Regioselective Synthesis of Functionalized Furans by Cyclization of 1,3-Bis-Silyl Enol Ethers with 1-Chloro-2,2-dimethoxyethane

Esen Bellur[a] and Helmar Görls,[b]Peter Langer*[a,c]

Keywords: Cyclization / Chemoselectivity / Silyl enol ethers / Regioselectivity / Tetrahydrofurans

Cyclization of 1,3-bis-silyl enol ethers with 1-chloro-2,2-dimethoxyethane allowed an efficient, regio- and diastereoselective synthesis of a variety of 2-alkylidene-4-methoxytetrahydrofurans. The TFA-mediated elimination of methanol resulted in the formation of functionalized furans. Similarly, 2,3,3a,4,5,6-hexahydro-2,3-benzofurans were prepared and transformed into 4,5,6,7-tetrahydro-2,3-benzofurans by treatment with TFA.
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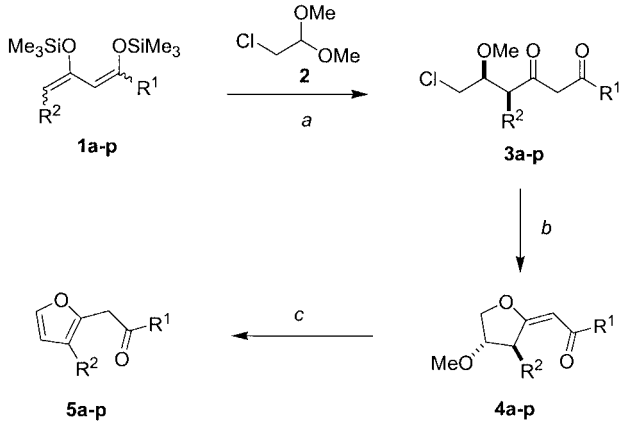
Introduction

Functionalized furans are of considerable pharmacological relevance and occur in a variety of natural products, such as terpenes. They include, for instance, the calicogorgins, furan fatty acids, cytotoxic furanocembranes, gersolanes, pseudopteranes, rosefuran, agassizin, furodysin, mikanifuran, and α-clausenan.[1,2] A number of synthetic approaches to furans have been reported.[2–8] Lewis-acid mediated condensation of silyl enol ethers—masked enolates—with aldehydes and acetals plays an important role in organic synthesis,[9,10] and a number of cyclization reactions have been reported in this context. As one example, the $TiCl_4$-mediated reaction of silyl enol ethers with α-bromoacetals has been reported to give β-alkoxy-γ-bromoketones that could be transformed into substituted furans.[11]

The reaction of 1,3-bis-silyl enol ethers—masked 1,3-dicarbonyl dianions[12]—with aldehydes and acetals is also of great synthetic importance.[13] Reactions between 1,3-bis-silyl enol ethers and enantiomerically pure α-substituted aldehydes often proceed with very good diastereoselectivity,[14] and the enantioselective condensation of a 1,3-bis-silyl enol ether with α-benzyloxyacetic aldehyde has recently been reported.[15] A number of cyclizations of 1,3-bis-silyl enol ethers and of 1-methoxy-3-trimethylsilyloxy-1,3-butadiene with functionalized aldehydes are known.[16] We have recently developed a new approach to 2-alkylidenetetrahydrofurans based on pioneering work by Chan,[17] through cyclizations of 1,3-bis-silyl enol ethers with 1-chloro-2,2-dimethoxyethane.[18] Here we wish to report studies related to the preparative scope of this reaction. With regard to our earlier publication, we have significantly extended its scope and have also studied its stereoselectivity in detail. In addition, the synthesis of furans through elimination reactions of 2-alkylidenetetrahydrofurans is reported. Our methodology allows a convenient synthesis of a great variety of functionalized mono- and bicyclic furans.

Results and Discussion

The Me_3SiOTf-catalysed reaction between 1,3-bis-silyl enol ether **1a**, prepared from methyl acetoacetate in two steps,[12b] and 1-chloro-2,2-dimethoxyethane (**2**) afforded the open-chained condensation product **3a** in 72% yield (Scheme 1, Table 1). Treatment of **3a** with DBU, by our recently published procedure,[18] resulted in regioselective cy-



Scheme 1. Synthesis of monocyclic furans. *a*) 0.5 equiv. Me_3SiOTf, CH_2Cl_2, –78 → 20 °C, *b*) 2.0 equiv. DBU, THF, 20 °C, *c*) TFA, CH_2Cl_2, 20 °C.

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Table 1. Products and yields.

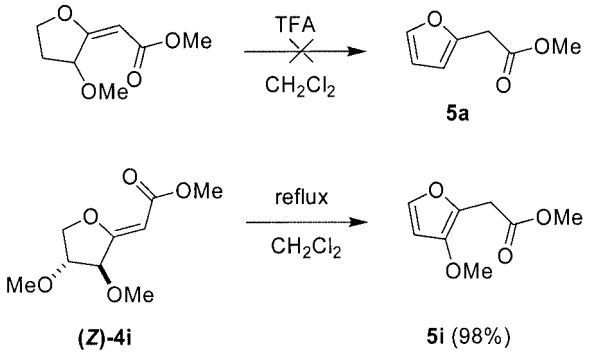
3,4,5	R^1	R^2	% (3)[a]	% (4)[a]	% (5)[a]	δ [ppm][b]	δ [ppm][c]	*E*/*Z*[d]
a	OMe	H	72	86	80	5.38	168.4	> 98:2
b	OEt	H	66	74	100	5.37	168.5	> 98:2
c	O*i*Pr	H	70	80	61	5.35	–	> 98:2
d	$O(CH_2)_2OMe$	H	67	68	100	5.43	167.9	> 98:2
e	OBn	H	51	94	100	5.44	168.3	> 98:2
f	Ph	H	51	–	70	–	–	–
g	OMe	Me	63	90	84	5.33	168.2	> 98:2
h	OEt	Et	83	99	79	5.33	167.9	> 98:2
i	OMe	OMe	64	49	–	5.54	167.8	> 98:2
i	OMe	OMe		33	98	5.05	165.5	< 2:98
j	OEt	Allyl	57	80	100	5.35	167.8	> 98:2
k	OEt	*n*Pr	87	79	100	5.35	167.6	> 98:2
l	OEt	*n*Bu	85	73	100	5.32	167.6	> 98:2
m	OEt	*n*Hex	88	76	100	5.31	167.6	> 98:2
n	OEt	*n*Oct	53	97	100	5.31	168.0	> 98:2
o	OEt	*n*Non	79	87	100	5.31	167.8	> 98:2
p	OEt	*n*Dec	86	70	100	5.31	167.7	> 98:2
q	OEt	$(CH_2)_6Cl$	78	93	76	5.32	167.8	> 98:2

[a] Yields of isolated products. For all compounds **4g**–**q**: *trans*/*cis* > 98:2. Compounds **3** were obtained as mixtures of keto/enol tautomers. In some cases a small amount of starting material (1,3-dicarbonyl compound derived from hydrolysis of 1,3-bis-silyl enol ether) could not be separated. [b] Chemical shift (^{1}H NMR, $CDCl_3$) of the hydrogen atom of the exocyclic double bond of **4**. [c] Chemical shift (^{13}C NMR, $CDCl_3$) of the carbonyl group of **4**. [d] *E*/*Z* ratio of the exocyclic double bond of **4**.

clization and formation of the 2-alkylidene-4-methoxytetrahydrofuran **4a** in 86% yield. The regioselectivity can be explained by stereoelectronic considerations.[19] The thermodynamically favoured isomer, containing an *E*-configured exocyclic double bond, was formed with very good selectivity. Treatment of **4a** with TFA afforded the furan **5a** by elimination of methanol.

Cyclizations of **2** with 1,3-bis-silyl enol ethers **1b**–**e** afforded **3b**–**e**, which were transformed into the known 2-alkylidenetetrahydrofurans **4b**–**e** (Scheme 1, Table 1).[18] The latter were treated with TFA to give the furans **5b**–**e** in good yields. Treatment of **2** with 1,3-bis-silyl enol ether **1f**, prepared from benzoylacetone, gave **3f**, and treatment of this with DBU directly afforded furan **5f**. The reactions between **2** and **1g**–**q** gave the corresponding open-chain products **3g**–**q** with very good diastereoselectivity, while treatment of **3g**–**q** with DBU afforded the 2-alkylidenetetrahydrofurans **4g**–**q**. The exocyclic double bond was formed with very good *E* diastereoselectivity (except in the case of **4i**), despite the presence of the substituent at C-3. The synthesis of **4g**, **4h** and **4l** has been reported by us previously.[18] Treatment of **4g**–**h** and **4j**–**q** with TFA afforded the substituted furans **5g**–**h** and **5j**–**q** in good yields. The furans **4q** and **5q**, prepared from the novel chloro-substituted 1,3-bis-silyl enol ether **1q**, are of special interest, due to their functionalized side-chain. For some derivatives of **3**, a small amount of 1,3-dicarbonyl compound (derived from hydrolysis of the 1,3-bis-silyl enol ether) could not be separated, but this impurity could be separated during the synthesis of **4**. Very good diastereoselectivities were observed for **3g**–**q** and **4g**–**q**. With regard to our initial procedure,[18] the employment of 0.5 rather than 1.0 equiv. of TMSOTf and the use of a higher concentration of the reactants proved preferable in terms of diastereoselectivity.

Treatment of the methoxy-substituted 2-alkylidenetetrahydrofurans (*E*)-**4i** and (*Z*)-**4i** with TFA resulted in isomerization to give *E*/*Z* mixtures of **4i** and small amounts of decomposition products. However, elimination of methanol and clean formation of methoxy-substituted furan **5i** could be achieved by heating of a CH_2Cl_2 solution of (*Z*)-**4i** at reflux. The corresponding reaction of (*E*)-**4i** has not been carried out. Treatment of methyl (3-methoxydihydrofuran-2-ylidene)acetate[20] with TFA was not successful and resulted in the formation of complex mixtures rather than furan **5a** (Scheme 2). This result and the formation of **5i** from (*Z*)-**4i** indicate that the presence of a methoxy group at C-4 is mandatory for a clean elimination and formation of a furan.



Scheme 2.

The configurations of the exocyclic double bonds of 2-alkylidenetetrahydrofurans **4** were established by NOESY experiments and by comparison of the chemical shifts of the hydrogen atoms of the exocyclic double bonds with those of related 2-alkylidenetetrahydrofurans (Table 1).[21,22] As would be expected, characteristic chemical shifts in the δ = 5.31–5.54 range were observed for all *E*-configured ester-derived 2-alkylidenetetrahydrofurans. In contrast, a resonance at δ = 5.05 was observed for the *Z*-configured isomer of **4i**. The *E*-configured 2-alkylidenetetrahydrofurans gen-

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erally showed a characteristic carbonyl ^{13}C NMR resonance in the δ = 167.6–168.5 range (for ester derivatives). In contrast, a resonance of δ = 165.6 was observed for the *Z*-configured isomer of **4i**.

Independent and unambiguous confirmation of the configuration was established by crystal structure analysis of **4g** (Figure 1). The crystal structure of **4g** revealed a *trans* (*erythro*) configuration of the C(2)–C(3) bond. Analysis of the coupling constants (Karplus) indicated that all the tetrahydrofurans **4g**–**q**, containing a substituent at C-3, possess *trans* configurations. However, the attribution of the relative stereochemistry in five-membered rings through *J* values has to be treated with great care and is not entirely unambiguous, due to the small differences between the dihedral angles of the *cis* and *trans* configurations. The excellent 1,2-diastereoselectivity can be explained by known stereoelectronic considerations (comparison of acyclic extended transition states with minimized electrostatic repulsion).[10,18] The transition state leading to the *trans* isomer is sterically favoured over that leading to the *cis* product. The configuration of the terminal double bond of the 1,3-bis-silyl enol ether is irrelevant to the stereoselection.

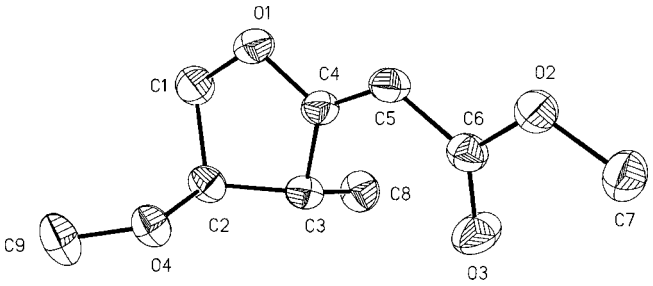
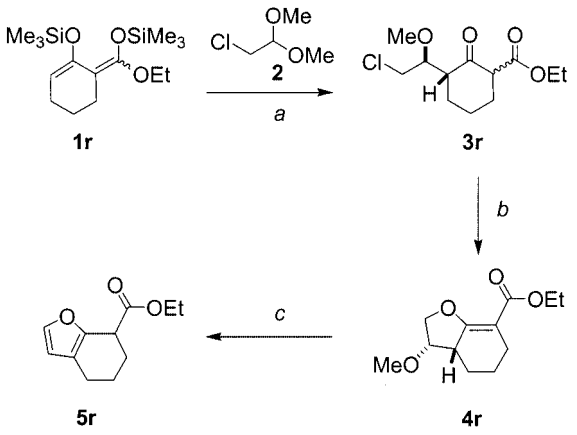


Figure 1. ORTEP plot of **4g**. Thermal ellipsoids of 50% probability are shown for the non-hydrogen atoms. Selected bond lengths (Å) and angles (°): O(1)–C(4) 1.3580(17), O(1)–C(1) 1.4548(19), O(3)–C(6) 1.2119(18), C(1)–C(2) 1.516(2), C(2)–C(3) 1.530(2), C(3)–C(4) 1.505(2), C(4)–C(5) 1.341(2), C(5)–C(6) 1.452(2); C(4)–O(1)–C(1) 109.57(11), O(1)–C(1)–C(2) 104.94(11), C(1)–C(2)–C(3) 102.00(12), C(4)–C(3)–C(8) 111.58(12), C(5)–C(4)–O(1) 119.17(13).

The reactions of cyclic 1,3-bis-silyl enol ethers[23] with 1-chloro-2,2-dimethoxyethane (**2**) were studied next (Scheme 3, Table 2). The reaction of **2** with **1r**, prepared from ethyl 2-oxocyclohexan-1-carboxylate, afforded the condensation product **3r** with very good 1,2-diastereoselectivity. Treatment of the latter with DBU afforded the *cis*-configured 3-methoxy-2,3,3a,4,5,6-hexahydro-2,3-benzofuran **4r**, and treatment of **4r** with TFA resulted in formation of the bicyclic furan **5r**.[24] The reaction between **2** and **1s**, prepared from ethyl 2-oxocyclopentan-1-carboxylate, afforded **3s** with very good diastereoselectivity. Treatment of **3s** with DBU afforded the diastereomerically pure *cis*-configured bicyclo[3.3.0]octene **4s**. All attempts to transform **4s** into furan **5s** resulted in decomposition. The 5,7-bicyclic tetrahydrofuran **4t** was prepared from the corresponding cyclic 1,3-bis-silyl enol ethers **1t**, again with very good *cis* diastereoselectivity. Treatment of **4t** with TFA afforded the



Scheme 3. Synthesis of **4r** and **5r**. *a*) 1.0 equiv. Me_3SiOTf, CH_2Cl_2, –78 → 20 °C, 49%, *b*) 2.0 equiv. DBU, THF, 20 °C, 77%, *c*) TFA, CH_2Cl_2, 20 °C, 76%.

novel bicyclic furan **5t**. A very good *trans* diastereoselectivity was observed for the synthesis of 5,8-bicyclic tetrahydrofuran **4u**, which was prepared from **1u**. Treatment of **4u** with TFA afforded the furan **5u**. The reaction between **2** and **1v** afforded **3v** with very good diastereoselectivity, treatment of **3v** with DBU afforded the *trans*-configured 5,12-bicyclic tetrahydrofuran **4v** as a separable mixture of *E*/*Z* isomers. The reaction of **4v** with TFA gave the furan **5v**. The reaction of **2** with **1w**, prepared from ethyl 4-methyl-2-oxocyclohexan-1-carboxylate, afforded **3w**. Three stereogenic centres were formed with very good double 1,2-diastereoselectivity. The diastereomerically pure, *cis*-configured 3-methoxyhexahydro-2,3-benzofuran **4w** was prepared from **3w**, treatment of **4w** with TFA affording furan **5w**. The reaction of **2** with **1x**, prepared from methyl 2-oxo-3-phenylcyclohexan-1-carboxylate, afforded **3x**, treatment of **3x** with DBU affording the *Z*-configured 3-methoxyhexahydro-2,3-benzofuran **4x** as a separable mixture of diastereomers. Heating of **4x** at reflux in dichloromethane afforded furan **5x** as an inseparable mixture of two diastereomers.

The structure of the 5,6-bicyclic 2-alkylidenetetrahydrofuran **4r** was studied by crystal structure analysis (Figure 2). A *cis* configuration was observed for the C(2)–C(3) bond of **4r**, in contrast to the monocyclic derivatives **4g**–**q**. Three stereogenic centres are present in the 5,6-bicyclic products **4w** and **4x**. The relative configuration of **4w** was established by analysis of the coupling constants (Karplus) and by comparison with **4r** and related 5,6-bicyclic 2-alkylidenetetrahydrofurans.[24] Analysis of the coupling constants (Karplus) also suggested that the 5,5- and 5,7-bicyclic heterocycles **4s**–**t** possess *cis* configurations. In contrast, a *trans* configuration is present in the case of the medium-sized 5,8-bicyclic product **4u**. However, attribution of the relative configuration through the *J* values is once again not entirely unambiguous, due to the small differences between the dihedral angles of the *cis* and *trans* configurations. This problem is particularly apparent for **4t** and **4u**, since no clear trend in the diastereoselectivity was observed. The crystal

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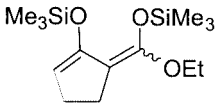
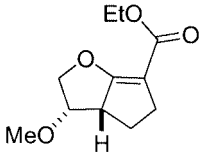
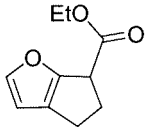
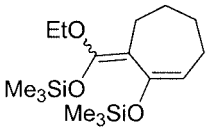
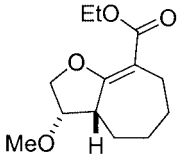
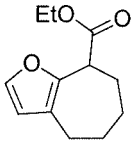
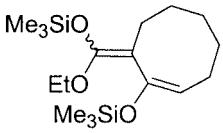
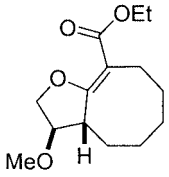
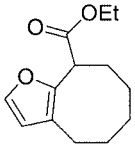
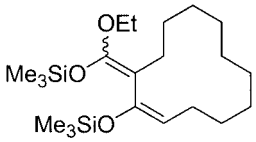
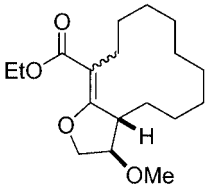
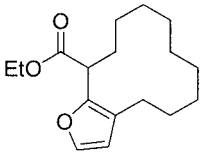
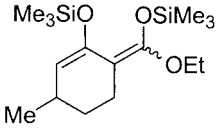
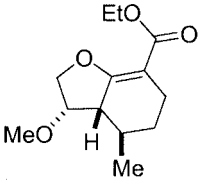
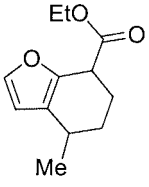
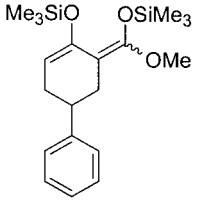
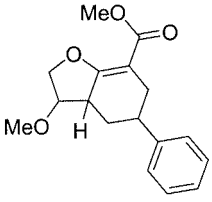
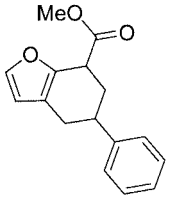
Table 2. Products and yields

	1	3[a]	4[a]	5[a]
s		42%	 91%	 0%
t		90%	 90%	 100%
u		65%	 80%	 84%
v		76%	 60% (*Z*), 38% (*E*)	 100%
w		86%	 68%	 100%
x		89%	 30%, 18%, 47%	 98%

[a] Yields of isolated products. For all products **4** (except for **4x**): *dr* > 98:2 in favour of the diastereomer drawn. The assignment of the relative configuration is not entirely unambiguous (except for **4r** and **4v**).

