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MOP-Phosphonites: A Novel Ligand Class for Asymmetric Catalysis

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. Tetrahydrofuran and dichloromethane were dried over sodium/benzophenone and calcium hydride respectively, and distilled prior to use. Toluene (Acros) was purchased in an anhydrous state and stored over molecular sieves. The preparations of (*S*)-[1,1'-binaphthalen]-2-ylphosphine ((*S*)-**1**) and (*R*)-(2'-methoxy-[1,1'-binaphthalen]-2-yl)phosphine ((*R*)-**2**) were carried out using literature procedures.[1] All other chemicals were used as received without further purification. Flash chromatography was performed on silica gel from Fluorochem (silica gel, 40-63u, 60A, LC301). Thin-layer-chromatography was performed on Merck aluminium-based plates with silica gel and fluorescent indicator 254 nm. For indicating, UV light or potassium permanganate solution (1.0 g $KMnO_4$, 6.7 g K_2CO_3, 0.1 g NaOH, 100 ml H_2O) was used. 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. Mass spectrometry was carried out by the EPSRC National Mass Spectrometry Service Centre, Swansea. Analytical high performance liquid chromatography (HPLC) was performed on a Varian Pro Star HPLC equipped with a variable wavelength detector.

X-ray Diffraction. All data were collected on an Oxford Diffraction Gemini A Ultra diffractometer at 150 K, using Mo Kα (λ = 0.71073Å) radiation. Semi-empirical absorption corrections were applied based on symmetry-equivalent and repeated reflections. Structures were solved by direct methods and refined on all unique F^2 values, with anisotropic non-H atoms and constrained riding isotropic H atoms. CrysAlisPro software was used for data collection, integration, and absorption corrections.[2] Structure solution, refinement, and graphics were made with the SHELXTL program.[3] A summary of key crystallographic experimental information is provided in Table S1.

NMR Spectroscopy. ^{1}H NMR, ^{11}B {^{1}H} NMR, ^{13}C {^{1}H} NMR, ^{19}F NMR, and ^{31}P {^{1}H} NMR spectra were recorded on a JEOL Lambda 500 (^{1}H 500.16 MHz) or JEOL ECS-400 (^{1}H 399.78 MHz) spectrometer at room temperature (21°C) if not otherwise stated, using the indicated solvent as internal reference. Two-dimensional NMR experiments (COSY, NOESY, HSQC, HMBC) were used for the assignment of proton and carbon resonances, the numbering scheme is given in Fig. S1. Full range NOESY spectra were acquired with 512 × 1024 data points and a spectral width of 9.0 ppm; mixing times were chosen between 10 and 500 ms. For the measurement of exchange rate constants in **8a**, the proton resonances of the methoxy group were used. Peak volumes were determined manually from the NOESY spectrum using MestReNova 6, and the rate constants were calculated with an estimated error of 10% using EXSYCalc.[4]

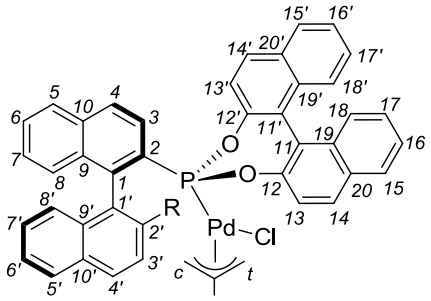

Fig. S1 Labelling scheme for binaphthyl compounds.

Table S1 Summary of X-Ray Crystallographic Data for **7a**, **7b**, **8a** and **8b**.

