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Atom-Economical Chemoselective Synthesis of 1,4-Enynes from Terminal Alkenes and Propargylic Alcohols Catalyzed by $Cu(OTf)_2$

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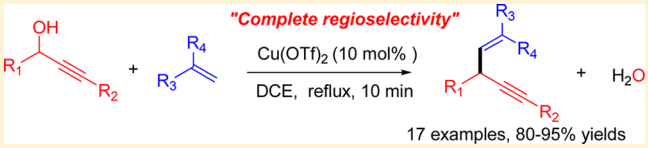
Supporting Information

ABSTRACT: A novel and efficient $Cu(OTf)_2$-catalyzed sp^3–sp^2 C–C bond formation reaction through the direct coupling of propargylic alcohols with terminal alkenes has been realized under mild conditions. The reaction is tolerant to air and is atom-economical, in accordance with the concept of modern green chemistry. The present protocol provides an attractive approach to a diverse range of 1,4-enynes in high to excellent yields.



Due to the electron-rich triple bond in combination with the fairly acidic features of the terminal acetylenic hydrogen atom, transition-metal-catalyzed nucleophilic reaction of terminal alkynes has become an important organic reaction, as it provides a direct and reliable approach to a wide variety of valuable products.[1] In contrast, related transition-metal-catalyzed nucleophilic reaction of terminal alkenes is rare because the C–H bond of simple alkenes is less reactive toward transition metals. The flexibility of the alkene functional group in organic synthesis makes the nucleophilic reaction of alkenes a desirable method for development. In addition to allowing access to saturated products by hydrogenation, the alkene moiety offers a handle for transformation into various other functional groups.

The nucleophilic substitution reactions of propargylic alcohols under metal catalysis or Brøsted acid have been recently extensively studied by using different nucleophiles such as alcohol, 1,3-diketones, arenes, silylalkenes.[2] Recently, an $FeCl_3$-catalyzed propargylic substitution reaction has been developed for the synthesis of diarylalkenyl propargylic compounds directly from propargylic alcohols with 1,1-diaryl alkenes in moderate to good yields.[3] However, the substrates are limited to 1,1-diaryl alkenes, and slightly longer reaction time is needed. Therefore, the development of a coupling reaction for the synthesis of 1,4-enynes directly from simple alkenes and propargylic alcohols is of significance. More recently, we have reported a convenient one-pot synthesis of 4,5-dihydropyrazole from aldehydes, hydrazines, and terminal alkenes using $Cu(OTf)_2$ as a multifunctional catalyst, where the alkenes were used as the nucleophile.[4] Naturally we attempted to extend the scope of the nucleophilic reaction of alkenes. Herein, we wish to report an efficient $Cu(OTf)_2$-catalyzed nucleophilic substitution reaction of terminal alkenes with propargylic alcohols bearing not only a terminal group but also a internal alkyne group to afford 1,4-enynes in high yields with complete regioselectivities under mild reaction conditions. The 1,4-enynes have been discovered to be one of the most efficient intermediates to access ring systems.[5]

Initially, we started to optimize the reaction parameters of this substitution reaction of alkenes with propargylic alcohols. A variety of catalysts and solvents were screened using 1,3-diphenylprop-2-yn-1-ol (**1a**) with styrene (**2a**) as a model system (Table 1). The reaction of **1a** and **2a** gave **3aa** in 90% yield in the presence of 10 mol % $Cu(OTf)_2$ in 1,2-dichloroethane (DCE) at reflux for 10 min (Table 1, entry 1). However, no improvement in the yield of **3aa** could be obtained, as the amount of $Cu(OTf)_2$ was increased to 15 mol % (Table 1, entry 3). In addition, the substitution reactions were obviously restrained when using CuCl, $FeCl_3$, $Pd(dba)_2$, or Brøsted acid as catalyst (Table 1, entries 4–8). Further optimization suggested that solvents also had a strong effect on this process (Table 1, entries 1 and 9–14).

