Stereoselective Synthesis of Carbobicyclics via Organoyttrium-Catalyzed Sequential Cyclization/Silylation Reactions

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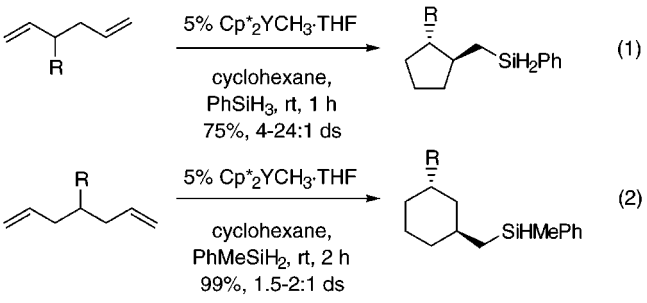
The sequential cyclization/silylation of 1,5-dienes and 1,6-dienes was effected under mild reaction conditions using catalytic quantities of Cp_2*YMe·THF. The process provides carbobicyclics in high yields and with excellent selectivities. The active catalyst is postulated to be Cp_2*YH·THF, which is generated in situ. A variety of alkenyl-substituted cyclopentane and cyclohexane substrates were examined. The high diastereoselectivities apparently originate from a preference for a chairlike transition structure that minimizes unfavorable steric interactions between the bulky Cp* ligands of the catalyst and the preexisting ring of the substrate. Acyclic triene precursors, 4-ethenyl-substituted 1,5-heptadienes and 5-ethenyl-substituted 1,8-nonadienes were also examined. These triene substrates, when exposed to the cyclization/silylation protocol, provide the strained *trans*-bicyclo[3.3.0]octanes and *trans*-decalin systems in high yield with excellent diastereoselectivity. The high selectivity is again attributed to the preference for a chairlike transition structure. The cyclized organosilane products isolated from these reactions were easily converted to the more versatile alcohols utilizing known oxidation methods.

Introduction

For the past several years we, along with others, have been developing selective cyclization[1] and silylation[2] reactions employing group 3 and organolanthanide catalysts. During the course of our research, the organoyttrium-catalyzed, stereoselective cyclization/silylation reaction of substituted 1,5- and 1,6-dienes was developed.[1f] A number of substituted dienes were cyclized in the presence of the precatalyst $Cp^*_2YCH_3$·THF and phenylsilanes to provide a variety of phenylsilyl-substituted carbocycles in high yield with moderate to excellent stereoselectivity (eqs 1 and 2). The resulting silanes could be easily oxidized to provide the more versatile alcohols. The air sensitive, Lewis acidic catalyst was compatible with ether, thioacetal, and tertiary amine functionalities.



To demonstrate the synthetic viability of this protocol, the catalytic cyclization/silylation method was utilized in the key step of a natural product synthesis.[3] The structural features of (±)-epilupinine, the simplest member of the lupin alkaloids, made it an ideal candidate for synthesis via an organoyttrium-catalyzed cyclization reaction. The requisite diene, *N*-(2-propenyl)-2-ethenylpiperidine, was easily synthesized in five steps from commercially available (±)-2-piperidinemethanol. When reacted with methylphenylsilane in the presence of $Cp^*_2YCH_3$·THF over 1 h, the expected phenylsilyl-substituted quinolizidine was obtained in high yield. Oxidation using the Woerpel oxidation conditions[4] provided the natural product (±)-epilupinine in yields ranging from 51% to 62% over two steps (eq 3). Remarkably, none of the trans isomer, naturally occurring (±)-lupinine, could be observed by NMR. The high diastereoselectivity associated with this process apparently results from the avoidance of interactions between the catalyst and the piperidine ring during the intramolecular insertion of the more hindered vinyl group of the diene.

The highly selective (±)-epilupinine synthesis suggested that the organoyttrium-catalyzed cyclization/silylation method could be used to prepare a variety of interesting polycyclic ring systems stereoselectively. Toward this end, a number of functionalized dienes and acyclic trienes were examined to ascertain stereoselectivity and functional group tolerances associated with polycyclic ring formation using this cyclization protocol.

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(2) (a) Sakakura, T.; Lautenschlager, H.-J.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1991**, 40. (b) Molander, G. A.; Julius, M. *J. Org. Chem.* **1992**, *57*, 6347. (c) Onozawa, S.-Y.; Sakakura, T.; Tanaka, M. *Tetrahedron Lett.* **1994**, *35*, 8177. (d) Molander, G. A.; Retsch, W. H. *Organometallics* **1995**, *14*, 4570. (e) Fu, P.-F.; Brard, L.; Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 7157. (f) Molander, G. A.; Winterfeld, J. *J. Organomet. Chem.* **1996**, *524*, 275.

(3) Molander, G. A.; Nichols, P. J. *J. Org. Chem.* **1996**, *61*, 6040.

(4) Smitrovich, J. H.; Woerpel, K. H. *J. Org. Chem.* **1996**, *61*, 6044.

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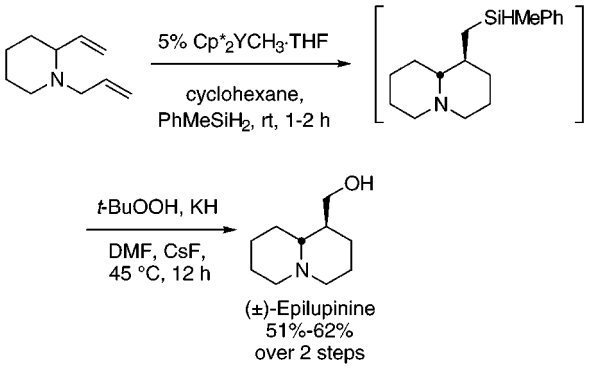
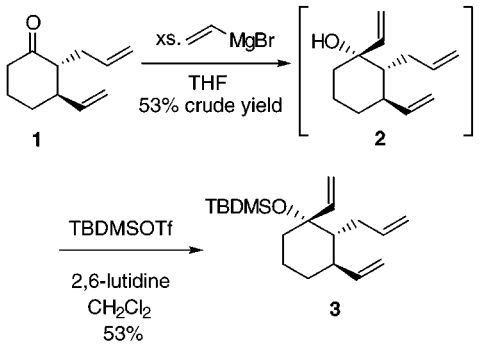


(3)

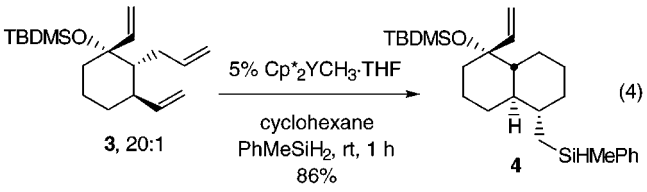
Scheme 1



The results described herein provide a detailed account of these annulation/silylation reactions mediated by an organoyttrium catalyst.

Results and Discussion

Cyclization of Monocyclic Precursors. Initial investigations of the catalytic cyclization/silylation reaction involved the examination of simple, polyalkenyl-substituted carbocycles. Triene **3** was prepared from the known ketone **1**[5] in two steps as outlined in Scheme 1. In a typical catalytic reaction, 5 mol % of the precatalyst $Cp^*_2YCH_3$·THF was dissolved in cyclohexane (0.5 M) followed by the addition of 1.1 equiv of methylphenylsilane and 1 equiv of the substrate at room temperature. The sterically bulky methylphenylsilane was used as the silylating agent because product dimerization had been observed previously in six-membered ring formation using phenylsilane.[1f] Thus the phenylsilane products derived from 1,6-diene cyclization/silylation compete with phenylsilane in the trapping of the cyclized organoyttrium intermediate resulting in unwanted product dimerization. Exposure of triene **3** to the cyclization/silylation protocol for 1 h at room temperature provided the bicyclic organosilane **4** in 86% isolated yield as what appeared to be a single diastereomer by gas chromatographic analysis (eq 4). The diastereoselectivity of the cyclization event in reactions that use methylphenylsilane as the silylating agent is difficult to assess. The σ-bond metathesis trapping of the cyclized organoyttrium intermediate with methylphenylsilane generates a product with a stereocenter on silicon in addition to any stereocenters formed in the annulation. Thus, when methylphenylsilane was utilized, the diastereoselectivity was determined after oxidation of the cyclized organosilane to the corresponding alcohol. Oxidation of silane **4** using the Woerpel oxidation conditions[4] provided alcohol **5** as a single diastereomer in 93% yield (eq 5). The structure of alcohol **5** was determined unambiguously by single-crystal X-ray crystallography of the corresponding diol generated by removal of the TBDMS protecting group.



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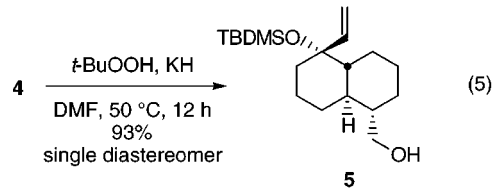
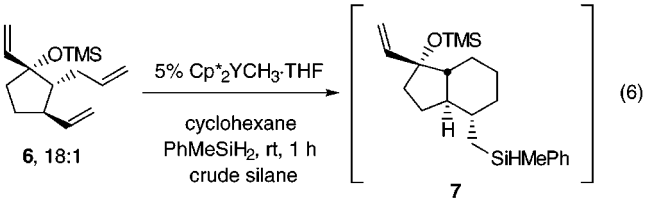
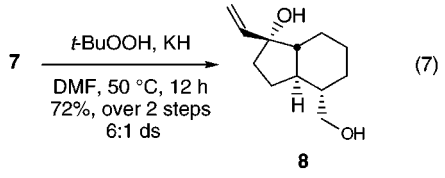


(5)

Triene **6** was prepared from (2*R**,3*R**)-3-ethenyl-2-(2-propenyl)cyclopentanone[6] following the same protocol outlined in Scheme 1. This substrate, in the presence of 1.1 equiv of $PhMeSiH_2$ and 5 mol % of the precatalyst $Cp^*_2YCH_3$·THF, provided the crude bicyclic organosilane **7** (eq 6). The crude silane mixture was then directly subjected to Woerpel oxidation conditions to give diol **8** as a 6:1 mixture of inseparable diastereomers in 72% yield (eq 7). Fortuitously, the Woerpel oxidation conditions removed the TMS protecting group and oxidized the silane, alleviating the need for a protecting group removal step as was necessary for alcohol **5**. The stereochemistry shown for the major diastereomer of silane **7** was based on the stereochemistry found previously for silane **4**.



(6)



(7)

There are several interesting aspects of the cyclization/silylation of substrates **3** and **6** that are worth noting. First, initial reaction of the active yttrium hydride catalyst occurs highly selectively at the least hindered of the three available olefins. The allyl group reacts in preference to the more hindered vinyl groups. This initial olefin insertion is followed by a rapid intramolecular cyclization resulting in a cyclic organoyttrium intermediate. This cyclization is presumed to be rapid because uncyclized silane products, the result of a σ-bond metathesis reaction between the uncyclized organoyttrium intermediate and the methylphenylsilane present in the

(5) Shimizu, I.; Ohashi, Y.; Tsuji, J. *Tetrahedron Lett.* **1983**, *24*, 3865.

(6) Posner, G. H.; Sterling, J. J.; Whitten, C. E.; Lentz, C. M.; Brunelle, D. J. *J. Am. Chem. Soc.* **1975**, *97*, 107.

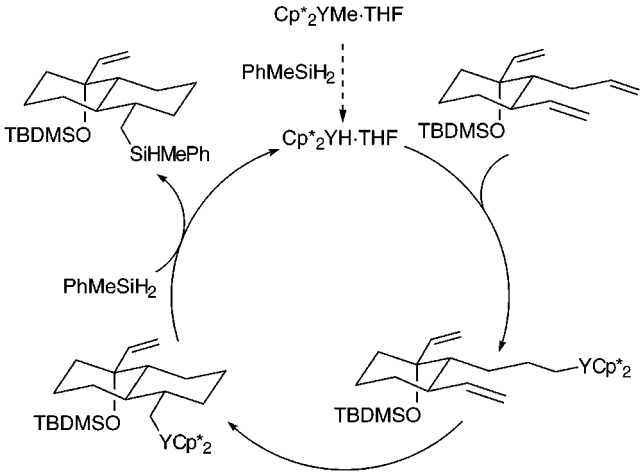
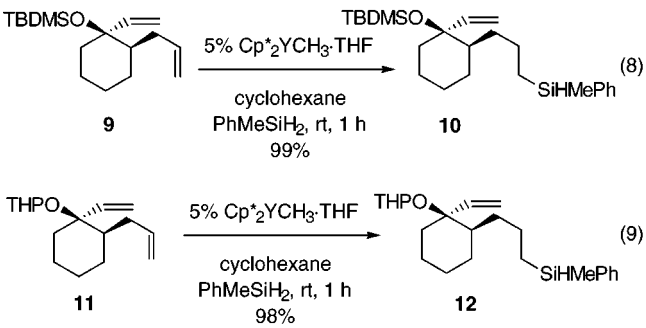


Figure 1. Proposed catalytic cycle for the organoyttrium-catalyzed cyclization of triene **3**.

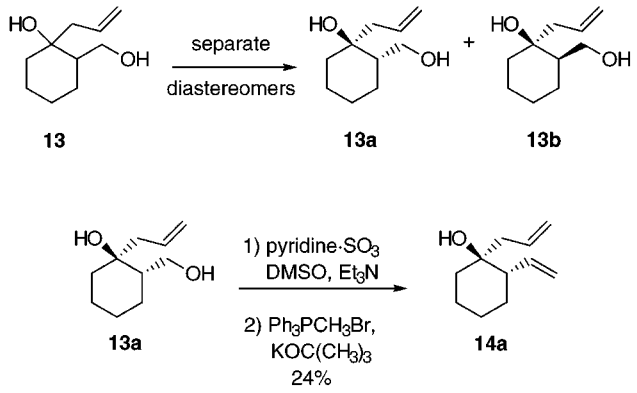
reaction mixture, are not observed. The intramolecular insertion reaction also occurs exclusively, this time at the less hindered of the two available vinyl groups. Subsequent σ-bond metathesis trapping of the cyclized organoyttrium intermediate with methylphenylsilane provides the bicyclic organosilane and regenerates the active hydride catalyst (Figure 1). The high selectivity associated with the cyclization of **3** is attributed to the chairlike transition structure shown in Figure 1. Unfavorable steric interactions between the bulky Cp* ligands of the catalyst and the preexisting cyclohexyl ring of the substrate may help to explain the high selectivity in the case of substrate **3**. The lower selectivity seen for the cyclization of substrate **6** may be attributed to diminished steric interations between the more fluxional cyclopentyl ring and the catalyst. The reaction of substrates **3** and **6** also demonstrates the ability of the catalyst to tolerate silyl protected alcohols.

