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Highly pH-Dependent Chemoselective Transfer Hydrogenation of α,β-Unsaturated Aldehydes in Water

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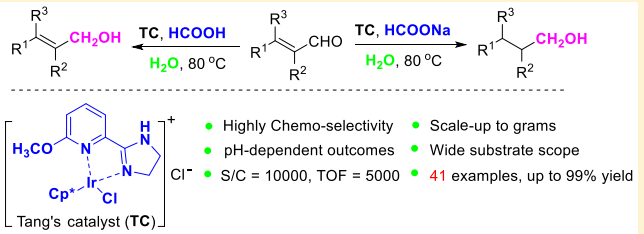
Supporting Information

ABSTRACT: The pH-dependent selective Ir-catalyzed hydrogenation of α,β-unsaturated aldehydes was realized in water. Using HCOOH as the hydride donor at low pH, the unsaturated alcohol products were obtained exclusively, while the saturated alcohol products were formed preferentially by employing HCOONa as the hydride donor at high pH. A wide range of functional groups including electron-rich as well as electron-poor substituents on the aryl group of α,β-unsaturated aldehydes can be tolerated, affording the corresponding products in excellent yields with high TOF values. High selectivity and yields were also observed for α,β-unsaturated aldehydes with aliphatic substituents. Our mechanistic investigations indicate that the pH value is critical to the chemoselectivity.



INTRODUCTION

Alcohols are versatile synthetic intermediates as well as ubiquitous structural motifs in natural products, materials, and bioactive compounds.[1] The reduction of aldehydes represents one of the most widely used methods to access the corresponding alcohols.[2] Among the available methods, transfer hydrogenation (TH) has proved to be one of the most efficient and practical methods. To date, many elegant TH processes have been developed for the conversion of α,β-unsaturated aldehydes to α,β-unsaturated alcohols by employing Ir,[3] Fe,[4] Mn,[5] Co,[6] Au,[7] and other transition-metal-based catalysts.[8] A number of protocols have also been developed for the reduction of both C═C bonds and C═O bonds of α,β-unsaturated aldehydes to produce saturated alcohols.[9]

Compared with the exclusive reduction of either the C═O bond or C═C bond, efforts toward highly efficient and chemoselective reduction of two unsaturated chemical bonds have been very limited.[10−14] Due to the preference for the hydrogenation of C═C bonds over C═O bonds,[15] selective TH of α,β-unsaturated aldehydes is challenging and more difficult to realize. Notably early excellent studies by Himeda and co-workers explored an iridium complex with 4,4′-dihydroxy-2,2′-bipyridine catalyzed TH of aldehydes/ketones.[10b] Frost and his group independently reported the Ru-catalyzed pH-dependent selective TH of α,β-unsaturated aldehydes in aqueous media.[11] The complex $DpRu(PTA)_2Cl_2$ was found to be effective for the selective hydrogenation of the C═O bond of cinnamaldehyde under acidic conditions, while the saturated alcohols were observed in the presence of sodium formate. However, the turnover frequencies (TOFs) were only 3.5 h^{-1} (Figure 1a). Recently, Dai and co-workers developed a method to obtain cinnamyl alcohol as the principal product using carbon-nanotube-supported PtFe nanoparticles.[12] The transformation was performed in moderate yield under 20 bar of hydrogen and exhibited poor selectivity toward C═C bond reduction (Figure 1b). Recently, Zaera and co-workers developed a strategy to provide cinnamyl alcohol as the major product with up to 85% yield by using alumina-supported platinum (SiO_2-ALD)-Pt/Al_2O_3 catalyst.[14]

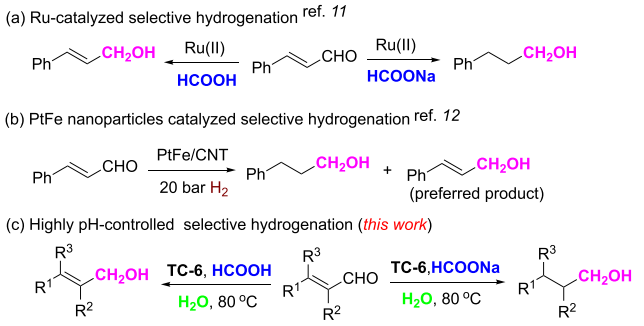


Figure 1. Selective TH of α,β-unsaturated aldehydes.

Despite these achievements, most previous methods have relatively low TOF, poor selectivity, and low yields.[10−15]

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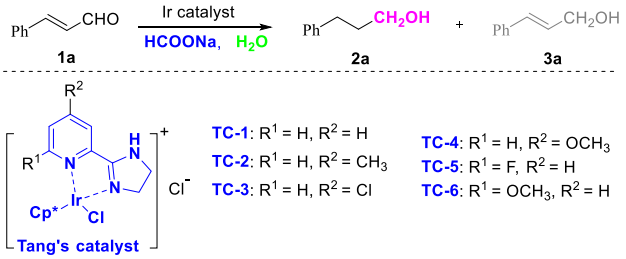
Therefore, developing a facile, efficient, and highly selective TH of unsaturated aldehydes is highly desirable. Herein, we describe a pH-dependent selective TH of unsaturated aldehydes by Ir catalyst in water. Both saturated alcohol (SA) and unsaturated alcohol (UA) products can be selectively obtained by the proper choice of pH; i.e., employing formic acid as a hydride donor yields the unsaturated alcohol products (>99/1 UA/SA), whereas utilizing sodium formate as the hydride donor promotes the formation of the saturated alcohol products (>99/1 SA/UA) (Figure 1c).

