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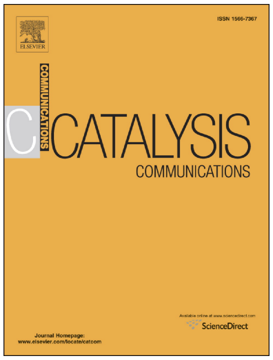

Functionalization of (-)-β-pinene and (-)-limonene via cross metathesis with symmetrical internal olefins

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Functionalization of (-)-β-pinene and (-)-limonene *via* cross metathesis with symmetrical internal olefins

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Abstract

The straightforward functionalization of sterically demanding α,α-disubstituted double bonds of the natural products β-pinene and limonene *via* cross metathesis with symmetrical internal olefins is described. The reaction is catalyzed by Hoveyda-Grubbs type ruthenium catalysts in dimethyl carbonate as green solvent and makes possible the clean introduction of ester and nitrile groups in one step without formation of byproducts.

Keywords: cross metathesis, terpenes, ruthenium catalysis

1. Introduction

Cyclic terpenes such as α-pinene, β-pinene, camphene and limonene are important bio-sourced components present in the resin of pine and citrus trees and are currently produced on an industrial scale. The world production of turpentine, which contains mainly these terpenes, is estimated at 350.000 tons/year [1], while that of limonene extracted from the peel of citrus fruits produced in fruit juice industry, containing about 90% of limonene [2], could result in approximately 65 kilotons per year [3]. Monoterpenes have already found direct applications in the field of fragrances and flavors [4] and constitute renewable building blocks for the access to sustainable polymers [5]. Several catalytic transformations of natural terpenes, such as oxidation, epoxidation, hydroformylation, hydrogenation, dehydrogenation, isomerization, rearrangement, have been achieved in order to produce added value chemicals for various applications [6,7].

Olefin metathesis, in particular cross metathesis, has an enormous potential for direct functionalization of olefins arising from natural resources [8,9]. The possibility of introducing

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ester, aldehyde, halogen, nitrile functional groups has already been demonstrated starting from 1,2-disubstituted internal double bonds of fatty acid derivatives [10,11] and terpenes featuring the trisubstituted prenyl end [12,13] with electron deficient olefins, allylic chlorides and esters as cross metathesis partners. We were especially interested in the functionalization of (1S)-(-)-β-pinene **1** and (S)-(-)-limonene **2** (Figure 1), which are bulky unsaturated monoterpenes featuring a terminal disubstituted carbon-carbon double bond. The first substrate is a sterically hindered methylenecyclohexane, and the second corresponds to a propen-2-ylcyclohexene derivative.

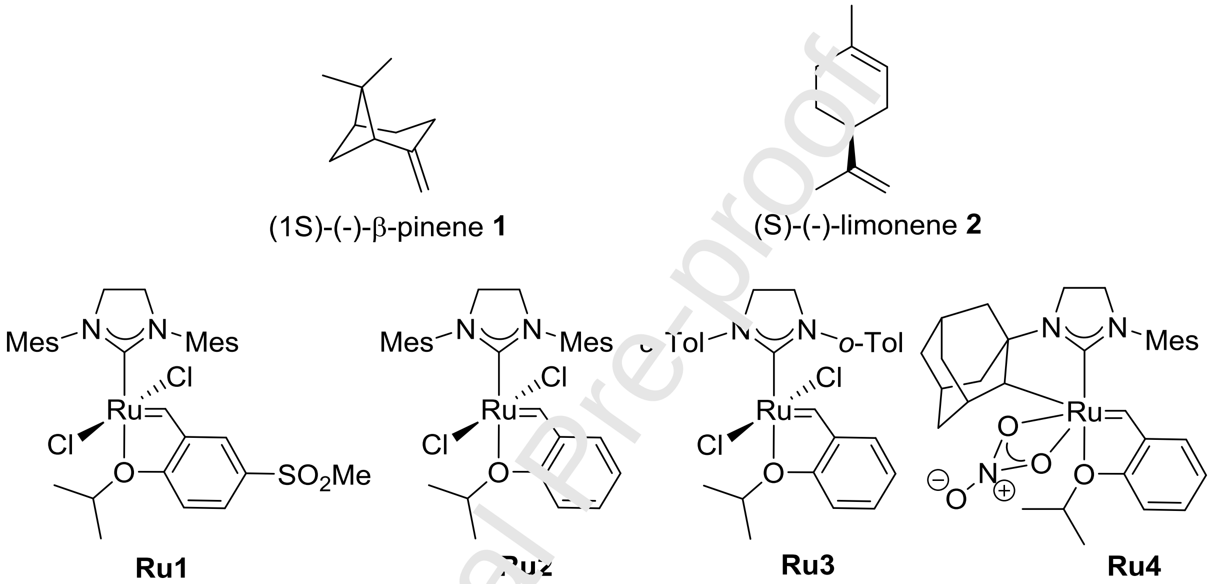

Figure 1: Cyclic monoterpenes and ruthenium catalysts used in this study

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A few examples of cross metathesis of *gem*-disubstituted cyclic olefins with terminal olefins have been reported from methylene cyclobutane, [14] -cyclopentane and -cyclohexane, [15] and the more difficult cross metathesis of olefins with sterically encumbered exocyclic methylene groups is much less documented [16,17]. Terpenes **1** and **2** have already been involved in olefin metathesis reactions with ruthenium catalysts, especially as chain transfer agents during cleavage of natural polyisoprene rubbers into terpene-terminated oligomers,[18] and during ring opening metathesis polymerization of dicyclopentadiene to control crosslinking and physical properties of the resulting polymers [19].

