Asian Journal of Chemistry; Vol. 28, No. 5 (2016), 960-964

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2016.19554

o-Eugenol: A Versatile Molecule for Production of Polyfunctional Alkenes *via* Organometallic Catalysis

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Received: 10 August 2015; *Accepted*: 15 December 2015; *Published online*: 30 January 2016; AJC-17726

In this study, the synthesis and cross metathesis of *o*-eugenol (2-allyl-6-methoxy phenol) has been investigated. Synthesis was conducted through two stages of reaction. The first step in the synthetic procedure was to obtain the intermediate 1-but-3-enyl-2-methoxy benzene. Then the heating of the obtained intermediate will initiate will initiate a [3,3] sigmatropic rearrangement to give the *o*-eugenol with a good yield. The ruthenium-catalyzed cross-metathesis of *o*-eugenol derivatives with electron deficient olefins including methyl acrylate, acrylonitrile and acrylamides was also reported. In addition the polymerization of 1-allyl-2-(allyloxy)-3-methoxybenzene was possible by acyclic diene metathesis and this allowed to synthesize a polymer from a natural substrate. All the resulting structures were supported by the spectroscopic data.

Keywords: Claisen rearrangement, *o*-Eugenol, Isomerization, O-Allylation, Benzoquinone, Cetyltrimethylammonium bromide.

INTRODUCTION

Phenols, specially flavonoids and anthocyanins show a great capacity to scavenge free radicals that causes the oxidative stress [1-4]. They have anti-inflammatory, antiallergic, antitrombotic, antimicrobial and antineoplasic activity [5-8]. *o*-Eugenol is a phenolic derivative commonly known as nail essence [9] that can also be extracted from pepper, bay leaves, cinnamon, nutmeg, camphor and some natural oils [10].

In the present study, we investigated the synthesis of *o*-eugenol as a contribution to possible future applications. In addition we report also a more systematic study on cross-metathesis of *o*-eugenol derivatives with electron deficient olefins including methyl acrylate, acrylonitrile and acrylamides leading to several polyfunctional phenol derivative.

EXPERIMENTAL

All the reactions were conducted under an inert atmosphere of argon using standard Schlenk tube techniques. Solvents were dried by distillation prior to use. Dimethyl carbonate and glycerol were distilled under atmospheric pressure and stored under argon over activated 3 Å molecular sieves. Methyl acrylate was purchased from Acros Organics and stored under argon over activated 3 Å molecular sieves prior to use. Acrylonitirile was distilled under atmospheric pressure and stored under argon over activated 3 Å molecular sieves. Acrylamide was purchased from Alfa Aesar and used as received (99.9 %).

General procedure for the cross-metathesis reactions with methyl acrylate: A dry and degassed Schlenk tube was loaded under argon with 100 mg of *o*-eugenol (0.48-0.61 mmol), 4 mg of Umicore M51 catalyst IV (6×10^{-3} mmol, 1 mol %) or 7.6 mg of Hoveyda catalyst (12×10^{-3} mmol, 2 mol %), 88-106 µL of methyl acrylate (~ 0.97-1.2 mmol, 2.5-3.3 mg of *para*-benzoquinone (~ 22-30 $\times 10^{-3}$ mmol, 5 mol %), or 5.2 mg of *para*-benzoquinone (~ 49×10^{-3} mmol, 10 mol %), 10 µL of dodecane as internal standard and 2 mL of solvent. The reaction was stirred under the mentioned conditions. After solvent evaporation, the products were purified by column chromatography on silica gel using of EtOAc/petroleum ether mixtures.

