The design of second generation MOP-phosphonites: efficient chiral hydrosilylation of functionalised styrenes

Supporting Information

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1. General Considerations and Chemical Analyses

**General Procedures.** All air- and/or water-sensitive reactions were performed under a nitrogen atmosphere using standard Schlenk line techniques in oven dried glassware. Solvents were freshly distilled prior to use; toluene was dried over sodium, tetrahydrofuran and diethyl ether were dried over sodium/benzophenone, dichloromethane was dried over calcium hydride and d-chloroform was dried over phosphorus pentoxide, distilled and stored over molecular sieves. (S)-[1,1’-binaphthalen]-2-ylphosphine ((S)-1), (R)-(2’-methoxy-[1,1’-binaphthalen]-2-yl)phosphine ((R)-2), (S)-[1,1’-binaphthalen]-2-yl diphenylphosphine ((S)-H-MOP), (R)-(2’-methoxy-[1,1’-binaphthalen]-2-yl)diphenylphosphine ((R)-MeO-MOP), (S,R)-[1,1’-binaphthalene]-2,2’-diyl [1,1’-binaphthalen]-2-ylphosphonite ((S,R)-Ia) and (S,S)-[1,1’-binaphthalene]-2,2’-diyl [1,1’-binaphthalen]-2-ylphosphonite ((S,S)-Ia) were prepared according to literature procedures. All other chemicals were used as received without further purification. Flash chromatography was performed on silica gel (Fluorochem, 60A, 40-63 μm) or neutral aluminum oxide (Acros Organics, 60A, 50-200 μm). Thin-layer chromatography was performed on Merck silica gel coated aluminium sheets with fluorescent indicator (UV254) or Machery-Nagel aluminum oxide coated polyester sheets with fluorescent indicator (UV254), UV light was used for indicating. Melting points were determined in open glass capillary tubes on a Stuart SMP3 melting point apparatus. Optical rotation values were determined on an Optical Activity Polaar 2001 device. Infrared spectra were measured on a Varian 800 FT-IR Scimitar Series spectrometer. $^1$H, $^{13}$C($^1$H) $^{19}$F and $^{31}$P($^1$H) NMR spectra were recorded on a Bruker 500 ($^1$H 500.15 MHz), JEOL 400 ($^1$H 399.78 MHz) or Bruker 300 ($^1$H 300.13 MHz) spectrometer at room temperature (21-25°C) if not otherwise stated, using the indicated solvent as internal reference. Two-dimensional NMR experiments ($^1$H-$^1$H COSY, $^1$H-$^1$H NOESY, HSQC, HMBC) were used for the assignment of proton and carbon resonances, the numbering schemes are given in Figure 1. High resolution mass spectrometry was carried out by the EPSRC National Mass Spectrometry Facility, Swansea. Analytical gas chromatography was performed on a Shimadzu GC2014 instrument with a flame ionisation detector, using a Supelco β-dex™ 225 capillary column (L = 30 m, I.D. = 0.25 mm, d_r = 0.25 μm) and helium (purge flow 3 ml/min) as the carrier gas.
Fig. 1 Numbering scheme used to assign proton and carbon resonances in the NMR spectra: phenoxy-derived ligands (left), biphenoxy-derived ligands (middle) and methallyl ligands (right).
2. Experimental Procedures

2.1 (S)-Diphenyl [1,1'-binaphthalen]-2-ylphosphite (S)-3a

(S)-[1,1'-Binaphthalen]-2-ylphosphine ((S)-1a, 286 mg, 1.00 mmol, 1.0 eq.) was dissolved in toluene (10 mL) and phosphorus pentachloride (458 mg, 2.20 mmol, 2.2 eq.) was added. The reaction mixture was stirred for 45 min, after which the volatiles were removed in vacuo. The residue was dissolved in THF (8 mL) and triethylamine (0.61 mL, 450 mg, 4.4 mmol, 4.4 eq.) was added. The reaction mixture was then left to stir for 10 min, before phenol (188 mg, 2.00 mmol, 1.0 eq.) was added and stirring continued overnight. The volatiles were removed in vacuo and the crude compound was filtered through a plug of alumina (diethyl ether) to yield the pure title compound as a white sticky solid (350 mg, 0.74 mmol, 74%). Rf = 0.95 (alumina; diethyl ether).

\[ \alpha_D^{19} = +56^\circ \text{ (CHCl}_3, c = 0.1). \]  
IR (neat): \( \nu = 3055.1 \text{ (w), 1483.3 (m), 1217.2 (m), 1193.4 (s), 1162.4 (m), 1120.2 (w), 1070.8 (w), 1023.4 (w), 852.9 (s), 758.7 (s), 716.5 (m), 687.3 (s), 632.4 (m) cm}^{-1}.\)  
\(^1\text{H NMR} (400 \text{ MHz, CDCl}_3): \delta (ppm) = 8.30 (dd, \text{J}_{HH} = 8.6 \text{ Hz}, \text{J}_{HP} = 2.8 \text{ Hz}, \text{H3}), 8.08 (d, \text{J}_{HH} = 8.6 \text{ Hz}, \text{H4}), 7.98-7.94 (m, \text{H2, H4'}/\text{H5'}), 7.91 (d, \text{J}_{HH} = 8.3 \text{ Hz}, \text{H1, H5}), 7.56-7.51 (m, \text{H3, H2'}/\text{H3'}/\text{H6'}), 7.56 (ddd, \text{J}_{HH} = 8.2 \text{ Hz}, \text{J}_{HH} = 8.2 \text{ Hz}, \text{J}_{PP} = 1.9 \text{ Hz}, \text{H6}), 7.32-7.21 (m, \text{H4, H7/H7'/H8'/H8'}), 7.19-7.13 (m, \text{H2, H13'}), 7.04-6.96 (m, \text{H3, H13/H14'}), 6.90-6.83 (m, \text{H3, H12'}/\text{H14}), 6.53-6.49 (m, \text{H2, H12}). \]  
\(^{13}\text{C}^1\text{H NMR} (101 \text{ MHz, CDCl}_3): \delta (ppm) = 155.3 (overlapping-d, \text{C11}/\text{C11'}), 143.2 (d, \text{J}_{CP} = 36.5 \text{ Hz}, \text{C1}), 137.7 (d, \text{J}_{CP} = 14.0 \text{ Hz}, \text{C2}), 135.4 (d, \text{J}_{CP} = 9.2 \text{ Hz}, \text{C1'}), 134.6 (\text{C10}), 133.6 (\text{C9'}), 123.9 (d, \text{J}_{CP} = 5.8 \text{ Hz}, \text{C9}), 129.6 (d, \text{J}_{CP} = 3.9 \text{ Hz}, \text{C2'}), 129.5 (\text{C13'}), 129.3 (\text{C13}), 128.8 (\text{C4}), 128.3, 128.2, 127.4 (\text{C6'}), 127.1 (d, \text{J}_{CP} = 2.8 \text{ Hz, C8}), 126.8 (\text{C6}), 126.6, 126.5, 126.1, 125.1 (\text{C3'}), 125.0 (d, \text{J}_{CP} = 3.3 \text{ Hz, C3}), 123.3 (\text{C14'}), 123.1 (\text{C14}), 119.9 (d, \text{J}_{CP} = 8.6 \text{ Hz, C12'}), 119.6 (d, \text{J}_{CP} = 8.9 \text{ Hz, C12}). \]  
\(^{31}\text{P}^1\text{H NMR} (162 \text{ MHz, CDCl}_3): \delta (ppm) = 154.8 (s). \text{HRMS (ASAP™, solid): Found: m/z = 471.1499. Calculated for [M + H]^+: m/z = 471.1508.}
2.2 (R)-Diphenyl (2'-methoxy-[1,1'-binaphthalen]-2-yl)phosphonite (R)-3b

(R)-(2'-Methoxy-[1,1'-binaphthalen]-2-yl)phosphine ((R)-1b, 316 mg, 1.00 mmol, 1.0 eq.) was dissolved in toluene (10 mL) and phosphorus pentachloride (458 mg, 2.20 mmol, 2.2 eq.) was added. The reaction mixture was stirred for 45 min, after which the volatiles were removed in vacuo. The residue was dissolved in THF (8 mL) and triethylamine (0.61 mL, 450 mg, 4.4 mmol, 4.4 eq.) was added. The reaction mixture was then left to stir for 10 min, before phenol (188 mg, 2.00 mmol, 1.0 eq.) was added and stirring continued overnight. The volatiles were removed in vacuo and the crude compound was filtered through a plug of alumina (toluene) to yield the pure title compound as a white solid (488 mg, 0.97 mmol, 97%). R<sub>i</sub> = 0.95 (alumina; toluene).

