DOI: 10.1002/ejoc.201100916

Cross-Metathesis Reactions of Homoallyl Methyl Malonates with Sterically Hindered Allylic Esters

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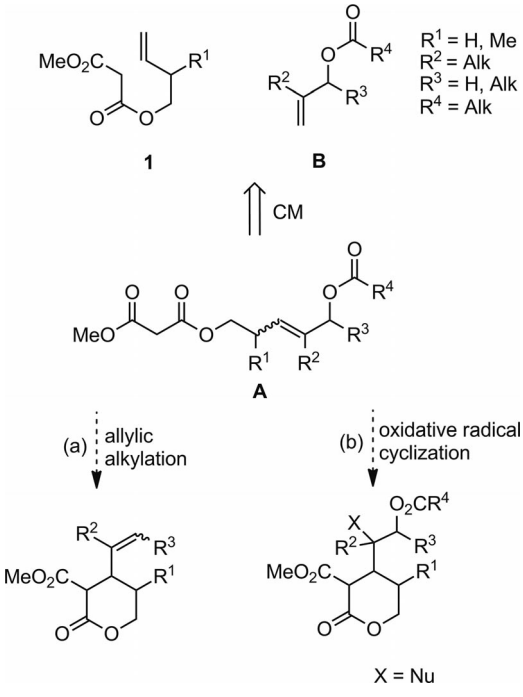
Keywords: Metathesis / Alkenes / Cross-coupling / Ruthenium / Homogeneous catalysis

The methyl malonate esters of 3-buten-1-ol and 2-methyl-3-buten-1-ol can be coupled efficiently to different methallylic esters in the presence of the second-generation Grubbs catalyst to yield trisubstituted olefins by the cross-metathesis reaction. Product selectivity and yields depend on the relative amounts of reagents and to a minor extent on the methallylic ester functional group. Alkyl substituents at either the allylic or the geminal positions significantly affect the product yields and the *E*/*Z* stereoselectivity.

Introduction

Among the various olefin metathesis processes,[1] cross metathesis (CM) has gained increasing relevance as a convenient synthetic tool in organic chemistry.[1,2] This is the result of the evolution of new catalysts and the advancements in the efficiency, selectivity, and functional group compatibility of the process. The continuous expansion of literature data has even led to a general model for predicting the product and stereoselectivity of a cross-metathesis reaction, depending on the type of catalyst and olefin functionalization.[3] As a consequence, the installation of structural elements within complex natural products or the synthesis of intermediates for further synthetic transformations are currently the most significant expressions of olefin CM. In recent years, our group has focused on the synthesis of γ- and δ-lactones by different synthetic methodologies, including ring-closing metathesis.[4] The development of this research enhanced our interest in the synthesis of intermediates of general structure **A** containing a trisubstituted double bond (Scheme 1). Taking aside the importance of trisubstituted double bond subunits in natural products,[2e] such intermediates could be subsequently transformed into lactone skeletons, either by an intramolecular metal-catalyzed allylic alkylation (Scheme 1, path a)[5] or by oxidative radical cyclization (Scheme 1, path b).[6] A concise retrosynthetic analysis carried out on compounds **A**, and the resulting disconnection of their trisubstituted double bond, clearly indicate CM of homoallyl malonate **1** and allyl esters **B** as a convenient approach for their preparation. Whereas allylic esters are known to react efficiently in CM reactions,[3,7] the use of an olefin bearing a malonate group as CM partner is rare. The reported cases include the reaction between acrylonitrile and diethyl 2-allylmalonate, $CH_2{=}CHCH_2CH(CO_2Et)_2$, which afforded the desired CM product in good yield,[8] and the incorporation of diallyl



Scheme 1. Retrosynthetic analysis of bifunctional trisubstituted olefins as potential precursors of lactone skeletons.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201100916.

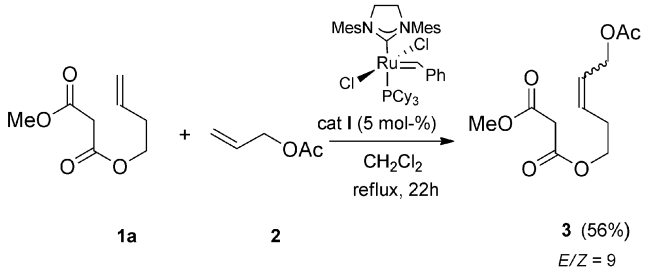
malonate into the backbone of polycyclooctene by a combination of ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis (ADMET) processes.[9]

These examples indicate that the C–H acidity and the chelating ability of the malonate group are not detrimental to the metathetic process catalyzed by carbene–ruthenium complexes.[10] However, the reactivity of linear allyl or homoallyl malonate esters in CM reactions can be regarded at present as virtually unknown. By contrast, the access to malonate-substituted olefins by CM and therefore to valuable intermediates for subsequent transformations would be highly desirable, the malonate moiety being one of the most versatile functional groups for C–C or C–O bond formation in organic synthesis.[11]

Herein we report on the CM reactions between the methyl homoallyl malonate derivatives of general formula CH_2=CH(CHR)$CH_2OCOCH_2CO_2Me$ [R = H (**1a**); Me (**1b**)] and allylic partners with different electronic and steric properties. In particular, we have addressed the effect of the position and steric hindrance of alkyl groups in the allylic moieties on the reaction, which is a key factor in the construction of alkyl-functionalized trisubstituted olefins.

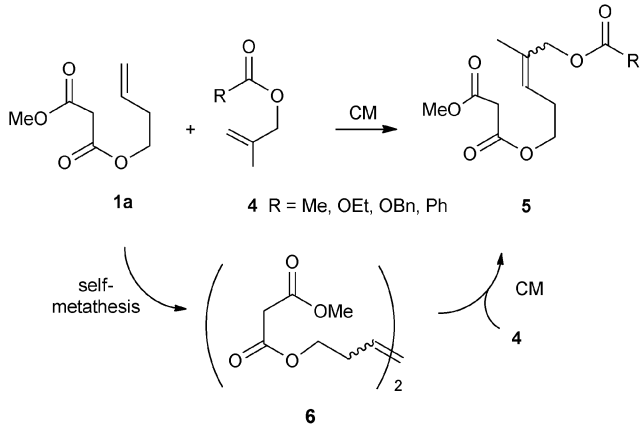
Results and Discussion

The olefin metathesis experiments were performed with the second-generation Grubbs catalyst **I** due to its tolerance towards polar functional groups and the recognized activity of the 1,3-disubstituted 4,5-dihydroimidazol-2-ylidene–ruthenium complexes in the formation of trisubstituted alkenes by CM.[3,12] Homoallyl methyl malonate **1a** was prepared by the reaction of 3-buten-1-ol with methyl malonyl chloride in the presence of NEt_3 and obtained as a light-yellow oil after column chromatography in 70% yield. The methyl-substituted analogue **1b** was obtained similarly from 2-methyl-3-buten-1-ol in 35% yield. To test the compatibility of the malonate moiety in the CM process, ester **1a** was treated with the monosubstituted allyl acetate (**2**; Scheme 2). Olefin **2** was used in 5 equiv. molar excess; in fact, the reaction between two terminal olefins, expected to exhibit fast homodimerization rates and similar reactivity of the homodimers and of the cross-products, requires the use of one of them in excess to avoid nonselective product mixtures.[3]



Scheme 2. CM reaction between homoallyl methyl malonate **1a** and allyl acetate (**2**).

