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3,4-Functionalized silacyclopentanes. Synthesis of *trans*-4-amino-, azido- and alkyloxy-1-silacyclopentan-3-ols from 6-oxa-3-silabicyclo[3.1.0]hexanes

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Abstract

The synthesis of novel *trans*-3,4-bifunctional silacyclopentane derivatives based on the reaction of 6-oxa-3-silabicyclo[3.1.0]-hexanes with aminated and oxygenated nucleophiles is described. One compound has potential as an antidepressant and anxiolytic agent.

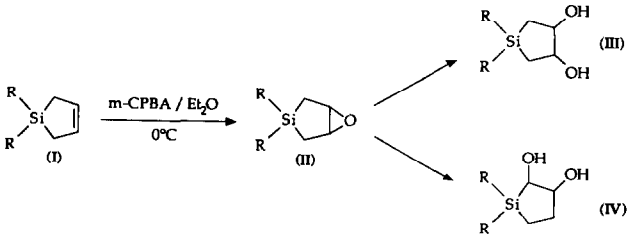
Keywords: Silicon; Synthesis; Silacyclopentanols; Serotonin antagonist

1. Introduction

Epoxides are particularly useful electrophilic reagents and intermediates in organic synthesis, mainly owing to their ring-opening reaction by nucleophiles, leading generally to *trans*-1,2-difunctionalized systems.

We have previously reported [1] the synthesis of the readily available 6-oxa-3-silabicyclo[3.1.0]hexanes **II**, obtained by oxidation of the corresponding 1-silacyclopent-3-enes **I** with 3-chloroperbenzoic acids (m-CPBA) and the easy preparation of *cis*- and *trans*-1-silacyclopentan-2,3- and -3,4-diols **III** and **IV** (Scheme 1).

With the common presence of β-amino alcohol groups in many biologically active compounds and our synthetic programme directed towards the preparation of novel structural types of silylated compounds, we undertook to investigate the synthesis of silylated β-amino alcohols. To our knowledge, only 1,1-dimethyl-4-(methylamino)-1-silacyclopentan-3-ol has been described in the silicon series [2]. This compound was prepared in 50% yield by a direct condensation of methylamine (25% aqueous solution) with the epoxide **IIa** (70°C, sealed ampoule, 5.5 h).



Scheme 1.

We report here the diastereoselective preparation of novel bifunctional silacyclopentanes **Va–i**, **VIIIa,b**, **IXa**, **Xa**, **XIa–d** and **XIIa,b**, by addition of various nucleophiles such as bromomagnesium alkylamides, azides, alcohols and free carboxylic acids to 6-oxa-3-silabicyclo[3.1.0]hexanes **IIa–c**.

2. Synthesis of *trans*-4-amino-1-silacyclopentan-3-ols (V), (X) and *trans*-4-azido-1-silacyclopentan-3-ols (IX)

Several classical chemical methods for preparing β-amino alcohols have been described, mainly using the direct ring-opening reaction of the corresponding epoxides by amines, often under drastic conditions. For example, weakly nucleophilic amines required elevated temperatures and sterically bulky amines afforded low

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R = Me, IIa
R = Ph, IIb
R = *p*F-Ph, IIc

(Va-i) (§ Table 1)

Scheme 2.

regiocontrol of the ring opening. These difficulties can be overcome by the utilization of either organometallic complexes as activating agents [3] (activation–complexation reaction on the oxygen atom of the oxirane) or of several metal amides as basic reagents including lithium [4], magnesium [5], organocopper [6], tin [7] or aluminium [8] amides.

We studied the addition of free amines and their corresponding metal amides to the readily available epoxide **IIa–c** [9] in order to prepare the *trans*-4-dialkylamino-1-silacyclopentan-3-ols **V** (Scheme 2).

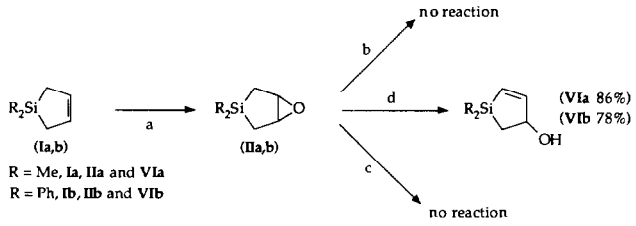
We started by studying the ring-opening reaction of epoxides **IIa,b** with diethylamine and sodium diethylamide. The epoxides **IIa,b** are stable towards diethylamine under different reaction conditions (EtOH or H_2O reflux; neat; sealed tube, 50°C) and sodium diethylamide in refluxing THF (Scheme 3).

With lithium diethylamide (strong base, poor nucleophile), the epoxide **IIa,b** underwent total transformation into the corresponding allylic alcohols **VIa,b** according to a process described previously [10]. These results are summarized in Scheme 3.

The preparation of various silylated β-amino alcohols **Va–i** was performed using bromomagnesium dialkylamides as nucleophilic agents (weak bases but strong nucleophiles) according to the method described by Caubère and co-workers [5] (Scheme 4). This route allowed the synthesis of a variety of *trans*-4-dialkylamino-1-silacyclopentan-3-ols **Va–i** in moderate-to-good yields as single diastereoisomers (Table 1) [11].

In none of these experiments were the products produced by abstraction of the α-proton observed.

Bromomagnesium dialkylamides were easily prepared from the corresponding secondary amines and Grignard reagents (EtMgBr or PhMgBr) in THF (20–



(Ia,b) (IIa,b)

R = Me, Ia, IIa and VIa
R = Ph, Ib, IIb and VIb

(VIa 86%)
(VIb 78%)

a: m-$ClC_6H_4CO_3H$, Et_2O, 0°C

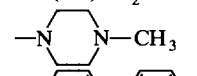
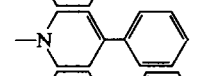
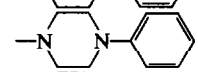
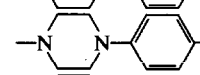
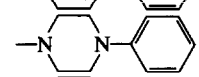
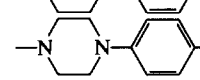
b: Et_2NH/ H_2O or EtOH reflux; neat, sealed tube, 50°C

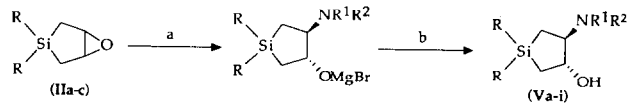
c: $NaEt_2N$, THF, reflux

d: $LiEt_2N$, hexane, 0°C,then H_2O

Scheme 3.

Table 1
Nature of R, R^1, R^2 in compounds V_{a-i}

R	NR^1R^2	Compounds V: yield (%)
Me	$-NMe_2$	**Va**: 72
Me	$-NEt_2$	**Vb**: 71
Me	$-N(Me)CH_2Ph$	**Vc**: 78
Me		**Vd**: 24
Ph		**Ve**: 56
Ph		**Vf**: 71
Ph		**Vg**: 69
*p*F-Ph		**Vh**: 56
*p*F-Ph		**Vi**: 67



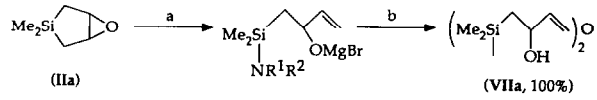
(IIa-c) (Va-i)

R = Me, **IIa**; R = Ph, **IIb**; R = *p*F-Ph, **IIc**
a : R^1R^2NMgBr / THF, 20-35°C (§ Table 1)
b : H_2O

Scheme 4.

