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Stereoselective Synthesis of (2*Z*,4*E*)-2,4-Pentadien-1-ols via Sequential 1,4-Elimination Reaction and [1,2]-Wittig Rearrangement Starting from (*E*)-4-Alkoxy-2-butenyl Benzoates

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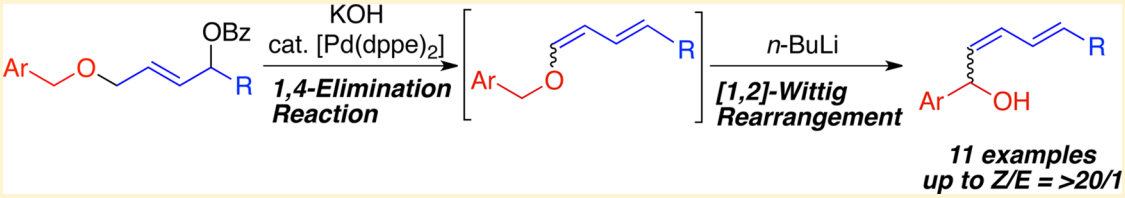
Supporting Information



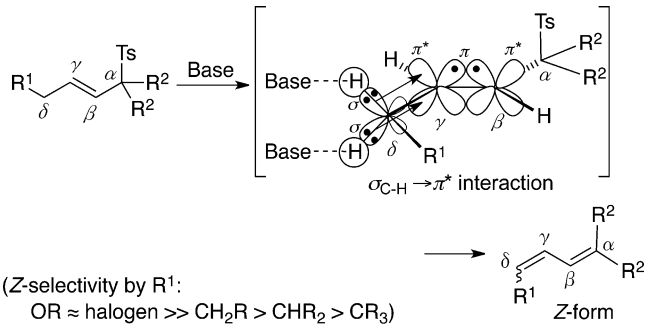
ABSTRACT: The sequential 1,4-elimination reaction of (*E*)-4-alkoxy-2-butenyl benzoates and [1,2]-Wittig rearrangement gave (2*Z*,4*E*)-2,4-pentadien-1-ols stereoselectively. *Z*-Selective formation of intermediary vinyl ethers, whose stereochemistry was well elucidated by the "*syn*-effect", was achieved by treatment of the 2-butenyl benzoates with KOH in the presence of Pd catalyst. The subsequent [1,2]-Wittg rearrangement by use of *n*-BuLi proceeded with retention of the stereochemistry of the intermediary vinyl ethers.

INTRODUCTION

Stereoselective synthesis of carbon−carbon double bonds as ubiquitous and versatile two-carbon units is among the most important and challenging tasks in organic chemistry.[1] Consequently, a large number of synthetic methodologies have been reported, e.g., (1) Wittig reaction, which utilizes the characteristics of phosphorus;[2] (2) Peterson reaction, which utilizes silicon;[3] (3) Julia olefination, which utilizes sulfones;[4,5] (4) reduction or carbometalation of alkynes, which takes advantage of organometallic reagents;[6] (5) [3,3]-sigmatoropic reactions such as Claisen rearrangement;[7] and (6) olefin metathesis, which is realized by the use of Grubbs catalysts.[8] However, these reactions depend on new C−C bond formation or reductive olefin formation from alkynes. On the other hand, while the elimination reaction is also a powerful method for the preparation of olefins, the stereochemistry of the products generally depends on the reaction pathway, i.e., E2 *anti*-elimination, *syn*-elimination, or E1 elimination. Several methods have been reported for stereoselective synthesis of olefins using simple elimination reactions.[9]

In our laboratory, stereoselective formation of sterically unfavorable (*Z*)-olefins was investigated with various types of elimination and isomerization reactions by treatment with a base.[10] We proposed that *Z*-selectivity was achieved by the "*syn*-effect", namely, a stereoelectronic effect owing to $\sigma_{C-H} \rightarrow \pi^*_{C=C}$ interaction as depicted in Scheme 1, in which the transition state of the 1,4-elimination of an allylic sulfone is depicted.[10c] Furthermore, it was found that *Z*-selectivity based on the "*syn*-effect" was enhanced when the δ-substituent (R^1 in Scheme 1) was an electron-withdrawing alkoxy or halogen group.

Scheme 1. Concept of the "*Syn*-Effect": $\sigma \rightarrow \pi^*$ Interaction in the Elimination Reaction of Allylic Sulfones



This methodology could then be applied to a stereoselective synthesis of (*Z*)-olefins in combination with C−C bond formation. We have reported a sequential 1,4-elimination reaction of δ-benzyloxy-substituted allylic sulfones followed by [1,2]-Wittig rearrangement[11] to give (*Z*)-dienyl alcohols (2,4-pentadien-1-ols), which are useful synthetic intermediates due to the presence of both an allylic alcohol moiety and a diene moiety (Scheme 2a).[12] However, the reaction was limited to only α,α-disubstituted allylic sulfones. When an α-monosubstituted allylic sulfone was subjected to the reaction, the elimination of the benzyloxy group proceeded preferentially via deprotonation of the more acidic α-proton (Scheme 2b).[13] In this situation, the stereocontrolled preparation of (2*Z*)-5-

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Scheme 2. Z-Selective Synthesis of Dienyl Alcohols

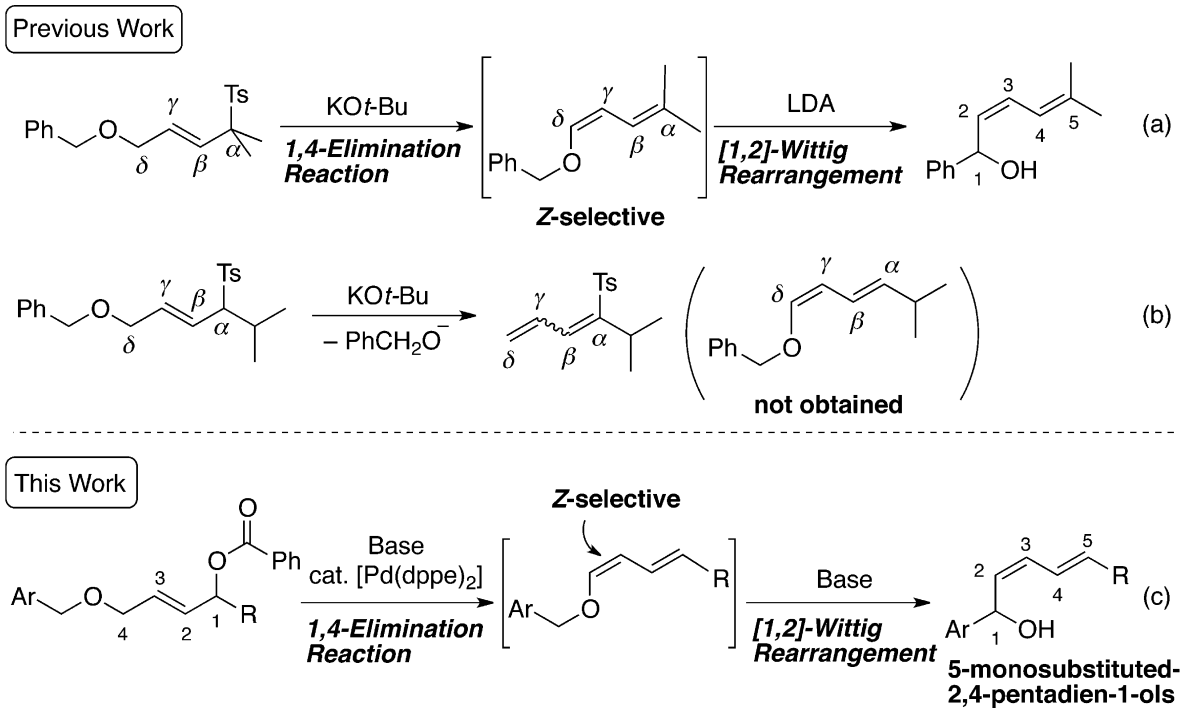
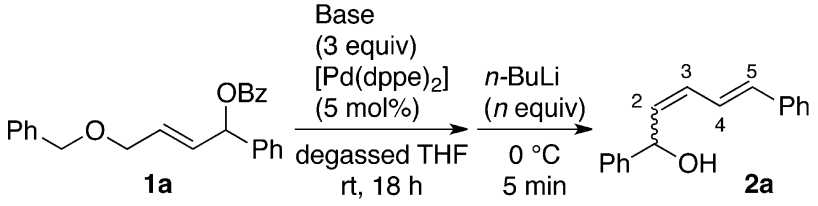
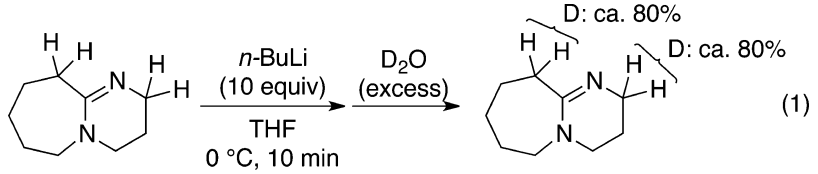