Other dienes were prepared to determine if the intermediate organometallic could cyclize to a vinyl group at a hindered quaternary center. Substrates **9** and **11** were easily prepared from 2-(2-propenyl)cyclohexanone[7] in two steps via vinylmagnesium bromide addition followed by the appropriate alcohol protection. When the substrates were exposed to the standard reaction protocol, clean formation of uncyclized organosilanes **10** and **12** resulted (eqs 8 and 9). This result is not surprising given the selectivity observed in eq 4. It is worth noting that the THP ether protecting group in substrate **12** tolerated the Lewis acidic catalyst.



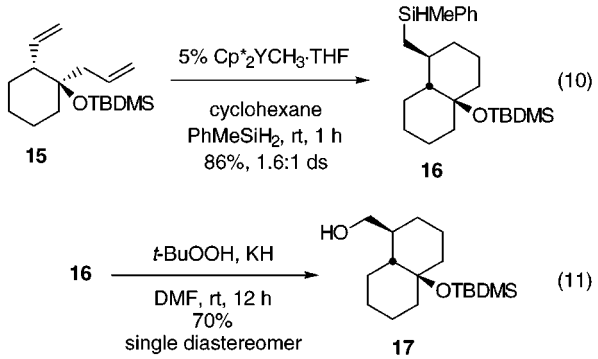
(7) Vanderwerf, C. A.; Lemmerman, V. L. *Org. Synth.* **1955**, Coll. Vol. 3, 44.

Scheme 2



The next cyclic substrates that were investigated possessed an allyl group at a quaternary center and a vinyl group substituted at a tertiary carbon. The known diol **13** was prepared following the addition of 2 equiv of allylmagnesium bromide to 2-(hydroxymethyl)cyclohexanone.[8] The two diastereomers were cleanly separated at this point by flash chromatography on silica gel (Scheme 2). Independent oxidation of the two diastereomers (one shown) followed by Wittig olefination provided alcohols **14a** and **14b** in diastereomerically pure form. Protection of the alcohols with either a TBDMS or TMS group provided the required substrates.

When substrate **15** was subjected to the standard cyclization/silylation conditions, a cyclized organosilane **16** was isolated in 86% yield as a 1.6:1 mixture of diastereomers along with 5% of other, nonseparable isomers (eq 10). As explained earlier, the diastereoselectivity of the annulation event could only be determined after oxidation in cases where methylphenylsilane was used as a silylating agent because of the silicon stereocenter. Oxidation of silane **16** provided alcohol **17** as a single diastereomer in 70% yield (eq 11). The stereochemistry of alcohol **17** was determined unambiguously from an X-ray crystal structure of the corresponding diol following TBDMS removal with TBAF.



Some interesting features were associated with the cyclization/silylation of diene **15**. The initial insertion of the organoyttrium hydride catalyst again takes place exclusively at the allyl group. The ensuing cyclization event occurs with complete selectivity. Presumably this selectivity is again associated with the desired chairlike transition structure and unfavorable interactions between the preexisting ring and the catalyst in a boatlike transition structure as depicted in Figure 2. The in-

(8) Kobayashi, S.; Hachiya, I. *J. Org. Chem.* **1994**, *59*, 3590.

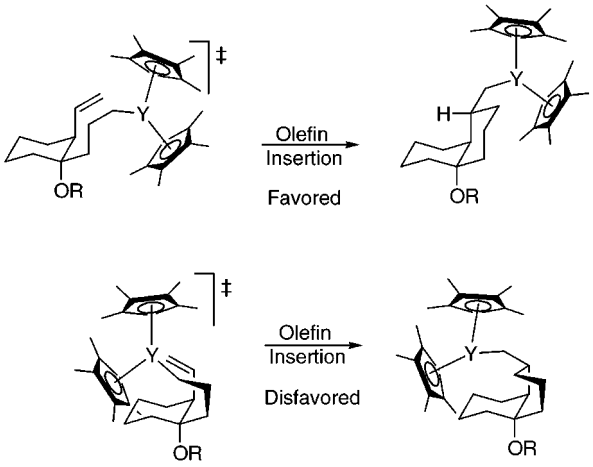
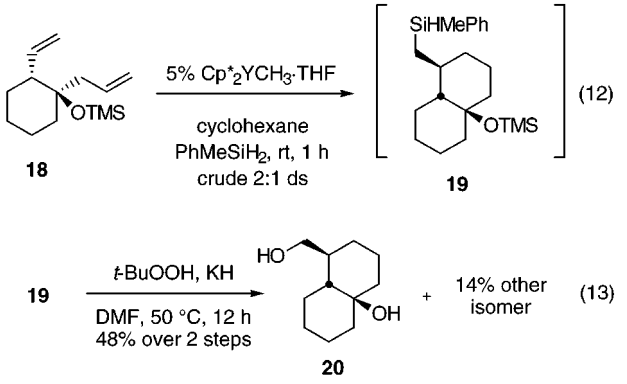


Figure 2. Proposed orientation required for intramolecular olefin insertion of diene **16**.

tramolecular insertion is again rapid as evidenced by the absence of uncyclized silylated products.

The analogous TMS protected diene **18** was also exposed to the reaction protocol. Diene **18**, in the presence of 1.1 equiv of $PhMeSiH_2$ and 5 mol % of the precatalyst $Cp^*_2YCH_3$·THF, provided the crude bicyclic organosilane **19** as a 2:1 diastereomeric mixture along with a significant amount of an additional, undetermined isomer (eq 12). The crude silane mixture was subjected to Woerpel oxidation conditions to provide diol **20** as a single diastereomer in 48% yield along with 14% of an unidentified isomer (eq 13). Again, the Woerpel oxidation conditions removed the TMS protecting group concurrent with oxidation of the silane.



The dienes that originated from alcohol **14b** were also examined to determine what effect the trans arrangement of the allyl and vinyl groups would have on the selectivity of the ring closure. When substrate **21** was exposed to the standard reaction conditions, the cyclized silane **22** was isolated in 93% yield as a 1.5:1 mixture of diastereomers (eq 14). Subsequent oxidation provided alcohol **23** in 68% yield as a 17.8:1 mixture of diastereomers (eq 15). Unfortunately, all attempts to remove the TBDMS protecting group in alcohol **23**, in hopes of obtaining a crystalline diol, were unsuccessful. Because TMS groups are much easier to remove, substrate **24** was prepared from alcohol **14b** and subjected to the standard cyclization/silylation conditions. Bicyclic organosilane **25** was isolated in 89% yield as a 1.5:1 mixture of diastereomers (eq 16). Subsequent Woerpel oxidation provided the desired diol **26** in 53% yield as a single diastereomer

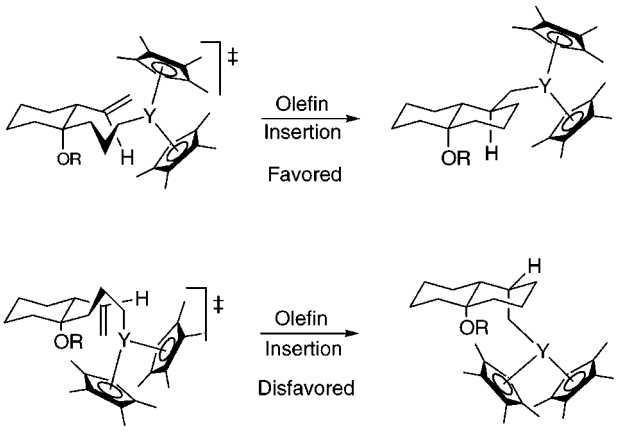
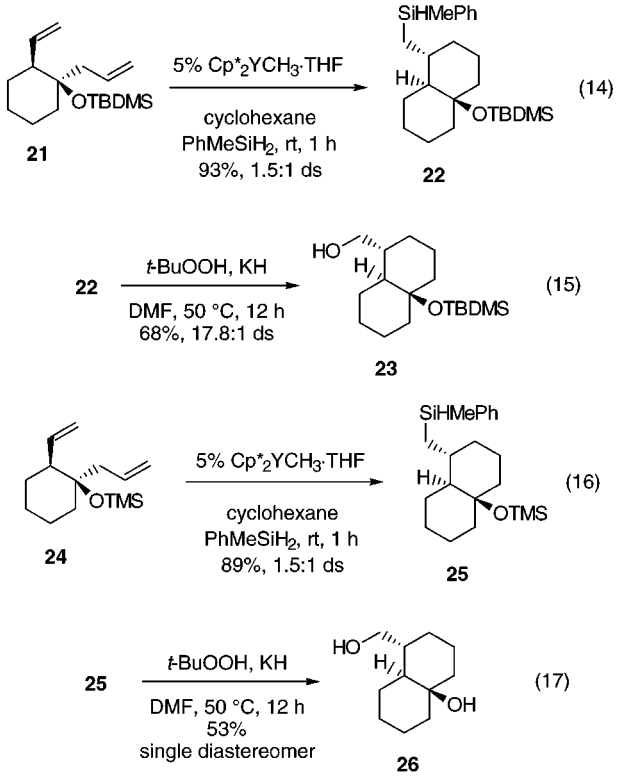


Figure 3. Proposed orientation required for intramolecular olefin insertion of dienes **22** and **25**.

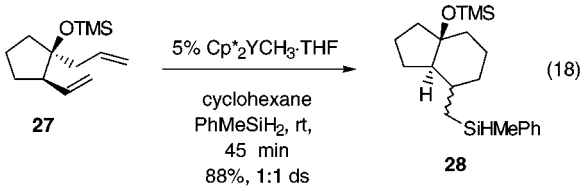
(eq 17). The stereochemistry of organosilanes **22** and **25** were subsequently proven unambiguously by obtaining a single-crystal X-ray structure of diol **26**.

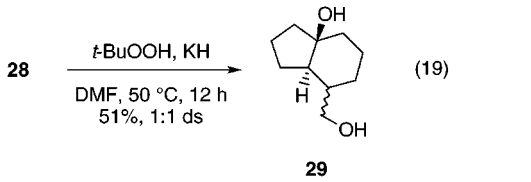


Some features of the cyclizations of dienes **21** and **24** are worth highlighting. The annulation event most likely proceeds exclusively though a chairlike transition structure and thus avoids unfavorable interactions between the catalyst and the preexisting ring as shown in Figure 3. The initial insertion of the organoyttium hydride catalyst is again completely chemoselective for the less hindered olefin. Catalytic annulation/silylation reactions of this type could be used to generate a wide variety of either cis or trans fused decalin systems in a highly selective manner.

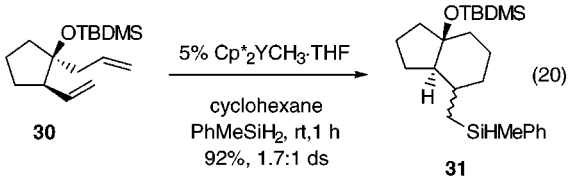
The cyclopentane analogue of substrate **24** was the next diene examined. (1*R**,2*S**)-2-ethenyl-1-(2-propenyl)-1-(trimethylsiloxy)cyclopentane (**27**) was prepared using the same reaction sequence outlined in Scheme 2 starting with allylmagnesium bromide addition to 2-(hy-

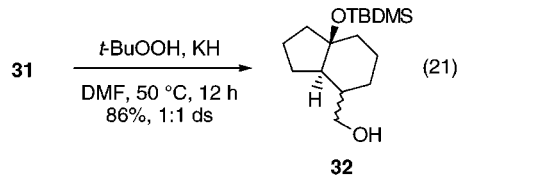
droxymethyl)cyclopentanone to prepare the requisite diol. When diene **27** was reacted with 1.1 equiv of $PhMeSiH_2$ at room temperature in the presence of 5 mol % of the precatalyst $Cp^*_2YCH_3$·THF for 45 min, bicyclic organosilane **28** was isolated in 88% yield as a 1:1 mixture of diastereomers (eq 18). The selectivity appeared similar in this case to some of the aforementioned cyclization reactions prior to oxidation of the silane stereocenter. Oxidation of silane **28** provided a 51% yield of diol **29** as a 1:1 mixture of diastereomers (eq 19). The lack of selectivity in this cyclization was unexpected given the results seen in the analogous cyclohexyl substrates. The fluxionality of the cyclopentane ring may account for the lack of selectivity in this reaction. There is apparently no bias toward a chairlike transition structure in this example. A single-crystal X-ray structure of one of the diol diastereomers **29** confirmed the structure of substrate **27** as well as the structure of the final product.



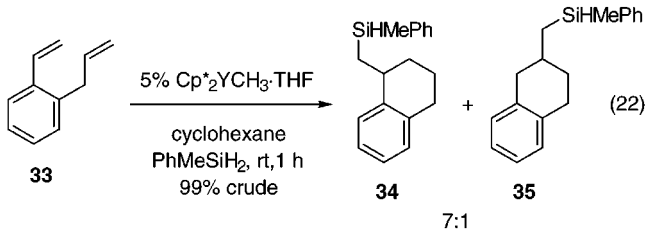


Hoping that a larger alcohol protecting group might lead to an increase in selectivity, the TMS substituent in substrate **27** was removed and replaced with a bulkier TBDMS protecting group providing diene **30**. Reaction under the standard cyclization/silylation protocol provided silane **31** in 92% yield as a 1.7:1 mixture of diastereomers (eq 20). We had hoped that oxidation of the silane stereocenter would reveal selective formation of the corresponding alcohol. Unfortunately, oxidation of silane **31** provided alcohol **32** in 86% yield as a 1:1 mixture of diastereomers (eq 21). Thus, no favorable steric bias was gained in this cyclization through the use of the larger TBDMS protecting group. Although the cyclizations of these alkenyl-substituted cyclopentanes lack selectivity, the annulation event was highly efficient and could provide a variety of substituted 5,6-ring systems from simple precursors.

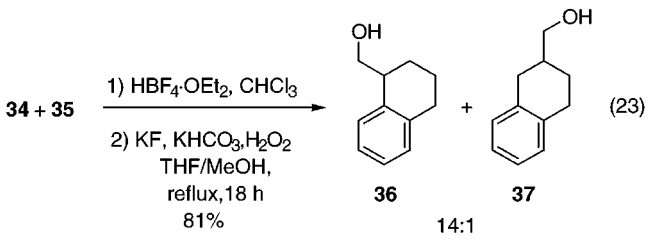




In a previous study the catalytic cyclization/silylation reaction of 1,2-divinylbenzene was reported.[3] From this experiment it was known that the active yttrium hydride catalyst was able to add to a vinyl substituent on an aromatic ring. The diene 1-ethenyl-2-(2-propenyl)benzene **33** was synthesized from the ozonolysis of indene followed by Wittig olefination of the crude dialdehyde. This substrate was prepared to examine the chemoselectivity for an allyl group versus a vinyl group ortho substituted on a benzene ring. When aromatic diene **33** was reacted under the standard cyclization/silylation reaction conditions two organosilane products (**34** and **35**) were isolated in 99% crude yield as a 7:1 mixture (eq 22). The major product **34** was the silane resulting from initial organoyttrium hydride insertion at the less hindered allyl substituent followed by cyclization and σ-bond metathesis trapping by $PhMeSiH_2$. The minor product was the cyclic organosilane resulting from initial yttrium hydride insertion at the more hindered vinyl group followed by cyclization and silane trapping. This was the first example, using the organoyttrium-catalyzed cyclization/silylation method, in which a significant amount of undesired material was produced via initial yttrium hydride insertion to a more hindered olefin. This lapse in chemoselectivity is perhaps due to the planarity of the aromatic ring which makes the vinyl group more accessible in this case, although electronic effects cannot be ruled out.



