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Synthesis of 1-Silabicyclo[4.4.0]dec-5-en-4-ones: A Model of the A and B Rings of 10-Silatestosterone

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1-Silabicyclo[4.4.0]dec-5-en-4-ones, a novel type of organosilicon compound, have been prepared from 2-methylidene-1-(3-oxopropyl)-1-silacyclohexanes by an ene reaction as the key transformation. Various routes to the starting aldehydes from 3-halopropyl, allyl, or 3-(4-methoxybenzyloxy)propylsilanes have been investigated.

Introduction

Siladrugs[1] are of interest due to the unique properties of the silicon atom.[2] Among them, silasteroids have been the subject of few studies. Two groups have reported independently the synthesis of 6,6-dimethyl-6-silasteroids.[3,4] This sila-substitution was performed to block the 6-hydroxylation pathway in order to prevent the aromatization of the B ring. Various compounds like dimethylsilaestradiol (**1**) and the analogue **2** of mestranol, a potent oral contraceptive agent, or some 5,6-secosilasteroids like **3** have been screened for estrogenic, anti-estrogenic, and post-coital activity (Figure 1). No significant estrogenic or anti-estrogenic activity was observed using doses 100–1000 times that of an estradiol standard. Compounds **1** and **3** exhibited post-coital activity in rats, but only at 10 mg kg^{-1}. The binding affinity of silaestradiol **1** towards the estrogen receptor protein of the rat uterus was found to be 0.3% that of estradiol. In these studies, two methyl groups were introduced onto the silicon atom to avoid the presence of Si–H bonds, a priori unstable in a biological environment. Therefore, the absence of estrogenicity could be due to steric or electronic effects.

We thought that sila-substitution of the steroid skeleton could lead to new compounds with interesting pharmacodynamic and/or pharmacokinetic properties if the replacement was carried out without the introduction of other new substituents to the parent steroid. Substitution of a quaternary carbon atom by a silicon atom fulfils this requirement and should yield stable compounds in biological media. So,

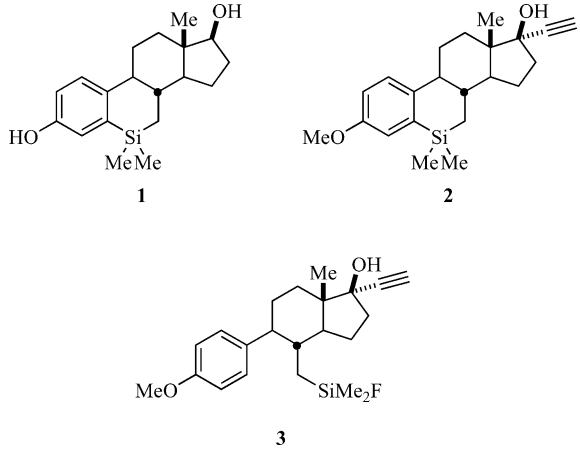

Figure 1. Some examples of 6-silasteroids and related compounds biologically tested.

two main groups of new compounds could be envisioned, the 10- and 13-silasteroids. Of the 10-silasteroids, we considered 10-silatestosterone (**4b**) an interesting target. One of the metabolic pathways of testosterone (**4a**) gives undesirable estradiol (Scheme 1)[5] and aromatization of the A ring of the sila analogue **4b** should be prevented by the presence of a silicon atom.[3,6] Theoretical[7] and experimental estimates[8] of the strength of the π bond of the C=Si double bond (ca. 39 kcal mol^{-1}) show that it is less stable than the C=C double bond (65 kcal mol^{-1}). Therefore, the formation of a C=Si double bond should need more energy than the formation of an analogous C=C double bond.

1-Silabicyclo[4.4.0]dec-5-en-4-ones of type **24**, models of the A and B rings of silatestosterone (**4b**), were our first goal because the paucity of reported methods for the preparation of bicyclo[*n.m.*0]alkanic compounds with a ring junction silicon atom is evident.[9–11] The formation of 3-methylidene-4-silacyclohexanols by the ene reaction from isopropenylsilanes bearing a 3-oxopropyl chain on the silicon atom has been reported.[12] We envisaged a synthesis of

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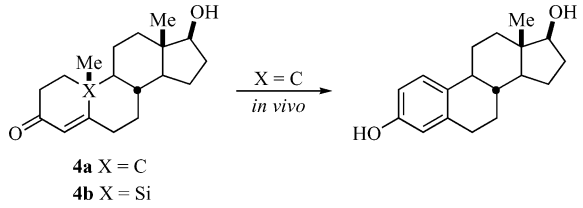
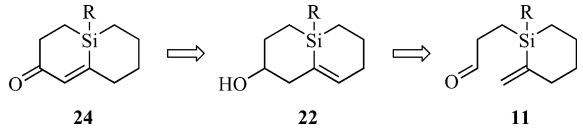


Scheme 1. Metabolic transformation of testosterone into estradiol.

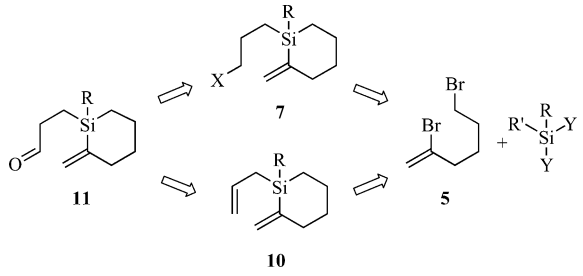
1-silabicyclo[4.4.0]dec-6-en-4-ols **22** starting from 2-methylidene-1-silacyclohexanes **11** and subsequent transformation to our goal (Scheme 2).



Scheme 2. Retrosynthesis of 1-silabicyclo[4.4.0]dec-5-en-4-ones **24**.

Results and Discussion

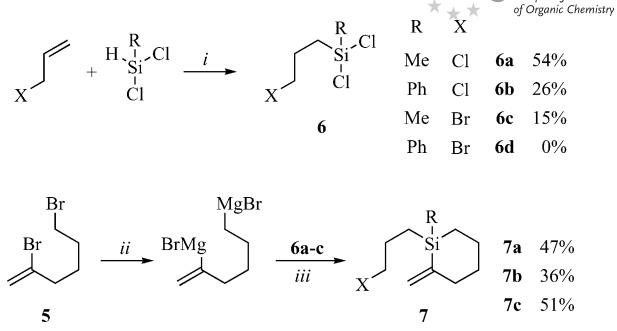
Among the various approaches to the required 2-methylidene-1-(3-oxopropyl)-1-silacyclohexanes **11** that have been tested, the intramolecular hydrosilylation of hex-5-ynylsilanes was successful.[13] But the shortest way to 2-methylidene-1-silacyclohexanes would be a priori from polyhalo- or polyethoxysilanes and 2,6-dibromohex-1-ene **5** using an organodimetallic derivative or Barbier-type conditions.[14] The synthesis of aldehydes **11** was attempted via the corresponding 3-halopropyl derivatives **7** or the allylsilanes **10** (Scheme 3).



Scheme 3. Retrosynthesis of 2-methylidene-1-silacyclohexanes **11**.

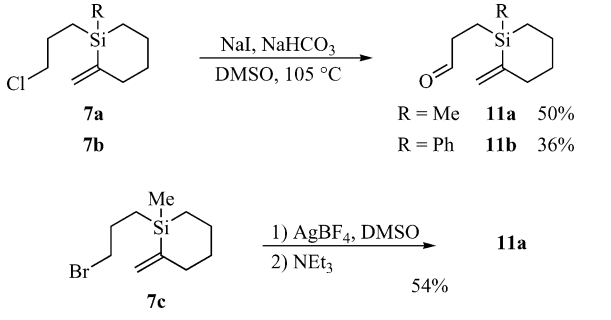
Synthesis of (3-Oxopropyl)silanes 11

The reactions at 65 °C of dichloro(3-halopropyl)silanes **6a**–**c** with the Grignard reagent prepared from 2,6-dibromohexene (**5**) in THF at 10 °C gave the 2-methylidenesilacyclohexanes **7a**–**c** in moderate yields after purification by silica gel chromatography.[14] The 3-halopropylsilanes **6** were generally isolated by distillation after reaction of the commercially available methyl- and phenyldichlorosilane with allyl bromide and chloride in the presence of $[H_2PtCl_6]$.[15] (3-Bromopropyl)phenylsilane (**6d**) was probably formed under these reaction conditions but polymerization occurred during the distillation under low pressure (Scheme 4).



Scheme 4. Preparation of 3-halopropylsilanes **7**. Reagents and conditions: *i*) for **6a** and **6c**, $[H_2PtCl_6]$, cyclohexane, reflux, 14 h; for **6b** and **6d**, $[H_2PtCl_6]$, without solvent; *ii*) THF, addition of **5** at 10 °C, then 3 h at 20 °C; *iii*) Grignard reagent (1 equiv.), THF, 65 °C, 1.4 h.