RESULTS AND DISCUSSION

We commenced our investigation on TH by subjecting (*E*)-3-phenylacrylaldehyde (**1a**) to conditions similar to those used for the previously reported hydrogenation reaction.[3a] Initially, various substituted Tang's catalysts were screened (Table 1,

Table 1. Optimization of the Conditions for Full Reduction[a]



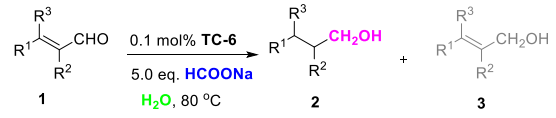
entry	[Ir]	time (h)	S/C ratio	TOF ($mol \cdot mol^{-1} \cdot h^{-1}$)	**2a**:**3a**[b]	yield of **2a**[c] (%)
1	TC-1	38	1000	26.4	99:1	91
2	TC-2	38	1000	26.4	97:3	90
3	TC-3	38	1000	26.4	97:3	90
4	TC-4	18	1000	27.8	98:2	92
5	TC-5	38	1000	26.4	98:2	91
6	TC-6	0.5	1000	2000	>99:1	93
7[d]	TC-6	38				
8[e]	TC-6	2	10000	5000	>99:1	91

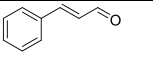
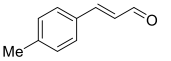
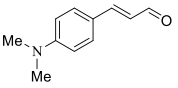
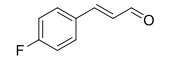
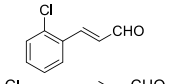
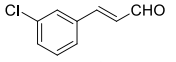
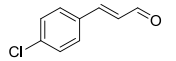
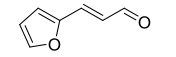
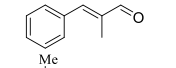
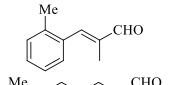
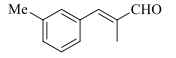
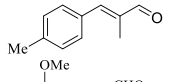
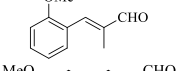
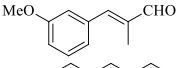
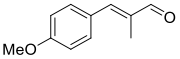
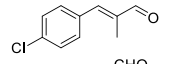
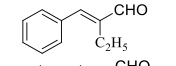
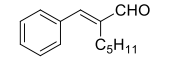
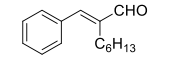
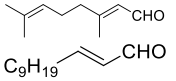
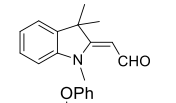
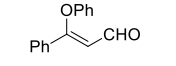
[a]Reaction conditions: **1a** (1.0 mmol), [Ir] (0.1 mol %), HCOONa (5.0 mmol), and H_2O (2 mL) at 80 °C. [b]Determined by GC-MS. [c]Yield of isolated product. [d]Performed at RT. [e]0.01 mol % Ir catalyst was used under N_2.

entries 2−6). In the presence of TC-1 catalyst and using HCOONa as the hydride donor at 80 °C for 38 h, the TH of **1a** afforded saturated alcohol **2a** in 91% yield with a 99/1 SA/UA ratio (Table 1, entry 1). Interestingly, when TC-6 was used as the catalyst, the yield of SA increased to 93% with a >99/1 SA/UA ratio (Table 1, entry 6). The TH reduction could be completed within 0.5 h, and SA **2a** was obtained as the only product. The effect of the reaction temperature was also studied. The transformation failed to proceed when the reaction was conducted at room temperature (Table 1, entry 7). Notably, decreasing the catalyst loading to 0.01 mol % affected the yield of product slightly under a N_2 environment (Table 1, entry 8).

Having identified the optimal reaction conditions, we next aimed to explore the generality of this TH protocol. As shown in Table 2, a variety of *β*-aryl substituted unsaturated aldehydes were exclusively reduced to the SA in excellent yields, and the observed selectivities were uniformly high (>99/1 SA/UA) regardless of the electron-neutral (**2a**, **2b**), -donating (**2c**), or

Table 2. Substrate Scope of Full Reduction[a]



Entry	**1**	**2**:**3**[b]	Yield of **2**[c]
1		>99:1	(**2a**) 93
2		97:3	(**2b**) 94
3		98:2	(**2c**) 96
4		>99:1	(**2d**) 98
5		>99:1	(**2e**) 95
6		>99:1	(**2f**) 94
7		>99:1	(**2g**) 96
8		>99:1	(**2h**) 90
9		>99:1	(**2i**) 97
10		>99:1	(**2j**) 96
11		98:2	(**2k**) 94
12		>99:1	(**2l**) 93
13		>99:1	(**2m**) 97
14		96:4	(**2n**) 95
15		>99:1	(**2o**) 94
16		97:3	(**2p**) 96
17		98:2	(**2q**) 91
18		5:2	(**2r**)92
19		2:1	(**2s**)91
20		9:1	(**2t**) 88
21		98:2	(**2u**)93
22		>99:1	(**2v**)95
23		--	--

[a]Reaction conditions: a mixture of **1** (1.0 mmol), TC-6 (0.1 mol %), HCOONa (5.0 mmol), and H_2O (2 mL) at 80 °C. [b]Determined by GC-MS. [c]Isolated yield.

-withdrawing (**2d**−**2g**) substituents at the *para*-, *meta*-, or *ortho*-positions of the phenyl group of cinnamaldehydes (Table 2, entries 1−7). The reduction of heterocycle substituted aldehydes, such as furan (**2h**), also proceeded efficiently in 90% yield with >99/1 SA/UA ratio (Table 2, entry 8). In

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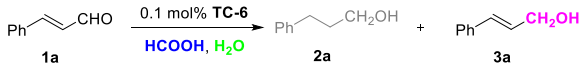
addition to substrates bearing a methyl or ethyl α-substituent, those with more sterically demanding substrates were also successfully transformed to the SA with high selectivity (**2i**–**2q**). A range of electron-donating (**2j**–**2o**) or -withdrawing (**2p**) β-aryl substituted aldehydes all afforded the corresponding SA efficiently with similarly high levels of selectivity. However, as the chain grows at the α-position, the reaction displays a much lower chemoselectivity (**2r**, **2s**). The possible reason is that the substitution groups at the α-position with high steric resistance affect the interaction between the C=C bond and iridium catalyst. Remarkably, high yields and selectivities of SA product were obtained for the aliphatic unsaturated aldehydes and TH occurred exclusively at the α-position C=C bond (**2t**, **2u**). It was noteworthy that a heterocyclic substituent at the β-position with high steric resistance also furnished a 95% yield with a >99/1 SA/UA ratio (**2v**). Unfortunately, the substituent of phenoxy at the β-position significantly affected the performance of the transformation (Table 2, entry 23).

