Amination of N-Aryl Prolinol via Ring-Expansion and Contraction: Application to Chiral Ligand for Catalytic Asymmetric Reaction

Takashi Mino,* Akio Saito, Youichi Tanaka, Shintaro Hasegawa, Yutaka Sato, Masami Sakamoto, and Tsutomu Fujita

Department of Applied Chemistry and Biotechnology, Faculty of Engineering, Chiba University, 1-33, Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

tmino@faculty.chiba-u.jp

Supporting Information Available: Figures S1-S4, full experimental procedures and characterization data, NMR spectra of new compounds, copies of HPLC charts of 8a, 8c, 4a, 4b, and 13a-d and X-ray crystallographic files (CIF) for 4b, 8a, 8c, and 10b. This material is available free of charge via the Internet at http://pubs.acs.org.
Table of Contents

FIGURE S1. X-Ray Crystal Structures of 8a ................................................................. S6
FIGURE S2. X-Ray Crystal Structures of 8c ................................................................. S7
FIGURE S3. X-Ray Crystal Structures of 4b ................................................................. S8
FIGURE S4. X-Ray Crystal Structures of 10b .............................................................. S9

General Experimental ................................................................................................. S10

Amination of 5 with DEAD and Pyrrolidine ............................................................. S10
Amination of 5 with CBr4-PPh3 and Pyrrolidine (Scheme 2) ..................................... S10
Characterization data for compound 6a ................................................................. S11
Characterization data for compound 7a ................................................................. S11

Bromination of 5 with CBr4-PPh3 (Scheme 3) ......................................................... S12
Characterization data for compound 8a ................................................................. S12

Iodonation of 5 (Table 1, Entry 1) ............................................................................... S13
Characterization data for compound 8b ................................................................. S13

Chlorination of 5 with carbon tetrachloride-triphenylphosphine (Table 1, Entry 2) ................................................................. S13
Characterization data for compound 8c ................................................................. S14
Characterization data for compound 9c ................................................................. S14

Chlorination of 5 with mesyl chloride (Table 1, Entry 3) ......................................... S15

Chlorination of 5 with thionyl chloride (Table 1, Entry 4) ......................................... S15

Ring Expansion Rearrangement of 9c (Scheme 4) ..................................................... S15
General procedure for amination of 8 with amines (Table 3) .................................................. S15
Characterization data for compound 6b ................................................................................... S16
Characterization data for compound 7b ................................................................................... S16
Characterization data for compound 6c ................................................................................... S17
Characterization data for compound 7c ................................................................................... S17
Characterization data for compound 6d ................................................................................... S18
Characterization data for compound 6e ................................................................................... S19
Characterization data for compound 7e ................................................................................... S19
Characterization data for compound 6f ................................................................................... S20
Characterization data for compound 7f ................................................................................... S20
Characterization data for compound 6g ................................................................................... S21
Characterization data for compound 7g ................................................................................... S21

General procedure for reduction of 4 or 10 ............................................................................. S22
Characterization data for compound 4a ................................................................................... S22
Characterization data for compound 10a ................................................................................ S23
Characterization data for compound 4b ................................................................................... S23
Characterization data for compound 10b ................................................................................ S24
Characterization data for compound 4c ................................................................................... S24
Characterization data for compound 4d ................................................................................... S25
Characterization data for compound 4e ................................................................................... S25
Characterization data for compound 4f ................................................................................... S26
Characterization data for compound 4g ................................................................................... S26

General procedure for direct preparation of 4 and 10 (Table 4) ............................................. S27
Characterization data for compound 4h ................................................................................... S28
Characterization data for compound 10h .............................................................................. S28
Characterization data for compound 4i ................................................................................... S29
Characterization data for compound 10i. ................................................................. S29

Acetylation of 4e. ............................................................................................................. S30
Characterization data for compound 4j. ......................................................................... S30

Acetylation of 4f. ............................................................................................................. S31
Characterization data for compound 4k. ......................................................................... S31

Bromination of ent-5 with CBr₄·PPh₃. .............................................................................. S32

Chlorination of ent-5 with thionyl chloride. ................................................................... S32

Direct preparation of ent-4a-b and ent-10a-b using ent-8a ............................................ S32

General procedure for the palladium-catalyzed allylic alkylation .................................. S32

Reference for SI. ............................................................................................................. S33

¹H, ¹³C, and ³¹P NMR of 6a. .......................................................................................... S34-36
¹H, ¹³C, and ³¹P NMR of 7a. .......................................................................................... S37-39
¹H, ¹³C, and ³¹P NMR of 8a. .......................................................................................... S40-42
¹H, ¹³C, and ³¹P NMR of 8b. .......................................................................................... S43-45
¹H, ¹³C, and ³¹P NMR of 8c. .......................................................................................... S46-48
¹H, ¹³C, and ³¹P NMR of 9c. .......................................................................................... S49-51
¹H, ¹³C, and ³¹P NMR of 6b. .......................................................................................... S52-54
¹H, ¹³C, and ³¹P NMR of 7b. .......................................................................................... S55-57
¹H, ¹³C, and ³¹P NMR of 6c. .......................................................................................... S58-60
¹H, ¹³C, and ³¹P NMR of 7c. .......................................................................................... S61-63
¹H, ¹³C, and ³¹P NMR of 6d. .......................................................................................... S64-66
1H, 13C, and 31P NMR of 6e……………………………………………………………………S67-69
1H, 13C, and 31P NMR of 7e……………………………………………………………………S70-72
1H, 13C, and 31P NMR of 6f……………………………………………………………………S73-75
1H, 13C, and 31P NMR of 7f……………………………………………………………………S76-78
1H, 13C, and 31P NMR of 6g……………………………………………………………………S79-81
1H, 13C, and 31P NMR of 7g……………………………………………………………………S82-84
1H, 13C, and 31P NMR of 4a……………………………………………………………………S85-87
1H, 13C, and 31P NMR of 10a……………………………………………………………………S88-90
1H, 13C, and 31P NMR of 4b……………………………………………………………………S91-93
1H, 13C, and 31P NMR of 10b……………………………………………………………………S94-96
1H, 13C, and 31P NMR of 4c……………………………………………………………………S97-99
1H, 13C, and 31P NMR of 4d……………………………………………………………………S100-102
1H, 13C, and 31P NMR of 4e……………………………………………………………………S103-105
1H, 13C, and 31P NMR of 4f……………………………………………………………………S106-108
1H, 13C, and 31P NMR of 4g……………………………………………………………………S109-111
1H, 13C, and 31P NMR of 4h……………………………………………………………………S112-114
1H, 13C, and 31P NMR of 10h……………………………………………………………………S115-117
1H, 13C, and 31P NMR of 4i……………………………………………………………………S118-120
1H, 13C, and 31P NMR of 10i……………………………………………………………………S121-123
1H, 13C, and 31P NMR of 4j……………………………………………………………………S124-126
1H, 13C, and 31P NMR of 4k……………………………………………………………………S127-129
Chiral phase HPLC chart of 8a……………………………………………………………………S130
Chiral phase HPLC chart of 8c……………………………………………………………………S131
Chiral phase HPLC chart of 4a……………………………………………………………………S132
Chiral phase HPLC chart of 4b……………………………………………………………………S133
Chiral phase HPLC chart of 13a……………………………………………………………………S134
Chiral phase HPLC chart of 13b……………………………………………………………………S134
Chiral phase HPLC chart of 13c……………………………………………………………………S135
Chiral phase HPLC chart of 13d……………………………………………………………………S135
FIGURE S1. X-Ray Crystal Structures of 8a.
FIGURE S2. X-Ray Crystal Structures of 8c.
FIGURE S3. X-Ray Crystal Structures of 4b.
FIGURE S4. X-Ray Crystal Structures of 10b.
General Experimental

Phosphine oxide $5^1$ and $ent$-$5$ were prepared according to the literature method.

$Ent$-$5$: 77%; $[\alpha]_D^{25} = 111.1^\circ$ (c 1.00, CHCl$_3$); $^1$H, $^{13}$C, and $^{31}$P NMR were matched the data of $5$.

Amination of 5 with DEAD and Pyrrolidine.

To the mixture of phosphine oxide 5 (0.21 g, 0.52 mmol), pyrrolidine (0.1 mL, 1.0 mmol) and triphenylphosphine (0.66 g, 2.53 mmol) in PhMe (4 mL) was added slowly DEAD in PhMe (1.0 g, 2.5 mmol, 40wt%) at room temperature for 10 min. After stirring at room temperature for 12 hr, the reaction mixture was heating at 80 °C for 24 h. The desired product was traced in the crude mixture analyzed by TLC and $^1$H NMR.

Amination of 5 with CBr$_r$PPh$_3$ and Pyrrolidine (Scheme 2).

To the mixture of 5 (0.201 g, 0.49 mmol), triphenylphosphine (0.153 g, 0.58 mmol) in acetonitrile (4 mL) was added carbon tetrabromide (0.196 g, 0.54 mmol) at room temperature. The mixture was added potassium carbonate (0.216 g, 1.6 mmol) and pyrrolidine (0.045 mL, 0.55 mmol) and refluxed for 6 h. After being cooled to room temperature, the mixture was filtrated by celite and concentrated under reduced pressure. The residue was purifed and separate 6a and 7a by silica gel chromatography (elution with $n$-hexane/EtOAc/McOH = 30/1/1).
$6a$: 0.108 g, 0.23 mmol, 47%; mp 141-142 °C; $[\alpha]_D^{25} = 109.7^\circ$ (c 1.01, CHCl₃); $^1$H NMR (CDCl₃) δ: 1.25-1.81 (m, 8H), 1.84-2.03 (m, 2H), 2.26 (br-s, 2H), 2.36 (br-s, 2H), 2.59 (br-s, 1H), 2.99 (br-s, 1H), 3.80 (br-s, 4H), 6.79 (ddd, $J = 1.5$, 7.3, and 13.4 Hz, 1H), 7.04-7.16 (m, 2H), 7.34-7.53 (m, 6H), 7.69-7.81 (m, 4H); $^{13}$C NMR (CDCl₃) δ: 23.2, 23.5, 30.6, 52.7, 54.5, 55.1, 59.8, 61.0, 116.0, 125.6, 125.8, 126.0, 126.2, 127.9, 128.1, 130.8, 130.9, 131.5 (d, $J_{cp} = 9.7$ Hz), 131.8, 131.9, 133.8, 134.7, 135.2, 136.1, 141.9, 159.3 (d, $J_{cp} = 11.3$ Hz); $^{31}$P NMR (CDCl₃) δ: 25.4; FAB-MS m/z (rel intensity): 461 (M⁺+1, 100); HRMS (FAB-MS) m/z calcd for C$_{28}$H$_{33}$N$_2$O$_2$P⁺H 461.2358, found 461.2362.

