Supporting Information

Catalytic Enantioselective Strecker Reaction of Ketoimines

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General: Infrared (IR) spectra were recorded on a JASCO FT/IR 410 Fourier transform infrared spectrophotometer. NMR spectra were recorded on a JEOL JNM-LA500 spectrometer, operating at 500 MHz for ^1H NMR, 125.65 MHz for ^{13}C NMR, and 202 MHz for ^{31}P NMR. Chemical shifts were reported downfield from TMS ($= 0$) for ^1H NMR. For ^{13}C NMR, chemical shifts were reported in the scale relative to the solvent used as an internal reference. ^{31}P NMR were carried out with phosphoric acid (85%) as an external standard. Optical rotations were measured on a JASCO P-1010 polarimeter. Column chromatographies were performed with silica gel Merck 60 (230-400 mesh ASTM), unless otherwise noted. The enantiomeric excesses (ee's) were determined by HPLC. HPLC analysis was performed on JASCO HPLC systems consisting of the following: pump, 880-PU or PU-980; detector, 875-UV or UV-970, measured at 254 nm; column, DAICEL CHIRALPAK AD-H, or DAICEL CHIRALCEL OJ-H, OD-H; mobile phase, hexane/2-propanol. EI mass spectra were measured on JEOL JMS-BU20 GCmate. In general, reactions were carried out in dry solvents under an argon atmosphere, unless noted otherwise. Dry solvents of tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were purchased from KANTO CHEMICAL CO., INC. Propionitrile was distilled from calcium hydride. Other reagents were purified by usual methods.

General procedure for the preparation of *N*-diphenylphosphinoylimine¹.

To a stirred solution of an oxime (prepared from the corresponding ketone and $\text{H}_2\text{NOH}\cdot\text{HCl}$ in pyridine) (0.05 mol) and triethylamine (5.05 g, 0.05 mol) in petroleum ether / CH_2Cl_2 (1/1, 150 ml), a solution of chlorodiphenylphosphine (11.0 g, 0.05 mol) in CH_2Cl_2 was added from a dropping funnel over 15 min at $-40\text{ }^\circ\text{C}$. After stirring for 1 h, the cooling bath was removed and the reaction temperature was gradually increased. The mixture was then allowed to stir for 1 h at room temperature before evaporating the solvent at lower than $20\text{ }^\circ\text{C}$. The residue was dissolved in dichloromethane, washed with water twice and with brine, dried over Na_2SO_4 , and concentrated to give a residue which was purified by silica gel flash column chromatography (KANTO silica gel 60N, spherical, neutral, particle size 0.040-0.100mm) (AcOEt /hexane) to give almost pure phosphinamide. The product was further purified by recrystallization from benzene/petroleum ether (**4a-4f**, **4h**, **4j**), or used without further purification (**4g**, **4i**). *N*-(1-Phenylethylidene)-diphenylphosphinamide (**4a**) and *N*-(1-naphthalen-2-ylidene)-

diphenylphosphinamide (**4d**) are known compounds¹.

***N*-(1-*p*-Chlorophenylethylidene)-diphenylphosphinamide (**4b**):**

white powder; ¹H NMR (C₆D₆): δ 8.18-8.24 (m, 4H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.00-7.17 (m, 8H), 2.60 (s, 3H); ¹³C NMR (C₆D₆): δ 179.1 (d, *J* = 7 Hz), 137.6, 137.5 (d, *J* = 27 Hz), 135.3 (d, *J* = 130 Hz), 131.2 (d, *J* = 8 Hz), 130.6 (d, *J* = 3 Hz), 128.7, 127.9, 127.8 (d, *J* = 12 Hz), 21.6 (d, *J* = 12 Hz); ³¹P NMR (C₆D₆): δ 16.5; IR (neat, cm⁻¹): 1637; EI-MS *m/z* 353 (M⁺); EI-HRMS Calcd for C₂₀H₁₇ClNOP (M⁺) : 353.0736, Found : 353.0744.

