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Radical Allylation of Aldehydes with Allenes by Photoredox Cobalt and Chromium Dual Catalysis

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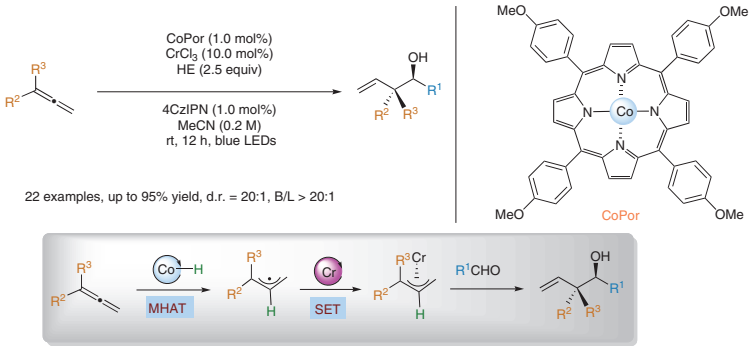

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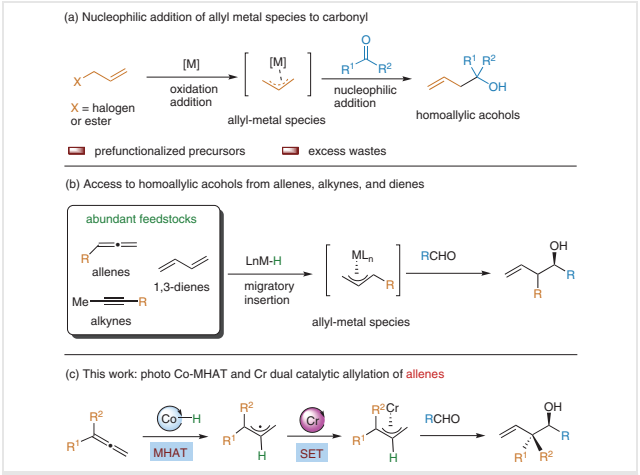
Abstract A dual cobalt and chromium photoredox-catalyzed allylation of aldehydes with allenes through a photo metal-hydride atom transfer (MHAT) process has been developed to yield homoallylic alcohols with exceptional diastereoselective control. This sustainable and efficient method holds significant promise for applications in the synthesis of valuable organic compounds.

Key words photocatalysis, metal-hydride atom transfer (MHAT), allenes, allylation, cobalt, homoallylic alcohols



Scheme 1 (a) Nucleophilic addition of allyl-metal to carbonyl; (b) traditional alkene functionalization via migrator insertion; (c) photo Co-MHAT and Cr dual catalysis for the allylation of allenes

Homoallylic alcohols are common building block for the synthesis of various natural products and pharmaceutically active compounds.[1] In light of the widespread applications of homoallylic alcohols, many synthetic methods have been developed for these high-value synthons. Classically, the most established approach is the addition of π-allylmetal species to carbonyl compounds.[2] Nevertheless, the tedious and uneconomical preparation of sensitive allylmetal complexes, that relies on pre-activated allylic halides and stoichiometric metallic reductants, has limited their broad application. This approach contradicts the principles of efficient synthesis and is not environmentally friendly (Scheme 1a). Consequently, it is essential to explore an efficient and sustainable approach to obtain homoallylic alcohols from abundant feedstock under mild reaction conditions.

Light olefins, such as 1,3-diene,[3] propyne,[3a,4] and allene,[3a,c,5] are products derived from petroleum cracking and have a substantial annual output, along with their derivatives. The direct conversion of these readily available feedstock into high-value products is of great importance in the field of chemical research.[6] For example, these feedstocks can undergo a migratory insertion process with H-metal species to form allyl-metal species, which then react with carbonyls to produce the corresponding homoallylic alcohols. In recent years, photoredox and transition metal catalysis has become an efficient synthetic strategy to access complex and attractive molecules from simple and abundant starting materials.[7] The photochemical reaction system efficiently controls the oxidation state of metals through single electron transfer (SET) processes. Recently, functionalizations of alkynes,[8] dienes,[9] and allenes[8a,10] by metallaphotoredox catalysis have been developed. Significantly, Glorius and co-workers introduced a dual photore-

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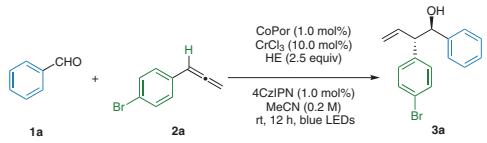
dox and chromium-catalyzed dialkylation of 1,3-dienes for the synthesis of homoallylic alcohols.[11] Xia and co-workers reported a nickel-catalyzed branch-selective reductive coupling of aldehydes to 1,3-dienes under visible light photoredox catalysis.[12] Breit and Xie described a general reductive allylation of aldehydes through coupling with allenes using an organophotoredox/nickel dual catalysis process (see Scheme 1b).[13]

The metal-hydride hydrogen atom transfer (MHAT), first reported by Halpern and Mukaiyama[14] and utilized by many research groups,[15] has proven to be an attractive strategy for conversion of alkenes into functional products. The mechanism of classical MHAT reactions generally begin with the oxidation of a low-valent metal to form a high-valent metal hydride, which subsequently undergoes hydrogen atom transfer to the alkene, generating a free carbon radical. This reactive radical further reacts with a radical acceptor to furnish the corresponding product. However, the generation of high-valent metal species typically requires a stoichiometric amount of chemical oxidant, frequently a peroxide or N-fluoro species.[16]

The integration of metallaphotoredox catalysis with MHAT has the potential to significantly enhance the versatility and applicability of traditional synthesis methods. For example, Ohmiya demonstrate Markovnikov hydroalkoxylation of unactivated alkenes using alcohols through a triple catalysis consisting of photoredox, cobalt, and Brønsted acid catalysts under visible light irradiation.[17] Luo presented the Giese reaction initiated by visible-light-facilitated dehydrogenated MHAT.[18] Teskey and co-workers reported the photoredox and MHAT-dual catalyzed reductive coupling of butadiene and a ketone.[19] These results have aroused our interest. We envisioned that an allyl radical could be generated by reaction between H-Co^{III} species and an allene via a MHAT process in the photocatalytic cycle. The resulting allyl radical would be rapidly captured by Cr^{II} to form an allyl-Cr^{III} intermediate. Then, the allyl-Cr^{III} complexes in the cross-coupling with aldehyde could yield homoallylic alcohol (Scheme 1c). Herein, we report the dual Co/Cr photoredox-catalyzed allylation of aldehydes with allenes to afford various homoallylic alcohols.

