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Nitroalkenes as Carbonyl Surrogates in Arylmethyl-homoallylic Alcohol Forming One-Pot Allylation Reactions in Water

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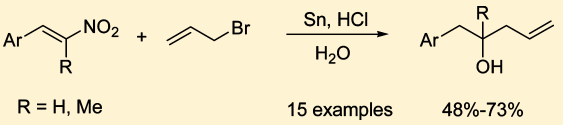
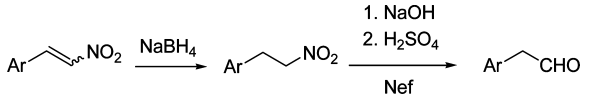
Supporting Information

ABSTRACT: A simple and practical approach has been developed for conducting direct, homoallylic alcohol forming allylation reactions of nitroalkenes in water. Employing the new method, various arylmethyl-homoallylic alcohols can be produced from the corresponding, readily prepared β-nitrostyrenes.



As a consequence of the fact that it is readily available and environmentally benign, water has received considerable attention recently as the solvent of choice for chemical reactions.[1] In particular, metal-mediated C−C bond forming reactions occurring in aqueous media have been intensively investigated.[2] In addition, nitroalkenes are known to be excellent Michael acceptors in conjugate addition reactions with organometallic reagents that are prepared in situ from allylic bromides and metals.[3] The general method for the conversion of nitroalkenes to carbonyl compounds involves a stepwise procedure that includes reduction to generate nitroalkanes followed by the Nef reaction (Scheme 1).[4] Only

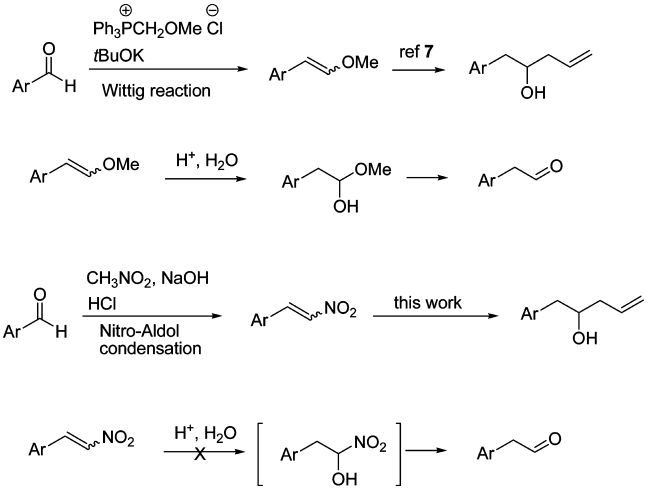
Scheme 1



a few examples of one-pot conversions of nitroalkenes to carbonyl compounds, utilizing reductive and oxidative procedures, have been described.[5] Although 2-arylacetaldehydes participate in allylation reactions that produce useful synthetic building blocks,[6] substrates of this type have limited commercially availability and exceptional lability.

We previously devised a simple method for the preparation of arylmethyl-homoallylic alcohols starting with β-methoxystyrenes,[7] which is superior to other more complicated approaches that utilize styrene oxide or methyl phenylacetate as phenylacetaldehyde equivalents.[8] Although β-methoxystyrenes can be readily prepared by using Wittig olefination reactions of the corresponding benzaldehydes, large scale production of these substances requires the use of large amounts of methoxymethyltriphenylphosphonium chloride and moisture-excluding conditions (Scheme 2). In contrast, β-nitrostyrenes are readily generated in a large scale manner through nitro-aldol condensation reactions of benzaldehydes followed by recrystallization. Until now, no reports exist describing the use of nitroalkenes as surrogates for carbonyl compounds in metal-mediated Barbier type allylation reactions. In the study described below, we have explored the potential for and

Scheme 2



scope of reactions in which nitroalkenes serve as substrates in organotin mediated allylation reactions in water. The results of this effort show that this process serves as a convenient method for the synthesis of arylmethyl-homoallylic alcohols.

