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Efficient access to polysubstituted tetrahydrofurans by electrophilic cyclization of vinylsilyl alcohols†

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Vinylsilyl alcohols undergo intramolecular cyclization to provide di-, tri- or tetrasubstituted-tetrahydrofurans. The influence of the number and position of substituents in the stereoselectivity of the process has been studied. Moreover, DFT calculations have been performed to get better insight into the influence of the substitution pattern of the vinylsilyl alcohol in the stereoselectivity of the cyclization.

Introduction

Five-membered oxacycles are abundant in several polycyclic and monocyclic natural bioactive products. Within them, the family of polyketide macrolides has emerged as a challenge for organic chemists. Most known macrolides contain THP rings in their structure or an array of THP and THF rings. However, lately there have been described several THF-containing macrolides with important therapeutic properties.[1]

For example, natural polyketide macrolides containing tetrahydrofuranyl moieties include nonactin,[2] ionophoric antibiotic isolated from the *Streptomyces*, chagosensine,[3] chlorinated macrolide isolated from the Red Sea calcareous sponge *Leucetta chagosensis*, amphidinolactone B,[4] cytotoxic macrolide isolated from the marine dinoflagellate *Amphidinium* sp. or phormidolide,[5] toxic metabolite isolated from the marine cyanobacterium *Phormidium* sp., within others (Fig. 1).

Numerous researchers have been attracted by the molecular complexity, stereochemical diversity and potential pharmacological properties of such systems. Particular attention has emerged towards the synthesis of substituted tetrahydrofurans, which are common structural features present in these natural products. The construction of such structures has been accomplished using a variety of methods. A powerful approach is the electrophilic cyclization of alkenes bearing a nucleophile. Different electrophilic sources have been reported, such as halogen,[6] selenium[7] or mercury.[8] The cyclization has shown to be dependent on the nature of the electrophile and steric and electronic factors. In most cases, the process affords a mixture of both possible stereoisomers, although one of them is usually obtained as the major one.

However, few successful examples have been reported on the acid-mediated cyclization of alkenols. Recently, Hosomi *et al.* have described the synthesis of disubstituted tetrahydrofurans by acid-catalyzed cyclization of vinylsilanes, comparing the behaviour of different silyl groups.[9]

On the other hand, while most of these synthetic methods deal with the synthesis of 2,5-disubstituted tetrahydrofurans, many of the 5-membered oxacycles found in natural macrolides are 2,3,5-tri- or 2,2,3,5-tetrasubstituted.

As part of our studies on the synthetic applications of allyl- and vinylsilanes towards the construction of different sized carbo-[10] and heterocycles,[11] we have recently published the intramolecular cyclization of allylsilyl alcohols to give silylated tetrahydrofurans in good yield.[12]

We now present ours results on the cyclization of vinylsilyl alcohols, bearing the phenyldimethylsilyl group, to give di-, tri- and tetrasubstituted tetrahydrofurans in a stereoselective manner.

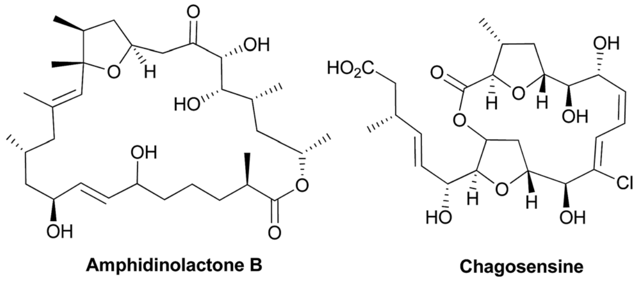

Fig. 1 Polyketide macrolides containing tetrahydrofuranyl moieties.

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† Electronic supplementary information (ESI) available: Computational details as well as copies of ^{1}H and ^{13}C NMR spectra for all new compounds are provided. See DOI: 10.1039/c5ra06640a

Results and discussion

The vinylsilyl alcohols needed for this study were readily prepared in two steps, with an initial silylcupration of alkynes followed by reaction with α,β-unsaturated carbonyl compounds to give oxovinylsilanes **1a–k**. The subsequent reduction with $LiAlH_4$ afforded the desired alcohols in nearly quantitative yields. The reduction of compounds **1h–i**, **k** provided an equimolar mixture of diastereoisomers **2h–i**, **k** and **3h–i**, **k** which could be separated by chromatography (Table 1).

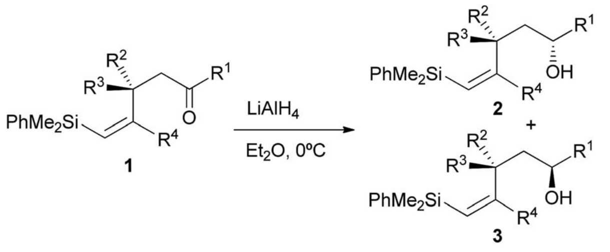
We used vinylsilyl alcohol **2g** as a model substrate and subjected it to cyclization using both acidic conditions (*p*-TsOH) and mercury-cyclization. The results are shown in Table 2.

From the results shown in Table 2 we can conclude that the stereoselectivity of the acid-catalyzed cyclization is moderate and dependent on the temperature of the reaction. Thus, a decrease in the temperature causes an increase in the *dr* of the cyclization, obtaining the best results when the reaction is conducted at room temperature. Lowering the temperature to 0 °C caused a remarkable decrease in the reaction rate, and after 25 hours of reaction a great amount of starting alcohol could be detected in the reaction mixture. Slightly lower stereoselectivities, together with longer reaction times, are obtained in the mercury-cyclization. In all cases the major stereoisomer is always the 2,5-*trans* tetrahydrofuran.

Next, we examined the scope of this cyclization using different vinylsilyl alcohols, in order to examine the influence of the substitution in the stereoselectivity of the process. The results are shown in Table 3.

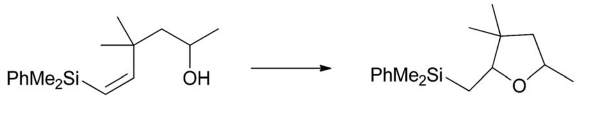
As illustrated in Table 3, the cyclization of vinylsilyl alcohols with allylic substituents **2b–d** ($R^1 = H$, $R^2 \neq H$) led to a unique 2,3-*trans*-disubstituted tetrahydrofuran, both using the acid-catalyzed or the mercury cyclization and independently of the bulkiness of the substituent (Table 3, entries 2–6). However, the mercury-cyclization is slower than the acid-catalyzed one (Table 3, entries 2–4). In contrast, cyclization of vinylsilanes **2e–2g** with an alkyl group on the carbon bounded to the hydroxy group ($R^1 \neq H$, $R^2 = R^3$) afforded substituted tetrahydrofurans with moderate 2,5-*trans* stereoselectivity (Table 3, entries 7–11). As it is shown (entries 7–8, 10–11) the effect of the temperature on the stereoselectivity of the process is well defined. Thus, the best stereoselectivity for cyclization of alcohol **2e** and **2g** was found when the reaction was performed at room temperature.

Table 1 Synthesis of vinylsilyl alcohols



	Compound						
Entry	R^1	R^2	R^3	R^4		Ratio **2/3**	Yield (%)
1	H	H	H	H	**2a**		93
2	H	Me	H	H	**2b**		90
3	H	Pr	H	H	**2c**		92
4	H	Ph	H	H	**2d**		89
5	Me	H	H	H	**2e**		94
6	Et	H	H	H	**2f**		91
7	Me	Me	Me	H	**2g**		90
8	Me	Ph	H	H	**2h/3h**	50 : 50	88
9	Me	^{i}Pr	H	H	**2i/3i**	50 : 50	92
10	H	Ph	H	Ph	**2j**		89
11	Ph	Ph	H	Ph	**2k/3k**	50 : 50	90

Table 2 Cyclization of vinylsilyl alcohol **2g**



2g **4g** (2,5-*trans*) / **5g** (2,5-*cis*)

Entry	Reagent	Temp/°C	Time/h	Ratio^a **4 : 5**	Yield (%)
1	$Hg(OTFA)_2$	−40 → 0	25	80 : 20	83
2	*p*-TsOH	0	25	85 : 15	49^b
3	*p*-TsOH	r. t.	10	84 : 16	90
4	*p*-TsOH	40	3	75 : 25	92

^{a} The ratio of isomers **4** and **5** were determined by ^{1}H-NMR analysis. ^{b} The reaction rate was very slow at 0 °C. A great amount of starting alcohol was recovered.

We next decided to study the cyclization of vinylsilyl alcohols bearing both types of substituents (one on the allylic position and the other on the carbon bounded to the hydroxy group). The results are shown in Scheme 1.

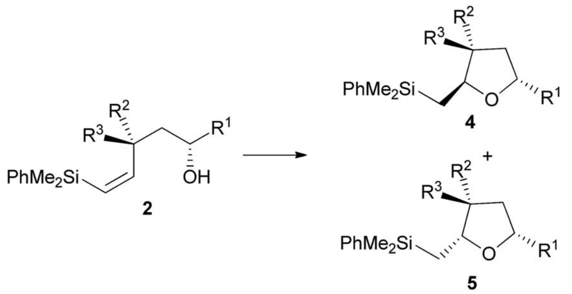
Interestingly, the cyclization of those substrates proceeds with excellent diastereocontrol (only one diastereoisomer could be detected in the reaction mixture), which seems to indicate that the influence of the allylic group (R^2) on the stereoselectivity is greater than that of the R^1 substituent. Moreover, the use of two diastereomeric vinylsilyl alcohols **2h–i** and **3h–i** allowed us to conclude that the allylic substituent is the one that controls the stereochemical outcome of the process since the final tetrahydrofurans always have the 2,3-*trans*-configuration.

Finally, we decided to study the cyclization of vinylsilyl alcohols bearing an additional substituent β to silicon. The results are shown in Scheme 2.

Surprisingly, this time the cyclization in the presence of *p*-TsOH is not stereoselective, affording an almost equimolar mixture of both diastereoisomeric tetrahydrofurans. Probably the presence of an extra substituent β to silicon will cause an unfavourable steric effect which will account for the shown loss of stereoselectivity.