In the presence of **I** (5 mol-%), the desired CM product **3** was isolated in 56% yield with an *E*/*Z* ratio of 9. Although the stereoselectivity is remarkably high, the moderate yield of the CM derivative may reflect a mild deactivating effect of the malonate group; yields of up to 80% are not uncommon for CM reactions involving two monosubstituted terminal olefins. Once the compatibility of the β-diester function in the metathetic process had been verified, we studied the reactivity of **1a** with methallylic esters for the synthesis of trisubstituted olefins (Scheme 3). When homoallyl malonate was treated with methallyl acetate (3.3 equiv. **4a**, 3 mol-% **I**), the CM product **5a** was obtained with 28% yield with a stereoisomeric ratio *E*/*Z* of 3.4. The result was encouraging and indicated the ability of an olefin bearing a malonate moiety to cross-react with a *gem*-disubstituted olefin partner, in spite of the increased steric hindrance of the allylic ester, in the presence of a relatively low catalyst load. The reaction between the same partners in a 4:1 molar ratio in the presence of the second-generation Hoveyda–Grubbs catalyst (4 mol-%) afforded the product **5a** in 21% yield, which indicates a higher activity of the Grubbs catalyst. Therefore the reaction of **1a** with methallylic partners **4** in the presence of complex **I** was investigated more systematically by varying the ester functionalities and the reaction conditions in an attempt to improve the yields of the trisubstituted olefins. The reactions were performed with an excess of either the methallyl substrate or the terminal olefin. Both conditions should assist selective cross metathesis.[3] The *gem*-disusbstituted ester, unreactive towards homodimerization due to the sterically hindered double bond, is expected to undergo the desired reaction with a terminal olefin. Conversely, a monosubstituted olefin used in excess can undergo both CM with the allylic ester and homodimerization by self-metathesis. The homodimer can react further with the methallyl ester in a secondary metathesis process, thus increasing the conversion into the desired heterodimer (Scheme 3). The products and yields obtained under the different conditions are presented in Table 1.



Scheme 3. Primary and secondary cross-metathesis processes in the reactions between methallylic esters **4** and homoallyl methyl malonate **1a**.

Table 1. Cross-metathesis reactions of homoallyl methyl malonate **1a** with methallyl esters **4**.

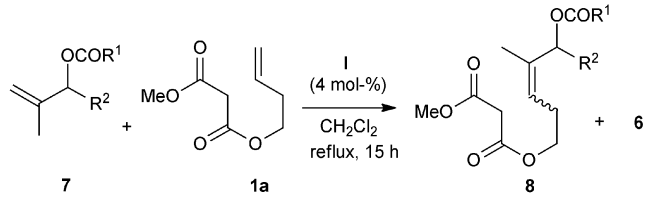
Entry	R	**4**/**1a**	Product	Yield [%][a]	*E*/*Z*	Yield of **6** [%][a]
1[b]	Me	3.3:1	**5a**	28	3.4	–
2[c]	Me	4:1	**5a**	78	5.0	trace
3[c]	Me	1:2	**5a**	28	3.4	57
4[b,d]	OEt	3.1:1	**5b**	24	3.7	–
5[c]	OEt	4:1	**5b**	58	3.7	15
6[b]	Ph	3.4:1	**5c**	20	3.4	–
7[c]	Ph	1:2.5	**5c**	43	3.9	–[e]
8[c,f]	Ph	1:2.5	**5c**	57	3.4	–[e]
9[c]	OBn	1:2	**5d**	40	3.7	42

[a] Isolated yield. [b] 3 mol-% **I**. [c] 4 mol-% **I**. [d] 22 h. [e] Not determined. [f] Addition of **I** over 6 h through a syringe pump.

When the methallyl ester was used in about a three-fold molar excess with respect to **1a**, the yields remained in the range of 20–30%, irrespective of the nature of the ester moiety, which was changed from acetate (Table 1, Entry 1) to ethyl carbonate (Table 1, Entry 4) to benzoate (Table 1, Entry 6). The CM efficiency improved appreciably by using 4 mol-% of catalyst **I** and a four-fold molar excess of the methallyl substrate (Table 1, Entries 2 and 5), the best yield and stereoselectivity being obtained in the case of the acetate (78%). In contrast, when using 2 equiv. of homoallyl methyl malonate, the yield of **5a** was the same (28%; Table 1, Entry 3) as that obtained under the conditions of Entry 1 (Table 1) and it was accompanied by a significant amount of the homodimer **6**, whereas the yield of the benzoate derivative **5c** was appreciably higher (Table 1, Entry 7). With the same molar ratio, the slow and constant addition of complex **I** in dichloromethane (0.015 M) to the reaction solution of **4c** (0.38 M) and **1a** over 6 h led to a significant increase in the amount of CM product (57%; Table 1, Entry 8).[13,14] In an attempt to reduce the interactions of the coordinating malonate group with the catalyst and so the presence of an inactive ruthenium species, the reactions of Entries 1 and 6 (Table 1) were repeated in the presence of $Ti(OiPr)_4$. Indeed, $Ti(OiPr)_4$ has proved to be a useful additive in RCM reactions of substrates with oxygen donor functional groups, in particular olefinic esters, due to their affinity for the electrophilic metal center.[15] However, in our case the addition of this Lewis acid led to the complete inhibition of the reaction when an equimolar amount with respect to **1** was used under the conditions of Entry 1 (Table 1), or a 25% yield of **5c** when a catalytic amount was used under the conditions of Entry 7 (Table 1).

We then investigated the influence of increased steric hindrance at the allylic carbon in the CM reaction with homoallyl methyl malonate. To choose the correct molar ratio between the two olefin types, the homodimer **6** was treated with ester **7b**. No products were observed from the reaction, which indicates the inability of the internal olefin to participate in CM with this ester. Therefore tertiary methallylic acetates **7** bearing alkyl groups R^2 of increasing steric bulk at the allylic carbon were treated with a four-fold molar excess of **1a**. These conditions resulted in productive CM (Table 2).

Table 2. Cross-metathesis reactions of homoallyl methyl malonate **1a** with tertiary allylic esters **7**.[a]



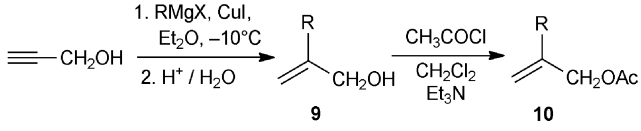
7 **1a** **8**

Entry	R^1	R^2	Product	Yield [%][b]	*E*/*Z*	Yield of **6** [%]
1	Me	Et	**8a**	31	20	39
2	Me	*n*Bu	**8b**	38	21	42
3	Me	$nC_{10}H_{21}$	**8c**	38	20	30
4	OBn	*n*Bu	**8d**	34	24	44
5	Me	*i*Pr	**8e**	11	all *E*	74
6	Me	*c*Pn[c]	**8f**	7	18	80

[a] Molar ratio of **7**/**1a** = 4:1. [b] Isolated yield. [c] *c*Pn = cyclopentyl.

The malonate derivatives **8** were prepared with excellent stereoselectivity; similar features were observed in the CM products of quaternary allylic olefins.[3] Although the yields remained low, the involvement of olefins with alkyl substituents at both the geminal and the allylic carbon atoms in CM reactions is not common. The length of the linear alkyl chain did not affect the actual outcomes (Table 2, Entries 1–3), but greater steric congestion at the allylic carbon due to the presence of secondary isopropyl or cyclopentyl groups reduced the CM product yield to around 10% (Table 2, Entries 5 and 6). In spite of the molar excess of esters **7**, consistent amounts of the homodimer **6** were recovered from these reactions.

The influence of alkyl groups R other than methyl at the quaternary sp^2 carbon in the allylic partner was studied by treating olefin **1a** with acetate esters of general formula $CH_2=C(R)CH_2OAc$ (**10**). These compounds were easily prepared starting from the corresponding alcohols **9**, accessible by literature procedures (Scheme 4).[16] Esters **10** were then treated with malonate **1a** and the results are shown in Table 3.

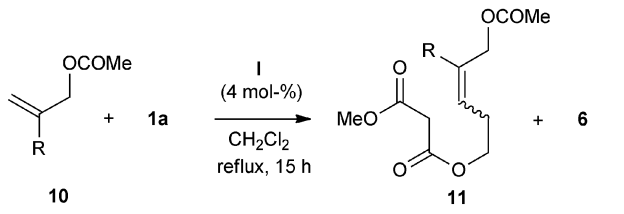


9 **10**

Scheme 4. Preparation of compounds **10** (R = Et, Bu, *c*Pn).