In previous studies, we have shown that several noncarbonyl compounds such as enol ethers,[7] formalin, and aldoximes participate in aqueous metal-mediated Barbier type allylation reactions.[9] Apparently, water plays a key role in these processes by participating in the formation of reactive aldehydes from the corresponding enol ethers, formalin, or aldoximes, which then undergo allylation in the presence of allyl anion equivalents. In water, enol ethers undergo hydration via oxocarbonium ion intermediates, which readily react with water to form hemiacetals and finally aldehydes. In contrast, hydration of β-nitrostyrene that introduces a hydroxyl group at the β-position only occurs with difficulty under acidic hydrolysis. In addition, α,β-unsaturated nitroalkenes undergo reduction reactions to yield oximes when treated with the types of metals or metal

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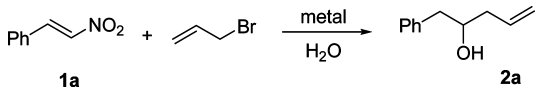
salts that are typically employed in Barbier type allylation reactions.[10] These features along with potential polymerization reactions of β-nitrostyrene are issues of concern in developing new Barbier type allylation reactions of β-nitrostyrenes.

In our initial investigations, we observed that treatment of β-nitrostyrene with allyl bromide and various metal combinations in aqueous solution either failed to generate or gave poor yields of products.[11] An exploratory study of tin mediated allylation reactions of β-nitrostyrene was then conducted employing allyl bromide and various in situ generated allylstannane sources (Table 1). The formation of the allylstannane intermediate in

Table 1. Tin-Mediated Allylation Reactions of β-Nitrostyrene[a]



1a 2a

entry	metal/additive	time (h)	yield (%)
1	Sn	4	0
2	Sn/$TiCl_3$	4	31
3	$SnCl_2$/$TiCl_3$	14	0
4[b]	Sn/HCl	1.5	47
5[c]	Sn/HCl	1.5	69
6[c]	Sn/HBr	1.5	55
7[c]	Sn/H_2SO_4	1	57
8[c]	Sn/CF_3SO_3H	1	53

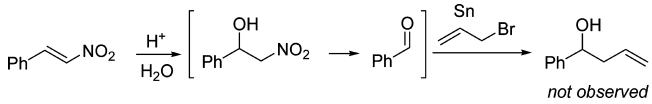
[a]Conditions: **1a** (1.0 mmol), allyl bromide (2.0 mmol), and indicated metal (2.0 mmol) in water (2.0 mL) at rt. [b]Conditions: To a suspension of **1a** (1.0 mmol), allyl bromide (2.0 mmol), and tin powder (2.0 mmol) in water (1.8 mL) at rt, HCl (0.2 mL) was added. [c]Conditions: To a suspension of allyl bromide (2.0 mmol), tin powder (2.0 mmol), and HCl (0.2 mL) in water (1.8 mL) at rt, **1a** (1.0 mmol) was added.

these processes by reaction of allyl bromide with tin appears to create a nonsufficiently acidic solution to promote hydration of the nitroalkene (Table 1, entry 1). It is known that conversion of a nitro into a carbonyl group requires an aqueous $TiCl_3$ solution with a pH lower than 1.[12] However, we observed that addition of 20% $TiCl_3$ in 3% hydrochloric acid to an aqueous solution of the in situ generated allylstannane does not promote formation of the aldehyde intermediate needed for the allylation reaction. Instead, the process occurring under these conditions results in the formation of a complicated mixture of products (Table 1, entry 2). In addition, the product forming reaction does not take place when allylstannane is generated in situ using less reactive $SnCl_2$ (Table 1, entry 3).

Taking into account the above findings, we envisioned that phenylacetaldehyde would be highly labile under reaction conditions in which $TiCl_3$ is present.[13] Therefore, a process, utilizing hydrochloric acid as a promoter, was probed. Indeed, a much cleaner reaction was found to take place (Table 1, entry 4 versus 2). Moreover, the efficiency of product formation in this reaction was observed to be strongly effected by the order in which the reagents are added (Table 1, entry 5 versus 4). The process carried out by adding the nitroalkene to the acid solution of the reagents gives a better yield than one in which hydrochloric acid is added to the mixture. The results of screening several strong acids (Table 1, entries 5–8) show that the reaction proceeds in each case, albeit in low yields (Table 1, entries 6–8), and that hydrochloric acid is the best promoter of the reaction, affording the arylmethyl-homoallylic alcohol product in 69% yield (entry 5). In addition, no significant yield is improved at higher temperature (**2a** was formed at 55 °C with 62% yield).