There are only few examples where these terpenes have been used as cross metathesis partners with olefins to form new fine chemicals. Thus, limonene has been reacted with the terminal olefin 1-hexene in the presence of 2 mol% of a second generation Grubbs catalyst without solvent to give the expected butyl-substituted limonene as a $E+Z$ mixture in 40% yield [20]. The extension to the non-conjugated 1,5-hexadiene has led to polyhexadiene together with hexadiene oligomers featuring one or two limonene end. Under these conditions β-pinene is not reactive, and cross metathesis products have been obtained only with neutral internal olefins partners using a ruthenium catalyst and a large excess of terpene [17,21]. On the other hand, even though the exocyclic double bond of limonene was reactive in intramolecular ring closing metathesis with an acrylic double bond, [22] a terminal electron deficient olefin such as an acrylate did not react intermolecularly with these terpenes but only provided the self-metathesis maleate/fumarate mixture [13]. These results showed that beside the nature of the catalyst, which is also a crucial parameter, cross metathesis of the bulky terpenes **1** and **2** with ruthenium catalysts took place favorably when the cross metathesis partner presented an internal carbon-carbon double bond. This observation provided impetus to investigate the ruthenium-catalyzed cross metathesis of terpenes **1** and **2** with symmetrical functional olefins, namely acrylic and allylic derivatives, in order to generate only one cross metathesis product.

2. Results and discussion

2.1. Cross metathesis of acrylic olefins with β-pinene 1

We first investigated the cross metathesis reaction of β-pinene **1** with dimethyl maleate **3** and fumarate **4** as symmetrical functional olefin (Figure 2 (1)) in the presence of the commercially available second generation ruthenium catalysts **Ru1**-**Ru4** (Figure 1).

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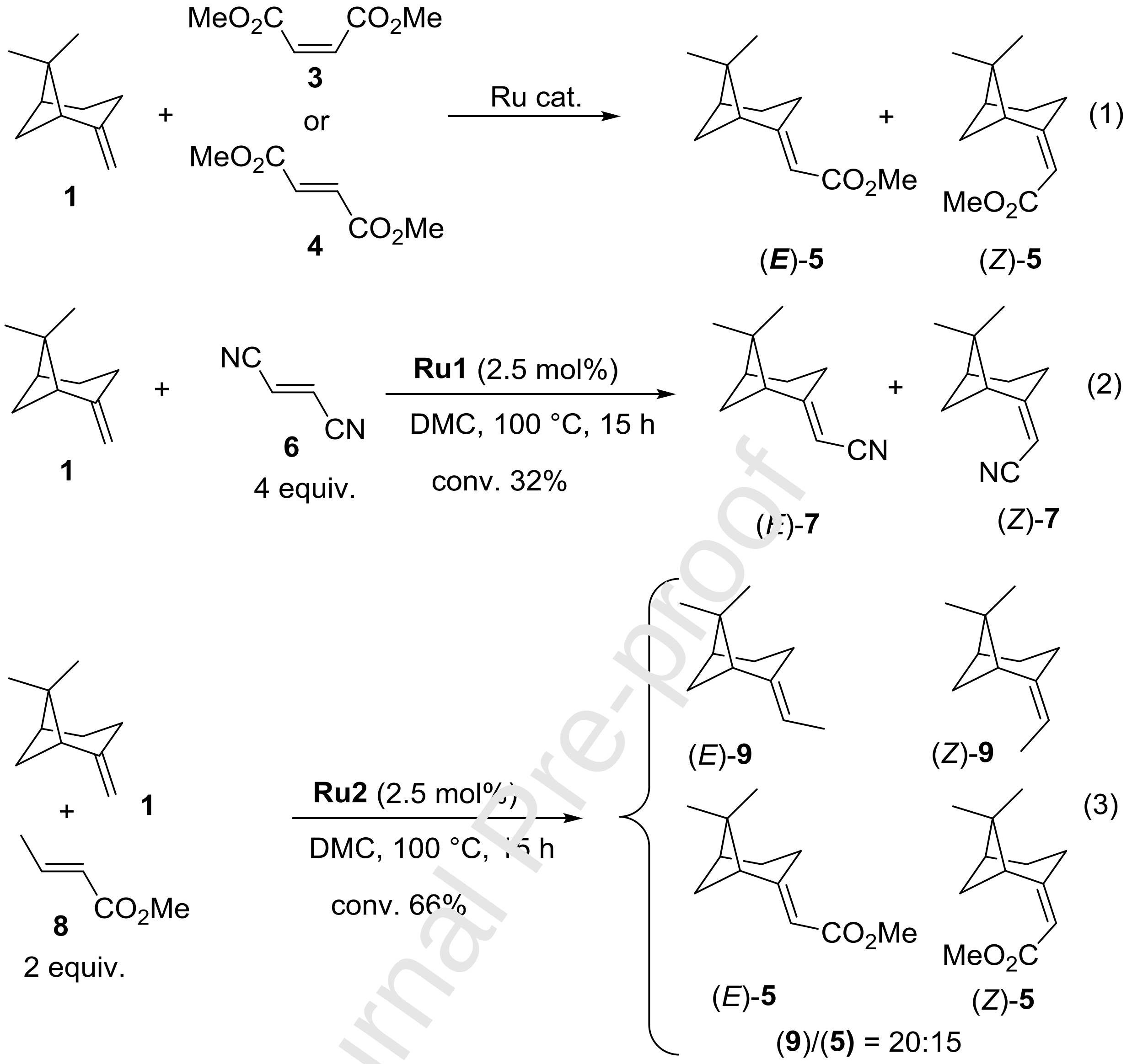

