Supporting Information

Asymmetric Hydroformylation Using Taddol-Based Chiral Phosphine-Phosphite Ligands

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Experimental Section

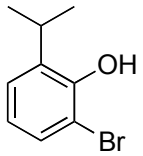
All reactions were carried out under an inert atmosphere and in heat-dried glasware. Anhydrous solvents were obtained by distillation from sodium benzophenone ketyl (THF) or distillation from CaH_2 (CH_2Cl_2). Flash column chromatography was performed on silica gel (particle size 40-63 mM, Acros). Reactions were monitored by analytical thin layer chromatography (TLC) using Merck silica gel 60 F_{254} aluminum plates and by GCMS. An Agilent Technologies Model GC 6890N gas chromatograph coupled with an HP 5973N series mass selective detector and an HP 7683 GC autosampler was employed for all GCMS analyses. Samples were separated on a 30-m x 0.25-mm, HP-5 MS column. The column temperature was initially held at 50 °C for 2 min, then the temperature was raised to 300 °C at a rate of 25 °C per min and held for 5 min. The total run time was 17 min. Injector temperature was maintained at 300 °C, and the injection volume was 1.0 μL in the split mode. Mass spectra were scanned from m/z 35-500. Electron impact ionization energy was 70 eV. NMR spectra were measured on Bruker instruments (Avance DPX 300 and Avance II 600) at 300 or 600 MHz for ^{1}H and 75 or 150 MHz for ^{13}C. Deuterated chloroform was used as a solvent. Proton shifts are reported in ppm (δ) downfield from TMS and were determined by reference to the residual solvent peak ($CDCl_3$: 7.24 ppm). Mass spectrometer MAT 900 (Finnigan) was used for the high resolution mass spectra (HRMS). Infrared spectra were recorded on a Paragon 100 FT IR instrument (Perkin-Elmer). Optical rotations were measured using a Perkin-Elmer 343 polarimeter, concentrations c are given in g/100 ml.

Synthesis of chiral Phosphine-Phosphite Ligands 12a, 12b, 13a

General procedure I: *ortho*-bromination to bromides of type **2**

In a flame-dried flask equipped with a Soxhlet apparatus and flushed with argon the substituted phenols of type **1** (1 equiv.) and diisopropylamine (0.1 equiv.) were dissolved in absolute CH_2Cl_2. The thimble was filled with NBS (1 equiv.) and the system was heated to reflux for 16 h. During this time, the NBS was slowly consumed. After cooling to RT the resulting mixture was treated with 2 M sulfuric acid. The layers were separated and the aqueous layer was extracted with *tert*-butylmethylether. The combined organic layers were washed with water and brine, and dried ($MgSO_4$). The solvent was removed under reduced pressure and the crude product was purified by flash chromatography.

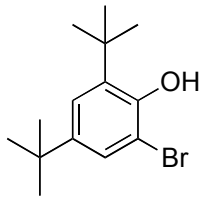
2-Bromo-6-isopropyl-phenol



According to general procedure **I**, 2-isopropylphenol (10.0 g, 73.40 mmol) and diisopropylamine (1.04 ml, 0.72 g, 7.34 mmol) were dissolved in CH_2Cl_2 (200 ml) and treated with NBS (13.07 g, 73.40 mmol) for 16 h at reflux. After cooling to RT the resulting mixture was treated with 2 M sulfuric acid (200 ml). The crude product was purified by flash chromatography (cyclohexane/EtOAc 40:1) to afford 2-bromo-6-isopropylphenol (15.31 g, 71.20 mmol, 97%) as a pale yellow liquid. TLC (cyclohexane/EtOAc 10:1): R_f = 0.41; ^{1}H NMR (300 MHz, CDCl3): δ [ppm] = 1.25 (d, 6H, 8-CH_3, 8´-CH_3), 3.33 (m, 1H, 7-H), 5.58 (s, 1H, OH), 6.78 (m, 1H, $^3J_{4,3}$ = 8.0 Hz, $^3J_{4,5}$ = 7.8 Hz, 4-H), 7.15 (dd, 1H, $^4J_{5,3}$ = 1.5 Hz, , $^3J_{5,4}$ = 7.8 Hz, 5-H), 7.30 (dd, 1H, $^4J_{3,5}$ = 1.5 Hz, , $^3J_{3,4}$ = 8.0 Hz, 3-H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ [ppm] = 22.4 (CH_3, C-8, C-8´), 28.0 (CH, C-7), 110.6 (C_q, C-2), 121.4 (CH, C-4), 125.9 (CH, C-5), 129.0 (CH, C-3), 136.3 (C_q, C-6), 149.4 (C_q, C-1); IR (ATR): $\tilde{\nu}$ [cm_{-1}] = 3507 (s, OH), 3067 (w, sp^2- CH), 3028 (w, sp^2-CH), 2959 (s, sp^3-CH), 2921 (s, sp^3-CH), 2868 (m, sp^3-CH), 1605 (m), 1490 (m), 1452 (s), 1406 (s), 1380 (m), 1361 (m), 1344 (m), 1316 (m), 1266 (s), 1210 (s), 1178 (s), 1153 (s), 1132 (m), 1114 (m), 1062 (m), 1031 (s), 954 (s), 892 (m), 805 (s), 782 (m), 744 (m), 706 (m), 615 (s); MS (EI, 70 eV): m/z (%) = 216 (36) [M^+], 214 (38) [M+], 201 (20) [M-CH_3]$^+$, 199 (22) [M-CH_3]$^+$, 120

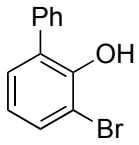
(100) [M-CH_3Br]$^+$, 115 (8), 107 (10), 102 (15), 91 (39), 77 (14), 63 (22),51 (12), 39 (17); HRMS $C_9H_{11}{}^{81}BrO$: calcd. 215.997; found 215.997.