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structure of the 5,12-bicyclic tetrahydrofuran **4v** (Figure 3) clearly showed the presence of a *trans*-configured C(3)–C(4) bond, which is also in agreement with the solution structure examined by NMR spectroscopy. The isomer studied by crystal structure analysis exhibited a *Z*-configured double bond. In summary, the reactions of medium-sized cyclic 1,3-bis-silyl enol ethers (**1v**, **1u**) and of open-chained 1,3-bis-silyl enol ethers (**1g**–**q**) lead to *trans*-configured 2-alkylidenetetrahydrofurans **4**. In contrast, the opposite stereochemistry (*cis*) was observed for **4r**–**t** and **4w**.

The reaction between 1,3-bis-silyl enol ether **1y**, prepared from 2-acetyl-γ-butyrolactone, and 1-chloro-2,2-dimethoxyethane (**2**) afforded the condensation product **3y** (Scheme 4). Treatment of the latter with DBU afforded the 2-alkylidenetetrahydrofuran **4y**. Heating of a dichloromethane solution of **4y** at reflux gave the furan **5y** in very good yield.

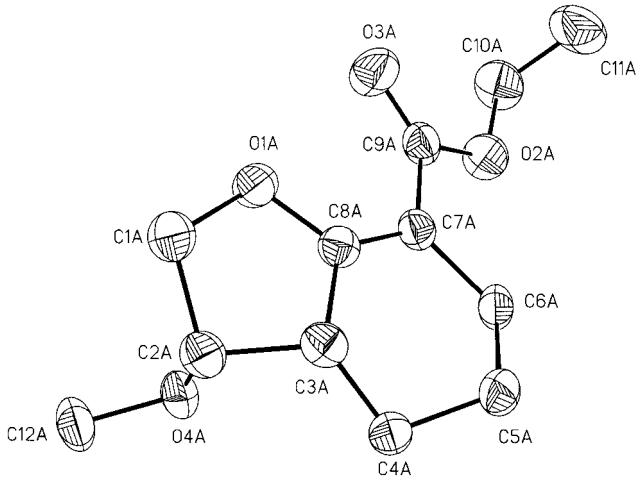


Figure 2. ORTEP plot of **4r**. Thermal ellipsoids of 50% probability are shown for the non-hydrogen atoms. Selected bond lengths (Å) and angles (°): O(1A)–C(8A) 1.356(2), O(1A)–C(1A) 1.460(2), C(1A)–C(2A) 1.521(3), C(2A)–C(3A) 1.522(3), C(3A)–C(8A) 1.507(2), C(6A)–C(7A) 1.516(3), C(7A)–C(8A) 1.343(3); C(8A)–O(1A)–C(1A) 108.72(14), C(1A)–C(2A)–C(3A) 100.19(15), C(8A)–C(3A)–C(4A) 112.06(15), C(8A)–C(3A)–C(2A) 101.37(14), C(4A)–C(5A)–C(6A) 111.73(15), C(8A)–C(7A)–C(9A) 121.74(17).

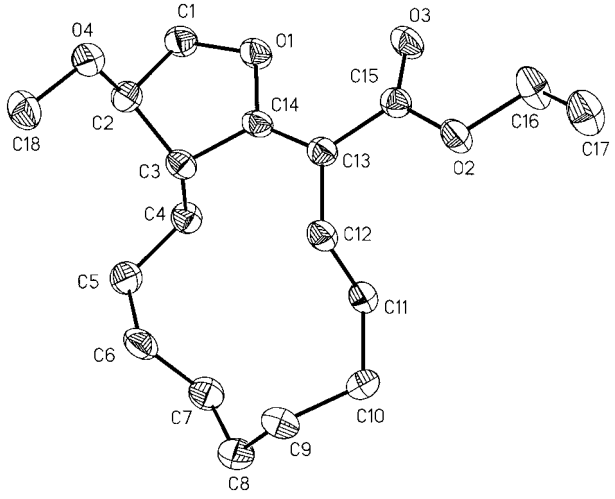
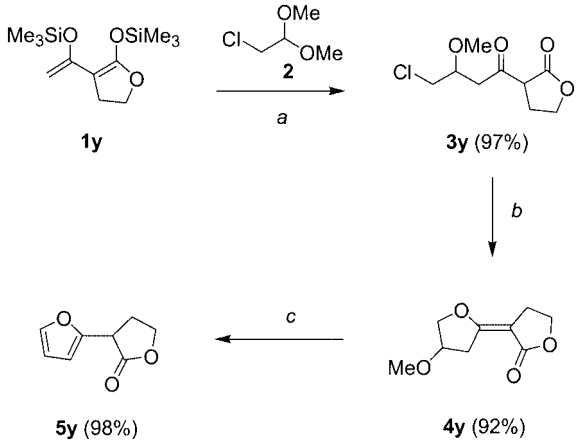
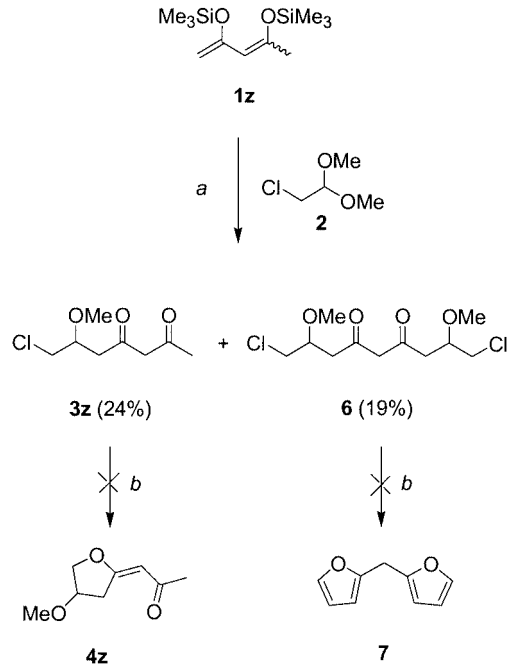


Figure 3. ORTEP plot of **4v**. Thermal ellipsoids of 50% probability are shown for the non-hydrogen atoms. Selected bond lengths (Å) and angles (°): O(1)–C(14) 1.363(3), O(1)–C(1) 1.459(4), C(1)–C(2) 1.504(5), C(2)–C(3) 1.536(4), C(3)–C(14) 1.506(4), C(3)–C(4) 1.541(4), C(13)–C(14) 1.349(4), C(13)–C(15) 1.474(4); C(14)–O(1)–C(1) 109.5(2), O(4)–C(2)–C(1) 108.2(2), C(14)–C(3)–C(2) 102.1(2), C(5)–C(4)–C(3) 112.7(3), C(5)–C(6)–C(7), 113.6(3), C(14)–C(13)–C(15) 120.4(3), C(15)–C(13)–C(12) 119.0(2), C(13)–C(14)–O(1) 122.4(3).



Scheme 4. Synthesis of **4y** and **5y**. *a*) 0.5 equiv. Me_3SiOTf, CH_2Cl_2, –78 → 20 °C, 97%. *b*) 2.0 equiv. DBU, THF, 20 °C, 92%. *c*) reflux in CH_2Cl_2, 98%.

The reaction between 2,4-bis(trimethylsilyloxy)penta-1,3-diene (**1z**), prepared from acetylacetone, and 1-chloro-2,2-dimethoxyethane (**2**) was studied next (Scheme 5). The reaction between **2** and **1z** afforded the open-chained products **3z** and **6**, the latter formed by reaction of **1z** with two equiv-



Scheme 5. Synthesis of **3z** and **6**. *a*) 0.5 equiv. Me_3SiOTf, CH_2Cl_2, –78 → 20 °C, *b*) 2.0 equiv. DBU, THF, 20 °C.

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alents of **2**. The reaction of **3z** and **6** with DBU resulted in decomposition rather than cyclization.

In summary, the cyclization of 1,3-bis-silyl enol ethers with 1-chloro-2,2-dimethoxyethane allowed an efficient synthesis of a variety of novel 2-alkylidene-4-methoxytetrahydrofurans. The reactions proceeded with very good chemo-, regio- and 1,2-diastereoselectivity. In addition, a new approach to functionalized furans based on elimination reactions of 2-alkylidenetetrahydrofurans was developed.

Experimental Section

General Procedure for Reactions between 1,3-Bis-silyl Enol Ethers and 1-Chloro-2,2-dimethoxyethane: Me_3SiOTf (0.5 equiv.) was added at –78 °C to a CH_2Cl_2 solution (4 mL mmol^{-1}) of **1** (1 equiv.) and **2** (1 equiv.), and the mixture was stirred for 2 h at –78 °C. The temperature of the reaction mixture was allowed to rise to 20 °C over 14 h, and the system was then stirred for 3 h at 20 °C. A saturated aqueous solution of $NaHCO_3$ was added to this solution, the organic layer was separated, and the aqueous layer was repeatedly extracted with dichloromethane. The combined organic extracts were dried over Na_2SO_4 and filtered, and the solvent of the filtrate was removed in vacuo. The residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc) to give **3**. Some products **3** contain a small amount of unknown impurity which was separated during the synthesis of **4**.

Compound 3a: This compound was produced from **2** (2.86 mL, 25.0 mmol), **1a** (6.512 g, 25.0 mmol) and Me_3SiOTf (2.778 g, 12.5 mmol) in CH_2Cl_2 (100 mL), **3a** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a yellow oil (3.76 g, 72%). ^{1}H NMR ($CDCl_3$, 300 MHz, 5% enol form): δ = 2.88 (d, J = 6.0 Hz, 2 H, CH_2), 3.41 (s, 3 H, OCH_3), 3.51 (s, 2 H, CH_2), 3.62 (dd, J = 3.9, 3.3 Hz, 2 H, CH_2Cl), 3.75 (s, 3 H, OCH_3), 3.95 (m, 1 H, CH), 5.10 (s, 1 H, CH=C from enol form), 12.10 (s, 1 H, OH from enol form) ppm.

Compound 3b: This compound was produced from **2** (1.14 mL, 10.0 mmol), **1b** (2.745 g, 10.0 mmol) and Me_3SiOTf (1.111 g, 5.0 mmol) in CH_2Cl_2 (100 mL), **3b** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a yellow oil (1.47 g, 66%). ^{1}H NMR ($CDCl_3$, 300 MHz, 5% enol form): δ = 1.29 (t, J = 7.2 Hz, 3 H, OCH_2CH_3), 2.88 (d, J = 6.0 Hz, 2 H, CH_2), 3.41 (s, 3 H, OCH_3), 3.49 (s, 2 H, CH_2), 3.62 (dd, J = 4.5, 3.3 Hz, 2 H, CH_2Cl), 3.94 (m, 1 H, CH), 4.20 (q, J = 7.2 Hz, 2 H, OCH_2CH_3), 5.09 (s, 1 H, CH=C from enol form), 12.15 (s, 1 H, OH from enol form) ppm.

Compound 3c: This compound was produced from **2** (1.14 mL, 10.0 mmol), **1c** (2.885 g, 10.0 mmol) and Me_3SiOTf (1.111 g, 5.0 mmol in CH_2Cl_2 (100 mL), **3c** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a yellow oil (1.66 g, 70%). ^{1}H NMR ($CDCl_3$, 300 MHz, 5% enol form): δ = 1.27 (d, J = 6.3 Hz, 6 H, $OCH(CH_3)_2$), 2.88 (d, J = 6.3 Hz, 2 H, CH_2), 3.41 (s, 3 H, OCH_3), 3.45 (s, 2 H, CH_2), 3.64 (dd, J = 4.5, 3.3 Hz, 2 H, CH_2Cl), 3.93 (m, 1 H, CH), 5.08 (sept, J = 6.3 Hz, 1 H, $OCH(CH_3)_2$), 5.11 (s, 1 H, CH=C from enol form), 12.22 (s, 1 H, OH from enol form) ppm.

Compound 3d: This compound was produced from **2** (1.14 mL, 10.0 mmol), **1d** (3.085 g, 10.0 mmol) and Me_3SiOTf (1.111 g, 5.0 mmol) in CH_2Cl_2 (100 mL), **3d** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a yellow oil (1.70 g, 67%). ^{1}H NMR ($CDCl_3$, 600 MHz, 5% enol form): δ = 2.83 (d, J = 6.0 Hz, 2 H, CH_2), 3.39 (s, 3 H, $OCH_2CH_2OCH_3$), 3.41 (s, 3 H, OCH_3), 3.54 (s, 2 H, CH_2), 3.59–3.65 (m, 4 H, $OCH_2CH_2OCH_3$, CH_2Cl), 3.95 (m, 1 H, CH), 4.32 (t, J = 6.0 Hz, 2 H, $OCH_2CH_2OCH_3$), 5.18 (s, 1 H, CH=C from enol form) ppm.

Compound 3e: This compound was produced from **2** (1.14 mL, 10.0 mmol), **1e** (3.366 g, 10.0 mmol) and Me_3SiOTf (1.111 g, 5.0 mmol) in CH_2Cl_2 (100 mL), **3e** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 10:1) as a yellow oil (1.45 g, 51%). ^{1}H NMR ($CDCl_3$, 300 MHz, 5% enol form): δ = 2.85 (d, J = 7.2 Hz, 2 H, CH_2), 3.37 (s, 3 H, OCH_3), 3.55 (s, 2 H, CH_2), 3.58 (dd, J = 4.5, 3.9 Hz, 2 H, CH_2Cl), 3.91 (m, 1 H, CH), 5.18 (s, 2 H, OCH_2Ph), 5.15 (s, 1 H, CH=C from enol form), 7.33–7.39 (m, 5 H, 5×CH from Ph), 12.20 (s, 1 H, OH from enol form) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 44.69 (CH_2), 45.17 (CH_2Cl), 49.85 (CH_2), 57.58 (OCH_3), 67.08 (OCH_2Ph), 75.84 (CH), 128.20, 128,37, 128.51 (CH from Ph), 135.11 (C from Ph), 166.54 (O–C=O), 200.21 (C=O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2957 (w), 2936 (m, C–H), 1744 (s, O–C=O), 1717 (s, C=O), 1651 (w), 1498 (w), 1456 (m), 1429 (w), 1409 (w), 1378 (m), 1322 (m), 1299 (w), 1264 (m), 1251 (m), 1231 (m), 1181 (m), 1151 (m), 1099 (s), 1028 (w), 996 (w), 750 (m), 699 (m) cm^{-1}. MS (EI, 70 eV): m/z (%) = 284 [M]$^+$ (48), 248 (19), 217 (23), 177 (100). $C_{14}H_{17}O_4Cl$ (284.739): C 59.06, H 6.02; found C 59.01, H 6.22.

Compound 3f: This compound was produced from **2** (1.14 mL, 10.0 mmol), **1f** (3.066 g, 10.0 mmol) and Me_3SiOTf (1.111 g, 5.0 mmol) in CH_2Cl_2 (100 mL), **3f** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a brown solid (1.29 g, 51%). ^{1}H NMR ($CDCl_3$, 300 MHz, 95% enol form, analysis for enol): δ = 2.76 (d, J = 7.2 Hz, 2 H, CH_2), 3.45 (s, 3 H, OCH_3), 3.63 (dd, J = 10.8, 4.5 Hz, 1 H, CH_2Cl), 3.71 (dd, J = 10.8, 4.5 Hz, 1 H, CH_2Cl), 3.98 (m, 1 H, CH), 6.24 (s, 1 H, CH from enol), 7.43–7.56 (m, 3 H, 3×H from Ph), 7.90 (d, J = 6.0 Hz, 2 H, 2×H from Ph), 16.07 (broad s, 1 H, OH from enol) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 41.83 (CH_2), 45.16 (CH_2Cl), 57.54 (OCH_3), 77.06 (CH), 97.21 (*C*H=C), 126.90, 128.49, 132.34 (CH from Ph), 134.30 (C from Ph), 182.83 (HO–*C*=CH), 193.34 (O=*C*–Ph) ppm. IR (KBr (cm^{-1})): $\tilde{\nu}$ = 2925 (w), 2919 (w, C–H), 1610 (s, C=C from enol from), 1575 (s), 1495 (m), 1458 (m), 129 (m), 1411 (w), 1371 (m), 1332 (w), 1303 (w), 1284 (w), 1263 (w), 1214 (w), 1188 (w), 1147 (m), 1094 (s), 1069 (m), 1002 (w), 947 (w), 830 (w), 765 (s), 702 (m), 690 (m) cm^{-1}. MS (EI, 70 eV): m/z (%) = 254 [M]$^+$ (37), 218 (48), 205 (59), 187 (100). $C_{13}H_{15}O_3Cl$ (254.713): C 61.39, H 5.94; found C 61.42, H 6.71. The exact molecular mass m/z = 254.0710 ± 2 ppm [M]$^+$ for $C_{13}H_{15}O_3Cl$ was confirmed by HRMS (EI, 70 eV).

