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$Cu(OTf)_2$-catalyzed arylmethylation of terminal alkynes with benzylic alcohols under ligand-, base-, and additive-free reaction conditions

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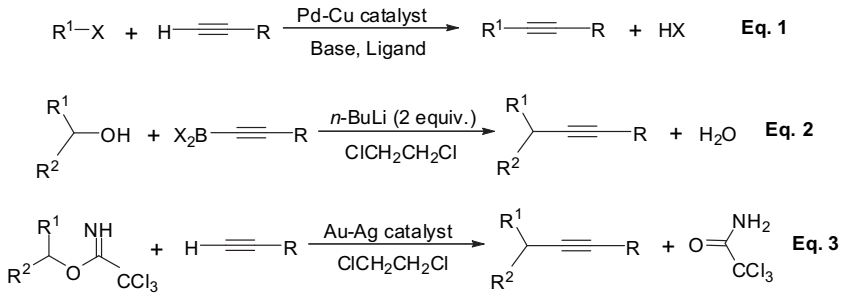
ABSTRACT

An effective, convenient, and mild coupling reaction of benzylic alcohols with terminal alkynes has been developed. As an effective Lewis acid, $Cu(OTf)_2$-catalyzed arylmethylation of terminal alkynes with benzylic alcohols generated the corresponding products in $BrCH_2CH_2Br$ with good yields in the absence of ligand, base, and additive.

1. Introduction

Because alkyne units have been found in a wide range of natural products,[1] bioactive compounds,[2] and as important building blocks in materials science[3] and organic synthesis,[4] the development of new methods for incorporating them into organic molecules is an important topic in organic synthesis. One of the practical methods for the synthesis of alkynes is the Sonogashira reaction[5] (palladium and copper-co-catalyzed coupling reaction of a terminal alkyne with an aryl halide) (Scheme 1, Eq. 1). However, the coupling of terminal alkynes with allylic, benzylic, and propargylic electrophiles for the formation of C_{sp}–C_{sp3} bond has been less widely explored,[6] most of them, usually require a strong base and a stoichiometric quantity of an organometallic reagent (organo-boron,[7] -zinc,[8] -magnesium,[9] -tin,[10] or -aluminum[11]). Recently, Fu and co-workers described the first applications of carbene ligands in Pd-catalyzed cross-couplings of



Scheme 1.

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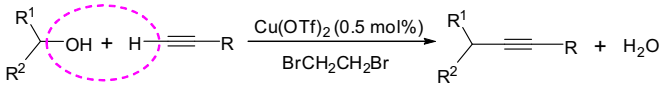
alkyl electrophiles (unactivated alkyl bromides and iodides) with terminal alkynes.[12] Although this method works well even on large scale, often it is associated with significant drawbacks including the use of strong base and production of large amounts of halide as by-products. Following that, Kabalka et al. demonstrated an efficient substitution reaction of benzylic alcohols with alkynylboron dihalides (Scheme 1, Eq. 2).[13] Benzylic alcohols as electrophiles would be quite useful since they would be both atom efficient and more environmentally sound. However, the use of alkynylboron dihalides as nucleophiles and the requirement of 2 equiv of *n*-BuLi limit its application. Recently, Wang's group developed the coupling reaction of trichloroacetimidate with terminal alkyne in the presence of 5.0 mol % of AuCl/AgOTf catalyst system, along with trichloroacetamide as by-product released and precious metals used in the reaction (Scheme 1, Eq. 3).[14] Therefore, the development of a practical and economical process for C–C (sp–sp^3) bond formation between terminal alkyne compounds and unmodified substrates is more essential. In this regard, alcohols as electrophiles would be attractive since it would be an atom-economic process with water being the only by-product.

The chemistry of alcohol derivatives has received much more attention for many years because of their plentiful and inexpensive properties, compared to alkyl halides or esters.[15] In addition, the direct coupling reaction of alcohol with C–H bond is environmentally benign, only generating H_2O as the side product. Very recently, an efficient and mild FeX_3-promoted strategy for the synthesis of various substituted alkenyl halides via intermolecular addition of benzylic alcohols to aromatic alkynes has been developed.[16] Meanwhile, a $Fe(OTf)_3$/TfOH co-catalyzed coupling reaction of terminal alkynes with benzylic alcohols has been also reported.[17] As Lewis acid catalyst, $Cu(OTf)_2$ has been proved to be powerful alkylnophilic one to activate the π-systems toward nucleophilic attack.[18] As part of our ongoing efforts devoted to the chemistry of benzylic alcohols to alkynes by using Lewis acids, herein we wish to report a *ligand-free* $Cu(OTf)_2$ (0.5 mol %) catalyzed arylmethylation of terminal alkynes with benzylic alcohols *in the absence of base and additive* in $BrCH_2CH_2Br$. The reactions generated the corresponding products in good to excellent yields (90–95%) (Scheme 2).

