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Ruthenium-Catalyzed Cross Metathesis of β-Myrcene and its Derivatives with Methyl Acrylate

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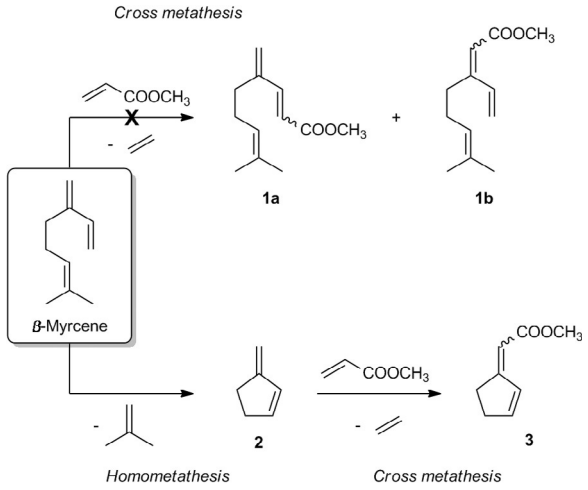
The reaction of β-myrcene with methyl acrylate produces 3-methylenecyclopent-1-ene in the presence of the Ru catalyst Neolyst M2 by ring-closing metathesis in the first step. In the second step, the generated methylidene unit reacts with methyl acrylate to give the corresponding unsaturated cyclic ester by cross metathesis. Under the optimized reaction conditions (80 °C, Neolyst M2, 16 equivalents of methyl acrylate), derivatives of β-myrcene, myrcenol, myrcenyl acetate, and β-ocimene, react to yield functionalized acyclic esters.

Since its discovery by Banks and Bailey in 1964 when they reacted propylene with ethylene and 2-butene,[1] metathesis has become powerful for both industrial applications[2] and academic research.[3] It constitutes an elegant route for direct C–C bond formation in organic chemistry,[3a,b] has a spectacular functional group tolerance, and Ru-catalyzed metathesis is often a key step in the total synthesis of natural[4] and biologically active compounds.[5]

Furthermore, because of its convenient reaction regime, it is of great importance for industrial applications, and thus industrially relevant compounds can be attained easily from bulk chemicals in a single step.[6] The production of cyclohexadecenone by Symrise, a flavor better known as Globanone, is an example of the successful application of metathesis.

To date, the metathesis of 1,3-dienes has been rarely reported in the literature. Cossy and co-workers attained high chemoselectivities and yields in the cross metathesis of methyl sorbate with 1-octene using a Hoveyda catalyst.[7] Additionally, a structurally related substrate was reacted with styrene in the presence of the Grubbs II catalyst.[8] With the use of this catalyst, the scope could be expanded to other functionalized dienes and reactants.[9] However, all of these examples have in common that either high catalyst loadings (up to 5 mol%) or long reaction times were required to achieve satisfactory yields.

Previously, the 1,3-diene β-myrcene (Scheme 1) has been examined exclusively in homometathesis to give functionalized



Scheme 1. Metathesis of β-myrcene with methyl acrylate.

cyclic pentenes.[10] Bilel and co-workers examined the cross metathesis of several terpenes[11] such as citronellal, citronellol, and citral with methyl acrylate to form terpenoids using a Hoveyda catalyst.[12] The range of substrates was expanded by Mauduit to other terpenes, which included citronellene.[13] However, for this substrate, which is similar to myrcene, an only moderate yield (<25%) could be realized. Quite recently, Fomine et al. examined the metathesis of α- and β-pinene by computational modeling.[14] Nevertheless, to the best of our knowledge, a cross metathesis of β-myrcene has not been described so far.

The demand for an easy access to unsaturated ester derivatives, which show potential features as flavors and fragrances,[15] has prompted us to undertake investigations in the field of terpene functionalization. Herein, we present a hitherto unknown derivatization of renewable β-myrcene with methyl acrylate by a cross-metathesis reaction.

Our initial studies were focused on the cross metathesis of β-myrcene with methyl acrylate (Scheme 1). Both C_{11}-ester **1a** and **1b**, respectively, derived from the direct cross metathesis, were not formed in the presence of all tested Ru catalysts (Table 1).

Instead, β-myrcene undergoes homometathesis to yield the ring-closed product (RCP), 3-methylenecyclopent-1-ene (**2**),[10,16] which is ready to react with methyl acrylate to yield the corresponding cross-metathesis product, methyl 2-(cyclopent-2-en-1-ylidene)acetate (**3**). Although its synthesis has already been suggested in a Horner–Wadsworth–Emmons reaction by Shibasaki et al.,[17] this compound has not been described so far. It

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Table 1. Precatalyst screening of the cross metathesis of β-myrcene and methyl acrylate at different temperatures.[a]

