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Ferrocenium hexafluorophosphate as an inexpensive, mild catalyst for the etherification of propargylic alcohols

Matthew J. Queensen, Jordan M. Rabus, Eike B. Bauer*

University of Missouri - St. Louis, Department of Chemistry and Biochemistry, One University Boulevard, St. Louis, MO 63121, USA

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ABSTRACT

Commercial ferrocenium hexafluorophosphate ($[FeCp_2]PF_6$) was found to be an efficient catalyst for the etherification of terminal, tertiary propargylic alcohols with primary and secondary alcohols (5 h to 3 days reaction time at 40 °C in CH_2Cl_2, 3 mol% catalyst loading). The propargylic ether products were isolated in 90–20% yields. The alcohols and propargylic alcohols were employed in an equimolar amount and no further additives were required. For a purely aromatic propargylic alcohol, the isolated yields were lower than those for a mixed aromatic-aliphatic propargylic alcohol. Through monitoring reactant consumption and product formation over time, we found that the aromatic propargylic alcohol undergoes yield-diminishing Meyer–Schuster rearrangements to the aldehyde more easily than the mixed aromatic-aliphatic propargylic alcohol. The employment of $[Fe(Cp)_2]PF_6$ as a single electron oxidant has the potential to add a new direction in the development of catalysts for the title reaction based on single electron transfer processes.

1. Introduction

Propargylic alcohols (**1** in Scheme 1) are valuable starting materials in organic synthesis [1,2]. They are easily accessible [3] and combine two functional groups – a triple bond and an —OH unit – in adjacent positions within one molecule, giving rise to a multifaceted reaction landscape [1,2]. Consequently, propargylic alcohols can be engaged in a great variety of organic transformations. Among other reactions, propargylic alcohols can undergo addition [4] or substitution reactions [2,5,6], they can be transformed to allenes [7] and can rearrange to carbonyl compounds [8,9,10], which has been synthetically useful in natural product syntheses [11]. Especially cyclization reactions [12] or addition/cyclization [13] or substitution/cyclization [14] sequences allow access to sophisticated synthetic targets from simple starting materials. Propargylic alcohols are, thus, powerful building blocks in organic syntheses.

Propargylic substitution reactions (i.e. the substitution of the —OH group by a nucleophile, Nu, to afford the substitution product **5**, Scheme 1) are frequently applied in the functionalization of propargylic alcohols [1,2,5,15]. The complex reaction landscape of propargylic substitution reactions shown in Scheme 1 poses a synthetic challenge [1]. In addition, —OH units are poor leaving groups, further complicating substitution chemistry. Potential propargylic carbocation intermediates **2** (Scheme 1) in substitution reactions can rearrange to allenic cations **3**, which can react with nucleophiles to afford allenes **6**. Furthermore, propargylic alcohols can undergo Meyer–Schuster rearrangements to aldehydes (**7** in Scheme 1) [8,9,16]. Catalysts are required for propargylic substitution reactions, which are, in most cases, Lewis acids. However, Lewis acid catalysts tend to also catalyze the Meyer–Schuster rearrangement to form aldehydes [8,9,17]. For example, $FeCl_3$ catalyzes both propargylic substitution [18] and Meyer–Schuster rearrangement reactions [19,20]. Thus, the challenge is to develop catalyst systems that promote the substitution reactions in high chemoselectivity.

Mechanistically, the substitution can proceed either through a carbocation **2** [21] or an allenylidene intermediate **4** (Scheme 1) [1,2,15,22]. Brønsted [23] as well as transition metal based Lewis acids have been employed as catalysts for the reaction [1]. It appears to be reasonable to assume that hard Lewis acids promote the carbocation route, whereas more highly sophisticated, soft transition metal complexes are more suitable to form an allenylidene intermediate (which greatly increases the selectivity of the catalyst) [24]. A variety of catalyst systems are known to substitute —OH groups by a variety of carbon- [25], nitrogen- [26] or phosphorus-centered [27] nucleophiles.

* Corresponding author. Fax: +1 314 516 5342.
E-mail address: bauere@umsl.edu (E.B. Bauer).

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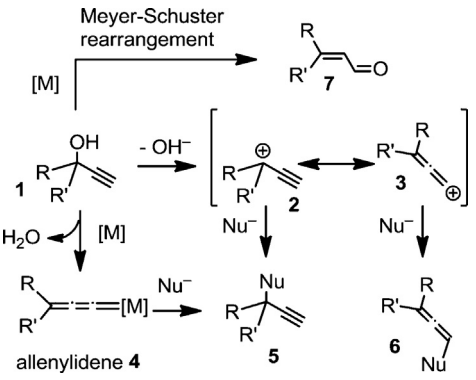


Scheme 1. Reaction landscape of propargylic alcohols.

The propargylic etherification reaction – i.e. the substitution of the OH group by an oxygen-centered nucleophile – is a specific version of a nucleophilic substitution reaction, where the nucleophile is an alcohol. A number of Brønsted [28] and Lewis acid catalyst systems have been reported for propargylic etherification reactions. Ruthenium-based systems have been widely employed [2,29,30], but catalyst systems based on copper [31], rhenium [32], bismuth [33] or gold [34] are known as well. With exceptions (as further outlined below), the reaction temperatures for substitution reactions of propargylic alcohols are typically above 60 °C. In some cases, additives are required for catalytic activity to unfold. There are catalysts known, that perform the reaction at room temperature, mainly based on Lewis acids in high oxidation states, such as $FeCl_3$ [18] and $BiCl_3$ [33]. The gold compound $Na[AuCl_4]$ also catalyzes the etherification of internal propargylic alcohols at room temperature [34]. In general, the catalytic systems that work at room temperature mainly employ internal propargylic alcohols [18,33,34] or utilize propargylic esters as starting material [35].

Iron catalysis has recently gained considerable interest; iron has a number of advantages compared to other transition metals typically employed in catalysis [36]. It is relatively non-toxic, abundant, and, therefore, inexpensive. As a consequence, iron is increasingly investigated as an alternative to more established transition metals. Accordingly, iron-based catalyst systems were also employed in propargylic etherification reactions. Zhan reported that $FeCl_3$ catalyzes the etherification of propargylic alcohols at room temperature within 5 h, but mainly internal propargylic alcohols were employed [18]. Zhan reported that $FeCl_3$ also catalyzes the etherification of internal propargylic esters, where the —OH has been replaced by an acetate group with increased leaving group abilities [35]. Zanotti described the iron complex $[Fe(Cp)(CO)_2]OTf$ to be catalytically active in the etherification of two different propargylic alcohols to give six different ethers with yields ranging from 9 to 72% [37]. As mentioned above, etherification (or enol etherification) [38] reactions of terminal propargylic alcohols frequently require elevated temperatures. To the best of our knowledge, Zhan's and Zanotti's pioneering reports are the only iron-catalyzed propargylic etherification examples; however, the alcohol nucleophiles were applied in excess and there is room for improvement with respect to some of the isolated yields and the substrate scope [18,37].

