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An Efficient Approach to 2-Bromoalken-3-ols by Regioselective Bromohydroxylation Reaction of Simple Allenes with NBS

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A regioselective bromohydroxylation reaction of simple allenes affording 2-bromoalken-3-ols in moderate-to-good yields has been developed by using NBS as the electrophilic reagent in a mixture of 1,4-dioxane/H_2O (1:1) at room temperature. Through this study it has been concluded that the regioselectivity is determined by various factors including steric and electronic effects of the substituents of the allene moiety.

Introduction

Halohydroxylations of carbon–carbon double bonds are one of the most important methods for providing 2-halo-substituted alcohols[1] as two functional groups, that is, X and OH, are introduced into the substrates in one synthetic operation. During the last 10 years we have developed highly regio- and stereoselective halohydroxylation (X = Cl, Br, I) reactions of allenyl sulfoxides,[2a,2b] sulfones,[2c] phosphane oxides,[2d,2e] sulfides,[3a,3b] selenides,[3c] and furanones.[4] The reactions of sulfoxides, sulfones, and phosphane oxides afforded (*E*) products, whereas those of sulfides, selenides, and furanones afforded (*Z*) products.[5]

Note that such reactions of simple allenes are usually nonselective, affording a mixture of products: The addition of chlorine to allenes to afford an almost equimolar mixture of 2,3-dichloropropene and propargyl chloride in moderate overall yields (approximately 50%) has been reported by Peer,[6] whereas the addition of hydrogen bromide to propa-1,2-diene produced the cyclodimerization products, *cis*- and *trans*-1,3-dibromo-1,3-dimethylcyclobutane, as well as the conventional adducts 2-bromopropene and 2,2-dibromopropane.[7] The reactions of sulfenyl chlorides with propa-1,2-diene yielded primary monoadducts (allyl chlorides), diadducts, vinyl chlorides (by rearrangement of the monoadducts), and 1,2-dichloropropanes (by hydrochlorination of the monoadducts).[8] This phenomenon can be attributed to the fact that the regio- and stereoselectivity of this reaction are strongly influenced by the nature of the electrophile and steric and electronic effects of the substituents on the allenes. In this paper we report our recent results on the regioselective halohydroxylation reactions of simple allenes.

Results and Discussion

First we used CH_3CN/H_2O (10:1), which is the most commonly used solvent[5] in the halohydroxylation of 4-phenyl-1,2-butadiene. However, the reaction afforded a mixture of regioisomeric products, 3-bromo-1-phenyl-3-buten-2-ol (**2a**) and (*Z*)-2-bromo-4-phenyl-2-buten-1-ol (*Z*)-**3a** [**2a**/(*Z*)-**3a** = 82:18] in 17% combined yield with the recovery of 20% of 4-phenyl-1,2-butadiene (**1a**; Entry 1, Table 1). Then a series of solvents, including 1,4-dioxane, CH_3NO_2, and CH_2Cl_2, were tested; 1,4-dioxane was found to be the best (Entries 1–4, Table 1). We studied the effect of the ratio of 1,4-dioxane/water and found that 1,4-dioxane/H_2O (1:1) gave the best results (Entries 2 and 5–8, Table 1). With 1.5 equiv. of NBS, the yield dropped unexpectedly (Entry 9, Table 1). Note that the reaction of **1a** with bromine afforded **2a** and (*Z*)-**3a** in 57% combined yield with a selectivity of 68:32 (Entry 11, Table 1). Finally, we defined the best reaction conditions for the bromohydroxylation of simple allenes to give 2-bromoalken-3-ols: NBS (1.0 equiv.) in 1,4-dixoane/H_2O (1:1) at room temperature (Entry 10, Table 1). Note that the bromohydroxylation reaction occurred at the more substituted C=C bond with the bromine atom adding to the central carbon atom of the allene. Thus, the regioselectivity is determined by the electronic effects (not the steric effect) of these two C=C bonds.

The results of the bromohydroxylation of different simple allenes with NBS under these standard reaction conditions are summarized in Table 2. Note that the monosubstituted allenes **1** reacted with NBS to afford 2-bromoalken-3-ols **2** in good yields with good selectivity towards the more substituted C=C bonds: R^1 may be benzyl (Entry 1, Table 2),

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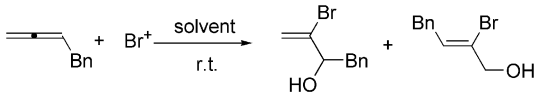
Table 1. Optimization of the reaction conditions for the bromohydroxylation reaction of 4-phenyl-1,2-butadiene (**1a**).[a]

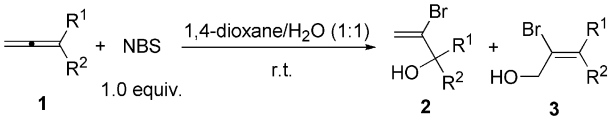


1a **2a** (*Z*)-**3a**

Entry	X (Quantity [equiv.])	Solvent	*t* [h]	Combined yield of **2a** + (*Z*)-**3a** [%][b]	**2a**/(*Z*)-**3a**[b]	Recovery of **1a** [%][b]
1	NBS (1.2)	CH_3CN/H_2O (10:1)	10.5	17	82:18	20
2	NBS (1.2)	dioxane/H_2O (10:1)	10.5	39	87:13	27
3	NBS (1.2)	CH_3NO_2/H_2O (10:1)	10.5	–	–	50
4	NBS (1.2)	CH_2Cl_2/H_2O (10:1)	17	24	63:37	24
5[c]	NBS (1.2)	dioxane/H_2O (1:1)	11.5	64	89:11	0
6	NBS (1.2)	dioxane	10	20	60:40	41
7	NBS (1.2)	dioxane/H_2O(1:10)	18	61	90:10	10
8	NBS (1.2)	H_2O	0.5	20	50:50	0
9	NBS (1.5)	dioxane/H_2O (1:1)	10	45	91:9	0
10	NBS (1.0)	dioxane/H_2O(1:1)	13	71	92:8	0
11	Br_2 (1.0)	dioxane/H_2O(1:1)	0.8	57	68:32	0

[a] All reactions used 0.3 mmol of **1a** unless otherwise noted. [b] Determined by ^{1}H NMR by using CH_2Br_2 as the internal standard. [c] 0.6 mmol **1a** was used.

Table 2. Bromohydroxylation reaction of simple allenes with NBS.



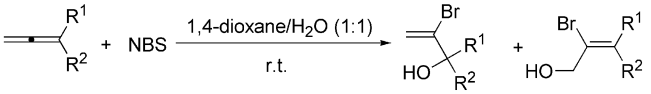
1 **2** **3**

Entry	**1** R^1	R^2	*t* [h]	NMR yield of **2** + **3** [%] (**2**/**3**)[a]	Isolated yield of **2** [%]	Isolated yield of **3** [%]
1	Bn	H (**1a**)	16	72 (91:9)	63 (**2a**)	4 [(*Z*)-**3a**]
2	*n*-$C_{10}H_{21}$	H (**1b**)	17	86 (94:6)	68 (**2b**)	5 [(*Z*)-**3b**]
3	*n*-C_8H_{17}	H (**1c**)	19	74 (96:4)	62 (**2c**)	5 [(*Z*)-**3c**]
4	*n*-C_7H_{15}	H (**1d**)	22	90 (94:6)	82 (**2d**)	5 [(*Z*)-**3d**]
5	*n*-C_6H_{13}	H (**1e**)	16	85 (93:7)	69 (**2e**)	4 [(*Z*)-**3e**]
6	*c*-C_6H_{11}	H (**1f**)	17	65 (89:11)	58 (**2f**)	3 [(*Z*)-**3f**]
7	Ph	H (**1g**)	16	74 (78:22)	59 (**2g**)	9 [(*Z*)-**3g**]
8	Et	Ph (**1h**)	23	76 (88:12)	65 (**2h**)	8 [(*E*)-**3h**]
9	*n*-C_4H_9	Ph (**1i**)	17.5	89 (85:15)	63 (**2i**)	11 [(*E*)-**3i**]
10	*n*-C_6H_{13}	Ph (**1j**)	20	76 (87:13)	64 (**2j**)	10 [(*E*)-**3j**]
11	allyl	Ph (**1k**)	12	76 (88:12)	60 (**2k**)	7 [(*E*)-**3k**]

