

Highly Stereoselective Synthesis of Bicyclo[*n*.3.0]alkanes by Titanium Tetrachloride Promoted [3 + 2] Cycloaddition of Allylsilanes and 1-Acetylcycloalkenes**

Hans-Joachim Knölker,* Norbert Foitzik, Helmut Goesmann, Regina Graf, Peter G. Jones, and Günter Wanzl

Abstract: The titanium tetrachloride promoted reaction of allylsilanes **1** with 1-acetylcyclohexene is shown to afford the silylbicyclo[4.3.0]nonanes **9** ([3 + 2] cycloaddition products) along with the 1-acetyl-2-allylcyclohexane **4** (Hosomi–Sakurai product). Here we report that systematic variation of the substituents at the silicon atom of **1** allows suppression of the classical Hosomi–Sakurai reaction in

favor of the [3 + 2] cycloaddition. Cycloaddition of the allylsilanes **1d**, **1i**, and **1k** with 1-acetylcycloalkenes **10**, containing a 5-, 6-, 7-, 8-, or 12-membered ring,

Keywords

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gives rise to the corresponding silylbicyclo[*n*.3.0]alkanes **11–13**. The cycloaddition of allyltriisopropylsilane (**1k**) and 1-acetyl-2-methylcycloalkenes **15** provides silylbicyclo[*n*.3.0]alkanes **16** with two contiguous quaternary carbon centers. The stereochemistry of the silylbicyclo[*n*.3.0]alkanes **11a–c** and **14** is unambiguously determined by X-ray analysis and ¹³C NMR spectroscopy.

Introduction

The formation of five-membered ring systems by [3 + 2] cycloaddition has received much attention in organic chemistry as an important method for the synthesis of cyclopentanoid products.^[1] We discovered the formation of trimethylsilylcyclopentanes^[2] as by-products in the Hosomi–Sakurai reaction.^[3] These by-products were originally considered to be silylmethylcyclobutanes^[4] and have been reassigned as silylcyclopentanes.^[2a, 5] They result from a [3 + 2] cycloaddition that involves a stereoselective cationic 1,2-silyl shift,^[6] thus generating a new silyl-substituted stereogenic center. A broad range of subsequent examples have confirmed our original findings.^[7] Related [3 + 2] cycloadditions of allenylsilanes were previously exploited by Danheiser et al. for the synthesis of silylcyclopentenes.^[8] The

advantage of our reaction is that new stereogenic centers are formed diastereoselectively, which opens up the possibility of asymmetric induction.

Our first objective was the optimization of the [3 + 2] cycloaddition of allylsilanes at the expense of the classical Hosomi–Sakurai reaction. This could be achieved by variation of the substituents at the silicon atom of the allylsilane.^[9] The scope and limitations of this novel [3 + 2] cycloaddition were investigated by reaction of 1-acetylcycloalkenes, with different ring sizes and different substitution patterns, with selected allylsilanes. The stereoselectivity of the reaction was ascertained by X-ray analysis and ¹³C NMR spectroscopy of the products.

Results and Discussion

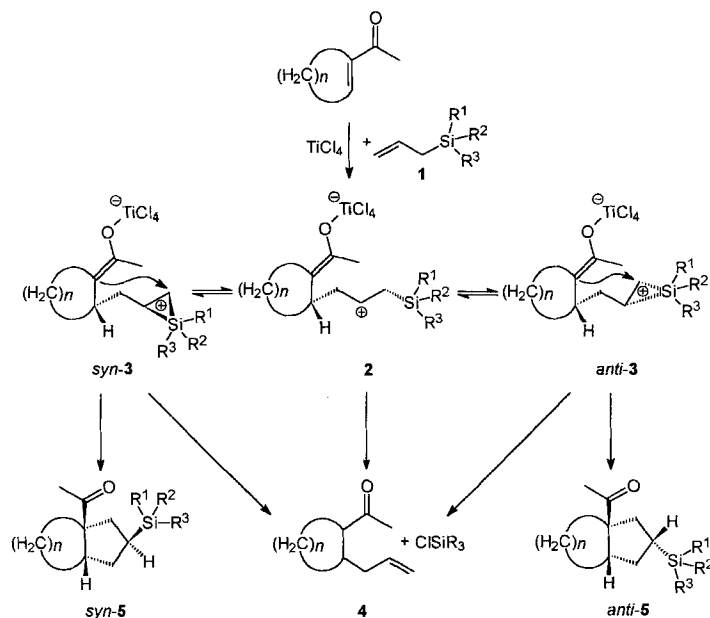
Mechanism and Optimization of the [3 + 2] Cycloaddition: The formation of cyclopentanes as products of the titanium tetrachloride promoted addition of allylsilanes to α,β -unsaturated ketones involves a β -silyl cation induced 1,2-silyl shift.^[6] The first step in this cyclopentane annulation is the nucleophilic attack of the allylsilane **1** at the β -enone position of the Lewis acid/enone complex (Scheme 1). In this process, the silyl group activating the double bond to electrophilic attack is oriented *anti* to the incoming nucleophile. The generated β -silyl cation **2** is stabilized by the so-called β -effect. Three different mechanisms of stabilization are considered to contribute to the β -effect:^[10]

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Scheme 1. Proposed mechanism of the [3+2] cycloaddition.

- 1) The positive charge in the β -position may be stabilized by through-bond σ -induction because silicon is more electropositive than carbon.
- 2) The carbon–silicon σ -bond is able to stabilize the positive charge by hyperconjugation (donation of C–Si σ -electrons to the empty carbon p-orbital) due to its high polarizability (“vertical stabilization” according to Traylor).
- 3) Stabilization of the positive charge by neighboring group participation of the silicon atom, which acts as an internal nucleophile to generate a siliranium ion^[11] (“nonvertical stabilization” according to Traylor).^[10a]

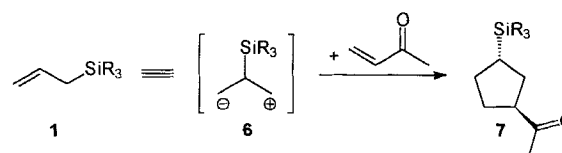
The stereoselective attack of the electrophile (the Lewis acid/enone complex) at the allylsilane **1** provides the intermediate cation **2** with the silyl group oriented *anti* relative to the new carbon–carbon bond. Cation **2** can directly form the bridged intermediate *anti*-**3**, which finally cyclizes to the product *anti*-**5**.

Abstract in German: Die Titanetetrachlorid-vermittelte Reaktion der Allylsilane **1** mit 1-Acetylcyclohexen liefert neben dem 1-Acetyl-2-allylcyclohexan **4** (Hosomi-Sakurai-Produkt) die Silylbicyclo[4.3.0]nonane **9** ([3+2]-Cycloadditionsprodukte). Wir berichten hier über die Unterdrückung der klassischen Hosomi-Sakurai-Reaktion zugunsten der [3+2]-Cycloaddition durch systematische Variation der Substituenten am Siliciumatom von **1**. Die Cycloaddition der Allylsilane **1d**, **1i** und **1k** an die 1-Acetylcycloalkene **10** verschiedener Ringgrößen (5-, 6-, 7-, 8- und 12-gliedrige Ringe) führt zu den Silylbicyclo[*n*.3.0]alkanen **11–13**. Die Cycloaddition von Allyltriisopropylsilan **1k** und den 1-Acetyl-2-methylcycloalkenen **15** liefert die Silylbicyclo[*n*.3.0]alkane **16** mit zwei aufeinanderfolgenden quartären Kohlenstoffatomen. Die Konfiguration der Silylbicyclo[*n*.3.0]alkane **11a–c** und **14** wird durch Röntgenstrukturanalysen und ¹³C-NMR-spektroskopisch zweifelsfrei belegt.

Alternatively, rotation about the carbon–carbon bond in cation **2** would result in the formation of the siliranium ion *syn*-**3**, which would afford the diastereoisomeric product *syn*-**5**.

The siliranium ion, a bridged nonclassical pentavalent silicon cation, is the crucial intermediate in the [3+2] cycloaddition. Nonvertical stabilization of the positive charge by the silicon atom generates two diastereoisomeric siliranium ions *syn*-**3** and *anti*-**3**. Both diastereoisomers can be interconverted via the β -silyl cation **2**. Intermolecular nucleophilic attack of a chloride ion at the silicon atom of any of the three cationic species (**2**, *syn*-**3**, and *anti*-**3**) affords chlorosilane and the product of the Hosomi–Sakurai reaction **4**, after hydrolysis during workup. Alternatively, the intramolecular nucleophilic attack of the titanium enolate at the primary carbon atom of the siliranium ions **3** provides the silylbicyclo[*n*.3.0]alkanes **5**. The cyclization of the siliranium ions **3** to give a silylcyclopentane requires an approach of the titanium enolate with a collinear arrangement of the enolate β -carbon, the primary carbon of the siliranium ion, and the silicon atom (5-*exo-tet* cyclization^[12]). The cyclization is highly stereospecific and occurs with retention of configuration of the carbon–silicon bond of *syn*-**3** and *anti*-**3**. Because of the stereoelectronic requirements, the cyclization via *anti*-**3** is preferred, since the conformation that enables adoption of the appropriate collinear arrangement is less strained for this diastereoisomer.

The present methodology of cyclopentane annulation by [3+2] cycloaddition of allylsilanes **1** to enones, which stereoselectively provides trialkylsilylcyclopentanes **7**, demonstrates that allylsilanes might serve as synthetic equivalents for a 2-trialkylsilyl-substituted 1,3-dipole **6** (Scheme 2).



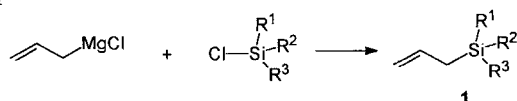
Scheme 2. Allylsilanes as synthetic equivalents of 2-silyl-substituted 1,3-dipoles.

Variation of the substituents at silicon should provide a tool to suppress nucleophilic attack of chloride at the silicon atom of the siliranium ion and thus prevent formation of the Hosomi–Sakurai product **4**. For this purpose, we investigated the reactivity of a variety of allylsilanes in the titanium tetrachloride promoted reaction with 1-acetylcyclohexene. The optimization achieved for the cyclopentane annulation can be seen by comparing the yields of the Hosomi–Sakurai product **4** and the silylbicyclo[4.3.0]nonanes **9** (Scheme 3, Table 1).

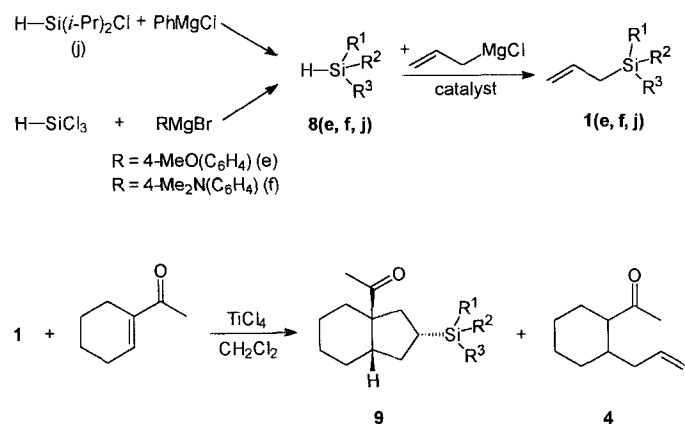
The allylsilanes **1** that are not commercially available were easily prepared by treatment of allylmagnesium chloride with the appropriate chlorosilanes (method A) or alternatively by transition metal catalyzed coupling of the corresponding hydrosilanes **8** with allylmagnesium chloride (method B).^[13]

An optimization of the reaction conditions led to the development of a standard reaction procedure, which provides a relatively high percentage of cycloadduct for the cycloaddition of 1-acetylcyclohexene and the parent allylsilane **1a**. According to this standard protocol, the titanium tetrachloride–enone com-

Method A:



Method B:

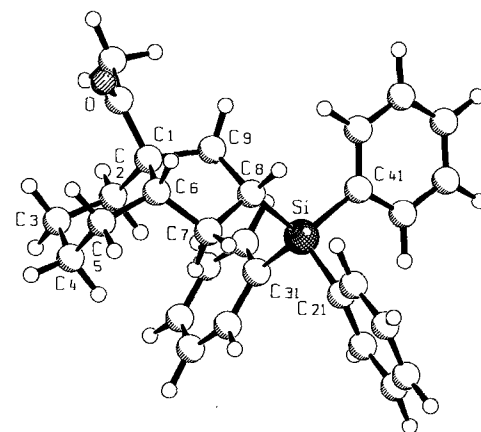
Scheme 3. Synthesis of allylsilanes **1** and [3+2] cycloadditions to silylbicyclo[4.3.0]nonanes **9**.Table 1. Optimization of the [3+2] cycloaddition of allylsilanes **1** with 1-acetylcyclohexene by variation of the substituents at silicon atom (see Scheme 3).

	R ¹	R ²	R ³	Yield [%]		
				1 (method) [a]	9	4
a	CH ₃	CH ₃	CH ₃	—	18	76
b	CH ₃	CH ₃	Ph	89 (A)	19	76
c	CH ₃	Ph	Ph	99 (A)	38	46
d	Ph	Ph	Ph	99 (A)	51	39
e	4-MeO(C ₆ H ₄)	4-MeO(C ₆ H ₄)	4-MeO(C ₆ H ₄)	64 (A) [b]; 77 (B)	—	55
f	4-Me ₂ N(C ₆ H ₄)	4-Me ₂ N(C ₆ H ₄)	4-Me ₂ N(C ₆ H ₄)	91 (B)	—	—
g	CH ₃	CH ₃	<i>t</i> Bu	—	40	—
h	CH ₃	CH ₃	thexyl	92 (A)	60	trace
i	<i>t</i> Bu	Ph	Ph	97 (A)	69	trace
j	<i>i</i> Pr	<i>i</i> Pr	Ph	61 (A) [c]; 61 (B)	68	trace
k	<i>i</i> Pr	<i>i</i> Pr	<i>i</i> Pr	—	86	2

[a] Method of preparation (see Scheme 3). [b] Yield based on tetrachlorosilane to which first 4-methoxyphenylmagnesium bromide and then allylmagnesium chloride were added. [c] Yield based on dichlorodisopropylsilane to which first phenylmagnesium chloride and then allylmagnesium chloride were added; by-product: diallyldisopropylsilane (18%).

plex is prepared in dichloromethane at -20°C , and the allylsilane (1.5 equiv) is added at -78°C . The reaction mixture is stirred at -20°C for 19 h and then quenched by addition of an aqueous ammonium chloride solution. By this technique the cycloadduct **9a** was obtained in a maximum yield of 18%. The *anti* stereochemistry of **9a**, which was obtained as a single diastereoisomer, was unequivocally confirmed by an X-ray crystal structure determination of the corresponding 2,4-dinitrophenylhydrazone.^[2a, 5a] The prefix *anti* refers to the position of the silyl group relative to the acetyl group. In order to achieve an optimization of the [3+2] cycloaddition by stabilization of the cationic intermediates **3** through steric and/or electronic effects, we tested allylsilanes **1b–d** in which the methyl groups are replaced successively by phenyl groups. Moreover, we envisaged a further synthetically useful transformation of the result-

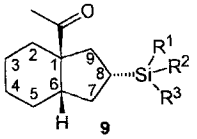
ing products by oxidative cleavage of the carbon–silicon bond to the corresponding carbinol.^[14] A significant increase of the yield of cycloadduct (38% of **9c**) was realized for the cycloaddition of allylmethyldiphenylsilane (**1c**). With allyltriphenylsilane (**1d**) the bicyclo[4.3.0]nonane **9** was obtained as the major product (51% of **9d**) for the first time. The stereochemistry of the triphenylsilyl derivative **9d** was assigned based on an X-ray analysis of single crystals, which again confirmed the *anti* arrangement of the silyl and acetyl groups (Figure 1, Table 2).

Figure 1. Molecular structure of **11b** (= **9d**) in the crystal (SCHAKAL representation; arbitrary numbering). Selected bond lengths [Å]: C8–C9 1.553(3), C1–C9 1.547(3), C1–C6 1.537(3), C6–C7 1.523(3), C7–C8 1.543(3), Si–C8 1.875(2), Si–C21 1.877(2), Si–C31 1.872(2), Si–C41 1.876(2).Table 2. X-ray crystal-structure analysis of **11a**, **11b** (= **9d**), and **11c**.

