Rapid and Solvent-Free Synthesis of Homoallyl or Homopropargyl Alcohols Mediated by Zinc Powder

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Received 20 April 2005; revised 19 May 2005

Abstract: A rapid and efficient procedure for the solvent-free synthesis of homoallylic and homopropargyl alcohols has been achieved by zinc-mediated Barbier-type reaction of carbonyl compounds at room temperature.

Key words: zinc powder, solvent-free, homoallylic alcohol, homopropargyl alcohol, carbonyl compounds

Being important building blocks and versatile synthons, homoallylic alcohols are highly featured in the organic syntheses of many biologically active molecules such as macrolides, polyhydroxylated natural products, and polyether antibiotics.[1] Among the existing means to construct these synthetically and biologically important molecules, metal-mediated allylation[2] is one of the easiest and most convenient. Since the 1980s, it has been gradually realized that carbonyl allylation can be achieved even in aqueous media through a Barbier-type reaction.[3] So far many metals have been reported to be effective in mediating the coupling between allyl halides and carbonyl compounds to give the corresponding homoallylic alcohols in aqueous media.

On the other hand, homopropargyl alcohols have received much attention as synthetic intermediates in organic synthesis and as the structural moiety in a variety of biologically active compounds.[4] Homopropargyl alcohols have been prepared by the reactions of propargyl organometallics of antimony,[5] borane,[6] cadium,[7] chromium,[8] indium,[9] magnesium,[4a] manganese,[10] tin,[11] lead,[12] and titanium[13] with aldehydes or ketones. However, these reactions involved the use of water, either pure or with co-solvent, as a medium for reactions with organic or organometallic reagents.[14]

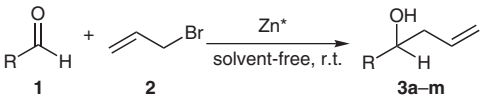
The allylation of carbonyl compounds mediated by zinc powder have been extensively reported.[15] But the yield of product was not high and the scope of substrate was limited. Some reaction occurred with the help of other catalyst or ultrasonic irradiation and the reaction needed longer time.

Developing more benign synthetic procedures in chemical synthesis is important in moving towards sustainable technologies, as a part of the rapidly emerging field of green chemistry.[16] For reducing the amount of waste, energy usage, and the use of volatile, toxic and flammable solvents, several approaches are available including avoiding the use of organic solvents as the reaction media.[16] Replacement media include non-volatile and recyclable ionic liquids,[17] H_2O,[18] supercritical CO_2,[19] polyethylene and polypropylene glycol.[20] An alternative approach avoids the use of the so-called 'solvent-free' or 'solventless' reaction.[21,22]

As a part of our program[23] to explore the synthetic applications of organozinc reagents, we have focused our attempts on developing rapid and novel green chemistry reactions. To our knowledge, solvent-free synthesis of homoallylic and homopropargyl alcohols is rarely reported and results in low yields.[24]

In this article, we wish to report an rapid, efficient, and zinc-mediated Barbier-type reaction that allows the synthesis of homoallylic and homopropargyl alcohols from carbonyl compounds with organic halides under solvent-free conditions.

To demonstrate this concept, initial experiments examined the reaction of *o*-chlorobenzaldehyde with allyl bromide mediated by zinc powder under solvent-free conditions (Scheme 1). As summarized in Tables 1, 1-(2-chlorophenyl)but-3-en-1-ol is typical of an effective protocol for synthesis homoallylic alcohols.



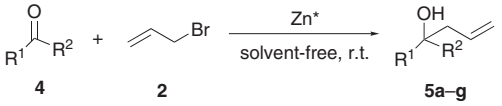
Scheme 1

From the results shown in Table 1, it can be seen that most of the reactions proceeded smoothly at room temperature in good to excellent yields and side reactions such as reduction and coupling were not observed. Interestingly, it was found that carbonyl compounds containing hydroxyl group could be efficiently allylated without any O-protection (Table 1, entry 7). This was clearly advantageous compared to the traditional allylation methods using the organometallic reagents. Further studies indicated that heteroaromatic aldehyde provided the allylation products in high yields (Table 1, entries 11 and 12). For cinnamaldehyde, the reaction occurred in a regiospecific manner

SYNTHESIS 2005, No. 17, pp 2838–2844
Advanced online publication: 16.08.2005
DOI: 10.1055/s-2005-872178; Art ID: F07505SS

and gave solely the 1,2-addition product (Table 1, entry 13). The reaction was not sensitive to the nature of the aldehydes used. The reaction proceeded well with either aromatic or aliphatic aldehydes. Furthermore, electron-withdrawing or -donating groups on the aromatic ring did not seem to affect the reaction significantly either in the yield of product or the rate of reaction.

