$Cu(OAc)_2{\cdot}H_2O$-promoted tandem β-alkynyl elimination of α- or β-hydroxy propargylic alcohols and homocoupling of the resulting alkynyl species

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α or β-hydroxy propargylic alcohols undergo tandem C(sp)–C(sp^3) bond cleavage via β-alkynyl elimination and homocoupling of the resulted alkynyl species in the presence of $Cu(OAc)_2{\cdot}H_2O$ to produce the corresponding hydroxycarbonyl compounds and 1,3-butadiynes.

Key words: C(sp)–C(sp^3) bond cleavage; β-alkynyl elimination; homocoupling; 1,3-butadiynes; propargylic alcohols

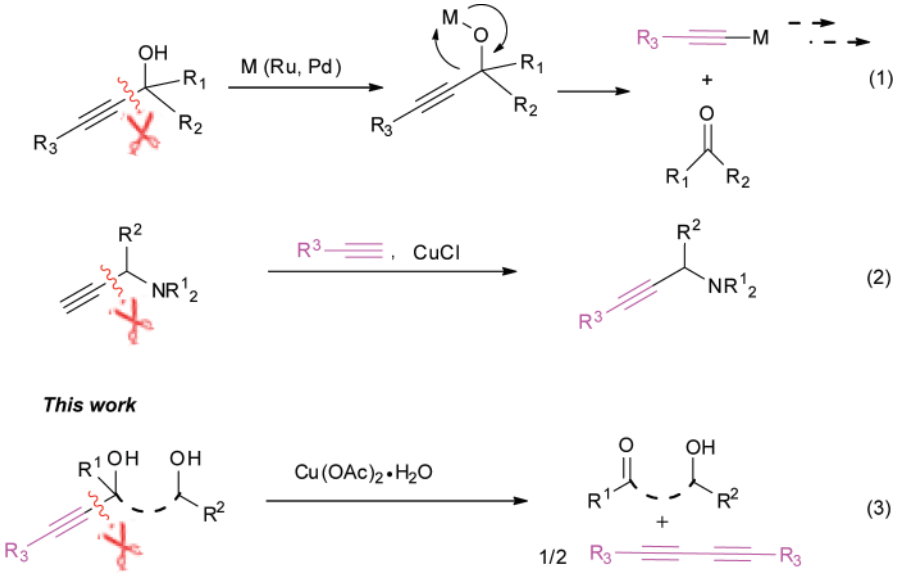
The C(sp)–C(sp^3) bond cleavage of propargylic alcohols via β-alkynyl elimination has attracted considerable attention since the resulted alkynyl species can employed in several successive reactions to construct useful tandem transformations [Scheme 1, Eqn (1)].[1–5] In general, these transformations have been catalysed by expensive Ru or Pd catalysts. Recently, by employing inexpensive copper(I) catalysts, the Nakamura group achieved a selective C(sp)–C(sp^3) bond cleavage of propargylic amines [Scheme 1, Eqn (2)].[6] The resultant copper acetylides and iminium intermediates can undergo further fragment exchange with additional aldehydes, amines, and alkynes to give new propargylic amines. Here, we disclose a copper-promoted tandem C(sp)–C(sp^3) bond cleavage and homocoupling of the resultant alkynyl species. To the best of our knowledge, this is the first example of copper-promoted C(sp)–C(sp^3) bond cleavage of propargylic alcohols via β-alkynyl elimination [Scheme 1, Eqn (3)].

Results and discussion

This discovery resulted from screening Lewis acids that we hoped might be effective catalysts for the cyclisation of **1a**.[7,8] We were surprised to discover that $Cu(OAc)_2{\cdot}H_2O$ produced salicylaldehyde and 1,4-diphenyl-1,3-butadiyne through an unexpected C(sp)–C(sp^3) bond cleavage of **1a**. Other copper salts such as CuCl, CuBr, CuI, $CuSO_4{\cdot}5H_2O$, $Cu(OTf)_2$, and $CuCl_2$ did not bring about this transformation. Other Lewis acids, such as $FeCl_3$ and $Yb(OTf)_3$, also showed no catalytic reactivity. Changing the loading of $Cu(OAc)_2{\cdot}H_2O$ from 0.5 equiv. to 0.2 and 1 equiv. afforded the compound **3a** in 56% and 76% yields, respectively. Among the solvents that were tested, DMF was also found to be effective for the reaction and afforded **3a** in 74% yield.

