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Ferrocenium Cations as Catalysts for the Etherification of Cyclopropyl-Substituted Propargylic Alcohols: Ene-yne Formation and Mechanistic Insights

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Abstract

Commercial ferrocenium hexafluorophosphate ($[FeCp_2]PF_6$) and ferrocenium boronic acid hexafluoroantimonate ($[FcB(OH)_2]SbF_6$) were found to be efficient catalysts for the etherification of terminal, tertiary, cyclopropyl-substituted propargylic alcohols through nucleophilic substitution with primary and secondary alcohols. The alcohol nucleophiles and the propargylic alcohols were employed in a nearly equimolar amount and no further additives were required. After 2 h reaction time at 40 °C in CH_2Cl_2 and 3 to 5 mol% catalyst load, aromatic, cyclopropyl-substituted propargylic alcohols gave rearranged, conjugated ene-yne products as single isomers in 35 to 73% isolated yields. Cyclopropyl-substituted propargylic alcohols bearing

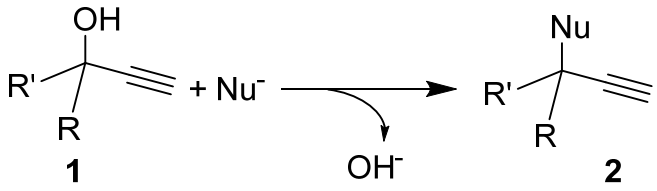
a thiophenyl substituent gave the corresponding cyclopropyl-substituted propargylic ethers in 27 to 56% isolated yields (45 °C, 2 h reaction time), where the cyclopropyl unit did not rearrange. Cyclobutyl-substituted propargylic alcohols gave the corresponding propargyl ether substituted products in 40 to 55% isolated yields (40 to 45 °C, around 16 h reaction time), and no rearrangement of the cyclobutyl unit was observed. Only minor amounts of side products were observed in the reaction mixtures. Experimental evidence points toward an ionic mechanism, since the more electron-rich thiophenyl-substituted substrates reacted faster.

Keywords: Homogeneous catalysis, iron, isomerization.

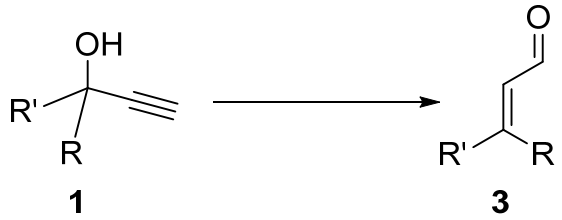
Introduction

Propargylic alcohols (**1** in Scheme 1) are valuable starting materials in organic synthesis.[1] They feature an alkyne and a hydroxyl unit in close proximity, and this bifunctionality allows for a variety of useful organic transformations.[2,3] The triple bond can be engaged in cycloaddition reactions[4] and if terminal, it can be deprotonated to act as nucleophile or undergo cross coupling reactions.[5] Intramolecular cyclization reactions involving propargylic alcohols have been investigated as well.[6] The hydroxyl group can be replaced in nucleophilic substitution reactions by a variety of nucleophiles (Scheme 1a).[7] Tandem reactions constituting of a propargylic nucleophilic substitution reaction followed by a cyclization can afford a variety of cyclic and heterocyclic ring systems.[8] As a consequence, propargylic alcohols are employed as starting materials in the synthesis of a variety of natural products,[9] pharmaceuticals[10] or other materials with valuable optical or mechanical properties.[11]

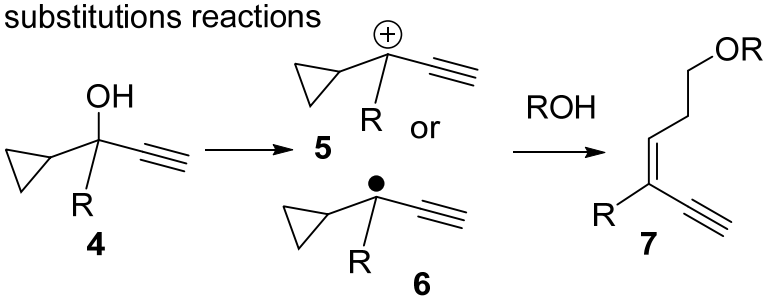
a) Propargylic substitution reaction



b) Meyer-Schuster rearrangement of propargylic alcohols



c) Potential cationic or radical intermediates in substitutions reactions



Scheme 1. Reactions of propargylic alcohols.

The bifunctionality of propargylic alcohols also enables rearrangement and isomerization reactions. The most common ones are the Meyer-Schuster rearrangement (Scheme 1b), the Rupe rearrangement and redox isomerization.[12] These reactions afford synthetically valuable α,β-unsaturated carbonyl compounds (such as **3** in Scheme 1b) and can be of value in their own right.[13] However, they can also cause yield-diminishing side reactions. Many catalyst systems, especially based on Lewis acids such as $FeCl_3$, can catalyze intramolecular rearrangement reactions of propargylic alcohols [14] as well as intermolecular reactions with other substrates

(e.g. in substitution reactions).[15] Thus, the search for catalyst systems that catalyze specifically one reaction over others is still ongoing.

As part of our long-range research activities in the area of catalytic activation of propargylic alcohols, we were especially interested in the substitution reaction of the –OH functionality of propargylic alcohols by other nucleophiles.[16] A number of catalyst systems are known for that reaction, and they are mainly based on transition metals such as ruthenium,[17] rhodium,[18] gold,[19] iridium,[20] copper[21] or iron.[22] However, main group compounds such as $BiCl_3$ can also catalyze propargylic substitution reactions.[23] Even Brønsted acids [24] can do so for certain substrates. Still, challenges remain. Some catalyst systems require high reaction temperatures, which may be problematic for the reaction of more highly sophisticated substrates. High reaction temperatures can also promote the catalyzed elimination of water from a propargylic starting material.[25] Furthermore, some catalyst systems are restricted to internal substrates[19] or show other substrate dependencies, like the restriction to propargylic acetates.[16a] The idea, that a proton can catalyze the substitution reaction for certain substrates appears appealing. However, a strong Brønsted acid such as HOTf may not be compatible with more highly sophisticated targets featuring other functional groups, giving rise to unwanted side reactions. Suppression of rearrangement side reactions such as the Meyer-Schuster rearrangement [16c] or others [26] can also be a challenge. As such, the search for catalyst systems that perform the reaction at reasonably low temperatures and with a high level of selectivity is still ongoing, as demonstrated by the number of publications and review articles on the topic that have appeared in the last few years.[7]

Iron catalysis is a vibrant area of research, because iron-based catalyst systems are affordable, environmentally benign and tend to be non-toxic.[27,28] Ferrocenium cations have been employed as stoichiometric oxidants in organic reactions previously,[29] but their *catalytic* activity is not very widely researched.[30,31] Recently, we disclosed that ferrocenium hexafluorophosphate, $[FeCp_2]PF_6$ (subsequently abbreviated as $FcPF_6$), catalyzes the substitution of the –OH group of aromatic propargylic alcohols by oxygen-centered nucleophiles to give the corresponding propargylic ethers (according to Scheme 1a, where Nu^- would formally be RO^-).[16c] Besides our own finding based on $FcPF_6$, we are only aware of two other iron based catalysts for the catalytic substitution of propargylic alcohols, $FeCl_3$ [15] and $[Fe(Cp)(CO)_2]^+$.[32] Interestingly, the substitution reactions catalyzed by $FcPF_6$ proceeded at 40 °C, which is lower than many other catalyst systems published by us[16] or others.[33] This led to speculation what the cause of the reduced reaction temperature for the $FcPF_6$ catalyst could be. Ferrocenium hexafluorophosphate is known to be a one electron oxidant,[29] which might enable radical reactions, and we were speculating if propargylic substitution reactions may proceed through a radical mechanism. To test this hypothesis, we decided to employ radical clock substrates in the reaction. Radical clocks rearrange when they form radicals throughout the course of a reaction, and the observation of rearranged products provides evidence for a radical mechanism.[34]

Accordingly, we decided to synthesize cyclopropyl-substituted propargylic alcohol substrates (**4** in Scheme 1c) to investigate whether the reaction proceeds through a radical mechanism. Cyclopropyl-substituted radicals **6** (Scheme 1c) may ring-open to form alkenes, but carbocation **5** may also have this tendency (*vide infra*). As exemplified in Scheme 1c, ene-ynes **7** can form

through rearrangement if a cyclopropyl-substituted propargylic alcohol **4** is employed.[35] The employment of cyclopropyl-substituted propargylic alcohols in reactions with alcohols to give conjugated, achiral enynes has been reported previously only four times, utilizing $Yb(OTf)_3$,[36a] triflic acid (TfOH),[36b] $HAuCl_4$[36c] and ruthenium complexes[36d] as catalysts. In these reports, the nucleophile was either the solvent[36b,c] or employed in large excess.[36a,d] Herein, we report ferrocenium-catalyzed substitution reactions with these substrates and isolated both ene-yne products and cyclopropyl-substituted products, depending on the substituent R in **4**. Experimental evidence points toward an ionic mechanism through carbocation **5** (Scheme 1c).[37]

Results

First, we needed to access cyclopropyl-substituted propargylic alcohols, which can be synthesized by the addition of an ethynyl anion to the carbonyl unit of the corresponding cycloalkyl ketone substrate precursors. Accordingly, the known cyclopropyl substituted propargylic alcohols **8**[36d] and **9**[36a] were synthesized following literature procedures as well as the known cyclobutyl-substituted propargylic alcohol **10** (Figure 1). [38]

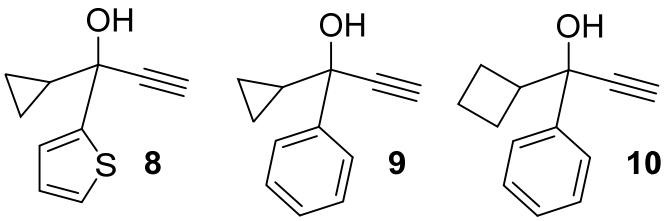
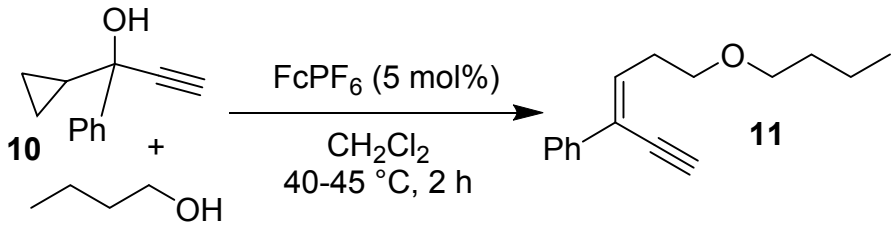


Figure 1. Propargylic alcohols utilized in the study.

From our previous work, we knew that $FcPF_6$ catalyzed the substitution of tertiary, aromatic propargylic alcohols by alcohol nucleophiles.[16c] Accordingly, we did not perform extensive

optimization efforts for the $FcPF_6$-catalyzed substitution reactions of the cyclopropyl-substituted propargylic alcohols. We assumed that our previously established reaction conditions (CH_2Cl_2 solvent, 40 °C reaction temperature, almost equimolar ratio of propargylic alcohol to alcohol nucleophile) would work for the cyclopropyl substrates as well, which turned out to be the case. For the test reaction between cyclopropyl alcohol **9** and *n*-butanol, the corresponding ene-yne product **11** (resulting from opening of the cyclopropyl ring) was obtained after 2 h at 40 °C in CH_2Cl_2 with a virtual complete conversion rate (Table 1, entry 1). No significant amounts of side products, e.g. from rearrangements as shown in Scheme 1b, were observed by GC. As investigated before, CH_2Cl_2 seems to be the solvent of choice for the reaction. The reaction also runs well in $ClCH_2CH_2Cl$ (entry 2). However, as can be seen in Table 1, solvents such as THF were less efficient (entry 3) and in toluene, the reaction did not proceed at all (presumably because the $FcPF_6$ catalyst is not sufficiently soluble in that solvent, entry 4). Some catalyst systems were reported where the alcohol nucleophile also serves as the solvent or an excess of the nucleophile over the propargylic alcohol was employed.[17,20] However, in our case, when *n*-butanol was used as the solvent, the conversion rate dropped to 25% (entry 5). It appears the alcohol solvent inhibits catalytic activity.