When comparing the reactivity of the ethyl-substituted ester **10a** with that of its methyl analogue **4a** under identical reaction conditions (78%; Table 1, Entry 2), it is evident that a secondary carbon group causes a significant reduction in the yield of the CM product (Table 3, Entry 1), which decreases further in the presence of the butyl group (Table 3, Entry 2). The CM reaction is suppressed for R = cyclopentyl. In addition, there is a complete loss of stereo-

Table 3. Cross-metathesis reactions of homoallyl methyl malonate **1a** with *gem*-disubstituted allylic acetates **10**.[a]



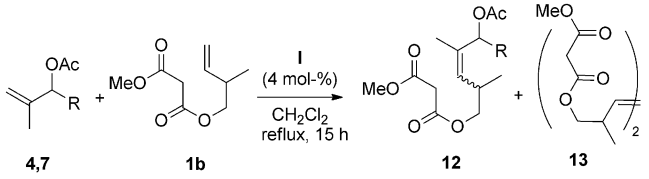
Entry	10	R	Product	Yield [%][b]	*E*/*Z*	Yield of 6 [%][b]
1	**10a**	Et	**11a**	59	1:1	–
2	**10b**	Bu	**11b**	36	1:1	51
3[c]	**10c**	*c*Pn	n.r.	–	–	63

[a] Molar ratio of **10/1a** = 4:1. [b] Isolated yield. [c] *c*Pn = cyclopentyl.

selectivity as a result of the comparable steric bulk of the *gem* substituents in esters **10**.

The methyl-substituted homoallyl methyl malonate **1b** was allowed to react with selected methallylic esters (**4a**, **7b**, **7f**) in order to evaluate the effect of steric hindrance on the malonate partner. The results are shown in Table 4.

Table 4. Cross-metathesis reactions of homoallyl methyl malonate **1b** with selected allylic esters **4** and **7**.[a]



Entry	Ester	R	Product	Yield [%][b]	*E*/*Z*	Yield of 13 [%]
1	**4a**	H	**12a**	43	4	45
2	**7b**	*n*Bu	**12b**	28	all *E*	68
3	**7f**	*c*Pn	n.r.	–	–	53

[a] Molar ratio of **7/1b** = 4:1. [b] Isolated yield.

The presence of the methyl group in **1b** resulted in a significant decrease in yield with respect to the analogous reactions carried out with malonate **1a**. This effect is particularly evident in the case of the methallylic partner **4a** (see for comparison Table 1, Entry 2; 78%) and becomes even larger for esters bearing an alkyl substituent at the allylic position. In fact, the presence of a secondary cyclopentyl group inhibits the CM reaction. In all cases, the homodimer **13** from the self-metathesis of **1b** was obtained. Note that only the *E* isomer was isolated from the reaction with **7b**.

Conclusions

The cross-metathesis reactions of malonate esters CH_2=CHCH(R)CH_2OCOCH_2CO_2Me (R = H, Me) with methallyl esters CH_2=C(R^3)CH(OCOR^1)R^2 featuring different alkyl groups afforded trisubstituted olefins functionalized with both the malonate and the allylic ester moieties. Thus, we have shown that homoallyl malonate derivatives are reactive CM partners for mono- and 1,1-disubstituted allylic esters. In the presence of alkyl groups at the allylic position, the CM products are formed with high *E*/*Z* stereoselectivity, which is important for the synthesis of naturally occurring compounds.

Experimental Section

General Methods: ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ with a 300 MHz Mercury Varian spectrometer. The calibration of spectra was carried out by using solvent signals ($CDCl_3$: δ_H = 7.25, δ_C = 77.0 ppm). The *E*/*Z* ratios were determined by NMR and GC–MS analysis, and the major isomer was deduced by the NOESY correlation of selected compounds (see the Supporting Information). IR spectra were recorded with a Shimadzu IR 470 spectrometer in $CHCl_3$ using NaCl cells. GC–MS analyses were performed with an HP 5890 gas chromatograph linked to an HP 5791 mass spectrometer. HRMS (ESI) spectra were recorded with a QTOF Micro spectrometer (Waters) operating in positive ion mode. Chemicals were commercially available and used without further purification. Dichloromethane was dried by distillation over P_2O_5. All the reactions were analyzed by TLC on silica gel plates (60 F_{254}). Column chromatography was performed on silica gel 60 (Merck, 70–230 mesh). The CM reactions were performed under Ar using standard Schlenk techniques. 2-Methyl-2-propenyl acetate (**4a**)[17a] and 2-methyl-2-propenyl benzoate (**4c**)[17b] were prepared as described in the literature.

Homoallyl Methyl Malonates 1a and 1b: Triethylamine (28 mL) was added to a solution of 3-buten-1-ol (2.03 g, 28 mmol) or 2-methyl-3-buten-1-ol (2.40 g, 28 mmol) in CH_2Cl_2 (25 mL) under argon. The resulting mixture was cooled in an ice bath and then a solution of methyl 3-chloro-3-oxopropionate (4.9 g, 36 mmol) in CH_2Cl_2 (15 mL) was added dropwise whilst stirring. The reaction was complete after 3 h (TLC). After addition of aq. 2 N HCl (6 mL), the reaction mixture was extracted with CH_2Cl_2 and the organic phase was washed with aq. sat. $NaHCO_3$ and then with water until neutrality. The organic phase was dried (Na_2SO_4) and the solvent evaporated under reduced pressure to give an oily residue, which was purified by column chromatography (silica gel, light petroleum ether/Et_2O, 7:3) to afford pure compounds **1** as colorless oils (3.37 g, 70% for **1a**; 1.82 g, 35% for **1b**). A previous report of **1a** did not report analytical and characterization data.[18]

Compound 1a: Colorless oil. IR ($CHCl_3$): $\tilde{\nu}$ = 1737, 1462, 1281 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.36 (qt, J = 6.7, 1.5 Hz, 2 H, CH_2C=), 3.35 [s, 2 H, $CH_2(C{=}O)_2$], 3.70 (s, 3 H, OCH_3), 4.16 (t, J = 6.7 Hz, 3 H, CH_2O), 5.07 (m, 2 H, CH_2=), 5.69 (ddt, J = 17.0, 10.3, 6.8 Hz, 1 H, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 31.7, 41.3, 52.4, 64.7, 117.4, 133.5, 166.3, 166.8 ppm. GC–MS (EI, 70 eV): *m*/*z* (%) = 101 (100), 59 (40), 55 (30), 54 (84).

Compound 1b: Colorless oil. IR ($CHCl_3$): $\tilde{\nu}$ = 2950, 1750, 1326 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.00 (d, J = 6.6 Hz, 3 H, CH_3CH), 2.50 (sext., J = 6.6 Hz, 1 H, CHCH$_3$), 3.34 [s, 2 H, $CH_2(C{=}O)_2$], 3.70 (s, 3 H, OCH_3), 3.99 (m, 2 H, CH_2O), 5.03 (m, 2 H, CH_2=), 5.69 (ddd, J = 17.6, 10.3, 7.3 Hz, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.2, 36.7, 41.2, 52.2, 69.1, 115.0, 139.5, 166.3, 166.8 ppm. HRMS (ESI): calcd. for $C_9H_{14}O_4$+Na [M + Na]$^+$ 209.0790; found 209.0794.

1-Acetoxy-5-(3′-methoxy-3′-oxopropionyloxy)-2-pentene (3): Allyl acetate **2** (1.32 g, 13.2 mmol) and ester **1a** (419 mg, 2.4 mmol) were

added whilst stirring to a CH_2Cl_2 solution (20 mL) of catalyst **I** (78 mg, 0.092 mmol). After 22 h at reflux, the solvent was removed under reduced pressure and the oily residue was purified by column chromatography (silica gel, light petroleum ether/Et_2O, 7:3) to afford pure compound **3** as a colorless oil (0.33 g, 56%). IR ($CHCl_3$): $\tilde{\nu}$ = 3010, 1735, 1430, 1240, 1100, 1020 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.97 (s, 3 H, CH_3CO), 2.37 (m, 2 H, CH_2CH_2CH=), 3.30 [s, 2 H, $CH_2(C{=}O)_2$], 3.65 (s, 3 H, OCH_3), 4.09 (t, J = 6.7 Hz, 2 H, Z isomer, CH_2CH_2O), 4.10 (t, J = 6.7 Hz, 2 H, E isomer, CH_2CH_2O), 4.43 (d, J = 5.4 Hz, 2 H=, E isomer, OCH_2CH), 4.53 (d, J = 5.4 Hz, 2 H, Z isomer, OCH_2CH=), 5.60 (m, 2 H, CH=CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 26.7, 31.2, 41.0, 52.3, 59.9, 64.1, 64.2, 64.5, 126.3, 126.8, 129.3, 130.3, 166.2, 166.7, 170.5 ppm. HRMS (ESI): calcd. for $C_{11}H_{16}O_6Na$ [M + Na]$^+$ 267.0845; found 267.0847.