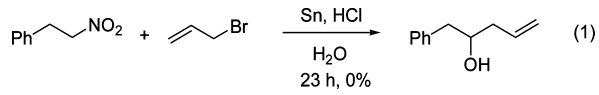
Although hydrolytic cleavage of nitroalkenes in strongly acidic aqueous solution has been described previously,[14] formation of the allylation product by reaction of benzaldehyde, which would be produced from β-nitrostyrene in this way, was not observed to occur under the optimal conditions (Scheme 3). The fact that high acidity is needed in order for the

Scheme 3



not observed

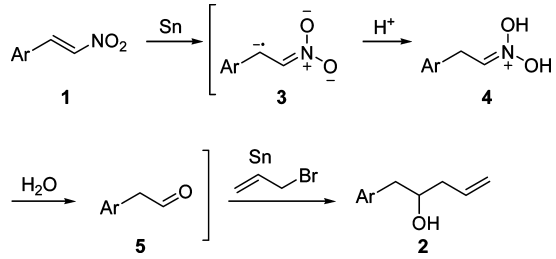
allylation reaction to occur[15] suggests that the presence of the carbon–carbon double bond in the substrate is crucial for the reaction. In accord with this proposal is the observation that (2-nitroethyl)benzene does not serve as a substrate for the allylation reaction (eq 1). Finally, comparison of the rates of



allylation reactions of aldoximes (overnight) vs nitroalkenes (1.5 h)[9b] demonstrates that tin-mediated allylation of nitroalkenes does not take place through aldoxime intermediates.

The observations described above have led to a proposal of a plausible mechanism shown in Scheme 4 for the allylation

Scheme 4. Plausible Mechanism



reaction.[16] The pathway involves initial generation of a nitrostyrene radical anion **3** by single electron transfer from tin followed by bis-protonation to produce the protonated nitronic acid **4**. Hydrolysis of **4** then occurs to generate the aldehyde intermediate **5**, which undergoes allylation to form the homoallylic alcohol **2**.

The scope of the newly developed allylation reaction was explored utilizing a variety of aryl-nitroalkenes (Table 2). The results show that this method can be used to prepare a wide variety of arylmethyl-homoallylic alcohols containing an assortment of *ortho*-, *meta*-, and *para*-positioned aryl ring substituents such as hydroxyl, methoxyl, chloro, bromo, ethyl, methyl, and cyano (Table 2, entries 2–13). It is worth noting that all of the nitroalkene substrates are insoluble in water yet the tin-mediated allylation reactions of these substances are performed using fully aqueous solutions. As expected, some of the low yields of the processes occurring in water can be significantly improved by utilizing THF, acetonitrile, and diethyl ether as cosolvents (Table 2, entries 8, 10, 12, and 14). A particularly significant finding, especially in light of the

