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Highly diastereoselective intramolecular Diels–Alder reaction of chiral silatrienes

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Abstract—New Si-chiral 2-silahexa-3,5-dienyl acrylates were prepared in six steps from dichloro(chloromethyl)methylsilane. The $EtAlCl_2$ catalysed intramolecular Diels–Alder reaction of these compounds gave chiral 4-sila-4a,7,8,8a-tetrahydroisochroman-1-ones in good yield. Very good diastereoselectivity was observed for a silatriene bearing a methyl and a 2-methoxyphenyl substituent on the chiral silicon atom.

1. Introduction

Asymmetric synthesis using compounds stereogenic at a carbon atom is very common. Since 1960s, several authors have reported studies on the use of silane derivatives bearing a stereogenic center on silicon as chiral inducers, despite the longer bonds to silicon than to a carbon atom.[1] Epoxidation of vinylsilanes,[2,3] reduction of ketones with mono-hydrogenosilanes[4,5] and radical monohydrogenolysis of a 1,1-dichloroethylsilane[6,7] were slightly diastereoselective (de≤20%). Low diastereoselectivities (de≤35%) were also noticed for Lewis acid-catalyzed reactions of an acetal with a silyl enol ether[5] or an allylic silane.[8] A thioacylsilane underwent rather good diastereselective nucleophilic additions on sulfur using organolithium reagents[9] (de≤76%) and a fairly good [2+4]-cycloaddition with buta-1,3-diene[10] (de≈50%). Noticeable diastereoselectivities (de≤76%) were also reported for the addition of electrophiles to anions adjacent to a chiral silyl group.[11,12] Since a long time, there has been some success with nucleophilic addition of Grignard reagents or organolithium derivatives on chiral acylsilane (de≤62%).[13,14] Recently an increase of diastereoselectivity (de=97%) was obtained at −100°C, using a silane bearing a benzyloxymethyl substituent.[15] This highly selective reaction occurs probably by chelation of the organometallic reagent with a 'quasi-intramolecular' attack of the carbonyl function.

In the last years we have studied the intramolecular Diels–Alder (IMDA) reaction of several chiral silicon compounds and in some cases a good diastereoselective induction was noticed.[16] The selectivity of this reaction seems to be very dependent on the steric effect of the silicon substituents. Thermal or Lewis acid-catalyzed IMDA reaction of 2-hydroxymethyl-2-methyl-2-silahexa-3,5-dienyl acrylate and the hydroxy protected derivatives have allowed the preparation of 4a,7,8,8a-tetrahydro-4-silaisochroman-1-ones,[16b] but the better diastereoselective reaction, obtained with the bulky triisopropylsilyl group as protecting group in the presence of $EtAlCl_2$, remained unsatisfactory, the four possible isomers were present in the ratio 20/6/71/3. In this work we describe the IMDA reaction of chiral silatrienes bearing rather hindering substituents such as phenyl, cyclohexyl and 2-methoxyphenyl on the silicon atom.

2. Results and discussion

2.1. Synthesis

The chiral silatrienes **5a–c** were prepared in six steps from commercially available dichloro(chloromethyl)methylsilane **1** as shown in Scheme 1. The chlorosilanes **2a**,**b** were obtained by reaction of (chloromethyl)dichlorosilane **1** with the Grignard reagents derived from bromobenzene and bromocyclohexane.[17] Chlorosilane **2c** was obtained by treating anisole with *n*-BuLi followed by reaction with dichlorosilane **1**.[18] These chlorosilanes **2a–c** were isolated by distillation and used immediately after isolation. The CuCN-catalyzed reaction of buta-1,3-dienylmagnesium chloride with chloro(chloromethyl)silanes **2a–c** gave mixtures of *E* and *Z* silahexadienes **3** ((*E*/*Z*) from 1/3 to 1/1) which were equilibrated by treatment with iodine in a benzenic solution. The ratio of *E* to *Z* silahexadienes **3** became better then 91/9. Replacement of the chlorine atom

Keywords: intramolecular Diels–Alder reactions; stereoselectivity; chiral silatrienes; silicon; 4-silatetrahydroisochroman-1-ones.

