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Synthesis of axially chiral C_{10}-BridgePHOS oxides and their use as organocatalysts in enantioselective allylations of aldehydes

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ABSTRACT

A series of C_{10}-BridgePHOS oxides possessing different substituted groups on the diphenyl phosphine system were synthesized and tested as organocatalysts in the allylation of aldehydes with allyltrichlorosilane, providing chiral homoallylic alcohols. These types of organocatalysts showed high catalytic activity and only 2 mol% catalyst loading was required to induce short reaction times. Under optimal reaction conditions, excellent product yields and up to 92% ee were obtained for a variety of substrates.
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1. Introduction

During the past decade there has been an explosive growth in the area of organocatalysis and asymmetric synthesis because of their stability to air and non-toxic properties.[1] Besides commonly used proline and its derivatives, not much attention has been given to using chiral bisphosphine oxides (such as BINAPO, Fig. 1) as potential organocatalysts in the field of asymmetric synthesis.[2] Few satisfactory examples concerning reaction activity and enantioselectivity have been reported with chiral bisphosphine oxides, although some progress has been made in enantioselective allylations,[3] epoxide openings,[4] aldol reactions[5] amongst others.[6] To some extent, the development of efficient chiral bisphosphine oxides remains a considerable challenge. Recently, our group has focused on the development of a class of axially chiral 5,5′-bridged biphenyl diphosphine ligands (Fig. 1, C_n-BridgePHOS). The axial chirality can be controlled by different length alkyl chains (n=7–12), which can affect asymmetric induction. C_{10}-BridgePHOS gave the best results in Pd-catalyzed asymmetric hydrogenation reactions.[7] To increase catalytic activity and selectivity, the diphenyl phosphine groups present in the C_{10}-BridgePHOS ligand were modified to change its steric and electronic properties. Considering the promising applications of BINAPO, we decided to investigate the use of diphosphine oxides of C_{10}-BridgePHOS (Fig. 1) as organocatalysts in the reaction between an aldehyde and allyltrichlorosilane.

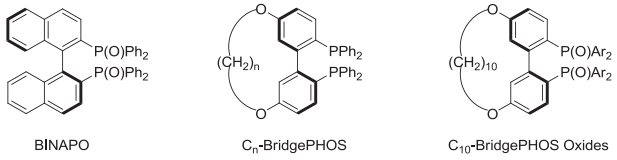

Fig. 1. C_{10}-BridgePHOS and its oxides.

2. Results and discussion

2.1. The synthesis of C_{10}-BridgePHOS oxides 1a–1d

Our synthetic approach to enantiopure C_{10}-BridgePHOS oxides (**1**) is outlined in Scheme 1. Commercially available 4-methoxyphenol was readily coupled in the presence of $FeCl_3$ and $AlCl_3$ at room temperature over 6 h to give 5,5′-dimethoxybiphenyl-2,2′-diol (**2**) in 62% yield. Reaction of **2** with $(CF_3SO_2)_2O$ in the presence of pyridine gave its triflate derivative (**3**) in almost quantitative yield. The important intermediate tetraethyl 5,5′-dimethoxybiphenyl-2,2′-diyldiphosphonate (**4**) was then obtained by phosphorylation of **3** via $Pd(OAc)_2$ catalysis in 86% yield.[8]

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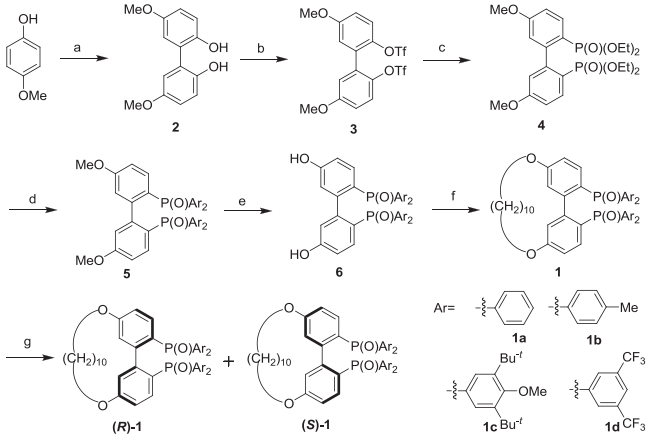
A series of aryl phosphine oxides **5a**–**5d** could be obtained in high yield by treating **4** with $SOCl_2$ in DMF followed with ArMgBr in THF. Reaction of **5a**–**5d** with BBr_3 provided their corresponding products **6a**–**6d** in quantitative yield. Finally, treatment of **6a**–**6d** with 1,10-dibromodecane in the presence of excess anhydrous K_2CO_3 in DMF furnished **1a**–**1d** in good yields. Compounds **1a**–**1d** were obtained optically pure via chiral preparative HPLC (Daicel Chiracel AD-H, IE, and IC-3 Columns).



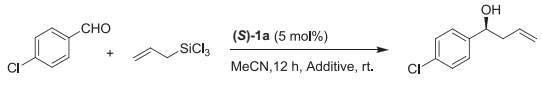
[a] $AlCl_3$, $FeCl_3$, $MeNO_2$, 62%; [b] Tf_2O, Py, CH_2Cl_2, 98%; [c] $HPO(OEt)_2$, $Pd(OAc)_2$, dppf, NEt_3,THF, 86%; [d] 1) DMF, $SOCl_2$; 2. ArMgBr, THF, **5a**: 87%, **5b**: 86%, **5c**: 90%, **5d**: 83%; [e] BBr_3, CH_2Cl_2, 100%; [f] $Br(CH_2)_{10}Br$, K_2CO_3, DMF, **1a**: 70%, **1b**: 72%, **1c**: 75%, **1d**: 64%; [g] Preparative Chromatography, 100%.

Scheme 1. The synthetic route of C_{10}-BridgePHOS oxides.

2.2. Screening of additive

Initially, 4-chlorobenzaldehyde (**7d**) was utilized in the reaction at room temperature in MeCN with **(*S*)-1a** (Scheme 1) as a chiral organocatalyst (Table 1). Only trace amounts of product were obtained in the absence of an additive (entry 1). However, 92% yield was obtained when diisopropylethylamine (DIPEA) was added to the reaction system, albeit with moderate enantioselectivity (entry 2, 41% ee). Addition of tetrabutylammonium iodide (TBAI) showed similar enantioselectivity but a very low reaction activity (entry 3). A combination of DIPEA and TBAI did not provide a better result (entry 4). Other additives such as *N*,*N*-dimethylaniline (DMA) and diethylamine (DEA) were also examined, and only trace amounts of products were obtained (entries 5 and 6). With the above results in hand, DIPEA was selected as the additive and used in subsequent reactions.

