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Stereocontrolled Synthesis and Cycloaddition of 1,2,4-Trioxygenated 1,3-Dienes

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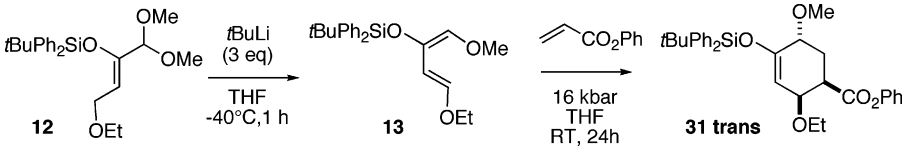

A new stereocontrolled synthetic pathway to 1,2,4-trioxygenated 1,3-dienes from pyruvic aldehyde dimethyl acetal (**14a**) is described. Reacting the cyclohexylamine-derived imine of this starting material with chloroalkyl ethers under basic conditions affords ketoacetals **18**−**20**, which were then transformed into eight different enoxysilanes **12**. A δ-elimination triggered by *tert*-butyllithium yields 1,2,4-trioxygenated dienes **13**. Increasing the bulkiness of the silyloxy group or that of the acetal moiety leads stereoselectively to the (1*E*,3*E*) or (1*Z*,3*E*) isomers of **13**, respectively. Hyperbaric [4 + 2] cycloadditions between **13** (**13c**, **13d**, **13g**) and *N*-methylmaleimide or methyl- and phenylacrylates give access to the expected cycloadducts with fine stereo- and regiocontrol.

Introduction

Oxygenated dienes exhibit a high reactivity and selectivity in various types of transformations.[1] They are also useful building blocks in the synthesis of natural products such as sugar derivatives.[1a,2−6] The most popular representative of this family of compounds is certainly the 1,3-dioxygenated 1,3-diene **4** (best known as the Danishefsky diene,[1j,2] Scheme 1), which is routinely used in Diels−Alder and hetero-Diels−Alder cycloadditions. In contrast, trioxygenated 1,3-dienic systems, which are expected to be more convergent reagents to access carbohydrates via a [4 + 2] cycloaddition, still show limited applications, probably because of the middle yields and low *Z*/*E* stereoselectivities associated with their synthesis. Three synthetic approaches are known to date to attain such structures. An early paper by Scheeren[7] describes the preparation of both 1,2,4- and 1,2,3-trioxygenated 1,3-dienes through a preliminary acid-

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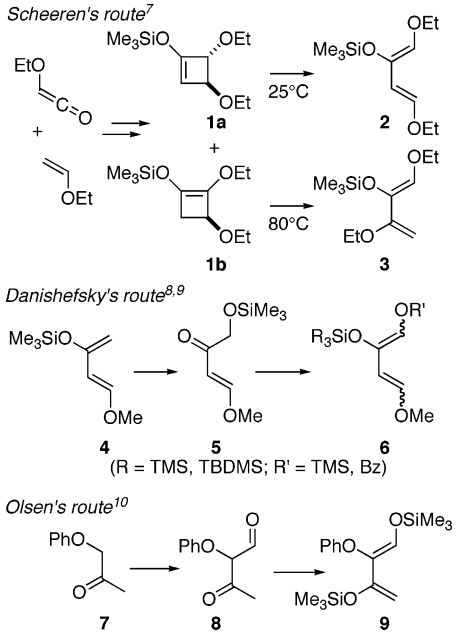
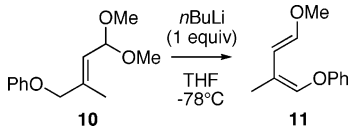
SCHEME 1. Known Routes to 1,2,3- and 1,2,4-Trioxygenated 1,3-Dienes



catalyzed [2 + 2] cycloaddition between a ketene and a vinyl ether (Scheme 1). The resulting alkoxycyclobutanone is transformed, by trimethylsilylation, into a mixture of silyloxycyclobutenes **1**. Cyclobutene **1a** undergoes an electrocyclic ring conrotatory opening at 25 °C to provide the single (1*Z*,3*E*)-1,4-dialkoxy-3-trimethylsilyloxybuta-1,3-diene **2**. The 1,2,3-isomer **3** is isolated after warming **1b** at 80 °C. Another strategy is proposed by Danishefsky[8] to attain 1,2,4-trioxygenated 1,3-dienes such as **6** (Scheme 1). It relies on the transformation of ketone **5** into its silyl enol ether. Ketone **5** results from a Rubottom[9] oxidation of the "classic" dioxygenated diene **4**. This route provides a mixture of three isomers. An additional way to 1,2,3-trioxygenated 1,3-dienes, for instance **9**, is described by Olsen.[10] It is based on the transformation of ketone **7** into keto aldehyde **8** that a double silylation turns into diene **9** (Scheme 1).

We present in this paper a new synthetic pathway affording 1,2,4-trioxygenated 1,3-dienes. This work takes advantage of our experience with the δ-elimination on α,β-unsaturated acetals such as **10** (Scheme 2),[4,11] triggered by *n*-butyllithium at low temperature. This procedure offers a relatively efficient one-step stereoselective access to (1*Z*,3*E*)-1,4-dialkoxy 1,3-dienes **11**.

SCHEME 2. Synthesis of 1,4-Dioxygenated 1,3-Diene via a δ-Elimination



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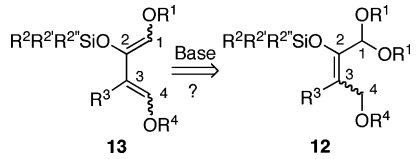
Extending the above methodology to α,β-unsaturated acetals bearing a silyloxy group at C^2 (**12**, Scheme 3) not only provides a relatively straightforward access to trioxygenated 1,3-dienes but also demonstrates that an enol ether double bond is an appropriate vector for a conjugate elimination reaction. No example of such a reaction seems to be described to date.

SCHEME 3. 1,2,4-Trioxygenated 1,3-Dienes via a δ-Elimination through an Enol Ether Double Bond?

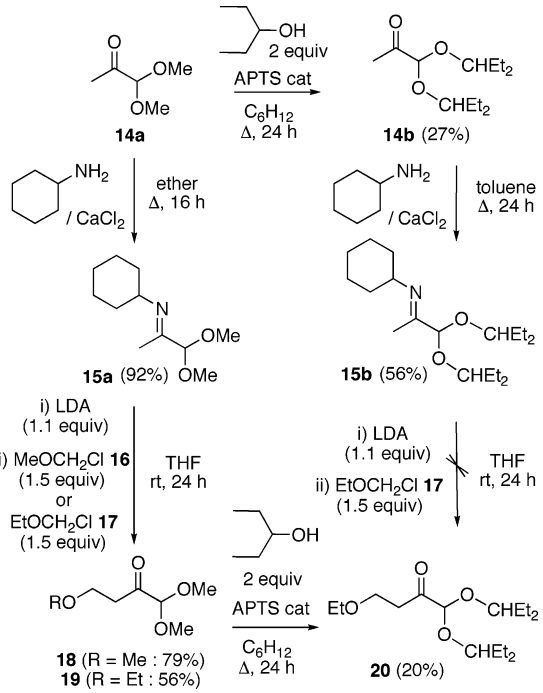


We present here the synthesis of **12** and its transformation into diene **13**. We conclude with a preliminary study concerning the reactivity of **13** in model Diels−Alder cycloadditions.

Results and Discussion

Preparation of Enoxysilanes 12. The required precursors, viz. 2-trialkylsilyloxy α,β-unsaturated acetals **12**, were prepared from pyruvic aldehyde dimethyl acetal **14a**, which revealed a convenient precursor (Scheme 4). To diversify the acetal group, and thus the OR^1 alkoxy substituent, on the final diene, a transacetalization of **14a** was considered. A bulky secondary alcohol was retained to evaluate a possible influence of the size of the leaving group on the chemical and stereochemical outcomes of the δ-elimination. Reacting **14a** with 2 equiv of pentan-3-ol in the presence of a catalytic amount of *p*-toluenesulfonic acid in cyclohexane led, after refluxing for 24 h in a Dean−Stark apparatus, to acetal **14b** in a modest 27% yield, comparable with results given in the literature.[12] The use of a larger amount

SCHEME 4. Syntheses of Butan-2-ones 18−20 from Pyruvic Aldehyde Dimethyl Acetal 14a



(12) Walker, L. F.; Bourghida, A.; Connolly, S.; Wills, M. *J. Chem. Soc., Perkin Trans. 1* **2002**, 965−981.

of alcohol was not retained even if it led to better conversions. Indeed, the difficulties encountered to eliminate the excess of pentan-3-ol when purifying **14b** prompted us to engage only 2 equiv of this alcohol, privileging the quality of **14b** to its quantity. Note that the precursor **14a** is cheap and commercially available.

The functionalization of the pyruvic methyl group was undertaken next. Deprotonating **14** by LDA in THF at low temperature and then trapping the resulting lithium enolate by various chloromethyl ethers was first examined.[13] This route was a dead-end, a product of self-condensation being most probably obtained,[14] together with starting material and unidentified byproducts (Figure 1). A possible chelation of the lithium of LDA by two oxygens of **14** could be at the origin of this result. This chelation would keep apart the nitrogen of the amide and the methyl group to be deprotonated. The Li^+ Lewis acid character would complementarily activate the carbonyl, facilitating the self-condensation by this method.

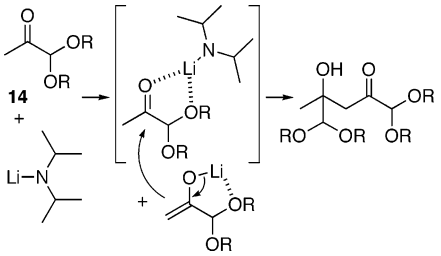


FIGURE 1. Proposed mechanism for the self-condensation of **14** in the presence of LDA.

The disappointing result above led us to first react ketoacetals **14** with cyclohexylamine, then to deprotonate the resulting iminoacetal and conduct the expected C-alkylation with chloromethyl ethers (Scheme 4). Such an alternative has been proposed to efficiently afford C-alkylation products from dialkylpyruvates in the presence of LDA.[15] Iminoacetals **15a** and **15b** (Scheme 4) were isolated in 92% and 56% crude yields, respectively. Immediate alkylation of the lithium enamide of **15**, generated by reacting LDA on **15**, with chloromethyl methyl ether **16** and chloromethyl ethyl ether **17** led to the expected butan-2-ones **18** and **19** from **15a** but failed with **15b**, probably because of the bulky acetal residue. We dodged this problem by preparing **20** from **19** in a late *trans*-acetalization step. The butan-2-one **20** was thus recovered in 20% yield after refluxing **19** in the presence of 2 equiv of pentan-3-ol in cyclohexane in a Dean−Stark apparatus.