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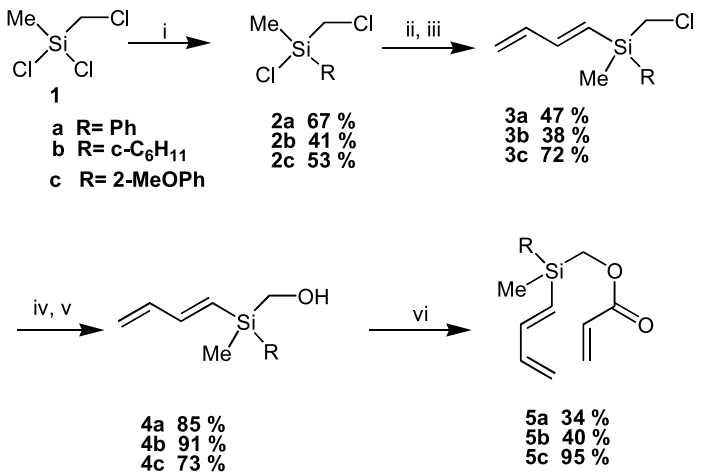


Scheme 1. (i) For **2a**, PhMgBr, Et_2O, reflux; for **2b**, *c*-C_6H_{11}MgBr, CuCN (5%), Et_2O, reflux; for **2c**, MeOPh, *n*-BuLi, Et_2O, reflux, (ii) $CH_2{=}CHCH{=}CH_2$-MgCl, CuCN (5%), THF, room temperature, (iii) I_2, reflux Benzene, (iv) KOAc, TiO_2, *n*-Bu_4NBr, (v) $LiAlH_4$ then H_2O, (vi) with **4a** and **4b**, DEAD, acrylic acid, PPh_3; with **4c**, acryloyl chloride, *N*,*N*-dimethylaniline.

of **3a–c** by an acetoxy group, in the presence of the phase transfer agent *n*-Bu_4NBr, gave the corresponding acetoxymethylsilanes which were reduced with $LiAlH_4$ to deliver the hydroxymethylsilanes **4a–c** and these were converted into the corresponding acrylic esters **5a–c**. While the Mitsunobu method (acrylic acid, DEAD, PPh_3) gave poor yields of the acrylic esters **5a**,**b**, the treatment of alcohol **4c** with acryloyl chloride in the presence of *N*,*N*-dimethylaniline gave the ester **5c** in quantitative yield.

2.2. Intramolecular Diels–Alder reaction

Treatment of silatrienes **5a–c** at room temperature in CH_2Cl_2 with 4 equiv. of $EtAlCl_2$ gave the 4-methyl-4a,7,8,8a-tetrahydro-4-silaisochromanones **6a–c**, which were isolated in medium to good yields (50–74%) as mixtures of 3 or 4 diastereomers. The diastereomeric ratios were determined by ^1H NMR spectroscopy through integration of the CH_3Si singlets (see Table 1, Scheme 2).

The reactions times of these reactions (1–2 h) were noticeably lower than those necessary, in the same conditions, to transform the similar silatrienes possessing CH_3 and CH_2OR groups (24–48 h).[16b] The diastereomeric ratios observed with compounds **6a–c** were generally higher than those obtained previously and the best result was obtained with silatriene **5c** bearing the 2-methoxyphenyl group; 90% of the silaisochromanones mixture **6c** was one isomer. Treatment of silatriene **5a** with 4 equiv. of $EtAlCl_2$, at −20°C gave similar results (47% yield, diast. ratios: 4/16/76/4) than those obtained at room temperature.

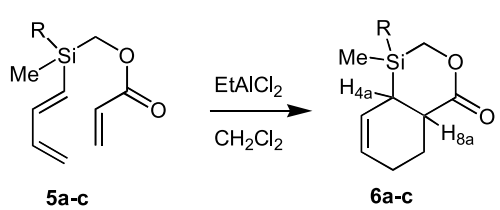
Heating of 0.02 M toluene solution of silatriene **5c** at 170°C for 20 h gave the 4-silatetrahydroisochromanone **6c** with 72% yield, very similar to the one obtained with $EtAlCl_2$, but the reaction was, as expected, less selective (diast. ratios: 11/20/53/16).

^1H NMR spectra of the 4-silatetrahydroisochroman-1-ones **6a–c** show signals around 3.00–3.15 ppm attributed to the proton H_{8a} of the major isomer. The coupling constants $J_{H8a-H4a}$ are between 4 and 7 Hz, which are consistent with a *cis* junction of cycles. The major isomers are thus formed via *endo* transition states (Scheme 3).

