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Asymmetric induction in the addition of enantiomerically pure *H*-phosphinate to chiral aldimines: diastereoselective generation of α-amino phosphinates with *P*,*C*-stereogenic centers

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ABSTRACT

α-Amino phosphinates with *P*,*C*-stereogenic centers were prepared from a *P*-retained addition of (R_P)-(−)-menthyl *H*-phenylphosphinate to (*R*)-aldimines with up to 86:14 dr under catalyst and solvent free condition at ambient temperature; the single (S_P,$S_{\alpha\text{-}C}$)-stereoisomers were isolated in moderate yields. Chirality on the nitrogen of chiral aldimine was proposed to control the stereoselectivity, and the (−)-menthoxyl showed mismatched asymmetric induction with (*S*)-aldimines.

1. Introduction

α-Amino phosphoric acid derivatives, especially stereogenic ones, have attracted much attention due to their widely pharmacological applications such as antibacterial action, enzyme inhibitors, HIV protease, herbicides, fungicides, plant growth regulators, antithrombotic agents, peptidases, and peptidase and protease inhibitors.[1–8] These compounds also have potential as auxiliaries and ligands,[9] or as precursors, in asymmetric catalysis.[10] Many research groups are committed to acquiring stereogenic α-amino phosphoric derivatives.[11] The developed approaches include Mannich type reactions of aldehydes/ketones, amines, and *H*-phosphites,[12] and nucleophilic additions of *H*-phosphites to imines[13] catalyzed by aluminum salalen complexes, chiral thioureas, binol-derived phosphoric acids and others.[14] Although several reviews have documented the preparation of α-amino phosphoric derivatives,[15] the synthesis of those that have *P*-stereogenic, especially *P*,*C*-stereogenic centers, has scarcely been involved.[16]

As reported, the chiral imines which were derived from (*S*)- or (*R*)-1-phenylethylamine reacted with P-H species to effectively induce the formation of new *C*-stereogenic centers in α-amino phosphoric derivatives.[17] However, when *P*-stereogenic P-H species are used in the reaction, to the best of our knowledge, their inducting behavior has scarcely been studied.[18,19] Herein the reaction of (R_P)-(−)-menthyl *H*-phenylphosphinate **1a**[18d] with chiral or non-chiral aldimines was examined. α-Amino phosphinates with *P*,*C*-stereogenic centers were obtained under catalyst and solvents-free conditions at ambient temperature. Although the chirality of the title compounds was controlled by stereogenic amine, rather than by (R_P)-**1a**, the latter exhibited matched or mismatched induction effects with (*R*)- or (*S*)-chiral amine, respectively.

2. Results and discussion

2.1. Addition of (R_P)-1a to (*R*)-1-phenylethanimines 2

When a mixture of (R_P/S_P)-**1a**/**1a**′ (50:50) was used to react with (*R*)-**2a**, which was generated from benzaldehyde and (*R*)-1-phenylthanamine, four stereoisomers were formed (Scheme 1). On ^{31}P NMR spectra, the corresponding peaks were observed at 38.18, 37.88, 37.47 and 36.22 ppm, in the ratio of 10:39:11:40. However, (R_P)-**1a** only afforded S_P,$S_{\alpha\text{-}C}$-**3a$_A$** (36.22 ppm) and S_P,$R_{\alpha\text{-}C}$-**3a$_B$** (38.18 ppm) in a ratio of 80:20 via a *P*-retention reaction (vide infra). Thus, the two other peaks at 37.88 and 37.47 ppm were assigned as **3a$_C$** and **3a$_D$** which was generated from (S_P)-**1a**′.

In a separate experiment, **1a**/**1a**′ (90:10) reacted with (*R*)-**2a** and gave four peaks in a ratio of 16:6:6:72 (Fig. 1). Among those, the 72:16 ratio of **3a$_A$**/**3a$_B$** was near to the above 40:10. The 88:12 ratio of **3a$_A$** + **3a$_B$**/**3a$_C$** + **3a$_D$** was near to the original ratio of **1a**/**1a**′. From the ^{1}H NMR spectra, the corresponding ratio of the four stereoisomers could also be distinguished.[20]

The reaction of (*R*)-**2a** with **1a** under various conditions was investigated (Table 1). Under neat conditions at 80 °C, **3a$_A$** and

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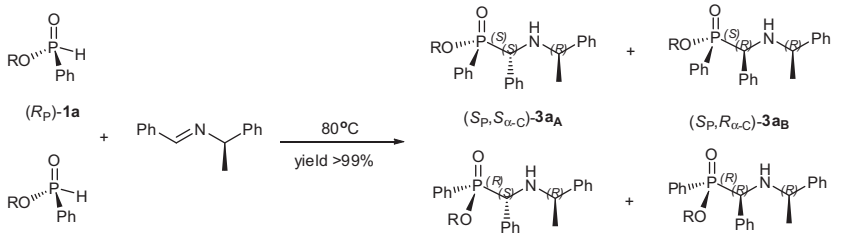


Scheme 1. The reaction of **1a** or **1a**/**1a**′ with (*R*)-**2a**.

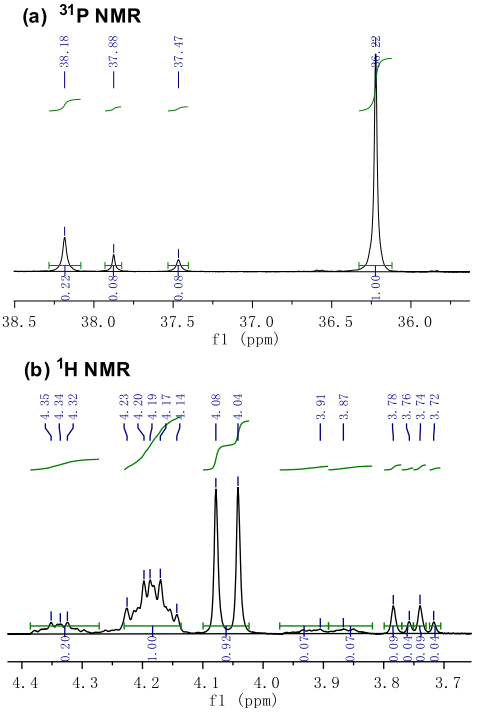


Figure 1. Selected peaks of $\mathbf{3a_A}$, $\mathbf{3a_B}$, $\mathbf{3a_C}$ and $\mathbf{3a_D}$ on ^{31}P NMR (a) and ^{1}H NMR (b) spectra for the reaction of (R_P/S_P)-**1a**/**1a**′ (90:10) with (*R*)-**2a**.

$\mathbf{3a_B}$ were formed in an 80:20 ratio and >99% yield (dr_C: the diastereomeric ratio on phosphorus and on α-carbon, respectively, entry 3). The formation of $\mathbf{3a_C}$ and $\mathbf{3a_D}$ was not detected. Thus, the dr_P was assigned as >99:1. Reducing the temperature led to the incomplete conversion of **1a**. For example, at 60 °C, **1a** was consumed in 67% after 12 h (entry 2). At room temperature, only trace amounts of **3a** were detected (entry 1). However, a higher temperature, such as 90 °C, resulted in a loss of chirality on phosphorus, as observed (97:3 dr_P) for the formation of $\mathbf{3a_A}$-$\mathbf{3a_D}$ (entry 4). Running the reaction in a solution or using an alkali catalyst did not afford **3a** (entries 5–13). Acidic catalysts, such as TsOH, showed weak activity, and **3a** was formed in poor yields (entries 14–15). By comparing entries 16 and 17, the presence of a radical initiator obviously accelerated the reaction, which indicated that the free radical seemed to be involved in the reaction.[21]

The reactions of various aldimines (*R*)-**2** were examined under neat conditions at 80 °C (Table 2). In most entries, compounds **3** were obtained in near complete yields. Compound (*R*)-**2** containing methoxyl, hydroxyl and halides reacted smoothly with **1a** (entries 4, 5–9). It seemed that electron donating groups on (*R*)-**2** could give better selectivity, as seen when **3b** to **3d** were formed in obviously higher dr_C than others (entry 2–4). Aliphatic aldimines such as (*R*)-**2j** also reacted with **1a** to afford **3j** in 83% yield and 83:17 dr_C (entry 10). The dr_C were significantly improved after recrystallization, and in most cases the single stereoisomers were isolated in moderate yields.

