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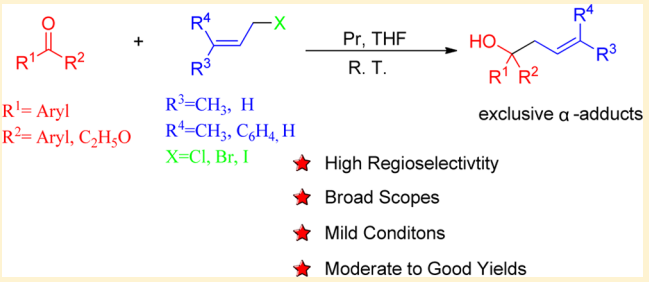
α-Regioselective Barbier Reaction of Carbonyl Compounds and Allyl Halides Mediated by Praseodymium

San Wu, Ying Li, and Songlin Zhang*

Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Dushu Lake Campus, Soochow University, Suzhou, 215123, People's Republic of China

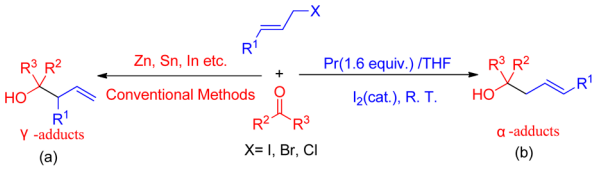
Supporting Information

ABSTRACT: The first utility of praseodymium as a mediating metal in the Barbier reaction of carbonyl compounds with allyl halides was reported in this paper. In contrast to the traditional metal-mediated or catalyzed Barbier reactions, exclusive α-adducts were obtained in this one-pot reaction with a broad scope of substrates and feasible reaction conditions.



The homoallylic alcohols are important building blocks to be applied in the synthesis of many biologically active molecules.[1] And the metal mediated or catalyzed addition of allylic agents to carbonyl compounds is the most efficient method to obtain such valuable compounds. Conventionally these metal-mediated Barbier reactions are highly γ-selective to give γ-adducts[2] (Scheme 1, reaction a), despite the fact that the

Scheme 1. Regioselective Barbier Reaction of Carbonyl Compounds and Allyl Halides



α-adduct 4-substituted homoallylic alcohols also play an important role in organic synthesis.[3] By far, the most straightforward approach to obtain 4-substituted homoallylic alcohols is metal-mediated α-selective allylation of carbonyl compounds. And many an endeavor has been made to realize α-selective allylation of aldehydes and ketones. The Yamamoto group reported the first direct preparation of allylbarium reagents in situ and their unexpected α-selective allylation reactions with carbonyl compounds.[4] And they explored metal effects on the α/γ selectivity in the reaction of various organometallic reagents with benzaldehyde. The first α-selective crotylation of aldehyde mediated by indium, zinc, and tin was reported by Loh's group.[5] However, the reaction appeared to be slow and lengthy. Wang's group[6] reported two examples of the regioselective allylation of benzaldehyde mediated by Sn in water in the presence of $NaBF_4$. And the α-selective allylation of ketone was first reported by Zhao and co-workers.[7] Since a high temperature leads to an increase of α-addition products, high boiling solvents were essential in their research. Thus, a more energy efficient and feasible method for α-selective allylation is still in demand.

The utilization of samarium diiodide in synthetic chemistry as an effective one-electron transfer reducing agent[8] has been extensively reported since the pioneering discovery study by Kagan et al.[9] Then, some other divalent lanthanide reagents with better solubility, LnX_2 (Ln = Nd,[10] Dy,[11] Tm,[12] X = I, Br, Cl), whose reduction potentials were similar to that of SmI_2 have been reported. In the meantime, the Barbier-type reactions of halides and carbonyl compounds mediated by these divalent lanthanide reagents were developed.[13] Due to the fact that these reagents are expensive and both moisture and oxygen sensitive unfortunately, the direct use of zerovalent lanthaniod metals was determined to be an alternative method in organic chemistry. However, the use of zerovalent lanthaniod metals in Barbier reaction was still limited to Sm.[14] To the best of our knowledge, only a few cases using praseodymium metal directly in organic synthesis have been reported.[15] Very recently, our group became deeply interested in the application of lanthanide metals in organic synthesis.[16] Herein, based on our recent work, we would like to report the utility of praseodymium as a mediating metal in the Barbier reaction of carbonyl compounds with allyl halides (Scheme 1, reaction b). And more importantly, the α-adducts can be obtained exclusively in this one-pot reaction.