As part of our continuing research in the area of the catalytic activation of propargylic alcohols [39], we are currently investigating ruthenium based systems to serve that purpose. During the course of our studies, we discovered that commercial ferrocenium hexafluorophosphate ($[FeCp_2]^+PF_6$, subsequently referred to as $[Fc]PF_6$) catalyzes the propargylic etherification of a number of substrates at low temperatures. Some experiments giving further insight into the course of the reaction are also presented.

2. Results and discussion

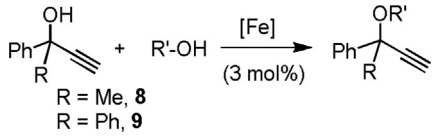
The starting point of our investigations was the consideration that Lewis acids were known to catalyze etherification reactions, but that Lewis acids also catalyze the Meyer–Schuster rearrangement (*vide supra*). It appeared that the rearrangements of inactivated substrates are mainly performed at elevated temperatures [8,9] and they might potentially compete with substitution reaction, resulting in unwanted side product formation. For these (and for general) reasons, we decided to look for a catalyst system that can perform the title reaction with terminal propargylic alcohols at lower temperatures. Test reaction in our laboratory showed that $FeCl_3$ and $FeCl_2$ catalyzed the etherification of 1,1-diphenylprop-2-yn-1-ol (**9**) and benzyl alcohol at 40 °C (Table 1). The conversion with $FeCl_2$ as the catalyst (Table 1, entry 2) was not complete after 18 h, but it was with $FeCl_3$ (Table 1, entry 1). However, we observed vapor formation when the alcohol starting materials and the strong Lewis acid $FeCl_3$ were combined. We speculated that the vapor was due to HCl and we set up a control reaction employing HCl as the catalyst (Table 1, entries 3 and 4). Indeed, HCl appeared to activate propargylic alcohols in some way. At different temperatures and HCl loads, the rearrangement product along with a small amount of the etherification product was observed by GC, albeit at relatively low overall conversions. Brønsted acids are known to catalyze the Meyer–Schuster rearrangement, which might be a competing reaction when $FeCl_3$ is utilized as catalyst [40].

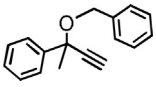
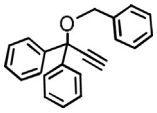
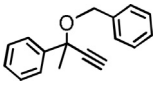
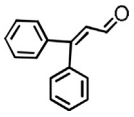
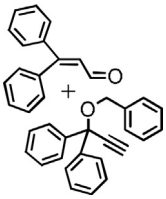
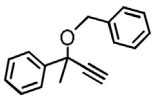
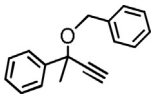
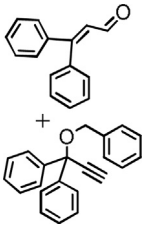
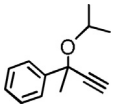
While simple catalyst systems can be very powerful, we were looking for a less reactive and more selective catalyst that could potentially be employed for more sophisticated target molecules where functional group selectivity might play a role. We envisaged $[Fc]PF_6$ as a mild yet reactive Lewis acid, because it is a 17 valence electron complex. Initial screening experiments employing $[Fc]PF_6$ revealed that it does indeed catalyze etherification reactions of propargylic alcohols (Table 1, entries 5 and 7). At room temperature, the catalyzed reaction is very slow, but at 40 °C, the reaction is reasonably fast (5 to 24 h) to become synthetically useful. In an attempt to increase the reaction rate, we performed the reactions at 65 °C (Table 1, entries 6 and 8). For the propargylic alcohol **9**, the product of the Meyer–Schuster rearrangement was observed in a 80% NMR yield (entry 6, vide infra). The propargylic alcohol **8** gave, at 65 °C, mainly substitution product (entry 8) but we found that 40 °C was sufficient for the very same reaction (entry 7). Isopropanol (*i*PrOH, a secondary alcohol) was also employed as the alcohol nucleophile, and gave reasonable yields (Table 1, entry 9).

After these optimization efforts, we found that at a catalyst load of 3 mol% $[Fc]PF_6$, one equivalent of the propargylic alcohol and one equivalent of an alcohol were converted to the corresponding propargylic ethers (CH_2Cl_2 solvent, 40 °C, 5 h to 3 days, Table 2). The exclusion of water and / or air was not necessary. As shown in Table 2, the isolated yields ranged from 90 to 20%. During screening as well as isolation of the products, no other species other than starting materials, products or occasional rearrangements were observed (*vide infra*). Most significantly, no dehydration of the propargylic alcohol **8** took place, providing the procedure chemoselectivity. Dehydration is occasionally observed when the reaction is performed at higher temperatures [9][9k]. We ascribe the lack of dehydration under conditions in Table 2 to the relatively low reaction temperature.

As can be seen from Table 2, tertiary propargylic alcohols can be employed for the reaction, however, at least one substituent on the propargylic alcohol (R or R') must be aromatic. Secondary propargylic alcohols could not successfully be converted to ethers under the reaction conditions and purely aliphatic secondary or tertiary ones gave GC yields below 20%. Both benzylic and aliphatic primary alcohols can be used. Secondary alcohols can also be utilized

Table 1
Screening reactions.



Entry	Catalyst	R′	Product	Yield/%[a]	Entry	Catalyst	R′	Product	Yield/%[a]
1	$FeCl_3$, CH_2Cl_2, 40 °C, 18 h	CH_2Ph		100	5	[Fc]PF_6 CH_2Cl_2 40 °C, 5 h	CH_2Ph		46[c]
2	$FeCl_2$, CH_2Cl_2, 40 °C, 18 h	CH_2Ph		45	6	[Fc]PF_6 Cl_2CH_2 65 °C, 5 h	CH_2Ph		80[d]
3	HCl (25 mol%) CH_2Cl_2, 40 °C, 18 h	CH_2Ph		34[b] 7[b]	7	[Fc]PF_6 CH_2Cl_2 40 °C, 5 h	CH_2Ph		89
					8	[Fc]PF_6 CH_2Cl_2 65 °C, 24 h	CH_2Ph		86
4	HCl (13 mol%) CH_2Cl_2, 80 °C, 2 days	CH_2Ph		30[b] 10[b]	9	[Fc]PF_6 CH_2Cl_2 40 °C, 3 days	*i*Pr		44[e]

[a] Determined by GC.
[b] Incomplete conversion to a number of products was observed, some of which remained unidentified.
[c] Isolated yield.
[d] 80% Meyer–Schsler rearrangement was detected by NMR.
[e] NMR yield.