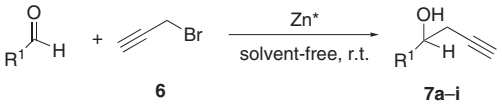
In order to define the scope and limitation of this method for synthesis of homoallylic alcohols, we have further examined the reaction of various ketones with allyl bromide mediated by zinc powder under solvent-free conditions (Scheme 2). The results are listed in Table 2.



Scheme 2

The allylation of acetophenone and propiophenone gave the corresponding products in 85% and 77% yields respectively (Table 2, entries 1 and 3). In the case of benzophenone, the ketone was not totally consumed, resulting in a moderate yield. This could result from steric hindrance due to the phenyl groups (Table 2, entry 2). In this case, an excess of allyl bromide was necessary (with 1.5 equiv of allyl bromide) to increase the yield.

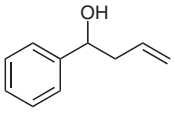
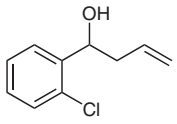
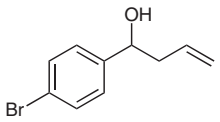
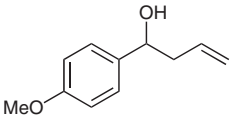
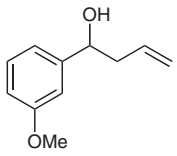
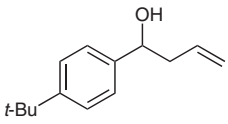
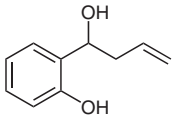
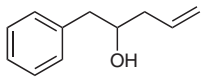
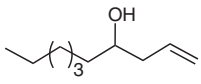
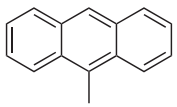
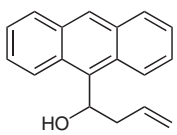
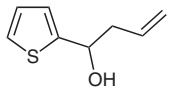
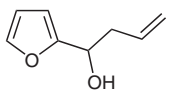
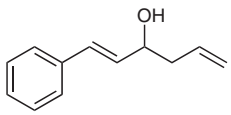
Encouraged by these preliminary results, we next investigated propargylation of several aldehydes under similar conditions (Scheme 3). The results described in Table 3 demonstrate that homopropargyl alcohols were produced in good yields under solvent-free conditions, but they required longer reaction time compared to homoallylic alcohols. Aromatic aldehydes, which were examined gave the corresponding products and the formation of allenyl alcohols were not detected from ^{1}H NMR and ^{13}C NMR spectra (Table 3, entries 1–8).



Scheme 3

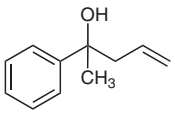
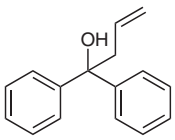
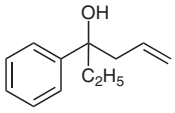
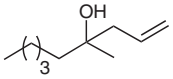
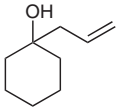
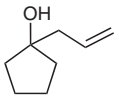
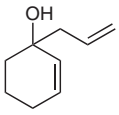
In contrast to the reported literature methods, the valuable features of our methodology include shorter reaction time and higher yield. Many metal-mediated Barbier-type reactions need longer reaction times[24–26] (range from few hours to several days) and some even require heat[27] or ultrasonic irradiation.[28] However, using our method, homoallylic alcohols can be synthesized in a highly efficient way. The yields of homoallylic alcohols are 68–91% and homopropargyl alcohols are 75–85%. All the reactions need only 10–30 minutes. The broader substrate scope lies in the fact that our methods are applicable to both aliphatic and aromatic carbonyl compounds. Even heterocyclic aldehydes and cyclic ketones can be allylated efficiently under solvent-free conditions. α,β-Unsaturated carbonyl

Table 1 Zinc-Mediated Carbonyl Allylation of Aldehydes under Solvent-Free Conditions

Entry[a]	R	Product		Time (min)	Yield (%)[b]
1	Ph		**3a**	15	81
2	2-Cl(C_6H_4)		**3b**	10	91
3	4-Br(C_6H_4)		**3c**	12	82
4	4-MeO(C_6H_4)		**3d**	15	86
5	3-MeO(C_6H_4)		**3e**	15	88
6	4-*t*-Bu(C_6H_4)		**3f**	25	78
7	2-OH(C_6H_4)		**3g**	20	83
8	$PhCH_2$		**3h**	30	74
9	$CH_3(CH_2)_3CH_2$		**3i**	20	80
10			**3j**	30	68
11			**3k**	20	84
12			**3l**	15	82
13	PhCH=CH		**3m**	15	77

[a] Reaction conditions: zinc powder (8 mmol), aldehydes (7 mmol), and allyl bromide (8 mmol).
[b] Isolated yield.

