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One-pot, solvent-free regioselective addition reactions of propargyl bromide to carbonyl compounds mediated by Zn–Cu couple

Xiaofang Ma [a], Jin-Xian Wang [a,b,*], Shunxi Li [a], Ke-Hu Wang [a], Danfeng Huang [a]

[a] Institute of Chemistry, Department of Chemistry, Northwest Normal University, 967 Anning Road (E.), Lanzhou 730070, PR China
[b] State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730070, PR China

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ABSTRACT

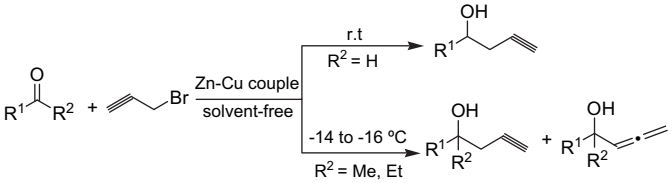
A Barbier-type propargylation of carbonyl compounds with propargyl bromide has been achieved with reactive zinc–copper couple under solvent-free conditions. The reaction of aldehydes with propargyl bromide produced the unique homopropargyl alcohols in excellent yields at room temperature without the formation of homoallenyl alcohols. The ketones reacted with propargyl bromide to give the corresponding homopropargyl alcohols in good to excellent yields at −14 to −16 °C. The advantages of this method are excellent yields, short reaction time, high regioselectivity, and avoidance of the use of organic solvents.

1. Introduction

In recent years, homopropargyl alcohols have received much attention as synthetic intermediates in organic synthesis and as the structural moieties in many biologically active compounds.[1] Numerous methods of propargylation of carbonyl compounds with propargyl bromide, such as using effective catalysts, aqueous phase reactions,[2] microwave,[2a,b] and ultrasound irradiation,[3] have been reported. The Barbier-type reactions have been widely applied to the synthesis of homopropargyl in laboratories and industries. Many metals including Sb,[4] Cr,[5] In,[2c,6] Mg,[1a] Mn,[7] Sn,[8] Pb,[9] Ti,[10] and Zn[11] have been reported to be effective in mediating the coupling between propargyl halides and carbonyl compounds to give the corresponding homopropargyl alcohols. In 2005, a new, efficient, and regioselective addition reaction of propargyl bromide to carbonyl compounds with gallium catalyzed by indium in THF was reported.[12a] However, these methods require long reaction time and use of organic solvents, such as THF, DMSO, and DMF, to improve the yields. The use of a great deal of organic solvents can potentially lead to some environmental pollution. Although the regiocontrolled synthesis of homopropargyl alcohols has been extensively studied, there are still not many satisfactory methods for the selective propargylation.[8b,12a–c]

In the solid organic reactions,[13] the micro-environment of reaction system is different from the environment of the reaction solution as no solvent molecules are involved. This often results in increase of reaction mixture concentration and improved efficiency. Moreover, in the solid state, molecules of the reaction are arranged in order, the directional reaction could be carried out and the reaction selectivity could be improved. In addition, in the solid-state chemical reaction, on account of the topology of control theory, the reaction would be performed in the absence of solvents, the higher concentration of reactants in the absence of solvents usually leads to more favorable kinetics than in solution. So it is possible for propargylation[2b,3,12] of carbonyl compounds selectively to introduce carbon–carbon triple bond into organic molecules under solvent-free conditions.

The reactivity of Zn–Cu couple in organic reactions has been described.[14,15] Zn–Cu couple has been considered as a moderate, non-toxic, low-cost metal mediator in organic reaction, and has the following advantages: simple post-processing, complete recovery of copper, and environmentally benign. With the great interest and demands of green chemistry,[16] herein we report an efficient Barbier-type reaction of carbonyl compounds with propargyl bromide mediated by Zn–Cu couple under solvent-free conditions to synthesize the homopropargyl alcohols (Scheme 1).



R^1 = Ph, Aryl, Heterocyclic, Aliphatic; R^2 = H, Me, Et.

Scheme 1. Zn–Cu couple mediated regioselective propargylation of carbonyl compounds with propargyl bromide under solvent-free conditions.

* Corresponding author.
E-mail address: wangjx@nwnu.edu.cn (J.-X. Wang).

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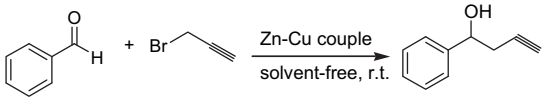
2. Results and discussion

We found that propargylation of aldehydes mediated by Zn–Cu couple generated homopropargyl alcohols under solvent-free conditions at room temperature in excellent yields.

First, to investigate the reactivity and regioselectivity of Zn–Cu couples, a variety of metals and solvents were examined in the reactions of benzaldehyde with propargyl bromide and the results are summarized in Table 1.

Table 1
Effects of the mediator and the amount of solvents on the formation of **3a**[a]



1a **2** **3a**

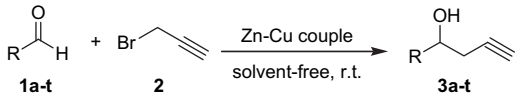
Entry	Mediator	Solvent	Time (h)	Yield[b] (%)
1	Zn–Cu	H_2O	8	Trace
2	Zn–Cu	H_2O	16	20
3	Zn–Cu	Et_2O	16	25
4	Zn–Cu	CH_2Cl_2	16	40
5	Zn–Cu	CH_3CN	3	42
6	Zn–Cu	EtOH	6	54
7	Zn–Cu	DMSO	1.2	60
8	Zn–Cu	THF	3	75
9	Zn–Cu	DMF	1.2	70
10	*Zn–Cu*	*None*	*0.5*	*85*
11	M[c]–Cu	None	16	NR[d]
12	Sn–Cu	None	1.2	56
13	Mg–Cu	None	1.5	12
14	M[e]	None	5–17	NR[d]
15	Sn	None	1	60
16	Zn	None	0.42	78

[a] Reaction conditions: **1a** (2.0 mmol), **2** (3.0 mmol), Zn–Cu couple or metal (4 mmol), solvent (2 mL), at room temperature.
[b] Isolated yields of homopropargyl alcohol **3a** after chromatography.
[c] M=Al–Cu, Fe–Cu, Mn–Cu, and Cd–Cu.
[d] NR: no reaction. Almost all of the benzaldehyde was recycled.
[e] M=Cd, Ni, Mn, Co, Fe, Al, W, Pb, Ti.

