Cycloadditions of Allylsilanes, Part *12*.[1] Regio- and Stereoselective Transformations of Silylbicyclo[n.3.0]alkanes

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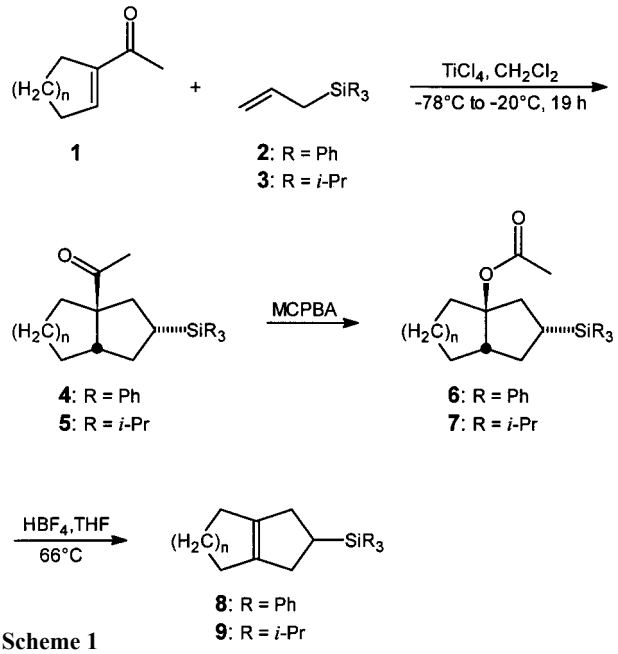
Abstract: Lewis acid promoted [3+2] cycloaddition of 1-acetylcycloalkenes and allylsilanes provides the silylbicyclo[*n*.3.0]-alkanes **4** and **5**. The sequence of regioselective Baeyer–Villiger oxidation and elimination of acetic acid affords the 3-silylbicyclo[3.3.0]oct-1(5)-enes **8a** and **9a** and the 8-(triphenylsilyl)bicyclo[4.3.0]non-1(6)-ene **(8b)**. Epoxidation and catalytic hydrogenation of these olefins proceeds with complete stereoselectivity *anti* relative to the silyl substituent. Ozonolysis of **8b** leads to 3-(triphenylsilyl)cyclononane-1,5-dione **(15)**.

Key words: allylsilanes, [3+2] cycloadditions, Baeyer–Villiger oxidation, molecular modelling, diastereoselective epoxidation

A few years ago the Lewis acid promoted [3+2] cycloaddition of allylsilanes and electron-deficient olefins was described as a side reaction of the Hosomi–Sakurai reaction.[2] It was found that allylsilanes containing bulky substituents at the silicon atom, especially allyl-triisopropylsilane, follow almost exclusively the course of the cycloaddition reaction.[3] Subsequently this reaction was developed to a useful synthetic method for the stereoselective construction of cyclopentanes.[4–6] Depending on the substrate and the reaction temperature a selective [2+2] cycloaddition of allylsilanes and electron-deficient olefins leading to silylmethylcyclobutanes was also observed.[7] Moreover, several related Lewis acid promoted cycloadditions of allylsilanes providing heterocyclic ring systems were reported.[8]

A broad range of angularly acetyl-substituted silylbicyclo[*n*.3.0]alkanes is stereoselectively available by Lewis acid promoted [3+2] cycloaddition of allylsilanes and 1-acetylcycloalkenes.[4] The chemo-, regio-, and stereoselective functionalization of these products directed toward potential applications to the synthesis of biologically active terpenes is currently under active investigation. One problem was the selective oxidative cleavage of the carbon–silicon bond containing a bulky silyl group by modifications of the classical Fleming–Tamao oxidation.[9] Recently this transformation was achieved for cycloadducts of allylsilanes containing the methyldiphenylsilyl,[10] triphenylsilyl,[10] dimethyltritylsilyl,[11] diisopropylsilyl,[1] and *tert*-butyldiphenylsilyl groups.[1] Using these modifications of the Fleming–Tamao oxidation the silylbicyclo[*n*.3.0]alkanes can be conveniently transformed to the corresponding hydroxybicyclo[*n*.3.0]alkanes with retention of configuration by oxidative cleavage of the sterically hindered carbon–silicon bond.[1,10] We now describe further synthetic transformations of the silylbicyclo[*n*.3.0]alkanes which are initiated by chemoselective oxidation of the angular acetyl group via a Baeyer–Villiger reaction. In this oxidation the silyl group is preserved and utilized as a stereodirecting group in subsequent reactions. Cycloaddition of the 1-acetylcycloalkenes **1** with the allylsilanes **2** and **3** provides the triphenylsilyl derivatives **4** and the triisopropylsilyl derivatives **5** of the bicyclo[3.3.0]octane **a**, bicyclo[4.3.0]nonane (hydrindane) **b**, and bicyclo[5.3.0]decane (hydroazulene) **c**, which represent important natural product frameworks found in many sesquiterpenes. The triphenylsilyl group was selected because it is easily transformed into a hydroxy group by a one-pot protodesilylation/Fleming–Tamao oxidation se-



