# A new synthetic approach to 3-methylene-1-cyclohexanols fused to five-, six- and seven-membered carbocycles through intramolecular cyclization of epoxyallylsilanes

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**Dedicated to Professor Benito Alcaide on occasion of his 60th birthday**

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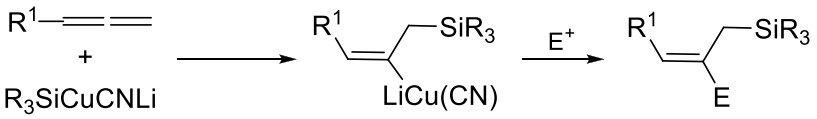
**Abstract**
Silylcupration of allene followed by conjugate addition to enones and carbonyl epoxidation provides a simple and high yielding route to epoxyallylsilanes carrying the useful phenyldimethylsilyl group. Lewis acid catalyzed intramolecular cyclization of epoxyallylsilanes is a powerful strategy for carbocyclic annulation of much potential in synthesis. In this article we show A general procedure for the synthesis of 3-methylene-1-cyclohexanols fused to five, six and seven-membered carbocycles by intramolecular cyclization of epoxyallylsilanes, which might be of great interest as an approach to bicyclic systems contained in many naturally occurring products, is described.

**Keywords:** Allylsilanes, allenes, silylcupration, epoxyallylsilanes, intramolecular cyclization, methylenecyclohexanols

## Introduction

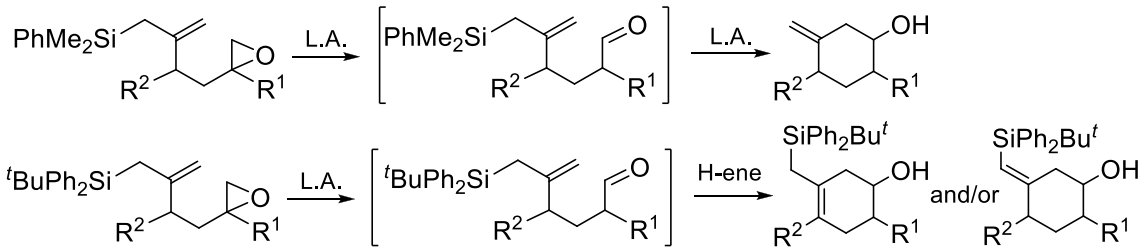
Organosilicon compounds and in particular allylsilane chemistry have attracted a great deal of attention due to the increasing number of new methodologies that allow useful synthetic transformations.[1] Over the last decade allenes have emerged as one of the best sources for the synthesis of allylsilanes.[2] They are readily attacked by silylcuprates giving rise to a great variety of allylsilanes with different substitution patterns.[3] The stoichiometry of the silylcuprate (higher or lower order) is responsible for the final regioselectivity of the reaction, leading selectively to allylsilanes when a lower order cyanosilylcuprate ($R_3SiCuCNLi$) is used.[4]




**Scheme 1**

α,β-Unsaturated oxocompounds have been successfully used in this reaction, leading to a wide range of oxo-functionalized allylsilanes, which are valuable intermediates for carbocyclic annulations.[4,5] In recent reviews, we have shown a general summary of the advances in allylsilane chemistry and their significance as precursors for the synthesis of three to seven-membered rings.[2b,6]

Despite its synthetic potential, the cyclization of epoxyallylsilanes has not been widely explored. Under Lewis acid conditions, nucleophilic substitution usually takes place at the most substituted carbon center of the epoxide[7] unless the presence of electron-withdrawing groups next to the epoxide destabilizes the developing carbocation.[8] Contrary to the normal 5-*exo*[9] or 6-*endo*[10,11] attack, we have recently reported that the acid-catalyzed reaction of epoxyallylsilanes containing the phenyldimethylsilyl[12] or the *tert*-butyldiphenylsilyl[13,14] group follows an unusual rearrangement-cyclization process which leads to methylenecyclohexanols[12] or to allyl- and vinylsilane-containing cyclohexanols[13] respectively (Scheme 2).



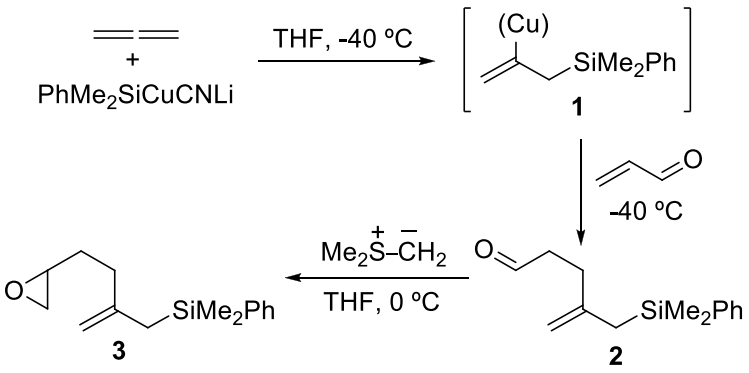

**Scheme 2**

## Results and Discussion

Epoxyallylsilanes have been previously prepared by Wittig reaction of an aldehyde with $Ph_3P{=}CHCH_2SiMe_3$ followed by epoxidation[15] and by cross metathesis of alkenyl epoxides and allylsilanes.[16] We have recently reported[12] a new route for the synthesis of epoxyallylsilanes by silylcupration of allene, followed by capture of the intermediate cuprate with enones and finally sulfur ylide-mediated epoxidation.

In the past years, we have been very actively involved in the study of the silyl- and stannylcupration of allenes and acetylenes and their synthetic applications.[2a,17] These reactions

take place by *syn*-addition of copper to one end of the multiple bond and Si or Sn to the other, affording cuprates with structures comparable to **1**. The intermediate allylsilane-vinylcuprate **1** can be captured by a great variety of electrophiles giving functionalized allylsilanes.[2a] For example, the use of α,β-unsaturated oxocompounds leads to oxoallylsilanes of type **2** which have been used as powerful building blocks for cyclopentane annelations.[2a,6a,18] Epoxidation of **2** via dimethylsulfonium-ylides gives epoxyallylsilanes **3** in high yield (Scheme 3).[12,13]