35°C, 1 h). Treatment of the crude bromomagnesium dialkylamide solutions with the epoxides **IIa–c** in THF (room temperature, overnight) afforded **Va–i**, which were readily purified by flash chromatography on silica gel. The temperature of the reaction is crucial. Above 35°C, nucleophilic addition to the silicon atom followed by ring opening takes place to give only **VIIa** (Scheme 5) [12].

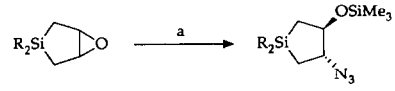
Oxirane ring cleavage with trimethylsilyl azide promoted by a catalytic amount of Lewis acid [$(^iPrO)_3Al$] in dichloromethane was accomplished with the epoxides **IIa,b** (Scheme 6) [13]. Thus *trans*-4-azido-3-tri-



(IIa) (VIIa, 100%)

a : R^1R^2NMgBr / THF, >35°C (R^1, R^2; § Table 1)
b : H_2O

Scheme 5.

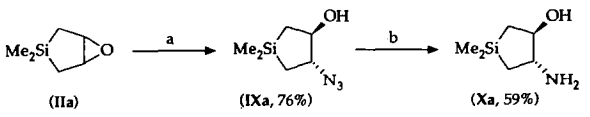


R = Me, IIa
R = Ph, IIb

R = Me, VIIIa, 64%
R = Ph, VIIIb, 92%

a: Me_3SiN_3, ε($Pr^iO)_3Al$, CH_2Cl_2, 20°C

Scheme 6.



a: NaN_3/ NH_4Cl, MeCOMe, H_2O, 40 h, reflux
b: $LiAlH_4$, Et_2O, 3 h reflux then H_2O

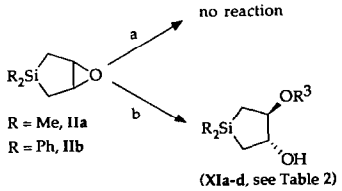
Scheme 7.

methylsilyloxy-1,1-dimethyl-(and 1,1-diphenyl)-1-silacyclopentanes **VIIIa,b** were obtained in good yield (64 and 92%, respectively). They were purified either by column chromatography on silica gel or by distillation.

A two-step synthesis, shown in Scheme 7, led to 4-amino-1-silacyclopentan-3-ol (**Xa**). In the first step, sodium azide reacts with **IIa** in a mixture of polar solvents (acetone/water), in the presence of ammonium chloride [14]. The 4-azido-1-silacyclopentan-3-ol **IXa** was then distilled and reduced by $LiAlH_4$ in diethyl ether to give the crystalline compound **Xa** in 45% overall yield.

3. Synthesis of *trans*-4-alkyloxy-1-silacyclopentan-3-ols (XI) and *trans*-4-acetoxy-1-silacyclopentan-3-ols (XII)

Whereas **IIa,b** are unreactive towards methanol, ethanol, 1-propanol and 1-butanol under several experimental conditions (50–80°C) [15] various *trans*-4-alkyloxy-1-silacyclopentan-3-ols (**XIa–d**) were obtained by reaction of **IIb** with alcohols at 0°C in the presence of catalytic amount of Lewis acid (boron trifluoride–diethyl ether complex) in almost quantitative yields (Scheme 8 and Table 2). This reaction seems to be general and applicable to various other alcohols. No products resulting from additions to silicon were isolated under these reaction conditions.

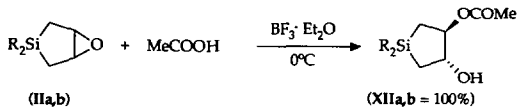


R^3 = Me, Et, Bu^t, $CH{\equiv}C\text{-}CH_2$-
a: R^3OH, neat, 50°C, R = Me [13]
b: R^3OH, $BF_3 \cdot Et_2O$, 0°C, R = Ph

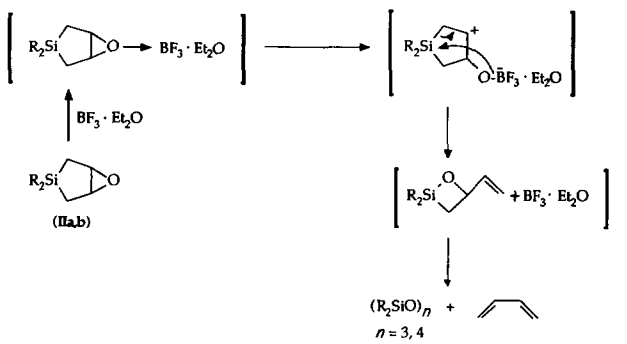
Scheme 8.

Table 2
Nature of R, R^3 in products **XIa–d**

R	Ph	Ph	Ph	Ph
R^3	Me	Et	^{t}Bu	$HC{\equiv}C\text{-}CH_2$-
Product **XI**	**XIa**	**XIb**	**XIc**	**XId**
Yield (%)	95	93	90	93



Scheme 9.



Scheme 10.

Lewis acid catalysis is also effective for the reaction between **IIa,b** and organic acids. The reaction between acetic acid and **IIa,b** in the presence of a catalytic amount of boron trifluoride–diethyl ether complex (0°C, 1 h) led quantitatively to *trans*-4-acetoxy-1-silacyclopentan-3-ols **XIIa,b** (Scheme 9). Compounds **XIIa,b** were also isolated in quantitative yield by heating **IIa,b** in neat acetic acid under reflux for 1 h [1].

However, this catalyst is ineffective for silaoxirane ring opening by amines since complexation of BF_3 occurs preferentially on the nitrogen atom of the base (Me_2NH or Et_2NH) even at 0°C.

In the absence of such a base, the boron trifluoride–diethyl ether complex decomposes the silacyclopentane **IIa,b** even at 20°C to give butadiene and siloxanes (Scheme 10).

4. Biological activity of *trans*-4-amino-1-silacyclopentan-3-ols (V–i)

The last step in our study was to test the biological properties of compounds **Ve–i** as serotonin antagonists. Serotonin (5-HT, 5-hydroxytryptamine) is considered to be involved in thermoregulation, appetite, memory, pain, sleep, sexual behaviour and psychiatric disorders such as anxiety and depression [16].

The silylated β-amino alcohols **Ve–i** showed moderate-to-high affinities for the 5-HT_{2A} receptor. The inhibitory concentration (IC_{50}), which is the concentration required to cause a reduction of 50% in the amount of specific binding of [^{3}H] ketanserin [16] are 25 nM (**Ve**), 4.4 nM (**Vf**), 2.2 nM (**Vg**), 23 nM (**Vh**) and 26 nM (**Vi**).

Central 5-HT_{2A} antagonistic activity in vivo was assessed by the ability of compounds to antagonize

mescaline-induced head twitches in mice [17]. A member of this series, **Vg**, displayed potent antagonist activity after oral administration. The dose (ED_{50}) which conferred protection on 50% of the animals was about 10 mg kg^{-1}.

