Supporting Information

A Highly Stereoselective Synthesis of Optically Active Tri-substituted 1,2-Ethylenediamines: The First Example of Grignard Addition to *N*-Diphenylphosphinoyl Ketimines Derived from Amino Acids

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General Experimental Procedures: NMR spectra were recorded in CDCl₃, operating at 500 MHz for ¹H NMR and 125.76 MHz for ¹³C NMR, at ambient temperature unless otherwise mentioned. All signals were expressed as ppm downfield from tetramethylsilane used as an internal standard (δ-value in CDCl₃). Infrared (IR) spectra were obtained recorded as KBr pellets. High resolution mass spectra were recorded using fast atom bombardment (HRFABMS). HPLC analysis of yield and diastereomeric excess was carried out at 40 °C, measured at 210 nm; column, YMC-pack ODS-AM (Column size: ID 4.6mm, Length 250mm, Particle size 5 μm) or ODS-AQ (Column size: ID 4.6mm, Length 250mm, Particle size 5 μm); mobile phase, 0.1% aqueous phosphoric acid/methanol or 0.1% aqueous phosphoric acid/acetonitrile. HPLC analysis of enantiomeric excess was carried out at 35 °C, measured at 254 nm or 220 nm, equipped with an appropriate optically active column (Column size: ID 4.6mm, Length 250mm). Column chromatography was performed with silica gel (230–400 mesh) or amino-modified silica gel¹ (NH-silica gel, 100-200 mesh). Preparative thin layer chromatography was performed on 0.5 mm × 20 cm × 20 cm silica gel plate. Reactions were carried out in dry solvents under nitrogen atmosphere if necessary. Enantiomeric excesses were determined by comparison with racemic samples. Phenylmagnesium bromide and methylmagnesium bromide were purchased from Kanto Chemical Co. 4-Fluorophenylmagnesium bromide and 4-methoxyphenylmagnesium bromide were purchased from Aldrich Chemical Co. *N*-(*tert*-Butoxycarbonyl)-L-alanine-*N'*-methoxy-*N'*-methylamide (**1a**) was purchased from HAMARI Chemicals, Ltd. *N*-(*tert*-Butoxycarbonyl)-L-valine-*N'*-methoxy-*N'*-methylamide (**1b**) was prepared from commercially available *N*-(*tert*-butoxycarbonyl)-L-valine according to the reported procedure.²

¹ Fuji Silysia, Chromatorex NH-DM1020.

² Maugras, I.; Poncet, J.; Jouin, P. *Tetrahedron* **1990**, *46*, 2807-2816.

***N*-Diphenylphosphinoyl Ketimines (4)**

***tert*-Butyl (Z)-*N*-{(2*S*)-1-[(diphenylphosphinoyl)imino]-1-(4-fluorophenyl)-2-propyl}carbamate (4b).** A colorless solid. Mp: 149-152 °C. $[\alpha]_D^{26} -18.3$ (*c* 1.05, CHCl₃, 99% ee). HPLC: DAICEL CHIRALPAK AD (hexane/2-propanol = 4/1, flow 0.5 mL/min) *t*_R 12.3 min (minor) and 18.3 min (major). ¹H NMR: δ 8.11 (dd, *J* = 8.8, 5.4 Hz, 2H), 8.03 (m, 2H), 7.89 (m, 2H), 7.65 (d, *J* = 9.5 Hz, 1H), 7.50–7.38 (m, 6H), 7.15 (dd, *J* = 8.6, 8.5 Hz, 2H), 5.37 (dq, *J* = 9.4, 7.3 Hz, 1H), 1.48 (d, *J* = 7.2 Hz, 3H), 1.21 (s, 9H). ¹³C NMR: δ 185.5 (d, *J* = 9 Hz), 165.5 (d, *J* = 255 Hz), 155.6, 134.5, 134.1 (d, *J* = 140 Hz), 133.8 (d, *J* = 130 Hz), 131.9 (d, *J* = 9 Hz), 131.6 (d, *J* = 3 Hz), 131.5 (d, *J* = 3 Hz), 131.4 (d, *J* = 9 Hz), 131.1 (d, *J* = 9 Hz), 128.6 (d, *J* = 13 Hz), 128.4 (d, *J* = 13 Hz), 115.9 (d, *J* = 22 Hz), 79.1, 49.8 (d, *J* = 10 Hz), 28.1, 19.3. IR (KBr): ν 3246, 3056, 2974, 2361, 1707, 1643, 1593, 1542, 1508, 1440, 1410, 1365, 1277, 1233, 1175, 1157, 1123, 1101, 1024, 726, 698, 551 cm⁻¹. HRFABMS *m/z*. Calcd for C₂₆H₂₈FN₂O₃PH (MH⁺): 467.1900, Found: 467.1872.

***tert*-Butyl (Z)-*N*-{(2*S*)-1-[(diphenylphosphinoyl)imino]-1-(4-fluorophenyl)-3-methyl-2-butyl}carbamate (4e).** A colorless solid. Mp: 119-122 °C. $[\alpha]_D^{27} -17.5$ (*c* 1.01, CHCl₃, 92% ee). HPLC: DAICEL CHIRALPAK AD (hexane/2-propanol = 9/1, flow 0.5 mL/min) *t*_R 11.1 min (minor) and 17.0 min (major). ¹H NMR: δ 8.13 (dd, *J* = 8.6, 5.5 Hz, 2H), 8.01 (m, 2H), 7.89 (dd, *J* = 12.0, 7.3 Hz, 2H), 7.56–7.37 (m, 7H), 7.15 (dd, *J* = 8.6, 8.5 Hz, 2H), 4.95 (dd, *J* = 9.6, 9.4 Hz, 1H), 2.35 (m, 1H), 1.25 (s, 9H), 1.03 (d, *J* = 6.5 Hz, 3H), 0.66 (d, *J* = 6.8 Hz, 3H). ¹³C NMR: δ 185.5, 165.4 (d, *J* = 254 Hz), 156.2, 136.5 (d, *J* = 22 Hz), 134.0 (d, *J* = 134 Hz), 133.9 (d, *J* = 138 Hz), 131.7 (d, *J* = 9 Hz), 131.6 (d, *J* = 10 Hz), 131.5, 131.3 (d, *J* = 9 Hz), 128.6 (d, *J* = 13 Hz), 128.4 (d, *J* = 13 Hz), 115.9 (d, *J* = 22 Hz), 79.0, 60.0 (d, *J* = 10 Hz), 32.6, 28.2, 20.1, 19.9. IR (KBr): ν 3288, 3060, 2968, 2931, 2871, 1703, 1641, 1594, 1508, 1440, 1365, 1288, 1236, 1189, 1158, 1119, 1106, 998, 887, 844, 773, 751, 725, 695, 593, 560, 550, 514 cm⁻¹. HRFABMS *m/z*. Calcd for C₂₈H₃₂FN₂O₃PH (MH⁺): 495.2213, Found: 495.2209.

***tert*-Butyl (Z)-*N*-{(2*S*)-1-[(diphenylphosphinoyl)imino]-1-(4-methoxyphenyl)-2-propyl}carbamate (4c).** 4-Methoxyphenylmagnesium bromide (0.5 M, THF solution, 96 mL, 48.0 mmol) was dropwise added to a stirred suspension of **1a** (4.46 g, 19.2 mmol) in THF (22.5 mL) at 0 °C,

