Supporting Information

Synthesis of P-Chiral Phosphine Compounds by Palladium-Catalyzed C–P Coupling Reactions

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1. General considerations

All manipulations of air-sensitive materials were carried out under an atmosphere of dry argon by using modified Schlenk line and glovebox techniques. Aryl halides, heteroaryl halides, bases, and catalysts were purchased from Alfa-Aesar and J&K Scientific Ltd. All solvents were distilled from appropriate drying agents under argon before use. The \( ^1 \text{H}, ^{13} \text{C}, ^{19} \text{F} \) and \( ^{31} \text{P} \) NMR spectroscopic data were recorded on Bruker Mercury Plus 400 MHz NMR spectrometers. Chemical shifts (\( \delta \)) for \( ^1 \text{H} \) and \( ^{13} \text{C} \) are referenced to internal solvent resonances and reported relative to SiMe\(_4\). Chemical shifts for \( ^{19} \text{F} \) are reported relative to an external CFCl\(_3\) standard. Chemical shifts for \( ^{31} \text{P} \) are reported relative to an external 85% H\(_3\)PO\(_4\) standard. High resolution mass analysis is performed on Varian 7.0T Fourier-transform mass spectrometry with ESI resource. High performance liquid chromatography (HPLC) was performed on Agilent 1100 series chromatographs using a Daicel Chiracel AD-H (4.6 mm \( \times \) 250 mm) or OD-H (4.6 mm \( \times \) 250 mm) or AS-H (4.6 mm \( \times \) 250 mm) column or IBN-H (4.6 mm \( \times \) 250 mm) with \( n \)-hexane/\( i \)-PrOH as an eluent. Microwave reaction was determined by Discover SP microwave instrument. (\( S \))-\textit{tert}-butyl(methyl)phosphine borane and (\( R \))-\textit{tert}-butyl(methyl)phosphine borane was synthesized according to the published procedures. \[1\]

![Scheme S1. Synthesis of optically pure P-stereogenic tert-butyl(methyl)phosphine borane\[1\]](image)

2. Procedures for palladium-catalyzed C–P coupling reactions

To a reaction tube, (\( S \))-\textit{tert}-butyl(methyl)phosphine borane (35.0 mg, 0.3 mmol), aryl and heteroaryl halides (0.5 mmol), Pd(OAc)\(_2\) (3.4 mg, 0.015 mmol), dppf (27.7 mg, 0.03 mmol), tBuONa (57.6 mg, 0.6 mmol) and toluene (3 mL) were added under argon. The mixture was stirred for 72 h at room temperature. After removal of volatile materials under reduced pressure, the crude product was purified by chromatograph on silica gel. (\( n \)-hexane / dichloromethane).

\((R\)-\textit{tert}-butyl(methyl)(napthalen-1-yl)phosphine Borane\)[2] Performed according to the general procedure to afford 41.0 mg (71%) of (\( R \))-2a as white solid. \(^1\text{H} \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.90 (d, \( J = 8.0 \) Hz, 1 H, Ar), 7.99 (d, \( J = 8.0 \) Hz, 1 H, Ar), 7.87 (d, \( J = 8.0 \) Hz, 1 H, Ar), 7.75 - 7.80 (m, 1 H, Ar), 7.61 - 7.75 (m, 1 H, Ar), 7.49 - 7.53 (m, 2 H, Ar),
1.78 (d, J = 12.0 Hz, 3 H, CH₃), 1.16 (d, J = 16.0 Hz, 9 H, C(CH₃)₃), 0.79 - 1.57 (m, 3 H, BH₃). ¹³C NMR (101 MHz, CDCl₃): δ 135.4 (d, JCP = 10.6 Hz, Ar), 133.9 (d, JCP = 7.7 Hz, Ar), 133.4 (d, JCP = 4.0 Hz, Ar), 132.4 (d, JCP = 2.6 Hz, Ar), 128.8 (s, Ar), 128.2 (d, JCP = 5.9 Hz, Ar), 126.6 (s, Ar), 126.3 (s, Ar), 125.0 (d, JCP = 44.8 Hz, Ar), 124.3 (d, JCP = 9.2 Hz, Ar), 30.5 (d, JCP = 31.5 Hz, C(CH₃)₃), 25.8 (d, JCP = 2.9 Hz, C(CH₃)₃), 8.9 (d, JCP = 39.6 Hz, CH₃). ³¹P NMR (162 MHz, CDCl₃): δ 23.8 (q, J = 69.7 Hz). HPLC (Daicel Chiralcel AS-H, n-hexane/i-PrOH = 95/5, UV = 254 nm, flow rate = 1.0 mL/min) tₑ₆ = 5.452 min (minor) and tₙ₂ = 6.546 min (major), ee = 91%. [α]ᵦ²⁵ = +8.5 (c = 2.0, CHCl₃).

(R)-tert-butyl(methyl)(phenyl)phosphine Borane.² Performed according to the general procedure to afford 41 mg (71%) of (R)-2b as white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.71 (t, J = 8.0 Hz, 2 H, Ar), 7.39 – 7.58 (m, 3 H, Ar), 1.58 (d, J = 8.0 Hz, 3 H, CH₃), 1.11 (d, J = 12.0 Hz, 9 H, C(CH₃)₃), 0.12 – 0.97 (m, 3 H, BH₃). ¹³C NMR (101 MHz, CDCl₃): δ 132.9 (d, JCP = 8.0 Hz, Ar), 131.1 (s, Ar), 128.3 (s, Ar), 128.2 (s, Ar), 28.5 (d, JCP = 33.3 Hz, C(CH₃)₃), 25.1 (d, JCP = 2.9 Hz, C(CH₃)₃), 5.2 (d, JCP = 37.8 Hz, CH₃). ³¹P NMR (162 MHz, CDCl₃): δ 25.0 (q, J = 64.8 Hz). HPLC (Daicel Chiralcel AS-H, n-hexane/i-PrOH = 95/5, UV = 254 nm, flow rate = 1.0 mL/min) tₑ₆ = 7.131 min (minor) and tₙ₂ = 8.103 min (major), ee = 65%. [α]ᵦ²⁵ = +23.0 (c = 2.0, CHCl₃).

(R)-tert-butyl(3,5-dimethylphenyl)(methyl)phosphine Borane. Performed according to the general procedure to afford 50 mg (75%) of (R)-2c as yellow solid. ¹H NMR (400 MHz, CDCl₃): δ 7.30 (s, 1 H, Ar), 7.27 (s, 1 H, Ar), 7.12 (s, 1 H, Ar), 2.36 (s, 6 H, CH₃), 1.53 (d, J = 8.0 Hz, 3 H, CH₃), 1.10 (d, J = 12.0 Hz, 9 H, C(CH₃)₃), 0.24 – 0.86 (m, 3 H, BH₃). ¹³C NMR (101 MHz, CDCl₃): δ 137.8 (d, JCP = 9.9 Hz, Ar), 132.8 (d, JCP = 2.6 Hz, Ar), 130.4 (d, JCP = 8.4 Hz, Ar), 127.2 (d, JCP = 50.3 Hz, Ar), 28.4 (d, JCP = 33.4 Hz, C(CH₃)₃), 25.2 (d, JCP = 2.6 Hz, C(CH₃)₃), 21.3 (s, CH₃), 5.3 (d, JCP = 37.8 Hz, CH₃). ³¹P NMR (162 MHz, CDCl₃): δ 24.3 (q, J = 69.7 Hz). HRMS (ESI): m/z: [M+H-BH₃]+ calculated for C₁₃H₂₁P: 209.1454, found 209.1455. HPLC (Daicel Chiralcel AS-H, n-hexane/i-PrOH = 95/5, UV = 220 nm, flow rate = 1.0 mL/min) tₐ₁ = 4.240 min (minor) and tₙ₂ = 5.678 min (major), ee = 94%. [α]ᵦ²⁵ = +38.0 (c = 2.0, CHCl₃).

(R)-tert-butyl(methyl)(o-tolylyphosphine Borane.² Performed according to the general procedure to afford 34 mg (42%) of (R)-2d as white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.52 - 7.56 (m, 1 H, Ar), 7.37 (t, J = 8.0 Hz, 1 H, Ar), 7.13 – 7.26 (m, 2 H, Ar), 2.66 (s, 3 H, CH₃), 1.64 (d, J = 8.0 Hz, 3 H, CH₃), 1.14 (d, J = 16.0 Hz, 9 H, C(CH₃)₃), 0.43 – 1.10 (m, 3 H, BH₃). ¹³C NMR (101 MHz, CDCl₃): δ 144.1 (d, JCP = 10.5 Hz, Ar), 133.9 (d, JCP = 6.1 Hz, Ar), 132.1 (d, JCP = 8.8 Hz, Ar), 131.0 (d, JCP = 2.4 Hz, Ar), 125.7 (d, JCP = 46.0 Hz, Ar), 125.3 (d, JCP = 8.3 Hz, Ar), 30.5 (d, JCP = 31.9 Hz, C(CH₃)₃), 25.4 (d, JCP = 2.7 Hz, C(CH₃)₃), 23.3 (d, J = 3.3 Hz, CH₃), 8.8 (d, JCP = 39.0 Hz, CH₃). ³¹P NMR (162 MHz, CDCl₃): δ 25.1 (q, J = 61.6 Hz). HPLC (Daicel Chiralcel OD-H, n-hexane/i-PrOH = 98/2, UV = 230 nm, flow rate = 0.5 mL/min) tₐ₁ = 12.580 min (minor) and tₙ₂ = 14.134 min (major), ee = 90%. [α]ᵦ²⁵ = +1.0 (c = 2.0, CHCl₃).
(R)-tert-butyl(4-{tert-butyl}phenyl)(methyl)phosphine Borane. Performed according to the general procedure to afford 67.5 mg (90%) of (R)-2e as yellow solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.61 – 7.65 (m, 2 H, Ar), 7.45 – 7.47 (m, 2 H, Ar), 1.55 (d, \(J = 8.0\) Hz, 3 H, CH\(_3\)), 1.33 (s, 9 H, C(CH\(_3\))\(_3\)), 1.11 (d, \(J = 12.0\) Hz, 9 H, C(CH\(_3\))\(_3\)), 0.48 – 1.05 (m, 3 H, BH\(_3\)). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 154.4 (d, \(J_{CP} = 2.4\) Hz, Ar), 132.7 (d, \(J_{CP} = 8.4\) Hz, Ar), 125.3 (d, \(J_{CP} = 9.7\) Hz, Ar), 124.2 (d, \(J_{CP} = 6.1\) Hz, Ar), 34.9 (s, C(CH\(_3\))\(_3\)), 31.2 (s, C(CH\(_3\))\(_3\)), 28.6 (d, \(J_{CP} = 33.3\) Hz, C(CH\(_3\))\(_3\)), 25.2 (d, \(J_{CP} = 3.0\) Hz, C(CH\(_3\))\(_3\)), 5.4 (d, \(J_{CP} = 30.3\) Hz, CH\(_3\)). \(^{31}\)P NMR (162 MHz, CDCl\(_3\)): \(\delta\) 23.7 (q, \(J = 66.4\) Hz). HRMS (ESI): m/z: [M+H-BH\(_3\)]\(^+\) calculated for C\(_8\)H\(_8\)P: 237.1767, found 237.1766. HPLC (Daicel Chiralcel AS-H, n-hexane/i-PrOH = 99/1, UV = 234 nm, flow rate = 1 mL/min) \(t_{R1} = 5.365\) min (major) and \(t_{R2} = 6.045\) min (minor), ee = 90%. [\(\alpha\)]\(_D\)\(^{25}\) = +13.0 (c = 2.0, CHCl\(_3\)).

(R)-tert-butyl(4-methoxyphenyl)(methyl)phosphine Borane. Performed according to the general procedures to afford 47 mg (70%) of (R)-2f as white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.69 – 7.78 (m, 2 H, Ar), 6.96 – 6.98 (m, 2 H, Ar), 3.85 (s, 3 H, OCH\(_3\)), 1.54 (d, \(J = 8.0\) Hz, 3 H, CH\(_3\)), 1.09 (d, \(J = 16.0\) Hz, 9 H, C(CH\(_3\))\(_3\)), 0.35 – 0.91 (m, 3 H, BH\(_3\)). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 161.8 (d, \(J_{CP} = 2.4\) Hz, Ar), 134.5 (d, \(J_{CP} = 9.4\) Hz, Ar), 118.4 (d, \(J_{CP} = 6.2\) Hz, Ar), 113.9 (d, \(J_{CP} = 10.3\) Hz, Ar), 55.3 (s, OCH\(_3\)), 28.7 (d, \(J_{CP} = 30.3\) Hz, C(CH\(_3\))\(_3\)), 25.2 (d, \(J_{CP} = 2.7\) Hz, C(CH\(_3\))\(_3\)), 5.5 (d, \(J_{CP} = 30.3\) Hz, CH\(_3\)). \(^{31}\)P NMR (162 MHz, CDCl\(_3\)): \(\delta\) 23.2 (q, \(J = 61.6\) Hz). HRMS (ESI): m/z: [M+H-BH\(_3\)]\(^+\) calculated for C\(_{12}\)H\(_{10}\)OP: 211.1246, found 211.1248. HPLC (Daicel Chiralcel AS-H, n-hexane/i-PrOH = 98/2, UV = 254 nm, flow rate = 0.8 mL/min) \(t_{R1} = 21.843\) min (minor) and \(t_{R2} = 23.093\) (major), ee = 98%. [\(\alpha\)]\(_D\)\(^{25}\) = +5.0 (c = 2.0, CHCl\(_3\)).

