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Fe(III) catalyzed enantioselective hydrophosphonylation of aldehydes promoted by chiral camphor Schiff bases

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ABSTRACT

Five novel chiral camphor Schiff bases were designed. Schiff base $\mathbf{L_3}$ showed high efficiency in Fe(III)-catalyzed asymmetric hydrophosphonylations of aldehydes, giving the corresponding products in high yields (up to 91%) along with moderate to good enantioselectivities (up to 82%).

1. Introduction

In recent years, the importance of α-hydroxyphosphonates has been well-recognized due to their biological activities. These compounds have been widely applied in medicine and biochemistry, as antibacterial agents, enzymes renin, thrombin, and anti-HIV agents.[1] Since the biological activity of these compounds is strongly related to the absolute configuration of the α-hydroxyphosphonates unit, it is not surprising that great efforts have focused on the synthesis of chiral α-hydroxyphosphonates derivatives.[2] The catalytic asymmetric hydrophosphonylation of aldehydes is one of the most powerful strategies for the synthesis of α-hydroxyphosphonates. Therefore, the development of new catalytic systems for the asymmetric hydrophosphonylation of aldehyde[3] has become a core work of this procedure.

Wynberg et al. first reported the preparation of enantiomerically enriched α-hydroxyphosphonates using amino alcohol as a catalyst.[4] Since this pioneering work, various catalytic systems, including organic molecules and chiral metal complexes, have been developed. The first transition metal catalyzed asymmetric hydrophosphonylation was discovered by Shibuya et al.[5] Shibasaki et al. reported the first highly enantioselective hydrophosphonylation of aldehydes using hetero-bimetallic complexes as catalysts.[6] Subsequently, a breakthrough was achieved with the C_1-symmetric [Al-(salalen)] complex by Katsuki et al.[7] Excellent results were also observed by Yamamoto et al.,[8] Feng et al.[9] and other groups.[10] Recently, the squaramine used to promote enantioselective hydrophosphonylation reactions was reported by Herrera et al..[11]

However, only limited types of chiral ligands have been successfully utilized in this reaction, which is in contrast to the many excellent chiral ligands and complexes, especially for chiral Schiff base and its complex. Clearly, the development of new efficient and practical catalytic systems for asymmetric hydrophosphonylation reaction is still a highly challenging topic.

From natural chiral sources, D-(+)-camphor often plays an important role in the asymmetric organic synthesis, in terms of its low-cost, easy-purification, and rigid structure.[12] Chiral camphor and its metal complexes have been shown to be highly efficient in many asymmetric reactions. We have paid much attention to modifying the chiral camphor frame. On the other hand, iron has unique properties, compared with rare metals and some sensitive metal salts, which are frequently used in asymmetric hydrophosphonylation reactions, such as being inexpensive, non-toxic, more abundant, and environmentally friendly. The development of iron catalysts is a primary long term goal in synthetic organic chemistry. Iron based catalysts are under-utilized in organic synthesis, especially in the field of asymmetric synthesis.[13] Therefore, the development of an iron complex with new chiral camphor derivatives for the synthesis of optically active α-hydroxyphosphonates is a reasonable target.

Chen et al. reported on the camphor-based tridentate Schiff base SBAIB ligands,[14] which were used in the asymmetric hydrophosphonylation of aldehydes to afford α-hydroxyphosphonates with high yields and good enantioselectivities.[14c] Inspired by this result and pursuit our interest in the development of cost effective and accessible catalysts based on the chiral camphor for the asymmetric catalytic synthesis, we herein report the synthesis of an unusual chiral camphor iron complex and its application as a catalyst in asymmetric hydrophosphonylation of aldehydes for the synthesis of optically active α-hydroxyphosphonates.

2. Results and discussion

At first, (1*S*,2*R*,4*R*)-1-amino-7,7-dimethylbicyclo[2.2.1]heptan-2-ol was prepared according to the procedure reported by

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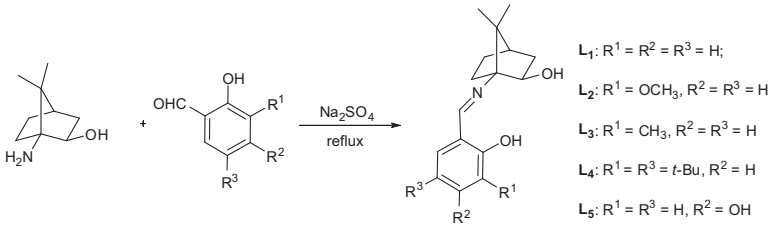
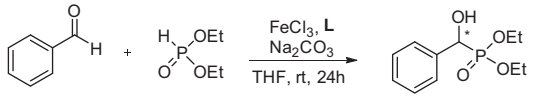


Scheme 1. Synthesis of chiral camphor Schiff bases.

Yan et al.[15] As shown in Scheme 1, the new Schiff bases **L₁**–**L₅** were prepared from (1*S*,2*R*,4*R*)-1-amino-7,7-dimethylbi-cyclo[2.2.1] heptan-2-ol by condensation with an appropriate commercially available aldehyde in MeOH/CH_2Cl_2 (1:3, v/v) in the presence of anhydrous Na_2SO_4 at reflux.