The enoxysilanes **12** were then isolated reacting **18**-**20** with lithium hexamethyldisilazane for 20 min at −78 °C and quenching the resulting enolates with a set of chlorotrialkylsilanes **21**−**25** (Scheme 5, Table 1). Eight acetalic enoxysilanes **12** (**12a**−**h**) were thus prepared in medium to good yields and used to evaluate the influence of the R^4 group (entry 1 vs 4, entry 3 vs 7), of the silyloxy substituent (entries 1−3, entries 4−7), and of the acetal appendage (entry 4 vs entry 8) on the consecutive δ-elimination.

SCHEME 5. Syntheses of Enoxysilanes 12 from butan-2-ones 18-20

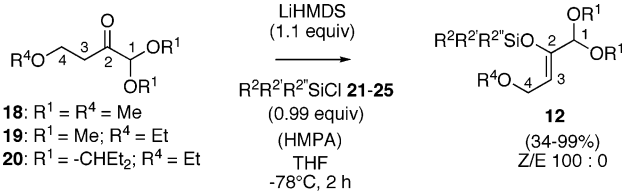


TABLE 1. Yields of Syntheses of 12

entry	ketone	R^1	R^4	$R^2R^{2'}R^{2''}SiCl$	R^2	$R^{2'}$	$R^{2''}$	**12**	yield (%)
1	**18**	Me	Me	**21**	Et	Et	Et	**12a**	99
2	**18**	Me	Me	**22**	*i*Bu	*i*Bu	*i*Bu	**12b**	37
3	**18**	Me	Me	**23**	Ph	Ph	*t*Bu	**12c**	34
4	**19**	Me	Et	**21**	Et	Et	Et	**12d**	99
5	**19**	Me	Et	**24**	Me	Me	*t*Bu	**12e**	43
6	**19**	Me	Et	**25**	*i*Pr	*i*Pr	*i*Pr	**12f**	65
7	**19**	Me	Et	**23**	Ph	Ph	*t*Bu	**12g**	52
8	**20**	$CHEt_2$	Et	**21**	Et	Et	Et	**12h**	96

Worthy of note is the selective recovery of the *Z*-isomers of **12** that could be proved thanks to bidimensional NMR studies such as NOESY experiments on **12a**. The main information given by this analytical technique is the correlation between H^3 and both H^1 and H^4 (Figure 2). Such a *Z*-stereoselectivity, previously observed in the literature from a β-alkoxy ketone,[16] may be rationalized considering a chelated transition state organizing the LiHMDS and the ketoacetal (Figure 2).

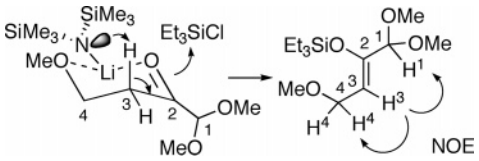


FIGURE 2. Possible origin for the *Z*-configuration of **12**.

Preparation of Dienes 13 by δ-Elimination from 12. The optimization of this key-step reaction has been conducted on the silyloxy acetal **12a**, which showed to be the easiest to prepare and was recovered with the best overall yield (72% from commercial **14a**). Resorting to our previous experimental conditions,[11] we tried to deprotonate the C^4 position of **12a** (Scheme 6) using 1−3 equiv of *n*-butyllithium at −40 °C in THF. However, only the starting material was recovered after workup. Increasing the quantity of this base and/or the temperature as well as the time of the reaction did not yield a trace of diene **12a**. The use of lithium and potassium amides (LDA, KDA) or potassium *tert*-butylate led to either **12a** or unidentified byproducts, respectively. We then decided to employ a stronger alkyllithium, viz. *tert*-butyllithium, and varied the solvent, the time, and the temperature of the reaction (Scheme 6). The results are gathered in Table 2.

No reaction was observed in the presence of 1 equiv of *tert*-butyllithium after 1 h at −78 °C in THF (entry 1). Increasing the amount of base (entries 2 and 3) in the same solvent allowed

(13) Narasaka, K.; Pai, F.-C. *Tetrahedron* **1984**, *40*, 2233−2238.

(14) This compound was identified in the crude mixture but not fully characterized: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.12 (3H, s), 2.46 (1H, d, J = 16.1 Hz), 2.85 (1H, d, J = 16.1 Hz), 3.29 (3H, s), 3.30 (3H, s), 3.40 (3H, s), 3.41 (3H, s), 4.00 (1H, s), 4.46 (1H, s).

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SCHEME 6. Synthesis of Diene 13a from 12a, via a *t*BuLi-Induced *δ*-Elimination

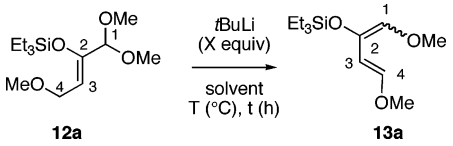


TABLE 2. Yields of the Synthesis of Dienes 13a from 12a via a *t*BuLi−Induced *δ*-Elimination

entry	solvent	*X* equiv	*T* (°C)	*t* (h)	conversion (%)	(1*E*,3*E*)/(1*Z*,3*E*)
1	THF	1	−78	1	0	
2	THF	1.5	−78	1	25	50:50
3	THF	3	−78	1	70	50:50
4	THF	3	−78	2	90	50:50
5	THF	3	−40	1	98	50:50
6	Et_2O	3	−40	1	*a*	
7	DME	3	−40	1	5	50:50
8	Toluene	3	−40	1	0	
9	Pentane	3	−40	1	0	

[a] Degradation of the starting material.

the formation of the expected diene. Actually, 25% of **13a** was formed using 1.5 equiv of *t*BuLi at −78 °C after 1 h (entry 2) and 70% with 3 equiv of the same base in similar conditions (entry 3). Increasing the time of the reaction (entry 4) or the temperature (entry 5) was efficient: 90% of **13a** was recovered by reacting **12a** with 3 equiv of the same base for 2 h at −78 °C in THF (entry 4), and an almost complete conversion (98%) of the enoxysilane into **13a** was observed after 1 h at −40 °C, still in THF and with 3 equiv of *t*BuLi (entry 5). Only two isomers of the expected dienes were formed in all cases and in an equivalent ratio. The configuration of these two species is discussed later. The influence of the solvent on the stereocontrol and the reactivity was examined next. Dimethoxymethyl ether (DME) was shown to be the only other solvent in which the formation of **13a** could proceed, but in a much lower yield and without any modification of the selectivity (entry 7). A complete degradation was observed in diethyl ether (entry 6), while no reaction occurred at all in toluene (entry 8) or pentane (entry 9). The influence of TMEDA, LiBr, or HMPA was also evaluated, but the results mentioned above were unchanged. This preliminary study suggested that the use of 3 equiv of *tert*-butyllithium in THF at −40 °C for 1 h was the best compromise in terms of yields and stereocontrol. These latter conditions were thus retained to extend the *δ*-elimination to the enoxysilanes **12b**−**h** (Scheme 7, Table 3). The experimental conditions optimized on **12a** and applied on **12b**−**h** were shown to be relatively general as all the enoxysilanes were almost quantitatively transformed into the corresponding dienes **13**. Comparing entries 1−3 to 4−8 suggests that R^4 has little if any influence on the reactivity and stereoselectivity of the *δ*-elimination. In contrast, increasing the bulkiness of the silyloxy group results in favoring one isomer, and excesses up to 74% were attained with the *tert*-butyldiphenylsilyloxy group (entries 3 and 7). The other isomer could be also formed with excess up to 74%, from a hindered acetal (entry 8). It is thus possible to synthesize at will one or the other of the two possible stereoisomers of **13**, simply swapping a bulky group for another on the precursor **12**.

SCHEME 7. Synthesis of 13a−h, via a *δ*-Elimination, from 12a−h

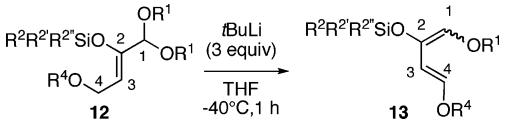


TABLE 3. Yields of the Synthesis of 13a−h, via a *δ*-Elimination, from 12a−h

entry	**12**	R^1	R^4	R^2	$R^{2'}$	$R^{2''}$	**13**	conversion (%)	(1*E*,3*E*)/(1*Z*,3*E*)
1	**12a**	Me	Me	Et	Et	Et	**13a**	98	50:50
2	**12b**	Me	Me	*i*Bu	*i*Bu	*i*Bu	**13b**	99	60:40
3	**12c**	Me	Me	Ph	Ph	*t*Bu	**13c**	91	87:13[a]
4	**12d**	Me	Et	Et	Et	Et	**13d**	98	50:50
5	**12e**	Me	Et	Me	Me	*t*Bu	**13e**	91	60:40
6	**12f**	Me	Et	*i*Pr	*i*Pr	*i*Pr	**13f**	91	75:25
7	**12g**	Me	Et	Ph	Ph	*t*Bu	**13g**	98	87:13
8	**12h**	$CHEt_2$	Et	Et	Et	Et	**13h**	95	13:87

[a] Ratio determined after [4 + 2] cycloaddition with *N*-methylmaleimide **26**.

To determine the stereochemistry of the two isomers, we measured the chemical shifts and the H^3-H^4 coupling constant (J_{H3-H4}) and compared these values to those reported in the literature.[7,8] The three isomers of the 1,2,4-trioxygenated diene

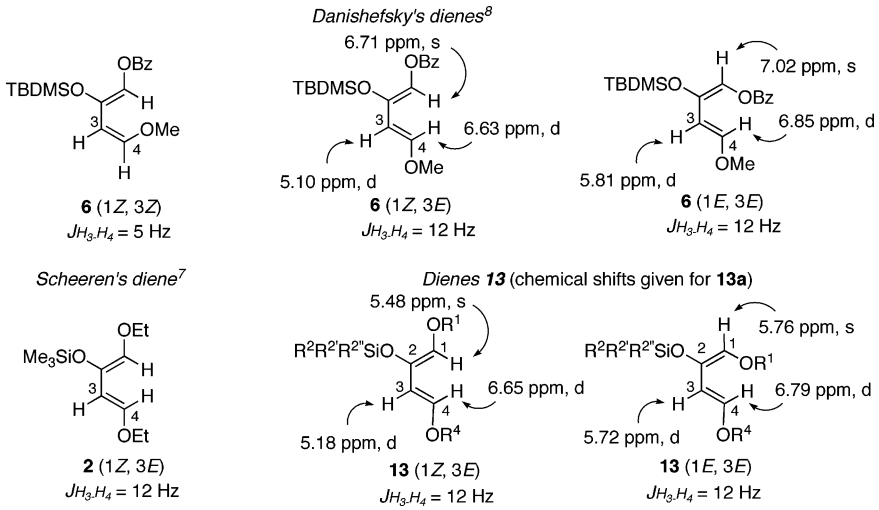
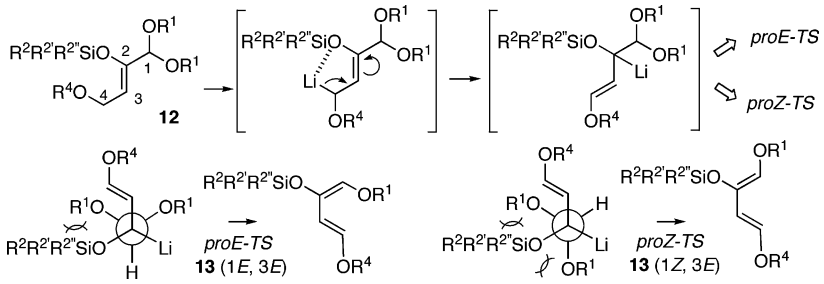


FIGURE 3. Coupling constants and chemical shifts of dienes **6**, **2**, and **13**.

