HAL
open science

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

Antoinette Fayad, Wassim El Malti, Bruno Ameduri, Ali Alaaeddine

To cite this version:

Antoinette Fayad, Wassim El Malti, Bruno Ameduri, Ali Alaaeddine. Synthesis and characterization of novel vinyl ethers that bear various functional groups. Comptes Rendus. Chimie, 2022, 25 (G1), pp.9-18. 10.5802/crchim.138 . hal-03562594

HAL Id: hal-03562594

https://hal.science/hal-03562594v1

Submitted on 9 Feb 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

Antoinette Fayad[a], Wassim El Malti[b], Bruno Ameduri[c], Ali Alaaeddine*[, a]

[a]*Laboratoire de Chimie Médicinale et des Produits Naturels & PRASE, EDST Lebanese University, Département de Chimie et de Biochimie, Faculté de Sciences 1, Campus de Hadath, Beyrouth, Liban. Correspondence to: A. Alaaeddine (E-mail:alikassem.alaaeddine@ul.edu.lb)*

[b]*College of Engineering and Technology, American University of the Middle East, Kuwait. Correspondence to: W. El Malti (E-mail:Wassim.elmalti@aum.edu.kw)*

[c]*Institut Charles Gerhardt, Ingénierie et Architectures Macromoléculaires, UMR CNRS 5253, Ecole Nationale Supérieure de Chimie de Montpellier, 8 Rue de l'Ecole Normale, 34296 Montpellier, France. Correspondence to: B. Ameduri (E-mail:bruno.ameduri@enscm.fr)*

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 ^{1}H and ^{13}C NMR spectroscopy.