Compound 3g: This compound was produced from **2** (1.37 mL, 12.0 mmol), **1g** (2.745 g, 10.0 mmol) and Me_3SiOTf (1.111 g, 5.0 mmol) in CH_2Cl_2 (100 mL), **3g** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a colourless oil (1.40 g, 63%). ^{1}H NMR ($CDCl_3$, 300 MHz, 5% enol form, contains a small amount of starting material): δ = 1.08 (d, J = 6.9 Hz, 3 H, CH_3), 3.11 (m, 1 H, CH), 3.35 (s, 3 H, OCH_3), 3.40–3.61 (m, 4 H, CH_2, CH_2Cl), 3.74 (s, 3 H, OCH_3), 3.84 (m, 1 H, CH), 5.11 (s, 1 H, CH=C from enol form), 12.12 (s, 1 H, OH from enol form) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 13.43 (CH_3), 42.80 (CH_2), 47.30 (CH), 49.68 (CH_2Cl), 51.81, 57.40 (OCH_3), 81.71 (CH), 167.14 (O–C=O), 204.98 (C=O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2980 (m), 2954 (s), 2942 (s), 2833 (w, C–H), 1749 (s, O=C–O), 1716 (s, C=O), 1656 (w), 1632 (w, C=C from enol form), 1455 (s), 1438 (s), 1405 (m), 1378 (m), 1327 (s), 1263 (s), 1248 (s), 1208 (s), 1180 (m), 1152 (s), 1127 (m), 1099 (s), 1047 (w), 1011 (m), 1004 (m) cm^{-1}.

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MS (EI, 70 eV): *m*/*z* (%) = 222 [*M*]$^+$ (5), 191 (15), 186 (12), 173 (100), 155 (29), 141 (31).

Compound 3h: This compound was produced from **2** (1.37 mL, 12.0 mmol), **1h** (3.026 g, 10.0 mmol) and Me_3SiOTf (1.111 g, 5.0 mmol) in CH_2Cl_2 (100 mL), **3h** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a yellow oil (2.07 g, 83%). ^{1}H NMR ($CDCl_3$, 300 MHz, 11% enol form): δ = 0.91 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.28 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3), 1.49–1.72 (m, 2 H, CH_2), 2.99–3.04 (m, 1 H, CH), 3.34 (s, 3 H, OCH_3), 3.43–3.59 (m, 4 H, CH_2, CH_2Cl), 3.82 (m, 1 H, CH), 4.20 (q, *J* = 7.2 Hz, 2 H, OCH_2CH_3), 5.09 (s, 1 H, CH=C from enol form), 12.19 (s, 1 H, OH from enol form) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 11.12, 13.86 (CH_3), 21.04, 43.16 (CH_2), 51.62 (CH_2Cl), 54.55 (CH), 57.69 (OCH_3), 60.87 (OCH_2CH_3), 81.30 (CH), 166.57 (O=C–O), 205.13 (C=O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2971 (s), 2937 (m), 2880 (w, C–H), 1746 (s, O–C=O), 1715 (s, C=O), 1649 (m, C=C from enol form), 1462 (m), 1448 (w), 1432 (w), 1409 (w),1387 (w), 1368 (m), 1306 (s), 1239 (s), 1205 (m), 1179 (m), 1154 (s), 1099 (s), 1062 (w), 1032 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 251 (100) [*M*]$^+$, 205 (62). $C_{11}H_{19}O_4Cl$ (250.722): C 52.70, H 7.64; found C 52.45, H 8.11.

Compound 3i: This compound was produced from **2** (1.37 mL, 12.0 mmol), **1i** (2.905 g, 10.0 mmol) and Me_3SiOTf (1.111 g, 5.0 mmol) in CH_2Cl_2 (100 mL), **3i** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a yellow oil (1.53 g, 64%). ^{1}H NMR ($CDCl_3$, 300 MHz, 25% enol form, contains ca. 40% of starting material): δ = 3.39 (s, 3 H, OCH_3), 3.44 (s, 3 H, OCH_3), 3.45 (s, 3 H, OCH_3), 3.53 (s, 2 H, CH_2), 3.62–3.73 (m, 2 H, CH_2Cl), 3.75 (d, *J* = 3.0 Hz, 1 H, CH), 3.98 (m, 1 H, CH), 5.31/5.40 (ds, 1 H, CH=C from enol forms of both isomers), 11.93/12.00 (ds, 1 H, OH from enol forms of both isomers) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 41.54 (CH_2), 46.09 (CH_2Cl), 51.97, 58.13, 60.35 (OCH_3), 82.21, 84.92 (CH), 167.36 (O=C–O), 205.12 (C=O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2992 (w), 2954 (s), 2941 (s), 2909 (w), 2809 (w), 2835 (m, C–H), 1751 (s, O–C=O), 1722 (s, C=O), 1660 (m), 1635 (w, C=C from enol form), 1439 (s), 1401 (w), 1323 (s), 1262 (s), 1228 (s), 1211 (s), 1122 (s), 1094 (s), 1022 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 238 [*M*]$^+$ (58), 207 (4), 146 (100). $C_9H_{15}O_5Cl$ (238.668): C 45.29, H 6.34; found C 45.31, H 6.39.

Compound 3j: This compound was produced from **2** (1.37 mL, 12.0 mmol), **1j** (3.146 g, 10.0 mmol) and Me_3SiOTf (1.111 g, 5.0 mmol) in CH_2Cl_2 (100 mL), **3j** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a yellow oil (1.49 g, 57%). ^{1}H NMR ($CDCl_3$, 300 MHz, 12% enol form): δ = 1.28 (t, *J* = 7.2 Hz, 3 H, CH_3), 2.20–2.41(m, 2 H, CH_2), 3.12 –3.20 (m, 1 H, CH), 3.35 (s, 3 H, OCH_3), 3.52 (s, 2 H, CH_2), 3.55–3.63 (m, 2 H, CH_2Cl), 3.79–3.84 (m, 1 H, CH), 4.19 (q, *J* = 7.2 Hz, 2 H, OCH_2), 5.00–5.22 (m, 2 H, CH_2=CH), 5.65–5.79 (m, 1 H, CH=CH_2), 12.22 (s, 1 H, OH from enol form) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2983 (m), 2937 (m), 2832 (w, C–H), 1746 (s, O=C–O), 1715 (s, C=O), 1643 (m, C=C from enol), 1463 (m), 1445 (m), 1417 (w), 1386 (w), 1369 (m), 1318 (m), 1305 (m), 1248 (m), 1205 (m), 1181 (m), 1153 (m), 1099 (s), 1032 (m), 999 (w), 845 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 262 [*M*]$^+$ (2), 230 (13), 217 (11), 213 (63), 181 (15), 169 (100).

Compound 3k: This compound was produced from **2** (1.37 mL, 12.0 mmol), **1k** (3.166 g, 10.0 mmol) and Me_3SiOTf (1.111 g, 5.0 mmol) in CH_2Cl_2 (100 mL), **3k** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a dark yellow oil (2.30 g, 87%). ^{1}H NMR ($CDCl_3$, 300 MHz, 24% enol form): δ = 0.91 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.27 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3), 1.23–1.35 (m, 2 H, CH_2), 1.58–1.66 (m, 2 H, CH_2), 3.08 (m, 1 H, CH), 3.34 (s, 3 H, OCH_3), 3.43 (s, 2 H, CH_2), 3.53–3.60 (m, 2 H, CH_2Cl), 3.81 (m, 1 H, CH), 4.20 (q, *J* = 7.2 Hz, 2 H, OCH_2), 5.09 (s, 1 H, CH=C from enol form), 12.20 (s, 1 H, OH from enol form) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C = 14.15 (CH_3), 20.25, 30.38 (CH_2), 43.40 (CH_2Cl), 51.83 (CH_2), 53.27 (CH), 57.93 (OCH_3), 61.11 (OCH_2), 81.84 (CH), 166.82 (O=C–O), 205.25 (C=O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2962 (s), 2935 (s), 2874 (m), 2832 (w, C–H), 1746 (s, O=C–O), 1715 (s, C=O), 1647 (m), 1463 (m), 1410 (w), 1369 (m), 1306 (s), 1234 (s), 1210 (m), 1179 (m), 1115 (s), 1099 (s), 1034 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 264 [*M*]$^+$ (11), 249 (19), 215 (100). $C_{12}H_{21}O_4Cl$ (264.749): C 54.44, H 8.00; found C 55.35, H 8.43.

Compound 3l: This compound was produced from **2** (1.37 mL, 12.0 mmol), **1l** (3.306 g, 10.0 mmol) and Me_3SiOTf (1.111 g, 5.0 mmol) in CH_2Cl_2 (100 mL), **3l** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a dark yellow oil (2.38 g, 85%). ^{1}H NMR ($CDCl_3$, 300 MHz, 24% enol form): δ = 0.88 (t, *J* = 6.9 Hz, 3 H, CH_3), 1.28 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3), 1.22–1.35 (m, 2 H, CH_2), 1.37–1.41 (m, 2 H, CH_2), 1.58–1.69 (m, 2 H, CH_2), 3.02–3.10 (m, 1 H, CH), 3.34 (s, 3 H, OCH_3), 3.43 (s, 2 H, CH_2), 3.52–3.57 (m, 2 H, CH_2Cl), 3.81 (m, 1 H, CH), 4.20 (q, *J* = 7.2 Hz, 2 H, OCH_2), 5.08 (s, 1 H, CH=C from enol form), 12.20 (s, 1 H, OH from enol form) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C = 14.15, 14.77 (CH_3), 22.35, 27.90, 29.26 (CH_2), 43.91 (CH_2Cl), 51.79 (CH_2), 53.38 (CH), 57.88 (OCH_3), 61.27 (OCH_2), 81.81 (CH), 166.80 (O=C–O), 205.18 (C=O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2959 (s), 2933 (s), 2869 (w, C–H), 1745 (s, O=C–O), 1716 (s, C=O), 1648 (w), 1631 (w), 1463 (w), 1412 (w), 1369 (w), 1308 (m), 1241 (m), 1209 (m), 1178 (w), 1155 (m), 1099 (s), 1033 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 278 [*M*]$^+$ (92), 265 (100), 229 (32).

Compound 3m: This compound was produced from **2** (1.37 mL, 12.0 mmol), **1m** (3.587 g, 10.0 mmol) and Me_3SiOTf (1.111 g, 5.0 mmol) in CH_2Cl_2 (100 mL), **3m** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a dark yellow oil (2.70 g, 88%). ^{1}H NMR ($CDCl_3$, 300 MHz, 11% enol form): δ = 0.87 (t, *J* = 6.9 Hz, 3 H, CH_3), 1.28 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3), 1.25–1.32 (m, 6 H, 3×H_2), 1.33–1.48 (m, 2 H,CH_2), 1.55–1.68 (m, 2 H, CH_2), 3.02–3.10 (m, 1 H, CH), 3.34 (s, 3 H, OCH_3), 3.43 (s, 2 H, CH_2), 3.49–3.56 (m, 2 H, CH_2Cl), 3.81 (m, 1 H, CH), 4.20 (q, *J* = 7.2 Hz, 2 H, OCH_2), 5.08 (s, 1 H, CH=C from enol form), 12.20 (s, 1 H, OH from enol form) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C = 14.26, 14.30 (CH_3), 22.60, 27.00, 28.36, 29.24, 31.69 (CH_2), 43.50 (CH_2Cl), 51.97 (CH_2), 53.54 (CH), 58.77 (OCH_3), 61.22 (OCH_2), 81.93 (CH), 166.91 (O=C–O), 205.27 (C=O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2956 (s), 2929 (s), 2857 (s, C–H), 1749 (s, O=C–O), 1715 (S, C=O), 1649 (m), 1463 (s), 1411 (m), 1306 (s), 1236 (s), 1178 (s), 1153 (s), 1099 (s), 1033 (s), 845 (w), 696 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 306 [*M*]$^+$ (3), 274 (6), 257 (100), 139 (33).

Compound 3n: This compound was produced from **2** (1.37 mL, 12.0 mmol), **1n** (3.867 g, 10.0 mmol) and Me_3SiOTf (1.111 g, 5.0 mmol), in CH_2Cl_2 (100 mL), **3n** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a brown oil (1.77 g, 53%). ^{1}H NMR ($CDCl_3$, 300 MHz, 25% enol form): δ = 0.88 (t, *J* = 6.8 Hz, 3 H, CH_3), 1.25–1.32 (m, 17 H, 7×H_2, CH_3), 3.05 (m, 1 H, CH), 3.34 (s, 3 H, OCH_3), 3.49–3.58 (m, 4 H, CH_2, CH_2Cl), 3.76–3.84 (m, 1 H, CH), 4.20 (q, *J* = 7.2 Hz, 2 H, OCH_2), 5.08 (s, 1 H, CH=C from enol form), 12.20 (s, 1 H, OH from enol form) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2955 (m), 2928 (s), 2856 (m, C–H), 1746 (s, O=C–O), 1716 (s, C=O), 1647 (m, C=C from enol),

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1463 (m), 1370 (w), 1307 (m), 1234 (m), 1179 (w), 1153 (m), 1100 (s), 1033 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 334 $[M]^+$ (3), 289 (15), 285 (100), 224 (36).

Compound 3o: This compound was produced from **2** (1.37 mL, 12.0 mmol), **1o** (4.01 g, 10.0 mmol) and Me_3SiOTf (1.111 g, 5.0 mmol) in CH_2Cl_2 (100 mL), **3o** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a dark yellow oil (2.75 g, 79%). ^1H NMR ($CDCl_3$, 300 MHz, 15% enol form): δ = 0.88 (t, J = 6.9 Hz, 3 H, CH_3), 1.20–1.34 (m, 15 H, 6×CH_2, CH_3), 1.37–1.48 (m, 2 H, CH_2), 1.59–1.68 (m, 2 H, CH_2), 3.01–3.10 (m, 1 H, CH), 3.33 (s, 3 H, OCH_3), 3.42 (s, 2 H, CH_2), 3.47–3.56 (m, 2 H, CH_2Cl), 3.81 (m, 1 H, CH), 4.20 (q, J = 7.2 Hz, 2 H, OCH_2), 5.07 (s, 1 H, CH=C from enol form), 12.23 (s, 1 H, OH from enol form) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 13.77, 13.89 (CH_3), 22.36, 26.67, 27.95, 28.97, 29.02, 29.18, 29.42, 31.55 (CH_2), 43.11 (CH_2Cl), 51.49 (CH_2), 53.15 (CH), 57.61 (OCH_3), 60.77 (OCH_2), 81.57 (CH), 166.48 (O=C–O), 205.13 (C=O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2927 (s), 2855 (s, C–H), 1746 (s, O=C–O), 1716 (s, C=O), 1649 (m), 1630 (m), 1463 (m), 1369 (m), 1307 (m), 1233 (s), 1154 (m), 1100 (s), 1033 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 348 $[M]^+$ (6), 316 (13), 299 (100), 281 (34). $C_{18}H_{33}O_4Cl$ (348.909): C 61.96, H 9.53; found C 62.71, H 8.85.

Compound 3p: This compound was produced from **2** (1.37 mL, 12.0 mmol), **1p** (4.148 g, 10.0 mmol) and Me_3SiOTf (1.111 g, 5.0 mmol) in CH_2Cl_2 (100 mL), **3p** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a dark yellow oil (3.12 g, 86%). ^1H NMR ($CDCl_3$, 300 MHz, 16% of enol form): δ = 0.89 (t, J = 6.9 Hz, 3 H, CH_3), 1.20–1.38 (m, 19 H, 8×CH_2, CH_3), 1.58–1.65 (m, 2 H, CH_2), 3.02–3.09 (m, 1 H, CH), 3.33 (s, 3 H, OCH_3), 3.42 (s, 2 H, CH_2), 3.43–3.59 (m, 2 H, CH_2Cl), 3.81 (m, 1 H, CH), 4.20 (q, J = 7.2 Hz, 2 H, OCH_2), 5.07 (s, 1 H, CH=C from enol form), 12.23 (s, 1 H, OH from enol form) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 13.87, 13.90 (CH_3), 22.46, 26.75, 27.52, 28.05, 29.09, 29.32, 29.34, 29.51, 31.67 (CH_2), 43.18 (CH_2Cl), 51.64 (CH_2), 53.24 (CH), 57.72 (OCH_3), 60.89 (OCH_2), 81.65 (CH), 166.58 (O=C–O), 205.29 (C=O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2927 (s), 2855 (s, C–H), 1745 (s, O=C–O), 1716 (s, C=O), 1649 (m), 1631 (m), 1463 (m), 1369 (m), 1306 (m), 1234 (s), 1155 (m), 1100 (s), 1034 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 362 $[M]^+$ (7), 330 (10), 313 (100), 295 (29).

Compound 3q: This compound was produced from **2** (0.14 mL, 1.2 mmol), **1q** (0.391 g, 1.0 mmol) and Me_3SiOTf (0.111 g, 0.5 mmol) in CH_2Cl_2 (30 mL), **3q** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a yellow oil (0.267 g, 78%). ^1H NMR ($CDCl_3$, 300 MHz, 15% enol form): δ = 1.29 (t, J = 7.2 Hz, 3 H, CH_3) 1.26–1.33 (m, 2 H, CH_2), 1.35–1.45 (m, 4 H, 2×CH_2), 1.58–1.69 (m, 2 H, CH_2), 1.70–1.76 (m, 2 H, CH_2), 3.01–3.11 (m, 1 H, CH), 3.34 (s, 3 H, OCH_3), 3.43 (s, 2 H, CH_2), 3.49–3.59 (m, 4 H, 2×CH_2–Cl), 3.82 (dd, J = 13.2, 4.2 Hz, 1 H, CH), 4.20 (q, J = 7.2 Hz, 2 H, OCH_2), 5.08 (s, 1 H, CH=C from enol form), 12.21 (s, 1 H, OH from enol form) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.09 (CH_3), 26.37, 26.66, 27.95, 28.79, 32.28 (CH_2), 43.23, 44.81 (CH_2–Cl), 51.74 (CH_2), 53.21 (CH), 57.82 (OCH_3), 61.03 (OCH_2), 81.69 (CH), 91.77 (*C*H=C from enol form), 166.67 (O=C–O), 172.45 (O=C–O from enol form), 176.83 (HO–*C*=CH from enol form), 205.35 (C=O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2954 (s), 2860 (m, C–H), 1745 (s, O=C–O), 1715 (s, C=O), 1646 (m), 1460 (m), 1408 (w), 1368 (w), 1307 (m), 1236 (s), 1153 (m), 1100 (s), 1033 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 324 $[M - Me]^+$ (26), 273 (13), 259 (9), 225 (63), 220 (4), 199 (3), 185 (9), 161 (37), 153 (10), 130 (24), 116 (79), 93 (13), 55 (100).

