Synthesis of ligand 4b. A mixture of 6 (1.50 g, 6.76 mmol) and 4-chlorodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine (4.74 g, 13.5 mmol) in toluene (60 mL) at -40 ºC was treated drop-wise with NEt₃ (3.0 mL, 21.4 mmol) in toluene (20 mL). The mixture was allowed to warm to room temperature overnight, then filtered and the solvent was removed under vacuum to give 4b as a colourless solid (6.37 g, 94 %). ¹H NMR (300 MHz; CDCl₃): 1.30 (18H, s, tBu), 7.02-7.22 (8H, m, ArH), 7.25-7.40 (6H, m, ArH), 7.52 (2H, d, J = 9 Hz, ArH), 7.49 (2H, d, J = 9 Hz, ArH), 7.74 (2H, d, J = 9 Hz, ArH), 7.78 (2H, d, J = 8 Hz, ArH), 7.82 (2H, d, J = 9 Hz, ArH), 7.86 (2H, d, J = 9 Hz, ArH); ³¹P NMR (121 MHz; CDCl₃): 144.6 (s). Anal. calcd for C₅₄H₄₄O₆P₂: C, 76.23; H, 5.21. Found: C, 76.01; H, 5.54.

Synthesis of 7. A mixture of 6 (5.0 g, 22.5 mmol) and PCl₃ (15.0 mL, 172 mmol) in toluene (80 mL) at -40 ºC was treated drop-wise with NEt₃ (25.0 mL, 180 mmol) in toluene (20 mL). The reaction was allowed to warm to room temperature overnight. The
filtrate was collected under nitrogen, and the filtrate residue washed with toluene (2 x 20 mL). The solvent from the combined filtrate and washing was removed under vacuum to give a white solid. Toluene (2 x 20 mL) was added to this solid and then removed under vacuum to ensure the full removal of PCl₃ to give 7 as a white solid (8.70 g, 91 %) and used without further purification. ¹H NMR (300 MHz; CDCl₃): 1.30 (18H, s, tBu), 7.31 (1H, s, ArH), 7.79 (1H, s, ArH); ³¹P NMR (121 MHz; CDCl₃): 183.6 (s).

**Synthesis of Ligand 4c.** A mixture of NEt₃ (6.0 mL, 43.0 mmol) and 7 (2.00 g, 4.72 mmol) in toluene (60 mL) at -40 °C was treated drop-wise with (2R,3R)-(−)-2,3-butanediol (0.86 mL, 9.42 mmol) in toluene (20 mL). The mixture was allowed to warm to room temperature overnight, then filtered and the filtrate residue washed with toluene (2 x 20 mL). The solvent from the filtrate was removed under vacuum to give 4c as a white solid. (3.10 g, 72.5 %). ¹H NMR (300 MHz; CDCl₃): 1.28 (18H, s, tBu), 1.32 (6H, d, J = 9 Hz, CH₃), 1.40 (6H, d, J = 5 Hz, CH₃), 3.80 (2H, dq, J = 6 & 5 Hz, OCH), 4.17 (2H, dq, J = 9 & 6 Hz, OCH), 6.79 (1H, s, ArH), 7.18 (1H, s, ArH); ³¹P NMR (121 MHz; CDCl₃): 135.4 (s); ¹³C NMR (75 MHz; CDCl₃) 18.45, 19.60 (s, CH₃), 30.55 (s, CH₃ tBu), 34.92 (s, C tBu), 78.47, 81.13 (s, OCH), 112.52 (t, J = 16 Hz, CH), 125.92, 134.43, 149.47.