**MP**: 142-144 °C. [α]<sub>D</sub><sup>20</sup> = +24° (CHCl<sub>3</sub>, c = 0.1). IR (neat): ν = 3233.1 (w), 3054.6 (w), 2935.7 (w), 2840.8 (w), 1592.2 (m), 1486.3 (m), 1334.5 (w), 1191.8 (s), 1162.9 (m), 1079.3 (m), 1052.5 (m), 1022.0 (m), 967.6 (m), 922.2 (s), 868.4 (m), 809.7 (s), 747.2 (s), 689.4 (s), 633.3 (m) cm<sup>-1</sup>.<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.32 (dd, 3<sup>JJHH</sup> = 8.5 Hz, 3<sup>JHP</sup> = 2.8 Hz, 1H, H3), 8.11 (d, 3<sup>JJHH</sup> = 8.5 Hz, 1H, H4), 8.03 (d, 3<sup>JJHH</sup> = 9.1 Hz, 1H, H4'), 8.00 (d, 3<sup>JJHH</sup> = 8.3 Hz, 1H, H5), 7.89 (d, 3<sup>JJHH</sup> = 8.2 Hz, 1H, H5'), 7.56 (apparent-t (dd), 3<sup>JJHH</sup> = 7.3 Hz, 1H, H6), 7.41 (d, 3<sup>JJHH</sup> = 9.1 Hz, 1H, H3'), 7.37-7.30 (m, 3H, H6'/H7/H8), 7.25-7.17 (m, 3H, H7'/H13'), 7.11 (d, 3<sup>JJHH</sup> = 8.5 Hz, 1H, H8'), 7.06-7.00 (m, 3H, H13/H14), 6.94-6.88 (m, 3H, H12'/H14'), 6.52 (d, 3<sup>JJHH</sup> = 8.3 Hz, 2H, H12), 3.72 (s, 3H, OCH<sub>3</sub>).<sup>13</sup>C<sup>(1)H</sup> NMR (101 MHz, CDCl<sub>3</sub>): δ (ppm) = 155.5 (overlapping-d, C11/C11'), 155.3 (d, 3<sup>JCP</sup> = 2.4 Hz, C2'), 139.9 (d, 3<sup>JCP</sup> = 38.3 Hz, C1), 138.0 (d, 3<sup>JCP</sup> = 13.4 Hz, C2), 135.1 (C10), 134.8 (d, 3<sup>JCP</sup> = 2.1 Hz, C9'), 132.9 (d, 3<sup>JCP</sup> = 6.4 Hz, C9), 130.7 (C4), 129.5 (C13'), 129.3 (C13), 128.9 (C10'), 128.4 (C5), 128.3 (d, 3<sup>JCP</sup> = 1.0 Hz, C4), 128.0 (C5'), 127.5 (C6), 127.1 (C7'), 126.6 (C7), 126.5 (d, 3<sup>JCP</sup> = 2.8 Hz, C8), 125.6 (C8'), 125.3 (d, 3<sup>JCP</sup> = 3.2 Hz, C3), 123.8 (C6'), 123.2 (C14'), 123.2 (C14), 120.9 (d, 3<sup>JCP</sup> = 7.1 Hz, C1'), 120.0 (d, 3<sup>JCP</sup> = 9.1 Hz, C12'), 119.8 (d, 3<sup>JCP</sup> = 8.8 Hz, C12), 113.1 (C3'), 56.3 (OCH<sub>3</sub>).<sup>31</sup>P<sup>(1)H</sup> NMR (162 MHz, CDCl<sub>3</sub>): δ (ppm) = 155.6 (s). HRMS (ASAP', solid): Found: m/z = 501.1602. Calculated for [M + H]<sup>+</sup>: m/z = 501.1614.
2.3 (S)-[1,1'-Biphenyl]-2,2'-diyl [1,1'-binaphthalen]-2-ylphosphonite (S)-4a

(S)-[1,1'-Binaphthalen]-2-ylphosphine ((S)-1a, 429 mg, 1.50 mmol, 1.0 eq.) was dissolved in toluene (12 mL) and phosphorus pentachloride (687 mg, 3.30 mmol, 2.2 eq.) was added. The reaction mixture was stirred for 45 min, after which the volatiles were removed in vacuo. The residue was dissolved in THF (12 mL) and triethylamine (0.92 mL, 670 mg, 6.6 mmol, 4.4 eq.) was added. The reaction mixture was then left to stir for 10 min before 2,2'-biphenol (279 mg, 1.50 mmol, 1.0 eq.) was added and stirring continued overnight. The volatiles were removed in vacuo and the crude compound was filtered through a plug of silica gel (toluene) to yield the pure title compound as a white solid (492 mg, 1.05 mmol, 70%). R<sub>t</sub> = 0.90 (silica gel; toluene).

**MP:** 137-139 °C. [α]<sub>D</sub> = +116° (CHCl<sub>3</sub>, c = 0.1). IR (neat): ν = 3048.0 (w), 1497.0 (m), 1473.1 (w), 1432.8 (m), 1244.5 (m), 1205.7 (m), 1180.0 (m), 1095.0 (w), 1022.0 (w), 946.1 (w), 893.2 (s), 851.6 (s), 821.3 (m), 800.7 (m), 761.8 (s), 700.2 (m), 630.5 (w), 603.2 (w) cm⁻¹. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.04 (d, <sup>3</sup>J<sub>NNN</sub> = 8.1 Hz, 1H, H4'), 7.98 (d, <sup>3</sup>J<sub>NNN</sub> = 8.2 Hz, 1H, H5'), 7.90 (d, <sup>3</sup>J<sub>NNN</sub> = 8.2 Hz, 1H, H5), 7.77-7.70 (m, 2H, H2'/H4), 7.69-7.64 (m, 1H, H3'), 7.57-7.49 (m, 3H, H3/H6/H6'), 7.48-7.43 (m, 2H, H16/H16'), 7.40-7.31 (m, 4H, H7/H7'/H8/H8'), 7.28-7.16 (m, 4H, H14/H14'/H15/H15'), 6.98-6.94 (m, 1H, H13'), 6.83 (d, <sup>3</sup>J<sub>NNN</sub> = 7.8 Hz, 1H, H13). <sup>13</sup>C<sup>{1}H</sup> NMR (101 MHz, CDCl<sub>3</sub>): δ (ppm) = 151.5 (d, <sup>2</sup>J<sub>CP</sub> = 4.4 Hz, C12), 151.3 (d, <sup>2</sup>J<sub>CP</sub> = 6.7 Hz, C12'), 145.0 (d, <sup>2</sup>J<sub>CP</sub> = 37.1 Hz, C1), 136.8 (d, <sup>2</sup>J<sub>CP</sub> = 39.1 Hz, C2), 135.0 (d, <sup>2</sup>J<sub>CP</sub> = 9.8 Hz, C1'), 134.9 (C10), 133.7 (d, <sup>4</sup>J<sub>CP</sub> = 2.6 Hz, C9'), 133.4 (C10'), 133.1 (d, <sup>3</sup>J<sub>CP</sub> = 4.6 Hz, C9), 132.3 (d, <sup>3</sup>J<sub>CP</sub> = 4.0 Hz, C11'), 131.9 (d, <sup>4</sup>J<sub>CP</sub> = 3.2 Hz, C11), 130.3 (d, <sup>4</sup>J<sub>CP</sub> = 5.4 Hz, C2'), 130.0 (C16 or C16'), 129.9 (C16 or C16'), 129.3 (C14 or C14'), 129.1 (C14 or C14'), 129.0 (C4'), 128.4 (C5'), 128.2 (C5), 127.7 (C6 or C6'), 127.3 (d, <sup>4</sup>J<sub>CP</sub> = 2.7 Hz, C8), 127.1 (C4), 126.9 (C8'), 126.6 (C7 or C7'), 126.5 (C7 or C7'), 126.2 (C6 or C6'), 125.1 (C3'), 125.0 (C15 or C15'), 124.9 (C15 or C15'), 124.4 (d, <sup>2</sup>J<sub>CP</sub> = 2.6 Hz, C3), 122.2 (overlapping-d, C13/C13'). <sup>31</sup>P<sup>{1}H</sup> NMR (162 MHz, CDCl<sub>3</sub>): δ (ppm) = 177.7 (s). HRMS (ASAP<sup>+</sup>, solid): Found: m/z = 469.1344. Calculated for [M + H]<sup>+</sup>: m/z = 469.1352.
2.4 \( (R)-[1,1^\prime\text{-Biphenyl}] \text{-} 2,2^\prime\text{-diyl (2'}-\text{methoxy-[1,1'}\text{-binaphthalen}] -2\text{-yl})\text{phosphonite (R)-}4b \)

(R)(2'-Methoxy-[1,1'-binaphthalen]-2-yl)phosphate \((\text{R}-1b, 474 \text{ mg, 1.50 mmol, 1.0 eq.})\) was dissolved in toluene (12 mL) and phosphorus pentachloride (687 mg, 3.30 mmol, 2.2 eq.) was added. The reaction mixture was stirred for 45 min, after which the volatiles were removed in vacuo. The residue was dissolved in THF (12 mL) and triethylamine (0.92 mL, 670 mg, 6.6 mmol, 4.4 eq.) was added. The reaction mixture was then left to stir for 10 min before 2,2'-biphenol (279 mg, 1.50 mmol, 1.0 eq.) was added and stirring continued overnight. The volatiles were removed in vacuo and the crude compound was filtered through a plug of silica gel (toluene) to yield the pure title compound as a white solid (510 mg, 1.02 mmol, 68%). \( 	ext{R}_f = 0.80 \) (silica gel; toluene).

