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First Transformation of Unsaturated Fatty Esters Involving Enyne Cross-Metathesis

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Dedicated to Professor Armin de Meijere on the occasion of his 70th birthday.

Abstract: The ruthenium-catalysed enyne cross-metathesis of several alkyne derivatives with terminal olefins was performed. These reactions were efficiently achieved under mild conditions in dimethyl carbonate, an eco-friendly solvent. A unique one-pot reaction based on an ethenolysis step followed by an enyne cross-metathesis allowed the efficient transformation of renewable unsaturated fatty esters into valuable conjugated 1,3-dienes of interest for further transformations.

Keywords: enynes; fatty esters; metathesis; renewable resources; ruthenium

Introduction

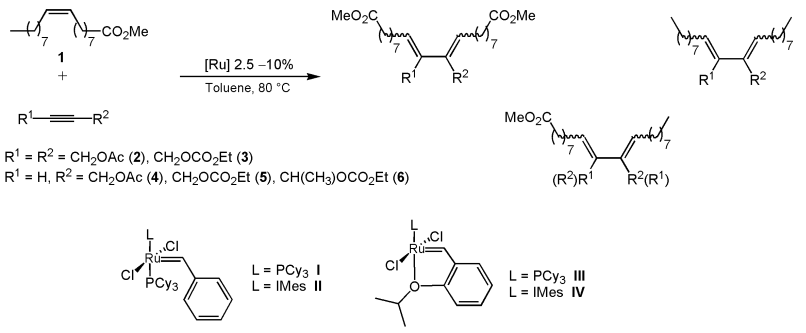
With the predicted end of the fossil era, the use of renewable resources as a supply of raw materials for the chemical industry is a domain of intense research.[1] In this context, vegetable fats and oils have been envisioned as green alternatives to petrochemical compounds.[2] Olefin metathesis[3] is a very powerful tool in organic[4] and polymer synthesis[5] that has already shown a high potential for the transformation of fats and oils.[6–10] Among the transformations achievable by metathetical processes, enyne metathesis[11] has emerged as a valuable route for the synthesis of 1,3-dienes. As for the transformation of olefins, intramolecular (ring-closing) and intermolecular (cross-metathesis) versions of enyne metathesis are possible. The intramolecular transformation was first reported in 1985 with a tungsten catalyst[12] and then with ruthenium complexes[13] followed in 1997 by the first examples of enyne cross-metathesis.[14] Since that time, several groups have contributed to the development of these transformations[15] but to the best of our knowledge, the transformation of fatty esters by enyne cross-metathesis has not been reported. Herein, we present the first transformation of fatty esters by an ethenolysis/enyne cross-metathesis sequence leading to bio-resourced 1,3-dienes.

Results and Discussion

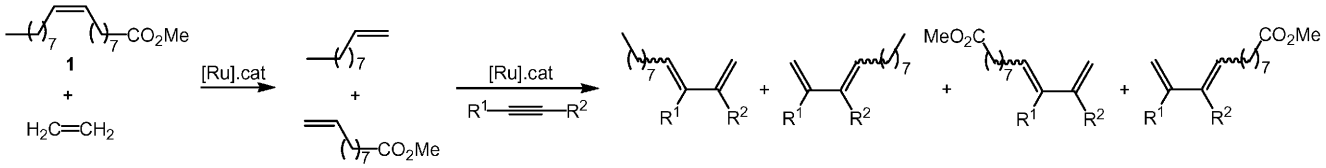
Until recently, the transformation of fatty esters by metathesis reactions was essentially performed by self-metathesis leading to internal olefins or by cross-metathesis with ethylene leading to terminal olefins.[7,8] To further extend the potential of metathesis for the transformation of fatty esters into end-functionalised long-chain alkenes, the direct introduction of functional groups is strongly desired. Thanks to the development of very active ruthenium catalysts the introduction of a polar functionality by cross-metathesis with electron-poor olefins such as acrylates[10a,b] and acrylonitriles[10c,d] is now possible. We now report the transformation of fatty esters by enyne cross-metathesis leading to conjugated 1,3-dienes that can be further transformed *via* tandem procedures.[11e,16,17]

First the reactivity of methyl oleate **1** with internal or terminal alkynes potentially leading to four different products was examined. Second generation Grubbs′ and Hoveyda catalysts **II** and **IV** were tested for this reaction but none of them allowed any conversion of the alkynes even when terminal alkynes were used. (Scheme 1).

