Palladium-catalyzed 1,4-addition of secondary alkylphenylphosphines to α,β-unsaturated carbonyl compounds for the synthesis of phosphorus- and carbon-stereogenic compounds

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General Methods

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under nitrogen. ¹H, ¹³C and ³¹P NMR spectra were recorded on a Varian instrument (400 MHz, 100 MHz and 162 MHz, respectively). ¹H, ¹³C NMR chemical shifts are reported vs tetramethylsilane signal or residual protio solvent signals.

Toluene and THF were distilled over sodium benzophenone ketyl under nitrogen. Dichloromethane and DMF were distilled over CaH₂ under nitrogen.

The catalysts **4**,¹ phenylalkylphosphine,² enones,³ and N-acylpyrrole⁴ were synthesized following the literature procedures. All other chemicals and solvents were purchased from commercial company and used as received.

Experimental Details and Characterization Data

Generanl Procedure for Table 2.

A mixture of catalyst (*S*,*S*)-**5a** (7.62 mg, 0.01 mmol; 5 mol%) and KOAc (9.8 mg, 0.1 mmol) in toluene (2.5 mL) was stirred at room temperature for 1 h. Then the temperature was reduced to -5 °C (realized with a refrigerated bath circulator), alkylphenylphosphine (0.20 mmol) and α , β -unsaturated carbonyl compound (0.30 mmol) were added into it, and the resulting solution was stirred for 24 h at -5 °C. Then 0.3 mL Me₂S·BH₃ (2 M in THF) was added into it and the resulting solution was stirred for 1.5 h. The excess borane was reacted with H₂O and the mixture was dried over MgSO₄, filtered and concentrated under vacuum. The residue was purified by silica gel chromatography with hexane/EtOAc = 4/1 to afford the product as a white solid.



Table 2, entry 1. White solid. 98% yield, dr = 1.1/1. The ee was determined on a Daicel Chiralcel OZ-3 column with hexane/2-propanol = 95/5, flow = 0.8 mL/min. Retention times: 11.3 min [(R_c, R_p) -diastereomer], 13.5 min [(S_c, S_p) -diastereomer], 14.8 min [(R_c, S_p) -diastereomer], 22.3 min [(S_c, R_p) -diastereomer]. 87% ee (major diastereomer), 96% ee (minor diastereomer). The absolute configuration was assigned by analogy with Table 2, entries 9 and 17.

¹H NMR (400 MHz, CDCl₃): δ 7.89-7.87 (m, 1H), 7.82-7.76 (m, 2H), 7.56-7.20 (m, 10H), 7.15-7.09 (m, 1H), 6.90-6.84 (m, 1H), 4.10-3.95 (m, 1H), 3.92-3.76 (m, 1H), 3.55 (ddd, *J* = 17.6, 10.0 and 4.0 Hz, 0.47H), 3.23 (ddd, *J* = 17.6, 10.4 and 2.8 Hz, 0.52H), 1.54 (d, *J* = 9.6 Hz, 1.38H), 1.34 (d, *J* = 10.0 Hz, 1.68H), 1.30-0.30 (m, 3H). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 18.1 (m).



Table 2, entry 2. White solid. 97% yield, dr = 1.1/1. The ee was determined on a Daicel Chiralcel OZ-3 column with hexane/2-propanol = 95/5, flow = 1.0 mL/min. Retention times: 10.4 min [(R_c,R_p) -diastereomer], 12.7 min [(S_c,S_p) -diastereomer], 14.3 min [(R_c,S_p) -diastereomer], 22.2 min [(S_c,R_p) -diastereomer]. 88% ee (major diastereomer), 95% ee (minor diastereomer). The absolute configuration was assigned by analogy with Table 2, entries 9 and 17.

¹H NMR (400 MHz, CDCl₃): δ 7.88 (d, J = 7.6 Hz, 1H), 7.78 (t, J = 8.0 Hz, 2H), 7.54-7.34 (m, 7H), 7.21 (d, J = 6.8 Hz, 1H), 7.08 (d, J = 7.6 Hz, 1H), 6.93 (d, J = 7.6 Hz, 1H), 6.74 (d, J = 6.8 Hz, 1H), 4.08-3.92 (m, 1H), 3.90-3.75 (m, 1H), 3.50 (ddd, J = 17.6, 10.0 and 6.8 Hz, 0.47H), 3.20 (ddd, J = 17.6, 10.4 and 2.8 Hz, 0.52H), 2.25 (s, 1.51H), 2.22 (s, 1.40H), 1.52 (d, J = 9.6 Hz, 1.41H), 1.33 (d, J = 10.0 Hz, 1.63H), 1.30-0.30 (m, 3H). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 18.5 (m).



Table 2, entry 3. White solid. 92% yield, dr = 1.2/1. The ee was determined on a Daicel Chiralcel OZ-3 column with hexane/2-propanol = 95/5, flow = 1.0 mL/min. Retention times: 16.6 min [(R_c, R_p) -diastereomer], 19.6 min [(S_c, S_p) -diastereomer], 22.6 min [(R_c, S_p) -diastereomer], 40.0 min [(S_c, R_p) -diastereomer]. 89% ee (major diastereomer), 95% ee (minor diastereomer). The absolute configuration was assigned by analogy with Table 2, entries 9 and 17.

¹H NMR (400 MHz, CDCl₃): δ 7.89-7.85 (m, 1H), 7.82-7.75 (m, 2H), 7.55-7.35 (m, 7H), 7.28-7.23 (m, 1H), 6.85-6.76 (m, 2H), 6.65 (d, J = 8.8 Hz, 1H), 4.05-3.90 (m, 1H), 3.87-3.76 (m, 1H), 3.73 (s, 1.7H), 3.72 (s, 1.3H), 3.49 (ddd, J = 17.6, 10.4 and 7.2 Hz, 0.45H), 3.20 (ddd, J = 18.0, 6.4 and 3.2 Hz, 0.53H), 1.53 (d, J = 9.6 Hz, 1.27H), 1.34 (d, J = 10.0 Hz, 1.64H), 1.30-0.30 (m, 3H). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 18.5 (m).



Table 2, entry 4. White solid. 94% yield, dr = 1.1/1. The ee was determined on a Daicel Chiralcel OZ-3 column with hexane/2-propanol = 98/2, flow = 0.8 mL/min. Retention times: 18.3 min [(R_c, R_p) -diastereomer], 24.5 min [(S_c, S_p) -diastereomer], 26.5 min [(R_c, S_p) -diastereomer], 38.7 min [(S_c, R_p) -diastereomer]. 87% ee (major diastereomer), 96% ee (minor diastereomer). The absolute configuration was assigned by analogy with Table 2, entries 9 and 17.

¹H NMR (400 MHz, CDCl₃): δ 7.90 (d, J = 7.2 Hz, 1H), 7.83-7.35 (m, 2H), 7.60-7.36 (m, 8H), 7.32-7.24 (m, 1H), 7.16 (t, J = 8.0 Hz, 0.50H), 7.01 (t, J = 8.0 Hz, 0.43H), 6.91-6.85 (m, 1H), 4.05-3.90 (m, 1H), 3.87-3.75 (m, 1H), 3.49 (ddd, J = 17.6, 10.0

and 7.2 Hz, 0.47H), 3.20 (ddd, J = 18.0, 6.4 and 2.8 Hz, 0.55H), 1.56 (d, J = 9.6 Hz, 1.36H), 1.37 (d, J = 9.6 Hz, 1.65H), 1.30-0.30 (m, 3H). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 19.4 (m).



Table 2, entry 5. White solid. 86% yield, dr = 1.1/1. The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 95/5, flow = 0.8 mL/min. Retention times: 24.1 min [(S_c, R_p) -diastereomer], 34.7 min [(S_c, S_p) -diastereomer], 48.0 min [(R_c, S_p) -diastereomer], 81.6 min [(R_c, R_p) -diastereomer]. 83% ee (major diastereomer), 96% ee (minor diastereomer). The absolute configuration was assigned by analogy with Table 2, entries 9 and 17.

¹H NMR (400 MHz, CDCl₃): δ 7.88 (d, J = 7.2 Hz, 1H), 7.81-7.74 (m, 2H), 7.58-7.35 (m, 8H), 7.26-7.20 (m, 2H), 6.75 (dd, J = 8.8 and 2.0 Hz, 1H), 4.05-3.92 (m, 1H), 3.86-3.75 (m, 1H), 3.54 (ddd, J = 17.6, 10.4 and 7.2 Hz, 0.46H), 3.19 (ddd, J = 17.6, 9.6 and 2.8 Hz, 0.54H), 1.56 (d, J = 9.6 Hz, 1.39H), 1.35 (d, J = 9.6 Hz, 1.73H), 1.30-0.30 (m, 3H). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 18.7 (m).