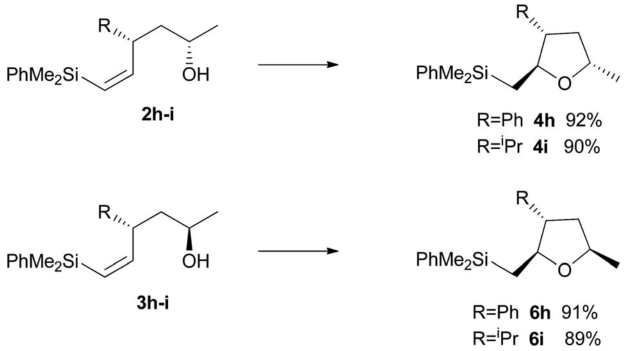
On the other hand, it has been reported that α-alkylsubstituted vinylsilanes undergo 1-2-silyl migration when subjected to acid-catalyzed cyclization to give silylated tetrahydropyrans.[13] In contrast, our β-substituted vinylsilanes **2j–k**, **3k** do not follow this pattern, probably due to the fact that such migration would lead to a very unstable primary carbocation.[14]

Table 3 Scope of the cyclization of vinylsilyl alcohols

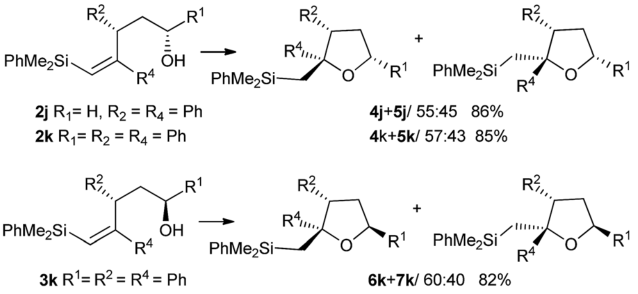


	Compound								
Entry	R^1	R^2	R^3		Reagent	Temp/°C	Time/h	Ratio[a] **4 : 5**	Yield (%)
1	H	H	H	**2a**	*p*-TsOH	40	3		92
2	H	Me	H	**2b**	$Hg(OTFA)_2$	r. t.	24	>95 : 5	89[b]
3	H	Me	H	**2b**	$Hg(OAc)_2$	r. t.	24	>95 : 5	90[b]
4	H	Me	H	**2b**	*p*-TsOH	40	15	>95 : 5	89
5	H	Pr	H	**2c**	*p*-TsOH	40	15	>95 : 5	80
6	H	Ph	H	**2d**	*p*-TsOH	40	16	>95 : 5	82
7	Me	H	H	**2e**	*p*-TsOH	40	5	80 : 20	89
8	Me	H	H	**2e**	*p*-TsOH	r. t.	12	89 : 11	80
9	Et	H	H	**2f**	*p*-TsOH	40	4	72 : 28	87
10	Me	Me	Me	**2g**	*p*-TsOH	40	3	75 : 25	92
11	Me	Me	Me	**2g**	*p*-TsOH	r. t.	10	84 : 16	90

[a] The ratio of isomers **4** and **5** were determined by ^1H-NMR analysis. [b] Reaction conditions: mercury salt (1.09 mmol), $CaCO_3$ (2.17 mmol), vinylsilyl alcohol (1 mmol), solvent THF.



Scheme 1 Stereoselective synthesis of 2,3,5-trisubstituted tetrahydrofurans.



Scheme 2 Synthesis of 2,2,3,5-tetrasubstituted tetrahydrofurans.

Mechanistic proposal

Following the models proposed by Houk[15] and Fleming[16] for the electrophilic attack on alkenes bearing an allylic stereogenic center, we could draw two chair-like reactive conformations for the cyclization of vinylsilyl alcohols **2b–d**. In the preferred conformation **A**, the largest substituent is antiperiplanar to the double bond, and the smallest allylic substituent (H) is located in the inside position. In the other possible conformation **B**, with R^2 inside, a severe 1,3-allylic steric interaction between R^2 and the silyl group can be seen which would explain the large preference for cyclization *via* conformer **A** (Fig. 2).

Regarding the acid-catalyzed reaction, and in accordance with Hosomi's mechanistical proposal,[9b] the reaction would then proceed through an initial acid–base reaction to give an oxonium ion which would undergo proton transfer leading to a stabilized β-carbocation to silicon (through rotation of the C–Si bond in order to be parallel to the empty p orbital). Final *syn*-addition of the hydroxy group would lead to the silylated tetrahydrofuran (Fig. 2).

On the other hand, it's known that the corresponding electrophilic mercury cyclization should occur in an *anti*-fashion. In this case, starting from preferred conformation **A**, the electrophilic attack would occur *anti* to the largest group to provide the corresponding mercuronium ion. The following intramolecular addition of the alcohol would provide the observed 2,3-*trans*-tetrahydrofuran **4b** (Fig. 3).

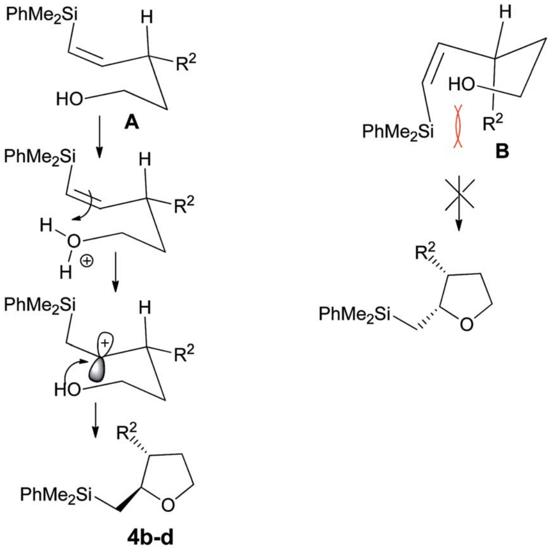


Fig. 2 Chair-like reactive conformations for alcohols **2b–d**.

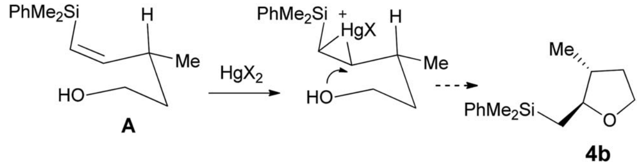


Fig. 3 Mechanism for the mercury-cyclization of alcohol **2b**.

Similarly, the moderate stereoselectivity observed in the acid-catalyzed cyclization of vinylsilyl alcohols **2e–f**, would indicate a small energy difference between conformers **C** and **D** in favour of conformation **C**. Thus, conformer **D** possesses a repulsive interaction between groups R^1 and SiR$_3$ on a 1,3-pseudoaxial orientation. As a result cyclization of **C** would proceed faster than that of conformer **D**, leading to a major *trans*-2,5-tetrahydrofuran (Fig. 4).

In addition, the loss of stereocontrol observed for the cyclization of vinylsilyl alcohols with a substituent R^4 β to silicon **2j, k**, **3k** can be again explained using Houk and Fleming's models since now, apart from the 1,3-allylic strain, there is a competing disfavouring interaction which is the 1,2-allylic strain between R^2 and R^4 (Fig. 5).

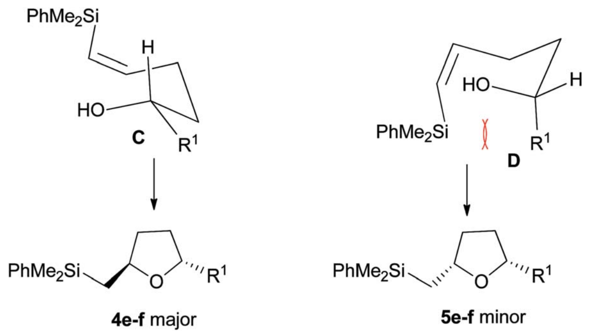


Fig. 4 Chair-like reactive conformations for alcohols **2e–f**.

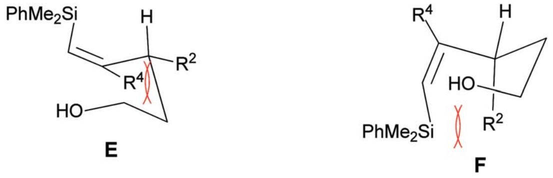


Fig. 5 Chair-like reactive conformations for alcohols **2j**, **k**, **3k**.

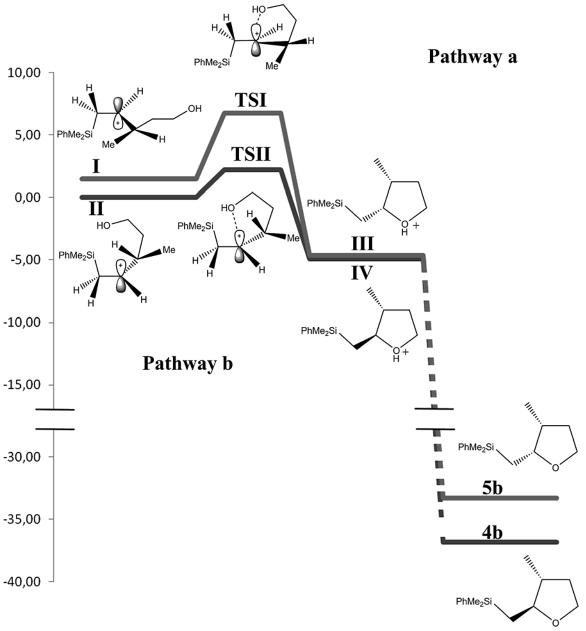


Fig. 6 Reaction pathways for the formation of **4b** and **5b**.

In order to get further insight into the substitution effect observed in the stereoselectivity of these reactions DFT calculations were conducted. The calculations were performed using compounds **2b** and **2e** as models for vinylsilyl alcohol with or without allylic substituents.[17] Calculations were initiated for compound **2b**. The two different reaction pathways leading to the corresponding 2,3-*trans* tetrahydrofuran **4b** and 2,3-*cis* tetrahydrofuran **5b** have been drawn, starting from the stabilized β-silylcarbocation (Fig. 6).

As shown, intermediate II is more stable than I by 1.46 kcal mol^{-1} and the activation energy of TSI is 3.08 kcal mol^{-1} higher than that of TSII (Table 4), which indicates that the cyclization through *path b* is kinetically more favorable than through *path a*. Moreover, the protonated tetrahydrofurans III and IV are similar in energy, but the final tetrahydrofuran **4b** is

Table 4 Free energies for the cyclization of **2b**

Pathway	$\Delta G\neq$ (kcal mol^{-1})	$\Delta G_{\text{reaction1}}$ (kcal mol^{-1})	$\Delta G_{\text{reaction2}}$[a] (kcal mol^{-1})
a	5.30	−3.19	−28.77
b	2.22	−4.92	−31.90

[a] Calculated from structures **III** and **IV** to **5b** and **4b**, respectively.

