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# 1 Synthesis and characterization of novel vinyl ethers that bear 2 various functional groups

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13 The synthesis of new functionalized vinyl ethers (VE) by *transesterification* reaction between ethyl vinyl ether  
14 (EVE) and different alcohols is presented in this study. An air-stable palladium catalyst generated *in situ*  
15 efficiently catalyzed the reaction leading to various VE in a single step with good conversion % (50-82%) and  
16 good yields (up to 75%). The reaction conditions were optimized in terms of the initial EVE/alcohol molar ratio,  
17 alcohol concentration, solvent, presence and nature of the ligand, amount of the catalyst, and choice of the metal  
18 precursor. All VE were characterized using <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

19 Keywords: vinyl ether; *transesterification*; catalysis; palladium; NMR.

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## 20 1. Introduction

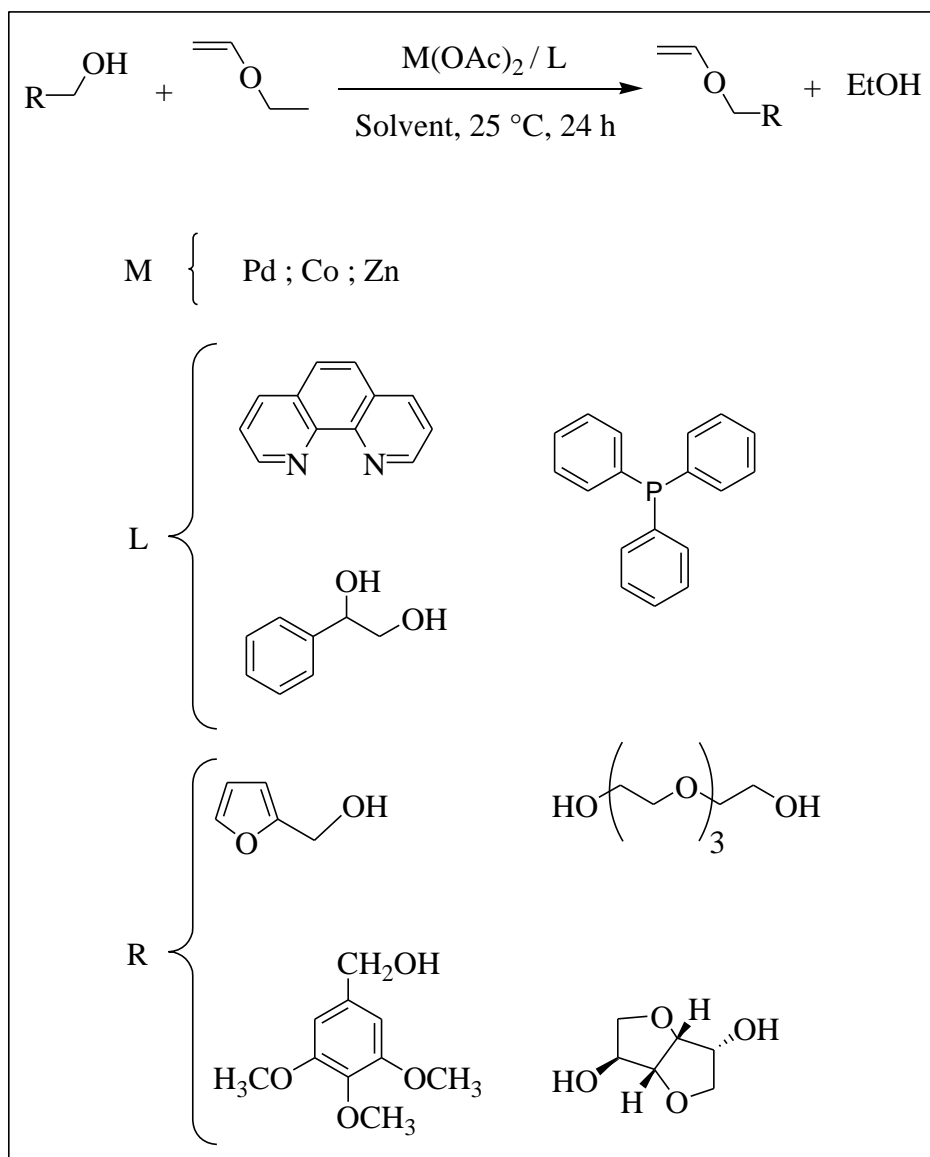
21 Enol ethers or vinyl ethers (VEs) are a class of chemical compounds that display ether  
22 and vinyl functional groups. These compounds have found numerous applications as key  
23 reagents in organic reactions such as the Diels-Alder reaction [1] and Claisen rearrangement  
24 [2], thanks to the remarkable reactivity of their electron-rich carbon-carbon double bond and  
25 the range of substituents that can bear [3,4]. They have been extensively polymerized under  
26 cationic initiation to produce polymeric materials endowed with excellent properties used in  
27 various industrial applications such as adhesives, paints, coating, and the synthesis of stimuli-  
28 sensitive materials [5-12]. Despite their simple structure, no universal method has been found  
29 to carry out their synthesis. Nevertheless, many methods have been developed to prepare vinyl  
30 ethers, particularly catalyzed *transesterification* using transition metals. Winternheimer et al.  
31 reported the main available pathways to synthesize vinyl ethers [2]. In the 1930's, Reppe and

