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

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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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zations of 1,3-bis-silyl enol ethers with 1-chloro-2,2-dimethoxyethane.^[18] Here we wish to report studies related to

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 TiCl₄-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 cycli-

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 Me₃SiOTf-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. Me₃SiOTf, CH₂Cl₂, $-78 \rightarrow 20$ °C, *b*) 2.0 equiv. DBU, THF, 20 °C, *c*) TFA, CH₂Cl₂, 20 °C.

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3,4,5	\mathbb{R}^1	\mathbb{R}^2	% (3) ^[a]	% (4) ^[a]	% (5) ^[a]	δ [ppm] ^[b]	δ [ppm] ^[c]	$E/Z^{[d]}$
a	OMe	Н	72	86	80	5.38	168.4	> 98:2
b	OEt	Н	66	74	100	5.37	168.5	> 98:2
c	O <i>i</i> Pr	Н	70	80	61	5.35	_	> 98:2
d	$O(CH_2)_2OMe$	Н	67	68	100	5.43	167.9	> 98:2
e	OBn	Н	51	94	100	5.44	168.3	> 98:2
f	Ph	Н	51	_	70	_	_	_
g	OMe	Me	63	90	84	5.33	168.2	> 98:2
ĥ	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	nPr	87	79	100	5.35	167.6	> 98:2
1	OEt	<i>n</i> Bu	85	73	100	5.32	167.6	> 98:2
m	OEt	nHex	88	76	100	5.31	167.6	> 98:2
n	OEt	nOct	53	97	100	5.31	168.0	> 98:2
0	OEt	<i>n</i> Non	79	87	100	5.31	167.8	> 98:2
р	OEt	nDec	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 (¹H NMR, CDCl₃) of the hydrogen atom of the exocyclic double bond of 4. [c] Chemical shift (¹C NMR, CDCl₃) 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-silvl 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-silvl 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 3gq with very good diastereoselectivity, while treatment of 3gq with DBU afforded the 2-alkylidenetetrahydrofurans 4gq. 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 41 has been reported by us previously.^[18] Treatment of 4g-h and 4j-q with TFA afforded the substituted furans 5gh 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 sidechain. For some derivatives of 3, a small amount of 1,3dicarbonyl compound (derived from hydrolysis of the 1,3bis-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 CH₂Cl₂ 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 2alkylidenetetrahydrofurans **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 esterderived 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-

erally showed a characteristic carbonyl ¹³C 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 **4**i.

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 1,3bis-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 1chloro-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 cisconfigured 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-silvl 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. Me₃SiOTf, CH₂Cl₂, $-78 \rightarrow 20$ °C, 49%, *b*) 2.0 equiv. DBU, THF, 20 °C, 77%, *c*) TFA, CH₂Cl₂, 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 1,2diastereoselectivity. 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 5,8bicyclic 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

Table 2. Products and yields



[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).

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-alkyl-



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).

idenetetrahydrofurans 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.



Scheme 4. Synthesis of **4y** and **5y**. *a*) 0.5 equiv. Me₃SiOTf, CH₂Cl₂, $-78 \rightarrow 20$ °C, 97%. *b*) 2.0 equiv. DBU, THF, 20 °C, 92%. *c*) reflux in CH₂Cl₂, 98%.

The reaction between 2,4-bis(trimethylsilyloxy)penta-1,3diene (1z), prepared from acetylacetone, and 1-chloro-2,2dimethoxyethane (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. Me₃SiOTf, CH₂Cl₂, $-78 \rightarrow 20$ °C, *b*) 2.0 equiv. DBU, THF, 20 °C.

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: Me₃SiOTf (0.5 equiv.) was added at -78 °C to a CH₂Cl₂ 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 NaHCO₃ 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 Na₂SO₄ 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 Me₃SiOTf (2.778 g, 12.5 mmol) in CH₂Cl₂ (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%). ¹H NMR (CDCl₃, 300 MHz, 5% enol form): δ = 2.88 (d, *J* = 6.0 Hz, 2 H, CH₂), 3.41 (s, 3 H, OCH₃), 3.51 (s, 2 H, CH₂), 3.62 (dd, *J* = 3.9, 3.3 Hz, 2 H, CH₂Cl), 3.75 (s, 3 H, OCH₃), 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 Me₃SiOTf (1.111 g, 5.0 mmol) in CH₂Cl₂ (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%). ¹H NMR (CDCl₃, 300 MHz, 5% enol form): δ = 1.29 (t, J = 7.2 Hz, 3 H, OCH₂CH₃), 2.88 (d, J = 6.0 Hz, 2 H, CH₂), 3.41 (s, 3 H, OCH₃), 3.49 (s, 2 H, CH₂), 3.62 (dd, J = 4.5, 3.3 Hz, 2 H, CH₂Cl), 3.94 (m, 1 H, CH), 4.20 (q, J = 7.2 Hz, 2 H, OCH₂CH₃), 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 Me₃SiOTf (1.111 g, 5.0 mmol in CH₂Cl₂ (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%). ¹H NMR (CDCl₃, 300 MHz, 5% enol form): δ = 1.27 (d, *J* = 6.3 Hz, 6 H, OCH(CH₃)₂), 2.88 (d, *J* = 6.3 Hz, 2 H, CH₂), 3.41 (s, 3 H, OCH₃), 3.45 (s, 2 H, CH₂), 3.64 (dd, *J* = 4.5, 3.3 Hz, 2 H, CH₂Cl), 3.93 (m, 1 H, CH), 5.08 (sept, *J* = 6.3 Hz, 1 H, OCH(CH₃)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 Me₃SiOTf (1.111 g, 5.0 mmol) in CH₂Cl₂ (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%). ¹H NMR (CDCl₃, 600 MHz, 5% enol form): δ = 2.83 (d, J = 6.0 Hz, 2 H, CH₂), 3.39 (s, 3 H, OCH₂CH₂OCH₃), 3.41 (s, 3 H, OCH₃), 3.54 (s, 2 H, CH₂), 3.59–3.65 (m, 4 H, OCH₂-CH₂OCH₃, CH₂Cl), 3.95 (m, 1 H, CH), 4.32 (t, J = 6.0 Hz, 2 H, OCH₂CH₂OCH₃), 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 Me₃SiOTf (1.111 g, 5.0 mmol) in CH₂Cl₂ (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%). ¹H NMR (CDCl₃, 300 MHz, 5% enol form): δ = 2.85 (d, J = 7.2 Hz, 2 H, CH₂), 3.37 (s, 3 H, OCH₃), 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, OCH₂Ph), 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. ¹³C NMR (CDCl₃, 75 MHz): $\delta_{\rm C}$ = 44.69 (CH₂), 45.17 (CH₂Cl), 49.85 (CH₂), 57.58 (OCH₃), 67.08 (OCH₂Ph), 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): $\tilde{v} = 2957$ (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 Me₃SiOTf (1.111 g, 5.0 mmol) in CH₂Cl₂ (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%). ¹H NMR (CDCl₃, 300 MHz, 95% enol form, analysis for enol): $\delta = 2.76$ (d, J = 7.2 Hz, 2 H, CH₂), 3.45 (s, 3 H, OCH₃), 3.63 (dd, *J* = 10.8, 4.5 Hz, 1 H, CH₂Cl), 3.71 (dd, *J* = 10.8, 4.5 Hz, 1 H, CH₂Cl), 3.98 (m, 1 H, CH), 6.24 (s, 1 H, CH from enol), 7.43–7.56 (m, 3 H, $3 \times$ 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. ¹³C NMR $(CDCl_3, 75 \text{ MHz}): \delta_C = 41.83 (CH_2), 45.16 (CH_2Cl), 57.54 (OCH_3),$ 77.06 (CH), 97.21 (CH=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)): $\tilde{v} = 2925$ (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). C₁₃H₁₅O₃Cl (254.713): C 61.39, H 5.94; found C 61.42, H 6.71. The exact molecular mass m/z = $254.0710 \pm 2 \text{ ppm } [M]^+$ for C₁₃H₁₅O₃Cl 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 Me₃SiOTf (1.111 g, 5.0 mmol) in CH₂Cl₂ (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%). ¹H NMR (CDCl₃, 300 MHz, 5% enol form, contains a small amount of starting material): $\delta = 1.08$ (d, J = 6.9 Hz, 3 H, CH₃), 3.11 (m, 1 H, CH), 3.35 (s, 3 H, OCH₃), 3.40–3.61 (m, 4 H, CH₂, CH₂Cl), 3.74 (s, 3 H, OCH₃), 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. ¹³C NMR (CDCl₃, 75 MHz): $\delta_{\rm C}$ = 13.43 (CH₃), 42.80 (CH₂), 47.30 (CH), 49.68 (CH₂Cl), 51.81, 57.40 (OCH₃), 81.71 (CH), 167.14 (O–C=O), 204.98 (C=O) ppm. IR (neat; cm⁻¹): $\tilde{v} =$ 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 Me₃SiOTf (1.111 g, 5.0 mmol) in CH₂Cl₂ (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%). ¹H NMR (CDCl₃, 300 MHz, 11% enol form): $\delta =$ 0.91 (t, J = 7.2 Hz, 3 H, CH₃), 1.28 (t, J = 7.2 Hz, 3 H, OCH₂CH₃), 1.49-1.72 (m, 2 H, CH₂), 2.99-3.04 (m, 1 H, CH), 3.34 (s, 3 H, OCH₃), 3.43–3.59 (m, 4 H, CH₂, CH₂Cl), 3.82 (m, 1 H, CH), 4.20 $(q, J = 7.2 \text{ Hz}, 2 \text{ H}, \text{ OC}H_2\text{C}H_3), 5.09 \text{ (s, 1 H, CH=C from enol})$ form), 12.19 (s, 1 H, OH from enol form) ppm. ¹³C NMR (CDCl₃, 75 MHz): $\delta_{\rm C}$ = 11.12, 13.86 (CH₃), 21.04, 43.16 (CH₂), 51.62 (CH₂Cl), 54.55 (CH), 57.69 (OCH₃), 60.87 (OCH₂CH₃), 81.30 (CH), 166.57 (O=C–O), 205.13 (C=O) ppm. IR (neat; cm⁻¹): $\tilde{v} =$ 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). C₁₁H₁₉O₄Cl (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 Me₃SiOTf (1.111 g, 5.0 mmol) in CH₂Cl₂ (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%). ¹H NMR (CDCl₃, 300 MHz, 25% enol form, contains ca. 40% of starting material): $\delta = 3.39$ (s, 3 H, OCH₃), 3.44 (s, 3 H, OCH₃), 3.45 (s, 3 H, OCH₃), 3.53 (s, 2 H, CH₂), 3.62-3.73 (m, 2 H, CH₂Cl), 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. ¹³C NMR (CDCl₃, 75 MHz): $\delta_{\rm C}$ = 41.54 (CH₂), 46.09 (CH₂Cl), 51.97, 58.13, 60.35 (OCH₃), 82.21, 84.92 (CH), 167.36 (O=C-O), 205.12 (C=O) ppm. IR (neat; cm⁻¹): $\tilde{v} = 2992$ (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). C9H15O5Cl (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 Me₃SiOTf (1.111 g, 5.0 mmol) in CH₂Cl₂ (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%). ¹H NMR (CDCl₃, 300 MHz, 12% enol form): δ = 1.28 (t, J = 7.2 Hz, 3 H, CH₃), 2.20–2.41(m, 2 H, CH₂), 3.12 –3.20 (m, 1 H, CH), 3.35 (s, 3 H, OCH₃), 3.52 (s, 2 H, CH₂), 3.55-3.63 (m, 2 H, CH₂Cl), 3.79-3.84 (m, 1 H, CH), 4.19 (q, J = 7.2 Hz, 2 H, OCH₂), 5.00-5.22 (m, 2 H, CH₂=CH), 5.65-5.79 (m, 1 H, CH=CH₂), 12.22 (s, 1 H, OH from enol form) ppm. IR (neat; cm⁻¹): $\tilde{v} = 2983$ (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 Me₃SiOTf (1.111 g, 5.0 mmol) in CH₂Cl₂ (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%). ¹H NMR (CDCl₃, 300 MHz, 24% enol form): δ = 0.91 (t, J = 7.2 Hz, 3 H, CH₃), 1.27 (t, J = 7.2 Hz, 3 H,