Table 1. Screening reactions.



Entry [a]	Solvent	Conversion (%)
1	CH_2Cl_2	97
2	$ClCH_2CH_2Cl$	95
3	THF	44
4	toluene	none
5	*n*-butanol	25%
6	CH_2Cl_2 / cat.$[CoCp_2]PF_6$	none
7	CH_2Cl_2 / TEMPO	34 [b]
8	CH_2Cl_2 / BHT	98 [c]

[a] Typical conditions: propargylic alcohol (around 0.6 mmol) and alcohol (around 0.6 mmol, equimolar) in the solvent (1 mL) catalyzed by $FcPF_6$ (5 mol%), at 40-45 °C for 2 hours. Conversions were determined by GC.
[b] In the presence of 20 mol% TEMPO for 16 h. In the presence of 100 mol% TEMPO, the conversion was 11%.
[c] In the presence of 20 or 100 mol% BHT for 16 h.

Interestingly, cobaltocenium hexafluorophosphate $[CoCp_2]PF_6$ does not catalyze the reaction (Table 1, entry 6). Cobaltocenium hexafluorophosphate is cationic but an 18 valence electron complex and not a one electron oxidant, whereas $FcPF_6$ is a 17 valence electron complex.

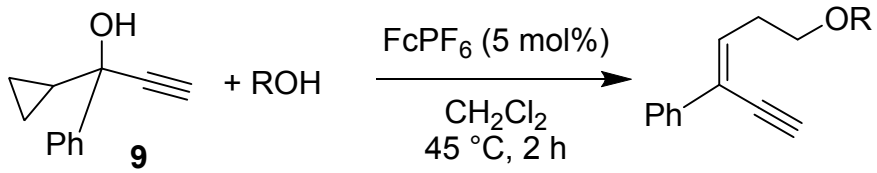
To further investigate the possibility of a radical mechanism, we performed the reaction in the presence of the radical scavengers (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) and 2,6-di-*tert*-butyl-4-methylphenol (BHT, entries 7 and 8).[39] As can be seen, BHT did not inhibit the reaction at all, and TEMPO slowed it down but did not completely stop it. This provides evidence that the reaction does not involve a free radical chain mechanism.

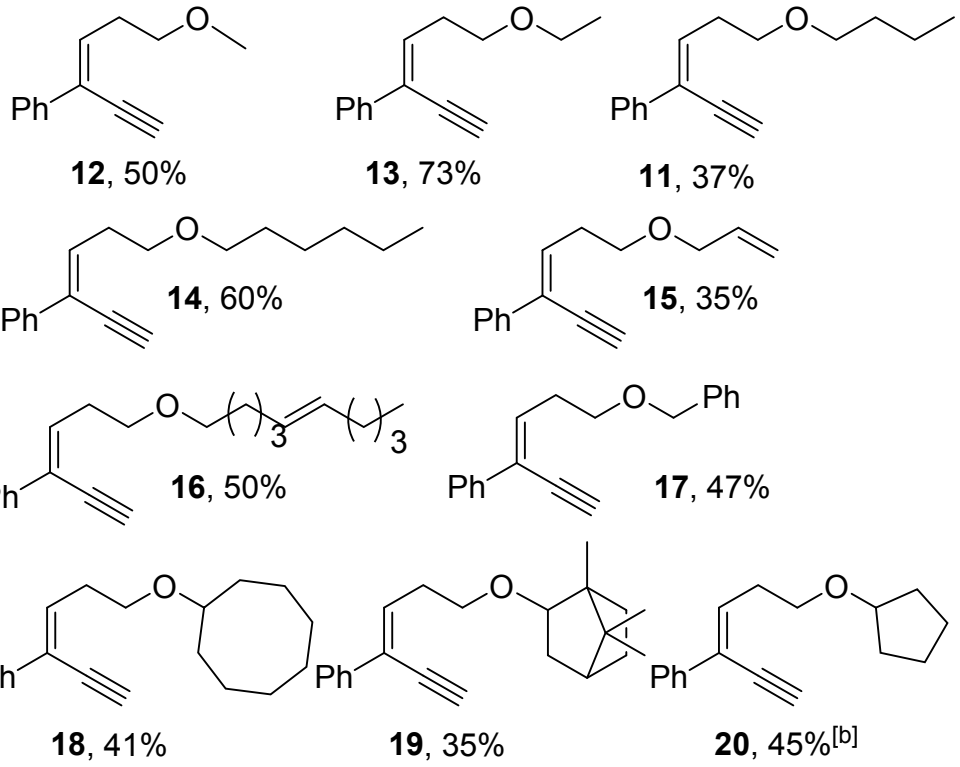
Taking the data in Table 1 together, preliminary results are somewhat inconclusive. The reaction may proceed through a radical mechanism:[40] the cyclopropyl substrate ring-opens to the ene-yne product. Cobaltocenium hexafluorophosphate, which does not act as a one-electron oxidant but possibly as a Lewis acid, is catalytically inactive. On the other hand, radical scavengers do not completely inhibit the reaction, and additional evidence collected throughout the course of our studies point toward an ionic mechanism (*vide infra*).

Next, we investigated the substrate scope of the reaction of the cyclopropyl propargylic alcohol **9** for the substitution reaction with a variety of alcohol nucleophiles (Table 2). As can be seen in Table 2, a variety of primary alcohols can be employed in the reaction to give the ene-yne products in isolated yields ranging from 35 to 73% after a 2 h reaction time. Secondary alcohols gave on average somewhat lower isolated yields of 35 to 45% (products **18** to **20**), which we tentatively attributed to the lower nucleophilicity of these alcohols. In all cases, the rearranged ene-yne products were isolated, as judged by NMR spectroscopy. Cyclopropyl rings give diagnostic peaks at around 2 and 3 ppm in their $^{13}C\{^{1}H\}$ NMR spectra and peaks below 0.8 ppm in their ^{1}H NMR spectra,[36a,b] which were absent in all products in Table 2. Furthermore, the olefinic methine =CH protons gave distinct triplets around 6.3 ppm in the ^{1}H NMR spectra, giving further evidence for the ene-yne products.[36a,b] The terminal alkyne unit was still present

in all products, as evidenced by resonances for the alkyne protons around 2.3 ppm in the ^{1}H NMR and around 83 and 80 ppm in the $^{13}C\{^{1}H\}$ NMR spectra. IR stretches around 3300 cm^{-1} were also observed for the terminal alkynes. Also, no –OH stretch for alcohols was observed in the IR spectra, demonstrating that the isolated products did not contain alcohols. In principle, all products in Table 2 can exist as *E* or *Z* isomers. However, only one product isomer was observed both by GC and NMR spectroscopy. We did not perform NOE NMR experiments for all products, but we did for **14**. We observed an NOE correlation between the olefinic methine =CH proton and a phenyl proton, pointing toward an *E* isomer. Product **13** matched literature values, which was also assigned by the authors to the *E* product.[36b] We tentatively assigned the configurations of all other products in Table 2 also to be the *E* isomers. The products in Table 2 turned out to be not very stable. They decompose in solution or in the solid state within days, and we could not obtain correct elemental analyses, they tended to be low on carbon by about 1%. Oxidative decomposition may take place, possibly catalyzed by trace amounts of iron present in the final products. GC-MS data taken of freshly prepared samples match the structures of the products and the NMR spectra exhibited baseline purity.

Table 2. Isolated yields under optimized conditions.[a]





[a] Typical conditions: propargylic alcohol (around 0.6 mmol) and alcohol (around 0.6 mmol, equimolar) in CH_2Cl_2 (1 mL) catalyzed by $FcPF_6$ (5 mol%), at 40 - 45 °C for 2 hours (in some cases, the reactions were run overnight, but were generally complete after 2 h). The products were isolated by column chromatography.
[b] With HBF_4 as catalyst.

The reaction times of 1 to 2 h to obtain the products in Table 2 are shorter than for our previously published $FcPF_6$ catalyzed reactions employing tertiary propargylic alcohols without a cyclopropyl unit (where the reaction times were between 16 h and 3 d).[16d] Consequently, it appears that the cyclopropyl unit accelerates the reaction significantly. The ring-opened ene-yne

products in Table 2 may provide evidence for a radical reaction. However, we observed by NMR and GC that first the substitution product with a ring-closed cyclopropyl unit formed, which subsequently ring-opened.

We monitored the reaction between cyclopropyl-substituted propargylic alcohol **9** and *n*-butanol over time. After about 20 minutes, the starting material was more or less consumed and the substitution product **21** with the ring-closed cyclopropyl unit had formed (as determined by GC and NMR, Scheme 2 and Figure 2). Over the course of another 20 minutes, the cyclopropyl ring opened to give the eneyne product. It was possible to intercept the intermediate **21** and purify it by column chromatography to identify its structure by NMR (albeit in only 23% isolated yield and 95% spectroscopic purity); the diagnostic peaks for the cyclopropyl ring around 2 and 3 ppm were still present in **21**. As such, the ring-closed product **21** forms first, which ring-opens in a second step to the eneyne **11**. The course of the reaction is illustrated in Figure 2, where for the reaction in Scheme 2 the relative ratios of starting material intermediate and ene-yne product are plotted versus the reaction time. As can be seen, the starting material first converts to the cyclopropyl-substituted intermediate, which then rearranges to the ene-yne product.

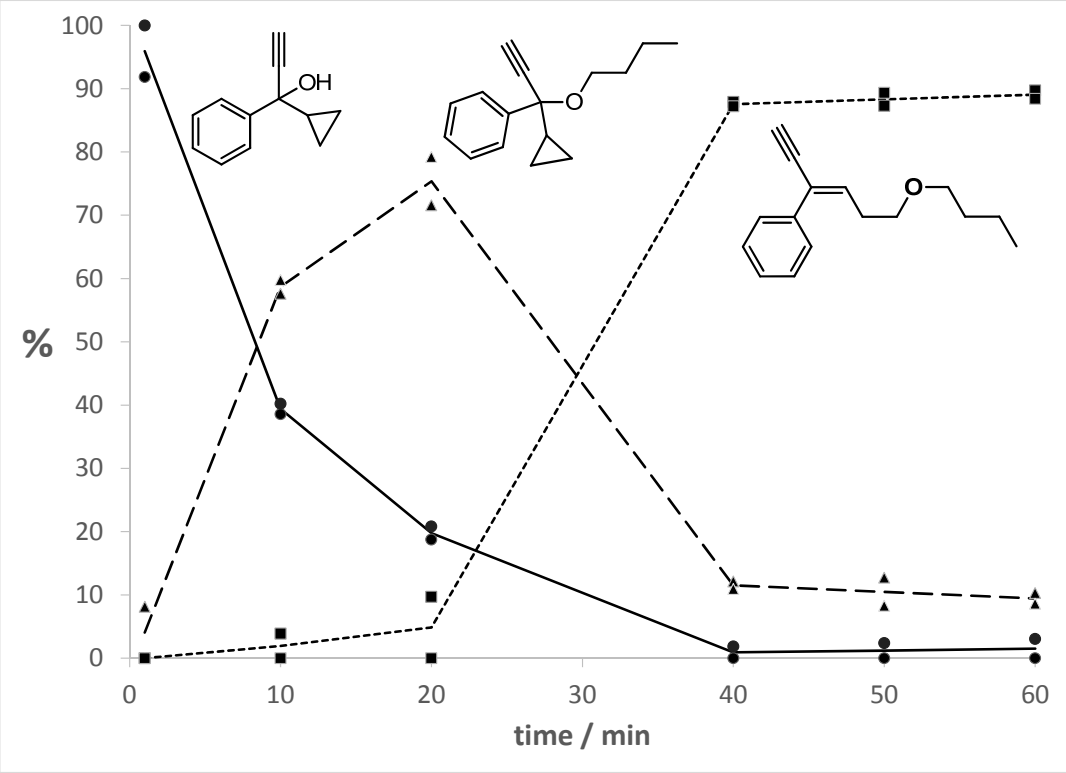
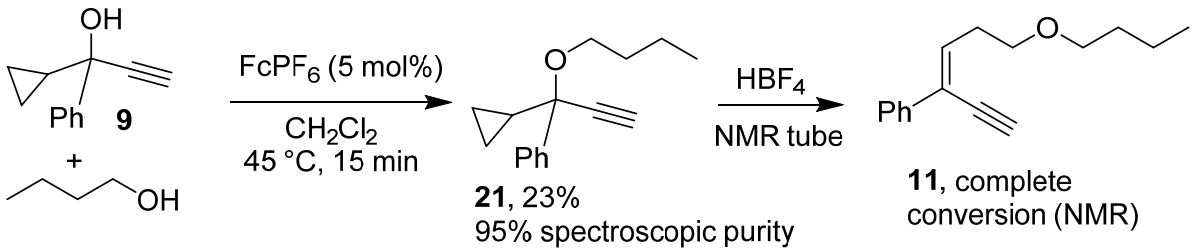


Figure 2. Formation of the ene-yne product over time, monitored by GC (average of two runs). Propargyl alcohol starting material **9**: solid line. Cyclopropyl intermediate **21**: dashed line. Ene-yne product **11**: dotted line.

