Palladium-Catalyzed Cyclization of Allylsilanes with Nucleophilic Displacement of the Silyl Group

István Macsári and Kálmán J. Szabó*[a]

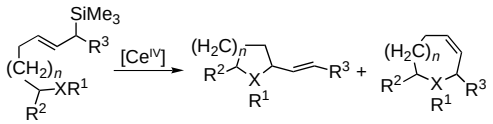
Abstract: Allylsilanes containing hydroxy or tosylamide groups undergo palladium(II)-catalyzed cyclization to afford derivatives of tetrahydrofuran, piperidine, and pyrrolidine. This catalytic reaction proceeds through an (η^3-allyl)-palladium intermediate that is generated by allylic displacement of the silyl group of the allylsilane precursors. The internal nucleophilic attack on the (η^3-allyl)palladium intermediates proceeds with high chemo- and regioselectivity. Benzoquinone and copper(II) chloride can be used for regeneration of the palladium(II) catalyst precursor. Mechanistic studies revealed that the copper(II) chloride reoxidant also activates the (η^3-allyl)palladium intermediate towards nucleophilic attack. Kinetic studies on the formation of the (η^3-allyl)palladium intermediates showed that the reaction rate is highly dependent on the concentration of chloride ligand and the solvent. The structure and reactivity of the key intermediates of the palladadesilylation process were studied by density functional theory (DFT) calculations, which showed that coordination of the electrophilic palladium(II) catalyst precursor to allylsilanes leads to a relatively weak β-silicon effect. The DFT studies also indicate that the cleavage of the carbon–silicon bond takes place by coordination of a chloride ion to the silicon atom.

Keywords: cyclizations · density functional calculations · heterocycles · homogeneous catalysis · palladium

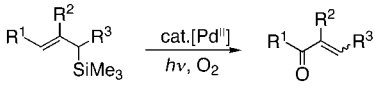
Introduction

Functionalized allylsilanes represent a useful class of reagents that continue to show high potential in regio- and stereocontrolled synthetic transformations.[1, 2] The highly selective transformations of allylsilanes are usually performed by electrophilic reagents.[3, 4] The driving force for electrophilic attack on allylsilanes is the formation of a β-silicon-stabilized carbocation intermediate.[5] Nucleophilic attack on allylsilanes, however, does not benefit from this stabilization, and this makes nucleophilic reagents less common in allylsilane chemistry. Allylsilanes can be made accessible to nucleophilic attack by employing organometallic reagents, electrochemical methods, or oxidizing agents.[6] The metal-mediated processes reported in the literature involve mercuration and thallation reactions of trimethylallylsilane to give allylic alcohols and amines.[6a–c, g–i]

Electrochemical oxidation of allylsilanes in the presence of alcohols or carboxylic acids was reported to form ether or ester derivatives.[6d] Cerium(IV)-mediated oxidative ring closure of allylsilanes bearing hydroxy and amine groups has been employed to prepare five- and eight-membered heterocycles [Eq. (1)].[6e] Palladium(II)-catalyzed oxidation of allylsilanes with UV light and molecular oxygen was used to prepare α,β-unsaturated carbonyl compounds [Eq. (2)].[6f]



(1)



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Palladium catalysis proceeding by nucleophilic attack of (η^3-allyl)palladium complexes is a possible alternative for nucleophilic displacement of the silyl group of allylsilanes. Catalytic transformations involving (η^3-allyl)palladium intermediates have been widely applied in a number of important chemical processes.[7–10] A wide range of allylic substrates, such as allylic halides, acetates, carbonates, and carbamates, undergo oxidative addition to palladium(0) to form (η^3-allyl)palladium complexes, which react with a great variety of nucleophiles. However, it is well known that many important allylic

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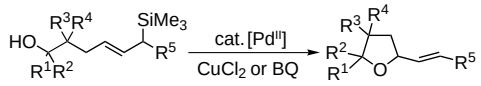
substrates, including allylsilanes, do not undergo palladium(0)-catalyzed allylic substitution. In fact, many palladium(0)-catalyzed transformations have been successfully employed for preparation of functionalized allylsilanes.[10, 12]

In a preliminarily communication we presented a palladium(II)-catalyzed procedure based on internal nucleophilic displacement of the silyl group of allylsilanes (Scheme 1).[11] This catalytic procedure could be used for preparation of substituted tetrahydrofuran derivatives in good yield.

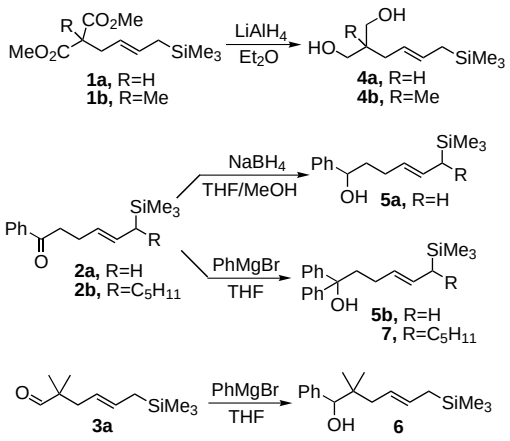


Scheme 1. Palladium(II)-catalyzed cyclization of allylsilanes.

Here we give a full account of our results on palladium(II)-catalyzed intramolecular cyclization of allylsilanes, and present an extension of this process. We also demonstrate that the employment of a silyl leaving group represents an interesting alternative to the acetate and carbonate groups which are commonly used in π-allylpalladium chemistry. To gain more insight into the mechanistic details of this reaction, the key steps of the catalytic transformation were investigated by kinetic and theoretical (DFT) studies.

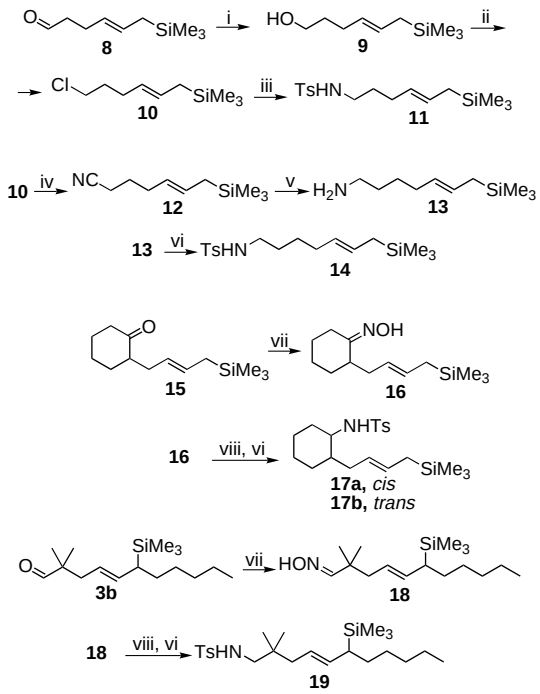
Results and Discussion

Synthesis of the starting materials: Allylsilane precursors with an internal O nucleophile were prepared from allylsilanes **1**–**3** (Scheme 2), which are readily available by a recently reported palladium(0)-catalyzed alkylation process.[12] These compounds were transformed into 6-trimethylsilylhex-4-en-1-ol derivatives **4**–**7** by Grignard reaction or reduction.



Scheme 2. Preparation of silylallyl alcohols **4**–**7**.

Allylsilanes functionalized with a toluene sulfonamide (NHTs) group were prepared from **3b, 8**, and **15**. Aldehyde **8**[13a, b] (Scheme 3) was reduced to alcohol **9**, followed by chlorination with NCS and PPh_3 to give **10**. Chloride **10** was treated with TsNHNa to furnish amide **11**. Compound **10** was also treated with NaCN to give nitrile **12**, which was reduced



Scheme 3. Preparation of toluenesulfonamides **11, 14, 17**, and **19**. i) $NaBH_4$, $CeCl_3 \cdot 7H_2O$, THF/MeOH 3/1, RT, 1 h; ii) NCS, PPh_3, THF, RT, 16 h; iii) TsNHNa, $TsNH_2$, DMSO, 60 °C, 16 h; iv) NaCN, DMSO, 90 °C, 16 h; v) $LiAlH_4$, Et_2O, RT, 2.5 h; vi) TsCl, Et_3N, CH_2Cl_2, 16 h, RT; vii) NaOAc, $NH_2OH \cdot HCl$, H_2O/EtOH 5/1, 60 °C, 16 h; viii) $LiAlH_4$, THF, reflux, 16 h. NCS = *N*-chlorosuccinimide.

to amine **13** followed by reaction with TsCl to give sulfonamide **14**. A different synthetic route was employed for the preparation of amides **17** and **19**: compounds **15** and **3b**[12] were transformed into the corresponding oximes **16** and **18** with $NH_2OH \cdot HCl$ followed by reduction with $LiAlH_4$ and acylation with TsCl.

The above-mentioned synthetic procedures provide simple access to the precursors of the catalytic reaction without affecting the allylsilyl group. Note that the commonly used substrates for palladium(0)-catalyzed allylic substitution reactions, such as allylic halides, acetates, and carbonates, cannot be transformed by the above synthetic methods unless their allylic functionality is protected.

Palladium(II)-catalyzed cyclization of allylsilanes: It is well documented that allylsilanes react with palladium(II) salts to give allylpalladium complexes.[14] Therefore, using this reaction in a catalytic procedure requires regeneration of the palladium(II) catalyst precursor. Since nucleophilic attack on an (η^3-allyl)palladium complex involves reduction of palladium(II) to palladium(0), the catalyst precursor must be reoxidized to maintain the catalytic cycle. Furthermore, the palladadesilylation of the allylsilane substrate must be sufficiently fast to obtain reasonable reaction times for the catalytic processes.

Benzoquinone (BQ) and $CuCl_2$ are frequently used reoxidants in palladium(II)-catalyzed procedures.[9] We found that both reagents can be used in the cyclization reaction, and accordingly developed two different methods for this catalytic procedure. Diol **4a** could be cyclized to give **20a** in good yield

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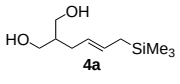
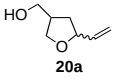
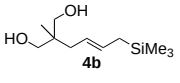
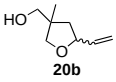
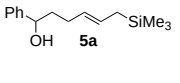
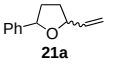
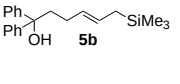
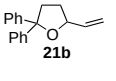
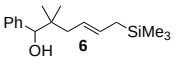
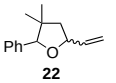
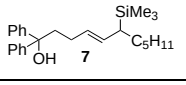
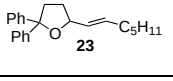
under mild, neutral conditions with $CuCl_2$ as reoxidant (Table 1, entry 1). However, using BQ as a reoxidant under acidic conditions required an extended reaction time (Table 1, entry 2) and gave **20a** in poor yield. Since cyclization of **4a** in the presence of $CuCl_2$ proceeds faster and in a better yield than the BQ-mediated procedure, we used $CuCl_2$ for the cyclization of allylsilyl alcohols **4b** and **5**–**7**.