(R)-4-{1,3-dioxolan-2-yl}phenyl(methyl)phosphine Borane. Performed according to the general procedure to afford 34 mg (42%) of (R)-2g as yellow solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.69 – 7.78 (m, 2 H, Ar), 7.56 – 7.58 (m, 2 H, Ar), 5.84 (s, 1 H, CH), 4.10 – 4.15 (m, 2 H, CH\(_2\)), 4.04 – 4.09 (m, 2 H, CH\(_2\)), 1.57 (d, \(J = 9.7\) Hz, 3 H, CH\(_3\)), 1.10 (d, \(J = 14.0\) Hz, 9 H, C(CH\(_3\))\(_3\)), 0.13 – 0.99 (m, 3 H, BH\(_3\)). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 141.1 (s, Ar), 133.0 (d, \(J_{CP} = 8.1\) Hz, Ar), 128.7 (d, \(J_{CP} = 50.5\) Hz, Ar), 126.3 (d, \(J_{CP} = 9.1\) Hz, Ar), 103.0 (s, CH), 65.4 (s, CH\(_2\)), 28.6 (d, \(J_{CP} = 40.4\) Hz, C(CH\(_3\))\(_3\)), 25.1 (d, \(J_{CP} = 2.7\) Hz, C(CH\(_3\))\(_3\)), 5.3 (d, \(J_{CP} = 40.4\) Hz, CH\(_3\)). \(^{31}\)P NMR (162 MHz, CDCl\(_3\)): \(\delta\) 25.2 (q, \(J = 66.4\) Hz). HRMS (ESI): m/z: [M+H-BH\(_3\)]\(^+\) calculated for C\(_{14}\)H\(_{20}\)OP: 253.1352, found 253.1352. HPLC (Daicel Chiralcel AS-H, n-hexane/i-PrOH = 98/2, UV = 250 nm, flow rate = 1.0 mL/min) \(t_{R1} = 26.610\) min (major) and \(t_{R2} = 34.227\) min (minor), ee = 89%. [\(\alpha\)]\(_D\)\(^{25}\) = +11.0 (c = 2.0, CHCl\(_3\)).

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(R)-4-(1,3-dioxolan-2-yl)phenyl)(tert-butyI)(methyl)phosphine Borane. Performed according to the general procedure to afford 34 mg (42%) of (R)-2h as yellow solid. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.75 – 7.80 (m, 2 H, Ar), 7.66 – 7.68 (m, 2 H, Ar), 7.60 – 7.61 (m, 2 H, Ar), 7.45 – 7.49 (m, 2 H, Ar), 7.37 – 7.41 (m, 1 H, Ar), 1.61 (d, $J$ = 9.7 Hz, 3 H, CH$_3$), 1.15 (d, $J$ = 14.0 Hz, 9 H, C(CH$_3$)$_3$), 0.41 – 0.87 (m, 3 H, CH$_2$). $^{13}$C NMR (101 MHz, CDCl$_3$): δ 143.9 (s, Ar), 139.9 (s, Ar), 133.3 (d, $J_{C,P}$ = 8.7 Hz, Ar), 128.9 (s, Ar), 128.0 (s, Ar), 127.2 (s, Ar), 126.9 (d, $J_{C,P}$ = 9.5 Hz, Ar), 126.3 (d, $J_{C,P}$ = 51.3 Hz, Ar), 28.6 (d, $J_{C,P}$ = 34.3 Hz, C(CH$_3$)$_3$). 1.16 (d, $J_{C,P}$ = 59.9 Hz). HRMS (ESI): m/z: [M+H-BH$_3$]+ calculated for C$_{16}$H$_{31}$OP: 221.1246, found 221.1246. HPLC (Daicel Chiralcel OD-H, n-hexane/i-PrOH = 95/5, UV = 254 nm, flow rate = 0.8 mL/min) $t_{R1}$ = 9.399 min (major) and $t_{R2}$ = 12.921 min (minor), ee = 84%. $[\alpha]_D^{25}$ = +58.0 (c = 2.0, CHCl$_3$).

(R)-4-(borane tert-butyI)(methyl)phosphino)phenyl)methanol. Performed according to the general procedure to afford 64 mg (95%) of (R)-2i as white solid. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.68 (t, $J$ = 8.7 Hz, 2 H, Ar), 7.44 (d, $J$ = 7.6 Hz, 2 H, Ar), 4.72 (s, 2 H, CH$_2$), 2.37 (s, 1 H, CH$_3$OH), 1.56 (d, $J$ = 9.7 Hz, 3 H, CH$_3$), 1.09 (d, $J$ = 14.0 Hz, 9 H, C(CH$_3$)$_3$). 1.17 – 0.91 (m, 3 H, CH$_2$). $^{13}$C NMR (101 MHz, CDCl$_3$): δ 144.1 (s, Ar), 133.0 (d, $J_{C,P}$ = 8.4 Hz, Ar), 126.4 (d, $J_{C,P}$ = 51.5 Hz, Ar), 126.4 (d, $J_{C,P}$ = 10.1 Hz, Ar), 64.4 (s, CH$_3$), 28.4 (d, $J_{C,P}$ = 33.0 Hz, C(CH$_3$)$_3$). 25.0 (d, $J_{C,P}$ = 2.6 Hz, C(CH$_3$)$_3$). 5.2 (d, $J_{C,P}$ = 37.8 Hz, CH$_3$). 31P NMR (162 MHz, CDCl$_3$): δ 22.4 (q, $J$ = 68.0 Hz). HRMS (ESI): m/z: [M+H-BH$_3$]+ calculated for C$_{16}$H$_{30}$OP: 211.1246, found 211.1246. HPLC (Daicel Chiralcel OD-H, n-hexane/i-PrOH = 90/10, UV = 254 nm, flow rate = 1.0 mL/min) $t_{R1}$ = 9.344 min (major) and $t_{R2}$ = 12.921 min (minor), ee = 84%. $[\alpha]_D^{25}$ = +58.0 (c = 2.0, CHCl$_3$).

(R)-tert-butyI(4-chlorophenyl)(methyl)phosphine Borane. Performed according to the general procedure to afford 46 mg (68%) of (R)-2j as white solid. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.61 – 7.69 (m, 2 H, Ar), 7.41 – 7.48 (m, 2 H, Ar), 1.57 (d, $J$ = 9.7 Hz, 3 H, CH$_3$), 1.10 (d, $J$ = 14.1 Hz, 9 H, C(CH$_3$)$_3$). 0.11 – 0.95 (m, 3 H, CH$_2$). $^{13}$C NMR (101 MHz, CDCl$_3$): δ 137.8 (s, Ar), 134.2 (d, $J_{C,P}$ = 8.9 Hz, Ar), 128.6 (d, $J_{C,P}$ = 9.9 Hz, Ar), 126.6 (d, $J_{C,P}$ = 50.5 Hz, Ar), 28.6 (d, $J_{C,P}$ = 30.3 Hz, C(CH$_3$)$_3$). 25.1 (d, $J_{C,P}$ = 2.7 Hz, C(CH$_3$)$_3$). 5.3 (d, $J_{C,P}$ = 38.4 Hz, CH$_3$). 31P NMR (162 MHz, CDCl$_3$): δ 25.5 (q, $J$ = 59.9 Hz). HRMS (ESI): m/z: [M+H-BH$_3$]+ calculated for C$_{16}$H$_{31}$ClP: 215.0751, found 215.0752. HPLC (Daicel Chiralcel AS-H, n-hexane/i-PrOH = 99/1, UV = 234 nm, flow rate = 1.0 mL/min) $t_{R1}$ = 9.339 min (major) and $t_{R2}$ = 11.765 min (minor), ee = 94%. $[\alpha]_D^{25}$ = +1.5 (c = 2.0, CHCl$_3$).
(R)-tert-butyl(methyl)[4-(trifluoromethyl)phenyl]phosphine Borane. Performed according to the general procedure to afford 47 mg (60%) of (R)-2k as yellow solid. 1H NMR (400 MHz, CDCl3): δ 7.83 - 7.88 (m, 2 H, Ar), 7.72 (d, J = 8.0 Hz, 2 H, Ar), 7.65 (m, 2 H, Ar), 1.61 (d, J = 9.5 Hz, 3 H, CH3), 1.12 (d, J = 14.2 Hz, 9 H, C(CH3)3), 0.21 - 0.94 (m, 3 H, BH3). 13C NMR (101 MHz, CDCl3): δ 133.3 (d, Jc,p = 8.4 Hz, Ar), 133.2 (d, Jc,p = 2.0 Hz, Ar), 133.0 (d, Jc,p = 5.1 Hz, Ar), 132.4 (s, Ar), 123.6 (q, Jc,F = 273.7 Hz, CF3), 122.2 (s, Ar), 28.6 (d, Jc,p = 32.6 Hz, C(CH3)3), 25.1 (d, Jc,p = 2.6 Hz, C(CH3)3), 5.2 (d, Jc,p = 37.0 Hz, CH3). 31P NMR (162 MHz, CDCl3): δ 26.9 (q, J = 40.5 Hz). 19F NMR (377 MHz, CDCl3): δ -63.1 (s). HRMS (ESI): m/z: [M+H-BH3]+ calculated for C12H12F3P: 249.1014, found 249.1016. HPLC (Daicel Chiralcel AS-H, n-hexane/i-ProOH = 99/1, UV = 254 nm, flow rate = 1.0 mL/min) tR1 = 6.392 min (minor) and tR2 = 6.672 min (major), ee = 89%. [α]D25 = +5.5 (c = 2.0, CHCl3).

(R)-1-[tert-butyl(methyl)phosphino]phenyl)ethan-1-one. Performed according to the general procedure to afford 22 mg (25%) of (R)-2l as white solid. 1H NMR (400 MHz, CDCl3): δ 7.79 - 8.05 (m, 2 H, Ar), 7.82 (t, J = 7.4 Hz, 2 H, Ar), 2.64 (d, J = 2.8 Hz, 3 H, COCH3), 1.61 (d, J = 6.8 Hz, 3 H, CH3), 1.12 (d, J = 14.2 Hz, 9 H, C(CH3)3). 13C NMR (101 MHz, CDCl3): δ 197.6 (s, COCH3), 138.8 (s, Ar), 133.2 (d, Jc,p = 8.1 Hz, Ar), 127.7 (d, Jc,p = 9.1 Hz, Ar), 28.8 (d, Jc,p =30.3 Hz, C(CH3)3), 28.5(s, COCH3), 25.1 (d, Jc,p = 2.7 Hz, C(CH3)3), 5.2 (d, Jc,p = 38.4 Hz, CH3). 31P NMR (162 MHz, CDCl3): δ 26.5 (q, J = 61.6 Hz). HRMS (ESI): m/z: [M+H-BH3]+ calculated for C13H12OP: 223.1246, found 223.1247. HPLC (Daicel Chiralcel OD-H, n-hexane/i-ProOH = 90/10, UV = 254 nm, flow rate = 1.0 mL/min) tR1 = 7.292 min (major) and tR2 = 8.536 min (minor), ee = 63%. [α]D25 = +1.5 (c = 2.0, CHCl3).

(R)-4-[tert-butyl(methyl)phosphino]phenyl)methanone. Performed according to the general procedure to afford 22 mg (25%) of (R)-2m as yellow solid. 1H NMR (400 MHz, CDCl3): δ 7.77 - 7.90 (m, 6 H, Ar), 7.61 - 7.65 (m, 1 H, Ar), 1.63 (d, J = 8.0 Hz, 3 H, CH3), 1.14 (d, J = 12.0 Hz, 9 H, C(CH3)3), 0.11 - 1.02 (m, 3 H, BH3). 13C NMR (101 MHz, CDCl3): δ 196.1 (s, CO), 139.8 (s, Ar), 136.8 (s, Ar), 133.0 (s, Ar), 132.8 (d, Jc,p = 8.1 Hz, Ar), 132.4 (s, Ar), 131.6 (s, Ar), 130.2(s, Ar), 129.4 (d, Jc,p = 10.0 Hz, Ar), 128.5 (s, Ar), 126.5 (s, Ar), 28.7 (d, Jc,p =32.3 Hz, C(CH3)3), 25.2 (d, Jc,p = 2.7 Hz, C(CH3)3), 5.2 (d, Jc,p = 37.4 Hz, CH3). 31P NMR (162 MHz, CDCl3): δ 26.5 (q, J = 76.1 Hz). HRMS (ESI): m/z: [M+H-BH3]+ calculated for C14H14OP: 285.1408, found 285.1413. HPLC (Daicel Chiralcel OD-H, n-hexane/i-ProOH = 98/2, UV = 250 nm, flow rate = 1.0 mL/min) tR1 = 54.504 min (minor) and tR2 = 57.362 min (major), ee = 65%. [α]D25 = +52.0 (c = 2.0, CHCl3).