With these optimal conditions in hand, we decided to explore the scope of this propargylic substitution reaction. Typical results are shown in Table 2. Among the propargylic alcohols **1a–1g** that were examined, propargylic alcohol **1b** possessing an electron-donating group (R^1 = 4-MeO-C_6H_4) gave the most desirable results, providing the 1,4-enynes in 90–95% yields (Table 2, entries 3–6). Substrate **1c** possessing an electron-withdrawing group (R^1 = 4-F-C_6H_4) at the benzene ring also reacted smoothly and afforded the desired products in high yields (Table 2, entries 8–10). What's more, fluorine has come to be recognized as a key element in materials science, and many fluorine-containing biologically active agents are finding applications as pharmaceuticals and agrochemicals.[6] Internal propargylic alcohol **1f** (R^2 = *n*-hexyl) also gave good results (Table 2, entries 14 and 15). To our delight, the reaction of terminal propargyl alcohol **1d** (R^2 = H) with styrene **2a** gave **3da** in 80% yield (Table 2, entry 12); this is in sharp

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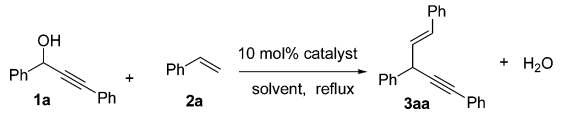
Table 1. Optimization of Reaction Conditions[a]



entry	catalyst	solvent	time	yield [%][b]
1	**$Cu(OTf)_2$**	**DCE**	**10 min**	**90**
2[c]	$Cu(OTf)_2$	DCE	15 h	72
3[d]	$Cu(OTf)_2$	DCE	10 min	91
4	CuCl	DCE	10 h	12
5	CuI	DCE	10 h	20
6	$Cu(OAc)_2$	DCE	10 h	16
5	$FeCl_3$	DCE	24 h	0
6	$Pd(dba)_2$	DCE	24 h	0
7	*p*-TSA	DCE	24 h	0
8	HOTf	DCE	24 h	0
9	$Cu(OTf)_2$	MeCN	24 h	0
10	$Cu(OTf)_2$	toluene	24 h	0
11	$Cu(OTf)_2$	DMF	24 h	0
12	$Cu(OTf)_2$	PhCl	24 h	0
13	$Cu(OTf)_2$	CH_3NO_2	24 h	0
14	$Cu(OTf)_2$	$CHCl_3$	24 h	0

[a]Reaction conditions: all reactions were carried out in a 5-mL flask using **1** (0.5 mmol), **2** (0.6 mmol) and catalyst (0.05 mmol) in solvent (2 mL) at reflux for 10 min. [b]Isolated yield of pure product based on **1a**. [c]The amount of $Cu(OTf)_2$ was decreased to 5 mol %. [d]The amount of $Cu(OTf)_2$ was increased to 15 mol %.

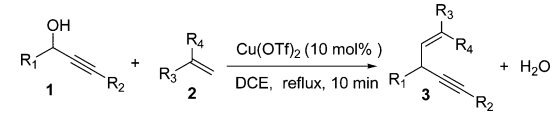
contrast to the $FeCl_3$-catalyzed reaction where the coupling reaction of 1-phenylprop-2-yn-1-ol **1d** with styrene **2a** was unsuccessful.[3] Moreover, **1g** (R^2 = TMS) reacted smoothly with **2a** giving **3ga** in 94% yield (Table 2, entry 16). Propargylic alcohol bearing a heterocyclic aromatic substituent such as 3-phenyl-1-(thiophen-2-yl)prop-2-yn-1-ol **1e** treated with **2d** also led to the desired product **3ed** in 93% yield (Table 2, entry 13).

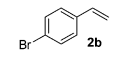
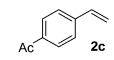
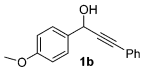
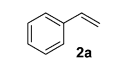
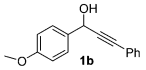
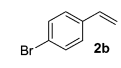
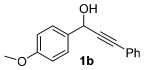
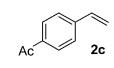
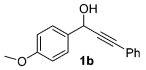
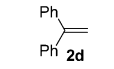
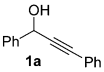
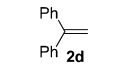
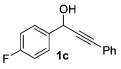
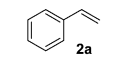
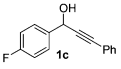
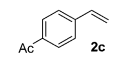
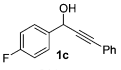
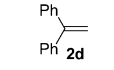
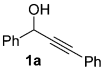
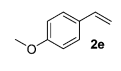
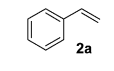
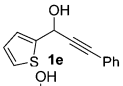
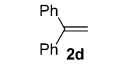
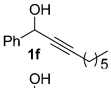
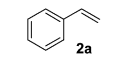
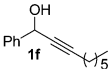
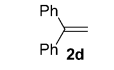
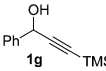
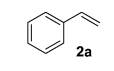
Additionally, a variety of alkenes **2** were employed to examine the generality of the method. Reactions of 4-bromostyrene (**2b**), 4-acetoxystyrene (**2c**), and 4-methoxystyrene (**2e**) with propargylic alcohol **1a** gave the corresponding 1,4-enynes **3ab**–**3ae** in 84–94% yields (Table 2, entries 1, 2, and 11). Obviously, electron-rich alkenes provided the desired products in higher yields than electron-poor alkenes did. In particular, 1,1-diphenylethylene **2d** (R^3 = Ph, R^4 = Ph) provided the desired products in high yields (Table 2, entries 6, 7, 10, 13, and 15). These results suggest that the geminally disubstituted alkenes are also good substrates on the propargyl substitution reaction.