Scheme 1

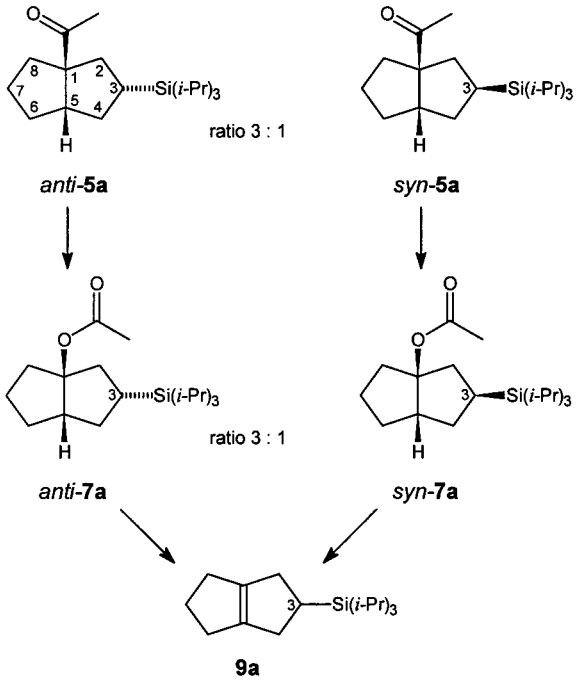
Table 1 Synthesis of the Cycloadducts **4** and **5** and Results of their Transformations to the Olefins **8** and **9**

	R	**a**, Yield (%)		**b**, Yield (%)	**c**, Yield (%)
		n = 1	*anti*/*syn*	n = 2	n = 3
4	Ph	25[4b]	1:0	51[4b]	34[4b]
6	Ph	81	1:0	87	0
8	Ph	87	–	96	–
5	*i*-Pr	71[4b]	3:1	86[4b]	68[4b]
7	*i*-Pr	93	3:1	23	0
9	*i*-Pr	45	–	–	–

quence with tetrabutylammonium fluoride/hydrogen peroxide recently developed in our laboratories.[10] On the other hand, the triisopropylsilyl derivatives are obtained in high yields.

Titanium(IV) chloride promoted [3+2] cycloaddition of the 1-acetylcycloalkenes **1** and either allyltriphenylsilane **2** or allyltriisopropylsilane **3** using our previously reported optimized reaction conditions provided the (triphenylsilyl)bicyclo[*n*.3.0]alkanes **4** and the (triisopropyl)-silylbicyclo[*n*.3.0]alkanes **5** (Scheme 1, Table 1).[4] By this procedure the bicyclo[3.3.0]octane **4a**, the bicyclo-[4.3.0]nonanes **4b** and **5b**, and the bicyclo[5.3.0]decanes **4c** and **5c** were obtained stereoselectively as the *anti* diastereoisomers, the bicyclo[3.3.0]octane **5a** was isolated as a 3:1 mixture of the anti and the syn diastereoisomer (anti and syn denote the position of the silyl relative to the acetyl group).[4] We envisaged a functionalization of the angular position of the silylbicyclo[*n*.3.0]alkanes **4** and **5** by a regioselective Baeyer–Villiger oxidation, which is known to occur with retention of configuration at the migrating carbon atom.[12] The triphenylsilyl-substituted bicyclo[3.3.0]octane **4a** and bicyclo[4.3.0]nonane **4b** were readily transformed to the corresponding acetoxy derivatives **6a** and **6b** by treatment with *m*-chloroperoxybenzoic acid (MCPBA) in dichloromethane for 5 days at reflux. However, the homologous bicyclo[5.3.0]decane **4c** did not undergo Baeyer–Villiger oxidation to **6c**. Neither under buffered basic (sodium hydrogen carbonate) or acidic (*p*-toluenesulfonic acid) reaction conditions with MCPBA nor using trifluoroperoxyacetic acid the formation of an acetoxy derivative was observed. The failure of the Baeyer–Villiger oxidation of **4c** was tentatively explained by the increased steric hindrance of the angular acetyl group caused by the annulated conformationally more flexible seven-membered ring. This attempted rationalization is supported by molecular model inspections (compare also the molecular structures of **4a**, **4b**, and **4c** in the crystal[4b]). The 1-acetoxy-3-(triphenylsilyl)bicyclo[3.3.0]octane **(6a)** and the 1-acetoxy-9-(triphenylsilyl)bicyclo[4.3.0]nonane **(6b)** were converted into the symmetrical bicyclic olefins **8a** and **8b** in excellent yields by tetrafluoroboric acid promoted elimination of acetic acid in tetrahydrofuran at reflux (Scheme 1, Table 1). The simple two-step sequence of Baeyer–Villiger oxidation and elimination opened up the way for the functionalization of both bridgehead carbon atoms of the cycloadducts **4a** and **4b**.

We next investigated the same sequence for the triisopropylsilyl derivatives **5a–c**. The Baeyer–Villiger oxidation of the 3:1 mixture of the *anti* and *syn* diastereoisomers of **5a** by treatment with MCPBA in dichloromethane for 22 hours at reflux afforded a 3:1 mixture of the corresponding acetoxy derivatives *anti*-**7a** and *syn*-**7a** in high yield (Scheme 2, Table 1). Tetrafluoroboric acid promoted elimination of acetic acid transformed both diastereoisomers of **7a** to the symmetrical 3-(triisopropylsilyl)-bicyclo[3.3.0]oct-1(5)-ene **(9a)**.