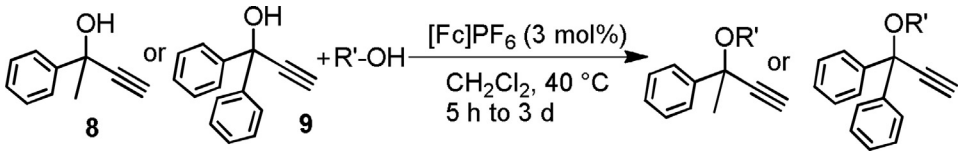
in the reaction as demonstrated with *l*-borneol (entry 4, where an almost 1:1 mixture of diastereomers was isolated) and isopropanol (*i*PrOH, entry 8). The secondary alcohols gave, in general, lower yields, which we tentatively ascribed to their lower nucleophilicity compared to primary alcohols.

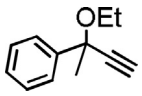
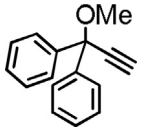
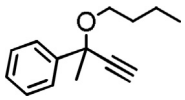
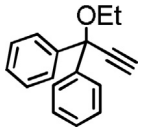
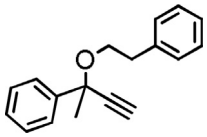
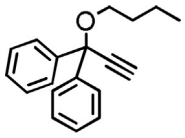
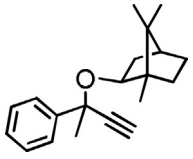
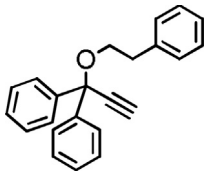
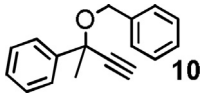
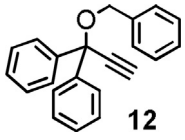
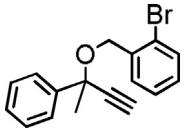
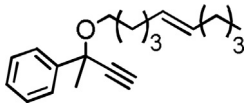
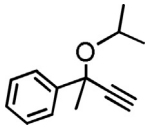
From the isolated yields in Table 2, some trends are obvious. It appears that the propargylic substrate 2-phenylbut-3-yn-2-ol (**8**) required, overall, a somewhat longer reaction time but gave in general higher yields compared to the aromatic propargylic substrate 1,1-diphenylprop-2-yn-1-ol (**9**). This aspect will be further discussed below. When methanol was employed as the alcohol substrate, the yields tended to be lower than for other alcohol substrates. With 2-phenylbut-3-yn-2-ol (**8**) as the propargyl alcohol, the yield of the resulting methoxy ether was so low that we decided to not list it in Table 2. We ascribe the low yield to the low stability of the product. A GC analysis of the crude reaction mixture of **8** and methanol showed almost complete consumption of the propargylic starting material and an intense peak for the ether product. However, all attempts to isolate the product chromatographically resulted in low to no yields, and we concluded that the product decomposes during workup on the column. An etherification reaction between aromatic propargylic substrate **9** and methanol (Table 2, entry 9) gave an isolated yield of only 21%, and only 80% conversion to the ether product was observed by GC. In general, when small alcohols, such as methanol, ethanol or *i*PrOH (Table 1, entry 9) were utilized, chromatographic separation of starting materials and products was not as easy and efficient compared to the ether products of larger alcohol nucleophiles. We tentatively ascribed that fact to the similar physical properties of propargylic starting material and ether product when small alcohols were used.

Pure $FeCl_2$ and $FeCl_3$ gave different product mixtures compared to [Fc]PF_6. For example, with $FeCl_3$, complete Meyer–Schuster rearrangement was observed when employed as catalyst under the conditions in Table 2, entry 11. Thus, potential iron chloride impurities cannot be responsible for the catalytic activity of [Fc]PF_6.

To further investigate the reaction, we decided to follow product formation and starting material consumption for selected reactions over time by GC. For the propargylic alcohols **8** (entry 5, Table 2 and Scheme 2, top; Fig. 1) and **9** (entry 13 and Scheme 2, bottom; Fig. 2), the reaction with benzyl alcohol was monitored. The reaction profile for **8** revealed a fast reaction at the early stage, and after 5 h, the concentration of the products virtually plateaued (Fig. 1). After one day, a slight decrease of the prod-

Table 2
Isolated yields.

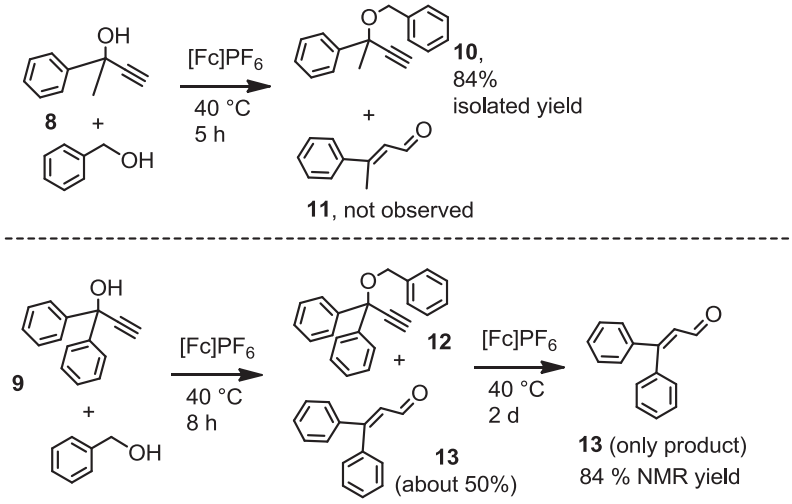


Entry[a]	Product	Isolated yield/%	Entry[a]	Product	Isolated yield/%
1		67	9[c]		21
2		74	10[c]		36
3		69	11[c]		40
4[b]		44	12[c]		35
5[d]	 10	84	13[c]	 12	46
6		86			
7		90			
8		20			

[a] General conditions: Propargylic alcohol (0.7 mol) and alcohol R′—OH (0.7 mmol) in CH_2Cl_2 (1 mL) catalyzed by $[Fc]PF_6$ (0.02 mol) at 40 °C for 3 days. The products were isolated chromatographically.
[b] A 50:50 mixture of diastereomers was isolated.
[c] 5 h reaction time.
[d] 18 h reaction time.

uct concentration can be observed, which we ascribed to product decomposition through hydrolysis (not shown in Fig. 1). Water from the atmosphere might have entered the reaction mixture, as the experiment was not performed under the exclusion of air. No Meyer–Schuster rearrangement to the aldehyde **11** was observed for this substrate in the presence of the benzyl alcohol nucleophile, which we also verified by NMR of the crude mixtures (Scheme 2, top).

