

Sn/I₂ Mediated allylation of carbonyl compounds with allyl (crotyl) halide in water

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Abstract

A novel mediator (Sn/I₂) has been developed and employed in the allylation and crotylation of various aldehydes and ketones with allyl (crotyl) halide in water. With a catalytic amount of I₂ and less than stoichiometric amounts of Sn, allyl (crotyl) bromide reacts with carbonyl compounds to produce the corresponding alcohols in quantitative yield. Even the inert allyl chloride and crotyl chloride can react with aldehydes to give the corresponding alcohols. The diastereoselectivity and regioselectivity of the reaction have also been studied. Sn/I₂ mediated allylations of aldehydes with crotyl bromide produced dominant γ -adducts with minor α -isomers while Sn/I₂ mediated allylations of aldehydes with crotyl chloride afforded dominant α -adducts with minor γ -isomers.

Keywords: Allylation, regioselectivity, carbonyl compounds, pure water

Introduction

Organic reactions in aqueous media is a significant branch of green chemistry utilizing a variety of organometallic reagents to accomplish Barbier-type carbonyl allylation in water.¹ As a typical Barbier-type allylation, metal-mediated allylation in aqueous media is studied widely. Metals such as indium², zinc³, gallium⁴, iron⁵ and tin⁶ are always used as mediators. However, in order to improve the reaction yield, more than stoichiometric amount of metals, long reaction time, the vast use of inorganic salt⁷ (e.g. NH₄Cl, SnCl₂), an organic co-solvent⁸ or ultrasonic irradiation⁹ are often involved. These facts prompted us to investigate a novel allylation reaction, which is very convenient to use, has a low cost, and does not require difficult techniques. Here, we discovered a novel mediator (Sn/I₂) for the allylation reaction in water. Using this new mediator, the dosage of tin metal can be decreased and the scope of substrates was extended. Even allyl chloride and crotyl chloride, which were inert to allylation in most cases, can be activated in the

allylation to afford the corresponding products in high yields. In addition, regioselectivity of the allylation can be achieved to some extent under the condition.

Results and Discussion

Tin & iodine mediated allylation of various aldehydes with allyl bromide

Conventionally, 1.5 to 2.0 equivalents of tin were used in the reaction of an aldehyde and allyl bromide in order to perform the allylation smoothly. Nevertheless, a long reaction time was usually required to improve the yield (13 h, 93%, entry 1, Table 1).

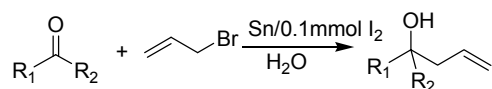
When a catalytic amount of iodine was added to the reaction mixture, the amount of tin consumed in the reaction could be markedly reduced to about 0.9 mmol, leading to a quantitative conversion (entry 2, Table 1). Afterwards, the scope of the substrates was extended. The results are listed in Table 1. Quantitative transformation was achieved in a short time for all the tested carbonyl compounds (entries 3-12, Table 1). After extracting the reaction mixture with ethyl ether, pure products were obtained directly without any other purification. No side-product was detected. The addition of iodine not only reduced the mediator loading but also accelerated the reaction largely. The reaction time was shortened from 13 hours to less than 7 hours.

Tin and iodine mediated allylation of aldehydes/ketones with allyl chloride

As far as we know, in aqueous media, the carbonyl allylation takes place only when allyl bromide is employed as a reaction substrate. The carbonyl allylation with allyl chloride does not give an ideal yield, and sometimes, does not work at all.

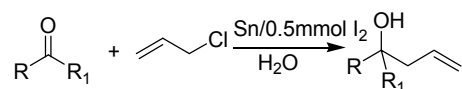
However, when a mixture of 0.5-0.6 equiv. of iodine and 1.2 equiv. of tin was employed as a mediator, the allylation can be carried out smoothly at room temperature to give rise to the corresponding product with a high yield (Table 2).

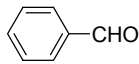
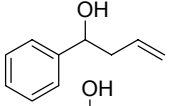
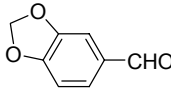
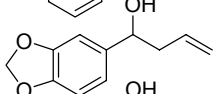
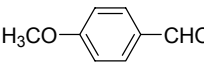
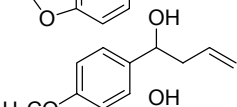
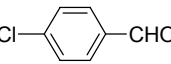
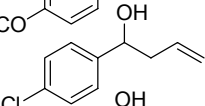
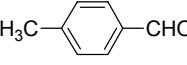
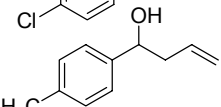
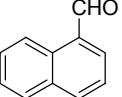
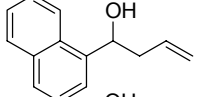
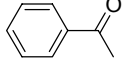
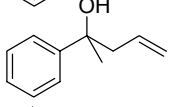
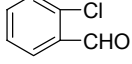
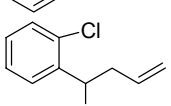
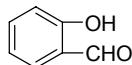
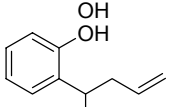