Unfortunately, when aliphatic olefins were used as the nucleophiles, substitution reactions of propargyl alcohols failed, generating the corresponding propargylic ethers (Scheme 1).[7]

On the basis of our and others' previous work,[8] our postulated reaction pathways are summarized in Scheme 2. Two competitive pathways could occur, leading to the formation of 1,4-enyne **3** and propargylic ether **4**. In the initial step, $Cu(OTf)_2$ triggers the dehydroxylation of propargylic alcohol **1** to form the intermediary propargylic cation **A**. The subsequent nucleophilic reaction of aromatic olefins **2** to the intermediary propargylic cation **A** leads to a stabilized benzylic carbocation intermediate **B** (Path I). Finally, intermediate **B** undergoes a dehydrogenation step to offer 1,4-enyne **3**. When aliphatic olefin is used, there is no benzylic stabilization, disfavoring Path I. Instead, the oxygen atom of the propargylic alcohol **1** attacks the intermediary propargylic cation **A** (Path II), leading to an intermediate **C**, which undergoes a dehydrogenation step to propargylic ether **4**.

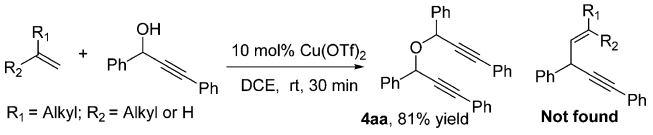
Table 2. Synthesis of Substituted 1,4-Enynes 3 Catalyzed by $Cu(OTf)_2$[a]



Entry	Substrate		Product	Yield [%][b]
1			**3ab**	84
2			**3ac**	92
3			**3ba**	93
4			**3bb**	90
5			**3bc**	93
6			**3bd**	95
7			**3ad**	94
8			**3ca**	84
9			**3cc**	85
10			**3cd**	87
11			**3ae**	94
12			**3da**	80
13			**3ed**	93
14			**3fa**	90
15			**3fd**	93
16			**3ga**	94

[a]Reaction conditions: all reactions were carried out in a 5-mL flask using **1** (0.5 mmol), **2** (0.6 mmol), and $Cu(OTf)_2$ (0.05 mmol) in DCE (2 mL) at reflux for 10 min. [b]Isolated yield of pure product based on **1a**.

Scheme 1. Synthesis of Propargylic Ether 4aa from Propargylic Alcohol 1a



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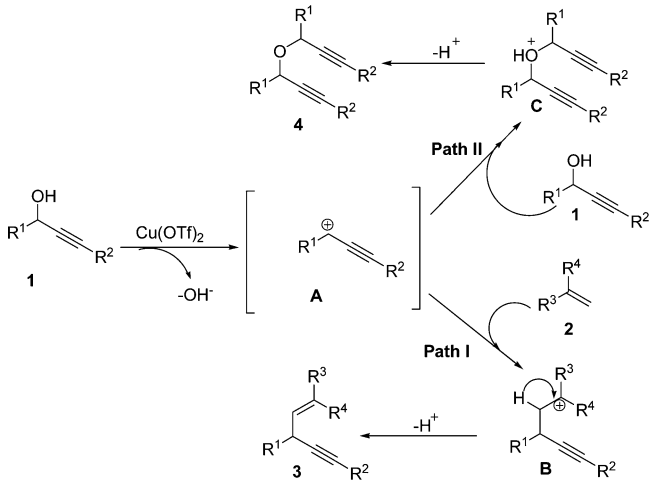
Scheme 2. Proposed Mechanism



In summary, we have documented a Cu-catalyzed reaction of simple terminal alkenes with propargylic alcohols. This operationally simple method gives a rapid access to the 1,4-enynes. Air-tolerant and atom-economical characteristics of the method are in accord with the concept of modern green chemistry and will be appealing for industries. Further development on this methodology is currently underway in our laboratory.

EXPERIMENTAL SECTION

General Description. Melting points are uncorrected. NMR spectra were in $CDCl_3$ (^1H at 500 MHz and ^{13} C at 125 MHz). Column chromatography was performed on silica gel (300−400 mesh). Unless otherwise noted, all reagents were obtained commercially and used without further purification.