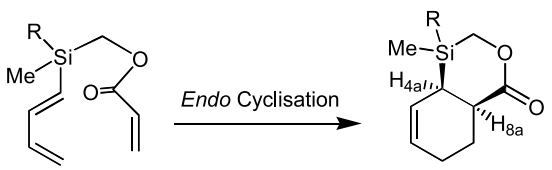
Generally the mixtures of diastereomeric 4-sila-4a,7,8,8a-tetrahydroisochroman-1-ones could not be separated by the usual silica gel column chromatography. For the 2-phenylsilaisochromanone **6a** it was possible to isolate by this technique a fraction containing 92% of the major isomer and a mixture of the three minor isomers. ^1H NMR spectra of the silatetrahydroisochromanones bearing on the silicon atom a cyclohexyl group, **6b**, or a protected or unprotected hydroxymethyl group[16b] show all the olefinic proton signals between 5.8 and 5.6 ppm. The olefinic protons of the major isomer of the phenylated and 2-methoxyphenylated compounds, **6a** and **6c**, appear also between 5.8 and 5.6 ppm. In the ^1H NMR spectrum of the mixture of the three minor isomers of **6a** (isolated by silica gel chromatography) a

Table 1. $EtAlCl_2$-catalysed IMDA reaction of silatrienes **5a–c**

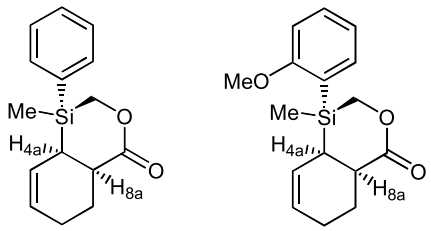
Silatriene **5a–c**	4-Silatetrahydroisochromanone **6a–c**		
	Time (h)	Yield	Diast. ratio
a R=Ph	2	50	3/15/79/3
b R=*c*-C_6H_{11}	1	68	21/74/5
c R=2-MeOPh	1.5	74	4/5/90/1



Scheme 2.



Scheme 3.



6a **6c**

Scheme 4.

signal at 3.13 ppm (ddd, J=4, 7, 7 Hz, H_{8a}) and a multiplet between 5.35 and 5.25 ppm were attributed to one isomer (for the two other isomers the olefinic protons were at lower field than 5.6 ppm). The coupling constants with the proton H_{8a} are lower or equal to 7 Hz so this isomer should be also with a *cis* junction of cycles. The presence of higher field olefinic proton for this isomer could be attributed to the shielding effect of the aromatic ring. It appears after examination of the Dreiding models of the various conformers of the *cis*-silatetrahydroisochromanone that one olefinic proton could be shielded when a phenyl group is in the *trans* relationship with the protons H_{8a} and H_{4a}. So, we suggest for the major isomer of **6a**, a *cis* relationship between the phenyl group and the proton H_{8a} and H_{4a}, it should be formed via a transition state where, related to the plane of the dienic part, the bulky aryl group is on the opposite side to that of the dienophile (Scheme 4).

The same suggestion concerning the major diastereomer of **6c** is made, because its olefinic protons are between 5.6 and 5.8 ppm and a signal between 5.25 and 5.35 ppm is clearly present in the ^{1}H NMR spectrum of the mixture of silaisochromanones isolated after the less selective thermal Diels–Alder reaction of **5c**. These results raise interesting mechanistic questions concerning a steric crowding or a chelate formation when a 2-methoxyphenyl group is present on the silicon atom. Further studies along these lines are in progress.

3. Conclusion

New 4-silatetrahydroisochroman-1-ones were prepared in good yields through $EtAlCl_2$ catalysed IMDA reactions of chiral silatrienes. Very good diastereoselectivity was observed for a silatriene bearing a methyl and a 2-methoxyphenyl substituent on the chiral silicon atom. The reaction proceeds, probably, via an *endo* transition state where, related to the plane of the dienic part, the silicon-bulky substituent is on the opposite side to that of the dienophile.

4. Experimental

4.1. Apparatus

^{1}H and ^{13}C spectra were recorded on Bruker AC200 (200 and 50.3 MHz, respectively) or Bruker AC250 (250 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 ionisation at 70 eV. IR spectra of neat products were registered on a Perkin–Elmer 682 spectrometer (wave numbers 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}). Dichloro(chloromethyl)methylsilane was obtained from commercial source (ABCR).