SCHEME 8. Proposed Model To Explain the (1*E*,3*E*) and (1*Z*,3*E*) Configurations of Dienes 13



6 isolated by Danishefsky were shown to be (1*Z*,3*Z*), (1*Z*,3*E*), and (1*E*,3*E*) (Figure 3). The difference between the 3*E* and the 3*Z* configuration translates into J_{H3-H4}, which is worth ~5 Hz and ~12 Hz, respectively. Similarly, the 3*E* configuration determined in Scheeren's diene **2** corresponds to a similar J_{H3-H4} value (12 Hz). As all dienes **13** isolated above exhibit a J_{H3-H4} = 12 Hz, we assumed that the δ-elimination conducted from the enoxysilanes **12** led to the two isomers (1*Z*,3*E*) and (1*E*,3*E*) (Figure 3). Each isomer was then identified by comparing the chemical shifts to those given by Danishefsky (Figure 3), and all of the above attributions were further supported by a series of bidimensional NOESY NMR experiments.

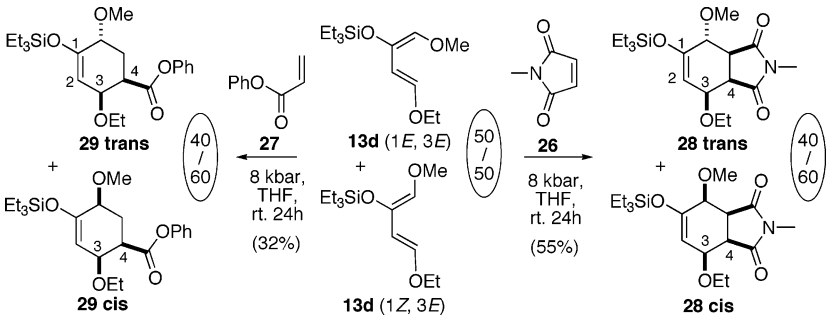
The 3*E* stereoselectivity can be rationalized considering an intramolecular coordination between the lithium atom and the oxygen of the silyloxy group (Scheme 8). This preference for the *E* configuration is in sharp contrast to the *Z* selectivity observed with allylic ethers in previous cases.[11] In the present case, the consecutive elimination of the methoxy group would involve an allylic α-silyloxy-lithiated intermediate, which could evolve through two transition states (*proE-TS*, *proZ-TS*). These later would be more or less isoenergetic for **13a**, **13b**, and **13d** since both isomers were isolated in 50:50 ratios. When increasing the bulkiness of the trialkylsilyloxy part, the isomer (1*E*,3*E*) became predominant. This suggests that the *proE-TS* would be favored by the steric constraint, provided the β-elimination takes place in a pure "anti" fashion. Indeed, as shown on the Newman projections placing one methoxy group anti to the lithium (Scheme 8), only one steric strain shows around the silyloxy group in the *proE-TS* against two in the *proZ-TS*. In contrast, the use of a bulky acetal enhances the proportion of the (1*Z*,3*E*) isomer. This preference is more difficult to justify on the basis of the simple unsolvated model below.

Cycloaddition of 13 with *N*-Methylmaleimide and Acrylates. The 1,2,4-trioxygenated-1,3-dienes **2** and **6** have been essentially used in heterocycloaddition toward activated aldehydes in the presence of mild Lewis acids.[7,8] Nevertheless, a few applications of these reagents in homo-Diels−Alder reactions have been reported, with a total regio- and endoselectivity.[6a,c,17] The relative reactivity of the dienes **13** has thus been evaluated in a set of [4 + 2] cycloadditions involving *N*-methylmaleimide and methyl- and phenylacrylates as dienophiles. The favorable effect of high pressure on the reactions described with 1,4-dialkoxy 1,3-dienes **11** with respect to classical thermal or Lewis acid activations[11] prompted us to conduct these cycloadditions under 8 to 16 kbar, at room temperature and for 24 h. The preliminary thermal experiments run with these dienes were not pursued because of their tendency to polymerize in these conditions.

The hyperbaric cycloaddition of the equimolar ratio of both isomers of **13d** with *N*-methylmaleimide **26** and phenyl acrylate **27** led to the expected cycloadducts **28** (55% overall yield) and **29** (32% overall yields), respectively (Scheme 9).

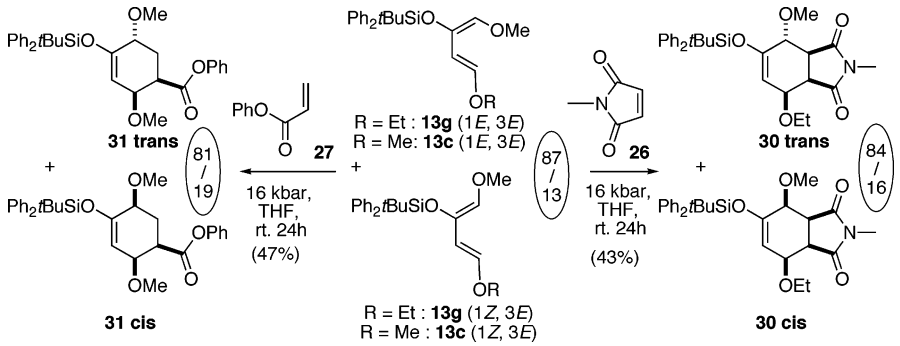
Each cycloaddition mainly led to two cycloadducts (*trans*, *cis*) that were separated by flash chromatography and isolated in an almost 50:50 ratio. The exact configurations and conformations of each adduct have been determined on account of mono- and bidimensional NMR studies. All cycloadducts were thus shown to derive from an *endo* approach since the main isomers presented a *syn* configuration between their C^3 and C^4 substituents (Scheme 9). This stereoselectivity is in fine agreement with comparable situations.[11,12] Adducts **29** correspond to half-chair conformations, while adducts **28** preferably adopt a convex boat-type folding. The preference of such flexible systems for convex conformation has been discussed in the literature for comparable systems.[18] The access to **29** pointed out the regiodirectivity related to dienes **13**. Both isomers **29 trans** and **29 cis** indeed place the silyloxy group and the phenyloxycarbonyl group in a 1−4 position on the cyclohexenyl moiety. Note that the presence of about 15% of the *exo* isomer was also noticed in this case. Close results were obtained with

SCHEME 9. [4 + 2] Cycloadditions of 13d with *N*-Methylmaleimide 26 and Phenyl Acrylate 27



methyl acrylate but in much lower overall yields (20%,

SCHEME 10. [4 + 2] Cycloadditions of 13c and 13g with *N*-Methylmaleimide 26 and Phenyl Acrylate 27



trans/*cis* = 60:40), probably because of the polymerization of this dienophile, which occurs very easily under hyperbaric conditions.[19]

Reacting *N*-methylmaleimide with **13g** and phenyl acrylate with **13c** transformed the mixtures of isomers of these two dienes into the corresponding *endo* cycloadducts **30** (43% overall yield) and **31** (47% overall yield), respectively. Interestingly, the *trans* and *cis* cycloadducts were formed in a 84:16 ratio for **30** and 81:19 ratio for **31** (Scheme 10). The resemblance of this latter values with the 87:13 ratio between the (1*E*,3*E*) and (1*Z*,3*E*) isomers of **13g** and **13c** suggests that these two compounds react at comparable rates. We can even generalize saying that isomers **13** (1*E*,3*E*) are the precursors of the adducts *trans* while **13** (1*Z*,3*E*) provides the *cis* cycloadducts.

Here again, all compounds could be perfectly characterized by NMR. The *endo* selectivity and convex boat-type folding were evidenced for adducts **30**. The *trans* relationship between the methoxy and ethoxy groups, imposed by the (1*E*,3*E*) configuration of the **13g** isomer, put the methoxy in an equatorial position and the ethoxy in an axial one, and could be confirmed in the case of **30 trans** by a single-crystal X-ray analysis (Figure 4). Complementarily, the regioselectivity of **13** was proven thanks to a second single-crystal X-ray analysis conducted on **31 trans** (Figure 4).

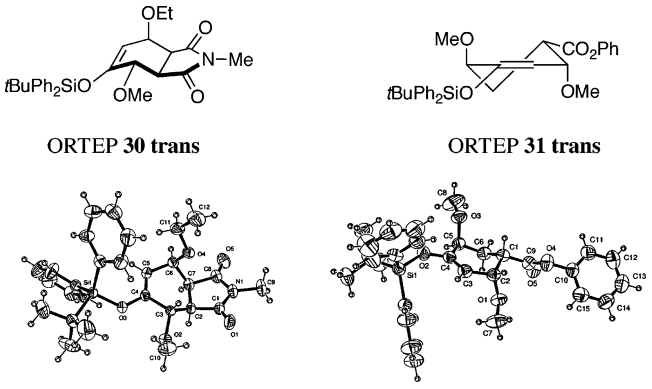


FIGURE 4. Single-crystal X-ray analyses of **30 trans** and **31 trans**.

(17) Tietze, L. F.; Günter, C.; Gericke, K. M.; Schuberth, I.; Bukoczi, G. *Eur. J. Org. Chem.* **2005**, 2459−2467.

(18) Maddaluno, J.; Gaonac'h, O.; Marcual, A.; Toupet, L., Giessner-Prettre, C. *J. Org. Chem.* **1996**, *61*, 5290−5306.

(19) The use of hydroquinone is usually required to avoid the polymerization of methyl acrylate when using hyperbaric activation. This radical inhibitor has not been introduced in our experimental conditions since it reacted with dienes **13**.

