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Hot Water–Promoted Cyclopropylcarbinyl Rearrangement Facilitates Construction of Homoallylic Alcohols

Pei-Fang Li, Cheng-Bo Yi, and Jin Qu*

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In the refluxing 9:1 (v/v) H_2O/1,4-dioxane and without additional catalyst, the rearrangements of various types of cyclopropyl carbinols were attempted. It was found that the reactions generally gave homoallylic alcohols in good to very high chemical yields. Rearrangements of bicyclic or tricyclic cyclopropyl carbinols readily gave the desired ring-expanded cyclic homoallylic alcohols which are difficult to synthesize by other means.

Introduction

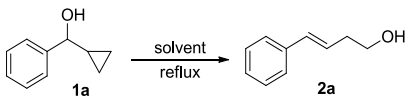
The homoallylic alcohol is a common structural motif in natural products and pharmaceuticals. The most widely used strategy for the synthesis of homoallylic alcohols is allylation of carbonyl compounds with allylmetal reagents, and very high enantioselectivities can be achieved with the assistance of chiral ligands.[1] Rearrangements of cyclopropyl carbinols can also lead to homoallylic alcohols,[2] including cyclic homoallylic alcohols with the double bond and the hydroxy group in the same ring, which are difficult to synthesize by other means. However, most of the recent reports have focused on tetrasubstituted cyclopropyl carbinol substrates.[2i–m] Furthermore, cyclopropylcarbinyl rearrangements in bicyclic and tricyclic ring systems have not been systematically studied.[3] Herein, we report that hot water promotes rearrangements of various types of cyclopropyl carbinols to afford acyclic or cyclic homoallylic alcohols in high yields.

In addition to being an extremely polar reaction medium, water has unique chemical and physical properties that allow it to catalyze organic reactions.[4] As temperature is increased, the selfionization of water increases substantially; the pK_w of water is 12.3 at 100 ℃, at which both the strong acid H_3O^+ and the strong base OH^- are more abundant than that at 25 ℃. We previously found that hot water acts as a mildly acidic catalyst to promote organic reactions traditionally catalyzed by Brønsted or Lewis acids.[5] Recently, we reported that 1,*n*-rearrangements (*n* = 3, 5, 7, 9) of allylic alcohols to conjugated polyene or enyne structural motifs occur in hot water in the absence of any additional catalyst,[5f] and we expected that cyclopropylcarbinyl rearrangements could be conducted under similar reaction conditions.

Results and discussion

In this study, we found that in refluxing water, rearrangement of phenyl-substituted cyclopropyl carbinol 1a gave corresponding homoallylic alcohol 2a, but in only 5% yield after 48 h (Table 1, entry 1). However, the addition of a small amount of an organic co-solvent to improve substrate dispersion speeded up the reaction, and etheric solvents were superior to other polar organic solvents (entries 2–7, note that no reaction occurred in any of the organic co-solvents alone). In 9:1 (v/v) H_2O/1,4-dioxane,[6] a 91% yield of 2a was obtained along with a small amount of an intermolecular etherification product. When the volume fraction of 1,4-dioxane was increased, the reaction rate decreased substantially (entries 8 and 9), perhaps owing to a reduction in the extent of ionization of water,[7] a decrease in the dielectric constant, or both.

Table 1. Rearrangement of **1a** in aqueous solutions under refluxing conditions.[a]



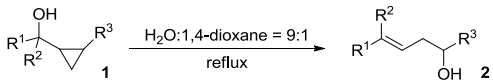
entry	solvent	time (h)	yield (%)[b]
1	H_2O	48	5
2	H_2O/dioxane, 9:1	27	91
3	H_2O/THF, 9:1	48	50
4	H_2O/DME, 9:1	30	87
5	H_2O/diglyme, 9:1	33	86
6	H_2O/CH_3CN, 9:1	48	11
7	H_2O/*i*-PrOH, 9:1	48	40
8	H_2O/dioxane, 4:1	48	82
9	H_2O/dioxane, 1:1	48	22

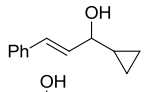
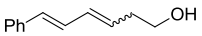
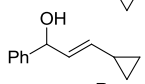
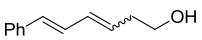
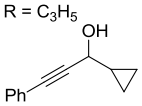
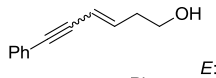
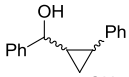
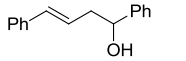
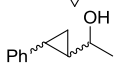
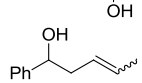
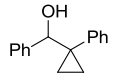
[a] Reaction conditions: 1 mmol of **1a** in solvent (25 mL), with vigorous stirring. [b] Isolated yield.

Various types of substituted cyclopropyl carbinol substrates were subsequently investigated (Table 2).[8] Secondary cyclopropyl carbinols with an electron-donating substituent reacted more readily than a substrate with a weakly electron-withdrawing chloride substituent (compare entries 2 and 3 with entry 4). Tertiary alcohol substrates provided the desired homoallylic alcohols with a trisubstituted alkene (entries 5 and 6). Both the reaction of 1g, which has a double bond between the hydroxy group and the phenyl group, and the reaction of 1h, which has a double bond between the hydroxy group and the

cyclopropyl ring, readily afforded the same diene with similar *E*/*Z* ratios (entries 7 and 8). Ring-opening reactions of alkyne-substituted cyclopropyl carbinols were also investigated for construction of conjugated enynes.[2i–m] Propargylic alcohol 1i, which is substituted with a terminal alkyne moiety, rearranged to afford conjugated enyne 2i in 80% yield (entry 9). Compounds 1j and 1k, each bearing an internal alkyne moiety, reacted smoothly to afford the corresponding conjugated enyne, 2j and 2k (entries 10 and 11), respectively. Although 1-cyclopropyl-2-propyn-1-ol 1l does not undergo ring opening upon treatment with trifluoromethanesulfonic acid,[2l] reaction of this substrate under our optimized conditions gave a 1:1 mixture of ring-opened products *E*- and *Z*-2l in 83% yield (entry 12). Cyclopropyl carbinol 1m, which bears a phenyl-substituted cyclopropane ring, provided desired product 2m in excellent yield (entry 13). Note that the reaction of cyclopropyl carbinol 1n, which has an aliphatic substituent, proceeded smoothly, and the homoallylic alcohol product did not undergo elimination reaction (entry 14). However, 1o, which has a geminally disubstituted cyclopropane ring, was unreactive under our reaction conditions (entry 15).