Entry	Precatalyst	Temperature								
		60 °C			80 °C			90 °C		
		X [%]	*Y*(**2**) [%]	*Y*(**3**) [%]	*X* [%]	*Y*(**2**) [%]	*Y*(**3**) [%]	*X* [%]	*Y*(**2**) [%]	*Y*(**3**) [%]
1	–	–	–	–	–	–	–	–	–	–
2	Grubbs I	2	2	–	3	3	–	7	2	–
3	Grubbs II	68	56	1	98	62	13	97	63	13
4	Neolyst M2	8	7	-	95	67	14	94	65	10
5	Neolyst M2py	29	28	-	82	66	6	77	61	4
6[b]	Neolyst M31	37	2	2	17	1	8	55	2	3
7[c]	Neolyst M51	9	9	–	21	17	–	28	23	–

[a] 0.5 mol% precatalyst, c(β-myrcene) = 0.1 mol L^{-1}, β-myrcene/methyl acrylate = 1:4, t = 1 h, toluene; conversion and yields were detected by GC (Abbreviations of the precatalysts: see Figure 1). [b] Addition of 50.0 mol% $PhSiCl_3$. [c] Addition of 0.5 mol% 0.1 M HCl. Abbreviations: X = conversion, Y = yield.

possesses a characteristic odor that can be described as "green", "buttery", or "plastic".

Among the various Ru precatalysts tested were those demonstrated previously to be successful in metathesis, such as first- and second-generation Grubbs catalysts and representatives of the Neolyst family (Figure 1). The main results of the screening of different precatalysts are presented in Table 1.

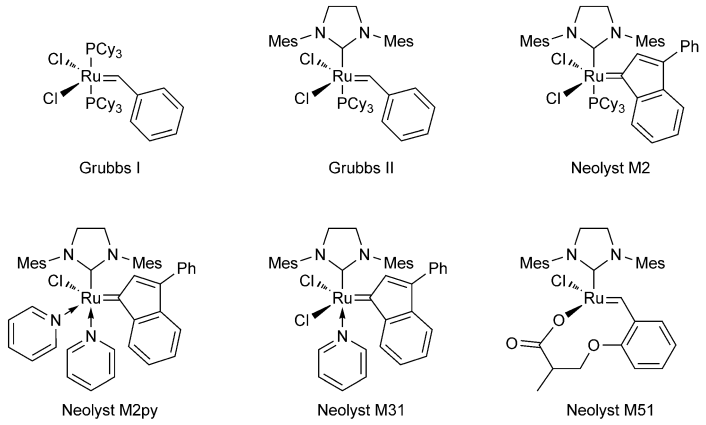


Figure 1. Selected Ru precatalysts for the cross metathesis of β-myrcene (Cy = cyclohexyl, Mes = mesityl).

The experiments were started at 60 °C, and only the reaction with the Grubbs II catalyst gave a satisfactory conversion (X) of β-myrcene with a good yield (Y) to the cyclic homometathesis product **2** of 56%, whereas only traces of the cyclic C_7-ester **3** could be detected in the final mixture (entry 3). However, a reaction with the structurally similar precatalyst Neolyst M2,[18] which bears an indenylidene at the metal center instead of benzylidene, gave the diene **2** only in poor yield (7%, entry 4). If the reaction temperature was increased to 80 °C, an enhanced conversion was noted in all cases. Using Grubbs II and Neolyst M2 catalysts led to similar results with almost full conversion after 1 h and a yield of the diene **2** of 62 and 67%, respectively. Fortunately, in addition to the homometathesis product, the ester **3** could be detected in up to 14% yield. A comparison of both runs showed that Neolyst M2 required higher temperatures to attain a similar activity to that of the Grubbs II catalyst. This observation was discussed previously by Grela et al. and is attributed to an easier dissociation of the benzylidene in Grubbs II than the indenylidene in Neolyst M2.[19]

The structurally related catalyst, Neolyst M2py, which has one chlorine and the phosphine ligand is substituted by pyridine, also demonstrated a good activity for the homometathesis to yield **2** in 66%, but less of product **3** was obtained (entry 5). Surprisingly, a reaction performed with Neolyst M31 resulted in low amounts of the desired products at all temperatures (entry 6). Significant differences between the conversion and yield indicated polymeric side reactions, for example, the ring-opening polymerization of cyclic diene **2**. This phenomenon was described by Sita in the polymerization of citronellene.[10a] Products derived from an acyclic diene metathesis of the substrate were not observed in all runs is in accordance with the results of Fogg et al. for highly dilute solutions.[20] The results from experiments in which Neolyst M51 was used as the precatalyst are in line with the work of Grela et al.,[21] as it is not thermally stable enough to perform ring-closing metathesis efficiently.

Encouraged by the results with Neolyst M2, different solvents were screened. With regard to the economy and eco-friendly credentials of metathesis, which usually works with expensive transition-metal catalysts synthesized in multistep reactions, the choice of the right solvent is essential. In particular, a suitable solvent could facilitate the recovery of the catalyst and would offer a better product separation. The results for the solvent screening are shown in Figure 2.

