Supporting Information

Catalytic Asymmetric Synthesis of Phosphine Boronates**
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**General Methods:**

Chromatography: Merck silica gel type 9385 230-400 mesh, TLC: Merck silica gel 60, 0.25 mm. Components were visualized by UV and potassium permanganate staining. Progress and conversion of the reaction were determined by GC-MS (GC, HP6890: MS HP5973) with an HP1 or HP5 column (Agilent Technologies, Palo Alto, CA) and $^{31}$P-NMR. Mass spectra were recorded on an AEI-MS-902 mass spectrometer (EI+) or a LTQ Orbitrap XL (ESI+). $^1$H-, $^{13}$C- and $^{31}$P-NMR spectra were recorded on a Varian AMX400 or a Varian VXR300 using CDCl$_3$ as solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard (CHCl$_3$: $\delta$ 7.26 for $^1$H, $\delta$ 77.0 for $^{13}$C). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. Optical rotations were measured on a *Schmidt + Haensch* polarimeter (Polartronic MH8) with a 10 cm cell ($c$ given in g/100 mL). Enantiomeric ratios were determined by HPLC analysis of both enantiomers for every compound using a Shimadzu LC-10ADVP HPLC equipped with a Shimadzu SPD-M10A VP diode array detector. All reactions were carried out under a nitrogen atmosphere using oven dried glassware and solvents and using standard Schlenk techniques. All copper-salts, alkynes, lithium and sodium tert-butoxide, bis(pinacolato)diboron, RhBr(PPh$_3$)$_3$, iodomethane, furan, sodium perborate tetrahydrate, $n$BuLi, NBS, HSiCl$_3$, Et$_3$N, (EtO)$_2$MeSiH, BH$_3$•THF, bis(4-nitrophenyl) hydrogen phosphate, ligands (1$R$2$R$)-N,N′-Dimethyl-1,2-diphenylethane-1,2-diamine, (S,R$_p$)-, (R,S$_p$)-Josiphos, (S)-Tol-BINAP, (a$R$,a$R$)-2,2′-Bis(a-NDimethylaminophenylmethyl)-(S,S)-1,1′-bis(diphenylphosphino)ferrocene (Mandyphos, SL-M001-1), (R)-1-[(R)-2-(2′-diphenylphosphino-phenyl)ferrocenyl]ethyl-di(bis-3,5-trifluoromethylphenyl)phosphine (Walphos, SL-W001-1), ((R,R)-Taniaphos, SL-T001-1), (R)-1-[(S)-2-dicyclohexylphosphino)-ferrocenyl]ethyl-diphenylphosphine (reverse-Josiphos, SL-J004-1) and (R)-(−)-2,2′-Bis[d(3,5-di-t-butyl-4-methoxyphenyl)phosphino]-diphenylphosphino)-6,6′-dimethoxy-1,1′-biphenyl ((R)-3,5-t-Bu-4-MeO-MeOBIPHEP) were purchased from Aldrich, and used without further purification. Diphenylphosphine oxide was purchased from TCI Europe.
Representative procedure for the synthesis of 1a-k: synthesis of (E)-oct-1-en-1-yldiphenylphosphine oxide (1a)

Diphenylphosphine oxide (1616 mg, 8.0 mmol), 1-octyne (926 mg, 1.24 mL, 8.4 mmol), and RhCl(PPh₃)₃ (222 mg, 3 mol %) were dissolved in 20 mL of dry toluene under nitrogen. The resulting transparent yellow solution was heated at 40 °C for 16h. The solvent was evaporated under reduced pressure to give a yellow semisolid. The crude product was then purified by column chromatography. White solid obtained after column chromatography (SiO₂, n-pentane/AcOEt 7:3), 2.32 g, 93% yield. Spectral data in accordance with lit. values.¹²

(E)-hex-1-en-1-yldiphenylphosphine oxide (1b)

Synthesized using diphenylphosphine oxide (404 mg, 2.0 mmol), 1-hexyne (172 mg, 241 µL, 2.1 mmol), and RhCl(PPh₃)₃ (55 mg, 3 mol %) in 5 mL of dry toluene. White solid obtained after column chromatography (SiO₂, n-pentane/AcOEt 1:1), 471 mg, 83% yield. HRMS (ESI+, m/z): calcd. for C₁₈H₂₂OP, [M+H⁺]: 285.1408; found: 285.1404. Spectral data in accordance with lit. values.³

(E)-dodec-1-en-1-yldiphenylphosphine oxide (1c)

Synthesized using diphenylphosphine oxide (404 mg, 2.0 mmol), 1-dodecyne (349 mg, 449 µL, 2.1 mmol), and RhCl(PPh₃)₃ (55 mg, 3 mol %) in 5 mL of dry toluene. White solid obtained after column chromatography (SiO₂, n-pentane/AcOEt 7:3), 553 mg, 75% yield. ¹H NMR (400 MHz, CDCl₃), δ: 7.71 – 7.63 (m, 4H), 7.51 – 7.39 (m, 6H), 6.78 – 6.64 (m, 1H), 6.20 (dd, JPH = 24.6, JHH = 17.1 Hz, 1H), 2.27 (q, J = 7.0 Hz, 2H), 1.45 (m, 2H), 1.33 – 1.19 (m, 14H), 0.85 (t, J = 6.5 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃), δ: 152.9, 133.3 (d, J = 104.7 Hz), 131.6 (d, J = 2.6 Hz), 131.3 (d, J = 9.9 Hz), 128.4 (d, J = 12.1 Hz), 121.6 (d, J = 103.1 Hz), 34.5 (d, J = 16.8 Hz), 31.9, 29.52, 29.50, 29.32, 29.27, 29.1, 27.9, 22.6, 14.1 ppm. ³¹P NMR (161.9 MHz, CDCl₃), δ: 23.4 ppm. HRMS (ESI+, m/z): calcd. for C₂₄H₃₄OP, [M+H⁺]: 369.2347; found: 369.2342.

(E)-diphenyl(4-phenylbut-1-en-1-yl)phosphine oxide (1d)