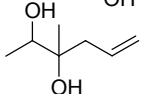
From Table 2, it was found that benzaldehyde, 4-chlorobenzaldehyde, 2-chlorobenzaldehyde could be converted to the corresponding homoallylic alcohol quantitatively (entries 1, 4, 8 in Table 2), which indicated that an electron-withdrawing group favored this allylation. Aliphatic ketone, 3-hydroxy-2-butanone, can also be a substrate in this allylation to give the corresponding homoallylic alcohol with a quantitative yield (entry 10, Table 1). An electron-donating group on the aromatic ring of an aldehyde has a negative influence on the corresponding allylation. For instance, the methanedioxy, methoxy, methyl, hydroxyl group can reduce the reaction yield significantly, as shown in entries 2, 3, 5, and 9. As for naphthyl aldehyde, the corresponding allylation produced the homoallylic alcohol with a moderate yield, perhaps due to the naphthyl ring being more electron-rich than the phenyl ring (entry 6). Overall, the Sn/I₂ mediator can promote this allylation effectively. Most of the allylations gave rise to the corresponding product with high yields under the conditions.

Table 1. Allylation of carbonyl compounds and allyl bromide mediated by Sn/I₂ in water

Entries	Substrates	Products	Time (h)	Yield %
1 ^a			13	93
2			4	>99
3			6	>99
4			7	>99
5			5	>99
6			6	>99
7			6	>99
8			6	>99
9			6	>99
10	$n\text{-C}_6\text{H}_{13}\text{CHO}$		6	>99
11			6	>99
12			6	>99

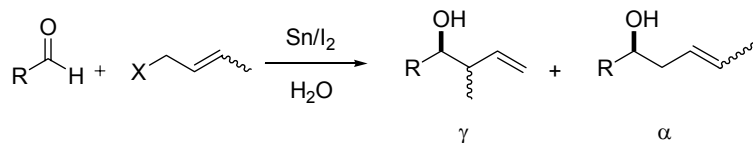
^aThe allylation was mediated by 1.5 mmol regular tin in water without I₂.

Table 2. Allylation of aldehydes/ketones and allyl chloride mediated by tin and iodine in water

Entries	Substrates	Products	Time (h)	Yield %
1			15	>99
2			20	51
3			17	78
4			15	>99
5			15	77
6			20	76
7			20	78
8			15	>99
9			20	77
10			20	>99

Tin & iodine mediated crotylation of various aldehydes and crotyl halides

The crotylation can also be promoted by this new mediator regardless of the use of crotyl bromide or crotyl chloride, affording the corresponding product in good yields (Table 3).

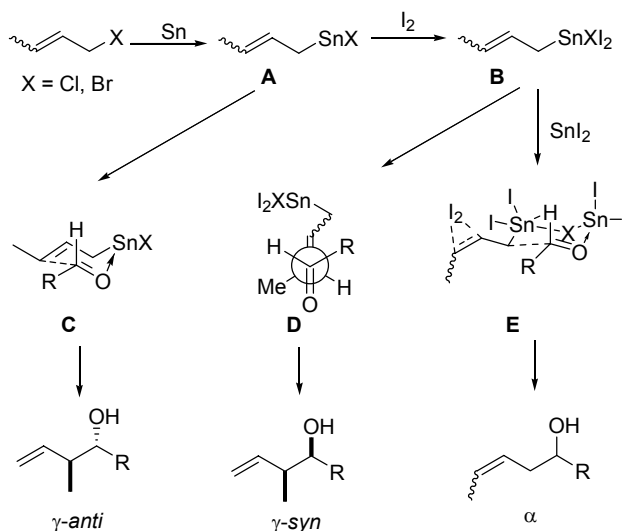
Table 3. Regio- and diastereoselectivity for tin/iodine mediated allylations of aldehydes with crotyl halide in water