General procedure for the cross-metathesis reactions with acrylonitrile: A dry and degassed Schlenk tube was loaded under argon with 100 mg of *o*-eugenol (0.48-0.61 mmol), 2.5-3.3 mg of *para*-benzoquinone (~ 22-30 $\times 10^{-3}$ mmol, 5 mol %), 64-80 µL of acrylonitrile (~ 0.97-1.2 mmol,

2 equiv.), 1.5 mL of solvent and then closed by a rubber septum. Another dry and degassed Schlenk tube was loaded under argon with 6.0-7.6 mg of Hoveyda catalyst II (12×10^{-3} mmol, 2 mol %), 10 µL of dodecane as internal standard and 0.5 mL of solvent. The ruthenium catalyst was then taken by a syringe and was slowly added into the first Schlenk tube through the septum by means of a syringe-pump during 2 h. After addition, the reaction mixture was stirred at 100 °C for additional 3 h. After solvent evaporation, the products were purified by column chromatography on silica gel using of EtOAc/petroleum ether mixtures.

General procedure for the cross-metathesis reactions with acrylamide: A dry and degassed Schlenk tube was loaded under argon with 125-157 mg of *o*-eugenol (0.76 mmol, 1.25 equiv.), 2.5-3.3 mg of *para*-benzoquinone (~ 22-30 × 10^{-3} mmol, 5 mol %), 43 mg of acrylamide (0.6 mmol, 1 equiv.), 10 µL of dodecane as internal standard and 1.5 mL of solvent and then closed by a rubber septum. Another dry and degassed Schlenk tube was loaded under argon with 7.6 mg of Hoveyda catalyst (12×10^{-3} mmol, 2 mol %), 10 µL of dodecane as internal standard and 0.5 mL of solvent. The ruthenium catalyst was then taken by a syringe and was slowly added into the first Schlenk tube through the septum by means of a syringe-pump during 2 h. After addition, the reaction mixture was stirred at 80 °C for additional time under the mentioned conditions. After solvent evaporation, the products were purified by column chromatography on basic alumina gel using of EtOAc/petroleum ether mixtures.

(E)-methyl 4-(2-hydroxy-3-methoxyphenyl)but-2-enoate (5): Yield = 60 %; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.54 (d, *J* = 6.4 Hz, 2H, $H_{1'}$), 3.70 (s, 3H, OCH_3), 3.88 (s, 3H, $COOCH_3$), 5.70 (s, 1H, OH), 5.81 (d, *J* = 15.6 Hz, 1H, $H_{3'}$), 6.70 (d, *J* = 6.8 Hz, 1Har, H_6), 6.76-6.79 (m, 2Har, $H_{4,5}$), 7.09-7.16 (m, 1H, $H_{2'}$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 32.3 ($C_{1'}$), 51.3 (OCH_3), 55.9 ($COOCH_3$), 109.1 (CH), 119.5 (C_4), 121.4 (C_5), 122.3 (C_6), 123.4 (C_1), 143.5 (C_2), 146.4 (C_3), 147.1 ($C_{3'}$), 167.0 (C=O). Anal. calcd. for $C_{12}H_{14}O_4$: C, 64.853 %; H, 6.350 %. Found: C, 64.8; H, 6.3; HRMS (ESI): $[M + Na]^+$ calculated for ($C_{12}H_{14}O_4Na$) = *m/z* 245.0789. Measured: *m/z* 245.0787; $C_{12}H_{14}O_4$: Theor. C 64.85, H 6.35 Exp. C 64.84, H 6.37.

