A Highly *syn*-Selective Allylation of Aldehydes in Water

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nBu$_4$NBr/PbI$_2$ acts as an effective catalyst for the allylation of aldehydes **2** with the allylic tin reagents **1** in water. A high *syn*-selectivity of **3** was achieved in water without any aprotic solvents in the reaction of the aromatic aldehydes **2** with the crotyltri-*n*-butyltin reagents **1b, 1c** irrespective of their *E*/*Z* geometry.

Introduction

Although a number of allylmetal reagents have been developed for the allylation of carbonyl compounds due to their high potentiality for carbon−carbon bond formation,[1] most of them are air and moisture sensitive. Recently, the allylation of aldehydes in water has been studied intensely because then there is no need for inflammable organic solvents, and any hydroxy or amino groups need not be protected.[2] Up to now, most aqueous allylations have been based on the Barbier-type conditions;[3] the use of indium metal is a quite recent development.[3b] Although *anti*-selective allylation in water has been investigated in the indium-mediated reaction with γ-substituted allyl halides,[4] hardly any *syn*-selective allylation in water has been performed so far[5] in spite of numerous diastereoselective methods under anhydrous conditions.[1] In aqueous Barbier-type reactions, where a single electron transfer (SET) mechanism on the metal surface or the generation of allylic metal intermediates has been postulated, the allylating species generated would be too labile to control the stereoselectivities.[3,4] If an allylic metal intermediate is adequately stable in water, the diastereoselectivity would be easily controlled as in anhydrous reactions. We are interested in allylic tributyltin reagents because they are inert toward water under neutral conditions. Traditional methods using allyl tributyltins require an equimolar amount of moisture-sensitive Lewis acid such as $BF_3{\cdot}OEt_2$, $TiCl_4$ or $SnCl_4$,[6] hence these reactions must be performed under strictly anhydrous conditions. Recently, lanthanide triflates have been developed as catalysts.[7] Among them, $Sc(OTf)_3$ could be used in a water-containing solvent (MeCN/H_2O= 9:1) for allylation with reactive tetraallyltin.[7c,7d] An alternative allylation with allyltributyltin in aqueous solvent has been performed, but requires strongly acidic conditions.[8] In all aqueous conditions, no diastereoselective reactions with γ-substituted allylic tins have been reported. We have already reported that PbI_2/HMPA acts as a gentle catalyst for allylation with allyltributyltin under aprotic conditions.[9] Although lead compounds are toxic, PbI_2/HMPA works especially well in only catalytic amounts for the chemoselective allylation of carbonyls to afford highly acid-sensitive allylated products. During our further investigation of the PbI_2-catalyzed allylation, we found that nBu$_4$NBr/PbI$_2$ effectively aided the catalytic allylation of aldehydes in water. Of particular interest is that a highly *syn*-selective allylation in water could be achieved without any aprotic solvent.

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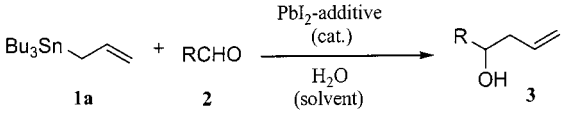
Results and Discussion

Initially, we investigated the allylation of *p*-chlorobenzaldehyde (**2a**) with allyltributyltin (**1a**) in water as shown in Table 1.

Table 1. Effect of the additive in the PbI_2-catalyzed allylation of aldehydes in H_2O[a]



1a 2 3

Entry	R		Additive	Conditions	Yield [%]
1	*p*-ClC$_6$H$_4$	**a**	none	rt, 48 h	4
2		**a**	HMPA	rt, 48 h	10
3		**a**	*n*-Bu$_4$NCl	rt, 48 h	36
4		**a**	*n*-Bu$_4$NI	rt, 48 h	65
5		**a**	*n*-Bu$_4$NBr	rt, 48 h	84
6		**a**	(*n*-C$_8$H$_{17}$)$_4$NBr	rt, 48 h	60
7		**a**	Et$_4$NBr	rt, 48 h	2
8		**a**	(*n*-C$_{16}$H$_{23}$NMe$_3$)Br	rt, 48 h	5
9		**a**	LiBr	rt, 48 h	5
10		**a**	*n*-Bu$_4$NBr	rt, 48 h	87[b]
11	Ph	**b**	*n*-Bu$_4$NBr	rt, 48 h	72
12	*p*-NO$_2$C$_6$H$_4$	**c**	*n*-Bu$_4$NBr	rt, 48 h	72
13	*o*-NO$_2$C$_6$H$_4$	**d**	*n*-Bu$_4$NBr	rt, 48 h	80
14	*o*-HOC$_6$H$_4$	**e**	*n*-Bu$_4$NBr	rt, 16 h	92
15		**f**	*n*-Bu$_4$NBr	rt, 48 h	21
16		**f**	*n*-Bu$_4$NBr	60 °C, 16 h	92
17	PhCH=CH	**g**	*n*-Bu$_4$NBr	60 °C, 48 h	80
18	PhCH$_2$CH$_2$	**h**	*n*-Bu$_4$NBr	rt, 48 h	43