The crystallography of $\mathbf{3a_A}$, $\mathbf{3b_A}$, $\mathbf{3d_A}$ and $\mathbf{3i_A}$ unambiguously showed the (*S*)-configurations on both phosphorus and α-carbon (Fig. 2).[22] The retained configuration on the phosphorus was thus confirmed. Since both $\mathbf{3a_A}$ and $\mathbf{3a_B}$ were generated from **1a**, the (S_P,$R_{α-C}$)-structure was confirmed for $\mathbf{3a_B}$. When a mixture of **1a**/**1a**′ (50:50) was used to react with (*R*)-**2a**, $\mathbf{3a_D}$/$\mathbf{3a_C}$ were formed from (S_P)-**1a**′ in 78:22 dr_C, and the dominant $\mathbf{3a_D}$ was similarly supposed to have an (*S*)-configuration on the α-carbon. Thus, the peaks at 37.88 and 37.47 ppm on ^{31}P NMR spectra, among the four ones in Figure 1 and Scheme 1 (also seen in entry 1 of Table 4), were assigned as (R_P,$S_{α-C}$)-$\mathbf{3a_D}$ (major) and (R_P,$R_{α-C}$)-$\mathbf{3a_C}$ (minor), respectively.

In most cases, the peaks of $\mathbf{3_A}$ were located at the upper field compared with $\mathbf{3_B}$ on the ^{31}P NMR spectra. However, the peak of S_P,$S_{α-C}$-$\mathbf{3i_A}$, whose structure was confirmed by X-ray diffraction, was located at downfield than $\mathbf{3i_B}$ (entry 9 of Table 2). The reversed peaks location might be due to the *ortho*-hydroxyl of salicylaldimine that took part in the formation of the chain structure. As shown in Part C and D of Figure 2, the nitrogen located near to P═O in $\mathbf{3_A}$, perhaps formed an intramolecular hydrogen bond. The presence of an *ortho*-hydroxyl in $\mathbf{3i_A}$/$\mathbf{3i_B}$ resulted in the variation of magnetic environment around the phosphorus.

Table 1
Hydrophosphorylation of **2a** with **1a** or **1a**/**1a**′

Entry	Catalyst (mol %)	Temp/time (°C/hr)	Solvent	Yield (%)[a,b]	dr_C (dr_P)[a,b]
1	No	rt/12	No	Trace	/
2	No	60/12	No	67	78:22
3	No	80/3	No	>99	80:20 (>99:1)
4	No	90/3	No	>99	80:20 (97:3)
5	No	80/5	EtOH	NA	/
6	No	45/12	THF	NA	/
7	No	45/12	DMSO	NA	/
8	Na_2CO_3 (20)	rt/12	No	NA	/
9	K_2CO_3 (20)	60/12	THF	NA	/
10	K_2CO_3 (20)	60/12	DMSO	NA	/
11	K_2CO_3 (100)	45/12	THF	NA	/
12	K_2CO_3 (100)	45/12	DMSO	NA[c]	/
13	KOH (20)	rt/12	DMSO	NA[c]	/
14	TsOH (50)	rt/12	No	21	77:23
15	TsOH (100)	rt/12	No	31	76:24
16	AIBN	80/0.5	No	62	79:21[d]
17	No	80/0.5	No	37	78:22[d]

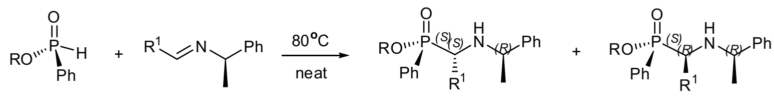
[a] The reactions were carried out with **1a** (dr >99:1) (1 mmol) and (*R*)-**2a** (1 mmol) in the presence of catalyst (if applicable) in some solvents (2 ml, if applicable).

[b] The yield and dr were estimated by ^{31}P NMR spectra based on **1a**. The dr_C were assigned as $\mathbf{3a_A}$/$\mathbf{3a_B}$ and dr_P (in parenthesis) as $\mathbf{3a_A}$ + $\mathbf{3a_B}$:$\mathbf{3a_C}$ + $\mathbf{3a_D}$.

[c] Phenylphosphinic acid was detected.

[d] A mixture of **1a**/**1a**′ was used, and the two stereoisomers $\mathbf{3a_A}$ and $\mathbf{3a_B}$ were confirmed based on Figure 1.

Table 2
Preparation of (S_P,$S_{\alpha\text{-}C}$)-$\mathbf{3_A}$ and (S_P,$R_{\alpha\text{-}C}$)-$\mathbf{3_B}$



Entry	R[1] of (*R*)-**2**	Yield % (dr)[a]	Isolated yield % (dr)[b]
1	Ph, **2a**	>99 (80:20)	$\mathbf{3a_A}$, 56 (>99:1)
2	*p*-MeC$_6$H$_4$, **2b**	>99 (83:17)	$\mathbf{3b_A}$, 60 (>99:1)
3	*p*-*i*PrC$_6$H$_4$, **2c**	>99 (86:14)	$\mathbf{3c_A}$, 63 (>99:1)
4	*p*-MeOC$_6$H$_4$, **2d**	>99 (85:15)	$\mathbf{3d_A}$, 65 (>99:1)
5	*p*-ClC$_6$H$_4$, **2e**	>99 (80:20)	$\mathbf{3e_A}$/$\mathbf{3e_B}$, 55 (84:16)
6	*m*-BrC$_6$H$_4$, **2f**	97 (80:20)	$\mathbf{3f_A}$/$\mathbf{3f_B}$, 54 (81:19)
7	*o*-FC$_6$H$_4$, **2g**	97 (75:15)	$\mathbf{3g_A}$, 56 (>99:1)
8	*o*-BrC$_6$H$_4$, **2h**	98 (80:20)	$\mathbf{3h_A}$, 52 (>99:1)
9	*o*–HOC$_6$H$_4$, **2i**	>99 (77:23)	$\mathbf{3i_A}$, 48 (>99:1)
10	*i*Pr, **2j**	83 (83:17)	$\mathbf{3j_A}$/$\mathbf{3j_B}$, 57 (85:15)

[a] **1a** and (*R*)-**2** were heated 80 °C for 8 h. The crude products were directly analyzed with ^{31}P NMR spectra, and the yield and dr were estimated. The dr$_P$ values obtained were >99:1 because of the *P*-stereospecific addition (vide infra). The dr$_C$ in the table were assigned as $\mathbf{3_A}$/$\mathbf{3_B}$.
[b] The products were isolated by recrystallization with dichloromethane/hexane.

2.2. Proposed stereochemistry for the addition of H-P species to aldimines

When aldimines **4**, which were derived from non-chiral amines were used to the addition, **1a** was also entirely consumed. However, two stereoisomers of adduct **5** were formed in a ratio of approximately 50:50 (Table 3). On the basis of the similarly retained configuration on phosphorus, $\mathbf{5_A}$ and $\mathbf{5_B}$ were supposed to have an (*S*)-configuration on the α-carbon, and an (*S*)- or (*R*)-configuration on phosphorus, respectively.

Relatively poor dr$_C$ values of $\mathbf{3_A}'$/$\mathbf{3_B}'$ were also observed for the reaction of **1a** with (*S*)-**2**′ that was derived from (*S*)-1-phenylethylamine (Scheme 2). When **1a**/**1a**′ (ca 69:31) was used to react with (*S*)-**2d**′, the two peaks originated from (S_P)-**1a**′ were also observed in the ratio near 1:1 on ^{31}P NMR spectra, which indicated (S_P)-**1a**′ also afforded the two stereoisomers $\mathbf{3_C}'$/$\mathbf{3_D}'$ in poor selectivity.

From the results of Tables 2 and 3, and Scheme 2, it was inferred that the ratio of $\mathbf{3_A}$/$\mathbf{3_B}$ (as well as aforementioned $\mathbf{3_D}$/$\mathbf{3_C}$) was controlled by chiral aldimine, rather by stereogenic phosphorus. Although the stereogenic phosphorus of **1a** did not contribute to the selectively of the formations of the two stereoisomers, it was noteworthy that the L-menthoxyl showed mismatched asymmetric induction to (*S*)-aldimine.