Table 2, entry 6. White solid. 86% yield, dr = 1.2/1. The ee was determined on a Daicel Chiralcel OZ-3 column with hexane/2-propanol = 95/5, flow = 1.0 mL/min. Retention times: 44.9 min [(R_c,R_p) -diastereomer], 52.7 min [(S_c,S_p) -diastereomer], 59.6 min [(R_c,S_p) -diastereomer], 65.0 min [(S_c,R_p) -diastereomer]. 87% ee (major diastereomer), 97% ee (minor diastereomer). The absolute configuration was assigned by analogy with Table 2, entries 9 and 17.

¹H NMR (400 MHz, CDCl₃): δ 8.15 (d, *J* = 8.4 Hz, 1H), 7.99-7.89 (m, 2H), 7.82-7.76

(m, 2H), 7.60-7.38 (m, 8H), 7.12-7.06 (dd, J = 8.8 and 1.6 Hz, 1H), 4.20-4.09 (m, 1H), 3.94-3.80 (m, 1H), 3.70 (ddd, J = 17.2, 10.0 and 7.2 Hz, 0.44H), 3.27 (ddd, J = 18.0, 9.6 and 2.8 Hz, 0.54H), 1.65 (d, J = 9.6 Hz, 1.31H), 1.40 (d, J = 10.0 Hz, 1.73H), 1.30-0.30 (m, 3H). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 19.6 (m).



Table 2, entry 7. 86% yield, dr = 1.3/1. The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 95/5, flow = 1.0 mL/min. Retention times: 13.2 min $[(S_c,R_p)$ -diastereomer], 25.7 min $[(R_c,S_p)$ -diastereomer]; 17.3 min $[(S_c,S_p)$ -diastereomer], 43.9 min $[(R_c,R_p)$ -diastereomer]. 81% ee (major diastereomer), 97% ee (minor diastereomer). The absolute configuration was assigned by analogy with Table 2, entries 9 and 17.



Major diastereomer, white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.84-7.75 (m, 4H), 7.58-7.44 (m, 8H), 7.40 (t, *J* = 7.6 Hz, 2H), 4.11 (ddd, *J* = 14.0, 11.8 and 2.8 Hz, 1H), 3.88 (ddd, *J* = 18.0, 11.2 and 4.2 Hz, 1H), 3.23 (ddd, *J* = 18.0, 10.0 and 3.2 Hz, 1H), 1.36 (d, *J* = 10.0 Hz, 3H). 1.30-0.30 (m, 3H). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 18.8 (m). [α]²⁰_D = -80.7 (c 1.10, CHCl₃). HRMS (ESI) calcd for C₂₃H₂₃BF₃OP (M)⁺ 413.1568, found 413.1561.



Minor diastereomer, white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.90 (d, J = 7.2 Hz,

2H), 7.60-7.35 (m, 10H), 7.01 (d, J = 7.6 Hz, 2H), 4.05 (ddd, J = 13.6, 10.0 and 3.6 Hz, 1H), 3.83 (ddd, J = 16.0, 10.0 and 4.0 Hz, 1H), 3.63 (ddd, J = 17.6, 9.6 and 6.8 Hz, 1H), 1.59 (d, J = 9.6 Hz, 3H), 1.30-0.30 (m, 3H). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 20.0 (m). $[\alpha]_{D}^{20} = -69.7$ (c 1.45, CHCl₃). HRMS (ESI) calcd for C₂₃H₂₃BF₃OP (M)⁺ 413.1568, found 413.1560.



Table 2, entry 8. White solid. 88% yield, dr = 1.2/1. The ee was determined on a Daicel Chiralpak IC column with hexane/2-propanol = 98/2, flow = 1.0 mL/min. Retention times: 22.6 min (major diastereomer), 26.9 min (major diastereomer), 38.3 min (minor diastereomer), 40.1 min (minor diastereomer). 89% ee (major diastereomer), 94% ee (minor diastereomer). The absolute configuration was assigned by analogy with Table 2, entries 9 and 17.

¹H NMR (400 MHz, CDCl₃): δ 7.78-7.73 (m, 2H), 7.65 (d, J = 8.4 Hz, 1H), 7.57 (d, J = 8.4 Hz, 1H), 7.53-7.37 (m, 5H), 7.30-7.24 (m, 38H), 7.14-7.08 (m, 1H), 6.85-6.81 (m, 1H), 4.04-3.91 (m, 1H), 3.83-3.74 (m, 1H), 3.48 (ddd, J = 17.6, 10.0 and 7.2 Hz, 0.52H), 3.21 (ddd, J = 17.6, 10.4 and 3.2 Hz, 0.51H), 1.54 (d, J = 9.6 Hz, 1.56H), 1.33 (d, J = 10.0 Hz, 1.49H), 1.30-0.30 (m, 3H). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 18.9 (m).



Table 2, entry 9. White solid. 98% yield, dr = 1.7/1. The ee was determined on a Daicel Chiralcel OZ-3 column with hexane/2-propanol = 95/5, flow = 1.0 mL/min. Retention times: $15.2 \text{ min } [(R_c, R_p)\text{-diastereomer}], 17.0 \text{ min } [(S_c, S_p)\text{-diastereomer}], 18.0 \text{$

23.3 min [(R_c,S_p) -diastereomer], 32.8 min [(S_c,R_p) -diastereomer]. 89% ee (major diastereomer), 94% ee (minor diastereomer). The absolute configuration of the major diastereomer was determined to be S_c,S_p by X-ray crystal analysis. The absolute configuration of the minor diastereomer was assigned by analogy with Table 2, entry 17.



Major diastereomer: ¹H NMR (400 MHz, CDCl₃): δ 7.73 (t, J = 9.2 Hz, 2H), 7.55-7.42 (m, 5H), 7.13 (d, J = 8.4 Hz, 2H), 3.78 (ddd, J = 14.4, 10.4 and 3.2 Hz, 1H), 3.17 (ddd, J = 17.6, 10.8 and 6.4 Hz, 1H), 2.72 (ddd, J = 18.0, 10.4 and 3.6 Hz, 1H), 1.97 (s, 3H), 1.31 (d, J = 9.6 Hz, 3H). 1.30-0.30 (m, 3H). ¹³C NMR (CDCl₃): δ 204.6 (d, $J_{CP} = 12.2$ Hz), 135.2 (d, $J_{CP} = 2.6$ Hz), 132.0 (d, $J_{CP} = 8.7$ Hz), 131.8 (d, $J_{CP} = 2.2$ Hz), 131.6 (d, $J_{CP} = 2.3$ Hz), 130.7 (d, $J_{CP} = 4.1$ Hz), 128.9 (d, $J_{CP} = 9.5$ Hz), 128.3 (d, $J_{CP} = 51.3$ Hz), 121.6 (d, $J_{CP} = 3.4$ Hz), 43.4 (d, $J_{CP} = 5.7$ Hz), 38.9 (d, $J_{CP} = 32.3$ Hz), 30.4 (d, $J_{CP} = 1.2$ Hz), 9.1 (d, $J_{CP} = 38.7$ Hz). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 18.0 (m). [α]²⁰_D = -103 (c 0.250, CHCl₃). HRMS (ESI) calcd for C₁₇H₂₂BBrOP (M+H)⁺ 362.0716, found 362.0716.



Minor diastereomer. ¹H NMR (400 MHz, CDCl₃): δ 7.51-7.38 (m, 10H), 7.26 (t, *J* = 4.0 Hz, 2H), 6.80 (d, *J* = 7.2 Hz, 2H), 3.75-3.69 (m, 1H), 3.24 (ddd, *J* = 18.0, 14.0 and 4.0 Hz, 1H), 2.95 (ddd, *J* = 17.6, 10.0 and 7.2 Hz, 1H), 2.09 (s, 3H), 1.52 (d, *J* = 9.6 Hz, 3H), 1.30-0.30 (m, 3H). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 19.0 (m). $[\alpha]^{20}_{D} =$

-103 (c 0.250, CHCl₃). HRMS (ESI) calcd for C₁₇H₂₂BBrOP (M+H)⁺ 362.0716, found 362.0714.



Table 2, entry 10. White solid. 91% yield, dr = 2.6/1. The ee was determined on a Daicel Chiralcel OZ-3 column with hexane/2-propanol = 95/5, flow = 1.0 mL/min. Retention times: 10.5 min [(S_c, R_p) -diastereomer], 11.3 min [(R_c, R_p) -diastereomer], 11.8 min [(R_c, S_p) -diastereomer], 12.6 min [(S_c, S_p) -diastereomer]. 72% ee (major diastereomer), 85% ee (minor diastereomer). The absolute configuration was assigned by analogy with Table 2, entries 9 and 17.

¹H NMR (300 MHz, CDCl₃): δ 7.80-7.65 (m, 4H), 7.55-7.30 (m, 6H), 3.15-2.90 (m, 3H), 2.40-2.20 (m, 1H), 1.67 (d, *J* = 10.2 Hz, 3H), 1.02 (d, *J* = 6.6 Hz, 6H), 1.30-0.30 (m, 3H). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 17.7 (m).