As far as we know there is only one example of enyne cross-metathesis involving cyclooctadiene as an internal alkene and it was shown that catalyst loadings of 5 mol% up to 20 mol% were necessary.[15c,e] In our case, increasing the loading of **IV** to 10 mol% failed to promote the cross-metathesis of **1** with al-



Scheme 1. Cross-metathesis of methyl oleate **1** with alkynes potentially leading to four dienes [Cy = cyclohexyl; IMes = 1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolinylidene].



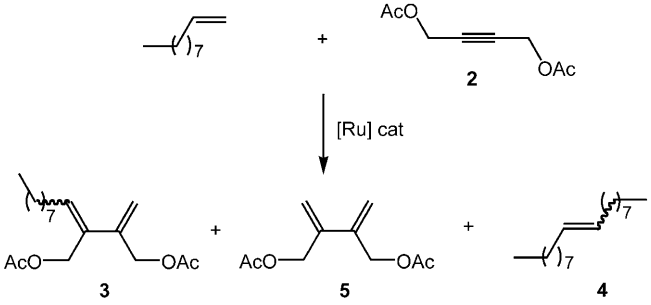
Scheme 2. One-pot ethenolysis/cross enyne metathesis.

kynes **2** and **6**, and only afforded products resulting from the self-metathesis of methyl oleate. To overcome this problem, we turned our attention to the one-pot ethenolysis/enyne cross-metathesis of methyl oleate **1** (Scheme 2).

Previous work in our group had shown that complex **III** was the most efficient catalyst to perform the ethenolysis of methyl oleate whereas catalysts **II** and **IV** resulted in unworkable mixtures of products due to a self-metathesis reaction of **1** and to double bond migration.[8a] Typically, catalyst **III** (2.5 mol%) allowed the ethenolysis of **1**, in dimethyl carbonate (DMC) used as an eco-friendly solvent,[18] at room temperature under 1 bar of ethylene leading with 93% conversion to *n*-decene and methyl 9-decenoate without double bond isomerisation and less than 4% of self-metathesis products.

With the first step of the one-pot sequence secured, we focused our efforts towards the optimisation of the enyne cross-metathesis by using *n*-decene and various terminal and internal alkynes. To initiate our investigations, we examined the cross-metathesis of *n*-decene with alkyne **2** (Scheme 3).

This reaction was initially performed in toluene using catalyst **II** and an excess of alkene. The expected formation of **3** was observed along with the formation of **4** resulting from the self-metathesis of *n*-decene and **5** resulting from the cross-metathesis of **2** with the *in situ* generated ethylene.[19] In this metathesis reaction, we have also found that dimethyl carbonate provided similarly good results as toluene or dichloromethane and was selected as the solvent of choice for this project. As summarised in Table 1 the



Scheme 3. Enyne cross-metathesis of *n*-decene with the symmetrical alkyne **2**

reaction was found to proceed efficiently under mild conditions using a low catalyst loading and it was also shown that catalysts **II** and **IV** displayed similar performances. Interestingly, reaction monitoring (Figure 1) showed that the formation of **4** was minor as long as the alkyne was not fully consumed, hence highlighting a favoured enyne cross-metathesis transformation with regard to an olefin metathesis reaction. It is also important to note that the reaction could be performed with only a two-fold excess of *n*-decene, which contrasts with previous intermolecular enyne metathesis reactions where larger excess of alkene were used.[20]

The scope of the reaction was extended to other internal and terminal functional alkynes using the optimised experimental conditions. The reactions proceeded efficiently for several substrates but different reactivities were observed with internal and terminal alkynes. Substitution of internal alkynes at the propar-

Table 1. Enyne cross-metathesis of *n*-decene with the symmetrical alkyne **2**.

Entry	Catalyst (mol%)	**2** [equiv.]	Solvent	Temp. [°C]	Time [h]	Conv. [%][a]	Yield of **3** [%][a]	*Z*/*E*[a]
1	**II** (5)	4	toluene	80	3	100	98	0.5/1
2	**II** (1)	2	toluene	40	0.6	100	97	0.56/1
3	**II** (1)	2	CH_2Cl_2	40	0.6	100	97	0.66/1
4	**II** (1)	2	dimethyl carbonate	r.t.	2.5	100	97	0.63/1
5	**II** (1)	2	dimethyl carbonate	40	0.5	100	95	0.64/1
6	**IV** (1)	2	dimethyl carbonate	40	0.6	100	95	0.63/1

[a] Determined by gas chromatography of the crude products.