The situation is fundamentally different for 1,1-diphenylprop-2-yn-1-ol **9** (Fig. 2 and Scheme 2, bottom). As can be seen, the propargylic ether product **12** formed over time, but also the Meyer–Schuster rearrangement product **13**. After 8 h, the ether and rearrangement products were observed in about equimolar amount by GC. Thus, the isolated yields for the etherification of 1,1-diphenylprop-2-yn-1-ol **9** (right side in Table 2) are lower because it rearranges during the reaction in a substantial amount to the aldehyde **13**. The aldehyde rearrangement side product **13** was not only observed by GC but also readily identified in the ^1H NMR of the crude reaction mixture, where it gave a distinct doublet at 9.4 ppm, coupling with the alkene proton.



Scheme 2. Etherification versus rearrangement for different propargylic alcohols as a function of time.

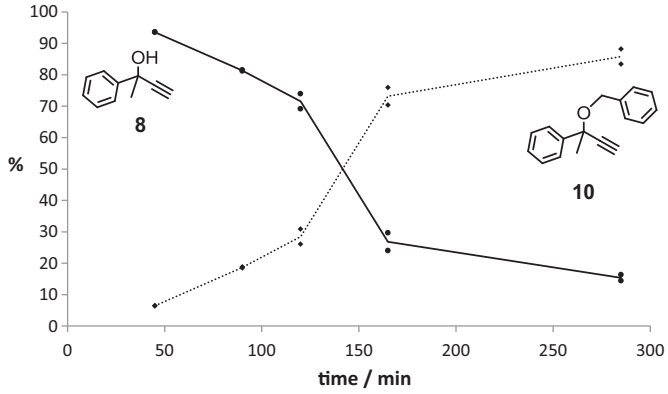


Fig. 1. Etherification of propargylic alcohol **8** (solid line) with benzyl alcohol followed over time by GC, average of two runs.

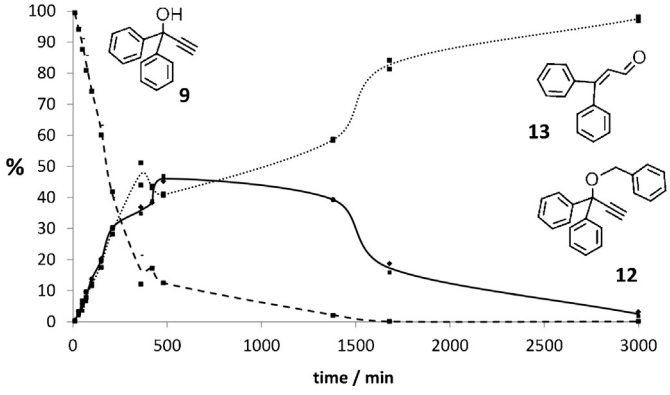


Fig. 2. Etherification of propargylic alcohol **9** (dashed line) with benzyl alcohol followed over time by GC, average of two runs.

When the reaction was continued for a total of three days (Fig. 2, Scheme 2), rearrangement continued; furthermore, the ether product **12** started decomposing after eight hours, presumably to the propargylic alcohol starting material **9**. After two days, only the rearrangement product **13** was observed by GC and NMR, which gave a 84% NMR yield (Scheme 2, bottom). After 8 h, the propargylic ether product **12** was isolated in 46% yield (Table 2, entry 13 and Scheme 2). Thus, it appeared that the reaction has a window for the formation of **12**. The propargylic ether product **12** seemed to form under kinetic control within the first eight hours and rearrangement occurs concurrently. When the reaction time is extended to 2 days, the ether product **12** converted and complete Meyer–Schuster rearrangement was observed, which is presumably a thermodynamically driven reaction. The 3,3-diphenylacrylaldehyde product **13** is probably more stable than both the propargylic alcohol starting material **9** and the ether product **12**.

Thus, the ether product **12** converts to the aldehyde **13**, which we did not observe for the 2-phenylbut-3-yn-2-ol ether product **10** (Fig. 1 and Scheme 2, top). Under the reaction conditions in Table 2, the propargylic alcohol starting material **8** either does not or only marginally rearrange to the aldehyde. We ascribe this difference in behavior of the propargylic alcohols **8** and **9** to the aldehyde product stabilities. Due to double conjugation, the aldehyde **13** is more stable than the aldehyde **11**, which might be a driving force for its formation.

When the propargylic alcohols **8** and **9** were subjected to catalytic conditions in Table 2 and Scheme 2 but without any alcohol nucleophile, some Meyer–Schuster rearrangement was observed by GC. The reactions were somewhat inconsistent when performed repeatedly and aldehyde products could not be isolated for both propargylic substrates. The $[Fc]PF_6$ is, thus, not a good catalyst for the Meyer–Schuster rearrangement at 40 °C; the rearrangement observed in Scheme 2 and Fig. 2 only efficiently takes place in the presence of alcohol substrate. At 65 °C, $[Fc]PF_6$ catalyzes the Meyer–Schuster rearrangement of the propargylic alcohol **9** to the corresponding aldehyde somewhat more efficiently (Table 1, entry 6).

We conclude that 1,1-diphenylprop-2-yn-1-ol **9** undergoes rearrangement more efficiently under the conditions in Table 2, which is responsible for the lower isolated yields but also for the faster reaction rate, because etherification and rearrangement take place concurrently. On the other hand, the 2-phenylbut-3-yn-2-ol **8** appears to not rearrange in presence of an alcohol substrate (Scheme 2, top). The lack of competing and yield-diminishing rearrangement is responsible for the higher propargylic ether yields observed for the propargylic alcohol **8**.

Further studies are needed in order to suggest a mechanism for the title reaction under the reaction conditions given in Table 2. However, some mechanistic aspects of the catalytic system presented herein can be elaborated. The allenylidene route (Scheme 1) requires that the propargylic alcohol substrate is activated through an allenylidene intermediate, which then is attacked by the alcohol nucleophile [41]. Iron allenylidene complexes are known [41b,42];

however, we do not have experimental evidence that an iron allenylidene intermediate is generated, as UV–vis and MS experiments have been, thus far, inconclusive. While the [Fc]PF_6 catalyst is a Lewis acid, it is not a very strong one and it is questionable if it is capable of ionizing a propargylic alcohol substrate. On the other hand, when the reaction of entry 12 in Table 2 was performed in the presence of either 2,2,6,6-(tetramethylpiperidin-1-yl) oxy (TEMPO) or 2,4,6-tri-*tert*-butylphenol (TTBP), which are both known to be radical scavengers, the reaction was completely inhibited. It is possible that the radical scavengers just deactivated the catalyst.