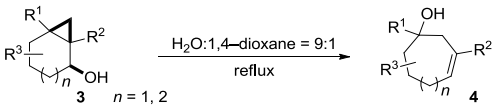
Table 2. Rearrangements of acyclic cyclopropyl carbinols.[a]

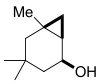
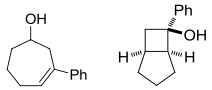
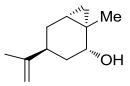
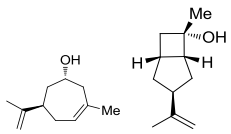
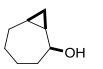
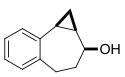
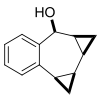
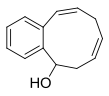
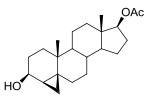
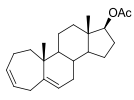
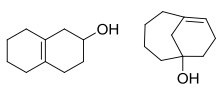


entry		substrate	time (h)		product	yield (%)[b]
1	**1a**	$R^1 = C_6H_5$	27	**2a**	$R^1 = C_6H_5$	91
2	**1b**	$R^1 = 4\text{-}MeOC_6H_5$	2	**2b**	$R^1 = 4\text{-}MeOC_6H_5$	82
3	**1c**	$R^1 = 2\text{-}HOC_6H_5$	18	**2c**	$R^1 = 2\text{-}HOC_6H_5$	81
4	**1d**	$R^1 = 4\text{-}ClC_6H_5$	48	**2d**	$R^1 = 4\text{-}ClC_6H_5$	66
5	**1e**	$R^1 = C_6H_5$, R^2 = Me	24	**2e**	$R^1 = C_6H_5$, R^2 = Me	75 *E*:*Z* = 13:1[c]
6	**1f**	R^1, $R^2 = C_6H_5$	24	**2f**	R^1, $R^2 = C_6H_5$	96
7[d]	**1g**		9	**2g**		85 *E*:*Z* = 8:1[c]
8[d]	**1h**		8	**2h**		88 *E*:*Z* = 7:1[c]
9	**1i**	R = H	16	**2i**	R = H	80
10	**1j**	$R = C_6H_5$	24	**2j**	$R = C_6H_5$	89
11	**1k**	$R = C_3H_5$	26	**2k**	$R = C_3H_5$	80
12[d]	**1l**		72	**2l**		83 *E*:*Z* = 1:1[c]
13	**1m**		15	**2m**		95
14	**1n**		36	**2n**		97 *E*:*Z* = 4:1[c]
15	**1o**		24			N. R.

[a] Reaction conditions: 1 mmol substrate in mixed solvent (H_2O:1,4-dioxane = 9:1, 25 mL), with vigorous stirring. [b] Isolated yield. [c] Determined by ^1H NMR spectroscopy. [d] H_2O:1,4-dioxane = 4:1.

Table 3. Rearrangements of cyclic cyclopropyl carbinols.[a]



entry		substrate	time (h)		product	yield (%)[b]
1	**3a**	$R^1 = Ph$	10	**4a**	$R^1 = Ph$	80
2	**3b**	$R^1 = 4\text{-}MeC_6H_4$	6	**4b**	$R^1 = 4\text{-}MeC_6H_4$	75
3	**3c**	$R^1 = 4\text{-}ClC_6H_4$	12	**4c**	$R^1 = 4\text{-}ClC_6H_4$	81
4	**3d**	R^1 = Me	4	**4d**	R^1 = Me	88
5	**3e**	$R^1 = n$-Bu	6	**4e**	$R^1 = n$-Bu	90
6[c]	**3f**	R^1 = H	12	**4f**	R^1 = H	91
7[d]	**3g**	R^1 = PhC≡C	36	**4g**	R^1 = PhC≡C	74
8	**3h**		5	**4h**		89
9	**3i**	R^2 = Me	24	**4i**	R^2 = Me	85
10	**3j**	$R^2 = n$-Bu	8	**4j**	$R^2 = n$-Bu	81
11	**3k**	$R^2 = Ph$	12	**4k-1** (77%) **4k-2** (11%)		
12	**3l**		26	**4l-1** (54%) **4l-2** (15%)		
13	**3m**		12	**4m**		85
14	**3n**		22	**4n**		80
15[d]	**3o**		24	**4o**		66
16[d]	**3p**		8	**4p**		73
17	**3q**		22	**4q-1** (62%) **4q-2** (12%)		

[a] Reaction conditions: 1 mmol substrate in mixed solvent (H_2O:1,4-dioxane = 9:1, 25 mL), with vigorous stirring. [b] Isolated yield. [c] 90 ℃. [d] H_2O:1,4-dioxane = 4:1.

With the aim of synthesizing seven- or eight-membered-ring homoallylic alcohols via rearrangements of bicyclic cyclopropyl carbinols accompanied by ring enlargement, we investigated the reactions of several bicyclo[4.1.0] or bicyclo[5.1.0] substrates (Table 3). Phenyl-substituted secondary cyclopropyl carbinol **3a** afforded ring-enlarged tertiary alcohol **4a** in 80% yield along with 14% of cyclic dienes resulting from the elimination of the hydroxy group (Table 3, entry 1). The same substrate would gave less desired product but more elimination products even under slightly acidic reaction conditions.[2m,9] When the rearrangement of **3a** was carried out in 1 gram scale, a parallel chemical yield was obtained without elongation of the reaction time (82% yield in 12 h,). Other R^1 substituents, including electron-rich and electron-poor aryl groups, alkyl groups, hydrogen, and an alkynyl group, generally gave the corresponding seven-membered ring homoallylic alcohols in good to high yields (entries 2–8). Analogous reactions of alcohols bearing alkyl or aryl R^2 substituents also afforded the ring-expanded products in yields of 54–85% (entries 9–12). However, small amounts of bicyclo[3.2.0]heptan-2-ol products such as **4k-2** and **4l-2** were also produced by the reaction.[3h] Substrates **3m** and **3n** reacted smoothly to give the corresponding eight-membered-ring products (entries 13–14). Sequential rearrangements of **3o**, which contains two cyclopropane rings, gave nine-membered-ring product **4o** in an acceptable yield (entry 15). The rearrangement of androstanediol derivative **3p** gave the desired ring-expanded homoallylic alcohol, but the product underwent further dehydration under the reaction conditions to give a diene product (entry 16), as has been reported previously under the acidic reaction condition.[10] Reaction of tricyclo[4.3.1.0]decanol **3q** gave two bicyclic homoallylic alcohols, **4q-1** and **4q-2**, in 62% and 12% yields, respectively (entry 17).[3g,3i,11]

Conclusions

In summary, we report for the first time that without additional catalyst, cyclopropylcarbinyl rearrangements produced homoallylic alcohols in good to excellent yields in a refluxing mixture of water and an organic solvent. Rearrangements of bicyclic or tricyclic cyclopropyl carbinols readily gave the desired ring-expanded cyclic homoallylic alcohols. More importantly, the unique catalytic power of water observed in the current study adds to our understanding of water as both a reaction medium and a catalyst of organic reactions.