[a] Combined yields of **2** and **3** were determined by ^{1}H NMR spectroscopy using CH_2Br_2 as the internal standard. The ratios of **2**/**3** are given in parentheses.

normal alkyl (Entries 2–5, Table 2), cyclic alkyl (Entry 6, Table 2), or phenyl (Entry 7, Table 2). Even with geminally disubstituted substrates, when R^1 is an alkyl group and R^2 is a phenyl group, the corresponding products were afforded in satisfactory yields and relatively high selectivities (Entries 8–10, Table 2). With R^1 being an allyl group, no reaction occurred at the allylic C=C bond. Note that products **2** and (*Z*)-**3** may be separated easily by chromatography on silica gel, and the byproduct (*Z*)-**3** is formed with a single configuration, as determined by an NOE study (see the Supporting Information).

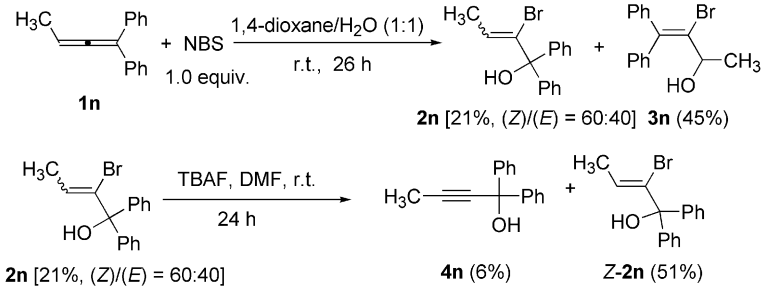
The substrates with both R^1 and R^2 as alkyl or phenyl groups led to a low regioselectivity, probably due to the increased steric effect of the coexistence of R^1 and R^2 resulting in a more electrophilic attack at the terminal C=C double bond (Scheme 1). These two products may also be easily separated by chromatography on silica gel.



1l: R^1 = R^2 = Ph 13 h **2l** (37%) **3l** (20%)
1m: R^1 = R^2 = *n*-C_4H_9 25 h **2m** (40%) **3m** (22%)

Scheme 1.

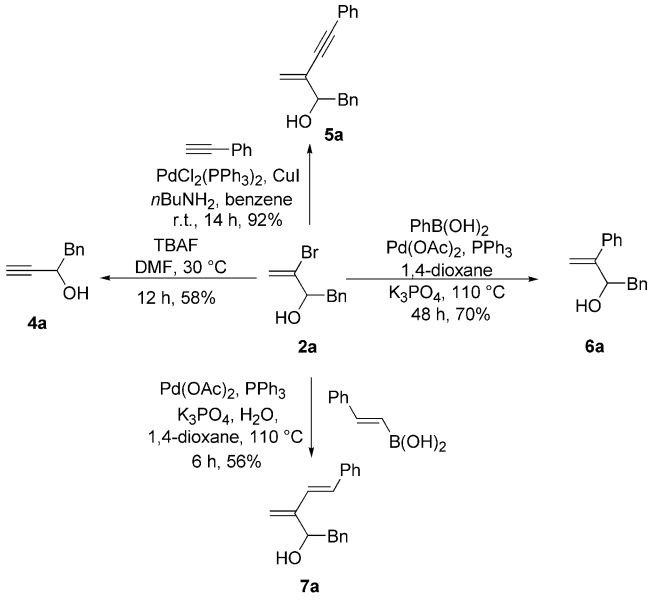
With trisubstituted substrate **1n**, due to the influence of the two phenyl substituents, regioisomer **3n** with the hy-



Scheme 2.

droxy group at the less hindered terminal is the main product, which indicates that the regioselectivity is a combination of electronic and steric effects (Scheme 2). Note that pure (*Z*)-**2n**, as determined by an NOE study (see the Supporting Information), can be obtained in 51% isolated yield by highly selective elimination of (*E*)-**2n** to give 1,1-diphenylbut-2-yn-1-ol (**4n)** using TBAF[9] (Scheme 2).

2-Bromoalken-3-ols are very useful building blocks in organic synthesis and can be exploited for the fast introduction of molecular complexity. The synthetic potential of this methodology was demonstrated by the reactions of **2a** (Scheme 3). By coupling protocols of the C–Br bond in **2a**, 1-alkynyl, aryl, and styryl groups can be introduced into the 2-position.[10] Elimination of HBr from **2a** afforded propargylic alcohol **4a**.[9]



Scheme 3.

Conclusions

We have developed a convenient method for the efficient synthesis of 2-bromo-substituted allylic alcohols by the regioselective bromohydroxylation of simple allenes with NBS. Owing to the ready availability of the starting allenes[11] and NBS, as well as the potential of the 2-bromoalken-3-ols formed, this reaction may be useful in organic synthesis. The regioselectivity of the reaction is determined by electronic effects or in some cases by a combination of electronic and steric effects. Further studies on the synthetic applications of this reaction are being conducted in our laboratory.

Experimental Section

General: ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AM 300 MHz. IR spectra were recorded with a Perkin–Elmer 983G instrument. Elemental analyses were recorded with a Carlo-Erba EA1110 elementary analysis instrument. Mass spectrometry was performed with an HP 5989A system. High-resolution mass spectrometry was determined with a Finnigan MAT 8430 or Bruker APEXIII instrument. Unless otherwise indicated, chemicals and solvents were purchased from commercial suppliers.

Synthesis of 2-Bromoalk-2-enols: The 1,2-allenes used in this study were prepared according to a reported procedure.[11]

3-Bromo-1-phenyl-3-buten-2-ol (2a) and (*Z*)-2-Bromo-4-phenyl-2-buten-1-ol [(*Z*)-3a]. Typical Procedure: NBS (1780.2 mg, 10.0 mmol) and H_2O (20 mL) were sequentially added to a solution of buta-2,3-dienylbenzene (**1a**; 1300.4 mg, 10.0 mmol) in dioxane (20 mL). After stirring at room temp. for 16 h, the reaction was complete, as monitored by TLC. The mixture was then quenched with a saturated aqueous solution of $Na_2S_2O_3$ (20 mL), and then water (50 mL) was added. This mixture was extracted with diethyl ether (3 × 30 mL), washed with a saturated aqueous solution of NaCl (3 × 20 mL), and dried with anhydrous Na_2SO_4. After filtration and concentration, the NMR yield of **2a** was 65% and the ratio of **2a**/(*Z*)-**3a** was 91:9, as determined by ^{1}H NMR analysis using CH_2Br_2 as the internal standard. Chromatography on silica gel (petroleum ether/ethyl acetate, 10:1) of the crude product afforded **2a** (1416.6 mg, 63%) and (*Z*)-**3a** (93.0 mg, 4%).

2a: Liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.20 (m, 5 H, ArH), 5.76 (dd, J = 2.1 and 0.9 Hz, 1 H, =CH), 5.53 (d, J = 1.8 Hz, 1 H, =CH), 4.33 (q, J = 6.3 Hz, 1 H, CHO), 3.06 (dd, J = 13.7 and 5.6 Hz, 1 H, one proton in $ArCH_2$), 2.90 (dd, J = 13.7 and 7.4 Hz, 1 H, one proton in $ArCH_2$), 2.12–2.02 (m, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.7, 135.8, 129.5, 128.5, 126.8, 117.6, 76.9, 41.8 ppm. IR (neat): $\tilde{\nu}$ = 3396, 3062, 3028, 2924, 1625, 1603, 1496, 1454, 1383, 1257, 1187, 1127, 1076, 1053, 1026 cm^{-1}. MS (70 eV, EI): *m/z* (%) = 147 (11.35) [M – Br]$^+$, 91 (100). $C_{10}H_{11}BrO$ (226.00): calcd. C 52.89, H 4.88; found C 52.91, H 4.94.