Table 2 Allylation of Ketones Mediated by Zn Powder under Solvent-Free Conditions

Entry[a]	R^1	R^2	Product		Time (min)	Yield (%)[b]
1	Ph	CH_3		**5a**	20	85
2	Ph	Ph		**5b**	30	80
3	Ph	C_2H_5		**5c**	30	77
4	C_5H_{11}	CH_3		**5d**	20	74
5	$(CH_2)_5$			**5e**	20	71
6	$(CH_2)_4$			**5f**	25	70
7	$(CH_2)_3CH{=}CH$			**5g**	20	78

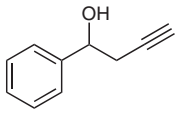
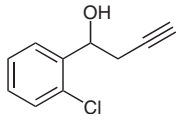
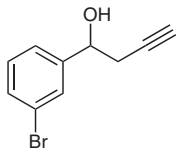
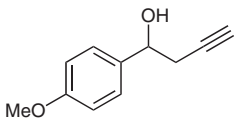
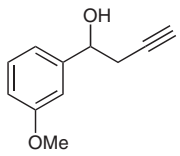
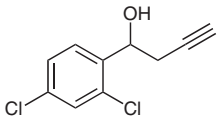
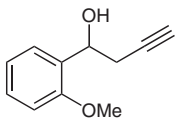
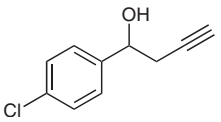
[a] Reaction conditions: zinc powder (8 mmol), ketones (7 mmol), and allyl bromide (8 mmol).
[b] Isolated yield.

compounds regioselectively give corresponding 1,2-addition product. More importantly, we find that our method can be applicable to propargyl bromide and achieve the propargylation of carbonyl compounds.

In conclusion, this solvent-free reaction provides a rapid, convenient and efficient process for synthesis of homoallylic and homopropargyl alcohols by coupling carbonyl compounds with allyl bromide or propargyl bromide mediated by zinc powder. More importantly, advantages of the present method are the excellent yields (benzaldehye: 81%; 2-chlorobenzaldehye: 91%; cinnamaldehyde: 77%; 3-methoxybenzaldehye: 88%; thiophene-2-carboxaldehyde: 84%; acetophenone: 85%; benzophenone: 80%), shorter time (10–30 min), environmentally benign reaction conditions and its abroad applicability to both aldehydes and ketones.

IR spectra were measured on thin-film samples, using an Alpha Centauri FT-IR spectrophotometer. ^{1}H NMR spectra (400 MHz) were recorded using a Bruker AC-E 400 MHz spectrometer in $CDCl_3$ with TMS as an internal standard. Mass spectra measurements were performed on a QP-1000A GC–MS spectrometer by EI ionization at 70 eV. Purification of products was performed via flash chromatography with 200–400 mesh silica gel [petroleum ether (bp 60–90 °C)–EtOAc, 15:1]. The chemicals were obtained from commercial sources.

Table 3 Synthesis of Homopropargyl Alcohols Mediated by Zinc Powder under Solvent-Free Conditions

Entry[a]	R^1	Product		Time (min)	Yield (%)[b]
1	Ph		**7a**	25	78
2	2-Cl(C_6H_4)		**7b**	20	84
3	3-Br(C_6H_4)		**7c**	30	80
4	4-MeO(C_6H_4)		**7d**	30	85
5	3-MeO(C_6H_4)		**7e**	30	81
6	2,4-Cl_2(C_6H_3)		**7f**	25	82
7	2-MeO(C_6H_4)		**7g**	30	79
8	4-Cl(C_6H_4)		**7h**	30	87

[a] The reaction was carried out using zinc powder (6 mmol), carbonyl compounds (5 mmol), and propargyl bromide (6 mmol) at r.t.
[b] Isolated yield.

Solvent-Free Synthesis of Homoallyl or Homopropargyl Alcohols; Typical Procedure

Activated zinc powder was placed (0.52 g, 8 mmol) in a flame-dried round-bottom flask (50 mL) fitted with a magnetic stir bar. Then aldehyde (7 mmol) and allyl bromide (0.96 g, 8 mmol) were added via the dropping funnel. The resulting mixture was vigorously stirred at r.t. After reaction completed, sat. NH_4Cl solution was poured into the mixture and stirred for several minutes. Et_2O was added and the organic layer was separated and dried over anhyd $MgSO_4$. The residue was purified by flash chromatography on silica gel using petroleum ether–EtOAc (15:1) as the eluent. This afforded corresponding homoallylic alcohols.

The Activated Method for Zinc Powder

Method 1:[29] Zn powder (100 g) and water (0.9 L) were placed into a 1-L Erlenmeyer flask equipped with a stir bar. Concd HCl (10 mL) was added with stirring over 1 min. The slurry was stirred for 20 min and the water was decanted. The metal was washed with water (3 × 250 mL), acetone (3 × 150 mL), and Et_2O (2 × 100 mL). The metal was then transferred to a flask equipped with a vacuum take-off and dried under full vacuum for 3 h.