2-Bromo-4,6-di-tert-butylphenol



According to general procedure **I**, 2,4-di-tert-butylphenol (5.0 g, 24.23 mmol) and diisopropylamine (0.42 ml, 0.32 g, 2.42 mmol) were dissolved in CH_2Cl_2 (100 ml) and treated with NBS (5.23 g, 24.23 mmol) for 16 h at reflux. After cooling to RT the resulting mixture was treated with 2M sulfuric acid (100 ml). The crude product was purified by flash chromatography (cyclohexane/EtOAc 40:1) to afford 2-Bromo-4,6-di-tert-butylphenol (4.67 g, 16.15 mmol, 66%) as a pale yellow solid. TLC (cyclohexane/EtOAc 10:1): R_f = 0.49; ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 1.29 (s, 9H, 8-H), 1.42 (s, 9H, 10-H), 5.66 (s, 1H, OH), 7.25 (d, 1H, ^4J = 2.3 Hz, 3-H or 5-H), 7.33 (d, 1H, ^4J = 2.3 Hz, 3-H or 5-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 29.4 (9C, $C(CH_3)_3$), 31.5 (9C, $C(CH_3)_3$), 34.4 ($C(CH_3)_3$), 35.6 ($C(CH_3)_3$), 111.9 (C_q), 123.7 (CH), 126.3 (CH), 136.7 (C_q), 143.7 (C_q), 148.0 (C_q); IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3510 (s, OH), 3071 (w, sp^2-CH), 2960 (s, sp^3-CH), 2867 (s, sp^3-CH), 1594 (m), 1472 (s), 1441 (s), 1382 (m), 1362 (m), 1326 (s), 1270 (m), 1236 (s), 1206 (s), 1173 (s), 1150 (m), 1113 (m), 1047 (s), 897 (m), 827 (s), 771 (s), 733 (s), 621 (s); MS (EI, 70 eV): m/z (%) = 286 (99) [M]$^+$, 284 (99) [M]$^+$, 271 (99) [M-CH_3]$^+$, 269 (99) [M-CH_3]$^+$, 255 (19), 243 (76), 241 (83), 227 (17), 213 (10), 206 (4) [M$^+$-Br], 199 (9), 191 (14), 175 (17), 159 (16), 141 (14), 128 (24), 115 (34), 105 (19), 91 (27), 77 (17), 65 (7), 57 (100) [C_4H_9]$^+$, 41 (56); HRMS $C_{14}H_{21}{}^{79}BrO$: calcd. 284.078; found 284.078.

3-bromobiphenyl-2-ol



According to general procedure **I**, 2-phenylphenol (10.0 g, 58.75 mmol) and diisopropylamine (0.83 ml, 0.89 g, 5.87 mmol) were dissolved in CH_2Cl_2 (200 ml) and treated with NBS (10.46 g, 58.75 mmol) for 16 h at reflux. After cooling to RT the resulting mixture was treated with 2M sulfuric acid (200 ml). The crude product was purified by flash chromatography (cyclohexane/EtOAc 40:1) to afford 3-bromobiphenyl-2-ol (14.05 g, 56.40 mmol, 96%) as a pale yellow liquid. TLC (cyclohexane/EtOAc 10:1): $R_f = 0.37$; ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 5.70 (s, 1H, OH), 6.90 (m, J_1 = 7.7 Hz, J_2= 7.9 Hz, 1H, 4-H), 7.27 (dd, J_1 = 7.7 Hz, J_2= 1.5 Hz, 1H, 3-H), 7.29 – 7.57 (m, 6H, 5-H, 8-H, 9-H, 8´-H, 9´-H, 10-H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ [ppm] = 111.0 (C_q, C-2), 121.6 (CH, C-4), 127.8 (CH, C-10), 128.5 (CH, C-8, C-8´), 129.1 (CH, C-9, C-9´), 129.7 (C_q, C-6), 130.1 (CH, C-5), 131.4 (CH, C-3), 137.1 (C_q, C-7), 149.2 (C_q, C-1); IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3494 (s, OH), 3058 (m, sp^2-CH), 3031 (m, sp^2-CH), 1599 (m), 1577 (m), 1562 (m), 1497 (m), 1465 (s), 1453 (s), 1427 (s), 1326 (s), 1285 (m), 1274 (m), 1253 (m), 1232 (s), 1169 (s), 1125 (s), 1068 (m), 1041 (m), 1015 (m), 997 (m), 829 (s), 783 (m), 767 (s), 752 (s), 730 (s), 696 (s), 639 (s), 619 (w).; MS (EI, 70 eV): m/z (%) = 250 (98) $[M]^+$, 248 (100) $[M]^+$, 168 (37) $[M\text{-}Br]^+$, 139 (59), 115 (41), 102 (5), 89 (8), 74 (7), 63 (12), 51 (7), 39 (5); HRMS $C_{12}H_9{}^{79}BrO$: calcd. 247.984; found 247.982.

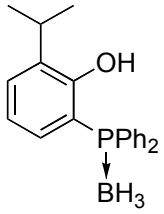
General procedure II: synthesis of BH_3-protected phosphinites of type 7

A flame-dried Schlenk flask was charged under argon with a substituted 2-bromo-phenol of type **6**, 1 equiv.) and DABCO (1.1 equiv.) and dissolved in CH_2Cl_2. This solution was stirred for 5 min at RT then cooled to 0 °C and the chlorophosphine (1.1 equiv.) was added dropwise via syringe. The resulting suspension was stirred 10 min at this temperature, warmed to RT and stirred for another 2 h. The reaction mixture was then cooled to 0 °C and a solution of BH_3 in THF (2 equiv.) was added. This resulting solution was stirred 15 min at 0 °C and 1 h at RT before it was quenched with H_2O (Strong H_2 gas formation) and extracted with *tert*-butyl-methylether. The ethereal phase was washed with brine and dried ($MgSO_4$). The solvent was evaporated to give the crude product of type **7**, which was used without further purification.

General procedure III: Rearrangement of BH_3-protected phosphinites to 2-boranatodiphenylphosphanyl-phenols of type 8

In a flame-dried Schlenk flask under argon a solution of a BH_3-protected phosphinite (**7**, 1 equiv.) in THF was cooled to 0 °C and treated with *n*-BuLi (1.5 equiv.). The mixture was stirred for 2 h at this temperature, then quenched with H_2O, extracted with *tert*-butyl-methylether and washed with NH_4Cl-solution. The organic layers were dried ($MgSO_4$) and concentrated under reduced pressure to give the crude product, which was purified by flash chromatography to provide the phosphines of type **8** as white solids.

