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PAPER

Eugenol as a renewable feedstock for the production of polyfunctional alkenes via olefin cross-metathesis†

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The ruthenium-catalyzed cross-metathesis of eugenol derivatives with electron deficient olefins is reported. It is shown that in the presence of ruthenium catalysts, eugenol and its *O*-protected derivatives have a high tendency to undergo carbon–carbon double bond migration before and after metathesis leading to the formation of conjugated styrene derivatives. The addition of 1,4-benzoquinone suppresses these isomerization reactions and provides an efficient access to new polyfunctional phenol derivatives upon cross-metathesis of the biosourced eugenol with acrylates, acrylonitrile and acrylamides.

Introduction

Due to the foreseen depletion of fossil oil as a main feedstock for fine chemistry, chemists are more and more interested in transformations of renewable resources both towards large tonnage industry, especially for energy supplies and polymers, and for niche products with high added value.¹ Catalysis, both heterogeneous and homogeneous, including organometallic, organo and biocatalysis, plays a crucial role in this field and forms the basis of biorefining processes.² Several families of natural products contain carbon–carbon double bonds, which are particularly suited for their transformation *via* olefin metathesis processes.^{1f,g,3} Direct applications have been successfully developed in oleochemistry, especially for the cleavage of unsaturated fatty derivatives to produce shorter aliphatic esters and olefins *via* ethenolysis,⁴ α,ω -bifunctional molecules *via* cross-metathesis with functional olefins,⁵ and polymers *via* acyclic diene metathesis polymerization⁶ or ring opening metathesis polymerization.⁷ A few reports have recently appeared on the transformation by olefin metathesis of terpenes, another class of valuable natural products.⁸ Eugenol, featuring a phenolic allylbenzene structure, is representative of the kind of unsaturated compounds that can be extracted from lignocellulosic biomass and transformed *via* olefin metathesis. Only a few scarce examples of direct self-metathesis⁹ and cross-metathesis of eugenol with symmetrical internal olefins¹⁰ and electron deficient olefins^{10a,b,11} with ruthenium benzylidene and indenylidene catalysts have been reported. Beside these direct applications of eugenol, a bis(allyl)benzene diene constructed from

eugenol has also been converted by acyclic diene metathesis polymerization.¹²

We now report a more systematic study on cross-metathesis of eugenol, *O*-protected eugenol derivatives and *ortho*-eugenol with electron deficient olefins including methyl acrylate, methyl methacrylate, acrylonitrile and acrylamides¹³ leading to several new and bio-sourced polyfunctional phenol derivatives.

Results and discussion

The cross-metathesis reactions were investigated with the four second generation ruthenium catalysts **I–IV** (Fig. 1).¹⁴

Cross-metathesis of eugenol with methyl acrylate was first investigated in toluene and the greener dimethyl carbonate¹⁵ (DMC) (Scheme 1). Whatever the catalyst used, complete conversion of eugenol **1** was obtained in relatively short reaction times at 80 °C (Table 1, entries 1–4 and 6–7) and even at room temperature (Table 1, entry 5). However, the reaction was not selective and other cross-metathesis products (Fig. 2) could be detected by gas chromatography and ¹H NMR of the crude reaction mixtures. These products were identified *via* selected cross-metathesis transformations.

The two major byproducts were compound **4**, resulting from isomerization of the carbon–carbon double bond of **3**, and to a lesser extent the styrene derivative **6**, arising from cross-metathesis of isoeugenol, resulting from migration of the allylic bond prior to the cross-metathesis with **2** (Fig. 2).

Compound **4** was clearly identified by a tandem cross-metathesis (**1** + **2**) promoted by catalyst **I** followed by hydrogenation of the resulting reaction mixture. Whereas GC analysis of the cross-metathesis reaction mixture showed two major peaks, the GC trace of the hydrogenated reaction mixture showed only one major peak that was assigned by GC-MS as the saturated product **5** (Scheme 2, (a)).