Synthesized using diphenylphosphine oxide (404 mg, 2.0 mmol), but-3-yn-1-ylbenzene (273 mg, 295 µL, 2.1 mmol), and RhCl(PPh₃)₃ (55 mg, 3 mol %) in 5 mL of dry toluene. White solid obtained after column chromatography (SiO₂, n-pentane/AcOEt 1:1), 652 mg, 98% yield. ¹H NMR (400 MHz, CDCl₃), δ: 7.61 – 7.54 (m, 4H), 7.52 – 7.46 (m, 2H), 7.44 – 7.38 (m, 4H), 7.29 – 7.24 (m, 2H), 7.23 – 7.18 (m, 1H), 7.16 – 7.12 (m, 2H), 6.76 – 6.63 (m, 1H), 6.16 (dd, JPH = 24.1, JHH = 17.0 Hz, 1H), 2.80 (t, J = 7.5 Hz, 2H), 2.62 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃), δ: 151.29, 151.27, 140.6, 132.9 (d, J = 105.0 Hz), 131.7 (d, J = 2.8 Hz), 131.3 (d, J = 10.0 Hz), 128.5, 128.4 (d, J = 12.1 Hz), 126.1, 122.9 (d, J = 101.9 Hz), 36.0 (d, J = 17.1 Hz), 34.1 ppm. ³¹P NMR (161.9 MHz, CDCl₃), δ: 23.5 ppm. HRMS (ESI+, m/z): calcd. for C₂₂H₂₂OP, [M+H⁺]: 333.1408; found: 333.1405.
(E)-(3-cyclopentylprop-1-en-1-yl)diphenylphosphine oxide (1e)
Synthesized using diphenylphosphine oxide (404 mg, 2.0 mmol), prop-2-yn-1-ylcyclopentane (227 mg, 275 µL, 2.1 mmol), and RhCl(PPh₃)₃ (55 mg, 3 mol %) in 5 mL of dry toluene. White solid obtained after column chromatography (SiO₂, n-pentane/AcOEt 1:1), 503 mg, 81% yield. ¹H NMR (400 MHz, CDCl₃), δ 7.73 – 7.65 (m, 4H), 7.53 – 7.42 (m, 6H), 6.77 – 6.65 (m, 1H), 6.22 (ddt, JₚΗ = 24.8, JₗΗ = 17.0 Hz, JHH = 1.3 Hz, 1H), 2.30 (tt, J = 7.1 Hz, J = 2.3 Hz, 2H), 1.97 (m, 1H), 1.76 (m, 2H), 1.64 – 1.47 (m, 4H), 1.14 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃), δ 152.3, 133.3 (d, J = 104.7 Hz), 131.6 (d, J = 2.8 Hz), 131.3 (J = 9.8 Hz), 128.5 (d, J = 11.9 Hz), 122.1 (d, J = 102.7 Hz), 41.1 (J = 16.7 Hz), 38.8, 32.4, 25.1 ppm. ³¹P NMR (161.9 MHz, CDCl₃), δ: 23.4 ppm. HRMS (ESI+, m/z): calcd. for C₂₀H₂₄OP, [M+H⁺]: 311.1565; found: 311.1562.

(E)-(3-cyclohexylprop-1-en-1-yl)diphenylphosphine oxide (1f)
Synthesized using diphenylphosphine oxide (404 mg, 2.0 mmol), prop-2-yn-1-ylcyclohexane (257 mg, 303 µL, 2.1 mmol), and RhCl(PPh₃)₃ (55 mg, 3 mol %) in 5 mL of dry toluene. White solid obtained after column chromatography (SiO₂, n-pentane/AcOEt 1:1), 597 mg, 92% yield. ¹H NMR (400 MHz, CDCl₃), δ 7.72 – 7.64 (m, 4H), 7.54 – 7.41 (m, 6H), 6.77 – 6.63 (m, 1H), 6.21 (ddt, JₚΗ = 25.1, JₗΗ = 16.9 Hz, JHH = 1.3 Hz, 1H), 2.19 (t, J = 6.9 Hz, 2H), 1.69 (m, 4H), 1.62 (m, 1H), 1.44 (m, 1H), 1.19 (m, 3H), 0.93 (m, 1H) ppm. ¹³C NMR (101 MHz, CDCl₃), δ 151.8, 133.2 (d, J = 104.6 Hz), 131.6 (d, J = 2.7 Hz), 131.3 (d, J = 9.9 Hz), 128.5 (d, J = 12.0 Hz), 122.6 (d, J = 102.8 Hz), 42.7 (d, J = 16.7 Hz), 37.1, 33.1, 26.3, 26.1 ppm. ³¹P NMR (161.9 MHz, CDCl₃), δ:
23.5 ppm. HRMS (ESI+, m/z): calcd. for C_{21}H_{26}OP, [M+H^+]: 325.1721; found: 325.1720.

(E)-(2-cyclopropylvinyl)diphenylphosphine oxide (1g)
Synthesized using diphenylphosphine oxide (404 mg, 2.0 mmol), ethynylcyclopropane (139 mg, 178 µL, 2.1 mmol), and RhCl(PPh$_3$)$_3$ (55 mg, 3 mol %) in 5 mL of dry toluene. White solid obtained after column chromatography (SiO$_2$, n-pentane/AcOEt 1:1), 413 mg, 77% yield. $^1$H NMR (400 MHz, CDCl$_3$), δ 7.71 – 7.64 (m, 4H), 7.50 – 7.39 (m, 6H), 6.29 – 6.10 (m, 2H), 1.65 (m, 1H), 0.93 – 0.83 (m, 2H), 0.65 – 0.56 (m, 2H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$), δ 156.7 (d, $J$ = 3.1 Hz), 133.5 (d, $J$ = 105.0 Hz), 131.6 (d, $J$ = 2.9 Hz), 131.2 (d, $J$ = 9.9 Hz), 128.4 (d, $J$ = 12.2 Hz), 117.7 (d, $J$ = 106.3 Hz), 16.5 (d, $J$ = 21.7 Hz), 8.48 ppm. $^{31}$P NMR (161.9 MHz, CDCl$_3$), δ 23.1 ppm. HRMS (ESI+, m/z): calcd. for C$_{17}$H$_{18}$OP, [M+H$^+$]: 269.1095; found: 269.1093.

(E)-(4-hydroxybut-1-en-1-yl)diphenylphosphine oxide (1h$^\prime$)
Synthesized using diphenylphosphine oxide (404 mg, 2.0 mmol), 3-butyn-1-ol (147 mg, 159 µL, 2.1 mmol), and RhCl(PPh$_3$)$_3$ (55 mg, 3 mol %) in 5 mL of dry toluene. White solid obtained after column chromatography (SiO$_2$, n-pentane/AcOEt 1:1), 485 mg, 89% yield.
(E)-4-(diphenylphosphoryl)but-3-en-1-yl propionate (1h)

1h' (300 mg, 1.1 mmol) and triethylamine (223 mg, 300 µL, 2.20 mmol) was dissolved in THF (10 ml) and the solution was cooled to 0°C. Propionyl chloride (144 µL, 153 mg, 1.65 mmol) was then added and the reaction mixture was stirred for 2h at rt. Water (5 mL) was then added, the resulting mixture was extracted with AcOEt (2× 10 mL), and the combined organic layer was washed with brine, dried over Na2SO4, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (SiO2, n-pentane/AcOEt 1:1) to afford the propionate ester 1h. 314 mg, 87% yield. 1H NMR (400 MHz, CDCl3), δ 7.72 – 7.64 (m, 4H), 7.55 – 7.49 (m, 2H), 7.49 – 7.42 (m, 4H), 6.77 – 6.65 (m, 1H), 6.33 (ddt, JPH = 23.9, JHH = 17.1 Hz, JHH = 1.3 Hz, 1H), 4.21 (t, J = 6.4 Hz, 2H), 2.63 (q, J = 6.4 Hz, 2H), 2.28 (q, J = 7.6 Hz, 2H), 1.08 (d, J = 7.6 Hz, 3H) ppm. 13C NMR (101 MHz, CDCl3), δ 174.2, 147.6, 132.6 (d, J = 105.3 Hz), 131.9 (d, J = 2.6 Hz), 131.3 (d, J = 10.0 Hz), 128.6 (d, J = 12.1 Hz), 124.5 (d, J = 102.2 Hz), 62.0, 33.6 (d, J = 17.3 Hz), 27.5, 9.0 ppm. 31P NMR (161.9 MHz, CDCl3), δ: 23.4 ppm. HRMS (ESI+, m/z): calcd. for C19H22O3P, [M+H+] : 329.1307; found: 329.1305.