Method 2:[30] In a flame-dried round-bottom flask fitted with magnetic stir bar, dropping funnel, and N_2 inlet, zinc powder was placed and the flask was flushed with anhyd N_2. Then 1,2-dibromoethane (0.1 mL, 2 mL THF) was added and the reaction mixture was heated to 65 °C until the solvent began to reflux. A few minutes (ca 2 min) later it was cooled and trimethylchlorosilane (0.1 mL, 1 mL THF) was added. The solution was stirred at r.t. for 15 min and the organic solvent was evaporated.

1-Phenylbut-3-en-1-ol (3a)
Oil.[26]

IR: 3372, 3073, 2916, 1641, 1493, 1446, 1041, 999, 916, 757 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.36–7.25 (m, 5 H), 5.86–5.75 (m, 1 H), 5.18–5.12 (m, 2 H), 4.73 (q, *J* = 5.6 Hz, 1 H), 2.55–2.47 (m, 2 H), 2.16 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 143.82, 134.42, 128.39, 127.52, 125.78, 118.42, 73.25, 43.81.

MS (EI, 70 eV): *m*/*z* (%) = 148 (0.3) [M^+], 131 (3.0), 107 (100.0), 91 (2.8), 79 (88.6), 77 (54.8), 51 (22.9), 39 (43.5).

1-(2-Chlorophenyl)but-3-en-1-ol (3b)
Oil.[31]

IR: 3302, 3073, 2939, 1639, 1472, 1409, 1340, 1096, 1035, 916, 753 cm^{-1}.

^1H NMR (400 MHz $CDCl_3$, TMS): δ = 7.59–7.54 (m, 1 H), 7.36–7.19 (m, 3 H), 5.98–5.75 (m, 1 H), 5.25–5.17 (m, 2 H), 5.15–5.13 (t, 1 H), 2.69–2.30 (m, 2 H), 2.18 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 141.12, 134.21, 131.65, 129.35, 128.42, 127.03, 127.00, 118.74, 69.55, 42.00.

MS (EI, 70 eV): *m*/*z* (%) = 184 (0.2) [M^+ + 2], 182 (0.6) [M^+], 147 (1.9), 141 (74.7), 113 (20.8), 105 (5.5), 77 (100.0).

1-(4-Bromophenyl)but-3-en-1-ol (3c)
Oil.[32]

IR: 3369, 3076, 2987, 2932, 1641, 1592, 1488, 1405, 1070, 1009, 826 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.50–7.43 (m, 2 H), 7.26–7.19 (m, 2 H), 5.88–5.67 (m, 1 H), 5.21–5.09 (m, 2 H), 4.67 (t, *J* = 5.6 Hz, 1 H), 2.51–2.42 (m, 2 H), 2.14 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 142.78, 133.91, 131.46, 127.53, 121.24, 118.93, 72.53, 43.82.

MS (EI, 70 eV): *m*/*z* (%) = 228 (1.1) [M^+ + 2], 226 (1.1) [M^+], 209 (0.1), 185 (92.5), 157 (21.7), 105 (7.5), 77 (100.0), 51 (22.5), 39 (32.7).

1-(4-Methoxyphenyl)but-3-en-1-ol (3d)
Oil.[25,26]

IR: 3398, 3070, 2922, 1883, 1612, 1511, 1446, 1247, 1035, 920, 826 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.28–7.25 (m, 2 H), 6.89–6.86 (m, 2 H), 5.82–5.76 (m, 1 H), 5.16–5.11 (m, 2 H), 4.68 (t, *J* = 6.0 Hz, 1 H), 3.81 (s, 3 H), 2.51–2.47 (m, 2 H), 2.04 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 159.00, 136.00, 134.59, 127.04, 118.24, 113.75, 72.93, 55.25, 43.74.

MS (EI, 70 eV): *m*/*z* (%) = 178 (0.6) [M^+], 161 (0.5), 144 (26.0), 137 (100.0), 109 (41.9), 94 (38.8), 77 (40.0), 51 (13.0), 39 (46.1).

1-(3-Methoxyphenyl)but-3-en-1-ol (3e)
Oil.[33]

IR: 3409, 3075, 2937, 2908, 2836, 1640, 1603, 1488, 1261, 1044, 995 cm^{-1}.

^1H NMR (400 MHz $CDCl_3$, TMS): δ = 7.28–6.80 (m, 4 H), 5.86–5.75 (m, 1 H), 5.19–5.13 (m, 2 H), 4.71 (q, *J* = 5.6 Hz, 1 H), 3.81 (s, 3 H), 2.55–2.46 (m, 2 H), 2.00 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 159.67, 145.58, 134.40, 129.40, 118.42, 118.08, 112.96, 111.24, 73.15, 55.18, 43.76.

MS (EI, 70 eV): *m*/*z* (%) = 178 (8.8) [M^+], 161 (0.6), 147 (0.3), 137 (99.6), 109 (100.0), 94 (40.4), 77 (35.0), 51 (8.4), 39 (24.9).

