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1 Synthesis and characterization of novel vinyl ethers that bear

2 various functional groups

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

19 Keywords: vinyl ether; *trans*etherification; catalysis; palladium; NMR.

20 1. Introduction

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

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

In 2013, our group published the *trans*etherification between ethyl vinyl ether and various alcohols leading to the corresponding original vinyl ethers with 40-84% yield in a single step synthesis [18,28-33]. A series of vinyl ether monomers that bear diverse functional groups, such as halogenomethyl, amino, carbonate, oligo(ethylene oxide) side-groups, and oligo(fluoroether) chains, were prepared and characterized by NMR spectroscopy. The palladium complex has been found to accelerate the reaction equilibrium, followed by using
an excess of either vinyl ether or alcohol.

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



67

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



-

80 2. Results and Discussion

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



84

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

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

91 **Table I.** *Trans*etherification of EVE and furfuryl alcohol in different reaction conditions^a

Entry	M(OAc) ₂ (X%)	Ligand (Y eq.)	Solvent	Initial EVE/ alcohol molar ratio	[alcohol] (mol/L)	Conv. ^b (%)
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	69
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	$Pd(OAc)_2(2\%)$	1,10-phenanthroline (1.5)	CH_2Cl_2	12	4.4	65
15	$Pd(OAc)_2(2\%)$	1,10-phenanthroline (1.5)	CH_2Cl_2	12	0.5	37
16	$Pd(OAc)_2(2\%)$	1,10-phenanthroline (1.5)	CH_2Cl_2	12	1	52
17	$Pd(OAc)_2(2\%)$	1,10-phenanthroline (1)	CH_2Cl_2	12	2.2	65
18	$Pd(OAc)_2(2\%)$	1,10-phenanthroline (2)	CH_2Cl_2	12	2.2	63
19	$Pd(OAc)_2(2\%)$	1,10-phenanthroline (3)	CH_2Cl_2	12	2.2	59
20	$Pd(OAc)_2(1\%)$	1,10-phenanthroline (1.5)	CH_2Cl_2	12	2.2	52
21	$Pd(OAc)_2(5\%)$	1,10-phenanthroline (1.5)	CH_2Cl_2	12	2.2	69
22	Pd(OAc) ₂ (10%)	1,10-phenanthroline (1.5)	CH_2Cl_2	12	2.2	66

92 ^a Reaction conditions : Solvent or bulk (entry 11), 24 h, 20 °C, M(OAc)₂ (X %), ligand (X eq /Pd(OAc)₂). ^b% conversion was assessed by 93 ¹H NMR spectroscopy; Conv. (%) = $\frac{\int 4.71 \ CH20(VE)/2}{\int 4.71 \ CH20(VE)/2 + \int 4.61 \ CH20H \ alchool/2} \times 100$, where \int_i represent the integral of the signal centered at 94 i ppm in ¹H NMR spectrum

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

In order to assess the impact of the metal used in the catalyst, the employment of $Zn(OAc)_2$ and $Co(OAc)_2$ complex catalysts did not result in the formation of the desired product (entries 5-6). However, using Pd(OAc)_2 led to the formation of the desired vinyl ether with 69% conversion. These results align with B. Boutevin et al. work. They demonstrated that the 1,10-phenanthroline-palladium (II) acetate complex led to vinyl ethers by *trans*etherification of ethyl vinyl ether in fair % yields [15].

While studying the effect of the solvent nature, moderate conversions were observed with 1,4-dioxane or toluene (entries 9-10). On the other hand, poor conversions were obtained using THF and DMF (entries 7-8). Dichloromethane was observed to be the best solvent for this reaction, with the highest conversion % (entry 4). This variation in the catalytic activity can be related to the solubility of the catalyst, which differs from one solvent to another depending on the solvent polarity. A slight decrease in the catalytic activity (66% conversion)
was observed when the reaction was conducted without solvent (entry 11).