The reaction between the benzophenone **1a** and allyl iodide was selected as a model reaction to optimize reaction conditions (Table 1, entries 1−10). First, the ratio of Pr and allyl iodide and temperature were examined, and the results were summarized in Table 1. To our delight, the yield could be improved to 82% by optimizing the molar ratio of **1a**/Pr/**2**

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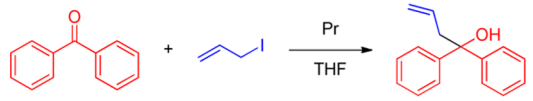
Table 1. Optimization of Reaction Conditions[a]



1a 2 3a

entry	1a:Pr:2	time (h)	temp (°C)	yield[b] (%)
1	1:2:6	2	rt	74
2	1:2:4	2	rt	79
3	1:2:2.4	2	rt	75
4	1:1.6:1.6	2	rt	81
5	1:1.6:2	2	rt	82
6	1:2.0:2	2	rt	82
7	1:1.6:2	2	0	45
8	1:1.6:2	2	−20	23
9	1:1.6:2	4	rt	84
10	1:1.6:2	1	rt	70
11	1:2:6	2	rt	74
12	1:2:4	2	rt	79
13	1:2:2.4	2	rt	75

[a]Unless noted, to a solution of **1a** (0.5 mmol), Pr (*X* mmol), and **2** (*Y* mmol) in THF (3 mL) under a nitrogen atmosphere, and the mixture was stirred. [b]Isolated yield based on **3a** after silica gel chromatography.

(Table 1, entries 5 vs 1−4 and 6). When the reaction was carried out at a lower temperature, the yield decreased significantly (Table 1, entries 7−8). Thus, a 1.0/1.6/2.0 molar ratio of **1a**/Pr/**2** at room temperature proved to be the optimal reaction conditions. And the reaction time was able to be shortened to 2 h.

With the optimized reaction conditions in hand, the substrate scope of the reaction of various benzophenones with allyl iodide was subsequently explored and the results were summarized in Table 2. As shown in Table 2, we found ketones bearing an electron-donating substituent gave high yields, such as 4,4′-dimethoxy, 4-methyl-, and 4-phenyl-benzophenone (Table 2, entries 2−4). For ketones bearing electron-withdrawing groups on aryl rings, such as 4,4′-dichloro-, 4,4′-difluoro-, and 3,4-dichlorobenzaldehyde, the products were obtained in moderate yields (Table 2, entries 5−7). The above-mentioned results indicated that electron-donating groups on the aryl ring were favored in the reaction rather than electron-withdrawing groups. Ethyl benzoate also gave the product **3h** in 56% yield (Table 2, entry 8). To broaden the scope of this reaction, allyl bromides were also examined (Table 2, entries 9−10). To our delight, the corresponding homoallylic alcohols were obtained in high yields as well.

Next, we turned our attention to the regioselectivity of this Barbier-type reaction. First, 3,3-dimethylallyl chloride was employed to investigate the regioselectivity (Table 3, entries 1−2). To our surprise, no γ-adducts, which are the dominant products in conventional Barbier reactions, were observed. 4,4-Dimethylallyl homoallylic alcohols were obtained in moderate to good yields. Then, to broaden the reaction scope, 3,3-dimethylallyl bromide was employed to react with a series of benzophenones (Table 3, entries 3−8). And the α-adducts were obtained exclusively in moderate to good yields. When cinnamon bromide reacted with benzophenones, *trans*-4-phenyl homoallylic alcohols could be gained in moderate yields (Table 3, entries 9−15). The results indicated that the Praseodymium-mediated Barbier-type reaction was highly α-regioselective. Finally, crotyl bromide was employed to investigate whether the steric hindrance affects the regioselectivity (Table 3, entries 16−17). A mixture of *E* and *Z* α-addition products was obtained in moderate yields which indicated the hindrance had no effect on regioselectivity.

In summary, we have documented the first Barbier-type reaction of allyl halides with carbonyl compounds mediated by praseodymium. As a complement to the traditional metal-mediated or catalyzed Barbier reactions, this reaction was highly α-regioselective and the reaction was conveniently carried out under mild conditions in a one-pot fashion. In this work, a straightforward strategy to synthesize 4-substituent homoallylic alcohols was developed. This strategy provides a broad scope and moderate to good yields of the products in a relatively short reaction time.