***N*-(1-*p*-Methylphenylethylidene)-diphenylphosphinamide (**4c**):**

white powder; ¹H NMR (C₆D₆): δ 8.29 (dd, *J* = 11.3, 7.1 Hz, 4H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.04-7.13 (m, 6H), 6.93 (d, *J* = 8.3 Hz, 2H), 2.77 (d, *J* = 2.2 Hz, 3H), 2.04 (s, 3H); ¹³C NMR (CDCl₃): δ 181.5 (d, *J* = 7 Hz), 143.3, 137.0 (d, *J* = 24 Hz), 135.1 (d, *J* = 132 Hz), 131.7 (d, *J* = 9 Hz), 131.4 (d, *J* = 3 Hz), 129.4, 128.5 (d, *J* = 12 Hz), 128.2, 23.1 (d, *J* = 12 Hz), 21.7; ³¹P NMR (C₆D₆): δ 16.1; IR (neat, cm⁻¹): 1632; EI-MS *m/z* 333 (M⁺); EI-HRMS Calcd for C₂₁H₂₀ClNOP (M⁺) : 333.1283, Found : 333.1289.

***N*-(1-Phenylpropylidene)-diphenylphosphinamide (**4e**):**

white powder; ¹H NMR (C₆D₆): δ 8.24-8.28 (m, 4H), 7.84-7.86 (m, 2H), 7.00-7.15 (m, 9H), 3.36 (q, *J* = 7.6 Hz, 2H), 1.07 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (C₆D₆): δ 186.5 (d, *J* = 7 Hz), 138.7 (d, *J* = 24 Hz), 136.5 (d, *J* = 130 Hz), 132.3 (d, *J* = 9 Hz), 132.1 (d, *J* = 9 Hz), 132.0, 131.2 (d, *J* = 3 Hz), 128.6 (d, *J* = 5 Hz), 128.5 (d, *J* = 9 Hz), 28.9 (d, *J* = 11 Hz), 13.4; ³¹P NMR (C₆D₆): δ 15.7; IR (neat, cm⁻¹): 1626; EI-MS *m/z* 333 (M⁺); EI-HRMS Calcd for C₂₁H₂₀NOP (M⁺) : 333.1283, Found : 353.1283.

***N*-(1-Methyl-3-phenylpropylidene)-diphenylphosphinamide (**4f**):**

white powder; ¹H NMR (CDCl₃): δ 7.82-7.89 (m, 4H), 7.35-7.48 (m, 6H), 7.16-7.29 (m, 5H), 3.04 (t, *J* = 7.6 Hz, 2H), 2.90 (t, *J* = 7.6 Hz, 2H), 2.47 (d, *J* = 1.9 Hz, 3H); ¹³C NMR (CDCl₃): δ 190.9 (d, *J* = 10 Hz), 141.0, 134.7 (d, *J* = 130 Hz), 131.7 (d, *J* = 9 Hz), 131.4 (d, *J* = 3 Hz), 128.6, 128.4 (d, *J* = 11 Hz), 128.4, 126.2, 45.2 (d, *J* = 21 Hz), 31.8, 27.3 (d, *J* = 16 Hz); ³¹P NMR (CDCl₃): δ 18.0; IR (neat, cm⁻¹): 1656; EI-MS *m/z* 347 (M⁺); EI-HRMS Calcd for C₂₂H₂₂NOP (M⁺) : 347.1439, Found : 347.1436.

***N*-(1-Methylhexylidene)-diphenylphosphinamide (**4g**):**

pale yellow oil; ¹H NMR (C₆D₆): δ 8.23 (dd, *J* = 11.6, 7.1 Hz, 4H), 6.99-7.15 (m, 6H), 2.20 (s, 3H), 2.07 (t, *J* = 7.3 Hz, 2H), 1.42-1.48 (m, 2H), 1.15-1.23 (m, 2H), 1.05-1.12 (m, 2H), 0.83 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (C₆D₆): δ 190.6 (d, *J* = 10 Hz), 135.6 (d, *J* = 128 Hz), 131.2 (d, *J* = 8 Hz), 130.4

(d, $J = 2$ Hz), 127.6 (d, $J = 11$ Hz), 42.6 (d, $J = 20$ Hz), 30.7, 25.9 (d, $J = 14$ Hz), 24.9, 22.0, 13.4; ^{31}P NMR (C_6D_6): δ 15.1; IR (neat, cm^{-1}): 1659; EI-MS m/z 313 (M^+); EI-HRMS Calcd for $\text{C}_{19}\text{H}_{24}\text{NOP}$ (M^+) : 313.1596, Found : 313.1595.