Scheme 2

We performed an extensive ^{13}C NMR spectroscopic investigation of the silylbicyclo[*n*.3.0]alkanes resulting from Lewis acid promoted [3+2] cycloaddition of 1-acetylcycloalkenes and allylsilanes. The chemical shift of the signal for the CH α to the silyl group at the five-membered ring proved to be dependent on the ring size of the additional annulated ring, the substituents at the silicon atom, and the relative stereochemistry at this carbon atom (*anti* or *syn* arrangement of the silyl group relative to the acetyl group).[4] Thus, for the triisopropylsilyl derivatives in the bicyclo[3.3.0]octane series a stereochemical assignment is possible by comparison of the characteristic ^{13}C NMR data with those of the corresponding triphenylsilyl derivatives. An X-ray analysis unequivocally confirmed the *anti* stereochemistry for **4a** and consequently also for the acetoxy derivative **6a**.[4b] Based on the comparison of the chemical shifts of the signals for the αSi-CH group (C3) the major diastereoisomers of **5a** and **7a** were assigned to have *anti* stereochemistry (Table 2). A high field shift is observed for the corresponding signals of the *syn* diastereoisomers.

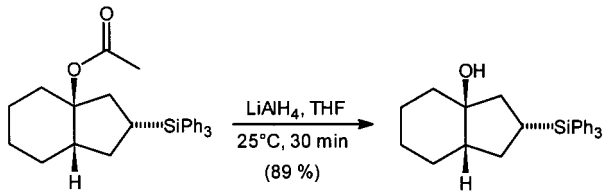
The Baeyer–Villiger oxidation of the bicyclo[4.3.0]nonane **5b** required more drastic reaction conditions (MCPBA, $CHCl_3$, reflux) and afforded the acetoxy

Table 2 Chemical Shift of the α-Silyl Carbon Atom (C3) in the ^{13}C NMR Spectrum (100 MHz, $CDCl_3$) for Various Silylbicyclo[3.3.0]octane Derivatives

R = Ph	δ (C3)	R = *i*-Pr	δ (C3)
4a	25.23 (*anti*)	**5a**	24.94 (*anti*) 21.14 (*syn*)
6a	24.42 (*anti*)	**7a**	23.76 (*anti*) 21.27 (*syn*)
8a	26.07	**9a**	25.16
11	25.65	**12**	24.56

derivative **7b** in only 23% yield along with 31% of starting material. As described above for the triphenylsilyl derivative **4c**, the triisopropylsilyl derivative **5c** did not undergo Baeyer–Villiger oxidation using MCPBA and trifluoroperoxyacetic acid. Obviously, Baeyer–Villiger oxidation of bicyclo[5.3.0]nonanes containing an acetyl group in the angular position can not be achieved by the applied conditions.

The Baeyer–Villiger oxidation of the 1-acetylbicyclo[*n*.3.0]alkanes followed by cleavage of the resulting acetic acid ester enables the introduction of an angular hydroxy group. Saponification of the acetoxy derivative **6b** by treatment with potassium hydroxide in ethanol/dichloromethane (5:1) at reflux for 2 days provided the 1-hydroxybicyclo[4.3.0]nonane **10** in only 57% yield. The low yield is explained by the rather harsh reaction conditions which are required for *tert*-alkyl esters. However, removal of the acetyl group by reduction of **6b** using lithium aluminum hydride in tetrahydrofuran at room temperature for 30 minutes afforded the carbinol **10** in 89% yield (Scheme 3).



6b **10**

Scheme 3

The olefins **8** and **9** were considered as good starting materials for further transformations at both bridgehead carbon atoms simultaneously. Because of the rigid conformation of the bicyclo[3.3.0]octene and bicyclo[4.3.0]nonene frameworks and the steric hindrance exhibited by the silyl moiety a high degree of stereoselectivity was expected for reactions at the central double bond. The bulky triphenylsilyl and triisopropylsilyl substituents were expected to function as stereodirecting groups which enforce an approach of reagents from the face opposite to silicon (*anti* selectivity). This prediction for the stereoselectivity of subsequent reactions at the central double bond derived support from molecular modelling studies. The minimum energy conformation of the triphenylsilyl-substituted bicyclo[4.3.0]nonene **8b** was calculated using the *HyperChem* program.[13] The structure of the olefin **8b** as determined by molecular mechanics calculations (MM+) is presented in Figure 1.[14] The bond lengths for the triphenylsilyl moiety of **8b** calculated by molecular mechanics are in good agreement with those obtained by the X-ray crystal structure analysis of **4b**.[4b] The space filling model of **8b** generated based on the molecular mechanics result shows that one face of the symmetrical olefin is shielded by the bulky triphenylsilyl group (Figure 2). Thus, based on steric arguments an attack of reagents at the central double bond should take

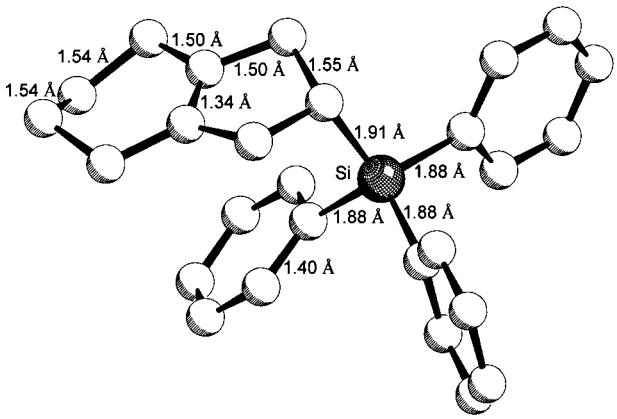


Figure 1 Calculated structure and bond lengths of **8b** determined by molecular mechanics[13] (SCHAKAL representation).[14]

