

Metathesis of a novel dienediyne system: A unique example involving the usage of in situ generated ethylene as cross-enyne metathesis partner

Sambasivarao Kotha *, Kalyaneswar Mandal

Department of Chemistry, Indian Institute of Technology, Bombay, Powai, Mumbai 400 076, India

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Abstract

A unique example of sequential ring-closing metathesis and cross-enyne metathesis is reported. Here, the in situ generated ethylene by product from ring-closing metathesis is trapped by alkyne moiety. No metathesis product formation was observed with more reactive second generation catalyst in the absence of ethylene. Differential chemoselectivity with the first and second generation Grubbs' catalyst has been observed when the reaction was performed in presence of the external source of ethylene.

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1. Introduction

Olefin metathesis has emerged as an extremely useful strategy in designing various polycyclics and heterocyclics of different ring size [1]. Among various modes of olefin metathesis, the intramolecular version ring-closing metathesis (RCM) has become more popular than other metathesis processes. Surprisingly, enyne metathesis (EM) is relatively less explored as compared to other metathesis routes [2]. Recently, the commercially available ruthenium-based catalysts **1–3** (Fig. 1) paved way for the construction of intricate molecular frames by using various metathesis strategies [3]. Besides, a superior reaction condition have been reported where the EM reaction can be performed under ethylene atmosphere, thereby enhancing its scope to generate various functionalized 1,3-dienes [4].

Herein, we report a unique example where in situ generated ethylene from RCM is trapped by an alkyne moiety providing a cross-enyne metathesis (CEM) sequence [5].

2. Results and discussion

At the outset, preparation of the key building block **4** was accomplished via a two-step procedure (Scheme 1). Esterification of the malonic acid **5** with propargyl alcohol followed by diallylation of **6** with allyl bromide using potassium carbonate in presence of a catalytic amount of tetrabutylammonium hydrogen sulfate (TBAHS) gave the desired dienediyne unit **4** in 90% overall yield.

Next, we systematically investigated the metathesis behavior of dienediyne building block **4** with various ruthenium-based catalysts. For example, exposure of **4** to the Grubbs' 1st generation catalyst **1** in absence of ethylene at r.t. in DCM gave metathesis products (**8** and **9**) along with the RCM product **7** (Scheme 2). This critical observation prompted us to investigate this transformation in detail and the results are summarized in Table 1. No detectable change in product ratio was observed under high dilution conditions (entry 2, Table 1). Gratifyingly, the yield of the metathesis products (**8** and **9**) was significantly improved when the reaction was performed in a closed vessel (entry 3, Table 1) and

* Corresponding author. Tel.: +91 22 2572 7160; fax: +91 22 2572 3480.
E-mail address: srk@chem.iitb.ac.in (S. Kotha).

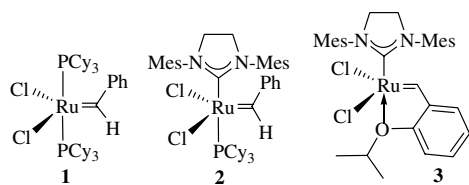


Fig. 1. Ruthenium based metathesis catalysts.

the relative product distribution is shown in Fig. 2. The reaction was stopped after the optimized time (30 min). Prolonged continuation (1.5 h) did not lead to the complete or increased conversion of **7** into **8** and/or **9** as indicated from ^1H NMR. When the reaction was performed under continuous nitrogen bubbling conditions the yield of CEM products was drastically reduced and compelled a higher catalyst loading. Moreover, much longer reaction time was required for the completion of the reaction (entry 4, Table 1). However, when the compound **7** was independently treated with the catalyst **1**, its conversion to **8** or **9** was not realized. Therefore, it was assumed that in situ generated ethylene byproduct is critical for the formation of the sequential RCM and CEM products **8** and **9**.

