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Synthesis of 4-alkoxycarbonyl-butenolides by uncatalyzed one-pot cyclization of 1,3-bis(silyloxy)alk-1-enes with oxalyl chloride

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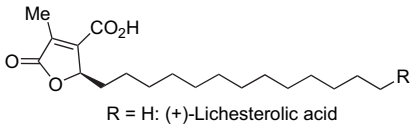
Abstract—3-Hydroxy-4-alkoxycarbonyl-butenolides were prepared by one-pot cyclizations of 1,3-bis(silyloxy)alk-1-enes with oxalyl chloride.

1. Introduction

4-Carboxy-, 4-alkoxycarbonyl-, and 4-acyl-butenolides are of considerable pharmacological relevance and occur in a variety of natural products.[1] This includes, for example, (+)- and (−)-lichesterolic acid,[2] neuropogolic acid,[3] isomuronic acid (Scheme 1),[3a] (+)-praesorediosic acid,[4] dihydroconstiputic acid,[5] paniculid C,[6] and medium-sized bicycles such as 8,14-dioxo-7,11-dehydro-11,13-dihydroacanthospermolide,[7] cyclospinosolide,[8] pachyclavulariolide P,[9] and phlogacanthoside B.[10] 4-Alkoxycarbonyl-butenolides are also important synthetic building blocks. For example, (+)-nephrosteranic acid and related γ-lactones were prepared by diastereoselective hydrogenation of 5-alkyl-3-mesyloxy-4-ethoxycarbonyl-butenolides.[11] Isotetronic acid derivatives, containing a hydroxy group at carbon atom C-3 of the butenolide moiety, are also occurring in many natural products. This includes (+)-leptosphaerin[12] and compound WF-3681,[13] distomadine B,[14] various ascorbic acid derivatives,[15] and many other pharmacologically relevant natural products.[16] Isotetronic acids have been used also as synthetic building blocks during the synthesis of (−)-tetrodotoxin,[17] 6-thiosialic and neuraminic acids,[18–21] nactins,[22] and erythronolide A.[23]



Scheme 1. Naturally occurring 4-carboxy-butenolides.

3-Hydroxy-4-alkoxycarbonyl-butenolides and related structures have been previously prepared mainly by base-mediated cyclization reactions. This includes the reaction of pyruvates with aldehydes,[24] of benzaldehyde with dimethyl methoxyfumarate,[25] of acetophenones with formaldehyde and diethyl oxalate,[26] and by DABCO mediated dimerization of methyl 2,4-dioxopentanoate.[27] A different approach relies on the PPh_3 mediated reaction of ketones with methyl acetoxypropynoate.[28] Nair et al. reported the synthesis of spirocycles based on PPh_3 mediated reactions of 1,2-quinones.[29] Saalfrank and co-workers reported the synthesis of 5-alkylidene-3-hydroxy-4-alkoxycarbonyl-butenolides by cyclization of 1,3-dicarbonyl compounds with oxalyl chloride.[30] Sonoda and co-workers reported the synthesis of 2,3-dioxo-2,3-dihydrofurans by cyclization of acetophenone derived silyl enol ethers with oxalyl chloride.[31]

We developed an efficient approach to 3-hydroxy-5-alkylidenebutenolides by cyclization of 1,3-bis(silyloxy)buta-1,3-dienes[32] with oxalyl chloride.[33] Recently, we reported[34] a convenient one-pot synthesis of 3-hydroxy-4-alkoxycarbonyl-butenolides by cyclization of oxalyl chloride with 1-alkoxy-1,3-bis(silyloxy)alk-1-enes,[35] which can be regarded as bis-silylated 3-hydroxyesters. Herein, we report full details of these studies. With regard to our preliminary communication, we significantly extended the preparative scope. In addition, we report the application of our methodology to the synthesis of an enantiomerically pure butenolide and the functionalization of the products by Suzuki reactions. The reactions reported herein proceed under mild conditions; and the starting materials are readily available.

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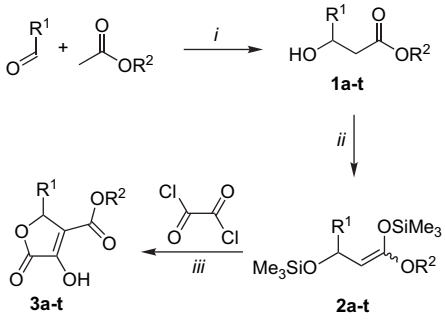
2. Results and discussion

1,3-Bis(silyloxy)alk-1-enes **2a–t** were prepared by the reaction of dilithiated 3-hydroxyesters **1a–t** (available by aldol reaction) with trimethylchlorosilane (Scheme 2, Tables 1 and 2). The cyclization of **2a–t** with oxalyl chloride afforded the 3-hydroxy-4-alkoxycarbonyl-butenolides **3a–t**. The best yields were obtained when the reactions were carried out *without* the presence of a Lewis acid (Table 2). Noteworthy, the reaction of 1,3-bis(silyl enol ethers) with simple acid chlorides[36] and the condensation of silyl ketene acetals with oxalyl chloride[37] were reported to be best carried out in the absence of Lewis acid. In contrast, the cyclization reactions of 1,3-bis(silyl enol ethers)[33] and 1,1-bis(silyloxy)-ketene acetals[38] with oxalyl chloride were reported to require the use of catalytic amounts of Me_3SiOTf.



Scheme 2. Synthesis of 4-alkoxycarbonyl-butenolides **3a–t**. Conditions: (i) LDA, THF, 5 min, −78 °C; (ii) (1) LDA (2.2 equiv), THF, 1 h, −78 °C, (2) Me_3SiCl (2.5 equiv), −78→20 °C, 24 h; (iii) −78→20 °C, 18 h.

Most butenolides **3a–t** were isolated in moderate to good yields. The relatively low yields of **3j**, **3l**, and **3d**,**h** can be explained by steric hindrance of the *tert*-butyl group, the unstable nature of the vinyl group, and the cleavage of the *tert*-butyl ester (by HCl formed during the cyclization), respectively. The cyclization of oxalyl chloride with 1,3-bis(silyloxy)alk-1-ene **2u**, prepared from acetone and ethyl acetate, gave the 5,5-dimethyl-butenolide **3u** in low yield, presumably due to the steric hindrance (Scheme 3).

Table 1. Synthesis of 4-(alkoxycarbonyl)-butenolides **3a–t**

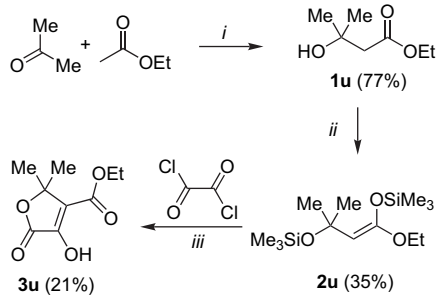
1–3	R^1	R^2	% (**1**)[a]	% (**2**)[a]	% (**3**)[a]
a	Me	Me	54	73	52
b	Me	Et	[b]	75	54
c	Et	Et	83	99	77
d	Et	*t*-Bu	89	97	32
e	*n*-Pr	Et	71	79	71
f	*i*-Pr	Et	78	86	65
g	*n*-Bu	Et	83	100	75
h	*n*-Bu	*t*-Bu	92	76	21
i	*i*-Bu	Et	62	75	63
j	*t*-Bu	Me	60	73	35
k	*n*-Hex	Me	65	91	61
l	CH_2=CH	Et	70	52	34
m	CH_2=$CH(CH_2)_8$	Et	65	93	83
n	$PhCH_2$	Me	77	87	38
o	Ph	Et	78	92	62
p	4-MeC_6H_4	Et	73	95	67
q	4-$(MeO)C_6H_4$	Et	83	91	32
r	2-$(Me)C_6H_4$	Me	69	74	50
s	2-$(MeO)C_6H_4$	Et	37	88	60
t	4-ClC_6H_4	Et	76	95	43

[a] Isolated yields.
[b] Commercially available.

Table 2. Optimization of the synthesis of **3a**

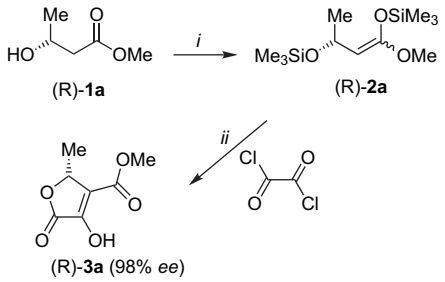
Entry	Lewis acid (equiv)	$(COCl)_2$ (equiv)	*c* (**2a**) [M]	*t* [h], *T* [°C]	% (**3a**)[a]
1	Me_3SiOTf (0.5)	2.0	0.12	0.5 h, −78 °C, 96 h, 20 °C	51
2	Me_3SiOTf (0.5)	2.5	0.075	0.5 h, −78 °C, 2 h, 50 °C	14
3	Me_3SiOTf (0.5)	1.3	0.15	18 h, 20 °C	50
4	Me_3SiOTf (1.0)	1.3	0.12	0.5 h, −78 °C, 96 h, 20 °C	53
5	Me_3SiOTf (4.0)	4.3	0.03	72 h, −78→20 °C	30
6	Me_3SiOTf (4.0)	4.3	0.03	72 h, 0→20 °C	23
7	none	1.0	0.10	18 h, −78→20 °C	54
8	$BF_3{\cdot}OEt_2$ (2.0)	1.3	0.12	0.5 h, −78 °C, 96 h, 20 °C	40
9	$TiCl_4$ (2.0)	1.3	0.12	72 h, −78→20 °C	0[b]
10	$TiCl_4$ (2.0)	1.3	0.12	72 h, −78→20 °C	0[b]

[a] Isolated yields.
[b] Complex mixture.



Scheme 3. Synthesis of 5,5-dimethyl-butenolide **3u**. Conditions: (i) LDA, THF, 5 min, −78 °C; (ii) (1) LDA (2.2 equiv), THF, 1 h, −78 °C, (2) Me_3SiCl (2.5 equiv), −78→20 °C, 24 h; (iii) −78→20 °C, 18 h.

Butenolides **3a–t** were prepared in racemic form (as racemic 3-hydroxyesters **1** were employed). Starting with (*R*)-**1a**, the optically pure butenolide (*R*)-**3a** could be successfully prepared (Scheme 4, Fig. 1). This experiment shows that no racemization occurred during the formation of 1,3-bis-(trimethylsilyloxy)alk-1-ene (*R*)-**2a** and the subsequent cyclization.



Scheme 4. Synthesis of optically pure butenolide (*R*)-**3a**. Conditions: (i) LDA, THF, 5 min, −78 °C; (ii) (1) LDA (2.2 equiv), THF, 1 h, −78 °C, (2) Me_3SiCl (2.5 equiv), −78→20 °C, 24 h; (iii) −78→20 °C, 18 h.

The hydroxy group of the isotetronic acid was successfully functionalized by transition metal catalyzed cross-coupling reactions (Scheme 5, Table 3). The products were isolated in moderate to good yields, except for **5d** prepared from 2-(methoxyphenyl)boronic acid.

In conclusion, a variety of 3-hydroxy-4-alkoxycarbonyl-butenolides were prepared by one-pot cyclizations of

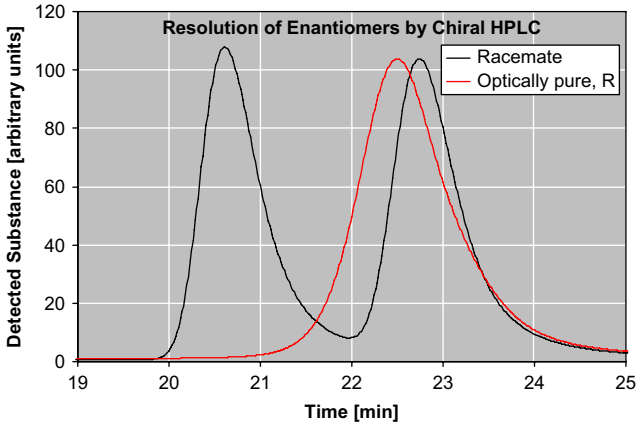
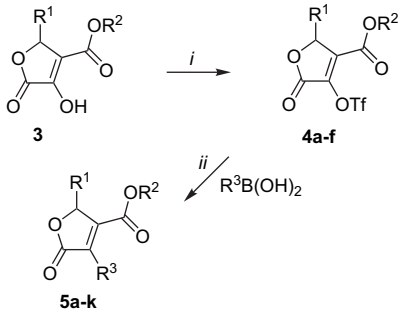


Figure 1. Determination of the enantiomeric excess of butenolide (*R*)-**3a**: chiral HPLC on a CHIRALCEL OD-H column. Conditions: hexane/ethanol=95:5+0.1% CF_3COOH (0.5 mL/min). Maxima after 20.61/22.50/22.74 min.



Scheme 5. Synthesis of butenolides **5a–k**. Conditions: (i) Tf_2O, pyridine, −78 to −10 °C; (ii) $Pd(PPh_3)_4$ (3 mol %), K_3PO_4 (1.5 equiv), dioxane, reflux.

Table 3. Synthesis of butenolides **5a–k**

3	4	5	R^1	R^2	R^3	% (**4**)[a]	% (**5**)[a]
f	**a**	**a**	*i*-Pr	Et	Ph	91	63
g	**b**	**b**	*n*-Bu	Et	Ph	84	76
g	**b**	**c**	*n*-Bu	Et	4-MeC_6H_4	84	45
g	**b**	**d**	*n*-Bu	Et	2-$MeOC_6H_4$	84	24
g	**b**	**e**	*n*-Bu	Et	3,4-$(MeO)_2C_6H_3$	84	56
g	**b**	**f**	*n*-Bu	Et	3,4,5-$(MeO)_3C_6H_2$	84	64
g	**b**	**g**	*n*-Bu	Et	Thien-2-yl	84	66
i	**c**	**h**	*i*-Bu	Et	4-$MeOC_6H_4$	86	57
j	**d**	**i**	*t*-Bu	Me	Ph	51	86
k	**e**	**j**	*n*-Hex	Me	Ph	77	61
o	**f**	**k**	Ph	Et	Ph	53	45

[a] Isolated yields.

1,3-bis(silyloxy)alk-1-enes with oxalyl chloride. The method is applicable to the synthesis of enantiomerically pure butenolides. This is useful, since there exist many methods for the enantioselective synthesis of 3-hydroxyesters. The oxalyl derived hydroxy group can be functionalized by Suzuki cross-coupling reactions of the enol triflate.

3. Experimental section

3.1. General comments

All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. For ^1H and ^{13}C NMR spectra the deuterated solvents indicated were used. Mass spectrometric data (MS) were obtained by electron ionization (EI, 70 eV), chemical ionization (CI, H_2O), or electrospray ionization (ESI). For preparative scale chromatography, silica gel (60–200 mesh) was used. Melting points are uncorrected.

3.2. General procedure for the preparation of 4-alkoxycarbonyl-butenolides 3a–u

To a CH_2Cl_2 solution of **2a–u** was added a CH_2Cl_2 solution of oxalyl chloride at −78 °C. The reaction mixture was allowed to warm to 20 °C within 15–24 h. Ether (60 mL) and brine (20 mL) were added, the organic and the aqueous layer were separated, and the latter was extracted with ether (3×30 mL). The combined organic layers were washed with water (10 mL), dried (Na_2SO_4), and filtered. The filtrate was concentrated in vacuo. The residue was purified by column chromatography (silica gel) or recrystallized (CH_2Cl_2/*n*-hexane) to give 4-alkoxycarbonyl-butenolides **3a–u**.

3.2.1. Methyl 4-hydroxy-2-methyl-5-oxo-2,5-dihydrofuran-3-carboxylate (3a). Starting with **2a** (261 mg, 0.99 mmol), CH_2Cl_2 (10 mL), and oxalyl chloride (2.0 M in CH_2Cl_2, 0.50 mL, 1.00 mmol), **3a** was isolated by column chromatography (*n*-hexane/Et_2O=1:1) as a slightly yellow solid (89 mg, 52%). Mp 48–49 °C; R_f 0.25 (tailing; Et_2O). Reaction time: 17 h. ^1H NMR (250 MHz, $CDCl_3$): δ=1.55 (d, ^3J=6.4 Hz, 3H, $CHCH_3$), 3.91 (s, 3H, OCH_3), 5.16 (q, ^3J=6.4 Hz, 1H, $CHCH_3$), 8.4 (br, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=19.4 ($CHCH_3$), 52.5 (OCH_3), 74.8 (OCH), 119.8 (*C*CH), 151.6 (COH), 164.6, 165.7 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3395 (br, s), 3344 (s), 2958 (w), 1781 (s), 1717 (s), 1456 (m), 1336 (m), 1229 (s), 1139 (s), 1053 (m), 772 (m). MS (EI, 70 eV): *m*/*z* (%)=172 (M^+, 15), 127 (27), 112 (18), 100 (37), 85 (56), 70 (100), 53 (20), 39 (40), 29 (21). Anal. Calcd for $C_7H_8O_5$ (172.14): C, 48.84; H, 4.68. Found: C, 49.01; H, 4.81.