(*Z*)-3a: Liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.15 (m, 5 H, ArH), 6.17 (tt, J = 7.1 and 1.1 Hz, 1 H, =CH), 4.24 (d, J = 5.7 Hz, 2 H, CH_2O), 3.55 (d, J = 6.9 Hz, 2 H, $ArCH_2$), 2.36 (t, J

= 6.2 Hz, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.7, 128.8, 128.6, 128.4, 127.2, 126.4, 68.2, 37.0 ppm. IR (neat): $\tilde{\nu}$ = 3363, 3062, 3027, 2917, 2861, 1655, 1602, 1495, 1453, 1263, 1201, 1095, 1010 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 228 (3.67) [M(^{81}Br)]$^+$, 226 (3.77) [M(^{79}Br)]$^+$, 129 (100). HRMS: calcd. for $C_{10}H_{11}{}^{79}BrO$ [M]$^+$ 225.9993; found 225.9989.

The following compounds **2b**–**2n** and **3b**–**3n** were prepared according to this procedure.

2-Bromo-1-tridecen-3-ol (2b) and (*Z*)-2-Bromo-2-tridecen-1-ol [(*Z*)-3b]: The reaction of trideca-1,2-diene (**1b**; 900.9 mg, 5.0 mmol) and NBS (895.6 mg, 5.0 mmol) in 1,4-dioxane (10.0 mL) and H_2O (10.0 mL) at room temp. for 17 h afforded **2b** (963.2 mg, 68%) and (*Z*)-**3b** (61.8 mg, 5%) (petroleum ether/ethyl acetate, 50:1 → 40:1 → 30:1 → 20:1 → 10:1). The ratio of **2b**/(*Z*)-**3b** was 94:6, as determined by ^{1}H NMR spectroscopy using CH_2Br_2 as the internal standard.

2b: Liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.86 (d, *J* = 1.5 Hz, 1 H, =CH), 5.55 (d, *J* = 1.8 Hz, 1 H, =CH), 4.07 (q, *J* = 6.3 Hz, 1 H, CHO), 1.98 (d, *J* = 5.7 Hz, 1 H, OH), 1.75–1.50 (m, 2 H, CH_2), 1.41–1.12 (m, 16 H, 8 CH_2), 0.87 (t, *J* = 6.6 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.6, 116.9, 76.1, 35.3, 31.9, 29.6, 29.54, 29.49, 29.3, 25.2, 22.7, 14.1 ppm. IR (neat): $\tilde{\nu}$ = 3354, 2924, 2854, 1627, 1466, 1378, 1309, 1162, 1073 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 197 (11.67) [M – Br]$^+$, 136 (100). $C_{13}H_{25}BrO$ (276.11): calcd. C 56.32, H 9.09; found C 56.33, H 8.93.

(*Z*)-3b: Liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.00 (t, *J* = 7.1 Hz, 1 H, =CH), 4.24 (s, 2 H, CH_2O), 2.29 (br. s, 1 H, OH), 2.19 (q, *J* = 7.1 Hz, 2 H, CH_2), 1.50–1.20 (m, 16 H, 8 CH_2), 0.88 (t, *J* = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 130.6, 126.4, 68.4, 31.9, 30.8, 29.6, 29.5, 29.4, 29.3, 29.2, 28.2, 22.7, 14.1 ppm. IR (neat): $\tilde{\nu}$ = 3334, 2925, 2854, 1657, 1462, 1377, 1296, 1221, 1131, 1093, 1011 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 278 (3.04) [M(^{81}Br)]$^+$, 276 (2.96) [M(^{79}Br)]$^+$, 197 (2.44) [M – Br]$^+$, 179 (15.50) [M – Br – H_2O]$^+$, 95 (100). HRMS: calcd. for $C_{13}H_{25}{}^{79}BrO$ [M]$^+$ 276.1089; found 276.1084.

2-Bromo-1-undecen-3-ol (2c) and (*Z*)-2-Bromo-2-undecen-1-ol [(*Z*)-3c]: The reaction of undeca-1,2-diene (**1c**; 760.1 mg, 5.0 mmol) and NBS (895.6 mg, 5.0 mmol) in 1,4-dioxane (10.0 mL) and H_2O (10.0 mL) at room temp. for 19 h afforded **2c** (772.1 mg, 62%) and (*Z*)-**3c** (58.6 mg, 5%) (petroleum ether/ethyl acetate, 50:1 → 40:1 → 30:1 → 20:1 → 10:1). The ratio of **2c**/(*Z*)-**3c** was 96:4 as determined by ^{1}H NMR spectroscopy using CH_2Br_2 as the internal standard.

2c: Liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.85 (d, *J* = 0.9 Hz, 1 H, =CH), 5.53 (d, *J* = 1.5 Hz, 1 H, =CH), 4.06 (t, *J* = 6.5 Hz, 1 H, CHO), 2.27 (br. s, 1 H, OH), 1.80–1.45 (m, 2 H, CH_2), 1.41–1.12 (m, 12 H, 6 CH_2), 0.86 (t, *J* = 6.6 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.5, 116.9, 76.0, 35.2, 31.8, 29.4, 29.3, 29.2, 25.1, 22.6, 14.1 ppm. IR (neat): $\tilde{\nu}$ = 3357, 2925, 2856, 1628, 1465, 1379, 1305, 1069 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 169 (10.64) [M – Br]$^+$, 41 (100). $C_{11}H_{21}BrO$ (248.08): calcd. C 53.02, H 8.49; found C 53.10, H 8.47.

(*Z*)-3c: Liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.00 (t, *J* = 6.9 Hz, 1 H, =CH), 4.24 (s, 2 H, CH_2O), 2.19 (q, *J* = 7.1 Hz, 2 H, CH_2), 2.11 (br. s, 1 H, OH), 1.45–1.18 (m, 12 H, 6 CH_2), 0.88 (t, *J* = 6.6 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 130.6, 126.4, 68.5, 31.8, 30.8, 29.4, 29.20, 29.19, 28.2, 22.6, 14.1 ppm. IR (neat): $\tilde{\nu}$ = 3333, 2925, 2855, 1657, 1461, 1377, 1292, 1263, 1221, 1131, 1092, 1014 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 250 (4.88) [M(^{81}Br)]$^+$, 248 (5.07) [M(^{79}Br)]$^+$, 151 (16.64) [M – Br – H_2O]$^+$, 95 (100). HRMS: calcd. for $C_{11}H_{21}{}^{79}BrO$ [M]$^+$ 248.0776; found 248.0768.

2-Bromo-1-decen-3-ol (2d) and (*Z*)-2-Bromo-2-decen-1-ol [(*Z*)-3d]: The reaction of deca-1,2-diene (**1d**; 276.1 mg, 2.0 mmol) and NBS (358.3 mg, 2.0 mmol) in 1,4-dioxane (7.0 mL) and H_2O (7.0 mL) at room temp. for 22 h afforded **2d** (385.8 mg, 82%) and (*Z*)-**3d** (25.3 mg, 5%) (petroleum ether/ethyl acetate, 50:1 → 30:1 → 20:1). The ratio of **2d**/(*Z*)-**3d** was 94:6 as determined by ^{1}H NMR spectroscopy using CH_2Br_2 as the internal standard.