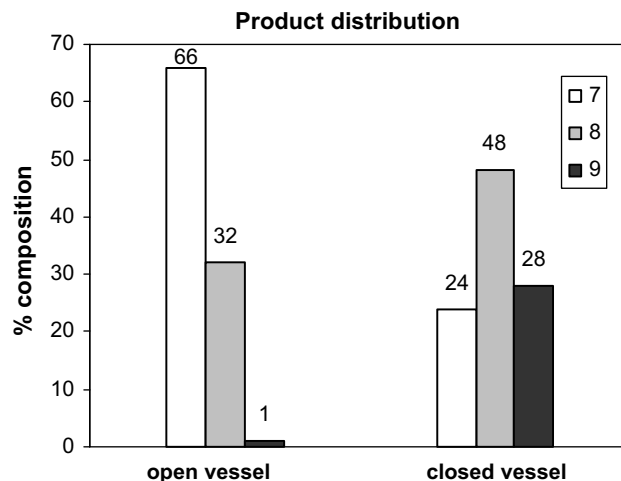


Fig. 2. Product distributions in open system and closed system.

In view of the above observations, we reasoned out that the closed system did not allow the ethylene to escape from the reaction mixture and hence the concentration of the active ruthenium carbene species in the solution is increased due to the reaction of ethylene maintaining a degenerate equilibrium with $\text{Ru}=\text{CH}_2$ [6]. Consequently,

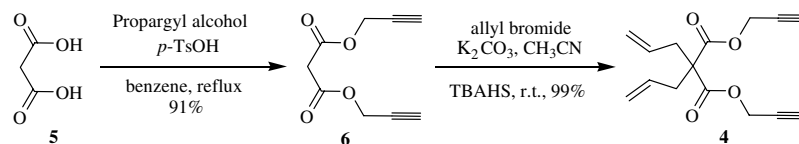
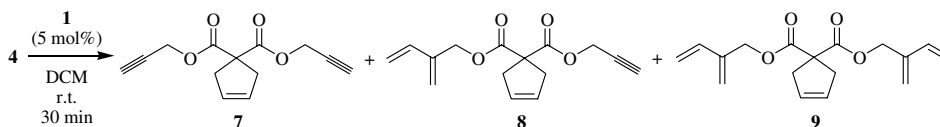
Scheme 1. Synthesis of **4**.Scheme 2. Metathesis of **4** in presence of Grubbs' 1st generation catalyst.

Table 1
Metathesis of **4** in the absence of the external source of ethylene

Entry	Ru-catalyst	Conditions	Time	Yield ^a (%)		
				7	8	9
1	1 (5 mol%)	DCM (0.1 M), r.t., open system	30 min	55	24	1
2	1 (5 mol%)	DCM (0.005 M), r.t.	30 min	50	20	1
3	1 (5 mol%)	DCM (0.2 M), r.t., closed system	30 min	17	31	16
4	1 (25 mol%) ^b	DCM, r.t. (continuous N_2 bubbling)	7 h	67	6	–
5	2 (10 mol%)	DCM, r.t.	24 h	NP ^c		
6	2 (10 mol%)	DCM reflux	11 h	NP ^c		
7	2 (10 mol%)	Benzene reflux	24 h	NP ^c		
8	3 (10 mol%)	DCM, r.t.	24 h	NP ^c		
9	3 (10 mol%)	Toluene, 80 °C	24 h	NP ^c		

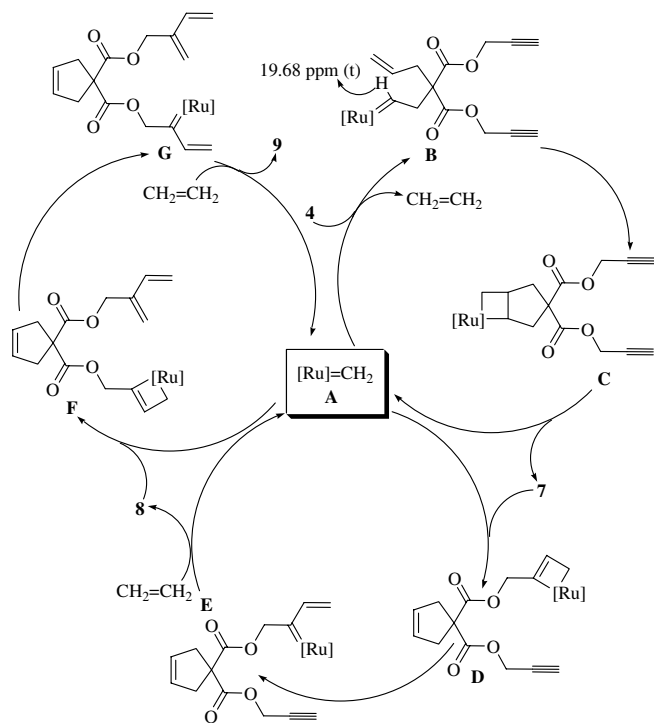
^a Isolated yield.