Under the optimised reaction conditions, the scope of this copper-promoted C(sp)–C(sp^3) bond cleavage reaction was demonstrated with a series of propargylic alcohols (Table 2). Propargylic alcohols derived from salicylaldehyde derivatives with methyl, methoxyl, chloro, bromo, and strong electron-withdrawing groups such as nitro all underwent the C–C bond cleavage. The reaction also worked smoothly with propargylic alcohols derived from substituted phenylacetylenes with methyl, methoxyl, isopropyl, chloro, bromo groups. Although the electron-withdrawing substrates showed less reactivity, good yield could be obtained at higher reaction temperature using DMF as solvent. Similarly, propargylic alcohols derived from *o*-acetylphenol and *o*-benzoylphenol derivatives gave the corresponding 1,3–diyne in good yields. Notably, α-hydroxy propargylic alcohol such as **1s** could also be used and gave 1,4-diphenyl-1,3-butadiyne in 72% yield (Scheme 2).

The coordinating ability of the dihydroxy compounds with the metal could be one of the key factors for the C(sp)–C(sp^3) bond cleavage. Moreover, the lack of formation of any 1,3-diynes and carbonyl compounds with simple propargylic alcohols such as **1t-v** under the standard conditions (Scheme 3) supports this hypothesis. It is worth mentioning that this transformation might have potential application as a carbonyl protecting group for hydroxycarbonyl compounds, since the propargylic alcohols could easily synthesized in good yield by the addition of lithium acetylides to hydroxycarbonyl compounds.



Scheme 1 Selective C(sp)–C(sp^3) bond cleavage.

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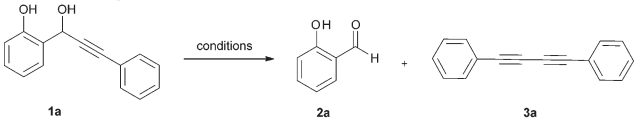
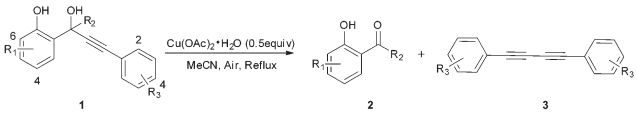
Table 1 Optimisation of reaction conditions[a]



Entry	Metal salts	Solvent	Yield/%[b]
1	CuCl	MeCN	0
2	CuBr	MeCN	0
3	CuI	MeCN	Trace
4	$CuSO_4·5H_2O$	MeCN	0
5	$Cu(OTf)_2$	MeCN	0
6	$CuCl_2$	MeCN	Trace
7	**$Cu(OAc)_2·H_2O$**	**MeCN**	**79**
8	$FeCl_3$	MeCN	0
9	$Yb(OTf)_3$	MeCN	0
10[c]	$Cu(OAc)_2·H_2O$	MeCN	56
11[d]	$Cu(OAc)_2·H_2O$	MeCN	76
11[e]	$Cu(OAc)_2·H_2O$	DMF	74
12	$Cu(OAc)_2·H_2O$	dioxane	25
13	$Cu(OAc)_2·H_2O$	toluene	0
14	$Cu(OAc)_2·H_2O$	DCM	0
15	$Cu(OAc)_2·H_2O$	DCE	0
16	$Cu(OAc)_2·H_2O$	THF	0

[a]Reaction conditions: **1a** (0.2 mmol) and metal salts (0.1 mmol) in solvents (2 mL) at reflux for 4 h. [b]Isolated yield based on **3a**. [c]20 mol% of $Cu(OAc)_2·H_2O$. [d]1 equiv. of $Cu(OAc)_2·H_2O$. [e]At 110 °C.