	11a	11b (= 9d)	11c
Crystal data			
empirical formula	C ₂₄ H ₃₀ OSi	C ₂₉ H ₃₂ OSi	C ₃₀ H ₃₄ OSi
formula weight	410.6	424.6	438.7
color, habit	colorless tablet	colorless tablet	colorless tablet
crystal size [mm]	0.28 × 0.20 × 0.10	0.85 × 0.50 × 0.25	—
crystal system	monoclinic	monoclinic	triclinic
space group	P2 ₁ /c	C2/c	P1
a [Å]	10.024(5)	26.567(4)	10.441(5)
b [Å]	11.123(7)	9.680(2)	11.956(6)
c [Å]	20.896(11)	19.552(4)	12.069(6)
α [°]	90	90	88.27(3)
β [°]	103.28(4)	103.29(2)	65.14(2)
γ [°]	90	90	69.55(3)
V [Å ³]	2268(2)	4894(2)	1269
Z	4	8	2
ρ _{calcd} [g cm ⁻³]	1.203	1.153	1.15
absorption coeff. [mm ⁻¹]	0.121	0.114	0.077
F(000)	880	1824	472
Data collection			
λ [Å]	0.71073	0.71073	0.71073
T [K]	200	293	290
θ range [°]	5.26–28.21	3.15–25.03	1.5–28.0
reflns collected	14116	4638	6441
independent reflns	5447	4318	5069
Refinement			
method	full-matrix least squares on F ²	full-matrix least squares on F ²	full-matrix least squares on F
data-to-parameter ratio	13.9:1	15.3:1	9.9:1
final R indices [I > 2σ(I)]	R ₁ = 0.0586 wR ₂ = 0.1500	R ₁ = 0.0444 wR ₂ = 0.1122	R = 0.053 Rw = 0.050
max. resid. electron density [e Å ⁻³]	0.35	0.24	0.45
CSD no. [15]	59415	405717	57205

The phenyl-substituted bicyclo[4.3.0]nonanes **9b–d** were obtained exclusively as single diastereoisomers. All products were completely characterized by ^1H and ^{13}C NMR spectroscopy (see Experimental Section). Comparison of some characteristic ^1H and ^{13}C NMR data of **9b** and **9c** with those of **9a** and **9d** (Table 3), whose stereochemistry was determined by X-ray analysis, unambiguously confirms the *anti* stereochemistry in all cases.

Table 3. Selected ^1H and ^{13}C NMR data (CDCl_3) of bicyclo[4.3.0]nonanes **9**.



	R ¹	R ²	R ³	$\delta(\text{H}-\text{C}6)$	$\delta(\text{C}6)$	$\delta(\text{C}8)$
9a	CH ₃	CH ₃	CH ₃	2.44	41.61	23.55
9b	CH ₃	CH ₃	Ph	2.45	41.40	22.70
9c	CH ₃	Ph	Ph	2.49	41.31	21.15
9d	Ph	Ph	Ph	2.48	41.04	19.94
9g	CH ₃	CH ₃	<i>t</i> Bu	2.42	41.46	20.48
9h	CH ₃	CH ₃	hexyl	2.41	41.42	21.84
9i	<i>t</i> Bu	Ph	Ph	2.42	40.94	18.39
9j	<i>i</i> Pr	<i>i</i> Pr	Ph	2.41	41.24	19.87
9k	<i>i</i> Pr	<i>i</i> Pr	<i>i</i> Pr	2.40	41.56	20.88

Encouraged by the results obtained with allyltriphenylsilane **1d**, we synthesized the allyltriarylsilanes **1e** and **1f**, substituted at the *para* positions with donor groups. Allyltri(4-methoxyphenyl)silane (**1e**) was prepared in 64% yield by method A, by treatment of tetrachlorosilane with 3.3 equiv of 4-methoxyphenylmagnesium bromide and then 1.2 equiv allylmagnesium chloride. Addition of a smaller excess of 4-methoxyphenylmagnesium bromide caused the formation of diallyldi(4-methoxyphenyl)silane. Method B was found to be superior for the synthesis of the allylsilanes **1e** and **1f**. Treatment of trichlorosilane with a threefold excess of the corresponding Grignard reagent afforded the hydridosilanes **8e** and **8f**, which were subjected to a nickel(II)-catalyzed coupling with allylmagnesium chloride.^[13] The titanium tetrachloride promoted addition of **1e** and 1-acetylcyclohexene provided only the Hosomi–Sakurai reaction product **4** in 55% yield. With allylsilane **1f** no product was obtained. Further attempts to achieve titanium tetrachloride promoted cycloadditions of 1-acetylcyclohexene with allyl-*tert*-butoxydiphenylsilane and allyltriethoxysilane resulted in decomposition of the allylsilane.

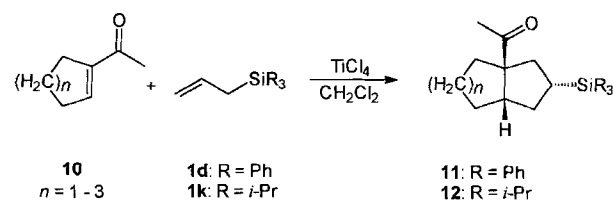
We next investigated the Lewis acid promoted cycloaddition of 1-acetylcyclohexene with allylsilanes having sterically demanding substituents. The synthesis of allyldiisopropylphenylsilane (**1j**) by method A (by successive addition of phenylmagnesium chloride and then allylmagnesium chloride to dichlorodiisopropylsilane) afforded the desired product (61% yield) and diallyldiisopropylsilane (18% yield), which were difficult to separate. Alternatively, **1j** was prepared by method B in 61% yield by addition of phenylmagnesium chloride to chlorodiisopropylsilane and subsequent [bis(triphenylphosphine)]nickel dichloride catalyzed coupling^[13] of the intermediate diisopropylphenylsilane (**8j**) with allylmagnesium chloride.

The results of the [3 + 2] cycloadditions of 1-acetylcyclohexene and the allylsilanes **1g–k** led us to the conclusion that in-

creasing steric demand of the substituents at the silicon atom gives increasing yields of the silylbicyclo[4.3.0]nonanes **9**. High yields of the cycloadducts were obtained with bulky alkyl substituents at the allylsilane moiety, presumably because the nucleophilic attack at silicon at the stage of the intermediate cations **2** and **3** is inhibited. A similar effect has been reported by Mayr et al. for the Lewis acid promoted reaction of diarylmethyl chlorides with allylsilanes.^[16] In all examples investigated for this silylcyclopentane annulation at 1-acetylcyclohexene, only one stereoisomer of product **9** was isolated under our optimized reaction conditions. The structural assignments of the 8-silylbicyclo[4.3.0]nonanes **9g–k** are based on a full characterization by 400 MHz ^1H NMR and 100 MHz ^{13}C NMR spectra. The assignments of the signals were confirmed by additional COSY, $^1\text{H}/^{13}\text{C}$ -correlated, and DEPT spectra. The *anti* arrangement of the silyl and the acetyl group of compounds **9a**^[2a, 5a] and **9d** was unequivocally determined by X-ray analysis (Figure 1, Table 2). The *anti* stereochemistry of the compounds **9g–k** was confirmed by comparison of selected NMR data with those of **9a** and **9d** (Table 3). The signal for the angular proton at C6 appears as a characteristic multiplet in the region of $\delta = 2.4$ –2.5. For all derivatives, the ^{13}C NMR signal of C6 is observed at $\delta = 41$ –42. The characteristic ^{13}C NMR signal of C8 (α to Si) for this type of compound generally appears in the region $\delta = 18.4$ –23.6.

Our major achievement here is the suppression of the classical Hosomi–Sakurai reaction in favor of the [3 + 2] cycloaddition by using bulky substituents at the silicon atom of the allylsilane **1**. Thus, the addition of allyltriisopropylsilane (**1k**) and 1-acetylcyclohexene according to our optimized reaction procedure provided **9k** as a single diastereoisomer in 86% yield. Danheiser et al. have reported the synthesis of **9k** in 45% yield as a mixture of diastereoisomers.^[7a]

Variation of the Ring Size: We next investigated the [3 + 2] cycloaddition of allylsilanes (**1d** and **1k**) with 1-acetylcycloalkenes **10** of different ring size (five- to seven-membered rings) (Scheme 4, Table 4). The 1-acetylcycloalkenes can be prepared



Scheme 4. Variation of the ring size of the 1-acetylcycloalkene **10**.

Table 4. [3 + 2] Cycloadditions of allylsilanes **1d** (R = Ph) and **1k** (R = *i*Pr) with 1-acetylcycloalkenes **10a–c** ($n = 1$ –3; Scheme 4).

Product	R	<i>n</i>	Yield [%]	Stereochem. [a]	$\delta(\text{C}-\text{Si})$ [b]
11a	Ph	1	25	<i>anti</i>	25.23
11b (= 9d)	Ph	2	51	<i>anti</i>	19.94
11c	Ph	3	34	<i>anti</i>	23.09
12a	<i>i</i> Pr	1	71	<i>anti/syn</i> = 3:1	24.94/21.14
12b (= 9k)	<i>i</i> Pr	2	86	<i>anti</i>	20.88
12c	<i>i</i> Pr	3	68	<i>anti</i>	22.65

[a] Position of the silyl group relative to the acetyl group. [b] Chemical shift of the CH group α to Si in the ^{13}C NMR spectrum (100 MHz, CDCl_3).

by Friedel–Crafts acylation of the corresponding cycloalkenes.^[17] However, much higher yields were obtained by Rupe rearrangement of 1-ethynylcycloalkanols (see Table 5).^[18] We selected the allylsilanes **1d** and **1k** because the former generates crystalline products and provides suitable crystals for X-ray analyses, while the latter gives the best yields of cyclopentane derivatives. It was of special interest to us whether the same stereoselectivity would be observed with 1-acetylcyclopentene (**10a**) and 1-acetylcycloheptene (**10c**) as in the cycloaddition of 1-acetylcyclohexene (**10b**).

The stereochemical assignments of the bicycloalkanes **12a** and **12c** are based on the X-ray analyses of **11a** and **11c** (Figure 2 and 3, Table 2) and a comparison of the corresponding characteristic NMR data.

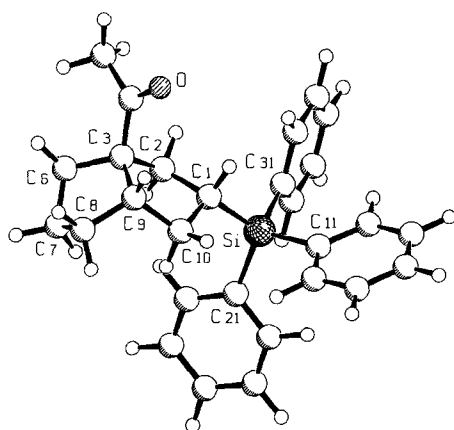


Figure 2. Molecular structure of **11a** in the crystal (SCHAKAL representation; arbitrary numbering). Selected bond lengths [Å]: C1–C2 1.524(3), C2–C3 1.555(3), C3–C9 1.551(3), C9–C10 1.534(3), C1–C10 1.521(3), Si–C1 1.881(2), Si–C11 1.873(2), Si–C21 1.873(2), Si–C31 1.862(2).

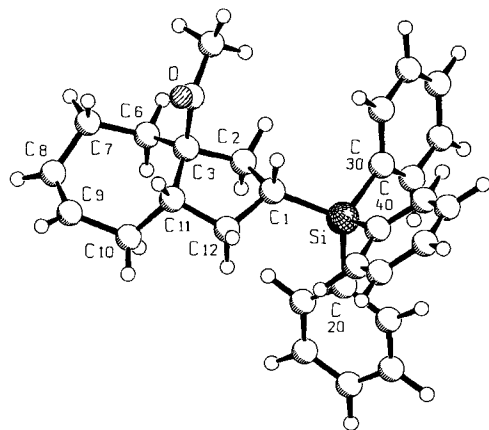
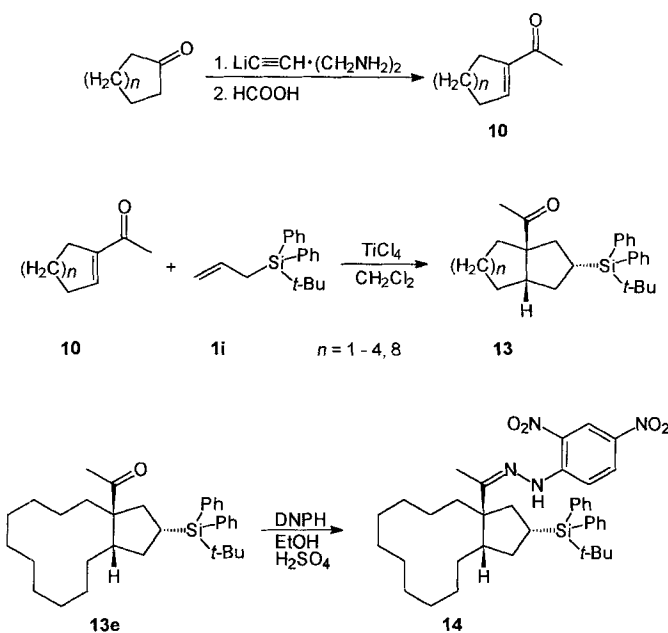


Figure 3. Molecular structure of **11c** in the crystal (SCHAKAL representation; arbitrary numbering). Selected bond lengths [Å]: C1–C2 1.543(5), C2–C3 1.543(5), C3–C11 1.557(5), C11–C12 1.546(4), C1–C12 1.534(6), Si–C1 1.879(4), Si–C20 1.878(3), Si–C30 1.884(4), Si–C40 1.876(3).

The cycloaddition of allyltriisopropylsilane (**1k**) to 1-acetylcyclopentene (**10a**) gives only a 3:1 selectivity (*anti*-**12a**:*syn*-**12a**) in favor of the product with the bulky triisopropylsilyl group in an *anti* position relative to the acetyl group (Table 4). Steric reasons are responsible for this loss of stereoselectivity. In *anti*-**12a** the bulky triisopropylsilyl group is in a sterically con-

gested region on the *endo* side, that is, the concave face of the roof-shaped molecule. In all other cycloadditions the *anti* diastereoisomer was formed exclusively.

For potential synthetic applications of the Lewis acid promoted cycloaddition of allylsilanes, we must be able to remove the sterically hindered silyl groups from the cycloaddition products. The appropriate methodology is the oxidative cleavage of the carbon–silicon bond.^[14] Fleming et al. demonstrated the conversion of dimethylphenylsilylalkanes into hydroxyalkanes.^[19] A related transformation has been described by Tamao et al. with diethoxymethylsilylalkanes.^[20] Our own investigations with the methylphenylsilyl derivative **9c** and the triphenylsilyl derivative **9d** demonstrated that the cleavage of even more sterically hindered silylalkanes is possible in high yields by modification of the reaction conditions.^[21] Therefore, we additionally investigated the [3 + 2] cycloaddition of allyl-*tert*-butyldiphenylsilane (**1i**) with 1-acetylcycloalkenes **10** of different ring size including medium-sized ring systems (Scheme 5, Table 5). 1-Acetylcyclooctene (**10d**) and 1-acetylcyclododecene (**10e**) can readily be prepared from the corresponding cycloalkanones by treatment with ethynyllithium and subsequent Rupe rearrangement of the intermediate 1-ethynylcycloalkanols (see Experimental Section).^[18]



Scheme 5. Rupe rearrangement to the 1-acetylcycloalkenes **10** of different ring sizes (top) and their [3 + 2] cycloaddition with **1i** (middle); synthesis of **14** (bottom).

Table 5. [3 + 2] Cycloadditions of allyl-*tert*-butyldiphenylsilane (**1i**) with 1-acetylcycloalkenes **10**.

10 (yield [a])	<i>n</i>	Product	Yield [%]	Stereochem. [b]	$\delta(\text{C} - \text{Si})$ [c]
a (84)	1	13a	53	<i>anti</i>	23.84
b (–)	2	13b (= 9i)	69	<i>anti</i>	18.39
c (72)	3	13c	50	<i>anti</i>	21.53
d (44)	4	13d	82	<i>anti</i>	18.14
e (60)	8	13e	65	<i>anti</i>	17.66

[a] Yield [%] obtained by the Rupe rearrangement (Scheme 5, top). [b] Position of the silyl group relative to the acetyl group. [c] Chemical shift of the CH group α to Si in the ¹³C NMR spectrum (100 MHz, CDCl₃).