However, [Fc]PF_6 has another role as a single electron oxidant [43]. It is, at this point, too early to suggest a mechanism for the reaction, but it appears to be possible that the title reaction proceeds through a single electron transfer mechanism under the reaction conditions described herein [43b,44,45]. We think the employment of a single electron oxidant has the potential to inspire a new direction in the development of catalysts for the title reaction based on single electron transfer processes [45].

Compared to other iron based catalyst systems known in the literature, [Fc]PF_6 performs well and complements existing systems. As already mentioned, the strict exclusion of air or water is not necessary. The reaction is restricted to tertiary alcohols and complements, thus, the catalyst systems that primarily work for secondary propargylic alcohols [1,2,30,32]. The reaction temperature is 40 °C, which is lower than for many other catalyst systems reported in the literature [1]. Room temperature systems have been reported [37], but they mainly employ internal propargylic alcohols [33,34,35]. We think the low reaction temperature allows for the employment of propargylic alcohols with hydrogens in a β position, which tend to eliminate at higher temperatures [9][9k]. Many reports of substitution reactions utilize propargylic alcohols without β -hydrogen atoms [1,32]. Most significantly, as opposed to other systems reported in the literature, the alcohol substrate has not to be in excess over the propargylic alcohol substrate, which makes the employment of [Fc]PF_6 attractive in cases where an expensive alcohol substrate is one of the reactants. As demonstrated in Table 1 (entries 3 and 4), HCl potentially interferes with the title reaction, and we encourage researchers in the area employing very strong Lewis acids such as $FeCl_3$ to carefully look for side product formation.

3. Conclusion

We presented herein a new catalyst system based on [Fc]PF_6 (ferrocenium hexafluorophosphate) for the conversion of propargylic alcohols to the corresponding propargylic ethers (90 to 20% isolated yields). The reaction can be conducted at 40 °C, which is lower than for many other known catalyst systems for the reaction. The reagents can be employed in equimolar amounts. No additives are required and no dehydration was observed. For a purely aromatic propargylic alcohol, the etherification reaction competes with an rearrangement of the alcohol to the aldehyde, which appeared to also be catalyzed by [Fc]PF_6 and which lowered the yield for that specific substrate. Further mechanistic investigations are ongoing.

Experimental

General. All reactions were carried out in open air. CH_2Cl_2, 2-phenyl-3-butyn-2-ol, 1,1-diphenyl-2-propyn-3-ol, MeOH, *n*-butanol, benzyl alcohol, 2-phenylethanol, (2-bromophenyl)methanol, *l*-borneol, (*E*)-dec-5-en-1-ol, 2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO), 2,4,6-tri-*tert*-butylphenol (TTBP), [Fc]PF_6 (all Sigma–Aldrich), EtOH (Decon), and *i*PrOH (Fischer) were used as received.

NMR spectra were obtained at room temperature on a Bruker Avance 300 MHz or a Varian Unity Plus 300 MHz instrument and referenced to a residual solvent signal; all assignments are tentative. EI and exact masses were recorded on a JEOL MStation [JMS-700] Mass Spectrometer and HP 5988A GC–MS instrument. Gas chromatograms were recorded on a HP 5890 instrument. IR spectra were recorded on Thermo Nicolett 670 FTIR. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA, USA.

Characterization data for the known propargylic ethers in Table 2 are listed in the Supporting information.

General procedure for the etherification of 2-phenyl-3-butyn-2-ol: (2-Ethoxybut-3-yn-2-yl)benzene (Table 2, entry 1) [39a]: 2-phenyl-3-butyn-2-ol (0.106 g, 0.728 mmol) was added to a 5-mL screw cap vial and dissolved in CH_2Cl_2 (1 mL). Ethanol (0.036 g, 0.897 mmol) was added followed by the addition of [Fc]PF_6 (0.007 g, 0.022 mmol). The vial was then sealed and heated at 40 °C for 3 days. The solvent was removed and the residue was chromatographed on a neutral alumina oxide (Aluminar®) column (2.5 × 30 cm, hexane and then CH_2Cl_2) to give the product as a yellow solid (0.085 g, 0.487 mmol, 67%). NMR (δ, $CDCl_3$) ^{1}H: 7.67–7.29 (m, 7H, aromatic), 3.69 (doublet of quintets, 1 H, $^2J_{HH}$ = 7.2 Hz, $^2J_{HH}$ = 4.2 Hz, OC*H*H'), 3.22 (doublet of quintets, 1H, $^2J_{HH}$ = 7.2 Hz, $^2J_{HH}$ = 4.2 Hz, OCH*H*'), 2.74 (s, 1H, C≡C*H*), 1.78 (s, 3H, CH_3), 1.24 (t, 3H, $^2J_{HH}$ = 7.2 Hz, OCH_2CH_3) ppm. ^{13}C{^{1}H}: 143.3 (s, aromatic ipso), 128.6 (s, aromatic), 128.5 (s, aromatic), 127.9 (s, aromatic), 127.6 (s, aromatic*), 126.1 (s, aromatic), 84.7 (s, *C*≡CH), 75.9 (s, *C*C≡CH), 75.2 (s, C≡*C*H), 60.6 (s, OCH_2), 33.2 (s, CH_3), 15.6 (s, OCH_2CH_3) ppm. IR (ATR, Neat): 3284 (m), 3055 (w), 2973 (m), 2926(w), 1714 (s), 1670 (s), 1575 (s), 1491 (s), 1335 (s), 1264 (s), 1057 (s), 997 (s) ν.