\textbf{MP:} 225-227 °C. \([\alpha]_D^{20} = +162^\circ \) (CHCl₃, c = 0.1). \textbf{IR} (neat): \( \nu = 3062.8 \) (w), 2969.0 (w), 1619.9 (w), 1592.5 (w), 1496.0 (m), 1471.6 (w), 1435.6 (m), 1269.1 (m), 1248.4 (s), 1197.6 (s), 1181.9 (m), 1124.4 (w), 1077.5 (m), 1049.8 (w), 1020.3 (w), 867.9 (m), 839.6 (m), 811.5 (m), 769.3 (s), 745.0 (s), 693.4 (m), 631.9 (m) cm\(^{-1}\). \textbf{\( ^1\text{H NMR} \)} (400 MHz, CDCl₃): \( \delta \) (ppm) = 8.05 (d, \( \beta_{jHH} = 9.1 \) Hz, 1H, \( H'4 \)), 7.94 (apparent-t (dd), \( \beta_{jHH} = 8.3 \) Hz, 2H, \( H5/H5' \)), 7.71 (d, \( \beta_{jHH} = 8.6 \) Hz, 1H, \( H4 \)), 7.55-7.22 (m, 5H, \( H3/H3'/H6/H16/H16' \)), 7.38-7.26 (m, 4H, \( H6'/H7/H7'/H8 \)), 7.25-7.20 (m, 3H, \( H14 \) or \( H14'/H15/H15' \)), 7.17 (apparent-t (dd), \( \beta_{jHH} = 7.8 \) Hz, 1H, \( H14 \) or \( H14' \)), 7.08 (d, \( \beta_{jHH} = 8.5 \) Hz, 1H, \( H8' \)), 6.95-6.92 (m, 1H, \( H13' \)), 6.82 (d, \( \beta_{jHH} = 8.0 \) Hz, 1H, \( H13 \)), 3.89 (s, 3H, OCH₃). \textbf{\( ^{13}\text{C}[^{1}\text{H}]\text{NMR} \)} (101 MHz, CDCl₃): \( \delta \) (ppm) = 155.9 (d, \( \delta_{JCp} = 3.3 \) Hz, \( C2' \)), 151.5 (overlapping-d, \( C12/C12' \)), 141.6 (d, \( \delta_{JCp} = 38.0 \) Hz, \( C1 \)), 136.7 (d, \( \delta_{JCp} = 37.3 \) Hz, \( C2 \)), 135.3 (C10), 135.0 (d, \( \delta_{JCp} = 2.4 \) Hz, \( C9' \)), 132.9 (d, \( \delta_{JCp} = 5.0 \) Hz, \( C9 \)), 132.4 (d, \( \delta_{JCp} = 4.0 \) Hz, \( C11' \)), 132.1 (d, \( \delta_{JCp} = 2.9 \) Hz, \( C11 \)), 130.8 (C4'), 129.9 (C16 or C16'), 129.7 (C16 or C16'), 129.2 (C14 or C14'), 129.0 (C14 or C14'), 128.7 (C10'), 128.3 (C5 or C5'), 128.1 (C5 or C5'), 127.6 (C6), 127.0 (C4), 126.9 (C7 or C7'), 126.6 (d, \( \delta_{JCp} = 2.3 \) Hz, \( C8 \)), 126.4 (C7 or C7'), 125.7 (C8'), 125.0 (C15'), 124.8 (C15), 124.6 (d, \( \delta_{JCp} = 1.9 \) Hz, \( C3 \)), 123.8 (C6'), 122.6 (C13), 122.3 (C13'), 119.3 (d, \( \beta_{jHH} = 10.1 \) Hz, \( C1' \)), 112.9 (C3'), 56.3 (OCH₃). \textbf{\( ^{31}\text{P}[^{1}\text{H}]\text{NMR} \)} (162 MHz, CDCl₃): \( \delta \) (ppm) = 180.0 (s). \textbf{HRMS} (ASAP, solid): Found: \( m/z = 499.1449 \). Calculated for \([\text{M} + \text{H}]^+\): \( m/z = 499.1458 \).
2.5 (S)-3,3'-Dimethyl-[1,1'-biphenyl]-2,2'-diyl [1,1'-binaphthalen]-2-yl)phosphonite (S)-5a

(S)-[1,1'-Binaphthalen]-2-yl)phosphine ((S)-1a, 429 mg, 1.50 mmol, 1.0 eq.) was dissolved in toluene (10 mL) and phosphorus pentachloride (687 mg, 3.30 mmol, 2.2 eq.) was added. The reaction mixture was stirred for 45 min, after which the volatiles were removed in vacuo. The residue was dissolved in diethyl ether (14 mL) and triethylamine (0.92 mL, 668 mg, 6.60 mmol, 4.4 eq.) was added. The reaction mixture was then left to stir for 10 min before 3,3'-dimethyl-[1,1'-biphenyl]-2,2'-diol (321 mg, 1.50 mmol, 1.0 eq.) was added and stirring continued overnight. The volatiles were removed in vacuo and the crude compound was filtered through a plug of alumina (diethyl ether) to yield the pure title compound as a white solid (678 mg, 1.37 mmol, 91%). Rf = 0.95 (alumina; diethyl ether).

**MP**: 202-203 °C. [α]20D = +58° (CHCl3, c = 0.1). **IR** (neat): ν = 3054.7 (w), 1455.4 (s), 1417.0 (m), 1364.0 (w), 1318.2 (w), 1250.4 (w), 1195.6 (m), 1165.0 (m), 1120.5 (w), 1082.0 (m), 1025.4 (w), 922.0 (w), 878.1 (s), 798.4 (m), 769.2 (s), 736.0 (s), 696.0 (s), 630.7 (m) cm⁻¹. **1H NMR** (400 MHz, CDCl3): δ (ppm) = 8.02 (dd, 1H), 7.62 (1H), 7.64 (3H), 7.21 (3H), 7.10 (3H), 6.89 (3H), 5.85 (3H), 5.36 (3H), 4.75 (3H), 4.44 (3H), 3.24 (3H), 2.22 (s, 3H), 1.78 (s, 3H), 1.50 (s, 3H), 1.30 (s, 3H). **13C{1H} NMR** (101 MHz, CDCl3): δ (ppm) = 149.6 (overlapping-d, C12/C12'), 144.6 (d, 3JCP = 38.2 Hz, C1), 138.3 (d, 3JCP = 39.0 Hz, C2), 135.5 (d, 3JCP = 10.4 Hz, C1'), 135.0 (C10), 134.0 (d, 3JCP = 3.7 Hz, C9'), 133.4 (C10'), 133.0 (d, 3JCP = 4.9 Hz, C9), 132.4 (d, 3JCP = 4.6 Hz, C11 or C11'), 131.9 (d, 3JCP = 2.7 Hz, C11 or C11'), 130.9, 130.7, 130.6 (C14'), 130.4 (C14), 129.7 (d, 3JCP = 5.5 Hz, C2'), 128.8 (C4'), 128.5 (C5'), 128.2 (C5), 128.0, 127.8, 127.7, 127.4, 127.4 (C4), 126.7, 126.6, 126.5, 126.1, 125.0 (C3'), 124.6 (C15 or C15'), 124.4 (C15 or C15'), 123.9 (C3), 16.7 (CH3'), 16.4 (CH3). **31P{1H} NMR** (162 MHz, CDCl3): δ (ppm) = 172.4 (s). **HRMS** (ASAP, solid): Found: m/z = 497.1657. Calculated for [M + H]+: m/z = 497.1665.
2.6 (R)-3,3’-Dimethyl-[1,1’-biphenyl]-2,2’-diyl (2’-methoxy-[1,1’-binaphthalen]-2-yl) phosphonite (R)-5b

(R)-(2’-Methoxy-[1,1’-binaphthalen]-2-yl)phosphine ((R)-1b, 474 mg, 1.50 mmol, 1.0 eq.) was dissolved in toluene (10 mL) and phosphorus pentachloride (687 mg, 3.30 mmol, 2.2 eq.) was added. The reaction mixture was stirred for 45 min, after which the volatiles were removed in vacuo. The residue was dissolved in THF (14 mL) and triethylamine (0.92 mL, 668 mg, 6.60 mmol, 4.4 eq.) was added. The reaction mixture was then left to stir for 10 min, before 3,3’-dimethyl-[1,1’-biphenyl]-2,2’-diol (321 mg, 1.50 mmol, 1.0 eq.) was added and stirring continued overnight. The volatiles were removed in vacuo and the crude compound was filtered through a plug of alumina (diethyl ether) to yield the pure title compound as a white solid (695 mg, 1.32 mmol, 88%). Rf = 0.90 (alumina; diethyl ether).