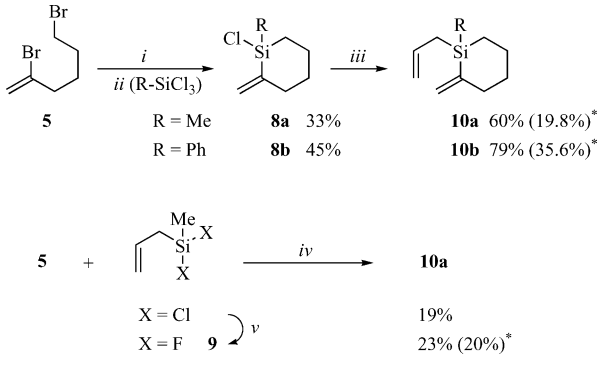
Oxidation of the chloropropylsilanes **7a**,**b** at 105 °C under modified Kornblum conditions[16] gave the expected aldehydes **11a**,**b** in 50 and 36% yields, respectively (Scheme 5). The aldehyde **11a** was obtained in a slightly better yield (54%) by reaction at 20 °C of the bromopropylsilane **7c** with DMSO in the presence of silver tetrafluoroborate and subsequent treatment with triethylamine.[17] The very low yield observed for the preparation of bromopropylsilane **6c** makes this reaction sequence via the brominated derivative **7c** less efficient than the one via chloropropylsilane **7a**.



Scheme 5. Preparation of 3-oxopropylsilanes **11** from halopropylsilanes.

Reactions of the commercially available methyl- and phenyltrichlorosilane with the Grignard reagent obtained from 2,6-dibromohexene (**5**), as described above, have allowed the synthesis of the 1-chloro-2-methylidenesilacyclohexanes **8a** and **8b** in 33 and 45% yields, respectively, after purification by distillation.[14] Initially, the introduction of a masked 3-oxopropyl chain was attempted. Aldehyde **11a** was not detected after reaction in diethyl ether of the chlorosilane **8a** with the Grignard reagent prepared from 3-bromopropanal dimethyl acetal[18] followed by acid treatment (oxalic acid/silica gel[19]). Reaction of **8a** with the lithiated derivative[20] of *N*-allylpyrrolidine and subsequent acid hydrolysis (3 N aqueous HCl) gave the aldehyde **11a** in 12% yield only. Much better results were obtained by indirect formation via the 1-allyl-2-methylidenesilacyclohexanes

10a,**b** synthesized by addition of a solution of allylmagnesium chloride in THF to the chlorosilanes **8a**,**b** and purification by silica gel chromatography (Scheme 6).

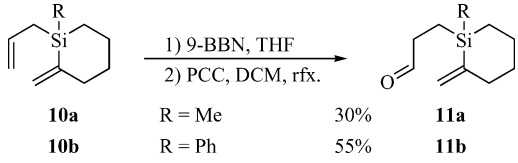


* In parentheses overall yield from the corresponding polychlorosilane

Scheme 6. Preparation of allylsilanes **10**. Reagents and conditions: *i*) THF, addition of **5** at 10 °C, then 3 h at 20 °C; *ii*) Grignard reagent (1 equiv.), THF, 65 °C, 1.4 h; *iii*) Grignard reagent (1 equiv.), THF, addition at 0 °C then 14 h at 20 °C; *iv*) Mg, THF, slow addition of reactants then 2 h at 60 °C; *v*) $NaBF_4$, tetraglyme, 70 °C.

The methylated silane **10a** was also prepared in similar yields from the commercially available allyldichloromethylsilane or the corresponding difluorosilane **9**[21] and dibromohexene **5** under Barbier-type conditions. With these dihalosilanes, lower yields of silane **10a** were obtained with the preformed Grignard reagent (5% from the dichlorosilane and 20% from compound **9**).

Treatment of the allylsilanes **10a**,**b** with 9-borabicyclononane (9-BBN) at 20 °C for 2 h and subsequent oxidation with pyridinium chlorochromate (PCC) on Celite®[22] in refluxing dichloromethane gave the expected aldehydes **11a** and **11b** in 30 and 55% yields, respectively (Scheme 7).

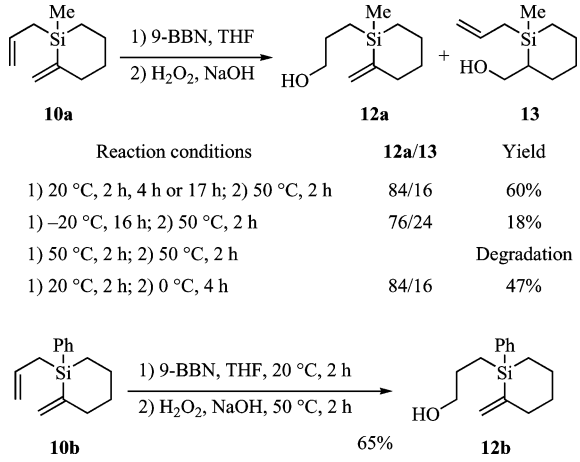


Scheme 7. Preparation of 3-oxopropylsilanes **11** from allylsilanes.

This synthesis of the phenylated aldehyde **11b** from trichlorophenylsilane was more efficient (overall yield 20%) than the approach via chloropropylsilane **7b** (overall yield 3.5%). The preparation of the methylated aldehyde **11a** via chloropropylsilane **7a** was more efficient than all the methods studied (overall yield 23.5%).

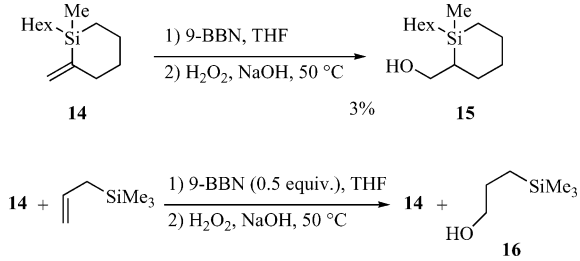
Comments on the Hydroboration of 1-Allyl-2-methylidenesilacyclohexanes 10

When the hydroboration reactions of allylsilanes **10a** and **10b** with 9-BBN were followed by oxidative cleavage with a basic solution of hydrogen peroxide at 50 °C,[23] the alcohols **12a** and **12b** were isolated in moderate yields (50–65%). The reaction of the methylated silane **10a** also delivered, in a minor amount, alcohol **13** as a result of the hydroboration of the exocyclic double bond, which could be easily separated from alcohol **12a** by silica gel chromatography. No improvements in yield or the **12a/13** ratio were observed by modifying the reaction time or the temperature of the hydroboration step or by decreasing the temperature of the oxidative step. The presence of such a byproduct was not observed in the case of the phenylated silane **10b** (Scheme 8).



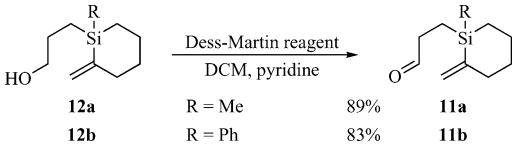
Scheme 8. Formation of (3-hydroxypropyl)silanes **12** from the allylsilanes **10**.

This difference in reactivity led us to study this transformation further. Reaction of 1-hexyl-1-methyl-2-methylidenesilacyclohexane (**14**) under the aforementioned conditions afforded the corresponding 2-(hydroxymethyl)silacyclohexane **15** in 3% yield. Treatment of an equimolar mixture of the hexylsilane **14** and allyltrimethylsilane under the same conditions led only to the formation of (3-hydroxypropyl)trimethylsilane (**16**; Scheme 9). Therefore, the unusually high reactivity of the exocyclic double bond of 1-allyl-2-methylidenesilacyclohexane **10a** seems due to the presence of the allyl group.



Scheme 9. Hydroboration of vinylsilane **14** and allyltrimethylsilane.

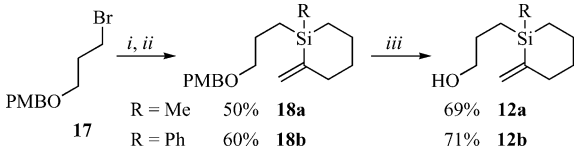
Oxidation of the (3-hydroxypropyl)silanes **12a**,**b** with the Dess–Martin reagent[24] gave the expected aldehydes **11a**,**b** in good yields[25] (Scheme 10). However, allylsilanes **10a** and **10b** were converted into the corresponding aldehydes **11** in better overall yields when the intermediate boranes were treated with PCC (see above).



Scheme 10. Preparation of 3-oxopropylsilanes **11** from alcohols **12**.

Other Syntheses of the (3-Hydroxypropyl)silanes 12

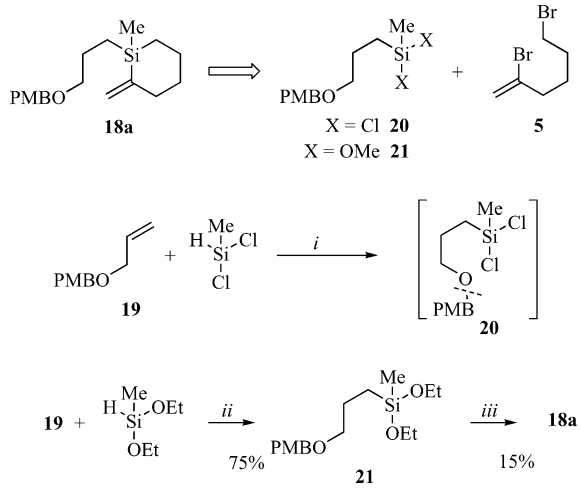
The 3-hydroxypropylsilanes **12a**,**b** were also synthesized by reaction of the chloromethylidenesilacyclohexanes **8a** and **8b** with the Grignard reagent prepared from 3-bromo-1-(4-methoxybenzyloxy)propane (**17**) and subsequent treatment of the ethers **18a**,**b** with 2,3-dichloro-5,6-dicyanoquinone (DDQ)[26] (Scheme 11).