General Experimental Procedure for Synthesis of 1,4-Enynes 3. To a 5-mL flask were added propargyl alcohol **1** (0.5 mmol), alkene **2** (0.6 mmol), 1,2-dichloroethane (DCE) (2.0 mL) and $Cu(OTf)_2$ (0.05 mmol) successively. The reaction mixture was stirred at reflux and monitored periodically by TLC. Upon completion (normally 10 min), DCE was removed under reduced pressure by an aspirator, and then the residue was purified by flash chromatography (hexane/ethyl acetate) on silica gel to afford 1,4-enynes **3**.

(*E*)-1,3,5-Triphenylpent-1-en-4-yne[9] (3aa). A pale yellow oil in 90% yield (132 mg, 0.45 mmol); ^1H NMR (500 MHz, $CDCl_3$) δ 7.56−7.51 (m, 4H), 7.43−7.39 (m, 4H), 7.39−7.32 (m, 6H), 7.29−7.27 (m, 1H), 6.84 (d, J = 15.6 Hz, 1H), 6.40 (dd, J = 15.6 and 6.5 Hz, 1H), 4.81 (d, J = 6.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.3, 136.8, 131.7, 130.4, 129.6, 128.7, 128.5, 128.2, 128.0, 127.7, 127.5, 127.1, 126.5, 123.4, 88.8, 85.4, 41.2. HRAPCIMS calcd for $C_{23}H_{19}$ (M + H)$^+$ 295.1487; found 295.1485.

(*E*)-1-Bromo-4-(3,5-diphenylpent-en-4-ynyl)benzene (3ab). A yellow oil in 84% yield (156 mg, 0.42 mmol); ^1H NMR (500 MHz, $CDCl_3$) δ 7.55−7.51 (m, 4H), 7.48−7.39 (m, 5H), 7.38−7.32 (m, 4H), 7.28−7.25 (m, 1H), 6.75 (d, J = 15.7 Hz, 1H), 6.37 (dd, J = 15.7 and 6.5 Hz, 1H), 4.78 (d, J = 6.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.0, 135.7, 131.7, 131.6, 130.4, 129.2, 128.74, 128.65, 128.2, 128.0, 127.7, 127.2, 123.3, 121.2, 88.5, 85.6, 41.2. HRAPCIMS calcd for $C_{23}H_{16}Br$ (M + H)$^+$ 371.0435, 373.0415; found 371.0433, 373.0413.

(*E*)-4-(3,5-Diphenyipent-1-en-4-ynyl)phenyl Acetate (3ac). A yellow oil in 92% yield (161 mg, 0.46 mmol); ^1H NMR (500 MHz, $CDCl_3$) δ 7.58−7.55 (m, 4H), 7.46−7.41 (m, 4H), 7.40−7.32 (m, 4H), 7.10 (d, J = 8.5 Hz, 2H), 6.82 (d, J = 15.6 Hz, 1H), 6.36 (dd, J = 15.6 and 6.5 Hz, 1H), 4.81 (d, J = 6.5 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.3, 149.9, 140.1, 134.5, 131.6, 129.8, 129.4, 128.7, 128.2, 128.0, 127.6, 127.4, 127.1, 123.3, 121.6, 88.7, 85.4, 41.1, 21.0. HRAPCIMS calcd for $C_{25}H_{21}O_2$ (M + H)$^+$ 353.1542; found 353.1539.

(*E*)-1-(1,5-Diphenylpent-1-en-4-yn-3-yl)-4-methoxybenzene (3ba). A yellow oil in 93% yield (150 mg, 0.47 mmol); ^1H NMR (500 MHz, $CDCl_3$) δ 7.57−7.51 (m, 2H), 7.44−7.40 (m, 4H), 7.38−7.31 (m, 6H), 6.95 (d, J = 8.8 Hz, 2H), 6.79 (d, J = 15.6 Hz, 1H), 6.37 (dd, J = 15.6 and 6.5 Hz, 1H), 4.75 (d, J = 6.5 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.7, 136.9, 132.3, 131.7, 130.2, 129.9, 128.7, 128.5, 128.2, 127.9, 127.5, 126.5, 123.5, 114.1, 89.1, 85.2, 55.27, 40.36. HRAPCIMS calcd for $C_{24}H_{19}O$ (M − H)$^+$ 323.1436; found 323.1432.