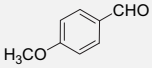
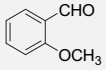
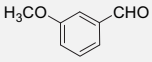
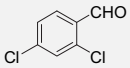
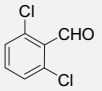
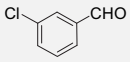
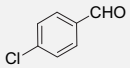
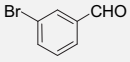
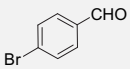
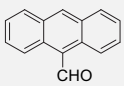
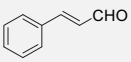
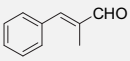
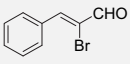
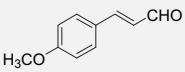
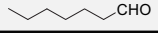
As shown in Table 1, propargylation of benzaldehyde mediated by Zn–Cu couple in H_2O, Et_2O, CH_2Cl_2 or CH_3CN did not give the desired addition product even after prolonged reaction time (Table 1, entries 1–5). The product was produced in EtOH and DMSO in moderate yields (Table 1, entries 6 and 7). The same reaction gave the corresponding homopropargyl alcohol in THF and DMF in good yields (75% and 70%, respectively) (Table 1, entries 8 and 9). The yield of homopropargyl alcohol was enhanced to 85% using Zn–Cu couple as the mediator under the solvent-free condition (Table 1, entry 10). Different M–Cu couples or metals were tested to mediate the propargylation of benzaldehyde in the absence of solvent. Al–Cu, Fe–Cu, Mn–Cu, and Cd–Cu couples were not effective to produce the desired products (Table 1, entry 11). Using Sn–Cu and Mg–Cu couples as mediators in the absence of solvent, the homopropargyl alcohols were gained in 56% and 12% yields, respectively (Table 1, entries 12 and 13). It was found that various metals, such as Cd, Ni, Mn, Co, Fe, Al, W, Pb, and Ti, were not effective to mediate the propargylation of benzaldehyde (Table 1, entry 14). When the mediator was Sn, the product was produced in moderate yield (Table 1, entry 15). The product in 78% yield was obtained when Zn powder was used as mediator under solvent-free condition (Table 1, entry 16). So the optimized conditions are Zn–Cu couple as mediator under solvent-free condition at room temperature.

The scope of this reaction was studied with various aldehydes and the experiment results are listed in Table 2. Aromatic aldehydes, whether 2-substituted, 3-substituted or 4-substituted benzaldehyde, reacted, respectively, with propargyl bromide to give the

Table 2
Zn–Cu couple mediated regioselective propargylation of various aldehydes with propargyl bromide[a]



1a-t **2** **3a-t**

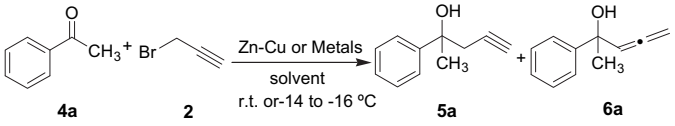
Entry	RCHO	Product[b]	Time (min)	Yield[c] (%)
1		**3a**	30	85 (78[16b])
2		**3b**	30	88 (85[16b])
3		**3c**	30	86 (79[16b])
4		**3d**	30	84 (81[16b])
5		**3e**	45	83 (82[16b])
6		**3f**	45	83
7		**3g**	45	90 (84[16b])
8		**3h**	45	89
9		**3i**	45	89 (87[16b])
10		**3j**	25	88 (80[16b])
11		**3k**	25	84 (78[16b])
12		**3l**	25	83
13		**3m**	30	80 (68[16b])
14		**3n**	30	90 (79[16b])
15		**3o**	30	90 (80[16b])
16		**3p**	55	85 (75[16b])
17		**3q**	60	84 (78[16b])
18		**3r**	55	88 (80[16b])
19		**3s**	55	80
20		**3t**	55	60 (74[16b])

[a] All reactions were conducted on the scale of 2 mmol of aldehydes with 3 mmol of propargyl bromide, and 4 mmol of Zn–Cu couple at room temperature.
[b] All products were characterized by IR, ^1H NMR, ^{13}C NMR, MS, and elemental analyses for all new compounds.
[c] Isolated yields.

corresponding homopropargyl alcohols in good yields (Table 2, entries 2–4, 7–12). 2,4-Dichlorobenzaldehyde or 2,6-dichlorobenzaldehyde reacted with propargyl bromide to produce the product in good yields (Table 2, entries 5 and 6). Moreover, anthracene-10-carbaldehyde reacted with propargyl bromide to produce the product in 80% yield (Table 2, entry 13). These results clearly show that the substituent on the phenyl ring, whether electron-donating or electron-withdrawing, has no dramatic influence on the product yields. Moreover, the position of the substituent on the phenyl ring also has no dramatic influence on the product yields. Heterocyclic aldehydes reacted with propargyl bromide to afford the corresponding homopropargyl alcohols in good yields (90% and 90%, respectively) (Table 2, entries 14 and 15). α,β-Unsaturated aldehydes were also propargylated in good yields (Table 2, entries 16–19), only the 1,2-addition products were obtained regioselectively. When the substrate was aliphatic aldehydes, homopropargyl alcohol was also obtained in 60% yield (Table 2, entry 20).

Encouraged by the previous results, we further investigated the propargylation of ketones mediated by Zn–Cu couple in the absence of solvent at room temperature. First, we chose acetophenone as substrate, a mixture of acetophenone, propargyl bromide, solvents, Zn–Cu couple or metals was stirred. The results are summarized in Table 3.