Scheme 11. Preparation of (3-hydroxypropyl)silanes **12** from the bromopropanol derivative **17**. Reagents and conditions: *i*) Mg, THF, 60 °C; *ii*) **8a** or **8b** (0.9 equiv.), THF, 20 °C, 1.4 h; *iii*) DDQ (1.3 equiv.), DCM/H_2O, 20 °C, 0.5 h.

In this approach, (3-oxopropyl)silanes **11a** and **11b** were prepared via the protected 3-hydroxypropylsilanes **18** in 10 and 16% overall yields, respectively. These yields are lower than those obtained via chloropropylsilane **7a** for the methylated product and via allylsilane **10b** for the phenylated product.

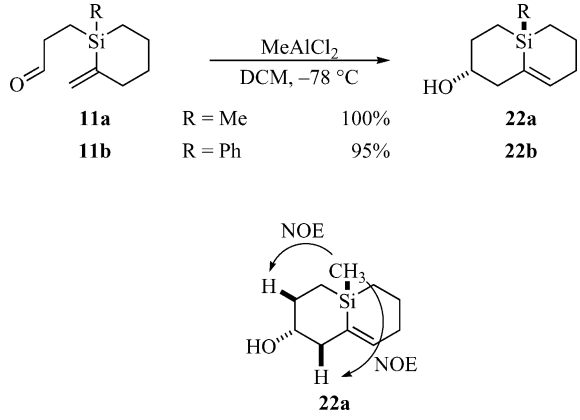
A more convergent approach to **18a** was envisaged from dibromohexene **5** and dichlorosilane **20** bearing a (4-methoxybenzyloxy)propyl chain. Allyl 4-methoxybenzyl ether (**19**) reacted with dichloromethylsilane in the presence of Speier's catalyst,[27] but the expected silane **20** could not be isolated. The ^{1}H NMR spectrum of the crude reaction mixture showed the absence of ethylenic protons and of protons characteristic of the methoxybenzyloxy group (Scheme 12). Benzyl ethers can be easily cleaved by trimethylsilyl iodide[28] or bromide.[29] In our case, a similar intramolecular reaction of the chlorosilane **20** could explain its subsequent transformation. When the allyl ether **19** was treated with dichloromethylsilane in the presence of Wilkinson's catalyst in refluxing benzene, 4-methoxybenzyl chloride was the only product isolated by distillation. Moreover, treatment in THF at 20 °C of the unconcentrated crude reaction mixture of this hydrosilylation with the Grignard reagent prepared from dibromohexene **5** gave the methylidenesilacyclohexane **18a**, but in less than 5% yield. When the temperature of the last step was increased to reflux temperature, the expected compound **18a** was not detected. Alternatively, hydrosilylation of the allyl ether **19** with diethoxymethylsilane, in refluxing cyclohexane in the presence of Speier's catalyst and air[30] satisfactorily gave the expected silane **21**, which was unstable over silica gel. No reaction occurred at room temperature with Speier's catalyst, even in the absence of solvent. In the presence of Wilkinson's catalyst[31] at 80 °C without solvent, a mixture of oligomers was obtained. Compound **18a** was not detected after treatment of the diethoxysilane **21** with the Grignard reagent obtained from dibromohexene **5**. However, reaction of an equimolar amount of the diethoxysilane **21** with the dilithiated reagent prepared from **5** and lithium gave the methylidenesilacyclohexane **18a** in too low a yield (15%) for synthetic purposes (Scheme 12).



Scheme 12. Retrosynthesis of (3-benzyloxypropyl)silane **18a** and preparation from a diethoxysilane. Reagents and conditions: *i*) [H_2PtCl_6], DCM, 20 °C, 14 h; *ii*) [H_2PtCl_6], air, cyclohexane, reflux, 3 h; *iii*) a) **5** and Li, Et_2O, –5 °C, 14 h; b) **21** and dilithiated reagent (1 equiv.), 20 °C, 10 h.

Synthesis of the Silabicyclodecenones 24

Treatment of the 3-oxopropylsilanes **11a** and **11b** with an excess of dichloromethylaluminium in dichloromethane at –78 °C led to the preparation of the bicyclic compounds **22** in excellent yields.[12] Gratifyingly, only one diastereoisomer was formed under these reaction conditions (Scheme 13).



Scheme 13. Preparation of silabicyclodec-6-en-4-ols **22** by the ene reaction and NOE effects.

The ^{1}H NMR spectra of these alcohols are very similar for the silabicyclic core protons and show a broad singlet at around 4.07 ppm. This signal, attributed to the proton

linked to the carbon bearing the hydroxy group, indicates that this proton is in an equatorial position. Moreover, a NOESY experiment performed on the alcohol **22a** showed cross-peaks between the protons of the methyl on the silicon atom and one of the protons on C-3 and one of those on C-5. Therefore it can be deduced that these stereoselective ene reactions delivered the silabicyclodecenols **22** with a *trans* relationship between the hydroxy group and the methyl on the silicon atom. Minimized molecular modeling geometries[32] of *cis*- and *trans*-silabicyclodecenol **22a** showed a chair conformation for the silacyclohexanol part of the two isomers (Figure 2). The *trans* isomer is the only one that agrees with the observed NMR features.

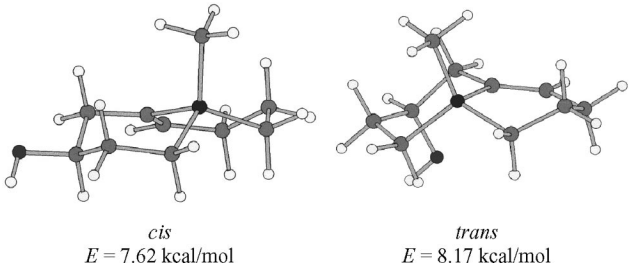


Figure 2. MM$^+$-minimized geometries of the *cis* and *trans* isomers **22a**.

Such *trans* diastereoisomers should be obtained by transfer of the allylic proton of the starting aldehyde **11**, which is on the same face as the oxopropyl chain. Examination of a Dreiding molecular model shows this proton is the only one accessible to undergo an ene reaction. Interactions of the oxygen and carbon atoms of the carbonyl group with this allylic proton and the methylene group carbon atom, respectively, lead to a *trans* diastereoisomer (Figure 3). The same type of *trans* diastereoisomer has been proposed for a product resulting from a molybdenum(II)-complex-catalyzed ene cyclization of a carbon analogue of the silacyclohexanes **11**.[33]

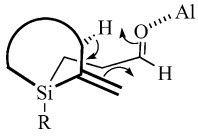
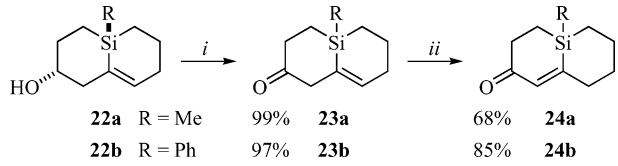


Figure 3. Dreiding model of the ene reaction with aldehydes **11**.

Initially the preparation of the α,β-ethylenic ketones **24** was attempted by Oppenauer oxidation of homoallylic alcohols **22** using a large excess of tris(isopropoxy)aluminum in the presence of cyclohexanone as cosolvent.[34] From the methylated silane **22a**, it was not possible to detect the expected ketone **24a** among the various compounds resulting from the aldol condensation of cyclohexanone. With the phenylated alcohol **22b**, the ketone **24b** was isolated in 9% yield after silica gel chromatography. A catalytic method with the dichlorotris(triphenylphosphane)ruthenium complex in the presence of potassium carbonate in acetone allowed the Oppenauer oxidation of various steroidic homoallylic alcohols with the hydroxy group in the equatorial position to α,β-ethylenic ketones.[35] No reaction was observed with **22a** under these conditions. This lack of reactivity may be related to the axial position of the hydroxy group.

However, the α,β-ethylenic ketones **24** were easily obtained by a two-step method.[36] Oxidation of the alcohols **22a**,**b** with Jones' reagent in acetone gave the β,γ-ethylenic ketones **23a**,**b** in excellent yields. Migration of the carbon–carbon double bond under basic conditions followed by neutralization afforded the expected ketones **24a** and **24b**, which were isolated in medium-to-good yields after silica gel chromatography (Scheme 14).



Scheme 14. Preparation of silabicyclodec-5-en-4-ones **24**. Reagents and conditions: *i*) CrO_3/H_2SO_4, acetone, 20 °C, 10 min; *ii*) KOH (cat.), MeOH, 50–60 °C, 50 min, then neutralization with acetic acid.

Finally, comparison of the chemical shifts of the ethylenic protons of the silabicyclo[4.4.0]decenones **24a** and **24b** and that of the α-hydrogen of 4,4-dimethyl-4-silacyclohex-2-en-1-one (**25**)[37] with those of the carbon analogues **26a**,[38] **26b**,[39] and **27**[40] shows the silicon atom exerts a similar downfield effect on these protons (Figure 4 and Table 1).

26a (R = Me), **26b** (R = Ph) **25** (X = Si), **27** (X = C)

Figure 4. Selected cycloalkenones for NMR comparison.

Table 1. NMR chemical shifts of the vinylic proton α to the carbonyl group.

Silacyclohexenones		Carbon analogues	
Compound	δ [ppm]	Compound	δ [ppm]
24a	6.33[a]	**26a**	5.70[a]
24b	6.54[a]	**26b**	6.10[a]
25	6.47[b]	**27**	5.71[b]

[a] In $CDCl_3$. [b] In CCl_4.

