Synthesis of Functionalized 2-Alkylidenetetrahydrofurans by Cyclization of 1,3-Bis(trimethylsilyloxy)-1,3-butadienes with Epoxides

Peter Langer,*[a, c] Holger Armbrust,[a] Tobias Eckardt,[a] and Jörg Magull[b]

Abstract: The Lewis acid mediated cyclization of epoxides with 1,3-bis(trimethylsilyloxy)-1,3-butadienes, electroneutral equivalents of 1,3-dicarbonyl dianions, results in the formation of 2-alkylidenetetrahydrofurans with a great variety of substitution patterns and functional groups. This includes the synthesis of 2,3′-bifuranylidenes and 7-oxabicyclo[4.3.0]nonanes. The cyclization of dienes with functionalized epoxides containing base-labile groups proceeds with good chemoselectivity. In all reactions, good regio- and *E* diastereoselectivities are observed. Based on the stereoselectivities observed for reactions of 1,2-disubstituted epoxides, a working hypothesis for the mechanism of the reaction is suggested.

Keywords: cyclization · epoxides · heterocycles · Lewis acids · stereoselective syntheses

Introduction

Despite their potential synthetic usefulness, cyclization reactions of dianions[1, 2] with 1,2-dielectrophiles are problematic since they can suffer from various side reactions, such as polymerization, decomposition,[3] formation of open-chain products,[4] elimination,[5] or SET (Single-Electron Transfer) reactions.[6] These problems result from the fact that both dianions and 1,2-dielectrophiles are highly reactive compounds (low reactivity matching). In addition, a number of 1,2-dielectrophiles are rather unstable in reactions with strong nucleophiles. To overcome these problems, Lewis acid mediated reactions of electroneutral dianion equivalents (masked dianions) have been developed. During the past years, we have developed a number of cyclization[7] and multicomponent reactions[8] of dianions with a variety of 1,2-dielectrophiles. In this context, we have also developed Lewis acid mediated cyclizations of 1,3-bis(trimethylsilyloxy)-1,3-butadienes, masked 1,3-dicarbonyl dianions,[9] with oxalyl chloride, α-chloroacetic chloride, chloroacetic aldehyde dimethylacetal, 1,2-diketones, and phthalic dialdehyde.[10]

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Cyclization reactions of free or masked dianions with epoxides are relatively rare: for example, the cyclization of 1,3-dicarbonyl dianions with epoxides, which was first reported by Bryson.[11] Cyclizations of carbohydrate-derived epoxytriflates with 1,3-dicarbonyl dianions have been reported by Voelter and co-workers.[12] Recently, we have reported the synthesis of 2-alkylidene-5-hydroxymethyltetrahydrofurans by reaction of 1,3-dicarbonyl dianions with epibromohydrin.[13] Molander and co-worker have reported the SnF_2-mediated cyclization of epoxyaldehydes with 3-iodo-2-[(trimethylsilyl)methyl]propene (an electroneutral equivalent of the trimethylenemethane dianion).[14] This reaction proceeds by regioselective attack of the dianion on the aldehyde and subsequent cyclization through the terminal carbon of the epoxide to give cyclohexane derivatives.

The reaction of 1,3-dicarbonyl dianions with epoxides suffers from several drawbacks. The preparative scope of these reactions is limited to epoxides containing no sterically hindered substituents or base-labile functional groups. As a result of the basic conditions, the cyclizations have to be carried out in two steps rather than as one-pot reactions (addition of the dianion onto the epoxide and subsequent acid-mediated cyclization of the open-chain product). To overcome these problems, we have recently developed the first Lewis acid mediated cyclizations of 1,3-bis(trimethylsilyloxy)-1,3-butadienes with epoxides.[15, 16] These reactions allow an efficient synthesis of a great variety of 2-alkylidenetetrahydrofurans, which can be transformed into functionalized tetrahydrofurans by hydrogenation. Herein, we wish to report full details of this cyclization reaction and studies related to the mechanism. With regard to our preliminary report, the scope of the reaction was significantly extended and now includes the synthesis of 2,3′-bifuranylidenes and 7-oxabicyclo[4.3.0]nonanes. In addition, the regiochemical influence of the substituents of the epoxide was studied.

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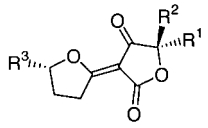
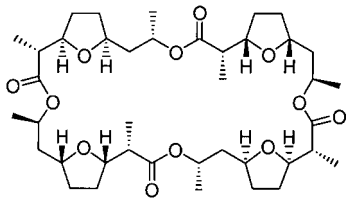


Charlic acid: $R^1 = H$, $R^2 = CH_2CO_2H$, $R^3 = H$

Charolic acid: $R^1 = Me$, $R^2 = R^3 = H$

Terrestric acid: $R^1 = Me$, $R^2 = H$, $R^3 = Et$

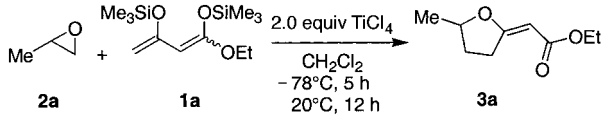


Nonactin

The 2-alkylidenetetrahydrofurans available by our methodology are direct precursors of biologically relevant tetrahydrofurans. We have recently reported the application of our methodology to the synthesis of methyl 8-*epi*-homononactate.[15] (±)-Methyl homononactate and methyl 8-*epi*-homononactate are subunits of the nactins, a class of macrotetrolide antibiotics isolated from a variety of *Streptomyces* cultures.[17, 18] The 2,3′-bifuranylidenes are also present in a number of natural products. This includes, for example, charlic acid, charolic acid, and terrestric acid, which are metabolites of *Penicillium charlesii* and *Penicillium terrestre*, respectively.[19]

Results and Discussion

Optimization: The reaction of 1,2-propenoxide (**2a**) with 1-ethoxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene (**1a**), which is available from ethyl acetoacetate in two steps,[9] afforded the 2-alkylidenetetrahydrofuran **3a** in up to 70% yield (Scheme 1). Proper tuning of the reaction temperature



Scheme 1. Cyclization of 1,3-bis(trimethylsilyloxy)-1,3-diene **1a** with 1,2-butenoxide.

Abstract in German: *Die $TiCl_4$-vermittelte Cyclisierung von Epoxiden mit 1,3-Bis(trimethylsilyloxy)-1,3-butadienen, elektroneutralen Äquivalenten von 1,3-Dicarbonyldianionen, erlaubt einen effizienten Zugang zu einer großen Bandbreite von 2-Alkylidentetrahydrofuranen. Dies schließt die Synthese von 2,3′-Bifuranylidenen und 7-Oxabicyclo[4.3.0]nonanen ein. Die Cyclisierung funktionalisierter Epoxide, die basenlabile Gruppen tragen, verläuft mit guter Chemoselektivität. Alle Produkte wurden mit guter Regio- und E-Diastereoselektivität gebildet. Eine experimentell begründete Arbeitshypothese für den Mechanismus der Cyclisierung wird vorgeschlagen.*

(stirring at −78–20 °C for 5 h and at 20 °C for 12 h) and the choice of the Lewis acid ($TiCl_4$, 2.0 equiv) proved important parameters for the optimization of the reaction (Table 1). The cyclization proceeded by attack of the terminal carbon of the diene on the sterically less hindered carbon atom of the epoxide and subsequent regioselective cyclization through the oxygen atom. The exocyclic double bond was formed with excellent *E* diastereoselectivity.

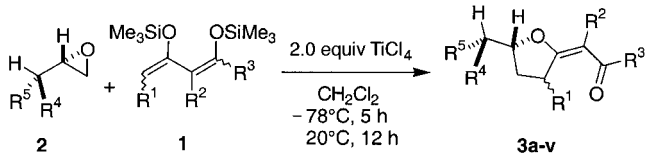
Table 1. Optimization of the cyclization of **1a** with **2a**.

	Lewis acid [equiv]	**2a** [equiv]	*t* [h][a]	[%][b]
1	$BF_3 \cdot Et_2O$ (2.0)	1.0	5+12	0
2	Me_3SiOTf (2.0)	1.0	5+12	0
3	$ZnCl_2$ (2.0)	1.0	0+12	0
4	$TiCl_4$ (2.0)	1.0	0+12[c]	0
5	$TiCl_4$ (2.0)	1.0	5+0	12
6	$TiCl_4$ (2.0)	1.0	5+5	57
7	$TiCl_4$ (2.0)	1.0	5+12	70
8	$TiCl_4$ (2.0)	1.5	5+12	62
9	$TiCl_4$ (1.0)	1.0	5+12	24

[a] Reaction time at −78–20 °C and at 20 °C. [b] Isolated yields. [c] The reaction was started at 0 °C.

Preparative scope: To study the preparative scope of the cyclization, the substituents of the 1,3-bis(trimethylsilyloxy)-1,3-butadiene and of the epoxide were systematically varied (Scheme 2, Table 2). The reaction of diene **1a** with 1,2-propenoxide, 1,2-butenoxide, 1,2-hexenoxide, 5,6-epoxy-1-hexene, and 1-benzyloxy-2,3-propenoxide afforded the 2-alkylidenetetrahydrofurans **3a**–**e** with good regio- and *E* diastereoselectivities.

The reaction of **1a** with epichloro- and epibromohydrin afforded the chloro- and bromo-substituted 2-alkylidenetetrahydrofurans **3f** and **3g**, respectively, in acceptable yields and with good regio- and *E* diastereoselectivities. Interestingly, the reaction proceeded with good chemoselectivity with exclusive attack of the silyl enol ether on the epoxide rather than on the alkyl halide function. In contrast, the reaction of the dianion of ethyl acetoacetate with epibromohydrin resulted in the formation of a 5-hydroxymethyl-2-alkylidenetetrahydrofuran (Scheme 3).[13] The reaction of bis-silyl enol ether **1a** with *threo*-3-bromo-1,2-butenoxide gave the diastereomerically pure 2-alkylidenetetrahydrofuran **3h** with again good *E* diastereoselectivity and without epimerization at the carbon attached to the bromine atom. Tetrahydrofurans containing chloro or bromo substituents in the side chain



Scheme 2. Cyclization of 1,3-bis(trimethylsilyloxy)-1,3-dienes **1** with epoxides **2** (for R^1–R^5 see Table 2).

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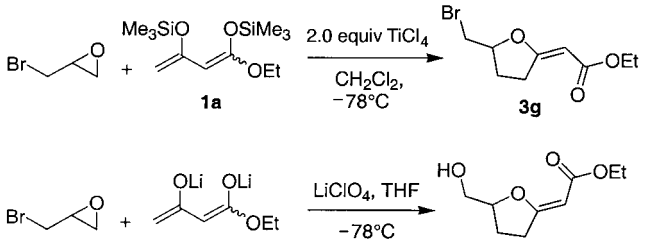
Table 2. Synthesis of 2-alkylidenetetrahydrofurans **3a–v**.

1	3	R^1	R^2	R^3	R^4	R^5	δ[a]	δ[b]	[%][c, d]
a	**a**	H	H	OEt	H	H	5.25	168.7	70
a	**b**	H	H	OEt	Me	H	5.23	168.7	62
a	**c**	H	H	OEt	Pr	H	5.22	168.7	44
a	**d**	H	H	OEt	$CH_2CH{=}CH_2$	H	5.23	168.6	30
a	**e**	H	H	OEt	OBn	H	5.33	168.5	58
a	**f**	H	H	OEt	Cl	H	5.31	168.2	52
a	**g**	H	H	OEt	Br	H	5.31	168.3	48
a	**h**	H	H	OEt	Br	Me	5.19	167.4	41
c	**i**	H	H	OMe	CH_2CO_2Et	H	5.24	169.0	51
b	**j**	H	Me	OEt	CO_2Et	H	–	169.0	50
b	**k**	H	Me	OEt	Me	H	–	169.5	58
b	**l**	H	Me	OEt	$CH_2CH{=}CH_2$	H	–	169.4	32
b	**m**	H	Me	OEt	Cl	H	–	168.8	45
d	**n**	H	Et	OEt	H	H	–	169.2	50
d	**o**	H	Et	OEt	Br	H	–	168.7	44
e	**p**	Me	H	OMe	Me	H	5.15	168.3	46
f	**q**	H	H	Ph	Me	H	6.50	190.2	62
f	**r**	H	H	Ph	Cl	H	6.58	190.1	51
f	**s**	H	H	Ph	Br	H	6.55	190.1	44
f	**t**	H	H	Ph	CO_2Et	H	6.53	190.3	41
g	**u**	H	H	CH_2OMe	Cl	H	5.94	197.1	45
g	**v**	H	H	CH_2OMe	Me	H	5.92	197.2	40

[a] Chemical shift (^{1}H NMR) of the hydrogen atoms of the exocyclic double bond. [b] Chemical shift (^{13}C NMR) of the exocyclic carbonyl group. [c] Isolated yields. For **3a–o** and **3q–v**: $E/Z > 98{:}2$; for **3p**: $E/Z = 5{:}1$. [d] Diastereoselectivity for **3h**: $ds > 98{:}2$ in favor of the drawn isomer (ds = diastereoselectivity). For **3p**: $ds = 4{:}1$.



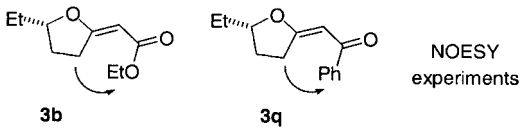
Scheme 3. Chemoselectivity of the cyclization of epibromohydrin with bis-silyl enol ethers and 1,3-dicarbonyl dianions.

have demonstrated considerable synthetic utility in functionalization reactions during natural product syntheses.[20] In addition, halogenated tetrahydrofurans are interesting in their own right as they occur in biologically relevant marine natural products.[21]

The reaction of ethyl 4,5-epoxypentanoate with bis-silyl enol ether **1c**, prepared from methyl acetoacetate, afforded the 2-alkylidenetetrahydrofuran **3i**. The cyclization of ethyl 3,4-epoxybutanoate with bis-silyl enol ether **1b**, which was prepared from ethyl 2-methylacetoacetate, afforded the 2-alkylidenetetrahydrofuran **3j**. The formation of **3i,j** proceeded again with good chemoselectivity with exclusive attack of the diene on the epoxide rather than on the ester function. In contrast, complex mixtures were obtained in the reaction of ester-substituted epoxides with the dianion of ethyl acetoacetate. Despite the presence of a methyl group at the exocyclic double bond, product **3j** was formed with good *E* diastereoselectivity. The cyclization of diene **1b** with 1,2-butenoxide, 5,6-epoxy-1-hexene, and epichlorohydrin afforded the 2-alkylidenetetrahydrofurans **3k–m**, containing a methyl group at the exocyclic double bond, with again good *E* diastereoselectivity. Diene **1d** was prepared from ethyl 2-ethylacetoacetate. The cyclization of **1d** with 1,2-propenoxide and epibromohydrin gave the ethyl-substituted 2-alkylidenetetrahydrofurans **3n** and **3o**, respectively.

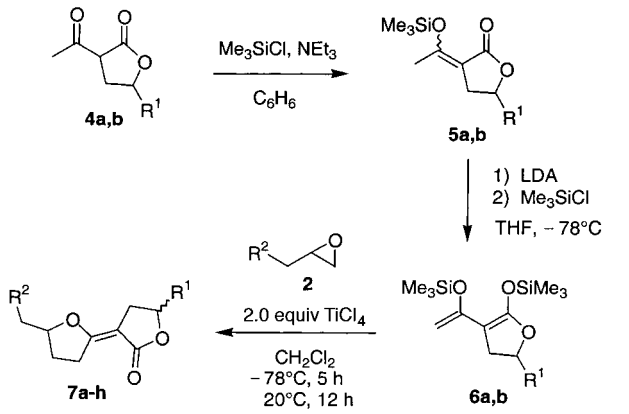
The reaction of 1,2-butenoxide with the diene of methyl 3-oxopentanoate **1e** afforded the 2-alkylidenetetrahydrofuran **3p** as a mixture of diastereomers. Despite the steric influence of the substituent R^1 = Me, the product was formed with good *E* diastereoselectivity. The cyclization of 1,2-butenoxide with diene **1f**, which was prepared from benzoylacetone, afforded the 2-alkylidenetetrahydrofuran **3q**. Similarly, the chloro-, bromo-, and ethoxycarbonyl-substituted 2-alkylidenetetrahydrofurans **3r–t** were prepared with good chemo-, regio-, and *E* diastereoselectivity. The reaction of epichlorohydrin and 1,2-butenoxide with 2,4-bis(trimethylsilyloxy)-5-methoxy-1,3-pentadiene (**1g**) afforded the 2-alkylidenetetrahydrofurans **3u** and **3v**.

The configuration of 2-alkylidenetetrahydrofurans **3b** and **3q** was proven by NOESY experiments. For **3b**, a NOE was observed between the ester and the $C(3)H_2$ group. In contrast, no NOE was detected between the latter and the CH group of the exocyclic double bond. For tetrahydrofuran **3q**, a NOE was observed between the phenyl and the $C(3)H_2$ group.

