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Cross-metathesis of methyl 10-undecenoate with dimethyl maleate: an efficient protocol with nearly quantitative yields

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In this cross metathesis of the renewable raw material methyl 10-undecenoate with dimethyl maleate, an α,ω-difunctional product was produced. Detailed optimizations led to nearly quantitative yields of the desired product. The cross metathesis of methyl 10-undecenoate with methyl acrylate yielded high conversions of the substrate. The product was accessed under mild reaction conditions with the use of a small amount of a commercially available homogeneous ruthenium catalyst. The *in situ* synthesis of dimethyl maleate from maleic anhydride was also possible in this reaction system.

Introduction

In terms of the resource-intensive processing required for oleochemical research, positive contributions to protect the reserves of existing fossil fuels can be made, or these petrochemicals can be partially substituted by using renewable resources. The link between oleo- and petrochemistry is the first step toward generating new and conventional products in a more environmentally-friendly way by using renewable resources. Oleochemical metathesis plays an important role in generating a broad range of mainly difunctional substrates, which are interesting starting materials for the polymer industry.[1–6]

Castor oil is the renewable source material used to produce methyl 10-undecenoate for these experiments. To obtain pure oil, several steps to refine it had to be taken. Detailed information pertaining to the regeneration was reviewed by Meier *et al.*[7] Undecenoic acid was derived from the thermal cleavage of ricinoleic acid, followed by transesterification, methyl 10-undecenoate could be produced. Undecenoic acid and its corresponding methyl ester have great potential for industrial applications, for example, for use as a basic building block in the production of polyesters, polyolefins or polyethers.[8] Their fungicidal and bactericidal properties further enhance this broad range of applications.[9]

The second substrate of our work was dimethyl maleate. It can be generated by acid[10] or TMSCHN$_2$ (trimethylsilyldiazomethane)[11] catalyzed reactions of maleic anhydride, or by esterification of maleic acid in methanol.[12]

This article describes the ruthenium catalyzed cross metathesis of methyl 10-undecenoate **1** and dimethyl maleate **2**. The resulting product was the α,ω-dicarboxylic acid methyl ester **3** with methyl acrylate **4** as a by-product (Fig. 1).

The product **3** can be used in the manufacture for high-molecular weight polyesters, polyamides and as a macrocyclic compound, because of its α,ω-difunctional system.[13] Moreover, dicarboxylic-derivatives are important intermediates for synthesizing biodegradable polymers used in the production of lubricants and plasticizers, and are therefore important intermediates in chemical engineering.[13–15] **3** was achieved in 2007 through a cross metathesis with methyl acrylate by Meier *et al.*, resulting in satisfactory yields.[16]

Detailed investigations of the cross metathesis of methyl 10-undecenoate **1** with diethyl maleate have been performed. As a result, a reaction network was identified that resulted in high product yields.[17]

Several descriptions of metathesis reactions of maleic acid-derivatives have been published. For example, the isomerization of dimethyl maleate and fumarate during their self-metathesis,[18] as well as the investigations of the low reactivity of methyl maleate in cross metathesis with ethylene.[19] Methyl

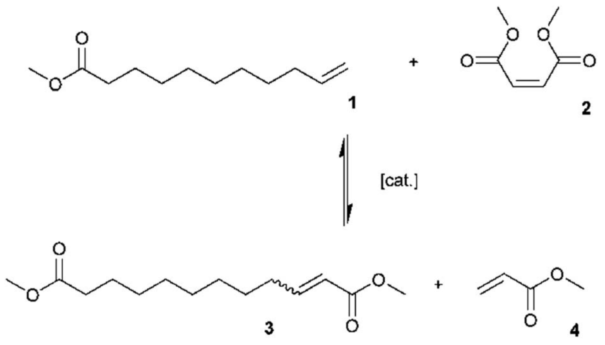

Fig. 1 Cross metathesis of methyl 10-undencenoate **1** and dimethyl maleate **2**.