32 Wolff developed a process to form VEs from acetylene and primary alcohols under rigorous  
33 pressure and temperature conditions and using a large amount of basic catalyst [13,14]. Then,  
34 four additional synthetic pathways have been developed for the chemical conversion of  
35 alcohols to vinyl ether: i) addition onto acetylene [13,14], ii) phase transfer catalysis based on  
36 Williamson reaction between an alkoxide and 2-chloroethyl vinyl ether [15], iii) modification  
37 of vinyl acetate in the presence of an iridium complex [16,17], and iv) *transesterification* [18].  
38 The latter strategy has been widely studied in the presence of either mercuric acetate [19,20]  
39 or palladium acetate [21-24] catalysts producing various vinyl ethers in fair to good yields.  
40 Complexes of palladium acetate and trifluoroacetate with bidentate ligands, such as 1,10-  
41 phenanthroline, have proven to efficiently catalyze most of the vinyl ethers **preparations, and**  
42 its catalysis mechanism was proposed by Handerson and Schlaf [23]. They successfully used  
43 (L-L) Pd(OAc)<sub>2</sub> catalyst, where L-L stands for 2,2'-bipyridyl or 1,10-phenanthroline chelate,  
44 for the transfer vinylation of protected monosaccharides. The efficiency of palladium (II)  
45 complex in transfer vinylation has been **initially** described by McKeon and Fitton [25]. To the  
46 best of our knowledge, only two other examples of catalyzed transfer vinylation were reported  
47 in literature: vinylation of steroids [22] and synthesis of glycidol vinyl ether [26]. In 2010,  
48 Pichavant et al. described the synthesis of a vinyl ether by *transesterification* catalyzed by a  
49 palladium(II) complex in the presence of ethyl vinyl ether in dichloromethane [27]. The  
50 iridium-catalyzed reaction of vinyl acetate with alcohols **later appeared** as a complementary  
51 method to palladium-catalyzed *transesterification* [**16,17**].

52 In 2013, our group published the *transesterification* between ethyl vinyl ether and  
53 various alcohols leading to the corresponding original vinyl ethers with 40-84% yield in a  
54 single step synthesis [18,28-33]. A series of vinyl ether monomers that bear diverse functional  
55 groups, such as halogenomethyl, amino, carbonate, oligo(ethylene oxide) side-groups, and  
56 oligo(fluoroether) chains, were prepared and characterized by NMR spectroscopy. The

57 palladium complex has been found to accelerate the reaction equilibrium, followed by using  
58 an excess of either vinyl ether or alcohol.

59 In this work, a detailed study on the transesterification reaction of ethyl vinyl ethers  
60 was carried out. The aim was to prepare new vinyl ethers with various side chain functional  
61 groups (Scheme 1) and can be widely used in the synthesis of polymeric materials and other  
62 applications. These vinyl ethers were synthesized from the corresponding alcohols through  
63 transesterification of ethyl vinyl ether catalyzed by an organometallic complex generated *in*  
64 *situ* (Scheme 1). Several reaction parameters were studied: the initial EVE/alcohol molar  
65 ratio, alcohol concentration, nature of the solvent, presence and nature of the ligand, amount  
66 of the organometallic complex, and choice of the metal precursor.



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68 **Scheme 1.** Synthesis of vinyl ethers bearing various functional groups by *transesterification* of the  
 69 corresponding alcohol and ethyl vinyl ether

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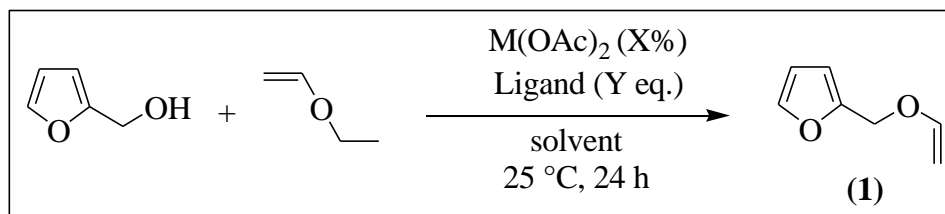
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## 80 2. Results and Discussion

81 In this study, liquid vinyl ethers bearing various side chains were prepared from four  
 82 different alcohols (Scheme 1). Furfuryl alcohol was chosen to undergo a series of  
 83 *transesterifications reactions to determine* the optimal experimental conditions (Scheme 2).



85 **Scheme 2.** Synthesis of 2-(vinylloxymethyl) furan by *transesterification* of the furfuryl alcohol and ethyl vinyl  
 86 ether

87 Using our typical procedure, the following key parameters were investigated: the  
 88 initial EVE/alcohol molar ratio, alcohol concentration, nature of the solvent, presence and  
 89 nature of the ligand, amount of the catalyst, and choice of the metal precursor. The results are  
 90 summarized in Table I.

91 **Table I.** *Transesterification* of EVE and furfuryl alcohol in different reaction conditions<sup>a</sup>