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

1. Introduction

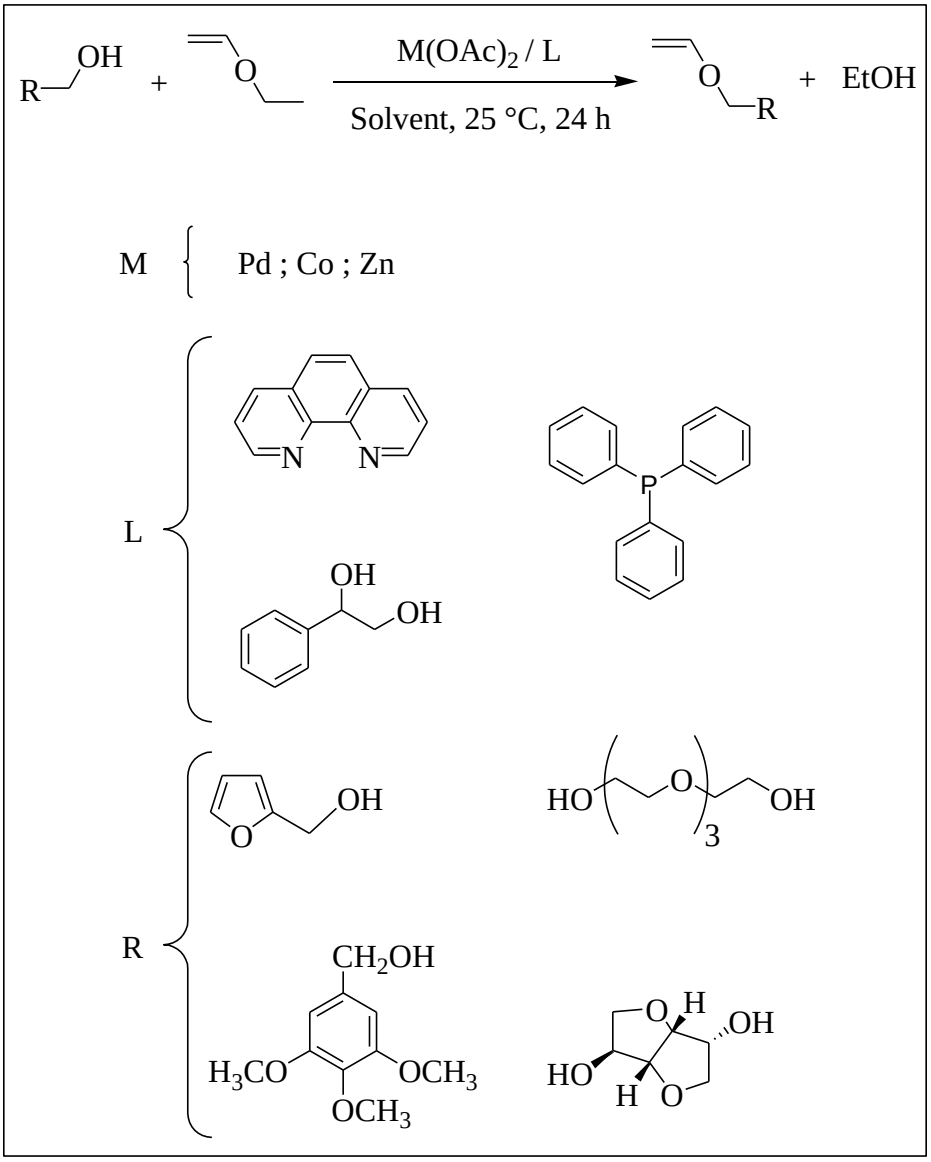
Enol ethers or vinyl ethers (VEs) are a class of chemical compounds that display ether and vinyl functional groups. These compounds have found numerous applications as key reagents in organic reactions such as the Diels-Alder reaction [1] and Claisen rearrangement [2], thanks to the remarkable reactivity of their electron-rich carbon-carbon double bond and the range of substituents that can bear [3,4]. They have been extensively polymerized under cationic initiation to produce polymeric materials endowed with excellent properties used in various industrial applications such as adhesives, paints, coating, and the synthesis of stimuli-sensitive materials [5-12]. Despite their simple structure, no universal method has been found to carry out their synthesis. Nevertheless, many methods have been developed to prepare vinyl ethers, particularly catalyzed *trans*etherification using transition metals. Winternheimer et al. 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 pressure and temperature conditions and using a large amount of basic catalyst [13,14]. Then, four additional synthetic pathways have been developed for the chemical conversion of alcohols to vinyl ether: i) addition onto acetylene [13,14], ii) phase transfer catalysis based on Williamson reaction between an alkoxide and 2-chloroethyl vinyl ether [15], iii) modification of vinyl acetate in the presence of an iridium complex [16,17], and iv) *trans*etherification [18]. The latter strategy has been widely studied in the presence of either mercuric acetate [19,20] or palladium acetate [21-24] catalysts producing various vinyl ethers in fair to good yields. Complexes of palladium acetate and trifluoroacetate with bidentate ligands, such as 1,10-phenanthroline, have proven to efficiently catalyze most of the vinyl ethers preparations, and its catalysis mechanism was proposed by Handerson and Schlaf [23]. They successfully used (L–L) $Pd(OAc)_2$ catalyst, where L–L stands for 2,2'-bipyridyl or 1,10-phenanthroline chelate, 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 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, Pichavant et al. described the synthesis of a vinyl ether by *trans*etherification catalyzed by a palladium(II) complex in the presence of ethyl vinyl ether in dichloromethane [27]. The iridium-catalyzed reaction of vinyl acetate with alcohols later appeared as a complementary method to palladium-catalyzed *trans*etherification [16,17].

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.

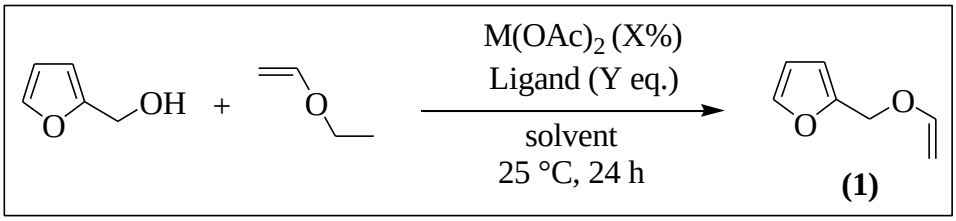
In this work, a detailed study on the *trans*etherification reaction of ethyl vinyl ethers was carried out. The aim was to prepare new vinyl ethers with various side chain functional groups (Scheme 1) and can be widely used in the synthesis of polymeric materials and other applications. These vinyl ethers were synthesized from the corresponding alcohols through *trans*etherification of ethyl vinyl ether catalyzed by an organometallic complex generated *in 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 of the organometallic complex, and choice of the metal precursor.