The stereochemistry of the addition is proposed in Figure 3, in which the conformation of $\mathbf{3_A}$ and $\mathbf{3_B}$ were referred to X-ray diffraction structures (Fig. 2). The strong repulsion (*a*) between the lone pair of electrons of the nitrogen to α-aryl in $\mathbf{3_B}$ (or $\mathbf{3_C}$, the minor stereoisomer) was supposed to result in its lower stability, and therefore, less formation. Thus, the ratio of $\mathbf{3_A}$/$\mathbf{3_B}$ (or $\mathbf{3_D}$/$\mathbf{3_C}$) depended on the possible ratio of (R_N)/(S_N) which was controlled by chiral carbon skeleton of (*R*)-**2**. When (R_P)-**1a** was reacted with (*S*)-**2**′, the interaction (*b*) between α-aryl to *o*-isopropyl of $\mathbf{3_B}'$ became significant. Thus, $\mathbf{3_A}'$ and $\mathbf{3_B}'$ showed the similarly stabilities, and the selectivity for the formation of them was quite poor.[23]

Petnehazya et al. reported the dominant formation of two stereoisomers during the addition of ethyl phenylphosphinate **1c** to chiral imines.[17a] In order to further investigate the induction behaviors, the reaction of *H*-phosphinates having various alkoxyl groups with (*R*)-**2a** was examined (Table 4). The four stereoisomers were similarly formed, in a ratio of (S_C)-**3**:(R_C)-**3** of 72:28 to 78:22 [the two dominant ones were assigned as (S_C)-stereoisomers]. The alkoxyl groups of **1** slightly influenced the selectivity. For example, the methoxyl and ethoxyl of **1b** and **1c** seemed to give worse dr than others (entries 2 and 3). The menthoxyl of (S_P)-**1a**′ gave similar dr to *t*-butoxyl of **1d** (in 39:11 or 78:22 dr). We supposed that the bigger alkoxyl groups tended to enhance the interaction (*a*) of Figure 3 and the asymmetric induction of chiral imine. L-Menthoxyl of (R_P)-**1a** showed the stronger enhancement than other alkoxyl groups. A discussion about the volume of menthoxyl or alkoxyl in phenylphosphinates could also be found in our previous publication.[24]

The induction of L-menthoxyl to the selective formation of α-amino phosphoric derivatives was also found in the reported reactions of (*R*)-**2** or (*S*)-**2**′ with *P*-symmetric di- or trimenthoxyl phosphites.[17b–d] Recently, Ordoñez et al. reported an improved selectivity, up to 93:7 dr, by employing the more bulky (*S*)-3,3-dimethyl-2-butylamine as chiral source, in a one-pot process utilizing non-chiral dimethyl phosphites, chiral amines and aldehydes.[17e] They studied the conformation of imines and proposed the major diastereomers were afforded from the *re* face attacking from the less hindered side to the imines by phosphite.

In addition to Ordoñez's proposal, as we supposed, the flexible configuration of the nitrogen should be alternatively considered for the selective formation of α-amino phosphoric derivatives. As can be seen in entries 1–5 in Table 2, (*R*)-**2** containing electron donating groups gave better dr$_C$ than those containing electron withdrawing groups. The spatial interaction between aryl and chiral amine moiety should be similar in the two types of (*R*)-**2**. The electron donating group-substituted α-aryl possessing increased electron cloud density, might enhance the repulsion with the lone pair of electrons of the nitrogen, and result in a bigger stability-difference between $\mathbf{3_A}$ and $\mathbf{3_B}$. Conversely, the long distance but matched or mismatched asymmetric induction between menthoxyl to chiral aldimine indicated that the configuration of nitrogen controlled the stabilities of $\mathbf{3_A}$ and $\mathbf{3_B}$. The DFT calculation also indicated $\mathbf{3a_A}$ was more stable than $\mathbf{3a_B}$ by 1.339 Kcal/mol (for details, please see SI).

Compared to the catalytic reactions for the preparation of α-amino phosphorus derivatives, our procedure employed two types of auxiliaries that were inexpensive and can be conveniently removed by means of the well-established procedure, avoiding the usage of expensive metallic catalyst or chiral ligands. Petnehazya et al. reported the stereoselective preparation of α-amino phosphinic acids from the hydrolysis of *N*-1-phenylethyl ethyl α-amino phosphinate (the compound same to our entry 3 of Table 4) with concentrated HCl in glacial acetic acid. The following *N*-deprotection was realized via Pd/C catalyzed hydrogenolysis, in 20–60% yield and with good to excellent er.[17a,25] On the basis of

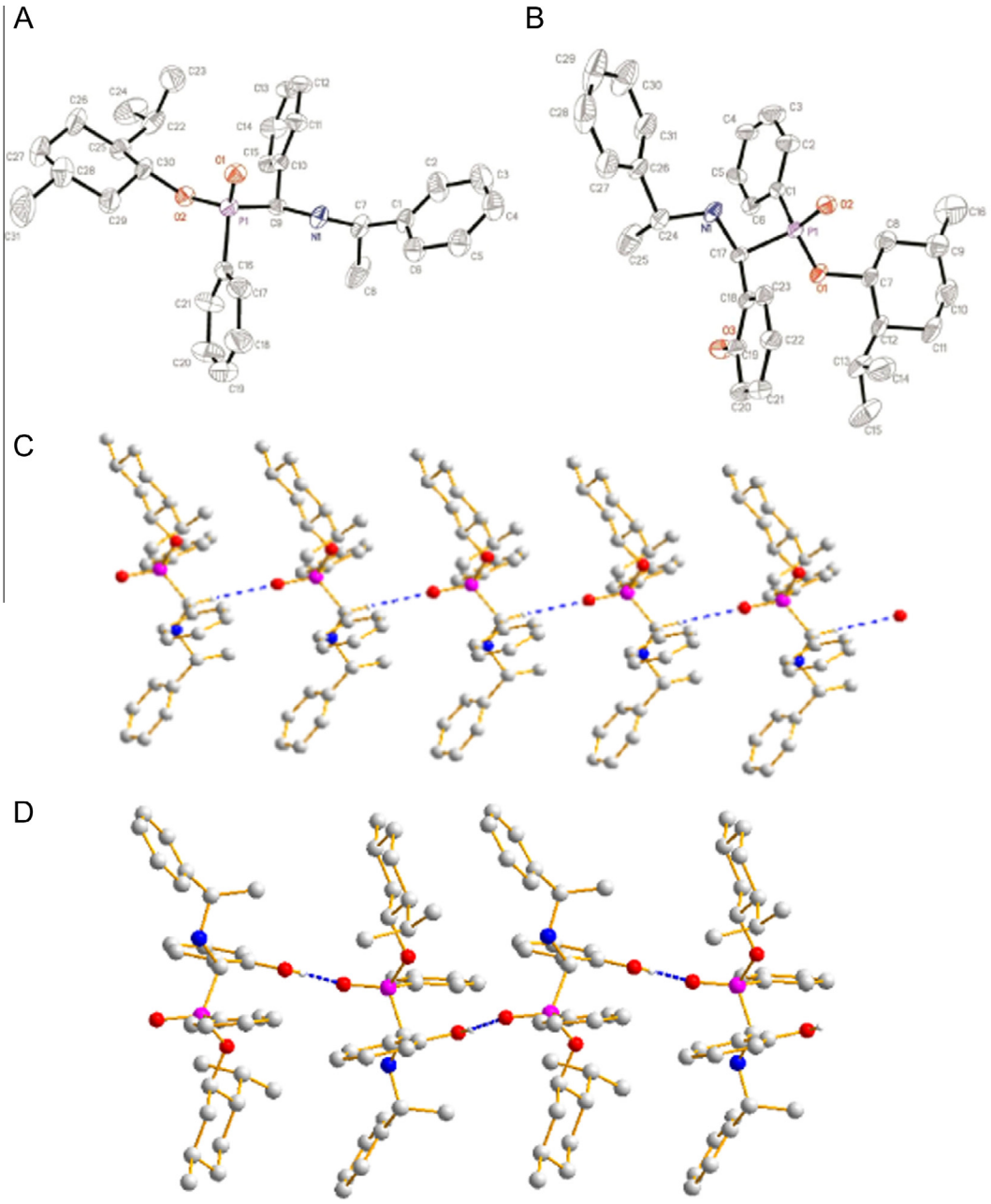


Figure 2. ORTEP drawing for $\mathbf{3a_A}$ (A) and $\mathbf{3i_A}$ (B), one-dimensional chain structures for $\mathbf{3a_A}$ (C) and $\mathbf{3i_A}$ (D).

their procedure, our products **3** would be similarly converted into α-amino phosphinic acids. Due to the hydrolysis, the reported *P*-inversed substitution of another auxiliary (−)-menthoxyl with nucleophilic reagents, such as alkyl,[26] amino,[27] and alkoxyl,[28] accomplished the *P*-deprotection and stereoselective conversion of the products to various *P*,*C*-stereogenic compounds.