Table 1. Optimization of Reaction Conditions



entry	base	*n*	yield (%)	Z/E^a
1	DBU	12	84	10/1
2	NaO*t*-Bu	7	<82	10/1
3	NaO*t*-Bu[b]		0[c]	
4	KO*t*-Bu[b]		0[c]	
5[d]	NaOH	6	73	10/1
6[d]	KOH	6	68	>20/1

[a]The ratios were determined by 400 MHz ^{1}H NMR spectra. Stereochemistries at C4═C5 were *E*. [b]Sublimed NaO*t*-Bu or KO*t*-Bu was used. [c]A complex mixture of products was obtained. [d]MS4A were added after the elimination reaction.



monosubstituted-2,4-pentadien-1-ols still remained to be solved. Previously, we found that (1*Z*,3*E*)-1,3-dienes were produced stereoselectively in the Pd-catalyzed elimination reaction of acyclic (*E*)-allylic acetates with a base.[10g] We anticipated this protocol would be applicable to the sequential 1,4-elimination reaction and [1,2]-Wittig rearrangement. Herein we describe the sequential reaction of stereoselective 1,4-elimination of (*E*)-4-alkoxy-2-butenyl benzoates via the π-allylic palladium complex and subsequent [1,2]-Wittig rearrangement to afford (2*Z*,4*E*)-5-monosubstituted-2,4-pentadien-1-ols (Scheme 2c).

RESULTS AND DISCUSSION

We chose (*E*)-4-benzyloxy-1-phenyl-2-butenyl benzoate (**1a**) as a model substrate for the optimization of the reaction conditions.[14,15] Under our previously reported conditions for allylic acetates using DBU, the Pd-catalyzed [1,4]-elimination reaction of **1a** did not proceed reproducibly. Deactivation of the Pd(0) complex by molecular oxygen contamination was

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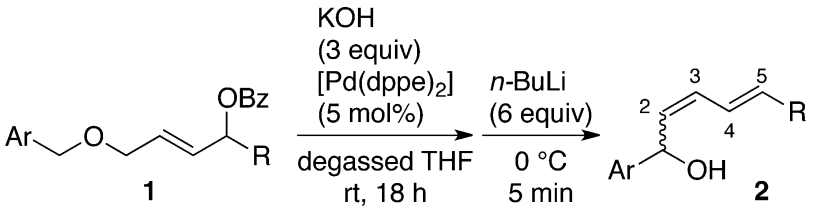
Table 2. Scope of Substrates



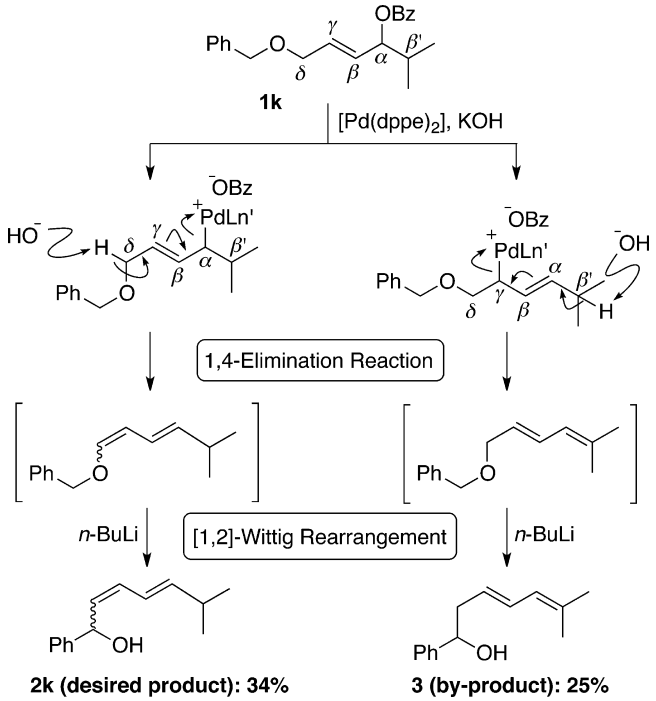
entry	Ar	R		yield (%)	Z/E^a
1	Ph	Ph	**a**	68	>20/1
2	2-MeC_6H_4	Ph	**b**	65	18/1
3	3-MeC_6H_4	Ph	**c**	58	>20/1
4	4-MeC_6H_4	Ph	**d**	63	>20/1
5	4-$MeOC_6H_4$	Ph	**e**	71	19/1
6	4-ClC_6H_4	Ph	**f**	63	15/1
7	2-Naph	Ph	**g**	68	>20/1
8	Ph	4-MeC_6H_4	**h**	72	>20/1
9	Ph	2-Naph	**i**	67	17/1
10	Ph	*t*-Bu	**j**	53	>20/1
11	Ph	*i*-Pr	**k**	34	>20/1

[a]The ratios were determined by 400 MHz ^{1}H NMR spectra. Stereochemistries at C4═C5 were *E*.

suspected as the cause. In order to prevent this deactivation, degassed THF was used as the solvent, and the 1,4-elimination reaction was found to proceed reproducibly. After the 1,4-elimination by treatment with DBU,[16] an excess amount of *n*-BuLi was added to the reaction mixture to give the desired (2*Z*,4*E*)-dienyl alcohol **2a** in good yield with high *Z*-selectivity at the C2−C3 double bond (Table 1, entry 1).[17] However, a large excess (12 equiv) of *n*-BuLi was required to complete the [1,2]-Wittig rearrangement.[17] The deprotonation of DBU with excess amounts of *n*-BuLi was confirmed by deuterium-labeling experiment (eq 1). After the search for a base that did not react with *n*-BuLi, NaO*t*-Bu could reduce the amount of *n*-BuLi to 7 equiv for the [1,2]-Wittig rearrangement (entry 2). However, the desired product **2a** was not obtained with NaO*t*-Bu or KO*t*-Bu purified by sublimation (entries 3 and 4). We supposed the actual base might be NaOH or KOH, which was generated by partial hydrolysis of NaO*t*-Bu or KO*t*-Bu. Therefore, we employed NaOH and KOH as bases for the initial elimination. To our delight, elimination proceeded[18] reproducibly, and further treatment with *n*-BuLi (6 equiv) gave **2a** in good yield with excellent *Z*-selectivity at the C2−C3 double bond (entries 5 and 6).