Table 3
Effects of the mediator and the amount of solvents on the formation of **5a** and **6a**[a]

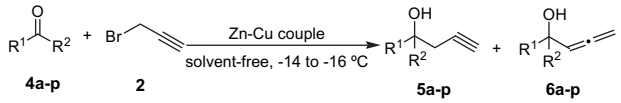


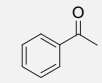
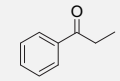
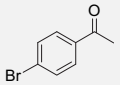
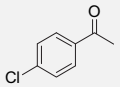
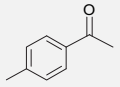
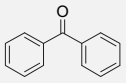
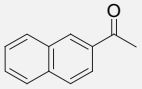
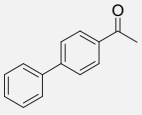
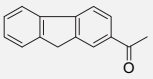
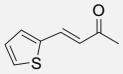
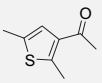
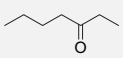
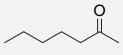
Entry	Mediator	Solvent	Time (h)	Yield[b] (%)	
				rt	−14 to −16 °C
1	Zn–Cu	H_2O	13	NR[c]	NR[c]
2	Zn–Cu	Et_2O	18	NR[c]	NR[c]
3	Zn–Cu	CH_2Cl_2	13	NR[c]	NR[c]
4	Zn–Cu	CH_3CN	2	NR[c]	NR[c]
5	Zn–Cu	DMSO	1.5	76 (84:16)	42 (100:0)
6	Zn–Cu	THF	1.5	60 (91:9)	NR[c]
7	Zn–Cu	DMF	1	64 (82:18)	73 (100:0)
8	*Zn–Cu*	*None*	*0.5*	*87 (85:15)*	*92 (100:0)*
9	Zn	None	1	75 (100:0)	24 (100:0)
10	Cu	None	0.5	NR[c]	NR[c]

[a] Reaction conditions: **4a** (2.0 mmol), **2** (3.0 mmol), Zn–Cu couple or metal (4 mmol), and solvent (2 mL).
[b] Isolated yields of homopropargyl alcohol **5a** and homoallenyl alcohol **6a** after chromatography. Ratios were obtained in GC.
[c] NR: no reaction. Almost all of the acetophenone was recycled.

It can be seen that the propargylation of acetophenone mediated by Zn–Cu couple in H_2O, Et_2O, CH_2Cl_2 or CH_3CN did not give the addition product even after prolonged reaction time (Table 3, entries 1–4). When the solvent was DMSO, THF or DMF, the product was a mixture of homopropargyl alcohol and homoallenyl alcohols in 76% (**5a**/**6a**=84:16), 60% (**5a**/**6a**=91:9) and 64% (**5a**:**6a**=82:18) yields, respectively, at room temperature. But the homopropargyl alcohol was regioselectively afforded when the temperature was decreased to −14 to −16 °C (Table 3, entries 5–7) except in THF. The reaction proceeded smoothly in the absence of solvent at room temperature for 0.5 h with good yield of 87% (**5a**/**6a**=85:15). When the reaction was performed at −14 to −16 °C, the yield of the homopropargyl alcohol was enhanced to 92% (**5a**/**6a**=100:0) (Table 3, entry 8). When using Cu, the reaction did not produce the addition product whether at room temperature or at −14 to −16 °C even after prolonged reaction time (Table 3, entry 10). With Zn powder, the product was generated in good yield (75%) at room temperature and 24% at −14 to −16 °C (Table 3, entry 9). According to our investigation, the efficient

Table 4
Zn–Cu couple mediated regioselective propargylation of various ketones with propargyl bromide[a]



Entry	R^1COR^2	Product[b]	Time (min)	Yield[c] [% (**5a–p**/**6a–p**)]
1		**5a**	30	92 (100:0), 75[d]
2		**5b**	35	92 (100:0), 74[d]
3		**5c**	35	92 (100:0), 74[d]
4		**5d**	35	91 (100:0), 81[16f]
5		**5e**	35	90 (100:0), 80[d]
6		**5f**+**6f**	40	91 (91:9), 75[d]
7		**5g**	30	82 (100:0)
8		**5h**	30	90 (100:0)
9		**5i**	30	90 (100:0)
10		**5j**	30	90 (100:0)
11		**5k**	30	90 (100:0)
12		**5l**	33	80 (100:0)
13		**5m**	30	85 (100:0)
14		**5n**	30	87 (100:0), 72[16f]
15		**5o**	45	85 (100:0), 70[d]
16		**5p**	38	80 (100:0), 73[d]

[a] All reactions were conducted on the scale of 2 mmol of ketones with 3 mmol of propargyl bromide and 4 mmol of Zn–Cu couple at −14 to −16 °C.
[b] All products were identified by IR, ^1H NMR, ^{13}C NMR, MS, and elemental analyses for all new compounds.
[c] Yields of isolated products. Ratios were obtained in GC.
[d] The reaction was mediated by Zn powder at room temperature.

conditions for the propargylation of acetophenone were at −14 to −16 °C mediated by Zn–Cu couple under the solvent-free conditions.

These results encouraged us to explore the propargylation of various ketones mediated by Zn–Cu couple under solvent-free conditions at −14 to −16 °C. The experiment results are listed in Table 4.

As shown in Table 4, it can be seen that the aromatic ketones reacted with propargyl bromide and generated the corresponding homopropargyl alcohols at −14 to −16 °C in excellent yields (Table 4, entries 1–5). If the substrate was benzophenone, a mixture of **5f** and **6f** was gained in 91% (**5f**/**6f**=91:9) yield (Table 4, entry 6). When the ketones were 1-(naphthalen-2-yl)ethanone, 1-(4-biphenyl)-ethanone, and 1-(9*H*-fluoren-7-yl)ethanone, the corresponding products were obtained in excellent yields (Table 4, entries 7–9). The results clearly showed that a substituent on the phenyl ring has no significant influence on the product yields, but has a little influence on the selectivity of the products. If the substrates were heterocyclic ketones, the corresponding homopropargyl alcohols were obtained in high yields (Table 4, entries 10–12). For α,β-unsaturated ketones, only the 1,2-addition products were obtained regioselectively in 90% and 80% good yields, respectively (Table 4, entries 11 and 16). Aliphatic ketones also produced the addition products in good yields (Table 4, entries 13–16).

Compared to the propargylation of ketones mediated by Zn powder at room temperature, when the propargylation of ketones was performed at −14 to −16 °C mediated by Zn–Cu couple in the absence of solvent, homopropargyl alcohols were regioselectively produced in good to excellent yields. The yields of the products were improved 7–17% and the reaction time was shortened.

3. Conclusion

We report an efficient, one-pot, and green synthesis of homopropargyl alcohols mediated by Zn–Cu couple under solvent-free conditions in good to excellent yields. In contrast to the methods in the literature, the main advantages of this method are: the excellent yields when Zn–Cu couple is used as mediator (the yields rise as high as 80–90% from 68–87% for aldehydes and the yields rise as high as 80–92% from 70–81% for ketones), short reaction time, high regioselectivity, and avoidance of the use of organic solvent. Our work showed that substantial progress could be made in organic reactions under the solvent-free conditions. This method could be potentially applied to the synthesis of natural products or other biological intriguing compounds.