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

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).



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

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

[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 ^{1}H NMR spectroscopy; Conv. (%) = $\frac{\int 4.71\ CH2O(VE)/2}{\int 4.71\ CH2O(VE)/2 + \int 4.61\ CH2OH\ alchool/2}$ x 100, where $\int_i$ represent the integral of the signal centered at i ppm in ^{1}H 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.

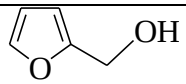
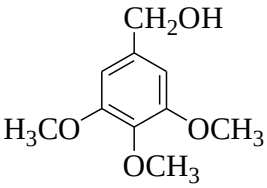
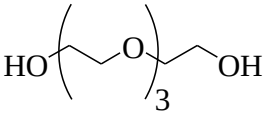
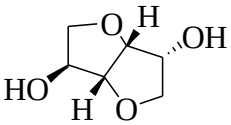
The effect of the initial alcohol concentration was examined as well. 69% conversion was obtained with a concentration of 2.2 mol/L (entry 4). A similar % conversion was obtained when the alcohol concentration was raised to 4.4 mol/L (entry 14), showing that the maximum possible % conversion was already 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 1,10-phenanthroline 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.

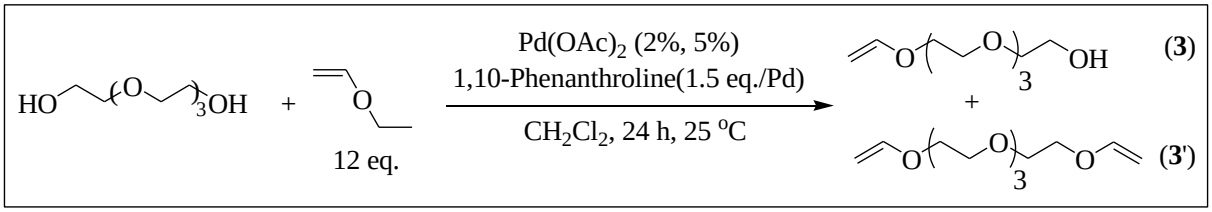
Table II. *Trans*etherification of primary alcohols that bear various side groups with ethyl vinyl ether[a]

Entry	ROH	VE	$Pd(OAc)_2$ (x%)	Conv.[b] (%)	Yield[c] (%)
1		*2-(vinyloxymethyl) furan* **(1)**	2	69	59
2		*1,2,3 trimethoxy-5-(vinyloxymethyl) benzene* **(2)**	2	82	75
3		*2-(2-(vinyloxy)ethoxy) ethanol* (mono-**3**)	2	75	50
		(2-(2-(vinyloxy)ethoxy)ethoxy) ethene (bis-**3'**)	5	61	40
4[d]		*6-(vinyloxy)-hexahydrofuro[3,2-b]furan-3-ol* **(4)**	2	50	42

[a] **Reaction conditions:** 20 °C, 24 h, $Pd(OAc)_2$ (2%) generated *in situ*, 1,10-phenanthroline (1.5 eq /$Pd(OAc)_2$). [b]Conversion was assessed by ^{1}H NMR spectroscopy; Conv. (%) = $\frac{\int 4.71\ CH2O(VE)/2}{\int 4.71\ CH2O(VE)/2 + \int 4.61\ CH2OH\ alchool/2}$ x 100. [c]isolated yield. [d]reaction 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 ^{1}H 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/CH_2Cl_2 due to its low solubility in dichloromethane. The desired vinyl ether (**4**) was obtained with 50 % conversion and 42 % yield (entry 4).