5. Conclusion

We have shown that the 6-oxa-3-silabicyclo[3.1.0]-hexanes **IIa–c** are useful synthons for the preparation of a novel class of 3,4-functional-1-silacyclopentanes such as 4-amino-, 4-azido- and 4-alkyloxy-1-silacyclopentan-3-ols under mild conditions.

The preparation of a variety of *trans*-dialkylamino-1-silacyclopentan-3-ols (**Va–i**) was achieved in moderate-to-high yields using bromomagnesium diethylamides as nucleophilic agents, whereas *trans*-4-alkyloxy-1-silacyclopentan-3-ols (**XI**) were easily prepared from **IIa,b** using the corresponding alcohols and boron trifluoride–diethyl ether complex as catalyst.

Compound **Vg** has potential as an antidepressant and anxiolytic agent.

Further investigations on the scope of these reactions and on the pharmacological properties of **Vg** are in progress.

6. Experimental

Solvents were either distilled immediately before use from sodium benzophenone ketyl or dried over 4Å molecular sieves. Commercially available reagents were used as received.

The progress of the reactions was monitored by TLC on silica gel (Merck Kieselgel 60 F_{254}).

Melting points were determined using a Reicher–Kofler apparatus and are uncorrected.

^1H NMR spectra were recorded on a Bruker AC 80, 200 WP spectrometer and ^{13}C NMR on a Bruker AC 200 spectrometer with broad-band proton decoupling. IR spectra were recorded on a Perkin-Elmer 1600 FT or a Nicolet 60 SXR spectrophotometer using samples in KBr pellets. GC/MS was carried out at an ionizing voltage of 70 eV on a Hewlett-Packard 5989A mass spectrometer. A Hewlett-Packard 5890 gas chromatograph was coupled to the mass spectrometer and was used as the MS inlet.

Mass spectra were obtained on a Finigan 3000 apparatus at an ionizing voltage of 70 eV.

All glassware was dried overnight in an oven at 120°C. The apparatus was assembled and was then flame-dried while being swept with argon or dinitrogen. All reactions and transfers were conducted under purified argon or dinitrogen.

Elemental analyses were performed at the Centre de Recherches de Vitry-Alforville (Rhône-Poulenc Rorer) or at the Ecole Nationale Supérieure de Chimie de Toulouse.

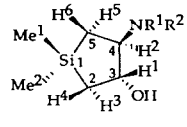
Flash column chromatography was performed on silica gel (Merck Kieselgel, 203–400 mesh).

6.1. General procedure for the preparation of trans-4-amino-1-silacyclopentan-3-ols Va–d

6.1.1. Method A: Typical procedure for the preparation of compounds Va–d

Amido magnesium reagents were prepared according Caubère and co-workers [5].

The Grignard reagent was prepared from magnesium turnings (1.21 g, 50 mmol) and ethyl bromide (4.36 g, 40 mmol) in diethyl ether (20 ml) and introduced into a 250 ml two-necked round-bottomed flask equipped with a Teflon-covered magnetic stirring bar and a reflux condenser topped with a calcium chloride drying tube. An excess of the desired amine in THF (10 ml) was then slowly added. Stirring was continued for 2 h under heating (35°C). After cooling the dimethyl silaoxirane **IIa** (2.5 g, 20 mmol) in diethyl ether (10 ml) was slowly introduced in order to hold the temperature below 20°C. Stirring was continued for 12 h at room temperature. The mixture was then hydrolysed with a saturated solution of ammonium chloride, washed several times with water and extracted with diethyl ether. Organic layers were dried over sodium sulphate. Solvents were removed and compounds **Va–d** were distilled under reduced pressure.



$NR^1R^2 = NMe_2$, Va
$NR^1R^2 = NEt_2$, Vb
$NR^1R^2 = NMe(CH_2Ph)$, Vc
$NR^1R^2 =$ N⟨⟩N–Me, Vd

trans-4-N,N-Dimethylamino-1,1-dimethyl-1-silacyclopentan 3-ol (Va).

According to the general procedure, oxirane **IIa** (2.5 g, 20 mmol) was allowed to react with Me_2NMgBr solution obtained from dimethylamine (3 g, excess) in THF (10 ml) and an ethereal solution of ethylmagnesium bromide, prepared from magnesium turnings (1.21 g, 50 mmol) and ethyl bromide (4.36 g, 40 mmol) in Et_2O (20 ml). After the usual workup, **Va** was purified by fractional distillation: 2.27 g, yield 72%, b.p. 84°C/9 mm Hg. Anal Found: C, 55.70; H, 11.00. $C_8H_{19}NOSi$ calc.: C, 55.44; H, 11.05%. IR: 3453 (OH), 2950, 2903, 2866, 2827, 2782, 1456, 1410, 1384, 1338, 1251, 1211, 1172, 1148, 1127, 1075, 1022, 978, 839, 812, 731, 703, 637 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz) δ: 0.03 (s, 3H, Me^1Si), 0.05 (s, 3H, Me^2Si), 0.52 (m, 3H, H^4, H^5, H^6), 1.15 (dd, J (H^3H^4) = 13.8 Hz; ^3J (H^3H^1) = 7.0 Hz, 1H,

H^3), 2.08 (s, 6H, NMe_2), 2.36 (ddd, ^3J (H^2H^1) = 10.1 Hz; ^3J (H^2H^5) = 12.2 Hz; ^3J (H^2H^6) = 6.6 Hz, 1H, H^2), 3.45 (ddd, ^3J (H^1H^2) = ^3J (H^1H^4) = 10.1 Hz; ^3J (H^1H^3) = 7.0 Hz, 1H, H^1), 3.50 (m, 1H, OH). ^{13}C NMR ($CDCl_3$, 200 MHz) δ: −0.75 (Me^1Si), −0.72 (Me^2Si) 4.35 (C^5), 19.86 (C^2), 40.11 (Me_2N), 71.60 (C^4), 71.83 (C^3). GC MS *m/z* (relative intensity%): 173 (3) M^+, 129 (7) ($[Me_2SiCH_2CHNMe_2]^+$), 114 (27) ($[M - Me_2SiH]^+$), 75 (100) ($[Me_2SiOH]^+$), 59 (14) ($[Me_2SiH]^+$), 45 (12) ($[Me_2NH]^+$), 44 (6) ($[CH_3CHO]^+$).

trans-4-N,N-Diethylamino-1,1-dimethyl-1-silacyclopentan-3-ol (***Vb***).