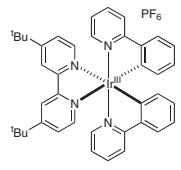
We chose 1-bromo-4-(propa-1,2-dien-1-yl)benzene (**2a**) as the allyl precursor and commenced our study with reaction of benzaldehyde (**1a**) (Table 1). After implementing extensive optimizations, we were pleased to discover that utilizing CoPor and $CrCl_3$ as metal catalysts, 4CzIPN as the organic photocatalyst, Hantzsch ester (HE) as the sacrificial electron donor, the reaction proceeded smoothly in MeCN, yielding the desired product **3a** in 85% yield with excellent diastereoselectivity 20:1 and >20:1 B/L ratio (Table 1, entry 1). Solvent screening revealed that MeCN was superior to DCM and THF, while the polar solvent DMF resulted in much decreased yield and diastereoselectivity (Table 1, entries 2–4). Replacing 4CzIPN with metal photocatalysts

Table 1 Reaction Optimization

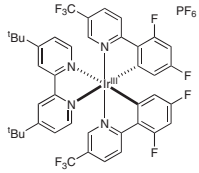


1a 2a 3a

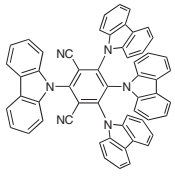
Entry[a]	Variation from standard conditions	Yield (%)[b]	d.r.[c]
1	none	85	20:1
2	DCM instead of MeCN	35	8:1
3	THF instead of MeCN	43	8:1
4	DMF instead of MeCN	11	5:1
5	**Ir-1** instead of 4CzIPN	63	7:1
6	**Ir-2** instead of 4CzIPN	62	3:1
7	5 mol% CoPor instead of 1 mol% CoPor	48	7:1
8	0.1 mol% CoPor instead of 1 mol% CoPor	26	>10:1
9	5 mol% $CrCl_3$ instead of 10 mol% $CrCl_3$	42	10:1
10	2.5 mol% $CrCl_3$ instead of 10 mol% $CrCl_3$	13	>20:1
11	1 mol% $CrCl_3$ instead of 10 mol% $CrCl_3$	0	
12	no light	0	
13	no CoPor	0	
14	no 4CzIPN	0	
15	no $CrCl_3$	0	
16	no HE	0	



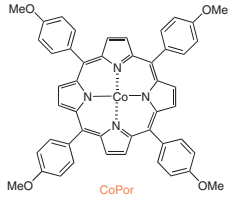
$Ir(ppy)_2(dtbbpy)PF_6$ **Ir-1**



$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ **Ir-2**



4CzIPN



CoPor

[a] *Reaction conditions*: **1a** (1.0 mmol, 1.0 equiv), **2a** (2.0 mmol, 2.0 equiv), CoPor (1.0 mol%), $CrCl_3$ (10.0 mol%), 4CzIPN (1.0 mol%), HE (2.5 mmol, 2.5 equiv), MeCN (5.0 mL), rt, blue LED light (10-W, 450 nm LEDs), 12 h.
[b] The yields were determined by ^1H NMR with 1,3,5-trimethoxybenzene as an internal standard.
[c] Diastereoselective ratio (d.r.) was determined by ^1H NMR spectroscopy of the crude mixture.

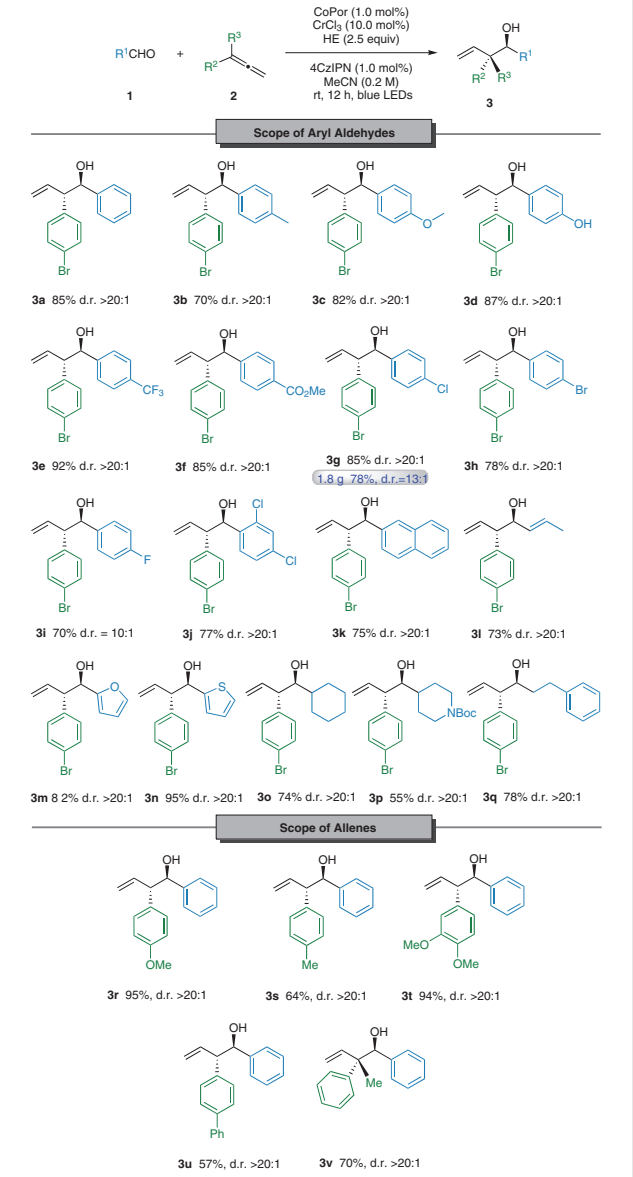
such as $Ir(ppy)_2(dtbbpy)PF_6$ (**Ir-1**) and $Ir((dF(CF_3)ppy)_2(dtbbpy)PF_6$ (**Ir-2**) exhibited modest yields and lower diastereoselectivities (Table 1, entries 5 and 6). Variation of the CoPor catalyst loading revealed that 1 mol% provided optimal results (Table 1, entries 1, 7, and 8). Increasing the