2d: Liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.86 (dd, *J* = 2.0 and 0.8 Hz, 1 H, =CH), 5.54 (d, *J* = 1.8 Hz, 1 H, =CH), 4.07 (q, *J* = 6.2 Hz, 1 H, CHO), 2.16–2.00 (m, 1 H, OH), 1.73–1.50 (m, 2 H, CH_2), 1.42–1.13 (m, 10 H, 5 CH_2), 0.87 (t, *J* = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.6, 116.9, 76.0, 35.2, 31.7, 29.3, 29.2, 25.2, 22.6, 14.1 ppm. IR (neat): $\tilde{\nu}$ = 3373, 2955, 2926, 2856, 1627, 1465, 1414, 1379, 1164, 1104, 1054 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 155 (10.90) [M – Br]$^+$, 57 (100). $C_{10}H_{19}BrO$ (234.06): calcd. C 51.07, H 8.14; found C 51.18, H 8.13.

(*Z*)-3d:[12] Liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.00 (t, *J* = 6.9 Hz, 1 H, =CH), 4.24 (d, *J* = 5.4 Hz, 2 H, CH_2O), 2.19 (q, *J* = 7.2 Hz, 2 H, CH_2), 2.07 (br. s, 1 H, OH), 1.50–1.18 (m, 10 H, 5 CH_2), 0.89 (t, *J* = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 130.6, 126.5, 68.5, 31.8, 30.8, 29.15, 29.07, 28.2, 22.6, 14.1 ppm. IR (neat): $\tilde{\nu}$ = 3345, 2925, 2857, 1659, 1459 1377, 1281, 1221, 1134, 1091, 1017 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 236 (5.10) [M(^{81}Br)]$^+$, 234 (5.17) [M(^{79}Br)]$^+$, 137 (27.93) [M – Br – H_2O]$^+$, 81 (100).

2-Bromo-1-nonen-3-ol (2e) and (*Z*)-2-Bromo-2-nonen-1-ol [(*Z*)-3e]: The reaction of nona-1,2-diene (**1e**; 621.0 mg, 5.0 mmol) and NBS (895.3 mg, 5.0 mmol) in 1,4-dioxane (10.0 mL) and H_2O (10.0 mL) at room temp. for 16 h afforded **2e** (766.5 mg, 69%) and (*Z*)-**3e** (44.9 mg, 4%) (petroleum ether/ethyl acetate, 50:1 → 40:1 → 30:1 → 20:1). The ratio of **2e**/(*Z*)-**3e** was 93:7 as determined by ^{1}H NMR spectroscopy using CH_2Br_2 as the internal standard.

2e: Liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.84 (d, *J* = 1.2 Hz, 1 H, =CH), 5.52 (d, *J* = 1.8 Hz, 1 H, =CH), 4.05 (t, *J* = 6.5 Hz, 1 H, CHO), 2.44 (br. s, 1 H, OH), 1.75–1.43 (m, 2 H, CH_2), 1.41–1.12 (m, 8 H, 4 CH_2), 0.86 (t, *J* = 6.3 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.5, 116.8, 76.0, 35.1, 31.6, 28.9, 25.1, 22.5, 14.0 ppm. IR (neat): $\tilde{\nu}$ = 3373, 2961, 2927, 2858, 1626, 1466, 1379, 1160, 1098, 1065, 1046 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 123 (85.22) [M – Br – H_2O]$^+$, 43 (100). $C_9H_{17}BrO$ (220.05): calcd. C 48.88, H 7.75; found C 48.93, H 7.80.

(*Z*)-3e:[13] Liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.00 (t, *J* = 7.1 Hz, 1 H, =CH), 4.24 (s, 2 H, CH_2O), 2.19 (q, *J* = 7.2 Hz, 2 H, CH_2), 2.08 (br. s, 1 H, OH), 1.50–1.15 (m, 8 H, 4 CH_2), 0.89 (t, *J* = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 130.6, 126.5, 68.5, 31.6, 30.8, 28.8, 28.2, 22.5, 14.1 ppm. IR (neat): $\tilde{\nu}$ = 3329, 2956, 2926, 2857, 1651, 1459, 1374, 1134, 1092, 1015 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 222 (3.01) [M(^{81}Br)]$^+$, 220 (3.43) [M(^{79}Br)]$^+$, 123 (26.22) [M – Br – H_2O]$^+$, 43 (100).

2-Bromo-1-cyclohexyl-2-propen-1-ol (2f) and (*Z*)-2-Bromo-3-cyclohexyl-2-propen-1-ol [(*Z*)-3f]: The reaction of propa-1,2-dienylcyclohexane (**1f**; 611.1 mg, 5.0 mmol) and NBS (895.5 mg, 5.0 mmol) in 1,4-dioxane (10.0 mL) and H_2O (10.0 mL) at room temp. for 17 h afforded **2f** (632.3 mg, 58%) and (*Z*)-**3f** (31.1 mg, 3%) (petroleum ether/ethyl acetate, 50:1 → 40:1 → 30:1 → 20:1 → 15:1). The ratio of **2f**/(*Z*)-**3f** was 89:11 as determined by ^{1}H NMR spectroscopy using CH_2Br_2 as the internal standard.

2f: Liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.82–5.77 (m, 1 H, =CH), 5.55 (d, *J* = 1.8 Hz, 1 H, =CH), 3.70 (t, *J* = 7.1 Hz, 1 H,

CHO), 2.11 (d, J = 6.6 Hz, 1 H, CH), 1.96 (d, J = 12.9 Hz, 1 H, OH), 1.82–1.45 (m, 5 H, one proton in CH_2 and 2 CH_2), 1.35–0.80 (m, 5 H, one proton in CH_2 and 2 CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.5, 118.0, 80.6, 40.9, 29.3, 27.9, 26.2, 25.8, 25.7 ppm. IR (neat): $\tilde{\nu}$ = 3385, 2926, 2852, 1626, 1450, 1384, 1309, 1261, 1209, 1191, 1156, 1081, 1054, 1028 cm^{-1}. MS (70 eV, EI): m/z (%) = 220 (0.85) $[M(^{81}Br)]^+$, 218 (0.90) $[M(^{79}Br)]^+$, 83 (100). $C_9H_{15}BrO$ (218.03): calcd. C 49.33, H 6.90; found C 49.28, H 6.88.

(*Z*)-3f: Liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.83 (d, J = 8.7 Hz, 1 H, =CH), 4.22 (d, J = 4.2 Hz, 2 H, CH_2O), 2.50–2.30 (m, 1 H, CH), 2.09 (br. s, 1 H, OH), 1.80–1.58 (m, 5 H, one proton in CH_2 and 2 CH_2), 1.40–1.00 (m, 5 H, one proton in CH_2 and 2 CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.6, 124.5, 68.5, 39.9, 31.6, 25.9, 25.5 ppm. IR (neat): $\tilde{\nu}$ = 3332, 2925, 2851, 1654, 1448, 1314, 1276, 1215, 1146, 1081, 1005 cm^{-1}. MS (70 eV, EI): m/z (%) = 220 (1.57) $[M(^{81}Br)]^+$, 218 (1.56) $[M(^{79}Br)]^+$, 121 (25.87) [M – Br – H_2O]$^+$, 99 (100). HRMS: calcd. for $C_9H_{15}{}^{79}BrO$ $[M]^+$ 218.0306; found 218.0313.

2-Bromo-1-phenyl-2-propen-1-ol (2g) and (*Z*)-2-Bromo-3-phenyl-2-propen-1-ol [(*Z*)-3g]: The reaction of propa-1,2-dienylbenzene (**1g**; 232.2 mg, 2.0 mmol) and NBS (358.4 mg, 2.0 mmol) in 1,4-dioxane (7.0 mL) and H_2O (7.0 mL) at room temp. for 16 h afforded **2g** (251.3 mg, 59%) and (*Z*)-**3g** (39.2 mg, 9%) (petroleum ether/diethyl ether, 10:1 → 8:1). The ratio of **2g**/(*Z*)-**3g** was 78:22 as determined by ^1H NMR spectroscopy using CH_2Br_2 as the internal standard.