Conclusions

We have established various synthetic routes to 1-silabicyclo[4.4.0]dec-5-en-4-ones **24**, a new class of compounds with a silicon atom at the ring junction. The silabicyclic core was built by a diastereoselective ene reaction from a 1-(3-oxopropyl)-2-methylidene-1-silacyclohexane. The methylated compound **24a** was prepared in five steps from dichloro(3-chloropropyl)methylsilane in 16% overall yield. The phenylated analogue **24b** was synthesized in seven steps from trichlorophenylsilane in 15% yield via an allylated in-

termediate. The silabicyclodecenone **24a** is a model of the A and B rings of 10-silatestosterone. Our results concerning the silasteroid will be published in due course.

Experimental Section

General: All reactions were performed under argon using oven-dried glassware. All the commercially available silanes **6a**–**e**, **6g**, and **6h** were used without further purification. Sodium tetrafluoroborate and hexachloroplatinic acid were kept in a desiccator filled with P_2O_5. THF was distilled prior to use over the radical anion of benzophenone. Cyclohexane was filtered through basic alumina prior to use. Column chromatography was performed on silica gel SDS (70–200 μm).

NMR spectra were recorded with a Bruker AC 200, AC 250, or DRX 400 spectrometer at room temperature. Chemical shifts (δ) are reported in ppm with respect to tetramethylsilane; a solvent signal ($CDCl_3$) was used as the internal reference ($CHCl_3$: 7.27; $CDCl_3$: 77.0 ppm). Certain signals were assigned on the basis of COSY, HSQC, HMBC, DEPT, or TOCSY experiments. IR spectra were recorded with a Perkin–Elmer FT-IR Spectrum One instrument with neat samples on NaCl plates. Mass spectra were recorded using the electron ionization method (70 eV) with a Nermag R10–10 instrument coupled to an OKI DP125 chromatographer (low resolution) or with a Finnigan MAT 95 S instrument (high resolution). Elemental analyses were performed by the Microanalyse Service of the Institut de Chimie des Substances Naturelles at Gif-sur-Yvette (ICSN).

The syntheses and/or spectroscopic data of 2,6-dibromohexene (**5**), dihalosilanes **6a**–**c** and **9**, and methylidenesilacyclohexanes **7a**–**c**, **8a**,**b**, and **10a** have already been reported.[14] 3-Bromo-1-(4-methoxybenzyloxy)propane (**17**)[41] was prepared by a three-step sequence from propane-1,3-diol via 3-(4-methoxybenzyloxy)propan-1-ol.[42] The hydroxy group was replaced by a bromine atom by treatment of the corresponding mesylate (MsCl, NEt_3, DCM, 0 °C, 2 h) with LiBr in *N*-methylpyrrolidinone at 20 °C for 3 d (82% yield from the alcohol).

1-Allyl-1-methyl-2-methylidene-1-silacyclohexane (10b): A 0.65 M solution of allylmagnesium chloride in THF (2.8 mL, 1.8 mmol) was added dropwise to 1-chloro-1-methyl-2-methylidene-1-silacyclohexane (**8a**) (0.29 g, 1.8 mmol) maintained at 0 °C. The reaction mixture was stirred at 20 °C for 14 h and a saturated NH_4Cl aqueous solution was added. The organic product was extracted with diethyl ether and, after separation, the aqueous phase was extracted twice with diethyl ether. The combined organic phases were washed with water, dried with Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (pentane) to afford the allylmethylsilacyclohexane **10a** (0.18 g, 60%) as a colorless oil.[14]

1-Allyl-2-methylidene-1-phenyl-1-silacyclohexane (10b): Following the same procedure as above, 1-choro-2-methylidene-1-phenyl-1-silacyclohexane (**8b**) (0.70 g, 3.14 mmol) and a 0.65 M solution of allylmagnesium chloride in THF (4.85 mL, 3.15 mmol) afforded, after silica gel column chromatography (pentane), **10b** (0.57 g, 79%) as a colorless oil. R_f (pentane) = 0.48. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.90 (ddd, J = 4.6, 10.1, 14.6 Hz, 1 H, 6-H), 1.14 (ddd, J = 3.8, 7.4, 14.6 Hz, 1 H, 6′-H), 1.40–1.57 (m, 1 H, 4-H), 1.57–1.82 (m, 2 H, 4'-H, 5-H), 1.82–2.02 (m, 5'-H) and 1.93 (d, J = 8.2 Hz, $CH_2CH{=}CH_2$) (3 H), 2.21–2.54 (m, 2 H, 3-H, 3'-H), 4.86 (d, J = 9.3 Hz, 1 H, CH=CH_2 *cis*), 4.88 (d, J = 17.2 Hz, 1 H, CH=CH_2 *trans*), 5.28 (d, J = 2.9 Hz, 1 H, C=CH_2), 5.66 (d, J = 2.9 Hz, 1 H, C=CH_2), 5.78 (ddt, J = 9.3, 17.2, 8.2 Hz, 1 H, CH=CH_2), 7.30–7.49 (m, 3 H, *m*- and *p*-H_{Ar}), 7.49–7.56 (m, 2 H, *o*-H_{Ar}) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.1 (C-6), 20.3 (Si-CH_{2Allyl}), 24.1 (C-5), 30.6 (C-4), 39.8 (C-3), 113.8 (CH=CH_2), 124.2 (C=CH_2), 127.7 (*m*-CH_{Ar}), 129.1 (*p*-CH_{Ar}), 133.9 ($CH{=}CH_2$), 134.4 (*o*-CH_{Ar}), 134.9 (C_{Ar}), 148.7 (C-2) ppm. LRMS: *m*/*z* (%) = 228 (8) $[M]^+$, 188 (19), 187 (100), 159 (27), 145 (12), 131 (12), 109 (34), 107 (42), 105 (75), 81 (12), 79 (12), 53 (11). IR: $\tilde{\nu}$ = 3069 ($\nu_{=CH}$), 3048 ($\nu_{=CH}$), 2918, 1630 ($\nu_{C=C}$), 1428 (ν_{Si-Ar}), 1111 (δ_{Si-Ar}), 893 ($\delta_{=CH}$), 699 cm^{-1}. HRMS: calcd. for $C_{14}H_{20}Si$ $[M]^+$ 228.1334; found 228.1336.

1-Methyl-2-methylidene-1-(3-oxopropyl)-1-silacyclohexane (11a)

From the (3-Chloropropyl)silane 7a: A mixture of chloropropylsilane **7a** (0.107 g, 0.453 mmol), $NaHCO_3$ (91.5 mg, 1.0 mmol), NaI (195 mg, 1.3 mmol), and DMSO (3 mL) was heated at 105 °C for 2 h. After cooling, water was added and the organic products were extracted with diethyl ether. After separation, the aqueous phase was extracted twice with diethyl ether. The combined organic phases were washed with water, dried with Na_2SO_4, and concentrated under reduced pressure. Silica gel column chromatography (pentane/Et_2O, 9:1) allowed the isolation of the starting material **7a** (33.5 mg, conversion: 73.5%) and the (3-oxopropyl)silane **11a** (35.3 mg, 50%) as colorless oils.

From the (3-Bromopropyl)silane 7c: A solution of (bromopropyl)silane **7c** (0.103 g, 0.42 mmol) in DMSO (1 mL) was added to a mixture of silver tetrafluoroborate (0.108 g, 0.55 mmol) and DMSO (0.5 mL) and the reaction mixture was stirred at 20 °C for 14 h. After addition of triethylamine (0.15 mL, 1.07 mmol) the reaction mixture was stirred 15 min and water and diethyl ether were added. The separated aqueous phase was extracted twice with diethyl ether. The combined organic phases were washed with brine, dried with Na_2SO_4, and concentrated under reduced pressure. Silica gel column chromatography (pentane/Et_2O, 8:2) allowed the isolation of the starting material **7c** (27 mg, conversion: 71%) and the (3-oxopropyl)silane **11a** (30.4 mg, 54%) as colorless oils.

From the (3-Hydroxypropyl)silane 12a: Dess–Martin reagent (0.19 g, 0.44 mmol) was added to a solution of (hydroxypropyl)silane **12a** (49.2 mg, 0.27 mmol) in pyridine (6.5 mL) and dichloromethane (1 mL) maintained at 0 °C. The reaction mixture was stirred at 20 °C for 1.4 h and diethyl ether was added. The organic phase was washed, successively, with a saturated aqueous sodium thiosulfate solution, a saturated aqueous sodium hydrogen carbonate solution, and water. The organic phase was dried with Na_2SO_4, concentrated under low pressure, and the (3-oxopropyl)silane **11a** (43.6 mg, 89%) was isolated as a colorless oil after silica gel column chromatography (pentane/Et_2O, 9:1).