$7a$: 0.053 g, 0.11 mmol, 23%; mp 172-174 °C; $[\alpha]_D^{25} = -49.0^\circ$ (c 1.00, CHCl₃); $^1$H NMR (CDCl₃) δ: 0.940-1.17 (m, 2H), 1.25-1.32 (m, 1H), 1.49-1.56 (m 1H) 1.69 (br-s, 4H), 1.72-1.93 (m, 1H), 2.26-2.42 (m, 4H), 2.75 (d, $J = 10.6$ Hz, 1H), 2.93-3.08 (m, 3H), 3.80 (s, 3H), 6.52 (ddd, $J = 2.4$, 9.0, and 19.5 Hz, 1H), 7.04-7.12 (m, 2H), 7.38-7.52 (m, 6H), 7.65-7.73 (m, 4H); $^{13}$C NMR (CDCl₃) δ: 23.0, 23.3, 30.1, 50.9, 51.2, 55.2, 55.6, 60.1, 116.1 (d, $J_{cp} = 2.0$ Hz), 125.6, 125.7, 126.3, 126.5, 127.9, 128.1 (d, $J_{cp} = 4.2$ Hz), 128.2, 130.7 (d, $J_{cp} = 2.6$ Hz), 130.9, 131.0 (d, $J_{cp} = 4.6$ Hz), 131.1, 133.4, 134.1 (d, $J_{cp} = 8.3$ Hz), 134.8, 135.5 (d, $J_{cp} = 8.8$ Hz), 144.6 (d, $J_{cp} = 4.2$ Hz), 160.1 (d, $J_{cp} = 10.5$ Hz); $^{31}$P NMR (CDCl₃) δ: 26.1; FAB-MS m/z (rel intensity): 461 (M⁺+1, 100); HRMS (FAB-MS) m/z calcd for C$_{28}$H$_{33}$N$_2$O$_2$P⁺H 461.2358, found 461.2355.
Bromination of 5 with CBr₄-PPh₃ (Scheme 3).

To the mixture of 5 (1.22 g, 3.0 mmol), triphenylphosphine (0.866 g, 3.3 mmol) in acetonitrile (5 mL) was added carbon tetrabromide (1.09 g, 3.3 mmol) in acetonitrile (2 mL) at room temperature, and stirring was continued for 3 h at room temperature. The mixture was filtrated by celite and concentrated under reduced pressure. The residue was purified by silica gel chromatography (elution with n-hexane/EtOAc = 1/1).

\[
\begin{align*}
&\text{8a: 1.30 g, 2.76 mmol, 92%; mp 185-187 °C; } [\alpha]_D^{25} = -98.3° (c 0.99, \text{CHCl}_3): \text{ }^1\text{H NMR (CDCl}_3) \delta: 1.23-1.38 (m, 2H), 1.44-1.56 (m, 1H), 2.00-2.10 (m, 1H), 2.80-2.98 (m, 3H), 3.04 (dt, } J = 3.0 \text{ and } 11.1 \text{ Hz, 1H), 3.32 (t, } J = 10.8 \text{ Hz, 1H), 3.83 (s, 3H), 6.51 (ddd, } J = 1.9, 7.0, \text{ and } 13.0 \text{ Hz, 1H), 7.04-7.13 (m, 2H), 7.38-7.57 (m, 6H), 7.63-7.74 (m, 4H); } ^{13}\text{C NMR (CDCl}_3) \delta: 25.5, 35.3, 47.1, 50.2, 54.8, 58.9, 115.8, 125.1, 125.2, 126.2, 126.5, 127.6 (d, } J_{cp} = 5.9 \text{ Hz), 127.8 (d, } J_{cp} = 6.3 \text{ Hz), 130.0, 130.2, 130.5, 130.9, 131.0, 133.1, 133.7, 134.3, 135.1, 142.6, 159.2 (d, } J_{cp} = 10.1 \text{ Hz); } ^{31}\text{P NMR (CDCl}_3) \delta: 26.4; \text{ FAB-MS m/z (rel intensity): 470 (M'}^+1, 77); \text{ HRMS (FAB-MS) m/z calcd for C}_{28}\text{H}_{26}\text{BrNO}_2\text{P+H 470.0885, found 470.0905.}}
\end{align*}
\]
Iodonation of 5 (Table 1, Entry 1).

To the mixture of 5 (0.404 g, 0.99 mmol), triphenylphosphine (0.381 g, 1.5 mmol), imidazole (0.136 g, 2.0 mmol) in ether (5 mL) was added iodine (0.381 g, 1.5 mmol) at room temperature, and stirring was continued for 3 h at room temperature. The mixture was diluted with chloroform and water. The organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (elution with n-hexane/EtOAc = 1/1).

\[
\text{8b: 0.486 g, 0.94 mmol, 95%; mp 157-158 °C; } [\alpha]_{D}^{25} = -131.1° \text{ (c 1.01, CHCl}_3) ; \]

\[
1^H \text{ NMR (CDCl}_3) \delta: 1.23-1.40 \text{ (m, 2H)}, 1.69 \text{ (qd, } J = 12.4 \text{ and } 4.5 \text{ Hz, 1H)}, 2.10-2.20 \text{ (m, 1H)}, 2.86-3.13 \text{ (m, 4H)}, 3.49 \text{ (t, } J = 11.2 \text{ Hz, 1H)}, 3.83 \text{ (s, 3H)}, 6.51 \text{ (ddd, } J = 12.9, 7.2 \text{ and } 1.7 \text{ Hz, 1H)}, 7.03-7.13 \text{ (m, 2H)}, 7.40-7.69 \text{ (m, 6H)}, 7.65-7.75 \text{ (m, 4H)}; \]

\[
1^3C \text{ NMR (CDCl}_3) \delta: 26.7, 27.6, 37.8, 50.9, 55.4, 61.2, 116.2 \text{ (d, } J_{cp} = 2.1 \text{ Hz)}, 125.6, 125.7, 126.8, 127.0, 128.1 (d, } J_{cp} = 8.7 \text{ Hz)}, 128.4 \text{ (d, } J_{cp} = 8.9 \text{ Hz)}, 130.5, 130.6, 131.0 \text{ (d, } J_{cp} = 2.7 \text{ Hz)}, 131.5, 131.6, 133.6 \text{ (d, } J_{cp} = 17.0 \text{ Hz)}, 134.3, 134.9 \text{ (d, } J_{cp} = 20.1 \text{ Hz)}, 135.7, 143.0 \text{ (d, } J_{cp} = 4.1 \text{ Hz)}, 159.6 \text{ (d, } J_{cp} = 10.4 \text{ Hz)}; \]

\[
3^1P \text{ NMR (CDCl}_3) \delta: 26.4; \text{ FAB-MS m/z (rel intensity): } 518 \text{ (M}^+1, 95) ; \text{ HRMS (FAB-MS) m/z calcd for C}_{24}H_{25}INO_2P+H 518.0746, \text{ found 518.0775.} \]

Chlorination of 5 with carbon tetrachloride-triphenylphosphine (Table 1, Entry 2).

To the mixture of 5 (0.204 g, 0.5 mmol), triphenylphosphine (0.144 g, 0.55 mmol) in acetonitrile (3 mL) was added carbon tetrachloride (0.052 mL, 0.55 mmol) at room temperature, and stirring was continued for 24 h at room temperature. The mixture was filtrated by celite and concentrated under reduced pressure. The residue was purified and separate 8c and 9c by silica gel chromatography (elution with n-hexane/EtOAc = 2/1).
8c: 64.0 mg, 0.15 mmol, 30%; mp 216-217 °C; \([\alpha]_D^{25} = -84.1^\circ\) (c 1.02, CHCl₃): \(^1\)H NMR (CDCl₃) \(\delta\): 1.17-1.40 (m, 3H), 1.94-1.99 (m, 1H), 2.77-3.04 (m, 4H), 3.17 (t, \(J = 10.5\) Hz, 1H), 3.83 (s, 3H), 6.51 (dd, \(J = 1.9, 7.0,\) and 12.9 Hz, 1H), 7.04-7.13 (m, 2H), 7.40-7.58 (m, 6H), 7.64-7.77 (m, 4H); \(^{13}\)C NMR (CDCl₃) \(\delta\): 24.8, 35.1, 50.7, 55.0, 55.3, 59.0, 116.3 (d, \(J_{\text{cp}} = 2.0\) Hz), 125.6, 125.8, 126.8, 127.0, 128.1 (d, \(J_{\text{cp}} = 4.4\) Hz), 128.3 (d, \(J_{\text{cp}} = 4.8\) Hz), 130.6, 130.8, 131.0, 131.4, 131.5, 134.2, 134.9, 135.1, 135.6, 143.3, 159.8 (d, \(J_{\text{cp}} = 10.2\) Hz); \(^{31}\)P NMR (CDCl₃) \(\delta\): 26.4; FAB-MS m/z (rel intensity): 426 (M⁺+1, 100); HRMS (FAB-MS) m/z calcd for C₂₄H₂₅ClNO₂P⁺H 426.1390, found 426.1384.

