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Control of diastereoselectivity in the crotylation and cinnamylation of aldehydes by the selection of ligands on allylic indium reagents

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Diastereoselective couplings of salicylaldehyde, anisaldehyde and 2-pyridylaldehyde with crotyl- and cinnamylindium reagents were studied. The *syn*/*anti* selectivity was found to depend largely on the ligands on the indium atom of the allylic indium reagents. A *syn*-selective cinnamylation of salicylaldehyde was realized by the combination of cinnamyl acetate and indium(I) iodide, whereas an *anti*-selective coupling with salicylaldehyde was achieved by the indium trichloride/aluminium-mediated cinnamylation.

Introduction

Diastereoselective allylation of aldehyde or ketone is the most fundamental reaction in carbon–carbon bond formation.[1] Diastereoselectivity in the addition of allylic organometallic compounds to α-substituted carbonyl compounds is explained by two models: steric and stereoelectronic effects of an α-substituent (Cram–Felkin–Anh's model)[2a–d] and chelation of an α-hetero atom to the organometallic reagents (Cram's cyclic model).[2e,f] Various allylic metal reagents have been utilized for this purpose, of which allylindium reagents have received much interest in the past decade.[3] Even in water, high diastereoselectivities have been realized on the basis of the chelation of a hetero atom in the substrates, where a free hydroxyl group at the α- or β-position serves as a good chelator to indium.[3a–i] The stereochemical outcome has hitherto been argued on the Barbier-type In-mediated allylation of aldehydes, where the active allylindium reagents are considered to be allylindium(III) sesquihalides or allylindium(I).[4] On the other hand, the diastereoselectivity involving other types of allylindium reagents, such as allylindium dihalides and triallylindium reagents, has not been investigated. We have recently described the preparation of allylindium reagents by umpolung reaction of π-allylpalladium(II) with indium(I) iodide, which leads to homoallylic alcohols upon coupling with aldehydes.[5] Higher availability of usable allylic substrates, including allylic chlorides and allylic acetates, facilitates preparation of allylindium reagents possessing a variety of ligands on the indium atom such as Cl and OAc. These reagents can not be prepared by the conventional oxidative addition of indium metal to allylic chlorides and allylic acetates. Here we report a Pd-catalyzed crotylation and cinnamylation by the above umpolung procedure, where the ligands on the indium atom exert a significant effect on control of the diastereoselectivity for the allylation of aromatic aldehydes possessing a chelating unit at the α-position.

Results and discussion

Halides as ligand

At first, diastereoselectivity was surveyed in the reaction of crotylindium sesquihalide with benzaldehyde by changing the solvent and reaction temperature. Crotylindium sesquibromide was prepared from crotyl bromide and indium at room temperature for 1 h, and then benzaldehyde was added. (Method A, Table 1, Entries 1–7). The outcome of stereoselectivity was none; the *syn*- and *anti*-adducts were obtained in almost equal ratios. Only in DMF at low temperature, a slight preference for the *syn*-adduct was observed. (Entry 7). The crotylindium reagent, generated from crotyl chloride and indium(I) iodide in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium(0) (Method B-1), gave a modest *anti*-adduct selectivity (Entry 8). The use of InBr gave a similar result (Entry 9). The regioisomer of crotyl chloride, 3-chlorobut-1-ene, gave the corresponding homoallylic alcohol with loss of the diastereoselectivity (Entries 10 and 11).

On the contrary, crotylation of 2-pyridylaldehyde gave the *syn*-adduct mainly. The solvent and temperature did not largely affect the diastereoselectivity (Entries 12–15). This *syn*-selectivity is explained by a general chelation model as shown in Fig. 1. It is known that the In-mediated reaction of 2-pyridylaldehyde with 3-bromo-1-trifluoromethylprop-1-ene proceeds stereoselectively giving the corresponding *syn*-adduct.[3j,k] The *syn*-adduct was also obtained from salicylaldehyde by a similar chelation-assisted procedure (Entries 16 and 17). Such chelation effect of salicylaldehyde was observed with a crotylstannane reagent.[6]

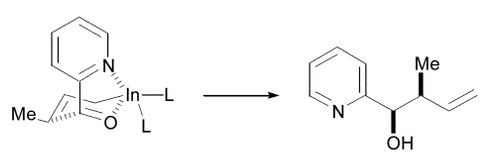

Fig. 1 A proposed transition state for the *syn* crotylation of 2-pyridyl aldehyde.