(E)-(4-((tert-butyldimethylsilyl)oxy)but-1-en-1-yl)diphenylphosphine oxide (1i)

Synthesized using diphenylphosphine oxide (404 mg, 2.0 mmol), 4-((tert-butyldimethylsilyloxy)1-butyne (387 mg, 434 µL, 2.1 mmol), and RhCl(PPh3)3 (55 mg, 3 mol %) in 5 mL of dry toluene. White solid obtained after column chromatography (SiO2, n-pentane/AcOEt 7:3), 580 mg, 75% yield. 1H NMR (400 MHz, CDCl3), δ 7.73 – 7.65 (m, 4H), 7.53 – 7.39 (m, 6H), 6.72 – 6.59 (m, 1H), 6.31 (dd, JPH = 23.7, JHH = 17.3 Hz, 1H), 3.74 (t, J = 6.1 Hz, 2H), 2.50 (m, 2H), 0.84 (s, 9H), 0.01 (s, 6H) ppm. 13C NMR (101 MHz, CDCl3), δ 149.5, 133.0 (d, J = 105.0 Hz), 131.7 (d, J = 2.8 Hz), 131.4 (d, J = 9.9 Hz), 128.5 (d, J = 12.1 Hz), 123.8 (d, J = 102.5 Hz), 61.2, 37.9 (d, J = 16.9 Hz), 25.8, 18.2, 5.4 ppm. 31P NMR (161.9 MHz, CDCl3), δ: 23.7 ppm. HRMS (ESI+, m/z): calcd. for C22H32O2PSi, [M+H+] : 387.1909; found: 387.1907.
(E)-diphenyl(styryl)phosphine oxide (1j)
Synthesized using diphenylphosphine oxide (1212 mg, 6.0 mmol), ethynylbenzene (612 mg, 660 µL, 6.0 mmol), and RhCl(PPh₃)₃ (165 mg, 3 mol %) in 10 mL of dry toluene. White solid obtained after column chromatography (SiO₂, n-pentane/AcOEt 1:1), 1.02 g, 56% yield. Spectral data in accordance with lit. values.²

(E)-diphenyl(2-(trimethylsilyl)vinyl)phosphine oxide (1k)
Synthesized using diphenylphosphine oxide (404 mg, 2.0 mmol), ethynyltrimethylsilane (206 mg, 297 µL, 2.1 mmol), and RhCl(PPh₃)₃ (55 mg, 3 mol %) in 5 mL of dry toluene. White solid obtained after column chromatography (SiO₂, n-pentane/AcOEt 1:1), 336 mg, 56% yield. Spectral data in accordance with lit. values.²

General procedure for the asymmetric copper-catalyzed conjugate boration of α,β-unsaturated phosphine oxides: Synthesis of (R)-diphenyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl)phosphine oxide (2a).

A) Reaction performed using 0.2 mmol of substrate 1a
THF (500 µL) was added to a mixture of bis(pinacolato)diboron (78 mg, 0.3 mmol), 1a (63 mg, 0.2 mmol), CuPF₆(CH₃CN)₄ (7.5 mg, 0.02 mmol), and (R,Sp)-Josiphos (15.4 mg, 0.024 mmol), and the mixture was stirred for 10 min at room temperature. A THF
solution of 1 M lithium tert-butoxide (30 μL, 0.03 mmol) and subsequently MeOH (13 mg, 16 μL, 0.4 mmol) were then added, and the solution was stirred for 16 h. The reaction mixture was diluted with EtOAc (10 mL), water (5 mL) was added, and the mixture was stirred for 5 min. The resulting aqueous phase was extracted with AcOEt (2× 10 mL), and the combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO₂, n-pentane/AcOEt 7:3), affording product 2a (78 mg, 89% yield, 97:3 e.r.) as a colorless oil.

**B) Reaction performed using 4 mmol of substrate 1a**

THF (6 mL) was added to a mixture of bis(pinacolato)diboron (1524 mg, 6 mmol), 1a (1250 mg, 4 mmol), CuPF₆(CH₃CN)₄ (150 mg, 0.4 mmol), and (R,S₉)-Josiphos (308 mg, 0.48 mmol), and the mixture was stirred for 10 min at room temperature. A THF solution of 1 M lithium tert-butoxide (600 μL, 0.60 mmol) was then added dropwise, subsequently MeOH (192 mg, 243 μL, 6 mmol) was slowly added over 5 min and the solution was stirred for 16 h. The reaction mixture was diluted with EtOAc (20 mL), water (10 mL) was added, and the mixture was stirred for 5 min. The resulting aqueous phase was extracted with AcOEt (2× 10 mL), and the combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO₂, n-pentane/AcOEt 7:3), affording product 2a (1620 mg, 92% yield, 97:3 e.r.) as a colorless oil. ¹H NMR (400 MHz, CDCl₃), δ: 7.78 – 7.70 (m, 4H), 7.50 – 7.39 (m, 6H), 2.58 – 2.49 (m, 1H), 2.25 – 2.16 (m, 1H), 1.50 – 1.35 (m, 3H), 1.28 – 1.10 (m, 20H), 0.83 (t, J = 6.8 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃), δ: 134.0 (d, J = 96.0 Hz, 1C), 133.9 (d, J = 96.0 Hz, 1C), 131.3 (m, 2C), 130.9 (d, J = 9.0 Hz, 2C), 130.9 (d, J = 9.0 Hz, 2C), 128.4 (d, J = 11.4 Hz, 4C), 83.3, 32.6 (d, J = 10.4 Hz), 31.7, 30.5 (d, J = 71.6 Hz), 29.3, 28.3, 24.84 (2C), 24.76 (2C), 24.6 (2C), 22.5, 14.0 ppm. ³¹P NMR (161.9 MHz, CDCl₃), δ: 32.6 ppm. [α]D²⁰ = -7.0 (c = 1.0, CHCl₃).

HRMS (ESI+, m/z): calcd. for C₂₆H₃₉BO₃P, [M+H⁺]: 441.2730; found: 441.2728.

Enantiomeric ratio was determined by chiral HPLC analysis, Chiralpak AS-H column, n-heptane/i-PrOH 98:2, 40 °C, retention times (min): 13.1 (minor) and 15.5 (major).
(R)-Diphenyl{(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)phosphine oxide (2b)

The title compound was prepared from 1b (57 mg, 0.2 mmol) following general procedure A. Purification by column chromatography (SiO₂, n-pentane/EtOAc 7:3) afforded 2b (71 mg, 86% yield, 97:3 e.r.) as a colorless oil. ¹H NMR (400 MHz, CDCl₃), δ 7.78 – 7.67 (m, 4H), 7.49 – 7.38 (m, 6H), 2.60 – 2.48 (m, 1H), 2.29 – 2.15 (m, 1H), 1.52 – 1.33 (m, 3H), 1.29 – 1.08 (m, 14H), 0.90 – 0.82 (m, 2H), 0.79 (t, J = 7.0 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃), δ: 133.9 (d, J = 98.1 Hz, 1C), 133.8 (d, J = 97.3 Hz, 1C), 131.3 (m, 2C), 130.9 (d, J = 9.2 Hz, 2C), 130.8 (d, J = 9.0 Hz, 2C), 128.4 (d, J = 11.3 Hz, 4C), 83.3, 32.2 (d, J = 10.2 Hz), 30.5, 30.4 (d, J = 71.7 Hz), 24.8 (2C), 24.7 (2C), 24.5 (2C), 22.6, 13.9 ppm. ³¹P NMR (161.9 MHz, CDCl₃), δ: 32.9 ppm.

[α]D²⁰ = -7.0 (c = 1.0, CHCl₃).

HRMS (ESI+, m/z): calcd. for C₂₄H₃₅BO₃P, [M+H⁺]: 413.2417; found: 413.2416.
Enantiomeric ratio was determined by chiral HPLC analysis, Chiralpak AS-H column, n-heptane/i-PrOH 98:2, 40 °C, retention times (min): 15.7 (minor) and 18.8 (major).