OCH₂CH₃), 1.23–1.35 (m, 2 H, CH₂), 1.58–1.66 (m, 2 H, CH₂), 3.08 (m, 1 H, CH), 3.34 (s, 3 H, OCH₃), 3.43 (s, 2 H, CH₂), 3.53–3.60 (m, 2 H, CH₂Cl), 3.81 (m, 1 H, CH), 4.20 (q, J = 7.2 Hz, 2 H, OCH₂), 5.09 (s, 1 H, CH=C from enol form), 12.20 (s, 1 H, OH from enol form) ppm. ¹³C NMR (CDCl₃, 150 MHz): $\delta_{\rm C} = 14.15$ (CH₃), 20.25, 30.38 (CH₂), 43.40 (CH₂Cl), 51.83 (CH₂), 53.27 (CH), 57.93 (OCH₃), 61.11 (OCH₂), 81.84 (CH), 166.82 (O=C–O), 205.25 (C=O) ppm. IR (neat; cm⁻¹): $\tilde{v} = 2962$ (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). C₁₂H₂₁O₄Cl (264.749): C 54.44, H 8.00; found C 55.35, H 8.43.

Compound 31: This compound was produced from 2 (1.37 mL, 12.0 mmol), 11 (3.306 g, 10.0 mmol) and Me₃SiOTf (1.111 g, 5.0 mmol) in CH₂Cl₂ (100 mL), 31 being isolated after chromatography (silica gel, n-hexane/EtOAc, 100:1 to 1:1) as a dark yellow oil (2.38 g, 85%). ¹H NMR (CDCl₃, 300 MHz, 24% enol form): δ = 0.88 (t, J = 6.9 Hz, 3 H, CH₃), 1.28 (t, J = 7.2 Hz, 3 H, OCH₂CH₃), 1.22–1.35 (m, 2 H, CH₂), 1.37–1.41 (m, 2 H, CH₂), 1.58–1.69 (m, 2 H, CH₂), 3.02–3.10 (m, 1 H, CH), 3.34 (s, 3 H, OCH₃), 3.43 (s, 2 H, CH₂), 3.52–3.57 (m, 2 H, CH₂Cl), 3.81 (m, 1 H, CH), 4.20 (q, J = 7.2 Hz, 2 H, OCH₂), 5.08 (s, 1 H, CH=C from enol form), 12.20 (s, 1 H, OH from enol form) ppm. ¹³C NMR (CDCl₃, 150 MHz): $\delta_{\rm C}$ = 14.15, 14.77 (CH₃), 22.35, 27.90, 29.26 (CH₂), 43.91 (CH₂Cl), 51.79 (CH₂), 53.38 (CH), 57.88 (OCH₃), 61.27 (OCH₂), 81.81 (CH), 166.80 (O=C-O), 205.18 (C=O) ppm. IR (neat; cm⁻¹): $\tilde{v} = 2959$ (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 Me₃SiOTf (1.111 g, 5.0 mmol) in CH₂Cl₂ (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%). ¹H NMR (CDCl₃, 300 MHz, 11% enol form): δ = 0.87 (t, J = 6.9 Hz, 3 H, CH₃), 1.28 (t, J = 7.2 Hz, 3 H, OCH₂CH₃), 1.25–1.32 (m, 6 H, 3×H₂), 1.33–1.48 (m, 2 H,CH₂), 1.55-1.68 (m, 2 H, CH₂), 3.02-3.10 (m, 1 H, CH), 3.34 (s, 3 H, OCH₃), 3.43 (s, 2 H, CH₂), 3.49–3.56 (m, 2 H, CH₂Cl), 3.81 (m, 1 H, CH), 4.20 (q, J = 7.2 Hz, 2 H, OCH₂), 5.08 (s, 1 H, CH=C from enol form), 12.20 (s, 1 H, OH from enol form) ppm. ¹³C NMR (CDCl₃, 150 MHz): $\delta_{\rm C}$ = 14.26, 14.30 (CH₃), 22.60, 27.00, 28.36, 29.24, 31.69 (CH₂), 43.50 (CH₂Cl), 51.97 (CH₂), 53.54 (CH), 58.77 (OCH₃), 61.22 (OCH₂), 81.93 (CH), 166.91 (O=C-O), 205.27 (C=O) ppm. IR (neat; cm⁻¹): $\tilde{v} = 2956$ (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 Me₃SiOTf (1.111 g, 5.0 mmol), in CH₂Cl₂ (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%). ¹H NMR (CDCl₃, 300 MHz, 25% enol form): δ = 0.88 (t, *J* = 6.8 Hz, 3 H, CH₃), 1.25–1.32 (m, 17 H, 7×H₂, CH₃), 3.05 (m, 1 H, CH), 3.34 (s, 3 H, OCH₃), 3.49–3.58 (m, 4 H, CH₂, CH₂Cl), 3.76–3.84 (m, 1 H, CH), 4.20 (q, *J* = 7.2 Hz, 2 H, OCH₂), 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{v} = 2955 (m), 2928 (s), 2856 (m, C–H), 1746 (s, O=C–O), 1716 (s, C=O), 1647 (m, C=C from enol),