Among a number of solvents, the catalyst showed a comparable activity and selectivity for the desired products in toluene, heptane, and 1,4-dioxane. More polar solvents such as methyl *tert*-butyl ether (MTBE) and THF have worse characteristics towards the reaction, and only traces of the cyclic ester were formed. In contrast to the low-boiling-point solvents, only propylene carbonate (PC, high boiling) has the ability to give **2** and its consecutive product **3** in promising yields. With regard to a beneficial product separation by distillation, this solvent has to be considered.[22] Furthermore, no reaction took

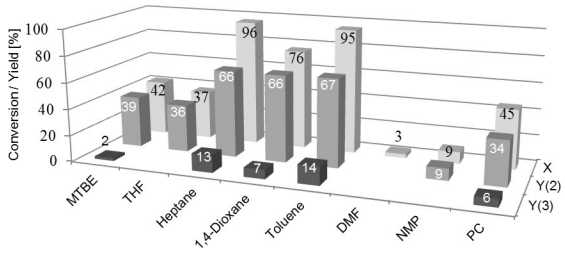


Figure 2. Optimization of the solvent in the cross metathesis of β-myrcene with methyl acrylate. Conditions: 0.5 mol% Neolyst M2, c(β-myrcene) = 0.1 mol L^{-1}, β-myrcene/methyl acrylate = 1:4, T = 80 °C or reflux, t = 1 h; conversions and yields were detected by GC (MTBE = methyl *tert*-butyl ether, NMP = *N*-methyl-2-pyrrolidone, PC = propylene carbonate). Abbreviations: X = conversion, Y = yield.

place in solvents such as dichloromethane, methanol, DMSO, and ethylene glycol.

Our attention was then focused on the variation of the catalyst loading to minimize side reactions and thus to force the final cross metathesis to give **3** using toluene as the solvent (Figure 3). It may be assumed that an enhanced concentration of the active catalyst will promote the second reaction step of the cross metathesis with methyl acrylate.

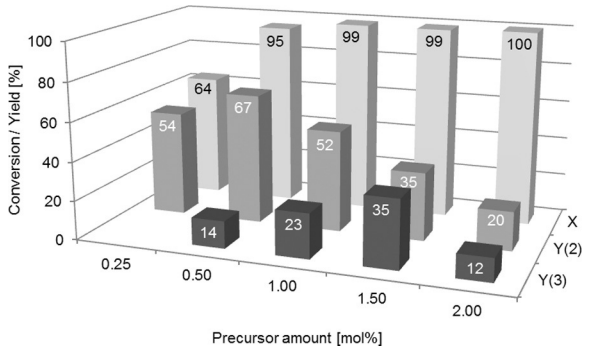


Figure 3. Optimization of the catalyst loading in the cross metathesis of β-myrcene with methyl acrylate. Conditions: Neolyst M2, c(β-myrcene) = 0.1 mol L^{-1}, β-myrcene/methyl acrylate = 1:4, T = 80 °C, t = 1 h, toluene; conversion and yields were detected by GC. Abbreviations: X = conversion, Y = yield.

If the concentration of the precatalyst is doubled to 1 mol%, the detected amount of 3-methylenecyclopent-1-ene (**2**) in the final mixture decreased, whereas the yield of the cyclic ester **3** increased. A further increase of the catalyst concentration to 1.5 mol% affected the homometathesis but generated the consecutive product in up to 35% yield. Unfortunately, this trend was not observed using 2 mol% of Neolyst M2. Indeed, despite the full conversion, less of the ring-closing metathesis product **2** and less of the cross-metathesis product **3** were generated. It can be supposed that Neolyst M2 catalyzes the ring-opening metathesis polymerization (ROMP)[23] of **2** in addition to the ring-closing metathesis of β-myrcene to give **3**. If 0.25 mol% of the catalyst was employed, the conversion decreased, but a higher selectivity for the diene (54%) was achieved. Unfortunately, no cyclic ester could be detected.

Furthermore, the dependence on the amount of methyl acrylate was examined in the hope to promote the reaction in favor of either diene **2** or cyclic ester **3**. The results are illustrated in Figure 4.

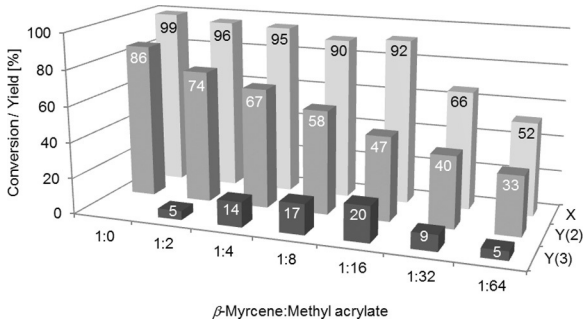


Figure 4. Optimization of the β-myrcene/methyl acrylate molar ratio in the cross metathesis of β-myrcene with methyl acrylate. Conditions: 0.5 mol% Neolyst M2, c(β-myrcene) = 0.1 mol L^{-1}, T = 80 °C, t = 1 h, toluene; conversion and yields were detected by GC. Abbreviations: X = conversion, Y = yield.

An increase of the ratio of β-myrcene to methyl acrylate from 1:4 to 1:8 and finally to 1:16 gave an improved yield for the consecutive product **3** of up to 20%, as expected. The use of methyl acrylate in a great excess, such as 1:32 or even 1:64, seems to inhibit the reaction and both the homo- and cross-metathesis products were detected in lower amounts. At a lower ratio of only 1:2, more diene **2** (74%) and less C_7-ester **3** (5%) were formed. Consequently, if no methyl acrylate is added to the reaction, a maximum yield of 86% of **2** was detected.