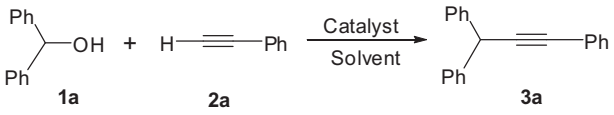


Scheme 2.

2. Results and discussion

For initial optimization of the reaction conditions and the identification of the best catalyst, solvent, and reaction temperature, diphenylmethanol and phenylacetylene were chosen as model substrates. The results were summarized in Table 1. To our delight, 91% of **3a** was obtained when the model reaction was carried out in $BrCH_2CH_2Br$ and 0.5 mol % of $Cu(OTf)_2$ was used as catalyst at 120 °C for 12 h (Table 1, entry 3). Other Lewis acids, such as $In(OTf)_3$, Zn $(OTf)_2$, and $Fe(OTf)_3$ could catalyze this transformation, but their efficiencies were much lower than that of $Cu(OTf)_2$, especially under low loading of catalyst reaction conditions (Table 1, entries 1–4). In addition, Brønsted acid, TfOH gave the desired compound **3a** in 38% yield with 2.0 mol % loading of TfOH used in the reaction, but trace amount of **3a** was obtained with 0.5 mol % loading of TfOH (Table 1, entry 5). However, H_2SO_4 and HCl failed to catalyze the reaction and no desired **3a** was obtained, even in high loading of catalyst used (Table 1, entries 6 and 7). Notably, the combination of $Fe(OTf)_3$ (2.0 mol %) and TfOH (4.0 mol %) gave **3a** in 75% isolated yield (Table 1, entry 4).[17] When other Lewis acid, such as $AlCl_3$ or $FeCl_3$ was used for the reaction, only corresponding alkenyl chloride was obtained (Table 1, entries 8 and 9).[19] With respect to the catalyst loading, when 0.25 mol % of $Cu(OTf)_2$ was used, the reaction did not go to completion, but that a higher loading (1.0 mol %) of the catalyst gave a very good result (Table 1, entry 18). However, with an increased loading of the catalyst up to 2.0 mol % there was no increase in the isolated yield of the product (Table 1, entry 3). Thus, 0.5 mol % of Cu $(OTf)_2$ is enough to accomplish this reaction. Moreover, this reaction was strongly influenced by the solvents. No any desired product was isolated when the reaction was carried out in DMSO, DMF, C_2H_5OH, CH_3NO_2 or CH_3CN (Table 1, entries 10–14). The use of $ClCH_2CH_2Cl$ to replace $BrCH_2CH_2Br$ as solvent resulted in decreasing isolated yield of the product (Table 1, entry 15). However, in the case of $BrCH_2CH_2Br$ used as solvent, at a relative low temperature (80, 100 °C), 65 and 77% yield of **3a** was isolated, respectively (Table 1, entries 16 and 17). Therefore, 0.5 mol % of $Cu(OTf)_2$ in 1,2-dibromoethane was considered as an efficient catalyst system at 120 °C for this cross-coupling reaction.

Table 1
Optimization of reaction conditions for the model reaction[a]