Compound **6** was unambiguously identified after cross-metathesis of methyl acrylate **2** with the *E*-isoeugenol quantitatively obtained

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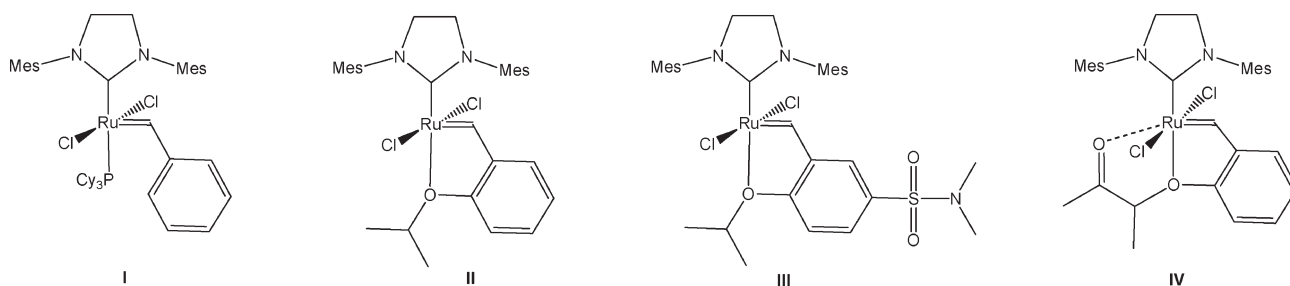
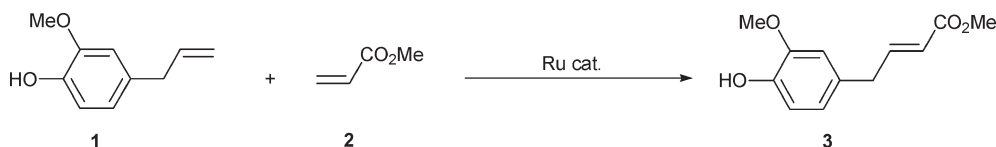


Fig. 1 Olefin metathesis catalysts.



Scheme 1 Cross-metathesis of eugenol with methyl acrylate.

by treatment of eugenol **1** with 2 mol% of $\text{RuCl}_2(\text{PPh}_3)_3$, an isomerization catalyst, in methanol at 60 °C during 17 h (Scheme 2, (b)). Compound **6** was isolated as the sole metathesis product and as the pure *E*-isomer.

Whereas it was reported that ruthenium indenylidene catalysts gave noticeable amounts of self-metathesis products, such as **8**, with preferred formation of the *E*-stereoisomer during cross-metathesis of allylphenols and functional allylbenzene derivatives with electron deficient olefins such as acrylic acid, esters, amides, and conjugated enones,^{10b} the reaction carried out with catalysts **II**, **III** and **IV** in dimethyl carbonate gave almost no self-metathesis product from **1**. The formation of the self-metathesis product **8** was also less important when benzylidene ruthenium complexes featuring a bulky unsymmetrical *N*-heterocyclic carbene ligand were used.^{10a} It was also reported that self-metathesis of eugenol without an olefinic partner occurred at 25 °C under neat conditions in the presence of Grubbs first generation catalyst $\text{RuCl}_2(\text{=CHPh})(\text{PCy}_3)_2$ *in vacuo*.⁹ In contrast, the treatment of eugenol **1** with catalyst **II** in dimethyl carbonate at 80 °C for 3 h provided complete conversion into the functional *trans*-stilbene **7** resulting from self-metathesis of isoeugenol.

From these preliminary tests, it appeared that catalysts bearing a chelating benzylidene ligand proved to be the most selective for the formation of **3**. Of note, it was observed that a longer reaction time of 24 h led to higher formation of **6** (Table 1, entries 2, 4), which indicated that a double migration operated from **3** to give **4**, and that cross-metathesis of **4** with the excess of methyl acrylate **2** also took place to give **6**.

These results clearly indicated that pre- and post-cross-metathesis double bond migration reactions were the origin of undesired side reactions preventing efficient production of cross-metathesis products with electron deficient olefins.¹⁶ Limitation of this type of ruthenium-catalyzed olefin migration by the utilization of additives has already been investigated and the beneficial effect of 1,4-benzoquinone was found¹⁷ and already exploited in various metathesis transformations of natural products.¹⁸ We thus carried out cross-metathesis of eugenol **1** with **2** in the presence of 5 to 20 mol% of 1,4-benzoquinone. As a result, almost all isomerization products disappeared from the GC traces. This made the isolation of pure **3** possible by chromatography, whereas in the absence of 1,4-benzoquinone the mixture of cross-metathesis products could not be simply separated by chromatography over silica gel. The best results