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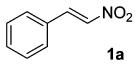
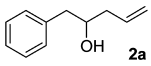
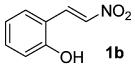
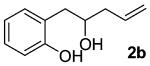
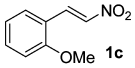
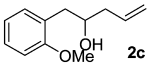
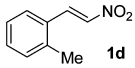
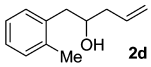
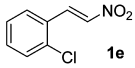
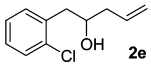
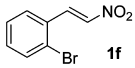
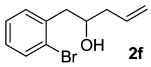
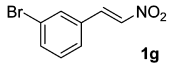
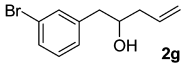
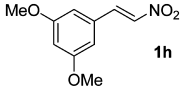
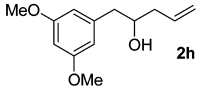
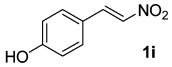
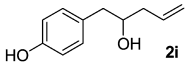
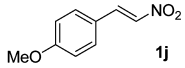
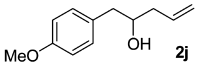
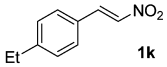
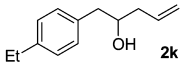
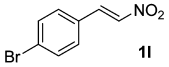
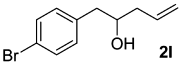
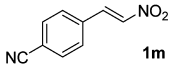
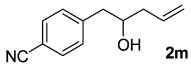
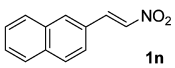
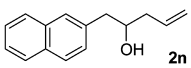
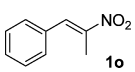
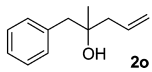
Table 2. Tin-Mediated Allylation Reactions of Arylnitroalkenes[a]

entry	substrate	product	yield (%)[a]
1	 **1a**	 **2a**	69
2	 **1b**	 **2b**	73
3	 **1c**	 **2c**	63
4	 **1d**	 **2d**	54
5	 **1e**	 **2e**	58
6	 **1f**	 **2f**	49
7	 **1g**	 **2g**	49
8	 **1h**	 **2h**	21 (59)[b]
9	 **1i**	 **2i**	60
10	 **1j**	 **2j**	35 (51)[c]
11	 **1k**	 **2k**	52
12	 **1l**	 **2l**	25 (50)[d]
13	 **1m**	 **2m**	68
14	 **1n**	 **2n**	21 (57)[d]
15	 **1o**	 **2o**	48

[a]Conditions: To a suspension of allyl bromide (2.0 mmol), tin powder (2.0 mmol), and HCl (0.2 mL) in water (1.8 mL) at rt, nitroalkene (1.0 mmol) was added. [b]Conditions: THF (1 mL) and water (0.8 mL) were used as solvent. [c]Conditions: CH_3CN (1 mL) and water (0.8 mL) were used as solvent. [d]Conditions: Et_2O (1 mL) and water (0.8 mL) were used as solvent.

fact that the preparation of α-aryl methyl ketones is a challenging synthetic problem,[17] is that reaction of nitroalkene **1o** generates a substance in this family (Table 2, entry 15).

In conclusion, the studies described above have led to the development of a new, simple, inexpensive, and potentially scalable method for the synthesis of arylmethyl-homoallylic alcohols from nitroalkenes.

EXPERIMENTAL SECTION

General Information and Materials. All commercially available chemicals were used without further purification. β-nitrostyrenes[18] were prepared from reported procedures. TLC analyses were run on a TLC glass plate (Silica gel 60 F254) and were visualized using UV and a solution of phosphomolybdic acid in ethanol (5 wt %) or *p*-anisaldehyde stain. Flash chromatography was performed using silica gel (70−230 mesh). ^1H and ^{13}C NMR spectra were recorded on a 300 MHz spectrometer. Chemical shifts are reported relative to $CHCl_3$ [δ_H 7.24, δ_C (central line) 77.0]. Mass spectra were recorded under fast atom bombardment (FAB), and high-resolution mass spectra were recorded by electron impact ionization with a magnetic sector analyzer.

General Procedure for Tin-Mediated Allylation Reactions of Nitroalkenes. To a mixture of allyl bromide (2.0 mmol), tin powder (2.0 mmol), and 37% aqueous hydrochloric acid (0.2 mL) in water (1.8 mL), β-nitrostyrene (1.0 mmol) was added. The resulting mixture was stirred at ambient temperature. The reaction was monitored by TLC until no starting material was observed, and normally the reaction was stirred at rt for 1.5 h. Et_2O (5 mL) was then added to the reaction, and the mixture was transferred to a separatory funnel. The organic layer was back extracted with Et_2O (5 mL). The combined organic layers were washed with brine (3 mL × 2), dried over $MgSO_4$, and concentrated in a rotary evaporator. The residue was purified by silica-gel chromatography using EtOAc/hexanes (1:25) as eluent to give the product.