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 30: This compound was produced from 2 (1.37 mL, 12.0 mmol), 10 (4.01 g, 10.0 mmol) and Me₃SiOTf (1.111 g, 5.0 mmol) in CH₂Cl₂ (100 mL), **30** 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 (CDCl₃, 300 MHz, 15% enol form): δ = 0.88 (t, J = 6.9 Hz, 3 H, CH₃), 1.20–1.34 (m, 15 H, $6 \times$ CH₂, CH₃), 1.37-1.48 (m, 2 H, CH₂), 1.59-1.68 (m, 2 H, CH₂), 3.01-3.10 (m, 1 H, CH), 3.33 (s, 3 H, OCH₃), 3.42 (s, 2 H, CH₂), 3.47-3.56 (m, 2 H, CH₂Cl), 3.81 (m, 1 H, CH), 4.20 (q, J = 7.2 Hz, 2 H, OCH₂), 5.07 (s, 1 H, CH=C from enol form), 12.23 (s, 1 H, OH from enol form) ppm. ¹³C NMR (CDCl₃, 75 MHz): $\delta_{\rm C}$ = 13.77, 13.89 (CH₃), 22.36, 26.67, 27.95, 28.97, 29.02, 29.18, 29.42, 31.55 (CH₂), 43.11 (CH₂Cl), 51.49 (CH₂), 53.15 (CH), 57.61 (OCH₃), 60.77 (OCH₂), 81.57 (CH), 166.48 (O=C-O), 205.13 (C=O) ppm. IR (neat; cm⁻¹): $\tilde{v} = 2927$ (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). C₁₈H₃₃O₄Cl (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 Me₃SiOTf (1.111 g, 5.0 mmol) in CH₂Cl₂ (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 (CDCl₃, 300 MHz, 16% of enol form): $\delta = 0.89$ (t, J = 6.9 Hz, 3 H, CH₃), 1.20–1.38 (m, 19 H, 8×CH₂) CH₃), 1.58–1.65 (m, 2 H, CH₂), 3.02–3.09 (m, 1 H, CH), 3.33 (s, 3 H, OCH₃), 3.42 (s, 2 H, CH₂), 3.43-3.59 (m, 2 H, CH₂Cl), 3.81 (m, 1 H, CH), 4.20 (q, J = 7.2 Hz, 2 H, OCH₂), 5.07 (s, 1 H, CH=C from enol form), 12.23 (s, 1 H, OH from enol form) ppm. ¹³C NMR (CDCl₃, 75 MHz): $\delta_{\rm C}$ = 13.87, 13.90 (CH₃), 22.46, 26.75, 27.52, 28.05, 29.09, 29.32, 29.34, 29.51, 31.67 (CH₂), 43.18 (CH₂Cl), 51.64 (CH₂), 53.24 (CH), 57.72 (OCH₃), 60.89 (OCH₂), 81.65 (CH), 166.58 (O=C-O), 205.29 (C=O) ppm. IR (neat; cm⁻¹): ṽ = 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 Me₃SiOTf (0.111 g, 0.5 mmol) in CH₂Cl₂ (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 (CDCl₃, 300 MHz, 15% enol form): δ = 1.29 (t, J = 7.2 Hz, 3 H, CH₃) 1.26–1.33 (m, 2 H, CH₂), 1.35–1.45 (m, 4 H, 2×CH₂), 1.58–1.69 (m, 2 H, CH₂), 1.70–1.76 (m, 2 H, CH₂), 3.01–3.11 (m, 1 H, CH), 3.34 (s, 3 H, OCH₃), 3.43 (s, 2 H, CH₂), 3.49–3.59 (m, 4 H, $2 \times$ CH₂–Cl), 3.82 (dd, J = 13.2, 4.2 Hz, 1 H, CH), 4.20 (q, J = 7.2 Hz, 2 H, OCH₂), 5.08 (s, 1 H, CH=C from enol form), 12.21 (s, 1 H, OH from enol form) ppm. ¹³C NMR (CDCl₃, 75 MHz): $\delta_{\rm C}$ = 14.09 (CH₃), 26.37, 26.66, 27.95, 28.79, 32.28 (CH₂), 43.23, 44.81 (CH₂-Cl), 51.74 (CH₂), 53.21 (CH), 57.82 (OCH₃), 61.03 (OCH₂), 81.69 (CH), 91.77 (CH=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): $\tilde{v} = 2954$ (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 Me₃SiOTf (1.111 g, 5.0 mmol) in CH₂Cl₂ (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 (CDCl₃, 300 MHz, 55% enol form): δ = 1.25–1.33 (m, 3 H, OCH₂CH₃), 1.38–1.58 (m, 2 H, CH₂), 1.62–1.85 (m, 2 H, CH₂), 1.97–2.39 (m, 2 H, CH₂), 2.69–3.09 (m, 1 H, CH), 3.40/3.50 (ds, 3 H, OCH₃), 3.43–3.48 (m, 1 H, CH), 3.59–3.70 (m, 2 H, CH₂Cl), 3.72–3.92 (m, 1 H, CH), 4.22 (q, *J* = 7.1 Hz, 2 H, OCH₂CH₃), 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 Me₃SiOTf (1.111 g, 5.0 mmol), in CH₂Cl₂ (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 (CDCl₃, 300MHz): δ = 1.24–1.32 (m, 3 H, CH₃), 1.59–1.66 (m, 1 H, CH₂), 1.98–2.08 (m, 1 H, CH₂), 2.18–2.45 (m, 2 H, CH₂), 3.45 (s, 3 H, OCH₃), 3.49 (m, 1 H, CH), 3.66 (m, 1 H, CH), 3.75–3.85 (m, 2 H, CH₂Cl), 4.12–4.23 (m, 2 H, OCH₂), 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 Me₃SiOTf (0.222 g, 1.0 mmol) in CH₂Cl₂ (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 (CDCl₃, 300 MHz): $\delta = 1.26$ (t, J = 7.2 Hz, 3 H, CH₃), 1.31-1.40 (m, 2 H, CH₂), 1.73-1.87 (m, 2 H, CH₂), 1.88-2.03 (m, 4 H, 2×H₂), 2.11–2.26 (m, 1 H, CH₂), 2.94–3.01 (m, 1 H, CH), 3.45 (s, 3 H, OCH₃), 3,52-3.63 (m, 2 H, CH₂Cl), 3.71-3.77 (m, 1 H, CH), 4.18 (q, J = 7.2 Hz, 2 H, OCH₂) ppm. ¹³C NMR (CDCl₃, 75 MHz): δ = 13.86 (CH₃), 26.26, 27.27, 27.41, 28.40 (CH₂), 43.36 (CH₂Cl), 53.54 (OCH₃), 58.05, 59.31 (CH), 61 12 (OCH₂), 80.89 (CH), 169.73 (O=C–O), 209.47 (C=O) ppm. IR (neat; cm⁻¹): \tilde{v} = 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). C13H21O4Cl (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 Me₃SiOTf (0.556 g, 2.5 mmol) in CH₂Cl₂ (50 mL), **3u** being isolated as a yellow oil (0.95 g, 65%). ¹H NMR (CDCl₃, 300 MHz, 19% enol form): δ = 1.20–1.34 (m, 7 H, 2×H₂, CH₃), 1.53–1.65 (m, 2 H, CH₂), 1.66–1.83 (m, 2 H, CH₂), 2.01–2.35 (m, 2 H, CH₂), 2.41–2.55 (m, 1 H, CH), 2.61–2.71 (m, 1 H, CH), 3.48 (s, 3 H, OCH₃), 3.52–3.78 (m, 2 H, CH₂Cl), 3.85–4.05 (m, 1 H, CH), 4.13–4.24 (m, 2 H, OCH₂), 12.80 (s, 1 H, OH from enol form) ppm. IR (neat; cm⁻¹): \tilde{v} = 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 Me₃SiOTf (1.111 g, 5.0 mmol) in CH₂Cl₂ (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 (CDCl₃, 300 MHz, 9% enol form, 30% minor diastereomer, spectra analysis for the main isomer): δ = 1.22–1.43 (m, 17 H, 7×H₂, CH₃), 1.55–1.70 (m, 2 H, CH₂), 1.73–2.01 (m, 2 H, CH₂), 2.25–2.38 (m, 1 H, CH), 3.31/3.44 (ds, 3 H, OCH₃), 3.47–3.57 (m, 2 H, CH₂Cl), 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, OCH₂CH₃), 1.300 (s,

1 H, OH from enol form) ppm. ¹³C NMR (CDCl₃, 50 MHz): $\delta_{\rm C}$ = 14.01 (CH₃), 19.94, 22.03, 23.06, 23.26, 23.92, 24.14, 24.36, 26.15, 26.79 (CH₂), 44.07 (CH₂Cl), 52.72, 54.33 (CH), 57.47 (OCH₃), 61.79 (OCH₂CH₃), 79.33 (CH), 169.36 (O=C–O), 205.96 (C=O) ppm. IR (neat; cm⁻¹): \tilde{v} = 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 Me₃SiOTf (0.56 g, 2.5 mmol) in CH₂Cl₂ (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%). ¹H NMR (CDCl₃, 300 MHz, 48% enol form): δ = 1.04 (dd, *J* = 12, 6.6 Hz, 3 H, CH₃), 1.26–1.34 (m, 3 H, OCH₂CH₃), 1.59–2.01 (m, 2 H, CH₂), 2.06–2.35 (m, 2 H, CH₂), 2.45–2.54 (m, 1 H, CH), 3.45 (s, 3 H, OCH₃), 3.52 (m, 1 H, CH), 3.59 (m, 1 H, CH), 3.68–3.85 (m, 2 H, CH₂Cl), 4.15–4.21 (m, 1 H, CH), 4.22–4.29 (m, 2 H, OCH₂CH₃), 12.20/12.45 (ds, 1 H, OH from two possible enol forms) ppm. IR (neat; cm⁻¹): \tilde{v} = 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 Me₃SiOTf (1.111 g, 5 mmol), in CH₂Cl₂ (100 mL), 3x being isolated after chromatography (silica gel, *n*-hexane/EtOAc, 100:1 to 1:1) as a vellow oil (2.890 g, 89%). ¹H NMR (CDCl₃, 300 MHz, 70% enol form, analysis for enol form): $\delta = 1.80-2.15$ (m, 2 H, CH₂), 2.23-2.42 (m, 2 H, CH₂), 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, OCH₃), 3.41-3.61 (m, 1 H, CH₂-Cl), 3.68-3.81 (m, 5 H, CH₂-Cl, OCH₃, 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): $\tilde{v} = 3085$ (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). C₁₇H₂₁O₄Cl (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 Me₃SiOTf (0.222 g, 10 mmol) in CH₂CL₂ (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%). ¹H NMR (CDCl₃, 300 MHz): δ = 2.24–2.39 (m, 2 H, CH₂), 3.42 (s, 3 H, OCH₃), 3.60-3.66 (m, 2 H, CH₂-Cl), 3.71-3.77 (m, 1 H, CH), 3.93–3.99 (m, 1 H, CH), 4.28–4.43 (m, 2 H, OCH₂) ppm. ¹³C NMR (CDCl₃, 150 MHz): $\delta_c = (23.85, 44.16 (CH_2), 45.10 (CH_2-$ Cl), 53.06 (CH), 57.63 (OCH₃), 67.45 (OCH₃), 76.09 (CH), 172.77 (O=C-O), 200.58 (C=O) ppm. IR (neat; cm⁻¹): $\tilde{v} = 3519$ (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 Me₃SiOTf (1.111 g, 5 mmol) in CH₂Cl₂ (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) ¹H NMR (CDCl₃, 300 MHz): δ = 2.07 (s, 3 H, CH₃), 2.61 (m, 2 H, CH₂), 3.42 (s, 3 H, OCH₃), 3.56–3.69 (m, 2 H, CH₂Cl), 3.90 (m, 1 H, CH), 5.56 (s, 1 H, CH from enol), 15.58 (broad s, 1 H, OH from enol) ppm. ¹³C NMR (CDCl₃, 75 MHz): δ_C = 24.51 (CH₃), 40.95 (CH₂), 45.08 (CH₂Cl), 57.52 (OCH₃), 76.99 (CH), 101.02 (CH from enol), 190.78, 190.85 (C=O and C=*C*–OH) ppm. IR (neat; cm⁻¹): \tilde{v} = 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* – CH₃]⁺ (100), 161 (62), 143 (29).

Compound 6: (75% of enol form) ¹H NMR (CDCl₃, 300 MHz): δ = 2.63 (m, 4 H, 2×H₂), 3.40 (s, 2 H, CH₂ from keto form), 3.42 (s, 6 H, 2×OCH₃), 3.64 (m, 4 H, 2×H₂-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. ¹³C NMR (CDCl₃, 75 MHz): $\delta_{\rm C}$ = 40.77 (2×H₂), 44.96 (2×H₂-Cl), 57.47 (2×OCH₃), 76.91 (2×H), 101.63 (*CH*=C), 190.40 (O–*C*=CH) ppm. IR (neat; cm⁻¹): \tilde{v} = 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 C₁₁H₁₈O₄Cl₂ 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: ¹H NMR (CDCl₃, 300 MHz): $\delta = 3.36$ (s, 3 H, OCH₃), 3.51 (s, 3 H, OCH₃), 3.70 (s, 3 H, OCH₃), 3.89 (d, J = 3.2 Hz, 1 H, CH), 4.24 (d, J = 10 Hz, 1 H, OCH₂), 4.33 (dd, J = 10, 3.2 Hz, 1 H, OCH₂), 5.08 (s, 1 H, CH), 5.54 (s, 1 H, CH=C) ppm. ¹³C NMR (CDCl₃, 50 MHz): $\delta_C = 50.88$, 56.81, 57.77 (OCH₃), 74.44 (C–5), 79.05, 81.41 (CH), 94.57 (CH=C), 167.75 (O=C–O), 171.42 (O–C=CH) ppm. IR (neat; cm⁻¹): $\tilde{v} = 2992$ (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 (%) = 202.0841±2 ppm [M]⁺ for C₉H₁₄O₅ was confirmed by HRMS (EI, 70 eV).