The reactions of cinnamylindium and aromatic aldehydes were then studied. Although an α- or a β-hydroxyl group in carbonyl compounds is reported to be the most effective for chelation to indium,[3a–i] salicylaldehyde gave only low *syn*-stereoselectivities (Entries 18 and 19). The *anti*-diastereoselectivity observed for the coupling with *o*-anisaldehyde indicates that chelation control by the methoxy group is not operational (Entries 20 and 21).

Acetoxy group as ligand

Next, crotyl and cinnamyl acetates were used for allylating compounds. Crotylation of benzaldehyde with crotyl acetate (*E* : *Z* = 85 : 15) by Method B-2 gave the *anti*-homoallylic

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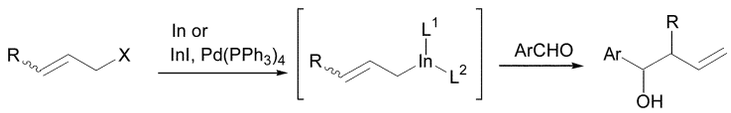
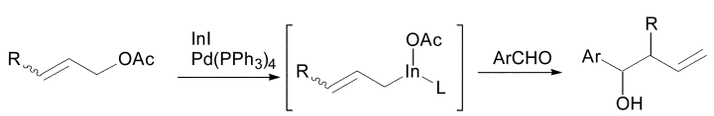
Table 1 Reaction of crotyl and cinnamyl halides with aromatic aldehydes[a]



Entry	R	X	Ar	Method[b]	*t*/h	Solvent	*T*/°C	L^1	L^2	Product	Yield (%)	*syn* : *anti*
1	Me	Br	Ph	**A**	2	MeOH	rt	Crotyl, Br		**1a**	99	54 : 46
2	Me	Br	Ph	**A**	2	MeOH	−78	Crotyl, Br		**1a**	67	50 : 50
3	Me	Br	Ph	**A**	2	THF	rt	Crotyl, Br		**1a**	78	56 : 44
4	Me	Br	Ph	**A**	2	THF	−78	Crotyl, Br		**1a**	77	46 : 54
5	Me	Br	Ph	**A**	2	ether	rt	Crotyl, Br		**1a**	53	43 : 57
6	Me	Br	Ph	**A**	2	ether	−78	Crotyl, Br		**1a**	35	55 : 45
7	Me	Br	Ph	**A**	2	DMF	−60	Crotyl, Br		**1a**	95	64 : 36
8	Me	Cl	Ph	**B-1**	1.5	THF	rt	I	Cl	**1a**	96	37 : 63
9	Me	Cl	Ph	**B-1**[c]	1.5	THF	rt	Br	Cl	**1a**	80	33 : 67
10	Me	Cl	Ph	**B-1**[d]	1.5	THF	rt	I	Cl	**1a**	92	58 : 42
11	Me	Cl	Ph	**B-1**[c,d]	1.5	THF	rt	Br	Cl	**1a**	89	47 : 53
12	Me	Cl	2-Pyridyl	**B-1**	2	DMI	rt	I	Cl	**1b**	43	83 : 17
13	Me	Cl	2-Pyridyl	**B-1**	2	THF	rt	I	Cl	**1b**	72	84 : 16
14	Me	Cl	2-Pyridyl	**B-1**	7	THF	−40	I	Cl	**1b**	50	83 : 17
15	Me	Cl	2-Pyridyl	**B-1**	24	THF	−78	I	Cl	**1b**	49	78 : 22
16	Me	Cl	*o*-C_6H_4OH	**B-1**	2	DMI	rt	I	Cl	**1c**	90	78 : 22
17	Me	Cl	*o*-C_6H_4OH	**B-1**	7	THF	rt	I	Cl	**1c**	88	75 : 25
18	Ph	Cl	*o*-C_6H_4OH	**B-1**	1	DMI	rt	I	Cl	**2c**	100	55 : 45
19	Ph	Cl	*o*-C_6H_4OH	**B-1**	2	THF	rt	I	Cl	**2c**	95	56 : 44
20	Ph	Cl	*o*-C_6H_4OMe	**B-1**	1	DMI	rt	I	Cl	**2d**	86	33 : 67
21	Ph	Cl	*o*-C_6H_4OMe	**B-1**	2	THF	rt	I	Cl	**2d**	86	24 : 76