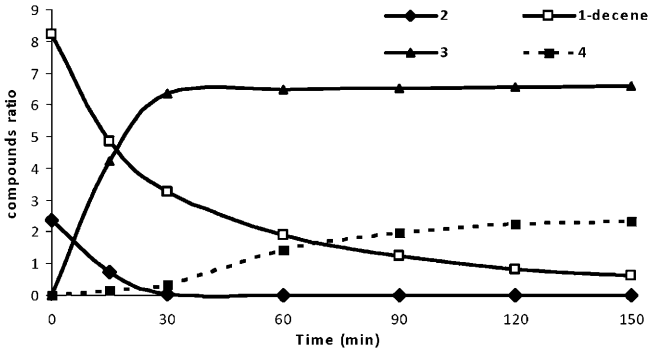


Figure 1. Reaction profile as product ratio = f(t). Ratios determined by integration *vs* internal standard.

gylic position totally inhibited the reactions (Table 2, entries 1–4) whereas this substitution was found to be necessary for the transformation of terminal alkynes (Table 2, entries 5–9). If the lack of reactivity of substrates **7** and **8** might be attributed to steric hindrance resulting in the self-metathesis of *n*-decene only, substrates **12** and **13** were found to inhibit any metathesis reactions. It is noteworthy that the cross-metathesis with monosubstituted propargylic esters and carbonates leads to the regioselective formation of dienes and no trisubstituted double bond was observed.

Next, the one-pot ethenolysis/cross-metathesis of methyl oleate **1** was performed in dimethyl carbonate using the Hoveyda catalyst **III** for the ethenolysis step and Grubbs catalyst **II** for the cross-metathesis of the generated olefins with alkynes. Catalyst **II** and the alkyne derivative were directly added to the crude reaction mixture after the ethenolysis was completed (Scheme 4).

As depicted in Scheme 4 the ethenolysis step furnished *n*-decene and methyl 9-decenoate in equal proportions and small amounts of self-metathesis products **4** (3%) and **22** (2%). Based on the products ratio measured by gas chromatography, the ethenolysis reaction furnished 1.7 equiv. of terminal olefins, which were reacted with one equiv. of alkyne. This led to the formation of the desired products **18** and **23** both in high 48% yield measured by gas chromatography with internal calibration (maximum theoretical yield assuming equal reactivity of *n*-decene and methyl 9-decenoate = 50%). The same one-pot sequence repeated with the internal alkyne **2** led to products **3** and **24** (Figure 2) obtained again in high yields, 45% and 53%, respectively (GC yields).

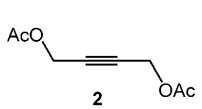
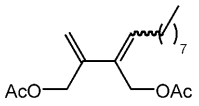
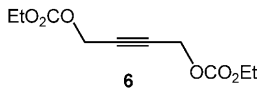
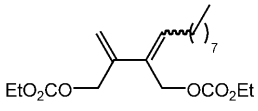
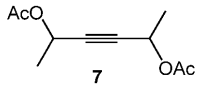
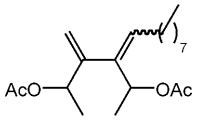
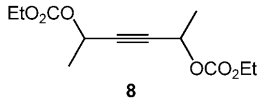
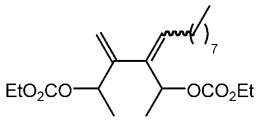
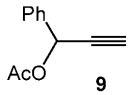
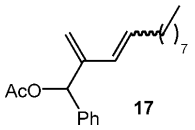
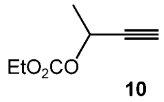
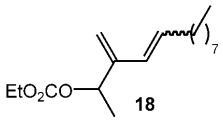
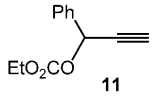
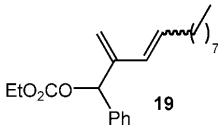
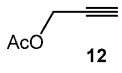
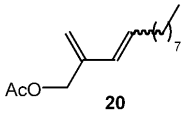
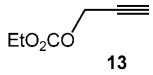
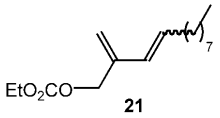
In both reactions involving terminal or internal alkynes, the expected dienes were obtained in a mixture of several compounds containing unreacted methyl oleate **1**, terminal olefins (*n*-decene, methyl 9-decenoate) and self-metathesis products **4** and **22**. Although these products were present in small quantities and isolable owing to different polarities and boiling points, it would be interesting to find alternative routes for a cleaner production of the desired conjugated dienes. An elegant route would be to perform the one-pot sequence starting from a symmetrical olefin obtained by self-metathesis of methyl oleate[6,7] or from fermentation of oleic acid.[21] Thus, the diester **22** was engaged in a one-pot sequence as previously described for methyl oleate **1** (Scheme 5).