Experimental Section

General

All reactions were carried out in aerial atmosphere. 1,4-Dioxane (HPLC grade) was used as received from Alfa Aesar®. We used either water purified with a Milli-Q Ultrapure Water Purification System or Watson's distilled water (pH = 5.5 6.5). Substrates were synthesized according to the known procedures. Flash column chromatography was performed using the indicated solvent system on Qingdao-Haiyang® silica gel (200–300 mesh). All of the compounds were characterized by ^{1}H NMR and ^{13}C NMR. Peaks recorded are relative to the internal standards: TMS (δ = 0.00) for ^{1}H NMR and $CDCl_3$ (δ = 77.00) for ^{13}C NMR spectra. High resolution mass spectral analyses were measured on a Finnigan/MAT95 mass spectrometer.

Preparation of cyclopropyl carbinols 1a–1o.

Cyclopropyl carbinols **1a**,[2m] **1b**,[12] **1d**,[13] **1e**,[14] **1f**,[15] **1g**,[16] **1h**,[17] **1i-1k**,[2k] **1l**,[2l] **1m**,[18] **1n**[19] and **1o**[20] were prepared according to previously reported procedures.

2-(Cyclopropyl(hydroxy)methyl)phenol (1c)

To a solution of 2-bromophenol (865 mg, 5.0 mmol) in Et_2O (20 mL) at 0 ℃ was added *n*-BuLi solution (2.4 M in hexane, 4.2 mL, 10.0 mmol). The solution was stirred at 0 ℃ for 30 min. Then the solution was cooled to –78 ℃ and cyclopropanecarbaldehyde (350 mg, 5 mmol) in Et_2O (5 mL) was added. The reaction mixture was allowed to warm to 0 ℃ and stirred at 0 ℃ for 2 h. Diluted aqueous NH_4Cl solution (20 mL) was added to quench the reaction and the reaction mixture was extracted with EtOAc (2 × 50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc/hexane = 1:5) to afford the desired product **1c** (460 mg, 56%). Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.24–7.15 (m, 1H), 7.07 (m, 1H), 6.93–6.81 (m, 2H), 4.13 (dd, *J* = 8.9, 2.6 Hz, 1H), 2.73 (d, *J* = 2.8 Hz, 1H), 1.46–1.35 (m, 1H), 0.70–0.62 (m, 2H), 0.45–0.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 129.1, 127.3, 126.1, 119.7, 117.1, 80.5, 17.9, 3.63, 3.60; HRMS (EI) for $C_{10}H_{12}O_2$ calcd for $[M]^+$ *m/z* 164.0837, found 164.0841.

General Procedure for Preparation of cyclopropyl carbinols 3a–3q.

6-Phenylbicyclo[4.1.0]heptan-2-ol (3a).

To a solution of diiodomethane (5.36 g, 20.0 mmol) in dried CH_2Cl_2 (50 mL) was added diethylzinc (1.0 M in hexane, 10.0 mL, 10.0 mmol) slowly at –20 ℃. The reaction mixture was allowed to stir at –20 ℃ for 0.5 h. Then 3-phenylcyclohex-2-enol (870 mg, 5.0 mmol) in CH_2Cl_2 (5 mL) was added to the reaction mixture at –20 ℃. After stirring at –20 ℃ for 0.5 h, the reaction mixture was allowed to warm to room temperature and further stirred at room temperature for 3 h. Diluted aqueous NH_4Cl solution (5 mL) was added to quench the reaction, the reaction mixture was filtered through celite and the filtrate was washed with water (50 mL), extracted with CH_2Cl_2 (2 × 100 mL). The combined organic layers were dried with $MgSO_4$, filtered and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (MTBE/hexane = 1:4) to afford the title alcohol. Slight yellow oil (58%, 545 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.23 (m, 4H), 7.22–7.12 (m, 1H), 4.41 (m, 1H), 2.01–1.86 (m, 2H), 1.71–1.58 (m, 2H), 1.55–1.33 (m, 3H), 1.32–1.23 (m, 1H), 0.97–0.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 128.3, 127.4, 125.9, 65.9, 31.2, 30.2, 28.0, 26.2, 19.3, 13.6; HRMS (EI) for $C_{13}H_{16}O$ calcd for $[M]^+$ *m/z* 188.1201, found 188.1203.

6-(p-Tolyl) bicyclo[4.1.0]heptan-2-ol (3b). White solid (59 %): mp = 38–39.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 4.46–4.35 (m, 1H), 2.32 (s, 3H), 1.97–1.83 (m, 2H), 1.67–1.55 (m, 2H), 1.52–1.42 (m, 2H), 1.41–1.32 (m, 1H), 1.32–1.22 (m, 1H), 0.96–0.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 135.4, 129.0, 127.4,

65.9, 31.4, 30.2, 27.6, 26.2, 21.0, 19.3, 13.5; HRMS (EI) for $C_{14}H_{18}O$ calcd for $[M]^+$ *m/z* 202.1358, found 202.1364.

6-(4-Chlorophenyl)bicyclo[4.1.0]heptan-2-ol (3c). White solid (77 %): mp = 55–56.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 4.46–4.36 (m, 1H), 1.98–1.81 (m, 2H), 1.69–1.55 (m, 3H), 1.54–1.33 (m, 3H), 1.33–1.23 (m, 1H), 0.96 (t, *J* = 5.3 Hz, 1H), 0.90 (dd, *J* = 9.4, 4.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 131.5, 128.9, 128.4, 65.7, 31.1, 30.1, 27.5, 26.2, 19.2, 13.7; HRMS (EI) for $C_{13}H_{15}ClO$ calcd for $[M]^+$ *m/z* 222.0811, found 222.0812.

6-Methylbicyclo[4.1.0]heptan-2-ol (3d).[21] Colorless oil (67%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (m, 1H), 1.62 (ddd, *J* = 13.6, 8.4, 5.2 Hz, 1H), 1.57–1.47 (m, 2H), 1.40–1.29 (m, 1H), 1.39 (s, 1H), 1.27–1.16 (m, 1H), 1.14–1.03 (m, 2H), 1.08 (s, 3H), 0.51 (t, *J* = 4.9 Hz, 1H), 0.31 (dd, *J* = 9.0, 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 66.4, 30.03, 29.96, 27.2, 26.4, 19.3, 18.7, 13.5.

6-Butylbicyclo[4.1.0]heptan-2-ol (3e).[21] Colorless oil (66%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.25–4.12 (m, 1H), 1.66–1.54 (m, 2H), 1.53–1.44 (m, 1H), 1.44–1.24 (m, 6H), 1.23–1.09 (m, 3H), 1.09–0.95 (m, 2H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.45 (t, *J* = 5.0 Hz, 1H), 0.35 (dd, *J* = 8.9, 4.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 67.0, 41.0, 30.0, 28.8, 27.8, 25.6, 23.4, 22.9, 20.3, 14.2, 13.6.

Bicyclo[4.1.0]heptan-2-ol (3f).[22] Colorless oil (74%): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.19 (dt, *J* = 8.7, 5.8 Hz, 1H), 1.90–1.80 (m, 1H), 1.68–1.58 (m, 1H), 1.46–1.35 (m, 3H), 1.31–1.10 (m, 3H), 1.03–0.92 (m, 1H), 0.57 (td, *J* = 8.7, 4.7 Hz, 1H), 0.30 (q, *J* = 5.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 67.3, 29.9, 22.7, 20.7, 17.7, 12.8, 7.2.