All cycloaddition products **13** were obtained as single diastereoisomers with an *anti* arrangement of the silyl substituent relative to the angular acetyl group. The structural and stereochemical assignments of the bicycloalkanes **13a–d** are based on a complete characterization by ^1H and ^{13}C NMR spectroscopy and a comparison of the chemical shift for the CH signal α to silicon with the corresponding data of **11a–c** (Table 4) which were characterized by X-ray analyses.

Additionally, the *anti* stereochemistry of **13e** was unequivocally confirmed by an X-ray crystal structure determination of the corresponding 2,4-dinitrophenylhydrazone derivative **14** (Scheme 5; Figure 4, top). The side view of the molecular structure of **14** in the crystal (Figure 4, bottom) emphasizes the corrugated conformation of the 12-membered ring in the solid state.

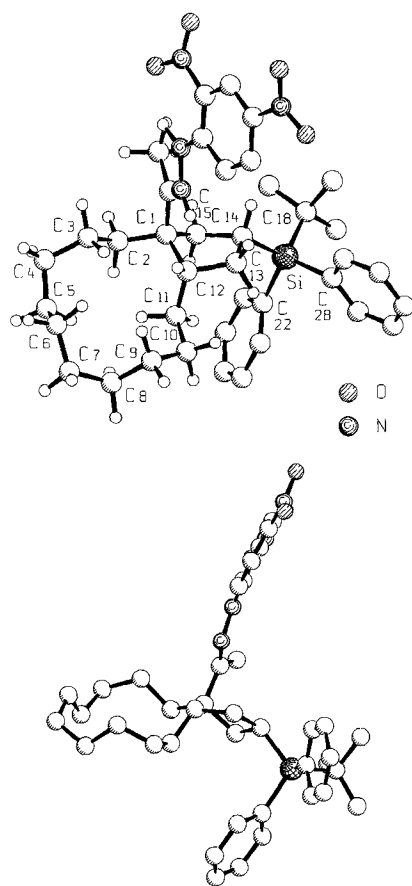


Figure 4. Molecular structure of **14** in the crystal (SCHAKAL representation). Top: hydrogen atoms of the aryl rings and the *tert*-butyl group omitted for clarity. Bottom: side view; hydrogen atoms omitted for clarity. Selected bond lengths [$\text{\AA}$]: C1–C2 1.551(3), C1–C12 1.561(3), C1–C15 1.544(3), C2–C3 1.529(3), C3–C4 1.520(3), C4–C5 1.531(4), C5–C6 1.512(4), C6–C7 1.532(4), C7–C8 1.505(5), C8–C9 1.554(4), C9–C10 1.484(4), C10–C11 1.523(4), C11–C12 1.535(3), C12–C13 1.546(3), C13–C14 1.563(3), C14–C15 1.550(3), Si–C14 1.889(3), Si–C18 1.902(3), Si–C22 1.890(3), Si–C28 1.885(3).

A characteristic feature of the ^1H NMR spectra of the bicyclo[10.3.0]pentadecanes **13e** and **14** is a high-field signal at $\delta = -0.52$ for **13e** and at -0.42 for **14**, each corresponding to one proton. For the parent compound **13e** an assignment of this proton signal was achieved by means of the 2D NMR spectra. The ^1H , ^1H correlated NMR spectrum of **13e** (Figure 5) reveals a coupling between the high-field proton ($\delta = -0.52$) and the

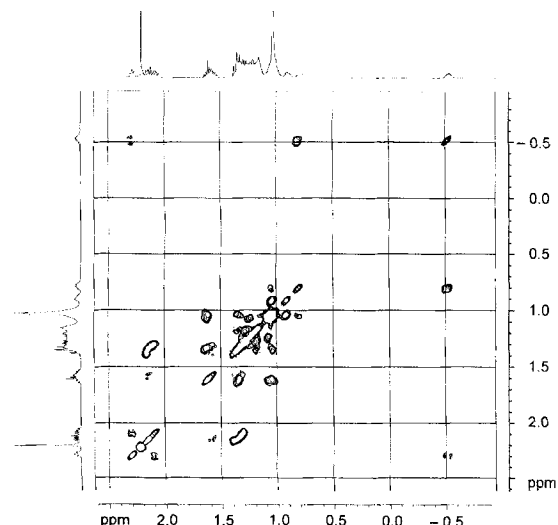


Figure 5. ^1H , ^1H -correlated NMR spectrum of **13e** (500 MHz, CDCl_3).

angular proton of the bicyclic ring system (proton at C12, $\delta = 2.28$). The ^{13}C , ^1H correlated NMR spectrum (Figure 6) shows that the high-field proton and a second proton with a signal only slightly shifted to high field ($\delta = 0.80$) are bound to the same carbon atom (signal at $\delta = 26.44$). From the two correlations it can be concluded that the signals at $\delta = -0.52$ and 0.80 belong to the protons at C11.

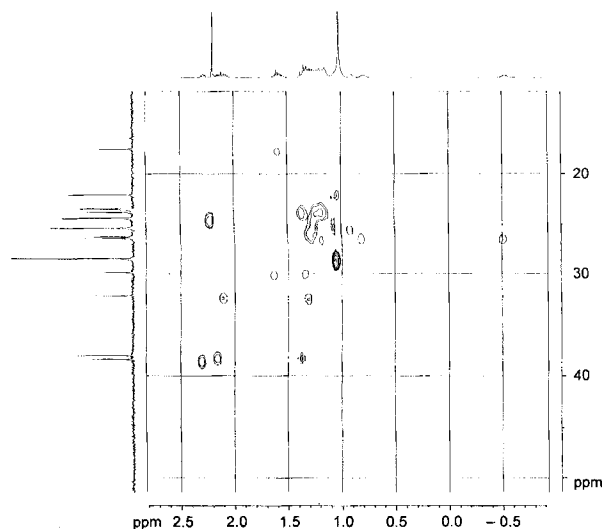


Figure 6. ^{13}C , ^1H -correlated NMR spectrum of **13e** (125/500 MHz, CDCl_3).

Assuming that the five-membered ring and its substituents adopt a similar conformation in the solid state and in solution, the molecular structure of the bicyclo[10.3.0]pentadecane derivative **14** can be used in order to explain the high-field shift of the signals in the ^1H NMR spectra of **13e** and **14**. The protons at C11 are shielded owing to the anisotropy caused by one of the phenyl substituents at the silicon atom. A view onto the plane of one of the phenyl rings in the crystal structure of **14** shows that the C11 methylene group is arranged just below the aromatic nucleus (Figure 7, top). One proton of this methylene group points directly towards the aromatic ring, as shown by side-view

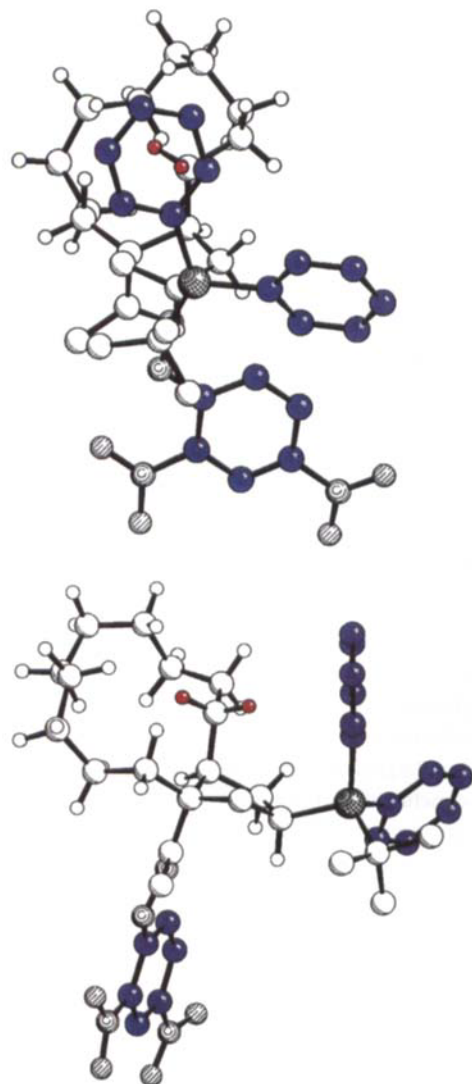
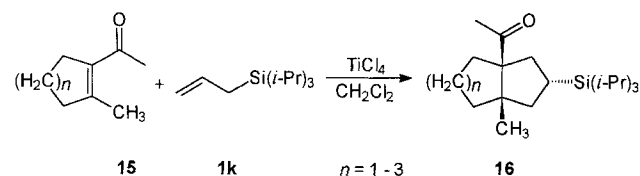


Figure 7. Molecular structure of **14** in the crystal (SCHAKAL representation; the hydrogen atoms of the substituents at the bicyclo[10.3.0]pentadecane ring system have been omitted for clarity; aromatic C atoms in blue, hydrogen atoms at C11 in red). Top: view onto the plane of one of the phenyl ring. Bottom: side-view of the phenyl ring.

of the phenyl ring (Figure 7, bottom). The signal at $\delta = -0.52$ in the ^1H NMR spectrum of **13e** ($\delta = -0.42$ for **14**) is assigned to this proton. In the crystal of the hydrazone derivative **14** the closest distance to the aromatic ring $\text{H}_\text{A} 11-\text{C} 23$ is calculated to be 2.87 Å. The closest distance for the second methylene proton to the aromatic ring $\text{H}_\text{B} 11-\text{C} 23$ is calculated to be 4.42 Å. The observed high-field shift of one methylene proton of the annulated ring to negative δ values is a special effect due to the conformation of the 12-membered ring system in **13e** and its hydrazone derivative **14** and is not observed for any of the lower homologues (**13a–d**) in the series of *tert*-butyldiphenylsilylcyclopentanes incorporated in a bicyclo[*n*.3.0]-alkane ring system.

Construction of Two Contiguous Quaternary Carbon Atoms: The [3 + 2] cycloaddition of 1-acetyl-2-methylcycloalkenes **15** and allylsilanes can be used for the diastereoselective synthesis of bicyclic ring systems with concomitant construction of two ad-

jacent quaternary carbon centers. The compounds **15** were prepared according to literature procedures.^[17b, 22] Reaction of **15** and allyltriisopropylsilane (**1k**) provided the bicyclo[*n*.3.0]-alkanes **16** (Scheme 6, Table 6).



Scheme 6. [3 + 2] Cycloadditions of allyltriisopropylsilane **1k** and 1-acetyl-2-methylcycloalkenes **15** to give silylbicyclo[*n*.3.0]alkanes **16**.

Table 6. [3 + 2] Cycloadditions of allyltriisopropylsilane **1k** with 1-acetyl-2-methylcycloalkenes **15**.

Product	<i>n</i>	Yield [%]	Stereochem. [a]	$\delta(\text{C}-\text{Si})$ [b]
16a	1	92	<i>anti/syn</i> = 5:1	23.76/20.78
16b	2	46	<i>anti</i>	15.48
16c	3	54	<i>anti</i>	19.27

[a] Position of the silyl group relative to the acetyl group. [b] Chemical shift of the CH group α to Si(*i*Pr)₃ in the ^{13}C NMR spectrum (100 MHz, CDCl_3).

The best yield was obtained for the bicyclo[3.3.0]octane derivative **16a**, which was isolated as a 5:1 mixture of the *anti* and *syn* diastereoisomers. The increased reactivity of the five-membered ring double bond may be explained by strain release on cycloaddition with the allylsilane. The formation of the *syn* diastereoisomer results from the steric hindrance caused by the bulky triisopropylsilyl group in the *endo* position of the bicyclo[3.3.0]octane ring. Because of the additional methyl group, the selectivity in favor of the *anti* diastereoisomer of **16a** is higher than that for **12a**. The hydrindane **16b** and the hydroazulene **16c** were isolated as pure diastereoisomers. The stereochemical assignment for **16a–c** is based on comparison of selected NMR data with those of **12a–c**.

Conclusion

The titanium tetrachloride promoted addition of sterically hindered allylsilanes and 1-acetylcycloalkenes containing five- to twelve-membered rings provides diastereoselectively the corresponding silylbicyclo[*n*.3.0]alkanes. In all cases the cycloaddition product with an *anti* orientation of the silyl and angular acetyl groups is either obtained as the only diastereoisomer or as the major diastereoisomer. All stereochemical assignments are unequivocally confirmed by X-ray crystal structure determinations of selected compounds and comparison of characteristic NMR spectral data.

Experimental Section

General: All reactions were carried out in dry solvents under inert gas. Flash chromatography: Baker or Merck silica gel (0.03–0.06 mm). Melting points: Leitz hot stage and Büchi 535. Bulb-to-bulb distillation: Büchi glass tube oven GKR-51. IR: Bruker IFS 25, Bruker IFS 88 (FT-IR), Perkin-Elmer 882

and Perkin-Elmer 1710 (FT-IR); $\tilde{\nu}$ in cm^{-1} . ^1H and ^{13}C NMR: Bruker WP-200, AM-300, AM-400, and DRX-500; δ in ppm, J in Hz. MS: Finnigan MAT-312 and MAT-90, at 70 eV. Elemental analysis: Heraeus CHN-Rapid.

Allyldimethylphenylsilane^[23] (**1b**): Chlorodimethylphenylsilane (1.88 g, 1.83 mL, 11.0 mmol) was added slowly to a cold 1 M solution of allylmagnesium chloride in THF (11.0 mL, 11.0 mmol). After stirring at RT for 1.5 h, the mixture was quenched by addition of an aqueous solution of ammonium chloride. The organic layer was separated and the aqueous layer was extracted three times with Et_2O . The combined organic layers were dried over magnesium sulfate. The solvent was evaporated and the residue subjected to flash chromatography (light petroleum ether/ Et_2O 7:1, silica gel): **1b** (1.73 g, 89%). Colorless oil. ^1H NMR (200 MHz, CDCl_3): δ = 0.31 (s, 6H), 1.78 (dt, J = 8.1, 1.1 Hz, 2H), 4.89 (m, 2H), 5.81 (m, 1H), 7.39 (m, 3H), 7.54 (m, 2H). For further data, see ref. [23].

Allylmethyldiphenylsilane^[23a] (**1c**): Chloromethyldiphenylsilane (3.86 g, 3.5 mL, 16.6 mmol) was added slowly to a cold 1 M solution of allylmagnesium chloride in THF (19.0 mL, 19.0 mmol) and the mixture was stirred vigorously for 1.5 h at RT. The mixture was poured into an aqueous solution of ammonium chloride, the aqueous layer extracted three times with Et_2O , the combined organic layers dried (MgSO_4), and the solvent evaporated. Bulb-to-bulb distillation of the residue at 115 °C/0.2 mbar provided **1c** (3.93 g, 99%). Colorless oil. B.p. 113–114 °C/0.2 mbar (Lit.^[23a]: b.p. 310–311 °C/740 torr); IR (CHCl_3): $\tilde{\nu}$ = 3071, 3054, 3000, 1629, 1590, 1428, 1255, 1153, 1113, 901, 813, 795 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): δ = 0.60 (s, 3H), 2.12 (dt, J = 7.9, 1.2 Hz, 2H), 4.94 (m, 2H), 5.84 (ddt, J = 17.0, 10.1, 8.0 Hz, 1H), 7.40 (m, 6H), 7.54 (m, 4H); ^{13}C NMR and DEPT (75 MHz, CDCl_3): δ = –4.77 (CH_3), 22.19 (CH_2), 114.29 (CH_2), 127.86 (4CH), 129.32 (2CH), 134.10 (CH), 134.58 (4CH), 136.61 (2C); MS: m/z (%) = 238 (12, M^+), 200 (26), 199 (38), 198 (42), 197 (100), 181 (30), 180 (23), 165 (29), 121 (19), 119 (28), 105 (35); HRMS: 238.1178 ($\text{C}_{16}\text{H}_{18}\text{Si}$, calcd. 238.1178).