Table 1. Palladium(II)-catalyzed cyclization of silylallyl alcohols **4**–**7**.

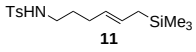
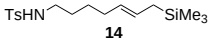
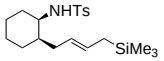
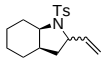
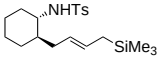
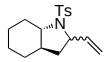
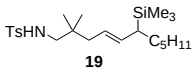
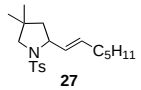
Entry	Substrate	Conditions[a] °C	h	Product	Yield[b] [%]
1	 **4a**	25	1.5	 **20a**	86
2	**4a**	25	14[c]	**20a**	40
3	 **4b**	25	2.5	 **20b**	62
4	 **5a**	40	1.5	 **21a**	69
5	 **5b**	40	2.5[d]	 **21b**	60
6	 **6**	20	14	 **22**	53
7	 **7**	20	4[d]	 **23**	66[e]

[a] The reactions were conducted in *i*PrOH (5 mL) with allylsilane (0.5 mmol), $Li_2[PdCl_4]$ (0.025 mmol, 5 mol%) and $CuCl_2$ (1.25 mmol). [b] Yield of isolated product. [c] Allylsilane (0.5 mmol), $Pd(OAc)_2$ (0.025 mmol, 5 mol%), BQ (1.1 mmol), and H_3PO_4 (0.135 mmol) in CH_2Cl_2/MeOH (10/1, 5 mL). [d] The substrate was added by syringe pump (0.5 and 3 h for **5b** and **7**, respectively) to the stirred reaction mixture. [e] About 15% of the *cis* isomer was also formed.

Cyclization of alcohols **4**–**7** was complete within 2–4 h, but a longer reaction time was required when methyl substituents were present at the 3-position of the substrate (Table 1, entry 6). The relatively short reaction time is particularly important for cyclization of tertiary alcohols **5b** and **7**, since these compounds readily eliminate water even under mild reaction conditions. Since cyclization proceeded much faster under neutral conditions than under acidic conditions (cf. Table 1, entries 1 and 2), we attempted to use basic reaction conditions to further accelerate the catalytic process. However, under these conditions only the unconverted starting materials could be recovered after 24 h.

The palladium-catalyzed cyclization reaction was also extended to allylsilanes containing toluenesulfonamide groups (Table 2). Amides **11** and **19** were cyclized to give substituted pyrrolidine derivatives in good yields. Cyclization of the homologous **14** gave piperidine derivative **25**. The diastereomers of **17** were separated and subjected to the ring-closure reaction to afford fused ring systems **26a** and **26b**, respectively.

Table 2. Palladium(II)-catalyzed cyclization of sulfonamides.

Entry	Substrate	Conditions[a] °C	h	Product	Yield[b] [%]
1	 **11**	45	3.5	 **24**	74
2	 **14**	45	4	 **25**	66
3	 **17a**	45	2	 **26a**	80
4	 **17b**	45	2	 **26b**	64
5	 **19**	45	4	 **27**	80[c]

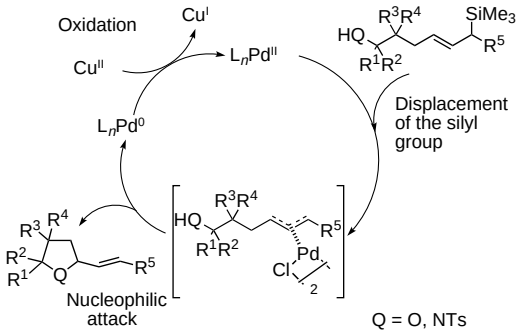
[a] The reactions were conducted in *t*BuOH (5 mL) with allylsilane (0.5 mmol), $Li_2[PdCl_4]$ (0.025 mmol, 5 mol%), and $CuCl_2$ (1.25 mmol). [b] Yield of isolated product. [c] About 20% of the *cis* isomer was also formed.

In the cyclization reactions the best results were obtained by using alcohol solvents such as MeOH, *i*PrOH, and *t*BuOH. In other solvents, such as acetonitrile, THF, DMSO, CH_2Cl_2, and DMF slow reactions with poor yields were observed. Cyclization of silylallyl alcohols **4**–**7** could be readily achieved in *i*PrOH. However, when the same solvent was used for the ring closure of amides, considerable amounts of acyclic isopropylallyl ether derivatives were also obtained. Formation of this by-product is due to nucleophilic attack of the solvent on the (η^3-allyl)palladium intermediates of the reaction. The fact that isopropylallyl ether derivatives are not formed on cyclization of **4**–**7** indicates that nucleophilic attack by the internal hydroxy group is much faster than that by an external secondary alcohol (e.g., the *i*PrOH solvent), and it also shows that the tosylamides **11**, **14**, **17** and **19** are much less nucleophilic than the corresponding alcohols **4**–**7**. Therefore, for cyclization of tosylamides, *t*BuOH was used as solvent, which is less nucleophilic than *i*PrOH. Conducting the reaction in *t*BuOH leads to longer reaction times, but formation of the alkylallyl ether by-products was completely avoided.

The regio- and chemoselectivity of the reaction are very high. Ring closure of **4**–**7**, **11**, **17**, and **19** provided exclusively five-membered rings, while formation of seven-membered rings was not observed. Similarly, cyclization of **14** led only to six-membered piperidine derivative **25**. However, the diastereoselectivity of the ring closure is poor, because the two diastereomers of **20a** **20b**, **21a**, **22**, **26a**, and **26b** were formed in approximately equal amounts.

Mechanistic Aspects

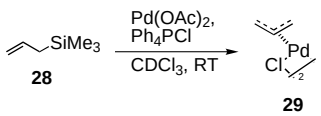
The palladium(II)-catalyzed nucleophilic substitution reaction discussed above has three important steps: 1) palladadesilylation to give the (η^3-allyl)palladium intermediate; 2) intramolecular nucleophilic attack on this complex; and 3) reoxidation of the catalyst to complete the catalytic cycle (Scheme 4). In particular steps 1 and 3 differ significantly



Scheme 4. Catalytic cycle of the ring-closure reaction.

from the mechanisms of the more common palladium(0)-catalyzed nucleophilic displacement reactions. Therefore, we studied the effects of ligands and solvents on the palladadesilylation process, as well as the role of the reoxidants in activating the nucleophilic attack.

Mechanistic investigations on the palladadesilylation reaction: A rapid and clean palladadesilylation process is a prerequisite for a synthetically useful catalytic nucleophilic substitution of allylsilanes. The above results suggested that the chloride concentration has a major influence on the rate of the reaction. Using $Li_2[PdCl_4]$ as catalyst precursor gave a much faster catalytic reaction than with $Pd(OAc)_2$ (cf. Table 1, entries 1 and 2). The influence of the chloride ligand concentration on the formation of the (η^3-allyl)palladium complexes was studied on a model system. The palladium(II) precursor for palladadesilylation was generated by mixing $Pd(OAc)_2$ with various amounts of Ph_4PCl in $CDCl_3$. The progress of the formation of the (η^3-allyl)palladium complex from this precursor and allyltrimethylsilane (Scheme 5) was monitored by ^1H NMR spectroscopy at 25 °C.



Scheme 5. Model reaction for the kinetic studies.

The palladadesilylation reaction was very slow in the absence of chloride ligand. After 20 min less than 15% of the allylsilane was converted to (η^3-allyl)palladium complex **29**. The rate of formation of **29** increased on increasing the Pd/Cl ratio to 1/2 (Figure 1), and complete conversion of the allylsilane substrate occurred within 10 min. However, a large

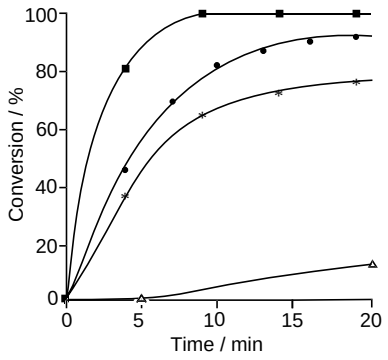


Figure 1. Rate of formation of the allylpalladium complex as a function of the chloride ion concentration. Pd/Cl ratio: 10/1 (△); 1/1 (●); 1/2 (■); and 1/10 (*).

increase in chloride concentration (Pd/Cl = 1/10) decreased the rate of complex formation.

The solvent effect of methanol on the rate of complex formation was studied at low chloride concentrations (Pd/Cl = 10/1) in $CDCl_3$. The reaction rate increased with increasing amount of CD_3OD in the solvent mixture (Figure 2). Addition of only 10% of CD_3OD doubles the rate of

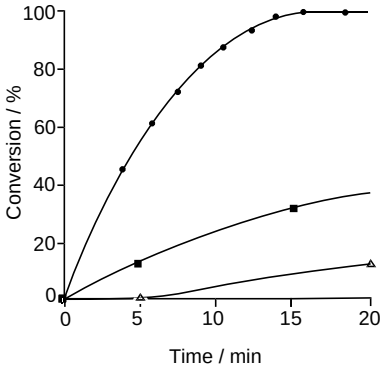
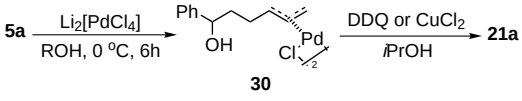


Figure 2. Rate of formation of the allylpalladium complex as a function of CD_3OD concentration in $CDCl_3$: 0% (△); 10% (■); 50% (●).

complex formation. With 50% CD_3OD complex formation was complete after 15 min, and in pure CD_3OD **28** was completely converted to **29** in less than two minutes.

These results indicate that the employment of a moderately high chloride concentration and alcohol solvents dramatically increases the rate of the palladadesilylation process and hence the overall catalytic reactions.

Reaction of the allylpalladium complexes: The allylpalladium intermediate **30** was prepared by palladadesilylation of **5a** (Scheme 6). Complex **30** is air-stable and does not undergo



Scheme 6. Preparation of allylpalladium complex **30** by palladadesilylation of **5a**.

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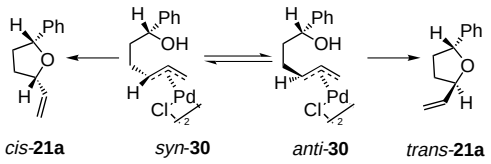
spontaneous cyclization. Therefore, **30** must be activated to allow nucleophilic attack by the hydroxy group. This activation could be achieved by addition of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) or $CuCl_2$ to a solution of **30** in *i*PrOH. Thus $CuCl_2$ has a dual role in the catalytic process: 1) it serves as an oxidizing agent for regeneration of the palladium(II) catalyst; 2) it activates the (η^3-allyl)palladium intermediates towards nucleophilic attack.