6-(Phenylethynyl)bicyclo[4.1.0]heptan-2-ol (3g). Slight yellow solid (95%): mp = 57.5–59 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.32 (m, 2H), 7.32–7.22 (m, 3H), 4.38–4.28 (m, 1H), 2.08 (dt, *J* = 14.3, 6.1 Hz, 1H), 1.86 (ddd, *J* = 14.1, 9.0, 5.3 Hz, 1H), 1.76 (dt, *J* = 9.3, 6.4 Hz, 1H), 1.70–1.60 (m, 1H), 1.49 (d, *J* = 4.7 Hz, 1H), 1.46–1.29 (m, 2H), 1.16–1.04 (m, 2H), 0.93 (dd, *J* = 6.4, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.5, 128.1, 127.5, 123.7, 96.4, 76.0, 65.5, 29.25, 29.19, 28.2, 19.3, 16.9, 14.1; HRMS (EI) for $C_{15}H_{16}O$ calcd for $[M]^+$ *m/z* 212.1201, found 212.1193.

4,4,6-Trimethylbicyclo[4.1.0]heptan-2-ol (3h). White solid (54%): mp = 46–48 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.36–4.24 (m, 1H), 1.48 (dd, *J* = 12.8, 6.3 Hz, 1H), 1.38–1.23 (m, 3H), 1.13–1.05 (m, 1H), 1.10 (s, 3H), 0.87 (s, 3H), 0.83 (s, 3H), 0.69 (t, *J* = 12.0 Hz, 1H), 0.41 (dd, *J* = 8.9, 4.4 Hz, 1H), 0.26 (t, *J* = 5.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 66.0, 44.6, 41.5, 32.2, 31.4, 28.3, 25.8, 25.4, 18.8, 16.0; HRMS (EI) for $C_{10}H_{18}O$ calcd for $[M]^+$ *m/z* 154.1358, found 154.1353.

1-Methylbicyclo[4.1.0]heptan-2-ol (3i).[23] Colorless oil (49%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (dd, *J* = 9.1, 5.8 Hz, 1H), 1.95–1.83 (m, 1H), 1.75–1.65 (m, 1H), 1.46–1.29 (m, 3H), 1.22–1.10 (m, 1H), 1.18 (s, 3H), 0.98–0.86 (m, 2H), 0.45–0.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 72.9, 30.5, 24.7, 23.6, 22.6, 21.9, 21.2, 15.5.

1-Butylbicyclo[4.1.0]heptan-2-ol (3j). Colorless oil (76%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.09–3.96 (m, 1H), 1.89–1.77 (m, 1H), 1.74–1.54 (m, 2H), 1.49–1.21 (m, 7H), 1.18–0.99 (m, 2H), 0.98–0.83 (m, 5H), 0.44–0.37 (m, 1H), 0.37–0.29 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 69.4, 38.1, 30.8, 29.0, 27.0, 23.6, 23.0, 20.5, 19.8, 14.2; HRMS (EI) for $C_{11}H_{20}O$ calcd for $[M]^+$ *m/z* 168.1514, found 168.1521.

1-Phenylbicyclo[4.1.0]heptan-2-ol (3k).[24] White solid (68%): mp = 58.5–60 ℃ (lit.[17] mp = 57 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.27 (m, 4H), 7.21 (t, *J* = 7.0 Hz, 1H), 4.26–4.17 (m, 1H), 2.10–2.00 (m, 1H), 1.87–1.77 (m, 1H), 1.65–1.46 (m, 3H), 1.40–1.28 (m, 2H), 1.16–1.02 (m, 2H), 0.85 (t, *J* = 5.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 128.8, 128.4, 126.3, 72.7, 32.7, 29.8, 23.4, 22.6, 21.3, 15.1.

1-Methyl-4-(prop-1-en-2-yl)bicyclo[4.1.0]heptan-2-ol (3l).[3h] Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.76 (s,1H), 4.73 (s,1H), 3.94–3.83 (m, 1H), 1.87–1.75 (m, 5H), 1.73 (s, 3H), 1.37–1.25 (m, 1H), 1.12 (s, 3H), 1.00–0.90 (m, 1H), 0.41 (dd, *J* = 8.8, 4.8 Hz, 1H), 0.23 (t, *J* = 5.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 109.1, 71.8, 36.5, 36.4, 28.7, 21.8, 20.8, 19.6, 17.0.

Bicyclo[5.1.0]octan-2-ol (3m).[25] White solid (50%, 315 mg): mp = 41.5–42.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.29–4.12 (m, 1H), 1.91–1.79 (m, 1H), 1.79–1.68 (m, 2H), 1.67–1.35 (m, 4H), 1.34–1.21 (m, 1H), 1.19–0.94 (m, 3H), 0.60–0.51 (m, 1H), 0.48–0.36 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 71.2, 35.7, 28.6, 26.9, 25.0, 22.7, 14.9, 3.1.

Compound 3n. White solid (90%): mp = 61–62 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.4 Hz, 1H), 7.23–7.01 (m, 3H), 4.29 (m, 1H), 3.18 (ddd, *J* = 13.9, 12.0, 5.4 Hz, 1H), 2.54 (dt, *J* = 13.6, 4.0 Hz, 1H), 2.28–2.11 (m, 2H), 1.86–1.72 (m, 1H), 1.52–1.38 (m, 1H), 1.01 (td, *J* = 8.9, 4.5 Hz, 1H), 0.77 (dd, *J* = 10.3, 5.7 Hz, 1H), 0.47 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 139.7, 130.9, 128.6, 126.7, 126.5, 68.3, 34.6, 29.9, 19.8, 17.3, 7.8; HRMS (EI) for $C_{12}H_{14}O$ calcd for $[M]^+$ *m/z* 174.1045, found 174.1045.

Compound 3o. Yellow solid (11%): mp = 97–100 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.2 Hz, 1H), 7.40 (d, *J* = 6.8 Hz, 1H), 7.30–7.19 (m, 2H), 4.73 (d, *J* = 9.2 Hz, 1H), 2.01 (br s, 1H), 1.94–1.86 (m, 1H), 1.29 (td, *J* = 9.1, 4.2 Hz, 1H), 1.15–1.06 (m, 2H), 1.04–0.94 (m, 1H), 0.84–0.77 (m, 1H), 0.73 (dd, *J* = 9.8, 5.0 Hz, 1H), 0.44 (dd, *J* = 10.0, 5.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 135.8, 131.9, 126.9, 126.3, 121.3, 74.1, 26.6, 18.7, 16.9, 15.3, 14.7, 11.3; HRMS (EI) for $C_{13}H_{14}O$ calcd for $[M]^+$ *m/z* 186.1045, found 186.1040.