	7a	**7b**	**8a**	**8b**
formula	$C_{45}H_{34}Cl_3O_2PPd$	$C_{45}H_{34}Cl_3O_2PPd$	$C_{46}H_{36}Cl_3O_3PPd$	$C_{49}H_{44}ClO_4PPd$
formula wt	850.44	850.44	880.47	869.66
cryst syst	orthorhombic	orthorhombic	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a, Å; *α*, deg	11.9353(3); 90	12.0059(4); 90	10.4065(4); 90	12.1370(2); 90
b, Å; *β*, deg	13.7947(4); 90	13.8615(4); 90	17.4563(4); 90	14.4938(3); 90
c, Å; *γ*, deg	22.2867(6); 90	22.5034(7); 90	21.7841(5); 90	23.2109(5); 90
V, Å^3	3669.37(17)	3745.0(2)	3957.3(2)	4083.06(14)
Z	4	4	4	4
ρ_{calc}, g cm^{-3}	1.539	1.508	1.478	1.415
μ, mm^{-1}	0.808	0.791	0.753	0.604
F(000)	1728	1728	1792	1792
T_{min}/T_{max}	0.97796/1.00000	0.82919/1.00000	0.7945/0.8639	0.8395/0.9420
hkl range	–12 to 15, –16 to 18, –27 to 28	–15 to 14, –18 to 18, –22 to 30	–9 to 12, –17 to 22, –21 to 29	–16 to 16, –19 to 19, –30 to 31
θ range, deg	2.9 to 28.6	2.9 to 28.6	2.9 to 28.5	3.0 to 28.6
no. of measd rflns	19447	21950	22011	48358
no. of unique rflns (R_{int})	7808 (0.0373)	8064 (0.0447)	8320 (0.0394)	9182 (0.0525)
no. of obsd rflns, $I > 2\sigma(I)$	6453	6146	7461	6798
refined params/restraints	470/0	471/0	463/24	509/0
goodness of fit	0.88	0.876	1.038	0.893
Abs. structure param.	–0.024(14)	–0.020(16)	0.03(2)	–0.028(16)
R1/wR2 ($I > 2\sigma(I)$)	0.0281/0.0444	0.0311/0.0500	0.0385/0.0887	0.0300/0.0548
R1/wR2 (all data)	0.0396/0.0457	0.0509/0.0525	0.0455/0.0931	0.0511/0.0575
resid electron dens, e Å^{-3}	0.29/–0.41	0.64/–0.69	0.38/–0.54	0.42/–0.40

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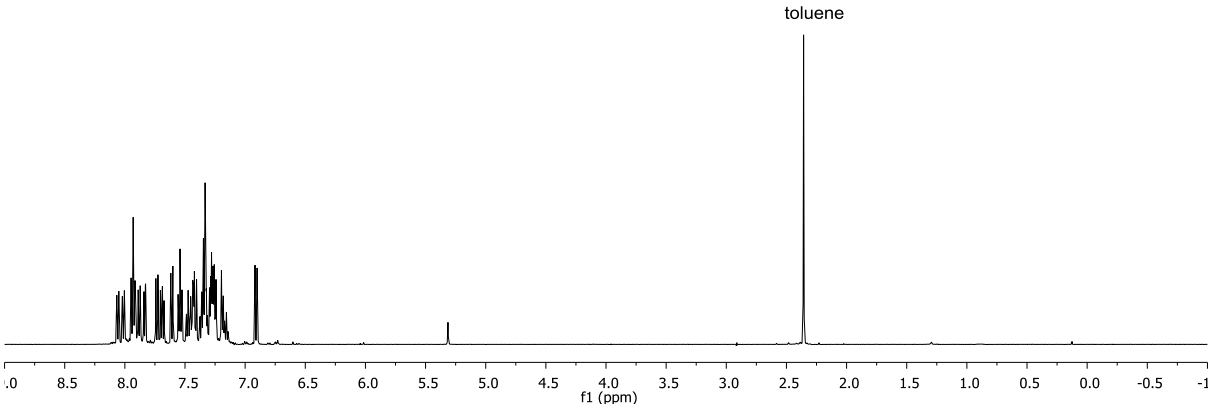
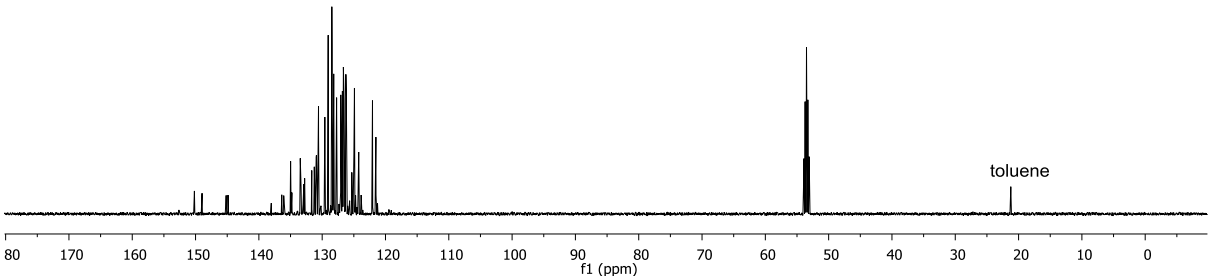
2 Experimental Procedures