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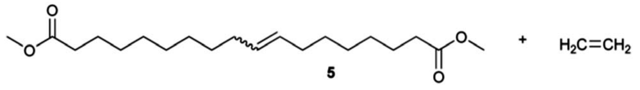

Fig. 2 Self metathesis products of methyl 10-undecenoate **1**.

acrylate **4** as by-product of the cross metathesis investigated was easily separated from the reaction mixture by way of thermal separation. It also has a broad spectrum of applications, for example in comonomers for polymerization.[20]

Methyl acrylate **4** is manufactured at a large industrial scale using acetylene, propylene or methyl formate, which are basic petrochemical compounds.[21–23] This substrate is both the asymmetrical analogue to dimethyl maleate **2** and a widely-used cosubstrate in oleochemistry.[16,24–30]

The self metathesis of methyl 10-undecenoate **1** to dimethyl icos-10-enedioate **5** through the release of ethylene was the only side reaction observed for the cross metathesis in question (Fig. 2).

This C-20 dicarboxylic acid methyl ester **5** is also an intermediate used in the synthesis of biodegradable polymers and is therefore considered to be a value-added product.[31] Different methods for the cross metathesis of fatty-derivatives have been published. Several of the cosubstrates include allylchloride,[25] acrylo- and fumaronitril,[25,26,32,33] acrolein,[34] ethyl acrylate[35] and *cis*-2-buten-1,4-diyl diacetate.[36]

However, only a few means of cross metathesis with symmetrical maleate esters have been published to this day.[18] The oleochemical cross metathesis of methyl 10-undecenoate **1** with dimethyl maleate **2** under homogeneous catalysis is outlined below.

To the best of our knowledge, no systematic investigation of this particular cross metathesis has been published to date.

Results

Only the primary metathesis products are specified for the results of this portion of the experiment. Therefore, only those substrates with a double bond in the position shown in the figures before are listed. However, slice deviations may appear in the yields and conversions. The yields of **3** and **5** contain the respective *cis-* and *trans*-isomeres of the substrates. The described reactions of this work were carried out in closed reactors to prevent the escape of the formed ethylene. The catalyst system was of great importance for controlling the reaction. No reliable conclusions as to the reactivity of a substrate were made prior to optimizing a system, though several approaches were used as guidelines.[37,38] First, a detailed catalyst screening with the homogeneous ruthenium complexes **[Ru]-1** to **[Ru]-13** was carried out (Fig. 3).

Methyl 10-undecenoate **1** and dimethyl maleate **2** in a ratio of 1/10 were stirred for 3 hours at 50 °C in toluene. A catalyst concentration of 1 mol% (based on **1**) was used. The catalysts which were most likely in this reaction are available in Table 1.

Only the catalysts with a NHC-ligand showed noteworthy results in this cross metathesis. As a result of the ligand, they possess increased activity.[39] In comparing the catalyst systems, the catalysts with the 3-phenylindenylidene ligand were more appropriate for the desired product **3** than the systems with the benzylidene ligand. These ligands were found to have a greater group tolerance than their benzylidene counterparts.[38]

When using **[Ru]-10**, both quantitative conversion and yield of **3** are possible. However, the disadvantage of this system was the use of $PhSiCl_3$ as an activating additive.[40] The authors' investigations were done without this catalyst due to its high risk potential[41] in accordance with the guidelines of "green chemistry".[42] The catalyst for further investigations is **[Ru]-4**, because for example this catalyst is stable at high