1-Phenylpent-4-en-2-ol (2a, Table 2, entry 1). 112 mg (69%). An oil; TLC (EtOAc/hexanes (1:4)) R_f = 0.43; ^1H NMR (300 MHz, $CDCl_3$) δ 1.76 (br s, 1 H), 2.15−2.37 (m, 2 H), 2.67−2.84 (m, 2 H), 3.82−3.91 (m, 1 H), 5.11−5.17 (m, 2 H), 5.78−5.92 (m, 1 H), 7.19−7.32 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.1 (CH_2), 43.2 (CH_2), 71.6 (CH), 118.1 (CH_2), 126.4 (CH), 128.4 (2 × CH), 129.3 (2 × CH), 134.6 (CH), 138.3 (C). These data are in agreement with those reported in the literature.[7]

2-(2-Hydroxypent-4-enyl)phenol (2b, Table 2, entry 2). 130 mg (73%). An oil; TLC (EtOAc/hexanes (1:4)) R_f = 0.33; ^1H NMR (300 MHz, $CDCl_3$) δ 2.16−2.21 (m, 1 H), 2.30−2.37 (m, 1 H), 2.73−2.92 (m, 3 H), 3.97−4.01 (m, 1 H), 5.11−5.19 (m, 2 H), 5.76−5.81 (m, 1 H), 6.79−7.16 (m, 4 H), 8.21 (br s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 38.5 (CH_2), 41.2 (CH_2), 72.6 (CH), 117.1 (CH), 119.0 (CH_2), 120.3 (CH), 125.0 (C), 128.3 (CH), 131.5 (CH), 133.9 (CH), 155.3 (C). These data are in agreement with those reported in the literature.[7]

1-(2-Methoxyphenyl)pent-4-en-2-ol (2c, Table 2, entry 3). 121 mg (63%). An oil; TLC (EtOAc/hexanes (1:4)) R_f = 0.43; ^1H NMR (300 MHz, $CDCl_3$) δ 2.16 (s, 1 H), 2.19−2.30 (m, 2 H), 2.73 (dd, J = 13.5, 7.2 Hz, 1 H), 2.87 (dd, J = 13.5, 4.5 Hz, 1 H), 3.81 (s, 3 H), 3.85−3.95 (m, 1 H), 5.08−5.16 (m, 2 H), 5.80−5.92 (m, 1 H), 6.84−6.92 (m, 2 H), 7.12−7.23 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.9 (CH_2), 41.4 (CH_2), 55.2 (CH_3), 70.9 (CH), 110.4 (CH), 117.5 (CH_2), 120.6 (CH), 126.9 (C), 127.8 (CH), 131.3 (CH), 135.1 (CH), 157.5 (C); EI-MS m/z (rel intensity) 192 (M^+, 12), 151 (52), 122 (100), 91 (76). HRMS: $[M]^+$ calcd for $C_{12}H_{16}O_2$, 192.1150; found, 192.1156.

1-*o*-Tolylpent-4-en-2-ol (2d, Table 2, entry 4). 95 mg (54%). An oil; TLC (EtOAc/hexanes (1:4)) R_f = 0.50; ^1H NMR (300 MHz, $CDCl_3$) δ 1.70 (d, J = 2.1 Hz, 1 H), 2.22−2.39 (m, 5 H), 2.73 (dd, J = 13.8, 8.1 Hz, 1 H), 2.82 (dd, J = 13.8, 5.1 Hz, 1 H), 3.83−3.89 (m, 1 H), 5.12−5.19 (m, 2 H), 5.79−5.93 (m, 1 H), 7.11−7.17 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.6 (CH_3), 40.4 (CH_2), 41.4 (CH_2), 70.7 (CH), 118.1 (CH_2), 125.9 (CH), 126.6 (CH), 130.1 (CH), 130.4 (CH), 134.7 (CH), 136.6 (C), 136.7 (C); EI-MS m/z (rel intensity) 176 (M^+, 5), 135 (33), 117 (20), 106 (100). HRMS: $[M]^+$ calcd for $C_{12}H_{16}O$, 176.1201; found, 176.1197.