3.2.2. Ethyl 2,5-dihydro-4-hydroxy-2-methyl-5-oxofuran-3-carboxylate (3b). Starting with **2b** (0.41 g, 1.50 mmol), CH_2Cl_2 (15 mL), and oxalyl chloride (2.0 M in CH_2Cl_2, 0.75 mL, 1.50 mmol), **3b** was isolated by column chromatography (*n*-hexane/Et_2O=1:1) as a slightly yellow oil (0.151 g, 54%). Reaction time: 17 h. ^1H NMR ($CDCl_3$, 300 MHz): δ=1.34 (t, 3H, ^3J=7.1 Hz, OCH_2CH_3), 1.57 (d, 3H, ^3J=6.5 Hz, CH_3), 4.33–4.44 (m, 2H, CH_2), 5.10 (q, 1H, ^3J=6.5 Hz, CH), 8.75 (br s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=14.2 (OCH_2CH_3), 19.6 (CH_3), 62.0 (CH_2), 74.79 (CH), 120.14 (*C*), 152.19 (COH), 164.64 (CO), 165.55 ($CO_2CH_2CH_3$). IR (KBr, cm^{-1}): $\tilde{\nu}$=3328 (w), 2985 (m), 2938 (w), 2876 (w), 1781 (s), 1709 (s), 1443 (m), 1332 (m), 1225 (s), 1184 (s), 1102 (m), 1052 (m), 923 (w), 769 (w). UV–vis (MeCN, nm): λ (log ε)= 205.51 (3.49), 251.03 (4.04). MS (EI, 70 eV): *m*/*z* (%)=186 ($[M]^+$, 1.5), 187 (1.5), 141 (85), 130 (15), 112 (78), 99 (48), 86 (50), 70 (100), 53 (12), 43 (66), 29 (57). Anal. Calcd for $C_8H_{10}O_5$: C, 51.61; H, 5.41. Found: C, 51.2; H, 5.82.

3.2.3. Ethyl 2-ethyl-4-hydroxy-5-oxo-2,5-dihydrofuran-3-carboxylate (3c). Starting with **2c** (322 mg, 1.11 mmol), CH_2Cl_2 (10 mL), and oxalyl chloride (2.0 M in CH_2Cl_2,

0.55 mL, 1.10 mmol), **3c** was isolated by column chromatography (*n*-hexane/Et_2O=1:1) as a slightly brown oil (170 mg, 77%); R_f 0.50 (tailing; Et_2O). Reaction time: 17 h. ^1H NMR (300 MHz, $CDCl_3$): δ=0.97 (t, ^3J=7.3 Hz, 3H, $CHCH_2CH_3$), 1.38 (t, ^3J=7.1 Hz, 3H, OCH_2CH_3), 1.62–1.76 (m, 1H, $CHCH_AH_B$), 2.10–2.23 (m, 1H, $CHCH_AH_B$), 4.39 (m, 2H, OCH_2), 5.09 (dd, $^3J_1$=7.3 Hz, $^3J_2$=3.2 Hz, 1H, CH), 8.78 (br, 1H, OH). ^{13}C NMR (150 MHz, $CDCl_3$): δ=8.2, 14.0 (CH_3), 26.0 ($CHCH_2$), 61.9 (OCH_2), 79.1 (CH), 118.4 (*C*CH), 152.1 (COH), 164.4, 165.9 (CO). IR (neat, cm^{-1}): $\tilde{\nu}$=3326 (br, s), 2980 (s), 2939 (m), 1781 (s), 1703 (s), 1447 (s), 1379 (m), 1303 (s), 1224 (s), 1184 (s), 1137 (s), 1083 (m), 771 (m). MS (EI, 70 eV): *m*/*z* (%)=200 (M^+, 33), 155 (47), 143 (72), 114 (100), 70 (85), 29 (99). HRMS (EI, 70 eV): calcd for $C_9H_{12}O_5$ (M^+) 200.06792; found 200.06746.

3.2.4. *tert*-Butyl 2,5-dihydro-4-hydroxy-2-ethyl-5-oxofuran-3-carboxylate (3d). Starting with **2d** (0.52 g, 1.50 mol), CH_2Cl_2 (10 mL), and oxalyl chloride (2.0 M in CH_2Cl_2, 0.55 mL, 1.10 mmol), **3d** was isolated by column chromatography (*n*-hexane/Et_2O=1:1) as a slightly brown oil (0.110 g, 32%); R_f 0.50 (tailing; Et_2O). Reaction time: 17 h. ^1H NMR ($CDCl_3$, 300 MHz): δ=0.94 (t, 3H, ^3J=7.4 Hz, CH_2CH_3), 1.57 (s, 9H, CH_3), 1.60–1.80 (m, 1H, CH_AH_B), 2.14 (sextd, 1H, ^3J=7.4, 3.2 Hz, CH_AH_B), 5.05 (dd, 1H, ^3J=3.2, 7.1 Hz, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=8.2 (CH_2CH_3), 25.9 (CH_2CH_3), 28.0 (CH_3), 79.1 (*C*H), 84.2 ($C(CH_3)_3$), 119.7 (*C*), 152.1 (*C*OH), 164.1 (*C*O), 166.0 (CO_2-*t*-Bu). IR (KBr, cm^{-1}): $\tilde{\nu}$=3404 (w), 2978 (w), 1782 (m), 1688 (m), 1440 (w), 1372 (w), 1239 (w), 1149 (m), 1081 (w). MS (EI, 70 eV): *m*/*z* (%)=228 ($[M]^+$, 1), 184 (1), 155 (7), 142 (1), 127 (5), 108 (1), 77 (1), 59 (2), 57 (22), 28 (100). A correct elemental analysis or HRMS data could not be obtained, due to decomposition.

3.2.5. Ethyl 2,5-dihydro-4-hydroxy-2-propyl-5-oxofuran-3-carboxylate (3e). Starting with **2e** (0.442 g, 1.5 mmol), CH_2Cl_2 (15 mL), and oxalyl chloride (2.0 M in CH_2Cl_2, 0.75 mL, 1.5 mmol), **3e** was isolated by column chromatography (*n*-hexane/Et_2O=1:1) as a slightly brown oil (0.227 g, 71%); R_f 0.50 (tailing; Et_2O). Reaction time: 17 h. ^1H NMR ($CDCl_3$, 300 MHz): δ=0.96 (t, 3H, ^3J=7.3 Hz, CH_3), 1.38 (t, 3H, ^3J=7.1 Hz, OCH_2CH_3), 1.43–1.49 (m, 2H, CH_2CH_3), 1.53–1.63 (m, 1H, $CH_AH_BCH_2CH_3$), 2.04–2.15 (m, 1H, $CH_ACH_BCH_2CH_3$), 4.30–4.45 (m, 2H, OCH_2CH_3), 5.11 (dd, 1H, ^3J=3, 8.1 Hz, CH), 8.78 (br s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=13.7 (CH_3), 14.1 (OCH_2CH_3), 17.8 (CH_2CH_3), 35.2 ($CH_2CH_2CH_3$), 61.9 (OCH_2CH_3), 78.1 (CH), 118.2 (*C*), 152.2 (*C*OH), 164.6 (*C*O), 165.7 ($CO_2CH_2CH_3$). IR (KBr, cm^{-1}): $\tilde{\nu}$=2977 (m), 2934 (m), 2865 (m), 1781 (w), 1742 (w), 1710 (w), 1447 (m), 1383 (m), 1238 (w), 1126 (s), 1044 (w), 795 (w). MS (EI, 70 eV): *m*/*z* (%)=215 ($[M+1^+]$, 2), 214 ($[M]^+$, 8), 169 (28), 143 (48), 123 (11), 113 (48), 86 (20), 70 (41), 43 (43), 28 (100). Anal. Calcd for $C_{10}H_{14}O_5$: C, 56.07; H, 6.59. Found: C, 56.34; H, 7.13.

3.2.6. Ethyl 4-hydroxy-2-isopropyl-5-oxo-2,5-dihydrofuran-3-carboxylate (3f). Starting with **2f** (287 mg, 0.94 mmol), CH_2Cl_2 (10 mL), and oxalyl chloride (2.0 M in CH_2Cl_2, 0.47 mL, 0.94 mmol), **3f** was isolated by column chromatography (*n*-hexane/Et_2O=1:1) as a slightly yellow solid (109 mg, 54%). Mp 52–54 °C; R_f 0.38 (tailing; Et_2O). Reaction time: 16 h. ^1H NMR (300 MHz, $CDCl_3$): δ=0.72 (d, ^3J=6.9 Hz, 3H, $CHCH_3$), 1.18 (d, ^3J=7.0 Hz, 3H, $CHCH_3$), 1.38 (t, ^3J=7.1 Hz, 3H, OCH_2CH_3), 2.39 (m, 1H, $CH(CH_3)_2$), 4.38 (m, 2H, OCH_2), 5.06 (d, ^3J=2.5 Hz, 1H, OCH), 8.2 (br, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.7, 14.0 (OCH_2CH_3, $CHCH_3$), 19.4 ($CHCH_3$), 30.0 ($CH(CH_3)_2$), 61.9 (OCH_2), 82.2 (OCH), 117.8 (*C*CH), 152.4 (COH), 164.6, 166.1 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3332 (m), 2976 (m), 1786 (s), 1693 (s), 1440 (m), 1377 (m), 1303 (m), 1222 (s), 1185 (m), 1123 (m), 1000 (m). MS (EI, 70 eV): *m*/*z* (%)=214 (M^+, 18), 172 (100), 144 (36), 126 (49), 114 (28), 70 (32), 43 (38). Anal. Calcd for $C_{10}H_{14}O_5$ (214.22): C, 56.07; H, 6.59. Found: C, 56.25; H, 6.75.

3.2.7. Ethyl 2-butyl-4-hydroxy-5-oxo-2,5-dihydrofuran-3-carboxylate (3g). Starting with **2g** (322 mg, 1.01 mmol), CH_2Cl_2 (10 mL), and oxalyl chloride (2.0 M in CH_2Cl_2, 0.50 mL, 1.00 mmol), **3g** was isolated by column chromatography (*n*-hexane/Et_2O=1:1) as a slightly orange solid (173 mg, 75%). Mp=40 °C; R_f 0.45 (tailing; Et_2O). Reaction time: 17 h. ^1H NMR (300 MHz, $CDCl_3$): δ=0.91 (t, ^3J=7.1 Hz, 3H, $CH_2CH_2CH_3$), 1.25–1.45 (m, 7H, OCH_2CH_3, $CH_2CH_2CH_3$), 1.50–1.70 (m, 1H, $CHCH_AH_B$), 2.00–2.20 (m, 1H, $CHCH_AH_B$), 4.39 (m, 2H, OCH_2), 5.11 (dd, $^3J_1$=7.9 Hz, $^3J_2$=2.9 Hz, 1H, CH), 8.1 (br, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.7, 14.1 (CH_3), 22.2, 26.3, 32.7 (CH_2), 61.9 (OCH_2), 78.3 (CH), 118.7 (*C*CH), 152.1 (COH), 164.5, 165.9 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3330 (br, w), 2960 (m), 2935 (m), 2870 (w), 1780 (s), 1708 (s), 1662 (m), 1443 (m), 1378 (w), 1336 (m), 1301 (m), 1226 (m), 1183 (m), 1138 (m), 1103 (m), 1018 (w), 770 (w). MS (EI, 70 eV): *m*/*z* (%)=228 (M^+, 3), 183 (43), 172 (25), 143 (100), 126 (33), 114 (92), 113 (89), 97 (46), 86 (52), 70 (71), 41 (60), 29.0 (90), 28 (47), 27 (47). Anal. Calcd for $C_{11}H_{16}O_5$ (228.24): C, 57.88; H, 7.07. Found: C, 57.52; H, 7.12.

3.2.8. *tert*-Butyl 2-butyl-4-hydroxy-5-oxo-2,5-dihydrofuran-3-carboxylate (3h). Starting with **2h** (674 mg, 1.94 mmol), CH_2Cl_2 (20 mL), and oxalyl chloride (2.0 M in CH_2Cl_2, 0.97 mL, 1.94 mmol), **3h** was isolated by column chromatography (*n*-hexane/Et_2O=4:1) as a slightly brown oil (104 mg, 21%); R_f 0.59–0.77 (tailing; Et_2O). Reaction time: 22 h. ^1H NMR (300 MHz, $CDCl_3$): δ=0.91 (m, 3H, CH_2CH_3), 1.25–1.50 (m, 4H, $CH_2CH_2CH_3$), 1.57 (s, 9H, $C(CH_3)_3$), 1.59–1.70 (m, 1H, $CHCH_AH_B$), 2.03–2.15 (m, 1H, $CHCH_AH_B$), 5.06 (dd, $^3J_1$=7.7 Hz, $^3J_2$=2.9 Hz, 1H, CH), 8.7 (br, 1H, OH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=13.7 (CH_2CH_3), 22.1, 26.1 (CH_2), 28.0 ($C(CH_3)_3$), 32.4 (CH_2), 78.3 (OCH), 84.1 ($C(CH_3)_3$), 120.1 (*C*CH), 151.9 (COH), 164.1, 165.9 (CO). IR (neat, cm^{-1}): $\tilde{\nu}$=3327 (br, s), 2960 (s), 2933 (s), 2874 (s), 1786 (s), 1685 (s), 1458 (m), 1371 (s), 1237 (s), 1151 (s), 771 (m). MS (CI, isobutane): *m*/*z* (%)=257 ($[M+1]^+$, 19), 202 (21), 201 (100), 157 (11).

3.2.9. Ethyl 4-hydroxy-2-isobutyl-5-oxo-2,5-dihydrofuran-3-carboxylate (3i). Starting with **2i** (306 mg, 0.96 mmol), CH_2Cl_2 (10 mL), and oxalyl chloride (2.0 M in CH_2Cl_2, 0.48 mL, 0.96 mmol), **3i** was isolated by column chromatography (*n*-hexane/Et_2O=1:1) as a colorless solid

(138 mg, 63%). Mp 99–100 °C; R_f 0.38 (tailing; Et_2O). Reaction time: 16 h. ^1H NMR (300 MHz, $CDCl_3$): δ=0.97 (d, ^3J=6.4 Hz, 3H, $CHCH_3$), 1.01 (d, ^3J=6.2 Hz, 3H, $CHCH_3$), 1.38 (t, ^3J=7.1 Hz, 3H, OCH_2CH_3), 1.46 (m, 1H, CH_AH_BCH), 1.85–2.00 (m, 2H, $CH_AH_BCH(CH_3)_2$), 4.39 (m, 2H, OCH_2CH_3), 5.13 (dd, $^3J_1$=9.9 Hz, $^3J_2$=2.0 Hz, 1H, CH), 8.7 (br, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.0 (OCH_2CH_3), 21.6, 23.4, 24.8 ($CH(CH_3)_2$), 42.5 ($CHCH_2$), 61.8 (OCH_2), 77.0 (OCH), 119.3 (CCH), 151.8 (COH), 164.5, 165.8 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3276 (br, w), 2958 (m), 1747 (s), 1710 (s), 1676 (w), 1464 (w), 1344 (w), 1299 (m), 1218 (m), 1190 (m), 1144 (w). MS (EI, 70 eV): *m/z* (%)=228 (M^+, 2), 184 (40), 172 (72), 143 (100), 126 (50), 114 (93), 86 (42), 70 (68), 41 (81), 29 (77). Anal. Calcd for $C_{11}H_{16}O_5$ (228.24): C, 57.88; H, 7.07. Found: C, 58.16; H, 7.43.

3.2.10. Methyl 2-*tert*-butyl-4-hydroxy-5-oxo-2,5-dihydrofuran-3-carboxylate (3j). Starting with **2j** (4.07 g, 13.4 mmol), CH_2Cl_2 (100 mL), and oxalyl chloride (2.0 M in CH_2Cl_2, 6.68 mL, 13.4 mmol), **3j** was isolated by column chromatography (*n*-hexane/Et_2O=2:1→1:1) as an orange oil (1.01 g, 35%); R_f 0.18–0.37 (tailing; Et_2O). Reaction time: 15 h. ^1H NMR (300 MHz, $CDCl_3$): δ=0.99 (s, 9H, $C(CH_3)_3$), 3.90 (s, 3H, OCH_3), 4.93 (s, 1H, CH), 7.3 (br, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=25.8 ($C(CH_3)_3$), 36.5 ($C(CH_3)_3$), 52.4 (OCH_3), 85.5 (OCH), 117.6 (C=COH), 153.2 (COH), 165.5, 165.6 (CO). IR (neat, cm^{-1}): $\tilde{\nu}$=3348 (br, w), 2966 (m), 1776 (s), 1724 (s), 1654 (m), 1456 (m), 1324 (m), 1231 (s), 1180 (m), 1128 (m), 1019 (w), 979 (w), 773 (w). MS (EI, 70 eV): *m/z* (%)=214 (M^+, 0.53), 158 (100), 126 (22), 70 (33), 57 (98), 29 (27).

3.2.11. Methyl 2-hexyl-4-hydroxy-5-oxo-2,5-dihydrofuran-3-carboxylate (3k). Starting with **2k** (377 mg, 1.13 mmol), CH_2Cl_2 (10 mL), and oxalyl chloride (2.0 M in CH_2Cl_2, 0.57 mL, 1.14 mmol), **3k** was isolated by column chromatography (*n*-hexane/Et_2O=1:1) as a slightly yellow solid (168 mg, 61%). Mp 73–74 °C; R_f 0.42 (tailing; Et_2O). Reaction time: 15 h. ^1H NMR (300 MHz, $CDCl_3$): δ=0.88 (t, ^3J=6.6 Hz, 3H, CH_2CH_3), 1.18–1.49 (m, 8H, $(CH_2)_4CH_3$), 1.52–1.67 (m, 1H, $CHCH_AH_B$), 2.05–2.18 (m, 1H, $CHCH_AH_B$), 3.92 (s, 3H, OCH_3), 5.11 (dd, $^3J_1$=8.1 Hz, $^3J_2$=2.8 Hz, 1H, CH), 8.38 (br, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.8 (CH_2CH_3), 22.3, 24.2, 28.7, 31.4, 33.0 (CH_2), 52.4 (OCH_3), 78.4 (OCH), 118.3 (CCH), 151.6 (COH), 164.6, 166.1 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3321 (s), 2925 (s), 2857 (m), 1788 (s), 1699 (s), 1456 (m), 1343 (m), 1309 (m), 1220 (s), 1115 (m), 994 (w), 772 (w). MS (EI, 70 eV): *m/z* (%)=242 (M^+, 2), 186 (37), 158 (82), 129 (100), 100 (72), 70 (28). Anal. Calcd for $C_{12}H_{18}O_5$ (242.27): C, 59.49; H, 7.49. Found: C, 59.68; H, 7.66.