Conclusion

These results show that 1,2,4-trioxygenated 1,3-dienes can be prepared from commercially available pyruvic aldehyde dimethyl acetal **14a** in four synthetic steps and with overall yields in the 4−72% range. Reacting **14a** with cyclohexylamine and then chloroalkyl ethers under basic conditions led to ketoacetals **18** to **20**, which were treated by LiHMDS and then chlorotrialkylsilanes to afford eight enoxysilanes **12**. δ-Eliminations prompted on **12** by *tert*-butyllithium gave the expected 1,2,4-trioxygenated 1,3-dienes **13**. These latter transformations were performed in quantitative yields and led to two isomers ((1*Z*,3*E*) and (1*E*,3*E*)) on the four possible ones. Stereoselective approaches favoring either **13** (1*Z*,3*E*) or **13** (1*E*,3*E*) were finally worked out. While bulky trialkylsilyloxy substituent increase the proportion of dienes (1*E*,3*E*), bulky acetals rather provide dienes (1*Z*,3*E*). Three dienes (**13c**, **13d**, and **13g**) were reacted with *N*-methylmaleimide and acrylates (phenyl, methyl) at room temperature, for 24 h in THF and under hyperbaric conditions. They all gave the corresponding *endo* cycloadducts, the (1*E*,3*E*) and (1*Z*,3*E*) isomers reacting in comparable rates. The regioselectivity of the reaction could be evidenced using the acrylates as dienophiles.

Experimental Section

1,1-Bis(1-ethylpropyloxy)propan-2-one 14b. Pentan-3-ol (10.1 mL, 93.4 mmol, 2.2 equiv) was added, in a Dean−Stark apparatus, to a mixture of pyruvic aldehyde dimethyl acetal **14a** (5 g, 42.3 mmol, 1 equiv) and *p*-toluenesulfonic acid monohydrate (0.08 g, 0.42 mmol, 0.01 equiv) in cyclohexane (50 mL). The resulting reaction mixture was stirred at 81 °C for 24 h and then cooled to room temperature. After evaporation of the solvent and then dilution with diethyl ether (20 mL), the organic layer was washed with a 0.1 M solution of NaOH (20 mL). The aqueous layer was twice extracted with diethyl ether (2 × 20 mL), and the combined organics were dried ($MgSO_4$), filtered, and concentrated. Purification of the residue by flash chromatography on silica (heptane/AcOEt 90:10) gave **14b** as a yellow oil (2.68 g, 27%): IR (neat) ν 1729, 1462, 1351, 1103, 1010 cm^{-1}; EIMS (70 eV) *m*/*z* 230 (M^+, <1), 217 (100), 187 (M^+ − MeC═O, 10), 143 (M^+ − $OCH(Et)_2$, 17), 87 ($[OCH(Et)_2]^+$, 64), 71 ($[CH(Et)_2]^+$, 81); ^1H NMR (300 MHz) δ 0.73 (6H, t, J = 7.2), 0.83 (6H, t, J = 7.2), 1.33−1.51 (8H, m), 2.07 (3H, s), 3.31 (1H, t, J = 5.8), 3.34 (1H, t, J = 5.8), 4.39 (1H, s); ^{13}C NMR (75 MHz) δ 9.2, 9.7, 23.2, 26.1, 26.5, 80.3, 102.2, 204.9. Anal. Calcd for $C_{13}H_{26}O_3$: C, 67.79; H, 11.38. Found: C, 67.53; H, 11.67.

Cyclohexyl(2,2-dimethoxy-1-methylethylidene)amine 15a. Pyruvic aldehyde dimethyl acetal **14a** (10 g, 84.6 mmol, 1 equiv) was added to a mixture of cyclohexylamine (11 mL, 96.1 mmol, 1.1 equiv) and calcium chloride (500 mg) in diethyl ether (50 mL). The resulting reaction mixture was stirred at 45 °C for 16 h. After

the mixture was cooled to room temperature, the solvent was evaporated to give **15a** as a yellow oil (15.54 g, 92%): IR (neat) ν 1667, 1447, 1358, 1070 cm^{-1}; CI (NH_3) *m*/*z* 200 (MH^+, 100); ^{1}H NMR (200 MHz) δ 1.19−1.78 (10H, m), 1.78 (3H, s), 3.34 (6H, s), 3.22−3.37 (1H, m), 4.38 (1H, s); ^{13}C NMR (75 MHz) δ 11.7, 25.1, 25.9, 33.6, 55.2, 59.4, 109.2, 164.0.

2,2-Bis(1-ethylpropyloxy)-1-methylethylidenecyclohexylamine 15b. 1,1-Bis(1-ethylpropyloxy)propan-2-one **14b** (1 g, 4.34 mmol, 1equiv) was added, in a Dean−Stark apparatus, to a mixture of cyclohexylamine (496 μL, 4.34 mmol, 1 equiv) and calcium chloride (50 mg) in toluene (5 mL). The resulting reaction mixture was stirred at 110 °C for 24 h. After the mixture was cooled to room temperature, the solvent was evaporated to give **15b** as a yellow oil (759 mg, 56%): IR (neat) ν 1668, 1461, 1328, 1105, 1008 cm^{-1}; CI (NH_3) *m*/*z* 312 (MH^+, 100); ^{1}H NMR (200 MHz) δ 0.81 (6H, t, J = 7.3), 0.91 (6H, t, J = 7.3), 1.24−1.83 (18H, m), 1.87 (3H, s), 3.23−3.45 (3H, m), 4.64 (1H, s); ^{13}C NMR (50 MHz) δ 9.8, 10.0, 11.9, 25.3, 26.0, 26.3, 26.7, 33.5, 59.1, 79.3, 105.5, 166.0.

1,1,4-Trimethoxybutan-2-one 18. *n*BuLi 2.4 M (4.6 mL, 11.04 mmol, 1.1 equiv) was added at −78 °C to a solution of diisopropylamine (1.70 mL, 12.1 mmol, 1.2 equiv) in freshly distilled THF (10 mL). After 30 min of stirring at this temperature, a solution of 2,2-dimethoxy-1-methylethylidenecyclohexylamine **15a** (2 g, 10.03 mmol, 1 equiv) in dry THF (5 mL) was introduced, followed, after an additional 2 h of stirring at −78 °C, by a solution of chloromethyl methyl ether **16** (1.14 mL, 15.0 mmol, 1.5 equiv) in dry THF (2 mL). The resulting reaction mixture was stirred at room temperature for 24 h before the reaction was quenched by the addition of a saturated solution of $NaHCO_3$ (10 mL). The aqueous layer was extracted with diethyl ether (2 × 10 mL), and the combined organics were dried ($MgSO_4$), filtered, and concentrated. Purification of the residue by flash chromatography (heptane/AcOEt 70:30) gave **18** as a yellow oil (1.29 g, 79%): IR (neat) ν 1731, 1450, 1389, 1193, 1073 cm^{-1}; EIMS (70 eV) *m*/*z* 162 (M^+, <1), 131 (M^+ − OMe, 28), 75 ($[CH(OMe)_2]^+$, 100); ^{1}H NMR (300 MHz) δ 2.81 (2H, t, J = 6.4), 3.33 (3H, s), 3.41 (6H, s), 3.66 (2H, t, J = 6.4), 4.49 (1H, s); ^{13}C NMR (75 MHz) δ 37.7, 54.7, 58.8, 67.0, 104.0, 203.9. Anal. Calcd for $C_7H_{14}O_4$: C, 51.84; H, 8.70. Found: C, 51.88; H, 8.92.

4-Ethoxy-1,1-dimethoxybutan-2-one 19. *n*BuLi 2.25 M (12.3 mL, 27.7 mmol, 1.1 equiv) was added at −78 °C to a solution of diisopropylamine (4.26 mL, 30.4 mmol, 1.2 equiv) in freshly distilled THF (20 mL). After 30 min of stirring at this temperature, a solution of 2,2-dimethoxy-1-methylethylidenecyclohexylamine **15a** (5 g, 25.1 mmol, 1 equiv) in dry THF (10 mL) was introduced, followed, after an additional 2 h of stirring at −78 °C, by a solution of chloromethyl ethyl ether **17** (3.49 mL, 37.6 mmol, 1.5 equiv) in dry THF (5 mL). The resulting reaction mixture was stirred at room temperature for 24 h before the reaction was quenched by the addition of a saturated solution of $NaHCO_3$ (20 mL). The aqueous layer was extracted with diethyl ether (2 × 20 mL), and the combined organics were dried ($MgSO_4$), filtered, and concentrated. Purification of the residue by flash chromatography (heptane/AcOEt 70:30) gave **19** as a yellow oil (2.5 g, 56%): IR (neat) ν 1731, 1445, 1379, 1105, 1072 cm^{-1}; CI (NH_3) *m*/*z* 194 ($MH^+ + NH_3$, 100), 177 (MH^+, 25); ^{1}H NMR (300 MHz) δ 1.14 (3H, t, J = 7.1), 2.80 (2H, t, J = 6.4), 3.38 (6H, s), 3.45 (2H, q, J = 7.1), 3.68 (2H, t, J = 6.4), 4.49 (1H, s); ^{13}C NMR (75 MHz) δ 15.4, 38.3, 54.9, 65.1, 66.7, 104.1, 204.3. Anal. Calcd for $C_8H_{16}O_4$: C, 54.53; H, 9.15. Found: C, 54.62; H, 9.41.

4-Ethoxy-1,1-bis(1-ethylpropyloxy)butan-2-one 20. 4-Ethoxy-1,1-dimethoxybutan-2-one **19** (0.5 g, 2.84 mmol, 1 equiv) was added, in a Dean−Stark apparatus, to a mixture of pentan-3-ol (645 μL, 5.96 mmol, 2.1 equiv) and *p*-toluenesulfonic acid monohydrate (6 mg, 0.03 mmol, 0.01 equiv) in cyclohexane (20 mL). The resulting reaction mixture was stirred at 81 °C for 24 h and then cooled to room temperature. After evaporation of the solvent, the residue was dissolved in diethyl ether (10 mL) and washed with a 0.1 M solution of NaOH (5 mL). The aqueous layer was twice extracted with diethyl ether (2 × 5 mL), and the combined organics were dried ($MgSO_4$), filtered, and concentrated. Purification of the residue by flash chromatography on silica (heptane/AcOEt 90:10) gave **20** as a yellow oil (165 mg, 20%): IR (neat) ν 1728, 1463, 1379, 1104, 1021 cm^{-1}; EIMS (70 eV) *m*/*z* 288 (M^+, <1), 201 (M^+ − $OCH(Et)_2$, 25), 71 ($[CH(Et)_2]^+$, 100); ^{1}H NMR (300 MHz) δ 0.82 (6H, t, J = 7.5), 0.92 (6H, t, J = 7.5), 1.17 (3H, t, J = 7.1), 1.42−1.59 (8H, m), 2.93 (2H, t, J = 6.8), 3.41−3.52 (4H, m), 3.70 (2H, t, J = 6.8), 4.54 (1H, s); ^{13}C NMR (75 MHz) δ 9.4, 9.9, 15.4, 26.1, 26.5, 36.3, 65.3, 66.5, 80.4, 101.9, 205.2. Anal. Calcd for $C_{16}H_{32}O_4$: C, 66.63; H, 11.18. Found: C, 66.68; H, 11.52.