4. Experimental

4.1. General remarks

^{1}H NMR spectra were recorded on a Brucker AM 400 MHz and Brucker AC-E 200 MHz spectrometers in $CDCl_3$ with TMS as an internal standard. ^{13}C NMR spectra were obtained on a Brucker AM-400 operating at 100 MHz or a Brucker AC-E 200 operating at 50 MHz. IR spectra were recorded on an Alpha Centauri FI-IR spectrometer. Mass spectra were recorded on an HP 5988A and GC/MS/DS instruments. Elemental analyses were carried out on Carlo Erba-1106 instruments. Purification of products was performed via flash chromatography with 200–400 mesh silica gel (15:1 petroleum–diethyl ether). All substrates and reagents were obtained commercially, which were prepared by standard procedures.

4.2. Typical experimental procedure for the synthesis of homopropargyl alcohols

Zn–Cu couple (324 mg) was placed in a flame dried round-bottom flask (50 mL) fitted with magnetic bar. Then carbonyl compounds (2 mmol) and propargyl bromide (3 mmol) were added. The resulting mixture was stirred and the reaction was monitored by TLC. After complete conversion, saturated NH_4Cl (15 mL) solution was poured into the mixture. The mixture was extracted with Et_2O (3×10 mL) and the organic layer was separated, dried over anhydrous $MgSO_4$, and evaporated. The pure product was obtained by column chromatograph of the crude mixture on silica gel using petroleum/ethyl acetate as an eluent. All the isolated products were characterized by IR, ^{1}H NMR, ^{13}C NMR, and MS, and elemental analysis for all the new compounds.

4.3. Typical experimental procedure for the synthesis of Zn–Cu couple

Zinc powder (178 mmol) and distilled water (80 mL) were placed into a 100 mL round-bottom flask equipped with a stir bar. With stirring, add HCl (37%, 2×1 mL) over 10 min. Then anhydrous $CuSO_4$ (30 mmol) was added into the flask with stirring and went on stirring for about 15 min. Finally, the mixture was filtered and the solid was washed with water (3×30 mL), acetone (3×10 mL), and ethyl ether (2×10 mL). Transfer the solid to a flask equipped with vacuum take-off and dry under vacuum for 3 h at 100 °C.

4.3.1. 1-Phenylbut-3-yn-1-ol ***3a***. Colorless oil,[17] IR (ν/cm^{-1}): 3393, 3295, 3032, 2912, 2119, 1956, 1684, 1604, 1451, 862, 756, 701, 642; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.41–7.26 (m, 5H), 4.88 (t, J=6.4 Hz, 1H), 2.65 (q, J=6.4, 2.8 Hz, 2H), 2.40 (s, 1H), 2.08 (t, J=2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=142.4, 128.5, 128.0, 125.7, 80.6, 72.3, 71.0, 29.4; EIMS (m/z, %) 146 (M^+), 107, 79, 77, 51, 39.

4.3.2. 1-(4-Methoxyphenyl)but-3-yn-1-ol ***3b***. Colorless oil,[18] IR (ν/cm^{-1}): 3422, 3291, 2912, 2838, 2118, 1646, 1613, 1514, 1248, 1034, 833, 644; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.33–7.26 (m, 2H), 6.90–6.87 (m, 2H), 4.83 (q, J=6.0, 2.8 Hz, 1H), 3.80 (s, 3H), 2.64–2.61 (m, 2H), 2.34 (s, 1H), 2.07 (t, J=2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=159.3, 134.6, 127.0, 113.8, 80.8, 72.0, 70.9, 55.3, 29.4; EIMS (m/z, %) 176 (M^+), 137, 122, 109, 94, 77, 51, 39.

4.3.3. 1-(2-Methoxyphenyl)but-3-yn-1-ol ***3c***. Colorless oil,[16b] IR (ν/cm^{-1}): 3427, 3294, 3069, 2940, 2118, 1953, 1597, 1491, 1462, 1242, 1051, 864, 757, 638; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.42–7.25 (m, 2H), 7.00–6.87 (m, 2H), 5.08 (q, J=7.2 Hz, 1H), 3.86 (s, 3H), 2.87 (s, 1H), 2.80–2.60 (m, 2H), 2.04 (t, J=2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=156.2, 130.2, 128.8, 126.8, 120.7, 110.3, 81.3, 70.4, 69.0, 55.2, 27.4; EIMS (m/z, %) 176 (M^+), 137, 121, 107, 94, 77, 51, 39.

4.3.4. 1-(3-Methoxyphenyl)but-3-yn-1-ol ***3d***. Colorless oil,[19] IR (ν/cm^{-1}): 3424, 3290, 3053, 2915, 2118, 1952, 1599, 1487, 1460, 1261, 1154, 1043, 864, 787, 699, 647; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.29–6.83 (m, 4H), 4.85 (t, J=6.4 Hz, 1H), 3.80 (s, 3H), 2.65–2.62 (m, 2H), 2.42 (s, 1H). 2.09 (t, J=2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=159.7, 144.1, 129.5, 118.0, 113.4, 111.2, 80.6, 72.2, 71.0, 55.2, 29.4; EIMS (m/z, %) 176 (M^+), 137, 122, 109, 94, 77, 51, 39.

4.3.5. 1-(2,4-Dichlorophenyl)but-3-yn-1-ol ***3e***. White solid, mp 50–51 °C,[16b] 48–49 °C, IR (ν/cm^{-1}): 3297, 2930, 2117, 1912, 1645, 1589, 1472, 1385, 1043, 862, 820; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.58–7.26 (m, 3H), 5.23 (q, J=6.4 Hz, 1H), 2.86–2.76 (m, 1H), 2.56–2.49 (m, 2H), 2.11 (t, J=2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=138.3, 134.0, 132.2, 129.1, 128.1, 127.4, 79.8, 71.5, 68.3, 27.7; EIMS (m/z, %): 214 (M^+), 179, 175, 145, 141, 105, 77, 51, 39.