3.2.12. Ethyl 2,5-dihydro-4-hydroxy-5-oxo-2-vinylfuran-3-carboxylate (3l). Starting with **2l** (0.432 g, 1.5 mmol), CH_2Cl_2 (15 mL), and oxalyl chloride (2.0 M in CH_2Cl_2, 0.75 mL, 1.5 mmol), **3l** was isolated by column chromatography (*n*-hexane/Et_2O=1:1) as a slightly yellow oil (0.100 g, 34%). Reaction time: 15 h. ^1H NMR ($CDCl_3$, 300 MHz): δ=1.35 (t, 3H, ^3J=7.1 Hz, –CH_3), 4.35 (m, 2H, CH_2), 5.39 (dt, 1H, ^4J=1.0 Hz, ^3J=10.2 Hz, CH), 5.47 (dt, 1H, ^4J=1.0 Hz, ^3J=6.5 Hz, $CHCHCH_{Acis}H_{Btrans}$), 5.53 (dt, 1H, ^4J=1.0 Hz, ^3J=17.0 Hz, $CHCHCH_{Acis}H_{Btrans}$), 5.778 (m, 1H, $CHCH_2$), 8.78 (br s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=14.2 (CH_3), 62.0 (CH_2), 78.1 ($CHCHCH_2$), 118.0 (C), 120.3 ($CHCHCH_2$), 131.6 ($CHCHCH_2$), 152.0 (COH), 164.5 (CO), 165.4 (CO_2Et). IR (KBr, cm^{-1}): $\tilde{\nu}$=2984 (w), 1782 (s), 1708 (s), 1665 (m), 1442 (w), 1379 (w), 1307 (m), 1224 (m), 1126 (m), 1011 (w), 941 (w). MS (EI, 70 eV): *m/z* (%)=198 ($[M]^+$, 7), 170 (12), 152 (34), 142 (16), 125 (63), 107 (79), 97 (42), 80 (44), 55 (25), 43 (14), 28 (100).

3.2.13. Ethyl 2-(9-decenyl)-4-hydroxy-5-oxo-2,5-dihydrofuran-3-carboxylate (3m). Starting with **2m** (374 mg, 0.93 mmol), CH_2Cl_2 (10 mL), and oxalyl chloride (2.0 M in CH_2Cl_2, 0.42 mL, 0.84 mmol), **3m** was isolated by column chromatography (*n*-hexane/Et_2O=1:1) as a slightly yellow oil (216 mg, 83%). Reaction time: 24 h. ^1H NMR (250 MHz, $CDCl_3$): δ=1.23–1.45 (m, 15H, $OCHCH_2(CH_2)_6$, CH_3), 1.52–1.67 (m, 1H, $OCHCH_AH_B$), 1.97–2.16 (m, 3H, H_2C=$CHCH_2$, $OCHCH_AH_B$), 4.37 (m, 2H, OCH_2), 4.89–5.02 (m, 2H, H_2C=CH), 5.09 (dd, $^3J_1$=7.8 Hz, $^3J_2$=2.9 Hz, 1H, OCH), 5.80 (ddt, $^3J_1$=17.0 Hz, $^3J_2$=10.3 Hz, $^3J_3$=6.7 Hz, 1H, H_2C=CH), 8.70 (br, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.1 (CH_3), 24.3, 28.8, 29.0, 29.1, 29.2, 29.3, 33.0, 33.7 ($OCH(CH_2)_8$), 61.9 (OCH_2), 78.3 (OCH), 114.1 (H_2C=CH), 118.9 (CCH), 139.1 (H_2C=CH), 152.2 (COH), 164.6, 165.7 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3393 (br, s), 2980 (m), 2924 (s), 2854 (s), 1784 (s), 1748 (s), 1710 (s), 1669 (m), 1467 (m), 1300 (m), 1218 (s), 1190 (s), 776 (m). MS (CI, isobutane): *m/z* (%)=311 ($[M+1]^+$, 100), 265 (49). Anal. Calcd for $C_{17}H_{26}O_5$ (310.39): C, 65.78; H, 8.44. Found: C, 65.82; H, 8.65.

3.2.14. Methyl 2-benzyl-2,5-dihydro-4-hydroxy-5-oxofuran-3-carboxylate (3n). Starting with **2n** (0.49 g, 1.50 mmol), CH_2Cl_2 (10 mL), and oxalyl chloride (2.0 M in CH_2Cl_2, 0.75 mL, 1.5 mmol), **3n** was isolated by column chromatography (*n*-hexane/Et_2O=1:1) as a slightly yellow oil (0.148 g, 38%). Reaction time: 24 h. ^1H NMR ($CDCl_3$, 300 MHz): δ=3.02 (dd, 1H, ^3J=6.2 Hz, ^2J=14.5 Hz, CH_ACH_B), 3.42 (dd, 1H, ^3J=3.3 Hz, ^2J=14.5 Hz, CH_ACH_B), 3.96 (s, 1H, OCH_3), 5.34 (dd, 1H, ^3J=6.23, 3.38 Hz, CH), 7.95–7.15 (m, 2H, Ar), 7.19–7.31 (m, 3H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=38.7 (CH_2), 52.6 (OCH_3), 77.9 (CH), 117.5 (C), 127.2 (Ar), 128.5 (Ar), 129.5 (Ar), 134.2 (Ar), 152.3 (COH), 164.5 (CO), 165.4 (CO_2Me). IR (KBr, cm^{-1}): $\tilde{\nu}$=3400 (m), 2979 (w), 1777 (s), 1713 (s), 1660 (m), 1515 (w), 1455 (m), 1341 (w), 1224 (m), 1172 (m), 1123 (m), 1044 (w), 771 (w). MS (EI, 70 eV): *m/z* (%)=248 ($[M]^+$, 11), 278 (2), 223 (1), 205 (1), 177 (2), 160 (3), 114 (6), 91 (100), 66 (8).

3.2.15. Ethyl 4-hydroxy-5-oxo-2-phenyl-2,5-dihydrofuran-3-carboxylate (3o). Starting with **2o** (314 mg, 0.93 mmol), CH_2Cl_2 (10 mL), and oxalyl chloride (2.0 M in CH_2Cl_2, 0.46 mL, 0.92 mmol), **3o** was isolated by column chromatography (*n*-hexane/Et_2O=1:1) as a slightly yellow solid (143 mg, 62%). Mp 105 °C; R_f 0.25 (tailing; Et_2O). Reaction time: 17 h. ^1H NMR (300 MHz, $CDCl_3$): δ=1.16 (t, ^3J=7.1 Hz, 3H, CH_3), 4.21 (q, ^3J=7.1 Hz, 2H, OCH_2), 6.00 (s, 1H, OCH), 7.26–7.31 (m, 2H, Ph), 7.35–7.40 (m, 3H, Ph), 8.87 (br, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$):

δ=13.8 (CH_3), 61.8 (OCH_2), 79.4 (OCH), 118.9 (*C*=COH), 127.2, 128.7, 129.6 (CH_{Ar}), 134.2 (C_{Ar}), 152.0 (COH), 164.3, 165.7 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3300 (br, m), 2992 (w), 1749 (s), 1715 (s), 1674 (m), 1456 (w), 1319 (m), 1207 (s), 1179 (s), 1127 (m), 998 (m). MS (EI, 70 eV): *m*/*z* (%)=248 (M^+, 33), 203 (21), 175 (16), 158 (41), 130 (59), 105 (39), 77 (47), 28 (100). Anal. Calcd for $C_{13}H_{12}O_5$ (248.23): C, 62.90; H, 4.87. Found: C, 62.82; H, 4.93.

3.2.16. Ethyl 4-hydroxy-2-(4-methylphenyl)-5-oxo-2,5-dihydrofuran-3-carboxylate (3p). Starting with **2p** (337 mg, 0.96 mmol), CH_2Cl_2 (10 mL), and oxalyl chloride (2.0 M in CH_2Cl_2, 0.45 mL, 0.90 mmol), and recrystallization from a mixture of CH_2Cl_2 (3 mL) and *n*-hexane (25 mL) at −24 °C yielded **3p** as a slightly brown solid (159 mg, 67%); mp 113–114 °C. Reaction time: 24 h. ^1H NMR (250 MHz, $CDCl_3$): δ=1.18 (t, ^3J=7.1 Hz, 3H, CH_2CH_3), 2.36 (s, 3H, $ArCH_3$), 4.21 (m, 2H, OCH_2), 5.98 (s, 1H, OCH), 7.17 (s, 4H, Ar), 8.8 (br, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.8 (CH_2CH_3), 21.2 ($ArCH_3$), 61.9 (OCH_2), 79.3 (OCH), 118.9 (*C*=COH), 127.2, 129.4 (CH_{Ar}), 131.2, 139.6 (C_{Ar}), 152.0 (COH), 164.4, 165.8 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3316 (br, m), 2997 (m), 1753 (s), 1744 (s), 1716 (s), 1671 (s), 1460 (m), 1318 (s), 1201 (s), 1174 (s), 992 (s), 775 (m). MS (EI, 70 eV): *m*/*z* (%)=262 (M^+, 49), 217 (28), 189 (25), 145 (58), 144 (100), 121 (56), 119 (80), 117 (54), 116 (36), 115 (71), 91 (66), 44 (70). Anal. Calcd for $C_{14}H_{14}O_5$ (262.26): C, 64.12; H, 5.38. Found: C, 63.97; H, 5.22.

3.2.17. Ethyl 2,5-dihydro-4-hydroxy-2-(4′-methoxyphenyl)-5-oxofuran-3-carboxylate (3q). Starting with **2q** (0.55 g, 1.50 mmol), CH_2Cl_2 (15 mL), and oxalyl chloride (2.0 M in CH_2Cl_2, 0.75 mL, 1.5 mmol), **3q** was isolated by column chromatography (*n*-hexane/Et_2O=1:1) as a slightly yellow solid (0.134 g, 32%); mp 97.6–100.3 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ=1.18 (t, 3H, ^3J=7.1 Hz, CH_3), 3.82 (s, 3H, OCH_3), 4.21 (q, 2H, CH_2), 5.97 (s, 1H, CH), 6.89 (dd, 2H, ^3J=6.8 Hz, ^4J=1.9 Hz, Ar), 7.20 (dd, 2H, ^3J=6.7 Hz, ^4J=2 Hz, Ar), 8.78 (br s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=13.9 (CH_3), 55.3 (OCH_3), 61.8 (CH_2), 79.2 (CH), 114.1 (*C*), 118.8 (Ar), 126.1 (Ar), 128.7 (Ar), 152.1 (COH), 160.6 (Ar), 164.5 (CO), 165.7 (CO_2Et). IR (KBr, cm^{-1}): $\tilde{\nu}$=3299 (w), 1742 (s), 1676 (m), 1612 (w), 1515 (w), 1460 (w), 1315 (s), 1256 (m), 1174 (s), 1126 (w), 1024 (w), 992 (m), 838 (w). MS (EI, 70 eV): *m*/*z* (%)=278 ($[M]^+$, 45), 279 (3), 233 (19), 205 (14), 178 (11), 160 (100), 117 (21), 89 (36), 77 (25), 28 (63). Anal. Calcd for $C_{14}H_{14}O_6$: C, 60.43; H, 5.07. Found: C, 60.05; H, 5.10.

3.2.18. Methyl 2,5-dihydro-4-hydroxy-5-oxo-2-*ortho*-tolylfuran-3-carboxylate (3r). Starting with **2q** (0.49 g, 1.50 mmol), CH_2Cl_2 (15 mL), and oxalyl chloride (2.0 M in CH_2Cl_2, 0.75 mL, 1.5 mmol), **3r** was isolated by column chromatography (*n*-hexane/Et_2O=1:1) as a slightly yellow oil (0.172 g, 49%). ^1H NMR ($CDCl_3$, 300 MHz): δ=2.50 (s, 3H, $ArCH_3$), 3.75 (s, 3H, OCH_3), 6.32 (s, 1H, Ar), 6.97 (dd, 1H, ^3J=8.3 Hz, ^4J=0.6 Hz, Ar), 6.98–7.29 (m, 3H, Ar), 8.77 (br s, 1H, OH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=19.0 (CH_3), 52.5 (OCH_3), 76.2 (CH), 118.1 (*C*), 126.3 (Ar), 126.3 (Ar), 129.6 (Ar), 131.0 (Ar), 132.1 (Ar), 137.5 (Ar), 152.4 (COH), 164.7 (CO), 165.8 (CO_2Me). IR (KBr, cm^{-1}): $\tilde{\nu}$=3366 (w), 1776 (s), 1727 (s), 1666 (w), 1460 (w), 1315 (m), 1208 (s), 1172 (m), 1129 (m), 1006 (w), 772 (w). MS (EI, 70 eV): *m*/*z* (%)=248 ($[M]^+$, 23), 216 (5), 203 (39), 171 (52), 144 (34), 115 (78), 114 (100), 91 (78), 66 (20), 28 (15). Anal. Calcd for $C_{13}H_{12}O_5$: C, 62.9; H, 4.87. Found: C, 62.82; H, 4.98.

3.2.19. Ethyl 4-hydroxy-2-(2-methoxyphenyl)-5-oxo-2,5-dihydrofuran-3-carboxylate (3s). Starting with **2s** (317 mg, 0.86 mmol), CH_2Cl_2 (10 mL), and oxalyl chloride (2.0 M in CH_2Cl_2, 0.41 mL, 0.82 mmol), and recrystallization from a mixture of CH_2Cl_2 (2.5 mL) and *n*-hexane (25 mL) at −24 °C yielded **2s** as a slightly brown solid (137 mg, 60%); mp 111–112 °C. Reaction time: 24 h. ^1H NMR (250 MHz, $CDCl_3$): δ=1.13 (t, ^3J=7.1 Hz, 3H, CH_2CH_3), 3.83 (s, 3H, OCH_3), 4.19 (q, ^3J=7.1 Hz, 2H, OCH_2), 6.36 (s, 1H, OCH), 6.89–6.96 (m, 2H, Ar), 7.06–7.10 (m, 1H, Ar), 7.31–7.38 (m, 1H, Ar), 8.9 (br, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.8 (CH_2CH_3), 55.7 (OCH_3), 61.6 (OCH_2), 75.3 (OCH), 111.3 (CH_{Ar}), 118.2 (C), 120.5 (CH_{Ar}), 122.0 (C), 128.7, 131.0 (CH_{Ar}), 152.6, 158.1, 164.7, 166.1 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=3272 (s), 2979 (m), 2939 (w), 1787 (s), 1749 (s), 1704 (s), 1690 (s), 1602 (m), 1496 (m), 1234 (s), 1186 (s), 761 (m). MS (EI, 70 eV): *m*/*z* (%)=278 (M^+, 100), 233 (68), 188 (37), 161 (59), 135 (63), 131 (85), 44 (66). Anal. Calcd for $C_{14}H_{14}O_6$ (278.26): C, 60.43; H, 5.07. Found: C, 60.73; H, 5.29.

3.2.20. Ethyl 2-(4-chlorophenyl)-4-hydroxy-5-oxo-2,5-dihydrofuran-3-carboxylate (3t). Starting with **2t** (336 mg, 0.90 mmol), CH_2Cl_2 (10 mL), and oxalyl chloride (2.0 M in CH_2Cl_2, 0.41 mL, 0.82 mmol), and recrystallization from a mixture of CH_2Cl_2 (5 mL) and *n*-hexane (20 mL) at −24 °C yielded **3t** as a slightly brown solid (99 mg, 43%); mp 115–116 °C. Reaction time: 24 h. ^1H NMR (250 MHz, $CDCl_3$): δ=1.19 (t, ^3J=7.1 Hz, 3H, CH_3), 4.22 (q, ^3J=7.1 Hz, 2H, OCH_2), 5.97 (s, 1H, OCH), 7.18–7.27 (m, 2H, Ar), 7.32–7.39 (m, 2H, Ar), 8.90 (br, 1H, OH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=13.8 (CH_3), 61.9 (OCH_2), 78.6 (OCH), 118.4 (*C*=COH), 128.6, 128.9 (CH_{Ar}), 132.9, 135.5 (C_{Ar}), 152.0 (COH), 164.0, 165.8 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3363 (br, s), 2999 (m), 1749 (s), 1713 (s), 1672 (s), 1496 (m), 1318 (s), 1202 (s), 1178 (s), 997 (s), 835 (m). Anal. Calcd for $C_{13}H_{11}ClO_5$ (282.68): C, 55.24; H, 3.92. Found: C, 55.28; H, 4.30.

3.2.21. Ethyl 4-hydroxy-2,2-dimethyl-5-oxo-2,5-dihydrofuran-3-carboxylate (3u). Starting with **2u** (291 mg, 1.00 mmol), CH_2Cl_2 (10 mL), and oxalyl chloride (2.0 M in CH_2Cl_2, 0.50 mL, 1.00 mmol), **3u** was isolated by column chromatography (*n*-heptane/Et_2O=1:1) as a slightly yellow solid (43 mg, 21%). Mp 61–62 °C; R_f 0.22 (tailing; Et_2O). Reaction time: 22 h. ^1H NMR (250 MHz, $CDCl_3$): δ=1.38 (t, ^3J=7.1 Hz, 3H, CH_2CH_3), 1.59 (s, 6H, $C(CH_3)_2$), 4.38 (q, ^3J=7.1 Hz, 2H, CH_2), 7.0 (br, 1H, OH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=14.1 (CH_2CH_3), 25.9 ($C(CH_3)_2$), 61.9 (OCH_2), 83.4 ($OC(CH_3)_2$), 123.3 (*C*=COH), 151.7 (COH), 164.6, 165.0 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3314 (br, s), 2981 (m), 1747 (s), 1707 (s), 1664 (s), 1448 (m), 1368 (m), 1315 (s), 1249 (s), 1182 (s), 1128 (s), 1065 (s), 986 (m), 772 (m). MS (EI, 70 eV): *m*/*z* (%)=200 (M^+, 24), 185

(20), 157 (31), 155 (42), 129 (28), 100 (33), 86 (60), 84 (100), 69 (30), 49 (62). HRMS (EI, 70 eV): calcd for $C_9H_{12}O_5$ (M^+) 200.06792; found 200.06864.