Entry	R	X	I ₂ (mmol)	Time (h)	Yield ^a (%)	
					γ (syn:anti) ^b	α (Z:E) ^b
1	Ph-	Br	0.1	6	88(54:46)	11(67:33)
2	4-Cl-C ₆ H ₄ -	Br	0.1	9	83(52:48)	17(68:32)
3	2-Cl-C ₆ H ₄ -	Br	0.1	10	85(53:47)	15(68:32)
4	4-CH ₃ -C ₆ H ₄ -	Br	0.1	12	75(49:51)	25(63:36)
5	n-C ₆ H ₁₃ -	Br	0.1	10	68(57:43)	32(75:25)
6	4-CH ₃ O-C ₆ H ₄ -	Br	0.1	12	89(65:35)	11(52:48)
7	2-CH ₃ O-C ₆ H ₄ -	Br	0.1	8	65(57:43)	27(58:42)
8	Ph-	Cl	0.5	15	27(76:24)	53(64:36)
9	4-Cl-C ₆ H ₄ -	Cl	0.5	15	22(70:30)	53(68:32)
10	2-Cl-C ₆ H ₄ -	Cl	0.5	15	18(50:50)	57(56:44)
11	4-CH ₃ -C ₆ H ₄ -	Cl	0.5	15	31(67:33)	41(65:35)
12	n-C ₆ H ₁₃ -	Cl	0.5	15	34(52:48)	65(75:25)
13	4-CH ₃ O-C ₆ H ₄ -	Cl	0.2	15	51(51:49)	29(50:50)
14	2-CH ₃ O-C ₆ H ₄ -	Cl	0.2	15	51(52:48)	46(64:36)

^aIsolated yield. ^bThe ratio of α to γ was determined by ¹H NMR, ¹³C NMR.

As shown in Table 3, using only a catalytic amount of iodine, the carbonyl crotylation by crotyl bromide can be carried out smoothly to generate the corresponding alcohols with excellent to quantitative yields in 6-12 hours (entries 1-7, Table 3). Under these conditions, the reaction preferred the *syn*-isomer in dominant γ -adduct. When crotyl chloride was employed in the carbonyl crotylation, a bigger amount of iodine (0.5 mmol) was needed to mediate the crotylation, perhaps due to the low reactivity of crotyl chloride. The Sn/I₂ promoted crotylation using crotyl chloride produced the corresponding alcohols with good to excellent yields (entries 8-12, Table 3). Compared to the allylation of crotyl bromide, the crotylation of crotyl chloride gave α -adducts as the predominant products. For 4-methoxybenzaldehyde or 2-methoxybenzaldehyde, when 0.5 of mmol I₂ was used to promote the crotylation of crotyl chloride, side reactions increased. Nevertheless, the suitable reduction of the iodine dosage had little influence on the allylation for these two substrates. When the amount of I₂ was reduced to 0.2 mmol in order to eliminate the side reactions, the γ -adduct product was obtained as the predominant product (entries 13-14, Table 3).

Plausible mechanisms are shown in Scheme 1. The γ -*anti* product likely forms via the usual six-membered cyclic chair transition state (**C**). The stannous intermediate (**A**) behaves as a Lewis acid¹⁰ and coordinates with the carbonyl oxygen. When a catalytic amount of iodine was added in the reaction, iodine can coordinate with the stannous bromide to afford an intermediate (**B**), in which the Lewis acidity of stannous is reduced while the steric hindrance of the α -C of the allylic halide is increased due to the iodine coordination. As a result, the nucleophilicity of the γ -C in the allylic halide is enhanced and this γ -C attacks a substrate aldehyde directly to afford an acyclic antiperiplanar transition (**D**). This acyclic antiperiplanar transition, in which the steric hindrance is reduced most, leads to a γ -*syn* product¹¹. With the addition of iodine, the amount of stannous iodide is increased and the excess of iodine maybe results in the formation of iodonium. Either this iodonium or stannous iodide can promote the formation of a chair-formed six-membered cyclic transition state (**E**), in which the γ -position is occupied by iodine and the electron density of the α -C is increased, resulting in the α -nucleophilic attack to afford the α -adduct product.^{6g} The iodine in iodonium is inclined to bind to a neighboring stannic iodide, which pushes the methyl group to the same side as that of the α -C, as shown in (**E**) and prefers the formation of a *Z*-isomer in an α -adduct product. According to this proposed mechanism, the experimental results and the diastereoselectivity can be explained to some extent.



Scheme 1. Proposed mechanisms.

Conclusions

In conclusion, Sn/I₂ efficiently mediates the Barbier-type allylation of carbonyl compounds with crotyl (allyl) halide (Br or Cl) in water afford the corresponding homoallylic alcohols with good to excellent yields. The addition of iodine led to the reduction of the mediator loading of the

metal (tin). Moreover, the regio- and diastereoselectivity in crotylations were affected by the variation of the iodine addition. Further research is in process in our laboratory.