4.2. Synthesis of chlorosilanes (2a,b)

Chloro(chloromethyl)methylphenylsilane **2a** was prepared through reaction of the dichloro(chloromethyl)methylsilane with a solution of PhMgBr in diethyl ether.[17] Chloro(chloromethyl)cyclohexylmethyllsilane **2b** was prepared through reaction of dichloro(chloromethyl)methylsilane with a solution of PhMgBr in diethyl ether in the presence of CuCN. Both chlorosilanes were isolated through distillation and used immediately.

4.2.1. Chloro(chloromethyl)(2-methoxyphenyl)methylsilane (2c). Yield: 53%. 26.7 mL of a solution of *n*-BuLi (1.5 M, 40.0 mmol) in hexane were added dropwise to a solution of anisole (4.30 mL, 40.0 mmol) in 50 mL of dry diethyl ether under argon atmosphere. The solution was heated under reflux for 36 h. After return to room temperature dichloro(chloromethyl)methylsilane (4.50 mL, 27.6 mmol) was added and the mixture refluxed for another 4 h. The suspension was then filtered and the filtrate distilled under reduced pressure (0.01 mm Hg) giving 3.45 g of chlorosilane **2c** (bp 90–100°C). ^{1}H NMR: 0.79 (s, 3H, $SiCH_3$), 3.66 (s, 3H, MeO), 3.15 (d, J=13.9 Hz), 3.30 (d, J=13.8 Hz) (AB system, 2H), 6.89 (d, J=8.3 Hz, 1H), 7.06 (t, J=7.3 Hz, 1H), 7.4–7.6 (m, 1H), 7.64 (dd, J=1.8, 7.3 Hz, 1H).

4.3. Synthesis of (*E*)-(buta-1,3-dienyl)methylsilanes (3a–c): general procedure

A solution of buta-1,3-dien-1-ylmagnesium chloride in THF was prepared as follows: magnesium (5.00, 206 mmol) and zinc chloride (1.50, 11.0 mmol) were placed in a reaction vessel, under an argon atmosphere and heated for 2–3 min with a flame. After return 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 (*Z*/*E*=94/6) (10 mL, 100 mmol) and 1,2-dibromoethane (0.80 mL) dissolved in THF (70 mL) were then added dropwise for 1.5 h so as to maintain a gentle reflux. The reaction was heated under reflux for another 3 h and then left overnight at room temperature without stirring. Settlement of the resulting suspension leave 0.55 M orange solution of butadienylmagnesium chloride.

33.6 mmol of chlorosilane **2a–c** were added dropwise to a stirred mixture of CuCN (200 mg, 2.40 mmol) in 80 mL of a THF buta-1,3-dien-1-ylmagnesium chloride solution (44 mmol) under an argon atmosphere at 0°C. The reaction mixture was stirred overnight, quenched with aqueous NH_4Cl and extracted with *n*-hexane. The combined organic extracts were dried over anhydrous Na_2SO_4. After solvent evaporation, the crude product was purified by distillation

under reduced pressure (0.05 mm Hg) to yield butadienylsilanes **3a–c** as a mixture of *E* and *Z* isomers.

Isomerisation reaction. A solution of butadienylsilane **3a–c** (26.5 mmol) and iodine (0.340 g, 1.34 mmol, 5%) in benzene (100 mL) was heated under reflux for 3.5 h under an argon atmosphere. The reaction mixture was then quenched with aqueous $Na_2S_2O_3$, extracted with *n*-hexane and the combined organic extracts dried over anhydrous Na_2SO_4. After solvent evaporation, the crude chloromethylsilane **3** was purified by column chromatography (hexane/diethyl ether).

4.3.1. (*E*)-(Buta-1,3-dien-1-yl)(chloromethyl)methylphenylsilane (3a). *E*/*Z*=91/9. Yield: 47%. IR: 1630, 1580, 1260 ($SiCH_3$). ^{1}H NMR: 0.53 (s, 3H, $SiCH_3$), 3.06 (s, 2H, CH_2Cl), 5.23 (d, *J*=9.9 Hz, 1H), 5.31 (d, *J*=17.1 Hz, 1H), 6.03 (d, *J*=18.5 Hz, 1H), 6.42 (ddd, *J*=9.9, 9.9, 16.9 Hz, 1H), 6.69 (dd, *J*=18.5, 9.9 Hz, 1H), 7.3–7.5 (m, 3H, Ph), 7.5–7.6 (m, 2H, Ph). ^{13}C NMR: −6.0 ($SiCH_3$). 29.0 (CH_2Cl), 119.4, 127.2, 127.9, 129.8, 134.2, 134.3, 139.2, 148.5. MS: *m*/*z* (%) 209 (2.2), 207 (3.8), 173 (71), 145 (22), 121 (100), 105 (35), 95 (27), 93 (20), 91 (32), 63 (31), 43 (29).