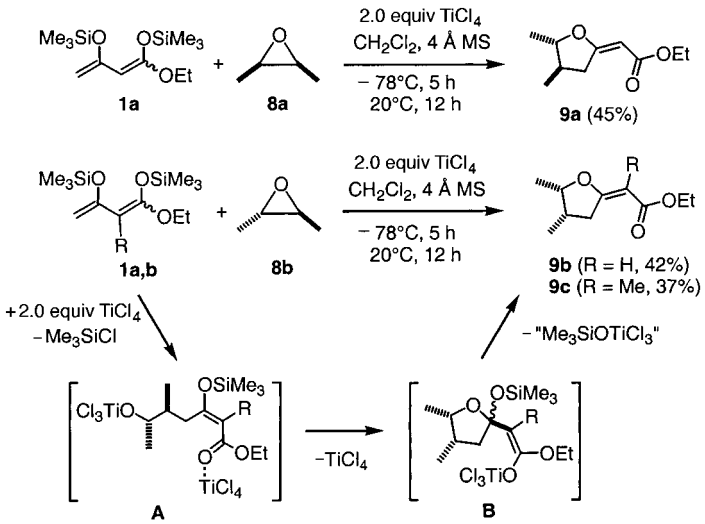


Comparison of the chemical shifts of the hydrogen atoms of the exocyclic double bond (Table 2) with those of related compounds allowed an independent confirmation of the *E* configuration of the 2-alkylidenetetrahydrofurans.[7, 10, 19] As expected, chemical shifts in the range of $\delta = 5.15–5.31$ were observed for ester-derived, *E* configured tetrahydrofurans. For benzoylacetone-derived tetrahydrofurans, chemical shifts in the typical range of $\delta = 6.50–6.58$ were found. The configuration of 2-alkylidenetetrahydrofurans **3j–o**, containing a tetrasubstituted exocyclic double bond, was established by analysis of the ^{13}C NMR chemical shifts (Table 2) of the carbonyl carbon atoms.[7, 10, 19] Additional evidence was obtained by NOESY experiments, for example, of tetrahydrofuran **3n**, and by a crystal structure analysis of a related compound (vide infra).

Synthesis of 2,3′-bifuranylidenes: The extension of our methodology to the preparation of dinuclear 2-alkylidenetetrahydrofurans (2,3′-bifuranylidenes) was of special interest since these compounds are present in a number of natural products (see Introduction).[19] In addition, these compounds represent versatile building blocks for the synthesis of naturally occurring spiroketals such as chalcogran.[22] Silylation of γ-butyrolactones **4a,b** with Me_3SiCl/NEt_3 afforded the silyl enol ethers **5a,b**, which were transformed in high yields into the bis-silyl enol ethers **6a,b** by treatment with LDA (lithium diisopropylamide) and Me_3SiCl (Scheme 4).[23]



Scheme 4. Cyclization of the γ-lactone-derived dienes **6a,b** with epoxides (for R^1, R^2 see Table 3).



Scheme 5. Cyclization of bis-silyl enol ethers with 1,2-disubstituted epoxides.

To our satisfaction, the $TiCl_4$-mediated reaction of **6a** with 1,2-propenoxide and 1,2-butenoxide afforded the 2,3′-bifuranylidenes **7a,b** with good regio- and *E* diastereoselectivity (Scheme 4, Table 3). The *E*-configured tetrahydrofurans **7c** and **7d** were prepared by reaction of **6a** with 1,2-hexenoxide and 5,6-epoxy-1-hexene, respectively. The reaction of **6a** with epichlorohydrin and epibromohydrin afforded the chloro- and bromo-substituted 2,3′-bifuranylidenes **7e,f** with again good chemo-, regio-, and *E* diastereoselectivity. Starting with the ethyl-substituted bis-silyl enol ether **6b**, the 2,3′-bifuranylidenes **7g,h** were obtained with good regio- and *E* diastereoselectivity but, as expected, without any remote diastereocontrol. The *E* configuration of 2,3′-bifuranylidenes **7a–h** was established by comparison of the ^{13}C NMR chemical shifts (Table 3) with those of tetrahydrofurans **3** (Table 2) and related compounds.[7, 10, 19] In addition, a crystal structure analysis of a related product was obtained (vide infra).

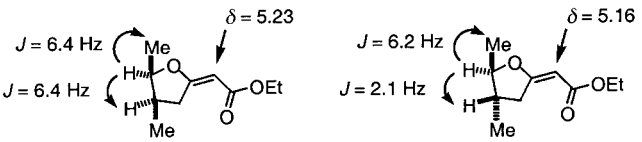
Table 3. Synthesis of the 2,3′-bifuranylidenes **7a–h**.

7	R^1	R^2	[%][a]	δ[b]	*E*/*Z*
a	H	H	42	169.1	> 98:2
b	H	Me	34	169.2	> 98:2
c	H	Pr	37	169.2	> 98:2
d	H	$CH_2CH{=}CH_2$	36	168.9	> 98:2
e	H	Cl	46	168.1	> 98:2
f	H	Br	62	167.8	> 98:2
g	Et	Me	57	168.7	> 98:2
h	Et	Br	82	167.6	> 98:2

[a] Isolated yields. [b] Chemical shift (^{13}C NMR) of the exocyclic carbonyl group.

Cyclization reactions of 1,2-disubstituted epoxides: To get some insight into the mechanism of the reaction, we have studied the reaction of 1,3-bis(trimethylsilyloxy)-1,3-diene **1a** with 1,2-disubstituted epoxides (Scheme 5): the reaction of **1a** with *cis*-2,3-butenoxide (**8a**) afforded the *E*-configured 2-alkylidenetetrahydrofuran **9a** containing two *trans*-configured methyl groups in good yield. In contrast, reaction of **1a** with *trans*-2,3-butenoxide (**8b**) gave the 2-alkylidenetetrahydrofuran **9b** containing two *cis*-configured methyl groups. Similarly, tetrahydrofuran **9c** was prepared from diene **1b** with good *E* and *cis* diastereoselectivity.

The configuration of tetrahydrofurans **9a–c** was proven by NOESY measurements and by analysis of the coupling constants. As expected, the value of the $J_{5\text{-H},4\text{-H}}$ coupling constant is significantly higher for the *cis*-configured tetrahydrofuran **9b** than for the *trans*-configured isomer **9a**. This observation was independently confirmed by comparison of the ^1H NMR data of products **9a–c** (chemical shifts and coupling constants) with those of related compounds with known configuration.[24] The *E* configuration of the exocyclic double bond was established by comparison of the chemical shifts of the CH signals of the exocyclic double bond with those of tetrahydrofurans **3**.



The observed stereoselectivity suggested that the formation of 2-alkylidenetetrahydrofurans **3a–v**, **7a–h**, and **9a–c** can be explained by the following mechanism: regioselective attack of the terminal carbon of the diene on the epoxide afforded intermediate **A** with inversion of the configuration. The retention of the configuration of the carbon attached to the oxygen atom suggests that the cyclization proceeded by $TiCl_4$-mediated conjugate addition of the epoxide-derived hydroxy group onto the α,β-unsaturated ester moiety to give intermediate **B**. In contrast, attack of the silyl enol ether derived oxygen atom of **A** on the carbon attached to the hydroxy group would have resulted in an inversion of the configuration. The final product was formed by elimination of silanolate. The presence of the Lewis acid seems to be important for both the initial condensation and the subsequent cyclization and elimination. The stereoselectivity can be explained by the higher thermodynamic stability of the products containing *E*-configured exocyclic double bonds

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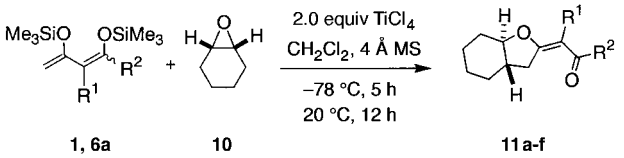
(minimization of the dipole–dipole repulsion of the oxygen atoms).[25, 26]

Synthesis of 7-oxabicyclo[4.3.0]nonanes: Based on the stereochemical observations outlined in the preceeding paragraph, we reasoned that the reaction of bis-silyl enol ethers with *cis*-configured cyclic epoxides should result in the formation of *trans*-configured bicyclic 2-alkylidenetetrahydrofurans. In fact, the reaction of diene **1a** with cyclohexenoxide **10** afforded the 7-oxabicyclo[4.3.0]nonane **11a** with high regioselectivity and with good *E* and *trans* diastereoselectivity (Scheme 6, Table 4). The cyclization of **10** with dienes **1c**, **1h**, **1i**, and **1f**, prepared from methyl acetoacetate, isopropyl acetoacetate, isobutyl acetoacetate, and benzoylacetone, respectively,



1, 6a **10** **11a-f**

Scheme 6. Cyclization of bis-silyl enol ethers with cyclic epoxides (for R^1, R^2 see Table 4).

Table 4. Synthesis of 7-oxabicyclo[4.3.0]nonanes **11a–f**.

1	11	R^1	R^2	Yield [%][a]	δ[b]
a	**a**	H	OEt	26	5.40
c	**b**	H	OMe	30	5.27
h	**c**	H	O*i*Pr	32	5.26
i	**d**	H	O*i*Bu	31[c]	5.32
f	**e**	H	Ph	24	6.52
6a	**f**		CH_2CH_2O	26	–

[a] Isolated yields. For all products: $E/Z > 98:2$. [b] Chemical shift (^{1}H NMR) of the hydrogen atoms of the exocyclic double bond. [c] Impurities could not be completely removed.

resulted in diastereoselective formation of the 7-oxabicyclo[4.3.0]nonanes **11b–e**. The dinuclear 7-oxabicyclo[4.3.0]-nonane **11f** was prepared from diene **6a** with good *E* and *trans* diastereoselectivity. Complex mixtures were obtained in the reaction of **1a** with cyclopentenoxide, cyclooctenoxide, and cyclododecenoxide.

The configuration of **11a–f** was established by analysis of the chemical shifts of the hydrogen atoms located at the exocyclic double bond and by analogy to the stereoselectivity observed in the formation of tetrahydrofurans **9a–c**. The structure of **11f** was independently confirmed by crystal structure analysis (Figure 1). Compound **11f** possesses an *E*-configured exocyclic double bond. The 7-oxabicyclo[4.3.0]nonane system exhibits a *trans* configuration. A chair conformation is observed for the cyclohexane moiety. The two heterocyclic moieties of the bifuranylidene system of **11f** are nearly in plane.

Influence of the epoxide on the regioselectivity: To study the parameters which direct the regioselectivity of cyclization, we have studied reactions of bis-silyl enol ethers with styrenoxide and 3,4-epoxy-1-butene. The reaction of **1a** with styrenoxide **12a** resulted in a change of the regioselectivity and formation of the *E*-configured 2-alkylidenetetrahydrofuran **13a** containing the phenyl substituent at carbon C-4 rather than C-5 (Scheme 7, Table 5). Similarly, the reaction of

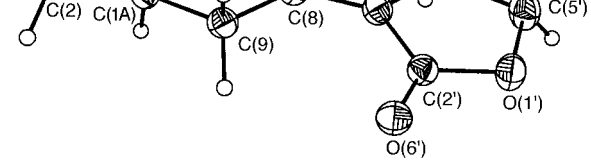
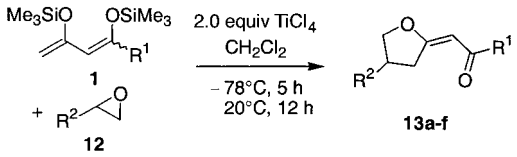


Figure 1. ORTEP plot of **11f**. The thermal ellipsoids of 50% probability are shown for the non-hydrogen atoms. Selected bond lengths [Å] and angles [°]: C(1A)–C(6A) 1.501(6), C(1A)–C(9) 1.549(4), O(7)–C(8) 136.0(2), O(1′)–C(2′) 1.362(2), O(1′)–C(5′) 1.454(2), C(2′)–C(3′) 1.453(3), C(3′)–C(4′) 1.502(2), C(6A)–O(7) 1.536(4); C(6A)–C(1A)–C(2) 107.7(3), C(6A)–C(1A)–C(9) 100.6(3), C(1A)–C(2)–C(3A) 104.6(2), C(1A)–C(6A)–O(7) 97.6(3), C(8)–O(7)–C(6A) 105.78(18), C(3′)–C(8)–O(7) 120.02(16), C(2′)–O(1′)–C(5′) 110.75(14), O(1′)–C(2′)–C(3′) 109.26(15).



Scheme 7. Influence of the substituents of the epoxide on the regioselectivity (for R^1, R^2 see Table 5).

Table 5. Synthesis of 2-alkylidenetetrahydrofurans **13a–f**.

1	13	R^1	R^2	Yield [%][a]	δ[d]
a	**a**	OEt	Ph	30	5.40
f	**b**	Ph	$CH{=}CH_2$	38	6.54
f	**c**	Ph	Me	45	6.52
g	**d**	CH_2OMe	Me	42	5.95
j	**e**	Me	Me	36[b]	5.75, 5.78
j	**f**	Me	Et	15 + 6[c]	5.74, 5.75

[a] Isolated yields. For all products: $E/Z > 98:2$. [b] Inseparable mixture of regioisomers. For the main isomer, the methyl group is located at carbon C-5. [c] Isolated yields of regioisomers. For the main isomer, the ethyl group is located at carbon C-4. [d] Chemical shift (^{1}H NMR) of the hydrogen atoms of the exocyclic double bond.

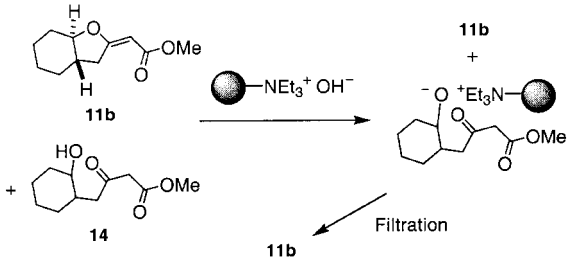
1,3-bis(trimethylsilyloxy)-1-phenyl-1,3-butadiene with 3,4-epoxy-1-butene **12b** afforded the vinyl-substituted tetrahydrofuran **13b**.

The cyclization of ester-derived dienes with 1,2-propenoxide afforded tetrahydrofurans **3a** and **3n** containing a methyl group at carbon C-5. In contrast, the reaction of 1,2-propenoxide with bis-silyl enol ethers **1f** and **1g** afforded tetrahydrofurans **13c** and **13d**, respectively, containing the methyl group at carbon C-4 rather than C-5. The reaction of 2,4-bis(trimethylsilyloxy)-1,3-pentadiene (**1j**) with 1,2-propenoxide and 1,2-butenoxide resulted in the formation of tetrahydrofurans **13e** and **13f**, respectively, which were each obtained as mixtures of regioisomers. The structure of

tetrahydrofurans **13a–f** was established by DEPT experiments. The *E* configuration of the exocyclic double bond was again proven by comparison of the chemical shifts of the respective CH signals with those of tetrahydrofurans **3**.

The change of the regioselectivity can be explained as follows: bis-silyl enol ethers prepared from 1,3-diketones are less reactive than those derived from β-ketoesters. The nucleophilic attack of a bis-silyl enol ether on an epoxide is slower for ketone- than for ester-derived dienes. Therefore, the $TiCl_4$-mediated ring opening of the epoxide and formation of a carbocation is faster than nucleophilic attack of the diene on the epoxide. The change in the regioselectivity observed for styrenoxide and 3,4-epoxy-1-butene can be explained by the fact that the phenyl and vinyl group efficiently stabilize a carbocation. In contrast, alkyl groups stabilize a carbocation less efficiently. For reactions of bis-silyl enol ethers with alkyl-substituted epoxides, a change in the regioselectivity is most likely for reactions of ketone-derived dienes with 1,2-propenoxide due to the low reactivity of the diene and the low steric hindrance of the methyl group of the epoxide.

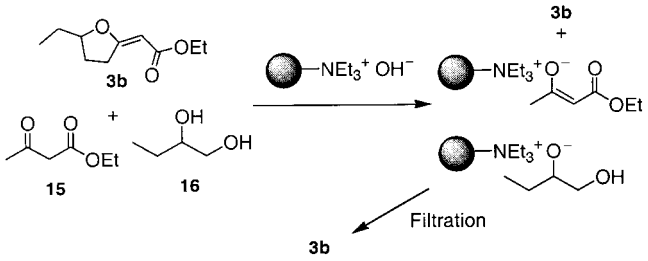
Optimization of the isolation and purification procedure: During our synthetic studies, we have developed a new method, which greatly simplified the purification and isolation of 2-alkylidenetetrahydrofurans. Herein, we wish to report the results of our efforts. Analysis of the crude product of the reaction of cyclohexenoxide **10** with 1-methoxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene indicated that, besides the desired product **11b**, significant amounts of the 1:1 condensation product **14** had been formed. Similar by-products were formed in all cyclization reactions of bis-silyl enol ethers with **10**. As a result of the presence of a hydroxy and a 1,3-dicarbonyl group, **14** was expected to be considerably more acidic than **11b**. Therefore, a solution of the mixture in diethyl ether was treated with the basic ion-exchange resin Ambersep 900-OH (Scheme 8). After stirring for 2 h, the resin was



Scheme 8. Purification of **11b** by Ambersep 900-OH.

filtered off, and the filtrate was concentrated in vacuo. This procedure was repeated one time. Much to our satisfaction, the major impurity was selectively removed. The pure product was isolated by column chromatography, which was easy to carry out as a result of the absence of **14**. In contrast, two tedious chromatographic separations were required during the conventional purification procedure. The isolated yields of **11b** were comparable for either purification method.