This is an important observation. First, the initial formation of the ring-closed product would indicate an ionic mechanism, and the cyclopropyl substituent efficiently stabilizes that positive charge.[41] Second, it appears possible that the cyclopropyl-substituted propargylic ether **21** rearranges in the presence of a Lewis acid. To support this assumption, we added a small amount of the Brønsted acid HBF_4 to an NMR sample of the cyclopropyl-substituted propargylic ether **21** (Scheme 2). Indeed, ring opening to the ene-yne product **11** (in addition to some side products) was observed by NMR after an hour. Finally, a tertiary radical intermediate like **6** in Scheme 1c may not have a large tendency to ring-open to a primary radical. These findings

support an ionic mechanism, and that the ring-opening is possible in the presence of Brønsted acids.



Scheme 2. Formation of the cyclopropyl-substituted intermediate **21** and ring-opening

More evidence that Lewis acids can ring-open the cyclopropyl ring in **9** provides product **20** in Table 2. Ene-yne **20** was obtained with HBF_4 as the catalyst. Under these reaction conditions, it appears unlikely that radicals form, further excluding a radical mechanism for the ring-opening.

We next turned our attention to the cyclobutyl-substituted propargylic alcohol **10**. We were speculating as to whether cyclic substituents as part of the propargylic alcohol can, in general, accelerate the substitution reactions, whereas we were not expecting the cyclobutyl substituent to ring-open. Indeed, the substitution reactions also worked for this substrate with five different alcohols (Table 3), and the cyclobutyl ring system stayed intact. However, the reaction times for the cyclobutyl-substituted propargylic alcohol **10** were much longer; it took at least 8 hours for the reaction to go to completion and reactions were typically run overnight. As such, the cyclobutyl ring does not accelerate the reaction, giving the cyclopropyl substituent a special role in the substitution reactions described herein.

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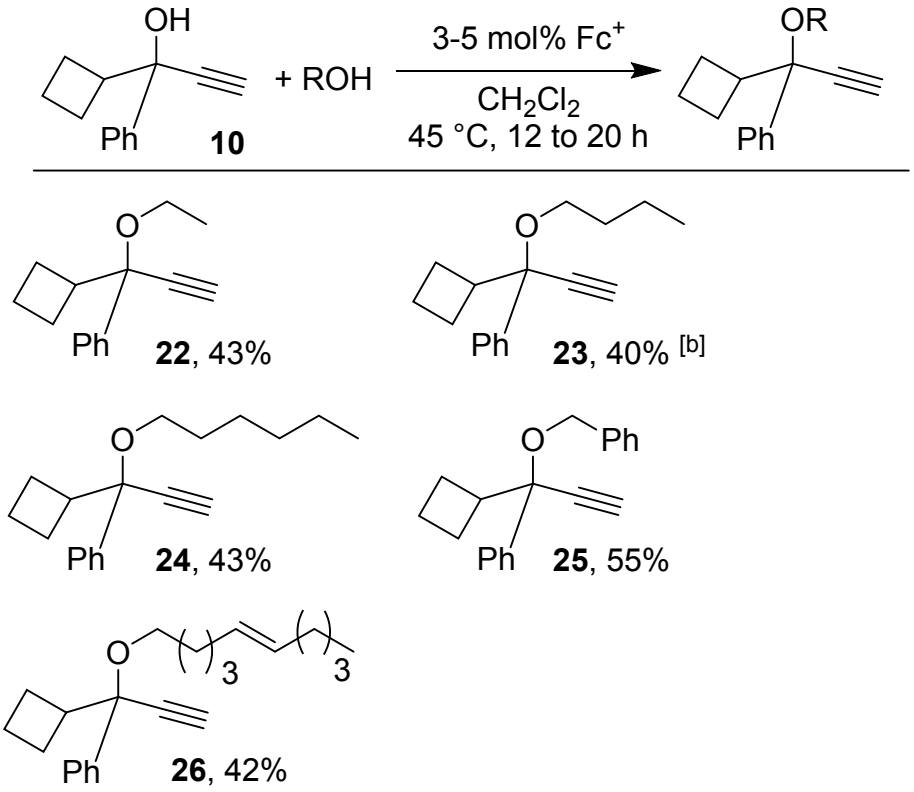
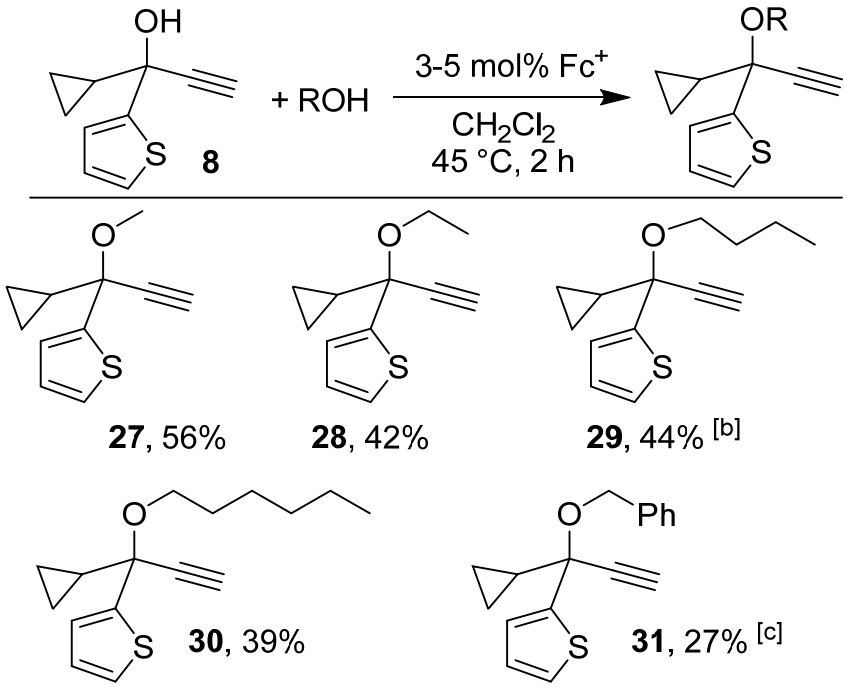
Table 3. Isolated yields under optimized conditions.[a]



[a] Typical conditions: propargylic alcohol (around 0.600 mmol) and alcohol (around 0.600 mmol) in CH_2Cl_2 (1 mL) catalyzed by $[FcB(OH)_2]SbF_6$ (3 mol%), at 45 °C for 12 to 20 hours. The products were isolated by column chromatography.
[b] $FcPF_6$ catalyst (5 mol%).

Finally, we became interested in what impact the aromatic ring substituent on the propargylic alcohol has on the course of the reaction. We employed the thiophenyl-substituted, aromatic propargylic alcohol **8** in substitution reactions (Table 4), and the results were surprising.

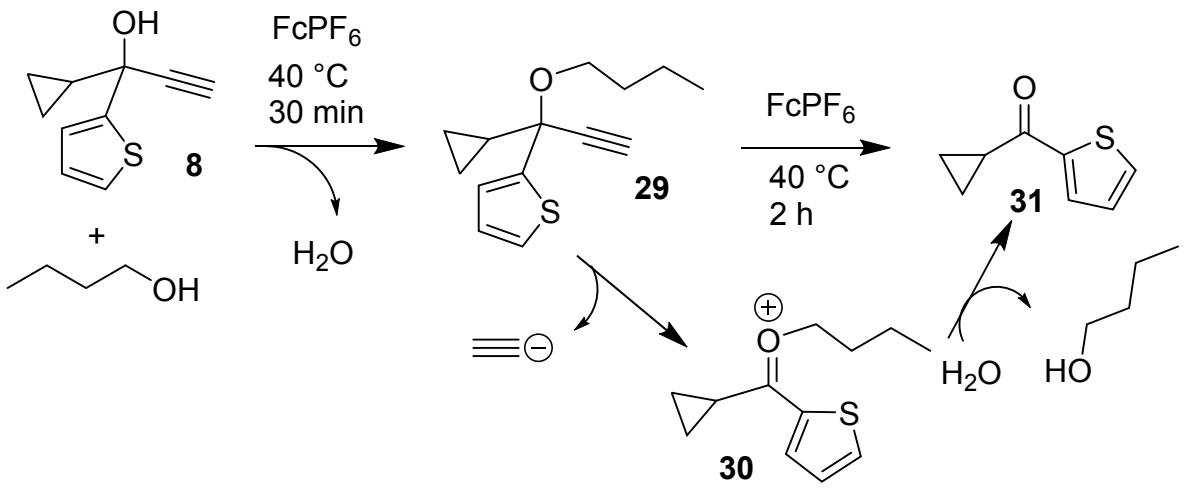
Table 4. Isolated yields under optimized conditions.[a]



[a] Typical conditions: propargylic alcohol (around 0.6 mmol) and alcohol (around 0.6 mmol) in CH_2Cl_2 (1 mL) catalyzed by $FcPF_6$ (5 mol%), at 45 °C for 1-2 hours. The products were isolated by column chromatography.
[b] $[FcB(OH)_2]SbF_6$ catalyst (3 mol%), reaction run overnight at room temperature.
[c] $FcPF_6$ 8 to 16 h reaction time at room temperature.

No ring opening of the cyclopropyl unit took place no matter the length of the reaction time. The corresponding cyclopropyl-substituted propargylic ethers were isolated in 27 to 52% isolated yields. All thiophenyl-substituted products still featured peaks around 2 and 3 ppm in the $^{13}C\{^1H\}$ NMR spectra, indicating that the cyclopropyl substituent remained intact. Another feature of the thiophenyl-substituted propargylic alcohol **8** was a dramatically increased reaction rate with $FcPF_6$ as the catalyst. As established by GC, the formation of **29** (Table 4) was 80% complete after 10 minutes and it was 100% complete after 30 minutes, which is even somewhat

faster compared to the phenyl-substituted propargylic alcohol **9**. As such, the thiophenyl substituent in **8** has an additional accelerating effect on the reaction compared to the phenyl-substituted substrate **9**. In addition, an extended reaction time of 2 h and longer resulted in conversion of the product **29** back to the ketone **31** (Scheme 3), as established by GC. Loss of the alkynyl group may give the cationic intermediate **30**, which can be hydrolyzed to the ketone **7** with the water generated during the formation of the ether **29**.