The identities of silanes **34** and **35** were confirmed by oxidation[9] to the corresponding alcohols and comparison of their NMR spectra to those previously reported in the literature (eq 23).[10] Curiously, the oxidation resulted in isolation of alcohols **36** and **37** in 81% yield as a 14:1 mixture of isomers. The observed selectivity essentially doubled from the cyclization/silylation event. The most likely explanation for this peculiar result is partial decomposition of the minor product during oxidation or isolation.



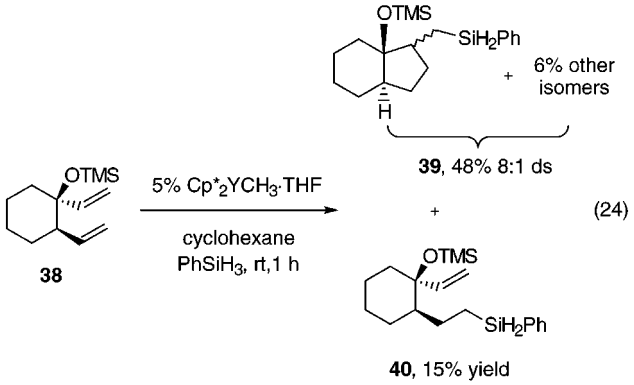
The reaction of diene **33** is noteworthy for a few reasons. First, preferential insertion of the yttrium hydride catalyst still occurs at the allyl double bond.

(9) Bergens, S. H.; Nogeda, P.; Whelan J.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 2121.

(10) (a) Taylor, S. K.; Davisson, M. E.; Hissom, B. R., Jr.; Brown, S. L.; Pristach, H. A.; Schramm, S. B.; Harvey, S. M. *J. Org. Chem.* **1987**, *52*, 425. (b) Bijoy, P.; Rao, G. S. R. S. *Synth. Commun.* **1993**, *23*, 2701. (c) Beckwith, A. L. J.; Gerba, S. *Aust. J. Chem.* **1992**, *45*, 289.

Additionally, the organometallic that is initially formed through insertion of the vinyl group has the metallocene complex placed at the terminus of the alkene rather than at the internal carbon. This observation is consistent with our previous results using the yttrium-based catalyst but is in contrast to selectivities reported elsewhere for the silylation of styrene using sterically more open samarium[2e] and neodymium[2a] catalysts. Steric concerns are critically important in the reaction of a organolanthanide hydrides to styrene, and the less open Cp^*_2YH catalyst has always been observed to undergo olefin insertion in a manner that places the metallocene complex at the terminal carbon of the original monosubstituted alkene unit.

Diene **38** was prepared in an identical fashion to diene **24** from 2-(hydroxymethyl)cyclohexanone using vinyl in place of allyl to prepare the required diol (Scheme 2). The results for cyclization of dienes **9** and **11** indicated that diene **38** would be too sterically encumbered to cyclize. Nonetheless, reaction of substrate **38** with $PhSiH_3$ using the standard reaction protocol provided the cyclized organosilane **39**, along with a small amount of other isomers, in 48% yield as an 8:1 mixture of diastereomers (eq 24). Some of the uncyclized silane **40** was also isolated. This result served to illustrate that the 5-exo cyclization onto a vinyl group at a quaternary center is possible. The isolation of the uncyclized silane **40** indicates that σ-bond metathesis with the silane is competing with a sterically inhibited cyclization event.



(24)

A bulkier silane was utilized in an attempt to slow the σ-bond metathesis reaction enough to allow clean cyclization to occur. Thus, diene **38** was reacted with $PhMeSiH_2$ using the standard reaction protocol. The reaction with $PhMeSiH_2$ was slower, requiring 6 h at ambient temperature. Isolation of the cyclic organosilane **41** was achieved in 80% yield as a 4.4:1 mixture of diastereomers (eq 25). No uncyclized material was isolated in this case which indicated that bulkier silanes could be used effectively to enhance cyclization reactions of this type. Determination of the stereoselectivity of the cyclization again required oxidation of the silane to remove the silicon stereocenter. In a subsequent NMR experiment, diene **38** was reacted with $PhMeSiH_2$ in the presence of 5 mol % of the precatalyst $Cp^*_2YCH_3$·THF in benzene-d_6 over the course of 7 h at room temperature. The crude cyclic organosilane **41** was isolated and immediately oxidized to give diol **42** in 48% yield over two steps as a single diastereomer (eq 26). Thus, not only do bulky divinyl substrates of this type cyclize, they apparently do so with complete selectivity. The stereochemistry of silane **41** was determined unambiguously by a single-crystal X-ray structure of diol **42**.

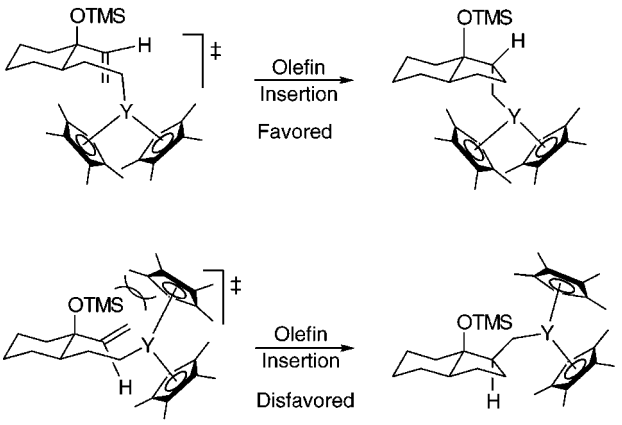
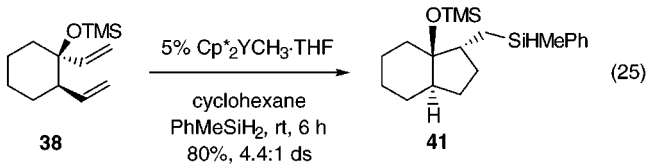
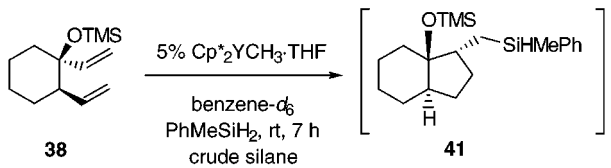
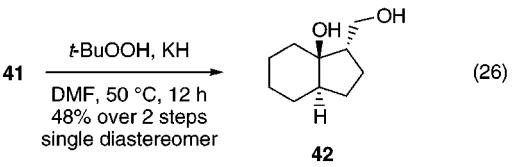


Figure 4. Proposed orientation required for intramolecular olefin insertion of diene **39**.



(25)





(26)

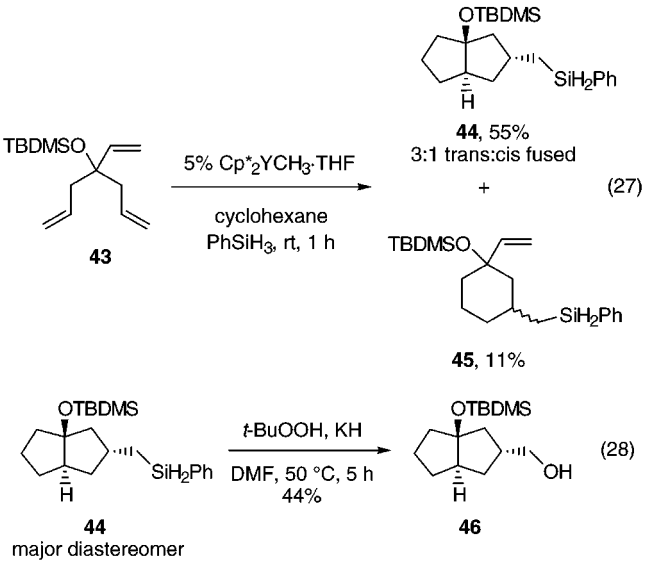
Interestingly, the stereochemistry of silane **41** is different from that which would be predicted by a chairlike transition structure. The cyclization of diene **38** proceeds exclusively through a boatlike transition structure. This mode of cyclization had not been previously observed in these cyclization reactions. Unfavorable interactions between the bulky Cp* rings of the catalyst and the TMS ether apparently favor a boatlike transition structure as shown in Figure 4. Additionally, unfavorable interactions ($A^{1,3}$-strain) between the OTMS group and the vinyl group also contribute to the preference for the boatlike transition structure. This result suggests that the organoyttrium-catalyzed cyclization/silylation protocol can be used to selectively prepare substituted cyclopentane rings from a variety of cyclic, divinyl substrates.

Cyclization of Acyclic Polyene Precursors

The selective conversion of simple acyclic polyene precursors to complex polycyclic molecules is an important transformation in organic synthesis. Cyclizations of this type has been reported by Negishi and co-workers

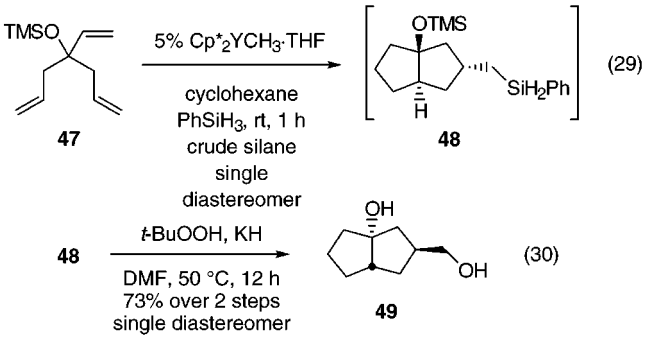
using catalytic titanium alkoxide.[11] Additionally, a variety of elegant palladium(II)-catalyzed "zipper" reactions of enynes have been reported by Trost and co-workers.[12] The only lanthanide-catalyzed polyene cyclization was disclosed by Marks and co-workers, who used dienes and enynes to prepare nitrogen-containing bicycles via a catalytic hydroamination reaction.[13] In an attempt to expand the organoyttrium-catalyzed cyclization/silylation method, a variety of triene precursors were prepared to examine the propensity for multiple cyclization reactions and study relevant stereochemistry issues.

The first triene substrate prepared was the symmetrical substrate **43**. This substrate was prepared in two steps by reacting methyl acrylate with 2 equiv of allylmagnesium bromide followed by TBDMS protection of the resulting alcohol. It was uncertain that this triene precursor would even cyclize because it had already been established that a vinyl substituent at a quaternary center on a cyclohexane ring would not undergo cyclization with an adjacent allyl group. Nonetheless, when triene **43** was treated with $PhSiH_3$ in the presence of 5 mol % of the precatalyst $Cp^*_2YCH_3$·THF in cyclohexane (0.5 M) the major product, bicyclic silane **44**, was isolated in 55% yield in a 3:1 diastereomeric ratio (eq 27). Interestingly, a significant amount of the six-membered ring byproduct **45** was also isolated. The major diastereomer of silane **44** was easily isolated and was later determined to be the trans 5,5-ring system shown. Oxidation of the major diastereomer provided alcohol **46** in 44% yield (eq 28). A single-crystal X-ray structure of alcohol **46** confirmed the stereochemistry shown for silane **44**. Because the second 5-exo-trig cyclization event was presumed to proceed preferentially through a chair-like transition structure, the minor diastereomer of silane **44** was assumed to be the cis fused bicyclic silane. However, precise stereochemical identification of the minor diastereomer of silane **44** was not possible.



Some distinct features of the multiple cyclization of triene substrate **43** should be mentioned. From the structures of the isolated products it is apparent that the initial organoyttrium hydride insertion occurs exclusively at one of the two (equivalent) less hindered allyl substituents. An ensuing intramolecular cyclization event then takes place that favors formation of a five-membered ring over a six-membered ring by a 5:1 ratio. Notably, a more sterically inhibited 5-exo-trig cyclization is favored over the 6-exo-trig cyclization. The organoyttrium intermediate from the first 5-exo-trig cyclization is apparently not trapped by the $PhSiH_3$ in the reaction mixture. Instead, this intermediate rapidly undergoes a second 5-exo-trig cyclization, and the resulting organometallic is then converted to the corresponding silane **44** via a σ-bond metathesis reaction with $PhSiH_3$. Any organometallic generated by a 6-exo process is transformed by a σ-bond metathesis reaction with $PhSiH_3$ because the second cyclization event (which would generate a bridged bicyclic sytem) is slow.

Thinking that the OTBDMS group was bulky enough to slow the 5-exo-trig cyclization pathway and allow for the formation of silane **45**, a second triene was prepared which replaced the OTBDMS group with the smaller OTMS substituent. Substrate **47** was prepared in fashion similar to triene **43**. The reaction of the OTMS containing precursor **47** under the standard organoyttrium-catalyzed cyclization/silylation protocol provided the crude bicyclic silane **48** as a single diastereomer (eq 29). Attempts to purify silane **48** resulted in partial decomposition of the product. Thus, direct oxidation of the crude silane product provided diol **49** in 73% yield over two steps as a single diastereomer (eq 30). No other significant byproducts were isolated. Removal of the TBDMS group in the known alcohol **46** and subsequent ^1H NMR spectral comparison with diol **49** provided the structural verification of silane **48**. Remarkably, three stereocenters are produced with complete selectivity from the simple, achiral triene **47** via the organoyttrium-catalyzed cyclization/silylation protocol.



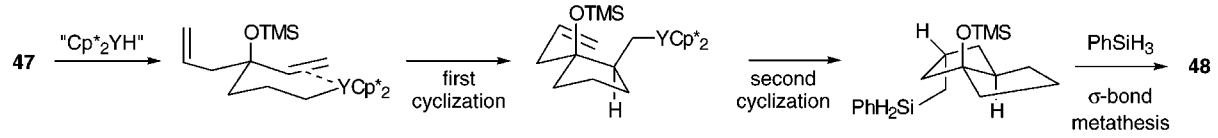
There are again several interesting features associated with this unique transformation. First, none of the silane product from a 6-exo-trig cyclization was observed. Apparently, the smaller OTMS group allows complete preference for the 5-exo cyclization pathway. Additionally, following the initial cyclization event the smaller OTMS substituent must prefer the pseudoaxial orientation, allowing for the generation of a single trans-fused

(11) Negishi, E.-I.; Jensen, M. D.; Kondakov, D. Y.; Wang, S. *J. Am. Chem. Soc.* **1994**, *116*, 8404.