In the case of the synthesis of 2-alkylidenetetrahydrofurans **3**, 1,3-dicarbonyl compounds and diols were common by-products, which were formed by hydrolysis of the bis-silyl enol ethers and epoxides, respectively. The purification of **3b** was again greatly improved by the use of Ambersep 900-OH, which efficiently scavenged the relatively acidic by-products **15** and **16** (Scheme 9). The isolated yield of **3b** was similar to that obtained by the more tedious conventional purification procedure.



Scheme 9. Purification of **3b** by Ambersep 900-OH.

In summary, we have reported the, to our knowledge, first cyclizations of 1,3-bis(trimethylsilyloxy)-1,3-butadienes, masked 1,3-dicarbonyl dianions, with epoxides. These reactions allow an efficient, chemo-, regio-, and diastereoselective synthesis of a variety of functionalized 2-alkylidenetetrahydrofurans, 2,3′-bifuranylidenes, and 7-oxabicyclo[4.3.0]nonanes, which represent useful precursors to biologically relevant tetrahydrofurans and natural products. Reactions of 1,2-disubstituted epoxides with bis-silyl enol ethers proceeded with good stereoselectivity and suggest that in all cyclizations the dienes react as 1,2-nucleophiles/electrophiles rather than 1,3-dinucleophiles; the epoxides can be regarded as 1,3-electrophiles/nucleophiles rather than 1,2-dielectrophiles. Further studies relating to the application of our methodology for the synthesis of natural products are in progress.

Experimental Section

General: All solvents were dried by standard methods, and all reactions were carried out under an inert atmosphere. For the ^1H and ^{13}C NMR spectra (^1H NMR: 250 and 300 MHz, 20 °C; ^{13}C NMR: 62.5 and 75 MHz, 20 °C), the deuterated solvents indicated were used. Bruker AM 250 (250 MHz), Varian VXR-200 (200 MHz), Varian Mercury 200 (200 MHz), Varian Unity 300 (300 MHz), Bruker AMX 300 (300 MHz), and Varian Inova 500 (500 MHz) were used. Mass spectrometric data (MS) were obtained by using electron ionization (EI, 70 eV, Finnigan MAT 95), chemical ionization (CI, 200 eV, H_2O), or electrospray ionization (Finnigan LC-Q, ESI). FT-IR: Bruker Vector 22 and Bruker IFS-66 were used. For preparative scale chromatography, Merck silica gel 60 (0.063–0.200 mm, 230–400 mesh) or Macherey-Nagel silica gel 60 (0.040–0.063 mm, 200–400 mesh) was used. Thin-layer chromatography (TLC): Macherey-Nagel silica gel 60 F_{254} was used. Melting points were uncorrected. Elemental analyses were performed at the microanalytical laboratory of the University of Göttingen. A LECO CHN 2000 analyzer with combined HERAEUS combustion apparatus Mikro U/D was used. All starting materials were used as purchased. Bis-silyl enol ethers **1** were prepared according to literature procedures.[9c] Ethyl 3,4-epoxybutanoate was prepared in three steps from ethyl 4-chloroacetoacetate.[27] Ethyl 4,5-epoxypentanoate was prepared in three steps from diethyl 2-allylmalonate.[28]

General procedure for the cyclization of epoxides with 1,3-bis(trimethylsilyloxy)-1,3-butadienes: Compound 1,2-butenoxide (130 mg, 0.15 mL, 1.8 mmol, $d = 0.837\ g\,cm^{-3}$) at 20 °C was added to a solution (30 mL) of

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1,3-bis(trimethylsilyloxy)-1-ethoxy-1,3-butadiene (1.8 mmol, 0.5 g) in CH_2Cl_2 and molecular sieves (4 Å). The solution was cooled to −78 °C, and subsequently $TiCl_4$ (3.6 mmol, 0.40 mL, $d = 1.726\ g\,cm^{-3}$) was added. After warming of the solution to 20 °C over 6 h, the solution was stirred for 12 h. A saturated aqueous solution of NaCl (150 mL) was added, and the organic layer was separated. The aqueous layer was extracted with diethyl ether (4 × 150 mL). The organic layer was dried ($MgSO_4$), filtered, and the filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel, diethyl ether/petroleum ether = 1:3) to give **3b** as a colorless oil (205 mg, 62 %). In some cases, two chromatographic purifications were required.

Purification of 3b by ion-exchange resins: A solution (20 mL) of the crude product mixture of **3b** in diethyl ether was treated with the basic ion-exchange resin Ambersep 900-OH. After stirring for 2 h, the resin was filtered off, and the filtrate was concentrated in vacuo. This procedure was repeated one time. After evaporation of the solvent, the residue was purified by chromatography to give **3b** as a colorless oil (210 mg, 63 %).

2-(*E*)-(Ethoxycarbonylmethylidene)-5-methyltetrahydrofuran (3a): Starting with 1,3-bis(trimethylsilyloxy)-1-ethoxy-1,3-butadiene (0.50 g, 1.8 mmol), 1,2-propenoxide (0.13 mL, $d = 0.829\ g\,cm^{-3}$, 1.8 mmol), and $TiCl_4$ (0.40 mL, $d = 1.726\ g\,cm^{-3}$, 3.6 mmol), **3a** was isolated after chromatography (silica gel, diethyl ether/petroleum ether = 1:3) as a colorless oil (216 mg, 70 %, $E/Z > 98{:}2$). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.25$ (t, $J =$ 7.1 Hz, 3H; OCH_2CH_3), 1.35 (d, $J = 5.3$ Hz, 3H; $CHCH_3$), 1.51 – 1.72 (m, 1H; 4-H), 2.15 – 2.27 (m, 1H; 4-H), 2.95 (dddd, $J = 18.3$, 9.1, 9.1, 2.0 Hz, 1H; 3-H), 3.31 (dddd, $J = 18.4$, 8.9, 4.0, 1.5 Hz, 1H; 3-H), 4.11 (q, $J = 7.1$ Hz, 2H; OCH_2CH_3), 4.47 – 4.56 (m, 1H; 5-H), 5.25 (t, $J = 1.7$ Hz, 1H; $CHCO_2Et$); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 14.43$ (OCH_2CH_3), 20.33 (CH_3), 30.74, 31.00 (C-3, C-4), 59.07 (OCH_2CH_3), 80.23 (C-5), 89.16 ($CHCO_2Et$), 168.67 (C=O), 176.42 (C-2); MS (70 eV, EI): *m*/*z* (%): 170 (66) [M^+], 142 (29), 125 (100), 69 (68); the exact molecular mass for $C_9H_{14}O_3$: *m*/*z* (%): 170.0943 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV).

2-(*E*)-(Ethoxycarbonylmethylidene)-5-ethyltetrahydrofuran (3b): Starting with 1,3-bis(trimethylsilyloxy)-1-ethoxy-1,3-butadiene (0.50 g, 1.8 mmol), 1,2-butenoxide (0.15 mL, 1.8 mmol), and $TiCl_4$ (0.40 mL, $d = 1.726\ g\,cm^{-3}$, 3.6 mmol), **3b** was isolated after chromatography (silica gel, diethyl ether/petroleum ether = 1:3) as a colorless oil (205 mg, 62 %, $E/Z > 98{:}2$). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.95$ (t, $J = 7.4$ Hz, 3H; CH_2CH_3), 1.23 (t, $J = 7.1$ Hz, 3H; OCH_2CH_3), 1.51 – 1.80 (m, 3H; 4-H, CH_2CH_3), 2.09 – 2.22 (m, 1H; 4-H), 2.92 (dddd, $J = 18.4$, 9.1, 9.1, 2.0 Hz, 1H; 3-H), 3.27 (dddd, $J = 18.4$, 9.1, 4.0, 1.5 Hz, 1H; 3-H), 4.09 (q, $J = 7.1$ Hz, 2H; OCH_2CH_3), 4.23 – 4.35 (m, 1H; 5-H), 5.23 – 5.24 (m, 1H; CHC=O); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 9.72$ (CH_2CH_3), 14.44 (OCH_2CH_3), 27.81, 28.71, 30.54 (C-3, C-4, C-1), 59.06 (OCH_2CH_3), 85.35 (C-5), 89.03 ($CHCO_2Et$), 168.74 (C=O), 176.55 (C-2); MS (70 eV, EI): *m*/*z* (%): 184 (71) [M^+], 179 (4), 166 (4), 155 (10), 139 (100), 112 (24); the exact molecular mass for $C_{10}H_{16}O_3$: *m*/*z* (%): 184.1099 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV).

2-(*E*)-(Ethoxycarbonylmethylidene)-5-butyltetrahydrofuran (3c): Starting with 1,3-bis(trimethylsilyloxy)-1-ethoxy-1,3-butadiene (3.1 mmol, 0.87 g), 1,2-hexenoxide (0.31 g, 0.38 mL, $d = 0.831\ g\,cm^{-3}$, 3.1 mmol), and $TiCl_4$ (6.2 mmol, 0.68 mL, $d = 1.726\ g\,cm^{-3}$), **3c** was isolated after chromatography (silica gel, diethyl ether/petroleum ether = 1:3) as a colorless oil (286 mg, 44 %, $E/Z > 98{:}2$). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.85 – 0.91$ (m, 3H; $CH_2CH_2CH_3$), 1.19 – 1.41 (m, 7H; OCH_2CH_3, $CH_2CH_2CH_2CH_3$), 1.46 – 1.68 (m, 3H; 4-H, CH_2 to C-5), 2.09 – 2.26 (m, 1H; 4-H), 2.90 (dddd, $J = 18.3$, 9.2, 9.2, 1.9 Hz, 1H; 3-H), 3.26 (dddd, $J = 18.4$, 9.2, 4.0, 1.4 Hz, 1H; 3-H), 4.09 (q, 2H; OCH_2CH_3), 4.26 – 4.41 (m, 1H; 5-H), 5.21 – 5.22 (m, 1H; CHC=O); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 13.85$, 14.40 (OCH_2CH_3, CH_3), 22.47, 27.67, 29.12, 30.52, 34.55 (C-3, C-4, 3 × CH_2), 59.00 (OCH_2CH_3), 84.16, 89.00 (CHC=O, C-5), 168.69 (C=O), 176.47 (C-2); MS (70 eV, EI): *m*/*z* (%): 212 (89) [M^+], 167 (100), 103 (60), 85 (66), 43 (89); the exact molecular mass for $C_{12}H_{20}O_3$: *m*/*z* (%): 212.1412 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV).

2-(*E*)-(Ethoxycarbonylmethylidene)-5-(3-butenyl)tetrahydrofuran (3d): Starting with 1,3-bis(trimethylsilyloxy)-1-ethoxy-1,3-butadiene (0.97 g, 3.5 mmol), 5,6-epoxy-1-hexene (0.39 mL, $d = 0.870\ g\,cm^{-3}$, 3.5 mmol), and $TiCl_4$ (0.77 mL, $d = 1.726\ g\,cm^{-3}$, 7.0 mmol), **3d** was isolated after chromatography (silica gel, diethyl ether/petroleum ether 1:3) as a colorless oil (220 mg, 30 %, $E/Z > 98{:}2$). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.22$ (t, $J =$ 7.1 Hz, 3H; OCH_2CH_3), 1.58 – 1.84 (m, 4H; CH_2), 2.09 – 2.23 (m, 2H; 4-H), 2.91 (dddd, $J = 18.3$, 9.2, 9.2, 2.0 Hz, 1H; 3-H), 3.27 (dddd, $J = 18.4$, 9.1, 4.1, 1.4 Hz, 1H; 3-H), 4.09 (q, $J = 7.1$ Hz, 2H; OCH_2CH_3), 4.32 – 4.38 (m, 1H; 5-H), 4.94 – 5.07 (m, 2H; CH=CH_2), 5.22 – 5.24 (m, 1H; $CHCO_2Et$), 5.70 – 5.84 (m, 1H; CH=CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 14.37$ (OCH_2CH_3), 29.23, 29.70, 30.43, 33.96 (CH_2, C-3, C-4, C-1′, C-2′), 58.98 (OCH_2CH_3), 83.31 (C-5), 89.15 (CH=CO_2), 115.18 (CH=CH_2), 137.27 (CH=CH_2), 168.57 (C=O), 176.22 (C-2); MS (70 eV, EI): *m*/*z* (%): 210 (89) [M^+], 170 (45), 106 (60), 89 (66), 43 (100); the exact molecular mass for $C_{12}H_{18}O_3$: *m*/*z* (%): 210.1256 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV).

2-(*E*)-(Ethoxycarbonylmethylidene)-5-(benzyloxymethyl)tetrahydrofuran (3e): Starting with 1,3-bis(trimethylsilyloxy)-1-ethoxy-1,3-butadiene (0.97 g, 3.5 mmol), 1-(benzyloxy)-2-propenoxide (0.57 g, 3.5 mmol), and $TiCl_4$ (0.77 mL, $d = 1.726\ g\,cm^{-3}$, 7.0 mmol), **3e** was isolated after chromatography (silica gel, diethyl ether/petroleum ether = 1:3) as a colorless oil (560 mg, 58 %, $E/Z > 98{:}2$). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.26$ (t, $J =$ 7.1 Hz, 3H; OCH_2CH_3), 1.85 – 1.94 (m, 1H; 4-H), 2.10 – 2.16 (m, 1H; 4-H), 2.97 – 3.08 (m, 1H; 3-H), 3.20 – 3.27 (m, 1H; 3-H), 3.50 – 3.66 (m, 2H; CH_2OCH_2Ph), 4.12 (q, $J = 7.1$ Hz, 2H; OCH_2CH_3), 4.54 – 4.62 (m, 3H; 5-H, CH_2OCH_2Ph), 5.33 – 5.34 (m, 1H; CHC=O), 7.35 (m, 5H; Ph); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 14.36$ (OCH_2CH_3), 25.59, 30.15 (C-3, C-4), 59.07 (OCH_2CH_3), 71.21, 73.34 (CH_2OCH_2Ph, CH_2OCH_2Ph), 82.46, 89.59 (C-5, CHC=O), 127.56, 127.61, 128.32 (CH, Ph), 137.64 (C, Ph), 168.49 (C=O), 176.32 (C-2); IR (neat): $\tilde{\nu} = 3088$ (w), 3064 (w), 3031 (w), 2980 (m), 2937 (m), 2871 (m), 1722 (s), 1641 (m), 1453 (m), 1393 (m), 1372 (m), 1274 (s), 1113 (s), 1070 (m), 1048 cm^{-1} (m); MS (70 eV, EI): *m*/*z* (%): 276 (25) [M^+], 231 (36), 91 (100); the exact molecular mass for $C_{16}H_{20}O_4$: *m*/*z* (%): 276.1361 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV).

2-(*E*)-(Ethoxycarbonylmethylidene)-5-(chloromethyl)tetrahydrofuran (3f): Starting with 1,3-bis(trimethylsilyloxy)-1-ethoxy-1,3-butadiene (0.99 g, 3.6 mmol), epichlorohydrin (0.39 g, 0.33 mL, $d = 1.180\ g\,cm^{-3}$, 3.6 mmol), and $TiCl_4$ (0.79 mL, $d = 1.726\ g\,cm^{-3}$, 7.2 mmol), **3f** was isolated after chromatography (silica gel, diethyl ether/petroleum ether = 1:3) as a colorless oil (378 mg, 52 %, $E/Z > 98{:}2$). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta =$ 1.23 (t, $J = 7.1$ Hz, 3H; OCH_2CH_3), 1.89 – 2.04 (m, 1H; 4-H), 2.15 – 2.33 (m, 1H; 4-H), 2.93 – 3.11 (m, 1H; 3-H), 3.02 (dddd, $J = 18.5$ Hz, 9.1, 4.1, 1.5 Hz, 1H; 3-H), 3.62 (d, $J = 5.1$ Hz, 2H; CH_2Cl), 4.09 (q, $J = 7.1$ Hz, 2H; OCH_2CH_3), 4.56 – 4.71 (m, 1H; 5-H), 5.31 (m, 1H; $CHCO_2Et$); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 14.28$ (OCH_2CH_3), 26.67, 29.88 (C-3, C-4), 45.38 (CH_2Cl), 59.15 (OCH_2CH_3), 81.91 (C-5), 90.17 ($CHCO_2Et$), 168.15 (C=O, 175.30 (C-2); IR (neat): $\tilde{\nu} = 2961$ (s), 2938 (s), 1778 (s), 1713 (s), 1643 (s), 1461 (m), 1445 (m), 1428 (m), 1372 (s), 1331 (m), 1301 (m), 1174 (m), 1117 (s), 1048 cm^{-1} (s); MS (70 eV, EI): *m*/*z* (%): 204 (44) [M^+], 176 (13), 161 (34), 159 (100); the exact molecular mass for $C_9H_{13}O_3Cl$: *m*/*z* (%): 204.0553 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV).