Compound 3r: This compound was produced from **2** (1.14 mL, 10.0 mmol), **1r** (3.15 g, 10.0 mmol) and Me_3SiOTf (1.111 g, 5.0 mmol) in CH_2Cl_2 (100 mL), **3r** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 40:1) as a yellow oil (1.29 g, 49%). ^1H NMR ($CDCl_3$, 300 MHz, 55% enol form): δ = 1.25–1.33 (m, 3 H, OCH_2CH_3), 1.38–1.58 (m, 2 H, CH_2), 1.62–1.85 (m, 2 H, CH_2), 1.97–2.39 (m, 2 H, CH_2), 2.69–3.09 (m, 1 H, CH), 3.40/3.50 (ds, 3 H, OCH_3), 3.43–3.48 (m, 1 H, CH), 3.59–3.70 (m, 2 H, CH_2Cl), 3.72–3.92 (m, 1 H, CH), 4.22 (q, J = 7.1 Hz, 2 H, OCH_2CH_3), 12.53/12.61 (ds, 1 H, OH from two possible enol forms) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 262 (100) $[M]^+$, 230 (59), 226 (66), 217 (70).

Compound 3s: This compound was produced from **2** (1.14 mL, 10.0 mmol), **1s** (3.00 g, 10.0 mmol) and Me_3SiOTf (1.111 g, 5.0 mmol), in CH_2Cl_2 (100 mL), **3s** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a yellow oil (1.03 g, 42%). ^1H NMR ($CDCl_3$, 300MHz): δ = 1.24–1.32 (m, 3 H, CH_3), 1.59–1.66 (m, 1 H, CH_2), 1.98–2.08 (m, 1 H, CH_2), 2.18–2.45 (m, 2 H, CH_2), 3.45 (s, 3 H, OCH_3), 3.49 (m, 1 H, CH), 3.66 (m, 1 H, CH), 3.75–3.85 (m, 2 H, CH_2Cl), 4.12–4.23 (m, 2 H, OCH_2), 4.58–4.61 (m, 1 H, CH) ppm. MS (EI, 70 eV): *m*/*z* (%) = 213 $[M - Cl]^+$ (33), 198 (24), 153 (100).

Compound 3t: This compound was produced from **2** (0.3 mL, 2.4 mmol), **1t** (0.66 g, 2.0 mmol) and Me_3SiOTf (0.222 g, 1.0 mmol) in CH_2Cl_2 (30 mL), **3t** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a yellow oil (0.50 g, 90%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.26 (t, J = 7.2 Hz, 3 H, CH_3), 1.31–1.40 (m, 2 H, CH_2), 1.73–1.87 (m, 2 H, CH_2), 1.88–2.03 (m, 4 H, 2×H_2), 2.11–2.26 (m, 1 H, CH_2), 2.94–3.01 (m, 1 H, CH), 3.45 (s, 3 H, OCH_3), 3,52–3.63 (m, 2 H, CH_2Cl), 3.71–3.77 (m, 1 H, CH), 4.18 (q, J = 7.2 Hz, 2 H, OCH_2) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 13.86 (CH_3), 26.26, 27.27, 27.41, 28.40 (CH_2), 43.36 (CH_2Cl), 53.54 (OCH_3), 58.05, 59.31 (CH), 61 12 (OCH_2), 80.89 (CH), 169.73 (O=C–O), 209.47 (C=O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2981 (s), 2934 (s), 2859 (s), 2832 (m, C–H), 1747 (s, O=C–O), 1704 (s, C=O), 1637 (w), 1451 (s), 1372 (s), 1352 (m), 1305 (s), 1241 (s), 1186 (s), 1142 (s), 1100 (s), 1027 (s), 943 (m), 863 (w), 751 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 276 $[M]^+$ (3), 240 (39), 231 (17), 227 (100). $C_{13}H_{21}O_4Cl$ (276.60): C 56.42, H 7.65; found C 56.28, H 7.89.

Compound 3u: This compound was produced from **2** (0.75 mL, 0.6 mmol), **1u** (1.71 g, 5.0 mmol) and Me_3SiOTf (0.556 g, 2.5 mmol) in CH_2Cl_2 (50 mL), **3u** being isolated as a yellow oil (0.95 g, 65%). ^1H NMR ($CDCl_3$, 300 MHz, 19% enol form): δ = 1.20–1.34 (m, 7 H, 2×H_2, CH_3), 1.53–1.65 (m, 2 H, CH_2), 1.66–1.83 (m, 2 H, CH_2), 2.01–2.35 (m, 2 H, CH_2), 2.41–2.55 (m, 1 H, CH), 2.61–2.71 (m, 1 H, CH), 3.48 (s, 3 H, OCH_3), 3.52–3.78 (m, 2 H, CH_2Cl), 3.85–4.05 (m, 1 H, CH), 4.13–4.24 (m, 2 H, OCH_2), 12.80 (s, 1 H, OH from enol form) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2933 (s), 2859 (m, C–H), 1745 (s, O=C–O), 1706 (s, C=O), 1644 (s), 1617 (m), 1463 (m), 1449 (m), 1399 (w), 1374 (m), 1328 (m), 1306 (m), 1299 (m), 1247 (s), 1201 (m), 1184 (m), 1011 (s), 847 (s), 792 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 290 $[M]^+$ (13), 275 (26), 241 (100).

Compound 3v: This compound was produced from **2** (1.37 mL, 12.0 mmol), **1v** (3.97 g, 10.0 mmol) and Me_3SiOTf (1.111 g, 5.0 mmol) in CH_2Cl_2 (100 mL), **3v** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a yellow oil (2.62 g, 76%). ^1H NMR ($CDCl_3$, 300 MHz, 9% enol form, 30% minor diastereomer, spectra analysis for the main isomer): δ = 1.22–1.43 (m, 17 H, 7×H_2, CH_3), 1.55–1.70 (m, 2 H, CH_2), 1.73–2.01 (m, 2 H, CH_2), 2.25–2.38 (m, 1 H, CH), 3.31/3.44 (ds, 3 H, OCH_3), 3.47–3.57 (m, 2 H, CH_2Cl), 3.80–3.88 (m, 1 H, CH), 3.96–4.06 (m, 1 H, CH), 4.16 (q, J = 7.2 Hz, 2 H, OCH_2CH_3), 13.00 (s,

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1 H, OH from enol form) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ_C = 14.01 (CH_3), 19.94, 22.03, 23.06, 23.26, 23.92, 24.14, 24.36, 26.15, 26.79 (CH_2), 44.07 (CH_2Cl), 52.72, 54.33 (CH), 57.47 (OCH_3), 61.79 (OCH_2CH_3), 79.33 (CH), 169.36 (O=C–O), 205.96 (C=O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2932 (s), 2867 (m, C–H), 1743 (s, O=C–O), 1711 (s, C=O), 1469 (m), 1444 (w), 1369 (w), 1291 (w), 1263 (m), 1248 (m), 1203 (m), 1178 (s), 1155 (m), 1102 (s), 1028 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 347 $[M]^+$ (27), 315 (56), 280 (100).

Compound 3w: This compound was produced from **2** (0.7 mL, 6.0 mmol), **1w** (1.643 g, 5.0 mmol) and Me_3SiOTf (0.56 g, 2.5 mmol) in CH_2Cl_2 (50 mL), **3w** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a yellow oil (1.19 g, 86%). ^{1}H NMR ($CDCl_3$, 300 MHz, 48% enol form): δ = 1.04 (dd, *J* = 12, 6.6 Hz, 3 H, CH_3), 1.26–1.34 (m, 3 H, OCH_2CH_3), 1.59–2.01 (m, 2 H, CH_2), 2.06–2.35 (m, 2 H, CH_2), 2.45–2.54 (m, 1 H, CH), 3.45 (s, 3 H, OCH_3), 3.52 (m, 1 H, CH), 3.59 (m, 1 H, CH), 3.68–3.85 (m, 2 H, CH_2Cl), 4.15–4.21 (m, 1 H, CH), 4.22–4.29 (m, 2 H, OCH_2CH_3), 12.20/12.45 (ds, 1 H, OH from two possible enol forms) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2957 (s), 2932 (s), 2873 (s, C–H), 1741 (s, O=C–O), 1715 (s, C=O), 1652 (s), 1617 (s), 1458 (s), 1428 (m), 1402 (s), 1374 (s), 1304 (s), 1276 (s), 1216 (s), 1159 (s), 1096 (s), 1029 (s), 975 (w), 827 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 276 $[M]^+$ (29), 244 (41), 227 (62), 213 (100).

Compound 3x: This compound was produced from **2** (1.37 mL, 12 mmol), **1x** (3.777 g, 10 mmol), and Me_3SiOTf (1.111 g, 5 mmol), in CH_2Cl_2 (100 mL), **3x** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a yellow oil (2.890 g, 89%). ^{1}H NMR ($CDCl_3$, 300 MHz, 70% enol form, analysis for enol form): δ = 1.80–2.15 (m, 2 H, CH_2), 2.23–2.42 (m, 2 H, CH_2), 2.62–2.70 (m, 1 H, CH), 2.87–3.15 (m, 1 H, CH), 3.45–3.46, 3.49 (ts, 3 H, OCH_3), 3.41–3.61 (m, 1 H, CH_2–Cl), 3.68–3.81 (m, 5 H, CH_2–Cl, OCH_3, CH), 7.19–7.31 (m, 5 H, 5 × H from Ph), 12.18, 12.43, 12.44 (ts, 1 H, OH) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 3085 (w), 3061 (w), 3028 (m), 2998 (m), 2951 (s), 2935 (s), 2858 (m), 2833 (m, C–H), 1745 (m, O=C–O), 1716 (m, C=O), 1659 (s), 1618 (s), 1495 (m), 1443 (s), 1361 (s), 1333 (s), 1286 (s), 1260 (s), 1247 (s), 1225 (s), 1205 (s), 1094 (s), 1035 (m), 1011 (m), 958 (w), 906 (w), 844 (s), 761 (s), 702 (s), 527 (w), 435 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 324 $[M]^+$ (30), 294 (5), 292 (21), 275 (3), 232 (97), 219 (17), 200 (11), 171 (26), 157 (5), 104 (59), 95 (35), 93 (100), 91 (42), 77 (12). $C_{17}H_{21}O_4Cl$ (324.804): C 62.87, H 6.52; found C 63.20, H 7.02.

Compound 3y: This compound was produced from **2** (2.74 mL, 24 mmol), **1y** (5.450 g, 20 mmol) and Me_3SiOTf (0.222 g, 10 mmol) in CH_2CL_2 (200 mL), **3y** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 50:1 to 1:1) as a yellow oil (4.260 g, 97%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.24–2.39 (m, 2 H, CH_2), 3.42 (s, 3 H, OCH_3), 3.60–3.66 (m, 2 H, CH_2–Cl), 3.71–3.77 (m, 1 H, CH), 3.93–3.99 (m, 1 H, CH), 4.28–4.43 (m, 2 H, OCH_2) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): δ_c = (23.85, 44.16 (CH_2), 45.10 (CH_2–Cl), 53.06 (CH), 57.63 (OCH_3), 67.45 (OCH_3), 76.09 (CH), 172.77 (O=C–O), 200.58 (C=O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 3519 (w, OH from enol form), 2988 (s), 2922 (s), 2832 (m, C–H), 1770 (s, O=C–O), 1721 (s, C=O), 1655 (m, C=C from enol form), 1482 (m), 1457 (s), 1430 (m), 1379 (s), 1307 (m), 1218 (m), 1174 (s), 1161 (s), 1127 (m), 1097 (s), 1025 (s), 969 (w), 946 (m), 883 (w), 863 (w) 844 (w), 790 (w), 748 (m), 695 (m), 683 (m), 591 (w), 531 (w), 468 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 220 $[M]^+$ (1), 184 (2), 171 (87), 155 (2), 139 (6), 135 (11), 128 (17), 112 (22), 95 (28), 93 (84), 85 (100).

Compound 3z: This compound was produced from **2** (1.37 mL, 12 mmol), **1z** (2.445 g, 10 mmol) and Me_3SiOTf (1.111 g, 5 mmol) in CH_2Cl_2 (100 mL), with **3z** (0.466 g, 24%) and **6** (0.536 g, 19%) being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as yellow oils.

Compound 3z: (75% of enol form) ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.07 (s, 3 H, CH_3), 2.61 (m, 2 H, CH_2), 3.42 (s, 3 H, OCH_3), 3.56–3.69 (m, 2 H, CH_2Cl), 3.90 (m, 1 H, CH), 5.56 (s, 1 H, CH from enol), 15.58 (broad s, 1 H, OH from enol) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 24.51 (CH_3), 40.95 (CH_2), 45.08 (CH_2Cl), 57.52 (OCH_3), 76.99 (CH), 101.02 (CH from enol), 190.78, 190.85 (C=O and C=*C*–OH) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 3408 (broad, O–H from enol), 2960 (w), 2932 (w, C–H), 1765 (w), 1722 (m), 1704 (m), 1663 (s), 1612 (s, C=C from enol), 1431 (m), 1401 (m), 1365 (m), 1339 (m), 1299 (w), 1247 (m), 1208 (w), 1167 (w), 1100 (s), 1052 (w), 1027 (w), 968 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 177 $[M - CH_3]^+$ (100), 161 (62), 143 (29).

Compound 6: (75% of enol form) ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.63 (m, 4 H, 2 × H_2), 3.40 (s, 2 H, CH_2 from keto form), 3.42 (s, 6 H, 2 × OCH_3), 3.64 (m, 4 H, 2 × H_2–Cl), 3.87–3.93 (m, 2 H, 2 × H), 5.63 (s, 1 H, CH=C from enol), 15.30 (broad s, 1 H, OH from enol) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 40.77 (2 × H_2), 44.96 (2 × H_2–Cl), 57.47 (2 × OCH_3), 76.91 (2 × H), 101.63 (*CH*=C), 190.40 (O–*C*=CH) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 3404 (w, O–H), 2935 (m), 2831 (w, C–H), 1726 (w), 1706 (m, C=O), 1613 (s, C=C–O), 1458 (m), 1447 (m), 1431 (m), 1352 (m), 1313 (m), 1236 (m), 1202 (m), 1185 (m), 1153 (w), 1101 (s), 1019 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 285 $[M]^+$ (4), 249 (4), 217 (17), 203 (55), 192 (30), 187 (7), 177 (100), 160 (10), 145 (35), 141 (19), 127 (8). The exact molecular mass *m*/*z* = 284.0582 ± 2 ppm $[M]^+$ for $C_{11}H_{18}O_4Cl_2$ was confirmed by HRMS (EI, 70 eV).

General Procedure for the Preparation of (*E*)-2-Alkylidene-4-methoxytetrahydrofurans (4): DBU (2 equiv.) was added to a THF solution (3 mL mmol^{-1}) of **3** (1 equiv.), and the mixture was stirred for 12 h at 20 °C. The solvent was removed in vacuo and the residue was purified by chromatography (silica gel, *n*-hexane/EtOAc, 50:1 to 1:1) to give **4**.

Compound 4i: This compound was produced from **3i** (1.40 g, 5.9 mmol) and DBU (1.75 mL, 11.7 mmol) in THF (10 mL); (*E*)-**4i** (0.583 g, 49%) and (*Z*)-**4i** (0.40 g, 33%) were isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as yellow oils.

Compound (*E*)-4i: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.36 (s, 3 H, OCH_3), 3.51 (s, 3 H, OCH_3), 3.70 (s, 3 H, OCH_3), 3.89 (d, *J* = 3.2 Hz, 1 H, CH), 4.24 (d, *J* = 10 Hz, 1 H, OCH_2), 4.33 (dd, *J* = 10, 3.2 Hz, 1 H, OCH_2), 5.08 (s, 1 H, CH), 5.54 (s, 1 H, CH=C) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ_C = 50.88, 56.81, 57.77 (OCH_3), 74.44 (C–5), 79.05, 81.41 (CH), 94.57 (*C*H=C), 167.75 (O=C–O), 171.42 (O–*C*=CH) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2992 (w), 2952 (m), 2831 (w, C–H), 1713 (s, C=C–O), 1658 (s, C=C–C=O), 1641 (m), 1437 (m), 1385 (m), 1356 (m), 1318 (w), 1296 (w), 1254 (w), 1234 (w), 1192 (m), 1186 (m), 1127 (s), 1110 (s), 1050 (m), 1032 (w), 980 (m), 952 (w), 848 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 202 (100) $[M]^+$, 171 (74), 155 (5). The exact molecular mass *m*/*z* = 202.0841 ± 2 ppm $[M]^+$ for $C_9H_{14}O_5$ was confirmed by HRMS (EI, 70 eV).

Compound (*Z*)-4i: ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 3.35 (s, 3 H, OCH_3), 3.39 (s, 3 H, OCH_3), 3.68 (s, 3 H, OCH_3), 3.88 (d, *J* = 3.2 Hz, 1 H, CH), 4.05 (s, 1 H, CH), 4.38 (d, *J* = 10 Hz, 1 H, OCH_2), 4.47 (dd, *J* = 10, 3.2 Hz, 1 H, OCH_2), 5.05 (s, 1 H, CH=C) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ_C = 50.93, 56.78, 57.02 (OCH_3), 75.66 (C–5), 81.06, 84.22 (CH), 92.71 (*C*H=C), 165.59 (O=C–O), 166.74 (O–*C*=CH) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2993 (w), 2951 (m), 2831 (w, C–H), 1716 (s, C=C–O), 1663 (s, C=C–C=O),

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1461 (m), 1438 (m), 1400 (w), 1357 (w), 1315 (w), 1276 (m), 1247 (w), 1197 (s), 1139 (m), 1113 (s), 1094 (m), 1049 (m), 996 (m), 849 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 202 $[M]^+$ (94), 171 (100), 156 (50), 125 (35). $C_9H_{14}O_5$ (202.207): C 53.46, H 6.98; found C 52.97, H 6.97.

Compound 4j: This compound was produced from **3j** (0.25 g, 0.9 mmol) and DBU (0.28 mL, 1.9 mmol) in THF (10 mL), **4j** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a yellow oil (0.17 g, 80%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.27 (t, *J* = 7.2 Hz, 3 H, CH_3), 2.03–2.11 (m, 1 H, CH_2), 2.54–2.61 (m, 1 H, CH_2), 3.30 (s, 3 H, OCH_3), 3.80 (dd, *J* = 10.5, 3.3 Hz, 1 H, CH), 3.83 (d, *J* = 3.3 Hz, 1 H, CH), 4.14 (dq, *J* = 7.2, 4.2 Hz, 2 H, OCH_2CH_3), 4.22–4.32 (m, 2 H, OCH_2), 5.10 (s, 1 H, CH_2=CH), 5.16 (dd, *J* = 4.5, 1.5 Hz, 1 H, CH_2=CH), 5.35 (s, 1 H, CH=C), 5.80–5.88 (m, 1 H, CH=CH_2) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.34 (CH_3), 34.66 (CH_2), 46.90 (CH), 56.04 (OCH_3), 59.24 (OCH_2), 74.34 (C–5), 82.23 (CH), 90.76 (*C*H=C), 117.44 (*C*H_2=CH), 135.20 (*C*H=CH_2), 167.80 (O=C–O),178.04 (O–*C*=CH) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2983 (m), 2934 (m), 2907 (m, C–H), 1701 (s, C=C–O), 1644 (s, C=C–C=O), 1464 (m), 1444 (m), 1376 (m), 1343 (m), 1319 (w), 1288 (m), 1247 (m), 1224 (m), 1169 (m), 1124 (s), 1099 (s), 1050 (s), 1008 (m), 971 (w), 923 (m), 830 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 226 $[M]^+$ (6), 195 (100), 181 (51), 165 (20). The exact molecular mass *m*/*z* = 226.1205 ±2 ppm $[M]^+$ for $C_{12}H_{18}O_4$ was confirmed by HRMS (EI, 70 eV).