1-(4-*tert*-Butylphenyl)but-3-en-1-ol (3f)
Oil.[26]

IR: 3364, 3075, 2963, 2905, 1641, 1511, 1409, 1269, 1050, 914, 833 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.40–7.25 (m, 4 H), 5.85–5.77 (m, 1 H), 5.22–5.12 (m, 2 H), 4.74 (t, *J* = 6.0 Hz, 1 H), 2.55–2.48 (q, 2 H), 1.96 (s, 1 H), 1.32 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 150.48, 140.86, 134.70, 125.33, 125.31, 118.22, 73.10, 43.63, 34.49, 31.33.

MS (EI, 70 eV): *m*/*z* (%) = 204 (0.5) [M^+], 187 (1.2), 163 (46.3), 148 (6.8), 133 (8.0), 119 (1.9), 105 (8.3), 91 (12.9), 77 (9.0), 57 (100.0), 41 (44.6).

1-(2-Hydroxyphenyl)but-3-en-1-ol (3g)
Oil.[33]

IR: 3331, 3079, 2926, 1598, 1447, 1236, 997, 924, 755 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 8.03 (s, 1 H), 7.25–6.81 (m, 4 H), 5.89–5.81 (m, 1 H), 5.25–5.19 (m, 2 H), 4.89–4.85 (m, 1 H), 2.66–2.56 (m, 2 H), 2.16 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 155.53, 133.84, 128.99, 127.08, 126.17, 119.76, 119.54, 117.26, 74.69, 42.13.

MS (EI, 70 eV): *m*/*z* (%) = 164 (43.2) [M^+], 147 (10.5), 145 (53.5), 131 (58.8), 129 (16.8), 123 (100.0), 95 (59.0), 77 (75.0), 65 (19.0), 51 (32.0), 39 (65.0).

1-Phenylpent-4-en-2-ol (3h)
Oil.[25]

IR: 3394, 3068, 3027, 2927, 1640, 1494, 1451, 1076, 1033, 915 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.37–7.13 (m, 5 H), 5.91–5.81 (m, 1 H), 5.18–5.13 (m, 2 H), 3.91–3.85 (m, 1 H), 2.84–2.70 (m, 2 H), 2.37–2.18 (m, 2 H), 1.81 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 138.34, 134.65, 129.40, 128.52, 126.46, 118.15, 71.66, 43.25, 41.15.

MS (EI, 70 eV): *m*/*z* (%) = 162 (1.1) [M^+], 144 (0.9), 121 (38.2), 103 (30.1), 92 (100.0), 77 (15.9).

Dec-1-en-4-ol (3i)
Oil.[34]

IR: 3363, 3074, 2927, 2857, 1828, 1641, 1458, 1377, 995, 912 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 5.88–5.78 (m, 1 H), 5.15–5.11 (m, 2 H), 3.67–3.61 (m, 1 H), 2.33–2.12 (m, 2 H), 1.79 (s, 1 H), 1.49–1.37 (m, 10 H), 0.90–0.86 (t, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 134.91, 118.06, 70.65, 41.92, 36.80, 31.80, 29.30, 25.62, 22.60, 14.06.

MS (EI, 70 eV): *m*/*z* (%) = 139 (0.6) [M^+ – OH], 115 (13.7), 97 (38.3), 69 (15.9), 55 (100.0), 41 (55.4).

1-(9-Anthryl)but-3-en-1-ol (3j)
Oil.[35]

IR: 3410, 3070, 2923, 2853, 1723, 1666, 1446, 1315, 1285, 1036, 917, 735 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 8.64–7.22 (m, 9 H), 6.30 (q, *J* = 5.2 Hz, 1 H), 5.98–5.89 (m, 1 H), 5.26–5.12 (m, 2 H), 3.23–2.82 (m, 2 H), 2.23 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 138.05, 135.18, 133.95, 131.64, 129.32, 129.20, 128.19, 125.56, 124.76, 118.00, 70.61, 42.06.

MS (EI, 70 eV): *m*/*z* (%) = 248 (8.4) [M^+], 231 (0.1), 207 (51.5), 178 (34.2), 152 (57.0), 137 (3.9), 123 (96.8), 106 (6.3), 95 (10.2), 73 (21.2), 61 (16.3), 43 (100.0).

1-(2-Thienyl)but-3-en-1-ol (3k)
Oil.[36]

IR: 3374, 3075, 2932, 2905, 1641, 1436, 1034, 919, 852 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.25–7.24 (m, 1 H), 6.99–6.96 (m, 2 H), 5.88–5.78 (m, 1 H), 5.22–5.15 (m, 2 H), 4.99 (t, *J* = 6.4 Hz, 1 H), 2.64–2.60 (m, 2 H), 2.17 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 147.75, 133.79, 126.62, 124.56, 123.67, 118.84, 69.33, 43.76.