Interestingly, cyclization of **30** does not occur in the presence of BQ, probably because BQ is a weaker activator for nucleophilic attack on (η^3-allyl)palladium complexes than DDQ, especially in the presence of chloride ligands.[15] Therefore, the BQ-mediated catalytic reaction should be performed under chloride-free conditions (Table 1, entry 2). Employment of BQ as activator and reoxidant requires acidic reaction conditions, since a protonation step is involved in the reduction of BQ to hydroquinone. However, using acidic conditions and BQ as the reoxidant leads to a very slow reaction with a low yield. This can be explained by the fact that the ring closure involves deprotonation of the OH group, which is hindered in the presence of acid. Cyclization with BQ or $CuCl_2$ does not proceed under basic conditions. Neutral conditions gave the best results, which were achieved with $CuCl_2$ as reoxidant and activator. Employment of alcoholic solvents was also beneficial, because the solvent molecules can also act as weak bases that assist in the deprotonation of the hydroxyl or amide groups.

Like the catalytic process, the stoichiometric cyclization reaction proceeds with high regioselectivity, but the diastereoselectivity is low. This can be explained by the fact that **30** readily undergoes *syn*–*anti* isomerization and is therefore present in two diastereomeric forms (Scheme 7). If the



Scheme 7. Cyclization is faster than *syn*–*anti* isomerization.

stability of the diastereomers were markedly different, the complex would isomerize to the thermodynamically favored form, which would undergo internal nucleophilic attack to give one of the cyclic diastereomers.[16] However, in our experiments the heterocyclic products were obtained as 1/1 mixtures of diastereomers, and this indicates that the thermodynamic stabilities of the diastereomeric (η^3-allyl)palladium intermediates, such as *syn*-**30** and *anti*-**30**, are about equal.

Theoretical Studies on the Palladadesilylation Process

The above studies on the palladium(II)-catalyzed cyclization of allylsilanes showed that formation of the allylpalladium intermediate is influenced by the chloride concentration and by the choice of the solvent. Therefore, we further investigated the mechanistic aspects of the palladadesilylation reaction by performing density functional calculations on the structure and reactivity of adducts in which trimethylallylsilane is coordinated to a $PdCl_3^-$ (**31a**) or to a $PdCl_2$ (**32a**) fragment. Adduct **31a** can be formed from $PdCl_4^{2-}$ by ligand substitution of one of the chloride ligands. Dissociation of a second chloride ion (**32a**) leads to the free coordination site necessary for the $\eta^2 \rightarrow \eta^3$ conversion.

Computational methods: The geometries were fully optimized by employing a Becke-type[17a] three-parameter density functional model B3PW91. This so-called hybrid functional includes the exact (Hartree–Fock) exchange, the gradient-corrected exchange functional of Becke,[17a] and the more recent correlation functional of Perdew and Wang[17b]. All calculations were carried out with a double-ζ(DZ) + P basis set constructed from the LANL2DZ basis set[17c–e] by adding one set of d-polarization functions to the heavy atoms (exponents: C 0.63, Cl 0.514, O 1.154, Si 0.262) and one set of diffuse d-functions on palladium (exponent: 0.0628). All calculations were performed with the Gaussian 98 program package.[17f]

Structure of (η^2-allyl)palladium complexes: Harmonic vibration analysis of the fully optimized structures of **31a** and **32a** gave only real frequencies, indicating that these complexes represent minima on the potential energy surface. In these complexes (Figure 3) the C–Si bonds are perpendicular to the allyl moiety (the C1-C2-C3-Si dihedral angles τ are 91.2 and 99.7°, respectively). Furthermore, the carbon–silicon bonds in both complexes are somewhat longer than a normal C–Si bond. Rotation of the silyl group by 90° leads to shortening of the C–Si bond and thermodynamic destabilization of the complex. The geometrical and energy changes caused by the 90° rotation are more pronounced in **32a** than in **31a**. Elongation of the C–Si bond in **32a** also weakens it, and this facilitates the C–Si bond cleavage required for formation of the (η^3-allyl)palladium intermediate. Clearly, the (η^3-allyl)-palladium intermediate is more easily formed from **32a** than from **31a**.

The above results clearly indicate the presence of hyperconjugative interactions between the C–Si bond and the π system of the (η^2-trimethylsilylallyl)palladium fragment in **32a**. This interaction is very similar to the hyperconjugative interaction between the C–Si(σ) orbital and the p_π orbital in β-silyl-substituted carbocations. This interaction forms the basis of the β-silicon effect,[3, 5] which is the driving force of electrophilic attack on vinyl- and allylsilanes. Theoretical studies by Jorgensen et al.[5a] showed that the C–Si bond is strongly elongated (2.070 Å) in β-silyl carbocations, and that a 90° rotation of the silyl group from the conjugated upright conformation (cf. **32a**) to the unconjugated form (cf. **32b**) leads to a destabilization by 22.2 kcal mol^{-1}. Clearly, electrophilic attack (e.g., protonation) on an allylsilane generates much larger β-silicon effect than the coordination of an electrophilic palladium(II) species such as $PdCl_2$ (**32a**). This also implies that the cleavage of the C–Si bond is more difficult in palladium(II) adducts than in β-silyl carbocations.

The relatively weak β-silicon effect in **32a** compared to β-silyl carbocations (Scheme 8) can be explained by the fact that

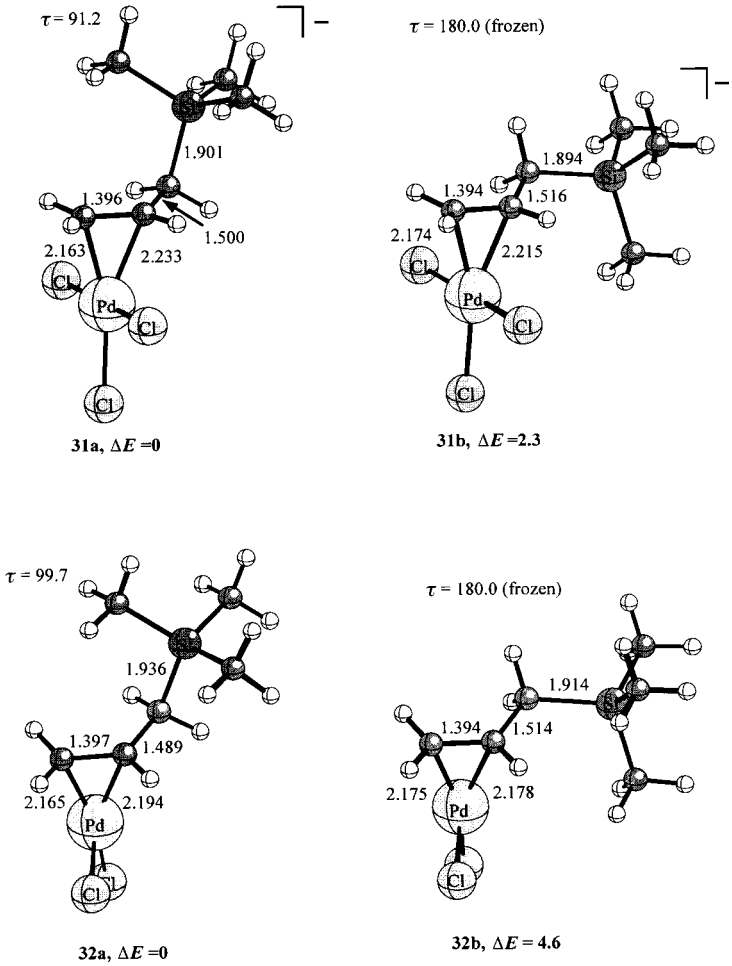
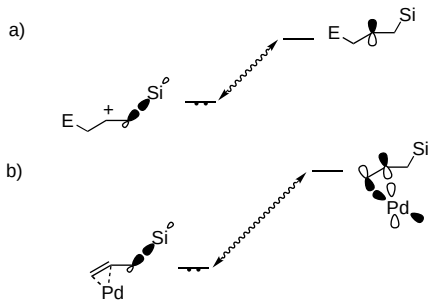


Figure 3. Selected B3PW91/LANL2DZ + P geometrical parameters for (η^2-allyl)palladium complexes **31** and **32** (bond lengths in Å, angles in degrees, energies in kcal mol^{-1}).



Scheme 8. β-Silicon effect in a) β-silyl carbocations and b) in allyltrimethylsilane – $PdCl_2$ adduct.

the electrophilic attack by palladium(II) does not lead to formation of a carbocation center at C2; instead, the palladium atom coordinates to C1–C2 in an η^2 manner. This also means that the C–Si(σ) MO is not able to conjugate with a low-lying p_π MO, as in a β-silyl carbocation. Instead, interaction of C–Si(σ) with a high-lying PdCC(π*) MO leads to relatively weak hyperconjugation (Scheme 8).

Factors promoting C–Si bond cleavage: A weak electrostatic interaction of the silicon atom of **32** with a methanol molecule (Figure 4) leads to a slightly elongated C–Si bond length of 1.941 Å (**33**). However, this interaction does not contribute significantly to the cleavage of the C–Si bond. On the other hand, the approach of a free chloride ion to the silicon atom leads to immediate C–Si bond cleavage accompanied by formation of chlorotrimethylsilane. This process leads to formation of an (η^3-allyl)palladium complex without an activation barrier.

A more realistic model of the desilylation reaction in a condensed phase involves coordination of two methanol molecules to the attacking chloride ion (**34**, Figure 4). According to harmonic frequency analysis, **34** represents a minimum on the potential energy surface, and it is characterized by a strongly elongated C–Si bond. In fact, the C–Si bond in **34** (2.016 Å) is about as long as the C–Si bond in β-silyl carbocations (2.070 Å), and therefore it can be assumed that the cleavage of the C–Si bond in **34** is about as facile as in β-silyl carbocations. The activation barrier to C–Si bond cleavage is extremely low (< 0.5 kcal mol^{-1}), and therefore it was not determined. Formation of the (η^3-allyl)palladium complex (**35**) and chlorotrimethylsilane from **34** is a highly exothermic process (-32.2 kcal mol^{-1}). Although this process certainly requires a higher activation energy in a condensed phase such as in methanol solution, and the reaction is less exothermic than in this model calculation, it can be concluded that the coordination of chloride to the silicon atom of **32a** considerably facilitates C–Si bond cleavage.

The above theoretical results clearly indicate that the location at which the chloride ion coordinates has a major influence on the palladadesilylation process. The chloride ion can coordinate to two centers in **32a**. Coordination to the silicon atom (**34**) facilitates C–Si bond cleavage and formation of the (η^3-allyl)palladium intermediate of the catalytic reaction (**35**). However, coordination to palladium leads to formation of **31a**, in which the C–Si bond is strong, and therefore formation of the (η^3-allyl)palladium intermediate is not feasible. These conclusions are also in agreement with our mechanistic results (Figure 1): at very low chloride concentrations complex **34** cannot be formed, and formation of the (η^3-allyl)palladium intermediate is slow. At very high chloride concentration, dissociation of chloride ion from **31a** is hindered, and this also decelerates formation of the complex. The alcohol solvents probably do not have a direct influence on the palladadesilylation process. They react immediately with chlorotrimethylsilane to give the alkyl trimethylsilyl ether and release chloride ions for the palladadesilylation process. This can explain the finding that addition of methanol accelerates the formation of the (η^3-allyl)palladium complex even at low chloride concentration (Figure 2).