With the chiral camphor Schiff bases in hand, the asymmetric induced properties were initially examined in the hydrophosphonylation of benzaldehyde with diethyl phosphate in the presence of sodium carbonate at room temperature in THF according to the literature.[16] The catalytic metal salt was fixed to $FeCl_3$ and kept in a 1:1 ratio to Schiff based as Sekar's results. The experimental results are listed in Table 1. Iron trichloride cooperated with chiral camphor Schiff bases **L₃** to give diethyl hydroxy(phenyl)methyl phosphonate with the highest yield (85%) and ee (76%) among the Schiff bases **L₁**–**L₅**. This implied that the Schiff bases **L₃** cooperated with iron trichloride and was most powerful for the model reaction. The optimization of reaction conditions then focused on Fe promoted by chiral camphor Schiff bases **L₃** as the catalyst for model reaction.

Table 1
Screen asymmetric induced properties of the chiral Schiff bases **L₁**–**L₅**[a]



1a 2a 3aa

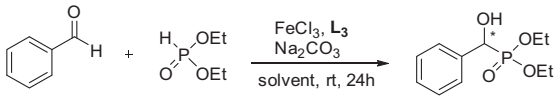
Entry[a]	**L** (mol %)	Yield[b] (%)	ee[c] (%)
1	**L₁** (10)	77	20
2	**L₂** (10)	80	17
3	**L₃** (10)	85	76
4	**L₄** (10)	82	70
5	**L₅** (10)	75	11

[a] Reaction conditions: benzaldehyde **1a** (53 mg, 0.5 mmol), diethyl phosphate **2a** (76 mg, 0.55 mmol), $FeCl_3$ (8 mg, 10 mol %), **L** (10 mol %), Na_2CO_3 (53 mg, 0.5 mmol), THF (5 mL), under N_2.
[b] Isolated yields.
[c] Determined by HPLC analysis (Chiralcel OD-H).

The reaction solvent is an important factor with regards to chemical reactions. Several solvents were chosen to test the solvent factor for the asymmetric hydrophosphonylation reaction catalyzed by chiral Schiff base **L₃** and $FeCl_3$ (Table 2, entries 1–9). Among the different solvents, THF was established as the best choice for this reaction system (Table 2, entry 1, 85% yield, 76% ee).

Next, the effects of various bases were examined using chiral Schiff base **L₃** and $FeCl_3$ as the catalyst. Inorganic bases and organic bases were tested in THF. The results are summarized in Table 3. It can be seen that $NaHCO_3$ (one equivalent) provided the product with an excellent yield (87%) and enantioselectivity (80%), which was better than other bases for the model reaction. Moreover, the amount of $NaHCO_3$ was changed from 0.5–1.5 equiv in the hydrophosphonylation reaction (Table 3, entries 2, 10, and 11). The results indicated that an excess of $NaHCO_3$ did not improve the chemical yield or the enantiomeric excess. The temperature effect was also explored

Table 2
Effects of solvent on the asymmetric hydrophosphonylation reaction under the chiral Schiff base **L₃** and $FeCl_3$[a]

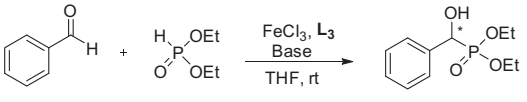


1a 2a 3aa

Entry	Solvent	Yield[b] (%)	ee[c] (%)
1	THF	85	76
2	DCM	83	59
3	DCE	35	51
4	Toluene	75	64
5	Dioxane	58	66
6	$CHCl_3$	80	62
7	EtOH	60	28
8	CH_3CN	65	61
9	DMF	54	50

[a] Reaction conditions: benzaldehyde **1a** (53 mg, 0.5 mmol), diethyl phosphate **2a** (76 mg, 0.55 mmol), $FeCl_3$ (8 mg, 10 mol %), **L₃** (14 mg, 10 mol %), Na_2CO_3 (53 mg, 0.5 mmol), solvent (5 mL), under N_2.
[b] Isolated yields.
[c] Determined by HPLC analysis (Chiracel OD-H).

Table 3
Effects of base on the asymmetric hydrophosphonylation reaction catalyzed by the chiral Schiff base **L₃** and $FeCl_3$[a]

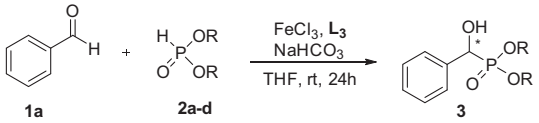


1a 2a 3aa

Entry	Base	Time (h)	Yield[b] (%)	ee[c] (%)
1	Na_2CO_3	24	85	76
2	$NaHCO_3$	24	87	80
3	K_2CO_3	24	77	12
4	Na_2SO_3	24	56	63
5	K_3PO_4	24	40	33
6	DABCO	24	82	73
7	TEA	24	75	74
8	DBU	24	70	11
9	DIPEA	24	73	72
10[d]	$NaHCO_3$	24	80	76
11[e]	$NaHCO_3$	24	85	75
12[f]	$NaHCO_3$	30	71	70
13[g]	$NaHCO_3$	15	86	59