EXPERIMENTAL SECTION

General Details. All of the reagents and solvents were used directly as obtained commercially unless otherwise noted. The petroleum ether (PE) used refers to the 60−90 °C boiling point fraction of petroleum. Column chromatography was performed with 200−300 mesh silica gel using flash column techniques. ^{1}H and ^{13}C NMR spectra were determined in $CDCl_3$ or DMSO-d_6 on a 400 MHz spectrometer. Chemical shifts in ^{1}H NMR spectra are reported in parts per million (ppm, δ) downfield from the internal standard Me_4Si (TMS, δ = 0.00 ppm) or DMSO (2.50 ppm). Chemical shifts in ^{13}C NMR spectra are reported relative to the central line of the chloroform signal (δ = 77.00 ppm) or DMSO signal (δ = 40.00 ppm). High-resolution mass spectra were obtained with a GCT-TOF instrument.

General Procedure for Synthesis of Alcohol. Allyl halides (1.0 mmol), ketones (0.5 mmol), and Pr powder (0.8 mmol) were mixed in dry THF (3 mL) under a nitrogen atmosphere at room temperature. The mixture was stirred for about 2 h (the reaction was monitored by TLC). The reaction mixture was then quenched with dilute hydrochloric acid. The resulting mixture was extracted with diethyl ether (3 × 10 mL) and dried over anhydrous Na_2SO_4. The solvent was removed by evaporation under reduced pressure. Purification by column chromatography on silica gel (eluent: EtOAc/Pet ether = 1/20) afforded alcohols.

1,1-Diphenylbut-3-en-1-ol (***3a***).[17] The title compound was obtained according to the general procedure. Pale yellow oil; yield 82% (91.9 mg); IR (KBr): 3556, 3047, 2910, 2840, 1944, 1769, 1640, 1550, 1470, 1386, 1160, 992, 812, 769, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.40−7.20 (m, 10H), 5.60−5.47 (m, 1H), 5.15−5.06 (m, 2H), 2.96 (d, *J* = 7.10 Hz, 2H), 2.49 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 146.9, 133.9, 128.6, 127.3, 126.4, 121.0, 77.3, 47.1; HRMS (EI$^+$) calcd for $C_{16}H_{16}O$ (M^+): 224.1202; found 224.1203.

1,1-Bis(4-methoxyphenyl)but-3-en-1-ol (***3b***).[18] The title compound was obtained according to the general procedure. Pale yellow oil; yield 89% (126.4 mg); IR (KBr): 3490, 3074, 2930, 2830, 2545, 2048, 1890, 1610, 1510, 1465, 1380, 990, 829, 735 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.26 (d, *J* = 8.4 Hz, 2H), 6.75 (d, *J* = 8.4 Hz, 2H), 5.62−5.52 (m, 1H), 5.15−5.04 (m, 2H), 3.67(s, 6H), 2.92 (d, *J* = 6.9 Hz, 2H), 2.44 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 158.3, 139.0, 133.7, 133.6, 127.4, 126.9, 120.1, 113.6, 113.2, 76.4, 55.3, 55.0, 46.9; HRMS (EI$^+$) calcd for $C_{18}H_{20}O_3$ (M^+): 284.1412; found 284.1410.

1-Phenyl-1-p-tolylbut-3-en-1-ol (***3c***).[19] The title compound was obtained according to the general procedure. Pale yellow oil; yield 74% (88.1 mg); IR (KBr): 3555, 3060, 3025, 2975, 2920, 1955, 1639, 1510, 1445, 1383, 998, 810, 765, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.34−7.03 (m, 9H), 5.61−5.51 (m, 1H), 5.14−5.03 (m, 2H), 2.96 (d, *J* = 7.1 Hz, 2H), 2.44 (s, 1H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 147.1, 144.0, 136.8, 134.0, 129.3, 128.5, 127.2, 126.5, 126.3, 120.7, 77.1, 47.1, 21.4; HRMS (EI$^+$) calcd for $C_{17}H_{18}O$ (M^+): 238.1358; found: 238.1354.

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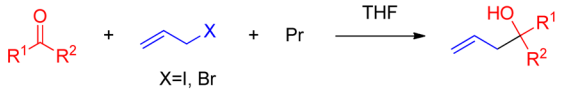
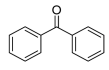
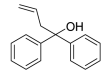
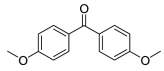
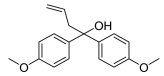
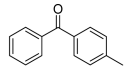
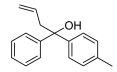
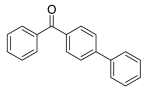
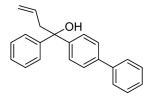
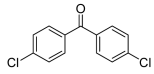
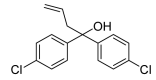
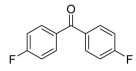
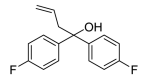
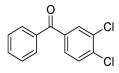
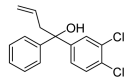
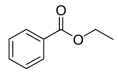
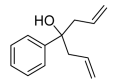
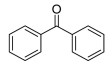
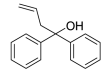
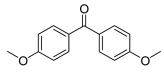
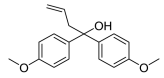
Table 2. Reactions of Ketone Compounds with Allyl Iodide Promoted by Praseodymium Metal[a]