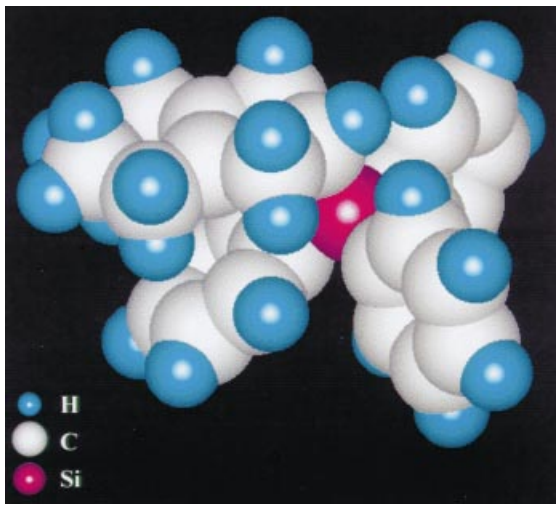
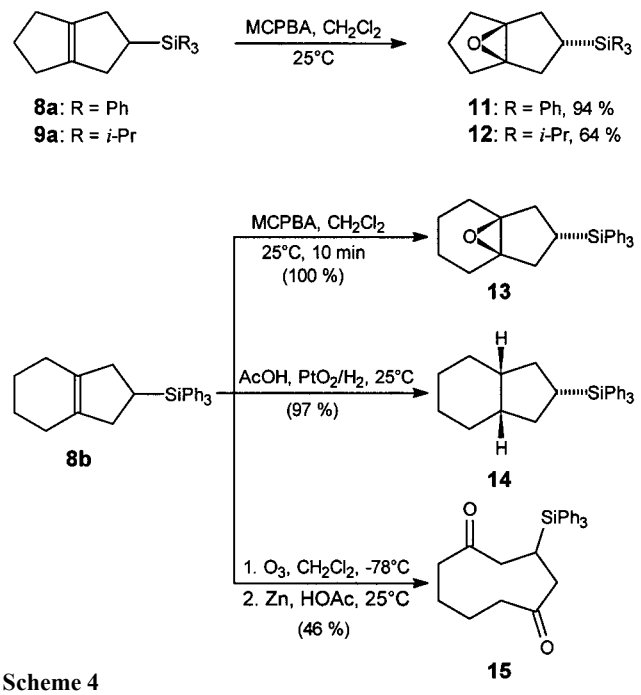


Figure 2 Space filling model of **8b** (*HyperChem* program).[13]

place *anti* relative to the silyl substituent. The same mode of stereoselectivity was expected for reactions of the olefins **8a** and **9a**.

Epoxidation of the triphenylsilyl-substituted bicyclo[3.3.0]octene **8a** with MCPBA in dichloromethane at room temperature proceeded in 10 minutes and provided stereoselectively the (triphenylsilyl)oxapropellane **11** in 94% yield (Scheme 4). The same reaction with the triisopropylsilyl-substituted bicyclo[3.3.0]octene **9a** required 45 minutes and afforded the epoxide **12** in only 64% yield.

Epoxidation of the triphenylsilylbicyclo[4.3.0]nonene **8b** by reaction with MCPBA for 10 minutes at room temperature provided quantitatively the (triphenylsilyl)oxapropellane **13** (Scheme 4). Catalytic hydrogenation of the olefin **8b** with platinum dioxide in acetic acid under a hydrogen atmosphere at room temperature afforded almost quantitatively the bicyclo[4.3.0]nonane **14**. The epoxidations of the bicyclic olefins **8** and **9a** to the epoxides **11**, **12**, and **13** and the catalytic hydrogenation of **8b** to **14** proceeded with complete stereoselectivity. The relative stereochemistry of these products was assigned based on the steric considerations described above.



Scheme 4

Cleavage of the central double bond of the bicyclo[4.3.0]nonene **8b** by ozonolysis[15] afforded 3-(triphenylsilyl)cyclononane-1,5-dione **(15)** and shows the potential of the bicyclic olefins as synthetic precursors for functionalized medium-sized ring compounds.

All reactions were carried out using anhydrous and degassed solvents under an inert gas atmosphere. MCPBA from Acros Chimica (art. 25.579.68, peracid content: 70%) was used. Flash chromatography: Baker or Merck silica gel (0.03–0.06 mm). Mps: Büchi 535. IR spectra: Perkin–Elmer 1710, Bruker IFS-88. ^{1}H NMR and ^{13}C NMR spectra: Bruker AM-400; internal standard: the signal of the deuterated solvent; coupling constants *J* in Hz. MS: Finnigan MAT-312 and MAT-90; ionization potential: 70 eV.

1-Acetoxy-3-(triphenylsilyl)bicyclo[3.3.0]octane (6a)
$NaHCO_3$ (1.23 g, 14.6 mmol) and MCPBA (1.80 g, content 70%; 7.30 mmol of MCPBA) were added in small portions over a period of 2 d to a refluxing solution of **4a** (1.00 g, 2.44 mmol) in CH_2Cl_2 (40 mL). After a reaction time of 5 d the cold mixture was quenched with aq $NaHCO_3$ (40 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 40 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated in vacuo. The residue was subjected to flash chromatography (silica gel, hexane/Et_2O 7:1) to provide **6a** as colorless crystals, yield: 840 mg (81%); mp 85–86 °C.

IR (KBr): ν = 1723 cm^{-1} (C=O)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.07–1.26 (m, 4H), 1.51 (dt, *J* = 2.8, 14.0 Hz, 1H), 1.60 (m, 1H), 1.74 (m, 2H), 2.02 (s, 3H), 2.13 (m, 1H), 2.28 (m, 1H), 2.61 (m, 2H), 7.34–7.42 (m, 9H), 7.53 (m, 6H).