Table 1
Effect of additive[a]



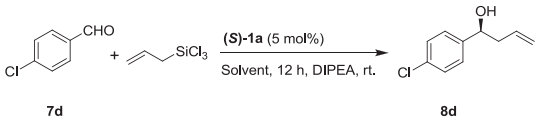
Entry	Additive	Yield[b] (%)	ee[c,d] (%)
1	None	<5	—
2	DIPEA	92	41 (*S*)
3	TBAI	53	41 (*S*)
4	DIPEA/TBAI	93	41 (*S*)
5	DMA	<5	—
6	DEA	<5	—

[a] Reactions were conducted using 4-chlorobenzaldehyde (0.60 mmol) and allyltrichlorosilane (0.90 mmol) in MeCN (8 mL) in the presence of **(*S*)-1a** (5 mol %) and additive (5 mol %) at rt for 12 h.
[b] Isolated yield.
[c] Determined by HPLC.
[d] The absolute configuration of product was assigned through comparison of the sign of specific rotations with the literature data.[9]

2.3. Screening of solvent

Solvent had an obvious effect on the reaction activity and enantioselectivity (Table 2). Use of MeCN and $PhCH_2CN$ provided products in excellent yield and up to 41% ee in the enantioselective allylation reactions (entries 1 and 2). DCM gave the desired product in 91% yield but only 28% ee (entry 3). However, other halogenated solvents such as $CHCl_3$ and PhCl, only provided the desired products in low to moderate yields and enantioselectivities (entries 4 and 5). Other commonly used solvents (toluene, THF, acetone, and Et_2O) were found unsuitable for this reaction (entries 6–9). MeCN was selected and used in subsequent reactions.

Table 2
Effect of solvent[a]



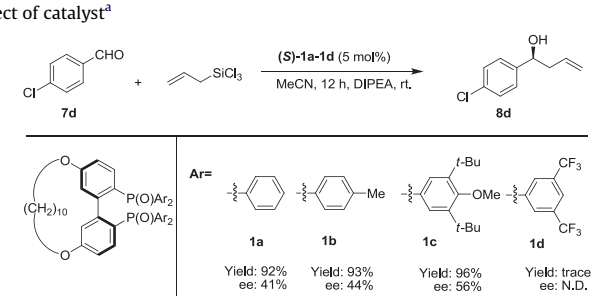
Entry	Solvent	Yield[b] (%)	ee[c,d] (%)
1	MeCN	92	41 (*S*)
2	$PhCH_2CN$	92	41 (*S*)
3	DCM	91	28 (*S*)
4	$CHCl_3$	57	16 (*S*)
5	PhCl	34	18 (*S*)
6	$PhCH_3$	16	0
7	DMF	<5	—
8	Acetone	<5	—
9	THF	<5	—

[a] Reactions were conducted using 4-chlorobenzaldehyde (0.60 mmol) and allyltrichlorosilane (0.90 mmol) in a suitable solvent (8 mL) in the presence of **(*S*)-1a** (5 mol %) and DIPEA (5 mol %) at rt for 12 h.
[b] Isolated yield.
[c] Determined by HPLC.
[d] The absolute configuration of product was assigned through comparison of the sign of specific rotations with the literature data.[9]

2.4. Screening of catalyst

Catalysts containing different steric and electronic properties had a significant effect on the reaction. As shown in Table 3, catalyst **(*S*)-1b** containing a Me group provided better enantioselectivity than **(*S*)-1a** (44% ee than 41% ee). Subsequently, **(*S*)-1c** possessing a bulky electron-donating group was used as a catalyst, and the desired product **8d** was obtained readily in almost quantitative yield and with 56% ee. However, catalyst **(*S*)-1d** possessing a bulky

Table 3
Effect of catalyst[a]



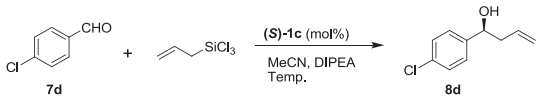
[a] Reactions were conducted using 4-chlorobenzaldehyde (0.60 mmol) and allyltrichlorosilane (0.90 mmol) in MeCN (8 mL) in the presence of **1** (5 mol %) and DIPEA (5 mol %) at rt for 12 h. The enantioselectivities were determined by HPLC.

electron-withdrawing group showed a negative effect on reaction activity. According to the above catalytic behavior, **(*S*)-1c** was selected as the chiral organocatalyst for further investigation.

2.5. Screening of temperature and catalyst loading

Accordingly, the effect of temperature on the reaction was examined (Table 4). Decreasing the reaction temperature from rt to 0 °C provided the desired product in 92% yield and 56% ee after 2 h (entry 2). Further decreasing the temperature to −40 °C gave the desired product in 56% ee but an obvious decrease in reactivity activity was observed (entry 3). Further investigation focused on a low catalyst loading with the aim of improving reaction efficiency. When decreasing the catalyst loading from 5 mol % to 2 mol %, the reaction still proceeded smoothly with high reaction activity, providing similar catalytic results (entries 1 and 4). However, the product was only obtained in 83% yield when 1% catalyst loading was used (entry 5). Following reactions were examined at room temperature by using 2 mol % catalyst loading.

Table 4
Effect of temperature and catalyst loading[a]



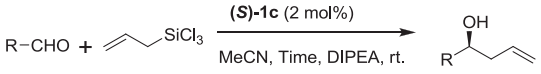
Entry	**(*S*)-1c** (mol %)	Temp (°C)	Time (h)	Yield[b] (%)	ee[c,d] (%)
1	5	rt	1	96	56 (*S*)
2	5	0	2	92	56 (*S*)
3	5	−40	8	32	56 (*S*)
4	2	rt	6	91	56 (*S*)
5	1	rt	36	83	56 (*S*)

[a] Reactions were conducted using 4-chlorobenzaldehyde (0.60 mmol) and allyltrichlorosilane (0.90 mmol) in MeCN (8 mL) in the presence of **(*S*)-1c** (1–5 mol %) and additive (5 mol %) at certain temperature.
[b] Isolated yield.
[c] Determined by HPLC.
[d] The absolute configuration of product was assigned through comparison of the sign of specific rotations with the literature data.[9]

2.6. The scope of substrate

With the optimal reaction conditions in hand, we investigated the applicability of this catalytic system for a series of aldehydes. Thus, a number of simple aldehydes were subjected to the optimized reaction conditions using **(*S*)-1c** (2 mol %) as an organocatalyst in the presence of DIPEA at rt in MeCN (Table 5). First, benzaldehyde was used as a substrate in the reaction and the product was obtained in excellent yield and 57% ee. Substrates with electron-withdrawing groups located at the 2-, 3- and 4-position of the phenyl ring were next examined. Products were obtained in more than 90% yield, in addition to moderate to good enantioselectivities were obtained, and substrates with a 3-position group on the phenyl ring provided the best results (entries 2–4). Other substrates with electron-withdrawing groups at the 3-position were then examined and good enantioselectivities were also obtained (entries 5–8). However, substrates with electron-withdrawing groups at the 2- and 6-position gave lower enantioselectivity (entry 9). A similar phenomenon was also found for the substrates possessing electron-donating groups located at the 2-, 3- and 4-position of the phenyl ring motifs (entries 10–15). To our delight, products with up to 92% ee were obtained when substrates with 3,5-disubstituted electron-donating groups were used (entries 16–18).