Table 1 Cross-metathesis of eugenol **1** with methyl acrylate **2**^a

Entry	Catalyst	Benzoquinone	<i>t</i> (h)	Conv. (%) ^b	3 : 4 : 6 GC area ratio	Yield of 3 (%) ^c
1	I (2 mol%)	no	3	100	34 : 60 : 6	nd
2	II (2 mol%)	no	3	100	36 : 42 : 22	65 ^f
3	II (2 mol%) ^d	no	3	100	46 : 42 : 12	50 ^f
4	II (2 mol%)	no	24	100	27 : 6 : 67	62 ^f
5	II (0.5 mol%)	no	3	100 ^e	57 : 43 : nd	nd
6	III (2 mol%)	no	3	100	44 : 42 : 14	nd
7	IV (2 mol%)	no	3	100	65 : 20 : 15	80 ^f
8	II (1 mol%)	5 mol%	16	100	92 : 8 : 0	nd
9	IV (1 mol%)	5 mol%	8	100	91 : 9 : 0	73
10	IV (1 mol%)	5 mol%	16	100	91 : 9 : 0	78
11	IV (0.5 mol%)	5 mol%	3	74	94 : 6 : 0	nd

^a Conditions: eugenol **1** (0.6 mmol), methyl acrylate **2** (1.2 mmol), solvent: dimethyl carbonate (2 ml), temperature: 80 °C, nd: not determined.

^b Conversion determined by GC. ^c Isolated yield. ^d Solvent: toluene. ^e Reaction carried out at room temperature. ^f Isolated yield for the mixture **3** + **4** + **6**.

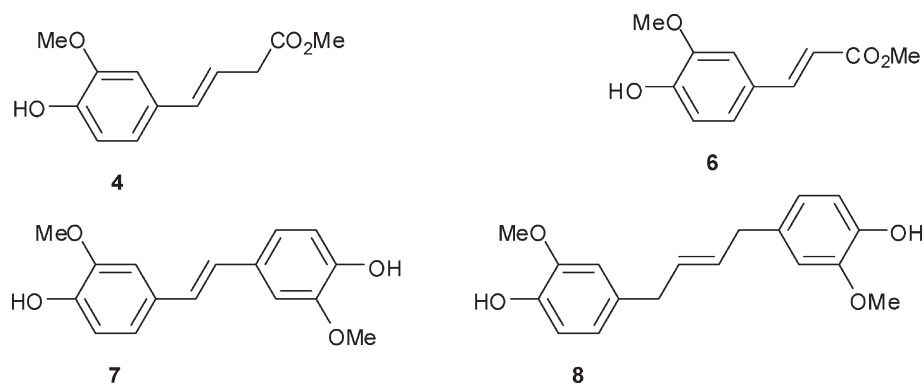


Fig. 2 Undesired products from cross-metathesis reactions involving eugenol.

were obtained with 1 mol% of catalyst **II** or **IV** and 5 mol% of 1,4-benzoquinone in dimethyl carbonate at 80 °C. Under these conditions, complete conversion of **1** was achieved with highly selective formation of **3** isolated in 78% yield (Table 1, entry 10). By contrast with the self-metathesis reaction of eugenol performed without 1,4-benzoquinone, it is noteworthy that in the presence of 5 mol% of 1,4-benzoquinone and 2 mol% of catalyst **II** in DMC at 80 °C for 3 h, eugenol was converted in 92% yield into its self-metathesis product **8** without any trace of **7**. However, in the presence of methyl acrylate and 1,4-benzoquinone, no self-metathesis product **8** was detected by GC analysis.