[a] PbI_2 0.1 mmol, additive 0.1 mmol, **1a** 1 mmol, **2** 1 mmol, H_2O 1 mL. − [b] THF (1 mL) was used as solvent.

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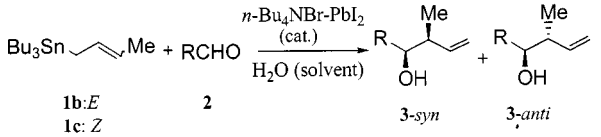
With PbI_2 as a catalyst (10 mol %), the reaction did not proceed at room temp. for 48 h (entry 1). The catalytic system PbI_2/HMPA, which has previously been used in anhydrous solvents,[9] did not promote the allylation in water (entry 2). However, the addition of tetrabutylammonium halides increased the yields of the homoallyl alcohol **3a** (entries 3−5). Among the ammonium salts examined, tetrabutylammonium bromide (nBu$_4$NBr) was the best with a yield of **3a** of 84% (entry 5). Other ammonium bromides and lithium bromide were less effective (entries 7−9). The catalytic activity in water was of a similar degree as that in anhydrous THF (entry 10). By using nBu$_4$NBr/PbI_2 as a catalyst, other aromatic aldehydes **2b**−**2e** reacted smoothly to give the homoallyl alcohols **3b**−**3e** under mild conditions at room temp. (entries 11−14). In the case of the bulky substrate **2f**, a high yield of 92% was achieved at 60 °C (entry 16). For the unsaturated aldehyde **2g**, the 1,2 adduct **3g** was obtained as the sole product (entry 17). In the reaction of the aliphatic aldehyde **2h**, the product **3h** was obtained in moderate yield (entry 18).

Table 2 shows the stereoselectivity in the reaction of crotyltin reagents (**1b**,**c**) with aromatic aldehydes.

Table 2. The *syn*-selective crotylation of aldehydes in H_2O[a]



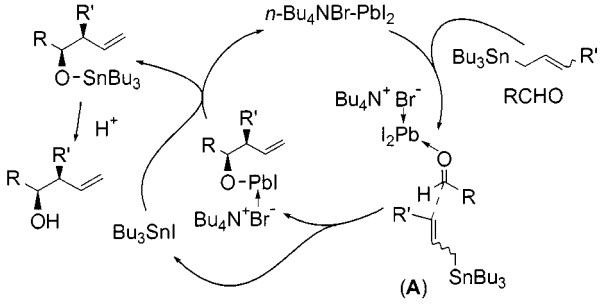
1b:*E* **1c**: *Z* **2** **3**-*syn* **3**-*anti*

Entry	R	Crotyl Tin	Product	Yield [%]	*syn* : *anti*
1	*p*-ClC_6H_4	**1b**	**3i**	90	89 : 11
2		**1c**	**3i**	91	96 : 4
3	Ph	**1b**	**3j**	80	90 : 10
4		**1c**	**3j**	93	93 : 7
5	*p*-$CH_3C_6H_4$	**1b**	**3k**	90	90 : 10
6		**1c**	**3k**	90	90 : 10
7	*p*-MeOC_6H_4	**1b**	**3l**	70	85 : 15
8		**1c**	**3l**	75	88 : 12
9	*o*-HOC_6H_4	**1b**	**3m**	82	82 : 18
10		**1c**	**3m**	99	85 : 15
11	*o*-$NO_2C_6H_4$	**1b**	**3n**	76	82 : 18
12	*p*-NCC_6H_4	**1b**	**3o**	94	80 : 20
13	PhCH=CH	**1b**	**3p**	80	87 : 13
14	$PhCH_2CH_2$	**1b**	**3q**	47	70 : 30

[a] PbI_2 0.1 mmol, nBu$_4$NBr 0.1 mmol, crotyltin 1 mmol, **2** 1 mmol, H_2O 1 mL, 60 °C, 48 h.