Compound 3p. White solid (52%): mp = 120–122 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.60 (t, *J* = 8.4 Hz, 1H), 4.38 (t, *J* = 6.9 Hz, 1H), 2.25–2.12 (m, 1H), 2.11– 1.98 (m, 1H), 2.06 (s, 3H), 1.75 (dt, *J* = 12.4, 3.2 Hz, 1H), 1.71–1.56 (m, 3H), 1.56–1.43 (m, 3H), 1.38–1.02 (m, 10H), 1.00 (s, 3H), 0.97–0.88 (m, 1H), 0.81 (s, 3H), 0.72 (t, *J* = 4.8 Hz, 1H), 0.60 (dt, *J* = 13.7, 3.2 Hz, 1H), 0.10 (dd, *J* = 9.2, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 82.8, 63.7, 50.8, 46.1, 42.4, 37.0, 35.4, 34.1, 33.1, 30.4, 30.2, 27.6, 27.5, 26.4, 26.3, 23.6, 21.3, 21.2, 21.0, 12.0, 10.6. HRMS (EI) for $C_{22}H_{34}O_3$ calcd for $[M]^+$ *m/z* 346.2508, found 346.2500.

Compound 3q. Slight yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23 (t, *J* = 8.1 Hz, 1H), 1.96–1.72 (m, 5H), 1.60–1.46 (m, 2H), 1.38 (bs, 1H), 1.31–1.12 (m, 4H), 1.11–0.98 (m, 1H), 0.74 (d, *J* = 4.5 Hz, 1H), 0.22 (d, *J* = 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 81.0, 32.7, 31.1, 30.2, 29.4, 27.3, 26.5, 21.4, 21.1, 14.3; HRMS (EI) for $C_{10}H_{16}O$ calcd for $[M]^+$ *m/z* 152.1201, found 152.1197.

General procedure for rearrangements of cyclopropyl carbinols in Table 2.

Cinnamyl alcohol (2a).[26]

To a 50 mL round-bottom flask containing the substrate **1a** (148 mg, 1 mmol) was added 1,4-dioxane (2.5 mL), and then to the solution was added H_2O (22.5 mL). The flask was fitted with a condenser, stirred vigorously under refluxing condition. After completion judged by TLC, the resulting solution was cooled to room temperature. The mixture was extracted with

EtOAc (3 × 50 mL), washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc/hexane = 1:5) to afford the desired product **2a** (134 mg, 91%). Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.34 (m, 2H), 7.33–7.27 (m, 2H), 7.25–7.18 (m, 1H), 6.50 (d, *J* = 15.9 Hz, 1H), 6.21 (dt, *J* = 15.8, 7.2 Hz, 1H), 3.76 (m, 2H), 2.49 (m, 2H), 1.55 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 132.8, 128.5, 127.3, 126.3, 126.0, 62.0, 36.4.

(*E*)-4-(4-Methoxyphenyl)but-3-en-1-ol (2b).[26] White solid (146 mg, 82%): mp = 80–81 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.45 (d, *J* = 15.9 Hz, 1H), 6.06 (dt, *J* = 15.8, 7.2 Hz, 1H), 3.81 (s, 3H), 3.77–3.71 (m, 2H), 2.51–2.43 (m, 2H), 1.51 (t, *J* = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 132.3, 130.0, 127.2, 124.0, 113.9, 62.1, 55.3, 36.4.

(*E*)-2-(4-Hydroxybut-1-en-1-yl)phenol (2c). White solid (133 mg, 81%): mp = 74–76 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.7, 1H), 7.09 (t, *J* = 7.9, 1H), 6.87 (t, *J* = 7.5, 1H), 6.79 (d, *J* = 8.1, 1H), 6.70 (d, *J* = 16.0 Hz, 1H), 6.29 (s, 1H), 6.15 (dt, *J* = 15.9, 7.1 Hz, 1H), 3.77 (t, *J* = 5.8 Hz, 2H), 2.54–2.44 (m, 2H), 2.25 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 128.3, 128.1, 127.5, 127.3, 124.7, 120.7, 116.0, 61.8, 36.5; HRMS (ESI) for $C_{10}H_{12}O_2$ calcd for $[M–H]^-$ *m*/*z* 163.0759, found 163.0763.

(*E*)-4-(4-Chlorophenyl)but-3-en-1-ol (2d).[26] Colorless oil (120 mg, 66%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.24 (m, 4H), 6.45 (d, *J* = 15.9 Hz, 1H), 6.19 (dt, *J* = 15.8, 7.1 Hz, 1H), 3.81–3.71 (m, 2H), 2.48 (m, 2H), 1.54 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.7, 132.8, 131.5, 128.6, 127.2, 127.1, 61.9, 36.3.

(*E* or *Z*)-4-Phenylpent-3-en-1-ol (2e).[2d,14] (*E*:*Z* = 13:1) Colorless oil (121 mg, 75%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.17 (m, 5H), 5.79 (td, *J* = 7.3, 1.3 Hz, 0.93H, *E* isomer), 5.48 (td, *J* = 7.5, 1.4 Hz, 0.07H, *Z* isomer), 3.75 (s, 1.86H, *E* isomer), 3.62 (s, 0.14H, *Z* isomer), 2.50 (m, 1.86H, *E* isomer), 2.26 (m, 0.14H), 2.08 (s, 3H), 1.49 (s, 1H).

4,4-Diphenylbut-3-en-1-ol (2f).[27] Colorless oil (215 mg, 96%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.15 (m, 10H), 6.11 (t, *J* = 7.5 Hz, 1H), 3.72 (s, 2H), 2.40 (m, 2H), 1.42 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 142.3, 139.8, 129.8, 128.2, 128.1, 127.2, 127.1, 127.1, 125.2, 62.6, 33.3.

6-Phenylhexa-3(*E* or *Z*), 5(*E*)-dien-1-ol (2g).[28] (3*E*:3*Z* = 8:1) Colorless oil (148 mg, 85%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.18 (m, 5H), 7.08 (ddd, *J* = 15.5, 11.1, 1.1 Hz, 0.11H, *Z* isomer), 6.77 (dd, *J* = 15.7, 10.4 Hz, 0.89H, *E* isomer), 6.58 (d, *J* = 15.5 Hz, 0.11H, *Z* isomer), 6.49 (d, *J* = 15.7 Hz, 0.89H, *E* isomer), 6.40–6.25 (m, 1H), 5.80 (dt, *J* = 14.9, 7.3 Hz, 0.89H, *E* isomer), 5.53 (dt, *J* = 10.9, 7.9 Hz, 0.11H, *Z* isomer), 3.72 (m, 2H), 2.58 (qd, *J* = 6.5, 1.4 Hz, 0.22H, *Z* isomer), 2.43 (qd, *J* = 6.4, 1.0 Hz, 1.88H, *E* isomer), 1.50 (br s, 1H).