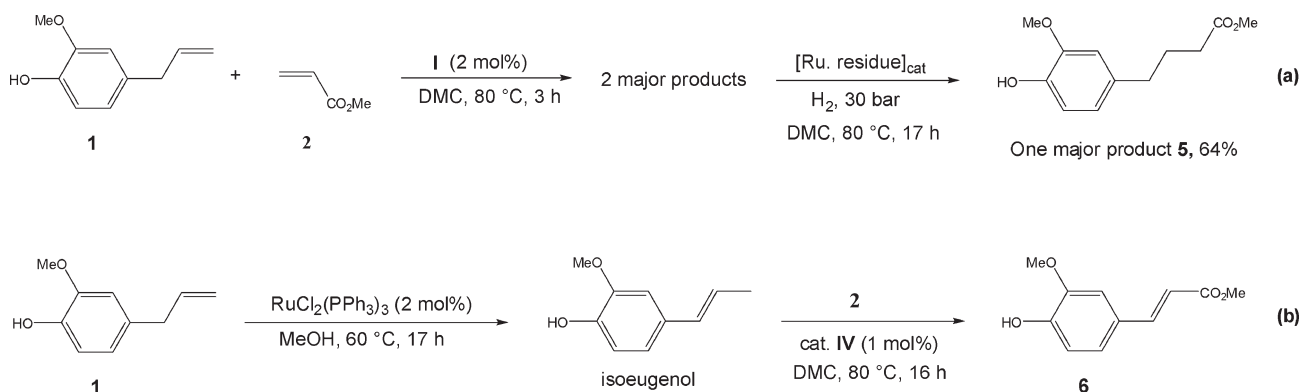
On the basis of these initial results obtained with methyl acrylate **2**, other electron deficient olefins were successfully applied in cross-metathesis with eugenol **1** (Scheme 3, Table 2).

Thus, under conditions inspired from cross-metathesis with terpene derivatives,^{8a} when the more sterically hindered methyl methacrylate **9** was reacted with eugenol **1** in the presence of 2 mol% of catalyst **II** and 5 mol% of 1,4-benzoquinone without solvent, complete conversion of **1** was obtained after 16 h at 90 °C (Table 2, entry 1). No self-metathesis product **8** was formed, and compound **10** was isolated in 60% yield as the sole *E*-stereoisomer as shown by 2D NMR analysis.

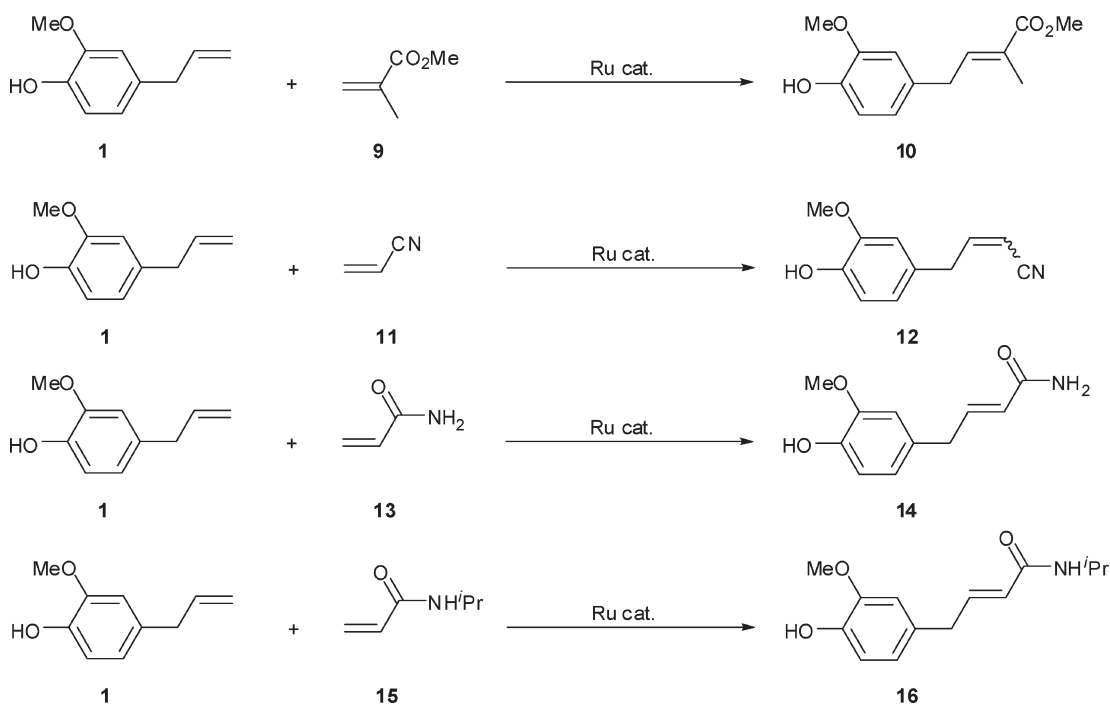
The cross-metathesis with acrylonitrile and acrylamide turned out to be more difficult to perform with high efficiency probably due to the fast degradation of the catalytic species under the experimental conditions used. We have already shown that important efficiency improvements in the cross-metathesis of