The effect of pH was further investigated using HCOOH as a hydride donor (Table 3). First, different amounts of

Table 3. Optimization of the Conditions for Semi-Reduction[a]



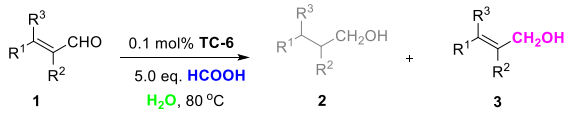
entry	hydrogen source	temperature (°C)	time (h)	3a:2a[b]	yield[c] (%)
1	1.0 equiv of HCOOH	80	18	>99:1	14
2	2.0 equiv of HCOOH	80	18	>99:1	31
3	3.0 equiv of HCOOH	80	18	>99:1	41
4	5.0 equiv of HCOOH	80	0.5	>99:1	91
5	5.0 equiv of HCOOH	rt	18	>99:1	25
6	5.0 equiv of HCOOH, 2.0 equiv of Et_3N	rt	0.5	62:38	92[d]
7	5.0 equiv of HCOOH, 5.0 equiv of Et_3N	rt	0.5	69:31	94[d]
8	5.0 equiv of HCOOH, 5.0 equiv of Et_3N	80	0.5	74:26	95[d]

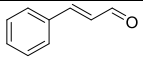
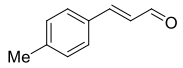
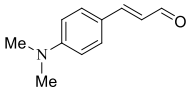
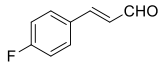
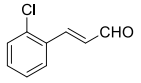
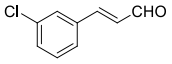
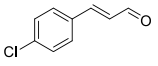
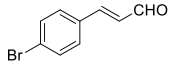
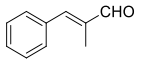
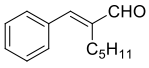
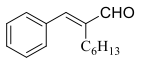
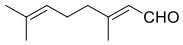
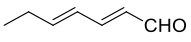
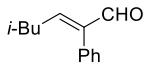
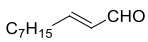
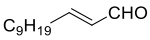
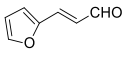
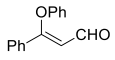
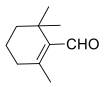
[a]Reaction conditions: **1a** (1.0 mmol), Ir catalyst (0.1 mol %), and H_2O (2 mL). [b]Determined by GC-MS. [c]Isolated yield of **3a**. [d]Mixed yield of **3a** and **2a**.

HCOOH were studied (Table 3, entries 1–4). When 1 equiv of formic acid was used as the hydride donor, the transformation proceeded with high selectivity to afford the unsaturated alcohol (>99/1 UA/SA) but with only 14% yield (Table 3, entry 1). To our delight, when the amount of HCOOH was increased to 5 equiv, the yield of UA was increased drastically up to 91% yield with high selectivity in a short period of 0.5 h time (Table 3, entry 4). Further optimization of the reaction temperature demonstrated that only 25% yield of UA was obtained when the reaction was conducted at room temperature (Table 3, entry 5). Additive Et_3N improved the yield at room temperature (Table 3, entries 6–8). Et_3N could promote the TH, affording UA in excellent yields but with poor selectivity, even under a reaction temperature of 80 °C (Table 3, entry 8).

With the optimized conditions in hand, we then turned our attention to the scope of α,β-unsaturated aldehyde derivatives (Table 4). A wide range of substrates bearing electron-donating, electron-withdrawing, and halogen substituents on the aromatic ring were tolerated (**3a**–**3h**). Moreover, excellent

Table 4. Substrate Scope of Semi-Reduction[a]



Entry	1	3:2[b]	Yield of 3(%)[c]
1		>99:1	(**3a**)91
2		>99:1	(**3b**)95
3		>99:1	(**3c**)94
4		>99:1	(**3d**)94
5		>99:1	(**3e**)97
6		>99:1	(**3f**)95
7		>99:1	(**3g**)96
8		>99:1	(**3h**)86
9		>99:1	(**3i**)91
10		>99:1	(**3j**)94
11		>99:1	(**3k**)93
12		>99:1	(**3l**)90
13		>99:1	(**3m**)93
14		>99:1	(**3n**)95
15		>99:1	(**3o**)91
16		>99:1	(**3p**)92
17		>99:1	(**3q**)92
18		100	(**3r**)92
19		>99:1	(**3s**)92

[a]Reaction conditions: a mixture of **1** (1.0 mmol), TC-6 (0.1 mol %), HCOOH (5.0 mmol), and H_2O (2 mL) at 80 °C. [b]Determined by GC-MS. [c]Isolated yield.

yields with high chemoselectivity were observed (>99/1 UA/SA). Additionally, substituents on the α-position could be tolerated, such as (*E*)-2-methyl-3-phenylacrylaldehyde and (*E*)-2-hexyl-3-phenylacrylaldehyde. These substrates afforded

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the corresponding products (**3i**–**3k**) in high yields and excellent selectivity under the reaction conditions. Both alkene and aliphatic substituted enals were also suitable for this reaction, delivering the UA product in excellent yields and >99/1 UA/SA ratios (**3l**–**3p**). In addition, a heterocyclic substituent is compatible with this protocol, giving the desired product of 92% yield and >99/1 UA/SA ratio (**3q**). More importantly, the presence of a β-disubstituent in **1** did not affect the overall efficiency and the completely unsaturated alcohol product was highly obtained (**3r**). Notably, 2,6,6-trimethylcyclohex-1-enecarbaldehyde with steric hindrance also worked well, resulting in the corresponding product **3s** in high yield and excellent chemoselectivity.

