Intramolecular Diels−Alder Reaction of Chiral Silatrienes: Synthesis of 4a,7,8,8a-Tetrahydro-4-silaisochroman-1-ones

Paulo J. Coelho*[a] and Luis Blanco[a]

Keywords: Intramolecular Diels−Alder reaction / Cycloadditions / Chirality / Silicon / Tetrahydro-4-silaisochroman-1-ones

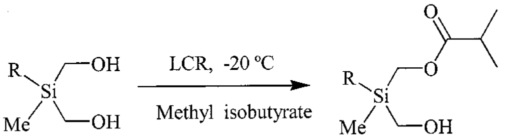
Intramolecular Diels–Alder reactions of chiral 2-silahexa-3,5-dienyl α,β-unsaturated esters have been found to afford tetrahydro-4-silaisochroman-1-ones in moderate yields. The best diastereoselectivity was achieved in the reaction of silatriene **8c**, in which methyl and triisopropylsilyloxymethyl groups are attached to the silicon atom, with an acrylate as the dienophile under $EtAlCl_2$-catalyzed conditions.

Introduction

Silicon compounds find wide application in organic synthesis, for example as protective groups, as reagents for functional group transformation or for carbon−carbon bond formation.[1] More recently, silicon compounds have been used with great success as a temporary tether between two reacting groups in intramolecular reactions. Highly regio- and stereoselective transformations have been reported using this approach, specifically in radical additions,[2] hydrosilylations,[3] [2 + 2] cycloadditions,[4] and Diels−Alder reactions.[5] Since Si−O and Si−C bonds can be selectively cleaved, it is possible to perform chemical transformations that are impossible by means of intermolecular reactions, either due to a lack of reactivity of the reagents or to inherently low selectivity.

Since the pioneering work of Sommer's group on the synthesis and reactions of optically active methylnaphthylphenylsilyl compounds,[6] there have been only a few reports on the use of Si-centered chiral compounds as chiral auxiliaries.[7] This lack of interest is partially due to the low diastereoselectivities hitherto observed. However, such studies have been almost exclusively undertaken by using methylnaphthylphenylsilyl derivatives. In these systems, the selectivity stems mainly from the steric differentiation of the methyl, naphthyl, and phenyl groups. Recently, Bienz and Chapeaurouge[8] showed that high diastereoselectivity can be achieved in the addition of organometallic compounds, at very low temperatures, to chiral acylsilanes bearing alkyloxymethyl groups at their silicon atoms.

The lack of available methods for the synthesis of optically active silicon compounds has also contributed to the slow development of their application in asymmetric synthesis. In this context, a new method for the synthesis of these compounds has been developed in our laboratory. It uses enzymes for the monotransesterification of esters with prochiral 2-silapropane-1,3-diols.[9] This approach has allowed us to synthesize several optically active 2,2-disubstituted 2-silapropanes (*ee* ≤ 70%) in 50−80% yield (Scheme 1).



Scheme 1. Transesterification of prochiral 2-silapropane-1,3-diols

Results and Discussion

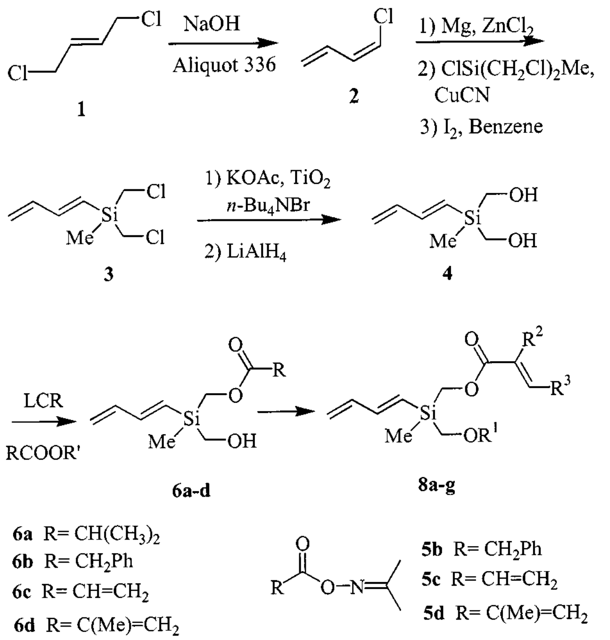
In this paper, we describe a study of the regio- and diastereoselectivity of the intramolecular Diels−Alder reaction (IMDA) between a diene and a dienophile linked by a chiral silicon atom through Si−C bonds. The enantiomerically enriched silatrienes **8a−g** and **6c** (*ee* ≥ 34%) were prepared in good yield in six or seven steps from (*E*)-1,4-dichlorobut-2-ene (**1**) as shown in Scheme 2. Dehydrochlorination of **1** in aqueous NaOH in the presence of the phase-transfer agent Aliquat 336 at 50−60 °C under reduced pressure gave 1-chlorobuta-1,3-diene (**2**) (*E*/*Z* = 6:94) in good yield (86%). The CuCN-catalyzed reaction of buta-1,3-dienylmagnesium chloride with bis(chloromethyl)methylchlorosilane gave a mixture of silabutadienes **3** (*E*/*Z* = 1:2) in 79% yield.[10] Viehe[11] showed that heating benzene solutions of 1-chlorobuta-1,3-diene containing 1% iodine yielded an equilibrium mixture of *E* and *Z* isomers [*E*/*Z* = (70 ± 5):(30 ± 5)]. When applied to a mixture of silabutadienes, (*Z*)-**3** and (*E*)-**3**, this reaction gave rise to a mixture highly enriched in the *Z* isomer (*E*/*Z* = 97:3), which could be isolated in 88% yield by distillation. Replacement of the chloro substituents by acetate groups in the presence of the phase-transfer agent n-Bu_4NBr gave bis(acetoxy)silane, which was reduced to 2-silapropanediol **4** with $LiAlH_4$ in excellent yield (96%). This compound was found to be rather unstable at room temper-

---

[a] Laboratoire des Carbocycles (associe au CNRS), Institut de Chimie Moleculaire d'Orsay, Bat. 420, Universite de Paris-Sud, F-91405 Orsay, France
E-mail: pcoelho@marao.utad.pt

1434−193X/00/0917−3039 $ 17.50+.50/0

ature, but could be stored for months at −20 °C without noticeable decomposition.



Scheme 2. Synthesis of silatrienes **8a–g**, **6c**

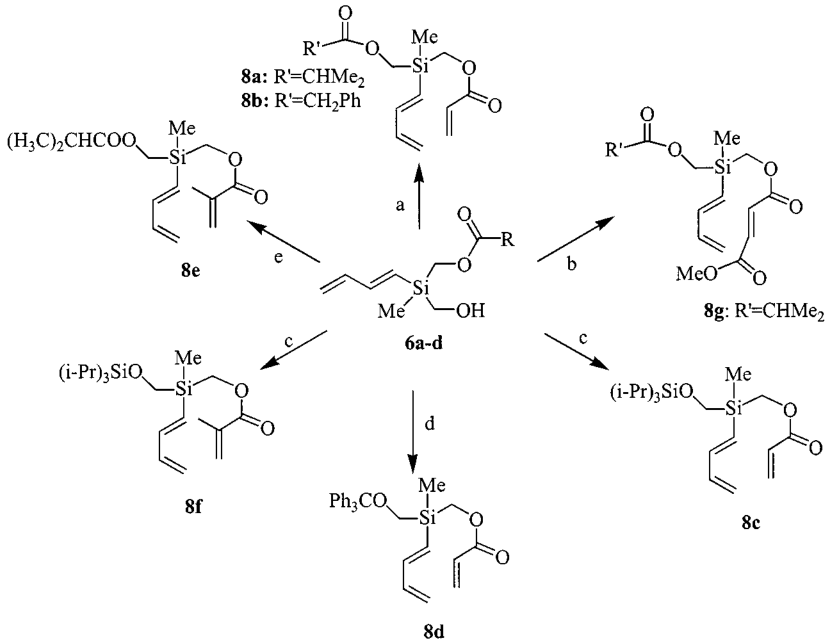
Transesterifications of methyl isobutyrate and acetoxime esters **5b–d** with prochiral 2-silapropanediol **4** catalyzed by the lipase from *Candida rugosa* (LCR) gave rise to optically active 2-(hydroxymethyl)-2-silapropyl esters **6a–d**,[9] together with small amounts of the corresponding diesters **7a–d**. The transesterification of methyl isobutyrate was carried out in the neat liquid, while the transesterifications of oximes **5b–d** were performed in diisopropyl ether. All enzymatic reactions were carried out at −20 °C[12] (Table 1). The transesterifications of the α,β-unsaturated oximes led to silatrienes, which incorporate a diene, a dienophile, and a hydroxymethyl group amenable to further functionalization. However, the silatrienes prepared in this way were found to be formed with low *ee*. Thus, it was concluded that the synthetic sequence leading to silatrienes with high enantiomeric purity involves the transesterification of methyl isobutyrate with subsequent introduction of the dienophile.