High *syn*-selectivities were obtained irrespective of the *E*/*Z* geometry of the crotyltributyltins (entries 1 and 2). Although an elevated temperature (60 °C) was required, the crotylated γ adduct **3i** was obtained in water in high yields. In the case of benzaldehyde (entries 3 and 4), the *syn*-selectivity in **3j** was comparable with that of the anhydrous method using BF_3·OEt_2.[6g] The reactions of other aromatic aldehydes gave the γ adducts **3k**−**3o** also with high *syn*-selectivities (entries 5−12). The reaction of an unsaturated aldehyde also occurred with *syn*-selectivity (entry 13). In the case of an aliphatic aldehyde, the yield and *syn*-selectivity of **3q** were only moderate (entry 14). These results are in sharp contrast to the *anti*-selectivity which is observed in the indium-mediated aqueous Barbier-type allylation where the Zimmerman−Traxler transition state involving an (*E*)-γ-substituted allylic indium intermediate is proposed.[4a] While *syn*-selectivity is traditionally promoted under anhydrous conditions,[6] these results provide the first highly *syn*-selective allylation in water without any aprotic solvent.

We assume that nBu$_4$NBr/PbI_2 behaves as a Lewis acid, although the possibility of forming active allylic lead species by a metal exchange between Sn and Pb cannot be excluded.[10] Scheme 1 shows a proposed catalytic cycle. The high *syn*-selectivity from both the reactions of (*E*)-crotyltin **1b** and (*Z*)-crotyltin **1c** indicates that the reaction proceeds through an antiperiplanar acyclic transition state (**A**).[6h,11] We do not know why nBu$_4$NBr is a more effective additive compared to other ammonium salts, although the reasons could include the ability of nBu$_4$NBr to coordinate to the Pb atom or the formation of suitable colloid particles.



Scheme 1

Conclusion

In conclusion, nBu$_4$NBr/PbI_2 acts as an effective catalyst for the allylation of aldehydes with allylic tin compounds. The following characteristic features are noted: (i) The reactions can be carried out smoothly in water without aprotic solvent; (ii) A catalytic amount of nBu$_4$NBr/PbI_2 is sufficient; (iii) The reaction conditions are neutral and mild; (iv) Finally, it is noteworthy that the reaction with crotyltributyltin provides a high *syn*-selectivity. We are investigating the mechanism and further applications of this catalyst.

Experimental Section

General: IR spectra were recorded as thin films on a Horiba FT-720 spectrometer. All the ^1H and ^{13}C spectra were recorded with a JEOL JNM-GSX-270 (270 and 67.9 MHz, respectively) in deuterochloroform ($CDCl_3$) containing 0.03% (w/v) of tetramethylsilane. Mass spectra were recorded on a JEOL JMS-DS-303. Column chromatography was performed by using Fuji Davison silica gel FL-100DX. Preparative TLC was carried out on Wakogel B-5F silica gel.

Allyl tributyltin (nBu$_3$SnCH$_2$CH=CH$_2$) (**1a**) was prepared by the reaction of allyl Grignard with nBu$_3$SnCl. (*E*)- and (*Z*)-Crotyltributyltins (nBu$_3$SnCH$_2$CH=CHCH$_3$; **1b**, **c**) were also prepared from the tributylstannyllithium with the corresponding (*E*)- or (*Z*)-allylic chlorides. PbI_2 and nBu$_4$NBr are commercially available and were used without purification. All aldehydes **2** used here were commercial samples. THF was freshly distilled from sodium benzophenone ketyl. All reactions were carried out under dry nitrogen.

Representative Procedure for the Reaction between Allyltributyltin (1a) and 2a Catalyzed by nBu$_4$NBr/PbI$_2$: PbI_2 (0.046 g, 0.1 mmol) and nBu$_4$NBr (0.033 g, 0.1 mmol) were successively added to deionized water (1 mL). Initially, PbI_2 only slightly dissolved in water. After 10 min., the yellow solid PbI_2 changed to give a pale yellow suspension. To the mixture were added aldehyde **2a** (0.14 g, 1 mmol) and allyltributyltin (0.33 g, **1a**) (1 mmol). After stirring at room temp. for 48 h, 10 mL of H_2O was added and the mixture was extracted with ether (3 × 50 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and then evaporated. The residue was subjected to column chromatography eluting with hexane/EtOAc (1:1) to give product **3a** (0.153 g). Further purification was performed by silica gel TLC with hexane/Et_2O (7:1).