From the Allylsilane 10a: A 0.5 M solution of 9-BBN in THF (3.8 mL, 1.9 mmol) was added dropwise to allylsilane **10a** (0.32 g, 1.9 mmol). After stirring for 3 h at 20 °C, the reaction solution was transferred through a cannula into a suspension of a 50:50 mixture of PCC and Celite® (7.4 g, 17.1 mmol) in dichloromethane (30 mL). The reaction mixture was heated at reflux for 2 h and was filtered, after cooling, through a silica gel pad (EtOAc). After concentration under low pressure silica gel column chromatography (pentane/Et_2O, 8:2) afforded the starting material **10a** (37.4 mg, conversion: 88%) and the (3-oxopropyl)silane **11a** (90.1 mg, 30%) as colorless oils. R_f (pentane/Et_2O, 4:1) = 0.48. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.11 (s, 3 H, $SiCH_3$), 0.65 (ddd, J = 4.6, 10.2, 14.6 Hz, 1 H, 6-H), 0.80–1.10 (m, CH_2CH_2CHO) and 0.90 (ddd, J = 4.6, 7.5, 14.6 Hz, 6′-H) (3 H), 1.33–1.55 (m, 1 H, 4-H), 1.55–1.77 (m, 2 H, 4'-H, 5-H), 1.77–1.89 (m, 1 H, 5'-H), 2.21–2.43 (m, 2 H, 3-H, 3'-H), 2.46–2.72 (m, 2 H, CH_2-CHO), 5.14 (d, J =

3.2 Hz, 1 H, C=CH_2), 5.50 (d, J = 3.2 Hz, 1 H, C=CH_2), 9.76 (t, J = 1.4 Hz, 1 H, CHO) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –5.6 ($SiCH_3$), 4.5 (CH_2CH_2CHO), 13.3 (C-6), 24.3 (C-5), 30.8 (C-4), 38.3 (CH_2CHO), 39.7 (C-3), 122.4 (C=CH_2), 153.6 (C-2), 202.9 (CHO) ppm. LRMS: m/z (%) = 182 (2) $[M]^+$, 167 (10), 154 (15), 126 (21), 125 (23), 113 (15), 112 (28), 111 (23), 101 (100), 99 (97), 97 (47), 95 (14), 85 (30), 83 (10), 71 (20), 61 (15), 59 (23), 55 (17), 53 (10), 45 (43), 43 (42). IR: $\tilde{\nu}$ = 3040 ($\nu_{=CH}$), 2917, 2852, 2714 (ν_{OC-H}), 1725 ($\nu_{C=O}$), 1630 ($\nu_{C=C}$), 1446, 1408, 1252 (δ_{Si-CH3}), 1177, 921, 894 ($\delta_{=CH}$), 797 cm^{-1}. HRMS: calcd. for $C_{10}H_{18}OSi$ $[M]^+$ 182.1126; found 182.1124.

2-Methylidene-1-(3-oxopropyl)-1-phenyl-1-silacyclohexane (11b): Following the same procedure as above for the synthesis of aldehyde **11a** from allylsilane **10a**, addition of 9-BBN to 1-allyl-2-methylidene-1-phenyl-1-silacyclohexane (**8b**) (0.52 g, 2.28 mmol) followed by oxidation of the resulting borane with PCC afforded, after silica gel column chromatography (pentane/Et_2O, 4:1), **11b** (0.31 g, 55%) as a colorless oil. R_f (pentane/Et_2O, 1:1) = 0.65. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.83 (ddd, J = 4.5, 10.3, 14.6 Hz, 1 H, 6-H), 1.07–1.26 (m, CH_2CH_2CHO) and 1.22 (ddd, J = 4.5, 7.5, 14.6 Hz, 6′-H) (3 H), 1.44–1.57 (m, 1 H, 4-H), 1.62–1.77 (m, 2 H, 4'-H, 5-H), 1.86–2.00 (m, 1 H, 5'-H), 2.30–2.40 (m, 1 H, 3-H), 2.40–2.51 (m, 3 H, 3'-H, CH_2CHO), 5.21 (d, J = 2.9 Hz, 1 H, C=CH_2), 5.61 (d, J = 2.9 Hz, 1 H, C=CH_2), 7.23–7.37 (m, 3 H, m- and p-H_{Ar}), 7.40–7.54 (m, 2 H, o-H_{Ar}), 9.66 (t, J = 1.5 Hz, 1 H, CHO) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 3.8 (CH_2CH_2CHO), 11.4 (C-6), 24.1 (C-5), 30.5 (C-4), 38.2 (CH_2CHO), 39.7 (C-3), 124.3 (C=CH_2), 128.0 (m-CH_{Ar}), 129.4 (p-CH_{Ar}), 134.3 (o-CH_{Ar}), 134.4 (C_{Ar}), 148.4 (C-2), 202.6 (CHO) ppm. LRMS: m/z (%) = 244 (3) $[M]^+$, 217 (14), 216 (62), 215 (14), 189 (11), 188 (26), 187 (30), 175 (30), 174 (38), 167 (22), 164 (18), 163 (100), 162 (37), 161 (88), 160 (22), 159 (39), 147 (13), 145 (17), 133 (12), 131 (18), 123 (23), 117 (11), 109 (12), 107 (31), 105 (47), 84 (15). IR: $\tilde{\nu}$ = 3068 ($\nu_{=CH}$), 3045 ($\nu_{=CH}$), 2918, 2852, 2717 (ν_{OC-H}), 1723 ($\nu_{C=O}$), 1428 (ν_{Si-Ar}), 1176, 1111 (δ_{Si-Ar}), 924, 892 ($\delta_{=CH}$), 737, 701 cm^{-1}. HRMS: calcd. for $C_{15}H_{20}OSi$ $[M]^+$ 244.1283; found 224.1284.

1-(3-Hydroxypropyl)-1-methyl-2-methylidene-1-silacyclohexane (12a)

From the Allylsilane 10a: A 0.5 M solution of 9-BBN in THF (2.24 mL, 1.12 mmol) was added dropwise to allylsilane **10a** (0.18 g, 1.12 mmol). After stirring for 3 h at 20 °C, a 3 M aqueous solution of NaOH (0.34 mL, 1.01 mmol) and a 35% aqueous solution of H_2O_2 (0.3 mL, 3.36 mmol) were added. The reaction mixture was heated at 50 °C for 1 h and after cooling the organic products were extracted with pentane. The organic phases were dried with Na_2SO_4 and concentrated under reduced pressure. Silica gel column chromatography (pentane/Et_2O, 1:1) allowed the isolation of the starting material **10a** (41 mg, conversion: 78%), **12a** (80 mg, 50%) and 1-allyl-2-hydroxymethyl-1-methyl-1-silacyclohexane (**13**) (15mg, 9.4%) as colorless oils.

From the [3-(4-Methoxybenzyloxy)propyl]silane 18a: DDQ (0.149 g, 0.54 mmol) was added to a mixture of **18a** (0.124 g, 0.41 mmol), water (0.220 mL), and dichloromethane (4 mL) maintained at 5 °C. After stirring at 20 °C for 0.5 h, a saturated aqueous sodium hydrogen carbonate solution was added and the organic products were extracted with dichloromethane. The combined organic phases were dried with Na_2SO_4 and concentrated under reduced pressure. The (3-hydroxypropyl)silane **12a** (52.2 mg, 69%) was isolated as a colorless oil after silica gel column chromatography (pentane/Et_2O, 3:1). R_f (pentane/Et_2O, 1:1) = 0.28. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.11 (s, 3 H, $SiCH_3$), 0.50–0.64 (m, 6-H) and 0.53–0.75 (m, $CH_2CH_2CH_2OH$), and 0.64–0.70 (m, 6′-H) (4 H), 1.32–1.48 (m, 1 H, 4-H), 1.48–1.62 (m, 4'-H) and 1.60 (quint, J = 6.5 Hz, CH_2CH_2OH) (3 H), 1.62–1.73 (m, 1 H, 5-H), 1.73–1.86 (m, 1 H, 5'-H), 2.33–2.46 (m, 2 H, 3-H), 3.62 (t, J = 6.5 Hz, 2 H, CH_2OH), 5.14 (d, J = 3.5 Hz, 1 H, C=CH_2), 5.48 (d, J = 3.5 Hz, 1 H, C=CH_2) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –5.6 ($SiCH_3$), 8.4 ($CH_2CH_2CH_2OH$), 13.4 (C-6), 24.4 (C-5), 26.9 (CH_2CH_2OH), 30.9 (C-4), 39.8 (C-3), 65.5 (CH_2OH), 121.6 (C=CH_2), 151.6 (C-2) ppm. LRMS: m/z (%) = 184 (1) $[M]^+$, 169 (7), 141 (12), 127 (17), 125 (16), 109 (10), 102 (11), 101 (100), 99 (24), 97 (28), 87 (13), 75 (26), 74 (36), 61 (35), 59 (25), 45 (12), 43 (12). IR: $\tilde{\nu}$ = 3328 (ν_{OH}), 3039 ($\nu_{=CH}$), 2915, 1631 ($\nu_{C=C}$), 1437, 1248 (δ_{Si-CH3}), 1052 (ν_{C-O}), 918, 892 ($\delta_{=CH}$), 866, 791 cm^{-1}. HRMS: calcd. for $C_{10}H_{20}OSi$ $[M]^+$ 184.1283; found 184.1282.