1-(2-Chlorophenyl)pent-4-en-2-ol (2e, Table 2, entry 5). 114 mg (58%). An oil; TLC (EtOAc/hexanes (1:4)) R_f = 0.45; ^1H NMR (300 MHz, $CDCl_3$) δ 1.71 (d, J = 3.9 Hz, 1 H), 2.21−2.35 (m, 2 H), 2.80 (dd, J = 13.8, 8.1 Hz, 1 H), 2.99 (dd, J = 13.8, 4.8 Hz, 1 H), 3.90−4.05 (m, 1 H), 5.12−5.19 (m, 2 H), 5.79−5.90 (m, 1 H), 7.14−7.36 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 40.8 (CH_2), 41.4 (CH_2), 70.0 (CH), 118.3 (CH_2), 126.7 (CH), 127.9 (CH), 129.6 (CH), 131.7 (CH), 134.3 (C), 134.4 (CH), 136.3 (C); EI-MS m/z (rel intensity) 196 (M^+, 3), 155 (62), 126 (90), 91 (100). HRMS: $[M]^+$ calcd for $C_{11}H_{13}ClO$, 196.0655; found, 196.0648.

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1-(2-Bromophenyl)pent-4-en-2-ol (2f, Table 2, entry 6). 118 mg (49%). An oil; TLC (EtOAc/hexanes (1:4)) R_f = 0.45; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.71 (d, J = 3.6 Hz, 1 H), 2.31−2.36 (m, 2 H), 2.81 (dd, J = 13.8, 8.1 Hz, 1 H), 3.00 (d, J = 13.8, 4.8 Hz, 1 H), 3.90−4.05 (m, 1 H), 5.12−5.19 (m, 2 H), 5.79−5.87 (m, 1 H), 7.04−7.10 (m, 1 H), 7.20−7.27 (m, 2 H), 7.53 (d, J = 7.8 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.4 (CH_2), 43.2 (CH_2), 70.0 (CH), 118.2 (CH_2), 124.8 (C), 127.3 (CH), 128.1 (CH), 131.7 (CH), 132.8 (CH), 134.4 (CH), 138.0 (C); EI-MS m/z (rel intensity) 240 (M^+, 5), 199 (34), 172 (58), 91 (100). HRMS: $[M]^+$ calcd for $C_{11}H_{13}BrO$, 240.0150; found, 240.0155.

1-(3-Bromophenyl)pent-4-en-2-ol (2g, Table 2, entry 7). 118 mg (49%). An oil; TLC (EtOAc/hexanes (1:4)) R_f = 0.38; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.73 (d, J = 3.3 Hz, 1 H), 2.16−2.31 (m, 2 H), 2.66 (dd, J = 13.8, 7.8 Hz, 1 H), 2.76 (dd, J = 13.8, 4.8 Hz, 1 H), 3.75−3.90 (m, 1 H), 5.10−5.17 (m, 2 H), 5.75−5.87 (m, 1 H), 7.13−7.18 (m, 2 H), 7.32−7.37 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.2 (CH_2), 42.7 (CH_2), 71.3 (CH), 118.4 (CH_2), 122.4 (C), 128.0 (CH), 129.5 (CH), 129.9 (CH), 132.3 (CH), 134.2 (CH), 140.8 (C); EI-MS m/z (rel intensity) 240 (M^+, 7), 199 (28), 170 (63), 91 (100). HRMS: $[M]^+$ calcd for $C_{11}H_{13}BrO$, 240.0150; found, 240.0145.