Compound 4k: This compound was produced from **3k** (0.70 g, 2.6 mmol) and DBU (0.79 mL, 5.3 mmol) in THF (20 mL), **4k** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a yellow oil (0.48 g, 79%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.99 (t, *J* = 6.9 Hz, 3 H, CH_3), 1.27 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3), 1.21–1.31 (m, 1 H, CH_2), 1.55 (sextet, *J* = 7.2 Hz, 2 H, CH_2), 1.65–1.71 (m, 1 H, CH_2), 3.32 (s, 3 H, OCH_3), 3.69 (dd, *J* = 10.8, 3.3 Hz, 1 H, CH), 3.82 (d, *J* = 3.3 Hz, 1 H, CH), 4.09–4.18 (m, 2 H, OCH_2CH_3), 4.22–4.32 (m, 2 H, OCH_2), 5.32 (s, 1 H, CH=C) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 13.64, 14.16 (CH_3), 21.07, 32.41 (CH_2), 47.20 (CH), 55.80 (OCH_3), 58.88 (OCH_2), 74.09 (C–5), 82.43 (CH), 90.17 (*C*H=C–O), 167.55 (O=C–O), 178.96 (O–*C*=CH) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2962 (w), 2934 (w, C–H), 1702 (s, C=C–O), 1644 (s, C=C–C=O), 1463 (w), 1385 (w), 1339 (w), 1170 (w), 1123 (s), 1094(s), 1048 (m), 1019 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 228 $[M]^+$ (7), 197 (18), 183 (39), 155 (100). $C_{12}H_{20}O_4$ (228.288): C 63.14, H 8.83; found C 62.69, H 8.39.

Compound 4m: This compound was produced from **3m** (0.50 g, 1.6 mmol) and DBU (0.49 mL, 3.3 mmol) in THF (20 mL), **4m** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a yellow oil (0.33 g, 76%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.89 (t, *J* = 6.9 Hz, 3 H, CH_3), 1.26 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3), 1.22–1.35 (m, 6 H, 3×CH_2), 1.36–1.40 (m, 1 H, CH_2), 1.43–1.49 (m, 2 H, CH_2), 1.68–1.78 (m, 1 H, CH_2), 3.32 (s, 3 H, OCH_3), 3.67 (dd, *J* = 10.8, 3.3 Hz, 1 H, CH), 3.82 (d, *J* = 3.3 Hz, 1 H, CH), 4.15 (dq, *J* = 7.2, 3.3 Hz, 2 H, OCH_2CH_3), 4.22–4.32 (m, 2 H, OCH_2), 5.31 (s, 1 H, CH=C) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 13.86, 14.25 (CH_3), 22.39, 28.02, 29.02, 30.50, 31.54 (CH_2), 47.52 (CH), 55.88 (OCH_3), 58.98 (OCH_2), 74.17 (C–5), 82.54 (CH), 90.29 (*C*H=C–O), 167.64 (O=C–O), 179.01 (O–*C*=CH) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2956 (m), 2929 (s), 2858 (w, C–H), 1703 (s, C=C–O), 1644 (s, C=C–C=O), 1464 (m), 1417 (m), 1384 (m), 1338 (w), 1169 (w), 1122 (s), 1097 (s), 1051 (m), 1014 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 270 $[M]^+$ (11), 241 (15), 240 (100), 239 (89), 226 (61). $C_{15}H_{26}O_4$ (270.368): C 66.64, H 9.69; found C 67.04, H 10.12.

Compound 4n: This compound was produced from **3n** (0.35 g, 1.0 mmol) and DBU (0.31 mL, 2.1 mmol) in THF (20 mL), **4n** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a colourless oil (0.30 g, 97%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.88 (t, *J* = 6.9 Hz, 3 H, CH_3), 1.22–1.29 (m, 13 H, 5×H_2, CH_3), 1.33–1.51 (m, 3 H, CH_2), 1.68–1.79 (m, 1 H, CH_2), 3.32 (s, 3 H, OCH_3), 3.68 (dd, *J* = 10.8, 3.3 Hz, 1 H, CH), 3.82 (d, *J* = 3.3 Hz, 1 H, CH), 4.13 (dq, *J* = 7.2, 3.3 Hz, 2 H, OCH_2CH_3), 4.22–4.32 (m, 2 H, OCH_2), 5.31 (s, 1 H, CH=C) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.08, 14.42 (CH_3), 22.63, 27.17, 29.20, 29.32, 29.37, 31.79, 32.03 (CH_2), 50.30 (CH), 56.43 (OCH_3), 59.31 (OCH_2), 75.99 (C–5), 82.36 (CH), 89.65 (*C*H=C), 165.84 (O=C–O), 174.23 (O–*C*=CH) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2954 (m), 2928 (s), 2856 (m, C–H), 1713 (s, O=C–O); 1697 (s, C=C–O), 1650 (s, C=C–C=O), 1464 (m), 1371 (w), 1318 (w), 1267 (m), 1189 (s), 1137 (m), 1102 (m), 1048 (m), 1022 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 298 $[M]^+$ (3), 267 (100), 253 (77). The exact molecular mass *m*/*z* = 298.2144 ± 2 ppm $[M]^+$ for $C_{17}H_{30}O_4$ was confirmed by HRMS (EI, 70 eV).

Compound 4o: This compound was produced from **3o** (0.85 g, 2.44 mmol) and DBU (0.73 mL, 4.9 mmol) in THF (20 mL), **4o** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a yellow oil (0.66 g, 87%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.88 (t, *J* = 6.9 Hz, 3 H, CH_3), 1.26 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3), 1.19–1.29 (m, 12 H, 6×CH_2), 1.30–1.41 (m, 1 H, CH_2), 1.43–1.50 (m, 2 H, CH_2), 1.66–1.73 (m, 1 H, CH_2), 3.32 (s, 3 H, OCH_3), 3.68 (dd, *J* = 10.8, 3.3 Hz, 1 H, CH), 3.82 (d, *J* = 3.3 Hz, 1 H, CH), 4.14 (dq, *J* = 7.2, 3.3 Hz, 2 H, OCH_2CH_3), 4.22–4.32 (m, 2 H, OCH_2), 5.31 (s, 1 H, CH=C) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.00, 14.36 (CH_3), 22.57, 28.16, 29.21, 29.38, 29.44 (2C), 30.60, 31.78 (CH_2), 47.59 (CH), 56.01 (OCH_3), 59.10 (OCH_2), 74.28 (C–5),82.63 (CH), 90.45 (*C*H=C–O), 167.77 (O=C–O), 179.05 (O–*C*=CH) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2927 (s), 2856 (m, C–H), 1704 (s, C=C–O), 1644 (s, C=C–C=O), 1463 (w), 1376 (w), 1168 (w), 1121 (s), 1098 (s), 1050 (m), 1019 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%): 312 $[M]^+$ (11), 281 (91), 267 (100). Anal. calcd. for $C_{18}H_{32}O_4$ (312.448): C 69.20, H 10.32; found C 69.18, H 10.49.

Compound 4p: This compound was produced from **3p** (0.83 g, 2.3 mmol), and DBU (0.68 mL, 4.6 mmol) in THF (20 mL), **4p** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a yellow oil (0.53 g, 70%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.88 (t, *J* = 6.9 Hz, 3 H, CH_3), 1.26 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3), 1.19–1.29 (m, 14 H, 7×CH_2), 1.30–1.40 (m, 1 H, CH_2), 1.41–1.49 (m, 2 H, CH_2), 1.66–1.74 (m, 1 H, CH_2), 3.32 (s, 3 H, OCH_3), 3.68 (dd, *J* = 10.8, 3.3 Hz, 1 H, CH), 3.82 (d, *J* = 3.3 Hz, 1 H, CH), 4.14 (dq, *J* = 7.2, 3.3 Hz, 2 H, OCH_2CH_3), 4.22–4.32 (m, 2 H, OCH_2), 5.31 (s, 1 H, CH=C) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C = 13.93, 14.29 (CH_3), 22.52, 28.10, 29.16, 29.37, 29.39, 29.43, 30.52, 31.74, 31.79 (CH_2), 47.56 (CH), 55.95 (OCH_3), 59.04 (OCH_2), 74.23 (C-5), 82.60 (CH), 90.35 (CH=C), 167.71 (O=C–O), 179.03 (O–*C*=CH) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2927 (s), 2855 (m, C–H), 1704 (s, C=C–O), 1644 (s, C=C–C=O), 1464 (m), 1377 (m), 1339 (w), 1288 (w), 1246 (w), 1223 (w), 1168 (w), 1123 (s), 1099 (s), 1050 (m), 1019 (w), 937 (w), 828 (w), 723 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 326 $[M]^+$ (3), 295 (100), 281 (48). $C_{19}H_{34}O_4$ (326.475): C 69.90, H 10.50; found C 69.80, H 10.74.

Compound 4q: This compound was produced from **3q** (0.154 g, 0.45 mmol) and DBU (0.13 mL, 0.90 mmol) in THF (5 mL), **4q** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a slightly yellow oil (0.128 g, 93%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.29 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.32–1.39 (m, 6 H, 3×CH_2), 1.65–1.84 (m, 4 H, 2×CH_2), 3.32 (s, 3 H, OCH_3), 3.54 (t, *J* = 6.6 Hz, 2 H, CH_2–Cl), 3.68 (dd, *J* = 10.8, 3.3 Hz, 1 H, CH), 3.82 (d, *J* = 3.3 Hz, 1 H, CH), 4.15 (dq, *J* = 7.2,

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3.3 Hz, 2 H, OCH_2CH$_3$), 4.29–4.33 (m, 2 H, OCH$_2$), 5.32 (s, 1 H, CH=C) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz): δ_C = 14.39 (CH$_3$), 26.64, 27.95, 28.65, 30.44, 32.43 (CH$_2$), 44.98 (CH$_2$–Cl), 47.51 (CH), 56.08 (OCH$_3$), 59.18 (OCH$_2$), 74.27 (C–5), 82.62 (CH), 90.52 (*C*H=C–O), 167.81 (O=C–O), 178.92 (O–*C*=CH) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2981 (m), 2933 (s), 2860 (m), 2828 (w, C–H), 1701 (s, C=C–O), 1641 (s, C=C–C=O), 1377 (m), 1338 (m), 1290 (m), 1225 (m), 1168 (m), 1121 (s), 1099 (s), 1050 (s), 1020 (m), 936 (w), 828 (m), 725 (w), 650 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 304 [*M*]$^+$ (2), 273 (32), 259 (17), 245 (2), 237 (8), 213 (2), 199 (11), 195 (3), 186 (16), 181 (5), 167 (6), 155 (100). $C_{15}H_{25}O_4Cl$ (304.813): C 59.11, H 8.27; found C 59.84, H 8.25.

Compound 4r: This compound was produced from **3r** (0.80 g, 3.0 mmol) and DBU (0.91 mL, 6.1 mmol) in THF (10 mL), **4r** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 50:1 to 1:1) as a white solid (0.53 g, 77%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 1.27 (t, *J* = 7.2 Hz, 3 H, OCH$_2$CH_3), 1.41–1.56 (m, 1 H, CH$_2$), 1.61–1.75 (m, 1 H, CH$_2$), 1.88–2.02 (m, 2 H, CH$_2$), 2.26–2.39 (m, 2 H, CH$_2$), 2.64–2.73 (m, 1 H, CH), 3.35 (s, 3 H, OCH$_3$), 3.92 (m, 1 H, CH), 4.15 (m, 1 H, OCH$_2$), 4.17 (q, *J* = 7.2 Hz, 2 H, OCH_2CH$_3$), 4.49 (d, *J* = 10.5 Hz, 1 H, OCH$_2$) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz): δ_C = 14.13 (CH$_3$), 21.17, 21.89, 23.61 (CH$_2$), 45.46 (CH), 56.77 (OCH$_3$), 59.14 (O*C*H$_2$CH$_3$), 74.13 (C-5), 78.88 (CH), 97.66 (C=C), 166.29 (O–C=O), 166.45 (O–C=C) ppm. IR (KBr (cm^{-1})): $\tilde{\nu}$ = 2948 (w, C–H), 1708 (s, C=C–O), 16.84 (w), 1642 (s, C=C–C=O), 1293 (w), 1270 (m), 1240 (m) 1201 (s), 1147 (m), 1122 (m), 1102 (s), 1074 (w), 1063 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 226 [*M*]$^+$ (71), 197 (27), 181 (100). The exact molecular mass *m*/*z* = 226.1205 ± 2 ppm [*M*]$^+$ for $C_{12}H_{18}O_4$ was confirmed by HRMS (EI, 70 eV).

Compound 4s: This compound was produced from **3s** (0.20 g, 0.8 mmol) and DBU (0.24 mL, 1.6 mmol) in THF (10 mL), **4s** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a colourless oil (0.15 g, 91%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 1.29 (t, *J* = 7.2 Hz, 3 H, CH$_3$), 1.83–1.89 (m, 1 H, CH$_2$), 2.26–2.35 (m, 2 H, CH$_2$), 2.81–2.85 (m, 1 H, CH$_2$), 3.15 (t, *J* = 9.0 Hz, 1 H, CH), 3.37 (s, 3 H, OCH$_3$), 3.77 (dd, *J* = 5.1, 3.0 Hz, 1 H, CH), 4.18 (q, *J* = 7.2 Hz, 2 H, OCH_2CH$_3$), 4.63 (dd, *J* = 10.8, 3.0 Hz, 1 H, OCH$_2$), 4.84 (d, *J* = 10.8 Hz, 1 H, OCH$_2$) ppm. ^{13}C NMR (CDCl$_3$, 150 MHz): δ_C = 14.36 (CH$_3$), 21.16, 27.59 (CH$_2$), 54.18 (CH), 57.47 (OCH$_3$), 59.80 (OCH$_2$), 77.04 (CH), 84.32 (C–5), 96.45 (*C*=C–O), 164.78 (O=C–O), 169.64 (O–C=C) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2962 (m), 2938 (m), 2836 (w, C–H), 1755 (s, O=C–O), 1725 (s, C=C–O), 1461 (m), 1449 (m), 1365 (w), 1257 (m), 1237 (m), 1192 (m), 1153 (m), 1114 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 313 [*M*]$^+$ (68), 199 (36), 181 (19), 167 (100), 152 (31). The exact molecular mass *m*/*z* = 212.1049 ± 2 ppm [*M*]$^+$ for $C_{11}H_{16}O_4$ was confirmed by HRMS (EI, 70 eV).

Compound 4t: This compound was produced from **3t** (0.27 g, 0.98 mmol) and DBU (0.29 mL, 2.0 mmol) in THF (15 mL), **4t** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a yellow oil (0.21 g, 90%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 1.28 (t, *J* = 7.2 Hz, 3 H, CH$_3$), 1.47–1.50 (m, 2 H, CH$_2$), 1.59–1.69 (m, 1 H, CH$_2$), 1.75–1.87 (m, 2 H, CH$_2$), 1.98–2.13 (m, 2 H, CH$_2$), 2.86 (dd, *J* = 15.3, 6.9 Hz, 1 H, CH$_2$), 3.08 (dt, *J* = 12.3, 2.1 Hz, 1 H, CH), 3.34 (s, 3 H, OCH$_3$), 3.65–3.68 (m, 1 H, CH), 4.19 (q, *J* = 7.2 Hz, 2 H, OCH_2CH$_3$), 4.38 (d, *J* = 3.6 Hz, 2 H, OCH$_2$) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz): δ_C = 14.20 (CH$_3$), 26.81, 26.87, 29.30, 31.13 (CH$_2$), 51.21 (CH), 56.38 (OCH$_3$), 59.56 (OCH$_2$), 75.02 (C-5), 84.71 (CH), 103.00 (*C*=C–O), 167.04 (O=C–O), 172.03 (O–*C*=C) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2981 (m), 2926 (s), 2953 (m, C–H), 1705 (s, O=C–O), 1677 (s, C=C–O), 1640 (s, C=C–C=O), 1447 (m), 1388 (m), 1370 (m), 1328 (w), 1301 (m), 1278 (m), 1250 (m), 1222 (m), 1178 (s), 1150 (s), 1122 (m), 1102 (s), 1050 (s), 998 (m), 962 (m), 939 (w), 876 (w), 856 (w), 831 (w), 783 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 240 [*M*]$^+$ (100), 211 (32), 195 (90). $C_{13}H_{20}O_4$ (240.299): C 64.98, H 8.39; found C 64.75, H 8.97.

Compound 4u: This compound was produced from **3u** (0.50 g, 1.7 mmol) and DBU (0.51 mL, 3.4 mmol) in THF (10 mL), **4u** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a yellow oil (0.35 g, 80%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 1.27 (t, *J* = 7.2 Hz, 3 H, CH$_3$), 1.31–1.42 (m, 2 H, CH$_2$), 1.54–1.72 (m, 4 H, 2 × CH$_2$), 1.77–1.92 (m, 2 H, CH$_2$), 2.01–2.12 (m, 1 H, CH$_2$), 2.75 (dt, *J* = 14.3, 3.7 Hz, 1 H, CH$_2$), 3.08 (dd, *J* = 12.3, 3.3 Hz, 1 H, CH), 3.32 (s, 3 H, OCH$_3$), 3.63 (d, *J* = 3.3 Hz, 1 H, CH), 4.17 (dq, *J* = 7.2, 1.5 Hz, 2 H, OCH_2CH$_3$), 4.36 (dd, *J* = 10.5, 3.3 Hz, 1 H, OCH$_2$), 4.50 (d, *J* = 10.8 Hz, 1 H, OCH$_2$) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz): δ_C = 14.24 (CH$_3$), 24.98, 25.99, 26.51, 28.98, 33.33 (CH$_2$), 49.47 (CH), 56.01 (OCH$_3$), 59.25 (OCH$_2$), 74.47 (C–5), 84.29 (CH), 99.73 (*C*=C–O), 166.38 (O=C–O), 169.31 (O–*C*=C) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2979 (s), 2926 (s), 2855 (s), 2827 (m, C–H), 1708 (s, O=C–O), 1676 (s, C=C–O), 1639 (s, C=C–C=O), 1457 (s), 1386 (s), 1367 (s), 1329 (m), 1305 (s), 1261 (m), 1243 (m), 1226 (w), 1173 (s), 1138 (s), 1104 (s), 1022 (m), 1047 (s), 988 (m), 952 (m), 226 (w), 884 (w), 849 (m), 818 (w), 791 (m), 751 (m), 731 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 254 (100) [*M*]$^+$, 223 (31), 209 (94). $C_{14}H_{22}O_4$ (254.325): C 66.12, H 8.72; found C 65.62, H 8.44.