Co catalyst loading would accelerate the generation of allyl radicals, which cannot be adequately captured by Cr metal, eventually leading to a decrease in yield. Moreover, gradually decreasing the amount of $CrCl_3$ did not affect the diastereoselectivity, however, it led to significantly decreased yields of **3a** (Table 1, entries 9–11). Finally, a series of control experiments demonstrated that photocatalyst, $CrCl_3$, CoPor, Hantzsch ester, and blue LED were all indispensable for this allylation reaction (Table 1, entries 12–16).

With the optimized reaction conditions in hand, the substrate scope was investigated (Scheme 2). First, we explored the various aldehydes with the allene **2a** as coupling partner. A range of homoallylic alcohols were readily obtained. Benzaldehyde derivatives with varying electronic properties, including electron-neutral (**3a**), electron-donating (such as 4-methyl (**3b**), 4-methoxy (**3c**), and 4-hydroxy (**3d**)), and electron-withdrawing groups (such as CF_3 (**3e**) and CO_2Me (**3f**)), exhibited superior reactivity under the standard conditions and yielded the respective products with excellent diastereoselectivities and satisfactory yields. In addition, the halogen functionalities remained intact after the coupling. For examples, aryl aldehydes containing chloro (**3g**), bromo (**3h**), fluoro (**3i**), and 2,4-dichloro groups (**3j**), were all well tolerated. Using naphthalene-2-carbaldehyde and acrolein, the yields of related products (**3k**, **3l**) slightly decreased, while the diastereoselectivity remained high. Considering the wide presence of heterocyclic structures in the biologically important molecules, heterocyclic substrates furan-2-carbaldehyde and thiophene-2-carbaldehyde reacted smoothly with **2a** to give the homoallylic alcohol products in 82% and 95% yields, respectively (**3m**, **3n**). Notably, cyclic alkyl aldehydes (**3o**, **3p**) or linear aliphatic aldehydes (**3q**) were also compatible with this transformation.

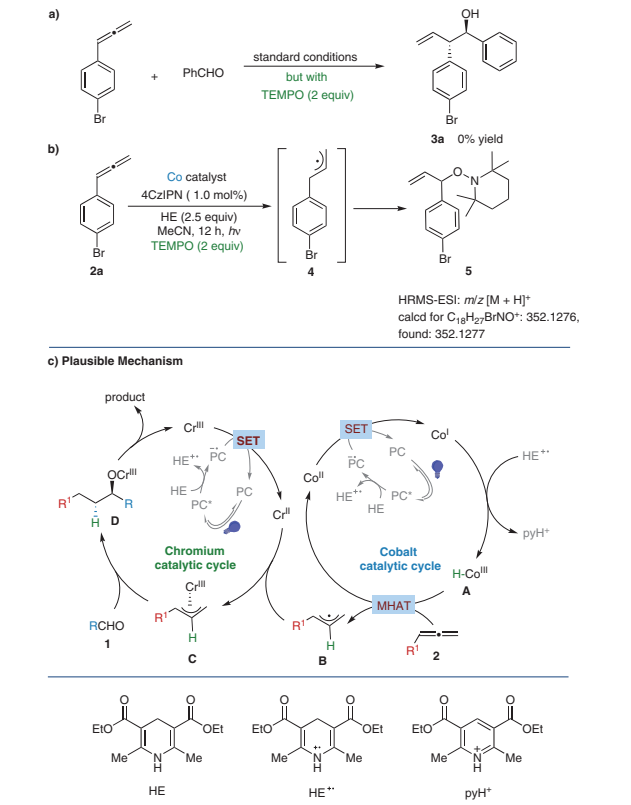
Next, we investigated the versatility of the allene component. Aryl allenes bearing electron-donating group successfully yielded the desired homoallylic alcohols through our protocol, demonstrating satisfactory diastereoselectivity (**3r–3u**). Notably, a 1,1′-disubstituted allene also effectively coupled with benzaldehyde under the optimized conditions to afford homoallylic alcohol **3v** in 70% yield and a diastereomeric ratio of 20:1. In order to determine the utility of this catalytic reaction, gram-scale reactions were carried out with satisfactory results. We successfully obtained product **3g** in 1.8 g (78%) yield with d.r. 13:1.

Further mechanistic experiments were conducted to confirm the radical nature of the reaction. It was discovered that 2,2,6,6-tetramethylpiperidinooxy (TEMPO) could effectively inhibit the reaction under standard conditions (Scheme 3a). When **2a** reacted without $CrCl_3$ and aldehydes, the allyl radical adduct was detected (Scheme 3b). Based on previous work and current results, a plausible reaction mechanism pathway is proposed (Scheme 3c). Under the irradiation of blue LEDs, the excited photocatalyst 4CzIPN* [$E_{1/2}$ (4CzIPN*/4CzIPN$^-$) = +1.43 V vs SCE][20] is quenched by HE to generate the reduced state 4CzIPN$^{-\bullet}$ and HE$^{+\bullet}$ ($E_{HE}^{+}/_{HE}$ = +1.0 V vs SCE).[21] The Co^{II} and Cr^{III} species subsequently undergo single-electron reduction with 4CzIPN$^{-\bullet}$ to give Co^{I} and Cr^{II} species, respectively. This Co^{I} captures H^+ to afford H-Co^{III} species **A**. On the other hand, the allyl radical **B** is generated from the metal-hydrogen atom transfer (MHAT) of the H-Co^{III} species to the allene, along with the



Scheme 2 Scope of allylation reactions. *Reagents and conditions*: CoPor (1.0 mol%), $CrCl_3$ (10.0 mol%), 4CzIPN (1.0 mol%), HE (2.5 mmol, 2.5 equiv), MeCN (5.0 mL), rt, blue LED light (10-W, 450 nm LEDs), 12 h. The diastereoselective ratio (d.r.) was determined by ^{1}H NMR spectroscopy of the crude mixture.