Under the optimized conditions, the sequential 1,4-elimination reaction and [1,2]-Wittig rearrangement of various substrates were performed (Table 2). Benzyl-type ethers **1b**−**1d** with *o*-, *m*-, and *p*-methyl groups produced the corresponding (2*Z*,4*E*)-dienyl alcohols **2b**−**2d** (entries 2−4). When 2-butenyl benzoates **1e** and **1f** bearing electron-donating or electron-withdrawing groups on the aromatic ring were employed, the desired products were also obtained with excellent *Z*-selectivities (entries 5 and 6). 4-(2-Naphthylmethyloxy)butenyl benzoate **1g** was also converted into the corresponding (2*Z*,4*E*)-dienyl alcohol **2g** (entry 7). Next, we examined the generality of the sequential reaction for (*E*)-2-butenyl benzoates bearing various substituents at the α-position of the butenyl group. The desired products **2h**−**2j** were obtained in good yields with excellent *Z*-selectivities from 2-butenyl benzoates **1h**−**1j** bearing an aryl or *t*-Bu substituent on the α-carbon (entries 8−10). However, in the case of a benzoate **1k** with an *i*-Pr group at the α-position of the butenyl group, dienyl alcohol **2k** was obtained in low yield, while excellent *Z*-selectivity was retained. In this case, byproduct **3**, derived from deprotonation of not Hδ but Hβ' followed by [1,2]-Wittig rearrangement, was obtained (Scheme 3).[19]

Scheme 3. Generation of Byproduct 3 in the Reaction of 2-Butenyl Benzoate 1k Bearing an Isopropyl Substituent at the α-Position



In conclusion, we achieved a stereoselective synthesis of (2*Z*,4*E*)-2,4-pentadien-1-ols via sequential 1,4-elimination reaction and [1,2]-Wittig rearrangement starting from (*E*)-4-alkoxy-2-butenyl benzoates. The present method would be applicable in synthetic chemistry, because the stereochemistry can be predicted correctly by universal stereoelectronic

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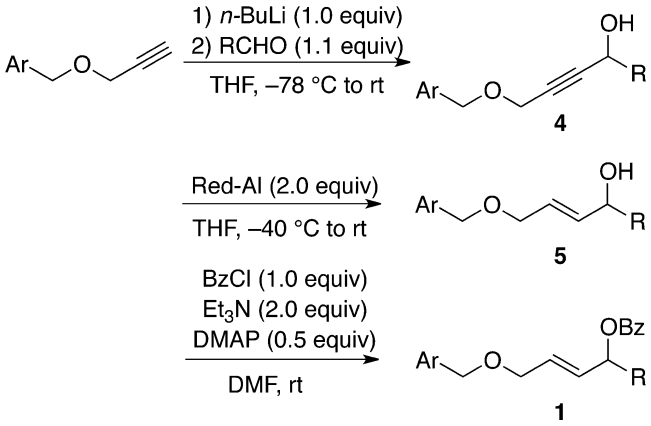
effects.[20] Development of other *Z*-selective reactions based on this strategy is currently underway in our laboratory.

EXPERIMENTAL SECTION

General Method. ^{1}H NMR spectra were recorded on a 400 MHz NMR spectrometer. Chemical shifts δ are reported in ppm using TMS as an internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (J), and integration. ^{13}C NMR spectra were recorded on a 100 MHz NMR spectrometer. The chemical shifts are reported relative to $CDCl_3$ (δ = 77.0 ppm). The wavenumbers of maximum absorption peaks in IR spectra are presented in cm^{-1}. HRMS (EI positive, ESI-TOF) spectra were measured with quadrupole and TOF mass spectrometers. All of the melting points were measured with a micro melting point apparatus. THF was freshly distilled from sodium diphenylketyl. THF used for 1,4-elimination was degassed by three freeze−pump−thaw cycles prior to use. DMF was distilled and stored over drying agents.

(*E*)-4-Alkoxy-2-butenyl benzoates **1** were prepared from the corresponding propargyl ethers and aldehydes according to the following scheme:



Representative Procedure for Preparation of 4-Alkoxy-2-butyn-1-ol 4a. To a solution of benzyl propargyl ether (4.00 g, 27.4 mmol) in THF (45 mL) was added *n*-BuLi (16.9 mL of 1.62 M solution in hexane, 27.4 mmol) dropwise at −78 °C. After 20 min of stirring, benzaldehyde (3.19 g, 30.1 mmol) was added, and the resulting solution was stirred for 30 min at −78 °C, warmed to room temperature, and stirred for 3 h.[21] The reaction mixture was quenched with a satd aq solution of NH_4Cl. After the solvent was evaporated, the aqueous layer was separated and extracted with Et_2O. The combined organic extracts were washed with H_2O and brine and dried over Na_2SO_4. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 5/1) to give **4a** (6.01 g, 87%) as an oil.

In a similar manner, 4-alkoxy-2-butyn-1-ols **4b**−**4k** were prepared from the corresponding propargyl ethers.

4-(Benzyloxy)-1-phenyl-2-butyn-1-ol (4a).[21] ^{1}H NMR (400 MHz, $CDCl_3$): 2.25 (d, J = 5.9 Hz, 1H), 4.27 (d, J = 1.8 Hz, 2H), 4.61 (s, 2H), 5.53 (d, J = 5.9 Hz, 1H), 7.28−7.41 (m, 8H), 7.55 (d, J = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 57.0, 63.9, 71.3, 81.8, 86.3, 126.3, 127.6, 127.8, 128.0, 128.1, 128.2, 136.8, 140.2. IR (neat): 3390, 3062, 3030, 2857, 2227, 1644, 1494, 1454, 1387, 1354, 1313, 1264, 1193, 1120, 1071, 1026, 918, 738, 698 cm^{-1}. HRMS (EI): calcd for $C_{17}H_{16}O_2$ [M$^+$] 252.1150, found 252.1155.

4-((2-Methylbenzyl)oxy)-1-phenyl-2-butyn-1-ol (4b). Compound **4b** (3.63 g, 91% from 15.0 mmol of 2-methylbenzyl propargyl ether) was obtained as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): 2.25 (d, J = 6.0 Hz, 1H), 2.34 (s, 3H), 4.28 (d, J = 1.8 Hz, 2H), 4.60 (s, 2H), 5.53 (d, J = 6.0 Hz, 1H), 7.15−7.24 (m, 3H), 7.25−7.43 (m, 4H), 7.54 (d, J = 6.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 18.6, 57.3, 64.2, 69.8, 82.2, 86.4, 125.6, 126.4, 128.0, 128.1, 128.4, 129.0, 130.1, 134.9, 136.9, 140.3. IR (neat): 3391, 3063, 3029, 2864, 2235, 1604, 1493, 1454, 1353, 1262, 1189, 1121, 1072, 945, 918, 843, 809, 745, 699 cm^{-1}. HRMS (EI): calcd for $C_{18}H_{18}O_2$ [M$^+$] 266.1307, found 266.1313.

4-((3-Methylbenzyl)oxy)-1-phenyl-2-butyn-1-ol (4c). Compound **4c** (2.81 g, 86% from 12.3 mmol of 3-methylbenzyl propargyl ether) was obtained as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): 2.21 (d, J = 5.9 Hz, 1H), 2.35 (s, 3H), 4.27 (d, J = 1.8 Hz, 2H), 4.57 (s, 2H), 5.53 (d, J = 5.9 Hz, 1H), 7.11−7.17 (m, 3H), 7.23 (d, J = 7.4 Hz, 1H), 7.32−7.42 (m, 3H), 7.55 (d, J = 6.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 21.1, 57.0, 64.0, 71.3, 82.0, 86.4, 125.0, 126.4, 128.0, 128.1, 128.3, 128.4, 128.6, 136.8, 137.8, 140.0. IR (neat): 3391, 3029, 2857, 2230, 1609, 1492, 1454, 1380, 1353, 1255, 1192, 1157, 1120, 1078, 1003, 918, 785, 742, 698 cm^{-1}. HRMS (EI): calcd for $C_{18}H_{18}O_2$ [M$^+$] 266.1307, found 266.1305.

4-((4-Methylbenzyl)oxy)-1-phenyl-2-butyn-1-ol (4d). Compound **4d** (2.79 g, 92% from 11.4 mmol of 4-methylbenzyl propargyl ether) was obtained as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): 2.23 (d, J = 6.0 Hz, 1H), 2.34 (s, 3H), 4.24 (d, J = 1.8 Hz, 2H), 4.57 (s, 2H), 5.53 (d, J = 6.0 Hz, 1H), 7.15 (d, J = 7.8 Hz, 2H), 7.23 (d, J = 7.8 Hz, 2H), 7.32−7.41 (m, 3H), 7.55 (d, J = 6.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 21.3, 57.3, 64.4, 71.6, 82.5, 86.8, 126.8, 128.4, 128.5, 128.7, 129.3, 134.2, 137.8, 140.7. IR (neat): 3392, 3029, 2857, 2230, 1617, 1515, 1493, 1453, 1382, 1354, 1309, 1262, 1193, 1120, 1077, 1021, 945, 918, 843, 806, 754, 732, 699 cm^{-1}. HRMS (EI): calcd for $C_{18}H_{18}O_2$ [M$^+$] 266.1307, found 266.1306.