unsaturated fatty acid derivatives with acrylonitrile were obtained when the catalyst was slowly added to the reaction mixture.^{5d,e} Following this procedure almost complete conversion of **1** was achieved in diethyl carbonate (DEC) when 2 mol% of catalyst **II** was introduced during 2 h (0.5 ml h⁻¹) and the reaction maintained at 100 °C for 3 additional hours. Under these conditions, **12** was isolated in 82% yield as a mixture of (*Z*)- and (*E*)-isomers in a 2 : 1 respective ratio, and no self-metathesis product **8** or other by-products resulting from pre- or post-isomerization were detected (Table 2, entry 2). The cross-metathesis of eugenol **1** with 2 equivalents of acrylamide **13** proved to be more difficult. When the reaction was carried out for 16 h in the presence of 2 mol% of catalyst **II** in either dimethyl carbonate at 80 °C or toluene at 100 °C it led to low 66% and 25% respective conversions of **1**. Furthermore, it was found that the separation of the two primary acrylic amides **13** and **14** by silica gel chromatography was very difficult. To overcome these problems, catalyst **II** was slowly added to the reaction mixture and a slight excess of eugenol (**1** : **13** molar ratio = 1.25) was used to facilitate purification. With this protocol a conversion of 97% of **13** was obtained and **14** was isolated as the (*E*)-isomer in 60% yield after column chromatography over basic alumina (Table 2, entry 4). Transferring these conditions to the cross-metathesis with isopropylacrylamide **15**, 98% conversion of **15** was obtained and (*E*)-**16** was isolated in 70% yield (Table 2, entry 5).

O-Protected eugenol derivatives were then applied in cross-metathesis reactions with the same electron deficient olefins



Scheme 2 Side-products identification.

Scheme 3 Cross-metathesis of eugenol **1** with functional olefins.

under the best conditions found for the cross-metathesis with eugenol (Scheme 4). The results obtained with the phenol functionality protected as an isopropoxy ether (compound **17**) are collected in Table 3. Conditions could always be found to reach complete conversion of the substrate **17** and in all cases the addition of 1,4-benzoquinone was found beneficial and

improved the isolated yields of the expected products. The isolation of amide derivatives **21** and **22** was again more difficult and moderate isolated yields were obtained even after chromatography over basic alumina, but starting from the olefins **2**, **9** and **11**, products **18**, **19** and **20** were isolated in good yields

Table 2 Cross-metathesis of eugenol **1** with electron deficient olefins^a

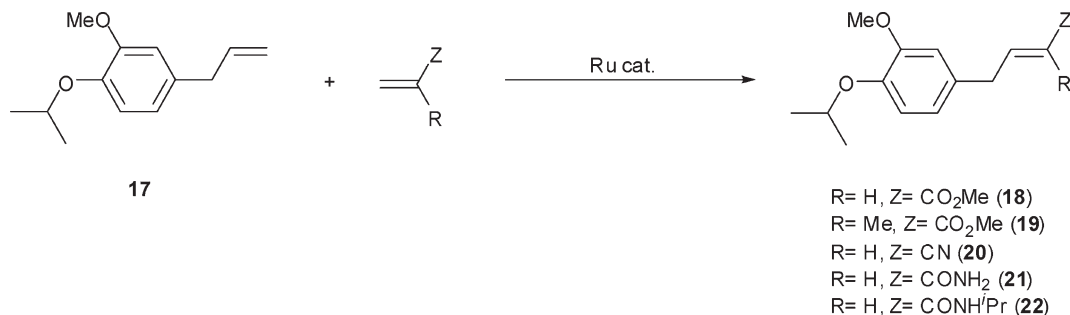
Entry	Olefin	Solvent	<i>T</i> (°C)	<i>t</i> (h)	Conv. (%)	Isolated yield (%)
1	9	Neat ^b	90	16	100	60
2	11	DEC	100	(2 + 3) ^c	97	82
3	13	DMC	80	(2 + 2) ^c	93 ^d	40 ^e
4	13	DMC	80	(2 + 2) ^c	97 ^f	60 ^e
5	15	DMC	80	(2 + 15) ^c	98 ^g	70 ^h