Allyltriphenylsilane^[23b] (**1d**): A 2 M solution of allylmagnesium chloride (18.7 mL, 37.4 mmol) was added slowly to a cold solution of chlorotriphenylsilane (10.0 g, 33.9 mmol) in THF (20 mL). After stirring at RT for 5 h, the mixture was poured into an aqueous solution of ammonium chloride. The aqueous layer was extracted with Et_2O (3 $\times$) and the combined organic layers were dried over magnesium sulfate. Evaporation of the solvent and recrystallization of the residue from Et_2O provided **1d** (10.1 g, 99%). Colorless crystals. M.p. 89–90 °C (Lit.^[23b]: m.p. 90–91 °C); IR (KBr): $\tilde{\nu}$ = 3066, 3047, 3041, 3011, 2996, 1428, 1420, 1388, 1162, 1156, 1113, 1102, 734, 699 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): δ = 2.41 (dt, J = 7.9, 1.3 Hz, 2H), 4.94 (m, 2H), 5.89 (ddt, J = 17.0, 10.0, 7.9 Hz, 1H), 7.40 (m, 9H), 7.54 (m, 6H); ^{13}C NMR and DEPT (75 MHz, CDCl_3): δ = 21.24 (CH_2), 115.11 (CH_2), 127.87 (6CH), 129.57 (3CH), 133.84 (CH), 134.62 (3C), 135.79 (6CH); MS: m/z (%) = 299 (2, $M^+ - 1$), 261 (30), 260 (47), 259 (100), 258 (11), 257 (28), 182 (26), 181 (35), 180 (30), 155 (28), 105 (31); Anal. calcd. for $\text{C}_{21}\text{H}_{20}\text{Si}$: C 83.94, H 6.71; found: C 83.70, H 6.78.

Allyltri(4-methoxyphenyl)silane (**1e**) and **diallyldi(4-methoxyphenyl)silane**: A 1.8 M solution of 4-methoxyphenylmagnesium bromide in THF (15 mL, 27 mmol) was added to a solution of SiCl_4 (1.53 g, 1.03 mL, 8.98 mmol) in THF (5 mL) and the mixture was heated under reflux for 4 h. After cooling to RT, a 2 M solution of allylmagnesium chloride in THF (4.84 mL, 9.68 mmol) was added and the reaction mixture was stirred at RT for an additional 1 h, then poured into an aqueous solution of NH_4Cl , and the layers separated. The aqueous layer was extracted with Et_2O (3 $\times$), the combined organic layers were dried (MgSO_4), and the solvent was evaporated. The residue was subjected to flash chromatography (light petroleum ether/ Et_2O 7:1, silica gel) and provided as the less polar product **diallyldi(4-methoxyphenyl)silane** (921 mg, 32%, colorless oil) and as the more polar product **1e** (1.06 g, 30%, colorless solid).

1e: IR (CHCl_3): $\tilde{\nu}$ = 2960, 2912, 2836, 1628, 1592, 1564, 1500, 1464, 1312, 1276, 1248, 1220, 1180, 1152, 1112, 1032, 580, 532 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): δ = 2.31 (dt, J = 7.9, 1.2 Hz, 2H), 3.81 (s, 9H), 4.90 (m, 2H), 5.86 (ddt, J = 17.0, 10.0, 7.9 Hz, 1H), 6.91 (m, 6H), 7.48 (m, 6H); ^{13}C NMR and DEPT (75 MHz, CDCl_3): δ = 21.88 (CH_2), 55.01 (3 CH_3), 113.60 (6CH), 114.68 (CH_2), 126.10 (3C), 134.34 (CH), 137.18 (6CH), 160.73 (3C); MS: m/z (%) = 351 (14), 350 (52), 349 (100, $M^+ - 41$), 318 (1), 243 (5), 242 (2), 214 (9), 199 (9), 174 (11).

Diallyldi(4-methoxyphenyl)silane: IR (CHCl_3): $\tilde{\nu}$ = 3080, 3000, 2960, 2912, 2836, 1628, 1592, 1564, 1500, 1396, 1312, 1276, 1248, 1180, 1152, 1112, 1032, 932, 900, 564, 524 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): δ = 2.07 (dt, J = 7.9, 1.2 Hz, 4H), 3.81 (s, 6H), 4.90 (m, 4H), 5.79 (ddt, J = 16.9, 10.1, 8.0 Hz, 2H), 6.90 (m, 4H), 7.43 (m, 4H); ^{13}C NMR and DEPT (75 MHz, CDCl_3): δ = 20.54 (2 CH_2), 54.99 (2 CH_3), 113.59 (4CH), 114.46 (2 CH_2), 125.96 (2C), 134.09 (2CH), 136.47 (4CH), 160.70 (2C); MS: m/z (%) = 324 (2, M^+), 285 (15), 284 (56), 283 (100), 243 (28), 214 (63), 199 (44), 175 (21), 171 (13), 145 (12), 135 (19).

Allyltri(4-methoxyphenyl)silane (**1e**): A 1.8 M solution of 4-methoxyphenylmagnesium bromide in THF (50 mL, 90 mmol) was added to a solution of SiCl_4 (4.58 g, 3.09 mL, 26.9 mmol) in THF (10 mL) and the mixture was heated under reflux for 5 h. After cooling to RT, a 2 M solution of allylmagnesium chloride in THF (16.2 mL, 32.4 mmol) was added and the reaction mixture was heated under reflux for an additional 1 h. The cold mixture was poured into an aqueous solution of NH_4Cl and the layers separated. The aqueous layer was extracted with Et_2O (3 $\times$), the combined organic layers were dried (MgSO_4), and the solvent was evaporated. Recrystallization of the residue from Et_2O afforded **1e** (6.75 g, 64%). Colorless solid. Spectral data, see above.

Allyltri(4-methoxyphenyl)silane (**1e**): A solution of tri(4-methoxyphenyl)silane (**8e**) (665 mg, 1.90 mmol) in THF (10 mL) was added to 5 mol % of [1,1'-bis(diphenylphosphine)ferrocene]nickel dichloride^[13] (65 mg, 95 μmol). While stirring, a 2 M solution of allylmagnesium chloride in THF (4.74 mL, 9.48 mmol) was added and the reaction mixture was heated under reflux for 14 d. The cold mixture was poured into an aqueous solution of NH_4Cl , the aqueous layer was extracted with Et_2O , and the combined organic layers were dried (MgSO_4). Evaporation of the solvent and flash chromatography (light petroleum ether/ Et_2O 5:1, silica gel) afforded **1e** (571 mg, 77%). Colorless solid. Spectral data, see above.

Allyltri(4-*N,N*-dimethylaminophenyl)silane (**1f**): A 2 M solution of allylmagnesium chloride in THF (32.1 mL, 64.2 mmol) was added to a solution of [bis(triphenylphosphine)]nickel dichloride^[13] (420 mg, 0.642 mmol, 5 mol %) and tri(4-*N,N*-dimethylaminophenyl)silane (**8f**) (5.0 g, 12.8 mmol) in THF (30 mL). The reaction mixture was heated under reflux for 14 d and then quenched by addition of an aqueous solution of ammonium chloride (pH = 7–8). The layers were separated, the aqueous layer extracted with Et_2O , the combined organic layers were dried (MgSO_4), and the solvent evaporated. Recrystallization of the residue afforded **1f** (4.97 g, 91%). Yellow-brownish crystals. M.p. 104–105 °C; IR (KBr): $\tilde{\nu}$ = 3081, 2980, 2883, 2847, 2792, 1592, 1508, 1357, 1203, 1107, 1060, 803, 776 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 2.29 (d, J = 7.9 Hz, 2H), 2.96 (s, 18H), 4.89 (m, 2H), 5.92 (ddt, J = 17.0, 10.0, 7.9 Hz, 1H), 6.72 (d, J = 8.7 Hz, 6H), 7.40 (d, J = 8.7 Hz, 6H); ^{13}C NMR and DEPT (100 MHz, CDCl_3): δ = 22.41 (CH_2), 40.17 (6 CH_3), 111.66 (6CH), 113.78 (CH_2), 121.26 (3C), 135.44 (CH), 136.85 (6CH), 150.90 (3C); MS: m/z (%) = 429 (1, M^+), 388 (100), 372 (9), 309 (8), 194 (9); HRMS: 429.2614 ($\text{C}_{27}\text{H}_{35}\text{N}_3\text{Si}$, calcd. 429.2600); Anal. calcd. for $\text{C}_{27}\text{H}_{35}\text{N}_3\text{Si}$: C 75.48, H 8.22, N 9.79; found: C 74.90, H 8.29, N 9.59.

Allyldimethylthexylsilane (**1h**): A 2 M solution of allylmagnesium chloride in THF (12.0 mL, 24.0 mmol) was added slowly at 0 °C to a solution of chlorodimethylthexylsilane (3.58 g, 3.95 mL, 20.0 mmol) in THF (15 mL). The mixture was stirred for 2 h at RT, poured into an aqueous solution of ammonium chloride, and extracted three times with Et_2O . The combined organic layers were dried (Na_2SO_4), the solvent evaporated, and the residue subjected to flash chromatography (pentane, silica gel): **1h** (3.39 g, 92%). Colorless oil. IR (film): $\tilde{\nu}$ = 3078, 2960, 2868, 1631, 1467, 1391, 1378, 1366, 1252, 1155, 874, 837, 817 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 0.01 (s, 6H), 0.85 (s, 6H), 0.88 (d, J = 6.9 Hz, 6H), 1.58 (dt, J = 8.2, 1.1 Hz, 2H), 1.62 (sept., J = 6.9 Hz, 1H), 4.81–4.88 (m, 2H), 5.80 (ddt, J = 16.9, 10.1, 8.2 Hz, 1H); ^{13}C NMR and DEPT (100 MHz, CDCl_3): δ = –4.31 (2 CH_3), 18.58 (2 CH_3), 20.92 (2 CH_3), 22.22 (CH_2), 23.51 (C), 34.76 (CH), 112.70 (CH_2), 135.82 (CH); MS: m/z (%) = 184 (1, M^+), 143 (27), 99 (43), 73 (100), 59 (19); HRMS: 184.1637 ($\text{C}_{11}\text{H}_{24}\text{Si}$, calcd. 184.1647).

Allyl-*tert*-butyldiphenylsilane (**1i**): A 2 M solution of allylmagnesium chloride in THF (11.7 mL, 23.4 mmol) was added to a cold solution of *tert*-butylchlorodiphenylsilane (5.37 g, 5.0 mL, 19.5 mmol) in THF (15 mL). Af-

ter stirring for 5 h at RT, the mixture was poured into an aqueous solution of ammonium chloride, and the aqueous layer was extracted three times with Et₂O. The combined organic layers were dried over sodium sulfate, the solvent was evaporated, and the residue subjected to flash chromatography (pentane/Et₂O 20:1, silica gel): **1i** (5.33 g, 97%). Colorless oil. B.p. 134–135 °C/0.3 mbar; IR (film): $\tilde{\nu}$ = 3072, 3050, 2998, 2961, 2930, 2887, 2858, 1630, 1589, 1471, 1463, 1428, 1108, 766, 736, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 1.12 (s, 9H), 2.25 (dt, J = 7.9, 1.3 Hz, 2H), 4.85 (ddt, J = 10.0, 2.0, 1.1 Hz, 1H), 4.96 (m, 1H), 5.83 (ddt, J = 16.9, 10.0, 7.9 Hz, 1H), 7.38–7.44 (m, 6H), 7.67 (m, 4H); ¹³C NMR and DEPT (100 MHz, CDCl₃): δ = 18.53 (C), 18.80 (CH₂), 27.90 (3CH₃), 114.56 (CH₂), 127.57 (4CH), 129.13 (2CH), 134.45 (2C), 134.72 (CH), 136.04 (4CH); MS: m/z (%) = 280 (10, M^+), 239 (66), 223 (100), 217 (26), 197 (36), 183 (20), 181 (23), 145 (11), 135 (72), 105 (23); HRMS: 280.1630 (C₁₉H₂₄Si, calcd. 280.1647).

Allyldiisopropylphenylsilane (1j) and diallyldiisopropylsilane: A 2 M solution of phenylmagnesium chloride (12 mL, 24 mmol) was added to a solution of dichlorodiisopropylsilane (3.70 g, 20.0 mmol) in THF (20 mL). The mixture was heated under reflux for 16 h, and subsequently cooled to 0 °C, and then a 2 M solution of allylmagnesium chloride (12 mL, 24 mmol) was added. After stirring for 5 h at RT, the reaction mixture was poured slowly into an aqueous solution of ammonium chloride. The aqueous layer was extracted three times with Et₂O and the combined organic layers were dried over magnesium sulfate. The solvent was evaporated and the residue subjected to flash chromatography (pentane, silica gel). Diallyldiisopropylsilane (720 mg, 18%), followed by **1j** (2.82 g, 61%) were eluted, both as colorless oils.

1j: B.p. 74–76 °C/0.3 mbar; IR (film): $\tilde{\nu}$ = 3071, 2943, 2891, 2865, 1630, 1463, 1427, 1108, 733, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 1.05 (d, J = 7.4 Hz, 6H), 1.08 (d, J = 7.4 Hz, 6H), 1.33 (sept., J = 7.4 Hz, 2H), 1.99 (dt, J = 8.1, 1.2 Hz, 2H), 4.90 (m, 1H), 5.03 (m, 1H), 5.96 (ddt, J = 16.9, 10.0, 8.1 Hz, 1H), 7.38 (m, 3H), 7.53 (m, 2H); ¹³C NMR and DEPT (100 MHz, CDCl₃): δ = 10.95 (2CH), 17.25 (CH₂), 17.93 (2CH₃), 17.99 (2CH₃), 113.69 (CH₂), 127.57 (2CH), 128.83 (CH), 134.88 (2CH), 134.95 (C), 135.35 (CH); MS: m/z (%) = 232 (6, M^+), 191 (100), 161 (11), 149 (63), 147 (20), 135 (37), 121 (90), 107 (24), 105 (51); HRMS: 232.1667 (C₁₅H₂₄Si, calcd. 232.1647).

Diallyldiisopropylsilane: IR (film): $\tilde{\nu}$ = 3078, 2942, 2891, 2867, 1630, 1463, 1156, 893 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 1.04 (m, 14H), 1.63 (d, J = 8.1 Hz, 4H), 4.84 (m, 2H), 4.92 (m, 2H), 5.86 (ddt, J = 17.0, 10.0, 8.1 Hz, 2H); ¹³C NMR and DEPT (100 MHz, CDCl₃): δ = 11.31 (2CH), 17.76 (2CH₂), 18.14 (4CH₃), 113.12 (2CH₂), 135.39 (2CH); MS: m/z (%) = 196 (0.3, M^+), 155 (93), 153 (27), 127 (17), 113 (66), 111 (15), 99 (26), 97 (12), 85 (100), 83 (17), 71 (29), 69 (23), 59 (48); HRMS: 196.1658 (C₁₂H₂₀Si, calcd. 196.1647).

Allyldiisopropylphenylsilane (1j): A solution of diisopropylphenylsilane (**8j**) (3.00 g, 15.6 mmol) in THF (40 mL) was added to [bis(triphenylphosphine)]nickel dichloride^[13] (510 mg, 780 μ mol, 5 mol %). While stirring vigorously, a 2 M solution of allylmagnesium chloride in THF (39 mL, 78 mmol) was added and the mixture was heated under reflux for 18 d. The cold mixture was poured slowly into an aqueous solution of ammonium chloride and extracted with Et₂O (3 $\times$). The combined organic layers were dried (MgSO₄), the solvent was evaporated, and the residue subjected to flash chromatography (pentane, silica gel): **1j** (2.20 g, 61%), followed by starting material **8j** (340 mg, 11%) were eluted, both as colorless oils. Spectral data, see above.