2g: Liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.50–7.30 (m, 5 H, ArH), 6.05 (dd, J = 1.7 and 1.1 Hz, 1 H, =CH), 5.69 (d, J = 1.8 Hz, 1 H, =CH), 5.26 (s, 1 H, CHO), 2.61 (br. s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.6, 135.5, 128.5, 128.3, 126.6, 117.6, 77.8 ppm. IR (neat): $\tilde{\nu}$ = 3378, 3063, 3031, 2880, 1625, 1494, 1454, 1387, 1233, 1193, 1151, 1113, 1079, 1034, 1024 cm^{-1}. MS (70 eV, EI): m/z (%) = 214 (37.73) $[M(^{81}Br)]^+$, 212 (38.35) $[M(^{79}Br)]^+$, 107 (100). HRMS: calcd. for $C_9H_9{}^{79}BrO$ $[M]^+$ 211.9837; found 211.9834.

(*Z*)-3g:[14] Liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.69–7.59 (m, 2 H, ArH), 7.45–7.30 (m, 3 H, ArH), 7.10 (s, 1 H, =CH), 4.42 (d, J = 3.6 Hz, 2 H, CH_2O), 3.30 (br. s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.8, 128.9, 128.1, 128.0, 127.6, 125.1, 69.1 ppm. IR (neat): $\tilde{\nu}$ = 3333, 3056, 3025, 2917, 2859, 1647, 1603, 1491, 1446, 1367, 1285, 1089, 1071 cm^{-1}. MS (70 eV, EI): m/z (%) = 214 (29.75) $[M(^{81}Br)]^+$, 212 (29.70) $[M(^{79}Br)]^+$, 133 (100) [M – Br]$^+$. HRMS: calcd. for $C_9H_9{}^{79}BrO$ $[M]^+$ 211.9837; found 211.9836.

2-Bromo-3-phenyl-1-penten-3-ol (2h) and (*E*)-2-Bromo-3-phenyl-2-penten-1-ol [(*E*)-3h]: The reaction of penta-1,2-dien-3-ylbenzene (**1h**; 288.0 mg, 2.0 mmol) and NBS (358.4 mg, 2.0 mmol) in 1,4-dioxane (7.0 mL) and H_2O (7.0 mL) at room temp. for 23 h afforded **2h** (311.9 mg, 65%) and (*E*)-**3h** (39.3 mg, 8%) [eluent: first time, petroleum ether/ethyl acetate, 40:1 → 30:1 → 20:1; after this separation, (*E*)-**3h** was not pure; second time, petroleum ether/ethyl acetate, 30:1 → 20:1 gave pure (*E*)-**3h**]. The ratio of **2h**/(*E*)-**3h** was 88:12 as determined by ^1H NMR spectroscopy using CH_2Br_2 as the internal standard.

2h: Liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.33 (m, 2 H, ArH), 7.32–7.14 (m, 3 H, ArH), 5.95 (d, J = 2.4 Hz, 1 H, =CH), 5.63 (d, J = 2.4 Hz, 1 H, =CH), 2.38 (br. s, 1 H, OH), 2.22–2.06 (m, 1 H, CH_2), 2.05–1.88 (m, 1 H, CH_2), 0.80 (t, J = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.7, 140.6, 128.1, 127.4, 125.7, 117.3, 79.9, 32.1, 8.1 ppm. IR (neat): $\tilde{\nu}$ = 3557, 3465, 3087, 3060, 3028, 2974, 2938, 2880, 1621, 1493, 1447, 1376, 1348, 1311, 1271, 1199, 1126, 1077, 1055, 1032 cm^{-1}. MS (70 eV, EI): m/z (%) = 242 (8.33) $[M(^{81}Br)]^+$, 240 (8.53) $[M(^{79}Br)]^+$, 211 (100). HRMS: calcd. for $C_{11}H_{13}{}^{81}BrO$ $[M]^+$ 242.0129; found 242.0129.

(*E*)-3h: Liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.24 (m, 3 H, ArH), 7.20–7.08 (m, 2 H, ArH), 4.13 (d, J = 6.3 Hz, 2 H, CH_2O), 2.62 (q, J = 7.5 Hz, 2 H, CH_2), 1.98 (br. s, 1 H, OH), 0.95 (t, J = 7.7 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.5, 139.3, 128.4, 128.0, 127.6, 124.2, 65.6, 32.3, 11.3 ppm. IR (neat): $\tilde{\nu}$ = 3386, 3058, 3024, 2970, 2930, 2873, 1621, 1491, 1443, 1375, 1239, 1200, 1113, 1086, 1057, 1010 cm^{-1}. MS (70 eV, EI): m/z (%) = 242 (43.11) $[M(^{81}Br)]^+$, 240 (43.88) $[M(^{79}Br)]^+$, 161 (58.19) [M – Br]$^+$, 143 (100) [M – Br – H_2O]$^+$. HRMS: calcd. for $C_{11}H_{13}{}^{79}BrO$ $[M]^+$ 240.0150; found 240.0142.

2-Bromo-3-phenyl-1-hepten-3-ol (2i) and (*E*)-2-Bromo-3-phenyl-2-hepten-1-ol [(*E*)-3i]: The reaction of hepta-1,2-dien-3-ylbenzene (**1i**; 861.1 mg, 5.0 mmol) and NBS (895.1 mg, 5.0 mmol) in 1,4-dioxane (10.0 mL) and H_2O (10.0 mL) at room temp. for 17.5 h afforded **2i** (845.4 mg, 63%) and (*E*)-**3i** (151.8 mg, 11%) (petroleum ether/ethyl acetate, 40:1 → 30:1 → 20:1). The ratio of **2i**/(*E*)-**3i** was 85:15 as determined by ^1H NMR spectroscopy using CH_2Br_2 as the internal standard.

2i: Liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.48–7.41 (m, 2 H, ArH), 7.40–7.24 (m, 3 H, ArH), 6.04 (d, J = 2.1 Hz, 1 H, =CH), 5.71 (d, J = 2.4 Hz, 1 H, =CH), 2.45 (s, 1 H, OH), 2.23–2.10 (m, 1 H, one proton in CH_2), 2.08–1.93 (m, 1 H, one proton in CH_2), 1.50–1.02 (m, 4 H, 2 CH_2), 0.87 (t, J = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.1, 141.0, 128.1, 127.5, 125.6, 117.2, 79.8, 39.1, 25.8, 23.0, 14.0 ppm. IR (neat): $\tilde{\nu}$ = 3556, 3473, 3088, 3060, 3028, 2957, 2931, 2871, 1621, 1494, 1467, 1447, 1378, 1323, 1258, 1127, 1090, 1051, 1033 cm^{-1}. MS (70 eV, EI): m/z (%) = 270 (4.14) $[M(^{81}Br)]^+$, 268 (4.25) $[M(^{79}Br)]^+$, 211 (100). $C_{13}H_{17}BrO$ (268.05): calcd. C 58.01, H 6.37; found C 58.09, H 6.64.

(*E*)-3i: Liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.24 (m, 3 H, ArH), 7.18–7.11 (m, 2 H, ArH), 4.12 (d, J = 6.0 Hz, 2 H, CH_2O), 2.65–2.50 (m, 2 H, =CCH_2), 2.13 (br. s, 1 H, OH), 1.40–1.20 (m, 4 H, 2 CH_2), 0.86 (t, J = 6.9 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.4, 139.6, 128.4, 128.0, 127.5, 124.8, 65.6, 38.7, 28.9, 22.4, 13.8 ppm. IR (neat): $\tilde{\nu}$ = 3403, 3058, 3024, 2956, 2937, 2865, 1626, 1490, 1451, 1381, 1228, 1128, 1069, 1009 cm^{-1}. MS (70 eV, EI): m/z (%) = 270 (19.21) $[M(^{81}Br)]^+$, 268 (20.41) $[M(^{79}Br)]^+$, 189 (26.98) [M – Br]$^+$, 171 (18.26) [M – Br – H_2O]$^+$, 129 (100). HRMS: calcd. for $C_{13}H_{17}{}^{79}BrO$ $[M]^+$ 268.0463; found 268.0458.