[a] All reactions were carried out with allylic substrates–aldehyde = 2 : 1. [b] Method **A**; crotyl bromide and indium were premixed at rt for 1 h, and then benzaldehyde was added. Method **B-1**; Crotyl chloride (*E* : *Z* = 85 : 15) or cinnamyl chloride (*E* only) and InI were used in the presence of $Pd(PPh_3)_4$ (5 mol%). [c] InBr was used in place of InI. [d] 3-Chlorobut-1-ene was used in place of crotyl chloride.

Table 2 Reaction of crotyl and cinnamyl acetates with aromatic aldehydes[a]



Entry	R	Ar	Method[b]	*t*/h	Solvent	L	Product	Yield (%)	*syn* : *anti*
1	Me	Ph	**B-2**	1.5	THF	I	**1a**	98	32 : 68
2	Me[c]	Ph	**B-2**	1.5	THF	I	**1a**	72	71 : 29
3[d]	Me	2-Pyridyl	**B-2**	7	THF	I	**1b**	61	93 : 7
4[d]	Me[c]	2-Pyridyl	**B-2**	7	THF	I	**1b**	73	86 : 14
5	Me	*o*-C_6H_4OH	**B-2**	2	DMI	I	**1c**	82	75 : 25
6	Ph	Ph	**B-2**	1.5	THF	I	**2a**	100	14 : 86
7	Ph	2-Pyridyl	**B-2**	6	DMI	I	**2b**	73	100 : 0
8	Ph	2-Pyridyl	**B-2**	48	DCM	I	**2b**	83	100 : 0
9	Ph	*o*-C_6H_4OH	**B-2**	2	DMI	I	**2c**	100	96 : 4
10	Ph	*o*-C_6H_4OH	**B-2**	2	THF	I	**2c**	87	82 : 18
11	Ph	*o*-C_6H_4OH	**B-2**	7	DCM	I	**2c**	90	63 : 37
12	Ph	*o*-C_6H_4OH	**B-2**	24	THF–H_2O (1 : 1)	I	**2c**	59	44 : 56
13	Ph	*o*-C_6H_4OH	**B-2**	24	H_2O	I	**2c**	44	34 : 66
14	Ph	*o*-C_6H_4OH	**C**	2	DMI	Cl	**2c**	92	2 : 98
15	Ph	*o*-C_6H_4OH	**B-2**[e]	2	DMI	Cl	**2c**	50	76 : 24
16	Ph	*o*-C_6H_4OH	**B-2**[f]	6	DMI	I	**2c**	85	64 : 36
17	Ph	*o*-C_6H_4OH	**B-2**[g]	3	DMI	I	**2c**	55	11 : 89
18	Ph	*o*-C_6H_4OMe	**B-2**	1	DMI	I	**2d**	90	21 : 79
19	Ph	*o*-C_6H_4OMe	**B-2**	2	THF	I	**2d**	86	21 : 79
20	Ph	*o*-C_6H_4OMe	**B-2**	7	DCM	I	**2d**	92	27 : 73
21	Ph	*o*-C_6H_4OMe	**C**	24	DMI	Cl	**2d**	63	7 : 93