Table 2, entry 11. White solid. 84% Yield, dr = 1.2/1. The ee was determined on a Daicel Chiralpak IC column with hexane/2-propanol = 95/5, flow = 1.0 mL/min. Retention times: 9.4 min [(R_c, R_p) -diastereomer], 10.1 min [(S_c, S_p) -diastereomer], 16.0 min [(S_c, R_p) -diastereomer], 16.9 min [(R_c, S_p) -diastereomer]. 86% ee (major diastereomer), 93% ee (minor diastereomer). The absolute configuration was assigned by analogy with Table 2, entries 9 and 17.

¹H NMR (400 MHz, CDCl₃): δ 7.79 (t, J = 6.4 Hz, 1H), 7.55-7.12 (m, 10H), 6.85 (d, J = 6.0 Hz, 1H), 6.23 (dt, J = 20.4 and 2.0 Hz, 2H), 4.03-3.85 (m, 1H), 3.76-3.55 (m, 1H), 3.31 (ddd, J = 17.2, 10.4 and 6.8 Hz, 0.47H), 3.13 (ddd, J = 17.6, 10.0 and 3.2 Hz, 0.53H), 1.56 (d, J = 9.6 Hz, 1.49H), 1.33 (d, J = 10.0 Hz, 1.76H), 1.30-0.30 (m,

3H). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 18.3 (m).



Table 2, entry 12. White solid. 97% yield, dr = 1.2/1. The ee was determined on a Daicel Chiralpak IC column with hexane/2-propanol = 95/5, flow = 1.0 mL/min. Retention times: 8.4 min [(S_c, S_p) -diastereomer], 9.5 min [(R_c, R_p) -diastereomer], 15.3 min [(S_c, R_p) -diastereomer], 16.3 min [(R_c, S_p) -diastereomer]. 84% ee (major diastereomer), 93% ee (minor diastereomer). The absolute configuration was assigned by analogy with Table 2, entries 9 and 17.

¹H NMR (400 MHz, CDCl₃): δ 7.79 (t, *J* = 8.0 Hz, 1H), 7.55-7.36 (m, 4H), 7.26-7.20 (m, 2H), 7.17-7.09 (m, 2H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 6.8 Hz, 1H), 6.26-6.18 (m, 2H), 3.97-3.81 (m, 1H), 3.70 (ddd, *J* = 17.2, 9.2 and 3.6 Hz, 0.48H), 3.59 (ddd, *J* = 17.2, 11.2 and 6.4 Hz, 0.54H), 3.25 (ddd, *J* = 17.2, 10.8 and 6.4 Hz, 0.47H), 3.09 (ddd, *J* = 17.2, 9.6 and 3.2 Hz, 0.53H), 2.30 (s, 1.57H), 2.24 (s, 1.37H), 1.53 (d, *J* = 9.6 Hz, 1.35H), 1.32 (d, *J* = 10.0 Hz, 1.67H), 1.30-0.30 (m, 3H). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 18.7 (m).



Table 2, entry 13. White solid. 91% yield, dr = 1.2/1. The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 95/5, flow = 1.0 mL/min. Retention times: 20.0 min [(S_c , S_p)-diastereomer], 31.1 min [(R_c , R_p)-diastereomer], 34.7 min [(S_c , R_p)-diastereomer], 46.8 min [(R_c , S_p)-diastereomer]. 85% ee (major diastereomer), 93% ee (minor diastereomer). The absolute configuration was assigned by analogy with Table 2, entries 9 and 17.

¹H NMR (300 MHz, CDCl₃): δ 7.87-7.73 (m, 4H), 7.66-6.95 (m, 11H), 6.26-6.21 (m, 2H), 4.19-4.00 (m, 1H), 3.88-3.68 (m, 1H), 3.37 (ddd, *J* = 17.1, 10.5 and 6.0 Hz, 0.45H), 3.20 (ddd, *J* = 17.1, 9.3 and 2.4 Hz, 0.54H), 1.56 (d, *J* = 9.6 Hz, 1.66H), 1.34 (d, *J* = 10.2 Hz, 1.74H), 1.30-0.30 (m, 3H). ³¹P{¹H} NMR (121 MHz, CDCl₃): δ 18.1 (m).



Table 2, entry 14. White solid. 95% yield, dr = 1.1/1. The ee was determined on a Daicel Chiralpak IC column with hexane/2-propanol = 95/5, flow = 1.0 mL/min. Retention times: 15.6 min [(S_c, S_p) -diastereomer], 17.6 min [(R_c, R_p) -diastereomer], 29.2 min [(S_c, R_p) -diastereomer], 32.5 min [(R_c, S_p) -diastereomer]. 83% ee (major diastereomer), 92% ee (minor diastereomer). The absolute configuration was assigned by analogy with Table 2, entries 9 and 17.

¹H NMR (400 MHz, CDCl₃): δ 7.78 (t, J = 8.8 Hz, 1H), 7.51-7. 15 (m, 7H), 6.84 (d, J = 8.4 Hz, 1H), 6.77 (d, J = 7.2 Hz, 1H), 6.68 (d, J = 8.4 Hz, 1H), 6.26-6.20 (m, 2H), 3.94-3.71 (m, 1H), 3.76 (s, 1.51H), 3.71 (s, 1.40H), 3.58-3.51 (m, 1H), 3.24 (ddd, J = 17.2, 10.8 and 2.4 Hz, 0.48H), 3.08 (ddd, J = 17.2, 9.2 and 2.8 Hz, 0.52H), 1.54 (d, J = 9.6 Hz, 1.35H), 1.33 (d, J = 10.4 Hz, 1.67H), 1.30-0.30 (m, 3H). ³¹P{¹H} NMR (121 MHz, CDCl₃): δ 18.1 (m).



Table 2, entry 15. White solid. 97% yield, dr = 1.1/1. The ee was determined on a Daicel Chiralcel OZ-H column with hexane/2-propanol = 95/5, flow = 0.8 mL/min. Retention times: 47.9 min [(S_c , S_p)-diastereomer], 60.7 min [(R_c , R_p)-diastereomer],

72.0 min $[(R_c, S_p)$ -diastereomer], 97.9 min $[(S_c, R_p)$ -diastereomer]. 85% ee (major diastereomer), 93% ee (minor diastereomer). The absolute configuration was assigned by analogy with Table 2, entries 9 and 17.

¹H NMR (300 MHz, CDCl₃): δ 8.20 (d, J = 8.7 Hz, 1H), 7.99 (d, J = 8.4 Hz, 1H), 7.80 (t, J = 8.4 Hz, 1H), 7.61-7.38 (m, 5H), 7.26 (s, 1H), 7.14 (s, 1H), 7.08 (d, J = 7.8 Hz, 1H), 6.34-6.20 (m, 2H), 4.13-3.97 (m, 1H), 3.80-3.56 (m, 1H), 3.45 (ddd, J = 17.4, 10.8 and 6.9 Hz, 0.44H), 3.13 (ddd, J = 17.4, 8.7 and 3.0 Hz, 0.50H), 1.66 (d, J = 9.3 Hz, 1.99H), 1.39 (d, J = 9.9 Hz, 1.78H), 1.30-0.30 (m, 3H). ³¹P{¹H} NMR (121 MHz, CDCl₃): δ 18.9 (m).



Table 2, entry 16. White solid. 98% yield, dr = 1.2/1. The ee was determined on a Daicel Chiralcel OZ-H column with hexane/2-propanol = 95/5, flow = 0.8 mL/min. Retention times: 10.8 min [(R_c,R_p) -diastereomer], 11.6 min [(S_c,S_p) -diastereomer], 15.5 min [(R_c,S_p) -diastereomer], 22.2 min [(S_c,R_p) -diastereomer]. 84% ee (major diastereomer), 95% ee (minor diastereomer). The absolute configuration was assigned by analogy with Table 2, entries 9 and 17.

¹H NMR (400 MHz, CDCl₃): δ 7.77 (t, J = 7.6 Hz, 1H), 7.60-6.84 (m, 10H), 6.27-6.22 (m, 2H), 3.97-3.80 (m, 1H), 3.78-3.48 (m, 1H), 3.32-3.20 (m, 0.46H), 3.18-3.06 (m, 0.51H), 1.58 (d, J = 9.6 Hz, 1.42H), 1.36 (d, J = 9.6 Hz, 1.64H), 1.30-0.30 (m, 3H). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 19.4 (m).



Table 2, entry 17. White solid. 98% yield, dr = 1.2/1. The ee was determined on a

Daicel Chiralcel OZ-H column with hexane/2-propanol = 95/5, flow = 0.8 mL/min. Retention times: 15.3 min [(S_c, S_p) -diastereomer], 18.1 min [(R_c, R_p) -diastereomer], 22.9 min [(R_c, S_p) -diastereomer], 33.8 min [(S_c, R_p) -diastereomer]. 86% ee (major diastereomer), 96% ee (minor diastereomer). The absolute configuration of the major diastereomer was assigned by analogy with Table 2, entry 9. The absolute configuration of the minor diastereomer was determined to be S_c, R_p by X-ray crystal analysis.