^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 22.25 (CH_3), 24.42 (CH), 25.09 (CH_2), 30.32 (CH_2), 36.40 (CH_2), 38.40 (CH_2), 41.44 (CH_2), 51.78 (CH), 100.49 (C), 127.83 (6 CH), 129.43 (3 CH), 134.40 (3 C), 135.94 (6 CH), 170.82 (C=O).

MS (150 °C): *m*/*z* (%) = 366 (M^+ – HOAc, 13), 259 (100), 241 (56), 199 (8), 181 (11).

1-Acetoxy-8-(triphenylsilyl)bicyclo[4.3.0]nonane (6b)
A solution of **4b** (1.00 g, 2.35 mmol) in anhyd CH_2Cl_2 (50 mL) was added to MCPBA (1.72 g, content: 70%; 6.98 mmol of MCPBA) and $NaHCO_3$ (198 mg, 2.36 mmol). The mixture was stirred at reflux. Further MCPBA was added after 24 h (470 mg, content: 70%; 1.91 mmol of MCPBA) and 48 h (1.00 g, content: 70%; 4.06 mmol of MCPBA). After a reaction time of 5 d at reflux the cold mixture was stirred over solid $NaHCO_3$ and then poured into aq $NaHCO_3$ (50 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL) and the combined organic layers were dried ($MgSO_4$). The solvent was evaporated in vacuo and the residue subjected to flash chromatography (silica gel, hexane/Et_2O 7:1). Recrystallization from Et_2O at –20 °C afforded **6b** as colorless crystals; yield: 905 mg (87%); mp 87–89 °C (Et_2O).

IR (KBr): ν = 1720 cm^{-1} (C=O)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.59 (m, 1H), 1.02 (m, 1H), 1.14 (m, 2H), 1.30 (m, 2H), 1.44–1.58 (m, 2H), 1.80 (ddd, *J* = 13.6, 9.0, 4.2 Hz, 1H), 2.00 (dd, *J* = 13.8, 10.7 Hz, 1H), 2.03 (s, 3H), 2.17 (m, 2H), 2.34 (quint, *J* = 9.4 Hz, 1H), 2.52 (dd, *J* = 13.8, 9.6 Hz, 1H), 7.41 (m, 9H), 7.60 (m, 6H).

^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = *1*7.95 (CH), 22.48 (CH_3), 22.61 (CH_2), 23.07 (CH_2), 27.97 (CH_2), 30.39 (CH_2), 31.31 (CH_2), 35.77 (CH_2), 44.73 (CH), 91.56 (C), 127.83 (6 CH), 129.47 (3 CH), 134.62 (3 C), 136.04 (6 CH), 170.70 (C=O).

MS (100 °C): *m*/*z* (%) = 381 (M^+ – OAc, 4), 332 (30), 330 (28), 327 (11), 259 (49), 214 (11), 199 (15), 86 (69), 84 (100), 81 (21), 79 (10), 59 (5).

1-Acetoxy-3-(triisopropylsilyl)bicyclo[3.3.0]octane (7a)
MCPBA (1.20 g, content: 70%; 4.87 mmol of MCPBA) was added to a solution of **5a** (mixture of diastereoisomers, *anti*/*syn* 3:1, 500 mg, 1.62 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred at reflux for 22 h. After cooling to r.t. the solution was poured into aq $NaHCO_3$ (20 mL) and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL), the combined organic layers were dried ($MgSO_4$), and the solvent was evaporated in vacuo. Flash chromatography (silica, gel, hexane/Et_2O 15:1) of the residue provided **7a** as a mixture of diastereoisomers (*anti*/*syn* 3:1) as a colorless oil; yield: 490 mg (93%).

IR (film): ν = 1736 cm^{-1} (C=O).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.83–0.89 (m, 1H), 1.06 (m, 21H), 1.13–1.37 (m, 4H), 1.41–1.61 (m, 3H), 1.65–1.85 (m, 2H), 1.98 (s) and 1.99 (s, Σ 3H), 2.10–2.21 (m, 1H), 2.43–2.52 (m, 1H).

^{13}C NMR and DEPT (100 MHz, $CDCl_3$):

anti-**7a**: δ = 11.38 (3 CH), 19.18 (6 CH_3), 22.19 (CH_3), 23.76 (CH), 25.30 (CH_2), 30.42 (CH_2), 37.22 (CH_2), 38.66 (CH_2), 42.19 (CH_2), 51.90 (CH), 100.32 (C), 170.83 (C=O).

syn-**7a**: δ = 11.38 (3 CH), 19.18 (6 CH_3), 21.27 (CH), 22.19 (CH_3), 26.07 (CH_2), 33.63 (CH_2), 33.89 (CH_2), 39.36 (CH_2), 41.91 (CH_2), 50.59 (CH), 99.73 (C), 170.83 (C=O).

MS (30 °C): *m*/*z* (%) = 324 (M^+, 0.3), 264 (1), 221 (3), 173 (100), 131 (4).

HRMS: calcd for $C_{19}H_{36}O_2Si$ (M^+): 324.2485. Found: 324.2493.