[a] Unless otherwise noted, reactions were carried out with crotyl acetate (*E* : *Z* = 85 : 15) or cinnamyl acetate (*E* only) in the ratio of allylic substrates–aldehyde–InI = 2 : 1 : 2. [b] Method **B-2**; cinnamyl acetate and InI were used in the presence of $Pd(PPh_3)_4$ (5 mol%). Method **C**; cinnamyl acetate, $InCl_3 \cdot nH_2O$ (n = 3–4), and Al were used in the presence of $Pd(PPh_3)_4$ (5 mol%). [c] Crotyl acetate (*Z*-only) was used. [d] Allylic substrates–aldehyde–InI = 2 : 1 : 1. [e] InCl was used in place of InI. [f] In the presence of an equimolar amount of $InCl_3 \cdot nH_2O$ (n = 3–4) to cinnamyl acetate. [g] In the presence of an equimolar amount of $AlCl_3$ to cinnamyl acetate.

alcohol preferentially (Table 2, Entry 1), though (*Z*)-crotyl acetate gave the *syn*-adduct dominantly (Entry 2). In contrast, 2-pyridylaldehyde and salicylaldehyde gave the *syn*-products selectively regardless of the geometry of the starting crotyl acetate (Entries 3–5), based on the chelation control. The chelating effect was also observed for the reaction of cinnamylindium derived from cinnamyl acetate: benzaldehyde gave the *anti*-adduct (Entry 6), and 2-pyridylaldehyde gave the *syn*-product exclusively (Entries 7 and 8). A dramatic improvement of the diastereoselectivity was observed in the coupling of

salicylaldehyde by using cinnamyl acetate in place of cinnamyl chloride (Entries 9–11).

In this reaction, the ligands on the indium atom are considered to be I and OAc. A plausible transition state is depicted in Fig. 2, which involves an intramolecular hydrogen bonding between the acetoxy group on the indium atom and the α-hydroxyl group of salicylaldehyde. In aqueous media, the reaction proceeded more slowly and the selectivity was reversed to *anti*, indicating that the chelation of the hydroxyl group to the indium atom did not work (Entries 12 and 13). A combination of indium trichloride hydrate and metallic aluminium powder[5b] is also usable in the coupling of salicylaldehyde with cinnamyl acetate (Method C). Interestingly, the cinnamylation by this method gave the *anti*-adduct highly selectively (Entry 14). In this case, one of the ligands on the indium atom of the cinnamylindium reagent is considered to be Cl instead of I, because this reagent is prepared from π-cinnamylpalladium and indium(I) chloride generated *in situ*. In order to check the role of Cl on the indium atom, the reaction of salicylaldehyde with cinnamyl acetate was performed by changing indium(I) iodide to indium(I) chloride, which resulted in the formation of **2c** with the ratio of *syn* : *anti* = 76 : 24 (Entry 15). This fact indicates that Cl on the indium atom does not affect the inversion of the *syn* : *anti* ratio. Therefore, the observed highly *anti*-selective cinnamylation of salicylaldehyde may occur under the influence of indium trichloride or aluminium trichloride formed *in situ*. These Lewis acids are considered to coordinate to the carbonyl and hydroxyl groups of salicylaldehyde prior to the attack of cinnamylindium and prevent the chelation of the hydroxyl group to the cinnamylindium reagent. In order to check this possibility, the reactions were performed in the presence of indium trichloride hydrate or aluminium trichloride, and homoallylic alcohol **2c** was formed in 85% (*syn* : *anti* = 64 : 36) and 55% yields (*syn* : *anti* = 11 : 89), respectively (Entries 16 and 17). These results indicate that the chelation of the hydroxyl group is prevented by aluminium trichloride in the $InCl_3$–Al mediated reaction. The reaction of *o*-anisaldehyde gave the *anti*-adduct predominantly by Method B-2 (Entries 18–20), indicating again the negligible chelation of the methoxy group. Method C also gave high *anti*-selectivity for this substrate (Entry 21).

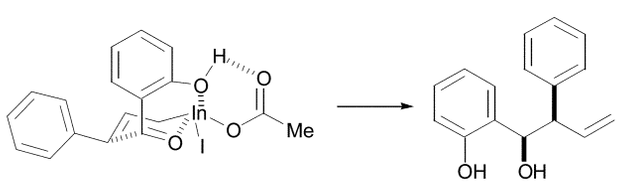


Fig. 2 A plausible transition state for the *syn* allylation of salicylaldehyde with the cinnamylindium reagent derived from cinnamyl acetate.