^b Catalyst added portion wise at different time interval.

^c NP = no product formation was observed indicated from the ^1H NMR.

the amount of the CEM product is increased. No traces of other metathesis products (such as ring-opening/cross-metathesis involving **7** and **4**) have been detected from the ^1H NMR of the reaction mixture. Similarly, continuous bubbling of nitrogen removes the volatile ethylene as and when it was generated and thereby reducing the yield of the CEM product.

The formation of the products **7**, **8** and **9** has been rationalized with the aid of three catalytic cycles shown in Scheme 3. Formation of metathesis products most likely



Scheme 3. Possible mechanistic pathways.

involves the initial formation of ruthenium alkylidene intermediate **B** from **4** followed by [2+2] cycloaddition to give metallacyclobutane **C**. Bond reorganization of **C** affords compound **7** with the generation of ruthenium methylidene **A**. The propagating carbene **A** on reaction with the alkyne moiety of **7** generates a new vinyl alkylidene **E** in the second catalytic cycle via **D**. Transfer of methylene unit from a molecule of in situ generated ethylene results in the formation of the diene **8** and regeneration of methylidene **A**. Repetition of the similar catalytic cycle with substrate **8** in principle generates another vinyl alkylidene species **G** through the intermediacy of **F**, which upon methylene transfer with ethylene provides **9**. However, the possibility of transfer of methylene to the vinyl carbene (**E** and **G**) from another molecule of the enyne substrate **4** cannot be ruled out.

An extra support of this reaction pathway has been obtained by monitoring the reaction with the aid of ^1H NMR spectroscopy. When the substrate **4** (0.2 M) and Grubbs' catalyst **1** (5 mol%; $\text{Ru}=\text{CHPh}$ at $\delta = 19.99$ ppm) were combined in CDCl_3 at r.t., a new transient proton signal (triplet at $\delta = 19.68$ ppm) corresponding to ruthenium alkylidene intermediate **B** appeared immediately besides styrene signals. Appearance of the propagating methylidene singlet at $\delta = 18.93$ ppm with concomitant disappearance of the terminal olefinic proton signal clearly indicated the initial generation of the metallacyclobutane intermediate **C** from the reaction of **4** with **1**. As metathesis proceeds, the benzylidene carbene proton singlet and alkylidene proton triplet disappears and the methylidene singlet becomes apparent. The first catalytic cycle produced a molecule of ethylene which emerged as a sharp singlet at $\delta = 5.40$ ppm and disappeared slowly as the reaction proceeded to completion (Fig. 3a).

To probe the formation of products **7–9** more reactive ruthenium catalysts containing *N*-heterocyclic carbene