Table 1. LCR-catalyzed transesterification of methyl isobutyrate and oximes **5b–d** with 2-silapropanediol **4**

Ester	Time (h)	Mono-ester	*ee* (%)	Yield (%)	Diester	Yield (%)
Methyl isobutyrate	120	**6a**	62	70	7a	8
5b	44	**6b**	34	64	**7b**	12
5c	28	**6c**	40	71	**7c**	9
5d	48	**6d**	58	79	**7d**	10

It is noteworthy that the *ee* of monoester **6d** (58%), prepared by transesterification of methacrylate oxime **5d**, was superior to that of monoester **6c** (40%) prepared by transesterification of acrylate oxime **5c**, and very similar to that of monoester **6a** (62%). Hence, it would seem that the enantioselectivity of the LCR-catalyzed transesterification is particularly influenced by the presence of substituents α to the ester group. On the other hand, the degree of unsaturation of the ester function is seen to have a strong effect on the rate of the reaction but does not seem to modify its enantioselectivity.

The hydroxymethyl(butadienyl)silanes **6a–d** were then converted into compounds **8a–g** by one of two methods, namely introduction of the dienophile by esterification of the hydroxymethyl function (compounds **6a**,**b**) or, in the case of compounds **6c–d** that already incorporated the di-



Scheme 3. Synthesis of silatrienes **8a–g**.

Table 2. Intramolecular Diels−Alder reactions of silatrienes **8a−f** and **6c**

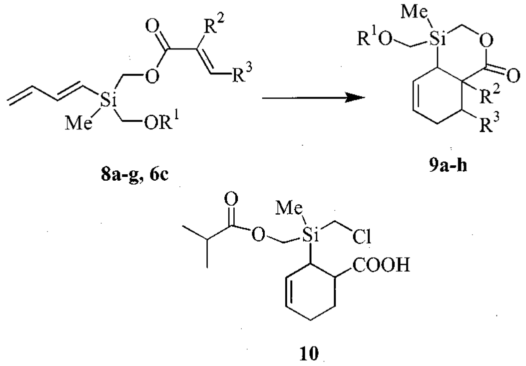
Silatriene				Thermal reaction			EtAlCl$_2$-catalysed reaction			
	R^1	R^2	R^3	Conditions (°C)	Yield (%)	Diast. ratio	Product	Yield (%)	Diast. ratio	Time
8a	COCHMe$_2$	H	H	150 °C, 48h	51	6:29:45:19	**9a**	23 [a]	1:14:68:17	24 h
8b	COCH$_2$Ph	H	H	160 °C, 48h	51	6:33:47:14	**9b**	60	4:28:61:17	24 h
8c	Si(*i*Pr)$_3$	H	H	150 °C, 48h	56	25:13:44:18	**9c**	25	20:6:71:3	48 h
8d	CPh$_3$	H	H	200 °C, 48h	56	24:16:44:16	**9d**	[b]		
6c	H	H	H	150 °C, 48h	44	29:14:35:22	**9h**	[b]		
8e	COCHMe$_2$	Me	H	205 °C, 48h	30	32:8:58:2	**9e**	[b]		
8f	Si(*i*Pr)$_3$	Me	H	220 °C, 48h	53	31:9:50:10	**9f**	[c]		
8g	COCHMe$_2$	H	COOMe	140 °C, 24h	27	22:28:33:27	**9g**	50	28:43:14:5	30 min

[a] 41% of the acid **10** was also isolated. − [b] Decomposition. − [c] No reaction.

enophile function, by protection of the hydroxymethyl function (Scheme 3).

Intramolecular Diels−Alder Reactions

The DA reactions of silatrienes **8a−g** and **6c** were performed under thermal conditions or by adding a Lewis acid catalyst. The thermal reaction involved heating 0.02 M toluene solutions of the silatrienes at 140−220 °C. This led to almost complete consumption of the starting material in 1−2 days. The catalyzed reactions were run at room temperature in CH$_2$Cl$_2$ using 4 equivalents of EtAlCl$_2$. The results are presented in Table 2. The DA reactions of silatrienes **8a−g** and **6c** gave 4-methyl-4a,7,8,8a-tetrahydro-4-silaisochroman-1-ones **9a−h** in 23−56% yield as mixtures of four diastereomers (Scheme 4). The diastereomeric ratios were determined by ^{1}H NMR spectroscopy through integration of the CH$_3$Si singlets. The EtAlCl$_2$-catalyzed IMDA of silatriene **8a** gave a mixture of four diastereomers of the tetrahydro-4-silaisochromanone **9a** (23%), along with 41% of the acid **10**. Treatment of a CH$_2$Cl$_2$ solution of tetrahydro-4-silaisochromanone **9a** with EtAlCl$_2$ at room temperature for two days, followed by hydrolysis gave acid **10**. This result would seem to indicate that the acid **10**, isolated after treatment of the silatriene **8a** with EtAlCl$_2$, was formed by reaction of the Lewis acid with the tetrahydro-4-silaisochromanone **9a**.

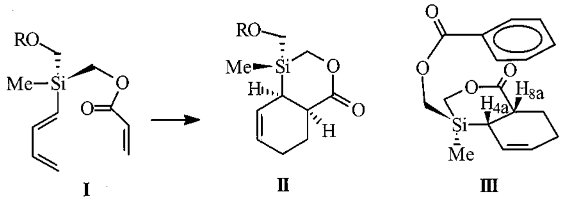


Scheme 4. Diels−Alder reaction of silatrienes **8a−g**, **6c**; reagents: (a) DEAD, Ph$_3$P, CH$_2$CHCOOH; (b) DMAP, Et$_3$N, CH$_3$O(O)CCHCHCOCl; (c) (*i*Pr)$_3$SiOTf, 2,6-dimethylpyridine; (d) Ph$_3$CCl, Et$_3$N; (e) DEAD, Ph$_3$P, (CH$_3$)$_2$CHCOOH

As expected, the fumarate **8g** proved to be the most reactive silatriene. The thermal reaction occurred at a lower temperature (140 °C) and the EtAlCl$_2$-catalyzed reaction required only 30 min for complete consumption of the starting material. Under thermal conditions, the best diastereomeric ratio was observed in the cyclization of compound **8e** (32:8:58:2). The diastereoselectivities observed in the cyclizations of silatrienes **8a−d**, in which the hydroxymethyl function is protected as an isobutyric ester, a phenylacetyl ester, a trisopropylsilyl ether, and a triphenylmethyl ether, respectively, were somewhat higher, but the nature of the protective group did not have a marked influence on the diastereoselectivity. The diastereoselectivities of the EtAlCl$_2$-catalyzed IMDA reactions of silatrienes **8a−c**,**g** were found to be significantly higher than those obtained under thermal conditions. Under EtAlCl$_2$-catalyzed conditions, the best diastereoselectivities were observed in the cyclizations of acrylates **8a** and **8c**, where the major diastereomers of tetrahydro-4-silaisochromanones **9a**,**c** constituted 68% and 71%, respectively, of the product mixtures.

Structure Elucidation

The reactions of all the silatrienes gave mixtures of the four diastereomers of tetrahydro-4-silaisochroman-1-one **9**, which could not be separated by column chromatography, except in the case of the diastereomeric alcohols **9h**. The major isomer and a mixture of the remaining 3 isomers were resolved by preparative thin-layer chromatography. Analysis of the ^{1}H NMR spectra of the various mixtures allowed us to determine the coupling constant $J_{\text{H4a-H8a}}$ (Scheme 5). The two major isomers have $J_{\text{H4a-H8a}} < 7$ Hz, which is consistent with a *cis* configuration for these two protons, while the other two isomers have $J_{\text{H4a-H8a}} = 11$ Hz, indicating a *trans* configuration. The two major diastereomers were thus formed through *endo* cyclization, while the two minor diastereomers were formed through *exo* cyclization. This means that the *endo* cyclization is favored over the *exo* cyclization by a factor of 1.8, the diastereoselectivity of the latter being rather low (9%).



Scheme 5

Treatment of tetrahydro-4-silaisochromanone **9h** with isobutyryl chloride or phenylacetyl chloride in CH_2Cl_2 in the presence of triethylamine gave tetrahydro-4-silaisochromanones **9a** and **9b**, respectively. ^1H NMR analysis of these products showed that the two major diastereomers had the same configuration as the two major diastereomers obtained in the cyclization of silatrienes **8a** and **8b**. Table 3 shows the *endo/exo* selectivity and the *de* of the *endo* cyclization of silatrienes **6c**, **8a**, and **8b**. The *endo/exo* stereoselectivity of the $EtAlCl_2$-catalyzed IMDA reaction can be seen to be superior to that obtained under thermal conditions. The diastereoselectivity imposed by the chiral silicon atom in the *endo* cyclization is also greater under $EtAlCl_2$ catalysis. The diastereoselectivities observed in the cyclizations of acrylates **8a**,**b**, which have protected hydroxyl functions, are higher than those achieved with the hydroxymethylsilatriene **6c**. However, this increase is rather slight, probably because the silicon atom is too distant to exercise a significant steric control.