1,1,4-Trimethoxy-2-triethylsilyloxybut-2-ene 12a. *n*BuLi 2.1 M (3.23 mL, 6.78 mmol, 1.1 equiv) was added at −78 °C to a solution of hexamethyldisilazane (1.55 mL, 7.34 mmol, 1.2 equiv) in freshly distilled THF (5 mL). After 30 min of stirring at this temperature, chlorotriethylsilane **21** (1.03 mL, 6.13 mmol, 0.99 equiv) was introduced, followed by a solution of 1,1,4-trimethoxybutan-2-one **18** (1 g, 6.16 mmol, 1 equiv) in dry THF (1 mL). The resulting reaction mixture was stirred at −78 °C for 2 h and then at room temperature for 2 h before the reaction was quenched by the addition of a 0.1 M solution of NaOH (5 mL). The aqueous layer was extracted with diethyl ether (2 × 10 mL), and the combined organics were dried ($MgSO_4$), filtered, and concentrated to give **12a** as a yellow oil (1.7 g, 99%), which could be purified by flash chromatography on silica (cyclohexane/AcOEt 80:20): IR (neat) ν 1675, 1458, 1198, 1114 cm^{-1}; CI (NH_3) *m*/*z* 294 ($MH^+ + NH_3$, 35), 277 (MH^+, 5), 262 (MH^+ − Me, 95), 245 (MH^+ − MeOH, 100); ^{1}H NMR (300 MHz) δ 0.67 (6H, q, J = 8.0), 0.96 (9H, t, J = 8.0), 3.30 (3H, s), 3.31 (6H, s), 4.02 (2H, d, J = 6.9), 4.50 (1H, s), 5.11 (1H, t, J = 6.9); ^{13}C NMR (75 MHz) δ 5.7, 7.0, 53.8, 58.1, 66.6, 102.8, 107.5, 148.4. Anal. Calcd for $C_{13}H_{28}O_4Si$: C, 56.48; H, 10.21. Found: C, 56.65; H, 10.46.

1,1,4-Trimethoxy-2-triisobutylsilyloxybut-2-ene 12b. *n*BuLi 2.2 M (925 μL, 2.03 mmol, 1.1 equiv) was added at −78 °C to a solution of hexamethyldisilazane (465 μL, 2.2 mmol, 1.2 equiv) in freshly distilled THF (5 mL). After 30 min of stirring at this temperature, chlorotriisobutylsilane **22** (495 μL, 1.84 mmol, 0.99 equiv) was introduced, followed by a solution of 1,1,4-trimethoxybutan-2-one **18** (0.3 g, 1.85 mmol, 1 equiv) in dry THF (2 mL). The resulting reaction mixture was stirred at −78 °C for 2 h and then at room temperature for 2 h before the reaction was quenched by the addition of a 0.1 M solution of NaOH (5 mL). The aqueous layer was extracted with diethyl ether (2 × 10 mL), and the combined organics were dried ($MgSO_4$), filtered, and concentrated to give **12b** as a yellow oil (0.25 g, 37%), which may be purified by flash chromatography on silica (cyclohexane/AcOEt 80:20): IR (neat) ν 1674, 1464, 1363, 1218, 1088 cm^{-1}; EIMS (70 eV) *m*/*z* 360 (MH^+, <1), 161 (MH^+ − $Si(iBu)_3$, 41), 75 ($[CH(OMe)_2]^+$, 100); ^{1}H NMR (300 MHz) δ 0.71 (6H, d, J = 6.8), 0.95 (18H, d, J = 6.4), 1.79−1.93 (3H, m), 3.31 (3H, s), 3.32 (6H, s), 4.03 (2H, d, J = 6.6), 4.52 (1H, s), 5.11 (1H, t, J = 6.6); ^{13}C NMR (75 MHz) δ 24.4, 26.6, 26.8, 53.7, 58.1, 66.8, 102.6, 107.1, 148.1. Anal. Calcd for $C_{19}H_{40}O_4Si$: C, 63.28; H, 11.18. Found: C, 63.34; H, 11.29.

2-(*tert*-Butyldiphenylsilyloxy)-1,1,4-trimethoxybut-2-ene 12c. *n*BuLi 2.25 M (1.5 mL, 3.37 mmol, 1.1 equiv) was added at −78 °C to a mixture of hexamethyldisilazane (775 μL, 3.67 mmol, 1.2 equiv) and HMPA (1 mL) in freshly distilled THF (5 mL). After 30 min of stirring at this temperature, *tert*-butylchlorodiphenylsilane **23** (800 μL, 3.08 mmol, 1 equiv) was introduced, followed by a solution of 1,1,4-trimethoxybutan-2-one **18** (0.5 g, 3.08 mmol, 1 equiv) in dry THF (1 mL). The resulting reaction mixture was stirred at −78 °C for 2 h and then at room temperature for 2 h before the reaction was quenched by the addition of a 0.1 M solution of NaOH (5 mL). The aqueous layer was extracted with diethyl ether (2 × 10 mL), and the combined organics were dried ($MgSO_4$), filtered, and concentrated. The residue was purified by flash chromatography on silica (heptane/AcOEt 90:10) to give **12c** as a pale yellow oil

(0.419 g, 34%): IR (neat) ν 1677, 1427, 1195, 1112 cm^{-1}; EIMS (70 eV) *m/z* 400 (MH$^+$, <1), 199 (100), 183 (Ph_2SiH^+, 63), 167 (86), 145 ([MeOCH2CH=C(CH(OMe)$_2$]$^+$, 75), 75 ([CH(OMe)$_2$]$^+$, 36), 57 (*t*Bu$^+$, 67); ^{1}H NMR (300 MHz) δ 1.08 (9H, s), 3.02 (6H, s), 3.20 (3H, m), 3.96 (2H, d, J = 6.8), 4.30 (1H, s), 5.17 (1H, t, J = 6.8), 7.36−7.44 (6H, m), 7.71−7.75 (4H, m); ^{13}C NMR (75 MHz) δ 26.9, 53.8, 58.0, 66.8, 102.2, 106.9, 127.9, 130.1, 133.6, 135.1, 135.8, 148.2. Anal. Calcd for $C_{23}H_{32}O_4Si$: C, 68.96; H, 8.05. Found: C, 69.41; H, 8.13.

4-Ethoxy-1,1-dimethoxy-2-triethylsilyloxybut-2-ene 12d. *n*BuLi 2.1 M (2.97 mL, 6.24 mmol, 1.1 equiv) was added at −78 °C to a solution of hexamethyldisilazane (1.43 mL, 6.78 mmol, 1.2 equiv) in freshly distilled THF (10 mL). After 30 min of stirring at this temperature, chlorotriethylsilane **21** (1.03 mL, 6.14 mmol, 1.1 equiv) was introduced, followed by a solution of 4-ethoxy-1,1-dimethoxybutan-2-one **19** (1 g, 5.67 mmol, 1 equiv) in dry THF (5 mL). The resulting reaction mixture was stirred at −78 °C for 2 h and then at room temperature for 2 h before the reaction was quenched by the addition of a 0.1 M solution of NaOH (5 mL). The aqueous layer was extracted with diethyl ether (2 × 10 mL) and the combined organics were dried ($MgSO_4$), filtered, and concentrated to give **12d** as a yellow oil (1.63 g, 99%): IR (neat) ν 1675, 1458, 1198, 1114 cm^{-1}; CI (NH_3) *m/z* 308 (MH$^+$ + NH_3, 88), 276 (MH$^+$ − Me, 100), 259 (MH$^+$ − MeOH, 77); ^{1}H NMR (300 MHz) δ 0.68 (6H, q, J = 7.5), 0.98 (9H, t, J = 7.5), 1.19 (3H, t, J = 7.2), 3.32 (6H, s), 3.46 (2H, q, J = 7.2), 4.07 (2H, d, J = 6.8), 4.51 (1H, s), 5.13 (1H, t, J = 6.8); ^{13}C NMR (75 MHz) δ 5.7, 7.0, 15.6, 53.8, 64.8, 65.7, 102.9, 108.0, 148.0.

2-(*tert*-Butyldimethylsilyloxy)-4-ethoxy-1,1-dimethoxybut-2-ene 12e. *n*BuLi 2.25 M (416 μL, 0.94 mmol, 1.1 equiv) was added at −78 °C to a mixture of hexamethyldisilazane (214 μL, 1.01 mmol, 1.3 equiv) and HMPA (0.8 mL) in freshly distilled THF (3 mL). After 30 min of stirring at this temperature, *tert*-butylchlorodimethylsilane **24** (128 mg, 0.85 mmol, 1 equiv) was introduced, followed by a solution of 4-ethoxy-1,1-dimethoxybutan-2-one **19** (0.15 g, 0.85 mmol, 1 equiv) in dry THF (1 mL). The resulting reaction mixture was stirred at −78 °C for 2 h and then at room temperature for 2 h before the reaction was quenched by the addition of a 0.1 M solution of NaOH (5 mL). The aqueous layer was extracted with diethyl ether (2 × 10 mL), and the combined organics were dried ($MgSO_4$), filtered, and concentrated. The residue was purified by flash chromatography on silica (heptane/AcOEt 90:10) to give **12e** as a yellow oil (0.106 g, 43%): IR (neat) ν 1677, 1471, 1252, 1112 cm^{-1}; EIMS (70 eV) *m/z* 290 (M$^+$, <1), 259 (M$^+$ − OMe, 7), 245 (M$^+$ − OEt, 15), 75 ([CH(OMe)$_2$]$^+$, 75), 59 ([CH_2OEt]$^+$, 100); ^{1}H NMR (300 MHz) δ 0.14 (6H, s), 0.94 (9H, s), 1.19 (3H, t, J = 7.2), 3.30 (6H, s), 3.46 (2H, q, J = 7.2), 4.07 (2H, d, J = 6.8), 4.52 (1H, s), 5.16 (1H, t, J = 6.8); ^{13}C NMR (75 MHz) δ 15.6, 18.8, 26.1, 53.5, 64.8, 65.7, 102.4, 108.1, 147.9.