4.3.6. 1-(2,6-Dichlorophenyl)but-3-yn-1-ol ***3f***. Colorless oil, IR (ν/cm^{-1}): 3300, 2922, 2120, 1866, 1648, 1562, 1434, 1049, 778, 730, 643; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.33–7.17 (m, 3H), 5.66 (q, J=6.4, 2.8 Hz, 1H), 3.13–3.06 (m, 2H), 2.87 (q, J=6.4, 2.4 Hz, 1H), 2.03 (t, J=2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=135.9, 134.5, 129.4,

129.4, 79.8, 70.6, 70.2, 25.3; EIMS (*m*/*z*, %): 179, 175 (M^+−39), 147, 111, 77, 51, 39. Anal. Calcd for $C_{10}H_8OCl_2$: C, 55.85; H, 3.75. Found: C, 56.07; H, 3.73.

4.3.7. 1-(2-Chlorophenyl)but-3-yn-1-ol ***3g***. Colorless oil,[20a] IR (ν/cm^{-1}): 3399, 3298, 3068, 2920, 2120, 1957, 1624, 1595, 1472, 1439, 1040, 864, 757, 643; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.64–7.22 (m, 4H), 5.28 (q, *J*=6.4 Hz, 1H), 2.84–2.79 (m, 2H), 2.54 (s, 1H), 2.11 (t, *J*=2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=139.6, 131.6, 129.4, 128.9, 127.1, 127.0, 80.3, 71.2, 68.7, 27.7; EIMS (*m*/*z*, %): 182, 180 (M^+), 141, 113, 77, 51, 39.

4.3.8. 1-(3-Chlorophenyl)but-3-yn-1-ol ***3h***. Colorless oil, IR (ν/cm^{-1}): 3390, 3298, 3067, 2913, 2120, 1946, 1694, 1576, 1476, 1428, 1056, 885, 788, 692; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.45–7.26 (m, 4H), 4.86 (q, *J*=6.4 Hz, 1H), 2.69–2.57 (m, 2H), 2.44 (s, 1H), 2.09 (t, *J*=2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=144.4, 134.4, 129.7, 128.1, 126.0, 123.9, 80.1, 71.6, 71.4, 29.5; EIMS (*m*/*z*, %): 181 (M^++1), 141, 113, 77, 51, 39. Anal. Calcd for $C_{10}H_9OCl$: C, 66.49; H, 5.02. Found: C, 66.28; H, 5.00.

4.3.9. 1-(4-Chlorophenyl)but-3-yn-1-ol ***3i***. Colorless oil,[20] IR (ν/cm^{-1}): 3392, 3298, 3062, 2913, 2120, 1955, 1902, 1650, 1598, 1491, 1413, 1057, 866, 829, 644; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.34–7.26 (m, 4H), 4.85 (t, *J*=6.4 Hz, 1H), 2.63–2.58 (m, 2H), 2.43 (s, 1H), 2.08 (t, *J*=2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=140.8, 133.7, 128.6, 127.2, 80.2, 71.6, 71.3, 29.5; EIMS (*m*/*z*, %): 180 (M^+), 165, 163, 141, 113, 77, 51, 39.

4.3.10. 1-(3-Bromophenyl)but-3-yn-1-ol ***3j***. Colorless oil,[20b] IR (ν/cm^{-1}): 3393, 3296, 3063, 2912, 2119, 1952, 1642, 1569, 1424, 1061, 883, 785, 648; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.57–7.21 (m, 4H), 4.85 (q, *J*=6.8 Hz, 1H), 2.67–2.62 (m, 2H), 2.43 (s, 1H), 2.10 (t, *J*=2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=144.6, 131.0, 130.0, 128.9, 124.4, 122.6, 80.0, 71.6, 71.4, 29.5; EIMS (*m*/*z*, %): 226, 224 (M^+), 209, 207, 185, 157, 77, 63, 51, 39.

4.3.11. 1-(4-Bromophenyl)but-3-yn-1-ol ***3k***. Colorless oil,[20a] IR (ν/cm^{-1}): 3391, 3296, 3061, 2912, 2119, 1903, 1593, 1487, 1404, 1065, 1009, 866, 825, 646; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.50–7.44 (m, 2H), 7.29–7.22 (m, 2H), 4.85 (q, *J*=6.4 Hz, 1H), 2.67–2.56 (m, 2H), 2.39 (s, 1H), 2.08 (t, *J*=2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=141.3, 131.6, 127.5, 121.8, 80.1, 71.6, 71.4, 29.4; EIMS (*m*/*z*, %): 226, 224 (M^+), 209, 185, 157, 145, 128, 105, 89, 77, 63, 51, 39.

4.3.12. 1-(2-Bromophenyl)but-3-yn-1-ol ***3l***. Colorless oil, IR (ν/cm^{-1}): 3395, 3297, 3065, 2919, 2120, 1952, 1648, 1565, 1519, 1467, 1434, 1024, 863, 755, 644; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.63–7.14 (m, 4H), 5. 23 (q, *J*=6.8 Hz, 1H), 2.84 (d, *J*=2.8 Hz, 1H), 2.57–2.50 (m, 2H), 2.11 (t, *J*=2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=141.1, 132.6, 129.3, 127.7, 127.3, 121.7, 80.2, 71.2, 70.9, 27.7; EIMS (*m*/*z*, %): 226, 224 (M^+), 209, 207, 185, 157, 77, 63, 51, 39. Anal. Calcd for $C_{10}H_9OBr$: C, 53.36; H, 4.03. Found: C, 53.28; H, 4.00.

4.3.13. 1-(Anthracen-9-yl)but-3-yn-1-ol ***3m***. Colorless oil,[21] IR (ν/cm^{-1}): 3429, 3296, 3053, 2955, 2926, 2119, 1952, 1666, 1587, 1528, 1449, 1070, 957, 889, 735, 638; ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.45–8.36 (m, 2H), 8.17 (s, 1H), 7.80–7.78 (m, 2H), 7.36–7.27 (m, 4H), 6.20 (q, *J*=6.8, 2.8 Hz, 1H), 3.17–3.04 (m, 2H), 2.75–2.68 (m, 1H), 1.97 (t, *J*=2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=132.1, 131.3, 129.1, 129.0, 128.4, 125.6, 125.5, 124.5, 81.3, 70.8, 69.1, 27.3; EIMS (*m*/*z*, %): 246 (M^+), 229, 207, 189, 178, 151, 89, 74, 59, 45, 39.