Compound (*Z*)-**4i:** ¹H NMR (CDCl₃, 600 MHz): δ = 3.35 (s, 3 H, OCH₃), 3.39 (s, 3 H, OCH₃), 3.68 (s, 3 H, OCH₃), 3.88 (d, *J* = 3.2 Hz, 1 H, CH), 4.05 (s, 1 H, CH), 4.38 (d, *J* = 10 Hz, 1 H, OCH₂), 4.47 (dd, *J* = 10, 3.2 Hz, 1 H, OCH₂), 5.05 (s, 1 H, CH=C) ppm. ¹³C NMR (CDCl₃, 50 MHz): δ_C = 50.93, 56.78, 57.02 (OCH₃), 75.66 (C–5), 81.06, 84.22 (CH), 92.71 (CH=C), 165.59 (O=C–O), 166.74 (O–C=CH) ppm. IR (neat; cm⁻¹): \tilde{v} = 2993 (w), 2951 (m), 2831 (w, C–H), 1716 (s, C=C–O), 1663 (s, C=C–C=O),

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). C₉H₁₄O₅ (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%). ¹H NMR (CDCl₃, 300 MHz): δ = 1.27 (t, J = 7.2 Hz, 3 H, CH₃), 2.03–2.11 (m, 1 H, CH₂), 2.54–2.61 (m, 1 H, CH₂), 3.30 (s, 3 H, OCH₃), 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, OCH₂CH₃), 4.22–4.32 (m, 2 H, OCH₂), 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=CH₂) ppm. ¹³C NMR $(CDCl_3, 75 \text{ MHz}): \delta_C = 14.34 (CH_3), 34.66 (CH_2), 46.90 (CH),$ 56.04 (OCH₃), 59.24 (OCH₂), 74.34 (C-5), 82.23 (CH), 90.76 (CH=C), 117.44 (CH₂=CH), 135.20 (CH=CH₂), 167.80 (O=C-O),178.04 (O–C=CH) ppm. IR (neat; cm⁻¹): $\tilde{v} = 2983$ (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 $\pm 2 \text{ ppm } [M]^+$ for C₁₂H₁₈O₄ 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%). ¹H NMR (CDCl₃, 300 MHz): $\delta = 0.99$ (t, J = 6.9 Hz, 3 H, CH₃), 1.27 (t, J = 7.2 Hz, 3 H, OCH₂CH₃), 1.21–1.31 (m, 1 H, CH₂), 1.55 (sextet, J = 7.2 Hz, 2 H, CH₂), 1.65–1.71 (m, 1 H, CH₂), 3.32 (s, 3 H, OCH₃), 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, OCH₂CH₃), 4.22-4.32 (m, 2 H, OCH₂), 5.32 (s, 1 H, CH=C) ppm. ¹³C NMR (CDCl₃, 75 MHz): $\delta_{\rm C}$ = 13.64, 14.16 (CH₃), 21.07, 32.41 (CH₂), 47.20 (CH), 55.80 (OCH₃), 58.88 (OCH₂), 74.09 (C-5), 82.43 (CH), 90.17 (CH=C-O), 167.55 (O=C-O), 178.96 (O–C=CH) ppm. IR (neat; cm⁻¹): $\tilde{v} = 2962$ (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). C₁₂H₂₀O₄ (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%). ¹H NMR (CDCl₃, 300 MHz): δ = 0.89 (t, J = 6.9 Hz, 3 H, CH₃), 1.26 (t, J = 7.2 Hz, 3 H, OCH₂CH₃), 1.22–1.35 (m, 6 H, 3×CH₂), 1.36–1.40 (m, 1 H, CH₂), 1.43–1.49 (m, 2 H, CH₂), 1.68–1.78 (m, 1 H, CH₂), 3.32 (s, 3 H, OCH₃), 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, OCH₂CH₃), 4.22– 4.32 (m, 2 H, OCH₂), 5.31 (s, 1 H, CH=C) ppm. ¹³C NMR (CDCl₃, 75 MHz): $\delta_{\rm C}$ = 13.86, 14.25 (CH₃), 22.39, 28.02, 29.02, 30.50, 31.54 (CH₂), 47.52 (CH), 55.88 (OCH₃), 58.98 (OCH₂), 74.17 (C-5), 82.54 (CH), 90.29 (CH=C-O), 167.64 (O=C-O), 179.01 (O-*C*=CH) ppm. IR (neat; cm⁻¹): $\tilde{v} = 2956$ (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** be-

ing isolated after chromatography (silica gel, n-hexane/EtOAc, 100:1 to 1:1) as a colourless oil (0.30 g, 97%). ¹H NMR (CDCl₃, 300 MHz): $\delta = 0.88$ (t, J = 6.9 Hz, 3 H, CH₃), 1.22–1.29 (m, 13 H, $5 \times H_2$, CH₃), 1.33–1.51 (m, 3 H, CH₂), 1.68–1.79 (m, 1 H, CH₂), 3.32 (s, 3 H, OCH₃), 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, OC H_2 CH₃), 4.22–4.32 (m, 2 H, OCH₂), 5.31 (s, 1 H, CH=C) ppm. ¹³C NMR (CDCl₃, 75 MHz): $\delta_{\rm C}$ = 14.08, 14.42 (CH₃), 22.63, 27.17, 29.20, 29.32, 29.37, 31.79, 32.03 (CH₂), 50.30 (CH), 56.43 (OCH₃), 59.31 (OCH₂), 75.99 (C-5), 82.36 (CH), 89.65 (CH=C), 165.84 (O=C-O), 174.23 (O–C=CH) ppm. IR (neat; cm⁻¹): $\tilde{v} = 2954$ (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 C₁₇H₃₀O₄ was confirmed by HRMS (EI, 70 eV).

Compound 40: This compound was produced from 30 (0.85 g, 2.44 mmol) and DBU (0.73 mL, 4.9 mmol) in THF (20 mL), 40 being isolated after chromatography (silica gel, n-hexane/EtOAc, 100:1 to 1:1) as a yellow oil (0.66 g, 87%). ¹H NMR (CDCl₃, 300 MHz): $\delta = 0.88$ (t, J = 6.9 Hz, 3 H, CH₃), 1.26 (t, J = 7.2 Hz, 3 H, OCH₂CH₃), 1.19–1.29 (m, 12 H, 6×CH₂), 1.30–1.41 (m, 1 H, CH₂), 1.43–1.50 (m, 2 H, CH₂), 1.66–1.73 (m, 1 H, CH₂), 3.32 (s, 3 H, OCH₃), 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, OCH₂CH₃), 4.22– 4.32 (m, 2 H, OCH₂), 5.31 (s, 1 H, CH=C) ppm. ¹³C NMR (CDCl₃, 75 MHz): $\delta_{\rm C}$ = 14.00, 14.36 (CH₃), 22.57, 28.16, 29.21, 29.38, 29.44 (2C), 30.60, 31.78 (CH₂), 47.59 (CH), 56.01 (OCH₃), 59.10 (OCH₂), 74.28 (C-5),82.63 (CH), 90.45 (CH=C-O), 167.77 (O=C-O), 179.05 (O–C=CH) ppm. IR (neat; cm⁻¹): $\tilde{v} = 2927$ (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 C₁₈H₃₂O₄ (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%). ¹H NMR (CDCl₃, 300 MHz): δ = 0.88 (t, J = 6.9 Hz, 3 H, CH₃), 1.26 (t, J = 7.2 Hz, 3 H, OCH₂CH₃), 1.19–1.29 (m, 14 H, 7×CH₂), 1.30–1.40 (m, 1 H, CH₂), 1.41–1.49 (m, 2 H, CH₂), 1.66–1.74 (m, 1 H, CH₂), 3.32 (s, 3 H, OCH₃), 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, OCH₂CH₃), 4.22– 4.32 (m, 2 H, OCH₂), 5.31 (s, 1 H, CH=C) ppm. ¹³C NMR (CDCl₃, 150 MHz): $\delta_{\rm C}$ = 13.93, 14.29 (CH₃), 22.52, 28.10, 29.16, 29.37, 29.39, 29.43, 30.52, 31.74, 31.79 (CH₂), 47.56 (CH), 55.95 (OCH₃), 59.04 (OCH₂), 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): $\tilde{v} = 2927$ (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%). ¹H NMR (CDCl₃, 300 MHz): $\delta = 1.29$ (t, J = 7.2 Hz, 3 H, CH₃), 1.32–1.39 (m, 6 H, 3×CH₂), 1.65–1.84 (m, 4 H, 2×CH₂), 3.32 (s, 3 H, OCH₃), 3.54 (t, J = 6.6 Hz, 2 H, CH₂–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,