Table 5 Estimated Boltzmann distribution in solution at room temperature for TSI and TSII

Transition state	$\Delta G/k_bT$	% Distribution (25 °C)	% Experimental ratio
TSII	0.00	92.1	>95
TSI	2.46	7.9	<5

Table 6 Free energies for the cyclization of **2e**

Pathway	$\Delta G\neq$ (kcal mol^{-1})	$\Delta G_{\text{reaction1}}$ (kcal mol^{-1})	$\Delta G_{\text{reaction2}}$[a] (kcal mol^{-1})
c	3.18	−4.38	−28.53
d	3.15	−6.89	−27.34

[a] Calculated from structures **VII** and **VIII** to **5e** and **4e**, respectively.

Table 7 Estimated Boltzmann distribution in solution at room temperature for TSIV and TSIII

Transition state	$\Delta G/k_bT$	% Distribution (25 °C)	% Experimental ratio
TSIV	0.00	86.7	89
TSIII	1.83	13.3	11

significantly more stable than **5b** in thermodynamics (by 3.5 kcal mol^{-1}). Overall, the shown calculations are in agreement with the high stereoselectivity towards **4b** observed when the vinylsilyl alcohol **2b**, with an allylic substituent, is submitted to cyclization.

Moreover, optimization of structures **I** and **II** give us additional information relative to the influence of the allylic substituent in the stereoselectivity of this cyclization. Thus, the optimized structure for **II**, which corresponds to the stabilized β to silicon cation of conformation **A** with H inside, shows a boat-like conformation where the intermediate carbocation is easily accessible by the OH group. However, the optimized structure for **I**, with Me inside, is a quasi linear conformation in which the OH group is far apart from the carbocation atom (Fig. 6).[18] This means that in order to be able to cyclize, structure **I** has to rotate to get a suitable orientation between the reactive groups, which in consequence will require a higher energy.

Moreover, the calculated Boltzmann distribution for **TSI** and **TSII** correlate perfectly with the experimental ratio obtained in the cyclization for tetrahydrofurans **4b** and **5b** (Table 5).

Noteworthy, calculations for compound **2e** reveal several differences (Fig. 7). Now tetrahydrofurans **4e** and **5e** have almost the same energy (being **4e** 0.24 kcal mol^{-1} more stable than **5e**). Moreover, protonated furans **VII** and **VIII** are close in energy (being **VIII** 2.514 kcal mol^{-1} more stable) and a similar trend is observed for structures **V** and **VI**, which have a difference in energy of 1.08 kcal mol^{-1}. In addition, the free energy barriers for both pathways only differ in 0.03 kcal mol^{-1} (Table 6). On the basis of these computational studies we can conclude that although *path d* is more favorable than *path c*, the difference in their energy profiles makes feasible the obtention of mixtures of both stereoisomers.

The observation of the corresponding optimized structures **V** and **VI** is also in agreement with this conclusion. Thus, the optimization without restrictions of these structures show that the preferred conformation for **V** and **VI** are essentially extended zig-zag conformations. Neither of these conformations is appropriate for cyclization, suggesting a moderate preference for either *path c* or *d* (Fig. 7).

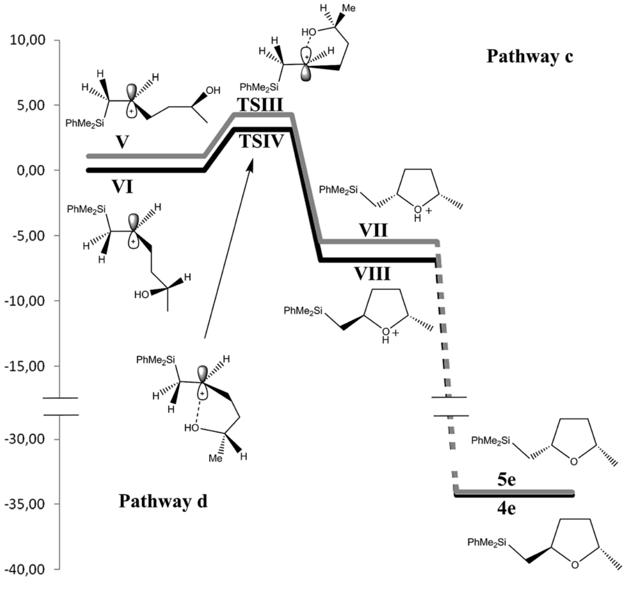


Fig. 7 Reaction pathways for the formation of **4e** and **5e**.

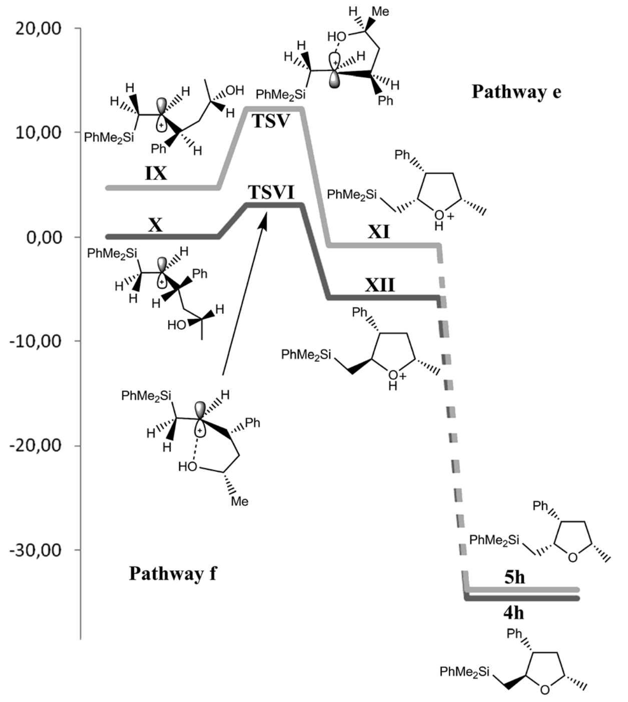


Fig. 8 Reaction pathways for the formation of **4h** and **5h**.

Table 8 Free energies for the cyclization of **2h**

Pathway	$\Delta G\neq$ (kcal mol^{-1})	$\Delta G_{\text{reaction1}}$ (kcal mol^{-1})	$\Delta G_{\text{reaction2}}$ (kcal mol^{-1})
e	7.60	−5.42	−32.98
f	3.04	−5.79	−28.85

Again, the estimated Boltzmann distribution for **TSIV** and **TSIII** (Table 7) is consistent with the experimental results (Table 3, entry 7).

Finally, we decided to study the behaviour of a vinylsilyl alcohol **2h** with two substituents ($R^1 \neq H$, $R^2 \neq H$) on the alkylic chain. As depicted in Fig. 8, the predicted lower energy *pathway f* is consistent with the experimental results (Scheme 1). These results confirm unambiguously the great influence of the allylic substituent in the stereocontrol of this process. The difference in energy between intermediate **IX**, which is the corresponding carbocation from **B** with $R^2 = Ph$ inside (Fig. 2), and **X**, with H inside, is 4.66 kcal mol^{-1} and between the predicted barriers for **TSV** and **TSVI** is 4.56 kcal mol^{-1} (Table 8), favouring the formation of tetrahydrofuran **4h**. As shown in **TSV**, the bulky phenyl group is blocking the approach of the hydroxy group to the reactive alkene moiety, which is consistent with the high energy barrier for *pathway e*.

Finally, the calculate Boltzmann distribution for **TSVI** and **TSV** (Table 9) are also consistent with the experimental obtention of a unique diastereoisomer **4h** (Scheme 1).

Conclusions

In conclusion, we have described an efficient and stereoselective synthesis of di-, tri- and tetrasubstituted tetrahydrofurans through the intramolecular cyclization of vinylsilyl alcohols. This methodology is a general approach to the synthesis of a wide range of tetrahydrofurans bearing substituents on C-2, C-3 or C-5, which represent the most frequent structures in the framework of many natural oxacycles. Moreover, the presence of the silyl group in the substrate provides an easy entry to further functionalization, due to the ability of silicon to be oxidized under mild conditions (Fleming–Tamao oxidation).

Experimental

General experimental

All the reactions were carried out under an atmosphere of argon or nitrogen in dried glassware unless otherwise indicated. Materials were obtained from commercial suppliers and used without further purification except when otherwise noted. Solvents were dried and distilled according to the standard protocols. Flash column chromatography was performed on silica gel using the indicated solvent.

Table 9 Estimated Boltzmann distribution in solution at room temperature for **TSVI** and **TSV**

Transition state	$\Delta G/k_bT$	% Distribution (25 °C)	% Experimental ratio
TSVI	0.00	99.99	>95
TSV	1.83	0.001	<5

Synthesis of vinylsilyl aldehydes or ketones 1a–k

To a stirred suspension of CuCN (6 mmol) in dry THF (10 ml), under nitrogen, was added a solution of $PhMe_2SiLi$ (6 mmol) and the mixture stirred for 30 min. at 0 °C. The solution was then cooled to −78 °C and the acetylene (6 mmol) was added and stirred for an additional hour. $BF_3 \cdot OEt_2$ (6 mmol) or TMSCl (6 mmol) was then added and, after 5 min stirring at −78 °C, the α,β-unsaturated carbonyl compound (7 mmol) was added dropwise. The resulting mixture was allowed to warm to 0 °C, quenched with basic saturated ammonium chloride solution (15 ml) and extracted with ether (3 × 15 ml). The organic layer was dried over MgSO4 and the solvent rotoevaporated. Purification by flash chromatography gave the vinylsilyl aldehydes or ketones **1a–k**. The synthesis and spectroscopic data of vinylsilyl ketones **1e, f, h, i** have been previously described.[11a]

(*Z*)-5-Dimethylphenylsilyl-4-pentenal (1a). Colorless oil (87%); IR ν_{max}(film)/cm^{-1} 1728, 1605, 1249, 1109; ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 9.62$ (s, 1H), 7.60–7.52 (m, 2H), 7.40–7.36 (m, 3H), 6.44–6.34 (m, 1H), 5.76 (d, $J = 14.0$ Hz, 1H), 2.39–2.36 (m, 4H), 0.42 (s, 6H, $(CH_3)_2Si$); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 201.5$ (CHO), 147.7 (CH), 139.2 (C), 133.6 (CH), 129.0 (CH), 128.9 (CH), 127.8 (CH), 43.3 (CH_2), 26.1 (CH_2), −1.1 (CH_3); MS (CI): *m*/*z* 219 ($M^+ + 1$), 203 ($M^+ - Me$), 135 ($SiMe_2Ph$); HRMS (ESI+) *m*/*z* calcd for $C_{13}H_{18}NaOSi$ ($[M + Na]^+$): 241.1019, found 241.1024.