**MP**: 203-205 °C. [α]_D^20 = +48° (CHCl₃, c = 0.1). **IR** (neat): ν = 3054.3 (w), 2924.8 (w), 1602.1 (w), 1593.6 (w), 1510.1 (w), 1458.7 (m), 1414.9 (m), 1333.9 (w), 1203.6 (m), 1077.0 (m), 1021.5 (m), 918.0 (w), 885.0 (m), 869.0 (m), 809.8 (m), 769.6 (m), 746.5 (m), 696.6 (m), 632.1 (m) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.05 (d, J_HH = 9.1 Hz, 1H, H₄”), 7.94 (d, J_HH = 8.2 Hz, 2H, H₅/H₅’), 7.74 (d, 8.5 Hz, 1H, H₄), 7.53 (apparent-t (dd), J_HH = 7.4 Hz, 1H, H₆), 7.49-7.44 (m, 2H, H₃/H₃’), 7.38-7.24 (m, 6H, H₆'/H₇'/H₈'/H₁₆'/H₁₆’), 7.17-7.15 (m, 2H, H₁₄/H₁₄’), 7.13-7.10 (m, 3H, H₈’/H₁₅/H₁₅’), 3.86 (s, 3H, OCH₃), 1.99 (s, 3H, CH₃’), 1.87 (s, 3H, CH₃). ¹³C(¹H) NMR (101 MHz, CDCl₃): δ (ppm) = 155.4 (d, J_CP = 3.3 Hz, C₂’), 149.8 (overlapping-d, C₁₂/C₁₂’), 141.4 (d, J_CP = 40.6 Hz, C₁), 138.4 (d, J_CP = 37.8 Hz, C₂), 135.4 (C₁₀), 135.0 (d, J_CP = 3.2 Hz, C₉’), 132.8 (d, J_CP = 5.9 Hz, C₉), 132.3 (d, J_CP = 3.8 Hz, C₁₁ or C₁1’), 132.0 (1H, H₁ or C₁1’), 131.0 (C₁₆ or C₁₆’), 130.7 (C₁₆ or C₁₆’), 130.6 (C₄’), 130.5 (C₄’), 130.5 (C₁₄), 128.8 (C₁₀’), 128.3 (C₅), 128.2 (C₅’), 127.9 (C₁₃ or C₁₃’), 127.8 (C₁₃ or C₁₃’), 127.6 (C₆), 127.3 (C₄), 127.0 (d, J_CP = 2.4 Hz, C₈), 126.9 (C₇’), 126.5 (C₇), 125.5 (C₈’), 124.5 (C₁₅ or C₁₅’), 124.4 (C₁₅ or C₁₅’), 124.2 (d, J_CP = 1.2 Hz, C₃), 123.7 (C₆’), 119.9 (d, J_CP = 10.6 Hz, C₁’), 112.8 (C₃’), 56.3 (OCH₃), 16.4 (CH₃’), 16.2 (CH₃). ³¹P(¹H) NMR (162 MHz, CDCl₃): δ (ppm) = 174.2 (s). **HRMS** (NSI⁺, DCM/MeOH): Found: m/z = 527.1761. Calculated for [M + H]⁺: m/z = 527.1771.
2.7 2,2'-Dihydroxy-3,3'-dimethyl-1,1'-biphenyl

2.7.1 2,2'-Dimethoxy-1,1'-biphenyl

2,2'-Dihydroxy-1,1'-biphenyl (5.00 g, 26.9 mmol, 1.0 eq.) was dissolved in acetone (100 mL). Potassium hydroxide (6.04 g, 108 mmol, 4.0 eq.) was added to the solution and the reaction mixture was stirred for 15 min, after which methyl iodide (6.70 mL, 15.3 g, 108 mmol, 4.0 eq.) was added. The reaction mixture was stirred for 16 h, the volatiles were removed in vacuo and the residue dissolved in diethyl ether (100 mL). The organic phase was washed with water (100 mL), 1 M aq. HCl (50 mL) and 0.2 M aq. NaHCO₃ (50 mL), dried over MgSO₄ and the volatiles were removed in vacuo. Silica gel flash chromatography (petrol/ethyl acetate, 9:1) yielded the pure title compound as a white solid (4.63 g, 21.6 mmol, 80%). Rf = 0.50 (silica gel; petrol/ethyl acetate, 9:1). The physical and spectroscopic properties matched those reported in the literature.⁵

MP: 156-158 °C (Lit.⁵ 155-156 °C). ¹H NMR (400 MHz, CDCl₃): δ = 7.33 (ddd, J = 7.8 Hz, J = 7.8 Hz, J = 1.8 Hz, 2H), 7.25 (dd, J = 7.4 Hz, J = 1.8 Hz, 2H), 7.03-6.96 (m, 4H), 3.77 (s, 6H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃): δ = 157.1, 131.6, 128.7, 127.9, 120.4, 111.2, 55.8 ppm.

2.7.2 2,2'-Dimethoxy-3,3'-dimethyl-1,1'-biphenyl

2,2'-Dimethoxy-1,1'-biphenyl (2.00 g, 9.33 mmol, 1.0 eq.) was dissolved in diethyl ether (120 mL). N,N,N',N'-Tetramethylethlenediamine (6.8 mL, 5.3 g, 45 mmol, 4.8 eq.) was added and the reaction mixture was cooled to 0 °C. n-Butyllithium (2.2 M solution in hexanes, 19 mL, 2.7 g, 42 mmol, 4.5 eq.) was added and the reaction mixture was left to stir at 0 °C for 1 h, after which it was heated to 40 °C and refluxed for 18 h. After cooling to 0 °C, methyl iodide (3.0 mL, 6.8 g, 48 mmol, 5.1 eq.) was added and the reaction mixture was left to stir for 1.5 h, before the reaction was quenched with 1 M aq. HCl (20 mL). The organic layer was separated, washed with 2.0 M aq. NaHCO₃ (2 x 50 mL) and brine (2 x 50 mL), dried over MgSO₄ and the volatiles were removed in vacuo. The title compound was obtained
as a yellow oil (2.12 g, 8.75 mmol, 94 %) and reacted without purification. The physical and spectroscopic properties matched those reported in the literature.\(^6\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.20\text{-}7.14\) (m, 4H), 7.25 (apparent-t (dd), \(J = 7.5\) Hz, 2H), 3.40 (s, 6H), 2.34 (s, 6H) ppm.

2.7.3 2,2'-Dihydroxy-3,3'-dimethyl-1,1'-biphenyl

Boron tribromide (1.0 M solution in DCM, 12 mL, 3.0 g, 12 mmol, 4.0 eq.) was diluted with DCM (10 mL) and cooled to 0 °C. 2,2'-Dimethoxy-3,3'-dimethyl-1,1'-biphenyl (730 mg, 3.0 mmol, 1.0 eq.) was dissolved in DCM (20 mL) and added to the solution. The reaction mixture was allowed to warm to room temperature and stirred for 18 h. The reaction mixture was cooled to 0 °C and quenched with water (20 mL). The organic phase was separated and the aqueous phase washed with DCM (20 mL). The combined organic extracts were washed with brine (3 x 20 mL), dried over MgSO\(_4\) and the volatiles were removed \textit{in vacuo}. Silica gel flash chromatography (petrol/ethyl acetate, 20:1) yielded the pure title compound as a dark pink solid (540 mg, 2.52 mmol, 84%). \(R_t = 0.20\) (silica gel; petrol/ethyl acetate, 20:1).