As detailed before, silaoxirane **IIa** (2.5 g) and Et_2NMgBr lead to 2.47 g of **Vb**, yield 71%, b.p. 50°C/0.1 mmHg. Anal. Found: C, 59.95; H, 11.4. $C_{10}H_{23}NOSi$ calc.: C, 59.64; H, 11.51%. IR: 3465 (OH), 2967, 2907, 2873, 2822, 1470, 1451, 1419, 1381, 1337, 1295, 1272, 1250, 1205, 1165, 1146, 1104, 1063, 1027, 1000, 975, 845, 785, 747, 730, 703, 639 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz) δ: 0.11 (s, 3H, Me^1Si), 0.13 (s, 3H, Me^2Si), 0.85 (m, 4H, H^3, H^4, H^5, H^6), 1.01 (t, J = 6.8 Hz, 6H, $(CH_2CH_3)_2$), 2.35 (q, J = 6.8 Hz, 4H, $(CH_2CH_3)_2$), 2.42 (m, 1H, H^2), 3.49 (m, 1H, H^1). ^{13}C NMR ($CDCl_3$, 200 MHz) δ: −0.76 (Me^1Si), −0.67 (Me^2Si), 7.21 (C^5), 14.44 (CH_3CH_2N), 19.22 (C^2), 43.41 (CH_3CH_2N), 66.13 (C^4), 71.51 (C^3). GC MS *m/z* (relative intensity, %): 201 (20) M^+, 172 (9) ($M - Et)^+$, 157 (28) ($[M - Et - Me]^+$), 142 (31) ($[M - Et - 2Me]^+$), 128 (100) ($[M - Et_2NH]^+$), 98 (97) ($[M - Et_2NH - 2Me]^+$), 75 (58) ($[Me_2SiOH]^+$), 73 (14) ($[Et_2NH]^+$), 59 (31) ($[Me_2SiH]^+$), 58 (12) ($[Me_2Si]^+$).

trans-4-N,N-Methyl(benzyl)amino-1,1-dimethyl-1-silacyclopentan-3-ol (***Vc***).

From *N*-methylbenzylamine (5.0 g, 40 mmol) and 2.5 g (20 mmol) of **IIa**, **Vc** (3.85 g) was obtained after distillation, yield 78% b.p. 98°C/0.05 mmHg. Anal. Found: C, 67.22; H, 9.01. $C_{14}H_{23}NOSi$ calc.: C, 67.42; H, 9.29%. IR: 3470 (OH), 3085, 3061, 3027, 2949, 2904, 2847, 2796, 1644, 1602, 1494, 1453, 1417, 1370, 1250, 1217, 1164, 1146, 1112, 1075, 1023, 982, 840, 813, 739, 699, 646 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz) δ: 0.16 (s, 6H, Me_2Si), 0.62 (m, 3H, H^4, H^5, H^6), 1.28 (dd, J (H^3H^4) = 13.8 Hz; ^3J (H^3H^1) = 7.0 Hz 1H, H^3), 2.11 (s, 3H, NMe), 2.44 (m, 1H, H^2), 3.50 (dd, $J(H_AH_B)$ = 13.0 Hz, 2H, H_A, H_B), 3.60 (m, 1H, OH), 3.65 (m, 1H, H^1). ^{13}C NMR ($CDCl_3$, 200 MHz) δ: −0.59 (Me^1Si), −0.51 (Me^2Si), 5.71 (C^5), 19.71 (C^2), 36.05 (N*Me*), 58.69 (CH_2Ph), 71.00 (C^4), 71.79 (C^3), 127.10, 128.03, 128.86, 139.40 (C arom.). GC MS *m/z* (relative intensity, %): 249 (5) M^+, 204 (4) ($[M - CH_3CHOH]^+$), 158 (6) ($[M - C_7H_7]^+$), 134 (6) ($[PhCH_2N(Me)CH_2]^+$), 121 (3) ($[PhCH_2N(Me)H]^+$), 114 (100) ($[Me_2SiCH_2$-$CH{=}NMe]^+$), 101 (4) ($[Me_2SiCH_2CHO]^+$), 91 (69) ($[C_7H_7]]^+$), 75 (19) ($[Me_2SiOH]^+$), 59 (19) ($[Me_2SiH]^+$), 45 (4) ($[CH_3CHOH]^+$), 42 (11) ($[C_3H_6]^+$).

trans-4-(N-Methylpiperazino-1,1-dimethyl-1-silacyclopentan-3-ol (***Vd***).

From 4.0 g (40 mmol) of 1-methylpiperazine and 2.5 g (20 mmol) of epoxide **IIa**, **Vd** (1.1 g) was obtained after distillation, yield 24%, b.p. 90% 0.05 mmHg. Anal. Found: C, 57.76; H, 10.58. $C_{11}H_{24}N_2OSi$ calc.: C, 57.84; H, 10.59%. IR: 3474 (OH), 2934, 2842, 2796, 2768, 1456, 1420, 1368, 1353, 1338, 1286, 1251, 1183, 1174, 1147, 1139, 1073, 1049, 1028, 1012, 980 cm^{-1}. ^1H NMR ($CDCl_3$ 80 MHz) δ: 0.13 (s, 3H, Me^1Si), 0.14 (s, 3H, Me^2Si), 0.57 (m, 2H, H^5, H^6), 1.24 (m, 2H, H^3, H^4), 2.26 (s, 3H, NMe), 2.48 (m, 8H, CH_2CH_2N), 3.50 (m, 2H, H^1, H^2). ^{13}C NMR ($CDCl_3$, 200 MHz) δ: −0.70 (Me^1Si), −0.63 (Me^2Si), 6.40 (C^5), 19.63 (C^2), 46.10 (MeN), 56.60 (CH_2N), 71.03 (C^4), 71.87 (C^3), GC MS *m/z* (relative intensity, %): 228 (3) M^+, 210 (6) ($[M\text{-}H_2O]^+$), 200 (11) ($[M\text{-}C_2H_4]^+$), 183 (4) ($[M\text{-}CH_3CHOH]^+$), 169 (3) ($[M\text{-}C_2H_5CHOH]^+$), 155 (3) ($[M\text{-}C_3H_7CHOH]^+$), 115 (6) ($[Me_2SiCH_2CH_2CHO]^+$), 113 (100) ($[MeN(CH_2)_4NCH_2]^+$), 101 (14) ($[Me_2Si$-$CH_2CHO]^+$), 100 (9) ($[MeN(CH_2)_4NH]^+$), 85 (36) ($[HN(CH_2)_4N]^+$), 75 (40) ($[Me_2SiOH]^+$), 70 (92) ($[C_4H_8N]^+$), 59 (25) ($[Me_2SiH]^+$), 44 (10) ($[CH_3$-$CHO]^+$), 42 (22) ($[C_3H_6]^+$).

6.1.2. Method B: typical procedure for the preparation of compounds Ve–i

Phenylmagnesium bromide (1.25 eq., 3 M solution in diethyl ether) was added dropwise to a solution of the desired amine (1.25 eq.) in dry THF (45 ml) at such a rate that the temperature was maintained at 35°C. The resulting mixture was then stirred at this temperature for 1 h. After cooling to 20°C, a solution of silaoxirane **IIa** or **IIb** (1 eq.) in THF (20 ml) was added. Stirring was continued for 20 h at room temperature and the reaction mixture was quenched with water (100 ml) then extracted with diethyl ether (3 × 50 ml). The combined organic extracts were dried over sodium sulphate, filtered and concentrated under reduced pressure to give crude compounds **Ve–i** which were purified by flash column chromatography on silica gel.

trans-4-(4-Phenyl-1,2,3,6-tetrahydropyridinyl)-1,1-diphenyl-3-hydroxy-1-silacyclopentane (***Ve***).