3.2.22. Determination of the enantiomeric excess of (*R*)-3a. The enantiomeric excess (ee) was determined by HPLC on an analytical column (CHIRALCEL OD-H). Conditions: hexane/ethanol=95:5+0.1% CF_3COOH (0.5 mL/min). Maxima after 20.61/22.50/22.74 min.

3.3. General procedure for the preparation of triflates 4a–f

To a CH_2Cl_2 solution of the appropriate isotetronic acids **3f**,**g**,**i**–**o** was added pyridine. After stirring for 15 min the solution was cooled to −78 °C and Tf_2O was added. The reaction mixture was allowed to warm to 0 °C within 90–120 min and the reaction mixture was directly purified (without aqueous work-up) by column chromatography (silica gel) to give the triflates **4a–f**.

3.3.1. Ethyl 2,5-dihydro-2-isopropyl-4-trifluormethanesulfonyloxy-5-oxofuran-3-carboxylate (4a). Starting with **3f** (0.161 g, 0.752 mmol), CH_2Cl_2 (100 mL), pyridine (0.118 g, 1.53 mmol), and Tf_2O (0.318 g, 1.127 mmol), **4a** was isolated as a yellow liquid (0.237 g, 91%); R_f 0.78 (CH_2Cl_2). After stirring for 120 min, the reaction mixture (temperature: −5 °C) was purified by column chromatography (CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 300 MHz): δ=0.76 (d, 3H, ^3J=6.9 Hz, CH_3), 1.21 (d, 3H, ^3J=7.0 Hz, CH_3), 1.40 (t, 3H, ^3J=7.1 Hz, CH_2CH_3), 2.54 (septd, 1H, ^3J=7.0, 2.6 Hz, $CH(CH_3)_2$), 4.41 (q, 2H, ^3J=7.1 Hz, CH_2CH_3), 5.22 (d, 1H, ^3J=2.6 Hz, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=13.8 (CH_3), 13.8 (CH_2CH_3), 19.4 (CH_3), 30.4 ($CH(CH_3)_2$), 63.2 (CH_2CH_3), 83.2 (CH), 118.3 (q, $^1J_{C-F}$=321 Hz, CF_3), 137.8 (C), 141.43 (COS), 158.74 (CO), 163.4 (CO_2Et). IR (KBr, cm^{-1}): $\tilde{\nu}$=3438 (m), 2977 (w), 1796 (s), 1735 (s), 1676 (w), 1439 (s), 1385 (w), 1218 (s), 1131 (s), 1011 (w), 753.86 (w), 609 (m). MS (EI, 70 eV): *m*/*z* (%)=304 ([M^+, C_3H_3], 6), 222 (5), 171 (19), 143 (100), 114 (59), 70 (50), 43 (56), 29 (35). Anal. Calcd for $C_{11}H_{13}F_3O_7S$: C, 38.15; H, 3.78. Found: C, 38.37; H, 3.60.

3.3.2. Ethyl 2-butyl-5-oxo-4-trifluoromethanesulfonyloxy-2,5-dihydrofuran-3-carboxylate (4b). Starting with **3g** (1.16 g, 5.10 mmol), CH_2Cl_2 (100 mL), pyridine (1.03 g, 13.0 mmol), and Tf_2O (1.93 g, 6.84 mmol), **4b** was isolated as a yellow liquid (1.54 g, 84%); R_f 0.78 (CH_2Cl_2). After stirring for 120 min, the reaction mixture (temperature: −5 °C) was purified by column chromatography (CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.92 (m, 3H, $CH_2CH_2CH_3$), 1.25–1.50 (m, 7H, OCH_2CH_3, $CH_2CH_2CH_3$), 1.70–1.85 (m, 1H, $CHCH_AH_B$), 2.15–2.28 (m, 1H, $CHCH_AH_B$), 4.42 (m, 2H, OCH_2), 5.30 (dd, $^3J_1$=7.6 Hz, $^3J_2$=3.2 Hz, 1H, OCH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.6, 13.7 (CH_3), 22.1, 26.0, 32.0 ($(CH_2)_3$), 63.2 (OCH_2), 79.3 (OCH), 118.3 (q, $^1J_{CF}$=321 Hz, CF_3), 137.7, 141.8 (C=C), 158.6, 163.2 (CO). IR (neat, cm^{-1}): $\tilde{\nu}$=2964 (m), 2936 (m), 2877 (w), 1796 (s), 1735 (s), 1438 (s), 1254 (s), 1220 (s), 1135 (s), 608 (m). MS (EI, 70 eV): *m*/*z* (%)=361 ([M+1]$^+$, 0.4), 304 (5), 143 (100). HRMS (EI, 70 eV): calcd for $C_{12}H_{16}F_3O_7S$ ([M+1]$^+$) 361.05633; found 361.05555. Anal. Calcd for $C_{12}H_{15}F_3O_7S$ (360.30): C, 40.00; H, 4.20. Found: C, 40.34; H, 4.09.

3.3.3. Ethyl 2-isobutyl-5-oxo-4-trifluoromethanesulfonyloxy-2,5-dihydrofuran-3-carboxylate (4c). Starting with **3i** (106 mg, 0.46 mmol), CH_2Cl_2 (10 mL), pyridine (95 mg, 1.2 mmol), and Tf_2O (205 mg, 0.73 mmol), **4c** was isolated as a yellow oil (144 mg, 86%); R_f 0.79 (CH_2Cl_2). After stirring for 90 min, the reaction mixture (temperature: 12 °C) was purified by column chromatography (CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.99 (d, ^3J=6.4 Hz, 3H, $CHCH_3$), 1.03 (d, ^3J=6.3 Hz, 3H, $CHCH_3$), 1.41 (t, ^3J=7.2 Hz, 3H, OCH_2CH_3), 1.55 (m, 1H, $CHCH_AH_B$), 1.88–2.04 (m, 2H, $CH_AH_BCH(CH_3)_2$), 4.42 (m, 2H, OCH_2), 5.31 (dd, $^3J_1$=9.9 Hz, $^3J_2$=2.2 Hz, 1H, OCH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.8 (OCH_2CH_3), 21.4, 23.3, 24.9 ($CH(CH_3)_2$), 41.7 ($CHCH_2$), 63.2 (OCH_2), 78.2 (OCH), 118.3 (q, $^1J_{CF}$=321 Hz, CF_3), 137.6, 142.4 (C=C), 158.7, 163.2 (CO). IR (neat, cm^{-1}): $\tilde{\nu}$=2964 (m), 2876 (w), 1796 (s), 1735 (s), 1438 (s), 1254 (s), 1221 (s), 1134 (s), 1100 (m), 819 (m), 608 (m). MS (CI, isobutane): *m*/*z* (%)=361 ([M+1]$^+$, 35).

3.3.4. Methyl 2-*tert*-butyl-5-oxo-4-trifluoromethanesulfonyloxy-2,5-dihydrofuran-3-carboxylate (4d). Starting with **3j** (900 mg, 4.20 mmol), CH_2Cl_2 (100 mL), pyridine (831 mg, 10.5 mmol), and Tf_2O (1.42 g, 5.04 mmol), **4d** was isolated as an orange oil (736 mg, 51%); R_f 0.76 (CH_2Cl_2). After stirring for 100 min, the reaction mixture (temperature: 0 °C) was purified by column chromatography (CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.02 (s, 9H, $C(CH_3)_3$), 3.95 (s, 3H, OCH_3), 5.12 (s, 1H, OCH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=25.6 ($C(CH_3)_3$), 36.7 ($C(CH_3)_3$), 53.4 (OCH_3), 86.0 (OCH), 118.3 (q, $^1J_{CF}$=321 Hz, CF_3), 137.3, 142.4 (C=C), 159.9, 162.8 (CO). IR (neat, cm^{-1}): $\tilde{\nu}$=2971 (m), 2878 (w), 1798 (s), 1744 (s), 1438 (s), 1255 (s), 1225 (s), 1134 (s), 1107 (s), 609 (m). MS (EI, 70 eV): *m*/*z* (%)=347 ([M+1]$^+$, 0.2). HRMS (EI, 70 eV): calcd for $C_{11}H_{14}F_3O_7S$ ([M+1]$^+$) 347.04068; found 347.04000. Anal. Calcd for $C_{11}H_{13}F_3O_7S$ (346.28): C, 38.15; H, 3.78. Found: C, 38.39; H, 3.78.

3.3.5. Methyl 2-hexyl-5-oxo-4-trifluoromethanesulfonyloxy-2,5-dihydrofuran-3-carboxylate (4e). Starting with **3j** (1.52 g, 6.27 mmol), CH_2Cl_2 (100 mL), pyridine (1.24 g, 15.7 mmol), and Tf_2O (2.12 g, 7.52 mmol), **4e** was isolated as an orange liquid (1.81 g, 77%); R_f 0.80 (CH_2Cl_2). After stirring for 100 min, the reaction mixture (temperature: 0 °C) was purified by column chromatography (CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.88 (t, ^3J=6.8 Hz, 3H, CH_2CH_3), 1.20–1.48 (m, 8H, $(CH_2)_4CH_3$), 1.77 (m, 1H, $CHCH_AH_B$), 2.12–2.27 (m, 1H, $CHCH_AH_B$), 3.96 (s, 3H, OCH_3), 5.31 (dd, $^3J_1$=7.7 Hz, $^3J_2$=3.2 Hz, 1H, OCH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.9 (CH_2CH_3), 22.4, 23.9, 28.6, 31.4, 32.3 (CH_2), 53.2 (OCH_3), 79.2 (OCH), 118.3 (q, $^1J_{CF}$=321 Hz, CF_3), 138.1, 141.2 (C=C), 159.0, 163.1 (CO). IR (neat, cm^{-1}): $\tilde{\nu}$=2960 (m), 2932 (m), 2861 (m), 1797 (s), 1740 (s), 1440 (s), 1255 (s), 1221 (s), 1134 (s), 608 (m). MS (EI, 70 eV): *m*/*z* (%)=375 ([M+1]$^+$, 0.2). HRMS (EI, 70 eV): calcd for $C_{13}H_{18}F_3O_7S$ ([M+1]$^+$) 375.07198; found 375.07116. Anal. Calcd for $C_{13}H_{17}F_3O_7S$ (374.33): C, 41.71; H, 4.58. Found: C, 42.15; H, 4.68.

3.3.6. Ethyl 5-oxo-2-phenyl-4-trifluoromethanesulfonyloxy-2,5-dihydrofuran-3-carboxylate (4f). Starting with **3o** (62 mg, 0.25 mmol), CH_2Cl_2 (5 mL), pyridine (50 mg, 0.63 mmol), and Tf_2O (92 mg, 0.33 mmol), **4f** was isolated as an orange solid (50 mg, 53%); R_f 0.74 (CH_2Cl_2). After stirring for 110 min, the reaction mixture (temperature: 5 °C) was purified by column chromatography (CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.27 (t, ^3J=7.2 Hz, 3H, CH_3), 4.28 (m, 2H, OCH_2), 6.20 (s, 1H, OCH), 7.28–7.34 (m, 2H, Ph), 7.39–7.47 (m, 3H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.6 (CH_3), 63.2 (OCH_2), 80.3 (OCH), 118.4 (q, $^1J_{CF}$=321 Hz, CF_3), 127.4, 129.2, 130.4 (CH_{Ar}), 131.6, 137.7, 141.2 (C), 158.2, 163.3 (CO). IR (Nujol, cm^{-1}): $\tilde{\nu}$=1785 (s), 1726 (s), 1258 (s), 1224 (s), 1153 (s), 1117 (s), 1005 (m), 813 (m), 761 (m), 608 (m). MS (EI, 70 eV): *m*/*z* (%)=380 (M^+, 11), 105 (100), 77 (34), 69 (27). HRMS (EI, 70 eV): calcd for $C_{14}H_{11}F_3O_7S$ (M^+) 380.01721; found 380.01671. Anal. Calcd for $C_{14}H_{11}F_3O_7S$ (380.29): C, 44.22; H, 2.92. Found: C, 44.53; H, 2.83.

3.4. General procedure for the synthesis of aryl-substituted isotetronic acids 5a–k

A mixture of triflates **4a–f**, K_3PO_4, arylboronic acids, $Pd(PPh_3)_4$, and 1,4-dioxane was heated at 90–95 °C for 4–8 h. To the solution was added ether, the mixture was filtered, and the filtrate was concentrated in vacuo. The coupling products **5a–k** were isolated by column chromatography (silica gel).

3.4.1. Ethyl 2,5-dihydro-2-isopropyl-5-oxo-phenylfuran-3-carboxylate (5a). Starting with **4a** (89.00 mg, 0.25 mmol), K_3PO_4 (85 mg, 0.4 mmol), phenylboronic acid (40 mg, 0.325 mmol), $Pd(PPh_3)_4$ (9 mg, 0.007 mmol), and 1,4-dioxane (4.0 mL), **5a** was isolated by column chromatography (silica gel; *n*-hexane/EtOAc=20:1) as a slightly yellow oil (41 mg, 63%); R_f 0.20 (*n*-hexane/EtOAc=10:1). Reaction time: 4 h. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=0.84 (d, 3H, ^3J=6.9 Hz, CH_3), 1.21 (d, ^3J=7.3 Hz, CH_3), 1.24 (t, 3H, ^3J=7.2 Hz, CH_2CH_3), 2.38 (septd, 3H, ^3J=2.9, 6.9 Hz, CH(CH_3)$_2$), 4.14–4.35 (m, 2H, CH_2CH$_3$), 5.21 (d, 1H, ^3J=2.9 Hz, CH), 7.38–7.45 (m, 3H, Ar), 7.52–7.6 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=13.8 (CH_3), 14.5 (CH_2CH_3), 19.5 (CH_3), 30.7 (CH(CH_3)$_2$), 61.9 (CH_2CH$_3$), 84.9 (CH), 128.0 (Ar), 128.5 (Ar), 129.4 (Ar), 129.8 (Ar), 135.3 (C), 148.7 (CAr), 162.7 (CO_2Et), 171.3 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3405 (w), 3061 (w), 2968 (m), 2361 (w), 1765 (s), 1725 (s), 1494 (w), 1465 (m), 1374 (m), 1396 (m), 1294 (m), 1222 (s), 1176 (s), 1111 (w), 1011 (m), 957 (w), 783 (w), 696 (m). MS (EI, 70 eV): *m*/*z* (%)=274 ([M]$^+$, 10), 232 (10), 229 (1), 186 (28), 175 (9), 146 (7.67), 129 (12), 103 (5), 77 (5), 57 (1), 28 (100).

3.4.2. Ethyl 2-butyl-5-oxo-4-phenyl-2,5-dihydrofuran-3-carboxylate (5b). Starting with **4b** (215 mg, 0.60 mmol), K_3PO_4 (190 mg, 0.90 mmol), phenylboronic acid (100 mg, 0.82 mmol), $Pd(PPh_3)_4$ (21 mg, 0.018 mmol), and 1,4-dioxane (3.0 mL), **5b** was isolated by column chromatography (silica gel; *n*-hexane/EtOAc=20:1) as a slightly yellow oil (130 mg, 76%); R_f 0.20 (*n*-hexane/EtOAc=10:1). Reaction time: 4 h. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.92 (t, ^3J=7.1 Hz, 3H, $CH_2CH_2CH_3$), 1.22 (t, ^3J=7.1 Hz, 3H, OCH_2CH_3), 1.32–1.53 (m, 4H, $CH_2CH_2CH_3$), 1.65–1.78 (m, 1H, CHCH_AH$_B$), 2.05–2.17 (m, 1H, CHCH$_A$$H_B$), 4.26 (m, 2H, OCH_2CH_3), 5.27 (dd, $^3J_1$=7.8 Hz, $^3J_2$=3.3 Hz, 1H, OCH), 7.38–7.44 (m, 3H, Ph), 7.52–7.59 (m, 2H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.7 (2×CH_3), 22.2, 26.6, 32.3 ((CH_2)$_3$), 61.7 (OCH_2), 80.8 (OCH), 127.8 (CH_{Ar}), 128.4 (C), 129.4, 129.7 (CH_{Ar}), 135.4, 148.9 (C), 162.2, 171.1 (CO). IR (neat, cm^{-1}): $\tilde{\nu}$=2959 (m), 2932 (m), 2873 (w), 1766 (s), 1721 (s), 1377 (w), 1224 (m), 1177 (m), 1015 (m), 696 (m). MS (EI, 70 eV): *m*/*z* (%)=288 (M^+, 32), 243 (16), 204 (99), 203 (100), 175 (97), 147 (39), 129 (31), 77 (8), 57 (17). HRMS (EI, 70 eV): calcd for $C_{17}H_{20}O_4$ (M^+) 288.13561; found 288.13484.