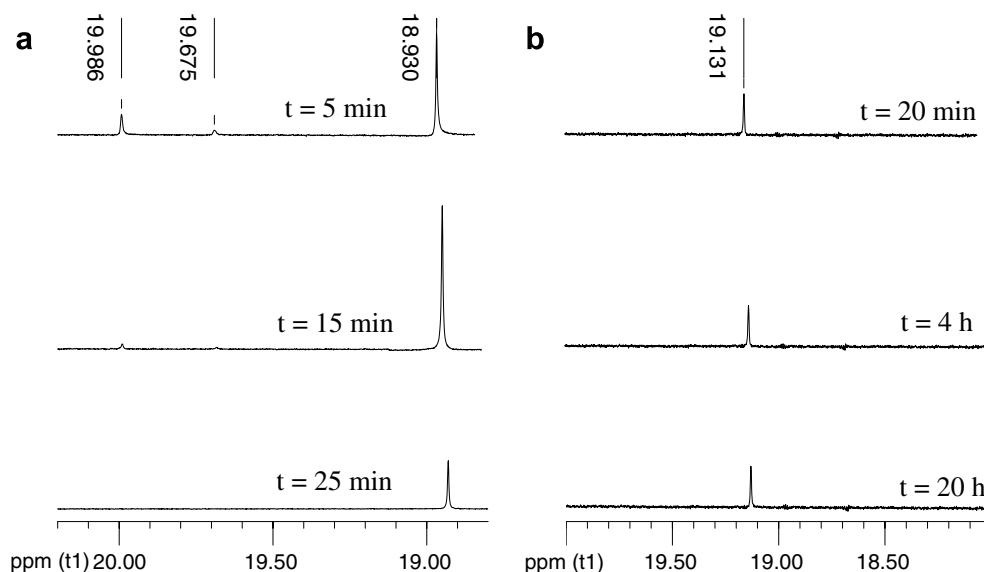


Fig. 3. Partial ^1H NMR spectra showing the change over time. Carbene signal of catalyst **1** (a) and catalyst **2** (b).

(NHC) ligands such as **2** (or **3**) were employed. To our surprise, no metathesis product formation was observed when compound **4** was reacted with the catalysts **2** or **3** (entries 5–9, Table 1). Even under forcing conditions no detectable amount of the metathesis products (entries 7 and 9, Table 1) were observed. It is known that metathesis process is highly dependent on the steric and electronic effects of the substrate employed. There are literature reports where, no reaction or incomplete conversion was observed when Grubbs' 2nd generation catalyst was employed with sterically hindered substrates. Whereas, sterically less hindered Grubbs' 1st generation catalyst was effectively used to give the complete conversion and good yield of the products with the same substrate [7]. Therefore, steric factor may be responsible for the absence of product whilst the sterically hindered 2nd generation catalyst cannot approach the olefin moiety of the sterically demanding substrate **4**. However, the possible coordination of the triple bond to the ruthenium centre leading to an inactive η^2 -alkyne or η^1 -vinylidene species also cannot be ruled out.

Monitoring the reaction with ^1H NMR (substrate **4** (0.02 M) and catalyst **2** (12 mol%) in CDCl_3 at r.t.) showed the presence of benzylidene proton singlet at $\delta = 19.13$ ppm which remained unaltered up to 20 h (Fig. 3b). No extra signal (corresponding to styrene or ruthenium methylidene) was detected and no trace amount of the product peak was observed. Starting material was completely unchanged.

Further, compounds **4** and **8** were independently exposed to Grubbs' catalyst **1** in presence of external ethylene, the anticipated CEM products were observed in a moderate yield. But, the reaction took longer time to obtain higher conversion (entries 1 and 2, Table 2). Interestingly, a different mode of reactivity has been observed when compound **4** was treated with Grubbs' 2nd generation catalyst **2** in presence of ethylene (Scheme 4). No RCM product was observed and the CEM products (**10** and **11**) were obtained in low yield [8]. Also, higher catalyst loading and longer reaction time was necessary for complete conversion of the starting material (entry 4, Table 2). The low yields can be accounted because; the multi-olefinic compounds are known to be sensitive at higher temperature or longer exposure to Grubbs' catalyst due to their propensity to polymerization.

When compound **10** was subjected to metathesis reaction with catalyst **1** in absence of ethylene, the expected RCM product **8** along with sequential RCM and CEM product **9** was observed in moderate yield (Scheme 5).

The intramolecular ring-closing enyne metathesis (RCEM) products such as **12** were not formed under the present reaction conditions (Scheme 6) [9]. Probably, the extra strain associated with the transition state of the RCCEM as compared to alkene metathesis (RCM) is responsible for the observed product. Though strained seven membered ring formations by RCCEM is well known, the present observation indicates that if there is a competi-

Table 2
Metathesis under ethylene atmosphere^a

Entry	Substrate	Ru-catalyst	Conditions	Time (h)	Yield ^b
1	4	1 (6 mol%)	DCM, r.t.	17	7 (12%), 8 (40%), 9 (22%)
2	8	1 (10 mol%)	DCM, r.t.	39	9 (43%) ^c
3	4	2 (10 mol%)	DCM, r.t.	15	10 (26%) ^d , 11 (3%) ^d
4	4	2 (20 mol%) ^e	DCM, r.t.	78	10 (9%), 11 (13%)