Figure 2. Cross metathesis of β-pinene **1** with various acrylic substrates

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Most of the experiments were carried out in a closed Schlenk reactor under argon atmosphere at 100 °C during 15 h and the results were based on GC analysis of crude mixtures. The effect of temperature, concentration of substrates, catalyst loading and nature of the solvent were first examined (Table 1).

Our first attempts revealed that good conversion of β-pinene **1** into **5** was obtained with the symmetrical electron deficient olefins **3** and **4** in the presence of 2.5 mol% of the Zhan-1-B **Ru1** and the Hoveyda **Ru2** catalysts. Surprisingly, when the less hindered catalyst **Ru3** and the more bulky *Z*-selective catalyst **Ru4** were used under the conditions of Table 1, entry 2 and 3, no conversion of β-pinene was observed. We found that dimethyl carbonate as green solvent provided better results than toluene, which is commonly used in olefin metathesis operating at high temperature. Indeed, a temperature of 100 °C was necessary to get high conversion of the terpene and this temperature was adopted for further investigation. With both olefins **3** and **4**, the effect of the concentration of the terpene was relatively weak as its conversion remained in the same range when the concentration was varied from 0.074 to 0.74 mol/L with the two catalysts (entries 4, 5; 9, 10; 14, 15; 17, 18). In addition, it was possible to perform the cross metathesis reaction under neat conditions with an excess of fumarate **3** or maleate **4** (entries 11, 19). On the other hand, a higher catalyst loading of 5 mol% appeared to give slightly higher conversion than with 2.5 mol% (entries 4, 6; 8, 9; 16, 17).

Table 1 Cross metathesis of β-pinene **1** with dimethyl maleate **3** and fumarate **4**[a]

Entry	**3/1** or **4/1** (mol. ratio)	Catalyst (mol%)	Conc. (mol/L)	Temp. (°C)	Solvent	Conv. (%)[b]	Yield (%)[b] (%)[c]	(*E*)/(*Z*)-**5** ratio[d]
1	**3/1** (2)	**Ru1** (2.5)	0.37	115	toluene	51	49	62:38
2	**3/1** (2)	**Ru1** (2.5)	0.37	130	toluene	61	57	60:40
3	**3/1** (2)	**Ru1** (2.5)	0.37	100	DMC	55	47	60:40
4	**3/1** (4)	**Ru1** (2.5)	0.37	100	DMC	67	66	61:39
5	**3/1** (4)	**Ru1** (2.5)	0.074	100	DMC	69	48	61:39
6	**3/1** (4)	**Ru1** (5)	0.37	100	DMC	77	70 (66)	62:38
7	**3/1** (4)	**Ru1** (5)	0.74	100	DMC	76	72 (48)	62:38
8	**3/1** (4)	**Ru2** (2.5)	0.37	100	DMC	70	68	62:38
9	**3/1** (4)	**Ru2** (5)	0.37	100	DMC	85	79 (57)	61:39
10	**3/1** (4)	**Ru2** (5)	0.74	100	DMC	91	91 (65)	57:43
11	**3/1**	**Ru2** (5)		100	neat	80	80	55:45
12	**4/1** (2)	**Ru1** (2.5)	0.37	115	toluene	54	52	76:24
13	**4/1** (2)	**Ru1** (2.5)	0.37	100	DMC	43	37 (30)	73:27
14	**4/1** (2)	**Ru1** (2.5)	0.37	100	DMC	59	58 (39)	77:23
15	**4/1** (4)	**Ru1** (2.5)	0.74	100	DMC	55	47	73:27
16	**4/1** (4)	**Ru2** (2.5)	**0.37**	100	DMC	69	66 (40)	69:31
17	**4/1** (4)	**Ru2** (5)	0.37	100	DMC	85	79 (57)	68:32
18	**4/1** (4)	**Ru2** (5)	0.74	100	DMC	74	71 (57)	70:30
19	**4/1**	**Ru2** (5)		100	neat	57	52 (37)	69:31

[a] General conditions: β-pinene **1** (100 mg, 0.7 mmol), solvent (1, 2 or 10 mL), reaction time (15 h), [b] Conversion and GC yield determined using hexadecane as internal standard, [c] Isolated yield, [d] *E*/*Z* ratio determined by GC of the crude mixture.

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It is noteworthy that in a general manner, starting from fumarate or maleate, catalyst **Ru2** provided the best conversion of β-pinene **1**. In all cases, due to the presence of an excess of fumarate or maleate, a mixture of these two stereoisomers was observed at the end of the reaction resulting from their self-metathesis reaction. In addition, we confirmed that when methyl acrylate was used, no cross-metathesis product was formed, β-pinene **1** was recovered and only the self-metathesis products dimethyl fumarate **3** and maleate **4** were formed [13]. This result contrasts with the easy formation of cross metathesis products from acrylic acid esters as well as maleate by cross metathesis with non-sterically hindered monosubstituted terminal olefins [23,24]. Indeed, maleates and fumarates have been efficiently used in olefin cross metathesis in place of acrylates, especially with the objective of reducing the number of possible cross metathesis products, but they had never been shown to be suitable substrates when acrylates did not work.