S6
**COOEt**

3

**COOEt**

3

(R)-**ethyl 4-borane tert-butyl(methyl)phosphino**benzoate. Performed according to the general procedure to afford 37 mg (40%) of (R)-2a as yellow solid. **1H NMR (400 MHz, CDCl3): δ 8.08 – 8.14 (m, 2 H, Ar), 7.76 – 7.83 (m, 2 H, Ar), 4.41 (q, J = 7.0 Hz, 2 H, CH3CH2), 1.61 (d, J = 9.8 Hz, 3 H, CH3), 1.41 (t, J = 7.0 Hz, 3 H, CH3), 1.11 (d, J = 14.0 Hz, 9 H, C(CH3)3), 0.19 – 0.94 (m, 3 H, BH3). **13C NMR (101 MHz, CDCl3): δ 165.9 (s, CO2Et), 133.4 (d, JCP = 2.0 Hz, Ar), 132.9 (d, JCP = 8.3 Hz, Ar), 132.8 (d, JCP = 2.0 Hz, Ar), 129.1 (d, JCP = 9.5 Hz, Ar), 61.4 (s, CO2CH2CH3), 28.7 (d, JCP = 33.3 Hz, C(CH3)3), 25.1 (d, JCP = 2.8 Hz, C(CH3)3), 14.3 (s, CO2CH2CH3), 5.2 (d, JCP = 37.4 Hz, CH3). **31P NMR (162 MHz, CDCl3): δ 26.4 (q, J = 66.4 Hz). HRMS (ESI): m/z: [M+H-BH3]+ calculated for C20H20O2P: 206.1094, found 206.1093. HPLC (Daicel Chiralcel OD-H, n-hexane/i-PrOH = 98/2, UV = 230 nm, flow rate = 0.8 mL/min) tR = 15.308 min (major) and tR = 16.976 min (minor), ee = 92%. [α]D25 = +11.0 (c = 2.0, CHCl3).

(R)-**4-(borane tert-butyl(methyl)phosphino)benzonitrile.** Performed according to the general procedure to afford 24 mg (36%) of (R)-2o as white solid. **1H NMR (400 MHz, CDCl3): δ 7.85 (d, J = 6.0 Hz, 2 H, Ar), 7.77 (d, J = 5.0 Hz, 2 H, Ar), 1.63 (d, J = 7.0 Hz, 3 H, CH3), 0.98 – 1.19 (d, J = 14.0 Hz, 9 H, C(CH3)3), 0.11 – 0.95 (m, 3 H, BH3). **13C NMR (101 MHz, CDCl3): δ 153.4 (s, CO2Et), 133.5 (d, JCP = 8.1 Hz, Ar), 117.9 (s, CN), 115.0 (d, JCP = 40.0 Hz, Ar), 28.6 (d, JCP = 30.0 Hz, C(CH3)3), 25.1 (d, JCP = 2.7 Hz, C(CH3)3), 5.1 (d, JCP = 40.4 Hz, CH3). **31P NMR (162 MHz, CDCl3): δ 28.1 (q, J = 71.3 Hz). HRMS (ESI): m/z: [M+H-BH3]+ calculated for C19H17NP: 206.1093, found 206.1094. HPLC (Daicel Chiralcel OD-H, n-hexane/i-PrOH = 90/10, UV = 250 nm, flow rate = 1.0 mL/min) tR = 7.383 min (major) and tR = 8.712 min (minor), ee = 74%. [α]D25 = +4.7 (c = 2.0, CHCl3).

**COOEt**

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**COOEt**

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(R)-**tert-butyl(4-methoxynaphthalen-1-yl)(methyl)phosphine Borane.** Performed according to the general procedure to afford 37 mg (40%) of (R)-2p as white solid. **1H NMR (400 MHz, CDCl3): δ 8.79 (d, J = 8.4 Hz, 1 H, Ar), 8.33 (d, J = 8.4 Hz, 1 H, Ar), 7.74 (s, 1 H, Ar), 7.47 – 7.63 (m, 2 H, Ar), 6.86 (d, J = 8.2 Hz, 1 H, Ar), 4.05 (s, 3 H, OCH3), 1.76 (d, J = 9.0 Hz, 3H, CH3), 1.15 (d, J = 14.0 Hz, 9 H, C(CH3)3), 0.21 - 0.88 (m, 3 H, BH3). **13C NMR (101 MHz, CDCl3): δ 158.4 (d, JCP = 3.0 Hz, Ar), 136.4 (d, JCP = 11.1 Hz, Ar), 134.7 (d, JCP = 6.1 Hz, Ar), 127.9 (d, JCP = 5.1 Hz, Ar), 127.1 (s, Ar), 126.0 (d, JCP = 8.1 Hz, Ar), 125.6 (s, Ar), 122.4 (s, Ar), 115.7 (d, JCP = 49.5 Hz, Ar), 102.7 (d, JCP = 11.1 Hz, Ar), 55.7 (s, OMe), 30.7 (d, JCP = 32.3 Hz, C(CH3)3), 25.9 (d, JCP = 3.0 Hz, C(CH3)3), 9.0 (d, JCP = 39.4 Hz, CH3). **31P NMR (162 MHz, CDCl3): δ 22.4 (q, J = 68.0 Hz). HRMS (ESI): m/z: [M+H-BH3]+ calculated for C26H25OP: 261.1403, found 261.1403. HPLC (Daicel Chiralcel OD-H, n-hexane/i-PrOH = 98/2, UV = 250 nm, flow rate = 1 mL/min) tR = 7.585 min (minor) and tR = 12.549 min (major), ee = 46%. [α]D25 = +16.0 (c = 2.0, CHCl3).

S7
(R)-tert-butyl(9,9-dimethyl-9H-fluoren-2-yl)(methyl)phosphine Borane. Performed according to the general procedure to afford 76 mg (82%) of (R)-2q as white solid. 1H NMR (400 MHz, CDCl3): δ 7.72 – 7.81 (m, 3 H, Ar), 7.67 (t, J = 8.6 Hz, 1 H, Ar), 7.43 – 7.49 (m, 1 H, Ar), 7.34 – 7.38 (m, 2 H, Ar), 1.62 (t, J = 7.6 Hz, 3 H, CH3), 1.51 (d, J = 4.0 Hz, 6 H, Ar), 1.12 (d, J = 16.0 Hz, 9 H, C(CH3)3), 0.11 – 0.09 (m, 3 H, BH3). 13C NMR (101 MHz, CDCl3): δ 154.1 (s, Ar), 153.5 (d, Jc,p = 9.1 Hz, Ar), 142.2 (s, Ar), 138.0 (d, Jc,p = 10.0 Hz, Ar), 131.8 (s, Ar), 131.7 (d, Jc,p = 5.0 Hz, Ar), 128.4 (s, Ar), 127.2 (d, Jc,p = 8.1 Hz, Ar), 126.0 (s, Ar), 122.8 (s, Ar), 120.7 (s, Ar), 119.7 (d, Jc,p = 10.0 Hz, Ar), 47.0 (s, C(CH3)3), 28.6 (d, Jc,p = 34.4 Hz, C(CH3)3), 27.0 (s, C(CH3)3), 25.2 (d, Jc,p = 2.8 Hz, C(CH3)3), 5.5 (d, Jc,p = 38.4 Hz, CH3).

31P NMR (162 MHz, CDCl3): δ 25.3 (q, J = 72.9 Hz). HRMS (ESI): m/z: [M+H-BH3]+ calculated for C26H28P: 297.1767, found 297.1769. HPLC (Daicel Chiralcel IBN-H, n-hexane/i-ProOH = 99/1, UV = 254 nm, flow rate = 0.5 mL/min) tR1 = 11.612 min (minor) and tR2 = 12.325 min (major), ee = 74%. [α]D25 = +7.5 (c = 2.0, CHCl3).

(R)-tert-butyl(methyl)(phenanthren-9-yl)phosphine Borane. Performed according to the general procedure to afford 79 mg (85%) of (R)-2r as white solid. 1H NMR (400 MHz, CDCl3): δ 8.96 (d, J = 8.1 Hz, 1 H, Ar), 8.68 – 8.74 (m, 2 H, Ar), 8.08 (d, J = 12.4 Hz, 1 H, Ar), 7.94 (d, J = 7.7 Hz, 1 H, Ar), 7.61 – 7.80 (m, 4 H, Ar), 1.87 (d, J = 9.0 Hz, 3 H, CH3), 1.21 (d, J = 14.1 Hz, 9 H, C(CH3)3), 0.11 - 0.94 (m, 3 H, BH3). 13C NMR (101 MHz, CDCl3): δ 136.2 (d, Jc,p = 4.0 Hz, Ar), 132.7 (d, Jc,p = 7.1 Hz, Ar), 131.7 (d, Jc,p = 2.0 Hz, Ar), 130.6 (d, Jc,p = 7.1 Hz, Ar), 130.0 (d, Jc,p = 10.0 Hz, Ar), 129.5 (s, Ar), 129.4 (d, Jc,p = 17.2 Hz, Ar), 128.8 (s, Ar), 127.1 (d, Jc,p = 6.1 Hz, Ar), 126.6 (s, Ar), 124.3 (d, Jc,p = 47.5 Hz, Ar), 122.8 (d, Jc,p = 38.4 Hz, Ar), 30.7 (d, Jc,p = 30.3 Hz, C(CH3)3), 26.1 (d, Jc,p = 2.8 Hz, C(CH3)3), 9.2 (d, Jc,p = 40.4 Hz, CH3). 31P NMR (162 MHz, CDCl3): δ 24.6 (q, J = 58.3 Hz). HRMS (ESI): m/z: [M+H-BH3]+ calculated for C26H28P: 281.1454, found 281.1455. HPLC (Daicel Chiralcel AS-H, n-hexane/i-ProOH = 90/10, UV = 254 nm, flow rate = 1.0 mL/min) tR1 = 13.414 min (minor) and tR2 = 28.472 min (major), ee =91%. [α]D25 = +13.5 (c = 2.0, CHCl3).

(R)-3-(borane tert-butyl(methyl)phosphino)-N,N-dimethylaniline. Performed according to the general procedure to afford 37 mg (52%) of (R)-3a as yellow solid. 1H NMR (400 MHz, CDCl3): δ 7.26 – 7.39 (m, 1 H, Ar), 7.09 (d, J = 12.0 Hz, 1 H, Ar), 6.92 – 6.96 (m, 1 H, Ar), 6.82 (d, J = 8.0 Hz, 1 H, Ar), 2.98 (s, 6 H, N(CH3)2), 1.54 (d, J = 12.0 Hz, 3 H, CH3), 1.12 (d, J = 24.0 Hz, 9 H, C(CH3)3), 0.18 – 0.74 (m, 3 H, BH3). 13C NMR (101 MHz, CDCl3): δ 150.1 (d, Jc,p = 11.8 Hz, Ar), 128.8 (d, Jc,p = 10.3 Hz, Ar), 127.3 (d, Jc,p = 51.5 Hz, Ar), 120.1 (d, Jc,p = 6.0 Hz, Ar), 117.2 (d, Jc,p = 12.8 Hz, Ar), 114.8 (d, Jc,p = 2.3 Hz, Ar), 40.4 (s, N(CH3)2), 28.5 (d, Jc,p = 30.3 Hz, C(CH3)3), 25.4 (d, Jc,p = 2.7 Hz, C(CH3)3), 5.4 (d, Jc,p = 38.4 Hz, CH3). 31P NMR (162 MHz, CDCl3): δ 25.6 (q, J = 64.8 Hz). HRMS (ESI): m/z: [M+H-BH3]+ calculated for C13H20NP: 224.1563, found 224.1562. HPLC (Daicel Chiralcel OD-H, n-hexane/i-ProOH = 98/2,
UV = 250 nm, flow rate = 0.8 mL/min \( t_{91} = 8.667 \text{ min (minor)} \) and \( t_{92} = 10.155 \text{ min (major)} \), ee = 80%. \( [\alpha]_{D25}^{25} = +24.0 \) (c = 2.0, CHCl₃).