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

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

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

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

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

141 **Table II.** *Trans*etherification of primary alcohols that bear various side groups with ethyl vinyl ether^a

Entry	ROH	VE	Pd(OAc) ₂ (x%)	Conv. ^b (%)	Yield ^c (%)
1	ОН	2-(vinyloxymethyl) furan (1)	2	69	59
2	CH ₂ OH H ₃ CO OCH ₃	1,2,3 trimethoxy-5-(vinyloxymethyl) benzene (2)	2	82	75
3	но (О) ОН	2-(2-(vinyloxy)ethoxy) ethanol (mono- 3) (2-(2-(vinyloxy)ethoxy) ethene (bis- 3')	2 5	75 61	50 40
4 ^d	HO HO	6-(vinyloxy)-hexahydrofuro[3,2-b]furan-3-ol (4)	2	50	42

^{142 &}lt;sup>a</sup> Reaction conditions: 20 °C, 24 h, Pd(OAc)₂ (2%) generated *in situ*, 1,10-phenanthroline (1.5 eq /Pd(OAc)₂). ^bConversion was assessed by 143 ¹H NMR spectroscopy; Conv. (%) = $\frac{\int 4.71 CH2O(VE)/2}{\int 4.71 CH2O(VE)/2 + \int 4.61 CH2OH alchool/2} \times 100$. ^cisolated yield. ^dreaction carried out in THF

²⁻⁽Vinyloxymethyl) furan (1) was prepared under the optimal conditions by *trans*etherification catalyzed by a palladium (II) complex generated *in situ*. 69% conversion and 59% yield were obtained (entry 1). 1,2,3-trimethoxy-5-(vinyloxymethyl) benzene (2) was synthesized under the same conditions with 82% conversion and 75% yield (entry 2). The *trans*etherification of tetraethylene glycol and ethyl vinyl ether (Scheme 3) led to mono-vinyl ether (3) with 75% conversion calculated based on the ¹H NMR analysis of the reaction mixture. Surprisingly, in a random experimental trial, when the amount of the catalyst was

raised to 5%, telechelic bis vinyl-ether (**3**') was formed as a major product, and the % yield dropped from 50 to 40 (entry 3). Finally, the *trans*etherification of dianhydro-D-glucitol was exceptionally performed in THF/CH₂Cl₂ due to its low solubility in dichloromethane. The desired vinyl ether (**4**) was obtained with 50 % conversion and 42 % yield (entry 4).





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

All synthesized vinyl ethers (1-4) were characterized by ¹H and ¹³C NMR 158 spectroscopy. In the following section, the ¹H and ¹³C NMR spectra of 2-(vinyloxymethyl) 159 furan (1) are provided as a representative sample. The ¹H NMR spectrum (Figure 1) of vinyl 160 161 ether (1) shows both nonequivalent protons ($H_2C=$) of the vinyl group as two doublets of doublets centered at 4.11 and 4.34 ppm (${}^{3}J_{HHgem} = 2.21$ Hz, ${}^{3}J_{HHcis} = 6.78$ Hz, ${}^{3}J_{HHtrans} = 14.26$ 162 Hz). Furthermore, the VE's vinyl proton (=CH-) is located at 6.53 ppm as a doublet of 163 doublets. Similar signals with identical multiplicities, integrations, and close chemical shifts 164 have been observed for the other synthesized vinyl ethers (2-4), confirming the success of the 165 *trans*etherification process. For vinyl ether (1), the methylenic protons of CH_2 -O exhibit very 166 close signals at around 4.7 ppm. Another singlet can be observed at 4.6 ppm corresponding to 167 the methylenic protons of the alcohol precursor that was not totally removed by purification. 168

The ¹³C NMR spectrum of 2-(vinyloxymethyl) furan (1) (Figure 2) shows the characteristic signals of both carbon atoms of the C=C double bond, at 151.14 ppm and 87.67 ppm. These signals appear in opposite phases as the former is tertiary while the latter is secondary. In the same manner, the methylenic carbon exhibits a negative signal at 62.34 ppm. Finally, the positive signals of the carbons of the furan ring appear at 107.77, 110.35, and 142.58 ppm, confirming the structure of the product. Similar results have been obtainedfor the other vinyl ethers (2-4).



177 Figure 1. ¹H NMR spectrum of 2-(vinyloxymethyl) furan (1) (CDCl₃, 20 °C, 300 MHz), * represents the signal

178 of the alcohol precursor remaining traces



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176

180 Figure 2. ¹³C NMR spectrum of 2-(vinyloxymethyl) furan (1) (CDCl₃, 20 °C, 300 MHz)

182 **3. EXPERIMENTAL SECTION**

183 3.1. Materials

Ethyl vinyl ether, cobalt (II) acetate tetrahydrate, zinc (II) acetate, palladium (II) 184 185 acetate, 1,10-phenanthroline, 1,2-phenylethanediol, triphenylphosphine, 2-(hydroxymethyl) furan, 3,4,5-trimethoxybenzylalcohol, tetraethylene glycol, dianhydro-D-glucitol, 186 dichloromethane (99.9%), THF (anhydrous, 99.9%), sodium sulfate, were purchased from 187 Sigma Aldrich. Deuterated chloroform (99.96 atom % D), 1.4-dioxane (anhydrous, 99.8% 188 purity), DMF (anhydrous, 99.8% purity), and toluene (anhydrous, 99.8%) were purchased 189 from Euriso-top, JTBaker, Riedel de Haen and Merck, respectively. THF was dried over 190 sodium/benzophenone and distilled before using it. 191