1 **2** **3**

Entry	Substrate	Product	Yield (%)[b]
1	 **1a**	 **3a**	82
2	 **1b**	 **3b**	89
3	 **1c**	 **3c**	74
4	 **1d**	 **3d**	88
5	 **1e**	 **3e**	74
6	 **1f**	 **3f**	85
7	 **1g**	 **3g**	72
8[c]	 **1h**	 **3h**	56
9[d]	 **1a**	 **3a**	80
10[d]	 **1b**	 **3b**	85

[a]Unless noted, to a solution of **1a** (0.5 mmol), Pr (0.8 mmol), and allyl iodide (1.0 mmol) in THF (3 mL) were added under a nitrogen atmosphere, and the mixture was stirred for 2 h. [b]Isolated yield based on **1a** after silica gel chromatography. [c]To a solution of **1a** (0.5 mmol), Pr (3.0 mmol), and **2** (3.5 mmol)in THF (6 mL) were added under a nitrogen atmosphere, and the mixture was stirred for 2 h. [d]Allyl bromide was used instead of allyl iodide.

1-Phenyl-1-(4′-phenyl)phenylbut-3-en-1-ol (***3d***). The title compound was obtained according to the general procedure. Pale yellow oil; yield 88% (132.1 mg); IR (KBr): 3555, 3071, 2920, 2835, 1951, 1770, 1625, 1510, 1460, 1385, 1175, 930, 815, 769, 689 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.46−7.11 (m, 14H), 5.61−5.55 (m, 1H), 5.15−5.03 (m, 2H), 2.97 (d, J = 7.1 Hz, 2H), 2.50 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 146.5, 145.7, 140.7, 139.7, 133.5, 128.8, 128.3, 127.3, 127.1, 127.0, 127.0, 126.5, 126.1, 120.7, 76.8, 46.8; HRMS (EI^+) calcd for $C_{22}H_{20}O$ (M^+): 300.1514; found: 300.1510.

DOI: 10.1021/acs.joc.6b01466
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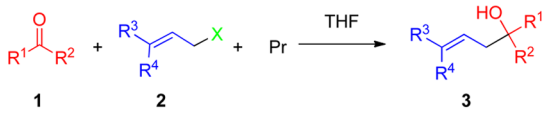
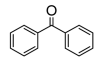
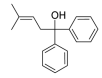
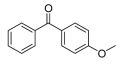
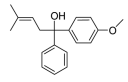
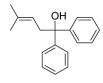
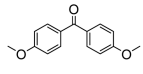
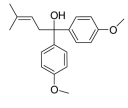
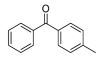
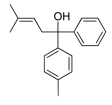
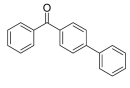
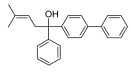
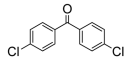
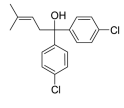
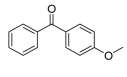
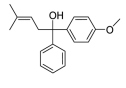
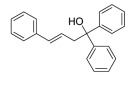
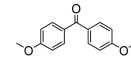
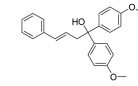
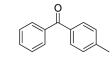
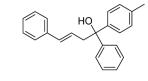
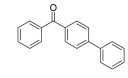
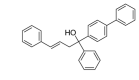
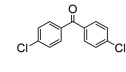
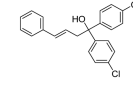
Table 3. Reactions of Ketone Compounds with Allyl Iodide Promoted by Praseodymium Metal[a]



Entry[a]	allyl halide	Substrate	Product	Yield (%)[b]
1		 **1a**	 **4a**	67
2		 **1c**	 **4c**	72
3		 **1a**	 **4a**	61
4		 **1b**	 **4b**	77
5		 **1c**	 **4c**	76
6		 **1d**	 **4d**	66
7		 **1e**	 **4e**	63
8		 **1i**	 **4i**	71
9		 **1a**	 **5a**	68
10		 **1b**	 **5b**	57
11		 **1c**	 **5c**	70
12		 **1d**	 **5d**	67
13		 **1e**	 **5e**	54
14		**1f**	**5f**	37
15		**1i**	**5i**	61
16		**1a**	**6a**	70
17		**1c**	**6c**	65

[a]Unless noted, to a solution of **1a** (0.5 mmol), Pr (0.8 mmol), and **2** (1.0 mmol) in THF (3 mL) were added under a nitrogen atmosphere, and the mixture was stirred for 2 h. [b]Isolated yield based on **1a** after silica gel chromatography.