and the mixture was stirred for 30 h at 25 °C. After cooling to 0 °C, aqueous KHSO₄ solution (7.84 g, 57.6 mmol in 67.5 mL of water) was added. The reaction mixture was stirred for 1 h at ambient temperature and extracted with *tert*-butyl methyl ether (45 mL × 2). The organic layer was washed with water (45 mL) and brine (22.5 mL), dried over Na₂SO₄, and concentrated in vacuo. 10.67 g of crude ketone **2c** was obtained as a pale yellow oil. Crude **2c** (10.67 g, 19.2 mmol) was dissolved in ethanol (107 mL). To it was added hydroxylamine hydrochloride (3.33 g, 48.0 mmol), sodium acetate (3.94 g, 48.0 mmol), and water (21 mL). The mixture was stirred for 4 h under reflux, cooled to rt, diluted with water (27 mL), and concentrated under reduced pressure to remove ethanol. The residual solution was extracted with ethyl acetate (54 mL × 3). The organic layer was washed with saturated aqueous NaHCO₃ (27 mL) and brine (27 mL), dried over Na₂SO₄, and concentrated in vacuo. The residue was passed through a pad of silica gel (heptane/ethyl acetate = 4/1 to 1/1). 5.59 g of crude oxime **3c** was obtained as a colorless solid. Crude **3c** (5.59 g, 19.0 mmol) was dissolved in THF (56 mL), followed by the addition of triethylamine (3.2 mL, 22.8 mmol) and it was cooled to –30 °C. Chlorodiphenylphosphine (3.4 mL, 19.0 mmol) was added dropwise at –30 °C, and the mixture was stirred for 3 h at the same temperature. It was warmed to rt over 2 h. Water (56 mL) was added and the organic layer was separated. The aqueous layer was extracted with *tert*-butyl methyl ether (56 mL × 2). The combined organic layer was dried over Na₂SO₄ and concentrated in vacuo. The orange oily residue was chromatographed on silica gel (heptane/*tert*-butyl methyl ether = 1/1) to give **4c** as a colorless solid (3.62 g, 40%). Mp: 54–58 °C. [α]_D²⁶ –13.1 (*c* 1.07, CH₃OH, 99% ee). HPLC: DAICEL CHIRALPAK AD (hexane/2-propanol = 4/1, flow 0.5 mL/min) *t*_R 14.2 min (minor) and 23.2 min (major). ¹H NMR: δ 8.11 (d, *J* = 8.9 Hz, 2H), 8.04 (m, 2H), 7.89 (m, 2H), 7.77 (d, *J* = 9.5 Hz, 1H), 7.49–7.36 (m, 6H), 6.97 (d, *J* = 9.0 Hz, 2H), 5.44 (dq, *J* = 9.5, 7.3 Hz, 1H), 3.88 (s, 3H), 1.48 (d, *J* = 7.2 Hz, 3H), 1.21 (s, 9H). ¹³C NMR: δ 185.2 (d, *J* = 9 Hz), 163.5, 155.6, 134.6 (d, *J* = 141 Hz), 134.3 (d, *J* = 130 Hz), 131.9 (d, *J* = 9 Hz), 131.5 (d, *J* = 9 Hz), 131.4 (d, *J* = 3 Hz), 131.3 (d, *J* = 3 Hz), 130.9, 130.5 (d, *J* = 22 Hz), 128.5 (d, *J* = 13 Hz), 128.4 (d, *J* = 13 Hz), 114.1, 78.9, 49.1 (d, *J* = 10 Hz), 28.2, 19.7. IR (KBr): ν 3276, 3058, 2977, 2932, 2365, 1706, 1638, 1597, 1571, 1511, 1439, 1366, 1242, 1168, 1121, 1103, 1023, 972, 863, 725, 695, 552, 522 cm^{–1}. HRFABMS *m/z*. Calcd for C₂₇H₃₁N₂O₄PH (MH⁺): 479.2100, Found: 479.2116.

Grignard Addition to *N*-Diphenylphosphinoyl Ketimines (4)

***tert*-Butyl *N*-{(2*S*)-1-[(diphenylphosphinoyl)amino]-1,1-diphenyl-2-propyl}carbamate (5aa).** A colorless solid. $[\alpha]_D^{27} -70.4$ (*c* 1.02, CHCl₃, 98% ee). HPLC: DAICEL CHIRALPAK AD (hexane/2-propanol = 4/1, flow 0.5 mL/min) *t*_R 12.5 min (minor) and 25.0 min (major). ¹H NMR: δ 7.76 (m, 2H), 7.62 (m, 2H), 7.39–7.24 (m, 14H), 6.88–6.83 (m, 3H), 5.03 (m, 1H), 4.52 (br, 1H), 1.45 (s, 9H), 1.04 (d, *J* = 6.5 Hz, 3H). ¹³C NMR: δ 156.5, 142.2, 138.9, 134.6 (d, *J* = 124 Hz), 134.2 (d, *J* = 131 Hz), 131.7 (d, *J* = 9 Hz), 131.3 (d, *J* = 9 Hz), 131.1 (d, *J* = 2 Hz), 130.7, 130.4, 128.5, 128.2 (d, *J* = 13 Hz), 127.9 (d, *J* = 13 Hz), 127.5, 127.4, 127.2, 127.1, 79.9, 69.0, 53.5, 28.4, 17.8. IR (KBr): ν 3432, 3222, 3057, 2977, 2930, 1701, 1497, 1539, 1366, 1312, 1170, 1121, 1054, 915, 859, 752, 724, 699, 539 cm⁻¹. HRFABMS *m/z*. Calcd for C₃₂H₃₅N₂O₃PH (MH⁺): 527.2464, Found: 527.2487.

Yields in Table 1 were determined by HPLC assay with following conditions; Column: YMC AM-303 (0.1% aqueous phosphoric acid/methanol = 3/7, flow 1.0 mL/min) *t*_R 12.5 min (**6a**), 15.1 min (**4a**), and 26.1 min (**5aa**).

***tert*-Butyl *N*-{(1*S*,2*S*)-1-[(diphenylphosphinoyl)amino]-1-(4-methoxyphenyl)-1-phenyl-2-propyl}carbamate (5ac).** Yield was determined by HPLC assay with following conditions; Column: YMC AQ-303 (0.1% aqueous phosphoric acid/acetonitrile = 50/50 to 5/95 in 30 min, flow 1.0 mL/min) *t*_R 14.2 min (**6a**), 17.3 min (**5ac**), and 17.5 min (**5ca**). After work-up, this product was obtained as a mixture of **5ac** and **6a**. Authentic sample was prepared as following procedure³: To a stirred solution of a mixture of **5ac** and **6a** (487 mg) in toluene (2.4 mL) was added 2,6-lutidine (0.26 mL, 2.23 mmol). Trimethylsilyl trifluoromethanesulfonate (0.30 mL, 1.67 mmol) was added at 0 °C. The mixture was warmed to 70 °C, stirred for 1 h, and cooled to 0 °C. Saturated aqueous NaHCO₃ (2.4 mL) was added at 0 °C and the mixture was stirred for 30 min at rt, and extracted with ethyl acetate (2.4 mL × 3). The organic layer was dried over Na₂SO₄ and concentrated in vacuo. An orange oily residue was chromatographed on silica gel (CHCl₃/methanol = 19/1 to 9/1) to give des-Boc **5ac** as a pale yellow solid (295 mg). To a stirred

³ Yamanoi, K.; Ohfuné, Y. *Tetrahedron Lett.* **1988**, 29, 1181–1184.

solution of des-Boc **5ac** (20.0 mg, 0.0438 mmol) in dioxane (0.4 mL) was added aqueous NaOH (1 N, 0.044 mL, 0.0438 mmol) and di-*tert*-butyl dicarbonate (10.5 mg, 0.0482 mmol). The mixture was stirred for 3.5 h at 40 °C and directly subjected to column chromatography (heptane/ethyl acetate = 1/1) to give **5ac** as a colorless solid (22.8 mg, 93%). $[\alpha]_D^{26}$ -82.2 (c 0.84, CHCl₃, 99% ee, 80% de). HPLC: DAICEL CHIRALPAK AD (hexane/2-propanol = 4/1, flow 0.5 mL/min) t_R 14.3 min (minor) and 71.1 min (major). ¹H NMR: δ 7.79 (m, 2H), 7.61 (m, 2H), 7.40–7.23 (m, 12H), 7.13 (d, J = 8.5 Hz, 2H), 6.34 (d, J = 8.7 Hz, 2H), 4.99 (m, 1H), 4.56 (br, 1H), 3.64 (s, 3H), 1.46 (s, 9H), 1.03 (d, J = 6.0 Hz, 3H). ¹³C NMR: δ 158.5, 156.5, 142.1, 134.8 (d, J = 126 Hz), 134.3 (d, J = 132 Hz), 131.9, 131.8 (d, J = 10 Hz), 131.3 (d, J = 9 Hz), 131.1, 130.6, 130.5, 128.6, 128.3 (d, J = 12 Hz), 127.7 (d, J = 13 Hz), 127.5, 127.1, 112.5, 79.9, 68.4, 55.0, 53.9, 28.4, 17.8. IR (KBr): ν 3432, 3230, 3057, 2976, 2932, 1701, 1610, 1514, 1439, 1366, 1253, 1179, 1120, 1053, 859, 754, 721, 699, 540 cm⁻¹. HRFABMS m/z . Calcd for C₃₃H₃₇N₂O₄PH (MH⁺): 557.2569, Found: 557.2555.