3.4.3. Ethyl 2-butyl-5-oxo-4-(4-tolyl)-2,5-dihydrofuran-3-carboxylate (5c). Starting with **4b** (220 mg, 0.61 mmol), K_3PO_4 (194 mg, 0.91 mmol), 4-tolylboronic acid (108 mg, 0.79 mmol), $Pd(PPh_3)_4$ (21 mg, 0.018 mmol), and 1,4-dioxane (3.0 mL), **5c** was isolated by column chromatography (silica gel; *n*-hexane/EtOAc=100:1→20:1) as a colorless oil (84 mg, 45%); R_f 0.24 (*n*-hexane/EtOAc=10:1). Reaction time: 6 h. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.92 (t, ^3J=7.2 Hz, 3H, $CH_2CH_2CH_3$), 1.25 (t, ^3J=7.1 Hz, 3H, OCH_2CH_3), 1.29–1.52 (m, 4H, $CH_2CH_2CH_3$), 1.64–1.76 (m, 1H, CHCH_AH$_B$), 2.04–2.17 (m, 1H, CHCH$_A$$H_B$), 2.38 (s, 3H, $ArCH_3$), 4.27 (m, 2H, OCH_2CH_3), 5.25 (dd, $^3J_1$=7.8 Hz, $^3J_2$=3.3 Hz, 1H, OCH), 7.22 (d, ^3J=8.2 Hz, 2H, Ar), 7.48 (m, 2H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.8, 13.9 (CH_2CH_3), 21.5 ($ArCH_3$), 22.3, 26.7, 32.5 ((CH_2)$_3$), 61.8 (OCH_2CH_3), 80.9 (OCH), 125.5 (C), 128.7, 129.5 (CH_{Ar}), 135.5, 140.2, 148.1 (C), 162.5, 171.4 (CO). IR (neat, cm^{-1}): $\tilde{\nu}$=2959 (m), 2932 (m), 2873 (w), 1765 (s), 1729 (s), 1718 (s), 1376 (w), 1225 (m), 1177 (m), 1015 (m). MS (EI, 70 eV): *m*/*z* (%)=302 (M^+, 69), 257 (23), 229 (25), 218 (99), 217 (99), 189 (100), 161 (76), 143 (37), 115 (30), 91 (11), 57 (21). Anal. Calcd for $C_{18}H_{22}O_4$ (302.36): C, 71.50; H, 7.33. Found: C, 71.34; H, 7.41.

3.4.4. Ethyl 2-butyl-4-(2-methoxyphenyl)-5-oxo-2,5-dihydrofuran-3-carboxylate (5d). Starting with **4b** (211 mg, 0.59 mmol), K_3PO_4 (186 mg, 0.88 mmol), 2-methoxyphenylboronic acid (116 mg, 0.76 mmol), $Pd(PPh_3)_4$ (20 mg, 0.017 mmol), and 1,4-dioxane (3.0 mL), **5d** was isolated by column chromatography (silica gel; *n*-hexane/EtOAc=1:0→15:1) as a slightly yellow solid (44 mg, 24%). Mp 71–72 °C; R_f 0.13 (*n*-hexane/EtOAc=10:1). Reaction time: 6 h. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.92 (t, ^3J=7.1 Hz, 3H, $CH_2CH_2CH_3$), 1.14 (t, ^3J=7.1 Hz, 3H, OCH_2CH_3), 1.30–1.50 (m, 4H, $CH_2CH_2CH_3$), 1.63–1.80 (m, 1H, CHCH_AH$_B$), 2.03–2.17 (m, 1H, CHCH$_A$$H_B$), 3.76 (m, 3H, OCH_3), 4.19 (m, 2H, OCH_2), 5.30 (dd, $^3J_1$=7.7 Hz, $^3J_2$=3.3 Hz, 1H, OCH), 6.89 (d, ^3J=8.0 Hz, 1H, Ar), 7.03 (dt, ^3J=7.5 Hz, ^4J=1.0 Hz, 1H, Ar), 7.35–7.44 (m, 2H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.75, 13.83 (CH_2CH_3), 22.3, 26.6, 32.3 ((CH_2)$_3$), 55.3 (OCH_3), 61.3 (OCH_2), 81.0 (OCH), 110.6 (CH_{Ar}), 118.2 (C), 120.3, 130.4, 130.9 (CH_{Ar}), 132.1, 151.0, 156.9 (C), 162.5, 171.5 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=2958 (m), 2936 (m), 2873 (w), 1762 (s), 1723 (s), 1494 (m), 1467 (m), 1381 (m), 1253 (m), 1240 (m), 1172 (m), 1016 (m), 763 (m). MS (EI, 70 eV): *m*/*z* (%)=318 (M^+, 81), 272 (53), 257 (22), 234 (64), 233 (100), 205 (92), 177 (13), 159 (33), 57 (15). HRMS (EI, 70 eV): calcd for $C_{18}H_{22}O_5$ (M^+) 318.14618; found 318.14636.

3.4.5. Ethyl 2-butyl-4-(3,4-dimethoxyphenyl)-5-oxo-2,5-dihydrofuran-3-carboxylate (5e). Starting with **4b** (195 mg, 0.54 mmol), K_3PO_4 (172 mg, 0.81 mmol), 3,4-dimethoxyphenylboronic acid (128 mg, 0.70 mmol), $Pd(PPh_3)_4$ (19 mg, 0.016 mmol), and 1,4-dioxane (3.0 mL), **5e** was isolated by column chromatography (silica gel; *n*-hexane/EtOAc=5:1) as a slightly turbid yellow oil (105 mg, 56%); R_f 0.31 (*n*-hexane/EtOAc=3:1). Reaction time: 6 h. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.93 (t, ^3J=7.1 Hz, 3H, CH_2CH_2-CH_3), 1.29 (t, ^3J=7.2 Hz, 3H, OCH_2CH_3), 1.32–1.53 (m, 4H, $CH_2CH_2CH_3$), 1.62–1.76 (m, 1H, $CHCH_AH_B$), 2.03–2.14 (m, 1H, $CHCH_AH_B$), 3.91 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 4.30 (m, 2H, OCH_2), 5.25 (dd, $^3J_1$=7.9 Hz, $^3J_2$=3.3 Hz, 1H, OCH), 6.91 (d, ^3J=8.2 Hz, 1H, Ar), 7.23 (d, ^4J=2.0 Hz, 1H, Ar), 7.25 (dd, ^3J=8.2 Hz, ^4J=2.0 Hz, 1H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.7, 13.9 (CH_2CH_3), 22.2, 26.6, 32.4 ($(CH_2)_3$), 55.76, 55.80 (OCH_3), 61.7 (OCH_2), 80.7 (OCH), 110.3, 112.6 (CH_{Ar}), 120.8 (C), 123.0 (CH_{Ar}), 134.6, 147.2, 148.2, 150.4 (C), 162.5, 171.3 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=3007 (m), 2957 (s), 2935 (m), 2869 (m), 1763 (s), 1728 (s), 1603 (m), 1515 (s), 1466 (m), 1327 (m), 1262 (s), 1208 (s), 1143 (s), 1024 (s), 760 (m). MS (EI, 70 eV): *m*/*z* (%)=348 (M^+, 100), 302 (28), 275 (32), 264 (49), 263 (94), 236 (33), 235 (90), 207 (72), 189 (17), 57 (13). Anal. Calcd for $C_{19}H_{24}O_6$ (348.39): C, 65.50; H, 6.94. Found: C, 65.73; H, 7.08.

3.4.6. Ethyl 2-butyl-5-oxo-4-(3,4,5-trimethoxyphenyl)-2,5-dihydrofuran-3-carboxylate (5f). Starting with **4b** (154 mg, 0.43 mmol), K_3PO_4 (136 mg, 0.64 mmol), 3,4,5-trimethoxyphenylboronic acid (118 mg, 0.56 mmol), $Pd(PPh_3)_4$ (15 mg, 0.013 mmol), and 1,4-dioxane (2.5 mL), **5f** was isolated by column chromatography (silica gel; *n*-hexane/EtOAc=10:1→5:1) as a yellow oil (104 mg, 64%); R_f 0.25 (*n*-hexane/EtOAc=3:1). Reaction time: 6 h. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.93 (t, ^3J=7.2 Hz, 3H, $CH_2CH_2CH_3$), 1.28 (t, ^3J=7.1 Hz, 3H, OCH_2CH_3), 1.32–1.54 (m, 4H, $CH_2CH_2CH_3$), 1.64–1.80 (m, 1H, $CHCH_AH_B$), 2.03–2.14 (m, 1H, $CHCH_AH_B$), 3.88 (s, 6H, OCH_3), 3.89 (s, 3H, OCH_3), 4.30 (m, 2H, OCH_2), 5.26 (dd, $^3J_1$=7.9 Hz, $^3J_2$=3.3 Hz, 1H, OCH), 6.89 (s, 2H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.7, 13.9 (CH_2CH_3), 22.2, 26.6, 32.4 ($(CH_2)_3$), 56.1, 60.7 (OCH_3), 61.8 (OCH_2), 80.7 (OCH), 106.9 (CH_{Ar}), 123.5, 134.5, 139.4, 148.6, 152.7 (C), 162.4, 171.0 (CO). IR (neat, cm^{-1}): $\tilde{\nu}$=2959 (m), 2938 (m), 2873 (w), 1764 (s), 1726 (m), 1582 (m), 1507 (m), 1461 (m), 1418 (m), 1294 (m), 1246 (m), 1211 (m), 1129 (s), 1010 (m). MS (EI, 70 eV): *m*/*z* (%)=378 (M^+, 100), 332 (19), 305 (26), 293 (84), 265 (77), 237 (39), 57 (16). Anal. Calcd for $C_{20}H_{26}O_7$ (378.42): C, 63.48; H, 6.93. Found: C, 63.46; H, 7.08.

3.4.7. Ethyl 2-butyl-5-oxo-4-(thien-2-yl)-2,5-dihydrofuran-3-carboxylate (5g). Starting with **4b** (188 mg, 0.52 mmol), K_3PO_4 (166 mg, 0.78 mmol), (thien-2-yl)boronic acid (87 mg, 0.68 mmol), $Pd(PPh_3)_4$ (18 mg, 0.016 mmol), and 1,4-dioxane (3.0 mL), **5g** was isolated by column chromatography (silica gel; *n*-hexane/EtOAc=20:1) as a yellow oil (101 mg, 66%); R_f 0.32 (*n*-hexane/EtOAc=10:1). Reaction time: 4 h. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.91 (t, ^3J=7.1 Hz, 3H, $CH_2CH_2CH_3$), 1.25–1.50 (m, 7H, OCH_2CH_3, $CH_2CH_2CH_3$), 1.60–1.75 (m, 1H, $CHCH_AH_B$), 2.01–2.13 (m, 1H, $CHCH_AH_B$), 4.40 (m, 2H, OCH_2), 5.27 (dd, $^3J_1$=7.7 Hz, $^3J_2$=3.2 Hz, 1H, OCH), 7.14 (dd, $^3J_1$=5.1 Hz, $^3J_2$=3.9 Hz, 1H, Ar), 7.58 (dd, $^3J_1$=5.1 Hz, $^3J_2$=1.0 Hz, 1H, Ar), 8.31 (dd, $^3J_1$=3.9 Hz, $^3J_2$=1.0 Hz, 1H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.7, 14.0 (CH_3), 22.2, 26.6, 32.6 ($(CH_2)_3$), 61.9 (OCH_2), 80.9 (OCH), 127.1 (CH_{Ar}), 128.1, 129.5 (C), 131.1, 132.9 (CH_{Ar}), 142.5 (C), 162.3, 170.5 (CO). IR (neat, cm^{-1}): $\tilde{\nu}$=2959 (m), 2932 (m), 2872 (w), 1764 (s), 1721 (s), 1306 (m), 1237 (s), 1204 (s), 1136 (m), 1016 (m). MS (EI, 70 eV): *m*/*z* (%)=294 (M^+, 65), 237 (26), 210 (88), 209 (99), 181 (100), 153 (44), 135 (21), 57 (23). HRMS (EI, 70 eV): calcd for $C_{15}H_{18}O_4S$ (M^+) 294.09203; found 294.09169.

3.4.8. Ethyl 2-isobutyl-4-(4-methoxyphenyl)-5-oxo-2,5-dihydrofuran-3-carboxylate (5h). Starting with **4c** (40 mg, 0.11 mmol), K_3PO_4 (35 mg, 0.16 mmol), 4-methoxyphenylboronic acid (22 mg, 0.14 mmol), $Pd(PPh_3)_4$ (6 mg, 0.005 mmol), and 1,4-dioxane (1.5 mL), **5h** was isolated by column chromatography (silica gel; *n*-heptane/EtOAc=20:1) as a colorless solid (20 mg, 57%). Mp 56–58 °C; R_f 0.13 (*n*-heptane/EtOAc=10:1). Reaction time: 8 h. ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.99 (d, ^3J=6.4 Hz, 3H, $CHCH_3$), 1.04 (d, ^3J=6.4 Hz, 3H, $CHCH_3$), 1.27 (t, ^3J=7.0 Hz, 3H, OCH_2CH_3), 1.52 (ddd, ^2J=14.0 Hz, $^3J_1$=9.8 Hz, $^3J_2$=4.3 Hz, 1H, $CHCH_AH_B$), 1.84 (ddd, ^2J=14.0 Hz, $^3J_1$=9.2 Hz, $^3J_2$=2.7 Hz, 1H, $CHCH_AH_B$), 1.92–2.05 (m, 1H, $CH(CH_3)_2$), 3.84 (s, 3H, OCH_3), 4.28 (m, 2H, OCH_2), 5.27 (dd, $^3J_1$=9.8 Hz, $^3J_2$=2.7 Hz, 1H, OCH), 6.94 (m, 2H, Ar), 7.58 (m, 2H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.9 (OCH_2CH_3), 21.6, 23.5, 25.3 ($CH(CH_3)_2$), 42.3 ($CHCH_2$), 55.3 (OCH_3), 61.8 (OCH_2), 79.7 (OCH), 113.5 (CH_{Ar}), 120.8 (C), 131.4 (CH_{Ar}), 134.8, 147.5 (C), 161.0, 162.5 (C, CO), 171.6 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=2950 (s), 2867 (m), 1747 (s), 1712 (s), 1607 (s), 1514 (s), 1300 (s), 1261 (s), 1247 (s), 1190 (s), 1184 (s), 1018 (s), 1001 (s), 769 (m). MS (EI, 70 eV): *m*/*z* (%)=318 (M^+, 59), 272 (25), 234 (57), 233 (100), 205 (91), 177 (68), 57 (15). HRMS (EI, 70 eV): calcd for $C_{18}H_{22}O_5$ (M^+) 318.14618; found 318.14633.

3.4.9. Methyl 2-*tert*-butyl-5-oxo-4-phenyl-2,5-dihydrofuran-3-carboxylate (5i). Starting with **4d** (295 mg, 0.85 mmol), K_3PO_4 (271 mg, 1.28 mmol), phenylboronic acid (135 mg, 1.11 mmol), $Pd(PPh_3)_4$ (30 mg, 0.026 mmol), and 1,4-dioxane (4.0 mL), **5i** was isolated by column chromatography (silica gel; *n*-heptane/EtOAc=20:1→10:1) as a colorless oil (201 mg, 86%); R_f 0.17 (*n*-heptane/EtOAc=10:1). Reaction time: 8 h. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.03 (s, 9H, $C(CH_3)_3$), 3.79 (s, 3H, OCH_3), 5.05 (s, 1H, OCH), 7.38–7.45 (m, 3H, Ph), 7.53–7.62 (m, 2H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ=25.5 ($C(CH_3)_3$), 36.3 ($C(CH_3)_3$), 52.7 (OCH_3), 88.0 (OCH), 128.29 (C), 128.34, 129.0, 129.9 (CH_{Ar}), 133.7, 149.3 (C), 164.7, 170.7 (CO). IR (neat, cm^{-1}): $\tilde{\nu}$=2967 (m), 2911 (w), 2874 (w), 1767 (s), 1735 (s), 1437 (m), 1369 (m), 1319 (m), 1232 (s), 1166 (s), 1117 (m), 1043 (m), 977 (m), 696 (m). MS (EI, 70 eV): *m*/*z* (%)=274 (M^+, 2), 218 (100), 186 (99), 129 (50), 57 (86). HRMS (EI, 70 eV): calcd for $C_{16}H_{18}O_4$ (M^+) 274.11996; found 274.11928.

3.4.10. Methyl 2-hexyl-5-oxo-4-phenyl-2,5-dihydrofuran-3-carboxylate (5j). Starting with **4e** (208 mg, 0.56 mmol), K_3PO_4 (177 mg, 0.83 mmol), phenylboronic

acid (88 mg, 0.72 mmol), $Pd(PPh_3)_4$ (19 mg, 0.016 mmol), and 1,4-dioxane (3.0 mL), **5j** was isolated by column chromatography (silica gel; *n*-hexane/EtOAc=1:0→50:1) as a slightly yellow oil (103 mg, 61%); R_f 0.30 (*n*-hexane/EtOAc=10:1). Reaction time: 4 h. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.89 (t, ^3J=6.8 Hz, 3H, CH_2CH_3), 1.20–1.42 (m, 6H, CH_2), 1.48 (m, 2H, CH_2), 1.63–1.76 (m, 1H, $CHCH_AH_B$), 2.03–2.15 (m, 1H, $CHCH_AH_B$), 3.78 (s, 3H, OCH_3), 5.26 (dd, $^3J_1$=7.9 Hz, $^3J_2$=3.3 Hz, 1H, OCH), 7.38–7.46 (m, 3H, Ph), 7.51–7.58 (m, 2H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.9 (CH_2CH_3), 22.4, 24.5, 28.8, 31.4, 32.7 (CH_2), 52.4 (OCH_3), 80.8 (OCH), 128.0 (CH_{Ar}), 128.3 (C), 129.4, 129.8 (CH_{Ar}), 135.6, 148.4 (C), 162.7, 171.0 (CO). IR (neat, cm^{-1}): $\tilde{\nu}$=2955 (s), 2929 (s), 2858 (m), 1766 (s), 1733 (s), 1437 (m), 1225 (s), 1170 (s), 982 (m), 695 (m). MS (EI, 70 eV): *m*/*z* (%)=302 (M^+, 36), 273 (26), 190 (99), 189 (100), 186 (34), 172 (12), 161 (66), 129 (49), 113 (67), 85 (16), 57 (8). Anal. Calcd for $C_{18}H_{22}O_4$ (302.36): C, 71.50; H, 7.33. Found: C, 71.48; H, 7.45.