Major diastereomer. ¹H NMR (400 MHz, CDCl₃): δ 7.79 (t, J = 8.8 Hz, 1H), 7.58-7.44 (m, 5H), 7.25-7.15 (m, 4H), 6.23 (s, 2H), 3.95-3.85 (m, 1H), 3.54 (ddd, J = 17.6, 11.2 and 5.2 Hz, 1H), 3.08 (ddd, J = 17.6, 9.2 and 2.8 Hz, 1H), 1.35 (d, J = 10.0 Hz, 3H), 1.30-0.30 (m, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 167.3 (d, $J_{CP} = 15.9$ Hz), 134.5 (d, $J_{CP} = 2.3$ Hz), 132.1 (d, $J_{CP} = 2.3$ Hz), 132.0 (d, $J_{CP} = 8.7$ Hz), 131.8 (d, $J_{CP} = 1.9$ Hz), 130.6 (d, $J_{CP} = 3.8$ Hz), 129.1 (d, $J_{CP} = 9.9$ Hz), 128.0 (d, $J_{CP} = 51.3$ Hz), 121.9 (d, $J_{CP} = 3.4$ Hz), 118.8, 113.5, 39.8 (d, $J_{CP} = 32.3$ Hz), 35.0 (d, $J_{CP} = 8.4$ Hz), 9.3 (d, $J_{CP} = 39.0$ Hz). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 19.4 (m). [α]²⁰_D = -75.4 (c 0.60, CHCl₃).



Minor diastereomer. ¹H NMR (400 MHz, CDCl₃): δ 7.55-7.21 (m, 9H), 6.74 (d, *J* = 7.2 Hz, 2H), 6.28 (s, 2H), 3.91-3.82 (m, 1H), 3.71-3.65 (m, 1H), 3.32-3.21 (m, 1H), 3.08 (ddd, *J* = 17.6, 9.2 and 2.8 Hz, 1H), 1.58 (d, *J* = 9.6 Hz, 3H), 1.30-0.30 (m, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 167.4 (d, $J_{CP} = 15.2$ Hz), 134.4 (d, $J_{CP} = 5.7$ Hz), 132.4 (d, $J_{CP} = 9.2$ Hz), 132.0 (d, $J_{CP} = 2.2$ Hz), 131.3 (d, $J_{CP} = 1.9$ Hz), 130.2 (d, $J_{CP} = 4.2$ Hz), 128.6 (d, $J_{CP} = 9.9$ Hz), 125.9 (d, $J_{CP} = 52.3$ Hz), 121.6 (d, $J_{CP} = 3.0$ Hz), 118.9, 113.6, 39.9 (d, $J_{CP} = 30.4$ Hz), 34.9 (d, $J_{CP} = 7.6$ Hz), 9.0 (d, $J_{CP} = 39.5$ Hz). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 19.6 (m). [α]²⁰_D = -43.5 (c 1.00, CHCl₃).

Generanl Procedure for Table 3.

Isopropylphenylphosphine **2d** (30.4 mg, 0.20 mmol) was added to a solution of (*S*,*S*)-**4** (2.7 mg, 4 µmol Pd) and α , β -unsaturated carbonyl compound **1** (0.30 mmol) in toluene (2.5 mL) at -5 °C (realized with a refrigerated bath circulator), then the resulting solution was stirred for 24 h at the same temperature. Then 0.3 mL Me₂S·BH₃ (2 M in THF) was added into it and the resulting solution was stirred for 1.5 h. The excess borane was reacted with H₂O and the mixture was dried over MgSO₄, filtered and concentrated under vacuum. The residue was purified by silica gel chromatography with hexane/EtOAc = 4/1 to afford the product as a white solid.



Table 3, entry 1. White solid. 80% yield, dr> 10/1. The ee was determined on a Daicel Chiralcel OZ-3 column with hexane/2-propanol = 95/5, flow = 1.0 mL/min. Retention times: 8.7 min [(R_c , S_p)-diastereomer], 18.5 min [(S_c , R_p)-diastereomer]. 98% ee. [α]²⁰_D = -11.1 (c 0.750, CHCl₃). The absolute configuration was determined to be S_c , R_p by X-ray crystal analysis.

¹H NMR (400 MHz, CDCl₃): δ 7.85 (d, *J* = 7.6 Hz, 2H), 7.54-7.35 (m, 8H), 7.14-7.12 (m, 3H), 6.80-6.76 (m, 1H), 4.24-4.15 (m, 1H), 3.84 (ddd, *J* = 18.0, 9.2 and 2.8 Hz, 1H), 3.43 (ddd, *J* = 16.8, 11.2 and 4.0 Hz, 1H), 2.27-2.19 (m, 1H), 1.43 (dd, *J* = 15.6

and 6.8 Hz, 3H), 0.98 (dd, J = 15.6 and 7.2 Hz, 3H), 1.30-0.30 (m, 3H). ¹³C NMR (CDCl₃): δ 196.6 (d, $J_{CP} = 13.3$ Hz), 136.5 (d, $J_{CP} = 1.1$ Hz), 136.2 (d, $J_{CP} = 7.3$ Hz), 133.9 (d, $J_{CP} = 2.2$ Hz), 133.2, 131.5 (d, $J_{CP} = 2.7$ Hz), 128.8 (d, $J_{CP} = 3.8$ Hz), 128.5, 128.1 (d, $J_{CP} = 6.5$ Hz), 128.0 (d, $J_{CP} = 0.8$ Hz), 127.9, 127.1 (d, $J_{CP} = 2.3$ Hz), 124.5 (d, $J_{CP} = 48.2$ Hz), 39.1 (d, $J_{CP} = 6.1$ Hz), 36.1 (d, $J_{CP} = 28.5$ Hz), 20.5 (d, $J_{CP} = 36.1$ Hz), 16.8 (d, $J_{CP} = 1.9$ Hz). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 34.6 (m). HRMS (ESI) calcd for C₂₄H₂₉BO₂P (M+H)⁺ 374.2080, found 374.2075.



Table 3, entry 2. White solid. 84% yield, dr> 10/1. The ee was determined on a Daicel Chiralcel OZ-3 column with hexane/2-propanol = 95/5, flow = 1.0 mL/min. Retention times: 13.2 min [(R_c, S_p) -diastereomer], 42.5 min [(S_c, R_p) -diastereomer]. 98% ee. [α]²⁰_D = -25.0 (c 2.00, CHCl₃). The absolute configuration was assigned by analogy with Table 3, entry 1.

¹H NMR (300 MHz, CDCl₃): δ 7.84 (d, J = 7.5 Hz, 2H), 7.54-7.38 (m, 8H), 6.79 (d, J = 8.1 Hz, 2H), 7.84 (d, J = 8.7 Hz, 2H), 4.18-4.09 (m, 1H), 3.82 (ddd, J = 17.7, 9.0 and 3.0 Hz, 1H), 3.36 (ddd, J = 17.1, 11.4 and 5.1 Hz, 1H), 2.30-2.16 (m, 1H), 1.40 (dd, J = 15.6 and 6.6 Hz, 3H), 1.00 (dd, J = 15.6 and 6.9 Hz, 3H), 1.30-0.30 (m, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 196.7 (d, J_{CP} = 13.6 Hz), 158.4 (d, J_{CP} = 1.9 Hz), 136.4 (d, J_{CP} = 1.5 Hz), 134.0 (d, J_{CP} = 7.6 Hz), 133.1, 131.4 (d, J_{CP} = 2.2 Hz), 129.8 (d, J_{CP} = 3.8 Hz), 128.5, 128.1 (d, J_{CP} = 9.1 Hz), 127.89, 127.87 (d, J_{CP} = 6.2 Hz), 124.5 (d, J_{CP} = 48.5 Hz), 113.4 (d, J_{CP} = 1.9 Hz), 55.0, 39.1 (d, J_{CP} = 6.5 Hz), 35.4 (d, J_{CP} = 29.6 Hz), 20.4 (d, J_{CP} = 36.1 Hz), 16.8 (d, J_{CP} = 1.9 Hz). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 35.2 (m). HRMS (ESI) calcd for C₂₅H₃₁BO₂P (M+H)⁺ 404.2186, found 404.2187.



Table 3, entry 3. White solid. 85% yield, dr> 10/1. The ee was determined on a Daicel Chiralcel OZ-3 column with hexane/2-propanol = 95/5, flow = 1.0 mL/min. Retention times: 33.3 min [(R_c, S_p) -diastereomer], 39.9 min [(S_c, R_p) -diastereomer]. 99% ee. [α]²⁰_D = -34.4 (c 1.73, CHCl₃). The absolute configuration was assigned by analogy with Table 3, entry 1.