***tert*-Butyl *N*-{(1*R*,2*S*)-1-[(diphenylphosphinoyl)amino]-1-methyl-1-phenyl-2-propyl}carbamate (**5ad**).** A colorless solid. $[\alpha]_D^{27}$ -40.2 (c 0.99, CHCl₃, 99% ee, >96% de). HPLC: DAICEL CHIRALPAK AD (hexane/2-propanol = 9/1, flow 0.5 mL/min) t_R 20.1 min (minor) and 24.1 min (major). ¹H NMR: δ 8.01 (m, 2H), 7.93 (m, 2H), 7.55–7.37 (m, 10H), 7.28 (d, J = 7.2 Hz, 1H), 7.09 (d, J = 8.9 Hz, 1H), 4.29 (dq, J = 9.1, 6.8 Hz, 1H), 3.43 (d, J = 4.7 Hz, 1H), 1.49 (s, 9H), 1.39 (s, 3H), 0.89 (d, J = 6.7 Hz, 3H). ¹³C NMR: δ 156.7, 146.1 (d, J = 8 Hz), 134.4 (d, J = 127 Hz), 133.6 (d, J = 133 Hz), 132.5 (d, J = 10 Hz), 132.0 (d, J = 2 Hz), 131.8 (d, J = 3 Hz), 131.0 (d, J = 9 Hz), 128.8 (d, J = 13 Hz), 128.7, 128.5 (d, J = 13 Hz), 127.0, 125.0, 78.8, 64.7, 54.7, 28.6, 26.4, 16.0. IR (KBr): ν 3274, 3055, 2973, 2931, 1689, 1534, 1440, 1365, 1251, 1176, 1120, 1023, 973, 857, 754, 728, 698, 528 cm⁻¹. HRFABMS m/z . Calcd for C₂₇H₃₃N₂O₃PH (MH⁺): 465.2307, Found: 465.2281.

***tert*-Butyl *N*-{(1*R*,2*S*)-1-[(diphenylphosphinoyl)amino]-1-(4-fluorophenyl)-1-phenyl-2-propyl}carbamate (**5ba**).** A colorless solid. $[\alpha]_D^{26}$ -67.1 (c 1.02, CHCl₃, 98% ee, 83% de). HPLC: DAICEL CHIRALPAK AD (hexane/2-propanol = 4/1, flow 0.5 mL/min) t_R 14.5 min (minor) and 18.3 min (major). ¹H NMR: δ 7.76 (m, 2H), 7.53 (m, 2H), 7.41–7.19 (m, 11H), 6.98

(dd, $J = 8.6, 8.6$ Hz, 2H), 6.90 (m, 3H), 5.03 (dq, $J = 9.5, 6.8$ Hz, 1H), 4.61 (br, 1H), 1.61 (s, 9H), 1.04 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR: δ 162.0 (d, $J = 247$ Hz), 156.5, 138.9, 137.1, 134.8 (d, $J = 127$ Hz), 133.9 (d, $J = 131$ Hz), 131.7 (d, $J = 10$ Hz), 131.2 (d, $J = 3$ Hz), 131.1 (d, $J = 9$ Hz), 130.8 (d, $J = 8$ Hz), 130.5, 130.2, 128.3 (d, $J = 13$ Hz), 127.8 (d, $J = 13$ Hz), 127.6, 127.4, 114.1 (d, $J = 21$ Hz), 80.1, 68.7, 53.6, 28.4, 17.8. IR (KBr): ν 3434, 3234, 3058, 2978, 2931, 1701, 1604, 1508, 1439, 1366, 1162, 1121, 1052, 865, 831, 753, 722, 697, 540 cm^{-1} . HRFABMS m/z . Calcd for $\text{C}_{32}\text{H}_{34}\text{FN}_2\text{O}_3\text{PH}$ (MH^+): 545.2369, Found: 545.2390.

***tert*-Butyl *N*-{(2*S*)-1-[(diphenylphosphinoyl)amino]-1,1-bis(4-fluorophenyl)-2-propyl}carbamate (5bb).** A colorless solid. $[\alpha]_{\text{D}}^{27} -63.5$ (c 1.00, CHCl_3 , 99% ee). HPLC: DAICEL CHIRALPAK AD (hexane/2-propanol = 4/1, flow 0.5 mL/min) t_{R} 16.2 min (minor) and 30.5 min (major). ^1H NMR: δ 7.77 (m, 2H), 7.55 (m, 2H), 7.43–7.32 (m, 6H), 7.31–7.20 (m, 5H), 7.02 (dd, $J = 8.8, 8.6$ Hz, 2H), 6.52 (dd, $J = 8.7, 8.7$ Hz, 2H), 4.97 (m, 1H), 4.67 (br, 1H), 1.44 (s, 9H), 1.02 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR: δ 162.0 (d, $J = 247$ Hz), 161.8 (d, $J = 248$ Hz), 156.6, 137.0, 134.6 (d, $J = 127$ Hz), 134.6, 134.0 (d, $J = 131$ Hz), 132.3 (d, $J = 7$ Hz), 131.4 (d, $J = 10$ Hz), 131.3 (d, $J = 2$ Hz), 131.0 (d, $J = 9$ Hz), 130.7, 130.6 (d, $J = 8$ Hz), 128.4 (d, $J = 12$ Hz), 127.8 (d, $J = 13$ Hz), 114.3 (d, $J = 21$ Hz), 114.1 (d, $J = 21$ Hz), 80.3, 68.2, 53.9, 28.4, 17.7. IR (KBr): ν 3436, 3232, 3056, 2979, 2931, 1700, 1604, 1509, 1439, 1366, 1234, 1161, 1121, 1052, 828, 721, 697, 540 cm^{-1} . HRFABMS m/z . Calcd for $\text{C}_{32}\text{H}_{33}\text{F}_2\text{N}_2\text{O}_3\text{PH}$ (MH^+): 563.2275, Found: 563.2256.

***tert*-Butyl *N*-{(1*R*,2*S*)-1-[(diphenylphosphinoyl)amino]-1-(4-methoxyphenyl)-1-phenyl-2-propyl}carbamate (5ca).** A colorless solid. $[\alpha]_{\text{D}}^{26} -80.2$ (c 1.03, CHCl_3 , 99% ee, 96% de). HPLC: DAICEL CHIRALPAK AD (hexane/2-propanol = 4/1, flow 0.5 mL/min) t_{R} 17.2 min (minor) and 23.2 min (major). ^1H NMR: δ 7.75 (m, 2H), 7.58 (m, 2H), 7.39–7.21 (m, 11H), 6.87 (m, 3H), 6.82 (d, $J = 8.7$ Hz, 2H), 5.01 (m, 1H), 4.51 (br, 1H), 3.80 (s, 3H), 1.44 (s, 9H), 1.04 (d, $J = 6.0$ Hz, 3H). ^{13}C NMR: δ 158.6, 156.4, 139.2, 134.8 (d, $J = 128$ Hz), 134.2 (d, $J = 130$ Hz), 133.8, 131.7 (d, $J = 10$ Hz), 131.2 (d, $J = 9$ Hz), 131.1 (d, $J = 2$ Hz), 130.6, 130.3, 129.9, 128.2 (d, $J = 13$ Hz), 127.8 (d, $J = 13$ Hz), 127.4, 127.2, 112.8, 79.8, 68.6, 55.2, 53.6, 28.4, 17.8. IR (KBr): ν 3387, 3231, 3057, 2977, 2932, 2837, 1701, 1609, 1510, 1439, 1366, 1252, 1177, 1120,

1053, 911, 861, 828, 753, 723, 698, 540 cm^{-1} . HRFABMS m/z . Calcd for $\text{C}_{33}\text{H}_{37}\text{N}_2\text{O}_4\text{PH}$ (MH^+): 557.2569, Found: 557.2556.