2.1 (*S*,*R*$_b$)-[1,1'-binaphthalene]-2,2'-diyl [1,1'-binaphthalen]-2-ylphosphonite (**5a**)

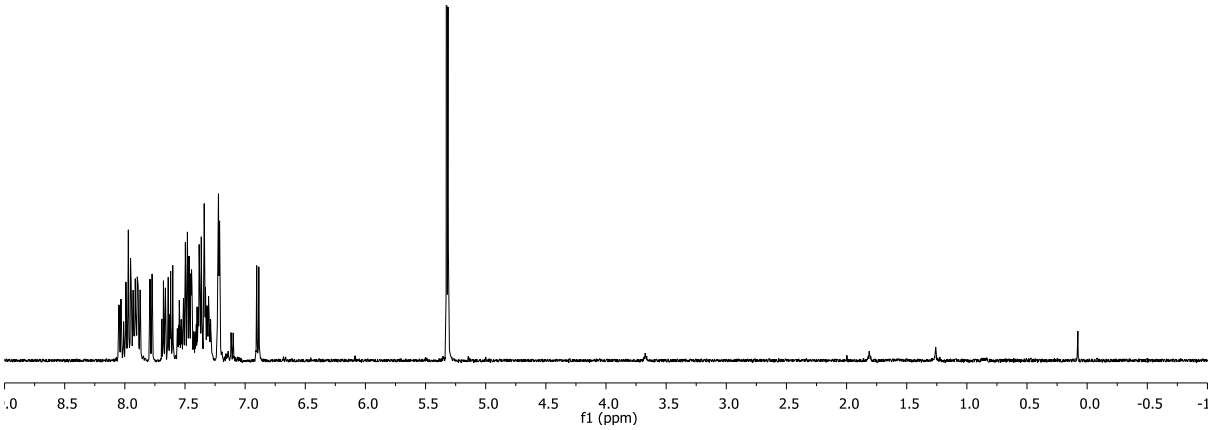
Phosphorus pentachloride (458 mg, 2.20 mmol) was dissolved in toluene (8 mL). (*S*)-**1** (286 mg, 1.00 mmol) was added and the reaction mixture was left to stir for 45 minutes. The volatiles were removed *in vacuo* to give (*S*)-**3** (^{31}P {^{1}H} NMR, $CDCl_3$: δ = 157.1 ppm) as a yellow oil. Tetrahydrofuran (8 mL), triethylamine (448 mg, 0.64 mL, 4.40 mmol) and (*R*)-BINOL (286 mg, 1.00 mmol) were subsequently added and the solution was left to stir overnight. The volatiles were removed *in vacuo* and the crude product was filtered through a plug of silica in toluene. The title product was obtained after removal of the solvent as a white solid. Yield: 404 mg (71%). **MP**: 158 °C. **OR** (*c* = 1.0 mg/ml, $CHCl_3$): $[\alpha]_D^{20}$ = +238°. **IR** (neat): *v* 3055.4, 2981.3, 1588.6, 1505.9, 1462.5, 1362.2, 1326.4, 1228.2, 1203.1, 1154.9, 1070.0, 949.2, 869.5, 818.8, 782.0, 747.7, 629.4 cm^{-1}. **^{1}H NMR** (CD_2Cl_2, 500 MHz): δ (ppm) 8.06 (d, $^3J_{HH}$ = 8.3 Hz, 1H, *H*4'), 8.01 (d, $^3J_{HH}$ = 8.3 Hz, 1H, Ar*H*), 7.95-7.91 (m, 3H, *H*14/Ar*H*), 7.88 (d, $^3J_{HH}$ = 8.2 Hz, 1H, Ar*H*), 7.84 (dd, $^3J_{HH}$ = 7.0 Hz, $^5J_{HP}$ = 1.0 Hz, 1H, *H*2'), 7.73 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *H*14'), 7.69 (dd, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 7.0 Hz, 1H, *H*3'), 7.61 (d, $^3J_{HH}$ = 8.6 Hz, 1H, *H*4), 7.56-7.52, (m, 2H, Ar*H*), 7.49-7.40 (m, 4H, *H*13/Ar*H*), 7.38-7.31 (m, 5H, Ar*H*), 7.30-7.24 (m, 3H, *H*3/Ar*H*), 6.91 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *H*13'). **^{13}C {^{1}H} NMR** (CD_2Cl_2, 126 MHz): δ (ppm) 150.2 (d, $^2J_{CP}$ = 2.4 Hz, *C*12), 149.0 (d, $^2J_{CP}$ = 6.1 Hz, *C*12'), 145.0 (d, $^2J_{CP}$ = 37.2 Hz, *C*1), 136.2 (d, $^1J_{CP}$ = 38.9 Hz, *C*2), 135.0, 134.8 (d, J_{CP} = 10.0 Hz), 133.5, 133.3 (d, J_{CP} = 2.1 Hz), 133.0 (d, J_{CP} = 4.7 Hz), 132.9 (d, J_{CP} = 1.5 Hz), 132.8 (d, J_{CP} = 1.0 Hz), 131.7, 131.2, 130.9 (d, $^4J_{CP}$ = 5.8 Hz, *C*2'), 130.6 (*C*14), 129.6 (d, $^4J_{CP}$ = 0.7 Hz, *C*14'), 129.1 (*C*4'), 128.5, 128.4, 128.3, 128.2, 127.7, 127.1 (*C*4), 127.0 (d, J_{CP} = 2.8 Hz), 126.8, 126.7, 126.6, 126.6, 126.5, 126.3, 126.3, 126.2, 125.0, 124.9 (*C*3'), 124.9, 124.7 (d, $^3J_{CP}$ = 5.7 Hz, *C*11), 124.2 (d, $^2J_{CP}$ = 2.7 Hz, *C*3), 123.8 (d, $^3J_{CP}$ = 2.6 Hz, *C*11'), 122.2 (*C*13'), 121.5 (d, $^3J_{CP}$ = 1.4 Hz, *C*13). **^{31}P {^{1}H} NMR** (CD_2Cl_2, 202 MHz,): δ (ppm) 177.4. **HRMS** (*m*/*z*, ESI$^+$, MeOH): found 585.1605, calcd for $[M + H_2O]^+$ 585.1614.