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

All synthesized vinyl ethers (**1-4**) were characterized by ^{1}H and ^{13}C NMR spectroscopy. In the following section, the ^{1}H and ^{13}C NMR spectra of 2-(vinyloxymethyl) furan (**1**) are provided as a representative sample. The ^{1}H NMR spectrum (Figure 1) of vinyl 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 Hz). Furthermore, the VE's vinyl proton (=CH-) is located at 6.53 ppm as a doublet of doublets. Similar signals with identical multiplicities, integrations, and close chemical shifts have been observed for the other synthesized vinyl ethers (**2-4**), confirming the success of the *trans*etherification process. For vinyl ether (**1**), the methylenic protons of CH_2-O exhibit very close signals at around 4.7 ppm. Another singlet can be observed at 4.6 ppm corresponding to the methylenic protons of the alcohol precursor that was not totally removed by purification.

The ^{13}C 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 obtained for the other vinyl ethers (**2-4**).

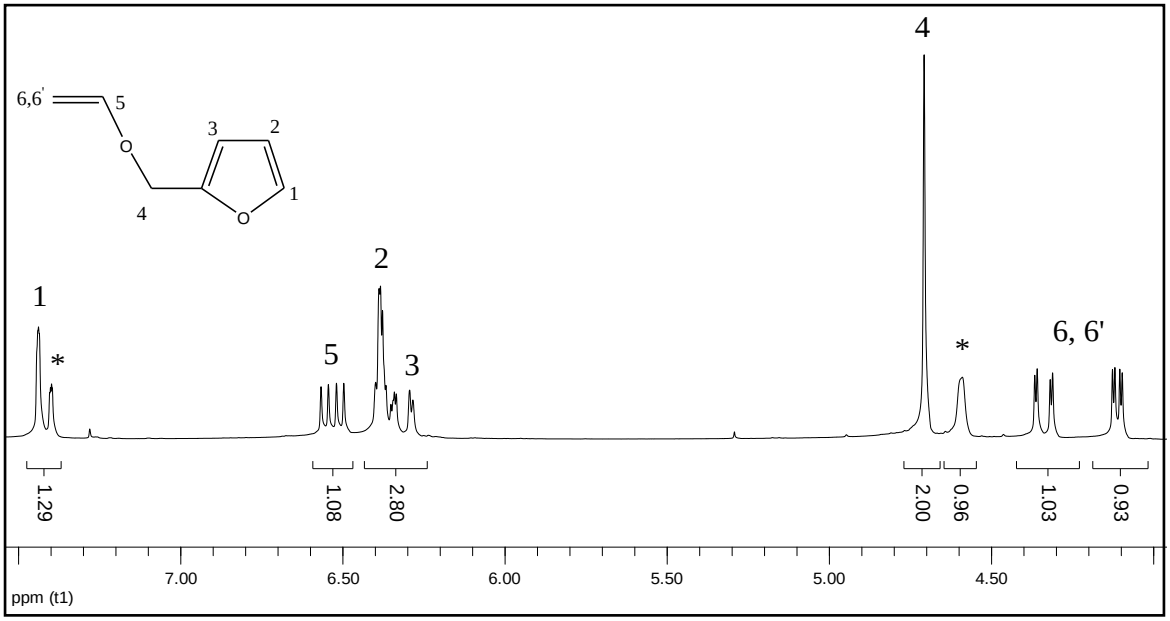


Figure 1. ^{1}H NMR spectrum of 2-(vinyloxymethyl) furan **(1)** ($CDCl_3$, 20 °C, 300 MHz), * represents the signal of the alcohol precursor remaining traces