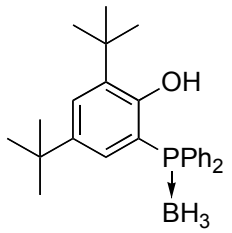
2-Boranatodiphenylphosphanyl-6-isopropyl-phenol



According to procedure **II** and **III**, 2-Bromo-6-isopropyl-phenol (1.0 g, 4.67 mmol) and DABCO (0.58 g, 5.14 mmol) were dissolved in CH_2Cl_2 (15 ml) and treated with chlorodiphenylphosphine (1.13 g, 0.92 ml, 5.14 mmol). After addition of BH_3 in THF (1 M, 9.34 ml, 9.34 mmol) the reaction was quenched with water to afford after evaporation the corresponding borane-protected phosphinite (1.78 g, 4.31 mmol). The crude product was dissolved in THF (25 ml) and treated with *n*-BuLi (1.60 M in THF, 4.05 ml, 6.48 mmol) and quenched with water. The crude product was purified by flash chromatography (cyclohexane/EtOAc 10:1) to afford 2-boranato-diphenylphosphanyl-6-isopropyl-phenol (1.3 g, 3.89 mmol, 85% over two steps) as a white solid. TLC (cyclohexane/EtOAc 10:1): R_f = 0.28; ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 1.24 (d, 6H, ^3J = 6.9 Hz, $CH(CH_3)_2$, 8-H, 8´-H), 1.25 (m, 1H, ^3J = 6.9 Hz, $CH(CH_3)_2$, 7-H), 6.73 (m, 1H, J_1 = 1.7 Hz , J_2 = 10.7 Hz , 3- H), 6.86 (m, 1H, J_1 = 1.5 Hz , J_2 = 7.7 Hz), 7.30 – 7.70 (m, 12H, CH, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 22.5 (2C, $CH(CH_3)_2$), 26.8 ($CH(CH_3)_2$), 111.1 (d, J_{CP} = 58.8 Hz, C_q, C-2), 120.4 (d, J_{CP} = 8.4 Hz, CH), 128.8 (d, 4C, J_{CP} = 10.6 Hz), 130.5 (CH), 131.4 (2C, CH), 131.6 (CH), 132.1 (d, 2C, J_{CP} = 8.9 Hz, C_q), 133.0 (d, 4C, J_{CP} = 9.9 Hz, CH), 137.7 (d, J_{CP} = 5.7 Hz, C_q), 157.1 (d, J_{CP} = 9.4 Hz, C_q, C-1); ^{31}P NMR (121.6 MHz, $CDCl_3$): δ [ppm] = 13.8; ^{11}B NMR (96.3 MHz, $CDCl_3$) : δ [ppm] = -36.7; MS (EI, 70 eV): m/z (%) = 320 (100) $[M\text{-}BH_3]^+$, 305 (76) $[M\text{-}CH_6B]^+$, 292 (52), 277 (5), 241 (3), 227 (9), 213 (11), 199 (14), 183

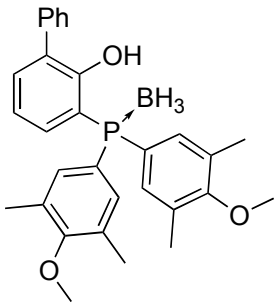
(39), 165 (23), 152 (10), 108 (11), 91 (6), 78 (14), 51 (7); HRMS (EI) $C_{21}H_{21}OP$ = $[M\text{-}BH]^+$.: calcd. 320.133; found 320.133.

2-Boranatodiphenylphosphanyl-4,6-di-*tert*-butyl-phenol



According to procedure **II** and **III** 2-Bromo-4,6-di-tert-butylphenol (1.43 g, 5.0 mmol) and DABCO (0.62 g, 5.5 mmol) were dissolved in CH_2Cl_2 (15 ml) and treated with chlorodiphenylphosphane (1.21 g, 0.99 ml, 5.5 mmol). After addition of BH_3 in THF (1 M, 10.0 ml, 10.0 mmol) the reaction was quenched with water to afford after evaporation the corresponding boran-protected phosphinite (2.17 g, 4.63 mmol). The crude product was dissolved in THF (12 ml) and treated with *n*-BuLi (1.42 M in THF, 4.89 ml, 6.95 mmol) and quenched with water. The crude product was purified by flash chromatography (cyclohexane/EtOAc 10:1) to afford 2-Boranatodiphenylphosphanyl-4,6-di-*tert*-butyl-phenol (1.38 g, 4.32 mmol, 81% over two steps) as a white solid. TLC (cyclohexane/EtOAc 10:1): R_f = 0.37; ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 1.12 (s, 9H, $C(CH_3)_3$), 1.42 (s, 9H, $C(CH_3)_3$), 6.68 (dd, 1H, J_1 = 2.4 Hz, J_2 = 11.7 Hz, 3-H), 7.30 – 7.60 (m, 12H, CH-OH); ^{13}C NMR (75 MHz, $CDCl_3$) : δ [ppm] = 29.6 (3C, $C(CH_3)_3$), 31.2 (3C, $C(CH_3)_3$), 34.3 ($C(CH_3)_3$), 35.4 ($C(CH_3)_3$), 111.2 (d, J_{CP} = 58.7 Hz, C_q, C-2), 128.2 (C_q), 128.5 (CH, C-5), 128.6 (CH), 128.8 (d, 4C, J_{CP} = 10.6 Hz), 131.4 (2C, CH), 132.9 (d, 4C, J_{CP} = 9.8 Hz), 138.0 (d, 2C, J_{CP} = 5.8 Hz, C_q), 142.1 (d, J_{CP} = 8.0 Hz, C_q,), 157.1 (d, J_{CP} = 9.8 Hz, C_q, C-1); ^{31}P NMR (121.6 MHz, $CDCl_3$) : δ = 13.8; ^{11}B NMR (96.3 MHz, $CDCl_3$) : δ [ppm] = -36.7; IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3360 (s, OH), 3057 (m), 2957 (s), 2909 (m), 2867 (m), 2376 (m), 1587 (w), 1574 (w), 1475 (m), 1466 (m), 1454 (m), 1435 (s), 1407 (m), 1390 (m), 1361 (s), 1341 (m), 1286 (m), 1247 (s), 1215 (s), 1186 (s), 1141 (m), 1116 (m), 1104 (s), 1067 (s), 1025 (m), 887 (m), 819 (m), 767 (m), 740 (s), 699 (s), 691 (s), 626 (s), 608 (s); MS (EI, 70 eV): m/z (%) = 390 (84) $[M\text{-}BH_3]^+$, 375 (66) $[M\text{-}CH_6B]^+$, 348 (39), 333 (30), 297 (30), 269 (9), 255 (14), 221 (14), 201 (23), 183 (100), 166 (17), 152 (20), 133 (20), 108 (97), 91 (33), 78 (66), 57 (58) $[C_4H_9]^+$, 41 (44); HRMS (EI) $C_{26}H_{31}OP$ = $[M\text{-}BH_3]^+$.: calcd. 390.211; found 390.211.