9c: 31.2 mg, 0.073 mmol, 15%; mp 223-224 °C; \([\alpha]_D^{25} = 65.0^\circ\) (c 0.43, CHCl₃): \(^1\)H NMR (CDCl₃) \(\delta\): 1.38-1.50 (m, 2H), 1.63-1.73 (m, 1H), 1.98-2.10 (m, 1H), 2.35-2.70 (m, 2H), 3.07 (t, \(J = 10.7\) Hz, 1H), 3.43 (dd, \(J = 3.6\) and 10.7 Hz, 1H), 3.75-3.84 (br-m, 1H), 3.82 (s, 3H), 6.71 (dd, \(J = 1.8, 7.2,\) and 13.5 Hz, 1H), 7.06-7.18 (m, 2H), 7.39-7.54 (m, 6H), 7.69-7.81 (m, 4H); \(^{13}\)C NMR (CDCl₃) \(\delta\): 24.5, 30.2, 47.6, 53.1, 55.7, 65.0, 116.6, 126.2, 126.4, 126.8, 127.0, 128.4 (d, \(J_{\text{cp}} = 7.8\) Hz), 128.6 (d, \(J_{\text{cp}} = 7.7\) Hz), 131.3 (d, \(J_{\text{cp}} = 2.8\) Hz), 131.6 (d, \(J_{\text{cp}} = 2.6\) Hz), 131.9 (d, \(J_{\text{cp}} = 9.3\) Hz), 132.1 (d, \(J_{\text{cp}} = 9.0\) Hz), 133.7, 134.2, 135.1, 135.6, 135.9, 137.3, 159.3 (d, \(J_{\text{cp}} = 11.3\) Hz); \(^{31}\)P NMR (CDCl₃) \(\delta\): 25.1; FAB-MS m/z (rel intensity): 426 (M⁺+1, 100); HRMS (FAB-MS) m/z calcd for C₂₄H₂₅ClNO₂P⁺H 426.1390, found 426.1384.
Chlorination of 5 with mesyl chloride (Table 1, Entry 3).
To the mixture of 5 (0.204 g, 0.5 mmol), triethylamine (0.28 mL, 2.0 mmol) in THF (2 mL) was added mesyl chloride (0.043 mL, 0.55 mmol) at 0 °C for 5 min, and refluxed for 3 h. After being cooled to room temperature, the mixture was diluted with chloroform and quenched 2M NaOH aq. The organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified and separate 8c (0.119 g, 0.28 mmol, 56%) and 9c (0.046 g, 0.11 mmol, 22%) by silica gel chromatography.

Chlorination of 5 with thionyl chloride (Table 1, Entry 4).
To the mixture of 5 (0.409 g, 1.0 mmol), triethylamine (0.2 mL, 1.4 mmol) in chloroform (2 mL) was added thionyl chloride (0.08 mL, 1.1 mmol), and stirring was continued for 2 h at room temperature. The mixture was diluted with chloroform and quenched with water. The organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified and separate 8c (0.218 g, 0.51 mmol, 51%) and 9c (0.132 g, 0.31 mmol, 31%) by silica gel chromatography.

Ring Expansion Rearrangement of 9c (Scheme 4).
The solution of 9c (0.426 g, 0.1 mmol) in chloroform (0.5 mL) was heated at 50 °C for 5 h. After being cooled to room temperature, the mixture was concentrated under reduced pressure. The desired product 8c was obtained analytically pure by TLC and ¹H and ³¹P NMR of the crude analysis.

General procedure for amination of 8 with amines (Table 3).
To the mixture of 8 (0.3 mmol) in acetonitrile (1 mL) was added potassium carbonate (0.083 g, 0.6 mmol) and amines (0.33 mmol) and refluxed for 6 h. After being cooled to room temperature, the mixture was filtrated by celite and concentrated under reduced pressure. The residue was purified and separate 6 and 7 by silica gel chromatography (elution with n-hexane/MeOH/EtN₃ = 30/2/1).
6b: 54%; mp 179-180 °C; [α]₀^25 = 111.7° (c 0.98, CHCl₃): \(^1\)H NMR (CDCl₃) \(\delta\): 1.25-1.43 (m, 8H), 1.49-1.60 (m, 2H), 1.82-1.96 (m, 2H), 2.07 (br-s, 2H), 2.16 (br-s, 2H), 2.54 (br-s, 1H), 3.03 (br-s, 1H), 3.78 (s, 3H), 3.88 (br-s, 1H), 6.78 (ddd, \(J = 1.4, 7.4, \text{ and } 13.4 \text{ Hz}, 1H), 7.01-7.12 (m, 2H), 7.33-7.49 (m, 6H), 7.69-7.81 (m, 4H); \(^{13}\)C NMR (CDCl₃) \(\delta\): 23.3, 24.4, 25.9, 30.4, 52.0, 54.9, 55.0, 59.5, 62.3, 115.6, 125.2, 125.4, 125.9, 126.1, 127.8, 128.0 (d, \(J_{cp} = 1.5 \text{ Hz})\), 130.7, 131.3, 131.4, 131.8, 131.9, 134.1, 134.5, 135.4, 136.0, 142.0, 159.6 (d, \(J_{cp} = 11.1 \text{ Hz})\); \(^{31}\)P NMR (CDCl₃) \(\delta\): 24.8; FAB-MS m/z (rel intensity): 475 (M⁺+1, 100); HRMS (FAB-MS) m/z calcd for C₂₉H₃₅N₂O₂P⁺H 475.2514, found 475.2535.

7b: 40%; mp 165-166 °C; [α]₀^25 = -37.2° (c 1.00, CHCl₃): \(^1\)H NMR (CDCl₃) \(\delta\): 0.78-0.92 (m, 1H), 1.10 (dq, \(J = 3.6 \text{ and } 12.4 \text{ Hz}, 1H), 1.25-1.40 (m, 3H) 1.45-1.60 (m, 4H), 1.65-1.88 (m, 2H), 2.28-2.45 (m, 4H), 2.68 (d, \(J = 10.4 \text{ Hz}, 1H), 2.93-3.07 (m, 3H), 3.81 (s, 3H), 6.46-6.55 (m, 1H), 7.03-7.11 (m, 2H), 7.36-7.54 (m, 6H), 7.65-7.74 (m, 4H); \(^{13}\)C NMR (CDCl₃) \(\delta\): 23.8, 24.8, 26.3, 27.4, 50.9, 51.1, 53.1, 55.3, 60.0, 116.4, 125.7, 125.9, 126.2, 126.4, 128.0, 128.1 (d, \(J_{cp} = 3.4 \text{ Hz})\), 128.2, 130.6 (d, \(J_{cp} = 2.7 \text{ Hz})\), 130.8, 131.0 (d, \(J_{cp} = 7.7 \text{ Hz})\), 131.1 (d, \(J_{cp} = 9.2 \text{ Hz})\), 133.5, 134.1 (d, \(J_{cp} = 8.6 \text{ Hz})\), 135.0, 135.6 (d, \(J_{cp} = 9.0 \text{ Hz})\), 144.7, 160.1 (d, \(J_{cp} = 10.6 \text{ Hz})\); \(^{31}\)P NMR (CDCl₃) \(\delta\): 26.1; FAB-MS m/z (rel intensity): 475 (M⁺+1, 100); HRMS (FAB-MS) m/z calcd for C₂₉H₃₅N₂O₂P⁺H 475.2514, found 475.2552.
6c: 55%; mp 195-196 °C; [α]_D^{25} = 106.5° (c 0.87, CHCl₃); \textsuperscript{1}H NMR (CDCl₃) δ: 1.20-1.49 (m, 3H), 1.60-1.89 (m, 2H), 2.04-2.23 (m, 5H), 2.48 (br-s, 1H), 2.93 (br-s, 1H), 3.39-3.47 (m, 4H), 3.79 (s, 3H), 3.96 (br, 1H), 6.73 (ddd, J = 1.3, 7.4, and 13.4 Hz, 1H), 7.01-7.13 (m, 2H), 7.36-7.49 (m, 6H), 7.65-7.80 (m, 4H); \textsuperscript{13}C NMR (CDCl₃) δ: 23.4, 30.1, 51.6, 53.9, 55.1, 59.0, 62.0, 67.0, 116.0, 125.3, 125.5, 126.0, 126.2, 127.9, 128.1, 130.8 (d, J_c = 3.8 Hz), 131.3, 131.4, 131.7, 131.9, 134.0, 134.6, 135.4, 136.0, 142.1, 159.7 (d, J_c = 10.6 Hz); \textsuperscript{31}P NMR (CDCl₃) δ: 24.8; FAB-MS m/z (rel intensity): 477 (M⁺+1, 89); HRMS (FAB-MS) m/z calcd for C₂₈H₃₃N₂O₂P⁺H 477.2310, found 477.2309.

7c: 34%; mp 101-103 °C; [α]_D^{25} = -43.7° (c 0.72, CHCl₃); \textsuperscript{1}H NMR (CDCl₃) δ: 0.80-1.18 (m, 2H), 1.25-1.35 (m, 1H), 1.72-1.76 (m, 2H), 2.41 (br, 4H), 2.74 (d, J = 10.4 Hz, 1H), 2.93-3.06 (m, 3H), 3.66 (t, J = 4.5 Hz, 4H), 3.81 (s, 3H), 6.51 (ddd, J = 2.5, 6.4, and 13.0 Hz, 1H), 7.04-7.13 (m, 2H), 7.38-7.54 (m, 6H), 7.65-7.73 (m, 4H); \textsuperscript{13}C NMR (CDCl₃) δ: 23.6, 27.3, 50.1, 51.1, 53.3, 55.3, 59.6, 67.3, 116.4 (d, J_c = 2.2 Hz), 125.7, 125.9, 126.4, 126.6, 128.0, 128.2 (d, J_c = 3.9 Hz), 128.3, 130.8 (d, J_c = 2.6 Hz), 130.9 (d, J_c = 2.7 Hz), 131.0 (d, J_c = 3.5 Hz), 131.1 (d, J_c = 3.3 Hz), 133.4, 134.1 (d, J_c = 10.7 Hz), 134.9, 135.6 (d, J_c = 10.8 Hz), 144.5 (d, J_c = 4.3 Hz), 160.1 (d, J_c = 10.4 Hz); \textsuperscript{31}P NMR (CDCl₃) δ: 26.4; FAB-MS m/z (rel intensity): 477 (M⁺+1, 91); HRMS (FAB-MS) m/z calcd for C₂₈H₃₃N₂O₂P⁺H 477.2307, found 477.2325.
6d: 82%; mp 61-62 °C; $[\alpha]_{D}^{25} = 80.8^\circ$ (c 0.87, CHCl₃). $^1$H NMR (CDCl₃) $\delta$: 0.84-1.29 (m, 11H), 1.29-1.60 (m, 8H), 1.61-1.72 (m, 4H), 1.72-2.11 (m, 2H), 2.12-2.29 (m, 2H), 2.66-2.76 (m, 1H), 3.17-3.24 (m, 1H), 3.56-3.62 (m, 1H), 3.81 (s, 3H), 6.89 (ddd, $J = 1.5$, 7.5 and 13.3 Hz, 1H), 7.04 (d, $J = 7.3$ Hz, 1H), 7.09-7.16 (m, 1H), 7.39-7.54 (m, 6H), 7.63-7.81 (m, 4H);