As shown in Scheme 5, **22** was first transformed by ethenolysis into methyl 9-decenoate, which was further engaged in an enyne cross-metathesis with **9** or **2**. Thus, using the bio-resourced fatty diester **22**, dienes **24** and **25** were obtained in high yields and selectivities. As anticipated the purification of the products was facilitated since the reaction mixtures now only consisted in the desired product, the unreacted starting diester **22** and the intermediate methyl 9-decenoate as minor products. The dienes **24** and **25** were easily purified by column chromatography and isolated in 90% and 81% yields, respectively.

Conclusions

In conclusion, we have shown that the enyne cross-metathesis of long-chain terminal olefins resulting from ethenolysis of unsaturated fatty esters could be efficiently and selectively performed under mild conditions in an eco-friendly solvent. The scope of the reaction was extended to several internal and terminal alkynes bearing functional groups providing an access to various functional dienes. This transformation was included in a one-pot ethenolysis/enyne cross-metathesis sequence performed from renewable unsaturat-

Table 2. Cross-metathesis of alkynes with *n*-decene.[a]

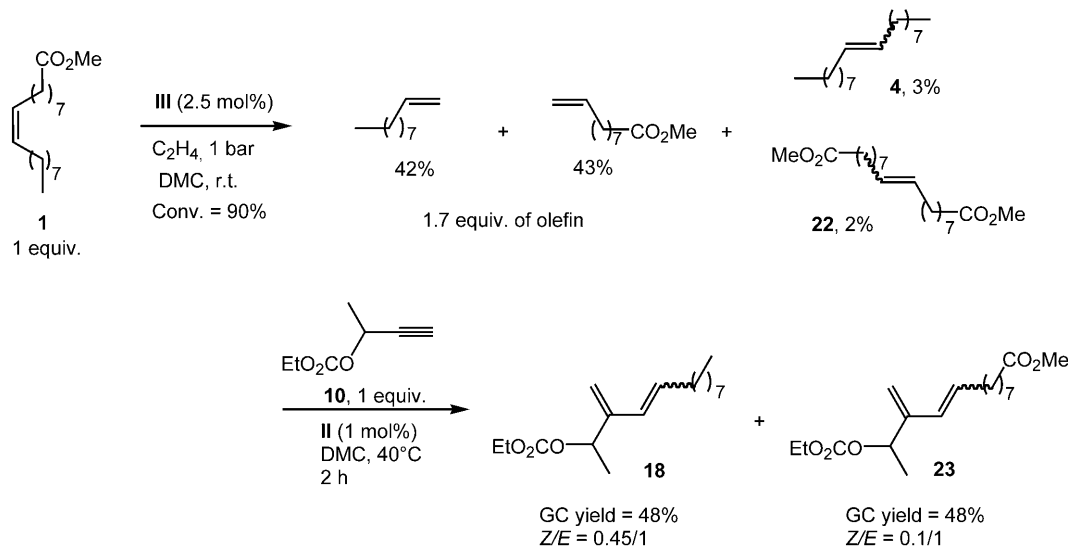
Entry	Alkyne	Product	Conversion/yield[b]	*Z*/*E*[c]
1	 **2**	 **3**	100/97/94	0.64/1
2	 **6**	 **14**	100/96/70	0.85/1
3	 **7**	 **15**		–
4	 **8**	 **16**		–
5	 **9**	 **17**	100/91/80	$E > 99\%$ [d]
6	 **10**	 **18**	100/98/79	0.34/1
7	 **11**	 **19**	100/93/70	0.4/1[d]
8	 **12**	 **20**		–
9	 **13**	 **21**		–

[a] Catalyst **II**, (1 mol%), alkyne (0.3 mmol), *n*-decene (0.6 mmol) dimethyl carbonate (2.5 mL), 40 °C, 2 h.
[b] Conversion/GC yield/isolated yield (%).
[c] Determined by gas chromatography.
[d] Determined by ^{1}H NMR (isolated product).

ed fatty esters. The expected dienes were formed starting from methyl oleate together with small amounts of internal alkenes resulting from secondary self metathesis reactions. The use of a symmetrical diester provides an important advantage as it facilitates the purification of the expected dienes. This new reaction sequence based on two efficient catalytic metathesis reactions provides a useful method in oleochemistry for the transformation of natural oils into functional compounds or intermediates of interest for further transformations.

Experimental Section

All reactions were carried out under an inert atmosphere of argon using Schlenck tube techniques. Solvents were freshly distilled and dried prior to use according to classical proce-



Scheme 4. One-pot ethenolysis/enyne cross-metathesis of methyl oleate **1** with propargyl carbonate **10** (*Z*/*E* determined by GC of the crude products).