3-Boranato-(bis(4-methoxy-3,5-dimethylphenyl)phosphino)biphenyl-2-ol



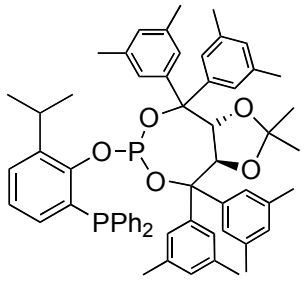
According to procedure **II** and **III** 3-bromobiphenyl-2-ol (0.45 g, 1.8 mmol) and DABCO (0.22 g, 2.0 mmol) were dissolved in CH_2Cl_2 (6 ml) and treated with chlorobis(4-methoxy-3,5-dimethylphenyl)phosphine (0.67 g, 2.0 mmol). After addition of BH_3 in THF (1 M, 3.6 ml, 3.6 mmol) the reaction was quenched with water to afford after evaporation the corresponding boran-protected phosphinite. The crude product was dissolved in THF (7 ml) and treated with *n*-BuLi (1.46 M in hexane, 1.85 ml, 2.7 mmol) and quenched with water. The crude product was purified by flash chromatography (cyclohexane/EtOAc 5:1) to afford 3-Boranato-(bis(4-methoxy-3,5-dimethylphenyl)phosphino)biphenyl-2-ol (0.49 g, 1.01 mmol, 56% over two steps) as a white solid. TLC (cyclohexane/EtOAc, 5:1): R_f = 0.37; ^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 2.26 (s, 12H, CH_3), 3.74 (s, 6H, OCH_3), 6.95-7.03 (m, 2H), 7.21 (Ψd, *J* = 11.3 Hz, 4H), 7.31-7.36 (m, 2H), 7.41 (Ψt, *J* = 7.8 Hz, 2H, 7.43-7.47 (m, 1H), 7.51 (Ψd, *J* = 7.2 Hz, 2H); ^{31}P NMR (121.5 MHz, $CDCl_3$): δ [ppm] = 11.42; ^{11}B NMR (96.3 MHz, $CDCl_3$): δ [ppm] = -36.4; IR (ATP) $\tilde{\nu}$ [cm^{-1}] = 3340 (s), 3053 (w), 3028 (w), 2986 (w), 2937 (m), 2376 (s), 2298 (w), 1586 (m), 1477 (s), 1449 (s), 1421 (s), 1344 (m), 1277 (s), 1223 (s), 1191 (w), 1114 (s), 1065 (m), 1008 (s), 908 (m), 832 (w), 798 (w), 759 (m), 731 (m), 698 (m), 631 (w); MS (EI, 70 eV): m/z (%) = 481 (31), 471 (31), 470 (100, $[M\text{-}BH_3]^+$), 319 (45), 303 (26), 183 (26), 166 (20), 152 (19), 136 (16), 121 (22), 105 (19), 91 (26), 77 (19); HRMS (EI, 70 eV): calcd. für $[M\text{-}BH_3]^+$: 470.201, found.: 470.201.

General procedure IV: Synthesis of chiral phosphine-phosphite-ligands.

A flame-dried Schlenk flask was put under argon and the phosphine (1.0 equiv.) and DABCO (10 equiv.) were dissolved in absolute CH_2Cl_2. The resulting solution was stirred for 10 min at

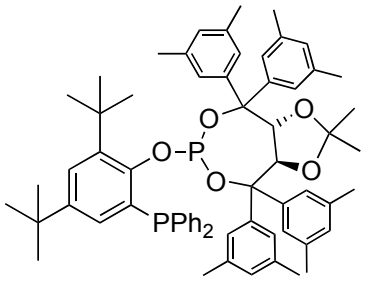
RT, then cooled to 0 °C and a solution of PCl_3 in CH_2Cl_2 (1.0 equiv.) was added drop wise via syringe. The reaction mixture was stirred for 30 min at this temperature, warmed to RT and stirred for 3 h. The milky suspension was cooled to 0 °C and a solution of the chiral diol (1.5 equiv.) in CH_2Cl_2 was added. After 30 min the resulting solution was allowed to warm to RT and stirring was continued for another 20 h. The solvent was evaporated to give the crude product, which was purified by flash chromatography to afford ligands (**12a**, **12b**, **13a**) as white foams.

(3a*R*,8a*R*)-4,4,8,8-tetrakis(3,5-dimethylphenyl)-6-(2-(diphenylphosphino)-6-isopropylphenoxy)-2,2-dimethyltetrahydro-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepine (12a)



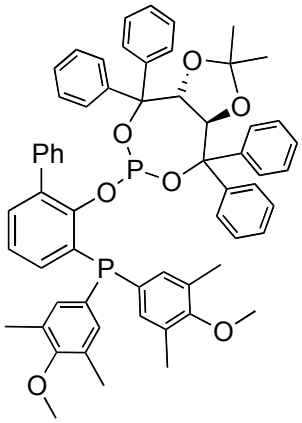
According to general procedure **IV**, a solution of 2-Boranatodiphenylphosphanyl-6-isopropylphenol (0.50 g, 1.50 mmol) was treated with DABCO (1.35 g, 12.0 mmol) and PCl_3 (2M, 0.98 ml, 1.95 mmol) in CH_2Cl_2 (10 ml) and (*R,R*)-Xylyl-Taddol (0.96 g, 1.65 mmol) in CH_2Cl_2 (10 ml). The crude product was purified by flash chromatography (cyclohexane/EtOAc 3:1) to afford **12b** (0. 274 g, 20%) as white foam. TLC (cyclohexane/EtOAc, 10:1): R_f = 0.5; ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 0.34 (s, 3H, CH_3), 1.14 (d, $^1J_{HH}$ = 6.9, 3H, $CH(CH_3)_2$), 1.17 (d, $^1J_{HH}$ = 6.9, 3H, $CH(CH_3)_2$), 1.28 (s, 3H, CH_3), 2.11 (s, 6H, $C(CH_3)$), 2.19 ((s, 6H, $C(CH_3)$), 2.22 (s, 6H, $C(CH_3)$), 2.24 (s, 6H, $C(CH_3)$), 3.90 (m, 1H), 4.92 (d, J = 8.3 Hz, 1H, OCH), 4.97 (d, J_1 = 8.3 Hz, J_2 = 2.4 Hz, 1H, OCH), 6.67-6.72 (m, 1H), 6.76 (m, 5H), 6.99-7.22 (m, 17H), 7.52, (s, 2H); ^{31}P NMR {^{1}H} (121.5 MHz, $CDCl_3$): d = -18.72 (d, J = 73.3 Hz), 149.57 (d, J = 73.3 Hz); IR (ATR): $\tilde{\nu}$ = 3051 (w), 2961 (w), 2915 (m), 2864 (w), 1601 (m), 1458 (m), 1433 (m), 1418 (m), 1379 (m), 1245 (m), 1211 (m), 1160 (m, 1083 (w), 1067 (w), 1043 (s), 940 (w), 905 (m), 886 (m), 855 (s), 803 (m), 760 (m), 740 (s), 690 (m); $[\alpha]_\lambda$ (20 °C, CH_2Cl_2, c = 0.115 g/100 ml): $[\alpha]_{589}$: -174; $[\alpha]_{546}$ = -211; $[\alpha]_{405}$ = -492; $[\alpha]_{365}$ = -709; $[\alpha]_{334}$ = -1064.