\textbf{MP:} 90-92 °C (Lit.\(^7\) 85-86 °C). \textbf{IR (neat):} \(\nu = 3029.6\) (s), 1587.5 (w), 1451.4 (m), 1324.0 (m), 1240.1 (m), 1198.9 (s), 1165.9 (m), 1124.9 (m), 1088.9 (m), 839.6 (m), 759.5 (s) cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.19\) (d, \(3J_{HH} = 7.5\) Hz, 2H, \(H_4\)), 7.06 (d, \(3J_{HH} = 7.5\) Hz, 2H, \(H_6\)), 6.93 (dd, \(3J_{HH} = 7.5\) Hz, \(3J_{HH} = 7.5\) Hz, 2H, \(H_5\)), 5.17 (s, 2H, \(OH\)), 2.31 (s, 6H, \(CH_3\)) ppm. \(^{13}\)C\(^{1}\)H NMR (101 MHz, CDCl\(_3\)): \(\delta = 151.6\) (C2), 131.6 (C4), 128.4 (C6), 125.6 (C3), 122.1 (C1), 121.0 (C5), 16.3 (CH\(_3\)) ppm. \textbf{HRMS (ASAP*, solid):} Found: \(m/z = 215.1067\). Calculated for [M + H]^+: \(m/z = 215.1067\).
(S)-4a (18.7 mg, 39.9 μmol, 1.0 eq.) and [Pd(η^3-C₄H₇)Cl]_2 (7.9 mg, 20 μmol, 0.5 eq.) were dissolved in DCM (0.5 mL) and stirred for 10 min; the title complex formed quantitatively as two isomers (isomer A 58%; isomer B 42%). Single crystals were grown by slow diffusion of diethyl ether into a DCM solution.

**MP**: 142-144 °C (decomp.). IR (neat): ν = 3059.6 (w), 1497.7 (m), 1475.9 (m), 1433.1 (s), 1367.6 (w), 1339.1 (m), 1259.4 (m), 1210.4 (w), 1095.7 (m), 1044.3 (w), 946.6 (w), 905.8 (s), 884.8 (m), 834.6 (w), 783.6 (s), 771.5 (s), 713.3 (m), 688.9 (m), 636.6 (m), 605.6 (m). ^1H NMR (500 MHz, CD₂Cl₂, −20 °C): δ (ppm) = 8.16 (dd, ^3_J_H = 7.0 Hz, ^3_J_HH = 0.9 Hz, 1H, H4^a), 8.04-7.96 (m, 6H), 7.95-7.89 (m, 3H, H3^b/H4^a/H4^b), 7.83 (dd, ^3_J_H = 7.0 Hz, ^3_J_HH = 0.9 Hz, 1H, H4^b), 7.76 (dd, ^3_J_H = 8.7 Hz, ^3_J_HH = 5.1 Hz, 1H, H3^a), 7.75-7.70 (m, 2H, H3^b/H3^a), 7.65-7.61 (m, 2H), 7.60-7.46 (m, 10H), 7.44-7.30 (m, 10H), 7.29-7.24 (m, 2H), 7.22 (d, ^3_J_HH = 8.6 Hz, 1H, H^b), 7.18 (d, ^3_J_HH = 8.6 Hz, 1H, H^a), 6.97 (d, ^3_J_HH = 8.1 Hz, 1H, H13^b), 6.78 (d, ^3_J_H = 8.1 Hz, 1H, H13^a), 4.20 (dd, ^3_J_HH = 10.1 Hz, ^3_J_HH = 2.9 Hz, 1H, allyl-Ht^syn), 3.77 (dd, ^3_J_HH = 9.8 Hz, ^3_J_HH = 2.9 Hz, 1H, H^a), 2.67-2.62 (m, 2H, allyl-Ht^syn/allyl-Ht^anti), 2.44 (br s, 1H, allyl-Ht^syn), 1.58 (d, ^3_J_HH = 14.1 Hz, 1H, H^a), 1.17 (s, 3H, allyl-CH₃^a), 1.16 (s, 3H, allyl-CH₃^b), 0.82 (br s, 1H, allyl-Hc^anti), 0.61 (br s, 1H, allyl-Hc^anti). ^13C{^1H} NMR (126 MHz, CD₂Cl₂, −20 °C): δ (ppm) = 150.1 (m, C12^b/C12^a/C12^b/C12^b), 144.7 (overlapping-d, C1^a/C1^a), 135.3, 135.1, 134.4 (d, ^3_J_Cp = 10.1 Hz, C1^a), 134.2 (d, ^3_J_Cp = 9.4 Hz, C1^a), 133.9 (C9^a), 133.6, 133.5, 133.5, 133.4, 133.3, 133.2, 133.1, 132.8 (C9^b), 131.2 (C4^b), 131.0, 130.8, 130.7, 130.5, 130.4, 130.3, 129.9, 129.4, 129.2, 129.1, 128.9, 128.6, 128.4, 128.3, 128.2, 127.9, 127.7, 127.5, 127.2, 127.1, 127.0, 126.9, 126.9, 126.8, 126.5, 126.3, 126.1, 125.9, 125.8, 125.6, 125.4, 124.7, 124.3, 123.2, 123.0, 121.6 (C13^a), 120.9 (C13^b), 77.4 (d, ^3_J_Cp = 46.3 Hz, allyl-C^b), 76.5 (d, ^3_J_Cp = 44.8 Hz, allyl-C^a), 57.4 (allyl-C^b), 56.3 (allyl-C^a), 22.8 (allyl-CH₃^a/allyl-CH₃^b). ^31P{^1H} NMR (202 MHz, CD₂Cl₂, −20 °C): δ (ppm) = 173.6 (s, P^a), 172.0 (s, P^b). HRMS (ASAP⁺, solid): Found: m/z = 625.0888. Calculated for [M − Cl]⁺: m/z = 625.0878.
2.9 \([\eta^3\text{-C}_4\text{H}_7]\text{PdCl(S)-5a} \) (S)-7a

(S)-5a (19.9 mg, 40.0 μmol, 1.0 eq.) and [Pd(\eta^3\text{-C}_4\text{H}_7)Cl]_2 (7.9 mg, 20 μmol, 0.5 eq.) were dissolved in DCM (0.5 mL) and stirred for 10 min; the title complex formed quantitatively as two isomers (isomer A 58%; isomer B 42%). Single crystals were grown by hexane layering of a DCM solution.