Co^{II} formed. Finally, the allyl radical is rapidly captured by Cr^{II} to form an allyl-Cr^{III} intermediate **C**, which couples with aldehydes to obtain the homoallyl alcohol product and Cr^{III}.



Scheme 3 Plausible reaction mechanism

In conclusion, we have developed a bimetallic Co and Cr photoredox catalysis enabling the carbonyl allylation with allenes involving the MHAT process of H-Co^{III} to allenes. This method utilizes commercially available catalyst, has a wide substrate scope, and accommodates various functional groups with excellent diastereoselectivity. It is poised to have further applications in the synthesis of drugs and natural products.

All reactions of were conducted in flame-dried glassware under a N_2 atmosphere using anhyd solvent. Commercially available reagents were used without further purification. Thin layer chromatography (TLC) was performed using Huanghai TLC silica gel plates HSG F254 and visualized using UV light, anisaldehyde, or $KMnO_4$. The photocatalytic reactions were performed on a WATTCAS Parallel Light Reactor (WP–TEC–1020L) with 10-W LED. ^1H and ^{13}C NMR spectra were recorded on a Bruker 400M spectrometer with internal standard of residual $CDCl_3$ (δ = 7.26, ^1H) and the central peak of $CDCl_3$ (δ = 77.00, ^{13}C). ESI mass spectra were obtained from an HPLC-Q-Tof mass spectrometer using acetonitrile as the mobile phase. UV-vis spectra were collected on an HP 8453 spectrometer.

Radical Allylation; General Procedure

To a solution of aldehyde **1** (1.0 mmol, 1.0 equiv), HE (2.5 mmol, 2.5 equiv), CoPor (1.0 mol%), $CrCl_3$ (10.0 mol%), and 4CzIPN (1.0 mol%) in MeCN (0.2 M) was added allene **2** (2.0 mmol, 2.0 equiv). The mixture was stirred at rt using 10-W blue LED for 12 h. The mixture was concentrated under reduced pressure to give a crude residue that was purified by chromatography (silica gel) to afford **3**.

Procedure for the synthesis of compound 5

An oven-dried Schlenk tube containing a stir bar was charged with TEMPO (1 mmol, 2.0 equiv), Co catalyst (0.0005 mmol, 0.1 mol%), 4CzIPN (0.005 mmol, 1.0 mol%) and HE (1.25 mmol, 2.5 equiv) in MeCN (5 mL, 0.1 M) under argon. Then, **2a** (0.5 mmol, 1.0 equiv) was added. The reaction was stirred at room temperature under 450 nm LED irradiation for 12 h. After completing, the reaction mixture was concentrated in vacuo.

HRMS-ESI: *m*/*z* [M + H]$^+$ calcd for $C_{18}H^{27}BrNO^+$: 352.1276, found: 352.1277.

2-(4-Bromophenyl)-1-phenylbut-3-en-1-ol (3a)

Chromatography (EtOAc/PE 1:10); colorless oil; yield: 128.4 mg (85%); R_f = 0.5 (EtOAc/PE 1:4).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.32 (m, 1 H), 7.32–7.30 (m, 1 H), 7.26–7.17 (m, 3 H), 7.16–7.09 (m, 2 H), 6.94–6.92 (m, 1 H), 6.92–6.90 (m, 1 H), 6.20 (ddd, *J* = 17.1, 10.2, 8.7 Hz, 1 H), 5.31–5.24 (m, 1 H), 5.24–5.18 (m, 1 H), 4.80 (d, *J* = 7.7 Hz, 1 H), 3.53 (t, *J* = 8.2 Hz, 1 H), 2.31 (s, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.52, 139.64, 137.33, 131.34, 130.06, 128.05, 127.62, 126.61, 120.40, 118.70, 77.06, 58.39.

HRMS-ESI: *m*/*z* [M – OH]$^+$ calcd for $C_{16}H_{14}Br$: 285.0273; found: 285.0269.

2-(4-Bromophenyl)-1-(*p*-tolyl)but-3-en-1-ol (3b)

Chromatography (EtOAc/PE 1:10); colorless oil; yield: 110.6 mg (70%); R_f = 0.6 (EtOAc/PE 1:4).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.33 (s, 1 H), 7.31 (s, 1 H), 7.03 (s, 4 H), 6.93 (d, *J* = 8.4 Hz, 2 H), 6.19 (ddd, *J* = 17.1, 10.2, 8.7 Hz, 1 H), 5.30–5.24 (m, 1 H), 5.23–5.16 (m, 1 H), 4.77 (dd, *J* = 7.8, 2.5 Hz, 1 H), 3.53 (t, *J* = 8.2 Hz, 1 H), 2.29 (s, 3 H), 2.25 (d, *J* = 2.6 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 139.79, 138.53, 137.55, 137.23, 131.32, 130.09, 128.76, 126.53, 120.32, 118.52, 76.86, 58.27, 21.08.

HRMS-ESI: *m*/*z* [M – OH]$^+$ calcd for $C_{17}H_{16}Br$: 299.0430; found: 299.0434.

2-(4-Bromophenyl)-1-(4-methoxyphenyl)but-3-en-1-ol (3c)

Chromatography (EtOAc/PE 1:10); colorless oil; yield: 136.1 mg (82%); R_f = 0.3 (EtOAc/PE 1:4).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.31 (m, 1 H), 7.31–7.29 (m, 1 H), 7.07–7.05 (m, 1 H), 7.04–7.02 (m, 1 H), 6.92–6.91 (m, 1 H), 6.90–6.89 (m, 1 H), 6.77–6.75 (m, 1 H), 6.75–6.72 (m, 1 H), 6.19 (ddd, *J* = 17.0, 10.3, 8.8 Hz, 1 H), 5.30–5.26 (m, 1 H), 5.25–5.20 (m, 1 H), 4.75 (d, *J* = 8.0 Hz, 1 H), 3.76 (s, 3 H), 3.50 (t, *J* = 8.4 Hz, 1 H), 2.27 (s, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.91, 139.71, 137.67, 133.58, 131.33, 130.04, 127.81, 120.31, 118.59, 113.40, 76.64, 58.53, 55.15.