Table 3. *endo/exo* Selectivity and *endo* diastereoselectivity of the IMDA

Silatriene R^1	*endo/exo* ratio		*endo* diastereoselectivity	
	Thermal reaction	Catalyzed reaction	Thermal reaction	Catalyzed reaction
6c H	1.8:1		9	66
8a $CH_2COCHMe_2$	3.0:1	4.6:1	22	37
8b CH_2COCH_2Ph	4.0:1	8.1:1	18	

The relative configurations of the tetrahydro-4-silaisochromanones **9a**,**b**,**h** could be established by analysis of the chemical shifts of the H_{8a} protons. For tetrahydro-4-silaisochromanones **9h**, the two major diastereomers have $\delta(H_{8a}) = 3.05$ and 3.07. Protection of the hydroxyl group as an isobutyric ester did not have a significant effect on these chemical shifts. However, the chemical shift of this proton was greatly affected when the hydroxyl function was protected as a phenylacetyl ester. While one of the diastereomers exhibits almost the same chemical shift as tetrahydro-4-silaisochromanones **9h** and **9a**, $\delta(H_{8a}) = 3.02$, in the major diastereomer this signal is shifted upfield to $\delta(H_{8a}) = 2.79$. The fact that only one diastereomer of tetrahydro-4-silaisochromanone **9b** was affected by the presence of the phenylacetyl group indicates that in this diastereomer the H_{8a} proton and the aromatic ring are on the same side of the molecule (III) (Scheme 5).

Since the major diastereomers of tetrahydro-4-silaisochromanone **9a**,**b**,**h** have the same relative configuration, we can suppose that they are formed through an *endo* transition state where the bulky silicon substituent, $ROCH_2$, and the dienophile are on opposite sides of the plane defined by the diene (I). Further studies involving the use of more bulky silicon substituents are currently in progress in our laboratory and the results will be reported in due course.

Experimental Section

General Remarks: ^1H and ^{13}C NMR spectra were recorded on Bruker AC200 (200 MHz and 50.3 MHz, respectively) or Bruker AC250 (250 MHz and 62.9 MHz, respectively) spectrometers. All spectra were recorded from samples in $CDCl_3$ solution. Chemical shifts are given in ppm. − Mass spectra were obtained on a NERMAG R10−10 spectrometer using electron ionization at 70 eV. − IR spectra were recorded on a Perkin−Elmer 682 spectrometer (wavenumbers in cm^{-1}). − The products were isolated by column chromatography on silica gel (SDS 70−230 mesh). − TLC was performed on 0.25 mm thick silica gel plates (Merck 60 F_{254}). − The enantiomeric excesses were determined by ^1H NMR in the presence of chiral $Eu(hfc)_3$. − Chlorobis(chloromethyl)methylsilane and lipase LCR were obtained from commercial sources (ABCR and Sigma L1754, respectively).

(*Z*)-1-Chlorobuta-1,3-diene (2): NaOH (71.0 g, 1.78 mol), water (105 mL), and Aliquat 336 (60 drops) were placed in a reaction vessel equipped for distillation and maintained under reduced pressure (10 Torr) at 50−60 °C. (*E*)-1,4-Dichlorobut-2-ene (**1**) (*E/Z* = 97:3) (30 mL, 0.282 mol) was then added dropwise over a period of 4 h. The diene collected in the collector flask, which was kept at −78 °C, was then dried over Na_2SO_4 and redistilled to give 21.5 g (86%) of **2** (*Z/E* = 94:6). − ***Z*-Isomer:** ^1H NMR: $\delta = 5.32$ (d, $J = 10.3$ Hz, 1 H), 5.39 (dd, $J = 17.1, 0.9$ Hz, 1 H), 6.04 (d, $J = 7.1$ Hz, 1 H), 6.33 (dd, $J = 10.3, 6.1$ Hz, 1 H), 6.77 (ddd, $J = 10.3, 10.3, 17.1$ Hz, 1 H); ***E*-Isomer:** $\delta = 5.15$ (d, $J = 10.4$ Hz, 1 H), 5.24 (d, $J = 16.7$ Hz, 1 H), 6.20 (m, 2 H), 6.48 (dd, $J = 10.5, 13$ Hz, 1 H).

(Buta-1,3-dienyl)bis(chloromethyl)methylsilane (3): A solution of buta-1,3-dienylmagnesium chloride in THF was prepared as follows: magnesium turnings (5.00 g, 206 mmol) and zinc chloride (1.50 g, 11.0 mmol) were placed in a reaction vessel under an argon atmosphere and heated for 2−3 min with a flame. Once the flask had cooled to room temperature, THF (7.0 mL) and dibromoethane (0.300 mL) were added. After ethene evolution, the mixture was diluted with THF (15 mL) and heated to 45−50 °C. A solution of 1-chlorobuta-1,3-diene (**2**) (*Z/E* = 94:6) (10 mL, 100 mmol) and 1,2-dibromoethane (0.800 mL) in THF (70 mL) was then added dropwise over a period of 1.5 h so as to maintain a gentle reflux. The reaction mixture was heated under reflux for a further 3 h and then left overnight at room temperature without stirring. Decantation of the resulting suspension provided an orange 0.55 M solution of butadienylmagnesium chloride.

Chlorobis(chloromethyl)methylsilane (5.60 mL, 33.6 mmol) was added dropwise to a stirred mixture of CuCN (220 mg, 2.40 mmol) and the aforementioned solution of buta-1,3-dienylmagnesium chloride in THF (80 mL, 44 mmol) under argon at 0 °C. The reaction mixture was stirred overnight, then quenched with aqueous NH_4Cl, and the resulting mixture was extracted with *n*-hexane. The combined organic extracts were dried over anhydrous Na_2SO_4. After evaporation of the solvent, the crude product was purified by distillation under reduced pressure (0.05 Torr) to yield 5.180 g (79%) of (buta-1,3-dienyl)bis(chloromethyl)methylsilane **3** (*E*/*Z* = 1:2).

Isomerization Reaction: A solution of butadienylsilane **3** (*E*/*Z* = 1:2) (5.18 g, 26.5 mmol) and iodine (0.340 g, 1.34 mmol, 5%) in benzene (100 mL) was refluxed for 3.5 h under argon. The reaction was then quenched with aqueous $Na_2S_2O_3$, the resulting mixture was extracted with *n*-hexane, and the combined organic extracts were dried over anhydrous Na_2SO_4. After evaporation of the solvent, the crude product was purified by distillation under reduced pressure (0.05 Torr) to yield 4.55 g (88%) of butadienylsilane **3** (*E*/*Z* = 97:3). − IR (neat): ν = 1630, 1580, 1260 cm^{-1}. − ^1H NMR: δ = 0.36 (s, 3 H), 2.99 (s, 4 H), 5.27 (dd, *J* = 10.1, 1.1 Hz, 1 H), 5.35 (dd, *J* = 17.1, 1.1 Hz, 1 H), 5.85 (d, *J* = 18.5 Hz, 1 H), 6.12 (dd, *J* = 18.5, 10.2 Hz, 1 H), 6.39 (ddd, *J* = 10.1, 10.2, 17.1 Hz, 1 H). − ^{13}C NMR: δ = −7.4, 27.1, 120.3, 124.9, 139.0, 149.1. − MS: *m*/*z* (%) = 196 (6.7), 194 (9.5), 147 (28), 145 (87), 79 (100).

(*E*)-(Buta-1,3-dienyl)bis(hydroxymethyl)methylsilane (4): A mixture of bis(chloromethyl)silane **3** (3.39 g, 17.4 mmol), potassium acetate (4.0 g, 41 mmol), tetrabutylammonium bromide (170 mg, 0.530 mmol), and titanium oxide (680 mg, 8.51 mmol) was stirred under argon at 80−90 °C for 3 h. Once the mixture had cooled to room temperature, silica gel (10 g) and diethyl ether (10 mL) were added. The resulting suspension was stirred for 5 min, then filtered, and the collected solid was washed 10 times with diethyl ether. After evaporation of the solvent from the combined filtrate and washings, the crude product was purified by column chromatography (*n*-hexane/Et_2O) to yield 3.37 g (80%) of (*E*)-[acetoxymethyl(buta-1,3-dienyl)methylsilyl]methyl acetate: − IR (neat): ν = 1740, 1630, 1290, 1220 cm^{-1}. − ^1H NMR: δ = 0.25 (s, 3 H), 2.06 (s, 6 H), 3.92 (s, 4 H), 5.24 (d, *J* = 9.8 Hz, 1 H), 5.32 (dd, *J* = 16.8, 0.9 Hz, 1 H), 5.78 (d, *J* = 18.5 Hz, 1 H), 6.38 (ddd, *J* = 10.1, 9.8, 16.8 Hz, 1 H), 6.67 (dd, *J* = 18.5, 10.1 Hz, 1 H). − ^{13}C NMR: δ = −7.0, 20.7, 54.4, 119.8, 125.6, 139.2, 148.6, 171.7. − MS: *m*/*z* (%) = 228 (1.09), 227 (6.14), 189 (25), 169 (61), 109 (100). − $C_{11}H_{18}O_4Si$: calcd. C 54.52, H 7.49; found C 54.28, H 7.26.