Indeed, with the application of a combination of both steering effects, a catalyst concentration of 1.5 mol% and an excess of methyl acrylate of 16:1 gave a 22% yield of the ring-closing metathesis product and a maximum of 42% for the corresponding cyclic ester **3**.

With regard to the economy of this reaction, we tried to optimize the space time yield by increasing the substrate concentration (Figure 5).

An enhanced β-myrcene concentration (up to 0.5 mol L^{-1}) has no significant influence on reactivity and selectivity. However, if the reaction mixture is more concentrated, the conver-

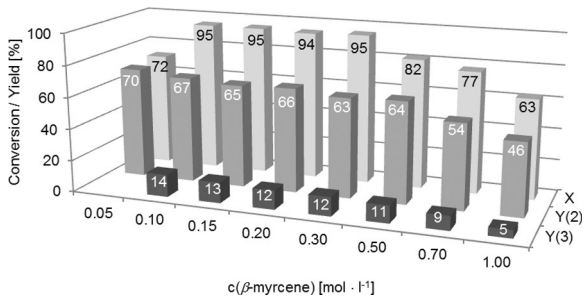


Figure 5. Optimization of the β-myrcene concentration in the cross metathesis of β-myrcene with methyl acrylate. Conditions: 0.5 mol% Neolyst M2, β-myrcene/methyl acrylate = 1:4, T = 80 °C, t = 1 h, toluene; conversion and yields were detected by GC. Abbreviations: X = conversion, Y = yield.

sion and thus the yield for both products decreased. Possibly, at higher concentrations, a catalyst deactivation occurs caused by substrate inhibition. At a low concentration of 0.05 mol L^{-1}, the yield for the homometathesis product could be slightly improved (70%), but surprisingly, no ring-closed product was obtained.

These results illustrated that the reaction path of an intramolecular homometathesis (to give **2**) is much faster than the direct cross metathesis of β-myrcene itself (to give **1a**,**b**). To prevent the ring-closing reaction, the (isolated) threefold substituted double bond was functionalized so that the remaining diene unit of the molecule can react exclusively with the reactant. Therefore, myrcenol as well as its O-acetylated derivative, myrcenyl acetate, were applied to the reaction. The latter was synthesized by treatment of the alcohol with acetyl chloride in the presence of pyridine. Moreover, the reaction of isomeric β-ocimene was examined (Figure 6).

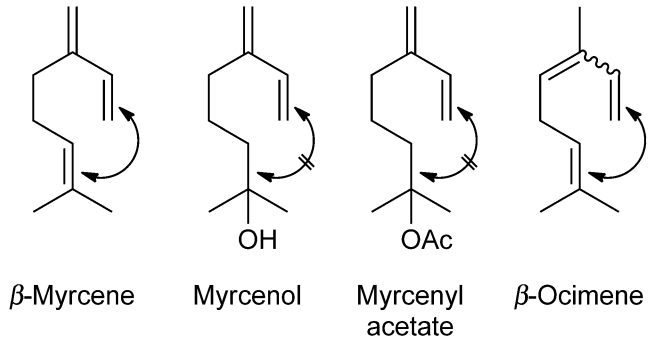


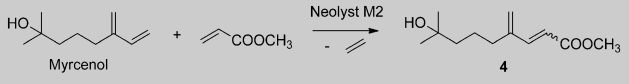
Figure 6. Applied structurally related dienes for the cross metathesis with methyl acrylate (double arrow: possible ring-closing metathesis reaction).

The first investigations were undertaken with myrcenol, and the results of the reaction with methyl acrylate in the presence of Neolyst M2 are shown in Table 2.

All experiments were performed with Neolyst M2 in toluene by adapting the reaction conditions from the reaction of β-myrcene. Indeed, the direct cross-metathesis product is generated in all cases, however, the formation of Diels–Alder adducts (DAA) was also detected. An increase of the catalyst loading from 0.5 to 3 mol% led to an increased conversion to 23% to give the ester **4** in a maximum 4% yield (entries 1–3). If the excess of methyl acrylate was increased to 1:16, 14% of the desired product could be detected (entry 4). Remarkably, a further enhancement of the acrylate and an increased reaction time (entries 5 and 6, respectively) promoted the undesired Diels–Alder reaction.

Additionally, myrcenyl acetate was used in the reaction, and the results are given in Table 3.

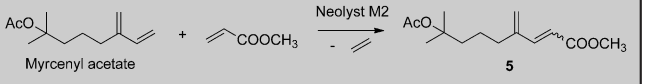
Table 2. Cross metathesis of myrcenol with methyl acrylate with Neolyst M2 in toluene.[a]



Entry	Precatalyst [mol%]	Myrcenol/ methyl acrylate	*X* [%]	*Y*(**4**) [%]	*Y*(DAA) [%]
1	0.5	1:4	5	1	1
2	1.0	1:4	8	1	4
3	3.0	1:4	23	4	3
4	3.0	1:16	44	14	8
5[b]	3.0	1:16	72	11	15
6	3.0	1:32	59	9	13

[a] Neolyst M2, *c*(myrcenol) = 0.1 mol L^{-1}, *T* = 80 °C, *t* = 1 h, toluene; conversion and yields were detected by GC. [b] *t* = 8 h. Abbreviations: *X* = conversion, *Y* = yield.