(*Z*)-5-Dimethylphenylsilyl-3-methyl-4-pentenal (1b). Colorless oil (85%); IR ν_{max}(film)/cm^{-1} 1724, 1605, 1249, 1113; ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 9.44$ (s, 1H), 7.62–7.56 (m, 2H), 7.41–7.35 (m, 3H), 6.23 (dd, $J = 14.0$ and 10.1 Hz, 1H), 5.71 (d, $J = 14.0$ Hz, 1H), 2.89–2.79 (m, 1H), 2.30–2.21 (m, 2H), 0.98 (d, $J = 6.6$ Hz, 3H), 0.48 (s, 3H, CH_3Si), 0.46 (s, 3H, CH_3Si); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 201.6$ (CHO), 153.5 (CH), 139.2 (C), 133.7 (CH), 129.1 (CH), 127.9 (CH), 126.8 (CH), 50.3 (CH_2), 33.0 (CH), 20.6 (CH_3), −0.9 (CH_3), −1.1 (CH_3); MS (CI): *m*/*z* 233 ($M^+ + 1$), 217 ($M^+ - Me$), 155 ($M^+ - Ph$), 135 ($SiMe_2Ph$); HRMS (ESI+) *m*/*z* calcd for $C_{14}H_{20}NaOSi$ ($[M + Na]^+$): 255.1176, found 255.1181.

(*Z*)-5-Dimethylphenylsilyl-3-propyl-4-pentenal (1c). Colorless oil (79%); IR ν_{max}(film)/cm^{-1} 1724, 1605, 1249, 1109; ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 9.40$ (t, $J = 2.4$ Hz, 1H), 7.61–7.53 (m, 2H), 7.43–7.38 (m, 3H), 6.17 (dd, $J = 14.0$ and 10.1 Hz, 1H), 5.74 (d, $J = 14.0$ Hz, 1H), 2.74–2.62 (m, 1H), 2.32 (ddd, $J = 15.8$, 6.6 and 2.4 Hz 1H), 2.15 (ddd, $J = 15.8$, 7.0 and 2.4 Hz, 1H), 1.41–1.15 (m, 4H), 0.85 (t, $J = 6.6$ Hz, 3H), 0.47 (s, 3H, CH_3Si), 0.44 (s, 3H, CH_3Si); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 201.8$ (CHO), 152.6 (CH), 139.2 (C), 133.7 (CH), 129.0 (CH), 128.0 (CH), 127.8 (CH), 48.9 (CH_2), 37.9 (CH), 37.3 (CH_2), 20.2 (CH_2), 14.1 (CH_3), −1.0 (CH_3), −1.2 (CH_3); MS (CI): *m*/*z* 261 ($M^+ + 1$), 245 ($M^+ - Me$), 183 ($M^+ - Ph$), 135 ($SiMe_2Ph$); HRMS (ESI+) *m*/*z* calcd for $C_{16}H_{24}NaOSi$ ($[M + Na]^+$): 283.1489, found 283.1491.

(*Z*)-5-Dimethylphenylsilyl-3-phenyl-4-pentenal (1d). Colorless oil (83%); IR ν_{max}(film)/cm^{-1} 1721, 1595, 1249, 1109; ^{1}H

NMR (300 MHz, $CDCl_3$) $\delta = 9.44$ (t, $J = 2.0$ Hz, 1H), 7.66–7.62 (m, 2H), 7.49–7.42 (m, 3H), 7.34–7.21 (m, 3H), 7.09–7.02 (m, 2H), 6.56 (dd, $J = 14.0$ and 10.3 Hz, 1H), 5.82 (d, $J = 14.0$ Hz, 1H), 4.09–3.95 (m, 1H), 2.78 (ddd, $J = 16.2$, 7.9 and 2.0 Hz, 1H), 2.57 (ddd, $J = 16.2$, 7.0 and 2.0 Hz, 1H), 0.44 (s, 6H, $(CH_3)_2Si$); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 200.8$ (CHO), 150.7 (CH), 142.3 (C), 138.9 (C), 133.9 (CH), 129.2 (CH), 128.7 (CH), 128.2 (CH), 128.0 (CH), 127.1 (CH), 126.6 (CH), 49.7 (CH_2), 43.3 (CH), −1.0 (CH_3), −1.2 (CH_3); MS (CI): m/z 293 ($M^+ - 1$), 279 ($M^+ - Me$), 217 ($M^+ - Ph$), 135 ($SiMe_2Ph$).

(*Z*)-6-Dimethylphenylsilyl-4,4-dimethyl-5-hexen-2-one (1g). Colorless oil (87%); IR ν_{max}(film)/cm^{-1} 1716, 1595, 1249, 1111; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 7.55$–7.53 (m, 2H), 7.35–7.32 (m, 3H), 6.53 (d, $J = 15.7$ Hz, 1H), 5.63 (d, $J = 15.7$ Hz, 1H), 2.33 (s, 2H), 1.97 (s, 3H), 1.04 (s, 6H), 0.42 (s, 6H, $(CH_3)_2Si$); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 208.2$ (CO), 159.6 (CH), 140.8 (C), 134.1 (CH), 129.2 (CH), 128.1 (CH), 124.8 (CH), 55.9 (CH_2), 38.4 (C), 32.2 (CH_3), 28.2 ($2 \times CH_3$), 0.98 ($2 \times CH_3$); MS (CI): m/z 261 ($M^+ + 1$), 245 ($M^+ - Me$), 183 ($M^+ - Ph$), 135 ($SiMe_2Ph$).

(*E*)-5-Dimethylphenylsilyl-3,4-diphenyl-4-pentenal (1j). Colorless oil (89%); IR ν_{max}(film)/cm^{-1} 1728, 1249, 1110; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 9.32$ (s, 1H), 7.70–7.67 (m, 2H), 7.42–7.41 (m, 3H), 7.27–7.14 (m, 6H), 7.05–7.03 (m, 2H), 6.82–6.80 (m, 2H), 5.94 (s, 1H), 4.64 (dd, $J = 8.8$ and 6.6 Hz, 1H), 2.89 (dd, $J = 16.7$ and 8.8 Hz, 1H), 2.54 (dd, $J = 16.7$ and 6.6 Hz, 1H), 0.62 (s, 3H), 0.56 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 201.4$ (CH), 160.0 (C), 142.7 (C), 140.3 (C), 139.2 (C), 134.1 (CH), 130.8 (CH), 129.5 (CH), 128.6 (CH), 128.3 (CH), 128.2 (CH), 127.8 (CH), 127.4 (CH), 126.9 (CH), 46.3 (CH_2), 44.8 (CH), −0.5 (CH_3), −1.0 (CH_3); MS (CI) m/z (%) 371 ($M^+ + 1$), 370 (M^+), 369 ($M^+ - 1$), 355 ($M^+ - Me$), 341 ($M^+ - CHO$), 293 ($M^+ - Ph$), 235 ($M^+ - SiMe_2Ph$), 135 ($SiMe_2Ph$).

(*E*)-5-Dimethylphenylsilyl-1,3,4-triphenyl-4-penten-1-one (1k). Colorless oil (82%); IR ν_{max}(film)/cm^{-1} 1680, 1260, 1110; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 7.84$–6.91 (m, 20H), 5.96 (s, 1H), 5.12 (dd, $J = 8.7$ and 5.1 Hz, 1H) 3.65 (dd, $J = 17.4$ and 8.7 Hz, 1H) (m, 1H), 3.18 (dd, $J = 17.4$ and 5.1 Hz, 1H), 0.61 (s, 3H, CH_3Si), 0.58 (s, 3H, CH_3Si); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 197.6$ (C), 160.1 (C), 143.4 (C), 141.3 (C), 139.3 (C), 137.1 (C), 134.0 (CH), 133.0 (CH), 130.5 (CH), 129.0 (CH), 128.5 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.7 (CH), 127.6 (CH), 127.1 (CH), 126.2 (CH), 45.4 (CH), 41.5 (CH_2), −0.9 (CH_3), −1.1 (CH_3).

Synthesis of vinylsilyl alcohols 2 and 3

To a suspension of 1.7 mmol of $LiAlH_4$ in dry ether (8 ml), under nitrogen, was added a solution of the vinylsilyl aldehydes or ketones **1a–k** (2 mmol) in dry ether (2 ml) at 0 °C. The mixture was stirred for 45 min at 0 °C and then quenched with 4 ml of $NaHCO_3$ (10%) and 4 ml of NaOH (20%). The organic layer was dried, the solvent evaporated and the mixture was purified by flash chromatography (EtOAc/hexane 1 : 10) to give alcohols **2** and **3**. The spectroscopic data of vinylsilyl alcohol **2d** has been previously described.[9b]

(*Z*)-5-Dimethylphenylsilyl-4-penten-1-ol (2a). Colorless oil (93%); IR ν_{max}(film)/cm^{-1} 3331, 1605, 1249, 1106; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 7.69$–7.59 (m, 2H), 7.48–7.41 (m, 3H), 6.55–6.46 (m, 1H), 5.77 (d, $J = 14.0$ Hz, 1H), 3.51 (t, $J = 6.6$ Hz, 2H), 2.18 (q, $J = 7.5$ Hz, 2H), 2.11–2.09 (br s, 1H, OH), 1.65–1.52 (m, 2H), 0.47 (s, 6H, $(CH_3)_2Si$); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 150.1$ (CH), 139.7 (C), 133.8 (CH), 129.0 (CH), 127.9 (CH), 127.5 (CH), 62.1 (CH_2), 32.4 (CH_2), 30.1 (CH_2), −0.8 (CH_3); MS (CI): m/z 219 ($M^+ - 1$), 205 ($M^+ - Me$), 142 ($M^+ - Ph$), 135 ($SiMe_2Ph$); HRMS (ESI+) m/z calcd for $C_{13}H_{20}NaOSi$ ($[M + Na]^+$): 243.1176, found 243.1178.

(*Z*)-5-Dimethylphenylsilyl-3-methyl-4-penten-1-ol (2b). Colorless oil (90%); IR ν_{max}(film)/cm^{-1} 3331, 1605, 1249, 1113; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 7.68$–7.62 (m, 2H), 7.44–7.40 (m, 3H), 6.24 (dd, $J = 14.0$ and 10.1 Hz, 1H), 5.70 (d $J = 14.0$ Hz, 1H), 3.51–3.37 (m, 2H), 2.48–2.34 (m, 1H), 1.78 (s, 1H, OH), 1.59–1.40 (m, 2H), 0.97 (d, $J = 6.6$ Hz, 3H), 0.49 (s, 3H, CH_3Si), 0.46 (s, 3H, CH_3Si); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 156.2$ (CH), 139.8 (C), 133.7 (CH), 129.0 (CH), 127.9 (CH), 125.8 (CH), 60.9 (CH_2), 39.8 (CH_2), 34.9 (CH), 21.0 (CH_3), −0.6 (CH_3), −1.0 (CH_3); MS (CI): m/z 219 ($M^+ - Me$), 157 ($M^+ - Ph$), 135 ($SiMe_2Ph$); HRMS (ESI+) m/z calcd for $C_{13}H_{18}NaOSi$ ($[M + Na]^+$): 257.1332, found 257.1330.