Experimental Section

General Procedures. A mixture of benzaldehyde (0.10 mL, 1.0 mmol, 1 equiv.), tin powder (0.10 g, 0.9 mmol), I₂ (25mg, 10% mmol) and allyl bromide (0.14 mL, 1.5 mmol) in water (2-4 mL) was stirred in a 10 mL round-bottom flask equipped with a glass septum at room temperature for several hours. Then the reaction mixture was extracted with ethyl acetate (3×10ml). The combined organic layer was washed with 10 mL of water and 10 mL of brine respectively, and dried over anhydrous magnesium sulfate. The mixture was then filtered. Pure product was obtained after evaporating the solvent with a yield of 99% (160mg).

Phenyl-3-buten-1-ol. ¹H NMR (300Hz, CDCl₃): δ 2.49-2.57 (m, 2H), 2.64-2.72 (br, 1H), 4.71 (t, J=6.06 Hz, 1H), 5.12-5.25 (m, 2H), 5.77-5.91 (m, 1H), 7.25-7.44 (m, 5H); ¹³C HMR (75Hz, CDCl₃): δ 43.6, 73.4, 117.9, 125.9, 127.4, 128.3, 134.6, 144.0; IR (film): 3385, 3075, 1641 cm⁻¹; HRMS (EI): calc. for C₁₀H₁₀ (M⁺-H₂O) 130.0783, found 130.0769.

1-Benzo[1,3]dioxol-5-yl-but-3-en-1-ol. ¹H NMR(300Hz, CDCl₃) δ: 2.02-2.19 (br, 1H), 2.46 (dd, J=6.58, 6.92 Hz, 2H), 4.64 (t, J=6.49 Hz, 1H), 5.10-5.19 (m, 2H), 5.70-5.85 (m, 1H), 5.95 (s, 2H), 6.73-6.83 (m, 2H), 6.87 (s, 1H); ¹³C NMR (75Hz, CDCl₃): 43.8, 73.7, 101.0, 106.5, 108.1, 118.2, 119.3, 134.8, 138.2, 146.9, 147.7; IR (film): 3383, 3075, 1640 cm⁻¹; IR (film): 3383.3, 3075.4, 1640.4 cm⁻¹. HRMS (EI): calc. for C₁₁H₁₀O₂ (M⁺-H₂O) 174.0681, found 174.0665.

1-(4-Methoxyphenyl)-3-beten-1-ol. ¹H NMR (300Hz, CDCl₃): 2.03-2.27 (br, 1H), 2.48 (dd, J=6.66, 6.66 Hz, 2H), 3.79 (s, 3H), 4.66 (t, J= 6.54 Hz, 1H), 5.08-5.19 (m, 2H), 5.71-5.87 (m, 1H), 6.84-6.93 (d, 8.61 Hz, 2H), 7.21-7.36 (d, 8.55 Hz, 2H); ¹³C NMR (75Hz, CDCl₃): 43.6, 76.0, 78.7, 113.7, 117.8, 127.1, 134.8, 136.3, 158.9; IR (film): 3371, 3078, 1642 cm⁻¹; HRMS (EI): calc. for C₁₁H₁₂O (M⁺-H₂O) 160.0888, found 160.0855.

1-(4-Chlorophenyl)-3-buten-1-ol. ¹H NMR (300Hz, CDCl₃): δ 1.90-2.32 (br, 1H), 2.45 (dd, J=5.63, 6.64 Hz, 2H), 4.68 (t, J=7.29, 1H), 5.15 (d, J=11.7 Hz, 2H), 5.66-5.83 (m, 1H), 7.21-7.32 (m, 4H); ¹³C HNMR (75Hz, CDCl₃): δ 43.6, 72.7, 118.4, 127.3, 128.4, 133.0, 134.0, 142.4. IR (film): 3371, 3078, 1642 cm⁻¹; HRMS (EI): calc for C₁₀H₉Cl (M⁺-H₂O) 164.0393, found 164.0382.

1-(4-Methylphenyl)-3-buten-1-ol. ¹H NMR (300Hz, CDCl₃): δ 2.02-2.19 (br, 1H), 2.33 (s, 3H), 2.48 (dd, J=6.58, 6.92 Hz, 2H), 4.67 (t, J=6.49, 6.30 Hz, 1H), 5.07-5.19 (m, 2H), 5.70-5.87 (m, 1H), 7.14 (d, J=7.2 Hz, 2H), 7.22 (d, J=7.80 Hz, 2H); ¹³C NMR (75Hz, CDCl₃): 21.2, 43.8, 73.7, 118.2, 125.9, 129.2, 134.8, 137.2, 141.1; IR (film): 3383, 3075, 1640 cm⁻¹; HRMS (EI): calc. for C₁₁H₁₂ (M⁺-H₂O) 144.0939, found 144.0924.