**MP:** 147-149 °C (decomp.). IR (neat): ν = 3048.8 (w), 1558.2 (w), 1454.9 (m), 1418.3 (m), 1187.0 (m), 1126.3 (w), 1087.3 (m), 1025.8 (w), 947.3 (w), 888.3 (s), 802.3 (m), 770.3 (s), 710.2 (m), 635.1 (s), 610.1 (m) cm⁻¹. **1H NMR** (500 MHz, CDCl₃, −20 °C): δ (ppm) = 8.33 (dd, 3J_HH = 14.0 Hz, 3J_Hh = 4.8 Hz, 1H, H3⁵), 8.17 (d, 3J_HH = 8.7 Hz, 1H, H4⁶), 8.04-7.95 (m, 4H, H3², 2H, H4⁴/H5⁴), 7.91-7.87 (m, 2H, H4⁴/H5⁴), 7.79 (d, 3J_Hh = 8.3 Hz, 1H, H6⁵), 7.70 (d, 3J_Hh = 8.2 Hz, 1H, H6⁵), 7.63-7.58 (m, 2H), 7.52 (d, 3J_Hh = 6.9 Hz, 1H, H2⁴), 7.48-7.38 (m, 3H), 7.35-7.09 (m, 20H, H8⁶/H8⁸/H14⁴⁸/H14⁵⁸/H15⁴⁸/H15⁵⁸/H15⁶⁸/H15⁷⁸/H16⁴⁸/H16⁵⁸/H16⁶⁸/H16⁷⁸/H16⁸⁸), 7.05-7.01 (m, 2H, H14⁵⁸/H14⁶⁸), 4.43 (dd, 3J_HH = 9.9 Hz, 3J_Hh = 2.8 Hz, 1H, allyl-Hts⁷), 4.06 (dd, 3J_HH = 10.2 Hz, 3J_Hh = 2.8 Hz, 1H, allyl-Hts⁷), 3.25 (br s, 1H, allyl-Hts⁷), 3.16 (d, 3J_HH = 13.8 Hz, 1H, allyl-Hts⁷), 3.00 (br s, 1H, allyl-Hts⁷), 2.57 (d, 3J_HH = 14.3 Hz, 1H, allyl-Hts⁷), 2.27 (br s, 1H, allyl-Hts⁷), 2.24 (s, 3H, CH₃⁷), 2.13 (br s, 1H, allyl-Hts⁷), 1.81 (s, 3H, CH₃⁷), 1.63 (s, 6H, CH₃⁷/CH₃⁸), 1.52 (s, 3H, allyl-CH₃⁷), 1.47 (s, 3H, allyl-CH₃⁷). **13C{¹H} NMR** (126 MHz, CDCl₃, −20 °C): δ (ppm) = 148.8 (d, 2J_Cp = 13.4 Hz, C1²⁸), 148.4 (d, 2J_Cp = 12.8 Hz, C1²⁸), 148.0 (d, 2J_Cp = 7.4 Hz, C1²⁸), 147.3 (d, 2J_Cp = 7.6 Hz, C1²⁸), 143.3 (d, 2J_Cp = 18.2 Hz, C1³⁰), 142.6 (d, 2J_Cp = 6.7 Hz, C1³⁰), 135.5 (d, 2J_Cp = 2.5 Hz, C1³⁰), 135.2 (d, 2J_Cp = 7.1 Hz, C1³⁰), 134.9, 134.8, 134.7 (d, 2J_Cp = 8.8 Hz, allyl-C⁶⁴), 134.0 (d, 2J_Cp = 9.0 Hz, allyl-C⁶⁴), 133.9 (C9⁸), 133.5, 133.2, 133.1, 133.0, 132.5, 131.5, 131.5, 131.3, 131.2 (d, 2J_Cp = 2.8 Hz), 131.0 (d, 2J_Cp = 2.2 Hz), 130.9, 130.8, 130.7 (d, 2J_Cp = 2.2 Hz), 130.7, 130.5 (d, 2J_Cp = 2.8 Hz), 130.4 (d, 2J_Cp = 2.8 Hz), 130.2 (d, 2J_Cp = 2.2 Hz), 130.2 (d, 2J_Cp = 1.9 Hz), 128.8 (C²⁹), 128.6, 128.4, 128.3 (C⁴⁳), 128.3, 128.3, 128.1, 128.0, 127.9, 127.8, 127.6, 127.5, 127.0, 126.9, 126.8, 126.8, 126.0, 125.9, 125.8, 125.8, 125.6, 125.5, 125.4, 125.4, 125.1, 124.3 (C³⁴/C³⁵), 78.3 (d, 2J_Cp = 44.7 Hz, allyl-Cl⁶⁴), 77.8 (d, 2J_Cp = 45.7 Hz, allyl-Cl⁶⁴), 59.3 (d, 2J_Cp = 5.1 Hz, allyl-Cl⁶⁴), 57.4 (d, 2J_Cp = 3.5 Hz, allyl-Cl⁶⁴), 22.9 (allyl-CH₃⁴), 22.8 (allyl-CH₃⁴), 17.6 (CH₃⁴), 17.2 (CH₃⁴), 16.8 (CH₃⁴), 16.5 (CH₃⁴). **31P{¹H} NMR** (202 MHz, CDCl₃, −20 °C): δ (ppm) = 177.6 (s, P¹), 172.9 (s, P¹). **HRMS** (NSI⁺, DCM/MeOH + NH₄OAc): Found: m/z = 653.1190. Calculated for [M − Cl]⁺: m/z = 653.1191.
(S)-5a (19.9 mg, 40.0 μmol, 1.0 eq.) and [Pd(η^3-C₄H₇)Cl]₂ (7.9 mg, 20 μmol, 0.5 eq.) were dissolved in DCM (2.0 mL) and stirred for 10 min, before sodium tetraakis[3,5-bis(trifluoromethyl)phenyl]borate (35.4 mg, 40 μmol, 1.0 eq.) was added and stirred for 30 min. The reaction mixture was filtered through Celite® to yield the title complex quantitatively as two isomers (isomer A 48%; isomer B 52%).

**MP**: 128-130 °C. IR (neat): ν = 3068.1 (w), 1610.9 (w), 1504.7 (w), 1462.7 (w), 1421.6 (w), 1353.9 (s), 1273.8 (s), 1160.6 (m), 1117.5 (s), 948.6 (w), 909.9 (m), 887.1 (m), 839.0 (m), 803.0 (m), 765.5 (m), 745.1 (m), 712.4 (s), 681.5 (s), 669.7 (s), 637.1 (m) cm⁻¹. ¹H NMR (500 MHz, CD₂Cl₂, 0 °C): 6 (ppm) = 8.34 (dd, ³JHH = 8.4 Hz, ³JHH = 6.4 Hz, 1H, H₃A), 8.27 (dd, ³JHH = 8.5 Hz, ³JHH = 6.4 Hz, 1H, H₃B), 8.16 (d, ³JHH = 8.2 Hz, 1H, H₅B), 8.13 (d, ³JHH = 8.2 Hz, 1H, H₅A), 8.11-8.00 (m, 6H, H₄A/H₄B/H₄A/H₄B/H₅A/H₅B), 7.81-7.75 (m, 18H, H₆A/H₆B/ortho-BAr⁷), 7.68-7.33 (m, 23H, H₂A/H₆A/H₆B/H₇A/H₇B/H₈A/H₈B/H₄A/H₄B/H₄A/H₄B/H₆A/H₆B/H₆A/para-BAr⁷), 7.30-7.25 (m, 2H, H₇A/H₇B), 7.21-6.91 (m, 7H, H₂B/H₃A/H₃B/H₅A/H₅B/H₁⁵A/H₁⁵B), 6.05 (d, ³JHH = 8.6 Hz, 1H, H₈A), 5.99 (d, ³JHH = 8.6 Hz, 1H, H₈B), 4.13 (d, ³JHP = 13.8 Hz, 1H, allyl-H₃sym⁸), 3.43 (dd, ³JHP = 9.7 Hz, ³JHP = 2.4 Hz, 1H, allyl-H₃sym⁸), 3.09 (br s, 1H, allyl-H₃sym⁸), 3.00 (br s, 1H, allyl-H₃sym⁸), 2.59 (br d, ³JHP = 9.0 Hz, 1H, allyl-H₃sym⁸), 2.48 (d, ³JHP = 13.6 Hz, 1H, allyl-H₃sym⁸), 2.35 (br s, 4H, allyl-H₃sym⁸/aryl-CH₃), 2.31 (br s, 4H, allyl-H₃sym⁸/aryl-CH₃), 2.11 (s, 3H, allyl-CH₃), 2.02 (s, 3H, allyl-CH₃), 1.88 (s, 3H, allyl-CH₃), 0.96 (s, 3H, allyl-CH₃). ¹³B NMR (160 MHz, CD₂Cl₂, 0 °C): δ (ppm) = -6.6 (s). ¹³C[¹H] NMR (126 MHz, CD₂Cl₂, 0 °C): δ (ppm) = 161.8 (q, ³JCB = 49.7 Hz, ipso-BAr⁷), 147.8 (m, C₁₂A/C₁₂B/C₁₂A/C₁₂B), 144.1 (overlapping-d, C₁⁴/C¹⁸), 140.8 (d, ³JCP = 10.7 Hz, allyl-C⁸), 138.3 (d, ³JCP = 10.4 Hz, allyl-C⁴), 137.5 (d, ³JCP = 45.4 Hz, C₂⁸), 137.2 (d, ³JCP = 44.7 Hz, C₂⁸), 136.5 (d, ³JCP = 1.0 Hz, C₁⁰⁸), 136.5 (d, ³JCP = 1.0 Hz, C₁⁰⁸), 134.8 (ortho-BAr⁷), 133.7 (C₉⁸), 133.4 (C₉⁸), 133.0 (d, ³JCP = 4.6 Hz), 132.5 (d, ³JCP = 3.2 Hz), 132.3 (d, ³JCP = 5.4 Hz, C₉⁸), 132.2 (d, ³JCP = 4.9 Hz, C₉⁸), 131.8, 131.7, 131.7, 131.2 (d, ³JCP = 3.4 Hz), 131.0 (C₃⁸), 130.8 (C₃⁸), 130.7, 130.7, 130.5, 130.0, 129.8 (m), 129.7 (d, ³JCP = 2.8 Hz), 129.6 (d, ³JCP = 3.2 Hz), 129.5 (C₅⁸), 129.4, 129.3 (C₅⁸), 129.2, 129.1, 129.0, 128.9 (m), 128.8, 128.7 (m), 128.5, 128.4 (m), 128.3, 128.2 (d, ³JCP = 10.0 Hz), 128.1 (m), 128.0, 128.0, 127.7 (d, ³JCP = 8.3 Hz, C₁⁰⁸), 127.5 (d, ³JCP = 7.7 Hz, C₁⁰⁸), 127.2, 127.1, 127.0, 126.8, 126.4, 126.1 (m), 126.0, 125.9, 125.8 (C₈⁸/C₈⁸), 125.1 (d, ³JCP = 10.7 Hz, C₃⁸), 124.7 (d, ³JCP = 7.3 Hz, C₃⁸), 124.6 (q, ³JCS =
273 Hz, CF₃), 122.6, 122.5, 117.5 (septet, 3JCF = 3.8 Hz, para-BAr²), 109.0 (C2¹A), 107.5 (C2¹B), 101.9 (d, 2JCP = 40.3 Hz, allyl-Ct⁴), 98.4 (d, 2JCP = 40.5 Hz, allyl-Ct⁶), 57.3 (d, 2JCP = 6.1 Hz, allyl-Cc⁸), 54.8 (d, 2JCP = 6.6 Hz, allyl-Cc⁶), 22.7 (allyl-CH₃), 21.4 (allyl-CH₃), 17.1 (aryl-CH₃), 16.8 (aryl-CH₃), 16.7 (aryl-CH₃), 16.6 (aryl-CH₃). ¹⁹F NMR (471 MHz, CD₂Cl₂, 0 °C): δ (ppm) = −62.7 (s). ³¹P{¹H} NMR (202 MHz, CD₂Cl₂, 0 °C): δ (ppm) = 170.1 (s, P⁰), 169.5 (s, P⁴). HRMS (NSI⁺, DCM/MeOH + NH₄OAc): Found: m/z = 653.1194. Calculated for [M – BAr²]⁺: m/z = 653.1191.
2.11 General procedure for the asymmetric hydrosilylation of styrene derivatives

\[
\begin{align*}
\text{Ar} & \xrightarrow{[\text{Pd}, \text{HSiCl}_3, \text{chiral ligand}]} \text{SiCl}_3 \xrightarrow{[\text{O}]} \text{OH}
\end{align*}
\]