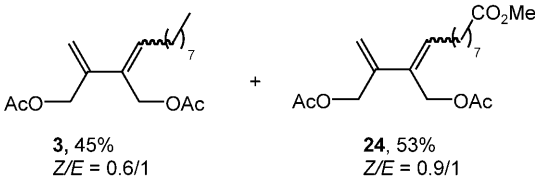
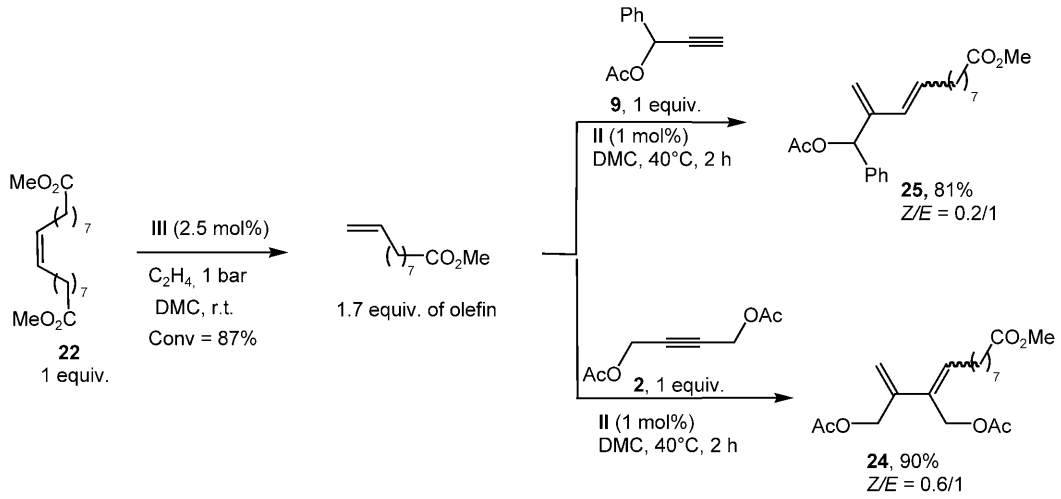


Figure 2. Products of the one pot ethenolysis/enyne cross-metathesis of methyl oleate **1** with the alkyne **2** (*Z*/*E* determined by GC of the crude products).

dures; over CaH_2 for dichloromethane, Na for THF and toluene. Dimethyl carbonate was purchased from Alfa Aesar and stored over 4 A molecular sieves after distillation. Ruthenium catalysts were purchased from Aldrich and stored under argon. Methyl oleate **1** was purchased from Fluka and used as received. Compounds **2** and **12** were purchased from Alfa Aesar and Acros organics, respectively, and used as received. Compounds **9** and **11** were prepared according to reported procedures.[22] Sample products were characterised by NMR analysis using Bruker 200 dpx and Bruker avance 300 MHz NMR spectrometers. Gas chromatography analyses were performed on a Shimadzu 2014 gas chromatograph with internal calibration. GC/MS analyses were performed on a Shimadzu QP2010 apparatus.

General Procedure for the Preparation of Propargylic Compounds

Ethyl prop-2-yn-1-yl carbonate (13): To a stirred solution of prop-2-yn-1-ol (2.3 mL, 42.8 mmol, 1.0 equiv.), dimethylaminopyridine (30 mg, 0.25 mmol) and triethylamine (9.1 mL, 64.2 mmol, 1.5 equiv.) in CH_2Cl_2 (60 mL) at 0 °C was added



Scheme 5. One-pot ethenolysis/enyne cross-metathesis of diester **22** with terminal and internal alkynes (*Z*/*E* determined by ^{1}H NMR of the isolated products).

dropwise ethyl chloroformate[23] (6.1 mL, 64.2 mmol, 1.5 equiv.). The reaction mixture was stirred overnight (15 h) at room temperature. The reaction mixture was quenched with saturated NH_4Cl and extracted with AcOEt. The combined extracts were washed with brine and the organic layer was separated and dried over anhydrous Na_2SO_4. The solvent was carefully evaporated (product very volatile) under vacuum (rotatory evaporator). The residue obtained was then purified by distillation or chromatographed on silica gel with pentane/diethyl ether (90:10 v/v) as eluent to give propargylic carbonate **13** as a colourless oil; yield: 5.26 g (96%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.68$ (d, $J = 2.5$ Hz, 2H), 4.19 (q, $J = 7.1$ Hz, 2H), 2.50 (t, $J = 2.5$ Hz, 1H), 1.28 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 154.6$, 77.16, 75.6, 64.6, 55.1, 14.3.

But-2-yne-1,4-diyl diethyl biscarbonate (6): Yield: 93%. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.76$ (s, 4H), 4.22 (q, $J = 7.0$ Hz, 4H), 1.31 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 154.6$, 81.0, 64.7, 55.3, 14.3.