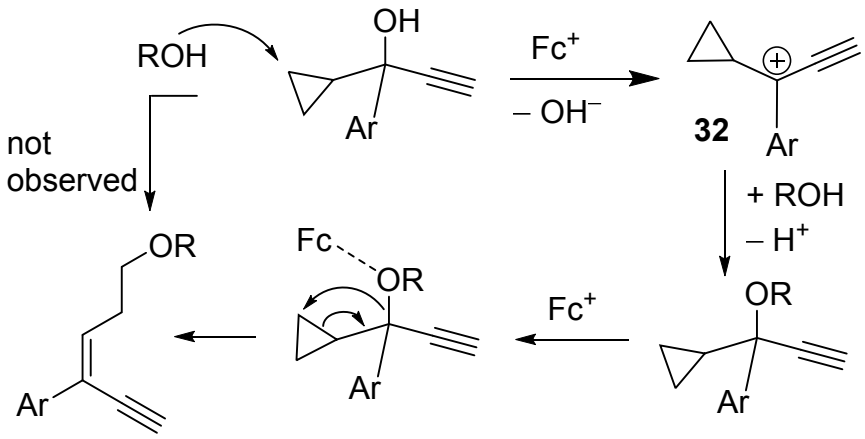
Scheme 3. Speculated reactivity of thiophene-substituted propargylic alcohol **8**.

Overall, it was determined that the course of the reaction of cyclopropyl-substituted propargylic alcohols depended on the other substituent present on the propargylic substrate. Phenyl substituents afforded the corresponding ene-yne products after one to two hours, whereas thiophenyl-substituted substrates gave only cyclopropyl-substituted products after 10 to 30 minutes. The isolated yields were moderate to good. Although we typically observed complete conversion by GC with only small amounts of side products, we also observed that we lost product during chromatographic workup. The products appeared to not be especially stable, and as exemplified in Scheme 3, may decompose over time.

Some of the reactions in Tables 3 and 4 were performed with the known ferrocenium boronic acid hexafluoroantimonate ($[FcB(OH)_2]SbF_6$) as the catalyst.[30c] This catalyst appears to be a little less reactive, as demonstrated with product **29** (Table 4), where the reaction needed to be run overnight. Ferrocenium boronic acid hexafluoroantimonate gave inseparable ring-opened and ring-closed product mixtures for the reactions in Table 2. However, for some substrates in Tables 3 and 4, they gave, as opposed to $FcPF_6$, analytically pure samples. The influence of the ferrocenium architecture and the counterion is currently under investigation.

Discussion

The above findings shed some light on the mechanism of propargylic substitution reactions and the ring-opening behavior of cyclopropyl rings. The above data clearly give evidence for an ionic, S_N1-type mechanism (Scheme 4, pathway to the right). As such, $FcPF_6$ assists in the formation of the carbocation **32**, which subsequently reacts with the nucleophilic alcohol to give the propargylic ether. The ether may rearrange, assisted by the Fc^+ ion, another Lewis acid, or a proton, to the ene-yne product, possibly through an intramolecular process. Other authors also suggested an ionic mechanism for the formation of ene-ynes from cyclopropyl-substituted propargylic alcohols.[36b]



Scheme 4. Suggested mechanistic sequence.

Several data points give evidence for an ionic mechanism. First, the initial substitution products for both cyclopropyl-substituted propargylic alcohols are the ring-closed cyclopropyl propargylic ethers. The proparglic ethers bearing a phenyl-substituent cause an opening of the cyclopropyl ring over time, whereas the ethers with a thiophenyl substituent do not. As mentioned above, the thiophenyl-substituted propargylic alcohol **8** reacts much faster than the phenyl-substituted alcohol **9**. The thiophenyl substituent is more electron-rich, facilitating the formation of the carbocation intermediate **32** in Scheme 4. The cyclobutyl-substituted propargylic alcohol **10** is the least reactive among those tested in this study, requiring a longer reaction time of at least 8 hours. The cyclobutyl substituent in **10** seems to behave like a "regular" substituent in a tertiary propargylic alcohol. We tested tertiary propargylic alcohols with a methyl instead of a cyclopropyl substituent in previous work, and they also required reaction times above 8 hours.[16c] As such, the cyclopropyl ring alone activates the propargylic alcohols for nucleophilic substitution reactions compared to an alkyl substituent. This is in line with the increased aptitude of the cyclopropyl ring to stabilize a positive charge (as in **32**) compared to a methyl substituent,[41] further supporting an ionic mechanism.

As such, a radical mechanism appears unlikely. Some radical ring opening mechanisms were reported to proceed under oxidative conditions with an oxidant present in stoichiometric amounts.[40] We employed $FcPF_6$ (potentially an oxidant) in catalytic amounts. Finally, the ring-opening could also take place by direct attack of the alcohol on the cyclopropyl ring (Scheme 4, left pathway). However, such a direct attack is primarily observed with electrophilic cyclopropanes,[42] and the cyclopropyl substituents in our starting material may just not be electrophilic enough.

An open question, however, is why the phenyl-substituted cyclopropyl ether **21** rearranges to the ene-yne product **11** under ionic conditions (Scheme 2), and the thiophenyl-substituted ethers do not. As shown in the experiment in Scheme 2 and mechanistically depicted in Scheme 4, a Lewis acid may catalyze the rearrangement from a cyclopropyl-substituted propargylic alcohol to the corresponding ene-yne. One explanation may be that the sulfur atom in the thiophenyl ring system disturbs the ring opening process.

Some of the yields of the reactions in Tables 2 to 4 were only moderate. However, with the exception of product **13** in Table 2, all catalysis products are new. Especially the quaternary, cyclobutyl- and thiophenyl-substituted propargyl ethers constitute a new class of compounds, to which the ferrocenium catalysts provide a new synthetic pathway. This is of importance, because some ene-ynes[43] and propargylic ethers[44] were demonstrated to exhibit pharmaceutical activity.

Conclusion

We demonstrated that ferrocenium cations serve as catalysts in the substitution of –OH groups in propargylic alcohols by alcohol nucleophiles. Cyclopropyl-substituted propargylic alcohols

afforded ene-ynes through ring opening of the cyclopropyl ring, which took place after the substitution reaction. Thiophenyl- and cyclobutyl-substituted propargylic alcohols afforded the corresponding propargylic ethers, and no ring-opening took place. These quaternary propargylic alcohols with a thiophenyl- and cyclopropyl ring are a new compound class, to which ferrocenium catalysts provide access. We think carbocation intermediates formed during the reaction, because electron-rich substituents accelerated the reaction and the substitution itself took place without cyclopropyl ring-opening, which may be more prevalent when a radical intermediate forms. Also, radical scavengers did at best slow down the reaction but did not completely inhibit it.

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Supplementary data

^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of all catalysis products in Tables 2 to 4 and for the reaction in Scheme 2. Supplementary data associated with this article can be found, in the online version, at xxx.

Experimental

General. All chemicals, ferrocenium hexafluorophosphate ($FcPF_6$) and cobaltocenium hexafluorophosphate ($[CoCp_2]PF_6$) were used as supplied from Sigma-Aldrich. CH_2Cl_2 was

freshly distilled from CaH_2. 1-Cyclopropyl-1-phenylprop-2-yn-1-ol (**9**),[36a] 1-cyclopropyl-1-(thiophen-2-yl)prop-2-yn-1-ol (**8**),[36d] 1-cyclobutyl-1-phenylprop-2-yn-1-ol (**10**),[38] and ferrocenium boronic acid hexafluoroantimonate ($[FcB(OH)_2]SbF_6$) were synthesized following the literature.[30c] All NMR spectra for characterization were collected at room temperature on a Bruker Avance 300 MHz instrument; all chemical shifts (δ) are reported in ppm and are referenced to a residual solvent signal. All assignments are tentative. IR spectra were collected on a Thermo Nicolet 360 FT-IR spectrometer. HRMS measurements were performed on a MaXis plus quadrupole time-of-flight mass spectrometer (Bruker) with atmospheric pressure photoionization (APPI). EI masses were recorded on a HP 5988A GC-MS instrument. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA, USA.

(6-Methoxyhex-3-en-1-yn-3-yl)benzene (**12,** Table 2): In a screw-cap pressure vial, 1-phenyl-1-cyclopropyl-2-yne-1-ol (0.100 g, 0.581 mmol) was dissolved in CH_2Cl_2 (2 mL). Methanol (0.0185 g, 0.593 mmol) and $FcPF_6$ (0.010 g, 0.030 mmol) were added and the sealed vial was heated at 45 °C for 2.5 hours. The reaction mixture was filtered through a short pad of silica gel using CH_2Cl_2 (2–4 mL). The product was obtained by column chromatography on alumina (2.5 × 30 cm, 9:1 v/v hexanes : EtOAc) as an orange colored oil (0.054 g, 0.290 mmol, 50%). ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.69–7.65 (m, 2H, aromatic), 7.42–7.31 (m, 3H, aromatic), 6.61 (t, J_{HH} = 7 Hz, C=CH, 1H), 3.60 (t, J = 7 Hz, 2H, OCH_2), 3.44 (s, 3H, CH_3), 3.41 (s, ≡CH, 1H), 2.86 (q, J_{HH} = 7 Hz, 2H, OCH_2) ppm; $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ =137.5 (s, *C*=CH), 136.2 (s, aromatic), 128.4 (s, aromatic), 127.8 (s, aromatic), 126.0 (s, aromatic), 124.1 (s, C=*C*H), 83.5 (s, HC≡), 80.7 (s, HC≡*C*), 71.5 (s, =C*C*H_2), 58.7 (s, CH_2O), 31.7 (s, CH_3); IR (ATR, neat): $\tilde{\nu}$ = 3283 (m), 2922 (m), 2870 (m), 2825 (m) cm^{-1}; MS (70 eV): *m*/*z* (%):

185 (30) $[M–H]^+$, 171 (10) $[M–CH_3]^+$, 156 (50) $[M+H–OCH_3]^+$, 141 (100) $[M–C_2H_5O]^+$, 128 (60) $[M+H–C_3H_7O]^+$, 115 (100) $[M+H–C_4H_8O]^+$, 45 (90) $[C_2H_5O]^+$.

6-Ethoxy-3-phenyl-3-en-1-yne (**13**, Table 2):[36b] In a screw cap pressure vial, 1-phenyl-1-cyclopropyl-2-yne-1-ol (0.116 g, 0.623 mmol) was dissolved in CH_2Cl_2 (2 mL). Ethanol (0.031 g, 0.674 mmol) and $FcPF_6$ (0.010 g, 0.030 mmol) were added and the sealed vial was heated at 45 °C for 75 minutes. The reaction mixture filtered through a short pad of silica gel and the filtrate was chromatographed (2 × 30 cm alumina, 1:1 v/v EtOAc/hexanes 1:9) to obtain the product 6-ethoxy-3-phenyl-3-en-1-yne (0.091 g, 0.455 mmol, 73%) as an orange oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.66 (d, J_{HH}=7.0 Hz, 2H, aromatic), 7.46–7.31 (m, 3H, aromatic), 6.61 (t, J_{HH}=7.4 Hz, C=C*H*, 1H), 3.65–3.54 (m, 4H, CH_2OCH_2), 3.28 (s, ≡C*H*, 1H), 2.72 (q, J_{HH}=7.0 Hz, 2H, CH_2CH_3), 1.15 (t, J_{HH}=7.0 Hz, 3H, CH_3) ppm; $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ = 137.5 (s, *C*=CH), 136.4 (s, aromatic), 128.4 (s, aromatic), 127.7 (s, aromatic), 126.0 (s, aromatic), 124.0 (s, C=*C*H), 83.4 (s, C≡*C*H), 80.7 (s, *C*≡CH), 69.3 (s, OCH_2), 66.2 (s, C=CHCH_2), 31.9 (s, *C*HCH_2O), 15.5 (s, CH_3) ppm.