4.3.14. 1-(Furan-2-yl)but-3-yn-1-ol ***3n***. Pale yellow oil,[3] IR (ν/cm^{-1}): 3383, 3295, 2918, 2121, 1618, 1503, 1054, 1015, 816, 744, 650; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.40 (d, 1H), 6.36–6.34 (m, 2H), 4.89 (t, *J*=6.0 Hz, 1H), 2.78 (q, *J*=6.0, 2.8 Hz, 2H), 2.39 (s, 1H), 2.08 (t, *J*=2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=154.6, 142.3, 110.2, 106.6, 79.8, 71.2, 66.1, 26.1; EIMS (*m*/*z*, %): 136 (M^+), 119, 97, 79, 69, 51, 41, 39.

4.3.15. 1-(Thiophen-2-yl)but-3-yn-1-ol ***3o***. Pale yellow oil,[3] IR (ν/cm^{-1}): 3393, 3293, 3107, 2919, 2119, 1955, 1646, 1039, 853, 705, 646; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.28–7.26 (m, 1H), 7.05–6.94 (m, 2H), 5.12 (q, *J*=6.4 Hz, 1H), 2.76 (q, *J*=6.8, 2.8 Hz, 2H), 2.51 (s, 1H), 2.11 (t, *J*=2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=146.1, 126.7, 125.0, 124.1, 80.0, 71.5, 68.5, 29.5; EIMS (*m*/*z*, %): 152 (M^+), 134, 113, 85, 45, 39.

4.3.16. (E)-1-Phenylhex-1-en-5-yn-3-ol ***3p***. Pale yellow oil,[22] IR (ν/cm^{-1}): 3389, 3295, 3029, 2913, 2119, 1953, 1600, 1495, 1445, 1101, 1037, 969, 751, 692, 645; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.41–7.21 (m, 5H), 6.67 (d, *J*=16.4 Hz, 1H), 6.28 (dd, *J*=16.4, 6.4 Hz, 1H), 4.48 (q, *J*=6.4 Hz, 1H), 2.62–2.50 (m, 2H), 2.18 (s, 1H), 2.09 (t, *J*=2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=136.3, 131.3, 129.9, 128.6, 127.9, 126.6, 80.2, 71.1, 70.7, 27.7; EIMS (*m*/*z*, %): 172 (M^+), 133, 115, 105, 91, 77, 55, 39.

4.3.17. (E)-2-Methyl-1-phenylhex-1-en-5-yn-3-ol ***3q***. Pale yellow oil,[16b] IR (ν/cm^{-1}): 3394, 3296, 3025, 2923, 2118, 1953, 1655, 1596, 1562, 1493, 1445, 1019, 870, 749, 699, 644; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.36–7.21 (m, 5H), 6.60 (s, 1H), 4.37 (t, *J*=6.4 Hz, 1H), 2.59–2.57 (m, 2H), 2.15 (s, 1H), 2.09 (t, *J*=2.8 Hz, 1H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=138.0, 137.2, 129.0, 128.1, 126.6, 126.5, 80.6, 75.5, 70.9, 26.1, 13.5; EIMS (*m*/*z*, %): 186 (M^+), 171, 147, 129, 115, 91, 77, 69, 55, 39.

4.3.18. (Z)-2-Bromo-1-phenylhex-1-en-5-yn-3-ol ***3r***. Colorless oil,[16b] IR (ν/cm^{-1}): 3393, 3296, 3027, 2918, 2120, 1955, 1641, 1492, 1443, 1043, 923, 864, 755, 694, 645; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.62–7.26 (m, 5H), 7.18 (s, 1H), 4.49 (q, *J*=6.0 Hz, 1H), 2.80–268 (m, 2H), 2.47 (s, 1H), 2.11 (t, *J*=2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=134.8, 129.2, 129.1, 128.3, 128.2, 127.0, 79.4, 75.5, 71.6, 26.6; EIMS (*m*/*z*, %): 252, 250 (M^+), 213, 211, 195, 193, 171, 131, 115, 103, 89, 77, 63, 51, 39.

4.3.19. (E)-1-(4-Methoxyphenyl)hex-1-en-5-yn-3-ol ***3s***. Pale yellow oil, IR (ν/cm^{-1}): 3400, 3291, 3005, 2932, 2118, 2015, 1830, 1651, 1607, 1513, 1460, 1033, 847, 813, 644; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.35–7.26 (m, 2H), 6.90–6.80 (m, 2H), 6.60 (d, *J*=16 Hz, 1H), 6.18–6.12 (m, 1H), 4.45 (q, *J*=6.0 Hz, 1H), 3.85–3.76 (m, 3H), 2.61–2.49 (m, 2H), 2.18 (s, 1H), 2.09 (t, *J*=2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=159.4, 130.9, 129.0, 127.8, 127.7, 114.0, 80.4, 71.0, 70.9, 55.3, 27.8; EIMS (*m*/*z*, %): 202 (M^+), 163, 145, 135, 121, 91, 77, 55, 39. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.07; H, 6.97.

4.3.20. Dec-1-yn-4-ol ***3t***. Colorless oil,[23] IR (ν/cm^{-1}): 3387, 3310, 2928, 2858, 2119, 1649, 1460, 1048, 850, 633; ^{1}H NMR (400 MHz, $CDCl_3$): δ=3.78–3.75 (m, 1H), 2.47–2.29 (m, 2H), 2.07–1.91 (m, 2H), 1.61 (s, 1H), 1.57–1.29 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=80.9, 70.8, 69.9, 36.2, 31.8, 29.2, 27.3, 25.5, 22.6, 14.1; EIMS (*m*/*z*, %): 139 (M^+−15), 125, 115, 97, 81, 69, 55, 39.

4.3.21. 2-Phenylpent-4-yn-2-ol ***5a***. Colorless oil,[12o] IR (ν/cm^{-1}): 3433, 3294, 3061, 2979, 2118, 1956, 1603, 1494, 1100, 946, 852, 765, 643; ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.50–7.26 (m, 5H), 2.80–2.67 (m, 2H), 2.39 (s, 1H), 2.05 (t, *J*=2.8 Hz, 1H), 1.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=146.3, 128.2, 127.1, 124.7, 80.4, 73.2, 71.7, 34.6, 29.2; EIMS (*m*/*z*, %) 159 (M^+−H), 121, 105, 77, 51, 43, 39.