(2-Phenethoxybut-3-yn-2-yl)benzene (Table 2, entry 3): 2-phenyl-3-butyn-2-ol (0.111 g, 0.757 mmol), 2-phenylethanol (0.093 g, 0.759 mmol), and [Fc]PF_6 (0.007 g, 0.021 mmol) were combined and worked up as described above for (2-ethoxybut-3-yn-2-yl)benzene to give (2-phenethoxybut-3-yn-2-yl)benzene as a yellow oil (0.118 g, 0.443 mmol, 69 %). Anal. calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.25; H, 7.14. NMR (δ, $CDCl_3$) ^{1}H: 7.41–7.38 (m, 2H, aromatic), 7.21–7.04 (m, 8H, aromatic), 3.72 (doublet of quintets, 1H, $^2J_{HH}$ = 1.7 Hz, $^2J_{HH}$ = 7.3 Hz, $^2J_{HH}$ = 8.5 Hz, OC*H*H'), 3.24 (doublet of quintets, 1H, $^2J_{HH}$ = 1.7 Hz, $^2J_{HH}$ = 7.3 Hz, $^2J_{HH}$ = 8.5 Hz, OCH*H*'), 2.79 (m, 2H, OCH_2CH_2Ph), 2.55 (s, 1H, C≡C*H*), 1.61 (s, 3H, CH_3) ppm. ^{13}C{^{1}H}: 142.8 (s, aromatic), 139.2 (s, aromatic), 129.4 (s, aromatic), 129.1 (s, aromatic), 128.6 (s, aromatic), 128.3 (s, aromatic), 128.1 (s, aromatic), 126.1 (s, aromatic), 125.9 (s, aromatic), 84.3 (s, *C*≡CH), 75.9 (CR_4), 75.6 (s, C≡*C*H), 66.1 (s, OCH_2), 36.7 (s, CH_2CH_2Ph), 33.1 (s, CH_3) ppm. IR (ATR, neat): ν 3063 (w), 2864 (w), 1708 (s), 1575 (s), 1494 (s), 1356 (s), 1218 (s), 1045 (s) cm^{-1}. ESI-MS: *m*/*z* 235 ([M−CH_3], 10%), 129 ([M−OCH_2CH_2Ph], 100%). EI-MS: HRMS *m*/*z* calculated for $C_{17}H_{15}O$ (corresponds to [M−CH_3]): 235.1123. Found: 235.1124.

(2-Borneoylbut-3-yn-2-yl)benzene (Table 2, entry 4): 2-phenyl-3-butyn-2-ol (0.105 g, 0.716 mmol), l-borneol (0.112 g, 0.726 mmol), and [Fc]PF_6 (0.008 g, 0.024 mmol) were combined and worked up as described above for (2-ethoxybut-3-yn-2-yl)benzene to give (2-borneoylbut-3-yn-2-yl)benzene as a yellow solid as a 1:1 mixture of diastereomers (0.089 g, 0.355 mmol, 44 %). NMR (δ, $CDCl_3$) ^{1}H: 7.74–7.71 (m, 3H, aromatic + aromatic'), 7.43–7.30 (m, 2H, aromatic + aromatic'), 4.10 (d, 1H, $^2J_{HH}$ = 9.2 Hz, OC*H*'), 3.97 (d, 1H, $^2J_{HH}$ = 9.1 Hz, OC*H*), 2.68 (s, 1H, C≡C*H*'), 2.67 (s, 1H, C≡C*H*), 2.35–2.24 (m, 1H,$OCHCH_2$'), 2.22–2.13 (m, 1H, $OCHCH_2$), 1.81 (s, 3H, C≡CCH_3'), 1.79 (s, 3H, C≡CCH_3), 1.68 (t, 2H, $^2J_{HH}$ = 4.6 Hz, $OCHCH_2$'), 1.55 (t, 2H, $^2J_{HH}$ = 4.5 Hz, $OCHCH_2$),

1.41–1.22 (m, 4H, $CH_2CH_2 + CH_2CH_2$'), 0.96 (s, 3H, CCH_3'), 0.88 (s, 3H, CCH_3), 0.86 (s, 3H, CCH_3'), 0.85 (s, 3H, CCH_3), 0.78 (s, 3H, $CH_3 + CH_3$') ppm. $^{13}C\{^1H\}$: 144.5 (s, aromatic), 128.2 (s, aromatic), 127.8 (s, aromatic), 126.5 (s, aromatic), 126.4 (s, aromatic), 86.6 (s, *C*≡CH), 86.4 (s, *C*≡CH'), 80.3 (s, *CC*≡CH), 80.0 (s, *CC*≡CH'), 75.2 (s, C≡*C*H), 75.2 (s, C≡*C*H'), 75.0 (br s, O*C*H + O*C*H'), 49.8 (s, OCH*C*), 49.7 (s, OCHC'), 47.4 (s, *CC*≡CH), 47.2 (s, *CC*≡CH'), 45.7 (s, OCHCH_2CH), 45.5 (s, OCHCH_2CH'), 39.5 (s, OCHCH_2), 38.0 (s, OCHCH_2'), 32.5 (s, C≡CCH_3), 31.9 (s, C≡CCH_3'), 28.5 (s, CH_2CH_2), 28.5 (s, CH_2CH_2'), 27.3 (s, CH_2CH_2), 27.2 (s, CH_2CH_2'), 20.0 (s, CH_3'), 20.0 (s, CH_3), 19.2 (br s, $CH_3 + CH_3$'), 13.9 (s, CH_3'), 13.7 (s, CH3) ppm. IR (ATR, neat): ν 3302 (m), 2947 (s), 1704 (m), 1489 (s), 1446 (s), 1364 (s), 1223 (s), 1085 (s), 992 (s) cm^{-1}. EI-MS: *m*/*z* 282 ([M], 10%), 258 ([M—C≡C], 10%), 243 ([M—C≡C—CH_3], 10%), 129 ([M–borneol], 100 %).

1-Bromo-2-(((2-phenylbut-3-yn-2-yl)oxy)methyl)benzene (Table 2, entry 6): 2-phenyl-3-butyn-2-ol (0.850 g, 5.778 mmol), (2-bromophenyl)methanol (0.721 g, 5.80 mmol), and [Fc]PF_6 (0.571 g, 0.174 mmol) were added to a evacuated and nitrogen flushed 2 neck round bottom flask and suspended in 20 mL of CH_2Cl_2. The reaction was stirred at 40 °C for 2 days and then purified by column chromatography (2 × 30 cm alumina column) using hexane as eluent to give 1-bromo-2-(((2-phenylbut-3-yn-2-yl)oxy)methyl)benzene as a yellow oil (1.269 g, 4.968 mmol, 86%). NMR (δ, $CDCl_3$) ^1H :7.81–7.17 (m, 14H, aromatic), 5.32 (s, CH_2Cl_2), 4.83 (t, 1H, $^2J_{HH}$=12 Hz, OC*H*H'), 4.39 (d, 1H, $^2J_{HH}$ = 12 Hz, OCH*H*'), 2.87 (d, 1H, $^2J_{HH}$ = 2.5 Hz, C≡C*H*), 1.95 (d, 3H, $^2J_{HH}$ = 2.5 Hz, CH_3) ppm. $^{13}C\{^1H\}$: 142.7 (s, aromatic), 138.4 (s, aromatic), 132.6 (s, aromatic), 129.6 (s, aromatic), 129.1 (s, aromatic), 128.9 (s, aromatic), 128.7 (s, aromatic), 128.6 (s, aromatic), 128.3 (s, aromatic), 127.9 (s, aromatic), 127.6 (s, aromatic), 126.2 (s, aromatic), 125.2 (s, aromatic), 122.9 (s, aromatic), 84.1 (s, *C*≡CH), 76.6 (s, *CC*≡CH), 76.3 (s, C≡*C*H), 66.8 (s, OCH_2), 33.1 (s, CH_3) ppm. IR (ATR, neat): ν 3290 (m), 3057 (m), 2985 (m), 2929 (w), 1729 (m), 1668 (m), 1568 (s), 1469 (s), 1441 (s), 1377 (m), 1268 (m), 1223 (m), 1089 (s), 1021 (s), 908 (m) cm^{-1}. FAB-MS: HRMS *m*/*z* calculated for $C_{17}H_{15}BrONa$: 337.0204 and 339.0184. Found: 337.0216 and 339.0196.