Diethyl hex-3-yne-2,5-diyl diacetate (7): Yield: 76%; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.47$ (q, $J = 6.6$ Hz, 2H), 2.06 (s, 6H), 1.47 (d, $J = 6.6$ Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 169.8$, 83.1, 60.2, 21.4, 21.2.

Diethyl hex-3-yne-2,5-diyl biscarbonate (8): Yield: 90%; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.35$ (q, $J = 6.6$ Hz, 2H), 4.21 (q, $J = 7.1$ Hz, 4H), 1.52 (d, $J = 6.6$ Hz, 6H), 1.31 (t, $J = 7.1$, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 154.2$, 83.4, 64.4, 64.0, 21.4, 14.4.

Ethyl 1-methylprop-2-yn-1-yl carbonate (10): Yield: 93%; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.29$ (q, $J = 6.6$ Hz, 1H), 4.21 (q, $J = 7.1$ Hz, 2H), 2.49 (s, 1H), 1.55 (d, $J = 6.6$ Hz, 3H), 1.31 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 154.3, 81.6, 73.8, 64.4, 63.9, 21.4, 14.3.

General Procedure for the Preparation of New 1,3-Diene Compounds

3-[(Acetyloxy)methyl]-2-methylenedodec-3-en-1-yl acetate (3): A dried Schlenk tube was loaded with 2.5 mg of **II** (0.003 mmol, 1 mol%), 50 mg of **2** (0.295 mmol, 1.0 equiv.) and 2.5 mL of dimethyl carbonate. 110 μL of 1-decene (0.590 mmol, 2.0 equiv.) and 26 μL of hexadecane (internal standard) were then introduced into the stirred solution. The reaction mixture was heated at 40 °C for a period of 40 min (until all 1,4-diacetoxy but-2-yne was consumed). The solvent was evaporated under vacuum to give a dark coloured oil. This oil was then purified by chromatography on silica gel with diethyl ether/petroleum ether (98:2 v/v) as the eluant to give **3** as a colorless oil; yield: 86.5 mg (94%). Compound **3** was obtained as a mixture of isomers. Isomers were identified by NOESY experiments. Silica gel purification was found to modify the *Z*/*E* ratio. *Z*/*E* crude (gas chromatography): 0.64/1; purified product (gas chromatography): 0.25/1, (^{1}H NMR): 0.26/1. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.82$ (t, $J = 7.5$ Hz, 0.26H), 5.66 (t, $J = 7.4$ Hz, 1.00H), 5.31 (s, 1.01H), 5.25 (s, 0.23H), 5.22 (s, 0.23H), 5.00 (s, 1.00H), 4.81 (s, 0.45H), 4.75 (s, 0.45H), 4.60 (s, 1.93H), 4.57 (s, 1.93H), 1.26 (m, 0.41H), 2.11–2.04 (m, 8.72H), 1.33–1.25 (m, 14.75H), 0.87 (t, $J = 6.9$ Hz, 3.87H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 170.8$, 170.6, 140.6, 134.8, 133.5, 117.2, 68.0, 65.9, 32.0, 29.8, 29.6, 29.5, 29.4, 28.9, 22.8, 21.1, 21.0, 14.3; HR-MS: $m/z = 190.1722$ $[M-2CH_3COOH]^+$, calcd. for $C_{18}H_{30}O_4$: 310.2144; elemental anal. calcd. for $C_{18}H_{30}O_4$: C 69.64, H 9.74; found: C 69.37, H 9.73.

3-{[(Ethoxycarbonyl)oxy]methyl}-2-methylidenedodec-3-en-1-yl ethyl carbonate (14): Compound **14** was obtained as a mixture of isomers. Isomers were identified by analogy to **3**. Silica gel purification was found to modify the *Z*/*E* ratio. *Z*/*E*: crude (gas chromatography): 0.85/1; purified product (gas chromatography): 0.34/1, (^{1}H NMR): 0.35/1. Yield: 70%. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.86$ (t, $J = 7.4$ Hz, 0.35H), 5.72 (t, $J = 7.4$ Hz, 1.00H), 5.37 (s, 0.95H), 5.32 (s, 0.33H), 5.28 (s, 0.32H), 5.06 (s, 0.98H), 4.87 (s, 0.68H), 4.80 (s, 0.64H), 4.66 (s, 1.90H), 4.63 (s, 1.92H), 4.22–4.14 (m, 4.72H), 2.25 (q, $J = 7.5$ Hz, 0.63H), 2.08 (q, $J = 7.3$ Hz, 1.94H), 1.32–1.25 (m, 22.87H), 0.87 (t, $J = 7.0$ Hz, 4.17H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 155.1$, 155.0, 139.8, 135.9, 132.8, 118.0, 115.5, 77.4, 71.0, 68.9, 64.3, 64.2, 64.1, 63.0, 32.0, 29.7, 29.6, 29.4, 29.3, 28.9, 22.8, 14.4, 14.3; HR-MS: $m/z = 190.1724$ $[M-2C_3H_6O_3]^+$, calcd. for $C_{20}H_{34}O_6$: 370.2355; elemental anal. calcd. for $C_{20}H_{34}O_6$: C 64.84, H 9.25; found: C 64.60, H 9.21.