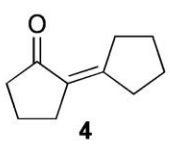
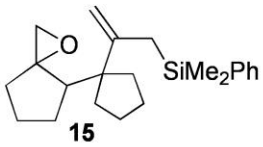
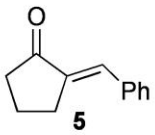
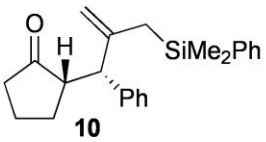
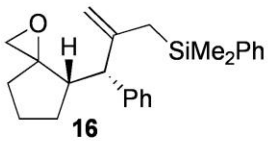
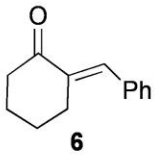
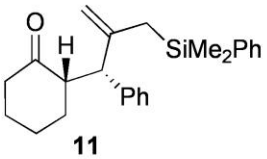
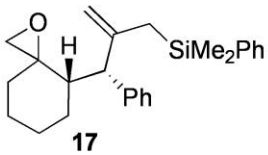
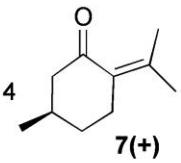
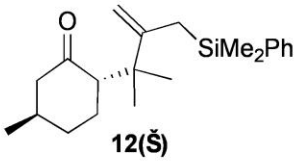
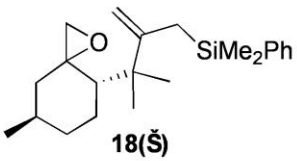
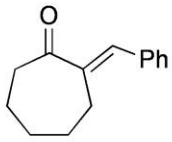
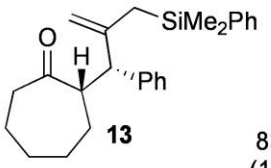
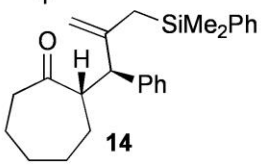
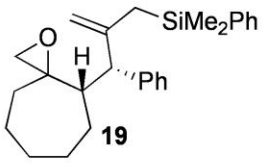
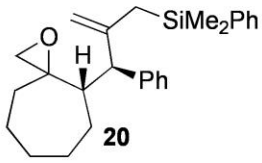



**Scheme 3**

In this paper we describe the synthesis and cyclization of epoxyallylsilanes containing five-, six- and seven-membered carbocycles as an efficient route for the construction of bicyclic 3-methylene-1-cyclohexanols systems which are present in the skeleton of many terpenoid products. As it is shown, Lewis acid-catalyzed intramolecular cyclization seems to occur with concomitant rearrangement of the epoxy group and trapping of the intermediate aldehyde (Table 2).[19]

Phenyldimethylsilylcyanocuprate[20] reacts with allene at –40ºC giving an allylsilane-vinylcopper intermediate **1**, which was treated with cyclic α,β-unsaturated ketones **4-8** to afford the products of conjugate addition **9-14** in good yield. All the reactions were carried out in the presence of $BF_3.OEt_2$ or TMSCl, which considerably increased the yield (Table 1). The cyclic oxoallylsilanes thus obtained were treated with dimethylsulfonium methylide to give in good yield the corresponding epoxides **15-20** (Table 1) apparently as a single diastereomer (single sharp signals in $^{13}C$ NMR spectra).[21] No attempt was made to assign configurations to the epoxides.

**Table 1.** Synthesis of oxo- and epoxyallylsilanes.

| entry | enone | oxoallylsilane[a] | yield(%) | epoxyallylsilane[a] | yield(%) |
|---|---|---|---|---|---|
| 1 |  **4** |  **9** | 79[b] |  **15** | 64 |
| 2 |  **5** |  **10** | 82[c] |  **16** | 65 |
| 3 |  **6** |  **11** | 85[b] |  **17** | 67 |
| 4 |  **7(+)** |  **12(Š)** | 82[b] |  **18(Š)** | 70 |
| 5[d] |  **8** |  **13** +  **14** | 83[b] (1:1) |  **19**  **20** | 65 67 |

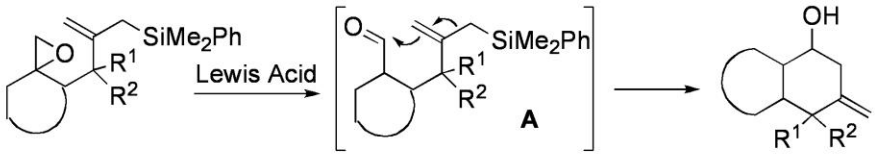
[a]THF was used as solvent. [b]$BF_3.Et_2O$ was use as activant. [c]TMSCl was use as activant. [d]Compounds **13** and **14** separated by LC (ratio 1:1).

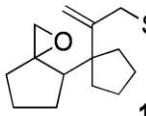
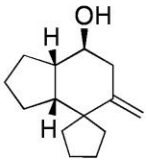
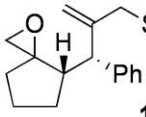
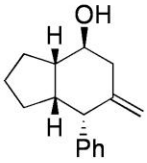
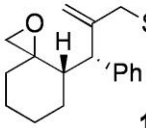
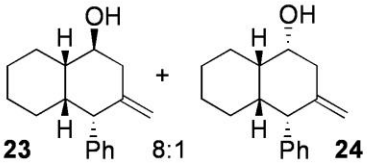
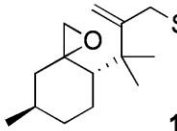
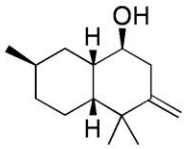
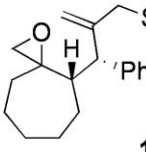
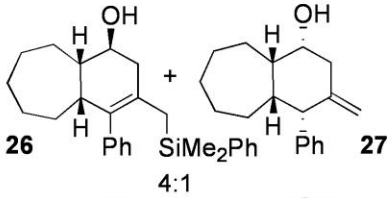
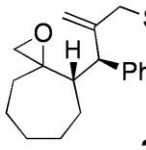
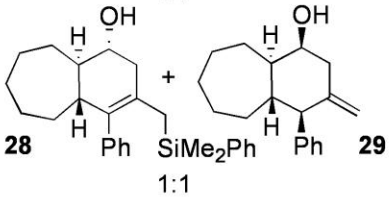
The stereochemistry of the isolated compound was established by COSY and NOESY spectra, and by examining their $^1H$ coupling constants. For the entry 5, both diastereomers **13** and **14** could be well separated by LC, and their relative stereochemistry assigned. Both were efficiently epoxidated with retention of their initial configuration.