3.3 Hz, 2 H, OCH₂CH₃), 4.29–4.33 (m, 2 H, OCH₂), 5.32 (s, 1 H, CH=C) ppm. ¹³C NMR (CDCl₃, 75 MHz): $\delta_{\rm C}$ = 14.39 (CH₃), 26.64, 27.95, 28.65, 30.44, 32.43 (CH₂), 44.98 (CH₂–Cl), 47.51 (CH), 56.08 (OCH₃), 59.18 (OCH₂), 74.27 (C–5), 82.62 (CH), 90.52 (CH=C–O), 167.81 (O=C–O), 178.92 (O–C=CH) ppm. IR (neat; cm⁻¹): \tilde{v} = 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). C₁₅H₂₅O₄Cl (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%). ¹H NMR (CDCl₃, 300 MHz): $\delta = 1.27$ (t, J = 7.2 Hz, 3 H, OCH₂CH₃), 1.41–1.56 (m, 1 H, CH₂), 1.61-1.75 (m, 1 H, CH₂), 1.88-2.02 (m, 2 H, CH₂), 2.26-2.39 (m, 2 H, CH₂), 2.64–2.73 (m, 1 H, CH), 3.35 (s, 3 H, OCH₃), 3.92 (m, 1 H, CH), 4.15 (m, 1 H, OCH₂), 4.17 (q, J = 7.2 Hz, 2 H, OCH_2CH_3), 4.49 (d, J = 10.5 Hz, 1 H, OCH_2) ppm. ¹³C NMR $(CDCl_3, 75 \text{ MHz}): \delta_C = 14.13 (CH_3), 21.17, 21.89, 23.61 (CH_2),$ 45.46 (CH), 56.77 (OCH₃), 59.14 (OCH₂CH₃), 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)): $\tilde{v} = 2948$ (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 $m/z = 226.1205 \pm 2 \text{ ppm } [M]^+$ 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%). ¹H NMR (CDCl₃, 300 MHz): δ = 1.29 (t, J = 7.2 Hz, 3 H, CH₃), 1.83–1.89 (m, 1 H, CH₂), 2.26-2.35 (m, 2 H, CH₂), 2.81-2.85 (m, 1 H, CH₂), 3.15 (t, J = 9.0 Hz, 1 H, CH), 3.37 (s, 3 H, OCH₃), 3.77 (dd, J = 5.1, 3.0 Hz, 1 H, CH), 4.18 (q, J = 7.2 Hz, 2 H, OCH₂CH₃), 4.63 (dd, J = 10.8, 3.0 Hz, 1 H, OCH₂), 4.84 (d, J = 10.8 Hz, 1 H, OCH₂) ppm. ¹³C NMR (CDCl₃, 150 MHz): $\delta_{\rm C}$ = 14.36 (CH₃), 21.16, 27.59 (CH₂), 54.18 (CH), 57.47 (OCH₃), 59.80 (OCH₂), 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): $\tilde{v} = 2962$ (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 $m/z = 212.1049 \pm 2$ ppm $[M]^+$ for C₁₁H₁₆O₄ 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%). ¹H NMR (CDCl₃, 300 MHz): $\delta = 1.28$ (t, J = 7.2 Hz, 3 H, CH₃), 1.47–1.50 (m, 2 H, CH₂), 1.59–1.69 (m, 1 H, CH₂), 1.75–1.87 (m, 2 H, CH₂), 1.98–2.13 (m, 2 H, CH₂), 2.86 (dd, J = 15.3, 6.9 Hz, 1 H, CH₂), 3.08 (dt, J = 12.3, 2.1 Hz, 1 H, CH), 3.34 (s, 3 H, OCH₃), 3.65–3.68 (m, 1 H, CH), 4.19 (q, J = 7.2 Hz, 2 H, OCH₂CH₃), 4.38 (d, J = 3.6 Hz, 2 H, OCH₂) ppm. ¹³C NMR (CDCl₃, 75 MHz): $\delta_C = 14.20$ (CH₃), 26.81, 26.87, 29.30, 31.13 (CH₂), 51.21 (CH), 56.38 (OCH₃), 59.56 (OCH₂), 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): $\tilde{v} = 2981$ (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). C₁₃H₂₀O₄ (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%). ¹H NMR (CDCl₃, 300 MHz): $\delta = 1.27$ (t, J = 7.2 Hz, 3 H, CH₃), 1.31–1.42 (m, 2 H, CH₂), 1.54–1.72 (m, 4 H, 2×CH₂), 1.77–1.92 (m, 2 H, CH₂), 2.01– 2.12 (m, 1 H, CH₂), 2.75 (dt, J = 14.3, 3.7 Hz, 1 H, CH₂), 3.08 (dd, J = 12.3, 3.3 Hz, 1 H, CH), 3.32 (s, 3 H, OCH₃), 3.63 (d, J = 3.3 Hz, 1 H, CH), 4.17 (dq, J = 7.2, 1.5 Hz, 2 H, OCH₂CH₃), 4.36 $(dd, J = 10.5, 3.3 Hz, 1 H, OCH_2), 4.50 (d, J = 10.8 Hz, 1 H,$ OCH₂) ppm. ¹³C NMR (CDCl₃, 75 MHz): $\delta_{\rm C}$ = 14.24 (CH₃), 24.98, 25.99, 26.51, 28.98, 33.33 (CH₂), 49.47 (CH), 56.01 (OCH₃), 59.25 (OCH₂), 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): $\tilde{v} = 2979$ (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). C₁₄H₂₂O₄ (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: ¹H NMR (CDCl₃, 300 MHz): $\delta = 1.14-1.39$ (m, 12 H, $6 \times CH_2$), 1.28 (t, J = 7.2 Hz, 3 H, CH_3), 1.49–1.62 (m, 2 H, CH₂), 2.00–2.12 (m, 2 H, CH₂), 2.28–2.38 (m, 2 H, CH₂), 2.49– 2.61 (m, 1 H, CH₂), 3.31 (s, 3 H, OCH₃), 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, 2 H) OCH_2CH_3), 4.31 (d, J = 3.9 Hz, 2 H, OCH_2) ppm. ¹³C NMR (CDCl₃, 50 MHz): $\delta_{\rm C}$ = 14.35 (CH₃), 21.62, 22.39, 23.60, 24.15, 24.25, 25.40, 25.83, 26.31, 29.07 (CH₂), 47.55 (CH), 56.10 (OCH₃), 59.34 (OCH₂), 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): $\tilde{v} = 2931$ (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 $m/z = 310.2144 \pm 2 \text{ ppm } [M]^+$ for C₁₈H₃₀O₄ was confirmed by HRMS (EI, 70 eV).

Compound (Z)-4v: M.p. 77.5 °C. ¹H NMR (CDCl₃, 600 MHz): δ = 1.10 (t, J = 7.2 Hz, 3 H, CH₃), 1.18–1.22 (m, 10 H, 5×H₂), 1.24–1.41 (m, 2 H, CH₂), 1.47–1.53 (m, 2 H, CH₂), 1.54–1.60 (m, 1 H, CH₂), 1.62–1.69 (m, 1 H, CH₂), 1.97 (m, 1 H, CH₂), 2.13–2.19 (m, 1 H, CH₂), 2.97 (dd, J = 11, 5.5 Hz, 1 H, CH), 3.14 (s, 3 H, OCH₃), 3.48 (d, J = 5.5 Hz, 1 H, CH), 3.95–4.02 (m, 1 H, OCH₂CH₃), 4.03–4.08 (m, 1 H, OCH₂CH₃), 4.21 (dd, J = 11, 5.5 Hz, 1 H, OCH₂), 4.29 (d, J = 11 Hz, 1 H, OCH₂) ppm. ¹³C NMR (CDCl₃, 50 MHz): δ_{C} = 14.37 (CH₃), 21.52, 23.15, 25.40, 25.87, 26.75, 27.16, 27.36, 27.53, 29.84 (CH₂), 46.81 (CH), 56.11 (OCH₃), 59.47 (OCH₂), 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{v} = 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 C₁₈H₃₀O₄ 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 ¹H NMR $(CDCl_3, 300 \text{ MHz}): \delta = 1.13 \text{ (d, } J = 6.6 \text{ Hz}, 3 \text{ H}, \text{ CH}_3\text{)}, 1.28 \text{ (t, } J$ $= 7.2 \text{ Hz}, 3 \text{ H}, \text{ OCH}_2\text{C}H_3$, 1.21–1.31 (m, 1 H, CH₂), 1.49–1.61 (m, 1 H, CH₂), 1.75–1.87 (m, 1 H, CH), 2.28–2.38 (m, 3 H, CH₂, CH), 3.39 (s, 3 H, OCH₃), 3.81 (dt, J = 6.6, 9.0 Hz, 1 H, CH), 3.94 (t, J= 8.4 Hz, 1 H, OCH₂), 4.18 (q, J = 7.2 Hz, 2 H, OCH₂CH₃), 4.55 (dd, $J = 6.6, 8.4 \text{ Hz}, 1 \text{ H}, \text{ OCH}_2$) ppm. ¹³C NMR (CDCl₃, 150 MHz): $\delta_{\rm C}$ = 14.62, 19.66 (CH₃), 24.41, 31.63 (CH₂), 33.95, 51.70 (CH), 58.53 (OCH₃), 59.84 (OCH₂), 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)): $\tilde{v} = 2979$ (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 = $240.1362 \pm 2 \text{ ppm } [M]^+$ 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): ¹H NMR (CDCl₃, 300 MHz): δ = 1.69 (q, J = 12.0 Hz, 1 H, CH₂), 2.29–2.43 (m, 2 H, CH₂, CH), 2.65–2.73 (m, 1 H, CH), 2.81–2.97 (m, 2 H, CH₂), 3.44 (s, 3 H, OCH₃), 3.72 (s, 3 H, OCH₃), 3.85-3.90 (m, 1 H, CH), 4.01 (dd, J = 8.7, 8.7 Hz, 1 H, OCH₂), 4.58 (dd, J = 8.7, 6.9 Hz, 1 H, OCH₂), 7.20–7.35 (m, 5 H, 5×CH from Ph) ppm. ¹³C NMR (CDCl₃, 150 MHz): $\delta_{\rm C}$ = 32.79, 33.28 (CH₂), 40.38, 47.47 (CH), 51.28, 58.85 (OCH₃), 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)): $\tilde{v} = 2946$ (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 C₁₇H₂₀O₄ was confirmed by HRMS (EI, 70 eV).

Compound 4x (2): ¹H NMR (CDCl₃, 300 MHz): $\delta = 1.98-2.21$ (m, 2 H, CH₂), 2.35–2.41 (m, 1 H, CH), 2.65–2.73 (m, 2 H, CH₂), 3.33 (s, 3 H, OCH₃), 3.37–3.44 (m, 1 H, CH), 3.78 (s, 3 H, OCH₃), 3.98–4.10 (m, 1 H, CH), 4.08 (dd, J = 10.5, 2.6 Hz, 1 H, OCH₂), 4.49 (d, J = 10.5 Hz, 1 H, OCH₂), 7.19–7.32 (m, 5 H, 5×CH from Ph) ppm. ¹³C NMR (CDCl₃, 150 MHz): $\delta_{\rm C} = 28.22$, 28.44 (CH₂), 36.56, 41.09 (CH), 51.41, 57.31 (OCH₃), 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): $\tilde{v} = 3027$ (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 $m/z = 288.1362 \pm 2 \text{ ppm } [M]^+$ for C₁₇H₂₀O₄ was confirmed by HRMS (EI, 70 eV).