3. Conclusion

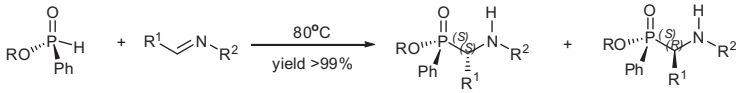
In conclusion, *P*,*C*-stereogenic α-amino phosphinates were prepared from stereogenic aldimines and *H*-phosphinate (R_P)-**1a** in high 86:14 dr_C. In most cases, the single (S_P,$S_{α\text{-}C}$)-stereoisomers were isolated in moderate yields. The reactions were carried out under neat conditions, which were simple, convenient, environmentally friendly, and therefore practical. The *P*-retention mechanism was confirmed. During the reaction of (R_P)-**1a** with (*R*)-aldimine, the chirality on the α-carbon was induced by (*R*)-aldimine. Non-chiral aldimine, as well as the reaction of (R_P)-**1a** with (*S*)-aldimine, did not show selectivity. On the basis of these results, the configuration of the α-carbon atom was supposed to be controlled by chiral aldimines via strong repulsion between the lone electron pair of nitrogen to α-aryl groups. The menthoxyl in (R_P)-**1a** enhanced the asymmetric induction of chiral aldimines. In the reaction of (R_P)-**1a** with (*S*)-aldimines, the mismatched induction was caused by the interaction between ortho-isopropyl of menthyl to α-aryl.

4. Experimental

4.1. General procedure for synthesis of α-aminophosphinates

Under nitrogen, (R_P)-**1a** (280 mg, 1 mmol)[18d] and aldimine (1 mmol) were added in a flask, the mixture was stirred for 8 h at 80 °C. The crude product was obtained as a pale yellow solid.

Table 3
The addition of **1a** to **4**



R = L-menthyl;
R^1 = Ph, *p*-MeC_6H_4, *p*-$iPrC_6H_4$, *p*-$MeOC_6H_4$;
R^2 = *n*Bu, *t*Bu

Entry	R^1	R^2	(dr)[a]	Isolated yield % (dr)[b]
1	Ph	*t*Bu	**5a$_A$/5a$_B$**, 45:55	89 (44:56)
2	*p*-MeC_6H_4	*t*Bu	**5b$_A$/5b$_B$**, 53:47	85 (54:46)
3	*p*-$iPrC_6H_4$	*t*Bu	**5c$_A$/5c$_B$**, 50:50	85 (47:53)
4	*p*-$MeOC_6H_4$	*t*Bu	**5d$_A$/5d$_B$**, 49:51	81 (47:53)
5	Ph	*n*Bu	**5e$_A$/5e$_B$**, 37:63	80 (40:60)
6	*p*-MeC_6H_4	*n*Bu	**5f$_A$/5f$_B$**, 53:47	87 (52:48)
7	*p*-$iPrC_6H_4$	*n*Bu	**5g$_A$/5g$_B$**, 40:60	82 (43:57)
8	*p*-$MeOC_6H_4$	*n*Bu	**5h$_A$/5h$_B$**, 57:43	86 (57:43)

[a] Yield and dr were estimated by ^{31}P NMR spectra, dr were assigned as **5$_A$/5$_B$**. The structures of **5$_A$** and **5$_B$** were determined based on peaks in the upfield and downfield regions of the ^{31}P NMR spectra, respectively.
[b] The products were isolated by recrystallization with dichloromethane/hexane.

After recrystallization with petroleum ether and dichloromethane, the resulting solid was filtered and dried in vacuo.

4.2. (S_P,$S_{\alpha\text{-}C}$)-L-Menthyl [(*R*)-1-phenylethylaminophenyl methyl] phenylphosphinate 3a$_A$

White solid (274 mg, 56%, >99:1 dr$_C$), mp 176–179 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.88–7.74 (m, 2H), 7.56 (t, *J* = 6.9 Hz, 1H), 7.46 (dt, *J* = 7.4, 3.4 Hz, 2H), 7.34–7.12 (m, 8H), 7.12–7.02 (m, 2H), 4.19 (qd, *J* = 11.1, 4.6 Hz, 1H), 4.07 (d, *J* = 14.7 Hz, 1H), 3.52 (q, *J* = 6.4 Hz, 1H), 2.17–2.12 (m, 1H), 1.65 (s, 1H), 1.62 (s, 1H), 1.60–1.09 (m, 6H), 1.05 (d, *J* = 6.5 Hz, 3H), 1.01–0.60 (m, 7H), 0.49 (d, *J* = 6.9 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.22 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6 (s), 137.0 (d, *J* = 3.0 Hz), 133.5 (s), 132.6 (d, *J* = 9.3 Hz), 132.1 (t, *J* = 15.2 Hz), 129.2 (d, *J* = 5.7 Hz), 128.6–128.0 (m), 127.7 (d, *J* = 2.5 Hz), 127.0 (d, *J* = 19.0 Hz), 61.3 (s), 60.2 (s), 55.3 (d, *J* = 12.3 Hz), 49.0 (d, *J* = 5.6 Hz), 43.3 (s), 34.2 (s), 31.6 (s), 24.9 (s), 22.7 (s), 22.1 (d, *J* = 2.7 Hz), 21.4 (s), 15.4 (s). Calcd for $C_{31}H_{40}NO_2P$: C, 76.04; H, 8.23. Found: C, 75.79; H, 8.18.

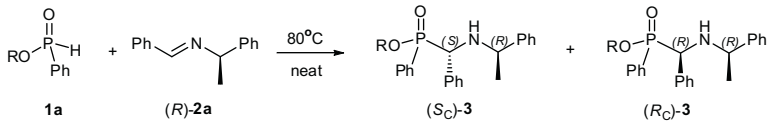
4.3. (S_P,$S_{\alpha\text{-}C}$)-L-Menthyl [(*R*)-1-phenylethylamino-*p*-tolylmethyl] phenylphosphinate 3b$_A$

White solid (302 mg, 60%, >99:1 dr$_C$), mp 170–174 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84–7.75 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.46 (dd, *J* = 7.5, 3.1 Hz, 2H), 7.29 (s, 1H), 7.26 (s, 1H), 7.19 (dd, *J* = 15.3, 7.6 Hz, 5H), 7.12–7.02 (m, 2H), 4.18 (dd, *J* = 13.1, 8.8 Hz, 1H), 4.03 (d, *J* = 14.5 Hz, 1H), 3.51 (q, *J* = 6.4 Hz, 1H), 2.34 (s, 3H), 1.94 (br, 1H), 1.61 (d, *J* = 12.0 Hz, 1H), 1.52 (d, *J* = 10.7 Hz, 1H), 1.42–1.28 (m, 2H), 1.27–1.11 (m, 2H), 1.02 (d, *J* = 6.4 Hz, 3H), 0.94–0.78 (m, 2H), 0.71 (dd, *J* = 22.4, 9.5 Hz, 4H), 0.63 (d, *J* = 7.0 Hz, 3H), 0.48 (d, *J* = 6.9 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.01 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8 (s), 137.3 (s), 133.8 (d, *J* = 5.3 Hz), 132.6 (d, *J* = 9.2 Hz), 131.9 (d, *J* = 2.7 Hz), 128.9 (s), 129.0 (s), 129.1 (s), 128.5–127.9 (m), 126.9 (d, *J* = 13.6 Hz), 61.0 (s), 59.8 (s), 55.1 (d, *J* = 12.4 Hz), 49.1 (d, *J* = 5.5 Hz), 43.3 (s), 34.3 (s), 31.6 (s), 24.8 (s), 22.7 (s), 22.0 (d, *J* = 7.7 Hz), 21.3 (d, *J* = 4.7 Hz), 15.4 (s). Calcd for $C_{32}H_{42}NO_2P$: C, 76.31; H, 8.41. Found: C, 75.86; H, 8.33.