Table 5
The scope of substrates[a]



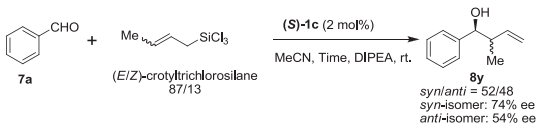
Entry	R	Time (h)	Product	Yield[b] (%)	ee[c,d] (%)
1	C_6H_5	6	**8a**	93	57 (*S*)
2	2-ClC_6H_4	3	**8b**	94	66 (*S*)
3	3-ClC_6H_4	6	**8c**	93	75 (*S*)
4	4-ClC_6H_4	6	**8d**	96	56 (*S*)
5	3-FC_6H_4	3	**8e**	89	62 (*S*)
6	3-BrC_6H_4	3	**8f**	93	70 (*S*)
7	3-$NO_2C_6H_4$	3	**8g**	90	67 (*S*)
8	3,5-$Cl_2C_6H_3$	3	**8h**	96	77 (*S*)
9	2,6-$Cl_2C_6H_3$	3	**8i**	93	50 (*S*)
10	2-MeC_6H_4	6	**8j**	92	63 (*S*)
11	3-MeC_6H_4	6	**8k**	90	77 (*S*)
12	4-MeC_6H_4	9	**8l**	86	60 (*S*)
13	2-$MeOC_6H_4$	3	**8m**	91	72 (*S*)
14	3-$MeOC_6H_4$	6	**8n**	91	74 (*S*)
15	4-$MeOC_6H_4$	6	**8o**	87	60 (*S*)
16	3,5-$Me_2C_6H_3$	3	**8p**	93	81 (*S*)
17	3,5-$(MeO)_2C_6H_3$	3	**8q**	95	80 (*S*)
18	3,5-$(t\text{-}Bu)_2C_6H_3$	2	**8r**	96	92 (−)
19	1-Naphthyl	6	**8s**	93	77 (*S*)
20	2-Naphthyl	12	**8t**	80	71 (*S*)
21	2-Furyl	12	**8u**	84	43 (*S*)
22	2-Thienyl	12	**8v**	82	70 (*S*)
23	$C_6H_4CH_2CH_2$	6	**8w**	72	8 (*R*)
24	C_6H_4CHCH	6	**8x**	78	16 (*S*)

[a] Reactions were conducted using **7** (0.60 mmol) and allyltrichlorosilane (0.90 mmol) in MeCN (8 mL) in the presence of **(*S*)-1c** (2 mol %) and DIPEA (5 mol %) at rt.
[b] Isolated yield.
[c] Determined by HPLC.
[d] The absolute configuration of product was assigned through comparison of the sign of specific rotations with the literature data.[9]

Replacement of the phenyl ring by a naphthalene ring, such as 1-naphthaldehyde or 2-naphthaldehyde, gave products in high yields and with enantioselectivities of 77% and 71%, respectively (entries 19 and 20). When the phenyl ring was replaced by heterocyclic motifs (a furan or a thiophene ring), excellent catalytic activity and moderate to high enantioselectivities were also observed (entries 21 and 22). The present catalytic system is therefore suitable for the allylation of a series of aldehydes.

We also performed the reactions using benzenepropanal and cinnamyl aldehyde. The reactants provided high reaction activity and high yield, but a low enantioselectivities (entries 23 and 24).

Finally, the allylation was carried out by using a mixture of (*E*)-crotyltrichlorosilane and (*Z*)-crotyltrichlorosilane (*E*/*Z*=87:13) instead of the simple allyltrichlorosilane. The result showed that a mixture of diastereoisomeric alcohols (*syn* and *anti* in 52:48 ratio) was obtained in 89% yield (Scheme 2).



Scheme 2. The allylation with (*E*)- and (*Z*)-crotyltrichlorosilane.

3. Conclusions

In conclusion, a series of C_{10}-BridgePHOS oxides possessing different substituted groups at the phenyl rings were synthesized. They were used as efficient organocatalysts in the allylation of

aldehydes with excellent catalytic behavior. These types of organocatalysts showed high catalytic activity, therefore only 2 mol% catalyst loading was required to promote the reaction. Under optimal reaction conditions, excellent product yields and up to 92% ee were obtained for a variety of substrates.

4. Experimental

4.1. General

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Varian MERCURY plus-400 spectrometer with TMS as an internal standard. HRMS was performed at the Analysis Center of Shanghai Jiao Tong University. Enantioselectivity was measured by high performance liquid chromatography (HPLC) using Daicel Chiralcel OD-H, AD-H, OJ-H, IE-H, and IC-3 columns with hexane/2-propanol as eluent. Column chromatography was performed using 100–200 mesh silica gel. Melting points were measured with SGW X-4 micro melting point apparatus. Optical rotations were measured on a Rudolph Research Analytical Autopol VI automatic polarimeter using a 50 mm path-length cell at 589 nm.

4.2. Synthesis of C_{10}-BridgePHOS oxides 1a–1d

*4.2.1. 5,5′-Dimethoxybiphenyl-2,2′-diol (**2**).*[10] A solution of 4-methoxyphenol (6.2 g, 50.0 mmol) in dry $MeNO_2$ (40 mL) was added to a stirred solution of $AlCl_3$ (0.6 equiv) in dry $MeNO_2$ (20 mL) under nitrogen at room temperature. After 30 min, a solution of anhydrous $FeCl_3$ (1.0 equiv) in dry $MeNO_2$ (20 mL) was added and the mixture was continued to stir for 6 h at room temperature. The reaction was quenched with aqueous HCl solution (1 N, 50 mL) and the resulting mixture was extracted with EtOAc (3×50 mL). The organic phase was dried over Na_2SO_4 and solvent evaporated. The residue was purified on a silica gel column with petrol ether–EtOAc as eluent to afford a white solid **2** (3.8 g, 62%). Mp 88–89 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (2H, d, J=8.4 Hz), 6.89 (2H, dd, J=9.2, 3.2 Hz), 6.82 (2H, d, J=2.8 Hz), 3.79 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 146.7, 125.5, 118.0, 116.2, 115.6, 77.6, 77.3, 77.0, 56.1.

*4.2.2. 5,5′-Dimethoxybiphenyl-2,2′-diyl bis(trifluoromethanesulfonate) (**3**).* To a stirring solution of **2** (2.5 g, 10.0 mmol) and pyridine (5 equiv) in DCM (20 mL) at 0 °C was added dropwise Tf_2O (2.2 equiv) at a rate to maintain the reaction temperature below 10 °C. The reaction was allowed to warm to ambient temperature and its progress was monitored by thin layer chromatography (TLC). When the material disappeared, the reaction was quenched with aqueous HCl solution (1 N, 2 mL) and the resulting mixture was extracted with DCM (3×10 mL). The combined organic phase was dried over Na_2SO_4, filtered, and concentrated under vacuum at rt. The residue was purified by flash chromatography with an ethyl acetate–petrol ether mixture as eluent to give **3** as colorless oil (5.1 g, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (2H, d, J=8.8 Hz), 7.01 (2H, dd, J=9.2, 3.2 Hz), 6.95 (2H, d, J=3.2 Hz), 3.85 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 140.3, 130.6, 122.9, 120.1, 117.4, 115.9, 56.1; HRMS (ESI-MS) calcd for $C_{16}H_{12}F_6O_8S_2$ 528.0222, found: 528.0233.