4-((4-Methoxybenzyl)oxy)-1-phenyl-2-butyn-1-ol (4e). Compound **4e** (1.36 g, 89% from 5.4 mmol of 4-methoxybenzyl propargyl ether) was obtained as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): 2.21 (br, 1H), 3.80 (s, 3H), 4.23 (d, J = 1.2 Hz, 2H), 4.54 (s, 2H), 5.53 (s, 1H), 6.87 (d, J = 8.7 Hz, 2H), 7.27 (d, J = 8.7 Hz, 2H) 7.32−7.41 (m, 3H), 7.55 (d, J = 6.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 55.3, 57.1, 64.4, 71.3, 82.5, 86.7, 113.9, 126.7, 128.4, 128.7, 129.3, 130.0, 140.7, 159.4. IR (neat): 3401, 3062, 3031, 2837, 2226, 1612, 1585, 1512, 1493, 1455, 1354, 1302, 1249, 1175, 1118, 1074, 1032, 918, 818, 759, 700 cm^{-1}. HRMS (EI): calcd for $C_{18}H_{18}O_3$ [M$^+$] 282.1256, found 282.1253.

4-((4-Chlorobenzyl)oxy)-1-phenyl-2-butyn-1-ol (4f). Compound **4f** (2.67 g, 85% from 11.0 mmol of 4-chlorobenzyl propargyl ether) was obtained as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): 2.18 (br, 1H), 4.27 (d, J = 1.8 Hz, 2H), 4.57 (s, 2H), 5.54 (s, 1H), 7.27−7.42 (m, 7H), 7.54 (d, J = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 57.4, 64.2, 70.7, 82.0, 86.6, 126.4, 128.0, 128.2, 128.4, 129.2, 133.5, 135.5, 140.3. IR (neat): 3378, 3031, 2861, 1598, 1540, 1491, 1455, 1408, 1354, 1262, 1193, 1120, 1086, 1015, 918, 841, 806, 733, 699, 674 cm^{-1}. HRMS (EI): calcd for $C_{17}H_{15}ClO_2$ [M$^+$] 286.0761, found 286.0765.

4-(2-Naphthalenylmethoxy)-1-phenyl-2-butyn-1-ol (4g). Compound **4e** (1.86 g, 73% from 8.4 mmol of 2-naphthalenylmethoxy propargyl ether) was obtained as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): 2.23 (br, 1H), 4.31 (d, J = 1.8 Hz, 2H), 4.78 (s, 2H), 5.54 (s, 1H), 7.33−7.42 (m, 3H), 7.46−7.49 (m, 3H), 7.55−7.57 (m, 2H), 7.80−7.84 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): 57.2, 64.3, 71.6, 82.3, 86.5, 125.8, 125.9, 126.0, 126.5, 126.9, 127.5, 127.8, 128.1, 128.2, 128.5, 132.9, 133.0, 134.5, 140.3. IR (neat): 3381, 3057, 2854, 2230, 1601, 1509, 1492, 1454, 1355, 1271, 1173, 1123, 1078, 1003, 918, 856, 818, 754, 699 cm^{-1}. HRMS (EI): calcd for $C_{21}H_{18}O_2$ [M$^+$] 302.1307, found 302.1305.

4-(Benzyloxy)-1-(4-tolyl)-2-butyn-1-ol (4h). Compound **4h** (2.13 g, 76% from 10.5 mmol of benzyl propargyl ether) was obtained as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): 2.15 (d, J = 6.0 Hz, 1H), 2.36 (s, 3H), 4.27 (d, J = 1.8 Hz, 2H), 4.61 (s, 2H), 5.49 (d, J = 6.0 Hz, 1H), 7.20 (d, J = 7.8 Hz, 2H), 7.29−7.38 (m, 5H), 7.43 (d, J = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 20.9, 57.1, 63.8, 71.3, 81.7, 86.7, 126.3, 127.6, 127.9, 128.2, 128.9, 136.9, 137.5, 137.7. IR (neat): 3396, 3029, 2858, 2235, 1605, 1511, 1496, 1454, 1354, 1264, 1196, 1178, 1114, 1071, 1026, 942, 821, 742, 699 cm^{-1}. HRMS (EI): calcd for $C_{18}H_{18}O_2$ [M$^+$] 266.1307, found 266.1300.

4-(Benzyloxy)-1-(2-naphthalenyl)-2-butyn-1-ol (4i). Compound **4i** (1.44 g, 81% from 5.8 mmol of benzyl propargyl ether) was obtained as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): 2.34 (br, 1H),

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4.30 (d, J = 0.9 Hz, 2H), 4.63 (s, 2H), 5.69 (s, 1H), 7.28−7.35 (m, 5H), 7.47−7.52 (m, 2H), 7.66 (d, J = 8.2 Hz, 1H), 7.82−7.89 (m, 3H), 8.00 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 57.1, 64.2, 71.4, 82.3, 86.4, 124.4, 125.1, 126.0, 127.4, 127.7, 127.9, 128.0, 128.2, 128.3, 132.9, 133.0, 136.9, 137.7. IR (neat): 3375, 3057, 2857, 2225, 1601, 1507, 1495, 1455, 1355, 1269, 1167, 1113, 1071, 1025, 951, 903, 861, 821, 748, 699 cm^{-1}. HRMS (EI): calcd for $C_{21}H_{18}O_2$ [M$^+$] 302.1307, found 302.1306.

6-(Benzyloxy)-2,2-dimethyl-4-hexyn-3-ol (4j).[22] Compound **4j** (1.16 g, 42% from 11.9 mmol of benzyl propargyl ether) was obtained as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): 1.01 (s, 9H), 1.72 (br, 1H), 4.07 (s, 1H), 4.23 (d, J = 1.8 Hz, 2H), 4.60 (s, 2H), 7.26−7.36 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): 25.2, 35.6, 57.2, 71.1, 71.3, 81.2, 86.3, 127.7, 128.0, 128.3, 137.2. IR (neat): 3446, 3030, 2956, 2867, 2215, 1606, 1540, 1478, 1455, 1363, 1321, 1240, 1123, 1072, 1008, 936, 743, 698 cm^{-1}. HRMS (EI): calcd for $C_{15}H_{20}O_2$ [M$^+$] 232.1463, found 232.1464.

6-(Benzyloxy)-2-methyl-4-hexyn-3-ol (4k).[22] Compound **4k** (2.53 g, 94% from 12.3 mmol of benzyl propargyl ether) was obtained as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): 1.01 (d, J = 7.3 Hz, 3H), 1.03 (d, J = 7.3 Hz, 3H), 1.60 (br, 1H), 1.87−1.93 (m, 1H), 4.23 (s, 2H), 4.23−4.25 (m, 1H), 4.60 (s, 2H), 7.28−7.36 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): 17.3, 18.0, 34.2, 57.2, 67.6, 71.3, 81.1, 86.4, 127.7, 128.0, 128.3, 137.1. IR (neat): 3402, 3031, 2962, 2872, 2215, 1620, 1496, 1455, 1384, 1352, 1261, 1207, 1144, 1073, 1027, 936, 743, 699 cm^{-1}. HRMS (EI): calcd for $C_{14}H_{18}O_2$ [M$^+$] 218.1307, found 218.1311.

Representative Procedure for Preparation of (*E*)-4-Alkoxy-2-butenyl Benzoate 1a. To a solution of compound **4a** (2.52 g, 10 mmol) in THF (20 mL) was added Red-Al (5.6 mL of 3.6 M solution in toluene, 20 mmol) dropwise at −40 °C. The reaction mixture was warmed to room temperature, stirred for 3 h, and quenched with a satd aq solution of Na_2SO_4. After insoluble substance was filtered off through a bed of Celite, the solvent was evaporated. The residue was passed through a short silica gel column (hexane/AcOEt = 2/1) to afford the almost pure (*E*)-2-buten-1-ol **5a**[23] (2.53 g). This material was used for the conversion to the corresponding benzoate **1a** without further purification. To a solution of the obtained **5a** (2.53 g) in DMF (40 mL) were added Et_3N (2.02 g, 20 mmol), benzoyl chloride (1.40 g, 10 mmol), and DMAP (610 mg, 5 mmol) at room temperature, and the resulting solution was stirred overnight. The reaction mixture was quenched with a satd aq solution of NH_4Cl. The aqueous layer was separated and extracted with AcOEt. The combined organic extracts were washed with H_2O and brine and dried over Na_2SO_4. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 15/1) to give **1a** (2.51 g, 70% for 2 steps) as an oil.