HRMS-ESI: *m*/*z* [M – OH]$^+$ calcd for $C_{17}H_{16}BrO$: 315.0375; found: 315.0379.

2-(4-Bromophenyl)-1-hydroxybut-3-en-1-yl)phenol (3d)

Chromatography (EtOAc/PE 1:10); colorless oil; yield: 133.6 mg (87%); R_f = 0.1 (EtOAc/PE 1:4).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.17 (s, 1 H), 7.39–7.37 (m, 1 H), 7.38–7.33 (m, 1 H), 7.10–7.08 (m, 1 H), 7.08–7.06 (m, 1 H), 7.00–6.98 (m, 1 H), 6.98–6.96 (m, 1 H), 6.60–6.58 (m, 1 H), 6.58–6.56 (m, 1 H), 6.20 (ddd, *J* = 17.2, 10.3, 8.1 Hz, 1 H), 5.24 (d, *J* = 4.5 Hz, 1 H), 5.03 (dd, *J* = 10.2, 1.5 Hz, 1 H), 4.87 (ddd, *J* = 17.2, 2.1, 1.1 Hz, 1 H), 4.66 (dd, *J* = 6.9, 4.5 Hz, 1 H), 3.50 (t, *J* = 7.6 Hz, 1 H).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 156.41, 142.24, 139.51, 134.86, 131.31, 131.14, 128.20, 119.37, 116.76, 114.79, 75.95, 57.43.

HRMS-ESI: *m*/*z* [M – OH]$^+$ calcd for $C_{16}H_{14}BrO$: 301.0223; found: 301.0220.

2-(4-Bromophenyl)-1-(4-(trifluoromethyl)phenyl)but-3-en-1-ol (3e)

Chromatography (EtOAc/PE 1:10); colorless oil; yield: 170.2 mg (92%); R_f = 0.4 (EtOAc/PE 1:4).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 8.1 Hz, 2 H), 7.38 (d, *J* = 8.4 Hz, 2 H), 7.27 (d, *J* = 8.0 Hz, 2 H), 6.95 (d, *J* = 8.4 Hz, 2 H), 6.19 (ddd, *J* = 17.0, 10.2, 8.8 Hz, 1 H), 5.33 (dd, *J* = 10.2, 1.3 Hz, 1 H), 5.24 (dt, *J* = 17.1, 1.2 Hz, 1 H), 4.88 (d, *J* = 6.6 Hz, 1 H), 3.51 (t, *J* = 8.2 Hz, 1 H), 2.42 (d, *J* = 2.4 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.48, 139.03, 136.57, 131.60, 131.15, 130.69, 129.95, 129.28 (d, *J* = 32.9 Hz), 128.34, 126.94, 126.75, 124.97 (q, *J* = 3.9 Hz).124.03 (d, *J* = 270.7 Hz Hz), 120.79, 119.42, 76.43, 58.49.

HRMS-ESI: *m*/*z* [M – H_3O]$^-$ calcd for $C_{17}H_{11}BrF_3$: 351.0002; found: 350.9999.

Methyl 4-(2-(4-Bromophenyl)-1-hydroxybut-3-en-1-yl)benzoate (3f)

Chromatography (EtOAc/PE 1:10); colorless oil; yield: 153.0 mg (85%); R_f = 0.3 (EtOAc/PE 1:4).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89–7.88 (m, 1 H), 7.87–7.86 (m, 1 H), 7.34–7.32 (m, 1 H), 7.32–7.30 (m, 1 H), 7.20–7.19 (m, 1 H), 7.18–7.17 (m, 1 H), 6.92–6.91 (m, 1 H), 6.90–6.89 (m, 1 H), 6.17 (ddd, *J* = 17.0, 10.2, 8.8 Hz, 1 H), 5.28 (dd, *J* = 10.2, 1.1 Hz, 1 H), 5.20 (dt, *J* = 17.1, 1.2 Hz, 1 H), 4.84 (d, *J* = 7.6 Hz, 1 H), 3.88 (s, 3 H), 3.49 (t, *J* = 8.2 Hz, 1 H), 2.48 (s, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.85, 146.68, 139.12, 136.73, 131.49, 129.95, 129.30, 126.59, 120.65, 119.16, 76.64, 58.42, 52.04.

HRMS-ESI: *m*/*z* [M – OH]$^+$ calcd for $C_{18}H_{16}BrO_2$: 343.0328; found: 343.0326.

2-(4-Bromophenyl)-1-(4-chlorophenyl)but-3-en-1-ol (3g)

Chromatography (EtOAc/PE 1:10); colorless oil; yield: 128.4 mg (85%); R_f = 0.5 (EtOAc/PE 1:4).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.34 (m, 1 H), 7.34–7.32 (m, 1 H), 7.21–7.19 (m, 1 H), 7.19–7.17 (m, 1 H), 7.07–7.05 (m, 1 H), 7.05–7.03 (m, 1 H), 6.93–6.91 (m, 1 H), 6.90–6.88 (m, 1 H), 6.16 (ddd, *J* = 17.0, 10.2, 8.8 Hz, 1 H), 5.29 (dd, *J* = 10.2, 0.9 Hz, 1 H), 5.22 (dt, *J* = 17.1, 1.2 Hz, 1 H), 4.76 (d, *J* = 7.8 Hz, 1 H), 3.45 (t, *J* = 8.3 Hz, 1 H), 2.35 (s, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 139.97, 139.21, 136.97, 133.26, 131.51, 129.97, 128.19, 127.97, 120.62, 119.12, 76.38, 58.56.