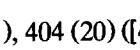
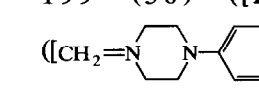
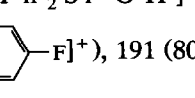
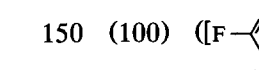
The above procedure was performed on **IIb** (6.3 g; 25 mmol), phenylmagnesium bromide (10 ml; 30 mmol), 4-phenyl-1,2,3,6-tetrahydropyridine (4.77 g; 30 mmol) and THF (45 ml). The residue was purified by flash column chromatography on silica gel using dichloromethane/methanol (98:2) as eluent. The resulting orange solid was recrystallized from boiling 2-propanol to deliver 2.9 g (56% yield) of *trans*-4-(4-phenyl,1,2,3,6-

tetrahydropyridinyl)-1,1-diphenyl-3-hydroxy-1-silacyclopentane as a white solid, m.p. 142°C. Anal. Found (0.12% H_2O) C, 78.79; H, 7.10; N, 3.33. $C_{27}H_{29}NOSi$ calc. C, 78.79; H, 7.10; N, 3.40%. NMR ($CDCl_3$, 200 MHz) δ (ppm): from 1.00 to 1.90 (m, 4H, $-CH_2-Si-CH_2-$), from 2.60 to 3.10 (m, 5H, $N-CH_2-CH_2-C$ and $N-CH-$), 3.40 (m, 2H, $N-CH_2-CH=$), 4.05 (m, 1H, $CH-OH$), 6.10 (t, 1H, $-CH=C$), from 7.25 to 7.60 (m, 15H aromatics). IR (KBr): 3440 (ν, O–H), 3070, 3055, 3025 (ν C–H benzene and ethylene), 2960, 2910 (ν_{as} CH_2), 2830, 2820 (ν_s CH_2), 1650 (ν C=C), 1600, 1590, 1495, 1430, 1115, 750, 730, 700, 505 cm^{-1}. MS *m/z* (relative intensity, %): 411 (8) M^+, 199 (40) ($[Ph_2Si=OH]^+$), 184 (100) ($[Ph_2SiH_2]^+$).

*trans-4-(4-Phenylpiperazinyl)-1,1-diphenyl-3-hydroxy-1-silacyclopentane (**Vf**).*

The above procedure was performed on **IIb** (12.6 g; 50 mmol), phenylmagnesium bromide (20 ml; 60 mmol), 4-phenyl-1-piperazine (9.7 g; 60 mmol) and THF (45 ml). The residue was purified by flash column chromatography on silica gel using dichloromethane/methanol (99:1) as eluent. The resulting orange solid was recrystallized from boiling 2-propanol to deliver 14.2 g (71% yield) of *trans*-4-(4-phenylpiperazinyl)-1,1-diphenyl-3-hydroxy-1-silacyclopentane) (**Vf**) as a pale-yellow solid, m.p. 123°C. Anal. Found: C, 75.65; H, 7.49; N, 6.63. $C_{26}H_{30}N_2OSi$ calc.: C, 75.32; H, 7.29; N, 6.76%. NMR ($CDCl_3$, 200 MHz) δ (ppm): from 0.90 to 1.90 (m, 4H, $-CH_2-Si-CH_2-$), from 2.60 to 3.30 (m, 8H, 4 $N-CH_2-$), 2.80 (m, 1H, $N-CH-$), 3.70 (s, 1H, $-OH$), 3.95 (m, 1H, $CH-OH$), from 6.90 to 7.60 (m, 15H aromatics). IR (KBr): 3420 (ν O–H), 3065, 3045, 3020 (ν C–H benzene) 2945, 2900 (ν_{as} CH_2), 2880, 2825 (ν_s CH_2), 1595, 1575, 1490, 1450, 1425, 1110, 730, 695, 500 cm^{-1}. MS *m/z* (relative intensity, %): 414 (30) M^+, 396 (20) ($[414-H_2O]^+$), 386 (70) ($[414-C_2H_4]^+$), 238 (65) ($[Ph_2Si(CH_2)_4]^+$), 210 (30) ($[238-C_2H_4]^+$), 199 (50) ($[Ph_2Si=OH]^+$), 183 (50) ($[Ph_2SiH]^+$), 132 (60) ($[PhN(=CH_2)-CH=CH_2]^+$).

*trans-4-[1-(4-Fluorophenyl)piperazinyl]-1,1-diphenyl-3-hydroxy-1-silacyclopentane (**Vg**).*

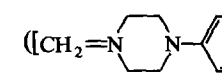
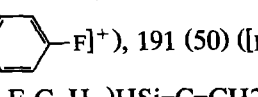
The above procedure was performed on **IIb** (12.6 g; 50 mmol), phenylmagnesium bromide (20 ml; 60 mmol), 1-(4-fluorophenyl)piperazine (10.8 g; 60 mmol) and THF (50 ml). The residue was purified by flash column chromatography on silica gel using dichloromethane/methanol (99:1) as eluent. The resulting orange solid was recrystallized from boiling 2-propanol to deliver 11.1 g (69% yield) of *trans*-4-[1-(4-fluorophenyl)piperazinyl]-1,1-diphenyl-3-hydroxy-1-silacyclopentane (**Vg**) as a white solid, m.p. 123°C. Anal. Found: C, 72.48; H, 6.90; F, 4.22; N, 6.43. $C_{26}H_{29}FN_2OSi$ calc.: C, 72.18; H, 6.76; F, 4.39; N, 6.48%. NMR ($CDCl_3$, 200 MHz) δ (ppm): from 1.00 to 1.90 (m, 4H, $-CH_2Si-CH_2-$), from 2.40 to 3.20 (m, 8H, 4 $N-CH_2-$), 2.80 (m, 1H, $N-CH-$), 3.60 (bs, 1H, $-OH$), 3.90 (m, 1H, $CHOH$), from 6.85 to 7.05 (m, 4H aromatics, NC_6H_4F), from 7.40 to 7.60 (m, 10H aromatics). IR (KBr): 3445 (ν O–H), 3070, 3045, 3020, 3005, 3000 (ν C–H benzene), 2950, 2900 (ν_{as} CH_2), 2875, 2825 (ν_s CH_2), 1585, 1510, 1490, 1425, 1115, 825, 815, 735, 700, 505 cm^{-1}. MS *m/z* (relative intensity, %): 432 (10) M^+, 414 (5) ($[432-H_2O]^+$), 404 (20) ($[432-C_2H_4]^+$), 238 (25) (), 199 (30) ($[Ph_2Si=OH]^+$), 193 (70) (), 191 (80) (), 150 (100) (), 137 (45) ($[Ph(CH_3)Si=OH]^+$), 122 (60) ($[Ph(H)Si=O]^+$), 105 (30) ($[PhSi]^+$).