Tri(4-methoxyphenyl)silane (8e): A 2 M solution of 4-methoxyphenylmagnesium bromide in THF (5 mL, 10 mmol) was added to a solution of trichlorosilane (407 mg, 303 μ L, 3 mmol) in THF (5 mL). The reaction mixture was stirred for 1 h at RT, then poured into an aqueous solution of NH₄Cl, extracted three times with Et₂O, and the combined organic layers were dried over magnesium sulfate. Evaporation and flash chromatography (light petroleum ether/Et₂O 3:1, silica gel) afforded **8e** (1.05 g, 100%). Colorless crystals. M.p. 70–71 °C; IR (CHCl₃): $\tilde{\nu}$ = 3000, 2960, 2912, 2836, 2120, 1592, 1564, 1500, 1464, 1396, 1308, 1280, 1248, 1180, 1112, 1032, 804 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ = 3.81 (s, 9H), 5.41 (s) and (d, J_{HSi} = 196.0 Hz, Σ = 1H), 6.92 (brd, J = 8.7 Hz, 6H), 7.48 (brd, J = 8.7 Hz, 6H); ¹³C NMR and DEPT (75 MHz, CDCl₃): δ = 55.06 (3CH₃), 113.88 (6CH), 124.95 (3C), 137.26 (6CH), 161.00 (3C); MS: m/z (%) = 350 (46, M^+), 349 (22), 335 (14), 304 (3), 274 (11), 273 (54), 243 (59),

242 (100), 241 (19), 214 (18), 199 (19), 135 (24); HRMS: 350.1297 (C₂₁H₂₂O₃Si, calcd. 350.1298); Anal. calcd. for C₂₁H₂₂O₃Si: C 71.97, H 6.33; found: C 71.46, H 6.33.

Tri(4-*N,N*-dimethylphenyl)silane (8f): A 2 M solution of 4-*N,N*-dimethylaminophenylmagnesium bromide in THF (30 mL, 60 mmol) was added to a solution of trichlorosilane (2.27 g, 1.69 mL, 16.7 mmol) in THF (30 mL) at 0 °C while stirring vigorously. The reaction mixture was warmed to RT and stirred for 14 h at this temperature. The mixture was poured into an aqueous solution of ammonium chloride, the layers were separated, and the aqueous layer was extracted with Et₂O (3 $\times$). The combined organic layers were dried (MgSO₄) and the solvent was evaporated. Recrystallization of the residue from Et₂O at –20 °C provided **8f** (6.51 g, 100%). Colorless crystals. M.p. 158–159 °C; IR (KBr): $\tilde{\nu}$ = 3080, 3001, 2881, 2850, 2801, 2072, 1594, 1507, 1351, 1224, 1201, 1111, 792 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 2.97 (s, 18H), 5.39 (s) and (d, J_{HSi} = 192.0 Hz, Σ = 1H), 6.74 (d, J = 8.5 Hz, 6H), 7.46 (d, J = 8.5 Hz, 6H); ¹³C NMR and DEPT (100 MHz, CDCl₃): δ = 40.22 (6CH₃), 111.95 (6CH), 120.17 (3C), 136.89 (6CH), 151.20 (3C); MS: m/z (%) = 389 (100, M^+), 388 (17), 269 (25), 268 (72), 224 (8), 158 (9), 121 (12), 120 (20); HRMS: 389.2299 (C₂₄H₃₁N₃Si, calcd. 389.2287); Anal. calcd. for C₂₄H₃₁N₃Si: C 73.99, H 8.03, N 10.79; found: C 73.19, H 8.02, N 10.80.

Diisopropylphenylsilane (8j): A 2 M solution of phenylmagnesium chloride in THF (30 mL, 60 mmol) was added to a solution of chlorodiisopropylsilane (7.54 g, 8.67 mL, 50 mmol) in THF (20 mL) at 0 °C. The reaction mixture was stirred for 1 h at RT, then quenched by addition of a dilute aqueous solution of NH₄Cl, and the layers were separated. The aqueous phase was extracted with Et₂O (3 $\times$), the combined organic layers were dried over sodium sulfate, the solvent was evaporated, and the residue subjected to flash chromatography (pentane, silica gel): **8j** (9.59 g, 100%). Colorless oil. IR (film): $\tilde{\nu}$ = 3071, 3053, 2943, 2892, 2865, 2101, 1459, 1111, 999, 801 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 1.05 (d, J = 7.3 Hz, 6H), 1.12 (d, J = 7.3 Hz, 6H), 1.29 (dsept., J = 3.1, 7.3 Hz, 2H), 4.00 (t, J = 3.1 Hz) and (dt, J_{HSi} = 183.5 Hz, 3.1, Σ = 1H), 7.40 (m, 3H), 7.56 (m, 2H); ¹³C NMR and DEPT (100 MHz, CDCl₃): δ = 10.72 (2CH), 18.50 (2CH₃), 18.68 (2CH₃), 127.65 (2CH), 129.09 (CH), 134.17 (C), 135.49 (2CH); MS: m/z (%) = 192 (42, M^+), 149 (100), 121 (97), 107 (43), 105 (22); HRMS: 192.1328 (C₁₂H₂₀Si, calcd. 192.1334).

1-Acetyl-8-dimethylphenylsilylbicyclo[4.3.0]nonane (9b): A solution of 1-acetylcyclohexene (500 mg, 0.52 mL, 4.03 mmol) in dichloromethane (2 mL) was added to a stirred solution of titanium tetrachloride (840 mg, 0.49 mL, 4.43 mmol) in dichloromethane (5 mL) at –20 °C. The formation of the Lewis acid/enone complex was indicated by the intense yellow color of the resulting suspension. The reaction mixture was cooled to –78 °C and a solution of allyldimethylphenylsilane (**1b**) (1.06 g, 1.2 mL, 6.04 mmol) in dichloromethane (6 mL) was added. After stirring for 4 h at –78 °C the reaction temperature was raised to –20 °C, during which the color changed to an intense red-violet. The reaction mixture was stirred for an additional 15 h at this temperature and the cold mixture was poured into an aqueous solution of ammonium chloride. The organic layer was separated and the aqueous layer was extracted three times with cold CH₂Cl₂. The combined organic layers were dried over magnesium sulfate, the solvent evaporated, and the residue subjected to flash chromatography (light petroleum ether/Et₂O 7:1, silica gel). Bulb-to-bulb distillation of the resulting colorless oil provided 1-acetyl-2-allylcyclohexane (**4**) at 70 °C/0.15 mbar (505 mg, 76%) and the bicyclononane **9b** (229 mg, 19%) at 160 °C/0.15 mbar, both as colorless oils.

9b: IR (CHCl₃): $\tilde{\nu}$ = 2936, 2864, 1693, 1427, 1367, 1356, 1351, 1250, 1150, 1134, 1114, 834, 813 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 0.30 (s, 6H), 1.13 (m, 1H), 1.20–1.61 (m, 9H), 1.69–1.79 (m, 2H), 1.91 (m, 1H), 2.12 (s, 3H), 2.45 (m, 1H), 7.37 (m, 3H), 7.54 (m, 2H); ¹³C NMR and DEPT (100 MHz, CDCl₃): δ = –4.65 (CH₃), –4.49 (CH₃), 21.91 (CH₂), 22.70 (CH), 23.46 (CH₂), 25.47 (CH₃), 26.35 (CH₂), 31.03 (CH₂), 32.02 (CH₂), 37.62 (CH₂), 41.40 (CH), 58.38 (C), 127.67 (2CH), 128.92 (CH), 133.76 (2CH), 138.36 (C), 212.91 (C=O); MS: m/z (%) = 300 (3, M^+), 285 (1), 260 (18), 222 (11), 137 (7), 135 (100), 125 (14); HRMS: 300.1910 (C₁₉H₂₈SiO, calcd. 300.1909).

1-Acetyl-8-methyldiphenylsilylbicyclo[4.3.0]nonane (9c): A solution of 1-acetylcyclohexene (1.38 g, 1.43 mL, 11.1 mmol) in CH₂Cl₂ (5 mL) was added

to a stirred solution of titanium tetrachloride (2.33 g, 1.35 mL, 12.3 mmol) in CH_2Cl_2 (14 mL) at -20°C . The resulting yellow suspension of the Lewis acid/enone complex was cooled to -78°C and a solution of allyl-methyldiphenylsilane (**1c**) (4.0 g, 16.8 mmol) in CH_2Cl_2 (16 mL) was added. The color of the reaction mixture spontaneously changed to red-violet. The reaction temperature was raised to -20°C over a period of 4 h, the mixture stirred for an additional 15 h at this temperature, and then poured into an aqueous solution of ammonium chloride. The organic layer was separated immediately and the aqueous layer extracted three times with cold dichloromethane. The combined organic layers were dried (MgSO_4) and the solvent was evaporated. 1-Acetyl-2-allylcyclohexene **4** (847 mg, 46%) was isolated by bulb-to-bulb distillation at $70^\circ\text{C}/0.15$ mbar as a colorless oil. The residue was subjected to flash chromatography (hexane/ Et_2O 15:1, silica gel): **9c** (1.52 g, 38%). Colorless oil. IR (film): $\tilde{\nu} = 3068, 3048, 2928, 2861, 1699, 1448, 1428, 1349, 1251, 1149, 1133, 1113, 787, 737, 721, 701\text{ cm}^{-1}$; ^1H NMR (400 MHz, CDCl_3): $\delta = 0.59$ (s, 3H), 1.11 (m, 2H), 1.25–1.38 (m, 5H), 1.49–1.86 (m, 5H), 2.01 (m, 1H), 2.14 (s, 3H), 2.49 (m, 1H), 7.39 (m, 6H), 7.54 (m, 4H); ^{13}C NMR and DEPT (100 MHz, CDCl_3): $\delta = -5.98$ (CH_3), 21.15 (CH), 21.94 (CH_2), 23.46 (CH_2), 25.63 (CH_3), 26.28 (CH_2), 30.90 (CH_2), 32.28 (CH_2), 37.78 (CH_2), 41.31 (CH), 58.47 (C), 127.83 (4CH), 129.29 (2CH), 134.80 (2CH), 134.82 (2CH), 136.46 (C), 136.54 (C), 213.00 (C=O); MS: m/z (%) = 362 (2, M^+), 322 (11), 321 (41), 284 (14), 197 (100), 125 (6), 105 (4); HRMS: 362.2051 ($\text{C}_{24}\text{H}_{30}\text{OSi}$, calcd. 362.2066).

1-Acetyl-8-triphenylsilylbicyclo[4.3.0]nonane (9d): A solution of 1-acetylcyclohexene (500 mg, 0.52 mL, 4.03 mmol) in dichloromethane (2 mL) was added to a solution of titanium tetrachloride (840 mg, 0.49 mL, 4.43 mmol) in CH_2Cl_2 (5 mL) at -20°C . The resulting yellow suspension indicated the formation of the Lewis acid/enone complex. After cooling to -78°C a solution of allyltriphenylsilane (**1d**) (1.82 g, 6.04 mmol) in dichloromethane (6 mL) was added. After stirring for 4 h at -78°C the reaction mixture was warmed to -20°C , during which the color changed to a deep red-violet. The reaction mixture was stirred for an additional 15 h at this temperature and then poured into an aqueous solution of ammonium chloride. The organic layer was separated, the aqueous layer extracted with CH_2Cl_2 (3 $\times$), the combined organic layers were dried (MgSO_4), and the solvent was evaporated. The residue was subjected to flash chromatography (pentane/ Et_2O 6:1, silica gel). 1-Acetyl-2-allylcyclohexene (**4**) (258 mg, 39%) was separated from this crude product by bulb-to-bulb distillation at $70^\circ\text{C}/0.15$ mbar. Recrystallization of the residue from Et_2O afforded **9d** (872 mg, 51%). Colorless crystals. M.p. $114\text{--}115^\circ\text{C}$; IR (KBr): $\tilde{\nu} = 3067, 3045, 2923, 2858, 1695, 1428, 1229, 1216, 1133, 1110, 742, 702, 536, 512\text{ cm}^{-1}$; ^1H NMR (400 MHz, CDCl_3): $\delta = 0.73$ (m, 1H), 0.98 (m, 1H), 1.08 (m, 1H), 1.18 (m, 3H), 1.36–1.47 (m, 2H), 1.60–1.73 (m, 2H), 1.98 (m, 1H), 2.10–2.19 (m, 2H), 2.12 (s, 3H), 2.48 (m, 1H), 7.40 (m, 9H), 7.61 (m, 6H); ^{13}C NMR and DEPT (100 MHz, CDCl_3): $\delta = 19.94$ (CH), 21.85 (CH_2), 23.29 (CH_2), 25.63 (CH_3), 26.06 (CH_2), 30.37 (CH_2), 32.51 (CH_2), 37.79 (CH_2), 41.04 (CH), 58.46 (C), 127.85 (6CH), 129.51 (3CH), 134.54 (3C), 135.99 (6CH), 213.00 (C=O); MS: m/z (%) = 424 (3, M^+), 383 (83), 347 (18), 261 (26), 260 (83), 259 (100), 199 (18), 183 (14), 181 (47); Anal. calcd. for $\text{C}_{29}\text{H}_{32}\text{SiO}$: C 82.02, H 7.60; found: C 81.86, H 7.62.

1-Acetyl-8-tert-butyltrimethylsilylbicyclo[4.3.0]nonane (9g): A solution of 1-acetylcyclohexene (500 mg, 0.52 mL, 4.03 mmol) in dichloromethane (2 mL) was added to a solution of TiCl_4 (840 mg, 0.49 mL, 4.43 mmol) in dichloromethane (5 mL) at -20°C . The formation of the Lewis acid/enone complex was indicated by the intense yellow color of the resulting suspension. The reaction mixture was cooled to -78°C and a solution of allyl-tert-butyltrimethylsilane (944 mg, 6.04 mmol) in CH_2Cl_2 (5 mL) was added slowly. During a period of 4 h the reaction mixture was warmed to -20°C and then stirred for an additional 16 h at this temperature. The mixture was poured into an aqueous solution of ammonium chloride and the aqueous layer was extracted three times with dichloromethane. The combined organic layers were dried over sodium sulfate, the solvent was evaporated, and the residue subjected to flash chromatography (pentane/ Et_2O 20:1, silica gel). Bulb-to-bulb distillation of the resulting yellow oil at $90^\circ\text{C}/0.03$ mbar provided **9g** (450 mg, 40%). Colorless oil. IR (film): $\tilde{\nu} = 2930, 2857, 1695, 1464, 1246, 1147, 1131, 915, 828, 803, 766, 733\text{ cm}^{-1}$; ^1H NMR (400 MHz, CDCl_3): $\delta = -0.09$ (s, 3H), -0.08 (s, 3H), 0.85 (s, 9H), 1.17 (m, 2H), 1.31–1.58 (m, 8H), 1.68 (m, 1H), 1.85 (m, 2H), 2.12 (s, 3H), 2.42 (m, 1H); ^{13}C NMR and DEPT (100 MHz, CDCl_3): $\delta = -7.63$ (CH_3), -7.56 (CH_3), 16.92 (C), 20.48 (CH), 21.97 (CH_2), 23.60 (CH_2), 25.51 (CH_3), 26.43 (CH_2),

27.00 (3 CH_3), 31.33 (CH_2), 33.09 (CH_2), 38.78 (CH_2), 41.46 (CH), 58.27 (C), 213.06 (C=O); MS: m/z (%) = 280 (9, M^+), 223 (100), 179 (15), 147 (92), 105 (19), 103 (18), 75 (99.7), 73 (80); HRMS: 280.2206 ($\text{C}_{17}\text{H}_{32}\text{OSi}$, calcd. 280.2222).