4.3.2. (*E*)-(Buta-1,3-dien-1-yl)(chloromethyl)cyclohexylmethylsilane (3b). *E*/*Z*=96/4. Yield: 38%. IR: 1580, 1500, 1255 ($SiCH_3$). ^{1}H NMR: 0.18 (s, 3H, $SiCH_3$), 0.8–1.0 (m, 1H), 1.0–1.4 (m, 5H), 1.6–1.8 (m, 5H), 2.87 (s, 2H, CH_2Cl), 5.19 (d, *J*=9.5 Hz, 1H), 5.28 (d, *J*=16.7 Hz, 1H), 5.82 (d, *J*=18.4 Hz, 1H), 6.38 (ddd, *J*=9.9, 9.9, 16.7 Hz, 1H), 6.62 (dd, *J*=18.2, 9.9 Hz, 1H). MS: *m*/*z* (%) 228 (0.3, M^+), 179 (7), 109 (23), 97 (100), 81 (20), 79 (34).

4.3.3. (*E*)-(Buta-1,3-dien-1-yl)(chloromethyl)(2-methoxyphenyl)methylsilane (3c). *E*/*Z*=92/8. Yield: 72%. IR: 1590, 1570, 1240 ($SiCH_3$). ^{1}H NMR: 0.52 (s, 3H, $SiCH_3$), 3.17 (s, 2H, CH_2Cl), 3.83 (s, 3H, CH_3O), 5.20 (dd, *J*=9.7, 1.0 Hz, 1H), 5.29 (dd, *J*=16.6, 1.0 Hz, 1H), 6.44 (ddd, *J*=9.9, 9.9, 16.5 Hz, 1H), 6.69 (dd, *J*=10.1, 18.5 Hz, 1H), 6.86 (d, *J*=8.5 Hz, 1H), 6.99 (t, *J*=7.3 Hz, 1H), 7.35–7.45 (m, 2H). ^{13}C NMR: −6.2 ($SiCH_3$), 29.5 (CH_2Cl), 55.0 (OCH_3), 109.6, 118.8, 120.7, 122.4, 128.3, 132.7, 135.9, 139.5, 147.6, 164.0. MS: *m*/*z* (%) 254 (2.7), 252 (4.5, M^+), 239 (8), 237 (19), 203 (60), 201 (20), 173 (36), 151 (40), 145 (41), 129 (35), 121 (85), 105 (37), 91 (42), 75 (100), 59 (46).

4.4. Synthesis of hydroxymethylsilanes (4a–c): general procedure

A mixture of chloromethylsilane **3a–c** (17.4 mmol), potassium acetate (4.0 g, 41 mmol), tetrabutylammonium bromide (140 mg, 0.530 mmol) and titanium oxide (680 mg, 8.51 mmol) was stirred under an argon atmosphere, at 80–90°C, for 3 h. After return to room temperature, 10 g of silica gel and 10 mL of diethyl ether were added. The suspension was stirred for 5 min, filtered and the residue washed 10 times with diethyl ether. After solvent evaporation, the crude product was purified by column chromatography (*n*-hexane/Et_2O) to yield the corresponding acetoxymethylsilanes.

In the next step, 37 mL of a 1 M $LiAlH_4$ solution (37 mmol) in diethyl ether were added dropwise to a stirred solution of the acetoxymethylsilane in diethyl ether at −20°C. The suspension was stirred for 30 min at room temperature then 2–3 g of hydrated Na_2SO_4 were added very slowly (violent reaction) followed by 10 mL of water. After decantation, the aqueous phase was extracted with diethyl ether (4×50 mL). The combined organic extracts were dried over Na_2SO_4 and the solvent removed under reduced pressure, leaving the pure hydroxymethyl)silane **4a–c**.