Table 2 C(sp)–C(sp³) bond cleavage of phenol derivatives[a]



Entry	Substrates	Time/h	Yield/%[b]
1	**1a** $R_1 = R_2 = R_3 = H$	4	79
2	**1b** R_1 = 4-Me, $R_2 = R_3 = H$	1.5	66
3	**1c** R_1 = 4-OMe, $R_2 = R_3 = H$	2	72
4	**1d** R_1 = 6-Me, $R_2 = R_3 = H$	3.5	78
5	**1e** R_1 = 4,6-dimethyl, $R_2 = R_3 = H$	1.5	92
6	**1f** R_1 = 4-Cl, $R_2 = R_3 = H$	3.5	48(64)[c]
7	**1g** R_1 = 4,6-dibromo, $R_2 = R_3 = H$	(5)[c]	(82)[c]
8	**1h** R_1 = 4-NO_2, $R_2 = R_3 = H$	6(5)[c]	25(91)[c]
9	**1i** $R_1 = R_2 = H$, R_3 = 4-Me	6.5	67
10	**1j** $R_1 = R_2 = H$, R_3 = 4-OMe	6	70
11	**1k** $R_1 = R_2 = H$, R_3 = 4-Cl	17(4)[c]	67(70)[c]
12	**1l** $R_1 = R_2 = H$, R_3 = 2-Cl	2.5	33
13	**1m** $R_1 = R_2 = H$, R_3 = 4-Br	22	20
14	**1n** R_1 = 4-Cl, $R_2 = H$, R_3 = 4-Cl	(4)[c]	(83)[c]
15	**1o** $R_1 = H$, R_2 = Me, $R_3 = H$	4	71
16	**1p** $R_1 = H$, R_2 = Me, R_3 = 4-Pr	4	73
17	**1q** $R_1 = H$, R_2 = Me, R_3 =4-Cl	3.5	77
18	**1r** R_1 = 4-Me, R_2 = *p*-MePh, $R_3 = H$	3	84

[a]Reaction conditions: propargylic alcohols (0.2 mmol), $Cu(OAc)_2·H_2O$ (0.1 mmol) in MeCN (2.0 mL) at reflux, air. [b]Isolated yield based on **3**. [c]DMF, 110 °C.

Although the mechanism of this transformation is not completely clear, on the basis of these preliminary data and literature precedents, a plausible reaction mechanism is suggested in Scheme 4. Intermediate **I** is initially generated by the coordination of copper to the substrate.[9] **I** then undergoes C(sp)–C(sp³) bond cleavage via β-alkynyl elimination to form intermediate II with release of **2**. Intermediate II then decomposes into phenylacetylene radicals and CuOAc. Finally, the dimerisation of the phenylacetylene radicals provides **3** with the oxidisation of CuOAc to $Cu(OAc)_2$ in the presence of AcOH and O_2.[10]

In summary, an unprecedented tandem Cu(II)-promoted selective C(sp)–C(sp³) bond cleavage of α or β-hydroxy propargylic alcohols via β-alkynyl elimination and homocoupling of the resulted alkynyl radicals has been established. The coordination of the dihydroxy group with the metal is essential for the C(sp)–C(sp³) bond cleavage. Further studies regarding the mechanistic details and the potential application of this transformation for successive reactions and as a carbonyl protecting group are in progress.

Experimental

All reagents and solvents were purchased from commercial suppliers and used without purifications. Melting points were measured on a Büchi B-545. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker Avance III 500 (500 MHz) instrument in $CDCl_3$ or DMSO using tetramethylsilane (TMS) as the internal standard. Chemical shifts (δ) are reported in ppm and coupling constants *J* are given in Hz. ESI-MS spectra and high resolution mass spectra (HRMS) were obtained on a Agilent 6210 LC/TOF-MS with ESI source. The propargylic alcohols were synthesised by the addition of lithium acetylides to hydroxycarbonyl compounds according to literature method.[1]

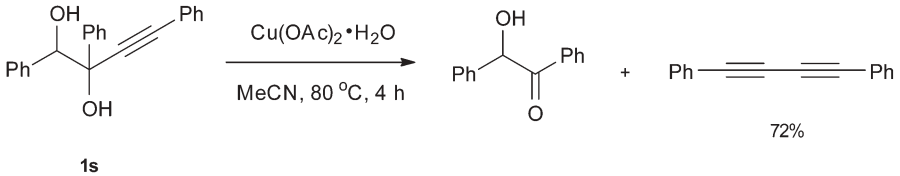
General experimental procedure and spectroscopic data: Propargylic alcohol (0.2 mmol) in acetonitrile (2.0 mL) was added $Cu(OAc)_2·H_2O$ (0.1 mmol) at room temperature. The reaction mixture was heated at reflux, in air. After completion of the reaction as indicated by TLC, the solvent was removed under reduced pressure, and the residue was purified by chromatography on silica gel (100–200 mesh) using petroleum ether/EtOAc (9/1, v/v) as the eluent to give 1,3-butadiynes.