[a] Reaction conditions: benzaldehyde **1a** (53 mg, 0.5 mmol), diethyl phosphate **2a** (76 mg, 0.55 mmol), $FeCl_3$ (8 mg, 10 mol %), **L₃** (14 mg, 10 mol %), Base (0.5 mmol), THF (5 mL), under N_2.
[b] Isolated yields.
[c] Determined by HPLC analysis (Chiracel OD-H).
[d] 0.5 equiv $NaHCO_3$ was used.
[e] 1.5 equiv $NaHCO_3$ was used.
[f] Reaction temperature was 0 °C.
[g] Reaction temperature was 55 °C.

Table 4
Influence of catalyst loading on the asymmetric hydrophosphonylation reaction catalyzed by chiral Schiff base $\mathbf{L_3}$ and $FeCl_3$ and the performance of different disubstituted phosphites[a]



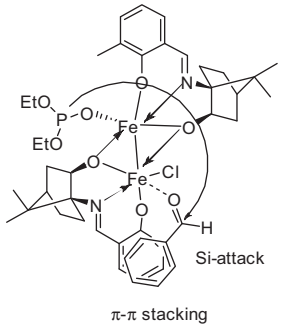
Entry	R	$\mathbf{L_3}$ (mol %)	$FeCl_3$ (mol %)	Yield[b] (%)	ee[c] (%)
1	Et	5	5	86	78
2	Et	10	10	87	80
3	Et	20	20	87	76
4	Et	30	30	85	74
5	Me	10	10	68	79
6	Bu	10	10	73	75
7	Ph	10	10	nr	—

[a] Reaction conditions: benzaldehyde **1a** (53 mg, 0.5 mmol), diethyl phosphate **2** (0.55 mmol), $NaHCO_3$ (42 mg, 0.5 mmol), THF (5 mL), under N_2.
[b] Isolated yields.
[c] Determined by HPLC analysis (Chiracel OD-H).

(Table 3, entries 12 and 13). It was found that room temperature was the best while increasing or decreasing the reaction temperature resulted in a lower enantioselectivity. Subsequently, the effect of the catalyst loading was examined and the results are shown in Table 4. It was seen that 10 mol % was the optimal catalyst loading (Table 4, entry 2). With the optimized reaction conditions in hand, other disubstituted phosphites, such as dimethyl phosphite, dibutyl phosphite, and diphenyl phosphite, were next evaluated (Table 4, entries 5 and 6). All of the dialkyl phosphites smoothly gave the desired products in good yield and enantioselectivity. Diethyl phosphite showed the best performance (87% yield, 80% ee). However, the diphenyl phosphite failed to generate any product in this transformation and the reason was unclear.

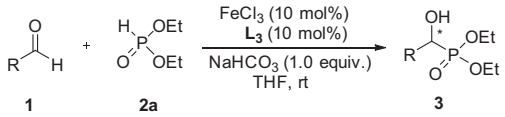
After the optimal reaction conditions were established, the asymmetric hydrophosphonylation reaction was performed between diethyl phosphate and aldehydes under the optimized reaction conditions. The results are summarized in Table 5. The aromatic aldehydes underwent the asymmetric hydrophosphonylation reaction smoothly with good chemical yields and enantiomeric excess values with electron-withdrawing and electron-donating groups. 1-Naphthaldehyde also successfully afforded the desired product in good yield and with acceptable enantioselectivity. Although aliphatic aldehyde smoothly generated the phosphate, the enantioselectivity decreased sharply. The absolute configurations of all α-hydroxyphosphonates with a known absolute configuration in the literature, produced by our procedure, had an (*S*)-configuration. However, Chen's result[14c] gave (*R*)-absolute configuration products based on the iron complex of SBAIB ligand, which is a camphor based Schiff base derived from the 3-amino group of (1*R*,2*S*,3*R*)-3-amino-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol. This means a combination of our catalytic system and Chen's system will produce either an (*S*) or (*R*) absolute configuration α-hydroxyphosphonates as desired.

A key intermediate for the explanation of the absolute configurations of the obtained phosphonates is given in Scheme 2 on the



Scheme 2. A possible intermediate for the generation of phosphonate.