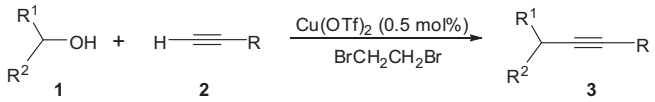
1a 2a 3a

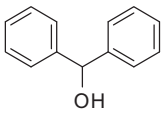
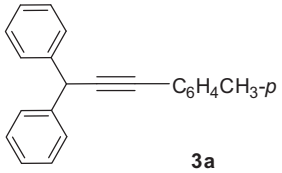
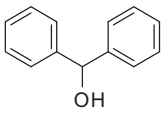
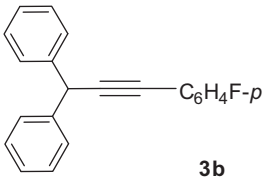
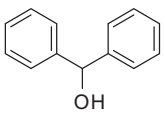
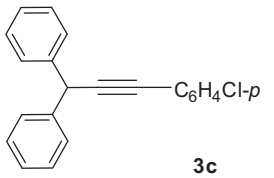
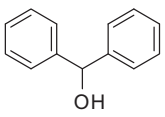
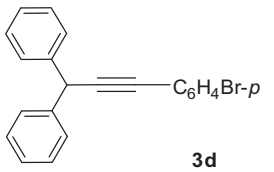
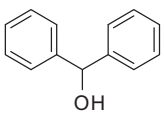
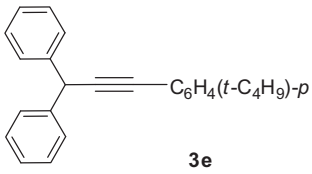
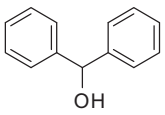
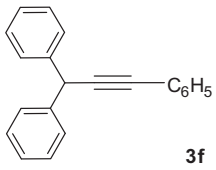
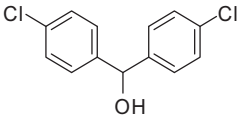
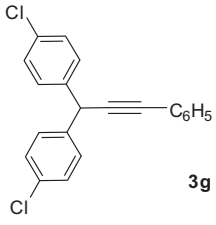
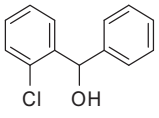
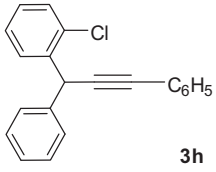
Entry	Catalyst	Solvent	Temp (°C)/time (h)	Yield [b](%)
1	$Zn(OTf)_2$	$BrCH_2CH_2Br$	120/12	Trace, 23[c]
2	$In(OTf)_3$	$BrCH_2CH_2Br$	120/12	Trace, 53[c]
3	$Cu(OTf)_2$	$BrCH_2CH_2Br$	120/12	91, 91[c]
4	$Fe(OTf)_3$	$BrCH_2CH_2Br$	120/12	52, 68[c], 75[d]
5	TfOH	$BrCH_2CH_2Br$	120/12	Trace, 38 [c]
6	H_2SO_4	$BrCH_2CH_2Br$	120/12	0, 0[e]
7	HCl	$BrCH_2CH_2Br$	120/12	0, 0[e]
8	$AlCl_3$	$BrCH_2CH_2Br$	120/12	0
9	$FeCl_3$	$BrCH_2CH_2Br$	120/12	0
10	$Cu(OTf)_2$	DMSO	120/12	0
11	$Cu(OTf)_2$	DMF	120/12	0
12	$Cu(OTf)_2$	C_2H_5OH	80/24	0
13	$Cu(OTf)_2$	CH_3CN	80/24	0
14	$Cu(OTf)_2$	CH_3NO_2	80/24	0
15	$Cu(OTf)_2$	$ClCH_2CH_2Cl$	90/24	51
16	$Cu(OTf)_2$	$BrCH_2CH_2Br$	80/12	65
17	$Cu(OTf)_2$	$BrCH_2CH_2Br$	100/12	77
18	$Cu(OTf)_2$	$BrCH_2CH_2Br$	120/12	91[f], 58[g]

[a] Reaction conditions: diphenylmethanol (1.0 equiv), phenylacetylene (1.1 equiv), catalyst (0.5 mol %), solvent (1.0 mL $mmol^{-1}$), 12 h.
[b] Isolated yields.
[c] The catalyst (2.0 mol %) was used.
[d] $Fe(OTf)_3$ (2.0 mol %) and TfOH (4.0 mol %) were used.
[e] Acid (5.0 mol %) was used.
[f] $Cu(OTf)_2$ (1.0 mol %) was used.
[g] $Cu(OTf)_2$ (0.25 mol %) was used.

To probe the generality of this reaction, a series of arylmethylation products of terminal alkynes with benzylic alcohols were then prepared through this cross-coupling protocol. Under the optimized reaction conditions, a variety of terminal alkynes and benzylic alcohols were chosen as substrates for the reaction in the presence of 0.5 mol % $Cu(OTf)_2$ in $BrCH_2CH_2Br$ at 120 °C for 12 h without base, ligand, and additive. The results in Table 2 indicated that arylalkynes with both electron-donating and electron-withdrawing functional groups on the benzene rings, such as CH_3, *t*-C_4H_9, F, Cl, and Br groups reacted smoothly with diphenylmethanol to afford the corresponding products **3a**–**e** in excellent yields (Table 2, entries 1–5). Fortunately, phenylacetylene also gave a high yield of the desired product, **3f** (Table 2, entry 6). However, no desired coupling product was detected when aliphatic alkyne was used as one of the substrate in the reaction and starting materials were unchanged. In an effort to

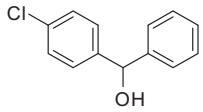
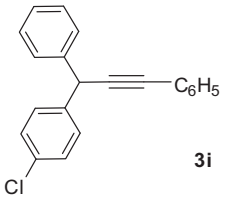
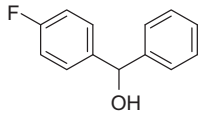
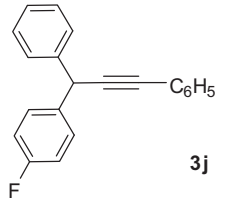
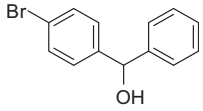
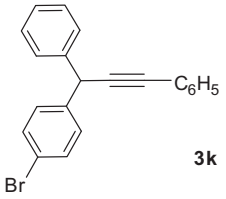
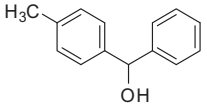
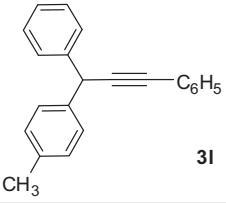
Table 2
$Cu(OTf)_2$-catalyzed coupling of benzylic alcohols and alkynes[a]