| Entry | $M(OAc)_2$ (X%)  | Ligand (Y eq.)                | Solvent    | Initial EVE/<br>alcohol<br>molar ratio | [alcohol]<br>(mol/L) | Conv. <sup>b</sup><br>(%) |
|-------|------------------|-------------------------------|------------|--|----------------------|---------------------------|
| 1     | $Pd(OAc)_2$ (2%) | -                             | $CH_2Cl_2$ | 12                                     | 2.2                  | 0                         |
| 2     | $Pd(OAc)_2$ (2%) | 1-Phenyl-1,2-ethanediol (1.5) | $CH_2Cl_2$ | 12                                     | 2.2                  | 0                         |
| 3     | $Pd(OAc)_2$ (2%) | Triphenylphosphine (2)        | $CH_2Cl_2$ | 12                                     | 2.2                  | 0                         |
| 4     | $Pd(OAc)_2$ (2%) | 1,10-phenanthroline (1.5)     | $CH_2Cl_2$ | 12                                     | 2.2                  | <b>69</b>                 |
| 5     | $Zn(OAc)_2$ (2%) | 1,10-phenanthroline (1.5)     | $CH_2Cl_2$ | 12                                     | 2.2                  | 0                         |
| 6     | $Co(OAc)_2$ (2%) | 1,10-phenanthroline (1.5)     | $CH_2Cl_2$ | 12                                     | 2.2                  | 0                         |
| 7     | $Pd(OAc)_2$ (2%) | 1,10-phenanthroline (1.5)     | DMF        | 12                                     | 2.2                  | 8                         |
| 8     | $Pd(OAc)_2$ (2%) | 1,10-phenanthroline (1.5)     | THF        | 12                                     | 2.2                  | 16                        |
| 9     | $Pd(OAc)_2$ (2%) | 1,10-phenanthroline (1.5)     | Dioxane    | 12                                     | 2.2                  | 50                        |
| 10    | $Pd(OAc)_2$ (2%) | 1,10-phenanthroline (1.5)     | Toluene    | 12                                     | 2.2                  | 57                        |
| 11    | $Pd(OAc)_2$ (2%) | 1,10-phenanthroline (1.5)     | -          | 12                                     | 2.2                  | 66                        |
| 12    | $Pd(OAc)_2$ (2%) | 1,10-phenanthroline (1.5)     | $CH_2Cl_2$ | 6                                      | 2.2                  | 60                        |
| 13    | $Pd(OAc)_2$ (2%) | 1,10-phenanthroline (1.5)     | $CH_2Cl_2$ | 24                                     | 2.2                  | 57                        |

|    |                            |                           |                                 |    |     |           |
|----|----------------------------|---------------------------|---------------------------------|----|-----|-----------|
| 14 | Pd(OAc) <sub>2</sub> (2%)  | 1,10-phenanthroline (1.5) | CH <sub>2</sub> Cl <sub>2</sub> | 12 | 4.4 | 65        |
| 15 | Pd(OAc) <sub>2</sub> (2%)  | 1,10-phenanthroline (1.5) | CH <sub>2</sub> Cl <sub>2</sub> | 12 | 0.5 | 37        |
| 16 | Pd(OAc) <sub>2</sub> (2%)  | 1,10-phenanthroline (1.5) | CH <sub>2</sub> Cl <sub>2</sub> | 12 | 1   | 52        |
| 17 | Pd(OAc) <sub>2</sub> (2%)  | 1,10-phenanthroline (1)   | CH <sub>2</sub> Cl <sub>2</sub> | 12 | 2.2 | 65        |
| 18 | Pd(OAc) <sub>2</sub> (2%)  | 1,10-phenanthroline (2)   | CH <sub>2</sub> Cl <sub>2</sub> | 12 | 2.2 | 63        |
| 19 | Pd(OAc) <sub>2</sub> (2%)  | 1,10-phenanthroline (3)   | CH <sub>2</sub> Cl <sub>2</sub> | 12 | 2.2 | 59        |
| 20 | Pd(OAc) <sub>2</sub> (1%)  | 1,10-phenanthroline (1.5) | CH <sub>2</sub> Cl <sub>2</sub> | 12 | 2.2 | 52        |
| 21 | Pd(OAc) <sub>2</sub> (5%)  | 1,10-phenanthroline (1.5) | CH <sub>2</sub> Cl <sub>2</sub> | 12 | 2.2 | <b>69</b> |
| 22 | Pd(OAc) <sub>2</sub> (10%) | 1,10-phenanthroline (1.5) | CH <sub>2</sub> Cl <sub>2</sub> | 12 | 2.2 | 66        |

92 <sup>a</sup> **Reaction conditions** : Solvent or bulk (entry 11), 24 h, 20 °C, M(OAc)<sub>2</sub> (X %), ligand (X eq /Pd(OAc)<sub>2</sub>). <sup>b</sup>% conversion was assessed by  
93 <sup>1</sup>H NMR spectroscopy; **Conv.** (%) =  $\frac{\int_{4.71} CH_2O(VE)/2}{\int_{4.71} CH_2O(VE)/2 + \int_{4.61} CH_2OH alcohol/2}$  x 100, where  $\int_i$  represent the integral of the signal centered at  
94  $i$  ppm in <sup>1</sup>H NMR spectrum

95 The presence of the ligand played an essential role in the *trans*etherification reaction.  
96 This was proven in entry 1 that was carried out without ligand, for which no transformation  
97 was observed. Using 1-phenyl-1,2-ethanediol (entry 2) and triphenylphosphine (entry 3)  
98 ligands did not lead to the desired product. However, the 1,10-phenanthroline ligand showed a  
99 remarkable catalytic activity of Pd(OAc)<sub>2</sub> with 69% conversion, obtained after 24 hours of  
100 stirring at 20 °C (entry 4).

101 In order **to assess** the impact of the metal used in the catalyst, the employment of  
102 Zn(OAc)<sub>2</sub> and Co(OAc)<sub>2</sub> complex **catalysts did** not result in the formation of the desired  
103 product (entries 5-6). However, using Pd(OAc)<sub>2</sub> led to the formation of the desired vinyl ether  
104 with 69% conversion. **These results align with B. Boutevin et al. work. They demonstrated**  
105 **that** the 1,10-phenanthroline-palladium (II) acetate complex led to vinyl ethers by  
106 *trans*etherification of ethyl vinyl ether in fair % yields [15].