(R)-4-(4-(borane tert-butyl(methyl)phosphino)phenyl)morpholine. Performed according to the general procedure to afford 44 mg (53%) of (R)-3b as white solid. \(^1\)H NMR (400 MHz, CDCl₃): \( \delta \) 7.55 – 7.60 (m, 2 H, Ar), 6.91 – 6.94 (m, 2 H, Ar), 3.84 – 3.87 (m, 4 H, \( \text{CH}_2 \)), 2.52 – 2.55 (m, 4 H, CH₂). \(^13\)C NMR (101 MHz, CDCl₃): \( \delta \) 15.3 (s, Ar), 120.5 (d, \( J = 13.9 \text{ Hz} \), 3 H, CH); 1.09 (d, \( J = 10.0 \text{ Hz} \), 3 H, Ar), 116.0 (d, \( J_c = 9.1 \text{ Hz} \), Ar), 114.1 (d, \( J_c = 10.1 \text{ Hz} \), Ar), 66.6 (s, CH₂), 47.8 (s, CH₂), 28.7 (d, \( J_c = 34.3 \text{ Hz} \), C(CH₃)), 25.1 (d, \( J_c = 3.0 \text{ Hz} \), C(CH₂)), 5.3 (d, \( J_c = 38.4 \text{ Hz} \), CH₂). HRMS (ESI): \( m/z \): [M+H-BH₃]⁺ calculated for \( C_{13}H_{23}NOP: 266.1406 \), found 266.1407. HPLC (Daicel Chiralcel OD-H, n-hexane/i-PrOH = 90/10, UV = 250 nm, flow rate = 1.0 mL/min) \( t_{81} = 11.953 \text{ min (major)} \) and \( t_{82} = 16.618 \text{ min (minor)} \), ee = 46%. \( [\alpha]_{D25}^{25} = +24.0 \) (c = 2.0, CHCl₃).

(R)-1-(4-(borane tert-butyl(methyl)phosphino)phenyl)-1H-pyrrole. Performed according to the general procedure to afford 57 mg (74%) of (R)-3c as white solid. \(^1\)H NMR (400 MHz, CDCl₃): \( \delta \) 7.74 – 7.79 (m, 2 H, Ar), 7.46 – 7.49 (m, 2 H, Ar), 7.13 – 7.15 (m, 2 H, Ar), 6.38 – 6.39 (m, 2 H, Ar), 1.59 (d, \( J = 3.0 \text{ Hz} \), 3 H, CH₃), 1.13 (d, \( J = 4.0 \text{ Hz} \), 9 H, C(CH₃)₃), 0.11 – 1.07 (m, 3 H, Me). \(^13\)C NMR (101 MHz, CDCl₃): \( \delta \) 142.7 (d, \( J_c = 3.0 \text{ Hz} \), Ar), 134.4 (d, \( J_c = 9.9 \text{ Hz} \), Ar), 124.2 (d, \( J_c = 51.2 \text{ Hz} \), Ar), 119.5 (d, \( J_c = 10.0 \text{ Hz} \), Ar), 119.0 (s, Ar), 111.4 (s, Ar), 28.7 (d, \( J_c = 33.3 \text{ Hz} \), C(CH₃)), 25.1 (d, \( J_c = 3.0 \text{ Hz} \), C(CH₂)), 5.3 (d, \( J_c = 37.4 \text{ Hz} \), CH₂). HRMS (ESI): \( m/z \): [M+H-BH₃]⁺ calculated for \( C_{15}H_{27}NOP: 246.1406 \), found 246.1407. HPLC (Daicel Chiralcel OD-H, n-hexane/i-PrOH = 98/2, UV = 254 nm, flow rate = 0.8 mL/min) \( t_{81} = 13.659 \text{ min (minor)} \) and \( t_{82} = 15.300 \text{ min (major)} \), ee = 94%. \( [\alpha]_{D25}^{25} = +0.5 \) (c = 2.0, CHCl₃).

(R)-9-(4-(borane tert-butyl(methyl)phosphino)phenyl)-9H-carbazole. Performed according to the general procedure to afford 67.8 mg (63%) of (R)-3d as white solid. \(^1\)H NMR (400 MHz, CDCl₃): \( \delta \) 8.15 (d, \( J = 8.0 \text{ Hz} \), 2 H, Ar), 7.93 – 7.98 (m, 2 H, Ar), 7.70 – 7.72 (m, 2 H, Ar), 7.41 – 7.49 (m, 4 H, Ar), 7.30 – 7.34 (m, 2 H, Ar), 1.67 (d, \( J = 8.0 \text{ Hz} \), 3 H, CH₃), 1.21 (d, \( J = 16.0 \text{ Hz} \), 9 H, C(CH₃)₃), 0.26 – 0.93 (m, 3 H, BH₂). \(^13\)C NMR (101 MHz, CDCl₃): \( \delta \) 140.5 (d, \( J_c = 2.0 \text{ Hz} \), Ar), 140.2 (s, Ar), 134.5 (d, \( J_c = 9.1 \text{ Hz} \), Ar), 126.7 (s, Ar), 126.3 (d, \( J_c = 10.0 \text{ Hz} \), Ar), 126.1 (s, Ar), 123.7 (s, Ar), 120.5 (d, \( J_c = 6.1 \text{ Hz} \), Ar), 109.7 (s, Ar), 28.7 (d, \( J_c = 33.3 \text{ Hz} \), C(CH₂)), 25.2 (d, \( J_c = 3.0 \text{ Hz} \), C(CH₃)).
\[ 5.4 \text{ (d, } J_{C-P} = 37.4 \text{ Hz, CH}_3) \] 31P NMR (162 MHz, CDCl\(_3\)): \( \delta 25.6 \text{ (q, } J = 53.5 \text{ Hz). HRMS (ESI)}: m/z: [M+H-BH_3]^+ \text{ calculated for } \text{C}_3\text{H}_3\text{NP: 346.1719, found 346.1721. HPLC (Daicel Chiralcel AS-H, } n\text{-hexane}/\text{-i-PrOH = 98/2, UV = 254 nm, flow rate = 0.5 mL/min) } t_{R1} = 18.239 \text{ min (major) and } t_{R2} = 20.275 \text{ min (minor), ee = 69%. } [\alpha]_D^{25} = +4.5 \text{ (c = 2.0, CHCl}_3) \].

\[ \text{(R)-4-(borane tert-butyl(methyl)phosphino)-N,N-diphenylaniline. Performed according to the general procedure to afford 58 mg (47%) of (R)-3e as white solid. } ^1\text{H NMR (400 MHz, CDCl}_3\text{): } \delta 7.46 - 7.51 \text{ (m, 2 H, Ar), 7.28 - 7.32 (m, 4 H, Ar), 7.09 - 7.14 (m, 6 H, Ar), 7.02 - 7.04 (m, 2 H, Ar), 1.52 \text{ (d, } J = 8.0 \text{ Hz, 3 H, CH}_3)\text{, 1.11 (d, } J = 12.0 \text{ Hz, 9 H, C(CH}_3)_2\text{), 0.26 - 0.86 (m, 3 H, BH}_3\text{). 13C NMR (101 MHz, CDCl}_3\text{): } \delta 150.3 \text{ (d, } J_{C-P} = 2.0 \text{ Hz, Ar), 146.7 \text{ (s, Ar), 133.8 (d, } J_{C-P} = 9.1 \text{ Hz, Ar), 125.6 (s, Ar), 124.2 (s, Ar), 120.4 \text{ (d, } J_{C-P} = 10.0 \text{ Hz, Ar), 118.4 (s, Ar), 117.8 (s, Ar), 28.7 (d, } J_{C-P} = 33.3 \text{ Hz, C(CH}_3)_2\text{), 25.2 (d, } J_{C-P} = 3.0 \text{ Hz, C(CH}_3)_2\text{), } 5.4 \text{ (d, } J_{C-P} = 38.4 \text{ Hz, CH}_3)\text{. 31P NMR (162 MHz, CDCl}_3\text{): } \delta 25.4 \text{ (q, } J = 61.6 \text{ Hz). HRMS (ESI)}: m/z: [M+H-BH}_3\text{]^+ calculated for } \text{C}_3\text{H}_3\text{NP: 348.1876, found 348.1877. HPLC (Daicel Chiralcel OD-H, } n\text{-hexane}/\text{-i-PrOH = 98/2, UV = 250 nm, flow rate = 1.0 mL/min) } t_{R1} = 5.476 \text{ min (minor) and } t_{R2} = 5.912 \text{ min (major), ee = 84%. } [\alpha]_D^{25} = +8.0 \text{ (c = 2.0, CHCl}_3) \].

\[ \text{(R)-4-(borane tert-butyl(methyl)phosphino)-N,N-bis(4-iodophenylaniline. Performed according to the general procedure to afford 93.7 mg (51%) of (R)-3f as white solid. } ^1\text{H NMR (400 MHz, CDCl}_3\text{): } \delta 7.46 - 7.51 \text{ (m, 2 H, Ar), 7.28 - 7.32 (m, 4 H, Ar), 7.13 \text{ (d, } J = 8.0 \text{ Hz, 4 H, Ar), 7.02 - 7.04 (m, 2 H, Ar), 1.52 \text{ (d, } J = 8.0 \text{ Hz, 3 H, CH}_3)\text{, 1.12 (d, } J = 12.0 \text{ Hz, 9 H, C(CH}_3)_2\text{), 0.26 - 0.86 (m, 3 H, BH}_3\text{). 13C NMR (101 MHz, CDCl}_3\text{): } \delta 149.2 \text{ (d, } J_{C-P} = 3.0 \text{ Hz, Ar), 146.1 \text{ (s, Ar), 138.6 (s, Ar), 134.0 \text{ (d, } J_{C-P} = 9.1 \text{ Hz, Ar), 127.7 \text{ (d, } J_{C-P} = 39.9 \text{ Hz, Ar), 121.6 \text{ (d, } J_{C-P} = 10.1 \text{ Hz, Ar), 120.5 (s, Ar), 87.6 (s, Ar), 28.6 (d, } J_{C-P} = 33.3 \text{ Hz, C(CH}_3)_2\text{), 25.2 (d, } J_{C-P} = 2.0 \text{ Hz, C(CH}_3)_2\text{), 5.3 (d, } J_{C-P} = 38.4 \text{ Hz, CH}_3)\text{. 31P NMR (162 MHz, CDCl}_3\text{): } \delta 23.7 \text{ (q, } J = 38.9 \text{ Hz). HRMS (ESI)}: m/z: [M+H-BH}_3\text{]^+ calculated for } \text{C}_3\text{H}_3\text{iNP: 599.9808, found 599.9811. HPLC (Daicel Chiralcel OD-H, } n\text{-hexane}/\text{-i-PrOH = 90/10, UV = 254 nm, flow rate = 1.0 mL/min) } t_{R1} = 9.428 \text{ min (major) and } t_{R2} = 11.065 \text{ min (minor), ee = 94%. } [\alpha]_D^{25} = +1.5 \text{ (c = 2.0, CHCl}_3) \].

\[ \text{(R)-2-(borane tert-butyl(methyl)phosphino)-6-fluoropyridine. Performed according to the general procedure to afford 59 mg (62%) of (R)-3g as white solid. } ^1\text{H NMR (400 MHz, CDCl}_3\text{): } \delta 7.88 - 7.92 \text{ (m, 1 H, Ar), 7.69 - 7.73 (m, 1 H, Ar), 7.37 \text{ (d, } J = 8.0 \text{ Hz, 1 H, Ar), 1.60 (d, } J = 8.0 \text{ Hz, 3 H, CH}_3)\text{, 1.11 (d, } J = 16.0 \text{ Hz, 9 H, C(CH}_3)_2\text{), 0.26 - 0.98 (m, 3 H, BH}_3\text{). 13C NMR (101 MHz, CDCl}_3\text{): } \delta 154.5 \text{ (d, } J_{C-P} = 61.6 \text{ Hz, Ar), 151.5 \text{ (d, } J_{C-P} = 11.1 \text{ Hz, Ar), 138.4 (d, } J_{C-P} = 10.0 \text{ Hz, Ar), 129.1 \text{ (d, } J_{C-P} = 23.2 \text{ Hz, Ar), 125.7 (d, } J_{C-P} = 2.0 \text{ Hz, Ar), 28.8 (d, } J_{C-P} = 32.3 \text{ Hz, C(CH}_3)_2\text{), 25.2 (d, } J_{C-P} = 3.0 \text{ Hz, C(CH}_3)_2\text{), 4.5 (d, } J_{C-P} = 39.4 \text{ Hz, CH}_3)\text{. 31P NMR (162 MHz, CDCl}_3\text{): } \delta 30.3 \text{ (q, } J = 61.6 \text{ Hz). 19F NMR (376 MHz, CDCl}_3\text{): } \delta -68.4 \text{ (s). HRMS (ESI)}: m/z: [M+H-BH}_3\text{]^+ calculated for } \text{C}_3\text{H}_3\text{iFNP: 200.0999, found 200.1001. HPLC (Daicel Chiralcel OD-H, } n\text{-hexane/i-PrOH = 90/10, UV = 254 nm, flow rate = 1.0 mL/min) } t_{R1} = 9.500 \text{ min (major) and } t_{R2} = 10.482 \text{ min (minor), ee = 94%. } [\alpha]_D^{25} = +2.0 \text{ (c = 2.0, CHCl}_3) \].}
Chiralcel AS-H, n-hexane/i-ProOH = 98/2, UV = 250 nm, flow rate = 1.0 mL/min) \( t_{R1} = 11.503 \) min (minor) and \( t_{R2} = 12.124 \) min (major), ee = 97\%. \([\alpha]_{D}^{25} = +12.0 (c = 2.0, CHCl_3)\).