4-(2-Hydroxy-3-methoxy-phenyl) but-2-enenitrile (6): Yield = 65 %; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.54, 3.76 (2d, *J* = 6.0 Hz, 7.2 Hz, 2H, $H_{1'}$, *cis* + *trans*), 3.89 (s, 3H, OCH_3), 5.29, 5.36 (2d, *J* = 16.0 Hz, *J* = 10.8 Hz, 1H, $H_{3'}$, *cis* + *trans*), 5.78, 5.80 (2s, 1H, OH, *cis* + *trans*), 6.64-6.70 (m, 1H, $H_{2'}$), 6.78-6.80 (m, 3Har, $H_{4,5,6}$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 32.3, 33.4 (C1', *cis* + *trans*), 55.9 (OCH_3), 99.3, 100.1 ($C_{3'}$, *cis* + *trans*), 109.4, 109.5 (CH, *cis* + *trans*),116.0, 117.5 (CN, *cis* + *trans*), 119.7 (C_4), 122.0, 122.2 (C_5, *cis* + *trans*), 122.6 (C1), 143.5 (C_2), 146.4 (C_3), 152.4, 153.4 (C_2, *cis* + *trans*). Anal. calcd. for $C_{11}H_{11}O_2N$: C, 69.826 %; H, 5.860 %. Found: C, 69.8; H, 5.8; HRMS (ESI): $[M + Na]^+$ calculated for ($C_{11}H_{11}NO_2Na$) = *m/z* 212.0687. Measured: *m/z* 212.0688; $C_{11}H_{11}NO_2$: Theor. C 69.83, H 5.86, N 7.4 Exp. C 69.29, H 5.76, N 7.03.

(E)-4-(2-Hydroxy-3-methoxyphenyl) but-2-enamide (7): Yield = 56 %; ^{1}H NMR (400 MHz, Methanol-d_4, ppm): 3.49 (d, *J* = 7.6 Hz, 2H, $H_{1'}$), 3.82 (s, 3H, OCH_3), 5.88 (s, 1H, $H_{3'}$), 6.24-6.26 (m, 1H, OH), 6.62 (s, 1H, $H_{2'}$), 6.73 (d, *J* = 8.0 Hz, 1Har, H_6), 6.80 (dd, 1Har, *J* = 7.6 Hz, *J* = 7.6 Hz, H_5), 6.92(d, 1H, *J* = 8.0 Hz, H_4). ^{13}C NMR (100 MHz, Methanol-d_4, ppm): 33.1 ($C_{1'}$), 56.2 (OCH_3), 110.7 (C_4), 120.1 (C_5), 123.0 (C_6), 124.2 ($C_{3'}$), 125.6 (C_1), 144.9 ($C_{2'}$), 145.2 (C_2), 148.6 (C_3), 171.0 ($CONH_2$). Anal. calcd. for $C_{11}H_{13}O_3$: C, 68.377 %; H, 6.782 %. Found: C, 68.3 H, 6.7; HRMS (ESI): $[M + Na]^+$ calculated for ($C_{11}H_{13}NO_3Na$) = *m/z* 230.0793. Measured: *m/z* 230.0796

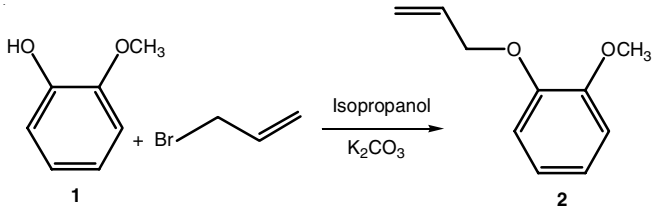
1-Allyl-2-(allyloxy)-3-methoxybenzene (8): A mixture of *o*-eugenol (**1**, 16.4 g, 0.1 mol), NaOH (6 g, 0.15 mol), dichloromethane (50 mL), CTAB (1.21×10^2 mM) and distilled water (50 mL) were placed in 500 mL round bottom flask. Allyl bromide (24.2 g, 0.2 mol) was added drop wise and the mixture was then stirred at room temperature for 5 h. After completion, the organic layer was separated and aqueous layer was extracted with dichloromethane (2 × 20 mL). The combined organic phase was washed with distilled water (2 × 50 mL), dried with anhydrous Na_2SO_4 and concentrated to give compound (**2**) (16.60 g, 81.10 %) as yellowish liquid. IR (ATR) ν_{max}, cm^{-1}): 3078,2908-2839, 1843, 1589 and 1512, 1458, 1419, 1226 and 1141, 995, 918, 856 and 739. ^{1}H NMR spectrum (500 MHz, $CDCl_3$): δ 6.71-6.74 ppm (3H, m, ArH), 5.95-5.97 (2H, m, =CH), 5.26-5.32 (2H, m, $=CH_2$), 5.05 (2H, t, *J* = 15.6 Hz, $=CH_2$), 4.57 (2H,d, *J* = 15.6 Hz, CH_2O), 3.81 (3H, s, OCH_3) and 3.31 (2H, d, *J* = *8.6* Hz, CH_2). ^{13}C NMR spectrum (125 MHz,$CDCl_3$,): δ 39.80 (CH_2), 55.81 (OCH_3), 69.96 (OCH_2),115.61 and 117.73 9 (CH_2=), 133.55 and 137.62 (=CH), 112.20, 113.58, 120.33, 133.03, 146.30 and 149.36 (ArC). Mass spectrum (EI): *m/z* 204 (M, 40 %),163 (100), 135 (15), 103 (70), 91 (50), 77 (23), 41 (70). Anal. calcd. for $C_{13}H_{16}O_2$: C, 76.440 %; H, 7.895 %. Found: C, 76.4, H, 7.8