107 While studying the effect of the solvent nature, moderate conversions were observed  
108 with 1,4-dioxane or toluene (entries 9-10). On the other hand, poor conversions were obtained  
109 using THF and DMF (entries 7-8). Dichloromethane was observed to be the best solvent for  
110 this **reaction, with** the highest **conversion %** (entry 4). This variation in the catalytic activity  
111 can be related to the solubility of the **catalyst, which** differs from one solvent to another

112 depending on the solvent polarity. A slight decrease in the catalytic activity (66% conversion)  
113 was observed when the reaction was conducted without solvent (entry 11).

114 It was noticed that the increase in the initial EVE/alcohol molar ratio from 6 to 12 eq.  
115 shifted the equilibrium in favor of the desired vinyl ether product (entries 4 and 12).  
116 Furthermore, an increase in the number of EVE equivalents for more than 12 did not benefit  
117 the % conversion (entry 13). This may be due to the dilution effect. Thus, 12 eq. of EVE was  
118 sufficient to promote this reaction.

119 The effect of the initial alcohol concentration was examined as well. 69% conversion  
120 was obtained with a concentration of 2.2 mol/L (entry 4). A similar % conversion was  
121 obtained when the alcohol concentration was raised to 4.4 mol/L (entry 14), showing that the  
122 maximum possible % conversion was already reached with a concentration of 2.2 mol/L.  
123 Dropping the [alcohol] to 0.5 mol/L (entry 15), lessened the conversion to 37%. Thus,  
124 medium concentration ( $\approx 2.2$  mol/L) was good enough to be used for the catalyst to be  
125 effective and give high % conversions.

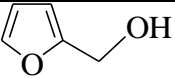
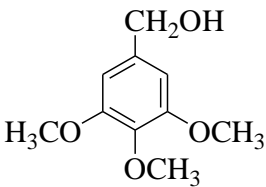
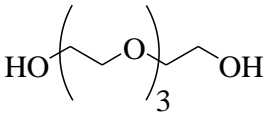
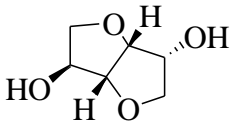
126 Since the presence of the ligand was determined to be crucial, the variation of the  
127 number of equivalents of 1,10-phenanthroline was studied. When the number of the 1,10-  
128 phenanthroline ligand equivalents was augmented from 1.0 to 1.5, it improved the conversion  
129 from 65 % to 69% (entries 4 and 17). In entry 18, a slightly lower % conversion was obtained  
130 with 2 ligand equivalents (63%). Furthermore, adding 3 equivalents of the ligand resulted in  
131 an apparent reduction of the % conversion (entry 19).

132 A significant increment in the conversion % was marked by increasing the amount of  
133 catalyst from 1 to 2% (entries 4 and 20). Adding a 5% catalyst (entry 21) did not show any  
134 notable advantage. However, the 10% catalyst (entry 22) marked a slight drop in the %  
135 conversion, indicating that a 2% catalyst is sufficient to achieve the highest conversion % in  
136 this transesterification reaction.



137 A series of vinyl ethers (**1-4**) was then synthesized by *transesterification* catalyzed by  
 138 2% palladium (II) acetate generated *in situ*. The reactions were carried out in dichloromethane  
 139 in the presence of 1.5 equivalents of 1,10-phenanthroline and excess of EVE (12 eq.). The  
 140 reaction was stirred at room temperature for 24 hours. The results are summarized in Table II.

141 **Table II.** *Transesterification* of primary alcohols that bear various side groups with ethyl vinyl ether<sup>a</sup>

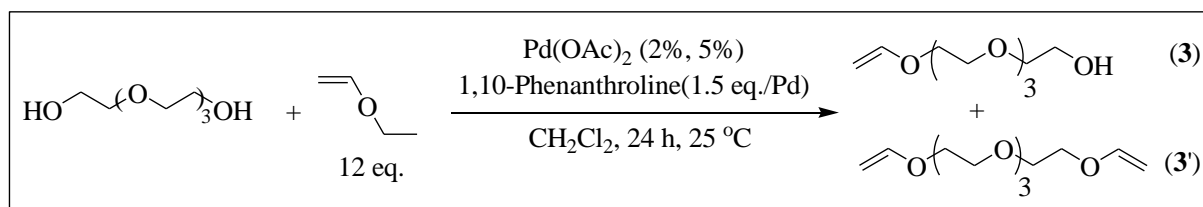
| Entry          | ROH   | VE  | Pd(OAc) <sub>2</sub><br>(x%) | Conv. <sup>b</sup><br>(%) | Yield <sup>c</sup><br>(%) |
|----------------|---|---|------------------------------|---------------------------|---------------------------|
| 1              |    | 2-(vinylloxymethyl) furan ( <b>1</b> )                    | 2                            | 69                        | 59                        |
| 2              |    | 1,2,3 trimethoxy-5-(vinylloxymethyl) benzene ( <b>2</b> ) | 2                            | 82                        | 75                        |
| 3              |  | 2-(2-(vinyloxy)ethoxy) ethanol (mono- <b>3</b> )          | 2                            | 75                        | 50                        |
|                |   | (2-(2-(vinyloxy)ethoxy)ethoxy) ethene (bis- <b>3'</b> )   | 5                            | 61                        | 40                        |
| 4 <sup>d</sup> |  | 6-(vinyloxy)-hexahydrofuro[3,2-b]furan-3-ol ( <b>4</b> )  | 2                            | 50                        | 42                        |

142 <sup>a</sup> Reaction conditions: 20 °C, 24 h, Pd(OAc)<sub>2</sub> (2%) generated *in situ*, 1,10-phenanthroline (1.5 eq /Pd(OAc)<sub>2</sub>). <sup>b</sup>Conversion was assessed by