Compound 4x (3): M.p. 155 °C. ¹H NMR (CDCl₃, 300 MHz): δ = 2.02-2.17 (m, 2 H, CH₂), 2.34-2.45 (m, 1 H, CH), 2.63-2.71 (m, 1 H, CH), 2.84-2.98 (m, 2 H, CH₂), 3.37 (s, 3 H, OCH₃), 3.71 (s, 3 H, OCH₃), 3.95 (dd, *J* = 4.8, 3.0 Hz, 1 H, CH), 4.24 (dd, *J* = 10.5, 3.0 Hz, 1 H, OCH₂), 4.58 (d, J = 10.5 Hz, 1 H, OCH₂), 7.19–7.35 (m, 5 H, 5×CH from Ph) ppm. ¹³C NMR (CDCl₃, 150 MHz): $\delta_{\rm C}$ = 28.27, 33.24 (CH₂), 40.80, 46.95 (CH), 51.20, 57.30 (OCH₃), 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)): $\tilde{v} = 2948$ (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). C₁₇H₂₀O₄ (288.343): C 70.81, H 6.99; found C 70.17, H 6.96. The exact molecular mass $m/z = 288.1362 \pm 2 \text{ ppm } [M]^+$ 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%). ¹H NMR (CDCl₃, 150 MHz): $\delta = 2.87 - 2.96$ (m, 3 H, 2×CH₂), 3.34 (s, 3 H, OCH₃), 3.55-3.62 (dm, J = 18.3, 1.4 Hz, 1 H, CH₂), 4.16-4.42 (m, 5 H, $2 \times OCH_2$, CH) ppm. ¹³C NMR (CDCl₃, 150 MHz): $\delta_C = 24.68$, 34.80 (CH₂), 56.17 (OCH₃), 65.03 (OCH₂), 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): $\tilde{v} = 2986$ (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 C₉H₁₂O₄ (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 CH₂Cl₂ 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 Na₂CO₃ was added. The organic layer was separated, and the aqueous layer was repeatedly extracted with diethyl ether. The combined organic extracts were dried (Na₂SO₄) and filtered, and the filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel, nhexane/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 CH₂Cl₂, 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 CH₂Cl₂ (20 mL), **5a** being isolated without further purification as a yellow oil (0.20 g, 80%). ¹H NMR (CDCl₃, 300 MHz): δ = 3.68 (s, 2 H, CH₂), 3.73 (s, 3 H, OCH₃), 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. ¹³C NMR (CDCl₃, 75 MHz): δ _C = 33.79 (CH₂), 52.15 (OCH₃), 107.96, 110.44, 142.02 (CH), 147.52 (C), 169.78 (O=C–O) ppm. IR (neat; cm⁻¹): \tilde{v} = 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 C₇H₈O₃ 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 CH₂Cl₂ (5 mL), **5b** being isolated without further purification as a yellow oil (0.08 g, 100%). ¹H NMR (CDCl₃, 300 MHz): $\delta = 1.27$ (t, J = 7.2 Hz, 3 H, CH₃), 3.68 (s, 2 H, CH₂), 4.19 (q, J = 7.2 Hz, 2 H, OCH₂CH₃), 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. ¹³C NMR (CDCl₃, 75 MHz): $\delta_{\rm C} = 14.15$ (CH₃), 34.15 (CH₂), 61.19 (OCH₂), 107.98, 110.52, 142.06 (CH), 147.79 (C), 169.47 (O=C–O) ppm. IR (neat; cm⁻¹): $\tilde{v} = 2964$ (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 $m/z = 154.0630 \pm 2$ ppm [M]⁺ for C₈H₁₀O₃ 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 CH₂Cl₂ (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 (CDCl₃, 300 MHz): δ = 1.25 (d, *J* = 6.3 Hz, 6 H, 2×CH₃), 3.64 (s, 2 H, CH₂), 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. ¹³C NMR (CDCl₃, 75 MHz): δ_{C} = 21.74 (2CH₃), 34.46 (CH₂), 68.63 (OCH), 107.84, 110.49, 141.97 (CH), 148.02 (C), 168.98 (O=C–O) ppm. IR (neat; cm⁻¹): \tilde{v} = 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 C₉H₁₂O₃ 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 CH₂Cl₂ (5 mL), 5d being isolated without further purification as a vellow oil (0.13 g, 100%). ¹H NMR (CDCl₃, 300 MHz): δ = 3.38 (s, 3 H, OCH₃), 3.61 $(t, J = 4.8 \text{ Hz}, 2 \text{ H}, \text{ OCH}_2\text{CH}_2\text{OCH}_3), 3.73 (s, 2 \text{ H}, \text{CH}_2), 4.28 (t, 2 \text{ H}, \text{CH}_2),$ J = 4.8 Hz, 2 H, OCH₂CH₂OCH₃), 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. ¹³C NMR (CDCl₃, 75 MHz): $\delta_{\rm C}$ = 33.71 (CH₂), 58.76 (OCH₃), 63.98 (OCH₂CH₂OCH₃), 70.09 (OCH₂CH₂OCH₃), 107.92, 110.34, 141.88 (CH), 147.40 (C), 169.23 (O=C-O) ppm. IR (neat; cm⁻¹): $\tilde{v} = 2977$ (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 $m/z = 184.0736 \pm 2 \text{ ppm } [M]^+$ for C₉H₁₂O₄ 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 CH₂Cl₂ (5 mL), **5e** being isolated without further purification as a yellow oil (0.07 g, 100%). ¹H NMR (CDCl₃, 300 MHz): δ = 3.73 (s, 2 H, CH₂), 5.16 (s, 2 H, OCH₂), 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. ¹³C NMR (CDCl₃, 75 MHz): δ_{C} = 34.09 (CH₂), 66.87 (OCH₂), 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{v} = 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 $m/z = 216.0786 \pm 2$ ppm $[M]^+$ for C₁₃H₁₂O₃ 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 (CDCl₃, 600 MHz): δ = 4.29 (s, 2 H, CH₂), 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. ¹³C NMR (CDCl₃, 50 MHz): δ = 38.30 (CH₂), 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): $\tilde{v} = 2955$ (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 = $186.0681 \pm 2 \text{ ppm } [M]^+$ 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 CH₂Cl₂ (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 (CDCl₃, 300 MHz): $\delta = 1.99$ (s, 3 H, CH₃), 3.62 (s, 2 H, CH₂), 3.71 (s, 3 H, OCH₃), 6.21 (d, J = 1.8 Hz, 1 H, CH), 7.27 (d, J = 1.8 Hz, 1 H, CH) ppm. ¹³C NMR (CDCl₃, 75 MHz): $\delta_{\rm C} = 9.77$ (CH₃), 32.03 (CH₂), 52.20 (OCH₃), 113.01 (CH), 116.95 (C), 141.10 (CH), 143.09 (C), 170.08 (O=C–O) ppm. IR (neat; cm⁻¹): $\tilde{v} = 2960$ (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 C₈H₁₀O₃ 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 CH₂Cl₂ (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 (CDCl₃, 300 MHz): δ = 1.15 (t, J = 7.5 Hz, 3 H, CH₃), 1.26 (t, J = 7.2 Hz, 3 H, OCH₂CH₃), 2.93 (q, J = 7.5 Hz, 2 H, CH₂), 3.61 (s, 2 H, CH₂), 4.16 (q, J = 7.2 Hz, 2 H, OCH₂CH₃), 6.26 (d, J = 1.8 Hz, 1 H, CH), 7.28 (d, J = 1.8 Hz, 1 H, CH) ppm. ¹³C NMR (CDCl₃, 150 MHz): $\delta_{\rm C}$ = 14.05, 14.69 (CH₃), 17.84, 22.61 (CH₂), 60.89 (OCH₂), 111.19 (CH), 123.51 (C), 141.19 (CH), 142.55 (C), 169.70 (O=C–O) ppm. IR (neat; cm⁻¹): $\tilde{v} = 2965$ (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 $m/z = 182.0943 \pm 2 \text{ ppm } [M]^+$ 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 (CDCl₃, 300 MHz): δ = 3.64 (s, 2 H, CH₂), 3.71 (s, 3 H, OCH₃), 3.75 (s, 3 H, OCH₃), 6.31 (d, *J* = 2.1 Hz, 1 H, CH), 7.19 (d, *J* = 2.1 Hz, 1

H, CH) ppm. ¹³C NMR (CDCl₃, 75 MHz): $\delta_{\rm C}$ = 30.76 (CH₂), 52.07, 59.12 (OCH₃), 102.77 (CH), 131.43 (C), 140.38 (CH), 145.19 (C), 170.06 (O=C-O) ppm. IR (neat; cm⁻¹): \tilde{v} = 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 5*j*: This compound was produced from 4*j* (0.10 g, 0.4 mmol) and TFA (0.44 mL, 5.7 mmol) in CH₂Cl₂ (10 mL), 5j being isolated without further purification as a colourless oil (0.09 g, 100%). ¹H NMR (CDCl₃, 300 MHz): $\delta = 1.25$ (t, J =7.2 Hz, 3 H, CH₃), 3.14 (dt, J = 6.3, 1.5 Hz, 2 H, CH₂), 3.61 (s, 2 H, CH₂), 4.16 (q, J = 7.2 Hz, 2 H, OCH₂), 5.01–5.09 (m, 2 H, CH_2 =CH), 5.82–5.95 (m, 1 H, CH=CH₂), 6.23 (d, J = 1.8 Hz, 1 H, CH), 7.30 (d, J = 1.8 Hz, 1 H, CH) ppm. ¹³C NMR (CDCl₃, 75 MHz): $\delta_{\rm C} = 14.11$ (CH₃), 29.12, 32.37 (CH₂), 61.06 (OCH₂), 112.07 (CH), 115.46 (CH₂=CH), 119.41 (C), 136.21 (CH=CH₂), 141.25 (CH), 143.56 (C), 169.48 (O=C-O) ppm. IR (neat; cm⁻¹): v = 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 C₁₁H₁₄O₃ 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 CH₂Cl₂ (10 mL), 5k being isolated without further purification as a colourless oil (0.11 g, 100%). ¹H NMR (CDCl₃, 300 MHz): $\delta = 0.92$ (t, J =7.2 Hz, 3 H, CH₃), 1.25 (t, J = 7.2 Hz, 3 H, OCH₂CH₃), 1.55 (sextet, J = 7.2 Hz, 2 H, CH₂), 2.33 (t, J = 7.2 Hz, 2 H, CH₂), 3.60 (s, 2 H, CH₂), 4.16 (q, J = 7.2 Hz, 2 H, OCH₂), 6.23 (d, J = 1.8 Hz, 1 H, CH), 7.28 (d, J = 1.8 Hz, 1 H, CH) ppm. ¹³C NMR (CDCl₃, 150 MHz): $\delta_{\rm C}$ = 13.58, 13.98 (CH₃), 23.25, 26.55, 32.21 (CH₂), 60.88 (OCH₂), 111.54 (CH), 121.71 (C), 141.01 (CH), 143.02 (C), 169. 52 (O=C-O) ppm. IR (neat; cm⁻¹): $\tilde{v} = 2962$ (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 $m/z = 196.1099 \pm 2 \text{ ppm } [M]^+$ for $C_{11}H_{16}O_3$ was confirmed by HRMS (EI, 70 eV).