tert-Butyl N-[(2S)-1-[(diphenylphosphinoyl)amino]-3-methyl-1,1-diphenyl-2-butyl]carbamate (5da). Yields were determined by HPLC assay with following conditions; Column: YMC AQ-303 (0.1% aqueous phosphoric acid/acetonitrile = 50/50 to 5/95 in 30 min, flow 1.0 mL/min) t_r 12.5 min (**7da**), 19.7 min (**4d**), and 21.4 min (**5da**). After work-up, this product was obtained as a mixture of **5da** and **7da**. Authentic samples were prepared in similar manner as **5db** and **7db**. A colorless solid. $[\alpha]_D^{27}$ -37.8 (c 0.99, CHCl_3 , 97% ee). HPLC: DAICEL CHIRALPAK AD (hexane/2-propanol = 19/1, flow 0.5 mL/min) t_r 45.7 min (minor) and 54.2 min (major). ^1H NMR: δ 7.74 (dd, $J = 11.5$, 7.7 Hz, 2H), 7.60 (dd, $J = 12.0$, 7.4 Hz, 2H), 7.41–7.21 (m, 13H), 6.88 (m, 3H), 5.20 (br, 1H), 4.85 (d, $J = 10.6$ Hz, 1H), 4.46 (d, $J = 7.4$ Hz, 1H), 1.91 (m, 1H), 1.47 (s, 9H), 0.98 (d, $J = 6.7$ Hz, 3H), 0.22 (d, $J = 6.3$ Hz, 3H). ^{13}C NMR: δ 157.3, 142.6, 139.2, 135.0 (d, $J = 127$ Hz), 134.0 (d, $J = 131$ Hz), 131.8 (d, $J = 10$ Hz), 131.1 (d, $J = 9$ Hz), 131.0 (d, $J = 3$ Hz), 130.5, 130.3, 128.5, 128.3 (d, $J = 12$ Hz), 127.8 (d, $J = 13$ Hz), 127.7, 127.5, 127.3, 127.2, 79.8, 69.1, 61.1, 28.4, 28.3, 23.7, 17.2. IR (KBr): ν 3443, 3222, 3058, 2965, 2931, 2873, 1703, 1497, 1440, 1390, 1366, 1250, 1171, 1121, 1065, 922, 868, 753, 724, 699, 537 cm^{-1} . HRFABMS m/z . Calcd for $\text{C}_{34}\text{H}_{39}\text{N}_2\text{O}_3\text{PH}$ (MH^+): 555.2777, Found: 555.2768.

N-[(2S)-1-[(Diphenylphosphinoyl)imino]-1-phenyl-3-methyl-2-butyl]benzamide (7da). A colorless solid. $[\alpha]_D^{27}$ -222.8 (c 1.03, CHCl_3 , 96% ee). HPLC: DAICEL CHIRALPAK AD (hexane/2-propanol = 4/1, flow 0.5 mL/min) t_r 21.9 min (major) and 40.1 min (minor). ^1H NMR: δ 7.95 (dd, $J = 13.2$, 7.8 Hz, 2H), 7.71 (d, $J = 7.9$ Hz, 2H), 7.57 (dd, $J = 7.5$, 7.1 Hz, 1H), 7.49 (m, 2H), 7.43 (m, 2H), 7.30–7.20 (m, 7H), 7.07 (m, 2H), 6.92 (dd, $J = 13.3$, 7.9 Hz, 2H), 5.93 (br, 1H), 4.17 (s, 1H), 1.27 (m, 1H), 0.73 (d, $J = 6.5$ Hz, 3H), 0.72 (d, $J = 7.1$ Hz, 3H). ^{13}C NMR: δ 161.4 (d, $J = 7$ Hz), 146.2, 138.5, 133.2 (d, $J = 130$ Hz), 132.4 (d, $J = 11$ Hz), 132.0 (d, $J = 123$ Hz), 131.9 (d, $J = 11$ Hz), 131.8 (d, $J = 3$ Hz), 131.2 (d, $J = 3$ Hz), 129.8, 129.7, 128.2 (d, $J = 14$ Hz), 128.0, 127.6, 127.1 (d, $J = 14$ Hz), 127.1, 126.8, 76.4, 69.9 (d, $J = 6$ Hz), 30.0, 21.4, 15.1. IR (KBr): ν 3424, 3215, 3059, 2963, 2933, 2874, 1705, 1438, 1384, 1315, 1252, 1223, 1121, 1062, 825, 749, 727, 700, 587, 539, 525 cm^{-1} . HRFABMS m/z . Calcd for $\text{C}_{30}\text{H}_{29}\text{N}_2\text{O}_2\text{PH}$ (MH^+): 481.2045, Found: 481.2022.

***tert*-Butyl *N*-{(1*R*,2*S*)-1-[(diphenylphosphinoyl)amino]-1-(4-fluorophenyl)-3-methyl-1-phenyl-2-butyl}carbamate (5ea).** Yields were determined by HPLC assay with following conditions; Column: YMC AQ-303 (0.1% aqueous phosphoric acid/acetonitrile = 50/50 to 5/95 in 30 min, flow 1.0 mL/min) t_R 12.9 min (**7ea**), 20.1 min (**4e**), and 21.0 min (**5ea**). After work-up, this product was obtained as a mixture of **5ea** and **7ea**. Authentic samples were prepared in similar manner as **5db** and **7db**. A colorless solid. $[\alpha]_D^{26}$ -29.0 (c 0.29, CHCl_3 , 92% ee, >96% de). HPLC: DAICEL CHIRALCEL OD-H (hexane/2-propanol = 97/3, flow 0.5 mL/min) t_R 11.9 min (major) and 18.8 min (minor). ^1H NMR: δ 7.73 (ddd, J = 11.2, 8.1, 8.0 Hz, 2H), 7.53 (ddd, J = 12.2, 12.1, 7.3 Hz, 2H), 7.40–7.24 (m, 8H), 7.18 (m, 2H), 6.94–6.91 (m, 5H), 4.85 (m, 2H), 4.47 (d, J = 8.1 Hz, 1H), 1.94 (m, 1H), 1.44 (s, 9H), 1.01 (d, J = 6.7 Hz, 3H), 0.17 (d, J = 6.5 Hz, 3H). ^{13}C NMR: δ 162.1 (d, J = 247 Hz), 157.2, 139.4, 137.6, 135.0 (d, J = 126 Hz), 133.9 (d, J = 131 Hz), 131.7 (d, J = 10 Hz), 131.1, 131.0 (d, J = 9 Hz), 130.5, 129.9, 128.3 (d, J = 12 Hz), 127.8 (d, J = 13 Hz), 127.7, 127.6, 114.3 (d, J = 21 Hz), 80.1, 68.6, 61.2, 28.4, 28.1, 23.7, 17.1. IR (KBr): ν 3447, 3384, 3222, 3059, 2978, 2934, 2874, 1809, 1705, 1604, 1508, 1439, 1392, 1370, 1310, 1213, 1163, 1120, 1069, 868, 840, 753, 722, 698, 536 cm^{-1} . HRFABMS m/z . Calcd for $\text{C}_{34}\text{H}_{38}\text{FN}_2\text{O}_3\text{PH}$ (MH^+): 573.2682, Found: 573.2702.

***N*-{(2*S*)-1-[(Diphenylphosphinoyl)imino]-1-(4-fluorophenyl)-3-methyl-2-butyl}benzamide (7ea).** A colorless solid. $[\alpha]_D^{27}$ -215.8 (c 1.03, CHCl_3 , 92% ee). HPLC: DAICEL CHIRALPAK AD (hexane/2-propanol = 4/1, flow 0.5 mL/min) t_R 21.3 min (major) and 44.4 min (minor). ^1H NMR: δ 7.92 (dd, J = 13.2, 7.2 Hz, 2H), 7.69 (d, J = 7.6 Hz, 2H), 7.59 (dd, J = 7.7, 7.2 Hz, 1H), 7.50 (ddd, J = 7.9, 7.4, 3.5 Hz, 2H), 7.42 (dd, J = 8.8, 5.2 Hz, 2H), 7.31–7.21 (m, 4H), 7.08 (ddd, J = 7.8, 7.7, 3.6 Hz, 2H), 6.99–6.93 (m, 4H), 5.36 (s, 1H), 4.16 (d, J = 1.9 Hz, 1H), 1.35 (m, 1H), 0.76 (d, J = 7.1 Hz, 3H), 0.74 (d, J = 6.5 Hz, 3H). ^{13}C NMR: δ 161.8 (d, J = 247 Hz), 160.6 (d, J = 7 Hz), 145.7, 134.2 (d, J = 3 Hz), 133.0 (d, J = 130 Hz), 132.3 (d, J = 11 Hz), 132.3, 132.0 (d, J = 3 Hz), 131.9 (d, J = 11 Hz), 131.5 (d, J = 8 Hz), 131.4 (d, J = 3 Hz), 129.6, 128.3 (d, J = 14 Hz), 128.2, 127.7, 127.2 (d, J = 14 Hz), 113.7 (d, J = 22 Hz), 76.1, 69.6 (d, J = 6 Hz), 29.9, 21.6, 15.3. IR (KBr): ν 3431, 3214, 3060, 2962, 2932, 2874, 1709, 1603, 1510, 1437, 1384, 1315, 1227, 1121, 1014, 837, 749, 727, 700, 570, 532 cm^{-1} . HRFABMS m/z . Calcd for $\text{C}_{30}\text{H}_{28}\text{FN}_2\text{O}_2\text{PH}$ (MH^+): 499.1951, Found: 499.1931.