¹H NMR (400 MHz, CDCl₃): δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.86 (d, *J* = 8.8 and 1.6 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.54-7.36 (m, 7H), 7.10 (dd, *J* = 8.8 and 1.6 Hz, 2H), 4.32 (td, *J* = 10.8 and 2.8 Hz, 1H), 3.90 (ddd, *J* = 18.0, 8.4 and 2.4 Hz, 1H), 3.58 (ddd, *J* = 18.1, 11.2 and 4.4 Hz, 1H), 2.34-2.21 (m, 1H), 1.40 (dd, *J* = 15.6 and 6.8 Hz, 3H), 1.07 (dd, *J* = 15.2 and 6.8 Hz, 3H), 1.30-0.30 (m, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 195.9 (d, *J*_{CP} = 12.5 Hz), 146.6 (d, *J*_{CP} = 2.3 Hz), 144.7 (d, *J*_{CP} = 6.4 Hz), 135.9 (d, *J*_{CP} = 1.2 Hz), 133.6 (d, *J*_{CP} = 9.5 Hz), 127.9, 123.8 (d, *J*_{CP} = 48.6 Hz), 123.1 (d, *J*_{CP} = 1.5 Hz), 39.3 (d, *J*_{CP} = 5.3 Hz), 36.2 (d, *J*_{CP} = 27.3 Hz), 21.3 (d, *J*_{CP} = 34.5 Hz), 16.9 (d, *J*_{CP} = 1.9 Hz). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 35.8 (m). HRMS (ESI) calcd for C₂₄H₂₈BNO₃P (M+H)⁺ 419.1931, found 419.1930.



Table 3, entry 4. White solid. 88% yield, dr> 10/1. The ee was determined on a Daicel Chiralcel OZ-3 column with hexane/2-propanol = 95/5, flow = 1.0 mL/min. Retention times: 8.0 min [(R_c, S_p) -diastereomer], 13.8 min [(S_c, R_p) -diastereomer]. 99% ee. [α]²⁰_D = -30.4 (c 3.00, CHCl₃). The absolute configuration was assigned by analogy with Table 3, entry 1.

¹H NMR (400 MHz, CDCl₃): δ 7.86 (d, J = 7.2 Hz, 2H), 7.56-7.36 (m, 8H), 7.28-7.25

(m, 1H), 7.03 (t, J = 7.6 Hz, 1H), 6.92 (d, J = 7.6 Hz, 1H), 6.85-6.81 (m, 1H), 4.17-4.11 (m, 1H), 3.86 (ddd, J = 18.0, 9.2 and 2.8 Hz, 1H), 3.38 (ddd, J = 17.6, 10.8 and 4.8 Hz, 1H), 2.28-2.19 (m, 1H), 1.42 (dd, J = 16.0 and 6.8 Hz, 3H), 1.03 (dd, J = 15.6 and 6.8 Hz, 3H), 1.30-0.30 (m, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 196.1 (d, $J_{CP} = 12.3$ Hz), 138.8 (d, $J_{CP} = 7.0$ Hz), 136.2 (d, $J_{CP} = 1.6$ Hz), 133.8 (d, $J_{CP} = 7.8$ Hz), 133.3, 131.8 (d, $J_{CP} = 2.4$ Hz), 131.5 (d, $J_{CP} = 3.7$ Hz), 130.2 (d, $J_{CP} = 1.5$ Hz), 129.5 (d, $J_{CP} = 1.7$ Hz), 128.6, 128.2 (d, $J_{CP} = 9.1$ Hz), 127.9, 127.6 (d, $J_{CP} = 3.7$ Hz), 124.0 (d, $J_{CP} = 48.6$ Hz), 122.1 (d, $J_{CP} = 2.0$ Hz), 39.0 (d, $J_{CP} = 5.8$ Hz), 35.8 (d, $J_{CP} = 28.1$ Hz), 20.5 (d, $J_{CP} = 35.5$ Hz), 16.8, 16.7 (d, $J_{CP} = 2.4$ Hz). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 35.0 (m). HRMS (ESI) calcd for C₂₄H₂₈BBrOP (M+H)⁺ 452.1185, found 452.1162.



Table 3, entry 5. White solid. 83% yield, dr = 7/1. The ee was determined on a Daicel Chiralcel OZ-3 column with hexane/2-propanol = 95/5, flow = 1.0 mL/min. Retention times: 8.5 min [(R_c, S_p) -diastereomer], 14.6 min [(S_c, R_p) -diastereomer]. 98% ee. [α]²⁰_D = -8.32 (c 2.40, CHCl₃). The absolute configuration was assigned by analogy with Table 3, entry 1.

¹H NMR (400 MHz, CDCl₃): δ 7.51-7.48 (m, 1H), 7.47-7.36 (m, 4H), 7.22-7.13 (m, 5H), 6.89-6.85 (m, 2H), 6.24 (d, J = 2.4 Hz, 2H), 4.10 (ddd, J = 11.2, 9.6 and 2.8 Hz, 1H), 3.78 (ddd, J = 17.2, 8.4 and 2.8 Hz, 1H), 3.17 (ddd, J = 17.2, 11.6 and 4.8 Hz, 1H), 2.31-2.19 (m, 1H), 1.44 (dd, J = 15.6 and 6.8 Hz, 3H), 1.01 (dd, J = 15.6 and 6.8 Hz, 3H), 1.30-0.30 (m, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 167.7 (d, $J_{CP} = 16.4$ Hz), 135.4 (d, $J_{CP} = 9.6$ Hz), 133.9 (d, $J_{CP} = 8.0$ Hz), 131.7 (d, $J_{CP} = 2.7$ Hz), 128.7 (d, $J_{CP} = 3.8$ Hz), 128.22, 128.17 (d, $J_{CP} = 6.8$ Hz), 127.5 (d, $J_{CP} = 2.3$ Hz), 123.9 (d, $J_{CP} = 48.6$ Hz), 118.9, 113.2, 36.7 (d, $J_{CP} = 28.8$ Hz), 35.3 (d, $J_{CP} = 6.8$ Hz), 20.4 (d, $J_{CP} = 36.0$ Hz), 16.8 (d, $J_{CP} = 2.2$ Hz). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 35.3 (m).

HRMS (ESI) calcd for $C_{22}H_{31}BBrN_2OP (M+NH_4)^+$ 380.2298, found 380.2295.



Table 3, entry 6. White solid. 80% yield, dr = 5/1. The ee was determined on a Daicel Chiralcel OZ-3 column with hexane/2-propanol = 95/5, flow = 1.0 mL/min. Retention times: 10.7 min [(R_c , S_p)-diastereomer], 15.7 min [(S_c , R_p)-diastereomer]. 99.6% ee. $[\alpha]^{20}_{D} = -78$ (c 0.15, CHCl₃). The absolute configuration was assigned by analogy with Table 3, entry 1.

¹H NMR (400 MHz, CDCl₃): δ 7.51-7.48 (m, 1H), 7.47-7.36 (m, 4H), 7.22-7.13 (m, 4H), 6.75 (d, *J* = 7.6 Hz, 2H), 6.24 (t, *J* = 2.0 Hz, 2H), 4.09-4.03 (m, 1H), 3.76 (ddd, *J* = 17.2, 8.0 and 2.4 Hz, 1H), 3.13 (ddd, *J* = 17.2, 12.0 and 4.4 Hz, 1H), 2.28-2.19 (m, 1H), 1.41 (dd, *J* = 16.0 and 6.8 Hz, 3H), 1.03 (dd, *J* = 15.6 and 6.8 Hz, 3H), 1.30-0.30 (m, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 167.4 (d, *J*_{CP} = 16.0 Hz), 134.7 (d, *J*_{CP} = 7.0 Hz), 133.8 (d, *J*_{CP} = 7.8 Hz), 131.9 (d, *J*_{CP} = 2.6 Hz), 131.3 (d, *J*_{CP} = 1.1 Hz), 130.3 (d, *J*_{CP} = 3.7 Hz), 128.4 (d, *J*_{CP} = 9.3 Hz), 123.6 (d, *J*_{CP} = 48.3 Hz), 121.4 (d, *J*_{CP} = 3.6 Hz), 118.8, 113.4, 36.3 (d, *J*_{CP} = 28.6 Hz), 35.4 (d, *J*_{CP} = 6.7 Hz), 20.7 (d, *J*_{CP} = 35.3 Hz), 16.8 (d, *J*_{CP} = 2.2 Hz). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 34.7 (m). HRMS (ESI) calcd for C₂₂H₃₀BBrN₂OP (M+NH₄)⁺ 458.1403, found.458.1400.



Table 3, entry 7. White solid. 81% yield, dr = 6/1. The ee was determined on a Daicel Chiralcel OZ-3 column with hexane/2-propanol = 95/5, flow = 1.0 mL/min. Retention times: 8.0 min [(R_c, S_p) -diastereomer], 13.0 min [(S_c, R_p) -diastereomer]. 99% ee. [α]²⁰_D = -10.0 (c 2.60, CHCl₃). The absolute configuration was assigned by analogy with Table 3, entry 1.