Conclusion

We have described a new palladium(II)-catalyzed cyclization reaction involving nucleophilic displacement of the silyl group of allylsilanes. This procedure is suitable for the preparation of derivatives of tetrahydrofuran, pyrrolidine, and piperidine under mild reaction conditions in good yields (Tables 1 and 2). The cyclization reaction gave the best results under neutral conditions with $CuCl_2$ as activator and reoxidant. Mechanistic studies indicate that the palladadesilylation of allylsilanes is

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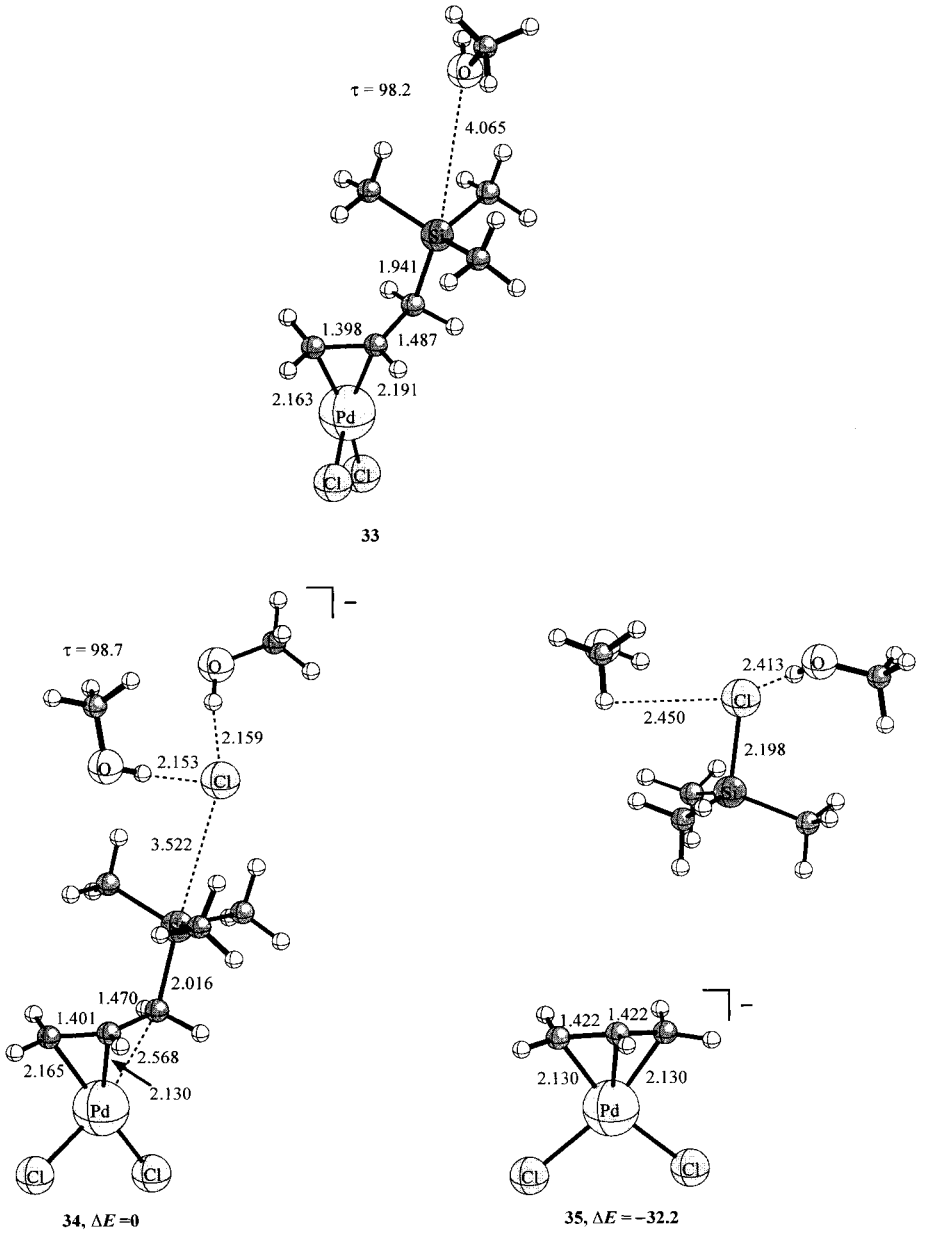

Figure 4. Selected B3PW91/LANL2DZ + P geometrical parameters for **33, 34**, and (η^3-allyl)palladium complex **35** (bond lengths in Å, angles in degrees, energies in kcal mol^{-1}).

strongly influenced by the concentration of chloride ions. The optimal rate of formation of the (η^3-allyl)palladium complex is obtained with a Pd/Cl ratio of 1/2 (Figure 1). The DFT calculations show that in the adduct formed by electrophilic attack of palladium(II) on allyltrimethylsilane (**31a**), the β-silicon effect is relatively weak. Cleavage of the C–Si bond requires coordination of a chloride ion to the silicon atom (**34**). On the other hand, a high chloride concentration leads to formation of **31a**, which slows down the palladadesilylation process.

Experimental Section

The starting materials were purchased from Aldrich and Lancaster. All solvents were freshly distilled prior to use. All reactions were conducted under an argon atmosphere by employing standard manifold techniques. NMR spectra were recorded in $CDCl_3$ (^{1}H at 400 MHz and ^{13}C at 100.5 MHz) with $CDCl_3$ ($\delta(^1H) = 7.26$, $\delta(^{13}C) = 77.0$) as internal standard. For column chromatography, Merck silica gel 60 (230–400 mesh) was used.

Reduction of 1a, b: The corresponding diester[12] (2.1 mmol) in diethyl ether (4.8 mL) was added dropwise to a suspension of $LiAlH_4$ (0.21 g, 6.3 mmol) in diethyl ether (6 mL) at 0 °C. The mixture was stirred for 2.5 h at room temperature. It was then cooled to 0 °C, and water (0.2 mL) was added. The resulting mixture was allowed to warm to room temperature, then an aqueous solution of NaOH (15%, 0.2 mL) and water (0.61 mL) were added. A white slurry was formed, which was filtered through Celite and washed with EtOAc (3 × 10 mL). The organic solvents were removed, and the resulting oil was purified by chromatography (diethyl ether).

2-[(*E*)-4′-Trimethylsilylbut-2′-enyl]-propane-1,3-diol (4a): Colorless crystals (86% yield). M.p. 48–49 °C; ^{1}H NMR: $\delta = 5.45$ (m, 1H; H3′), 5.23 (m, 1H; H2′), 3.83 (dd, $J = 10.8$, 10.2 Hz, 2H; H1a, H3a), 3.66 (dd, $J = 10.8$, 10.4 Hz, 2H; H1b, H3b), 2.09 (s, 2H; OH), 2.00 (t, $J = 6.8$ Hz, 2H; H1′), 1.82 (m, 1H; H2), 1.42 (d, $J = 8.0$ Hz, 2H; H4′), −0.01 (s, 9H; $Si(CH_3)_3$); ^{13}C NMR: $\delta = 128.9$ (C3′), 125.9 (C2′), 66.5 (C1, C3), 42.9 (C2), 32.0 (C1′), 23.2 (C4′), −1.4 ($Si(CH_3)_3$); elemental analysis (%) calcd for $C_{10}H_{22}O_2Si$ (202.37): C 59.35, H 10.96; found: C 59.22, H 10.64.

2-Methyl-2-[(*E*)-4′-trimethylsilylbut-2′-enyl]propane-1,3-diol (4b): Colorless crystals (95% yield). M.p. 59–60 °C; ^{1}H NMR: $\delta = 5.47$ (m, 1H; H3′), 5.26 (m, 1H; H2′), 3.50 (m, 4H; H1, H3), 2.38 (s, 2H; OH), 2.02 (t, $J =$ 7.4 Hz, 2H; H1′), 1.44 (d, $J = 8.0$ Hz, 2H; H4′), 0.83 (s, 3H; CH_3), −0.01 (s, 9H; $Si(CH_3)_3$); ^{13}C NMR: $\delta = 130.1$ (C3′), 123.7 (C2′), 70.7 (C1, C3), 40.0 (C2), 38.1 (C1′), 23.4 (C4′), 19.1 (CH_3), −1.4 ($Si(CH_3)_3$). MS (CI): *m*/*z* (%): 226 (1) $[M]^+$, 201 (1) $[M - CH_3]^+$, 183 (2) $[C_{10}H_{20}OSi]^+$, 143 (4) $[C_8H_{15}O_2]^+$, 129 (10) $[C_7H_{13}O_2]^+$, 93 (20), 73 (100) $[C_3H_9Si]^+$.

(*E*)-1-Phenyl-6-trimethylsilanylhex-4-en-1-ol (5a): $NaBH_4$ (0.081 g, 2.15 mmol) was carefully added in small portions to a solution of ketone **2a** (0.220 g, 0.89 mmol) and $CeCl_3 \cdot 7H_2O$ (0.33 g, 0.89 mmol) in THF/methanol (3/1, 12 mL) at 0 °C. The resulting mixture was stirred at room temperature for 1 h. Then it was quenched with a saturated aqueous solution of NH_4Cl (4.4 mL), filtered through Celite, and washed with CH_2Cl_2 (3 × 10 mL). The organic solvents were removed, and the aqueous residue was diluted with brine and extracted with CH_2Cl_2 (3 × 10 mL) and diethyl ether (2 × 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated. The product was obtained after chromatography (pentane/diethyl ether 4/1) as a colorless oil (79% yield). ^{1}H NMR: $\delta = 7.34$ (m, 4H; Ar), 7.28 (m, 1H; Ar), 5.44 (m, 1H; H5), 5.26 (m, 1H; H4), 4.69 (m, 1H; H1), 2.08 (m, 2H; H3), 1.91–1.75 (br m, 2H; H2), 1.42 (d, $J = 7.6$ Hz, 2H; H6), −0.01 (s, 9H; $Si(CH_3)_3$); ^{13}C NMR: $\delta =$ 145.0, 128.7, 127.7, 126.1 (Ar), 128.1 (C5), 127.3 (C4), 74.5 (C1), 39.7 (C2), 29.6 (C3), 23.2 (C6), −1.4 ($Si(CH_3)_3$); MS (CI): *m*/*z* (%): 249 (2) $[M+1]^+$,

248 (2) $[M]^+$, 233 (3) $[M-CH_3]^+$, 205 (15) $[C_{14}H_{19}Si]^+$, 158 (17) $[C_{12}H_{14}]^+$, 143 (4) $[C_8H_{19}Si]^+$, 120 (9) $[C_8H_8O]^+$, 105 (100) $[C_7H_5O]^+$, 73 (50) $[C_3H_9Si]^+$.