To demonstrate the synthetic utility of this transformation, the selective full reduction of 2-methyl-3-phenyl-propenal (**1i**) was performed at a gram scale (Figure 2). Product **2i** could be prepared by the proper choice of pH in excellent yields, further highlighting the utility of our protocol.

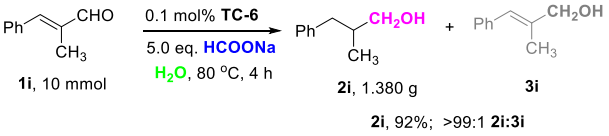

Figure 2. Gram-scale selective full conduction of **1i**.

There are two possibilities for the formation of a fully reduced product. (1) The C═O bond is reduced first to produce an allylic alcohol intermediate, and it is followed by C═C bond reduction. (2) The C═C bond is reduced first to produce a saturated aldehyde intermediate, and it is followed by C═O bond reduction. To elucidate the mechanism of our reaction, several control experiments were performed. The corresponding UA of **3a** was prepared and subjected to the standard reaction conditions. As indicated in Figure 3b, a trace

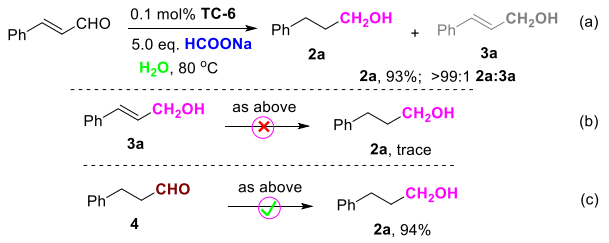

Figure 3. Preliminary mechanistic studies.

amount of SA product was formed. In contrast, the direct reduction of saturated aldehyde 3-phenylpropanal **4** afforded SA product **2a** in 94% yield (Figure 3c). This result rules out the involvement of allylic alcohol as an intermediate and suggests that the saturated aldehyde is likely the intermediate, which is consistent with previous reports.[16]

On the basis of our experimental results, a possible reaction mechanism is proposed in Figure 4. Initially, the intermediate **A** could be formed by ligand exchange from iridium catalyst, hydride donor, and water, followed by further extruding carbon dioxide to generate active catalyst **B**. Subsequent selective TH of α,β-unsaturated aldehydes is proposed, and the selectivity of C═C bond hydrogenation exhibits a strong dependence on the pH value. When HCOOH is used as the hydride donor (pH ≈ 2), the proton-activated α,β-unsaturated aldehydes can be preferentially coordinated to the iridium hydride **B** to form

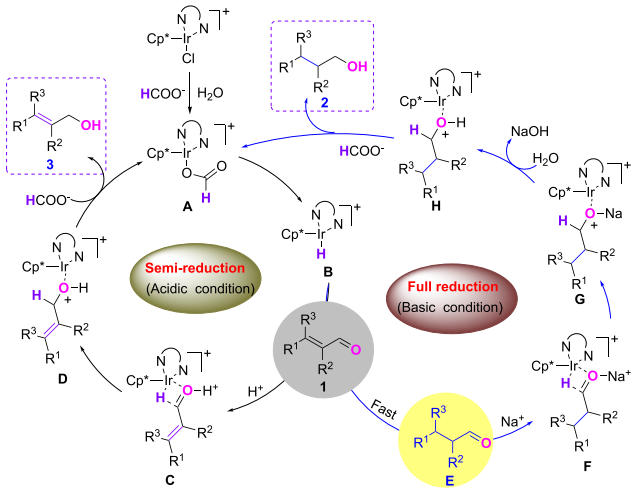

Figure 4. Proposed mechanism for the pH-dependent selectivity TH of α,β-unsaturated aldehydes.

intermediate **C** through a four-membered transition state, thus leading to selective reduction of the C═O bond of α,β-unsaturated aldehydes. Finally, ligand exchange between the intermediate **D** and formate anion gives the desired UA product **3** and regenerates **A** for the next cycle. When 5.0 equiv of HCOONa was employed as the hydride donor, the pH value of the aqueous solution is about 8. It is known that hydrogenation of C═C bonds is preferred over that of C═O bonds under basic conditions.[15] In our case, the active iridium catalyst **B** selectively reduced the C═C bond, giving rise to intermediate SA **E**. This reaction featured a fast reaction rate. The pathway was experimentally supported by TH of 3-phenylpropanal (Figure 3c), which suggested that the intermediate **E** might be formed before the C═O bond reduction. Subsequent C═O bond reduction resulted in intermediate **F** through a similar four-membered transition state. Finally, full reduction generated product **2** and released catalyst **A**.

CONCLUSIONS

In conclusion, we have developed a pH-dependent chemoselective TH of α,β-unsaturated aldehydes under mild conditions in water, affording SA or UA by simply changing the pH value. These results demonstrate that the pH value is critical to the chemoselectivity of the TH process. Further investigations on the reaction mechanism as well as exploration of asymmetric hydrogenation of α,β-unsaturated aldehydes are in progress.

EXPERIMENTAL SECTION

General Information. ^{1}H and ^{13}C NMR spectra were recorded using a 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, and $CDCl_3$ is solvent with TMS as the internal standard. GC-MS was obtained using electron ionization. TLC was performed by using commercially prepared 100–400 mesh silica gel plates, and visualization was effected at 254 nm. Starting materials of α-substituted α,β-unsaturated aldehydes were prepared according to previously reported methods.[17] Other starting materials of α,β-unsaturated aldehydes were commercially available.

General Procedure for Synthesis of Saturated Alcohols. In a 10 mL Schlenk tube, α,β-unsaturated aldehydes **1** (1 mmol) were added to a stirred solution of HCOONa (340 mg, 5 mmol) and TC-6 catalyst (0.55 mg, 0.1 mol %) in deionized water (2 mL) at 80 °C.