The cross metathesis of **1** with methyl acrylate can formally generate two types of ruthenium carbene species: a methoxycarbonylmethylidene [**Ru3**] and a cyclohexylidene [**Ru4**] (Figure 3). [**Ru3**] is a well-known ruthenium enoic carbene intermediate that has been reported in catalytic transformations including self-metathesis of acrylates with second generation ruthenium catalysts, and described as fast initiating but unstable olefin metathesis catalyst [25]. The ruthenium moiety [**Ru4**] has been proposed as active species during the previously reported metathesis transformations of β-pinene with internal olefins,[17] and proposed in predictive calculations for cross metathesis of β-pinene with (*Z*)-3-methylpent-2-ene with a second generation Grubbs catalyst [26]. [**Ru3**] can interact with methyl acrylate to generate the self-metathesis products **3**+**4** (Fig. 3 (a)), and with β-pinene, (Fig. 3 (b)), en route to the expected cross metathesis product, which is however not formed experimentally. Route (Fig. 3-(c)) is a non-productive pathway but constitutes nevertheless a pathway for the formation of **[Ru4]**. [**Ru4**] can interact with methyl acrylate according to two regioselectivities. Route (Fig. 3 (e)) is the non-productive reverse reaction of (Fig. 3-(c)) and only route (Fig. 3 (d)) would give the expected product and this one also does not take place experimentally. The productive interaction of [**Ru4**] with β-pinene (Fig. 3-(f)) would lead to the self-metathesis product but this reaction is unlikely and not observed as it was shown that the less substituted methylenecyclohexane did not give self-metathesis, [27] and more generally 1,1-disubstituted olefins were reluctant to self-metathesis with ruthenium catalysts [28]. Thus, the sole productive reaction is the self-metathesis of methyl acrylate, which leads to the formation of dimethyl fumarate and maleate (Fig. 3 (a)).

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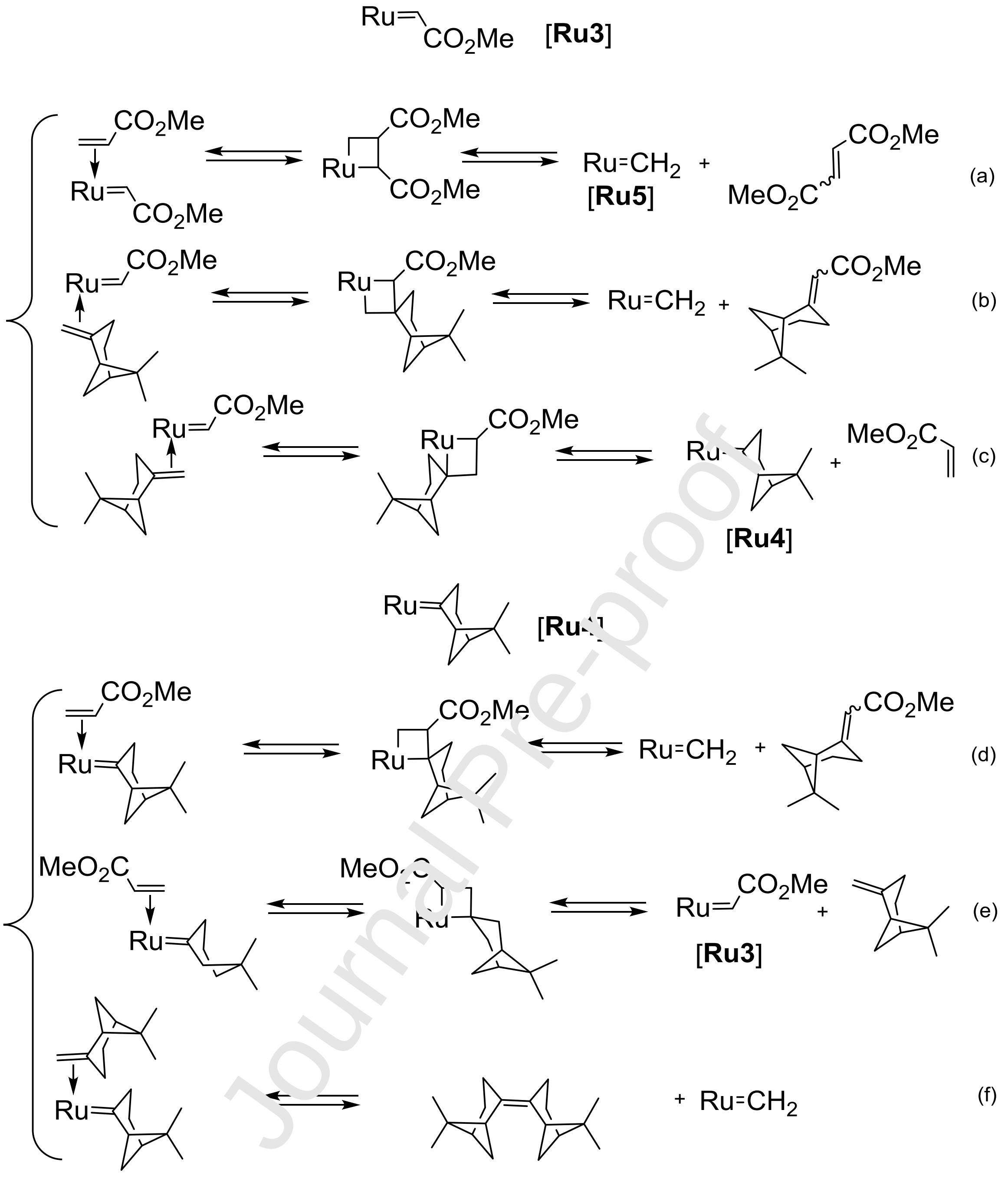