**Synthesis of ligand 4d.** A mixture of NEt₃ (3.0 mL, 21.5 mmol) and 7 (1.00 g, 2.36 mmol) in toluene (60 mL) at -40 °C was treated drop-wise with (D)-mannitoldiol (1.24 g, 4.72 mmol) in toluene (20 mL). The mixture was allowed to warm to room temperature overnight, then filtered and the filtrate residue washed with toluene (2 x 20 mL). The solvent from the solution was removed under vacuum to give 4d as a very hygroscopic white solid (2.61 g, 69 %). ¹H NMR (300 MHz; CDCl₃): 1.25 (6H, s, CH₃), 1.26 (18H, s, tBu), 1.33 (6H, s, CH₃), 1.39 (6H, s, CH₃), 1.42 (6H, s, CH₃), 3.98-4.19 (12H, m, OCH & OCH₂), 4.19-4.27 (2H, m, OCH), 4.47-4.50 (2H, m, OCH), 6.56 (1H, s, ArH), 7.21 (1H, s, ArH); ³¹P NMR (121 MHz; CDCl₃): 136.7 (s); ¹³C NMR (75 MHz; CDCl₃) 25.36, 25.68, 26.89, 27.22 (s, CH₃), 30.09 (s, CH₃ tBu), 34.93 (s, C tBu), 66.18 (s, C(Me)₂), 66.58, 67.17 (s, CH₂), 67.69 (s, C(Me)₂), 76.38, 76.89, 80.13, 81.37 (s, OCH), 110.49, 113.11 (t, J = 15 Hz, Ar CH), 129.44, 135.50.
Synthesis of complex 5a. Method A. A mixture of ligand 4a (0.30 g, 0.4 mmol) and [PdCl2(NCPh)2] (0.15 g, 0.4 mmol) in 1,2-dichloroethane (20 mL) was heated to reflux during which time a white suspension was formed. The mixture was maintained at reflux until a clear yellow solution was obtained (approx. 6 days). The solvent was removed under vacuum, the residue was re-dissolved in THF and filtered through celite. The solvent was removed under vacuum and trituration with pentane to give 5a as a pale yellow powder (0.27 g, 77.5 %). Crystals suitable for X-ray analysis were grown from CDCl3. 1H NMR (300 MHz; CDCl3): 6.80 (2H, d, J = 8 Hz, ArH), 7.21-7.68 (9H, m, ArH), 7.87-8.08 (16H, m, ArH); 31P NMR (CDCl3): 147.2 (s); MS (EI): m/z = 878 (M⁺), 843 (M⁺ - Cl), 738 (M⁺ - PdCl).

Method B. Ligand 4a (0.404 g, 0.547 mmol), [PdCl2(NCMe)2] (0.142 g, 0.546 mmol) and 1,2-dichloroethane (2.5 mL) where placed in microwave reaction vessel and heated in a CEM Discover 300 W microwave reactor at 150 ºC for 1h. Work-up as method A (91.5 %).

General method for the synthesis of complexes 5b - d: A mixture of the appropriate ligand 4 (0.08 mmol) and [PdCl2(NCMe)2] (0.021 g, 0.08 mmol) in 1,2-dichloroethane (2 mL) was treated with NEt₃ (0.011 mL, 0.08 mmol) and then heated at 80 ºC for 2h. The resultant mixture was filtered through celite, the solvent was removed under vacuum and the residue crystallised from CH₂Cl₂/Et₂O

Complex 5b: Grey solid (0.041 g, 51 %). 1H NMR (300 MHz; CDCl3): 1.17 (18H, s, 1Bu), 7.24 (1H, s, ArH), 7.27 (2H, ddd, J = 8, 7 & 1 Hz, ArH), 7.34 (2H, d, J = 9 Hz, ArH), 7.35 (2H, ddd, J = 8, 7 & 1 Hz, ArH), 7.44 (2H, ddd, J = 8, 7 & 1 Hz, ArH), 7.46 (2H, d, J = 9 Hz, ArH), 7.48 (2H, d, J = 9 Hz, ArH), 7.53 (2H, ddd, J = 8, 7 & 1 Hz, ArH), 7.64 (2H, d, J = 9 Hz, ArH), 7.88 (2H, d, J = 8 Hz, ArH), 7.95 (2H, d, J = 9 Hz, ArH), 8.00 (2H, d, J = 8 Hz, ArH), 8.02 (2H, d, J = 9 Hz, ArH); 31P NMR (121 MHz; CDCl3): 147.3 (s); Anal. calcd for C₅₄H₄₃ClO₆P₂Pd·CDCl₃: C, 59.40; H, 4.08. Found: C, 59.55; H, 3.85.
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**Complex 5c:** Grey solid (0.021 g, 47.5 %); $^1$H NMR (300 MHz; CDCl$_3$): 1.24 (18H, br s, tBu), 1.48 (12H, br s, CH$_3$), 4.32 (4H, br s, CH), 7.02 (1H, s, ArH); $^{31}$P NMR (121 MHz; CDCl$_3$): 147.6 (s); $^{13}$C NMR (75 MHz; CDCl$_3$): 18.78, 19.18 (s, CH$_3$), 30.19 (s, CH$_3$tBu), 35.15 (s, C$^3$Bu), 81.49, 82.89 (s, OCH), 125.23, 130.01, 146.51, 151.90.