In similar manner, (*E*)-4-alkoxy-2-butenyl benzoates **1b**−**1k** were prepared from the corresponding 4-alkoxy-2-butyn-1-ols **4b**−**4k**.

(*E*)-4-(Benzyloxy)-1-phenyl-2-buten-1-yl Benzoate (1a). ^{1}H NMR (400 MHz, $CDCl_3$): 4.07 (d, J = 5.5 Hz, 2H), 4.52 (s, 2H), 5.96 (dt, J = 15.6, 5.5 Hz, 1H), 6.04 (dd, J = 15.6, 6.0 Hz, 1H), 6.54 (d, J = 6.0 Hz, 1H), 7.26−7.58 (m, 13H), 8.09 (d, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 69.6, 72.3, 75.9, 127.0, 127.6, 127.7, 128.1, 128.3, 128.5, 128.6, 129.5, 129.6, 130.1, 130.6, 133.0, 137.9, 139.0, 165.4. IR (neat): 3063, 3031, 2855, 1717, 1600, 1584, 1494, 1452, 1315, 1267, 1176, 1107, 1069, 1025, 968, 751, 712 cm^{-1}. HRMS (EI): calcd for $C_{24}H_{22}O_3$ [M$^+$] 358.1569, found 358.1573.

(*E*)-4-((2-Methylbenzyl)oxy)-1-phenyl-2-buten-1-yl Benzoate (1b). Starting from 5.0 mmol of **4b**, almost pure **5b** (1.22 g) was obtained. Then 708 mg of the intermediary **5b** was used to give **1b** (644 mg, 61% for 2 steps) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): 2.30 (s, 3H), 4.08 (d, J = 5.0 Hz, 2H), 4.50 (s, 2H), 5.97 (dt, J = 15.6, 5.0 Hz, 1H), 6.05 (dd, J = 15.6, 5.5 Hz, 1H), 6.54 (d, J = 5.5 Hz, 1H), 7.15−7.58 (m, 12H), 8.09 (d, J = 9.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 18.7, 69.7, 70.5, 75.8, 125.6, 126.9, 127.7, 128.1, 128.3, 128.5, 129.6, 130.1, 130.6, 132.9, 135.8, 136.6, 139.0, 165.3. IR (neat): 3063, 3031, 2855, 1719, 1601, 1493, 1452, 1314, 1266, 1176, 1107, 1070, 1025, 968, 746, 712 cm^{-1}. HRMS (EI): calcd for $C_{25}H_{24}O_3$ [M$^+$] 372.1725, found 372.1728.

(*E*)-4-((3-Methylbenzyl)oxy)-1-phenyl-2-buten-1-yl Benzoate (1c). Starting from 5.5 mmol of **4c**, almost pure **5c** (1.33 g) was obtained. Then 707 mg of the intermediary **5c** was used to give **1c** (678 mg, 69% for 2 steps) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): 2.33 (s, 3H), 4.06 (d, J = 5.5 Hz, 2H), 4.47 (s, 2H), 5.97 (dt, J = 15.5, 5.5 Hz, 1H), 6.05 (dd, J = 15.5, 5.9 Hz, 1H), 6.54 (d, J = 5.9 Hz, 1H), 7.09−7.58 (m, 12H), 8.09 (d, J = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 21.3, 69.7, 72.4, 75.9, 124.9, 127.0, 128.1, 128.2, 128.3, 128.4, 128.6, 129.6, 129.7, 130.1, 130.7, 133.0, 137.8, 137.9, 139.0, 165.4. IR (neat): 3061, 3031, 2919, 2855, 1718, 1601, 1585, 1492, 1451, 1314, 1266, 1176, 1158, 1107, 1069, 1025, 968, 907, 780, 757, 712 cm^{-1}. HRMS (EI): calcd for $C_{25}H_{24}O_3$ [M$^+$] 372.1725, found 372.1721.

(*E*)-4-((4-Methylbenzyl)oxy)-1-phenyl-2-buten-1-yl Benzoate (1d). Starting from 6.4 mmol of **4d**, almost pure **5d** (1.45 g) was obtained. Then 570 mg of the intermediary **5d** was used to give **1d** (546 mg, 58% for 2 steps) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): 2.33 (s, 3H), 4.04 (d, J = 5.5 Hz, 2H), 4.46 (s, 2H), 5.95 (dt, J = 15.5, 5.5 Hz, 1H), 6.02 (dd, J = 15.5, 6.0 Hz, 1H), 6.53 (d, J = 6.0 Hz, 1H), 7.10−7.58 (m, 12H), 8.10 (d, J = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 21.1, 69.5, 72.2, 75.9, 127.0, 127.9, 128.1, 128.3, 128.6, 129.0, 129.7, 130.2, 130.6, 133.0, 133.5, 134.9, 137.3, 139.1, 165.5. IR (neat): 3031, 2921, 2856, 1719, 1601, 1515, 1493, 1451, 1315, 1267, 1176, 1107, 1070, 1025, 969, 806, 756, 712 cm^{-1}. HRMS (EI): calcd for $C_{25}H_{24}O_3$ [M$^+$] 372.1725, found 372.1726.

(*E*)-4-((4-Methoxybenzyl)oxy)-1-phenyl-2-buten-1-yl Benzoate (1e). Starting from 3.6 mmol of **4e**, almost pure **5e** (986 mg) was obtained. Then 781 mg of the intermediary **5e** was used to give **1e** (619 mg, 56% for 2 steps) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): 3.80 (s, 3H), 4.03 (d, J = 5.5 Hz, 2H), 4.44 (s, 2H), 5.95 (dt, J = 15.6, 5.5 Hz, 1H), 6.03 (dd, J = 15.6, 5.5 Hz, 1H), 6.54 (d, J = 5.5 Hz, 1H), 6.86 (d, J = 8.7 Hz, 2H), 7.22−7.58 (m, 10H), 8.09 (d, J = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 55.2, 69.4, 72.0, 75.9, 113.7, 127.0, 128.1, 128.3, 128.6, 129.4, 129.7, 130.0, 130.2, 130.6, 133.0, 139.1, 159.2, 165.4. IR (neat): 3062, 3032, 2934, 2836, 1718, 1612, 1585, 1512, 1493, 1452, 1361, 1314, 1266, 1175, 1107, 1026, 968, 820, 756, 713 cm^{-1}. HRMS (EI): calcd for $C_{25}H_{24}O_4$ [M$^+$] 388.1675, found 388.1683.

(*E*)-4-((4-Chlorobenzyl)oxy)-1-phenyl-2-buten-1-yl Benzoate (1f). Starting from 7.0 mmol of **4f**, almost pure **5f** (1.87 g) was obtained. Then 800 mg of the intermediary **5f** was used to give **1f** (783 mg, 67% for 2 steps) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): 4.05 (d, J = 5.5 Hz, 2H), 4.46 (s, 2H), 5.95 (dt, J = 16.4, 5.5 Hz, 1H), 6.03 (dd, J = 16.4, 5.9 Hz, 1H), 6.53 (d, J = 5.9 Hz, 1H), 7.25−7.59 (m, 12H), 8.09 (d, J = 8.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 69.8, 71.5, 75.8, 126.9, 128.1, 128.3, 128.4, 128.6, 129.0, 129.3, 129.6, 130.1, 130.8, 133.0, 133.3, 136.5, 138.9, 165.4. IR (neat): 3062, 3032, 2854, 1718, 1600, 1584, 1491, 1451, 1396, 1314, 1267, 1200, 1176, 1108, 1025, 1015, 968, 841, 807, 757, 712 cm^{-1}. HRMS (EI): calcd for $C_{24}H_{21}ClO_3$ [M$^+$] 392.1179, found 392.1175.