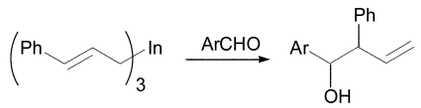
Tricinnamylindium

The reaction of tricinnamylindium, prepared by transmetallation of cinnamyllithium with indium trichloride in THF (Method D), was tested on the coupling with benzaldehyde, 2-pyridylaldehyde, salicylaldehyde and *o*-anisaldehyde (Table 3). The observed diastereoselectivities were almost coincident to the cases with cinnamyl chloride by Method B-1; benzaldehyde and *o*-anisaldehyde gave the *anti*-adducts, whereas 2-pyridylaldehyde and salicylaldehyde afforded the *syn*-adducts, but in somewhat lower selectivity than that with cinnamyl acetate.

Mechanistic consideration

The *syn*–*anti* selectivity of reactions involving γ-substituted allylic indium reagents and aldehydes can be explained by a series of cyclic transition states illustrated in Fig. 3, where the

Table 3 Reaction of tricinnamylindium with aromatic aldehydes[a]



Entry	Ar	Product	Yield (%)	*syn* : *anti*
1	Ph	**2a**	74	19 : 81
2	2-Pyridyl	**2b**	76	74 : 26
3	*o*-C_6H_4OH	**2c**	82	61 : 39
4	*o*-C_6H_4OMe	**2d**	50	27 : 73

[a] All reactions were carried out with tricinnamylindium–aldehyde = 2 : 1 in THF at room temperature for 2 h.

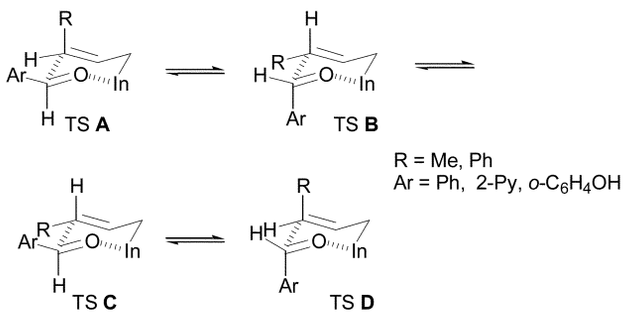


Fig. 3 Proposed transition states.

allylindium reagent coordinates intramolecularly to the oxygen atom of the carbonyl group. TS **A** and/or TS **B** allow the formation of the *syn*-adduct, while the *anti*-product is obtained from TS **C** and/or TS **D**. Generally, TS **C** leading to the *anti*-adduct is most favourable from the steric point of view unless some other intramolecular chelation operates, because both the R and Ar groups adopt equatorial positions and the allylic indium exists as the *E*-form. However, when the aldehyde possesses chelating units such as a hydroxyl group, the second intramolecular coordination to the allylindium reagent must be taken into consideration. In TS **B** and TS **D**, the hetero atom of the *o*-hydroxylphenyl or 2-pyridyl group is capable of coordinating to the indium atom. As cinnamylindium couples with aldehyde as the (*E*)-form irrespective of the geometry of the starting bromide,[7] the stereoselectivity is considered to be the outcome of the orientation of Ar. The low stereoselectivities observed in the reactions of salicylaldehyde in Table 1 and Table 3 indicate that the hydroxyl group on salicylaldehyde does not efficiently coordinate to the indium atom of the cinnamylindium reagents. High *syn*-selectivity is realized by fixing more tightly by the aid of the second chelation from the acetoxy group as seen in Fig. 2.