(R)-Diphenyl{(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dodecyl)phosphine oxide (2c)

The title compound was prepared from 1c (74 mg, 0.2 mmol) following general procedure A. Purification by column chromatography (SiO₂, n-pentane/EtOAc 7:3) afforded 2c (89 mg, 90% yield, 96:4 e.r.) as a colorless oil. ¹H NMR (400 MHz, CDCl₃),
δ 7.75 – 7.68 (m, 4H), 7.47 – 7.36 (m, 6H), 2.58 – 2.46 (m, 1H), 2.25 – 2.14 (m, 1H), 1.48 – 1.35 (m, 3H), 1.31 – 1.04 (m, 28H), 0.85 (t, J = 6.7 Hz, 3H) ppm. 13C NMR (101 MHz, CDCl3), δ: 133.8 (d, J = 97.4 Hz, 1C), 133.8 (d, J = 96.5 Hz, 1C), 131.3 (m, 2C), 130.9 (d, J = 9.1 Hz, 2C), 130.8 (d, J = 8.8 Hz, 2C), 128.4 (d, J = 11.4 Hz, 4C), 82.2, 32.5 (d, J = 10.4 Hz), 31.8, 30.3 (d, J = 71.7 Hz), 29.5, 29.4, 29.3, 29.2, 28.2, 24.7 (2C), 24.6 (2C), 24.4 (2C), 22.6, 14.0 ppm. 31P NMR (161.9 MHz, CDCl3), δ: 32.5 ppm.


Enantiomeric ratio was determined by chiral HPLC analysis, Chiralpak AS-H column, n-heptane/i-PrOH 98:2, 40 °C, retention times (min): 11.0 (minor) and 12.5 (major).

\[(R)-\text{Diphenyl}(4\text{-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl}}\text{phosphine oxide (2d)}\]

The title compound was prepared from 1d (67 mg, 0.2 mmol) following general procedure A. Purification by column chromatography (SiO2, n-pentane/EtOAc 1:1) afforded 2d (69 mg, 75% yield, 96:4 e.r.) as a colorless oil. 1H NMR (400 MHz, CDCl3), δ 7.78 – 7.70 (m, 4H), 7.50 – 7.39 (m, 6H), 7.26 – 7.18 (m, 2H), 7.13 (t, J = 7.1 Hz, 1H), 7.06 (t, J = 7.4 Hz, 2H), 2.64 – 2.49 (m, 2H), 2.32 – 2.23 (m, 1H), 1.86 – 1.73 (m, 2H), 1.55 – 1.45 (m, 1H), 1.25 (m, 1H), 1.23 (s, 12H) ppm. 13C NMR (101 MHz, CDCl3), δ: 142.3, 133.7 (d, J = 96.4 Hz, 2C), 131.4 (m, 2C), 131.0 (d, J = 9.2 Hz, 2C), 130.9 (d, J = 9.2 Hz, 2C), 128.5 (d, J = 11.4 Hz, 2C), 128.4 (d, J = 11.4 Hz, 2C), 128.3, 128.2, 125.6, 83.5, 34.8, 34.5 (d, J = 10.3 Hz), 30.5 (d, J = 71.5 Hz), 24.9 (2C), 24.8 (2C), 24.6 (2C) ppm. 31P NMR (161.9 MHz, CDCl3), δ: 32.4 ppm.

\[[\alpha]_D^{20} = +1.6 \ (c = 1.0, \text{CHCl}_3)\].

Enantiomeric ratio was determined by chiral HPLC analysis, Chiralpak AS-H column, n-heptane/i-PrOH 98:2, 40 °C, retention times (min): 21.3 (minor) and 31.7 (major).

\[
(R)-(3\text{-Cyclopentyl-2-}(4,4,5,5\text{-tetramethyl-1,3,2-dioxaborolan-2-yl})\text{propyl})\text{diphenylphosphine oxide (2e)}
\]

The title compound was prepared from 1e (62 mg, 0.2 mmol) following general procedure A. Purification by column chromatography (SiO₂, n-pentane/EtOAc 7:3) afforded 2e (75 mg, 86% yield, 98:2 e.r.) as a colorless oil. 

\[
\begin{align*}
    &\text{δ} 7.77 – 7.69 (m, 4H), 7.48 – 7.38 (m, 6H), 2.55 – 2.45 (m, 1H), 2.28 – 2.19 (m, 1H), 1.78 – 1.70 (m, 1H), 1.69 – 1.61 (m, 1H), 1.57 – 1.46 (m, 3H), 1.44 – 1.36 (m, 3H), 1.23 – 1.20 (m, 1H), 1.01 – 0.87 (m, 2H) ppm. \\
    &\text{13C NMR (101 MHz, CDCl₃), δ: 134.0 (d, } J = 96.6 \text{ Hz, 1C), 133.7 (d, } J = 96.9 \text{ Hz, 1C), 131.3 (m, 2C), 130.9 (d, } J = 9.3 \text{ Hz, 4C), 128.4 (d, } J = 11.5 \text{ Hz, 4C), 83.3, 38.92 (d, } J = 10.9 \text{ Hz), 38.90, 32.7, 32.5, 30.8 (d, } J = 71.3 \text{ Hz), 25.1, 25.0, 24.9 (2C), 24.8 (2C), 24.6 (2C) ppm.} \\
    &\text{31P NMR (161.9 MHz, CDCl₃), δ: 32.4 ppm.}
\end{align*}
\]

\[\alpha_D^{20} = -10.0 \ (c = 1.0, \text{CHCl₃}).\]

HRMS (ESI+, m/z): calcd. for C₂₆H₃₇BO₃P, [M+H⁺]: 439.2573; found: 439.2573.

Enantiomeric ratio was determined by chiral HPLC analysis, Chiralpak AS-H column, n-heptane/i-PrOH 99:1, 40 °C, retention times (min): 29.4 (minor) and 33.2 (major).
(R)-(3-cyclohexyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)diphenyl-phosphine oxide (2f)

The title compound was prepared from 1f (65 mg, 0.2 mmol) following general procedure A. Purification by column chromatography (SiO₂, n-pentane/EtOAc 7:3) afforded 2f (72 mg, 80% yield, 97:3 e.r.) as a colorless oil. ¹H NMR (400 MHz, CDCl₃), δ 7.75 – 7.67 (m, 4H), 7.46 – 7.35 (m, 6H), 2.51 – 2.42 (m, 1H), 2.20 – 2.13 (m, 1H), 1.61 – 1.50 (m, 4H), 1.47 – 1.36 (m, 1H), 1.36 – 1.25 (m, 4H), 1.25 – 1.14 (m, 14H), 1.10 – 0.96 (m, 2H), 0.75 – 0.61 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃), δ: 133.8 (d, J = 96.8 Hz, 1C), 133.5 (d, J = 96.8 Hz, 1C), 131.4 (m, 2C), 131.0 (d, J = 9.3 Hz, 4C), 128.4 (d, J = 11.5 Hz, 4C), 83.3, 40.1 (d, J = 10.9 Hz), 36.3, 33.2, 33.1, 30.7 (d, J = 71.6 Hz), 26.5, 26.30, 26.27, 24.8 (2C), 24.5 (2C), 24.1 (2C) ppm. ³¹P NMR (161.9 MHz, CDCl₃), δ: 32.8 ppm.

[α]D²⁰ = -11.0 (c = 1.0, CHCl₃).