2-(*E*)-(Ethoxycarbonylmethylidene)-5-(bromomethyl)tetrahydrofuran (3g): Starting with 1,3-bis(trimethylsilyloxy)-1-ethoxy-1,3-butadiene (0.60 g, 2.2 mmol), epibromohydrin (0.20 mL, $d = 1.655\ g\,cm^{-3}$, 2.2 mmol), and $TiCl_4$ (0.44 mL, $d = 1.726\ g\,cm^{-3}$, 4.4 mmol), **3g** was isolated after chromatography (silica gel, diethyl ether/petroleum ether = 1:3) as a colorless oil (260 mg, 48 %, $E/Z > 98{:}2$). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.22$ (t, $J = 7.1$ Hz, 3H; OCH_2CH_3), 1.83 – 2.01 (m, 1H; 4-H), 2.21 – 2.39 (m, 1H; 4-H), 2.94 – 3.05 (m, 1H; 3-H), 3.21 – 3.52 (m, 3H; 3-H, CH_2Br), 4.10 (q, $J = 7.1$ Hz, 2H; OCH_2CH_3), 4.55 – 4.65 (m, 1H; 5-H), 5.31 (m, 1H; CHC=O); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 14.28$ (OCH_2CH_3), 27.70, 29.91 (C-3, C-4), 33.61 (CH_2Br), 59.15 (OCH_2CH_3), 82.01 (C-5), 90.18 ($CHCO_2Et$), 168.25 (C=O), 176.130 (C-2); MS (70 eV, EI): *m*/*z* (%): 248 (60) [M^+], 203 (94), 176 (23), 69 (100); the exact molecular mass for $C_9H_{13}O_3Br$: *m*/*z* (%): 248.0048 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV).

***threo*-2-(*E*)-(Ethoxycarbonylmethylidene)-5-(bromoethyl)tetrahydrofuran (3h)**: Starting with 1,3-bis(trimethylsilyloxy)-1-ethoxy-1,3-butadiene (0.41 g, 1.5 mmol), *threo*-2-bromo-3,4-butenoxide (0.25 g, 1.5 mmol), and $TiCl_4$ (0.33 mL, $d = 1.726\ g\,cm^{-3}$, 3.0 mmol), **3h** was isolated after chromatography (silica gel, diethyl ether/petroleum ether = 1:3) as a colorless oil (161 mg, 41 %, $E/Z > 98{:}2$). ^{1}H NMR (250 MHz, [D$_6$]acetone): $\delta = 1.19$ (t, $J = 7.1$ Hz, 3H; OCH_2CH_3), 1.70 (d, $J = 6.9$ Hz, 3H; $CHBrCH_3$), 1.88 – 2.01 (m, 1H; 4-H), 2.24 – 2.39 (m, 1H; 4-H), 2.97 (dddd, $J = 18.5$, 9.8, 9.8, 1.8 Hz, 1H; 3-H), 3.31 (dddd, $J = 18.5$, 9.8, 4.3, 1.6 Hz, 1H; 3-H), 3.05 (q, $J = 7.1$ Hz, 2H; OCH_2CH_3), 4.28 – 4.38 (m, 1H; $CHBrCH_3$), 4.52 – 4.60 (m, 1H; 5-H),

5.19 (dd, $J = 1.7$, 1.7 Hz, 1H; C*H*CO_2Et); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 13.94$ (OCH_2CH_3), 21.42 ($CHBrCH_3$), 26.80, 30.29 (C-3, C-4), 51.06 (*C*HBrCH_3), 58.58 (OCH_2CH_3), 86.43 (C-5), 89.04 (*C*HC=O), 167.44 (C=O), 176.18 (C-2); MS (70 eV, EI): *m/z* (%): 262 (50) [M^+], 217 (66), 155 (26), 137 (88), 109 (30), 87 (36), 69 (100).

2-(*E*)-[1-(Methoxycarbonyl)methylidene]-5-(ethoxycarbonylethyl)tetrahydrofuran (3i): Starting with 1,3-bis(trimethylsilyloxy)-1-methoxy-1,3-butadiene (0.83 g, 3.2 mmol), ethyl 4,5-epoxypentanoate (0.47 g, 3.2 mmol), and $TiCl_4$ (0.70 mL, $d = 1.726$ g cm^{-3}, 6.2 mmol), **3i** was isolated after chromatography (silica gel, diethyl ether/petroleum ether = 1:3) as a colorless oil (418 mg, 51%, $E/Z > 98:2$). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta =$ 1.24 (t, $J = 7.1$ Hz, 3H; OCH_2CH_3), 1.61 – 2.01 (m, 3H; CH_2CH_2C=O, 4-H), 2.13 – 2.26 (m, 1H; 4-H), 2.33 – 2.51 (m, 2H; CH_2CH_2C=O), 2.92 (dddd, $J =$ 18.2, 9.0, 9.0, 2.0 Hz, 1H; 3-H), 3.27 (dddd, $J = 18.5$, 9.1, 4.2, 1.5 Hz, 1H; 3-H), 3.63 (s, 3H; OCH_3), 4.12 (q, $J = 7.1$ Hz, 2H; OCH_2CH_3), 4.35 – 4.45 (m, 1H; 5-H), 5.22 – 5.25 (m, 1H; CHC=O); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.15$ (OCH_2CH_3), 29.02, 29.10, 29.97 (C-3, C-4, CH_2CH_2C=O), 49.85 (CH_2CH_2C=O), 50.60 (OCH_3), 60.53 (OCH_2CH_3), 82.88 (C-5), 89.11 (*C*HC=O), 168.97, 172.76 (2 × C=O), 176.18 (C-2); MS (70 eV, EI): *m/z* (%): 242 (22) [M^+], 210 (70), 169 (23), 122 (100), 118 (58); the exact molecular mass for $C_{12}H_{18}O_5$: *m/z* (%): 242.1154 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV).

2-(*E*)-[1-(Ethoxycarbonyl)ethylidene]-5-(ethoxycarbonylmethyl)tetrahydrofuran (3j): Starting with 1,3-bis(trimethylsilyloxy)-1-ethoxy-2-methyl-1,3-butadiene (0.43 g, 1.5 mmol), ethyl 3,4-epoxybutanoate (0.16 g, 1.2 mmol), and $TiCl_4$ (0.27 mL, $d = 1.726$ g cm^{-3}, 2.4 mmol), **3j** was isolated after chromatography (silica gel, diethyl ether/petroleum ether = 1:3) as a colorless oil (154 mg, 50%, $E/Z > 98:2$). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta =$ 1.22 (t, $J = 7.1$ Hz, 6H; 2 × OCH_2CH_3), 1.64 – 1.79 (m, 4H; 4-H, CCH_3), 2.18 – 2.31 (m, 1H; 4-H′), AB signal ($\delta_A = 2.51$, $\delta_B = 2.69$, $J_{A,B} = 15.6$ Hz, $J_{A,X} = 6.4$, $J_{B,X} = 6.0$ Hz, 2H; CH_2C=O), 2.91 (dddd, $J = 18.2$, 9.0, 9.0, 1.7 Hz, 1H; 3-H), 3.16 (dddd, $J = 18.2$, 7.4, 4.4, 1.3 Hz, 1H; 3-H′), 4.19 (m, 4H; 2 × OCH_2CH_3), 4.87 (quint, $J = 7.0$ Hz, 1H; 2-H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 11.19$ (CCH_3), 14.06, 14.35 (2 × OCH_2CH_3), 29.73, 30.66 (C-3, C-4), 39.94 (CH_2C=O), 59.37, 60.61 (2 × OCH_2CH_3), 78.77 (C-5), 97.94 (CH_3CC=O), 169.04, 169.13, 170.03 (C-2, 2 × C=O); IR (neat): $\tilde{\nu} = 3466$ (br), 2984 (s), 2941 (m), 1778 (s), 1733 (s), 1643 (w), 1448 (m), 1371 (s), 1300 (s), 1260 (s), 1176 (s), 1113 (s), 1026 cm^{-1} (s); MS (70 eV, EI): *m/z* (%): 256 (20) [M^+], 210 (72), 122 (100); the exact molecular mass for $C_{13}H_{20}O_5$: *m/z* (%): 256.1310 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV); elemental analysis calcd (%) for $C_{13}H_{20}O_5$ (256.3): C 60.92, H 7.87; found: C 60.74, H 7.77.

2-(*E*)-[1-(Ethoxycarbonyl)ethylidene]-5-ethyltetrahydrofuran (3k): Starting with 1,3-bis(trimethylsilyloxy)-1-ethoxy-2-methyl-1,3-butadiene (0.75 g, 2.6 mmol), butenoxide (0.20 mL, $d = 1.180$ g cm^{-3}, 2.6 mmol). and $TiCl_4$ (0.57 mL, $d = 1.726$ g cm^{-3}, 5.2 mmol), **3k** was isolated after chromatography (silica gel, diethyl ether/petroleum ether = 1:3) as a colorless oil (298 mg, 58%, $E/Z > 98:2$). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.96$ (t, $J =$ 7.0 Hz, 3H; CH_2CH_3), 1.23 (t, $J = 7.1$ Hz, 3H; OCH_2CH_3), 1.50 – 1.76 (m, 3H; CH_2CH_3, 4-H), 1.79 (t, $J = 1.5$ Hz, 3H; CH_3), 2.05 – 2.20 (m, 1H; 4-H), 2.92 (dddd, $J = 18.1$, 9.1, 9.1, 1.6 Hz, 1H; 3-H), 3.20 (dddd, $J = 18.1$, 7.4, 4.4, 1.3 Hz, 1H; 3-H′), 4.12 (q, $J = 7.0$ Hz, 2H; OCH_2CH_3), 4.26 (quint, $J =$ 6.8 Hz, 1H; 5-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 9.83$, 11.25 (CH_3), 14.45 (OCH_2CH_3), 28.02, 29.41, 31.16 (C-3, C-4, CCH_2CH_3), 59.32 (OCH_2CH_3), 84.51 (C-5), 96.94 (CCO_2Et), 169.49, 170.26 (C-2, C=O); MS (70 eV, EI): *m/z* (%): 198 (74) [M^+], 169 (12), 153 (100); the exact molecular mass for $C_{11}H_{18}O_3$: *m/z* (%): 198.1256 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV).

2-(*E*)-[1-(Ethoxycarbonyl)ethylidene]-5-(3-butenyl)tetrahydrofuran (3l): Starting with 1,3-bis(trimethylsilyloxy)-1-ethoxy-2-methyl-1,3-butadiene (0.75 g, 2.6 mmol), 5,6-epoxy-1-hexene (0.29 mL, $d = 0.870$ g cm^{-3}, 3.5 mmol), and $TiCl_4$ (0.57 mL, $d = 1.726$ g cm^{-3}, 5.2 mmol), **3l** was isolated after chromatography (silica gel, diethyl ether/petroleum ether = 1:3) as a colorless oil (186 mg, 32%, $E/Z > 98:2$). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta =$ 1.26 (t, $J = 7.0$ Hz, 3H; OCH_2CH_3), 1.20 – 1.40 (m, 2H; CH_2), 1.60 – 1.80 (m, 2H; CH_2), 1.84 (t, $J = 1.5$ Hz, 3H; CH_2), 2.10 – 2.30 (m, 2H; CH_2), 2.93 (dddd, $J = 18.2$, 9.2, 9.2, 1.9 Hz, 1H; 3-H), 3.24 (dddd, $J = 18.4$, 9.2, 4.1, 1.4 Hz, 1H; 3-H), 4.15 (q, $J = 7.0$ Hz, 2H; OCH_2CH_3), 4.30 – 4.42 (m, 1H; 5-H), 4.95 – 5.10 (m, 2H; CH=CH_2), 5.74 – 5.95 (m, 1H; C*H*=CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 12.32$, 15.61 (CH_3), 30.01, 30.12, 31.89, 35.02 (CH_2, C-3, C-4, C-1′, C-2′), 59.60 (OCH_2CH_3), 83.22 (C-5), 97.60 (*C*=CO_2Et), 115.81 (CH=*C*H_2), 137.60 (*C*H=CH_2), 168.88 (C=O), 170.02 (C-2); MS (70 eV, EI): *m/z* (%): 224 (58) [M^+], 195 (42), 179 (100); the exact molecular mass for $C_{13}H_{20}O_3$: *m/z* (%): 224.1412 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV).

2-(*E*)-[1-(Ethoxycarbonyl)ethylidene]-5-(chloromethyl)tetrahydrofuran (3m): Starting with 1,3-bis(trimethylsilyloxy)-1-ethoxy-2-methyl-1,3-butadiene (0.75 g, 2.6 mmol), epichlorohydrin (0.20 mL, $d = 1.180$ g cm^{-3}, 2.6 mmol), and $TiCl_4$ (0.57 mL, $d = 1.726$ g cm^{-3}, 5.2 mmol), **3m** was isolated after chromatography (silica gel, diethyl ether/petroleum ether = 1:3) as a colorless oil (250 mg, 45%, $E/Z > 98:2$). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.25$ (t, $J = 7.1$ Hz, 3H; OCH_2CH_3), 1.79 (t, $J = 1.6$ Hz, 3H; CH_3), 1.82 – 2.02 (m, 1H; 4-H), 2.16 – 2.30 (m, 1H; 4-H), 2.92 – 3.07 (m, 1H; 3-H), 3.14 – 3.27 (m, 1H; 3-H), 3.54 – 3.69 (m, 2H; CH_2Cl), 4.12 (q, $J =$ 7.1 Hz, 2H; OCH_2CH_3), 4.55 – 4.64 (m, 1H; 5-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 11.02$ (CH_3), 14.12 (OCH_2CH_3), 27.18, 30.31 (C-3, C-4), 45.39 (CH_2Cl), 59.29 (OCH_2CH_3), 81.13 (C-5), 97.12 (CCO_2Et), 168.83, 168.99 (C-2, C=O); MS (70 eV, EI): *m/z* (%): 218 (80) [M^+], 172 (100), 146 (24), 137 (48), 83 (94); the exact molecular mass for $C_{10}H_{15}O_3Cl$: *m/z* (%): 218.0710 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV).

2-(*E*)-[1-(Ethoxycarbonyl)propylidene]-5-methyltetrahydrofuran (3n): Starting with 1,3-bis(trimethylsilyloxy)-1-ethoxy-2-ethyl-1,3-butadiene (0.70 g, 2.3 mmol), 1,2-propenoxide (0.17 mL, $d = 0.829$ g cm^{-3}, 2.3 mmol), and $TiCl_4$ (0.51 mL, $d = 1.726$ g cm^{-3}, 4.6 mmol), **3n** was isolated after chromatography (silica gel, diethyl ether/petroleum ether = 1:3) as a colorless oil (228 mg, 50%, $E/Z > 98:2$). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.97$ (t, $J = 7.4$ Hz, 3H; CH_2CH_3), 1.26 (t, $J = 7.1$ Hz, 3H; OCH_2CH_3), 1.33 (d, $J = 6.4$ Hz, 3H; CH_3 to C-5), 1.37 – 1.69 (m, 1H; 4-H), 2.11 – 2.23 (m, 1H; 4-H), 2.30 (q, $J = 7.4$ Hz, 2H; CH_2CH_3), 2.93 (ddd, $J = 9.0$, 9.0, 9.0 Hz, 1H; 3-H), 3.21 (ddd, $J = 18.4$, 9.1, 4.6 Hz, 1H; 3-H), 4.13 (q, $J =$ 7.1 Hz, 2H; OCH_2CH_3), 4.42 – 4.55 (m, 1H; 5-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 13.80$, 14.47, 20.57 (3 × CH_3), 19.38 (CH_2CH_3), 31.47, 31.53 (C-3, C-4), 59.22 (OCH_2CH_3), 79.38 (C-5), 103.97 (*C*C=O), 169.25, (C=O), 170.16 (C-2); MS (70 eV, EI): *m/z* (%): 198 (60) [M^+], 171 (49), 149 (100), 73 (88); the exact molecular mass for $C_{11}H_{18}O_3$: *m/z* (%): 198.1256 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV).

2-(*E*)-[1-(Ethoxycarbonyl)propylidene]-5-(bromomethyl)tetrahydrofuran (3o): Starting with 1,3-bis(trimethylsilyloxy)-1-ethoxy-2-ethyl-1,3-butadiene (0.91 g, 3.0 mmol), epibromohydrin (0.27 mL, 3.0 mmol, $d =$ 1.655 g cm^{-3}), and $TiCl_4$ (0.66 mL, $d = 1.726$ g cm^{-3}, 6.0 mmol), **3o** was isolated after chromatography (silica gel, diethyl ether/petroleum ether = 1:3) as an orange solid (366 mg, 44%, $E/Z > 98:2$). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.94$ (t, $J = 7.3$ Hz, 3H; CH_2CH_3), 1.23 (t, $J = 7.2$ Hz, 3H; OCH_2CH_3), 1.84 – 1.99 (m, 1H; 3-H), 2.15 – 2.31 (m, 3H; CH_2CH_3, 3-H′), 2.89 – 3.04 (m, 1H; 4-H), 3.18 (ddd, $J = 18.4$, 9.5, 5.3 Hz, 1H; 4-H′), AB signal ($\delta_A = 3.41$, $\delta_B = 3.47$, $J_{AB} = 10.4$, $J_{A,X} = 6.2$, $J_{B,X} = 4.9$ Hz, 2H; CH_2Br), 4.10 (q, $J = 7.2$ Hz, 2H; OCH_2CH_3), 4.52 – 4.62 (m, 1H; 5-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 13.60$ (CH_2CH_3), 14.32 (OCH_2CH_3), 19.32 (CH_2CH_3), 28.27, 30.58 (C-3, C-4), 33.77 (CH_2Br), 59.31 (OCH_2CH_3), 80.85 (C-5), 105.02 (*C*HC=O), 168.70, 168.90 (C-2, C=O); IR (neat): $\tilde{\nu} =$ 2975 (s), 2937 (m), 1781 (m), 1731 (s), 1698 (s), 1634 (s), 1461 (m), 1445 (m), 1370 (m), 1298 (m), 1254 (s), 1189 (s), 1166 (m), 1099 cm^{-1} (s); MS (70 eV, EI): *m/z* (%): 276 (36) [M^+], 231 (42), 197 (50), 151 (100); the exact molecular mass for $C_{11}H_{17}O_3Br$: *m/z* (%): 276.0361 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV); elemental analysis calcd (%) for $C_{11}H_{17}O_3Br$ (277.2): C 47.67, H 6.18; found: C 47.82, H 6.03.