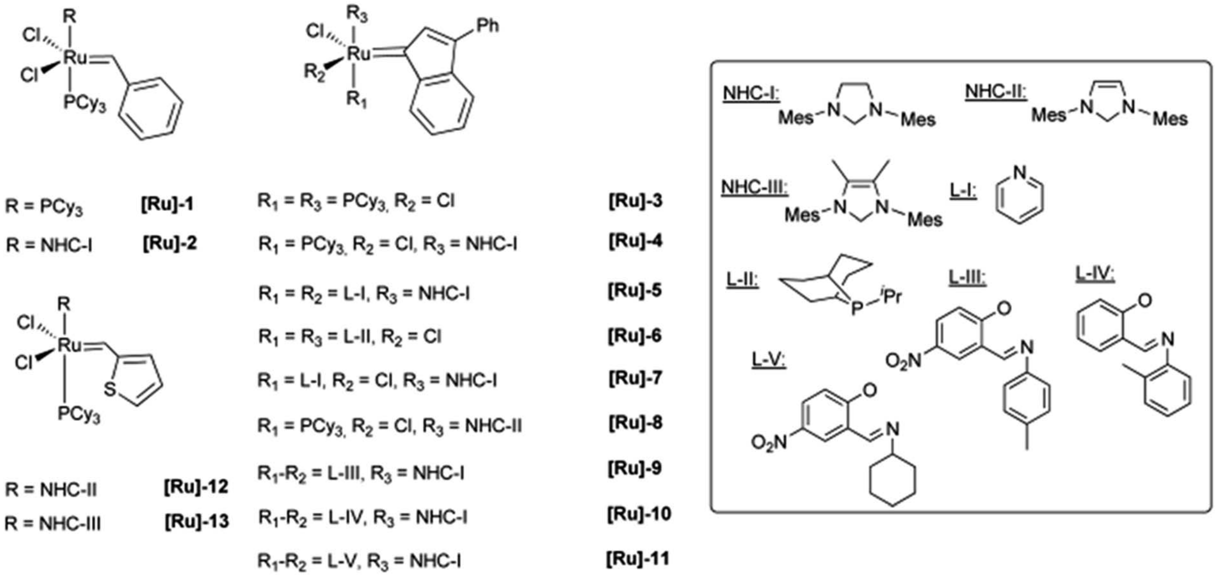

Fig. 3 Investigated metathesis catalysts.

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Table 1 Best catalysts in the cross metathesis of **1** and **2**. Reaction conditions: $T = 50$ °C, $t = 3$ h, solvent = toluene, 1.0 mol% catalyst, **1/2**: 1/10, * = 100 eq. $PhSiCl_3$ (based on catalyst)

Catalyst	X (1) [%]	Y (3) [%]	Y (5) [%]
[Ru]-2	71	32	13
[Ru]-4	92	50	17
[Ru]-9*	49	26	0
[Ru]-10*	>99	99	0
[Ru]-11*	49	18	1

Table 2 Variation of the catalyst concentration in the CM of **1** and **2**. Reaction conditions: $T = 50$ °C, $t = 3$ h, solvent = toluene, catalyst = [Ru]-4, **1/2**: 1/10

Concentration [mol%]	X (**1**) [%]	Y (**3**) [%]	Y (**5**) [%]
0.1	11	3	7
0.25	34	10	14
0.5	59	26	19
0.75	80	50	19
1.0	92	50	17
1.5	96	70	14
2.0	>99	99	2

temperatures.[43] The objective of the further investigations is to achieve results comparable to **[Ru]-10** by using the catalyst system **[Ru]-4**.

The variation of the catalyst concentration within the range of 0.1 mol% to 2.0 mol% produced a significant trend in the yields to product **3** (Table 2).

It should be noted that increasing the catalyst concentration increased the conversion of methyl 10-undecenoate **1** and the yields of **3**. The course of the parallel undergoing self metathesis is remarkable. The yields of **5** first increased, but then fell to a minimum at a concentration of 2.0 mol%. The same series of experiments was carried out with a reaction time of 24 hours to avoid side reactions. Identical results were achieved, so no side reactions could proceed.

Quantitative conversions and yields were possible at a high catalyst concentration of 2.0 mol%, but the financial burden of the catalyst was prohibitive. Also at this concentration an isomerization of the oleochemical compound **1** could be detected. Therefore, a concentration of 0.75 mol% was used for subsequent investigations to determine whether similar results could be achieved with a reduced amount of catalyst.