Table 5
Enantioselective hydrophosphonylation of various aldehydes catalyzed by chiral Schiff base $\mathbf{L_3}$ and $FeCl_3$[a]



Entry	Aldehyde	Product	Time (h)	Yield[b] (%)	ee[c] (%)	Configuration[d]
1	PhCHO	**3aa**	24	87	80	(*S*)
2	4-$MeOC_6H_4CHO$	**3ab**	24	86	80	(*S*)
3	3-$MeOC_6H_4CHO$	**3ac**	24	85	79	—
4	2-$MeOC_6H_4CHO$	**3ad**	24	82	76	—
5	4-MeC_6H_4CHO	**3ae**	23	84	79	(*S*)
6	3-MeC_6H_4CHO	**3af**	23	83	78	(*S*)
7	4-$Me_2NC_6H_4CHO$	**3ag**	21	85	72	—
8	2,3,4-Trimethoxybenzaldehyde	**3ah**	24	81	78	(*S*)
9	4-FC_6H_4CHO	**3ai**	10	90	74	(*S*)
10	4-BrC_6H_4CHO	**3aj**	11	91	72	(*S*)
11	3-ClC_6H_4CHO	**3ak**	13	89	71	—
12	Thiophene-2-carboxaldehyde	**3al**	20	83	75	(*S*)
13	5-Methylthiophene-2-carboxaldehyde	**3am**	20	80	81	(*S*)
14	Cinnamaldehyde	**3an**	15	85	82	(*S*)
15	α-Methyl-trans-cinnamaldehyde	**3ao**	15	83	79	—
16	1-Naphthaldehyde	**3ap**	20	80	63	(*S*)
17	Phenylpropyl aldehyde	**3aq**	24	73	41	—

[a] Reaction conditions: aldehyde **1** (0.5 mmol), diethyl phosphate **2** (76 mg, 0.55 mmol), $FeCl_3$ (8 mg, 10 mol %), $\mathbf{L_3}$ (14 mg, 10 mol %), $NaHCO_3$ (42 mg, 0.5 mmol), THF (5 mL), under N_2.
[b] Isolated yields.
[c] Determined by HPLC analysis (Chiralcel OD-H or Chiralpak AD columns).
[d] Configuration was assigned on the basis of a thorough literature survey.

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basis of Chen's proposed mechanism.[14c] The addition of the phosphite group to the benzaldehyde occured on the *si*-face of the benzaldehyde, since there was steric hindrance from the bridge dimethyl group of the camphor moiety if the addition occured on the *re*-face of the benzaldehyde. Thus phosphonates with an (*S*)-absolute configuration were favored.

3. Conclusion

In conclusion, five novel chiral camphor-based Schiff bases derived from the 1-amino group of (1*S*,2*R*,4*R*)-1-amino-7,7-dimethyl-bicyclo[2.2.1]hep-tan-2-ol have been designed and applied to form the corresponding Fe(III) complexes as catalysts in the asymmetric hydrophosphonylation of aldehydes. Schiff base **L_3** showed the best chirality induction ability. The electron-rich and electron-deficient aromatic aldehydes were well tolerated in the reaction system with good chemical yields and enantiomeric excess values. The absolute configurations of all α-hydroxyphosphonates with a known absolute configuration in the literature were (*S*), which is contrary to Chen's results in which an (*R*)-configuration was observed using the camphor based Schiff base derived from 3-amino group of (1*R*,2*S*,3*R*)-3-amino-1,7,7-trimetylbicyclo-[2.2.1]heptan-2-ol. The application of these camphor-based Schiff bases in other asymmetric reactions is currently under investigation.

4. Experimental section

4.1. General procedure for synthesis of Schiff base ligands

(1*S*,2*R*,4*R*)-1-Amino-7,7-dimethylbicyclo[2.2.1]heptan-2-ol (5 mmol, 776 mg) was reacted with 2-hydroxy-1-aromaticaldehydes (5 mmol) in MeOH/CH_2Cl_2 (1:3, v/v) (8 mL) in the presence of anhydrous Na_2SO_4 under a nitrogen atmosphere at room temperature. The reaction mixture was then stirred for 12 h. Subsequently, filtration and concentration of the filtrate gave a residue, which was purified by silica gel column chromatography (eluents: petroleum ether/ethyl acetate = 6:1–1:2) to give the target product.

4.1.1. (1*S*,2*R*,4*R*)-1-(2-Hydroxybenzylideneamino)-7,7-dimethyl-bicyclo[2.2.1]heptan-2-ol L_1

Yellow solid; yield 75%; mp 99–101 °C; $[\alpha]_D^{22} = -110.8$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 14.12 (s, 1H), 8.41 (s, 1H), 7.36–7.32 (m, 1H), 7.29–7.27 (m, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.88 (t, *J* = 7.4 Hz, 1H), 3.92–3.89 (m, 1H), 2.33 (s, 1H), 2.12–2.06 (m, 1H), 2.03–1.87 (m, 4H), 1.36–1.27 (m, 5H), 0.87 (s, 3H); ^{13}C NMR (101 MHz, CDCl3): δ 164.6, 162.9, 132.7, 131.7, 118.8, 117.9, 78.6, 74.6, 48.3, 43.6, 39.9, 27.8, 27.1, 19.9; HRMS (ESI) $[M+H]^+$ calcd for $C_{16}H_{21}NO_2$: 260.1645; found: 260.1643.