1-(Naphthalen-1-yl)-but-3-en-1-ol. ^1H NMR: δ 2.47-2.70 (m, 3H), 5.09-5.17 (m, 2H), 5.40-5.42 (m, 1H), 5.78-5.91(m, 1H), 7.17-7.99 (m, 7H); ^{13}C NMR: δ 43.1, 70.2, 118.6, 123.1, 123.2, 125.6, 125.7, 126.3, 128.2, 129.2, 130.5, 135.0, 139.6; IR (film): 3380, 3070, 1640 cm^{-1} ; HRMS: calc. for $\text{C}_{14}\text{H}_{14}\text{O}$ (M^+) 198.1045, found 198.1058.

1-(2-Chlorophenyl)-3-buten-1-ol. ^1H NMR (300Hz, CDCl_3): δ 2.26-2.43 (m, 1H), 2.43-2.53 (br, 1H), 2.53-2.66 (m, 1H), 5.07-5.21 (m, 3H), 5.75-5.93 (m, 1H), 7.12-7.35 (m, 3H), 7.53 (d, $J=9.15$ Hz, 1H); ^{13}C NMR (75Hz, CDCl_3): δ 42.2, 69.8, 118.8, 127.2, 127.3, 128.6, 129.5, 131.9, 134.4, 141.4; IR (film): 3381, 3074, 1641 cm^{-1} ; HRMS (EI): calc. for $\text{C}_{10}\text{H}_{11}\text{OCl}$ (M^+): 182.0498. Found: 182.0496.

1-(2-Hydroxyphenyl)-3-beten-1-ol. ^1H NMR (300Hz, CDCl_3): δ 2.50-2.70 (m, 2H), 2.90-3.13 (br, 1H), 4.85 (t, $J=5.96$ Hz, 1H), 5.19 (d, $J=12.95$ Hz, 2H), 5.73-5.94 (m, 1H), 6.67-7.29 (m, 4H), 8.07 (s, 1H); ^{13}C NMR (75Hz, CDCl_3): δ 42.1, 74.5, 117.2, 119.1, 120.0, 126.7, 127.23, 129.0, 134.0, 155.3; IR (film): 3346, 3085, 1640 cm^{-1} ; HRMS (EI): calc. for $\text{C}_{10}\text{H}_{11}\text{O}$ (M^+) 164.0837, found 164.0831.

Dec-1-en-4-ol. ^1H NMR (300Hz, CDCl_3): δ 0.86 (t, $J = 6.7$ Hz, 3H), 1.27-1.44 (m, 10H), 1.70-1.90 (br, 1H), 2.06-2.16 (m, 1H), 2.24-2.32 (m, 1H), 3.60-3.66 (m, 1H), 5.08-5.14 (m, 2H), 5.77-5.86 (m, 1H); ^{13}C NMR (75Hz, CDCl_3): δ 14.0, 22.6, 25.6, 29.3 31.8, 36.8, 41.9, 70.7, 117.7, 134.9; IR (film): 3356, 2928, 1641 cm^{-1} . HRMS (EI): calc. for $\text{C}_{10}\text{H}_{20}\text{O}$ (M^+) 156.1514, found 156.1503.

2-Phenylpent-4-en-2-ol. ^1H NMR (300Hz, CDCl_3): δ 1.54 (s, 3H), 1.98-2.17 (br, 1H), 2.45-2.50 (m, 1H), 2.65-2.71 (m, 1H), 5.09-5.15 (m, 2H), 5.55-5.69 (m, 1H), 7.20-7.45 (m, 5H); ^{13}C NMR (75Hz, CDCl_3): δ 30.3, 48.7, 73.8, 119.6, 124.9, 126.8, 128.3, 133.9, 147.8; IR (film): 3418, 3085, 1647 cm^{-1} ; HRMS: calc. for $\text{C}_{11}\text{H}_{14}\text{O}$ (M^+) 162.0790, found 162.0794.

3-methyl-hex-5-ene-2,3-diol. ^1H NMR (300Hz, CDCl_3): δ 1.12-1.25 (m, 6H), 1.50-1.70 (br, 1H), 1.93-2.05 (br, 1H), 2.10-2.32 (m, 2H), 3.62-3.69 (m, 1H), 5.11-5.19 (m, 2H), 5.85-5.94 (m, 1H); ^{13}C NMR (75Hz, CDCl_3): δ 17.2, 17.3, 20.7, 23.5, 40.3, 43.7, 72.5, 73.8, 74.4, 74.7, 118.6, 118.7, 133.6, 133.8; IR (film): 3420, 3074, 1639 cm^{-1} ; HRMS: calc. for C_7H_{10} ($\text{M}^+-2\text{H}_2\text{O}$) 94.0783, found 94.0781.