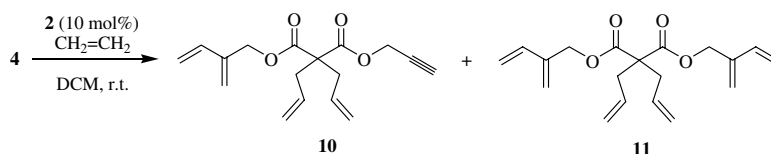
^a All the reactions were carried out at balloon pressure of ethylene.

^b Isolated yield.

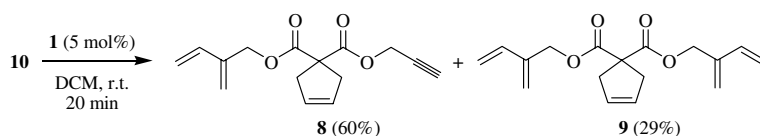
^c Yield based on starting material recovered determined at 42% conversion.

^d Yield based on starting material recovered determined at 61% conversion.

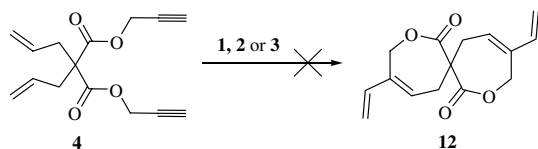
^e Catalyst added portion wise at different time intervals.



Scheme 4. Metathesis of **4** with **2** in presence of ethylene.



Scheme 5. Metathesis of **10** in presence of Grubbs' 1st generation catalyst.



Scheme 6. No RCEM product formation.

tion between the formation of five member ring and seven member ring, the five member ring formation is the preferred outcome.

3. Conclusions

In conclusion, we have described a unique example of the sequential RCM and CEM reaction where in situ generated ethylene is trapped by alkyne moiety in the absence of the external source of ethylene. In this process, cyclopentene ring and conjugated dienes are assembled in a single step. No metathesis product formation was observed with more reactive second generation catalyst in the absence of ethylene. A differential chemoselectivity of Grubbs' first generation and second generation catalyst was observed when the reaction was performed in presence of ethylene.

4. Experimental

Analytical thin-layer chromatography (TLC) was performed on glass plates coated with Acme's silica gel G or GF 254 (containing 13% calcium sulfate as a binder). Visualization of the spots on TLC plates was achieved either by exposure to iodine vapour or UV light. Flash chromatography was performed using Acme's silica gel (100–200 mesh). Petroleum ether refers to fraction having boiling point 60–80 °C. Metathesis catalysts were purchased from Sigma–Aldrich Chemical Co. All the commercial grade reagents were used without further purification. Infrared spectra were recorded on a Nicolet 400 FT-IR spectrometer in KBr/CHCl₃/CCl₄ and the absorptions are reported in cm⁻¹. ¹H NMR spectra were determined on a Bruker 300 MHz or 400 MHz spectrometer as CDCl₃ solutions. Coupling constants (*J* values) are given in hertz (Hz). Chemical shifts are expressed in parts per million (ppm) downfield from internal reference tetramethylsilane.

4.1. Diprop-2-ynyl 2,2-diallylmalonate (**4**)

To a solution of dipropargyl malonate (953 mg, 5.29 mmol) in dry acetonitrile (20 mL), anhydrous powdered potassium carbonate (3.5 g, 25.4 mmol), allyl bromide (1.53 g, 12.7 mmol), and a pinch of tetrabutyl ammoniumhydrogensulfate (TBAHS) were added. The reaction mixture was then allowed to stir at r.t. for 6 h and then filtered through a celite pad. The residue was washed with dichloromethane (3 × 10 mL) and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (silica gel,