192 3.2. Characterization by Nuclear Magnetic Resonance

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

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205 3.3. Synthetic procedures

206 3.3.1. Synthesis of 2-(vinyloxymethyl) furan (1)



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The catalyst solution was initially prepared by dissolving palladium (II) acetate (91.00 208 mg, 4.00*10⁻⁴ mol) in 2 mL of dichloromethane. A solution of 1,10-phenanthroline (110.20 209 mg, $6.00*10^{-4}$ mol) in dichloromethane (2 mL) was then charged drop-wise. The reaction 210 211 medium was stirred at room temperature for 30 minutes to generate the palladium catalyst in situ. Then, a solution of 2-(hydroxymethyl) furan (2.00 g, 0.02 mol) and ethyl vinyl ether 212 (17.30 g, 0.24 mol) in dichloromethane (5 mL) was added to the catalytic solution. The 213 214 reaction mixture was stirred at room temperature for 24 hours. The % conversion was tracked by withdrawing a 0.2 ml sample and drying it under vacuum to eliminate the EVE residue. 215 The conversion was 69%. The purification of the synthesized EV was conducted by adding 50 216 217 mL of distilled water; the solution was extracted with dichloromethane (2 x 50 mL). The organic phase was then dried over Na₂SO₄, filtered, and the solvent was evaporated under 218 vacuum to give the desired product (1) in the form of a brown liquid (1.46 g, 59% yield). 1 H 219 NMR (300 MHz, CDCl₃) δ (ppm): 7.40 (d, -CH-O, 1H, H7), 6.53 (dd, -CH=CH₂, 1H, H3, 220 ${}^{3}J_{\text{trans}}$ =14.27 Hz, ${}^{3}j_{\text{cis}}$ =6.78 Hz), 6.34 (m, -CH=CH-O, 1H, H6), 6.29 (d, -CH=C-O, 1H, H5, 221 ³J=2.27 Hz), 4.70 (s, -CH₂-O-, 2H, H4), 4,34 (dd, CH_aH_b=CH (E), 1H, H1, ³J_{cis}=6.78 Hz, 222 ${}^{2}J_{\text{gem}}$ =2.23 Hz), 4.11 (dd, CH_aH_b=CH (Z), 1H, H2, ${}^{3}J_{\text{trans}}$ =14.26 Hz, ${}^{2}J_{\text{gem}}$ =2.21 Hz). ¹³C 223 NMR (300 MHz, CDCl₃) δ (ppm): 151.14 (-CH=CH₂, 1C, C3), 142.58 (-CH-O, 1C, C7), 224

225 110.35 (-CH=CH-O, 1C, C6), 107.77 (-CH=C-O, 1C, C5), 87.67 (CH₂=CH, 1C, C1), 62.34 (226 CH₂-O-, 1C, C4).

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



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The same procedure for (1) was applied to 3,4,5-trimethoxybenzylalcohol (2.00 g, 0.01 229 mol) and ethyl vinyl ether (8.65 g, 0.12 mol) that were dissolved in 2.5 ml of 230 dichloromethane. The solution was then added to the catalytic solution that was prepared by 231 palladium (II) acetate (112.50 mg, 5.00*10⁻⁴ mol) and 1,10-phenanthroline (135.15 mg, 232 7.50*10⁻⁴ mol) in 2 mL of dichloromethane. The ¹H NMR analysis of an aliquot in CDCl₃ 233 showed 82% conversion. The product was then purified in the same manner as described for 234 (1). 1,2,3-trimethoxy-5-(vinyloxymethyl) benzene (2) was obtained as an orange-yellow 235 liquid (2.67 g, 75% yield). ¹**H NMR** (300 MHz, CDCl₃) δ (ppm): 6.52 (s, C**H** of benzene, 2H, 236 H5), 6.45 (dd, -CH=CH₂, 1H, H3, ³J_{trans}=14.25 Hz, ³J_{cis}=6.80 Hz), 4,52 (s, CH₂-O, 2H, H4), 237 4.25 (dd, CH_aH_b=CH, 1H, H1, ${}^{3}J_{trans}$ =14.3 Hz, ${}^{2}J_{gem}$ =2.16 Hz), 4.00 (dd, CH_aH_b=CH, 1H, H2, 238 ³J_{cis}=6.8 Hz, ²J_{gem}=2.16 Hz), 3.78 (s, CH₃-O, 9H, H6). ¹³C NMR (300 MHz, CDCl₃) δ (ppm): 239 151.50 (-CH=CH₂, 1C, C3), 104.54 (C of benzene, 2C, C5), 87.72 (CH₂=CH, 1C, C1), 70.23 240 (CH₂-O, 1C, C4), 60.80-56.01 (CH₃-O, 3C, C6). 241