(*E*)-4-(2-Naphthalenylmethoxy)-1-phenyl-2-buten-1-yl Benzoate (1g). Starting from 5.5 mmol of **4g**, almost pure **5g** (1.35 g) was obtained. Then 802 mg of the intermediary **5g** was used to give **1g** (463 mg, 35% for 2 steps) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): 4.11 (d, J = 5.5 Hz, 2H), 4.67 (s, 2H), 5.98 (dt, J = 15.5, 5.5 Hz, 1H), 6.06 (dd, J = 15.5, 5.5 Hz, 1H), 6.55 (d, J = 5.5 Hz, 1H), 7.30−7.58 (m, 11H), 7.75−7.84 (m, 4H), 8.09 (d, J = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 69.7, 72.4, 75.9, 125.7, 125.8, 126.0, 126.5, 127.0, 127.6, 127.8, 128.1, 128.3, 128.6, 129.5, 129.6, 130.1, 130.7, 132.8, 132.9, 133.1, 135.4, 139.0, 165.4. IR (neat): 3058, 2852, 1716, 1601, 1508, 1492, 1451, 1314, 1267, 1175, 1107, 1069, 1025, 966, 856, 818, 753, 712 cm^{-1}. HRMS (EI): calcd for $C_{28}H_{24}O_3$ [M$^+$] 408.1725, found 408.1729.

(*E*)-4-(Benzyloxy)-1-(4-tolyl)-2-buten-1-yl Benzoate (1h). Starting from 5.2 mmol of **4h**, almost pure **5h** (1.32 g) was obtained. Then 715 mg of the intermediary **5h** was used to give **1h** (615 mg, 58% for 2 steps) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): 2.34 (s, 3H), 4.06 (d, J = 5.0 Hz, 2H), 4.50 (s, 2H), 5.95 (dt, J = 15.5, 5.0 Hz, 1H), 6.03 (dd, J = 15.5, 5.5 Hz, 1H), 6.50 (d, J = 5.5 Hz, 1H), 7.16−7.57 (m, 12H), 8.08 (d, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 21.2, 69.8, 72.3, 75.9, 127.1, 127.6, 127.8, 128.3, 128.4, 128.6, 129.2,

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129.3, 129.7, 130.2, 130.9, 133.0, 136.0, 138.0, 165.5. IR (neat): 3030, 2921, 2857, 1717, 1601, 1514, 1495, 1452, 1315, 1267, 1176, 1108, 1069, 1025, 968, 816, 737, 711 cm^{-1}. HRMS (EI): calcd for $C_{25}H_{24}O_3$ [M^+] 372.1725, found 372.1730.

(*E*)-4-(Benzyloxy)-1-(2-naphthalenyl)-2-buten-1-yl Benzoate (1i). Starting from 4.8 mmol of **4i**, almost pure **5i** (1.29 g) was obtained. Then 667 mg of the intermediary **5i** was used to give **1i** (528 mg, 53% for 2 steps) as an oil. ^1H NMR (400 MHz, $CDCl_3$): 4.08 (d, *J* = 5.5 Hz, 2H), 4.51 (s, 2H), 5.99 (dt, *J* = 15.5, 5.5 Hz, 1H), 6.13 (dd, *J* = 15.5, 5.9 Hz, 1H), 6.71 (d, *J* = 5.9 Hz, 1H), 7.24−7.61 (m, 11H), 7.80−7.93 (m, 4H), 8.12 (d, *J* = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 70.7, 73.3, 77.0, 125.7, 127.10, 127.16, 127.19, 128.6, 128.7, 129.0, 129.3, 129.4, 130.6, 130.7, 131.1, 131.5, 133.9, 134.0, 137.3, 138.8, 166.4. IR (neat): 3059, 2853, 1717, 1601, 1508, 1452, 1361, 1314, 1266, 1175, 1106, 1069, 1025, 968, 858, 818, 749, 711 cm^{-1}. HRMS (EI): calcd for $C_{28}H_{24}O_3$ [M^+] 408.1725, found 408.1727.

(*E*)-6-(Benzyloxy)-2,2-dimethyl-4-hexen-3-yl Benzoate (1j). Starting from 4.6 mmol of **4j**, almost pure **5j** (866 mg) was obtained. Then 494 mg of the intermediary **5j** was used to give **1j** (328 mg, 37% for 2 steps) as an oil. ^1H NMR (400 MHz, $CDCl_3$): 1.02 (s, 9H), 4.04 (d, *J* = 4.5 Hz, 2H), 4.50 (s, 2H), 5.28 (d, *J* = 6.0 Hz, 1H), 5.84 (dd, *J* = 15.5, 6.0 Hz, 1H), 5.86 (dt, *J* = 15.5, 4.5 Hz, 1H), 7.26−7.38 (m, 5H), 7.45 (dd, *J* = 7.8, 7.7 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 1H), 8.07 (d, *J* = 7.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 25.9, 34.7, 69.7, 71.9, 81.4, 127.5, 127.7, 127.9, 128.3, 129.5, 130.5, 130.7, 132.8, 138.0, 165.6. IR (neat): 3063, 3031, 2965, 2868, 1718, 1601, 1452, 1395, 1365, 1316, 1270, 1176, 1111, 1069, 1025, 970, 736, 711 cm^{-1}. HRMS (EI): calcd for $C_{22}H_{26}O_3$ [M^+] 338.1882, found 338.1878.

(*E*)-6-(Benzyloxy)-2-methyl-4-hexen-3-yl Benzoate (1k). Starting from 7.4 mmol of **4k**, almost pure **5k** (1.58 g) was obtained. Then 547 mg of the intermediary **5k** was used to give **1k** (528 mg, 57% for 2 steps) as an oil. ^1H NMR (400 MHz, $CDCl_3$): 1.00 (d, *J* = 6.9 Hz, 3H), 1.01 (d, *J* = 6.4 Hz, 3H), 1.99−2.10 (m, 1H), 4.04 (d, *J* = 5.5 Hz, 2H), 4.50 (s, 2H), 5.35 (t, *J* = 6.4 Hz, 2H), 5.80 (dd, *J* = 16.5, 6.4 Hz, 1H), 5.87 (dt, *J* = 16.5, 5.5 Hz, 1H), 7.26−7.58 (m, 8H), 8.06 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 18.0, 18.2, 32.2, 69.8, 72.0, 78.9, 127.5, 127.7, 128.2, 128.3, 129.1, 129.5, 130.0, 132.8, 138.0, 165.7. IR (neat): 3063, 3031, 2965, 2873, 1717, 1601, 1584, 1494, 1452, 1387, 1368, 1270, 1176, 1111, 1069, 1025, 971, 738, 712 cm^{-1}. HRMS (EI): calcd for $C_{21}H_{24}O_3$ [M^+] 324.1725, found 324.1721.

Representative Procedure for Sequential 1,4-Elimination Reaction and [1,2]-Wittig Rearrangement of (*E*)-2-Butenyl Benzoate 1a (Table 2, entry 1). To a mixture of powdered KOH (21 mg, 1.05 mmol) and [Pd(dppe)$_2$] (16 mg, 0.018 mmol) was added compound **1a** (125 mg, 0.35 mmol) in THF (12 mL) dropwise at room temperature, and the reaction mixture was stirred for 18 h. After MS4A was added and the resulting mixture was stirred for 30 min, the mixture was cooled to 0 °C, and *n*-BuLi (1.27 mL of 1.62 M solution in hexane, 2.1 mmol) was added. After 5 min, the reaction mixture was quenched with a satd aq solution of NH_4Cl. The aqueous layer was separated and extracted with Et_2O. The combined organic extracts were washed with H_2O and brine and dried over Na_2SO_4. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 10/1 with 1% Et_3N) to give **2a** (56 mg, 68%, *Z*/*E* = >20/1) as an oil.

In a similar manner, (2*Z*,4*E*)-2,4-pentadien-1-ols **2b**−**2k** were obtained from **1b**−**1k**.

(2*Z*,4*E*)-1,5-Diphenyl-2,4-pentadien-1-ol (2a).[24] ^1H NMR (400 MHz, $CDCl_3$): δ 2.04 (br s, 1H), 5.69 (dd, *J* = 11.0, 8.7 Hz, 1H), 5.81 (d, *J* = 8.7 Hz, 1H), 6.30 (t, *J* = 11.0 Hz, 1H), 6.64 (d, *J* = 15.5 Hz, 1H), 7.21 (dd, *J* = 15.5, 11.0 Hz, 1H), 7.26−7.45 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 70.0, 123.6, 125.9, 126.6, 127.5, 127.9, 128.5, 128.6, 130.1, 133.1, 134.9, 136.9, 143.1. IR (neat): 3366, 3027, 1599, 1492, 1449, 1280, 1073, 1027, 986, 945, 859, 740, 697 cm^{-1}. HRMS (EI): calcd for $C_{17}H_{16}O$ [M^+] 236.1201, found 236.1207.