2% EtOAc in petroleum ether) to provide compound **4** as a colourless liquid (1.36 g, 99%). *R*_f = 0.29 (silica gel, EtOAc/petroleum ether 1:9); IR (neat): $\tilde{\nu}$ = 3303 cm⁻¹ (≡CH) and 1740 cm⁻¹ (C=O); ¹H NMR (300 MHz, CDCl₃): δ = 2.48 (*t*, *J* = 2.4 Hz, 2H; 2 × ≡CH); 2.69 (*d*, *J* = 7.2 Hz, 4H; 2 × CH₂=CHCH₂); 4.72 (*d*, *J* = 2.4 Hz, 4H; 2 × OCH₂); 5.12–5.19 (*m*, 4H; 2 × CH₂=CHCH₂); 5.60–5.74 (*m*, 2H; 2 × CH₂=CHCH₂); ¹³C NMR (75.4 MHz, CDCl₃): δ = 36.7, 52.8, 57.3, 75.4, 120.0, 131.6, 169.6; HRMS (Q-Tof): *m/z* calc. for C₁₅H₁₆O₄Na (M+Na): 283.0946; found: 283.0946.

4.2. Representative metathesis of diprop-2-ynyl 2,2-diallylmalonate (**4**) with Grubbs' 1st generation catalyst **1** in the absence of the external source of ethylene (entry 3, Table 1)

Into a test tube equipped with a magnetic stir bar was added compound **4** (39 mg, 0.15 mmol) and Grubbs' catalyst **1** (7 mg, 8.5 μmol) in dry, degassed DCM (0.7 mL, degassed with argon for 10 min) and then tightly closed with glass stopper. The reaction mixture was stirred at r.t. for 30 min and concentrated. The crude product was purified by silica gel column chromatography. Elution of the column with 1.5% EtOAc in petroleum ether afforded bis(2-methylenebut-3-enyl) cyclopent-3-ene-1,1-dicarboxylate (**9**) (7 mg, 16%) as a colourless oil. *R*_f = 0.43 (silica gel, EtOAc/petroleum ether 1:9); IR (neat): $\tilde{\nu}$ = 1734 cm⁻¹ (C=O); ¹H NMR (300 MHz, CDCl₃): δ = 3.05 (*s*, 4H; 2 × cyclopentene CH₂), 4.81 (*s*, 4H; 2 × OCH₂), 5.10–5.62 (*m*, 8H; 2 × C=CH₂ and 2 × CH=CH₂), 5.62 (*s*, 2H; cyclopentene =CH), 6.35 (*dd*, *J* = 17.4, 11.1 Hz, 2H; 2 × CH=CH₂); ¹³C NMR (75.4 MHz, CDCl₃): δ = 40.7, 58.8, 64.5, 114.5, 118.2, 127.6, 135.8, 139.9, 171.4; HRMS (Q-Tof): *m/z* calc. for C₁₇H₂₀O₄Na (M+Na): 311.1259; found: 311.1256. Continuous elution of the column with the same polarity gave 1-(2-methylenebut-3-enyl) 1-prop-2-ynyl cyclopent-3-ene-1,1-dicarboxylate (**8**) (12 mg, 31%) as a colourless oil. *R*_f = 0.34 (silica gel, EtOAc/petroleum ether 1:9); IR (neat): $\tilde{\nu}$ = 3294 cm⁻¹ (≡CH) and 1735 cm⁻¹ (C=O); ¹H NMR (300 MHz, CDCl₃): δ = 2.46 (*t*, *J* = 2.4 Hz, 1H; ≡CH); 3.06 (*s*, 4H; 2 × cyclopentene CH₂); 4.71 (*d*, *J* = 2.4 Hz, 2H; OCH₂C≡CH); 4.83 (*s*, 2H; OCH₂C(=CH₂)CH=CH₂); 5.12–5.26 (*m*, 4H; OCH₂C(=CH₂)CH=CH₂ and OCH₂C(=CH₂)CH=CH₂); 5.62 (*s*, 2H; 2 × cyclopentene =CH); 6.36 (*dd*, *J* = 18, 11.4 Hz, 1H; CH=CH₂); ¹³C NMR (75.4 MHz, CDCl₃): δ = 41.0, 53.1, 58.8, 64.9, 75.3, 114.8, 118.6, 127.8, 136.0, 140.1, 171.3, 171.5; HRMS (Q-Tof): *m/z* calc. for C₁₅H₁₆O₄Na (M+Na): 283.0946; found: 283.0938. Further elution of column with 2% EtOAc/petroleum ether provided diprop-2-ynyl cyclopent-3-ene-1,1-dicarboxylate (**7**) (6 mg, 17%) as a colourless oil. *R*_f = 0.24 (silica gel, EtOAc/petroleum ether 1:9); IR (neat): $\tilde{\nu}$ = 3293 cm⁻¹ (≡CH) and 1734 cm⁻¹ (C=O); ¹H NMR (300 MHz, CDCl₃): δ = 2.47 (*t*, 2.6 Hz, 2H; 2 × C≡CH); 3.06 (*s*, 4H; 2 × cyclopentene CH₂); 4.74 (*d*, *J* = 2.4 Hz, 4H; 2 × OCH₂); 5.62 (*s*, 2H;