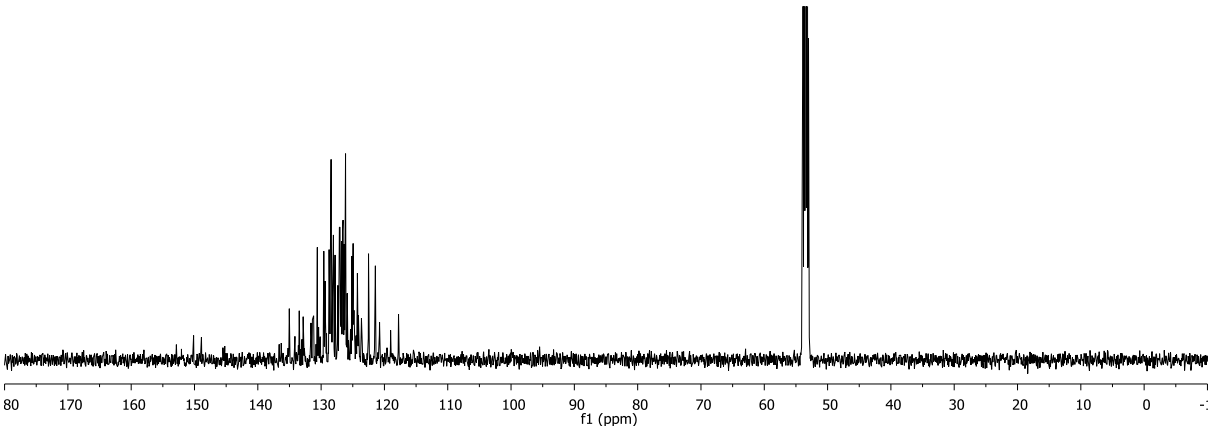




2.2 (*S*,*S*$_b$)-[1,1'-binaphthalene]-2,2'-diyl [1,1'-binaphthalen]-2-ylphosphonite (**5b**)