143 <sup>1</sup>H NMR spectroscopy; Conv. (%) =  $\frac{\int 4.71 \text{ CH}_2\text{O(VE)}/2}{\int 4.71 \text{ CH}_2\text{O(VE)}/2 + \int 4.61 \text{ CH}_2\text{OH alcohol}/2} \times 100$ . <sup>c</sup>isolated yield. <sup>d</sup>reaction carried out in THF

144 2-(Vinylloxymethyl) furan (**1**) was prepared under the optimal conditions by  
 145 *transesterification* catalyzed by a palladium (II) complex generated *in situ*. 69% conversion  
 146 and 59% yield were obtained (entry 1). 1,2,3-trimethoxy-5-(vinylloxymethyl) benzene (**2**) was  
 147 synthesized under the same conditions with 82% conversion and 75% yield (entry 2). The  
 148 *transesterification* of tetraethylene glycol and ethyl vinyl ether (Scheme 3) led to mono-vinyl  
 149 ether (**3**) with 75% conversion calculated based on the <sup>1</sup>H NMR analysis of the reaction  
 150 mixture. Surprisingly, in a random experimental trial, when the amount of the catalyst was

151 raised to 5%, telechelic bis vinyl-ether (**3'**) was formed as a major product, and the % yield  
 152 dropped from 50 to 40 (entry 3). Finally, the *transesterification* of dianhydro-D-glucitol was  
 153 exceptionally performed in THF/CH<sub>2</sub>Cl<sub>2</sub> due to its low solubility in dichloromethane. The  
 154 desired vinyl ether (**4**) was obtained with 50 % conversion and 42 % yield (entry 4).

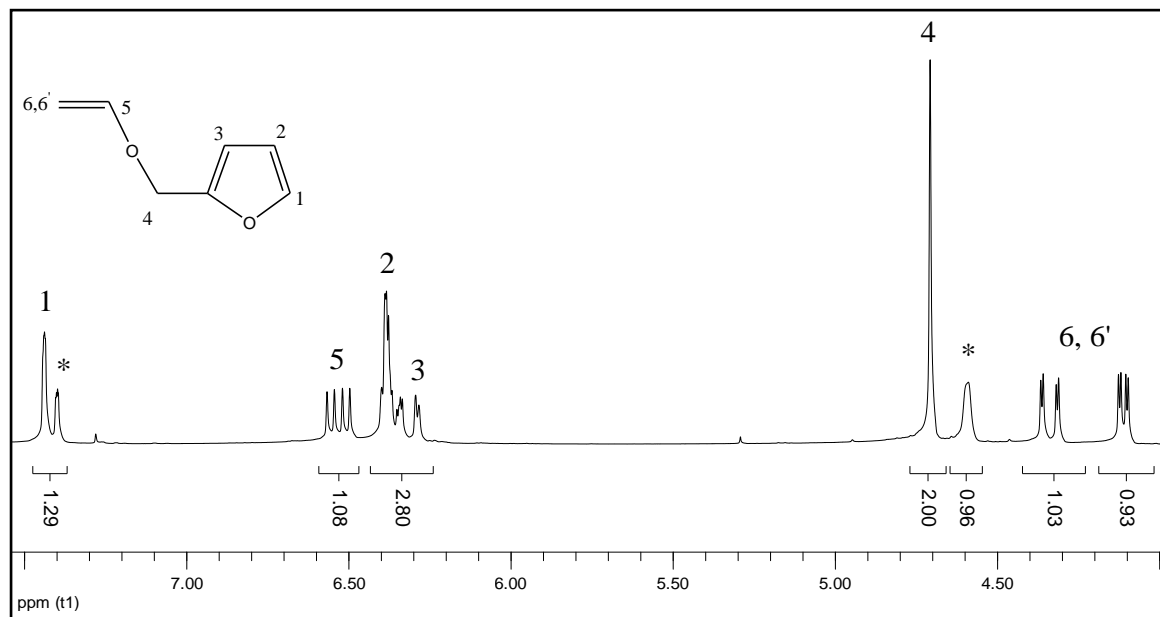


156 **Scheme 3.** *Transesterification* of bis(2-(hydroxyethoxy)ethyl)ether and EVE leading to either mono-functional  
 157 VE (**3**) or bis-functional VE (**3'**)