Preparation of 5b, 6, and 7: Phenylmagnesium bromide (4.0 mmol) was added dropwise to a solution of the corresponding ketone or aldehyde[12] (0.5 mmol) in THF (1 mL) at 0 °C. The reaction mixture was stirred at 40 °C, and the progress of the reaction was monitored by TLC. When the reaction was complete, it was quenched with a saturated aqueous solution of NH_4Cl. The resulting mixture was diluted with diethyl ether (10 mL) and washed with brine. The organic layer was dried over anhydrous $MgSO_4$, concentrated, and purified by chromatography (pentane/diethyl ether 9/1).

(*E*)-1,1-Diphenyl-6-trimethylsilylhex-4-en-1-ol (5b): Colorless crystals (68% yield). M.p. 54–56 °C. ^{1}H NMR: $\delta = 7.42$ (m, 4H; Ar), 7.32 (m, 4H; Ar), 7.21 (m, 2H; Ar), 5.36 (m, 2H; H4, H5), 2.35 (m, 2H; H2), 2.00 (m, 2H; H2), 1.39 (d, $J = 7.6$ Hz, 2H; H6), −0.02 (s, 9H; $Si(CH_3)_3$); ^{13}C NMR: $\delta = 147.2$, 128.3, 127.0, 126.3 (Ar), 128.5 (C5), 127.3 (C4), 78.8 (C1), 42.4 (C2), 28.0 (C3), 23.2 (C6), −1.4 ($Si(CH_3)_3$); MS (CI): *m*/*z* (%): 324 (1) $[M]^+$, 306 (6) $[M-H_2O]^+$, 232 (8) $[C_{18}H_{16}]^+$, 183 (20) $[C_{13}H_{11}O]^+$, 180 (100) $[C_{14}H_{12}]^+$, 165 (22) $[C_{13}H_9]^+$, 105 (24) $[C_7H_5O]^+$, 73 (13) $[C_3H_9Si]^+$.

(*E*)-2,2-Dimethyl-1-phenyl-6-trimethylsilylhex-4-en-1-ol (6): Colorless oil (93% yield). ^{1}H NMR: $\delta = 7.32$ (m, 4H; Ar), 7.25 (m, 1H; Ar), 5.44 (m, 1H; H5), 5.36 (m, 1H; H4), 4.46 (d, $J = 2.8$ Hz, 1H; H1), 2.12 (dd, $J = 13.6$, 6.8 Hz, 1H; H3), 1.94 (dd, $J = 13.6$, 6.8 Hz, 1H; H3), 1.45 (d, $J = 7.6$ Hz, 2H; H6), 0.88 (s, 3H; CH_3), 0.80 (s, 3H; CH_3), 0.01 (s, 9H; $Si(CH_3)_3$); ^{13}C NMR: $\delta = 142.2$, 128.1, 127.8, 127.5 (Ar), 129.6 (C5), 125.0 (C4), 81.3 (C1), 43.0 (C2), 39.2 (C3), 24.0 (CH_3), 23.5 (C6), 22.7 (CH_3), −1.3 ($Si(CH_3)_3$); MS (CI): *m*/*z* (%): 277 (2) $[M+1]^+$, 276 (3) $[M]^+$, 261 (15) $[M-CH_3]^+$, 203 (12) $[C_{14}H_{19}O]^+$, 155 (24) $[C_9H_{19}Si]^+$, 113 (10) $[C_6H_{13}Si]^+$, 105 (100) $[C_7H_5O]^+$, 73 (62) $[C_3H_9Si]^+$.

(*E*)-1,1-Diphenyl-6-trimethylsilanyl-undec-4-en-1-ol (7): Colorless oil (80% yield). ^{1}H NMR: $\delta = 7.42$ (m, 4H; Ar), 7.32 (m, 4H; Ar), 7.21 (m, 2H; Ar), 5.36 (m, 2H; H4, H5), 2.35 (m, 2H; H2), 2.00 (m, 2H; H3), 1.44–1.13 (br m, 9H; H6–H10), 8.88 (t, $J = 7.2$ Hz, 3H; H11), −0.05 (s, 9H; $Si(CH_3)_3$); ^{13}C NMR: $\delta = 147.2$, 128.3, 127.0, 126.3 (Ar), 132.9 (C5), 127.6 (C4), 78.8 (C1), 42.6 (C2), 33.6 (C6), 32.2 (C7), 29.5 (C8), 29.3 (C9), 28.2 (C3), 23.1 (C10), 14.7 (C11), −2.6 ($Si(CH_3)_3$); elemental analysis (%) calcd for $C_{26}H_{38}OSi$ (394.68): C 79.12, H 9.70; found: C 78.97, H 9.87.

***N*-[(*E*)-6-Trimethylsilylhex-4-enyl]toluene-4-sulfonamide (11)**: Aldehyde **8**[13a,b] was reduced by $NaBH_4$ to alcohol **9** (93% yield) by the method described for reduction of alcohol **5a**. The NMR data for **9** were identical with those given in the literature for the same compound prepared by an alternative procedure.[18] Alcohol **9** was chlorinated by the following procedure: PPh_3 (0.904 g, 3.4 mmol) in THF (4 mL) was added to a suspension of *N*-chlorosuccinimide (0.464 g, 3.4 mmol) in THF (4 mL) at 0 °C. The resulting pink slurry was stirred at room temperature for 0.5 h, followed by addition of alcohol **9** in THF (4 mL), and this mixture was stirred overnight at the same temperature. Thereafter, the solvent was removed, and the crude product was purified by column chromatography (pentane) to give **10** (81% yield). The NMR data of this product were identical with the literature data for the same compound prepared by an alternative procedure.[19] A solution of **10** (0.26 g, 1.36 mmol), $TsNH_2$ (0.233 g, 1.36 mmol), and TsNHNa (0.263 g, 1.36 mmol) in DMSO (6 mL) was stirred for 16 h at 60 °C. Thereafter, the reaction mixture was diluted with brine and extracted with diethyl ether. The solvent was removed, and purification by chromatography (pentane/diethyl ether 2/1) afforded **11** as a colorless oil (68% yield). ^{1}H NMR: $\delta = 7.75$ (d, $J = 8.0$ Hz, 2H; Ar), 7.30 (d, $J = 8.0$ Hz, 2H; Ar), 5.33 (m, 1H; H5), 5.10 (m, 1H; H4), 4.53 (t, $J = 2.0$ Hz, 1H; N*H*), 2.92 (dd, $J = 13.2$, 6.8 Hz, 2H; H1), 2.42 (s, 3H; ArCH_3), 1.94 (dd, $J = 13.8$, 7.0 Hz, 2H; H3), 1.48 (m, 2H; H2), 1.34 (d, $J = 8.0$ Hz, 2H; H6), −0.05 (s, 9H; $Si(CH_3)_3$); ^{13}C NMR: $\delta = 143.6$, 137.4, 130.0, 127.4 (Ar), 127.9 (C5), 127.3 (C4), 43.0 (C1), 30.0 (C2, C3), 23.0 (C6), 21.8 (ArCH_3), −1.7 ($Si(CH_3)_3$); elemental analysis (%) calcd for $C_{16}H_{27}NO_2SSi$ (325.56): C 59.03, H 8.36, N 4.30; found: C 58.86, H 8.38, N 4.44.

***N*-[(*E*)-7-Trimethylsilylhept-5-enyl]toluene-4-sulfonamide (14)**: Chloride **10** (0.11 g, 0.58 mmol) and NaCN (0.088 g, 1.8 mmol) in DMSO (3 mL) were stirred overnight at 90 °C. Thereafter, the reaction mixture was diluted with water (20 mL) and extracted with diethyl ether (5 × 10 mL) and CH_2Cl_2 (2 × 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$, concentrated, and purified by chromatography (pentane/diethyl ether 9/1) to afford nitrile **12** as a colorless oil (88% yield). The NMR data of **12** were identical with the literature data for the same product prepared by an alternative procedure.[20] Nitrile **12** (0.086 g, 0.48 mmol) was reduced to amine **13**[20] by the procedure described for reduction of alcohols **4a, b** to give a colorless oil (86% yield). A solution of **13** (0.075 g, 0.4 mmol), TsCl (0.152 g, 0.8 mmol), and Et_3N (0.135 mL, 1.0 mmol) in CH_2Cl_2 (1.2 mL) was stirred for overnight at room temperature. Thereafter, the reaction mixture was diluted with diethyl ether (20 mL) and washed with water (10 mL). The aqueous layer was extracted with diethyl ether (3 × 8 mL), and the organic layer was dried over anhydrous $MgSO_4$. Subsequently, the solvent was removed, and the residual oil was purified by chromatography (pentane/diethyl ether 13/10) to give **14** as a colorless oil (93% yield). ^{1}H NMR: $\delta = 7.75$ (d, $J = 8.0$ Hz, 2H; Ar), 7.30 (d, $J = 8.0$ Hz, 2H; Ar), 5.33 (m, 1H; H6), 5.13 (m, 1H; H5), 4.11 (m, 1H; N*H*), 2.92 (m, 2H; H1), 2.43 (s, 3H; ArCH_3), 1.90 (m, 2H; H4), 1.44 (m, 2H; H2), 1.36 (d, $J = 8.0$ Hz, 2H; H7), 1.29 (m, 2H; H3), −0.04 (s, 9H; $Si(CH_3)_3$); ^{13}C NMR: $\delta = 143.7$, 137.4, 130.0, 127.5 (Ar), 128.2 (C6), 127.2 (C5), 43.5 (C1), 32.5 (C4), 29.3 (C3), 27.2 (C2), 22.9 (C7), 21.9 (ArCH_3), −1.6 ($Si(CH_3)_3$); MS (CI): *m*/*z* (%): 340 (2) $[M+1]^+$, 339 (7) $[M]^+$, 324 (10) $[M-CH_3]^+$, 256 (12), 228 (20), 180 (100) $[C_{10}H_{18}NSi]^+$, 149 (12), 91 (12) $[C_7H_7]^+$, 73 (27) $[C_3H_9Si]^+$.

Preparation of oximes 16 and 18: The corresponding aldehyde or ketone[12] (4.1 mmol) in ethanol (1.5 mL) was added to a solution of NaOAc (0.330 g, 4.1 mmol) and $NH_2OH \cdot HCl$ (0.422 g, 6.15 mmol) in water/ethanol (5/1, 8.6 mL) at 60 °C. After 1 h ethanol (4.5 mL) was added, and the mixture was stirred overnight. Thereafter, the reaction mixture was diluted with ice water (40 mL), extracted with diethyl ether, and dried over anhydrous Na_2SO_4. Subsequently, the solvent was removed, and the residual yellow oil was purified by column chromatography (pentane/diethyl ether).