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

$$\begin{bmatrix} 1 & 3 & 4 & 0 & 5 & 6 \\ 2 & 0 & 3 & 0 \\ (3) & \\ C_{10}H_{20}O_5 & (220 \text{ g/mol}) \end{bmatrix}$$

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The same procedure for (1) was applied to tetraethylene glycol (2.00 g, 0.01 mol) and 244 ethyl vinyl ether (8.65 g, 0.12 mol) that were dissolved in 2.5 ml of dichloromethane. The 245 solution was then added to the catalytic solution that was prepared by palladium (II) acetate 246 (44.90 mg, 2.00*10⁻⁴ mol) and 1.10-phenanthroline (54.06 mg, 3.00*10⁻⁴ mol) in 2 mL of 247 dichloromethane. The ¹H NMR analysis of an aliquot in CDCl₃ showed 75% conversion. The 248 product was then purified in the same manner as described for (1). 2-(2-249 (vinyloxy)ethoxy)ethanol was obtained as a yellow liquid (0.60 g, 50% yield). ¹H NMR (300 250 MHz, CDCl₃) δ (ppm): 6.40 (dd, -C**H**=CH₂, 1H, H**3**, ³J_{trans}=14.34 Hz, ³J_{cis}=6.79 Hz), 4.10 (dd, 251 $CH_aH_b=CH$, 1H, H1, ${}^{3}J_{trans}=14.33$ Hz, ${}^{2}J_{gem}=1.66$ Hz), 3.90 (dd, $CH_aH_b=CH$, 1H, H2, 252 ${}^{3}J_{cis}$ =6.77 Hz, ${}^{2}J_{gem}$ =1.06 Hz), 3.80-3.50 (m, CH₂ on the terminal chain, 16H, H4-6). ${}^{13}C$ 253 NMR (300 MHz, CDCl₃) δ (ppm): 151.63 (-CH=CH₂, 1C, C3), 86.55 (CH₂=CH, 1C, C1), 254 72.90 (1C, C5), 70.50-67.19 (6C, C4), 61.55 (-CH₂-OH, 1C, C6). 255

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



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

solution was then added to the catalytic solution that was prepared by palladium (II) acetate 260 $(0.038 \text{ mg}, 1.70*10^{-4} \text{ mol})$ and 1,10-phenanthroline $(0.045 \text{ mg}, 2.55*10^{-4} \text{ mol})$ in 2 mL of 261 CH₂Cl₂. ¹H NMR analysis of an aliquot in acetone-d6 showed 50% conversion. The product 262 was then purified in the same manner as described for (1). 6-(Vinyloxy)-hexahydrofuro[3,2-263 b]furan-3-ol (4) was obtained as an orange-yellow liquid (0.25 g, 42% yield). ¹H NMR (300 264 MHz, acetone-d6) δ (ppm): 6.49 (dd, -CH=CH₂, 1H, H3, ³J_{trans}=14.37 Hz, ³J_{cis}=6.87 Hz), 4.10 265 (dd, CH_aH_b=CH, 1H, H1, ${}^{3}J_{cis}$ =6.76 Hz, ${}^{2}J_{gem}$ =2.03 Hz), 3.90 (dd, CH_aH_b=CH, 1H, H2), 4.50-266 3.50 (cyclic CH₂ and CH, 8H). ¹³C NMR (300 MHz, CDCl₃) δ (ppm): 151.00 (-CH=CH₂, 267 1C, C2), 88.90 (cyclic CH, 2C, C4 and C7), 78.00 (CH-O-CH=, 1C, C3), 72.00 (-CH-OH, 268 1C, C6), 82.50 (CH=CH₂, 1C, C1), 76.50 et 73.10 (cyclic CH₂, 2C, C8 and C5). 269

270 4. CONCLUSION

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

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