Nonenzymatic kinetic resolution of racemic β-hydroxyalkane phosphonates with chiral copper catalyst

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Abstract: Kinetic resolution of β-hydroxyalkane phosphonates was efficiently performed by 2-fluorobenzoylation in the presence of copper(II) triflate and (R,R)-Ph-BOX as a catalyst with good $s$ value of up to 21.

Keywords: Kinetic resolution; Asymmetric acylation; β-Hydroxyalkane phosphonates; Chiral copper complex; Molecular recognition

1. Introduction

Optically active β-hydroxyalkane phosphonic acid derivatives are important precursors for biologically active compounds. Although a multitude of enzymatic kinetic resolution methods have been developed for preparation of enantiomerically enriched β-hydroxyalkane phosphonic acid derivatives, to the best of our knowledge, nonenzymatic methods have not been reported. We recently reported an efficient method for kinetic resolution of 1,2-diols, vic-amino alcohols, and α- or β-hydroxyalkanamides with copper(II) ion associated with chiral ligand (R,R)-Ph-BOX by acylation to obtain optically active alcohols with excellent enantioselectivity. More recently, we have found that copper catalyst efficiently mediated kinetic resolution of α-hydroxyalkane phosphonates. In this report, we applied our methodology to kinetic resolution of β-hydroxyalkane phosphonates to afford optically active β-acyloxyalkane phosphonates in high yields and enantioselectivities. This is based on molecular recognition by Cu(II)–(R,R)-Ph-BOX complex to form the activated intermediates $A$ or $A'$ followed by benzylation (Scheme 1).
Scheme 1. Kinetic resolution of β-hydroxyalkanephosphonates with chiral copper catalyst.

2. Result and discussion
2.1 Effect of chiral catalyst

We began by surveying the effect of chiral catalysts composed of metal salt and chiral ligand to optimize their effect. The kinetic resolution of dimethyl (2-hydroxy-2-phenylethyl)phosphonate (1a) with benzoyl chloride (0.5 equiv) in CH$_2$Cl$_2$ was carried out in the presence of K$_2$CO$_3$ (1 equiv), metal salt (0.05 equiv) and chiral ligand (0.05 equiv). The results are shown in Table 1. The selectivity $s$ value$^8$ of a combination of Cu(OTf)$_2$ and (R,R)-Ph-BOX shown in Entry 1 was higher than those of other combinations (Entries 2—13). For instance, a combination of Zn(OTf)$_2$ and (R,R)-Ph-BOX promoted the benzoylation well, while the selectivity was somewhat low (Entry 2). Combinations of other metal triflates, copper dichloride, or palladium diacetate and (R,R)-Ph-BOX did not promote any kinetic resolution (Entries 3—11). (R,R)-Bn-BOX and (S,S)-t-Bu-BOX were not applicable to the kinetic resolution (Entries 12 and 13).

Table 1.
Effect of chiral catalyst on kinetic resolution of DL-1a.$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Metal salt</th>
<th>Chiral ligand</th>
<th>Product (S)-2a(Bz)</th>
<th>Recovered (R)-1a</th>
<th>$s$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Yield (%)</td>
<td>ee (%)$^b$</td>
<td>Yield (%)</td>
</tr>
<tr>
<td>1</td>
<td>Cu(OTf)$_2$</td>
<td>(R,R)-Ph-BOX</td>
<td>24</td>
<td>62</td>
<td>73</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: BzCl (0.5 equiv) / MX$_n$ (0.05 equiv) / chiral ligand (0.05 equiv) / K$_2$CO$_3$ (1.0 equiv) / CH$_2$Cl$_2$ / 0 °C to rt, 20 h.
2.2 Effect of acylating agents

We then set to investigate the effect of acylating agent to improve the selectivity. Table 2 summarizes the effect of different acylating agents on the kinetic resolution of DL-1a. Use of benzoic anhydride and N-benzoylimidazole which have lower reactivity compared with benzoyl chloride gave no benzoylated product (S)-2a(Bz) (Entries 1 and 2). On the other hand, use of 2-methylbenzoyl chloride afforded (S)-2a(2-MeBz) with moderate s value (Entry 3), while use of 2-methoxylbenzoyl chloride afforded (S)-2a(2-MeOBz) with low s value (Entry 4).

Among the 2-halogenated benzoyl chlorides which gave improved results (Entries 5, 10 and 11), 2-fluorobenzoyl chloride gave the best result. 3- or 4-fluorobenzoyl chloride was unfavorable when compared to 2-fluorobenzoyl chloride (Entries 6-9). On the other hand, 1- or 2-naphthoyl chloride gave moderate selectivities (Entries 12 and 13). Aliphatic acyl chloride such as acetyl, pivaloyl, and chloroacetyl chloride did not give good results (Entries 14-16). Interestingly, the reaction of DL-1a with phenyl isocyanate gave the opposite stereoselectivity (Entry 17). On the other hand, p-TsCl and CIP(O)(OEt)2 did not react with DL-1a (Entries 18 and 19).

<table>
<thead>
<tr>
<th>No.</th>
<th>Metal Salt</th>
<th>Chiral Ligand</th>
<th>s</th>
<th>r</th>
<th>Selectivity</th>
</tr>
</thead>
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<td>2</td>
<td>Zn(OTf)2</td>
<td>(R,R)-Ph-BOX</td>
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<td>23</td>
<td>53</td>
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<tr>
<td>3</td>
<td>Mg(OTf)2</td>
<td>(R,R)-Ph-BOX</td>
<td>23</td>
<td>6</td>
<td>76</td>
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<tr>
<td>4</td>
<td>Sn(OTf)2</td>
<td>(R,R)-Ph-BOX</td>
<td>trace</td>
<td>43</td>
<td>6</td>
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<tr>
<td>5</td>
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<tr>
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<td>Cu(OTf)2</td>
<td>(S,S)-t-Bu-BOX</td>
<td>10</td>
<td>−4c</td>
<td>89</td>
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</table>

a DL-1a (0.5 mmol), metal salt (0.025 mmol), chiral ligand (0.025 mmol), BzCl (0.25 mmol), K2CO3 (0.5 mmol) in CH2Cl2 (3.0 mL) at 0 °C to rt for 20 h. b Determined by HPLC. c (R)-2a(Bz) was obtained. d (S)-1a was recovered.
Table 2.
Effect of acylating agent on kinetic resolution.\textsuperscript{a}

\begin{table}[h]
\centering
\begin{tabular}{cccccc}
\hline
\textbf{Entry} & \textbf{Acylating agent} & \textbf{Product} & \textbf{Recovered (R)-1a} & \textbf{Yield (\%)} & \textbf{ee (\%)} \\
\hline
\textbf{1} & Bz₂O & (S)-2a(Bz) & 0 & - & >99 & - \\
\textbf{2} & N-Bz-imidazole & (S)-2a(Bz) & trace & - & 96 & - \\
\textbf{3} & 2-MeBzCl & (S)-2a(2-MeBz) & 23 & 69 & 69 & 16 & 6 \\
\textbf{4} & 2-MeOBzCl & (S)-2a(2-MeOBz) & 31 & 6 & 66 & 0 & 0 \\
\textbf{5} & 2-FBzCl & (S)-2a(2-FBz) & 32 & 80 & 66 & 28 & 12 \\
\textbf{6} & 3-FBzCl & (S)-2a(3-FBz) & 19 & 59 & 53 & 30 & 5 \\
\textbf{7} & 4-FBzCl & (S)-2a(4-FBz) & 27 & 52 & 60 & 30 & 4 \\
\textbf{8} & 2,6-F₂BzCl & (S)-2a(2,6-F₂Bz) & 22 & 56 & 63 & 27 & 5 \\
\textbf{9} & C₆F₅COCl & (S)-2a(C₆F₅CO) & 23 & 47 & 70 & 13 & 3 \\
\textbf{10} & 2-ClBzCl & (S)-2a(2-ClBz) & 30 & 72 & 70 & 20 & 7 \\
\textbf{11} & 2-BrBzCl & (S)-2a(2-BrBz) & 15 & 61 & 85 & 5 & 4 \\
\textbf{12} & 1-naphthoyl-Cl & (S)-2a(1-naphthoyl) & 20 & 64 & 78 & 8 & 5 \\
\textbf{13} & 2-naphthoyl-Cl & (S)-2a(2-naphthoyl) & 30 & 55 & 63 & 23 & 4 \\
\textbf{14} & AcCl & (S)-2a(Ac) & 36 & 16 & 59 & 10 & 2 \\
\textbf{15} & t-BuCOCl & (S)-2a(t-BuCO) & trace & - & >99 & - & - \\
\textbf{16} & CICH₂COCl & (S)-2a(CICH₂CO) & 20 & 8 & 68 & 7 & 1 \\
\textbf{17} & PhNCO & (R)-2a(PhNHCO) & 45 & 29 & 55 & -24\textsuperscript{d} & 2 \\
\textbf{18} & p-TsCl & (S)-2a(p-Ts) & 0 & - & >99 & - & - \\
\textbf{19} & CI(\text{O}(\text{OEt})₂) & (S)-2a(\text{CI}(\text{O}(\text{OEt})₂) & 0 & - & >99 & - & - \\
\hline
\end{tabular}
\caption{Effect of acylating agent on kinetic resolution.}
\end{table}

\textsuperscript{a} DL-1a (0.5 mmol), Cu(OTf)₂ (0.025 mmol), (R,R)-Ph-BOX (0.025 mmol), acylating agent (0.25 mmol), K₂CO₃ (0.5 mmol) in CH₂Cl₂ (3.0 mL) at 0 °C to rt for 20 h. \textsuperscript{b} Determined by HPLC. \textsuperscript{c} Without K₂CO₃, at -40 °C, for 20 min. \textsuperscript{d} (S)-1a was recovered.
2.3 Solvent effect

Table 3 summarizes the effect of solvents on the kinetic resolution of DL-1a. Alcohols as protic solvents did not work to accelerate the 2-fluorobenzoylation (Entries 1-4). Acetonitrile, acetone, and AcOEt which might coordinate with Cu(II) gave (S)-2a(2-FBz) with low s value (Entries 5, 8, and 9), while DMF and DMSO as polar solvents did not work at all (Entries 6 and 7). Use of ethereal or aromatic solvents improved the yields and enantioselectivities (Entries 10-15). Halogenated aliphatic solvents were suitable for the kinetic resolution (Entries 16-19). Especially CH₂Cl₂ was the most suitable solvent for the kinetic resolution. On the other hand, fluorobenzene or chlorobenzene gave moderate selectivities (Entries 20 and 21).

Table 3.
Effect of solvents on kinetic resolution.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Product (S)-2a(2-FBz)</th>
<th>Recovered (R)-1a</th>
<th>s</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Yield (%)</td>
<td>ee (%)\textsuperscript{b}</td>
<td>Yield (%)</td>
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<td>MeOH</td>
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<td>-</td>
<td>&gt;99</td>
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<td>EtOH</td>
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<td>-</td>
<td>&gt;99</td>
</tr>
<tr>
<td>3</td>
<td>(i)-PrOH</td>
<td>trace</td>
<td>-</td>
<td>&gt;99</td>
</tr>
<tr>
<td>4</td>
<td>(t)-BuOH</td>
<td>trace</td>
<td>-</td>
<td>&gt;99</td>
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<td>6</td>
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<td>&gt;99</td>
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<td>9</td>
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<td>Et₂O</td>
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<tr>
<td>12</td>
<td>(i)-Pr₂O</td>
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<td>56</td>
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<td>Entry</td>
<td>Base</td>
<td>Product (S)-2a(2-FBz)</td>
<td>Recovered (R)-1a</td>
<td>$s$</td>
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<tr>
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<td>-----------------------</td>
<td>------------------</td>
<td>------</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Yield (%)</td>
<td>$ee$ (%)$^b$</td>
<td>Yield (%)</td>
</tr>
<tr>
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<td>K$_2$CO$_3$</td>
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<td>66</td>
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<tr>
<td>2</td>
<td>Na$_2$CO$_3$</td>
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<td>70</td>
<td>58</td>
</tr>
<tr>
<td>3</td>
<td>NaHCO$_3$</td>
<td>30</td>
<td>53</td>
<td>61</td>
</tr>
</tbody>
</table>

$^a$ DL-1a (0.5 mmol), Cu(OTf)$_2$ (0.025 mmol), (R,R)-Ph-BOX (0.025 mmol), 2-FBzCl (0.25 mmol), K$_2$CO$_3$ (0.5 mmol) in solvent (3.0 mL) at 0 °C to rt for 20 h. $^b$ Determined by HPLC.

### 2.4 Effect of base

Table 4 summarizes the effect of bases on the kinetic resolution of DL-1a. Use of K$_2$CO$_3$, Na$_2$CO$_3$, or NaHCO$_3$ as a base gave 2-fluorobenzyolated product (S)-2a(2-FBz) with good $s$ values (Entries 1—3), while other carbonate salts such as Li$_2$CO$_3$, ZnCO$_3$, BaCO$_3$, CaCO$_3$, Cs$_2$CO$_3$ and (NH$_4$)$_2$CO$_3$ did not effectively accelerate the kinetic resolution (Entries 4-9). On the other hand, diisopropylethylamine (DIPEA) gave (S)-2a(2-FBz) with low yield and selectivity (Entry 10).

**Table 4.**

Effect of bases on the kinetic resolution.$^a$
Next, we surveyed the effect of ester substituents of β-hydroxyalkanephosphonates 1 to optimize their effect. The kinetic resolution of β-hydroxy-β-phenylethanephosphonates 1a-d with benzoyl or 2-fluorobenzoyl chloride (0.5 equiv) in CH$_2$Cl$_2$ was carried out in the presence of K$_2$CO$_3$ (1 equiv), Cu(OTf)$_2$ (0.05 equiv) and (R,R)-Ph-BOX (0.05 equiv). The results are shown in Table 5. In the case of benzoylation of 1a-d, the $s$ values for substrates 1a,d substituted with methyl or n-butyl ester were slightly lower than those of 1b,c substituted with ethyl or isopropyl ester (Entries 1—4). The $s$ values of 2-fluorobenzoylation for 1a-d was somewhat higher than those of benzoylation for 1a-d (Entries 1—8). Among 2-fluorobenzoylation for 1a-d, the $s$ value for substrate 1b was slightly better than those of 1a,c,d (Entries 4—8).