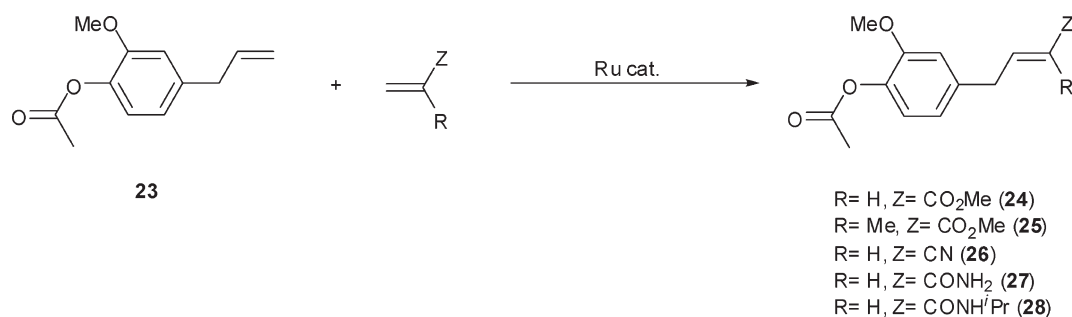
^a Conditions: eugenol (0.6 mmol), olefin (1.2 mmol), catalyst **II** (2 mol%), 1,4-benzoquinone (5 mol%), isolated yield based on **1**, nd = not determined. ^b 2 ml of methyl methacrylate (31 equiv.). ^c Slow addition of the catalyst within 2 h at 0.5 ml h⁻¹. ^d **1** : **13** molar ratio = 1. ^e Isolated yield based on **13**. ^f **1** : **13** molar ratio = 1.25. ^g **1** : **15** molar ratio = 1.25. ^h Isolated yield based on **15**.

Table 3 Cross-metathesis of **17** with electron deficient olefins^a

Entry	Olefin	Solvent	<i>T</i> (°C)	<i>t</i> (h)	Conv. (%)	Isolated yield (%)
1	2	DMC	80	3	100	18 (75) ^g
2 ^b	2	DMC	80	8	100	18 (85) ^g
3	9	Neat ^c	90	16	100	19 (75) ^g
4	9	Neat ^c	90	16	100	19 (78) ^g
5	11	DEC	100	(2 + 3) ^d	98	20 (80) ^g
6	13	DMC	80	(2 + 15) ^d	98 ^e	21 (57) ^h
7	15	DMC	80	(2 + 15) ^d	98 ^f	22 (53) ^h

^a **17** (0.6 mmol), olefin (1.2 mmol), catalyst **II** (2 mol%), 1,4-benzoquinone (5 mol%), conversion based on **17**. ^b Catalyst **IV**. ^c 2 ml of methyl methacrylate (39 equiv.). ^d Slow addition of the catalyst within 2 h at 0.5 ml h⁻¹. ^e **17** : **13** molar ratio = 1.25. ^f **17** : **15** molar ratio = 1.25. ^g Yield based on **17**. ^h Yield based on the electron deficient olefin.

Scheme 4 Cross-metathesis of eugenol derivative **17** with functional olefins.

Scheme 5 Cross-metathesis of eugenol derived **23**.

ranging from 75–85%. From methyl methacrylate the best yields were obtained in neat conditions, and for the cross-metathesis with acrylonitrile and acrylamides the slow addition of the catalyst proved to be the most convenient procedure. The effect of 1,4-benzoquinone was much less pronounced when the reaction was performed in neat methyl methacrylate, which indicated that the excess of methacrylate disfavored the isomerization and self-metathesis of **16**. The (*E*)-isomers of products **18**, **19**, **21** and **22** were formed as the major products with very high stereoselectivity, whereas **20** was isolated as a mixture of (*Z*) and (*E*)-isomers in a 2 : 1 ratio.

Compound **23**, obtained by *O*-acylation of eugenol, was also submitted to cross-metathesis under the best conditions identified during the experiments with eugenol for each olefin partner (Scheme 5). The best results are gathered in Table 4. As depicted for the cross-metathesis of **17**, all reactions proceeded with high to full conversion and the cross-metathesis products were isolated in moderate to good yields. Again, the slow addition of catalyst was necessary to ensure high conversion with acrylonitrile and acrylamide derivatives. Products **24**, **25**, **27** and **28** were obtained as (*E*)-isomers whereas **26** was obtained as a mixture of (*Z*)/(*E*) isomers in a 3 : 1 ratio.