4.3.22. 3-Phenylhex-5-yn-3-ol ***5b***. Colorless oil,[12o] IR (ν/cm^{-1}): 3463, 3296, 3061, 2971, 2932, 2117, 1955, 1604, 1493, 1131, 987, 762, 701, 644; ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.44–7.25 (m, 5H), 2.81–2.69 (m, 2H), 2.33 (s, 1H), 2.03 (t, *J*=2.8 Hz, 1H), 2.01–1.88 (m, 2H), 0.77 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=144.5, 128.1, 126.9, 125.3, 80.3,

75.7, 71.8, 34.3, 33.1, 7.98; EIMS (*m*/*z*, %) 174 (M^+), 145, 135, 115, 105, 91, 77, 57, 51, 39.

4.3.23. 2-(4-Bromophenyl)pent-4-yn-2-ol ***5c***. Colorless oil,[12o] IR (ν/cm^{-1}): 3440, 3296, 3063, 2978, 2926, 2118, 1954, 1649, 1487, 1395, 1085, 1008, 946, 824, 645; ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.52–7.48 (m, 2H), 7.40–7.28 (m, 2H), 2.74–2.70 (m, 2H), 2.41 (s, 1H), 2.08 (t, *J*=2.8 Hz, 1H), 1.65–1.60 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=145.3, 131.3, 126.7, 121.1, 79.9, 73.0, 72.1, 34.5, 29.2; EIMS (*m*/*z*, %) 238 (M^+), 199, 183, 155, 105, 91, 77, 43, 39.

4.3.24. 2-(4-Chlorophenyl)pent-4-yn-2-ol ***5d***. Colorless oil,[12o] IR (ν/cm^{-1}): 3437, 3299, 3064, 2978, 2928, 2119, 1492, 1093, 828, 750, 644; ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.44–7.40 (m, 2H), 7.34–7.26 (m, 2H), 2.76–2.39 (m, 2H), 2.17 (s, 1H), 2.06 (t, *J*=2.8 Hz, 1H), 1.64–1.57 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=144.8, 132.9, 128.3, 126.3, 79.9, 72.9, 72.0, 34.5, 29.2; EIMS (*m*/*z*, %) 194 (M^+), 155, 139, 111, 75, 51, 43, 39.

4.3.25. 2-p-Tolylpent-4-yn-2-ol ***5e***. Colorless oil,[3] IR (ν/cm^{-1}): 3435, 3295, 3026, 2978, 2925, 2870, 2118, 1956, 1514, 1450, 1095, 944, 855, 818, 722, 642; ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.40–7.36 (m, 2H), 7.26–7.16 (m, 2H), 2.78–2.65 (m, 2H), 2.37 (s, 1H), 2.05 (t, *J*=2.8 Hz, 1H), 1.65–1.58 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=143.4, 136.7, 128.9, 124.6, 80.5, 73.1, 71.6, 34.5, 29.3, 21.0; EIMS (*m*/*z*, %) 174 (M^+), 135, 119, 105, 91, 77, 65, 43, 39.

4.3.26. 1,1-Diphenylbut-3-yn-1-ol and 1,1-diphenylbuta-2,3-dien-1-ol ***5f***+***6f***. Colorless oil,[12o] IR (ν/cm^{-1}): 3463, 3293, 3030, 2922, 2854, 2118, 1957, 1492, 1447, 1168, 1051, 758, 700, 655; ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.46–7.23 (m, 10H), 5.95 (t, *J*=6.4 Hz, 1H), 4.98 (d, *J*=6.4 Hz, 2H), 3.16 (t, *J*=2.8 Hz, 2H), 2.95 (s, 1H), 2.62 (s, 1H), 2.04 (t, *J*=2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=145.4, 128.2, 127.3, 126.1, 80.4, 80.2, 72.5, 33.3; EIMS (*m*/*z*, %) 222 (M^+), 205, 183, 165, 105, 77, 51, 39.

4.3.27. 2-(Naphthalen-6-yl)pent-4-yn-2-ol ***5g***. Colorless oil,[12o] IR (ν/cm^{-1}): 3433, 3295, 3057, 2929, 2118, 1954, 1600, 1506, 1455, 1123, 943, 858, 749, 642; ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.96–7.81 (m, 4H), 7.58–7.44 (m, 3H), 2.89–2.76 (m, 2H), 2.55 (s, 1H), 2.04 (t, *J*=2.8 Hz, 1H), 1.74–1.69 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=143.6, 133.1, 132.4, 128.2, 128.0, 127.5, 126.1, 125.9, 123.31, 123.2, 80.3, 73.4, 71.9, 34.5, 29.2; EIMS (*m*/*z*, %) 210 (M^+), 171, 155, 127, 77, 63, 51, 43, 39.

4.3.28. 2-(4-Biphenyl)pent-4-yn-2-ol ***5h***. White solid, mp 32–33 °C, IR (ν/cm^{-1}): 3437, 3293, 3057, 2977, 2926, 2118, 1955, 1602, 1560, 1487, 1450, 1183, 1095, 943, 840, 767, 643; ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.60–7.34 (m, 9H), 2.84–2.71 (m, 2H), 2.43 (s, 1H), 2.08 (t, *J*=2.8 Hz, 1H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=145.3, 140.7, 140.0, 128.8, 127.3, 127.1, 127.0, 125.2, 80.4, 73.1, 71.9, 34.6, 29.2; EIMS (*m*/*z*, %) 236 (M^+), 197, 152, 115, 43, 39. Anal. Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.82. Found: C, 86.37; H, 6.80.

4.3.29. 2-(9H-Fluoren-7-yl)pent-4-yn-2-ol ***5i***. White solid, mp 82–83 °C, IR (ν/cm^{-1}): 3463, 3277, 3055, 2971, 2923, 2115, 1948, 1651, 1589, 1453, 1121, 1083, 951, 833, 770, 643; ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.78–7.69 (m, 3H), 7.55–7.25 (m, 4H), 3.90 (s, 2H), 2.85–2.72 (m, 2H), 2.46 (s, 1H), 2.07 (t, *J*=2.8 Hz, 1H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=145.0, 143.4, 143.3, 141.3, 140.7, 126.7, 126.6, 125.0, 123.4, 121.5, 119.9, 119.5, 80.5, 73.5, 71.8, 37.0, 34.8, 29.4; EIMS (*m*/*z*, %) 248 (M^+), 209, 193, 165, 152, 115, 43, 39. Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.49. Found: C, 86.89; H, 6.47.