Table 5.  
Effect of ester substituents of DL-1a—d.$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Recovered (R)-1a—d</th>
<th>$s$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Yield (%)</td>
<td>ee (%)$^b$</td>
<td>Yield (%)</td>
</tr>
</tbody>
</table>

$^a$ DL-1a (0.5 mmol), Cu(OTf)$_2$ (0.025 mmol), (R,R)-Ph-BOX (0.025 mmol), 2-FBzCl (0.25 mmol), base (0.5 mmol) in solvent (3.0 mL) at 0 °C to rt for 20 h.  
$^b$ Determined by HPLC.
1. \( \text{R}^1 = \text{Me} \) (S)-2a(Bz) 24 62 (R)-1a 73 22 5
2. \( \text{R}^1 = \text{Et} \) (S)-2b(Bz) 26 66 (R)-1b 55 41 7
3. \( \text{R}^1 = i-\text{Pr} \) (S)-2c(Bz) 34 66 (R)-1c 51 36 7
4. \( \text{R}^1 = n-\text{Bu} \) (S)-2d(Bz) 29 56 (R)-1d 60 20 4
5. \( \text{R}^1 = \text{Me} \) (2-FBz) 32 80 (R)-1a 66 28 12
6. \( \text{R}^1 = \text{Et} \) (2-FBz) 32 83 (R)-1b 53 36 15
7. \( \text{R}^1 = i-\text{Pr} \) (2-FBz) 36 77 (R)-1c 57 29 10
8. \( \text{R}^1 = n-\text{Bu} \) (2-FBz) 20 82 (R)-1d 71 28 13

* DL-1a—d (0.5 mmol), Cu(OTf)_2 (0.025 mmol), (R,R)-Ph-BOX (0.025 mmol), BzCl or 2-FBzCl (0.25 mmol), K_2CO_3 (0.5 mmol) in CH_2Cl_2 (3.0 mL) at 0 °C to rt for 20 h. Determined by HPLC.

However, these selectivities were relatively lower than those of \( \alpha \)-hydroxyphosphonates (Scheme 2).

\[
\text{Ph} \quad \text{OH} \quad \text{P} \quad \text{OEt} \quad \text{OEt} \\
\text{DL-3} \quad \text{BzCl (0.5 equiv)} \quad \text{Cu(OTf)}_2 (0.05 equiv) \quad \text{(R,R)-Ph-BOX (0.05 equiv)}
\]

\[
\text{K}_2\text{CO}_3 (1 \text{ equiv}) \quad \text{CH}_2\text{Cl}_2 \quad \text{0°C to rt, 12 h} \quad \text{s=18} \quad 39\% \text{ yield} \quad 83\% \text{ ee} \\
\text{Ph} \quad \text{OEt} \quad \text{P} \quad \text{OEt} \quad \text{OH} \\
\text{(S)-3} \quad \text{39\% yield} \quad 83\% \text{ ee} \quad 48\% \text{ yield} \quad 52\% \text{ ee}
\]

**Scheme 2.** Kinetic resolution of \( \alpha \)-hydroxyphosphonate.

To clarify the reason for the different selectivities, a competitive reaction of \( \beta \)-hydroxyphosphonate DL-1b and \( \alpha \)-hydroxyphosphonate DL-3 with benzoyl chloride under the optimized reaction condition was examined (Scheme 3). The reactivity of \( \beta \)-isomer DL-1b was much lower than that of \( \alpha \)-isomer DL-3. This result may imply that the formation of the activated intermediates A or A\' composed of Cu(II)(R,R)-Ph-BOX complex and DL-1b (in Scheme 1) was slower than the formation of the corresponding intermediate Cu(II)(R,R)-Ph-BOX complex and DL-3.
Scheme 3. Competitive reaction of \( \alpha \)- and \( \beta \)-hydroxyphosphonate.

2.6 Kinetic resolution of various \( \beta \)-hydroxyalkanephosphonates

Kinetic resolution of various dimethyl or diethyl \( \beta \)-hydroxyalkanephosphonates DL-1e-r or DL-1s-v by 2-fluorobenzoylation under the optimized reaction conditions is summarized in Table 6. First, substrates having 2, 3, or 4-methylated phenyl group 1e-g efficiently afforded the corresponding optically active 2-fluorobenzoylated compounds (S)-2e-g (Entries 1-3). Especially, the kinetic resolution of DL-1e gave the best \( s \) value of 21 among dimethyl phosphonates DL-1e-r. On the other hand, 4-methoxyphenylated alcohol DL-1i afforded somewhat better result than 2-methoxyphenylated alcohol DL-1h (Entries 4 and 5). In case of alcohols DL-1j-m which contain electron withdrawing substituents such as nitro or halogen group at the 4-position the selectivities were moderate (Entries 6-9). The kinetic resolution of 1- or 2-naphthylated alcohols DL-1n or 1o was effectively proceeded (Entries 10 and 11). Also, this method was applicable to kinetic resolution of aliphatic alcohols DL-1p-r to give moderate selectivities (Entries 12-14). The \( s \) value for 2-fluorobenzoylation of diethyl phosphonate DL-1v improved that of the corresponding dimethyl ester DL-1p (Entries 12 and 18), while the \( s \) values for 2-fluorobenzoylation of diethyl phosphonates DL-1s-u did not improve those of the corresponding dimethyl esters DL-1e,i,n (Entries 1 and 15, 5 and 16, 10 and 17).
Table 6.
Kinetic resolution of various $\beta$-hydroxyalkanephosphonates DL-1e—v. $^a$

![Chemical structure diagram]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>$(S)$-2e—r</th>
<th>Recovered $(R)$-1e—r $^s$</th>
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<td>$R^2$</td>
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<td>36</td>
<td>78</td>
</tr>
<tr>
<td>16</td>
<td>Et</td>
<td>4-MeOPh</td>
<td>33</td>
<td>77</td>
</tr>
<tr>
<td>17</td>
<td>Et</td>
<td>1-naphthyl</td>
<td>36</td>
<td>61</td>
</tr>
<tr>
<td>18</td>
<td>Et</td>
<td>Me</td>
<td>39</td>
<td>56</td>
</tr>
</tbody>
</table>

$^a$ DL-1e—v (0.5 mmol), Cu(OTf)$_2$ (0.025 mmol), (R,R)-Ph-BOX (0.025 mmol), 2-FBzCl (0.25 mmol), K$_2$CO$_3$ (0.5 mmol) in CH$_2$Cl$_2$ (3.0 mL) at 0 °C to rt for 20 h. $^b$ Determined by HPLC.

2.7 Acceleration effect of catalyst

Next, we investigated the 2-fluorobenzoylation of $\beta$-hydroxyphosphonate (DL-1a) to see whether it could be accelerated by chiral copper(II) complex or not. The results are shown in Table 7. In the absence of Cu(OTf)$_2$, and (R,R)-Ph-BOX the reaction of DL-1a
with 2-fluorobenzoyl chloride was very slow (Entry 1), while in the presence of Cu(OTf)$_2$, the yield of 2-fluorobenzoylated compound 2a(2-FBz) was somewhat improved (Entry 2). Further improvement was accomplished by using a combination of Cu(OTf)$_2$ and (R,R)-Ph-BOX to afford 2a(2-FBz) in 32% yield (Entry 3). These results suggest that DL-1a is recognized by Cu(II)-(R,R)-Ph-BOX complex in the same way as in kinetic resolution of α-hydroxyphosphonates.\(^7\)

**Table 7.**
2-Fluorobenzoylation of DL-1a with or without a catalyst.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amount (equiv)</th>
<th>2a(2-FBz)</th>
<th>1a</th>
</tr>
</thead>
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<tr>
<td></td>
<td>X: Cu(OTf)$_2$</td>
<td>Y: (R,R)-Ph-BOX</td>
<td>Yield (%)</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>0.05</td>
<td>0.05</td>
<td>32</td>
</tr>
</tbody>
</table>

$^a$ DL-3a (0.5 mmol), Cu(OTf)$_2$ (X equiv), (R,R)-Ph-BOX (Y equiv), 2-FBzCl (0.25 mmol), K$_2$CO$_3$ (0.5 mmol) in CH$_2$Cl$_2$ (3.0 mL) at 0 °C to rt for 20 h. $^b$ Determined by HPLC.

2.8 Stereochemistry

Plausible stereochemical course is shown in Scheme 2. Firstly, Cu(II)-(R,R)-Ph-BOX complex B might be formed.\(^6\)\(^b\) B can approach (R)- or (S)-1 to generate the activated intermediates A'(R)-complex or A'(S)-complex, respectively. Since A'(S)-complex has steric hindrance between phenyl group on oxazoline ring and R$^2$ group on (S)-1, A'(R)-complex might form more quickly than A'(S)-complex. Reactive phenyl isocyanate quickly reacted with A'(R)-complex to give (R)-2a(PhNHCO) (path a, Entry 17 in Table 2). On the other hand, although less reactive 2-fluorobenzoyl chloride than phenyl isocyanate, hardly closes to A'(R)-complex by the steric hindrance (path b), 2-fluorobenzoyl chloride easily closes to A'(S)-complex to produce (S)-2 with good selectivity (path c).
Scheme 4. Plausible stereochemical course.
2.9 Conclusion

In conclusion, we have demonstrated a new non-enzymatic method for kinetic resolution of β-hydroxyalkanephosphonates. Synthetic applications of this enantiomerically enriched 2-fluorobenzoylation of racemic β-hydroxyalkanephosphonates are underway.

3. Experimental Section

3.1. General

$^1$H NMR and $^{13}$C NMR spectra were measured on a Varian Gemini 300 or 400 spectrometer with TMS as an internal standard. IR spectra were obtained on a Shimadzu FTIR-8100A. Mass spectra were obtained on a JEOL JMS-700N instrument. HPLC analyses were achieved by using a LC-10AT VP and a SPD-10A VP of Shimadzu Seisakusho, Inc. Specific rotations were measured with JASCO DIP-1000. Melting points are uncorrected.

All reagents and solvents were used as supplied without further purification.

3.2. Preparation of racemic β-hydroxyphosphonates 1a-o, q-u: Typical procedure\textsuperscript{9}

Under an argon atmosphere 1.6 M of $n$-butyl lithium (15 mL, 24 mmol) was slowly added to a solution of dimethyl methylphosphonate (2.14 mL, 20 mmol) in THF (40 mL) at −70 °C. After stirring for 30 min, to the solution was added slowly a solution of 4-chlorobenzaldehyde (3.37 g, 24 mmol) in THF (10 mL). After stirring for 1 h, to the resulting solution was added acetic acid (1.49 mL, 24 mmol). Solvent was removed under reduced pressure and water (25 mL) added to the residue. Organic portion was extracted with CH$_2$Cl$_2$ (3 x 30mL), then dried over MgSO$_4$, and the filtrate was concentrated under reduced pressure. The residue was subjected to silica gel column chromatography ($n$-hexane/AcOEt = 1/4). Further recrystallization from Et$_2$O and $n$-hexane afforded 1l (84% yield) as white crystals.

3.3. Preparation of racemic β-hydroxyphosphonates 1p, v

To a solution of dimethyl 2-oxopropylphosphonate (0.69 mL, 5 mmol) in methanol
(10 mL) was added sodium borohydride (0.76 g, 20 mmol) at 0 °C. After stirring for 16 h at room temperature, to the reaction mixture, 2M aq. HCl was added. The resulting mixture was concentrated under reduced pressure. To the residue was added H2O (10 mL), and the organic portion was extracted with AcOEt (3 x 25 mL). The organic layer was then dried over MgSO4, and the filtrate was concentrated under reduced pressure. The residue was subjected to silica gel column chromatography (AcOEt) to afford 1p (51% yield).

3.4. Kinetic resolution of racemic β-hydroxyphosphonate, typical procedure

A typical procedure for kinetic resolution of DL-1a: Under an aerobic atmosphere, a solution of Cu(OTf)2 (9.0 mg, 0.025 mmol) and (R,R)-Ph-BOX (8.4 mg, 0.025 mmol) in CH2Cl2 (3 mL) was stirred for 10 min. Into the solution were added DL-1a (115 mg, 0.5 mmol), K2CO3 (69 mg, 0.5 mmol) and 2-fluorobenzoyl chloride (30 μL, 0.25 mmol) at 0 °C. The resulting mixture was allowed to stand until it warmed to room temperature and stirred for 20 h. To the solution was poured water (20 mL) and extracted with CH2Cl2 (20 mL x 3). The combined organic layer was dried over MgSO4 and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (n-hexane : AcOEt = 1 : 1) to afford (S)-2a(2-FBz) (32% yield, 80% ee) as colorless oil and (R)-1a (66% yield, 28% ee) as white solid.

Dimethyl (R)-(2-hydroxy-2-phenylethyl)phosphonate (1a)1b: White solid; Mp 57.5—58.0 °C (Et2O); [α]D20 —14.5 (c 1.3, acetone, 49% ee); 1H NMR (300 MHz, CDCl3) δ 2.15—2.34 (m, 2H), 3.66 (br s, 1H), 3.73 (d, J = 10.8 Hz, 3H), 3.78 (d, J = 11.1 Hz, 3H), 5.08—5.17 (m, 1H), 7.27—7.41 (m, 5H); HPLC chiralcel OB column (4.6 mm x 250 mm), n-hexane : 2-propanol = 20 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 11.9 min, 15.9 min (enriched).

Dimethyl (S)-(2-benzoyloxy-2-phenylethyl)phosphonate (2a(Bz)): Colorless oil; [α]D20 —12.8 (c 0.53, acetone, 62% ee); IR(neat) 2955, 1721, 1269, 1111, 1034, 714 cm⁻¹; 1H NMR (300 MHz, CDCl3) δ 2.36—2.50 (m, 1H), 2.63—2.78 (m, 1H), 3.63 (d,
J = 10.8 Hz, 3H), 3.64 (d, J = 10.8 Hz, 3H), 6.27—6.35 (m, 1H), 7.28—7.60 (m, 8H), 8.09 (d, J = 7.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 32.4 (d, J = 140 Hz), 52.0 (d, J = 6.6 Hz), 52.2 (d, J = 6.6 Hz), 71.1, 126.1 (2C), 128.1 (2C), 128.2, 128.3 (2C), 129.4 (2C), 129.6, 132.8, 139.5 (d, J = 10.7 Hz), 164.9; MS [HR-EI (M⁺)] calcd for C₁₇H₁₉O₅P 334.0970 found 334.0965; HPLC chiralcel OJ-H column (4.6 mmφ, 250 mm), n-hexane : 2-propanol = 10 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 31.4 min (enriched), 36.6 min.