(E)-Methyl 4-(2-methoxy-4-((E)-4-methoxy-4-oxobut-2-enyl) phenoxy)but-2-enoate (9): Yield = 72 % ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.46 (d, 6.0 Hz, 2H, $H_{1'}$), 3.72 (s, 3H, CH 3), 3.74 (s, 3H, CH_3), 3.86 (s, 3H, CH_3), 4.74-4.75 (m, 2H, CH_2), 5.81 (d, *J* = 15.6 Hz, 1H, $H_{3'}$), 6.18 (d, *J* = 15.6 Hz, 1H, H_6), 6.66-6.68 (m, 2Har, $H_{4,5}$), 6.77 (d, *J* = 8.4 Hz, 1Har, H_6), 7.05-7.11 (m, 2H, CH, $H_{2',5'}$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 38.0 ($C_{1'}$), 51.4 (CH_3), 51.5 (CH_3), 55.8 (CH), 67.7 ($C_{4'}$), 112.5 (C_4), 114.0 (C_5), 120.7 ($C_{6'}$), 121.7 (C_6), 121.7 (C_5), 131.3 (C_1), 142.8 (C_2), 146.2 (C_3), 147.5 ($C_{5'}$), 149.6 (C_2), 166.3 ($COOCH_3$), 166. 8 ($COOCH_3$). Anal. calcd. for $C_{16}H_{18}O_6$: C, 62.737 %; H, 5.923 %. Found: C, 62.7, H, 5.9; HRMS (ESI): $[M + Na]^+$ calculated for ($C_{17}H_{20}O_6Na$) = 343.1157. Measured: 343.1160; $C_{17}H_{20}O_6$: Theor. C 63.74, H 6.29 Exp. C 64.01, H 6.26

Poly *bis*-allyl-benzene *o*-eugenol (10): The product was obtained after decanting into cold methanol to obtain 187 g of polymer having the following characteristics: M_n: 2959 (g/mol); M_w: 8145; PDi: 2.7526 determined by gel permeation chromatography GPC (calibrated against polystyrene in chloro-form). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.32 (bd, 13.2 Hz, 2H, CH_2), 3.82 (s, 3H, CH_3), 4.57 (bd, 2H, CH_2), 5.65-6.08 (m, 2H, CH), 6.65-6.70 (m, 2Har, CH), 6.78 (d, 6.4 Hz, 1Har, CH).