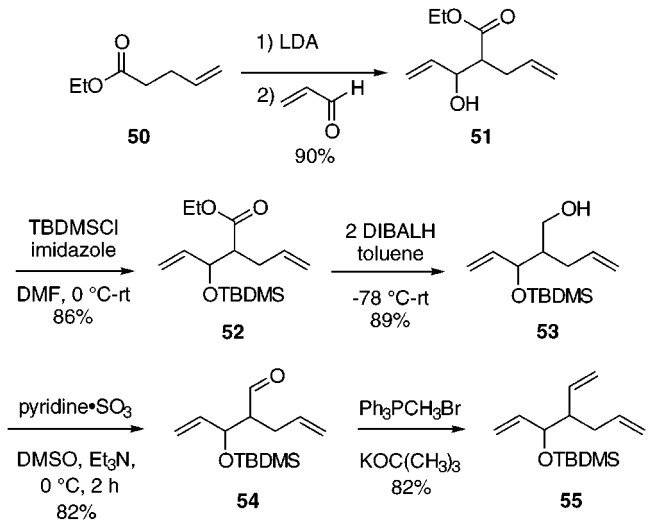
(12) (a) For a review, see: Trost, B. M. *Acc. Chem. Res.* **1990**, *23*, 34. (b) Trost, B. M.; Lee, D. C.; Rise, F. *Tetrahedron Lett.* **1989**, *30*, 651. (c) Trost, B. M.; Pedregal, C. *J. Am. Chem. Soc.* **1992**, *114*, 7292. (d) Trost, B. M.; Czeskis, A. *Tetrahedron Lett.* **1994**, *35*, 211. (e) Trost, B. M.; Chung, J. Y. L. *J. Am. Chem. Soc.* **1985**, *107*, 4586. (f) Trost, B. M.; Tanoury, G. J. *J. Am. Chem. Soc.* **1987**, *109*, 4753. (g) Trost, B. M.; Lee, D. C. *J. Org. Chem.* **1989**, *54*, 2271. (h) Trost, B. M.; Shi, Y. *J. Am. Chem. Soc.* **1991**, *113*, 701. (i) Trost, B. M.; Shi, Y. *J. Am. Chem. Soc.* **1993**, *115*, 9421. (j) Trost, B. M.; Shi, Y. *J. Am. Chem. Soc.* **1992**, *114*, 791.

(13) Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 707.

Scheme 3



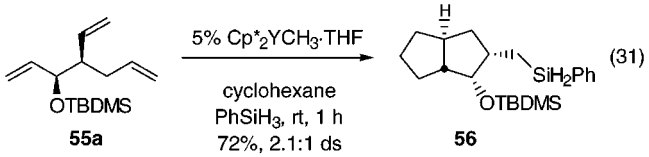
Scheme 4



diastereomer as shown in Scheme 3. The isolation of a single diastereomer also suggests that the second 5-exo cyclization is extremely selective as was assumed for the reaction of triene **43**. The outstanding selectivity can be attributed to the preference for the two chairlike transition structures that minimize unfavorable steric interactions between the bulky Cp* rings of the catalyst and the substrate. Again, no uncyclized or partially cyclized hydrosilylated products were observed, indicating that the second cyclization event is faster than silane trapping. The generation of 3-substituted *trans*-bicyclo[3.3.0]octanes via a tandem anionic cyclization reaction has been disclosed by Bailey and co-workers.[14] The results herein demonstrate that the organoyttrium-catalyzed cyclization/silylation reaction is also well suited for the selective synthesis of the strained trans 5,5-ring system. Finally, the isolation of the thermodynamically less favored *trans*-bicyclo[3.3.0] system speaks to the kinetic nature of the cyclization reactions. It has been noted previously that olefin insertion reactions of organolanthanides are extremely exothermic and effectively irreversible under reasonable reaction conditions.[15]

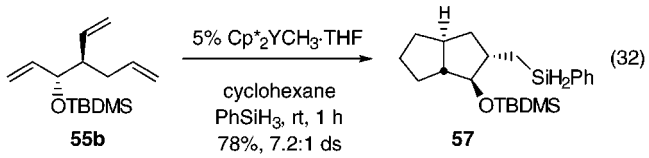
To demonstrate the versatility of this method further, an additional triene precursor of the trans 5,5-ring system was synthesized. The triene 3-(*tert*-butyldimethylsiloxy)-4-ethenyl-1,6-heptadiene (**55**) was efficiently prepared over five steps as outlined in Scheme 4. The addition of the ester enolate **50**[16] to acrolein provided alcohol **51**. Protection of alcohol **51** as the TBDMS ether **52** and subsequent DIBALH reduction of the ester provided alcohol **53**. Oxidation of alcohol **53** to aldehyde **54** followed by a Wittig olefination provided the desired triene **55** as a 1:1 diastereomeric mixture. Following extensive purification by flash chromatography, both diastereomers could be isolated in pure form.

Triene substrate **55a** was first reacted under the organoyttrium-catalyzed cyclization/silylation conditions. In the presence of 5 mol % of the precatalyst $Cp^*_2YCH_3$·THF, the reaction with $PhSiH_3$ was complete in 1 h at room temperature providing bicyclic silane **56** in 72% yield as a 2.1:1 mixture of diastereomers, presumably at the nonbridgehead stereocenter (eq 31). Unfortunately, the two diastereomers could not be separated, and all attempts at oxidation of this silane mixture resulted in decomposition of the products. Therefore, the relative stereochemistry of the major product could not be established with certainty.



(31)

The second diastereomer of triene **55**, substrate **55b**, was also subjected to the annulation/silylation reaction conditions. Reaction with $PhSiH_3$ over the course of 1 h at ambient temperature provided the bicyclic organosilane product **57** in 78% yield as a 7.2:1 diastereomeric mixture, again presumably at the nonbridgehead stereocenter (eq 32). As in the case of substrate **55a**, separation of the diastereomers was not possible. Additionally, all attempts at oxidation and TBDMS removal resulted in product decomposition. Thus, the relative stereochemistry of the major product could again not be established with certainty. The major silane products **56** and **57** depict the relative stereochemistry that would result from both of the cyclizations proceeding through chairlike transition structures.



(32)

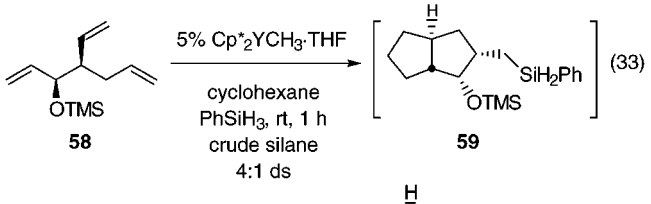
To gain insight regarding the stereochemistry of these cyclizations the TMS protecting group was again used because it could be easily removed during oxidation. The TBDMS protecting group in substrate **55a** was removed and replaced with a TMS group providing triene **58**. Reaction of substrate **58** with $PhSiH_3$ in the presence of 5 mol % of the precatalyst $Cp^*_2YCH_3$·THF provided the crude silane **59** as a 4:1 mixture of diastereomers (eq 33). Direct oxidation of the silane mixture **59** provided the expected diol **60** in 37% yield over two steps as a 4:1 mixture of diastereomers at the nonbridgehead stereocenter (eq 34). The major diastereomer was isolated and the structure was determined unambiguously from a single-crystal X-ray structure. From the cyclization result of triene **47** it is likely that the annulation/

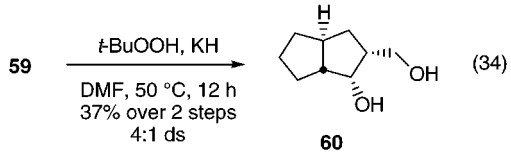
(14) (a) Bailey, W. F.; Khanolkar, A. D. *Tetrahedron Lett.* **1990**, *31*, 5993. (b) Bailey, W. F.; Khanolkar, A. D.; Gavaskar, K. V. *J. Am. Chem. Soc.* **1992**, *114*, 8053.

(15) Haar, C. M.; Stern, C. L.; Marks, T. J. *Organometallics* **1996**, *15*, 1765.

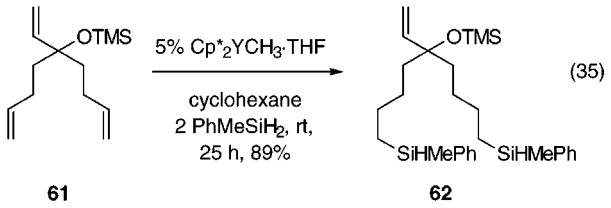
(16) Procedure adapted from: Lotz, B. T.; Miller, M. J. *J. Org. Chem.* **1993**, *58*, 618.

silylation reactions of substrates **55a** and **55b**, which both contain vinyl groups at a tertiary center, provide trans-fused 5,5-rings exclusively (Scheme 3). Therefore, the diastereomeric mixtures observed in the above reactions must originate from the second 5-exo-trig cyclization event where the transition structure of the second ring closure is apparently influenced by the sterically bulky ether substituent. Nonetheless, these reactions serve to demonstrate that highly functionalized trans-fused 5,5-bicycles can be prepared using the organoyttrium-catalyzed cyclization/silylation protocol.



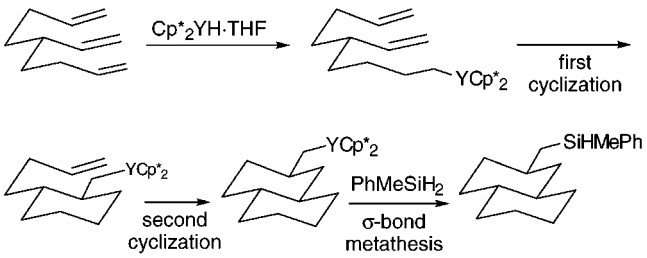


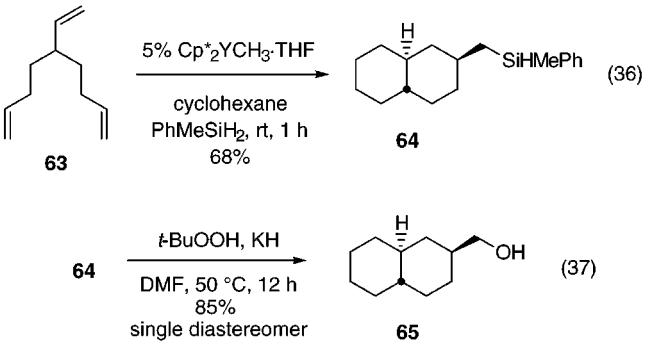
Attention was next focused on the synthesis of *trans*-decalin ring systems from triene precursors. The first precursor examined was analogous to substrate **47**. Substrate **61** was prepared in two steps from 1,8-nonadien-5-one[17] by vinylmagnesium bromide addition and subsequent TMS protection. Reaction of substrate **61** under the standard reaction conditions provided only uncyclized material. When triene **61** was reacted with 2 equiv of $PhMeSiH_2$ over the extended reaction time of 25 h at room temperature the disilylated product **62** was cleanly isolated in 89% yield (eq 35). This result was puzzling for a number of reasons. First, the analogous substrate, triene **47**, cyclized very efficiently to generate the strained trans 5,5 ring system. Next, the reaction time of 25 h was abnormally long considering most cyclization/silylation reactions using the organoyttrium precatalyst $Cp^*_2YCH_3$·THF were complete within 1 h. These results and the results observed for cyclic substrates **9** and **11** confirmed that cyclization onto a vinyl group at a quaternary center to form a six-membered ring is difficult using this protocol.



The next *trans*-decalin precursor examined was the known triene **63**.[11] Reaction of substrate **63** using the standard reaction protocol provided the bicyclic silane **64** in 68% yield as a diastereomeric mixture (eq 36). As in previous six-membered ring cyclizations, the use of $PhMeSiH_2$ was required to prevent product dimerization. Thus, the diastereoselectivity of the ring closure could only be determined after oxidation of the silane stereocenter. Oxidation of silane **64** provided alcohol **65** in 85% yield as a single diastereomer (eq 37). Subsequent PDC oxidation and melting point comparison of the derived acid with known literature values[18] verified the stereochemistry shown. A similar cyclization of triene **63** was reported by Negishi and co-workers using catalytic $Ti(i\text{-}OPr)_4$ in the presence of Et_2AlCl.[11] This cascade carbometalation reaction required 3 days for completion and gave a 3.3:2.3:1 ratio of three diastereomeric alcohols **65**.

Scheme 5





The origin of stereoselectivity in the cyclization of substrate **63** is very similar to that found for the cyclization of substrate **47**. Initial insertion of the organoyttrium hydride occurs exclusively at one of the least hindered olefins (Scheme 5). The first cyclization event occurs through a chairlike transition structure providing a cyclized organoyttrium intermediate. A second, rapid cyclization then ensues, providing a bicyclic organoyttrium species. This intermediate undergoes a σ-bond metathesis reaction with $PhMeSiH_2$, liberating the product and regenerating the active catalyst. These results suggest that the organoyttrium-catalyzed cyclization/silylation method may be used to prepare a variety of functionalized *trans*-decalin ring systems in a highly selective fashion starting with simple polyene precursors.

Conclusions

The reactions described herein serve to demonstrate the usefulness and versatility of the organoyttrium-catalyzed cyclization/silylation method. A wide variety of polycyclic molecules were prepared from simple precursors in a highly selective manner using this reaction protocol. The intrinsic steric bulk of the catalyst dictates the mode of cyclization and accounts for the high diastereoselectivies observed in these reactions. The cyclization and subsequent silylation reaction of acyclic precursors best illustrates this selectivity as three new stereocenters are created with complete selectivity. The bicyclic organosilanes generated by this method were

(17) Nagai, M.; Lazor, J.; Wilcox, C. S. *J. Org. Chem.* **1990**, *55*, 3440.

(18) (a) Chapman, N. B.; Shorter, J.; Toyne, K. J. *J. Chem. Soc.* **1964**, 1077. (b) Dauben, W. G.; Tweit, R. L.; Mannerskantz, C. *J. Am. Chem. Soc.* **1954**, *76*, 4420. (c) DiBiase, S. A.; Wolak, R. P.; Dishong, D. M.; Gokel, G. W. *J. Org. Chem.* **1980**, *45*, 3630.

easily oxidized in most cases using known literature procedures to provide the more versatile alcohols in good to modest yields. The results outlined above demonstrate the utility of the organoyttrium-catalyzed cyclization/silylation method in the selective preparation of useful, cyclic organic molecules.

Experimental Section

Materials and Methods. All catalytic organoyttrium reactions were performed in a nitrogen-filled Vacuum Atmospheres glovebox unless otherwise noted. All substrates were extensively purified by flash chromatography and/or distillation. Prior to use, all substrates were freeze/pump/thaw-degassed. Cyclohexane was purchased from Aldrich Chemical Co., distilled from Na, and degassed before using. The organoyttrium precatalyst $Cp^*_2YCH_3$·THF was synthesized from the literature procedure[19] using Schlenk techniques. Phenylsilane (Aldrich, 99%) was degassed and stored in the glovebox. Methylphenylsilane was purchased from United Chemical Technologies and freeze/pump/thaw-degassed prior to storage in a glovebox. Diethyl ether and THF were distilled from sodium benzophenone ketyl under argon immediately prior to use. CH_2Cl_2 was distilled from CaH_2 immediately prior to use. Triethylamine, DMSO, and DMF were all distilled from CaH_2 and stored over molecular sieves. Potassium hydride was purchased as a 35% dispersion in mineral oil from Aldrich. The white solid was isolated under argon after several washings with dry hexane using Schlenk techniques.[20] Deuterated NMR solvents ($CDCl_3$) were purchased from Cambridge Isotope Laboratories and stored over 4 Å molecular sieves. All other materials were commercially available and were used without further purification unless otherwise noted.