2-Methyl-1-phenyl-3-buten-1-ol.¹² ^1H NMR (300 MHz, CDCl_3) *syn isomers*: δ 0.98 (d, $J=6.87$ Hz, 3H), 1.99-2.19 (br, 1H), 2.35-2.62 (m, 1H), 4.57 (d, $J=5.84$ Hz, 1H), 4.99-5.09 (m, 2H), 5.64-5.88 (m, 1H), 7.16-7.39 (m, 5H); *anti isomers*: δ 0.86 (d, $J=6.83$ Hz, 3H), 1.99-2.19 (br, 1H), 2.35-2.62 (m, 1H), 4.32 (d, $J=7.64$ Hz, 1H), 5.13-5.23 (m, 2H), 5.64-5.88 (m, 1H), 7.16-7.39 (m, 5H). ^{13}C NMR (75 MHz, CDCl_3) *syn isomers*: δ 14.1, 44.6, 77.1, 115.5, 126.5, 127.4, 128.1, 140.3, 142.6; *anti isomers*: δ , 16.5, 46.2, 77.4, 116.8, 126.9, 127.7, 128.3, 140.6, 142.4. IR (film): 3417, 3080, 1640 cm^{-1} . HRMS (EI): calc. for $\text{C}_{11}\text{H}_{14}\text{O}$ (M^+): 162.1045, found 162.1042.

2-Methyl-1-(4-chlorophenyl)-3-buten-1-ol.¹² ^1H NMR (400 MHz, CDCl_3) *syn isomers*: δ 0.97 (d, $J=6.84$ Hz, 3H), 2.36-2.56 (m, 2H), 2.38-2.55 (br, 1H), 4.52 (d, $J=5.54$ Hz, 1H), 4.99-5.06 (m, 2H), 5.66-5.80 (m, 1H), 7.18-7.32 (m, 4H); *anti isomers*: δ 0.86 (d, $J=6.82$ Hz, 3H), 2.36-2.56 (m, 2H), 2.38-2.55 (br, 1H), 4.31 (d, $J=7.58$ Hz, 1H), 5.13-5.19 (m, 2H), 5.66-5.80 (m, 1H), 7.18-7.32 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) *syn isomers*: δ 14.1, 44.6, 77.4, 115.8, 128.2,

128.2, 132.9, 139.9, 141.1; *anti isomers*: δ 16.3, 46.2, 76.8, 117.0, 127.9, 128.3, 133.2, 140.2, 140.9. IR (film): 3406, 3080, 1640 cm^{-1} . HRMS (EI): calc. for $\text{C}_{11}\text{H}_{13}\text{OCl}$ (M^+): 196.0655, found 196.0652.

2-Methyl-1-(2-chlorophenyl)-3-buten-1-ol.¹³ ^1H NMR (300 MHz, CDCl_3) *syn isomers*: δ 1.00 (d, $J=6.81$ Hz, 3H), 1.82-2.14 (br, 1H), 2.50 (q, $J=5.91, 6.93$ Hz, 1H), 04-5.23 (m, 3H), 5.84-6.02 (m, 1H), 7.11-7.65 (m, 4H); *anti isomers*: δ 0.96 (d, $J=6.81$ Hz, 3H), 1.82-2.14 (br, 1H), 2.55 (q, $J=5.91, 6.93$ Hz, 1H), 5.04-5.23 (m, 3H), 5.84-6.02 (m, 1H), 7.11-7.65 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3) *syn isomers*: δ 16.6, 45.1, 73.5, 117.1, 126.0, 127.9, 128.2, 129.4, 131.4, 133.3, 140.3, 140.5; *anti isomers*: δ 12.8, 42.6, 73.3, 115.6, 126.8, 127.0, 128.4, 128.6, 132.1, 132.7, 139.7, 140.7. IR (film): 3406, 3071, 1639 cm^{-1} . HRMS (EI): calc. for $\text{C}_{11}\text{H}_{13}\text{OCl}$ (M^+): 196.0655, found 196.0648.

2-Methyl-1-(4-methylphenyl)-3-buten-1-ol.¹² ^1H NMR (300 MHz, CDCl_3) *syn isomers*: 1.00 (d, $J=6.84$ Hz, 3H), 2.33 (s, 3H), 2.39-2.63 (m, 1H), 4.53 (d, $J=6.00$ Hz, 1H), 4.99-5.06 (m, 2H), 5.66-5.86 (m, 1H), 7.10-7.25 (m, 4H); *anti isomers*: δ 0.85 (d, $J=6.00$ Hz, 3H), 2.05 (s, 3H) 2.39-2.63 (m, 1H), 4.30 (d, $J=9.00$ Hz, 1H), 5.13-5.22 (m, 2H), 5.66-5.86(m, 1H), 7.10-7.25 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3) *syn isomers*: δ 13.9, 20.8, 44.3, 76.3, 115.0, 126.2, 128.4, 136.6, 139.4, 140.1; *anti isomers*: 16.2, 20.8, 45.8, 77.4, 116.2, 126.4, 128.6, 136.9, 139.2, 140.5. IR (film): 3418, 3079, 1639 cm^{-1} . HRMS (EI): calc. for $\text{C}_{12}\text{H}_{16}\text{O}$ (M^+): 176.1201, found 176.1201.