Table 3. Cross metathesis of myrcenyl acetate with methyl acrylate with Neolyst M2 in toluene.[a]



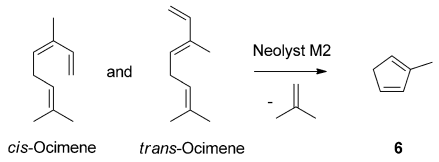
Entry	Precatalyst [mol%]	Myrcenyl acetate/ methyl acrylate	*X* [%]	*Y*(**5**) [%]	*Y*(DAA) [%]
1	0.5	1:4	30	1	1
2	0.5	1:16	37	4	6
3	1.5	1:4	29	4	2

[a] Neolyst M2, *c*(myrcenyl acetate) = 0.1 mol L^{-1}, *T* = 80 °C, *t* = 3 h, toluene; conversion and yields were detected by GC. Abbreviations: *X* = conversion, *Y* = yield.

Under the optimized reaction conditions, only traces of product **5** were detected (entry 1). Although the catalyst loading and/or amount of methyl acrylate were increased, only a negligible yield for the cross-metathesis product was obtained (entries 2 and 3). Clearly, the substituent of the substrate seems to have a dramatic influence on the reaction. Previous investigations by Hoye and Zhao[10b] on linalool showed that a nucleophilic hydroxyl group is able to coordinate to the metal center of the catalyst by substitution of a chlorine or phosphine to lead to an increased reaction rate. A non-nucleophilic acetyl function, which is present in myrcenyl acetate, does not have these characteristics, which explains the low conversion rates in a reaction with methyl acrylate.

As β-myrcene seemed to be highly reactive in ring-closing metathesis, the isomer β-ocimene was taken into consideration for direct cross metathesis with methyl acrylate. A mixture of both the *cis* and *trans* isomers (*cis*/*trans* = 33:67) was first reacted in the presence of Neolyst M2 without any additional acrylate to give the corresponding methyl cyclopentadiene (**6**; Scheme 2). The results of the temperature dependence of the reaction are shown in Figure 7.

In accordance with the results for the cross metathesis of β-myrcene (see above), the highest activity for Neolyst M2 was achieved at reaction temperatures above 80 °C, which yielded up to 25% of **6**. In addition, it also indicated that a ring-closing reaction takes place for the *cis* rather than for the *trans* isomer, which might be caused by the physical configuration/distance between the double bonds (Scheme 3). As a result, a maximum



Scheme 2. Ring-closing metathesis of a *cis*/*trans* mixture of β-ocimene.

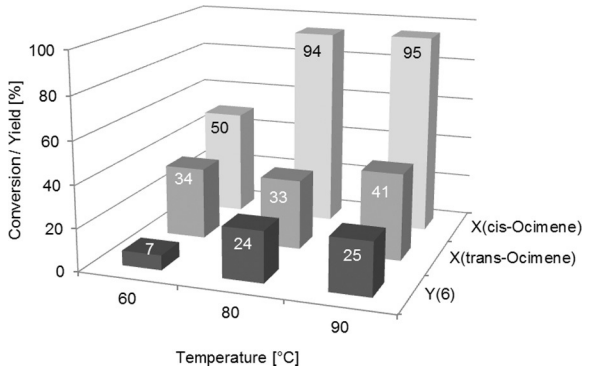


Figure 7. Optimization of the temperature in the homometathesis of β-ocimene. Conditions: 0.5 mol% Neolyst M2, c(β-ocimene) = 0.1 mol L^{-1}, t = 1 h, toluene; conversions and yield were detected by GC. Abbreviations: X = conversion, Y = yield.

of 41% conversion was achieved for the *trans* isomer, whereas a conversion of more than 94% *cis*-ocimene was observed.

Furthermore, the conversion of β-ocimene is significantly higher than the yield of the cyclic product. It is supposed that this is caused by the modified 1,3-diene unit in β-ocimene: the diene unit of β-myrcene contains two terminal double bonds. However, in β-ocimene an internal double bond is present next to the terminal one, which seems to affect the activity of the entire 1,3-diene unit towards homometathesis. Finally, β-ocimene is more able to react in an acyclic diene metathesis (ADMET), which is in agreement with the ring-closing metathesis and is one of the possible side reactions.

To counteract those unintended reactions and simultaneously increase the yield of **6**, the dependence of the catalyst loading was examined (Table 4). An increased amount of Neolyst M2 caused an increased conversion of both *cis*- and *trans*-ocimene. Simultaneously, the yield of **6** was increased to 25% using 1 mol% of the precatalyst (entry 4). Surprisingly, a prolonged reaction time improved the conversion but affected the amount of product (4%; entry 6). This observation can be explained by the fact that methyl cyclopentadiene might further react in consecutive metathesis reactions (e.g., ROMP).