2-(1-Hydroxy-3-phenylprop-2-yn-1-yl)phenol (**1a**):[11] Pale white solid, m.p. 88–90 °C(lit. 88 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49–7.43 (m, 3H), 7.36–7.31 (m, 3H), 7.29–7.25 (m, 2H), 6.92 (t, *J* = 7.6 Hz, 2H), 5.91 (d, *J* = 4.3 Hz, 1H), 3.00 (d, *J* = 5.3 Hz, 1H).

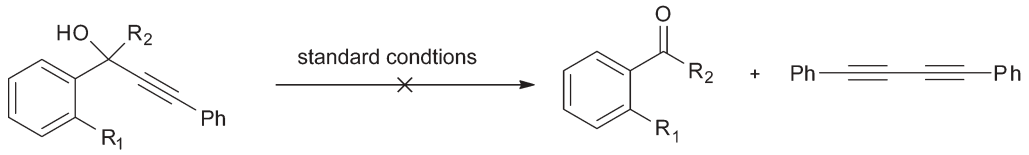
2-(1-Hydroxy-3-phenylprop-2-yn-1-yl)-4-methylphenol (**1b**): Brown solid, m.p. 80–82 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49–7.46 (m, 2H), 7.35–7.30 (m, 3H), 7.21 (d, *J* = 1.9 Hz, 1H), 7.07 (s, 1H), 7.03 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.81 (d, *J* = 8.2 Hz, 1H), 5.85 (d, *J* = 5.4 Hz, 1H), 3.06 (d, *J* = 5.6 Hz, 1H), 2.27 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.81, 131.86, 130.56, 129.57, 128.83, 128.36, 128.18, 124.45, 122.12, 116.94, 87.94, 86.87, 64.26, 20.54. HRMS (ESI): *m/z* calcd for $C_{16}H_{14}O_2Na$ [M + Na]: 261.0891; found: 261.0890.

2-(1-Hydroxy-3-phenylprop-2-yn-1-yl)-4-methoxyphenol (**1c**): Pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.35–7.31 (m, 3H), 7.03 (d, *J* = 3.0 Hz, 1H), 6.88 (s, 1H), 6.85 (d, *J* = 8.8 Hz, 1H), 6.79 (dd, *J* = 8.8, 3.0 Hz, 1H), 5.86 (d, *J* = 4.1 Hz, 1H), 3.76 (s, 3H), 3.16 (d, *J* = 5.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.22, 148.95, 131.84, 128.88, 128.37, 125.56, 122.00, 117.76, 115.12, 113.43, 88.08, 86.60, 64.07, 55.84. HRMS (ESI): *m/z* calcd for $C_{16}H_{14}O_3Na$ [M + Na]: 277.0841; found: 277.0839.

2-(1-Hydroxy-3-phenylprop-2-yn-1-yl)-6-methylphenol (**1d**): White solid, m.p. 89–91 °C; ^{1}H NMR (500 MHz, DMSO) δ 8.57 (s, 1H), 7.42–7.34 (m, 6H), 7.06–7.02 (m, 1H), 6.79 (t, *J* = 7.5 Hz, 1H), 6.22 (d, *J* = 5.5 Hz, 1H), 5.89 (d, *J* = 5.2 Hz, 1H), 2.19 (s, 3H). ^{13}C NMR (125 MHz, DMSO) δ 152.07, 131.22, 129.96, 128.60, 128.44, 128.17, 124.97, 124.82, 122.36, 119.29, 91.32, 83.68, 58.99, 16.29. HRMS (ESI): *m/z* calcd for $C_{16}H_{14}O_2Na$ [M + Na]: 261.0891; found: 261.0891.