Phosphonite ligand (0.25 mol\% or 0.50 mol\%) and \([\text{Pd}(\eta^3-C_3\text{H}_5)\text{Cl}]_2\) (0.125 mol\%) were dissolved in the styrene (1.0 eq.) and stirred at room temperature for 20 min; for reactions at an external temperature of 0 °C, the reaction mixture was subsequently stirred for 20 min at this temperature. Trichlorosilane (1.2 eq.) was added and the conversion of the reaction was followed by \(^1\text{H}\) NMR spectroscopy. The product was purified by Kugelrohr distillation (reduced pressure; 150-180 °C).

The product (400 mg) was dissolved in methanol (30 mL) and THF (30 mL); potassium carbonate (1.40 g, 10.1 mmol), potassium fluoride (600 mg, 10.3 mmol) and hydrogen peroxide solution (35 wt. % in water, 1.8 mL) were added and the reaction mixture left to stir overnight. The suspension was filtered and the volatiles were removed in vacuo. The residue was dissolved in diethyl ether (50 mL) and washed with water (3 x 50 mL), dried over MgSO\(_4\) and the volatiles were removed in vacuo. Silica gel flash chromatography (petrol/ethyl acetate, 3:1) yielded the pure alcohol products, which were all obtained as colourless oils.

The \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectroscopic data matched that of commercially acquired samples or data reported in the literature, and the HRMS data was in accordance with the calculated values. The enantiomeric excess was determined by chiral GC or HPLC analysis; the absolute configuration was assigned by comparison of the measured sign of the optical rotation to literature data.

2.11.1 1-Phenylethanol

\(R_f = 0.60\) (silica gel; petrol/ethyl acetate, 3:1). \(^1\text{H}\) NMR (300 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 7.44-7.26 (m, 5H), 4.91 (q, \(\delta_{J_{HH}} = 6.5\) Hz, 1H), 2.08 (br s, 1H), 1.52 (d, \(\delta_{J_{HH}} = 6.5\) Hz, 3H). \(^{13}\text{C}\{^1\text{H}\}\) NMR (75 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 145.9, 128.5, 127.5, 125.4, 70.4, 25.2. HRMS (ASAP\(^+\), solid): Found: \(m/z = 121.0646\). Calculated for \([\text{M} - \text{H}]^+\): \(m/z = 121.0648\).

2.11.2 1-[4-(Chloro)phenyl]ethanol

\(R_f = 0.50\) (silica gel; petrol/ethyl acetate, 3:1). \(^1\text{H}\) NMR (300 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 7.25-7.17 (m, 4H), 4.77 (q, \(\delta_{J_{HH}} = 6.4\) Hz, 1H), 2.09 (br s, 1H), 1.37 (d, \(\delta_{J_{HH}} = 6.4\) Hz, 3H). \(^{13}\text{C}\{^1\text{H}\}\) NMR (75 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 144.3, 133.1, 128.6, 126.8, 69.7, 25.3. HRMS (ASAP\(^+\), solid): Found: \(m/z = 155.0256\). Calculated for \([\text{M} - \text{H}]^+\): \(m/z = 155.0258\).
2.11.3 1-[4-(Methoxy)phenyl]ethanol

$R_f = 0.30$ (silica gel; petrol/ethyl acetate, 3:1). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm) = 7.23 (d, $^3J_{HH} = 8.7$ Hz, 2H), 6.81 (d, $^3J_{HH} = 8.7$ Hz, 2H), 4.78 (q, $^1J_{HH} = 6.4$ Hz, 1H), 3.73 (s, 3H), 1.71 (br s, 1H), 1.51 (d, $^3J_{HH} = 6.4$ Hz, 3H). $^{13}$C{^1}H NMR (75 MHz, CDCl$_3$): $\delta$ (ppm) = 159.0, 138.0, 126.7, 113.9, 70.0, 55.3, 25.0.

3. Density Functional Theory Calculations

Performed with the B3LYP functional and 6-31G* basis set, using the Spartan program. In each case the calculations were considered to be complete and converged to a minimum on the potential energy surface after vibrational frequency analysis did not report any negative frequencies.

3.1 (S)-H-MOP and (R)-MeO-MOP

$\text{-(S)-H-MOP}$ and $\text{(R)-MeO-MOP}$

$\text{LUMO} - 1.15 \text{ eV}$

$\text{HOMO} - 1.06 \text{ eV}$

$\text{LUMO} - 5.51 \text{ eV}$

$\text{HOMO} - 5.27 \text{ eV}$
3.2 (S)-3a and (R)-3b

\[
\begin{align*}
\text{HOMO} & \quad -5.80 \text{ eV} \\
\text{LUMO} & \quad -1.29 \text{ eV}
\end{align*}
\]

\[
\begin{align*}
\text{HOMO} & \quad -5.51 \text{ eV} \\
\text{LUMO} & \quad -1.21 \text{ eV}
\end{align*}
\]
3.3 (S)-4a and (R)-4b

-1.33 eV

LUMO

-1.21 eV

-5.76 eV

HOMO

-5.47 eV
3.4 (S)-5a and (R)-5b

LUMO

HOMO

-1.34 eV

-1.22 eV

-5.76 eV

-5.48 eV
4. X-ray Diffraction

Fig. 2  Molecular structure of one of the two independent molecules of (R)-3b (the asymmetric unit comprises two molecules in different conformations). Hydrogen atoms have been omitted for clarity. Selected average bond distances (Å) and angles (°): P1–C2 1.818(3), P1–O1 1.6489(18), P1–O2 1.6675(17), O1–C12A 1.400(10), O2–C12' 1.390(3), C1–C1' 1.495(3); O1–P1–O2 98.80(9), O1–P1–C2 96.62(10), O2–P1–C2 97.37(10), C2–C1–C1'–C2' −102.2(3).

Fig. 3  Molecular structure of one of the two independent molecules of (S)-7a (the asymmetric unit comprises two molecules in different conformations). Hydrogen atoms have been omitted for clarity. Selected average bond distances (Å) and angles (°): Pd2A–P2 2.250(3), Pd2A–Cl2 2.363(3), Pd2A–C39 2.166(5), Pd2A–C40A 2.119(8), Pd2A–C41A 2.091(9), P2–C23 1.814(4), P2–O3 1.625(3), P2–O4 1.606(3), C32–C32' 1.475(6); P2–Pd2A–Cl2 93.59(11), P2–Pd2A–C40A 165.9(3), P2–Pd2A–C41A 98.50(3), C40A–Pd2A–C41A 67.5(3), C40A–C39–C41A 118.5(6), C23–C22–C22'–C23' –96.7(5), C33–C32–C32'–C33' 48.6(6).
Measurements were made at 150 K on an Oxford Diffraction (Agilent Technologies) Gemini A Ultra diffractometer, using CuKα radiation (1.54184 Å) for (R)-3b and MoKα radiation (λ = 0.71073 Å) for (R)-4b, (S)-6a and (S)-7a. Cell parameters were refined from the observed positions of all strong reflections. Intensities were corrected for absorption, using a semi-empirical method based on symmetry-equivalent and repeated reflections for (R)-4b and (S)-6a and analytically using a multi-faceted crystal model for (R)-3b and (S)-7a. The structures were solved by direct methods and refined on F² values for all unique data. All non-hydrogen atoms were refined anisotropically, and H atoms were positioned with idealised geometry and the thermal parameters constrained using the riding model; U(H) was set at 1.2 times Ueq for the parent C atom. One phenyl group of one of the crystallographically independent molecules of (R)-3b and the palladium atom and methallyl ligand of one crystallographically independent molecule of (S)-7a were modeled as disordered over two positions with the use of restraints. Continuous solvent-accessible channels were observed along the crystallographic [010] direction in the structure of (S)-6a. The disordered diethyl ether molecules therein could not be modeled in a sensible way and were resolved using the Olex2 solvent mask routine, details of which can be found in the CIF. Oxford Diffraction CrysAlisPro was used for data collection and processing,¹¹ and Olex2¹² using SHELX¹³ for structure solution, refinement, and to generate the molecular overlap figures. Crystal Impact Diamond was used to generate all other molecular graphics with displacement ellipsoids drawn at the 50% probability level.¹⁴