The results of the crotylation of benzaldehyde with (*E*)- and (*Z*)-crotyl acetates (Entries 1 and 2, Table 2) indicate that, in contrast to cinnamylation, the geometry of the starting acetates is reflected in the products to some extent. In Entries 3 and 4 in Table 2, both (*E*)- and (*Z*)-crotyl acetates gave the *syn*-adduct upon the reaction with 2-pyridylaldehyde. These facts suggest that (*E*)-crotylindium was formed from both (*E*)- and (*Z*)-acetates and reacted with 2-pyridylaldehyde *via* TS **B**. The crotylation of salicylaldehyde (Entry 5) undergoes less *syn*-selectively than the cinnamylindium case (Entry 9). This observation can be accounted for by the existence of (*Z*)-crotylindium derived from the (*Z*)-isomer contained in the starting acetate. The high *syn*-selectivity in the reactions of both (*E*)- and (*Z*)-crotyl acetates with 2-pyridylaldehyde can be rationalized by assuming that TS **D** is energetically too unfavourable; hence, crotylation proceeds *via* TS **B** after isomerization of (*Z*)-crotylindium to (*E*)-crotylindium.

Table 4 The chemical shifts of the olefinic proton –C*H*=CH_2 of **2a**–**d**

Product	*syn* (δ_H)	*anti* (δ_H)
2a	5.90	6.26
2b	6.11	6.24
2c	5.90	6.29
2d	6.00	6.30

Stereochemistry

The stereochemistry of compounds **1a**,[8] **1b**[9] **1c**,[10] **2a**[11] and **2b**[12] was confirmed according to the literature. The assignment of the *syn*-and *anti*-isomers of compounds **2c** and **2d** was made by comparison of the ^{1}H NMR with those of **2a** and **2b**. Compounds **2c** and **2d** give a similar ^{1}H-NMR pattern to **2a** and **2b**, and the *syn*-isomers show the signals of the olefinic proton –C*H*=CH_2 at higher field than the *anti*-isomers (Table 4).

Conclusion

The stereoselectivity associated with carbonyl allylation by allylindium reagents has hitherto been studied using various modified carbonyl compounds and allylic indium reagents;[3a–i] however, the influence of the ligands on the indium atom has received little attention.[13] The present study demonstrated for the first time that the diastereoselectivity of the indium-mediated allylation of aldehydes can be controlled not only by the α-oxygenated substitution in aldehydes, but also by a proper choice of the ligands on allylindium reagents.

Experimental

General

All reactions were carried out under a positive pressure of argon. THF was distilled from lithium aluminium hydride before use. Indium(I) iodide and indium(I) chloride were purchased from Aldrich Chemical Co. and were used directly as received. Indium trichloride was purchased from Katayama Chemical Co. and used as obtained. $Pd(PPh_3)_4$ was prepared according to the reported procedure.[14] Aldehydes were distilled prior to use. (*Z*)-Crotyl acetate was prepared from (*Z*)-crotyl alcohol according to the literature.[15] Infrared spectra were recorded on a JASCO IRA-102 spectrometer. ^{1}H-NMR spectra were recorded on a Varian Gemini-200 spectrometer (200 MHz). All NMR data were obtained in $CDCl_3$ solutions containing tetramethylsilane as an internal standard; *J*-values are given in Hz. Elemental analyses were performed at the Elemental Analysis Centre of Kyoto University.

Method **A**: (Entry 1 in Table 1) a mixture of crotyl bromide (206 μL, 2.0 mmol) and indium (115 mg, 1.0 mmol) was stirred in MeOH (2 mL) at room temperature for 1 h, and then benzaldehyde (102 μL, 1.0 mmol) was added. The reaction mixture was stirred at room temperature for 2 h and quenched with diluted 1 M HCl. The product was extracted with diethyl ether, and washed with water, then brine. The extracts were dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The product was purified by column chromatography on silica gel (elution with CH_2Cl_2) to afford 2-methyl-1-phenybut-3-en-1-ol (**1a**)[8] (160 mg, 99%, *syn* : *anti* = 54 : 46).