*4.2.3. Tetraethyl 5,5′-dimethoxybiphenyl-2,2′-diyldiphosphonate (**4**).* To a three-necked flask under nitrogen, $Pd(OAc)_2$ (0.2 equiv of **3**), DPPF (0.21 equiv), KOAc (0.02 equiv), and anhydrous DMF (5 mL) were added and the reaction mixture was stirred under 60 °C for 30 min. DIPEA (1.5 equiv) and diethylphosphite (3.0 equiv) were added and the mixture stirred for 15 min. A solution of **3** (2.5 g, 5.0 mmol) in DMF (20 mL) was added slowly. The reaction mixture was heated to 100 °C and stirred for another 12 h. The volatiles were removed in vacuo to give a dark brown oil. Upon biphasic work-up (20 mL water/3×25 mL diethyl ether), the yellow organic layer was separated, dried over Na_2SO_4, and concentrated under vacuum. The residue was purified by column chromatography with ethyl acetate–petrol ether as eluent to yield a white solid **4** (2.0 g, 86%). Mp 138–140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (2H, dd, J=14.0, 8.8 Hz), 7.01 (2H, dd, J=4.4, 2.4 Hz), 6.94 (2H, dt, J=8.8, 2.8 Hz), 3.96–3.72 (8H, m), 3.85 (6H, s), 1.11 (12H, dt, J=21.6, 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 135.4, 120.1, 118.2, 117.6, 113.1, 61.9, 55.6, 16.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ 19.88; HRMS (ESI-MS) calcd for $C_{22}H_{32}O_8P_2$ $[M+1]^+$ 487.1650, found: 487.1649.

*4.2.4. General procedure for the synthesis of **5a–5d**.* In a 100 mL three-neck flask with a condenser, **4** (1.00 g, 2.1 mmol), dry DMF (5 mL), and thionyl chloride (10.0 equiv) were added and warmed to 80 °C under an argon atmosphere. After 5 h, the excess thionyl chloride and DMF were evaporated under vacuum. Dry THF (5 mL) was added, and evaporated under vacuum while stirred for 5 min. Another small amount of THF (5 mL) was added, followed by the dropwise addition of the Grignard reagent prepared from different aryl bromides (6.0 equiv) and magnesium granules (20.0 equiv) at −50 °C. The reaction mixture was allowed to warm to room temperature within 30 min to form a yellow solution and was further stirred for 6 h. The reaction was quenched by addition of saturated NH_4Cl solution (5 mL). The organic layer was separated, washed with saturated NaCl solution (3×10 mL), dried over anhydrous Na_2SO_4, and evaporated under vacuum. The residue was purified by column chromatography with petroleum ether/ethyl acetate to give the pure products **5a–5d**.

*4.2.4.1. (5,5′-Dimethoxybiphenyl-2,2′-diyl)bis(diphenylphosphine oxide) (**5a**).* White solid (1.10 g, 87%); mp 246–247 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81–7.70 (4H, m), 7.69–7.59 (4H, m), 7.55–7.40 (6H, m), 7.38–7.27 (6H, m), 7.05 (2H, dd, J=13.6, 8.8 Hz), 6.81 (2H, t, J=2.8 Hz), 6.64–6.59 (2H, m), 3.48 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 161.1, 147.1, 147.0, 149.9, 146.9, 136.1, 135.9, 135.8, 134.8, 134.4, 133.3, 132.3, 132.2, 132.0, 131.9, 131.6, 131.5, 131.2, 131.1, 128.7, 128.6, 128.2, 128.1, 122.4, 121.3, 117.5, 117.4, 114.4, 114.2, 55.2; ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.15; HRMS (ESI-MS) calcd for $C_{38}H_{32}O_4P_2$ $[M+1]^+$ 615.1854, found: 615.1832.

*4.2.4.2. (5,5′-Dimethoxybiphenyl-2,2′-diyl)bis(di(4-methylphenyl)phosphine oxide) (**5b**).* White solid (1.20 g, 87%); mp 212–214 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (4H, dd, J=11.2, 8.0 Hz), 7.48 (4H, dd, J=12.0, 8.0 Hz), 7.26–7.24 (4H, m), 7.10 (4H, dd, J=7.6, 2.0 Hz), 7.04 (2H, dd, J=13.2, 8.8 Hz), 6.86 (2H, t, J=2.4 Hz), 6.63 (2H, dt, J=8.8, 1.6 Hz), 3.50 (6H, s), 2.35 (12H, d, J=35.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 166.7, 144.3, 141.8, 135.9, 132.3, 132.2, 132.1, 132.0, 129.4, 129.3, 128.9, 128.8, 117.6, 55.2, 29.9, 21.7; ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.33; HRMS (ESI-MS) calcd for $C_{42}H_{40}O_4P_2$ $[M+1]^+$ 671.2486, found: 671.2468.

*4.2.4.3. (5,5′-Dimethoxybiphenyl-2,2′-diyl)bis(di(3,5-di-tert-butyl-4-methoxyphenyl)phosphine oxide) (**5c**).* White solid (2.19 g, 90%); mp 205–208 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (4H, d, J=12.8 Hz), 7.43 (4H, d, J=12.8 Hz), 7.08 (2H, dd, J=13.2, 8.4 Hz), 6.72 (2H, dt, J=8.4, 2.4 Hz), 6.35 (2H, t, J=2.8 Hz), 3.67 (12H, s), 3.30 (6H, s), 1.33 (72H, d, J=8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 162.4, 162.3, 162.2, 162.1, 160.5, 160.4, 158.4, 147.8, 147.7, 145.4, 144.2, 144.0, 143.6, 143.5, 142.8, 138.9, 135.7, 135.5, 132.0, 131.9, 130.5, 130.4, 130.1, 129.1, 129.0, 127.9, 126.9, 124.7, 124.0, 123.3, 122.3, 116.8, 116.7, 113.0, 112.9, 64.7, 64.6, 64.5, 54.7, 36.4, 36.2, 36.1, 32.3, 32.2, 32.1, 32.1; ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.75; HRMS (ESI-MS) calcd for $C_{74}H_{104}O_8P_2$ $[M+1]^+$ 1183.7284, found:1183.7299.

*4.2.4.4. (5,5′-Dimethoxybiphenyl-2,2′-diyl)bis(di(3,5-bis(trifluoromethyl)phenyl)phosphine oxide) (**5d**).* White solid (1.98 g, 83%);

mp 217–220 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (4H, d, J=11.2 Hz), 8.18 (4H, dd, J=11.2, 1.6 Hz), 8.06 (2H, s), 7.90 (2H, s), 7.16 (2H, dd, J=14.0, 9.2 Hz), 6.73 (2H, dt, J=8.4, 2.0 Hz), 6.36 (2H, t, J=2.8 Hz), 3.67 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 161.9, 144.8, 144.7, 144.6, 144.5, 138.0, 137.0, 135.5, 135.4, 134.4, 132.8, 132.7, 132.6, 132.5, 132.4, 132.3, 132.2, 132.1, 132.0, 131.9, 131.8, 131.7, 131.6, 126.1, 126.0, 125.9, 124.3, 124.2, 121.6, 121.4, 121.2, 120.1, 120.0, 112.9, 112.7, 55.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ 23.16; ^{19}F NMR (376 MHz, $CDCl_3$): δ 10.57, 10.50; HRMS(ESI-MS) calcd for $C_{46}H_{24}F_{24}O_4P_2$ $[M+1]^+$ 1159.0845, found: 1159.0835.

4.2.5. General procedure for the synthesis of ***6a*****–****6d***. To a stirring solution of **5a**–**5d** (1.0 mmol, 1.0 equiv) in DCM (20 mL), boron tribromide (2.0 equiv) was added dropwise over 30 min at −78 °C. After the addition the reaction mixture was warmed to room temperature and stirred for another 8 h. The reaction was quenched by the addition of a cold brine solution (10 mL) and aqueous HCl solution (1 N, 10 mL). The suspension was filtered and the obtained white precipitate was washed with hot water and ether to give white solids, which were used without further purification.