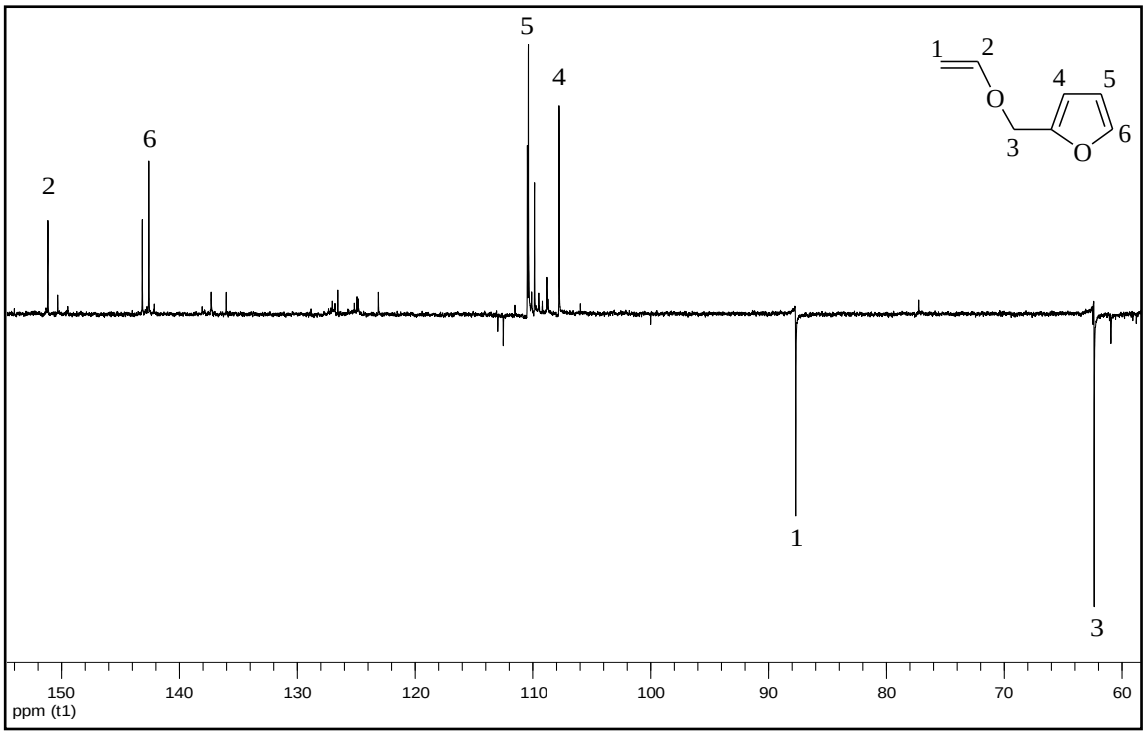


Figure 2. ^{13}C NMR spectrum of 2-(vinyloxymethyl) furan **(1)** ($CDCl_3$, 20 °C, 300 MHz)

3. EXPERIMENTAL SECTION

3.1. Materials

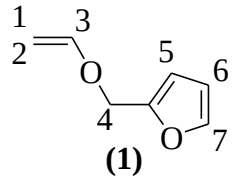
Ethyl vinyl ether, cobalt (II) acetate tetrahydrate, zinc (II) acetate, palladium (II) acetate, 1,10-phenanthroline, 1,2-phenylethanediol, triphenylphosphine, 2-(hydroxymethyl) furan, 3,4,5-trimethoxybenzylalcohol, tetraethylene glycol, dianhydro-D-glucitol, dichloromethane (99.9%), THF (anhydrous, 99.9%),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

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 ^{1}H and ^{13}C 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).

3.3. Synthetic procedures

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



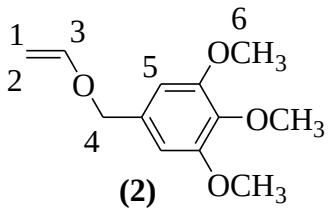
(1)

$C_7H_8O_2$ (124 g/mol)