1-(3-Hydroxypropyl)-2-methylidene-1-phenyl-1-silacyclohexane (12b): Following the same procedure as above for the synthesis of alcohol **12a** from silane **18a**, the reaction of DDQ with **18b** (0.46 g, 1.26 mmol) afforded, after silica gel column chromatography (pentane/Et_2O, 4:1), **12b** (0.22 g, 71%) as a colorless oil. R_f (pentane/Et_2O, 1:1) = 0.23. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (ddd, J = 4.6, 10.7, 12.5 Hz, 6-H) and 0.90–1.00 (m, $CH_2CH_2CH_2OH$) (3 H), 1.21 (ddd, J = 4.6, 7.0, 12.5 Hz, 1 H, 6′-H), 1.46–1.57 (m, 1 H, 4-H), 1.61–1.80 (m, CH_2CH_2OH) and 1.65–1.77 (m, 4'-H, 5-H) (4 H), 1.92–2.03 (m, 1 H, 5'-H), 2.32–2.55 (m, 2 H, 3-H, 3'-H), 3.60 (t, J = 7.0 Hz, 2 H, CH_2OH), 5.28 (d, J = 3.0 Hz, 1 H, C=CH_2), 5.65 (d, J = 3.0 Hz, 1 H, C=CH_2), 7.31–7.46 (m, 3 H, m- and p-H_{Ar}), 7.46–7.62 (m, 2 H, o-H_{Ar}) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 8.1 (C-6), 11.5 ($CH_2CH_2CH_2OH$), 24.2 (C-5), 26.9 (CH_2CH_2OH), 30.7 (C-4), 39.9 (C-3), 65.5 (CH_2OH), 123.9 (C=CH_2), 127.8 (m-CH_{Ar}), 129.1 (p-CH_{Ar}), 134.3 (o-CH_{Ar}), 135.5 (C_{Ar}), 149.3 (C-2) ppm. LRMS: m/z (%) = 246 (1) $[M]^+$, 187 (7), 168 (7), 164 (17), 163 (100), 159 (14), 145 (7), 136 (30), 123 (23), 109 (11), 107 (17), 105 (28), 92 (11), 91 (7), 80 (10), 78 (8), 44 (24). IR: $\tilde{\nu}$ = 3326 (ν_{OH}), 3068 ($\nu_{=CH}$), 3045 ($\nu_{=CH}$), 2918, 1428 (ν_{Si-Ar}), 1110 (δ_{Si-Ar}), 1054 (ν_{C-O}), 923, 892 ($\delta_{=CH}$), 733, 700 cm^{-1}. HRMS: calcd. for $C_{15}H_{22}OSi$ $[M]^+$ 246.1440; found 246.1442.

1-[3-(4-Methoxybenzyloxy)propyl]-1-methyl-2-methylidene-1-silacyclohexane (18a)

From the Diethoxysilane 21: A solution of 2,5-dibromohexene (**5**) (1.92 g, 7.9 mmol) in diethyl ether (15 mL) was added dropwise to a suspension of lithium (0.24 g, 34.3 mmol) in diethyl ether (3 mL) maintained at –5 °C. The reaction mixture was stirred at –5 °C for 14 h and the resulting organometallic solution was titrated by acid/base reaction (0.385 M, assuming formation of a dilithiated species, 87%). The diethoxysilane **21** (0.826 g, 2.65 mmol) was added to this solution of organolithiated reagent (6.9 mL, 2.65 mmol). After 10 h at 20 °C, a saturated aqueous ammonium chloride solution was added and the organic products were extracted three times with diethyl ether. The combined organic phases were washed with water, dried with Na_2SO_4, and concentrated under reduced pressure. **18a** (0.134 g, 15%) was isolated as a colorless oil after silica gel column chromatography (pentane/Et_2O, 9:1).

From the Chlorosilacyclohexane 8a: A solution of 1-chloro-1-methyl-2-methylidene-1-silacyclohexane (**8a**) (0.22 g, 1.36 mmol) in THF (1.5 mL) was added dropwise to a 0.56 M solution of 3-(4-methoxybenzyloxy)propylmagnesium bromide in THF (2.7 mL, 1.5 mmol) prepared by reaction for 6 h of 3-bromo-1-(4-methoxybenzyloxy)propane (**17**) with magnesium in THF at 60 °C. After 14 h at 20 °C, a saturated aqueous ammonium chloride solution was added and the organic products were extracted three times with diethyl ether. The combined organic phases were washed with water, dried with Na_2SO_4, and concentrated under reduced pressure. The silane **18a** (0.205 g, 50%) was isolated as a colorless oil

after silica gel column chromatography (pentane/Et_2O, 4:1). R_f (pentane/Et_2O, 1:1) = 0.58. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.12 (s, 3 H, $SiCH_3$), 0.59–0.74 (m, $CH_2CH_2CH_2O$) and 0.61 (ddd, J = 4.6, 9.9, 14.4 Hz, 6-H), and 0.76 (ddd, J = 4.6, 7.7, 14.4 Hz, 6′-H) (4 H), 1.39–1.52 (m, 1 H, 4-H), 1.53–1.64 (m, 4'-H) and 1.58–1.71 (m, CH_2CH_2O), and 1.64–1.76 (m, 5-H) (4 H), 1.76–1.87 (m, 1 H, 5'-H), 2.27–2.44 (m, 2 H, 3-H, 3'-H), 3.45 (t, J = 6.9 Hz, 2 H, CH_2CH_2O), 3.82 (s, 3 H, OCH_3), 4.47 (s, 2 H, OCH_2C_{Ar}), 5.13 (d, J = 3.5 Hz, 1 H, C=CH_2), 5.49 (d, J = 3.5 Hz, 1 H, C=CH_2), 6.90 (d, J = 8.7 Hz, 2 H, m-H_{Ar}), 7.28 (d, J = 8.7 Hz, 2 H, o-H_{Ar}) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –5.6 ($SiCH_3$), 8.8 ($CH_2CH_2CH_2O$), 13.4 (C-6), 24.0 (CH_2CH_2O), 24.4 (C-5), 30.9 (C-4), 39.8 (C-3), 55.2 (OCH_3), 72.4 (OCH_2C_{Ar}), 72.9 (CH_2CH_2O), 113.7 (m-CH_{Ar}), 121.6 (C=CH_2), 129.2 (o-CH_{Ar}), 130.7 ($C_{Ar}CH_2$), 151.7 (C-2), 159.0 ($C_{Ar}O$) ppm. LRMS: m/z (%) = 304 (32) $[M]^+$, 247 (15), 208 (13), 207 (29), 162 (23), 161 (38), 135 (12), 126 (10), 125 (42), 123 (13), 122 (88), 121 (100), 102 (10), 101 (84), 99 (22), 97 (67), 91 (18), 85 (10), 78 (19), 77 (24), 71 (17), 59 (21), 43 (8). IR: $\tilde{\nu}$ = 3038 ($\nu_{=CH}$), 2915, 2851, 1608 ($\nu_{C=C}$), 1513 ($\nu_{C=CO}$), 1250 (δ_{Si-CH3} or δ_{Ar-O}), 1171, 1098 (ν_{C-O}), 1036 (ν_{Si-OC}), 820 ($\delta_{=CH}$) cm^{-1}. HRMS: calcd. for $C_{18}H_{28}O_2Si$ $[M]^+$ 304.1858; found 304.1847.

1-[3-(4-Methoxybenzyloxy)propyl]-2-methylidene-1-phenyl-1-silacyclohexane (18b): Following the same procedure as above for the synthesis of silane **18a** from chlorosilane **8a**, reaction of a 0.56 M of 3-(4-methoxybenzyloxy)propylmagnesium bromide in THF (4.85 mL, 2.72 mmol) with 1-chloro-2-methylidene-1-phenyl-1-silacyclohexane (**8b**) (0.605 g, 2.72 mmol) afforded **18b** (0.60 g, 60%) as a colorless oil after silica gel column chromatography (pentane/Et_2O, 4:1). R_f (pentane/Et_2O, 4:1) = 0.52. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.70–0.98 (m, 4 H, 6-H, $CH_2CH_2CH_2O$), 1.00–1.25 (m, 1 H, 5-H), 1.32–1.52 (m, 1 H, 5'-H), 1.53–1.62 (m, 3 H, 4-H, CH_2CH_2O), 1.62–1.93 (m, 1 H, 4'-H), 2.16–2.43 (m, 2 H, 3-H), 3.54 (t, J = 6.3 Hz, 2 H, CH_2CH_2O), 3.80 (s, 3 H, OCH_3), 4.42 (s, 2 H, OCH_2C_{Ar}), 5.25 (d, J = 3.4 Hz, 1 H, C=CH_2), 5.63 (d, J = 3.4 Hz, 1 H, C=CH_2), 6.87 (d, J = 8.6 Hz, 2 H, m-H_{Ar} for $CH_2C_6H_4O$), 7.23 (d, J = 8.6 Hz, 2 H, o-H_{Ar} for $CH_2C_6H_4O$), 7.30–7.44 (m, 3 H, m- and p-H_{Ar} for PhSi), 7.55–7.64 (m, 2 H, o-H_{Ar} for PhSi) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.3 ($CH_2CH_2CH_2O$), 11.4 (C-6), 23.6 and 24.1 (CH_2CH_2O, C-5), 30.6 (C-4), 39.8 (C-3), 55.0 (OCH_3), 72.3 and 72.9 (CH_2CH_2O, OCH_2C_{Ar}), 113.6 (m-CH_{Ar} for $CH_2C_6H_4O$), 123.7 (C=CH_2), 127.7 (m-CH_{Ar} for PhSi), 129.1 and 129.2 (o-CH_{Ar} for $CH_2C_6H_4O$, p-CH_{Ar} for PhSi), 130.6 ($C_{Ar}CH_2$), 134.3 (o-CH_{Ar} for PhSi), 135.5 ($C_{Ar}Si$), 151.7 (C-2), 159.0 ($C_{Ar}O$) ppm. IR: $\tilde{\nu}$ = 3064 ($\nu_{=CH}$), 3043 ($\nu_{=CH}$), 2916, 2852, 1613 ($\nu_{C=C}$), 1587, 1513 ($\nu_{C=CO}$), 1428, 1302, 1248 (δ_{Si-CH3} or δ_{Ar-O}), 1172, 1098 (ν_{C-O}), 1037 (ν_{Si-OC}), 924, 821 ($\delta_{=CH}$) cm^{-1}. HRMS: calcd. for $C_{23}H_{30}O_2NaSi$ $[M + Na]^+$ 389.1907; found 389.1907.