Compound 4v: This compound was produced from **3v** (2.40 g, 6.9 mmol) and DBU (2.07 mL, 13.8 mmol) in THF (10 mL), with (*E*)-**4v** (0.77 g, 60%) and (*Z*)-**4v** (0.50 g, 38%) being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as yellow oils.

Compound (*E*)-4v: ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 1.14–1.39 (m, 12 H, 6 × CH$_2$), 1.28 (t, *J* = 7.2 Hz, 3 H, CH$_3$), 1.49–1.62 (m, 2 H, CH$_2$), 2.00–2.12 (m, 2 H, CH$_2$), 2.28–2.38 (m, 2 H, CH$_2$), 2.49–2.61 (m, 1 H, CH$_2$), 3.31 (s, 3 H, OCH$_3$), 3.82 (t, *J* = 3.9 Hz, 1 H, CH), 3.95 (dd, *J* = 5.7, 3.9 Hz, 1 H, CH), 4.11–4.24 (m, 2 H, OCH_2CH$_3$), 4.31 (d, *J* = 3.9 Hz, 2 H, OCH$_2$) ppm. ^{13}C NMR (CDCl$_3$, 50 MHz): δ_C = 14.35 (CH$_3$), 21.62, 22.39, 23.60, 24.15, 24.25, 25.40, 25.83, 26.31, 29.07 (CH$_2$), 47.55 (CH), 56.10 (OCH$_3$), 59.34 (OCH$_2$), 75.38 (C–5), 83.95 (CH), 104.62 (*C*=C–O), 168.79 (O=C–O), 173.25 (O–*C*=C) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2931 (s), 2861 (m, C–H), 1741 (w), 1693 (s, C=C–O), 1622 (s, C=C–C=O), 1465 (m), 1446 (m), 1383 (w), 1366 (w), 1302 (m), 1283 (m), 1238 (m), 1218 (w), 1196 (m), 1176 (m), 1150 (m), 1097 (s), 1049 (s), 1020 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 310 [*M*]$^+$ (29), 279 (100), 265 (11). The exact molecular mass *m*/*z* = 310.2144 ± 2 ppm [*M*]$^+$ for $C_{18}H_{30}O_4$ was confirmed by HRMS (EI, 70 eV).

Compound (*Z*)-4v: M.p. 77.5 °C. ^{1}H NMR (CDCl$_3$, 600 MHz): δ = 1.10 (t, *J* = 7.2 Hz, 3 H, CH$_3$), 1.18–1.22 (m, 10 H, 5 × H$_2$), 1.24–1.41 (m, 2 H, CH$_2$), 1.47–1.53 (m, 2 H, CH$_2$), 1.54–1.60 (m, 1 H, CH$_2$), 1.62–1.69 (m, 1 H, CH$_2$), 1.97 (m, 1 H, CH$_2$), 2.13–2.19 (m, 1 H, CH$_2$), 2.97 (dd, *J* = 11, 5.5 Hz, 1 H, CH), 3.14 (s, 3 H, OCH$_3$), 3.48 (d, *J* = 5.5 Hz, 1 H, CH), 3.95–4.02 (m, 1 H, OCH_2CH$_3$), 4.03–4.08 (m, 1 H, OCH_2CH$_3$), 4.21 (dd, *J* = 11, 5.5 Hz, 1 H, OCH$_2$), 4.29 (d, *J* = 11 Hz, 1 H, OCH$_2$) ppm. ^{13}C NMR (CDCl$_3$, 50 MHz): δ_C = 14.37 (CH$_3$), 21.52, 23.15, 25.40, 25.87, 26.75, 27.16, 27.36, 27.53, 29.84 (CH$_2$), 46.81 (CH), 56.11 (OCH$_3$), 59.47 (OCH$_2$), 74.64 (C–5), 82.88 (CH), 102.96 (*C*=C–O), 167.19 (O=C–O), 169.13 (O–*C*=C) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2975 (m), 2930 (s), 28.62 (m), 28.28 (w, C–H), 1708 (s, C=C–O), 1680 (s, C=C–C=O), 1630 (s), 1469 (m), 1446 (m), 1382 (w), 1367 (m), 1353 (w), 1339 (w), 1322 (m), 1295 (m), 1281 (m), 1232 (m), 1170 (s), 1145 (s),

1105 (s), 1095 (s), 1047 (m), 1032 (m), 1012 (w), 959 (w), 735 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 310 $[M]^+$ (30), 279 (100), 265 (26). The exact molecular mass *m*/*z* = 310.2144 ± 2 ppm $[M]^+$ for $C_{18}H_{30}O_4$ was confirmed by HRMS (EI, 70 eV).

Compound 4w: This compound was produced from **3w** (0.24 g, 0.87 mmol) and DBU (0.26 mL, 1.7 mmol) in THF (10 mL), **4w** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a yellow solid (0.14 g, 68%). M.p. 59 °C ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.13 (d, *J* = 6.6 Hz, 3 H, CH_3), 1.28 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3), 1.21–1.31 (m, 1 H, CH_2), 1.49–1.61 (m, 1 H, CH_2), 1.75–1.87 (m, 1 H, CH), 2.28–2.38 (m, 3 H, CH_2, CH), 3.39 (s, 3 H, OCH_3), 3.81 (dt, *J* = 6.6, 9.0 Hz, 1 H, CH), 3.94 (t, *J* = 8.4 Hz, 1 H, OCH_2), 4.18 (q, *J* = 7.2 Hz, 2 H, OCH_2CH_3), 4.55 (dd, *J* = 6.6, 8.4 Hz, 1 H, OCH_2) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C = 14.62, 19.66 (CH_3), 24.41, 31.63 (CH_2), 33.95, 51.70 (CH), 58.53 (OCH_3), 59.84 (OCH_2), 73.68 (C–5), 82.56 (CH), 98.89 (*C*=C–O), 165.95 (O=C–O), 166.83 (O(O–*C*=C) ppm. IR (KBr (cm^{-1})): $\tilde{\nu}$ = 2979 (w), 2954 (m), 2929 (m), 2894 (w, C–H), 1708 (s, O=C–O), 1685 (s, C=C–O), 1652 (s, C=C–C=O), 1371 (w), 1295 (m), 1276 (m), 1228 (m), 1200 (m), 1155 (m), 1131 (s), 1096 (m), 1047 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 240 $[M]^+$ (38), 211 (16), 195 (47), 167 (100). The exact molecular mass *m*/*z* = 240.1362 ± 2 ppm $[M]^+$ for $C_{13}H_{20}O_4$ was confirmed by HRMS (EI, 70 eV).

Compound 4x: This compound was produced from **3x** (0.300 g, 0.92 mmol) and DBU (0.28 mL, 1.85 mmol) in THF (10 mL), with **4x (1)** (0.079 g, 30%), **4x (2)** (0.047 g, 18%) and **4x (3)** (0.124 g, 47%) being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 50:1 to 1:1) as a slightly yellow solid, an oil and a solid, respectively.

Compound 4x (1): ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.69 (q, *J* = 12.0 Hz, 1 H, CH_2), 2.29–2.43 (m, 2 H, CH_2, CH), 2.65–2.73 (m, 1 H, CH), 2.81–2.97 (m, 2 H, CH_2), 3.44 (s, 3 H, OCH_3), 3.72 (s, 3 H, OCH_3), 3.85–3.90 (m, 1 H, CH), 4.01 (dd, *J* = 8.7, 8.7 Hz, 1 H, OCH_2), 4.58 (dd, *J* = 8.7, 6.9 Hz, 1 H, OCH_2), 7.20–7.35 (m, 5 H, 5 × CH from Ph) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C = 32.79, 33.28 (CH_2), 40.38, 47.47 (CH), 51.28, 58.85 (OCH_3), 73.93 (C–5), 82.32 (CH), 98.65 (*C*=C–O), 126.67, 126.91 (2 C), 128.86 (2 C) (CH from Ph), 145.20 (C from Ph), 166.12 (O=C–O), 166.84 (O–*C*=C) ppm. IR (KBr (cm^{-1})): $\tilde{\nu}$ = 2946 (w, C–H), 1711 (s, O=C–O), 1683 (m), 1655 (s, *C*=C–O), 1454 (w), 1438 (w), 1392 (w), 1302 (w), 1258 (s), 1198 (s), 1134 (s), 110 (s), 1080 (s), 1010 (w), 978 (w), 769 (m), 704 (m).) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 288 $[M]^+$ (43), 257 (12), 230 (6), 213 (5), 197 (3), 184 (27), 169 (9), 152 (100), 121 (12), 93 (27), 91 (16), 77 (7). The exact molecular mass *m*/*z* = 288.1362 ± 2 ppm $[M]^+$ for $C_{17}H_{20}O_4$ was confirmed by HRMS (EI, 70 eV).

Compound 4x (2): ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.98–2.21 (m, 2 H, CH_2), 2.35–2.41 (m, 1 H, CH), 2.65–2.73 (m, 2 H, CH_2), 3.33 (s, 3 H, OCH_3), 3.37–3.44 (m, 1 H, CH), 3.78 (s, 3 H, OCH_3), 3.98–4.10 (m, 1 H, CH), 4.08 (dd, *J* = 10.5, 2.6 Hz, 1 H, OCH_2), 4.49 (d, *J* = 10.5 Hz, 1 H, OCH_2), 7.19–7.32 (m, 5 H, 5 × CH from Ph) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C = 28.22, 28.44 (CH_2), 36.56, 41.09 (CH), 51.41, 57.31 (OCH_3), 74.71 (C–5), 79.71 (CH), 97.31 (*C*=C–O), 126.37, 127.23 (2 C), 128.51 (2 C), (CH from Ph), 145.26 (C from Ph), 166.81 (O=C–O), 167.13 (O–*C*=C) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 3027 (w), 2975 (w), 2935 (m), 2900 (m), 2867 (w, C–H), 1711 (s, O=C–O), 1686 (s), 1656 (s, *C*=C–O), 1494 (w), 1439 (m), 1388 (m), 1365 (w), 1332 (w), 1299 (w), 1268 (m), 1245 (m), 1201 (m), 1148 (m), 1109 (s), 1080 (m), 1059 (w), 1017 (w), 989 (w), 939 (w), 917 (w), 761 (w), 703 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 288 $[M]^+$ (20), 184 (17), 152 (100), 121 (2), 98 (26), 93 (7), 91 (12). The exact molecular mass *m*/*z* = 288.1362 ± 2 ppm $[M]^+$ for $C_{17}H_{20}O_4$ was confirmed by HRMS (EI, 70 eV).

Compound 4x (3): M.p. 155 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.02–2.17 (m, 2 H, CH_2), 2.34–2.45 (m, 1 H, CH), 2.63–2.71 (m, 1 H, CH), 2.84–2.98 (m, 2 H, CH_2), 3.37 (s, 3 H, OCH_3), 3.71 (s, 3 H, OCH_3), 3.95 (dd, *J* = 4.8, 3.0 Hz, 1 H, CH), 4.24 (dd, *J* = 10.5, 3.0 Hz, 1 H, OCH_2), 4.58 (d, *J* = 10.5 Hz, 1 H, OCH_2), 7.19–7.35 (m, 5 H, 5 × CH from Ph) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C = 28.27, 33.24 (CH_2), 40.80, 46.95 (CH), 51.20, 57.30 (OCH_3), 75.16 (C–5), 79.29 (CH), 97.88 (*C*=C–O), 126.59, 127.02 (2 C), 128.64 (2 C) (CH from Ph), 145.57 (C from Ph), 166.37 (O=C–O), 166.98 (O–*C*=C) ppm. IR (KBr (cm^{-1})): $\tilde{\nu}$ = 2948 (w), 2933 (w), 2901 (w), 2845 (w, C–H), 1714 (s, O=C–O), 1683 (w), 1650 (s, C=C–O), 1495 (w), 1459 (w), 1432 (w), 1389 (w), 1358 (w), 1291 (w), 1255 (s), 1195 (s), 1146 (s), 1126 (m), 1091 (s), 1056 (m), 1015 (m), 966 (w), 940 (m), 856 (w), 839 (w), 768 (m), 707 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 288 $[M]^+$ (41), 257 (11), 230 (5), 213 (13), 197 (4), 184 (27), 169 (8), 152 (100), 121 (17), 93 (24), 91 (21), 77 (10). $C_{17}H_{20}O_4$ (288.343): C 70.81, H 6.99; found C 70.17, H 6.96. The exact molecular mass *m*/*z* = 288.1362 ± 2 ppm $[M]^+$ for $C_{17}H_{20}O_4$ was confirmed by HRMS (EI, 70 eV).

Compound 4y: This compound was produced from **3y** (0.500 g, 2.27 mmol) and DBU (0.68 mL, 4.53 mmol) in THF (20 mL), **4y** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 30:1 to 1:1) as a yellow oil (0.384 g, 92%). ^{1}H NMR ($CDCl_3$, 150 MHz): δ = 2.87–2.96 (m, 3 H, 2 × CH_2), 3.34 (s, 3 H, OCH_3), 3.55–3.62 (dm, *J* = 18.3, 1.4 Hz, 1 H, CH_2), 4.16–4.42 (m, 5 H, 2 × OCH_2, CH) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C = 24.68, 34.80 (CH_2), 56.17 (OCH_3), 65.03 (OCH_2), 76.13 (C–5), 77.92 (CH), 94.06 (*C*=C–O), 167.27 (O=C–O), 172.65 (O–*C*=C) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2986 (m), 2925 (s), 2916 (s), 2830 (w, C–H), 1738 (s, O=C–O), 1679 (s, C=C–O), 1462 (m), 1414 (w), 1372 (s), 1307 (m), 1263 (s), 1241 (s), 1213 (s), 1160 (m), 1100 (s), 1039 (s), 1002 (s), 948 (m), 927 (w), 841 (w), 801 (w), 772 (w), 753 (m), 695 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 184 $[M]^+$ (17), 152 (100), 126 (11), 116 (1), 95 (27), 84 (5), 68 (9). Anal.: calcd. for $C_9H_{12}O_4$ (184.191): C 58.69, H 6.57; found C 58.52, H 6.42.

General Procedure for the Synthesis of Furans 5: TFA (0.88 mL, 11.5 mmol) was added to a CH_2Cl_2 solution (10 mL) of **4** (0.9 mmol). After the mixture had been stirred for 4 h at room temperature, a saturated aqueous solution of Na_2CO_3 was added. The organic layer was separated, and the aqueous layer was repeatedly extracted with diethyl ether. The combined organic extracts were dried (Na_2SO_4) and filtered, and the filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) to give **5**. These furan derivatives are not UV-active (neither short nor long wavelength). To make the product visible on TLC, the following mixture was used as a dying agent: MeOH/AcOH/anisaldehyde, 85:14:1. Alternatively, production of furans from 2-alkylidene-4-methoxy tetrahydrofurans by elimination of methanol was achieved successfully by heating at reflux in CH_2Cl_2, and for some of them in 1,4-dioxane, with very good yields.

Compound 5a: This compound was produced from **4a** (0.30 g, 1.7 mmol) and TFA (1.75 mL, 22.7 mmol) in CH_2Cl_2 (20 mL), **5a** being isolated without further purification as a yellow oil (0.20 g, 80%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.68 (s, 2 H, CH_2), 3.73 (s, 3 H, OCH_3), 6.22 (dt, *J* = 3.3, 0.9 Hz, 1 H, CH), 6.34 (dd, *J* = 3.3, 1.2 Hz, 1 H, CH), 7.36 (dd, *J* = 1.2, 0.9 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 33.79 (CH_2), 52.15 (OCH_3), 107.96, 110.44, 142.02 (CH), 147.52 (C), 169.78 (O=C–O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2962 (s), 2923 (s), 2852 (w, C–H), 1738 (s, O=C–

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O), 1719 (s), 1647 (w), 1439 (m), 1414 (w), 1342 (w), 1308 (m), 1261 (s), 1197 (s), 1096 (s), 1020 (s), 866 (m), 800 (s) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 140 $[M]^+$ (31), 81 (100). The exact molecular mass *m/z* = 140.0473 ± 2 ppm $[M]^+$ for $C_7H_8O_3$ was confirmed by HRMS (EI, 70 eV).

Compound 5b: This compound was produced from **4b** (0.10 g, 0.54 mmol) and TFA (0.54 mL, 7.0 mmol) in CH_2Cl_2 (5 mL), **5b** being isolated without further purification as a yellow oil (0.08 g, 100%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.27 (t, *J* = 7.2 Hz, 3 H, CH_3), 3.68 (s, 2 H, CH_2), 4.19 (q, *J* = 7.2 Hz, 2 H, OCH_2CH_3), 6.22 (dt, *J* = 3.3, 0.9 Hz, 1 H, CH), 6.33 (dd, *J* = 3.3, 1.8 Hz, 1 H, CH), 7.36 (dd, *J* = 1.8, 0.9 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.15 (CH_3), 34.15 (CH_2), 61.19 (OCH_2), 107.98, 110.52, 142.06 (CH), 147.79 (C), 169.47 (O=C–O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2964 (m, C–H), 1638 (m, O=C–O), 1261 (s), 1222 (w), 1180 (m), 1095 (s), 1022 (s), 866 (w), 800 (s) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 154 $[M]^+$ (74), 125 (33), 93 (87), 81 (100). The exact molecular mass *m/z* = 154.0630 ± 2 ppm $[M]^+$ for $C_8H_{10}O_3$ was confirmed by HRMS (EI, 70 eV).

Compound 5c: This compound was produced from **4c** (0.25 g, 1.3 mmol) and TFA (1.3 mL, 16.2 mmol) in CH_2Cl_2 (10 mL), **5c** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a yellow oil (0.13 g, 61%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.25 (d, *J* = 6.3 Hz, 6 H, 2×CH_3), 3.64 (s, 2 H, CH_2), 5.04 (sept, *J* = 6.3 Hz, 1 H, OCH), 6.22 (dt, *J* = 3.3, 0.9 Hz, 1 H, CH), 6.33 (dd, *J* = 3.3, 1.8 Hz, 1 H, CH), 7.35 (dd, *J* = 1.8, 0.9 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 21.74 ($2CH_3$), 34.46 (CH_2), 68.63 (OCH), 107.84, 110.49, 141.97 (CH), 148.02 (C), 168.98 (O=C–O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2963 (m), 2927 (w, C–H), 1739 (w, O=C–O), 1261 (s), 1178 (w), 1100 (s), 1020 (s), 800 (s) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 168 $[M]^+$ (31), 125 (93), 108 (100). The exact molecular mass *m/z* = 168.0786 ± 2 ppm $[M]^+$ for $C_9H_{12}O_3$ was confirmed by HRMS (EI, 70eV).