(*E*)-1-Bromo-4-(3-(4-methoxypheyl)-5-phenylpent-1-en-4-ynyl)benzene (3bb). A pale yellow oil in 90% yield (180 mg, 0.45 mmol); ^1H NMR (500 MHz, $CDCl_3$) δ 7.53−7.50 (m, 2H), 7.47−7.40 (m, 5H), 7.37−7.32 (m, 3H), 7.30−7.24 (m, 1H), 7.04−6.87 (m, 2H), 6.71 (dd, J = 15.6 and 1.8 Hz, 1H), 6.35 (dd, J = 15.6 and 6.4 Hz, 1H), 4.72 (d, J = 6.4 Hz, 1H), 3.83 (s, 3H). ^{13} C NMR (125 MHz, $CDCl_3$) δ 158.7, 135.8, 132.0, 131.7, 131.6, 130.7, 129.4, 128.9, 128.7, 128.3, 128.0, 123.3, 121.2, 114.1, 88.8, 85.3, 55.3, 40.3. HRAPCIMS calcd for $C_{24}H_{18}BrO$ (M − H)$^+$ 401.0541, 403.0521; found 401.0594, 403.0569.

(*E*)-4-(3-(4-Methoxyphenyl)-5-phenylpent-1-en-4-ynyl)-phenyl Acetate (3bc). A yellow oil in 93% yield (177 mg, 0.47 mmol); ^1H NMR (500 MHz, $CDCl_3$) δ 7.49−7.45 (m, 2H), 7.40−7.36 (m, 4H), 7.34−7.30 (m, 3H), 7.04 (d, J = 8.7 Hz, 2H), 6.91 (d, J = 8.7 Hz, 2H), 6.74 (d, J = 15.6 Hz, 1H), 6.28 (dd, J = 15.6 and 6.5 Hz, 1H), 4.71 (d, J = 6.5 Hz, 1H), 3.81 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 158.8, 150.0, 134.8, 132.3, 131.7, 130.2, 129.2, 128.8, 128.3, 128.0, 127.5, 123.5, 121.7, 114.1, 89.0, 85.3, 55.4, 40.4, 21.1. HRAPCIMS calcd for $C_{26}H_{23}O_3$ (M + H)$^+$ 383.1647; found 383.1629.

1-Methoxy-4-(1,1,5-triphenylpent-1-en-4-yn-3-yl)benzene (3bd). A yellow oil in 95% yield (190 mg, 0.48 mmol); ^1H NMR (500 MHz, $CDCl_3$) δ 7.59−7.55 (m, 2H), 7.52−7.49 (m, 2H), 7.47−7.41 (m, 5H), 7.39- 7.30 (m, 8H), 6.96 (dd, J = 8.7 and 1.1 Hz, 2H), 6.31 (d, J = 10.1 Hz, 1H), 4.78 (d, J = 10.1 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.5, 141.8, 141.4, 139.2, 132.7, 131.7, 129.9, 128.7, 128.5, 128.4, 128.2, 128.1, 127.9, 127.5, 127.4, 123.6, 113.9, 90.1, 83.8, 55.2, 37.1. HRAPCIMS calcd for $C_{30}H_{25}O$ (M + H)$^+$ 401.1905; found 401.1883.

1,1,3,5-Tetraphenylpent-1-en-4-yne[3] (3ad). A yellow oil in 94% yield (174 mg, 0.47 mmol); ^1H NMR (500 MHz, $CDCl_3$) δ 7.62−7.58 (m, 2H), 7.57−7.53 (m, 4H), 7.50−7.43 (m, 5H), 7.42−7.33 (m, 9H), 6.36 (d, J = 10.1 Hz, 1H), 4.87 (d, J = 10.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.91, 141.87, 140.8, 139.3, 131.9, 130.1, 128.8, 128.7, 128.6, 128.4, 128.3, 128.1, 127.7, 127.64, 127.56, 127.0, 123.8, 120.0, 89.9, 84.2, 38.0. HRAPCIMS calcd for $C_{29}H_{23}$ (M + H)$^+$ 371.1800; found 371.1778.

(*E*)-1-(1,5-Diphenylpent-1-en-4-yn-3-yl)-4-fluorobenzene (3ca). A yellow oil in 84% yield (131 mg, 0.42 mmol); ^1H NMR (500 MHz, $CDCl_3$) δ 7.55−7.52 (m, 2H), 7.48−7.44 (m, 2H), 7.42 (d, J = 7.5 Hz, 2H), 7.37−7.31 (m, 6H), 7.08−7.04 (m, 2H), 6.79 (d, J = 15.6 Hz, 1H), 6.34 (dd, J = 15.6 and 6.6 Hz, 1H), 4.76 (d, J = 6.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.9 and 160.9, 136.7, 131.7, 130.6, 129.34, 129.28, 129.2, 128.5, 128.3, 128.1, 127.6, 126.5, 123.3, 115.6 and 115.4, 88.6, 85.6, 40.5. HRAPCIMS calcd for $C_{23}H_{16}F$ (M − H)$^+$ 311.1236; found 311.1216.