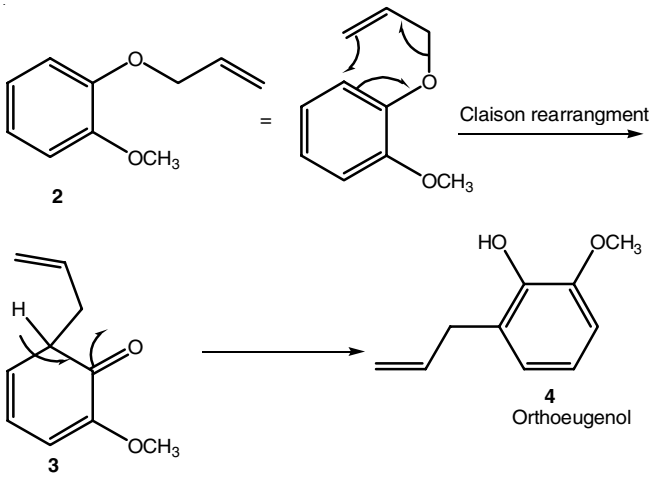
RESULTS AND DISCUSSION

Synthesis of *o*-eugenol: In this study, *o*-eugenol was prepared [11-13]; the first step in the synthetic procedure was to obtain the intermediate **2** this was accomplished by reaction of guaiacol with 3-bromo-1-propene and anhydrous potassium carbonate in dry 2-propanol at reflux for 8 h (**Scheme-I**).



Scheme-I: Synthesis of intermediate **2**

Then the heating of the intermediate **2** will initiate a [3,3] sigmatropic rearrangement to give the *o*-eugenol with a good yield. **Scheme-II**.



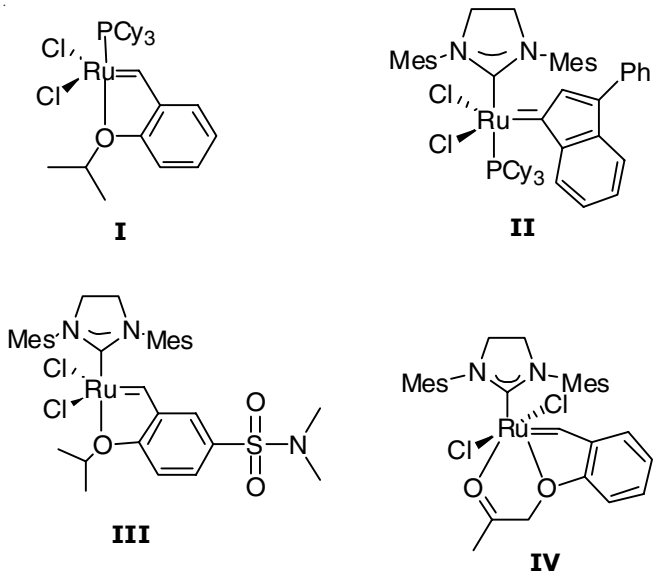
Scheme-II: Protocol synthesis of *o*-eugenol **4**

The resulting structure **4** is supported by all the spectroscopic data.

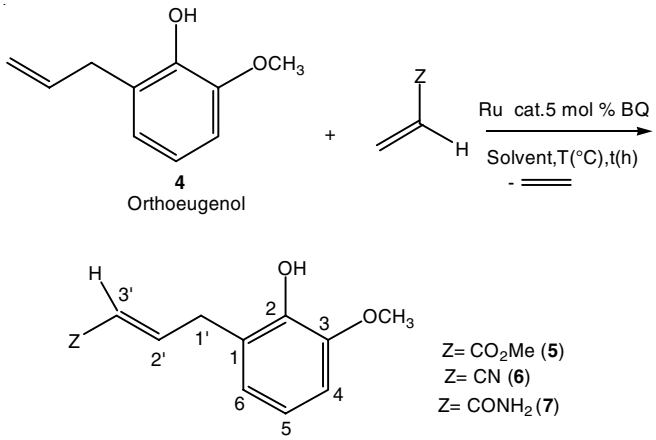
The cross-metathesis reactions of *o*-eugenol were investigated with the four second generation ruthenium catalysts I-IV (**Scheme-III**).

Cross metathesis of *o*-eugenol: The cross-metathesis of *o*-eugenol was carried out with methyl acrylate, acrylonitrile and acrylamide are outlined in **Scheme-IV**.