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The resulting suspension was vigorously stirred at 80 °C for 0.5 h. After completion of the reaction, the mixture was extracted with ethyl acetate (3 × 10 mL). The combined ethyl acetate layer was then dried over magnesium sulfate and concentrated in a vacuum. The resulting crude product was purified by silica gel chromatography using a mixture of 1/5 EtOA/petroleum ether as eluent to afford the saturated alcohol product selectively.

General Procedure for Synthesis of Unsaturated Alcohols. In a 10 mL Schlenk tube, formic acid (400 μL, 5 mmol) in four batches was added to a stirred solution of α,β-unsaturated aldehydes **1** (1 mmol) and TC-6 catalyst (0.1 mol %) in deionized water (2 mL) at 80 °C. The resulting suspension was stirred for 0.5 h. After completion of the reaction, the mixture was extracted with ethyl acetate (3 × 10 mL). The combined ethyl acetate layer was then dried over magnesium sulfate and concentrated in a vacuum. The resulting crude product was purified by silica gel chromatography using a mixture of EtOAc/petroleum ether (1/5) as eluent to afford the unsaturated alcohol product.

Procedure for Gram-Scale Selective Full Conduction of α,β-Unsaturated Aldehyde. A mixture of (*E*)-2-methyl-3-phenyl-acrylaldehyde **1i** (10 mmol, 1.460 g), TC-6 catalyst (0.1 mol %, 5.50 mg), HCOONa (50 mmol, 3.400 g, 5.0 equiv), and 20 mL of water was added to a 100 mL Schlenk tube, which was connected with a condenser sealing and then vigorously stirred together at 80 °C for 4 h. After completion of the reaction, the mixture was extracted with ethyl acetate (3 × 60 mL). The combined ethyl acetate layer was then dried over sodium sulfate and concentrated in a vacuum. After evaporation of the solvent, the crude mixture was purified by silica gel column chromatography to afford **2i** (1.380 g, >98% purity, 92% yield, >99/1 **2i**/**3i**).

3-Phenyl-propan-1-ol (***2a***). Colorless oil. Yield: 126.5 mg, 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.32 (m, 2H), 7.26−7.22 (m, 3H), 3.70 (t, *J* = 6.5 Hz, 2H), 2.74 (t, *J* = 8.0 Hz, 2H), 2.24 (s, 1H), 1.97−1.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 128.5, 128.4, 125.9, 62.2, 34.2, 32.1.

3-p-Tolyl-propan-1-ol (***2b***). Colorless oil. Yield: 141.1 mg, 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15−7.13 (m, 4H), 3.70 (t, *J* = 6.5 Hz, 2H), 2.71 (t, *J* = 8.0 Hz, 2H), 2.38 (s, 3H), 2.10 (s, 1H), 1.95−1.88 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 135.3, 129.1, 128.4, 62.2, 34.4, 31.7, 21.1.

3-(4-Dimethylamino-phenyl)-propan-1-ol (***2c***). Colorless oil. Yield: 171.8 mg, 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14−7.44 (m, 2H), 6.78−6.74 (m, 2H), 3.69 (t, *J* = 6.5 Hz, 2H), 2.95 (s, 6H), 2.65 (t, *J* = 8.0 Hz, 2H), 2.00 (s, 1H), 1.92−1.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 130.2, 129.1, 113.3, 62.4, 41.1, 34.5, 31.1.

3-(4-Fluoro-phenyl)-propan-1-ol (***2d***). Colorless oil. Yield: 151.0 mg, 98%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17−7.13 (m, 2H), 7.00−6.95 (m, 2H), 3.65 (t, *J* = 6.5 Hz, 2H), 2.83 (s, 1H), 2.68 (t, *J* = 8.0 Hz, 2H), 1.90−1.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 160.1, 137.5, 137.5, 129.8, 129.7, 115.2, 115.0, 61.8, 34.3, 31.2.

3-(2-Chloro-phenyl)-propan-1-ol (***2e***). Colorless oil. Yield: 161.5 mg, 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.26 (m, 5H), 4.28−4.22 (m, 1H), 3.86−3.81 (m, 1H), 3.75−3.69 (m, 1H), 3.20−3.15 (m, 1H), 3.11−3.05 (m, 1H), 2.39 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 129.4, 128.6, 127.0, 65.9, 64.9, 40.79.

3-(3-Chloro-phenyl)-ropan-1-ol (***2f***). Colorless oil. Yield: 159.8 mg, 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23−7.20 (m, 3H), 7.11−7.08 (m, 1H), 3.68 (t, *J* = 6.4 Hz, 2H), 2.72−2.69 (m, 2H), 1.91−1.85 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 134.1, 129.7, 128.6, 126.7, 126.1, 61.9, 33.9, 31.7.

3-(4-Chloro-phenyl)-propan-1-ol (***2g***). Colorless oil. Yield: 163.2 mg, 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 3.63 (t, *J* = 6.5 Hz, 2H), 3.27 (s, 1H), 2.66 (d, *J* = 8.0 Hz, 2H), 1.88−1.81 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 131.5, 129.8, 128.5, 61.7, 34.0, 31.4.

3-Furan-2-yl-propan-1-ol (***2h***). Light yellow oil. Yield: 113.4 mg, 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (br, 1H), 6.28−6.27 (m, 1H), 6.00 (d, *J* = 2.9 Hz, 1H), 3.66 (t, *J* = 6.4 Hz, 2H), 2.72 (t, *J* = 7.5 Hz, 2H), 1.93−1.86 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 140.9, 110.1, 105.0, 61.9, 30.9, 24.3.

2-Methyl-3-phenyl-propan-1-ol (***2i***). Colorless oil. Yield: 145.6 mg, 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.30 (m, 2H), 7.25−7.20 (m, 3H), 3.52 (q, *J* = 10.6 Hz, 2H), 2.79 (d, *J* = 13.4 Hz, 1H), 2.44 (d, *J* = 13.4 Hz, 1H), 1.97 (s, 1H), 0.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 129.2, 128.3, 125.9, 67.6, 39.6, 16.4.