***N*-(1-Methyl-3-phenylallylidene)-diphenylphosphinamide (4h)**: white powder; ^1H NMR (C_6D_6): δ 8.28 (dd, $J = 11.6, 7.0$ Hz, 4H), 7.01-7.32 (m, 12H), 6.91 (d, $J = 16.5$ Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (CDCl_3): δ 181.3 (d, $J = 8$ Hz), 141.9, 135.1, 134.9 (d, $J = 131$ Hz), 131.7 (d, $J = 9$ Hz), 131.4 (d, $J = 2$ Hz), 130.3, 130.0 (d, $J = 23$ Hz), 129.0, 128.5 (d, $J = 12$ Hz), 128.3, 23.8 (d, $J = 15$ Hz); ^{31}P NMR (C_6D_6): δ 16.3; IR (neat, cm^{-1}): 1614; EI-MS m/z 345 (M^+); EI-HRMS Calcd for $\text{C}_{22}\text{H}_{20}\text{NOP}$ (M^+) : 345.1283, Found : 345.1285.

***N*-(1-Methyloct-2-enylidene)-diphenylphosphinamide (4i)**: pale yellow oil; ^1H NMR (C_6D_6): δ 8.25 (dd, $J = 11.3, 6.7$ Hz, 4H), 7.00-7.16 (m, 7H), 6.10-6.17 (m, 1H), 2.33 (s, 3H), 1.83 (q, $J = 7.3$ Hz, 2H), 1.00-1.20 (m, 6H), 0.83 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (C_6D_6): δ 180.3 (d, $J = 8$ Hz), 145.2, 135.6 (d, $J = 129$ Hz), 132.5 (d, $J = 22$ Hz), 131.3 (d, $J = 9$ Hz), 130.3 (d, $J = 3$ Hz), 127.6 (d, $J = 12$ Hz), 32.1, 30.8, 27.4, 22.3 (d, $J = 15$ Hz), 21.9, 13.3; ^{31}P NMR (C_6D_6): δ 15.9; IR (neat, cm^{-1}): 1612; EI-MS m/z 339 (M^+); EI-HRMS Calcd for $\text{C}_{21}\text{H}_{26}\text{NOP}$ (M^+) : 339.1752, Found : 339.1751.

***N*-(1-Cyclohex-1-enylethylidene)-diphenylphosphinamide (4j)**: pale yellow powder; ^1H NMR (C_6D_6): δ 8.23-8.28 (m, 4H), 7.02-7.19 (m, 6H), 6.12 (s, 1H), 2.54 (d, $J = 2.2$ Hz, 3H), 2.39-2.44 (m, 2H), 1.72-1.78 (m, 2H), 1.40-1.47 (m, 2H), 1.25-1.31 (m, 2H); ^{13}C NMR (C_6D_6): δ 180.8 (d, $J = 8$ Hz), 139.8 (d, $J = 25$ Hz), 137.9, 136.1 (d, $J = 130$ Hz), 131.3 (d, $J = 8$ Hz), 130.3 (d, $J = 3$ Hz), 127.7 (d, $J = 11$ Hz), 25.6, 24.0, 21.8, 21.0, 20.3 (d, $J = 12$ Hz); ^{31}P NMR (C_6D_6): δ 15.3; IR (neat, cm^{-1}): 1615; EI-MS m/z 323 (M^+); EI-HRMS Calcd for $\text{C}_{20}\text{H}_{22}\text{NOP}$ (M^+) : 323.1439, Found : 323.1436.

Representative procedure for the catalytic enantioselective Strecker-type reaction

***N*-(1-Cyano-1-phenylethyl)-diphenylphosphinamide (5a)**: A solution of $\text{Gd}(\text{O}i\text{Pr})_3$ (0.2 M in THF, 37.5 μL , 0.0075 mmol, purchased from Kojundo Chemical Laboratory Co., Ltd. Fax: +81-492-84-1351) was added to a solution of ligand **3** (7.5 mg, 0.015 mmol) in THF 0.15 mL in an ice bath. The mixture was stirred for 30 min at 45 $^\circ\text{C}$, and then the solvent was evaporated. After drying the resulting pre-catalyst under vacuum (~ 5 mmHg) for 1 h, substrate **4a** (96 mg, 0.3 mmol) was added as a solid in one portion. Propionitrile (0.1 mL) and then TMSCN (60 μL , 0.45 mmol) were added to the mixture at -40 $^\circ\text{C}$ to start the reaction. After the reaction period shown in Table 2, H_2O was added followed by the addition of EtOAc. The organic layer was separated and the water layer