6-Phenylhexa-3(*E* or *Z*), 5(*E*)-dien-1-ol (2h).[28] (3*E*:3*Z* = 7:1) Colorless oil (153 mg, 88%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.17 (m, 5H), 7.07 (ddd, *J* = 15.5, 11.1, 0.9 Hz, 0.12H, *Z* isomer), 6.76 (dd, *J* = 15.7, 10.4 Hz, 0.88H, *E* isomer), 6.57 (d, *J* = 15.6 Hz, 0.12H, *Z* isomer), 6.49 (d, *J* = 15.7 Hz, 0.88H, *E* isomer), 6.32 (ddd, *J* = 15.2, 10.4, 0.6 Hz, 1H), 5.80 (dt, *J* = 14.9, 7.3 Hz, 0.88H, *E* isomer), 5.53 (dt, *J* = 10.7, 7.8 Hz, 0.12H, *Z* isomer), 3.72 (m, 2H), 2.62–2.54 (m, 0.24H, *Z* isomer), 2.47–2.37 (m, 1.76H, *E* isomer), 1.52 (br s, 1H).

(*E*)-4-Phenylhex-3-en-5-yn-1-ol (2i).[2i] Brown oil (137 mg, 80%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.57 (m, 2H), 7.37–7.24 (m, 3H), 6.54 (t, *J* = 7.5 Hz, 1H), 3.81 (t, *J* = 6.3 Hz, 2H), 3.35 (s, 1H), 2.83–2.74 (m, 2H), 1.61 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 135.6, 128.4, 127.8, 125.9, 124.9, 83.5, 80.7, 61.9, 34.7.

(*Z*)-4,6-diphenylhex-3-en-5-yn-1-ol (2j).[2m] Colorless oil (220 mg, 89%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71–7.63 (m, 2H), 7.57–7.50 (m, 2H), 7.40–7.26 (m, 6H), 6.51 (t, *J* = 7.5 Hz, 1H), 3.86 (t, *J* = 6.4 Hz, 2H), 2.87 (m, 2H), 1.55 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 133.8, 131.5, 128.39, 128.36, 127.8, 126.0, 125.8, 123.2, 95.6, 86.4, 62.1, 34.9.

(*Z*)-6-Cyclopropyl-4-phenylhex-3-en-5-yn-1-ol (2k). Colorless oil (170 mg, 80%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.28–7.21 (m, 1H), 6.35 (t, *J* = 7.4 Hz, 1H), 3.79 (t, *J* = 6.3 Hz, 2H), 2.78–2.67 (m, 2H), 1.53–1.44 (m, 1H), 0.94–0.84 (m, 2H), 0.84–0.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 132.4, 128.2, 127.5, 126.1, 125.9, 100.0, 72.7, 62.1, 34.6, 8.9, 0.3; HRMS (EI) for $C_{15}H_{16}O$ calcd for $[M]^+$ *m*/*z* 212.1201, found 212.1200.

(*E* or *Z*)-6-Phenylhex-3-en-5-yn-1-ol (2l).[29] (*E*:*Z* = 1:1) Slight yellow oil (143 mg, 83%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.40 (m, 2H), 7.35–7.27 (m, 3H), 6.23 (dt, *J* = 15.8, 7.3 Hz, 0.5H, *E* isomer), 6.03 (dt, *J* = 10.8, 7.4 Hz, 0.5H, *Z* isomer), 5.88–5.76 (m, 1H), 3.77 (t, *J* = 6.3 Hz, 1H), 3.72 (t, *J* = 6.1 Hz, 1H), 2.68 (qd, *J* = 6.5, 1.3 Hz, 1H), 2.48–2.39 (m, 1H), 1.71 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 139.5, 131.4, 128.28, 128.26, 128.2, 128.0, 123.3, 112.4, 111.6, 94.0, 88.6, 87.7, 85.9, 61.8, 61.5, 36.5, 33.8.

(*E*)-1,4-Diphenylbut-3-en-1-ol (2m).[30] White solid (212 mg, 95%): mp = 94–94.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.18 (m, 10H), 6.50 (d, *J* = 15.9 Hz, 1H), 6.20 (dt, *J* = 15.8, 7.3 Hz, 1H), 4.85–4.75 (m, 1H), 2.71–2.61 (m, 2H), 2.11 (d, *J* = 3.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 137.2, 133.4, 128.50, 128.45, 127.6, 127.3, 126.1, 125.9, 125.8, 73.7, 43.1.

1-Phenylpent-3(*E* or *Z*)-en-1-ol (2n).[30] (*E*:*Z* = 4:1) Colorless oil (157 mg, 97%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.23 (m, 5H), 5.69–5.54 (m, 1H), 5.49–5.36 (m, 1H), 4.75–4.62 (m, 1H), 2.63–2.33 (m, 2H), 2.09 (d, *J* = 2.1 Hz, 0.81H, *E* isomer), 2.04 (d, *J* = 4.2 Hz, 0.19H, *Z* isomer), 1.69 (d, *J* = 6.3 Hz, 2.43H, *E* isomer), 1.60 (d, *J* = 7.1 Hz, 0.57H, *Z* isomer);

General procedure for rearrangements of cyclopropyl carbinols in Table 3.

1-Phenylcyclohept-3-enol (4a).

To a 50 mL round-bottom flask containing the substrate **3a** (188 mg, 1.0 mmol) was added 1,4-dioxane (2.5 mL), and then to the solution was added H_2O (22.5 mL). The flask was fitted with a condenser, stirred vigorously under refluxing condition. After completion judged by TLC, the resulting solution was cooled to room temperature. The mixture was extracted with EtOAc (3 × 50 mL), washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (MTBE/hexane = 1:5) to afford the desired product **4a** (150 mg, 80%). Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.47 (m, 2H), 7.39–7.29 (m, 2H), 7.27–7.20 (m, 1H), 6.19–6.09 (m, 1H), 5.71–5.62 (m, 1H), 2.91–2.83 (m, 1H), 2.46 (ddd, *J* = 14.8, 8.1, 1.9 Hz, 1H), 2.37–2.27 (m, 2H), 2.26–2.00 (m, 3H), 1.71–1.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 136.1, 128.1, 126.4, 126.1, 124.1, 72.4, 45.7, 41.4, 28.7, 21.8; HRMS (EI) for $C_{13}H_{16}O$ calcd for $[M]^+$ *m*/*z* 188.1201, found 188.1210.

1-(*p*-Polyl)cyclohept-3-enol (4b). White solid (151 mg, 75%): mp =39–41 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.16–6.08 (m, 1H), 5.70–5.62 (m, 1H), 2.89–2.81 (m, 1H), 2.45 (ddd, *J* = 14.8, 8.1, 1.8 Hz, 1H), 2.34 (s, 3H), 2.33–2.27 (m, 1H), 2.27 (s, 1H),

2.23–2.07 (m, 2H), 2.07–1.98 (m, 1H), 1.67–1.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 136.0, 128.80, 128.79, 126.2, 124.1, 72.4, 45.7, 41.5, 28.7, 21.8, 20.9; HRMS (EI) for $C_{14}H_{18}O$ calcd for $[M]^+$ *m/z* 202.1358, found 202.1356.