Table 4 Cross-metathesis of **23** with electron deficient olefins^a

Entry	Olefin	Solvent	<i>T</i> (°C)	<i>t</i> (h)	Conv. (%)	Isolated yield (%)
1	2	DMC	80	8	100	24 (81) ^c
2	9	Neat ^b	90	16	99	25 (72) ^c
3	11	DEC	100	(2 + 3) ^d	96	26 (79) ^c
4	13	DMC	80	(2 + 15) ^d	92 ^f	27 (65) ^e
5	15	DMC	80	(2 + 3) ^d	98 ^g	28 (53) ^e

^a **23** (0.6 mmol), olefin (1.2 mmol), catalyst **II** (2 mol%), 1,4-benzoquinone (5 mol%). ^b 2 ml of methyl methacrylate (39 equiv.). ^c Yield based on **23**. ^d Slow addition of the catalyst within 2 h at 0.5 ml h⁻¹. ^e Yield based on the electron deficient olefin. ^f **23** : **13** molar ratio = 1.25. ^g **23** : **15** molar ratio = 1.25.

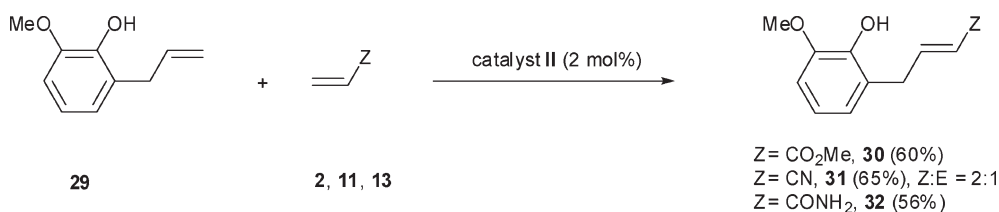
The best conditions identified for the cross-metathesis of eugenol with methyl acrylate, acrylonitrile and acrylamide were used to perform the cross-metathesis with 2-allyl-6-methoxyphenol **29** (*o*-eugenol), an isomer of eugenol (Scheme 6). Complete conversion of **29** was obtained with 2 equivalents of methyl acrylate **2** and the product **30** was isolated in 60% yield when the reaction was carried out in the presence of 2 mol% of catalyst **II** and 5 mol% of 1,4-benzoquinone in dimethyl carbonate at 80 °C for 24 h.

The reactions with acrylonitrile and acrylamide were conducted in the presence of 5 mol% of 1,4-benzoquinone using the slow addition of 2 mol% of catalyst **II** within 2 h followed by 3 h at the reaction temperature. The reaction with acrylonitrile **11** performed at 100 °C in diethyl carbonate led to 95% conversion of **29** and **31** was isolated in 65% yield as a 2 : 1 mixture of (*Z*) and (*E*)-isomers, respectively. From acrylamide, the reaction carried out at 80 °C in dimethyl carbonate with a **29** : **13** molar ratio of 1.25 produced a lower conversion of the amide (75%) and the acrylic amide **32** was isolated as the (*E*) isomer in 56% yield.

The cross-metathesis reaction with **29** required more severe conditions than with eugenol **1**. This is probably due to the presence of the OH group in *ortho*-position of the reactive allyl group. A steric interaction can take place but the coordinating ability of the hydroxyl group that can interact with a catalytic metal intermediate might also have an inhibiting effect.

Conclusion

We have shown that cross-metathesis of eugenol (4-allyl-2-methoxyphenol) with electron deficient olefins in the presence of second generation ruthenium catalysts is subject to concurrent isomerization reactions catalyzed by the metathesis catalyst precursor, which hampers the production of the expected products. This problem has been solved by using 5 mol% of 1,4-benzoquinone, which inhibits the isomerization of the allyl group of eugenol derivatives before cross-metathesis, and also

Scheme 6 Cross-metathesis of *o*-eugenol **29**.

the double bond migration from the formed metathesis products. Putting in action different procedures such as reactions under neat conditions with methyl methacrylate or slow addition of the catalyst in the case of acrylonitrile and acrylamides, it was possible to prepare a variety of functionalized phenol derivatives. Cross-metathesis from the eugenol isomer 2-allyl-6-methoxyphenol proved to be less productive. All these transformations were carried out without solvent or in green solvents, mainly dialkyl carbonates, and they open the route to the preparation of a variety of polyfunctional products from renewable feedstocks.

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