In the next step, a 1 M $LiAlH_4$ solution in diethyl ether (37 mL, 37 mmol) was added dropwise to a stirred solution of (*E*)-[acetoxymethyl(buta-1,3-dienyl)methylsilyl]methyl acetate (3.34 g, 13.8 mmol) in diethyl ether at −20 °C. The resulting suspension was stirred for 30 min at room temperature, then hydrated Na_2SO_4 (2−3 g) was slowly added in small portions (violent reaction!) followed by water (10 mL). After decantation, the aqueous phase was extracted 4 times with diethyl ether. The combined organic extracts were dried over Na_2SO_4, and then the solvent was removed under reduced pressure to leave the pure bis(hydroxymethyl)silane **4** (2.09 g, 96%). − IR (neat): ν = 3450, 1575, 1265 cm^{-1}. − ^1H NMR: δ = 0.23 (s, 3 H), 1.81 (br. s, 2 H), 3.72 (d, *J* = 13.9 Hz) and 3.63 (d, *J* = 13.9 Hz, AB system, 4 H], 5.22 (d, *J* = 9.8 Hz, 1 H), 5.31 (d, *J* = 16.8 Hz, 1 H), 5.84 (d, *J* = 18.5 Hz, 1 H), 6.38 (ddd, *J* = 9.8, 10.1, 16.8 Hz, 1 H), 6.72 (dd, *J* = 18.5, 10.1 Hz, 1 H). − ^{13}C NMR: δ = −7.9, 54.5, 119.3, 126.8, 139.3, 148.2. − MS: *m*/*z* (%) = 143 (0.88), 127 (22), 109 (21), 61 (100). − $C_7H_{14}O_2Si$: calcd. C 53.12, H 8.92; found C 53.01, H 8.95.

Enzymatic Transesterification of Methyl Isobutyrate with (*E*)-(Buta-1,3-dienyl)bis(hydroxymethyl)methylsilane (4): A mixture of **4** (0.318 g, 2.00 mmol), methyl isobutyrate (3 mL), and lipase LCR (1.2 g) was kept at −20 °C for 5 days. The reaction was monitored by TLC and was terminated when the amounts of the diester and diol were approximately equal. The suspension was filtered through Celite and the filtrate was washed several times with diethyl ether. After evaporation of the solvent, the products were separated by silica gel column chromatography (*n*-hexane/Et_2O).

(*E*)-[Buta-1,3-dienyl(hydroxymethyl)methylsilyl]methyl Isobutyrate (6a): Yield 70%. − IR (neat): ν = 3450, 1740, 1575, 1250 cm^{-1}. − ^1H NMR: δ = 0.21 (s, 3 H), 1.17 (d, *J* = 6.9 Hz, 6 H), 2.0 (br. s, 1 H), 2.58 (sept., *J* = 6.9 Hz, 1 H), 3.48 (d, *J* = 14 Hz) and 3.56 (d, *J* = 14 Hz) [AB system, 2 H], 3.98 (s, 2 H), 5.22 (d, *J* = 9.9 Hz, 1 H), 5.31 (d, *J* = 17.1 Hz, 1 H), 5.79 (d, *J* = 18.5 Hz, 1 H), 6.36 (ddd, *J* = 10.0, 9.9, 17.1 Hz, 1 H), 6.69 (dd, *J* = 10.0, 18.5 Hz, 1 H). − ^{13}C NMR: δ = −7.9, 19.0, 33.0, 52.7, 55.1, 119.4, 126.1, 139.2, 148.3, 178.1. − MS: *m*/*z* (%) = 213 (3), 197 (91), 175 (90), 109 (59), 43 (100).

(*E*)-[Buta-1,3-dienyl(isobutyryloxymethyl)methylsilyl]methyl Isobutyrate (7a): Yield 7.5%. − IR (neat): ν = 1750, 1580, 1265 cm^{-1}. − ^1H NMR: δ = 0.24 (s, 3 H), 1.15 (d, *J* = 6.9 Hz, 12 H), 2.55 (sept., *J* = 6.9 Hz, 2 H), 3.92 (s, 4 H), 5.21 (d, *J* = 9.9 Hz, 1 H), 5.29 (d, *J* = 17.0 Hz, 1 H), 5.77 (d, *J* = 18.5 Hz, 1 H), 6.35 (ddd, *J* = 9.9, 9.9, 17.0 Hz, 1 H), 6.65 (dd, *J* = 10.1, 18.5 Hz, 1 H). − ^{13}C NMR: δ = −7.3, 19.1, 34.0, 54.4, 119.7, 125.7, 139.2, 148.5, 177.7. − MS: *m*/*z* (%) = 284 (1.79), 283 (7.05), 245 (29), 197 (100), 109 (29).

Enzymatic Transesterification of Oximes 5b−d with (*E*)-(Buta-1,3-dienyl)bis(hydroxymethyl)methylsilane (4): A mixture of bis(hydroxymethyl)silane **4** (0.100 g, 0.633 mmol), oxime **5b−d** (0.633 mmol), lipase LCR (300 mg), and diisopropyl ether (2 mL) was kept at −20 °C. The reaction was monitored by TLC and was terminated after complete consumption of the oxime or diol. The suspension was then filtered through Celite and the collected solid was washed several times with diethyl ether. After evaporation of the solvent from the combined filtrate and washings, the products, monoesters **6b−d** and diesters **7b−d**, were separated by silica gel column chromatography (*n*-hexane/Et_2O).

(*E*)-[Buta-1,3-dienyl(hydroxymethyl)methylsilyl]methyl Phenylacetate (6b): Yield 64%. − IR (neat): ν = 3450, 1735, 1575, 1250 cm^{-1}. − ^1H NMR: δ = 0.14 (s, 3 H), 1.6 (br. s, 1 H), 3.38 (d, *J* = 13.8 Hz) and 3.45 (d, *J* = 13.8 Hz) [AB system, 2 H], 3.64 (s, 2 H), 4.00 (s, 2 H), 5.22 (d, *J* = 9.8 Hz, 1 H), 5.29 (d, *J* = 16.8 Hz, 1 H), 5.71 (d, *J* = 18.5 Hz, 1 H), 6.32 (ddd, *J* = 9.8, 10, 16.8 Hz, 1 H), 6.62 (dd, *J* = 10, 18.5 Hz, 1 H), 7.20−7.40 (m, 5 H). − MS: *m*/*z* (%) = 262 (0.44), 261 (2.88), 246 (22), 245 (100), 223 (8), 109 (50), 91 (93).

(*E*)-[(Buta-1,3-dienyl)methyl(phenylacetoxymethyl)silyl]methyl Phenylacetate (7b): Yield 12%. − IR (neat): ν = 1735, 1605, 1575, 1235 cm^{-1}. − ^1H NMR: δ = 0.11 (s, 3 H), 3.60 (s, 4 H), 3.88 (s, 4 H), 5.22 (d, *J* = 9.8 Hz, 1 H), 5.27 (d, *J* = 16.8 Hz, 1 H), 5.63 (d, *J* = 18.5 Hz, 1 H), 6.30 (ddd, *J* = 9.8, 10.0, 16.8 Hz, 1 H), 6.54 (dd, *J* = 10.0, 18.5 Hz, 1 H), 7.2−7.4 (m, 10 H). − ^{13}C NMR: δ = −7.5, 41.3, 54.9, 119.8, 125.3, 127.1, 128.5, 129.2, 134.0, 139.1, 148.6, 172.1. − MS: *m*/*z* (%) = 379 (7.2), 342 (5), 341 (18), 245 (100), 109 (21), 91 (60).

(*E*)-[Buta-1,3-dienyl(hydroxymethyl)methylsilyl]methyl Acrylate (6c): Yield 71%. − IR (neat): ν = 3420, 1730, 1575, 1255 cm^{-1}. − ^1H NMR: δ = 0.24 (s, 3 H), 1.6 (br. s, 1 H), 3.57 (d, *J* = 14 Hz) and 3.50 (d, *J* = 14 Hz) [AB system, 2 H], 4.08 (s, 2 H), 5.23 (d, *J* = 9.7 Hz, 1 H), 5.32 (d, *J* = 17.3 Hz, 1 H), 5.81 (d, *J* = 18.5 Hz, 1 H), 5.85 (dd, *J* = 10.3, 1.1 Hz, 1 H), 6.15 (dd, *J* = 10.3, 17.1 Hz, 1 H), 6.35 (ddd, *J* = 9.8, 10.0, 17.3 Hz) and 6.40 (dd, *J* = 1.1, 17.1 Hz) (2 H), 6.70 (dd, *J* = 9.8, 18.5 Hz, 1 H). − ^{13}C NMR: δ = −8.1, 52.3, 55.1, 119.2, 126.0, 127.9, 130.6, 139.1, 148.1, 167.1. −

MS: *m/z* (%) = 198 (0.49), 197 (3.41), 182 (17), 181 (100), 159 (12), 109 (62).