2-Bromo-3-phenyl-1-nonen-3-ol (2j) and (*E*)-2-Bromo-3-phenyl-2-nonen-1-ol [(*E*)-3j]: The reaction of nona-1,2-dien-3-ylbenzene (**1j**; 399.0 mg, 2.0 mmol) and NBS (358.2 mg, 2.0 mmol) in 1,4-dioxane (7.0 mL) and H_2O (7.0 mL) at room temp. for 20 h afforded **2j** (376.1 mg, 64%) and (*E*)-**3j** (60.1 mg, 10%) (petroleum ether/ethyl acetate, 40:1 → 30:1 → 20:1). The ratio of **2j**/(*E*)-**3j** was 87:13 as determined by ^1H NMR spectroscopy using CH_2Br_2 as the internal standard.

2j: Liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.44–7.34 (m, 2 H, ArH), 7.33–7.18 (m, 3 H, ArH), 5.97 (d, J = 2.7 Hz, 1 H, =CH), 5.64 (d, J = 2.7 Hz, 1 H, =CH), 2.35 (s, 1 H, OH), 2.16–2.02 (m, 1 H, one proton in CH_2CO), 2.00–1.86 (m, 1 H, one proton in CH_2CO), 1.45–1.28 (m, 1 H, one proton in CH_2), 1.26–0.96 (m, 7 H, one proton in CH_2 and 3 CH_2), 0.78 (t, J = 6.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.0, 140.9, 128.1, 127.4, 125.6, 117.1, 79.7, 39.3, 31.6, 29.5, 23.6, 22.5, 14.0 ppm. IR (neat): $\tilde{\nu}$ = 3560, 3470, 3087, 3060, 3028, 2955, 2928, 2856, 1621, 1494, 1447, 1377, 1328, 1261, 1127, 1094, 1062, 1032 cm^{-1}. MS (70 eV, EI): m/z (%) = 298 (3.30) $[M(^{81}Br)]^+$, 296 (3.29) $[M(^{79}Br)]^+$, 211

(100). HRMS: calcd. for $C_{15}H_{21}{}^{79}BrO$ $[M]^+$ 296.0776; found 296.0774.

(*E*)-3j: Liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.26 (m, 3 H, ArH), 7.18–7.11 (m, 2 H, ArH), 4.13 (d, J = 6.3 Hz, 2 H, CH_2O), 2.59 (t, J = 7.4 Hz, 2 H, $=CCH_2$), 2.10–1.96 (m, 1 H, OH), 1.40–1.19 (m, 8 H, 4 CH_2), 0.85 (t, J = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.4, 139.6, 128.4, 128.0, 127.6, 124.7, 65.6, 39.0, 31.5, 28.9, 26.7, 22.5, 14.0 ppm. IR (neat): $\tilde{\nu}$ = 3373, 2955, 2926, 2857, 1628, 1597, 1492, 1462, 1442, 1378, 1230, 1206, 1073, 1009 cm^{-1}. MS (70 eV, EI): m/z (%) = 298 (8.67) $[M(^{81}Br)]^+$, 296 (8.86) $[M(^{79}Br)]^+$, 129 (100). HRMS: calcd. for $C_{15}H_{21}{}^{79}BrO$ $[M]^+$ 296.0776; found 296.0775.

2-Bromo-3-phenyl-1,5-hexadien-3-ol (2k) and (*E*)-2-Bromo-3-phenyl-2,5-hexadien-1-ol [(*E*)-3k]: The reaction of hexa-1,2,5-trien-3-ylbenzene (**1k**; 15.1 mg, 2.0 mmol) and NBS (357.5 mg, 2.0 mmol) in 1,4-dioxane (6.8 mL) and H_2O (6.8 mL) at room temp. for 12 h afforded **2k** (306.5 mg, 60%) and (*E*)-**3k** (36.4 mg, 7%) (petroleum ether/ethyl acetate, 20:1 → 10:1). The ratio of **2k**/(*E*)-**3k** was 88:12 as determined by ^1H NMR spectroscopy using CH_2Br_2 as the internal standard.

2k: Liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.54–7.44 (m, 2 H, ArH), 7.42–7.22 (m, 3 H, ArH), 6.07 (d, J = 2.4 Hz, 1 H, one proton in $=CH_2$), 5.83–5.64 (m, 2 H, one proton in $=CH_2$ and =CH), 5.21 (d, J = 4.2 Hz, 1 H, one proton in $=CH_2$), 5.16 (s, 1 H, one proton in $=CH_2$), 3.08 (dd, J = 14.1 and 6.6 Hz, 1 H, one proton in CH_2), 2.79 (dd, J = 13.8 and 7.5 Hz, 1 H, one proton in CH_2), 2.63 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.4, 139.4, 132.6, 128.2, 127.7, 125.8, 120.2, 117.7, 78.5, 43.7 ppm. IR (neat): $\tilde{\nu}$ = 3545, 3076, 3028, 2979, 1640, 1620, 1494, 1447, 1345, 1176, 1128, 1091, 1061 cm^{-1}. MS (70 eV, EI): m/z (%) = 254 (0.22) $[M(^{81}Br)]^+$, 252 (0.22) $[M(^{79}Br)]^+$, 211 (100). $C_{12}H_{13}BrO$ (252.01): calcd. C 56.94, H 5.18; found C 56.80, H 5.28.

(*E*)-3k: Liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.27 (m, 3 H, ArH), 7.20–7.13 (m, 2 H, ArH), 5.80–5.64 (m, 1 H, =CH), 5.12–5.49 (m, 2 H, $=CH_2$), 4.18 (d, J = 5.7 Hz, 2 H, CH_2O), 3.36 (dt, J = 6.6 and 1.5 Hz, 2 H, CH_2), 1.99 (t, J = 6.5 Hz, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.6, 139.3, 132.8, 128.4, 128.1, 127.7, 126.0, 117.0, 65.6, 43.4 ppm. IR (neat): $\tilde{\nu}$ = 3385, 3079, 3059, 2921, 2872, 1638, 1600, 1491, 1442, 1432, 1412, 1227, 1072, 1000 cm^{-1}. MS (70 eV, EI): m/z (%) = 254 (5.44) $[M(^{81}Br)]^+$, 252 (5.33) $[M(^{79}Br)]^+$, 155 (100). HRMS: calcd. for $C_{12}H_{13}{}^{79}BrO$ $[M]^+$ 252.0150; found 252.0148.

2-Bromo-1,1-diphenyl-2-propen-1-ol (2l) and 2-Bromo-3,3-diphenyl-2-propen-1-ol (3l): The reaction of 1,1-diphenylpropa-1,2-diene (**1l**; 192.4 mg, 1.0 mmol) and NBS (178.3 mg, 1.0 mmol) in 1,4-dioxane (3.4 mL) and H_2O (3.4 mL) at room temp. for 13 h afforded **2l** (105.9 mg, 37%) and **3l** (56.6 mg, 20%) (petroleum ether/ethyl acetate, 400:1 → 100:1 → 20:1).