1-(4-Chlorophenyl)-3-buten-1-ol (3a):[12] 84% yield (0.153 g, 0.47 mmol). − IR (neat): $\tilde{\nu}$ = 3400, 1600 cm^{-1}. − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 2.04 (d, J = 3.2 Hz, 1 H), 2.42−2.52 (m, 2 H), 4.73 (ddd, J = 3.2, 5.6 and 7.1 Hz), 5.12 5.20 (m, 2 H), 5.71−5.86 (m, 1 H), 7.27−7.34 (m, 4 H). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 43.72, 72.52, 118.64, 127.15, 128.43, 133.06, 133.92, 142.26. − CI-HRMS [M$^+$ + 1]: calcd. for $C_{10}H_{11}ClO$ 182.0498; found 183.0574.

1-(2-Hydroxyphenyl)-3-buten-1-ol (3e):[13] Prepared by the typical procedure (room temp.) from **1a** (1 mmol) and **2e** (1 mmol) in 84% yield (0.138 g, 0.84 mmol). − IR (neat): $\tilde{\nu}$ = 3200, 1600 cm^{-1}. − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 2.56−2.67 (m, 2 H), 2.77 (d, J = 2.9 Hz, 1 H), 4.85−4.90 (m, 2 H), 5.19−5.25 (m, 2 H), 5.73−5.90 (m, 1 H), 6.81−7.20 (m, 4 H), 7.99 (s, 1 H). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 42.0, 74.4, 119.0, 126.5, 117.0, 119.8, 127.0, 128.8, 133.8, 155.2. − $C_{10}H_{12}O_2$ (164.2): calcd. C 73.15, H 7.37; found C 72.97, H 7.49.

1-(2-Amino-3,5-dibromophenyl)-3-buten-1-ol (3f): Prepared by the typical procedure (60 °C, 16 h) from **1a** (1 mmol) and **2f** (1 mmol) in 92% yield (0.293 g, 0.92 mmol). − IR (neat): $\tilde{\nu}$ = 3150, 1685, 1457, 1234 cm^{-1}. − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 2.25 (d, J = 3.4 Hz, 1 H), 2.53−2.74 (m, 2 H), 4.67 (ddd, J = 3.4, 5.1 and 8.4 Hz, 1 H), 4.82 (s, 2 H), 5.18−5.24 (m, 2 H), 5.74−5.89 (m, 1 H), 7.12 (d, J = 2.0 Hz, 1 H), 7.49 (d, J = 2.0 Hz, 1 H). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 39.4, 73.1, 108.8, 111.3, 119.2, 129.4, 134.0, 134.3, 141.9. − HRMS: calcd. for $C_{10}H_{11}Br_2NO$ 318.9207; found 318.9205.

1-Phenylhex-1,5-dien-3-ol (3g):[14] Prepared by the typical procedure (60 °C, 48 h) from **1a** (1 mmol) and **2g** (1 mmol) in 80% yield (0.139 g, 0.80 mmol). − IR (neat): $\tilde{\nu}$ = 3350, 1640 cm^{-1}. − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.85 (s, 1 H), 2.34−2.48 (m, 2 H), 4.36 (q, J = 6.4 Hz, 1 H), 5.15−5.20 (m, 2 H), 5.81−5.91 (m, 1 H), 6.24 (dd, J = 6.4 and 15.6 Hz), 6.61 (d, J = 15.6 Hz, 1 H), 7.22−7.39 (m, 5 H). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 42.0, 71.7, 118.2, 126.4, 127.5, 128.4, 130.2, 131.4, 133.9, 136.5. − $C_{12}H_{14}O$ (174.2): calcd. C 82.72, H 8.10; found C 82.65, H 8.25.