The products **5-7** were obtained under optimized conditions during the cross metathesis of *o*-eugenol with methylacrylate [14] and the results are given in Table-1.



Scheme-III: Olefin metathesis catalysts



Scheme-IV: Cross metathesis of *o*-eugenol with methyl acrylate, acrylonitrile and acrylamide

The cross-metathesis with methyl acrylate was first experimented out with 1 mol % of catalyst Umicore M51 (**IV**); in the DMC at 80 °C for 8 and 16 h. Conversions were 67 and 82 % obtained respectively. Then the catalyst was exchanged by the second generation Hoveyda catalyst and we kept the same conditions. In this case a conversion of 92 % of *o*-eugenol was obtained.

The last test was performed with 2 mol % of Hoveyda 2nd generation catalyst in DMC at 80 °C for 24 h and *o*-eugenol was converting up to 97 %. The yield of the obtained product was reached up to 60 % and with a 100 % E stereochemistry (Table-1, entry 1).

TABLE-1
CROSS METHATHESIS OF *o*-EUGENOL WITH DIFFERENTS OLEFINES

Entry	Olefin	Solvent	Catalyst (%)	Addition[a]	T (°C)	t (h)	Conv. (%)[b]	Yield (%)[c]
1	Methyl acrylate	Glycerol	Hoveyda II: 2	Total	80	24	97	**(5)** 60
2	Acrylonitrile	DMC	Hoveyda II: 2	Slow	100	(2 + 3)	95	**(6)** 65
3[c]	Acrylamide	Glycerol	Hoveyda II: 2	Slow	80	(2 + 2)	75	**(7)** 56

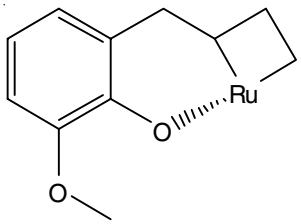
[a]Slow addition of the catalyst was made with a syringe pump for 2 h with a flow rate 0.5 mL/h, [b]The conversion was determined using dodecane as internal standard, [c]The cross-metathesis with acrylamide was made with 1.25 equiv. *o*-eugenol and the yield was calculated relative to the acrylamide.

In order to achieve the target results, we then studied the cross metathesis of *o*-eugenol with acrylonitrile in presence of the DEC at 100 °C for 5 h by adding the catalyst slowly for the first 2 h. Consequently, we convert *o*-eugenol up to 95 % and the isolated yield was 65 % in both form of two isomers Z/E: 2/1 (Table-1, entry 2).

On the other hand cross-metathesis of *o*-eugenol with acrylamide produced a conversion of 75 % after 4 h and it remained constant even after 6 h and 24 h.

The cross-metathesis of *o*-eugenol with a small excess of acrylamide and 2 mol % of Hoveyda 2nd generation catalyst during 2 h gave the results. The target product was isolated on the basic alumina column with a yield of 56 % and a 100 % E stereochemistry (Table-1, entry 3).

It should be noted that the cross-metathesis of *o*-eugenol requires more hard conditions which can be due to the OH group position. Its suggested that during the catalytic cycle of cross metathesis, the OH group could chelate the catalytic species and thereby inhibit its activity (**Scheme-V**).

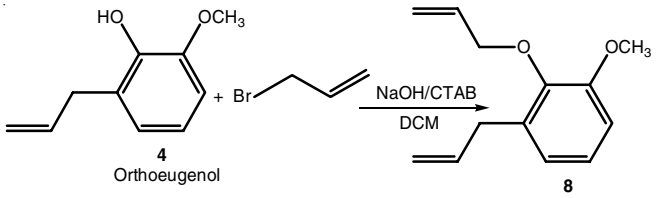


Scheme-V: Proposed structure of the interaction of *o*-eugenol with the metal center during metathesis reactions

Cross metathesis of 1-allyl-2-(allyloxy)-3-methoxy benzene

Synthesis of 1-allyl-2-(allyloxy)-3-methoxy benzene (8): Compound of 1-allyl-2-(allyloxy)-3-methoxy benzene (**8**) was synthesized by CTAB catalyzed O-allylation of *o*-eugenol with allyl bromide in dichloromethane-water biphasic systems. The allyl bromide was previously prepared from allyl alcohol and hydrogen bromide by the method of Kamm and Marvel. Reaction was carried out at room temperature.