1-(4-Chlorophenyl)cyclohept-3-enol (4c). Colorless oil (180 mg, 81%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 6.20–6.10 (m, 1H), 5.70–5.60 (m, 1H), 2.87–2.78 (m, 1H), 2.42 (ddd, *J* = 14.8, 8.2, 1.4 Hz, 1H), 2.36 (s, 1H), 2.35–2.27 (m, 1H), 2.24–2.12 (m, 1H), 2.11–1.96 (m, 2H), 1.71–1.55 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 136.5, 132.1, 128.2, 125.8, 125.7, 72.1, 45.6, 41.4, 28.6, 21.7; HRMS (EI) for $C_{13}H_{15}ClO$ calcd for $[M]^+$ *m/z* 222.0811, found 222.0820.

1-Methylcyclohept-3-enol (4d). Colorless oil (111 mg, 88%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (dt, *J* = 12.0, 6.2 Hz, 1H), 5.66–5.55 (m, 1H), 2.32 (d, *J* = 6.6 Hz, 2H), 2.23–2.04 (m, 2H), 1.91–1.82 (m, 2H), 1.80–1.70 (m, 1H), 1.58–1.49 (m, 2H), 1.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.0, 126.6, 69.8, 45.6, 41.5, 29.6, 28.4, 22.3; HRMS (EI) for $C_8H_{14}O$ calcd for $[M]^+$ *m/z* 126.1045, found 126.1041.

1-Butylcyclohept-3-enol (4e). Colorless oil (151 mg, 90%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.04–5.92 (m, 1H), 5.66–5.55 (m, 1H), 2.36–2.23 (m, 2H), 2.23–2.04 (m, 2H), 1.84–1.75 (m, 2H), 1.67 (d, *J* = 1.6 Hz, 1H), 1.61–1.43 (m, 4H), 1.41–1.25 (m, 4H), 0.91 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.8, 126.5, 71.6, 43.7, 41.3, 39.7, 28.5, 25.5, 23.3, 22.2, 14.1; HRMS (EI) for $C_{11}H_{20}O$ calcd for $[M]^+$ *m/z* 168.1514, found 168.1515.

Cyclohept-3-enol (4f).[31] Colorless oil (102 mg, 91%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.99–5.89 (m, 1H), 5.69–5.57 (m, 1H), 3.78–3.64 (m, 1H), 2.41–2.34 (m, 2H), 2.20–2.00 (m, 3H), 1.81–1.64 (m, 2H), 1.60 (s, 1H), 1.47–1.35 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.8, 125.9, 69.1, 40.8, 37.3, 28.3, 23.2.

1-(Phenylethynyl)cyclohept-3-enol (4g). Slight yellow oil (156 mg, 74%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.38 (m, 2H), 7.34–7.26 (m, 3H), 6.08–5.98 (m, 1H), 5.73–5.62 (m, 1H), 2.74–2.58 (m, 2H), 2.32–2.02 (m, 5H), 1.75–1.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 131.6, 128.2, 125.4, 122.8, 92.6, 84.2, 68.6, 46.2, 41.8, 28.2, 23.0; HRMS (EI) for $C_{15}H_{16}O$ calcd for $[M]^+$ *m/z* 212.1201, found 212.1198.

1,6,6-Trimethylcyclohept-3-enol (4h). Slight yellow oil (137mg, 89%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 (dt, *J* = 10.5, 6.8 Hz, 1H), 5.74 (dt, *J* = 10.4, 6.4 Hz, 1H), 2.40–2.27 (m, 2H), 2.15–2.00 (m, 2H), 1.77–1.57 (m, 2H), 1.23 (s, 3H), 1.03 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.9, 127.9, 71.4, 58.2, 40.5, 40.2, 32.8, 32.1, 31.7, 29.6; HRMS (EI) for $C_{10}H_{18}O$ calcd for $[M]^+$ *m/z* 154.1358, found 154.1353.

3-Methylcyclohept-3-enol (4i). Colorless oil (89 mg, 71%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.67 (s, 1H), 3.77–3.62 (m, 1H), 2.47 (t, *J* = 11.8 Hz, 1H), 2.24 (d, *J* = 14.1 Hz, 1H), 2.12–1.92 (m, 3H), 1.82–1.53 (m, 3H), 1.75 (s, 3H), 1.45–1.31 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.5, 127.8, 68.3, 42.5, 41.1, 27.6, 26.7, 23.7; HRMS (EI) for $C_8H_{14}O$ calcd for $[M]^+$ *m/z* 126.1045, found 126.1048.

3-Butylcyclohept-3-enol (4j). Colorless oil (136 mg, 81%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.65 (t, *J* = 6.4 Hz, 1H), 3.64 (br s, 1H), 2.52–2.39 (m, 1H), 2.24 (d, *J* = 14.1 Hz, 1H), 2.11–1.91 (m, 5H), 1.77–1.67 (m, 2H), 1.50 (s, 1H), 1.43–1.21 (m, 5H), 0.89 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 127.5, 68.8, 41.4, 41.3, 40.0, 30.0, 27.5, 24.0, 22.4, 12.0; HRMS (EI) for $C_{11}H_{20}O$ calcd for $[M]^+$ *m/z* 168.1514, found 168.1521.

3-Phenylcyclohept-3-enol (4k-1). White solid (145 mg, 77%): mp = 79–80 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.34 (m, 2H), 7.33–7.27 (m, 2H), 7.25–7.18 (m, 1H), 6.22 (t, *J* = 6.9 Hz, 1H), 3.91–3.80 (m, 1H), 2.92 (dd, *J* = 14.3, 9.2 Hz, 1H), 2.82 (dt, *J* = 14.3, 1.7 Hz, 1H), 2.34–2.19 (m, 2H), 2.18–2.09 (m, 1H), 1.90–1.78 (m, 1H), 1.78–1.68 (m, 1H), 1.68–1.56 (br s, 1H), 1.55–1.43 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 138.8, 131.9, 128.2, 126.6, 125.8, 68.4, 41.3, 41.1, 28.1, 23.3; HRMS (EI) for $C_{13}H_{16}O$ calcd for $[M]^+$ *m/z* 188.1201, found 188.1203.

6-Phenylbicyclo[3.2.0]heptan-6-ol (4k-2).[24] Slight yellow oil (20 mg, 11%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.51 (m, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.29–7.22 (m, 1H), 3.02–2.92 (m, 1H), 2.75–2.66 (m, 1H), 2.66–2.56 (m, 1H), 2.10 (dd, *J* = 13.4, 6.6 Hz, 1H), 2.00–1.79 (m, 3H), 1.75 (br s, 1H), 1.64 (dd, *J* = 12.5, 6.2 Hz, 1H), 1.59–1.49 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 128.3, 126.6, 124.2, 72.7, 50.9, 41.6, 32.7, 31.1, 26.6, 25.9.