*1,1-Bis(4-chlorophenyl)but-3-en-1-ol (**3e**).*[20] The title compound was obtained according to the general procedure. Pale yellow oil; yield 74% (108.1 mg); IR (KBr): 3555, 3085, 2979, 2855, 1910, 1777, 1640, 1595, 1495, 1410, 1095, 930, 825, 759, 670 cm^{-1}; ^1H NMR ($CDCl_3$,

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400 MHz, TMS): δ 7.24 (d, J = 8.4 Hz, 4H), 7.15 (d, J = 8.4 Hz, 4H), 5.52−5.50 (m, 1H), 5.15−5.06 (m, 2H), 2.89 (d, J = 7.2 Hz 2H), 2.51 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 144.6, 133.0, 132.6, 128.4, 127.4, 121.3, 76.3, 46.5; HRMS (EI$^+$) calcd for $C_{16}H_{14}Cl_2O$ (M^+): 292.0422 and 294.0392; found: 292.0422 and 294.0393.

1,1-Bis(4-fluorophenyl)but-3-en-1-ol (**3f**).[18] The title compound was obtained according to the general procedure. Pale yellow oil; yield 85% (110.6 mg); IR (KBr): 3555, 3080, 2910, 2845, 1955, 1730, 1640, 1560, 1490, 1360, 1110, 989, 821, 769, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.29 (dd, J = 14.0 Hz, J = 3.06 Hz, 4H), 6.90 (t, J = 8.6 Hz, 4H), 5.57−5.50 (m, 1H), 5.17−5.09 (m, 2H), 2.93 (d, J = 7.18 Hz, 2H), 2.50 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 160.20 (d, $^1J_{C-F}$ = 244.0 Hz), 142.6 (d, $^3J_{C-F}$ = 3.0 Hz), 133.3, 128.1, 121.4, 115.4 (d, $^2J_{C-F}$ = 21 Hz), 76.7, 47.3; HRMS (EI$^+$) calcdfor $C_{16}H_{14}F_2O$ (M^+): 260.1013; found 260.1010.

1-(3,4-Dichlorophenyl)-1-phenylbut-3-en-1-ol (**3g**).[21] The title compound was obtained according to the general procedure. Pale yellow oil; yield 72% (105.5 mg); IR (KBr): 3540, 3065, 2920, 2845, 1955, 1760, 1640, 1560, 1468, 1382, 1175, 992, 820, 765, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.48−7.13 (m, 8H), 5.53−5.49 (m, 1H), 5.17−5.12 (m, 2H), 297−2.84 (m, 2H), 2.52 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 147.1, 145.6, 132.7, 132.5, 131.0, 130.3, 130.2, 128.6, 128.3, 127.5, 126.0, 121.4, 76.4, 46.6; HRMS(EI$^+$) calcd for $C_{16}H_{14}Cl_2O$ (M^+): 292.0422 and 294.0392; found: 292.0420 and 294.0393.

4-Phenylhepta-1,6-dien-4-ol (**3h**).[22] The title compound was obtained according to the general procedure. Pale yellow oil; yield 56% (52.7 mg); IR (KBr): 3555, 3070, 2979, 1945, 1630, 1490, 1440, 1383, 998, 915, 865, 766, 659 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.44−7.38 (m, 2H), 7.36−7.23 (m, 2H), 7.25−7.20 (m, 2H),5.67−5.53 (m, 2H), 5.14−5.05 (m, 2H), 2.69 (q, d, J = 8.0 Hz, 2H), 2.52 (q, d, J = 4.0 Hz, 2H), 2.19 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): 135.8, 133.5, 128.1, 126.6, 125.3, 119.2, 75.1, 46.9; HRMS(EI$^+$) calcd for $C_{13}H_{16}O$ (M^+): 188.1201; found: 188.1200.