1-(3,5-Dimethoxyphenyl)pent-4-en-2-ol (2h, Table 2, entry 8). 131 mg (59%). An oil; TLC (EtOAc/hexanes (1:4)) R_f = 0.25; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.77 (br s, 1 H), 2.16−2.34 (m, 2 H), 2.62 (dd, J = 13.5, 8.1 Hz, 1 H), 2.73 (dd, J = 13.5, 4.8 Hz, 1 H), 3.75 (s, 6 H), 3.77−3.88 (m, 1 H), 5.10−5.17 (m, 2 H), 5.78−5.91 (m, 1 H), 6.31−6.36 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.1 (CH_2), 43.5 (CH_2), 55.2 (2 × CH_3), 71.5 (CH), 98.4 (CH), 107.3 (CH), 118.0 (CH_2), 134.6 (2 × CH), 140.6 (C), 160.8 (2 × C); EI-MS m/z (rel intensity) 222 (M^+, 9), 204 (15), 181 (17), 152 (100). HRMS: $[M]^+$ calcd for $C_{13}H_{18}O_3$, 222.1256; found, 222.1249.

4-(2-Hydroxypent-4-enyl)phenol (2i, Table 2, entry 9). 107 mg (60%). Pale yellow solid, mp 61−62 °C; TLC (EtOAc/hexanes (1:4)) R_f = 0.23; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.77 (br s, 1 H), 2.17−2.34 (m, 2 H), 2.62 (dd, J = 13.8, 8.1 Hz, 1 H), 2.74 (dd, J = 13.8, 4.8 Hz, 1 H), 3.78−3.88 (m, 1 H), 5.10−5.16 (m, 2 H), 5.50 (br s, 1 H), 5.77−5.90 (m, 1 H), 6.73 (d, J = 9.3 Hz, 2 H), 7.04 (d, J = 9.3 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) 40.9 (CH_2), 42.1 (CH_2), 72.0 (CH), 115.4 (2 × CH), 118.2 (CH_2), 129.8 (C), 130.4 (2 × CH), 134.5 (CH), 154.4 (C); EI-MS m/z (rel intensity) 178 (M^+, 14), 137 (19), 108 (100), 91 (16). HRMS: $[M]^+$ calcd for $C_{11}H_{14}O_2$, 178.0994; found, 178.0986.

1-(4-Methoxyphenyl)pent-4-en-2-ol (2j, Table 2, enrty 10). 98 mg (51%). An oil; TLC (EtOAc/hexanes (1:4)) R_f = 0.45; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.75 (d, J = 3.3 Hz, 1 H), 2.18−2.32 (m, 2 H), 2.63 (dd, J = 13.8, 7.8 Hz, 1 H), 2.74 (dd, J = 13.8, 5.1 Hz, 1 H), 3.77 (s, 3 H), 3.78−3.84 (m, 1 H), 5.10−5.16 (m, 1 H), 5.77−5.89 (m, 1 H), 6.83 (d, J = 8.4 Hz, 2 H), 7.13 (d, J = 8.4 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.0 (CH_2), 42.3 (CH_2), 55.2 (CH_3), 71.7 (CH), 113.9 (2 × CH), 117.9 (CH_2), 130.3 (C), 134.7 (2 × CH), 134.7 (CH), 158.2 (C). These data are in agreement with those reported in the literature.[7]

1-(4-Ethylphenyl)pent-4-en-2-ol (2k, Table 2, entry 11). 99 mg (52%). An oil; TLC (EtOAc/hexanes (1:4)) R_f = 0.53; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.22 (t, J = 7.5 Hz, 3 H), 1.70 (d, J = 3.3 Hz, 1 H), 2.18−2.35 (m, 2 H), 2.58−2.71 (m, 3 H), 2.79 (dd, J = 13.5, 5.1 Hz, 1 H), 3.84−3.88 (m, 1 H), 5.11−5.17 (m, 2 H), 5.81−5.90 (m, 1 H), 7.12−7.13 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.5 (CH_3), 28.4 (CH_2), 41.1 (CH_2), 42.8 (CH_2), 71.7 (CH), 117.9 (CH_2), 128.0 (2 × CH), 129.3 (2 × CH), 134.7 (CH), 135.4 (C), 142.4 (C). These data are in agreement with those reported in the literature.[7]