Various tests with different ratio of substrate **1/2** in a range of 1/1 to 1/20 were carried out to reduce the amount of undesired products and the unnecessary use of substrate. In general, the self metathesis to **5** could be suppressed with an increased excess of **2**, which increased the yields of product **3** at the same time. A compromise of high excess and high yields was reached at a substrate–cosubstrate ratio (**1/2**) of 1/5. This ratio was retained for subsequent steps in the experiment. To avoid unnecessarily lengthy reaction times, different time experiments were performed. They were carried out in the range of 5 minutes to 24 hours. A constant conversion of methyl 10-undecenoate **1** was recorded after a reaction time of 1 hour. As the reaction time increased, yields of self metathesis product **5** increased proportionally; therefore a constant reaction time of 1 hour had to be capped in the subsequent optimization.

The findings of the reaction temperatures investigated clearly demonstrated that an increase in temperature resulted in an increase of conversion and in product yields (Fig. 4).

At the same time, the conversion of **5** decreased. This yield was reduced to 1% at a reaction temperature of 80 °C. Under these reaction conditions, the conversion of methyl 10-undecenoate **1**, as well as the yield of **3** are nearly quantitative at >99%. The positive effect of the reaction temperature was attributed to decreases in substrate viscosity. The resulting acceleration of transport processed of catalyst to substrate was simplified. Also the thermal activation of the cosubstrate **2** seemed to be necessary due to its steric hindrance.

By maintaining a temperature of 80 °C, an isomerization of the substrates was prevented, which arise with increasing temperature. Different solvents were investigated to account possible coordinative effects. Had this not been applied, a clear classification within the different solvents could not have showed any clear trend. Comparably high yields could be reached with the standard metathesis solvents ethyl acetate and dichloromethane. Lower yields and conversion (20%) were generated using simple alcohols such as methanol and isopropanol. Toluene was used in subsequent investigations as it resulted in the highest yields, and due to its low production costs compared to the other solvents tested, which was particularly beneficial.[44]

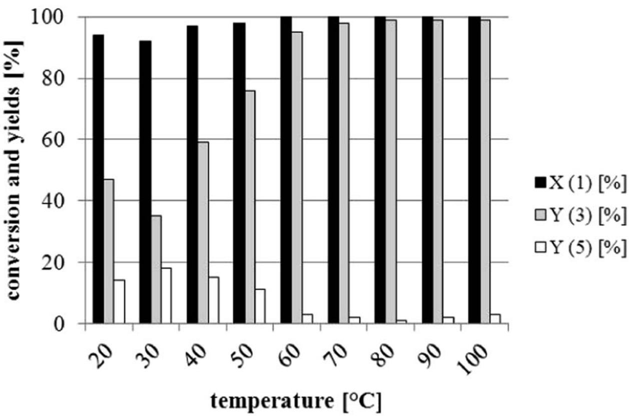

Fig. 4 Variation of reaction temperature. Reaction conditions: $t = 1$ h, solvent: toluene, catalyst: 0.75 mol% [Ru]-4, **1/2**: 1/5.

Table 3 Variation of the catalyst concentration. Reaction conditions: $T = 80$ °C, $t = 1$ h, solvent: toluene, catalyst: [Ru]-4, **1/2**: 1/5

Concentration [mol%]	X (**1**) [%]	Y (**3**) [%]	Y (**5**) [%]
0.1	44	8	18
0.25	56	16	19
0.5	81	51	14
0.75	>99	99	1
1.0	>99	99	1

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Having optimized the reaction conditions by this point, a second stage reduction of the catalyst concentration was carried out to further reduce the amount of catalyst (Table 3).

0.75 mol% of the catalyst was sufficient to achieve nearly quantitative conversions and yields. A further reduction of the concentration led to a collapse of the results of up to 50% of the maximal value, which was therefore not useful.

Environmentally friendly variations to the ratio of substrate to solvent were investigated, as the best solvent is no solvent in green chemistry. The ratio was tested within the range of 10 wt % substrate up to no solvent at all (Fig. 5). The previous attempts were made at 65 wt% substrate.