**Dimethyl (S)-[2-phenyl-2-(2-toluoyloxy)ethyl]phosphonate (2a(2-MeBz))**: Colorless solid; Mp 94.0—96.0 °C (Et₂O); [α]_D²⁰ +3.7 (c 1.1, acetone, 69% ee); IR(neat) 3463, 2955, 1725, 1458, 1267, 1082, cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.33—2.49 (m, 1H), 2.57 (s, 3H), 2.61—2.74 (m, 1H), 3.63 (d, J = 11.4 Hz, 6H), 6.26—6.33 (m, 1H), 7.21—7.48 (m, 8H), 8.00—8.03 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 21.6, 32.7 (d, J = 140 Hz), 52.2 (d, J = 6.6 Hz), 52.4 (d, J = 6.6 Hz), 71.0, 125.6, 126.4 (2C), 128.4, 128.6 (2C), 129.1, 130.5, 131.6, 132.0, 139.9 (d, J = 10.7 Hz), 140.4, 165.8; MS [HR-EI (M⁺)] calcd for C₁₈H₂₁O₅P 348.1126 found 348.1134; HPLC chiralcel OJ-H column (4.6 mmφ, 250 mm), n-hexane : 2-propanol = 20 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 30.5 min (enriched), 35.1 min.

**Dimethyl (S)-[2-(2-methoxybenzoyloxy)-2-phenylethyl]phosphonate (2a(2-MeOBz))**: White solid; Mp 109—110 °C (Et₂O); [α]_D²⁰ —0.15 (c 1.4, acetone, 6% ee); IR(neat) 3456, 2955, 1738, 1495, 1266, 1082 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.34—2.49 (m, 1H), 2.61—2.74 (m, 1H), 3.62 (d, J = 11.1 Hz, 3H), 3.63 (d, J = 11.1 Hz, 3H), 3.88 (s, 3H), 6.24—6.32 (m, 1H), 6.95—7.01 (m, 2H), 7.10—7.18 (m, 3H), 7.44—7.50 (m, 3H), 7.89—7.92 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 32.6 (d, J = 139 Hz), 52.1 (d, J = 6.6 Hz), 52.2 (d, J = 6.6 Hz), 55.7, 70.9, 111.8, 119.3, 119.9, 126.4 (2C), 128.1, 128.3 (2C), 131.6, 133.6, 139.8 (d, J = 9.9 Hz), 159.3, 164.2; MS [HR-EI (M⁺)] calcd for C₁₈H₂₁O₆P 364.1076 found 364.1090; HPLC chiralcel OJ-H column (4.6 mmφ, 250 mm), n-hexane : ethanol = 5 : 1, wavelength: 254 nm, flow rate: 0.3 mL/min, retention time: 46.9 min (enriched), 50.5 min.
Dimethyl \((S)-[2-(2-fluorobenzoyloxy)-2-phenylethyl]phosphonate\) (2a(2-FBz)):

Colorless oil; \([\alpha]_D^{20} = -6.5\) (c 0.69, acetone, 80% ee); IR(neat) 3465, 2955, 1732, 1456, 1262, 1044 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 2.35—2.49 (m, 1H), 2.62—2.76 (m, 1H), 3.62 (d, \(J = 11.1\) Hz, 3H), 3.64 (d, \(J = 11.1\) Hz, 3H), 6.29—6.37 (m, 1H), 7.10—7.23 (m, 2H), 7.29—7.41 (m, 3H), 7.46—7.53 (m, 3H), 7.99 (td, \(J = 1.5, 7.5\) Hz, 1H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 32.8 (d, \(J = 140\) Hz), 52.5 (d, \(J = 6.6\) Hz), 52.6 (d, \(J = 6.6\) Hz), 71.8, 117.1 (d, \(J = 22.2\) Hz), 118.6 (d, \(J = 9.9\) Hz), 124.2 (d, \(J = 3.3\) Hz), 126.7 (2C), 128.7, 128.8 (2C), 132.4, 134.9 (d, \(J = 9.1\) Hz), 139.7 (d, \(J = 10.7\) Hz), 162.1 (d, \(J = 259\) Hz), 163.0 (d, \(J = 4.1\) Hz); MS [HR-EI (M\(^+\))] calcd for C\(_{17}\)H\(_{18}\)FO\(_5\)P 352.0876 found 352.0872; HPLC chiralcel OD-H column (4.6 mm\(\phi\), 250 mm) \(\times\) 2, \(n\)-hexane : 2-propanol = 5 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 19.8 min (enriched), 25.6 min.

Dimethyl \((S)-[2-(3-fluorobenzoyloxy)-2-phenylethyl]phosphonate\) (2a(3-FBz)):

Colorless oil; \([\alpha]_D^{20} = -7.9\) (c 0.70, acetone, 59% ee); IR(neat) 2955, 1727, 1447, 1272, 1202, 1030 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 2.35—2.49 (m, 1H), 2.62—2.77 (m, 1H), 3.63 (d, \(J = 11.1\) Hz, 3H), 3.65 (d, \(J = 11.1\) Hz, 3H), 6.26—6.35 (m, 1H), 7.22—7.47 (m, 7H), 7.72—7.78 (m, 1H), 7.86—7.90 (m, 1H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 32.4 (d, \(J = 140\) Hz), 52.1 (d, \(J = 6.6\) Hz) 52.3 (d, \(J = 6.6\) Hz), 71.6 (d, \(J = 1.7\) Hz), 116.3 (d, \(J = 23.1\) Hz), 120.0 (d, \(J = 20.6\) Hz), 125.3 (d, \(J = 3.3\) Hz), 126.2 (2C), 128.4, 128.5 (2C), 129.9 (d, \(J = 7.4\) Hz), 131.9 (d, \(J = 7.4\) Hz), 139.3 (d, \(J = 10.7\) Hz), 162.3 (d, \(J = 246\) Hz), 163.9 (d, \(J = 2.5\) Hz); MS [HR-EI (M\(^+\))] calcd for C\(_{17}\)H\(_{18}\)FO\(_5\)P 352.0876 found 352.0869; HPLC chiralcel OJ-H column (4.6 mm\(\phi\), 250 mm), \(n\)-hexane : 2-propanol = 10 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 28.4 min (enriched), 34.7 min.

Dimethyl \((S)-[2-(4-fluorobenzoyloxy)-2-phenylethyl]phosphonate\) (2a(4-FBz)):

Colorless oil; \([\alpha]_D^{20} = -6.6\) (c 1.1, acetone, 52% ee); IR(neat) 2955, 1725, 1605, 1273, 1034 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 2.35—2.47 (m, 1H), 2.62—2.77 (m, 1H), 3.63 (d, \(J = 10.8\) Hz, 3H), 3.64 (d, \(J = 10.8\) Hz, 3H), 6.25—6.33 (m, 1H), 7.11 (t, \(J = 9.0\) Hz, 2H), 7.30—7.46 (m, 5H), 8.07—8.13 (m, 2H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 32.5
(d, $J = 140$ Hz), 52.1 (d, $J = 6.6$ Hz), 52.3 (d, $J = 6.6$ Hz), 71.4 (d, $J = 1.7$ Hz), 115.3 (d, $J = 21.4$ Hz, 2C), 126.0, 126.2 (2C), 128.4, 128.5 (2C), 132.1 (d, $J = 9.1$ Hz, 2C), 139.5 (d, $J = 10.7$ Hz), 164.0, 165.6 (d, $J = 253$ Hz); MS [HR-EI (M$^+$)] calcd for C$_{17}$H$_{18}$FO$_5$P 352.0876 found 352.0869; HPLC chiralcel OJ-H column (4.6 mm$\phi$, 250 mm), $n$-hexane : 2-propanol = 10 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 33.2 min (enriched), 43.7 min.

**Dimethyl (S)-[2-(2,6-difluorobenzoyloxy)-2-phenylethyl]phosphonate (2a(2,6-F$_2$Bz))**: Colorless oil; [α]$_D^{20}$ +7.1 (c 1.2, acetone, 56% ee); IR(neat) 2957, 1732, 1626, 1472, 1269, 1061 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 2.36—2.49 (m, 1H), 2.60—2.75 (m, 1H), 3.61 (d, $J = 11.1$ Hz, 3H), 3.63 (d, $J = 11.1$ Hz, 3H), 6.29—6.37 (m, 1H), 6.94 (t, $J = 8.4$ Hz, 2H), 7.32—7.51 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 32.5 (d, $J = 140$ Hz), 52.1 (d, $J = 6.6$ Hz), 52.3 (d, $J = 6.6$ Hz), 71.4, 110.5 (t, $J = 17.3$ Hz), 111.8 (t, $J = 2.5$ Hz), 112.0 (t, $J = 2.5$ Hz), 126.5 (2C), 128.47 (2C), 128.51, 132.9 (t, $J = 10.7$ Hz), 138.9 (d, $J = 9.9$ Hz), 160.0, 160.6 (dd, $J = 5.8$, 256 Hz, 2C); MS [HR-EI (M$^+$)] calcd for C$_{17}$H$_{17}$F$_2$O$_5$P 370.0781 found 370.0780; HPLC chiralcel OD-H column (4.6 mm$\phi$, 250 mm), $n$-hexane : 2-propanol = 10 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 16.0 min (enriched), 20.4 min.

**Dimethyl (S)-(2-pentafluorobenzoyloxy-2-phenylethyl)phosphonate (2a(C$_6$F$_5$CO))**: Colorless oil; [α]$_D^{20}$ +3.4 (c 0.96, acetone, 47% ee); IR(neat) 2957, 1742, 1653, 1497, 1221, 1026 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 2.36—2.48 (m, 1H), 2.57—2.72 (m, 1H), 3.63 (d, $J = 10.8$ Hz, 3H), 3.65 (d, $J = 10.8$ Hz, 3H), 6.31—6.39 (m, 1H), 7.33—7.48 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 32.3 (d, $J = 140$ Hz), 52.1 (d, $J = 6.6$ Hz), 52.4 (d, $J = 6.6$ Hz), 73.3, 107.7 (dt, $J = 4.1$, 15.6 Hz), 126.6 (2C), 128.6 (2C), 128.8, 136.1—136.4 (m), 138.3 (d, $J = 9.1$ Hz), 138.6—138.9 (m), 141.7—142.0 (m), 144.0—144.6 (m), 146.6—146.8 (m), 157.5; MS [HR-FAB (M+H$^+$)] calcd for C$_{17}$H$_{15}$F$_5$O$_5$P 425.0577 found 425.0592; HPLC chiralcel OD-H column (4.6 mm$\phi$, 250 mm), $n$-hexane : 2-propanol = 10 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 15.5 min (enriched), 17.9 min.
**Dimethyl (S)-[2-(2-chlorobenzoyloxy)-2-phenylethyl]phosphonate (2a(2-ClBz)):**

Colorless solid; Mp 62.0—63.0 °C; $\alpha_\text{D}^{20} +4.1$ (c 1.3, acetone, 72% ee); IR(neat) 2955, 1733, 1256, 1051, 772 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 2.37—2.50 (m, 1H), 2.63—2.76 (m, 1H), 3.631 (d, $J = 11.1$ Hz, 3H), 3.634 (d, $J = 11.1$ Hz, 3H), 6.28—6.36 (m, 1H), 7.31—7.50 (m, 8H), 7.91—7.95 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 32.5 (d, $J = 139$ Hz), 52.2 (d, $J = 6.6$ Hz), 52.3 (d, $J = 6.6$ Hz), 71.9, 126.47, 126.53 (2C), 128.45, 128.50 (2C), 129.5, 130.9, 131.5, 132.5, 133.6, 139.2 (d, $J = 9.9$ Hz), 163.9; MS [HR-EI (M$^+$)] calcd for C$_{17}$H$_{18}$ClO$_5$P 368.0580 found 368.0590; HPLC chiralcel OD-H column (4.6 mmφ, 250 mm) x 2, n-hexane : 2-propanol = 5 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 21.2 min (enriched), 24.7 min.

**Dimethyl (S)-[2-(2-bromobenzoyloxy)-2-phenylethyl]phosphonate (2a(2-BrBz)):**

Colorless oil; $\alpha_\text{D}^{20} —6.2$ (c 1.2, acetone, 61% ee); IR (neat) 2955, 1748, 1293, 1136, 772 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 2.38—2.51 (m, 1H), 2.64—2.78 (m, 1H), 3.63 (d, $J = 11.1$ Hz, 3H), 3.64 (d, $J = 11.1$ Hz, 3H), 6.28—6.36 (m, 1H), 7.29—7.42 (m, 5H), 7.48—7.51 (m, 2H), 7.65 (dd, $J = 1.8$, 7.8 Hz, 1H), 7.90 (dd, $J = 2.1$, 7.5 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 32.4 (d, $J = 139$ Hz), 52.2 (d, $J = 6.6$ Hz), 52.4 (d, $J = 6.6$ Hz), 72.0, 121.6, 126.6 (2C), 127.0, 128.5 (3C), 131.4, 131.5, 132.6, 134.2, 139.0 (d, $J = 9.9$ Hz), 164.4; MS [HR-FAB (M+H)$^+$] calcd for C$_{17}$H$_{19}$BrO$_3$P 413.0153 found 413.0155; HPLC chiralcel OD-H column (4.6 mmφ, 250 mm) x 2, n-hexane : 2-propanol = 5 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 22.4 min (enriched), 25.8 min.

**Dimethyl (S)-[2-(1-naphthoyloxy)-2-phenylethyl]phosphonate (2a(1-naphthoyl)):**

Colorless oil; $\alpha_\text{D}^{20} +28.7$ (c 0.40, acetone, 64% ee); IR(neat) 2953, 1717, 1242, 1196, 1132, 1030 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 2.40—2.54 (m, 1H), 2.68—2.82 (m, 1H), 3.646 (d, $J = 11.1$ Hz, 3H), 3.655 (d, $J = 11.1$ Hz, 3H), 6.39—6.47 (m, 1H), 7.33—7.42 (m, 3H), 7.49—7.61 (m, 5H), 7.87 (dd, $J = 1.8$, 7.8 Hz, 1H), 8.03 (d, $J = 8.1$ Hz, 1H), 8.32 (dd, $J = 1.2$, 7.2 Hz, 1H), 8.87 (d, $J = 9.0$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 32.6 (d, $J = 139$ Hz), 52.2 (d, $J = 6.6$ Hz), 52.3 (d, $J = 6.6$ Hz), 71.2 (d, $J = 1.6$ Hz), 124.3, 125.5, 126.0, 126.3 (2C), 126.4, 127.6, 128.29, 128.32, 128.5 (2C), 130.2,
131.2, 133.4, 133.5, 139.7 (d, J = 10.7 Hz), 165.7; MS [HR-EI (M⁺)] calcd for C₂₁H₂₁O₅P 384.1127 found 384.1108; HPLC chiralcel OJ-H column (4.6 mmϕ, 250 mm), n-hexane : 2-propanol = 10 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 31.9 min (enriched), 38.8 min.