The most remarkable feature observed in the epoxyallylsilane cyclization is the absence of products resulting from 5-*exo* or 6-*endo* cyclization (the normal epoxide cleavage). Instead, we selectively obtained bicyclic 3-methylene-1-cyclohexanols **21-29** derived from an unusual rearrangement-cyclization process (Table 2). The rearrangement of a carbonyl group into an epoxide is known process that is enhanced by the presence of acids.[22] However, this is the first time that this sequential tandem reaction is observed in epoxyallylsilanes. The substituents on the silyl group should play an important role because epoxyallylsilanes carrying TMS groups give normal products of 5-*exo* or 6-*endo* attack.[11]

The results collected in Table 2 seems to indicate that in the case of epoxyallylsilanes bearing $PhMe_2Si$ groups, rearrangement occurs faster than the nucleophilic substitution on the epoxy group. A two-step mechanism involving rearrangement to intermediate **A** followed by intramolecular Sakurai-Hosomi cyclization has been proposed (Table 2). The second step (cyclization) must be a fast reaction since aldehyde intermediates of type **A** never were isolated. To optimize the procedure, several combinations of solvent, temperature, time and Lewis acid were carefully tested. Boron trifluoride etherate in dichloromethane was proven to be the best choice for good yield (table 2). From a synthetic point of view, the reported methodology is highly attractive because it provides an efficient strategy for the construction of bicyclic 3-methylene-1-cyclohexanols fused to five-, six- and seven-membered ring systems contained in many natural products.

**Table 2.**



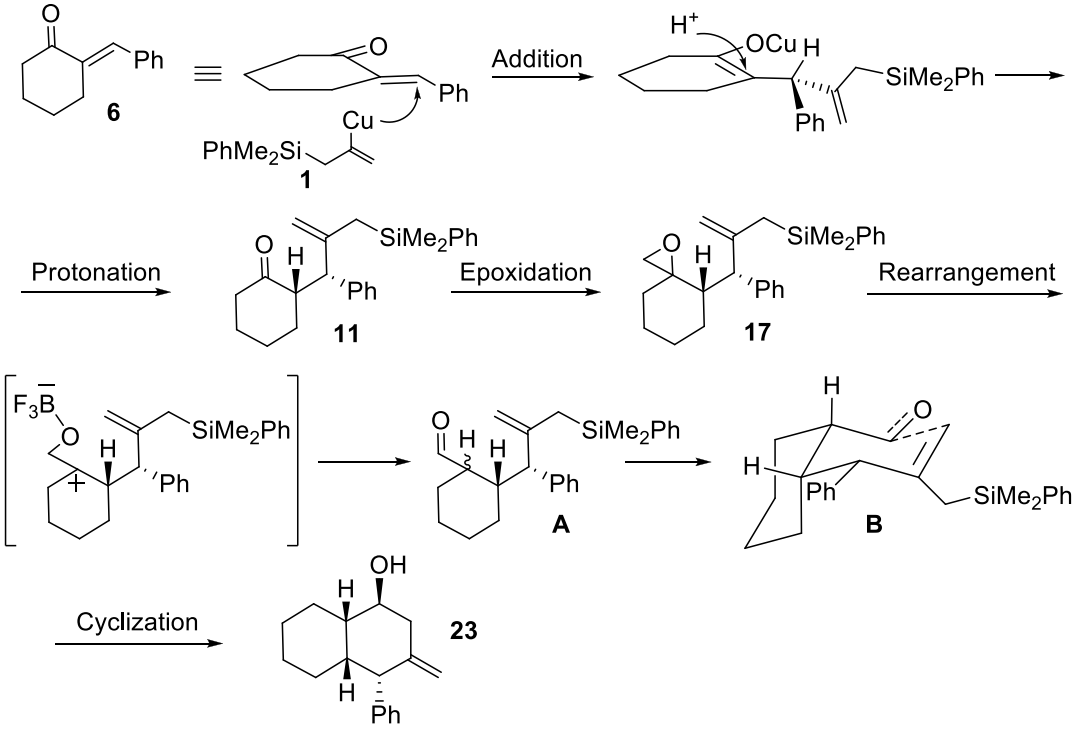

| Entry | Epoxiallylsilane | Lewis Acid[a] solvent | T (ºC) react. time (min) | Methylenecyclohexanols (ratio)[b] | Yield (%)[c] |
|---|---|---|---|---|---|
| 1 |  **15** | $BF_3.OEt_2$ DCM | 0 40 |  **21** | 89 |
| 2 |  **16** | $BF_3.OEt_2$ DCM | 0 40 |  **22** | 85 |
| 3 |  **17** | $BF_3.OEt_2$ DCM | 0 40 |  **23** 8:1 **24** | 88 |
| 4 |  **18(Š)** | $BF_3.OEt_2$ DCM | 0 40 |  **25(+)** | 88 |
| 5 |  **19** | $BF_3.OEt_2$ DCM | 0 40 |  **26** **27** 4:1 | 80 |
| 6 |  **20** | $BF_3.OEt_2$ DCM | 0 40 |  **28** **29** 1:1 | 75 |

[a]1.2 Equivalents used. [b]Separated by LC (hexanes-ethyl acetate). [c]Isolated pure compounds.

High levels of stereoselectivity were found in the formation and cyclization of epoxyallylsilanes. Except for compound **20**, all epoxyallylsilane cyclizations afford selectively *cis*-fused bicyclic systems. Moreover, formation of **26** and **27** seems to point out that, in some cases, the loss of proton competes favorably with the leaving of silyl group.

The *cis* stereochemistry of fused rings and the configurations of the phenyl and hydroxyl bearing carbons were assigned by examining their COSY and NOESY spectra. For example, in compound **23** observation of coupling patterns for H(1) δ=4.1 ppm and H(4) δ=3.53 ppm clearly indicates that they are axial (OH/Ph, *trans* di- equatorial). The former protons also have clear COSY correlations with H(8a) δ=1.86 ppm and H(4a) δ=1.95 ppm respectively. Examination of the NOE correlations between H(4a) and H(8a) shows strong cross-peaks at the coordinates, which support *cis*-fused stereochemistry. H(4a) also has an intense NOE correlation with H(4) which suggest that both protons are in a *syn* relationship (Ph/H(4a): *anti*). Finally, no cross-peaks were found for the correlation H(1)-H(8a), however *syn*-protons H(1) and $H_{eq}$(2) δ=2.23 ppm show NOE correlation, thus confirming the *anti* relationship of H(1) and H(8a).