3.4.11. Ethyl 5-oxo-2,4-diphenyl-2,5-dihydrofuran-3-carboxylate (5k). Starting with **4f** (190 mg, 0.50 mmol), K_3PO_4 (159 mg, 0.75 mmol), phenylboronic acid (79 mg, 0.65 mmol), $Pd(PPh_3)_4$ (17 mg, 0.015 mmol), and 1,4-dioxane (2.5 mL), **5k** was isolated by column chromatography (silica gel; *n*-hexane/EtOAc=1:0→20:1) as a slightly yellow solid (70 mg, 45%). Mp 110–112 °C; R_f 0.13 (*n*-hexane/EtOAc=10:1). Reaction time: 4 h. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.06 (t, ^3J=7.1 Hz, 3H, CH_3), 4.11 (m, 2H, OCH_2), 6.20 (s, 1H, OCH), 7.30–7.42 (m, 5H, Ph), 7.42–7.48 (m, 3H, Ph), 7.63–7.71 (m, 2H, Ph). ^{13}C NMR (150 MHz, $CDCl_3$): δ=13.6 (CH_3), 61.8 (OCH_2), 82.2 (OCH), 127.3, 128.05 (CH_{Ar}), 128.12 (C), 128.9, 129.6, 129.7, 130.1 (CH_{Ar}), 133.8, 134.8, 148.4 (C), 161.8, 171.2 (CO). IR (KBr, cm^{-1}): $\tilde{\nu}$=2981 (m), 1758 (s), 1729 (m), 1651 (m), 1494 (m), 1446 (m), 1369 (m), 1288 (m), 1220 (s), 1117 (m), 1014 (s), 792 (m), 692 (m). MS (EI, 70 eV): *m*/*z* (%)=308 (M^+, 23), 279 (22), 235 (34), 203 (22), 175 (21), 105 (100), 77 (18). HRMS (EI, 70 eV): calcd for $C_{19}H_{16}O_4$ (M^+) 308.10431; found 308.10351.

3.5. General procedure for the preparation of 3-hydroxyesters 1a–u

An LDA solution was prepared by the addition of *n*-BuLi to a THF solution of diisopropylamine at 0 °C. After stirring for 1 h, the solution was cooled to −78 °C and the respective ester or ketone was dropwise added. After stirring for 1 h at −78 °C, the appropriate electrophile was added within 30 s. After stirring for 3–5 min, hydrochloric acid was added. The organic and the aqueous layer were separated and the solvents were removed under reduced pressure. The aqueous layer was extracted with ethyl acetate (2×150 mL). The combined organic layers were washed with a saturated aqueous solution of $NaHCO_3$ (2×50 mL), dried (Na_2SO_4), and filtered. The filtrate was concentrated in vacuo. The residue was purified by vacuum destillation or by column chromatography (silica gel) to give 3-hydroxyesters **1a**–**u**. The synthesis of **1a**,[39] **1b**,[40] **1c**,[41] **1d**,[42] **1e**,[43] **1f**,[43] **1g**,[44] **1h**,[45] **1i**,[46] **1j**,[47] **1k**,[48] **1l**,[49] **1n**,[47] **1o**,[50] **1p**,[51] **1q**,[51] **1r**,[52] **1s**,[53] and **1t**[53] was previously reported.

3.5.1. Methyl 3-hydroxybutyrate (1a). Starting with diisopropylamine (10.12 g, 100 mmol), THF (100 mL), *n*-BuLi (2.5 M in hexanes, 41 mL, 103 mmol), methyl acetate (7.41 g, 100 mmol), acetaldehyde (5.29 g, 120 mmol), and hydrochloric acid (2.0 M, 50 mL), **1a** was isolated by destillation as a clear colorless liquid (6.43 g, 54%); bp 34 °C (0.1 mbar). Reaction time: 3.5 min. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.24 (d, ^3J=6.3 Hz, 3H, $CHCH_3$), 2.43 (dd, ^2J=16.5 Hz, ^3J=7.4 Hz, 1H, CH_AH_B), 2.51 (dd, ^2J=16.5 Hz, ^3J=3.8 Hz, 1H, CH_AH_B), 2.8 (br, 1H, OH), 3.72 (s, 3H, OCH_3), 4.21 (m, 1H, CHOH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=22.3 ($CHCH_3$), 42.6 (CH_2), 51.4 (OCH_3), 64.0 (CH), 172.9 (CO). IR (neat, cm^{-1}): $\tilde{\nu}$=3431 (br, s), 2974 (m), 2935 (w), 1737 (s), 1439 (m), 1377 (m), 1297 (m), 1196 (m), 1176 (m), 1126 (m), 1089 (m), 946 (w). MS (GC–EI, 70 eV): *m*/*z* (%)=117 ($[M-1]^+$, 2), 103 (38), 100 (6), 87 (29), 74 (83), 71 (45), 59 (18), 45 (57), 43 (100).

3.5.2. Ethyl 3-hydroxyvalerate (1c). Starting with diisopropylamine (10.12 g, 100 mmol), THF (100 mL), *n*-BuLi (2.5 M in hexanes, 41 mL, 103 mmol), ethyl acetate (8.81 g, 100 mmol), propionaldehyde (6.97 g, 120 mmol), and hydrochloric acid (2.0 M, 50 mL), **1c** was isolated by destillation as a clear colorless liquid (12.09 g, 83%); bp 100 °C (5 mbar). Reaction time: 3.5 min. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.97 (t, ^3J=7.4 Hz, 3H, CH_3CH_2-CH), 1.28 (t, ^3J=7.1 Hz, 3H, OCH_2CH_3), 1.52 (m, 2H, CH_3CH_2CH), 2.40 (dd, ^2J=16.4 Hz, ^3J=8.9 Hz, 1H, CH_AH_BCO), 2.51 (dd, ^2J=16.4 Hz, ^3J=3.3 Hz, 1H, CH_AH_BCO), 2.85 (br, 1H, OH), 3.94 (dddd, $^3J_1$=8.9 Hz, $^3J_2$=7.0 Hz, $^3J_3$=5.5 Hz, $^3J_4$=3.3 Hz, 1H, CHOH), 4.18 (q, ^3J=7.1 Hz, 2H, OCH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ=9.7 (CH_3CH_2CH), 14.0 (OCH_2CH_3), 29.3 (CH_3CH_2CH), 40.9 (CH_2CO), 60.5 (OCH_2), 69.2 (CHOH), 172.9 (CO). IR (neat, cm^{-1}): $\tilde{\nu}$=3447 (br, m), 2968 (m), 2936 (m), 2880 (w), 1735 (s), 1465 (w), 1374 (m), 1282 (m), 1250 (m), 1179 (s), 1112 (m), 1034 (m), 983 (m). MS (GC–EI, 70 eV): *m*/*z* (%)=145 ($[M-1]^+$, 1), 128 (3), 117 (100), 101 (29), 89 (48), 71 (93), 59 (40), 43 (49). HRMS (EI, 70 eV): calcd for $C_7H_{13}O_3$ ($[M-1]^+$) 145.08592; found 145.08556.

3.5.3. Ethyl 3-hydroxyheptanoate (1g). Starting with diisopropylamine (10.12 g, 100 mmol), THF (100 mL), *n*-BuLi (2.5 M in hexanes, 41 mL, 103 mmol), ethyl acetate (8.81 g, 100 mmol), valeraldehyde (10.34 g, 120 mmol), and hydrochloric acid (2.0 M, 50 mL), **1g** was isolated by destillation as a clear colorless liquid (14.52 g, 83%); bp 70 °C (0.1 mbar). Reaction time: 3.5 min. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.91 (t, ^3J=7.1 Hz, 3H, CH_3CH_2-CH_2), 1.28 (t, ^3J=7.1 Hz, 3H, OCH_2CH_3), 1.30–1.60 (m, 6H, $(CH_2)_3$), 2.40 (dd, ^2J=16.4 Hz, ^3J=8.8 Hz, 1H, CH_AH_BCO), 2.51 (dd, ^2J=16.4 Hz, ^3J=3.3 Hz, 1H, CH_AH_BCO), 2.89 (br, 1H, OH), 4.00 (m, 1H, CHOH), 4.17 (q, ^3J=7.1 Hz, 2H, OCH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.9, 14.1 (CH_3), 22.5, 27.5, 36.2 ($(CH_2)_3$), 41.3 (CH_2CO), 60.5 (OCH_2), 67.9 (CHOH), 173.0 (CO). IR (neat, cm^{-1}): $\tilde{\nu}$=3447 (br, m), 2959 (s), 2933 (s), 2873 (m), 2862 (m), 1735 (s), 1374 (m), 1300 (m), 1249 (m), 1176 (m), 1028 (m). MS (GC–EI, 70 eV): *m*/*z* (%)=173 ($[M-1]^+$, 0.5), 156 (2), 117 (100), 89 (33), 88 (31), 71 (59), 43 (30). HRMS (EI, 70 eV): calcd for $C_9H_{17}O_3$ ($[M-1]^+$) 173.11722; found 173.11724.

3.5.4. *tert*-Butyl 3-hydroxyheptanoate (1h). Starting with diisopropylamine (10.12 g, 100 mmol), THF (100 mL), *n*-BuLi (2.5 M in hexanes, 41 mL, 103 mmol), *tert*-butyl acetate (11.62 g, 100 mmol), valeraldehyde (10.34 g, 120 mmol), and hydrochloric acid (2.0 M, 50 mL), **1h** was isolated by destillation as a clear colorless liquid (18.55 g, 92%); bp 78 °C (0.1 mbar). Reaction time: 3.5 min. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.91 (t, ^3J=7.1 Hz, 3H, CH_3CH$_2$), 1.25–1.55 (m, 6H, (CH$_2$)$_3$), 1.47 (s, 9H, C(CH$_3$)$_3$), 2.31 (dd, ^2J=16.3 Hz, ^3J=8.8 Hz, 1H, CH$_A$H$_B$CO), 2.43 (dd, ^2J=16.3 Hz, ^3J=3.3 Hz, 1H, CH$_A$H$_B$CO), 2.94 (br, 1H, OH), 3.96 (m, 1H, C*H*OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.9 (*C*H$_3$CH$_2$), 22.6, 27.6 (CH$_2$), 28.1 (C(*C*H$_3$)$_3$), 36.1 (CH$_2$), 42.3 (*C*H$_2$CO), 68.1 (CHOH), 81.1 (*C*(CH$_3$)$_3$), 172.5 (CO). IR (neat, cm^{-1}): $\tilde{\nu}$=3443 (br, m), 2959 (s), 2933 (s), 2873 (m), 2862 (m), 1730 (s), 1458 (m), 1393 (m), 1368 (s), 1298 (m), 1255 (m), 1156 (s), 1039 (w). MS (CI, isobutane): *m*/*z* (%)=203 ([M+1]$^+$, 1), 147 (100).

3.5.5. Methyl 3-hydroxy-4,4-dimethylvalerate (1j). Starting with diisopropylamine (7.08 g, 70 mmol), THF (70 mL), *n*-BuLi (2.5 M in hexanes, 29 mL, 72 mmol), methyl acetate (5.19 g, 70 mmol), pivalaldehyde (7.24 g, 84 mmol), and hydrochloric acid (2.0 M, 35 mL), **1j** was isolated by destillation as a clear colorless liquid (6.76 g, 60%); bp 69 °C (0.1 mbar). Reaction time: 4 min. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.92 (s, 9H, C(CH$_3$)$_3$), 2.36 (dd, ^2J=16.1 Hz, ^3J=10.5 Hz, 1H, CH_AH$_B$CO), 2.54 (dd, ^2J=16.1 Hz, ^3J=2.3 Hz, 1H, CH$_A$$H_B$CO), 2.85 (br, 1H, OH), 3.71 (dd, $^3J_1$=10.5 Hz, $^3J_2$=2.3 Hz, 1H, C*H*OH), 3.72 (s, 3H, OCH$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ=25.5 (C(*C*H$_3$)$_3$), 34.3 (*C*CH), 36.4 (CH$_2$), 51.8 (OCH$_3$), 75.4 (CHOH), 174.2 (CO). IR (neat, cm^{-1}): $\tilde{\nu}$=3515 (br, m), 2957 (s), 2909 (m), 2873 (m), 1731 (s), 1439 (m), 1366 (m), 1304 (m), 1166 (m), 1015 (m). MS (GC–EI, 70 eV): *m*/*z* (%)=159 ([M−1]$^+$, 0.1), 103 (100), 87 (14), 71 (65), 57 (35), 43 (41). HRMS (EI, 70 eV): calcd for $C_8H_{15}O_3$ ([M−1]$^+$) 159.10157; found 159.10226.

3.5.6. Methyl 3-hydroxynonanoate (1k). Starting with diisopropylamine (8.91 g, 88 mmol), THF (80 mL), *n*-BuLi (2.5 M in hexanes, 36 mL, 90 mmol), methyl acetate (5.93 g, 80 mmol), heptanal (9.14 g, 80 mmol), and hydrochloric acid (2.0 M, 44 mL), **1k** was isolated by destillation as a clear colorless liquid (9.83 g, 65%); bp 77 °C (0.1 mbar). Reaction time: 4 min. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.88 (t, ^3J=6.8 Hz, 3H, CH_3CH$_2$), 1.15–1.60 (m, 10H, (CH$_2$)$_5$), 2.41 (dd, ^2J=16.4 Hz, ^3J=8.8 Hz, 1H, CH_AH$_B$CO), 2.52 (dd, ^2J=16.4 Hz, ^3J=3.4 Hz, 1H, CH$_A$$H_B$CO), 2.94 (br, 1H, OH), 3.71 (s, 3H, OCH$_3$), 4.00 (m, 1H, C*H*OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.9 (*C*H$_3$CH$_2$), 22.5, 25.3, 29.1, 31.7, 36.5 ((CH$_2$)$_5$), 41.1 (*C*H$_2$CO), 51.6 (OCH$_3$), 67.9 (CHOH), 173.3 (CO). IR (neat, cm^{-1}): $\tilde{\nu}$=3457 (br, m), 2955 (s), 2930 (s), 2858 (m), 1740 (s), 1438 (m), 1290 (m), 1197 (m), 1167 (m), 1056 (w). MS (GC–EI, 70 eV): *m*/*z* (%)=187 ([M−1]$^+$, 0.5), 170 (0.6), 103 (100), 74 (33), 71 (35), 55 (19), 43 (34). HRMS (EI, 70 eV): calcd for $C_{10}H_{19}O_3$ ([M−1]$^+$) 187.13287; found 187.13289.

3.5.7. Ethyl 3-hydroxy-12-tridecenoate (1m). Starting with diisopropylamine (10.12 g, 100 mmol), THF (100 mL), *n*-BuLi (2.5 M in hexanes, 41 mL, 103 mmol), ethyl acetate (8.81 g, 100 mmol), 10-undecenal (13.46 g, 80 mmol), and hydrochloric acid (2.0 M, 50 mL), **1m** was isolated by column chromatography (silica gel; *n*-heptane/ethyl acetate=7:1→5:1) as a clear slightly yellow oil (13.23 g, 65%); R_f 0.33 (*n*-heptane/ethyl acetate=5:1). Reaction time: 4.5 min. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.23–1.55 (m, 17H, CHOH(CH_2)$_7$, CH$_3$), 2.03 (m, 2H, H$_2$C=CHCH_2), 2.38 (dd, ^2J=16.4 Hz, ^3J=8.7 Hz, 1H, CH_AH$_B$CO), 2.50 (dd, ^2J=16.4 Hz, ^3J=3.4 Hz, 1H, CH$_A$$H_B$CO), 2.66 (br, 1H, OH), 3.99 (m, 1H, C*H*OH), 4.16 (q, ^3J=7.1 Hz, 2H, OCH$_2$), 4.88–5.03 (m, 2H, H_2C=CH), 5.80 (ddt, $^3J_1$=17.0 Hz, $^3J_2$=10.3 Hz, $^3J_3$=6.7 Hz, 1H, H$_2$C=C*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.2 (CH$_3$), 25.5, 28.9, 29.1, 29.4, 29.5, 29.5, 33.8, 36.5, 41.3 ((CH$_2$)$_8$, *C*H$_2$CO), 60.7 (OCH$_2$), 68.0 (CHOH), 114.1 (H$_2$*C*=CH), 139.2 (H$_2$C=*C*H), 173.1 (CO). IR (neat, cm^{-1}): $\tilde{\nu}$=3454 (br, w), 2979 (m), 2927 (s), 2855 (m), 1736 (s), 1641 (w), 1465 (m), 1373 (m), 1301 (m), 1182 (m), 1030 (m), 910 (m). MS (CI, isobutane): *m*/*z* (%)=257 ([M+1]$^+$, 100), 239 (20). Anal. Calcd for $C_{15}H_{28}O_3$ (256.38): C, 70.27; H, 11.01. Found: C, 70.10; H, 11.20.

3.5.8. Ethyl 3-hydroxy-3-phenylpropionate (1o). Starting with diisopropylamine (6.07 g, 60 mmol), THF (70 mL), *n*-BuLi (2.5 M in hexanes, 25 mL, 63 mmol), ethyl acetate (4.85 g, 55 mmol), benzaldehyde (5.31 g, 50 mmol), and hydrochloric acid (2.0 M, 28 mL), **1o** was isolated by destillation as a clear slightly yellow liquid (7.58 g, 78%); bp 110 °C (0.1 mbar). Reaction time: 4 min. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.25 (t, ^3J=7.1 Hz, 3H, CH$_3$), 2.68 (dd, ^2J=16.3 Hz, ^3J=4.4 Hz, 1H, CH_AH$_B$CO), 2.75 (dd, ^2J=16.3 Hz, ^3J=8.4 Hz, 1H, CH$_A$$H_B$CO), 3.34 (d, ^3J=3.5 Hz, 1H, OH), 4.17 (q, ^3J=7.1 Hz, 2H, OCH$_2$), 5.12 (m, 1H, C*H*OH), 7.24–7.39 (m, 5H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.0 (CH$_3$), 43.3 (*C*H$_2$CO), 60.7 (OCH$_2$), 70.2 (CHOH), 125.6, 127.6, 128.4 (CH$_{Ar}$), 142.5 (C$_{Ar}$), 172.2 (CO). IR (neat, cm^{-1}): $\tilde{\nu}$=3458 (br, m), 2982 (w), 1732 (s), 1454 (w), 1372 (m), 1298 (m), 1268 (m), 1196 (m), 1162 (m), 1038 (m), 701 (m). MS (EI, 70 eV): *m*/*z* (%)=194 (M$^+$, 39), 147 (10), 120 (19), 107 (100), 106 (25), 105 (75), 88 (19), 79 (65), 77 (53). HRMS (EI, 70 eV): calcd for $C_{11}H_{14}O_3$ (M$^+$) 194.09375; found 194.09339.