4.4.1. (*E*)-2-Methyl-2-phenyl-2-silahexa-3,5-dien-1-ol (4a). Yield: 85%. IR: 3350 (OH), 1580, 1250 ($SiCH_3$). ^{1}H NMR: 0.46 (s, 3H, $SiCH_3$), 3.70 (m, 3H, CH_2OH and OH), 5.15–5.35 (m, 2H), 6.02 (d, *J*=18.2 Hz, 1H), 6.43 (ddd, *J*=9.9, 9.9, 16.9 Hz, 1H), 6.72 (dd, *J*=18.2, 9.8 Hz, 1H), 7.3–7.5 (m, 3H, Ph), 7.50–7.65 (m, 2H, Ph). ^{13}C NMR: −6.5 ($SiCH_3$), 53.9 (CH_2OH), 118.9, 127.8, 128.2, 129.4, 134.2, 135.1, 139.3, 148.0. MS: *m*/*z* (%) 189 (0.6), 173 (54), 137 (54), 121 (100), 105 (21).

4.4.2. (*E*)-2-Cyclohexyl-2-methyl-2-silahexa-3,5-dien-1-ol (4b). Yield: 91%. IR: 3360 (OH), 1580, 1250 ($SiCH_3$). ^{1}H NMR: 0.12 (s, 3H, $SiCH_3$), 0.75–1.0 (m, 2H), 1.0–1.4 (m, 5H), 1.6–1.8 (m, 5H), 3.51 (s, 2H, CH_2OH), 5.17 (d, *J*=9.4 Hz, 1H), 5.27 (d, *J*=16.2 Hz, 1H), 5.84 (d, *J*=18.4 Hz, 1H), 6.38 (ddd, *J*=10.1, 10.1, 16.7 Hz, 1H), 6.64 (dd, *J*=18.6, 10.2 Hz, 1H). ^{13}C NMR: −8.9 ($SiCH_3$), 23.4, 26.7, 27.3, 27.4, 27.8, 52.8 (CH_2OH), 118.1, 128.8, 139.6, 147.2. MS: *m*/*z* (%) 180 (0.5), 179 (3.2), 143 (20), 97 (100), 61 (28).

4.4.3. (*E*)-2-(2-Methoxyphenyl)-2-methyl-2-silahexa-3,5-dien-1-ol (4c). Yield: 73%. IR: 3400 (OH), 1590, l240 ($SiCH_3$). ^{1}H NMR: 0.46 (s, 3H, $SiCH_3$), 1.91 (m, OH, 1H), 3.70 (s, 2H, CH_2OH), 3.86 (s, 3H, CH_3O), 5.20 (d, *J*=9.8 Hz, 1H), 5.29 (d, *J*=16.4 Hz, 1H), 6.09 (d, *J*=18.4 Hz, 1H), 6.45 (ddd, *J*=10.0, 10.0, 16.3 Hz, 1H), 6.72 (dd, *J*=10.1, 18.3 Hz, 1H), 6.90 (d, *J*=8.3 Hz, 1H), 7.02 (t, *J*=7.3 Hz, 2H), 7.35–7.45 (m, 2H, Ph). ^{13}C NMR: −6.4 ($SiCH_3$), 54.3 (CH_2OH), 55.0, 109.6, 118.3, 120.8, 123.4, 128.8, 131.2, 135.9, 139.5, 147.2, 163.7. MS: *m*/*z* (%) 220 (2), 219 (6.9), 203 (82), 173 (57), 151 (47), 145 (44), 129 (25), 128 (30), 121 (100), 105 (30), 91 (44), 75 (84), 59 (65), 45 (39).

4.5. Synthesis of acrylates (5a,b): general procedure

Diethyl azodicarboxylate (105 μL, 0.660 mmol) (DEAD) was added dropwise to a stirred solution of (hydroxymethyl)silane **4a**,**b** (0.439 mmol), triphenylphosphine (173 mg, 0.660 mmol) and acrylic acid (38 mg, 0.527 mmol) in 20 mL THF, at −78°C, under an argon atmosphere. The reaction mixture was then stirred for 20 min at room temperature. After solvent evaporation, the crude acrylate **5** was purified by chromatography (*n*-hexane/Et_2O 80/20).

4.5.1. (*E*)-2-Methyl-2-phenyl-2-silahexa-3,5-dien-1-yl acrylate (5a). Yield: 34%. IR: 1735 (C=O), 1575, 1260 ($SiCH_3$). ^{1}H NMR: 0.47 (s, 3H, $SiCH_3$), 4.16 (s, 2H), 5.20–5.35 (m, 2H), 5.80 (dd, *J*=10.3, 1.8 Hz, 1H), 6.00 (d, *J*=18.2 Hz, 1H), 6.13 (dd, *J*=10.3, 17.3 Hz, 1H), 6.3–6.5 (m, 2H), 6.67 (dd, *J*=18.3, 9.9 Hz, 1H), 7.3–7.5 (m, 3H),

7.5–7.6 (m, 2H). ^{13}C NMR: −5.8 ($SiCH_3$), 55.8 (CH_2O), 119.4, 127.5, 128.0, 128.4, 129.7, 130.4, 134.3, 134.5, 139.3, 148.4, 166.9 (C═O). MS: *m/z* (%) 258 (0.9, M^+), 243 (23), 205 (67), 181 (40), 173 (39), 145 (31), 137 (25), 128 (100), 121 (97), 105 (44), 95 (26), 91 (20), 55 (81), 53 (20), 43 (34).