(*E*)-4-(3-(4-Fluorophenyl)-5-phenylpent-1-en-4-ynyl)phenyl Acetate (3cc). A yellow oil in 85% yield (157 mg, 0.43 mmol); ^1H NMR (500 MHz, $CDCl_3$) δ 7.52−7.48 (m, 2H), 7.47−7.43 (m, 2H), 7.42−7.39 (m, 2H), 7.35−7.31 (m, 3H), 7.10−7.02 (m, 4H), 6.75 (dd, J = 15.7 and 1.4 Hz, 1H), 6.27 (dd, J = 15.7 and 6.5 Hz, 1H), 4.73 (d, J = 6.5 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.4, 162.9 and 161.0, 150.1, 135.9, 134.5, 131.7, 129.6, 129.3, 129.2, 128.3, 128.1, 127.5, 123.2, 121.7, 115.6 and 115.4, 88.4, 85.6, 40.4, 21.1. HRAPCIMS calcd for $C_{25}H_{20}FO_2$ (M + H)$^+$ 371.1447; found 371.1436.

1-Fluoro-4-(1,1,5-triphenylpent-1-en-4-yn-3-yl)benzene (3cd). A yellow oil in 87% yield (169 mg, 0.44 mmol); ^1H NMR (500 MHz, $CDCl_3$) δ 7.60−7.57 (m, 2H), 7.55−7.51 (m, 2H), 7.50−7.44

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(m, 5H), 7.42−7.37 (m, 3H), 7.36−7.31 (m, 5H), 7.17−7.06 (m, 2H), 6.31 (d, J = 10.1 Hz, 1H), 4.82(d, J = 10.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.9 and 161.0, 142.1, 141.7, 139.2, 136.5, 131.9, 130.0, 129.1, 129.0, 128.7, 128.4, 128.3, 128.2, 127.8, 127.7, 127.7, 123.6, 115.6 and 115.4, 89.7, 84.3, 37.3. HRAPCIMS calcd for $C_{29}H_{22}F$ $(M + H)^+$ 389.1706; found 389.1688.

(*E*)-1-(3,5-Diphenylpent-1-en-4-ynyl)-4-methoxybenzene (3ae). A yellow oil in 94% yield (152 mg, 0.47 mmol); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54−7.49 (m, 4H), 7.37−7.34 (m, 3H), 7.35−7.31 (m, 4H), 7.31−7.27 (m, 1H), 6.86 (d, J = 8.8 Hz, 2H), 6.73 (d, J = 15.6 Hz, 1H), 6.22 (dd, J = 15.6 and 6.6 Hz, 1H), 4.75 (d, J = 6.6 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 140.5, 131.7, 129.8, 129.6, 128.7, 128.2, 128.0, 127.70, 127.65, 127.5, 127.0, 123.5, 113.9, 89.0, 85.2, 55.3, 41.2. HRAPCIMS calcd for $C_{24}H_{21}O$ $(M + H)^+$ 325.1592; found 325.1592.

(*E*)-1,3-Diphenylpent-1-en-4-yne[10] (3da). A yellow oil in 80% yield (87 mg, 0.40 mmol); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51−7.47 (m, 2H), 7.42−7.38 (m, 4H), 7.35−7.31 (m, 4H), 6.81 (d, J = 15.7 Hz, 1H), 6.33−6.29 (m, 1H), 4.61 (d, J = 6.4 Hz, 1H), 2.55 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.7, 136.6, 130.6, 128.9, 128.7, 128.5, 127.6, 127.5, 127.2, 126.5, 83.3, 73.3, 40.3. HRAPCIMS calcd for $C_{17}H_{13}$ $(M - H)^+$217.1017; found 217.1010.