3.5.9. Ethyl 3-hydroxy-3-(4-methylphenyl)-propionate (1p). Starting with diisopropylamine (10.12 g, 100 mmol), THF (100 mL), *n*-BuLi (2.5 M in hexanes, 42 mL, 105 mmol), ethyl acetate (8.81 g, 100 mmol), 4-methylbenzaldehyde (9.57 g, 80 mmol), and hydrochloric acid (2.0 M, 50 mL), **1p** was isolated by column chromatography (silica gel; *n*-heptane/ethyl acetate=5:1) as a clear yellow oil (12.17 g, 73%); R_f 0.22 (*n*-heptane/ethyl acetate=5:1). Reaction time: 5 min. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.26 (t, ^3J=7.1 Hz, 3H, CH$_2$CH_3), 2.34 (s, 3H, ArCH$_3$), 2.67 (dd, ^2J=16.1 Hz, ^3J=4.3 Hz, 1H, CH_AH$_B$CO), 2.76 (dd, ^2J=16.1 Hz, ^3J=8.4 Hz, 1H, CH$_A$$H_B$CO), 3.21 (br, 1H, OH), 4.18 (q, ^3J=7.1 Hz, 2H, OCH$_2$), 5.10 (dd, $^3J_1$=8.6 Hz, $^3J_2$=4.3 Hz, 1H, C*H*OH), 7.14–7.28 (m, 4H, Ar). ^{13}C NMR (62 MHz, $CDCl_3$): δ=14.1 (CH$_2$CH_3), 21.1 (ArCH$_3$), 43.3 (*C*H$_2$CO), 60.8 (OCH$_2$), 70.1 (CHOH), 125.6, 129.2 (CH$_{Ar}$), 137.5, 139.5 (C$_{Ar}$), 172.4 (CO). IR (neat, cm^{-1}): $\tilde{\nu}$=3459 (br, s), 2982 (m), 2925 (m), 1734

(s), 1515 (m), 1372 (m), 1195 (m), 1160 (m), 1038 (m), 819 (m). MS (EI, 70 eV): *m/z* (%)=208 (M^+, 12), 190 (13), 145 (29), 121 (67), 120 (64), 119 (100), 93 (21), 91 (90), 65 (20). Anal. Calcd for $C_{12}H_{16}O_3$ (208.25): C, 69.21; H, 7.74. Found: C, 69.09; H, 7.85.

3.5.10. Ethyl 3-hydroxy-3-(2-methoxyphenyl)-propionate (1s). Starting with diisopropylamine (20.24 g, 200 mmol), THF (180 mL), *n*-BuLi (2.5 M in hexanes, 82 mL, 205 mmol), ethyl acetate (17.62 g, 200 mmol), 2-methoxybenzaldehyde (21.78 g, 160 mmol), dissolved in THF (20 mL), and hydrochloric acid (2.0 M, 100 mL), **1s** was isolated by column chromatography (silica gel; *n*-heptane/ethyl acetate=3:1) as a clear slightly yellow oil (16.41 g, 37%*); R_f 0.27 (*n*-heptane/ethyl acetate=3:1). Reaction time: 4.5 min. *Only 55% of the raw product was used for column chromatography. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.26 (t, ^3J=7.1 Hz, 3H, CH_2CH_3), 2.69 (dd, ^2J=16.1 Hz, ^3J=9.0 Hz, 1H, CH_AH_BCO), 2.83 (dd, ^2J=16.1 Hz, ^3J=4.0 Hz, 1H, CH_AH_BCO), 3.2 (br, 1H, OH), 3.85 (s, 3H, OCH_3), 4.17 (q, 7.1 Hz, 2H, OCH_2), 5.36 (dd, $^3J_1$=8.9 Hz, $^3J_2$=3.7 Hz, 1H, CHOH), 6.87 (dd, ^3J=8.2 Hz, ^4J=0.9 Hz, 1H, Ar), 6.97 (m, 1H, Ar), 7.26 (m, 1H, Ar), 7.43 (dd, ^3J=7.6 Hz, ^4J=1.5 Hz, 1H, Ar). ^{13}C NMR (62 MHz, $CDCl_3$): δ=14.0 (CH_2CH_3), 41.6 (CH_2CO), 55.1 (OCH_3), 60.5 (OCH_2), 66.3 (CHOH), 110.1, 120.6, 126.4, 128.4 (CH_{Ar}), 130.5 ($C_{Ar}CHOH$), 155.9 ($C_{Ar}OCH_3$), 172.5 (CO). IR (neat, cm^{-1}): $\tilde{\nu}$=3497 (br, s), 2981 (m), 2939 (m), 1733 (s), 1602 (m), 1492 (s), 1465 (s), 1286 (s), 1243 (s), 1190 (s), 1159 (s), 1029 (s), 756 (s). MS (EI, 70 eV): *m/z* (%)=224 (M^+, 14), 206 (8), 175 (9), 161 (14), 150 (28), 137 (100), 135 (44), 107 (44), 77 (22). Anal. Calcd for $C_{12}H_{16}O_4$ (224.25): C, 64.27; H, 7.19. Found: C, 64.25; H, 7.26.

3.5.11. Ethyl 3-(4-chlorophenyl)-3-hydroxypropionate (1t). Starting with diisopropylamine (10.12 g, 100 mmol), THF (90 mL), *n*-BuLi (2.5 M in hexanes, 41 mL, 103 mmol), ethyl acetate (8.81 g, 100 mmol), 4-chlorobenzaldehyde (11.25 g, 80 mmol), dissolved in THF (10 mL), and hydrochloric acid (2.0 M, 50 mL), **1t** was isolated by column chromatography (silica gel; *n*-heptane/ethyl acetate=3:1) as a clear slightly yellow oil (13.91 g, 76%); R_f 0.30 (*n*-heptane/ethyl acetate=3:1). Reaction time: 4.5 min. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.26 (t, ^3J=7.1 Hz, 3H, CH_3), 2.68 (s, 1H, CH_AH_BCO), 2.70 (d, ^3J=2.1 Hz, 1H, CH_AH_BCO), 3.2 (br, 1H, OH), 4.18 (q, ^3J=7.1 Hz, 2H, OCH_2), 5.10 (dd, $^3J_1$=7.3 Hz, $^3J_2$=5.5 Hz, 1H, CHOH), 7.31 (s, 4H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.1 (CH_3), 43.2 (CH_2CO), 61.0 (OCH_2), 69.6 (CHOH), 127.1, 128.7 (CH_{Ar}), 133.5, 141.0 (C_{Ar}), 172.3 (CO). IR (neat, cm^{-1}): $\tilde{\nu}$=3457 (br, s), 2983 (m), 1732 (s), 1493 (m), 1373 (m), 1194 (s), 1162 (m), 1091 (m), 1014 (s), 831 (m). MS (EI, 70 eV): *m/z* (%)=230 (M^+, ^{37}Cl, 4), 228 (M^+, ^{35}Cl, 9), 165 (25), 141 (77), 140 (52), 139 (100), 111 (34), 88 (20), 77 (36). Anal. Calcd for $C_{11}H_{13}ClO_3$ (228.67): C, 57.78; H, 5.73. Found: C, 57.66; H, 5.78.

3.5.12. Ethyl 3-hydroxy-3-methylbutyrate (1u). Starting with diisopropylamine (10.12 g, 100 mmol), THF (100 mL), *n*-BuLi (2.5 M in hexanes, 41 mL, 103 mmol), ethyl acetate (8.81 g, 100 mmol), acetone (6.97 g, 120 mmol), and hydrochloric acid (2.0 M, 50 mL), **1u** was isolated by destillation as a clear colorless liquid (11.33 g, 77%); bp 48 °C (0.1 mbar). Reaction time: 10 min (−60 °C). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.25 (m, 9H, CH_2CH_3, $C(CH_3)_2$), 2.45 (s, 2H, CH_2CO), 3.59 (s, 1H, OH), 4.15 (q, ^3J=7.1 Hz, 2H, OCH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.1 (CH_2CH_3), 29.1 ($C(CH_3)_2$), 46.3 (CH_2CO), 60.5 (OCH_2), 68.9 (COH), 172.9 (CO).

3.6. General procedure for the preparation of 1,3-bis(trimethylsilyloxy)alk-1-enes 2a–u

An LDA solution was prepared by the addition of *n*-BuLi to a THF solution of diisopropylamine at 0 °C. After stirring for 1 h, the solution was cooled to −78 °C and the respective 3-hydroxyesters (**1a–u**) were added. After stirring for 1 h at −78 °C, TMSCl was added and the solution was allowed to warm to 20 °C within 14–24 h. The solvent and volatile compounds were removed in vacuo. The residue was dissolved in *n*-hexane and the suspension was filtered under inert atmosphere. The filtrate was concentrated in vacuo to give 1,3-bis(trimethylsilyloxy)alk-1-enes **2a–u**, which were used without further purification. Due to their low stability, products **2a–u** could be only characterized by NMR.

3.6.1. 1-Methoxy-1,3-bis(trimethylsilyloxy)but-1-ene (2a). Starting with **1a** (2.66 g, 22.5 mmol) and TMSCl (6.11 g, 56.3 mmol), **2a** was obtained as a slightly yellow liquid (4.34 g, 73%). Reaction time: 18 h. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.08 (s, 9H, $Si(CH_3)_3$), 0.18 (s, 9H, $Si(CH_3)_3$), 1.20 (d, ^3J=6.3 Hz, 3H, $CHCH_3$), 3.46 (s, 3H, OCH_3), 3.59 (d, ^3J=8.8 Hz, 1H, CCH), 4.60 (dq, $^3J_1$=8.8 Hz, $^3J_2$=6.3 Hz, 1H, OCH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=0.2, 0.3 ($Si(CH_3)_3$), 25.9 ($CHCH_3$), 54.3 (OCH_3), 64.6, 81.9 (CH), 156.5 (C).

3.6.2. 1,3-Bis(trimethylsilyloxy)-1-ethoxy-but-1-ene (2b). Starting with **1b** (2.64 g, 20.00 mmol) and TMSCl (6.11 g, 56.3 mmol), **2b** was obtained as a slightly yellow liquid (4.143 g, 75%). Reaction time: 18 h. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=0.06 (s, 9H, $Si(CH_3)_3$), 0.17 (s, 9H, $COSi(CH_3)_3$-OEt), 1.18 (d, 3H, ^3J=6.3 Hz, CH_3), 1.22 (t, 3H, ^3J=7.0 Hz, CH_2CH_3), 3.54 (d, 1H, ^3J=8.8 Hz, C=CH), 3.66 (dq, 2H, ^3J=7.0 Hz, ^2J=1.7 Hz, CH_2), 4.52–4.64 (m, 1H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=0.3 ($Si(CH_3)_3$), 0.5 ($Si(CH_3)_3$), 14.3 (CH_2CH_3), 26.0 (CH_3), 62.8 (CH_2), 64.7 (CCH_3), 82.3 (CH), 155.5 (COEt).

3.6.3. 1-Ethoxy-1,3-bis(trimethylsilyloxy)pent-1-ene (2c). Starting with **1c** (6.58 g, 45.0 mmol) and TMSCl (12.22 g, 112 mmol), **2c** was obtained as a clear yellow liquid (12.92 g, 99%). Reaction time: 19 h. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.09 (s, 9H, $Si(CH_3)_3$), 0.21 (s, 9H, $Si(CH_3)_3$), 0.85 (t, ^3J=7.4 Hz, 3H, $CHCH_AH_BCH_3$), 1.28 (t, ^3J=7.1 Hz, 3H, OCH_2CH_3), 1.33–1.65 (m, 2H, $CHCH_AH_B$), 3.51 (d, ^3J=8.9 Hz, 1H, CCH), 3.72 (q, ^3J=7.1 Hz, 2H, OCH_2), 4.33 (dt, $^3J_1$=8.9 Hz, $^3J_2$=6.6 Hz, 1H, OCH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=0.3, 0.4 ($Si(CH_3)_3$), 10.3, 14.3 (CH_3), 32.3 ($CHCH_2$), 62.8 (OCH_2), 70.0, 80.7 (CH), 156.1 (C). MS (EI, 70 eV): *m/z* (%)=292 ($[M+2]^+$, 2), 261 (16), 143 (29), 131 (33), 75 (50), 74 (100), 28 (75).

3.6.4. 1-*tert*-Butoxy-1,3-bis(trimethylsilyloxy)-pent-1-ene (2d). Starting with **1d** (3.48 g, 20.00 mmol) and TMSCl

(12.22 g, 112 mmol), **2d** was obtained as a clear yellow liquid (6.178 g, 97%). Reaction time: 19 h. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=0.11 (s, 9H, Si(CH_3)$_3$), 0.22 (s, 9H, COSi(CH_3)$_3$O-*t*-Bu), 0.87 (t, >3H, CH_3), 1.34 (s, 9H, C(CH_3)$_3$), 1.45 (m, >2H, CH_2), 3.94 (d, 1H, ^3J=9 Hz, C=C*H*), 4.28 (m, 1H, C*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=0.3 (Si(*C*H$_3$)$_3$), 0.6 (COSi(*C*H$_3$)$_3$O-*t*-Bu), 10.4 (CH$_2$*C*H$_3$), 28.4 (C(*C*H$_3$)$_3$), 32.0 (*C*H$_2$CH$_3$), 70.3 (C=*C*H), 78.8 (*C*(CH$_3$)$_3$), 93.7 (*C*H), 151.6 (*C*O$_2$-*t*-Bu).

3.6.5. 1,3-Bis(trimethylsilyloxy)-1-ethoxy-hex-1-ene (2e). Starting with **1e** (3.2 g, 20.0 mmol) and TMSCl (3.447 g, 32 mmol), **2e** was obtained as a clear yellow liquid (4.811 g, 79%) Reaction time: 19 h. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=0.06 (s, 9H, Si(CH_3)$_3$), 0.17 (s, 9H, COSi-(CH_3)$_3$OEt), 0.91 (t, 3H, CH_3), 1.23 (t, 3H, ^3J=6.9 Hz, OCH$_2$CH_3), 1.18–1.50 (signal overlap, 4H, CH_2CH_2CH$_3$), 3.49 (d, 1H, ^3J=8.9 Hz, C=C*H*), 3.71 (q, ^3J=7.0 Hz, 2H, OCH_2CH$_3$), 4.46–4.39 (m, 1H, C*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=0.3 (Si(*C*H$_3$)$_3$), 0.4 (COSi(*C*H$_3$)$_3$OEt), 13.9 (*C*H$_3$), 14.3 (OCH$_2$*C*H$_3$), 19.1 (CH$_2$*C*H$_2$CH$_3$), 41.8 (*C*H$_2$CH$_2$CH$_3$), 62.8 (O*C*H$_2$CH$_3$), 68.3 (C=*C*H), 80.9 (*C*H), 156.0 (*C*OEt).

3.6.6. 1,3-Bis(trimethylsilyloxy)-1-ethoxy-4-methyl-pent-1-ene (2f). Starting with **1f** (3.2 g, 20.0 mmol) and TMSCl (3.447 g, 32 mmol), **2f** was obtained as a clear yellow liquid (5.221 g, 86%). Reaction time: 19 h. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=0.09 (s, 9H, Si(CH_3)$_3$), 0.20 (s, 9H, COSi-(CH_3)$_3$OEt), 0.82 (d, 3H, ^3J=6.7 Hz, CH$_3$), 0.87 (d, 3H, ^3J=6.7 Hz, CH$_3$), 1.28 (t, 3H, ^3J=7.0 Hz, CH$_2$CH_3), 1.6 (m, 1H, C*H*(CH$_3$)$_2$), 3.5 (d, 1H, ^3J=9 Hz, C=C*H*), 3.72 (q, 2H, ^3J=7.0 Hz, CH$_2$), 4.08–4.21 (m, >1H, C*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=0.3 (Si(*C*H$_3$)$_3$), 0.5 (COSi-(*C*H$_3$)$_3$OEt), 14.4 (CH$_2$*C*H$_3$), 18.3 (CH$_3$), 18.9 (CH$_3$), 35.6 (*C*H(CH$_3$)$_2$), 62.8 (CH$_2$), 73.7 (C=*C*H), 87.7 (C*H*), 156.3 (*C*OEt).

3.6.7. 1-Ethoxy-1,3-bis(trimethylsilyloxy)hept-1-ene (2g). Starting with **1g** (3.92 g, 22.5 mmol) and TMSCl (6.11 g, 56.3 mmol), **2g** was obtained as a clear yellow liquid (7.17 g, 100%). Reaction time: 24 h. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.10 (s, 9H, Si(CH$_3$)$_3$), 0.21 (s, 9H, Si(CH$_3$)$_3$), 0.86–0.94 (m, 3H, CH$_2$CH$_2$CH_3), 1.20–1.60 (m, 9H, (CH_2)$_3$, OCH$_2$CH_3), 3.51 (d, ^3J=8.9 Hz, 1H, CCH), 3.72 (q, ^3J=7.1 Hz, 2H, OCH$_2$), 4.41 (m, 1H, OCH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=0.3, 0.5 (Si(CH$_3$)$_3$), 14.1, 14.3 (CH$_3$), 22.6, 28.1, 39.3 (CH$_2$), 62.8 (OCH$_2$), 68.6, 81.0 (CH), 156.0 (C). MS (EI, 70 eV): *m*/*z* (%)=318 (M$^+$, 0.2), 261 (42), 231 (11), 189 (13), 159 (12), 146 (25), 143 (100), 110 (19), 28 (20).