4.4. (S_P,$S_{\alpha\text{-}C}$)-L-Menthyl [(*R*)-1-phenylethylamino-*p*-isopropyl phenylmethyl]phenylphosphinate 3c$_A$

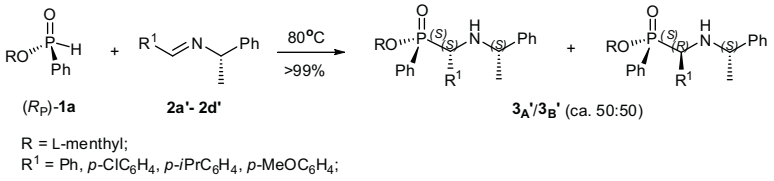
White solid (335 mg, 63%, >99:1 dr$_C$), mp 160–164 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 10.5, 7.6 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.44 (td, *J* = 7.4, 3.3 Hz, 2H), 7.16 (dt, *J* = 14.4, 7.6 Hz, 7H), 7.04 (d, *J* = 6.3 Hz, 2H), 4.16 (dt, *J* = 15.0, 11.0 Hz, 1H), 4.02 (d, *J* = 14.3 Hz, 1H), 3.49 (q, *J* = 6.4 Hz, 1H), 2.89 (dt, *J* = 13.7, 6.9 Hz, 1H), 2.00 (br, 1H), 1.62 (d, *J* = 11.4 Hz, 1H), 1.61–1.21 (m, 10H), 1.21–1.04 (m, 2H), 1.01 (d, *J* = 6.5 Hz, 3H), 0.82 (ddd, *J* = 35.0, 26.4, 10.0 Hz, 2H), 0.73–0.60 (m, 6H), 0.45 (d, *J* = 6.9 Hz, 3H). ^{31}P

Table 4
The diastereomeric ratio for the reaction of (*R*)-**2a** with **1**



Entry	R	S_C-**3**:R_C-**3**[a]
1	Men, **1a**/**1a**′	(40 + 39):(10 + 11)[b]
2	Me, **1b**	73:27
3	Et, **1c**	72:28
4	*i*Pr, **1d**	78:22
5	*t*Bu, **1e**	76:24
6	*c*Hex, **1f**	75:25

[a] The ratio were estimated by ^{31}P NMR spectra. For **1b** to **1f**, the two higher peaks located at down field were assigned as (S_C)-**3**, and the two lower ones were assigned as (R_C)-**3**.
[b] The ratio of (S_P,S_C)-**3a$_A$** + (R_P,S_C)-**3a$_D$**:(S_P,R_C)-**3a$_B$** + (R_P,R_C)-**3a$_C$**.



Scheme 2. The reaction of **1a** with (*S*)-**2′**.

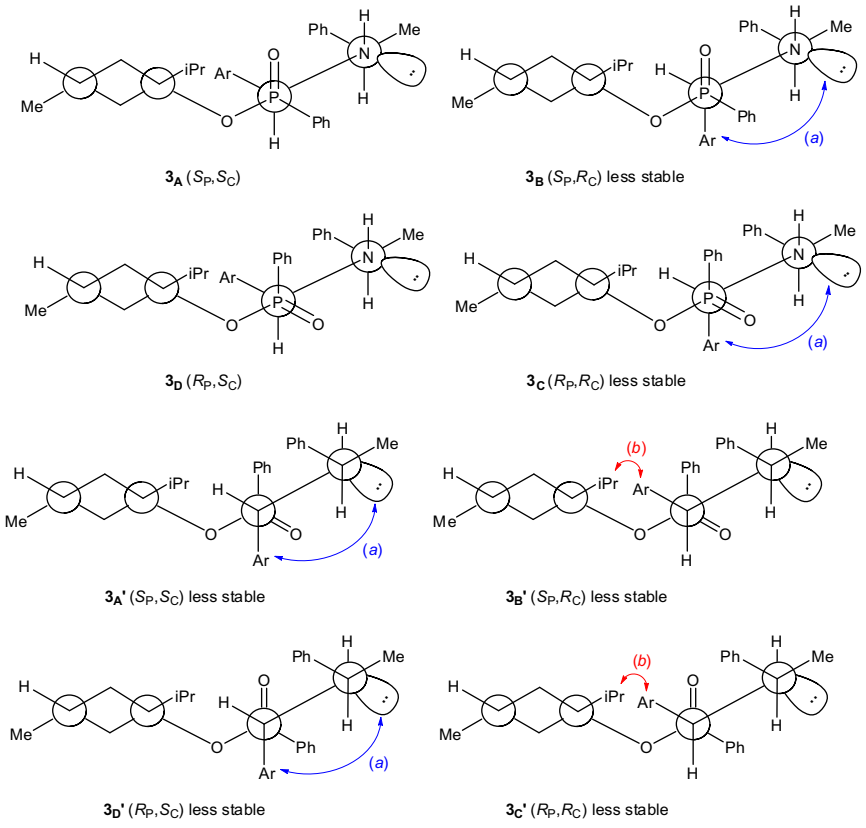


Figure 3. Supposed conformation for $\mathbf{3_A}$–$\mathbf{3_B}$ and $\mathbf{3_A'}$–$\mathbf{3_D'}$.

NMR (162 MHz, $CDCl_3$) δ 36.10 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0 (d, J = 2.6 Hz), 145.6 (s), 134.0 (d, J = 2.9 Hz), 133.7 (s), 132.5 (s), 132.4 (s), 132.3 (s), 131.7 (d, J = 2.7 Hz), 128.9 (d, J = 5.8 Hz), 128.1 (s), 127.8 (d, J = 12.3 Hz), 126.7 (d, J = 11.6 Hz), 126.2 (d, J = 1.6 Hz), 60.6 (s), 59.5 (s), 55.0 (d, J = 12.5 Hz), 48.8 (d, J = 5.7 Hz), 43.1 (s), 34.1 (s), 33.8 (s), 31.4 (s), 24.7 (s), 24.0 (s), 22.5 (s), 21.9 (s), 21.1 (s), 15.2 (s). Calcd for $C_{34}H_{46}NO_2P$: C, 76.80; H, 8.72. Found: C, 76.75; H, 8.60.

4.5. (S_P,$S_{\alpha\text{-}C}$)-L-Menthyl [(*R*)-1-phenylethylamino-*p*-methoxyl phenylmethyl]phenylphosphinate 3d$_A$

White solid (338 mg, 65%, >99:1 dr$_C$), mp 159–162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, J = 11.1, 7.1 Hz, 2H), 7.54 (t, J = 6.9 Hz, 1H), 7.44 (td, J = 7.4, 3.3 Hz, 2H), 7.19 (p, J = 6.5 Hz, 5H), 7.08–7.02 (m, 2H), 6.81 (d, J = 8.6 Hz, 2H), 4.18 (dd, J = 7.0, 4.1 Hz, 1H), 4.01 (d, J = 14.3 Hz, 1H), 3.80 (s, 3H), 3.51 (q, J = 6.3 Hz, 1H), 1.88 (br, 1H), 1.62 (d, J = 12.0 Hz, 1H), 1.53 (d, J = 11.9 Hz, 2H), 1.42 (dd, J = 8.1, 5.7 Hz, 1H), 1.28–1.11 (m, 4H), 1.04 (d, J = 6.5 Hz, 3H), 0.88 (dt, J = 11.8, 9.3 Hz, 2H), 0.68 (t, J = 7.4 Hz, 6H), 0.51 (d, J = 6.9 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.08 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4 (d, J = 2.4 Hz), 145.7 (s), 133.6 (s), 132.6 (s), 132.5 (s), 132.0 (d, J = 2.7 Hz), 130.2 (d, J = 5.8 Hz), 128.9 (d, J = 3.2 Hz), 128.4 (s), 128.–127.9 (m), 126.9 (d, J = 15.7 Hz), 113.8 (d, J = 1.5 Hz), 60.6 (s), 59.5 (s), 55.4 (s), 55.2 (d, J = 12.3 Hz), 49.1 (d, J = 5.5 Hz), 43.3 (s), 34.3 (s), 31.6 (s), 24.9 (s), 22.7 (s), 22.1 (d, J = 5.9 Hz), 21.4 (s), 15.5 (s). Calcd for $C_{32}H_{42}NO_3P$: C, 73.96; H, 8.15. Found: C, 75.79; H, 8.07.