2-(*E*)-(Methoxycarbonylmethylidene)-3-methyl-5-ethyltetrahydrofuran (3p): Starting with 1-methoxy-1,3-bis(trimethylsilyloxy)-1,3-pentadiene (0.52 g, 2.0 mmol), 1,2-butenoxide (0.17 mL, $d = 0.837$ g cm^{-3}, 2.0 mmol), and $TiCl_4$ (0.44 mL, $d = 1.726$ g cm^{-3}, 4.0 mmol), **3p** was isolated after chromatography (silica gel, diethyl ether/petroleum ether = 1:3) as a colorless oil (169 mg, 46%, $E/Z = 5:1$, $ds = 4:1$). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.96$ (t, $J = 7.5$ Hz, 3H; CH_2CH_3), 1.22 (d, $J = 7.2$ Hz, 3H; $CHCH_3$), 1.33 – 1.88 (m, 4H; CH_2CH_3, 4-H), 3.62 (s, 3H; OCH_3), 3.63 – 3.76 (m, 1H; 3-H), 4.33 – 4.42 (m, 1H; 5-H), 5.15, 5.21 (2 × m, 1H; C*H*C=O, both diastereomers); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 9.72$ (CH_2CH_3), 18.67 (CH_3 to C-3), 27.86 (CH_2CH_3), 37.02 (C-3), 37.41 (C-4), 50.49 (OCH_3), 83.37, 87.80 (*C*HC=O, C-5), 168.32 (C-2), 181.10 (C=O); MS (70 eV, EI): *m/z* (%): 184 (68) [M^+], 179 (4), 166 (9), 155 (10), 139 (100); the exact molecular mass for $C_{10}H_{16}O_3$: *m/z* (%): 184.1099 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV).

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2-(*E*)-(Phenylcarbonylmethylidene)-5-ethyltetrahydrofuran (3q): Starting with 1,3-bis(trimethylsilyloxy)-1-phenyl-1,3-butadiene (0.58 g, 1.9 mmol), 1,2-butenoxide (0.16 mL, $d = 0.837\,g\,cm^{-3}$, 1.9 mmol), and $TiCl_4$ (0.42 mL, $d = 1.726\,g\,cm^{-3}$, 3.8 mmol), **3q** was isolated after chromatography (silica gel, diethyl ether/petroleum ether = 1:3) as an orange oil (255 mg, 62%, $E/Z > 98:2$). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.02$ (t, $J = 7.3$ Hz, 3H; CH_2CH_3), 1.59–1.83 (m, 3H; 4-H, CH_2CH_3), 2.19–2.32 (m, 1H; 4-H), 3.14 (dddd, $J = 14.3$, 9.2, 9.2, 1.9 Hz, 1H; 3-H), 3.49 (dddd, $J = 17.9$, 9.8, 4.4, 1.5 Hz, 1H; 3-H), 4.35–4.46 (m, 1H; 5-H), 6.50–6.51 (m, 1H; CHC=O), 7.30–7.53 (m, 3H; Ph), 7.88–7.92 (m, 2H; Ph); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 9.72$ (CH_2CH_3), 27.79, 28.59, 31.79 (C-3, C-4, CH_2CH_3), 85.62 (C-5), 94.61 (CHC=O), 127.41, 128.17, 131.51 (CH, Ph), 139.76 (C, Ph), 179.13 (C-2), 190.24 (C=O); IR (neat): $\tilde{\nu} = 3084$ (w), 3061 (w), 3030 (w), 2966 (s), 2933 (s), 2879 (m), 2855 (m), 1654 (s), 1587 (s), 1571 (m), 1456 (m), 1447 (m), 1386 (s), 1167 cm^{-1} (s); MS (70 eV, EI): *m/z* (%): 216 (70) [M^+], 201 (100), 176 (13), 161 (20), 139 (22), 119 (45); the exact molecular mass for $C_{14}H_{16}O_2$: *m/z* (%): 216.1150 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV); elemental analysis calcd (%) for $C_{14}H_{16}O_2$ (216.3): C 77.75, H 7.46; found: C 76.88, H 7.60.

2-(*E*)-(Phenylcarbonylmethylidene)-5-(chloromethyl)tetrahydrofuran (3r): Starting with 1,3-bis(trimethylsilyloxy)-1-phenyl-1,3-butadiene (0.67 g, 2.2 mmol), epichlorohydrin (0.17 mL, $d = 1.180\,g\,cm^{-3}$, 2.2 mmol), and $TiCl_4$ (0.48 mL, $d = 1.726\,g\,cm^{-3}$, 4.4 mmol), **3r** was isolated after chromatography (silica gel, diethyl ether/petroleum ether = 1:3) as a colorless oil (265 mg, 51%, $E/Z > 98:2$). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.98–2.13$ (m, 1H; 4-H), 2.26–2.37 (m, 1H; 4-H), 3.16–3.31 (m, 1H; 3-H), 3.42–3.56 (m, 1H; 3-H), 3.69 (dd, $J = 5.1$, 0.9 Hz, 2H; CH_2Cl), 4.68–4.78 (m, 1H; 5-H), 6.58 (t, $J = 1.7$ Hz, 1H; $CHCO_2Et$), 7.39–7.53 (m, 3H; Ph), 7.88–7.93 (m, 2H; Ph); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 26.59$, 31.16 (C-3, C-4), 45.44 (CH_2Cl), 82.10 (C-5), 95.29 (*C*HCOPh), 127.40, 128.22, 131.71 (*C*H, Ph), 139.37 (C, Ph), 177.69 (C-2), 190.06 (*C*OPh); IR (KBr): $\tilde{\nu} = 3099$ (w), 3083 (w), 3055 (w), 2984 (w), 2919 (w), 1663 (s), 1598 (s), 1583 (s), 1566 (s), 1383 (m), 1374 (m), 1167 cm^{-1} (s); MS (70 eV, EI): *m/z* (%): 236 (100) [M^+], 159 (52), 105 (46), 77 (33), 69 (48); the exact molecular mass for $C_{13}H_{13}O_2Cl$: *m/z* (%): 236.0604 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV); elemental analysis calcd (%) for $C_{13}H_{13}O_2Cl$ (236.7): C 65.97, H 5.54; found: C 66.10, H 5.61.

2-(*E*)-(Phenylcarbonylmethylidene)-5-(bromomethyl)tetrahydrofuran (3s): Starting with 1,3-bis(trimethylsilyloxy)-1-phenyl-1,3-butadiene (0.74 g, 2.4 mmol), epibromohydrin (0.21 mL, $d = 1.655\,g\,cm^{-3}$, 2.4 mmol), and $TiCl_4$ (0.53 mL, $d = 1.726\,g\,cm^{-3}$, 4.8 mmol), **3s** was isolated after chromatography (silica gel, diethyl ether/petroleum ether = 1:3) as an orange solid (298 mg, 44%, $E/Z > 98:2$). ^1H NMR (250 MHz, $CDCl_3$): $\delta =$ 1.92–2.04 (m, 1H; 4-H), 2.25–2.33 (m, 1H; 4-H), 3.14–3.26 (m, 1H; 3-H), 3.40–3.54 (m, 3H; 3-H, CH_2Br), 4.64–4.70 (m, 1H; 5-H), 6.54–6.56 (m, 1H; CHC=O), 7.36–7.50 (m, 3H; Ph), 7.86–7.90 (m, 2H; Ph); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 27.78$, 31.24 (C-3, C-4), 33.43 (CH_2Br), 81.85 (C-5), 95.34 (*C*HC=O), 127.42, 128.23, 131.73 (CH, Ph), 139.36 (C, Ph), 177.64 (C-2) 190.09 (C=O); IR (KBr): $\tilde{\nu} = 3098$ (w), 3054 (w), 3026 (w), 2981 (w), 2945 (w), 2917 (w), 1660 (s), 1596 (s), 1567 (s), 1457 (m), 1433 (m), 1380 (s), 1165 cm^{-1} (s); MS (70 eV, EI): *m/z* (%): 280 (60) [M^+], 203 (24), 180 (18), 147 (35), 122 (33), 105 (100); the exact molecular mass for $C_{13}H_{13}O_2Br$: *m/z* (%): 280.0099 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV); elemental analysis calcd (%) for $C_{13}H_{13}O_2Br$ (281.1): C 55.54, H 4.66; found: C 55.32, H 4.46.

2-(*E*)-[1-(Phenylcarbonyl)methylidene]-5-(ethoxycarbonylmethyl)tetrahydrofuran (3t): Starting with 1,3-bis(trimethylsilyloxy)-1-phenyl-1,3-butadiene (0.18 g, 0.6 mmol), 3,4-ethyl epoxybutanoate (0.08 g, 0.6 mmol), and $TiCl_4$ (0.13 mL, $d = 1.726\,g\,cm^{-3}$, 1.2 mmol), **3t** was isolated after chromatography (silica gel, ether/petroleum ether = 1:3) as a colorless oil (68 mg, 41%, $E/Z > 98:2$). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.28$ (t, $J =$ 7.1 Hz, 3H; OCH_2CH_3), 1.76–1.91 (m, 1H; 4-H), 2.31–2.44 (m, 1H; 4-H), AB signal ($\delta_A = 2.61$, $\delta_B = 2.74$, $J_{AB} = 16.0$, $J_{A,X} = 6.0$, $J_{B,X} = 7.2$ Hz, 2H; CH_2C=O), 3.16 (dddd, $J = 18.0$, 9.1, 9.1, 1.9 Hz, 1H; 3-H), 3.48 (dddd, $J =$ 19.2, 9.1, 4.3, 1.4 Hz, 1H; 3-H), 4.19 (q, $J = 7.1$ Hz, 2H; OCH_2CH_3), 4.87 (quint, $J = 7.0$ Hz, 1H; 2-H), 6.53 (t, $J = 1.7$ Hz, 1H; CHC=O), 7.38–7.52 (m, 3H; Ph), 7.87–7.91 (m, 2H; Ph); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta =$ 14.12 (OCH_2CH_3), 29.09, 31.38 (C-3, C-4), 39.73 (CH*C*H$_2$C=O), 60.90 (OCH_2CH_3), 79.73 (C-5), 95.41 (*C*HC=O), 127.52, 128.30, 131.73 (CH, Ph), 139.63 (C, Ph), 169.91 (C=O), 177.89 (C-2), 190.29 (C=O); MS (70 eV, EI): *m/z* (%): 274 (40) [M^+], 186 (100), 122 (22), 117 (34), 105 (64); the exact molecular mass for $C_{16}H_{18}O_4$: *m/z* (%): 274.1205 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV); elemental analysis calcd (%) for $C_{16}H_{18}O_4$ (274.3): C 70.06, H 6.61; found: C 69.72, H 6.63.

2-(*E*)-(3-Methoxy-2-oxopropylidene)-5-(chloromethyl)tetrahydrofuran (3u): Starting with 2,4-bis(trimethylsilyloxy)-1-methoxy-2,4-pentadiene (0.49 g, 1.8 mmol), epichlorohydrin (0.14 mL, $d = 1.180\,g\,cm^{-3}$, 1.8 mmol), and $TiCl_4$ (0.40 mL, $d = 1.726\,g\,cm^{-3}$, 3.6 mmol), **3u** was isolated after chromatography (silica gel, diethyl ether/petroleum ether = 1:3) as a colorless oil (165 mg, 45%, $E/Z > 98:2$). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.82–2.03$ (m, 1H; 4-H), 2.10–2.31 (m, 1H; 4-H′), 2.92–3.10 (m, 1H; 3-H), 3.17–3.44 (m, 1H; 3-H), 3.31 (s, 3H; OCH_3), 3.55–3.70 (m, 2H; CH_2Cl), 3.88 (s, 2H; CH_2OCH_3), 4.55–4.73 (m, 1H; 5-H), 5.94 (m, 1H; $CHCO_2Et$); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 26.37$, 31.05 (C-3, C-4), 45.33 (CH_2Cl), 58.93 (OCH_3), 77.58 (CH_2OCH_3), 82.08 (C-5), 94.14 (*C*HCOCH$_2$), 177.14 (C-2), 197.08 (*C*OCH$_2$); MS (70 eV, EI): *m/z* (%): 204 (67) [M^+], 176 (34), 161 (27), 159 (100); the exact molecular mass for $C_9H_{13}O_3Cl$: *m/z* (%): 204.0553 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV).

2-(*E*)-(3-Methoxy-2-oxopropylidene)-5-ethyltetrahydrofuran (3v): Starting with 2,4-bis(trimethylsilyloxy)-1-methoxy-2,4-pentadiene (0.96 g, 3.5 mmol), 1,2-butenoxide (0.30 mL, 3.5 mmol, $d = 0.837\,g\,cm^{-3}$), and $TiCl_4$ (0.77 mL, $d = 1.726\,g\,cm^{-3}$, 7.0 mmol), **3v** was isolated after chromatography (silica gel, diethyl ether/petroleum ether = 1:3) as a colorless oil (258 mg, 40%, $E/Z > 98:2$). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.96$ (t, $J =$ 7.5 Hz, 3H; CH_2CH_3), 1.53–1.77 (m, 3H; 4-H, CH_2CH_3), 2.12–2.25 (m, 1H; 4-H), 2.99 (dddd, $J = 18.3$, 9.1, 9.1, 1.8 Hz, 1H; 3-H), 3.27–3.42 (m, 4H; OCH_3, 3-H), 3.92 (s, 2H; CH_2OCH_3), 4.32–4.38 (m, 1H; 5-H), 5.92 (s, 1H; *C*HC=OCH$_2$); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 9.73$ (CH_2CH_3), 27.82, 28.54, 31.77 (CH_2CH_3, C-3, C-4), 59.12 (OCH_3), 77.79 (CH_2OCH_3), 85.75 (C-5), 93.53 (*C*HC=O), 178.59 (C-2), 197.23 (C=O); MS (70 eV, DCI, NH_3): *m/z* (%): 185 (100) [M+1$^+$], 202 (82) [M+18$^+$].

2-Oxo-3-(1-trimethylsilyloxy)ethenyl-4,5-dihydrofuran (5a): Triethylamine (11.36 mL, 81.9 mmol, $d = 0.73\,g\,cm^{-3}$) was added to a solution (250 mL) of 3-acetyl-2-oxo-4,5-dihydrofuran (7.0 g, 54.6 mmol, $d = 1.19\,g\,cm^{-3}$) in benzene at 0 °C. The solution was stirred for 30 min, and subsequently trimethylchlorosilane (12.42 mL, 98.3 mmol, $d = 0.83\,g\,cm^{-3}$) was slowly added. The solution was warmed to ambient temperature over 6 h and subsequently stirred for 18 h. The solvent was removed in vacuo, and pentane was added to the residue (100 mL). The suspension was filtered under nitrogen, and the filtrate was concentrated in vacuo to give **5a** as a slightly yellow oil (10.06 g, 92%). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.20$ (s, 9H; $Si(CH_3)_3$), 2.25 (t, $J = 1.5$ Hz, 3H; CCH_3), 2.77 (tt, $J = 7.5$, 1.5 Hz, 2H; 4-H), 4.15 (t, $J = 7.5$ Hz, 2H; 5-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 0.87$ ($Si(CH_3)_3$), 18.47 (C*C*H$_3$), 25.99 (C-4), 64.22 (C-5), 104.55 (C-3), 162.39 (Me_3SiOC), 172.31 (C-2); MS (70 eV, EI): *m/z* (%): 200 (23) [M^+], 185 (100), 141 (19), 110 (9), 73 (47); the exact molecular mass for $C_9H_{16}O_3Si$: *m/z* (%): 200.0868 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV).

5-Ethyl-2-oxo-3-(1-trimethylsilyloxy)ethenyl-4,5-dihydrofuran (5b): Triethylamine (2.56 mL, 18.5 mmol, $d = 0.73\,g\,cm^{-3}$) and trimethylchlorosilane (2.81 mL, 22.5 mmol, $d = 0.83\,g\,cm^{-3}$) at 0 °C were slowly added to a solution (50 mL) of 3-acetyl-5-ethyl-2-oxo-4,5-dihydrofuran (1.93 g, 12.36 mmol) in benzene. The solution was stirred for 30 min, warmed to ambient temperature over 6 h, and subsequently stirred at 20 °C for 48 h. The solvent was removed in vacuo, and pentane (20 mL) was added to the residue. The suspension was filtered under nitrogen, and the filtrate was concentrated in vacuo to give **5b** as a slightly yellow oil (2.57 g, 91%). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.23$ (s, 9H; $Si(CH_3)_3$), 0.94 (t, $J = 6.9$ Hz, 3H; CH_2CH_3), 1.62 (dq, $J = 6.9$, 7.3 Hz, 2H; CH_2CH_3), 2.28 (t, $J = 1.9$ Hz, 3H; CH_3), 2.25–2.35 (m, 1H; 4-H), 2.88 (dq, $J = 7.3$, 1.9 Hz, 1H; 4-H), 4.22–4.33 (m, 1H; 5-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 0.93$ ($Si(CH_3)_3$), 18.63 (CH_3), 29.29 (CH_2CH_3), 31.57 (C-4), 77.36 (C-5), 105.78 (C-3), 162.06 (R_3SiOC), 172.01 (C-2); MS (70 eV, EI): *m/z* (%): 228 (15) [M^+], 213 (100), 171 (79), 147 (44), 127 (50); the exact molecular mass for $C_{11}H_{20}O_3Si$: *m/z* (%): 228.1182 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV).