(6-Butoxyhex-3-en-1-yn-3-yl) benzene (**11,** Table 2): In a screw cap pressure vial, 1-phenyl-1-cyclopropyl-2-yne-1-ol (0.105 g, 0.610 mmol) was dissolved in CH_2Cl_2 (2 mL). *n*-Butanol (0.045 g, 0.608 mmol) and $FcPF_6$ (0.010 g, 0.030 mmol) were added and the vial was sealed and heated at 45 °C for 2 hours. The reaction mixture was filtered through silica gel, using CH_2Cl_2 (2–4 mL). The product was obtained by column chromatography on alumina (2.5 × 30 cm, 9:1 v/v hexanes : EtOAc) as a yellow colored oil (0.052 g, 0.228 mmol, 37%). ^{1}H NMR (300 MHz,

$CDCl_3$): δ =7.53–7.51 (m, 2H, aromatic), 7.28–7.16 (m, 3H, aromatic), 6.48 (t, 1H, $^2J_{HH}$=7 Hz, =CH), 3.49 (t, $^2J_{HH}$=7 Hz, 2H, OCH_2), 3.38 (t, 2H, $^2J_{HH}$=7 Hz, OCH_2), 3.27 (s, 1H, ≡CH), 2.72 (q, $^2J_{HH}$=7 Hz, 2H, CH_2), 1.54–1.34 (m, 2H, CH_2), 1.36–1.26 (m, 2H, CH_2), 0.85 (t, 3H, $^2J_{HH}$=7 Hz, CH_3) ppm; $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ = 137.6 (s, *C*=CH), 136.5 (s, aromatic), 128.4 (s, aromatic), 127.7 (s, aromatic), 126.0 (s, aromatic), 123.9 (s, C=*C*H), 83.4 (s, C≡*C*H), 80.8 (s, *C*≡CH), 70.8 (s, OCH_2), 69.5 (s, OCH_2), 31.90 (s, CH_2), 31.86 (s, CH_2), 19.4 (s, CH_2), 14.0 (s, CH_3) ppm; IR (ATR, neat): $\tilde{\nu}$ = 3288 (m), 3055 (w), 2973 (m), 2926 (w) cm^{-1}; MS (70 eV): *m*/*z* (%): 185 (20) $[M–C_3H_7]^+$, 155 (15) $[M–C_4H_9O]^+$, 141 (50) $[M–C_5H_{11}O]^+$, 128 (40) $[M–C_6H_{12}O]^+$, 115 (50) $[M–C_7H_{13}O]^+$, 57 (100) $[C_4H_9]^+$.

(6-(Hexyloxy)hex-3-en-1-yn-3-yl)benzene (**14,** Table 2): 1-Cyclopropyl-1-phenylprop-2-yn-1-ol (0.103 g, 0.598 mmol) was added to a screw cap pressure vial and dissolved in CH_2Cl_2 (2 mL). 1-Hexanol (0.075 g, 0.669 mmol) was added followed by $FcPF_6$ (0.012 g, 0.037 mmol). The sealed vial was then heated to 45 °C for 2 hours. The mixture was filtered through a short pad of silica using CH_2Cl_2 (2–4 mL). The product was obtained by chromatography on a neutral alumina oxide (Aluminar®) column (2.5 × 30 cm, 9:1 v/v hexanes : EtOAc) to give the product as a yellow colored oil (0.093 g, 0.361 mmol, 60%). ^1H NMR (300 MHz, $CDCl_3$): δ =7.54–7.51 (m, 2H, aromatic), 7.28–7.19 (m, 3H, aromatic), 6.48 (t, $^2J_{HH}$ = 7 Hz, 1H, alkene), 4.07 (s, 0.16H, ferrocene), 3.48 (t, $^2J_{HH}$ = 7 Hz, 2H), 3.36 (t, $^2J_{HH}$ = 7 Hz, 2H), 3.26 (s, 1H), 2.75–2.68 (q, $^2J_{HH}$ = 7 Hz, 2H), 1.50 (q, $^2J_{HH}$ = 7 Hz, 2H), 1.31–1.22 (m, 6H), 0.80 (t, $^2J_{HH}$ = 7 Hz, 3H)

ppm; $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ = 137.6 (s, *C*=CH), 136.5 (s, aromatic), 128.4 (s, aromatic), 127.8 (s, aromatic), 126.0 (s, aromatic), 124.0 (s, C=*C*H), 83.5 (s, C≡*C*H), 80.8 (s, *C*≡CH), 71.1 (s, CH_2O), 69.5 (s, CH_2O), 68.0 (s, trace amount ferrocene), 31.9 (s, CH_2), 31.8 (s, CH_2), 29.8 (s, CH_2), 26.0 (s, CH_2), 22.7 (s, CH_2), 14.2 (s, CH_3) ppm; IR (ATR, neat): $\tilde{\nu}$ = 3288 (m), 3060 (w), 3024 (w), 2927 (s), 2854 (s), 2790 (m) cm^{-1}; MS (70 eV): *m*/*z* (%): 255 (5) $[M–1]^+$, 155 (30) $[M–C_6H_{13}O]^+$, 141 (100) $[M–C_7H_{15}O]^+$, 128 (70) $[M–C_8H_{16}O]^+$, 115 (95) $[M–C_9H_{17}O]^+$; HRMS (APPI): *m*/*z* calcd for $C_{18}H_{25}O$: 257.1905 $[M+H]^+$; found: 257.1900.

6-Alloxy-3-phenyl-3-en-1-yne (**15,** Table 2): In a screw cap pressure vial, 1-phenyl-1-cyclopropyl-2-yne-1-ol (0.094 g, 0.547 mmol) was dissolved in CH_2Cl_2 (2 mL). Allyl alcohol (0.031 g, 0.534 mmol) and $FcPF_6$ (0.010 g, 0.030 mmol) was added and the vial was sealed and heated at 45 °C overnight. The reaction mixture was filtered through a short pad of silica gel with CH_2Cl_2 (2–4 mL). The product was obtained by column chromatography on alumina (2.5 × 30 cm, 9:1 v/v hexanes : EtOAc) as an orange colored oil (0.041 g, 0.193 mmol, 35%). ^1H NMR (300 MHz, $CDCl_3$): δ =7.54–7.49 (m, 2H, aromatic), 7.28–7.19 (m, 3H, aromatic), 6.48 (t, J_{HH} = 7 Hz, C=CH, 1H), 5.90–5.80 (m, CH=CH_2, 2H), 4.16 (t, J_{HH} = 5.48 Hz, OCH_2, 2H), 3.93 (t, J_{HH} = 7 Hz, OCH_2, 2H), 3.52 (t, J_{HH} = 7.4 Hz, OCH_2CH_2, 2H), 3.27 (s, C≡CH, 1H), 2.73 (q, J_{HH} = 7.3 Hz, CHCH_2, 2H) ppm; $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ =137.5 (s, C=), 136.4 (s, aromatic), 136.2 (s, C=), 128.4 (s, aromatic), 127.8 (s, aromatic), 126.0 (s, aromatic), 124.1 (s, C=), 117.1 (C=*C*H_2), 83.5 (s, C≡*C*H), 80.7 (s, *C*≡CH), 71.9 (s, OCH_2), 69.1 (s, OCH_2), 68.0 (s, trace amount ferrocene), 31.9 (s, =CH*C*H_2) ppm; IR (ATR, neat): $\tilde{\nu}$ = 3267 (m), 3023 (w), 2853

(m) cm^{-1}; MS (70 eV): *m*/*z* (%): 184 (10) $[M–C_2H_4]^+$, 155 (20) $[M–C_3H_5O]^+$, 141 (50) $[M–C_4H_7O]^+$, 128 (40) $[M–C_5H_8O]^+$, 115 (50) $[M–C_6H_9O]^+$, 41 ($[C_3H_5]^+$, 100%).

6-(*trans*-5-Decoxy)-3-phenyl-3-en-1-yne (**16,** Table 2): In a screw cap pressure vial, 1-phenyl-1-cyclopropyl-2-yne-1-ol (0.110 g, 0.639 mmol) was dissolved in CH_2Cl_2 (2 mL) and *trans*-5-decanol (0.100 g, 0.641 mmol) and $FcPF_6$ (0.010 mg, 0.030 mmol) were added. The sealed vial was heated at 45 °C for 2 hours. The reaction mixture was filtered through a short pad of silica gel by using CH_2Cl_2 (2–4 mL). The product was obtained by column chromatography on alumina (2.5 × 30 cm, 9:1 v/v hexanes : EtOAc) as an orange colored oil (0.099 g, 0.319 mmol, 50%). ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.54–7.52 (m, 2H, aromatic), 7.29–7.18 (m, 3H, aromatic), 6.49 (t, J_{HH}=7 Hz, 1H, C=CH), 5.32 (q, J_{HH}=3 Hz, 2H, *H*C=C*H*), 3.50 (t, J_{HH} = 7 Hz, 2H, OCH_2), 3.36 (t, J_{HH} = 7 Hz, 2H, OCH_2), 3.27 (s, 1H, ≡CH), 2.72 (q, J_{HH} = 7 Hz, 2H, CH_2), 1.96–1.80 (m, 4H, $2CH_2$), 1.55–1.47 (m, 2H, CH_2), 1.39–1.31 (m, 2H, CH_2), 1.29–1.22 (m, 4H, $2CH_2$), 0.82 (t, J_{HH} = 7 Hz, 3H, CH_3) ppm; $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ = 137.6 (s, C=), 136.5 (s, aromatic), 130.8 (s, C=), 130.0 (s, C=), 128.4 (s, aromatic), 127.7 (s, aromatic), 126.0 (s, aromatic), 123.9 (s, C=*C*H), 83.4 (s, C≡*C*H), 80.8 (s, *C*≡CH), 70.9 (s, OCH_2), 69.5 (s, OCH_2), 32.4 (s, CH_2), 32.4 (s, CH_2), 31.89 (s, CH_2), 31.85 (s, CH_2), 29.2 (s, CH_2), 26.2 (s, CH_2), 22.3 (s, CH_2), 14.1 (s, CH_3) ppm; MS (70 eV): *m*/*z* (%): 309 (5) $[M–1]^+$, 155 (30) $[M–C_{10}H_{19}O]^+$, 141 (60) $[M–C_{11}H_{21}O]^+$, 128 (50) $[M–C_{12}H_{22}O]^+$, 115 (100) $[M–C_{13}H_{23}O]^+$; IR (ATR, neat): $\tilde{\nu}$ = 3289 (m), 3021 (w), 2923 (s), 2853 (s), 2790 (w) cm^{-1}.

6-Benzoxy-3-phenyl-3-en-1-yne (**17,** Table 2): In a screw cap pressure vial, 1-phenyl-1-cyclopropyl-2-yne-1-ol (0.108 g, 0.627 mmol) was dissolved in CH_2Cl_2 (2 mL) and benzyl alcohol (0.068 g, 0.630 mmol) and $FcPF_6$ (0.010 g, 0.030 mmol) were added. Then the vial was sealed and heated at 45 °C for 75 minutes. The reaction mixture was filtered through a short pad of silica gel using CH_2Cl_2 (2-4 mL). The product 6-benzoxy-3-phenyl-3-en-1-yne was obtained by column chromatography on alumina (2.5 × 30 cm, 9:1 v/v hexanes : EtOAc) as an orange colored oil (0.077 g, 0.294 mmol, 47%). ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.63–7.59 (m, 2H, aromatic), 7.37–7.26 (m, 8H, aromatic), 6.57 (t, $^2J_{HH}$ = 7 Hz, C=CH, 1H), 4.55 (s, 2H, OCH_2Ph), 4.16 (0.5 H, ferrocene), 3.36 (t, $^2J_{HH}$ = 7 Hz, 2H, OCH_2), 3.35 (s, 1H, C≡CH), 2.85 (q, $^2J_{HH}$ = 7 Hz, 2H, CHCH_2) ppm; $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ = 138.4 (s, C=), 137.6 (s, aromatic), 136.42 (s, aromatic), 136.38 (s, aromatic), 128.53 (s, aromatic), 128.49 (s, aromatic), 127.8 (s, aromatic), 127.7 (s, aromatic), 126.0 (s, aromatic), 124.2 (s, =C), 83.7 (s, C≡*C*H), 80.8 (s, *C*≡CH), 73.0 (s, OCH_2), 69.1 (s, OCH_2), 31.9 (s, CH*C*H_2) ppm; MS (70 eV): *m*/*z* (%): 261 (5) [*M*–1]$^+$, 141 (20) [*M*–C_8H_9O]$^+$, 114 (20) [*M*–$C_{10}H_{12}O$]$^+$, 91 (100) [C_7H_7]$^+$; IR (ATR, neat): $\tilde{\nu}$ = 3282 (w), 3026 (m), 2853 (m) cm^{-1}.