was extracted with EtOAc three times and the combined organic layer was washed with brine, dried (Na_2SO_4), and concentrated to give a crude product which was recrystallized from CH_2Cl_2 /hexane to give enantiomerically pure (>99% ee) **5a** (48.0 mg, 0.25 mmol; 84%) as white powder. ^1H NMR (CDCl_3): δ 7.95-8.03 (m, 2H), 7.70-7.83 (m, 4H), 7.31-7.58 (m, 9H), 3.92 (d, J = 7.9 Hz, 1H), 1.91 (s, 3H); ^{13}C NMR (CDCl_3): δ 141.4, 141.3, 141.3, 135.6, 132.9, 132.6, 132.5, 132.4, 132.4, 132.3, 132.2, 131.9, 131.5, 131.4, 129.1, 129.0, 129.0, 128.9, 128.8, 128.7, (128-142 ppm : multiple peaks), 121.5 (d, J = 3 Hz), 57.0, 29.7 (d, J = 3 Hz); ^{31}P NMR (CDCl_3): δ 20.3; IR (neat, cm^{-1}): 3142, 1438, 1191; EI-MS m/z 346 (M^+); EI-HRMS Calcd for $\text{C}_{21}\text{H}_{19}\text{N}_2\text{OP}$ (M^+) : 346.1235, Found : 346.1233; $[\alpha]_{\text{D}}^{23}$ -19.1 (c = 1.00, CHCl_3) (>99% ee); HPLC (DAICEL CHIRALCEL OJ-H, hexane/2-propanol 9/1, 1.0 ml/min) t_{R} 8.6 min (major), 12.9 min (minor).

Representative procedure for the conversion to oxazolidone (7).

12 N HCl aq. (1 mL) was added to a crude mixture of the Strecker reactant (from **4i**, 30.1 mg, 0.0698 mmol) at room temperature, and the mixture was stirred at 100 °C for 10 h. After cooling down to room temperature, the solvent was removed and pyridine (0.5 mL) was added to the residue. Then to the mixture, benzoyl chloride (25 μL , 0.210 mmol) and DMAP (1 mg) was added at room temperature. After stirring for 2 h, water was added followed by the addition of ether. The organic layer was separated, and the aqueous phase was further extracted twice with ether. The combined organic layer was washed with water twice and brine, dried (Na_2SO_4), and concentrated to give a residue which was purified by silica gel flash chromatography (AcOEt/hexane, 1/25) to give oxazolidone **7i** (18.8 mg, 0.0694 mmol; 99% from **4i**) as colorless oil.

4-(4-Methylphenyl)-4-methyl-2-phenyl-4H-oxazol-5-one (7c):

colorless oil; ^1H NMR (CDCl_3): δ 8.09 (d, $J = 7.6$ Hz, 2H), 7.50-7.64 (m, 5H), 7.19 (d, $J = 8.3$ Hz, 2H), 2.35 (s, 3H), 1.87 (s, 3H); ^{13}C NMR (CDCl_3): δ 179.5, 160.3, 138.3, 135.9, 133.0, 129.6, 129.0, 128.2, 126.1, 125.4, 70.7, 27.0, 21.2; IR (neat, cm^{-1}): 1819, 1656, 1005; EI-MS m/z 265 (M^+); EI-HRMS Calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_2$ (M^+) : 265.1103, Found : 265.1102; $[\alpha]_{\text{D}}^{23} +134.1$ ($c = 0.920$, CHCl_3) (98% ee); HPLC (DAICEL CHIRALCEL OJ-H, hexane/2-propanol 1000/1, 1.0 ml/min) t_{R} 23.2 min (minor), 27.6 min (major).