**Dimethyl (S)-[2-(2-naphthoyloxy)-2-phenylethyl]phosphonate (2a(2-naphthoyl)):**
Colorless oil; [α]₀²⁰ —37.3 (c 0.51, acetone, 55% ee); IR(neat) 2953, 1717, 1277, 1225, 1196, 1026 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.41—2.54 (m, 1H), 2.69—2.83 (m, 1H), 3.64 (d, J = 11.1 Hz, 3H), 3.65 (d, J = 11.1 Hz, 3H), 6.34—6.42 (m, 1H), 7.32—7.42 (m, 3H), 7.50—7.62 (m, 4H), 7.88 (d, J = 8.7 Hz, 2H), 7.97 (d, J = 7.5 Hz, 1H), 8.09 (dd, J = 1.8, 8.7 Hz, 1H), 8.66 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 32.8 (d, J = 140 Hz), 52.3 (d, J = 6.6 Hz), 52.5 (d, J = 6.6 Hz), 71.5 (d, J = 2.5 Hz), 125.2, 126.4 (2C), 126.6, 127.1, 127.7, 128.1, 128.3, 128.5, 128.7 (2C), 129.3, 131.2, 132.4, 135.5, 139.8 (d, J = 10.7 Hz), 165.3; MS [HR-EI (M⁺)] calcd for C₂₁H₂₁O₅P 384.1127 found 384.1116; HPLC chiralcel OJ-H column (4.6 mmϕ, 250 mm), n-hexane : 2-propanol = 5 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 30.6 min (enriched), 46.0 min.

**Dimethyl (S)-(2-acetoxy-2-phenylethyl)phosphonate (2a(Ac)):**
Colorless oil; [α]₀²⁰ +2.6 (c 1.0, acetone, 16% ee); IR(neat) 2957, 1744, 1248, 1049, 820, 544 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.08 (s, 3H), 2.22—2.37 (m, 1H), 2.46—2.60 (m, 1H), 3.65 (d, J = 11.1 Hz, 6H), 6.05—6.12 (m, 1H), 7.30—7.40 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 21.0, 32.4 (d, J = 140 Hz), 52.3 (d, J = 6.6 Hz), 52.5 (d, J = 6.6 Hz), 70.5, 126.5 (2C), 128.4, 128.6 (2C), 139.6 (d, J = 10.7 Hz), 169.6; MS [HR-EI (M⁺)] calcd for C₁₂H₁₇O₅P 272.0814 found 272.0802; HPLC chiralcel OD-H column (4.6 mmϕ, 250 mm), n-hexane : 2-propanol = 10 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 14.8 min (enriched), 17.3 min.

**Dimethyl (S)-(2-chloroacetoxy-2-phenylethyl)phosphonate ((S)-2a(ClCH₂CO)):**
Colorless oil; [α]₀²⁰ +4.7 (c 0.93, acetone, 8% ee); IR(neat) 2957, 1761, 1268, 1173, 1046, 820 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.25—2.40 (m, 1H), 2.56—2.63 (m,
1H), 3.66 (d, J = 10.8 Hz, 3H), 3.67 (d, J = 10.8 Hz, 3H), 4.08 (d, J = 3.6 Hz, 2H),
6.13—6.21 (m, 1H), 7.30—7.43 (m, 5H); 13C NMR (100 MHz, CDCl3) δ 32.2 (d, J =
140 Hz), 40.9, 52.4 (d, J = 6.6 Hz), 52.6 (d, J = 6.6 Hz), 72.5, 126.6 (2C), 128.7 (2C),
128.9, 138.7 (d, J = 10.7 Hz), 166.0; MS [HR-EI (M+)] calcd for C12H16ClO5P 306.0424
found 306.0400; HPLC chiralcel OD-H column (4.6 mmφ, 250 mm), n-hexane : 2-propanol = 10 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 16.0
min (enriched), 18.5 min.

Dimethyl (R)-(2-phenyl-2-phenylaminocarbonyloxyethyl)phosphonate
((R)-2a(PhNHCO): Colorless solid; Mp 128—130 °C (AcOEt and n-hexane); [α]D20
—6.7 (c 1.2, acetone, 29% ee); IR(neat) 2955, 1732, 1549, 1233, 1049, 758 cm−1; 1H
NMR (300 MHz, CDCl3) δ 2.17—2.42 (m, 1H), 2.52—2.66 (m, 1H), 3.64 (d, J = 10.8
Hz, 3H), 3.67 (d, J = 10.8 Hz, 3H), 6.04—6.11 (m, 1H), 6.96 (br s, 1H), 7.04 (t, J = 7.2
Hz, 1H), 7.25—7.39 (m, 9H); 13C NMR (100 MHz, CDCl3) δ 32.6 (d, J = 139 Hz), 52.2
(d, J = 6.6 Hz), 52.5 (d, J = 6.6 Hz), 71.3, 118.5 (2C), 123.1, 126.2 (2C), 128.3, 128.5
(2C), 128.7 (2C), 137.9, 139.7 (d, J = 10.7 Hz), 152.2; MS [HR-EI (M+)] calcd for
C17H20NO5P 349.1079 found 349.1065; HPLC chiralcel OD-H column (4.6 mmφ, 250
mm) x 2, n-hexane : 2-propanol = 15 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min,
retention time: 42.3 min (enriched), 49.3 min.

Diethyl (R)-(2-hydroxy-2-phenylethyl)phosphonate (1b): Colorless oil; [α]D20
—10.8 (c 1.1, acetone, 41% ee); 1H NMR (300 MHz, CDCl3) δ 1.30 (t, J = 7.2 Hz, 3H),
1.36 (t, J = 7.2 Hz, 3H), 2.17—2.25 (m, 2H), 3.87 (br s, 1H), 4.03—4.21 (m, 4H),
5.07—5.18 (m, 1H), 7.26—7.40 (m, 5H); HPLC chiralcel OD-H column (4.6 mm x 250
mm), n-hexane : 2-propanol = 50 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min,
retention time: 30.5 min (enriched), 35.1 min.

Diethyl (S)-(2-benzoyloxy-2-phenylethyl)phosphonate (2b(Bz)): Colorless oil; [α]D20
—7.8 (c 1.0, acetone, 66% ee); IR(neat) 2984, 1725, 1275, 1111, 1080, 716 cm−1; 1H
NMR (300 MHz, CDCl3) δ 1.17—1.23 (m, 6H), 2.35—2.48 (m, 1H), 2.62—2.75 (m,
1H), 3.94—4.07 (m, 4H), 6.28—6.35 (m, 1H), 7.30—7.48 (m, 7H), 7.53—7.58 (m, 1H),
8.07—8.11 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 16.4, 16.5, 33.9 (d, $J = 140$ Hz), 62.1 (d, $J = 6.6$ Hz), 62.3 (d, $J = 6.6$ Hz), 71.8, 126.7 (2C), 128.6 (2C), 128.7, 128.9 (2C), 130.0 (2C), 130.3, 133.3, 140.2 (d, $J = 10.7$ Hz), 165.5; MS [HR-EI (M$^+$)] calcd for C$_{19}$H$_{23}$O$_5$P 362.1283 found 362.1288; HPLC chiral cel OJ-H column (4.6 mmφ, 250 mm), $n$-hexane : 2-propanol = 30 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 33.1 min (enriched), 45.6 min.

**Diethyl (S)-[2-(2-fluorobenzoyloxy)-2-phenylethyl]phosphonate (2b[2-FBz]):**

Colorless oil; [α]$_D^{20}$ +2.0 (c 1.2, acetone, 83% ee); IR(neat) 2986, 1728, 1294, 1256, 1030, 758 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 1.18—1.23 (m, 6H), 2.35—2.48 (m, 1H), 2.61—2.75 (m, 1H), 3.94—4.08 (m, 4H), 6.30—6.37 (m, 1H), 7.10—7.23 (m, 2H), 7.28—7.40 (m, 3H), 7.46—7.55 (m, 3H), 8.00 (td, $J = 1.8$, 7.2 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 15.96, 16.03, 33.4 (d, $J = 140$ Hz), 61.5 (d, $J = 6.6$ Hz), 61.7 (d, $J = 6.6$ Hz), 71.7, 116.7 (d, $J = 22.2$ Hz), 118.3 (d, $J = 9.1$ Hz), 123.8 (d, $J = 4.1$ Hz), 126.4 (2C), 128.3, 128.4 (2C), 132.0, 134.5 (d, $J = 9.1$ Hz), 139.5 (d, $J = 10.7$ Hz), 161.8 (d, $J = 256$ Hz), 162.6; MS [HR-FAB (M+H) +] calcd for C$_{19}$H$_{23}$FO$_5$P 381.1267 found 381.1271; HPLC chiralcel OD-H column (4.6 mmφ, 250 mm), $n$-hexane : 2-propanol = 30 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 20.4 min (enriched), 30.8 min.

**Diisopropyl (R)-(2-hydroxy-2-phenylethyl)phosphonate (1c)$_{10}$:** White solid; Mp 69.0—69.5 °C (Et$_2$O); [α]$_D^{20}$ —10.1 (c 1.4, acetone, 36% ee); $^1$H NMR (300 MHz, CDCl$_3$) δ 1.28—1.38 (m, 12H), 2.12 (d, $J = 6.3$ Hz, 1H), 2.18 (d, $J = 6.3$ Hz, 1H), 4.13 (br s, 1H), 4.64—4.82 (m, 2H), 5.03—5.12 (m, 1H), 7.24—7.41 (m, 5H); HPLC chiralcel OD-H column (4.6 mmφ, 250 mm) x 2, $n$-hexane : 2-propanol = 50 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 32.7 min (enriched), 36.3 min.

**Diisopropyl (S)-(2-benzoyloxy-2-phenylethyl)phosphonate (2c[Bz]):** Colorless oil; [α]$_D^{20}$ —11.6 (c 1.4, acetone, 66% ee); IR(neat) 2980, 1725, 1275, 1111, 1017, 712 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 1.18—1.25 (m, 12H), 2.29—2.43 (m, 1H),
2.57—2.71 (m, 1H), 4.60—4.71 (m, 2H), 6.26—6.34 (m, 1H), 7.29—7.47 (m, 7H), 7.53—7.58 (m, 1H), 8.09—8.12 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 23.70 (d, $J$ = 3.3 Hz, 2C), 23.73 (d, $J$ = 3.3 Hz), 23.77 (d, $J$ = 3.3 Hz), 34.8 (d, $J$ = 141 Hz), 70.4 (d, $J$ = 6.6 Hz), 70.6 (d, $J$ = 6.6 Hz), 71.6, 126.4 (2C), 128.1 (2C), 128.2, 128.4 (2C), 129.6 (2C), 130.0, 132.9, 140.1 (d, $J$ = 10.7 Hz), 165.1; MS [HR-EI (M$^+$)] calcd for C$_{21}$H$_{27}$O$_5$P 390.1596 found 390.1578; HPLC chiral cel OJ-H column (4.6 mmφ, 250 mm), $n$-hexane : 2-propanol = 30 : 1, wavelength: 254 nm, flow rate: 0.5 mL/min, retention time: 24.1 min, 30.3 min (enriched).

**Diisopropyl (S)-[2-(2-fluorobenzoyloxy)-2-phenylethyl]phosphonate (2c(2-FBz))**:
Colorless oil; [$\alpha$]$_D$$^{20}$ +2.9 (c 1.1, acetone, 77% ee); IR(neat) 2980, 1736, 1456, 1264, 1019, 762 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 1.18—1.25 (m, 1H), 2.29—2.43 (m, 4H), 2.56—2.70 (m, 1H), 4.59—4.70 (m, 2H), 6.29—6.37 (m, 1H), 7.09—7.23 (m, 2H), 7.26—7.39 (m, 3H), 7.46—7.55 (m, 3H), 8.02 (td, $J$ = 1.8, 7.5 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 23.55 (d, $J$ = 3.3 Hz), 23.59 (d, $J$ = 3.3 Hz), 23.62 (d, $J$ = 3.3 Hz), 23.65 (d, $J$ = 3.3 Hz), 34.7 (d, $J$ = 141 Hz), 70.2 (d, $J$ = 6.6 Hz), 70.3 (d, $J$ = 6.6 Hz), 71.8, 116.6 (d, $J$ = 22.2 Hz), 118.4 (d, $J$ = 9.1 Hz), 123.7 (d, $J$ = 4.1 Hz), 126.4 (2C), 128.1, 128.3 (2C), 132.0, 134.3 (d, $J$ = 9.1 Hz), 139.7 (d, $J$ = 10.7 Hz), 161.7 (d, $J$ = 259 Hz), 162.6 (d, $J$ = 3.3 Hz); MS [HR-FAB (M+H)$^+$] calcd for C$_{21}$H$_{27}$FO$_5$P 408.1580 found 408.1602; HPLC chiralcel OD-H column (4.6 mmφ, 250 mm), $n$-hexane : 2-propanol = 30 : 1, wavelength: 254 nm, flow rate: 0.7 ml/min, retention time: 15.2 min (enriched), 23.1 min.

**Dibutyl (R)-(2-hydroxy-2-phenylethyl)phosphonate (1d)**: Colorless oil; [$\alpha$]$_D$$^{20}$ —11.7 (c 1.2, acetone, 20% ee); IR(neat) 3360, 2961, 1240, 1221, 1026 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 0.90—0.98 (m, 6H), 1.31—1.47 (m, 4H), 1.55—1.72 (m, 4H), 2.17—2.25 (m, 2H), 3.92 (br s, 1H), 3.98—4.17 (m, 4H), 5.07—5.16 (m, 1H), 7.26—7.41 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 13.2 (2C), 18.3 (2C), 32.00, 32.05, 35.5 (d, $J$ = 136 Hz), 65.0, 65.3, 68.3, 125.3 (2C), 127.1, 127.9 (2C), 143.7; MS [HR-EI (M$^+$)] calcd for C$_{16}$H$_{27}$O$_4$P 314.1647 found 314.1651; HPLC chiralcel OD-H column (4.6 mmφ, 250 mm) x 2, $n$-hexane : 2-propanol = 50 : 1, wavelength: 254 nm, flow rate:
1.0 mL/min, retention time: 39.6 min (enriched), 42.1 min.