1-Acetyl-8-dimethylhexylbicyclo[4.3.0]nonane (9h): A solution of 1-acetylcyclohexene (250 mg, 0.26 mL, 2.01 mmol) in CH_2Cl_2 (1 mL) was added slowly to a solution of titanium tetrachloride (420 mg, 0.25 mL, 2.21 mmol) in CH_2Cl_2 (2.5 mL) at -20°C . The intense yellow color of the resulting suspension indicated the formation of the Lewis acid/enone complex. The reaction mixture was cooled to -78°C and a solution of allyldimethylhexylsilane (**1h**) (741 mg, 4.02 mmol) in dichloromethane (3 mL) was added. The mixture was warmed to 0°C over a period of 4 h (the color changed to an intense red-violet), stirred vigorously for an additional 16 h at this temperature, poured into an aqueous solution of ammonium chloride, and the aqueous layer was extracted with dichloromethane (3 $\times$). The combined organic layers were dried over sodium sulfate, the solvent was evaporated, and the residue subjected to flash chromatography (pentane/ Et_2O 20:1, silica gel): **9h** (371 mg, 60%). Colorless oil. IR (film): $\tilde{\nu} = 2929, 2864, 1696, 1463, 1374, 1348, 1247, 1146, 1129, 830, 809, 767\text{ cm}^{-1}$; ^1H NMR (400 MHz, CDCl_3): $\delta = -0.04$ (s, 3H), -0.03 (s, 3H), 0.72–0.89 (m, 1H), 0.799 (s, 3H), 0.804 (s, 3H), 0.82 (d, $J = 6.8$ Hz, 6H), 1.10–1.91 (m, 13H), 2.12 (s, 3H), 2.41 (m, 1H); ^{13}C NMR and DEPT (100 MHz, CDCl_3): $\delta = -5.25$ (CH_3), -5.14 (CH_3), 18.49 (CH_3), 18.62 (CH_3), 21.12 (CH_3), 21.29 (CH_3), 21.84 (CH), 21.97 (CH_2), 23.62 (C, CH_3), 25.53 (CH_3), 26.40 (CH_2), 31.44 (CH_2), 33.30 (CH_2), 34.66 (CH), 39.04 (CH_2), 41.42 (CH), 58.14 (C), 213.03 (C=O); MS: m/z (%) = 308 (2, M^+), 223 (75), 179 (14), 147 (94), 105 (16), 103 (13), 84 (100), 75 (94), 73 (62), 59 (32); HRMS: 308.2508 ($\text{C}_{19}\text{H}_{36}\text{OSi}$, calcd. 308.2535).

1-Acetyl-8-tert-butylphenylsilylbicyclo[4.3.0]nonane (9i): A solution of 1-acetylcyclohexene (500 mg, 0.52 mL, 4.03 mmol) in dichloromethane (2 mL) was added to a solution of TiCl_4 (840 mg, 0.49 mL, 4.43 mmol) in dichloromethane (5 mL) at -20°C (yellow suspension). After cooling to -78°C , a solution of allyl-tert-butylphenylsilane (**1i**) (1.69 g, 6.04 mmol) in CH_2Cl_2 (6 mL) was added, the reaction mixture warmed slowly to 0°C (the color changed to red-violet), and stirred vigorously for 19 h at this temperature. A solution of allyl-tert-butylphenylsilane **1i** (1.13 g, 4.03 mmol) in dichloromethane was added, the mixture stirred for an additional 24 h, and then poured into an aqueous solution of ammonium chloride. The organic layer was separated, the aqueous layer extracted three times with dichloromethane, and the combined organic layers dried over sodium sulfate. The solvent was evaporated and the residue subjected to flash chromatography (pentane/ Et_2O 20:1, silica gel): **9i** (1.12 g, 69%). Colorless crystals. M.p. $115\text{--}116^\circ\text{C}$; IR (KBr): $\tilde{\nu} = 3068, 3050, 2929, 2855, 1690, 1465, 1423, 1359, 1139, 1103, 817, 739, 701, 605, 555\text{ cm}^{-1}$; ^1H NMR (400 MHz, CDCl_3): $\delta = 0.54$ (m, 1H), 0.92–1.17 (m, 6H), 1.07 (s, 9H), 1.35 (m, 1H), 1.54 (m, 2H), 1.93 (m, 2H), 2.05 (m, 1H), 2.10 (s, 3H), 2.42 (m, 1H), 7.40 (m, 6H), 7.65 (m, 4H); ^{13}C NMR and DEPT (100 MHz, CDCl_3): $\delta = 18.39$ (CH), 18.64 (C), 21.84 (CH_2), 23.31 (CH_2), 25.63 (CH_3), 26.00 (CH_2), 28.53 (3 CH_3), 30.12 (CH_2), 32.99 (CH_2), 38.36 (CH_2), 40.94 (CH), 58.27 (C), 127.42 (2CH), 127.47 (2CH), 129.13 (2CH), 134.13 (C), 134.18 (C), 136.74 (2CH), 136.79 (2CH), 213.19 (C=O); MS: m/z (%) = 404 (1, M^+), 347 (100), 199 (83), 183 (75), 181 (12), 147 (11), 135 (15); HRMS: 404.2545 ($\text{C}_{27}\text{H}_{36}\text{OSi}$, calcd. 404.2535); Anal. calcd. for $\text{C}_{27}\text{H}_{36}\text{OSi}$: C 80.15, H 8.97; found: C 80.16, H 9.06.

1-Acetyl-8-diisopropylphenylsilylbicyclo[4.3.0]nonane (9j): A solution of 1-acetylcyclohexene (500 mg, 0.52 mL, 4.03 mmol) in dichloromethane (2 mL) was added to a solution of titanium tetrachloride (840 mg, 0.49 mL, 4.43 mmol) in CH_2Cl_2 (5 mL) at -20°C . The formation of the Lewis acid/enone complex was indicated by the intense yellow color of the resulting suspension. A solution of allyldiisopropylphenylsilane (**1j**) (1.41 g, 6.04 mmol) in CH_2Cl_2 (6 mL) was added slowly at -78°C and the reaction mixture was warmed over a period of 4 h to -20°C (the color changed to red-violet). After stirring for an additional 16 h at this temperature, the reaction mixture was poured into an aqueous layer of ammonium chloride. The organic layer was separated, the aqueous layer extracted three times with dichloromethane, and the combined organic layers dried (MgSO_4). Evaporation of the solvent and flash chromatography of the residue (pentane/ Et_2O 20:1, silica gel) provided **9j** (974 mg, 68%). Colorless oil. IR (film): $\tilde{\nu} = 3070, 2938, 2864, 1700, 1461, 1427, 1350, 1106, 883, 738, 702\text{ cm}^{-1}$; ^1H NMR

(400 MHz, CDCl_3): δ = 0.97 (m, 1H), 1.12 (m, 12H), 1.17–1.68 (m, 12H), 1.79 (m, 1H), 1.95 (m, 1H), 2.11 (s, 3H), 2.41 (m, 1H), 7.36 (m, 3H), 7.52 (m, 2H); ^{13}C NMR and DEPT (100 MHz, CDCl_3): δ = 11.30 (CH), 11.40 (CH), 18.69 (CH_3), 18.73 (CH_3), 18.90 (CH_3), 18.92 (CH_3), 19.87 (CH), 21.94 (CH_2), 23.49 (CH_2), 25.60 (CH_3), 26.28 (CH_2), 31.09 (CH_2), 32.57 (CH_2), 38.12 (CH_2), 41.24 (CH), 58.18 (C), 127.59 (2CH), 128.82 (CH), 134.62 (C), 135.28 (2CH), 213.11 (C=O); MS: m/z (%) = 356 (2, M^+), 313 (100), 235 (12), 165 (29), 149 (24), 147 (19), 137 (22), 121 (44), 107 (16); HRMS: 356.2540 ($\text{C}_{23}\text{H}_{36}\text{OSi}$, calcd. 356.2535).

1-Acetyl-8-triisopropylsilylbicyclo[4.3.0]nonane (9k): A solution of titanium tetrachloride (840 mg, 0.49 mL, 4.43 mmol) in dichloromethane (5 mL) was cooled to -20°C and a solution of 1-acetylcyclohexene (500 mg, 0.52 mL, 4.03 mmol) in dichloromethane (2 mL) was added (formation of the Lewis acid/enone complex as a yellow suspension). After cooling to -78°C , a solution of allyltriisopropylsilane (1.20 g, 1.46 mL, 6.04 mmol) in dichloromethane (6 mL) was added. The reaction temperature was raised to -20°C over a period of 4 h (the color changed to red-violet), the mixture was stirred for an additional 16 h at this temperature, and poured into an aqueous solution of ammonium chloride. The organic layer was separated, the aqueous layer extracted three times with dichloromethane, and the combined organic layers were dried over sodium sulfate. Evaporation of the solvent and flash chromatography (pentane/ Et_2O 20:1, silica gel) afforded first the less polar 1-acetyl-2-allylcyclohexene (**4**) (16 mg, 2%) as a colorless oil and then **9k** (1.12 g, 86%). Colorless oil. IR (film): $\tilde{\nu}$ = 2933, 2865, 1696, 1460, 1381, 1347, 1145, 1131, 1013, 997, 916, 881, 664 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 1.00–1.17 (m, 21H), 1.22–1.77 (m, 11H), 1.92 (m, 2H), 2.14 (s, 3H), 2.40 (m, 1H); ^{13}C NMR and DEPT (100 MHz, CDCl_3): δ = 11.21 (3CH), 19.23 (6 CH_3), 20.88 (CH), 22.10 (CH_2), 23.66 (CH_2), 25.57 (CH_3), 26.56 (CH_2), 31.97 (CH_2), 33.58 (CH_2), 39.17 (CH_2), 41.56 (CH), 58.04 (C), 213.10 (C=O); MS: m/z (%) = 322 (1, M^+), 281 (9), 279 (100), 277 (15), 147 (22), 131 (19), 103 (11); HRMS: 322.2674 ($\text{C}_{20}\text{H}_{38}\text{OSi}$, calcd. 322.2692).

1-Acetylcyclopentene (10a): A solution of 1-ethynylcyclopentan-1-ol (5.0 g, 45.4 mmol) in formic acid (40 mL) was heated under reflux for 3 h. After cooling to RT, brine (100 mL) and Et_2O (100 mL) were added and then the mixture was neutralized by addition of solid KOH at 0°C . The layers were separated, the aqueous layer was extracted with Et_2O (3 $\times$), and the combined organic layers were dried over magnesium sulfate. The solvent was evaporated and the residue was purified by bulb-to-bulb distillation at $50^\circ\text{C}/0.2$ mbar: **10a** (4.21 g, 84%). Colorless oil. IR (film): $\tilde{\nu}$ = 2928, 2860, 1711, 1670, 1634, 1469, 1445, 1384, 1349, 1280, 1208, 1158, 958, 726 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ = 1.17 (m, 2H), 1.24–1.42 (m, 11H), 1.47 (m, 2H), 1.56 (m, 2H), 2.25 (m, 1H), 2.27 (s, 3H), 2.32 (t, J = 6.8 Hz, 2H), 6.58 (t, J = 8.0 Hz, 1H); ^{13}C NMR and DEPT (125 MHz, CDCl_3): δ = 22.12 (CH_2), 22.62 (CH_2), 22.96 (CH_2), 23.59 (CH_2), 25.01 (CH_2), 25.05 (CH_2), 25.18 (CH_2), 26.01 (CH_3), 26.11 (CH_2), 26.25 (CH_2), 26.36 (CH_2), 142.11 (C), 144.11 (CH), 200.18 (C=O); MS: m/z (%) = 208 (100, M^+), 151 (15), 137 (27), 123 (12), 109 (22), 95 (23), 83 (24), 81 (20), 55 (28), 43 (64); HRMS: 208.1838 ($\text{C}_{14}\text{H}_{24}\text{O}$, calcd. 208.1827).

1-Acetylcycloheptene (10c): A solution of cycloheptanone (5.79 g, 6.09 mL, 51.6 mmol) in THF (50 mL) was added to a solution of lithium acetylide ethylenediamine complex (5 g, 54.3 mmol) in THF (50 mL) at 35°C . The reaction mixture was stirred for 1.5 h at RT, H_2O (100 mL) was added, and the mixture was heated for 1 h under reflux. The layers were separated, the aqueous phase was extracted with Et_2O (3 $\times$), the combined organic layers were dried over magnesium sulfate, and the solvent was evaporated. Formic acid (100 mL) was added to the residue and the reaction mixture was heated under reflux for 3 h. Brine (100 mL) and Et_2O (100 mL) were added at RT and the mixture was neutralized cautiously by addition of solid KOH at 0°C . The aqueous layer was extracted three times with diethyl ether, the combined organic layers were dried (MgSO_4), the solvent was evaporated, and the residue was purified by bulb-to-bulb distillation at $50^\circ\text{C}/0.2$ mbar: **10c** (5.12 g, 72%). Colorless oil. ^1H NMR (500 MHz, CDCl_3): δ = 1.42 (m, 2H), 1.53 (m, 2H), 1.75 (m, 2H), 2.27 (s, 3H), 2.32 (m, 2H), 2.46 (m, 2H), 7.06 (t, J = 6.7 Hz, 1H); ^{13}C NMR and DEPT (125 MHz, CDCl_3): δ = 25.24 (CH_2), 25.38 (CH_3), 25.82 (CH_2), 26.09 (CH_2), 29.14 (CH_2), 32.27 (CH_2), 145.60 (CH), 146.57 (C), 199.21 (C=O). For further data, see ref. [17b].

1-Acetylcyclooctene (10d): A solution of cyclooctanone (7.40 g, 58.6 mmol) in THF (50 mL) was added to a suspension of lithium acetylide ethylenediamine complex (5.30 g, 57.6 mmol) in THF (50 mL) at 35°C , stirred for 1.5 h at RT, and then H_2O (100 mL) was added. This reaction mixture was heated under reflux for 1 h, the organic layer separated, and the aqueous layer was extracted with Et_2O (3 $\times$). The combined organic layers were dried over magnesium

sulfate and the solvent was evaporated. Formic acid (100 mL) was added to the residue and this mixture was heated under reflux for an additional 3 h. The mixture was quenched by addition of brine (100 mL) and diethyl ether (100 mL) and neutralized cautiously with solid KOH at 0°C . The aqueous layer was extracted three times with Et_2O , the combined organic layers were washed with a sat. aqueous solution of NaHCO_3 and dried (MgSO_4). Evaporation of the solvent and bulb-to-bulb distillation ($75^\circ\text{C}/0.2$ mbar) of the residue afforded a crude product, which was subjected to flash chromatography (hexane/ Et_2O 1:1, silica gel): **10d** (3.91 g, 44%). Colorless oil. IR (film): $\tilde{\nu}$ = 2925, 2853, 1666, 1636, 1465, 1447, 1385, 1286, 1200 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 1.33–1.50 (m, 6H), 1.58 (m, 2H), 2.26 (s, 3H), 2.29 (m, 2H), 2.39 (m, 2H), 6.83 (t, J = 8.3 Hz, 1H); ^{13}C NMR and DEPT (100 MHz, CDCl_3): δ = 23.48 (CH_2), 25.55 (CH_3), 26.25 (CH_2), 26.69 (CH_2), 27.69 (CH_2), 29.21 (CH_2), 29.31 (CH_2), 143.22 (C), 143.76 (CH), 199.20 (C=O); MS: m/z (%) = 152 (100, M^+), 137 (52), 123 (16), 109 (66), 81 (19), 79 (16), 67 (63), 55 (20), 43 (90); HRMS: 152.1209 ($\text{C}_{10}\text{H}_{16}\text{O}$, calcd. 152.1201).

1-Acetylcyclododecene (10e): A solution of cyclododecanone (3.13 g, 17.2 mmol) in THF (25 mL) was added to a suspension of lithium acetylide ethylenediamine complex (5.0 g, 54.3 mmol) in THF (50 mL) at 35°C (to maintain this temperature the mixture must be cooled). The reaction mixture was stirred for 7 d at RT, lithium acetylide ethylenediamine complex (2 g, 21.7 mmol) was added, and the mixture was stirred for an additional 7 d at this temperature. H_2O (100 mL) was added and this mixture was heated under reflux for 1 h. The layers were separated, the aqueous layer was extracted with Et_2O (3 $\times$), the combined organic layers were dried (MgSO_4), and the solvent was evaporated. Formic acid (100 mL) was added to the residue and this reaction mixture was heated under reflux for 3 h. Brine (100 mL) and Et_2O (100 mL) were added at 20°C . While stirring vigorously, the mixture was neutralized by addition of solid KOH at 0°C . The aqueous layer was extracted three times with diethyl ether, the combined organic layers were dried over magnesium sulfate, and the solvent was evaporated. The residue was purified twice by bulb-to-bulb distillation (90°C , 0.2 mbar): **10e** (2.15 g, 60%). Colorless oil. IR (film): $\tilde{\nu}$ = 2928, 2860, 1711, 1670, 1634, 1469, 1445, 1384, 1349, 1280, 1208, 1158, 958, 726 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ = 1.17 (m, 2H), 1.24–1.42 (m, 11H), 1.47 (m, 2H), 1.56 (m, 2H), 2.25 (m, 1H), 2.27 (s, 3H), 2.32 (t, J = 6.8 Hz, 2H), 6.58 (t, J = 8.0 Hz, 1H); ^{13}C NMR and DEPT (125 MHz, CDCl_3): δ = 22.12 (CH_2), 22.62 (CH_2), 22.96 (CH_2), 23.59 (CH_2), 25.01 (CH_2), 25.05 (CH_2), 25.18 (CH_2), 26.01 (CH_3), 26.11 (CH_2), 26.25 (CH_2), 26.36 (CH_2), 142.11 (C), 144.11 (CH), 200.18 (C=O); MS: m/z (%) = 208 (100, M^+), 151 (15), 137 (27), 123 (12), 109 (22), 95 (23), 83 (24), 81 (20), 55 (28), 43 (64); HRMS: 208.1838 ($\text{C}_{14}\text{H}_{24}\text{O}$, calcd. 208.1827).