HRMS-ESI: *m*/*z* [M – OH]$^+$ calcd for $C_{16}H_{13}BrCl$: 318.9884; found: 318.9880.

1,2-Bis(4-bromophenyl)but-3-en-1-ol (3h)

Chromatography (EtOAc/PE 1:10); colorless oil; yield: 297.2 mg (78%); R_f = 0.4 (EtOAc/PE 1:4).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.34 (m, 2 H), 7.34–7.32 (m, 2 H), 7.03–6.98 (m, 1 H), 7.01–6.96 (m, 1 H), 6.94–6.89 (m, 1 H), 6.92–6.87 (m, 1 H), 6.16 (ddd, *J* = 17.1, 10.2, 8.8 Hz, 1 H), 5.32–5.26 (m, 1 H), 5.22 (dt, *J* = 17.0, 1.2 Hz, 1 H), 4.75 (d, *J* = 7.8 Hz, 1 H), 3.45 (t, *J* = 8.3 Hz, 1 H), 2.30 (s, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 140.49, 139.18, 136.91, 131.50, 131.11, 129.97, 128.31, 121.42, 120.62, 119.12, 76.39, 58.46.

HRMS-ESI: *m*/*z* [M – H_2O]$^-$ calcd for $C_{16}H_{12}Br_2$: 362.9212; found: 362.9213.

2-(4-Bromophenyl)-1-(4-fluorophenyl)but-3-en-1-ol (3i)

Chromatography (EtOAc/PE 1:10); colorless oil; yield: 112.0 mg (70%); R_f = 0.5 (EtOAc/PE 1:4).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.31 (m, 1 H), 7.34–7.29 (m, 1 H), 7.13–7.03 (m, 2 H), 6.95–6.85 (m, 4 H), 6.18 (ddd, *J* = 17.0, 10.2, 8.8 Hz, 1 H), 5.33–5.26 (m, 1 H), 5.28–5.19 (m, 1 H), 4.77 (dd, *J* = 8.0, 2.2 Hz, 1 H), 3.46 (t, *J* = 8.4 Hz, 1 H), 2.36 (d, *J* = 2.4 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.31, 160.87, 139.31, 137.17, 131.45, 131.15, 130.53, 129.96, 128.26, 120.53, 119.03, 115.01, 114.79, 76.40, 58.76.

HRMS-ESI: *m*/*z* [M – H_3O]$^-$ calcd for $C_{16}H_{11}BrF$: 301.0034; found: 301.0034.

2-(4-Bromophenyl)-1-(2,4-dichlorophenyl)but-3-en-1-ol (3j)

Chromatography (EtOAc/PE 1:10); colorless oil; yield: 142.1 mg (77%); R_f = 0.5 (EtOAc/PE 1:4).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 8.4 Hz, 1 H), 7.45–7.39 (m, 1 H), 7.42–7.37 (m, 1 H), 7.30–7.28 (m, 1 H), 7.27–7.23 (m, 1 H), 7.18–7.13 (m, 1 H), 7.16–7.10 (m, 1 H), 6.19 (ddd, *J* = 17.1, 10.2, 8.9 Hz, 1 H), 5.27 (d, *J* = 5.1 Hz, 1 H), 5.20 (dd, *J* = 10.3, 1.5 Hz, 1 H), 5.00 (dt, *J* = 17.1, 1.2 Hz, 1 H), 3.65 (dd, *J* = 8.9, 5.1 Hz, 1 H), 2.14 (s, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.16, 137.81, 131.69, 129.69, 120.24, 118.02, 77.94, 52.91, 39.65, 30.11, 26.50, 26.35, 26.24, 25.90.

HRMS-ES: *m*/*z* [M – H]$^-$ calcd for $C_{16}H_{12}BrCl_2O$: 368.9454; found: 368.9449.

2-(4-Bromophenyl)-1-(naphthalen-2-yl)but-3-en-1-ol (3k)

Chromatography (EtOAc/PE 1:10); colorless oil; yield: 132.8 mg (75%); R_f = 0.5 (EtOAc/PE 1:4).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77–7.66 (m, 3 H), 7.58 (s, 1 H), 7.46–7.37 (m, 2 H), 7.29–7.27 (m, 1 H), 7.27–7.21 (m, 2 H), 6.97–6.91 (m, 1 H), 6.95–6.89 (m, 1 H), 6.20 (ddd, *J* = 17.1, 10.3, 8.7 Hz, 1 H), 5.28–5.23 (m, 1 H), 5.19 (dt, *J* = 17.1, 1.2 Hz, 1 H), 4.95 (d, *J* = 7.6 Hz, 1 H), 3.62 (t, *J* = 8.1 Hz, 1 H), 2.05 (s, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 139.62, 139.02, 137.24, 132.99, 132.91, 131.42, 130.08, 127.95, 127.79, 127.59, 126.01, 125.85, 125.70, 124.52, 120.48, 118.84, 77.12, 58.22.

HRMS-ESI: *m*/*z* [M – OH]$^+$ calcd for $C_{20}H_{16}Br$: 335.0430; found: 335.0425.

(*E*)-3-(4-Bromophenyl)hepta-1,5-dien-4-ol (3l)

Chromatography (EtOAc/PE 1:10); colorless oil; yield: 97.1 mg (73%); R_f = 0.4 (EtOAc/PE 1:4).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.49 (m, 1 H), 7.49–7.47 (m, 1 H), 7.38–7.36 (m, 1 H), 7.36–7.34 (m, 1 H), 7.27–7.25 (m, 1 H), 7.24 (s, 1 H), 6.95–6.94 (m, 1 H), 6.94–6.91 (m, 1 H), 6.17 (ddd, *J* = 17.0, 10.2, 8.8 Hz, 1 H), 5.35–5.27 (m, 1 H), 5.26–5.19 (m, 1 H), 4.86 (d, *J* = 7.3 Hz, 1 H), 3.49 (t, *J* = 8.2 Hz, 1 H), 2.40 (d, *J* = 2.4 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 140.00, 137.51, 131.44, 131.02, 130.17, 128.51, 120.41, 118.15, 75.04, 56.51, 17.67.