2-Methylene-1-phenyldodec-3-en-1-yl acetate (17): Product **17** was obtained as the single *E* isomer. ^{1}H NMR (300 MHz, $CDCl_3$): $<\iota\tau>\delta</\iota\tau> = 7.38$–7.27 (m, 5H), 6.52 (s, 1H), 5.98 (d, $J = 16.2$ Hz, 1H), 5.68 (dt, $J = 6.7$ Hz, $J = 16.1$ Hz, 1H), 5.21 (s, 1H), 5.18 (s, 1H), 2.11 (s, 3H), 1.99 (q, $J = 6.8$ Hz, 2H), 1.31–1.22 (m, 12H), 0.88 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $<\iota\tau>\delta</\iota\tau> = 170.1$, 144.3, 138.8, 133.2, 128.6, 128.5, 128.3 127.8, 114.2, 100.13, 77.4, 75.1, 33.2, 32.0, 29.6, 29.4, 29.2, 29.1, 22.8, 21.4, 14.3; HR-MS: $m/z = 337.2140$ $[M+Na]^+$, calcd. for $C_{21}H_{30}O_2$: 314.2246; elemental anal. cal. for $C_{17}H_{30}O_3$: C 80.21, H 9.62; found: C 80.34, H 9.55.

Ethyl-2-methylene-1-methyldodec-3-en-1-yl carbonate (18): Product **18** was obtained as a mixture of isomers. Silica gel purification was found to modify the *Z*/*E* ratio. *Z*/*E* crude (gas chromatography): 0.34/1; purified product (gas chromatography): 0.52/1, (^{1}H NMR): 0.55/1. Yield: 79%. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.01$ (d, $J = 16.1$ Hz, 1.00H), 5.84–5.75 (m, 1.55H), 5.64 (dt, $J = 7.1$ Hz, $J = 11.7$ Hz, 0.61H), 5.40 (q, $J = 6.5$ Hz, 0.98H), 5.27 (s, 0.59H), 5.19–5.12 (m, 1.52H), 5.04 (s, 0.94H), 4.99 (s, 0.57H), 4.22–4.15 (m, 2.91H), 2.19 (q, $J = 7.2$ Hz, 1.15H), 2.09 (q, $J = 7.0$ Hz, 1.88H), 1.45–1.26 (m, 28.57H), 0.88 (t, $J = 6.9$ Hz, 5.14H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 154.7$, 146.2, 135.7, 132.0, 128.6, 125.2, 114.0, 112.3, 77.0, 74.0, 64.0, 63.9, 33.3, 32.0, 30.1, 29.7, 29.6, 29.5, 29.4, 29.3, 28.9, 22.8, 20.7, 19.9, 14.4, 14.3; HR-MS: $m/z = 192.1890$ $[M-C_3H_6O_3]^+$, calculated for $C_{17}H_{30}O_3$: 282.2195; elemental anal. calcd. for $C_{17}H_{30}O_3$: C 72.30, H 10.71; found: C 72.43, H 10.78.

Ethyl-2-methylene-1-phenyldodec-3-en-1-yl carbonate (19): Product **19** was obtained as a mixture of isomers. *Z*/*E* crude (^{1}H NMR): 0.4/1; purified product (^{1}H NMR): 0.43/1. Yield: 70%. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.42$–7.28 (m, 6.89H), 6.34 (s, 1.00H), 6.05 (s, 0.38H), 5.98 (d, $J = 16.0$ Hz, 1.02H), 5.76–5.66 (m, 1.44H), 5.55 (dt, $J = 7.1$ Hz, $J = 11.6$ Hz, 0.44H), 5.45 (s, 0.41H), 5.27 (s, 1.05H), 5.25 (s, 1.04H), 5.13 (s, 0.40H), 4.25–4.17 (m, 2.85), 2.14 (q, $J = 6.6$ Hz, 0.81H), 2.02 (q, $J = 6.9$ Hz, 2.05H), 1.36–1.24 (m, 22.57H), 0.91 (t, $J = 6.9$ Hz, 4.41H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 154.6$, 143.9, 143.0, 138.2, 135.9, 133.2, 128.6, 128.5, 128.4, 128.3, 127.7, 127.3, 125.3, 114.9, 114.2, 100.1, 81.5, 78.9, 64.3, 33.2, 32.0, 29.9, 29.6, 29.5, 29.4, 29.3, 29.2,

29.1, 28.9, 22.8, 14.4, 14.3; HR-MS: $m/z = 344.2380$ $[M]^+$, calcd. for $C_{22}H_{32}O_3$: 344.2351; elemental anal. calcd. for $C_{22}H_{32}O_3$: C 76.70, H 9.36; found: C 76.24, H 9.38.