4-Methyl-1,1-diphenylpent-3-en-1-ol (**4a**).[18] The title compound was obtained according to the general procedure. Pale yellow oil; yield 67% (84.5 mg); IR (KBr): 3550, 3080, 3030, 2925, 1950, 1665, 1600, 1445, 1380, 1265, 1169, 1055, 905, 754, 642 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.38−7.08 (m, 10H), 4.96 (t, J = 7.2 Hz, 1H), 2.92 (d, J = 7.3 Hz, 2H), 2.47 (s, 1H), 1.58 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 147.3, 146.7, 138.2, 128.8, 128.4, 127.6, 127.0, 127.0, 126.4, 118.8, 78.0, 41.2, 26.5, 18.7; HRMS (EI$^+$) calcd for $C_{24}H_{24}O$ (M^+): 328.1827; found 328.1829.

1,1-Bis(4-methoxyphenyl)-4-methylpent-3-en-1-ol (**4b**). The title compound was obtained according to the general procedure. Pale yellow oil; yield 77% (120.3 mg); IR (KBr): 3545, 3030, 1899, 1765, 1605, 1449, 1405, 1380, 1155, 975, 835, 745, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.33 (d, J = 8.0 Hz, 4H), 6.83 (d, J = 8.0 Hz, 4H), 5.04 (t, J = 8.0 Hz, 1H), 3.78(s, 6H), 2.95(d, J = 8.0 Hz, 2H), 2.45(s, 1H), 1.68(d, J = 4.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.3, 139.6, 129.7, 127.3, 118.8, 113.4, 112.5, 77.2, 55.2, 41.1, 26.2, 18.3; HRMS (EI$^+$) calcd for $C_{20}H_{24}O_3$ (M^+): 312.1725; found 312.1723.

4-Methyl-1-phenyl-1-m-tolylpent-3-en-1-ol (**4c**). The title compound was obtained according to the general procedure. Pale yellow oil; yield 76% (101.2 mg); IR (KBr): 3550, 3020, 2925, 1945, 1805, 1678, 1605, 1510, 1446, 1383, 1169, 1058, 1009, 879, 815, 761, 646 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.43 (d, J = 8.0 Hz, 2H), 7.34−7.17 (m, 5H), 7.10 (d, J = 8.0 Hz, 2H), 5.04 (t, J = 8.0 Hz, 1H), 2.99 (d, J = 8.0 Hz, 2H),2.56 (s, 1H), 2.30 (s, 3H), 1.66 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.65, 143.90, 138.20, 136.79, 129.72, 128.52, 127.06, 126.44, 119.02, 78.00, 41.30, 26.56, 21.44, 18.76; HRMS (EI$^+$) calcd for $C_{14}H_{12}O$ (M^+): 196.0888; found 196.0889.

4-Methyl-1-phenyl-1-(4′-phenyl)phenylpent-3-en-1-ol (**4d**). The title compound was obtained according to the general procedure. Pale yellow oil; yield 66% (108.4 mg); IR (KBr): 3555, 3055, 3040, 2910, 1950, 1670, 1600, 1465, 1380, 1259, 1168, 1055, 905, 750, 709, 649 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.48−7.11 (m, 14H), 4.98 (s, 1H), 2.95 (d, J = 7.1 Hz, 2H), 2.51 (s, 1H), 1.59(s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 147.3, 146.4, 141.2, 139.9, 138.4, 129.1, 128.6, 127.6, 127.4, 127.2, 127.2, 126.9, 126.4, 118.8, 78.0, 41.2, 26.5, 18.7; HRMS (EI$^+$) calcd for $C_{24}H_{24}O$ (M^+): 328.1827; found 328.1821.

1,1-Bis(4-chlorophenyl)-4-methylpent-3-en-1-ol (**4e**). The title compound was obtained according to the general procedure. Pale yellow oil; yield 63% (101.2 mg); IR (KBr): 3545, 3025, 1890, 1765, 1605, 1450, 1406, 1380, 1155, 971, 835, 748, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 7.28−7.23 (m, 4H), 7.20−7.15 (m, 4H), 4.90 (t, J = 6.8 Hz, 1H), 2.85 (d, J = 7.2 Hz, 2H), 2.48 (s, 1H), 1.60−1.54 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 145.1, 138.8, 132.8, 128.4, 127.5, 127.5, 117.7, 77.0, 40.7, 26.2, 18.3; HRMS (EI$^+$) calcd for $C_{18}H_{18}Cl_2O$ (M^+): 320.0735; found 320.0733.