1-Acetyl-3-triphenylsilylbicyclo[3.3.0]octane (11a): A solution of 1-acetylcyclopentene (2.01 g, 2.10 mL, 18.2 mmol) in dichloromethane (10 mL) was added to a solution of titanium tetrachloride (3.79 g, 2.19 mL, 20.0 mmol) in dichloromethane (25 mL) at -20°C . The formation of the Lewis acid/enone complex was indicated by the yellow color of the resulting suspension. A solution of allyltriphenylsilane (**1d**) (8.20 g, 27.3 mmol) in dichloromethane (30 mL) was added at -78°C . Over a period of 3.5 h the reaction mixture was warmed to -20°C , during which the color changed to an intense red-violet. After stirring for an additional 16 h at this temperature, the mixture was poured into a cold aqueous solution of ammonium chloride and the organic layer was separated immediately. The aqueous layer was extracted with dichloromethane (3 $\times$), the combined organic layers were dried over sodium sulfate, and the solvent evaporated. Recrystallization of the residue from Et_2O at -20°C afforded **11a** (1.89 g, 25%). Colorless crystals. M.p. $103\text{--}104^\circ\text{C}$; IR (KBr): $\tilde{\nu}$ = 3069, 3050, 3016, 2950, 2858, 1689, 1481, 1426, 1353, 1243, 1223, 1186, 1156, 1106, 740, 702, 545 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 1.15–1.36 (m, 3H), 1.41 (m, 1H), 1.57 (m, 1H), 1.69 (m, 1H), 1.87 (m, 1H), 2.20 (s, 3H), 2.32 (m, 1H), 2.63 (ddd, J = 13.0, 5.8, 1.7 Hz, 1H), 2.85 (m, 1H), 7.40 (m, 9H), 7.57 (m, 6H); ^{13}C NMR and DEPT (100 MHz, CDCl_3): δ = 24.86 (CH_2), 25.23 (CH), 25.95 (CH_3), 33.16 (CH_2), 36.99 (CH_2), 37.68 (CH_2), 39.93 (CH_2), 47.72 (CH), 68.87 (C), 127.85 (6CH), 129.44 (3CH), 134.55 (3C), 135.94 (6CH), 211.85 (C=O); MS: m/z (%) = 410 (1, M^+), 370 (11), 369 (39), 260 (20), 259 (100), 181 (10); HRMS: 410.2046 ($\text{C}_{28}\text{H}_{30}\text{OSi}$, calcd. 410.2066).

1-Acetyl-9-triphenylsilylbicyclo[5.3.0]decane (11c): A solution of 1-acetylcycloheptene (1.10 g, 8.00 mmol) in dichloromethane (4 mL) was added to a

solution of titanium tetrachloride (1.68 g, 0.98 mL, 8.86 mmol) in dichloromethane (5 mL) at -20°C . The color of the reaction mixture turned to an intense dark red. After cooling to -78°C , a solution of allyltriphenylsilane (**1d**) (3.64 g, 12.08 mmol) in dichloromethane (12 mL) was added. The reaction mixture was warmed slowly to -20°C and stirred for 19 h at this temperature. The cold mixture was quenched by addition of an aqueous solution of ammonium chloride, the organic layer separated immediately, and the aqueous layer extracted with dichloromethane ($3\times$). The combined organic layers were dried over magnesium sulfate, the solvent was evaporated, and the residue subjected to flash chromatography (hexane/Et₂O 7:1, silica gel): **11c** (1.20 g, 34%). Colorless crystals. M.p. $107\text{--}108^{\circ}\text{C}$; IR (KBr): $\tilde{\nu} = 3067, 3048, 2927, 2852, 1692, 1425, 1348, 1186, 1133, 1108, 739, 701, 555\text{ cm}^{-1}$; ¹H NMR (400 MHz, CDCl₃): $\delta = 0.89\text{--}1.30$ (m, 5H), $1.43\text{--}1.76$ (m, 8H), $2.01\text{--}2.07$ (m, 1H), 2.22 (s, 3H), $2.24\text{--}2.31$ (m, 1H), 3.01 (m, 1H), 7.39 (m, 9H), 7.53 (m, 6H); ¹³C NMR and DEPT (100 MHz, CDCl₃): $\delta = 23.09$ (CH), 25.14 (CH₃), 26.06 (CH₂), 28.15 (CH₂), 31.04 (CH₂), 33.04 (CH₂), 34.91 (CH₂), 38.07 (CH₂), 42.26 (CH₂), 42.51 (CH), 64.37 (C), 127.85 (CH), 129.45 (3CH), 134.45 (3C), 135.90 (6CH), 213.11 (C=O); MS: m/z (%) = 438 (1, *M*⁺), 398 (4), 397 (15), 361 (3), 360 (4), 276 (3), 260 (22), 259 (100), 181 (7); HRMS: 438.2392 (C₃₀H₃₄OSi, calcd. 438.2379).

1-Acetyl-3-triisopropylsilylbicyclo[3.3.0]octane (12a): A solution of titanium tetrachloride (840 mg, 0.49 mL, 4.43 mmol) in CH₂Cl₂ (5 mL) was cooled to -20°C and a solution of 1-acetylcyclopentene (443 mg, 4.03 mmol) in CH₂Cl₂ (3 mL) was added. After cooling to -78°C , a solution of allyltriisopropylsilane (1.20 g, 1.46 mL, 6.05 mmol) in CH₂Cl₂ (5 mL) was added. Over a period of 2 h the reaction mixture was warmed to -20°C and stirred for an additional 17 h at this temperature. The cold mixture was poured into an aqueous solution of ammonium chloride, the organic layer separated immediately, and the aqueous layer extracted with dichloromethane ($3\times$). The combined organic layers were dried over magnesium sulfate, the solvent was evaporated, and the residue subjected to flash chromatography (hexane/Et₂O 30:1, silica gel): **12a** (881 mg, 71%, *anti/syn* = 3:1). Colorless oil. IR (film): $\tilde{\nu} = 3382, 2943, 2891, 2865, 1701, 1463, 1354, 1160, 999, 882, 666\text{ cm}^{-1}$; ¹H NMR (400 MHz, CDCl₃): $\delta = 0.99\text{--}1.07$ (m, 21H), $1.16\text{--}1.73$ (m, 9H), $2.09\text{--}2.16$ (m, 1H), 2.13 (s, *syn*-**12a**) and 2.14 (s, *anti*-**12a**, $\Sigma = 3\text{H}$), 2.44 (ddd, $J = 12.9, 5.6, 2.0\text{ Hz}$, 1H), 2.70 (m, 1H); ¹³C NMR and DEPT (100 MHz, CDCl₃): *anti*-**12a**: $\delta = 11.42$ (3CH), 19.15 (6CH₃), 24.94 (CH), 24.97 (CH₂), 25.77 (CH₃), 33.15 (CH₂), 37.16 (CH₂), 38.37 (CH₂), 40.59 (CH₂), 47.50 (CH), 68.56 (C), 211.77 (C=O); *syn*-**12a**: $\delta = 11.42$ (3CH), 19.15 (6CH₃), 21.14 (CH), 25.96 (CH₃), 26.99 (CH₂), 35.04 (CH₂), 36.83 (CH₂), 37.24 (CH₂), 40.68 (CH₂), 47.04 (CH), 68.35 (C), 211.87 (C=O); MS: m/z (%) = 308 (4, *M*⁺), 267 (9), 265 (100), 263 (28), 183 (5), 133 (12), 131 (22), 103 (16); HRMS: 308.2519 (C₁₉H₃₆OSi, calcd. 308.2535).

1-Acetyl-9-triisopropylsilylbicyclo[5.3.0]decane (12c): A solution of 1-acetylcycloheptene (440 mg, 3.19 mmol) in dichloromethane (2 mL) was added to a solution of titanium tetrachloride (668 mg, 0.39 mL, 3.53 mmol) in dichloromethane (5 mL) at -20°C . A solution of allyltriisopropylsilane (948 mg, 1.15 mL, 4.78 mmol) in dichloromethane (4 mL) was added at -78°C . The reaction mixture was warmed to -20°C and stirred for 19 h at this temperature. The cold mixture was poured into an aqueous solution of ammonium chloride, the organic layer separated immediately, and the aqueous layer extracted three times with dichloromethane. The combined organic layers were dried over magnesium sulfate, the solvent was evaporated, and the residue subjected to flash chromatography (hexane/Et₂O 30:1, silica gel): **12c** (723 mg, 68%). Colorless oil. IR (film): $\tilde{\nu} = 2940, 2865, 1701, 1463, 1350, 1241, 1164, 1136, 1072, 999, 917, 883, 784, 664\text{ cm}^{-1}$; ¹H NMR (400 MHz, CDCl₃): $\delta = 0.85$ (m, 1H), $0.99\text{--}1.04$ (m, 21H), $1.17\text{--}1.76$ (m, 11H), $2.00\text{--}2.20$ (m, 3H), 2.16 (s, 3H), 2.84 (m, 1H); ¹³C NMR and DEPT (100 MHz, CDCl₃): $\delta = 11.33$ (3CH), 19.15 (6CH₃), 22.65 (CH), 24.95 (CH₃), 26.16 (CH₂), 28.32 (CH₂), 31.18 (CH₂), 33.46 (CH₂), 35.16 (CH₂), 38.91 (CH₂), 42.13 (CH), 43.17 (CH₂), 64.26 (C), 213.31 (C=O); MS: m/z (%) = 336 (4, *M*⁺), 293 (100), 249 (2), 161 (16), 159 (6), 133 (3), 131 (30); HRMS: 336.2866 (C₂₁H₄₀OSi, calcd. 336.2848).

1-Acetyl-3-tert-butylphenylsilylbicyclo[3.3.0]octane (13a): A solution of 1-acetylcyclopentene (444 mg, 4.03 mmol) in dichloromethane (7 mL) was added to a solution of titanium tetrachloride (840 mg, 0.49 mL, 4.43 mmol) in dichloromethane (7 mL) at -20°C . The resulting yellow suspension (Lewis acid/enone complex) was cooled to -78°C and a solution of allyl-tert-butylphenylsilane (**1i**) (1.70 g, 6.06 mmol) in dichloromethane (7 mL)

was added slowly. After warming to -20°C (the color changed to red-violet), the reaction mixture was stirred for 19 h at this temperature and then quenched by addition of an aqueous solution of ammonium chloride. The aqueous layer was extracted three times with dichloromethane, the combined organic layers were dried over magnesium sulfate, and the solvent was evaporated. Recrystallization from Et₂O afforded **13a** (828 mg, 53%). Colorless crystals. M.p. $89\text{--}92^{\circ}\text{C}$; IR (KBr): $\tilde{\nu} = 3069, 2996, 2954, 2860, 1695, 1470, 1447, 1426, 1360, 1229, 1158, 1108, 820, 742, 701, 684, 607\text{ cm}^{-1}$; ¹H NMR (400 MHz, CDCl₃): $\delta = 0.98\text{--}1.18$ (m, 3H), 1.06 (s, 9H), 1.33 (m, 1H), $1.42\text{--}1.65$ (m, 5H), 2.15 (s, 3H), 2.21 (m, 1H), 2.50 (ddd, $J = 13.0, 5.7, 1.9\text{ Hz}$, 1H), 2.75 (m, 1H), 7.37 (m, 6H), 7.60 (m, 4H); ¹³C NMR and DEPT (100 MHz, CDCl₃): $\delta = 18.56$ (C), 23.84 (CH), 24.68 (CH₃), 25.88 (CH₃), 28.42 (3CH₃), 33.08 (CH₂), 36.93 (CH₂), 37.93 (CH₂), 40.22 (CH₂), 47.45 (CH), 68.59 (C), 127.33 (2CH), 127.37 (2CH), 128.94 (2CH), 134.29 (C), 134.38 (C), 136.47 (2CH), 136.48 (2CH), 212.03 (C=O); MS: m/z (%) = 390 (1, *M*⁺), 333 (100), 199 (80), 197 (10), 183 (91), 181 (15), 135 (17); HRMS: 390.2390 (C₂₆H₃₄OSi, calcd. 390.2379); Anal. calcd. for C₂₆H₃₄OSi: C 79.95, H 8.78; found: C 79.80, H 8.67.

1-Acetyl-9-tert-butylphenylsilylbicyclo[5.3.0]decane (13c): A solution of titanium tetrachloride (840 mg, 0.49 mL, 4.43 mmol) in dichloromethane (7 mL) was cooled to -20°C and a solution of 1-acetylcycloheptene (560 mg, 4.05 mmol) in dichloromethane (7 mL) was added. The formation of the Lewis acid/enone complex was indicated by the yellow color of the resulting suspension. After cooling to -78°C , a solution of allyl-tert-butylphenylsilane (**1i**) (1.70 g, 6.06 mmol) in dichloromethane (7 mL) was added slowly. The reaction mixture was warmed to -20°C and stirred for 19 h at this temperature, then quenched by addition of an aqueous solution of ammonium chloride, and the organic layer was separated. The aqueous layer was extracted with dichloromethane ($3\times$), the combined organic layers were dried (MgSO₄), and the solvent was evaporated. The residue was subjected to flash chromatography (hexane/Et₂O 15:1, silica gel): **13c** (853 mg, 50%). Colorless oil. IR (film): $\tilde{\nu} = 3071, 3047, 3014, 2996, 2926, 2855, 1700, 1471, 1427, 1391, 1362, 1351, 1165, 1134, 1107, 911, 820, 740, 702, 686, 609\text{ cm}^{-1}$; ¹H NMR (400 MHz, CDCl₃): $\delta = 0.88\text{--}1.64$ (m, 13H), 1.04 (s, 9H), 1.96 (dd, $J = 14.8, 7.7\text{ Hz}$, 1H), 2.15 (m, 1H), 2.19 (s, 3H), 2.91 (m, 1H), 7.40 (m, 6H), 7.60 (m, 4H); ¹³C NMR and DEPT (100 MHz, CDCl₃): $\delta = 18.50$ (C), 21.53 (CH), 24.96 (CH₃), 25.86 (CH₂), 27.99 (CH₂), 28.35 (3CH₃), 30.90 (CH₂), 32.85 (CH₂), 34.75 (CH₂), 38.22 (CH₂), 42.19 (CH), 42.50 (CH₂), 64.01 (C), 127.27 (2CH), 127.31 (2CH), 128.89 (2CH), 133.96 (C), 134.34 (C), 136.31 (2CH), 136.44 (2CH), 213.26 (C=O); MS: m/z (%) = 418 (1, *M*⁺), 361 (100), 199 (48), 197 (10), 183 (73), 135 (20); HRMS: 418.2684 (C₂₈H₃₈OSi, calcd. 418.2692).