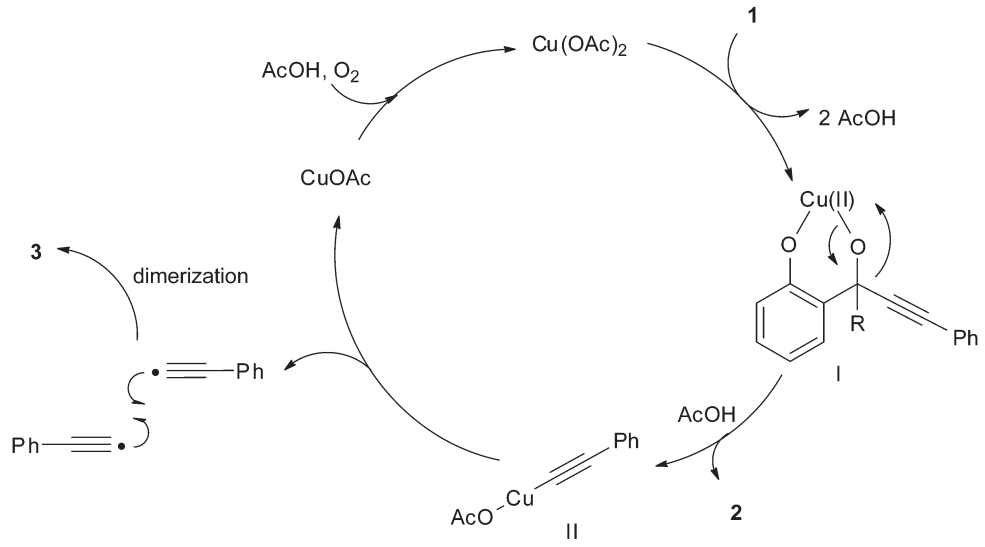


Scheme 2 C(sp)–C(sp³) bond cleavage of **1s**.



1t, R_1 = Br, R_2 = H
1u, R_1 = H, R_2 = Me
1v, R_1= H, R_2 = Ph

Scheme 3 The reaction of simple propargylic alcohols.



Scheme 4 Proposed mechanism.

2-(1-Hydroxy-3-phenylprop-2-yn-1-yl)-4,6-dimethylphenol (**1e**): White solid, m.p. 89–92 °C; ^{1}H NMR (500 MHz, DMSO) δ 8.31 (s, 1H), 7.42–7.36 (m, 5H), 7.14 (s, 1H), 6.85 (s, 1H), 6.16 (s, 1H), 5.85 (s, 1H), 2.20 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (125 MHz, DMSO) δ 149.68, 131.22, 130.50, 128.61, 128.41, 128.06, 127.68, 125.23, 124.71, 122.41, 91.49, 83.52, 58.90, 20.24, 16.27. HRMS (ESI): *m/z* calcd for $C_{17}H_{16}O_2Na$ [M + Na]: 275.1048; found: 275.1044.

4-Chloro-2-(1-hydroxy-3-phenylprop-2-yn-1-yl)phenol (**1f**): Pink solid, m.p. 91–93 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.42 (d, *J* = 2.5 Hz, 1H), 7.38–7.34 (m, 3H), 7.26 (s, 1H), 7.21 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 1H), 5.88 (d, *J* = 5.2 Hz, 1H), 2.84 (d, *J* = 5.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.00, 131.92, 129.95, 129.17, 128.47, 127.55, 125.91, 125.05, 121.67, 118.60, 88.81, 85.75, 64.03. HRMS (ESI): *m/z* calcd for $C_{15}H_{11}ClO_2Na$ [M + Na]: 281.0345; found: 281.0343.

2,4-Dibromo-6-(1-hydroxy-3-phenylprop-2-yn-1-yl)phenol (**1g**): Yellow oil; ^{1}H NMR (500 MHz, DMSO) δ 9.75 (s, 1H), 7.70 (d, *J* = 2.4 Hz, 1H), 7.65 (d, *J* = 2.4 Hz, 1H), 7.44–7.42 (m, 2H), 7.40–7.37 (m, 3H), 6.46 (s, 1H), 5.86 (s, 1H). ^{13}C NMR (125 MHz, DMSO) δ 150.12, 133.54, 133.26, 131.34, 129.09, 128.72, 128.67, 121.94, 112.48, 111.25, 90.08, 84.01, 58.27. HRMS (ESI): *m/z* calcd for $C_{15}H_{10}Br_2O_2Na$ [M + Na]: 402.8945; found: 402.8942.