2 × cyclopentene C=CH); ^{13}C NMR (100.6 MHz, CDCl_3): $\delta = 41.0, 53.3, 58.7, 75.4, 127.9, 171.1$; HRMS (Q-Tof): m/z calc. for $\text{C}_{13}\text{H}_{12}\text{O}_4\text{Na}$ (M+Na): 255.0633; found: 255.0642.

4.3. Metathesis of diprop-2-ynyl 2,2-diallylmalonate (**4**) with Grubbs' 1st generation catalyst **1** in the presence of the external source of ethylene (entry 1, Table 2)

Compound **4** (100 mg, 0.384 mmol) in dry DCM (7 mL) was degassed with nitrogen for 15 min and then with ethylene gas for 10 min. Grubbs' catalyst **1** (20 mg, 0.024 mmol, portion wise addition at different time intervals) was then added and finally, the vessel was kept under 1 atm. ethylene pressure (using balloon pressure). The reaction mixture was then stirred at r.t. Starting material was disappeared within 30 min. However, the stirring was continued to get better conversion of the cross-enyne metathesis products. After 17 h the pressure was released and the resulting brown solution was concentrated under reduced pressure and the crude product was purified by silica gel flash chromatography. Elution of the column with 1.5% EtOAc in petroleum ether afforded compound **9** (24 mg, 22%) as a colourless oil. Continuous elution of the column with the same polarity gave compound **8** (40 mg, 40%) as a colourless oil. Further elution of column with 2% EtOAc/petroleum ether provided **7** (11 mg, 12%) as a colourless oil.

4.4. Metathesis of **8** with Grubbs' 1st generation catalyst **1** in the presence of the external source of ethylene (entry 2, Table 2)

Compound **8** (45 mg, 0.17 mmol) in dry DCM (3 mL) was degassed with nitrogen for 15 min and then with ethylene gas for 10 min. Grubbs' catalyst **1** (14 mg, 0.017 mmol, portion wise addition at different time intervals) was then added and finally, the vessel was kept under 1 atm. ethylene pressure (using balloon pressure). The reaction mixture was then stirred at r.t. for 39 h. The pressure was released and the resulting brown solution was concentrated under reduced pressure and the crude reaction mixture was then subjected to flash chromatographic purification (silica gel, 1–1.5% EtOAc in petroleum ether) to afford compound **9** as a colourless liquid (9 mg, 43%, based on starting material recovered) along with unreacted starting material **8** (26 mg, 58%).

4.5. Representative metathesis of diprop-2-ynyl 2,2-diallylmalonate (**4**) with Grubbs' 2nd generation catalyst **2** in the presence of the external source of ethylene (entry 4, Table 2)