2-Methyl-3-o-tolyl-propan-1-ol (***2j***). Colorless oil. Yield: 157.5 mg, 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25−7.21 (m, 4H), 3.64−3.53 (m, 2H), 2.89−2.84 (m, 2H), 2.49−2.35 (m, 4H), 2.07−1.97 (m, 1H), 1.03 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 136.3, 130.4, 13.0, 126.1, 125.8, 67.9, 37.0, 36.7, 19.6, 16.7.

2-Methyl-3-m-tolyl-propan-1-ol (***2k***). Colorless oil. Yield: 154.2 mg, 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.5 Hz, 1H), 7.11−7.06 (m, 3H), 3.62−3.51 (m, 2H), 2.82 (dd, *J* = 13.4, 6.1 Hz, 2H), 2.45−2.42 (m, 4H), 2.04−1.96 (m, 1H), 1.00 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 137.8, 130.1, 128.2, 126.7, 126.3, 67.6, 39.75 (s), 37.9, 21.5, 16.6.

2-Methyl-3-p-tolyl-propan-1-ol (***2l***). Colorless oil. Yield: 152.6 mg, 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20−7.15 (m, 4H), 3.61−3.50 (m, 2H), 2.92 (s, 1H), 2.85−2.80 (m, 1H), 2.47−2.42 (m, 4H), 2.02−1.96 (m, 1H), 1.00 (br, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.7, 135.3, 129.2, 129.0, 67.6, 39.3, 37.9, 21.1, 16.6.

3-(2-Methoxy-phenyl)-2-methyl-propan-1-ol (***2m***). Colorless oil. Yield: 174.7 mg, 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16−7.11 (m, 1H), 7.08 (d, *J* = 7.3 Hz, 1H), 6.85 (t, *J* = 7.4 Hz, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 3.72 (s, 3H), 3.42−3.34 (m, 2H), 3.27 (s, 1H), 2.71 (dd, *J* = 13.3, 6.7 Hz, 1H), 2.45 (dd, *J* = 13.3, 7.3 Hz, 1H), 1.96−1.91 (m, 1H), 0.90 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 131.2, 129.0, 127.3, 120.6, 110.4, 67.1, 55.3, 36.6, 33.5, 16.9.

3-(3-Methoxy-phenyl)-2-methyl-propan-1-ol (***2n***). Colorless oil. Yield: 171.1 mg, 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24−7.20 (m, 1H), 6.80−6.76 (m, 3H), 3.81 (s, 3H), 3.58−3.46 (m, 2H), 2.77 (dd, *J* = 13.4, 6.2 Hz, 1H), 2.40 (dd, *J* = 13.4, 8.3 Hz, 1H), 2.18 (s, 1H), 2.00−1.94 (m, 1H), 0.93 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 142.3, 129.2, 121.6, 114.9, 111.1, 67.7, 55.2, 39.8, 37.7, 16.5.

3-(4-Methoxy-phenyl)-2-methyl-propan-1-ol (***2o***). Colorless oil. Yield: 169.3 mg, 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H), 3.55−3.44 (m, 2H), 3.07 (s, 1H), 2.75 (dd, *J* = 13.5, 6.0 Hz, 1H), 2.37 (dd, *J* = 13.5, 8.2 Hz, 1H), 1.92 (dq, *J* = 13.0, 6.4 Hz, 1H), 0.93 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 132.8, 130.1, 113.7, 67.4, 55.2, 38.8, 37.9, 16.4.

3-(4-Chlorophenyl)-2-methylpropan-1-ol (***2p***). Colorless oil. Yield: 176.7 mg, 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 3.75 (s, 1H), 3.51−3.43 (m, 2H), 2.76 (dd, *J* = 13.5, 5.9 Hz, 1H), 2.35 (dd, *J* = 13.5, 8.4 Hz, 1H), 1.93−1.84 (m, 2H), 0.90 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 131.5, 130.6, 128.3, 67.1, 38.9, 37.7, 16.3.

2-Benzyl-butan-1-ol (***2q***). Colorless oil. Yield: 149.3 mg, 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.31 (m, 2H), 7.25−7.22 (m, 3H), 3.57 (d, *J* = 5.4 Hz, 2H), 2.69−2.66 (m, 2H), 1.85 (s, 1H), 1.80−1.74 (m, 1H), 1.48−1.38 (m, 2H), 0.98 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (102 MHz, $CDCl_3$) δ 140.9, 129.2, 128.3, 125.9, 64.4, 44.1, 37.3, 23.3, 11.4.

2-Benzyl-heptan-1-ol (***2r***). Colorless oil. Yield: 189.7 mg, 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−6.99 (m, 7.3H), 6.51 (s, 0.4H), 4.20 (s, 0.8H), 3.50 (d, *J* = 5.3 Hz, 2H), 2.62 (dd, *J* = 7.1, 3.1 Hz, 2H), 2.29−2.25 (m, 0.9H), 1.82−1.74 (m, 1H), 1.53−1.44 (m, 9H), 1.40−1.18 (m, 10.4H), 0.87 (br, 4.3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 140.9, 137.7, 129.2, 128.7, 128.3, 128.2, 126.4, 125.9, 125.2, 66.9, 64.8, 42.6, 37.7, 32.2, 32.1, 30.8, 28.8, 28.1, 26.7, 22.7, 22.5, 14.1, 14.0.

2-Benzyl-octan-1-ol (***2s***). Colorless oil. Yield: 200.4 mg, 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.21 (m, 7.7H), 6.56 (s, 0.5H), 4.25 (d, *J* = 1.3 Hz, 1H), 3.55 (d, *J* = 5.3 Hz, 2H), 2.67 (dd, *J* = 7.1, 2.2 Hz, 2H), 2.32 (br, 1H), 1.84−1.79 (m, 1.6H), 1.55−1.49 (m, 1H), 1.38−1.30 (m, 14H), 0.94−0.89 (m, 3.0 Hz, 4.8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 140.9, 137.6, 129.2, 128.7, 128.3, 128.2, 126.5, 125.9, 125.2, 67.0, 64.8, 42.6, 37.7, 31.9, 31.6, 30.8, 29.6, 29.6, 28.8, 28.4, 27.0, 22.7, 22.7, 14.2, 14.1.