2-(1-Hydroxy-3-phenylprop-2-yn-1-yl)-4-nitrophenol (**1h**):[11] Yellow solid, m.p. 133–135 °C(lit. 137–138 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42–8.35 (m, 2H), 8.18 (dd, *J* = 9.0, 2.7 Hz, 1H), 7.51 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.40–7.34 (m, 3H), 7.02 (d, *J* = 9.0 Hz, 1H), 6.00 (s, 1H), 3.06 (s, 1H).

2-(1-Hydroxy-3-(p-tolyl)prop-2-yn-1-yl)phenol (**1i**): Pale grey solid, m.p. 98–100 °C; ^{1}H NMR (500 MHz, CDC_{l3}) δ 7.45 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 3.8 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.93 (dd, *J* = 7.8, 2.7 Hz, 2H), 5.91 (d, *J* = 5.8 Hz, 1H), 2.79 (d, *J* = 5.9 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (125 MHz, CDC_{l3}) δ 155.37, 139.17, 131.75, 130.18, 129.13, 127.76, 124.57, 120.24, 118.85, 117.18, 88.55, 85.79, 64.55, 21.50. HRMS (ESI): *m/z* calcd for $C_{16}H_{14}O_2Na$ [M + Na]: 261.0891; found: 261.0887.

2-(1-Hydroxy-3-(4-methoxyphenyl)prop-2-yn-1-yl)phenol (**1j**):[11] Pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 4.9 Hz, 1H), 7.43–7.41 (m, 1H), 7.40–7.38 (m, 2H), 7.20–7.24 (m, 1H), 6.90 (d, *J* = 7.7 Hz, 2H), 6.83–6.81 (m, 2H), 5.88 (s, 1H), 3.78 (s, 3H), 3.33 (s, 1H).

2-(3-(4-Chlorophenyl)-1-hydroxyprop-2-yn-1-yl)phenol (**1k**):[11] White solid, m.p. 120–121 °C (lit. 122 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.40 (m, 3H), 7.32–7.25 (m, 4H), 7.13 (s, 1H), 6.93 (d, *J* = 7.7 Hz, 2H), 5.90 (s, 1H), 2.85 (s, 1H).

2-(3-(2-chlorophenyl)-1-hydroxyprop-2-yn-1-yl)phenol (**1l**): Orange solid, m.p. 73–75°C; ^{1}H NMR (500 MHz, DMSO) δ 9.66 (s, 1H), 7.60 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.55–7.51 (m, 2H), 7.40–7.32 (m, 2H), 7.12–7.16 (m, 1H), 6.88–6.84 (m, 2H), 5.99 (s, 1H), 5.89 (s, 1H). ^{13}C NMR (125 MHz, DMSO) δ 154.01, 134.61, 133.45, 130.02, 129.31, 128.77, 127.97, 127.71, 127.27, 122.19, 119.00, 115.26, 97.00, 80.00, 57.54. HRMS (ESI): *m/z* calcd for $C_{15}H_{11}ClO_2Na$ [M + Na]: 281.0345; found: 281.0344.

2-(3-(4-Bromophenyl)-1-hydroxyprop-2-yn-1-yl)phenol (**1m**): White solid, m.p. 128–129 °C; ^{1}H NMR (500 MHz, DMSO) δ 9.62 (s, 1H), 7.63–7.47 (m, 3H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.12 (t, *J* = 7.3 Hz, 1H), 6.84 (t, *J* = 8.0 Hz, 2H), 5.94 (s, 1H), 5.80 (s, 1H). ^{13}C NMR (125 MHz, DMSO) δ 153.87, 133.19, 131.68, 128.62, 128.05, 127.40, 121.75, 121.72, 118.98, 115.22, 93.08, 82.04, 57.41. HRMS (ESI): *m/z* calcd for $C_{15}H_{11}BrO_2Na$ [M + Na]: 324.9840; found: 324.9837.

4-Chloro-2-(3-(4-chlorophenyl)-1-hydroxyprop-2-yn-1-yl)phenol (**1n**): White solid, m.p. 130–131 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43–7.40 (m, 2H), 7.38 (d, *J* = 2.5 Hz, 1H), 7.34–7.31 (m, 2H), 7.26 (s, 1H), 7.21 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 1H), 5.86 (s, 1H), 2.92 (d, *J* = 35.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.96, 135.33, 133.14, 130.01, 128.85, 127.48, 125.80, 125.08, 120.19, 118.64, 87.50, 86.84, 63.95. HRMS (ESI): *m/z* calcd for $C_{15}H_{10}Cl_2O_2Na$ [M + Na]: 314.9956; found: 314.9955.