1-Acetoxy-8-(triisopropylsilyl)bicyclo[4.3.0]nonane (7b)
A solution of **5b** (394 mg, 1.22 mmol) in $CHCl_3$ (15 mL) was added to MCPBA (956 mg, content: 70%; 3.88 mmol of MCPBA) and $NaHCO_3$ (493 mg, 5.87 mmol). The mixture was stirred at reflux for 4 d, the cold mixture was quenched by addition of sat. aq $NaHCO_3$ (15 mL), and the layers were separated. The aqueous layer was extracted with $CHCl_3$ (3 × 15 mL), the combined organic layers were dried ($MgSO_4$), and the solvent was evaporated in vacuo. Flash chromatography (silica gel, pentane/Et_2O 60:1) of the residue af-

forded **7b** as the less polar fraction (light yellow oil, yield: 95 mg, 23%) and the starting material **5b** as the more polar fraction (yield: 122 mg, 31%).

IR (film): ν = 1733 cm^{-1} (C=O).

^1H NMR (400 MHz, $CDCl_3$): δ = 1.07 (m, 21H), 1.33 (m, 4H), 1.44–1.52 (m, 3H), 1.68 (m, 1H), 1.85–2.00 (m, 3H), 1.98 (s, 3H), 2.10 (m, 2H), 2.29 (dd, *J* = 14.0, 8.5 Hz, 1H).

^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 11.16 (3 CH), 18.36 (CH), 19.26 (6 CH_3), 22.40 (CH_3), 22.61 (CH_2), 23.03 (CH_2), 28.65 (CH_2), 31.47 (CH_2), 32.24 (CH_2), 37.04 (CH_2), 45.24 (CH), 91.01 (C), 170.62 (C=O).

MS (70 °C): *m/z* (%) = 278 (M^+ – HOAc, 5), 235 (18), 172 (100), 157 (3).

3-(Triphenylsilyl)bicyclo[3.3.0]oct-1(5)-ene (8a)

54% HBF_4 in Et_2O (0.22 mL, 140 mg, 1.60 mmol of acid) was added to a solution of **6a** (200 mg, 0.469 mmol) in THF (10 mL). The mixture was heated at reflux for 20 h and then quenched by addition of aq $NaHCO_3$ (6 mL). The layers were separated, the aqueous layer was extracted with Et_2O (3 × 10 mL), and the combined organic layers were dried ($MgSO_4$). Removing of the solvent in vacuo and flash chromatography (silica gel, hexane/Et_2O 10:1) of the residue provided **8a** as colorless crystals; yield: 150 mg (87%); mp 92–93 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.04 (m, 2H), 2.12 (m, 2H), 2.19 (m, 2H), 2.43 (m, 2H), 2.57 (m, 2H), 2.85 (tt, *J* = 9.9, 7.6 Hz, 1H), 7.32–7.42 (m, 9H), 7.53 (m, 6H).

^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 26.07 (CH), 28.65 (CH_2), 29.13 (2 CH_2), 32.34 (2 CH_2), 127.75 (6 CH), 129.26 (3 CH), 135.24 (3 C), 135.85 (6 CH), 146.49 (2 C).

MS (90 °C): *m/z* (%) = 366 (M^+, 2), 288 (40), 259 (100), 183 (7), 181 (10).

HRMS: calcd for $C_{26}H_{26}Si$ (M^+): 366.1804. Found: 366.1818.

8-(Triphenylsilyl)bicyclo[4.3.0]non-1(6)-ene (8b)

54% HBF_4 in Et_2O (72 μL, 46 mg, 0.523 mmol of acid) was added to a solution of **6b** (200 mg, 0.454 mmol) in THF (10 mL) and the mixture was heated at reflux for 3 h. After cooling to r.t. the mixture was quenched by addition of aq $NaHCO_3$ (10 mL). The aqueous layer was extracted with Et_2O (3 × 10 mL), the combined organic layers were dried ($MgSO_4$), and the solvent was removed in vacuo. Flash chromatography (pentane/Et_2O 7:1) of the residue afforded **8b** as colorless crystals; yield: 166 mg (96%); mp 89–90 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.57 (m, 4H), 1.76–1.99 (m, 4H), 2.38 (tt, *J* = 10.1, 7.4 Hz, 1H), 2.53 (m, 2H), 2.71 (m, 2H), 7.35–7.44 (m, 9H), 7.58 (m, 6H).

^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 18.55 (CH), 23.12 (2 CH_2), 25.75 (2 CH_2), 39.26 (2 CH_2), 127.76 (6 CH), 129.26 (3 CH), 134.51 (2 C), 135.36 (3 C), 135.89 (6 CH).

MS (25 °C): *m/z* (%) = 380 (M^+, 3), 303 (16), 302 (57), 260 (27), 259 (100), 224 (5), 183 (22), 182 (10), 181 (15), 120 (11).

HRMS: calcd for $C_{27}H_{28}Si$ (M^+): 380.1960. Found: 380.1947.

3-(Triisopropylsilyl)bicyclo[3.3.0]oct-1(5)-ene (9a)

54% HBF_4 in Et_2O (0.4 mL, 255 mg, 2.90 mmol of acid) was added to a solution of **7a** (242 mg, 0.746 mmol) in THF (15 mL). The mixture was heated at reflux for 5 d. The mixture was poured into aq $NaHCO_3$ (20 mL) and the aqueous layer was extracted with Et_2O (3 × 20 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated. The residue was subjected twice to flash chromatography (silica gel, 1. pentane/Et_2O 20:1; 2. pentane) to afford **9a** as a colorless oil; yield: 89 mg (45%).

^1H NMR (400 MHz, $CDCl_3$): δ = 1.03–1.18 (m, 21H), 2.12–2.36 (m, 11H).

^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 11.34 (3 CH), 19.25 (6 CH_3), 25.16 (CH), 28.81 (CH_2), 29.33 (2 CH_2), 32.33 (2 CH_2), 146.67 (2 C).