Deprotection of *N*-*tert*-Butoxycarbonyl Group from 5

(2*S*)-1-[(Diphenylphosphinoyl)amino]-1,1-diphenyl-2-propylamine (9aa). A colorless solid. $[\alpha]_D^{27} -4.4$ (*c* 1.02, CHCl₃, 98% ee). ¹H NMR: δ 7.74 (m, 2H), 7.49 (m, 2H), 7.42–7.26 (m, 9H), 7.19 (ddd, *J* = 7.6, 7.6, 3.3 Hz, 2H), 7.15 (dd, *J* = 7.4, 1.3 Hz, 2H), 6.99 (dd, *J* = 7.3, 7.3 Hz, 1H), 6.93 (dd, *J* = 7.8, 7.2 Hz, 2H), 5.21 (br, 1H), 4.31 (q, *J* = 6.6 Hz, 1H), 2.84 (br, 2H), 1.12 (d, *J* = 6.5 Hz, 3H). ¹³C NMR: δ 140.6 (d, *J* = 121 Hz), 140.6 (d, *J* = 117 Hz), 134.8, 133.8, 133.4, 131.8 (d, *J* = 10 Hz), 131.3 (d, *J* = 9 Hz), 131.3, 130.9 (d, *J* = 3 Hz), 130.2, 129.2, 128.3 (d, *J* = 12 Hz), 128.0 (d, *J* = 13 Hz), 127.5, 127.4, 127.3, 69.2 (d, *J* = 2 Hz), 52.8 (d, *J* = 2 Hz), 20.2. IR (KBr): ν 3375, 3290, 3054, 2966, 1591, 1494, 1438, 1371, 1212, 1185, 1122, 1068, 911, 858, 755, 725, 700, 646, 542, 526 cm⁻¹. HRFABMS *m/z*. Calcd for C₂₇H₂₇N₂OPH (MH⁺): 427.1939, Found: 427.1943.

(1*R*,2*S*)-1-[(Diphenylphosphinoyl)amino]-1-(4-fluorophenyl)-1-phenyl-2-propylamine (9ba). A colorless solid. $[\alpha]_D^{27} -13.7$ (*c* 1.03, CHCl₃, 99% ee, 83% de). ¹H NMR: δ 7.68 (m, 2H), 7.56 (m, 2H), 7.34–7.21 (m, 10H), 6.99–6.92 (m, 5H), 5.52 (br, 1H), 4.18 (q, *J* = 6.4 Hz, 1H), 1.56 (br, 2H), 1.05 (d, *J* = 6.5 Hz, 3H). ¹³C NMR: δ 161.9 (d, *J* = 246 Hz), 139.6 (d, *J* = 3 Hz), 137.0 (d, *J* = 3 Hz), 136.9 (d, *J* = 3 Hz), 134.9 (d, *J* = 130 Hz), 134.3 (d, *J* = 130 Hz), 131.5 (d, *J* = 10 Hz), 131.4 (d, *J* = 9 Hz), 130.8 (d, *J* = 3 Hz), 130.7 (d, *J* = 3 Hz), 130.6, 128.0 (d, *J* = 10 Hz), 127.9 (d, *J* = 10 Hz), 127.5, 127.1, 113.7 (d, *J* = 21 Hz), 68.8 (d, *J* = 2 Hz), 53.1 (d, *J* = 3 Hz), 21.3. IR (KBr): ν 3389, 3313, 3166, 3058, 2968, 2932, 2876, 1603, 1506, 1139, 1378, 1206, 1121, 1087, 934, 830, 754, 725, 698, 612, 563, 543, 527 cm⁻¹. HRFABMS *m/z*. Calcd for C₂₇H₂₆FN₂OPH (MH⁺): 445.1845, Found: 445.1821.

(2*S*)-1-[(Diphenylphosphinoyl)amino]-1,1-bis(4-fluorophenyl)-2-propylamine (9bb). A colorless solid. $[\alpha]_D^{27} -15.6$ (*c* 0.65, CHCl₃, 99% ee). ¹H NMR: δ 7.70 (m, 2H), 7.56 (m, 2H), 7.38–7.29 (m, 6H), 7.23 (ddd, *J* = 7.8, 7.4, 3.3 Hz, 2H), 7.17 (dd, *J* = 8.8, 5.4 Hz, 2H), 6.99 (dd, *J* = 8.8, 8.6 Hz, 2H), 6.56 (dd, *J* = 8.8, 8.7 Hz, 2H), 5.80 (br, 1H), 4.11 (q, *J* = 6.5 Hz, 1H), 1.55 (br, 2H), 1.05 (d, *J* = 6.5 Hz, 3H). ¹³C NMR: δ 162.1 (d, *J* = 247 Hz), 161.8 (d, *J* = 248 Hz), 136.7, 135.3, 133.9 (d, *J* = 130 Hz), 133.0 (d, *J* = 130 Hz), 132.4 (d, *J* = 8 Hz), 131.6 (d, *J* = 10

Hz), 131.4 (d, $J = 2$ Hz), 131.3 (d, $J = 9$ Hz), 131.1 (d, $J = 2$ Hz), 130.9 (d, $J = 8$ Hz), 128.3 (d, $J = 13$ Hz), 128.0 (d, $J = 13$ Hz), 114.2 (d, $J = 21$ Hz), 114.0 (d, $J = 21$ Hz), 68.1, 53.4, 20.2. IR (KBr): ν 3399, 3059, 2974, 2933, 1754, 1686, 1604, 1509, 1439, 1381, 1232, 1165, 1122, 1069, 1015, 872, 837, 753, 722, 697, 602, 539 cm^{-1} . HRFABMS m/z . Calcd for $\text{C}_{27}\text{H}_{25}\text{F}_2\text{N}_2\text{OPH}$ (MH^+): 463.1751, Found: 463.1763.

Preparation of tri-substituted diamine 10

Enantiomeric excesses of **10aa**, **10ba**, and **10bb** were determined by analysis of corresponding imidazolidinone. Diastomeric excess of **10ba** was determined by reversed phase HPLC: YMC AQ-303 (0.1% aqueous phosphoric acid/acetonitrile = 95/5 to 90/10 in 20 min, to 80/20 in 10 min, flow 1.0 mL/min) t_R 17.5 min (**10ab**) and 18.2 min (**10ba**).

(2S)-1,1-Diphenyl-1,2-propanediamine (10aa). A colorless solid. $[\alpha]_D^{27} +12.8$ (c 1.05, CHCl_3 , 99% ee). HPLC: DAICEL CHIRALPAK AD (hexane/2-propanol = 4/1, flow 0.5 mL/min) t_R 15.9 min (minor) and 22.2 min (major). ^1H NMR: δ 7.53 (dd, $J = 8.6, 1.2$ Hz, 2H), 7.47 (dd, $J = 8.6, 1.2$ Hz, 2H), 7.29 (dd, $J = 7.9, 7.3$ Hz, 4H), 7.18 (dd, $J = 7.6, 7.0$ Hz, 2H), 4.05 (q, $J = 6.4$ Hz, 1H), 1.55 (br, 4H), 1.01 (d, $J = 6.4$ Hz, 3H). ^{13}C NMR: δ 147.1, 146.4, 128.3, 128.1, 126.6, 126.6, 126.3, 126.3, 64.3, 52.1, 17.8. IR (KBr): ν 3448, 3356, 3337, 3273, 3080, 3059, 3020, 2979, 2936, 1594, 1492, 1445, 1201, 1003, 940, 892, 865, 769, 752, 705, 629, 541 cm^{-1} . HRFABMS m/z . Calcd for $\text{C}_{15}\text{H}_{18}\text{N}_2\text{H}$ (MH^+): 227.1548, Found: 227.1572.