Figure 3. Catalytic steps for the cross metathesis of β-pinene **1** with methyl acrylate

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The same carbenic species [**Ru3**] and [**Ru4**] are formed during the cross metathesis of β-pinene with dimethyl fumarate **3** and maleate **4** (Fig. 4). The interaction of [**Ru3**] with maleate is responsible for the isomerization of the starting olefin into dimethyl fumarate **3** (Fig. 4 (a)). The route described in Fig. 4 (b) is the same as the one of Fig. 3 (b) that is not operative using methyl acrylate. In Fig. 4, route (c) does not lead to cross metathesis product and route (e) similar to Fig. 3 route (f) does not take place for steric reason. Finally, from **3** or **4** only routes Fig. 4 (b) and (d) would lead to the expected cross metathesis product **5**. It is however difficult to conclude which one is the predominant or the sole one. Route (d) represents a similar pathway as the one proposed by A.J. Robinson for the cross metathesis of an excess of β-pinene (30 equiv.) with isoprenyl olefins [17] and M.A. Tlenkopatchev for the cross metathesis of stoichiometric amounts of β-pinene and the less hindered 3-methylpent-2-ene [26] involving ruthenium carbene species such as [**Ru4**] arising from the terpene. Even though the route described in Fig. 3 (b) is not productive from methyl acrylate, the same pathway described in Fig. 4 (b) involving [**Ru3**] and β-pinene might be productive from dimethyl maleate **3** or fumarate **4**. This might be the result of the competitive interaction of [**Ru3**] with acrylates *versus* β-pinene, which is much more favored with methyl acrylate (Fig. 3 (a) *vs* Fig. 3 (b)), considering steric factors and the excess of methyl acrylate hence leading preferentially to the self-metathesis products **3** and **4**. The steric discrimination is much less important between methyl fumarate or maleate *versus* β-pinene as depicted in ruthenacycle formation (Fig.4 (a) and (b)) thus making the productive formation of the cross-metathesis product feasible. It must be noted that a similar competition between self-metathesis *versus* cross metathesis of acrylate has previously been observed when an acrylate and a moderately hindered *gem*-disubstituted olefins such as 2-methylheptene or methylenecyclohexane were reacted in the presence of a second generation ruthenium catalyst [25].

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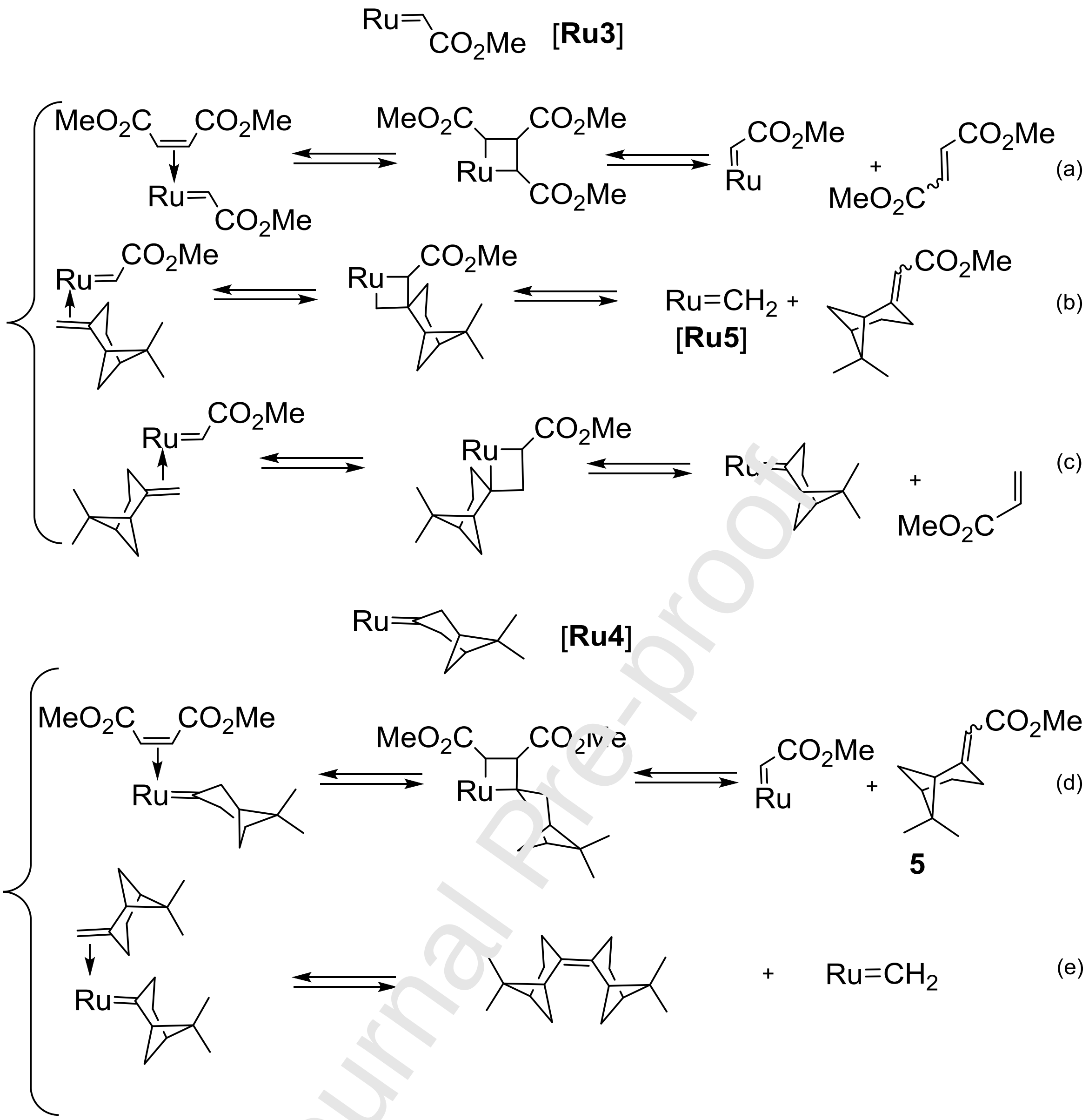