$^{13}$C NMR (CDCl₃) $\delta$: 22.9, 25.3, 26.2, 26.6, 26.7, 30.4, 31.5, 32.7, 34.3, 48.9, 53.3, 55.1, 58.1, 62.7, 115.6, 125.4, 125.6, 126.2, 126.3, 128.0, 128.1, 130.8 (d, $J_{cp} = 9.5$ Hz), 131.4 (d, $J_{cp} = 9.5$ Hz), 132.1 (d, $J_{cp} = 8.9$ Hz), 134.0, 134.1, 134.6, 135.4, 135.5, 136.0, 142.1 (d, $J_{cp} = 4.4$ Hz), 159.3 (d, $J_{cp} = 11.3$ Hz); $^{31}$P NMR (CDCl₃) $\delta$: 25.4; FAB-MS m/z (rel intensity): 571 (M⁺+1, 100); HRMS (FAB-MS) m/z calcd for C₃₆H₄₇N₂O₂P⁺H 571.3453, found 571.3486.
6e: 54%; mp 79-80 °C; $[\alpha]_D^{25} = 82.4^\circ$ (c 1.03, CHCl$_3$): $^1$H NMR (CDCl$_3$) $\delta$: 0.83 (t, $J = 7.1$ Hz, 3H), 1.26-1.49 (m, 3H), 1.76 (br-s, 1H), 1.80-1.90 (m, 1H), 2.19 (dd, $J = 3.7$ and 12.3 Hz, 1H), 2.26-2.50 (m, 4H), 2.59 (br-s, 1H), 2.88 (br-s, 1H), 3.12 (br-s, 1H), 3.36-3.40 (m, 2H), 3.81 (br-s, 1H), 3.83 (s, 3H), 6.76 (ddd, $J = 1.6$, 7.3, and 13.4 Hz, 1H), 7.04-7.15 (m, 2H), 7.36-7.50 (m, 6H), 7.70-7.81 (m, 4H); $^{13}$C NMR (CDCl$_3$) $\delta$: 12.3, 23.6, 31.1, 48.3, 53.6, 55.5, 55.9, 57.2, 58.8, 60.9, 116.3, 126.1, 126.3, 126.5, 126.7, 128.4, 128.5, 131.2, 131.9, 132.1, 132.2, 134.2, 134.3, 135.4, 135.6 (d, $J_{cp} = 7.4$ Hz), 136.8, 142.0, 159.8 (d, $J_{cp} = 11.1$ Hz); $^{31}$P NMR (CDCl$_3$) $\delta$: 25.1; FAB-MS m/z (rel intensity): 479 (M$^+$+1, 55); HRMS (FAB-MS) m/z calcd for C$_{28}$H$_{35}$N$_2$O$_3$P+H 497.2464, found 479.2459.

7e: 43%; mp 73-75 °C; $[\alpha]_D^{25} = 4.46^\circ$ (c 1.01, CHCl$_3$): $^1$H NMR (CDCl$_3$) $\delta$: 0.50-0.64 (m, 1H), 0.99 (t, $J = 7.1$ Hz, 3H) 1.06-1.26 (m, 2H), 1.52-1.59 (m, 1H) 2.35-2.62 (m, 6H), 2.92-3.29 (m, 4H), 3.48 (t, $J = 5.4$ Hz, 2H), 3.82 (s, 3H), 6.50 (ddd, $J = 3.2$, 5.8, and 13.0 Hz, 1H), 7.04-7.12 (m, 2H), 7.38-7.52 (m, 6H), 7.65-7.73 (m, 4H); $^{13}$C NMR (CDCl$_3$) $\delta$: 14.6, 23.9, 27.3, 44.3, 50.9, 51.3, 53.7, 55.3, 56.4, 59.1, 116.5, 125.8, 126.0, 126.3, 126.5, 128.0, 128.2, 130.7, 130.8 (d, $J_{cp} = 3.5$ Hz), 130.9, 131.4, 131.5, 133.5 (d, $J_{cp} = 23.3$ Hz), 134.2, 134.9 (d, $J_{cp} = 20.3$ Hz), 135.6, 144.4 (d, $J_{cp} = 3.9$ Hz), 160.0 (d, $J_{cp} = 10.5$ Hz); $^{31}$P NMR (CDCl$_3$) $\delta$: 26.8; FAB-MS m/z (rel intensity): 479 (M$^+$+1, 76); HRMS (FAB-MS) m/z calcd for C$_{28}$H$_{35}$N$_2$O$_3$P+H 479.2464, found 479.2494.
6f: 61%; mp 52-54 °C; \([\alpha]_D^{25} = 80.1 \text{ (c 1.01, CHCl}_3\); \(^1^H\) NMR (CDCl\(_3\), 50 °C) \(\delta\): 1.00-1.53 (m, 3H), 1.75-1.94 (m, 1H), 1.94-2.13 (m, 1H), 2.28-2.58 (m, 5H), 2.60-3.30 (m, 3H), 3.30-3.50 (m, 4H), 3.50-3.75 (m, 1H), 3.81 (s, 3H), 3.85-4.23 (m, 1H), 6.71 (ddd, \(J = 2.5, 7.1\) and 13.5 Hz, 1H), 7.03-7.18 (m, 2H), 7.31-7.55 (m, 6H), 7.56-7.88 (m, 4H); \(^1^C\) NMR (CDCl\(_3\)) \(\delta\): 23.7, 25.9, 50.3, 52.1, 54.9, 55.3, 56.2, 60.3, 116.5, 126.4, 126.7 (d, \(J_{cp} = 11.7\) Hz), 128.4, 128.6, 131.4, 132.0-132.1 (m), 133.5, 134.9, 135.0, 135.1, 136.4, 159.8 (d, \(J_{cp} = 11.3\) Hz); \(^{31}\)P NMR (CDCl\(_3\)) \(\delta\): 26.00; FAB-MS m/z (rel intensity): 495 (M\(^{+1}\), 100); HRMS (FAB-MS) m/z calcd for C\(_{28}\)H\(_{35}\)N\(_2\)O\(_4\)P+H 495.2413, found 495.2408.

7f: 26%; mp 74-76 °C; \([\alpha]_D^{25} = 69.9^\circ \text{ (c 1.05, CHCl}_3\); \(^1^H\) NMR (CDCl\(_3\)) \(\delta\): 0.14-0.20 (m, 1H), 1.07-1.18 (m, 2H), 1.55-1.58 (m, 1H), 2.36 (br-d, \(J = 9.8\) Hz, 1H), 2.59-2.66 (m, 4H), 2.83-2.92 (m, 2H), 3.07 (t, \(J = 10.7\) Hz, 1H), 3.26 (d, \(J = 6.8\) Hz, 1H), 3.51-3.62 (m, 4H), 3.84 (s, 3H), 3.98 (br-s, 2H), 6.50 (ddd, \(J = 2.5, 6.4,\) and 13.0 Hz, 1H), 7.04-7.12 (m, 2H), 7.38-7.52 (m, 6H), 7.65-7.73 (m, 4H); \(^1^C\) NMR (CDCl\(_3\)) \(\delta\): 23.8, 26.4, 50.5, 51.9, 54.8, 55.2, 56.2, 60.6, 116.5, 125.8, 126.0, 126.3, 126.5, 128.1 (d, \(J_{cp} = 3.4\) Hz), 128.2 (d, \(J_{cp} = 4.6\) Hz), 130.1, 130.2, 130.7, 131.1, 131.8, 131.9, 132.9, 134.3 (d, \(J_{cp} = 4.4\) Hz), 135.7, 144.3 (d, \(J_{cp} = 4.1\) Hz), 159.9 (d, \(J_{cp} = 10.4\) Hz); \(^{31}\)P NMR (CDCl\(_3\)) \(\delta\): 27.5; FAB-MS m/z (rel intensity): 495 (M\(^{+1}\), 50); HRMS (FAB-MS) m/z calcd for C\(_{28}\)H\(_{33}\)N\(_2\)O\(_3\)P+H 495.2413, found 495.2375.
**6g**: 32%; yellow liquid; $[\alpha]_D^{25} = 81.4^\circ$ (c 1.04, CHCl$_3$): $^1$H NMR (CDCl$_3$) $\delta$: 1.22 (t, $J = 7.1$ Hz, 6H), 1.29-1.42 (m, 2H), 1.51-1.65 (m, 2H), 1.71-1.98 (m, 1H), 2.44 (dd, $J = 3.8$ and 12.9 Hz, 2H), 2.60 (br-s, 1H), 3.01-3.17 (m, 1H), 3.34 (dd, $J = 17.5$ and 32.0 Hz, 4H), 3.71-3.87 (m, 1H), 3.79 (s, 3H), 4.08 (q, $J = 7.1$ Hz, 4H), 6.73 (ddd, $J = 1.9$, 7.2, and 13.4 Hz, 1H), 7.00-7.12 (m, 2H), 7.36-7.51 (m, 6H), 7.67-7.81 (m, 4H); $^{13}$C NMR (CDCl$_3$) $\delta$: 14.2, 22.3, 30.1, 52.6, 55.1, 55.2, 57.5, 60.0, 60.1, 115.9, 125.5, 125.7, 126.0, 126.2, 127.9, 128.1, 130.7 (d, $J_{cp} = 2.6$ Hz), 130.8 (d, $J_{cp} = 2.6$ Hz), 131.4 (d, $J_{cp} = 9.1$ Hz), 131.9 (d, $J_{cp} = 8.8$ Hz), 133.7 (d, $J_{cp} = 10.2$ Hz), 134.8, 135.0, 135.2, 136.2, 141.4, 159.3 (d, $J_{cp} = 11.3$ Hz), 171.5; $^{31}$P NMR (CDCl$_3$) $\delta$: 24.8; FAB-MS m/z (rel intensity): 579 (M$^+$+1, 62); HRMS (FAB-MS) m/z calcd for C$_{32}$H$_{39}$N$_2$O$_2$P+H 579.2634, found 579.2584.