4.5.2. (*E*)-2-Cyclohexyl-2-methyl-2-silahexa-3,5-dien-1-yl acrylate (5b). Yield: 40%. IR: 1740 (C═O), 1535, 1260 ($SiCH_3$). ^{1}H NMR: 0.13 (s, 3H, $SiCH_3$), 0.7–1.0 (m, 1H), 1.1–1.35 (m, 5H), 1.6–1.8 (m, 5H), 3.97 (s, 2H), 5.18 (d, *J*=9.8 Hz, 1H), 5.27 (d, *J*=18.4 Hz, 1H), 5.81 (dd, *J*=10.3, 1.5 Hz, 1H), 5.81 (d, *J*=18.7 Hz, 1H), 6.14 (dd, *J*=10.3, 17.5 Hz, 1H), 6.25–6.45 (m, 2H), 6.60 (dd, *J*=10.3, 18.6 Hz, 1H). ^{13}C NMR: −8.3 ($SiCH_3$), 23.8, 26.7, 27.2, 27.3, 27.9, 54.8 (CH_2O), 118.5, 128.0, 128.5, 130.2, 139.5, 147.3, 167.0 (C═O). MS: *m/z* (%) 250 (0.5), 249 (1.4), 211 (4.7), 181 (100), 109 (38), 97 (27), 95 (19), 55 (52).

4.5.3. (*E*)-2-(2-Methoxyphenyl)-2-methyl-2-silahexa-3,5-dien-1-yl acrylate (5c). Acryloyl chloride (0.200 mL, 2.4 mmol) was added dropwise to a stirred solution of hydroxymethylsilane **4c** (190 mg, 0.812 mmol) and *N*,*N*-dimethylaniline (0.200 mL) in CH_2C1_2 (25 mL) at 0°C under argon atmosphere. After stirring for 30 min at room temperature the solution was quenched with HCl 1 M (10 mL) and the resulting mixture was extracted with CH_2C1_2. The combined organic extracts were dried over anhydrous Na_2SO_4, concentrated and the product was purified by column chromatography (*n*-hexane/ether 80/20) to give 223 mg of acrylate **5c** (95% yield). IR: 1730 (C═O), 1590, 1240 ($SiCH_3$). ^{1}H NMR: 0.47 (s, 3H), 3.82 (s, 3H), 4.22 (s, 2H), 5.15–5.30 (m, 2H), 5.77 (dd, *J*=1.9, 10.2 Hz, 1H), 6.05 (d, *J*=18.4 Hz, 1H), 6.11 (dd, *J*=10.2, 17.2 Hz, 1H), 6.3–6.5 (m, 2H), 6.67 (dd, *J*=10.1, 18.4 Hz, 1H), 6.85 (d, *J*=8.5 Hz, 1H), 6.98 (t, *J*=7.2 Hz, 1H), 7.35–7.45 (m, 2H). ^{13}C NMR: −6.0 ($SiCH_3$), 55.0, 56.1, 109.5, 118.5, 120.6, 122.6, 126.5, 128.6, 130.0, 131.6, 135.8, 139.6, 147.3, 164.2, 167.0 (C═O). MS: *m/z* (%) 289 (0.6), 288 (1.3, M^+), 273 (29), 236 (24), 235 (86), 203 (21), 181 (40), 173 (40), 151 (31), 145 (32), 128 (100), 121 (84), 105 (36), 91 (33), 77 (30), 75 (72), 59 (41), 55 (67).

4.6. Lewis acid intramolecular Diels–Alder catalysed reaction: general procedure

A 1 M $EtAlCl_2$ solution in CH_2Cl_2 (4.0 mL, 4.0 mmol) was added to a solution of silatriene **5a–c** (1.0 mmol) in CH_2Cl_2 (20 mL) under argon. After complete consumption of the silatriene (TLC), the reaction mixture 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 crude silaisochromanone **6** was purified by silica gel column chromatography (*n*-hexane/Et_2O).