Figure 4. Catalytic steps for the cross metathesis of β-pinene **1** with dimethyl maleate **4**

The comparison of the productive pathways in Fig. 3 and Fig. 4 reveals that with methyl acrylate a ruthenium methylidene [**Ru5**] is formed, which then generates ethylene to restore [**Ru3**] from methyl acrylate, and that on the other hand, Ru=CHCO$_2$Me [**Ru3**] is generated in the productive routes Fig.4 (a) and (d). The formation of [**Ru5**] is known to facilitate decomposition of the catalyst [29], and the presence of ethylene has also been reported as detrimental to some metathesis reactions, [30] which might contribute to explain the absence of cross metathesis of β-pinene **1** with methyl acrylate. It is also surprising that during the reaction with methyl acrylate, the dimethyl maleate and fumarate, which are generated *in situ* are not involved in further cross metathesis with β-pinene. This observation suggests that the

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self-metathesis of methyl acrylate is much faster than the cross metathesis reaction with the terpene and during this transformation after full consumption of methyl acrylate the amount of active catalyst is decreased due to fast decomposition of the catalytic species at 100 °C.

The new products (*E*)-**5** and (*Z*)-**5** were produced in satisfactory yields but could not be separated by column chromatography. A fine NMR analysis of their mixture based on NOESY and HSQC experiments (see Supporting Information for details) together with data from the literature on β-pinene **1**, [31,32] made possible the full characterization of each stereoisomer. In particular, the stereochemistry was clarified by Nuclear Overhauser Effect study, which revealed interaction between the ethylenic proton C(10)H (at 4.46 ppm) with the C(1) H proton in the (*E*)-**5** isomer (at 2.46 ppm), and interaction of the same ethylenic proton C(10)H (at 5.60 ppm) with one of the proton of the methylene group at C(3) in the (*Z*)-**5** isomer (at 2.21 ppm).

Using dimethyl fumarate **4** led to a slightly higher *E*/*Z* ratio as compared to dimethyl maleate (average value E/Z= 71:29 from **4**, and E/Z = 60:40 from **3**). It is noteworthy that the stereoselectivity in favour of the *E*-isomer is much less pronounced than that obtained with less bulky linear terpenes [12].

Similarly, the cross metathesis of acrylonitrile with **1** did not lead to the cross metathesis product but following the same principle, the symmetrical fumaronitrile **6** led to a mixture of (E)-**7** and (Z)-**7** stereoisomers according to equation (2) (Figure 2). With this cross metathesis partner, the conversion of β-pinene **1** was much lower than starting from dimethyl fumarate **3** as in the best case a conversion of 32% (14% isolated yield) was obtained in DMC at 100 °C for 15 h in the presence of 2.5 mol% of catalyst [**Ru1**] with a β-pinene concentration of 0.37 mol/L. The structure of the stereoisomers has also been determined by NOE experiments and the major stereoisomer was found to be the (*E*)-**7** isomer, which contrasts with all previous results reported with acrylonitrile where the (*Z*)-isomer is the major one.[11,33] Indeed, interaction between the ethylenic proton C(10)H (at 4.95 ppm) with the C(1) H proton in the (*E*)-**7** isomer (at 2.58 ppm), and interactions of the same ethylenic proton C(10)H (at 5.04 ppm) with one of the protons of the methylene group at C(3) in the (*Z*)-**7** isomer (at 2.40 and 2.70 ppm) were observed in the NOESY spectrum (see Supporting Information).

Then, we investigated the cross metathesis of β-pinene **1** with the non-symmetrical methyl crotonate **8** featuring an internal double bond (Figure 2 - (3)). In the presence of catalyst **Ru2** (2.5 mol%), the cross metathesis reaction of **1** with a twofold excess of **8** took place in DMC

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([**1**]= 0.74 mol/L) at 100 °C leading to 66% conversion of β-pinene but the reaction was not selective and beside the functional derivatives **5** (*E*+*Z*), the purely aliphatic stereoisomers of the β-pinene derivative **9** were formed in a (**9**)/(**5**) molar ratio of 57:43 (1.3) as determined by GC analysis of the crude reaction mixture. When the reaction was carried out without solvent in the presence of 5 mol% of **Ru2**, 48% conversion of **1** was obtained and the (**9**)/(**5**) ratio was much higher (6.25). As expected, (*E*)-**5** was the major acrylic isomer but the (*E*)- and (*Z*)-stereoisomers of **9** were not separated by GC and thus it was not possible to give the corresponding stereoisomeric ratio.