**Dibutyl (S)-(2-benzoyloxy-2-phenylethyl)phosphonate (2d(Bz))**: Colorless oil; \([\alpha]_D^{20} = -7.8\) (c 1.1, acetone, 56% ee); IR(neat) 2961, 1725, 1273, 1109, 1026, 716 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 0.82—0.88 (m, 6H), 1.23—1.35 (m, 4H), 1.46—1.57 (m, 4H), 2.36—2.49 (m, 1H), 2.62—2.76 (m, 1H), 3.86—4.00 (m, 4H), 6.27—6.34 (m, 1H), 7.30—7.47 (m, 7H), 7.53—7.60 (m, 1H), 8.07—8.10 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 13.4 (2C), 18.5 (2C), 32.27, 32.33, 33.4 (d, \(J = 140\) Hz), 65.5 (d, \(J = 6.6\) Hz), 65.7 (d, \(J = 6.6\) Hz), 71.5, 126.4 (2C), 128.2 (2C), 128.3, 128.5 (2C), 129.6 (2C), 129.8, 133.0, 139.9 (d, \(J = 9.9\) Hz), 165.1; MS [HR-EI (M\(^+\))] calcd for C\(_{23}\)H\(_{31}\)O\(_5\)P 418.1910 found 418.1902; HPLC chiralcel OJ-H column (4.6 mm\(\phi\), 250 mm), n-hexane : ethanol = 30 : 1, wavelength: 254 nm, flow rate: 0.3 mL/min, retention time: 24.1 min (enriched), 27.5 min.

**Dibutyl (S)-(2-(2-fluorobenzoyloxy)-2-phenylethyl)phosphonate (2d(2-FBz))**: Colorless oil; \([\alpha]_D^{20} = -2.7\) (c 1.1, acetone, 82% ee); IR(neat) 2960, 1732, 1458, 1260, 1034, 760 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 0.83—0.89 (m, 6H), 1.23—1.36 (m, 4H), 1.46—1.57 (m, 4H), 2.35—2.48 (m, 1H), 2.61—2.75 (m, 1H), 3.87—3.99 (m, 4H), 6.29—6.36 (m, 1H), 7.09—7.22 (m, 2H), 7.27—7.39 (m, 3H), 7.45—7.55 (m, 3H), 7.97—8.02 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 13.4 (2C), 18.5 (2C), 32.18, 32.25, 33.3 (d, \(J = 139\) Hz), 65.3 (d, \(J = 6.6\) Hz), 65.5 (d, \(J = 6.6\) Hz), 71.8, 116.8 (d, \(J = 22.2\) Hz), 118.4 (d, \(J = 9.1\) Hz), 123.8 (d, \(J = 4.1\) Hz), 126.5 (2C), 128.3, 128.5 (2C), 132.1, 134.5 (d, \(J = 9.1\) Hz), 139.6 (d, \(J = 9.9\) Hz), 161.9 (d, \(J = 256\) Hz), 162.68; MS [HR-FAB (M+H\(^+\))] calcd for C\(_{23}\)H\(_{31}\)FO\(_5\)P 437.1894 found 437.1941; HPLC chiralcel OJ-H column (4.6 mm\(\phi\), 250 mm), n-hexane : ethanol = 60 : 1, wavelength: 254 nm, flow rate: 0.5 ml/min, retention time: 31.4 min (enriched), 43.5 min.

**Dimethyl (R)-(2-hydroxy-2-(2-methylphenyl)ethyl)phosphonate (1e)**: Colorless oil; \([\alpha]_D^{20} = -21.0\) (c 1.4, acetone, 38% ee); IR(neat) 3350, 2955, 1462, 1227, 1075 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 2.06—2.26 (m, 2H), 2.34 (s, 3H), 3.56 (br s, 1H), 3.76 (d, \(J = 11.1\) Hz, 3H), 3.80 (d, \(J = 11.1\) Hz, 3H), 5.29—5.38 (m, 1H), 7.11—7.27 (m, 3H),
7.54 (d, $J = 7.2$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 18.6, 33.6 (d, $J = 7.2$ Hz), 52.1 (d, $J = 7.4$ Hz), 52.4 (d, $J = 7.4$ Hz), 64.9 (d, $J = 4.1$ Hz), 124.8, 126.1, 127.2, 130.1, 133.7, 141.7 (d, $J = 14.8$ Hz); MS [HR-EI (M$^+$)] calcd for C$_{11}$H$_7$O$_4$P 244.0865 found 244.0861; The ee of the dimethyl (R)-[2-hydroxy-2-(2-methylphenyl)ethyl]phosphonate (1e) was determined by HPLC of the corresponding dimethyl (S)-[2-(2-fluorobenzoyloxy)-2-(2-methylphenyl)ethyl]phosphonate (2e).

**Dimethyl (S)-[2-(2-fluorobenzoyloxy)-2-(2-methylphenyl)ethyl]phosphonate (2e):**

Colorless oil; [α]$_D^{20}$ $-27.0$ (c 0.83, acetone, 87% ee); IR(neat) 2955, 1728, 1300, 1262, 1040, 760 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 2.30—2.43 (m, 1H), 2.53 (s, 3H), 2.58—2.72 (m, 1H), 3.63 (d, $J = 11.1$ Hz, 3H), 3.64 (d, $J = 11.1$ Hz, 3H), 6.49—6.57 (m, 1H), 7.10—7.26 (m, 5H), 7.43—7.56 (m, 2H), 7.97—8.02 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 18.9, 32.0 (d, $J = 139$ Hz), 52.2 (d, $J = 6.6$ Hz), 52.3 (d, $J = 6.6$ Hz), 68.4, 116.8 (d, $J = 22.2$ Hz), 118.2 (d, $J = 9.9$ Hz), 123.9 (d, $J = 3.3$ Hz), 125.7, 126.3, 128.1, 130.5, 132.1, 134.5 (d, $J = 9.1$ Hz), 135.1, 138.1 (d, $J = 10.7$ Hz), 161.9 (d, $J = 259$ Hz), 162.7 (d, $J = 3.3$ Hz); MS [HR-EI (M$^+$)] calcd for C$_{18}$H$_{20}$FO$_5$P 366.1033 found 366.1021; HPLC chiralcel OJ-H column (4.6 mmφ, 250 mm), n-hexane : 2-propanol = 5 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 14.4 min (enriched), 18.3 min.

**Dimethyl (R)-[2-hydroxy-2-(3-methylphenyl)ethyl]phosphonate (1f):**

Colorless oil; [α]$_D^{20}$ $-11.3$ (c 1.2, acetone, 31% ee); IR(neat) 3370, 2956, 1489, 1248, 1082 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 2.10—2.34 (m, 2H), 2.36 (s, 3H), 3.62 (br s, 1H), 3.74 (d, $J = 11.1$ Hz, 3H), 3.78 (d, $J = 11.1$ Hz, 3H), 5.03—5.14 (m, 1H), 7.07—7.28 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 21.1, 34.8 (d, $J = 136$ Hz), 52.0 (d, $J = 6.6$ Hz), 52.3 (d, $J = 6.6$ Hz), 68.3 (d, $J = 4.1$ Hz), 122.3, 125.9, 128.1 (2C), 137.8, 143.7 (d, $J = 15.6$ Hz); MS [HR-EI (M$^+$)] calcd for C$_{11}$H$_{17}$O$_4$P 244.0865 found 244.0859; HPLC chiralcel OD-H column (4.6 mmφ, 250 mm) x 2, n-hexane : 2-propanol = 10 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 23.1 min (enriched), 25.4 min.

**Dimethyl (S)-[2-(2-fluorobenzoyloxy)-2-(3-methylphenyl)ethyl]phosphonate (2f):**
Colorless oil; $[\alpha]_D^{20} +9.2$ (c 1.4, acetone, 83% ee); IR(neat) 2955, 1732, 1615, 1456, 1264, 1048 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 2.33—2.46 (m, 1H), 2.36 (s, 3H), 2.61—2.75 (m, 1H), 3.63 (d, $J = 11.1$ Hz, 3H), 3.65 (d, $J = 11.1$ Hz, 3H), 6.26—6.33 (m, 1H), 7.09—7.30 (m, 6H), 7.47—7.55 (m, 1H), 7.97—8.02 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 21.2, 32.6 (d, $J = 140$ Hz), 52.1 (d, $J = 6.6$ Hz), 52.3 (d, $J = 6.6$ Hz), 71.5 (d, $J = 2.5$ Hz), 116.7 (d, $J = 22.2$ Hz), 118.3 (d, $J = 9.9$ Hz), 123.3, 123.8 (d, $J = 4.1$ Hz), 127.0, 128.4, 129.1, 132.1, 134.5 (d, $J = 9.1$ Hz), 138.1, 139.4 (d, $J = 11.5$ Hz), 161.8 (d, $J = 259$ Hz), 162.7 (d, $J = 4.1$ Hz); MS [HR-EI (M$^+$)] calcd for C$_{18}$H$_{20}$FO$_5$P 366.1032 found 366.1023; HPLC chiralcel OJ-H column (4.6 mm $\phi$, 250 mm), n-hexane : 2-propanol = 10 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 24.4 min (enriched), 31.1 min.

**Dimethyl (R)-[2-hydroxy-2-(4-methylphenyl)ethyl]phosphonate (1g):** White solid; Mp 57.0—57.5 °C (Et$_2$O); $[\alpha]_D^{20} —12.5$ (c 1.3, acetone, 38% ee); IR(neat) 3380, 2955, 1242, 1051, 830 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 2.10—2.29 (m, 2H), 2.34 (s, 3H), 3.56 (br s, 1H), 3.73 (d, $J = 11.1$ Hz, 3H), 3.75 (d, $J = 11.1$ Hz, 3H), 5.05—5.14 (m, 1H), 7.16 (d, $J = 9.0$ Hz, 2H), 7.28 (d, $J = 9.0$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 21.9, 34.9 (d, $J = 135$ Hz), 52.2 (d, $J = 6.6$ Hz), 52.4 (d, $J = 135$ Hz), 68.4 (d, $J = 4.1$ Hz), 125.3 (2C), 129.0 (2C), 137.2, 140.7 (d, $J = 15.6$ Hz); MS [HR-EI (M$^+$)] calcd for C$_{11}$H$_{17}$O$_4$P 244.0864 found 244.0869; The ee of the Dimethyl (R)-[2-hydroxy-2-(4-methylphenyl)ethyl]phosphonate (1g) was determined by HPLC of the corresponding Dimethyl (S)-[2-(2-fluorobenzoyloxy)-2-(4-methylphenyl)ethyl]phosphonate (2g).

**Dimethyl (S)-[2-(2-fluorobenzoyloxy)-2-(4-methylphenyl)ethyl]phosphonate (2g):** Colorless oil; $[\alpha]_D^{20} +2.8$ (c 1.3, acetone, 75% ee); IR(neat) 2955, 1738, 1615, 1456, 1266, 1084 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 2.31—2.48 (m, 1H), 2.34 (s, 3H), 2.62—2.76 (m, 1H), 3.63 (d, $J = 11.1$ Hz, 3H), 3.65 (d, $J = 11.1$ Hz, 3H), 6.26—6.34 (m, 1H), 7.09—7.22 (m, 4H), 7.37 (d, $J = 8.1$ Hz, 2H), 7.47—7.55 (m, 1H), 7.95—8.01 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 21.0, 32.4 (d, $J = 139$ Hz), 52.1 (d, $J = 6.6$ Hz), 52.3 (d, $J = 6.6$ Hz), 71.4, 116.7 (d, $J = 22.2$ Hz), 118.3 (d, $J = 9.1$ Hz), 123.8 (d, $J = 4.1$
Hz), 126.4 (2C), 129.1 (2C), 132.0, 134.4 (d, \( J = 9.1 \) Hz), 136.5 (d, \( J = 9.9 \) Hz), 138.2, 161.8 (d, \( J = 259 \) Hz), 162.7 (d, \( J = 4.1 \) Hz); MS \( [\text{HR-EI (M}^+\text{)}] \) calcd for \( \text{C}_{18}\text{H}_{20}\text{FO}_5\text{P} \) 366.1033 found 366.1021; HPLC chiral cel OD-H column (4.6 mmϕ, 250 mm) x 2, \( n \)-hexane : 2-propanol = 5 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 17.9 min (enriched), 21.0 min.

**Dimethyl (\( R \))-\([2\)-hydroxy-\( \text{-2-(2-methoxyphenyl)ethyl}\)]phosphonate (1h):** White solid; Mp 77.5—78.0 °C (Et\(_2\)O); \([\alpha]_D^{20}\) —20.4 (c 3.5, acetone, 38% ee); IR(neat) 3380, 2957, 1491, 1250, 1078 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta 2.16—2.43 \) (m, 2H), 3.70 (d, \( J = 11.1 \) Hz, 3H), 3.75 (br s, 1H), 3.78 (d, \( J = 11.1 \) Hz, 3H), 3.85 (s, 3H), 5.26—5.37 (m, 1H), 6.87 (d, \( J = 8.1 \) Hz, 1H), 6.99 (t, \( J = 7.5 \) Hz, 1H), 7.24—7.29 (m, 1H), 7.49 (d, \( J = 7.2 \) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta 32.6 \) (d, \( J = 134 \) Hz), 51.9 (d, \( J = 6.6 \) Hz), 52.1 (d, \( J = 6.6 \) Hz), 54.9, 64.0 (d, \( J = 4.9 \) Hz), 109.8, 120.4, 125.9, 128.1, 131.5 (d, \( J = 14.8 \) Hz), 155.3; MS \( [\text{HR-EI (M}^+\text{)}] \) calcd for \( \text{C}_{11}\text{H}_{17}\text{O}_5\text{P} \) 260.0814 found 260.0795; HPLC chiralcel OJ-H column (4.6 mmϕ, 250 mm), \( n \)-hexane : 2-propanol = 10 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 12.4 min, 14.5 min (enriched).