4-Methyl-4-naphthalen-2-yl-2-phenyl-4H-oxazol-5-one (7d):

colorless oil; ^1H NMR (CDCl_3): δ 8.08-8.15 (m, 3H), 7.78-7.90 (m, 4H), 7.48-7.64 (m, 5H), 1.98 (s, 3H); ^{13}C NMR (CDCl_3): δ 179.3, 160.5, 136.2, 133.2, 133.1, 133.1, 129.0, 128.8, 128.4, 128.3, 127.7, 126.6, 126.6, 124.6, 123.3, 71.0, 27.3; IR (neat, cm^{-1}): 1820, 1656, 1005; EI-MS m/z 301 (M^+); EI-HRMS Calcd for $\text{C}_{20}\text{H}_{15}\text{NO}_2$ (M^+) : 301.1103, Found : 301.1102; $[\alpha]_{\text{D}}^{24} +101.0$ ($c = 0.675$, CHCl_3) (94% ee); HPLC (DAICEL CHIRALCEL OJ-H, hexane/2-propanol 99/1, 1.0 ml/min) t_{R} 21.1 min (minor), 34.4 min (major).

4-Ethyl-2,4-diphenyl-4H-oxazol-5-one (7e):

colorless oil; ^1H NMR (CDCl_3): δ 8.11 (d, $J = 7.3$ Hz, 2H), 7.68 (d, $J = 7.3$ Hz, 2H), 7.49-7.62 (m, 3H), 7.30-7.41 (m, 3H), 2.25 (q, $J = 7.3$ Hz, 2H), 0.93 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (CDCl_3): δ 178.9, 160.2, 138.2, 132.8, 128.8, 128.6, 128.1, 128.1, 125.9, 125.7, 74.9, 34.4, 8.6; IR (neat, cm^{-1}): 1813, 1655, 1021; EI-MS m/z 265 (M^+); EI-HRMS Calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_2$ (M^+) : 265.1103, Found : 265.1103; $[\alpha]_{\text{D}}^{22} +105.4$ ($c = 0.81$, CHCl_3) (85% ee); HPLC (DAICEL CHIRALCEL OJ-H, hexane/2-propanol 499/1, 1.0 ml/min) t_{R} 14.8 min (minor), 20.0 min (major).

4-Methyl-4-phenethyl-2-phenyl-4H-oxazol-5-one (7f):

colorless oil; ^1H NMR (CDCl_3): δ 8.02 (d, $J = 7.0$ Hz, 2H), 7.46-7.61 (m, 3H), 7.13-7.27 (m, 5H), 2.60-2.66 (m, 1H), 2.45-2.52 (m, 1H), 2.18-2.25 (m, 2H), 1.57 (s, 3H); ^{13}C NMR (CDCl_3): δ 180.3, 160.3, 140.5, 132.9, 129.0, 128.6, 128.5, 128.1, 126.3, 126.0, 69.6, 40.1, 30.6, 24.2; IR (neat, cm^{-1}): 1822, 1653, 1004; EI-MS m/z 279 (M^+); EI-HRMS Calcd for $\text{C}_{18}\text{H}_{17}\text{NO}_2$ (M^+) : 279.1259, Found : 279.1254; $[\alpha]_{\text{D}}^{25} +3.6$ ($c = 0.675$, CHCl_3) (89% ee); HPLC (DAICEL CHIRALCEL OJ-H, hexane/2-propanol 99/1, 1.0 ml/min) t_{R} 17.8 min (minor), 31.6 min (major).

4-Methyl-4-pentyl-2-phenyl-4H-oxazol-5-one (7g):

colorless oil; ^1H NMR (CDCl_3): δ 8.00 (d, $J = 7.3$ Hz, 2H), 7.46-7.59 (m, 3H), 1.84-1.89 (m, 2H), 1.51 (s, 3H), 1.14-1.33 (m, 6H), 0.82-0.86 (m, 3H); ^{13}C NMR (CDCl_3): δ 181.0, 159.7, 132.6, 128.8, 127.9, 126.0, 69.6, 38.3, 31.5, 23.9, 23.6, 22.3, 13.9; IR

(neat, cm^{-1}): 1822, 1655, 1004; EI-MS m/z 245 (M^+); EI-HRMS Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_2$ (M^+) : 245.1416, Found : 245.1420; $[\alpha]_{\text{D}}^{22} +4.2$ ($c = 0.88$, CHCl_3) (61% ee); HPLC (DAICEL CHIRALCEL OJ-H, hexane/2-propanol 499/1, 1.0 ml/min) t_{R} 6.6 min (minor), 8.0 min (major).