General Procedure for Preparation of Methallyl Carbonates 4b and 4d: A solution of 2-methyl-2-propen-1-ol (1.17 mL, 13.9 mmol) and the desired ethyl or benzyl chloroformate (20 mmol) in CH_2Cl_2 (36 mL) was cooled to 0 °C. Pyridine (1.61 mL, 20 mmol) was added dropwise over 45 min. After 12 h, the reaction mixture was diluted with additional CH_2Cl_2 (10 mL), washed with 2 N HCl (2 × 10 mL), then with aq. sat. $NaHCO_3$ (3 × 5 mL). The organic phase was dried with Na_2SO_4 and the solvent removed under reduced pressure. The resulting oily residue was purified by column chromatography (silica gel, light petroleum ether/Et_2O, 95:5) to afford pure **4**.

Ethyl 2-Methyl-2-propenyl Carbonate (4b): Colorless oil; yield: 77%. IR ($CHCl_3$): $\tilde{\nu}$ = 2980, 1740, 1480, 1400, 1290 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.27 (t, J = 7.1 Hz, 3 H, CH_3CH_2), 1.73 (s, 3 H, CH_3C=), 4.16 (q, J = 7.1 Hz, 2 H, CH_3CH_2O), 4.49 (s, 2 H, CH_2O), 4.94 (m, 2 H, CH_2=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.2, 19.3, 63.9, 70.9, 113.3, 139.4, 155.0 ppm. HRMS (ESI): calcd. for $C_7H_{12}O_3Na$ [M + Na]$^+$ 167.0684; found 167.0690.

Benzyl 2-Methyl-2-propenyl Carbonate (4d): Colorless oil; yield: 41%. IR ($CHCl_3$): $\tilde{\nu}$ = 2965, 1742, 1398, 1282 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.77 (s, 3 H, CH_3C=), 4.56 (s, 2 H, CH_2O), 4.97 (m, 2 H, CH_2=), 5.17 (s, 2 H, OCH_2Ph), 7.37 (m, 5 H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.2, 69.5, 71.1, 113.5, 128.2, 128.4, 128.5, 135.3, 139.3, 155.0 ppm. GC–MS (EI, 70 eV): m/z (%) = 151 (16), 107 (14), 91 (100). HRMS (ESI): calcd. for $C_{12}H_{14}O_3Na$ [M + Na]$^+$ 229.0841; found 229.0834.

General CM Procedure for the Synthesis of Compounds 5: Homoallyl malonate **1a** (0.5 mmol) and up to 4 equiv. of ester **4** (2.0 mmol) were dissolved in CH_2Cl_2 (10 mL). The mixture was heated at reflux and a solution of catalyst **I** (0.015 or 0.02 mmol) in CH_2Cl_2 (6 mL) was added dropwise through a syringe pump over 45 min. The mixture was heated at reflux for 15 h. Removal of solvent under reduced pressure afforded an oily residue that was purified by column chromatography (silica gel, light petroleum ether/Et_2O, 8:2) to afford pure compound **5** and homodimer **6**, both as colorless oils. Reaction yields are reported in Table 1.

1-Acetoxy-5-(3′-methoxy-3′-oxopropionyloxy)-2-methyl-2-pentene (5a, Table 1, Entries 1–3): Colorless oil. IR ($CHCl_3$): $\tilde{\nu}$ = 3010, 1743, 1446, 1390, 1345, 1291 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.64 (s, 3 H, E isomer, CH_3C=), 1.74 (s, 3 H, Z isomer, CH_3C=), 2.04 (s, 3 H, Z isomer, CH_3CO), 2.05 (s, 3 H, E isomer, CH_3CO), 2.40 (m, 2 H, CH_2CH_2CH=), 3.35 [s, 2 H, $CH_2(C{=}O)_2$], 3.71 (s, 3 H, OCH_3), 4.12 (t, J = 6.6 Hz, 2 H, OCH_2CH_2), 4.42 (s, 2 H, E isomer, CH_2OAc), 4.54 (s, 2 H, Z isomer, CH_2OAc), 5.38 (m, 1 H, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9, 20.7, 20.8, 21.4, 26.9, 27.0, 41.2, 52.4, 64.4, 64.6, 68.2, 123.4, 124.9, 133.1, 166.3, 166.8, 170.7, 170.8 ppm. GC–MS (EI, 70 eV): m/z (%) = 140 (40), 98 (100), 80 (96), 81 (64), 59 (36). HRMS (ESI): calcd. for $C_{12}H_{18}O_6Na$ [M + Na]$^+$ 281.1001; found 281.1005.

Ethyl 2′-Methyl-5′-(3′′-methoxy-3′′-oxopropionyloxy)pent-2′-enyl Carbonate (5b, Table 1, Entries 4 and 5): Colorless oil; E/Z = 3.7:1. IR ($CHCl_3$): $\tilde{\nu}$ = 2934, 1748, 1716, 1420, 1362, 1232 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.27 (t, J = 7.0 Hz, 3 H, CH_3CH_2O), 1.66 (s, 3 H, E isomer, CH_3C=), 1.76 (s, 3 H, Z isomer, CH_3C=), 2.40 (m, 2 H, CH_2CH_2CH=), 3.33 [s, 2 H, $CH_2(C{=}O)_2$], 3.70 (s, 3 H, OCH_3), 4.13 (m, 4 H, CH_3CH_2O), 4.47 (s, 2 H, E isomer, $CH_2OC{=}O$), 4.59 (s, 2 H, Z isomer, $CH_2OC{=}O$), 5.36 (m, 1 H, E isomer, CH=), 5.44 (m, 1 H, Z isomer) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9, 14.2, 21.3, 27.0, 27.1, 41.2, 52.4, 63.9, 64.4, 65.9, 72.7, 124.1, 125.6, 132.7 ppm. GC–MS (EI, 70 eV): m/z (%) = 170 (23), 101 (50), 81 (88), 80 (100), 79 (53), 69 (33), 59 (35). HRMS (ESI): calcd. for $C_{13}H_{20}O_7Na$ [M + Na]$^+$ 311.1107; found 311.1112.

1-Benzoyloxy-5-(3′-methoxy-3′-oxopropionyloxy)-2-methyl-2-pentene (5c, Table 1, Entries 6–8): Colorless oil. IR ($CHCl_3$): $\tilde{\nu}$ = 2950, 1718, 1452, 1386, 1315, 1274, 1177, 1070 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.74 (s, 3 H, E isomer, CH_3C=), 1.85 (s, 3 H, Z isomer, CH_3C=), 2.44 (m, 2 H, CH_2CH_2CH=), 3.35 [s, 2 H, $CH_2(C{=}O)_2$], 3.72 (s, 3 H, OCH_3), 4.07 (t, J = 6.9 Hz, 2 H, Z isomer, OCH_2CH_2), 4.09 (t, J = 6.9 Hz, 2 H, E isomer, OCH_2CH_2), 4.71 (s, 2 H, E isomer, CH_2OBz), 4.83 (s, 2 H, Z isomer, CH_2OBz), 5.36 (m, 1 H, Z isomer, CH=), 5.53 (m, 1 H, E isomer, CH=), 7.43 (m, 2 H, Ar), 7.55 (tt, J = 7.4, 1.3 Hz, 1 H, Ar), 8.03 (m, 2 H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5, 15.6, 21.3, 21.9, 27.6, 27.7, 63.9, 64.1, 66.2, 70.4, 124.4, 125.9, 128.7, 130.0, 130.6, 133.3, 133.5, 166.7, 171.4 ppm. GC–MS (EI, 70 eV): m/z (%) = 105 (100), 77 (18). HRMS (ESI): calcd. for $C_{17}H_{20}O_6Na$ [M + Na]$^+$ 343.1158; found 343.1156.