Method **B-2**: (Entry 7 in Table 2) to a mixture of indium(I) iodide (240 mg, 1.0 mmol) and $Pd(PPh_3)_4$ (30 mg, 0.025 mmol) in DMF (3 mL), cinnamyl acetate (165 μL, 1.0 mmol) and salicylaldehyde (53 μL, 0.50 mmol) were added at room temperature. The reaction mixture was stirred for 1 h and quenched with diluted 1 M HCl. The product was extracted with diethyl ether and washed with water, then brine. The extracts were dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The product was purified by column chromatography on silica gel (elution with hexane : CH_2Cl_2 = 1 : 2) to afford 1-(2-hydroxyphenyl)-2-phenylbut-3-en-1-ol (**2b**) (120 mg, 100%, *syn* : *anti* = 96 : 4).

Method **C**: (Entry 12 in Table 2) to a mixture of cinnamyl acetate (165 μL, 1.0 mmol), $Pd(PPh_3)_4$ (30 mg, 0.03 mmol), aluminium powder (100 mg, 3.7 mmol) and $InCl_3 \cdot nH_2O$ (*n* = 3 to 4, 0.30 g, 1.0 mmol), salicylaldehyde (53 μL, 0.50 mmol) was added at room temperature. The reaction mixture was stirred for 2 h and quenched with diluted HCl. The product was extracted with diethyl ether and washed with water, then brine. The extracts were dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The product was purified by column chromatography on silica gel (elution with EtOAc : hexane = 1 : 9 then 2 : 8) to give 1-(2-hydroxyphenyl)-2-phenylbut-3-en-1-ol (**2c**) (110 mg, 92%, *syn* : *anti* = 2 : 98).

Method **D**: (Entry 1 in Table 3): to a solution of allylbenzene (160 μL, 1.2 mmol) in THF (5 mL), *sec*-BuLi (1.0 M in cyclohexane, 1.2 mL, 1.2 mmol) was added at −78 °C and a solution of $InCl_3$ (89 mg, 0.40 mmol) in THF (3 mL) was then added. The reaction mixture was kept for 30 min at this temperature. Benzaldehyde (103 μL, 1.0 mmol) was added and the reaction was performed at −78 °C for 2 h. After being warmed to room temperature, the reaction mixture was treated with saturated aqueous ammonium chloride (5 mL) The product was extracted with ether, washed with water, then brine. The extracts were dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The product was purified by column chromatography on silica gel (elution with EtOAc : hexane = 2 : 8) to give 1,2-diphenylbut-3-en-1-ol (**2a**)[11] (170 mg, 74%, *syn* : *anti* = 19 : 81).

2-Methyl-1-(2-pyridyl)but-3-en-1-ol (1b)[9]

ν_{MAX}(film)/cm^{-1} 3400, 2990, 1598, 1436, 1004, 918, and 750; *syn*-isomer δ_H 0.91 (3 H, d, *J* 6.9, Me), 2.62 (1 H, m, MeC*H*), 4.13 (1 H, d, *J* 5.0, OH), 4.71 (1 H, t, *J* 5.0, C*H*OH), 5.07 (2 H, m, CH_2=), 5.92 (1 H, ddd, *J* 18, 10, 7.3, –CH=), 7.20 (1 H, dd, *J* 7.0, 5.0, pyr), 7.24 (1 H, d, *J* 6.9, pyr), 7.67 (1 H, dt, *J* 1.6, 7.5, pyr) and 8.55 (1 H, d, *J* 4.9, pyr); *anti*-isomer δ_H 1.08 (3 H, d, *J* 6.9, Me), 4.64 (1 H, d, *J* 5.6, C*H*OH) and 5.77 (1 H, ddd, *J* 17, 6.6, 6.1, –C*H*=).

1-(2-Hydroxyphenyl)-2-methylbut-3-en-1-ol (1c)[10]

ν_{MAX}(film)/cm^{-1} 3350, 2990, 1584, 1484, 1240, 1000, 916 and 752; *syn*-isomer δ_H 1.10 (3 H, d, *J* 6.8, Me), 2.53–2.81 (2 H, m, C*H*Me and OH), 4.82 (1 H, dd, *J* 5.1, 2.6, C*H*OH), 5.07–5.32 (2 H, m, CH_2=), 5.71–5.91 (1 H, m, C*H*=CH_2), 6.78–6.98 (3 H, m, Ph), 7.13–7.21 (1 H, m, Ph) and 8.10 (1 H, s, C_6H_4OH); *anti*-isomer δ_H 0.90 (3 H, d, *J* 6.8, Me), 4.44 (1 H, dd, *J* 9.8, 1.7, C*H*OH) and 7.94 (1 H, s, C_6H_4OH). (Found C, 73.93; H, 8.06. $C_{11}H_{17}O_2$ requires C, 74.12; H, 7.93%).