6-(2,4-Di-*tert*-Butyl-6-diphenylphosphanyl-phenoxy)-2,2-α,α,α',α'-tetraxylyl-tetrahydro-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepin (12b)



According to general procedure **IV**, a solution of 2-Boranatodiphenylphosphanyl-4,6-di-*tert*-butyl-phenol (0.30 g, 0.74 mmol) was treated with DABCO (0.825 g, 7.35 mmol) and PCl_3 (2M, 0.41 ml, 0.82 mmol) in CH_2Cl_2 (7 ml) and (*R,R*)-Xylyl-Taddol (0.498 g, 0.86 mmol) in CH_2Cl_2 (7 ml). The crude product was purified by flash chromatography (cyclohexane/EtOAc 40:1) to afford **12b** (0.389 g, 53%) as white foam. TLC (cyclohexane/EtOAc, 40:1): R_f = 0.37; ^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 0.34 (s, 3H, CH_3), 1.15 (s, 9H, $C(CH_3)_3$), 1.20 (s, 3H, CH_3), 1.52 (s, 9H, $C(CH_3)_3$), 2.07 (s, 6H, $C(CH_3)$), 2.18 ((s, 6H, $C(CH_3)$), 2.21 (s, 6H, $C(CH_3)$), 2.25 (s, 6H, $C(CH_3)$), 5.00 (dd, *J* = 8.25 Hz, 1.86 Hz, 1H, OCH), 5.05 (d, *J* = 8.22 Hz, 1H, OCH), 6.73 (s, br, 1H, CH), 6.80 (s, br, 2H, CH), 6.87 (m, 3H, CH), 6.94 (s, 3H, CH), 7.00 (t, *J* = 7.38 Hz, 2H, CH) 7.11 (m, 10H, CH), 7.37 (d, *J* = 2.4 Hz, 1H, CH), 7.48 (s, br, 2H, CH); ^{31}P NMR {^{1}H} (202 MHz, $CDCl_3$): δ = -19.81 (d, *J* = 159.1 Hz), 145.01 (d, *J* = 159.1 Hz); IR (ATR): $\tilde{\nu}$ = 3051 (w), 2958 (m), 2860 (w), 2730 (w), 2244 (w), 1945 (w), 1877 (w), 1796 (w), 1598 (m), 1476 (m), 1432 (m), 1419 (m), 1391 (m), 1379 (m), 1361 (m), 1213 (m), 1159 (m), 1040 (s), 939 (m), 905 (s), 884 (s), 851 (s), 801 (s); MS (ESI, EtOAc/MeOH, Ag^+ OAc^-): *m/z* (%) = 1105.22 (3, $[M+Ag]^+$), 1051.28 (3), 1032.29 (6),1031.29 (15), 1030.30 (84), 1029.29 (100), 1019.27 (3), 543.20 (24), 487.06 (90), 455.06 (42), 392.13 (2), 216.24 (6), 131.16 (16); $[\alpha]_\lambda$ (20 °C, $CHCl_3$, c = 0.15 g/100 ml): $[\alpha]_{589}$: -162; $[\alpha]_{546}$ = -195; $[\alpha]_{405}$ = -452; $[\alpha]_{365}$ = -659.

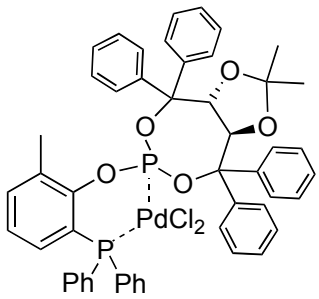
(3a*R*,8a*R*)-6-(3-(bis(4-methoxy-3,5-dimethylphenyl)phosphino)biphenyl-2-yloxy)-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepine



According to general procedure **IV**, a solution of 3-Boranato-(bis(4-methoxy-3,5-dimethylphenyl)phosphino)biphenyl-2-ol (0.47 g, 0.97 mmol) was treated with DABCO (0.88 g, 7.76 mmol) and PCl_3 (2M, 0.54 ml, 1.07 mmol) in CH_2Cl_2 (7 ml) and (*R*,*R*)-Taddol (0.51 g, 1.07 mmol) in CH_2Cl_2 (7 ml). The crude product was purified by flash chromatography (cyclohexane/EtOAc 10:1) to afford **12b** (0.45 g, 0.48 mmol, 49%) as white foam. TLC (cyclohexane/EtOAc, 10:1): R_f = 0.23; ^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 0.31 (s, 3H, CH_3), 0.91 (s, 3H, CH_3), 2.14 (s, 6H, CH_3), 2.19 (s, 6H, CH_3), 3.69 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 4.94 (d, *J* = 8.2 Hz), 4.98 (d, *J* = 8.2 Hz), 6.81 (Ψd, *J* = 7.0 Hz, 2H) 6.85 (Ψd, *J* = 7.5 Hz, 2H), 6.89 (Ψd, *J* = 7.2 Hz, 2H), 6.90- 6.92 (m, 1H), 7.03-7.10 (m, 4H), 7.12-7.16 (m, 2H), 7.16-7.22 (m, 7H), 7.25-7.32 (m, 10H), 7.42 (Ψd, *J* = 7.4 Hz, 2H), 7.49-7.52 (m, 2H); ^{31}P NMR (121.5 MHz, $CDCl_3$): δ [ppm] = -19.18 (d, *J* = 86.3 Hz, PR_3), 143.44 (d, *J* = 86.3 Hz, POR_3); IR (ATP) $\tilde{\nu}$ [cm^{-1}] = 3024 (w), 3055 (w), 2985 (w), 2933 (m), 2857 (w), 2822 (w), 1595 (w), 1582 (w), 1493 (m), 1474 (m), 1446 (m), 1404 (m), 1275 (m), 1214 (s), 1166 (m), 1111 (s), 1088 (m), 1034 (m), 1012 (s)m 905 (m), 882 (s), 817 (w), 764 (m), 727 (s), 697 (s), 609 (w); MS (ESI, MeOH/CH_2Cl_2): *m/z* (%) = 987.39 (94) $[M+Na]^+$, 965.40 (100) $[M]^+$, 563.18 (35), 406.13 (81); $[\alpha]_\lambda$ (20 °C, CH_2Cl_2, c= 0.14 g/100 ml): $[\alpha]_{589}$ = -195°, $[\alpha]_{546}$ = -233°, $[\alpha]_{405}$ = -525°, $[\alpha]_{365}$ = -767°.

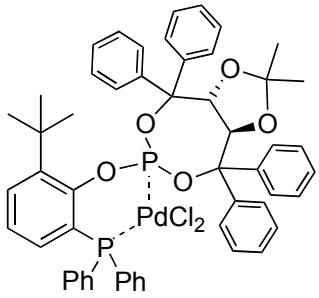
Synthesis of the Pd(II)-Complexes

Synthesis of the Complex [Pd(**10b**)Cl_2]



Ligand **10b** (47.2 mg, 60.0 μmol) and [$PdCl_2(PhCN)_2$] (23.0 mg, 60.0 μmol) were dissolved in toluene (2.5 ml) and stirred for 90 min at RT. Hexane was then added to precipitate the Pd(II) complex. After centrifugation, the precipitate (product) was washed with hexane and dried in vacuo to afford the Pd(II)-complex [Pd(**10b**)Cl_2] (57 mg, 59.0 μmol, 99%) as a grey solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 0.26 (s, 3H, CH_3), 0.99 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 5.54 (Ψt, J = 7.3 Hz, 2H, OCH), 6.53 (Ψt, J = 9.0 Hz, 1H), 6.88 (Ψdt, J_1 = 7.6 Hz, J_2 = 1.2, 1H), 6.97-7.06 (m, 3H), 7.07-7.69 (m, 26 H), 7.84 (Ψt, J = 7.4 Hz, 2H). ^{31}P NMR {^{1}H} (121.6 MHz, $CDCl_3$): d = 10.78 (s, PR_3), 82.91 (s, PO_3R); IR (ATR): $\tilde{\nu}$ = 3056 (w), 2990 (w), 2929 (w), 2228 (w), 1573 (w), 1493 (w), 1447 (m), 1435 (m), 1409 (w), 1383 (w), 1253 (w), 1213 (m), 1154 (m), 1098 (m), 1050 (m), 1009 (s), 996 (s), 909 (s), 852 (w), 726 (s), 697 (s), 661 (w);

Synthesis of the Complex [Pd(**10i**)Cl_2]



Ligand **10i** (49.7 mg, 60.0 μmol) and [$PdCl_2(PhCN)_2$] (23.0 mg, 60.0 μmol) were dissolved in toluene (2.5 ml) and stirred for 90 min at RT. Hexane was then added to precipitate the Pd(II) complex. After centrifugation, the precipitate (product) was washed with hexane and dried in vacuo to afford the Pd(II)-complex [Pd(**10i**)Cl_2] (55 mg, 54.0 μmol, 90%) as a grey solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 0.48 (s, 3H, CH_3), 0.84 (s, 3H, CH_3), 0.88 (s, 9H, CH_3), 5.32 (d, J = 7.4 Hz, 1H, OCH), 6.25 (d, J = 7.4 Hz, 1H, OCH), 6.58 (Ψt, J = 8.7 Hz, 1H), 7.05 (Ψdt, J_1 = 7.8 Hz, J_2 = 1.3 Hz, 1H), 7.09-7.20 (m, 8H), 7.07-7.69 (m, 21H), 7.92 (Ψd, J = 7.3 Hz,

2H); ^{31}P NMR {^{1}H} (121.5 MHz, $CDCl_3$): d = 9.94 (d, *J* = 6.6 Hz, PR_3), 91.53 (d, *J* = 6.6 Hz, PO_3R); IR (ATR): $\tilde{\nu}$ = 3057 (w), 2986 (w), 2933 (w), 2226 (w), 1494 (w), 1480 (w), 1447 (m), 1435 (m), 1403 (m), 1392 (w), 1382 (w), 1232 (w), 1214 (w), 1164 (w), 1112 (m), 1099 (m), 1050 (m), 1031 (m), 1006 (s), 995 (s), 912 (m), 887 (m), 855 (m), 742 (s), 725 (s), 695 (s);

Table 1. Summary of crystallographic data and structure refinement results for Pd(**10b**)Cl_2 and Pd(**10i**)Cl_2.