2-[(*E*)-4′-Trimethylsilylbut-2′-enyl]cyclohexanone oxime (16): Compound **16** was obtained from **15** as a colorless oil (59% yield). ^{1}H NMR: $\delta = 8.69$ (s, 1H; OH), 5.40 (m, 1H; H3′), 5.21 (m, 1H; H2′), 2.75 (m, 1H; $H6_{eq}$), 2.38 (m, 1H; H1′), 2.20 (br m, 2H; $H2_{ax}$, $H6_{ax}$), 2.04 (m, 1H; H1′), 1.85 (m, 1H; $H3_{eq}$), 1.69 (br m, 2H; $H5_{eq}$, $H4_{eq}$), 1.56 (m, 1H; $H5_{ax}$), 1.49 (m, 1H; $H4_{ax}$), 1.40 (d, $J = 8.0$ Hz, 2H; H4′), 1.37 (m, 1H; $H3_{ax}$), −0.02 (s, 9H; $Si(CH_3)_3$); ^{13}C NMR: $\delta = 163.0$ (C1), 128.5 (C3′), 126.6 (C2′), 42.8 (C2), 34.5 (C1′), 32.3 (C3), 26.5 (C5), 24.0 (C4), 23.4 (C6), 23.1 (C4′), −1.6 ($Si(CH_3)_3$); MS (CI): *m*/*z* (%): 240 (1) $[M+1]^+$, 239 (4) $[M]^+$, 224 (42) $[M-CH_3]^+$, 210 (13) $[C_{11}H_{20}NOSi]^+$, 166 (100) $[C_{10}H_{16}NO]^+$, 113 (7) $[C_6H_{13}Si]^+$, 73 (68) $[C_3H_9Si]^+$.

(*E*)-2,2-Dimethyl-6-trimethylsilylundec-4-enal oxime (18): Compound **18** was prepared from **3b** as a pale yellow oil (87% yield). ^{1}H NMR: $\delta = 7.49$ (s, 1H; OH), 7.33 (s, 1H; H1), 5.19 (m, 2H; H5, H4), 2.10 (d, $J = 6.0$ Hz, 2H; H3), 1.44–1.10 (br m, 9H; H6–10), 1.06 (s, 6H; 2 × CH_3), 0.86 (t, $J = 7.2$ Hz, 3H; H11), −0.04 (s, 9H; $Si(CH_3)_3$); ^{13}C NMR: $\delta = 159.6$ (C1), 136.0 (C5), 123.0 (C4), 45.0 (C3), 37.4 (C2), 33.6 (C6), 32.0 (C9), 29.5 (C8), 29.3 (C7), 25.4 (CH_3), 25.3 (CH_3), 23.0 (C10), 14.5 (C11), −2.8 ($Si(CH_3)_3$); MS (CI): *m*/*z* (%): 283 (2) $[M]^+$, 282 (5) $[M-1]^+$, 266 (10) $[M-OH]^+$, 210 (8) $[C_{13}H_{24}NO]^+$, 159 (25), 141 (22) $[C_8H_{17}Si]^+$, 73 (27) $[C_3H_9Si]^+$.

Preparation of sulfonamides 17 and 19: The oximes were reduced by a procedure similar to the reduction described for preparation of **4a**, **b**. The modifications were that THF was used as solvent and the reaction mixture was heated to reflux overnight. The amine intermediates were used without further purification. The acylation with TsCl was performed by the procedure described for preparation of **14**.

***N*-{2-[(*E*)-4′-Trimethylsilylbut-2′-enyl)]cyclohexyl}toluene-4-sulfonamide (17)** was obtained as a 2/1 mixture of diastereomers in 64% yield. For identification of the diastereomers **17a** and **17b**, we used the NMR data given for *cis*- and *trans*-*N*-tosyl-2-allylcyclohexylamine.[21] According to the literature data, the δ(H1) signal of *cis*-*N*-tosyl-2-allylcyclohexylamine is observed at lower field than the that of the *trans* isomer. ***cis*-17a**: Colorless crystals, m.p. 116–118 °C. ^{1}H NMR: $\delta = 7.75$ (d, $J = 8.0$ Hz, 2H; Ar), 7.28 (d, $J = 8.0$ Hz, 2H; Ar), 5.26 (m, 1H; H3′), 4.98 (m, 1H; H2′), 4.46 (d, $J = 8.4$ Hz, 1H; N*H*), 3.43 (m, 1H; H1), 2.42 (s, 3H; ArCH_3), 1.84 (m, 2H; H1′), 1.60–1.06 (br m, 10H; H2–6), 1.33 (d, $J = 8.0$ Hz, 2H; H4′), −0.04 (s, 9H; $Si(CH_3)_3$); ^{13}C NMR: $\delta = 143.5$, 138.9, 130.0, 127.4 (Ar), 128.4 (C3′), 126.5 (C2′), 53.7 (C1), 41.2 (C2), 34.6 (C1′), 30.9 (C3), 27.3 (C6), 24.1 (C4), 23.1 (C4′), 21.9 (ArCH_3), 21.5 (C5), −1.6 ($Si(CH_3)_3$). ***trans*-17b**: ^{1}H NMR: $\delta = 7.76$ (d, $J = 8.0$ Hz, 2H; Ar), 7.26 (d, $J = 8.0$ Hz, 2H; Ar), 5.26 (m, 1H; H3′), 4.99 (m, 1H; H2′), 4.45 (d, $J = 8.8$ Hz, 1H; N*H*), 2.83 (m, 1H; H1), 2.41 (s, 3H; ArCH_3), 1.75 (m, 2H; H1′), 1.59 (br m, 4H; H3–$H6_{eq}$), 1.35 (d,

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$J = 8.0$ Hz, 2H; H4′), 1.23 (br m, 3H; H4 – H6$_{ax}$), 0.88 (m, 1H; H3$_{ax}$), −0.04 (s, 9H; Si(CH$_3$)$_3$); ^{13}C NMR: $\delta = 143.4$, 138.9, 129.9, 127.3 (Ar), 128.6 (C3′), 126.2 (C2′), 57.4 (C1), 43.8 (C2), 36.0 (C1′), 34.7 (C3), 31.0 (C6), 25.5 (C4), 25.3 (C5), 23.1 (C4′), 21.9 (ArCH$_3$), −1.6 (Si(CH$_3$)$_3$); elemental analysis (%) calcd for $C_{20}H_{33}NO_2SSi$ (379.65): C 63.27, H 8.76, N 3.69; found: C 63.45, H 8.56, N 3.73.

***N*-[(*E*)-2,2-Dimethyl-6-trimethylsilylundec-4-enyl]toluene-4-sulfonamide (19)**: Compound was obtained as a colorless oil (87% yield). ^{1}H NMR: $\delta =$ 7.74 (d, $J = 8.0$ Hz, 2H; Ar), 7.29 (d, $J = 8.0$ Hz, 2H; Ar), 5.12 (m, 2H; H5, H4), 4.43 (br s, 1H; NH), 2.67 (d, $J = 6.8$ Hz, 2H; H1), 2.42 (s, 3H; ArCH$_3$), 1.88 (d, $J = 6.4$ Hz, 2H; H3), 1.40 – 1.10 (br m, 9H; H6 – 10), 0.86 (t, $J =$ 7.2 Hz, 3H; H11), 0.83 (s, 6H; 2 × CH$_3$), −0.09 (s, 9H; Si(CH$_3$)$_3$); ^{13}C NMR: $\delta = 143.5$, 137.5, 130.0, 127.4 (Ar), 135.8 (C5), 123.2 (C4), 53.3 (C1), 43.5 (C3), 37.8 (C2), 33.6 (C6), 32.0 (C9), 29.3 (C8), 29.0 (C7), 25.2 (CH$_3$), 25.1 (CH$_3$), 23.0 (C10), 21.8 (ArCH$_3$), 14.5 (C11), −2.8 (Si(CH$_3$)$_3$). MS (CI): *m*/*z* (%): 424 (4) $[M+1]^+$, 423 (12) $[M]^+$, 408 (9) $[M - CH_3]^+$, 366 (11) $[C_{19}H_{32}NO_2SSi]^+$, 256 (34) $[C_{13}H_{22}NO_2S]^+$, 228 (12) $[C_{11}H_{18}NO_2S]^+$, 180 (11) $[C_{13}H_{24}]^+$, 133 (100), 91 (12) $[C_7H_7]^+$, 74 (62), 73 (30) $[C_3H_9Si]^+$.

Representative procedure for palladium(II)-catalyzed cyclization: The corresponding allylsilane (0.5 mmol), $Li_2[PdCl_4]$ (0.007 g, 0.025 mmol, 5 mol%), and $CuCl_2$ (0.168 g, 1.25 mmol) in *i*PrOH or *t*BuOH (5 mL) were stirred for the temperatures and times listed in Tables 1 and 2. When the reaction was complete, the reaction mixture was diluted with diethyl ether (25 mL) and extracted with brine (2 × 10 mL), followed by drying over anhydrous $MgSO_4$. The solvent was removed, and the products were purified by chromatography (pentane/diethyl ether).

4-Hydroxymethyl-2-vinyltetrahydrofuran (20a): Colorless oil. *cis* isomer: ^{1}H NMR: $\delta = 5.86$ (m, 1H; CHCH$_2$), 5.25 (dt, $J = 16.8$, 1.4 Hz, 1H; CHCH$_2$), 5.11 (dt, $J = 10.4$, 1.4 Hz, 1H; CHCH$_2$), 4.28 (m, 1H; H2), 3.86 (dd, $J = 8.8$, 7.6 Hz, 1H; H5), 3.75 (dd, $J = 8.8$, 5.6 Hz, 1H; H5), 3.60 (m, 2H; CH$_2$OH), 2.52 (m, 1H; H4), 2.20 (m, 1H; H3), 1.34 (m, 1H; H3). ^{13}C NMR: $\delta = 138.9$ (CHCH$_2$), 116.2 (CHCH$_2$), 80.9 (C2), 70.9 (C5), 65.5 (CH$_2$OH), 42.5 (C4), 35.7 (C3); *trans* isomer: ^{1}H NMR: $\delta = 5.82$ (m, 1H; CHCH$_2$), 5.23 (dt, $J = 16.8$, 1.4 Hz, 1H; CHCH$_2$), 5.09 (dt, $J = 10.4$, 1.4 Hz, 1H; CHCH$_2$), 4.38 (q, $J = 7.2$ Hz, 1H; H2), 4.03 (dd, $J = 8.8$, 7.0 Hz, 1H; H5), 3.60 (m, 3H; H5, CH$_2$OH), 2.52 (m, 1H; H4), 1.89 (m, 1H; H3), 1.80 (m, 1H; H3). ^{13}C NMR: $\delta = 139.1$ (CHCH$_2$), 115.6 (CHCH$_2$), 79.7 (C2), 70.8 (C5), 65.0 (CH$_2$OH), 41.8 (C4), 35.1 (C3); MS (CI): *m*/*z* (%): 130 (6) $[M+2]^+$, 129 (5) $[M+1]^+$, 115 (14) $[C_6H_{11}O_2]^+$, 94 (16), 81 (8) $[C_6H_9]^+$, 79 (55), 75 (54) $[C_3H_7O_2]^+$, 73 (100) $[C_4H_9O]^+$, 67 (53) $[C_5H_7]^+$.