2-(1,1,5-Triphenylpent-1-en-4-yn-3-yl)thiophene[3] (3ed). A yellow oil in 93% yield (175 mg, 0.47 mmol); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59−7.54 (m, 2H), 7.53−7.48 (m, 2H), 7.47−7.42 (m, 3H), 7.41−7.32 (m, 8H), 7.28 (dd, J = 5.1 and 1.2 Hz, 1H), 7.14 (m,1H), 7.04 (dd, J = 5.1 and 3.5 Hz, 1H), 6.38 (d, J = 10.0 Hz, 1H), 5.00 (dd, J = 10.0 and 1.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 142.2, 141.5, 138.7, 131.7, 129.8, 128.5, 128.19, 128.17, 128.1, 127.7, 127.6, 127.4, 126.9, 124.52, 124.45, 123.2, 89.1, 83.4, 33.6. HRAPCIMS calcd for $C_{27}H_{21}S$ $(M + H)^+$377.1364; found 377.1357.

(*E*)-1,3-Diphenylundec-1-en-4-yne (3fa). A yellow oil in 90% yield (136 mg, 0.45 mmol); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46−7.43 (m, 2H), 7.42−7.35 (m, 4H), 7.32−7.29 (m, 3H), 7.24 (m, 1H), 6.75 (d, J = 15.6 Hz, 1H), 6.30 (dd, J = 15.6 and 6.5 Hz, 1H), 4.55 (d, J = 6.5 Hz, 1H), 2.33 (td, J = 7.1 and 2.2 Hz, 2H), 1.61−1.58(m, 2H), 1.52−1.45 (m, 2H), 1.40−1.31 (m, 4H), 0.94 (t, J = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.0, 137.0, 130.5, 129.8, 128.5, 128.4, 127.6, 127.3, 126.8, 126.4, 85.8, 79.1, 40.7, 31.3, 28.9, 28.6, 22.6, 18.9, 14.1. HRAPCIMS calcd for $C_{23}H_{25}$ $(M + H)^+$ 301.1956; found 301.1948.

1,1,3-Triphenylundec-1-en-4-yne (3fd). A yellow oil in 93% yield (176 mg, 0.47 mmol); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49−7.46 (m, 4H), 7.45−7.42 (m, 3H), 7.41−7.37 (m, 2H), 7.33−7.28 (m, 6H), 6.23 (d, J = 10.2 Hz, 1H), 4.59 (d, J = 10.2 Hz, 1H), 2.36 (td, J = 7.1 and 2.3 Hz, 2H), 1.65−1.61 (m, 2H), 1.53−1.49 (m, 2H), 1.41−1.38 (m, 4H), 0.99 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.9, 141.3, 140.9, 139.3, 129.9, 129.5, 128.4, 128.4, 128.1, 127.5, 127.4, 127.34, 127.28, 126.6, 84.3, 80.1, 37.3, 31.3, 28.9, 28.5, 22.6, 19.0, 14.1. HRAPCIMS calcd for $C_{29}H_{31}$ $(M + H)^+$ 379.2426; found 379.2423.

(*E*)-(3,5-Diphenylpent-4-en-1-ynyl)trimethylsilane (3ga). A yellow oil in 94% yield (136 mg, 0.47 mmol); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47−7.43 (m, 2H), 7.40−7.37 (m, 4H), 7.36−7.31 (m, 4H), 6.74 (d, J = 15.7 Hz, 1H), 6.29 (dd, J = 15.7 and 6.6 Hz, 1H), 4.60 (d, J = 6.6 Hz, 1H), 0.28 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.9, 136.8, 130.4, 129.5, 128.6, 128.5, 127.7, 127.5, 127.0, 126.5, 89.7, 73.3, 41.6, 0.1. HRAPCIMS calcd for $C_{20}H_{21}Si$ $(M - H)^+$ 289.1413; found 289.1413.