	Pd(**10b**)Cl_2	Pd(**10i**)Cl_2
chem. formula	$C_{53}H_{47}Cl_{11}O_5P_2Pd$	$C_{55}H_{52}Cl_8O_5P_2Pd$
formular weight	1322.20	1244.91
cryst size, mm	0.2 x 0.06 x 0.03	0.3 x 0.2 x 0.2
crystal system	orthorhombic	monoclinic
space group	P212121	P21
a, Å	11.1298(4)	11.7707(10)
b, Å	18.3889(7)	14.8558(10)
c, Å	27.0464(10)	15.7168(10)
α, deg	90	90
β, deg	90	99.1439(10)
γ, deg	90	90
V, Å^3	5535.4(4)	2713.4(3)
Z	4	2
D_{calcd}, g cm^{-3}	1.587	1.524
μ, mm^{-1}	0.971	0.843
F(000)	2672	1268
θ range, deg	1.34 to 27.00	1.75 to 27.00
no. of measd reflns	24637	12637
no. of unique reflns	11587	9664
no of data/restraints/param	11587 / 0 / 652	9664 / 1 / 646
final R indices [I>2σ(I)]	R1 = 0.0316, wR2 = 0.0654	R1 = 0.0455, wR2 = 0.0857
R indices (all data)	R1 = 0.0391, wR2 = 0.0672	R1 = 0.0710, wR2 = 0.1030
observed reflections	10324	7448
absolute structure parameter[17]	-0.020(15)	-0.01(3)

High-pressure NMR experiments

In a typical experiment a 5 mm sapphire high-pressure NMR tube was filled with a solution of [Rh(acac)$(CO)_2$] (4.0 mg, 0.016 mmol), ligand (0.047 mmol), and benzene-d6 (0.5 ml). The tube was purged three times with 5 bar of H_2/CO (1:1), pressurized with 5 bar of H_2/CO (1:1), and left for 4 h at 50 °C. After cooling to room temperature the NMR spectra were recorded. For VT-NMR, benzene-d_6 was replaced by toluene-d_8.

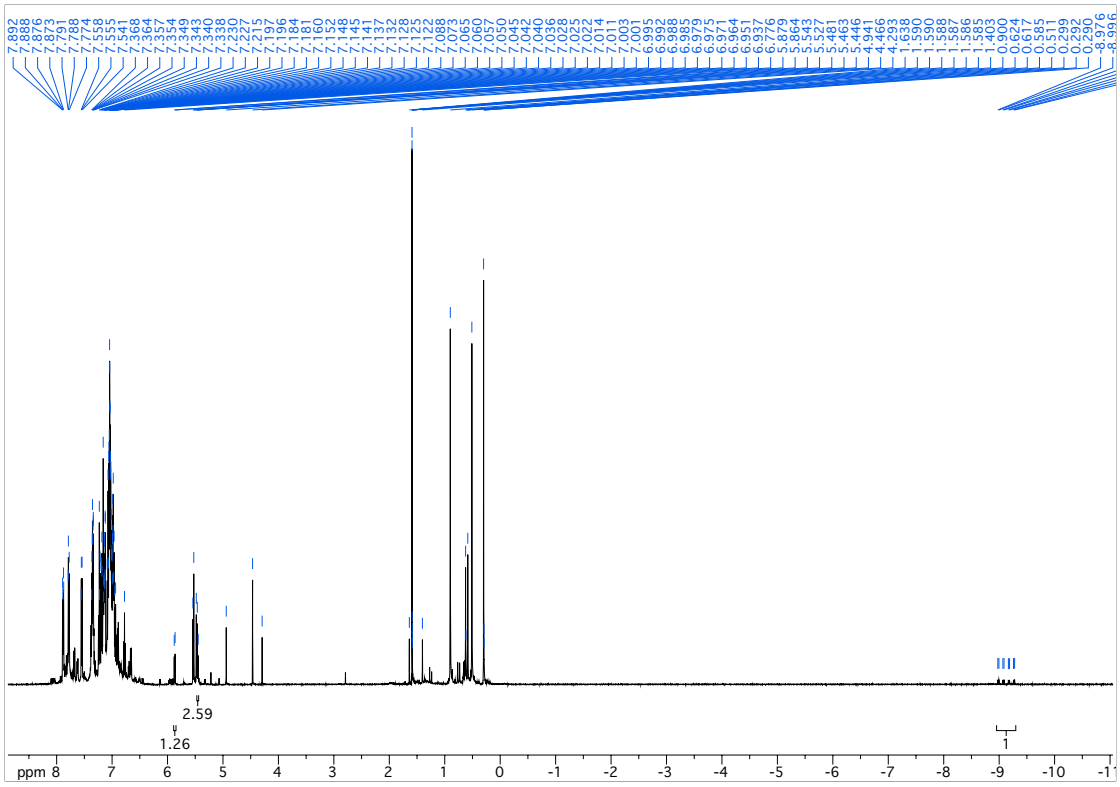


Figure 1. ^{1}H NMR spectra of [Rh(H)(**10h**)$(CO)_2$].

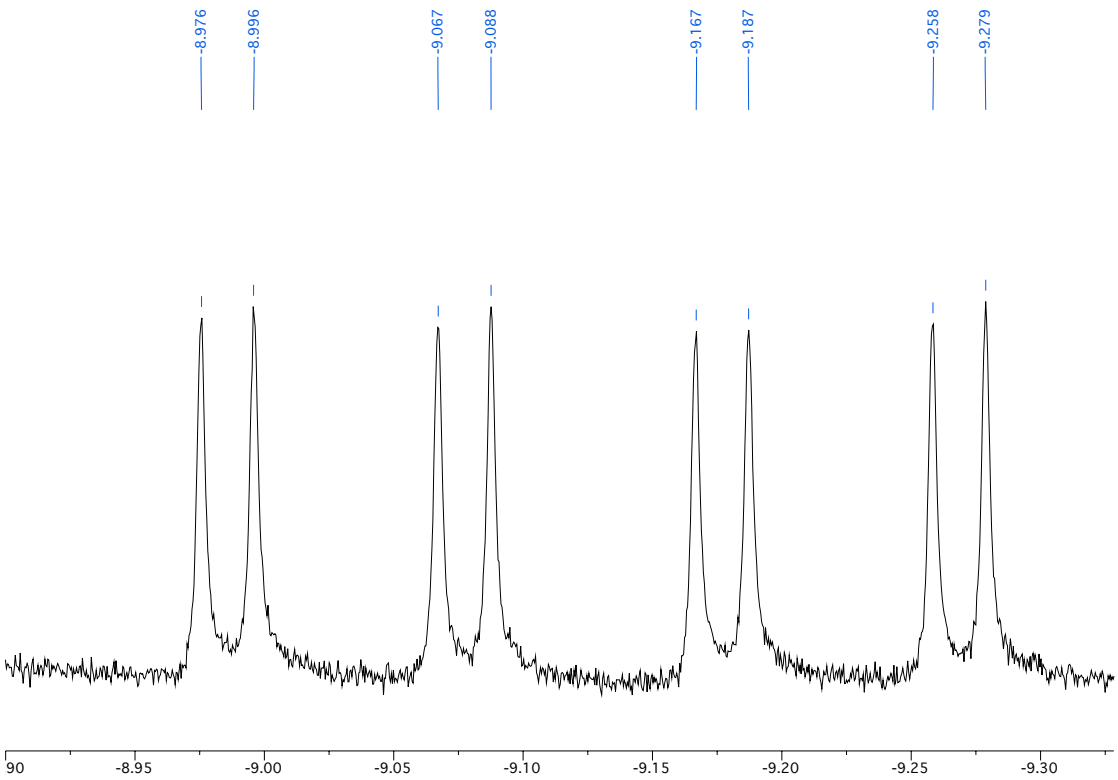


Figure 2. Hydride region of the ^{1}H NMR spectra of [Rh(H)(**10h**)$(CO)_2$].