**\((R)\)-methyl 6-(borane-(R)-methyl)phosphino)picolinate.** Performed according to the general procedure to afford 35.7 mg (47\%) of \((R)\)-3h as white solid. \(^1\)H NMR (400 MHz, CDCl_3): \( \delta \) 8.11 – 8.15 (m, 2 H, Ar), 7.86 – 7.91 (m, 1 H, Ar), 3.97 (s, 3 H, Ar), 7.57 – 7.64 (m, 1 H, Ar), 7.42 – 7.45 (m, 1 H, Ar), 2.10 (d, \( J = 8.0 \) Hz, \( 3 \) H, \( CD_2 \)). \(^1^3\)C NMR (101 MHz, CDCl_3): \( \delta \) 165.2 (s, CO), 154.3 (d, \( J_{C-P} = 64.6 \) Hz, Ar), 148.1 (d, \( J_{C-P} = 11.1 \) Hz, Ar), 136.7 (d, \( J_{C-P} = 8.1 \) Hz, Ar), 132.9 (d, \( J_{C-P} = 25.3 \) Hz, Ar), 125.8 (d, \( J_{C-P} = 2.0 \) Hz, Ar), 52.8 (s, CH_3), 28.8 (d, \( J_{C-P} = 32.3 \) Hz, C(CH_3)_2), 25.3 (d, \( J_{C-P} = 2.5 \) Hz, C(CH_3)_3), 4.6 (d, \( J_{C-P} = 39.4 \) Hz, CH_2). \(^{31}\)P NMR (162 MHz, CDCl_3): \( \delta \) 30.3 (q, \( J = 66.4 \) Hz). HRMS (ESI): m/z: [M+H-BH_3]^+ calculated for C_{16}H_{21}NO_4P: 240.1148, found 240.1150. HPLC (Daicel Chiralcel AS-H, n-hexane/i-ProOH = 95/5, UV = 230 nm, flow rate = 1.0 mL/min) \( t_{R1} = 8.140 \) min (minor) and \( t_{R2} = 9.308 \) min (major), ee = 73\%. \([\alpha]_{D}^{25} = +42.0 (c = 2.0, CHCl_3)\).

\(\text{(R)-2-(borane tert-buty1(methyl)phosphino)quinoline.} \) Performed according to the general procedure to afford 68 mg (56\%) of \((R)\)-3i as white solid. \(^1\)H NMR (400 MHz, CDCl_3): \( \delta \) 8.20 – 8.22 (m, 1 H, Ar), 8.15 (d, \( J = 8.0 \) Hz, 1 H, Ar), 8.02 – 8.05 (m, 1 H, Ar), 7.87 (d, \( J = 8.0 \) Hz, 1 H, Ar), 7.75 – 7.79 (m, 1 H, Ar), 7.60 – 7.64 (m, 1 H, Ar), 1.76 (d, \( J = 8.0 \) Hz, \( 3 \) H, \( CH_2 \)), 1.18 (d, \( J = 16.0 \) Hz, 9 H, C(CH_3)_2), 0.25 – 1.11 (m, 3 H, BH_3). \(^{1^3}\)C NMR (101 MHz, CDCl_3): \( \delta \) 154.7 (s, Ar), 154.1 (s, Ar), 148.0 (d, \( J_{C-P} = 13.1 \) Hz, Ar), 135.1 (d, \( J_{C-P} = 10.0 \) Hz, Ar), 130.1 (s, Ar), 129.9 (s, Ar), 127.8 (s, Ar), 125.6 (d, \( J_{C-P} = 26.3 \) Hz, Ar), 29.1 (d, \( J_{C-P} = 32.3 \) Hz, C(CH_3)_2), 25.4 (d, \( J_{C-P} = 3.0 \) Hz, C(CH_3)_3), 4.6 (d, \( J_{C-P} = 40.4 \) Hz, CH_3). \(^{31}\)P NMR (162 MHz, CDCl_3): \( \delta \) 30.1 (q, \( J = 63.2 \) Hz). HRMS (ESI): m/z: [M+H-BH_3]^+ calculated for C_{16}H_{19}NP: 232.1250, found 232.1250. HPLC (Daicel Chiralcel AS-H, n-hexane/i-ProOH = 98/2, UV = 250 nm, flow rate = 0.8 mL/min) \( t_{R1} = 6.452 \) min (minor) and \( t_{R2} = 6.937 \) min (major), ee = 81\%. \([\alpha]_{D}^{25} = +49.5 (c = 2.0, CHCl_3)\).

\(\text{(R)-8-(borane tert-buty1(methyl)phosphino)quinoline.} \) Performed according to the general procedure to afford 20.7 mg (20\%) of \((R)\)-3j as white solid. \(^1\)H NMR (400 MHz, CDCl_3): \( \delta \) 8.91 – 8.93 (m, 1 H, Ar), 8.50 – 8.55 (m, 1 H, Ar), 8.19 (d, \( J = 8.0 \) Hz, 1 H, Ar), 7.96 (d, \( J = 8.0 \) Hz, 1 H, Ar), 7.57 – 7.64 (m, 1 H, Ar), 7.42 – 7.45 (m, 1 H, Ar), 2.10 (d, \( J = 8.0 \) Hz, 3 H, \( CH_2 \)), 2.38 (d, \( J = 12.0 \) Hz, 9 H, C(CH_3)_2), 0.26 – 0.90 (m, 3 H, BH_3). \(^{1^3}\)C NMR (101 MHz, CDCl_3): \( \delta \) 149.6 (d, \( J_{C-P} = 2.0 \) Hz, Ar), 149.4 (s, Ar), 140.2 (d, \( J_{C-P} = 16.2 \) Hz, Ar), 136.6 (s, Ar), 132.0 (d, \( J_{C-P} = 2.5 \) Hz, Ar), 128.4 (d, \( J_{C-P} = 5.1 \) Hz, Ar), 126.0 (s, Ar), 125.9 (s, Ar), 125.9 (s, Ar), 30.3 (d, \( J_{C-P} = 34.3 \) Hz, C(CH_3)_2), 26.6 (d, \( J_{C-P} = 3.0 \) Hz, C(CH_3)_2), 8.6 (d, \( J_{C-P} = 39.4 \) Hz, CH_3). \(^{31}\)P NMR (162 MHz, CDCl_3): \( \delta \) 31.0 (q, \( J = 58.3 \) Hz). HRMS (ESI): m/z: [M+H-BH_3]^+ calculated for C_{16}H_{22}NP: 232.1250, found 232.1250. HPLC (Daicel Chiralcel OD-H, n-hexane/i-ProOH = 98/2, UV = 250 nm, flow rate = 1.0 mL/min) \( t_{R1} = 6.324 \) min (minor) and \( t_{R2} = 7.473 \) min (major), ee = 71\%. \([\alpha]_{D}^{25} = +42.0 (c = 2.0, CHCl_3)\).
(R)-2-(borane tert-butyl(methyl)phosphino)-5-methoxy pyrazine. Performed according to the general procedure to afford 40.0 mg (59%) of (R)-3k as white solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.66 (s, 1 H, Ar), 8.31 (s, 1 H, Ar), 4.01 (s, 3 H, OCH$_3$), 1.58 (d, $J$ = 8.0 Hz, 3 H, CH$_3$), 1.14 (d, $J$ = 12.0 Hz, 9 H, C(CH$_3$)$_3$), 0.20 – 0.98 (m, 3 H, BH$_3$). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 161.0 (d, $J_{CP}$ = 20.0 Hz, Ar), 147.5 (d, $J_{CP}$ = 28.3 Hz, Ar), 138.7 (d, $J_{CP}$ = 66.7 Hz, Ar), 136.2 (d, $J_{CP}$ = 10.0 Hz, Ar), 55.0 (s, OMe), 28.9 (d, $J_{CP}$ = 33.3 Hz, C(CH$_3$)$_3$), 25.3 (d, $J_{CP}$ = 3.0 Hz, C(CH$_3$)$_3$), 4.7 (d, $J_{CP}$ = 39.4 Hz, CH$_3$). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 24.4 (q, $J$ = 59.9 Hz). HRMS (ESI): m/z: [M+H-BH$_3$]$^+$ calculated for C$_{15}$H$_{18}$N$_2$PO: 213.1151, found 213.1152. HPLC (Daicel Chiralcel OD-H, n-hexane/i-PrOH = 98/2, UV = 254 nm, flow rate = 0.8 mL/min) $t_{R1}$ = 5.752 min (major) and $t_{R2}$ = 6.206 min (minor), ee = 77%. $[\alpha]_{D}^{25}$ = +9.5 ($c$ = 2.0, CHCl$_3$).

(R)-2-(borane tert-butyl(methyl)phosphino)-3-chloroquinoline. Performed according to the general procedure to afford 64 mg (76%) of (R)-3l as yellow solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.15 – 8.17 (m, 1 H, Ar), 8.05 – 8.08 (m, 1 H, Ar), 7.83 – 7.92 (m, 2 H, Ar), 1.81 (d, $J$ = 8.0 Hz, 3 H, CH$_3$), 1.28 (d, $J$ = 12.0 Hz, 9 H, C(CH$_3$)$_3$), 0.18 – 1.14 (m, 3 H, BH$_3$). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 150.3 (d, $J_{CP}$ = 22.6 Hz, Ar), 149.9 (d, $J_{CP}$ = 9.3 Hz, Ar), 141.4 (s, Ar), 140.3 (s, Ar), 132.9 (s, Ar), 130.8 (s, Ar), 129.6 (s, Ar), 128.3 (s, Ar), 31.5 (d, $J_{CP}$ = 29.3 Hz, C(CH$_3$)$_3$), 26.0 (d, $J_{CP}$ = 2.0 Hz, C(CH$_3$)$_3$), 7.7 (d, $J_{CP}$ = 41.4 Hz, CH$_3$). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 37.9 (q, $J$ = 53.5 Hz). HRMS (ESI): m/z: [M+H-BH$_3$]$^+$ calculated for C$_{15}$H$_{18}$ClN$_2$P: 267.0812, found 267.0813. HPLC (Daicel Chiralcel OD-H, n-hexane/i-PrOH = 98/2, UV = 250 nm, n-hexane/i-PrOH = 98/2, UV = 250 nm, flow rate = 0.8 mL/min) $t_{R1}$ = 11.847 min (minor) and $t_{R2}$ = 13.672 min (major), ee = 94%. $[\alpha]_{D}^{25}$ = +2.5 ($c$ = 2.0, CHCl$_3$).

3. Procedures of palladium-catalyzed C–P coupling reactions under microwave conditions

To a reaction tube, (R)-tert-butyl(methyl)phosphine borane (35 mg, 0.3 mmol), aryl and heteroaryl halides (0.5 mmol), Pd(OAc)$_2$ (3.37 mg, 0.015 mmol), dpf (27.75 mg, 0.03 mmol), tBuONa (57.66 mg, 0.60 mmol) and toluene (3 mL) were added under argon. The mixture was stirred for 6 h under microwave conditions. After removal of the volatile materials under reduced pressure, the crude product was purified by chromatograph on silica gel. (n-hexane / dichloromethane).

(S)-tert-butyl(methyl)(naphthalen-1-yl)phosphine Borane.2 Performed according to the microwave reactions procedure to afford 47.2 mg (64%) of (S)-2a as white solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.90 (d, $J$ = 8.0 Hz, 1 H, Ar), 7.99 (d, $J$ = 8.0 Hz, 1 H, Ar), 7.87 (d, $J$ = 8.0 Hz, 1 H, Ar), 7.75 – 7.80 (m, 1 H, Ar), 7.61 – 7.75 (m, 1 H, Ar), 7.49 - 7.53 (m, 2 H, Ar), 1.78 (d, $J$ = 12.0 Hz, 3 H, CH$_3$), 1.16 (d, $J$ = 16.0 Hz, 9 H, C(CH$_3$)$_3$), 0.79 - 1.57 (m, 3 H, BH$_3$). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 23.9 (q, $J$ = 66.4 Hz). HPLC (Daicel Chiralcel AS-H, n-hexane/i-PrOH = 95/5, UV = 250 nm, flow rate = 1.0 mL/min) $t_{R1}$ = 5.430 min (major), ee = 99%. $[\alpha]_{D}^{25}$ = -23.0 ($c$ = 2.0, CHCl$_3$).
(5)-tert-butyl(methyl)(phenyl)phosphine Borane. Performed according to the microwave reactions procedure to afford 50.6 mg (87%) of (5)-2b as white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.69 – 7.73 (m, 2 H, Ar), 7.43 – 7.52 (m, 3 H, Ar), 1.58 (d, J = 12.0 Hz, 3 H, CH₃), 1.11 (d, J = 12.0 Hz, 9 H, C(CH₃)₃), 0.24 – 1.07 (m, 3 H, BH₃). ³¹P NMR (162 MHz, CDCl₃): δ 25.0 (q, J = 63.2 Hz). HPLC (Daicel Chiralcel AS-H, n-hexane/i-PrOH = 95/5, UV = 230 nm, flow rate = 1.0 mL/min) tᵣ₁ = 7.908 min (major) and tᵣ₂ = 8.829 min (minor), ee = 99%. [α]ᵣ25 = -14.5 (c = 2.0, CHCl₃).