MS (25 °C): *m/z* (%) = 264 (M^+, 13), 221 (100), 179 (9), 115 (8), 105 (11), 87 (10), 73 (15), 59 (22).

HRMS: calcd for $C_{17}H_{32}Si$ (M^+): 264.2273. Found: 264.2260.

1-Hydroxy-8-(triphenylsilyl)bicyclo[4.3.0]nonane (10)

By Reduction of 6b with $LiAlH_4$

A solution of **6b** (150 mg, 0.340 mmol) in THF (5 mL) was added slowly to a stirred suspension of $LiAlH_4$ (13 mg, 0.343 mmol) in THF (5 mL). After 30 min at r.t. the mixture was quenched by addition of ice (20 g) and 1 M HCl (0.4 mL). The aqueous layer was extracted with Et_2O (3 × 20 mL) and the combined organic layers were dried ($MgSO_4$). Evaporation of the solvent in vacuo and flash chromatography (silica gel, hexane/Et_2O 2:1) of the residue afforded the carbinol **10** as a colorless oil; yield: 120 mg (89%).

IR (drift): ν = 3371 cm^{-1} (O–H).

^1H NMR (400 MHz, $CDCl_3$): δ = 0.17 (m, 1H), 1.04 (m, 2H), 1.22 (m, 2H), 1.45 (m, 3H), 1.65–1.84 (m, 4H), 1.94 (m, 1H), 2.42–2.50 (m, 1H), 2.60 (tt, *J* = 11.3, 8.4 Hz, 1H), 7.36–7.45 (m, 9H), 7.65 (m, 6H).

^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 17.62 (CH), 23.30 (CH_2), 24.53 (CH_2), 30.12 (CH_2), 32.54 (CH_2), 35.54 (CH_2), 38.17 (CH_2), 46.97 (CH), 81.52 (C), 127.78 (6 CH), 129.40 (3 CH), 134.87 (3 C), 136.04 (6 CH).

MS (105 °C): *m/z* (%) = 398 (M^+, 0.4), 276 (15), 259 (100), 199 (14), 181 (8), 122 (13).

HRMS: calcd for $C_{27}H_{30}OSi$ (M^+): 398.2066. Found: 398.2076.

By Saponification of 6b with KOH

KOH (28 mg, 0.5 mmol) was added to a solution of **6b** (200 mg, 0.454 mmol) in EtOH (5 mL)/CH_2Cl_2 (1 mL) and then heated at reflux for 24 h. Additional KOH (28 mg, 0.5 mmol) was added and the mixture was heated at reflux for further 24 h. The cold mixture was poured into water (10 mL) and the aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was removed in vacuo. Flash chromatography (silica gel, hexane/Et_2O 2:1) of the residue provided the alcohol **10** as a colorless oil; yield: 103 mg (57%), spectral data, see above.

3-(Triphenylsilyl)-9-oxatricyclo[3.3.1.$0^{1,5}$]nonane (11)

A solution of MCPBA (34 mg, content 70%; 0.138 mmol of MCPBA) in CH_2Cl_2 (2 mL) was added to a stirred solution of the bicyclooctene **8a** (50 mg, 0.136 mmol) in CH_2Cl_2 (1 mL). After a reaction time of 10 min at r.t. the mixture was quenched by the addition of aq $NaHCO_3$ (10 mL) and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL) and the combined organic layers were dried ($MgSO_4$). Evaporation of the solvent provides **11** as colorless crystals; yield: 49 mg (94%); mp 118 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.47 (m, 2H), 1.69 (dd, *J* = 13.8, 11.1 Hz, 2H), 1.89 (m, 4H), 2.19 (dd, *J* = 13.8, 7.6 Hz, 2H), 2.60 (tt, *J* = 11.1, 7.6 Hz, 1H), 7.35–7.45 (m, 9H), 7.54 (m, 6H).

^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 25.65 (CH), 27.52 (2 CH_2), 27.84 (CH_2), 30.60 (2 CH_2), 77.34 (2 C), 127.90 (6 CH), 129.51 (3 CH), 134.45 (3 C), 135.88 (6 CH).

MS (44 °C): *m/z* (%) = 382 (M^+, 4), 278 (90), 259 (100), 201 (78), 199 (38), 181 (14), 154 (50), 149 (36), 123 (10), 111 (16), 109 (12), 97 (25), 95 (17), 85 (20), 83 (32), 81 (14), 71 (25), 69 (25), 57 (39).

HRMS: calcd for $C_{26}H_{26}OSi$ (M^+): 382.1753. Found: 382.1777.

3-(Triisopropylsilyl)-9-oxatricyclo[3.3.1.0^{1,5}]nonane (12)
A solution of **9a** (110 mg, 0.416 mmol) in CH_2Cl_2 (8 mL) was added to MCPBA (124 mg, content: 70%; 0.503 mmol of MCPBA). After stirring for 45 min at r.t. the mixture was poured into aq $NaHCO_3$ (10 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL), the combined organic layers were dried ($MgSO_4$), and the solvent was evaporated. Flash chromatography (silica gel, pentane/Et_2O 20:1) of the residue provided **12** as a colorless oil; yield: 75 mg (64%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 (m, 21H), 1.52 (m, 2H), 1.64 (m, 2H), 1.80 (m, 1H), 1.85–1.98 (m, 6H).

^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 11.34 (3 CH), 19.17 (6 CH_3), 24.56 (CH), 27.75 (2 CH_2), 27.85 (CH_2), 30.63 (2 CH_2), 77.29 (2 C).