1-(4-Bromophenyl)pent-4-en-2-ol (2l, Table 2, entry 12). 121 mg (50%). An oil; TLC (EtOAc/hexanes (1:4)) R_f = 0.38; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.85 (s, 1 H), 2.13−2.31 (m, 2 H), 2.63 (dd, J = 13.8, 7.8 Hz, 1 H), 2.85 (dd, J = 13.8, 5.1 Hz, 1 H), 3.78−3.83 (m, 1 H), 5.08−5.15 (m, 2 H), 5.77−5.80 (m, 1 H), 7.07 (d, J = 8.4 Hz, 2 H), 7.40 (d, J = 8.4 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.1 (CH_2), 42.4 (CH_2), 71.3 (CH), 118.2 (CH_2), 120.2 (C), 131.0 (2 × CH), 131.4 (2 × CH), 134.3 (CH), 137.4 (C). These data are in agreement with those reported in the literature.[19]

4-(2-Hydroxypent-4-enyl)benzonitrile (2m, Table 2, entry 13). 127 mg (68%). An oil; TLC (EtOAc/hexanes (1:4)) R_f = 0.20; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.78 (s, 1 H), 2.15−2.34 (m, 2 H), 2.75 (dd, J = 13.8, 7.8 Hz, 1 H), 2.85 (dd, J = 13.8, 4.5 Hz, 1 H), 3.78−3.92 (m, 1 H), 5.10−5.17 (m, 2 H), 5.74−5.85 (m, 1 H), 7.31 (d, J = 8.1 Hz, 2 H), 7.56 (d, J = 8.1 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.4 (CH_2), 43.0 (CH_2), 70.9 (CH), 110.1 (C), 118.7 (CH_2), 118.9 (C), 130.1 (2 × CH), 132.0 (2 × CH), 133.9 (CH), 144.4 (C); EI-MS m/z (rel intensity) 187 (M^+, 0.1), 146 (32), 118 (21), 117 (100). HRMS: $[M]^+$ calcd for $C_{12}H_{13}NO$, 187.0997; found, 187.0990.

1-(Naphthalen-2-yl)pent-4-en-2-ol (2n, Table 2, entry 14). 121 mg (57%). An oil; TLC (EtOAc/hexanes (1:4)) R_f = 0.35; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.87 (br s, 1 H), 2.24−2.37 (m, 2 H), 2.88 (dd, J = 13.8, 7.8 Hz, 1 H), 2.98 (dd, J = 13.8, 5.1 Hz, 1 H), 3.90−4.05 (m, 1 H), 5.14−5.21 (m, 2 H), 5.82−5.93 (m, 1 H), 7.36 (dd, J = 8.4, 1.5 Hz, 1 H), 7.42−7.50 (m, 2 H), 7.67 (s, 1 H), 7.78−7.84 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.1 (CH_2), 43.3 (CH_2), 71.5 (CH), 118.0 (CH_2), 125.4 (CH), 126.0 (CH), 127.4 (CH), 127.5 (CH), 127.7 (CH), 127.8 (CH), 128.0 (CH), 132.2 (C), 133.4 (C), 134.6 (CH), 135.8 (C). These data are in agreement with those reported in the literature.[20]

2-Methyl-1-phenylpent-4-en-2-ol (2o, Table 2, entry 15). 85 mg (48%). An oil; TLC (EtOAc/hexanes (1:4)) R_f = 0.45; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.13 (s, 3 H), 1.53 (s, 1 H), 2.23 (dd, J = 7.2, 0.9 Hz, 2 H), 2.72 (d, J = 13.5 Hz, 1 H), 2.78 (d, J = 13.5 Hz, 1 H), 5.08−5.18 (m, 2 H), 5.84−5.98 (m, 1 H), 7.19−7.32 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.5 (CH_3), 46.2 (CH_2), 47.8 (CH_2), 72.0 (C), 118.7 (CH_2), 126.4 (CH), 128.1 (CH_2 × 2), 130.5 (CH_2 × 2), 134.0 (CH), 137.3 (C); EI-MS m/z (rel intensity) 176 (M^+, 5), 135 (33), 117 (20), 106 (100). These data are in agreement with those reported in the literature.[21]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Complete characterization data (^{1}H and ^{13}C NMR and mass spectral data) for all compounds. 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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