**Dimethyl (\( S \))-\([2\)-\( \text{2-fluorobenzoyloxy}-\text{-2-(2-methoxyphenyl)ethyl}\)]phosphonate (2h):** Colorless oil; \([\alpha]_D^{20}\) —17.4 (c 1.4, acetone, 74% ee); IR(neat) 2955, 1732, 1493, 1246, 1026 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta 2.54 \) (dd, \( J = 6.6, 16.2 \) Hz, 2H), 3.66 (d, \( J = 10.8 \) Hz, 3H), 3.68 (d, \( J = 10.8 \) Hz, 3H), 3.89 (s, 3H), 6.61—6.70 (m, 1H), 6.89—6.98 (m, 2H), 7.11—7.29 (m, 3H), 7.41—7.45 (m, 1H), 7.48—7.57 (m, 1H), 8.03—8.09 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta 30.6 \) (d, \( J = 138 \) Hz), 52.0 (d, \( J = 5.8 \) Hz), 52.1 (d, \( J = 5.8 \) Hz), 55.2, 66.7 (d, \( J = 4.1 \) Hz), 110.4, 116.6 (d, \( J = 22.2 \) Hz), 118.3 (d, \( J = 9.1 \) Hz), 120.4, 123.7 (d, \( J = 3.3 \) Hz), 126.0, 127.9 (d, \( J = 12.4 \) Hz), 129.0, 132.0, 134.3 (d, \( J = 8.2 \) Hz), 155.6, 161.7 (d, \( J = 259 \) Hz), 162.4 (d, \( J = 3.3 \) Hz); MS \( [\text{HR-EI (M}^+\text{)}] \) calcd for \( \text{C}_{18}\text{H}_{20}\text{FO}_5\text{P} \) 382.0982 found 382.0995; HPLC chiralcel OD-H column (4.6 mmϕ, 250 mm), \( n \)-hexane : 2-propanol = 10 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 21.9 min (enriched), 38.2 min.
Dimethyl (R)-[2-hydroxy-2-(4-methoxyphenyl)ethyl]phosphonate (1i): Colorless oil; $[\alpha]_D^{20} = -7.1$ (c 3.8, acetone, 29% ee); IR (neat) 3350, 2955, 1514, 1254, 1048, 837 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 2.04—2.34 (m, 2H), 3.53 (br s, 1H), 3.74 (d, $J = 10.8$ Hz, 3H), 3.77 (d, $J = 10.8$ Hz, 3H), 3.81 (s, 3H), 5.02—5.13 (m, 1H), 6.89 (d, $J = 8.7$ Hz, 2H), 7.31 (d, $J = 8.7$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 34.7 (d, $J = 136$ Hz), 51.9 (d, $J = 5.8$ Hz), 52.2 (d, $J = 5.8$ Hz), 54.8, 67.9, 113.4 (2C), 126.5 (2C), 135.9 (d, $J = 14.0$ Hz), 158.7; MS [HR-EI (M$^+$)] calcd for C$_{11}$H$_{17}$O$_5$P 260.0814 found 260.0800; HPLC chiralcel AY-H column (4.6 mm $\phi$, 250 mm), n-hexane : 2-propanol = 5 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 33.2 min (enriched), 41.4 min.

Dimethyl (S)-[2-(2-fluorobenzoyloxy)-2-(4-methoxyphenyl)ethyl]phosphonate (2i): Colorless oil; $[\alpha]_D^{20} = +1.7$ (c 1.4, acetone, 84% ee); IR (neat) 2955, 1728, 1613, 1516, 1248, 1030 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 2.34—2.48 (m, 1H), 2.66—2.76 (m, 1H), 3.62 (d, $J = 11.1$ Hz, 3H), 3.64 (d, $J = 11.1$ Hz, 3H), 3.80 (s, 3H), 6.25—6.33 (m, 1H), 6.90 (d, $J = 9.0$ Hz, 2H), 7.09—7.22 (m, 2H), 7.42 (d, $J = 9.0$ Hz, 2H), 7.47—7.54 (m, 1H), 7.94—8.00 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 32.3 (d, $J = 139$ Hz), 52.1 (d, $J = 6.6$ Hz), 52.2 (d, $J = 6.6$ Hz), 55.0, 71.2, 113.7 (2C), 116.7 (d, $J = 22.2$ Hz), 118.3 (d, $J = 9.9$ Hz), 123.7 (d, $J = 4.1$ Hz), 127.9 (2C), 131.4 (d, $J = 9.9$ Hz), 131.9, 134.4 (d, $J = 9.1$ Hz), 159.5, 161.7 (d, $J = 259$ Hz), 162.7 (d, $J = 3.3$ Hz); MS [HR-EI (M$^+$)] calcd for C$_{18}$H$_{20}$FO$_6$P 382.0982 found 382.0995; HPLC chiralcel OD-H column (4.6 mm $\phi$, 250 mm) x 2, n-hexane : 2-propanol = 5 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 28.4 min (enriched), 35.0 min.

Dimethyl (R)-[2-hydroxy-2-(4-nitrophenyl)ethyl]phosphonate (1j)$^{11}$: Pale yellow solid; Mp 115—116 °C (Et$_2$O); $[\alpha]_D^{20} = -7.6$ (c 1.0, acetone, 29% ee); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 2.16—2.24 (m, 2H), 3.75 (d, $J = 10.8$ Hz, 3H), 3.81 (d, $J = 10.8$ Hz, 3H), 4.29 (br s, 1H), 5.18—5.26 (m, 1H), 7.58 (d, $J = 8.4$ Hz, 2H), 8.22 (d, $J = 8.7$ Hz, 2H); The ee of the Dimethyl (R)-[2-hydroxy-2-(4-nitrophenyl)ethyl]phosphonate (1j) was determined by HPLC of the corresponding Dimethyl (S)-[2-(2-fluorobenzoyloxy)-2-(4-nitrophenyl)ethyl]phosphonate (2j).
Dimethyl (S)-[2-(2-fluorobenzoyloxy)-2-(4-nitrophenyl)ethyl]phosphonate (2j): Pale yellow oil; \([\alpha]_D^{20} = -2.3\) (c 1.3, acetone, 57% ee); IR(neat) 2957, 1738, 1615, 1219, 1123, 772 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 2.34—2.49 (m, 1H), 2.61—2.74 (m, 1H), 3.67 (d, \(J = 11.1\) Hz, 3H), 3.69 (d, \(J = 11.1\) Hz, 3H), 6.34—6.32 (m, 1H), 7.13—7.24 (m, 2H), 7.52—7.60 (m, 1H), 7.67 (d, \(J = 9.3\) Hz, 2H), 7.96—8.02 (m, 1H), 8.25 (d, \(J = 9.0\) Hz, 2H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 32.4 (d, \(J = 141\) Hz), 52.4 (d, \(J = 5.8\) Hz), 52.5 (d, \(J = 5.8\) Hz), 70.7, 117.0 (d, \(J = 22.2\) Hz), 117.7 (d, \(J = 9.1\) Hz), 123.8 (2C), 124.1 (d, \(J = 4.1\) Hz), 127.4 (2C), 132.2, 135.1 (d, \(J = 9.1\) Hz), 146.5 (d, \(J = 9.9\) Hz), 147.7, 161.9 (d, \(J = 259\) Hz), 162.8 (d, \(J = 3.3\) Hz); MS [HR-EI (M\(^+\))] calcd for C\(_{17}\)H\(_{17}\)F\(_2\)N\(_2\)O\(_7\)P 397.0726 found 397.0735; HPLC chiralcel AS column (4.6 mm\(\phi\), 250 mm) x 2, n-hexane : 2-propanol = 1 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 34.9 min (enriched), 42.1 min.

Dimethyl (R)-[2-hydroxy-2-(4-fluorophenyl)ethyl]phosphonate (1k): Colorless oil; \([\alpha]_D^{20} = -12.3\) (c 1.0, acetone, 41% ee); IR(neat) 3360, 2957, 1514, 1258, 1076, 845 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 2.09—2.30 (m, 2H), 3.71 (br s, 1H), 3.74 (d, \(J = 10.8\) Hz, 3H), 3.78 (d, \(J = 10.8\) Hz, 3H), 5.05—5.16 (m, 1H), 7.01—7.07 (m, 2H), 7.34—7.19 (m, 2H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 34.8 (d, \(J = 137\) Hz), 51.9 (d, \(J = 6.6\) Hz), 52.2 (d, \(J = 6.6\) Hz), 67.7, 114.8 (d, \(J = 21.4\) Hz, 2C), 127.0 (d, \(J = 8.2\) Hz, 2C), 139.7 (d, \(J = 14.0\) Hz), 161.8 (d, \(J = 245\) Hz); MS [HR-EI (M\(^+\))] calcd for C\(_{10}\)H\(_{14}\)FO\(_4\)P 248.0614 found 248.0592; HPLC chiralcel AY-H column (4.6 mm\(\phi\), 250 mm), n-hexane : 2-propanol = 20 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 38.1 min (enriched), 41.5 min.

Dimethyl (S)-[2-(2-fluorobenzoyloxy)-2-(4-fluorophenyl)ethyl]phosphonate (2k): Colorless oil; \([\alpha]_D^{20} = +2.1\) (c 2.4, acetone, 72% ee); IR(neat) 2957, 1732, 1615, 1514, 1264, 1080 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 2.32—2.47 (m, 1H), 2.61—2.74 (m, 1H), 3.63 (d, \(J = 10.8\) Hz, 3H), 3.65 (d, \(J = 10.8\) Hz, 3H), 6.27—6.34 (m, 1H), 7.04—7.23 (m, 4H), 7.43—7.56 (m, 3H), 7.94—8.00 (m, 1H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 32.4 (d, \(J = 140\) Hz), 52.2 (d, \(J = 6.6\) Hz), 52.3 (d, \(J = 6.6\) Hz), 71.0, 115.4 (d,
\( J = 21.4 \text{ Hz, } 2 \text{C} \), 116.8 (d, \( J = 22.2 \text{ Hz} \)), 118.1 (d, \( J = 9.1 \text{ Hz} \)), 123.9 (d, \( J = 4.1 \text{ Hz} \)), 128.4 (d, \( J = 8.2 \text{ Hz, } 2 \text{C} \)), 132.1, 134.7 (d, \( J = 8.2 \text{ Hz} \)), 135.3 (dd, \( J = 3.3, 9.9 \text{ Hz} \)), 161.8 (d, \( J = 259 \text{ Hz} \)), 162.5 (d, \( J = 246 \text{ Hz} \)), 162.8; MS [HR-EI (M⁺)] calcd for \( \text{C}_{17}\text{H}_{17}\text{F}_{2}\text{O}_{5}\text{P} \) 370.0782 found 370.0756; HPLC chiralcel OD-H column (4.6 mmϕ, 250 mm) x 2, \( n \)-hexane : 2-propanol = 5: 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 21.5 min (enriched), 24.2 min.

**Dimethyl \((R)\)-[2-hydroxy-2-(4-chlorophenyl)ethyl]phosphonate (1l):**  White solid; Mp 60.5—61.0 °C (Et₂O and \( n \)-hexane); \([\alpha]_D^{20} \) —9.2 (c 1.8, acetone, 37% ee); IR(neat) 3350, 2955, 1242, 1051, 835, 546 cm⁻¹; \(^1\text{H NMR} \) (300 MHz, CDCl₃) \( \delta \) 2.10—2.26 (m, 2H), 3.73 (d, \( J = 11.1 \text{ Hz, } 3 \text{H} \)), 3.78 (d, \( J = 11.1 \text{ Hz, } 3 \text{H} \)), 3.82 (s, 1H), 5.05—5.14 (m, 1H), 7.30—7.36 (m, 4H); \(^{13}\text{C NMR} \) (100 MHz, CDCl₃) \( \delta \) 34.5 (d, \( J = 137 \text{ Hz} \)), 51.7 (d, \( J = 5.8 \text{ Hz} \)), 52.1 (d, \( J = 5.8 \text{ Hz} \)), 67.5 (d, \( J = 3.3 \text{ Hz} \)), 126.7 (2C), 128.0 (2C), 132.6, 142.5 (d, \( J = 14.8 \text{ Hz} \)); MS [HR-EI (M⁺)] calcd for \( \text{C}_{10}\text{H}_{14}\text{ClO}_{4}\text{P} \) 264.0319 found 264.0303; HPLC chiralcel AY-H column (4.6 mmϕ, 250 mm), \( n \)-hexane : 2-propanol = 10 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 22.6 min (enriched), 29.4 min.

**Dimethyl \((S)\)-[2-(4-chlorophenyl)-2-(2-fluorobenzoyloxy)ethyl]phosphonate (2l):**  Colorless oil; \([\alpha]_D^{20} \) —9.0 (c 1.2, acetone, 66% ee); IR(neat) 3350, 2955, 1732, 1294, 1260, 1040, 758 cm⁻¹; \(^1\text{H NMR} \) (300 MHz, CDCl₃) \( \delta \) 2.31—2.46 (m, 1H), 2.59—2.72 (m, 1H), 3.64 (d, \( J = 10.8 \text{ Hz, } 3 \text{H} \)), 3.66 (d, \( J = 10.8 \text{ Hz, } 3 \text{H} \)), 6.25—6.32 (m, 1H), 7.10—7.24 (m, 2H), 7.35 (d, \( J = 8.4 \text{ Hz, } 2 \text{H} \)), 7.43 (d, \( J = 8.4 \text{ Hz, } 2 \text{H} \)), 7.49—7.57 (m, 1H), 7.94—8.00 (m, 1H); \(^{13}\text{C NMR} \) (100 MHz, CDCl₃) \( \delta \) 32.3 (d, \( J = 140 \text{ Hz} \)), 52.2 (d, \( J = 5.8 \text{ Hz} \)), 52.3 (d, \( J = 5.8 \text{ Hz} \)), 70.9, 116.8 (d, \( J = 22.2 \text{ Hz} \)), 118.0 (d, \( J = 9.9 \text{ Hz} \)), 123.9 (d, \( J = 4.1 \text{ Hz} \)), 127.9 (2C), 128.6 (2C), 132.0, 134.1, 134.6 (d, \( J = 9.1 \text{ Hz} \)), 137.9 (d, \( J = 9.9 \text{ Hz} \)), 161.8 (d, \( J = 259 \text{ Hz} \)), 162.6 (d, \( J = 4.1 \text{ Hz} \)); MS [HR-EI (M⁺)] calcd for \( \text{C}_{17}\text{H}_{17}\text{ClF}_{3}\text{O}_{5}\text{P} \) 386.0486 found 386.0500; HPLC chiralcel OD-H column (4.6 mmϕ, 250 mm) x 2, \( n \)-hexane : 2-propanol = 5: 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 21.2 min (enriched), 24.4 min.
Dimethyl (R)-[2-hydroxy-2-(4-bromophenyl)ethyl]phosphonate (1m): White solid; Mp 91.0—92.0 °C (Et₂O); [α]D²⁰ —11.5 (c 0.68, acetone, 49% ee); IR(neat) 3365, 2955, 1242, 1069, 828, 544 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.06—2.25 (m, 2H), 3.70—3.80 (m, 6H), 3.98 (br s, 1H), 5.01—5.13 (m, 1H), 7.25—7.29 (m, 2H), 7.44—7.51 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 34.7 (d, J = 137 Hz), 52.1 (d, J = 6.6 Hz), 52.4 (d, J = 6.6 Hz), 67.8 (d, J = 4.1 Hz), 121.1, 127.1 (2C), 131.3 (2C), 142.9 (d, J = 14.8 Hz); MS [HR-EI (M⁺)] calcd for C₁₀H₁₄⁷⁹BrO₄P 307.9814 found 307.9789; HPLC chiralcel AY-H column (4.6 mmϕ, 250 mm), n-hexane : 2-propanol = 10 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 23.4 min (enriched), 33.8 min.