((4-Phenylhex-3-en-5-yn-1-yl)oxy)cyclooctane (**18,** Table 2): 1-phenyl-1-cyclopropyl-2-yne-1-ol (0.071 g, 0.413 mmol) was added to a screw cap vial and dissolved in CH_2Cl_2 (1 mL). Cyclooctanol (0.076 g, 0.593 mmol) was added followed by the addition of $FcPF_6$ (0.012 g, 0.037 mmol). The sealed vial was heated to 45 °C for 100 minutes. The solvent was removed, and the residue was chromatographed on a neutral alumina (Aluminar®) column (2.5 × 30 cm, 9:1 v/v hexanes : EtOAc) to give the product as an orange colored oil (0.060 g, 0.213 mmol, 52%). For further purification, the product was chromatographed on a silica column (2.5 × 10

cm, 9:1 v/v hexanes : EtOAc) to give the product as a yellow colored oil (0.048 g, 0.170 mmol, 41%). ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.54–7.50 (m, 2H, aromatic), 7.28–7.16 (m, 3H, aromatic), 6.49 (t, $^{2}J_{HH}$ = 7Hz, 1H, =CH), 4.08 (s, 0.16H, ferrocene), 3.49 (t, $^{2}J_{HH}$ = 7 Hz, 2H, CH_2), 3.39–3.33 (m, 1H, *H*COH), 3.26 (s, 1H, C≡CH), 2.69 (q, $^{2}J_{HH}$ = 7 Hz, 2H), 1.80–1.30 (m, 14H, 7CH_2) ppm; $^{13}C\{^{1}H\}$ (75 MHz, $CDCl_3$): δ =137.6 (s, =C), 136.8 (s, aromatic), 128.4 (s, aromatic), 127.8 (s, aromatic), 126.0 (s, aromatic), 123.8 (s, =C), 83.4 (s, C≡*C*H), 80.8 (s, *C*≡CH), 79.9 (s, *C*H_2O), 68.0 (s, trace amount ferrocene), 66.9 (s, *C*HO), 32.3 (s, CH_2), 31.6 (s, CH_2), 27.4 (s, CH_2), 25.5 (s, CH_2), 23.2 (s, CH_2) ppm; IR (ATR, neat): $\tilde{\nu}$ = 3289 (m), 3026 (w), 2915 (s), 2849 (s) cm^{-1}; MS (70 eV): *m*/*z* (%): 281 (5) $[M-1]^+$, 141(80) $[M-C_9H_{17}O]^+$, 128 (75) $[M-C_{10}H_{18}O]^+$, 114 (100) $[M-C_{11}H_{20}O]^+$; HRMS (APPI): *m*/*z* calcd for $C_{20}H_{27}O$: 283.2061 $[M+H]^+$; found: 283.2056.

1,7,7-Trimethyl-2-((4-phenylhex-3-en-5-yn-1-yl)oxy)bicyclo[2.2.1]heptane (**19,** Table 2): 1-phenyl-1-cyclopropyl-2-yne-1-ol (0.100 g, 0.581 mmol) was added to a screw cap vial and dissolved in CH_2Cl_2 (1 mL). *l*-Borneol (1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol, 0.089 g, 0.576 mmol) was added followed by the addition of $FcPF_6$ (0.010 g, 0.037 mmol). The vial was heated to 45 °C for 120 minutes. The solvent was removed, and the residue was chromatographed on a neutral alumina oxide (Aluminar®) column (2.5 × 30 cm, 9:1 v/v hexanes: EtOAc) to give the product as an orange colored oil (0.063 g, 0.204 mmol, 35%). ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.53–7.50 (m, 2H, aromatic), 7.28–7.16 (m, 3H, aromatic), 6.50 (t, J_{HH} = 7 Hz, 1H, =CH), 4.07 (s, 0.4H, ferrocene), 3.55–3.42 (m, 3H), 3.27 (s, 1H, ≡CH), 2.68 (q, $^{2}J_{HH}$ = 7 Hz, 2H), 2.05–1.89

(m, 2H), 1.62–1.53 (m, 2H), 1.19–1.11 (m, 2H), 0.94 (dd, J_{HH} = 13 Hz, J_{HH} = 3 Hz, 1H), 0.80 (s, 3H), 0.76 (s, 6H) ppm; $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ =137.7 (s, =C), 137.2 (s, aromatic), 128.4 (s, aromatic), 127.7 (s, aromatic), 125.9 (s, aromatic), 123.6 (s, =C), 84.7 (s, C≡*C*H), 83.3 (s, OCH), 80.9 (s, *C*≡CH), 68.9 (s, CH_2O), 68.0 (trace amount ferrocene), 49.3 (s, CH), 47.8 (s, CH), 45.0 (s, CH), 36.4 (s, CH), 32.3 (s, CH), 28.4 (s, CH), 26.7 (s, CH), 19.9 (s, CH_3), 18.9 (s, CH_3), 14.1 (s, CH_3) ppm; IR (ATR, neat): $\tilde{\nu}$ = 3303 (m), 3056 (w), 3024 (w), 2945 (s), 2869 (s) cm^{-1}; HRMS (APPI): *m*/*z* calcd for $C_{22}H_{29}O$: 309.2218 $[M+H]^+$; found: 309.2210.

(6-(Cyclopentyloxy)hex-3-en-1-yn-3-yl)benzene (**20,** Table 2): 1-Cyclopropyl-1-phenylprop-2-yn-1-ol (0.103 g, 0.598 mmol) was added to a 5-mL screw cap vial and dissolved in CH_2Cl_2 (1 mL). Cyclopentanol (0.050 g, 0.581 mmol) was added followed by the addition of HBF_4 (ca 5.0 μL of a diethyl ether complex). The vial was then heated at 40 °C for 1 hour and the solvent was removed. The residue was chromatographed on a neutral alumina oxide (Aluminar®) column (2.5 × 30 cm, 9:1 v/v hexanes : EtOAc) to give the product as an orange oil (0.065 g, 0.270 mmol, 45 %). ^1H NMR (300 MHz, $CDCl_3$): δ =7.69–7.65 (m, 2H, aromatic), 7.43–7.31 (m, 3H, aromatic), 6.62 (t, 1H, $^2J_{HH}$=7 Hz, C=C*H*), 4.02–3.97 (m, 1H, OCH), 3.60 (t, 2H, $^2J_{HH}$ = 7 Hz, OCH_2), 3.42 (s, 1H, C≡C*H*), 2.84 (q, 2H, $^2J_{HH}$ = 7 Hz, OCH_2CH_2), 1.84–1.50 (m, 8H, 4CH_2) ppm; $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ = 137.6 (s, =C), 136.7 (s, aromatic), 128.4 (s, aromatic), 127.7 (s, aromatic), 125.9 (s, aromatic), 123.9 (s, =C), 83.4 (s, H*C*≡C), 81.4 (s, O*C*H), 80.8 (s, HC≡*C*), 67.5 (s, CH_2O), 32.4 (s, CH_2), 32.2 (s, CH_2), 23.6 (s, CH_2) ppm. MS (70 eV):

m/*z* (%): 239 (10) [*M*–H]$^+$, 141 (100) [$C_6H_{11}O$]$^+$, 128 (70) [*M*–$C_7H_{12}O$]$^+$, 114 (75) [*M*–$C_8H_{14}O$]$^+$, 69 (50) [C_5H_9]$^+$.

(1-Cyclobutyl-1-ethoxyprop-2-yn-1-yl)benzene (**22,** Table 3): In a screw-cap pressure vial, 1-cyclobutyl-2-yn-ol (0.100 g, 0.537 mmol) was dissolved in CH_2Cl_2 (1 mL) and ethanol (0.025 g, 0.543 mmol) and [$FcB(OH)_2$]SbF_6 (0.008 g, 0.017 mmol) were added. Then the vial was heated at 45 °C overnight. The product was filtered through a short pad of silica gel using CH_2Cl_2 (2–4 mL). The product (1-cyclobutyl-1-ethoxyprop-2-yn-1-yl)benzene was obtained by column chromatography on alumina (2.5 × 30 cm, 9:1 v/v hexanes : EtOAc) as a yellow colored oil (0.050 g, 0.233 mmol, 43%). ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.46–7.43 (m, 2H, aromatic), 7.27–7.16 (m, 3H, aromatic), 3.58–3.53 (dd, 1H, J_{HH} = 7 Hz, J_{HH} = 2.1 Hz, OC*H*H'), 3.12–3.07 (dd, 1H, J_{HH} = 7.2 Hz, J_{HH} = 1.8 Hz, OCH*H*'), 2.64 (s, 1H, C≡C*H*), 2.60 (q, J_{HH} = 8 Hz, CH), 2.19 (qint, J_{HH} = 10.5 Hz, 1H, CH), 1.89–1.86 (m, 2H, 2CH), 1.65–1.60 (m, 3H, 3CH), 1.11 (t, J_{HH} = 7.0 Hz, 3H, CH_3) ppm; ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ = 140.8 (s, aromatic), 128.0 (s, aromatic), 127.6 (s, aromatic), 126.3 (s, aromatic), 82.2 (s, C≡C), 81.8 (s, C≡C), 76.5 (s, *C*C≡CH), 47.1 (s, CH), 23.8 (s, CH_2), 23.5 (s, CH_2), 16.2 (s, CH_2), 15.4 (s, CH_3) ppm; IR (ATR, neat): ṽ = 3303 (m), 3056 (w), 3024 (w), 2945 (s), 2869 (s) cm^{-1}; MS (70 eV): *m*/*z* (%): 214 (5) [*M*]$^+$, 159 (20) [*M*–C_4H_7]$^+$, 115 (50) [*M*+H–C_4H_7–OCH_2CH_3]$^+$, 77 (40) [Ph]$^+$, 53 (100) [C_4H_5]$^+$; HRMS (APPI): *m*/*z* calcd for $C_{15}H_{18}O$, 214.1357 [*M*]$^+$; found 214.1360; elemental analysis calcd (%) for $C_{15}H_{18}O$: C 84.07, H 8.47; found: C 83.88, H 8.28.

(1-Cyclobutyl-1-butoxyprop-2-yn-1-yl)benzene (**23,** Table 3): In a screw-cap pressure vial, 1-cyclobutyl-2-yn-ol (0.100 g, 0.537 mmol) was dissolved in CH_2Cl_2 (1 mL) and *n*-butanol (0.040 g, 0.540 mmol) and $FcPF_6$ (0.010 g, 0.030 mmol) were added. Then the vial was heated at 45 °C for overnight. The product was filtered through a short pad of silica gel using CH_2Cl_2 (2–4 mL). The product (1-cyclobutyl-1-butoxyprop-2-yn-1-yl)benzene was obtained by column chromatography on alumina (2.5 × 30 cm, 9:1 v/v hexanes : EtOAc) as an orange colored oil (0.052 g, 0.214 mmol, 40%). ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.46–7.42 (m, 2H, aromatic), 7.27–7.16 (m, 3H, aromatic), 3.50 (dd, 1H, J_{HH} = 6 Hz, J_{HH} = 2 Hz, OC*H*H'), 3.05 (dd, 1H, J_{HH} = 6 Hz, J_{HH} = 2 Hz, OCH*H*'), 2.64 (s, 1H, C≡C*H*), 2.60 (quin, 1H, J_{HH} = 8 Hz, CH), 2.20 (dquin, J_{HH} = 10 Hz, J_{HH} = 1 Hz, 1H, CH), 1.91 (quin, 1H, J_{HH} = 9 Hz, CH), 1.85–1.79 (m, 1H, CH), 1.66–1.57 (m, 2H, CH_2), 1.53 – 1.45 (m, 3H, CH+CH_2), 1.30 (quin, J_{HH} = 7 Hz, 2H, CH_2), 0.817 (t, J_{HH} = 7 Hz, 3H, CH_3) ppm; ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ =140.8 (s, aromatic), 128.0 (s, aromatic), 127.5 (s, aromatic), 126.4 (s, aromatic), 82.3 (s, *C*≡), 81.5 (s, *C*≡), 76.5 (s, *C*C≡CH), 64.6 (s, OCH_2), 47.1 (s, OCH), 32.1 (s, CH_2), 23.7 (s, CH_2), 23.5 (s, CH_2), 19.5 (s, CH_2), 16.9 (s, CH_2), 14.4 (s, CH_3) ppm; MS (70 eV): *m*/*z* (%): 241 (5) $[M–H]^+$, 186 (50) $[M–C_4H_9]^+$, 115 (50) $[M+H–C_4H_9O–C_4H_7]^+$, 55 (50) $[C_4H_7]^+$; IR (ATR, neat): $\tilde{\nu}$ = 3302 (m), 3059 (w), 2956 (s), 2932 (s), 2866 (s) cm^{-1}.