Fig. 5 shows that this cross metathesis is favored by a high substrate-concentration. At 60 wt% substrates, the resulting ongoing self metathesis was almost completely suppressed. A further advantage was the reduced amount of solvent, making the reaction more cost effective.[45]

The same difunctional product **3** was generated *via* the cross metathesis of methyl 10-undecenoate **1** and methyl acrylate **4** (Fig. 6).

The advantage of this reaction is that no by-product was observed except the self metathesis product of methyl 10-undecenoate **1** the C-20 dicarboxylic acid methyl ester **5** (Fig. 2). The other product observed was dimethyl maleate **2**, which generated the same product **3**, and was therefore not a typical by-product.

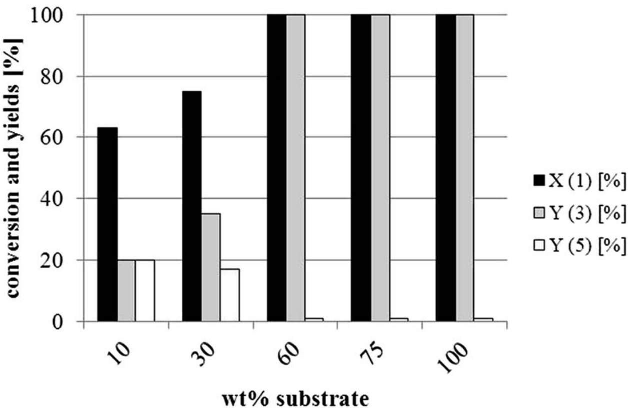

Fig. 5 Variation of substrate to solvent ratio. Reaction conditions: $T = 80$ °C, $t = 1$ h, solvent: toluene, catalyst: 0.75 mol% **[Ru]-4**, **1/2**: 1/5.

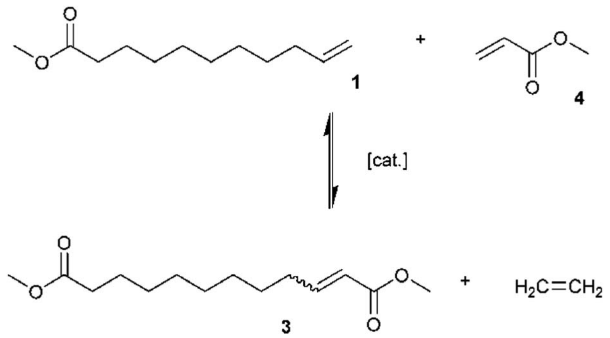

Fig. 6 Cross metathesis of **1** and methyl acrylate **4**.

As described previously, several investigations of the cross metathesis have been published. These reactions were investigated under the optimized reactions conditions of the metathesis with dimethyl maleate **2** in order to verify whether the relativities of the symmetric and asymmetric analogue molecules result in the same yields, and whether direct conclusions for their use in other cross metathesis reactions could be drawn.

Under the same reaction conditions (80 °C, ratio **1/4**: 1/5, toluene), only 0.5 mol% of **[Ru]-4** and a reaction time of 30 minutes were necessary to achieve 97% of the desired product **3**. Hence, this reaction was faster, and a lower catalyst load was necessary than in cross metathesis with dimethyl maleate **2**. The self metathesis to product **5** was not observed under these reaction conditions.

The variation of substrate concentration showed similar trends to the above-mentioned cross metathesis (Table 4).

Here only 30 wt% of the substrate, thus 70 wt% solvent, yielded a nearly quantitative conversion and yield. The same yields were also achieved without using a solvent. A reaction dilution was not necessary in this case, which was also observed with dimethyl maleate **2**. The investigation of the catalyst activity with methyl acrylate **4** as the cosubstrate demonstrated that the same catalysts as those in the reaction with **2** were active. Also, the same solvent effects were observed.

Therefore, the optimized reaction conditions were almost transferable to the unsymmetrical substrate. This point might be applied to other cross metathesis systems, though this must be tested in each case.