Compound 5d: This compound was produced from **4d** (0.15 g, 0.69 mmol) and TFA (0.7 mL, 9.0 mmol) in CH_2Cl_2 (5 mL), **5d** being isolated without further purification as a yellow oil (0.13 g, 100%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 3.38 (s, 3 H, OCH_3), 3.61 (t, *J* = 4.8 Hz, 2 H, $OCH_2CH_2OCH_3$), 3.73 (s, 2 H, CH_2), 4.28 (t, *J* = 4.8 Hz, 2 H, $OCH_2CH_2OCH_3$), 6.23 (dt, *J* = 3.3, 0.9 Hz, 1 H, CH), 6.33 (dd, *J* = 3.3, 1.8 Hz, 1 H, CH), 7.36 (dd, *J* = 1.8, 0.9 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 33.71 (CH_2), 58.76 (OCH_3), 63.98 ($OCH_2CH_2OCH_3$), 70.09 ($OCH_2CH_2OCH_3$), 107.92, 110.34, 141.88 (CH), 147.40 (C), 169.23 (O=C–O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2977 (s), 2931 (s), 2880 (s), 2823 (w, C–H), 1792 (w), 1745 (s), 1741 (s, O=C–O), 1646 (m), 1604 (w), 1506 (w), 1453 (m), 1405 (m), 1384 (m), 1374 (m), 1338 (m), 1261 (m), 1227 (m), 1198 (s), 1180 (s), 1149 (s), 1128 (s), 1077 (m), 1037 (s), 1015 (m), 950 (w), 940 (w), 843 (w), 817 (w), 740 (w) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 184 (100) $[M]^+$, 139 (2), 125 (8), 109 (2). The exact molecular mass *m/z* = 184.0736 ± 2 ppm $[M]^+$ for $C_9H_{12}O_4$ was confirmed by HRMS (EI, 70 eV).

Compound 5e: This compound was produced from **4e** (0.08 g, 0.30 mmol) and TFA (0.3 mL, 0.39 mmol) in CH_2Cl_2 (5 mL), **5e** being isolated without further purification as a yellow oil (0.07 g, 100%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 3.73 (s, 2 H, CH_2), 5.16 (s, 2 H, OCH_2), 6.23 (dd, *J* = 3.3, 0.6 Hz, 1 H, CH), 6.33 (t, *J* = 3.3 Hz, 1 H, CH), 7.31–7.38 (m, 6 H, CH, 5×CH from Ph) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 34.09 (CH_2), 66.87 (OCH_2), 108.14, 110.55 (CH), 128.18, 128.31, 128.57 (CH from Ph), 135.61 (C from Ph), 142.11 (CH), 147.53 (C), 169.26 (O=C–O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2962 (w, C–H), 1741 (s, O=C–O), 1455 (w), 1382 (w), 1338 (w), 1262 (s), 1224 (m), 1206 (m), 1180 (m), 1153 (s), 1079 (m), 1014 (s), 800 (m), 740 (m), 699 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 216 $[M]^+$ (15), 91 (100), 81 (77). The exact molecular mass *m/z* = 216.0786 ± 2 ppm $[M]^+$ for $C_{13}H_{12}O_3$ was confirmed by HRMS (EI, 70 eV).

Compound 5f: This compound was produced from **3f** (0.550 g, 2.2 mmol) and DBU (0.65 mL, 4.3 mmol) in THF (10 mL), **5f** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a black oil (0.29 g, 72%). ^1H NMR ($CDCl_3$, 600 MHz): δ = 4.29 (s, 2 H, CH_2), 6.22 (dd, *J* = 3.3, 0.9 Hz, 1 H, CH), 6.32 (dt, *J* = 3.3, 1.2 Hz, 1 H, CH), 7.35 (d, *J* = 1.2, 0.9 Hz, 1 H, CH), 7.45 (t, *J* = 6.0 Hz, 2 H, 2×CH from Ph), 7.55 (t, *J* = 6.0 Hz, 1 H, CH from Ph), 7.99 (d, *J* = 6.0 Hz, 2 H, 2×CH from Ph) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 38.30 (CH_2), 108.25, 110.58 (CH), 128.35, 128.49, 128.57 (CH from Ph), 136.04 (C from Ph), 141.98 (CH), 148.14 (C), 171.25 (O=C–O) ppm. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2955 (w, C–H), 1719 (w), 1691 (s, O=C–O), 1598 (m), 1582 (w), 1568 (w), 1505 (w), 1449 (m), 1385 (w), 1337 (w), 1319 (w), 1279 (m), 1226 (m), 1208 (m), 1181 (w), 1152 (w), 1074 (w), 1014 (m), 996 (w), 737 (m), 715 (w), 689 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 186 (100) [*M*]. The exact molecular mass *m/z* = 186.0681 ± 2 ppm $[M]^+$ for $C_{12}H_{10}O_2$ was confirmed by HRMS (EI, 70 eV).

Compound 5g: This compound was produced from **4g** (0.08 g, 0.4 mmol) and TFA (0.40 mL, 5.2 mmol) in CH_2Cl_2 (5 mL), **5g** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a colourless oil (0.05 g, 84%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.99 (s, 3 H, CH_3), 3.62 (s, 2 H, CH_2), 3.71 (s, 3 H, OCH_3), 6.21 (d, *J* = 1.8 Hz, 1 H, CH), 7.27 (d, *J* = 1.8 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 9.77 (CH_3), 32.03 (CH_2), 52.20 (OCH_3), 113.01 (CH), 116.95 (C), 141.10 (CH), 143.09 (C), 170.08 (O=C–O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2960 (m), 2925 (s), 2855 (w, C–H), 1727 (m, O=C–O), 1675 (w), 1458 (m), 1442 (m), 1406 (w), 1386 (w), 1319 (w), 1261 (s), 1200 (m), 1175 (m), 1161 (m), 1120 (m), 1118 (m), 1095 (s), 1022 (s), 800 (s) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 154 (100) $[M]^+$, 139 (18), 123 (19), 95 (60). The exact molecular mass *m/z* = 154.0630 ± 2 ppm $[M]^+$ for $C_8H_{10}O_3$ was confirmed by HRMS (EI, 70 eV).

Compound 5h: This compound was produced from **4h** (0.15 g, 0.7 mmol) and TFA (0.70 mL, 9.1 mmol) in CH_2Cl_2 (15 mL), **5h** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a yellow oil (0.10 g, 79%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.15 (t, *J* = 7.5 Hz, 3 H, CH_3), 1.26 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3), 2.93 (q, *J* = 7.5 Hz, 2 H, CH_2), 3.61 (s, 2 H, CH_2), 4.16 (q, *J* = 7.2 Hz, 2 H, OCH_2CH_3), 6.26 (d, *J* = 1.8 Hz, 1 H, CH), 7.28 (d, *J* = 1.8 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C = 14.05, 14.69 (CH_3), 17.84, 22.61 (CH_2), 60.89 (OCH_2), 111.19 (CH), 123.51 (C), 141.19 (CH), 142.55 (C), 169.70 (O=C–O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2965 (m), 2928 (m), 2879 (w), 2857 (w, C–H), 1742 (s, O=C–O), 1648 (w), 1600 (w), 1463 (m), 1446 (w), 1433 (w), 1400 (w), 1369 (w), 1332 (w), 1300 (w), 1264 (m), 1246 (w), 1214 (m), 1180 (m), 1162 (m), 1095 (m), 1069 (w), 1032 (m), 893 (w), 737 (w) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 182 $[M]^+$ (94), 153 (32), 152 (27), 137 (100), 109 (49), 107 (90), 93 (12). The exact molecular mass *m/z* = 182.0943 ± 2 ppm $[M]^+$ for $C_{10}H_{14}O_3$ was confirmed by HRMS (EI, 70 eV).

Compound 5i: The reaction was carried out by heating of a CH_2Cl_2 solution (5 mL) of **4i** (0.100 g, 0.495 mmol) under reflux for 24 h. The solvent was removed in vacuo and the residue was purified by chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 50:1) to give **5i** as a slight yellow oil (0.082 g, 98%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 3.64 (s, 2 H, CH_2), 3.71 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3), 6.31 (d, *J* = 2.1 Hz, 1 H, CH), 7.19 (d, *J* = 2.1 Hz, 1

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H, CH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 30.76 (CH_2), 52.07, 59.12 (OCH_3), 102.77 (CH), 131.43 (C), 140.38 (CH), 145.19 (C), 170.06 (O=C–O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 3004 (w), 2953 (m), 2846 (w, C–H), 1742 (m, O=C–O), 1665 (m), 1642 (m), 1508 (w), 1458 (m), 1441 (m), 1413 (m), 1340 (m), 1284 (s), 1239 (s), 1196 (s), 1173 (s), 1101 (s), 1011 (s), 890 (w), 786 (w), 736 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 170 $[M]^+$ (19), 110 (100).

Compound 5j: This compound was produced from **4j** (0.10 g, 0.4 mmol) and TFA (0.44 mL, 5.7 mmol) in CH_2Cl_2 (10 mL), **5j** being isolated without further purification as a colourless oil (0.09 g, 100%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.25 (t, J = 7.2 Hz, 3 H, CH_3), 3.14 (dt, J = 6.3, 1.5 Hz, 2 H, CH_2), 3.61 (s, 2 H, CH_2), 4.16 (q, J = 7.2 Hz, 2 H, OCH_2), 5.01–5.09 (m, 2 H, CH_2=CH), 5.82–5.95 (m, 1 H, CH=CH_2), 6.23 (d, J = 1.8 Hz, 1 H, CH), 7.30 (d, J = 1.8 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.11 (CH_3), 29.12, 32.37 (CH_2), 61.06 (OCH_2), 112.07 (CH), 115.46 (CH_2=CH), 119.41 (C), 136.21 (CH=CH_2), 141.25 (CH), 143.56 (C), 169.48 (O=C–O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2982 (m), 2932 (w, C–H), 1741 (s, O=C–O), 1641 (m), 1512 (w), 1440 (m), 1417 (m), 1369 (w), 1334 (m), 1302 (m), 1264 (m), 1235 (m), 1180 (s), 1160 (s), 1100 (m), 1060 (m), 1030 (s), 997 (w), 918 (m), 894 (w), 737 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 194 $[M]^+$ (48), 165 (5), 121 (100). The exact molecular mass *m*/*z* = 194.0943 ± 2 ppm $[M]^+$ for $C_{11}H_{14}O_3$ was confirmed by HRMS (EI, 70 eV).

Compound 5k: This compound was produced from **4k** (0.13 g, 0.6 mmol) and TFA (0.57 mL, 7.4 mmol), in CH_2Cl_2 (10 mL), **5k** being isolated without further purification as a colourless oil (0.11 g, 100%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.92 (t, J = 7.2 Hz, 3 H, CH_3), 1.25 (t, J = 7.2 Hz, 3 H, OCH_2CH_3), 1.55 (sextet, J = 7.2 Hz, 2 H, CH_2), 2.33 (t, J = 7.2 Hz, 2 H, CH_2), 3.60 (s, 2 H, CH_2), 4.16 (q, J = 7.2 Hz, 2 H, OCH_2), 6.23 (d, J = 1.8 Hz, 1 H, CH), 7.28 (d, J = 1.8 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C = 13.58, 13.98 (CH_3), 23.25, 26.55, 32.21 (CH_2), 60.88 (OCH_2), 111.54 (CH), 121.71 (C), 141.01 (CH), 143.02 (C), 169. 52 (O=C–O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2962 (m), 2932 (m), 2872 (w, C–H), 1741 (s, O=C–O), 1510 (w), 1462 (m), 1415 (w), 1402 (w), 1370 (w), 1333 (w), 1302 (w), 1263 (m), 1239 (m), 1208 (m), 1163 (s), 1097 (m), 1031 (s), 801 (w), 735 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 196 $[M]^+$ (24), 166 (96), 123 (100). The exact molecular mass *m*/*z* = 196.1099 ± 2 ppm $[M]^+$ for $C_{11}H_{16}O_3$ was confirmed by HRMS (EI, 70 eV).

Compound 5l: This compound was produced from **4l** (0.10 g, 0.4 mmol) and TFA (0.41 mL, 5.4 mmol) in CH_2Cl_2 (10 mL), **5l** being isolated without further purification as a colourless oil (0.09 g, 100%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.91 (t, J = 7.2 Hz, 3 H, CH_3), 1.25 (t, J = 7.2 Hz, 3 H, OCH_2CH_3), 1.33 (sextet, J = 7.2 Hz, 2 H, CH_2), 1.50 (quint, J = 7.2 Hz, 2 H, CH_2), 2.35 (t, J = 7.2 Hz, 2 H, CH_2), 3.60 (s, 2 H, CH_2), 4.16 (q, J = 7.2 Hz, 2 H, OCH_2), 6.23 (d, J = 1.8 Hz, 1 H, CH), 7.28 (d, J = 1.8 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C = 13.82, 14.07 (CH_3), 22.22, 24.28, 32.30, 32.32 (CH_2), 60.98 (OCH_2), 111.61 (CH), 121.98 (C), 141.08 (CH), 142.94 (C), 169.63 (O=C–O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2962 (w), 2931 (w), 2860 (w, C–H), 1743 (s, O=C–O), 1462 (w), 1261 (s), 1230 (m), 1097 (s), 1026 (s), 800 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 210 (100) $[M]^+$, 181 (10), 166 (99), 137 (86). The exact molecular mass *m*/*z* = 210.1256 ± 2 ppm $[M]^+$ for $C_{12}H_{18}O_3$ was confirmed by HRMS (EI, 70 eV).

Compound 5m: This compound was produced from **4m** (0.13 g, 0.5 mmol) and TFA (0.46 mL, 6.0 mmol) in CH_2Cl_2 (10 mL), **5m** being isolated without further purification as a colourless oil (0.11 g, 100%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.88 (t, J = 7.2 Hz, 3 H, CH_3), 1.25 (t, J = 7.2 Hz, 3 H, OCH_2CH_3), 1.26–1.35 (m, 6 H, 3 × CH_2), 1.51 (quint, J = 7.2 Hz, 2 H, CH_2), 2.34 (t, J = 7.2 Hz, 2 H, CH_2), 3.60 (s, 2 H, CH_2), 4.16 (q, J = 7.2 Hz, 2 H, OCH_2), 6.23 (d, J = 1.8 Hz, 1 H, CH), 7.28 (d, J = 1.8 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C = 13.99, 14.07 (CH_3), 22.54, 24.59, 28.85, 30.14, 31.61, 32.29 (CH_2), 60.96 (OCH_2), 111.59 (CH), 122.01 (C), 141.07 (CH), 142.92(C), 169.60 (O=C–O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2958 (m), 2930 (s), 2857 (m, C–H), 1742 (s, O=C–O), 1463 (m), 1401 (w), 1370 (w), 1333 (w), 1264 (m), 1226 (m), 1211 (m), 1179 (m), 1160 (s), 1119 (w), 1099 (m), 1030 (m), 733 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 238 $[M]^+$ (94), 210 (23), 194 (11), 165 (100). The exact molecular mass *m*/*z* = 238.1569 ± 2 ppm $[M]^+$ for $C_{14}H_{22}O_3$ was confirmed by HRMS (EI, 70 eV).

Compound 5n: This compound was produced from **4n** (0.10 g, 0.3 mmol) and TFA (0.34 mL, 4.4 mmol) in CH_2Cl_2 (10 mL), **5n** being isolated without further purification as a yellow oil (0.09 g, 100%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.88 (t, J = 7.2 Hz, 3 H, CH_3), 1.19–1.28 (m, 13 H, 5 × H_2, OCH_2CH_3), 1.45 (t, J = 7.2 Hz, 2 H, CH_2), 2.34 (t, J = 7.2 Hz, 2 H, CH_2), 3.60 (s, 2 H, CH_2), 4.16 (q, J = 7.2 Hz, 2 H, OCH_2CH_3), 6.23 (d, J = 1.8 Hz, 1 H, CH), 7.28 (d, J = 1.8 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.05, 14.11 (CH_3), 22.63, 24.63, 29.22, 29.24, 29.41, 30.21, 31.84, 32.34 (CH_2), 61.00 (OCH_2), 111.63 (CH), 122.06 (C), 141.11 (CH), 142.93 (C), 169.64 (O=C–O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2957 (w), 2928 (s), 2856 (m, C–H), 1743 (s, O=C–O), 1463 (w), 1266 (w), 1215 (w), 1177 (m), 1159 (m), 1101 (w), 1032 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 266 (100) $[M]^+$, 193 (86). The exact molecular mass *m*/*z* = 266.1882 ± 2 ppm $[M]^+$ for $C_{16}H_{26}O_3$ was confirmed by HRMS (EI, 70 eV).

Compound 5o: This compound was produced from **4o** (0.12 g, 0.4 mmol) and TFA (0.38 mL, 5.0 mmol) in CH_2Cl_2 (10 mL), **5o** being isolated without further purification as a yellow oil (0.11 g, 100%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.88 (t, J = 7.2 Hz, 3 H, CH_3), 1.23–1.32 (m, 15 H, 6 × CH_2, CH_3), 1.51 (quint, J = 7.2 Hz, 2 H, CH_2), 2.34 (t, J = 7.2 Hz, 2 H, CH_2), 3.60 (s, 2 H, CH_2), 4.16 (q, J = 7.2 Hz, 2 H, OCH_2), 6.23 (d, J = 1.8 Hz, 1 H, CH), 7.28 (d, J = 1.8 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C = 14.02, 14.07 (CH_3), 22.60, 24.59, 29.20, 29.26, 29.42, 29.50, 30.23, 31.83, 32.29 (CH_2), 60.95 (OCH_2), 111.59 (CH), 122.01 (C), 141.07 (CH), 142.92 (C), 169.58 (O=C–O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2960 (m), 2927 (s), 2856 (m, C–H), 1744 (s, O=C–O), 1463 (m), 1262 (m), 1210 (w), 1175 (m), 1158 (m), 1100 (m), 1078 (m), 1031 (s), 799 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 280 (100) $[M]^+$, 207 (79). The exact molecular mass *m*/*z* = 280.2038 ± 2 ppm $[M]^+$ for $C_{17}H_{28}O_3$ was confirmed by HRMS (EI, 70 eV).