(5)-tert-butyl(methyl)(o-tolyl)phosphine Borane. Performed according to the microwave reactions procedure to afford 40.7 mg (65%) of (5)-2d as white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.52 – 7.56 (m, 1 H, Ar), 7.35 – 7.39 (m, 1 H, Ar), 7.23 – 7.26 (m, 2 H, Ar), 2.66 (s, 3 H, CH₃), 1.64 (d, J = 8.0 Hz, 3 H, CH₃), 1.14 (d, J = 16.0 Hz, 9 H, C(CH₃)₃), 0.19 – 1.10 (m, 3 H, BH₃). ³¹P NMR (162 MHz, CDCl₃): δ 25.1 (q, J = 59.9 Hz). HPLC (Daicel Chiralcel OD-H, n-hexane/i-PrOH = 98/2, UV = 230 nm, flow rate = 0.5 mL/min) tᵣ₁ = 13.211 min (major) and tᵣ₂ = 14.302 min (minor), ee = 92%. [α]ᵣ25 = -12.5 (c = 2.0, CHCl₃).

(5)-tert-butyl(4-(tert-butyl)phenyl)(methyl)phosphine Borane. Performed according to the microwave reactions procedure to afford 35.3 mg (50%) of (5)-2e as white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.61 – 7.65 (m, 2 H, Ar), 7.45 – 7.47 (m, 2 H, Ar), 1.55 (d, J = 8.0 Hz, 3 H, CH₃), 1.33 (d, J = 12.0 Hz, 9 H, C(CH₃)₃), 0.18 – 1.05 (m, 3 H, BH₃). ³¹P NMR (162 MHz, CDCl₃): δ 23.7 (q, J = 66.4 Hz). HPLC (Daicel Chiralcel AS-H, n-hexane/i-PrOH = 99/1, UV = 254 nm, flow rate = 1.0 mL/min) tᵣ₁ = 4.992 min (minor) and tᵣ₂ = 5.519 min (major), ee = 88%. [α]ᵣ25 = -7.3 (c = 2.0, CHCl₃).

(5)-tert-butyl(4-methoxyphenyl)(methyl)phosphine Borane. Performed according to the microwave reactions procedure to afford 53.7 mg (80%) of (5)-2f as white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.61 – 7.65 (m, 2 H, Ar), 6.96 – 6.98 (m, 2 H, Ar), 3.85 (s, 3 H, OCH₃), 1.54 (d, J = 8.0 Hz, 3 H, CH₃), 1.09 (d, J = 16.0 Hz, 9 H, C(CH₃)₃), 0.35 – 0.91 (m, 3 H, BH₃). ³¹P NMR (162 MHz, CDCl₃): δ 23.2 (q, J = 69.7 Hz). HPLC (Daicel Chiralcel AS-H, n-hexane/i-PrOH = 98/2, UV = 250 nm, flow rate = 0.8 mL/min) tᵣ₁ = 21.932 min (major) and tᵣ₂ = 24.014 min (minor), ee = 95%. [α]ᵣ25 = -8.3 (c = 2.0, CHCl₃).

(5)-[1,1′-biphenyl]-4-yl(tert-butyl)(methyl)phosphine Borane. Performed according to the microwave reactions procedure to afford 57.4 mg (70%) of (5)-2h as white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.75 – 7.81 (m, 2 H, Ar), 7.66 – 7.68 (m, 2 H, Ar), 7.61 (d, J = 4.0 Hz, 2 H, Ar), 7.45 – 7.49 (m, 2 H, Ar), 7.37 – 7.41 (m, 1 H, Ar), 1.61 (d, J = 12.0 Hz, 3 H, CH₃), 1.14 (d, J = 12.0 Hz, 9 H, C(CH₃)₃), 0.24 – 0.95 (m, 3 H, BH₃). ³¹P NMR (162 MHz, CDCl₃): δ 24.7 (q, J = 77.8 Hz). HPLC (Daicel Chiralcel OD-H, n-hexane/i-PrOH = 95/5, UV = 250 nm, flow rate = 0.8 mL/min) tᵣ₁ = 7.872 min (minor) and tᵣ₂ = 8.778 min (major), ee = 93%. [α]ᵣ25 = -12.0 (c = 2.0, CHCl₃).
(S)-tert-butyl(4-chlorophenyl)(methyl)phosphine Borane. Performed according to the microwave reactions procedure to afford 46.6 mg (68%) of (S)-2j as white solid. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.60 – 7.69 (m, 2 H, Ar), 7.37 – 7.51 (m, 2 H, Ar), 1.57 (d, $J = 12.0$ Hz, 3 H, CH$_3$), 1.10 (d, $J = 16.0$ Hz, 9 H, C(CH$_3$)$_3$), 0.22 – 0.85 (m, 3 H, BH$_3$). $^{31}$P NMR (162 MHz, CDCl$_3$): δ 25.4 (q, $J = 63.2$ Hz). HPLC (Daicel Chiralcel AS-H, n-hexane/i-PrOH = 99/1, UV = 234 nm, flow rate = 1.0 mL/min) $t_{R1} = 9.679$ min (major) and $t_{R2} = 12.252$ min (minor), ee = 95%. $[^{[a]}D_{25}]^{25} = -12.3$ (c = 2.0, CHCl$_3$).

(S)-tert-butyl(methyl)(4-(trifluoromethyl)phenyl)phosphine Borane. Performed according to the microwave reactions procedure to afford 31.4 mg (40%) of (S)-2k as white solid. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.83 – 7.88 (m, 2 H, Ar), 7.72 (d, $J = 8.0$ Hz, 2 H, Ar), 1.61 (d, $J = 12.0$ Hz, 3 H, CH$_3$), 1.13 (d, $J = 12.0$ Hz, 9 H, C(CH$_3$)$_3$), 0.25 – 0.85 (m, 3 H, BH$_3$). $^{31}$P NMR (162 MHz, CDCl$_3$): δ 26.9 (q, $J = 59.9$ Hz). HPLC (Daicel Chiralcel AS-H, n-hexane/i-PrOH = 99/1, UV = 254 nm, flow rate = 1.0 mL/min) $t_{R1} = 6.399$ min (major) and $t_{R2} = 6.745$ min (minor), ee = 94%. $[^{[a]}D_{25}]^{25} = -33.0$ (c = 2.0, CHCl$_3$).

(S)-ethyl 4-(borane tert-butyl(methyl)phosphino)benzoate. Performed according to the microwave reactions procedure to afford 50.3 mg (63%) of (S)-2n as white solid. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.10 – 8.12 (m, 2 H, Ar), 7.77 – 7.81 (m, 2 H, Ar), 4.41 (q, $J = 7.1$ Hz, 2 H, CH$_2$CH$_3$), 1.61 (d, $J = 12.0$ Hz, 3 H, CH$_3$), 1.39 – 1.43 (m, 3 H, CH$_3$), 1.11 (d, $J = 16.0$ Hz, 9 H, C(C$_2$H$_5$)$_3$), 0.21 – 0.87 (m, 3 H, BH$_3$). $^{31}$P NMR (162 MHz, CDCl$_3$): δ 26.4 (q, $J = 74.5$ Hz). HPLC (Daicel Chiralcel OD-H, n-hexane/i-PrOH = 98/2, UV = 230 nm, flow rate = 0.8 mL/min) $t_{R1} = 14.957$ min (minor) and $t_{R2} = 16.501$ min (major), ee = 97%. $[^{[a]}D_{25}]^{25} = -28.0$ (c = 2.0, CHCl$_3$).

(S)-4-(4-(borane tert-butyl(methyl)phosphino)phenyl)morpholine. Performed according to the microwave reactions procedure to afford 65.8 mg (79%) of (S)-2b as white solid. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.56 – 7.60 (m, 2 H, Ar), 6.91 – 6.94 (m, 2 H, Ar), 3.83 – 3.90 (m, 4 H, CH$_2$), 3.21 – 3.29 (m, 4 H, CH$_2$), 1.52 (d, $J = 12.0$ Hz, 3 H, CH$_3$), 1.09 (d, $J = 16.0$ Hz, 9 H, C(CH$_3$)$_3$), 0.19 – 0.88 (m, 3 H, BH$_3$). $^{31}$P NMR (162 MHz, CDCl$_3$): δ 22.4 (q, $J = 77.8$ Hz). HPLC (Daicel Chiralcel OD-H, n-hexane/i-PrOH = 90/10, UV = 250 nm, flow rate = 1.0 mL/min) $t_{R1} = 11.772$ min (major) and $t_{R2} = 16.287$ min (minor), ee = 91%. $[^{[a]}D_{25}]^{25} = -12.0$ (c = 2.0, CHCl$_3$).

(S)-9-(4-(borane tert-butyl(methyl)phosphino)phenyl)-9H-carbazole. Performed according to the microwave reactions procedure to afford 52.1 mg (43%) of (S)-2d as white solid. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.15 (d, $J = 8.0$ Hz, 1 H, Ar), 7.61 – 7.66 (m, 2 H, Ar), 7.47 – 7.51 (m, 2 H, Ar), 7.31 – 7.35 (m, 2 H, Ar), 7.13 – 7.16 (m, 1 H, Ar), 6.61 – 6.63 (m, 2 H, Ar), 3.22 – 3.26 (m, 4 H, CH$_2$), 1.52 (d, $J = 12.0$ Hz, 3 H, CH$_3$), 1.09 (d, $J = 16.0$ Hz, 9 H, C(CH$_3$)$_3$), 0.19 – 0.88 (m, 3 H, BH$_3$). $^{31}$P NMR (162 MHz, CDCl$_3$): δ 22.4 (q, $J = 77.8$ Hz). HPLC (Daicel Chiralcel OD-H, n-hexane/i-PrOH = 90/10, UV = 250 nm, flow rate = 1.0 mL/min) $t_{R1} = 11.772$ min (major) and $t_{R2} = 16.287$ min (minor), ee = 91%. $[^{[a]}D_{25}]^{25} = -12.0$ (c = 2.0, CHCl$_3$).
Hz, 2 H, Ar), 7.91 – 7.99 (m, 2 H, Ar), 7.67 – 7.74 (m, 2 H, Ar), 7.41 – 7.49 (m, 4 H, Ar), 7.29 – 7.35 (m, 2 H, Ar),
1.67 (d, J = 8.0 Hz, 3 H, CH), 1.21 (d, J = 16.0 Hz, 9 H, C(CH)3), 0.26 – 0.93 (m, 3 H, BH3). 31P NMR (162 MHz, CDCl3): δ 25.5 (q, J = 66.4 Hz). HPLC (Daicel Chiralcel AS-H, n-hexane/i-PrOH = 98/2, UV = 254 nm, flow rate = 0.5 mL/min) tR1 = 18.379 min (minor) and tR2 = 20.599 min (major), ee = 90%. [α]D25 = -6.0 (c = 2.0, CHCl3).

(5)-4-(borane tert-butyl(methyl)phosphino)-N,N-bis(4-iodophenyl)aniline. Performed according to the microwave reactions procedure to afford 81.5 mg (45%) of (S)-3f as white solid. 1H NMR (400 MHz, CDCl3): δ 7.46 – 7.51 (m, 2 H, Ar), 7.28 – 7.32 (m, 4 H, Ar), 7.13 (d, J = 8.0 Hz, 4 H, Ar), 7.02 – 7.04 (m, 2 H, Ar), 1.52 (d, J = 8.0 Hz, 3 H, C(CH)3), 1.12 (d, J = 12.0 Hz, 9 H, C(CH)3), 0.26 – 0.86 (m, 3 H, BH3). 31P NMR (162 MHz, CDCl3): δ 23.7 (q, J = 45.4 Hz). HPLC (Daicel Chiralcel OD-H, n-hexane/i-PrOH = 90/10, UV = 254 nm, flow rate = 1.0 mL/min) tR1 = 9.797 min (minor) and tR2 = 11.418 min (major), ee = 95%. [α]D25 = -6.5 (c = 2.0, CHCl3).

(5)-2-(borane tert-butyl(methyl)phosphino)-6-fluoropyridine. Performed according to the microwave reactions procedure to afford 43.2 mg (56%) of (S)-3g as white solid. 1H NMR (400 MHz, CDCl3): δ 7.88 – 7.92 (m, 1 H, Ar), 7.69 – 7.73 (m, 1 H, Ar), 7.37 (d, J = 8.0 Hz, 1 H, Ar), 1.60 (d, J = 8.0 Hz, 3 H, CH), 1.11 (d, J = 16.0 Hz, 9 H, C(CH)3), 0.26 – 0.98 (m, 3 H, BH3). 31P NMR (162 MHz, CDCl3): δ 30.5 (q, J = 61.6 Hz). HPLC (Daicel Chiralcel AS-H, n-hexane/i-PrOH = 98/2, UV = 250 nm, flow rate = 1.0 mL/min) tR1 = 11.471 min (major) and tR2 = 12.718 min (minor), ee = 93%. [α]D25 = -34.0 (c = 2.0, CHCl3).