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*3,7-Dimethyl-oct-6-en-1-ol (**2t**).* Colorless oil. Yield: 137.4 mg, 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.12−5.08 (m, 1H), 3.72−3.65 (m, 2H), 2.03−1.94 (m, 2H), 1.68 (d, J = 0.9 Hz, 3H), 1.63−1.58 (m, 4H), 1.41−1.31 (m, 2H), 1.27−1.16 (m, 2H), 0.91 (d, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.3, 124.7, 61.2, 39.9, 37.2, 29.1, 25.7, 25.5, 19.5, 17.7.

*Dodecan-1-ol (**2u**).* Colorless oil. Yield: 173.2 mg, 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.63 (t, J = 6.7 Hz, 2H), 1.58−1.55 (m, 3H), 1.37−1.26 (m, 18H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 63.0, 32.8, 31.9, 29.7, 29.6, 29.6, 29.6, 29.4, 29.3, 25.7, 22.7, 14.1.

*2-(1,3,3-Trimethyl-2,3-dihydro-1H-indol-2-yl)-ethanol (**2v**).* Purple oil. Yield: 194.9 mg, 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (td, J = 7.7, 1.3 Hz, 1H), 6.99 (dd, J = 7.3, 0.9 Hz, 1H), 6.73 (td, J = 7.4, 0.9 Hz, 1H), 6.51 (d, J = 7.8 Hz, 1H), 3.80−3.71 (m, 2H), 2.88 (dd, J = 7.3, 4.9 Hz, 1H), 2.71 (d, J = 4.1 Hz, 4H), 2.00−1.92 (m, 2H), 1.31 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.6, 139.4, 127.5, 121.6, 119.0, 108.4, 74.1, 60.8, 43.1, 35.3, 31.7, 27.0, 23.7.

*(E)-3-Phenylprop-2-en-1-ol (**3a**).* White solid. Yield: 121.9 mg, 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.20 (m, 5H), 6.55 (d, J = 15.9 Hz, 1H), 6.30 (dt, J = 15.9, 5.7 Hz, 1H), 4.24 (dd, J = 5.7, 1.5 Hz, 2H), 2.93 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 131.0, 128.7, 128.6, 127.7, 126.5, 63.5.

*3-p-Tolyl-prop-2-en-1-ol (**3b**).* White solid. Yield: 140.6 mg, 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 6.60 (d, J = 16.0 Hz, 1H), 6.33 (dt, J = 16.0, 5.8 Hz, 1H), 4.31 (dd, J = 5.8, 1.5 Hz, 2H), 2.63 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 134.0, 131.1, 129.3, 127.5, 126.4, 63.7, 21.2.

*3-(4-Dimethylamino-phenyl)-prop-2-en-1-ol (**3c**).* Yellow oil. Yield: 166.5 mg, 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.27−7.24 (m, 2H), 6.68−6.66 (m, 3H), 6.49 (d, J = 15.8 Hz, 1H), 6.15 (dt, J = 15.8, 6.2 Hz, 1H), 4.24 (dd, J = 6.2, 1.4 Hz, 2H), 2.94 (s, 6H), 2.07 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 131.7, 127.5, 125.2, 124.2, 112.5, 64.2, 40.6.

*3-(4-Fluoro-phenyl)-prop-2-en-1-ol (**3d**).* White solid. Yield: 142.9 mg, 94%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.29 (m, 2H), 7.03−6.98 (m, 2H), 6.57 (d, J = 15.9 Hz, 1H), 6.27 (dt, J = 15.9, 5.7 Hz, 1H), 4.30 (dd, J = 5.7, 1.4 Hz, 2H), 2.60 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6 (s), 161.1 (s), 132.9, 132.9, 129.8, 128.3, 128.2, 128.0, 127.9, 115.60, 115.4, 63.4.

*3-(2-Chloro-phenyl)-prop-2-en-1-ol (**3e**).* Colorless oil. Yield: 163.0 mg, 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62−7.59 (m, 2H), 7.35−7.31 (m, 2H), 7.29−7.25 (m, 1H), 6.74 (s, 1H), 4.29 (d, J = 0.8 Hz, 2H), 3.15 (s, 1H); ^{13}C NMR (102 MHz, $CDCl_3$) δ 134.2, 132.5, 129.3, 128.3, 128.2, 124.8, 67.6.

*3-(3-Chloro-phenyl)-prop-2-en-1-ol (**3f**).* Colorless oil. Yield: 159.6 mg, 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.27−7.23 (m, 3H), 6.57 (dt, J = 15.9, 1.5 Hz, 1H), 6.38 (dt, J = 15.9, 5.5 Hz, 1H), 4.34 (dd, J = 5.5, 1.5 Hz, 2H), 1.98 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 134.5, 130.1, 129.8, 129.5, 127.65, 126.4, 124.7, 63.4.

*3-(4-Chloro-phenyl)-prop-2-en-1-ol (**3g**).* White solid. Yield: 161.3 mg, 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.27 (m, 4H), 6.56 (dt, J = 15.9, 1.5 Hz, 1H), 6.33 (dt, J = 15.9, 5.6 Hz, 1H), 4.32 (dd, J = 5.6, 1.5 Hz, 2H), 2.28 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 133.3, 129.7, 129.2, 128.8, 127.7, 63.4.

*3-(4-Bromo-phenyl)-prop-2-en-1-ol (**3h**).* White solid. Yield: 182.3 mg, 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.44 (m, 2H), 7.26−7.24 (m, 2H), 6.57 (d, J = 15.9 Hz, 1H), 6.36 (dt, J = 15.9, 5.6 Hz, 1H), 4.33 (dd, J = 5.6, 1.5 Hz, 2H), 1.91 (s, 1H); ^{13}C NMR (102 MHz, $CDCl_3$) δ 135.6, 131.7, 129.8, 129.3, 128.0, 121.4, 63.5.