HRMS (ESI+, m/z): calcd. for C₂₇H₃₉BO₃P, [M+H⁺]: 453.2730; found: 453.2729.

Enantiomeric ratio was determined by chiral HPLC analysis, Chiralpak AS-H column, n-heptane/i-PrOH 98:2, 40 °C, retention times (min): 28.6 (minor) and 31.3 (major).

(S)-(2-Cyclopropyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)diphenyl-phosphine oxide (2g)

The title compound was prepared from 1g (54 mg, 0.2 mmol) following general procedure A using (S,Rp)-Josiphos as ligand. Reaction time: 48 h. Purification by column chromatography (SiO₂, n-pentane/EtOAc 7:3) afforded 2g (75 mg, 95% yield, 93:7 e.r.) as a colorless oil. ¹H NMR (400 MHz, CDCl₃), δ 7.77 – 7.69 (m, 4H), 7.47 – 7.36 (m, 6H), 2.68 – 2.59 (m, 1H), 2.46 – 2.38 (m, 1H), 1.23 (s, 6H), 1.20 (s, 3H), 1.19 (s, 3H), 0.79 – 0.67 (m, 2H), 0.40 – 0.33 (m, 1H), 0.30 – 0.23 (m, 1H), 0.18 – 0.11 (m, 1H), 0.00 – -0.05 (m, 1H) ppm. ¹³C NMR (101 MHz, CDCl₃), δ: 134.1 (d, J = 97.2 Hz, 1C), 133.5
(d, J = 97.0 Hz, 1C), 131.3 (m, 2C), 130.9 (d, J = 8.8 Hz, 2C), 130.8 (d, J = 9.5 Hz, 2C),
128.4 (d, J = 11.7 Hz, 2C), 128.3 (d, J = 11.4 Hz, 2C), 83.4, 31.4 (d, J = 71.1 Hz), 24.7
(1C), 24.7 (1C), 24.5 (2C), 24.1 (2C), 14.3 (d, J = 14.7 Hz), 5.6, 4.6 ppm. $^{31}$P NMR
(161.9 MHz, CDCl$_3$), $\delta$: 31.7 ppm.

$[\alpha]_D^{20} = +15.0$ (c = 1.0, CHCl$_3$).

HRMS (ESI+, m/z): calcd. for C$_{23}$H$_{31}$BO$_3$P, [M+H$^+$]: 397.2104; found: 397.2099.

Enantiomeric ratio was determined by chiral HPLC analysis, Chiralpak AS-H column, n-
heptane/i-PrOH 98:2, 40 °C, retention times (min): 19.0 (major) and 24.6 (minor).

\[\text{(R)-4-(Diphenylphosphoryl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl propionate (2h)}\]

The title compound was prepared from 1h (66 mg, 0.2 mmol) following general
procedure A. Reaction time: 24 h. Purification by column chromatography (SiO$_2$, n-
pentane/EtOAc 1:1) afforded 2h (62 mg, 68% yield, 97:3 e.r.) as a colorless oil. $^1$H NMR
(400 MHz, CDCl$_3$), $\delta$: 7.78 – 7.67 (m, 4H), 7.51 – 7.39 (m, 6H), 4.11 – 3.96 (m, 2H), 2.61
– 2.48 (m, 1H), 2.31 – 2.22 (m, 1H), 2.20 (q, J = 7.5 Hz, 2H), 1.82 (q, J = 6.5 Hz, 2H),
1.55 – 1.39 (m, 1H), 1.21 (s, 12H), 1.05 (t, J = 7.5 Hz, 3H) ppm. $^{13}$C NMR (101 MHz,
CDCl$_3$), $\delta$: 174.4, 133.7 (m, 2C), 131.5 (d, J = 6.7 Hz, 2C), 130.9 (m, 4C), 128.5 (m, 4C),
83.6, 63.0, 30.8, 30.2 (d, J = 74.5 Hz), 27.5, 24.8 (2C), 24.7 (2C), 24.6 (2C), 9.0 ppm. $^{31}$P
NMR (161.9 MHz, CDCl$_3$), $\delta$: 32.8 ppm.

$[\alpha]_D^{20} = -26.2$ (c = 1.0, CHCl$_3$).

HRMS (ESI+, m/z): calcd. for C$_{25}$H$_{35}$BO$_5$P, [M+H$^+$]: 457.2315; found: 457.2311.

Enantiomeric ratio was determined by chiral HPLC analysis, Chiralpak AS-H column, n-
heptane/i-PrOH 98:2, 40 °C, retention times (min): 38.2 (minor) and 42.0 (major).
(S)-(4-((tert-Butyldimethylsilyl)oxy)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)diphenylphosphine oxide (2i)

The title compound was prepared from 1i (77 mg, 0.2 mmol) following general procedure A using (S,Rp)-Josiphos as ligand. Reaction time: 48 h. Purification by column chromatography (SiO2, n-pentane/EtOAc 7:3) afforded 2i (90 mg, 87% yield, 96:4 e.r.) as a colorless oil. ¹H NMR (400 MHz, CDCl₃), δ 7.75 – 7.68 (m, 4H), 7.47 – 7.37 (m, 6H), 3.61 – 3.49 (m, 2H), 2.58 – 2.45 (m, 1H), 2.34 – 2.25 (m, 1H), 1.77 – 1.63 (m, 2H), 1.49 – 1.38 (m, 1H), 1.20 (s, 3H), 1.20 (s, 3H), 1.19 (s, 6H), 0.81 (s, 9H), 0.04 (s, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃), δ: 133.8 (d, J = 97.1 Hz, 1C), 133.7 (d, J = 97.0 Hz, 1C), 131.4 (m, 2C), 130.9 (d, J = 9.2 Hz, 2C), 130.9 (d, J = 9.2 Hz, 2C), 128.4 (d, J = 11.5 Hz, 2C), 128.4 (d, J = 11.5 Hz, 2C), 128.4 (d, J = 11.5 Hz, 2C), 83.4, 62.3, 35.4 (d, J = 10.4 Hz), 30.7 (d, J = 71.6 Hz), 25.9, 24.8 (1C), 24.8 (1C), 24.8 (2C), 24.6 (2C), 18.3, -5.3 ppm. ³¹P NMR (161.9 MHz, CDCl₃), δ: 32.5 ppm. [α]D²⁰ = +5.6 (c = 1.0, CHCl₃).

HRMS (ESI+, m/z): calcd. for C₂₈H₄₄BO₄PSi, [M+H⁺]: 515.2918; found: 515.2908.

Enantiomeric ratio was determined by chiral HPLC analysis, Chiralpak AS-H column, n-heptane/i-PrOH 98:2, 40 °C, retention times (min): 10.5 (major) and 13.4 (minor).

(R)-Diphenyl(2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phosphine oxide (2j)
The title compound was prepared from 1j (61 mg, 0.2 mmol) following general procedure A using (1R,2R)-N,N'-dimethyl-1,2-diphenylethane-1,2-diamine as ligand and DME as solvent. Reaction time: 24 h. Purification by column chromatography (SiO2, n-pentane/EtOAc 7:3) afforded 2j (62 mg, 72% yield, 90:10 e.r.) as a colorless oil. 1H NMR (400 MHz, CDCl3), δ 7.74 – 7.65 (m, 2H), 7.64 – 7.44 (m, 2H), 7.45 – 7.35 (m, 4H), 7.34 – 7.28 (m, 2H), 7.12 – 7.07 (m, 4H), 7.05 – 6.99 (m, 1H), 3.05 – 2.92 (m, 1H), 2.81 – 2.70 (m, 1H), 2.55 – 2.44 (m, 1H), 1.10 (s, 6H), 1.09 (s, 6H) ppm. 13C NMR (101 MHz, CDCl3), δ: 142.4, 131.3 (d, J = 17.8 Hz, 2C), 130.9 (d, J = 9.0 Hz, 2C), 130.7 (d, J = 9.0 Hz, 2C), 128.5 – 128.2 (m), 128.1, 125.6, 83.7, 32.5 (d, J = 70.1 Hz), 24.6 (2C), 24.5 (2C), 24.3 (2C) ppm. 31P NMR (161.9 MHz, CDCl3), δ: 31.4 ppm. HRMS (ESI+, m/z): calcd. for C26H31BO3P, [M+H+] : 433.2104; found: 433.2103.