Compound 5p: This compound was produced from **4p** (0.15 g, 0.5 mmol) and TFA (0.5 mL, 6.0 mmol) in CH_2Cl_2 (15 mL), **5p** being isolated without further purification as a yellow oil (0.14 g, 100%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.88 (t, J = 7.2 Hz, 3 H, CH_3), 1.19–1.28 (m, 17 H, 7 × CH_2, CH_3), 1.51 (quint, J = 7.2 Hz, 2 H, CH_2), 2.34 (t, J = 7.2 Hz, 2 H, CH_2), 3.60 (s, 2 H, CH_2), 4.16 (q, J = 7.2 Hz, 2 H, OCH_2), 6.23 (d, J = 1.8 Hz, 1 H, CH), 7.28 (d, J = 1.8 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.04, 14.09 (CH_3), 22.63, 24.61, 29.22, 29.29, 29.41, 29.43, 29.57, 30.20, 31.85, 32.31 (CH_2), 60.96 (OCH_2), 111.60 (CH), 122.01 (C), 141.06 (CH), 142.93 (C), 169.58 (O=C–O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2959 (m), 2927 (s), 2955 (m, C–H), 1744 (s, O=C–O), 1463 (w), 1262 (m), 1226 (w), 1210 (w), 1159 (m), 1100 (m), 1031 (m), 800 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 294 (100) $[M]^+$, 221 (68). The exact molecular mass *m*/*z* = 294.2195 ± 2 ppm $[M]^+$ for $C_{18}H_{30}O_3$ was confirmed by HRMS (EI, 70 eV).

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Compound 5q: This compound was produced from **4q** (0.100 g, 0.293 mmol) in CH_2Cl_2 (10 mL), **5q** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 10:1) as a slight yellow oil (0.061 g, 76%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.19 (t, J = 7.2 Hz, 3 H, CH_3), 1.23–1.51 (m, 6 H, 3×CH_2), 1.70 (quint, J = 6.9 Hz, 2 H, CH_2), 2.29 (t, J = 7.5 Hz, 2 H, CH_2), 3.46 (t, J = 6.6 Hz, 2 H, CH_2–Cl), 3.60 (s, 2 H, CH_2), 4.10 (q, J = 7.2 Hz, 2 H, OCH_2), 6.16 (d, J = 1.8 Hz, 1 H, CH), 7.22 (d, J = 1.8 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.15 (CH_3), 24.50, 26.65, 28.39, 29.98, 32.35, 32.50 (CH_2), 45.06 (CH_2–Cl), 61.07 (OCH_2), 111.59 (CH), 121.80 (C), 141.23 (CH), 143.06 (C), 169.64 (O=C–O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2983 (w), 2934 (s), 2859 (m, C–H), 1742 (s, O=C–O), 1510 (w), 1461 (m), 1444 (m), 1400 (w), 1369 (w), 1335 (w), 1303 (w), 1269 (m), 1204 (m), 1164 (s), 1118 (m), 1092 (m), 1031 (m), 894 (w), 736 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 272 [*M*]$^+$ (17), 258 (4), 199 (25), 184 (4), 168 (14), 148 (10), 121 (5), 107 (9), 95 (100).

Compound 5r: This compound was produced from **4r** (0.20 g, 0.88 mmol) and TFA (0.9 mL, 11.5 mmol) in CH_2Cl_2 (10 mL), **5r** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a yellow oil (0.13 g, 76%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.27 (t, J = 7.2 Hz, 3 H, CH_3), 1.68–1.79 (m, 1 H, CH_2), 1.81–1.94 (m, 1 H, CH_2), 1.97–2.08 (m, 1 H, CH_2), 2.09–2.18 (m, 1 H, CH_2), 2.37–2.55 (m, 2 H, CH_2), 3.69 (t, J = 7.2 Hz, 1 H, CH), 4.19 (q, J = 7.2 Hz, 2 H, O*C*H_2CH$_3$), 6.22 (d, J = 1.8 Hz, 1 H, CH), 7.30 (d, J = 1.8 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.24 (CH_3), 21.12, 21.90, 27.16 (CH_2), 40.261 (CH), 60.98 (OCH_2), 110.35 (CH), 119.13 (C), 141.53 (CH), 146.54 (C), 172.74 (O=C–O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2963 (s), 2931 (m), 2909 (m), 2856 (w, C–H), 1740 (m, O=C–O), 1446 (w), 1413 (w), 1261 (s), 1224 (w), 1176 (m), 1151 (m), 1096 (s), 1054 (s), 1024 (s), 865 (m), 798 (s), 703 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 194 [*M*]$^+$ (16), 121(100).

Compound 5t: This compound was produced from **4t** (0.10 g, 0.4 mmol) and TFA (0.42 mL, 5.4 mmol) in CH_2Cl_2 (10 mL), **5t** being isolated without further purification as a colourless oil (0.09 g, 100%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.25 (t, J = 7.2 Hz, 3 H, CH_3), 1.53–1.59 (m, 2 H, CH_2), 1.71–1.80 (m, 1 H, CH_2), 1.84–1.89 (m, 2 H, CH_2), 2.22–2.27 (m, 1 H, CH_2), 2.50–2.53 (m, 2 H, CH_2), 3.90 (t, J = 4.2 Hz, 1 H, CH), 4.19 (dq, J = 7.2, 2.9 Hz, 2 H, OCH_2), 6.16 (d, J = 1.5 Hz, 1 H, CH), 7.18 (d, J = 1.5 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 75 Hz): δ_C = 14.24 (CH_3), 25.58, 26.91, 28.22, 29.57 (CH_2), 45.29 (CH), 60.86 (OCH_2), 113.27 (CH), 122.75 (C), 139,74 (CH), 148.89 (C), 172.31 (O=C–O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2931 (m), 2857 (w, C–H), 1736 (s, O=C–O), 1707 (m), 1449 (m), 1371 (w), 1307 (w), 1259 (m), 1239 (m), 1222 (m), 1191 (m), 1157 (m), 1104 (m), 1080 (m), 1026 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 208 [*M*]$^+$ (13), 194 (12), 162 (8), 135 (100). The exact molecular mass *m*/*z* = 208.1099 ± 2 ppm [*M*]$^+$ for $C_{12}H_{16}O_3$ was confirmed by HRMS (EI, 70 eV).

Compound 5u: This compound was produced from **4u** (0.15 g, 0.6 mmol) and TFA (0.59 mL, 7.7 mmol) in CH_2Cl_2 (5 mL), **5u** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 20:1) as a colourless oil (0.11 g, 84%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.26 (t, J = 7.2 Hz, 3 H, CH_3), 1.30–1.49 (m, 2 H, CH_2), 1.52–1.71 (m, 4 H, 2×CH_2), 1.93–2.03 (m, 1 H, CH_2), 2.12–2.21 (m, 1 H, CH_2), 2.47–2.56 (m, 1 H, CH_2), 2.65–2.74 (m, 1 H, CH_2), 3.87 (dd, J = 11.1, 3.9 Hz, 1 H, CH), 4.21 (q, J = 7.2 Hz, 2 H, OCH_2), 6.14 (d, J = 1.8 Hz, 1 H, CH), 7.25 (d, J = 1.8 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.19 (CH_3), 23.85, 24.85, 25.26, 28.90, 29.60 (CH_2), 43.80 (CH), 60.87 (OCH_2), 112.67 (CH), 120.04 (C), 140.41 (CH), 147.38 (C), 172.57 (O=C–O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2928 (s), 2856 (w, C–H), 1739 (s, O=C–O), 1449 (m), 1370 (w), 1302 (m), 1265 (m), 1229 (m), 1176 (s), 1159 (m), 1097 (m), 1029 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 222 [*M*]$^+$ (9), 207 (54), 193 (8), 148 (100).

Compound 5v: This compound was produced from (*E*)-**4v** (0.40 g, 1.3 mmol) and TFA (1.3 mL, 17.0 mmol) in CH_2Cl_2 (5 mL), **5v** being isolated without further purification as an orange oil (0.36 g, 100%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.98–1.13 (m, 2 H, CH_2), 1.21 (t, J = 7.2 Hz, 3 H, CH_3), 1.15–1.29 (m, 6 H, 3×H_2), 1.31–1.46 (m, 4 H, 2×H_2), 1.57–1.66 (m, 2 H, CH_2), 1.92–2.03 (m, 1 H, CH_2), 2.06–2.15 (m, 1 H, CH_2), 2.38–2.53 (m, 2 H, CH_2), 3.84 (dd, J = 9.4, 5.9 Hz, 1 H, CH), 4.07–4.17 (dq, J = 7.2, 3.6 Hz, 2 H, OCH_2), 6.21 (d, J = 1.8 Hz, 1 H, CH), 7.32 (d, J = 1.8 Hz, 1 H, CH) ppm. ^{13} C NMR ($CDCl_3$, 75 MHz): δ_C = 13.99 (CH_3), 21.11, 22.07, 22.13, 23.67, 23.84, 23.91, 24.87, 27.12, 28,49 (CH_2), 40.03 (CH), 60.62 (OCH_2), 110.62 (CH), 121.28 (C), 141.42 (CH), 146.99 (C), 172.15 (O=C–O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2934 (s), 2860 (s, C–H), 1740 (s, O=C–O), 1512 (w), 1465 (s), 1445 (s), 1391 (w), 1369 (m), 1346 (w), 1260 (s), 1241 (s), 1221 (s), 1172 (s), 1151 (s), 1098 (s), 1030 (s), 891 (w), 804 (s), 738 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 278 [*M*]$^+$ (40), 205 (100). The exact molecular mass *m*/*z* = 278.1882 ± 2 ppm [*M*]$^+$ for $C_{17}H_{26}O_3$ was confirmed by HRMS (EI, 70 eV).

Compound 5w: This compound was produced from **4w** (0.08 g, 0.31 mmol) and TFA (0.31 mL, 4.1 mmol) in CH_2Cl_2 (5 mL), **5w** being isolated without further purification as a yellow oil (0.07 g, 100%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.15 (d, J = 6.9 Hz, 3 H, CH_3), 1.28 (t, J = 7.2 Hz, 3 H, OCH$_2$C*H*$_3$), 1.29–1.38 (m, 1 H, CH_2), 1.94–2.05 (m, 2 H, CH_2), 2.15–2.20 (m, 1 H, CH_2), 2.73 (sextet, J = 7.2 Hz, 1 H, CH), 3.68 (t, J = 6.3 Hz, 1 H, CH), 4.19 (q, J = 7.2 Hz, 2 H, O*C*H_2CH$_3$), 6.27 (d, J = 1.8 Hz, 1 H, CH), 7.29 (dd, J = 1.8, 0.9 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C = 14.24, 20.67 (CH_3), 25.87 (CH_2), 27.65 (CH), 30.41 (CH_2), 40.84 (CH), 60.98 (OCH_2), 109.10 (CH), 124.55 (C), 141.64 (CH), 146.03 (C), 172.82 (O=C–O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2959 (m), 2930 (s), 2856 (w, C–H), 1737 (s, O=C–O), 1453 (m), 1372 (w), 1310 (w), 1286 (w), 1260 (m), 1228 (w), 1179 (s), 1142 (m), 1122 (w), 1097 (m), 1032 (m), 736 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 208 [*M*]$^+$ (12), 125 (100). The exact molecular mass *m*/*z* = 208.1099 ± 2 ppm [*M*]$^+$ for $C_{12}H_{16}O_3$ was confirmed by HRMS (EI, 70 eV).

Compound 5x: This compound was produced from **4x** (0.100 g, 0.35 mmol) in CH_2Cl_2 (10 mL), **5x** being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 50:1) as a yellow oil (0.087 g, 98%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.15–2.48 (m, 2 H, CH_2), 2.54–2.82 (m, 2 H, CH_2), 2.94–3.04, 3.17–3.27 (dm, 1 H, *CH*–Ph), 3.74, 3.75 (ds, 3 H, OCH_3), 3.80–4.02 (dm, 1 H, CH), 6.24–6.27 (dd, J = 6.0, 1.8 Hz, 1 H, CH), 7.21–7.36 (m, 6 H, CH, 5×CH from Ph) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C = 29.90, 30.32 (1×CH), 33.71, 34.81 (1×CH_2), 38.07, 39.66 (1×*CH*–Ph), 40.96, 42.02 (1×H), 51.53, 52.43 (1×OCH_3), 110.43 (CH), 119.42, 119.61 (1×C), 126.64, 126.78 (1×CH from Ph), 127.04, 127.12 (2×CH from Ph), 128.68, 128.74 (2×CH from Ph), 142.21, 142.29 (1×CH), 144.97, 145.22 (1×C), 146.04, 146.28 (1×C), 172.83, 172.88 (1×O=C–O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 3062 (w), 3029 (w), 3002 (w), 2952 (m), 2927 (m), 2853 (w, C–H), 1740 (s, O=C–O), 1685 (w), 1608 (w), 1499 (m), 1448 (m), 1439 (m), 1354 (w), 1313 (w), 1282 (m), 1252 (s), 1230 (s), 1200 (s), 1169 (s), 1103 (w), 1975 (w), 1038 (m), 1016 (m), 844 (s), 762 (m), 738 (m), 701 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 256 [*M*]$^+$ (66), 197 (1009, 179 (8), 170 (7), 165 (6), 151 (29), 119 (9), 104 (27), 91 (43), 81 (17), 59 (11). The exact molecular mass *m*/*z* = 256.1099 ± 2 ppm [*M*]$^+$ for $C_{16}H_{16}O_3$ was confirmed by HRMS (EI, 70 eV).

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Compound 5y: A solution of **4y** (0.130 g, 0.71 mmol) in CH_2Cl_2 (100 mL) was heated at for 5 h and the solvent was removed in vacuo. The residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc, 20:1 to 5:1) to give **5y** as a yellow oil (0.105 g, 98%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.54–2.71 (m, 2 H, CH_2), 3.91 (t, J = 9.2 Hz, 1 H, CH), 4.32–4.40 (m, 1 H, OCH_2), 4.46–4.52 (m, 1 H, OCH_2), 6.31–6.33 (m, 1 H, CH), 6.36 (dd, J = 3.3, 1.8 Hz, 1 H, CH), 7.39 (dd, J = 1.8, 0.9 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C = 28.69 (CH_2), 39.66 (CH), 67.08 (OCH_2), 107.80, 110.66, 142.64 (CH), 149.36 (C), 175.18 (O=C–O) ppm. IR (neat; cm^{-1}): $\tilde{\nu}$ = 2917 (w, C–H), 1771 (s, O=C–O), 1506 (w), 1483 (w), 1455 (w), 1376 (m), 1262 (w), 1241 (w), 1203 (m), 1154 (s), 1097 (w), 1072 (w), 1023 (m), 951 (m), 885 (w), 742 (m), 689 (w) cm^{-1}. MS (EI, 70 eV): m/z (%) = 152 $[M]^+$ (29), 108 (73), 94 (21), 80 (100), 67 (17). The exact molecular mass m/z = 152.0473 ± 2 ppm $[M]^+$ for $C_8H_8O_3$ was confirmed by HRMS (EI, 70 eV).

Crystal Structure Determination: The intensity data for the compounds were collected on a Nonius Kappa CCD diffractometer, using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects, but not for absorption effects.[25,26] The structures were solved by direct methods (SHELXS)[27] and refined by full-matrix least-squares techniques against Fo^2 (SHELXL-97).[28] For the C3 group of both symmetry-independent molecules of **4r** the hydrogen atoms were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal Data for 4g:[29] $C_9H_{14}O_4$, Mr = 186.20 g mol^{-1}, colourless prism, size 0.03 × 0.03 × 0.03 mm, orthorhombic, space group *Pbca*, a = 13.4002(2), b = 8.0370(4), c = 17.9872(6) Å, V = 1937.1(1) Å^3, T = –90 °C, Z = 8, $\rho_{calcd.}$ = 1.277 g cm^{-3}, μ(Mo-K_α) = 1.0 cm^{-1}, F(000) = 800, 3998 reflections in h(–17/17), k(–10/10), l(–23/23), measured in the range 3.96° ≤ Θ ≤ 27.45°, completeness Θ_{max} = 99.4%, 2197 independent reflections, R_{int} = 0.021, 1696 reflections with $F_o > 4\sigma(F_o)$, 118 parameters, 0 restraints, $R1_{obs}$ = 0.044, wR^2_{obs} = 0.113, $R1_{all}$ = 0.061, wR^2_{all} = 0.124, GOOF = 1.033, largest difference peak and hole: 0.231/–0.184 e Å^{-3}.

Crystal Data for 4r:[29] $C_{12}H_{18}O_4$, Mr = 226.26 g mol^{-1}, colourless prism, size 0.03 × 0.03 × 0.02 mm, triclinic, space group $P\bar{1}$, a = 8.8743(2), b = 10.1470(3), c = 13.5326(4) Å, α = 101.701(1), β = 95.436(1), γ = 91.924(1)°, V = 1186.14(6) Å^3, T = –90 °C, Z = 4, $\rho_{calcd.}$ = 1.267 g cm^{-3}, μ(Mo-K_α) = 0.94 cm^{-1}, F(000) = 488, 8710 reflections in h(–11/11), k(–13/12), l(–17/16), measured in the range 2.05° ≤ Θ ≤ 27.46°, completeness Θ_{max} = 99.2%, 5390 independent reflections, R_{int} = 0.020, 3883 reflections with $F_o > 4\sigma(F_o)$, 297 parameters, 0 restraints, $R1_{obs}$ = 0.056, wR^2_{obs} = 0.138, $R1_{all}$ = 0.083, wR^2_{all} = 0.155, GOOF = 1.027, largest difference peak and hole: 0.523/–0.304 e Å^{-3}.

Crystal Data for 4v:[29] $C_{18}H_{28}O_4 \cdot 1/6\,C_6H_{14}$, Mr = 322.41 g mol^{-1}, colourless prism, size 0.03 × 0.03 × 0.02 mm, hexagonal, space group *P*6(5), a = 21.1201(4), b = 21.1201(4), c = 6.7753(2) Å, V = 2617.3(1) Å^3, T = –90 °C, Z = 6, $\rho_{calcd.}$ = 1.220 g cm^{-3}, μ(Mo-K_α) = 0.84 cm^{-1}, F(000) = 1044, 6661 reflections in h(–27/27), k(–23/21), l(–6/8), measured in the range 1.93° ≤ Θ ≤ 27.46°, completeness Θ_{max} = 99.9%, 3574 independent reflections, R_{int} = 0.036, 2704 reflections with $F_o > 4\sigma(F_o)$, 208 parameters, 1 restraints, $R1_{obs}$ = 0.056, wR^2_{obs} = 0.140, $R1_{all}$ = 0.082, wR^2_{all} = 0.155, GOOF = 1.054, Flack parameter 0.2(15) (the absolute structures could not be determined by Mo-radiation), largest difference peak and hole: 0.331/–0.396 e Å^{-3}.

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