As it is shown in the example of Scheme 4, addition of cuprate **1** to the enone **6** is followed by stereoselective protonation from the less hindered side of the enolate to give selectively oxoallylsilane **11** (8:1, Table 1). The epoxide **17** undergoes rearrangement, in the presence of boron trifluoride etherate, probably through a cationic intermediary (Scheme 4) to give an intermediate aldehyde **A** (not isolated). Subsequent cyclization to bicyclic methylenecyclohexanol **23** takes place via a low-energy transition state **B** (Scheme 4) where the bulky groups attain an equatorial conformation for minimal steric repulsions. The *cis*-fused ring pattern obtained in most cases might indicate that rearrangement give just the intermediate aldehyde **A** of *cis* stereochemistry, however, it is also feasible that the two possible α-epimers of the aldehyde **A** equilibrate, with the one which can cyclize to give *cis*-fused products reacting faster and therefore giving rise to the final products.




**Scheme 4**

In summary, a new route to methylenecyclohexanols fused to five, six and seven-membered carbocyclic rings via epoxyallylsilane cyclization is described. The stereoselectivity of the reaction allows the efficient preparation of 5/6, 6/6 and 7/6 cis-fused bicyclic systems contained in many natural products. An unusual rearrangement-cyclization tandem process has been proposed as a feasible mechanism for the general reaction reported.

## Experimental Section

**General Procedures.** Organometallic reagents were purchased from Aldrich and CuCN from Fluka. The latter was briefly dried in vacuo prior to use. 1,2-Propadiene (Allene) was supplied by Air Liquide S. A. in lecture bottles. All reactions were carried out under dry nitrogen. Elemental analyses were performed with a LECO CHNS-932 analyzer sited in the "Parque Científico Tecnológico de la UBU, Pza. Misael Bañuelos s/n, 09001 Burgos Spain". The stereochemistry of compounds has been assigned on the basis of COSY and NOESY experiments.

**Silylcupration of allene. General procedure**[4]

A solution of phenyldimethylsilyl-lithium[23] (3 mmol), prepared in THF (3 ml) from phenyldimethylchlorosilane and lithium shots (0 ºC to r.t. overnight), was added by syringe to a stirred suspension of copper(I) cyanide (269 mg, 3 mmol) in THF (5 ml) at 0 ºC, under argon atmosphere. The resulting black mixture was stirred at this temperature for 30 min, and then used immediately. The solution of the phenyldimethylsilylcyanocuprate[20] (3 mmol) in THF (8 ml) was cooled at –40 ºC and a slight excess of allene was added from a balloon. The mixture was stirred for 1 h at this temperature and the reagent **1** is ready to use. The intermediate cuprates resulting from addition to allene are stable enough in solution to be used without special precautions other than dry atmosphere, however long periods of times before using the reagent are not recommended.

**Reaction of the intermediate cuprate 1 with enones 4-8. Typical procedure**[4] $BF_3.Et_2O$ (0.38 ml, 3 mmol) was added at –78 ºC to a stirred solution of the intermediate cuprate **1** (3 mmol) and the mixture stirred for 10 min at this temperature, then 3.5 mmol of the α,β-unsaturated oxocompound **4-8** in THF (5 ml) were added dropwise at –40 ºC and the resulting mixture was kept at this temperature for 1 h. After gentle warming to 0 ºC (over 0.5 h) the mixture was quenched with aq sat. $NH_4Cl$ solution and extracted with $Et_2O$. The organic phase was dried, evaporated and chromatographed (EtOAc:hexanes) to give the corresponding oxoallylsilanes **9-14** (Table 1).

**1'-(3-Phenyldimethylsilylprop-1-en-2-yl)bi(cyclopentan)-2-one (9).** Viscous colorless oil, (79%); IR (neat): 1741 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz, δ): 7.58-7.35 (m, 5H), 4.81 (s, 1H), 4.78 (s, 1H), 2.30-1.48 (m, 15H), 1.75 (d, *J* = 13.5 Hz, 1H), 1.68 (d, *J* = 13.5 Hz, 1H), 0.38 (s, 3H, $CH_3Si$), 0.37 (s, 3H, $CH_3Si$); $^{13}C$ NMR ($CDCl_3$, 75 MHz, δ): 221.2, 148.9, 139.5, 133.6,

128.9, 127.7, 110.5, 55.5, 52.4, 40.9, 34.1, 32.2, 27.5, 23.4, 23.2, 21.0, 20.2, -2.1; Anal. Calcd. for $C_{21}H_{30}OSi$: C, 77.24; H, 9.26. Found: C, 77.55; H, 9.54.

**[2*R**,1'*R**]-2-(1'-Phenyl-2'-phenyldimethylsilylmethyl-2'-propen-1'-yl)cyclo- pentan-1-one (10).** Colorless oil, (82%); IR (neat): 1737, 1629 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz, δ): 7.70-7.15 (m, 10H), 4.89 (s, 1H), 4.83 (s, 1H), 3.51 (d, *J* = 6.7 Hz, 1H), 2.66 (q, *J* = 8.2 Hz, 1H), 2.35-2.25 (m, 1H), 2.19-2.09 (m, 2H), 1.98-1.80 (m, 3H), 1.74 (d, *J* = 14.3 Hz, 1H), 1.67 (d, *J* = 14.3 Hz, 1H), 0.44 (s, 3H, $CH_3Si$), 0.41 (s, 3H, $CH_3Si$); $^{13}C$ NMR ($CDCl_3$, 75 MHz, δ): 218.8, 146.8, 141.9, 138.9, 133.9, 129.1, 128.9, 128.2, 127.9, 126.5, 110.5, 52.6, 52.2, 38.5, 28.3, 25.5, 20.3, -2.5, -3.1; Anal. Calcd. for $C_{23}H_{28}OSi$: C, 79.26; H, 8.10. Found: C, 79.60; H, 8.38.

**[2*R**,1'*R**]-2-(1'-Phenyl-2'-phenyldimethylsilylmethyl-2'-propen-1'-yl)cyclohexan -1-one (11).** Colorless oil, (85%); IR (neat): 1725 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz, δ): 7.51-7.14 (m, 10H), 4.87 (s, 1H), 4.71 (s, 1H), 3.53 (d, *J* = 10.8 Hz, 1H), 3.09-3.01 (m, 1H), 2.26-2.21 (m, 2H), 2.12-2.04 (m, 1H), 1.94-1.89 (m, 1H), 1.81-1.70 (m, 2H), 1.66 (d, *J* = 14.5 Hz, 1H), 1.65-1.57 (m, 2H), 1.52 (d, *J* = 14.5 Hz, 1H), 0.21 (s, 3H, $CH_3Si$), 0.16 (s, 3H, $CH_3Si$); $^{13}C$ NMR ($CDCl_3$, 75 MHz, δ): 211.8, 146.6, 142.0, 139.1, 133.7, 129.1, 128.5, 128.2, 127.9, 126.4, 110.2, 53.1, 52.9, 42.4, 32.8, 29.0, 24.2, 23.1, -2.4, -2.8; Anal. Calcd. for $C_{24}H_{30}OSi$: C, 79.50; H, 8.34. Found: C, 79.87; H, 8.65.