4-Methyl-4-phenyl-2-styryl-4H-oxazol-5-one (7h): colorless oil; ^1H NMR (CDCl_3): δ 8.07 (d, $J = 7.1$ Hz, 2H), 7.49-7.63 (m, 3H), 7.24-7.40 (m, 5H), 6.76 (d, $J = 16.1$ Hz, 1H), 6.34 (d, $J = 16.1$ Hz, 1H), 1.73 (s, 3H); ^{13}C NMR (CDCl_3): δ 178.9, 160.4, 135.9, 133.0, 131.5, 129.0, 128.8, 128.4, 128.2,

126.9, 126.8, 126.1, 70.1, 25.0; IR (neat, cm^{-1}): 1822, 1655, 1006; EI-MS m/z 277 (M^+); EI-HRMS Calcd for $\text{C}_{18}\text{H}_{15}\text{NO}_2$ (M^+) : 277.1103, Found : 277.1111; $[\alpha]_{\text{D}}^{25} +31.6$ ($c = 0.095$, CHCl_3) (83% ee); HPLC (DAICEL CHIRALCEL OJ-H, hexane/2-propanol 99/1, 1.0 ml/min) t_{R} 18.6 min (minor), 33.4 min (major).

4-Hept-1-enyl-4-methyl-2-phenyl-4H-oxazol-5-one (7i): colorless oil; ^1H NMR (CDCl_3): δ 8.03 (dd, $J = 7.3, 1.3$ Hz, 2H), 7.47-7.60 (m, 3H), 5.81-5.87 (m, 1H), 5.60 (d, $J = 15.6$ Hz, 1H),

2.02-2.06 (m, 2H), 1.61 (s, 3H), 1.21-1.41 (m, 6H), 0.87 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (CDCl_3): δ 178.2, 159.0, 132.4, 131.8, 127.9, 127.0, 126.2, 125.1, 68.8, 31.3, 30.4, 27.5, 23.6, 21.5, 13.1; IR (neat, cm^{-1}): 1824, 1651, 1005; EI-MS m/z 271 (M^+); EI-HRMS Calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_2$ (M^+) : 271.1572, Found : 271.1570; $[\alpha]_{\text{D}}^{23} +1.3$ ($c = 0.79$, CHCl_3) (88% ee); HPLC (DAICEL CHIRALPAK AD-H, hexane/2-propanol 499/1, 1.0 ml/min) t_{R} 7.5 min (major), 8.7 min (minor).

4-Cyclohex-1-enyl-4-methyl-2-phenyl-4H-oxazol-5-one (7j): colorless oil; ^1H NMR (CDCl_3): δ 8.02 (d, $J = 7.3$ Hz, 2H), 7.47-7.59 (m, 3H), 5.90-5.92 (m, 1H), 1.95-2.22 (m, 4H), 1.62 (s, 3H), 1.48-1.70 (m, 4H); ^{13}C NMR (CDCl_3): δ 179.2, 159.9, 134.1, 132.6, 128.7, 127.9, 126.0, 125.0, 72.1, 25.2,

24.0, 22.6, 22.1, 21.8; IR (neat, cm^{-1}): 1820, 1651, 1002; EI-MS m/z 255 (M^+); EI-HRMS Calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_2$ (M^+) : 255.1259, Found : 255.1269; $[\alpha]_{\text{D}}^{23} +20.3$ ($c = 1.56$, CHCl_3) (90% ee); HPLC (DAICEL CHIRALCEL OJ-H, hexane/2-propanol 499/1, 0.5 ml/min) t_{R} 20.8 min (major), 23.1 min (minor).

Lanthanide metal effects

Gd-catalyst was selected based on the following metal-screening.

entry	lanthanide	yield of 7k (%)	ee of 7k (%)
1	Pr	69	11
2	Sm	69	10
3	Gd	74	51
4	Dy	79	-26
5	Er	21	0

Conversion of the Strecker-products and determination of the absolute configurations