The catalyst solution was initially prepared by dissolving palladium (II) acetate (91.00 mg, $4.00*10^{-4}$ mol) in 2 mL of dichloromethane. A solution of 1,10-phenanthroline (110.20 mg, $6.00*10^{-4}$ mol) in dichloromethane (2 mL) was then charged drop-wise. The reaction 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 (17.30 g, 0.24 mol) in dichloromethane (5 mL) was added to the catalytic solution. The 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. The conversion was 69%. The purification of the synthesized EV was conducted by adding 50 mL of distilled water; the solution was extracted with dichloromethane (2 x 50 mL). The organic phase was then dried over Na_2SO_4, filtered, and the solvent was evaporated under vacuum to give the desired product **(1)** in the form of a brown liquid (1.46 g, 59% yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm): 7.40 (d, -C**H**-O, 1H, H**7**), 6.53 (dd, -C**H**=CH_2, 1H, H**3**, $^3J_{trans}$=14.27 Hz, $^3j_{cis}$=6.78 Hz), 6.34 (m, -C**H**=CH-O, 1H, H**6**), 6.29 (d, -C**H**=C-O, 1H, H**5**, ^3J=2.27 Hz), 4.70 (s, -C$\mathbf{H_2}$-O-, 2H, H**4**), 4,34 (dd, C$\mathbf{H_a}$$H_b$=CH (E), 1H, H**1**, $^3J_{cis}$=6.78 Hz, $^2J_{gem}$=2.23 Hz), 4.11 (dd, $CH_a$$\mathbf{H_b}$=CH (Z), 1H, H**2**, $^3J_{trans}$=14.26 Hz, $^2J_{gem}$=2.21 Hz). **^{13}C NMR** (300 MHz, $CDCl_3$) δ (ppm): 151.14 (-**C**H=CH_2, 1C, C**3**), 142.58 (-**C**H-O, 1C, C**7**),

110.35 (-**C**H=CH-O, 1C, C**6**), 107.77 (-**C**H=C-O, 1C, C**5**), 87.67 (**C**H_2=CH, 1C, C**1**), 62.34 (-**C**H_2-O-, 1C, C**4**).

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

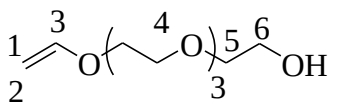


(2)

$C_{12}H_{16}O_4$ (224 g/mol)

The same procedure for **(1)** was applied to 3,4,5-trimethoxybenzylalcohol (2.00 g, 0.01 mol) and ethyl vinyl ether (8.65 g, 0.12 mol) that were dissolved in 2.5 ml of dichloromethane. The solution was then added to the catalytic solution that was prepared by palladium (II) acetate (112.50 mg, $5.00*10^{-4}$ mol) and 1,10-phenanthroline (135.15 mg, $7.50*10^{-4}$ mol) in 2 mL of dichloromethane. The ^{1}H NMR analysis of an aliquot in $CDCl_3$ showed 82% conversion. The product was then purified in the same manner as described for **(1)**. 1,2,3-trimethoxy-5-(vinyloxymethyl) benzene (**2**) was obtained as an orange-yellow liquid (2.67 g, 75% yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm): 6.52 (s, C**H** of benzene, 2H, H**5**), 6.45 (dd, -C**H**=CH_2, 1H, H**3**, $^3J_{trans}$=14.25 Hz, $^3J_{cis}$=6.80 Hz), 4,52 (s, C$\mathbf{H_2}$-O, 2H, H**4**), 4.25 (dd, C$\mathbf{H_a}$$H_b$=CH, 1H, H**1**, $^3J_{trans}$=14.3 Hz, $^2J_{gem}$=2.16 Hz), 4.00 (dd, $CH_a$$\mathbf{H_b}$=CH, 1H, H**2**, $^3J_{cis}$=6.8 Hz, $^2J_{gem}$=2.16 Hz), 3.78 (s, C$\mathbf{H_3}$-O, 9H, H**6**). **^{13}C NMR** (300 MHz, $CDCl_3$) δ (ppm): 151.50 (-C**H**=CH_2, 1C, C**3**), 104.54 (C of benzene, 2C, C**5**), 87.72 (**C**H_2=CH, 1C, C**1**), 70.23 (**C**H_2-O, 1C, C**4**), 60.80-56.01 (**C**H_3-O, 3C, C**6**).