**[2*S**,5*R**]-2-(3'-Phenyldimethylsilylmethyl-2'-methylbut-3'-en-2-yl)-5-methylcyclohexanone (12).** Colorless oil, (82%). $[\alpha]^{20}_D$ -7.1 (c 0.88, $HCCl_3$); IR (neat): 1712, 1630 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz, δ): 7.58-7.35 (m, 5H), 4.78 (s, 1H), 4.69 (s, 1H), 2.46 (dd, *J* = 12.3 and 4.4 Hz, 1H), 2.27 (dt, *J* = 11.6 and 2.7 Hz, 1H), 2.0 (t, *J* = 12.3 Hz, 1H), 1.95-1.77 (m, 3H), 1.70 (d, *J* = 16.8 Hz, 1H), 1.68 (d, *J* = 16.8 Hz, 1H), 1.38 (qd, *J* = 13.0 and 2.7 Hz, 1H), 1.25 (qd, *J* = 13.0 and 2.5 Hz, 1H), 1.15 (s, 3H), 1.13 (s, 3H), 0.99 (d, *J* = 6.1 Hz, 3H), 0.39 (s, 3H, $CH_3Si$), 0.35 (s, 3H, $CH_3Si$); $^{13}C$ NMR ($CDCl_3$, 75 MHz, δ): 211.6, 152.7, 139.7, 133.6, 128.9, 127.6, 109.1, 55.0, 52.4, 41.0, 36.1, 34.6, 28.9, 24.4, 22.3, 21.9, 19.5, -2.0, -2.2; Anal. Calcd. for $C_{21}H_{32}OSi$: C, 76.77; H, 9.82. Found: C, 77.01; H, 9.99.

**[2*R**,1'*R**]-2-(1'-Phenyl-2'-phenyldimethylsilylmethyl-2'-propen-1'-yl)cycloheptan-1-one (13).** Colorless oil, (41.5%); IR (neat): 1720 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz, δ): 7.62-7.19 (m, 10H), 5.02 (s, 1H), 4.86 (s, 1H), 3.46 (d, *J* = 10.8 Hz, 1H), 3.30 (td, *J* = 10.8 and 3.1 Hz, 1H), 2.22-2.05 (m, 3H), 1.95-1.75 (m, 4H), 1.76(d, *J* = 14.3 Hz, 1H), 1.65 (d, *J* = 14.3 Hz, 1H), 1.40-1.10 (m, 3H), 0.36 (s, 3H, $CH_3Si$), 0.34 (s, 3H, $CH_3Si$); $^{13}C$ NMR ($CDCl_3$, 75 MHz, δ): 213.7, 146.4, 141.4, 138.6, 133.4, 128.8, 128.1, 127.8, 127.5, 126.1, 108.7, 54.2, 53.9, 42.9, 30.2, 28.3, 28.1, 24.2, 23.7, -2.7, -3.3; Anal. Calcd. for $C_{25}H_{32}OSi$: C, 79.73; H, 8.56. Found: C, 80.09; H, 8.86.

**[2*R**,1'*S**]-2-(1'-Phenyl-2'-phenyldimethylsilylmethyl-2'-propen-1'-yl)cyclo- heptan-1-one (14).** Colorless oil, (41.5%); IR (neat): 1716 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz, δ): 7.55-7.05 (m, 10H), 4.72 (s, 1H), 4.61 (s, 1H), 3.49 (d, *J* = 11.0 Hz, 1H), 3.20 (td, *J* = 11.0 and 3.1 Hz, 1H), 2.62 (dt, *J* = 14.7 and 3.0 Hz, 1H), 2.47 (ddd, *J* = 14.7, 10.5 and 5.4 Hz, 1H), 1.92-1.70 (m, 2H), 1.66 (d, *J* = 14.0 Hz, 1H), 1.52 (d, *J* = 14.0 Hz, 1H), 1.40-1.11 (m, 4H), 1.07-0.85 (m, 2H), 0.41 (s, 3H, $CH_3Si$), 0.25 (s, 3H, $CH_3Si$); $^{13}C$ NMR ($CDCl_3$, 75 MHz, δ): 214.0, 149.2, 141.5, 139.5,

133.7, 129.0, 128.7, 128.2, 127.5, 126.5, 106.7, 54.1, 53.7, 43.9, 30.3, 28.9, 27.6, 26.4, 23.4, -2.6, -3.1.

**Synthesis of epoxyallylsilanes 15-20. Typical procedure**[12]

To a solution of trimethylsulphonium iodide (1 mmol) in dry THF (5 ml) was added dropwise n-BuLi (1 mmol, 1.6 M BuLi in hexanes) and the mixture stirred for 5 min at 0ºC. Then a solution of the oxoallylsilane **9-14** (0.8 mmol) in THF (1ml) is added. After stirring for an additional 30 min at 0ºC and 1 h at r.t. brine (10 ml) is added and the mixture extracted with ether, dried and evaporated to dryness. The residue was purified by chromatography to give the corresponding epoxyallylsilanes **15-20** (Table 1).

**[2-(1-(1-Oxaspiro[2.4]heptan-4-yl)cyclopentyl)allyl]dimethylphenylsilane (15).** Colorless oil, (64%); IR (neat): 1632 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$, δ): 7.60-7.35 (m, 5H), 4.87 (s, 1H), 4.76 (s, 1H), 2.68 (d, *J* = 5.6 Hz, 1H), 2.64 (d, *J* = 5.6 Hz, 1H), 2.44 (dd, *J* = 10.0 and 7.7 Hz, 1H), 1.89-1.40 (m, 16H), 0.38 (s, 6H, $(CH_3)_2Si$); $^{13}C$ NMR ($CDCl_3$, 75 MHz, δ): 149.3, 139.8, 133.6, 128.8, 127.7, 110.0, 65.6, 55.0, 54.1, 42.7, 35.6, 32.9, 31.4, 30.2, 24.0, 23.5, 22.1, 20.3, -2.0; Anal. Calcd. for $C_{22}H_{32}OSi$: C, 77.59; H, 9.47. Found: C, 77.90; H, 9.75.