2-(2-Hydroxy-4-phenylbut-3-yn-2-yl)phenol (**1o**):[12] Pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.54 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.50–7.46 (m, 2H), 7.36–7.31 (m, 3H), 7.23–7.19 (m, 1H), 6.92–6.86 (m, 2H), 3.40 (s, 1H), 1.94 (s, 3H).

2-(2-Hydroxy-4-(4-propylphenyl)but-3-yn-2-yl)phenol (**1p**): Brown oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.55 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.23–7.19 (m, 1H), 7.15 (d, *J* = 8.1 Hz, 2H), 6.92–6.86 (m, 2H), 3.23 (s, 1H), 2.59 (t, 2H), 1.93 (s, 3H), 1.66–1.61 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.85, 143.91, 131.72, 129.67, 128.59, 128.10, 127.02, 119.84, 119.10, 117.81, 89.86, 86.76, 73.18, 37.95, 31.38, 24.33, 13.73. HRMS (ESI): *m/z* calcd for $C_{19}H_{20}O_2Na$ [M + Na]: 303.1361; found: 303.1360.

2-(4-(4-Chlorophenyl)-2-hydroxybut-3-yn-2-yl)phenol (**1q**): Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.53 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.420–7.40 (m, 2H), 7.34–7.31 (m, 2H), 7.25–7.21 (m, 1H), 6.95–6.90 (m, 2H), 3.98 (s, 1H), 1.96 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.61, 134.88, 132.98, 129.68, 128.68, 127.91, 126.79, 120.47, 119.95, 117.76, 91.56, 85.08, 72.75, 31.21. HRMS (ESI): *m/z* calcd for $C_{16}H_{13}ClO_2Na$ [M + Na]: 295.0502; found: 295.0499.

2-(1-Hydroxy-3-phenyl-1-(p-tolyl)prop-2-yn-1-yl)phenol (**1r**): Pale orange solid, m.p. 136–137 °C; ^{1}H NMR (500 MHz, DMSO) δ 9.16 (s, 1H), 7.50–7.38 (m, 7H), 7.33 (d, *J* = 1.8 Hz, 1H), 7.21 (s, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.93 (dd, *J* = 8.1, 1.5 Hz, 1H), 6.63 (d, *J* = 8.1 Hz, 1H), 2.27 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (125 MHz, DMSO) δ 152.28, 142.08, 136.28, 131.24, 129.61, 129.07, 128.66, 128.57, 128.26, 127.30, 126.95, 126.03, 122.37, 116.33, 92.55, 84.97, 73.08, 20.57, 20.38. HRMS (ESI): *m/z* calcd for $C_{23}H_{20}O_2Na$ [M + Na]: 351.1361; found: 351.1360.

(2R)-1,2,4-Triphenylbut-3-yne-1,2-diol (**1s**): White solid, m.p. 156–158 °C; ^{1}H NMR (500 MHz, DMSO) δ 7.55 (d, *J* = 7.1 Hz, 2H), 7.45–7.37 (m, 5H), 7.32–7.18 (m, 8H), 6.20 (s, 1H), 5.54 (d, *J* = 4.7 Hz, 1H), 4.73 (d, *J* = 4.6 Hz, 1H). ^{13}C NMR (125 MHz, DMSO) δ 143.16, 141.27, 131.18, 128.67, 128.49, 127.11, 127.06, 127.00, 126.96, 126.54, 122.62, 92.34, 85.68, 79.84, 75.56. HRMS (ESI): *m/z* calcd for $C_{22}H_{18}O_2Na$ [M + Na]: 337.1204; found: 337.1203.

1,4-Diphenylbuta-1,3-diyne (**3a**):[13] White solid, m.p. 86–88 °C (lit. 86–87 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57–7.50 (m, 4H), 7.40–7.31 (m, 6H).