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**Fig. 4** Two views of an overlay image of the biphenyl moiety in the two independent molecules of (S)-7a.
4.1 Crystal data and structure refinement for (R)-3b

Empirical formula \( \text{C}_{33}\text{H}_{25}\text{O}_{3}\text{P} \)

Formula weight 500.50

Temperature/K 150.0(2)

Crystal system monoclinic

Space group \( \text{P}2_1 \)

\( a/\text{Å} \) 10.57860(7)

\( b/\text{Å} \) 16.52575(9)

\( c/\text{Å} \) 14.80544(8)

\( \alpha/^\circ \) 90

\( \beta/^\circ \) 95.7963(6)

\( \gamma/^\circ \) 90

Volume/\( \text{Å}^3 \) 2575.04(3)

\( Z \) 4

\( \rho_{\text{calc}} \text{g/cm}^3 \) 1.291

\( \mu/\text{mm}^{-1} \) 1.208

\( F(000) \) 1048.0

Crystal size/mm\(^3\) 0.27 \( \times \) 0.2 \( \times \) 0.13

Radiation CuK\( \alpha \) (\( \lambda = 1.54184 \))

2\( \Theta \) range for data collection/\(^\circ\) 6 to 133.998

Index ranges \(-12 \leq h \leq 12, -19 \leq k \leq 19, -17 \leq l \leq 17\)

Reflections collected 71384

Independent reflections 9138 \( [R_{\text{int}} = 0.0479, R_{\text{sigma}} = 0.0227]\)

Data/restraints/parameters 9138/14/687

Goodness-of-fit on \( F^2 \) 1.049

Final R indexes [\( I > 2\sigma (I) \)] \( R_1 = 0.0273, wR_2 = 0.0645 \)

Final R indexes [all data] \( R_1 = 0.0303, wR_2 = 0.0663 \)

Largest diff. peak/hole / e \( \text{Å}^3 \) 0.13/-0.19

Flack parameter 0.001(5)
### 4.2 Crystal data and structure refinement for (R)-4b

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<td>γ/*</td>
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4.3 Crystal data and structure refinement for (S)-6a

Empirical formula \( \text{C}_{36}\text{H}_{28}\text{O}_{2}\text{PClPd} \)

Formula weight 665.40

Temperature/K 150.0(2)

Crystal system orthorhombic

Space group \( \text{P2}_1\text{2}_1\text{2}_1 \)

\( a/\text{Å} \) 10.0618(3)

\( b/\text{Å} \) 14.4757(4)

\( c/\text{Å} \) 25.0065(10)

\( \alpha/° \) 90

\( \beta/° \) 90

\( \gamma/° \) 90

Volume/\( \text{Å}^3 \) 3642.2(2)

\( Z \) 4

\( \rho_{\text{calc}} \text{g/cm}^3 \) 1.213

\( \mu \text{mm}^{-1} \) 0.653

\( F(000) \) 1352.0

Crystal size/mm\(^3\) 0.4 × 0.12 × 0.02

Radiation MoK\( \alpha \) (\( \lambda = 0.71073 \))

2\( \Theta \) range for data collection/° 5.86 to 57.234

Index ranges \(-13 \leq h \leq 12, -17 \leq k \leq 17, -29 \leq l \leq 30\)

Reflections collected 7676

Independent reflections 7674 [\( R_{\text{int}} = 0.0000, R_{\text{sigma}} = 0.0471 \)]

Data/restraints/parameters 7674/0/371

Goodness-of-fit on \( F^2 \) 1.010

Final R indexes [\( I \geq 2\sigma (I) \)] \( R_1 = 0.0318, wR_2 = 0.0709 \)

Final R indexes [all data] \( R_1 = 0.0388, wR_2 = 0.0737 \)

Largest diff. peak/hole / e Å\(^3\) 0.37/-0.49

Flack parameter -0.034(13)
4.4 Crystal data and structure refinement for (S)-7a

Empirical formula \( \text{C}_{38}\text{H}_{32}\text{O}_{2}\text{PClPd} \)

Formula weight \( 693.45 \)

Temperature/K \( 150.01(10) \)

Crystal system monoclinic

Space group \( \text{P2}_1 \)

\( a/\text{Å} \) \( 11.4401(2) \)

\( b/\text{Å} \) \( 16.7063(3) \)

\( c/\text{Å} \) \( 16.3663(3) \)

\( \alpha/^{\circ} \) \( 90 \)

\( \beta/^{\circ} \) \( 90.6112(16) \)

\( \gamma/^{\circ} \) \( 90 \)

Volume/Å\(^3\) \( 3127.78(10) \)

\( Z \) \( 4 \)

\( \rho_{\text{calc}}/\text{g/cm}^3 \) \( 1.473 \)

\( \mu/\text{mm}^{-1} \) \( 0.763 \)

\( F(000) \) \( 1416.0 \)

Crystal size/mm\(^3\) \( 0.24 \times 0.18 \times 0.1 \)

Radiation \( \text{MoK}\alpha (\lambda = 0.71073) \)

\( 2\theta \) range for data collection/\(^{\circ} \) \( 5.544 \text{ to } 58.916 \)

Index ranges \(-15 \leq h \leq 15, -22 \leq k \leq 21, -22 \leq l \leq 22 \)

Reflections collected \( 96971 \)

Independent reflections \( 15384 [R_{int} = 0.0547, R_{sigma} = 0.0442] \)

Data/restraints/parameters \( 15384/826/795 \)

Goodness-of-fit on \( F^2 \) \( 1.051 \)

Final R indexes \( [I>2\sigma(I)] \) \( R_1 = 0.0355, wR_2 = 0.0629 \)

Final R indexes \( \text{[all data]} \) \( R_1 = 0.0560, wR_2 = 0.0708 \)

Largest diff. peak/hole / e Å\(^3\) \( 0.79/-0.55 \)

Flack parameter \(-0.056(8)\)
5. NMR Spectra

5.1 $^1$H and $^{13}$C NMR spectra for (S)-3a
5.2 $^1$H and $^{13}$C NMR spectra for (R)-3b
5.3 $^1$H and $^{13}$C NMR spectra for $(S)$-4a
5.4 $^1$H and $^{13}$C NMR spectra for (R)-4b
5.5 $^1$H and $^{13}$C NMR spectra for (S)-5a
5.6 $^1$H and $^{13}$C NMR spectra for (R)-5b
5.7 $^1$H and $^{13}$C NMR spectra for 2,2'-dihydroxy-3,3'-dimethyl-1,1'-biphenyl
5.8 $^1$H and $^{13}$C NMR spectra for (S)-6a
5.9 $^1$H and $^{13}$C NMR spectra for (S)-7a
5.10 $^1$H and $^{13}$C NMR spectra for (S)-8a
5.11 $^1$H and $^{13}$C NMR spectra for catalysis products

5.11.1 1-Phenylethanol
5.11.2 1-[4-(Chloro)phenyl]ethanol
5.11.3 1-[4-(Methoxy)phenyl]ethanol
6. Chiral GC and HPLC

6.1 1-Phenylethanol

GC conditions – injection temperature: 200 °C, detection temperature 200 °C, oven temperature: 80 °C for 45 min, then ramp to 130 °C at 10 °C/min, retention times: 51.8 min (R) and 52.8 min (S).

Racemic.

Table 1: Entry 18.

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<td>52.98</td>
<td>52.78</td>
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Table 1: Entry 18.
6.2 1-[4-(Chloro)phenyl]ethanol

GC conditions – injection temperature: 200 °C, detection temperature 200 °C, oven temperature: 100 °C for 45 min, then ramp to 180 °C at 10 °C/min, retention times: 53.9 min (R) and 54.2 min (S).

Racemic.

Table 2: Entry 2.
6.3 1-[4-(Methoxy)phenyl]ethanol

GC conditions – injection temperature: 200 °C, detection temperature 200 °C, oven temperature: 100 °C for 60 min, then ramp to 180 °C at 10 °C/min, retention times: 68.7 min (R) and 69.2 min (S).

Racemic.

Table 2: Entry 8.

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7. References