(*E*)-[(Acryloxymethyl)(buta-1,3-dienyl)methylsilyl]methyl Acrylate (7c): Yield 8.5%. − IR (neat): ν = 1735, 1645, 1260 cm^{-1}. − ^{1}H NMR: δ = 0.28 (s, 3 H), 4.04 (s, 4 H), 5.24 (d, *J* = 10.0 Hz, 1 H), 5.31 (d, *J* = 17.3 Hz, 1 H), 5.75−5.90 (m, 2 H), 6.13 (dd, *J* = 10.3, 16.9 Hz, 1 H), 6.38 (ddd, *J* = 10.0, 10.1, 17.3 Hz) and 6.40 (dd, *J* = 16.9, 1.7 Hz) (2 H), 6.69 (dd, *J* = 10.1, 18.5 Hz, 1 H). − ^{13}C NMR: δ = −7.3, 54.6, 119.8, 125.3, 128.1, 130.5, 139.1, 148.7, 166.8. − MS: *m/z* (%) = 252 (1.06), 251 (6.16), 213 (24), 181 (100), 109 (67). − $C_{13}H_{18}O_4Si$: calcd. C 58.62, H 6.81; found C 58.63, H 6.88.

(*E*)-[Buta-1,3-dienyl(hydroxymethyl)methylsilyl]methyl Methacrylate (6d): Yield 79%. − IR (neat): ν = 3500, 1735, 1645, 1200 cm^{-1}. − ^{1}H NMR: δ = 0.24 (s, 3 H), 1.6 (br. s, 1 H), 1.95 (s, 3 H), 3.57 (d, *J* = 14 Hz) and 3.50 (d, *J* = 14 Hz) [AB system, 2 H], 4.06 (s, 2 H), 5.23 (d, *J* = 10.0 Hz, 1 H), 5.31 (d, *J* = 17.2 Hz, 1 H), 5.54−5.60 (m, 1 H), 5.81 (d, *J* = 18.5 Hz, 1 H), 6.11 (s, 1 H), 6.37 (ddd, *J* = 10.0, 10.1, 17.2 Hz, 1 H), 6.70 (dd, *J* = 10.1, 18.5 Hz, 1 H). − ^{13}C NMR: δ = −7.9, 16.3, 52.7, 55.4, 119.4, 125.6, 126.1, 136.1, 139.1, 148.4, 168.4. − MS: *m/z* (%) = 196 (15), 195 (83), 173 (12), 109 (56), 41 (100).

(*E*)-[Buta-1,3-dienyl(methacryloxymethyl)methylsilyl]methyl Methacrylate (7d): Yield: 10%. − IR (neat): ν = 1730, 1645, 1260 cm^{-1}. − ^{1}H NMR: δ = 0.29 (s, 3 H), 1.94 (s, 6 H), 4.01 (s, 4 H), 5.23 (d, *J* = 10.0 Hz, 1 H), 5.31 (d, *J* = 17.0 Hz, 1 H), 5.52−5.58 (m, 2 H), 5.81 (d, *J* = 18.5 Hz, 1 H), 6.08 (s, 2 H), 6.37 (ddd, *J* = 10.0, 10.0, 17.0 Hz, 1 H), 6.67 (dd, *J* = 10.0, 18.5 Hz, 1 H). − ^{13}C NMR: δ = −7.2, 18.4, 54.7, 119.8, 125.4, 125.5, 136.2, 139.2, 148.7, 168.1. − MS: *m/z* (%) = 279 (7.6), 241 (26), 195 (93), 109 (40), 69 (100). − $C_{15}H_{22}O_4Si$: calcd. C 61.19, H 7.53; found C 61.11, H 7.42.

Synthesis of Silatrienes 8a,b: Diethyl azodicarboxylate (DEAD) (105 µL, 0.660 mmol) was added dropwise to a stirred solution of (hydroxymethyl)silane **6a**,**b** (0.439 mmol), triphenylphosphane (0.660 mmol), and acrylic acid (0.527 mmol) in THF (20 mL) at −78 °C under argon. The reaction mixture was stirred for 20 min at room temperature. After evaporation of the solvent, the crude product was purified by chromatography (*n*-hexane/Et_2O).

(*E*)-[Buta-1,3-dienyl(isobutyryloxymethyl)methylsilyl]methyl Acrylate (8a): Yield 73%. − IR (neat): ν = 1730, 1640, 1250 cm^{-1}. − ^{1}H NMR: δ = 0.27 (s, 3 H), 1.16 (d, *J* = 7.0 Hz, 6 H), 2.56 (sept., *J* = 7.0 Hz, 1 H), 3.93 (s, 2 H), 4.02 (s, 2 H), 5.23 (d, *J* = 10.0 Hz, 1 H), 5.30 (d, *J* = 17.3 Hz, 1 H), 5.79 (d, *J* = 18.5 Hz, 1 H), 5.83 (dd, *J* = 10.2, 1.6 Hz, 1 H), 6.13 (dd, *J* = 10.2, 17.3 Hz, 1 H), 6.37 (ddd, *J* = 10, 10, 17.3 Hz, 1 H), 6.40 (dd, *J* = 1.6, 17.3 Hz, 2 H), 6.67 (dd, *J* = 18.5, 10.0 Hz. 1 H). − ^{13}C NMR: δ = −7.3, 19.0, 33.9, 54.3, 54.7, 119.7, 125.5, 128.2, 130.5, 139.1, 148.6, 166.1, 177.6. − MS: *m/z* (%) = 267 (13), 230 (24), 229 (65), 198 (31), 197 (91), 182 (36), 181 (100), 110 (20), 109 (71).

(*E*)-[(Buta-1,3-dienyl)methyl(phenylacetoxymethyl)silyl]methyl Acrylate (8b): Yield 85%. − IR (neat): ν = 1735, 1265 cm^{-1}. − ^{1}H NMR: δ = 0.20 (s, 3 H), 3.62 (s, 2 H), 3.96 (s, 4 H), 5.23 (d, *J* = 10.2 Hz, 1 H), 5.29 (d, *J* = 17.0 Hz, 1 H), 5.72 (d, *J* = 18.6 Hz, 1 H), 5.82 (dd, *J* = 1.5, 10.3 Hz, 1 H), 6.11 (dd, *J* = 10.3, 17.3 Hz, 1 H), 6.33 (ddd, *J* = 10.0, 10.2, 17.0 Hz, 1 H), 6.39 (dd, *J* = 1.5, 17.3 Hz, 1 H), 6.61 (dd, *J* = 10.0, 18.6 Hz, 1 H), 7.40−7.20 (m, 5 H). − MS: *m/z* (%) = 316 (3.14), 315 (4.31), 277 (38), 245 (18), 182 (24), 181 (75), 109 (21), 91 (96), 55 (100).

(*E*)-[(Buta-1,3-dienyl)methyl(triphenylmethoxymethyl)methylsilyl]methyl Acrylate (8d): A mixture of triethylamine (200 µL, 143 mmol), hydroxymethylsilane **6c** (200 mg, 0.943 mmol), triphenylmethyl chloride (316 mg, 1.13 mmol), and CH_2Cl_2 (20 mL) was stirred under argon. After 2 days at room temperature, the reaction was quenched with saturated aqueous NH_4Cl and the resulting mixture was extracted with CH_2Cl_2. The combined organic extracts were dried over anhydrous Na_2SO_4, concentrated, and the residue was purified by column chromatography (*n*-hexane/Et_2O) to yield **8d** (415 mg, 97%). − IR (neat): ν = 1735, 1260, 1185 cm^{-1}. − ^{1}H NMR: δ = 0.27 (s, 3 H), 2.87 (s, 2 H), 4.08 (s, 2 H), 5.20 (d, *J* = 10.0 Hz, 1 H), 5.26 (d, *J* = 17.0 Hz, 1 H), 5.79 (dd, *J* = 10.3, 1.6 Hz, 1 H), 5.84 (d, *J* = 18.5 Hz, 1 H), 6.11 (dd, *J* = 10.3, 17.2 Hz, 1 H), 6.36 (dd, *J* = 1.6, 17.2 Hz) and 6.37 (ddd, *J* = 10, 10, 17.0 Hz, 2 H), 6.64 (dd, *J* = 9.9, 18.5 Hz, 1 H), 7.45−7.20 (m, 15 H). − ^{13}C NMR: δ = −7.1, 52.7, 55.5, 88.5, 119.1, 126.6, 128.3, 130.2, 139.2, 120.8, 127.6, 128.8, 143.7, 148.1, 167.4. − MS: *m/z* (%) = 244 (29), 243 (100), 181 (91), 166 (20), 165 (97), 109 (20). − CI-MS (NH_3): *m/z* (%) = 244 (63), 243 (100), 181 (6).