In situ preparation of dimethyl maleate 2 from maleic anhydride 6

Having optimized the reactions conditions for the cross metathesis of methyl 10-undecenoate **1** with dimethyl maleate **2**, the *in situ* preparation of **2** from maleic anhydride **6** was investigated, with subsequent use in cross metathesis (Fig. 7).

The use of maleic anhydride **6** enabled a 75% reduction in costs, thanks to the cheaper production of the substrate. The

Table 4 Variation of substrate concentration. Reaction conditions: $T = 80$ °C, $t = 30$ min, solvent: toluene, catalyst: 0.5 mol% **[Ru]-4**, **1/4**: 1/5

Weight%	X (**1**) [%]	Y (**3**) [%]
10	94	87
20	97	97
30	>99	>99
40	>99	>99
50	>99	>99

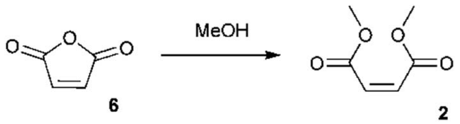

Fig. 7 *In situ* preparation of dimethyl maleate **2**.

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technical production process of maleic anhydride **6** is based on the oxidation of hydrocarbons at high temperatures of between 350 to 450 °C. Maleic anhydride **6** has a broad range of applications, for example in the production of maleic acid, tartaric acid, furanes and 1,4-butanediol.[46] Therefore, this reaction was of interest not only from an academic perspective, but also from an economic point of view. Another advantage of the *in situ* cross metathesis, as demonstrated by many preliminary investigations, is that maleic anhydride **6** is totally inactive in metathesis conversions with the type of catalysts used in this investigation.

At first, the transformation of maleic anhydride **6** to dimethyl maleate **2** was investigated without applying cross metathesis. Therefore, different acids were used in methanol to react with maleic anhydride **6** in different concentrations (sulfuric acid, potassium hydrogen sulfate, dodecyl sulfonic acid, Dowex 1X8). In this case, methanol performed two functions: it served both as the solvent—no other solvent was used—and as the reagent for converting the maleic anhydride **6**.

It turned out that Dowex 1X8 in an amount of 1 wt% (based of **6**) had the greatest impact on the formation of dimethyl maleate **2**. That detection had the benefit of allowing the acid to separate easily *via* filtration after the reaction. The cross metathesis was carried out under the above-mentioned reaction conditions with the addition of 1 wt% Dowex and maleic anhydride **6** instead of dimethyl maleate **2** and under an increased reaction time of 12 hours (**1**/**6** in a ratio of 1/5, solvent & reagent: methanol, 12 hours, 80 °C, 1 wt% Dowex, 1.0 mol% **[Ru]-4**). Under these conditions, the self metathesis of methyl 10-undecenoate **1** to **5** occurred at 9%. However, only a conversion of **1** of about 60% and a 40% yield of **3** were achieved. These low values were explained by the use of methanol, which resulted also in lower yields when using it in the cross metathesis with dimethyl maleate **2**. Another reason for these results may have been the heterogeneity of the systems, which occurred by adding a solid component to the homogeneous system, and which may have resulted in mass transport limitations and therefore lowered conversions and yields.

It was determined that it is, in principle, possible to use maleic anhydride **6** rather than dimethyl maleate **2**, which could be more attractive in terms of cost. However, under the optimized reaction conditions of the cross metathesis with dimethyl maleate **2**, only low yields were achieved. This problem might be solved by using another catalyst system that is stable in acid media and is highly active in methanol. Therefore, more detailed investigations should be conducted.