**[4*R**,1'*R**]-4-(1'-Phenyl-2'-phenyldimethylsilylmethyl-2'-propen-1'-yl)-1-oxaspiro[2,4]heptane (16)**. Colorless oil, (65%); IR (neat): 3050, 1625 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$, δ): 7.52-7.14 (m, 10H), 4.88 (s, 1H), 4.63 (s, 1H), 3.08 (d, *J* = 11 Hz, 1H), 2.69-2.60 (m, 1H), 2.27 (d, *J* = 5 Hz, 1H), 2.12-1.92 (m, 2H), 1.78-1.71 (m, 1H), 1.66 (d, *J* = 14.2 Hz, 1H), 1.51 (d, *J* = 5 Hz, 1H), 159-1.48 (m, 4H), 0.22 (s, 3H, $CH_3Si$), 0.20 (s, 3H, $CH_3Si$); $^{13}C$ NMR ($CDCl_3$, 75 MHz, δ): 148.8, 142.5, 139.2, 133.6, 128.9, 128.7, 127.7, 126.1, 108.7, 65.7, 53.6, 49.8, 42.4, 34.2, 32.1, 23.7, 21.7, -2.6, -2.9.

**[4*R**,1'*R**]-4-(1'-Phenyl-2'-phenyldimethylsilylmethyl-2'-propen-1'-yl)-1-oxaspiro[2,5]octane (17)**. Colorless oil, (67%); IR (neat): 3066, 1629, 1248, 1112, 874 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$, δ): 7.56-7.25 (m, 10H), 4.96 (s, 1H), 4.75 (s, 1H), 3.36 (d, *J* = 11.4 Hz, 1H), 2.36 (d, *J* = 4.6 Hz, 1H), 2.26 (d, *J* = 4.6 Hz, 1H), 2.25-2.15 (m, 1H), 1.90-1.40 (m, 8H), 1.62 (s, 2H), 0.22 (s, 3H, $CH_3Si$), 0.16 (s, 3H, $CH_3Si$); $^{13}C$ NMR ($CDCl_3$, 75 MHz, δ): 147.3, 142.5, 139.4, 133.7, 129.0, 128.6, 128.1, 127.8, 126.3, 110.0, 60.6, 53.7, 52.5, 41.2, 33.3, 29.2, 25.2, 23.3, 22.3, -2.4, -3.1; Anal. Calcd. for $C_{25}H_{32}OSi$: C, 79.73; H, 8.56. Found: C, 79.98; H, 8.77.

**[4*S**,7*R**]-4-(3'-Phenyldimethylsilylmethyl-2'-methylbut-3'-en-2-yl)-7-methyl-1-oxaspiro[2,5]octane (18).** Colorless oil, (70%). $[\alpha]^{20}_D$ -20.4 (c 1..32, $HCCl_3$); IR (neat): 1624, 1248 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz, δ): 7.62-7.43 (m, 5H), 4.88 (s, 1H), 4.70 (s, 1H), 3.43 (d, *J* = 4.5 Hz, 1H), 2.37 (d, *J* = 4.5 Hz, 1H), 1.95-1.84 (m, 3H), 1.80 (dd, *J* = 12.5 and 2.9 Hz, 1H), 1.75 (s, 2H), 1.59 (dd, *J* = 12.5 and 2.9 Hz, 1H), 1.51 (broad d, *J* = 12.7 Hz, 1H), 1.14-1.04 (m, 2H), 0.98 (s, 3H), 0.92 (d, *J* = 7.5 Hz, 3H), 0.91 (s, 3H), 0.40 (s, 3H), 0.39 (s, 3H); $^{13}C$ NMR ($CDCl_3$, 75 MHz, δ): 155.6, 139.6, 133.6 128.9, 127.8, 109.0, 62.0, 54.2, 46.1, 44.2, 41.5, 35.8, 31.0, 29.3, 25.6, 22.1 21.6, 19.7, -1.8, -1.9; Anal. Calcd. for $C_{22}H_{34}OSi$: C, 77.13; H, 10.00. Found: C, 77.39; H, 10.21.

**[4*R**,1'*R**]-4-(1'-Phenyl-2'-phenyldimethylsilylmethyl-2'-propen-1'-yl)-1-oxaspiro[2,6]nonane (19)**. Colorless oil, (65%); IR (neat): 1638 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$, δ): 7.51-7.20 (m, 10H), 4.89 (s, 1H), 4.67 (s, 1H), 3.17 (d, *J* = 11.5 Hz, 1H), 2.42 (d, *J* = 4.7 Hz, 1H), 2.29 (d, *J* = 4.7 Hz, 1H), 2.22-2.15 (m, 1H), 1.75-1.40 (m, 10H), 1.61 (d, *J* = 15.1 Hz, 1H), 1.53 (d, *J* = 15.1 Hz, 1H), 0.15 (s, 3H), 0.12 (s, 3H); $^{13}C$ NMR ($CDCl_3$, 75 MHz, δ): 147.5, 142.2, 139.4, 133.6, 128.9, 127.8, 127.7, 126.2, 109.8, 60.9, 56.0, 53.9, 42.8, 34.4, 30.2, 27.3, 26.6, 25.5, 22.1, -2.4, -3.2; Anal. Calcd. for $C_{26}H_{34}OSi$: C, 79.94; H, 8.77. Found: C, 80.21; H, 9.01.

**[4*R**,1'*S**]-4-(1'-Phenyl-2'-phenyldimethylsilylmethyl-2'-propen-1'-yl)-1-oxaspiro[2,6]nonane (20)**. Colorless oil, (67%); IR (neat): 1640, 1248 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$, δ): 7.45-7.15 (m, 10H), 5.01 (s, 1H), 4.76 (s, 1H), 3.11 (d, *J* = 10.2 Hz, 1H), 2.57 (d, *J* = 4.8 Hz, 1H), 2.52 (d, *J* = 4.8 Hz, 1H), 2.21 (ddd, *J* = 10.2, 8.9 and 4.3 Hz, 1H), 1.73 (d, *J* = 14.7 Hz, 1H), 1.69-1.47 (m, 7H), 1.58 (d, *J* = 14.7 Hz, 1H), 1.40-1.22 (m, 3H), 0.15 (s, 3H), 0.12 (s, 3H); $^{13}C$ NMR ($CDCl_3$, 75 MHz, δ): 148.3, 142.0, 139.4, 133.5, 129.1, 128.8, 128.1, 127.6, 126.3, 109.4, 61.5, 55.4, 55.1, 43.6, 35.0, 29.2, 27.0, 26.8, 25.8, 24.3, -2.5, -2.9.

**Cyclization of epoxyallylsilanes 15-20. Typical procedure**[12]

$BF_3.OEt_2$ (1.2 mmol) was slowly added to a solution of the epoxyallylsilane (1 mmol) in DCM (10 ml) under nitrogen at 0ºC. After stirring for 40 min at this temperature brine was added and the mixture extracted with ether. The organic layer was dried over $MgSO_4$, the solvent was evaporated and the residue purified by chromatography to give the corresponding methylenecyclohexanols **21-29** (Table 2).