General Procedure for the Organoyttrium-Catalyzed Cyclization/Silylation Reaction. In a nitrogen atmosphere glovebox $Cp^*_2YCH_3$·THF (5 mol %) was dissolved in cyclohexane (0.5 M) prior to the addition of either phenylsilane of methylphenylsilane (at least 1.1 equiv) and the substrate (1 equiv). Reaction progress was monitored by gas chromatography. Upon completion, the reaction mixture was removed from the glovebox and filtered through a small plug of Florisil to remove the catalyst prior to concentration by rotary evaporation. The crude product was purified by flash chromatography. Concentration under reduced pressure (0.06 mmHg) or Kugelrohr distillation provided the isolated silane products.

General Procedure for the Woerpel Oxidation of Silane Products.[4] To a dry 100 mL round-bottom flask equipped with a stopcock sidearm was added a 90% solution of *tert*-butyl hydroperoxide (10 equiv) and DMF (2 mL per 0.5 mmol silane) under argon. Next, solid potassium hydride (10 equiv) was slowly added at room temperature using Schlenk techniques under an atmosphere of argon. The addition was exothermic and provided a slightly pink foamy suspension. To this was added the silane (1 equiv) in DMF (0.2 M). The mixture was then stirred for 12 h at 50 °C. Sodium thiosulfate (1 g per 0.5 mmol silane) was then added, and the mixture was stirred for 0.5 h. The reaction mixture was then exposed to reduced pressure (0.06 mmHg) to remove the DMF. The resulting solid residue was extracted several times with chloroform and filtered through Celite. The filtrate was concentrated by rotary evaporation and purified by flash chromatography. Concentration under reduced pressure (0.06 mmHg) or Kugelrohr distillation provided the isolated alcohol products.

(1*R,2*R**,6*S**,7*S**)-2-(*tert*-Butyldimethylsiloxy)-2-ethenyl-7-[(methylphenylsilyl)methyl]bicyclo[4.4.0]decane (4).** Diene **3** (0.076 g, 0.25 mmol) was exposed to the general cyclization/silylation procedure given. The reaction was found to be complete in 1 h by gas chromatography. Following workup, the crude product was agitated in a Kugelrohr distillation apparatus at 70 °C at reduced pressure to remove any low molecular weight impurities. This provided **4** as a clear oil (0.092 g, 0.22 mmol, 86% yield) as what appeared to be a single diastereomer by gas chromatography: R_f 0.49 (hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56−7.50 (m, 2H), 7.37−7.31 (m, 3H), 5.04−4.92 (m, 1H), 4.46−4.36 (m, 2H), 2.08−1.96 (m, 1H), 1.79−1.58 (m, 5H), 1.57−1.44 (m, 2H), 1.32−1.06 (m, 5H), 1.04−0.82 (m, 11H), 0.78−0.58 (m, 3H), 0.32 (d, J = 3.8 Hz, 3H), 0.1−0.02 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 137.5, 134.3, 134.2, 129.0, 127.8, 111.6, 52.9, 52.8, 43.8, 40.1, 36.9, 35.4, 35.3, 30.6, 26.3, 26.1, 26.0, 21.2, 18.8, 18.7,−1.9, −2.3, −4.2, −4.8; IR (neat) 2928, 2117, 1250 cm^{-1}; HRMS Calcd for $C_{26}H_{43}OSi_2^+$(M − H)$^+$: 427.2853, found 427.2790; LRMS (EI) *m*/*z* 371 (31.2), 195 (47.3), 121 (100.0), 105 (16.1), 91 (12.9).

(1*R,2*R**,6*S**,7*S**)-2-(*tert*-Butyldimethylsiloxy)-2-ethenyl-7-(hydroxymethyl)bicyclo[4.4.0]decane (5).** Silane **4** (73 mg, 0.17 mmol) was exposed to the Woerpel oxidation procedure given. Following workup, the crude product was purified by flash chromatography. Concentration under reduced pressure (0.06 mmHg) provided **5** (51.5 mg, 0.16 mmol, 93% yield) as a single stereoisomer which was >99% pure by gas chromatography: R_f 0.30 (5:1 hexanes:EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.15 (dd, J = 17.6, 11.2 Hz, 1H), 5.05−4.92 (m, 2H), 3.70 (dd, J = 10.7, 3.2 Hz, 1H), 3.48 (dd, J = 10.7, 6.2 Hz, 1H), 1.92−1.83 (m, 1H), 1.80−1.61 (m, 5H), 1.60−1.46 (m, 2H), 1.45−1.32 (m, 1H), 1.31−1.01 (m, 5H), 0.99−0.76 (m, 11H), 0.02 (d, J = 4.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 111.8, 76.4, 65.9, 52.6, 45.5, 38.2, 36.6, 30.2, 29.8, 26.1, 25.9, 25.7, 20.9, 18.8, −1.9, −2.3; IR (neat) 3336, 2929, 2855, 1252 cm^{-1}; HRMS Calcd for $C_{19}H_{36}O_2Si^+$: 324.2485, found 324.2502; LRMS (EI) *m*/*z* 324 (0.5), 267 (75.3), 175 (33.3), 157 (18.2), 119 (22.0), 105 (22.1), 93 (39.0), 75 (100.0).

(1*R,2*R**,6*S**,7*S**)-7-Ethenyl-2-(hydroxymethyl)-bicyclo[4.4.0]nonan-7-ol (8).** (1*R**,2*R**,3*R**)-1,3-Diethenyl-2-(2-propenyl)-1-(trimethylsiloxy)cyclopentane (**6**) (62 mg, 0.25 mmol) was exposed to the general cyclization/silylation procedure given. The reaction mixture changed from faint yellow to a darker, cloudy yellow over 1 h after which no starting material was observed by gas chromatography. Following workup, the crude silane **7** was directly subjected to oxidation.

Crude silane **7** in 2.5 mL was subjected to the Woerpel oxidation procedure given. Following workup, the crude product was purified by flash chromatography. Concentration under reduced pressure (0.06 mmHg) provided **8** (35.2 mg, 0.18 mmol, 72% yield) as a 6:1 mixture of diastereomers which was >99% pure by gas chromatography. Spectral data reported for the major diastereomer: R_f 0.15 (1:1 hexanes:EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 (dd, J = 17.1, 10.7 Hz, 1H), 5.22 (dd, J = 17.1, 1.3 Hz, 1H), 5.04 (dd, J = 10.7, 1.3 Hz, 1H), 3.65 (dd, J = 10.7, 4.3 Hz, 1H), 3.52−3.38 (m, 1H), 2.02−1.73 (m, 4H), 1.72−1.38 (m, 5H), 1.37−1.14 (m, 3H), 1.13−0.76 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 111.6, 81.5, 67.1, 54.8, 46.5, 43.9, 39.3, 29.2, 27.6, 25.6, 23.7; IR (neat) 3374, 2925, 2857 cm^{-1}; HRMS Calcd for $C_{12}H_{20}O_2^+$: 196.1463, found 196.1471; LRMS (EI) *m*/*z* 196 (5.6), 147 (17.4), 120 (18.6), 119 (18.6), 109 (18.0), 108 (21.9), 95 (26.2), 79 (2.4), 70 (44.6), 55 (100.0).

(1*R,2*S**)-1-(*tert*-Butyldimethylsiloxy)-1-ethenyl-2-[3-(methylphenylsilyl)propyl]cyclohexane (10).** (1*R**,2*S**)-1-*tert*-(Butyldimethylsiloxy)-1-ethenyl-2-(2-propenyl)cyclohexane (**9**) (0.141 g, 0.50 mmol) was exposed to the general cyclization/silylation procedure given. The reaction mixture changed from clear to light yellow over 1 h and was found to be complete. Following workup, the crude product was agitated in a Kugelrohr distillation apparatus at 100 °C at reduced pressure to remove any low molecular weight impurities. This provided **10** as a clear oil (0.2008 g, 0.498 mmol, 99% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58−7.49 (m, 2H), 7.41−7.31 (m, 3H), 6.13 (dd, J = 17.8, 11.2 Hz, 1H), 5.03−4.97 (m, 2H), 4.37−4.30 (m, 1H), 1.73−1.58 (m, 3H), 1.58−1.39 (m, 4H), 1.39−1.09 (m, 6H), 0.90 (s, 9H), 0.84−0.72 (m,

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2H), 0.31 (d, J = 3.8 Hz, 3H), 0.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 136.8, 134.3, 134.2, 129.3, 129.1, 127.9, 127.8, 111.9, 47.3, 37.1, 33.4, 33.3, 27.1, 26.2, 26.1, 25.9, 22.5, 22.4, 21.7, 18.8, 13.7, 13.6, −1.9, −2.2, −5.5, −5.7; IR (neat) 2114 cm^{-1}; HRMS Calcd for $C_{24}H_{42}OSi_2^+$: 402.2774, found 402.2780; LRMS (EI) *m*/*z* 402 (4.7), 197 (11.0), 196 (19.4), 195 (100.0), 121 (37.2), 75 (43.7). Anal. Calcd for $C_{24}H_{42}OSi_2$: C, 71.57%; H, 10.51%. Found: C, 71.74%; H, 10.81%.

(1*R,2*S**)-1-Ethenyl-2-[3-(methylphenylsilyl)propyl]-1-(tetrahydropyranyloxy)cyclohexane (12).** (1*R**,2*S**)-1-Ethenyl-2-(2-propenyl)-1-(trimethylsiloxy)cyclohexane (**11**) (0.130 g, 0.52 mmol) was subjected to the general cyclization/silylation procedure given. The reaction mixture changed from faint yellow to dark yellow over 1 h and was found to be complete. Following workup, the crude product was purified by flash chromatography. The product was then agitated in a Kugelrohr distillation apparatus at 100 °C at reduced pressure to remove any low molecular weight impurities. This provided **12** as a clear oil (0.1914 g, 0.51 mmol, 98% yield): R_f 0.38 (10:1 hexanes: EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57−7.47 (m, 2H), 7.39−7.28 (m, 3H), 6.37 (dd, J = 17.8, 11.3 Hz, 0.5H), 5.86 (dd, J = 17.8, 11.3 Hz, 0.5H), 5.16−4.99 (m, 2H), 4.65−4.59 (m, 1H), 4.32 (q, J = 3.5 Hz, 1H), 4.03−3.93 (m, 1H), 3.48−3.39 (m, 1H), 1.93−1.10 (m, 19H), 0.92−0.67 (m, 2H), 0.31 (dd, J = 3.8, 1.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 143.8, 136.8, 134.3, 129.1, 127.8, 114.6, 113.2, 94.4, 93.4, 80.2, 79.6, 63.1, 62.8, 47.5, 46.5, 33.2, 33.1, 32.6, 32.4, 32.3, 26.9, 26.8, 25.8, 25.7, 25.3, 22.6, 22.5, 21.7, 20.1, 20.0, 13.6, 13.5, −5.6, −5.7; IR (neat) 2112 cm^{-1}; HRMS Calcd for $C_{23}H_{36}O_2Si^+$: 372.2485, found 372.2507; LRMS (EI) *m*/*z* 372 (0.1), 371 (0.1), 243 (12.1), 193 (13.8), 165 (15.0), 137 (34.6), 122 (13.5), 121 (75.0), 105 (12.9), 86 (17.3), 85 (100.0), 84 (33.7). Anal. Calcd for $C_{23}H_{36}O_2Si$: C, 74.13%; H, 9.74%. Found: C, 73.84%; H, 9.74%.

(1*R,5*S**,6*R**)-1-(*tert*-Butyldimethylsiloxy)-5-[(methylphenylsilyl)methyl]bicyclo[4.4.0]decane (16).** (1*R**,2*R**)-1-(*tert*-Butyldimethylsiloxy)-2-ethenyl-1-(2-propenyl-)cyclohexane (**15**) (147 mg, 0.52 mmol) was exposed to the general cyclization/silylation procedure given. The reaction mixture changed from faint yellow to a darker, cloudy yellow over 1 h after which no starting material was observed by gas chromatography. Following workup and purification, Kugelrohr distillation provided **16** as a 1.6:1 mixture of diastereomers (194 mg, 0.48 mmol, 92% yield) which also contained 6% of inseparable isomeric impurities by gas chromatography: at 160 °C/0.06 mmHg; R_f 0.48 (hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53−7.49 (m, 2H), 7.36−7.30 (m, 3H), 4.43−4.36 (m, 1H), 1.91−0.90 (m, 17H), 0.87 (s, 9H), 0.68−0.49 (m, 1H), 0.35−0.28 (m, 3H), 0.06−0.01 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 134.2, 129.1, 127.8, 75.5, 51.0, 32.8, 26.1, 21.9, 18.6, −1.5, −1.8, −4.9; IR (neat) 2932, 2118 cm^{-1}; HRMS Calcd for $C_{24}H_{41}OSi_2^+$ $(M - H)^+$: 401.2696, found 401.2674; LRMS (EI) *m*/*z* 196 (20.2), 195 (100.0), 121 (43.4), 105 (15.0).

(1*R,5*S**,6*R**)-1-(*tert*-Butyldimethylsiloxy)-5-(hydroxymethyl)bicyclo[4.4.0]decane (17).** Silane **16** (161 mg, 0.40 mmol) in 2 mL of DMF was subjected Woerpel oxidation conditions given previously. Following workup, the crude alcohol was purified by flash chromatography. After prolonged exposure to reduced pressure (0.06 mmHg), **17** (84 mg, 0.28 mmol, 70% yield) was isolated as a clear oil which was >96% pure by gas chromatography: ot 152 °C/0.06 mmHg; R_f 0.29 (2:1 hexane: Et_2O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (dd, J = 10.7, 3.7 Hz, 1H), 3.54−3.46 (m, 1H), 1.90−1.63 (m, 6H), 1.53−1.12 (m, 11H), 0.87 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 75.5, 65.8, 44.8, 26.1, 22.1, 18.5, −1.5, −1.8; IR (neat) 3336, 2933, 2858 cm^{-1}; HRMS Calcd for $C_{17}H_{34}O_2Si^+$: 298.2328, found 298.2328; LRMS (EI) *m*/*z* 267 (20.3), 159 (12.3), 150 (26.7), 149 (100.0), 145 (12.9), 107 (33.0). Anal. Calcd for $C_{17}H_{34}O_2Si$: C, 68.39; H, 11.48. Found: C, 69.38; H, 11.30.