**7g**: 6%; yellow liquid; $[\alpha]_D^{25} = -52.4^\circ$ (c 0.39, CHCl$_3$): $^1$H NMR (CDCl$_3$) $\delta$: 0.94-1.17 (m, 2H), 1.22-1.36 (m, 1H), 1.26 (t, $J = 7.1$ Hz, 6H), 1.65-1.70 (m, 1H), 2.04-2.16 (m, 1H), 2.71-2.83 (m, 2H), 2.89-2.97 (m, 2H), 3.41 (s, 4H), 3.81 (s, 3H), 4.14 (q, $J = 7.1$ Hz, 4H), 6.52 (ddd, $J = 2.6$, 6.4, and 13.0 Hz, 1H), 7.03-7.15 (m, 2H), 7.38-7.51 (m, 6H), 7.62-7.72 (m, 4H); $^{13}$C NMR (CDCl$_3$) $\delta$: 14.2, 23.9, 28.9, 50.9, 52.6, 54.4, 55.3, 58.7, 60.3, 116.4, 125.7, 125.9, 126.3, 126.5, 128.1 (d, $J_{cp} = 7.4$ Hz), 128.3 (d, $J_{cp} = 7.6$ Hz), 130.8, 130.9, 131.0, 131.2 (d, $J_{cp} = 9.2$ Hz), 133.4, 133.8, 134.9, 135.2, 135.6, 144.4, 160.1 (d, $J_{cp} = 10.7$ Hz), 172.5; $^{31}$P NMR (CDCl$_3$) $\delta$: 26.4; FAB-MS m/z (rel intensity): 579 (M$^+$+1, 63); HRMS (FAB-MS) m/z calcd for C$_{32}$H$_{39}$N$_2$O$_2$P+H 579.2634, found 579.2654.
General procedure for reduction of 4 or 10.

To a phosphine oxide (0.4 mmol) and triethylamine (1.0 mL, 7.0 mmol) in m-xylene (2 mL) was added trichlorosilane (1.0 mL, 10 mmol) at 0 °C under an argon atmosphere. The reaction mixture was refluxed for 6 h. After being cooled to room temperature, the mixture was diluted with ether and quenched with 2 M aqueous NaOH solution. The organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (elution with n-hexane/EtOAc = 15/1).

![Structure 4a](image)

4a: 84%; mp 112-113 °C; [α]D²⁵ = 41.7° (c 0.10, CHCl₃); ¹H NMR (CDCl₃) δ: 1.56-1.71 (m, 7H), 2.03-2.13 (m, 1H), 2.16-2.36 (m, 6H), 2.53-2.62 (m, 1H), 2.78 (dd, J = 7.6 and 15.4 Hz, 1H), 3.66-3.75 (m, 1H), 3.79 (s, 3H), 6.40 (ddd, J = 1.3, 2.8, and 7.6 Hz, 1H), 6.86 (dd, J = 0.6 and 8.0 Hz, 1H), 7.05 (ddd, J = 0.8, 7.9, and 8.7 Hz, 1H), 7.25-7.35 (m, 10H); ¹³C NMR (CDCl₃) δ: 23.4, 24.2, 31.5, 51.9, 54.7, 55.0, 61.1, 61.7 (d, Jcp = 3.3 Hz), 112.4, 124.9, 126.3, 128.1-128.2 (m), 134.0, 134.1, 134.3, 134.4, 138.7 (d, Jcp = 13.2 Hz), 139.2 (d, Jcp = 14.6 Hz), 140.5, 142.7 (d, Jcp = 4.1 Hz), 158.3 (d, Jcp = 3.6 Hz); ³¹P NMR (CDCl₃) δ: -15.1; FAB-MS m/z (rel intensity): 445 (M⁺+1, 100); HRMS (FAB-MS) m/z calcd for C₂₈H₃₃N₂OP+H 445.2409, found 445.2382.
10a: 77%; mp 150-151 °C; [α]$_D^{25}$ = 11.1° (c 0.10, CHCl$_3$): $^1$H NMR (CDCl$_3$) δ: 1.08-1.18 (m, 1H), 1.34-1.44 (m, 2H), 1.51-1.55 (m, 1H), 1.56-1.65 (m, 4H), 1.89 (d, $J$ = 11.5 Hz, 1H), 2.19-2.31 (m, 4H), 2.68-2.76 (m, 2H), 2.98-3.07 (m, 2H), 3.77 (s, 3H), 6.22 (ddd, $J$ = 1.2, 2.7, and 7.6 Hz, 1H), 6.85 (d, $J$ = 8.1 Hz, 1H), 7.03 (ddd, $J$ = 1.2, 7.6, and 8.1 Hz, 1H), 7.21-7.34 (m, 10H); $^{13}$C NMR (CDCl$_3$) δ: 23.0, 24.9, 30.5, 50.2, 51.3, 55.0, 55.1, 61.4, 112.4, 124.3, 124.8, 126.8, 128.1-128.3 (m), 133.8, 134.0, 134.1, 134.3, 138.9 (d, $J_{CP}$ = 9.7 Hz), 139.1 (d, $J_{CP}$ = 10.5 Hz), 140.9 (d, $J_{CP}$ = 2.8 Hz), 142.4 (d, $J_{CP}$ = 18.6 Hz), 159.0 (d, $J_{CP}$ = 2.6 Hz); $^{31}$P NMR (CDCl$_3$) δ: -13.5; FAB-MS m/z (rel intensity): 445 (M$^+$+1, 100); HRMS (FAB-MS) m/z calcd for C$_{28}$H$_{33}$N$_2$OP+H 445.2409, found 445.2369.

4b: 88%; mp 100 °C; [α]$_D^{25}$ = 48.0° (c 1.00, CHCl$_3$): $^1$H NMR (CDCl$_3$) δ: 1.25-1.43 (m, 6H), 1.52-1.66 (m, 3H), 1.95-2.28 (m, 7H), 2.51 (br, 1H), 2.75 (dd, $J$ = 7.7 and 15.4 Hz, 1H), 3.70-3.80 (m, 1H), 3.80 (s, 3H), 6.39 (ddd, $J$ = 1.3, 2.8, and 7.6 Hz, 1H), 6.85 (dd, $J$ = 0.6 and 8.1 Hz, 1H), 7.04 (ddd, $J$ = 0.9, 8.1, and 8.4 Hz, 1H), 7.23-7.32 (m, 10H); $^{13}$C NMR (CDCl$_3$) δ: 24.0, 24.4, 25.9, 31.6, 51.8, 54.9, 55.0, 59.3, 64.3, 112.2, 124.8, 126.2, 128.0-128.2 (m), 133.9, 134.2, 134.5, 138.7 (d, $J_{CP}$ = 13.1 Hz), 139.3 (d, $J_{CP}$ = 14.7 Hz), 140.8, 142.4, 158.3; $^{31}$P NMR (CDCl$_3$) δ: -15.0; FAB-MS m/z (rel intensity): 459 (M$^+$+1, 79); HRMS (FAB-MS) m/z calcd for C$_{29}$H$_{33}$N$_2$OP+H 459.2565, found 459.2555.

S23
10b: 58%; mp 134-135 °C; \([\alpha]_D^{25} = 4.2^\circ (c 0.45, \text{CHCl}_3)\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\): 1.12-1.22 (m, 1H), 1.26-1.51 (m, 8H), 2.12-2.30 (m, 4H), 2.69-2.77 (m, 2H), 2.93-3.02 (m, 2H), 3.78 (s, 3H), 6.22 (ddd, \(J = 1.2, 8.2\) Hz, 1H), 6.85 (d, \(J = 8.2\) Hz, 1H), 7.02 (ddd, \(J = 1.2, 8.0, \text{and} 8.9\) Hz, 1H), 7.21-7.34 (m, 10H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\): 24.8, 25.4, 26.4, 28.1, 50.4, 50.6, 75.1, 113.5, 124.4, 126.8, 128.1-128.4 (m), 133.7, 134.0, 134.0, 134.2, 138.9 (d, \(J_{cp} = 11.3\) Hz), 139.1 (d, \(J_{cp} = 13.0\) Hz), 140.8 (d, \(J_{cp} = 2.8\) Hz), 142.4 (d, \(J_{cp} = 18.4\) Hz), 159.0 (d, \(J_{cp} = 2.6\) Hz); \(^{31}\)P NMR (CDCl\(_3\)) \(\delta\): -13.3; FAB-MS m/z (rel intensity): 459 (M\(^+\)+1, 91); HRMS (FAB-MS) m/z calcd for C\(_{29}\)H\(_{35}\)N\(_2\)OP+H 459.2565, found 459.2523.