(E)-(2-(Dec-5-en-1-yloxy)but-3-yn-2-yl)benzene (Table 2, entry 7): 2-phenyl-3-butyn-2-ol (0.103 g, 0.705 mmol), (*E*)-dec-5-en-1-ol (0.111 g, 0.707 mmol), and [Fc]PF_6 (0.003 g, 0.011 mmol) were combined and worked up as described above for (2-ethoxybut-3-yn-2-yl)benzene to give (*E*)-(2-(dec-5-en-1-yloxy)but-3-yn-2-yl)benzene as a yellow oil (0.180 g, 0.634 mmol, 90%). NMR (δ, $CDCl_3$) ^1H : 7.72–7.70 (d, 2H, $^3J_{HH}$ = 8.3 Hz, aromatic), 7.47–7.37 (m, 3H, aromatic), 5.47 (br s, 2H, *HC* = *CH*), 3.68 (q, 1H, $^2J_{HH}$ = 6.5 Hz, OC*H*H'), 3.21 (q, 1H, $^2J_{HH}$ = 6.5 Hz, OCH*H*'), 2.78 (s, 1H, C≡C*H*), 2.07 (br. s, 4H, 2CH_2), 1.83 (s, CH_3), 1.66 (quint, 2H, $^2J_{HH}$ = 6.9 Hz, CH_2), 1.45–1.39 (m, 6H, 3CH_2), 0.99 (t, 3H, $^2J_{HH}$ = 6.9 Hz, CH_2CH_3) ppm. $^{13}C\{^1H\}$: 143.1 (s, aromatic), 130.1 (s, aromatic), 128.4 (s, aromatic), 127.8 (s, aromatic), 126.0 (s, aromatic), 84.4 (s, *C*≡CH), 75.8 (s, *CC*≡CH), 75.4 (s, C≡*C*H), 64.9 (s, *C*=*C*), 33.1 (s, CH_2), 32.5 (s, CH_2), 32.5 (s, CH_2), 32.0 (s, CH_2), 29.5 (s, CH_2), 26.3 (s, CH_2), 22.4 (s, CH_2), 14.2 (s, CH_2CH3) ppm. IR (ATR, neat): ν 3303 (m), 2926 (m), 2856 (w), 1723 (m), 1672 (w), 1575 (m), 1520 (m), 1464 (s), 1264 (m), 1093 (s), 905 (s) cm^{-1}. EI-MS: HRMS *m*/*z* calculated for $C_{20}H_{28}ONa$: 307.2038. Found: 307.2043.

(Isopropoxybut-3-yn-2-yl)benzene (Table 2 entry 8): 2-phenyl-3-butyn-2-ol (0.705 g, 4.827 mmol), isopropanol (0.491 g, 8.16 mmol), and [Fc]PF_6 (0.479 g, 0.145 mmol) were combined and worked up as described above for (2-ethoxybut-3-yn-2-yl)benzene to give the product as an orange oil (0.184 g, 0.968 mmol, 20%). NMR (δ, $CDCl_3$) ^1H : 7.81–7.79 (m, 1H, aromatic), 7.45–7.40 (m, 4H, aromatic), 3.95 (septet, 1H, $^2J_{HH}$ = 6.3 Hz, OC*H*), 2.78 (s, 1H, C≡C*H*), 1.84 (s, 3H, CH_3), 1.38 (d, 3H, $^2J_{HH}$ = 6.3 Hz, CHCH_3), 1.06 (d, 3H, $^2J_{HH}$ = 6.3 Hz, CHCH_3') ppm. $^{13}C\{^1H\}$: 144.1 (s), 128.3 (s), 128.0 (s), 126.6 (s, all aromatic), 85.6 (s, *C*≡CH), 75.4 (s, *CC*≡CH), 75.3 (s, C≡*C*H), 68.7 (s, OCH), 33.4 (s, CH_3), 24.4 (s, CH_3), 24.2 (s, CH_3) ppm. IR (ATR, neat): ν 3291 (m), 2969 (m), 2930 (m), 1597 (m), 1489 (s), 1444 (s), 1364 (s), 1220 (s), 1085 (s), 992 (s), 905 (s), 760 (s) cm^{-1}. EI-MS: *m*/*z* 173 ([M−CH_3], 50%), 129 ([M−*i*PrO], 100%).

General Procedure for the etherification of 1,1-diphenylprop-2-yn-1-ol: (1-methoxy-2-propyn-1-ylidene)bis-Benzene (Table 2, entry 9) [17] 1,1-diphenyl-2-propyn-3-ol (0.102 g, 0.491 mmol) was added to a 5 mL screw cap vial and dissolved in CH_2Cl_2 (1 mL). Methanol (0.016 g, 0.497 mmol) was then added followed by [Fc]PF_6 (0.005 g, 0.014 mmol). The vial was then sealed and heated to 40 °C for 5 h. The solvent was removed and the residue was chromatographed on a silica gel column (2.5 × 30 cm, 2:1 v/v hexanes/CH_2Cl_2) to give the product **8** as a yellow oil (0.022 g, 0.099 mmol, 21%). NMR (δ, $CDCl_3$) ^1H: 7.63–7.57 (m, 4H, aromatic), 7.41–7.30 (m, 6H, aromatic), 3.41 (d, 3H, $^2J_{HH}$ = 4.3 Hz, OCH_3), 2.94 (d, 1H, $^2J_{HH}$ = 4.3 Hz, C≡C*H*) ppm. $^{13}C\{^1H\}$: 143.2 (s, aromatic), 128.4 (s, aromatic), 127.9 (s, aromatic), 126.9 (s, aromatic), 83.4 (s, *CC*≡CH), 81.0 (s, *C*≡CH), 77.8 (s, CC≡*C*CH), 52.7 (s, OCH_3) ppm. IR (ATR, neat): ν 3302 (w), 1723 (m), 1672 (m), 1575 (s), 1470 (s), 1336 (s), 1266 (s), 1068 (s), 901 (s), 724 (s) cm^{-1}. EI-MS: *m*/*z* 222 ([M], 20%), 207 ([M−CH_3], 60%), 145 ([M–Ph], 100%). HRMS calculated for $C_{16}H_{14}O$: 222.1047. Found: 222.1045.