Table 4. Ring-closing metathesis of a *cis*/*trans* mixture of β-ocimene with Neolyst M2 in toluene.[a]

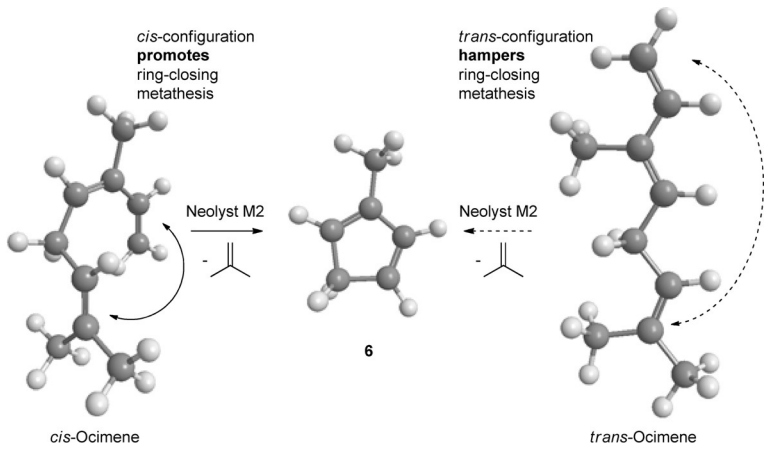
Entry	Precatalyst [%][mol%]	X(*cis*-ocimene) [%][%]	X(*trans*-ocimene) [%][%]	Y(**6**) [%][%]
1	0.1	36	24	4
2	0.3	62	27	13
3	0.5	94	33	24
4	1.0	99	49	25
5	1.5	99	59	24
6[b]	0.5	98	70	4

[a] Neolyst M2, c(β-ocimene) = 0.1 mol L^{-1}, T = 80 °C, t = 1 h, toluene; conversions and yield were detected by GC. [b] t = 16 h. Abbreviations: X = conversion, Y = yield.

The special electronic situation of the double bond in β-ocimene (see above) allows a direct cross metathesis with methyl acrylate to give the expected unsaturated acyclic ester **7**. Moreover, the threefold substituted double bond reacts too to give the corresponding product **8** with the dissociation of isobutene. As a result of their configurations, several diastereomers of **7** and **8** are possible. The results are summarized in Table 5.

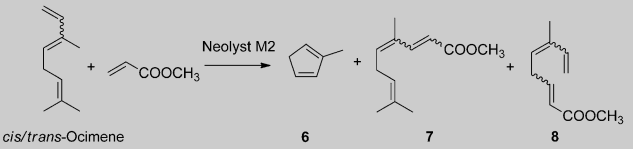
An increase of the reaction temperature from 60 to 90 °C promoted the conversion, and a maximum yield of the acyclic esters **7** and **8** of 10 and 18%, respectively, could be attained (entries 1–3). If 1.5 mol% of the precatalyst was applied, the amounts of the desired products could only be improved slightly (entry 4).

Furthermore, the influence of an excess of methyl acrylate was examined (Figure 8). With a β-ocimene/methyl acrylate ratio of 1:8 and 1:16, respectively, the highest yields of both



Scheme 3. Visualization of the reactivity of *cis*- and *trans*-ocimene in ring-closing metathesis.

Table 5. Cross metathesis of a *cis/trans* mixture of β-ocimene with methyl acrylate with Neolyst M2 in toluene.[a]



Entry	T [°C]	X [%]	Y(**6**) [%]	Y(**7**) [%]	Y(**8**) [%]
1	60	49	4	2	6
2	80	74	3	8	14
3	90	71	1	10	18
4[b]	80	84	2	13	17

[a] 0.5 mol% Neolyst M2, c(β-ocimene) = 0.1 mol L^{-1}, t = 1 h, toluene; conversion and yields were detected by GC. [b] 1.5 mol% Neolyst M2. Abbreviations: X = conversion, Y = yield.

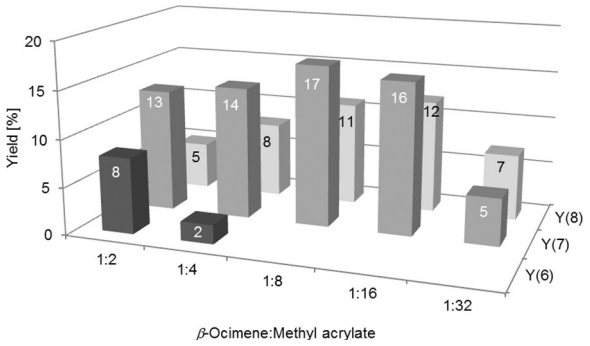


Figure 8. Optimization of the β-ocimene/methyl acrylate molar ratio in the cross metathesis of β-ocimene with methyl acrylate. Conditions: 0.5 mol% Neolyst M2, c(β-ocimene) = 0.1 mol L^{-1}, t = 1 h, toluene; yields were detected by GC. Abbreviations: X = conversion, Y = yield.

cross-metathesis products were attained. Interestingly, no cyclic diene was produced. Moreover, an excess of 1:32 seems to inhibit the reaction as already confirmed for the reaction of β-myrcene (see above). A slight excess of methyl acrylate (1:2) affects the yields of the direct cross-metathesis products but also promotes the ring-closing reaction.