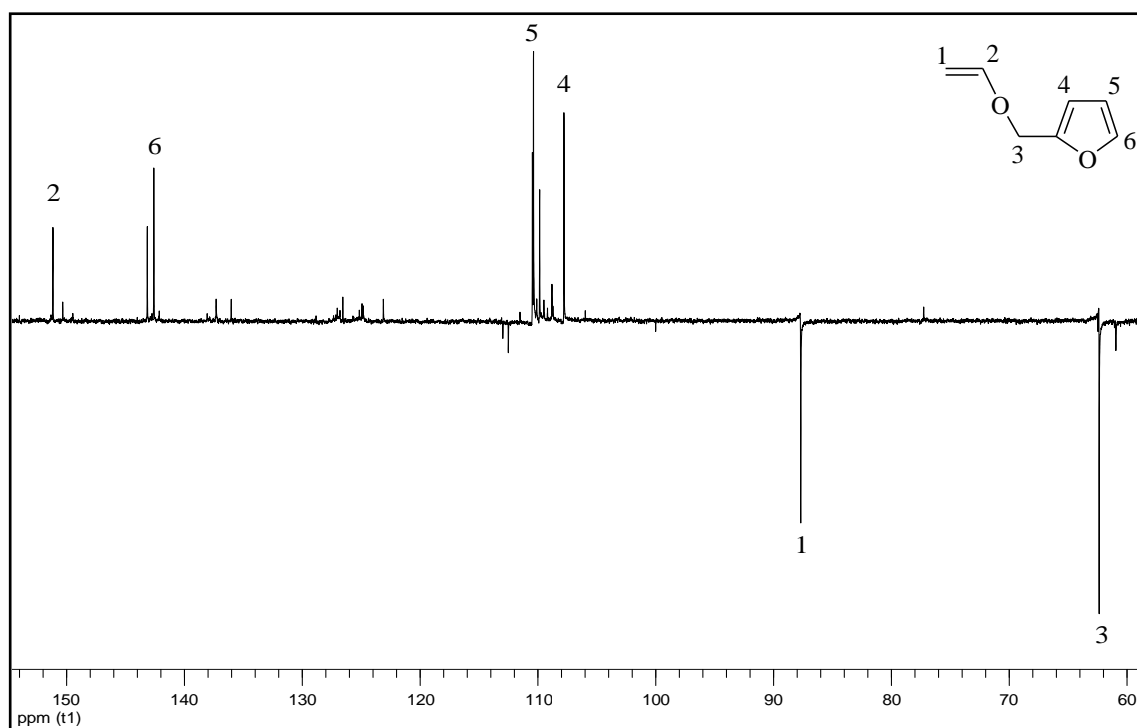
158 All synthesized vinyl ethers (**1-4**) were characterized by <sup>1</sup>H and <sup>13</sup>C NMR  
 159 spectroscopy. In the following section, the <sup>1</sup>H and <sup>13</sup>C NMR spectra of 2-(vinylloxymethyl)  
 160 furan (**1**) are provided as a representative sample. The <sup>1</sup>H NMR spectrum (Figure 1) of vinyl  
 161 ether (**1**) shows both nonequivalent protons (H<sub>2</sub>C=) of the vinyl group as two doublets of  
 162 doublets centered at 4.11 and 4.34 ppm (<sup>3</sup>J<sub>HHgem</sub> = 2.21 Hz, <sup>3</sup>J<sub>HHcis</sub> = 6.78 Hz, <sup>3</sup>J<sub>HHtrans</sub> = 14.26  
 163 Hz). Furthermore, the VE's vinyl proton (=CH-) is located at 6.53 ppm as a doublet of  
 164 doublets. Similar signals with identical multiplicities, integrations, and close chemical shifts  
 165 have been observed for the other synthesized vinyl ethers (**2-4**), confirming the success of the  
 166 *transesterification* process. For vinyl ether (**1**), the methylenic protons of CH<sub>2</sub>-O exhibit very  
 167 close signals at around 4.7 ppm. Another singlet can be observed at 4.6 ppm corresponding to  
 168 the methylenic protons of the alcohol precursor that was not totally removed by purification.

169 The <sup>13</sup>C NMR spectrum of 2-(vinylloxymethyl) furan (**1**) (Figure 2) shows the  
 170 characteristic signals of both carbon atoms of the C=C double bond, at 151.14 ppm and 87.67  
 171 ppm. These signals appear in opposite phases as the former is tertiary while the latter is  
 172 secondary. In the same manner, the methylenic carbon exhibits a negative signal at 62.34  
 173 ppm. Finally, the positive signals of the carbons of the furan ring appear at 107.77, 110.35,

174 and 142.58 ppm, confirming the structure of the product. Similar results have been obtained  
175 for the other vinyl ethers (2-4).



176  
177 **Figure 1.** <sup>1</sup>H NMR spectrum of 2-(vinylloxymethyl) furan (**1**) (CDCl<sub>3</sub>, 20 °C, 300 MHz), \* represents the signal  
178 of the alcohol precursor remaining traces



179  
180 **Figure 2.** <sup>13</sup>C NMR spectrum of 2-(vinylloxymethyl) furan (**1**) (CDCl<sub>3</sub>, 20 °C, 300 MHz)

181

### 182 3. EXPERIMENTAL SECTION

#### 183 3.1. Materials

184 Ethyl vinyl ether, cobalt (II) acetate tetrahydrate, zinc (II) acetate, palladium (II)  
185 acetate, 1,10-phenanthroline, 1,2-phenylethanediol, triphenylphosphine, 2-(hydroxymethyl)  
186 furan, 3,4,5-trimethoxybenzylalcohol, tetraethylene glycol, dianhydro-D-glucitol,  
187 dichloromethane (99.9%), THF (anhydrous, 99.9%), sodium sulfate, were purchased from  
188 Sigma Aldrich. Deuterated chloroform (99.96 atom % D), 1,4-dioxane (anhydrous, 99.8%  
189 purity), DMF (anhydrous, 99.8% purity), and toluene (anhydrous, 99.8%) were purchased  
190 from Euriso-top, JTBaker, Riedel de Haen and Merck, respectively. THF was dried over  
191 sodium/benzophenone and distilled before using it.

#### 192 3.2. Characterization by Nuclear Magnetic Resonance

193 The NMR spectra were recorded at room temperature on a Bruker AC 300 instrument  
194 using either *d*-chloroform or *d*-acetone as solvents and tetramethylsilane as reference.  
195 Coupling constant and chemical shifts ( $\delta$ ) are given in hertz (Hz) and part per million (ppm),  
196 respectively. The experimental conditions for recording  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were as  
197 follows: flip angle  $90^\circ$  (or  $30^\circ$ ), acquisition time 4.5 s (or 0.7 s), pulse delay 2 s (or 2 s), and a  
198 number of scans 128 (or 512).