1-(4-Methoxyphenyl)-4-methyl-1-phenylpent-3-en-1-ol (**4i**). The title compound was obtained according to the general procedure. Pale yellow oil; yield 72% (101.6 mg); IR (KBr): 3515, 3030, 2910, 2835, 2045, 1880, 1769, 1610, 1515, 1440, 1383, 1250, 1178, 905, 828, 769, 709 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.37−7.27 (m, 7H), 6.75−6.70 (m, 2H), 4.96 (s, 1H), 3.68 (s, 3H), 2.90 (d, J = 7.2 Hz, 2H), 2.45 (s, 1H), 1.59 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 158.4, 147.3, 139.3, 137.6, 128.1, 127.4, 126.7, 126.1, 118.7, 113.5, 77.5, 55.2, 41.0, 26.2, 18.4; HRMS (EI$^+$) calcd for $C_{19}H_{22}O_2$ (M^+): 282.1620; found 282.1618.

(E)-1,1,4-Triphenylbut-3-en-1-ol (**5a**).[23] The title compound was obtained according to the general procedure. Pale yellow oil; yield 68% (102.1 mg); IR (KBr): 3538, 3085, 2887, 1958, 1755, 1590, 1491, 1353, 1120, 968, 869, 776, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.51−7.45 (m, 4H), 7.39−7.35 (m, 3H), 7.30−7.24 (m, 7H), 6.61 (d, J = 15.8 Hz, 1H), 6.10−6.04 (m, 1H), 3.26 (d, J = 7.3 Hz, 2H), 2.64 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 146.8, 137.2, 135.6, 130.51, 128.8, 128.5, 127.8, 127.2, 126.8, 126.5, 126.3, 124.9, 119.4, 77.7, 46.3; HRMS (EI$^+$) calcd for $C_{22}H_{20}O$ (M^+): 300.1514; found 300.1516.

(E)-1,1-Bis(4-methoxyphenyl)-4-phenylbut-3-en-1-ol (**5b**). The title compound was obtained according to the general procedure. Pale yellow oil; yield 57% (102.7 mg); IR (KBr): 3550, 3083, 2885, 1955, 1751, 1599, 1485, 1383, 1190, 968, 867, 779, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.34 (d, J = 8.0 Hz, 4H), 7.27−7.13 (m, 5H), 6.83 (d, J = 8.0 Hz, 4H), 6.52 (d, J = 16.0 Hz, 1H), 6.10−6.00 (m, 1H), 3.74 (s, 6H), 3.14 (d, J = 8.0 Hz, 2H), 2.56 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 158.4, 139.2, 137.1, 135.0, 128.6, 127.5, 127.4, 126.3, 125.1, 113.5, 77.0, 55.3, 46.4; HRMS (EI$^+$) calcd for $C_{24}H_{24}O_3$ (M^+): 360.1725; found 360.1726.

(E)-1,4-DFiphenyl-1-p-tolylbut-3-en-1-ol (**5c**). The title compound was obtained according to the general procedure. Pale yellow oil; yield 70% (110.0 mg); IR (KBr): 3545, 3085, 2883, 1956, 1750, 1590, 1485, 1383, 1195, 978, 877, 789, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.51−7.05 (m, 14H), 6.54 (d, J = 16.0 Hz, 1H), 6.11−6.00 (m, 1H), 3.18 (d, J = 8.0 Hz, 2H), 2.54 (s, 1H), 2,30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 146.9, 143.8, 137.0, 136.6, 135.3, 129.0, 128.6, 128.3, 127.6, 127.0, 126.4, 126.1, 124.9, 77.4, 46.2, 21.1; HRMS (EI$^+$) calcd for $C_{23}H_{22}O$ (M^+): 314.1671; found 314.1672.

(E)-1-([1,1′-Biphenyl]-4-yl)-1,4-diphenylbut-3-en-1-ol (**5d**). The title compound was obtained according to the general procedure. Pale yellow oil; yield 67% (126.1 mg); IR (KBr): 3545, 3030, 2835, 1945, 1799, 1605, 1486, 1345, 1074, 988, 856, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.67−7.23 (m, 19H), 6.67 (d, J = 15.9 Hz, 1H), 6.19−6.14 (m, 1H), 3.33 (d, J = 7.2 Hz, 2H), 2.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): 146.8, 146.0, 141.0, 140.0, 137.2, 135.8, 129.1, 128.9, 128.6, 127.9, 127.6, 127.4, 127.3, 127.2, 126.8, 126.6, 126.4, 124.9, 77.7, 46.4; HRMS (EI$^+$) calcd for $C_{28}H_{24}O$ (M^+): 376.1827; found 376.1828.