5-Phenyl-1-hexen-3-ol (3h):[12] Prepared by the typical procedure from **1a** (1 mmol) and **2h** (1 mmol) in 43% yield (0.075 g, 0.43 mmol). − IR (neat): $\tilde{\nu}$ = 3300, 1640 cm^{-1}. − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.62 (br., 1 H), 1.76−1.82 (m, 2 H), 2.15−2.22 (m, 1 H), 2.29−2.36 (m, 1 H), 2.65−2.73 (m, 1 H), 2.78−2.85 (m, 1 H), 3.65−3.71 (m, 1 H), 5.12−5.17 (m, 2 H), 5.78−5.87 (m, 1 H), 7.17−7.30 (m, 5 H). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 32.0, 38.4, 42.0, 69.9, 118.0, 125.7, 128.3(2C), 134.5, 141.9. − EIMS: m/z = 176 [M$^+$], 158, 135, 117, 105, 91. − $C_{12}H_{16}O$ (176.3): calcd. C 81.77, H 9.15; found C 82.01, H9.22.

Diastereoselective Reaction between Crotyltributyltin (1b, c) and 2a Catalyzed by nBu$_4$NBr/PbI$_2$: PbI_2 (0.046 g, 0.1 mmol) and nBu$_4$NBr (0.033 g, 0.1 mmol) were successively added to deionized water (1 mL). After 10 min., the yellow PbI_2 changed to give a pale yellow suspension. To the mixture were added aldehyde **2a** (0.14 g, 1 mmol) and crotyltributyltin (**1b** or **1c**; 0.345 g, 1 mmol). After stirring at 60 °C for 48 h, 10 mL of H_2O was added and the mixture was extracted with ether (3 × 50 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and then evaporated. The diastereomeric ratio was determined by ^{1}H NMR spectroscopy. The residue was subjected to column chromatography eluting with hexane/EtOAc (1:1) to give **3i** as a *syn*/*anti* mixture (0.177 g). Further purification was performed by silica gel TLC with hexane/Et_2O (7:1).

1-(*p*-Chlorophenyl)-2-methyl-3-buten-1-ol (3i):[15] 90% yield (0.177 g, 0.90 mmol); *syn*:*anti* = 89:11. − IR (neat): $\tilde{\nu}$ = 3409, 2877, 1704 cm^{-1}. − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.85 (d, J = 7.3 Hz, 3 × 0.11 H) (*anti*), 1.00 (d, J = 6.8 Hz, 3 × 0.89 H) (*syn*), 2.05 (d, J = 3.9 Hz, 1 × 0.89 H) (*syn*), 2.25 (d, J = 2.4 Hz, 1 × 0.11 H) (*anti*), 2.35−2.50, (m, 1 × 0.11 H) (*anti*), 2.45−2.62 (m, 1 × 0.89 H) (*syn*), 4.33 (dd, J = 2.4 and 7.8 Hz, 1 × 0.11 H) (*anti*), 4.55 (dd, J = 3.9 and 4.9 Hz, 1 × 0.89 H) (*syn*), 5.00−5.15 (m, 2 × 0.89 H) (*syn*), 5.18−5.25 (m, 2 × 0.11 H) (*anti*), 5.65−5.85 (m, 1 H), 7.15−7.90 (m, 4 H). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 13.4 (*anti*), 13.7 (*syn*), 44.5 (*syn*), 46.1 (*anti*), 76.4, 115.9, 127.9, 128.2, 128.3, 139.9, 141.1. − HRMS: calcd. for $C_{11}H_{13}ClO$ 196.0655; found 196.0653.

2-Methyl-1-phenyl-3-buten-1-ol (3j):[16] Prepared by the typical procedure from **1b** (1 mmol) and **2b** (1 mmol) in 80% yield (0.130 g, 0.80 mmol); *syn*:*anti* = 90:10. − IR (neat): $\tilde{\nu}$ = 3424, 2977, 2877, 1457, 1002 cm^{-1}. − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.88 (d, J = 6.8 Hz, 3 × 0.10 H) (*anti*), 1.02 (d, J = 6.8 Hz, 3 × 0.90 H) (*syn*), 1.94 (d, J = 3.4 Hz, 1 × 0.90 H) (*syn*), 2.14 (d, J = 2.9 Hz, 1 × 0.10 H) (*anti*), 2.40−2.60, (m, 1 × 0.10 H) (*anti*), 2.50−2.70 (m, 1 × 0.90 H) (*syn*), 4.37 (dd, J = 2.9 and 7.5 Hz, 1 × 0.10 H) (*anti*), 4.63 (dd, J = 3.4 and 4.9 Hz, 1 × 0.90 H) (*syn*), 5.00−5.10 (m, 2 × 0.90 H) (*syn*), 5.18−5.25 (m, 2 × 0.10 H) (*anti*), 5.70−5.85 (m, 1 H), 7.20−7.45 (m, 5 H). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 13.3 (*anti*), 13.8 (*syn*), 44.4 (*syn*), 46.0 (*anti*), 76.8 (*syn*), 77.2 (*anti*), 115.3 (*syn*), 116.6 (*anti*), 126.2 (*syn*), 126.6 (*anti*), 127.1 (*syn*), 127.4 (*anti*), 127.8 (*syn*), 128.0 (*anti*), 140.0 (*syn*), 140.4 (*anti*), 142.3. − HRMS [M$^+$ + 1]: calcd. for $C_{11}H_{14}O$ 162.1045; found 163.1150.