The presence of NaOH without heating to avoid direct product of Claisen rearrangement to yield 1-allyl-2-(allyloxy)-3-methoxy-benzene (**8**) as yellowish liquid in 81.10 % yield (**Scheme-VI**).

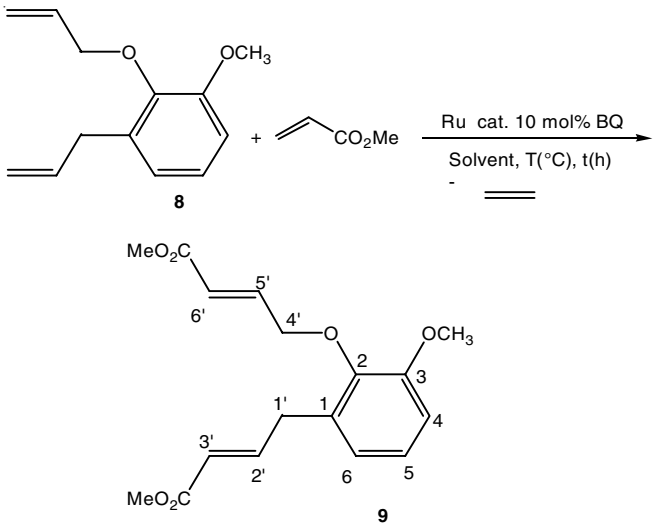


Scheme-VI: Synthesis of compound **8**

Clear evidence of allyloxy compound (**8**) was given by IR spectrum, which demonstrated the absence of hydroxy frequency in the range 3500-3400 cm^{-1} of the starting *o*-eugenol. It indicates that the reaction of O-allylation certainly take place effectively at room temperature in the presence of CTAB as micellar catalyst and no direct product of Claisen rearrangement.

The vinylidene allyloxy protons were found in ^1H NMR spectra of compound (**8**) as a multiplet at 5.26 ppm and these protons were shifted downfield with respect to 5.05 ppm in the vinylidene allyl due to the electron withdrawing of oxygen atom.

The presence of the two protons appearing as doublets at 4.57 ppm confirmed the OCH_2 groups. The ^{13}C NMR spectrum demonstrated thirteen peaks corresponding to thirteen carbon and this spectrum displayed signals at 69.96, 137.62 and 117.73 ppm originating from the corresponding OCH_2, =CH and $=CH_2$ carbons, respectively. Furthermore, the mass spectrum revealed a molecular ion peak at *m/z* 204 (40 %) together with a base peak at *m/z* 163 resulting from the loss of the allyl group. The resulting structure (**8**), which is 1-allyl-2-(allyloxy)-3-methoxy benzene is supported by all the spectroscopic data. The cross-metathesis of 1-allyl-2-(allyloxy)-3-methoxy benzene (**8**) with methylacrylate gave the di-functional product **9** (**Scheme-VII**).



Scheme-VII: Cross-metathesis of 1-allyl-2-(allyloxy)-3-methoxybenzene (**8**)

The cross-metathesis of the of 1-allyl-2-(allyloxy)-3-methoxy benzene (**8**) was investigated with methyl acrylate and the results are shown in Table-2.