3.6.8. 1-(*tert*-Butoxy)-1,3-bis(trimethylsilyloxy)hept-1-ene (2h). Starting with **1h** (4.56 g, 22.5 mmol) and TMSCl (6.11 g, 56.3 mmol), **2h** was obtained as a clear yellow liquid (5.95 g, 76%). Reaction time: 22 h. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.08 (s, 9H, Si(CH$_3$)$_3$), 0.18 (s, 9H, Si(CH$_3$)$_3$), 0.86 (m, 3H, CH$_2$CH_3), 1.13–1.52 (m, 15H, (CH$_2$)$_3$), C(CH$_3$)$_3$), 3.90 (d, ^3J=8.9 Hz, 1H, CCH), 4.33 (ddd, $^3J_1$=8.9 Hz, $^3J_2$=7.2 Hz, $^3J_3$=5.6 Hz, 1H, OCH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=0.3, 0.5 (Si(CH$_3$)$_3$), 14.1 (CH$_2$*C*H$_3$), 22.5, 28.1 (CH$_2$), 28.4 (C(*C*H$_3$)$_3$), 38.9 (CH$_2$), 68.8 (CH), 78.6 (O*C*(CH$_3$)$_3$), 93.8 (CH), 151.4 (*C*CH).

3.6.9. 1,3-Bis(trimethylsilyloxy)-1-ethoxy-5-methyl-hex-1-ene (2i). Starting with **1i** (3.48 g, 20.00 mmol) and TMSCl (3.447 g, 32 mmol), **2i** was obtained as a clear yellow liquid (4.754 g, 75%). Reaction time: 22 h. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=0.10 (s, 9H, Si(CH_3)$_3$), 0.20 (s, 9H, COSi(CH_3)$_3$OEt), 0.87 (d, 6H, ^3J=6.3 Hz, CH_3), 1.20–1.30 (m, 4H, CH_AH$_B$, CH_3), 1.36–1.48 (m, 1H, CH$_A$$H_B$), 1.55–1.65 (m, 1H, C*H*(CH$_3$)$_2$), 3.47 (d, 1H, ^3J=9 Hz, C=C*H*), 3.70 (q, 2H, ^3J=6.9 Hz, CH_2CH$_3$), 4.46–4.56 (m, 1H, C*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=0.3 (Si(*C*H$_3$)$_3$), 0.5 (COSi(*C*H$_3$)$_3$OEt), 14.3 (CH$_2$*C*H$_3$), 23.7 (*C*H(CH$_3$)$_2$), 24.8 (*C*H$_3$), 48.9 (*C*H$_2$), 62.8 (*C*H$_2$CH$_3$), 67.0 (C=*C*H), 81.1 (*C*H), 155.9 (*C*OEt).

3.6.10. 1-Methoxy-4,4-dimethyl-1,3-bis(trimethylsilyloxy)-pent-1-ene (2j). Starting with **1j** (3.58 g, 22.3 mmol) and TMSCl (6.11 g, 56.3 mmol), **2j** was obtained as a clear yellow liquid (4.97 g, 73%). Reaction time: 19 h. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.07 (s, 9H, Si(CH$_3$)$_3$), 0.20 (s, 9H, Si(CH$_3$)$_3$), 0.84 (s, 9H, C(CH$_3$)$_3$), 3.51 (s, 3H, OCH$_3$), 3.54 (d, ^3J=9.3 Hz, 1H, OCHC*H*), 4.07 (d, ^3J=9.3 Hz, 1H, OCH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=0.3, 0.5 (Si(CH$_3$)$_3$), 25.8 (C(*C*H$_3$)$_3$), 35.9 (*C*(CH$_3$)$_3$), 54.4 (OCH$_3$), 75.9, 77.1 (CH), 157.2 (*C*=CH).

3.6.11. 1-Methoxy-1,3-bis(trimethylsilyloxy)non-1-ene (2k). Starting with **1k** (4.23 g, 22.5 mmol) and TMSCl (6.11 g, 56.3 mmol), **2k** was obtained as a clear yellow liquid (6.81 g, 91%). Reaction time: 17 h. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.09 (s, 9H, Si(CH$_3$)$_3$), 0.20 (s, 9H, Si(CH$_3$)$_3$), 0.88 (m, 3H, CH$_2$CH_3), 1.15–1.60 (m, 10H, (CH$_2$)$_5$), 3.49 (s, 3H, OCH$_3$), 3.54 (d, ^3J=8.9 Hz, 1H, CCH), 4.40 (m, 1H, OCH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=0.27, 0.34 (Si(CH$_3$)$_3$), 14.0 (CH$_2$*C*H$_3$), 22.6, 25.8, 29.1, 31.9, 39.5 (CH$_2$), 54.4 (OCH$_3$), 68.5, 80.7 (CH), 157.0 (C).

3.6.12. 1,3-Bis(trimethylsilyloxy)-1-ethoxy-3-vinylprop-1-ene (2l). Starting with **1l** (2.88 g, 20.00 mmol) and TMSCl (3.447 g, 32 mmol), **2l** was obtained as a clear yellow liquid (3.024 g, 52%). Reaction time: 22 h. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=0.13 (s, 9H, Si(CH_3)$_3$), 0.23 (s, 9H, COSi(CH_3)$_3$OEt), 1.25–1.32 (m, overlap, 3H, CH_3), 3.58 (d, 1H, ^3J=9.1 Hz, C=C*H*), 3.74 (qd, 2H, ^2J=1.4 Hz, ^3J=7.0 Hz, CH_2), 4.06–4.26 (m, 1H, CH), 4.90–4.98 (m, 2H, CHCH_2), 5.79–5.94 (m, 1H, C*H*CH$_2$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=0.3 (Si(*C*H$_3$)$_3$), 0.4 (COSi(*C*H$_3$)$_3$OEt), 14.3 (CH$_3$), 62.9 (*C*H$_2$), 69.4 (C=*C*H), 79.3 (*C*H), 111.8 (CH*C*H$_2$), 142.1 (*C*HCH$_2$), 156.5 (*C*OEt).

3.6.13. 1-Ethoxy-1,3-bis(trimethylsilyloxy)trideca-1,12-diene (2m). Starting with **1m** (5.86 g, 22.9 mmol) and TMSCl (6.23 g, 57.3 mmol), **2m** was obtained as a clear yellow liquid (8.51 g, 93%). Reaction time: 20 h. ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.09 (s, 9H, Si(CH$_3$)$_3$), 0.20 (s, 9H, Si(CH$_3$)$_3$), 1.20–1.60 (m, 17H, OCH(CH_2)$_7$, CH$_3$), 2.03 (m, 2H, H$_2$C=CHCH_2), 3.49 (d, ^3J=8.9 Hz, 1H, CCH), 3.71 (q, ^3J=7.0 Hz, 2H, OCH$_2$), 4.40 (dt, $^3J_1$=8.9 Hz, $^3J_2$=6.4 Hz, 1H, OCH), 4.87–5.03 (m, 2H, H_2C=CH), 5.80 (ddt, $^3J_1$=17.0 Hz, $^3J_2$=10.3 Hz, $^3J_3$=6.7 Hz, 1H, H$_2$C=C*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ=0.3, 0.5 (Si(CH$_3$)$_3$), 14.3 (CH$_3$), 25.9, 28.9, 29.1, 29.5, 29.5, 29.6, 33.8, 39.5 ((CH$_2$)$_8$), 62.8 (OCH$_2$), 68.6, 81.0 (CH), 114.0 (*C*H$_2$CHCH$_2$CH$_2$), 139.1 (CH$_2$*C*HCH$_2$), 156.0 (C).

3.6.14. 1,3-Bis(trimethylsilyloxy)-1-methoxy-4-phenylbut-1-ene (2n). Starting with **1n** (3.88 g, 20.00 mmol) and TMSCl (3.447 g, 32 mmol), **2n** was obtained as a clear yellow liquid (5.877 g, 87%). Reaction time: 22 h. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=0.05 (s, 9H, Si(CH_3)$_3$), 0.19 (s, 9H, COSi(CH_3)$_3$OEt), 2.81 (qd, ^3J=7.4, 5.7 Hz, ^2J=13 Hz, 2H, CH_2), 3.51 (s, 3H, OMe), 3.70 (d, 1H, ^3J=8.9 Hz, –C=C*H*), 4.60–4.68 (m, 1H, C*H*), 7.10–7.45 (m, 5H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=0.01 (Si(*C*H$_3$)$_3$), 0.3 (COSi(*C*H$_3$)$_3$OEt), 46.0 (*C*H$_2$), 54.5 (OMe), 69.9 (C=*C*H), 80.1 (*C*H), 125.7 (Ar), 127.8 (Ar), 129.8 (Ar), 139.6 (Ar), 157.1 (*C*OMe).

3.6.15. 1-Ethoxy-3-phenyl-1,3-bis(trimethylsilyloxy)-prop-1-ene (2o). Starting with **1o** (4.35 g, 22.4 mmol) and TMSCl (6.11 g, 56.3 mmol), **2o** was obtained as a clear yellow-orange liquid (7.01 g, 92%). Reaction time: 17 h. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.25 (s, 9H, Si(CH$_3$)$_3$, major), 0.27 (s, 9H, Si(CH$_3$)$_3$, minor), 0.34 (s, 9H, Si(CH$_3$)$_3$, minor), 0.37 (s, 9H, Si(CH$_3$)$_3$, major), 1.37 (t, ^3J=7.0 Hz, 3H, CH$_3$, major), 1.38 (t, ^3J=7.0 Hz, 3H, CH$_3$, minor), 3.78–3.89 (m, 3H, OCH$_2$, OCHC*H*, major), 4.00–4.07 (m, 3H, OCH$_2$, OCHC*H*, minor), 5.72 (m, 1H, OCH, both), 7.30 (m, 1H, Ph, both), 7.39 (m, 2H, Ph, both), 7.49 (d, ^3J=7.3 Hz, 2H, Ph, both). ^{13}C NMR (75 MHz, $CDCl_3$): δ=0.3, 0.6 (Si(CH$_3$)$_3$), 14.3 (CH$_3$), 62.9 (OCH$_2$), 70.1, 81.6 (CH), 125.6, 126.2, 127.9 (CH$_{Ar}$), 146.7, 156.5 (C).

3.6.16. 1-Ethoxy-3-(4-tolyl)-1,3-bis(trimethylsilyloxy)-prop-1-ene (2p). Starting with **1p** (4.34 g, 20.8 mmol) and TMSCl (6.11 g, 56.3 mmol), **2p** was obtained as a clear orange liquid (6.97 g, 95%). Reaction time: 19 h. ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.13 (s, 9H, Si(CH$_3$)$_3$, major), 0.16 (s, 9H, Si(CH$_3$)$_3$, minor), 0.24 (s, 9H, Si(CH$_3$)$_3$, minor), 0.26 (s, 9H, Si(CH$_3$)$_3$, major), 1.27 (t, ^3J=7.0 Hz, 3H, CH$_3$, major), 1.28 (t, ^3J=7.0 Hz, 3H, CH$_3$, minor), 2.33 (s, 3H, ArCH$_3$, both), 3.66–3.79 (m, 3H, OCH$_2$, OCHC*H*, major), 3.88–3.97 (m, 3H, OCH$_2$, OCHC*H*, minor), 5.58 (m, 1H, OCH, both), 7.06–7.13 (m, 2H, Ar, both), 7.23–7.30 (m, 2H, Ar, both). ^{13}C NMR (75 MHz, $CDCl_3$): δ=0.3, 0.5 (Si(CH$_3$)$_3$), 14.3 (CH$_2$*C*H$_3$), 21.0 (ArCH$_3$), 62.9 (CH$_2$), 70.0, 81.8 (CH), 125.5, 128.6 (CH$_{Ar}$), 135.7, 143.7, 156.4 (C).

3.6.17. 1-Ethoxy-3-(4-methoxyphenyl)-1,3-bis(trimethylsilyloxy)prop-1-ene (2q). Starting with **1q** (4.34 g, 20.8 mmol) and TMSCl (6.11 g, 56.3 mmol), **2q** was obtained as a clear orange liquid (6.92 g, 91%). Reaction time: 19 h. The compound was used directly after its preparation, due to its unstable nature. Spectroscopic data were not obtained.

3.6.18. 1-([1,3-Bis(trimethylsilyloxy)]-3-methoxy-2-propenyl)-2-methylbenzene (2r). Starting with **1r** (3.88 g, 20.00 mmol) and TMSCl (3.447 g, 32 mmol), **2r** was obtained as a clear orange liquid (4.989 g, 74%). Reaction time: 19 h. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=0.16 (s, 9H, Si(CH_3)$_3$), 0.21 (s, 9H, COSi(CH_3)$_3$OEt), 2.3 (s, 3H, ArCH_3), 3.49 (s, 3H, OCH_3), 5.68 (d, 1H, ^3J=2.7 Hz, C*H*), 5.71 (d, 1H, ^3J=2.4 Hz, C=C*H*), 7.05–7.13 (m, 4H, –Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=0.3 (Si(*C*H$_3$)$_3$), 0.5 (COSi(*C*H$_3$)$_3$OEt), 19.0 (Ar*C*H$_3$), 54.6 (OMe), 67.6 (C=*C*H), 79.6 (*C*H), 125.2 (Ar), 125.8 (Ar), 126.1 (Ar), 129.8 (Ar), 133.9 (Ar), 144.7 (Ar), 157.5 (*C*OMe).

3.6.19. 3-1-Ethoxy-3-(2-methoxyphenyl)-1,3-bis(trimethylsilyloxy)prop-1-ene (2s). Starting with **1s** (5.05 g, 22.5 mmol) and TMSCl (6.11 g, 56.3 mmol), **2s** was obtained as a clear yellow-orange liquid (7.28 g, 88%). Reaction time: 17 h. ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.11 (s, 9H, Si(CH$_3$)$_3$), 0.28 (s, 9H, Si(CH$_3$)$_3$), 1.27 (t, ^3J=7.0 Hz, 3H, CH$_2$CH_3), 3.73 (q, ^3J=7.0 Hz, 2H, OCH$_2$), 3.80 (d, ^3J=9.2 Hz, 1H, OCHC*H*), 3.84 (s, 3H, OCH$_3$), 5.95 (d, ^3J=9.2 Hz, 1H, OCH), 6.82–7.03 (m, 2H, Ar), 7.17–7.29 (m, 1H, Ar), 7.50–7.57 (m, 1H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ=0.2, 0.4 (Si(CH$_3$)$_3$), 14.3 (CH$_2$*C*H$_3$), 55.3 (OCH$_3$), 62.8 (CH$_2$), 64.7, 80.9 (CH), 110.5, 120.5, 126.9, 127.3 (CH$_{Ar}$), 135.0, 155.6, 156.4 (C).

3.6.20. (4-Chlorophenyl)-1-ethoxy-1,3-bis(trimethylsilyloxy)prop-1-ene (2t). Starting with **1t** (5.11 g, 22.3 mmol) and TMSCl (6.19 g, 57.0 mmol), **2t** was obtained as a clear orange-red liquid (7.92 g, 95%). Reaction time: 17 h. ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.14 (s, 9H, Si(CH$_3$)$_3$, major), 0.16 (s, 9H, Si(CH$_3$)$_3$, minor), 0.23 (s, 9H, Si(CH$_3$)$_3$, minor), 0.27 (s, 9H, Si(CH$_3$)$_3$, major), 1.28 (t, ^3J=7.0 Hz, 3H, CH$_3$, both), 3.67 (d, ^3J=8.9 Hz, 1H, OCHC*H*, major), 3.73 (m, 2H, OCH$_2$, major), 3.85 (d, ^3J=8.9 Hz, 1H, OCHC*H*, minor), 3.93 (m, 2H, OCH$_2$, minor), 5.56 (d, ^3J=8.9 Hz, 1H, OCH, major), 5.59 (d, ^3J=8.9 Hz, 1H, OCH, minor), 7.23–7.34 (m, 4H, Ar, both). ^{13}C NMR (75 MHz, $CDCl_3$): δ=0.3, 0.6 (Si(CH$_3$)$_3$), 14.3 (CH$_3$), 63.0 (CH$_2$), 69.6, 81.2 (CH), 127.0, 128.0 (CH$_{Ar}$), 131.8, 145.3, 156.6 (C).

3.6.21. 1-Ethoxy-3-methyl-1,3-bis(trimethylsilyloxy)but-1-ene (2u). Starting with **1u** (3.29 g, 22.5 mmol) and TMSCl (6.11 g, 56.3 mmol), **2u** was obtained as a clear yellow liquid (2.32 g, 35%). Reaction time: 14 h. ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.10 (s, 9H, Si(CH$_3$)$_3$, major), 0.11 (s, 9H, Si(CH$_3$)$_3$, minor), 0.15 (s, 9H, Si(CH$_3$)$_3$, major), 0.21 (s, 9H, Si(CH$_3$)$_3$, minor), 1.26 (t, ^3J=7.2 Hz, 3H, CH$_2$CH_3, minor), 1.27 (t, ^3J=7.0 Hz, 3H, CH$_2$CH_3, major), 1.37 (s, 6H, C(CH$_3$)$_2$, minor), 1.39 (s, 6H, C(CH$_3$)$_2$, major), 3.61 (s, 1H, CH, major), 3.67 (q, ^3J=7.0 Hz, CH$_2$, major), 4.07–4.18 (m, 2H, CH$_2$ minor). ^{13}C NMR (75 MHz, $CDCl_3$): δ=0.5, 0.6 (Si(CH$_3$)$_3$), 14.4 (CH$_2$*C*H$_3$), 30.2 (C(*C*H$_3$)$_2$), 62.9 (CH$_2$), 72.7 (CH$_3$*C*), 85.5 (CH), 156.3 (*C*=CH).

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