(5)-8-(borane tert-butyl(methyl)phosphino)quinoline. Performed according to the microwave reactions procedure to afford 22.6 mg (26%) of (S)-3j as white solid. 1H NMR (400 MHz, CDCl3): δ 8.91 – 8.93 (m, 1 H, Ar), 8.50 – 8.55 (m, 1 H, Ar), 8.19 (d, J = 8.0 Hz, 1 H, Ar), 7.96 (d, J = 8.0 Hz, 1 H, Ar), 7.57 – 7.64 (m, 1 H, Ar), 7.42 – 7.45 (m, 1 H, Ar), 2.10 (d, J = 8.0 Hz, 3 H, CH), 1.18 (d, J = 12.0 Hz, 9 H, C(CH)3), 0.26 – 0.90 (m, 3 H, BH3). 31P NMR (162 MHz, CDCl3): δ 31.0 (q, J = 63.2 Hz). HPLC (Daicel Chiralcel OD-H, n-hexane/i-PrOH = 98/2, UV = 250 nm, flow rate = 1.0 mL/min) tR1 = 6.791 min (major) and tR2 = 7.931 min (minor), ee = 71%. [α]D25 = -27.0 (c = 2.0, CHCl3).

4. X-ray structural determination

The X-ray date was collected on a Rigaku Saturn CCDC diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least squares on F. All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model (SHELXL-97). The crystal data and structural refinements details are listed in Table S1. CCDC 2017943 ((S)-2q), and CCDC 2017887 ((R)-2h) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
Table S1. Crystal Data and Summary of X-ray Data Collection for compound \((S)-2q\) and \((R)-2h\)

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5. References

6. $^1$H, $^{13}$C, $^{19}$F and $^{31}$P NMR spectra for all products.

**Figure S1.** $^1$H NMR spectrum of (R)-2a in CDCl$_3$

**Figure S2.** $^{13}$C NMR spectrum of (R)-2a in CDCl$_3$
Figure S3. $^{31}$P NMR spectrum of (R)-2a in CDCl$_3$

Figure S4. $^1$H NMR spectrum of (R)-2b in CDCl$_3$
Figure S5. $^{13}$C NMR spectrum of (R)-2b in CDCl$_3$.

Figure S6. $^{31}$P NMR spectrum of (R)-2b in CDCl$_3$. 
**Figure S7.** $^1$H NMR spectrum of (R)-2c in CDCl$_3$

**Figure S8.** $^{13}$C NMR spectrum of (R)-2c in CDCl$_3$
Figure S9. $^{31}$P NMR spectrum of (R)-2c in CDCl$_3$

Figure S10. $^1$H NMR spectrum of (R)-2d in CDCl$_3$
Figure S11. $^{13}$C NMR spectrum of (R)-2d in CDCl$_3$

Figure S12. $^{31}$P NMR spectrum of (R)-2d in CDCl$_3$
Figure S13. $^1$H NMR spectrum of (R)-2e in CDCl$_3$

Figure S14. $^{13}$C NMR spectrum of (R)-2e in CDCl$_3$
Figure S15. $^{31}$P NMR spectrum of (R)-2e in CDCl$_3$

Figure S16. $^1$H NMR spectrum of (R)-2f in CDCl$_3$
**Figure S17.** $^{13}$C NMR spectrum of (R)-2f in CDCl$_3$

**Figure S18.** $^{31}$P NMR spectrum of (R)-2f in CDCl$_3$
Figure S19. $^1$H NMR spectrum of (R)-2g in CDCl$_3$

Figure S20. $^{13}$C NMR spectrum of (R)-2g in CDCl$_3$
Figure S21. $^{31}$P NMR spectrum of (R)-2g in CDCl$_3$

Figure S22. $^1$H NMR spectrum of (R)-2h in CDCl$_3$
**Figure S23.** $^{13}$C NMR spectrum of (R)-2h in CDCl$_3$

**Figure S24.** $^{31}$P NMR spectrum of (R)-2h in CDCl$_3$
Figure S25. $^1$H NMR spectrum of (R)-2i in CDCl$_3$

Figure S26. $^{13}$C NMR spectrum of (R)-2i in CDCl$_3$
Figure S27. $^{31}$P NMR spectrum of (R)-2i in CDCl$_3$

Figure S28. $^1$H NMR spectrum of (R)-2j in CDCl$_3$
Figure S29. $^{13}$C NMR spectrum of (R)-2j in CDCl$_3$

Figure S30. $^{31}$P NMR spectrum of (R)-2j in CDCl$_3$
Figure S31. $^1$H NMR spectrum of (R)-2k in CDCl$_3$

Figure S32. $^{13}$C NMR spectrum of (R)-2k in CDCl$_3$
Figure S33. \(^{31}\)P NMR spectrum of (R)-2k in CDCl$_3$

Figure S34. \(^{19}\)F NMR spectrum of (R)-2k in CDCl$_3$
Figure S35. $^1$H NMR spectrum of (R)-2I in CDCl$_3$

Figure S36. $^{13}$C NMR spectrum of (R)-2I in CDCl$_3$
Figure S37. $^{31}$P NMR spectrum of (R)-2l in CDCl$_3$

Figure S38. $^1$H NMR spectrum of (R)-2m in CDCl$_3$
Figure S39. $^{13}$C NMR spectrum of (R)-2m in CDCl$_3$.

Figure S40. $^{31}$P NMR spectrum of (R)-2m in CDCl$_3$. 
Figure S41. $^1$H NMR spectrum of (R)-2n in CDCl$_3$

Figure S42. $^{13}$C NMR spectrum of (R)-2n in CDCl$_3$
Figure S43. $^{31}$P NMR spectrum of (R)-2n in CDCl$_3$

Figure S44. $^1$H NMR spectrum of (R)-2o in CDCl$_3$
Figure S45. $^{13}$C NMR spectrum of (R)-2o in CDCl$_3$

Figure S46. $^{31}$P NMR spectrum of (R)-2o in CDCl$_3$
Figure S47. $^1$H NMR spectrum of (R)-2p in CDCl$_3$

Figure S48. $^{13}$C NMR spectrum of (R)-2p in CDCl$_3$
Figure S49. $^{31}\text{P}$ NMR spectrum of (R)-2p in CDCl$_3$

Figure S50. $^1\text{H}$ NMR spectrum of (R)-2q in CDCl$_3$

S41
Figure S51. $^{13}$C NMR spectrum of $(R)$-2q in CDCl$_3$.

Figure S52. $^{31}$P NMR spectrum of $(R)$-2q in CDCl$_3$. 

(S42)
Figure S53. $^1$H NMR spectrum of (R)-2r in CDCl$_3$

Figure S54. $^{13}$C NMR spectrum of (R)-2r in CDCl$_3$
Figure S55. $^{31}$P NMR spectrum of (R)-2r in CDCl$_3$

Figure S56. $^1$H NMR spectrum of (R)-3a in CDCl$_3$
Figure S57. $^{13}$C NMR spectrum of (R)-3a in CDCl$_3$.

Figure S58. $^{31}$P NMR spectrum of (R)-3a in CDCl$_3$. 

S45
Figure S59. $^1$H NMR spectrum of $(R)$-3b in CDCl$_3$

Figure S60. $^{13}$C NMR spectrum of $(R)$-3b in CDCl$_3$
Figure S61. $^{31}$P NMR spectrum of (R)-3b in CDCl$_3$

Figure S62. $^1$H NMR spectrum of (R)-3c in CDCl$_3$
Figure S63. $^{13}$C NMR spectrum of (R)-3c in CDCl$_3$

Figure S64. $^{31}$P NMR spectrum of (R)-3c in CDCl$_3$
Figure S65. $^1$H NMR spectrum of (R)-3d in CDCl$_3$

Figure S66. $^{13}$C NMR spectrum of (R)-3d in CDCl$_3$
Figure S67. $^{31}$P NMR spectrum of (R)-3d in CDCl$_3$

Figure S68. $^1$H NMR spectrum of (R)-3e in CDCl$_3$
Figure S69. $^{13}$C NMR spectrum of (R)-3e in CDCl$_3$

Figure S70. $^{31}$P NMR spectrum of (R)-3e in CDCl$_3$
Figure S71. $^1$H NMR spectrum of (R)-3f in CDCl$_3$.

Figure S72. $^{13}$C NMR spectrum of (R)-3f in CDCl$_3$.
Figure S73. \( ^{31}\text{P} \) NMR spectrum of (R)-3f in CDCl\(_3\)

Figure S74. \(^1\text{H} \) NMR spectrum of (R)-3g in CDCl\(_3\)
Figure S75. $^{13}$C NMR spectrum of (R)-3g in CDCl$_3$.

Figure S76. $^{31}$P NMR spectrum of (R)-3g in CDCl$_3$. 
Figure S77. $^{19}$F NMR spectrum of (R)-3g in CDCl$_3$

Figure S78. $^1$H NMR spectrum of (R)-3h in CDCl$_3$
Figure S79. $^{13}$C NMR spectrum of (R)-3h in CDCl$_3$

Figure S80. $^{31}$P NMR spectrum of (R)-3h in CDCl$_3$
Figure S81. $^1$H NMR spectrum of (R)-3i in CDCl$_3$

Figure S82. $^{13}$C NMR spectrum of (R)-3i in CDCl$_3$
**Figure S83.** $^{31}$P NMR spectrum of (R)-3i in CDCl$_3$

**Figure S84.** $^1$H NMR spectrum of (R)-3j in CDCl$_3$
Figure S85. $^{13}$C NMR spectrum of (R)-3j in CDCl$_3$

Figure S86. $^{31}$P NMR spectrum of (R)-3j in CDCl$_3$
Figure S87. $^1$H NMR spectrum of (R)-3k in CDCl$_3$.

Figure S88. $^{13}$C NMR spectrum of (R)-3k in CDCl$_3$. 
Figure S89. $^{31}$P NMR spectrum of (R)-3k in CDCl₃

Figure S90. $^1$H NMR spectrum of (R)-3l in CDCl₃
Figure S91. $^{13}$C NMR spectrum of (R)-3I in CDCl$_3$

Figure S92. $^{31}$P NMR spectrum of (R)-3I in CDCl$_3$
Figure S93. $^1$H NMR spectrum of (S)-2a in CDCl$_3$

Figure S94. $^{31}$P NMR spectrum of (S)-2a in CDCl$_3$
Figure S95. $^1$H NMR spectrum of (S)-2b in CDCl$_3$.

Figure S96. $^{31}$P NMR spectrum of (S)-2b in CDCl$_3$.
Figure S97. $^1$H NMR spectrum of (S)-2d in CDCl$_3$

Figure S98. $^{31}$P NMR spectrum of (S)-2d in CDCl$_3$
Figure S99. $^1$H NMR spectrum of (S)-2e in CDCl$_3$

Figure S100. $^{31}$P NMR spectrum of (S)-2e in CDCl$_3$
Figure S101. $^1$H NMR spectrum of (S)-2f in CDCl$_3$

Figure S102. $^{31}$P NMR spectrum of (S)-2f in CDCl$_3$
Figure S103. $^1$H NMR spectrum of (S)-2h in CDCl$_3$

Figure S104. $^{31}$P NMR spectrum of (S)-2h in CDCl$_3$
Figure S105. $^1$H NMR spectrum of (S)-3j in CDCl$_3$

Figure S106. $^{31}$P NMR spectrum of (S)-3j in CDCl$_3$
Figure S107. $^1$H NMR spectrum of (S)-2k in CDCl$_3$

Figure S108. $^{31}$P NMR spectrum of (S)-2k in CDCl$_3$
Figure S109. $^1$H NMR spectrum of (S)-2n in CDCl$_3$

Figure S110. $^{31}$P NMR spectrum of (S)-2n in CDCl$_3$
Figure S111. $^1$H NMR spectrum of (S)-3b in CDCl$_3$

Figure S112. $^{31}$P NMR spectrum of (S)-3b in CDCl$_3$
Figure S113. $^1$H NMR spectrum of (S)-3d in CDCl₃

Figure S114. $^{31}$P NMR spectrum of (S)-3d in CDCl₃
**Figure S115.** $^1$H NMR spectrum of (S)-3f in CDCl$_3$

**Figure S116.** $^{31}$P NMR spectrum of (S)-3f in CDCl$_3$
Figure S117. $^1$H NMR spectrum of (S)-3g in CDCl$_3$

Figure S118. $^{31}$P NMR spectrum of (S)-3g in CDCl$_3$
Figure S119. $^1$H NMR spectrum of (S)-3j in CDCl$_3$

Figure S120. $^{31}$P NMR spectrum of (S)-3j in CDCl$_3$
7. HPLC spectra for all products.

Chiral HPLC chromatographic analysis of (R)-2a
Condition: Daicel Chiralcel AS-H, n-hexane/i-PrOH = 95/5, UV = 250 nm, flow rate: 1.0 mL/min, retention time: t (minor) = 5.452 min, t (major) = 6.546 min, ee = 91%.

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Chiral HPLC chromatographic analysis of (S)-2a
Condition: Daicel Chiralcel AS-H, n-hexane/i-PrOH = 95/5, UV = 250 nm, flow rate: 1.0 mL/min, retention time: t (major) = 5.430 min, ee = 99%.