**Complex 5d:** Grey solid (0.052 g, 68.5 %); $^1$H NMR (300 MHz; CDCl$_3$): 1.24 (18H, s, tBu), 1.30 (6H, s, CH$_3$), 1.34 (6H, s, CH$_3$), 1.39 (6H, s, CH$_3$), 1.41 (6H, s, CH$_3$), 3.92-3.96 (2H, m, OCH), 4.02-4.09 (4H, m, OCH), 4.13-4.18 (2H, m, OCH), 4.29-4.32 (2H, m, OCH), 4.43-4.46 (2H, m, OCH), 4.52-4.58 (4H, m, OCH), 7.04 (1H, s, ArH); $^{31}$P NMR (121 MHz; CDCl$_3$): 151.2 (s); $^{13}$C NMR (75 MHz; CDCl$_3$): 25.23, 25.36, 27.17, 27.43 (s, CH$_3$), 30.06 (s, CH$_3$tBu), 35.08 (s, C$^3$Bu), 66.45 (s, C(Me)$_2$), 66.66, 66.92 (s, CH$_2$), 67.16 (s, C(Me)$_2$), 74.81, 74.94, 80.96, 81.42 (s, OCH), 125.51, 130.60, 146.75, 151.04; Anal. calcd for C$_{38}$H$_{59}$ClO$_{14}$P$_2$Pd: C, 48.36; H, 6.30. Found: C, 48.13; H, 6.61.

**Synthesis of complex 8.** Ligand 5b (0.504 g, 0.592 mmol) and [PdCl$_2$(NCMe)$_2$] (0154 g, 0.592 mmol) were dissolved in CH$_2$Cl$_2$ (10 mL) and stirred at room temperature for 1 h. The solution was concentrated under reduced pressure and ethanol (20 mL) added. The CH$_2$Cl$_2$ was removed under reduced pressure to induce precipitation of the product. The yellow crystalline solid was isolated by filtration and dried in vacuo to give 8 as a orange solid. (0.57 g, 93.5 %). Crystals suitable for X-ray analysis were grown from CH$_2$Cl$_2$:MeOH. $^1$H NMR (CDCl$_3$; 300 MHz): 0.28 (s, 18H, tBu), 1.23 (s, 18H, tBu), 6.01 (d, 2H, J = 9 Hz, Ar-H), 7.03-7.12 (m, 12H, Ar-H), 7.24-7.38 (m, 8H, Ar-H), 7.43 (d, 2H, J = 6 Hz, Ar-H), 7.51 (d, 4H, J = 6 Hz, Ar-H), 7.52 (d, 2H, J = 6 Hz, Ar-H), 7.69 (d, 2H, J = 7 Hz, Ar-H), 7.73 (dd, 4H, J = 3 & 9 Hz, Ar-H), 7.79 (d, 2H, J = 9 Hz, Ar-H), 7.95 (d, 4H, J = 9 Hz, Ar-H), 8.13 (d, 2H, J = 6 Hz, Ar-H), 8.22 (d, 2H, J = 6 Hz, Ar-H), 8.38 (s, 4H, Ar-H), 8.44 (br s, 2H, Ar-H). $^{31}$P NMR (CDCl$_3$; 121.5 MHz): 102.29 (d, $^2$J$_{PP}$ = 46.2 Hz), 104.28 (d, $^2$J$_{PP}$ = 46.2 Hz). $^{13}$C NMR (CDCl$_3$; 75.5 MHz): 28.61, 30.64 (s, CH$_3$tBu), 34.82, 35.27 (s, C$^3$Bu), 111.59, 120.03, 122.09, 122.34, 124.08, 125.46, 126.01, 126.62 (d, $^3$J$_{CP}$ = 10 Hz), 126.89, 127.15, 127.40, 127.71, 128.40 (d, $^3$J$_{CP}$ = 11 Hz), 128.79,
Figure S1. Molecular structure of complex 5a. Selected bond lengths (Å) and angles (°):
5a. Pd1-P1, 2.2615(19); Pd1-Pd2, 2.2445(18); Pd1-C21, 1.969(6); Pd1-Cl1, 2.3486(18); P1-O1, 1.613(5); P1-O2, 1.586(5); P1-O3, 1.597(5); P2-O4, 1.612(5); P2-O5, 1.587(5); P2-O6, 1.595(5); P1-Pd1-Cl1, 101.66(7); P2-Pd1-Cl1, 99.44(7); P2-Pd1-P1, 158.13(7); C21-Pd1-Cl1, 175.7(2); C21-Pd1-P1, 79.6(2); C21-Pd1-P2, 78.9(2); O2-P1-O1, 103.3(3);
O2-P1-O3, 105.3(3); O3-P1-O1, 97.8(3); O5-P2-O4, 97.9(3); O5-P2-O6, 103.0(2); O6-P2-O4, 106.6(3).