2-Methyl-1-(*p*-methylphenyl)-3-buten-1-ol (3k):[15] Prepared by the typical procedure from **1b** (1 mmol) and *p*-tolualdehyde (1 mmol) in 90% yield (0.159 g, 0.90 mmol); *syn*:*anti* = 90:10. − IR (neat): $\tilde{\nu}$ = 3417, 2977, 2869, 1635, 1511, 1457, 1002, 910 cm^{-1}. − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.87 (d J = 6.8 Hz, 3 × 0.1 H,) (*anti*), 1.05 (d, J = 6.8 Hz, 3 × 0.9 H) (*syn*), 1.93 (br., 1 × 0.9 H) (*syn*), 2.15 (br., 1 × 0.1 H) (*anti*), 2.34 (s, 3 H), 2.40−2.55 (m, 1 × 0.1 H) (*anti*), 2.50−2.65 (m, 1 × 0.9 H) (*syn*), 4.32 (d J = 8.3 Hz, 1 × 0.1 H,) (*anti*), 4.58 (d, J = 5.4 Hz, 1 × 0.9 H) (*syn*), 5.00−5.10 (m, 2 × 0.9 H) (*syn*), 5.15−5.25 (m, 2 × 0.1 H) (*anti*), 5.68−5.85 (m, 1 H), 7.10−7.30 (m, 4 H). − ^{13}C NMR (67.9 MHz, $CDCl_3$):

δ = 13.4 (*anti*), 14.0 (*syn*), 21.0, 44.5 (*syn*), 46.1 (*anti*), 77.2 (*syn*), 77.7 (*anti*), 115.4, 126.5, 128.8, 137.0, 140.5, 140.9. − HRMS [M^+ + 1]: calcd. for $C_{12}H_{16}O$ 176.1201; found 177.1282.

1-(4-Methoxyphenyl)-2-methyl-3-buten-1-ol (3l):[14] Prepared by the typical procedure from **1b** (1 mmol) and *p*-anisaldehyde (1 mmol) in 70% yield (0.134 g, 0.70 mmol); *syn*:*anti* = 85:15. − IR (neat): $\tilde{\nu}$ = 3417, 2977, 2869, 1635, 1511, 1457, 1002, 910 cm^{-1}. − ^1H NMR (270 MHz, $CDCl_3$): δ = 0.84 (d, *J* = 6.8 Hz, 3 × 0.15 H) (*anti*), 1.02 (d, *J* = 6.8 Hz, 3 × 0.85 H) (*syn*), 1.88 (d, *J* = 3.4 Hz, 1 × 0.85 H) (*syn*), 2.11 (d, *J* = 2.0 Hz, 1 × 0.15 H) (*anti*), 2.40−2.55 (m, 1 × 0.15 H) (*anti*), 2.50−2.65 (m, 1 × 0.85 H) (*syn*), 3.80 (s, 3 H), 4.28 (dd, *J* = 2.0 and 8.3 Hz, 1 × 0.15 H) (*anti*), 4.53 (dd, *J* = 3.4 and 6.3 Hz, 1 × 0.85 H) (*syn*), 5.00−5.10 (m, 2 × 0.85 H) (*syn*), 5.15−5.25 (m, 2 × 0.15 H) (*anti*), 5.68−5.85 (m, 1 H), 6.80−7.30 (m, 4 H). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 14.3 (*syn*), 16.5 (*anti*), 44.6 (*syn*), 46.3 (*anti*), 55.2, 77.0, 113.4, 113.6, 127.6, 134.8, 140.3, 158.8. − HRMS [M^+ + 1]: calcd. for $C_{12}H_{16}O_2$ 192.1150; found 193.1231.