Benzyl 2′-Methyl-5′-(3′′-methoxy-3′′-oxopropionyloxy)pent-2′-enyl Carbonate (5d, Table 1, Entry 9): Colorless oil; yield: 40%; E/Z = 3.7:1. IR ($CHCl_3$): $\tilde{\nu}$ = 2910, 1750, 1722, 1453, 1390, 1265 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.68 (s, 3 H, E isomer, CH_3C=), 1.78 (s, 3 H, Z isomer, CH_3C=), 2.40 (q, J = 7.3 Hz, 2 H, OCH_2CH_2CH=), 3.36 [s, 3 H, $CH_2(C{=}O)_2$], 3.73 (s, 3 H, OCH_3), 4.14 (t, J = 6.6 Hz, 2 H, OCH_2CH_2), 4.53 (s, 2 H, E isomer, $PhCH_2$), 4.64 (s, 2 H, $PhCH_2$), 5.46 (t, J = 7.3 Hz, 1 H, CH=), 7.36 (m, 5 H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.8, 27.0, 41.2, 52.3, 64.3, 69.6, 73.0, 124.2, 132.6, 135.2, 154.9, 166.3, 166.7 ppm. GC–MS (EI, 70 eV): m/z (%) = 170 (7), 101 (10),97 (24), 91 (100), 81 (16). HRMS (ESI): calcd. for $C_{18}H_{22}O_7Na$ [M + Na]$^+$ 373.1263; found 373.1265.

1,5-Bis(3′-methoxy-3′-oxopropionyloxy)-3-pentene (6, Table 1, Entries 3, 5, 9, Table 2, Table 3): Colorless oil; E/Z mixture. IR ($CHCl_3$): $\tilde{\nu}$ = 2974, 1725, 1489, 1358, 1249 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.33 (m, 4 H, OCH_2CH_2CH=), 3.38 [s, 4 H, $CH_2(C{=}O)_2$], 3.74 (s, 6 H, OCH_3), 4.15 (t, J = 7.3 Hz, 4 H, OCH_2CH_2), 5.49 (m, 2 H, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 31.7, 41.2, 52.3, 64.7, 128.1, 166.3, 166.8 ppm. HRMS (ESI): calcd. for $C_{14}H_{20}O_8Na$ [M + Na]$^+$ 339.1056; found 339.1049.

General Procedure for the Synthesis of Esters 7: A solution of methacrolein (3.0 mmol) was cooled in an ice bath under argon and the appropriate Grignard reagent ($BrMgR^2$; R^2 = Et, Bu, $nC_{10}H_{11}$, iPr, or cPn; 4.5 mmol, 2 M solution in THF) was added dropwise whilst stirring. After 4 h, the reaction mixture was poured into water (10 mL) and aq. 6 N HCl was added dropwise until the solid dissolved completely. After addition of CH_2Cl_2 (30 mL), the separated organic phase was washed with aq. sat. $NaHCO_3$, then with water, and finally dried (Na_2SO_4). Removal of solvent under reduced pressure afforded the desired crude methallyl alcohols as oils. Acetates **7a**–**c**,**e**,**f** were obtained by reaction of the methallyl alcohol

CH_2=C(Me)CH(R^2)OH with acetic anhydride in pyridine, whereas carbonate **7d** was obtained by reaction of CH_2=C(Me)CH(Bu)OH with benzoyl chloride in dichloromethane. The products were purified by column chromatography.

3-Acetoxy-2-methyl-1-pentene (7a): Colorless oil; obtained from CH_2=C(Me)CH(Et)OH; yield: 92%. IR ($CHCl_3$): $\tilde{\nu}$ = 2945, 1723, 1462, 1383, 1278, 1018 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.85 (t, J = 7.3 Hz, 3 H, CH_3CH$_2$), 1.63 (quint., J = 7.3 Hz, 2 H, CH$_3$CH_2), 1.69 (s, 3 H, CH_3C=), 2.04 (s, 3 H, CH_3CO), 4.88 (m, 2 H, CH_2=), 5.07 (t, J = 7.3 Hz, 1 H, CHO) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 9.6, 18.0, 21.1, 25.5, 78.5, 108.3, 112.6, 170.1 ppm. HRMS (ESI): calcd. for $C_8H_{14}O_2Na$ [M + Na]$^+$ 165.0891; found 165.0895.

3-Acetoxy-2-methyl-1-heptene (7b): Colorless oil; obtained from CH_2=C(Me)CH(Bu)OH; yield: 79%. IR ($CHCl_3$): $\tilde{\nu}$ = 3060, 1727, 1446, 1260, 1021 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.96 [t, J = 6.6 Hz, 3 H, (CH$_2$)$_3$CH_3], 1.43 (m, 6 H, CH_2CH_2CH_2), 1.71 (s, 3 H, CH_3C=), 2.01 (s, 3 H, CH_3CO), 4.90 (m, 2 H, CH_2=), 5.12 (t, J = 6.6 Hz, 1 H, CHO) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9, 17.4, 17.7, 23.2, 26.9, 31.5, 83.2, 107.2, 150.0, 171.5 ppm. HRMS (ESI): calcd. for $C_{10}H_{18}O_2Na$ [M + Na]$^+$ 193.1204; found 193.1200.

3-Acetoxy-2-methyl-1-tridecene (7c): Colorless oil; obtained from CH_2=C(Me)CH(nC$_{10}$H$_{11}$)OH; yield: 66%. IR ($CHCl_3$): $\tilde{\nu}$ = 2925, 1736, 1471, 1386, 1078 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.86 [t, J = 6.6 Hz, 3 H, (CH$_2$)$_9$CH_3], 1.42 [m, 18 H, (CH$_2$)$_9$], 1.71 (s, 3 H, CH_3C=), 2.01 (s, 3 H, CH_3CO), 4.90 (m, 2 H, CH_2=), 5.13 (t, J = 6.6 Hz, 1 H, CHO) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 18.1, 21.2, 22.7, 25.4, 25.5, 29.4, 29.6, 29.7, 32.0, 77.5, 112.6, 143.4, 170.3 ppm. HRMS (ESI): calcd. for $C_{16}H_{30}O_2Na$ [M + Na]$^+$ 277.2143; found 277.2145.

Benzyl 2′-Methylhept-1′-en-3′-yl Carbonate (7d): Colorless oil; obtained from CH_2=C(Me)CH(Bu)OH; yield: 35%. IR ($CHCl_3$): $\tilde{\nu}$ = 2965, 1735, 1462, 1394, 1200 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.98 [t, J = 7.3 Hz, 3 H, (CH$_2$)$_3$CH_3], 1.32 (m, 4 H, CH_2CH_2), 1.70 (m, 2 H, CH_2), 1.75 (s, 3 H, CH_3C=), 4.60 (s, 2 H, CH_2Ph), 5.00 (m, 3 H, CHO, CH_2=), 7.38 (m, 5 H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.8, 17.7, 22.3, 27.3, 32.3, 69.3, 81.8, 113.3, 128.2, 128.3, 128.5, 135.5, 142.7, 154.7 ppm. HRMS (ESI): calcd. for $C_{16}H_{22}O_3Na$ [M + Na]$^+$ 285.1467; found 285.1473.

3-Acetoxy-2,4-dimethyl-1-pentene (7e): Colorless oil; obtained from CH_2=C(Me)CH(iPr)OH; yield: 55%. IR ($CHCl_3$): $\tilde{\nu}$ = 2965, 1735, 1462, 1394, 1200 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 085 (d, J = 6.6 Hz, 3 H, CH_3CH), 0.89 (d, J = 6.6 Hz, 3 H, CH_3CH), 1.68 (s, 3 H, CH_3C=), 1.90 [m, 1 H, CH(CH$_3$)$_2$], 2.05 (s, 3 H, CH_3CO), 4.89 (m, 3 H, CHO, CH_2=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.9, 18.3, 19.0, 21.0, 29.7, 82.4, 113.6, 142.4, 170.3 ppm. HRMS (ESI): calcd. for $C_9H_{16}O_2Na$ [M + Na]$^+$ 179.1048; found 179.1044.