MS (EI, 70 eV): *m*/*z* (%) = 154 (1.1) [M^+], 137 (9.4), 113 (100.0), 85 (72.9), 83 (2.7), 58 (7.0), 45 (58.3), 41 (27.3), 39 (54.1).

1-(2-Furyl)but-3-en-1-ol (3l)
Oil.[25,26]

IR: 3370, 3078, 2918, 1841, 1643, 1431, 1029, 920 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.38–7.26 (m, 1 H), 6.34–6.25 (m, 2 H), 5.86–5.77 (m, 1 H), 5.20–5.13 (m, 2 H), 4.75 (t, *J* = 6.8 Hz, 1 H), 2.67–2.59 (m, 2 H), 2.07 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 155.95, 141.97, 133.64, 118.60, 110.12, 106.08, 66.88, 40.04.

MS (EI, 70 eV): *m*/*z* (%) = 138 (3.4) [M^+], 121 (5.3), 97 (100.0), 84 (24.7), 69 (16.4), 55 (24.5), 41 (38.5), 39 (36.2).

1-Phenylhexa-1,5-dien-3-ol (3m)
Oil.[25,26]

IR: 3374, 3070, 2925, 1640, 1438, 998, 915, 740, 687 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.39–7.21 (m, 5 H), 6.60 (d, *J* = 16.0 Hz, 1 H), 6.24 (dd, *J* = 16.0, 6.4 Hz, 1 H), 5.91–5.80 (m, 1 H), 5.21–5.14 (m, 2 H), 4.36 (q, *J* = 6.4 Hz, 1 H), 2.46–2.34 (m, 2 H), 1.98 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 136.60, 133.98, 131.48, 130.36, 128.55, 127.64, 126.46, 118.53, 71.69, 41.98.

MS (EI, 70 eV): *m*/*z* (%) = 174 (4.6) [M^+], 157 (5.3), 133 (75.3), 115 (31.8), 91 (15.0), 77 (35.7) 55 (100.0), 39 (52.7).

2-Phenylpent-4-en-2-ol (5a)
Oil.[25,26]

IR: 3425, 3070, 2975, 2925, 1646, 1440, 1364, 1059, 922 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.47–7.21 (m, 5 H), 5.60–5.56 (m, 1 H), 5.17–5.09 (m, 2 H), 2.71–2.44 (m, 2 H), 2.00 (s, 1 H), 1.54 (s, 3 H).

^{13}C NMR (100MHz, $CDCl_3$, TMS): δ = 147.59, 133.63, 128.15, 126.59, 124.73, 119.49, 73.58, 48.42, 29.89.

MS (EI, 70 eV): *m*/*z* (%) = 162 (0.3) [M^+], 145 (0.9), 121 (29.9), 105 (62.9), 77 (12.0), 51 (9.7), 43 (100.0).

1,1-Diphenylbut-3-en-1-ol (5b)
Oil.[25]

IR: 3549, 3475, 3068, 2930, 1817, 1639, 1440, 1171, 998, 918 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.46–7.19 (m, 10 H), 5.71–5.60 (m, 1 H), 5.26–5.16 (m, 2 H), 3.09–3.06 (m, 2 H), 2.55 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.46, 133.40, 128.17, 126.85, 125.95, 120.55, 76.84, 46.28.

MS (EI, 70 eV): *m*/*z* (%) = 224 (0.1) [M^+], 207 (1.5), 183 (79.6), 165 (2.0), 105 (100.0), 91 (11.4), 77 (66.0), 51 (16.3), 39 (13.3).

4-Phenylhex-1-en-4-ol (5c)
Oil.[37]

IR: 3474,3068, 3028, 2972, 2934, 1638, 1602, 1493, 1445, 978, 918, 762, 702, 567 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.40–7.21 (m, 5 H), 5.62–5.53 (m, 1 H), 5.16–5.09 (m, 2 H), 2.75–2.46 (m, 2 H), 2.02 (s, 1 H), 1.89–1.77 (q, 2 H), 0.76 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 145.71, 133.56, 128.03, 126.39, 125.37, 119.54, 75.97, 46.89, 35.22, 7.81.

MS (EI, 70 eV): *m*/*z* (%) = 159 (0.6) [M^+ – OH], 147 (0.6), 135 (40.2), 117 (3.5), 105 (21.8), 91 (5.5), 77 (23.2), 57 (100.0), 41 (22.8), 39 (34.1).

4-Methylnon-1-en-4-ol (5d)
Oil.[25]

IR: 3392, 3073, 2935, 1642, 1454, 1149, 1002, 917 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 6.08–5.87 (m, 1 H), 5.27–5.18 (m, 2 H), 2.35–2.28 (m, 2 H), 1.53–1.41 (m, 9 H), 1.28 (s, 3 H), 1.04–0.97 (t, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 134.10, 118.58, 72.17, 46.23, 41.81, 32.36, 26.69, 23.50, 22.62, 14.03.