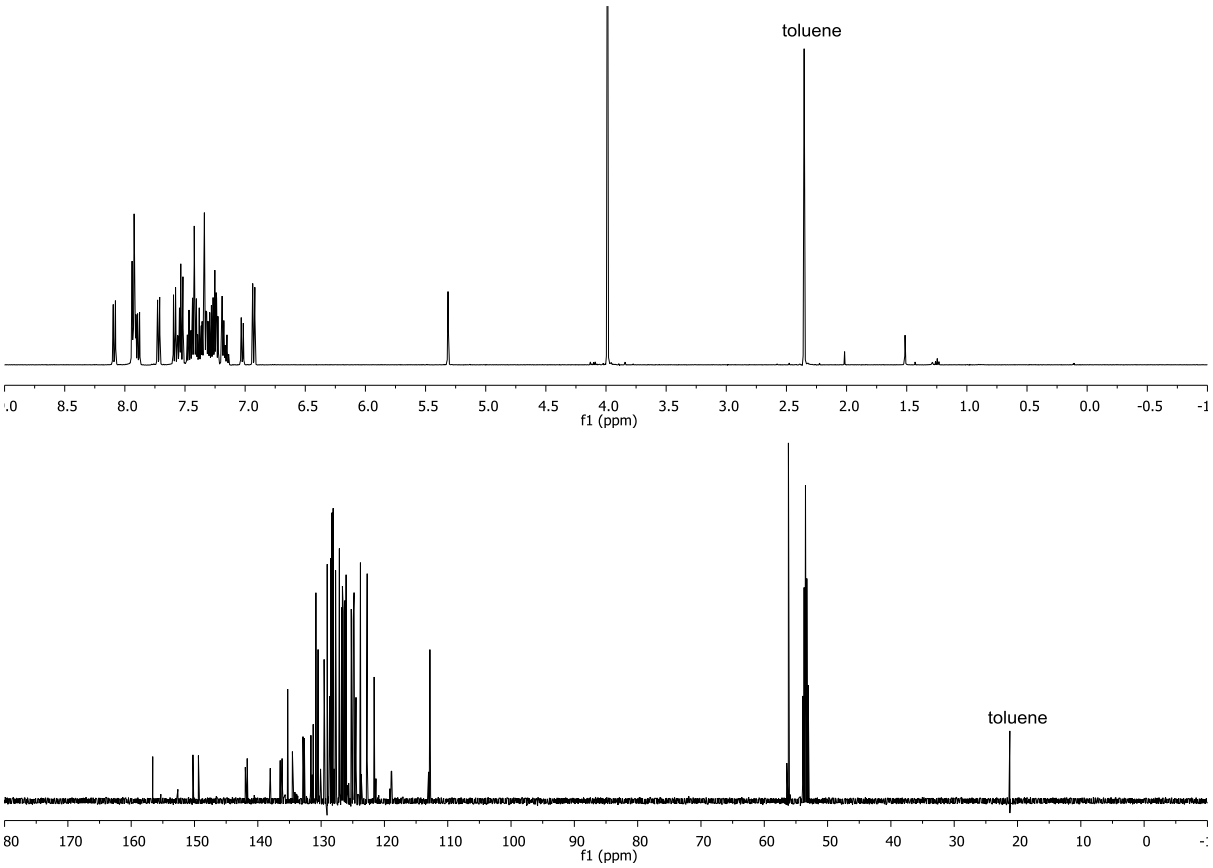
The same procedure was followed as for **5a**, except for using (*S*)-BINOL as the nucleophile. The title product was obtained as a white solid after removal of the solvent. Yield: 527 mg (93%). **MP**: 197 °C. **OR** (*c* = 1.0 mg/ml, $CHCl_3$): $[\alpha]_D^{20}$ = –264°. **IR** (neat): *v* 3060.6, 2981.3, 1588.6, 1506.5, 1466.0, 1366.0, 1330.0, 1262.7, 1232.0, 1204.0, 1141.6, 1141.6, 1072.2, 951.6, 869.5, 822.7, 789.4, 753.7, 684.6, 630.2 cm^{-1}. **^{1}H NMR** (CD_2Cl_2, 500 MHz): δ (ppm) 8.04 (d, $^3J_{HH}$ = 8.2 Hz, 1H, *H*4'), 7.99-7.89 (m, 4H, *H*14'/Ar*H*), 7.88 (d, $^3J_{HH}$ = 8.2 Hz, 1H, *H*5), 7.78 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *H*14), 7.68 (dd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 7.0 Hz, 1H, *H*3'), 7.63 (dd, $^3J_{HH}$ = 7.0 Hz, $^5J_{HP}$ = 1.2 Hz, 1H, *H*2'), 7.61 (d, $^3J_{HH}$ = 8.6 Hz, 1H, *H*4), 7.55 (ddd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 5.5 Hz, $^4J_{HH}$ = 