***N*-Boc- α -methylphenylglycine methyl ester (**6a**):** A suspension of **5a** (16.7 mg, 0.0482 mmol) in conc. HCl (1 mL) was heated at 100 °C for 10 h. After cooling to ambient temperature, the solvent was removed *in vacuo*, and the residue was dissolved in dry MeOH (0.5 mL). To this mixture, SOCl₂ (50 μ L) was added dropwise at room temperature then the reaction mixture was refluxed for 9 h. After cooling ambient temperature, the solvent was removed *in vacuo*, and the residue was dissolved in CH₃CN (2 mL). To this mixture, NaHCO₃ (300 mg, 3.6 mmol) and Boc₂O (45 mg, 0.206 mmol) was added respectively, and then the reaction mixture was heated at 70 °C for 12 h. After cooling to ambient temperature, the precipitate was removed by filtration and the filtrate was concentrated and the residue was purified by silica gel flash column chromatography (AcOEt/hexane, 1/6) to give the Boc protected amino acid **6a** (12.5 mg, 0.0448 mmol; 92% from **5a**) as white powder. From the optical rotation ($[\alpha]_D^{23} +44.1$ ($c = 0.625$, CHCl₃) (>99% ee)), the absolute configuration was determined to be *S* (lit.³ $[\alpha]_D^{21} +44.2$ ($c = 1.44$, CHCl₃) (>99% ee)).

2-Benzoylamino-2-methylnon-3-enoic acid methyl ester (7i-1**):** To a stirred solution of **7i** (88% ee) (23.2 mg, 0.0856 mmol) in dry MeOH (1 mL), SOCl₂ (73 μ L) was added dropwise at 0 °C. After the mixture was stirred at the same temperature for 1 h, the solvent was removed *in*

vacuo at 10 °C. The residue was purified by silica gel flash column chromatography (AcOEt/hexane, 1/3) to give methyl ester **7i-1** (23.5 mg, 0.0776 mmol; 91%) as a colorless oil; ¹H NMR (CDCl₃): δ 7.79 (d, *J* = 7.0 Hz, 2H), 7.41-7.52 (m, 3H), 6.83 (s, 1H), 5.72-5.77 (m, 2H), 3.77 (s, 3H), 2.04-2.09 (m, 2H), 1.79 (s, 3H), 1.21-1.41 (m, 6H), 0.87 (t, *J* = 6.7 Hz, 3H); ¹³C NMR (CDCl₃): δ 172.6, 165.2, 133.5, 131.8, 130.7, 128.4, 127.6, 126.1, 59.4, 52.0, 31.3, 30.4, 27.6, 21.7, 21.5, 13.1; IR (neat, cm⁻¹): 3310, 1742, 1639, 1531; EI-MS *m/z* 303 (M⁺); EI-HRMS Calcd for C₁₈H₂₅NO₃ (M⁺) : 303.1834, Found : 303.1830; [α]_D²⁴+22.9 (c = 1.12, CHCl₃) (88% ee).

2-Benzoylamino-2-methylnonanoic acid methyl ester (8i): Pd on carbon (5%) (5.0 mg) was added to a solution of the methyl ester **7i-1** (88% ee) (22.8 mg, 0.0751 mmol) in AcOEt (0.5 mL). The mixture was vigorously stirred under H₂ (1 atm), and after 6 h, the catalyst was filtered and washed with AcOEt. The filtrate was concentrated and the residue was purified by silica gel flash column chromatography (AcOEt/hexane, 1/3) to give **8i** (22.0 mg, 0.0721 mmol; 96%) as a colorless oil. The enantiomeric excess of **8i** was determined to be 89% using chiral HPLC analysis [DAICEL CHIRALCEL OJ-H, hexane/2-propanol 499/1, 0.5ml/min, *t_R* 15.7 min (minor), 16.5 min (major)]; ¹H NMR (CDCl₃): δ 7.79 (d, *J* = 7.0 Hz, 2H), 7.41-7.52 (m, 3H), 7.05 (s, 1H), 3.80 (s, 3H), 2.40-2.47 (m, 1H), 1.82-1.89 (m, 1H), 1.72 (s, 3H), 1.16-1.32 (m, 9H), 1.03-1.10 (m, 1H), 0.85 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (CDCl₃): δ 174.5, 165.3, 134.0, 130.5, 127.6, 126.0, 60.0, 51.9, 35.5, 30.8, 28.4, 28.2, 23.5, 22.3, 21.7, 13.2; IR (neat, cm⁻¹): 3325, 1742, 1641, 1530; EI-MS *m/z* 305 (M⁺); EI-HRMS Calcd for C₁₈H₂₇NO₃ (M⁺) : 305.1991, Found : 305.1986; [α]_D²²+18.4 (c = 0.87, CHCl₃) (89% ee).