2-Mythological-5-(prop-1-en-2-yl)cyclohept-2-enol (4l-1).[3h] Colorless oil (90 mg, 54%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74–5.66 (m, 1H), 4.71–4.65 (m, 2H), 4.09 (d, *J* = 4.1 Hz, 1H), 2.47 (d, *J* = 14.7 Hz, 1H), 2.38 (dd, *J* = 14.8, 7.4 Hz, 1H), 2.34–2.24 (m, 1H), 2.15–2.06 (m, 2H), 2.06–1.98 (m, 1H), 1.84–1.79 (m, 1H), 1.77 (s, 3H), 1.71 (s, 3H), 1.68–1.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 134.8, 126.0, 108.9, 66.6, 44.1, 40.3, 38.9, 33.1, 27.1, 20.5.

6-Mythology-3-(prop-1-en-2-yl)bicyclo[3.2.0]heptan-6-ol (4l-2).[3h] Colorless oil (15 mg, 15%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.76 (s, 1H), 4.72 (s, 1H), 2.84 (tt, *J* = 12.1, 6.1 Hz, 1H), 2.58 (t, *J* = 7.7 Hz, 1H), 2.51–2.40 (m, 1H), 2.23–2.12 (m, 1H), 2.01 (dd, *J* = 13.4, 6.6 Hz, 1H), 1.78 (s, 3H), 1.70–1.57 (m, 2H), 1.49–1.39 (m, 3H), 1.36 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 108.4, 69.5, 50.2, 45.7, 41.2, 37.3, 31.0, 30.6, 29.8, 21.6.

Cyclooct-3-enol (4m).[32] Colorless oil (107 mg, 85%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78–5.57 (m, 2H), 3.87–3.75 (m, 1H), 2.36 (t, *J* = 6.8 Hz, 2H), 2.29–2.17 (m, 1H), 2.15–2.05 (m, 1H), 1.87–1.77 (m, 1H), 1.74–1.29 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.3, 126.0, 72.1, 35.0, 34.0, 28.3, 25.7, 21.2.

Compound 4n. Colorless oil (140 mg, 80%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.32 (m, 1H), 7.27–7.17 (m, 2H), 7.12–7.02 (m, 1H), 5.57–5.34 (m, 2H), 5.23 (dd, *J* = 9.7, 7.3 Hz, 1H), 3.23 (ddd, *J* = 14.5, 11.1, 7.2 Hz, 1H), 2.95 (ddd, *J* = 14.5, 7.1, 3.5 Hz, 1H), 2.91–2.81 (m, 1H), 2.70–2.59 (m, 1H), 2.56–2.35 (m, 2H), 1.92 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 138.8, 130.3, 129.9, 127.7, 127.4, 126.7, 126.6, 73.9, 37.9, 33.1, 29.8; HRMS (EI) for $C_{12}H_{14}O$ calcd for $[M]^+$ *m/z* 174.1045, found 174.1041.

Compound 4o. Colorless oil (80%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.8 Hz, 1H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.21 (td, *J* = 7.5, 1.3 Hz, 1H), 7.07 (d, *J* = 7.7 Hz, 1H), 6.50 (dd, *J* = 11.6, 1.5 Hz, 1H), 5.81 (ddd, *J* = 11.6, 9.8, 4.5 Hz, 1H), 5.71–5.50 (m, 2H), 5.06 (dd, *J* = 6.9, 4.1 Hz, 1H), 2.86–2.67 (m, 2H), 2.66–2.55 (m, 1H), 2.55–2.43 (m, 1H), 1.90 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 134.6, 129.6, 129.0, 128.7, 128.2, 128.1, 127.7, 126.5, 124.9, 72.4, 37.1, 29.5; HRMS (EI) for $C_{13}H_{14}O$ calcd for $[M]^+$ *m/z* 186.1045, found 186.1038.

Compound 4p. White solid (73%): mp = 124–126 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.69–5.60 (m, 1H), 5.59–5.51 (m, 1H), 5.36 (d, *J* = 4.0 Hz, 1H), 4.61 (dd, *J* = 9.0, 7.9 Hz, 1H), 3.04 (d, *J* = 16.6 Hz, 1H), 2.48 (dd, *J* = 16.4, 7.8 Hz, 1H), 2.24–2.13 (m, 1H), 2.08–1.96 (m, 2H), 2.05 (s, 3H), 1.95–1.85 (m, 1H), 1.81–1.72 (m, 2H), 1.71–1.56 (m, 5H), 1.56–1.46 (m, 1H), 1.42–1.27 (m, 3H), 1.26–1.06 (m, 2H), 0.99 (s, 3H), 0.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 144.9, 130.1, 129.3, 122.2, 82.8, 51.4, 43.0, 42.4, 40.5, 36.9, 35.2, 34.2, 31.8, 31.0,

27.6, 24.0, 23.5, 22.9, 21.2, 20.9, 12.0; HRMS (EI) for $C_{22}H_{32}O$ calcd for $[M]^+$ *m/z* 328.2402, found 328.2410.

Compound 4q-1.[33] ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.01–3.88 (m, 1H), 2.25–2.13 (m, 1H), 2.03–1.95 (m, 2H), 1.92–1.80 (m, 6H), 1.65–1.50 (m, 5H), 1.25 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.6, 125.1, 67.5, 39.4, 31.3, 30.2, 29.8, 28.4, 23.0, 22.9.

Compound 4q-2.[33] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.66 (t, *J* = 5.0 Hz, 1H), 2.39–2.29 (m, 1H), 2.23–2.05 (m, 4H), 2.03–1.93 (m, 1H), 1.88–1.71 (m, 3H), 1.64–1.43 (m, 3H), 1.42–1.33 (m, 2H), 1.22–1.09 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 126.9, 75.0, 48.3, 40.7, 39.1, 33.4, 26.2, 23.2, 22.0.

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Notes and references

State Key Laboratory and Institute of Elemento-Organic Chemistry, Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin, 300071, China. E-mail: qujin@nankai.edu.cn

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6 For these reactions, we used either water purified with a Milli-Q Ultrapure Water Purification System or Watson's distilled water (pH = 5.5–6.5). Controlled reactions performed in PFA round-bottomed flasks (PFA: a copolymer of tetrafluoroethylene and perfluoroethers) furnished similar chemical yields, demonstrating that the glass surface was not responsible for promoting the reactions.

7 The pK_a* of water (K_a* is the apparent ionization constant of water) changes from 14 to 14.60 in an aqueous solution containing 20 vol% of 1,4-dioxane. See Woolley, E. M.; Hurkot, D. G.; Hepler, L. G. *J. Phys. Chem.* 1970, **74**, 3908.

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9 The rearrangement of substrate **3a** was also carried out under the acidic condition described by ref. 2m. In the mixed solvent of 4:1 (v/v) acetone/water and with 1 mol% of TfOH, the rearrangement of **3a** at 90 °C furnished 68% of **4a** in 15 min, please see supporting information for more details.

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