During the optimization of the reaction conditions, a mixture of (2*Z*,4*E*)-**2a** and the (2*E*,4*E*)-isomer was obtained as shown in Table 1. Selected NMR data for the (2*E*,4*E*)-isomer:[25] δ 5.32 (d, *J* = 6.4 Hz, 1H), 6.00 (dd, *J* = 15.1, 6.4 Hz, 1H), 6.47 (dd, *J* = 15.1, 10.5 Hz, 1H), 6.58 (d, *J* = 15.6 Hz, 1H), 6.78 (dd, *J* = 15.6, 10.5 Hz, 1H).

(2*Z*,4*E*)-1-(2-Methylphenyl)-5-phenyl-2,4-pentadien-1-ol (2b). Compound **2b** (56 mg, 65% from 0.35 mmol **1b**) was obtained as an oil. ^1H NMR (400 MHz, $CDCl_3$): 1.92 (br, 1H), 2.36 (s, 3H), 5.62 (dd, *J* = 11.0, 8.7 Hz, 1H), 5.95 (d, *J* = 8.7 Hz, 1H), 6.28 (t, *J* = 11.0 Hz, 1H), 6.63 (d, *J* = 15.6 Hz, 1H), 7.21 (dd, *J* = 15.6, 11.0 Hz, 1H), 7.24−7.59 (m, 9H). Selected data of (2*E*,4*E*)-isomer; 5.51 (d, *J* = 6.8 Hz, 1H), 5.81 (dd, *J* = 15.5, 6.4 Hz, 1H), 6.43 (dd, *J* = 15.5, 11.0 Hz, 1H), 6.58 (d, *J* = 16.0 Hz, 1H), 6.78 (dd, *J* = 16.0, 11.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 19.4, 67.4, 123.3, 125.3, 126.4, 126.6, 127.5, 128.0, 128.7, 130.4, 130.5, 132.3, 134.9, 135.1, 136.9, 141.2. IR (neat): 3440, 3024, 1599, 1489, 1457, 1372, 1241, 1158, 1046, 989, 749, 699 cm^{-1}. HRMS (EI): calcd for $C_{18}H_{18}O$ [M^+] 250.1358, found 250.1359.

(2*Z*,4*E*)-1-(3-Methylphenyl)-5-phenyl-2,4-pentadien-1-ol (2c). Compound **2c** (50 mg, 58% from 0.35 mmol **1c**) was obtained as an oil. ^1H NMR (400 MHz, $CDCl_3$): 1.97 (br, 1H), 2.40 (s, 3H), 5.68 (dd, *J* = 11.0, 9.1 Hz, 1H), 5.78 (d, *J* = 9.1 Hz, 1H), 6.29 (t, *J* = 11.0 Hz, 1H), 6.63 (d, *J* = 15.5 Hz, 1H), 7.08−7.12 (m, 1H), 7.23−7.44 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 21.5, 70.1, 123.0, 123.4, 126.55, 126.61, 128.0, 128.4, 128.5, 128.7, 130.2, 133.1, 135.0, 137.0, 138.4, 143.1. IR (neat): 3331, 3025, 1605, 1489, 1448, 1306, 1152, 1029, 987, 946, 779, 754, 692 cm^{-1}. HRMS (EI): calcd for $C_{18}H_{18}O$ [M^+] 250.1358, found 250.1347.

(2*Z*,4*E*)-1-(4-Methylphenyl)-5-phenyl-2,4-pentadien-1-ol (2d). Compound **2d** (55 mg, 63% from 0.35 mmol **1d**) was obtained as an oil. ^1H NMR (400 MHz, $CDCl_3$): 1.95 (br, 1H), 2.34 (s, 3H), 5.69 (dd, *J* = 11.0, 9.1 Hz, 1H), 5.79 (d, *J* = 9.1 Hz, 1H), 6.28 (t, *J* = 11.0 Hz, 1H), 6.63 (d, *J* = 15.1 Hz, 1H), 7.16−7.44 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): 21.1, 70.0, 123.4, 125.8, 126.6, 127.9, 128.7, 129.3, 130.1, 133.2, 134.9, 137.0, 137.4, 140.2. IR (neat): 3421, 3024, 2920, 1604, 1512, 1492, 1449, 1374, 1242, 1178, 1044, 986, 811, 749, 693 cm^{-1}. HRMS (EI): calcd for $C_{18}H_{18}O$ [M^+]: 250.1358, found 250.1363.

(2*Z*,4*E*)-1-(4-Methoxyphenyl)-5-phenyl-2,4-pentadien-1-ol (2e). Compound **2e** (66 mg, 71% from 0.35 mmol **1e**) was obtained as an oil. ^1H NMR (400 MHz, $CDCl_3$): 1.92 (br, 1H), 3.80 (s, 3H), 5.71 (dd, *J* = 11.0, 8.7 Hz, 1H), 5.77 (d, *J* = 8.7 Hz, 1H), 6.28 (t, *J* = 11.0 Hz, 1H), 6.63 (d, *J* = 15.5 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 2H), 7.18 (dd, *J* = 15.5, 11.0 Hz, 1H), 7.26−7.44 (m, 7H). Selected data of (2*E*,4*E*)-isomer; 5.29 (m, 1H), 5.99 (dd, *J* = 15.1, 6.4 Hz, 1H), 6.46 (dd, *J* = 15.1, 10.5 Hz, 1H), 6.57 (d, *J* = 15.5 Hz, 1H), 6.78 (dd, *J* = 15.5, 10.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 55.3, 69.7, 114.0, 123.4, 126.6, 127.2, 127.9, 128.6, 129.8, 133.2, 134.8, 135.3, 136.9, 159.1. IR (neat): 3382, 3026, 2956, 2834, 1610, 1584, 1509, 1449, 1302, 1247, 1173, 1033, 986, 946, 862, 830, 741, 692 cm^{-1}. HRMS (ESI-TOF): calcd for $C_{18}H_{18}O_2Na$ [M + Na^+] 289.1204, found 289.1198.

(2*Z*,4*E*)-1-(4-Chlorophenyl)-5-phenyl-2,4-pentadien-1-ol (2f). Compound **2f** (59 mg, 63% from 0.35 mmol **1f**) was obtained as an oil. ^1H NMR (400 MHz, $CDCl_3$): 1.98 (br, 1H), 5.62 (dd, *J* = 10.5, 9.1 Hz, 1H), 5.80 (d, *J* = 9.1 Hz, 1H), 6.31 (t, *J* = 10.5 Hz, 1H), 6.68 (d, *J* = 15.5 Hz, 1H), 7.20 (dd, *J* = 15.5, 10.5 Hz, 1H), 7.25−7.42 (m, 9H). Selected data of (2*E*,4*E*)-isomer; 5.30 (d, *J* = 6.4 Hz, 1H), 5.94 (dd, *J* = 15.1, 6.4 Hz, 1H), 6.46 (dd, *J* = 15.1, 11.0 Hz, 1H), 6.59 (d, *J* = 16.0 Hz, 1H), 6.77 (dd, *J* = 16.0, 11.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 69.3, 123.0, 126.6, 127.3, 128.1, 128.7, 130.6, 132.5, 133.3, 135.5, 136.8, 141.5. IR (neat): 3351, 3027, 1636, 1595, 1489, 1449, 1400, 1090, 1013, 986, 945, 861, 826, 744, 691 cm^{-1}. HRMS (EI): calcd for $C_{17}H_{15}OCl$ [M^+] 270.0811, found 270.0814.