MS (EI, 70 eV): *m*/*z* (%) = 139 (11.6) [M^+ – OH], 115 (23.2), 99 (100.0), 83 (12.1), 71 (55.3), 55 (34.3), 43 (92.4).

1-(Prop-2-enyl)cyclohexan-1-ol (5e)
Oil.[25,26]

IR: 3403, 3073, 2930, 1643, 1445, 1143, 969, 913 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 5.94–5.83 (m, 1 H), 5.16–5.08 (m, 2 H), 2.21 (d, *J* = 7.6 Hz, 2 H), 1.64–1.40 (m, 10 H), 1.31–1.25 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 133.69, 118.66, 70.91, 46.66, 37.35, 25.73, 22.15.

MS (EI, 70 eV): *m*/*z* (%) = 123 (0.9) [M^+ – OH], 99 (62.3), 81 (86.6), 69 (10.2), 55 (65.5), 41 (100.0).

1-(Prop-2-enyl)cyclopentan-1-ol (5f)
Oil.[2b]

IR: 3386, 3074, 2954, 1829, 1640, 1437, 1192, 995, 913 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 5.95–5.85 (m, 1 H), 5.16–5.12 (m, 2 H), 2.34 (d, *J* = 7.6 Hz, 2 H), 1.85–1.56 (m, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 134.53, 118.59, 73.29, 45.83, 39.38, 23.83.

MS (EI, 70 eV): *m*/*z* (%) = 126 (0.7) [M^+], 109 (0.6), 85 (100.0), 67 (77.8), 55 (51.9), 41 (57.2), 39 (51.1).

1-(Prop-2-enyl)-2-cyclohexen-1-ol (5g)
Oil.[25]

IR: 3386, 3073, 2931, 1829, 1642, 1435, 1172, 1084, 983, 915, 734, 621 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 5.93–5.80 (m, 2 H), 5.63–5.61 (m, 1 H), 5.15–5.10 (m, 2 H), 2.30 (d, *J* = 7.2 Hz, 2 H), 2.07–2.00 (m, 1 H), 1.74–1.60 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 133.66, 132.15, 130.18, 118.61, 69.13, 46.68, 35.51, 25.15, 18.92.

MS (EI, 70 eV): *m*/*z* (%) = 120 (0.5) [$M^+ - H_2O$], 97 (100.0), 79 (19.1), 67 (12.4), 55 (28.8), 41 (26.4).

1-Phenylbut-3-yn-1-ol (7a)
Oil.[7]

IR: 3381, 3294, 3032, 2914, 2118, 1955, 1636, 1451, 1049, 863, 701, 642 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.39–7.24 (m, 5 H), 4.86 (t, *J* = 6.4 Hz, 1 H), 2.64–2.61 (m, 2 H), 2.41 (s, 1 H), 2.06 (t, *J* = 2.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 142.38, 128.47, 127.99, 125.71, 80.63, 72.29, 70.96, 29.42

MS (EI, 70 eV): *m*/*z* (%) = 146 (0.3) [M^+], 128 (14.3), 107 (100.0), 79 (68.6), 77 (54.4), 51 (29.0), 39 (47.0).

1-(2-Chlorophenyl)but-3-yn-1-ol (7b)
Oil.[38]

IR: 3392, 3298, 3067, 2918, 2120, 1955, 1641, 1591, 1469, 1440, 1033, 859, 756, 641 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.63–7.20 (m, 4 H), 4.93 (q, *J* = 6.4 Hz, 1 H), 2.83–2.77 (m, 2 H), 2.62 (s, 1 H), 2.10 (t, *J* = 2.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 139.60, 131.63, 129.37, 128.91, 127.06, 126.99, 80.25, 71.20, 68.67, 27.66.

MS (EI, 70 eV): *m*/*z* (%) = 182 (0.1) [$M^+ + 2$], 180 (0.3) [M^+], 165 (0.1), 163 (0.3), 141 (51.4), 113 (15.7), 77 (100.0), 51 (40.6), 39 (47.6).

1-(3-Bromophenyl)but-3-yn-1-ol (7c)
Oil.[39]

IR: 3381, 3296, 3064, 2916, 2119, 1952, 1642, 1569, 1425, 1060, 882, 784, 644 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.56–7.21 (m, 4 H), 4.84 (q, *J* = 6.0 Hz, 1 H), 2.64–2.61 (m, 2 H), 2.44 (s, 1 H), 2.09 (t, *J* = 2.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 144.59, 131.02, 130.03, 128.88, 124.37, 122.58, 80.02, 71.54, 71.42, 29.46.

MS (EI, 70 eV): *m*/*z* (%) = 226 (0.6) [$M^+ + 2$], 224 (0.6) [M^+], 209 (0.1), 207 (0.1), 185 (31.9), 157 (13.8), 77 (100.0), 63 (6.9), 51 (40.5), 39 (56.3).