(1R,2S)-1-(4-Fluorophenyl)-1-phenyl-1,2-propanediamine (10ba). A colorless solid. $[\alpha]_D^{27} +7.6$ (c 1.05, CHCl_3 , 98% ee, 86% de). HPLC: DAICEL CHIRALPAK AD (hexane/2-propanol = 4/1, flow 0.5 mL/min) t_R 14.0 min (minor) and 19.7 min (major). ^1H NMR: δ 7.50 (d, $J = 7.6$ Hz, 2H), 7.44 (dd, $J = 8.7, 5.4$ Hz, 2H), 7.30 (dd, $J = 7.8, 7.5$ Hz, 2H), 7.19 (dd, $J = 7.4, 7.2$ Hz, 1H), 6.96 (dd, $J = 8.7, 8.7$ Hz, 2H), 4.04 (q, $J = 6.3$ Hz, 1H), 1.63 (br, 4H), 1.01 (d, $J = 6.3$ Hz, 3H). ^{13}C NMR: δ 161.3 (d, $J = 245$ Hz), 147.1, 142.1 (d, $J = 3$ Hz), 128.4, 128.3, 128.3, 126.4, 114.8 (d, $J = 21$ Hz), 63.9, 52.1, 17.8. IR (KBr): ν 3366, 3294, 3058, 3020, 2984, 2935, 2894, 1598, 1509, 1445, 1377, 1238, 1162, 1128, 1017, 916, 867, 823, 759, 722, 702, 626, 580, 541 cm^{-1} . HRFABMS m/z . Calcd for $\text{C}_{15}\text{H}_{17}\text{FN}_2\text{H}$ (MH^+): 245.1454, Found: 245.1443.

(2S)-1,1-Bis(4-fluorophenyl)-1,2-propanediamine (10bb). A colorless solid. $[\alpha]_D^{27} +12.6$ (*c* 0.98, CHCl₃, 99% ee). HPLC: DAICEL CHIRALPAK AD (hexane/2-propanol = 9/1, flow 0.5 mL/min) *t_R* 21.0 min (minor) and 36.0 min (major). ¹H NMR: δ 7.49 (dd, *J* = 8.9, 5.3 Hz, 2H), 7.42 (dd, *J* = 8.9, 5.4 Hz, 2H), 6.98 (ddd, *J* = 8.8, 8.6, 5.0 Hz, 4H), 4.01 (q, *J* = 6.3 Hz, 1H), 1.53 (br, 4H), 0.99 (d, *J* = 6.3 Hz, 3H). ¹³C NMR: δ 161.3 (d, *J* = 246 Hz), 161.3 (d, *J* = 246 Hz), 142.7 (d, *J* = 3 Hz), 142.0 (d, *J* = 3 Hz), 128.2 (d, *J* = 2 Hz), 128.2 (d, *J* = 2 Hz), 115.9 (d, *J* = 21 Hz), 114.9 (d, *J* = 21 Hz), 63.6, 52.1, 17.8. IR (KBr): ν 3373, 3338, 3279, 3069, 2986, 2963, 2931, 2892, 2873, 1910, 1601, 1504, 1408, 1378, 1307, 1222, 1160, 1123, 1014, 991, 872, 824, 785, 730, 672, 589, 567, 543 cm⁻¹. HRFABMS *m/z*. Calcd for C₁₅H₁₆F₂N₂H (MH⁺): 263.1360, Found: 263.1379.

Preparation of imidazolidinone 8ab and 8ba for NOE analysis. 10ab and 10ba were treated with 1,1'-carbonyldiimidazole in THF for several hours and they were directly subjected to preparative TLC (eluted with ethyl acetate) to give 8ab and 8ba, respectively.

(4S,5S)-4-(4-Fluorophenyl)-4-phenyl-1,3-imidazolidin-2-one (8ab). A colorless solid. $[\alpha]_D^{26} -313.3$ (*c* 0.112, CHCl₃, 98% ee, 95% de). ¹H NMR: δ 7.34–7.28 (m, 5H), 7.19 (d, *J* = 7.1 Hz, 2H), 7.03 (dd, *J* = 8.5, 8.5 Hz, 2H), 5.34 (br, 1H), 4.83 (br, 1H), 4.53 (q, *J* = 6.4 Hz, 1H), 0.89 (d, *J* = 6.4 Hz, 3H). ¹³C NMR: δ 162.0 (d, *J* = 248 Hz), 161.5, 141.2 (d, *J* = 4 Hz), 141.1, 128.2, 128.2 (d, *J* = 8 Hz), 127.7, 127.4, 115.5 (d, *J* = 21 Hz), 68.9, 56.7, 19.3. IR (KBr): ν 3436, 3212, 2975, 2928, 2881, 1709, 1512, 1242, 1165, 835, 700 cm⁻¹. HRFABMS *m/z*. Calcd for C₁₆H₁₅FN₂OH (MH⁺): 271.1247, Found: 271.1226.

(4R,5S)-4-(4-Fluorophenyl)-4-phenyl-1,3-imidazolidin-2-one (8ba). A colorless solid. $[\alpha]_D^{26} -266.1$ (*c* 0.124, CHCl₃, 98% ee, 86% de). ¹H NMR: δ 7.38–7.28 (m, 5H), 7.18 (m, 2H), 7.00 (dd, *J* = 8.7, 8.5 Hz, 2H), 5.30 (br, 1H), 4.78 (br, 1H), 4.59 (q, *J* = 6.4 Hz, 1H), 0.91 (d, *J* = 6.4 Hz, 3H). ¹³C NMR: δ 162.1 (d, *J* = 247 Hz), 161.4, 144.8, 137.3 (d, *J* = 3 Hz), 129.3 (d, *J* = 8 Hz), 128.8, 127.9, 126.2, 115.0 (d, *J* = 22 Hz), 68.9, 56.4, 19.2. IR (KBr): ν 3423, 3204, 3068, 2977, 2927, 2854, 1703, 1601, 1509, 1450, 1233, 1161, 832, 700 cm⁻¹. HRFABMS *m/z*. Calcd for C₁₆H₁₅FN₂OH (MH⁺): 271.1247, Found: 271.1270.

P133YMO-100

PL31950-100-2 4-F-COM-Imide

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PROCNO 1

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F2 - Processing parameters
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1183.15969 Rev01

S27

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 SW 1.00 Hz
 GB 0
 SC 0
 SS 0
 SW 1.00 Hz
 FIDRES 0.448211 Hz
 AQ 1.8913410 sec
 RG 16384
 IN 16.000 0000
 BS 16.00 0000
 GB 160.0 Hz
 GPC 3.0000000 sec
 DLI 0.1000000 sec

[illegible]

9ab

PL857P-002 colorless solid

PI185710-020 4-P-OMe-4-P-COM-de-Boc-amide

Current Data Parameters	
NAME	PI185710-020
EXPNO	10
PROCNO	1
F2 - Acquisition Parameters	
Date_	20101115
Time	11.26
EXPNO	4000
PROCNO	5
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PULPROG	zgpg30
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SCOUTPR	0
RG	1.034
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10ab

Current Data Parameters
 Name: 702050-88c-2
 Date: 10/10/10
 Sample: 1

1D - Acquisition Parameters
 Date_: 2001128
 Time: 7.41
 Instrument: spect
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 SFO: 500.135
 AQ: 1.00
 RG: 128
 SF: 128
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 F100: 100.625

Figure. ORTEP view of **4a** with the atom numbering scheme and 50% probability displacement ellipsoids. H atoms except those of the asymmetric center are omitted for clarity.