Enantiomeric ratio was determined by chiral HPLC analysis, Chiralpak AS-H column, n-heptane/i-PrOH 98:2, 40 °C, retention times (min): 25.9 (minor) and 31.5 (major).

![Chemical structure](image)

**(S)-Diphenyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)ethyl)phosphine oxide (2k)**

The title compound was prepared from 1k (60 mg, 0.2 mmol) following general procedure A using (1R,2R)-N,N'-dimethyl-1,2-diphenylethane-1,2-diamine as ligand and DME as solvent. Reaction time: 24 h. 82% conversion (determined by GC analysis and 31P NMR). Purification by column chromatography (SiO2, n-pentane/EtOAc 7:3) afforded 2k (58 mg, 68% yield, 85:15 e.r.) as a colorless oil. 1H NMR (400 MHz, CDCl3), δ 7.76 – 7.69 (m, 4H), 7.48 – 7.37 (m, 6H), 2.65 – 2.55 (m, 1H), 2.21 – 2.14 (m, 1H), 1.16 (s, 6H), 1.13 (s, 6H), 0.71 – 0.64 (m, 1H), 0.04 (s, 9H) ppm. 13C NMR (101 MHz, CDCl3), δ: 133.9 (d, J = 95.6 Hz, 1C), 133.3 (d, J = 96.6 Hz, 1C), 131.3 (m, 2C), 131.1 (d, J = 9.3 Hz, 2C), 131.0 (d, J = 9.4 Hz, 2C), 128.4 (d, J = 11.5 Hz, 2C), 128.3 (d,
\( J = 11.5 \text{ Hz, 2C}, 83.1, 25.3 \text{ (d, } J = 70.0 \text{ Hz), 25.2 (2C), 24.8 (2C), 24.8 (1C), 24.6 (1C), -1.9 \text{ ppm.} \)

\[ ^{31}\text{P NMR (161.9 MHz, CDCl}_3\text{), } \delta: 33.5 \text{ ppm.} \]

\([\alpha]^{20}_D = -3.0 \text{ (c = 1.0, CHCl}_3\text{).} \]

HRMS (ESI+, \( m/z \): calcd. for C\(_{23}\)H\(_{35}\)BO\(_3\)PSi, [M+H\(^+\)]: 429.2186; found: 429.2186.

Enantiomeric ratio was determined by chiral HPLC analysis, Chiralpak AS-H column, n-heptane/i-PrOH 98:2, 40 °C, retention times (min): 12.4 (minor) and 15.3 (major).

**Copper-catalyzed methylboration of 1a: Synthesis of diphenyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonan-2-yl)phosphine oxide (2l)**

THF (1.5 mL) was added to a mixture of bis(pinacolato) diboron (190 mg, 0.75 mmol), 1a (156 mg, 0.5 mmol), CuPF\(_6\)(CH\(_3\)CN\(_3\))\(_4\) (18.6 mg, 0.05 mmol), and (R,S\(_p\))-Josiphos (39 mg, 0.06 mmol), and the mixture was stirred for 10 min at room temperature. A THF solution of 1 M lithium tert-butoxide (0.55 mL, 0.55 mmol) and subsequently MeI (248 mg, 124 \( \mu \text{L, 2.0 mmol} \)) were then added, and the solution was stirred for 24 h. The reaction mixture was diluted with EtOAc (10 mL), water (5 mL) was added, and the mixture was stirred for 5 min. The resulting aqueous phase was extracted with AcOEt (2× 10 mL), and the combined organic layer was washed with brine, dried over Na\(_2\)SO\(_4\), and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO\(_2\), n-pentane/MeOH 7:3), affording product 2l (143 mg, 63% yield, 5.2:1 d.r.) as a colorless oil. \(^1\text{H NMR (400 MHz, CDCl}_3\text{), } \delta: 7.83 – 7.75 \text{ (m, 4H), 7.46 – 7.39 \text{ (m, 6H), 2.51 – 2.43 \text{ (m, 1H), 1.56 – 1.45 \text{ (m, 1H), 1.28 (s, 6H), 1.27 (s, 6H), 1.28 – 1.10 \text{ (m, 13H), 0.83 (t, } J = 6.9 \text{ Hz, 3H) ppm.} \)

\[^{13}\text{C NMR (101 MHz, CDCl}_3\text{), } \delta: 133.1 \text{ (d, } J = 94.0 \text{ Hz, 1C), 133.0 \text{ (d, } J = 93.0 \text{ Hz, 1C), 131.2 – 130.0 \text{ (m), 128.4 (d, } J = 11.4 \text{ Hz, 2C), 128.4 (d, } J = 11.4 \text{ Hz, 2C), 83.1, 34.4 (d, } J = 72.5 \text{ Hz), 31.6, 30.7 (d, } J = 33.0 \text{ Hz), 29.2, 28.7, 25.0 (2C), 24.9 (2C), 24.9 (2C), 22.5, 14.0, 10.8 (d, } J = 2.5 \text{ Hz) ppm.} \)

\[^{31}\text{P NMR (161.9 MHz, CDCl}_3\text{), } \delta: 37.0 \text{ ppm.} \)
Transformation from chiral organoboronate 2a to secondary alcohol: Synthesis of (R)-(2-hydroxyoctyl)diphenylphosphine oxide (3)

Sodium perborate tetrahydrate (128 mg, 0.83 mmol) was added in one portion to a solution of 2a (73 mg, 0.17 mmol, 96:4 e.r) in aqueous THF (2 mL, THF/H₂O = 1/1), and the mixture was stirred for 2 h. After diluting the reaction mixture with water (5 ml), the aqueous solution was extracted with EtOAc (3× 10 mL). The combined organic layer was dried over Na₂SO₄ and the solvent evaporated. The residue was purified by flash column chromatography (SiO₂, n-pentane/AcOEt 1:1), affording product 3 (47 mg, 86% yield, 96:4 e.r.) as a colorless oil. ¹H NMR (400 MHz, CDCl₃), δ 7.78 – 7.67 (m, 4H), 7.57 – 7.43 (m, 6H), 4.05 (m, 1H), 2.49 – 2.34 (m, 2H), 1.66 – 1.55 (m, 1H), 1.50 – 1.40 (m, 1H), 1.40 – 1.32 (m, 1H), 1.32 – 1.15 (m, 7H), 0.83 (t, J = 6.7 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃), δ: 133.4 (d, J = 99.5 Hz, 1C), 132.0 (m, 2C), 131.9 (d, J = 97.9 Hz, 1C), 130.9 (d, J = 9.6 Hz, 2C), 130.4 (d, J = 9.8 Hz, 2C), 128.8 (d, J = 11.7 Hz, 2C), 128.7 (d, J = 11.7 Hz, 2C), 66.9 (d, J = 5.1 Hz), 38.7 (d, J = 13.2 Hz), 36.3 (d, J = 71.6 Hz), 31.7, 29.1, 25.2, 22.5, 14.0 ppm. ³¹P NMR (161.9 MHz, CDCl₃), δ: 34.5 ppm. 