*4.2.5.1. 6,6′-Bis(diphenylphosphoryl)biphenyl-3,3′-diol (****6a****).* White solid; mp>260 °C; ^{1}H NMR (400 MHz, CD_3OD) δ 7.83–7.76 (4H, m), 7.72–7.66 (2H, m), 7.64–7.46 (14H, m), 7.04 (2H, dd, J=14.2, 8.6 Hz), 6.67–6.62 (2H, m), 6.10 (2H, dd, J=4.0, 2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 159.5, 147.1, 147.0, 146.9, 136.5, 135.8, 135.7, 135.6, 135.5, 134.6, 132.4, 132.3, 132.0, 131.9, 131.8, 131.5, 129.1, 129.0, 128.6, 128.5, 121.2, 120.1, 119.9, 119.8, 114.4, 114.2; ^{31}P NMR (162 MHz, CD_3OD): δ 27.61; HRMS (ESI-MS) calcd for $C_{36}H_{28}O_4P_2$ $[M+1]^+$ 587.1541, found: 587.1534.

*4.2.5.2. 6,6′-Bis(dip-tolylphosphoryl)biphenyl-3,3′-diol (****6b****).* White solid; mp>260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (4H, dd, J=11.2, 8.0 Hz), 7.48 (4H, dd, J=12.0, 8.0 Hz), 7.35–7.26 (8H, m), 7.01 (2H, dd, J=14.0, 8.4 Hz), 6.65 (2H, dt, J=8.4, 2.4 Hz), 5.95 (2H, dd, J=4.0, 2.4 Hz), 2.43 (12H, d, J=28.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 42.25; HRMS (ESI-MS) calcd for $C_{40}H_{36}O_4P_2$ $[M+1]^+$ 643.2167, found: 643.2119.

*4.2.5.3. 6,6′-Bis(bis(3,5-di-tert-butyl-4-methoxyphenyl)phosphoryl)biphenyl-3,3′-diol (****6c****).* White solid; mp>260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (4H, d, J=13.2 Hz), 7.31 (4H, d, J=13.2 Hz), 7.01 (2H, dd, J=14.0, 8.4 Hz), 6.75 (2H, dt, J=8.4, 2.8 Hz), 5.98 (2H, dd, J=3.2, 2.0 Hz), 3.78 (12H, d, J=7.2 Hz), 1.40 (72H, d, J=8.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 44.31; HRMS (ESI-MS) calcd for $C_{72}H_{100}O_8P_2$ $[M+1]^+$ 1155.6971, found: 1155.7006.

*4.2.5.4. 6,6′-Bis(bis(3,5-bis(trifluoromethyl)phenyl)phosphoryl) biphenyl-3,3′-diol (****6d****).* White solid; mp>260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (4H, d, J=11.6 Hz), 8.36 (4H, dd, J=11.6, 1.6 Hz), 8.23 (2H, s), 8.09 (2H, s), 7.16 (2H, dd, J=14.0, 8.4 Hz), 6.67 (2H, dt, J=8.8, 2.4 Hz), 6.20 (2H, dd, J=3.6, 2.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.88; ^{19}F NMR (376 MHz, $CDCl_3$) δ 17.31, 17.25; HRMS (ESI-MS) calcd for $C_{44}H_{20}O_4P_2$ $[M+1]^+$ 1131.0532, found: 1131.0527.

4.2.6. General procedure for the synthesis of ***1a*****–****1d***. A solution of **6a**–**6d** obtained from the previous step (1.0 equiv) and 1,10-dibromodecane (1.1 equiv) in DMF (200 mL) was added slowly to a suspension of anhydrous K_2CO_3 (10 equiv) in DMF (200 mL) at 80 °C. The mixture was stirred for 36 h before the solvent was removed under reduced pressure. The residue was extracted with ether, and the combined extracts were washed with water, brine, and dried over Na_2SO_4. After evaporation of solvent, a solid was obtained and was purified by column chromatography on silica gel with petroleum ether/ethyl acetate to give the pure products **1a**–**1d**.

*4.2.6.1. 5,5′-Decamethylenedioxy-2,2′-bis(diphenylphosphoryl)biphenyl (****1a****).* White solid (0.51 g, yield of two steps: 70%); mp 237–238 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74–7.64 (4H, m), 7.62–7.55 (4H, m), 7.55–7.36 (12H, m), 7.06 (2H, dd, J=12.8, 8.8 Hz), 6.71 (2H, dt, J=8.8, 2.4 Hz), 6.21 (2H, t, J=2.8 Hz), 3.82–3.76 (2H, m), 3.36–3.25 (2H, m), 1.57–0.82 (16H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 156.0, 146.6, 146.5, 135.8, 135.6, 135.5, 134.7, 134.2, 133.1, 132.5, 132.4, 132.1, 132.0, 131.4, 131.3, 131.2, 131.1, 128.7, 128.6, 128.2, 128.0, 122.4, 121.3, 117.5, 117.4, 116.3, 116.4, 66.9, 28.9, 28.8, 28.5, 28.1, 24.7, 24.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.74; HRMS (ESI) calcd for $C_{46}H_{46}O_4P_2$ $[M]^+$ 724.2871, found: 724.2886; Chiral HPLC: Daicel Chiralcel AD-H column (hexane/EtOH/2-propanol=82:10:8, 0.8 mL/min, 254 nm), t_R (R)=5.99 min, t_R (S)=9.09 min; **(*S*)-1a**: $[\alpha]_D^{25}$ −41.2 (c 0.50, $CHCl_3$).

*4.2.6.2. 5,5′-Decamethylenedioxy-2,2′-bis(di(4-methylphenyl) phosphoryl)biphenyl (****1b****).* White solid (0.56 g, yield of two steps: 72%); mp 229–232 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (4H, dd, J=11.6, 8.0 Hz), 7.48 (4H, dd, J=12.0, 8.0 Hz), 7.23 (4H, d, J=6.0 Hz), 7.08 (4H, dd, J=8.4, 2.0 Hz), 7.02 (2H, dd, J=13.2, 9.2 Hz), 6.62 (2H, dt, J=8.4, 2.0 Hz), 6.52 (2H, s), 3.86–3.83 (2H, m), 3.64–3.61 (2H, m), 2.36 (6H, s), 2.29 (6H, s), 1.37–0.93 (16H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 159.7, 146.8, 146.7, 146.6, 146.5, 141.7, 141.6, 141.2, 141.1, 135.5, 135.4, 132.5, 132.4, 132.2, 132.1, 131.1, 130.0, 129.4, 129.3, 128.9, 128.8, 122.7, 121.6, 117.6, 117.5, 116.1, 116.0, 66.7, 28.8, 28.5, 28.2, 24.7, 21.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.68; HRMS (ESI-MS) calcd for $C_{50}H_{54}O_4P_2$ $[M+1]^+$ 781.3575, found: 781.3571; Chiral HPLC: Daicel Chiralcel IC3-H column (hexane/MeOH/2-propanol=55:15:30, 0.5 mL/min, 254 nm), t_R (S)=19.99 min, t_R (R)=23.55 min; **(*S*)-1b**: $[\alpha]_D^{25}$ −14.5 (c 0.32, $CHCl_3$).