Diethoxy[3-(4-methoxybenzyloxy)propyl]methylsilane (21): Diethoxymethylsilane (0.5 mL, 3.1 mmol) and allyl 4-methoxybenzyl ether (**19**)[43] were added to a mixture of $[H_2PtCl_6]$ (ca. 0.5 mg) in cyclohexane (2 mL), protected from moisture with a calcium chloride guard tube. After heating at reflux for 3 h, solvent and impurities were removed under vacuum (0.1 Torr) to afford **21** (0.70 g, 75%) as a colorless oil. Gas chromatography showed a 96% pure product. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.13 (s, 3 H, $SiCH_3$), 0.58–0.61 (m, 2 H, $SiCH_2$), 1.22 (t, J = 7.1 Hz, 6 H, CH_3CH_2O), 1.60–1.76 (m, 2 H, $SiCH_2CH_2$), 3.43 (t, J = 8.7 Hz, 2 H, CH_2CH_2O), 3.77 (q, J = 7.1 Hz, 4 H, CH_3CH_2O), 3.82 (s, 3 H, OCH_3), 4.44 (s, 2 H, OCH_2C_{Ar}), 6.89 (d, J = 8.9 Hz, 2 H, m-H_{Ar}), 7.27 (d, J = 8.9 Hz, 2 H, o-H_{Ar}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = –5.0 ($SiCH_3$), 10.0 ($SiCH_2$), 18.3 (CH_3CH_2O), 23.1 ($SiCH_2CH_2$), 55.1 (OCH_3), 58.0 (CH_3CH_2O), 72.4 (OCH_2C_{Ar}), 72.5 (CH_2CH_2O), 113.7 (m-CH_{Ar}), 129.1 (o-CH_{Ar}), 130.7 ($C_{Ar}CH_2$), 159.0 ($C_{Ar}O$) ppm. LRMS: m/z (%) = 312 (0.1) $[M]^+$, 267 (13), 266 (69), 265 (39), 237 (21), 235 (35), 224 (10), 207 (12), 145 (18), 137 (49), 134 (30), 133 (90), 130 (13), 122 (24), 121 (100), 105 (21), 98 (11), 89 (23), 77 (26). IR: $\tilde{\nu}$ = 2972, 2929, 1613 ($\nu_{C=C}$), 1514 ($\nu_{C=CO}$), 1249 (δ_{Si-CH3} or ν_{Ar-O}), 1102 (ν_{C-O}), 1038 (ν_{Si-OC}), 822 ($\delta_{=CH}$) cm^{-1}. HRMS: calcd. for $C_{16}H_{28}O_4Si$ $[M]^+$ 312.1757; found 312.1770.

1-Methyl-1-silabicyclo[4.4.0]dec-6-en-4-ol (22a): A 1 M solution of $MeAlCl_2$ in hexanes (0.56 mL, 0.56 mmol) was added to a solution of aldehyde **11a** (56 mg, 0.31 mmol) in dichloromethane (2.3 mL) maintained at –78 °C. The reaction mixture was stirred at –78 °C for 6 h, then a saturated aqueous sodium hydrogen carbonate solution was added, and the organic products were extracted three times with dichloromethane. The combined organic phases were washed with water, dried with Na_2SO_4, and concentrated under reduced pressure. The siladecenol **22a** (56 mg, 100%) was isolated as a colorless oil after filtration through a silica gel pad (pentane/Et_2O, 1:1). R_f (pentane/Et_2O, 1:1) = 0.35. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.13 (s, 3 H, $SiCH_3$), 0.50–0.70 (m, 10-H) and 0.58–0.72 (m, 2-H) (2 H), 0.74–0.95 (m, 10′-H) and 0.78–0.93 (m, 2'-H) (2 H), 1.51–1.72 (m, 9-H) and 1.56–1.78 (m, 3-H) (2 H), 1.85–2.02 (m, 1 H, 9'-H), 2.08–2.27 (m, 3 H, 3'-H, 8-H, 8'-H), 2.34 (ddd, J = 2.3, 4.0, 13.7 Hz, 1 H, 5-H), 2.60 (ddddd, J = 2.6, 2.6, 2.6, 2.6, 13.7 Hz, 1 H, 5'-H), 4.07 (br. s, 1 H, 4-H), 6.38 (br. t, J = 4.7 Hz, 1 H, 7-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –5.6 ($SiCH_3$), 8.0 (C-2), 11.0 (C-10), 21.3 (C-9), 30.1 (C-3), 30.8 (C-8), 44.9 (C-5), 66.3 (C-4), 134.0 (C-6), 143.2 (C-7) ppm. LRMS: m/z (%) = 182 (31) $[M]^+$, 167 (74), 154 (32), 139 (64), 126 (40), 125 (43), 113 (52), 111 (61), 101 (59), 99 (78), 97 (57), 96 (47), 95 (44), 87 (42), 85 (38), 84 (38), 75 (46), 69 (32), 67 (36), 61 (100), 59 (42), 45 (61), 43 (35). IR: $\tilde{\nu}$ = 3400 (ν_{OH}), 3040 ($\nu_{=CH}$), 2907, 2852, 1713, 1623 ($\nu_{C=C}$), 1429 ($\delta_{=CH}$), 1249 (δ_{Si-CH3}), 1124, 1081, 1056, 1018, 916, 880, 832 ($\delta_{=CH}$), 773 cm^{-1}. HRMS: calcd. for $C_{10}H_{18}OSi$ $[M]^+$ 182.1126; found 182.1124.

1-Phenyl-1-silabicyclo[4.4.0]dec-6-en-4-ol (22b): Following the same procedure as above for the synthesis of siladecenol **22a**, reaction of aldehyde **11b** (95 mg, 0.31 mmol) with $MeAlCl_2$ afforded the siladecenol **22b** (90 mg, 95%) as a colorless oil after silica gel column chromatography (pentane/Et_2O, 1:1). R_f (pentane/Et_2O, 1:1) = 0.32. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.73 (ddd, J = 3.6, 13.0, 14.4 Hz, 1 H, 10-H), 0.98 (br. ddd, J = 2.7, 6.7, 14.4 Hz, 10'-H) and 1.00 (ddd, J = 5.0, 14.8, 14.8 Hz, 2-H), and 1.10 (ddd, J = 4.0, 4.0, 14.8 Hz, 2'-H) (3 H), 1.61 (dddd, J = 1.6, 4.0, 14.1, 14.1 Hz, 3'-H) and 1.69 (ddddd, J = 2.8, 4.6, 10.0, 13.0, 14.0 Hz, 9'-H) (2 H), 1.93 (m, 1 H, 9-H), 2.10–2.33 (m, 3 H, 3'-H, 8-H, 8'-H), 2.43 (ddd, J = 1.8, 3.7, 14.0 Hz, 1 H, 5-H), 2.62 (ddddd, J = 2.0, 2.5, 2.8, 2.8, 13.8 Hz, 1 H, 5'-H), 4.08 (br. s, 1 H, 4-H), 6.56 (br. t, J = 4.2 Hz, 1 H, 7-H), 7.31–7.51 (m, 3 H, m- and p-H_{Ar}), 7.51–7.71 (m, 2 H, o-H_{Ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 6.4 (C-2), 11.0 (C-10), 21.0 (C-9), 30.1 (C-3), 30.8 (C-8), 45.1 (C-5), 69.3 (C-4), 128.4 (m-CH_{Ar}), 129.7 (p-CH_{Ar}), 131.7 (C-6), 134.9 (o-CH_{Ar}), 136.4 (C_{Ar}), 145.3 (C-7) ppm. LRMS: m/z (%) = 244 (20) $[M]^+$, 216 (26), 198 (11), 189 (20), 188 (30), 187 (29), 175 (26), 174 (19), 167 (28), 166 (58), 161 (26), 149 (19), 139 (28), 138 (82), 131 (24), 125 (34), 124 (24), 123 (100), 121 (25), 107 (32), 105 (77), 91 (23). IR: $\tilde{\nu}$ = 3400 (ν_{OH}), 3040 ($\nu_{=CH}$), 2907, 2850, 1712, 1625 ($\nu_{C=C}$), 1427 (ν_{Si-Ar}), 1123 (δ_{Si-Ar}), 1123, 1082, 1053, 918, 887, 830 ($\delta_{=CH}$), 775 cm^{-1}. HRMS: calcd. for $C_{15}H_{20}OSi$ $[M]^+$ 244.1283; found 244.1276.