4c: 87%; mp 118 °C; \([\alpha]_D^{25} = 49.1 (c 1.00, \text{CHCl}_3)\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\): 1.48-1.68 (m, 3H), 1.87-2.08 (m, 2H), 2.09-2.34 (m, 5H), 2.52 (br, 1H), 2.77 (q, \(J = 7.7\) Hz, 1H), 3.51 (t, \(J = 4.7\) Hz, 4H), 3.68-3.80 (m, 1H), 3.78 (s, 3H), 6.40 (ddd, \(J = 1.3, 2.9\) and 7.6 Hz, 1H), 6.86 (d, \(J = 7.4\) Hz, 1H), 7.05 (ddd, \(J = 0.9, 8.5\) and 9.4 Hz, 1H), 7.22-7.33 (m, 10H). \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\): 24.0, 31.1, 52.0, 54.0, 55.0, 58.5, 64.9, 67.0, 112.3, 124.8, 126.3, 128.1-128.3 (m), 134.0, 134.2, 134.5, 138.7 (d, \(J_{cp} = 12.7\) Hz), 139.2 (d, \(J_{cp} = 14.6\) Hz), 140.7 (d, \(J_{cp} = 20.5\) Hz), 142.5 (d, \(J_{cp} = 4.0\) Hz), 158.3 (d, \(J_{cp} = 3.5\) Hz); \(^{31}\)P NMR (CDCl\(_3\)) \(\delta\): -14.7; FAB-MS m/z (rel intensity): 461 (M\(^+\)+1, 53); HRMS (FAB-MS) m/z calcd for C\(_{28}\)H\(_{35}\)N\(_2\)O\(_2\)P+H 461.2358, found 461.2347.
4d: 87%; mp 96 °C; $[\alpha]_D^{25} = 11.7$ (c 1.01, CHCl$_3$); $^1$H NMR (CDCl$_3$) $\delta$: 0.83-1.30 (m, 10H), 1.43-1.74 (m, 13H), 1.93-2.02 (m, 2H), 2.22-2.33 (m, 2H), 2.36 (dd, $J = 3.1$ and 13.7 Hz, 1H), 2.79-2.84 (m, 2H), 3.35-3.64 (m, 1H), 3.79 (s, 3H), 6.85 (d, $J = 8.1$ Hz, 1H), 7.04 (ddd, $J = 0.7$, 8.2, and 8.9 Hz, 1H), 7.20-7.34 (m, 10H); $^{13}$C NMR (CDCl$_3$) $\delta$: 23.7, 26.3, 26.6, 26.7, 31.0, 31.4, 32.6, 50.2, 52.3, 54.9, 58.5, 62.4, 112.3, 125.1, 126.1, 128.0-128.2 (m), 133.9, 134.0, 134.2, 134.3, 139.0 (d, $J_{cp} = 14.8$ Hz), 139.3 (d, $J_{cp} = 14.1$ Hz), 140.8, 141.1, 142.5 (d, $J_{cp} = 3.7$ Hz), 158.3 (d, $J_{cp} = 3.7$ Hz); $^{31}$P NMR (CDCl$_3$) $\delta$: -15.1; FAB-MS m/z (rel intensity): 555 (M$^+$+1, 38); HRMS (FAB-MS) m/z calcd for C$_{36}$H$_{47}$N$_2$OP+H 555.3504, found 555.3508.

4e: 77%; white liquid; $[\alpha]_D^{25} = 17.6$ (c 0.99, CHCl$_3$); $^1$H NMR (CDCl$_3$) $\delta$: 0.84 (t, $J = 7.1$ Hz, 3H), 1.45-1.60 (m, 3H), 1.95-2.11 (m, 2H), 2.22-2.50 (m, 5H), 2.52-2.63 (m, 2H), 2.79 (q, $J = 7.9$ Hz, 1H), 3.30-3.45 (m, 2H), 3.63-3.74 (m, 1H), 3.80 (s, 3H), 6.42 (ddd, $J = 1.3$, 2.8 and 7.7 Hz, 1H), 6.87 (d, $J = 7.5$ Hz, 1H), 7.06 (ddd, $J = 0.9$, 7.5 and 8.4 Hz, 1H), 7.23-7.33 (m, 10H), $^{13}$C NMR (CDCl$_3$) $\delta$: 12.1, 24.2, 31.6, 48.3, 52.5, 55.4, 55.8, 58.6, 58.9, 60.4, 112.8, 125.4, 126.9, 128.6-128.7 (m), 134.4, 134.6, 134.7, 134.9, 138.9 (d, $J_{cp} = 12.7$ Hz), 139.2 (d, $J_{cp} = 14.2$ Hz), 140.3 (d, $J_{cp} = 21.0$ Hz), 142.8 (d, $J_{cp} = 4.9$ Hz), 158.7 (d, $J_{cp} = 3.5$ Hz); $^{31}$P NMR (CDCl$_3$) $\delta$: -14.9; FAB-MS m/z (rel intensity): 463 (M$^+$+1, 28); HRMS (FAB-MS) m/z calcd for C$_{28}$H$_{35}$N$_2$O$_2$P+H 463.2514, found 463.2536.
4f: 79%; mp 101-102 °C; \([\alpha]_D^{25} = 28.0 (c 1.00, \text{CHCl}_3); \) ^1H NMR (CDCl\(_3\)) \(\delta: 1.42-1.75 (m, 3H), 1.95-2.65 (m, 10H), 2.77 (q, J = 7.8 Hz, 1H), 3.46 (t, J = 5.3 Hz, 4H), 3.66-3.77 (m, 1H), 3.81 (s, 3H), 6.43 (ddd, J = 1.3, 2.9 and 7.6 Hz, 1H), 6.89 (d, J = 8.1 Hz, 1H), 7.08 (t, J = 7.9 Hz, 1H), 7.23-7.42 (m, 10H); ^13C NMR (CDCl\(_3\)) \(\delta: 23.7, 31.3, 52.0, 55.1, 56.8, 59.5, 59.9, 60.0 (d, J_{cp} = 3.6 Hz), 112.5, 125.0, 126.6, 128.2-128.4 (m), 134.0, 134.2, 134.3, 134.5, 138.2 (d, J_{cp} = 11.7 Hz), 138.8 (d, J_{cp} = 13.5 Hz), 140.0 (d, J_{cp} = 20.5 Hz), 142.2 (d, J_{cp} = 4.0 Hz), 158.3 (d, J_{cp} = 3.4 Hz); ^31P NMR (CDCl\(_3\)) \(\delta: -14.78; \) FAB-MS m/z (rel intensity): 479 (M\(^+\), 52); HRMS (FAB-MS) m/z calcd for C\(_{28}\)H\(_{35}\)N\(_2\)O\(_3\)P+H 479.2464, found 479.2450.

4g: 23%; yellow liquid; \([\alpha]_D^{25} = 62.3° (c 0.33, \text{CHCl}_3); \) ^1H NMR (CDCl\(_3\)) \(\delta: 1.21 (t, J = 8.2 Hz, 6H), 1.60-1.68 (m, 3H), 1.97-2.09 (m, 1H), 2.22 (dd, J = 9.4 and 13.0 Hz, 1H), 2.53 (br-s, 1H), 2.64-2.77 (m, 2H), 3.38 (dd, J = 17.4 and 23.6 Hz, 4H), 3.67-3.77 (m, 1H), 3.79 (s, 3H), 4.08 (dq, J = 0.6 and 7.1 Hz, 4H), 6.80 (ddd, J = 1.3, 2.8, and 7.6 Hz, 1H), 6.85 (br-d, J = 7.5 Hz, 1H), 7.03 (dt, J = 0.8 and 8.4 Hz, 1H), 7.22-7.36 (m, 10H); ^13C NMR (CDCl\(_3\)) \(\delta: 14.2, 23.9, 30.8, 51.9, 54.9, 55.6, 60.1, 60.2, 112.3, 128.0-128.2 (m), 134.0, 134.2, 134.2, 134.5, 138.4, 138.5, 139.0, 139.2, 142.4 (d, J_{cp} = 4.1 Hz), 158.2 (d, J_{cp} = 3.4 Hz); ^31P NMR (CDCl\(_3\)) \(\delta: -14.9; \) FAB-MS m/z (rel intensity): 563 (M\(^+\), 9); HRMS (FAB-MS) m/z calcd for C\(_{32}\)H\(_{39}\)N\(_2\)O\(_5\)P+H 563.2675, found 563.2639.
General procedure for direct preparation of 4 and 10 (Table 4).

First step: To the mixture of 8 (0.5 mmol) in acetonitrile (3 mL) was added potassium carbonate (0.138 g, 1.0 mmol) and amines (1.0 mmol) and refluxed for 8 h. After being cooled to room temperature, the mixture was filtrated by celite and concentrated under reduced pressure. The mixture of 6 and 7 was obtained by silica gel chromatography (elution with n-hexane/EtOAc = 15/1). The mixture was used for the next step without further purification.

Second step: To the mixture of 6 and 7 and triethylamine (0.277 mL, 2.0 mmol) in m-xylene (2 mL) was added trichlorosilane (0.202 mL, 2.0 mmol) at 0 °C under an argon atmosphere. The reaction mixture was refluxed for 6 h. After being cooled to room temperature, the mixture was diluted with ether and quenched with 2 M aqueous NaOH solution. The organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (elution with n-hexane/EtOAc = 4/1).
4h: 41%; mp 63-65 °C; \( [\alpha]_{D}^{25} = 30.0^\circ \) (c 1.02, CHCl₃); \(^1\)H NMR (CDCl₃) δ: 1.66-1.77 (m, 3H), 2.05-2.16 (m, 1H), 2.57 (br, 1H), 2.80-2.94 (m, 4H), 3.08-3.32 (m, 3H), 3.37-3.40 (s, 3H), 3.90-4.00 (m, 1H), 6.30 (d, \( J = 7.7 \) Hz, 1H), 6.46 (dd, \( J = 1.1, 2.7, \) and 7.6 Hz, 1H), 6.61 (t, \( J = 7.1 \) Hz, 1H), 6.93 (d, \( J = 7.9 \) Hz, 1H), 7.03 (t, \( J = 7.8 \) Hz, 2H), 7.12 (d, \( J = 7.7 \) Hz, 1H), 7.24-7.41 (m, 10H); \(^{13}\)C NMR (CDCl₃) δ: 24.0, 28.7, 31.1, 51.9, 53.8, 54.3, 55.0, 60.4, 106.3, 112.3, 116.5, 124.0, 124.9, 126.6, 127.1, 128.2-128.3 (m), 129.4, 134.0, 134.2, 134.3, 134.6, 138.5 (d, \( J_{cp} = 12.7 \) Hz), 139.1 (d, \( J_{cp} = 14.7 \) Hz), 140.1 (d, \( J_{cp} = 20.0 \) Hz), 142.7 (d, \( J_{cp} = 4.4 \) Hz), 152.9, 158.3 (d, \( J_{cp} = 3.3 \) Hz); \(^{31}\)P NMR (CDCl₃) δ: -15.0; FAB-MS m/z (rel intensity): 491 (M⁺-1, 20); HRMS (FAB-MS) m/z calcd for C₃₂H₃₅N₂OP-H 491.2252, found 491.2253.