4.3.30. 2-(5-Methylfuran-2-yl)pent-4-yn-2-ol ***5j***. Pale yellow oil, IR (ν/cm^{-1}): 3417, 3297, 2984, 2923, 2120, 1958, 1663, 1561, 1517, 1450, 1108, 1023, 938, 787, 642; ^{1}H NMR (400 MHz, $CDCl_3$) δ=6.17–6.15 (m, 1H), 5.91–5.89 (m, 1H), 2.86–2.67 (m, 2H), 2.44–2.40 (m, 3H), 2.28 (s, 1H), 2.09–2.07 (m, 1H), 1.65–1.60 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=155.8, 151.6, 106.0, 105.9, 80.0, 71.5, 70.0, 32.1, 26.1, 13.6; EIMS (*m*/*z*, %) 164 (M^+), 125, 109, 53, 43, 39. Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.05; H, 7.33.

4.3.31. (E)-3-Methyl-1-(thiophen-2-yl)hex-1-en-5-yn-3-ol ***5k***. Pale yellow oil, IR (ν/cm^{-1}): 3422, 3297, 3106, 2976, 2928, 2118, 1796, 1649, 1592, 1520, 1424, 1114, 1043, 961, 855, 814, 644; ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.17–7.15 (m, 1H), 6.98–6.95 (m, 2H), 6.82 (d, *J*=3.6 Hz, 1H), 6.17 (d, *J*=3.6 Hz, 1H), 2.54–2.53 (m, 2H), 2.17(s, 1H), 2.12 (t, *J*=2.8 Hz, 1H), 1.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=141.8, 134.1, 127.4, 126.0, 124.3, 121.7, 80.0, 71.8, 71.7, 33.3, 27.4; EIMS (*m*/*z*, %) 192 (M^+), 153, 135, 109, 91, 69, 43, 39. Anal. Calcd for $C_{11}H_{12}OS$: C, 68.72; H, 6.29. Found: C, 68.69; H, 6.28.

4.3.32. 2-(2,5-Dimethylthiophen-3-yl)pent-4-yn-2-ol ***5l***. Pale yellow oil, IR (ν/cm^{-1}): 3435, 3294, 3069, 2974, 2921, 2118, 1956, 1659, 1553, 1481, 1448, 1142, 1113, 1033, 942, 829, 792, 640; ^{1}H NMR (400 MHz, $CDCl_3$) δ=6.57 (s, 1H), 2.81–2.62 (m, 2H), 2.54–2.41 (m, 3H), 2.37–2.29 (m, 3H), 2.28 (s, 1H), 2.08 (t, *J*=2.8 Hz, 1H), 1.64–1.55 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=140.7, 134.5, 132.4, 125.4, 80.6, 73.0, 71.6, 34.0, 28.7, 15.1, 14.9; EIMS (*m*/*z*, %) 194 (M^+), 155, 139, 113, 77, 67, 59, 43, 39. Anal. Calcd for $C_{11}H_{14}OS$: C, 68.00; H, 7.26. Found: C, 67.89; H, 7.24.

4.3.33. 4-Ethyloct-1-yn-4-ol ***5m***. Colorless oil, IR (ν/cm^{-1}): 3446, 3308, 2959, 2936, 2869, 2118, 1956, 1649, 1460, 1138, 981, 633; ^{1}H NMR (400 MHz, $CDCl_3$) δ=2.36–2.35 (m, 2H), 2.05 (t, *J*=2.8 Hz, 1H), 1.60 (s, 1H), 1.59–1.52 (m, 4H), 1.36–1.27 (m, 4H), 0.94–0.87 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=80.8, 73.6, 71.1, 37.8, 31.1, 29.7, 25.7, 23.2, 14.1, 7.93; EIMS (*m*/*z*, %) 115 (M^+−39), 97, 85, 59, 57, 55, 43, 39. Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.69; H, 11.73.

4.3.34. 4-Methylnon-1-yn-4-ol ***5n***. Colorless oil,[24] IR (ν/cm^{-1}): 3407, 3308, 2934, 2864, 2118, 1956, 1460, 1376, 1148, 918, 770, 633; ^{1}H NMR (400 MHz, $CDCl_3$) δ=2.37 (t, *J*=2.8 Hz, 2H), 2.08 (t, *J*=2.8 Hz, 1H), 1.77 (s, 1H), 1.61–1.25 (m, 11H), 0.92–0.88 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=80.9, 71.7, 71.2, 41.1, 32.4, 32.2, 26.2, 23.6, 22.6, 14.0; EIMS (*m*/*z*, %) 154 (M^+), 115, 99, 83, 71, 55, 43, 39.

4.3.35. 1-(Prop-2-ynyl)cyclohexanol ***5o***. Colorless oil,[12o] IR (ν/cm^{-1}): 3347, 3290, 2972, 2932, 2116, 1956, 1458, 1180, 1032, 945, 833, 725, 642; ^{1}H NMR (400 MHz, $CDCl_3$) δ=2.38–2.34 (m, 2H), 2.08 (t, *J*=2.8 Hz, 1H), 1.76 (s, 1H), 1.69–1.25 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=80.6, 71.4, 70.3, 36.7, 32.8, 25.5, 22.5; EIMS (*m*/*z*, %) 137 (M^+-H), 99, 81, 69, 55, 39.

4.3.36. 1-(Prop-2-ynyl)cyclohex-2-enol ***5p***. Colorless oil,[25] IR (ν/cm^{-1}): 3404, 3301, 3022, 2936, 2117, 1656, 1433, 1170, 1078, 988, 853, 734, 638; ^{1}H NMR (400 MHz, $CDCl_3$) δ=5.91–5.86 (m, 1H), 5.74–5.72 (m, 1H), 2.45–2.44 (m, 2H), 2.09–1.62 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=131.1, 130.8, 80.4, 71.1, 68.5, 35.2, 32.6, 25.1, 19.0; EIMS (*m*/*z*, %) 136 (M^+), 97, 79, 68, 55, 41, 39.

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