[α]_D^20 = -25.2 (c = 1.0, CHCl₃).

HRMS (ESI+, m/z): calcd. for C₂₀H₂₈O₂P, [M+H⁺]: 331.1827; found: 331.1824.

Enantiomeric ratio was determined by chiral HPLC analysis, Chiralpak AS-H column, n-heptane/i-PrOH 95:5, 40 °C, retention times (min): 16.6 (major) and 20.0 (minor).
C(sp\(^3\))-C(sp\(^2\)) coupling of 2a with furan using NBS: Synthesis of (S)-(2-(furan-2-yl)octyl)diphenylphosphine oxide (4)

A solution of furan (21 mg, 23 µL, 1.2 eq.) in THF (1.04 mL, 0.3M) was cooled to –78 °C and treated with \textit{n}-BuLi (195 µL, 1.2 eq., 1.6M in hexanes). The cooling bath was removed and the mixture was stirred at room temperature for 1 h. The mixture was cooled to –78 °C and 2a (96:4 e.r, 115 mg, 0.26 mmol, 1.0 eq.) was added dropwise as a solution in THF (0.5 mL, 0.5M). The mixture was stirred at –78 °C for 1 h followed by dropwise addition of a solution of NBS (56 mg, 0.312 mmol, 1.2 eq.) in THF (1 mL, 0.3M). After 1 h at –78 °C, Na\(_2\)S\(_2\)O\(_3\) aq. was added and the reaction mixture was allowed to warm to room temperature. The reaction mixture was diluted with EtOAc (10 mL) and water (5mL). The layers were separated and the aqueous layer was extracted with EtOAc (3× 10 mL). The combined organic layers were dried (Na\(_2\)SO\(_4\)), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO\(_2\), \textit{n}-pentane/AcOEt 8:2) or (C18-bonded silica, CH\(_3\)CN/H\(_2\)O 1:1), affording product 4 (79% conversion, 66 mg, 67% yield, 96:4 e.r.) as a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\): 7.73 – 7.65 (m, 2H), 7.63 – 7.55 (m, 2H), 7.48 – 7.30 (m, 6H), 7.07 (d, \(J = 1.2\) Hz, 1H), 5.98 (dd, \(J = 3.2, J = 1.9\) Hz, 1H), 5.8 (d, \(J = 3.1\) Hz, 1H), 3.37 – 3.27 (m, 1H), 2.77 – 2.69 (m, 1H), 2.51 (td, \(J = 14.3, J = 5.9\) Hz, 1H), 1.75 – 1.62 (m, 2H), 1.35 – 1.00 (m, 8H), 0.81 (t, \(J = 6.8\) Hz, 3H) ppm. \(^{13}\)C NMR (101 MHz, CDCl\(_3\), \(\delta\): 155.9 (d, \(J = 7.1\) Hz, 1C), 140.7, 134.2 (d, \(J = 98.9\) Hz, 1C), 132.0 (d, \(J = 99.0\) Hz, 1C), 131.5 (d, \(J = 2.7\) Hz, 1C), 131.2 (d, \(J = 2.7\) Hz, 1C), 130.7 (d, \(J = 9.4\) Hz, 2C), 130.4 (d, \(J = 9.4\) Hz, 2C), 128.5 (d, \(J = 11.7\) Hz, 2C), 128.3 (d, \(J = 11.7\) Hz, 2C), 109.8, 106.4, 35.7 (d, \(J = 8.7\) Hz), 34.8, 34.1, 32.8 (d, \(J = 3.4\) Hz), 31.6, 28.9, 27.0, 22.5 ppm. \(^{31}\)P NMR (161.9 MHz, CDCl\(_3\), \(\delta\): 30.2 ppm. 

[\(\alpha\)]\(_{D}^{20}\) = -2.2 (c = 1.0, CHCl\(_3\)).

HRMS (ESI+, \(m/z\): calcd. for C\(_{24}\)H\(_{30}\)O\(_2\)P, [M+H\(^+\)]: 381.1983; found: 381.1977.
Enantiomeric ratio was determined by chiral HPLC analysis, Chiralcel OD-H column, n-heptane/i-PrOH 98:2, 40 °C, retention times (min): 28.4 (minor) and 38.8 (major).

**Reduction of (S)-2a to phosphine boronate ester: Synthesis of (S)-diphenyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl)phosphane (5)**

**Method A)**

To a solution of (R)-2a (220 mg, 0.5 mmol) in toluene (4 mL) were added degassed triethylamine (144 µL, 1.05 mmol) and trichlorosilane (0.5 mL, 4.7 mmol). The mixture was stirred at 90 °C for 16h and the solvent removed in vacuo. After addition of Et₂O (20 mL), a yellow suspension was obtained which was filtered under a nitrogen atmosphere. The filtrate was diluted with degassed water and extracted with Et₂O. The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. Flash column chromatography (SiO₂, n-pentane/AcOEt 20:1), afforded product 5 (140 mg, 66% yield) as a colorless oil.

**Method B)**

A 25 mL dried Schlenk tube containing a stirring bar was charged with 5 (13.0 mg, 0.04 mmol) and (S)-2a (220 mg, 0.5 mmol). Under Ar flow, dry toluene (2 mL) and (EtO)₂MeSiH (320 µL, 2.0 mmol) were added, and the mixture was stirred at 110 °C for 16h. Then, the reaction mixture was cooled to r.t., diluted with EtOAc (10 mL) and water (5mL). The layers were separated and the aqueous layer was extracted with EtOAc (3×
10 mL). The combined organic layer was dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO₂, n-pentane/AcOEt 20:1), affording product 5 (77% conv., 124 mg, 58% yield) as a colorless oil.

\[ \text{H NMR (400 MHz, CDCl₃), } \delta \text{ 7.46 – 7.38 (m, 4H), 7.35 – 7.28 (m, 6H), 2.21 (dd, } J = 13.4, J = 9.2 \text{ Hz, 1H), 2.51 (ddd, } J = 13.4, J = 6.5 \text{ Hz, } J = 1.5 \text{ Hz, 1H), 1.51 (m, 2H), 1.30 – 1.18 \text{ (m, 8H), 1.27 (s, 12H), 1.05 (m, 1H), 0.86 (t, } J = 6.7 \text{ Hz, 3H ppm.} \]

\[ \text{C NMR (101 MHz, CDCl₃), } \delta: 139.4 \text{ (d, } J = 12.3 \text{ Hz, 1C), 139.0 \text{ (d, } J = 12.7 \text{ Hz, 1C), 133.1 (d, } J = 18.6 \text{ Hz, 2C), 132.5 (d, } J = 17.9 \text{ Hz, 2C), 128.5, 128.3 \text{ (d, } J = 6.5 \text{ Hz, 2C), 128.3 (d, } J = 6.5 \text{ Hz, 2C), 128.2, 83.1, 32.9 (d, } J = 13.1 \text{ Hz), 31.8, 30.2 (d, } J = 11.1 \text{ Hz), 29.4, 28.8, 24.87 (2C), 24.86 (2C), 22.6, 20.6, 14.1 ppm.} \]

\[ \text{P NMR (161.9 MHz, CDCl₃), } \delta: -17.2 \text{ ppm.} \]

\[ \text{EI-MS m/z: 424, 186 (100%).} \]