(1*R,5*S**,6*R**)-5-(Hydroxymethyl)bicyclo[4.4.0]-decanol (20).** The diene (1*R**,2*R**)-1-(trimethylsiloxy)-2-ethenyl-1-(2-propenyl)cyclohexane (**18**) (119 mg, 0.50 mmol) was reacted under the general cyclization/silylation conditions given. The reaction mixture changed from faint yellow to a darker, cloudy yellow over 1 h after which no starting material was observed by gas chromatography. Following workup, the crude product was purified by flash chromatography. Concentration under reduced pressure (0.06 mmHg) provided (1*R**,5*S**,6*R**)-1-(trimethylsiloxy)-5-[(methylphenylsilyl)methyl]bicyclo[4.4.0]decane (**19**) (157 mg, 0.44 mmol, 88% yield) as a 2:1 mixture of diastereomers which also contained another unidentified, cyclized isomer (approximately 18% of the isolated material by GC). In an attempt to determine the identity of this other isomer, an oxidation was performed on the silane mixture.

The mixture of **19** and the unknown cyclized silane isomer (157 mg, 0.44 mmol) was subjected to the Woerpel oxidation procedure given. Following workup, the major and minor products were separated by flash chromatography. Concentration of the major product under reduced pressure (0.06 mmHg) provided **20** (39.1 mg, 0.21 mmol, 48% yield) which was >99% pure by gas chromatography. The minor product was also isolated (11.1 mg, 0.06 mmol, 13.6% yield), but its structure was ambiguous. Characterization data is given for the major product: mp 110 °C; R_f 0.19 (3:1 EtOAc:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72 (dd, J = 10.7, 4.3 Hz, 1H), 3.65−3.57 (m, 1H), 1.81−1.53 (m, 9H), 1.51−1.21 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 71.7, 66.5, 44.3, 39.8, 22.7; IR (neat) 3347, 2927, 2861 cm^{-1}; HRMS Calcd for $C_{11}H_{20}O_2^+$: 184.1463, found 184.1471; LRMS (EI) *m*/*z* 184 (8.3), 153 (100.0), 111 (28.0), 97 (23.3). Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.77; H, 10.69.

(1*R,5*R**,6*S**)-1-(*tert*-Butyldimethylsiloxy)-5-[(methylphenylsilyl)methyl]bicyclo[4.4.0]decane (22).** The diene (1*R**,2*S**)-1-(*tert*-butyldimethylsiloxy)-2-ethenyl-1-(2-propenyl)cyclohexane (**21**) (143 mg, 0.51 mmol) was exposed to the general cyclization/silylation procedure. The reaction mixture changed from faint yellow to a darker, cloudy yellow over 1 h after which no starting material was observed by gas chromatography. Following workup, the crude product was purified by flash chromatography. Concentration under reduced pressure (0.06 mmHg) provided **22** as a 1.5:1 mixture of diastereomers (191 mg, 0.473 mmol, 93% yield) which was >98% pure by gas chromatography: R_f 0.53 (hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55−7.48 (m, 2H), 7.36−7.28 (m, 3H), 4.43−4.37 (m, 1H), 1.86−1.74 (m, 1H), 1.73−1.51 (m, 7H), 1.43−1.31 (m, 2H), 1.27−1.10 (m, 4H), 1.10−0.96 (m, 2H), 0.93−0.84 (m, 9H), 0.83−0.74 (m, 1H), 0.54−0.39 (m, 1H), 0.32−0.28 (m, 3H), 0.09−0.03 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 137.2, 134.3, 129.0, 128.9, 127.8, 74.6, 74.5, 53.5, 53.4, 40.1, 40.0, 35.7, 35.6, 33.3, 26.8, 26.7, 26.3, 26.2, 24.4, 21.7, 21.6, 19.1, 19.0, 17.9, 17.6, −1.79, −1.83, −1.87, −4.44, −5.12; IR (neat) 2927, 2854, 2116 cm^{-1}; HRMS Calcd for $C_{24}H_{42}OSi_2^+$: 402.2774, found 402.2754; LRMS (EI) *m*/*z* 402 (0.2), 346 (25.1), 345 (56.1), 270 (44.8), 269 (80.0), 201 (31.7), 196 (51.8), 195 (96.4), 191 (65.1), 122 (38.0), 121 (100.0), 107 (20.2), 105 (41.3), 91 (33.5).

(1*R,5*R**,6*S**)-1-(*tert*-Butyldimethylsiloxy)-5-(hydroxymethyl)bicyclo[4.4.0]decane (23).** Silane **22** (172 mg, 0.43 mmol) in 2 mL of DMF was subjected to the Woerpel oxidation procedure given. Following workup and purification, Kugelrohr distillation provided **23** as a 17.8:1 mixture of isomers (86.5 mg, 0.29 mmol, 68% yield) which was >98% pure by gas chromatography: ot 152 °C/0.06 mmHg; R_f 0.30 (3:1 hexanes:EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.59 (dd, J = 10.7, 3.2 Hz, 1H), 3.52 (dd, J = 10.7, 5.7 Hz, 1H), 1.77−0.96 (m, 17H), 0.91 (s, 9H), 0.08 (d, J = 1.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 74.3, 65.6, 47.6, 40.0, 39.8, 38.9, 29.9, 26.5, 26.4, 24.2, 21.4, 21.0, 19.1, −1.80, −1.83; IR (neat) 3331, 2928, 2855 cm^{-1}; HRMS Calcd for $C_{17}H_{34}O_2Si^+$: 298.2328, found 298.2316; LRMS (EI) *m*/*z* 298 (0.1), 267 (12.4), 150 (24.9), 149 (100.0), 107 (15.4).

(1*R,5*R**,6*S**)-5-[(Methylphenylsilyl)methyl]-1-(trimethylsiloxy)bicyclo[4.4.0]decane (25).** The diene (1*R**,2*S**)-2-ethenyl-1-(2-propenyl)-1-(trimethylsiloxy)cyclohexane (**24**) (121 mg, 0.51 mmol) was subjected to the general cyclization/silylation procedure given. The reaction mixture changed from faint yellow to a darker, cloudy yellow over 1 h after which no starting material was observed by gas chro-

matography. Following workup and purification by flash chromatography, concentration under reduced pressure (0.06 mmHg) at 80 °C provided **25** as an approximate 1.5:1 mixture of diastereomers (162 mg, 0.45 mmol, 89% yield) which was >98% pure by gas chromatography: R_f 0.41 (hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56−7.48 (m, 2H), 7.38−7.29 (m, 3H), 4.43−4.36 (m, 1H), 1.81−1.30 (m, 10H), 1.25−0.85 (m, 6H), 0.80−0.68 (m, 1H), 0.57−0.41 (m, 1H), 0.35−0.27 (m, 3H), 0.13−0.01 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 134.3, 129.0, 127.7, 74.8, 74.7, 52.9, 40.0, 39.9, 35.7, 35.5, 33.4, 26.7, 26.6, 24.5, 21.8, 21.7, 17.7, 17.6, 2.6, 2.5, −4.3, −4.9; IR (neat) 2930, 2850, 2116 cm^{-1}; HRMS Calcd for $C_{21}H_{36}OSi_2^+$: 360.2305, found 360.2323; LRMS (EI) *m*/*z* 360 (4.7), 303 (22.6), 225 (81.8), 209 (78.1), 192 (35.9), 121 (100.0), 105 (14.9). Anal. Calcd for $C_{21}H_{36}Si_2O$: C, 69.93; H, 10.06. Found: C, 70.25; H, 10.36.

(1*R,5*R**,6*S**)-5-(Hydroxymethyl)bicyclo[4.4.0]-decanol (26).** The 1.5:1 diastereomeric mixture of silanes **25** (140 mg, 0.39 mmol) in 2.0 mL of DMF was subjected to the Woerpel oxidation procedure given. After workup and purification, concentration under reduced pressure (0.06 mmHg) provided **26** (38 mg, 0.21 mmol, 53% yield) as a single stereoisomer which was >99% pure by gas chromatography. Recrystallization from chloroform and petroleum ether provided crystals suitable for X-ray crystallography. An X-ray crystal structure provided unambiguous structure identification of the major isomer: mp 111 °C; R_f 0.08 (3:1 hexanes: EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.05 (dd, J = 10.7, 3.1 Hz, 1H), 3.95 (dd, J = 10.7, 5.9 Hz, 1H), 2.30 (br s, 1H), 2.26−2.06 (m, 4H), 2.05−1.89 (m, 6H), 1.83 (br s, 1H), 1.79−1.66 (m, 3H), 1.65−1.55 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 70.2, 65.1, 44.9, 40.0, 39.9, 39.2, 29.7, 26.1, 24.3, 21.2, 20.8; IR (neat) 3382, 2927, 2855 cm^{-1}; HRMS Calcd for $C_{11}H_{20}O_2^+$: 184.1463, found 184.1467; LRMS (EI) *m*/*z* 184 (8.9), 154 (10.8), 153 (100.0), 111 (18.7), 97 (22.4). Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.96; H, 11.37.

(1*R,5*R**/*S**,6*S**)-5-[(Methylphenylsilyl)methyl]-1-(trimethylsiloxy)bicyclo[4.3.0]nonane (28).** (1*R**,2*S**)-2-Ethenyl-1-(2-propenyl)-1-(trimethylsiloxy)cyclopentane (**27**) (88 mg, 0.39 mmol) was exposed to the general cyclization/silylation procedure. The reaction mixture was initially bright yellow and faded to light yellow over 10 min. After 45 min no starting material was observed by gas chromatography. Following workup and purification, Kugelrohr distillation provided **28** (115 mg, 0.34 mmol, 88% yield) as a mixture of diastereomers which was >98% pure by gas chromatography: ot 136 °C/0.05 mmHg; R_f 0.44 (hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55−7.49 (m, 2H), 7.36−7.29 (m, 3H), 4.45−4.36 (m, 1H), 2.51−1.80 (m, 1H), 1.79−1.22 (m, 8H), 1.19−1.01 (m, 2H), 0.95−0.54 (m, 5H), 0.32−0.30 (m, 3H), 0.78−0.00 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.3, 129.1, 129.0, 127.8, 127.7, 82.1, 81.9, 57.5, 49.3, 46.7, 38.7, 37.9, 36.7, 36.5, 34.7, 33.1, 29.8, 29.7, 27.6, 26.4, 25.1, 22.2, 22.0, 20.8, 20.0, 19.2, 2.1, 2.0, −4.8, −4.9; IR (neat) 2116, 1052 cm^{-1}; HRMS Calcd for $C_{20}H_{34}OSi_2^+$: 346.2148, found 346.2138; LRMS (EI) *m*/*z* 346 (6.6), 211 (38.9), 209 (73.3), 178 (41.2), 121 (100.0), 75 (38.7), 73 (72.9).

(1*R,5*R**/*S**,6*S**)-5-(Hydroxymethyl)bicyclo-[4.3.0]nonanol (29).** The silane **28** (94 mg, 0.28 mmol) in 1.5 mL of DMF was subjected to the Woerpel oxidation procedure given. After workup, the products appeared to be a 1:1 mixture of diastereomeric diols by gas chromatography. The diastereomers could be easily separated by flash chromatography. Concentration under reduced pressure (0.06 mmHg) provided a crystalline solid for the separate diastereomers of **29** (25 mg, 0.15 mmol, 51% yield). Recrystallization of one of the diastereomers from chloroform provided crystals suitable for X-ray crystallography. An X-ray crystal structure provided unambiguous structure identification of this diastereomer. (1*R**,5*R**,6*S**)-5-(Hydroxymethyl)bicyclo[4.3.0]nonanol: mp 127 °C; R_f 0.21 (1:1 hexanes:EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.64 (dd, J = 10.7, 4.0 Hz, 1H), 3.44 (dd, J = 10.4, 6.7 Hz, 1H), 1.94−1.72 (m, 4H), 1.71−1.55 (m, 5H), 1.54−1.37 (m, 2H), 1.36−1.21 (m, 2H), 1.20−1.09 (m, 1H), 1.08−0.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 79.2, 67.0, 49.2, 39.7, 39.0, 36.3, 28.9, 25.8, 21.3, 20.1; IR (neat) 3331, 2936, 2849, 1042 cm^{-1}; HRMS Calcd for $C_{10}H_{18}O_2^+$: 170.1307, found 170.1303; LRMS (EI) *m*/*z* 170 (7.9), 139 (100.0), 121 (12.1), 109 (11.0), 97 (68.1). Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 71.10; H, 10.72.

(1*R**,5*S**,6*S**)-5-(Hydroxymethyl)bicyclo[4.3.0]nonanol: mp 88 °C; R_f 0.15 (1:1 hexanes:EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.4 (d, J = 5.9 Hz, 2H), 2.02−1.85 (m, 2H), 1.84−1.72 (m, 2H), 1.71−1.57 (m, 4H), 1.56−1.25 (m, 5H), 1.14 (br s, 1H), 1.08−0.88 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 78.8, 68.4, 47.7, 39.5, 38.8, 36.1, 29.2, 27.3, 24.6, 20.3; IR (neat) 3369, 2924, 2864, 1046 cm^{-1}; HRMS Calcd for $C_{10}H_{18}O_2^+$: 170.1307, found 170.1323; LRMS (EI) *m*/*z* 170 (21.0), 141 (52.4), 139 (67.4), 128 (61.8), 123 (47.8), 121 (14.6), 109 (28.4), 97 (100.0), 95 (46.6), 84 (66.0).

(1*R,5*R**/*S**,6*S**)-1-(*tert*-Butyldimethylsiloxy)-5-[(methylphenylsilyl)methyl]bicyclo[4.3.0]nonane (31).** (1*R**,2*S**)-1-(*tert*-Butyldimethylsiloxy)-2-ethenyl-1-(2-propenyl-)cyclopentane (**30**) (67 mg, 0.25 mmol) was exposed to the general cyclization/silylation procedure given. The reaction mixture was initially yellow and faded to a light, cloudy yellow over 1 h after which no starting material was observed by gas chromatography. Following workup and purification, Kugelrohr distillation provided **31** (90 mg, 0.23 mmol, 92% yield) as a 1.7:1 mixture of diastereomers which was >99% pure by gas chromatography: ot 152 °C/0.06 mmHg; R_f 0.60 (hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57−7.49 (m, 2H), 7.38−7.29 (m, 3H), 4.45−4.38 (m, 1H), 2.06−1.86 (m, 1H), 1.85−1.28 (m, 11H), 1.24−1.09 (m, 1H), 1.08−0.90 (m, 2H), 0.88−0.56 (m, 10H), 0.36−0.29 (m, 3H), 0.09- −0.08 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 134.3, 129.1, 129.0, 127.8, 127.7, 82.1, 82.0, 57.8, 49.7, 47.4, 47.1, 38.7, 38.0, 36.7, 36.2, 35.9, 34.9, 34.8, 32.9, 29.7, 29.6, 27.7, 26.5, 26.1, 25.1, 22.3, 22.1, 22.0, 20.8, 20.0, 19.1, 18.7, 18.6, −2.4, −2.5, −2.6, −2.7, −4.7, −5.2; IR (neat) 2115, 1046 cm^{-1}; LRMS (EI) *m*/*z* 388 (0.2), 332 (18.1), 333 (44.9), 256 (30.5), 255 (59.8), 253 (51.9), 196 (48.4), 195 (82.4), 178 (40.8), 177 (51.3), 122 (44.8), 121 (100.0), 107 (15.2), 105 (35.4), 75 (90.8). Anal. Calcd for $C_{23}H_{40}OSi_2$: C, 71.06; H, 10.37. Found: C, 71.30; H, 10.42.