(1-Cyclobutyl-1-hexoxyprop-2-yn-1-yl)benzene (**24,** Table 3): In a screw-cap pressure vial, 1-cyclobutyl-2-yn-ol (0.100 g, 0.537 mmol) was dissolved in CH_2Cl_2 (1 mL) and 1-hexanol (0.055 g, 0.539 mmol) and $[FcB(OH)_2]SbF_6$ (0.008 g, 0.017 mmol) were added. Then the vial

was heated at 45 °C overnight. The product was filtered through a short pad of silica gel using CH_2Cl_2 (2–4 mL). The product (1-cyclobutyl-1-hexoxyprop-2-yn-1-yl)benzene was obtained by column chromatography on alumina (2.5 × 30 cm, 9:1 v/v hexanes : EtOAc) as a pale yellow colored oil (0.063 g, 0.233 mmol, 43%). ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.46–7.42 (m, 2H, aromatic), 7.27–7.16 (m, 3H, aromatic), 3.48 (dd, 1H, J_{HH} = 6 Hz, J_{HH} = 2 Hz, OC*H*H'), 3.04 (dd, 1H, J_{HH} = 6.3 Hz, J_{HH} = 2.4 Hz, OCH*H*'), 2.63 (s, 1H, C≡C*H*), 2.60 (quin, 1H, J_{HH} = 8 Hz, CH), 2.20 (dquin, J_{HH} = 10 Hz, J_{HH} = 2 Hz, 1H, CH), 1.91 (quin, 1H, J_{HH} = 9 Hz, CH), 1.84–1.76 (m, 1H, CH), 1.68–1.56 (m, 2H, CH_2), 1.53 – 1.45 (m, 3H, CH+CH_2), 1.27–1.16 (m, 6H, 3CH_2), 0.80 (t, $^2J_{HH}$ = 8 Hz, 3H, CH_3) ppm; ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ =140.9 (s, aromatic), 128.0 (s, aromatic), 127.5 (s, aromatic), 126.4 (s, aromatic), 82.4 (s, C≡), 81.5 (s, C≡), 76.5 (s, *C*C≡CH), 65.0 (s, OCH_2), 47.1 (s,OCH), 31.8 (s, CH_2), 30.0 (s, CH_2), 25.9 (s, CH_2), 23.7 (s, CH_2), 23.5 (s, CH_2), 22.7 (s, CH_2), 16.9 (s, CH_2), 14.1 (s, CH_3) ppm; IR (ATR, neat): ṽ = 3303 (m), 3059 (w), 2929 (s), 2859 (m) cm^{-1}; elemental analysis calcd (%) for $C_{19}H_{26}O$: C 84.39, H 9.69; found: C 84.15, H 9.47.

(1-(Benzyloxy)-1-cyclobutylprop-2-yn-1-yl)benzene (**25,** Table 3): 1-Cyclobutyl-phenylprop-2-yn-ol (0.100 g, 0.537 mmol) was added to a screw cap vial and dissolved in CH_2Cl_2 (1 mL). Benzyl alcohol (0.058 g, 0.536 mmol) was added followed by $[FcB(OH)_2]SbF_6$ (0.008 g, 0.0034 mmol). The vial was then sealed and heated at 45 °C for 20 hours. The solvent was removed and the residue was chromatographed on a neutral alumina oxide (Aluminar®)

column (2.5 × 30 cm, 9:1 v/v hexanes : EtOAc) to give the product as a yellow oil (0.082 g, 0.297 mmol, 55 %).

^{1}H NMR (300 MHz, $CDCl_3$): δ =7.55–7.50 (m, 2H, aromatic), 7.29–7.17 (m, 8H, aromatic), 4.60 (d, J_{HH} = 11 Hz, 1H, OC*H*H'), 4.11 (d, J_{HH} = 11 Hz, 1H, OCH*H*'), 2.72-2.67 (m, 2H, ≡CH, CH), 2.27–2.24 (m, 1H, CH), 2.01–1.83 (m, 2H, 2CH), 1.69–1.56 (m, 3H, 3CH) ppm; ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ =140.4 (s, aromatic), 139.0 (s, aromatic), 128.3 (s, aromatic), 128.2 (s, aromatic), 127.9 (s, aromatic), 127.6 (s, aromatic), 127.4 (s, aromatic), 126.5 (s, aromatic), 82.2 (s, C≡), 82.0 (s, ≡C), 77.3 (s, *C*C≡CH), 67.0 (s, OCH_2), 47.2 (s, CH), 23.9 (s, CH_2), 23.7 (s, CH_2), 17.0 (s, CH_2) ppm; IR (ATR, neat): $\tilde{\nu}$ = 3286 (m), 3059 (w), 3027 (w), 2975 (m), 2937 (m), 2960 (m) cm^{-1}; elemental analysis calcd (%) for $C_{20}H_{20}O$: C 86.92, H 7.29; found: C 87.16, H 7.26%.

(*E*)-(1-Cyclobutyl-1-(hex-3-en-1-yloxy)prop-2-yn-1-yl)benzene (**26,** Table 3): In a vial, 1-phenyl-1-cyclobutyl-2-yne-1-ol (0.100 g, 0.537 mmol) was dissolved in CH_2Cl_2 (1 mL) and *trans*-5-decanol (0.082 g, 0.525 mmol) and $[FcB(OH)_2]SbF_6$ (0.008 g, 0.017 mmol) were added. The sealed vial was heated at 45 °C overnight. The product was filtered through a short pad of silica gel using CH_2Cl_2 (2–4 mL). The product 6-benzoxy-3-phenyl-3-en-1-yne was obtained by neutral Aluminar® column chromatography (2 × 30 cm, 9:1 v/v hexanes : EtOAc) as a yellow oil (0.074 g, 0.228 mmol, 42%). ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.60–7.57 (m, 2H, aromatic), 7.44–7.31 (m, 3H, aromatic), 5.45 (br s, 2H, CH═CH), 3.63 (q, J_{HH} = 7 Hz, 1H, OC*H*H'), 3.19 (q, J_{HH} = 7 Hz, 1H, OCH*H*'), 2.79 (s, 1H, ≡CH), 2.76 (q, J_{HH} = 8 Hz, 1H), 2.34 (quin, J_{HH} = 7

Hz, 1H), 2.11–2.04 (m, 6H, $3CH_2$), 1.82–1.60 (m, 5H), 1.51–1.34 (m, 6H, $3CH_2$), 0.95 (t, J_{HH} = 6 Hz, 3H, CH_3) ppm; $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ =140.8 (s, C=C), 130.7 (s, aromatic), 130.1 (s, aromatic), 128.0 (s, aromatic), 127.6 (s, aromatic), 126.4 (s, C=C), 82.3 (s, C≡), 81.6 (s, C≡), 76.6 (s, *C*C≡CH), 64.8 (s, OCH_2), 47.2 (s, CH), 32.5 (s, CH_2), 32.4 (s, CH_2), 31.9 (s, CH_2), 29.4 (s, CH_2), 26.2 (s, CH_2), 23.8 (s, CH_2), 23.5 (s, CH_2), 22.3 (s, CH_2), 16.9 (s, CH_2), 14.1 (s, CH_3) ppm; IR (ATR, neat): $\tilde{\nu}$ = 3302 (w), 2926 (s), 2858 (m) cm^{-1}; elemental analysis calcd (%) for $C_{23}H_{32}O$: C 85.13, H 9.94; found: C 85.12, H 9.88.

2-(1-Cyclopropyl-1-methoxyprop-2-yn-1-yl)thiophene (**27,** Table 4): In a screw-cap pressure vial, 1-thienyl-1-cyclopropyl-2-yne-1-ol (0.107 g, 0.600 mmol) was dissolved in CH_2Cl_2 (2 mL) and methanol (0.020 g, 0.625 mmol) and $FcPF_6$ (0.010 g, 0.030 mmol) were added. Then the vial was heated at 45 °C. After 45 minutes, the product was filtered through a short pad of silica gel using CH_2Cl_2 (2–4 mL). The product was obtained by column chromatography on alumina (2.5 × 30 cm, 9:1 v/v hexanes : EtOAc) as an orange oil (0.065 g, 0.338 mmol, 56%). ^1H NMR (300 MHz, $CDCl_3$): δ =7.21 (d, $^2J_{HH}$ = 6 Hz, 1H), 7.13 (d, $^2J_{HH}$ = 4 Hz, 1H), 6.90 (t, J_{HH} = 5 Hz, 1H), 3.24 (s, 3H, OCH_3), 2.55 (s, 1H, ≡CH), 1.41-1.36 (m, 1H, CH), 0.83–0.78 (m, 1H, CH), 0.59–0.43 (m, 3H, 3CH) ppm; $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ =144.7 (s, aromatic), 124.1 (s, aromatic), 123.8 (s, aromatic), 123.5 (s, aromatic), 77.8 (s, ≡C), 76.0 (s, C≡), 73.6 (s, *C*C≡CH), 50.4 (s, OCH_3), 20.6 (s, CH), 1.4 (s, CH_2), 0.0 (s, CH_2) ppm; IR (ATR, neat): $\tilde{\nu}$ = 3281 (w), 2933 (w), 2823 (m) cm^{-1}; elemental analysis calcd (%) for $C_{11}H_{12}OS$: C 68.71, H 6.29; found: C 68.55, H 6.08.

2-(1-Cyclopropyl-1-ethoxyprop-2-yn-1-yl) thiophene (**28,** Table 4): In a screw-capped pressure vial, 1-thienyl-1-cyclopropyl-2-yne-1-ol (0.140 g, 0.785 mmol) was dissolved in CH_2Cl_2 (2 mL) and ethanol (0.036 g, 0.781 mmol) and $FcPF_6$ (0.010 g, 0.030 mmol) were added. Then the vial was sealed and heated at 45 °C. After 60 minutes, the product was filtered through a short pad of silica gel using CH_2Cl_2 (2–4 mL). The product was obtained by column chromatography using alumina (2.5 × 30 cm, 9:1 v/v hexanes : EtOAc) as an orange oil (0.069 g, 0.334 mmol, 42%). ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.35 (d, J_{HH} = 5 Hz, 1H), 7.27 (d, J_{HH} = 4 Hz, 1H), 7.03 (t, J_{HH} = 4 Hz, 1H), 3.78 (q, J_{HH} = 8 Hz, 1H, OC*H*H'), 3.44 (q, J_{HH} = 7 Hz, 1H, OCH*H*'), 2.67 (s, ≡CH, 1H), 1.53–1.50 (m, 1H, CH), 1.27 (t, J_{HH} = 9 Hz, 3H, CH_3), 0.96–0.93 (m, 1H, CH), 0.71–0.59 (m, 3H, CH_2+CH) ppm; $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ =147.8 (s, aromatic), 126.2 (s, aromatic), 125.5 (s, aromatic), 125.4 (s, aromatic), 80.5 (s, ≡C), 75.2 (s, ≡C), 60.5 (s, OCH_2), 23.1 (s, CH), 15.4 (s, CH_3), 3.6 (s, CH_2), 2.2 (s, CH_2) ppm; IR (ATR, neat): $\tilde{\nu}$ = 3286 (m), 3007 (w), 2972 (m) cm^{-1}; MS (70 eV): m/z (%): 205 (10) $[M–H]^+$, 178 (30) $[M+H–CH_3CH_2]^+$, 165 (50) $[M–C_3H_5]^+$, 161 (30) $[M–CH_3CH_2O]^+$, 53 (100) $[C_4H_5]^+$, 45 (80) $[CH_3CH_2O]^+$.