(*E*)-[Buta-1,3-dienyl(isobutyryloxymethyl)methylsilyl]methyl Methacrylate (8e) : Diethyl azodicarboxylate (DEAD) (105 µL, 0.660 mmol) was added dropwise to a stirred solution of (hydroxymethyl)silane **6d** (0.439 mmol), triphenylphosphane (0.660 mmol), and isobutyric acid (0.527 mmol) in THF (20 mL) at −78 °C under argon. The reaction mixture was stirred for 20 min at room temperature. After evaporation of the solvent, the crude product was purified by chromatography (*n*-hexane/Et_2O). Yield: 74%. − IR (neat): ν = 1735, 1670, 1240 cm^{-1}. − ^{1}H NMR: δ = 0.27 (s, 3 H), 1.15 (d, *J* = 7.0 Hz, 6 H), 1.94 (d, *J* = 1.5 Hz, 3 H), 2.55 (sept., *J* = 7.0 Hz, 1 H), 3.94 (s, 2 H), 4.00 (s, 2 H), 5.22 (d, *J* = 9.7 Hz, 1 H), 5.30 (d, *J* = 16.9 Hz, 1 H), 5.52−5.58 (m, 1 H), 5.78 (d, *J* = 18.6 Hz, 1 H), 6.09 (d, *J* = 1.5 Hz, 1 H), 6.37 (ddd, *J* = 9.7, 9.9, 16.9 Hz, 1 H), 6.67 (dd, *J* = 9.9, 18.6 Hz, 1 H). − ^{13}C NMR: δ = −7.3, 18.3, 19.0, 33.9, 54.3, 54.6, 119.6, 125.2, 125.5, 136.6, 139.1, 148.5, 168.0, 177.5. − MS: *m/z* (%) = 281 (12.8), 243 (64), 197 (100), 195 (95), 109 (64). − $C_{15}H_{24}O_4Si$: calcd. C 60.78, H 8.16; found C 60.56, H 8.27.

(*E*)-[Buta-1,3-dienyl(isobutyryloxymethyl)methylsilyl]methyl Methyl Fumarate (8g): 3-(Methoxycarbonyl)acryloyl chloride (0.56 mmol) was added dropwise to a stirred solution of (hydroxymethyl)silane **6a** (0.37 mmol), triethylamine (0.56 mmol), and DMAP (10 mg) in CH_2Cl_2 (10 mL) at 0 °C under argon. The reaction mixture was stirred for 30 min at room temperature, then quenched with saturated aqueous NH_4Cl and the resulting mixture was extracted with CH_2Cl_2. The combined organic extracts were dried over anhydrous Na_2SO_4. After evaporation of the solvent, the crude product was purified by column chromatography (*n*-hexane/Et_2O) to give **8g** (88 mg, 70%). − IR (neat): ν = 1740, 1280 cm^{-1}. − ^{1}H NMR: δ = 0.27 (s, 3 H), 1.16 (d, *J* = 7.0 Hz, 6 H), 2.56 (sept., *J* = 7.0 Hz, 1 H), 3.82 (s, 3 H), 3.92 (s, 2 H), 4.08 (s, 2 H), 5.24 (d, *J* = 10.0 Hz, 1 H), 5.32 (d, *J* = 17.3 Hz, 1 H), 5.76 (d, *J* = 18.5 Hz, 1 H), 6.37 (ddd, *J* = 10.0, 10.0, 17.3 Hz, 1 H), 6.67 (dd, *J* = 18.5, 10.0 Hz, 1 H), 6.86 (s, 2 H). − ^{13}C NMR: δ = −7.4, 19.0, 33.9, 52.2, 54.2, 55.7, 119.9, 125.0, 133.1, 133.9, 139.0, 149.0, 165.3, 165.4, 177.5. − MS: *m/z* (%) = 282 (19.7), 287 (100), 239 (9), 199 (29), 197 (16), 189 (23). − $C_{16}H_{24}O_6Si$: calcd. C 56.45, H 7.11; found C 56.41, H 7.29.

Synthesis of Silatrienes 8c,f: Triisopropylsilyl trifluoromethanesulfonate (405 µL, 1.5 mmol) was added to a solution of (hydroxymethyl)silane **6a** (1.0 mmol) and 2,6-dimethylpyridine (240 µL, 2.0 mmol) in CH_2Cl_2 (20 mL) under argon. After stirring for 15 min, the reaction was quenched with saturated aqueous

$NaHCO_3$ and the resulting mixture was extracted with CH_2Cl_2. The combined organic extracts were dried over anhydrous Na_2SO_4, concentrated, and the product was purified by column chromatography (*n*-hexane/Et_2O).

(*E*)-[(Buta-1,3-dienyl)methyl(triisopropylsilyloxymethyl)silyl]-methyl Acrylate (8c): Yield 94%. − IR (neat): ν = 1740, 1255 cm^{-1}. − ^{1}H NMR: δ = 0.22 (s, 3 H), 1.15−1.00 (m, 21 H), 3.58 (s, 2 H), 4.03 (s, 2 H), 5.19 (d, J = 10.0 Hz, 1 H), 5.27 (d, J = 16.8 Hz, 1 H), 5.80 (dd, J = 10.2, 1.8 Hz, 1 H), 5.82 (d, J = 18.6 Hz, 1 H), 6.13 (dd, J = 10.2, 17.2 Hz, 1 H), 6.37 (ddd, J = 10.0, 10.0, 16.8 Hz, 1 H), 6.38 (dd, J = 17.2, 1.8 Hz, 1 H), 6.70 (dd, J = 10.0, 18.6 Hz, 1 H). − ^{13}C NMR: δ = −7.8, 11.8, 18.0, 53.5, 54.7, 118.9, 127.1, 128.5, 130.2, 139.5, 147.0, 167.0. − MS: *m*/*z* (%) = 326 (0.88), 325 (1.91), 315 (2), 181 (100), 109 (13). − $C_{19}H_{36}O_3Si_2$: calcd. C 61.90, H 9.84; found C 62.08, H 10.03.

(*E*)-[Buta-1,3-dienyl(triisopropylsilyloxymethyl)methylsilyl]methyl Methacrylate (8f): Yield 86%. − IR (neat): ν = 1735, 1650, 1260 cm^{-1}. − ^{1}H NMR: δ = 0.23 (s, 3 H), 1.15−1.00 (m, 21 H), 1.94 (d, J = 1.1 Hz, 3 H), 3.58 (s, 2 H), 4.01 (s, 2 H), 5.18 (d, J = 9.9 Hz, 1 H), 5.27 (d, J = 16.8 Hz, 1 H), 5.50−5.56 (m, 1 H), 5.84 (d, J = 18.5 Hz, 1 H), 6.08 (br. s, 1 H), 6.36 (ddd, J = 9.9, 9.9, 16.8 Hz, 1 H), 6.70 (dd, J = 9.9, 18.5 Hz, 1 H). − ^{13}C NMR: δ = −7.8, 11.8, 18.0, 18.4, 53.5, 54.6, 118.8, 125.0, 127.1, 136.4, 139.5, 147.9, 168.1. − MS: *m*/*z* (%) = 340 (0.95), 339 (2.94), 329 (0.8), 195 (100).

Intramolecular Diels−Alder Reaction

Thermal Reaction: The silatriene (0.40 mmol), phenothiazine (2 mg), and toluene (20 mL) were placed in a degassed vial, which was sealed and heated for 1−2 days (see Table 2). The vial was then opened, the solvent was evaporated, and the residue was purified by silica gel column chromatography (*n*-hexane/Et_2O).

Lewis Acid Catalyzed Reaction: A 1 M $EtAlCl_2$ solution in CH_2Cl_2 (4 mL, 4.0 mmol) was added to a solution of silatriene **8** (1.0 mmol) in CH_2Cl_2 (20 mL) under argon. After complete consumption of the silatriene (TLC), the reaction was quenched with saturated aqueous NH_4Cl and the resulting mixture was extracted with CH_2Cl_2. The combined organic extracts were dried over anhydrous Na_2SO_4, concentrated, and the residue was purified by silica gel column chromatography (*n*-hexane/Et_2O).

(4-Methyl-1-oxo-4a,7,8,8a-tetrahydro-4-silaisochroman-4-yl)methyl Isobutanoate (9a): IR (neat): ν = 1735, 1650, 1255 cm^{-1}. − ^{1}H NMR: δ = 0.18, 0.23, 0.30, and 0.35 (4 s, 3 H), 1.10−1.30 (m, 6 H), 1.5−2.5 (m, 5 H), 2.54 (sept., J = 7.0 Hz, 1 H), 2.98−3.12 (m, 1 H), 3.70−4.30 (m, 4 H), 5.50−5.80 (m, 2 H). − ^{13}C NMR: δ = −9.3, −8.0, −7.3, −6.2, 15.2, 18.0, 19.0, 21.1, 22.6, 23.0, 23.2, 24.0, 24.3, 33.8, 30.7, 39.3, 43.6, 53.6, 54.4, 54.9, 55.0, 59.6, 60.1, 122.1, 123.6, 123.2, 126.1, 127.1, 130.1, 175.5, 176.9, 178.3. − MS: *m*/*z* (%) = 284 (2.06), 283 (6.76), 282 (26), 281 (22), 267 (8), 175 (19), 161 (19), 158 (19), 143 (27), 43 (100).