Dimethyl (S)-[2-(4-bromophenyl)-2-(2-fluorobenzoyloxy)ethyl]phosphonate (2m): Colorless oil; [α]D²⁰ —9.6 (c 1.3, acetone, 60% ee); IR(neat) 2955, 1732, 1489, 1258, 1036, 758 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.30—2.45 (m, 1H), 2.59—2.72 (m, 1H), 3.64 (d, J = 10.8 Hz, 3H), 3.66 (d, J = 10.8 Hz, 3H), 6.23—6.31 (m, 1H), 7.10—7.23 (m, 2H), 7.36 (d, J = 8.7 Hz, 2H), 7.49—7.57 (m, 3H), 7.94—8.00 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 32.3 (d, J = 140 Hz), 52.2 (d, J = 6.6 Hz), 52.3 (d, J = 6.6 Hz), 70.9, 116.8 (d, J = 22.2 Hz), 117.9 (d, J = 9.9 Hz), 122.29, 123.9 (d, J = 4.1 Hz), 128.1 (2C), 131.6 (2C), 132.0, 134.7 (d, J = 9.1 Hz), 138.4 (d, J = 9.9 Hz), 161.7 (d, J = 259 Hz), 162.6 (d, J = 3.3 Hz); MS [HR-FAB (M+H)⁺] calcd for C₁₇H₁₈⁷⁹BrO₅P 431.0059 found 431.0085; HPLC chiralcel OD-H column (4.6 mmϕ, 250 mm) x 2, n-hexane : 2-propanol = 5 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 22.5 min (enriched), 26.2 min.

Dimethyl (R)-[2-hydroxy-2-(1-naphthyl)ethyl]phosphonate (1n): Colorless oil; [α]D²⁰ —27.6 (c 2.6, acetone, 43% ee); IR(neat) 3350, 2955, 1231, 1044, 781 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.24—2.48 (m, 2H), 3.77 (d, J = 10.8 Hz, 3H), 3.84 (d, J = 10.8 Hz, 3H), 3.89 (br s, 1H), 5.86—5.94 (m, 1H), 7.47—7.57 (m, 3H), 7.78 (t, J = 8.7 Hz, 2H), 7.86—7.90 (m, 1H), 8.01 (d, J = 8.1 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 33.9 (d, J = 136 Hz), 51.7 (d, J = 6.6 Hz), 52.3 (d, J = 6.6 Hz), 65.1 (d, J = 4.9 Hz), 122.4 (2C), 125.07, 125.10, 125.8, 127.5, 128.5, 129.3, 133.3, 139.5 (d, J = 15.6 Hz);
MS [HR-EI (M+)] calcd for C_{14}H_{17}O_{4}P 280.0865 found 280.0857; HPLC chiralcel OJ-H column (4.6 mmφ, 250 mm), n-hexane : 2-propanol = 20 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 20.9 min, 23.4 min (enriched).

Dimethyl (S)-[2-(2-fluorobenzoyloxy)-2-(1-naphthyl)ethyl]phosphonate (2n):
Colorless oil; [α]_D^{20} —60.0 (c 2.2, acetone, 79% ee); IR(neat) 2955, 1732, 1298, 1260, 1038, 758 cm^{-1}; ^1H NMR (300 MHz, CDCl₃) δ 2.54—2.67 (m, 1H), 2.73—2.86 (m, 1H), 3.65 (d, J = 11.1 Hz, 3H), 3.67 (d, J = 11.1 Hz, 3H), 7.05—7.28 (m, 3H), 7.44—7.63 (m, 4H), 7.69 (d, J = 7.2 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.88 (d, J = 8.1 Hz, 1H), 8.05 (dt, J = 1.8, 7.5 Hz, 1H), 8.26 (d, J = 8.4 Hz, 1H); ^13C NMR (100 MHz, CDCl₃) δ 32.2 (d, J = 139 Hz), 52.3 (d, J = 6.6 Hz), 52.4 (d, J = 6.6 Hz), 69.1, 116.9 (d, J = 22.2 Hz), 118.2 (d, J = 9.9 Hz), 122.9, 123.9, 124.0, 125.2, 125.8, 126.6, 128.91, 128.94, 129.6, 132.2, 133.8, 134.6 (d, J = 9.1 Hz), 135.5 (d, J = 12.3 Hz), 161.9 (d, J = 259 Hz), 162.8 (d, J = 4.1 Hz); MS [HR-FAB (M+H)] calcd for C_{21}H_{21}FO_{5}P 403.1110 found 403.1112; HPLC chiralcel OD-H column (4.6 mmφ, 250 mm), n-hexane : 2-propanol = 5 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 12.2 min, 20.0 min (enriched).

Dimethyl (R)-[2-hydroxy-2-(2-naphthyl)ethyl]phosphonate (1o):
White solid; Mp 57.0—57.5 °C (Et₂O); [α]_D^{20} —14.3 (c 1.0, acetone, 47% ee); IR(neat) 3330, 2955, 1423, 1049, 857 cm^{-1}; ^1H NMR (300 MHz, CDCl₃) δ 2.21—2.41 (m, 2H), 3.73 (d, J = 10.8 Hz, 3H), 3.80 (d, J = 10.8 Hz, 3H), 3.82 (br s, 1H), 5.24—5.35 (m, 1H), 7.45—7.53 (m, 3H), 7.81—7.88 (m, 4H); ^13C NMR (100 MHz, CDCl₃) δ 34.9 (d, J = 136 Hz), 52.2 (d, J = 6.6 Hz), 52.6 (d, J = 6.6 Hz), 68.7 (d, J = 4.1 Hz), 123.5, 124.1, 125.8, 126.1, 127.5, 127.9, 128.2, 132.8, 133.1, 141.0 (d, J = 15.6 Hz); MS [HR-EI (M⁺)] calcd for C_{14}H_{17}O_{4}P 280.0865 found 280.0857; HPLC chiralcel OD-H column (4.6 mmφ, 250 mm), n-hexane : 2-propanol = 5 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 11.3 min, 16.2 min (enriched).

Dimethyl (S)-[2-(2-fluorobenzoyloxy)-2-(2-naphthyl)ethyl]phosphonate (2o):
Colorless oil; [α]_D^{20} —24.6 (c 1.2, acetone, 72% ee); IR(neat) 2955, 1728, 1613, 1256,
1040, 760 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 2.44—2.57 (m, 1H), 2.72—2.86 (m, 1H), 3.61 (d, $J$ = 10.8 Hz, 3H), 3.65 (d, $J$ = 10.8 Hz, 3H), 6.47—6.55 (m, 1H), 7.10—7.24 (m, 2H), 7.47—7.60 (m, 4H), 7.80—7.88 (m, 3H), 7.94—8.04 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 32.4 (d, $J$ = 139 Hz), 52.1 (d, $J$ = 6.6 Hz), 52.2 (d, $J$ = 6.6 Hz), 71.6, 116.7 (d, $J$ = 22.2 Hz), 118.2 (d, $J$ = 9.9 Hz), 123.6, 123.8 (d, $J$ = 4.1 Hz), 125.8, 126.16, 126.18, 127.4, 127.9, 128.4, 123.0, 123.8, 133.0, 134.5 (d, $J$ = 9.1 Hz), 136.6 (d, $J$ = 9.9 Hz), 161.7 (d, $J$ = 259 Hz), 162.7 (d, $J$ = 3.3 Hz); MS [HR-FAB (M+H)$^+$] calcd for C$_{21}$H$_{21}$FO$_5$P 403.1110 found 403.1112; HPLC chiralcel OD-H column (4.6 mm$\phi$, 250 mm) x 2, $n$-hexane : 2-propanol = 5 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 36.8 min (enriched), 44.2 min.

**Dimethyl (R)-(2-hydroxypropyl)phosphonate (1p)$^{2c}$**: Colorless oil; [$\alpha$]$^D_{20}$ $-1.4$ (c 0.46, acetone, 10% ee); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.29 (dd, $J$ = 2.4, 6.3 Hz, 3H), 1.91—1.99 (m, 2H), 3.29 (br s, 1H), 3.77 (d, $J$ = 11.1 Hz, 3H), 3.78 (d, $J$ = 11.1 Hz, 3H), 4.14—4.27 (m, 1H); The ee of the dimethyl (R)-(2-hydroxypropyl)phosphonate (1p) was determined by HPLC of the corresponding dimethyl (S)-[2-(2-fluorobenzoyloxy)propyl]phosphonate (2p).

**Dimethyl (S)-[2-(2-fluorobenzoyloxy)propyl]phosphonate (2p)**: Colorless oil; [$\alpha$]$^D_{20}$ $+15.2$ (c 1.0, acetone, 57% ee); IR(neat) 2957, 1728, 1456, 1264, 1063, 762 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.52 (d, $J$ = 6.3 Hz, 3H), 2.08—2.22 (m, 1H), 2.32—2.44 (m, 1H), 3.74 (d, $J$ = 10.8 Hz, 3H), 3.76 (d, $J$ = 10.8 Hz, 3H), 5.40—5.51 (m, 1H), 7.11—7.23 (m, 2H), 7.50—7.57 (m, 1H), 7.92—7.99 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 21.1 (d, $J$ = 7.4 Hz), 31.7 (d, $J$ = 139 Hz), 52.4 (d, $J$ = 6.6 Hz, 2C), 67.1, 116.9 (d, $J$ = 21.4 Hz), 118.7 (d, $J$ = 9.1 Hz), 123.9 (d, $J$ = 4.1 Hz), 132.0, 134.5 (d, $J$ = 8.2 Hz), 161.9 (d, $J$ = 259 Hz), 163.3 (d, $J$ = 3.3 Hz); MS [HR-EI (M$^+$)] calcd for C$_{12}$H$_{16}$FO$_5$P 290.0719 found 290.0721; HPLC chiralcel OD-H column (4.6 mm$\phi$, 250 mm), $n$-hexane : 2-propanol = 10 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 13.4 min, 15.0 min (enriched).

**Dimethyl (E)-(R)-(2-hydroxy-4-phenylbut-3-enyl)phosphonate (1q)**: Colorless oil;...
\[ \alpha \]_D \, ^{20} +3.0 \ (c\ 1.2, \ \text{acetone, 38\% ee}); \ \text{IR(neat)} \ 3420, 2955, 1651, 1260, 1078 cm\textsuperscript{-1}; \ \text{H NMR (300 MHz, CDCl}_3) \ \delta \ 2.10—2.18 \ (m, 2H), 3.44 \ (br\ s, 1H), 3.77 \ (d, \ J = 10.8\ Hz, 3H), 3.79 \ (d, \ J = 10.8\ Hz, 3H), 4.67—4.80 \ (m, 1H), 6.24 \ (dd, \ J = 6.3, 15.9\ Hz, 1H), 6.67 \ (d, \ J = 15.9\ Hz, 1H), 7.23—7.41 \ (m, 5H); \ \text{C NMR (100 MHz, CDCl}_3) \ \delta \ 32.9 \ (d, \ J = 137\ Hz), 52.1 \ (d, \ J = 6.6\ Hz), 52.3 \ (d, \ J = 6.6\ Hz), 66.9 \ (d, \ J = 3.3\ Hz), 126.2 \ (2C), 127.4, 128.3 \ (2C), 129.8, 131.2 \ (d, \ J = 14.0\ Hz), 136.2; \ \text{MS [HR-EI (M\^+)] \ calcd for C}_{12}\text{H}_{17}\text{O}_4\text{P} 256.0865 \ \text{found} 256.0875; \ \text{HPLC chiralcel OD-H column (4.6 mmφ, 250 mm), n-hexane : 2-propanol = 10 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 21.0 min, 32.4 min (enriched).}

\textbf{Dimethyl (E)-(S)-[2-(2-fluorobenzoxyloxy)-4-phenylbut-3-enyl]phosphonate (2q):} Colorless oil; \[ \alpha \]_D \, ^{20} —13.3 \ (c\ 0.80, \ \text{acetone, 58\% ee}); \ \text{IR(neat)} \ 2955, 1728, 1293, 1252, 1032, 756 cm\textsuperscript{-1}; \ \text{H NMR (300 MHz, CDCl}_3) \ \delta \ 2.29—2.59 \ (m, 2H), 3.72 \ (d, \ J = 11.1\ Hz, 3H), 3.74 \ (d, \ J = 11.1\ Hz, 3H), 5.93—6.04 \ (m, 1H), 6.33 \ (dd, \ J = 7.5, 15.9\ Hz, 1H), 6.81 \ (d, \ J = 15.9\ Hz, 1H), 7.11—7.34 \ (m, 5H), 7.40—7.43 \ (m, 2H), 7.50—7.57 \ (m, 1H), 7.98—8.03 \ (m, 1H); \ \text{C NMR (100 MHz, CDCl}_3) \ \delta \ 30.8 \ (d, \ J = 139\ Hz), 52.3 \ (d, \ J = 6.6\ Hz), 52.5 \ (d, \ J = 6.6\ Hz), 70.4, 116.9 \ (d, \ J = 22.2\ Hz), 118.5 \ (d, \ J = 9.9\ Hz), 123.9 \ (d, \ J = 4.1\ Hz), 126.1 \ (d, \ J = 9.1\ Hz), 126.7 \ (2C), 128.1, 128.5 \ (2C), 132.1, 133.5, 134.6 \ (d, \ J = 9.1\ Hz), 135.7, 161.9 \ (d, \ J = 259\ Hz), 162.9 \ (d, \ J = 4.1\ Hz); \ \text{MS [HR-EI (M\^+)] \ calcd for C}_{19}\text{H}_{20}\text{FO}_5\text{P} 378.1032 \ \text{found} 378.1028; \ \text{HPLC chiralcel OJ-H column (4.6 mmφ, 250 mm), n-hexane : 2-propanol = 10 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 42.0 min (enriched), 52.6 min.}

\textbf{Dimethyl (R)-(2-hydroxy-4-phenylbut-3-ynyl)phosphonate (1r):} Colorless oil; \[ \alpha \]_D \, ^{20} +3.4 \ (c\ 0.99, \ \text{acetone, 50\% ee}); \ \text{IR(neat)} \ 3375, 2957, 2359, 1491, 1260, 1069 cm\textsuperscript{-1}; \ \text{H NMR (300 MHz, CDCl}_3) \ \delta \ 2.38 \ (dd, \ J = 5.7, 16.8\ Hz, 2H), 3.67 \ (br\ s, 1H), 3.80 \ (d, \ J = 11.1\ Hz, 3H), 3.81 \ (d, \ J = 11.1\ Hz, 3H), 4.94—5.07 \ (m, 1H), 7.30—7.36 \ (m, 3H), 7.41—7.46 \ (m, 2H); \ \text{C NMR (100 MHz, CDCl}_3) \ \delta \ 33.6 \ (d, \ J = 137\ Hz), 52.1 \ (d, \ J = 6.6\ Hz), 52.4 \ (d, \ J = 6.6\ Hz), 57.0, 84.1, 89.2 \ (d, \ J = 15.6\ Hz), 122.1, 127.9 \ (2C), 128.1, 131.2 \ (2C); \ \text{MS [HR-EI (M\^+)] \ calcd for C}_{12}\text{H}_{15}\text{O}_4\text{P} 254.0708 \ \text{found} 254.0700; \ \text{HPLC chiralcel OD-H column (4.6 mmφ, 250 mm), n-hexane : 2-propanol = 10 : 1,
wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 14.9 min, 19.3 min (enriched).