Entry	Alcohol	Alkyne	Product	Yield[b] (%)
1		*p*-$CH_3C_6H_4C{\equiv}CH$	 **3a**	90
2		*p*-$FC_6H_4C{\equiv}CH$	 **3b**	93
3		*p*-$ClC_6H_4C{\equiv}CH$	 **3c**	91
4		*p*-$BrC_6H_4C{\equiv}CH$	 **3d**	92
5		*t*-$C_4H_9C_6H_4C{\equiv}CH$	 **3e**	91
6		$C_6H_5C{\equiv}CH$	 **3f**	94
7		$C_6H_5C{\equiv}CH$	 **3g**	97
8		$C_6H_5C{\equiv}CH$	 **3h**	90

(*continued on next page*)

Table 2 (*continued*)

Entry	Alcohol	Alkyne	Product	Yield[b] (%)
9		$C_6H_5C{\equiv}CH$	 **3i**	96
10		$C_6H_5C{\equiv}CH$	 **3j**	91
11		$C_6H_5C{\equiv}CH$	 **3k**	92
12		$C_6H_5C{\equiv}CH$	 **3l**	93

[a] Reaction conditions: benzylic alcohol (1.0 mmol), alkyne (1.1 mmol), $Cu(OTf)_2$ (0.005 mmol), $BrCH_2CH_2Br$ (1.0 mL), 120 °C, 12 h.
[b] Isolated yields.

explore the scope of the reaction, we have screened the coupling of representative phenylacetylene with a variety of substituted benzylic alcohols. When benzylic alcohols bearing both electron-donating and electron-withdrawing functional groups on the benzene rings, such as CH_3, F, Cl, and Br groups also reacted smoothly with phenylacetylene to afford the expected products **3g**–**l** in high yields (Table 2, entries 7–12). Notably, sterically demanding *ortho* substituent did not hamper the reaction and the corresponding product **3h** was isolated in good yield (Table 2, entry 8). However, when other secondary or tertiary alcohols, such as *tert*-butyl alcohol, 2-propanol or cyclohexanol, were treated with phenylacetylene, no desired coupling products were obtained.

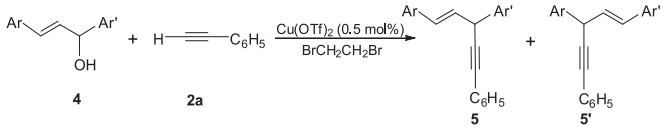
We next tried the coupling reaction of phenylacetylene with allylic alcohols under the present reaction conditions. When 1,3-diphenylprop-2-en-1-ol was reacted with phenylacetylene in the presence of 0.5 mol % of $Cu(OTf)_2$, the corresponding coupling product **5a** was isolated in good yield (Table 3, entry 1). Meanwhile, when 3-(4-chlorophenyl)-1-phenylprop-2-en-1-ol, 3-(4-methylphenyl)-1-phenylprop-2-en-1-ol, and 3-(2,4-dichlorophenyl)-1-phenylprop-2-en-1-ol were reacted with phenylacetylene, respectively, under the above reaction conditions, the corresponding coupling products, a mixture of regioisomers, **5b**/**5b′**, **5c**/**5c′**, and **5d**/**5d′** were obtained, respectively, in good yields with different ratios (Table 3, entries 2–4). Having the confirmed structure of **5a** in our hand, the structures of **5b** and **5b′**, **5c** and **5c′**, **5d** and **5d′**, were given by ^1H, ^{13}C NMR spectroscopic analysis, and HR-MS, even though they are new compounds. The ratios of two regioisomer products, **5b** and **5b′**, **5c** and **5c′**, **5d** and **5d′**, were determined by ^1H NMR spectral analysis. 1,3-Disubstituted allylic alcohol would presumably be first formed to a carbon cation as the intermediate in the presence of Lewis acid, $Cu(OTf)_2$, which probably possesses the resonance structures of allylic cation. The ratio of two regioisomers, **5** and **5′**, indicated in Table 3 accounts for the difference of the stability of two resonance structures in allylic cation (Scheme 3).