HRMS-ESI: *m*/*z* [M – OH]$^+$ calcd for $C_{13}H_{14}Br$: 249.0273; found: 249.0269.

2-(4-Bromophenyl)-1-(furan-2-yl)but-3-en-1-ol (3m)

Chromatography (EtOAc/PE 1:10); colorless oil; yield: 119.7 mg (82%); R_f = 0.4 (EtOAc/PE 1:4).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.36 (m, 1 H), 7.36–7.34 (m, 1 H), 7.31 (dd, *J* = 1.8, 0.8 Hz, 1 H), 7.03–7.01 (m, 1 H), 7.01–6.99 (m, 1 H), 6.22 (dd, *J* = 3.3, 1.9 Hz, 1 H), 6.19–6.11 (m, 1 H), 6.06 (d, *J* = 3.2 Hz, 1 H), 5.30–5.26 (m, 1 H), 5.23 (dt, *J* = 17.1, 1.3 Hz, 1 H), 4.85 (dd, *J* = 7.9, 3.1 Hz, 1 H), 3.80 (t, *J* = 8.1 Hz, 1 H), 2.26 (d, *J* = 4.1 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.83, 141.94, 139.38, 137.06, 131.46, 129.81, 120.61, 118.81, 110.12, 107.73, 70.72, 55.14.

HRMS-ESI: *m*/*z* [M – OH]$^+$ calcd for $C_{14}H_{12}BrO$: 275.0066; found: 275.0063.

2-(4-Bromophenyl)-1-(thiophen-2-yl)but-3-en-1-ol (3n)

Chromatography (EtOAc/PE 1:10); colorless oil; yield: 146.8 mg (95%); R_f = 0.1 (EtOAc/PE 1:4).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.37 (m, 1 H), 7.36–7.34 (m, 1 H), 7.17 (dd, *J* = 5.0, 1.2 Hz, 1 H), 7.02–7.00 (m, 1 H), 7.00–6.98 (m, 1 H), 6.83 (dd, *J* = 5.1, 3.5 Hz, 1 H), 6.66 (d, *J* = 3.2 Hz, 1 H), 6.19 (ddd, *J* = 17.1, 10.3, 8.5 Hz, 1 H), 5.32–5.28 (m, 1 H), 5.28–5.22 (m, 1 H), 5.08 (d, *J* = 7.9 Hz, 1 H), 3.59 (t, *J* = 8.2 Hz, 1 H), 2.50 (s, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.28, 139.43, 137.19, 131.45, 129.97, 126.34, 124.81, 124.65, 120.60, 119.03, 73.10, 58.70.

HRMS-ESI: *m*/*z* [M – OH]$^+$ calcd for $C_{14}H_{12}BrS$: 290.9838; found: 290.9835.

2-(4-Bromophenyl)-1-cyclohexylbut-3-en-1-ol (3o)

Chromatography (EtOAc/PE 1:10); colorless oil; yield: 114.7 mg (74%); R_f = 0.6 (EtOAc/PE 1:4).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.44 (m, 1 H), 7.43–7.41 (m, 1 H), 7.12–7.10 (m, 1 H), 7.09–7.07 (m, 1 H), 6.08 (ddd, *J* = 17.1, 10.2, 8.9 Hz, 1 H), 5.22 (dd, *J* = 10.3, 1.7 Hz, 1 H), 5.19–5.13 (m, 1 H), 3.52 (dd, *J* = 7.1, 4.0 Hz, 1 H), 3.45–3.38 (m, 1 H), 1.83–1.76 (m, 1 H), 1.74–1.67 (m, 2 H), 1.64–1.53 (m, 2 H), 1.26–1.04 (m, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.16, 137.81, 131.69, 129.69, 120.24, 118.02, 77.94, 77.32, 77.00, 76.68, 52.91, 39.65, 30.11, 26.50, 26.35, 26.24, 25.90.

HRMS-ESI: *m*/*z* [M – OH]$^+$ calcd for $C_{16}H_{20}Br$: 291.0743; found: 291.0740.

***tert*-Butyl 4-(2-(4-Bromophenyl)-1-hydroxybut-3-en-1-yl)piperidine-1-carboxylate (3p)**

Chromatography (EtOAc/PE 1:10); colorless oil; yield: 112.5 mg (55%); R_f = 0.2 (EtOAc/PE 1:4).

^{1}H NMR (400 MHz, CDCl3): δ = 7.46–7.44 (m, 1 H), 7.44–7.42 (m, 1 H), 7.11–7.08 (m, 1 H), 7.08–7.06 (m, 1 H), 6.09 (ddd, *J* = 17.1, 10.2, 9.0 Hz, 1 H), 5.23 (dd, *J* = 10.3, 1.6 Hz, 1 H), 5.17 (d, *J* = 17.1 Hz, 1 H), 4.15–4.03 (m, 2 H), 3.58–3.50 (m, 1 H), 3.45–3.34 (m, 1 H), 2.62–2.46 (m, 2 H), 1.85 (s, 1 H), 1.76–1.68 (m, 1 H), 1.54–1.48 (m, 1 H), 1.46–1.36 (m, 11 H), 1.33–1.23 (m, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.70, 140.73, 137.14, 131.83, 129.60, 120.47, 118.44, 79.24, 76.97, 52.88, 38.26, 28.83, 28.41, 26.10.

HRMS-ESI: *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{28}BrNNaO_3$: 432.1145; found: 432.1134.

4-(4-Bromophenyl)-1-phenylhex-5-en-3-ol (3q)

Chromatography (EtOAc/PE 1:10); colorless oil; yield: 128.7 mg (78%); R_f = 0.5 (EtOAc/PE 1:4).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.44 (m, 1 H), 7.44–7.43 (m, 1 H), 7.30–7.25 (m, 2 H), 7.22–7.17 (m, 1 H), 7.16–7.14 (m, 1 H), 7.13 (s, 1 H), 7.07–7.06 (m, 1 H), 7.06–7.04 (m, 1 H), 6.07 (ddd, *J* = 17.0, 10.2, 9.0 Hz, 1 H), 5.28–5.16 (m, 2 H), 3.78 (tt, *J* = 7.6, 3.8 Hz, 1 H), 3.31–3.21 (m, 1 H), 2.85 (ddd, *J* = 14.5, 9.1, 5.9 Hz, 1 H), 2.70–2.61 (m, 1 H), 1.89 (d, *J* = 3.5 Hz, 1 H), 1.73–1.61 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.76, 140.38, 137.59, 131.73, 129.66, 128.38, 128.31, 125.79, 120.48, 118.40, 72.93, 56.75, 36.05, 31.94.