3-Acetoxy-3-cyclopentyl-2-methyl-1-propene (7f): Colorless oil; obtained from CH_2=C(Me)CH(cPn)OH; yield: 78%. IR ($CHCl_3$): $\tilde{\nu}$ = 2944, 1738, 1423, 1372, 1225 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.38 (m, 8 H, $CH_2CH_2CH_2CH_2$), 1.71 (s, 3 H, CH_3C=), 1.97 (m, 1 H, CH_2CHCH$_2$), 2.06 (s, 3 H, CH_3CO), 4.53 (d, J = 7.2 Hz, 1 H, CHO), 4.96 (m, 2 H, CH_2=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.0, 23.8, 25.0, 31.4, 32.7, 43.5, 66.8, 110.0, 147.4, 170.7 ppm. HRMS (ESI): calcd. for $C_{11}H_{18}O_2Na$ [M + Na]$^+$ 205.1204; found 205.1206.

General Procedure for the Synthesis of Esters 8, 11, and 12: Compound **1** (0.5 mmol) and methallyl esters **7** or **10** (2 mmol) were dissolved in CH_2Cl_2 (10 mL) under argon. While keeping the reaction flask at 40 °C, a solution of catalyst **I** (4 mol-%) in CH_2Cl_2 (6 mL) was added dropwise over 45 min. The reaction was kept at reflux for 15 h and then the solvent was removed under reduced pressure. The oily residue was purified by column chromatography (silica gel, light petroleum ether/Et_2O, 8:2) to afford pure products **8** or **11** and homodimer **6**.

1-(3′-Methoxy-3′-oxopropionyloxy)-5-acetoxy-4-methyl-3-heptene (8a): Colorless oil; yield: 31%; E/Z = 20. IR ($CHCl_3$): $\tilde{\nu}$ = 2970, 1730, 1463, 1382, 1284, 1148, 1021 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.80 (t, J = 7.3 Hz, 3 H, CH$_2$CH_3), 1.60 (s, 3 H, CH_3C=), 1.65 (m, 2 H, CH_2CH$_3$), 2.03 (s, 3 H, CH_3CO), 2.36 (q, J = 7.3 Hz, 2 H, CH_2CH=), 3.35 [s, 2 H, CH_2(C=O)$_2$], 3.72 (s, 3 H, OCH_3), 4.12 (t, J = 7.0 Hz, 2 H, CH$_2$CH_2O), 5.01 (t, J = 7.3 Hz, 1 H, CHO), 5.37 (t, J = 7.3 Hz, 1 H, E isomer, CH=), 5.59 (t, J = 7.3 Hz, 1 H, Z isomer, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 9.7, 11.9, 21.1, 25.5, 27.0, 41.2, 52.4, 64.6, 80.1, 122.5, 136.1, 166.4, 166.8, 170.2 ppm. GC–MS (EI, 70 eV): m/z (%) = 126 (45), 109 (36), 108 (52), 101 (25), 97 (100), 93 (71), 59 (28), 57 (34). HRMS (ESI): calcd. for $C_{14}H_{22}O_6Na$ [M + Na]$^+$ 309.1314; found 309.1310.

1-(3′-Methoxy-3′-oxopropionyloxy)-5-acetoxy-4-methyl-3-nonene (8b): Colorless oil; yield: 38%; E/Z = 21. IR ($CHCl_3$): $\tilde{\nu}$ = 2965, 1730, 1464, 1383, 1150, 1016 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, J = 7.3 Hz, 3 H, CH_3CH$_2$), 1.23 (m, 4 H, CH_2CH_2), 1.57 (m, 2 H, CH_2), 1.60 (s, 3 H, CH_3C=), 2.01 (s, 3 H, CH_3CO), 2.36 (q, J = 7.3 Hz, 2 H, CH_2CH=), 3.35 [s, 2 H, CH_2(C=O)$_2$], 3.73 (s, 3 H, OCH_3), 4.12 (t, J = 7.3 Hz, 2 H, CH_2O), 5.08 (t, J = 7.3 Hz, 1 H, CHO), 5.37 (t, J = 7.3 Hz, 1 H, E isomer, CH=), 5.55 (t, J = 7.3 Hz, 1 H, Z isomer, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.0, 13.9, 21.7, 22.3, 27.0, 27.6, 32.3, 41.2, 52.4, 64.5, 78.9, 122.3, 136.5, 166.4, 166.8, 170.2 ppm. GC–MS (EI, 70 eV): m/z (%) = 154 (37), 136 (31), 101 (24), 97 (100), 93 (63), 81 (26), 59 (24), 57 (25). HRMS (ESI): calcd. for $C_{16}H_{26}O_6Na$ [M + Na]$^+$ 337.1627; found 337.1625.

1-(3′-Methoxy-3′-oxopropionyloxy)-5-acetoxy-4-methyl-3-pentadecene (8c): Colorless oil; yield: 38%; E/Z = 20. IR ($CHCl_3$): $\tilde{\nu}$ = 2953, 1750, 1480, 1290, 1200 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, J = 7.3 Hz, 3 H, CH$_2$CH_3), 1.23 [m, 18 H, CH$_2$-(CH$_2$)$_8$], 1.59 (s, 3 H, CH_3C=), 2.02 (s, 3 H, CH_3CO), 2.38 (q, J = 7.3 Hz, 2 H, CH_2CH=), 3.35 [s, 2 H, CH_2(C=O)$_2$], 3.73 (s, 3 H, OCH_3), 4.12 (t, J = 7.3 Hz, 2 H, CH$_2$CH_2O), 5.08 (m, 1 H, CHOAc), 5.37 (t, J = 7.3 Hz, 1 H, E isomer, CH=), 5.54 (t, J = 7.3 Hz, 1 H, Z isomer, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.1, 14.2, 15.3, 15.8, 15.9, 16.0, 17.5, 18.2, 18.6, 29.4, 29.6, 32.0, 32.7, 41.4, 52.5, 64.7, 76.5, 122.4, 136.7, 166.5, 167.0, 170.3 ppm. HRMS (ESI): calcd. for $C_{22}H_{38}O_6Na$ [M + Na]$^+$ 421.2566; found 421.2571.

Benzyl 1′-(3′′-Methoxy-3′′-oxopropionyloxy)-4′-methylnon-3′-ene-5′-yl Carbonate (8d): Colorless oil; yield: 34%; E/Z = 24. IR ($CHCl_3$): $\tilde{\nu}$ = 3160, 1783, 1432, 1325, 1169, 1043 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, J = 7.3 Hz, 3 H, CH$_2$CH_3), 1.31 (m, 4 H, CH_2CH_2), 1.65 (s, 3 H, overlapped, CH_3C=), 1.67 (m, 2 H, CH_2), 2.42 (q, J = 7.3 Hz, 2 H, CH_2CH=), 3.40 [s, 2 H, CH_2(C=O)$_2$], 3.76 (s, 3 H, OCH_3), 4.16 (t, J = 7.0 Hz, 2 H, CH$_2$CH_2O), 4.99 (t, J = 7.3 Hz, 1 H, CHO), 5.16 (s, 2 H, OCH_2Ph), 5.47 (t, J = 7.0 Hz, 1 H, E isomer, CH=), 5.65 (t, J = 7.0 Hz, 1 H, Z isomer, CH=), 7.34 (m, 5 H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.7, 13.8, 22.3, 26.9, 27.4, 32.2, 41.5, 52.3, 64.4, 69.3, 83.4, 123.2 ppm. GC–MS (EI, 70 eV): m/z (%) = 136 (15), 107 (13), 94 (30), 93 (100), 81 (16), 79 (22), 59 (15). HRMS (ESI): calcd. for $C_{22}H_{30}O_7Na$ [M + Na]$^+$ 429.1889; found 429.1891.