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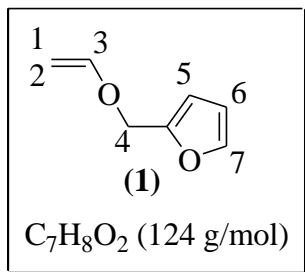
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205 3.3. Synthetic procedures

206 3.3.1. Synthesis of 2-(vinylloxymethyl) furan (**1**)

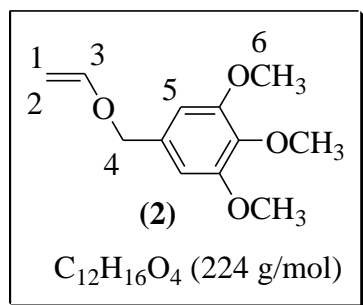


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208 The catalyst solution was initially prepared by dissolving palladium (II) acetate (91.00  
209 mg,  $4.00 \times 10^{-4}$  mol) in 2 mL of dichloromethane. A solution of 1,10-phenanthroline (110.20  
210 mg,  $6.00 \times 10^{-4}$  mol) in dichloromethane (2 mL) was then charged drop-wise. The reaction  
211 medium was stirred at room temperature for 30 minutes to generate the palladium catalyst *in*  
212 *situ*. Then, a solution of 2-(hydroxymethyl) furan (2.00 g, 0.02 mol) and ethyl vinyl ether  
213 (17.30 g, 0.24 mol) in dichloromethane (5 mL) was added to the catalytic solution. The  
214 reaction mixture was stirred at room temperature for 24 hours. The % conversion was tracked  
215 by withdrawing a 0.2 ml sample and drying it under vacuum to eliminate the EVE residue.  
216 The conversion was 69%. The purification of the synthesized EV was conducted by adding 50  
217 mL of distilled water; the solution was extracted with dichloromethane (2 x 50 mL). The  
218 organic phase was then dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvent was evaporated under  
219 vacuum to give the desired product (**1**) in the form of a brown liquid (1.46 g, 59% yield). <sup>1</sup>H  
220 NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 7.40 (d, -CH-O, 1H, H7), 6.53 (dd, -CH=CH<sub>2</sub>, 1H, H3,  
221 <sup>3</sup>J<sub>trans</sub>=14.27 Hz, <sup>3</sup>J<sub>cis</sub>=6.78 Hz), 6.34 (m, -CH=CH-O, 1H, H6), 6.29 (d, -CH=C-O, 1H, H5,  
222 <sup>3</sup>J=2.27 Hz), 4.70 (s, -CH<sub>2</sub>-O-, 2H, H4), 4.34 (dd, CH<sub>a</sub>H<sub>b</sub>=CH (E), 1H, H1, <sup>3</sup>J<sub>cis</sub>=6.78 Hz,  
223 <sup>2</sup>J<sub>gem</sub>=2.23 Hz), 4.11 (dd, CH<sub>a</sub>H<sub>b</sub>=CH (Z), 1H, H2, <sup>3</sup>J<sub>trans</sub>=14.26 Hz, <sup>2</sup>J<sub>gem</sub>=2.21 Hz). <sup>13</sup>C  
224 NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 151.14 (-CH=CH<sub>2</sub>, 1C, C3), 142.58 (-CH-O, 1C, C7),

225 110.35 (-CH=CH-O, 1C, C6), 107.77 (-CH=C-O, 1C, C5), 87.67 (CH<sub>2</sub>=CH, 1C, C1), 62.34 (-  
226 CH<sub>2</sub>-O-, 1C, C4).

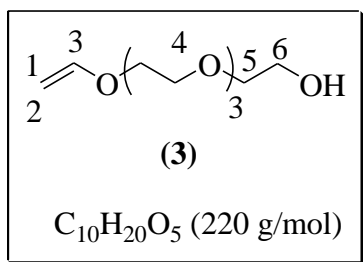
227 3.3.2. Synthesis of 1,2,3-trimethoxy-5-(vinylloxymethyl) benzene (**2**)



228

229 The same procedure for (**1**) was applied to 3,4,5-trimethoxybenzylalcohol (2.00 g, 0.01  
230 mol) and ethyl vinyl ether (8.65 g, 0.12 mol) that were dissolved in 2.5 ml of  
231 dichloromethane. The solution was then added to the catalytic solution that was prepared by  
232 palladium (II) acetate (112.50 mg, 5.00\*10<sup>-4</sup> mol) and 1,10-phenanthroline (135.15 mg,  
233 7.50\*10<sup>-4</sup> mol) in 2 mL of dichloromethane. The <sup>1</sup>H NMR analysis of an aliquot in CDCl<sub>3</sub>  
234 showed 82% conversion. The product was then purified in the same manner as described for  
235 (**1**). 1,2,3-trimethoxy-5-(vinylloxymethyl) benzene (**2**) was obtained as an orange-yellow  
236 liquid (2.67 g, 75% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 6.52 (s, CH of benzene, 2H,  
237 H5), 6.45 (dd, -CH=CH<sub>2</sub>, 1H, H3, <sup>3</sup>J<sub>trans</sub>=14.25 Hz, <sup>3</sup>J<sub>cis</sub>=6.80 Hz), 4.52 (s, CH<sub>2</sub>-O, 2H, H4),  
238 4.25 (dd, CH<sub>a</sub>H<sub>b</sub>=CH, 1H, H1, <sup>3</sup>J<sub>trans</sub>=14.3 Hz, <sup>2</sup>J<sub>gem</sub>=2.16 Hz), 4.00 (dd, CH<sub>a</sub>H<sub>b</sub>=CH, 1H, H2,  
239 <sup>3</sup>J<sub>cis</sub>=6.8 Hz, <sup>2</sup>J<sub>gem</sub>=2.16 Hz), 3.78 (s, CH<sub>3</sub>-O, 9H, H6). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm):  
240 151.50 (-CH=CH<sub>2</sub>, 1C, C3), 104.54 (C of benzene, 2C, C5), 87.72 (CH<sub>2</sub>=CH, 1C, C1), 70.23  
241 (CH<sub>2</sub>-O, 1C, C4), 60.80-56.01 (CH<sub>3</sub>-O, 3C, C6).