*4.2.6.3. 5,5′-Decamethylenedioxy-2,2′-bis(di(3,5-di-tert-butyl-4-methoxyphenyl)phosphoryl)biphenyl (****1c****).* White solid (0.97 g, yield of two steps: 75%); mp 225–228 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (4H, d, J=13.2 Hz), 7.37 (4H, d, J=13.2 Hz), 7.10 (2H, dd, J=14.0, 8.4 Hz), 6.71 (2H, dt, J=8.4, 2.8 Hz), 6.12 (2H, dd, J=3.2, 2.0 Hz), 3.82–3.77 (2H, m), 3.68 (12H, d, J=1.2 Hz), 3.57–3.52 (2H, m), 1.23 (88H, d, J=8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 162.2, 159.5, 159.4, 147.4, 147.3, 147.2, 147.1, 143.9, 143.8, 143.5, 143.4, 135.2, 135.0, 132.0, 131.9, 130.6, 130.5, 123.0, 128.9, 128.5, 127.4, 123.8, 122.7, 117.4, 117.2, 114.8, 114.7, 66.9, 64.5, 64.4, 36.2, 36.1, 32.2, 32.1, 28.9, 28.7, 27.9, 25.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.66; HRMS (ESI-MS) calcd for $C_{82}H_{118}O_8P_2$ $[M+1]^+$ 1293.8380, found: 1293.8391; Chiral HPLC: Daicel Chiralcel IE-H column (hexane/EtOH/2-propanol=80:10:10, 0.7 mL/min, 254 nm), t_R (S)=10.26 min, t_R (R)=11.91 min; **(*S*)-1c**: $[\alpha]_D^{25}$ −89.3 (c 0.50, $CHCl_3$).

*4.2.6.4. 5,5′-Decamethylenedioxy-2,2′-bis(di(3,5-bis(trifluoromethyl)phenyl)phosphoryl)biphenyl (****1d****).* White solid (0.81 g, yield of two steps: 64%); mp 146–149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (4H, d, J=11.6 Hz), 8.26 (4H, dd, J=11.6, 1.6 Hz), 8.03 (2H, s), 7.87 (2H, s), 7.11 (2H, dd, J=14.0, 8.4 Hz), 6.71 (2H, dt, J=8.8, 2.4 Hz), 6.22 (2H, dd, J=3.6, 2.0 Hz), 3.99–3.83 (4H, m), 1.66–1.03 (16H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 161.1, 145.0, 144.9, 144.8, 144.7, 137.6, 136.5, 136.4, 134.9, 134.8, 134.7, 133.9, 132.9, 132.8, 132.6, 132.5, 132.3, 132.2, 132.1, 132.0, 131.7, 131.6, 126.1, 126.0, 124.3, 124.2, 121.6, 121.5, 121.4, 120.3, 118.9, 117.7, 117.6, 117.4, 117.3, 67.9, 28.8, 28.6, 27.5, 24.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.10; ^{19}F NMR (376 MHz, $CDCl_3$) δ 14.75, 14.66; HRMS (ESI-MS) calcd for $C_{54}H_{38}O_4P_2$ $[M+1]^+$ 1269.1940, found: 1269.1957; Chiral HPLC: Daicel Chiralcel IE-H column (hexane/2-

propanol=99.5:0.5, 0.5 mL/min, 254 nm); t_R (*S*)=11.50 min, t_R (*R*)=15.91 min; **(*S*)-1d**: $[\alpha]_D^{25}$ −30.6 (*c* 0.22, $CHCl_3$).

4.3. General procedure for the enantioselective allylation of aldehydes

To a stirred solution of **1** (0.012 mmol) in acetonitrile (8 mL) at room temperature, an aldehyde (0.6 mmol) and DIPEA (3.0 mmol) were added. Allyltrichlorosilane (0.9 mmol) was then added dropwise by means of a syringe. The reaction was detected by thin layer chromatography (TLC) until the starting material disappeared and was then quenched by the addition of a saturated aqueous solution of $NaHCO_3$ (3 mL). Saturated NaCl (6 mL) and EtOAc (10 mL) were added and the organic phase was separated, dried over Na_2SO_4, filtered, and concentrated under vacuum at room temperature. The residue was purified on a flash chromatography with different ethyl acetate–petrol ether mixtures as eluent to give pure product for the determination of ee by chiral HPLC.

4.4. Analytical data

*4.4.1. 1-Phenylbut-3-en-1-ol (**8a**).*[11] As a pale yellow oil (83 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.25 (5H, m), 5.90–5.75 (1H, m), 5.18–5.06 (2H, m), 4.75 (1H, d, *J*=7.4 Hz), 2.50–2.38 (2H, m), 2.10 (1H, br s). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexane/2-propanol=97.5:2.5, 1.0 mL/min, 254 nm), t_{minor}=13.1 min (*R*), t_{major}=14.9 min (*S*), ee=57%.

*4.4.2. 1-(2-Chlorophenyl)-but-3-en-1-ol (**8b**).*[11] As a yellow oil (103 mg, 94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (1H, dd, *J*=7.6, 1.6 Hz), 7.27–7.20 (2H, m), 7.13 (1H, t, *J*=7.6 Hz), 5.85–5.74 (1H, m), 5.14–5.11 (3H, m), 2.59–2.52 (1H, m), 2.37–2.27 (1H, m), 2.09 (1H, s). Enantiomeric excess was determined by HPLC with a Chiralcel IE-H column (hexane/2-propanol=99:1, 0.8 mL/min, 210 nm), t_{minor}=10.9 min (*R*), t_{major}=12.6 min (*S*), ee=66%.

*4.4.3. 1-(3-Chlorophenyl)but-3-en-1-ol (**8c**).*[11] As a yellow oil (102 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (1H, s), 7.17–7.09 (3H, m), 5.69–5.60 (1H, m), 5.17–5.02 (2H, m), 4.60–4.55 (1H, m), 2.43–2.28 (2H, m), 2.04 (1H, s). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (hexane/2-propanol=98.5:1.5, 0.8 mL/min, 230 nm), t_{minor}=14.4 min (*R*), t_{major}=15.4 min (*S*), ee=75%.

*4.4.4. 1-(4-Chlorophenyl)-but-3-en-1-ol (**8d**).*[11] As a yellow oil (106 mg, 96%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.18 (4H, m), 5.73–5.65 (1H, m), 5.10–4.97 (2H, m), 4.65–4.61 (1H, m), 2.46–2.33 (2H, m), 2.07 (1H, s). Enantiomeric excess was determined by HPLC with a Chiralcel IE-H column (hexane/2-propanol=99.9:0.1, 1.0 mL/min, 230 nm), t_{minor}=26.1 min (*R*), t_{major}=27.6 min (*S*), ee=56%.

*4.4.5. 1-(3-Fluorophenyl)-3-buten-1-ol (**8e**).*[12] As a pale yellow oil (89 mg, 89%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.25 (1H, m), 7.13–7.05 (2H, m), 6.99–6.91 (1H, m), 5.85–5.70 (1H, m), 5.20–5.12 (2H, m), 4.70 (1H, t, *J*=6.4 Hz), 2.57–2.38 (2H, m), 2.25 (1H, s). Enantiomeric excess was determined by HPLC with a Chiralcel IC-3 column (hexane/2-propanol=98:2, 0.8 mL/min, 210 nm), t_{minor}=11.2 min (*R*), t_{major}=12.0 min (*S*), ee=62%.