¹H NMR (400 MHz, CDCl₃): δ 7.51-7.44 (m, 1H), 7.47-7.36 (m, 4H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.22 (t, *J* = 2.0 Hz, 2H), 7.06 (t, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 1H), 6.88-6.82 (m, 1H), 6.27 (t, *J* = 2.4 Hz, 2H), 4.05 (ddd, *J* = 11.6, 9.6 and 2.8 Hz, 1H), 3.78 (ddd, *J* = 17.6, 8.4 and 2.8 Hz, 1H), 3.12 (ddd, *J* = 17.2, 12.0 and 4.8 Hz, 1H), 2.27-2.17 (m, 1H), 1.42 (dd, *J* = 16.0 and 6.8 Hz, 3H), 1.03 (dd, *J* = 15.6 and 6.8 Hz, 3H), 1.30-0.30 (m, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 167.4 (d, *J*_{CP} = 15.9 Hz), 138.0 (d, *J*_{CP} = 7.6 Hz), 133.8 (d, *J*_{CP} = 7.9 Hz), 132.0 (d, *J*_{CP} = 2.2 Hz), 131.4 (d, *J*_{CP} = 3.4 Hz), 130.5 (d, *J*_{CP} = 1.6 Hz), 129.7 (d, *J*_{CP} = 1.5 Hz), 128.4 (d, *J*_{CP} = 8.5 Hz), 127.5 (d, *J*_{CP} = 3.8 Hz), 123.5 (d, *J*_{CP} = 7.2 Hz), 20.4 (d, *J*_{CP} = 35.7 Hz), 16.75, 16.69 (d, *J*_{CP} = 1.9 Hz). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 35.9 (m). HRMS (ESI) calcd for C₂₂H₃₀BBrN₂OP (M+NH₄)⁺ 458.1403, found 458.1397.



Table 3, entry 8. White solid. 78% yield, dr = 5/1. The ee was determined on a Daicel Chiralcel OZ-3 column with hexane/2-propanol = 95/5, flow = 1.0 mL/min. Retention times: 8.0 min [(R_c, S_p) -diastereomer], 13.0 min [(S_c, R_p) -diastereomer]. 99% ee. [α]²⁰_D = -61.1 (c 1.90, CHCl₃). The absolute configuration was assigned by analogy with Table 3, entry 1.

¹H NMR (400 MHz, CDCl₃): δ 7.78-7.75 (m, 1H), 7.67 (d, J = 8.8 Hz, 1H), 7.59-7.56 (m, 1H), 7.52-7.48 (m, 1H), 7.46-7.32 (m, 6H), 7.24-7.18 (m, 3H), 7.05 (d, J = 8.4 Hz, 1H), 6.23 (t, J = 2.0 Hz, 2H), 4.27 (ddd, J = 11.6, 9.2 and 2.4 Hz, 1H), 3.88 (ddd, J = 17.2, 8.4 and 2.8 Hz, 1H), 3.26 (ddd, J = 17.6, 11.6 and 4.4 Hz, 1H), 2.28-2.14 (m, 1H), 1.49 (dd, J = 15.6 and 6.4 Hz, 3H), 0.99 (dd, J = 15.6 and 6.8 Hz, 3H), 1.30-0.30 (m, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 167.6 (d, $J_{CP} = 16.2$ Hz), 134.0 (d, $J_{CP} = 7.7$ Hz), 132.8 (d, $J_{CP} = 7.7$ Hz), 132.7 (d, $J_{CP} = 1.6$ Hz), 132.5 (d, $J_{CP} = 1.6$ Hz), 131.8 (d, $J_{CP} = 2.5$ Hz), 128.2 (d, $J_{CP} = 9.3$ Hz), 127.9 (d, $J_{CP} = 1.2$ Hz), 127.63 (d, $J_{CP} = 0.8$

Hz), 127.57, 127.52 (d, $J_{CP} = 0.8$ Hz), 126.8 (d, $J_{CP} = 3.2$ Hz), 126.3 (d, $J_{CP} = 0.8$ Hz), 126.1 (d, $J_{CP} = 0.8$ Hz), 123.9 (d, $J_{CP} = 48.4$ Hz), 118.9, 113.3, 36.9 (d, $J_{CP} = 28.2$ Hz), 35.5 (d, $J_{CP} = 7.3$ Hz), 20.2 (d, $J_{CP} = 16.3$ Hz), 16.8 (d, $J_{CP} = 2.4$ Hz), 16.7 (d, $J_{CP} =$ 1.3 Hz). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 36.0 (m). HRMS (ESI) calcd for C₂₆H₃₃BN₂OP (M+NH₄)⁺ 430.2454, found 430.2452.



Table 1, entry 6. White solid. 96% yield, dr = 11/1. The ee was determined on a Daicel Chiralcel OZ-3 column with hexane/2-propanol = 95/5, flow = 0.8 mL/min. Retention times: 11.3 min (minor diastereomer), 12.4 min (minor diastereomer), 13.8 min (major diastereomer), 26.1 min (major diastereomer). 86% ee (major diastereomer), 65% ee (minor diastereomer).

Major diastereomer: ¹H NMR (400 MHz, CDCl₃): δ 7.89-7.87 (m, 2H), 7.58-7.52 (m, 1H), 7.48-7.35 (m, 7H), 7.14-7.08 (m, 3H), 6.90-6.84 (m, 2H), 4.03 (td, *J* = 10.4 and 3.2 Hz, 1H), 3.84 (ddd, *J* = 17.6, 9.6 and 3.2 Hz, 1H), 3.51 (ddd, *J* = 17.2, 10.0 and 6.8 Hz, 1H), 1.96-1.81 (m, 2H), 1.11 (dt, *J* = 16.8 and 7.6 Hz, 3H), 1.30-0.30 (m, 3H). ³¹P{¹H} NMR (121 MHz, CDCl₃): δ 27.2 (m).



Table 1, entry 7. White solid. 96% yield, dr = 4.7/1. The ee was determined on a Daicel Chiralcel OZ-3 column with hexane/2-propanol = 95/5, flow = 0.8 mL/min. Retention times: 8.4 min (minor diastereomer), 9.7 min (major diastereomer), 13.9 min (minor diastereomer), 16.0 min (major diastereomer). 58% ee (major diastereomer), 86% ee (minor diastereomer).

¹H NMR (400 MHz, CDCl₃): δ 7.89-7.76 (m, 2H), 7.58-6.84 (m, 13H), 4.09 (ddd, J = 15.2, 10.2 and 2.8 Hz, 0.25H), 4.02 (td, J = 10.8 and 2.8 Hz, 0.75H), 3.90 (ddd, J = 17.6, 10.2 and 4.8 Hz, 0.25H), 3.83 (ddd, J = 17.6, 9.6 and 3.6 Hz, 0.75H), 3.52 (ddd, J = 17.2, 10.4 and 6.8 Hz, 0.74H), 3.11 (ddd, J = 17.6, 10.0 and 2.8 Hz, 0.26H),

1.90-1.71 (m, 2H), 1.41-1.15 (m, 4H), 0.86 (t, J = 7.2 Hz, 2.25H), 0.73 (t, J = 6.8 Hz, 0.75H), 1.30-0.30 (m, 3H). ³¹P{¹H} NMR (121 MHz, CDCl₃): δ 24.2 (m).

Application for a P-Chiral Bisphosphine Synthesis



White solid. 62% yield. The ee was determined on a Daicel Chiralcel OZ-3 column with hexane/2-propanol = 90/10, flow = 1.0 mL/min. Retention times: 8.1 min [(R_c , S_p)-diastereomer], 12.0 min [(S_c , R_p)-diastereomer]. 99% ee.¹H NMR (400 MHz, CDCl₃): δ 7.96 (d, J = 7.2 Hz, 4H), 7.56 (t, J = 7.2 Hz, 2H), 7.44 (t, J = 7.2 Hz, 4H), 7.26 (t, J = 7.6 Hz, 2H), 7.20-7.07 (m, 9H), 6.66 (t, J = 8.0 Hz, 1H), 6.46 (d, J = 7.2 Hz, 2H), 4.18 (td, J = 10.8 and 2.8 Hz, 2H), 3.75 (ddd, J = 17.6, 9.6 and 2.4 Hz, 2H), 3.39 (ddd, J = 17.6, 10.4 and 6.4 Hz, 2H), 2.25-2.18 (m, 2H), 1.36 (dd, J = 16.0 and 7.2 Hz, 6H), 0.98 (dd, J = 15.2 and 7.2 Hz, 6H), 1.30-0.30 (m, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 196.7 (d, J_{CP} = 12.2 Hz), 137.23 (d, J_{CP} = 1.5 Hz), 137.18 (d, J_{CP} = 2.3 Hz), 130.2 (m), 128.6, 128.0, 127.98 (d, J_{CP} = 9.6 Hz), 127.6 (m), 124.6 (d, J_{CP} = 49.7 Hz), 39.8 (d, J_{CP} = 5.9 Hz), 35.7 (d, J_{CP} = 29.6 Hz), 21.8 (d, J_{CP} = 35.1 Hz), 17.01 (d, J_{CP} = 6.4 Hz), 17.00 (d, J_{CP} = 4.1 Hz). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 35.9 (m).