1-(4-Methoxyphenyl)but-3-yn-1-ol (7d)
Oil.[40]

IR: 3404, 3290, 2912, 2839, 2110, 1612, 1513, 1248, 1034, 833, 645 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.33–7.26 (m, 2 H), 6.91–6.87 (m, 2 H), 4.83 (t, *J* = 6.4 Hz, 1 H), 3.82 (s, 3 H), 2.64–2.61 (m, 2 H), 2.33 (s, 1 H), 2.07 (t, *J* = 2.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 158.01, 142.55, 130.50, 118.22, 80.20, 71.55, 69.80, 55.26, 29.41.

MS (EI, 70 eV): *m*/*z* (%) = 176 (2.5) [M^+], 159 (0.2), 137 (100.0), 122 (1.0), 109 (13.7), 94 (22.4), 77 (23.6), 51 (6.3), 39 (11.4).

1-(3-Methoxyphenyl)but-3-yn-1-ol (7e)
Oil.[41]

IR: 3408, 3290, 3055, 2917, 2118, 1953, 1598, 1460, 1261, 1154, 1042, 864, 787, 646 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.29–6.82 (m, 4 H), 4.85 (t, *J* = 6.4 Hz, 1 H), 3.81 (s, 3 H), 2.65–2.62 (m, 2 H), 2.41 (s, 1 H), 2.08 (t, *J* = 2.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 159.67, 144.08, 129.50, 117.97, 113.42, 111.20, 80.62, 72.19, 70.98, 55.21, 29.40.

MS (EI, 70 eV): *m*/*z* (%) = 176 (7.7) [M^+], 161 (1.9), 145 (3.7), 137 (79.6), 109 (100.0), 94 (61.5), 77 (71.9), 51 (25.2), 39 (85.1).

1-(2,4-Dichlorophenyl)but-3-yn-1-ol (7f)
Oil.

IR: 3294, 2921, 2119, 1955, 1910, 1645, 1469, 1382, 1042, 860, 817 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.67–7.26 (m, 3 H), 4.94 (q, *J* = 6.4 Hz, 1 H), 3.96 (s, 1 H), 2.81–2.48 (m, 2 H), 2.10 (t, *J* = 2.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 138.3, 134.0, 132.3, 129.2, 128.2, 127.4, 93.6, 71.5, 68.3, 27.7.

MS (EI, 70 eV): *m*/*z* (%) = 214 (10.7) [M^+], 186 (4.1), 179 (100.0), 175 (27.7), 145 (13.9), 141 (55.0), 105 (3.9), 77 (60.5), 51 (22.5), 39 (32.5).

HRMS: *m*/*z* [M – H] calcd for $C_{10}H_8Cl_2O$: 212.9879; found: 212.9879.

1-(2-Methoxyphenyl)but-3-yn-1-ol (7g)
Oil.

IR: 3412, 3293, 3069, 2921, 2117, 1955, 1596, 1462, 1241, 1049, 862, 756, 639 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.41–7.25 (m, 2 H), 6.99–6.87 (m, 2 H), 4.86 (q, *J* = 6.4 Hz, 1 H), 3.86 (s, 3 H), 2.90 (s, 1 H), 2.79–2.60 (m, 2 H), 2.04 (t, *J* = 2.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 156.3, 130.3, 128.7, 126.8, 120.7, 110.4, 94.2, 70.4, 68.9, 55.2, 27.4.

MS (EI, 70 eV): *m*/*z* (%) = 176 (1.3) [M^+], 161 (0.2), 159 (0.5), 145 (0.5), 137 (100.0), 121 (16.4), 107 (77.0), 94 (19.4), 77 (53.2), 51 (34.2), 39 (68.7).

HRMS: *m*/*z* [M – H_2O + H] calcd for $C_{11}H_{12}O_2$: 159.0804; found: 159.0806.

1-(4-Chlorophenyl)but-3-yn-1-ol (7h)
Oil.[38,39]

IR: 3382, 3297, 3066, 2912, 2119, 1955, 1902, 1646, 1597, 1489, 1411, 1055 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.33–7.26 (m, 4 H), 4.85 (t, *J* = 6.4 Hz, 1 H), 2.62–2.60 (m, 2 H), 2.46 (s, 1 H), 2.08 (t, *J* = 2.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 140.80, 133.65, 128.60, 137.13, 80.14, 71.58, 71.33, 29.46.

MS (EI, 70 eV): *m*/*z* (%) = 182 (0.2) [$M^+ + 2$], 180 (0.5) [M^+], 165 (1.0), 163 (3.0), 141 (60.9), 113 (19.5), 77 (100.0), 51 (36.1), 39 (98.4).

Acknowledgment

The work was supported by the National Natural Science Foundation of China (Grant 20272047), the Gansu Key Laboratory of Polymer Materials, and the Northwest Normal University Science and Technology Development Foundation of China.

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