Conclusion

A systematic optimization of the reaction parameters with the oleochemical raw material methyl 10-undecenoate **1** in cross metathesis was conducted successfully. The metathesis in question offers provided access to value-added and other interesting sustainable intermediates with the basic petrochemical metathesis partners, dimethyl maleate **2** and methyl acrylate **4**. Both reactions end in nearly quantitative yields of the desired product **3**. Using a small amount of commercial available catalyst **[Ru]-4** (0.75 mol%) at 80 °C, these high yields were achieved within a reaction time of 1 hour when using **2** as a cosubstrate. With methyl acrylate **4**, a lower amount of catalyst was necessary, and the reaction was completed within 30 minutes. The conditions were very similar for both reactions, which is a very important advantage for other cross metathesis compounds to be optimized within the same functional group. It was possible to synthesize dimethyl maleate **2** *in situ* in the reaction, though further studies are necessary to determine whether the basis of maleic anhydride **6** can achieve the high conversions described above.

Experimental

Analytic equipment and methods

Flash chromatography was conducted on silica gel 60 (Acros), substrates were visualized with *p*-anisaldehyde reagent through analytical thin-layer chromatography cards (VWR).

Both ^{1}H- and ^{13}C-nuclear magnetic resonance (NMR) spectra were recorded in deuterated chloroform on a Bruker Avance DRX 400 MHz and 500 MHz.

Gas chromatography (GC) analysis of the reaction solutions was carried out on a Hewlett-Packard gas chromatograph Series 6890 equipped with a HP5 capillary column (coating: 5% diphenyl-95%-dimethoxy-polysiloxane; length 30 m; diameter 0.25 mm, thickness 0.25 μm). A flame ionization detector (FID) connected to an autosampler was used to detect individual components. The oven temperature program was as follows: initial temperature 130 °C, hold for 6 min, increase by 25 °C min^{-1} up to 320 °C, hold for 4 min. Measurements were performed in split–split mode (ratio 70 : 1) using nitrogen as a carrier gas. The qualitative assignment of the chromatographically determined retention times of the individual components was carried out by comparing them to their respective pure substances. The quantitative determinations were made by the method with an internal standard.

The mass spectra were recorded by GC/MS. The mass spectrometer was a Hewlett Packard 5973 with electron energy of 70 eV and a scan range [m/z] of 50–700. The oven temperature program, the split–split mode and the specification of the carrier gas were similar to those in the GC-FID method.

Materials

Undecenoic acid (99%), maleic acid (99%), methanol (99.8%), methyl acrylate (99%), solvents and reagents were purchased from Acros. The benzylidene ruthenium catalysts (**[Ru]-1** and **[Ru]-2**) were obtained from Sigma-Aldrich, the thioether-catalysts (**[Ru]-12** and **[Ru]-13**) were provided by Evonik Industries and the remaining indenylidene catalysts (**[Ru]-3** till **[Ru]-11**) were provided by Umicore and were used as received.

Experimental procedures

Cross-metathesis of methyl 10-undecoate 1 with dimethyl maleate 2. All reactions were first conducted under argon to check whether this was necessary. They were performed at least twice to ensure accurate reproduction of the presented results.

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When using 0.4 g (2 mmol) of methyl 10-undecenoate **1**, 1.46 g (10 mmol) dimethyl maleate **2**, 16.74 g toluene (90 weight%) and an appropriate amount of catalyst, (1.0 mol% **[Ru]-4** = 0.019 g, 0.02 mmol) were added. The reaction was carried out in a closed reactor and heated to the desired temperature. After a defined reaction time, the reactor was placed directly into an ice bath to stop the reaction. Quenching the reaction by addition of ethyl vinyl ether led to the same results, so this procedure is for the examined reaction not necessary. After subsequent cooling, the GC samples were weighed (0.1 g reaction solution, 0.4 g isopropanol and 0.5 g *n*-pentadecane as internal standard) and analyzed accordingly.

Cross-metathesis of methyl 10-undecenoate 1 with *in situ* generated dimethyl maleate 2. When using 0.4 g (2 mmol) of methyl 10-undecenoate **1**, 0.99 g (10 mmol) maleic anhydride **6**, 20.00 g methanol (90 weight% + excess for the reaction with maleic anhydride **6**) and an appropriate amount of catalyst, (1.0 mol% **[Ru]-4** = 0.019 g, 0.02 mmol) and 0.01 g Dowex 1X8 (1 wt % based on **6**) were added. The reaction, the sample preparation and the product isolation occurred analogous to the cross metathesis described above.