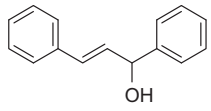
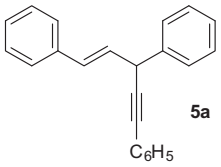
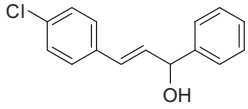
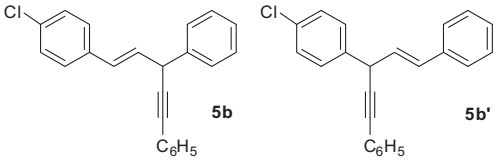
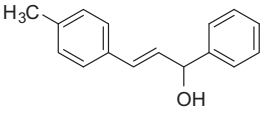
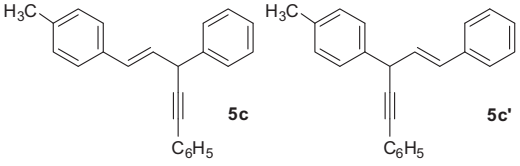
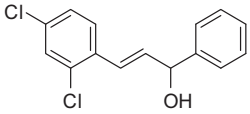
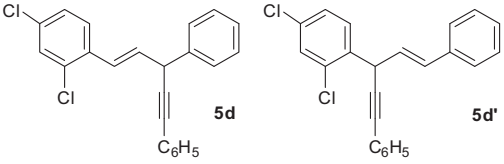
Based on the results obtained, a plausible mechanism of $Cu(OTf)_2$-catalyzed coupling reaction of terminal alkynes with benzylic alcohols was shown in Scheme 4. Benzyl alcohol was activated by the Lewis acid, $Cu(OTf)_2$, to form a carbocation intermediate **A**. The formed **A** attacks the electron-rich aromatic alkyne to generate vinyl cation **B**, followed by deprotonation to form the corresponding arylmethylation product.[17] When other Lewis acid, such as $FeBr_3$ or $FeCl_3$ was used as promoter for the reaction of benzylic alcohol with aromatic alkyne, the highly regio- and stereo-selective alkenyl bromides and chlorides were obtained. It was suggested that the sp-hybridized vinyl cation **B** could be attacked by a stronger nucleophile Br^- or Cl^- to generate the corresponding alkenyl halide in good stereoselectivity.[19]

3. Conclusions

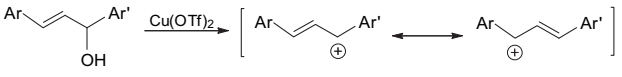
In summary, we have developed an effective, convenient, and mild direct coupling reaction of benzylic alcohols with terminal alkynes. As an effective Lewis acid, $Cu(OTf)_2$-catalyzed arylmethylation of terminal alkynes with benzylic alcohols generated the corresponding products in $BrCH_2CH_2Br$ with good yields in the absence of ligand, base, and additive. The successful alkynylation of allylic alcohols also provides a new route to 1,4-enynes, which are

Table 3
$Cu(OTf)_2$-catalyzed coupling of allylic alcohols to phenylacetylene [a]

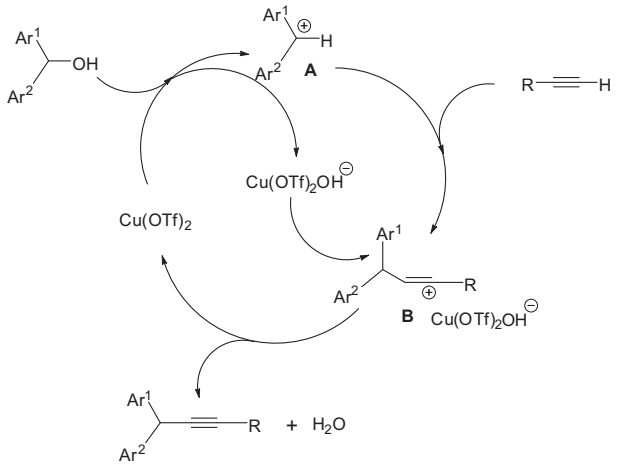


Entry	Alcohol	Product	Yield [b](%)/**5**:**5'**[c]
1		 **5a**	78
2		 **5b** **5b'**	80 (5:4)
3		 **5c** **5c'**	84 (5:6)
4		 **5d** **5d'**	71 (72:27)

[a] Reaction conditions: allylic alcohol (1.0 mmol), phenylacetylene (1.1 mmol), $Cu(OTf)_2$ (0.005 mmol), $BrCH_2CH_2Br$ (1.0 mL), 120 °C, 12 h.
[b] Isolated yields.
[c] Ratios were determined by ^1H NMR.



Scheme 3.



Scheme 4. Proposed mechanism of $Cu(OTf)_2$-catalyzed reaction of benzylic alcohol with terminal alkyne.

suitable for further elaboration. Furthermore, H_2O as the only by-product makes this transformation atom efficient. Further studies to extend the scope and synthetic utility for Cu-catalyzed cross-coupling reaction are in progress in our laboratory.

4. Experimental

4.1. General remarks

All reactions were carried out under an air atmosphere. All reagents were purchased from commercial suppliers and used after further purification. Products were purified by flash chromatography on 230–400 mesh silica gel, SiO_2. All ^1H NMR, ^{13}C NMR spectra were measured on a Bruker Avance NMR spectrometer (400 MHz or 100 MHz, respectively) with $CDCl_3$ as solvent and recorded in parts per million relative to internal tetramethylsilane standard.

4.2. Typical procedure for $Cu(OTf)_2$-catalyzed arylmethylation of terminal alkynes with benzylic alcohols without base, ligand, and additive

A 10 mL reaction tube was charged with diphenylmethanol (1.0 mmol), phenylacetylene (1.1 mmol), $Cu(OTf)_2$ (0.005 mmol), and $BrCH_2CH_2Br$ (1.0 mL). The reaction vessel was placed in an oil bath at 120 °C. After the reaction was carried out at this temperature for 12 h, it was cooled to room temperature, diluted with H_2O,

and extracted twice with Et_2O. The organic layers were combined, dried over Na_2SO_4, and concentrated to yield the crude product, which was further purified by flash chromatography on silica gel (eluant: petroleum ether) to give the desired cross-coupling product, 1,3,3-triphenyl-1-propyne (245 mg, 91% yield).