(1*R,5*R**/*S**,6*S**)-1-(*tert*-Butyldimethylsiloxy)-5-(hydroxymethyl)bicyclo[4.3.0]nonane (32).** Silane **31** (72 mg, 0.185 mmol) was subjected to the Woerpel oxidation conditions. Following workup, the products appeared to be a 1:1 mixture of diastereomeric alcohols by gas chromatography. The diastereomers were purified, but could not be separated by flash chromatography. Kugelrohr distillation provided **32** (41 mg, 0.16 mmol, 86% yield) as a 1:1 mixture of diastereomers which was >99% pure by gas chromatography: ot 132°/0.06 mmHg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.65−3.36 (m, 2H), 2.04−1.89 (m, 1H), 1.84−1.11 (m, 12H), 1.10−0.84 (m, 11H), 0.09−0.04 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 82.0, 81.5, 68.6, 67.2, 51.5, 50.1, 40.0, 39.2, 38.2, 38.0, 36.7, 36.0, 29.4, 29.0, 27.6, 26.1, 26.07, 26.0, 24.4, 21.4, 20.7, 20.5, 18.7, −2.3, −2.4, −2.6; IR (neat) 3326, 2928, 2856, 1046 cm^{-1}; LRMS (EI) *m*/*z* 254 (3.1), 253 (13.7), 171 (40.8), 151 (19.5), 136 (46.2), 135 (100.0), 107 (38.4), 105 (16.1), 93 (73.7), 79 (60.5), 75 (86.1). Anal. Calcd for $C_{16}H_{32}O_2Si$: C, 67.54; H, 11.34. Found: C, 67.83; H, 11.55.

1,2,3,4-Tetrahydro-1-naphthalenemethanol (36). The aromatic diene 1-ethenyl-2-(2-propenyl)benzene (**33**) (79 mg, 0.55 mmol) was exposed to the general cyclization/silylation procedure given. The reaction mixture changed from faint yellow to dark yellow over 1 h after which no starting material was observed by gas chromatography. Following workup, the crude product was purified by flash chromatography in hexanes and then concentrated to provide a 7:1 mixture of cyclized/silylated products (**34** and **35**) (145 mg, 0.542 mmol, 99% yield) as a clear oil which was >97% pure by GC analysis.

The silane mixture was then diluted with chloroform (5 mL) and cooled to 0 °C prior to the addition of HBF_4·OEt_2 (169 mg, 10.4 mmol). This mixture was stirred for 1 h at 0 °C. The mixture was then stirred for 15 min at 0 °C under reduced pressure (0.04 mmHg) prior to warming to room temperature for 5 min at reduced pressure. A light purple residue remained to which 5 mL of both THF and MeOH were added followed by KF (146 mg, 2.5 mmol), $KHCO_3$ (303 mg, 3.0 mmol), and a

30% H_2O_2 solution (1.2 g, 10.5 mmol). This mixture heated at reflux for 18 h. The mixture was then cooled to room temperature, and approximately 1 mL of water was added followed by enough K_2CO_3 to make a paste. The organics were separated, and the paste was extracted several times with EtOAc. The combined organics were concentrated by rotary evaporation, and the crude products were purified by flash chromatography. Kugelrohr distillation provided a 14:1 mixture of **36** and 1,2,3,4-tetrahydro-2-naphthalenemethanol (**37**) (71.7 mg, 0.442 mmol, 81% yield) as a clear oil which was >99% pure by GC analysis. The major product **36** could be partially isolated by flash chromatography to allow for complete characterization. The ^{1}H NMR spectra were in agreement with known literature spectra for **36**:[10] ot 104 °C/0.06 mmHg; R_f 0.13 (10:1 hexanes:EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24−7.19 (m, 1H), 7.16−7.07 (m, 3H), 3.78 (d, J = 6.4 Hz, 2H), 2.76 (pent, J = 5.6 Hz, 1H), 2.81−2.74 (m, 2H), 1.98−1.81 (m, 3H), 1.81−1.68 (m, 1H), 1.55 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 136.6, 129.3, 128.7, 126.1, 125.7, 67.1, 40.2, 29.7, 25.1, 19.7; IR (neat) 3334 br, 3060, 3016, 2930, 1035, 758 cm^{-1}; HRMS Calcd for $C_{11}H_{14}O^+$: 162.1045, found 162.1045; LRMS (EI) *m*/*z* 162 (10.7), 132 (12.0), 131 (100.0), 128 (10.2), 116 (10.4), 115 (12.9), 91 (25.8).

A small amount of the minor product **37** was also isolated allowing for NMR analysis. Both the ^{1}H NMR and ^{13}C NMR spectra were in good agreement with known literature spectra for **37**:[10] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (s, 4H), 3.62 (dd, J = 6.4, 2.6 Hz, 2H), 2.94−2.79 (m, 3H), 2.50 (dd, J = 16.5, 10.6 Hz, 1H), 2.07−1.91 (m, 2H), 1.58 (br s, 1H), 1.49−1.38 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7, 135.9, 129.2, 128.8, 125.6, 112.1, 67.7, 37.0, 32.4, 28.7, 25.9; IR (neat) 3342 br, 2920, 1065, 1024 cm^{-1}; HRMS Calcd for $C_{11}H_{14}O^+$: 162.1045, found 162.1073; LRMS (EI) *m*/*z* 162 (34.9), 144 (29.6), 129 (100.0), 116 (24.5).

(1*R,2*S**,5*S**)-2-[(Phenylsilyl)methyl]-1-(trimethylsiloxy)bicyclo[4.3.0]nonane (39).** The diene (1*R**,2*S**)-1,2-diethenyl-1-(trimethylsiloxy)cyclohexane (**38**) (55 mg, 0.245 mmol) was subjected to the general cyclization/silylation procedure. The reaction mixture was light yellow and became cloudy yellow over 1 h after which no starting material was observed by gas chromatography. Following workup, the crude products were separated and purified by flash chromatography. After exposure to reduced pressure (0.06 mmHg), the major product **39** (37 mg, 0.12 mmol, 48% yield) was isolated as an 8:1 mixture of diastereomers which also contained 6% of other, unidentified isomers by gas chromatography: R_f 0.46 (hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58−7.51 (m, 2H), 7.40−7.31 (m, 3H), 4.40−4.24 (m, 2H), 2.04−1.80 (m, 2H), 1.78−0.70 (m, 13H), 0.65−0.53 (m, 1H), 0.16- −0.06 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 134.4, 132.5, 129.6, 128.0, 85.0, 45.6, 44.9, 33.6, 30.1, 28.1, 25.9, 25.6, 21.7, 15.2, 3.0, 2.6, 2.1; IR (neat) 2135, 1046 cm^{-1}; HRMS Calcd for $C_{19}H_{32}OSi_2^+$: 332.1992, found 332.1967; LRMS (EI) *m*/*z* 332 (2.7), 259 (11.0), 195 (89.5), 183 (100.0), 121 (23.9), 107 (36.2), 105 (19.4).

A minor, uncyclized product, (1*R**,2*S**)-1-ethenyl-2-[(2-phenylsilyl)ethyl]-1-(trimethylsiloxy)cyclohexane (**40**) (11.5 mg, 0.04 mmol, 15% yield) was also isolated: R_f 0.28 (hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59−7.49 (m, 2H), 7.41−7.29 (m, 3H), 6.0 (dd, J = 17.0, 11.0 Hz, 1H), 5.15−4.94 (m, 2H), 4.2 (t, J = 3.6 Hz, 2H), 1.77−1.38 (m, 6H), 1.32−1.07 (m, 4H), 1.06−0.94 (m, 1H), 0.93−0.77 (m, 1H), 0.76−0.63 (m, 1H), 0.06 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 135.2, 132.9, 129.4, 127.9, 112.2, 77.7, 49.2, 37.1, 26.1, 25.5, 24.6, 21.8, 7.8, 2.5; IR (neat) 2131, 1046 cm^{-1}; HRMS Calcd for $C_{19}H_{32}OSi_2^+$: 332.1992, found 332.1958; LRMS (EI) *m*/*z* 332 (2.3), 259 (14.7), 195 (63.0), 181 (25.0), 155 (33.5), 107 (63.8), 105 (32.0), 78 (45.5), 73 (100.0).

(1*R,2*S**,5*R**)-2-[(Methylphenylsilyl)methyl]-1-(trimethylsiloxy)bicyclo[4.3.0]nonane (41).** (1*R**,2*S**)-1,2-Diethenyl-1-(trimethylsiloxy)cyclohexane (**38**) (111 mg, 0.495 mmol) was exposed to the cyclization/silylation procedure given. The reaction mixture was light yellow and became cloudy yellow over 6 h after which no starting material was observed by gas chromatography. Following workup and purification, Kugelrohr distillation provided **41** (142 mg, 0.396 mmol, 80% yield) as a 4.4:1 mixture of diastereomers which also contained 7% of other, unidentified isomers as indicated by gas chromatography: ot 122 °C/0.06 mmHg; R_f 0.45 (hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55−7.49 (m, 2H), 7.37−7.31 (m, 3H), 4.47−4.34 (m, 1H), 2.09−1.83 (m, 2H), 1.74−1.23 (m, 10H), 1.22−0.88 (m, 4H), 0.61−0.48 (m, 1H), 0.38−0.31 (m, 3H), 0.16−0.07 (m, 1H), 0.05−0.00 (m, 6H), −0.07 to −0.10 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 134.4, 134.3, 129.2, 127.9, 85.2, 45.6, 44.5, 33.6, 30.2, 28.2, 25.9, 25.7, 21.8, 18.2, 2.1, 2.0, −5.6; IR (neat) 2118, 1036 cm^{-1}; LRMS (EI) *m*/*z* 346 (16.4), 373 (13.0), 209 (73.5), 183 (100.0), 178 (33.9), 170 (31.7), 121 (93.0), 105 (14.4), 91 (19.9), 75 (35.3). Anal. Calcd for $C_{21}H_{34}OSi_2$: C, 70.32; H, 9.56. Found: C, 69.98; H, 9.59.

(1*R,2*S**,5*R**)-2-(Hydroxymethyl)bicyclo[4.3.0]nonan-1-ol (42).** In a nitrogen atmosphere glovebox, $Cp^*_2YCH_3$·THF (6 mg, 0.013 mmol) was dissolved in benzene-d_6 (0.5 mL) prior to the addition of methylphenylsilane (35 mg, 0.28 mmol) and **38** (56 mg, 0.25 mmol). The reaction mixture was transferred to a J. Young NMR tube and removed from the glovebox. The mixture remained light yellow over a 7 h period after which no starting material was observed by ^{1}H NMR. The reaction mixture was filtered through a small plug of Florisil to remove the catalyst prior to concentration by rotary evaporation. After further concentration under reduced pressure (0.06 mmHg), an oxidation was performed on the crude silane **41**.

The crude silane **41** (assume 0.25 mmol) in 1.5 mL of DMF was subjected to the Woerpel oxidation conditions given. Following workup and purification, concentration under reduced pressure (0.06 mmHg) provided the crystalline solid **42** as a single diastereomer (20 mg, 0.12 mmol, 48% yield) that was >99% pure by gas chromatography. Recrystallization from chloroform provided crystals suitable for X-ray crystallography. An X-ray crystal structure provided unambiguous structure identification of the diastereomers: mp 132 °C; R_f 0.47 (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.65−3.53 (m, 1H), 3.39−3.26 (m, 1H), 2.09−1.90 (m, 2H), 1.82 (d, J = 12.6 Hz, 1H), 1.75−1.49 (m, 5H), 1.48−1.06 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 79.7, 64.9, 51.7, 45.6, 33.7, 27.6, 25.5, 25.0, 21.1; IR (neat) 3322, 2939, 1061 cm^{-1}; LRMS (EI) *m*/*z* 170 (0.4), 152 (15.3), 98 (100.0).

(1*R,3*S**,5*S**)-1-(*tert*-Butyldimethylsiloxy)-3-[(phenylsilyl)methyl]bicyclo[3.3.0]octane (44).** The triene 4-*tert*-(butyldimethylsiloxy)-4-ethenyl-1,6-heptadiene (**43**) (0.127 g, 0.50 mmol) was exposed to the general cyclization/silylation procedure. The reaction mixture changed from faint yellow to dark yellow over 1 h and was found to be complete. Following workup, the crude products were purified by flash chromatography using hexanes. The diastereoselectivity was 3:1 by gas chromatography. The major diastereomer could be completely separated from the minor diastereomer and isomeric impurities. Kugelrohr distillation provided the clear oil **44** (0.0718 g, 0.2 mmol, 40% yield). The minor diastereomer was separated along with other isomers. Kugelrohr distillation provided the minor diastereomer [(1*R**,3*R**,5*R**) isomer] as a clear oil (0.0328 g, 0.09 mmol, 18% yield) which also contained 18% impurities by gas chromatography. The data are given for the isolated major diastereomer: ot 110°/0.05 mmHg; R_f 0.44 (hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62−7.47 (m, 2H), 7.41−7.24 (m, 3H), 4.28−4.24 (t, J = 3.7 Hz, 2H), 2.86−2.73 (m, 1H), 2.17−2.03 (m, 1H), 2.02−1.88 (m, 3H), 1.81−1.68 (m, 1H), 1.64−1.54 (m, 1H), 1.47−1.31 (m, 3H), 1.22−1.09 (m, 3H), 1.04 (dd, J = 12.6, 8.3 Hz, 1H), 0.82 (s, 9H), 0.02 (d, J = 16.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 132.8, 129.4, 127.9, 94.2, 56.0, 43.8, 40.3, 33.0, 32.5, 28.3, 25.8, 22.9, 20.0, 18.3, −3.1; IR (neat) 2134 cm^{-1}; HRMS Calcd for $C_{21}H_{35}OSi_2^+$ (M − H)$^+$: 359.2226, found 359.2219; LRMS (EI) *m*/*z* 359 (0.1), 303 (15.1), 228 (10.2), 227 (44.9), 199 (11.5), 183 (16.0), 182 (27.3), 181 (100.0), 151 (18.5), 121 (11.5), 107 (35.3), 105 (19.8). Anal. Calcd for $C_{21}H_{36}OSi_2$: C, 69.93%; H, 10.06%. Found: C, 70.32%; H, 10.38%.