HRMS-ESI: *m*/*z* [M – OH]$^+$ calculated for $C_{18}H_{18}Br$: 313.0586; found: 313.0578.

2-(4-methoxyphenyl)-1-phenylbut-3-en-1-ol (3r)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.25–7.12 (m, 5 H),7.01–6.93 (m, 2 H), 6.78–6.72 (m, 2 H), 6.22 (ddd, *J* = 17.1, 10.3, 8.8 Hz, 1 H), 5.25 (ddd, *J* = 10.2, 1.7, 0.7 Hz, 1 H), 5.20 (ddd, *J* = 17.1, 1.7, 1.0 Hz, 1 H), 4.82 (dd, *J* = 7.7, 2.1 Hz, 1 H), 3.75 (s, 3 H), 3.52 (t, *J* = 8.2 Hz, 1 H), 2.27 (d, *J* = 2.5 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.4, 142.1, 138.2, 129.4, 128.0, 127.5, 126.8, 118.1, 113.9, 77.4, 58.3, 55.3.

HR-MS (+ p APCI) *m*/*z*: [M + NH_4]$^+$ calcd for $C_{17}H_{22}NO_2^+$: 272.1645; found: 272.1646.

1-phenyl-2-(p-tolyl)but-3-en-1-ol (3s)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27–7.13 (m, 6 H),7.06–6.92 (m, 4 H), 6.24 (ddd, *J* = 17.1, 10.3, 8.9 Hz, 1 H), 5.24 (ddd, *J* = 15.4, 1.7, 0.8 Hz, 1 H), 5.21 (ddd, *J* = 22.2, 1.7, 0.8 Hz, 1 H), 4.85 (d, *J* = 7.6 Hz, 1 H), 3.59–3.48 (m, 1 H), 2.275 (s, 3 H), 2.271 (d, *J* = 2.4 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 142.1, 138.1, 137.7, 136.2, 129.2, 128.3, 128.0, 127.5, 126.8, 118.2, 77.3, 58.8, 21.1.

HR-MS (+ p APCI) *m*/*z*: [M + NH_4]$^+$ calcd for $C_{17}H_{22}NO^+$: 256.1696; found: 256.1695.

2-(3,4-dimethoxyphenyl)-1-phenylbut-3-en-1-ol (3t)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.25–7.12 (m, 5 H), 6.73 (d, *J* = 8.3 Hz, 1 H), 6.65 (ddd, *J* = 8.2, 2.0, 0.5 Hz, 1 H), 6.44 (d, *J* = 2.0 Hz, 1 H), 6.23 (ddd, *J* = 17.0, 10.3, 8.8 Hz, 1 H), 5.27 (ddd, *J* = 14.6, 1.7, 0.8 Hz, 1 H), 4.80 (d, *J*= 7.6 Hz, 1 H), 3.82 (s, 3 H), 3.71 (s, 3 H), 3.50 (t, *J* = 8.2 Hz, 1 H), 2.29 (brs, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 148.8, 147.8, 142.1, 138.0,133.2, 128.0, 127.5, 126.8, 120.3, 118.3, 112.1, 111.2, 77.5, 58.7, 55.9, 55.9.

HR-MS(+ p APCI) *m*/*z*: [M + NH_4]$^+$ calcd for $C_{18}H_{24}NO_3^+$: 302.1751; found: 302.1751.

2-([1,1'-biphenyl]-4-yl)-1-phenylbut-3-en-1-ol (3u)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.73–7.50 (m, 2 H), 7.49–7.38 (m, 4 H), 7.36–7.24 (m, 2 H), 7.23–7.13 (m, 6 H), 6.29 (ddd, *J* =17.1, 10.3, 8.9 Hz, 1 H), 5.30 (ddd, *J* = 10.3, 1.7, 0.7 Hz, 1 H), 5.25 (ddd, *J* = 17.1, 1.7, 1.0 Hz, 1 H), 4.90 (d, *J* = 7.5 Hz, 1 H), 3.62 (t, *J* = 8.2 Hz, 1 H), 2.32 (s, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 142.0, 140.9, 139.9, 139.5, 137.8, 128.9, 128.8, 128.1, 127.6, 127.3, 127.1, 127.1, 126.8, 118.6, 77.3, 58.8.

HR-MS (+ p APCI) *m*/*z*: $[M + NH_4]^+$ calcd for $C_{22}H_{24}NO^+$: 318.1852; found: 318.1855.

2-methyl-1,2-diphenylbut-3-en-1-ol (3v)

^{1}H NMR (400 MHz, Chloroform-d): δ = 7.41 (d, *J* = 7.7 Hz, 2 H), 7.35 (dd, *J* = 8.4, 6.7 Hz, 2 H), 7.31–7.19 (m, 5 H), 7.19–7.07 (m, 2 H), 6.59 (dd, *J* = 17.6, 10.9 Hz, 1 H), 5.35 (dd, *J* = 10.9 Hz, 1 H), 5.13 (dd, *J* = 17.7 Hz, 1 H), 5.08 (d, *J* = 2.1 Hz, 1 H), 2.17 (d, *J* = 2.3 Hz, 1 H), 1.32 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.1, 142.2, 140.2, 128.4, 128.0, 127.5, 127.4, 127.3, 126.6, 115.7, 80.4, 50.4, 20.7.

HR-MS (+ p APCI) *m*/*z*: $[M + NH_4]^+$ calcd for $C_{17}H_{22}NO^+$: 256.1696; found:256.1697.

Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information

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