2-Phenyl-1-(2-pyridyl)but-3-en-1-ol (2b)[12]

ν_{MAX}(film)/cm^{-1} 3200, 3100, 1600, 1440, 1060, 1008, 920, 754, 738 and 708; *syn*-isomer δ_H 3.78 (1 H, d, *J* 7.6, C*H*Ph), 3.92 (1 H, d, *J* 6.1, OH), 5.02–5.15 (2 H, m, CH_2=), 6.11 (1 H, ddd, *J* 17, 10, 7.6, C*H*=CH_2), 7.07–7.26 (7 H, m, pyr and Ph), 7.60 (1 H, dt, *J* 1.7, 7.7, pyr) and 8.48 (1 H, d, *J* 5.0, pyr); *anti*-isomer δ_H 4.23 (1 H, d, *J* 6.1, OH), 6.24 (1 H, ddd, *J* 17, 10, 7.6, C*H*=CH_2) and 8.53 (1 H, d, *J* 5.0, pyr). (Found C, 80.18; H, 6.70. N, 6.16. $C_{15}H_{15}NO$ requires C, 79.97; H, 6.71%, N, 6.22%).

1-(2-Hydroxyphenyl)-2-phenylbut-3-en-1-ol (2c)[16]

ν_{MAX}(film)/cm^{-1} 3350, 3050, 1584, 1488, 1452, 1240, 1040, 920, 750 and 698; *syn*-isomer δ_H 2.43 (1 H, d, *J* 2.1, OH), 3.80 (1 H, dd, *J* 9.1, 8.0, PhC*H*), 4.75–5.04 (3 H, m, CH_2= and C*H*OH), 5.90 (1 H, ddd, *J* 17, 10, 7.8, =CH–), 6.78–6.99 (3 H, m, Ph and C_6H_4OH), 7.16–7.44 (6 H, m, C_6H_4OH and Ph) and 7.75 (1 H, s, C_6H_4OH); *anti*-isomer δ_H 2.99 (1 H, d, *J* 1.9, OH), 3.75 (1 H,

t, *J* 9.2, PhC*H*), 4.89 (1 H, d, *J* 9.2, C*H*OH), 5.34 (1 H, d, *J* 17, *trans* =CH_2), 5.36 (1 H, d, *J* 10 Hz, *cis* =CH_2), 6.29 (1 H, ddd, *J* 17, 10, 9.2, =CH–) and 7.95 (1 H, s, C_6H_4OH); (Found C, 79.35; H, 6.69. $C_{16}H_{16}O_2$ requires C, 79.97; H, 6.71%).

1-(2-Methoxyphenyl)-2-phenylbut-3-en-1-ol (2d) [17]

ν_{MAX}(film)/cm^{-1} 3450, 3000, 1602, 1494, 1460, 1240, 1030, 920, 758 and 702; *anti*-isomer δ_H 2.65 (1 H, d, *J* 5.9, OH), 3.73 (3 H, s, MeO), 3.69–3.82 (1 H, m, C*H*Ph), 4.84–5.30 (3 H, m, CH=CH_2 and C*H*OH), 6.30 (1 H, ddd, *J* 17, 10, 8.5, –CH=), 6.75–7.03 (2 H, m, C_6H_4OH) and 7.11–7.33 (7 H, m, Ph and C_6H_4OH); *syn*-isomer: δ_H 2.45 (1 H, d, *J* 6.3, C*H*Ph), 3.80 (3 H, s, MeO) and 6.00 (1 H, ddd, *J* 17, 10, 8.0, –CH=).

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