Experimental

Data Collection

A colorless prismatic crystal of $C_{26}H_{29}N_2O_3P$ having approximate dimensions of 0.30 x 0.20 x 0.10 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Cu-K α radiation and a rotating anode generator.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $50.02 < 2\theta < 58.96^\circ$ corresponded to a primitive orthorhombic cell with dimensions:

$$a = 12.448(5) \text{ \AA}$$

$$b = 22.616(5) \text{ \AA}$$

$$c = 8.839(2) \text{ \AA}$$

$$V = 2488.5(1) \text{ \AA}^3$$

For $Z = 4$ and F.W. = 448.50, the calculated density is 1.20 g/cm³. The systematic absences of:

$$h00: h \pm 2n$$

$$0k0: k \pm 2n$$

$$00l: l \pm 2n$$

uniquely determine the space group to be:

P2₁2₁2₁ (#19)

The data were collected at a temperature of $25 \pm 1^\circ\text{C}$ using the ω - 2θ scan technique to a maximum 2θ value of 135.9° . Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.29° with a take-off angle of 6.0° . Scans of $(1.84 + 0.30 \tan \theta)^\circ$ were made at a speed of $16.0^\circ/\text{min}$ (in ω). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 7 scans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal to detector distance was 235 mm. The computer-controlled slits were set to 3.0 mm (horizontal) and 4.0 mm (vertical).

Data Reduction

Of the 4809 reflections that were collected, 2570 were unique ($R_{\text{int}} = 0.000$); equivalent reflections were merged. The intensities of three representative reflections were measured after every 150 reflections. No decay correction was applied.

The linear absorption coefficient, μ , for Cu-K α radiation is 12.1 cm^{-1} . The data were corrected for Lorentz and polarization effects. A correction for secondary extinction¹ was applied (coefficient = 12.380000).

Structure Solution and Refinement

The structure was solved by direct methods² and expanded using Fourier techniques.³ The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement⁴ on F was based on 2107 observed reflections ($I > 3.00\sigma(I)$) and 319 variable parameters and converged (largest parameter shift was 0.05 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.057$$

$$R_w = [\Sigma w (|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2} = 0.037$$

The standard deviation of an observation of unit weight⁵ was 5.44. The weighting scheme was based on counting statistics. Plots of $\Sigma w (|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin \theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.20 and -0.20 e⁻/Å³, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.⁶ Anomalous dispersion effects were included in Fcalc;⁷ the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.⁸ The values for the mass attenuation coefficients are those of Creagh and Hubbell.⁹ All calculations were performed using the CrystalStructure^{10,11} crystallographic software package.

References

(1) Larson, A.C. (1970), *Crystallographic Computing*, 291-294. F.R. Ahmed, ed. Munksgaard, Copenhagen (equation 22, with V replaced by the cell volume).

(2) SYSTEM90: Hou Yonggeng, Gao Min, Li Lipu, Hou Peixin. (1994) Acta Cryst. A50 748-753.

(3) DIRDIF99: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M.(1999). The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(4) Least Squares function minimized:

$$\sum w(|F_o| - |F_c|)^2 \quad \text{where } w = \text{Least Squares weights.}$$

(5) Standard deviation of an observation of unit weight:

$$[\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$$

where: N_o = number of observations

N_v = number of variables

(6) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(7) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(8) Creagh, D. C. & McAuley, W.J. ; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(9) Creagh, D. C. & Hubbell, J.H.; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(10) CrystalStructure 3.10: Crystal Structure Analysis Package, Rigaku and Rigaku/MSK
(2000-2002).

(11) CRYSTALS Issue 10: Watkin, D.J., Prout, C.K. Carruthers, J.R. & Betteridge, P.W.
Chemical Crystallography Laboratory, Oxford, UK.

Experimental Details

A. Crystal Data

Empirical Formula	C ₂₆ H ₂₉ N ₂ O ₃ P
Formula Weight	448.50
Crystal Color, Habit	colorless, prismatic
Crystal Dimensions	0.30 X 0.20 X 0.10 mm
Crystal System	orthorhombic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2 θ range)	25 (50.0 - 59.0 $^{\circ}$)
Omega Scan Peak Width at Half-height	0.29 $^{\circ}$
Lattice Parameters	a = 12.448(5) Å b = 22.616(5) Å c = 8.839(2) Å V = 2488.5(1) Å ³
Space Group	P2 ₁ 2 ₁ 2 ₁ (#19)
Z value	4
D _{calc}	1.197 g/cm ³
F ₀₀₀	952.00
μ (CuK α)	12.06 cm ⁻¹

B. Intensity Measurements

Diffractometer	Rigaku AFC7R
Radiation	CuK α ($\lambda = 1.54178 \text{ \AA}$) graphite monochromated
Attenuator	Ni foil (factor = 9.23)
Take-off Angle	6.0 $^{\circ}$
Detector Aperture	4.0 mm horizontal 3.0 mm vertical
Crystal to Detector Distance	235 mm
Voltage, Current	50kV, 200mA
Temperature	25.0 $^{\circ}$ C
Scan Type	ω -2 θ
Scan Rate	16.0 $^{\circ}$ /min (in ω) (up to 7 scans)
Scan Width	(1.84 + 0.30 tan θ) $^{\circ}$
2 θ_{max}	135.9 $^{\circ}$
No. of Reflections Measured	Total: 4809
Corrections	Unique: 2570 ($R_{\text{int}} = 0.000$) Lorentz-polarization Secondary Extinction (coefficient: 1.23800e+001)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SYSTEM90)
Refinement	Full-matrix least-squares on F
Function Minimized	$\Sigma w (F_o - F_c)^2$
Least Squares Weights	$1/\sigma^2(F_o)$
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I > 3.00\sigma(I)$)	2107
No. Variables	319
Reflection/Parameter Ratio	6.61
Residuals: R ($I > 3.00\sigma(I)$)	0.057
Residuals: R _w ($I > 3.00\sigma(I)$)	0.037
Goodness of Fit Indicator	5.44
Max Shift/Error in Final Cycle	0.05
Maximum peak in Final Diff. Map	0.20 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.20 e ⁻ /Å ³

Table 1. Atomic coordinates and $B_{\text{iso}}/B_{\text{eq}}$

atom	x	y	z	B_{eq}
P(1)	-0.0872(1)	-0.15733(6)	-0.1715(2)	6.44(4)
O(1)	-0.0373(3)	-0.1978(1)	-0.0602(4)	7.8(1)
O(2)	-0.2786(3)	-0.3728(1)	-0.0782(5)	7.4(1)
O(3)	-0.0968(3)	-0.3686(1)	-0.0640(4)	6.47(9)
N(1)	-0.2051(4)	-0.1734(2)	-0.2505(4)	6.2(1)
N(2)	-0.1889(3)	-0.2865(1)	-0.0739(5)	6.4(1)
C(1)	-0.1072(5)	-0.0850(2)	-0.0938(7)	6.6(2)
C(2)	-0.0004(6)	-0.1469(2)	-0.3325(8)	7.2(2)
C(3)	-0.2831(5)	-0.2501(2)	-0.0792(6)	6.3(1)
C(4)	-0.1962(5)	-0.3453(2)	-0.0732(6)	5.5(1)
C(5)	-0.0849(5)	-0.4332(2)	-0.0510(8)	6.9(2)
C(6)	-0.2814(5)	-0.2078(2)	-0.2159(6)	5.7(1)
C(7)	-0.3794(5)	-0.2070(2)	-0.3159(6)	6.0(1)
C(8)	-0.1356(5)	-0.4541(2)	0.0939(8)	10.7(2)
C(9)	-0.5566(6)	-0.2015(3)	-0.5035(8)	8.7(2)
C(10)	-0.4560(6)	-0.1901(3)	-0.5606(7)	8.4(2)
C(11)	-0.2985(5)	-0.2147(2)	0.0642(6)	7.5(2)
C(12)	0.0329(5)	-0.4399(2)	-0.0316(9)	11.0(2)
C(13)	-0.5700(6)	-0.2151(3)	-0.3524(8)	9.1(2)
C(14)	0.140(1)	-0.1269(5)	-0.565(1)	13.5(4)
C(15)	0.0387(9)	-0.1320(5)	-0.593(1)	13.6(4)
C(16)	-0.4818(6)	-0.2195(3)	-0.2607(7)	7.8(2)
C(17)	-0.3688(5)	-0.1923(2)	-0.4677(6)	7.3(2)
C(18)	-0.1833(5)	-0.0473(3)	-0.1407(8)	8.9(2)
C(19)	-0.1913(7)	0.0095(3)	-0.077(1)	11.7(3)
C(20)	-0.1202(8)	0.0283(4)	0.029(1)	13.3(4)
C(21)	-0.0394(9)	-0.0089(4)	0.070(1)	16.1(4)
C(22)	0.1795(8)	-0.1317(3)	-0.420(1)	12.8(3)
C(23)	0.1082(7)	-0.1417(3)	-0.3039(9)	8.9(2)
C(24)	-0.0362(7)	-0.0658(3)	0.0092(8)	11.4(3)
C(25)	-0.1196(6)	-0.4638(2)	-0.1943(8)	11.3(2)
C(26)	-0.0362(7)	-0.1395(3)	-0.4766(8)	10.4(3)
H(1)	-0.4908(6)	-0.2312(3)	-0.1583(7)	9.3(2)
H(2)	-0.6400(6)	-0.2209(3)	-0.3122(8)	10.9(2)
H(3)	-0.6169(6)	-0.2008(3)	-0.5693(8)	10.4(2)
H(4)	-0.4471(6)	-0.1796(3)	-0.6639(7)	10.0(2)
H(5)	-0.2995(5)	-0.1845(2)	-0.5082(6)	8.7(2)