General Procedure for the Preparation of Catalyst⁵



To a solution of amino alcohol (16.0 mmol) and triethyl amine (16.0 mmol) in dichloromethane (30 mL) at 0 °C was added dropwisely a solution of diacyl chloride (8.0 mmol) in dichloromethane, and the resulting mixture was stirred at room

temperature for 24 h. The mixture was filtered and washed with dichloromethane to afford the desired amide for the next step without further purification.

The obtained amide (1.5 mmol) was refluxed with SOCl₂ (8 mL) for 8 h, and the excess SOCl₂ was removed and the residue was dissolved with dichloromethane (5 mL). Then, it was added to a solution of anilines (3.3 mmol) and triethylamine (9 mmol) in dichloromethane (10 mL), and the resulting mixture was stirred at room temperature for 24 h. After addition of aqueous NaOH solution, the mixture was extracted with dichloromethane, and the organic phase was dried over MgSO₄, filtered and evaporated under vacumm. The residue was purified by silica gel chromatography to afford product as a solid.

The obtained oxazoline (0.2 mmol) was stirred with $Pd_2(dba)_3$ ·CHCl₃ (0.1 mmol) in toluene at 80 °C for 16 h. After cooling to room temperature, the mixture was filtered over celite and washed with dichloromethane, and the filtrate was concentrated under vacuum. The residue was purified by silica gel chromatography to afford product as a yellow solid.



White solid. 70% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.53-7.40 (m, 6H), 7.38-7.20 (m, 7H), 6.72-6.60 (m, 8H), 5.32 (t, *J* = 10.0 Hz, 2H), 4.27 (t, *J* = 10.0 Hz, 2H), 3.84 (t, *J* = 9.6 Hz, 2H), 3.64 (s, 6H). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 160.9, 155.6, 143.5, 134.5, 133.5, 131.3, 128.2, 126.9, 126.8, 126.6, 126.5, 122.5, 113.8, 67.4, 60.0, 54.9.



Yellow solid. 85% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.46 (d, *J* = 7.6 Hz, 4H), 7.31 (t, *J* = 7.2 Hz, 4H), 7.28-7.15 (m, 6H), 6.92 (d, *J* = 8.8 Hz, 4H), 6.61 (t, *J* = 7.6 Hz, 1H), 6.35 (d, *J* = 7.6 Hz, 2H), 5.44 (dd, *J* = 10.8 and 4.0 Hz, 2H), 4.39 (t, *J* = 10.4 Hz, 2H), 3.96 (dd, *J* = 9.6 and 3.6 Hz, 2H), 3.83 (s, 6H). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 174.6, 170.2, 159.1, 142.8, 132.9, 132.1, 128.4, 128.1, 127.3, 126.9, 126.7, 122.0, 114.8, 64.8, 63.8, 55.5. [α]²⁰_D = -150 (c 1.00, CHCl₃). HRMS (ESI) calcd for C₃₈H₃₂N₄O₂Pd (M-HBr)⁺ 678.1581, found 678.1564.



¹H NMR (400 MHz, CDCl₃): δ 7.25-7.08 (m, 13H), 6.53 (d, *J* = 9.2 Hz, 4H), 6.46 (d, *J* = 8.8 Hz, 4H), 4.51-4.45 (m, 2H), 3.89 (t, *J* = 10.0 Hz, 2H), 3.60 (s, 6H), 3.60-3.56 (m, 2H), 3.19 (dd, *J* = 13.6 and 4.8 Hz, 2H), 2.84 (dd, *J* = 13.6 and 8.4 Hz, 2H). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 160.0, 155.5, 137.8, 134.1, 133.2, 131.1, 129.1, 127.9, 126.7, 125.8, 122.5, 121.3, 113.5, 64.8, 56.1, 54.8, 41.3.



¹H NMR (400 MHz, CDCl₃): δ 7.47 (d, J = 6.0 Hz, 4H), 7.26-7.16 (m, 6H), 6.83 (d, J

= 8.0 Hz, 4H), 6.43 (d, J= 8.0 Hz, 1H), 6.10 (d, J= 7.6 Hz, 2H), 4.72-4.65 (m, 2H), 4.08 (t, J= 10.4 Hz, 2H), 3.80 (s, 6H), 3.35 (d, J= 4.8 Hz, 4H). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 173.3, 169.1, 158.8, 137.0, 132.8, 131.4, 130.0, 127.8, 127.6, 126.3, 126.1, 121.8, 114.4, 62.6, 58.0, 55.3, 40.5. $[\alpha]^{20}_{D}$ = 249 (c 1.00, CHCl₃). HRMS (ESI) calcd for C₄₀H₃₆N₄O₂Pd (M-HBr)⁺ 706.1894, found 706.1875.



¹H NMR (300 MHz, CDCl₃): δ 7.37-7.25 (m, 4H), 6.76-6.63 (m, 7H), 4.09-4.01 (m, 2H), 3.93 (t, *J* = 9.3 Hz, 2H), 3.73 (s, 6H), 3.65 (t, *J* = 9.3 Hz, 2H), 2.01-1.90 (m, 2H), 1.03 (d, *J* = 6.6 Hz, 6H), 0.98 (d, *J* = 6.6 Hz, 6H). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 159.3, 155.0, 134.3, 133.3, 130.7, 126.5, 122.0, 121.0, 113.3, 69.3, 54.4, 53.9, 32.1, 18.2. 17.4.



¹H NMR (400 MHz, CDCl₃): δ 7.12 (d, *J* = 8.8 Hz, 4H), 6.89 (d, *J* = 8.4 Hz, 4H), 6.49 (d, *J* = 7.6 Hz, 1H), 6.20 (d, *J* = 7.6 Hz, 2H), 4.35-4.29 (m, 2H), 3.94 (t, *J* = 10.0 Hz, 2H), 3.81 (s, 6H), 3.80-3.75 (m, 2H), 2.93-2.84 (m, 2H), 0.89 (d, *J* = 6.8 Hz, 6H), 0.85 (d, *J* = 6.4 Hz, 6H). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 173.2, 168.8, 158.9, 133.0, 132.4, 127.8, 126.4, 121.9, 114.7, 66.7, 55.5, 54.8, 30.2, 18.5, 14.2. [α]²⁰_D = -144 (c 1.00, CHCl₃). HRMS (ESI) calcd for C₃₂H₃₆N₄O₂Pd (M-HBr)⁺ 610.1894, found 610.1878.



¹H NMR (400 MHz, CDCl₃): δ 7.32-7.20 (m, 4H), 6.76-6.63 (m, 7H), 4.30-4.20 (m, 2H), 4.03 (t, *J* = 9.0 Hz, 2H), 3.72 (s, 6H), 3.54 (t, *J* = 8.4 Hz, 2H), 1.89-1.73 (m, 4H), 1.48-1.33 (m, 2H), 0.98 (d, *J* = 6.6 Hz, 6H), 0.96 (d, *J* = 6.6 Hz, 6H). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 158.9, 154.9, 134.1, 133.2, 130.6, 126.3, 121.7, 121.3, 113.2, 61.9, 57.3, 54.3, 45.1, 24.2, 22.2, 22.0.



¹H NMR (300 MHz, CDCl₃): δ 7.18 (d, J = 8.7 Hz, 4H), 6.92 (d, J = 9.0 Hz, 4H), 6.50 (d, J = 7.5 Hz, 1H), 6.23 (d, J = 7.8 Hz, 2H), 4.45-4.34 (m, 2H), 4.08 (t, J = 9.9 Hz, 2H), 3.85 (s, 6H), 3.77 (dd, J = 9.3 and 5.1 Hz, 2H), 1.85-1.42 (m, 6H), 1.04 (d, J = 6.3 Hz, 6H), 0.98 (d, J = 6.6 Hz, 6H). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 173.3, 168.7, 158.8, 133.1, 132.4, 127.7, 126.2, 121.7, 114.6, 60.9, 60.3, 55.4, 44.2, 25.0, 23.8, 21.5. [α]²⁰_D = -157 (c 1.00, CHCl₃). HRMS (ESI) calcd for C₃₄H₄₀N₄O₂Pd (M-HBr)⁺ 638.2207, found 638.2185.



¹H NMR (400 MHz, CDCl₃): δ 7.49 (d, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 7.2 Hz, 4H), 7.32 (m, 5H), 7.24 (t, *J* = 7.2 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 4H), 6.57 (d, *J* = 8.0 Hz, 4H), 5.32 (t, *J* = 10.0 Hz, 2H), 4.30 (t, *J* = 10.0 Hz, 2H), 3.90 (t, *J* = 9.2 Hz, 2H), 2.21 (s, 6H). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 160.4, 143.4, 137.7, 134.8, 132.3, 131.5, 129.2, 128.3, 127.2, 127.0, 126.7, 121.7, 120.0, 67.3, 59.4, 20.5.