*trans-4-(4-Phenylpiperazinyl)-1,1-di(4-fluorophenyl)-3-hydroxy-1-silacyclopentane (**Vh**).*

The above procedure was performed on **IIc** (2.34 g; 8 mmol), phenylmagnesium bromide (3.33 ml; 10 mmol), 4-phenyl-1-piperazine (1.58 g; 10 mmol) and THF (10 ml). The resulting oil was dissolved in diethyl ether (25 ml) and a solution of HCl (2 M; 9 ml) was added to yield 2.23 g (56%) of *trans*-4-(4-phenylpiperazinyl)-1,1-di(4-fluorophenyl)-3-hydroxy-1-silacyclopentane hydrochloride as a pale-yellow solid, m.p. 263°C. Anal. Found: C, 64.20; H, 6.30; Cl, 7.30; F, 7.7; N 5.90. $C_{26}H_{28}F_2N_2OSi \cdot HCl$ Calc.: C, 64.12; H, 6.00; Cl, 7.28; F, 7.80; N, 5.75%. NMR ($(D_3C)_2SO$, 200 MHz) δ (ppm): from 1.20 to 1.90 (m, 4H, $-CH_2-Si-CH_2-$), from 3.10 to 3.90 (m, 9H, $N-(CH_2)_2-N$ and $N-CH-$), 4.40 (m, 1H, $CH-OH$), 6.00 (s, 1H, $-OH$), from 6.80 to 7.70 (m, 13H aromatics, $2-C_6H_4F$ and $-C_6H_5$), 10.80 (s, 1H, $N-H$). IR (KBr): 3270 (ν O–H), 3100, 3070, 3030, ν C–H benzene), 2970, 2930 (ν_{as} CH_2), 2845 (ν_s CH_2), 2670, 2460 (ν N^+-H), 1605, 1590, 1500, 1115, 825, 735, 700, 500 cm^{-1}. MS *m/z* (relative intensity, %): 449 (15) ($[M-1]^+$), 431 (5) ($[449-H_2O]^+$), 421 (15) ($[449-C_2H_4]^+$), 260 (5) ($[(p\text{-}FC_6H_4)_2Si(CH_3)CH=CH_2]^+$), 245 (15) ($[(p\text{-}C_6H_4)_2SiCH=CH_2]^+$), 219 (30 ($[(p\text{-}FC_6H_4)_2SiH]^+$), 175 (100) ($[PhSiC_4H_4]^+$), 132 (95) ($[PhN(=CH_2)CH=CH_2]^+$).

*trans-4-[1-(4-Fluorophenyl)piperazinyl]-1,1-di(4-fluorophenyl)-3-hydroxy-1-silacyclopentane (**Vi**).*

The above procedure was performed on **IIc** (2.34 g; 8 mmol), phenylmagnesium bromide (3.33 ml; 10 mmol), 1-(4-fluorophenyl)piperazine (1.76 g; 10 mmol) and THF (10 ml). The resulting oil was dissolved in diethyl ether (25 ml) and a solution of HCl (2 M, 9 ml) was added to yield 2.74 g (67%) of *trans*-4-[1-(fluorophenyl)piperazinyl]-1,1-di(4-fluorophenyl)-3-hydroxy-1-silacyclopentane hydrochloride as a pale yellow solid,

m.p. 257°C. Anal. Found. C, 61.50; H, 5.90; Cl, 7.00; F, 11.20; N, 5.60. $C_{26}H_{27}F_3N_2OSi \cdot HCl$ Calc.: C, 61.83; H, 5.59; Cl, 7.02; F, 11.28; N, 5.55%. NMR ($(D_3C)_2SO$, 200 MHz) δ (ppm): from 1.20 to 1.90 (m, 4H, $-CH_2-Si-CH_2-$), from 3.10 to 3.80 (m, 8H, $N-(CH_2)_4-N$), 3.90 (m, 1H, N–CH–), 4.40 (m, 1H, CH–OH), 6.00 (s, 1H, –OH), from 7.00 to 7.70 (m, 12H aromatics, 3 $-C_6H_4F$) 10.80 (s, 1H, N–H). IR (KBr): 3280 (ν OH), 3060, 3020 (ν CH benzene), 2960, 2925, 2900 (ν_{as} CH_2), 2840 (ν_s CH_2), 2660, 2450 (ν N^+–H), 1585, 1510, 1500, 1110, 825, 520 cm^{-1}. MS *m/z* (relative intensity, %): 468 (15) M^+, 450 ($[468-H_2O]^+$), 440 ($[468-C_2H_4]^+$), 275 (5) ($[(p\text{-}F\text{-}C_6H_4)_2Si(CH_3)-CH_2-CO]^+$), 260 (5) ($[(p\text{-}F\text{-}C_6H_4)_2Si(CH_3)-CH{=}CH_2]^+$), 219 (25) ($[(p\text{-}F\text{-}C_6H_4)_2SiH]^+$), 193 (50)  , 191 (50)  , 150 (100) ($[p\text{-}F\text{-}C_6H_4)HSi{=}C{=}CH2]^+$), 137 (35) ($[Ph(CH_3)Si{=}OH]^+$), 122 ($[(Ph)HSi{=}O]^+$).

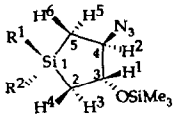
trans-4-Azido-3-trimethylsilyloxyl-1,1-dimethyl-1-silacyclopentane (***VIIIa***).

A 100 ml two-necked, round-bottomed flask equipped with a Teflon-covered magnetic stirring bar, a reflux condenser and topped with a calcium chloride drying tube was flushed with dinitrogen and charged with 0.2 g (0.98 mmol) of $Al(^iPrO)_3$ in 2 ml of dichloromethane. Azidotrimethylsilane (1.7 g, 15 mmol) was introduced by syringe. The mixture was stirred for 2 h at room temperature then neat epoxide **IIa** (1.28 g, 10 mmol) was added dropwise. The resulting mixture was stirred at room temperature for 24 h and filtered. The precipitate was washed several times with diethyl ether. The solvents were removed by evaporation and the residual liquid was distilled. We thus obtained (1.56 g) of **VIIIa**, yield 64%, b.p. 110°C/14 mmHg. IR: 2956, 2903, 2097 (N_3), 1408, 1365, 1332, 1301, 1251, 1189, 1157, 1147, 1086, 1046, 952, 882, 843 (O–$SiMe_3$), 749, 732 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz) δ: 0.12 (s, 9H, $OSiMe_3$), 0.15 (s, 6H, Me_2Si), 0.82 (m, 4H, H^3, H^4, H^5, H^6), 3.65 (m, 2H, H^1, H^2). ^{13}C NMR ($CDCl_3$, 200 MHz) δ: −0.87 (Me^1Si), −0.78 (Me^2Si), 0.15 ($OSiMe_3$), 16.58 (C^5), 21.85 (C^2), 68.37 (C^4), 77.79 (C^3).

trans-4-Azido-3-trimethylsilyloxy-1,1-diphenyl-1-silacyclopentane (***VIIIb***).

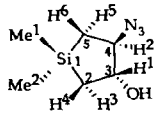
Compound **VIIIb** was prepared by the above procedure.

From **IIb** (1.0 g, 4 mmol), **VIIIb** (1.32 g) was obtained, after purification with a silica gel column using a pentane–diethyl ether (80:20) as eluent, yield 92%. IR: 3069, 3049, 3020, 2956, 2902, 2096 (N_3), 1486, 1428, 1406, 1334, 1301, 1251, 1188, 1147, 1115, 1085, 1045, 997, 949, 877, 842, 797, 731, 698 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz) δ: 0.24 (s, 9H, $OSiMe_3$), 1.52 (m, 4H, H^3, H^4, H^5, H^6), 4.08 (m, 2H, H^1, H^2), 7.3–7.8 (m, 10H, Ph_2Si). ^{13}C NMR ($CDCl_3$, 200 MHz) δ: 0.27 ($O-SiMe_3$), 15.71 (C^5), 20.72 (C^2), 68.49 (C^4), 77.83 (C^3), 128.07, 128.21, 128.32, 129.99, 130.03, 134.72, 134.83 (C arom.).



trans-4-Azido-1,1-dimethyl-1-silacyclopentan 3-ol (***IXa***).