Compound 51: This compound was produced from **41** (0.10 g, 0.4 mmol) and TFA (0.41 mL, 5.4 mmol) in CH₂Cl₂ (10 mL), 51 being isolated without further purification as a colourless oil (0.09 g, 100%). ¹H NMR (CDCl₃, 300 MHz): δ = 0.91 (t, J = 7.2 Hz, 3 H, CH₃), 1.25 (t, J = 7.2 Hz, 3 H, OCH₂CH₃), 1.33 (sextet, J = 7.2 Hz, 2 H, CH₂), 1.50 (quint, J = 7.2 Hz, 2 H, CH₂), 2.35 (t, J = 7.2 Hz, 2 H, CH₂), 3.60 (s, 2 H, CH₂), 4.16 (q, J =7.2 Hz, 2 H, OCH₂), 6.23 (d, J = 1.8 Hz, 1 H, CH), 7.28 (d, J = 1.8 Hz, 1 H, CH) ppm. ¹³C NMR (CDCl₃, 150 MHz): $\delta_{\rm C}$ = 13.82, 14.07 (CH₃), 22.22, 24.28, 32.30, 32.32 (CH₂), 60.98 (OCH₂), 111.61 (CH), 121.98 (C), 141.08 (CH), 142.94 (C), 169.63 (O=C-O) ppm. IR (neat; cm⁻¹): $\tilde{v} = 2962$ (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 = $210.1256 \pm 2 \text{ ppm} [M]^+$ for C₁₂H₁₈O₃ 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 CH₂Cl₂ (10 mL), 5m being isolated without further purification as a colourless oil

(0.11 g, 100%). ¹H NMR (CDCl₃, 300 MHz): $\delta = 0.88$ (t, J = 7.2 Hz, 3 H, CH₃), 1.25 (t, J = 7.2 Hz, 3 H, OCH₂CH₃), 1.26–1.35 (m, 6 H, 3×CH₂), 1.51 (quint, J = 7.2 Hz, 2 H, CH₂), 2.34 (t, J = 7.2 Hz, 2 H, CH₂), 3.60 (s, 2 H, CH₂), 4.16 (q, J = 7.2 Hz, 2 H, OCH₂), 6.23 (d, J = 1.8 Hz, 1 H, CH), 7.28 (d, J = 1.8 Hz, 1 H, CH) ppm. ¹³C NMR (CDCl₃, 150 MHz): $\delta_C = 13.99$, 14.07 (CH₃), 22.54, 24.59, 28.85, 30.14, 31.61, 32.29 (CH₂), 60.96 (OCH₂), 111.59 (CH), 122.01 (C), 141.07 (CH), 142.92(C), 169.60 (O=C–O) ppm. IR (neat; cm⁻¹): $\tilde{v} = 2958$ (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 $m/z = 238.1569 \pm 2$ ppm [M]⁺ for C₁₄H₂₂O₃ 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 CH₂Cl₂ (10 mL), 5n being isolated without further purification as a yellow oil (0.09 g, 100%). ¹H NMR (CDCl₃, 300 MHz): $\delta = 0.88$ (t, J = 7.2 Hz, 3 H, CH₃), 1.19–1.28 (m, 13 H, $5 \times H_2$, OCH₂CH₃), 1.45 (t, J = 7.2 Hz, 2 H, CH₂), 2.34 (t, J = 7.2 Hz, 2 H, CH₂), 3.60 (s, 2 H, CH₂), 4.16 $(q, J = 7.2 \text{ Hz}, 2 \text{ H}, \text{ OC}H_2\text{C}H_3), 6.23 \text{ (d}, J = 1.8 \text{ Hz}, 1 \text{ H}, \text{C}H),$ 7.28 (d, J = 1.8 Hz, 1 H, CH) ppm. ¹³C NMR (CDCl₃, 75 MHz): $\delta_{\rm C} = 14.05, 14.11 \text{ (CH}_3), 22.63, 24.63, 29.22, 29.24, 29.41, 30.21,$ 31.84, 32.34 (CH₂), 61.00 (OCH₂), 111.63 (CH), 122.06 (C), 141.11 (CH), 142.93 (C), 169.64 (O=C–O) ppm. IR (neat; cm⁻¹): $\tilde{v} = 2957$ (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 $m/z = 266.1882 \pm 2$ ppm $[M]^+$ for C₁₆H₂₆O₃ was confirmed by HRMS (EI, 70 eV).

Compound 50: This compound was produced from **40** (0.12 g, 0.4 mmol) and TFA (0.38 mL, 5.0 mmol) in CH₂Cl₂ (10 mL), 50 being isolated without further purification as a yellow oil (0.11 g, 100%). ¹H NMR (CDCl₃, 300 MHz): δ = 0.88 (t, J = 7.2 Hz, 3 H, CH₃), 1.23–1.32 (m, 15 H, $6 \times$ CH₂, CH₃), 1.51 (quint, J = 7.2 Hz, 2 H, CH₂), 2.34 (t, J = 7.2 Hz, 2 H, CH₂), 3.60 (s, 2 H, CH₂), 4.16 $(q, J = 7.2 \text{ Hz}, 2 \text{ H}, \text{ OCH}_2), 6.23 \text{ (d}, J = 1.8 \text{ Hz}, 1 \text{ H}, \text{ CH}), 7.28$ (d, J = 1.8 Hz, 1 H, CH) ppm. ¹³C NMR (CDCl₃, 150 MHz): $\delta_{\rm C}$ = 14.02, 14.07 (CH₃), 22.60, 24.59, 29.20, 29.26, 29.42, 29.50, 30.23, 31.83, 32.29 (CH₂), 60.95 (OCH₂), 111.59 (CH), 122.01 (C), 141.07 (CH), 142.92 (C), 169.58 (O=C–O) ppm. IR (neat; cm⁻¹): $\tilde{v} = 2960$ (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 $m/z = 280.2038 \pm 2 \text{ ppm} [M]^+$ for C₁₇H₂₈O₃ 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 CH₂Cl₂ (15 mL), 5p being isolated without further purification as a yellow oil (0.14 g, 100%). ¹H NMR (CDCl₃, 300 MHz): $\delta = 0.88$ (t, J = 7.2 Hz, 3 H, CH₃), 1.19–1.28 (m, 17 H, 7×CH₂, CH₃), 1.51 (quint, J = 7.2 Hz, 2 H, CH₂), 2.34 (t, *J* = 7.2 Hz, 2 H, CH₂), 3.60 (s, 2 H, CH₂), 4.16 $(q, J = 7.2 \text{ Hz}, 2 \text{ H}, \text{ OCH}_2), 6.23 \text{ (d}, J = 1.8 \text{ Hz}, 1 \text{ H}, \text{ CH}), 7.28$ (d, J = 1.8 Hz, 1 H, CH) ppm. ¹³C NMR (CDCl₃, 75 MHz): $\delta_{\rm C} =$ 14.04, 14.09 (CH₃), 22.63, 24.61, 29.22, 29.29, 29.41, 29.43, 29.57, 30.20, 31.85, 32.31 (CH₂), 60.96 (OCH₂), 111.60 (CH), 122.01 (C), 141.06 (CH), 142.93 (C), 169.58 (O=C-O) ppm. IR (neat; cm⁻¹): v = 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 $m/z = 294.2195 \pm 2 \text{ ppm } [M]^+$ for $C_{18}H_{30}O_3$ was confirmed by HRMS (EI, 70 eV).

Compound 5q: This compound was produced from 4q (0.100 g, 0.293 mmol) in CH₂Cl₂ (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%). ¹H NMR (CDCl₃, 300 MHz): $\delta = 1.19$ (t, J =7.2 Hz, 3 H, CH₃), 1.23–1.51 (m, 6 H, $3 \times$ CH₂), 1.70 (quint, J =6.9 Hz, 2 H, CH₂), 2.29 (t, J = 7.5 Hz, 2 H, CH₂), 3.46 (t, J =6.6 Hz, 2 H, CH₂-Cl), 3.60 (s, 2 H, CH₂), 4.10 (q, J = 7.2 Hz, 2 H, OCH₂), 6.16 (d, J = 1.8 Hz, 1 H, CH), 7.22 (d, J = 1.8 Hz, 1 H, CH) ppm. ¹³C NMR (CDCl₃, 75 MHz): $\delta_{\rm C}$ = 14.15 (CH₃), 24.50, 26.65, 28.39, 29.98, 32.35, 32.50 (CH₂), 45.06 (CH₂-Cl), 61.07 (OCH₂), 111.59 (CH), 121.80 (C), 141.23 (CH), 143.06 (C), 169.64 (O=C-O) ppm. IR (neat; cm⁻¹): $\tilde{v} = 2983$ (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 CH₂Cl₂ (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%). ¹H NMR (CDCl₃, 300 MHz): $\delta = 1.27$ (t, J = 7.2 Hz, 3 H, CH₃), 1.68–1.79 (m, 1 H, CH₂), 1.81–1.94 (m, 1 H, CH₂), 1.97–2.08 (m, 1 H, CH₂), 2.09– 2.18 (m, 1 H, CH₂), 2.37–2.55 (m, 2 H, CH₂), 3.69 (t, J = 7.2 Hz, 1 H, CH), 4.19 (q, J = 7.2 Hz, 2 H, OCH₂CH₃), 6.22 (d, J = 1.8 Hz, 1 H, CH), 7.30 (d, J = 1.8 Hz, 1 H, CH) ppm. ¹³C NMR (CDCl₃, 75 MHz): $\delta_{\rm C} = 14.24$ (CH₃), 21.12, 21.90, 27.16 (CH₂), 40.261 (CH), 60.98 (OCH₂), 110.35 (CH), 119.13 (C), 141.53 (CH), 146.54 (C), 172.74 (O=C–O) ppm. IR (neat; cm⁻¹): $\tilde{v} = 2963$ (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 CH₂Cl₂ (10 mL), 5t being isolated without further purification as a colourless oil (0.09 g, 100%). ¹H NMR (CDCl₃, 300 MHz): δ = 1.25 (t, J = 7.2 Hz, 3 H, CH₃), 1.53-1.59 (m, 2 H, CH₂), 1.71-1.80 (m, 1 H, CH₂), 1.84-1.89 (m, 2 H, CH₂), 2.22-2.27 (m, 1 H, CH₂), 2.50-2.53 (m, 2 H, CH₂), 3.90 (t, J = 4.2 Hz, 1 H, CH), 4.19 (dq, J =7.2, 2.9 Hz, 2 H, OCH₂), 6.16 (d, J = 1.5 Hz, 1 H, CH), 7.18 (d, J= 1.5 Hz, 1 H, CH) ppm. ¹³C NMR (CDCl₃, 75 Hz): $\delta_{\rm C}$ = 14.24 (CH₃), 25.58, 26.91, 28.22, 29.57 (CH₂), 45.29 (CH), 60.86 (OCH₂), 113.27 (CH), 122.75 (C), 139,74 (CH), 148.89 (C), 172.31 (O=C-O) ppm. IR (neat; cm⁻¹): $\tilde{v} = 2931$ (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 $m/z = 208.1099 \pm 2$ ppm $[M]^+$ for C₁₂H₁₆O₃ 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 CH₂Cl₂ (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%). ¹H NMR (CDCl₃, 300 MHz): $\delta = 1.26$ (t, J = 7.2 Hz, 3 H, CH₃), 1.30–1.49 (m, 2 H, CH₂), 1.52–1.71 (m, 4 H, 2×CH₂), 1.93–2.03 (m, 1 H, CH₂), 2.12–2.21 (m, 1 H, CH₂), 2.47–2.56 (m, 1 H, CH₂), 2.65–2.74 (m, 1 H, CH₂), 3.87 (dd, J = 11.1, 3.9 Hz, 1 H, CH), 4.21 (q, J = 7.2 Hz, 2 H, OCH₂), 6.14 (d, J = 1.8 Hz, 1 H, CH), 7.25 (d, J = 1.8 Hz, 1 H, CH) ppm. ¹³C NMR (CDCl₃, 75 MHz): $\delta_{C} = 14.19$ (CH₃), 23.85, 24.85, 25.26, 28.90, 29.60 (CH₂), 43.80 (CH), 60.87 (OCH₂), 112.67 (CH), 120.04 (C), 140.41 (CH), 147.38 (C), 172.57 (O=C–