2l: Liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.26 (m, 10 H, ArH), 5.81 (d, J = 2.1 Hz, 1 H, =CH), 5.33 (d, J = 2.4 Hz, 1 H, =CH), 3.18 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.5, 140.6, 128.1, 127.9, 127.6, 122.1, 83.1 ppm. IR (neat): $\tilde{\nu}$ = 3546, 3060, 3027, 1620, 1598, 1492, 1447, 1368, 1336, 1163, 1126, 1038, 1002 cm^{-1}. MS (70 eV, EI): m/z (%) = 290 (5.35) $[M(^{81}Br)]^+$, 288 (5.33) $[M(^{79}Br)]^+$, 183 (100). $C_{15}H_{13}BrO$ (288.01): calcd. C 62.30, H 4.53; found C 62.31, H 4.43.

3l:[15] Liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.48–7.05 (m, 10 H, ArH), 4.40 (s, 2 H, CH_2O), 2.36 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.7, 142.1, 139.7, 129.0, 128.4, 128.1, 127.9, 127.7, 125.6, 65.9 ppm. IR (neat): $\tilde{\nu}$ = 3386, 3056, 3026, 2926, 2870, 1597, 1576, 1493, 1443, 1381, 1290, 1209, 1173, 1086, 1032, 1001 cm^{-1}. MS (70 eV, EI): m/z (%) = 290 (21.41) $[M(^{81}Br)]^+$, 288 (21.92) $[M(^{79}Br)]^+$, 209 (100).

5-(1-Bromovinyl)nonen-5-ol (2m) and 2-Bromo-3-*n*-butyl-2-hepten-1-ol (3m): The reaction of 3-butylhepta-1,2-diene (**1m**; 90.9 mg, 0.6 mmol) and NBS (106.9 mg, 0.6 mmol) in 1,4-dioxane (2.0 mL) and H_2O (2.0 mL) at room temp. for 25 h afforded **2m** (60.0 mg, 40%) and **3m** (33.2 mg, 22%) (petroleum ether/ethyl acetate, 30:1).

2m: Liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.90 (d, J = 1.8 Hz, 1 H, =CH), 5.58 (d, J = 2.1 Hz, 1 H, =CH), 1.86–1.71 (m, 3 H, OH and CH_2), 1.65–1.48 (m, 2 H, CH_2), 1.40–1.18 (m, 8 H, 4 CH_2), 0.90 (t, J = 6.9 Hz, 6 H, 2 CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.9, 116.9, 78.9, 38.7, 25.2, 22.9, 14.0 ppm. IR (neat): $\tilde{\nu}$ = 3482, 2957, 2931, 2872, 1622, 1467, 1379, 1344, 1290, 1248, 1149, 1089, 1041 cm^{-1}. MS (70 eV, EI): m/z (%) = 250 (0.31) $[M(^{81}Br)]^+$, 248 (0.28) $[M(^{79}Br)]^+$, 191 (100). $C_{11}H_{21}BrO$ (246.06): calcd. C 53.02, H 8.49; found C 53.11, H 8.52.

3m: Liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.33 (d, J = 6.6 Hz, 2 H, CH_2O), 2.30–2.12 (m, 4 H, 2 CH_2), 1.95 (t, J = 6.3 Hz, 1 H, OH), 1.50–1.20 (m, 8 H, 4 CH_2), 1.00–0.81 (m, 6 H, 2 CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.1, 122.2, 64.4, 36.6, 32.4, 31.3, 29.5, 22.8, 22.6, 14.0, 13.9 ppm. IR (neat): $\tilde{\nu}$ = 3355, 2957, 2930, 2861, 1638, 1466, 1379, 1233, 1067, 1004 cm^{-1}. MS (70 eV, EI): m/z (%) = 250 (9.93) $[M(^{81}Br)]^+$, 248 (10.19) $[M(^{79}Br)]^+$, 109 (100). HRMS: calcd. for $C_{11}H_{21}{}^{81}BrO$ $[M]^+$ 250.0755; found 250.0758.

2-Bromo-1,1-diphenyl-2-buten-1-ol (2n) and 3-Bromo-4,4-diphenyl-3-buten-2-ol (3n): The reaction of 1,1-diphenylbuta-1,2-diene (**1n**; 123.3 mg, 0.6 mmol) and NBS (106.7 mg, 0.6 mmol) in 1,4-dioxane (2.0 mL) and H_2O (2.0 mL) at room temp. for 26 h afforded **2n** (37.2 mg, 21%) and **3n** (81.5 mg, 45%) (petroleum ether/ethyl acetate, 40:1 → 10:1).

2n: Liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.20 (m, 10 H, ArH), 6.30 [q, J = 7.7, 0.4 H, =CH(*E*)], 5.43 [q, J = 6.6 Hz, 0.6 H, =CH(*Z*)], 3.26 [s, 0.4 H, OH(*E*)], 3.20 [s, 0.6 H, OH(*Z*)], 1.72 [d, J = 6.9 Hz, 1.8 H, CH_3(*Z*)], 0.82 [d, J = 7.8 Hz, 1.2 H, CH_3(*E*)] ppm. IR (neat): $\tilde{\nu}$ = 3543, 3059, 3026, 3026, 2920, 2855, 1653, 1598, 1490, 1447, 1329, 1281, 1162, 1113, 1063, 1033, 1010 cm^{-1}. MS (70 eV, EI): m/z (%) = 304 (3.46) $[M(^{81}Br)]^+$, 302 (3.53) $[M(^{79}Br)]^+$, 183 (100). HRMS: calcd. for $C_{16}H_{15}{}^{79}BrO$ $[M]^+$ 302.0306; found 302.0310.

3n: Liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.31–7.01 (m, 10 H, ArH), 4.47 (q, J = 6.2 Hz, 1 H, CHO), 2.07 (br. s, 1 H, OH), 1.31 (d, J = 6.3 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.5, 142.1, 140.2, 132.3, 128.9, 128.6, 128.5, 128.0, 127.7, 127.4, 67.9, 23.2 ppm. IR (neat): $\tilde{\nu}$ = 3396, 3055, 3025, 2978, 2928, 1597, 1576, 1491, 1443, 1371, 1285, 1174, 1133, 1074, 1030 cm^{-1}. MS (70 eV, EI): m/z (%) = 304 (5.06) $[M(^{81}Br)]^+$, 302 (5.22) $[M(^{79}Br)]^+$, 223 (100). HRMS: calcd. for $C_{16}H_{15}{}^{79}BrO$ $[M]^+$ 302.0306; found 302.0305.

General Procedure for the Elimination of HBr from 2 To Afford Propargylic Alcohol 4[9]

1-Phenyl-3-butyn-2-ol (4a): TBAF (1.2 mL, 1 M in THF, 1.2 mmol) was slowly added to a solution of **2a** (91.0 mg, 0.4 mmol) and DMF (4 mL). After continuous stirring at room temp. for 12 h, the reaction was complete, as monitored by TLC. Then the mixture was diluted with diethyl ether (20 mL), quenched by the addition of saturated aqueous NH_4Cl (5 mL), washed with water, and dried with anhydrous Na_2SO_4. Concentration and column chromatography on silica gel (petroleum ether/ethyl acetate, 10:1) afforded **4a**[16] (33.9 mg, 58%) as a liquid. ^1H NMR (300 MHz, $CDCl_3$): δ

= 7.40–7.20 (m, 5 H, ArH), 4.56 (td, J = 6.5 and 2.1 Hz, 1 H, CHO), 3.08–2.93 (m, 2 H, $ArCH_2$), 2.47 (d, J = 2.4 Hz, 1 H, C≡CH), 2.19 (br. s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.2, 129.7, 128.4, 126.9, 84.1, 73.8, 62.9, 43.7 ppm. IR (neat): $\tilde{\nu}$ = 3539, 3374, 3288, 3086, 3063, 3030, 2950, 2926, 2860, 2117, 1602, 1496, 1454, 1435, 1390, 1335, 1289, 1079, 1032, 1004 cm^{-1}. MS (70 eV, EI): m/z (%) = 146 (1.65) $[M]^+$, 128 (16.15) $[M - H_2O]^+$, 91(100).