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

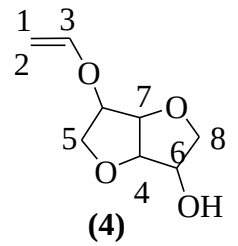


(3)

$C_{10}H_{20}O_5$ (220 g/mol)

The same procedure for **(1)** was applied to tetraethylene glycol (2.00 g, 0.01 mol) and ethyl vinyl ether (8.65 g, 0.12 mol) that were dissolved in 2.5 ml of dichloromethane. The solution was then added to the catalytic solution that was prepared by palladium (II) acetate (44.90 mg, $2.00*10^{-4}$ mol) and 1,10-phenanthroline (54,06 mg, $3.00*10^{-4}$ mol) in 2 mL of dichloromethane. The ^{1}H NMR analysis of an aliquot in $CDCl_3$ showed 75% conversion. The product was then purified in the same manner as described for **(1)**. 2-(2-(vinyloxy)ethoxy)ethanol was obtained as a yellow liquid (0.60 g, 50% yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ (ppm): 6.40 (dd, -C**H**=CH_2, 1H, H**3**, $^{3}J_{trans}$=14.34 Hz, $^{3}J_{cis}$=6.79 Hz), 4.10 (dd, C**H$_a$**H$_b$=CH, 1H, H**1**, $^{3}J_{trans}$=14.33 Hz, $^{2}J_{gem}$=1.66 Hz), 3.90 (dd, CH$_a$**H$_b$**=CH, 1H, H**2**, $^{3}J_{cis}$=6.77 Hz, $^{2}J_{gem}$=1.06 Hz), 3.80-3.50 (m, C**H**$_2$ on the terminal chain, 16H, H**4-6**). **^{13}C NMR** (300 MHz, $CDCl_3$) δ (ppm): 151.63 (-**C**H=CH_2, 1C, C**3**), 86.55 (**C**H$_2$=CH, 1C, C**1**), 72.90 (1C, C**5**), 70.50-67.19 (6C, C**4**), 61.55 (-**C**H$_2$-OH, 1C, C**6**).

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



(4)

$C_8H_{12}O_4$ (172 g/mol)

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 (0.038 mg, $1.70*10^{-4}$ mol) and 1,10-phenanthroline (0.045 mg, $2.55*10^{-4}$ mol) in 2 mL of CH_2Cl_2. ^{1}H NMR analysis of an aliquot in acetone-d6 showed 50% conversion. The product was then purified in the same manner as described for **(1)**. 6-(Vinyloxy)-hexahydrofuro[3,2-b]furan-3-ol (**4**) was obtained as an orange-yellow liquid (0.25 g, 42% yield). **^{1}H NMR** (300 MHz, acetone-d6) δ (ppm): 6.49 (dd, -C**H**=CH_2, 1H, H**3**, $^3J_{trans}$=14.37 Hz, $^3J_{cis}$=6.87 Hz), 4.10 (dd, C$\mathbf{H_a}$$H_b$=CH, 1H, H**1**, $^3J_{cis}$=6.76 Hz, $^2J_{gem}$=2.03 Hz), 3.90 (dd, $CH_a$$\mathbf{H_b}$=CH, 1H, H**2**), 4.50-3.50 (cyclic C$\mathbf{H_2}$ and C**H**, 8H). **^{13}C NMR** (300 MHz, $CDCl_3$) δ (ppm): 151.00 (-**C**H=CH_2, 1C, C**2**), 88.90 (cyclic **C**H, 2C, C**4** and C**7**), 78.00 (**C**H-O-CH=, 1C, C**3**), 72.00 (-**C**H-OH, 1C, C**6**), 82.50 (CH=**C**H_2, 1C, C**1**), 76.50 et 73.10 (cyclic **C**H_2, 2C, C**8** and C**5**).

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 ^{1}H and ^{13}C NMR spectroscopy. The newly synthesized VEs could bear various functional groups that can potentially induce remarkable properties and different polymerization applications.

ACKNOWLEDGEMENTS

The authors thank Ecole Nat. Sup. de Chimie de Montpellier (ENSCM) and Ecole doctorale à l'université Libanaise (EDST) as well as the Université Libanaise-programme de recherche for the financial support. Pr. Bernard Boutevin (ENSCM), and Dr. Ali Hachem and Dr. Iyad Karameh (Université Libanaise) are also acknowledged for their inputs.