1-(3′-Methoxy-3′-oxopropionyloxy)-5-acetoxy-4,6-dimethyl-3-heptene (8e): Colorless oil; yield: 11%; *E* isomer. IR ($CHCl_3$): $\tilde{\nu}$ = 2970, 1740, 1422, 1311, 1198 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.81 (d, J = 7.0 Hz, 3 H, CH_3CH), 0.90 (d, J = 7.0 Hz, 3 H, CH_3CH), 1.61 (s, 3 H, overlapped, CH_3C=), 1.68 (m, 2 H, overlapped, CH_2CH=), 2.07 (s, 3 H, CH_3CO), 2.42 [m, 1 H, CH-$(CH_3)_2$], 3.40 [s, 2 H, $CH_2(C{=}O)_2$], 3.76 (s, 3 H, OCH_3), 4.17 (m, 2 H, CH_2O), 4.81 (m, 1 H, CHO), 5.39 (m, 1 H, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.5, 19.0, 20.3, 26.5, 29.8, 41.4, 52.6, 64.4, 123.1, 136.7, 123.8, 133.2, 166.4, 166.8, 170.5 ppm. HRMS (ESI): calcd. for $C_{15}H_{24}O_6Na$ $[M + Na]^+$ 323.1471; found 323.1475.

1-Acetoxy-1-cyclopentyl-2-methyl-5-(3′-methoxy-3′-oxopropionyloxy)-2-pentene (8f): Colorless oil; yield: 7%; *E*/*Z* = 18. IR ($CHCl_3$): $\tilde{\nu}$ = 2934, 1725, 1430, 1350, 1250 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.53 [m, 8 H, overlapped, $CH_2(CH_2)_2CH_2$], 1.59 (s, 3 H overlapped, CH_3C=), 1.67 (m, 2 H, CH_2CH=), 2.01 (s, 3 H, *E* isomer, CH_3CO), 2.02 (s, 3 H, *Z* isomer, CH_3CO), 2.35 (m, 1 H, CH of cyclopentyl), 3.35 [s, 2 H, $CH_2(C{=}O)_2$], 3.72 (s, 3 H, OCH_3), 4.11 (d, J = 7.3 Hz, 1 H, *E* isomer, CHO), 4.14 (d, J = 7.3 Hz, 1 H, *Z* isomer, CHO), 5.38 (m, 1 H, *E* isomer, CH=), 5.56 (m, 1 H, *Z* isomer, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.3, 25.4, 27.0, 27.1, 29.1, 41.4, 41.8, 52.5, 64.7, 83.3, 123.5, 139.2 ppm. HRMS (ESI): calcd. for $C_{17}H_{26}O_6Na$ $[M + Na]^+$ 349.1627; found 349.1629.

1-Acetoxy-2-ethyl-5-(3′-methoxy-3′-oxopropionyloxy)-2-pentene (11a): Colorless oil; yield: 59%; *E*/*Z* = 1. IR ($CHCl_3$): $\tilde{\nu}$ = 2970, 1730, 1423, 1382, 1284, 1148, 1021 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.98 (t, J = 7.3 Hz, 3 H, *E* isomer, CH_3CH_2), 1.00 (t, J = 7.3 Hz, 3 H, *Z* isomer, CH_3CH_2), 2.04 (s, 3 H, *E* isomer, overlapped, CH_3CO), 2.05 (s, 3 H, *Z* isomer, overlapped, CH_3CO), 2.06 (m, 2 H, CH_3CH_2), 2.40 (q, J = 7.3 Hz, 2 H, *E* isomer, OCH_2CH_2), 2.44 (q, J = 7.3 Hz, 2 H, *Z* isomer, OCH_2CH_2), 3.37 [s, 2 H, $CH_2(C{=}O)_2$], 3.73 (s, 3 H, OCH_3), 4.13 (t, J = 6.6 Hz, 2 H, *E* isomer, OCH_2CH_2), 4.14 (t, J = 6.6 Hz, 2 H, *Z* isomer, OCH_2CH_2), 4.48 (s, 2 H, *E* isomer, CH_2OAc), 4.58 (s, 2 H, *Z* isomer, CH_2OAc), 5.32 (t, J = 6.6 Hz, 1 H, *E* isomer, CH=), 5.40 (t, J = 6.6 Hz, 1 H, *Z* isomer, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.0, 21.5, 26.7, 41.4, 52.6, 61.9, 64.8, 67.7, 123.5, 139.1, 166.5, 167.0, 170.9 ppm. GC–MS (EI, 70 eV): *m*/*z* (%) = 126 (45), 109 (36), 108 (52), 101, (25), 97 (100), 93 (71), 59 (28), 57 (34). HRMS (ESI): calcd. for $C_{13}H_{20}O_6Na$ $[M + Na]^+$ 295.1158; found 295.1162.

1-Acetoxy-2-butyl-5-(3′-methoxy-3′-oxopropionyloxy)-2-pentene (11b): Colorless oil; yield: 36%; *E*/*Z* = 1. IR ($CHCl_3$): $\tilde{\nu}$ = 2990, 1742, 1462, 1310, 1258, 1040 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, J = 7.3 Hz, 3 H, *E* isomer, CH_3CH_2), 0.89 (t, J = 7.3 Hz, 3 H, *Z* isomer, CH_3CH_2), 1.32 (m, 4 H, $CH_3CH_2CH_2$), 2.04 (s, 3 H, *E* isomer, overlapped, CH_3CO), 2.06 (s, 3 H, *Z* isomer, overlapped, CH_3CO), 2.07 (m, 2 H, CH_2CH_2C=), 2.40 (q, J = 7.3 Hz, 2 H, *E* isomer, OCH_2CH_2CH=), 2.43 (q, J = 7.3 Hz, 2 H, *Z* isomer, OCH_2CH_2CH=), 3.36 [s, 2 H, *E* isomer, $CH_2(C{=}O)_2$], 3.37 [s, 2 H, *Z* isomer, $CH_2(C{=}O)_2$], 3.72, (s, 3 H, OCH_3), 4.10 (t, J = 6.6 Hz, 2 H, *E* isomer, OCH_2CH_2), 4.11 (t, J = 6.6 Hz, 2 H, *Z* isomer, OCH_2CH_2), 4.47 (s, 2 H, *E* isomer, CH_2OAc), 4.56 (s, 2 H, *Z* isomer, CH_2OAc), 5.36 (t, J = 7.3 Hz, 1 H, *E* isomer, CH=), 5.40 (t, J = 7.3 Hz, 1 H, *Z* isomer, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 22.8, 27.1, 28.2, 30.52, 41.4, 52.5, 61.8, 64.8, 68.0, 123.9, 125.0, 137.7, 166.9, 167.0, 170.8 ppm. HRMS (ESI): calcd. for $C_{15}H_{24}O_6Na$ $[M + Na]^+$ 323.1471; found 323.1465.

General Procedure for the Synthesis of Alcohols 9 and Acetates 10: CuI (300 mg, 1.6 mmol) was added to a solution of prop-2-yn-1-ol (1.0 mL, 16.0 mmol) in anhyd. Et_2O (30 mL) whilst stirring at room temp. under argon. The reaction mixture was cooled to –10 °C and a 2 M solution of an appropriate Grignard reagent (16 mL, 32.0 mmol) was added dropwise over a period of 45 min. After 6 h, satd. aq. NH_4Cl (15 mL) was added to the reaction mixture while keeping the flask at 0 °C. The biphasic mixture was then separated and the aqueous phase was extracted with Et_2O (2 × 20 mL). The combined organic phases were washed with water and dried (Na_2SO_4). Removal of the solvent under reduced pressure afforded an oily residue, which was purified by column chromatography (silica gel, light petroleum ether/Et_2O, 9:1) to give pure alcohols **9**. The alcohols were subsequently converted into esters **10** by reaction with acetyl chloride/Et_3N in CH_2Cl_2. The esters **10** were purified by distillation at atmospheric pressure.