O) ppm. IR (neat; cm⁻¹): $\tilde{v} = 2928$ (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 CH₂Cl₂ (5 mL), 5v being isolated without further purification as an orange oil (0.36 g, 100%). ¹H NMR (CDCl₃, 300 MHz): $\delta = 0.98-1.13$ (m, 2 H, CH₂), 1.21 (t, J = 7.2 Hz, 3 H, CH₃), 1.15–1.29 (m, 6 H, $3 \times H_2$), 1.31– 1.46 (m, 4 H, 2×H₂), 1.57–1.66 (m, 2 H, CH₂), 1.92–2.03 (m, 1 H, CH₂), 2.06–2.15 (m, 1 H, CH₂), 2.38–2.53 (m, 2 H, CH₂), 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 (CDCl₃, 75 MHz): $\delta_{\rm C}$ = 13.99 (CH₃), 21.11, 22.07, 22.13, 23.67, 23.84, 23.91, 24.87, 27.12, 28,49 (CH₂), 40.03 (CH), 60.62 (OCH₂), 110.62 (CH), 121.28 (C), 141.42 (CH), 146.99 (C), 172.15 (O=C–O) ppm. IR (neat; cm⁻¹): $\tilde{v} = 2934$ (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 C₁₇H₂₆O₃ 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 CH₂Cl₂ (5 mL), 5w being isolated without further purification as a yellow oil (0.07 g, 100%). ¹H NMR (CDCl₃, 300 MHz): δ = 1.15 (d, J = 6.9 Hz, 3 H, CH₃), 1.28 (t, J = 7.2 Hz, 3 H, OCH₂CH₃), 1.29–1.38 (m, 1 H, CH₂), 1.94–2.05 (m, 2 H, CH₂), 2.15–2.20 (m, 1 H, CH₂), 2.73 (sextet, J = 7.2 Hz, 1 H, CH), 3.68 (t, J = 6.3 Hz, 1 H, CH), 4.19 $(q, J = 7.2 \text{ Hz}, 2 \text{ H}, \text{ OC}H_2\text{C}H_3), 6.27 \text{ (d}, J = 1.8 \text{ Hz}, 1 \text{ H}, \text{C}H),$ 7.29 (dd, J = 1.8, 0.9 Hz, 1 H, CH) ppm. ¹³C NMR (CDCl₃, 75 MHz): $\delta_{\rm C}$ = 14.24, 20.67 (CH₃), 25.87 (CH₂), 27.65 (CH), 30.41 (CH₂), 40.84 (CH), 60.98 (OCH₂), 109.10 (CH), 124.55 (C), 141.64 (CH), 146.03 (C), 172.82 (O=C–O) ppm. IR (neat; cm⁻¹): $\tilde{v} = 2959$ (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 C₁₂H₁₆O₃ was confirmed by HRMS (EI, 70 eV).

Compound 5x: This compound was produced from 4x (0.100 g, 0.35 mmol) in CH₂Cl₂ (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%). ¹H NMR (CDCl₃, 300 MHz): δ = 2.15–2.48 (m, 2 H, CH₂), 2.54–2.82 (m, 2 H, CH₂), 2.94–3.04, 3.17–3.27 (dm, 1 H, CH-Ph), 3.74, 3.75 (ds, 3 H, OCH₃), 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. ¹³C NMR (CDCl₃, 150 MHz): $\delta_{\rm C}$ = 29.90, 30.32 (1×CH), 33.71, 34.81 (1×CH₂), 38.07, 39.66 (1×CH-Ph), 40.96, 42.02 (1×H), 51.53, 52.43 (1×OCH₃), 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): $\tilde{v} = 3062$ (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 $m/z = 256.1099 \pm 2 \text{ ppm } [M]^+$ for $C_{16}H_{16}O_3$ was confirmed by HRMS (EI, 70 eV).

Compound 5y: A solution of 4y (0.130 g, 0.71 mmol) in CH₂Cl₂ (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%). ¹H NMR (CDCl₃, 300 MHz): δ = 2.54–2.71 (m, 2 H, CH₂), 3.91 (t, J = 9.2 Hz, 1 H, CH), 4.32–4.40 (m, 1 H, OCH₂), 4.46– 4.52 (m, 1 H, OCH₂), 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. ¹³C NMR (CDCl₃, 150 MHz): $\delta_{\rm C}$ = 28.69 (CH₂), 39.66 (CH), 67.08 (OCH₂), 107.80, 110.66, 142.64 (CH), 149.36 (C), 175.18 (O=C-O) ppm. IR (neat; cm⁻¹): $\tilde{v} = 2917$ (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 C₈H₈O₃ 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 Fo² (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] C₉H₁₄O₄, $Mr = 186.20 \text{ gmol}^{-1}$, colourless prism, size $0.03 \times 0.03 \times 0.03 \text{ mm}$, orthorhombic, space group *Pbca*, a = 13.4002(2), b = 8.0370(4), c = 17.9872(6) Å, V = 1937.1(1) Å³, T = -90 °C, Z = 8, $\rho_{\text{calcd.}} = 1.277 \text{ g cm}^{-3}$, $\mu(\text{Mo-}K_a) = 1.0 \text{ cm}^{-1}$, F(000) = 800, 3998 reflections in h(-17/17), k(-10/10), l(-23/23), measured in the range $3.96^{\circ} \le \Theta \le 27.45^{\circ}$, completeness $\Theta_{\text{max}} = 99.4\%$, 2197 independent reflections, $R_{\text{int}} = 0.021$, 1696 reflections with $F_o > 4\sigma(F_o)$, 118 parameters, 0 restraints, $RI_{\text{obs}} = 0.044$, $wR^2_{\text{obs}} = 0.113$, $RI_{\text{all}} = 0.061$, $wR^2_{\text{all}} = 0.124$, GOOF = 1.033, largest difference peak and hole: $0.231/-0.184 \text{ e}^{A^{-3}}$.

Crystal Data for 4r:^[29] C₁₂H₁₈O₄, $Mr = 226.26 \text{ gmol}^{-1}$, colourless prism, size $0.03 \times 0.03 \times 0.02 \text{ mm}$, triclinic, space group $P\bar{I}$, a = 8.8743(2), b = 10.1470(3), c = 13.5326(4) Å, a = 101.701(1), $\beta = 95.436(1)$, $\gamma = 91.924(1)^{\circ}$, V = 1186.14(6) Å³, T = -90 °C, Z = 4, $\rho_{\text{caled.}} = 1.267 \text{ g cm}^{-3}$, $\mu(\text{Mo-}K_{\alpha}) = 0.94 \text{ cm}^{-1}$, F(000) = 488, 8710 reflections in h(-11/11), k(-13/12), l(-17/16), measured in the range $2.05^{\circ} \le \Theta \le 27.46^{\circ}$, completeness $\Theta_{\text{max}} = 99.2\%$, 5390 independent reflections, $R_{\text{int}} = 0.020$, 3883 reflections with $F_{\text{o}} > 4\sigma(F_{\text{o}})$, 297 parameters, 0 restraints, $RI_{\text{obs}} = 0.056$, $wR^2_{\text{obs}} = 0.138$, $RI_{\text{all}} = 0.083$, $wR^2_{\text{all}} = 0.155$, GOOF = 1.027, largest difference peak and hole: 0.523/-0.304 e Å⁻³.

Crystal Data for 4v:^[29] C₁₈H₂₈O₄·1/6C₆H₁₄, *Mr* = 322.41 gmol⁻¹, colourless prism, size 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) Å³, *T* = -90 °C, *Z* = 6, $\rho_{calcd.}$ = 1.220 g cm⁻³, μ (Mo-*K*_a) = 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° $\leq \Theta \leq 27.46^{\circ}$, completeness $\Theta_{max} = 99.9\%$, 3574 independent reflections, *R*_{int} = 0.036, 2704 reflections with *F*_o > 4 σ (*F*_o), 208 parameters, 1 restraints, *RI*_{obs} = 0.056, *wR*²_{obs} = 0.140, *RI*_{all} = 0.082, *wR*²_{all} = 0.155, GOOF = 1.054, Flack parameter 0.2(15) (the absolute structures could not

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