**Conversion of (S)-5 into phosphine-borane complex (S)-6.**

In an oven dried Schlenk tube equipped with septum and stirring bar under a N₂ atmosphere, phosphine-borionate (S)-6 (69 mg, 0.16 mmol) was dissolved in anhydrous THF (1.0 mL), and BH₃-THF (1M solution in THF, 250 µL, 0.25 mmol) was then added dropwise. The reaction mixture was stirred for 1 h and the solvent was removed in vacuo. Flash column chromatography (SiO₂, n-pentane/AcOEt 9:1) afforded (S)-7 as a waxy solid. (58 mg, 83% yield).  

\[ \text{H NMR (400 MHz, CDCl₃), } \delta: 7.73 – 7.65 \text{ (m, 4H), 7.48 – 7.36 \text{ (m, 6H), 2.58 – 2.50 \text{ (m, 1H), 2.20 – 2.11 \text{ (m, 1H), 1.44 – 1.29 \text{ (m, 4H), 1.26 – 1.08 \text{ (m, 10H), 1.19 (s, 6H), 1.18 (s, 6H), 0.84 (t, } J = 6.7 \text{ Hz, 3H ppm.}} \]

\[ \text{C NMR (101 MHz, CDCl₃), } \delta: 132.3 \text{ (d, } J = 8.8 \text{ Hz, 1C), 132.3 (d, } J = 8.8 \text{ Hz, 1C), 130.9 (d, } J = 2.3 \text{ Hz, 2C), 130.8 (d, } J = 2.3 \text{ Hz, 2C), 130.6 (d, } J = 9.5 \text{ Hz, 2C), 130.1 (d, } J = 9.5 \text{ Hz, 2C), 128.6 (d, } J = 2.3 \text{ Hz, 1C), 128.5 (d, } J = 2.3 \text{ Hz, 1C), 83.4, 32.9 (d, } J = 8.8 \text{ Hz), 31.7, 29.3, 28.1, 26.0} \]
(d, $J = 35.4$ Hz), 24.9, 24.8, 22.5, 17.7, 14.1 ppm. $^{31}$P NMR (161.9 MHz, CDCl$_3$), $\delta$: 17.2 (d, $J_{PB} = 65$ Hz) ppm. 

$[\alpha]_D^{20} = +6.0$ (c = 1.0, CHCl$_3$).

HRMS (ESI+, m/z): calcd. for C$_{26}$H$_{40}$B$_2$O$_2$P', [M-H']$^-$: 437.2947; found: 437.2942.

**Synthesis of Pd-complex 7**

![Diagram of Pd-complex 7 synthesis](image)

In an oven dried Schlenk tube equipped with septum and stirring bar under a N$_2$ atmosphere, PdCl$_2$(CH$_3$CN)$_2$ (11.6 mg, 0.045 mmol) was dissolved in anhydrous THF (1.0 mL), and phosphine-boronate ($S$)-5 (38 mg, 0.09 mmol) in THF (1 mL) was added. The reaction mixture was stirred for 1 h and the solvent was concentrated in vacuo. Flash column chromatography (SiO$_2$, n-pentane/AcOEt 4:1) afforded 7 as a waxy solid. (25 mg). $^1$H NMR (400 MHz, CDCl$_3$), $\delta$: 7.81 – 7.74 (m, 2H), 7.72 – 7.66 (m, 2H), 7.42 – 7.31 (m, 6H), 2.81 – 2.72 (m, 1H), 2.54 – 2.44 (m, 1H), 1.34 – 0.95 (m, 11H), 1.12 (s, 6H), 1.11 (s, 6H), 0.84 (t, $J = 7.1$ Hz, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$), $\delta$: 134.1 (m), 130.1 (m), 128.0 (m), 83.1, 33.0, 31.7, 29.5, 28.5, 25.3 (2C), 24.9 (2C), 24.8 (2C), 22.5, 18.6, 14.1 ppm. $^{31}$P NMR (161.9 MHz, CDCl$_3$), $\delta$: 18.9 ppm.

HRMS (ESI+, m/z): calcd. for C$_{52}$H$_{76}$B$_2$ClO$_4$P$_2$Pd, [5$_2$+Pd+Cl]$^+$: 989.4128; found: 989.4152.

**Synthesis of Cu-complex 8**

![Diagram of Cu-complex 8 synthesis](image)
In an oven dried Schlenk tube equipped with septum and stirring bar under a N₂ atmosphere, CuBrSMe₂ (11 mg, 0.053 mmol) was dissolved in anhydrous CH₂Cl₂ (4 mL), and phosphine-boronate (S)-5 (45 mg, 0.106 mmol) in CH₂Cl₂ (1 mL) was added. The reaction mixture was stirred for 1 h and the solvent was concentrated in vacuo. Flash column chromatography (SiO₂, n-pentane/AcOEt 4:1) afforded 8 as a waxy solid. (20 mg). ¹H NMR (400 MHz, CDCl₃), δ: 7.73 – 7.60 (m, 4H), 7.40 – 7.29 (m, 6H), 2.50 – 2.39 (m, 1H), 2.23 – 2.12 (m, 1H), 1.66 – 1.55 (m, 1H), 1.55 – 1.44 (m, 1H), 1.37 – 1.27 (m, 1H), 1.24 – 1.06 (m, 9H), 1.19 (s, 6H), 1.17 (s, 6H), 0.81 (t, J = 6.8 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃), δ: 133.4 (d, J = 13.5 Hz), 133.1 (d, J = 13.5 Hz), 130.0 (m), 128.6 (m), 83.4, 32.3 (m), 31.7, 29.4, 28.3, 28.1 (m), 24.9, 24.8, 22.5, 14.1 ppm. ³¹P NMR (161.9 MHz, CDCl₃), δ: 6.4 ppm. HRMS (ESI⁺, m/z): calcd. for C₅₂H₇₆B₂CuO₄P₂, [5₂+Cu]⁺: 911.4701; found: 911.4704.
\(-^{1}H,\ ^{13}C\text{- and }^{31}P\text{ NMR spectra}\)
S35
The image contains a 1D NMR spectrum with peaks at various chemical shifts. The spectrum shows a series of resonances at different ppm values. The chemical structure labeled as "2h" is depicted below the spectrum. The peaks are labeled with their corresponding ppm values.
NL: 2.19E5
VHG_825#6-11  RT: 0.12-0.27  AV: 6  T: FTMS + p ESI Full ms [650.00-1250.00]

NL: 2.49E5
C_{52}H_{76}B_2O_4P_2Cu:
C_{52}H_{76}B_2O_4P_2Cu
pa Chrg 1
GC-MS data of compound 2a
GC-MS data of compound 5

S70
Representative HPLC traces

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PDA Ch1 229nm

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PDA Multi 1 228nm, 4nm

PDA Ch1 228nm

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X-ray structure determination of 2a

A suitable crystals of 2a was mounted on a cryo-loop and transferred into the cold nitrogen stream of a Bruker D8 Venture diffractometer. The final unit cell was obtained from the xyz centroids of 9925 reflections after integration. Intensity data were corrected for Lorentz and polarisation effects, scale variation, for decay and absorption: a multiscan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (SADABS). The structures were solved by direct methods using the program SHELXS. The hydrogen atoms were generated by geometrical considerations and constrained to idealised geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. Structure refinement was performed with the program package SHELXL. Crystal data and details on data collection and refinement are presented in Table S1.

CCDC 1049929 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Figure S1. ORTEP diagram of 2a. Hydrogen atoms have been omitted for clarity.

---

Table S1. Crystallographic data for 2a

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