Methyl-10,11-bis[(acetyloxy)methyl]dodeca-9,11-dienoate (24): A Schlenk flask (100 mL capacity) was loaded with 4.4 mg of catalyst **III** (0.007 mmol, 2.5 mol%), 0.110 g of diester **22**, 26 μL of hexadecane (internal standard) and 2.5 mL of dimethylcarbonate. The solution was stirred for 3 h at room temperature before addition of 50 mg of **2** (0.295 mmol, 1.0 equiv.) and 2.5 mg of catalyst **II** (0.003 mmol, 1 mol%). The reaction mixture was then heated at 40 °C for a period of 30–40 min (until all 1,4-diacetoxybut-2-yne was consumed). After cooling to to room temperature and solvent evaporation the dark crude oil was purified by chromatography on silica gel with diethyl ether/petroleum ether (95:5 v/v) as the eluant to give **24** as a clear oil; yield: 94.5 mg (90%). Product **24** was obtained as a mixture of isomers. Silica gel purification was found to modify the *Z*/*E* ratio. *Z*/*E* crude (gas chromatography): 0.95/1; purified product, (^{1}H NMR): 0.6/1. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.81$ (t, $J = 7.5$ Hz, 0.60H), 5.65 (t, $J = 7.3$ Hz, 1.00H), 5.31 (s, 1.04H), 5.25 (s, 0.56H), 5.22 (s, 0.57H), 4.99 (s, 1.02H), 4.80 (s, 1.14H), 4.75 (s, 1.11H), 4.60 (s, 1.95H), 4.57 (s, 1.98H), 3.66 (s, 4.58H), 2.32–2.18 (m, 3.17H), 2.08–2.04 (m, 12.24H), 1.63–1.58 (m, 3.30H), 1.29 (m, 9.78H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 174.4$, 170.8, 170.6, 141.4, 140.6, 139.6, 135.4, 134.6, 133.6, 131.7, 117.1, 114.64, 77.4, 67.9, 65.9, 65.4, 59.9, 51.6, 34.2, 29.7, 29.6, 29.2, 28.9, 28.5, 25.1, 21.1, 21.0; HR-MS: $m/z = 377.1938$ $[M+Na]^+$, calcd. for $C_{19}H_{30}O_6$: $m/z = 354.2042$; elemental anal. calcd. for $C_{19}H_{30}O_6$: C 64.39, H 8.53; found: C 64.46, H 8.69.

Ethyl 11-[(acetyloxy)(phenyl)methyl]dodeca-9,11-dienoate (25): Product **25** was obtained as a mixture of isomers. *Z*/*E* determined by ^{1}H NMR (pure product): 0.2/1. Yield: 81%. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.39$–7.28 (m, 6.06H), 6.51 (s, 1.00H), 6.22 (s, 0.20H), 5.97 (d, $J = 16.1$ Hz, 1.02H), 5.67 (dt, $J = 6.9$ Hz, $J = 16.0$ Hz, 1.24H), 5.51 (dt, $J = 7.0$ Hz, $J = 11.6$ Hz, 0.23H), 5.37 (s, 0.24H), 5.21 (s, 1.02H), 5.18 (s, 1.02H), 5.08 (s, 0.21H), 3.66 (s, 3.73H), 2.31–2.269 (m, 2.52H), 2.12–2.11 (m, 4.06H), 1.99 (q, $J = 7.0$ Hz, 2.05H), 1.61–1.56 (m, 2.55H), 1.30–1.16 (m, 10.02H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 174.4$, 170.0, 144.2, 138.7, 133.0, 128.7, 128.5, 128.4, 128.3, 127.8, 127.3, 114.2, 100.1, 75.1, 51.6, 34.2, 33.1, 29.2, 29.1, 28.9, 25.0, 21.4; HR-MS: $m/z = 381.2037$ $[M+Na]^+$, calcd. for $C_{22}H_{30}O_4$: 358.2144; elemental anal. calcd. for $C_{22}H_{30}O_4$: C 73.71, H 8.44; found: C 73.54, H 8.49.

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