4.6. (S_P)-L-Menthyl [(*R*)-1-phenylethylamino-*p*-chlorophenyl methyl]phenylphosphinate 3e$_A$/3e$_B$

White solid (288 mg, 55%, 84:16 dr$_C$), mp White solid; mp 165–169 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.74 (m, 2H), 7.73–7.62 (m, 1H), 7.57 (t, J = 7.4 Hz, 1H), 7.50–7.39 (m, 3H), 7.28–7.13 (m, 10H), 7.03 (d, J = 5.8 Hz, 2H), 4.34–4.24 (m, 0.16H), 4.18 (d, J = 11.2 Hz, 0.84H), 4.01 (d, J = 14.9 Hz, 1H), 3.45 (q, J = 6.4 Hz, 1H), 2.04 (s, 1H), 1.62 (s, 4H), 1.53 (d, J = 11.1 Hz, 3H), 1.33 (s, 1H), 1.27–1.11 (m, 2H), 1.05 (d, J = 6.5 Hz, 3H), 0.85 (d, J = 6.9 Hz, 2H), 0.77–0.63 (m, 9H), 0.51 (d, J = 6.9 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.57 (s, 16%), 34.38 (s, 84%). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2 (s), 135.6 (s), 133.4 (s), 133.1–132.2

(m), 132.1 (s), 130.3 (d, J = 5.6 Hz), 128.8 (s), 128.6–127.9 (m), 127.0 (s), 126.7 (s), 60.7 (s), 59.6 (s), 55.6 (d, J = 11.7 Hz), 48.9 (d, J = 5.4 Hz), 43.2 (s), 34.0 (s), 31.5 (d, J = 10.1 Hz), 24.8 (s), 22.6 (d, J = 18.3 Hz), 22.1 (s), 21.9 (s), 21.0 (s), 15.2 (s). Calcd for $C_{31}H_{39}ClNO_2P$: C, 71.05; H, 7.50. Found: C, 70.86; H, 7.42.

4.7. (S_P)-L-Menthyl [(*R*)-1-phenylethylamino-*m*-bromophenyl methyl]phenylphosphinate $3f_A/3f_B$

White solid (307 mg, 54%, 81:19 dr_C), mp 166–168 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.75 (m, 2H), 7.56 (t, J = 6.8 Hz, 1H), 7.52–7.43 (m, 3H), 7.39 (dd, J = 13.1, 4.8 Hz, 2H), 7.30 (dd, J = 7.5, 3.7 Hz, 1H), 7.26 (s, 1H), 7.24–7.07 (m, 6H), 7.07–6.95 (m, 3H), 4.32 (dd, J = 6.7, 4.2 Hz, 0.19H), 4.25–4.12 (m, 0.81H), 3.98 (d, J = 14.6 Hz, 0.81H), 3.73 (d, J = 18.1 Hz, 0.19H), 3.56–3.50 (m, 0.19H), 3.46 (q, J = 6.4 Hz, 0.81H), 2.20 (s, 1H), 1.68–1.58 (m, 2H), 1.53 (d, J = 11.6 Hz, 2H), 1.43 (s, 1H), 1.41–1.33 (m, 1H), 1.31 (d, J = 6.6 Hz, 1H), 1.28–1.13 (m, 2H), 1.03 (t, J = 8.5 Hz, 3H), 0.99–0.91 (m, 1H), 0.87 (ddd, J = 18.8, 10.6, 7.5 Hz, 2H), 0.79–0.63 (m, 8H), 0.50 (d, J = 6.9 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 37.32 (s, 19%), 35.41 (s, 81%). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1 (s), 144 (s), 140 (d, J = 2.9 Hz), 138.6 (s), 133.1 (s), 133.0–131.8 (m), 131.5 (d, J = 5.1 Hz), 130.8–129.8 (m), 129.6 (m, J = 9.4, 2.2 Hz), 128.8 (s), 128.5 (s), 128.4–127.9 (m), 127.9–127.3 (m), 127.0 (d, J = 12.4 Hz), 126.7 (s), 122.3 (s), 122.3 (s), 122.3 (s), 61.7 (s), 60.9 (s), 60.7 (s), 59.8 (s), 55.7 (d, J = 11.7 Hz), 55.3 (d, J = 14.5 Hz), 49.0 (dd, J = 17.6, 5.7 Hz), 43.2 (d, J = 10.8 Hz), 34.1 (d, J = 8.5 Hz), 31.5 (d, J = 11.9 Hz), 25.4 (s), 24.9 (d, J = 3.9 Hz), 22.8 (s), 22.5 (s), 22.4–22.3 (m), 22.0 (dd, J = 23.8, 21.3 Hz), 21.3 (s), 15.5 (s), 15.1 (s). Calcd for $C_{31}H_{39}BrNO_2P$: C, 65.49; H, 6.91. Found: C, 65.23; H, 6.81.

4.8. (S_P,$S_{\alpha\text{-}C}$)-L-Menthyl [(*R*)-1-phenylethylamino-*o*-fluro phenylmethyl]phenylphosphinate $3g_A$

White solid (284 mg, 56%, >99:1 dr_C), mp 175–178 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, J = 11.2, 7.5 Hz, 2H), 7.56 (q, J = 6.8 Hz, 2H), 7.48 (td, J = 7.4, 3.3 Hz, 2H), 7.23 (dd, J = 13.0, 6.8 Hz, 1H), 7.19–7.10 (m, 4H), 7.01 (dd, J = 9.1, 3.3 Hz, 2H), 6.95 (d, J = 8.9 Hz, 1H), 4.55 (d, J = 15.4 Hz, 1H), 4.19–4.09 (m, 1H), 3.47 (q, J = 6.6 Hz, 1H), 2.16 (br, 1H), 1.60 (d, J = 12.4 Hz, 1H), 1.50 (dd, J = 10.1, 3.1 Hz, 2H), 1.25 (d, J = 5.5 Hz, 1H), 1.24–1.10 (m, 3H), 1.01 (d, J = 6.4 Hz, 3H), 0.94–0.80 (m, 2H), 0.67 (d, J = 6.5 Hz, 3H), 0.60 (d, J = 7.0 Hz, 3H), 0.42 (d, J = 6.8 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.61 (d, J = 4.9 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5 (d, J = 6.3 Hz), 160.1 (d, J = 6.3 Hz), 145.4 (s), 133.7 (s), 132.4 (d, J = 9.5 Hz), 132.2 (d, J = 2.6 Hz), 130.0 (s), 129.1 (d, J = 6.0 Hz), 128.5–127.7 (m), 127.1 (d, J = 4.5 Hz), 126.8 (s), 124.7 (d, J = 15.1 Hz), 124.4 (s), 115.1 (s), 114.8 (s), 55.8 (d, J = 12.8 Hz), 53.9–52.5 (m), 51.8 (d, J = 114.6 Hz), 48.9 (d, J = 5.6 Hz), 43.2 (s), 34.2 (s), 31.6 (s), 29.9 (s), 24.7 (s), 22.6 (s), 22.4–21.8 (m), 21.3 (d, J = 4.8 Hz), 15.3 (s). Calcd for $C_{31}H_{39}FNO_2P$: C, 73.35; H, 7.74. Found: C, 73.26; H, 7.65.

4.9. (S_P,$S_{\alpha\text{-}C}$)-L-Menthyl [(*R*)-1-phenylethylamino-*o*-bromo phenylmethyl]phenylphosphinate $3h_A$

White solid (296 mg, 52%, >99:1 dr_C), mp 169–173 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, J = 11.2, 7.5 Hz, 2H), 7.56 (q, J = 6.8 Hz, 2H), 7.48 (td, J = 7.4, 3.3 Hz, 2H), 7.23 (dd, J = 13.0, 6.8 Hz, 1H), 7.19–7.10 (m, 4H), 7.01 (dd, J = 9.1, 3.3 Hz, 2H), 6.95 (d, J = 8.9 Hz, 1H), 4.55 (d, J = 15.4 Hz, 1H), 4.19–4.09 (m, 1H), 3.47 (q, J = 6.6 Hz, 1H), 2.16 (s, 1H), 1.60 (d, J = 12.4 Hz, 1H), 1.50 (dd, J = 10.1, 3.1 Hz, 2H), 1.25 (d, J = 5.5 Hz, 1H), 1.24–1.10 (m, 3H), 1.01 (d, J = 6.4 Hz, 3H), 0.94–0.80 (m, 2H), 0.67 (d, J = 6.5 Hz, 3H), 0.60 (d, J = 7.0 Hz, 3H), 0.42 (d, J = 6.8 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.63 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2 (s), 137.0 (s), 132.4 (m, J = 18.8, 9.1 Hz), 130.2 (d, J = 3.8 Hz), 129.0 (s), 128.3 (d, J = 12.6 Hz), 127.8 (d, J = 2.3 Hz), 127.1 (s), 126.8 (s), 126.0 (d, J = 7.6 Hz), 104.4 (s), 103.9 (s), 102.7 (d, J = 7.2 Hz), 77.5 (s), 64.0 (d, J = 1.7 Hz), 59.0 (s), 57.9 (s), 55.9 (d, J = 13.3 Hz), 49.0(d, J = 5.7 Hz), 43.1 (s), 34.1 (s), 31.5 (s), 29.9 (s), 24.6 (s), 22.6 (s), 22.3 (s), 22.0 (s), 21.4 (s), 18.8 (s), 18.2 (d, J = 13.7 Hz), 15.5 (s), 15.2 (s). Calcd for $C_{31}H_{39}BrNO_2P$: C, 65.49; H, 6.91. Found: C, 65.27; H, 6.84.