(2*Z*,4*E*)-1-(2-Naphthalenyl)-5-phenyl-2,4-pentadien-1-ol (2g). Compound **2g** (68 mg, 68% from 0.35 mmol **1g**) was obtained as an oil. ^1H NMR (400 MHz, $CDCl_3$): 2.09 (br, 1H), 5.76 (dd, *J* = 11.0, 8.7 Hz, 1H), 5.98 (d, *J* = 8.7 Hz, 1H), 6.35 (t, *J* = 11.0 Hz, 1H), 6.67 (d, *J* = 15.1 Hz, 1H), 7.26−7.55 (m, 9H), 7.81−7.91 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): 70.2, 123.3, 124.1, 124.3, 125.9, 126.2, 126.6, 127.6, 128.0, 128.4, 128.7, 130.4, 132.8, 132.9, 133.3, 135.2, 136.8, 140.4. IR (neat): 3447, 3024, 1599, 1507, 1492, 1449, 1371, 1242, 1158, 1123, 1046, 990, 896, 858, 818, 747, 693 cm^{-1}. HRMS (EI): calcd for $C_{21}H_{18}O$ [M^+] 286.1358, found 286.1353.

(2*Z*,4*E*)-5-(4-Methylphenyl)-1-phenyl-2,4-pentadien-1-ol (2h). Compound **2h** (63 mg, 72% from 0.35 mmol **1h**) was obtained as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): 1.98 (br, 1H), 2.35 (s, 3H), 5.66 (dd, J = 11.0, 8.7 Hz, 1H), 5.82 (d, J = 8.7 Hz, 1H), 6.29 (t, J = 11.0 Hz, 1H), 6.61 (d, J = 15.6 Hz, 1H), 7.13−7.48 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): 21.3, 70.0, 122.4, 125.9, 126.5, 127.6, 128.6, 129.4, 130.4, 132.4, 134.1, 135.0, 138.0, 143.1. IR (neat): 3293, 3023, 1630, 1603, 1509, 1490, 1453, 1343, 1287, 1191, 1017, 984, 954, 941, 908, 839, 806, 765, 735, 696 cm^{-1}. HRMS (EI): calcd for $C_{18}H_{18}O$ [M$^+$] 250.1358, found 250.1343.

(2*Z*,4*E*)-5-(2-Naphthalenyl)-1-phenyl-2,4-pentadien-1-ol (2i). Compound **2i** (67 mg, 67% from 0.35 mmol **1i**) was obtained as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): 2.05 (br, 1H), 5.73 (dd, J = 11.0, 9.1 Hz, 1H), 5.89 (d, J = 9.1 Hz, 1H), 6.37 (t, J = 11.0 Hz, 1H), 6.81 (d, J = 15.6 Hz, 1H), 7.32−7.48 (m, 8H), 7.66 (d, J = 7.8 Hz, 1H), 7.78−7.81 (m, 4H). Selected data of (2*E*,4*E*)-isomer; 5.35 (d, J = 5.9 Hz, 1H), 6.05 (dd, J = 15.1, 5.9 Hz, 1H), 6.54 (dd, J = 15.1, 9.6 Hz, 1H), 6.74 (d, J = 16.4 Hz, 1H), 6.88 (dd, J = 16.4, 9.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 70.1, 123.5, 123.6, 125.9, 126.1, 126.4, 126.9, 127.6, 127.7, 128.0, 128.3, 128.6, 130.3, 133.10, 133.15, 133.5, 134.4, 135.2, 143.0. IR (neat): 3397, 3030, 1626, 1600, 1506, 1491, 1454, 1268, 1115, 1008, 985, 953, 851, 822, 750, 700 cm^{-1}. HRMS (EI): calcd for $C_{21}H_{18}O$ [M$^+$] 286.1358, found 286.1363.

(2*Z*,4*E*)-6,6-Dimethyl-1-phenyl-2,4-heptadien-1-ol (2j). Compound **2j** (44 mg, 53% from 0.35 mmol **1j**) was obtained an oil. ^{1}H NMR (400 MHz, $CDCl_3$): 1.06 (s, 9H), 1.90 (br, 1H), 5.51 (dd, J = 11.0, 8.7 Hz, 1H), 5.72 (d, J = 8.7 Hz, 1H), 5.83 (d, J = 15.1 Hz, 1H), 6.10 (t, J = 11.0 Hz, 1H), 6.40 (dd, J = 15.1, 11.0 Hz, 1H), 7.26−7.42 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): 29.4, 33.5, 69.9, 119.5, 125.8, 127.4, 128.5, 130.5, 130.9, 143.4, 149.0. IR (neat): 3330, 3029, 2959, 2902, 2864, 1650, 1602, 1493, 1451, 1362, 1267, 1038, 985, 949, 743, 698 cm^{-1}. HRMS (EI): calcd for $C_{15}H_{20}O$ [M$^+$] 216.1514, found 216.1522.

A mixture of **2k** and **3** (40 mg, 59% from 0.35 mmol **1k**) was obtained as an oil. The yields of **2k** and **3** were determined by ^{1}H NMR spectrum of their mixture. After further separation of **2k** and **3** by column chromatography, the physical properties were measured.

(2*Z*,4*E*)-6-Methyl-1-phenyl-2,4-heptadien-1-ol (2k). Compound **2k** (34% from 0.35 mmol **1k**). ^{1}H NMR (400 MHz, $CDCl_3$): 1.03 (d, J = 6.9 Hz, 3H), 1.04 (d, J = 6.9 Hz, 3H), 1.89 (br, 1H), 2.35−2.43 (m, 1H), 5.50 (dd, J = 11.0, 8.7 Hz, 1H), 5.70 (d, J = 8.7 Hz, 1H), 5.80 (dd, J = 15.1, 6.8 Hz, 1H), 6.10 (t, J = 11.0 Hz, 1H), 6.43 (dd, J = 15.1, 11.0 Hz, 1H), 7.25−7.42 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): 22.20, 22.21, 31.4, 69.9, 121.8, 125.8, 127.5, 128.5, 130.5, 130.7, 143.4, 145.1. IR (neat): 3331, 3026, 2958, 2924, 1696, 1601, 1540, 1493, 1452, 1377, 1028, 986, 853, 746, 669 cm^{-1}. HRMS (EI): calcd for $C_{14}H_{18}O$ [M$^+$] 202.1358, found 202.1367.

(*E*)-6-Methyl-1-phenyl-3,5-heptadien-1-ol (3). Compound **3** (25% from 0.35 mmol **1k**). ^{1}H NMR (400 MHz, $CDCl_3$): 1.75 (s, 3H), 1.78 (s, 3H), 1.79 (br, 1H), 2.80 (ddd, J = 13.2, 12.4, 6.8 Hz, 1H), 2.89 (dd, J = 13.2, 5.0 Hz, 1H), 4.40 (dd, J = 12.4, 5.0 Hz, 1H), 5.62 (dd, J = 15.1, 6.8 Hz, 1H), 5.82 (d, J = 11.0 Hz, 1H), 6.44 (dd, J = 15.1, 11.0 Hz, 1H), 7.20−7.26 (m, 3H), 7.29−7.33 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 18.3, 26.0, 44.3, 76.7, 124.2, 126.5, 127.4, 128.5, 129.6, 132.0, 136.3, 137.9. IR (neat): 3404, 3026, 2922, 2855, 1659, 1602, 1494, 1453, 1376, 1260, 1094, 1029, 986, 959, 868, 801, 746, 700 cm^{-1}. HRMS (ESI-TOF): calcd for $C_{14}H_{18}ONa$ [M + Na$^+$] 225.1255, found 225.1255.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR and ^{13}C NMR spectra of compounds **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(16) When the reaction was quenched after the 1,4-elimination step, generation of a 10/1 mixture of (1*Z*,3*E*)-1-benzyloxy-4-phenyl-1,3-butadiene and its (1*E*,3*E*)-isomer[26] was confirmed by ^{1}H NMR spectrum of the crude products.
(17) The stereochemistry of a double bond between C4 and C5 in the obtained dienol was confirmed to be *E*-form.[10g] In the text, only the stereochemistry of C2═C3 was discussed.
(18) In the absence of Pd catalyst, 1,4-elimination did not proceed and **1a** was recovered.
(19) When the reaction was quenched after the 1,4-elimination step, generation of a mixture of 1-benzyloxy-5-methyl-1,3-butadiene and 1-benzyloxy-5-methyl-2,4-butadiene was confirmed by ^{1}H NMR spectrum of the crude products.
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