2,1′-Bis(trimethylsilyloxy)-(3-ethylene)-4,5-dihydrofuran (6a): *n*-Butyllithium (7.25 mL, 17.15 mmol, 2.36 M solution in *n*-hexane) was added to a solution (20 mL) of diisopropylamine (2.25 mL, 16.00 mmol, $d =$ 0.72 $g\,cm^{-3}$) in THF, and the solution was stirred for 30 min. This solution was added to a solution (50 mL) of 2-oxo-3-(1-trimethylsilyloxy)ethenyl-4,5-dihydrofuran **5a** (1.93 g, 12.36 mmol) in THF at −78 °C. The solution was stirred for 25 min, and subsequently trimethylchlorosilane (2.31 mL,

18.29 mmol, $d = 0.83\ g\,cm^{-3}$) was added. After stirring for 10 min at $-78\,^{\circ}C$, the solution was warmed to $20\,^{\circ}C$ over 45 min. The solvent was removed in vacuo, and pentane (20 mL) was added to the residue. The suspension was filtered under nitrogen, and the filtrate was concentrated in vacuo to give **6a** as a yellow oil (2.96 g, 95%). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.20, 0.24$ ($2 \times s$, $2 \times 9H$; $Si(CH_3)_3$), 2.75 (t, $J = 7.5$ Hz, 2H; 4-H), 3.88 (s, 1H; *cis*, $H_2C{=}C$), 3.98 (s, 1H; *trans*, $H_2C{=}C$), 4.24 (t, $J = 7.5$ Hz, 2H; 5-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 0.53, 0.93$ ($Si(CH_3)_3$), 30.18 (C-4), 66.04 (C-5), 81.66 ($C{=}CH_2$), 86.83 (C-3), 153.26 (Me_3SiOC), 155.05 (C-2); MS (70 eV, EI): *m*/*z* (%): 273 (18) [M^+], 257 (20), 245 (16), 185 (100), 158 (77).

2,1′-Bis(trimethylsilyloxy)-5-ethyl-3-ethylene-4,5-dihydrofuran (6b): *n*-Butyllithium (3.71 mL, 2.36 M solution in *n*-hexane, 8.77 mmol) was added to a solution (20 mL) of diisopropylamine (1.32 mL, 9.39 mmol, $d = 0.72\ g\,cm^{-3}$) in THF, and the solution was stirred for 30 min. This solution was added to a solution (50 mL) of 5-ethyl-2-oxo-3-(1-trimethylsilyloxy)ethenyl-4,5-dihydrofuran **5b** (1.43 g, 6.26 mmol) in THF at $-78\,^{\circ}C$. The solution was stirred for 25 min, and subsequently trimethylchlorosilane (1.34 mL, 10.65 mmol, $d = 0.83\ g\,cm^{-3}$) was slowly added. After stirring for 10 min at $-78\,^{\circ}C$, the solution was warmed to $20\,^{\circ}C$ over 45 min. The solvent was removed in vacuo, and pentane (20 mL) was added to the residue. The suspension was filtered under nitrogen, and the filtrate was concentrated in vacuo to give **6b** as a yellow oil (1.77 g, 94%). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.20, 0.26$ ($2 \times s$, $2 \times 9H$; $Si(CH_3)_3$), 0.95 (t, $J = 7.5$ Hz, 3H; CH_2CH_3), 1.57–1.69 (m, 2H; CH_2CH_3), 2.32–2.40 (m, 1H; 4-H), 2.72–2.83 (m, 1H; 4-H), 3.82 (s, 1H; *cis*, $H_2C{=}C$), 3.92 (s, 1H; *trans*, $H_2C{=}C$), 4.20–4.35 (m, 1H; 5-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 0.10, 0.51$ ($Si(CH_3)_3$), 9.38 (CH_3), 29.24 (CH_2CH_3), 35.38 (C-4), 78.96 (C-5), 81.22 ($C{=}CH_2$), 86.41 (C-3), 153.44 (Me_3SiOC), 158.32 (C-2); MS (70 eV, EI): *m*/*z* (%): 299 (11) [M^+], 213 (32), 171 (30), 147 (100), 73 (77).

General procedure for the synthesis of 2-alkylidenetetrahydrofurans (7): The compound 1,2-butenoxide (0.135 mL, $d = 0.837\ g\,cm^{-3}$, 1.5 mmol) at $20\,^{\circ}C$ in the presence of molecular sieves (4 Å) was added to a solution (30 mL) of **6a** (0.42 g, 1.5 mmol) in CH_2Cl_2. The solution was cooled to $-78\,^{\circ}C$, and $TiCl_4$ (3.6 mmol, 0.40 mL, $d = 1.726\ g\,cm^{-3}$) was slowly added. After warming of the solution to $20\,^{\circ}C$ over 6 h, the solution was stirred for 12 h. A saturated aqueous solution of NaCl (150 mL) was added, and the organic layer was separated. The aqueous layer was extracted with diethyl ether (4×150 mL). The organic layer was dried ($MgSO_4$), filtered, and the filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel, diethyl ether/petroleum ether = 1:2) to give **7b** as a colorless oil (90 mg, 34%).

(*E*)-5-Ethyltetrahydro-[2,3′]-bifuranyliden-2′-one (7b): ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.92$ (t, $J = 7.4$ Hz, 3H; CH_2CH_3), 1.52–1.71 (m, 3H; 4-H, CH_2CH_3), 2.14–2.18 (m, 1H; 4-H), 2.84 (dt, $J = 7.5$, 1.9 Hz, 2H; 4′-H), 2.90–2.98 (m, 1H; 3′-H), 3.18–3.31 (m, 1H; 3-H), 4.19–4.26 (t, $J = 7.5$ Hz, 2H; 5′-H), 4.30–4.36 (m, 1H; 5-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 9.60$ (CH_2CH_3), 24.92 (C-4), 27.68 (CH_2CH_3), 28.75, 29.07 (C-3, C-4′), 65.02 (C-5′), 85.99 (C-5), 92.20 (C-3′), 169.20 (C=O), 173.09 (C-2); IR (KBr): $\tilde{\nu} = 2963$ (s), 2925 (s), 2879 (m), 1761 (s), 1652 (m), 1456 (m), 1378 (m), 1188 (s), 1080 (s), 1020 (s), 953 (m), 790 cm^{-1} (w); MS (70 eV, EI): *m*/*z* (%): 182 (27) [M^+], 113 (29), 85 (100), 57 (17), 55 (19); the exact molecular mass for $C_{10}H_{14}O_3$: *m*/*z* (%): 182.0942 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV).

(*E*)-5-Methyltetrahydro-[2,3′]-bifuranyliden-2′-one (7a): Starting with 4-(1-trimethylsilyloxy)ethenyl-5-trimethylsilyloxy-2,3-dihydrofuran **6a** (0.42 g, 1.5 mmol), 1,2-propenoxide (0.109 mL, $d = 0.829\ g\,cm^{-3}$, 1.5 mmol), and $TiCl_4$ (0.35 mL, $d = 1.726\ g\,cm^{-3}$, 3.0 mmol), **7a** was isolated by chromatography (silica gel, diethyl ether/petroleum ether = 1:2) as a colorless solid (112 mg, 42%, $E/Z > 98{:}2$). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.00$ (d, $J = 6.6$ Hz, 3H; $CHCH_3$), 1.50–1.64 (m, 1H; 4-H), 2.09–2.21 (m, 1H; 4-H), 2.76 (t, $J = 7.0$ Hz, 2H; 4′-H) 2.82–2.91 (m, 1H; 3′-H), 3.16–3.25 (dddd, $J = 18.6$, 8.8, 3.9, 1.6 Hz, 1H; 3-H), 4.19 (t, $J = 7.5$ Hz, 5′-H), 4.46–4.54 (m, 1H; 5-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 20.16$ ($CHCH_3$), 24.82 (C-4), 29.21, 30.93 (C-3, C-4′), 64.92 (C-5′), 80.87 (C-5), 92.18 (C-3′), 169.07 (C=O), 172.93 (C-2); IR (KBr): $\tilde{\nu} = 2960$ (s), 2930 (s), 1768 (s), 1671 (m), 1430 (w), 1381 (m), 1259 (m), 1185 (s), 1025 (s), 752 (m), 694 cm^{-1} (w); MS (70 eV, EI): *m*/*z* (%): 168 (100) [M^+], 139 (23), 113 (68), 110 (20), 95 (13); the exact molecular mass for $C_9H_{12}O_3$: *m*/*z* (%): 168.0786 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV); elemental analysis calcd (%) for $C_9H_{12}O_3$: C 64.28, H 7.20; found: C 63.99, H 6.94.

(*E*)-5-Butyl-2′-oxotetrahydro-[2,3′]-bifuranylidene (7c): Starting with 2,1′-bis(trimethylsilyloxy)-3-ethylene-4,5-dihydrofuran **6a** (0.65 g, 2.4 mmol), 1,2-hexenoxide (0.287 mL, $d = 0.83\ g\,cm^{-3}$, 2.4 mmol), and $TiCl_4$ (0.525 mL, $d = 1.726\ g\,cm^{-3}$, 4.7 mmol), **7c** was isolated by chromatography (silica gel, diethyl ether/petroleum ether = 1:1) as a colorless oil (185 mg, 37%, $E/Z > 98{:}2$). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.85$ (t, $J = 6.6$ Hz, 3H; $(CH_2)_2CH_3$), 1.18–1.39 (m, 4H; $(CH_2)_2CH_3$), 1.39–1.70 (m, 3H; 4-H, $CHCH_2(CH_2)_2$), 2.10–2.20 (m, 1H; 4-H), 2.80 (dt, $J = 7.6$, 1.7 Hz, 2H; 4′-H), 2.85–2.93 (m, 1H; 3-H), 3.25 (dddd, $J = 17.7$, 8.9, 4.6, 1.9 Hz, 1H; 3-H), 4.22 (t, $J = 7.6$ Hz, 5′-H), 4.34–4.40 (m, 1H; 5-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 13.74$ ($(CH_2)_2CH_3$), 22.31 (CH_2CH_3), 24.93 ($CH_2CH_2CH_3$), 29.08, 29.27 (C-3, C-4′), 34.43 ($CHCH_2(CH_2)_2$), 65.00 (C-5′), 84.88 (C-5), 92.20 (C-3′), 169.17 (C=O), 173.07 (C-2); IR (KBr): $\tilde{\nu} = 2958$ (s), 2933 (s), 2873 (s), 1774 (s), 1658 (m), 1640 (m), 1382 (m), 1219 (s), 1190 (s), 1083 (w), 1025 cm^{-1} (s); MS (70 eV, EI): *m*/*z* (%): 210 (41) [M^+], 143 (16), 128 (29), 113 (57), 85 (100); the exact molecular mass for $C_{12}H_{18}O_3$: *m*/*z* (%): 210.1255 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV).

(*E*)-5-(3-Butylene)-2′-oxotetrahydro-[2,3′]-bifuranylidene (7d): Starting with 4-(1-trimethylsilyloxy)ethenyl-5-trimethylsiloxy-2,3-dihydrofuran **6a** (0.6 g, 2.2 mmol), 1,5-hexenmonoxide (0.25 mL, $d = 0.87\ g\,cm^{-3}$, 1.5 mmol), and $TiCl_4$ (0.35 mL, $d = 1.726\ g\,cm^{-3}$, 3.15 mmol), **7d** was isolated by chromatography (silica gel, diethyl ether/petroleum ether = 1:2) as a colorless oil (163 mg, 36%, $E/Z > 98{:}2$). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.58–1.75$ (m, 3H; 4-H, CH_2CH), 2.08–2.18 (m, 3H; 4-H, $H_2C{=}CHCH_2$), 2.80 (dt, $J = 7.6$, 1.6 Hz, 2H; 4′-H), 2.84–2.95 (m, 1H; 3-H), 3.18–3.25 (m, 1H; 3-H), 4.19 (t, $J = 7.6$ Hz, 2H; 5′-H), 4.37 (q, $J = 6.8$ Hz, 1H; 5-H), 4.90 (d, $J = 10.2$ Hz, 1H; *trans*, $H_2C{=}C$), 4.95 (d, $J = 16.8$ Hz, 1H; *cis*, $H_2C{=}C$); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 24.82$ (C-4), 28.94, 29.11, 29.53 (C4′, C3, $CH_2C{=}CHCH_2$), 24.82 (C-4, CH_2CH), 64.92 (C-5′), 83.96 (C-5), 92.29 (C-3′), 115.00 ($H_2C{=}CH$), 137.03 ($H_2C{=}CH$), 168.88 (C=O), 172.92 (C-2); IR (KBr): $\tilde{\nu} = 3078$ (m), 2937 (s), 1770 (s), 1664 (m), 1642 (m), 1382 (m), 1189 (s), 1054 (s), 1025 (s), 918 (m), 723 cm^{-1} (w); MS (70 eV, EI): *m*/*z* (%): 208 (93) [M^+], 167 (21), 153 (33), 128 (52), 113 (100); the exact molecular mass for $C_{12}H_{16}O_3$: *m*/*z* (%): 208.1099 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV).

(*E*)-5-Chloromethyl-2′-oxotetrahydro-[2,3′]-bifuranylidene (7e): Starting with 4-(1-trimethylsilyloxy)ethenyl-5-trimethylsilyloxy-2,3-dihydrofuran **6a** (0.6 g, 2.2 mmol), epichlorohydrin (0.173 mL, $d = 1.183\ g\,cm^{-3}$, 2.2 mmol), and $TiCl_4$ (0.49 mL, $d = 1.726\ g\,cm^{-3}$, 4.4 mmol, **7e** was isolated by chromatography (silica gel, diethyl ether/petroleum ether = 1:2) as a colorless oil (205 mg, 46%, $E/Z > 98{:}2$). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.96$ (ddt, $J = 8.5$, 5.9, 2.1 Hz, 1H; 4-H), 2.16–2.31 (m, 1H; 4-H), 2.81 (dt, $J = 7.7$, 1.9 Hz, 2H; 4′-H), 2.91–3.05 (m, 1H; 3-H), 3.23 (dddd, $J = 18.8$, 9.4, 4.2, 1.8 Hz, 1H; 3-H), 3.61 (dd, $J = 5.1$, 1.8 Hz, 2H; CH_2Cl), 4.23 (t, $J = 7.7$ Hz, 2H; 5′-H), 4.66 (q, $J = 6.0$ Hz, 1H; 5-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 24.79$ (C-4), 26.69 (C-4′), 28.56 (C-3), 45.36 (CH_2Cl), 65.07 (C-5′), 82.51 (C-5), 93.48 (C-3′), 168.09 (C=O), 172.68 (C-2); IR (KBr): $\tilde{\nu} = 2975$ (s), 2933 (s), 1772 (s), 1656 (m), 1458 (m), 1385 (s), 1261 (m), 1199 (s), 1181 (m), 1077 (m), 1053 (m), 1023 cm^{-1} (m); MS (70 eV, EI): *m*/*z* (%): 202 (40) [M^+], 167 (17), 144 (13), 113 (26), 85 (100); the exact molecular mass for $C_9H_{11}ClO_3$: *m*/*z* (%): 202.0396 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV).

(*E*)-5-Bromomethyl-2′-oxotetrahydro-[2,3′]-bifuranylidene (7f): Starting with 2,1′-bis(trimethylsilyloxy)-(3-ethylene)-4,5-dihydrofuran **6a** (0.65 g, 2.4 mmol), epibromohydrin (0.204 mL, $d = 0.83\ g\,cm^{-3}$, 2.4 mmol), and $TiCl_4$ (0.525 mL, $d = 1.726\ g\,cm^{-3}$, 4.7 mmol), **7f** was isolated by chromatography (silica gel, diethyl ether/petroleum ether = 1:1) as a colorless oil (365 mg, 62%, $E/Z > 98{:}2$). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.94–2.05$ (m, 1H; 4-H), 2.88 (dt, $J = 7.6$, 2.0 Hz, 2H; 4′-H), 3.01 (ddt, $J = 17.6$, 1.5 Hz, 1H; 3-H), 3.29 (dddd, $J = 17.5$, 9.3, 4.7, 2.4 Hz, 1H; 3-H), 3.50 (dd, $J = 6.4$, 1.8 Hz, 2H; CH_2Br), 4.30 (t, $J = 7.6$ Hz, 2H; 5′-H), 4.70 (q, $J = 5.9$ Hz, 1H; 5-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 24.58$ (C-4), 27.62 (C-4′), 28.42 (C-3), 33.45 (CH_2Br), 64.85 (C-5′), 82.02 (C-5), 93.22 (C-3′), 167.84 (C=O), 172.37 (C-2); IR (KBr): $\tilde{\nu} = 2965$ (w), 2926 (w), 1766 (s), 1672 (s), 1383 (m), 1259 (w), 1222 (s), 1199 (s), 1091 (w), 1024 (s), 863 cm^{-1} (w); MS (70 eV, EI): *m*/*z* (%): 246 (39) [M^+], 188 (7), 167 (23), 113 (46), 85 (100); the exact molecular mass for $C_9H_{11}BrO_3$: *m*/*z* (%): 245.9891 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV).