Compound **4** (50 mg, 0.19 mmol) in dry DCM (10 mL) was degassed with nitrogen for 15 min and then with ethylene gas for 10 min. Grubbs' catalyst **2** (32 mg, 0.038 mmol, portion wise addition at different time intervals) was then added and finally, the vessel was kept under 1 atm. ethylene pressure (using balloon pressure). The reaction mixture was

then stirred at r.t. After completion of the reaction (78 h, TLC monitoring), the pressure was released and the resulting brown solution was concentrated under reduced pressure and the crude product was purified by silica gel flash chromatography. Elution of the column with 1% EtOAc in petroleum ether afforded bis(2-methylenebut-3-enyl) 2,2-diallylmalonate (**11**) as a colourless oil. $R_f = 0.51$ (silica gel, EtOAc/petroleum ether 1:9); IR (neat): $\tilde{\nu} = 1735\text{ cm}^{-1}$ (C=O); ^1H NMR (300 MHz, CDCl_3): $\delta = 2.68$ (dt, $J = 7.3, 1.2$ Hz, 4H; $2 \times \text{CH}_2\text{CH}=\text{CH}_2$); 4.78 (d, $J = 0.6$ Hz, 4H; $2 \times \text{OCH}_2$); 5.09–5.26 (m, 12H; $2 \times \text{C}(\text{=CH}_2)\text{CH}=\text{CH}_2$ and $2 \times \text{CH}_2\text{CH}=\text{CH}_2$); 5.58–5.72 (m, 2H; $2 \times \text{CH}_2\text{CH}=\text{CH}_2$); 6.35 (dd, $J = 18.0, 11.1$ Hz, 2H; $2 \times \text{C}(\text{=CH}_2)\text{CH}=\text{CH}_2$); HRMS (Q-Tof): m/z calc. for $\text{C}_{19}\text{H}_{24}\text{O}_4\text{Na}$ (M+Na): 339.1572; found: 339.1562. Further elution of the column with 1.5% EtOAc in petroleum ether afforded 1-(2-methylenebut-3-enyl) 3-prop-2-ynyl 2,2-diallylmalonate (**10**) as a colourless oil. $R_f = 0.41$ (silica gel, EtOAc/petroleum ether 1:9); IR (neat): $\tilde{\nu} = 3305\text{ cm}^{-1}$ ($\equiv\text{CH}$) and 1735 cm^{-1} (C=O); ^1H NMR (300 MHz, CDCl_3): $\delta = 2.46$ (t, $J = 2.6$ Hz, 1H; $\equiv\text{CH}$); 2.68 (d, $J = 7.8$ Hz, 4H; $2 \times \text{CH}_2\text{CH}=\text{CH}_2$); 4.50 (d, $J = 2.4$ Hz, 2H; $\text{CH}_2\text{C}\equiv\text{CH}$); 4.81 (d, $J = 0.9$ Hz, 2H; $\text{OCH}_2\text{C}(\text{=CH}_2)\text{CH}=\text{CH}_2$); 5.11–5.28 (m, 8H; $\text{OCH}_2\text{C}(\text{=CH}_2)\text{CH}=\text{CH}_2$ and $2 \times \text{CH}_2\text{CH}=\text{CH}_2$); 5.59–5.71 (m, 2H; $2 \times \text{CH}_2\text{CH}=\text{CH}_2$); 6.63 (dd, $J = 18, 11.1$ Hz, 1H; $\text{OCH}_2\text{C}(\text{=CH}_2)\text{CH}=\text{CH}_2$); HRMS (Q-Tof): m/z calc. for $\text{C}_{17}\text{H}_{20}\text{O}_4\text{Na}$ (M+Na): 311.1259; found: 311.1262.

4.6. Metathesis of **10** with Grubbs' 1st generation catalyst **1** in the absence of the external source of ethylene

In a test tube equipped with a magnetic stir bar was added compound **10** (24 mg, 0.083 mmol) and Grubbs' catalyst **1** (4 mg, 4.9 μmol) in dry, degassed DCM (3 mL, degassed with argon for 10 min) and then tightly closed with glass stopper. The reaction mixture was stirred at r.t. After completion of the reaction (20 min, TLC monitoring) the brown solution was concentrated. The crude product was purified by silica gel column chromatography. Elution of the column with 1.5% EtOAc in petroleum ether afforded bis(2-methylenebut-3-enyl) cyclopent-3-ene-1,1-dicarboxylate (**9**) (7 mg, 29%) as a colourless oil. Continuous elution of the column with the same polarity gave 1-(2-methylenebut-3-enyl) 1-prop-2-ynyl cyclopent-3-ene-1,1-dicarboxylate (**8**) (13 mg, 60%) as a colourless oil.

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