3-Methyldec-1-en-4-ol.^{7c} ^1H NMR (400 MHz, CDCl_3) *syn isomers*: δ 0.88 (t, $J=6.9$ Hz, 3H), 1.00-1.06 (m, 3H), 1.37-1.69 (m, 10H), 2.20-2.26 (m, 1H), 3.49-3.50 (m, 1H), 5.05-5.13 (m, 2H), 5.70-5.80 (m, 1H); *anti isomers*: δ 0.88 (t, $J=6.9$ Hz, 3H), 1.00-1.06 (m, 3H), 1.37-1.69 (m, 10H), 2.20-2.26 (m, 1H), 3.38-3.40 (m, 1H), 5.05-5.13(m, 2H), 5.70-5.80(m, 1H). ^{13}C NMR (100 MHz, CDCl_3) *syn isomers*: δ 14.2, 16.4, 22.7, 26.2, 29.5, 31.9, 34.1, 44.2, 74.8, 115.2, 141.3; *anti isomers*: δ 14.2, 16.4, 22.7, 25.8, 29.3, 31.9, 34.4, 43.5, 74.8, 116.3, 140.5. IR (film): 3399, 3077, 1639 cm^{-1} . HRMS (EI): calc. for $\text{C}_{11}\text{H}_{22}\text{O}$ (M^+): 170.1671, found: 170.1667.

2-Methyl-1-(4-methoxyphenyl)-3-buten-1-ol.¹² ^1H NMR (300 MHz, CDCl_3) *syn isomers*: 1.01 (d, $J=6.6$ Hz, 3H), 1.94-2.23 (br, 1H), 2.39-2.60 (m, 1H), 3.78 (s, 3H), 4.52 (d, $J=6.0$ Hz, 1H), 4.99-5.06 (m, 2H), 5.65-5.87 (m, 1H), 6.82-6.90 (m, 2H), 7.17-7.27 (m, 2H); *anti isomers*: δ 0.84 (d, $J=6.9$ Hz, 3H), 1.94-2.23 (m, 2H), 2.44 (d, 1H), 3.78 (s, 3H), 4.29 (d, $J=8.7\text{Hz}$, 1H), 5.14-5.21 (m, 2H), 5.65-5.87 (m, 1H), 6.82-6.90 (m, 2H), 7.17-7.27 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3) *syn isomers*: δ 14.6, 44.8, 55.3, 77.2, 113.5, 115.3, 127.8, 135.0, 140.5, 158.9; *anti isomer*: δ 6.6, 46.3, 55.3, 76.8, 116.5, 128.1, 134.8, 141.0, 159.2. IR (film): 3442, 3075, 1612 cm^{-1} . HRMS (EI): calc. for $\text{C}_{12}\text{H}_{14}\text{O}$ (M^+-18): 174.1045, found: 174.1055.

2-Methyl-1-(2-methoxyphenyl)-3-buten-1-ol. ^1H NMR (300 MHz, CDCl_3) *syn isomers*: δ 1.04 (d, $J=6.81$ Hz, 3H), 2.35-2.57 (br, 1H), 2.61-2.76 (m, 1H), 3.84 (s, 3H), 4.77 (d, $J=6.06$ Hz, 1H), 4.91-5.03 (m, 2H), 5.71-5.86 (m, 1H), 6.81-6.99 (m, 2H), 7.16-7.32 (m, 2H); *anti isomers*: δ 0.91 (d, $J=6.9$ Hz, 3H), 2.25-2.57 (br, 1H), 2.53-2.69 (m, 1H), 3.83 (s, 3H), 4.69 (d, $J=7.55\text{Hz}$, 1H), 5.06-5.15 (m, 2H), 5.81-5.96 (m, 1H), 6.81-6.99 (m, 2H), 7.16-7.32 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3) *syn isomers*: δ 14.4, 43.3, 55.4, 74.3, 110.6, 114.7, 120.5, 128.1, 128.5, 130.9, 141.4, 156.6; *anti isomers*: 16.9, 44.8, 55.4, 73.9, 110.6, 115.8, 120.8, 128.3, 128.4, 131.0, 141.2, 156.9.

IR (film): 3437, 3075, 1638 cm^{-1} . HRMS (EI): calc. for $\text{C}_{12}\text{H}_{14}\text{O}$ (M^+ -18): 174.1045, found: 174.1047.