4-Hydroxymethyl-4-methyl-2-vinyltetrahydrofuran (20b): Colorless oil. *cis* isomer: ^{1}H NMR: $\delta = 5.85$ (m, 1H; CHCH$_2$), 5.23 (dt, $J = 17.2$, 1.4 Hz, 1H; CHCH$_2$), 5.09 (dt, $J = 10.4$, 1.4 Hz, 1H; CHCH$_2$), 4.38 (m, 1H; H2), 3.83 (d, $J = 8.8$ Hz, 1H; H5), 3.50 (br s, 2H; CH$_2$OH), 3.45 (d, $J = 8.8$ Hz, 1H; H5), 1.80 (dd, $J = 12.8$, 7.2 Hz, 1H; H3), 1.60 (dd, $J = 12.8$, 8.4 Hz, 1H; H3), 1.15 (s, 1H; CH$_3$); ^{13}C NMR: $\delta = 139.0$ (CHCH$_2$), 116.0 (CHCH$_2$), 80.5 (C2), 76.9 (C5), 70.1 (CH$_2$OH), 45.6 (C4), 42.7 (C3), 21.9 (CH$_3$). *trans* isomer: ^{1}H NMR: $\delta = 5.85$ (m, 1H; CHCH$_2$), 5.21 (dt, $J = 17.2$, 1.4 Hz, 1H; CHCH$_2$), 5.07 (dt, $J = 10.4$, 1.4 Hz, 1H; CHCH$_2$), 4.38 (m, 1H; H2), 3.71 (d, $J = 8.8$ Hz, 1H; H5), 3.50 (m, 3H; H5,CH$_2$OH), 2.08 (dd, $J = 12.8$, 7.2 Hz, 1H; H3), 1.42 (dd, $J = 12.8$, 8.8 Hz, 1H; H3), 1.13 (s, 1H; CH$_3$); ^{13}C NMR: $\delta = 139.3$ (CHCH$_2$), 115.4 (CHCH$_2$), 80.6 (C2), 76.3 (C5), 68.9 (CH$_2$OH), 45.9 (C4), 42.7 (C3), 22.3 (CH$_3$). MS (EI): *m*/*z* (%): 143 (100) $[M+1]^+$, 142 (18) $[M]^+$, 125 (19) $[M - OH]^+$, 111 (30) $[C_7H_{11}O]^+$, 109 (28) $[C_7H_9O]^+$, 95 (24) $[C_7H_{11}]^+$, 81 (19) $[C_6H_9]^+$, 67 (53) $[C_5H_7]^+$.

2-Phenyl-5-vinyltetrahydrofuran (21a): Colorless oil. This compound was previously reported[22] without NMR data. *cis* isomer: ^{1}H NMR: $\delta = 7.40$ – 7.25 (m, 5H), 6.01 (m, 1H; CHCH$_2$), 5.34 (dt, $J = 15.6$, 1.2 Hz, 1H; CHCH$_2$), 5.16 (dt, $J = 10.4$, 1.2 Hz, 1H; CHCH$_2$), 4.96 (t, $J = 7$ Hz, 1H; H2), 4.49 (q, $J = 7$ Hz, 1H; H5), 2.33 (m, 1H; H3), 2.16 (m, 1H; H3), 1.85 (m, 2H; H4); ^{13}C NMR: $\delta = 143.6$ (CHCH$_2$), 139.3, 128.5, 127.4, 126.1 (Ar), 115.8 (CHCH$_2$), 81.5 (C2), 81.1 (C5), 34.8 (C3), 32.4 (C4); *trans* isomer: ^{1}H NMR: $\delta = 7.40$ – 7.25 (m, 5H), 5.95 (m, 1H; CHCH$_2$), 5.32 (dt, $J = 16.8$, 1.4 Hz, 1H; CHCH$_2$), 5.14 (dt, $J = 10.4$, 1.4 Hz, 1H; CHCH$_2$), 5.08 (t, $J =$ 7.6 Hz, 1H; H2), 4.49 (q, $J = 6.4$ Hz, 1H; H5), 2.40 (m, 1H; H3), 2.20 (m, 1H; H3), 1.86 (m, 2H; H4); ^{13}C NMR: $\delta = 143.7$ (CHCH$_2$), 139.5, 128.5, 127.4, 125.8 (Ar), 115.3 (CHCH$_2$), 81.0 (C2), 80.9 (C5), 35.6 (C3), 33.2 (C4). MS (EI): *m*/*z* (%): 175 (5) $[M+1]^+$, 174 (33) $[M]^+$, 157 (100) $[M - OH]^+$, 145 (58) $[C_{10}H_9O]^+$, 117 (90) $[C_9H_9]^+$, 104 (32) $[C_8H_8]^+$, 91 (15) $[C_7H_7]^+$, 77 (13) $[C_6H_5]^+$, 67 (42) $[C_5H_7]^+$.

2,2-Diphenyl-5-vinyltetrahydrofuran (21b): Colorless crystals, m.p. 68 – 69 °C. ^{1}H NMR: $\delta = 7.49$ – 7.17 (m, 10H), 5.97 (m, 1H; CHCH$_2$), 5.29 (dt, $J = 17.2$, 1.2 Hz, 1H; CHCH$_2$), 5.12 (dt, $J = 10.4$, 1.2 Hz, 1H; CHCH$_2$), 4.61 (q, $J = 6.8$ Hz, 1H; H5), 2.70 – 2.52 (m, 2H; H3), 2.11 (m, 1H; H4), 1.77 (m, 1H; H4); ^{13}C NMR: $\delta = 147.1$, 146.7, 128.4, 128.2, 126.9, 126.8, 126.1, 126.0 (Ar), 139.6 (CHCH$_2$), 115.7 (CHCH$_2$), 88.8 (C2), 80.4 (C5), 38.9 (C3), 32.4 (C4); MS (EI): *m*/*z* (%): 251 (7) $[M+1]^+$, 250 (17) $[M]^+$, 234 (35) $[C_{18}H_{18}]^+$, 182 (33) $[C_{13}H_{10}O]^+$, 180 (100) $[C_{14}H_{12}]^+$, 173 (53) $[C_{12}H_{13}O]^+$, 154 (37), 105 (73) $[C_7H_5O]^+$, 77 (37) $[C_6H_5]^+$, 68 (32) $[C_5H_8]^+$. For alternative procedure for preparation of **21b**, see ref. [22]

3,3-Dimethyl-2-phenyl-5-vinyltetrahydrofuran (22): Colorless oil. *Cis* isomer: ^{1}H NMR: $\delta = 7.40$ – 7.25 (m, 5H), 6.08 (m, 1H; CHCH$_2$), 5.37 (dt, $J =$ 17.2, 1.6 Hz, 1H; CHCH$_2$), 5.17 (dt, $J = 10.4$, 1.6 Hz, 1H; CHCH$_2$), 4.57 (s, 1H; H2), 4.52 (m, 1H; H5), 2.07 (m, 1H; H4), 1.71 (m, 1H; H4), 1.19 (s, 3H; CH$_3$), 0.64 (s, 3H; CH$_3$). ^{13}C NMR: $\delta = 139.2$ (CHCH$_2$), 139.8, 128.1, 127.4, 126.6 (Ar), 115.4 (CHCH$_2$), 90.0 (C2), 78.1 (C5), 47.5 (C3), 43.0 (C4), 27.3, 25.2 (CH$_3$). *Trans* isomer: ^{1}H NMR: $\delta = 7.40$ – 7.25 (m, 5H), 5.97 (m, 1H; CHCH$_2$), 5.30 (dt, $J = 17.2$, 1.4 Hz, 1H; CHCH$_2$), 5.11 (dt, $J = 10.4$, 1.4 Hz, 1H; CHCH$_2$), 4.72 (m, 1H; H5), 4.66 (s, 1H; H2), 2.07 (m, 1H; H4), 1.77 (m, 1H; H4), 1.13 (s, 3H; CH$_3$), 0.69 (s, 3H; CH$_3$); ^{13}C NMR: $\delta = 140.2$ (CHCH$_2$), 139.8, 127.9, 127.4, 126.6 (Ar), 114.8 (CHCH$_2$), 88.9 (C2), 78.3 (C5), 48.7 (C3), 43.7 (C4), 25.5, 22.4 (CH$_3$); MS (EI): *m*/*z* (%): 203 (50) $[M+1]^+$, 202 (20) $[M]^+$, 201 (100) $[M-1]^+$, 185 (96) $[C_{14}H_{17}O]^+$, 159 (10) $[C_{11}H_{11}O]^+$, 125 (10) $[C_8H_{13}O]^+$, 96 (7) $[C_7H_{12}]^+$, 81 (39) $[C_6H_9]^+$.

(*E*/*Z*)-5-(Hept-1′-enyl)-2,2-diphenyltetrahydrofuran (23): Colorless oil. *E* isomer: ^{1}H NMR: $\delta = 7.49$ – 7.17 (m, 10H), 5.75 (m, 1H; H1′), 5.57 (m, 1H; H2′), 4.55 (q, $J = 7.2$ Hz, 1H; H5), 2.72 – 2.52 (m, 2H; H3), 2.06 (m, 3H; H4, H3′), 1.75 (m, 1H; H4), 1.45 – 1.27 (m, 6H; H4′ – H6′), 0.90 (t, $J = 6.8$ Hz, 3H; H7′); ^{13}C NMR: $\delta = 147.3$, 146.9, 128.3, 128.2, 126.8, 126.7, 126.2 (Ar), 133.2 (C1′), 131.2 (C2′), 88.5 (C2), 80.6 (C5), 39.4 (C3), 32.9 (C4), 32.6 (C5′), 31.9 (C3′), 29.2 (C4′), 23.0 (C6′), 14.5 (C7′); *Z* isomer: ^{1}H NMR: $\delta = 7.49$ – 7.17 (m, 10H), 5.57 (m, 1H; H1′ and H2′), 4.90 (q, $J = 7.2$ Hz, 1H; H5), 2.72 – 2.52 (m, 2H; H3), 2.06 (m, 3H; H4 and H3′), 1.75 (m, 1H; H4), 1.45 – 1.27 (m, 6H; H4′-6′), 0.90 (t, $J = 6.8$ Hz, 3H; H7′); ^{13}C NMR: $\delta = 147.3$, 146.9, 128.3, 128.2, 126.8, 126.7, 126.2 (Ar), 133.2 (C1′), 131.2 (C2′), 88.5 (C2), 75.2 (C5), 39.8 (C3), 33.3 (C4), 32.6 (C5′), 29.8 (C3′), 28.1 (C4′), 23.0 (C6′), 14.5 (C7′); elemental analysis (%) calcd for $C_{23}H_{28}O$ (320.47): C 86.20, H 8.81; found C 86.01, H 8.99.