4.1.2. (1*S*,2*R*,4*R*)-1-(2-Hydroxy-3-methoxybenzylideneamino)-7,7-dimethylbicyclo[2.2.1]heptan-2-ol L_2

Yellow solid; yield 78%; mp 60–61 °C; $[\alpha]_D^{22} = -157.2$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 14.83 (s, 1H), 8.25–8.13 (m, 1H), 6.84–6.59 (m, 3H), 3.96–3.88 (m, 4H), 3.28 (s, 1H), 2.08–1.89 (m, 5H), 1.32–1.25 (m, 5H), 0.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.1, 149.5, 123.3, 117.7, 116.3, 113.5, 78.2, 73.8, 55.9, 48.3, 43.4, 39.9, 27.6, 27.0, 19.8; HRMS (ESI) $[M+H]^+$ calcd for $C_{17}H_{23}NO_3$: 290.1751; found: 290.1755.

4.1.3. (1*S*,2*R*,4*R*)-1-(2-Hydroxy-3-methylbenzylideneamino)-7,7-dimethylbicyclo[2.2.1]heptan-2-ol L_3

Yellow solid; yield 81%; mp 147–149 °C; $[\alpha]_D^{22} = -56.1$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 14.20 (s, 1H), 8.39 (s, 1H), 7.16 (dd, *J* = 27.7, 7.3 Hz, 2H), 6.77 (t, *J* = 7.5 Hz, 1H), 3.86 (dd, *J* = 7.8, 3.5 Hz, 1H), 2.38 (s, 1H), 2.28 (s, 3H), 2.09–1.87 (m, 5H), 1.33–1.23 (m, 5H), 0.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.9, 160.7, 133.5, 129.3, 126.5, 118.1, 117.8, 78.7, 77.4, 48.2, 43.6, 39.9, 28.0, 27.1, 20.0, 15.6; HRMS (ESI) $[M+H]^+$ calcd for $C_{17}H_{23}NO_2$: 274.1802; found: 274.1807.

4.1.4. (1*S*,2*R*,4*R*)-1-((*E*)-3,5-Di-*tert*-butyl-2-hydroxybenzylideneamino)-7,7-dimethylbicyclo[2.2.1]heptan-2-ol L_4

Yellow solid; yield 85%; mp 149–151 °C; $[\alpha]_D^{22} = -51.4$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.97 (s, 1H), 8.46 (s, 1H), 7.40 (s, 1H), 7.14 (s, 1H), 3.86 (s, 1H), 2.15–1.88 (m, 6H), 1.45 (s, 9H), 1.32 (s, 9H), 1.30–1.25 (m, 5H), 0.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.0, 158.6, 140.0, 137.1, 127.1, 126.2, 118.1, 78.8, 74.8, 48.1, 43.7, 39.8, 35.1, 34.2, 31.5, 29.5, 27.9, 27.1, 20.2, 19.9; HRMS (ESI) $[M+H]^+$ calcd for $C_{24}H_{37}NO_2$: 272.2897; found: 372.2906.

4.1.5. 4-((*E*)-((1*S*,2*R*,4*R*)-2-Hydroxy-7,7-dimethylbicyclo[2.2.1]-heptan-1-ylimino)methyl)benzene-1,3-diol L_5

Yellow solid; yield 73%; mp 215–216 °C; $[\alpha]_D^{22} = -175.1$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO): δ 14.63 (s, 1H), 9.87 (s, 1H), 8.26 (d, *J* = 5.9 Hz, 1H), 7.13 (d, *J* = 8.6 Hz, 1H), 6.11–5.98 (m, 2H), 5.25–5.23 (m, 1H), 3.78–3.75 (m, 1H), 1.94–1.76 (m, 5H), 1.31–1.19 (m, 2H), 1.12 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (101 MHz, DMSO): δ 171.6, 163.0, 162.2, 134.2, 111.1, 105.9, 103.6, 75.6, 71.4, 47.3, 42.4, 40.4, 28.4, 26.6, 19.7; HRMS (ESI) $[M+H]^+$ calcd for $C_{16}H_{21}NO_3$: 276.1594; found: 276.1599.

4.2. General procedure for synthesis of optically active α-hydroxyphosphonates

Dialkyl phosphite (0.55 mmol, 76 mg) and aldehyde (0.5 mmol) were added to a THF (5 mL) solution of $FeCl_3$ (10 mol %, 8 mg), ligand **L_3** (10 mol %, 14 mg) and $NaHCO_3$ (1.0 equiv, 42 mg) under a nitrogen atmosphere. The reaction mixture was stirred for 10–23 h at room temperature, then the solvents were evaporated to give a residue. The final product was obtained by purification of the residue using silica gel column chromatography (eluents: petroleum ether/ethyl acetate = 2:1–1:7), which was characterized by NMR for confirming the chemical structure and the chiral HPLC for evaluating the enantiomeric excess using Chiralcel OD-H or Chiralpak AD columns.

4.2.1. (*S*)-Diethyl hydroxy(phenyl)methylphosphonate 3aa[9]

White solid; mp 76.1–77.0 °C; 87% yield, 80% ee, HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH, 95:5, 0.5 mL/min, 254 nm): t_R(minor) = 27.644 min, t_R(major) = 33.914 min; $[\alpha]_D^{22} = -28.3$ (*c* 1.0, $CHCl_3$) {lit.[9] $[\alpha]_D^{20} = -39.7$ (*c* 0.39, $CHCl_3$)}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.48 (m, 2H), 7.38–7.28 (m, 3H), 5.02 (dd, *J* = 10.9, 5.4 Hz, 1H), 4.09–3.98 (m, 4H), 1.28–1.20 (m, 6H).