1,1-Diphenyl-2-butyn-1-ol (4n) and (*Z*)-2-Bromo-1,1-diphenyl-2-buten-1-ol [(*Z*)-2n]: The reaction of **2n** (391.7 mg, 1.29 mmol) and TBAF (3.9 mL, 1 M in THF, 3.9 mmol) in DMF (13.0 mL) at room temp. for 24 h afforded (*Z*)-**2n** (198.8 mg, 51%) and **4n** (17.0 mg, 6%) (petroleum ether/ethyl acetate, 100:1 → 50:1 → 30:1).

4n:[17] Liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.70–7.50 (m, 4 H, ArH), 7.40–7.20 (m, 6 H, ArH), 2.52 (br. s, 1 H, OH), 1.97 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.4, 128.1, 127.5, 126.0, 83.7, 82.1, 74.4, 3.9 ppm. IR (neat): $\tilde{\nu}$ = 3404, 3084, 3060, 3027, 2972, 2920, 2852, 2233, 1599, 1490, 1449, 1382, 1350, 1280, 1180, 1157, 1142, 1105, 1077, 1032, 1011 cm^{-1}. MS (70 eV, EI): m/z (%) = 222 (40.04) $[M]^+$, 207 (100) $[M - CH_3]^+$.

(*Z*)-2n: Solid; m.p. 79.5–80.6 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.18 (m, 10 H, ArH), 5.44 (q, J = 6.5 Hz, 1 H, =CH), 3.20 (s, 1 H, OH), 1.72 (d, J = 6.3 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.5, 136.4, 129.1, 128.0, 127.8, 127.7, 83.3, 17.3 ppm. IR (KBr): $\tilde{\nu}$ = 3547, 3059, 3028, 2918, 2854, 1651, 1598, 1491, 1447, 1374, 1331, 1281, 1201, 1160, 1117, 1063, 1033, 1010 cm^{-1}. MS (70 eV, EI): m/z (%) = 304 (3.69) $[M(^{81}Br)]^+$, 302 (3.80) $[M(^{79}Br)]^+$, 183 (100). $C_{16}H_{15}BrO$ (302.03): calcd. C 63.38, H 4.99; found C 63.58, H 5.05.

Procedure for the Sonogashira Coupling of 2a. Synthesis of 3-Methylene-1,5-diphenyl-4-butyn-2-ol (5a): $[PdCl_2(PPh_3)_2]$ (11.0 mg, 0.015 mmol), CuI (3.1 mg, 0.015 mmol), **2a** (68.1 mg, 0.30 mmol), benzene (2 mL), ethynylbenzene (62.5 mg, 0.6 mmol), and nBuNH$_2$ (110.2 mg, 1.5 mmol) were sequentially added to a Schlenk tube at room temperature. After stirring for 14 h, the reaction was complete, as monitored by TLC. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate, 10:1) to give **5a** (68.1 mg, 92%) as a liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.53–7.42 (m, 2 H, ArH), 7.41–7.18 (m, 8 H, ArH), 5.53 (s, 1 H, =CH), 5.48 (s, 1 H, =CH), 4.49–4.36 (m, 1 H, CHO), 3.16 (dd, J = 13.5 and 5.1 Hz, 1 H, one proton in $ArCH_2$), 2.95 (dd, J = 13.7 and 7.7 Hz, 1 H, one proton in $ArCH_2$), 2.00 (br. s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.5, 133.6, 131.6, 129.5, 128.44, 128.39, 128.3, 126.6, 122.8, 121.4, 91.8, 86.7, 75.2, 42.6 ppm. IR (neat): $\tilde{\nu}$ = 3563, 3426, 3083, 3061, 3028, 2922, 1605, 1490, 1454, 1442, 1384, 1313, 1180, 1079, 1030 cm^{-1}. MS (70 eV, EI): m/z (%) = 248 (5.36) $[M]^+$, 128 (100). HRMS: calcd. for $C_{18}H_{16}O$ $[M]^+$ 248.1201; found 248.1201.

Procedure for the Suzuki Coupling Reaction

1,3-Diphenyl-3-buten-2-ol (6a): K_3PO_4 (222.6 mg, 1.05 mmol) was added to a rubber-capped Schlenk vessel. This vessel was flame-dried under vacuum and backfilled with nitrogen three times. Then $Pd(OAc)_2$ (2.0 mg, 0.009 mmol), phenylboronic acid (73.0 mg, 0.6 mmol), dioxane (1 mL), **2a** (68.6 mg, 0.3 mmol), dioxane (1 mL), PPh_3 (4.8 mg, 0.018 mmol), and water (16.5 μL, 0.9 mmol) were added sequentially to the Schlenk vessel at room temperature. The resulting mixture was heated at 110 °C with a preheated oil bath. After 48 h, the reaction was complete, as monitored by TLC. The reaction mixture was then cooled to room temperature and filtered through a short column of silica gel (CH_2Cl_2). Concentration and purification by chromatography (petroleum ether/ethyl acetate, 30:1) on silica gel afforded **6a** (47.2 mg, 70%) as a liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.48–7.15 (m, 10 H, ArH), 5.37 (d, J = 1.2 Hz, 1 H, =CH), 5.34 (s, 1 H, =CH), 4.90–4.80 (m, 1 H, CHO), 2.95 (dd, J = 14.0 and 3.8 Hz, 1 H, one proton in $ArCH_2$), 2.68 (dd, J = 14.0 and 8.6 Hz, 1 H, one proton in $ArCH_2$), 1.93 (br. s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.9, 139.8, 138.1, 129.4, 128.43, 128.40, 127.7, 126.8, 126.5, 113.0, 74.3, 42.7 ppm. IR (neat): $\tilde{\nu}$ = 3423, 3063, 3028, 2907, 2859, 1630, 1597, 1576, 1495, 1454, 1263, 1028 cm^{-1}. MS (70 eV, EI): m/z (%) = 224 (29.25) $[M]^+$, 105 (100). HRMS: calcd. for $C_{16}H_{16}O$ $[M]^+$ 224.1201; found 224.1192.

3-Styryl-1-phenyl-3-buten-2-ol (7a): The reaction of K_3PO_4 (222.6 mg, 1.05 mmol), $Pd(OAc)_2$ (2.1 mg, 0.009 mmol), styrylboronic acid (89.0 mg, 0.6 mmol), **2a** (68.3 mg, 0.3 mmol), 1,4-dioxane (2 mL), PPh_3 (4.7 mg, 0.018 mmol), and H_2O (16.5 μL, 0.9 mmol) at 110 °C for 6 h afforded **7a** (42.0 mg, 56%) (petroleum ether/ethyl acetate, 20:1) as a liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.48–7.38 (m, 2 H, ArH), 7.37–7.18 (m, 8 H, ArH), 6.82 (d, J = 16.5 Hz, 1 H, =CH), 6.75 (d, J = 16.5 Hz, 1 H, =CH), 5.29 (s, 2 H, $=CH_2$), 4.72 (d, J = 7.5 Hz, 1 H, CHO), 3.09 (dd, J = 14.0 and 3.8 Hz, 1 H, one proton in $ArCH_2$), 2.84 (dd, J = 13.7 and 8.6 Hz, 1 H, one proton in $ArCH_2$), 1.87 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.8, 138.3, 137.1, 129.4, 128.9, 128.6, 128.5, 128.0, 127.7, 126.6, 126.4, 114.9, 72.7, 43.2 ppm. IR (neat): $\tilde{\nu}$ = 3562, 3425, 3027, 2922, 2852, 1602, 1494, 1451, 1078 cm^{-1}. MS (70 eV, EI): m/z (%) = 250 (1.77) $[M]^+$, 91 (100). HRMS: calcd. for $C_{18}H_{18}O$ $[M]^+$ 250.1358; found 250.1357.

Supporting Information (see footnote on the first page of this article): ^1H and ^{13}C NMR spectra of all compounds.

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