(*Z*)-5-Dimethylphenylsilyl-3-propyl-4-penten-1-ol (2c). Colorless oil (92%); IR ν_{max}(film)/cm^{-1} 3331, 1605, 1249, 1109; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 7.61$–7.58 (m, 2H), 7.40–7.38 (m, 3H), 6.15 (dd, $J = 14.0$ and 10.1 Hz, 1H), 5.69 (d, $J = 14.0$ Hz, 1H), 3.50–3.35 (m, 2H), 2.28–2.17 (m, 1H), 1.63–1.52 (m, 1H), 1.41–1.14 (m, 6H), 0.85 (t, $J = 6.6$ Hz, 3H), 0.45 (s, 3H, CH_3Si), 0.41 (s, 3H, CH_3Si); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 155.2$ (CH), 139.8 (C), 133.8 (CH), 129.0 (CH), 127.8 (CH), 126.8 (CH), 61.0 (CH_2), 40.0 (CH), 37.9 (CH_2), 37.8 (CH_2), 20.2 (CH_2), 14.4 (CH_3), −0.7 (CH_3), −0.9 (CH_3); MS (CI): m/z 261 ($M^+ - 1$), 247 ($M^+ - Me$), 185 ($M^+ - Ph$), 135 ($SiMe_2Ph$); HRMS (ESI+) m/z calcd for $C_{16}H_{26}NaOSi$ ($[M + Na]^+$): 285.1645, found 285.1642.

(*Z*)-6-Dimethylphenylsilyl-5-hexen-2-ol (2e). Colorless oil (94%); IR ν_{max}(film)/cm^{-1} 3360, 1605, 1249, 1112; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 7.57$–7.55 (m, 2H), 7.36–7.34 (m, 3H), 6.50 (dt, $J = 14.3$ and 7.4 Hz, 1H), 5.74 (dd, $J = 14.3$ and 1.1 Hz, 1H), 3.73–3.61 (m, 1H), 2.23–2.09 (m, 2H), 1.80 (br s, 1H), 1.55–1.40 (m, 2H), 1.07 (d, $J = 6.3$ Hz, 3H), 0.46 (s, 3H, CH_3Si), 0.44 (s, 3H, CH_3Si); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 152.5$ (CH), 140.0 (C), 133.8 (CH), 129.4 (CH), 128.2 (CH), 128.0 (CH), 67.9 (CH), 39.2 (CH_2), 30.2 (CH_2), 23.9 (CH_3), −0.5 (CH_3), −0.6 (CH_3); MS (CI): m/z 233 ($M^+ - 1$), 219 ($M^+ - Me$), 157 ($M^+ - Ph$), 135 ($SiMe_2Ph$); HRMS (ESI+) m/z calcd for $C_{14}H_{22}NaOSi$ ($[M + Na]^+$): 257.1332, found 257.1331.

(*Z*)-7-Dimethylphenylsilyl-6-hepten-3-ol (2f). Colorless oil (91%); IR ν_{max}(film)/cm^{-1} 3402, 1605, 1248, 1112; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 7.57$–7.53 (m, 2H), 7.37–7.32 (m, 3H), 6.43 (dt, $J = 14.0$ and 7.0 Hz, 1H), 5.68 (d, $J = 14.0$ Hz, 1H), 3.40–3.30 (m, 1H), 2.20–2.08 (m, 2H), 1.42–1.27 (m, 4H), 1.27 (br s, 1H), 0.83 (t, $J = 7.0$ Hz, 3H), 0.41 (s, 3H, CH_3Si), 0.40 (s, 3H, CH_3Si); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 150.5$ (CH), 139.9 (C), 133.9 (CH), 129.1 (CH), 128.0 (CH), 127.5 (CH), 72.9 (CH), 36.6 (CH_2), 30.2 (CH_2), 30.1 (CH_2), 10.0 (CH_3), −0.7 (CH_3), −0.8 (CH_3); MS (CI): m/z 247 ($M^+ - 1$), 171 ($M^+ - Ph$), 135 ($SiMe_2Ph$); HRMS (ESI+) m/z calcd for $C_{15}H_{24}NaOSi$ ($[M + Na]^+$): 271.1489, found 271.1490.

(*Z*)-6-Dimethylphenylsilyl-4,4-dimethyl-5-hexen-2-ol (2g). Colorless oil (90%); IR ν_{max}(film)/cm^{-1} 3397, 1605, 1248, 1111; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 7.62$–7.58 (m, 2H), 7.40–7.38 (m, 3H), 6.59 (d, $J = 15.8$ Hz, 1H), 5.72 (d, $J = 15.4$ Hz, 1H), 3.88–3.82

(m, 1H), 1.73 (s, 1H), 1.69 (dd, $J = 14.0$ and 8.7 Hz, 1H), 1.36 (dd, $J = 14.0$ and 3.0 Hz, 1H), 1.08 (d, $J = 6.1$ Hz, 3H), 1.00 (s, 3H), 0.98 (s, 3H), 0.45 (s, 3H, CH_3Si), 0.43 (s, 3H, CH_3Si); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 160.9$ (CH), 140.5 (C), 133.7 (CH), 128.8 (CH), 127.8 (CH), 124.6 (CH), 65.5 (CH), 52.7 (CH_2), 38.5 (C), 29.1 (CH_3), 27.3 (CH_3), 24.9 (CH_3), 0.6 (CH_3), 0.5 (CH_3); MS (CI): *m/z* 261 ($M^+ - 1$), 247 ($M^+ - Me$), 185 ($M^+ - Ph$), 135 ($SiMe_2Ph$); HRMS (ESI+) *m/z* calcd for $C_{16}H_{26}NaOSi$ ($[M + Na]^+$): 285.1645, found 285.1647.

(*Z*,2*S,4*R**)-6-Dimethylphenylsilyl-4-phenyl-5-hexen-2-ol (2h).** Colorless oil (44%); IR ν_{max}(film)/cm^{-1} 3412, 1605, 1250, 1118; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 7.63$–7.55 (m, 2H), 7.44–7.38 (m, 3H), 7.28–7.23 (m, 2H), 7.20–7.15 (m, 1H), 7.05–7.00 (m, 2H), 6.63 (dd, $J = 14.0$ and 10.5 Hz, 1H), 5.72 (d, $J = 14.0$ Hz, 1H), 3.63–3.55 (m, 1H), 3.49–3.39 (m, 1H), 1.83–1.71 (m, 1H), 1.69–1.53 (m, 1H), 1.28 (s, 1H), 1.01 (d, $J = 6.1$ Hz, 3H), 0.46 (s, 3H, CH_3Si), 0.42 (s, 3H, CH_3Si); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 153.7$ (CH), 143.7 (C), 139.9 (C), 134.1 (CH), 129.3 (CH), 128.8 (CH), 128.1 (CH), 127.5 (CH), 126.4 (CH), 65.7 (CH), 46.7 (CH), 46.3 (CH_2), 24.1 (CH_3), −0.6 (CH_3), −0.9 (CH_3); MS (CI): *m/z* 309 ($M^+ - 1$), 295 ($M^+ - Me$), 233 ($M^+ - Ph$), 135 ($SiMe_2Ph$); HRMS (ESI+) *m/z* calcd for $C_{20}H_{26}NaOSi$ ($[M + Na]^+$): 333.1645, found 333.1646.

(*Z*,2*R,4*R**)-6-Dimethylphenylsilyl-4-phenyl-5-hexen-2-ol (3h).** White solid m.p. 52.5 °C (44%); IR ν_{max}(film)/cm^{-1} 3412, 1605, 1250, 1118; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 7.63$–7.55 (m, 2H), 7.44–7.38 (m, 3H), 7.28–7.23 (m, 2H), 7.20–7.15 (m, 1H), 7.05–7.00 (m, 2H), 6.51 (dd, $J = 14.0$ and 10.5 Hz, 1H), 5.69 (d, $J = 14.0$ Hz, 1H), 3.61–3.49 (m, 2H), 1.94–1.81 (m, 1H), 1.71–1.61 (m, 1H), 1.30–1.21 (brs, 1H), 1.05 (t, $J = 6.2$ Hz, 3H), 0.51 (s, 6H, $(CH_3)_2Si$); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 153.0$ (CH), 144.1 (C), 139.6 (C), 134.0 (CH), 129.2 (CH), 128.6 (CH), 128.1 (CH), 127.2 (CH), 126.2 (CH), 65.7 (CH), 46.3 (CH_2), 46.1 (CH), 23.4 (CH_3), −0.6 (CH_3), −1.1 (CH_3); MS (CI): *m/z* 309 ($M^+ - 1$), 295 ($M^+ - Me$), 233 ($M^+ - Ph$), 135 ($SiMe_2Ph$).

(*Z*,2*R,4*S**)-6-Dimethylphenylsilyl-4-isopropyl-5-hexen-2-ol (2i).** Colorless oil (46%); IR ν_{max}(film)/cm^{-1} 3371, 1252, 1114; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 7.59$–7.55 (m, 2H), 7.37–7.35 (m, 3H), 6.17 (dd, $J = 14.2$ and 10.7 Hz, 1H), 5.72 (d, $J = 14.2$ Hz, 1H), 3.56–3.51 (m, 1H), 2.19–2.12 (m, 1H), 1.55–1.51 (m, 2H), 1.40 (ddd, $J = 13.8$, 9.6 and 3.2 Hz, 1H), 1.19 (ddd, $J = 13.8$, 10.5 and 2.7 Hz, 1H), 1.06 (d, $J = 6.2$ Hz, 3H), 0.82 (d, $J = 6.8$ Hz, 3H), 0.81 (d, $J = 6.8$ Hz, 3H), 0.45 (s, 3H), 0.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 153.6$ (CH), 140.3 (C), 134.1 (CH), 129.4 (CH), 128.4 (CH), 128.3 (CH), 65.9 (CH), 45.4 (CH), 41.4 (CH_2), 32.9 (CH), 24.6 (CH_3), 20.1 (CH_3), 19.7 (CH_3), −0.1 (CH_3), −0.6 (CH_3); MS (CI): *m/z* 276 (M^+), 275 ($M^+ - 1$), 261 ($M^+ - Me$), 259 ($M^+ - OH$), 244 ($M^+ - {}^iPr$), 199 ($M^+ - Ph$), 135 ($SiMe_2Ph$); HRMS (ESI+) *m/z* calcd for $C_{17}H_{28}NaOSi$ ($[M + Na]^+$): 299.1805, found 299.1804.