4.3. Analytical data for the arylmethylation of terminal alkynes with benzylic alcohols products

*4.3.1. 1-(4-Methylphenyl)-3,3-diphenyl-1-propyne (**3a**)*[13]. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.44–7.42 (m, 4H), 7.36 (d, J=8.4 Hz, 2H), 7.30 (t, J=7.2 Hz, 4H), 7.23–7.19 (m, 2H), 7.09 (d, J=7.6 Hz, 2H), 5.19 (s, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=141.9, 138.0, 131.5, 128.9, 128.6, 127.8, 126.8, 120.4, 89.4, 84.9, 43.8, 21.4. IR (neat): ν=3461, 3049, 2534, 1955, 1599, 1505, 1492, 1014, 827, 749, 698 cm^{-1}.

*4.3.2. 1-(4-Fluorophenyl)-3,3-diphenyl-1-propyne (**3b**)*[17]. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.46–7.42 (m, 6H), 7.32 (t, J=8.0 Hz, 4H), 7.25–7.23 (m, 2H), 6.99 (t, J=8.8 Hz, 2H), 5.19 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=162.3 (d, J=247.4 Hz), 141.6, 133.5 (d, J=8.2 Hz), 128.6, 127.8, 126.9, 119.5 (d, J=3.5 Hz), 115.4 (d, J=21.9 Hz), 89.9 (d, J=1.5 Hz), 83.8, 43.6. IR (neat): ν=3463, 3052, 2536, 1954, 1592, 1507, 1490, 1017, 747, 693 cm^{-1}.

*4.3.3. 1-(4-Chlorophenyl)-3,3-diphenyl-1-propyne (**3c**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.42–7.37 (m, 6H), 7.33–7.30 (m, 4H), 7.01–6.96 (m, 4H), 5.18 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=141.4, 133.9, 132.9, 128.6, 128.5, 127.8, 126.9, 121.9, 91.2, 83.7, 43.7. IR (neat): ν=3461, 1952, 1589, 1510, 1489, 1014, 749, 698 cm^{-1}. Anal. Calcd for $C_{21}H_{15}Cl$: C, 83.30; H, 4.99. Found: C, 83.48; H, 5.04. HR-MS (ESI): m/z=302.0861 ([M]$^+$), calcd for $C_{21}H_{15}Cl$: 302.0862.

*4.3.4. 1-(4-Bromophenyl)-3,3-diphenyl-1-propyne (**3d**)*[17]. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.42–7.39 (m, 6H), 7.32–7.29 (m, 6H), 7.23–7.18 (m, 2H), 5.18 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=141.4, 133.1, 131.4, 128.7, 127.8, 126.9, 122.4, 122.1, 91.4, 83.8, 43.7. IR (neat): ν=3461, 1953, 1587, 1510, 1484, 1011, 756, 697 cm^{-1}.

*4.3.5. 1-(4-tert-Butylphenyl)-3,3-diphenyl-1-propyne (**3e**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.43 (t, J=8.4 Hz, 6H), 7.30 (t, J=8.0 Hz, 6H), 7.23–7.20 (m, 2H), 5.19 (s, 1H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=151.2, 141.9, 131.4, 128.6, 127.9, 126.8, 125.2, 120.4, 89.5, 84.9, 43.7, 34.7, 31.2. IR (neat): ν=3461, 1952, 1590, 1512, 1492, 1074, 763, 700 cm^{-1}. Anal. Calcd for $C_{25}H_{24}$: C, 92.54; H, 7.46. Found: C, 92.69; H, 7.31. HR-MS (ESI): m/z=324.1876 ([M]$^+$), calcd for $C_{25}H_{24}$: 324.1878.

*4.3.6. 1,3,3-Triphenyl-1-propyne (**3f**)*[13]. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.45–7.42 (m, 6H), 7.31–7.20 (m, 7H), 7.22–7.18 (m, 2H), 5.19 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=141.7, 131.6, 128.6, 128.2, 127.9, 126.9, 123.5, 90.2, 84.9, 43.7. IR (neat): ν=3452, 2943, 1953, 1580, 1483, 755, 697, 525 cm^{-1}.

*4.3.7. 1,1-Di(4-chlorophenyl)-3-phenyl-1-propyne (**3g**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.61–7.58 (m, 2H), 7.44–7.38 (m, 11H), 5.23 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=139.8, 133.0, 129.2, 128.9, 128.4, 123.0, 89.1, 85.7, 42.6. IR (neat): ν=3422, 1950, 1900, 1594, 1091, 756, 691 cm^{-1}. Anal. Calcd for $C_{21}H_{14}Cl_2$: C, 74.79; H, 4.18. Found: C, 75.01; H, 4.02. HR-MS (ESI): m/z=337.0471 ([M]$^+$), calcd for $C_{21}H_{14}Cl_2$: 337.0473.