1,4-Di-p-tolylbuta-1,3-diyne (**3i**):[13] White solid, m.p. 182–184 °C (lit. 186–187 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.1 Hz, 4H), 7.14 (d, *J* = 7.9 Hz, 4H), 2.36 (s, 6H).

1,4-Bis(4-methoxyphenyl)buta-1,3-diyne (**3j**):[13] White solid, m.p. 138–140 °C (lit. 140–141 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.8 Hz, 4H), 6.85 (d, *J* = 8.8 Hz, 4H), 3.82 (s, 6H).

1,4-Bis(4-chlorophenyl)buta-1,3-diyne (**3k**):[14] White solid, m.p. 257–259 °C (lit. 253 °C);[15] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 4H), 7.32 (d, *J* = 8.5 Hz, 4H).

1,4-Bis(2-chlorophenyl)buta-1,3-diyne (**3l**):[16] White solid, m.p. 138–140 °C (lit. 138–140 °C);[16] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.42 (dd, *J* = 8.1, 1.0 Hz, 2H), 7.33–7.29 (m, 2H), 7.25–7.21 (m, 2H).

1,4-Bis(4-bromophenyl)buta-1,3-diyne (**3m**):[17] Pale yellow solid, m.p. 138–140 °C (lit. 140–141 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.6 Hz, 4H), 7.38 (d, *J* = 8.6 Hz, 4H).

1,4-Bis(4-propylphenyl)buta-1,3-diyne (**3p**):[18] White solid, m.p. 108–109 °C (lit. 107–108 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.2 Hz, 4H), 7.14 (d, *J* = 8.1 Hz, 4H), 2.59 (t, *J* = 8.0 Hz, 4H), 1.67–1.59 (m, 4H), 0.93 (t, *J* = 7.3 Hz, 6H).

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References

1 R. Shintani, K. Takatsu, T. Katoh, T. Nishimura and T. Hayashi, *Angew. Chem. Int. Ed*., 2008, **47**, 1447.
2 A. Horita, H. Tsurugi, A. Funayama, T. Satoh and M. Miura, *Org. Lett*., 2007, **9**, 2231.
3 T. Nishimura, H. Araki, Y. Maeda and S. Uemura, *Org. Lett*., 2003, **5**, 2997.
4 T. Nishimura, T. Katoh, K. Takatsu, R. Shintani and T. Hayashi, *J. Am. Chem. Soc*., 2007, **129**, 14158.
5 A. Funayama, T. Satoh and M. Miura, *J. Am. Chem. Soc*., 2005, **127**, 15354
6 T. Sugiishi, A. Kimura and H. Nakamura, *J. Am. Chem. Soc*., 2010, **132**, 5332
7 D. Susanti, F. Koh, J.A. Kusuma, P. Kothandaraman and P.W.H. Chan, *J. Org. Chem*., 2012, **77**, 7166.
8 H. Harkat, A.L. Blanc, J.-M. Weibel and P. Pale, *J. Org. Chem*., 2008, **73**, 1620.
9 G.S. Kumar, C.U. Maheswari, R.A. Kumar, M.L. Kantam and K.R. Reddy, *Angew. Chem. Int. Ed*., 2011, **50**, 11748.
10 G. Egglinton and W. McRae, *Adv. Org. Chem*., 1963, **4**, 225.
11 H. Harkat, A.L. Blanc, J.–M. Weibel and P. Pale, *J. Org. Chem*., 2008, **73**, 1620.
12 M.I. Antczak, F. Cai and J.M. Ready, *Org. Lett*., 2011, **13**, 184.
13 S. Adimurthy, C.C. Malakar and U. Beifuss, *J. Org. Chem.*, 2009, **74**, 5648.
14 X. Meng, C.B. Li, B.C. Han, T.S. Wang and B.H. Chen, *Tetrahedron*., 2010, **66**, 4029.
15 M. Eugen, U. Dominik and M. Thomas J.J., *Eur. J. Org. Chem*., 2011, 238.
16 T.M. Wu, S.H. Huang and F.Y. Tsai, *Appl. Organomet. Chem*., 2011, **25**, 395.
17 V. Kumar, A. Chipeleme and K. Chibale, *Eur. J. Org. Chem*., 2008, 43.
18 K. Yin, C.J. Li, J. Li and X.S. Jia, *Green Chem*., 2011, **13**, 591.