Sodium azide (3.0 g, 46 mmol) and epoxide **IIa** (2.5 g, 20 mmol) in acetone were placed in a 150 ml two-necked round-bottomed flask equipped with a Teflon-covered magnetic stirring bar. Ammonium chloride solution (1.5 g, 28 mmol in 40 ml of H_2O) was then introduced and the reaction mixture was heated under reflux for 24 h with stirring. After cooling to room temperature, the mixture was extracted with diethyl ether (3 × 50 ml). The organic layers were combined and dried over sodium sulphate. The volatile solvents were removed by evaporation and the brown residue was distilled under reduced pressure. Azido alcohol **IXa** (2.25 g) was thus obtained in 76% yield, b.p. 53°C/0.05 mmHg.

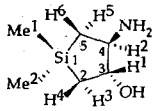


IR: 3381 (OH), 2955, 2903, 2100 (N_3), 1702, 1411, 1253, 1146, 1091, 1045, 996, 938, 845, 817, 733, 705, 631 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz) δ: 0.14 (s, 3H, Me^1Si), 0.16 (s, 3H, Me^2Si), 0.73 (m, 2H, H^5, H^6), 1.27 (m, 2H, H^3, H^4), 2.73 (m, 1H, OH), 3.59 (m, 2H, H^1, H^2). ^{13}C NMR ($CDCl_3$, 200 MHz) δ: −0.88 (Me_2Si), 16.44 (C^5), 20.48 (C^2), 68.69 (C^4), 76.52 (C^3). CI *m/z*: 189 ($[M+18]^+$). GC MS *m/z* (relative intensity, %): 128 (5) ($[Me_2SiCH_2CH_2N_3]^+$), 102 (23) ($[Me_2SiCH_2CHOH]^+$), 101 (20) ($[Me_2SiCH_2CHO]^+$), 100 (25) ($[Me_2SiN_3]^+$), 75 (40) ($[Me_2SiOH]^+$), 72 (100) ($[Me_2SiN]^+$), 59 (28) ($[Me_2SiH]^+$), 43 (47) ($[CH_3CHO]^+$), 29 (11) ($[HCO]^+$).

trans-4-Amino 1,1-dimethyl 1-silacyclopentan-3-ol (***Xa***).

Lithium aluminium hydride (1.0 g, 26 mmol) and 10 ml of diethyl ether were introduced in a 50 ml two-necked round-bottomed flask equipped with a reflux condenser which was topped with a calcium chloride drying tube. Azido alcohol **IXa** (2.0 g, 11.7 mmol) in 10 ml of diethyl of ether was syringed into the flask. The mixture was heated under reflux for 4 h, cooled and partially hydrolysed with H_2O (3 ml). The precipitate

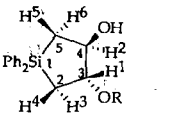
was filtered off (sintered crucible) and washed with diethyl ether. White crystals of the amino alcohol (1.0 g) of **Xa** were isolated by slow evaporation of solvents,



yield 59%, m.p. 45°C. IR (CCl_4): 3280, 2954, 2898, 1581, 1408, 1377, 1251, 1147, 1064, 1035, 954, 844, 796, 786, 746 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz) δ: 0.12 (s, 3H, Me^1Si), 0.13 (s, 3H, Me^2Si), 0.56 (m, 2H, H^5, H^6), 1.17 (m, 2H, H^3, H^4), 1.95 (m, 1H, OH), 1.95 (m, 2H, NH_2), 2.75 (m, 1H, H^2), 3.46 (m, 1H, H^1). ^{13}C NMR ($CDCl_3$, 200 MHz) δ: −0.76 (Me^1Si), −0.72 (Me^2Si), 21.48 (C^5), 21.53 (C^2), 59.11 (C^4), 78.67 (C^3). CI *m/z*: 146 ($[M+1]^+$). GC/MS *m/z* (relative intensity, %): 145 (2) M^+, 130 (4) ($[M-Me]^+$, 102 (8) ($[Me_2SiCH_2CHOH]^+$), 101 (24) ($[Me_2SiCH_2CHNH_2]^+$), 86 (100) ($[Me_2SiCH_2N]^+$), 75 (24) ($[Me_2SiOH]^+$), 74 (30) ($[Me_2SiNH_2]^+$), 59 (20) ($[Me_2SiH]^+$), 58 (12) ($[Me_2Si]^+$), 43 (18) ($[CH_3CHO]^+$).

6.2. General procedure for the preparation of 4-alkyloxy-1-silacyclopentan-3-ols (*XI*)

Epoxide **IIb** (1.0 g) and 10 ml of required alcohol were placed in a 50 ml two-necked round-bottomed flask equipped with a Teflon-covered bar and a reflux condenser topped with a calcium chloride drying tube. The mixture was stirred and cooled to 0°C, then 3 drops of the Lewis acid ($BF_3 \cdot Et_2O$) were added. The resulting stirred mixture was allowed to reach room temperature, treated with 20 ml of a saturated solution of ammonium chloride then extracted with a mixture of pentane and diethyl ether (3 × 50 ml). The combined organic layers were washed several times with water and dried over sodium sulphate. The solvents were removed under reduced pressure and the crude product was purified on a silica gel column using pentane/diethyl ether (80:20) mixture as eluent.



R = Me, XIa
R = Et, XIb
R = Bu^t, XIc
R = CH_2-C≡CH, XId

trans-3-Methoxy-1,1-diphenyl-1-silacyclopentan-4-ol (***XIa***).

Methanol was used in the above procedure and 1.06 g of **XIa** were isolated as a colourless liquid in 95% yield. Anal. Found: C, 71.70; H, 7.00. $C_{17}H_{20}O_2Si$ calcd: C, 71.79, H, 7.08%. IR: 3420 (associated OH), 3067, 3047, 2952, 2902, 2821, 1958, 1886, 1822, 1770, 1486, 1450, 1428, 1361, 1333, 1261, 1178, 1143, 1114, 1039, 996, 943, 797, 733, 699 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz) δ: 1.17 (m, 2H, H^3, H^4), 1.81 (m, 2H, H^5, H^6), 2.98 (m, 1H, OH), 3.44 (s, 3H, OMe), 3.65 (m, 1H, H^1), 4.09 (m, 1H, H^2), 7.3–7.8 (m, 10H arom.). ^{13}C NMR ($CDCl_3$, 200 MHz) δ: 14.99 (C^2), 18.15 (C^5), 56.77 (OMe), 76.38 (C^3), 87.00 (C^4), 128.22, 129.89, 134.77, 135.21 (C arom.). GC MS *m/z* (relative intensity, %): 269 (2) ($[M-Me]^+$), 240 (43) ($[Ph_2SiCH_2CHOMe]^+$), 225 (31) ($[Ph_2SiCH_2CHO]^+$), 213 (100) ($[Ph_2SiOMe]^+$), 208 (54) ($[Ph_2SiC_2H_2]^+$), 199 (58) ($[Ph_2SiOH]^+$), 183 (59) ($[Ph_2SiH]^+$), 182 (20) ($[Ph_2Si]^+$), 181 (66) ($[213-MeOH]^+$), 153 (25) ($[PhSiCH_4O_2]^+$), 136 (25) ($[PhSiOMe]^+$), 105 (32) ($[PhSi]^+$), 77 (15) ($[C_6H_5]^+$), 53 (12) ($[C_4H_5]^+$).

trans-3-Ethoxy-1,1-diphenyl-1-silacyclopentan-4-ol (***XIb***).