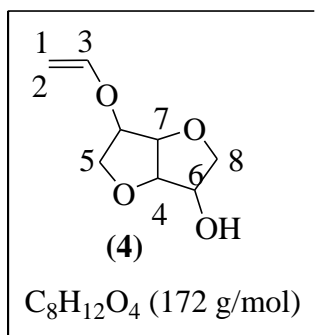
242 3.3.3. Synthesis of 2-(2-(vinylloxy)ethoxy)ethanol (**3**)



243

244 The same procedure for (1) was applied to tetraethylene glycol (2.00 g, 0.01 mol) and  
 245 ethyl vinyl ether (8.65 g, 0.12 mol) that were dissolved in 2.5 ml of dichloromethane. The  
 246 solution was then added to the catalytic solution that was prepared by palladium (II) acetate  
 247 (44.90 mg,  $2.00 \times 10^{-4}$  mol) and 1,10-phenanthroline (54,06 mg,  $3.00 \times 10^{-4}$  mol) in 2 mL of  
 248 **dichloromethane**. The  $^1H$  NMR analysis of an aliquot in  $CDCl_3$  showed 75% conversion. The  
 249 product was then purified in the same manner as described for (1). 2-(2-  
 250 (vinylloxy)ethoxy)ethanol was obtained as a yellow liquid (0.60 g, 50% yield).  $^1H$  NMR (300  
 251 MHz,  $CDCl_3$ )  $\delta$  (ppm): 6.40 (dd,  $-CH=CH_2$ , 1H, H3,  $^3J_{trans}=14.34$  Hz,  $^3J_{cis}=6.79$  Hz), 4.10 (dd,  
 252  $CH_aH_b=CH$ , 1H, H1,  $^3J_{trans}=14.33$  Hz,  $^2J_{gem}=1.66$  Hz), 3.90 (dd,  $CH_aH_b=CH$ , 1H, H2,  
 253  $^3J_{cis}=6.77$  Hz,  $^2J_{gem}=1.06$  Hz), 3.80-3.50 (m,  $CH_2$  on the terminal chain, 16H, H4-6).  $^{13}C$   
 254 NMR (300 MHz,  $CDCl_3$ )  $\delta$  (ppm): 151.63 ( $-CH=CH_2$ , 1C, C3), 86.55 ( $CH_2=CH$ , 1C, C1),  
 255 72.90 (1C, C5), 70.50-67.19 (6C, C4), 61.55 ( $-CH_2-OH$ , 1C, C6).

256 3.3.4. Synthesis of 6-(vinylloxy)-hexahydrofuro[3,2-b]furan-3-ol (4)



257

258 The same procedure for (1) was applied to dianhydro-D-glucitol (0.50 g,  $3.42 \times 10^{-3}$   
 259 mol) and ethyl vinyl ether (2.92 g, 0.041 mol) that were dissolved in 2.5 ml of THF. The

260 solution was then added to the catalytic solution that was prepared by palladium (II) acetate  
261 (0.038 mg,  $1.70 \times 10^{-4}$  mol) and 1,10-phenanthroline (0.045 mg,  $2.55 \times 10^{-4}$  mol) in 2 mL of  
262  $\text{CH}_2\text{Cl}_2$ .  $^1\text{H}$  NMR analysis of an aliquot in acetone- $d_6$  showed 50% conversion. The product  
263 was then purified in the same manner as described for (1). 6-(Vinyloxy)-hexahydrofuro[3,2-  
264 b]furan-3-ol (4) was obtained as an orange-yellow liquid (0.25 g, 42% yield).  $^1\text{H}$  NMR (300  
265 MHz, acetone- $d_6$ )  $\delta$  (ppm): 6.49 (dd,  $-\text{CH}=\text{CH}_2$ , 1H, H3,  $^3J_{\text{trans}}=14.37$  Hz,  $^3J_{\text{cis}}=6.87$  Hz), 4.10  
266 (dd,  $\text{CH}_a\text{H}_b=\text{CH}$ , 1H, H1,  $^3J_{\text{cis}}=6.76$  Hz,  $^2J_{\text{gem}}=2.03$  Hz), 3.90 (dd,  $\text{CH}_a\text{H}_b=\text{CH}$ , 1H, H2), 4.50-  
267 3.50 (cyclic  $\text{CH}_2$  and  $\text{CH}$ , 8H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 151.00 ( $-\text{CH}=\text{CH}_2$ ,  
268 1C, C2), 88.90 (cyclic  $\text{CH}$ , 2C, C4 and C7), 78.00 ( $\text{CH}-\text{O}-\text{CH}=\text{}$ , 1C, C3), 72.00 ( $-\text{CH}-\text{OH}$ ,  
269 1C, C6), 82.50 ( $\text{CH}=\text{CH}_2$ , 1C, C1), 76.50 et 73.10 (cyclic  $\text{CH}_2$ , 2C, C8 and C5).

#### 270 4. CONCLUSION

271 Several functionalized vinyl ethers were successfully synthesized by the  
272 *transesterification* catalyzed by a palladium complex generated in situ with conversions  
273 ranging between 50 and 82 and in 40-75% yields. Different experimental reaction parameters  
274 were optimized with a series of reactions carried out at room temperature for 24 hours using a  
275 high EVE excess. All vinyl ethers were characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. The  
276 newly synthesized VEs could bear various functional groups that can potentially induce  
277 remarkable properties and different polymerization applications.

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288       **References**

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