4.2.2. (*S*)-Diethyl hydroxy(4-methoxyphenyl)methylphosphonate 3ab[9]

White solid; mp 117.3–118.6 °C; 86% yield, 80% ee, HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH, 95:5, 0.5 mL/min, 254 nm): t_R(minor) = 39.487 min, t_R(major) = 58.233 min; $[\alpha]_D^{22} = -30.5$ (*c* 1.5, $CHCl_3$) {lit.[9] $[\alpha]_D^{20} = -38.6$ (*c* 0.76, $CHCl_3$)}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.40 (m, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 4.95 (dd, *J* = 10.0, 5.3 Hz, 1H), 4.09–3.91 (m, 4H), 3.81 (s, 3H), 1.29–1.20 (m, 6H).

4.2.3. Diethyl hydroxy(3-methoxyphenyl)methylphosphonate 3ac[9]

Colorless oil; 85% yield, 79% ee, HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH, 95:5, 0.5 mL/min, 254 nm): t_R(minor) = 38.992 min, t_R(major) = 59.256 min; $[\alpha]_D^{22} = -12.5$ (*c* 1.5, $CHCl_3$) {lit.[9]

$[\alpha]_D^{20} = -13.6$ (*c* 0.50, $CHCl_3$)}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.20 (t, *J* = 7.9 Hz, 1H), 7.01–6.97 (m, 2H), 6.78 (d, *J* = 8.2 Hz, 1H), 4.93 (dd, *J* = 10.9, 4.8 Hz, 1H), 4.03–3.89 (m, 4H), 3.74 (s, 3H), 1.23–1.14 (m, 6H).

4.2.4. Diethyl hydroxy(2-methoxyphenyl)methylphosphonate 3ad[9]

Colorless oil; 82% yield, 76% ee, HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH, 95:5, 0.5 mL/min, 254 nm): t_R(minor) = 35.387 min, t_R(major) = 43.051 min; $[\alpha]_D^{22} = -34.1$ (*c* 1.5, $CHCl_3$) {lit.[9] $[\alpha]_D^{20} = -43.4$ (*c* 0.78, $CHCl_3$)}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.48–7.45 (m, 1H), 7.24–7.19 (m, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 8.3 Hz, 1H), 5.35 (dd, *J* = 12.1, 7.2 Hz, 1H), 4.10–3.86 (m, 4H), 3.79 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H).

4.2.5. (*S*)-Diethyl hydroxy(*p*-tolyl)methylphosphonate 3ae[9]

White solid; mp 96.3–97.0 °C; 84% yield, 79% ee, HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH, 95:5, 0.5 mL/min, 254 nm): t_R(minor) = 23.815 min, t_R(major) = 27.382 min; $[\alpha]_D^{22} = -31.3$ (*c* 1.0, $CHCl_3$) {lit.[9] $[\alpha]_D^{20} = -40.0$ (*c* 0.81, $CHCl_3$)}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.38–7.36 (m, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 4.98 (dd, *J* = 10.4, 5.0 Hz, 1H), 4.10–3.92 (m, 4H), 3.18 (s, 1H), 2.35 (s, 3H), 1.30–1.21 (m, 6H).

4.2.6. (*S*)-Diethyl hydroxy(*m*-tolyl)methylphosphonate 3af[16]

Colorless oil; 83% yield, 78% ee, HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH, 95:5, 0.5 mL/min, 254 nm): t_R(minor) = 24.183 min, t_R(major) = 39.432 min; $[\alpha]_D^{22} = -17.6$ (*c* 1.0, $CHCl_3$) [lit.[16] $[\alpha]_D^{20} = -16.1$ (*c* 1.0, $CHCl_3$)]; ^1H NMR (400 MHz, $CDCl_3$): δ 7.23–7.14 (m, 3H), 7.04 (d, *J* = 6.7 Hz, 1H), 4.90 (dd, *J* = 10.9, 5.1 Hz, 1H), 4.21 (s, 1H), 4.03–3.87 (m, 4H), 2.28 (s, 3H), 1.12–1.21(m, 6H).

4.2.7. Diethyl(4-(dimethylamino)phenyl)(hydroxy)methylphosphonate 3ag[17]

Light yellow solid; mp 93.8–94.3 °C; 85% yield, 72% ee, HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH, 90:10, 0.5 mL/min, 254 nm): t_R(minor) = 26.234 min, t_R(major) = 35.252 min; $[\alpha]_D^{22} = -26.1$ (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.36–7.33 (m, 2H), 6.71 (d, *J* = 8.7 Hz, 2H), 4.88 (dd, *J* = 9.6, 5.0 Hz, 1H), 4.11–3.88 (m, 4H), 3.15 (s, 1H), 2.95 (s, 6H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H).