1-(2-Hydroxyphenyl)-2-methyl-3-buten-1-ol (3m): Prepared by the typical procedure from **1b** (1 mmol) and **2e** (1 mmol) in 82% yield (0.146 g, 0.82 mmol); *syn*:*anti* = 82:18. − IR (neat): $\tilde{\nu}$ = 3300, 2950, 2900, 1589, 1492, 1245 cm^{-1}. − ^1H NMR (270 MHz, $CDCl_3$): δ = 0.91 (d, *J* = 6.8 Hz, 3 × 0.18 H) (*anti*), 1.11 (d, *J* = 6.8 Hz, 3 × 0.82 H) (*syn*), 2.53 (d, *J* = 1.5 Hz, 1 × 0.82 H) (*syn*), 2.80 (s, *J* = 2.4 Hz, 1 × 0.18 H) (*anti*), 2.64−2.74 (m, 1 H), 4.43 (d, *J* = 8.8 Hz, 1 × 0.18 H) (*anti*), 4.83 (dd, *J* = 1.5 and 4.9 Hz, 1 × 0.82 H) (*syn*), 5.05−5.18 (m, 2 × 0.82 H) (*syn*), 5.25−5.35 (m, 2 × 0.18 H) (*anti*), 5.75−5.90 (m, 1 H), 6.80−7.30 (m, 4 H), 7.95 (s, 1 × 0.82 H) (*syn*), 8.12 (s, 1 × 0.18 H) (*anti*). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 13.3 (*syn*), 13.6 (*anti*), 44.4 (*syn*), 44.8 (*anti*), 79.3 (*syn*), 79.4 (*anti*), 116.2, 117.1, 119.3, 128.0, 128.8, 129.0, 140.0, 155.9. − HRMS [M^+ + 1]: calcd. for $C_{11}H_{14}O_2$ 178.0994; found 179.1097.

1-(2-Nitrophenyl)-2-methyl-3-buten-1-ol (3n): Prepared by the typical procedure from **1b** (1 mmol) and **2d** (1 mmol) in 76% yield (0.157 g, 0.76 mmol); *syn*:*anti* = 82:18. − IR (neat): $\tilde{\nu}$ = 3450, 2973, 1523, 1346, 1002 cm^{-1}. − ^1H NMR (270 MHz, $CDCl_3$): δ = 1.00 (d, *J* = 6.8 Hz, 3 × 0.82 H) (*syn*), 1.03 (d, *J* = 6.8 Hz, 3 × 0.18 H) (*anti*), 1.65 (br., 1 × 0.18 H) (*anti*), 2.35 (br, 1 × 0.82 H) (*syn*), 2.55−2.70 (m, 1 H), 5.00−5.08 (m, 2 × 0.82 H) (*syn*), 5.11−5.17 (m, 2 × 0.18 H) (*anti*), 5.30 (d, *J* = 4.9 Hz, 1 × 0.82 H) (*syn*), 5.72−5.90 (m, 3 × 0.18 H) (*anti*), 7.38−7.93 (m, 4 H). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 13.2 (*syn*), 13.6 (*anti*), 43.3 (*syn*), 45.1 (*anti*), 71.9 (*syn*), 72.0 (*anti*), 115.9, 124.4, 128.0, 128.9, 129.1, 133.0, 138.8, 140.2. − HRMS: calcd. for $C_{11}H_{13}NO_3$ 207.08953; found 208.0982 (CI, M^+ + 1).

1-(4-Cyanophenyl)-2-methyl-3-buten-1-ol (3o):[17] Prepared by the typical procedure from **1b** (1 mmol) and *p*-cyanobenzaldehyde (1 mmol) in 94% yield (0.176 g, 0.94 mmol); *syn*:*anti* = 80:20. − IR (neat): $\tilde{\nu}$ = 3486, 2977, 2877, 2229, 1704, 1411, 910 cm^{-1}. − ^1H NMR (270 MHz, $CDCl_3$): δ = 0.88 (d, *J* = 6.8 Hz, 3 × 0.20 H) (*anti*), 1.02 (d, *J* = 6.8 Hz, 3 × 0.80 H) (*syn*), 2.10 (d, *J* = 3.9 Hz, 1 × 0.80 H) (*syn*), 2.29 (d, *J* = 2.9 Hz, 1 × 0.20 H) (*anti*), 2.40−2.55 (m, 1 × 0.20 H) (*anti*), 2.50−2.65 (m, 1 × 0.80 H) (*syn*), 4.37 (dd, *J* = 2.9 and 8.3 Hz, 1 × 0.20 H) (*anti*), 4.63 (dd, *J* = 3.9 and 4.9 Hz, 1 × 0.80 H) (*syn*), 5.00−5.15 (m, 2 × 0.80 H) (*syn*), 5.15−5.25 (m, 2 × 0.20 H) (*anti*), 5.68−5.85 (m, 1 H), 7.40−8.05 (m, 4 H). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 13.4 (*syn*), 16.2 (*anti*), 44.5 (*syn*), 46.1 (*anti*), 76.2 (*syn*), 76.9 (*anti*), 110.8, 116.2, 118.8, 127.1, 131.7, 139.4, 148.0. − HRMS [M^+ + 1]: calcd. for $C_{12}H_{13}NO$ 187.0997; found 188.1074.