In conclusion, we report the first access to methyl 2-(cyclopent-2-en-1-ylidene)acetate from the reaction of renewable β-myrcene with methyl acrylate. This Ru-catalyzed tandem reaction consists of a ring-closing metathesis of β-myrcene and a subsequent cross metathesis with methyl acrylate and gives a convenient access to cyclic C_7-esters. Under the optimized reaction conditions, a temperature of 80 °C, a catalyst loading (Neolyst M2) of 1.5 mol%, and a methyl acrylate ratio of 1:16, the desired product was yielded in 42%. Further systematic examinations with other functionalized myrcene derivatives gave a detailed insight into the reaction pattern of the terpenyl scaffold. As a result of their modified structures, myrcenol and myrcenyl acetate were able to react directly in a cross metathesis with methyl acrylate to give the corresponding acyclic esters in up to 14%. In the reaction of β-ocimene, both the cyclic diene and acyclic esters could be achieved with yields of 25 and 18%, respectively.

Experimental Section

Laboratory experiments

All experiments in this work were performed in an oxygen-free environment using standard Schlenk techniques. Typically, Neolyst M2 (10.7 mg, 0.011 mmol, 1.5 mol%) and dry toluene (7.5 mL) were placed in a 100 mL two-necked round-bottomed flask equipped with a reflux condenser fitted with a bubble counter on top. The mixture was then placed into an ultrasonic bath for 2 min until the solid was dissolved completely. Subsequently, β-myrcene (102.2 mg, 0.75 mmol, 1.0 equiv.) and methyl acrylate (1033.1 mg, 12.0 mmol, 16.0 equiv.) were added, and the flask was immersed in a preheated oil bath at the desired temperature (e.g., 80 °C). After stirring for 1 h, the reaction was stopped by cooling to RT using an ice bath, and the mixture was analyzed by GC using di-*n*-butyl ether as the internal standard and isopropanol as an additional solvent.

Chemicals

All nonaqueous solvents used in this work were purchased dry from Acros Organics (Geel, Belgium) with a purity of 99% or higher. β-Myrcene was purchased from Acros Organics with a purity of 90%. Myrcenol and a *cis/trans* mixture of β-ocimene (*cis/trans* = 33:67) were used in a purity of 98% and were donated by Givaudan (Vernier, Switzerland). Other chemicals were purchased from commercial suppliers and were of the highest purity available. They were used as received without further purification. The Ru precatalysts denoted as "Neolyst" were donated by Umicore AG & Co. KG (Hanau, Germany). The Grubbs I and II precatalysts were purchased from Sigma Aldrich (St. Louis, Missouri, USA). Ar gas (99.998%) was purchased from Air Liquide Deutschland GmbH (Düsseldorf, Germany) and was used as received.

Analysis

Standard gas chromatographic analyses were performed by using a HP 6890 instrument (Hewlett–Packard GmbH, Waldbronn, Germany) equipped with a flame ionization detector (FID, 300 °C) and a HP5 capillary column (30 m, diameter 0.32 mm, film thickness 0.25 μm) connected to an autosampler. N_2 was used as the carrier gas. The injection volume of a sample was 1 μL.

GC–MS was performed by using a Hewlett–Packard 5973 instrument (70 eV).

All pure components were calibrated to determine the conversion (X) of the reaction and yield (Y) of the products.

^{1}H and ^{13}C NMR spectra were recorded by using a Bruker DRX400 (400 MHz for ^{1}H and 101 MHz for ^{13}C) and a Bruker DRX500 (500 MHz for ^{1}H and 126 MHz for ^{13}C) at RT (Bruker Corp., Billerica, Massachusetts, USA). All chemical shifts δ are given in ppm. Coupling constants are indicated as J and given in Hz. References: TMS (δ = 0.00 ppm) was taken as internal standard. The chemical shift for deuterated chloroform $CDCl_3$ is δ = 7.26 ppm. Peak characterization: s = singlet, d = doublet, dd = double doublet, t = triplet, dt = double triplet, m = multiplet.

Product isolation and characterization

3-Methylenecyclopent-1-ene (2): The reaction mixture was purified by distillation to yield the desired product (bp = 82 °C) accord-

ing to Hoye et al.[10c] ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.53$ (m, 4H, $2CH_2$), 4.77 (s, 1H, CH_2–H_A), 4.86 (s, 1H, CH_2–H_B), 6.15 ppm (m, 2H, CH=CH); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 29.1$ (CH_2), 32.4 (CH_2), 102.3 (=CH_2), 134.6 (CH), 139.6 (CH), 155.2 ppm (C).