4.2.8. (*S*)-Diethyl hydroxy(2,3,4-trimethoxyphenyl)methylphosphonate 3ah[16]

White solid; mp 82.3–83.8 °C; 81% yield, 78% ee, HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH, 90:10, 0.5 mL/min, 254 nm): t_R(minor) = 26.148 min, t_R(major) = 30.828 min; $[\alpha]_D^{22} = -13.7$ (*c* 1.0, $CHCl_3$) {lit.[16] $[\alpha]_D^{20} = -9.4$ (*c* 2.4, $CHCl_3$)}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.28–7.25 (m, 1H), 6.70 (d, *J* = 8.7 Hz, 1H), 5.28 (dd, *J* = 11.6, 7.1 Hz, 1H), 4.21–4.13 (m, 2H), 4.10–4.02 (m, 1H), 4.01–3.92 (m, 4H), 3.87 (s, 3H), 3.85 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

4.2.9. (*S*)-Diethyl(4-fluorophenyl)(hydroxy)methylphosphonate 3ai[16]

White solid; mp 56.3–57.1 °C; 90% yield, 74% ee, HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH, 97:3, 0.5 mL/min, 254 nm): t_R(minor) = 34.289 min, t_R(major) = 31.176 min; $[\alpha]_D^{22} = -23.6$ (*c* 1.5, $CHCl_3$) {lit.[16] $[\alpha]_D^{20} = -15.5$ (*c* 2.6, $CHCl_3$)}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.49–7.45 (m, 2H), 7.05 (t, *J* = 8.6 Hz, 2H), 5.00 (dd, *J* = 10.3, 5.3 Hz, 1H), 4.27–4.23 (m, 1H), 4.12–3.96 (m, 4H), 1.29–1.21 (m, 6H).

4.2.10. (*S*)-Diethyl(4-bromophenyl)(hydroxy)methylphosphonate 3aj[16]

White solid; mp 69.2–70.5 °C; 91% yield, 72% ee, HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH, 95:5, 0.5 mL/min, 254 nm): t_R(minor) = 28.636 min, t_R(major) = 24.880 min; $[\alpha]_D^{22} = -25.2$ (*c* 2.0, $CHCl_3$) {lit.[16] $[\alpha]_D^{20} = -17.4$ (*c* 1.4, $CHCl_3$)}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.3 Hz, 2H), 7.38–7.35(m, 2H), 4.98 (dd, *J* = 10.8, 3.5 Hz, 1H), 4.27 (s, 1H), 4.11–4.01 (m, 4H), 1.29–1.23 (m, 6H).

4.2.11. Diethyl(3-chlorophenyl)(hydroxy)methylphosphonate 3ak[9]

White solid; mp 54.5–55.3 °C; 89% yield, 71% ee, HPLC (Chiralpak AD, *n*-hexane/*i*-PrOH, 95:5, 0.5 mL/min, 254 nm): t_R(minor) = 33.972 min, t_R(major) = 31.105 min; $[\alpha]_D^{22} = -21.3$ (*c* 1.5, $CHCl_3$) {lit.[9] $[\alpha]_D^{20} = -25.3$ (*c* 0.46, $CHCl_3$)}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (s, 1H), 7.38–7.28 (m, 3H), 5.03 (d, *J* = 11.2 Hz, 1H), 4.66 (s, 1H), 4.16–4.03 (m, 4H), 1.32–1.24 (m, 6H).

4.2.12. (*S*)-Diethyl hydroxy(thiophen-2-yl)methylphosphonate 3al[9]

Colorless oil; 83% yield, 75% ee, HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH, 90:10, 0.5 mL/min, 254 nm): t_R(minor) = 18.878 min, t_R(major) = 31.172 min; $[\alpha]_D^{22} = -10.2$ (*c* 1.0, $CHCl_3$) {lit.[9] $[\alpha]_D^{20} = -11.3$ (*c* 0.57, $CHCl_3$)}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.23–7.20 (m, 1H), 7.12–7.10 (m, 1H), 6.93–6.91(m, 1H), 5.17 (d, *J* = 11.0 Hz, 1H), 4.85 (s, 1H), 4.11–3.95 (m, 4H), 1.24–1.16 (m, 6H).

4.2.13. (*S*)-Diethyl hydroxy(5-methylthiophen-2-yl)methylphosphonate 3am[5c]

White solid; mp 71.0–72.3 °C; 80% yield, 81% ee, HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH, 90:10, 0.5 mL/min, 254 nm): t_R(minor) = 16.341 min, t_R(major) = 32.851 min; $[\alpha]_D^{22} = -5.1$ (*c* 1.5, $CHCl_3$) {lit.[5c] $[\alpha]_D^{20} = -3.8$ (*c* 1.0, $CHCl_3$)}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.97 (s, 1H), 6.64 (s, 1H), 5.12 (dd, *J* = 10.9, 5.8 Hz, 1H), 4.63 (s, 1H), 4.19–4.06 (m, 4H), 2.47 (s, 3H), 1.34–1.26 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.5, 136.9, 126.4, 124.9, 67.8, 66.2, 63.6, 63.3, 16.4, 15.3; HRMS (ESI) $[M+Na]^+$ calcd for $C_{10}H_{17}O_4PS$: 287.0477; found: 287.0475.