1-Methyl-1-silabicyclo[4.4.0]dec-6-en-4-one (23a): A 0.67 M aqueous solution of Jones' reagent (0.64 mL, 2.4 mmol) was added to a

solution of alcohol **22a** (0.400 g, 2.2 mmol) in acetone (100 mL) maintained at 10 °C. After stirring for 10 min at 20 °C, the reaction mixture was diluted with dichloromethane and washed with water. The separated aqueous phase was extracted twice with dichloromethane. The combined organic phases were dried with Na_2SO_4 and concentrated under reduced pressure. The siladec-6-enone **23a** (0.396 g, 99%) was isolated as a colorless oil after silica gel column chromatography (pentane/Et_2O, 4:1). R_f (pentane/Et_2O, 3:1) = 0.33. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.38 (s, 3 H, $SiCH_3$), 0.43 (ddd, J = 4.0, 14.1, 14.1 Hz, 1 H, 10-H), 0.64–0.78 (m, 10'-H) and 0.65–0.77 (m, 2-H) (2 H), 0.83 (ddd, J = 3.0, 6.2, 13.9 Hz, 1 H, 2'-H), 1.53–1.67 (m, 1 H, 9-H), 1.72–1.84 (m, 1 H, 9'-H), 1.85–1.98 (m, 1 H, 8-H), 1.98–2.10 (m, 1 H, 8'-H), 2.32–2.47 (m, 2 H, 3-H), 2.83 (d, J = 15.0 Hz, 1 H, 5-H), 3.18 (dd, J = 3.0, 15.0 Hz, 1 H, 5'-H), 6.13 (br. q, J = 3.0 Hz, 1 H, 7-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –5.8 ($SiCH_3$), 9.1 (C-10), 9.8 (C-2), 20.0 (C-9), 29.8 (C-8), 38.4 (C-3), 52.6 (C-5), 131.4 (C-6), 141.6 (C-7), 210.5 (C-4) ppm. LRMS: m/z (%) = 180 (33) $[M]^+$, 152 (27), 138 (19), 137 (17), 125 (25), 124 (43), 109 (38), 97 (23), 96 (100), 81 (10), 59 (15), 55 (23), 53 (15), 45 (22), 43 (43). IR: $\tilde{\nu}$ = 3045 ($\nu_{=CH}$), 2909, 2854, 2251, 1705 ($\nu_{C=O}$), 1619 ($\nu_{C=C}$), 1429 ($\delta_{=CH}$), 1412, 1252 (δ_{Si-CH3}), 1114, 915, 824 ($\delta_{=CH}$) cm^{-1}. HRMS: calcd. for $C_{10}H_{16}OSi$ $[M]^+$ 180.0970; found 180.0966.

1-Phenyl-1-silabicyclo[4.4.0]dec-6-en-4-one (23b): Following the same procedure as above for the synthesis of siladec-6-enone **23a**, reaction of alcohol **22b** (21.1 mg, 0.086 mmol) with Jones' reagent afforded the siladec-6-enone **23b** (20.3 mg, 97%) as a colorless oil after silica gel column chromatography (pentane/Et_2O, 3:1). R_f (pentane/Et_2O, 3:1) = 0.28. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.74 (ddd, J = 3.6, 13.9, 13.9 Hz, 1 H, 10-H), 1.03–1.17 (m, 10'-H) and 1.03–1.17 (m, 2-H) (2 H), 1.42 (ddd, J = 3.6, 6.4, 13.9 Hz, 1 H, 2'-H), 1.67–1.80 (m, 1 H, 9-H), 1.88–2.02 (m, 1 H, 9'-H), 2.11–2.25 (m, 1 H, 8-H), 2.25–2.38 (m, 1 H, 8'-H), 2.47–2.68 (m, 2 H, 3-H), 3.13 (dd, J = 2.5, 16.5 Hz, 1 H, 5-H), 3.40 (ddd, J = 2.5, 6.0, 16.5 Hz, 1 H, 5'-H), 6.54 (br. q, J = 3.4 Hz, 1 H, 7-H), 7.37–7.50 (m, 3 H, m- and p-H_{Ar}), 7.59–7.69 (m, 2 H, o-H_{Ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.4 and 9.5 (C-2, C-10), 20.1 (C-9), 30.2 (C-8), 39.0 (C-3), 53.6 (C-5), 128.2 (m-CH_{Ar}), 129.7 (p-CH_{Ar}), 134.2 (C-6), 134.4 (o-CH_{Ar}), 135.0 (C_{Ar}), 144.2 (C-7), 211.2 (C-4) ppm. LRMS: m/z (%) = 242 (100) $[M]^+$, 215 (7), 214 (32), 200 (8), 199 (10), 188 (16), 187 (12), 186 (17), 160 (11), 159 (12), 158 (34), 131 (13), 130 (13), 108 (20), 107 (23), 106 (16), 105 (56), 93 (9), 79 (11), 53 (12). IR: $\tilde{\nu}$ = 3047 ($\nu_{=CH}$), 3012 ($\nu_{=CH}$), 2926, 2855, 1705 ($\nu_{C=O}$), 1618, 1589 ($\nu_{C=C}$), 1428 (ν_{Si-Ar}), 1265, 1112 (δ_{Si-Ar}), 862, 817, 726, 701, 667 cm^{-1}. HRMS: calcd. for $C_9H_{15}OSiNa$ $[M + Na]^+$ 265.1025; found 265.1005.

1-Methyl-1-silabicyclo[4.4.0]dec-5-en-4-one (24a): Seven drops (ca. 20 μL each) of a 10% aqueous KOH solution were added over 50 min to a solution of the siladec-6-enone **23a** (0.307 g, 1.7 mmol) in methanol (4 mL) maintained at 50–60 °C. After cooling, the reaction mixture was neutralized with acetic acid and taken off with water and diethyl ether. The separated aqueous phase was extracted twice with diethyl ether. The combined organic phases were washed with water to neutrality, dried with Na_2SO_4, and concentrated under reduced pressure. The siladec-5-enone **24a** (0.208 g, 68%) was isolated as a colorless oil after silica gel column chromatography (pentane/Et_2O, 4:1). R_f (pentane/Et_2O, 3:1) = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.29 (s, 3 H, $SiCH_3$), 0.59 (ddd, J = 4.0, 13.0, 13.0 Hz, 1 H, 10-H), 0.87–1.07 (m, 3 H, 2-H, 2'-H, 10'-H), 1.14–1.30 (m, 1 H, 8-H), 1.44–1.61 (m, 1 H, 9-H), 1.90–2.02 (m, 1 H, 8'-H), 2.03–2.17 (m, 1 H, 9'-H), 2.28–2.58 (m, 3 H, 3-H, 7-H, 7'-H), 2.62–2.80 (m, 1 H, 3'-H), 6.33 (s, 1 H, 5-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = –7.5 ($SiCH_3$), 8.7 (C-2), 13.9 (C-10), 23.7 (C-9), 30.4 (C-8), 35.9 (C-3), 38.7 (C-7), 137.9 (C-5), 167.6 (C-6), 202.0 (C-4) ppm. LRMS: m/z (%) = 180 (21) $[M]^+$, 153 (11), 152 (88), 125 (16), 124 (100), 109 (42), 97 (9), 96 (75), 95 (11), 79 (9), 69 (10), 68 (10), 67 (11), 55 (10), 43 (15). IR: $\tilde{\nu}$ = 3045 ($\nu_{=CH}$), 3016 ($\nu_{=CH}$), 2924, 2852, 1666 ($\nu_{C=O}$), 1590 ($\nu_{C=C}$), 1428, 1315, 1252 (δ_{Si-CH3}), 1123, 886, 840 ($\delta_{=CH}$), 789, 760 cm^{-1}. HRMS: calcd. for $C_{10}H_{16}OSi$ $[M]^+$ 180.0970; found 180.0973.

1-Phenyl-1-silabicyclo[4.4.0]dec-5-en-4-one (24b): Following the same procedure as above for the synthesis of siladec-5-enone **24a**, reaction of alcohol **23b** (64 mg, 0.26 mmol) with KOH in methanol afforded the siladec-5-enone **24b** (54 mg, 85%) as a colorless oil after silica gel column chromatography (pentane/Et_2O, 4:1). R_f (pentane/Et_2O, 4:1) = 0.26. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.78 (ddd, J = 4.7, 14.5, 14.5 Hz, 1 H, 10-H), 1.11–1.29 (m, 2 H, 2-H, 2'-H), 1.30–1.58 (m, 3 H, 10'-H, 9-H, 9'-H), 1.95–2.04 (m, 1 H, 8-H), 2.06–2.17 (m, 1 H, 8'-H), 2.41–2.53 (m, 1 H, 7-H), 2.54–2.62 (m, 2 H, 7'-H, 3-H), 2.76 (ddd, J = 5.0, 5.0, 16.0 Hz, 1 H, 3'-H), 6.54 (s, 1 H, 5-H), 7.38–7.53 (m, 3 H, m- and p-H_{Ar}), 7.53–7.68 (m, 2 H, o-H_{Ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.0 (C-2), 12.6 (C-10), 23.6 (C-9), 30.4 (C-8), 35.8 (C-3), 38.9 (C-7), 128.3 (m-CH_{Ar}), 130.0 (p-CH_{Ar}), 133.3 (C_{Ar}), 134.5 (o-CH_{Ar}), 139.8 (C-5), 165.0 (C-6), 202.3 (C-4) ppm. LRMS: m/z (%) = 242 (35) $[M]^+$, 215 (18), 214 (100), 187 (13), 186 (85), 159 (14), 158 (95), 157 (10), 145 (9), 144 (10), 131 (12), 130 (25), 129 (8), 107 (10), 105 (33). IR: $\tilde{\nu}$ = 3048 ($\nu_{=CH}$), 3056 ($\nu_{=CH}$), 2924, 2853, 1666 ($\nu_{C=O}$), 1590 ($\nu_{C=C}$), 1428 (ν_{Si-Ar}), 1314, 1269, 1120 (δ_{Si-Ar}), 885, 768 ($\delta_{=CH}$), 729, 698 cm^{-1}. HRMS: calcd. for $C_{15}H_{18}OSi$ $[M]^+$ 242.1127; found 242.1125. $C_{15}H_{18}OSi$ (242.39): calcd. C 74.33, H 7.49; found C 74.39, H 7.45.

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