(*E*)-3-Hydroxy-4-methyl-1-phenyl-1,5-hexadiene (3p):[18] Prepared by the typical procedure from **1b** (1 mmol) and **2g** (1 mmol) in 80% yield (0.175 g, 0.80 mmol); *syn*:*anti* = 87:13. − IR (neat): $\tilde{\nu}$ = 3450, 2958, 1450, 9702 cm^{-1}. − ^1H NMR (270 MHz, $CDCl_3$): δ = 1.06 (d, *J* = 6.8 Hz, 3 × 0.13 H) (*anti*), 1.09 (d, *J* = 6.8 Hz, 3 × 0.87 H) (*syn*), 1.70 (d, *J* = 4.9 Hz, 1 × 0.87 H) (*syn*), 1.85 (d, *J* = 3.4 Hz, 1 × 0.13 H) (*anti*), 2.30−2.45 (m, 1 × 0.13 H) (*anti*), 2.40−2.55 (m, 1 × 0.87 H) (*syn*), 4.00−4.10 (m, 1 × 0.13 H) (*anti*), 4.15−4.25 (m, 1 × 0.87 H) (*syn*), 5.00−5.25 (m, 2 H), 5.75−5.95 (m, 1 H), 6.23 (dd, *J* = 6.4 and 16.1 Hz, 1 H), 6.58 (d, *J* = 16.1 Hz, 1 H) 7.20−7.45 (m, 5 H). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 13.6 (*syn*), 16.0 (*anti*), 43.9 (*syn*), 44.7 (*anti*), 75.8 (*syn*), 76.1 (*anti*), 116.0 (*syn*), 116.7 (anti), 126.5, 127.6, 128.5, 129.9, 131.2, 136.7, 139.9. − HRMS [M^+ + 1]: calcd. for $C_{13}H_{16}O$ 188.1201; found 189.1291.

4-Hydroxy-3-methyl-6-phenyl-1-hexene (3q):[18] Prepared by the typical procedure (room temp.) from **1b** (1 mmol) and **2h** (1 mmol) in 47% yield (0.089 g, 0.47 mmol); *syn*:*anti* = 70:30. − IR (neat): $\tilde{\nu}$ = 3400, 2969, 1496, 1454 cm^{-1}. − ^1H NMR (270 MHz, $CDCl_3$): δ = 1.05 (d, *J* = 6.8 Hz, 3 × 0.70 H) (*syn*), 1.08 (d, *J* = 6.8 Hz, 3 × 0.30 H) (*anti*), 1.60−1.90 (m, 3 H), 2.20−2.35 (m, 1 H), 2.55−2.95 (m, 2 H), 3.35−3.45 (m, 1 × 0.70 H)(*anti*), 3.45−3.60 (m, 1 × 0.30 H) (*syn*), 5.00−5.15 (m, 2 H), 5.68−5.85 (m, 1 H), 7.10−7.40 (m, 5 H). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 14.2 (*syn*), 16.2 (*anti*), 32.1 (*anti*), 32.4 (*syn*), 35.8 (*syn*), 36.08 (*anti*), 43.7 (*syn*), 44.3 (*anti*), 73.98 (*anti*), 74.04 (*syn*), 115.5, 125.8, 128.4, 128.5, 140.65, 140.73. − HRMS [M^+ + 1]: calcd. for $C_{13}H_{18}O$ 190.1358; found 191.1434.

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[11] If allyllead species were formed by the Sn−Pb transmetallation, an *anti*-selectivity should be observed from (*E*)-crotytin **1b** through a Zimmerman−Traxler transition state as in the case of the indium-promoted allylation.[4]

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