4.10. (S_P,$S_{\alpha\text{-}C}$)-L-Menthyl [(*R*)-1-phenylethylamino-*o*-hydroxy phenylmethyl]phenylphosphinate $3i_A$

White solid (243 mg, 48%, >99:1 dr_C), mp 194–198 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.05 (s, 1H), 7.69 (dd, J = 11.2, 7.6 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.43 (td, J = 7.5, 3.5 Hz, 2H), 7.26 (s, 1H), 7.24–7.17 (m, 2H), 7.17–7.04 (m, 3H), 6.83 (d, J = 8.1 Hz, 1H), 6.71 (dt, J = 14.5, 7.3 Hz, 2H), 4.31 (dt, J = 15.1, 11.0 Hz, 1H), 4.15 (d, J = 16.1 Hz, 1H), 3.56 (q, J = 6.6 Hz, 1H), 2.44 (s, 1H), 1.70 (dd, J = 17.6, 10.4 Hz, 2H), 1.63–1.52 (m, 2H), 1.36–1.21 (m, 2H), 1.16 (d, J = 6.5 Hz, 3H), 1.05–0.83 (m, 3H), 0.71 (dd, J = 6.7, 2.8 Hz, 6H), 0.59 (d, J = 6.9 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 40.36 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1 (d, J = 4.1 Hz), 144.3 (s), 132.7 (s), 132.6 (s), 132.5 (s), 131.1 (d, J = 7.1 Hz), 129.9 (s), 129.3 (s), 128.4 (s), 128.1 (d, J = 12.7 Hz), 127.2 (s), 126.6 (s), 120.8 (s), 119.5 (s), 118.8 (s), 62.2 (s), 61.1 (s), 55.5 (d, J = 12.8 Hz), 48.8 (d, J = 5.3 Hz), 43.1 (s), 34.0 (s), 31.5 (s), 25.2 (s), 22.6 (s), 21.9 (s), 21.0 (s), 20.6 (s), 15.1 (s). Calcd for $C_{31}H_{40}NO_3P$: C, 73.64; H, 7.97. Found: C, 73.49; H, 7.88.

4.11. (S_P)-L-Menthyl [(*R*)-1-phenylethylamino-2-methylpropyl] phenylphosphinate $3j_A/3j_B$

White solid (260.0 mg, 57%, 85:15 dr_C), mp 194–198 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, J = 23.6, 15.3 Hz, 2H), 7.60–7.51 (m, 1H), 7.47 (dd, J = 13.1, 10.2 Hz, 2H), 7.23–7.11 (m, 3H), 6.98 (d, J = 6.2 Hz, 2H), 4.30–4.16 (m, 0.85H), 4.14 (d, J = 6.4 Hz, 0.15H), 3.52 (d, J = 6.3 Hz, 1H), 2.85 (d, J = 13.9 Hz, 1H), 2.37–2.11 (m, 2H), 1.92 (d, J = 6.5 Hz, 1H), 1.74–1.48 (m, 4H), 1.36 (t, J = 10.0 Hz, 1H), 1.26 (dd, J = 21.4, 12.7 Hz, 2H), 1.10 (d, J = 6.4 Hz, 3H), 1.05–0.62 (m, 21H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.24 (s, 15%), 39.83 (s, 85%). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6 (s), 145.0 (d, J = 7.0 Hz), 135.4 (d, J = 5.6 Hz), 134.3 (d, J = 5.5 Hz), 133.9 (s), 133.1–131.9 (m), 131.9 (s), 128.8–127.9 (m), 127.7 (d, J = 3.5 Hz), 127.1 (s), 127.1 (s), 127.0 (s), 60.3–59.3 (m), 59.3–57.2 (m), 56.8–56.4 (m), 56.4 (s), 49.4 (dd, J = 10.4, 4.8 Hz), 43.5 (s), 34.26 (s), 31.9–31.5 (m), 29.9 (s), 28.6 (t, J = 21.3 Hz), 28.3 (s), 25.7–24.6 (m), 24.6 (s), 24.3 (d, J = 8.8 Hz), 22.8 (t, J = 5.9 Hz), 22.6–21.9 (m), 21.9–21.5 (m), 21.4 (d, J = 3.7 Hz), 17.9–17.3 (m), 16.0–15.20 (m). Calcd for $C_{28}H_{42}NO_2P$: C, 73.81; H, 9.29. Found: C, 73.62; H, 9.20.

Acknowledgments

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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.tetasy.2016.06.022.