1-Cyclopropyl-1-(thiophen-2-yl)prop-2-yn-1-ol (**29,** Table 4): 1-cylopropyl-1-(thiophen-2-yl)prop-2-yn-1-ol (0.100 g, 0.561 mmol) was added to a screw cap vial and dissolved in CH_2Cl_2 (1 mL). *n*-Butanol (0.042 g, 0.568 mmol) was added followed by the addition of $[FcB(OH)_2]SbF_6$ (0.008 g, 0.017 mmol). Then the vial was kept at room temperature overnight.

The reaction mixture was filtered through a short pad of silica gel using CH_2Cl_2 (2–4 mL). The mixture was chromatographed on a neutral alumina oxide (Aluminar®) column (2.5 × 30 cm, 9:1 v/v hexanes : EtOAc) to give the product as a pale yellow oil (0.058 g, 0.247 mmol, 44%).

^{1}H NMR (300 MHz, $CDCl_3$): δ =7.19 (dd, J_{HH} = 5 Hz, J_{HH} = 1 Hz, 1H, aromatic), 7.12 (dd, J_{HH} = 4 Hz, J_{HH} = 1 Hz, 1H, aromatic), 6.88 (dd, J_{HH} = 5 Hz, J_{HH} = 4 Hz, 1H, aromatic), 4.09 (s, trace amount ferrocene), 3.57 (dt, J_{HH} = 6 Hz, J_{HH} = 2 Hz, 1H), 3.22 (dt, J_{HH} = 6 Hz, J_{HH} = 2 Hz, 1H), 2.52 (s, 1H, ≡CH), 1.52–1.18 (m, 5H, CH+2CH_2), 0.80 (t, J_{HH} = 7 Hz, 4H, CH_3+CH), 0.60–0.36 (m, 3H, CH+CH_2) ppm; $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ =147.8 (s, aromatic), 126.0 (s, aromatic), 125.4 (s, aromatic), 125.3 (s, aromatic), 80.8 (s, ≡CH), 76.9 (s, C≡), 75.0 (s, *C*C≡CH), 67.9 (s, ferrocene), 64.5 (s, CH_2O), 31.8 (s, CH), 23.1 (s, CH), 19.3 (s, CH), 13.9 (s, CH), 3.4 (s, CH), 2.1 (s, CH) ppm; HRMS (APPI): *m*/*z* calcd for $C_{14}H_{18}OS$: 234.1078 $[M]^+$; found: 234.1072. IR (ATR, neat): $\tilde{\nu}$ = 3287(m), 3081 (w), 3003 (w), 2955 (m), 2929 (m), 2868 (m) cm^{-1}; elemental analysis calcd (%) for $C_{14}H_{18}OS$: C 71.75, H 7.74; found: C 71.61, H 7.53.

2-(1-Cyclopropyl-1-(hexyloxy) prop-2-yn-1-yl)thiophene (**30,** Table 4): 1-cylopropyl-1-(thiophen-2-yl)prop-2-yn-1-ol (0.100 g, 0.561 mmol) was added to a screw-cap pressure vial and dissolved in CH_2Cl_2 (2 mL). 1-Hexanol (0.058 g, 0.568 mmol) was added followed by the addition of $FcPF_6$ (0.012 g, 0.037 mmol). The vial was then heated to 45 °C for 2 hours. The reaction mixture was filtered through a short pad of silica gel using CH_2Cl_2 (2–4 mL). The product was obtained by column chromatography on a neutral alumina oxide (Aluminar®)

column (2.5 × 30 cm, 9:1 v/v hexanes : EtOAc) as an orange oil (0.058 g, 0.221 mmol, 39%). ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.20 (dd, J_{HH} = 5 Hz, J_{HH} = 1 Hz, 1H, aromatic), 7.12 (dd, J_{HH} = 4 Hz, J_{HH} = 1 Hz, 1H, aromatic), 6.88 (dd, J_{HH} = 4 Hz, J_{HH} = 4 Hz, 1H, aromatic), 3.56 (dt, J_{HH} = 7 Hz, J_{HH} = 10 Hz, 1H, OC*H*H'), 3.22 (dt, J_{HH} = 10 Hz, J_{HH} = 7 Hz, 1H, OCH*H*'), 2.53 (s, ≡CH, 1H), 1.56–1.42 (m, 2H, CH_2), 1.42–1.38 (m, 1H, CH), 1.30–1.12 (m, 6H, $3CH_2$), 0.80 (t, J_{HH} = 7, 4H, CH_3+CH), 0.60–0.37 (m, 3H, CH+CH_2) ppm; $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ =147.8 (s, aromatic), 126.0 (s, aromatic), 125.4 (s, aromatic), 125.3 (s, aromatic), 80.7 (s, ≡C), 76.9 (s, *C*C≡CH, 75.0 (s, C≡), 67.9 (trace ferrocene), 64.8 (s, OCH_2), 31.6 (s, CH_2), 29.7 (s, CH_2), 25.8 (s, CH_2), 23.1 (s, CH_2), 22.6 (s, CH_2), 14.1 (s, CH_3), 3.5 (s, CH_2), 2.1 (s, CH_2) ppm; IR (ATR, neat): $\tilde{\nu}$ = 3300 (m), 3085 (w), 3008 (w), 2927 (s), 2857 (s), 2108 (w), 2070 (w), 1944 (w) cm^{-1}; MS (70 eV): *m*/*z* (%): 261 (5) $[M–H]^+$, 220 (70) $[M–C_6H_{13}]^+$, 137 (30) $[M–C_4H_3S–C_3H_5]^+$, 43 (100) $[C_3H_7]^+$, 41 (95) $[C_3H_5]^+$; HRMS (APPI): *m*/*z* calcd for $C_{16}H_{22}OS$: 262.1391 $[M]^+$; found: 262.1378.

2-(1-(Benzyloxy)-1-cyclopropylprop-2-yn-1-yl)thiophene (**31,** Table 4): 1-Cyclopropyl-1-(thiophen-2-yl)2-yn-1-ol (0.100 g, 0.561 mmol) was added to a screw-cap pressure vial and dissolved in CH_2Cl_2 (1 mL). Benzyl alcohol (0.060 g, 0.556 mmol) was added followed by $FcPF_6$ (0.010 g, 0.037 mmol). The vial was then sealed and kept at room temperature overnight. The solvent was removed and the residue was chromatographed on a neutral alumina oxide (Aluminar®) column (2.5 × 30 cm, 9:1 v/v hexanes : EtOAc) to give the product as yellow oil (0.04 g, 0.15 mmol, 27 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.28–7.16 (m, 7H, aromatic), 6.90 (dd, J_{HH}=4 Hz, J_{HH}=5 Hz,1H), 4.63 (d, 1H, J_{HH}=11 Hz, OC*H*H'), 4.30 (d, 1H, J_{HH}=11 Hz,

OCH*H'*), 4.08 (s, ferrocene), 2.61 (s, 1H, C≡C*H*), 1.51–1.42 (m, 1H, CH), 0.91–0.85 (m, 1H, CH), 0.60–0.44 (m, 3H, CH+CH_2) ppm; $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ =147.3 (s, aromatic), 138.5 (s, aromatic), 128.3 (s, aromatic), 127.8 (s, aromatic), 127.4 (s, aromatic), 126.2 (s, aromatic), 125.9 (s, aromatic), 125.7 (s, aromatic), 80.6 (s, ≡C), 75.7 (s, ≡C), 68.0 (s, CH_2O), 67.0 (s, trace ferrocene), 23.3 (s, CH), 3.7 (s, CH_2), 2.4 (s, CH_2) ppm; IR (ATR, neat): $\tilde{\nu}$ = 3283 (m), 3007 (m), 2902 (m), 2863 (m); MS (70 eV): *m*/*z* (%): 161 (30) [*M*–$OCH_2Ph]^+$, 91 (100) $[CH_2Ph]^+$, 77 (30) $[Ph]^+$.

(1-Butoxy-1-cyclopropylprop-2-yn-1-yl)benzene (**21**, Scheme 2): Cyclopropyl-phenylprop-2-yn-ol (0.124 g, 0.717 mmol) was added to a 5-mL screw cap vial and dissolved in CH_2Cl_2 (1 mL). *n*-Butanol (0.064 g, 0.863 mmol) was added followed by the addition of $FcPF_6$ (0.010 g, 0.031 mmol). The vial was then sealed and heated at 40 °C for 15 minutes. The sample was filtered through a short pad of silica and the solvent was removed. The residue was chromatographed on a neutral alumina oxide (Aluminar®) column (2.5 × 30 cm, 90:10 v/v hexanes : EtOAc) to give the product as an orange oil in about 95% spectroscopic purity (0.037 g, 0.162 mmol, 23 %). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.54–7.51 (m, 2H, aromatic), 7.31–7.16 (m, 3H, aromatic), 3.54 (dt, J_{HH} = 9 Hz, J_{HH} = 6 Hz, 1H, OC*H*H'), 3.13 (dt, J_{HH} = 9 Hz, J_{HH} = 6 Hz, 1H, OCH*H'*), 2.53 (s, 1H, C≡CH), 1.52–1.45 (m, 2H, CH_2), 1.35–1.20 (m, 3H, CH_2+CH), 0.81 (t, J_{HH}= 8 Hz, 3H, CH_3), 0.77–0.70 (m, 1H, CH), 0.49–0.30 (m, 3H, CH_3) ppm; $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ =142.5 (s, aromatic), 128.0 (s, aromatic), 127.6 (s, aromatic), 126.1 (s,

aromatic), 81.0 (s, *C*C≡), 80.2 (s, *C*≡CH), 76.0 (s, C≡*C*H), 64.5 (s, OCH_2), 32.0 (s, CH_2), 22.8 (s, CH_2), 19.4 (s, CH), 13.9 (s, CH_3), 3.3 (s, CH_2), 1.8 (s, CH_2) ppm.

Ring opening of **21** by HBF_4 to obtain enyne **11** (Scheme 3): The sample of **21** was dissolved in $CDCl_3$, one drop of HBF_4 (as diethyl ether complex) was added, and ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded. Due to the addition of the diethyl ether complex of HBF_4, the NMR spectra contained peaks for diethyl ether. The spectra matched the independently synthesized **11** (Table 2). NMR (δ, $CDCl_3$): ^1H 7.53–7.51 (m, 2H, aromatic), 7.28–7.16 (m, 3H, aromatic), 6.48 (t, 1H, $^2J_{HH}$ = 7 Hz, =CH), 3.49 (t, J_{HH} = 7 Hz, 2H, OCH_2), 3.40 (q, J_{HH}=7Hz, diethyl ether), 3.38 (t, 2H, $^2J_{HH}$ = 7 Hz, OCH_2), 3.27 (s, 1H, ≡CH), 2.72 (q, $^2J_{HH}$ = 7 Hz, 2H, CH_2), 1.54–1.34 (m, 2H, CH_2), 1.36–1.26 (m, 2H, CH_2), 1.13 (t, J_{HH} = 7 Hz, diethyl ether), 0.85 (t, 3H, $^2J_{HH}$ = 7 Hz, CH_3) ppm; $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ =137.6 (s, aromatic), 136.5 (s, $=CH_2$), 128.4 (s, aromatic), 127.7 (s, aromatic), 126.0 (s, aromatic), 123.9 (s, PhC=), 83.4 (s, *C*≡CH), 80.7 (s, C≡*C*H), 70.7 (s, OCH_2), 69.5 (s, OCH_2), 65.9 (s, diethyl ether), 31.9 (s, CH_2), 31.8 (s, CH_2), 19.4 (s, CH_2), 15.3 (s, diethyl ether), 14.0 (s, CH_3) ppm.

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