2.2. Cross metathesis of acrylic olefins with limonene 2

With the less sterically constrained terpene **2**, the reaction with methyl acrylate was also inefficient and only dimethyl maleate **3** and fumarate **4** were formed as previously reported [13]. However, the cross metathesis with the symmetrical maleate and fumarate in the presence of 2.5-5 mol% of **Ru1** and **Ru2** was successful and produced the expected and new acrylic stereoisomers of **10** according to equation (4) (Figure 5). Surprisingly, under the conditions described above for β-pinene **1** transformation, the productivities were generally lower, but reasonable conversions of 60% could be obtained with a (*E*/*Z*)-**10** ratio of 75:25 (Table 2 – see Supporting Information). The nature of the stereoisomers was also unambiguously determined by ^{1}H and ^{13}C NMR. In the (*E*)-isomer **10**, the acrylic proton at C(9) (5.68 ppm) is in interaction with protons at C(3), C(4) and C(5), whereas in the (*Z*)-isomer **10**, the same proton at C(9) (5.64 ppm) is in interaction with the methyl proton at C(10) (1.81 ppm) only. It can be noted that under the conditions of Table 2, entry 7, the complexes **Ru3** and **Ru4** were also inactive.

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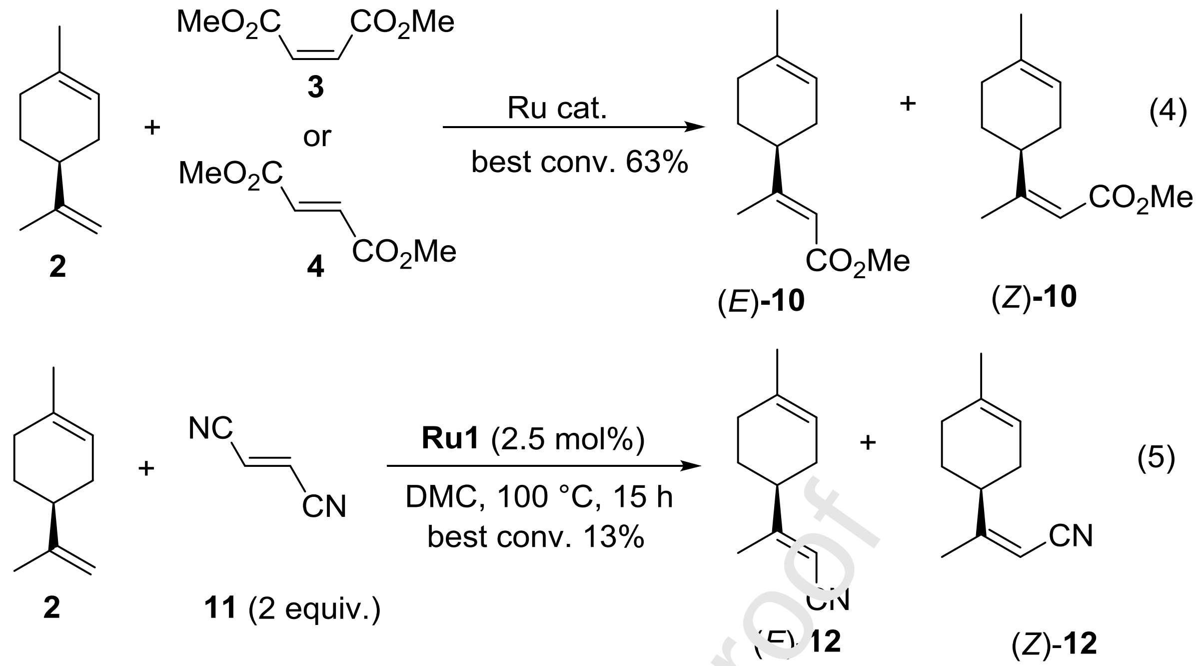

Figure 5. Cross metathesis of limonene with methyl fumarate, maleate and fumaronitrile

The nitrile derivatives **12** could also be formed upon reaction of limonene **2** with fumaronitrile **11** but in the presence of 2.5 mol% of **Ru1** at 100 °C for 15 h, a very low isolated yield of 7% was obtained corresponding to a conversion of only 13% (Figure 5 - equation (5)). In this case, the (*Z*)-**12** isomer was obtained as the major product (*Z*/*E*= 86:14).

2.3. Cross metathesis of allylic olefins with β-pinene 1 and limonene 2

Functional allylic esters and halides are suitable cross metathesis partners to introduce functional groups to the purely aliphatic terpenes **1** and **2**. Using this methodology, natural products including unsaturated fatty esters, acyclic terpenes and lignin-derived allylbenzene derivatives have been functionalized by cross metathesis with terminal olefinic partners such as allyl acetate and allyl halides or 1,4-diacetoxybut-2-ene as internal olefin [10]. Again when allyl acetate was used, no cross metathesis reaction took place with the terpenes **1** and **2**. On the other hand, the expected cross metathesis products **14** and **15** were formed in moderate yields when *cis*-1,4-diacetoxybut-2-ene **13** was used (Figure 6). With this cross metathesis partner, the (*E*)-isomers of **14** and **15** were formed as the major products (> 90% (*E*)-**14**, and (*Z*)-**15** was not detected by ^{1}H NMR).