References

1. Nicolaou, K. C.; Snyder, S. A.; Montagnon, T.; Vassilikogiannakis, G. Angew. Chem., Int. Ed. 2002, 41, 1668-1698.
2. Winternheimer, D. J.; Shade, R. E.; Merlic, C. A. Synthesis 2010, 15, 2497-2511.
3. Ziegler, F. E. Chem. Rev. 1988, 88, 1423-1452.
4. Rhoads, S. J.; Raulins, N. R. Org. React. 1975, 22, 1-252.
5. Fujimori, K. J. Macromol. Sci., Chem. 1975, A9, 495-504.
6. Kojima, K.; Sawamoto, M.; Higashimura, T. Macromolecules 1989, 22, 1552-1557.
7. Kohli, P.; Scranton, A. B.; Blanchard, G. J. Macromolecules 1998, 31, 5681-5689.
8. Kanazawa, A.; Kanaoka, S.; Aoshima, S. Chem. Lett. 2010, 39, 1232-1237.
9. Wang, J. F.; Tian, J.; Ye, P. Des. Monomers Polym. 2010, 13, 1-11.
10. Reyntjens, W. G. S.; Goethals, E. J. Polym. Adv. Technol. 2001, 12, 107-122.
11. Mueller, H. W. J. In Coatings Technology Handbook (3rd Edition); Tracton, A. A., Ed.; CRC Press LLC, 2006, pp 47/41-47/43.
12. Couture, G., Campagne, B., Alaaeddine, A., Ameduri, B.,. Polym Chem 2013, 4, 1960–1968.
13. Reppe, W.; Wolff, W. 1935/ 2012 assigned to I. G. Farbenindustrie AG .
14. Reppe, W. Justus Liebigs Ann. Chem. 1956, 601, 84-111.
15. Boutevin, B.; Youssef, B.; Boileau, S.; Garnault, A. M. J. Fluorine. Chem. 1987, 35, 399-410.
16. Okimoto, Y.; Sakaguchi, S.; Ishii, Y. J Am Chem Soc 2002, 124, 1590-1591.
17. Hirabayashi, T.; Sakaguchi, S.; Ishii, Y. Org. Synth. 2005, 82, 55.
18. Alaaeddine, A., Couture, G., Ameduri, B. Polym Chem 2013, 4, 4335–4347.
19. Boutevin, B.; Youssef, B. J. Fluorine Chem. 1989, 44, 395-412.
20. Boutevin, B.; Malek, F. Eur Polym J 1995, 31, 1279-1285.
21. Andersson, C. M.; Hallberg, A. J. Org. Chem. 1988, 53, 235-239.
22. Weintraub, P. M.; King, C.-H. R. J Org Chem 1997, 62, 1560-1562.
23. Handerson, S.; Schlaf, M. Org Lett 2002, 4, 407-409.
24. Peczuh, M. W.; Snyder, N. L. Tetrahedron Lett. 2003, 44, 4057-4061.
25. McKeon, J. E.; Fitton, P. Tetrahedron 1972, 28, 233-238.
26. Tachibana, T.; Aihara, T. 1989/, assigned to Seimi Chemical Co., Ltd., Japan.
27. Pichavant, L.; Guillermain, C.; Coqueret, X. Biomacromolecules 2010, 11, 2415-2421.
28. Alaaeddine, A., Hess, A., Boschet, F., Allcock, H., Ameduri, B.,. J. Polym. Sc. Part A : Polymer Chemistry 2013, 51, 977-986.

29. Alaaeddine, A.; Boschet, F.; Ameduri, B.; Boutevin, B. J. Polym. Sci., Part A: Polym. Chem. 2012, 50, 3303-3312.

30. Iftene, F.; David, G.; Boutevin, B.; Auvergne, R.; Alaaeddine, A.; Meghabar, R. J Polym Sci Part A: Polym Chem 2012, 50, 2432-2443.

31. Alaaeddine, A., Negrell, C., Ameduri, B. ACS Symposium Series, Advances in Fluorine-Containing Polymers 2012, 1106, Chapter 10, pp 141–169.

32. Martinent, A.; Alaaeddine, A.; Ameduri, B.; Capron, P. US 0190404-2011/, assigned to CEA, CNRS and ENSCM.

33. Galiano, H.; Ameduri, B.; Boutevin, B.; Alaaeddine, A. WO 049070-2012/, assigned to CEA and CNRS.