*4.4.6. 1-(3-Bromo-phenyl)but-3-en-1-ol (**8f**).*[12] As a yellow oil (126 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (1H, s), 7.41–7.28 (1H, m), 7.27–7.19 (2H, m), 5.84–5.72 (1H, m), 5.19–5.14 (2H, m), 4.72–4.68 (1H, m), 2.54–2.40 (2H, m), 2.11 (1H, s). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexane/2-propanol=98:2, 0.8 mL/min, 210 nm), t_{major}=18.4 min (*S*), t_{minor}=22.0 min (*R*), ee=70%.

*4.4.7. 1-(3-Nitrophenyl)-3-buten-1-ol (**8g**).*[13] As a yellow oil (105 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (1H, s), 8.13 (1H, d, *J*=1.2 Hz), 7.75 (1H, d, *J*=1.2 Hz), 7.52–7.40 (1H, m), 5.91–5.70 (1H, m), 5.26–5.12 (2H, m), 4.90–4.82 (1H, m), 2.65–2.50 (3H, m). Enantiomeric excess was determined by HPLC with a Chiralcel IC-3 column (hexane/2-propanol=92:8, 0.8 mL/min, 210 nm), t_{major}=13.3 min (*S*), t_{minor}=14.0 min (*R*), ee=67%.

*4.4.8. 1-(3,5-Dichlorophenyl)but-3-en-1-ol (**8h**).*[14] As a pale yellow oil (125 mg, 96%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.26 (3H, m), 5.82–5.71 (1H, m), 5.21–5.15 (2H, m), 4.68 (1H, dd, *J*=8.0, 4.8 Hz), 2.55–2.37 (2H, m), 2.12 (1H, br s). Enantiomeric excess was determined by HPLC with a Chiralcel OJ-H column (hexane/2-propanol=98:2, 0.8 mL/min, 210 nm), t_{major}=13.5 min (*S*), t_{minor}=14.4 min (*R*), ee=77%.

*4.4.9. 1-(2,6-Dichlorophenyl)but-3-en-1-ol (**8i**).*[9b] As a colorless oil (121 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (2H, d, *J*=8.0 Hz), 7.14 (1H, t, *J*=8.0 Hz), 5.86–5.81 (1H, m), 5.53–5.50 (1H, m), 5.15–5.08 (2H, m), 2.90 (1H, d, *J*=9.8 Hz), 2.87–2.82 (1H, m), 2.71–2.65 (1H, m). Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/2-propanol=98:2, 0.7 mL/min, 230 nm), t_{major}=11.7 min (*S*), t_{minor}=12.7 min (*R*), ee=50%.

*4.4.10. 1-o-Tolylbut-3-en-1-ol (**8j**).*[15] As a pale yellow oil (89 mg, 92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (1H, d, *J*=7.8 Hz), 7.23 (1H, t, *J*=7.2 Hz), 7.18 (1H, t, *J*=7.2 Hz), 7.13 (1H, d, *J*=7.2 Hz), 5.89–5.83 (1H, m), 5.20–5.15 (2H, m), 4.97 (1H, dd, *J*=8.4, 4.2 Hz), 2.53–2.49 (1H, m), 4.46–2.41 (1H, m), 2.34 (3H, s), 1.96 (1H, br s). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexane/2-propanol=98:2, 0.6 mL/min, 210 nm), t_{major}=20.3 min (*S*), t_{minor}=21.2 min (*R*), ee=63%.

*4.4.11. 1-m-Tolylbut-3-en-1-ol (**8k**).*[16] As a pale yellow oil (87 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20–7.04 (4H, m), 5.80–5.72 (1H, m), 5.13–5.08 (2H, m), 4.63 (1H, dd *J*=7.2, 5.4 Hz), 2.49–2.42 (2H, m), 2.32 (3H, s), 2.11 (1H, br s). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexane/2-propanol=98:2, 0.8 mL/min, 210 nm), t_{minor}=14.9 min (*R*), t_{major}=19.4 min (*S*), ee=77%.

*4.4.12. 1-p-Tolylbut-3-en-1-ol (**8l**).*[9b] As a pale yellow oil (84 mg, 86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (2H, d, *J*=5.6 Hz), 7.15 (2H, d, *J*=7.6 Hz), 5.83–5.80 (1H, m), 5.15 (2H, q, *J*=5.0 Hz), 4.72 (1H, t, *J*=4.0 Hz), 2.50 (2H, t, *J*=8.0 Hz), 2.35 (3H, s), 1.98 (1H, br s). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexane/2-propanol=98:2, 0.6 mL/min, 210 nm), t_{minor}=21.4 min (*R*), t_{major}=22.5 min (*S*), ee=60%.

*4.4.13. 1-(2-Methoxyphenyl)-but-3-en-1-ol (**8m**).*[11] As a pale yellow oil (97 mg, 91%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (1H, d, *J*=8.4 Hz), 7.19–7.15 (1H, m), 6.88 (1H, t, *J*=7.6 Hz), 6.80 (1H, d, *J*=8.4 Hz), 5.82–5.72 (1H, m), 5.09–5.01 (2H, m), 4.90–4.87 (1H, m), 3.77 (3H, s), 2.55–2.39 (3H, m). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexane/2-propanol=98:2, 0.8 mL/min, 210 nm), t_{major}=16.5 min (*S*), t_{minor}=18.6 min (*R*), ee=72%.

*4.4.14. 1-(3-Methoxyphenyl)-but-3-en-1-ol (**8n**).*[11] As a pale yellow oil (97 mg, 91%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20–7.16 (1H, m), 6.86–6.84 (2H, m), 6.75–6.73 (1H, m), 5.78–5.68 (1H, m), 5.12–5.05 (2H, m), 4.65–4.62 (1H, m), 3.74 (3H, s), 2.47–2.39 (2H,

m), 2.03 (1H, s). Enantiomeric excess was determined by HPLC with a Chiralcel IC-3 column (hexane/2-propanol=98:2, 0.8 mL/min, 210 nm), t_{major}=38.9 min (*S*), t_{minor}=43.3 min (*R*), ee=74%.

*4.4.15. 1-(4-Methoxyphenyl)but-3-en-1-ol (**8o**).*[11] As a pale yellow oil (93 mg, 87%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (2H, d, *J*=8.8 Hz), 6.87 (2H, d, *J*=8.8 Hz), 5.83–5.76 (1H, m), 5.18–5.11 (2H, m), 4.65 (1H, t, *J*=6.4 Hz), 3.80 (3H, s), 2.51 (2H, t, *J*=6.8 Hz), 2.01 (1H, s). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexane/2-propanol=98:2, 0.7 mL/min, 230 nm), t_{minor}=20.2 min (*R*), t_{major}=24.6 min (*S*), ee=60%.

*4.4.16. 1-(3,5-Dimethylphenyl)-but-3-en-1-ol (**8p**).*[11] As a pale yellow oil (98 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (2H, s), 6.83 (1H, s), 5.78–5.68 (1H, m), 5.10 (1H, s), 5.06 (1H, d, *J*=2.8 Hz), 4.56 (1H, t, *J*=5.6 Hz), 2.45–2.35 (2H, m), 2.24 (6H, s), 1.98 (1H, s). Enantiomeric excess was determined by HPLC with a Chiralcel IC-3 column (hexane/2-propanol=98:2, 0.8 mL/min, 210 nm), t_{major}=10.1 min (*S*), t_{minor}=11.1 min (*R*), ee=81%.