¹H NMR (400 MHz, CDCl₃): δ 7.46 (d, *J* = 6.8 Hz, 4H), 7.29-7.11 (m, 14H), 6.62 (t, *J* = 7.6 Hz, 1H), 6.44 (d, *J* = 7.6 Hz, 2H), 5.45 (d, *J* = 7.6 Hz, 2H), 4.43 (t, *J* = 9.6 Hz, 2H), 3.96 (d, *J* = 6.8 Hz, 2H), 2.39 (s, 6H). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 174.6, 169.7, 142.7, 137.9, 136.7, 132.8, 130.2, 128.3, 127.2, 126.9, 126.7, 126.2, 121.9, 64.7, 63.5, 21.0. [α]²⁰_D = -179 (c 1.00, CHCl₃). HRMS (ESI) calcd for C₃₈H₃₂N₄Pd (M-HBr)⁺ 646.1683, found 646.1669.



¹H NMR (400 MHz, CDCl₃): δ 7.45-7.26 (m, 10H), 7..03 (s, 2H), 6.70-6.64 (m, 8H), 5.34 (t, J = 9.6 Hz, 2H), 4.32 (t, J = 9.1 Hz, 2H), 3.89 (d, J = 9.0 Hz, 1H), 3.76 (s, 3H), 3.72 (s, 6H). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 160.7, 158.0, 155.5, 143.2, 135.1,



¹H NMR (400 MHz, CDCl₃): δ 7.51-7.42 (m, 4H), 7.32-7.15 (m, 10H), 6.92 (d, J = 8.8 Hz, 4H), 5.99 (s, 2H), 5.43-5.33 (m, 2H), 4.38 (t, J = 7.6 Hz, 2H), 3.99-3.92 (m, 2H), 3.82 (s, 6H), 3.26 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 169.9, 159.2, 154.9, 142.8, 132.8, 131.9, 128.4, 128.1, 127.3, 126.8, 126.7, 114.7, 113.3, 64.8, 63.7, 55.5, 55.1. [α]²⁰_D = 137 (c 1.10, CHCl₃). HRMS (ESI) calcd for C₃₉H₃₄N₄O₃Pd (M-HBr)⁺ 708.1687, found 708.1660.



A mixture of (S,S)-**5a** (110 mg, 0.144 mmol) and AgOAc (29 mg, 0.17 mmol) in dichloromethane (17 mL) was stirred at room temperature for 24 h, the mixture was filtered over celite and concentrated to afford the product (S,S)-**5i** (104 mg, 0.140 mmol; 97% yield).

¹H NMR (300 MHz, CDCl₃): δ 7.42-7.25 (m, 14H), 6.93 (d, *J* = 9.0 Hz, 4H), 6.55 (d, *J* = 6.0 Hz, 1H), 6.29 (d, *J* = 7.8 Hz, 2H), 5.50-5.30 (m, 2H), 4.42 (t, *J* = 7.8 Hz, 2H), 3.88 (t, *J* = 6.3 Hz, 2H), 3.84 (s, 6H), 2.00 (s, 3H). MS (ESI): 681.2 (M-HOAc)⁺.



A solution of (S,S)-**5i** (0.02 mmol) in dichloromethane (8 mL) and aqueous solution of NaCl or KI (0.20 mmol in 6 mL H₂O) was stirred at room temperature for 1 h. The organic phase was dried over MgSO₄, filtered, and concentrated to afford the desired products (S,S)-**5g** and (S,S)-**5h** in quantitative yield.



¹H NMR (400 MHz, CDCl₃): δ 7.50 (d, J = 7.6 Hz, 4H), 7.34 (d, J = 7.2 Hz, 4H), 7.28-7.18 (m, 6H), 6.93 (d, J = 9.2 Hz, 4H), 6.58 (d, J = 8.0 Hz, 1H), 6.33 (d, J = 8.0 Hz, 2H), 5.39 (dd, J = 10.8 and 4.4 Hz, 2H), 4.39 (t, J = 10.4 Hz, 2H), 4.02 (dd, J = 9.6 and 4.4 Hz, 2H), 3.85 (s, 6H). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 174.4, 169.9, 159.2, 142.7, 133.2, 132.3, 128.5, 128.1, 127.5, 126.94, 126.88, 121.9, 114.9, 64.5, 63.6, 55.5. [α]²⁰_D = 60 (c 0.70, CHCl₃). HRMS (ESI) calcd for C₃₈H₃₂N₄O₂Pd (M-HCl)⁺ 678.1581, found 678.1573.



¹H NMR (400 MHz, CDCl₃): δ 7.43 (d, J = 6.4 Hz, 4H), 7.34 (t, J = 6.4 Hz, 4H), 7.28-7.22 (m, 2H), 7.20 (d, J = 8.4 Hz, 4H), 6.93 (d, J = 8.4 Hz, 4H), 6.63 (t, J = 8.0

Hz, 1H), 6.37 (d, J = 7.6 Hz, 2H), 5.53 (dd, J = 10.8 and 4.0 Hz, 2H), 4.37 (t, J = 10.4 Hz, 2H), 3.96 (dd, J = 10.0 and 4.0 Hz, 2H), 3.84 (s, 6H). ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 175.2, 170.8, 159.3, 143.0, 132.8, 132.1, 128.6, 128.2, 127.4, 127.1, 126.8, 122.2, 114.9, 66.1, 64.1, 55.6. [α]²⁰_D = 65 (c 0.55, CHCl₃). HRMS (ESI) calcd for C₃₈H₃₂N₄O₂Pd (M-HI)⁺ 678.1581, found 678.1572.

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X-Ray Data



 $$\rm cd21370.\,tex$$ Table 1. Crystal data and structure refinement for cd21370.

Identification code	cd21370
Empirical formula	C17 H21 B Br O P
Formula weight	363. 03
Temperature	293(2) К
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P1
Unit cell dimensions	$ \begin{array}{llllllllllllllllllllllllllllllllllll$
Volume	915.0(4) A ³
Z, Calculated density	2, 1.318 Mg/m ³
Absorption coefficient	2.329 mm ⁻¹
F(000)	372
Crystal size	0.213 x 0.121 x 0.045 mm
Theta range for data collection	2.24 to 25.50 deg.
Limiting indices	$-7 \leq h \leq 7, -11 \leq k \leq 9, -18 \leq 1 \leq 18$
Reflections collected / unique	5255 / 4178 [R(int) = 0.0223]
Completeness to theta = 25.50	99.6 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.35197
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4178 / 3 / 407
Goodness-of-fit on F^2	1.019
Final R indices [I>2sigma(I)]	R1 = 0.0552, wR2 = 0.1448
R indices (all data)	R1 = 0.0789, $wR2 = 0.1598$
Absolute structure parameter	-0. 016 (13)
Largest diff. peak and hole	0.701 and -0.299 e.A^-3



 $$\rm cd212400.\,tex$$ Table 1. Crystal data and structure refinement for cd212400.

Thurst Circling and	ad212400
Identification code	CU212400
Empirical formula	C20 H22 B Br N O P
Formula weight	414.08
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	$ \begin{array}{llllllllllllllllllllllllllllllllllll$
Volume	2102.2(3) A ³
Z, Calculated density	4, 1.308 Mg/m ³
Absorption coefficient	2.038 mm ⁻¹
F (000)	848
Crystal size	0.156 x 0.112 x 0.056 mm
Theta range for data collection	1.57 to 26.00 deg.
Limiting indices	-7<=h<=7, -20<=k<=21, -23<=1<=18
Reflections collected / unique	11836 / 4132 [R(int) = 0.0635]
Completeness to theta = 26.00	99.9 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.08870
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4132 / 0 / 239
Goodness-of-fit on F^2	0.975
Final R indices [I>2sigma(I)]	R1 = 0.0497, wR2 = 0.1008
R indices (all data)	R1 = 0.0995, wR2 = 0.1189
Absolute structure parameter	0.001(13)
Largest diff. peak and hole	0.477 and -0.331 e.A^-3



cd21374.tex Table 1. Crystal data and structure refinement for cd21374.

Identification code	cd21374
Empirical formula	C24 H28 B 0 P
Formula weight	374.24
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	$ \begin{array}{llllllllllllllllllllllllllllllllllll$
Volume	2132(3) A ³
Z, Calculated density	4, 1.166 Mg/m ³
Absorption coefficient	0.139 mm ⁻¹
F(000)	800
Crystal size	0.212 x 0.158 x 0.137 mm
Theta range for data collection	2.00 to 26.00 deg.
Limiting indices	$-12 \le h \le 11$, $-16 \le k \le 16$, $-14 \le 1 \le 19$
Reflections collected / unique	13040 / 4197 [R(int) = 0.0326]
Completeness to theta = 26.00	100.0 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.66750
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4197 / 24 / 259
Goodness-of-fit on F^2	1.056
Final R indices [I>2sigma(I)]	R1 = 0.0355, $wR2 = 0.0902$
R indices (all data)	R1 = 0.0383, $wR2 = 0.0924$
Absolute structure parameter	-0.01(8)
Extinction coefficient	0. 0147 (19)
Largest diff. peak and hole 🍃	0.220 and -0.191 e.A -3