(*Z*,2*S,4*S**)-6-Dimethylphenylsilyl-4-isopropyl-5-hexen-2-ol (3i).** Colorless oil (46%); IR ν_{max}(film)/cm^{-1} 3383, 1252, 1113; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 7.57$–7.54 (m, 2H), 7.37–7.35 (m, 3H), 6.35 (dd, $J = 14.2$ and 10.7 Hz, 1H), 5.73 (d, $J = 14.2$ Hz, 1H), 3.61–3.57 (m, 1H), 2.09–2.04 (m, 1H), 1.58–1.51 (m, 2H), 1.46 (dt, $J = 13.8$ and 4.6 Hz, 1H), 1.33–1.25 (m, 1H), 1.02 (d, $J = 6.2$ Hz, 3H), 0.80 (d, $J = 6.8$ Hz, 3H), 0.75 (d, $J = 6.8$ Hz, 3H), 0.43 (s, 3H), 0.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 153.9$ (CH), 139.5 (C), 133.8 (CH), 129.0 (CH), 128.2 (CH), 127.8 (CH), 67.4 (CH), 46.5 (CH), 41.4 (CH_2), 31.9 (CH), 23.6 (CH_3), 19.6 (CH_3), 19.1 (CH_3), −0.6 (CH_3), −0.9 (CH_3).

(*E*)-5-Dimethylphenylsilyl-3,4-diphenyl-4-penten-1-ol (2j). Colorless oil (89%); IR ν_{max}(film)/cm^{-1} 3474, 1565, 1252, 1113; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 7.71$–7.68 (m, 2H), 7.45–7.44 (m, 3H), 7.27–7.15 (m, 7H), 7.08–7.05 (m, 1H), 6.88–6.85 (m, 2H), 5.89 (s, 1H), 4.13 (t, $J = 7.9$ Hz, 1H), 3.38–3.37 (m, 2H), 2.21–2.11 (m, 1H), 1.87–1.73 (m, 1H), 0.95 (s, 1H), 0.58 (s, 3H), 0.56 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 161.7$ (C), 143.4 (C), 141.7 (C), 139.9 (C), 134.2 (CH), 130.4 (CH), 129.5 (CH), 128.4 (CH), 128.3 (CH), 128.3 (CH), 127.7 (CH), 127.1 (CH), 126.5 (CH), 61.1 (CH_2), 47.2 (CH), 35.1 (CH_2), −0.3 (CH_3), −0.8 (CH_3); MS (CI) *m/z* (%): 373 ($M^+ + 1$), 372 (M^+), 357 ($M^+ - Me$), 355 ($M^+ - OH$), 295 ($M^+ - Ph$), 237 ($M^+ - PhMe_2Si$), 135 ($PhMe_2Si$).

(*E*,1*R,3*S**)-5-Dimethylphenylsilyl-1,3,4-triphenyl-4-penten-1-ol (2k).** White solid m.p. = 101–102 °C (45%); IR ν_{max}(film)/cm^{-1} 3476, 1551, 1259, 1106; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 7.74$–6.72 (m, 20H), 5.64 (s, 1H), 4.40–4.30 (m, 2H), 2.29–2.22 (m, 1H), 2.06–1.99 (m, 1H), 1.30 (brs, 1H, OH), 0.56 (s, 3H, CH_3Si), 0.55 (s, 3H, CH_3Si); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 163.2$ (C), 145.2 (C), 143.9 (C), 140.7 (C), 140.1 (C), 134.4 (CH), 129.3 (CH), 129.1 (CH), 128.8 (CH), 128.6 (CH), 128.5 (CH), 128.2 (CH), 128.1 (CH), 127.6 (CH), 127.4 (CH), 126.7 (CH), 126.5 (CH), 125.8 (CH), 71.90 (CH), 48.4 (CH), 42.5 (CH_2), −0.6 (CH_3), −0.7 (CH_3).

(*E*,1*S,3*S**)-5-Dimethylphenylsilyl-1,3,4-triphenyl-4-penten-1-ol (3k).** White solid m.p. = 77–78 °C (45%); IR ν_{max}(film)/cm^{-1} 3476, 1551, 1259, 1106; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 7.59$–6.88 (m, 20H), 5.95 (brs, 1H), 4.47 (dd, $J = 7.5$ and 4.1 Hz, 1H), 4.21 (dd, $J = 7.2$ and 6.2 Hz, 1H), 2.32–2.28 (m, 1H), 2.03–1.97 (m, 1H), 1.43 (brs, 1H, OH), 0.43 (s, 3H, CH_3Si), 0.42 (s, 3H, CH_3Si); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 160.9$ (C), 145.1 (C), 143.6 (C), 141.9 (C), 140.1 (C), 134.0 (CH), 131.3 (CH), 129.3 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 127.7 (CH), 127.5 (CH), 127.1 (CH), 126.4 (CH), 125.7 (CH), 72.0 (CH), 47.2 (CH), 42.1 (CH_2), −0.5 (CH_3), −1.0 (CH_3).

Synthesis of tetrahydrofurans 4, 5 using mercury salts

To a suspension of the mercury salt (1.09 mmol) and $CaCO_3$ (2.17 mmol) in 9 ml of dry THF was added a solution of the vinylsilyl alcohol (1 mmol) in dry THF (1 ml). The mixture was stirred at room temperature (Tables 2 and 3) and then $NaBH_4$ (0.72 mmol) in a 2.5 M solution of NaOH (4 ml) was added dropwise at 0 °C. The reaction mixture was vigorously stirred at 0 °C for l hour and then saturated NaCl solution was added (4 ml). The aqueous layer was extracted with ether and the combined extracts were washed with brine, dried over $MgSO_4$ and evaporated *in vacuo* to give an oil which was purified by chromatography (EtOAc/hexane 1 : 20).

Synthesis of tetrahydrofurans 4–7 using acid catalysis

To a solution of the vinylsilyl alcohol (1 mmol) in CH_2Cl_2 (5 ml) was added *p*-TsOH (1 mmol) in CH_2Cl_2 (0.5 ml) at room temperature. The mixture was stirred at the shown conditions (Table 3) and quenched with saturated solution of $NaHCO_3$ (5 ml). The organic layer was washed 3 times with $NaHCO_3$, dried over $MgSO_4$, evaporated *in vacuo* and purified by flash chromatography (EtOAc/hexane 1 : 20). The relative stereochemistry of all tetrahydrofurans was assigned on the basis of NOE experiments. The spectroscopic data of tetrahydrofuran **4d** has been previously described.[9b]

2-Dimethylphenylsilylmethyl-tetrahydrofuran (4a). Colorless oil (92%); IR ν_{max}(film)/cm^{-1} 1245, 1109; ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 7.59$–7.55 (m, 2H), 7.43–7.35 (m, 3H), 3.97–3.85 (m, 2H), 3.71–3.63 (m, 1H), 1.94–1.80 (m, 3H), 1.45–1.32 (m, 2H), 1.11 (dd, $J = 14.0$ y 8.3 Hz, 1H), 0.37 (s, 6H, $(CH_3)_2Si$); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 139.1$ (C), 133.5 (CH), 128.9 (CH), 127.7 (CH), 77.1 (CH), 66.9 (CH_2), 33.8 (CH_2), 25.9 (CH_2), 23.4 (CH_2), −2.1 (CH_3), −2.4 (CH_3); MS (CI): *m/z* 219 ($M^+ - 1$), 205 ($M^+ -$ Me), 143 ($M^+ -$ Ph), 135 ($SiMe_2Ph$); HRMS (ESI+) *m/z* calcd for $C_{13}H_{20}NaOSi$ ($[M + Na]^+$): 243.1176, found 243.1173.

(2*R,3*R**)-2-Dimethylphenylsilylmethyl-3-methyl-tetrahydrofuran (4b).** Colorless oil (90%); IR ν_{max}(film)/cm^{-1} 1249, 1109; ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 7.63$–7.58 (m, 2H), 7.46–7.39 (m, 3H), 3.92–3.85 (m, 1H), 3.82–3.75 (m, 1H), 3.51–3.44 (m, 1H), 2.17–2.05 (m, 1H), 1.83–1.73 (m, 1H), 1.58–1.45 (m, 1H), 1.21 (dd, $J = 14.5$ and 4.6 Hz, 1H), 1.06 (dd, $J = 14.5$ and 8.8 Hz, 1H), 1.01 (d, $J = 6.6$ Hz, 3H), 0.41 (s, 6H, $(CH_3)_2Si$); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 139.8$ (C), 133.6 (CH), 128.7 (CH), 127.7 (CH), 83.6 (CH), 66.2 (CH_2), 42.1 (CH), 34.2 (CH_2), 21.5 (CH_2), 17.0 (CH_3), −1.7 (CH_3), −2.4 (CH_3); MS (CI): *m/z* 233 ($M^+ - 1$), 213 ($M^+ -$ Me), 157 ($M^+ -$ Ph), 135 ($SiMe_2Ph$); HRMS (ESI+) *m/z* calcd for $C_{14}H_{22}NaOSi$ ($[M + Na]^+$): 257.1332, found 257.1333.

(2*R,3*R**)-2-Dimethylphenylsilylmethyl-3-propyl-tetrahydrofuran (4c).** Colorless oil (80%); IR ν_{max}(film)/cm^{-1} 1252, 1113; ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 7.61$–7.55 (m, 2H), 7.42–7.35 (m, 3H), 3.87–3.79 (m, 1H), 3.80–3.71 (m, 1H), 3.56–3.49 (m, 1H), 2.12–2.00 (m, 1H), 1.71–1.61 (m, 1H), 1.53–1.39 (m, 1H), 1.38–1.24 (m, 3H), 1.21–1.13 (m, 2H), 1.04 (dd, $J = 14.5$ y 8.8 Hz, 1H), 0.89 (t, $J = 7.0$ Hz, 3H), 0.36 (s, 3H, CH_3Si), 0.35 (s, 3H, CH_3Si); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 139.8$ (C), 133.6 (CH), 128.7 (CH), 127.6 (CH), 82.3 (CH), 66.3 (CH_2), 47.5 (CH), 35.0 (CH_2), 32.2 (CH_2), 22.2 (CH_2), 21.5 (CH_2), 14.2 (CH_3), −1.7 (CH_3), −2.5 (CH_3); MS (CI): *m/z* 261 ($M^+ - 1$), 247 ($M^+ -$ Me), 185 ($M^+ -$ Ph), 135 ($SiMe_2Ph$); HRMS (ESI+) *m/z* calcd for $C_{16}H_{26}NaOSi$ ($[M + Na]^+$): 285.1645, found 285.1643.