10h: 42%; mp 146-149 °C; \( [\alpha]_{D}^{25} = -55.4^\circ \) (c 1.00, CHCl₃); \(^1\)H NMR (CDCl₃) δ: 1.24-1.52 (m, 3H), 1.78-1.82 (m, 1H), 2.70 (br-d, \( J = 11.0 \) Hz, 1H), 2.83-2.90 (m, 3H), 3.01 (dt, \( J = 2.1 \) and 11.2 Hz, 1H), 3.11 (t, \( J = 10.5 \) Hz, 1H), 3.24-3.35 (m, 2H), 3.42 (q, \( J = 8.3 \) Hz, 1H), 3.77 (s, 3H), 6.11 (d, \( J = 8.1 \) Hz, 1H), 6.22 (dd, \( J = 1.3, 1.5, \) and 6.3 Hz, 1H), 6.53 (dd, \( J = 0.7, 7.2 \) and 7.9 Hz, 1H), 6.82 (d, \( J = 8.1 \) Hz, 1H), 6.95-7.03 (m, 3H), 7.23-7.39 (m, 10H); \(^{13}\)C NMR (CDCl₃) δ: 25.2, 27.5, 28.3, 47.4, 50.5, 50.9, 52.3, 55.1, 107.3 (d, \( J_{cp} = 3.4 \) Hz), 112.5, 116.3, 124.0, 124.6, 126.7, 127.1, 128.1-128.5 (m), 129.6, 133.7, 133.8, 134.0, 134.1, 138.9 (d, \( J_{cp} = 8.4 \) Hz), 140.6, 142.1, 142.3, 151.0, 158.7 (d, \( J_{cp} = 2.7 \) Hz); \(^{31}\)P NMR (CDCl₃) δ: -13.1; FAB-MS m/z (rel intensity): 493 (M⁺+1, 33); HRMS (FAB-MS) m/z calcd for C₃₂H₃₅N₂OP+H 493.2409, found 493.2434.
4i: 54%; yellow liquid: \([\alpha]_D^{25} = 26.4\ (c\ 1.00,\ CHCl_3)\); \(^1\)H NMR (CDCl_3) \(\delta\) : 0.84 (t, \(J = 7.1\) Hz, 3H), 1.54-1.67 (m, 3H), 1.98-2.08 (m, 1H), 2.09-2.44 (m, 4H), 2.56 (br, 1H), 2.77 (q, \(J = 7.6\) Hz, 1H), 3.24 (d, \(J = 13.9\) Hz, 1H), 3.52 (d, \(J = 13.9\) Hz, 1H), 3.69-3.77 (m, 1H), 3.76 (s, 3H), 6.40 (ddd, \(J = 1.3, 2.8\) and 7.6 Hz, 1H), 6.86 (d, \(J = 8.0\) Hz, 1H), 7.09 (ddd, \(J = 0.8, 7.4\) and 9.2 Hz, 1H), 7.13-7.33 (m, 15H); \(^13\)C NMR (CDCl_3) \(\delta\) : 12.3, 24.5, 31.7, 48.4, 52.6, 55.4, 58.8, 59.0, 60.8, 112.8, 125.4, 126.7 (d, \(J_{cp} = 4.7\) Hz), 128.3, 128.5-128.6 (m), 129.2, 134.1, 134.4, 134.6, 134.7, 134.9, 139.2 (d, \(J_{cp} = 13.2\) Hz), 139.2 (d, \(J_{cp} = 14.6\) Hz), 140.8, 141.0, 141.3, 142.9 (d, \(J_{cp} = 4.1\) Hz), 158.27 (d, \(J_{cp} = 3.5\) Hz); \(^3\)P NMR (CDCl_3) \(\delta\) : -15.2; FAB-MS m/z (rel intensity) : 509 (M\(^+\)+1, 63); HRMS (FAB-MS) m/z calcd for C\(_{33}\)H\(_{37}\)N\(_2\)OP+H 509.2722, found 509.2684.

10i: 26%; mp 138-139 °C; \([\alpha]_D^{25} = -17.8^\circ\ (c\ 1.00,\ CHCl_3)\); \(^1\)H NMR (CDCl_3) \(\delta\) : 0.81 (t, \(J = 7.1\) Hz, 3H), 1.09-1.30 (m, 2H), 1.40-1.44 (m, 1H), 1.75 (d, \(J = 9.6\) Hz, 1H), 2.26-2.50 (m, 3H), 2.59 (d, \(J = 11.0\) Hz, 1H), 2.84-2.88 (m, 1H), 3.01 (q, \(J = 10.9\) Hz, 2H), 3.42 (d, \(J = 14.5\) Hz, 1H), 3.56 (d, \(J = 14.5\) Hz, 1H), 3.79 (s, 3H), 6.23 (ddd, \(J = 1.3, 2.7\) and 7.6 Hz, 1H), 6.84 (d, \(J = 8.1\) Hz, 1H), 7.02 (dt, \(J = 1.2\) and 7.8 Hz, 1H), 7.15-7.33 (m, 15H); \(^13\)C NMR (CDCl_3) \(\delta\) : 13.9, 25.8, 28.5, 45.0, 50.9, 53.4, 54.5, 55.6, 58.0, 113.0, 124.9, 126.6, 128.3, 128.5-128.7 (m), 134.3, 134.5, 139.4 (d, \(J_{cp} = 12.3\) Hz), 139.7 (d, \(J_{cp} = 12.5\) Hz), 141.3 (d, \(J_{cp} = 3.2\) Hz), 142.5, 142.9, 143.1, 159.4; \(^3\)P NMR (CDCl_3) \(\delta\) : -13.1; FAB-MS m/z (rel intensity): 509 (M\(^+\)+1, 35); HRMS (FAB-MS) m/z calcd for C\(_{33}\)H\(_{37}\)N\(_2\)OP+H 509.2722, found 509.2746.
Acetylation of 4e.

To an aminophosphine 4e (0.159 g, 0.34 mmol) and triethylamine (1.0 mL, 7.2 mmol) in THF (5 mL) was added acetyl chloride (0.25 mL, 3.5 mmol) at 0 °C under an argon atmosphere. The reaction mixture was stirred for 20 min. The mixture was diluted with ether and quenched with water. The organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (elution with n-hexane/EtOAc = 15/1).

![Structure of 4j](image)

4j: 0.149 g, 0.30 mmol, 86%; white liquid; [α]D²⁵ = 18.2 (c 0.99, CHCl₃); ¹H NMR (CDCl₃) δ: 0.83 (t, J = 7.5 Hz, 3H), 1.50-1.70 (m, 3H), 2.02 (s, 5H), 1.20-2.67 (m, 6H), 2.78 (q, J = 7.7 Hz, 1H), 3.56-3.69 (m, 1H), 3.79 (s, 3H), 3.94 (dt J = 2.4 and 6.5 Hz, 2H), 6.40 (ddd, J = 1.3, 2.8 and 7.7 Hz, 1H), 6.87 (d, J = 8.1 Hz, 1H), 7.05 (ddd, J = 0.8, 8.3 and 9.1 Hz, 1H), 7.22-7.36 (m, 10H), ¹³C NMR (CDCl₃) δ: 12.3, 21.4, 24.3, 31.5, 49.3, 52.4, 52.9, 55.3, 59.3, 60.9, 62.3, 112.7, 125.3, 126.7, 128.5-128.6 (m), 134.4, 134.5, 134.6, 134.8, 139.0 (d, Jcp = 12.9 Hz), 139.4 (d, Jcp = 14.4 Hz), 140.8 (d, Jcp = 21.3 Hz), 142.8 (d, Jcp = 4.3 Hz), 158.6 (d, Jcp = 3.5 Hz), 171.4; ³¹P NMR (CDCl₃) δ: -15.0; FAB-MS m/z (rel intensity) : 505 (M⁺+1, 25); HRMS (FAB-MS) m/z calcld for C₃₀H₃₇N₂O₃P+H 505.2620, found 505.2644.
Acetylation of 4f.

To an aminophosphine 4f (0.120 g, 0.25 mmol) and triethylamine (1.0 mL, 7.2 mmol) in THF (2 mL) was added acetyl chloride (0.36 mL, 5.0 mmol) at 0 °C under an argon atmosphere. The reaction mixture was stirred for 15 min. The mixture was diluted with ether and quenched with water. The organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (elution with n-hexane/EtOAc = 5/1).

![Chemical structure of 4k](image)

4k: 0.132 g, 0.24 mmol, 94%; yellow liquid; [α]D²⁵ = 17.4 (c 1.00, CHCl₃); ¹H NMR (CDCl₃) δ: 1.49-1.69 (m, 3H), 1.91-2.10 (m, 2H), 2.02 (s, 6H), 2.32 (dd, J = 3.7 and 13.0 Hz, 1H), 2.47-2.68 (m, 5H), 2.77 (q, J = 7.8 Hz, 1H), 3.52-3.65 (m, 1H), 3.80 (s, 3H), 3.87-4.02 (m, 4H), 6.40 (ddd, J = 1.3, 2.8 and 7.6 Hz, 1H), 6.87 (d, J = 7.6 Hz, 1H), 7.06 (ddd, J = 0.8, 7.5 and 8.3 Hz, 1H), 7.22-7.35 (m, 10H); ¹³C NMR (CDCl₃) δ: 21.0, 23.9, 30.8, 52.2, 53.5, 55.0, 60.0, 60.5, 62.8, 112.5, 124.9, 126.4, 128.1-128.3 (m), 134.1, 134.2, 134.3, 134.4, 138.5 (d, Jcp = 12.8 Hz), 139.0 (d, Jcp = 14.2 Hz), 140.3 (d, Jcp = 21.0 Hz), 142.4 (d, Jcp = 4.4 Hz), 158.2 (d, Jcp = 3.5 Hz), 171.0; ³¹P NMR (CDCl₃) δ: -15.0; FAB-MS m/z (rel intensity): 563 (M⁺+1, 12); HRMS (FAB-MS) m/z calcd for C₃₂H₃₉N₂O₅P+H 563.2675, found 563.2666.
Bromination of ent-5 with CBr₄-PPh₃.