Table 1. Atomic coordinates and $B_{\text{iso}}/B_{\text{eq}}$ (continued)

atom	x	y	z	B_{eq}
H(6)	-0.3751(5)	-0.1895(2)	0.0652(6)	9.0(2)
H(7)	-0.2431(5)	-0.1835(2)	0.0772(6)	9.0(2)
H(8)	-0.3191(5)	-0.2405(2)	0.1472(6)	9.0(2)
H(9)	-0.3548(5)	-0.2788(2)	-0.0808(6)	7.6(2)
H(10)	-0.1202(3)	-0.2619(1)	-0.0945(5)	7.7(2)
H(11)	0.0533(5)	-0.4200(2)	-0.1017(9)	13.2(3)
H(12)	0.0703(5)	-0.4060(2)	0.0503(9)	13.2(3)
H(13)	0.0633(5)	-0.4780(2)	-0.0336(9)	13.2(3)
H(14)	-0.1028(6)	-0.5027(2)	-0.1888(8)	13.5(3)
H(15)	-0.0958(6)	-0.4307(2)	-0.2808(8)	13.5(3)
H(16)	-0.2206(6)	-0.4593(2)	-0.1954(8)	13.5(3)
H(17)	-0.2066(5)	-0.4615(2)	0.0485(8)	12.8(3)
H(18)	-0.1241(5)	-0.4971(2)	0.1101(8)	12.8(3)
H(19)	-0.1661(5)	-0.4321(2)	0.1431(8)	12.8(3)
H(20)	0.1340(7)	-0.1444(3)	-0.2030(9)	10.7(3)
H(21)	0.2547(8)	-0.1286(3)	-0.403(1)	15.4(4)
H(22)	0.189(1)	-0.1207(5)	-0.646(1)	16.2(6)
H(23)	0.0147(9)	-0.1288(5)	-0.695(1)	16.3(5)
H(24)	-0.1114(7)	-0.1409(3)	-0.4940(8)	12.5(3)
H(25)	0.0191(7)	-0.0922(3)	0.0398(8)	13.7(3)
H(26)	0.0139(9)	0.0042(4)	0.139(1)	19.3(5)
H(27)	-0.1265(8)	0.0664(4)	0.073(1)	16.0(5)
H(28)	-0.2469(7)	0.0355(3)	-0.109(1)	14.0(4)
H(29)	-0.2323(5)	-0.0601(3)	-0.2164(8)	10.7(2)

$$B_{\text{eq}} = 8/3 \pi^2 (U_{11}(\text{aa}^*)^2 + U_{22}(\text{bb}^*)^2 + U_{33}(\text{cc}^*)^2 + 2U_{12}(\text{aa}^*\text{bb}^*)\cos \gamma + 2U_{13}(\text{aa}^*\text{cc}^*)\cos \beta + 2U_{23}(\text{bb}^*\text{cc}^*)\cos \alpha)$$

Table 2. Anisotropic Displacement Parameters

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
P(1)	0.117(1)	0.0585(7)	0.0691(8)	0.0027(9)	0.009(1)	0.0161(7)
O(1)	0.118(3)	0.074(2)	0.103(3)	-0.005(2)	0.012(3)	0.035(2)
O(2)	0.103(3)	0.065(2)	0.115(3)	0.003(2)	-0.014(3)	0.002(2)
O(3)	0.099(3)	0.053(2)	0.094(3)	0.014(2)	-0.001(3)	0.009(2)
N(1)	0.109(4)	0.065(3)	0.063(3)	0.003(3)	0.002(3)	0.012(2)
N(2)	0.095(3)	0.045(2)	0.105(3)	0.014(2)	0.013(3)	0.023(3)
C(1)	0.120(5)	0.066(3)	0.067(3)	-0.000(4)	-0.004(4)	0.011(3)
C(2)	0.135(6)	0.045(3)	0.093(4)	-0.001(4)	0.025(5)	0.000(3)
C(3)	0.101(4)	0.067(3)	0.073(3)	0.016(3)	0.008(4)	0.024(3)
C(4)	0.094(4)	0.059(3)	0.056(3)	0.014(3)	-0.005(3)	0.010(3)
C(5)	0.095(5)	0.050(3)	0.118(5)	0.015(3)	-0.010(5)	0.010(3)
C(6)	0.112(5)	0.041(2)	0.065(3)	0.015(3)	0.013(3)	0.004(2)
C(7)	0.115(5)	0.055(3)	0.057(3)	0.019(3)	-0.003(4)	0.004(3)
C(8)	0.163(7)	0.086(4)	0.157(7)	0.032(5)	0.017(6)	0.053(5)
C(9)	0.136(7)	0.107(5)	0.087(5)	0.020(6)	-0.020(5)	-0.004(4)
C(10)	0.138(6)	0.120(5)	0.059(4)	0.034(5)	-0.003(4)	0.009(4)
C(11)	0.122(5)	0.091(4)	0.073(4)	0.021(4)	0.021(4)	0.023(4)
C(12)	0.123(5)	0.067(4)	0.227(9)	0.033(4)	-0.025(7)	0.021(5)
C(13)	0.108(6)	0.128(5)	0.109(6)	-0.003(5)	-0.016(5)	0.017(5)
C(14)	0.28(2)	0.092(6)	0.14(1)	-0.033(9)	0.12(1)	-0.026(7)
C(15)	0.30(1)	0.112(6)	0.102(7)	-0.06(1)	0.04(1)	-0.007(5)
C(16)	0.118(5)	0.100(4)	0.077(4)	-0.002(5)	-0.002(4)	0.017(4)
C(17)	0.117(6)	0.093(4)	0.067(4)	0.023(4)	0.012(4)	0.013(3)
C(18)	0.119(6)	0.083(4)	0.138(7)	-0.001(4)	0.003(6)	-0.009(5)
C(19)	0.165(9)	0.075(5)	0.20(1)	0.012(6)	0.049(9)	-0.015(6)
C(20)	0.26(1)	0.095(6)	0.147(9)	0.003(7)	0.06(1)	-0.046(6)
C(21)	0.35(2)	0.140(8)	0.126(7)	0.017(9)	-0.03(1)	-0.067(7)
C(22)	0.21(1)	0.092(5)	0.189(9)	0.011(6)	0.11(1)	0.005(7)
C(23)	0.141(7)	0.080(4)	0.119(6)	0.007(5)	0.035(6)	0.013(4)
C(24)	0.210(9)	0.119(6)	0.104(6)	0.034(6)	-0.042(6)	-0.029(5)
C(25)	0.203(8)	0.078(4)	0.148(6)	0.041(5)	-0.055(7)	-0.043(4)
C(26)	0.187(9)	0.137(6)	0.073(4)	-0.056(6)	0.020(5)	0.004(5)

The general temperature factor expression: $\exp(-2\pi^2(a^2U_{11}h^2 + b^2U_{22}k^2 + c^2U_{33}l^2 + 2a*b*U_{12}hk + 2a*c*U_{13}hl + 2b*c*U_{23}kl))$