4-Ethoxy-1,1-dimethoxy-2-triisopropylsilyloxybut-2-ene 12f. *n*BuLi 2.25 M (416 μL, 0.94 mmol, 1.1 equiv) was added at −78 °C to a mixture of hexamethyldisilazane (214 μL, 1.01 mmol, 1.2 equiv) and HMPA (0.8 mL) in freshly distilled THF (3 mL). After 30 min of stirring at this temperature, chlorotriisopropylsilane **25** (180 μL, 0.84 mmol, 0.99 equiv) was introduced, followed by a solution of 4-ethoxy-1,1-dimethoxybutan-2-one **19** (0.15 g, 0.85 mmol, 1 equiv) in dry THF (1 mL). The resulting reaction mixture was stirred at −78 °C for 2 h then at room temperature for 2 h before the reaction was quenched by the addition of a 0.1 M solution of NaOH (5 mL). The aqueous layer was extracted with diethyl ether (2 × 10 mL), and the combined organics were dried ($MgSO_4$), filtered, and concentrated. The residue was purified by flash chromatography on silica (heptane/AcOEt 90:10) to give **12f** as a yellow oil (0.185 g, 65%): IR (neat) ν 1673, 1464, 1383, 1196, 1113 cm^{-1}; EIMS (70 eV) *m/z* 332 (M$^+$, 1), 301 (M$^+$ − OMe, 5), 289 (MH$^+$ − *i*Pr, 35), 201 (100), 75 ([CH(OMe)$_2$]$^+$, 80), 59 ([CH_2OEt]$^+$, 75); ^{1}H NMR (300 MHz) δ 1.04−1.21 (24H, m), 3.30 (6H, s), 3.46 (2H, q, J = 7.2), 4.12 (2H, d, J = 6.0), 4.58 (1H, s), 5.15 (1H, t, J = 6.0); ^{13}C NMR (75 MHz) δ 13.7, 15.6, 18.3, 53.3, 65.0, 65.7, 102.3, 107.4, 147.8.

2-(*tert*-Butyldiphenylsilyloxy)-4-ethoxy-1,1-dimethoxybut-2-ene 12g. *n*BuLi 2.25 M (333 μL, 0.75 mmol, 1.1 equiv) was added at −78 °C to a mixture of hexamethyldisilazane (171 μL, 0.81 mmol, 1.2 equiv) and HMPA (1 mL) in freshly distilled THF (5 mL). After 30 min of stirring at this temperature, *tert*-butylchlorodiphenylsilane **23** (177 μL, 0.68 mmol, 1 equiv) was introduced, followed by a solution of 4-ethoxy-1,1-dimethoxybutan-2-one **19** (120 mg, 0.68 mmol, 1 equiv) in dry THF (1 mL). The resulting reaction mixture was stirred at −78 °C for 2 h then at room temperature for 2 h before the reaction was quenched by the addition of a 0.1M solution of NaOH (5 mL). The aqueous layer was extracted with diethyl ether (2 × 10 mL), and the combined organics were dried ($MgSO_4$), filtered and concentrated. The residue was purified by flash chromatography on silica (heptane/AcOEt 90:10) to give **12g** as a yellow oil (0.147 g, 52%): IR (neat) ν 1677, 1427, 1195, 1112 cm^{-1}; EIMS (70 eV) *m/z* 414 (M$^+$, <1), 357 (M$^+$ − *t*Bu, 6), 183 (100), 75 ([CH(OMe)$_2$]$^+$, 43), 57 (*t*Bu$^+$, 87); ^{1}H NMR (300 MHz) δ 1.07 (9H, s), 1.12 (3H, t, J = 7.2), 3.01 (6H, s), 3.32 (2H, q, J = 7.2), 3.99 (2H, d, J = 6.8), 4.29 (1H, s), 5.17 (1H, t, J = 6.8), 7.37−7.43 (6H, m), 7.70−7.72 (4H, m); ^{13}C NMR (75 MHz) δ 15.6, 20.1, 27.0, 53.8, 65.1, 65.7, 102.3, 107.5, 127.8, 130.1, 133.7, 135.9, 147.7.

4-Ethoxy-1-[bis(1-ethylpropyloxy)]-2-triethylsilyloxybut-2-ene 12h. *n*BuLi 3.00 M (210 μL, 0.63 mmol, 1.8 equiv) was added at −78 °C to a solution of hexamethyldisilazane (142 μL, 0.67 mmol, 1.9 equiv) in freshly distilled THF (5 mL). After 30 min of stirring at this temperature, chlorotriethylsilane **21** (95 μL, 0.56 mmol, 1.6 equiv) was introduced, followed by a solution of 4-ethoxy-1,1-bis(1-ethylpropyloxy)butan-2-one **20** (100 mg, 0.35 mmol, 1 equiv) in dry THF (1 mL). The resulting reaction mixture was stirred at −78 °C for 2 h then at room temperature for 2 h before the reaction was quenched by the addition of a 0.1 M solution of NaOH (5 mL). The aqueous layer was extracted with diethyl ether (2 × 10 mL), and the combined organics were dried ($MgSO_4$), filtered, and concentrated to give **12h** as a yellow oil, which did not require any further purification (135 mg, 96%): EIMS (70 eV) *m/z* 402 (M$^+$, <1), 358 (M$^+$ − EtOH, 8), 187 ([CH(OCHEt$_2$)$_2$]$^+$, 21), 87 ([OCHEt$_2$]$^+$, 44), 71 ([CHEt$_2$]$^+$, 100); ^{1}H NMR (200 MHz) δ 0.80−1.00 (27H, m), 1.19 (3H, t, J = 6.9), 1.45−1.56 (8H, m), 3.37−3.51 (4H, m), 4.06 (2H, d, J = 6.6), 4.62 (1H, s), 4.95 (1H, t, J = 6.6); ^{13}C NMR (50 MHz) δ 5.8, 6.1, 6.7, 7.1, 9.6, 9.9, 15.6, 26.0, 26.4, 65.0, 65.5, 78.9, 100.6, 107.7, 146.0.

1,4-Dimethoxy-2-triethylsilyloxy-1,3-butadiene 13a. *t*BuLi 1.5 M (362 μL, 0.54 mmol, 3.0 equiv) was added, at −40 °C and under nitrogen atmosphere, to a solution of 1,1,4-trimethoxy-2-triethylsilyloxybut-2-ene **12a** (50 mg, 0.18 mmol, 1 equiv) in freshly distilled THF (1 mL). The resulting reaction mixture was stirred for 1 h at −40 °C before the reaction was quenched by a 0.1 M solution of NaOH (2 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated to give **13a** as a yellow oil, which was not purified due to its low stability on silica (43 mg, 98%): IR (neat) ν 2956, 2877, 1670, 1463, 1114 cm^{-1}; (isomer 1*E*,3*E*) ^{1}H NMR (300 MHz) δ 0.67−0.73 (6H, m), 0.89−1.01 (9H, m), 3.53 (3H, s), 3.60 (3H, s), 5.72 (1H, d, J = 12.6), 5.76 (1H, s), 6.79 (1H, d, J = 12.6); ^{13}C NMR (75 MHz) *d* 5.2 or 5.6, 7.1 or 7.2, 56.5, 60.5, 97.9, 132.6, 137.3, 148.5; (isomer 1*Z*,3*E*) ^{1}H NMR (300 MHz) δ 0.67−0.73 (6H, m), 0.89−1.01 (9H, m), 3.54 (3H, s), 3.55 (3H, s), 5.18 (1H, d, J = 12.2), 5.48 (1H, s), 6.65 (1H, d, J = 12.2); ^{13}C NMR (75 MHz) δ 5.2 or 5.6, 7.1 or 7.2, 56.8, 59.7, 101.2, 130.8, 133.2, 146.7.

1,4-Dimethoxy-2-triisobutylsilyloxy-1,3-butadiene 13b. *t*BuLi 1.5 M (277 μL, 0.41 mmol, 3.0 equiv) was added, at −40 °C and under nitrogen atmosphere, to a solution of 1,1,4-trimethoxy-2-triisobutylsilyloxybut-2-ene **12b** (50 mg, 0.138 mmol, 1 equiv) in freshly distilled THF (1 mL). The resulting reaction mixture was stirred for 1 h at −40 °C before the reaction was quenched by a 0.1 M solution of NaOH (2 mL). The organic layer was dried

($MgSO_4$), filtered, and concentrated to give **13b** as a yellow oil, which was not purified due to its low stability on silica (45 mg, 99%): IR (neat) ν 1610, 1427, 1210, 1113 cm^{-1}; (isomer 1*E*,3*E*) ^1H NMR (200 MHz) δ 0.70 or 0.71 (6H, d, $J = 6.9$), 0.94 or 0.96 (18H, d, $J = 6.6$), 1.80−1.93 (3H, m), 3.52 (3H, s), 3.60 (3H, s), 5.71 (1H, d, $J = 12.8$), 5.74 (1H, s), 6.79 (1H, d, $J = 12.8$); ^{13}C NMR (50 MHz) δ 24.5, 26.1 or 26.6, 26.8, 56.5, 60.6, 98.0, 132.0, 137.9, 148.7; (isomer 1*Z*,3*E*) ^1H NMR (200 MHz) δ 0.70 or 0.71 (6H, d, $J = 6.9$), 0.94 or 0.96 (18H, d, $J = 6.9$), 1.80−1.93 (3H, m), 3.53 (3H, s), 3.54 (3H, s), 5.15 (1H, d, $J = 12.2$), 5.41 (1H, s), 6.66 (1H, d, $J = 12.2$); ^{13}C NMR (125 MHz) δ 24.5, 26.1 or 26.6, 26.8, 56.8, 59.6, 101.3, 129.6, 133.2, 146.8.

2-*tert*-Butyldiphenylsilyloxy-1,4-dimethoxy-1,3-butadiene 13c. *t*BuLi 1.5 M (277 μL, 0.41 mmol, 3.0 equiv) was added, at −40 °C and under nitrogen atmosphere, to a solution of 2-*tert*-butyldiphenylsilyloxy-1,1,4-trimethoxybut-2-ene **12c** (55 mg, 0.138 mmol, 1 equiv) in freshly distilled THF (1 mL). The resulting reaction mixture was stirred for 1 h at −40 °C before the mixture was quenched by a 0.1 M solution of NaOH (2 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated to give **13c** as a yellow oil, which was not purified due to its low stability on silica (46 mg, 91%). **13c** was not characterized furthermore since it was directly reacted with *N*-methylmaleimide **26**.