(4-Methyl-1-oxo-4a,7,8,8a-tetrahydro-4-silaisochroman-4-yl)methyl Phenylacetate (9b): ^{1}H NMR: δ = 0.10, 0.16, 0.21, and 0.28 (4 s, 3 H), 2.5−1.5 (m, 5 H), 2.79 (ddd, J = 3, 7, 7 Hz, 0.6 H), 3.02 (ddd, J = 4, 7, 7 Hz, 0.4 H), 3.55−3.70 (m, 2 H), 3.80−4.20 (m, 4 H), 5.40−5.80 (m, 2 H), 7.20−7.40 (m, 5 H). − ^{13}C NMR: δ = −8.3. −6.4, 20.5, 22.2, 22.6, 22.8, 23.9, 39.2, 38.6, 41.2, 53.5, 55.3, 59.1, 122.7, 123.2, 126.3, 127.3, 128.7, 129.1, 133.7, 172.5, 175.3.

4-Methyl-4-(triisopropylsilyloxymethyl)-4a,7,8,8a-tetrahydro-4-sila-isochroman-1-one (9c): IR (neat): ν = 1740, 1650, 1255 cm^{-1}. − ^{1}H NMR: δ = 0.09, 0.12, 0.30, and 0.32 (4 s, 3 H), 0.95−1.20 (m, 21 H), 1.75−2.60 (m, 5.21 H), 2.78 (ddd, J = 12, 12, 2 Hz, 0.13 H), 2.97−3.13 (m, 0.66 H), 3.50−3.65 (m, 2 H), [3.88 (d, J = 15.3 Hz) and 4.23 (d, J = 15.3 Hz) (AB system); 3.98 (d, J = 15.3 Hz) and 4.26 (d, J = 15.3 Hz) (AB system); 4.06 (d, J = 15.3 Hz) and 4.18 (d, J = 15.3 Hz) (AB system); 4.10 (d, J = 15.3 Hz) and 4.24 (d, J = 15.3 Hz) (AB system)] (2 H), 5.55−5.75 (m, 2 H). − ^{13}C NMR: δ = −8.6, −6.7, 11.7, 17.7, 18.0, 20.1, 22.5, 24.0, 24.1, 39.2, 39.0, 51.8, 53.2, 58.7, 123.1, 124.0, 125.8, 175.7. − MS: *m*/*z* (%) = 370 (9), 369 (24), 368 (18), 326 (11), 325 (12), 147 (50), 133 (23), 119 (100). − $C_{19}H_{36}O_3Si_2$: calcd. C 61.98, H 9.78; found C 62.17, H 9.86.

4-Methyl-4-(triphenylmethoxymethyl)-4a,7,8,8a-tetrahydro-4-sila-isochroman-1-one (9d): IR (neat): ν = 1750, 1650, 1500, 1260 cm^{-1}. − ^{1}H NMR: δ = 0.21, 0.25, 0.31, and 0.37 (4 s, 3 H), 1.60−2.50 (m, 5 H), 2.75−3.12 (m, 3 H), [3.41 (d, J = 15.3 Hz) and 4.25 (d, J = 15.3 Hz) (AB system); 4.02 (d, J = 15.3 Hz) and 4.22 (d, J = 15.3 Hz) (AB system); 4.08 (d, J = 15.3 Hz) and 4.18 (d, J = 15.3 Hz) (AB system)] (2 H), 5.50−5.80 (m, 2 H), 7.15−7.48 (m, 15 H). − ^{13}C NMR: δ = −9.6, −8.1, −6.5, −6.0, 15.2, 20.3, 22.4, 22.6, 22.9, 23.7, 24.0, 24.2, 24.7, 38.5, 39.0, 39.2, 51.0, 52.2, 52.3, 58.7, 58.9, 59.0, 88.4, 123.1, 123.7, 123.9, 125.5, 125.9, 126.6, 127.0, 127.7, 127.8, 128.7, 175.5, 176.4, 176.6. − MS: *m*/*z* (%) = 244 (24), 243 (100), 165 (100), 79 (13), 77 (14). − $C_{29}H_{30}O_3Si$: calcd. C 76.61, H 6.65; found C 76.36, H 6.85.

(4,8a-Dimethyl-1-oxo-4a,7,8,8a-tetrahydro-4-silaisochroman-4-yl)-methyl Isobutanoate (9e): IR (solution in CCl_4): ν = 1740, 1260 cm^{-1}. − ^{1}H NMR: δ = 0.17, 0.23, 0.26, and 0.32 (4 s, 3 H), 1.10−1.20 (m, 6 H), 1.26, 1.30, 1.37, and 1.39 (4 s, 3 H), 1.45−1.55 (m, 1 H), 1.83−1.85 (m, 1 H), 2.00−2.30 (m, 3 H), 2.49−2.68 (m, 1 H), 3.65−4.10 (m, 2 H), 4.10−4.45 (m, 2 H), 5.50−5.80 (m, 2 H). − ^{13}C NMR: δ = −7.0, −5.2, 19.0, 21.7, 21.9, 25.1, 25.2, 28.4, 30.2, 31.5, 31.7, 33.8, 33.8, 42.1, 53.9, 55.7, 59.7, 60.0, 123.5, 124.3, 124.6, 125.0, 177.1, 177.2, 177.9, 178.2. − MS: *m*/*z* (%) = 296 (4), 281 (3), 253 (4), 230 (25), 229 (62), 161 (37), 159 (51), 158 (100), 143 (40).

4,8a-Dimethyl-4-(triisopropylsilyloxymethyl)-4a,7,8,8a-tetrahydro-4-silaisochroman-1-one (9f): IR (neat): ν = 1740, 1270 cm^{-1}. − ^{1}H NMR: δ = 0.21, 0.23, 0.34, and 0.36 (4 s, 3 H), 0.90−1.20 (m, 21 H), 1.32, 1.33, 1.41, and 1.42 (4 s, 3 H), 1.43−1.60 (m, 1 H), 1.92−2.00 and 2.00−2.08 (2 m, 1 H), 2.10−2.45 (m, 3 H), 3.45−3.60 (m, 2 H), 4.05−4.35 (m, 2 H), 5.50−5.75 (m, 2 H). − ^{13}C NMR: δ = −5.6 and −7.6, 11.7, 15.3, 17.7, 18.0, 21.7, 22.0, 25.3, 27.4, 30.2, 31.6, 32.1, 42.1, 53.5 and 52.7, 59.2 and 59.3, 124.0, 124.9, 124.9, 126.8, 127.7, 128.9, 177.6. − MS: *m*/*z* (%) = 384 (2.87), 383 (6.22), 362 (7.76), 368 (15.8), 367 (23), 340 (1.44), 339 (2.6), 147 (40), 133 (42), 131 (25), 119 (100).

(8-Methoxycarbonyl-4-methyl-1-oxo-4a,7,8,8a-tetrahydro-4-silaiso-chroman-4-yl)methyl Isobutanoate (9g): IR (neat): ν = 1740, 1265 cm^{-1}. − ^{1}H NMR: δ = 0.16, 0.20, 0.23, and 0.33 (4 s, 3 H), 1.10−1.23 (m, 6 H), 1.77−2.95 (m, 4.35 H), 3.20−3.30 (m, 0.80 H), 3.35−3.45 (m, 0.85 H), 3.72 and 3.73 (2 s, 3 H), 3.75−4.32 (m, 4 H), 5.55−5.75 (m, 2 H). − ^{13}C NMR: δ = −9.3, −8.6, −6.6, 14.5, 18.2, 19.0, 20.2, 22.7, 23.4, 23.6, 28.5, 33.7, 33.8, 39.0, 39.5, 40.6, 40.7, 52.1, 52.2, 52.8, 54.7, 59.1, 59.5, 60.4, 122.5, 123.2, 124.0, 124.8, 173.8, 174.1, 176.8, 178.0, 178.2. − MS: *m*/*z* (%) = 345 (1.44), 340 (3.25), 325 (2), 309 (2), 281 (55), 175 (26), 43 (100). − $C_{16}H_{24}O_6Si$: calcd. C 56.45, H 7.11; found C 56.24, H 7.29.

4-(Hydroxymethyl)-4-methyl-4a,7,8,8a-tetrahydro-4-silaisochroman-1-one (9h): IR (solution in CCl_4): ν = 3640, 3450, 1750, 1265 cm^{-1}. − ^{1}H NMR: δ = 0.20, 0.23, 0.32, and 0.33 (4 s, 3 H), 1.40−2.40 (m, 5 H), 2.52 (ddd, J = 12, 12, 2 Hz, 0.24 H), 2.75 (ddd, J = 12, 12, 2 Hz, 0.14 H), 3.01−3.13 (m, 0.62 H), 3.65−3.50 (m, 2 H), [3.92 (d, J = 15.3 Hz) and 4.28 (d, J = 15.3 Hz) (AB system); 4.03 (d, J = 15.3 Hz) and 4.30 (d, J = 15.3 Hz) (AB system); 4.08 (d, J = 15.3 Hz) and 4.20 (d, J = 15.3 Hz) (AB system); 4.11 (d, J = 15.3 Hz) and 4.23 (d, J = 15.3 Hz) (AB system)] (2 H), 5.85−5.50 (m, 2 H). − ^{13}C NMR: δ = −10.2, −8.7, −6.8, 15.5, 19.9, 22.2, 22.5, 22.8, 23.7, 23.9, 24.0, 24.3, 24.3, 24.7, 38.7, 39.0, 39.2, 39.3, 51.3, 51.4, 52.3, 52.4, 58.5, 58.6, 58.7, 59.0, 123.0, 123.7, 123.2, 123.9, 125.9, 126.2, 126.8, 127.3, 175.6, 175.7. − MS: m/z (%) = 212 (16), 153 (16), 91 (29), 77 (100).