After 17 h of complete conversion the reaction was made with 2 mol % of Hoveyda 2nd generation catalyst in the DMC

TABLE-2
CROSS-METATHESIS OF DIENE 32 WITH METHYL ACRYLATE (AM)

Entry	Solvent	Catalyst (%)	AM (equiv.)	T (°C)	t (h)	Conversion (%)[a]	Isolated yield (%)
1	DMC	Hoveyda II: 2	4	80	17	100	42
2	DMC	Hoveyda II: 2	10	80	17	100	72
3	Glycerol	Hoveyda II: 2	10	100	17	100	68
4	DMC	Hoveyda II: 2	10	80	24	100	75

[a]Conversion was determined using dodecane as internal standard.

TABLE-3
OPTIMIZATION OF THE POLYMERIZATION OF THE DIENE 8 BY REACTION OF ACYCLIC DIENE METATHESIS

Entry	Solvent	Cata. (%)	T (°C)	t (h)	Conversion (%)[a]	Wight of polymer (mg)
1	DMC	Hoveyda II: 3	80	72	100	No polymer
2	DCM	Hoveyda II: 1	40	17	100	187 mg
3	Glycerol	Hoveyda II: 1	40	17	89	No polymer
4	Toluene	Hoveyda II: 1	80	17	96	No polymer

[a]The conversion was determined using dodecane as internal standard, the mass of the diene 8 = 300 mg.

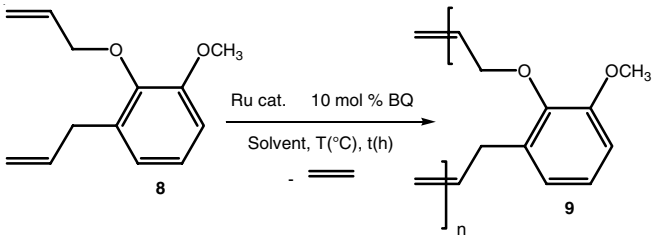
at 80 °C with 4 equivalents of methyl acrylate. The expected product was gained with yield of 42 %.

The obtained modest yield can be explained by a selective cross-metathesis of one of allyl moieties (Table-2, entry 1).

In order to solve this problem, we have reported the reaction again with 10 equivalents of methyl acrylate in this case, the obtained product was isolated with a good yield of about 72 % (Table-2, entry 2).

Eventhough, increasing the temperature up to 100 °C in DEC solvent for prolonged time up to 24 h could not ameliorate the yield of the reaction (Table-2, entry 3 and 4). The reaction product has been identified and it has a 100 % stereochemistry E. As noted that he migration of the double bond of the allyl moiety was avoided by the addition of 10 mol % of *p*-benzoquinone.

Polymerization of 1-allyl-2-(allyloxy)-3-methoxy benzene (8) The polymerization of diene **8** was possible by acyclic diene metathesis (ADMET) and this allowed to synthesize a polymer from a natural substrate (**Scheme-VIII**).



Scheme-VIII: Polymerization of diene **8**

The optimization of this reaction was studied and the results are summarized in Table-3.

Complete conversion was achieved with 3 mol % of Hoveyda 2nd generation catalyst in dimethyl carbonate and at 80 °C for 72 h. Under these conditions and after precipitation in methanol no polymer was obtained (Table-3, entry 1). While the use of 1 mol % of Hoveyda 2nd generation catalyst in DCM at 40 °C and after 17 h gave a polymer after precipitation (Table-3, entry 2). In order to carry out this reaction in a green solvent, the chlorinated solvent was replaced by dimethyl carbonate but no polymer was obtained (Table-3, entry 3). Eventhough, increasing temperature up to 80 °C could not allow to formation of polymer (Table-3, entry 4). All polymerization reactions were carried out in the presence of 10 mol % *p*-benzoquinone as an additive.

Conclusion

In this study synthesis and cross metathesis of *o*-eugenol has been investigated. The cross-metathesis of *o*-eugenol was carried out with different partners in the presence of catalyst ruthenium and has been optimized in some green solvents. A test for the polymerization of a monomer derived from *o*-eugenol was carried out and led to the formation of a polymer. Further studies will be needed to assess the value of the polymers obtained.

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