*4.3.8. 1,3-Diphenyl-3-(2-chlorophenyl)-1-propyne (**3h**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.86 (d, J=1.2 Hz, 1H), 7.67–7.64 (m, 4H), 7.50–7.42 (m, 8H), 7.32–7.28 (m, 1H), 5.96 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=140.5, 139.4, 133.3, 131.8, 130.2, 129.7, 128.7, 128.5, 128.3, 128.2, 128.0, 127.4, 127.1, 123.4, 89.8, 84.8, 40.4. IR (neat): ν=3446, 1951, 1902, 1590, 1070, 752, 692 cm^{-1}. Anal. Calcd for $C_{21}H_{15}Cl$: C, 83.30; H, 4.99. Found: C, 83.51; H, 4.75. HR-MS (ESI): m/z=302.0867 ([M]$^+$), calcd for $C_{21}H_{15}Cl$: 302.0862.

*4.3.9. 1,3-Diphenyl-3-(4-chlorophenyl)-1-propyne (**3i**)*[13]. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.60–7.59 (m, 2H), 7.54–7.52 (m, 2H), 7.49–7.35 (m, 10H), 5.28 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=141.3, 140.3, 132.8, 131.7, 129.3, 128.8, 128.3, 128.2, 127.9, 127.1, 123.3, 89.7, 85.3, 43.2. IR (neat): ν=3447, 1950, 1900, 1592, 1098, 753, 690 cm^{-1}.

*4.3.10. 1,3-Diphenyl-3-(4-fluorophenyl)-1-propyne (**3j**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.47–7.45 (m, 2H), 7.41–7.35 (m, 4H), 7.32–7.26 (m, 5H), 7.21 (t, J=7.2 Hz, 1H), 6.98 (t, J=8.8 Hz, 2H), 5.16 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=161.8 (d, J=243.9 Hz), 141.5, 137.5 (d, J=3.2 Hz), 131.6, 129.4 (d, J=8.0 Hz), 128.7, 128.2, 128.1, 127.8, 127.0, 123.3, 115.4 (d, J=21.4 Hz), 89.9, 85.1, 42.6 (d, J=2.2 Hz). IR (neat): ν=3443, 1953, 1902, 1590, 1088, 750, 687 cm^{-1}. Anal. Calcd for $C_{21}H_{15}F$: C, 88.09; H, 5.28. Found: C, 88.31; H, 5.07. HR-MS (ESI): m/z=286.1163 ([M]$^+$), calcd for $C_{21}H_{15}F$: 286.1158.

*4.3.11. 1,3-Diphenyl-3-(4-bromophenyl)-1-propyne (**3k**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.47–7.39 (m, 6H), 7.33–7.28 (m, 7H), 7.25–7.21 (m, 1H), 5.15 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=141.1, 140.8, 131.7, 131.6, 129.6, 128.7, 128.2, 128.1, 127.8, 127.1, 123.2, 120.8, 89.5, 85.2, 43.2. IR (neat): ν=3448, 3061, 1953, 1599, 1580, 1485, 1448, 1070, 1011, 841, 727, 697 cm^{-1}. Anal. Calcd for $C_{21}H_{15}Br$: C, 72.64; H, 4.35. Found: C, 72.69; H, 4.57. HR-MS (ESI): m/z=346.0359 ([M]$^+$), calcd for $C_{21}H_{15}Br$: 346.0357.

*4.3.12. 1,3-Diphenyl-3-(4-methylphenyl)-1-propyne (**3l**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.45–7.41 (m, 4H), 7.32–7.26 (m, 7H), 7.25–7.24 (m, 1H), 7.10 (d, J=8.0 Hz, 2H), 5.15 (s, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=141.9, 138.8, 136.4, 131.6, 129.3, 128.6, 128.2, 127.8, 127.7, 126.8, 123.6, 90.4, 84.7, 43.3, 21.0. IR (neat): ν=3444, 3063, 1950, 1599, 1512, 1489, 1447, 1072, 841, 729, 695 cm^{-1}. Anal. Calcd for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.38; H, 6.62. HR-MS (ESI): m/z=282.1406 ([M]$^+$), calcd for $C_{22}H_{18}$: 282.1409.

*4.3.13. (E)-1,3,5-Triphenylpent-4-yne-1-ene, (E)-**5a***[13]. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.49–7.47 (m, 4H), 7.38–7.32 (m, 4H), 7.30–7.25 (m, 5H), 7.23–7.16 (m, 1H), 6.76 (d, J=15.6 Hz, 1H), 6.32 (dd, J=15.6, 6.8 Hz, 1H), 4.73 (d, J=6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=140.3, 136.8, 131.7, 130.5, 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. IR (neat): ν=3462, 3053, 1951, 1665, 1597, 1512, 1489, 1448, 1112, 820, 754, 691 cm^{-1}.