(*E*/*Z*)-Methyl 2-(cyclopent-2-en-1-ylidene)acetate ((*E*/*Z*)-3): The reaction mixture was purified by column chromatography (silica 40 Å, cyclohexane/ethyl acetate 4:1) to yield the desired product as a *cis*/*trans* mixture (bp = 193 °C). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta =$ 2.56 (m, 2H, CH_2), 2.95 (m, 2H, CH_2), 3.64 (s, 3H, OCH_3), 5.55 (s, 1H, $CHCO_2CH_3$ of the *E* isomer), 5.70 (s, 1H, $CHCO_2CH_3$ of the *Z* isomer), 6.23 (m, 1H, CH), 6.55 ppm (m, 1H, CH); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 31.3$ (CH_2), 34.8 (CH_2), 52.3 (OCH_3), 109.7 (=CH_2), 136.1 (CH), 149.7 (CH), 154.4 (C), 169.6 ppm (C=O); MS (EI, 70 eV): *m*/*z* (%): 139 (7), 138 (M^+, 76), 123 (14), 108 (8), 107 (96), 106 (39), 105 (24), 95 (26), 80 (8), 79 (77), 78 (48), 77 (100), 67 (20), 53 (14), 52 (14), 51 (29), 50 (18).

Methyl-8-hydroxy-8-methyl-4-methylennon-2-enoate (4): MS (EI, 70 eV): *m*/*z* (%): 212 (M^+, 76), 194 (5), 179 (5), 165 (14), 151 (26), 135 (11), 125 (14), 119 (5), 107 (28), 95 (29), 91 (15), 79 (63), 66 (20), 63 (3), 59 (100), 55 (18).

Methyl-8-acetoxy-8-methyl-4-methylennon-2-enoate (5): MS (EI, 70 eV): *m*/*z* (%): 254 (M^+, 2), 194 (14), 179 (18), 165 (15), 151 (59), 135 (35), 125 (18), 119 (26), 107 (30), 95 (47), 79 (100), 69 (27), 59 (56), 55 (35), 52 (10).

2-Methyl-cyclopenta-1,3-diene (6): A typical experiment was performed in dichloromethane at 80 °C for 18 h. The mixture was cooled to RT, concentrated in vacuo, and purified by Kugelrohr distillation to yield the desired product as a colorless oil according to Korenevskii and Sergeyev[24] and Nicole et al.[25] ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.02$ (dt, $^4J_{H-H} = 1.9$ Hz, $^4J_{H-H} = 1.5$ Hz, 3H, CH_3), 2.95 (m, 2H, CH_2), 6.00 (m, 1H, CH), 6.41 ppm (m, 2H, CH=CH); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 15.2$ (CH_3), 41.4 (CH_2), 126.8 (CH), 133.7 (*C*H=CH), 135.8 (CH=*C*H), 142.2 ppm (C).

Methyl 4,8-dimethylnona-2,4,7-trienoate (7): MS (EI, 70 eV): *m*/*z* (%): 194 (M^+, 4), 179 (18), 147 (13), 135 (29), 125 (54), 119 (61), 112 (41), 105 (39), 91 (100), 77 (63), 69 (19), 65 (31), 59 (24), 53 (39).

Methyl 6-methylocta-2,5,7-trienoate (8): MS (EI, 70 eV): *m*/*z* (%): 166 (M^+, 3), 135 (2), 107 (4), 103 (1), 91 (12), 87 (3), 80 (100), 79 (42), 77 (10), 65 (6), 59 (2), 55 (12), 51 (5).

2-Methyl-6-methyleneoct-7-en-2-ylacetate (myrcenyl acetate): Myrcenol (1.00 g, 6.48 mmol, 1.0 equiv.) was dissolved in dichloromethane (25 mL), and pyridine (2.05 g, 25.92 mmol, 4.0 equiv.) was added. The mixture was cooled to 0 °C, and acetyl chloride (1.53 g, 19.44 mmol, 3.0 equiv.) was added dropwise. The solution was stirred at RT for 2 h before it was concentrated in vacuo, and the residue was purified by column chromatography (silica 40 Å, cyclohexane/ethyl acetate 8:1) to yield the desired product (0.71 g, 71 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.42$ (s, 6H, $3CH_3$), 1.51 (m, 2H, CH_2), 1.77 (m, 2H, CH_2), 1.96 (s, 3H, C(=O)CH_3), 2.20 (t, $^3J_{H-H} =$ 7.6 Hz, 2H, CCH_2CH_2), 4.99 (s, 1H, C(=CH_2–H_A)), 5.02 (s, 1H, C(=CH_2–H_B)), 5.06 (d, $^3J_{H-H_A} = 17.6$ Hz, 1H, CH=CH_2–H_A)), 5.21 (d, $^3J_{H-H_B} = 10.9$ Hz, 1H, CH=CH_2–H_B)), 6.37 ppm (dd, $^3J_{H-H_A} = 17.6$ Hz, $^3J_{H-H_B} = 10.8$ Hz, 1H, *C*H=CH_2); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 22.5$ (CH_2), 22.6 (CH_3), 22.6 (2C, C(CH_3)$_2$), 31.6 (CH_2), 40.7 (CH_2), 82.4 (*C*(CH_3)$_2$), 113.3 (CH=CH_2), 115.9 (C=CH_2), 138.9 (CH), 146.2 (*C*=CH_2), 154.4 (C), 170.6 ppm (C=O); MS (EI, 70 eV): *m*/*z* (%): 196 (M^+, 4), 136 (7), 121 (12), 105 (19), 91 (52), 79 (100), 77 (32), 67 (35), 65 (17), 63 (7), 55 (33), 53 (20), 51 (16).

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