1-Acetyl-10-tert-butylphenylsilylbicyclo[6.3.0]undecane (13d): A solution of 1-acetylcyclooctene (1.50 g, 9.85 mmol) in dichloromethane (15 mL) was added to a solution of titanium tetrachloride (2.08 g, 1.20 mL, 10.9 mmol) in dichloromethane (15 mL) at -20°C . After cooling to -78°C , a solution of allyl-tert-butylphenylsilane (**1i**) (4.15 g, 14.8 mmol) in dichloromethane (15 mL) was added. The reaction mixture was stirred for 60 min at this temperature and then quenched by addition of an aqueous solution of ammonium chloride. The organic layer was separated, the aqueous layer extracted with dichloromethane ($3\times$), and the combined organic layers were dried over magnesium sulfate. The solvent was evaporated and the residue subjected to flash chromatography (hexane/Et₂O 50:1, silica gel): **13d** (3.51 g, 82%). Colorless crystals. M.p. $108\text{--}111^{\circ}\text{C}$; IR (KBr): $\tilde{\nu} = 3075, 2955, 2928, 2857, 1697, 1468, 1426, 1132, 1110, 821, 741, 705, 611\text{ cm}^{-1}$; ¹H NMR (400 MHz, CDCl₃): $\delta = 0.93\text{--}1.63$ (m, 14H), 1.04 (s, 9H), 1.84 (dt, $J = 15.2, 3.7\text{ Hz}$, 1H), 2.14 (m, 1H), 2.21 (s, 3H), 2.42 (m, 1H), 2.75 (m, 1H), 7.39 (m, 6H), 7.62 (m, 4H); ¹³C NMR and DEPT (100 MHz, CDCl₃): $\delta = 18.14$ (CH), 18.46 (C), 24.50 (CH₂), 24.79 (CH₃), 25.73 (CH₂), 26.53 (CH₂), 28.32 (3CH₃), 29.43 (CH₂), 31.35 (CH₂), 33.61 (CH₂), 39.64 (CH), 40.17 (CH₂), 41.79 (CH₂), 64.10 (C), 127.24 (2CH), 127.27 (2CH), 128.88 (2CH), 133.79 (C), 134.38 (C), 136.29 (2CH), 136.45 (2CH), 212.80 (C=O); MS: m/z (%) = 432 (1, *M*⁺), 375 (100), 217 (9), 199 (51), 197 (16), 183 (98), 181 (14), 135 (28), 105 (19); HRMS: 432.2863 (C₂₉H₄₀OSi, calcd. 432.2848); Anal. calcd. for C₂₉H₄₀OSi: C 80.49, H 9.32; found: C 79.61, H 9.09.

1-Acetyl-14-tert-butylphenylsilylbicyclo[10.3.0]pentadecane (13e): A solution of titanium tetrachloride (840 mg, 0.49 mL, 4.43 mmol) in CH₂Cl₂ (7 mL) was cooled to -20°C and a solution of 1-acetylcyclododecene (840 mg, 4.03 mmol) in CH₂Cl₂ (7 mL) was added slowly. The mixture was

cooled to -78°C and a solution of allyl-*tert*-butyldiphenylsilane (**1i**) (1.69 g, 6.04 mmol) in dichloromethane (7 mL) was added. The reaction mixture was warmed to -20°C , stirred for 19 h at this temperature, and then quenched by addition of an aqueous solution of ammonium chloride. The aqueous layer was extracted three times with CH_2Cl_2 , the combined organic layers were dried (MgSO_4), and the solvent was evaporated. The residue was subjected to flash chromatography (hexane/ Et_2O 50:1, silica gel) and provided **13e** (1.28 g, 65%). Colorless, viscous oil. IR (KBr): $\tilde{\nu} = 2930, 2858, 1701, 1351, 1135, 1106, 910, 820, 737, 701, 686, 610\text{ cm}^{-1}$; ^1H NMR (500 MHz, CDCl_3): $\delta = -0.52$ (m, 1H), 0.80 (m, 1H), 0.91 (m, 1H), 1.00–1.38 (m, 16H), 1.03 (s, 9H), 1.59 (m, 3H), 2.12 (m, 3H), 2.20 (s, 3H), 2.28 (m, 1H), 7.37 (m, 6H), 7.59 (m, 4H); ^{13}C NMR and DEPT (125 MHz, CDCl_3): $\delta = 17.66$ (CH), 18.63 (C), 22.18 (CH_2), 23.58 (CH_2), 23.66 (CH_2), 23.95 (CH_2), 24.45 (CH_3), 24.55 (CH_2), 25.51 (CH_2), 25.54 (CH_2), 26.44 (CH_2), 26.55 (CH_2), 28.57 (3CH_3), 29.99 (CH_2), 32.31 (CH_2), 38.15 (CH_2), 38.52 (CH), 65.64 (C), 127.42 (4CH), 129.06 (2CH), 134.11 (C), 134.32 (C), 136.68 (2CH), 136.71 (2CH), 213.27 (C=O); MS: m/z (%) = 488 (0.1, M^+), 431 (65), 199 (23), 183 (35), 135 (12), 86 (61), 84 (100), 83 (14); HRMS: 488.3503 ($\text{C}_{33}\text{H}_{48}\text{OSi}$, calcd. 488.3474).

1-Acetyl-14-*tert*-butyldiphenylsilylbicyclo[10.3.0]pentadecane-(2,4-dinitrophenylhydrazone) (14): A solution of 2,4-dinitrophenylhydrazine (147 mg, 0.75 mmol) in conc. sulfuric acid (0.5 mL)/dry ethanol (3 mL) was added to a solution of **13e** (167 mg, 0.34 mmol) in dry ethanol (6 mL) at room temperature. The mixture was left for 15 h at room temperature, the precipitate was separated by filtration, washed carefully with water, and subsequently with a small amount of ethanol. Recrystallization from ethanol/ Et_2O (2:3) afforded the dinitrophenylhydrazone **14** (72 mg, 32%). Orange-yellow crystals. M.p. $218\text{--}220^{\circ}\text{C}$; IR (KBr): $\tilde{\nu} = 3322, 2930, 2858, 1618, 1592, 1518, 1471, 1446, 1426, 1362, 1334, 1312, 1283, 1222, 1136, 1107, 1082, 910, 833, 820, 739, 701\text{ cm}^{-1}$; ^1H NMR (500 MHz, CDCl_3): $\delta = -0.42$ (m, 1H), 0.90–1.42 (m, 20H), 1.02 (s, 9H), 1.50 (m, 1H), 1.61 (m, 1H), 2.04 (dd, $J = 12.7, 7.2\text{ Hz}$, 1H), 2.08 (s, 3H), 2.19 (m, 1H), 2.50 (m, 1H), 7.38 (m, 6H), 7.58 (m, 4H), 7.98 (d, $J = 9.6\text{ Hz}$, 1H), 8.36 (dd, $J = 9.6, 2.5\text{ Hz}$, 1H), 9.17 (d, $J = 2.5\text{ Hz}$, 1H), 11.16 (s, 1H); ^{13}C NMR and DEPT (125 MHz, CDCl_3): $\delta = 12.31$ (CH_3), 17.54 (CH), 18.68 (C), 22.40 (CH_2), 23.51 (CH_2), 23.60 (CH_2), 24.13 (CH_2), 24.98 (CH_2), 25.68 (CH_2), 25.84 (CH_2), 26.49 (CH_2), 26.64 (CH_2), 28.63 (3CH_3), 30.59 (CH_2), 32.26 (CH_2), 38.50 (CH_2), 40.10 (CH), 59.99 (C), 116.53 (CH), 123.63 (CH), 127.47 (4CH), 129.13 (2CH), 130.26 (CH), 134.18 (C), 134.39 (C), 136.69 (2CH), 136.72 (2CH), 137.70 (C), 145.57 (C), 160.85 (C=N), the signal of 1 C is missing due to overlap; MS: m/z (%) = 668 (37, M^+), 611 (100), 388 (7), 199 (54), 197 (23), 183 (69), 135 (48); HRMS: 668.3736 ($\text{C}_{39}\text{H}_{52}\text{N}_4\text{O}_4\text{Si}$, calcd. 668.3758); Anal. calcd. for $\text{C}_{39}\text{H}_{52}\text{N}_4\text{O}_4\text{Si}$: C 70.02, H 7.84, N 8.38; found: C 70.04, H 7.79, N 8.20.

X-ray crystal structure analysis of **14**. *Crystal data*: Empirical formula: $\text{C}_{39}\text{H}_{52}\text{N}_4\text{O}_4\text{Si}$; formula weight: 668.96; color, habit: orange-yellow tablet; crystal size: $0.60 \times 0.50 \times 0.25\text{ mm}$; crystal system: monoclinic; space group: $P2_1/n$. Unit cell dimensions: $a = 11.515(4)$, $b = 21.649(5)$, $c = 15.216(4)\text{ \AA}$; $\beta = 103.10(3)^{\circ}$; $V = 3695(2)\text{ \AA}^3$; $Z = 4$; $\rho_{\text{calcd}} = 1.210\text{ g cm}^{-3}$; absorption coefficient: 0.11 mm^{-1} ; $F(000)$: 1456. *Data collection*. $\lambda = 0.71073\text{ \AA}$; $T = 173\text{ K}$; θ range: $3.08\text{--}25.0^{\circ}$; reflections collected: 6506; independent reflections: 6482. *Refinement*: Full-matrix least squares on F^2 ; data-to-parameter ratio: 14.7:1; final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0492$, $wR_2 = 0.1090$; maximum residual electron density: $0.45\text{ e \AA}^{-3}$; CSD-405718.^[15]

1-Acetyl-3-triisopropyl-5-methylbicyclo[3.3.0]octane (16a): A solution of 1-acetyl-2-methylcyclopentene (500 mg, 4.03 mmol) in dichloromethane (2 mL) was added to a solution of TiCl_4 (840 mg, 0.49 mL, 4.43 mmol) in CH_2Cl_2 (5 mL) at -20°C . After cooling to -78°C , a solution of allyltriisopropylsilane (1.20 g, 1.46 mL, 6.04 mmol) in CH_2Cl_2 (5 mL) was added and the reaction mixture was warmed slowly (2 h) to -20°C . The mixture was stirred for an additional 17 h at this temperature and then poured into an aqueous solution of ammonium chloride. The layers were separated, the aqueous layer was extracted with CH_2Cl_2 ($3 \times$), and the combined organic layers were dried over magnesium sulfate. After filtration through a short plug of Celite, the solvent was evaporated and the residue subjected to flash chromatography (hexane/ Et_2O 10:1, silica gel): **16a** (1.19 g, 92%, *anti/syn* = 5:1). Colorless oil. IR (film): $\tilde{\nu} = 3369, 2942, 2890, 2866, 1694, 1461, 1383, 1351, 1184, 1156, 1015, 999, 917, 883, 763, 669, 643, 628\text{ cm}^{-1}$; ^1H NMR (400 MHz, CDCl_3): $\delta = 0.98$ (s, 3H), 1.01–1.14 (m, 21H), 1.34–1.49 (m, 4H), 1.54–1.74 (m, 5H), 2.137 (s, *anti*-**16a**) and 2.141 (s, *syn*-**16a**, $\Sigma = 3\text{H}$), 2.23 (m, 1H), 2.53 (m, 1H); ^{13}C NMR and DEPT (100 MHz,

CDCl_3): *anti*-**16a**: $\delta = 11.42$ (3CH), 19.21 (6CH₃), 23.67 (CH₂), 23.76 (CH), 24.75 (CH₃), 29.01 (CH₃), 37.99 (CH₂), 41.87 (CH₂), 42.92 (CH₂), 46.15 (CH₂), 57.01 (C), 68.02 (C), 213.44 (C=O). *syn*-**16a**: $\delta = 11.42$ (3CH), 19.21 (6CH₃), 20.78 (CH), 25.11 (CH₃), 26.28 (CH₂), 29.32 (CH₃), 38.99 (CH₂), 40.94 (CH₂), 42.98 (CH₂), 45.84 (CH₂), 56.45 (C), 68.26 (C), 213.74 (C=O); MS: m/z (%) = 322 (4, M^+), 279 (100), 277 (6), 185 (3), 147 (13), 131 (18), 103 (12); HRMS: 322.2698 ($\text{C}_{20}\text{H}_{38}\text{OSi}$, calcd. 322.2692).

1-Acetyl-8-triisopropyl-6-methylbicyclo[4.3.0]nonane (16b): A solution of TiCl_4 (840 mg, 0.49 mL, 4.43 mmol) in CH_2Cl_2 (5 mL) was cooled to -20°C and a solution of 1-acetyl-2-methylcyclohexene (556 mg, 4.03 mmol) in CH_2Cl_2 (3 mL) was added. The mixture was cooled to -78°C and a solution of allyltriisopropylsilane (1.20 g, 1.46 mL, 6.04 mmol) in CH_2Cl_2 (5 mL) was added. After warming to -20°C over a period of 2 h, the reaction mixture was stirred for an additional 17 h and then poured into an aqueous solution of NH_4Cl . The layers were separated and the aqueous layer was extracted with CH_2Cl_2 ($3 \times$). The combined organic layers were dried (MgSO_4) and then filtered through a short plug of Celite. Evaporation of the solvent and flash chromatography (hexane/ Et_2O 20:1, silica gel) provided **16b** (618 mg, 46%). Colorless oil. IR (film): $\tilde{\nu} = 2940, 2866, 2758, 2724, 1736, 1700, 1463, 1383, 1374, 1357, 1350, 1283, 1229, 1200, 1191, 1135, 1070, 1015, 1000, 919, 882, 749, 668, 649\text{ cm}^{-1}$; ^1H NMR (400 MHz, CDCl_3): $\delta = 0.96$ (s, 3H), 1.02–1.30 (m, 24H), 1.35–1.68 (m, 6H), 1.74–1.84 (m, 2H), 2.07 (s, 3H), 2.14 (t, $J = 12.6\text{ Hz}$, 1H), 2.28 (t, $J = 12.6\text{ Hz}$, 1H); ^{13}C NMR and DEPT (100 MHz, CDCl_3): $\delta = 11.06$ (3CH), 15.48 (CH), 19.28 (3CH₃), 19.35 (3CH₃), 21.73 (CH₂), 22.24 (CH₂), 24.44 (CH₃), 28.12 (CH₃), 33.39 (CH₂), 33.70 (CH₂), 37.28 (CH₂), 39.82 (CH₂), 43.29 (C), 59.75 (C), 211.88 (C=O); MS: m/z (%) = 336 (2, M^+), 295 (10), 293 (100), 291 (9), 251 (2), 183 (2), 161 (9), 131 (18); HRMS: 336.2854 ($\text{C}_{21}\text{H}_{40}\text{OSi}$, calcd. 336.2848).

1-Acetyl-9-triisopropyl-7-methylbicyclo[5.3.0]decane (16c): A solution of 1-acetyl-2-methylcycloheptene (613 mg, 4.03 mmol) in CH_2Cl_2 (3 mL) was added to a solution of TiCl_4 (840 mg, 0.49 mL, 4.43 mmol) in CH_2Cl_2 (5 mL) at -20°C . The mixture was cooled to -78°C and a solution of allyltriisopropylsilane (1.20 mg, 1.46 mL, 6.04 mmol) in CH_2Cl_2 (5 mL) was added. Over a period of 2 h the reaction mixture was warmed to -20°C , stirred at this temperature for an additional 17 h, and then quenched by addition of an aqueous solution of NH_4Cl . The layers were separated, the aqueous layer extracted three times (CH_2Cl_2), and the combined organic layers were dried over magnesium sulfate. Filtration through a short plug of Celite, evaporation of the solvent, and flash chromatography (hexane/ Et_2O 15:1, silica gel) afforded **16c** (768 mg, 54%). Colorless oil. IR (film): $\tilde{\nu} = 2941, 2865, 1701, 1461, 1382, 1366, 1347, 1239, 1169, 1015, 999, 972, 919, 882, 778, 668, 649\text{ cm}^{-1}$; ^1H NMR (400 MHz, CDCl_3): $\delta = 0.95$ (s, 3H), 1.04–1.16 (m, 21H), 1.25 (ddd, $J = 12.0, 5.4, 1.9\text{ Hz}$, 1H), 1.37–1.70 (m, 10H), 1.79–1.87 (m, 2H), 2.05 (m, 1H), 2.10 (s, 3H), 2.46 (ddd, $J = 13.2, 7.6, 1.9\text{ Hz}$, 1H); ^{13}C NMR and DEPT (100 MHz, CDCl_3): $\delta = 11.31$ (3CH), 19.27 (6CH₃, CH), 23.88 (CH₂), 24.77 (CH₂), 28.92 (CH₃), 28.94 (CH₃), 31.21 (CH₂), 37.43 (CH₂), 38.93 (CH₂), 39.86 (CH₂), 44.25 (CH₂), 47.73 (C), 64.38 (C), 212.47 (C=O); MS: m/z (%) = 350 (4, M^+), 307 (100), 305 (9), 263 (2), 175 (6), 157 (6), 131 (21); HRMS: 350.3014 ($\text{C}_{22}\text{H}_{42}\text{OSi}$, calcd. 350.3005).

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