(2*R,5*S**)-2-Dimethylphenylsilylmethyl-5-methyl-tetrahydrofuran (4e).** Colorless oil (71%); IR ν_{max}(film)/cm^{-1} 1249, 1109; ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 7.60$–7.52 (m, 2H), 7.37–7.34 (m, 3H), 4.17–4.06 (m, 2H), 2.07–1.88 (m, 2H), 1.51–1.33 (m, 3H), 1.18 (d, $J = 6.1$ Hz, 3H), 1.06 (dd, $J = 14.2$ and 9.0 Hz, 1H), 0.33 (s, 6H, $(CH_3)_2Si$); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 139.1$ (C), 133.5 (CH), 128.8 (CH), 127.7 (CH), 76.2 (CH), 73.6 (CH), 34.9 (CH_2), 34.5 (CH_2), 24.0 (CH_2), 21.5 (CH_3), −2.2 (CH_3), −2.4 (CH_3); MS (CI): *m/z* 233 ($M^+ - 1$), 219 ($M^+ -$ Me), 157 ($M^+ -$ Ph), 135 ($SiMe_2Ph$); HRMS (ESI+) *m/z* calcd for $C_{14}H_{22}NaOSi$ ($[M + Na]^+$): 257.1332, found 257.1331.

(2*S,5*S**)-2-Dimethylphenylsilylmethyl-5-methyl-tetrahydrofuran (5e).** Colorless oil (9%); IR ν_{max}(film)/cm^{-1} 1249, 1109; ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 7.60$–7.52 (m, 2H), 7.40–7.34 (m, 3H), 3.92–3.82 (m, 2H), 1.98–1.86 (m, 2H), 1.48–1.36 (m, 3H), 1.23 (d, $J = 6.1$ Hz, 3H), 1.08 (dd, $J = 14.0$ and 9.2 Hz, 1H), 0.32 (s, 6H, $(CH_3)_2Si$); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 139.1$ (C), 133.5 (CH), 128.8 (CH), 127.7 (CH), 77.2 (CH), 74.4 (CH), 33.6 (CH_2), 33.2 (CH_2), 24.0 (CH_2), 21.4 (CH_3), −2.1 (CH_3), −2.3 (CH_3); MS (CI): *m/z* 233 ($M^+ - 1$), 219 ($M^+ -$ Me), 157 ($M^+ -$ Ph), 135 ($SiMe_2Ph$).

(2*R,5*S**)-2-Dimethylphenylsilylmethyl-5-ethyl-tetrahydrofuran (4f).** Colorless oil (63%); IR ν_{max}(film)/cm^{-1} 1249, 1109; ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 7.60$–7.54 (m, 2H), 7.41–7.36 (m, 3H), 4.12–4.03 (m, 1H), 3.92–3.83 (m, 1H), 2.06–1.91 (m, 2H), 1.63–1.32 (m, 5H), 1.07 (dd, $J = 14.0$ y 8.3 Hz, 1H), 0.93 (t, $J = 7.5$ Hz, 3H), 0.35 (s, 3H, CH_3Si), 0.34 (s, 3H, CH_3Si); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 139.3$ (C), 133.5 (CH), 128.8 (CH), 127.7 (CH), 79.3 (CH), 76.2 (CH), 34.9 (CH_2), 32.1 (CH_2), 29.0 (CH_2), 23.9 (CH_2), 10.4 (CH_3), −2.1 (CH_3),−2.4 (CH_3); MS (CI): *m/z* 247 ($M^+ - 1$), 233 ($M^+ -$ Me), 171 ($M^+ -$ Ph), 135 ($SiMe_2Ph$); HRMS (ESI+) *m/z* calcd for $C_{15}H_{24}NaOSi$ ($[M + Na]^+$): 271.1489, found 271.1488.

(2*S,5*S**)-2-Dimethylphenylsilylmethyl-5-ethyl-tetrahydrofuran (5f).** Colorless oil (24%); IR ν_{max}(film)/cm^{-1} 1249, 1109; ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 7.61$–7.53 (m, 2H), 7.39–7.32 (m, 3H), 3.95–3.85 (m, 1H), 3.70–3.64 (m, 1H), 1.91–1.86 (m, 2H), 1.63–1.35 (m, 4H), 1.37 (dd, $J = 14.5$ and 5.7 Hz, 1H), 1.08 (dd, $J = 14.5$ and 8.6 Hz, 1H), 0.93 (t, $J = 7.5$ Hz, 3H), 0.34 (s, 3H, CH_3Si), 0.33 (s, 3H, CH_3Si); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 139.3$ (C), 133.5 (CH), 128.8 (CH), 127.6 (CH), 80.0 (CH), 76.9 (CH), 33.6 (CH_2), 31.0 (CH_2), 29.0 (CH_2), 23.9 (CH_2), 10.4 (CH_3), −2.1 (CH_3), −2.3 (CH_3); MS (CI): *m/z* 247 ($M^+ - 1$), 233 ($M^+ -$ Me), 171 ($M^+ -$ Ph), 135 ($SiMe_2Ph$); HRMS (ESI+) *m/z* calcd for $C_{15}H_{24}NaOSi$ ($[M + Na]^+$): 271.1489, found 271.1488.

(2*R,5*S**)-2-Dimethylphenylsilylmethyl-3,3,5-trimethyl-tetrahydrofuran (4g).** Colorless oil (76%); IR ν_{max}(film)/cm^{-1} 1249, 1109; ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 7.62$–7.57 (m, 2H), 7.37–7.27 (m, 3H), 4.16–4.09 (m, 1H), 3.57 (dd, $J = 10.5$ and 3.1 Hz, 1H), 1.86 (dd, $J = 12.1$ and 6.8 Hz, 1H), 1.31 (dd $J = 12.1$ and 8.5 Hz, 1H), 1.17 (d, $J = 6.1$ Hz, 3H), 0.95–0.80 (m, 2H), 0.92 (s, 3H), 0.88 (s, 3H), 0.37 (s, 3H, CH_3Si), 0.35 (s, 3H, CH_3Si); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 139.9$ (C), 133.7 (CH), 128.6 (CH), 127.5 (CH), 82.9 (CH), 71.5 (CH), 49.1 (CH_2), 42.5 (C), 24.9 (CH_3), 22.4 (CH_3), 21.2 (CH_3), 15.4 (CH_2), −1.8 (CH_3), −2.8 (CH_3); MS (CI): *m/z* 261 ($M^+ - 1$), 247 ($M^+ -$ Me), 185 ($M^+ -$ Ph), 135 ($SiMe_2Ph$); HRMS (ESI+) *m/z* calcd for $C_{16}H_{26}NaOSi$ ($[M + Na]^+$): 285.1645, found 285.1648.

(2*S,5*S**)-2-Dimethylphenylsilylmethyl-3,3,5-trimethyl-tetrahydrofuran (5g).** Colorless oil (14%); IR ν_{max}(film)/cm^{-1} 1249, 1109; ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 7.65$–7.61 (m, 2H), 7.42–7.38 (m, 3H), 4.03–3.93 (m, 1H), 3.52 (dd, $J = 11.5$ and 2.7 Hz, 1H), 1.84 (dd, $J = 12.3$ and 7.8 Hz, 1H), 1.37 (dd, $J = 12.3$ and 7.4 Hz, 1H), 1.27 (d, $J = 6.1$ Hz, 3H), 1.03–0.95 (m, 1H), 0.99 (s, 3H), 0.96 (s, 3H), 0.85 (dd, $J = 14.5$ and 2.7 Hz, 1H), 0.42 (s, 3H, CH_3Si), 0.41 (s, 3H, CH_3Si); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 140.1$ (C), 133.8 (CH), 128.7 (CH), 127.7 (CH), 85.2 (CH), 72.5 (CH), 48.4 (CH_2), 41.9 (C), 26.5 (CH_3), 24.3 (CH_3), 22.5 (CH_3), 17.0 (CH_2), −1.4 (CH_3), −2.5 (CH_3); MS (CI): *m/z* 261 ($M^+ - 1$), 247 ($M^+ -$ Me), 185 ($M^+ -$ Ph), 135 ($SiMe_2Ph$).

(2*R,3*S**,5*S**)-2-Dimethylphenylsilylmethyl-5-methyl-3-phenyltetrahydrofuran (4h).** Colorless oil (92%); IR ν_{max}(film)/cm^{-1} 1252, 1109; ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 7.52$–7.49 (m, 2H), 7.38–7.27 (m, 3H), 7.25–7.17 (m, 5H), 4.31–4.23 (m, 1H), 4.14–4.07 (m, 1H), 2.98–2.89 (m, 1H), 2.50–2.41 (m, 1H), 1.79–1.62

(m, 1H), 1.37–1.31 (m, 1H), 1.33 (d, $J = 6.1$ Hz, 3H), 1.13–1.10 (m, 1H), 0.32 (s, 3H, CH_3Si), 0.30 (s, 3H, CH_3Si); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 141.7$ (C), 139.7 (C), 133.6 (CH), 132.9 (CH), 128.6 (CH), 128.5 (CH), 127.6 (CH), 126.4 (CH), 82.6 (CH), 73.7 (CH), 55.7 (CH), 43.9 (CH_2), 21.7 (CH_3), 21.6 (CH_2), −1.8 (CH_3), −2.5 (CH_3); MS (CI): *m/z* 309 ($M^+ - 1$), 295 ($M^+ - Me$), 233 ($M^+ - Ph$), 135 ($SiMe_2Ph$); HRMS (ESI+) *m/z* calcd for $C_{20}H_{26}NaOSi$ ($[M + Na]^+$): 333.1645, found 333.1639.

(2*R,3*S**,5*R**)-2-Dimethylphenylsilylmethyl-5-methyl-3-phenyl-tetrahydrofuran (6h).** Colorless oil (91%); IR ν_{max}(film)/cm^{-1} 1252, 1109; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 7.62$–7.59 (m, 2H), 7.44–7.37 (m, 5H), 7.33–7.28 (m, 3H), 4.39–4.30 (m, 1H), 4.07–4.01 (m, 1H), 3.04–2.96 (m, 1H), 2.29–2.19 (m, 1H), 2.13–2.03 (m, 1H), 1.41 (d, $J = 6.1$ Hz, 3H), 1.24–1.22 (m, 2H), 0.44 (s, 3H, CH_3Si), 0.41 (s, 3H, CH_3Si); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 142.5$ (C), 139.8 (C), 133.7 (CH), 128.5 (CH), 127.8 (CH), 127.7 (CH), 126.4 (CH), 84.5 (CH), 74.4 (CH), 54.2 (CH), 42.6 (CH_2), 22.2 (CH_3), 21.6 (CH_2), −1.5 (CH_3), −2.3 (CH_3); MS (CI): *m/z* 309 ($M^+ - 1$), 295 ($M^+ - Me$), 233 ($M^+ - Ph$), 135 ($SiMe_2Ph$); HRMS (ESI+) *m/z* calcd for $C_{20}H_{26}NaOSi$ ($[M + Na]^+$): 333.1645, found 333.1641.