**[3a'*R**,7'*S**,7a'*S**]-5'-Methyleneoctahydrospiro[cyclopentane-1,4'-inden]-7'-ol (21)**. Colorless oil, (89%); IR (neat): 3622, 3373, 1640, 1039, 887 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$, δ): 4.83 (s, 1H), 4.70 (s, 1H), 3.34 (td, *J* = 11.6 and 4.9 Hz, 1H), 2.42 (dd, *J* = 12.2 and 5.0 Hz, 1H), 2.23 (t, *J* = 11.6 Hz, 1H), 1.92-1.80 (m, 4H), 1.79-1.50 (m, 11H), 1.45-1.32 (m, 1H), 1.29-1.15 (m, 1H); $^{13}C$ NMR ($CDCl_3$, 75 MHz, δ): 149.4 (C), 108.9 ($CH_2$), 71.6 (CH), 51.8 (CH), 50.6 (C), 46.9 (CH), 42.5 ($CH_2$), 38.9 ($CH_2$), 34.3 ($CH_2$), 27.9 ($CH_2$), 25.4 ($CH_2$), 23.8 ($CH_2$), 23.3 ($CH_2$), 21.2 ($CH_2$); Anal. Calcd. for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.79; H, 10.97.

**[3a*S**,4*S*,7*R**,7a*S**]-6-Methylene-7-phenyloctahydro-1*H*-inden-4-ol (22)**. White solid, (85%). m.p. 80.5-81.3 ºC; IR (neat): 3627, 3422, 1650, 903 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$, δ): 7.34-7.21 (m, 5H), 4.96 (s, 1H), 4.94 (s, 1H), 3.75 (d, *J* = 4 Hz, 1H), 3.57-345 (m, 1H), 2.75 (dt, *J* = 13.5 and 5.1 Hz, 1H), 2.57 (td, *J* = 13.5 and 2.0 Hz, 1H), 2.02-1.87 (m, 1H), 1.86-1.54 (m, 6H), 1.32-1.20 (m, 1H), 1.12-1.00 (m, 1H); $^{13}C$ NMR ($CDCl_3$, 75 MHz, δ): 149.7 (C), 142.8 (C), 130.3 (CH), 129,2 (CH), 127.3 (CH), 115.0 ($CH_2$), 77.5 (CH), 52.1 (CH), 48.9 ( CH), 47.3 (CH), 44.5 ($CH_2$), 29.3 ($CH_2$), 29.1 ($CH_2$), 23.4 ($CH_2$); Anal. Calcd. for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.40; H, 9.07.

**[1*S**,4*R**,4a*S**,8a*S**]-3-Methylene-4-phenyldecahydronaphthalen-1-ol (23)**. White solid, (78%). m.p. 107.3-108.1 ºC; IR (neat): 3626, 3367, 1644, 902 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$,

δ): 7.36-7.20 (m, 5H), 4.95 (d, *J* = 1.8 Hz, 1H), 4.75 (d, *J* = 1.8 Hz, 1H), 4.10 (td, *J* = 10.9 and 5.1 Hz, 1H), 3.53 (d, *J* = 3.0 Hz, 1H), 2.84 (dd, *J* = 12.8 and 5.1 Hz, 1H), 2.23 (dd, *J* = 12.8 and 10.9 Hz, 1H), 2.17 (dd, *J* = 10.4 and 2.4 Hz, 1 H), 1.95 (dq, *J* = 12.6 and 4.1 Hz, 1H), 1.90-1.82 (m, 1H), 1.81-1.73 (m, 1H), 1.71-1.35 (m, 5H), 1.23 (dd, J = 12.6 and 3.5 Hz, 1H),1.22-1.10 (m, 1H); $^{13}$C NMR ($CDCl_3$, 75 MHz, δ): 144.6 (C), 140.0 (C), 130.6 (CH), 127.7 (CH), 126.6 (CH), 110.9 ($CH_2$), 66.8 (CH), 55.0 (CH), 45.9 ($CH_2$),45.3 (CH), 43.6 (CH), 26.6 ($CH_2$) 26.2 ($CH_2$), 22.7 ($CH_2$), 20.4 ($CH_2$); Anal. Calcd. for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found: C, 84.60; H, 9.44.

**[1*R**,4*R**,4a*S**,8a*S**]-3-Methylene-4-phenyldecahydronaphthalen-1-ol (24)**. Colorless oil, (10%); IR (neat): 3569, 3460, 1640, 1068, 883 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$, δ): 7.47-7.19 (m, 5H), 5.06 (s, 1H), 4.81 (s, 1H), 3.98-3.91 (m, 1H), 3.54 (d, *J* = 4.5 Hz, 1H), 2.83 (ddd, *J* = 14.3, 3.5 and 1.6 Hz, 1H), 2.43 (dd, *J* = 14.3 and 3.1 Hz, 1H), 1.92-1.82 (m, 2H), 1.80-1.50 (m, 4H), 1.49-1.39 (m, 2H), 1.29-1.15 (m, 2H), 0.98-0.81 (m, 1H); $^{13}$C NMR ($CDCl_3$, 75 MHz, δ): 146.7 (C), 142.4 (C), 128.7 (CH), 128.2 (CH), 126.2 (CH), 113.5 ($CH_2$), 71.1 (CH), 54.7 (CH), 41.5 (CH), 39.9 ($CH_2$), 39.4 (CH), 30.8 ($CH_2$), 29.9 ($CH_2$), 26.2 ($CH_2$), 24.2 ($CH_2$).

**[1*S*,4a*R*,7*R*,8a*S*]-4,4,7-Trimethyl-3-methylenedecahydronaphthalen-1-ol (25)**. Colorless oil, (88%). $[\alpha]^{20}_D$ +15.3 (c 0.62, $HCCl_3$); IR (neat): 3331, 1640, 1048, 889 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$, δ): 4.78 (t, *J* = 1.6 Hz, 1H), 4.64 (t, *J* = 1.6 Hz, 1H), 3.82 (td, *J* = 11.1 and 5.5 Hz, 1H), 2.49 (dd, *J* = 12.7 and 5.5 Hz, 1H), 2.33 (dd, *J* = 12.7 and 11.1 Hz, 1H), 2.15-2.04 (m, 2H), 1.78-1.46 (m, 5H), 1.36 (dt, *J* = 12.5 and 4.1 Hz, 1H), 1.18 (s, 3H), 1.04 (s, 3H), 1.03-0.94 (m, 2H), 0.85 (d, *J* = 6.5 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz, δ): 151.5 (C), 108.6 ($CH_2$), 68.9 (CH), 48.4 (CH), 42.1 ($CH_2$), 40.0 (CH), 39.4 (C), 35.5 ($CH_2$), 35.4 ($CH_2$), 28.6 ($CH_3$), 25.9 (CH), 25.5 ($CH_3$), 23.4 ($CH_2$), 22.7 ($CH_3$); Anal. Calcd. for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 81.01; H, 11.86.