*Ent*-8a: 90%; \([\alpha]_D^{25} = 99.1^\circ (c \ 0.96, \text{CHCl}_3)\); \(^1\)H, \(^{13}\)C, and \(^{31}\)P NMR were matched the data of 8a.

Chlorination of ent-5 with thionyl chloride.

*Ent*-8c: 65%; \([\alpha]_D^{25} = 88.5^\circ (c \ 1.03, \text{CHCl}_3)\); \(^1\)H, \(^{13}\)C, and \(^{31}\)P NMR were matched the data of 8c.

Direct preparation of *ent*-4a-b and *ent*-10a-b from *ent*-8a.

*Ent*-4a: 46%; \([\alpha]_D^{25} = -43.5^\circ (c \ 1.01, \text{CHCl}_3)\); \(^1\)H, \(^{13}\)C, and \(^{31}\)P NMR were matched the data of 4a.

*Ent*-10a: 33%; \([\alpha]_D^{25} = -5.0^\circ (c \ 0.98, \text{CHCl}_3)\); \(^1\)H, \(^{13}\)C, and \(^{31}\)P NMR were matched the data of 10a.

*Ent*-4b: 50%; \([\alpha]_D^{25} = -50.2^\circ (c \ 0.98, \text{CHCl}_3)\); \(^1\)H, \(^{13}\)C, and \(^{31}\)P NMR were matched the data of 4b.

*Ent*-10b: 29%; \([\alpha]_D^{25} = -3.6^\circ (c \ 0.74, \text{CHCl}_3)\); \(^1\)H, \(^{13}\)C, and \(^{31}\)P NMR were matched the data of 10b.

General procedure for the palladium-catalyzed allylic alkylation.

To a mixture of [Pd(η³-C₃H₅)Cl]₂ (0.01 mmol, 0.004 g), chiral ligand 4 (0.02 mmol), and LiOAc (0.01 mmol) in a solvent (1 mL) was added BSA (1.5 mmol, 0.37 mL), and racemic allylic ester 11 (0.5 mmol) at room temperature under an Ar atmosphere. After 30 min, nucleophile 12 (1.5 mmol) was added, and stirring was continued for the time indicated in Table at the desired temperature. The reaction mixture was diluted with ether and water. The organic layer was washed with brine and dried over MgSO₄. The filtrate was concentrated with a rotary evaporator and the residue was purified by column chromatography.

*13a* (Table 5, entry 6): 99%; 95%ee; \([\alpha]_D^{25} = -19.7^\circ (c \ 1.01, \text{CHCl}_3)\); \(^1\)H and \(^{13}\)CNMR were matched the data of our authentic sample.!
13b (Table 6, entry 6): 71%; 98%ee; \([\alpha]_D^{25} = -17.1^\circ (c 1.08, \text{CHCl}_3)\); \(^1\)H and \(^{13}\)CNMR were matched the data of our authentic sample.\(^1\)

13c (Table 6, entry 3): 84%; 91%ee; \([\alpha]_D^{25} = -5.2^\circ (c 1.05, \text{CHCl}_3)\); \(^1\)H and \(^{13}\)CNMR were matched the data of our authentic sample.\(^1\)

13d (Table 6, entry 4): 91%; 95%ee; \([\alpha]_D^{25} = 37.2^\circ (c 1.01, \text{CHCl}_3)\); \(^1\)H and \(^{13}\)CNMR were matched the data of our authentic sample.\(^1\)

Reference

$^1$H NMR of 6a
$^{31}$P NMR of 6a
$^1$H NMR of 7a
$^{13}$C NMR of 7a
$^{31}$P NMR of 7a
$^{1}$H NMR of 8a
$^{13}$C NMR of 8a
$^{31}$P NMR of 8a
$^1$H NMR of 8b
\(^{13}\text{C} \text{NMR of 8b}\)
$^{31}\text{P NMR of } 8b$
$^{1}$H NMR of 8c
$^{13}$C NMR of 8c
$^{31}$P NMR of 8c
$^1$H NMR of 9c
$^{13}$C NMR of $9c$
$^{31}$P NMR of 9c
$^{13}$C NMR of 6b
$^{31}$P NMR of 6b
$^1$H NMR of 7b
$^{13}$C NMR of 7b
$^{31}P$ NMR of 7b
$^1$H NMR of 6c
$^{13}$C NMR of 6c
$^{31}$P NMR of 6c
$^1$H NMR of 7c
$^{13}$C NMR of 7c
$^{31}$P NMR of 7c
$^1$H NMR of 6d
$^{13}$C NMR of 6d
$^{31}$P NMR of 6d
$^1$H NMR of 6e
$^{13}$C NMR of 6e
$^{31}$P NMR of 6e
$^1$H NMR of 7e
$^{13}$C NMR of 7e
$^{31}$P NMR of 7e
$^1$H NMR of 6f
$^{13}$C NMR of 6f
$^{31}$P NMR of 6f
$^1$H NMR of 7f
$^{13}$C NMR of 7f
$^{31}\text{P NMR of } 7f$
$^1$H NMR of 6g
$^{13}$C NMR of 6g
$^3$P NMR of 6g
$^1$H NMR of 7g
$^{13}$C NMR of 7g
$^{31}\text{P NMR of 7g}$
^1H NMR of 4a
$^{13}$C NMR of 4a
$^{31}$P NMR of 4a
$^1$H NMR of 10a
$^{13}$C NMR of 10a
$^{31}$P NMR of 10a
$^1$H NMR of 4b
$^{13}$C NMR of 4b
$^3\text{P NMR of 4b}$
$^1\text{H}$ NMR of 10b
$^{13}$C NMR of 10b
$^{31}$P NMR of 10b
$^1$H NMR of 4c
$^{13}$C NMR of 4c
$^{31}$P NMR of 4c
$^1$H NMR of 4d
$^{13}$C NMR of 4d
$^{31}$P NMR of 4d
$^{1}H$ NMR of 4e
$^{13}$C NMR of 4e
$^{31}$P NMR of 4e
$^{31}$P NMR of 4f
$^1\text{H NMR of } 4g$
$^{13}$C NMR of 4g
$^{31}$P NMR of 4g
$^{1}H$ NMR of 4b
$^{13}$C NMR of 4h
$^{31}$P NMR of 4h
$^1$H NMR of 10h
$^{13}\text{C} \text{ NMR of 10h}$
$^{31}$P NMR of 10h
$^1$H NMR of 4i
$^{13}$C NMR of 4i
$^{31}$P NMR of 4i
$^1$H NMR of 10i
$^{13}$C NMR of 10i
$^{31}$P NMR of 10i
$^1$H NMR of 4j
$^{13}$C NMR of 4j
$^{31}$P NMR of 4j
$^1$H NMR of 4k
$^{13}$C NMR of 4k
$^{31}$P NMR of 4k
Chiral phase HPLC chart of \(8a\)

\[
\begin{array}{c}
\text{START DELAY} \quad 0.00 \text{ min} \\
\end{array}
\]

--- % CALCULATION RESULT ---

TEST-DATA

\[
\text{WINDOW} = 0 \% \quad \text{SCALE FACTOR} = 1.0000 \quad \text{PEAK AREA}
\]

\[
\begin{array}{cccccc}
\text{PEAK} & \text{RT(min)} & \text{AREA} & \text{HEIGHT} & \text{MK} & \text{AREA} \\
1 & 48.342 & 888486 & 2573 & & 100.0000 \\
\end{array}
\]

TOTAL 888486 2573 100.0000

Chiral phase HPLC chart of mixture of \(8a\) and \(\text{ent-8a}\)

\[
\begin{array}{c}
\text{START DELAY} \quad 0.00 \text{ min} \\
\end{array}
\]

--- % CALCULATION RESULT ---

TEST-DATA

\[
\text{WINDOW} = 0 \% \quad \text{SCALE FACTOR} = 1.0000 \quad \text{PEAK AREA}
\]

\[
\begin{array}{cccccc}
\text{PEAK} & \text{RT(min)} & \text{AREA} & \text{HEIGHT} & \text{MK} & \text{AREA} \\
1 & 35.775 & 227699 & 943 & V & 48.4753 \\
2 & 46.533 & 334864 & 969 & V & 59.5247 \\
\end{array}
\]

TOTAL 562562 1913 100.0000

Daicel CHIRALCEL OJ; Hexane : EtOH = 99 : 1; Flow : 0.5 mL/min
Chiral phase HPLC chart of 8c

Daicel CHIRALCEL OJ; Hexane : EtOH = 99 : 1; Flow : 0.5 mL/min
Chiral phase HPLC chart of 4a

Daicel CHIRALCEL OD-H; Hexane : i-ProOH = 99 : 1; Flow : 0.5 mL/min
Chiral phase HPLC chart of 4b

Daicel CHIRALCEL OD-H; Hexane : i-PrOH = 99.7 : 0.3; Flow : 0.3 mL/min
Chiral phase HPLC chart of \(13\text{a}\) (Table 5, entry 6); 95\%ee

Daicel CHIRALCEL OD-H; Hexane : i-PrOH = 99 : 1; Flow : 0.5 mL/min

Chiral phase HPLC chart of \(13\text{b}\) (Table 6, entry 6); 98\%ee

Daicel CHIRALPAK AD-H; Hexane : i-PrOH = 95 : 5; Flow : 1.0 mL/min
Chiral phase HPLC chart of $\textbf{13c}$ (Table 6, entry 3); 91% ee

Daicel CHIRALPAK AD-H; Hexane : $i$-PrOH = 90 : 10; Flow : 1.0 mL/min

Chiral phase HPLC chart of $\textbf{13d}$ (Table 6, entry 4); 95% ee

Daicel CHIRALPAK IA at 0 °C; Hexane : $i$-PrOH = 199 : 1; Flow : 0.15 mL/min