1-Phenyl-pent-3-en-1-ol (mixture of Z and E). ^1H NMR (400MHz, CDCl_3): δ 1.61-1.73 (m, 3H), 2.44-2.59 (m, 2H), 4.65-4.72 (m, 1H), 5.43-5.46 (m, 1H), 5.63-5.65 (m, 1H), 7.29-7.39 (m, 5H); ^{13}C NMR (100MHz, CDCl_3): δ 144.2, 144.1, 129.2, 128.4, 127.5, 127.4, 126.9, 126.0, 125.9, 125.8, 73.9, 73.6, 42.7, 36.9, 18.1, 13.0; IR (film): 3432, 3083, 1644 cm^{-1} . HRMS (EI) m/z calc. for $\text{C}_{11}\text{H}_{14}\text{O}$: 162.1045, found: 162.1049.

1-(4-Chlorophenyl)-pent-3-en-1-ol (mixture of Z and E). ^1H NMR (300 MHz, CDCl_3): δ 1.58 (d, $J=6.9$ Hz, E), 1.68 (d, $J=6.3$ Hz, Z), (E+Z, 3H) 2.02-2.25 (br, 1H), 2.27-2.62 (m, 2H), 4.59-4.72 (m, 1H), 5.31-5.46 (m, 1H), 5.51-5.72 (m, 1H), 7.22-7.44 (m, 4H). ^{13}C HNMR (75Hz, CDCl_3): δ 13.0, 18.1, 37.0, 42.8, 72.8, 73.2, 125.3, 126.4, 127.3, 128.0, 128.2, 128.5, 129.9, 133.1, 142.6. IR (film): 3384, 3021, 1655 cm^{-1} . HRMS (EI) m/z calc. for $\text{C}_{11}\text{H}_{13}\text{OCl}$: 196.0655, found: 196.0661.

1-(2-Chlorophenyl)-pent-3-en-1-ol (mixture of Z and E). ^1H NMR (300Hz, CDCl_3): δ 1.62 (d, $J=6.6$ Hz, E), 1.71 (d, $J=6.3$ Hz, Z), (E+Z, 3H), 2.06-2.30 (br, 1H), 2.38-2.76 (m, 2H), 5.04-5.29 (m, 1H), 5.41-5.60 (m, 1H), 5.61-5.84 (m, 1H), 7.11-7.45 (m, 3H), 7.50-7.76 (m, 1H). ^{13}C NMR (75Hz, CDCl_3): δ 12.9, 18.0, 35.1, 40.9, 69.9, 70.3, 125.4, 126.6, 127.0, 127.1, 128.0, 128.3, 128.4, 129.3, 129.7, 131.8, 141.4. IR (film): 3386, 3074, 1655 cm^{-1} . HRMS (EI) m/z calc. for $\text{C}_{11}\text{H}_{13}\text{OCl}$: 196.0655, found: 196.0663.

1-*p*-Tolyl-pent-3-en-1-ol (mixture of Z and E). ^1H NMR (300Hz, CDCl_3): δ 1.59 (d, $J=6.9$, E), 1.66 (d, $J=7.2$, Z), (E+Z, 3H) 2.10-2.19 (br, 1H), 2.33 (s, 3H), 2.37-2.60 (m, 2H), 4.56-4.67 (m, 1H), 5.33-5.47 (m, 1H), 5.49-5.68 (m, 1H), 7.10-7.31 (m, 4H). ^{13}C NMR (75Hz, CDCl_3): 13.0, 18.1, 21.3, 36.9, 44.2, 73.5, 73.8, 125.8, 125.9, 126.0, 129.2, 127.1, 127.3, 129.1, 129.1, 137.1, 141.3. IR (film): 3391, 3021, 1656 cm^{-1} . HRMS (EI) m/z calc. for $\text{C}_{12}\text{H}_{16}\text{O}$: 176.1201, found: 176.1201.

Undec-2-en-5-ol (mixture of Z and E). δ ^1H NMR (300Hz, CDCl_3): 0.90 (t, $J=6.9$ Hz, 3H), 1.23-1.58(m, 10H), 1.61-1.73 (m, 3H), 1.73-1.82 (br, 1H), 2.00-2.14 (m, E), 2.17-2.32 (m, Z) (Z+E, 2H), 3.53-3.71 (m, 1H), 5.38-5.73 (m, 2H). ^{13}C NMR (75Hz, CDCl_3): δ 13.0, 14.1, 18.1, 22.7, 25.7, 25.8, 29.4, 31.9, 35.0, 36.8, 36.9 40.8, 71.1, 71.5, 126.3, 127.1, 127.3, 128.8; IR (film): 3435, 1632 cm^{-1} . HRMS (EI) m/z calc. for $\text{C}_{11}\text{H}_{22}\text{O}$: 170.1671, found: 170.1695.

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