4-Ethoxy-1-methoxy-2-triethylsilyloxy-1,3-butadiene 13d. *t*BuLi 1.5 M (344 μL, 0.52 mmol, 3.0 equiv) was added, at −40 °C and under nitrogen atmosphere, to a solution of 4-ethoxy-1,1-dimethoxy-2-triethylsilyloxybut-2-ene **12d** (50 mg, 0.17 mmol, 1 equiv) in freshly distilled THF (1 mL). The resulting reaction mixture was stirred for 1 h at −40 °C before the reaction was quenched by a 0.1 M solution of NaOH (2 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated to give **13d** as a yellow oil, which was not purified due to its low stability on silica (43 mg, 98%): IR (neat) ν 1610, 1427, 1210, 1113 cm^{-1}; (isomer 1*E*,3*E*) ^1H NMR (200 MHz) δ 0.67 or 0.68 (6H, q, $J = 7.3$), 0.98 or 0.99 (9H, t, $J = 7.3$), 1.23−1.33 (3H, m), 3.51 (3H, s), 3.74 or 3.80 (2H, q, $J = 6.9$), 5.73 (1H, d, $J = 12.8$), 5.75 (1H, s), 6.73 (1H, d, $J = 12.8$); ^{13}C NMR (75 MHz) δ 5.2 or 5.6, 7.1 or 7.2, 56.5 or 56.9, 59.8, 66.0, 97.9, 132.5, 137.3, 148.5; (isomer 1*Z*,3*E*) ^1H NMR (200 MHz) δ 0.67 or 0.68 (6H, q, $J = 7.3$), 0.98 or 0.99 (9H, t, $J = 7.3$), 1.23−1.33 (3H, m), 3.53 (3H, s), 3.74 or 3.80 (2H, q, $J = 6.9$), 5.20 (1H, d, $J = 12.2$), 5.45 (1H, s), 6.60 (1H, d, $J = 12.2$); ^{13}C NMR (75 MHz) δ 5.2 or 5.6, 7.1 or 7.2, 56.5 or 56.9, 60.5, 63.4, 101.1, 130.8, 133.2, 146.7.

2-*tert*-Butyldimethylsilyloxy-4-ethoxy-1-methoxy-1,3-butadiene 13e. *t*BuLi 1.5 M (344 μL, 0.52 mmol, 3.0 equiv) was added, at −40 °C and under nitrogen atmosphere, to a solution of 2-*tert*-butyldimethylsilyloxy-4-ethoxy-1,1-dimethoxybut-2-ene **12e** (50 mg, 0.17 mmol, 1 equiv) in freshly distilled THF (1 mL). The resulting reaction mixture was stirred for 1 h at −40 °C before the reaction was quenched by a 0.1 M solution of NaOH (2 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated to give **13e** as a yellow oil, which was not purified due to its low stability on silica (40 mg, 91%): IR (neat) ν 1610, 1427, 1210, 1113 cm^{-1}; (isomer 1*E*,3*E*) ^1H NMR (300 MHz) δ 0.13 (6H, s), 0.95 (9H, s), 1.30 (3H, t, $J = 7.2$), 3.52 (3H, s), 3.80 (2H, q, $J = 7.2$), 5.73 (1H, d, $J = 12.8$), 5.74 (1H, s), 6.72 (1H, d, $J = 12.8$); ^{13}C NMR (75 MHz) δ −4.2, 15.0, 18.5, 26.2, 60.5, 65.3, 98.8, 133.0, 137.4, 147.6; (isomer 1*Z*,3*E*) ^1H NMR (300 MHz) δ 0.14 (6H, s), 0.96 (9H, s), 1.27 (3H, t, $J = 7.2$), 3.53 (3H, s), 3.74 (2H, q, $J = 7.2$), 5.20 (1H, d, $J = 12.4$), 5.45 (1H, s), 6.62 (1H, d, $J = 12.4$); ^{13}C NMR (75 MHz) δ −4.1, 15.2, 18.9, 26.4, 59.7, 65.8, 102.1, 130.7, 137.4, 145.8.

4-Ethoxy-1-methoxy-2-triisopropylsilyloxy-1,3-butadiene 13f. *t*BuLi 1.5 M (300 μL, 0.45 mmol, 3.0 equiv) was added, at −40 °C and under nitrogen atmosphere, to a solution of 4-ethoxy-1,1-dimethoxy-2-triisopropylsilyloxybut-2-ene **12f** (50 mg, 0.15 mmol, 1 equiv) in freshly distilled THF (1 mL). The resulting reaction mixture was stirred for 1 h at −40 °C before the reaction was quenched by a 0.1 M solution of NaOH (2 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated to give **13f** as a yellow oil, which was not purified due to its low stability on silica (41 mg, 91%): IR (neat) ν 1610, 1427, 1210, 1113 cm^{-1}; (isomer 1*E*,3*E*) ^1H NMR (200 MHz) δ 1.05−1.16 (21H, m), 1.30 (3H, t, $J = 6.9$), 3.50 (3H, s), 3.81 (2H, q, $J = 6.9$), 5.74 (1H, d, $J = 12.8$), 5.77 (1H, s), 6.83 (1H, d, $J = 12.8$); ^{13}C NMR (50 MHz) δ 13.2, 14.0, 18.5, 60.5, 65.3, 98.7, 131.8, 138.4, 147.8; (isomer 1*Z*,3*E*) ^1H NMR (200 MHz) δ 1.05−1.16 (21H, m), 1.27 (3H, t, $J = 6.9$), 3.51 (3H, s), 3.74 (2H, q, $J = 6.9$), 5.19 (1H, d, $J = 12.1$), 5.40 (1H, s), 6.68 (1H, d, $J = 12.1$); ^{13}C NMR (50 MHz) δ 12.5, 15.1, 18.1, 59.6, 65.7, 102.2, 130.0, 138.4, 145.7.

2-*tert*-Butyldiphenylsilyloxy-4-ethoxy-1-methoxy-1,3-butadiene 13g. *t*BuLi 1.5 M (241 μL, 0.36 mmol, 3.0 equiv) was added, at −40 °C and under nitrogen atmosphere, to a solution of 2-*tert*-butyldiphenylsilyloxy-4-ethoxy-1,1-dimethoxybut-2-ene **12g** (50 mg, 0.12 mmol, 1 equiv) in freshly distilled THF (1 mL). The resulting reaction mixture was stirred for 1 h at −40 °C before the reaction was quenched by a 0.1 M solution of NaOH (2 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated to give **13g** as a yellow oil, which was not purified due to its low stability on silica (45 mg, 98%): IR (neat) ν 1610, 1427, 1210, 1113 cm^{-1}; (isomer 1*E*,3*E*) ^1H NMR (300 MHz) δ 1.08 (9H, s), 1.33 (3H, t, $J = 7.2$), 3.16 (3H, s), 3.84 (2H, q, $J = 7.2$), 5.33 (1H, s), 5.77 (1H, d, $J = 12.8$), 7.04 (1H, d, $J = 12.8$), 7.37−7.40 (6H, m), 7.72−7.78 (4H, m); ^{13}C NMR (75 MHz) δ 15.1, 19.8, 27.0, 60.2, 65.3, 98.4, 128.0, 130.1, 133.2, 133.4, 135.8, 137.9, 147.5; (isomer 1*Z*,3*E*) ^1H NMR (300 MHz) δ 1.06 (9H, s), 1.29 (3H, t, $J = 7.2$), 3.32 (3H, s), 3.76 (2H, q, $J = 7.2$), 5.25 (1H, s), 5.26 (1H, d, $J = 12.1$), 6.86 (1H, d, $J = 12.1$), 7.37−7.40 (6H, m), 7.72−7.78 (4H, m); ^{13}C NMR (75 MHz) δ 15.2, 19.3, 26.9, 58.7, 65.8, 101.5, 127.5, 129.4, 130.0, 135.1, 135.5, 137.9, 146.0.

4-Ethoxy-1-(1-ethylpropyloxy)-2-triethylsilyloxy-1,3-butadiene 13h. *t*BuLi 1.5 M (248 μL, 0.37 mmol, 3.0 equiv) was added, at −40 °C and under nitrogen atmosphere, to a solution of 4-ethoxy-1-[bis(1-ethylpropyloxy)]-2-triethylsilyloxybut-2-ene **12h** (50 mg, 0.12 mmol, 1 equiv) in freshly distilled THF (1 mL). The resulting reaction mixture was stirred for 1 h at −40 °C before the reaction was quenched by a 0.1 M solution of NaOH (2 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated to give **13h** as a yellow oil, which was not purified due to its low stability on silica (36 mg, 95%): IR (neat) ν 1622, 1462, 1108, 1006 cm^{-1}; (isomer 1*E*,3*E*) ^1H NMR (300 MHz) δ 0.66−0.75 (6H, m), 0.84−1.00 (15H, m), 1.26 (3H, t, $J = 7.2$), 1.50−1.58 (4H, m), 3.34−3.42 (1H, m), 3.79 (2H, q, $J = 7.2$), 5.79 (1H, s), 5.80 (1H, d, $J = 12.8$), 6.69 (1H, d, $J = 12.8$); ^{13}C NMR (75 MHz) δ 6.7, 7.1, 9.6, 15.6, 26.5, 65.0, 84.8, 99.5, 130.5, 133.8, 146.9; (isomer 1*Z*,3*E*) ^1H NMR (300 MHz) δ 0.66−0.75 (6H, m), 0.84−1.00 (15H, m), 1.26 (3H, t, $J = 7.2$), 1.50−1.58 (4H, m), 3.34−3.42 (1H, m), 3.72 (2H, q, $J = 7.2$), 5.23 (1H, d, $J = 12.4$), 5.50 (1H, s), 6.55 (1H, d, $J = 12.4$); ^{13}C NMR (75 MHz) δ 5.7, 7.1, 10.1, 15.2, 27.1, 65.7, 85.6, 102.9, 129.9, 131.7, 144.6.