2-[(Chloromethyl)(isobutyryloxycarbonylmethyl)methylsilyl]cyclohex-3-enecarboxylic Acid (10): IR (neat): ν = 3700−3300, 1735, 1255 cm^{-1}. − ^{1}H NMR: δ = 0.25 (s, 3 H), 1.16 (d, J = 7.1 Hz, 6 H), 1.74−1.94 (m, 1 H), 1.94−2.09 (m, 1 H), 2.09−2.12 (m, 2 H), 2.32−2.44 (m, 1 H), 2.56 (sept, J = 7.0 Hz, 1 H), 2.89−3.04 (m) and 2.97 (s) (3 H), 3.96 (s, 2 H), 5.63−5.78 (m, 2 H). − ^{13}C NMR: δ = −7.0, 19.0, 23.7, 24.0, 25.2, 28.1, 34.0, 40.6, 54.2, 125.2, 125.9, 177.7, 181.2. − MS: m/z (%) = 284 (1.03), 283 (4.87), 282 (20.9), 281 (18), 268 (1.54), 267 (3.85), 184 (26), 175 (40), 161 (26), 158 (27), 147 (53), 144 (23), 143 (38), 77 (100). − CI-MS (NH$_3$): m/z (%) = 338 (1.08), 336 (1.89), 300 (19), 283 (100).

Treatment of **10** (20 mg) with a CH_2N_2 solution in diethyl ether afforded

Methyl 2-[(Chloromethyl)(isobutyryloxycarbonylmethyl)methylsilyl]-cyclohex-3-enecarboxylate. − IR (neat): ν = 1740, 1255 cm^{-1}. − ^{1}H NMR: δ = 0.22 (s, 3 H), 1.16 (d, J = 6.8 Hz, 6 H), 1.72−1.89 (m, 1 H), 1.90−2.04 (m, 1 H), 2.06−2.17 (m, 2 H), 2.30−2.38 (m, 1 H), 2.55 (sept, J = 7.0 Hz, 1 H), 2.91 (ddd, J = 3.2, 5.5, 8.7 Hz, 1 H), 2.95 (s, 2 H), 3.72 (s, 3 H), 3.95 (s, 2 H), 5.63−5.75 (m, 2 H). − ^{13}C NMR: δ = −7.0, 19.1, 23.9, 24.2, 25.4, 28.2, 34.1, 40.8, 51.8, 54.2, 125.4, 125.8, 176.1, 177.7. − MS: m/z (%) = 319 (0.29), 317 (0.77), 283 (5.65), 231 (14), 195 (33), 193 (100). − CI-MS (NH$_3$): m/z (%) = 352 (24), 351 (17), 350 (64), 333 (21), 245 (18), 195 (35), 193 (100).

Acknowledgments

We wish to thank the JNICT for awarding a Ph.D. grant to P. Coelho.

---

[1] R. J. P. Corriu, C. Guerin, J. J. E. Moreau, in *Topics In Stereochemistry* (Eds.: E. L. Eliel, S. H. Wilen, N. L. Allinger), John Wiley & Sons, New York, **1984**, Vol. 15, p. 43−198.

[2] [2a] H. Nishiyama, T. Kitajima, M. Matsumoto, K. Itoh, *J. Org. Chem.* **1984**, *49*, 2298−2300. − [2b] G. Stork, M. Kahn, *J. Am. Chem. Soc.* **1985**, *107*, 500−501. − [2c] G. Stork, M. J. Sofia, *J. Am. Chem. Soc.* **1986**, *108*, 6826−6828. − [2d] G. Stork, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 149−154. − [2e] R. V. Bonnert, M. J. Davies, J. Howarth, P. R. Jenkins, *J. Chem. Soc., Chem. Commun.* **1990**, 148−149. − [2f] K. Tamao, K. Maeda, T. Yamaguchi, Y. Ito, *J. Am. Chem. Soc.* **1989**, *111*, 4984−4985. − [2g] M. Koreeda, I. A. George, *J. Am. Chem. Soc.* **1986**, *108*, 8098−8100. − [2h] A. G. Myers, D. Y. Gin, K. L. Widdowson, *J. Am. Chem. Soc.* **1991**, *113*, 9661−9663.

[3] [3a] S. Anwar, A. P. Davis, *Tetrahedron* **1988**, *44*, 3761−3770. − [3b] K. Tamao, T. Nakajima, R. Sumiya, H. Arai, N. Higuchi, Y. Ito, *J. Am. Chem. Soc.* **1986**, *108*, 6090−6093. − [3c] M. R. Hale, A. H. Hoveyda, *J. Org. Chem.* **1992**, *57*, 1643−1645. − [3d] S. Anwar, G. Bradley, A. P. Davis, *J. Chem. Soc., Perkin Trans. 1* **1991**, 1383−1389. − [3e] K. Tamao, T. Tohma, N. Inui, O. Nakayama, Y. Ito, *Tetrahedron Lett.* **1990**, *31*, 7333−7336.

[4] [4a] K. Nakanishi, K. Mizuno, Y. Otsuji, *J. Chem. Soc., Chem. Commun.* **1991**, 90−92. − [4b] S. A. Fleming, S. C. Ward, *Tetrahedron Lett.* **1992**, *33*, 1013.

[5] [5a] K. Tamao, K. Kobayashi, Y. Ito, *J. Am. Chem. Soc.* **1989**, *111*, 6478−6480. − [5b] J. W. Gillard, R. Fortin, E. L. Grimm, M. Maillard, M. Tjepkema, M. A. Bernstein, R. Glaser, *Tetrahedron Lett.* **1991**, *32*, 1145−1148. − [5c] D. Craig, J. C. Reader, *Tetrahedron Lett.* **1990**, *31*, 6585−6588. − [5d] D. Craig, J. C. Reader, *Tetrahedron Lett.* **1992**, *33*, 4073−4076. − [5e] S. M. Sieburth, L. Fensterbank, *J. Org. Chem.* **1992**, *57*, 5279−5281. − [5f] G. Stork, T. Y. Chan, G. A. Breault, *J. Am. Chem. Soc.* **1992**, *114*, 7578−7579. − [5g] K. J. Shea, K. S. Zandi, A. J. Staab, R. Carr, *Tetrahedron Lett.* **1990**, *31*, 5885−5888. − [5h] K. J. Shea, A. J. Staab, K. S. Zandi, *Tetrahedron Lett.* **1991**, *32*, 2715−2718.

[6] L. H. Sommer, C. L. Frye, *J. Am. Chem. Soc.* **1959**, *81*, 1013.

[7] [7a] R. G. Daniels, L. A. Paquette, *Organometallics* **1982**, *1*, 1449−1453. − [7b] A. G. Brook, W. W. Limburg, *J. Am. Chem. Soc.* **1963**, *85*, 832−833. − [7c] A. G. Brook, J. D. Pascoe, *J. Am. Chem. Soc.* **1971**, *93*, 6224−6227.

[8] [8a] A. Chapeaurouge, S. Bienz, *Helv. Chim. Acta* **1993**, *76*, 1876−1889. − [8b] S. Bienz, A. Chapeaurouge, *Helv. Chim. Acta* **1991**, *74*, 1477−1488.

[9] [9a] A. Djerourou, L. Blanco, *Tetrahedron Lett.* **1991**, *32*, 6325−6326. − [9b] A. Djerourou, L. Blanco, *Phosphorus, Sulfur and Silicon* **1999**, *149*, 107.

[10] The preparation of buta-1,3-dienylmagnesium chloride from a mixture of (E)- and (Z)-chlorobutadiene (E/Z = 3:7) has been reported (see T. Ishii, N. Kawamura, S. Matsubara, K. Utimoto, S. Kozima, T Hitomi, *J. Org. Chem.* **1987**, *52*, 4416−4418). Treatment of isobutyraldehyde with this reagent gave a mixture of dienyl alcohols with a 3:7 E/Z ratio. This would seem to have been a fortuitous stereospecific reaction as these dienyl alcohols with the same E/Z ratio (3:7) were obtained starting from a mixture of chlorobutadienes with E/Z = 6:94.

[11] H. G. Viehe, *Angew. Chem. Int. Ed. Engl.* **1963**, *75*, 793−794.

[12] Transesterifications of methyl acrylate, phenyl acetate and fumarate with 2-silapropanediol **4** proved to be too slow at −20 °C. When these reactions were performed at room temperature, the monoesters **6b−d** were isolated in low yields (15−46%) and with very low *ee* (0−16%).

Received December 9, 1999
[O99665]