(2*R,3*S**,5*S**)-2-Dimethylphenylsilylmethyl-3-isopropyl-5-methyltetrahydrofuran (4i).** Colorless oil (90%); ^1H NMR (300 MHz, $CDCl_3$) $\delta = 7.62$–7.44 (m, 2H), 7.42–7.28 (m, 3H), 4.04–3.78 (m, 2H), 2.02–1.92 (m, 1H), 1.66–1.42 (m, 2H), 1.15 (d, $J = 6.0$ Hz, 3H), 1.15–1.09 (m, 2H), 1.05 (dd, $J = 14.7$ and 4.4 Hz, 1H), 0.83 (d, $J = 6.6$ Hz, 3H), 0.81 (d, $J = 6.6$ Hz, 3H), 0.33 (s, 3H, CH_3Si), 0.32 (s, 3H, CH_3Si); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 140.2$ (C), 133.7 (CH), 128.7 (CH), 127.7 (CH), 79.6 (CH), 73.1 (CH), 56.7 (CH), 38.5 (CH_2), 31.1 (CH), 24.7 (CH_2), 22.1 (CH_3), 21.0 (CH_3), 20.0 (CH_3), −1.6 (CH_3), −2.3 (CH_3); HRMS (ESI+) *m/z* calcd for $C_{17}H_{28}NaOSi$ ($[M + Na]^+$): 299.1802, found 299.1804.

(2*R,3*S**,5*R**)-2-Dimethylphenylsilylmethyl-3-isopropyl-5-methyltetrahydrofuran (6i).** Colorless oil (89%); ^1H NMR (300 MHz, $CDCl_3$) $\delta = 7.61$–7.46 (m, 2H), 7.43–7.27 (m, 3H), 3.93–3.78 (m, 1H), 3.75–3.55 (m, 1H), 1.80–1.65 (m, 1H), 1.63–1.39 (m, 3H), 1.17 (d, $J = 6.1$ Hz, 3H), 1.19–1.14 (m, 1H), 1.07 (dd, $J = 14.6$, 8.7 Hz, 1H), 0.83 (d, $J = 6.5$ Hz, 3H), 0.81 (d, $J = 6.5$ Hz, 3H), 0.33 (s, 3H, CH_3Si), 0.32 (s, 3H, CH_3Si); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 140.3$ (C), 133.8 (CH), 128.7 (CH), 127.7 (CH), 80.5 (CH), 74.1 (CH), 54.3, (CH) 36.7 (CH_2), 29.9 (CH), 24.3 (CH_2), 21.9 (CH_3), 19.8 (CH_3), −1.3 (CH_3), −2.1 (CH_3); HRMS (ESI+) *m/z* calcd for $C_{17}H_{28}NaOSi$ ($[M + Na]^+$): 299.1802, found 299.1805.

(2*S,3*S**)-2-Dimethylphenylsilylmethyl-2,3-diphenyl-tetrahydrofuran (4j) and (2*R**,3*S**)-2-dimethylphenylsilyl-methyl-2,3-diphenyltetrahydrofuran (5j).** Colorless oil (86%, 55 : 45 mixture of **4j** and **5j**); **4j:** ^1H NMR (300 MHz, $CDCl_3$) $\delta = 7.50$–6.67 (m, 15H), 4.40–4.30 (m, 1H), 4.10–4.04 (m, 1H), 3.36 (dd, $J = 10$ and 8.1 Hz, 1H), 2.21–2.13 (m, 2H), 1.76 (d, $J = 14.7$ Hz, 1H), 1.72 (d, $J = 14.7$ Hz, 1H), 0.30 (s, 3H, CH_3Si), 0.15 (s, 3H, CH_3Si); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 145.4$ (C), 140.9 (C), 139.1 (C), 133.4 (CH), 128.9 (CH), 128.4 (CH), 128.3 (CH), 127.4 (CH), 127.2 (CH), 126.5 (CH), 126.3 (CH), 125.6 (CH), 88.5 (C), 66.0 (CH_2), 58.6 (CH), 31.0 (CH_2), 30.5 (CH_2), −1.3 (CH_3), −1.8 (CH_3); **5j:** ^1H NMR (300 MHz, $CDCl_3$) $\delta = 7.50$–6.67 (m, 15H), 4.15–4.09 (m, 2H), 3.29 (dd, $J = 9.2$ and 7.4 Hz, 1H), 2.43–2.36 (m, 1H), 2.27–2.20 (m, 1H), 1.37 (d, $J = 15$ Hz, 1H), 1.07 (d, $J = 15$ Hz, 1H), −0.19 (s, 3H, CH_3Si), −0.11 (s, 3H, CH_3Si); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 145.4$ (C), 140.9 (C), 139.1 (C), 133.4 (CH), 128.9 (CH), 128.4 (CH), 128.3 (CH), 127.4 (CH), 127.2 (CH), 126.5 (CH), 126.3 (CH), 125.6 (CH), 89.2 (C), 66.4 (CH_2), 58.7 (CH), 32.1 (CH_2), 24.5 (CH_2), −1.3 (CH_3), −1.8 (CH_3).

(2*S,3*S**,5*R**)-2-Dimethylphenylsilylmethyl-2,3,5-triphenyl-tetrahydrofuran (4k) and (2*R**,3*S**,5*R**)-2-dimethylphenylsilyl-methyl-2,3,5-triphenyltetrahydrofuran (5k).** Colorless oil (85%, 57 : 43 mixture of **4k** and **5k**); **4k:** ^1H NMR (300 MHz, $CDCl_3$) $\delta =$ 7.57–6.72 (m, 20H), 5.29 (dd, $J = 10.9$ and 5.0 Hz, 1H), 3.70 (dd, $J = 12.1$ and 5.9 Hz, 1H), 2.57–2.50 (m, 1H), 2.25 (ddd, $J = 12.1$, 12.0 and 10.9 Hz, 1H), 1.96 (d, $J = 14.6$ Hz, 1H), 1.87 (d, $J = 14.6$ Hz, 1H), 0.28 (s, 3H, CH_3Si), −0.10 (s, 3H, CH_3Si); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 145.2$ (C), 143.9 (C), 140.7 (C), 140.1 (C), 134.3 (CH), 133.6 (CH), 129.3 (CH), 128.8 (CH), 128.6 (CH), 127.7 (CH), 127.3 (CH), 126.8 (CH), 126.4 (CH), 126.1 (CH), 125.8 (CH), 90.0 (C), 78.1 (CH), 61.3 (CH), 38.7 (CH_2), 31.8 (CH_2), −1.0 (CH_3), −1.6 (CH_3); **5k:** ^1H NMR (300 MHz, $CDCl_3$) $\delta = 7.57$–6.72 (m, 20H), 5.24 (dd, $J = 10.9$ and 4.9 Hz, 1H), 3.61 (dd, $J = 12.1$ and 6.4 Hz, 1H), 2.57–2.50 (m, 1H), 2.39 (ddd, $J = 12.1$, 12.0 and 10.9 Hz, 1H), 1.51 (d, $J = 14.5$ Hz, 1H), 1.04 (d, $J = 14.5$ Hz, 1H), 0.11 (s, 3H, CH_3Si), −0.24 (s, 3H, CH_3Si); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 145.2$ (C), 143.9 (C), 140.7 (C), 140.1 (C), 134.3 (CH), 133.6 (CH), 129.3 (CH), 128.8 (CH), 128.6 (CH), 127.7 (CH), 127.3 (CH), 126.8 (CH), 126.4 (CH), 126.1 (CH), 125.8 (CH), 88.5 (C), 79.9 (CH), 59.9 (CH), 42.2 (CH_2), 27.5 (CH_2), −0.9 (CH_3), −1.3 (CH_3).

(2*S,3*S**,5*S**)-2-Dimethylphenylsilylmethyl-2,3,5-triphenyl-tetrahydrofuran (6k) and (2*R**,3*S**,5*S**)-2-dimethylphenylsilyl-methyl-2,3,5-triphenyltetrahydrofuran (7k).** Colorless oil (82%, mixture of **6k** and **7k**); **6k:** ^1H NMR (300 MHz, $CDCl_3$) $\delta = 7.51$–6.71 (m, 20H), 5.64 (d, $J = 9.0$ Hz, 1H), 3.43–3.38 (m, 1H), 2.71–2.62 (m, 1H), 2.12–2.07 (m, 1H), 1.95 (d, $J = 14.5$ Hz, 1H), 1.75 (d, $J = 14.5$ Hz, 1H), 0.27 (CH_3), −0.26 (CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 145.49$ (C), 142.82 (C), 140.99 (C), 137.69 (C), 133.62 (CH), 129.13 (CH), 128.59 (CH), 128.29 (CH), 127.80 (CH), 127.55 (CH), 127.07 (CH), 126.95 (CH), 126.62 (CH), 125.52 (CH), 90.94, (C), 78.13 (CH), 58.68 (CH), 38.17 (CH_2), 30.90 (CH_2), −0.96 (CH_3), −1.89 (CH_3); **7k:** ^1H NMR (300 MHz, $CDCl_3$) $\delta = 7.49$–6.71 (m, 20H), 5.10 (dd, $J = 9.3$, 4.5 Hz, 1H), 3.38 (dd, $J = 11.4$ and 8.7 Hz, 1H), 3.02–2.93 (m, 1H), 2.33 (ddd, $J = 13.1$, 8.7 and 4.5 Hz, 1H), 1.75 (d, $J = 14.5$ Hz, 1H), 1.18 (d, $J = 14.5$ Hz, 1H), 0.16 (CH_3), −0.18 (CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta =$ 146.18 (C), 144.63 (C), 140.99 (C), 138.16 (C), 133.64 (CH), 129.69 (CH), 128.56 (CH), 127.99 (CH), 127.78 (CH), 127.70 (CH), 127.37 (CH), 126.39 (CH), 125.65 (CH), 89.36 (C), 77.17 (CH), 57.13 (CH), 40.04 (CH_2), 22.21 (CH_2), −1.47 (CH_3), −1.69 (CH_3).

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17 See ESI† for details about level of theory procedure followed.

18 Several attempts to optimize **I** in a conformation similar to that in **II** with and without restrictions were carried out and none of them resulted in a lower minimum than the one discussed.