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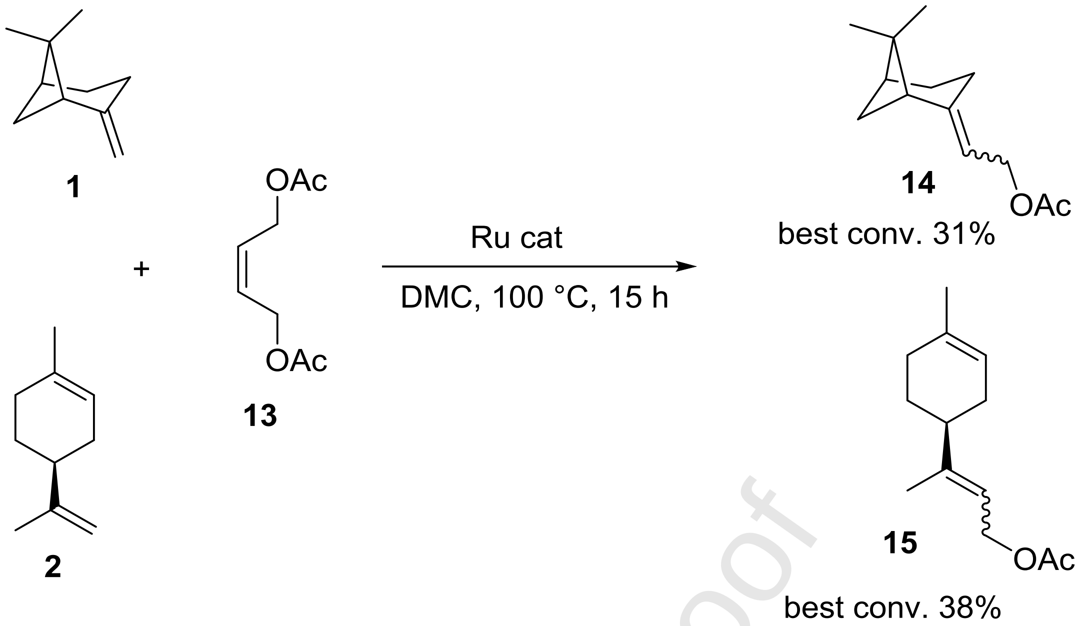

Figure 6. Cross metathesis of β-pinene **1** and limonene **2** with *cis*-1,4-diacetoxybut-2-ene **13**

However, the efficiency of these metathesis reactions was much lower with this cross metathesis partner than with acrylic esters. The influence of catalyst loading and substrates ratio were weak and the best conversions reaching 30-40% of the terpene were obtained under neat conditions (Table 3 – see Supporting Information).

2.4. Sequential cross metathesis/hydrogenation

It is now well established that the ruthenium residues resulting from olefin metathesis transformations are catalysts for subsequent hydrogenation of the formed carbon-carbon double bonds. This catalytic property, which was first used in metathesis polymerization (ROMP and ADMET)/hydrogenation processes [34] has known further developments in sequential cross metathesis/hydrogenation transformations [35]. We have shown that performing first the cross metathesis reaction of β-pinene **1** with dimethyl fumarate **4** in the presence of 5 mol% of **Ru2** as catalyst in DMC at 100 °C for 16 h and then applying a hydrogen pressure of 40 bar at 80 °C during 8 h led to full conversion of the terpene into the saturated ester **16** (see Supporting Information). ^{1}H NMR analysis confirmed that the *E* and *Z* isomers **5** disappeared and were hydrogenated into the same product **16** isolated in 40% yield.

3. Conclusion

The cross metathesis of sterically demanding *gem*-disubstituted olefins with terminal functional olefins in the presence of ruthenium catalysts is known to be a challenging

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reaction. Based on a few observations from the literature, we have developed a strategy involving more hindered symmetrical functional internal alkenes rather their terminal metathesis equivalents as cross metathesis partners for cross metathesis with bulky terpenes. Using Hoveyda-Grubbs type catalysts, it was thus possible to introduce ester and nitrile functional group to β-pinene **1** and limonene **2** *via* cross metathesis with dimethyl fumarate and maleate, fumaronitrile and 1,4-diacetoxybut-2-ene under neat conditions or in dimethyl carbonate as a green solvent without production of any byproduct. This cross metathesis reaction provides a straightforward access to new bio-sourced products. Wider catalysts screening involving the most recent ruthenium and molybdenum complexes might allow improvement of the productivity of these transformations.

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Author Contribution Statement

Luciana Sarmento Fernandes: experimental investigation, writing parts of the initial draft
Dalmo Mandelli: management of the project in Brazil, conceptualization
Wagner A. Carvalho: co-supervision in Brazil
Cédric Fischmeister: methodology, resources, preparation of published work, supervision
Christian Bruneau: conceptualization, project administration, funding acquisition, preparation of published work,

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Highlights

1. Olefin cross metathesis from sterically demanding natural terpenes
2. First evidence that fumarates and maleates are better cross metathesis partners than acrylates
3. Preparation of functionalized derivatives of □-pinene and limonene