References

1. (a) Orsini, F.; Sello, G.; Sisti, M. *Curr. Med. Chem.* **2010**, *17*, 264–289; (b) Lejczak, B.; Kafarski, P. *Top. Heterocycl. Chem.* **2009**, *20*, 31–63; (c) Collinsova, M.; Jiracek, J. *Curr. Med. Chem.* **2000**, *7*, 629–647; (d) Allen, M. C.; Fuhrer, W.; Tuck, B.; Wade, R.; Wood, J. M. *J. Med. Chem.* **1989**, *32*, 1652–1661; (e) Naydenova, E. D.; Todorov, P. T.; Troev, K. D. *Amino Acids* **2010**, *38*, 23–30; (f) Ye, M.-Y.; Yao, G.-Y.; Wei, J.-C.; Pan, Y.-M.; Liao, Z.-X.; Wang, H.-S. *Int. J. Mol. Sci.* **2013**, *14*, 9424–9439; (g) Kukhar', V. P.; Soloshonok, V. A.; Solodenko, V. A. *Phos. Sulf. Sil. Rel. Elem.* **1994**, *92*, 239–264; (h) Turcheniuk, K. V.; Kukhar, V. P.; Röschenthaler, G.-V.; Aceña, J. L.; Soloshonok, V. A.; Sorochinsky, A. E. *RSC Adv.* **2013**, *3*, 6693–6716.
2. Peyman, A.; Stahl, W.; Wagner, K.; Ruppert, D.; Budt, K. H. *Bioorg. Med. Chem. Lett.* **1994**, *4*, 2601–2604.
3. Maier, L.; Spoerri, H. *Phos. Sulf. Sil. Rel. Elem.* **1991**, *61*, 69–75.
4. Emsley, J.; Hall, D. In *The Chemistry of Phosphorous*; Harper & Row: London, 1976; p 494.
5. Meyer, J. H.; Bartlett, P. A. *J. Am. Chem. Soc.* **1998**, *120*, 4600–4609.
6. Miller, D. J.; Hammond, S. M.; Anderluzzi, D.; Bugg, T. D. *J. Chem. Soc., Perkin Trans. 1* **1998**, 131.
7. Bird, J.; Rachel, C. D. M.; Gregory, P. H.; David, J. H.; Eric, H. K.; Roger, E. M.; Anette, J. M.; Rahman, S. S.; Ward, R. W. *J. Med. Chem.* **1994**, *37*, 158–169.
8. Davis, F. A.; Lee, S.; Yan, H.; Titus, D. D. *Org. Lett.* **2001**, *3*, 1757–1760.
9. Zhang, J. F.; Cui, Z. W.; Miao, Z. W.; Chen, R. Y. *Chin. J. Org. Chem.* **2008**, *28*, 946–958; Zhao, G. P.; Wang, Y. Q.; Shen, B. A. *Chin. J. Synth. Chem.* **2008**, *16*, 247–251.
10. (a) Joly, G. D.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2004**, *126*, 4102–4103; (b) Cheng, X.; Goddard, R.; Buth, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 5079–5081.
11. (a) Cristau, H. J.; Pirat, J. L.; Virieux, D.; Onbrun, J.; Ciptadi, C. Y.; Bekro, A. *J. Organomet. Chem.* **2005**, *690*, 2472–2481; (b) Kaboudin, B. *Tetrahedron Lett.* **2003**, *44*, 1051–1054; (c) Ridder, D.; Wunderlich, H.; Braun, M. *Eur. J. Org. Chem.* **1998**, 1071–1076; (d) Ordóñez, M.; Sayago, F. J.; Cativiela, C. *Tetrahedron* **2012**, *68*, 6369–6412; (e) Ordóñez, M.; Viveros-Ceballos, J. L.; Cativiela, C.; Arizpe, A. *Curr. Org. Synth.* **2012**, *9*, 310–341; (f) Kudzin, Z. H.; Kudzin, M. H.; Drabowicz, J.; Stevens, C. V. *Curr. Org. Chem.* **2011**, *15*, 2015–2071; (g) Moonen, K.; Laureyn, I.; Stevens, C. V. *Chem. Rev.* **2004**, *104*, 6177–6215; (h) Röschenthaler, G.-V.; Kukhar, V. P.; Kulik, I. B.; Sorochinsky, A. E.; Soloshonok, V. A. *J. Fluor. Chem.* **2011**, *132*, 834–837; (i) Röschenthaler, G.-V.; Kukhar, V. P.; Kulik, I. B.; Belik, M. Yu.; Sorochinsky, A. E.; Rusanov, E. B.; Soloshonok, V. A. *Tetrahedron Lett.* **2012**, *53*, 539–542.
12. Brunel, J. M. *Chem. Rev.* **2005**, *105*, 857–897.
13. Verkade, J. M. M.; van Hemert, L. J. C.; Quaedflie, P. J. L. M.; Rutjes, F. P. J. T. *Chem. Soc. Rev.* **2008**, *37*, 29–41.
14. (a) Vovk, A. I.; Mischenko, I. M.; Tanchuk, V. Y.; Kachkovskii, G. A.; Sheiko, S. Y.; Kolodyazhnyi, O. I.; Kukhar, V. P. *Bioorg. Med. Chem. Lett.* **2008**, *18*, 4620–4623; (b) Schlemminger, I.; Saida, Y.; Groger, H.; Maison, W.; Durot, N.; Sasai, H.; Shibasaki, M.; Martens, J. *J. Org. Chem.* **2000**, *65*, 4818–4825.
15. (a) Akiyama, T.; Morita, H.; Itoh, J.; Fuchibe, K. *Org. Lett.* **2005**, *7*, 2583–2585; (b) Sawamura, M.; Ito, Y.; Hayashi, T. *Tetrahedron Lett.* **1989**, *30*, 2247–2250.
16. (a) Bhadury, P. S.; Song, B. A.; Yang, S.; Zhang, Y.; Zhang, S. *Curr. Org. Synth.* **2008**, *5*, 134–150; (b) Cherkasov, R. A.; Garifzyanov, A. R.; Koshkin, S. A. *Phos. Sulf. Sil. Rel. Elem.* **2011**, *65*, 782–784.
17. (a) Szabó, A.; Jászay, Z. M.; Hegedűs, L.; Tőke, L.; Petneházy, I. *Tetrahedron Lett.* **2003**, *44*, 4603–4606; (b) Kolodiazhnyi, O. I. *Phos. Sulf. Sil. Rel. Elem.* **2002**, *177*, 2111–2114; (c) Sergei, S.; Irina, G.; Evgeni, G.; Kolodiazhnyi, O. I. *Phos. Sulf. Sil. Rel. Elem.* **2002**, *177*, 2269–2270; (d) Kachkovskii, G. A.; Andrushko, N. V.; Sheiko, S. Yu.; Kolodyazhnyi, O. I. *Russ. J. Gen. Chem.* **2005**, *75*, 1735–1743; (e) Tibhe, G. D.; Lagunas-Rivera, S.; Vargas-Díaz, E.; García-Barradas, O.; Ordoñez, M. *Eur. J. Org. Chem.* **2010**, 6573–6581; (f) Li, S. S.; Wang, G. Q.; Li, Y.; Li, Y.; Yuan, C. Y. *Acta Chim. Sinica* **1993**, *51*, 1195–1202; (g) Tibhe, G. D.; Reyes-González, M. A.; Cativiela, C.; Ordóñez, M. *J. Mex. Chem. Soc.* **2012**, *56*, 183–187.
18. (a) Soloshonok, V. A.; Belokon, Y. N.; Kuzmina, N. A.; Maleev, V. I.; Svistunova, N. Y.; Solodenko, V. A.; Kukhar, V. P. *J. Chem. Soc., Perkin Trans. 1* **1992**, *12*, 1525–1529; (b) Xiao, W. M.; Sha, Z.; Song, Y.; Lin, H. J.; Pinaki, S. B.; De, Y. H.; Zhang, Y. P. *Molecules* **2010**, *15*, 5782–5796; (c) Chen, Q. Y.; Yuan, C. Y. *Synthesis* **2007**, 3779–3786; (d) Wang, W.-M.; Liu, L.-J.; Zhao, C.-Q.; Han, L.-B. *Eur. J. Org. Chem.* **2015**, 2342–2345.
19. Recently, we briefly reported the addition of RP-menthyl phenylphosphine oxide to chiral aldimines. Zhou, Z. Y.; Zhang, H.; Yao, L.; Wen, J. H.; Nie, S. Z.; Zhao, C. Q. *Chirality* **2016**, *28*, 132–135.
20. In the ^{1}H NMR spectra in Figure 1, multi peaks at 4.14 to 4.23 ppm were assigned as the α-proton of menthoxyl in $\mathbf{3a_A}$, and peaks at 4.32 to 4.35 ppm for similar proton in $\mathbf{3a_B}$. The ratio of two groups of peaks was 83:17. For $\mathbf{3a_C}$ and $\mathbf{3a_D}$, the similar protons located at 3.87 and 3.91 ppm, and the ratio of their total integration to $\mathbf{3a_A}$ + $\mathbf{3a_B}$ was 10:90. The doubled peaks of proton linked to α-carbon of $\mathbf{3a_A}$ and $\mathbf{3a_B}$ were observed at 4.06 and 3.76 ppm, respectively, with the coherent ratio of 84:16. For $\mathbf{3a_C}$ and $\mathbf{3a_D}$, the corresponding peaks were observed at 3.74 ppm and might be coincided and indistinguishable.
21. (a) Han, L.-B.; Zhao, C.-Q. *J. Org. Chem.* **2005**, *70*, 10121–10123; (b) Farnham, W. B.; Murray, R. K.; Mislow, K. *J. Am. Chem. Soc.* **1970**, *92*, 5809.
22. Yang, M.; Sun, Y. M.; Hou, Q. G.; Zhao, C.-Q. *Acta Cryst.* **2012**, *E68*, o2328.
23. Soloshonok, V. A.; Ellis, T. K.; Ueki, H.; Ono, T. *J. Am. Chem. Soc.* **2009**, *131*, 7208–7209.
24. Sun, Y.-M.; Xin, N.; Xu, Z.-Y.; Liu, L.-J.; Meng, F.-J.; Zhang, H.; Fu, B.-C.; Liang, Q.-J.; Zheng, H.-X.; Sun, L.-J.; Zhao, C.-Q.; Han, L.-B. *Org. Biomol. Chem.* **2014**, *12*, 9457–9465.
25. Francesco, I. N.; Wagner, A.; Colobert, F. *Chem. Commun.* **2010**, 2139–2141.
26. (a) Koide, Y.; Sakamoto, A.; Imamoto, T. *Tetrahedron Lett.* **1991**, *32*, 3375–3376; (b) Korpiun, O.; Lewis, R. A.; Chickos, J.; Mislow, K. *J. Am. Chem. Soc.* **1968**, *90*, 4842–4846; (c) Oshiki, T.; Imamoto, T. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3719–3721.
27. (a) Harger, M. J. P. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1882–1887; (b) Nudelman, A.; Cram, D. J. *J. Org. Chem.* **1971**, *36*, 335–337.
28. Kers, A.; Kers, I.; Stawinski, J.; Sobkowski, M.; Kraszewski, A. *Synthesis* **1995**, 427–430.