2-Amino-2-methylnonanoic acid methyl ester (9i): A solution of **8i** (17.6 mg, 0.0576 mmol) in conc. HCl (1 mL) was heated at 100 °C for 18 h. After cooling to ambient temperature, this mixture was washed with ether three times, and then evaporated to give almost pure 2-amino-2-methylnonanoic acid hydrochloride which was used in the next step without further purification. To a solution of this residue in dry MeOH (1 mL), SOCl₂ (220 μ L) was added dropwise at 0 °C. Then the reaction mixture was refluxed for 7 h. After cooling to ambient temperature, solvent was removed *in vacuo*, and the residue was dissolved in 1 N HCl. This mixture was washed with ether three times followed by evaporation to dryness. To the residue ether and concentrated aqueous ammonia were added to adjust the mixture to pH 9-10. The ether layer was separated and aqueous layer was extracted with ether twice. The combined organic layer was dried (Na₂SO₄), and concentrated to give a pure **9i** (10.0 mg, 0.0498 mmol; 88% from **8i**) as a white powder. From the optical rotation ([α]_D²²+11.0 (c = 1.00, EtOH) (89% ee)), the absolute configuration was determined to be *S* (lit.⁴[α]_D²⁰-12.9 (c = 0.6, EtOH) for *R* enantiomer, >95%

ee.); ^1H NMR (CDCl_3): δ 3.70 (s, 3H), 1.65-1.71 (m, 1H), 1.59-1.67 (bs, 2H), 1.50-1.56 (m, 1H), 1.31 (s, 3H), 1.10-1.30 (m, 10H), 0.87 (t, $J = 6.7$ Hz, 3H); ^{13}C NMR (CDCl_3): δ 177.5, 57.0, 51.3, 40.3, 30.9, 28.9, 28.3, 5.6, 23.3, 21.8, 13.2; IR (neat, cm^{-1}): 1734.

Studies to Observe the *E/Z* Isomers of *N*-diphenylphosphinoylketoimines

To observe relations between the enantioselectivity and *E/Z* ratio of the ketoimines, especially in the case of primary alkyl-substituted ketoimines, we planned to determine the *E/Z* ratio of the ketoimines. Based on the following results, however, we concluded that *N*-diphenylphosphonoylketoimines exist in a very fast equilibrium between *E*- and *Z*-isomers.

(1) Low temperature NMR studies using **4f** and **4g**: No peak separation was observed when ^1H and ^{31}P NMR were measured at -40 °C in CD_3CN (the solvent for the catalytic enantioselective reaction is propionitrile). ^{31}P NMR signals began to separate at -80 °C for **4f**, and at -94 °C for **4g**, in both ca. 4:1 ratio in CD_2Cl_2 (charts shown below). The results are in sharp contrast to that the precursor oximes exist as a mixture of the configurational isomers (ca. 3:1) even at ambient temperature. No conclusive 1D- and 2D-NOE of **4f** and **4g** were observed at room temperature to determine the C=N double geometry, probably due to a fast equilibrium compared to the NMR time scale. These results indicate that the energy barrier for the C=N rotation is low. Although the ratio of the separated peaks (thus, the position of the equilibrium) was similar for **4f** and **4g**, the resulting enantioselectivity was significantly different (89% ee from **4f** and 72% ee from **4g**). These results indicated that the *E/Z* ratio in the ground state is not the determining factor for the enantioselectivity.

(2) Analogy from the precedent studies using *N*-sulfonylimines: It is known that *N*-sulfonylimines exist in a fast equilibrium between *E*- and *Z*-isomers via in plane inversion.⁵ The mechanism of the facile isomerization was proposed to be through a stabilization of the transient linear structure by (p-d) π conjugation between sulfur and nitrogen atoms.⁶ Moreover, it is known that this type of conjugation is stronger between phosphorus and nitrogen atoms

than between sulfur and nitrogen atoms,⁷ which should result in a more facile isomerization of *N*-phosphinoylimines than *N*-sulfonylimines.

Based on the reasons described above, it appears to be reasonable to consider that *N*-phosphinoylimines exist in a very fast equilibrium between *E*- and *Z*-isomers even at -40 °C in propionitrile, and the reaction would proceed from one of these configurational isomers (controlled by Curtin–Hammet principle). Therefore, the *E/Z* ratio in the ground state may not be reflected to the enantioselectivity.

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