*4.3.14. (E)-1,3-Diphenyl-5-(4-chlorophenyl)-4-yne-1-ene (**5b**) and (E)-1,5-diphenyl-3-(4-chlorophenyl)-4-yne-1-ene (**5b**′), (**5b**/**5b**′=5/4).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.50–7.47 (m, 3H), 7.41–7.33 (m, 3H), 7.32–7.28 (m, 5H), 7.27–7.18 (m, 3H), 6.72 (d, J=15.6 Hz, 1H), 6.31–6.24 (m, 1H), 4.73–4.68 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=140.0, 138.8, 136.6, 135.3, 133.1, 132.9, 131.7 (d), 130.8, 130.3, 129.2, 129.1, 129.0, 128.8, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.7 (t), 127.2, 126.5, 123.3, 123.1, 88.5, 88.2, 85.7, 85.4, 41.1, 40.6. IR (neat): ν=3467, 3058, 1950, 1675, 1596, 1514, 1489, 1442, 1090, 823, 755, 691 cm^{-1}. Anal. Calcd for $C_{23}H_{17}Cl$: C, 84.01; H, 5.21. Found: C, 84.23; H, 5.15. HR-MS (ESI): m/z=328.1022 ([M]$^+$), calcd for $C_{23}H_{17}Cl$: 328.1019.

*4.3.15. (E)-1,3-Diphenyl-5-(4-methylphenyl)-4-yne-1-ene (**5c**) and (E)-1,5-diphenyl-3-(4-methylphenyl)-4-yne-1-ene (**5c**′), (**5c**/**5c**′=5/6).* ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.49–7.26 (m, 11H), 7.21–7.07 (m, 3H), 6.74 (dd, J=15.6, 8.8 Hz, 1H), 6.34–6.24 (m, 1H), 4.71 (m, 1H), 2.33 (s, 1.64H), 2.30 (s, 1.36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=140.4, 137.3 (d), 136.9, 136.7, 134.0, 131.7, 130.3, 130.2, 129.8, 129.4, 129.2, 128.7, 128.6, 128.5, 128.2, 128.0, 127.9, 127.7, 127.6, 127.4, 127.0,

126.5, 126.4, 126.1, 123.5, 123.4, 89.1, 89.0, 85.3, 85.2, 41.2, 40.8, 21.1, 21.0. IR (neat): ν=3465, 3055, 1952, 1660, 1598, 1510, 1490, 1448, 1112, 817, 756, 691 cm^{-1}. Anal. Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.28; H, 6.72. HR-MS (ESI): m/z=308.1569 ($[M]^+$), calcd for $C_{24}H_{20}$: 308.1565.

*4.3.16. (E)-1,3-Diphenyl-5-(2,4-dichlorophenyl)-4-yne-1-ene (**5d**) and (E)-1,5-diphenyl-3-(2,4-dichlorophenyl)-4-yne-1-ene (**5d′**), (**5d**/**5d′**=72/27).* ^1H NMR (400 MHz, $CDCl_3$): δ=7.63–7.46 (m, 4H), 7.38–7.34 (m, 4H), 7.30–7.22 (m, 5H), 7.19–7.11 (m, 2H), 6.30–6.22 (m, 1H), 5.18 (d, J=6.0 Hz, 0.27H), 4.75 (d, J=6.4 Hz, 0.72H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=139.7, 136.6, 136.5, 133.7, 133.6, 133.5, 133.4, 132.8, 131.7, 131.6, 131.2, 130.5, 129.4, 129.3, 128.8, 128.5, 128.3, 128.2, 128.1, 127.7, 127.6, 127.2, 127.1, 127.0, 126.5, 125.7, 123.2, 123.0, 88.2, 87.5, 85.9, 85.5, 41.4, 37.5. IR (neat): ν=3446, 3060, 1954, 1646, 1598, 1558, 1490, 1451, 1101, 867, 755, 691 cm^{-1}. Anal. Calcd for $C_{23}H_{16}Cl_2$: C, 76.04; H, 4.44. Found: C, 76.25; H, 4.27. HR-MS (ESI): m/z=363.0631 ($[M]^+$), calcd for $C_{23}H_{16}Cl_2$: 363.0629.

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Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.tet.2011.02.050. These data include MOL files and InChIKeys of the most important compounds described in this article.

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17. During the preparation of our manuscript, Jiao and co-workers reported the same reaction, they reported that Fe(OTf)3/TfOH co-catalyzed coupling reaction of terminal alkynes with benzylic alcohols, and the highest yield (77%) was reached co-catalyzed by Fe(OTf)3 (5 mol %) and TfOH (10 mol %) in DCE. Markedly, even when 2 mol % of Fe(OTf)3 and 5 mol % of TfOH were employed, the coupling went well giving 70% yield. See: Xiang, S. K.; Zhang, L. H.; Jiao, N. *Chem. Commun.* **2009**, 6487–6489 for detail.
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