1-(Toluene-4-sulfonyl)-2-vinylpiperidine (25): Colorless oil. ^{1}H NMR: $\delta =$ 7.67 (d, $J = 8.0$ Hz, 2H; Ar), 7.25 (d, $J = 8.0$ Hz, 2H; Ar), 5.68 (m, 1H; H1′), 5.16 (dt, $J = 17.5$, 1.5 Hz, 1H; CHCH$_2$), 5.13 (dt, $J = 10.5$, 1.5 Hz, 1H; CHCH$_2$), 4.58 (br s, 1H; H2), 3.66 (d, $J = 13.6$ Hz, 1H; H6$_{eq}$), 2.98 (ddd, $J =$ 13.2, 12.8, 2.4 Hz, 1H; H6$_{ax}$), 2.40 (s, 3H; ArCH$_3$), 1.70 – 1.36 (br m, 6H; H3 – 5); ^{13}C NMR: $\delta = 143.2$, 138.2, 129.8, 127.6 (Ar), 135.8 (CHCH$_2$), 117.4 (CHCH$_2$), 55.3 (C6), 41.9 (C2), 30.0 (C3), 25.3 (C5), 21.8 (ArCH$_3$), 19.4 (C4). For alternative literature procedure for preparation of **25**, see ref. [23]

1-(Toluene-4-sulfonyl)-2-vinyloctahydroindole (26a, b): **26a**: Obtained as a 1/1 mixture of diastereomers, colorless oil. Diastereomer 1: ^{1}H NMR: $\delta =$ 7.72 (d, $J = 8.0$ Hz, 2H; Ar), 7.29 (d, $J = 8.0$ Hz, 2H; Ar), 5.93 (m, 1H; CHCH$_2$), 5.25 (dt, $J = 17.2$, 1.2 Hz, 1H; CHCH$_2$), 5.08 (dt, $J = 10.0$, 1.2 Hz, 1H; CHCH$_2$), 3.99 (q, $J = 8.3$ Hz, 1H; H2), 3.68 (dt, $J = 11.2$, 6.6 Hz, 1H; H7a), 2.42 (s, 3H; ArCH$_3$), 1.95 (m, 1H; H7), 1.82 (dd, $J = 10.0$, 8.7 Hz, 2H; H3), 1.70 – 1.11 (br m, 8H; H3a, H4 – H6, H7); ^{13}C NMR: $\delta = 143.4$, 136.3, 129.8, 127.7 (Ar), 141.0 (CHCH$_2$), 115.0 (CHCH$_2$), 62.7 (C7a), 61.4 (C2), 36.8 (C3a), 35.4 (C3), 31.2 (C4), 26.1 (C7), 24.5 (C5), 21.7 (ArCH$_3$), 20.6 (C6). Diastereomer 2: ^{1}H NMR: $\delta = 7.70$ (d, $J = 8.0$ Hz, 2H; Ar), 7.24 (d, $J = 8.0$ Hz, 2H; Ar), 5.62 (m, 1H; CHCH$_2$), 5.12 (dt, $J = 17.2$, 0.8 Hz, 1H; CHCH$_2$), 4.94 (dt, $J = 9.6$, 0.8 Hz, 1H; CHCH$_2$), 4.25 (t, $J = 8.2$ Hz, 1H; H2), 3.82 (dt, $J = 10.8$, 5.3 Hz, 1H; H7a), 2.40 (s, 3H; ArCH$_3$), 2.29 (m, 2H; H3), 2.21 (m, 1H; H7), 1.70 – 1.11 (br m, 8H; H3a, H4 – H6, H7); ^{13}C NMR: $\delta = 142.8$, 139.6, 129.4, 127.7 (Ar), 139.5 (CHCH$_2$), 115.7 (CHCH$_2$), 61.4 (C7a), 61.0 (C2), 35.8 (C3a), 35.0 (C3), 29.4 (C4), 26.3 (C7), 24.0 (C5), 21.7 (ArCH$_3$), 20.6 (C6). **26b**: Formed as a 1/1 mixture of diastereomers as colorless crystals, m.p. 90 – 92 °C. Diastereomer 1: ^{1}H NMR: $\delta = 7.70$ (d, $J =$ 8.0 Hz, 2H; Ar), 7.30 (d, $J = 8.0$ Hz, 2H; Ar), 5.86 (m, 1H; CHCH$_2$), 5.35 (d, $J = 16.4$ Hz, 1H; CHCH$_2$), 5.14 (d, $J = 10.0$ Hz, 1H; CHCH$_2$), 4.40 (q, $J = 8.0$ Hz, 1H; H2), 2.78 (dt, $J = 10.4$, 3.6 Hz, 1H; H7a), 2.54 – 2.44 (br m, 2H; H3), 2.43 (s, 3H; ArCH$_3$), 1.85 – 0.95 (br m, 9H; H3a, H4 – H7); ^{13}C NMR: $\delta = 142.8$, 140.1, 129.6, 127.6 (Ar), 140.0 (CHCH$_2$), 115.5 (CHCH$_2$), 65.8 (C7a), 62.2 (C2), 45.8 (C3a), 36.2 (C3), 32.9 (C4), 30.3 (C7), 25.6 (C5), 25.0 (C4), 21.8 (ArCH$_3$). Diastereomer 2: ^{1}H NMR: $\delta = 7.69$ (d,

$J = 8.0$ Hz, 2H; Ar), 7.24 (d, $J = 8.0$ Hz, 2H; Ar), 5.65 (m, 1H; C*H*CH_2), 5.22 (d, $J = 16.8$ Hz, 1H; CHCH_2), 5.05 (d, $J = 10.4$ Hz, 1H; CHCH_2), 4.22 (m, 1H; H2), 2.54 – 2.44 (br m, 2H; H3), 2.40 (s, 3H; ArCH_3), 2.18 (m, 1H; H7a), 1.85 – 0.95 (br m, 9H; H3a, H4 – 7); ^{13}C NMR: $\delta = 143.6$, 135.1, 129.8, 128.1 (Ar), 139.7 (CHCH$_2$), 115.7 (CH*C*H$_2$), 67.2 (C7a), 63.6 (C2), 43.2 (C3a), 38.4 (C3), 31.2 (C4), 29.9 (C7), 25.7 (C5), 25.3 (C4), 21.9 (ArCH_3); MS (CI): *m*/*z* (%): 306 (13) $[M+1]^+$, 305 (63) $[M]^+$, 262 (100) $[C_{14}H_{16}NO_2S]^+$, 241 (17), 198 (6) $[C_9H_{12}NO_2S]^+$, 155 (14) $[C_7H_7O_2S]^+$, 150 (21) $[C_{10}H_{16}N]^+$, 107 (13) $[C_8H_{11}]^+$, 91 (29) $[C_7H_7]^+$.

2-(Hept-1′-enyl)-4,4-dimethyl-1-(toluene-4-sulfonyl)pyrrolidine (27): Obtained as a 4/1 mixture of *E* and *Z* isomers, colorless oil. ^{1}H NMR: $\delta = 7.67$ (d, $J = 8.0$ Hz, 2H; Ar), 7.26 (d, $J = 8.0$ Hz, 2H; Ar), 5.68 (m, 1H; H1′), 5.34 (m, 1H; H2′), 4.05 (q, $J = 7.9$ Hz, 1H; H2), 3.22 (dd, $J = 9.9$, 1.3 Hz, 1H; H5), 3.15 (dd, $J = 9.9$ Hz, 1H; H5), 2.42 (s, 3H; ArCH_3), 1.96 (m, 2H; H3′), 1.74 (ddd, $J = 12.7$, 7.4, 1.2 Hz, 1H; H3), 1.52 (dd, $J = 12.6$, 8.5 Hz, 1H; H3), 1.29 (br m, 6H; H4′ – H6′), 1.05 (s, 3H; CH_3), 0.88 (s, 3H; H7′), 0.76 (s, 3H; CH_3); ^{13}C NMR: $\delta = 143.2$, 136.7, 129.6, 127.9 (Ar), 132.6 (C1′), 131.3 (C2′), 62.3 (C5), 61.6 (C2), 48.3 (C3), 37.7 (C4), 32.3 (C3′), 31.8 (C5′), 29.0 (C4′), 26.8 (*C*H_3), 26.4 (*C*H_3), 22.9 (C6′), 21.8 (ArCH_3), 14.4 (C7′); elemental analysis (%) calcd for $C_{20}H_{31}NO_2S$ (349.54): C 68.72, H 8.94, N 4.01; found: C 68.59, H 9.06, N 4.16.

Formation of the (η^3-allyl)palladium complexes: The influence of the chloride concentration on the formation of the (η^3-allyl)palladium complex **29** was studied by mixing $Pd(OAc)_2$ (0.011 g, 0.05 mmol) with various amounts of Ph_4PCl in $CDCl_3$ (0.5 mL). This solution was transferred to an NMR tube followed by addition of **28** (0.006 g, 0.05 mmol) in $CDCl_3$ (0.2 mL). Formation of **29** was monitored by ^{1}H NMR spectroscopy. The solvent effect was studied by using $Pd(OAc)_2$ (0.011 g, 0.05 mmol), Ph_4PCl (0.002 g, 0.005 mmol), and **28** (0.006 g, 0.05 mmol) dissolved in various $CD_3OD/CDCl_3$ mixtures (0.7 mL).

Bis(μ-Chloro)bis[1-phenyl-(4,5,6-η^3)-hexen-1-ol]palladium (30): Allylsilane **5a** (0.040 g, 0.16 mmol) in methanol (3.5 mL) was added to a stirred solution of $Li_2[PdCl_4]$ (0.045 g, 0.17 mmol) in methanol (3.5 mL) at 0 °C. The progress of the reaction was monitored by TLC (pentane/diethyl ether 4/1). After completion of the reaction, the solvent was removed, and the residual yellow oil was purified by chromatography (CH_2Cl_2/MeOH 14/1) to afford **30** as yellow crystals (88% yield). Complex **30** was formed as a 1/1 mixture of diastereomers. ^{1}H NMR: $\delta = 7.34$ (m, 4H; Ar), 7.28 (m, 1H; Ar), 5.27 (m, 1H; H5), 4.75 (m, 1H; H4), 3.88 (m, 2H; H6), 2.82 (d, $J = 11.8$, 6.8 Hz, 1H; H1), 2.30 – 1.69 (br m, 2H; H2, H3); ^{13}C NMR: $\delta = 144.4$, 144.3, 128.7, 127.8, 126.1, 126.0 (Ar), 110.1, 110.0 (C5), 86.2, 86.1 (C4), 74.2, 73.8 (C1), 59.3 (C6), 38.2, 37.8 (C2), 28.9, 28.7 (C3); MS (CI): *m*/*z* (%): 634 (1) $[M+2]^+$, 175 (6) $[C_{12}H_{15}O]^+$, 157 (26) $[C_{12}H_{13}]^+$, 117 (47), 107 (43) $[C_7H_7O]^+$, 79 (100) $[C_6H_7]^+$, 77 (55) $[C_6H_5]^+$, 67 (40) $[C_5H_7]^+$.

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