Syntheses

Synthesis of methyl 10-undecenoate 1. 184.28 g (1.00 mol) methyl undec-10-acid, 82 mL (2.00 mol) methanol and 4.52 g (26 mmol) *p*-toluenesulfonic acid were dissolved in 200 mL dichloroethane and heated under reflux for 48 hours. After cooling to room temperature, the organic phase was washed with 100 mL distilled water, 100 mL of a 5% solution of sodium bicarbonate and once again with 100 mL of distilled water consecutively. The solvent was removed under reduced pressure after drying with sodium sulfate. Finally, a fractional distillation (82 °C, 10^{-3} mbar) to isolate methyl 10-undecenoate **1** was carried out with a purity of about 99% as a clear, colorless liquid.

Synthesis of dimethyl maleate 2. 58.05 g (0.50 mol) maleic acid is dissolved in 128.16 g (4.00 mol) methanol. 5.00 g (51 mmol) of concentrated sulfuric acid were added. The reaction mixture was stirred overnight. After the reaction, the resulting white solid was dissolved in 200 mL chloroform and the reaction mixture was washed three times with 100 mL of distilled water each. After that the organic phase was dried over sodium sulfate and the solvent was removed under reduced pressure. Subsequently, the dimethyl maleate **2** was isolated as a clear, colorless liquid with a purity of about 99%.

1,12-Dimethyl-dodec-2-enedioate 3. δ_H (400 MHz; $CDCl_3$; Me_4Si): 1.27 (10 H, s, $-CH_2-$), 1.50 (2 H, m, $-C(O)-CH_2-CH_2-$), 2.16 (2 H, m, $-CH_2-CH-$), 2.27 (2 H, t, $J = 7.5$, $-C(O)-CH_2-$), 3.64 (3 H, s, $-CH_3$), 3.70 (3 H, s, $-CH_3$), 5.79 (1 H, d, $J = 15.6$, $-CH-$), 6.94 (1 H, td, $J = 7.0$, 15.6, $-CH-$); δ_C (100 MHz; $CDCl_3$; Me_4Si): 24.8 ($-C(O)-CH_2-CH_2-$), 27.8, 28.8, 28.9, 29.0, 29.1, 32.1, 33.9, 51.3 ($-O-CH_3$), 120.7 ($-C(O)-CH-$), 149.6 ($-C(O)-CH-CH-$), 167.1 ($-C(O)-CH-$), 174.2 ($-C(O)-$); *m*/*z*: 257 (M^+, 1%), 225 (13), 206 (1), 192 (34), 183 (1), 174 (2), 164 (38), 147 (10), 136 (10), 123 (18), 109 (13), 95 (27), 87 (32), 81 (74), 74 (36), 67 (38), 55 (100), 41 (79), 29 (36).

1,20-Dimethyl-icos-10-enedioate 5. δ_H (500 MHz; $CDCl_3$; Me_4Si): 1.21 (20 H, m, $-CH_2-$), 1.58 (4 H, dd, $J = 7.1$, 14.2, $-CH_2-CH_2-C(O)-$), 1.96 (4 H, m, $-CH-CH_2-$) 2.27 (4 H, t, $J = 7.6$, $-CH_2-C(O)-$), 3.64 (6 H, s, $-O-CH_3-$), 5.33 (2 H, s, $-CH-$); δ_C (125 MHz; $CDCl_3$; Me_4Si): 24.9, 29.0, 29.1, 29.2, 29.3, 29.5, 32.5, 34.0, 51.4 ($-O-CH_3-$), 130.2 ($-CH-$), 174.2 ($-C(O)-$); *m*/*z*: 369 (M^+, 1%), 336 (9), 318 (2), 304 (4), 194 (1), 180 (2), 165 (2), 151 (3), 135 (4), 123 (5), 109 (9), 95 (20), 81 (27), 74 (25), 67 (28), 55 (64), 41 (39), 28 (100).

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