4.6.1. 4-Methyl-4-phenyl-4-sila-4a,7,8,8a-tetrahydroisochromanon-1-one (6a). Yield: 50%. ^{1}H NMR: 0.42, 0.48, 0.57 and 0.61 (4s, 3H, $SiCH_3$), 1.75–1.90 (m, 1H), 2.0–2.3 (m, 2H), 2.35–2.60 (m, 2H), 3.15 (ddd, *J*=4, 6, 6 Hz, 1H), 4.0–4.4 (m, 2H), 5.25–5.35 (m) and 5.5–5.8 (m) (2H), 7.35–7.60 (m, 5H). ^{13}C NMR: −7.3 ($SiCH_3$), 22.3, 22.5, 23.9, 38.9, 60.3, 123.6, 126.1, 128.4, 130.5, 133.4, 134.5, 175.6 (C═O). MS: *m/z* (%) 259 (15.1), 258 (67, M^+), 257 (10), 243 (5), 151 (29), 149 (26), 137 (47), 136 (36), 135 (72), 134 (69), 133 (35), 123 (50), 122 (21), 121 (100), 120 (44), 105 (87), 107 (30), 106 (26), 93 (25), 92 (23), 91 (60), 80 (61), 79 (96), 77 (55), 53 (33), 43 (38).

4.6.2. 4-Cyclohexyl-4-methyl-4-sila-4a,7,8,8a-tetrahydroisochromanon-1-one (6b). Yield: 68%. IR: 1735 (C═O), 1650, 1255 ($SiCH_3$). ^{1}H NMR: 0.05, 0.10, 0.17 (s, 3H, $SiCH_3$), 0.8–1.0 (m, 1H), 1.1–1.4 (m, 5H), 1.6–1.9 (m, 6H), 2.0–2.3 (m, 3H), 2.3–2.5 (m, 1H), 3.00 (ddd, *J*=3, 7, 7 Hz, 1H), 3.90 (d, *J*=14.7 Hz) and 4.19 (d, *J*=14.7 Hz) [AB system, minor isomer] and 4.00 (d, *J*=15.0 Hz) and 4.09 (d, *J*=15.0 Hz) [AB system, major isomer] (2H), 5.45–5.75 (m, 2H). ^{13}C NMR: −10.4, −9.0, −6.6, 20.3, 22.3, 22.4, 22.5, 22.9, 23.7, 23.8, 24.1, 24.3, 26.5, 26.6, 26.9, 26.98, 27.02, 27.4, 27.5, 27.7, 28.0, 38.8, 38.9, 39.4, 59.0, 59.2, 59.4, 123.8, 124.6, 125.3, 125.4, 126.4, 176.0 (C═O). MS: *m/z* (%) 266 (3.9), 265 (9.7), 264 (14.9, M^+), 181 (11), 137 (14), 99 (20), 81 (25), 80 (100), 79 (45), 77 (27), 75 (63), 61 (31), 59 (72), 58 (21), 55 (24), 45 (28), 43 (33).

4.6.3. 4-Methoxyphenyl-4-methyl-4-sila-4a,7,8,8a-tetrahydroisochromanon-1-one (6c). Yield: 74%. ^{1}H NMR: 0.34, 0.40, 0.47 and 0.54 (4 s, 3H, $SiCH_3$), 1.7–1.9 (m, 1H), 2.0–2.3 (m, 2H), 2.4–2.6 (m, 2H), 3.12 (ddd, *J*=4, 7, 6 Hz, 1H), 4.82 (s, 3H), 5.23 (d, *J*=14.7 Hz) and 5.42 (d, *J*=14.7 Hz) [AB system, 2H], 5.6–5.8 (m, 2H), 6.90 (d, *J*=7.5 Hz, 1H), 7.02 (t, *J*=7.5 Hz, 1H), 7.3–7.5 (m, 2H). ^{13}C NMR: −7.0 ($SiCH_3$), 21.0, 22.3, 24.0, 38.5, 55.2, 60.1, 109.7, 120.9, 121.8, 124.5, 125.6, 132.3, 135.1, 164.1, 176.1 (C═O). MS: *m/z* (%) 289 (11), 288 (33, M^+), 287 (7), 273 (2), 149 (100), 135 (29), 119 (31), 105 (41), 79 (48), 77 (23), 59 (28).

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