MS (20 °C): *m*/*z* (%) = 280 (M^+, 4), 237 (100), 121 (12), 103 (14), 75 (16), 61 (12), 59 (17).

HRMS: calcd for $C_{17}H_{32}OSi$ (M^+): 280.2222. Found: 280.2210.

8-(Triphenylsilyl)-10-oxatricyclo[4.3.1.0^{1,6}]decane (13)
A solution of **8b** (200 mg, 0.525 mmol) in CH_2Cl_2 (5 mL) was added slowly at 0 °C to a vigorously stirred solution of MCPBA (130 mg, content: 70%; 0.527 mmol of MCPBA) in CH_2Cl_2 (5 mL). After warming to r.t. the mixture was stirred for 10 min. The mixture was poured into aq $NaHCO_3$ (10 mL) and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL), the combined organic layers were dried ($MgSO_4$), and the solvent was evaporated in vacuo to afford **13** as colorless crystals; yield: 208 mg (100%); mp 125 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23 (m, 2H), 1.47 (m, 2H), 1.66 (dd, *J* = 13.6, 11.4 Hz, 2H), 1.67–1.72 (m, 2H), 1.96–2.10 (m, 3H), 2.31 (dd, *J* = 13.6, 7.6 Hz, 2H), 7.38–7.47 (m, 9H), 7.59 (m, 6H).

^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 17.13 (CH), 20.30 (2 CH_2), 26.49 (2 CH_2), 35.02 (2 CH_2), 67.15 (2 C), 127.93 (6 CH), 129.51 (3 CH), 134.61 (3 C), 135.94 (6 CH).

MS (70 °C): *m*/*z* (%) = 396 (M^+, 3), 278 (26), 277 (10), 276 (40), 260 (17), 259 (82), 201 (27), 199 (100), 181 (14), 154 (17), 122 (14), 69 (13), 57 (16).

HRMS: calcd for $C_{27}H_{28}OSi$ (M^+): 396.1909. Found: 396.1926.

8-(Triphenylsilyl)bicyclo[4.3.0]nonane (14)
PtO_2 (15 mg) was added to a solution of **8b** (200 mg, 0.525 mmol) in 100% HOAc (7 mL). The bicyclononene was hydrogenated by vigorous stirring of this mixture in a hydrogen atmosphere (1.1 atm) until no further hydrogen uptake was detected. HOAc was evaporated in vacuo, the residue was dissolved in Et_2O (10 mL), and the solution was neutralized by addition of sat. aq $NaHCO_3$ (10 mL). The layers were separated, the aqueous layer was extracted with Et_2O (3 × 10 mL), and the combined organic layers were dried ($MgSO_4$). After filtration the solvent was evaporated and the residue was subjected to flash chromatography (silica gelhexane/Et_2O 10:1) to afford **14** as colorless crystals; yield: 195 mg (97%); mp 68 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.98 (m, 2H), 1.22 (m, 4H), 1.26–1.35 (m, 2H), 1.59 (m, 2H), 1.97–2.24 (m, 5H), 7.40–7.48 (m, 9H), 7.65 (m, 6H).

^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 20.99 (CH), 23.76 (2 CH_2), 28.12 (2 CH_2), 32.73 (2 CH_2), 40.09 (2 CH), 127.77 (6 CH), 129.32 (3 CH), 135.40 (3 C), 136.15 (6 CH).

MS (56 °C): *m*/*z* (%) = 382 (M^+, 0.3), 305 (13), 278 (11), 259 (100), 201 (27), 183 (35).

HRMS: calcd for $C_{27}H_{30}Si$ (M^+): 382.2117. Found: 382.2162.

3-(Triphenylsilyl)cyclononane-1,5-dione (15)
A stream of ozone/oxygen was passed through a solution of **8b** (100 mg, 0.263 mmol) in CH_2Cl_2 (10 mL) at –78 °C until the blue color of the solution persisted. After purging with N_2 the mixture was warmed to r.t. and poured slowly into a suspension of zinc powder (500 mg, 7.65 mmol) in 50% HOAc (15 mL). This mixture was heated at reflux for 1 h, the layers were separated, and the aqueous layer was extracted with Et_2O (3 × 20 mL). The combined organic layers were neutralized by washing with aq $NaHCO_3$ (20 mL) and the layers were separated. The organic layer was dried ($MgSO_4$) and the solvent was evaporated in vacuo. Flash chromatography (silica gel, hexane/EtOAc 2:1) of the residue provided the dione **15** as a light yellow oil, yield: 50 mg (46%).

IR (drift): ν = 1703 cm^{-1} (C=O).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.64–1.90 (m, 4H), 1.92–2.08 (m, 1H), 2.14–2.74 (m, 7H), 2.78–2.87 (m, 1H), 7.31–7.48 (m, 9H), 7.53–7.67 (m, 6H).

^{13}C NMR and DEPT (100 MHz, $CDCl_3$): δ = 19.88 (CH), 23.84 (2 CH_2), 40.90 (2 CH_2), 43.36 (2 CH_2), 128.21 (6 CH), 129.94 (3 CH), 132.79 (3 C), 136.01 (6 CH), 215.33 (2 C=O).

MS (20 °C): *m*/*z* (%) = 412 (M^+, 0.3), 335 (48), 259 (100), 199 (7), 181 (10).

HRMS: calcd for $C_{27}H_{28}O_2Si$ (M^+): 412.1859. Found: 412.1865.

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