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Chiral HPLC chromatographic analysis of (R)-2b

Condition: Daicel Chiralcel AS-H, n-hexane/i-PrOH = 95/5, UV = 254 nm, flow rate: 1.0 mL/min, retention time: t (minor) = 7.131 min, t (major) = 8.103 min, ee = 65%.

Chiral HPLC chromatographic analysis of (S)-2b

Condition: Daicel Chiralcel AS-H, n-hexane/i-PrOH = 95/5, UV = 230 nm, flow rate: 1.0 mL/min, retention time: t (major) = 7.908 min, t (minor) = 8.829 min, ee = 99%.
Chiral HPLC chromatographic analysis of (R)-2c

Condition: Daicel Chiralcel AS-H, n-hexane/i-PrOH = 95/5, UV = 220 nm, flow rate: 1.0 mL/min, retention time: t (minor) = 4.240 min, t (major) = 5.678 min, ee = 94%.
Chiral HPLC chromatographic analysis of (R)-2d
Condition: Daicel Chiralcel OD-H, n-hexane/i-PrOH = 98/2, UV = 230 nm, flow rate: 0.5 mL/min, retention time: t (minor) = 12.580 min, t (major) = 14.134 min, ee = 90%.

Chiral HPLC chromatographic analysis of (S)-2d
Condition: Daicel Chiralcel OD-H, n-hexane/i-PrOH = 98/2, UV = 230 nm, flow rate: 0.5 mL/min, retention time: t (major) = 13.211 min, t (minor) = 14.302 min, ee = 92%.
Chiral HPLC chromatographic analysis of (R)-2e
Condition: Daicel Chiralcel AS-H, n-hexane/i-PrOH = 99/1, UV = 234 nm, flow rate: 1 mL/min, retention time: t (major) = 5.365 min, t (minor) = 6.045 min, ee = 90%.

Chiral HPLC chromatographic analysis of (S)-2e
Condition: Daicel Chiralcel AS-H, n-hexane/i-PrOH = 99/1, UV = 254 nm, flow rate: 1.0 mL/min, retention time: t (minor) = 4.992 min, t (major) = 5.519 min, ee = 88%.
Chiral HPLC chromatographic analysis of (R)-2f
Condition: Daicel Chiralcel AS-H, n-hexane/i-PrOH = 98/2, UV = 250 nm, flow rate: 0.8 mL/min, retention time: t (minor) = 21.843 min, t (major) = 23.093 min, ee = 98%.

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Chiral HPLC chromatographic analysis of (S)-2f
Condition: Daicel Chiralcel AS-H, n-hexane/i-PrOH = 98/2, UV = 250 nm, flow rate: 0.8 mL/min, retention time: t (major) = 21.932 min, t (minor) = 24.014 min, ee = 95%.

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Chiral HPLC chromatographic analysis of (S)-2f
Condition: Daicel Chiralcel AS-H, n-hexane/i-PrOH = 98/2, UV = 250 nm, flow rate: 0.8 mL/min, retention time: t (major) = 21.932 min, t (minor) = 24.014 min, ee = 95%.

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Chiral HPLC chromatographic analysis of (R)-2g
Condition: Daicel Chiralcel AS-H, n-hexane/i-PrOH = 98/2, UV = 250 nm, flow rate: 1.0 mL/min, retention time: t (major) = 26.610 min, t (minor) = 34.227 min, ee = 89%.
Chiral HPLC chromatographic analysis of (R)-2h
Condition: Daicel Chiralcel OD-H, n-hexane/i-ProH = 95/5, UV = 250 nm, flow rate: 0.8 mL/min, retention time: t (major) = 7.891 min, t (minor) = 8.692 min, ee = 79%.

Chiral HPLC chromatographic analysis of (S)-2h
Condition: Daicel Chiralcel OD-H, n-hexane/i-ProH = 95/5, UV = 250 nm, flow rate: 0.8 mL/min, retention time: t (minor) = 7.872 min, t (major) = 8.778 min, ee = 93%.
Chiral HPLC chromatographic analysis of (R)-2i
Condition: Daicel Chiralcel OD-H, n-hexane/i-PrOH = 90/10, UV = 254 nm, flow rate: 1.0 mL/min, retention time: t (major) = 9.399 min, t (minor) = 12.921 min, ee = 84%.

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Peak RetTime Type Width Area Height Area
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Chiral HPLC chromatographic analysis of (R)-2j
Condition: Daicel Chiralcel AS-H, n-hexane/i-PrOH = 99/1, UV = 234 nm, flow rate: 1.0 mL/min, retention time: t (minor) = 9.339 min, t (major) = 11.765 min, ee = 94%.

Chiral HPLC chromatographic analysis of (S)-2j
Condition: Daicel Chiralcel AS-H, n-hexane/i-PrOH = 99/1, UV = 234 nm, flow rate: 1.0 mL/min, retention time: t (major) = 9.679 min, t (minor) = 12.252 min, ee = 95%.
Chiral HPLC chromatographic analysis of (R)-2k
Condition: Daicel Chiralcel AS-H, n-hexane/i-PrOH = 99/1, UV = 254 nm, flow rate: 1.0 mL/min, retention time: t (minor) = 6.392 min, t (major) = 6.672 min, ee = 89%.

Chiral HPLC chromatographic analysis of (S)-2k
Condition: Daicel Chiralcel AS-H, n-hexane/i-PrOH = 99/1, UV = 254 nm, flow rate: 1.0 mL/min, retention time: t (major) = 6.399 min, t (minor) = 6.745 min, ee = 94%.
Chiral HPLC chromatographic analysis of (R)-2I
Condition: Daicel Chiralcel OD-H, n-hexane/i-PrOH = 90/10, UV = 254 nm, flow rate: 1.0 mL/min, retention time: t (major) = 7.292 min, t (minor) = 8.536 min, ee = 63%.
Chiral HPLC chromatographic analysis of (R)-2m

Condition: Daicel Chiralcel OD-H, n-hexane/i-ProOH = 98/2, UV = 250 nm, flow rate = 1.0 mL/min, retention time: t (minor) = 54.504 min, t (major) = 57.362 min, ee = 65%.
Chiral HPLC chromatographic analysis of \((R)-2n\)
Condition: Daicel Chiralcel OD-H, \(n\)-hexane/i-PrOH = 98/2, UV = 230 nm, flow rate: 0.8 mL/min, retention time: \(t_{\text{major}} = 15.308\) min, \(t_{\text{minor}} = 16.976\) min, ee = 92%.

Chiral HPLC chromatographic analysis of \((S)-2n\)
Condition: Daicel Chiralcel OD-H, \(n\)-hexane/i-PrOH = 98/2, UV = 230 nm, flow rate: 0.8 mL/min, retention time: \(t_{\text{minor}} = 14.957\) min, \(t_{\text{major}} = 16.501\) min, ee = 97%.
Chiral HPLC chromatographic analysis of (R)-2o

Condition: Daicel Chiralcel OD-H, n-hexane/i-PrOH = 90/10, UV = 250 nm, flow rate: 1.0 mL/min, retention time: t (major) = 7.383 min, t (minor) = 8.712 min, ee = 74%.
Chiral HPLC chromatographic analysis of (R)-2p

Condition: Daicel Chiralcel OD-H, n-hexane/i-PrOH = 98/2, UV = 250 nm, flow rate: 1 mL/min, retention time: t (minor) = 7.585 min, t (major) = 12.549 min, ee = 46%.
Chiral HPLC chromatographic analysis of (R)-2q
Condition: Daicel Chiralcel IBN-H, n-hexane/i-PrOH = 99/1, UV = 254 nm, flow rate: 0.5 mL/min, retention time: t (minor) = 11.612 min, t (major) = 12.325 min, ee = 74%.
Chiral HPLC chromatographic analysis of (R)-2r

Condition: Daicel Chiralcel AS-H, n-hexane/i-PrOH = 90/10, UV = 254 nm, flow rate: 1.0 mL/min, retention time: t (minor) = 13.414 min, t (major) = 28.472 min, ee = 91%.
Chiral HPLC chromatographic analysis of (R)-3a

Condition: Daicel Chiralcel OD-H, n-hexane/i-PrOH = 98/2, UV = 250 nm, flow rate: 0.8 mL/min, retention time: t (minor) = 8.667 min, t (major) = 10.155 min, ee = 80%.
Chiral HPLC chromatographic analysis of (R)-3b
Condition: Daicel Chiralcel OD-H, n-hexane/i-PrOH = 90/10, UV = 250 nm, flow rate: 1.0 mL/min, retention time: t (major) = 11.953 min, t (minor) = 16.618 min, ee = 46%.

Chiral HPLC chromatographic analysis of (S)-3b
Condition: Daicel Chiralcel OD-H, n-hexane/i-PrOH = 90/10, UV = 250 nm, flow rate: 1.0 mL/min, retention time: t (minor) = 11.772 min, t (major) = 16.287 min, ee = 91%.
Chiral HPLC chromatographic analysis of (R)-3c
Condition: Daicel Chiralcel OD-H, n-hexane/i-PrOH = 98/2, UV = 254 nm, flow rate: 0.8 mL/min, retention time: t (major) =13.659 min, t (minor) = 15.300 min, ee = 94%.
Chiral HPLC chromatographic analysis of (R)-3d
Condition: Daicel Chiralcel AS-H, n-hexane/i-PrOH = 98/2, UV = 254 nm, flow rate: 0.5 mL/min, retention time: t (major) = 18.239 min, t (minor) = 20.275 min, ee = 69%.

Chiral HPLC chromatographic analysis of (S)-3d
Condition: Daicel Chiralcel AS-H, n-hexane/i-PrOH = 98/2, UV = 254 nm, flow rate: 0.5 mL/min, retention time: t (minor) = 18.379 min, t (major) = 20.599 min, ee = 90%.
Chiral HPLC chromatographic analysis of (R)-3e
Condition: Daicel Chiralcel OD-H, n-hexane/i-PrOH = 98/2, UV = 250 nm, flow rate: 1.0 mL/min, retention time: $t_{\text{minor}} = 5.476$ min, $t_{\text{major}} = 5.912$ min, ee = 84%.
Chiral HPLC chromatographic analysis of (R)-3f
Condition: Daicel Chiralcel OD-H, n-hexane/i-PrOH = 90/10, UV = 254 nm, flow rate: 1.0 mL/min, retention time: t (major) = 9.428 min, t (minor) = 11.065 min, ee = 94%.

Chiral HPLC chromatographic analysis of (S)-3f
Condition: Daicel Chiralcel OD-H, n-hexane/i-PrOH = 90/10, UV = 254 nm, flow rate: 1.0 mL/min, retention time: t (minor) = 9.797 min, t (major) = 11.418 min, ee = 95%.
Chiral HPLC chromatographic analysis of (R)-3g
Condition: Daicel Chiralcel AS-H, n-hexane/i-PrOH = 98/2, UV = 250 nm, flow rate: 1.0 mL/min, retention time: t (minor) = 11.503 min, t (major) = 12.124 min, ee = 97%.

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Chiral HPLC chromatographic analysis of (S)-3g
Condition: Daicel Chiralcel AS-H, n-hexane/i-PrOH = 98/2, UV = 250 nm, flow rate: 1.0 mL/min, retention time: t (major) = 11.471 min, t (minor) = 12.718 min, ee = 93%.

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Chiral HPLC chromatographic analysis of (R)-3h
Condition: Daicel Chiralcel AS-H, n-hexane/i-PrOH = 95/5, UV = 230 nm, flow rate: 1.0 mL/min, retention time: t (minor) = 8.140 min, t (major) = 9.308 min, ee = 73%.
Chiral HPLC chromatographic analysis of (R)-3i

Condition: Daicel Chiralcel AS-H, n-hexane/i-PrOH = 98/2, UV = 250 nm, flow rate: 0.8 mL/min, retention time: $t_{(\text{minor})} = 6.452$ min, $t_{(\text{major})} = 6.937$ min, ee = 81%.
Chiral HPLC chromatographic analysis of (R)-3j
Condition: Daicel Chiralcel OD-H, n-hexane/i-PrOH = 98/2, UV = 250 nm, flow rate: 1.0 mL/min, retention time: t (minor) = 6.324 min, t (major) = 7.473 min, ee = 71%.

Chiral HPLC chromatographic analysis of (S)-3j
Condition: Daicel Chiralcel OD-H, n-hexane/i-PrOH = 98/2, UV = 250 nm, flow rate: 1.0 mL/min, retention time: t (major) = 6.791 min, t (minor) = 7.931 min, ee = 71%.
Chiral HPLC chromatographic analysis of (R)-3k
Condition: Daicel Chiralcel OD-H, n-hexane/i-PrOH = 98/2, UV = 254 nm, flow rate: 0.8 mL/min, retention time: t
(major) = 5.752 min, t (minor) = 6.206 min, ee = 77%.
Chiral HPLC chromatographic analysis of (R)-3I
Condition: Daicel Chiralcel OD-H, n-hexane/i-PrOH = 98/2, UV = 254 nm, flow rate: 0.8 mL/min, retention time: t (minor) = 11.874 min, t (major) = 13.672 min, ee = 94%.