(*E*)-5-Ethyl-5′-methyl-2′-oxotetrahydro-[2,3′]-bifuranylidene (7g): Starting with 2-ethyl-4-(1-trimethylsilyloxy)ethenyl-5-trimethylsilyloxy-2,3-dihydrofuran **6b** (0.42 g, 1.4 mmol), 1,2-propenoxide (0.096 mL, $d =$

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0.829 g cm^{-3}, 1.4 mmol), and $TiCl_4$ (0.308 mL, d = 1.726 g cm^{-3}, 2.8 mmol), **7g** was isolated by chromatography (silica gel, diethyl ether/petroleum ether = 1:2) as a colorless solid (156 mg, 57%, $E/Z > 98:2$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.97 (t, J = 7.3 Hz, 3H; CH_2CH_3), 1.35 (d, J = 6.2 Hz, 3H; $CHCH_3$), 1.55–1.76 (m, 2H; CH_2CH_3, 4-H), 2.16–2.24 (m, 1H; 4-H), 2.37–2.53 (m, 1H; 3-H), 2.87–2.98 (m, 2H; 3-H, 4′-H), 3.24–3.38 (m, 1H; 4′-H), 4.33–4.40 (m, 1H; 5′-H), 4.51–4.57 (m, 1H; 5-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 8.87 (CH_2CH_3), 20.15 ($CHCH_3$), 29.24, 29.28 (CH_2CH_3, C-4), 30.40, 30.98 (C-3, C-4′), 78.04 (C-5′), 80.76 (C-5), 93.22 (C-3′), 168.70 (C=O), 172.49 (C-2); IR (KBr): $\tilde{\nu}$ = 2975 (s), 2933 (s), 1772 (s), 1656 (m), 1458 (m), 1385 (s), 1261 (m), 1199 (s), 1181 (m), 1077 (m), 1053 (m), 1023 cm^{-1} (m); MS (70 eV, EI): m/z (%): 196 (100) [M^+], 167 (33), 154 (21), 114 (37), 110 (57); the exact molecular mass for $C_{11}H_{16}O_3$: m/z (%): 196.1099 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV).

(*E*)-5-Bromomethyl-2′-oxotetrahydro-[2,3′]-bifuranylidene (7h): Starting with 2-ethyl-4-(1-trimethylsilyloxy)ethenyl-5-trimethylsilyloxy-2,3-dihydrofuran **6b** (0.38 g, 1.3 mmol), epibromohydrin (0.99 mL, d = 0.829 g cm^{-3}, 1.3 mmol), and $TiCl_4$ (0.26 mL, d = 1.726 g cm^{-3}, 2.6 mmol), **7h** was isolated by chromatography (silica gel, diethyl ether/petroleum ether = 1:1) as a colorless oil (289 mg, 82%, $E/Z > 98:2$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.87 (t, J = 7.3 Hz, 3H; CH_2CH_3), 1.58 (dq, J = 7.3, 7.1 Hz, 2H; CH_2CH_3), 1.82–1.99 (m, 1H; 4-H), 2.17–2.32 (m, 1H; 4-H), 2.34–2.47 (m, 1H; 4′-H), 2.83–2.93 (m, 2H; 3-H, 4′-H), 3.18–3.31 (m, 1H; 3-H), 3.43 (d, J = 5.2 Hz, 2H), 4.27–4.34 (m, 1H; 5′-H), 4.59–4.64 (m, 1H; 5-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 8.84 (CH_2CH_3), 28.61 (CH_2CH_3), 29.08 (C-4), 30.05, 30.28 (C-3, C-4′), 33.42 (CH_2Br), 78.16 (C-5′), 82.00 (C-5), 94.56 (C-3′), 167.58 (C=O), 172.12 (C-2); IR (KBr): $\tilde{\nu}$ = 2963 (w), 2933 (w), 1759 (s), 1667 (s), 1512 (m), 1460 (w), 1354 (m), 1257 (m), 1197 (s), 1087 (w), 1021 (s), 799 cm^{-1} (s); MS (70 eV, EI): m/z (%): 274 (36) [M^+], 190 (23), 130 (27), 114 (55), 85 (100); the exact molecular mass for $C_{11}H_{15}BrO_3$: m/z (%): 274.0204 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV).

(±)-2-(*E*)-(Ethoxycarbonylmethylidene)-(4*S*,5*R*)-dimethyltetrahydrofuran (9a): Starting with 1,3-bis(trimethylsilyloxy)-1-ethoxy-1,3-butadiene (0.89 g, 3.2 mmol), *cis*-2,3-butenoxide (0.28 mL, d = 0.827 g cm^{-3}, 3.2 mmol), and $TiCl_4$ (0.68 mL, d = 1.726 g cm^{-3}, 6.2 mmol), **9a** was isolated after chromatography (silica gel, diethyl ether/petroleum ether = 1:3) as a colorless oil (265 mg, 45%, $E/Z > 98:2$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.03 (d, J = 6.6 Hz, 3H; CH_3 to C-4), 1.18 (t, J = 7.1 Hz, 3H; OCH_2CH_3), 1.27 (d, J = 6.2 Hz, 3H; CH_3 to C-5), 1.82–1.95 (m, 1H; 4-H), 2.47 (ddd, J = 18.1, 9.8, 2.1 Hz, 1H; 3-H), 3.44 (ddd, J = 18.0, 7.8, 1.3 Hz, 1H; 3-H), 3.91 (qd, J = 6.2, 2.1 Hz, 1H; 5-H), 4.04 (q, J = 7.1 Hz, 2H; OCH_2CH_3), 5.15–5.16 (m, 1H; $CHCO_2Et$); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.31 (OCH_2CH_3), 16.03, 18.50 (2 × CH_3), 38.83 (C-3), 39.01 (C-4), 58.93 (OCH_2CH_3), 85.71, 89.30 (C-5, $CHCO_2Et$), 168.48 (C=O), 175.59 (C-2); MS (70 eV, EI): m/z (%): 184 (56) [M^+], 169 (100), 139 (66), 123 (32), 69 (44); the exact molecular mass for $C_{10}H_{16}O_3$ m/z (%): 184.1099 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV).

(±)-2-(*E*)-(Ethoxycarbonylmethylidene)-(4*S*,5*S*)-dimethyltetrahydrofuran (9b): Starting with 1,3-bis(trimethylsilyloxy)-1-ethoxy-1,3-butadiene (0.89 g, 3.2 mmol), *trans*-2,3-butenoxide (0.28 mL, d = 0.804 g cm^{-3}, 3.2 mmol), and $TiCl_4$ (0.68 mL, d = 1.726 g cm^{-3}, 6.2 mmol), **9b** was isolated after chromatography (silica gel, diethyl ether/petroleum ether = 1:3) as a colorless oil (247 mg, 42%, $E/Z > 98:2$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.93 (d, J = 7.0 Hz, 3H; CH_3 to C-4), 1.21 (d, J = 6.5 Hz, 3H; CH_3 to C-5), 1.24 (t, J = 7.0 Hz, 3H; OCH_2CH_3), 2.36–2.45 (m, 1H; 4-H), 2.85–2.94 (m, 1H; 3-H), 3.15 (ddd, J = 18.0, 7.7, 1.4 Hz, 1H; 3-H), 4.10 (q, J = 7.0 Hz, 2H; OCH_2CH_3), 4.49 (dq, J = 6.4, 6.4 Hz, 1H; 5-H), 5.23–5.24 (m, 1H; $CHCO_2Et$); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.55, 14.44, 15.05 (OCH_2CH_3, 2 × CH_3), 34.31 (C-4), 38.42 (C-3), 59.09 (OCH_2CH_3), 82.03, 89.69 (C-5, $CHCO_2Et$), 168.75 (C=O), 175.79 (C-2); MS (70 eV, EI): m/z (%): 184 (59) [M^+], 169 (100), 139 (58), 123 (27), 69 (48); the exact molecular mass for $C_{10}H_{16}O_3$: m/z (%): 184.1099 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV).

(±)-2-(*E*)-[1-(Ethoxycarbonyl)ethylidene]-(4*S*,5*S*)-dimethyltetrahydrofuran (9c): Starting with 1,3-bis(trimethylsilyloxy)-1-ethoxy-2-methyl-1,3-butadiene (0.80 g, 2.8 mmol), *trans*-2,3-butenoxide (0.25 mL, d = 0.804 g cm^{-3}, 2.8 mmol), and $TiCl_4$ (0.62 mL, d = 1.726 g cm^{-3}, 5.6 mmol), **9c** was isolated after chromatography (silica gel, diethyl ether/petroleum ether = 1:3) as a colorless oil (205 mg, 37%, $E/Z > 98:2$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.94 (d, J = 7.0 Hz, 3H; CH_3 to C-4), 1.21 (d, J = 6.6 Hz, 3H; CH_3 to C-5), 1.27 (t, J = 7.0 Hz, 3H; OCH_2CH_3), 1.79 (t, J = 1.5 Hz, 3H; $=CCH_3$), 2.17–2.45 (m, 1H; 4-H), 2.83 (ddd, J = 17.9, 5.4, 1.4 Hz, 1H; 3-H), 3.14 (ddd, J = 17.9, 7.7, 1.6 Hz, 1H; 3-H′), 4.13 (q, J = 7.1 Hz, 2H; OCH_2CH_3), 4.48 (dt, J = 6.5, 6.5 Hz, 1H; 5-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.18, 13.70, 14.49, 15.32 (CH_3), 34.82 (C-4), 39.19 (C-3), 59.39 (OCH_2CH_3), 81.27 (C-5), 97.52 (C-2), 169.57 (C=O).

***trans*-2-(*E*)-(Ethoxycarbonylmethylidene)-7-oxabicyclo[4.3.0]nonane (11a)**: Following the general procedure, 1,3-bis(trimethylsilyloxy)-1-ethoxy-1,3-butadiene (0.50 g, 1.8 mmol), 1,2-cyclohexenoxide **10** (0.18 mL, d = 0.971 g cm^{-3}, 1.8 mmol), and $TiCl_4$ (0.40 mL, d = 1.726 g cm^{-3}, 3.6 mmol) were allowed to react. Chromatographic purification (silica gel, diethyl ether/petroleum ether = 1:3) afforded **11a** as a colorless solid (98 mg, 26%, $E/Z > 98:2$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.14–2.18 (m, 11H; CH_2CH_3, 1-H, CH_2), 2.22–2.36 (m, 1H; CH_2), 3.40–3.50 (m, 3H; 6-H, 9-H), 4.06 (q, J = 7.1 Hz, 2H; OCH_2CH_3), 5.23–5.25 (m, 1H; CHC=O); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.32 (OCH_2CH_3), 23.97, 25.22, 28.23, 30.23, 36.20 (C-9, CH_2), 44.31 (CH, C-1), 59.03 (OCH_2CH_3), 86.66, 90.84 (CHC=O, C-6), 168.27 (C=O), 175.51 (C-8); MS (70 eV, EI): m/z (%): 210 (100) [M^+], 165 (96), 122 (84), 115 (58), 81 (56); the exact molecular mass for $C_{12}H_{18}O_3$: m/z (%): 210.1255 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV); elemental analysis calcd (%) for $C_{12}H_{18}O_3$ (210.3): C 68.55, H 8.63; found: C 68.24, H 8.35.

***trans*-2-(*E*)-(Methoxycarbonylmethylidene)-7-oxabicyclo[4.3.0]nonane (11b)**: Starting with 1,3-bis(trimethylsilyloxy)-1-methoxy-1,3-butadiene (1.30 g, 5 mmol), 1,2-cyclohexenoxide (0.51 mL, d = 0.971 g cm^{-3}, 5 mmol), and $TiCl_4$ (1.10 mL, d = 1.726 g cm^{-3}, 10.0 mmol), **11b** was isolated by chromatography (silica gel, diethyl ether/petroleum ether = 1:2) as a colorless oil (282 mg, 30%, $E/Z > 98:2$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.15–1.58 (m, 9H; CH_2CH_2, 4-H), 2.24–2.37 (m, 2H; 1-H, 9-H), 3.41–3.53 (m, 2H; 6-H, 9-H), 3.60 (s, 3H; OCH_3), 5.27 (t, J = 1.1 Hz, 1H; C=CH); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 23.93, 25.28, 28.28, 30.27 (CH_2CH_2), 36.28 (C-9), 44.35 (C-1), 50.60 (OCH_3), 86.85 (C-6), 90.48 (C=CH), 168.81 (C=O), 175.90 (C-8); IR (KBr): $\tilde{\nu}$ = 2949 (s), 2863 (m), 1639 (s), 1436 (m), 1351 (m), 1236 (w), 1187 (w), 1140 (m), 1113 (m), 1076 (m), 1045 (m), 942 (m), 821 cm^{-1} (s); MS (70 eV, EI): m/z (%): 196 (100) [M^+], 165 (41), 122 (53), 101 (57), 81 (45); the exact molecular mass for $C_{11}H_{16}O_3$: m/z (%): 196.1099 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV).

Purification of 11b by ion-exchange resins: A solution (20 mL) of the crude product mixture of **11b** in ether was treated with the basic ion-exchange resin Ambersep 900-OH. After stirring for 2 h, the resin was filtered off, and the filtrate was concentrated in vacuo. This procedure was repeated one time. After evaporation of the solvent, the residue was purified by chromatography to give **11b** as a colorless oil (330 mg, 36%).

***trans*-2-(*E*)-(Isopropyloxycarbonylmethylidene)-7-oxabicyclo[4.3.0]nonane (11c)**: Starting with 1,3-bis(trimethylsilyloxy)-1-isopropyloxy-1,3-butadiene (0.52 g, 1.8 mmol), 1,2-cyclohexenoxide (0.18 mL, d = 0.971 g cm^{-3}, 1.8 mmol), and $TiCl_4$ (0.40 mL, d = 1.726 g cm^{-3}, 3.6 mmol), **11c** was isolated by chromatography (silica gel, diethyl ether/petroleum ether = 1:3) as a colorless solid (129 mg, 32%, $E/Z > 98:2$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.15–1.25 (d, J = 8.0 Hz, 6H; CH_3), 2.68–2.08 (m, 6H; 1-H, CH_2), 2.18–2.40 (m, 3H; CH_2), 3.38–3.58 (m, 3H; 6-H, 9-H), 4.97 (sept, J = 8.0 Hz, 1H; $CH(CH_3)_2$), 5.26 (t, J = 1.3 Hz, 1H; C=CH); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 22.00, 22.01 ($CH(CH_3)_2$), 24.03, 25.29, 28.30, 30.30, 36.26 (C-9, CH_2), 44.37 (CH, C-1), 66.09 ($OCH(CH_3)_2$), 86.64, 91.41 (CHC=O, C-6), 167.94 (C=O), 175.33 (C-8); MS (70 eV, EI): m/z (%): 224 (100) [M^+], 165 (40).

***trans*-2-(*E*)-[(2′-Methyl)propyloxycarbonylmethylidene]-7-oxabicyclo-[4.3.0]nonane (11d)**: Starting with 1,3-bis(trimethylsilyloxy)-1-(2′-methyl)-propyloxy-1,3-butadiene (0.91 g, 3.0 mmol), 1,2-cyclohexenoxide (0.30 mL, d = 0.971 g cm^{-3}, 3.0 mmol), and $TiCl_4$ (0.66 mL, d = 1.726 g cm^{-3}, 6.0 mmol), **11d** was isolated by chromatography (silica gel, diethyl ether/petroleum ether = 1:2) as a colorless oil (220 mg, 31%, $E/Z > 98:2$). Impurities could not be completely removed. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.92 (d, J = 6.7 Hz, 6H; CH_3), 1.01–2.03 (m, 11H; 1-H, CH_2, $CH(CH_3)_2$), 2.16–2.45 (m, 1H; 9-H), 3.44–3.56 (m, 2H; 6-H, 9-H), 3.82–3.92 (m, 2H; OCH_2), 5.32 (t, J = 1.2 Hz, 1H; C=CH); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 18.99 (CH_3), 24.07, 25.33, 27.82, 28.34 (CH_2CH_2), 30.34 (OCH_2CH), 36.34 (C-9), 44.43 (C-1), 69.56 (OCH_2), 86.79 (C-6), 91.02

(C=CH), 168.55 (C=O), 175.56 (C-8); MS (70 eV, EI): *m/z* (%): 238 (37) [M^+], 182 (51), 165 (100), 158 (44), 138 (47), 81 (45).