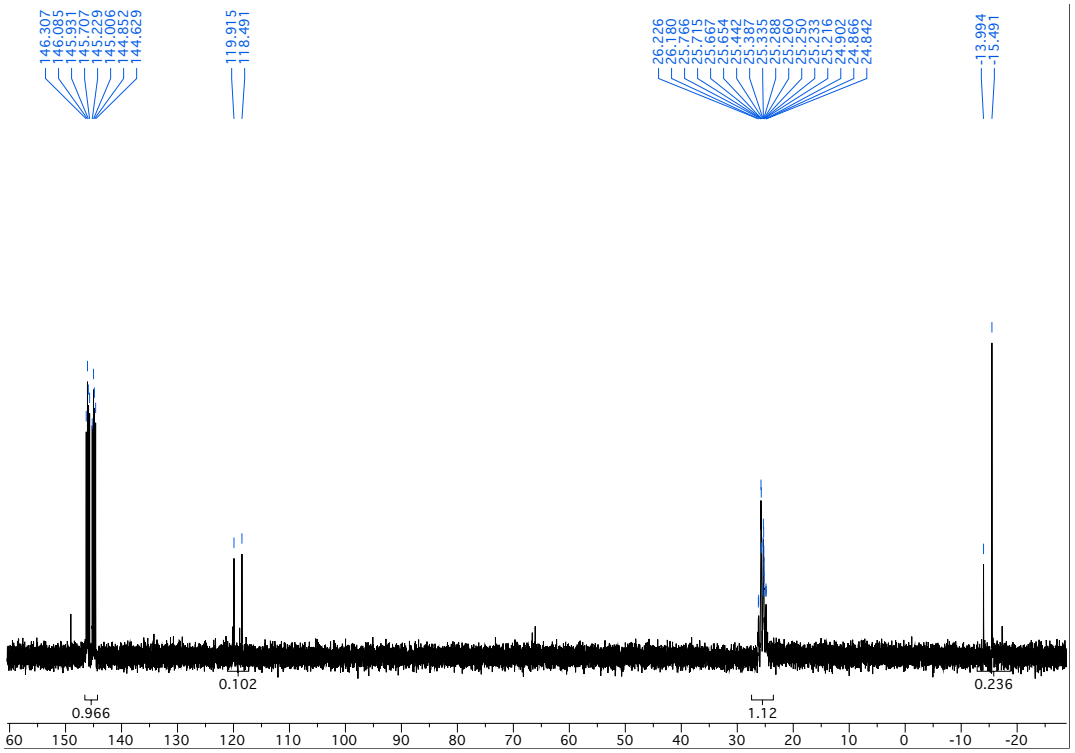


Figure 3. $^{31}P\{H\}$ NMR spectra of [Rh(H)(**10h**)$(CO)_2$].

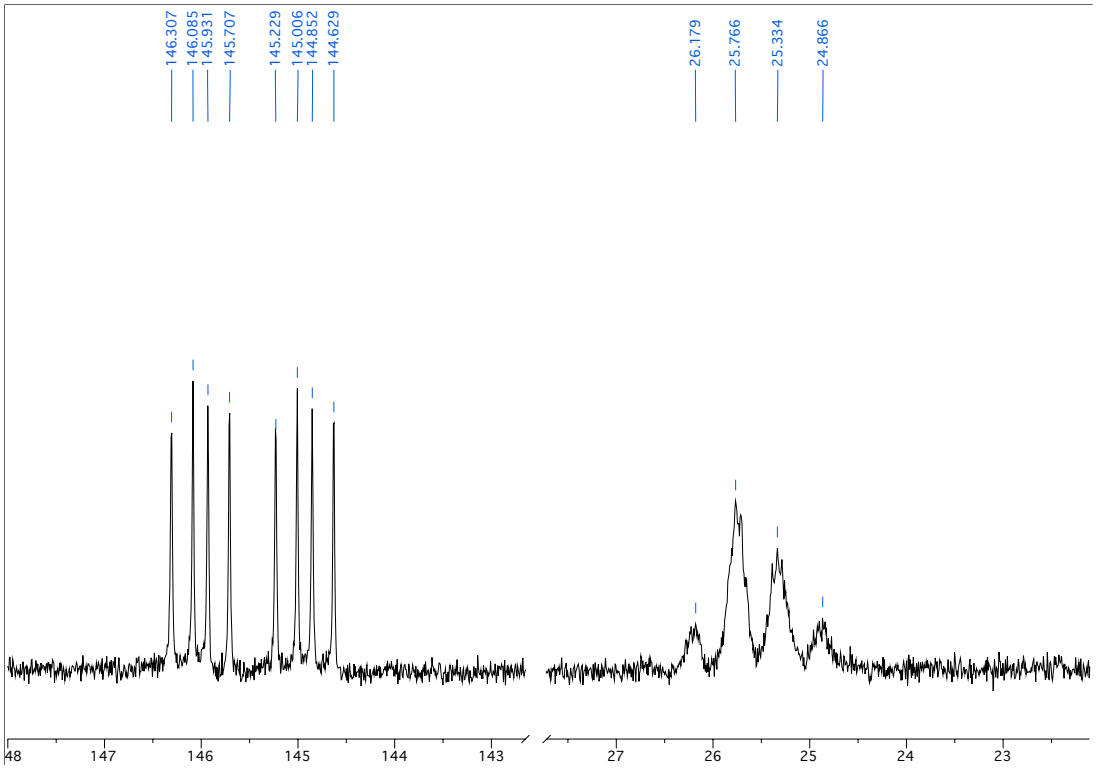


Figure 4. Phosphite and Phosphine region of $^{31}P\{H\}$ NMR spectra of [Rh(H)(**10h**)$(CO)_2$].