*4.4.17. 1-(3,5-Dimethoxyphenyl)but-3-en-1-ol (**8q**).*[17] As a yellow oil (121 mg, 95%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.56 (2H, d, *J*=2.4 Hz), 6.40 (1H, d, *J*=2.4 Hz), 5.87–5.81 (1H, m), 5.22–5.16 (2H, m), 4.71–4.68 (1H, m), 3.82 (6H, s), 2.56–2.47 (2H, m). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexane/2-propanol=95:5, 0.8 mL/min, 210 nm), t_{minor}=19.1 min (*R*), t_{major}=25.0 min (*S*), ee=80%.

*4.4.18. 1-(3,5-Di-tert-butylphenyl)but-3-en-1-ol (**8r**).* As a yellow oil (150 mg, 96%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (1H, s), 7.22 (2H, s), 5.93–5.83 (1H, m), 5.18 (2H, t, *J*=14.0 Hz), 4.73 (1H, t, *J*=6.4 Hz), 2.55–2.51 (2H, m), 2.05 (1H, br s), 1.34 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 143.3, 135.2, 121.9, 120.2, 118.3, 74.3, 44.1, 35.1, 31.7; HRMS (ESI-MS) calcd for $C_{18}H_{28}O$ $[M-1]^-$ 259.2062, found: 259.2056. Enantiomeric excess was determined by HPLC with a Chiralcel IC-3 column (hexane/2-propanol=98:2, 0.6 mL/min, 210 nm). t_{minor}=6.9 min, t_{major}=7.7 min, ee=92%; $[\alpha]_D^{25}$ −29.4 (*c* 0.37, $CHCl_3$).

*4.4.19. 1-(Naphthalen-1-yl)but-3-en-1-ol (**8s**).*[9b] As a pale yellow oil (110 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (1H, d, *J*=8.0 Hz), 7.89 (1H, d, *J*=7.2 Hz), 7.79 (1H, d, *J*=8.0 Hz), 7.67 (1H, d, *J*=7.2 Hz), 7.53–7.46 (3H, m), 5.99–5.89 (1H, m), 5.56–5.52 (1H, m), 5.24–5.17 (2H, m), 2.78–2.74 (1H, m), 2.63–2.57 (1H, m), 2.25 (1H, s). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexane/2-propanol=90:10, 1.0 mL/min, 210 nm), t_{major}=12.1 min (*S*), t_{minor}=21.6 min (*R*), ee=77%.

*4.4.20. 2-(Naphthalen-1-yl)but-3-en-1-ol (**8t**).*[18] As a pale yellow oil (95 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.80 (4H, m), 7.52–7.45 (3H, m), 5.90–5.80 (1H, m), 5.22–5.18 (1H, m), 5.16–5.12 (1H, m), 4.92 (1H, dd, *J*=7.6, 4.8 Hz), 2.66–2.54 (2H, m), 2.16 (1H, br s). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexane/2-propanol=95:5, 1.0 mL/min, 210 nm), t_{major}=16.5 min (*S*), t_{minor}=18.0 min (*R*), ee=71%.

*4.4.21. 1-(Furan-2-yl)but-3-en-1-ol (**8u**).*[19] As a pale yellow oil (70 mg, 84%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (1H, dd, *J*=1.2, 0.8 Hz), 6.32 (1H, dd, *J*=3.2, 1.6 Hz), 6.26 (1H, d, *J*=3.2 Hz), 5.81–5.77 (1H, m), 5.21–5.13 (2H, m), 4.74 (1H, dt, *J*=7.2, 5.6 Hz), 2.66–2.60 (2H, m), 2.06–2.03 (1H, m). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexane/2-propanol=99:1, 0.8 mL/min, 210 nm), t_{minor}=17.7 min (*R*), t_{major}=18.8 min (*S*), ee=43%.

*4.4.22. 1-(Thiophen-2-yl)but-3-en-1-ol (**8v**).*[9b] As a yellow oil (76 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.24 (1H, m), 7.00–6.98 (2H, m), 5.79–5.87 (1H, m), 5.23–5.16 (2H, m), 5.04–5.00 (1H, m), 2.67–2.59 (2H, m), 2.24 (1H, d, *J*=4.0 Hz). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexane/2-propanol=99:1, 1.0 mL/min, 210 nm), t_{minor}=22.5 min (*R*), t_{major}=23.6 min (*S*), ee=70%.

*4.4.23. 1-Phenylhex-5-en-3-ol (**8w**).*[4b] As a pale yellow oil (76 mg, 72%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.26 (2H, m), 7.23–7.18 (3H, m) 5.88–5.76 (1H, m), 5.18 (2H, dd, *J*=14.0, 1.2 Hz), 3.72–3.65 (1H, m), 2.82–2.77 (1H, m), 2.74–2.69 (1H, m), 2.35–2.28 (1H, m), 2.22–2.14 (1H, m), 1.82–1.77 (2H, m), 1.67 (1H, d, *J*=5.2 Hz). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexane/2-propanol=85:15, 0.5 mL/min, 210 nm), t_{minor}=10.7 min (*S*), t_{major}=14.1 min (*R*), ee=8%.

*4.4.24. 1-Phenyl-hexa-1,5-dien-3-ol (**8x**).*[4b] As a pale yellow oil (81 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.12 (5H, m), 6.53 (1H, d, *J*=16.0 Hz), 6.18 (1H, dd, *J*=16.0, 6.4 Hz), 5.82–5.74 (1H, m), 5.17–5.06 (2H, m), 4.32–4.27 (1H, m), 2.41–2.27 (2H, m), 1.78 (1H, s). Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexane/2-propanol=95:5, 1.0 mL/min, 210 nm), t_{major}=13.8 min (*S*), t_{minor}=18.0 min (*R*), ee=16%.

*4.4.25. 2-Methyl-1-phenylbut-3-en-1-ol (**8y**).*[5a] As a pale yellow oil (86 mg, 89%, *syn*/*anti*=52:48); *syn*-isomer δ 7.38–7.26 (5H, m), 5.78–5.70 (1H, m), 5.06–4.99 (2H, m), 4.60 (1H, d, *J*=5.2 Hz), 2.61–2.54 (1H, m), 1.02 (3H, d, *J*=7.6 Hz); ^{1}H NMR: *anti*-isomer δ 7.38–7.26 (5H, m), 5.85–5.76 (1H, m), 5.22–5.21 (1H, m), 5.20–5.15 (1H, m), 4.36 (1H, d, *J*=7.6 Hz), 2.51–2.45 (1H, m), 0.86 (3H, d, *J*=7.2 Hz). Enantiomeric excess was determined by HPLC with a Chiralcel IC-3 column (hexane/2-propanol=97.5:2.5, 0.6 mL/min, 210 nm), *syn*-isomer, t_{minor}=10.6 min (1*S*,2*R*), t_{major}=11.5 min (1*R*,2*S*), ee=74%; *anti*-isomer t_{minor}=12.3 min (1*R*,2*R*), t_{major}=13.2 min (1*S*,2*S*), ee=54%.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.07.030.

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