7-Ethoxy-4-methoxy-2-methyl-5-triethylsilyloxy-3a,4,7,7a-tetrahydroisoindole-1,3-dione 28. A solution of 4-ethoxy-1-methoxy-2-triethylsilyloxy-1,3-butadiene **13d** (0.2 g, 0.77 mmol, 1 equiv) in freshly distilled THF (2.5 mL) was added to a solution of *N*-methylmaleimide **26** (0.17 g, 1.16 mmol, 1.5 equiv) in dry THF (2.5 mL) in a high-pressure cell. After 24 h at room temperature and under 8 kbar, the solvent was evaporated and the residue was purified by flash chromatography on silica (heptane/AcOEt 95:5). Isomer **28 trans** (yellow oil, 64 mg, 22%): IR (neat) ν 1705, 1434, 1291, 1202, 1098 cm^{-1}; EIMS (70 eV) *m/z* 370 (M^+, 1), 258 (NMM^+, 100); ^1H NMR (300 MHz) δ 0.72 (6H, q, $J = 7.9$), 0.99 (9H, t, $J = 7.9$), 1.10 (3H, t, $J = 7.1$), 3.00 (3H, s), 3.07 (1H, dd, $J = 6.2$ and 10.4), 3.27 (1H, dd, $J = 6.2$ and 10.4), 3.37 (3H, s), 3.40−3.54 (2H, m), 4.09 (1H, dd, $J = 1.5$ and 6.7), 4.44 (1H, dd, $J = 6.4$ and 6.4), 5.28 (1H, dd, $J = 1.1$ and 6.8); ^{13}C NMR (75 MHz) δ 5.2, 6.9, 15.6, 25.3, 44.7, 45.7, 58.3, 64.2, 69.4, 75.2, 104.7, 157.3, 176.0, 176.3. Isomer **28 cis** (yellow oil, 95 mg, 33%): IR (neat) ν 1707, 1435, 1282, 1111 cm^{-1}; EIMS (70 eV) *m/z* 370 (M^+,

1), 258 (NMM$^+$, 100); ^{1}H NMR (300 MHz) δ 0.68 (6H, q, J = 8.3), 0.96 (9H, t, J = 8.3), 1.08 (3H, t, J = 7.1), 2.94 (3H, s), 3.14−3.15 (2H, m), 3.44−3.49 (2H, m), 3.51 (3H, s), 4.13−4.14 (1H, m), 4.34−4.38 (1H, m), 5.07 (1H, d, J = 4.9); ^{13}C NMR (75 MHz) δ 5.1, 6.8, 15.5, 24.9, 43.4, 46.5, 58.7, 64.3, 71.4, 75.0, 103.9, 154.5, 176.5, 178.5.

2-Ethoxy-5-methoxy-4-triethylsilyloxycyclohex-3-enecarboxylic Acid Phenyl Ester 29. A solution of 4-ethoxy-1-methoxy-2-triethylsilyloxy-1,3-butadiene **13d** (0.15 g, 0.58 mmol, 1 equiv) in freshly distilled THF (2.5 mL) was added to a solution of phenyl acrylate **27** (0.143 mL, 0,87 mmol, 1.5 equiv) in dry THF (2.5 mL) in a high-pressure cell. After 24 h at room temperature and under 8 kbar, the solvent was evaporated, and the residue was purified by flash chromatography on silica (heptane/AcOEt 95:5). Isomer **30 trans** (yellow oil, 28 mg, 13%): IR (neat) ν 1762, 1653, 1193, 1159 cm^{-1}; EIMS (70 eV) m/z 406 (M$^+$, 21), 374 (M$^+$-MeOH, 13), 258 (59, **13d**), 59 (100); ^{1}H NMR (300 MHz) δ 0,70 (6H, q, J = 7.9), 1.00 (9H, t, J = 8.0), 1.19 (3H, t, J = 6.8), 2.18 (1H, ddd, J = 3.8, 14.3 and 14.3), 2.31−2.23 (1H, m), 3.15 (1H, ddd, J = 4.2, 4.2 and 15.4), 3.44 (3H, s), 3.44−3.54 (1H, m), 3.58 (1H, dd, J = 2.3 and 3.4), 3.66 (1H, dq, J = 6.8 and 9.0), 4.37 (1H, dd, J = 4.9 and 4.9), 5.23 (1H, d, J = 5.3), 7.07 (2H, dd, J = 1.1 and 8.7), 7.22 (1H, dddd, J = 1.1, 1.1, 7.5 and 7.5), 7.38 (2H, dd, J = 7.5 and 7.5); ^{13}C NMR (75 MHz) δ 5.3, 7.0, 16.1, 25.1, 40.8, 58.5, 64.6, 72.2, 76.5, 104.6, 121.9, 125.9, 129.7, 151.4, 154.4, 172.0. Isomer **30 cis** (yellow oil, 39 mg, 19%): IR (neat) ν 1762, 1653, 1193, 1159 cm^{-1}; EIMS (70 eV) m/z 406 (M$^+$, 21), 374 (M$^+$-MeOH, 13), 258 (59), 59 (100); ^{1}H NMR (300 MHz) δ 0,72 (6H, q, J = 7.9), 1.00 (9H, t, J = 7.9), 1.18 (3H, t, J = 7.2), 2.23 (1H, ddd, J = 10.6, 13.2 and 13.2), 2.34 (1H, dddd, J = 1.1, 3.4, 6.4 and 13.2), 2.85 (1H, ddd, J = 3.4, 3.4 and 13.2), 3.39−3.47 (1H, m), 3.43 (3H, s), 3.66 (1H, dq, J = 7.2 and 9.0), 3.79 (1H, dd, J = 6.4 and 10.6), 4.36 (1H, dd, J = 4.5 and 4.9), 5.22 (1H, dd, J = 1.1 and 5.6), 7.07 (2H, dd, J = 1.1 and 8.7), 7.22 (1H, dddd, J = 1.1, 1.1, 7.5 and 7.5), 7.38 (2H, dd, J = 7.5 and 7.5); ^{13}C NMR (75 MHz) δ 5.4, 7.0, 16.0, 25.5, 44.4, 57.3, 64.0, 71.9, 76.3, 104.6, 121.8, 125.9, 129.7, 151.3, 156.1, 171.1.

5-*tert*-Butyldiphenylsilyloxy-7-ethoxy-4-methoxy-2-methyl-3a,4,7,7a-tetrahydroisoindole-1,3-dione 30. A solution of 2-(*tert*-butyldiphenylsilyloxy)-4-ethoxy-1-methoxy-1,3-butadiene **13g** (0.15 g, 0.39 mmol, 1 equiv) in freshly distilled THF (0.5 mL) was added to a solution of *N*-methylmaleimide **26** (60 mg, 0.54 mmol, 1.4 equiv) in dry THF (0.5 mL) in a high-pressure cell. After 24 h at room temperature and under 16 kbar, the solvent was evaporated and the residue was purified by flash chromatography on silica (heptane/AcOEt 95:5). Isomer **30 trans** (white solid, 71 mg, 36%): mp 120 °C (diethyl ether); IR (neat) ν 1705, 1429, 1114 cm^{-1}; EIMS (70 eV) m/z 493 (M$^+$, <1), 436 (M$^+$ − *t*Bu, 74), 213 (M$^+$ − *t*BuPh$_2$SiOC═CH, 100), 57 ([*t*Bu]$^+$, 75); ^{1}H NMR (300 MHz) δ 0.85 (3H, t, J = 7.1), 1.05 (9H, s), 2.86−2.99 (3H, m), 2.92 (3H, s), 3.10 (1H, dd, J = 4.5 and 9.4), 3.66 (3H, s), 4.02 (1H, dd, J = 5.3 and 5.3), 4.26 (1H, dd, J = 1.5 and 4.5), 4.72 (1H, dd, J = 1.1 and 5.3), 7.38−7.43 (6H, m), 7.68−7.74 (4H, m); ^{13}C NMR (75 MHz) δ 15.4, 19.7, 24.8, 26.6, 43.9, 46.8, 59.3, 63.6, 70.8, 74.1, 105.2, 128.1, 130.4, 132.2, 135.8, 154.5, 176.7, 178.6. Anal. Calcd for $C_{28}H_{35}NO_5Si$: C, 68.12; H, 7.15. Found: C, 68.19; H, 7.36. Isomer **30 cis** (yellow oil, 13 mg, 7%): IR (neat) ν 1705, 1428, 1289, 1203, 1113 cm^{-1}; EIMS (70 eV) m/z 493 (M$^+$, <1), 436 (M$^+$-*t*Bu, 74), 213 (M$^+$-*t*BuPh$_2$SiOC═CH, 100), 57 ([*t*Bu]$^+$, 75); ^{1}H NMR (300 MHz) δ 0.90 (3H, t, J = 6.8), 1.07 (9H, s), 2.84 (1H, dd, J = 6.0 and 10.5), 2.97 (3H, s), 3.03−3.14 (2H+1H, m), 3.50 (3H, s), 4.17 (1H, dd, J = 6.4 and 6.4), 4.24 (1H, dd, J = 1.5 and 6.8), 5.01 (1H, dd, J = 1.5 and 6.8), 7.37−7.46 (6H, m), 7.64−7.76 (4H, m); ^{13}C NMR (75 MHz) δ 15.3, 19.5, 25.2, 26.7, 44.6, 45.7, 58.8, 63.7, 68.8, 75.4, 108.0, 128.2, 130.5, 131.9, 135.8, 156.8, 176.0, 176.2.

4-*tert*-Butyldiphenylsilyloxy-2,5-dimethoxycyclohex-3-enecarboxylic Acid Phenyl Ester 31. A solution of 2-*tert*-butyldiphenylsilyloxy-1,4-dimethoxy-1,3-butadiene **13c** (0.15 g, 0.41 mmol, 1 equiv) in freshly distilled THF (2.5 mL) was added to a solution of phenyl acrylate **27** (0.093 mL, 0,67 mmol, 1.6 equiv) in dry THF (2.5 mL) in a high-pressure cell. After 24 h at room temperature and under 16 kbar, the solvent was evaporated and the residue was purified by flash chromatography on silica (heptane/AcOEt 95:5). Isomer **31 trans** (white solid, 80 mg, 38%): mp 136−137 °C (diethyl ether); IR (neat) ν 1765, 1658, 1492, 1427, 1195, 1083 cm^{-1}; EIMS (70 eV) m/z 516 (M$^+$, <1), 459 (M$^+$ − *t*Bu, 57), 427 (M$^+$ − *t*Bu − MeOH, 33), 213 (79), 135 (100); ^{1}H NMR (300 MHz) δ 1.06 (9H, s), 2.12 (1H, ddd, J = 4.1, 14.3 and 14.3), 2.19 (1H, ddd, J = 2.3, 3.0 and 14.3), 2.92 (3H, s), 3.10 (1H, ddd, J = 3.8, 3.8 and 12.4), 3.50 (3H, s), 3.73 (1H, dd, J = 2.3 and 3.4), 4.02 (1H, dd, J = 4.5 and 4.9), 4.89 (1H, d, J = 5.3), 7.01 (2H, dd, J = 1.1 and 8.3), 7.19 (1H, ddd, J = 1.1, 7.5 and 7.5), 7.33 (2H, d, J = 7.5), 7.36−7.46 (6H, m), 7.73−7.79 (4H, m); ^{13}C NMR (75 MHz) δ 19.6, 35.3, 36.7, 40.7, 56.1, 58.7, 73.3, 76.5, 105.1, 121.9, 125.9, 128.1, 129.7, 130.2, 130.3, 132.5, 132.7135.8, 151.3, 154.2, 172.0. Anal. Calcd for $C_{31}H_{36}O_5Si$: C, 72.06; H, 7.02. Found: C, 72.06; H, 7.18.

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Supporting Information Available: Experimental procedures, copies of the ^{1}H NMR and ^{13}C spectra for all compounds, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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