*2-Methyl-3-phenyl-prop-2-en-1-ol (**3i**).* Colorless oil. Yield: 134.7 mg, 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41−7.33 (m, 4H), 7.30−7.26 (m, 1H), 6.59 (s, 1H), 4.22 (s, 2H), 2.99 (s, 1H), 1.95 (d, J = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 137.7, 129.0, 128.2, 126.5, 124.9, 68.8, 15.4.

*2-Benzylidene-heptan-1-ol (**3j**).* Colorless oil. Yield: 191.9 mg, 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.34 (M, 2H), 7.29−7.25 (m, 3H), 6.56 (s, 1H), 4.25 (d, J = 1.3 Hz, 2H), 2.34−2.30 (m, 2H), 2.06 (s, 1H), 1.55−1.51 (m, 2H), 1.34−1.30 (m, 4H), 0.93−0.89 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 137.6, 128.7, 128.2, 126.4, 125.2, 67.0, 32.1, 28.8, 28.1, 22.5, 14.0.

*2-Benzylidene-octan-1-ol (**3k**).* Colorless oil. Yield: 202.9 mg, 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.34 (m, 2H), 7.29−7.23 (m, 3H), 6.56 (s, 1H), 4.25 (d, J = 1.4 Hz, 2H), 2.36−2.28 (m, 2H), 2.08 (s, 1H), 1.54−1.50 (m, 2H), 1.35−1.27 (m, 6H), 0.90 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 137.6, 128.7, 128.2, 126.5, 125.3, 67.0, 31.6, 29.5, 28.8, 28.4, 22.6, 14.1.

*3,7-Dimethyl-octa-2,6-dien-1-ol (**3l**).* Colorless oil. Yield: 138.7 mg, 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43−5.38 (m, 1H), 5.11−5.06 (m, 1H), 4.13 (d, J = 6.9 Hz, 1H), 4.07 (dd, J = 7.1, 0.8 Hz, 1H), 2.08−2.01 (m, 4H), 1.74−1.59 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 139.4, 132.3, 131.7, 124.5, 123.9, 123.8, 123.4, 59.2, 58.8, 39.5, 32.0, 26.5, 26.4, 25.6, 25.6, 23.4, 17.6, 17.6, 16.2.

*Hepta-2,4-dien-1-ol (**3m**).* Colorless oil. Yield: 104.3 mg, 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.21 (dd, J = 15.1, 10.3 Hz, 1H), 6.07−6.01 (m, 1H), 5.78−5.68 (m, 2H), 4.14 (d, J = 6.0 Hz, 2H), 2.12−2.06 (m, 3H), 1.01 (t, J = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.1, 132.0, 129.5, 128.4, 63.4, 25.6, 13.4.

*5-Methyl-2-phenyl-hex-2-en-1-ol (**3n**).* Colorless oil. Yield: 180.6 mg, 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.29 (m, 2H), 7.26−7.22 (m, 1H), 7.18−7.15 (m, 2H), 5.73−5.70 (m, 1H), 4.25 (s, 2H), 2.16 (br, 1H), 1.88 (t, J = 8.0 Hz, 2H), 1.64−1.58 (m, 1H), 0.84 (d, J = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9, 138.9, 128.8, 128.2, 127.8, 127.0, 68.0, 37.5, 28.8, 22.4.

*Dec-2-en-1-ol (**3o**).* Colorless oil. Yield: 142.1 mg, 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71−5.57 (m, 2H), 4.05 (d, J = 5.5 Hz, 2H), 2.42 (s, 1H), 2.06−2.01 (m, 2H), 1.39−1.27 (m, 10H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.2, 128.9, 63.5, 32.2, 31.8, 29.1, 22.6, 14.0.

*Dodec-2-en-1-ol (**3p**).* Colorless oil. Yield: 169.5 mg, 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72−5.58 (m, 2H), 4.07 (d, J = 5.3 Hz, 2H), 2.03 (dd, J = 13.8, 6.5 Hz, 2H), 1.85 (s, 1H), 1.32−1.27 (br, 14H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.4, 128.8, 63.7, 32.2, 31.9, 29.6, 29.5, 29.3, 29.2, 29.2, 22.7, 14.1.

*3-Furan-2-yl-prop-2-en-1-ol (**3q**).* Yellow oil. Yield: 114.1 mg, 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.27 (m, 1H), 6.48−6.44 (m, 1H), 6.39 (dd, J = 3.3, 1.9 Hz, 1H), 6.33−6.26 (m, 2H), 4.31 (dd, J = 5.5, 1.3 Hz, 2H), 1.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 142.0, 127.2, 119.3, 111.3, 108.03, 63.3.

*3-Phenoxy-3-phenyl-prop-2-en-1-ol (**3r**).* Yellow solid. Yield: 208.0 mg, 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.24−7.09 (m, 2H), 7.20−7.11 (m, 5H), 6.87−6.84 (m, 3H), 5.96 (t, J = 6.8 Hz, 1H), 4.26 (d, J = 6.7 Hz, 2H), 1.80 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 150.8, 134.5, 129.7, 128.7, 128.6, 125.8, 122.0, 116.1, 115.7, 57.7.

*(2,6,6-Trimethyl-cyclohex-1-enyl)-methanol (**3s**).* Colorless oil. Yield: 141.8 mg, 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.13 (s, 2H), 1.97 (t, J = 6.3 Hz, 2H), 1.74 (s, 3H), 1.61−1.58 (m, 2H), 1.46−1.43 (m, 2H), 1.37 (s, 1H), 1.04 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 133.5, 58.7, 39.4 (s), 34.0, 32.8, 28.5, 19.6, 19.3.

■ ASSOCIATED CONTENT

Supporting Information

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Typical experimental procedure and characterization for all products (PDF)

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Notes

The authors declare no competing financial interest.

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