2-Ethyl-2-propen-1-ol (9a): Colorless oil; yield: 55%. IR ($CHCl_3$): $\tilde{\nu}$ = 3625, 2946, 1465, 1029 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.04 (t, J = 7.3 Hz, 3 H, CH_3CH_2), 1.94 (q, J = 7.3 Hz, 2 H, CH_3CH_2), 2.05 (br. s, 1 H, OH), 4.05 (s, 2 H, CH_2O), 4.88 (m, 1 H, CH_A=), 4.99 (m, 1 H, CH_B=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.2, 25.8, 66.0, 108.1, 150.8 ppm. Spectral data are in agreement with those reported in the literature.[19a]

2-*n*-Butyl-2-propen-1-ol (9b): Colorless oil; yield: 24%. IR ($CHCl_3$): $\tilde{\nu}$ = 3630, 2935, 1239, 1043 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, J = 7.3 Hz, 3 H, CH_3CH_2), 1.34 (m, 4 H, $CH_3CH_2CH_2$), 2.02 [t, J = 7.3 Hz, 2 H, $CH_3(CH_2)_2CH_2C$ =], 2.21 (t, J = 5.8 Hz, 1 H, OH), 4.02 (d, J = 5.8 Hz, 2 H, CH_2O), 4.83 (m, 1 H, CH_A=), 4.98 (m, 1 H, CH_B=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 22.6, 30.0, 32.8, 65.9, 109.0, 149.3 ppm. Spectral data are in agreement with those reported in the literature.[19b]

2-Cyclopentyl-2-propen-1-ol (9c): Colorless oil; yield: 24%. IR ($CHCl_3$): $\tilde{\nu}$ = 3628, 2972, 1198, 1030 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.15–1.82 [m, 8 H, C$H_2(CH_2)_2CH_2$], 2.42 (quint., J = 8.3 Hz, 1 H, CH of cyclopentyl), 4.10 (s, 2 H, CH_2O), 4.88 (m, 1 H, CH_A=), 4.94 (m, 2 H, CH_B=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.9, 31.5, 43.1, 65.7, 106.9, 150.2 ppm. Spectral data are in agreement with those reported in the literature.[19c]

2-Ethylallyl Acetate (10a): Colorless oil; yield: 64%. IR ($CHCl_3$): $\tilde{\nu}$ = 2980, 1741, 1582, 1425, 1312, 1193 cm^{-1}. ^1H NMR (300 Hz, $CDCl_3$): δ = 1.05 (t, J = 7.3 Hz, 3 H, CH_3CH_2), 2.01 (q, J = 7.3 Hz, 2 H, CH_3CH_2), 2.07 (s, 3 H, CH_3CO), 4.51 (s, 2 H, CH_2O), 4.89 (m, 1 H, CH_A=), 5.00 (m, 1 H, CH_B=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.0, 21.0, 26.1, 67.0, 111.1, 145.7, 170.8 ppm. HRMS (ESI): calcd. for $C_7H_{12}O_2Na$ $[M + Na]^+$ 151.0735; found 151.0734.

2-Butylallyl Acetate (10b): Colorless oil; yield: 53%. IR ($CHCl_3$): $\tilde{\nu}$ = 2950, 1733, 1462, 1391, 1295, 1037 cm^{-1}. ^1H NMR (300 Hz, $CDCl_3$): δ = 0.88 (t, J = 7.3 Hz, 3 H, CH_3CH_2), 1.38 (m, 4 H, $CH_3CH_2CH_2$), 2.04 [q, J = 7.3 Hz, 2 H, $CH_3(CH_2)_2CH_2C$=], 2.06 (s, 3 H, CH_3CO), 4.49 (s, 2 H, CH_2O), 4.90 (m, 1 H, CH_A=), 4.98 (m, 1 H, CH_B=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9, 20.9, 22.4, 29.8, 33.0, 66.9, 112.0, 144.2, 170.7 ppm. HRMS (ESI): calcd. for $C_9H_{16}O_2Na$ $[M + Na]^+$ 179.1048; found 179.1040.

2-Cyclopentylallyl Acetate (10c): Colorless oil; yield: 28%. IR ($CHCl_3$): $\tilde{\nu}$ = 2936, 1742, 1444, 1319, 1040 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.15–1.64 [m, 8 H, C$H_2(CH_2)_2CH_2$], 2.06 (s, 3 H, CH_3CO), 2.46 (m, 1 H, CH of cyclopentyl), 4.53 (s, 2 H, CH_2O), 4.88 (m, 1 H, CH_A=), 4.98 (m, 1 H, CH_B=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.0, 23.8, 25.0, 31.4, 32.7, 43.5, 66.8, 110.0, 147.4, 170.7 ppm. HRMS (ESI): calcd. for $C_{10}H_{16}O_2Na$ $[M + Na]^+$ 191.1048; found 191.1052.

General Procedure for the Synthesis of Esters 12: Compound **1b** (0.5 mmol) and methallyl esters **4** or **7** (2 mmol) were dissolved in CH_2Cl_2 (10 mL) under argon. While keeping the reaction flask at 40 °C, a solution of catalyst **I** (4 mol-%) in CH_2Cl_2 (6 mL) was

added dropwise over 45 min. The reaction was kept at reflux for 15 h and then the solvent was removed under reduced pressure. The oily residue was purified by column chromatography (silica gel, light petroleum ether/Et_2O, 8:2) to afford pure products **12** and homodimer **13**.

1-Acetoxy-2,4-dimethyl-5-(3′-methoxy-3′-oxopropionyloxy)-2-pentene (12a): Colorless oil; yield 43%. IR ($CHCl_3$): $\tilde{\nu}$ = 2980, 1756, 1425, 1385, 1250 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.94 (d, J = 6.6 Hz, 3 H, CH_3CH), 1.64 (s, 3 H, CH_3C=), 2.03 (s, 3 H, CH_3CO), 2.78 (m, 1 H, CHCH$_3$), 3.34 [s, 2 H, CH_2(C=O)$_2$], 3.72 (s, 3 H, OCH_3), 3.94 [m, 2 H, CH(CH$_3$)CH_2O], 4.40 (s, 2 H, CH_2OAc), 5.17 (m, 1 H, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.2, 17.0, 20.9, 31.9, 41.4, 52.4, 63.2, 69.3, 130.1, 132.0, 166.4, 166.8, 170.8 ppm. HRMS (ESI): calcd. for $C_{13}H_{20}O_6Na$ [M + Na]$^+$ 295.1158; found 295.1152.

1-(3′-Methoxy-3′-oxopropionyloxy)-2,4-dimethyl-5-acetoxy-3-nonene (12b): Colorless oil; yield 28%. IR ($CHCl_3$): $\tilde{\nu}$ = 2965, 1732, 1411, 1323, 1190 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 [t, J = 7.3 Hz, 3 H, (CH$_2$)$_2$CH_3], 0.97 (dd, J = 7.3, 6.6 Hz, 3 H, CH_3CH), 1.24 (m, 4 H, CH$_3$CH_2CH_2), 1.60 (m, 2 H, CH$_3$CH$_2$CH$_2$CH_2), 1.61 (s, 3 H, CH_3C=), 2.02 (s, 3 H, CH_3CO), 2.77 (m, 1 H, CHCH$_3$), 3.36 and 3.37 [s, 2 H, CH_2(C=O)$_2$], 3.74 (s, 3 H, OCH_3), 3.94 [m, 2 H, CH(CH$_3$)CH_2O], 5.06 (t, J = 7.3 Hz, 1 H, CHOAc), 5.16 (d, J = 9.5 Hz, 1 H, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.3, 14.0, 17.2, 21.3, 22.5, 27.7, 31.7, 32.4, 41.4, 52.5, 69.4, 79.0, 129.1, 135.0, 166.5, 166.9, 170.2 ppm. HRMS (ESI): calcd. for $C_{17}H_{28}O_6Na$ [M + Na]$^+$ 351.1784; found 351.1781.

1,5-Bis(3′-methoxy-3′-oxopropionyloxy)-2,4-dimethyl-3-pentene (13): Colorless oil. IR ($CHCl_3$): $\tilde{\nu}$ = 2977, 1741, 1467, 1348, 1210 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.00 (d, J = 6.6 Hz, 6 H, CH_3CH), 2.35 (m, 2 H, CHCH$_3$), 3.34 [s, 4 H, CH_2(C=O)$_2$], 3.70 (s, 6 H, OCH_3), 4.02 (m, 4 H, CH_2O), 5.31 (m, 2 H, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.7, 35.9, 41.2, 52.3, 69.4, 132.1, 166.2, 166.8 ppm. HRMS (ESI): calcd. for $C_{16}H_{24}O_8Na$ [M + Na]$^+$ 367.1369; found 367.1365.

Supporting Information (see footnote on the first page of this article): ^1H and ^{13}C NMR spectra of compounds **1**, **5**–**8**, and **10**–**13**; NOESY spectra for compounds **5b** and **5c**.

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Received: June 23, 2011
Published Online: September 16, 2011