(E)-1,1-Bis(4-chlorophenyl)-4-phenylbut-3-en-1-ol (**5e**). The title compound was obtained according to the general procedure. Pale yellow oil; yield 54% (99.7 mg); IR (KBr): 3555, 3083, 2885, 1959, 1751, 1599, 1485, 1386, 1195, 968, 877, 779, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.37 (d, J = 8.0 Hz, 4H), 7.34−7.15 (m, 9H), 6.56 (d, J = 16.0 Hz, 1H), 6.03−5.90 (m, 1H), 3.14 (d, J = 8.0 Hz, 2H), 2.60 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 144.7, 136.6, 136.1, 133.1, 128.6, 128.5, 127.9, 127.5, 126.3, 123.6, 76.8, 45.9; HRMS (EI$^+$) calcd for $C_{22}H_{18}Cl_2O$ (M+): 368.0735; found 368.0737.

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*(E)-1,1-Bis(4-fluorophenyl)-4-phenylbut-3-en-1-ol (**5f**).* The title compound was obtained according to the general procedure. Pale yellow oil; yield 37% (62.2 mg); IR (KBr): 3550, 3088, 2879, 1955, 1730, 1595, 1490, 1338, 1189, 978, 865, 786, 697 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.46−7.40 (m, 4H), 7.28−7.20 (m, 5H), 7.04−7.00 (m, 4H), 6.58 (d, J = 15.9 Hz, 1H), 6.03−5.99 (m, 1H), 3.18 (d, J = 7.3 Hz, 2H), 2.62 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ162.1 (d, $^1J_{C-F}$ = 244.0 Hz), 142.5 (d, $^3J_{C-F}$ = 3.0 Hz), 137.0, 136.0, 128.9, 128.1, 128.0, 126.6, 124.2, 115.3 (d, $^2J_{C-F}$ = 21 Hz), 77.1, 77.0, 46.5; HRMS (EI^+) calcd for $C_{22}H_{18}F_2O$ (M^+): 336.1326; found 336.1328.

*(E)-1-(4-Methoxyphenyl)-1,4-diphenylbut-3-en-1-ol (**5i**).* The title compound was obtained according to the general procedure. Pale yellow oil; yield 61% (100.7 mg); IR (KBr): 3555, 3083, 2880, 1955, 1755, 1599, 1485, 1383, 1195, 968, 870, 779, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.44 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.34−7.10 (m, 8H), 6.83 (d, J = 8.0 Hz, 2H), 6.53 (d, J = 16.0 Hz, 1H), 6.10−5.90 (m, 1H), 3.73 (s, 3H), 3.17 (d, J = 8.0 Hz, 2H), 2.58 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 158.5, 135.2, 128.6, 128.3, 127.6, 127.4, 126.9, 126.4, 126.1, 124.9, 113.6, 77.3, 55.3, 46.3. HRMS (EI^+) calcd for $C_{23}H_{22}O_2$ (M^+): 330.1620; found 330.1621.

*1,1-Diphenylpent-3-en-1-ol (**6a**)[24] (E/Z = 4:1).* The title compound was obtained according to the general procedure. Pale yellow oil; yield 70% (83.3 mg); ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.46−7.17 (m, 10H), 5.70−5.64 (m, 1H), 5.31−5.25 (m, 1H), 3.08−2.97 (m, 2H), 2.63 and 2.53 (s, 1H), 1.66−1.61 (m, 3H); ^{13}C NMR (100 MHz, CDCl3, TMS): 146.7, 131.8, 129.3, 128.1, 126.7, 126.7, 125.9, 125.5, 124.6, 77.6, 76.8, 45.5, 39.5, 18.1, 13.2; HRMS (EI^+) calcd for $C_{17}H_{18}O$ (M^+): 238.1358; found 238.1360.

*1-Phenyl-1-(p-tolyl)pent-3-en-1-ol (**6c**) (E/Z = 3.3:1).* The title compound was obtained according to the general procedure. Pale yellow oil; yield 65% (81.9 mg); ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.45−7.09 (m, 9H), 5.71−5.62 (m, 1H), 5.33−5.23 (m, 1H), 3.05 and 2.96 (d, J = 7.6 and 7.2 Hz, 2H), 2.59 and 2.49 (s, 1H), 2.29 (s, 3H), 1.66−1.61 (m, 3H); ^{13}C NMR (100 MHz, CDCl3, TMS): 146.9, 143.8, 136.3, 136.2, 131.6, 129.1, 128.8, 128.8, 128.0, 128.0, 126.6, 126.6, 125.9, 125.6, 124.7, 77.5, 76.7, 45.6, 39.5, 20.9, 18.1, 13.2.; HRMS (EI^+) calcd for $C_{18}H_{20}O$ (M^+): 252.1514; found 252.1510.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01466.

^1H and ^{13}C NMR spectra for all compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: zhangsl@suda.edu.cn.

Notes

The authors declare no competing financial interest.

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