(1*R,3*S**,5*S**)-1-(*tert*-Butyldimethylsiloxy)-3-(hydroxymethyl)bicyclo[3.3.0]octane (46).** Silane **44** (125 mg, 0.35 mmol) was subjected to the Woerpel oxidation procedure given. The mixture was heated to 50 °C and stirred

for 5 h over which time it became a faint yellow color and contained a white precipitate. Following workup, the products were purified by flash chromatography. Concentration under reduced pressure (0.06 mmHg) provided **46** (39.6 mg, 0.15 mmol, 44% yield) as a single stereoisomer which was >99% pure by gas chromatography. Recrystallization from hexanes provided suitable crystals for X-ray crystallography. An X-ray crystal structure provided unambiguous structure identification of the major isomer: mp 95−96 °C; R_f 0.13 (5:1 hexanes:EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.61−3.49 (m, 2H), 2.80−2.74 (m, 1H), 2.19−2.06 (m, 1H), 2.05−1.91 (m, 1H), 1.90−1.77 (m, 2H), 1.69−1.53 (m, 2H), 1.49−1.32 (m, 4H), 1.30−1.19 (m, 1H), 1.10 (dd, J = 12.6, 8.0 Hz, 1H), 0.85 (s, 9H), 0.074 (s, 3H), 0.064 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 93.6, 67.8, 56.2, 46.6, 37.2, 32.8, 28.5, 26.2, 25.8, 22.7, 18.3, −3.0, −3.1; IR (neat) 3218, 2951, 2928, 2856 cm^{-1}; HRMS Calcd for $C_{15}H_{30}O_2Si^+$: 270.2019, found 270.1987; LRMS (EI) *m*/*z* 270 (0.4), 213 (10.9), 157 (17.6), 121 (79.2), 119 (12.1), 93 (37.5), 79 (42.8), 77 (11.7), 75 (100.0), 73 (31.4). Anal. Calcd for $C_{15}H_{30}O_2Si$: C, 66.60; H, 11.18. Found: C, 66.90; H, 11.50.

(1*R,3*S**,5*S**)-3-(Hydroxymethyl)bicyclo[3.3.0]-octanol (49).** The triene 4-ethenyl-4-(trimethylsiloxy)-1,6-heptadiene (**47**) (107 mg, 0.51 mmol) was exposed to the general cyclization/silylation procedure. The reaction mixture changed from faint yellow to bright yellow over 1 h after which no starting material was observed by gas chromatography. After workup and concentration under reduced pressure (0.06 mmHg), a ^{1}H NMR spectrum of the crude mixture showed no olefinic protons were present. The crude silane **48** appeared to be one isomer by gas chromatography. Because of difficulties in purification, an oxidation was performed on the crude silane.

The crude silane **48** (assume 0.51 mmol) in 2.5 mL of DMF was subjected to the Woerpel oxidation protocol given. Following workup, the products were purified by flash chromatography. Concentration under reduced pressure (0.06 mmHg) provided the crystalline solid **49**[21] as a single diastereomer (58 mg, 0.37 mmol, 73% yield) which was >99% pure by gas chromatography: mp 95−96 °C; R_f 0.15 (2:1 EtOAc:hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.61−4.49 (m, 2H), 2.93−2.79 (m, 1H), 2.28−2.12 (m, 1H), 2.11−1.99 (m, 1H), 1.99−1.88 (m, 1H), 1.78 (dd, J = 12.9, 8.0 Hz, 1H), 1.64−1.28 (m, 8H), 1.18 (dd, J = 12.9, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 91.9, 67.4, 54.1, 46.2, 36.9, 32.8, 28.0, 25.8, 22.4; IR (neat) 3363, 2953, 2868 cm^{-1}; HRMS Calcd for $C_9H_{16}O_2^+$: 156.1150, found 156.1158; LRMS (EI) *m*/*z* 156 (1.5), 138 (14.5), 127 (22.8), 125 (37.3), 123 (16.8), 114 (29.2), 109 (53.3), 97 (70.3), 83 (100.0), 81 (42.5). Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.36; H, 10.67.

(1*R,2*R**,3*R**/3*S**,5*S**)-2-(*tert*-Butyldimethylsiloxy)-3-[(phenylsilyl)methyl]bicyclo[3.3.0]octane (56).** The triene (3*R**,4*S**)-3-(*tert*-butyldimethylsiloxy)-4-ethenyl-1,6-heptadiene (**55a**) (127 mg, 0.50 mmol) was exposed to the general cyclization/silylation procedure given. The reaction mixture changed from faint yellow to dark yellow over 1 h after which no starting material was observed by gas chromatography. Following workup and purification, Kugelrohr distillation provided **56** as a 2:1 mixture of diastereomers (139 mg, 0.385 mmol, 77% yield) which also contained 7% of inseparable isomeric impurities by gas chromatography. The major product could be partially separated from the minor product by flash chromatography allowing for complete characterization: ot 130 °C/0.07 mmHg; R_f 0.34 (hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57−7.53 (m, 2H), 7.41−7.32 (m, 3H), 4.33−4.24 (m, 2H), 3.6 (d, J = 4.3 Hz, 1H), 2.39−2.29 (m, 1H), 2.15−2.04 (m, 1H), 2.04−1.93 (m, 3H), 1.65−1.51 (m, 2H), 1.38−1.23 (m, 3H), 1.05−0.93 (m, 2H), 0.84 (s, 9H), 0.71−0.60 (m, 1H), −0.02 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 132.5, 129.5, 128.0, 78.1, 57.5, 53.7, 48.6, 36.0, 29.0, 26.8, 25.9, 20.5, 18.2, 17.9, −4.6, −4.8; IR (neat) 2955, 2856, 2136 cm^{-1}; HRMS Calcd for $C_{21}H_{36}Si_2O^+$: 360.2305, found 360.2314; LRMS (EI) *m*/*z* 360 (1.1), 225 (16.5), 211 (52.9), 195 (10.6), 181 (100.0), 107 (15.2). Anal. Calcd for $C_{21}H_{36}Si_2O$: C, 69.93; H, 10.06. Found: C, 70.17; H, 10.24.

(1*R,2*S**,3*R**/3*S**,4*S**)-2-(*tert*-Butyldimethylsiloxy)-3-[(phenylsilyl)methyl]bicyclo[3.3.0]octane (57).** The triene (3*R**,4*R**)-3-(*tert*-butyldimethylsiloxy)-4-ethenyl-1,6-heptadiene (**55b**) (63 mg, 0.26 mmol) was subjected to the general cyclization/silylation procedure. The reaction mixture changed from faint yellow to dark yellow over 1 h after which no starting material was observed by gas chromatography. Following workup and purification, Kugelrohr distillation provided **57** as a 7.2:1 mixture of diastereomers (72 mg, 0.20 mmol, 78% yield) which was >97% pure by gas chromatography. The major product could be partially separated from the minor product by HPLC. The NMR data given is for the major product. All other characterization data was obtained on the diastereomeric mixture: ot 130 °C/0.07 mmHg; R_f 0.19 (hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57−7.53 (m, 2H), 7.39−7.31 (m, 3H), 4.31−4.24 (m, 2H), 3.44−3.40 (m, 1H), 2.39−2.31 (m, 1H), 1.98−1.89 (m, 2H), 1.82−1.52 (m, 5H), 1.37−1.29 (m, 2H), 1.12−1.06 (m, 3H), 1.85 (s, 9H), 0.20 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 132.6, 129.5, 128.0, 83.8, 59.6, 50.3, 47.8, 32.9, 28.6, 26.8, 25.9, 25.5, 18.0, 16.9, −4.0, −4.5; IR (neat) 2955, 2866, 2133 cm^{-1}; HRMS Calcd for $C_{21}H_{36}OSi_2^+$: 360.2305, found 360.2306; LRMS (EI) *m*/*z* 360 (0.07), 225 (15.5), 211 (52.4), 182 (29.8), 181 (100.0), 121 (11.6), 107 (28.7). Anal. Calcd for $C_{21}H_{36}OSi_2$: C, 69.93; H, 10.06. Found: C, 69.79; H, 10.33.

(1*R,2*R**,3*R**,5*S**)-3-(Hydroxymethyl)bicyclo[3.3.0]-octan-2-ol (60).** The triene (3*R**,4*S**)-4-ethenyl-3-(trimethylsiloxy)-1,6-heptadiene (**58**) (57 mg, 0.27 mmol) was subjected to the general cyclization/silylation protocol. The reaction mixture changed from faint yellow to clear over 1 h after which no starting material was observed by gas chromatography. After workup and concentration under reduced pressure (0.06 mmHg), a ^{1}H NMR spectrum of the crude mixture showed no olefinic protons were present. The crude silane **59** appeared to be a 4:1 diastereomeric mixture by gas chromatography. Because of difficulties in purification, an oxidation was performed on the crude silane.

The crude silane **59** (assume 0.27 mmol) in 1.5 mL of DMF was exposed to the Woerpel oxidation procedure given. Following workup and purification, concentration under reduced pressure (0.06 mmHg) provided the crystalline solid **60** (15.4 mg, 0.1 mmol, 37% yield over two steps) as a 4:1 mixture of diastereomers. The major diastereomer could be cleanly separated by flash chromatography. The structure of **60** was determined unambiguously from a single-crystal X-ray structure: mp 84 °C; R_f 0.26 (1:1 hexanes:EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.24−4.18 (m, 1H), 3.8 (dd, J = 11.0, 4.6 Hz, 1H), 3.74−3.66 (m, 1H), 2.79−2.57 (m, 2H), 2.20−1.95 (m, 4H), 1.71−1.57 (m, 2H), 1.49−1.20 (m, 4H), 1.10−0.91 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 71.0, 63.8, 59.2, 51.5, 47.6, 28.8, 28.1, 26.6, 19.7; IR (neat) 3362, 2935, 2865 cm^{-1}; HRMS Calcd for $C_9H_{14}O^+$ (M − H_2O)$^+$: 138.1045, found 138.1021; LRMS (EI) *m*/*z* 156 (0.5), 111 (11.2), 95 (32.3), 79 (36.6), 67 (99.5), 57 (56.9), 41 (100.0). Anal. Calcd for $C_9H_{16}O_2$: C, 69.16; H, 10.32. Found: C, 68.94; H, 10.46.

5-Ethenyl-1,9-bis(methylphenylsilyl)-5-(trimethylsiloxy)nonane (62). Following the general cyclization/silylation procedure given, $Cp^*_2YCH_3$·THF (12 mg, 0.025 mmol) was dissolved in cyclohexane (1 mL) prior to the addition of methylphenylsilane (141 mg, 1.15 mmol) and 5-ethenyl-5-(trimethylsiloxy)-1,8-nonadiene (**61**) (120 mg, 0.50 mmol). The reaction mixture was initially bright yellow and remained this color for 25 h after which no starting material was observed by gas chromatography. A small amount of monomeric silane, less than 4%, could still be observed by gas chromatography. Following workup, the crude product was purified by flash chromatography. Kugelrohr distillation provided **62** (215 mg, 0.45 mmol, 89% yield) as a clear oil which was >98% pure by gas chromatography: ot 180 °C/0.06 mmHg; R_f 0.29 (20:1 hexanes:EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55−7.49 (m, 4H), 7.39−7.31 (m, 6H), 5.78−5.69 (m, 1H), 5.12−4.97 (m, 2H), 4.34 (q, J = 3.5 Hz, 2H), 1.52−1.42 (m, 4H), 1.40−1.20 (m,

(21) The stereochemistry of **54** was confirmed after comparing NMR spectra with the diol obtained from alcohol **51** after TBDMS removal with TBAF.

8H), 0.92−0.76 (m, 4H), 0.32 (dd, J = 3.8, 1.1 Hz, 6H), 0.08 (d, J = 1.0 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 136.7, 134.3, 129.1, 127.8, 112.5, 78.4, 40.0, 27.3, 24.8, 13.4, 2.6, −5.7; IR (neat) 2938, 2113 cm^{-1}; LRMS (EI) *m/z* 305 (35.5), 215 (46.9), 211 (36.5), 210 (71.1), 209 (100.0), 135 (38.3), 133 (38.8), 121 (78.2), 105 (12.2), 73 (74.4). Anal. Calcd for $C_{28}H_{46}OSi_3$: C, 69.64; H, 9.60. Found: C, 70.05; H, 9.81.

(1*R,3*R**,6*R**)-3-[(Methylphenylsilyl)methyl]-bicyclo[4.4.0]decane (64).** The triene 5-ethenyl-1,8-nonadiene (**63**) (35 mg, 0.23 mmol) was subjected to the general cyclization/silylation procedure given. The reaction mixture was initially bright yellow and faded to light yellow over 1 h after which no starting material was observed by gas chromatography. Following workup and purification, Kugelrohr distillation provided **64** (43 mg, 0.16 mmol, 68% yield) as a 12.8:1 diastereomeric mixture which was >98% pure by gas chromatography: ot 118 °C/0.07 mmHg; R_f 0.71 (hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55−7.48 (m, 2H), 7.38−7.30 (m, 3H), 4.4 (q, J = 3.5 Hz, 1H), 1.78−1.36 (m, 7H), 1.30−1.10 (m, 3H), 1.07−0.62 (m, 9H), 0.31 (dd, J = 3.8, 1.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 134.3, 129.0, 127.8, 44.1, 44.0, 43.1, 43.0, 42.9, 36.5, 36.4, 34.6, 34.5, 34.1, 34.0, 33.8, 26.7, 26.6, 22.4, −4.8, −4.9; IR (neat) 2914, 2848, 2115 cm^{-1}; HRMS Calcd for $C_{18}H_{29}Si^+$ $(M + H)^+$: 273.2038, found 273.2005; LRMS (EI) *m/z* 272 (0.4), 195 (57.6), 135 (20.2), 121 (100.0), 107 (10.9), 105 (14.2). Anal. Calcd for $C_{18}H_{28}Si$: C, 79.33; H, 10.36. Found: C, 79.34; H, 10.43.

(1*R,3*R**,6*R**)-3-(Hydroxymethyl)bicyclo[4.4.0]-decane (65).** Silane **64** (89.5 mg, 0.33 mmol) in 1.5 mL of DMF was subjected to the Woerpel oxidation procedure given. Following workup and purification, Kugelrohr distillation provided the clear oil **65** (47.1 mg, 0.28 mmol, 85% yield) as a single diastereomer which was >97% pure by gas chromatography: ot 106 °C/0.07 mmHg; R_f 0.27 (5:1 hexanes: EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.44−3.38 (m, 2H), 1.78−1.45 (m, 8H), 1.39−1.31 (m, 1H), 1.28−1.14 (m, 2H), 1.04−0.76 (m, 6H), 0.72−0.58 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 68.8, 43.3, 42.5, 40.6, 36.9, 34.1, 33.8, 33.3, 29.4, 26.7, 26.6; IR (neat) 3358, 2915, 2849 cm^{-1}; HRMS Calcd for $C_{11}H_{20}O^+$: 168.1514, found 168.1524; LRMS (EI) *m/z* 168 (2.4), 150 (38.7), 137 (30.1), 121 (22.6), 108 (15.1), 95 (77.4), 81 (84.9), 67 (62.4), 41 (94.6), 31 (100.0); Analysis Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98; found: C, 78.54; H, 12.11.

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Supporting Information Available: Complete experimental details and ^{1}H NMR and ^{13}C NMR spectral data for the preparation of cyclization substrates and X-ray crystal structure data of the products described herein (136 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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