From 1.0 g of epoxide **IIb** and 10 ml of EtOH, 1.09 g of ethoxy alcohol **XIb** were isolated in 93% yield. Anal. Found: C, 72.38; H, 7.37. $C_{18}H_{22}O_2Si$ calc.: C, 72.41; H, 7.42%. IR: 3423, 3067, 3047, 2972, 2868, 1958, 1886, 1882, 1486, 1428, 1332, 1261, 1147, 1114, 1095, 1038, 999, 974, 798, 733, 690 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz) δ: 1.19 (m, 2H, H^3, H^4), 1.27 (t, J = 7.0 Hz, 3H, CH_2CH_3), 1.72 (dd, J (H^6H^5) = 6.8 Hz, ^3J (H^6H^2) = 2.6 Hz, 1H, H^6), 1.90 (dd, J (H^5H^6) = 6.8 Hz, ^3J (H^5H^2) = 2.6 Hz, 1H, H^5), 2.92 (m, 1H, OH), 3.58 (m, 1H, H^1), 3.63 (q, J = 7.0 Hz, CH_2CH_3), 4.14 (m, 1H, H^2), 7.3–7.8 (m, 10H, Ph_2Si). ^{13}C NMR ($CDCl_3$, 200 MHz) δ: 15.67 (CH_2CH_3), 15.71 (C^2), 17.96 (C^5), 64.49 (CH_2CH_3), 76.40 (C^3), 85.28 (C^4), 128.18, 128.22, 129.85, 129.87, 134.78, 135.30 (C arom.). GC MS *m/z* (relative intensity, %): 283 (1) ($[M-Me]^+$) 254 (17) ($[M-CH_3CHO]^+$), 227 (26) ($[Ph_2SiOEt]^+$), 226 (23) ($[Ph_2SiCH_2CHOH]^+$), 225 (100) ($[Ph_2SiCH_2CHO]^+$), 199 (35) ($[Ph_2SiOH]^+$), 183 (53) ($[Ph_2SiH]^+$), 182 (9) ($[Ph_2Si]^+$) 181 (31) ($[199-H_2O]^+$), 148 (4) ($[PhSiCH_2CHO]^+$), 105 (12) ($[PhSi]^+$), 77 (8) ($[C_6H_5]^+$), 53 (4) ($[C_4H_5]^+$).

trans-3-t-Butoxy-1,1-diphenyl-silacyclopentan-4-ol (***XIc***).

A 1.16 g amount of **XIc** as colourless oil was obtained from 1.0 g of epoxide **IIb** and 10 ml ^tBu OH in 90% yield. Anal. Found: C, 73.43; H, 7.98. $C_{20}H_{26}O_2Si$ calc.: C, 73.59; H, 8.03%. IR: 3424 (OH), 3068, 3048, 2971, 2909, 1957, 1884, 1820, 1772, 1654, 1567, 1486, 1472, 1428, 1389, 1364, 1333, 1253, 1195, 1140, 1113, 1067, 1037, 979, 882, 817, 800, 730, 698 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz) δ: 1.29 (s, 9H, O^tBu), 1.73 (m, 4H, H^3, H^4, H^5, H^6), 2.62 (m, 1H, OH), 3.94 (m, 2H, H^1, H^2), 7.3–7.8 (m, 10H, Ph_2Si). ^{13}C NMR ($CDCl_3$, 200 MHz) δ: 16.95 (C^2), 19.71 (C^5), 29.11 ($(CH_3)_3C$), 74.12 ($(CH_3)_3C$), 76.69 (C^3), 78.43 (C^4), 128.09, 128.21, 129.75, 129.81, 134.73, 134.76, 135.41, 135.49 (C arom.). GC MS *m/z* (relative intensity, %): 282 (2) ($[Ph_2SiCH_2CHO^tBu]^+$), 269 (8) ($[Ph_2SiCH_2O^tBu]^+$), 226 (19) ($[Ph_2SiCH_2CHOH]^+$), 225 (100) ($[Ph_2SiCH_2CHO]^+$), 199 (33) ($[Ph_2SiOH]^+$), 183 (36) ($[Ph_2$-

SiH]$^+$), 181 (17) ([199-H_2O]$^+$), 148 (6) ([PhSi-CH_2CHO]$^+$), 105 (9) ([PhSi]$^+$), 77 (6) ([C_6H_5]$^+$), 57 (13) ([C_4H_9]$^+$).

trans-3-Propynyloxy-1,1-diphenyl-1-silacyclopentan-4-ol (***XId***).

Using the above procedure, 1.13 g of alkoxy alcohol **XId** were isolated after purification with a silica gel column, yield 93%. IR: 3424 (OH), 3288, 3068, 3047, 3009, 2954, 2860, 1958, 1887, 1823, 1486, 1428, 1409, 1355, 1333, 1302, 1261, 1190, 1147, 1144, 1086, 1041, 997, 945, 799, 733, 699 cm^{-1}. ^{1}H NMR ($CDCl_3$, 80 MHz) δ: 1.17 (m, 2H, H^3, H^4), 1.81 (m, 2H, H^5, H^6), 2.44 (t, $J = 2.4$ Hz, 1H, $HC\equiv$), 3.93 (m, 2H, H^1, H^2), 4.27 (t, $J = 2.4$ Hz, 2H, OCH_2), 7.3 – 7.8 (m, 10H, Ph_2Si). ^{13}C NMR ($CDCl_3$ 200 MHz) δ: 15.27 (C^2), 18.03 (C^5), 56.43 (OCH_2), 74.59 (OCH_2C), 76.34 (C^3), 80.18 ($\equiv CH$), 84.83 (C^4), 128.22, 129.93, 134.72, 134.96 (C arom.). GC MS *m/z* (relative intensity, %): 308 (4) (M)$^+$, 269 (3) ([M – C_3H_3]$^+$), 254 (13) ([M – C_3H_2O]$^+$), 226 (19) ([Ph_2SiCH_2CHOH]$^+$), 225 (100) ([Ph_2SiCH_2CHO]$^+$), 199 (25) ([Ph_2SiOH]$^+$), 183 (52) ([Ph_2SiH]$^+$), 181 (28) ([199 – H_2O]$^+$), 148 (5) ([$PhSiCH_2CHO$]$^+$), 105 (19) ([PhSi]$^+$) 77 (10) ([C_6H_5]$^+$), 53 (6) ([C_4H_5]$^+$), 39 (14) ([C_3H_3]$^+$).

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