3-(1,3-Diphenylprop-2-ynyloxy)-1,3-diphenylprop-1-yne[7] (4aa). A colorless oil in 81% yield (161 mg, 0.41 mmol); NMR shows the presence of two geometrical isomers in a 1:0.64 ratio. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76−7.74 (m, 2H), 7.71−7.69 (m, 2H), 7.61−7.60 (m, 2H), 7.55−7.53 (m, 2H), 7.49−7.47 (m, 2H), 7.46−7.43 (m, 5H), 7.41−7.38 (m, 5H), 7.37−7.35 (m, 2H), 6.05 (s, 2H), 5.66 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ138.5, 138.9, 131.9, 131.8, 128.6, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 127.9, 127.7, 127.5, 122.51, 122.46, 88.1, 87.8, 87.1, 86.7, 70.2, 69.7. EI-MS (m/z) 399 $[M + H^+]$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Spectral data for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) For selected examples, see: (a) Trost, B. M.; McIntosh, M. C. *J. Am. Chem. Soc.* **1995**, *117*, 7255. (b) Trost, B. M.; Sorum, M. T.; Chan, C.; Harms, A. E.; Rühter, G. *J. Am. Chem. Soc.* **1997**, *119*, 698. (c) Frantz, D. E.; Fässler, R.; Carreira, E. M. *J. Am. Chem. Soc.* **1999**, *121*, 11245. (d) Trost, B. M.; Frontier, A. J. *J. Am. Chem. Soc.* **2000**, *122*, 11727. (e) Fischer, C.; Carreira, E. M. *Org. Lett.* **2001**, *3*, 4319. (f) Knöpfel, T. F.; Carreira, E. M. *J. Am. Chem. Soc.* **2003**, *125*, 6054. (g) Fischer, C.; Carreira, E. M. *Org. Lett.* **2004**, *6*, 1497. (h) Nishimura, T.; Washitake, Y.; Nishiguchi, Y.; Maeda, Y.; Uemura, S. *Chem. Commun.* **2004**, 1312. (i) Nishimura, T.; Washitake, Y.; Uemura, S. *Adv. Synth. Catal.* **2007**, *349*, 2563. (j) Zhou, L.; Chen, L.; Skouta, R.; Jiang, H.-F.; Li, C.-J. *Org. Biomol. Chem.* **2008**, *6*, 2969. (k) Ren, K.; Li, P.; Wang, L.; Zhang, X. *Tetrahedron* **2011**, *67*, 2753. (l) Suzuki, Y.; Naoe, S.; Oishi, S.; Fujii, N.; Ohno, H. *Org. Lett.* **2012**, *14*, 326. (m) Xu, Y.-L.; Pan, Y.-M.; Liu, P.; Wang, H.-S.; Tian, X.-Y.; Su, G.-F. *J. Org. Chem.* **2012**, *77*, 3557. (n) Liu, P.; Pan, Y.-M.; Xu, Y.-L.; Wang, H.-S. *Org. Biomol. Chem.* **2012**, *10*, 4696.

(2) For selected examples, see: (a) Pan, Y.-M.; Zhao, S.-Y.; Ji, W.-H.; Zhan, Z.-P. *J. Comb. Chem.* **2009**, *11*, 105. (b) Zhan, Z.-P.; Yu, J.-L.; Liu, H.-J.; Cui, Y.-Y.; Yang, R.-F.; Yang, W.-Z.; Li, J.-P. *J. Org. Chem.* **2006**, *71*, 8298. (c) Pan, Y.-M.; Zheng, F.-J.; Lin, H.-X.; Zhan, Z.-P. *J. Org. Chem.* **2009**, *74*, 3148.

(3) Peng, S.-Y.; Wang, L.; Wang, J. *Org. Biomol. Chem.* **2012**, *10*, 225.

(4) Wu, Q.; Liu, P.; Pan, Y.-M.; Xu, Y.-L.; Wang, H.-S. *RSC Adv.* **2012**, *2*, 10167.

(5) (a) Li, X.-X.; Huang, S.-Y.; Schienebeck, C.-M.; Shu, D.-X.; Tang, W.-P. *Org. Lett.* **2012**, *14*, 1484. (b) Sato, T.; Onuma, T.; Nakamura, I.; Terada, M. *Org. Lett.* **2011**, *13*, 4992.

(6) (a) Muller, K.; Faeh, C.; Diederich, F. *Science* **2007**, *317*, 1881. (b) Belisle, J. *Science* **1981**, *212*, 1509. (c) Shimizu, M.; Hiyama, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 214.

(7) Laali and coworkers also have reported that metallic triflates could promote self- or crossedcondensation of propargylic alcohols to synthesize a variety of bis-propargylic ethers in imidazolium ionic liquids. See: Aridoss, G.; Sarca, V.-D.; Ponder, J.-F., Jr; Crowe, J.; Laali, K.-K. *Org. Biomol. Chem.* **2011**, *9*, 2518.

(8) (a) Wang, T.; Chen, X.-L.; Chen, L.; Zhan, Z.-P. *Org. Lett.* **2011**, *13*, 3324. (b) Reference 2. (c) Georgy, M.; Boucard, V.; Campagne, J.-M. *J. Am. Chem. Soc.* **2005**, *127*, 14180. (d) Reference 3. (e) Reference 4.

(9) Paz, T.; Alejandro, B.; Carmen, N. *J. Org. Chem.* **2012**, *77*, 7344.

(10) Yue, H.-L.; Wei, W.; Li, M.-M.; Yang, Y.-R.; Ji, J.-X. *Adv. Synth. Catal.* **2011**, *353*, 3139.