**[1*S**,4a*R**,9a*S**]-3-(Phenyldimethylsilylmethyl)-4-phenyl-2,4a,5,6,7,8,9,9a-octahydro-1*H*-benzo[7]annulen-1-ol (26)**. Colorless oil, (64%); IR (neat): 3627, 3450, 1644, 1548, 1248, 1111 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$, δ): 7.40-7.20 (m, 8H), 7.03-6.90 (m, 2H), 3.77 (td, *J* = 8.0 and 4.8 Hz, 1H), 2.72-2.64 (m, 1H), 2.36 (dd, *J* = 16.2 and 4.8 Hz, 1H), 1.95 (dd, *J* = 16.2 and 8.0 Hz, 1H), 1.87 (d, *J* = 14.0 Hz, 1H), 1.86-1.72 (m, 3H), 1.70-1.51 (m, 4H), 1.46 (d, *J* = 14.0 Hz, 1H), 1.45-1.33 (m, 3H), 1.27-1.02 (m, 2H), 0.25 (s, 3H), 0.19 (s, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz, δ): 142.8 (C), 139.3 (C), 134.7 (C), 133.5 (CH), 129.5 (CH), 128.8 (CH), 127.8 (CH), 127.6 (CH), 126.9 (C), 125.8 (CH), 70.5 (CH), 44.4 (CH), 43.9 (CH), 40.1 ($CH_2$), 31.0 ($CH_2$), 29.3 ($CH_2$), 29.0 ($CH_2$), 28.5 ($CH_2$), 25.5 ($CH_2$), 23.9 ($CH_2$), -1.9 (2x$CH_3$); Anal. Calcd. for $C_{26}H_{34}OSi$: C, 79.94; H, 8.77. Found: C, 80.21; H, 8.90.

**[1*R**,4*R**,4a*S**,9a*S**]-3-Methylene-4-phenyldecahydro-1*H*-benzo[7]annulen-1-ol (27)**. Colorless oil, (16%); IR (neat): 3620, 3397, 1646, 1033 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$, δ): 7.40-7.20 (m, 5H), 5.05 (s, 1H), 4.81 (s, 1H), 3.90 (dd, *J* = 6.2 and 3.1 Hz, 1H), 3.62 (d, *J* = 4.2 Hz, 1H), 2.65-2.55 (m, 2H), 2.41 (dt, *J* = 9.4 and 4.2 Hz, 1H), 2.01 (dq, *J* = 10.2 and 2.7 Hz, 1H), 1.97-1.72 (m, 5H), 1.63-1.20 (m, 6H); $^{13}$C NMR ($CDCl_3$, 75 MHz, δ): 144.6 (C), 141.0 (C), 129.4 (CH), 127.8 (CH), 125.8 (CH), 112.0 ($CH_2$), 72.2 (CH), 53.5 (CH), 45.9 ($CH_2$), 43.9 (CH), 42.7 (CH), 31.7 ($CH_2$), 29.8 ($CH_2$), 29.2 ($CH_2$), 25.0 ($CH_2$), 24.6 ($CH_2$).

**[1*R**,4a*R**,9a*R**]-3-(Phenyldimethylsilylmethyl)-4-phenyl-2,4a,5,6,7,8,9,9a-octahydro-1*H*-benzo[7]annulen-1-ol (28)**. Colorless oil, (38%); IR (neat): 3627, 3420, 1456, 903 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$, δ): 7.37-7.20 (m, 8H), 6.96-6.90 (m, 2H), 3.92 (dt, *J* = 8.6 and 4.2 Hz, 1H), 2.75 (dt, *J* = 12.3 and 4.6 Hz, 1H), 2.20-2.03 (m, 2H), 1.99-1.90 (m, 1H), 1.83-1.70 (m, 3H), 1.68-1.05 (m, 9H), 0.92-0.83 (m, 1H), 0.23 (s, 3H), 0.17 (s, 3H); $^{13}C$ NMR ($CDCl_3$, 75 MHz, δ): 142.5 (C), 139.3 (C), 134.0 (C), 133.5 (CH), 129.4 (CH), 128.8 (CH), 127.8 (CH), 127.6 (CH), 127.3 (C), 125.7 (CH), 70.6 (CH), 44.2 (CH); 43.7 (CH), 37.4 ($CH_2$), 32.2 ($CH_2$), 31.4 ($CH_2$), 29.4 ($CH_2$), 25.6 ($CH_2$), 24.1 ($CH_2$), 22.7 ($CH_2$), -1.9 (2x$CH_3$); Anal. Calcd. for $C_{26}H_{34}OSi$: C, 79.94; H, 8.77. Found: C, 80.30; H, 8.98.

**[1*S**,4*S**,4a*S**,9a*R**]-3-Methylene-4-phenyldecahydro-1*H*-benzo[7]annulen-1-ol (29)**. Colorless oil, (37%); IR (neat): 3579, 3441, 1641, 1005 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$, δ): 7.32-7.10 (m, 5H), 4.82 (s, 1H), 4.14 (s, 1H), 3.94-3.90 (m, 1H), 2.96 (d, *J* = 11.5 Hz, 1H), 2.54 (s, 2H), 1.93 (qt, *J* = 11.0 and 2.4 Hz, 1H), 1.85-1.70 (m, 3H), 1.60-1.50 (m, 6H), 1.45-1.10 (m, 3H); $^{13}C$ NMR ($CDCl_3$, 75 MHz, δ): 147.9 (C), 141.8 (C), 129.3 (CH), 128.2 (CH), 126.2 (CH), 113.6 ($CH_2$), 73.4 (CH), 56.4 (CH), 49.2 (CH), 44.1 ($CH_2$), 43.3 (CH), 32.7 ($CH_2$), 32.5 ($CH_2$), 27.6 ($CH_2$), 25.6 ($CH_2$), 25.3 ($CH_2$); Anal. Calcd. for $C_{18}H_{24}O$: C, 84.32; H, 9.44. Found: C, 84.70; H, 9.73.

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