(1-Butoxyprop-2-yne-1,1-diyl)dibenzene (Table 2, entry 11): 1,1-Diphenyl-2-propyn-3-ol (0.104 g, 0.501 mmol), *n*-butanol (0.037 g, 0.502 mmol), and [Fc]PF_6 (0.005 g, 0.014 mmol) were combined and worked up as described above for (1-methoxy-prop-2-yne-1,1-diyl)dibenzene to give (1-butoxyprop-2-yne-1,1-diyl)dibenzene as a yellow oil (0.050 g, 0.189 mmol, 40%). Anal. Calc. for $C_{19}H_{20}O$: C, 86.32; H, 7.63 Found: C, 86.04; H, 7.38. NMR (δ, $CDCl_3$) ^1H: 7.50-7.47 (m, 4H, aromatic), 7.25-7.15 (m, 6H, aromatic), 3.40 (t, 2H, $^2J_{HH}$ = 6.4 Hz, OCH_2), 2.77 (s, 1H, C≡C*H*), 1.57 (quintet, 2H, $^2J_{HH}$ = 6.5 Hz, OCH_2CH_2), 1.38 (sextet, 2H, $^2J_{HH}$ = 7.4 Hz, CH_2CH_3), 0.83 (t, 3H, $^2J_{HH}$ = 7.3 Hz, CH_2CH_3) ppm. $^{13}C\{^1H\}$: 143.6 (s, aromatic), 128.2 (s, aromatic), 127.7 (s, aromatic), 126.7 (s, aromatic), 83.7 (s, *CC*≡CH), 79.8 (s, *C*≡CH), 76.7 (s, C≡*C*H), 64.4 (s, OCH_2), 32.1 (s, CH_2), 19.6 (s, CH_2), 14.1 (s, CH_3) ppm. IR (ATR, neat): ν 3282 (m), 3104 (m), 2957 (m), 1767 (m), 1697 (s), 1650 (s), 1548 (s), 1487 (s), 1445 (s), 1358 (s), 1024 (s), 741 (s) cm^{-1}. EI-MS: *m*/*z* 264 ([M], 30%), 191 ([M–O–*n*-Bu], 100%). HRMS *m*/*z* calculated for $C_{19}H_{20}O$: 264.1514. Found: 264.1519.

(1-Phenethoxyprop-2-yne-1,1-diyl)dibenzene (Table 2, entry 12): 1,1-Diphenyl-2-propyn-3-ol (0.099 g, 0.473 mmol), 2-phenylethanol (0.059 g, 0.500 mmol), and [Fc]PF_6 (0.005 g, 0.015 mmol) were combined and worked up as described above for 1-(methoxy)prop-2-yne-1,1-diyl)dibenzene to give (1-phenethoxyprop-2-yne-1,1-diyl)dibenzene as a yellow oil (0.055 g, 0.168 mmol, 35%). Anal. Calc. for $C_{23}H_{20}O$: C, 88.43; H, 6.45 found: C, 88.16; H, 6.39. NMR (δ, $CDCl_3$) ^1H: 7.41–7.38 (m, 3H, aromatic), 7.17–7.13 (m, 12H, aromatic), 3.63 (t, 2H, $^2J_{HH}$ = 7.0 Hz, OCH_2), 2.92 (t, 2H, $^2J_{HH}$ = 7.0 Hz, OCH_2CH_2), 2.75 (s, 1H, C≡CH) ppm. $^{13}C\{^1H\}$: 143.5 (s, aromatic), 136.4 (s, aromatic), 129.3 (s, aromatic), 128.5 (s, aromatic), 128.4 (s, aromatic), 128.4 (s, aromatic), 127.8 (s, aromatic), 126.7 (s, aromatic), 126.4 (s, aromatic), 83.5 (s, *CC*≡CH), 80.2 (s, *C*≡CH), 77.7 (s, C≡CH), 65.9 (s, OCH_2), 36.7 (s, OCH_2CH_2) ppm. IR (ATR, neat): ν 3283 (m), 3058 (m), 2933 (m), 2869 (m), 1728 (s), 1595 (s), 1487 (s), 1447 (s), 1211 (s), 1063 (s), 1023 (s), 741 cm^{-1}. EI-MS: *m*/*z* 311 ([M + H], 4%), 281 ([M–CH2 = O], 15%), 191 ([M–OCH_2CH_2Ph], 100%).

Meyer-Schuster rearrangement of 1,1-diphenyl-2-propyn-3-ol (Scheme 2, bottom): 1,1-diphenylprop-2-yn-1-ol (0.145 g, 0.697

mmol), benzyl alcohol (0.073 g, 0.678 mmol), and [Fc]PF_6 (0.007 g, 0.021 mmol) were combined in CH_2Cl_2 (3 mL) and heated at 40 °C for 3 days. The solvent was removed and the residue filtered through a short pad of silica gel. From the recovered mass (0.192 g), an NMR yield of 84% for the aldehyde **13** was calculated. The NMR showed besides the rearranged product only benzyl alcohol. NMR (δ, $CDCl_3$) ^{1}H: 9.43 (d, 0.65H, $^2J_{HH}$ = 8.0 Hz, *H*C = O of **13**), 7.35-7.20 (m, 18.3H, aromatic), 6.51 (d, 0.65H, $^2J_{HH}$ = 8.0 Hz, *CH*CHO of **13**), 4.75 (s, 2H, C*H*$_2$OH of benzyl alcohol), 2.55 (s, 1H, CH_2O*H* of benzyl alcohol). IR (ATR, neat): ν 3054 (w), 2840 (w), 1659 (s), 1589 (m), 1488 (m), 1442 (s), 1340 (s), 1263 (s), 1122 (s), 1028 (m), 768 (s), 731 (s) cm^{-1}.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2015.06.009

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