**Dimethyl (S)-[2-(2-fluorobenzoyloxy)-4-phenylbut-3-ynyl]phosphonate (2r):**
Colorless oil; \([\alpha]_D^{20} +4.6\) (c 0.59, acetone, 47% ee); IR(neat) 2955, 1736, 1491, 1252, 1036, 758 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 2.51—2.73 (m, 2H), 3.78 (d, \(J = 10.8\) Hz, 6H), 6.09—6.17 (m, 1H), 7.12—7.34 (m, 5H), 7.44—7.48 (m, 2H), 7.51—7.59 (m, 1H), 8.01—8.06 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 31.4 (d, \(J = 141\) Hz), 52.5 (d, \(J = 5.8\) Hz), 52.6 (d, \(J = 5.8\) Hz), 60.1, 85.0 (d, \(J = 12.4\) Hz), 86.2, 116.9 (d, \(J = 22.2\) Hz), 117.8 (d, \(J = 9.1\) Hz), 121.6, 123.9 (d, \(J = 4.1\) Hz), 128.1 (2C), 128.8, 131.7 (2C), 132.1, 134.8 (d, \(J = 9.1\) Hz), 162.0 (d, \(J = 260\) Hz), 162.4 (d, \(J = 4.1\) Hz); MS [HR-EI (M\(^+\))] calcd for C\(_{19}\)H\(_{18}\)FO\(_5\)P 376.0876 found 376.0866; HPLC chiralcel OJ-H column (4.6 mm\(\phi\), 250 mm), \(n\)-hexane : 2-propanol = 10 : 1, wavelength: 254 nm, flow rate: 1.0 mL/min, retention time: 42.6 min (enriched), 52.7 min.

**Diethyl (R)-[2-hydroxy-2-(2-methylphenyl)ethyl]phosphonate (1s):** White solid; Mp 52.5—54.5 °C (\(n\)-hexane); \([\alpha]_D^{20} —25.8\) (c 0.91, acetone, 60% ee); IR(neat) 3360, 2984, 1221, 1030, 965, 768 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 1.33 (t, \(J = 6.9\) Hz, 3H), 1.37 (t, \(J = 6.9\) Hz, 3H), 2.10—2.18 (m, 2H), 2.34 (s, 3H), 3.80 (s, 1H), 4.07—4.23 (m, 4H), 5.29—5.37 (m, 1H), 7.12—7.24 (m, 3H), 7.55 (d, \(J = 7.2\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 15.58 (d, \(J = 2.0\) Hz), 15.65 (d, \(J = 2.0\) Hz), 18.2, 34.2 (d, \(J = 135\) Hz), 60.9 (d, \(J = 6.6\) Hz), 61.1 (d, \(J = 6.6\) Hz), 64.4 (d, \(J = 4.1\) Hz), 124.6, 125.5, 126.5, 129.5, 133.3, 141.7 (d, \(J = 14.0\) Hz); MS [HR-EI (M\(^+\))] calcd for C\(_{13}\)H\(_{21}\)O\(_4\)P 272.1177 found 272.1096; HPLC chiralcel OD-H column (4.6 mm\(\phi\), 250 mm), \(n\)-hexane : 2-propanol = 30 : 1, wavelength: 254 nm, flow rate: 1.0 ml/min, retention time: 18.7 min (enriched), 24.1 min.

**Diethyl (S)-[2-(2-fluorobenzoyloxy)-2-(2-methylphenyl)ethyl]phosphonate (2s):** Colorless oil; \([\alpha]_D^{20} —24.1\) (c 1.1, acetone, 78% ee); IR(neat) 2986, 1728, 1298, 1250, 1026, 770 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 1.20 (t, \(J = 6.9\) Hz, 3H), 1.21 (t, \(J = 6.9\) Hz, 3H), 2.29—2.42 (m, 1H), 2.53 (s, 3H), 2.56—2.70 (m, 1H), 3.92—4.08 (m, 4H),
Diethyl (R)-[2-hydroxy-2-(4-methoxyphenyl)ethyl]phosphonate (1t): Colorless oil; 
$[\alpha]_D ^{20} = -12.4$ (c 1.6, acetone, 59% ee); IR(neat) 3360, 2986, 1514, 1254, 1044, 835 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.31 (t, $J = 7.2$ Hz, 3H), 1.35 (t, $J = 7.2$ Hz, 3H), 2.09—2.30 (m, 2H), 3.78 (s, 1H), 3.81 (s, 3H), 4.05—4.21 (m, 4H), 5.03—5.12 (m, 1H), 6.89 (d, $J = 9.0$ Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 2H); $^1$C NMR (100 MHz, CDCl$_3$) $\delta$ 16.0, 16.1, 35.6, 54.9, 61.4, 61.6, 68.1, 113.5, 115.4, 116.6, 118.4, 123.7, 127.9, 131.5, 131.9, 134.3, 135.1, 138.3, 161.9 (d, $J = 9.9$ Hz), 162.7 (d, $J = 4.1$ Hz); MS [HR-FAB (M+H)$^+$] calcd for C$_{20}$H$_{25}$FO$_5$P 395.1424 found 395.1438; HPLC chiralcel OD-H column (4.6 mmφ, 250 mm), $n$-hexane : 2-propanol = 20 : 1, wavelength: 254 nm, flow rate: 0.7 ml/min, retention time: 17.0 min (enriched), 22.9 min.

Diethyl (S)-[2-(2-fluorobenzoyloxy)-2-(4-methoxyphenyl)ethyl]phosphonate (2t): Colorless oil; $[\alpha]_D ^{20} = +0.95$ (c 0.96, acetone, 77% ee); IR(neat) 2986, 1728, 1615, 1516, 1254, 1034 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.20 (t, $J = 7.2$ Hz, 3H), 1.21 (t, $J = 7.2$ Hz, 3H), 2.33—2.47 (m, 1H), 2.61—2.75 (m, 1H), 3.80 (s, 3H), 3.94—4.08 (m, 4H), 6.26—6.33 (m, 1H), 6.89 (d, $J = 8.7$ Hz, 2H), 7.09—7.21 (m, 2H), 7.42 (d, $J = 8.7$ Hz, 2H), 7.47—7.54 (m, 1H), 7.95—8.01 (m, 1H); $^1$C NMR (100 MHz, CDCl$_3$) $\delta$ 15.94, 16.00, 33.2, 55.0, 61.4, 61.5, 61.5, 71.4, 113.7, 116.6, 118.4, 123.7, 127.9, 131.5, 131.9, 134.3, 135.1, 159.4, 161.7, 162.6 (d, $J = 3.3$ Hz); MS [HR-FAB (M+H)$^+$] calcd for C$_{20}$H$_{25}$FO$_6$P 411.1372 found
411.1376; HPLC chiralcel OD-H column (4.6 mmφ, 250 mm), n-hexane : 2-propanol = 10 : 1, wavelength: 254 nm, flow rate: 0.5 ml/min, retention time: 24.9 min (enriched), 30.7 min.

**Diethyl (R)-[2-hydroxy-2-(1-naphthyl)ethyl]phosphonate (1u):** White solid; Mp 44.0—46.0 °C (n-hexane); [α]D20 —31.5 (c 0.76, acetone, 47% ee); IR(neat) 3350, 2986, 1221, 1026, 776 cm−1; 1H NMR (300 MHz, CDCl3) δ 1.32 (t, J = 6.9 Hz, 3H), 1.42 (t, J = 6.9 Hz, 3H), 2.17—2.48 (m, 2H), 4.05—4.30 (m, 5H), 5.85—5.93 (m, 1H), 7.48—7.56 (m, 3H), 7.78 (t, J = 8.1 Hz, 2H), 7.88 (d, J = 8.7 Hz, 1H), 8.01 (d, J = 8.1 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ 15.59 (d, J = 3.3 Hz), 15.65 (d, J = 3.3 Hz), 34.7 (d, J = 136 Hz), 60.9 (d, J = 6.6 Hz), 61.4 (d, J = 6.6 Hz), 65.0 (d, J = 4.1 Hz), 122.27, 122.31, 124.80, 124.87, 125.4, 127.2, 128.2, 129.2, 133.1, 139.5 (d, J = 14.8 Hz); MS [HR-EI (M+)] calcd for C16H21O4P 308.1178 found 308.1165; HPLC chiralcel OD-H column (4.6 mmφ, 250 mm), n-hexane : 2-propanol = 30 : 1, wavelength: 254 nm, flow rate: 1.0 ml/min, retention time: 25.2 min (enriched), 32.5 min.

**Diethyl (S)-[2-(2-fluorobenzoyloxy)-2-(1-naphthyl)ethyl]phosphonate (2u):** Colorless oil; [α]D20 —44.9 (c 1.0, acetone, 61% ee); IR(neat) 2984, 1732, 1296, 1250, 1024, 970 cm−1; 1H NMR (300 MHz, CDCl3) δ 1.19 (t, J = 6.9 Hz, 3H), 1.20 (t, J = 6.9 Hz, 3H), 2.53—2.66 (m, 1H), 2.71—2.85 (m, 1H), 3.96—4.09 (m, 4H), 7.06—7.24 (m, 3H), 7.44—7.62 (m, 4H), 7.69 (d, J = 7.2 Hz, 1H), 7.82 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.1 Hz, 1H), 8.06 (td, J = 1.8, 7.5 Hz, 1H), 8.28 (d, J = 8.1 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ 16.00, 16.06, 33.2 (d, J = 139 Hz), 61.6 (d, J = 6.6 Hz), 61.7 (d, J = 6.6 Hz), 69.2, 116.8 (d, J = 22.2 Hz), 118.2, 122.9, 123.85 (d, J = 3.3 Hz), 123.93, 125.1, 125.7, 126.4, 128.8 (2C), 129.7, 132.2, 133.7, 134.5 (d, J = 9.1 Hz), 135.7 (d, J = 10.7 Hz), 161.9 (d, J = 259 Hz), 162.7; MS [HR-FAB (M+H)+] calcd for C23H25FO5P 431.1424 found 431.1454; HPLC chiralcel OD-H column (4.6 mmφ, 250 mm), n-hexane : 2-propanol = 30 : 1, wavelength: 254 nm, flow rate: 1.0 ml/min, retention time: 38.4 min (enriched), 48.5 min.

**Diethyl (R)-(2-hydroxypropyl)phosphonate (1v):** Colorless oil; [α]D20 —5.2 (c 0.87,
acetone, 49% ee); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.26—1.38 (m, 9H), 1.83—2.04 (m, 2H), 3.48 (br s, 1H), 4.07—4.23 (m, 5H); The ee of the Diethyl (R)-(2-hydroxypropyl)phosphonate (1v) was determined by HPLC of the corresponding Diethyl (S)-[2-(2-fluorobenzyloxy)propyl]phosphonate (2v).

**Diethyl (S)-[2-(2-fluorobenzyloxy)propyl]phosphonate (2v):** Colorless oil; $[\alpha]_D^{20}$ +15.1 (c 1.0, acetone, 56% ee); IR(neat) 2994, 1717, 1456, 1264, 1057, 772 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.28 (t, $J$ = 7.2 Hz, 3H), 1.32 (t, $J$ = 7.2 Hz, 3H), 1.52 (d, $J$ = 6.3 Hz, 3H), 2.04—2.21 (m, 1H), 2.31—2.44 (m, 1H), 4.06—4.17 (m, 4H), 5.40—5.50 (m, 1H), 7.10—7.23 (m, 2H), 7.48—7.55 (m, 1H), 7.93—7.99 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 16.1 (d, $J$ = 4.1 Hz), 16.2 (d, $J$ = 4.1 Hz), 21.0 (d, $J$ = 8.2 Hz), 32.6 (d, $J$ = 140 Hz), 61.7 (d, $J$ = 6.6 Hz, 2C), 67.1, 116.7 (d, $J$ = 22.2 Hz), 118.7 (d, $J$ = 9.9 Hz), 123.7 (d, $J$ = 4.1 Hz), 131.9, 134.3 (d, $J$ = 9.1 Hz), 161.8 (d, $J$ = 259 Hz), 163.1; MS [HR-EI (M$^+$)] calcd for C$_{14}$H$_{20}$FO$_5$P 318.1032 found 318.1033; HPLC chiralcel OD-H column (4.6 mm$^2$, 250 mm), $n$-hexane : 2-propanol = 30 : 1, wavelength: 254 nm, flow rate: 0.7 ml/min, retention time: 29.2 min, 32.4 min (enriched).

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**References and notes**