***trans*-2-(*E*)-(Phenylcarbonylmethylidene)-7-oxabicyclo[4.3.0]nonane (11e)**: Starting with 1,3-bis(trimethylsilyloxy)-1-phenyl-1,3-butadiene (1.53 g, 5 mmol), 1,2-cyclohexenoxide (0.51 mL, $d = 0.971\ g\,cm^{-3}$, 5.0 mmol), and $TiCl_4$ (1.10 mL, $d = 1.726\ g\,cm^{-3}$, 10.0 mmol), **11e** was isolated by chromatography (silica gel, diethyl ether/petroleum ether = 1:2) as an orange solid (290 mg, 24%, $E/Z > 98:2$). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.15-2.24$ (m, 11H; CH_2CH_2, 9-H, 1-H), 3.34–3.49 (m, 2H; 6-H, 9-H), 6.52 (t, $J = 2.1$ Hz, 1H; C=CH), 7.31–7.54 (m, 3H; Ph), 7.85–7.95 (m, 2H; Ph); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 24.12, 25.32, 28.34, 29.66$ (CH_2CH_2), 37.50 (C-9), 44.55 (C-1), 87.05 (C-6), 96.45 (C=CH), 127.58, 128.31, 131.73 (CH, Ph), 134.60 (C, Ph), 178.18 (C=O), 190.47 (C-8); MS (70 eV, EI): *m/z* (%): 242 (27) [M^+], 163 (95), 147 (67), 105 (100), 98 (39); the exact molecular mass for $C_{16}H_{18}O_2$: *m/z* (%): 242.1307 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV).

***trans*-2,3′-(*E*)-(2′-Oxofuranylidene)-7-oxabicyclo[4.3.0]nonane (11f)**: Starting with 2,1′-bis(trimethylsilyloxy)-(3-ethylene)-4,5-dihydrofuran (0.71 g, 2.6 mmol), 1,2-cyclohexenoxide (0.26 mL, $d = 0.971\ g\,cm^{-3}$, 2.6 mmol), and $TiCl_4$ (0.57 mL, $d = 1.726\ g\,cm^{-3}$, 5.2 mmol), **11f** was isolated by chromatography (silica gel, diethyl ether/petroleum ether = 1:2) as a colorless solid (141 mg, 26%, $E/Z > 98:2$). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.15-1.58$ (m, 6H; CH_2CH_2), 1.71–1.99 (m, 3H; CH_2), 2.18–2.34 (m, 2H; 1-H, 9-H), 2.82 (dt, $J = 7.6$, 2.8 Hz, 2H; 4′-H), 3.45–3.59 (m, 2H; 6-H, 9-H), 4.24 (t, $J = 7.7$ Hz, 2H; 5′-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 24.08, 25.02, 25.23, 28.31$ (CH_2CH_2), 34.95 (C-3), 44.60 (C-4), 65.18 (C-5′), 87.49 (C-5), 94.16 (C-3′), 168.62 (C=O), 172.99 (C-2); IR (KBr): $\tilde{\nu} =$ 2942 (s), 2687 (s), 1734 (s), 1684 (s), 1457 (s), 1373 (m), 1266 (s), 1220 (m), 1069 (m), 1019 cm^{-1} (s); MS (70 eV, EI): *m/z* (%): 208 (70) [M^+], 162 (11), 128 (14), 113 (100), 81 (26); the exact molecular mass for $C_{12}H_{16}O_3$: *m/z* (%): 208.1099 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV); elemental analysis calcd (%) for $C_{12}H_{16}O_3$: C 69.21, H 7.74; found: C 68.87, H 7.77.

2-(*E*)-(Ethoxycarbonylmethylidene)-4-phenyltetrahydrofuran (13a): Starting with 1,3-bis(trimethylsilyloxy)-1-ethoxy-1,3-butadiene (0.50 g, 1.8 mmol), styrenoxide (0.21 mL, $d = 1.051\ g\,cm^{-3}$, 1.8 mmol), and $TiCl_4$ (0.40 mL, $d = 1.726\ g\,cm^{-3}$, 3.6 mmol), **13a** was isolated after chromatography (silica gel, diethyl ether/petroleum ether = 1:3) as a colorless oil (125 mg, 30%, $E/Z > 98:2$). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.27$ (t, $J =$ 7.1 Hz, 3H; OCH_2CH_3), 3.13–3.26 (m, 1H; 3-H), 3.56–3.67 (m, 2H; 3-H, 4-H), 4.09–4.22 (m, 3H; OCH_2CH_3, 5-H), 4.52–4.59 (m, 1H; 5-H), 5.39–5.40 (m, 1H; CHC=O), 7.15–7.45 (m, 5H; Ph); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 14.36$ (OCH_2CH_3), 37.89 (C-3), 42.57 (C-4), 59.22 (OCH_2CH_3), 76.99 (C-5), 90.35 (CHC=O), 126.78, 127.10, 128.78 (CH, Ph), 140.26 (C, Ph), 168.28 (C=O), 175.69 (C-2); IR (neat): $\tilde{\nu} = 3466$ (br), 3086 (w), 3063 (w), 2980 (m), 2932 (m), 2901 (m), 1701 (s), 1643 (s), 1604 (m), 1495 (m), 1454 (m), 1371 (s), 1339 (s), 1238 (m), 1115 (s), 1047 cm^{-1} (s); MS (70 eV, EI): *m/z* (%): 232 (52) [M^+], 187 (26), 156 (26), 125 (100); the exact molecular mass for $C_{14}H_{16}O_3$: *m/z* (%): 232.1099 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV).

2-(*E*)-(Phenylcarbonylmethylidene)-4-vinyltetrahydrofuran (13b): Starting with 1,3-bis(trimethylsilyloxy)-1-phenyl-1,3-butadiene (1.07 g, 3.5 mmol), 3,4-epoxy-1-butene (0.28 mL, $d = 0.870\ g\,cm^{-3}$, 3.5 mmol), and $TiCl_4$ (0.77 mL, $d = 1.726\ g\,cm^{-3}$, 7.0 mmol), **13b** was isolated after chromatography (silica gel, diethyl ether/petroleum ether = 1:3) as a colorless oil (285 mg, 38%, $E/Z > 98:2$). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 2.96-3.19$ (m, 2H; 3-H), 3.40–3.62 (m, 1H; 4-H), 4.00 (t, $J = 7.9$ Hz, 1H; 5-H), 4.39 (t, $J = 7.9$ Hz, 1H; 5-H), 5.11–5.23 (m, 2H; CH=CH_2), 5.73–5.87 (m, 1H; CH=CH_2), 6.54 (m, 1H; CHC=O), 7.40–7.53 (m, 3H; Ph), 7.88–7.93 (m, 2H; Ph); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 37.50$ (C-3), 41.30 (C-4), 75.27 (C-5), 95.55 (CHC=O), 116.83 (CH=CH_2), 127.52, 128.27, 131.71 (CH, Ph), 136.20 (CH=CH_2) 139.58 (C, Ph), 178.13 (C-2), 190.12 (C=O); IR (KBr): $\tilde{\nu} = 3081$ (w), 3067 (w), 3028 (w), 2987 (w), 2954 (w), 2889 (w), 1647 (s), 1587 (s), 1567 (s), 1392 (m), 1175 cm^{-1} (s); MS (70 eV, EI): *m/z* (%): 214 (28) [M^+], 147 (69), 105 (65), 77 (52), 69 (100); the exact molecular mass for $C_{14}H_{14}O_2$: *m/z* (%): 214.0994 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV).

2-(*E*)-(Phenylcarbonylmethylidene)-4-methyltetrahydrofuran (13c): Starting with 1,3-bis(trimethylsilyloxy)-1-phenyl-1,3-butadiene (0.79 g, 2.5 mmol), 1,2-propenoxide (0.18 mL, $d = 0.829\ g\,cm^{-3}$, 2.5 mmol), and $TiCl_4$ (0.55 mL, $d = 1.726\ g\,cm^{-3}$, 5.0 mmol), **13c** was isolated after chromatography (silica gel, diethyl ether/petroleum ether = 1:3) as a colorless oil (228 mg, 45%, $E/Z > 98:2$). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.11$ (d, $J = 6.4$ Hz, 3H; CH_3), 2.47–2.61 (m, 1H; 4-H), 2.88 (ddd, $J = 18.7$, 6.8, 1.7 Hz, 1H; 3-H), 3.46 (ddd, $J = 18.7$, 8.0, 1.6 Hz, 1H; 3-H), 3.82 (dd, $J = 8.6$, 6.6 Hz, 1H; 5-H), 4.33 (dd, $J = 8.6$, 6.9 Hz, 1H; 5-H), 6.52 (t, $J = 1.7$ Hz, 1H; CHC=O), 7.37–7.51 (m, 3H; Ph), 7.87–7.92 (m, 2H; Ph); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 17.38$ (CH_3), 31.70 (C-4), 39.43 (C-3), 77.71 (C-5), 95.42 (CHC=O), 127.59, 128.22, 131.60 (CH, Ph), 139.68 (C, Ph), 179.05 (C-2), 190.15 (C=O); MS (70 eV, EI): *m/z* (%): 202 (70) [M^+], 187 (100), 162 (13), 147 (20), 125 (22), 105 (45); elemental analysis calcd (%) for $C_{13}H_{14}O_2$: C 77.20, H 6.98; found: C 76.86, H 7.09.

2-(*E*)-(3-Methoxy-2-oxopropylidene)-4-methyltetrahydrofuran (13d): Starting with 2,4-bis(trimethylsilyloxy)-1-methoxy-2,4-pentadiene (0.55 g, 2.0 mmol), 1,2-propenoxide (0.14 mL, $d = 0.829\ g\,cm^{-3}$, 2.0 mmol), and $TiCl_4$ (0.44 mL, $d = 1.726\ g\,cm^{-3}$, 4.0 mmol), **13d** was isolated after chromatography (silica gel, diethyl ether/petroleum ether = 1:3) as a colorless oil (143 mg, 42%, $E/Z > 98:2$). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.09$ (d, $J = 7.0$ Hz, 3H; CH_3 on C-4), 2.47–2.58 (m, 1H; 4-H), 2.70–2.81 (m, 1H; 3-H), 3.29–3.48 (m, 4H; 3-H, OCH_3), 3.80 (dd, $J = 8.6$, 6.7 Hz, 1H; 5-H), 3.94 (s, 2H; CH_2OCH_3), 4.32 (dd, $J = 8.6$, 6.9 Hz, 1H; 5-H), 5.94–5.96 (m, 1H; CHC=O); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 17.37$ (CH_3), 31.68, 39.39 (C-3, C-4), 59.13 (OCH_3), 77.80, 77.87 (C-5, CH_2OCH_3), 94.38 (CHC=O), 178.64 (C-2), 197.25 (C=O); MS (70 eV, DCI, NH_3): *m/z* (%): 171 (100) [M+1$^+$], 188 (82) [M+18$^+$], 358 (2) [2M+18$^+$].

2-(*E*)-(2-Oxopropylidene)-5-methyltetrahydrofuran (13e-1) and 2-(*E*)-(2-oxopropylidene)-4-methyltetrahydrofuran (13e-2): Starting with 2,4-bis(trimethylsilyloxy)-1,3-pentadiene (0.49 g, 2.0 mmol), 1,2-butenoxide (0.17 mL, $d = 0.837\ g\,cm^{-3}$, 2.0 mmol), and $TiCl_4$ (0.44 mL, $d =$ $1.726\ g\,cm^{-3}$, 4.0 mmol), **13e** was isolated by chromatography (silica gel, diethyl ether/petroleum ether = 1:3) as a colorless oil. The product was obtained as an inseparable 3:1 mixture of the regioisomers **13e-1** and **13e-2** (100 mg, 36%, $E/Z > 98:2$). **13e-1**: ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.35$ (d, $J = 6.3$ Hz, 3H; $CHCH_3$), 1.55–1.77 (m, 1H; 4-H), 2.10 (s, 3H; $COCH_3$), 2.10–2.28 (m, 1H; 4-H), 2.85–3.05 (dddd, $J = 18.8$, 9.0, 9.0, 2.0 Hz, 1H; 3-H), 3.25–3.40 (dddd, $J = 18.8$, 9.0, 4.1, 1.4 Hz, 1H; 3-H), 4.48–4.58 (m, 1H; 5-H), 5.74 (m, 1H; CHC=O); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 20.36$ (CH_2CH_3), 30.91, 31.13, 31.52 (C-3, C-4, CH_3, C=OCH_3), 80.21 (C-5), 98.28 (CHC=O), 176.56 (C-2), 197.60 (C=O); **13e-2**: ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.08$ (d, $J = 6.3$ Hz, 3H; $CHCH_3$), 2.11 (s, 3H; C=OCH_3), 2.12–2.38 (m, 1H; 4-H), 2.40–2.58 (ddd, $J = 18.5$, 7.4, 1.7 Hz, 1H; 3-H), 3.25–3.42 (ddd, $J = 18.5$, 8.3, 1.5 Hz, 1H; 3-H), 3.75 (dd, $J = 8.6$, 7.3 Hz, 1H; 5-H), 4.28 (dd, $J = 8.6$, 7.3 Hz, 1H; 5-H), 5.77 (t, $J = 1.5$ Hz, 1H; CHC=O); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 17.38, 31.76, 32.65, 38.98$ (C-3, C-4, CH_3, C=OCH_3), 77.20 (C-5), 98.98 (CHC=O), 176.58 (C-2), 197.60 (C=O); MS (70 eV, EI): *m/z* (%): 140 (18) [M^+], 125 (25); the exact molecular mass for $C_8H_{12}O_2$: *m/z* (%): 140.0837 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV).

2-(*E*)-(2-Oxopropylidene)-5-ethyltetrahydrofuran (13f-1) and 2-(*E*)-(2-oxopropylidene)-4-ethyltetrahydrofuran (13f-2): Starting with 2,4-bis(trimethylsilyloxy)-1,3-pentadiene (0.49 g, 2.0 mmol), 1,2-butenoxide (0.17 mL, $d = 0.837\ g\,cm^{-3}$, 2.0 mmol), and $TiCl_4$ (0.44 mL, $d =$ $1.726\ g\,cm^{-3}$, 4.0 mmol), the regioisomers **13f-1** (18 mg, 6%, $E/Z > 98:2$) and **13f-2** (46 mg, 15%, $E/Z > 98:2$) were isolated by chromatography (silica gel, diethyl ether/petroleum ether = 1:3) as colorless oils. **13f-1**: ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.97$ (t, $J = 7.5$ Hz, 3H; CH_2CH_3), 1.53–1.77 (m, 3H; 4-H, CH_2CH_3), 2.02–2.24 (m, 4H; 4-H, C=OCH_3), 2.94 (dddd, $J = 18.9$, 9.1, 9.1, 1.9 Hz, 1H; 3-H), 3.30 (dddd, $J = 18.9$, 9.2, 4.1, 1.4 Hz, 1H; 3-H), 4.26–4.34 (m, 1H; 5-H), 5.73–5.76 (m, 1H; CHC=O); **13f-2**: ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.92$ (t, $J = 7.4$ Hz, 3H; CH_2CH_3), 1.42 (quint, $J = 7.4$ Hz, 2H; CH_2CH_3), 2.09 (s, 3H; C=OCH_3), 2.12–2.38 (m, 1H; 4-H), 2.68 (ddd, $J = 18.6$, 7.3, 1.7 Hz, 1H; 3-H), 3.29 (ddd, $J = 18.6$, 8.4, 1.5 Hz, 1H; 3-H), 3.32 (dd, $J = 8.7$, 7.2 Hz, 1H; 5-H), 3.81 (dd, $J = 8.7$, 7.1 Hz, 1H; 5-H), 5.73–5.75 (m, 1H; CHC=O); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 12.14$ (CH_2CH_3), 25.56, 31.08, 37.01, 38.82 (C-3, C-4, CH_2CH_3, C=OCH_3), 75.95 (C-5), 98.76 (CHC=O), 176.88 (C-2), 197.53 (C=O); MS (70 eV, EI): *m/z* (%): 154 (16) [M^+], 139 (28), 125 (56), 111 (16), 71 (24), 69 (100); the exact molecular mass for $C_9H_{14}O_2$: *m/z* (%): 154.0994 ± 2 mD [M^+] was confirmed by HRMS (EI, 70 eV).

Crystal structure analysis:[29] For the data collection a Stoe IPDS II area detector system using graphite-monochromated $Mo_{K\alpha}$ radiation was used.

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No absorption corrections were made. The structures were solved by direct methods (SHELXS)[30] and refined by the full-matrix least squares techniques against F^2 (SHELXL-93).[31] The hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.

Crystallographic data of ***11f***: Empirical formula: $C_{12}H_{16}O_3$; formula weight: 208.25; temperature: 133(2) K; wavelength: 0.71073 Å; crystal system: monoclinic; space group: $P2_1/n$; unit cell dimensions: $a=6.6306(7)$ Å, $b=7.5994(11)$ Å, $\beta=98.199(9)^\circ$, $c=21.512(3)$ Å, $V=1072.9(2)$ Å^3, $Z=4$, ρ_{calcd}: 1.289 mg m^{-3}; absorption coefficient: 0.092 mm^{-1}; $F(000)$: 448; theta range for data collection: 1.91 to 24.71°; index ranges: $-7\le h\le 7$, $-8\le k\le 8$, $-23\le l\le 25$; reflections collected/unique: 6337/1784 [R(int) = 0.0491]; observed reflections: [$I>2\sigma(I)$]: 1433; completeness to $\theta=24.71$: 98.3 %; refinement method: full-matrix least-squares method on F^2; data/restraints/parameters: 1784/0/145; goodness-of-fit on F^2: 1.037; final R indices [$I>2\sigma(I)$] $R1=0.0457$, $wR2=0.1162$, R indices (all data): $R1=0.0573$, $wR2=0.1211$; largest diff. peak and hole: 0.312 and −0.202 e Å^{-3}.

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[29] Crystallographic data for the structure **11f** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. CCDC-171287 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

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