4.2.14. (*S*)-Diethyl 1-hydroxy-3-phenylallylphosphonate 3an[18]

White solid; mp 87.2–88.7 °C; 85% yield, 82% ee, HPLC (Chiralpak AD, *n*-hexane/*i*-PrOH, 90:10, 0.5 mL/min, 254 nm): t_R(minor) = 22.621 min, t_R(major) = 25.118 min; $[\alpha]_D^{22} = -12.1$ (*c* 1.0, $CHCl_3$) {lit.[18] $[\alpha]_D^{18} = +7.7$ (*c* 0.92, $CHCl_3$) for 49% ee (*R*)}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.27–7.23 (m, 1H), 6.81–6.76 (m, 1H), 6.36–6.29 (m, 1H), 4.70–4.65 (m, 1H), 4.23–4.16 (m, 4H), 3.73 (s, 1H), 1.36–1.31 (m, 6H).

4.2.15. Diethyl 1-hydroxy-2-methyl-3-phenylallylphosphonate 3ao[19]

Colorless oil; 83% yield, 79% ee, HPLC (Chiralpak AD, *n*-hexane/*i*-PrOH, 95:5, 0.5 mL/min, 254 nm): t_R(minor) = 35.924 min, t_R(major) = 37.682 min; $[\alpha]_D^{22} = -8.2$ (*c* 1.5, $CHCl_3$) {lit.[19] $[\alpha]_D^{20} = -17.4$ (*c* 1.4, $CHCl_3$)}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.28–7.13 (m, 5H), 6.61 (d, *J* = 4.8 Hz, 1H), 4.47 (d, *J* = 12.2 Hz, 1H), 4.14–4.08 (m, 4H), 1.95–1.93 (m, 3H), 1.28–1.23 (m, 6H).

4.2.16. (*S*)-Diethyl hydroxy(naphthalen-1-yl)methylphosphonate 3ao[20]

White solid; mp 111.2–112.6 °C; 80% yield, 63% ee, HPLC (Chiralpak AD, *n*-hexane/*i*-PrOH, 90:10, 0.5 mL/min, 254 nm): t_R(minor) = 33.960 min, t_R(major) = 32.051 min; $[\alpha]_D^{22} = -78.2$ (*c* 1.5, $CHCl_3$) {lit.[20] $[\alpha]_D^{20} = -100.5$ (*c* 0.6, $CHCl_3$)}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.12–8.10 (m, 1H), 7.92–7.83 (m, 3H), 7.56–7.48 (m, 3H), 5.90–5.86 (m, 1H), 4.11–3.95 (m, 4H), 1.25–1.05 (m, 6H).

4.2.17. Diethyl 1-hydroxy-3-phenylpropylphosphonate 3ap[20]

Colorless oil; 73% yield, 41% ee, HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH, 95:5, 0.5 mL/min, 254 nm): t_R(minor) = 17.488 min,

t_R(major) = 19.743 min; $[\alpha]_D^{22}$ = +10.7 (*c* 1.0, $CHCl_3$) {lit.[20] $[\alpha]_D^{20}$ = +14.5 (*c* 0.3, $CHCl_3$)}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–7.19 (m, 5H), 4.22–4.12 (m, 4H), 3.86 (s, 1H), 3.01–2.94 (m, 1H), 2.79–2.71 (m, 1H), 2.09–1.99 (m, 3H), 1.40–1.30 (m, 6H).

4.2.18. (*S*)-Dimethyl hydroxy(phenyl)methylphosphonate 3ba[6c]

White solid; mp 99.3–100.2 °C; 68% yield, 79% ee, HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH, 95:5, 0.5 mL/min, 254 nm): t_R(minor) = 47.617 min, t_R(major) = 50.259 min; $[\alpha]_D^{22}$ = −38.5° (*c* 1.0, $CHCl_3$) [lit.[6c] $[\alpha]_D^{25}$ = −44.3° (*c* 1.0, $CHCl_3$)]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51–7.50 (m, 2H), 7.40–7.31 (m, 3H), 5.07(d, *J* = 11.0 Hz, 1H), 4.33 (s, 1H), 3.73–3.67 (m, 6H).

4.2.19. (*S*)-Dibutyl hydroxy(phenyl)methylphosphonate 3ba[14c]

Colorless oil; 73% yield, 75% ee, HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH, 97:3, 0.5 mL/min, 254 nm): t_R(minor) = 23.434 min, t_R(major) = 26.176 min; $[\alpha]_D^{22}$ = −19.5 (*c* 1.0, $CHCl_3$) {lit.[14c] $[\alpha]_D^{21}$ = +25.8 (*c* 1.08, $CHCl_3$) for the (*R*)-enantiomer}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.48 (m, 2H), 7.38–7.29 (m, 3H), 5.04 (d, *J* = 10.9 Hz, 1H), 4.03–3.93 (m, 4H), 1.97 (s, 1H), 1.64–1.51 (m, 4H), 1.40–1.25 (m, 4H), 0.93–0.86 (m, 6H).

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