2.5 Hz, 1H, *H*6), 7.53-7.36 (m, 7H, *H*13'/Ar*H*), 7.35-7.28 (m, 3H, *H*7/*H*8/Ar*H*), 7.23-7.21 (m, 3H, *H*3/Ar*H*), 6.90 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *H*13). **^{13}C {^{1}H} NMR** (CD_2Cl_2, 126 MHz): δ (ppm) 150.1 (d, $^2J_{CP}$ = 1.9 Hz, *C*12'), 148.9 (d, $^2J_{CP}$ = 5.7 Hz, *C*12), 145.4 (d, $^2J_{CP}$ = 37.0 Hz, *C*1), 136.5 (d, $^1J_{CP}$ = 40.4 Hz, *C*2), 135.0 (d, J_{CP} = 7.9 Hz), 134.1 (d, J_{CP} = 2.9 Hz), 133.5, 133.0 (d, J_{CP} = 4.3 Hz), 132.9, 132.8, 131.6, 131.4, 131.2, 130.6 (*C*14'), 129.6 (*C*14), 129.4 (*C*2'), 128.7 (*C*4'), 128.5, 128.4, 128.4, 128.1 (*C*5), 127.8, 127.4 (d, J_{CP} = 2.6 Hz), 127.1 (*C*4), 127.0, 126.9, 126.8, 126.6, 126.5, 126.4, 126.2, 126.1, 125.9, 125.1 (*C*3'), 124.9, 124.8 (*C*11'), 124.3 (d, $^2J_{CP}$ = 2.6 Hz, *C*3), 123.6 (*C*11), 122.5 (*C*13), 121.4 (*C*13'). **^{31}P {^{1}H} NMR** (CD_2Cl_2, 202 MHz): δ (ppm) 175.7. **HRMS** (*m*/*z*, EI^+): found: = 567.1514, calcd for $[M - H]^+$ 567.1508.





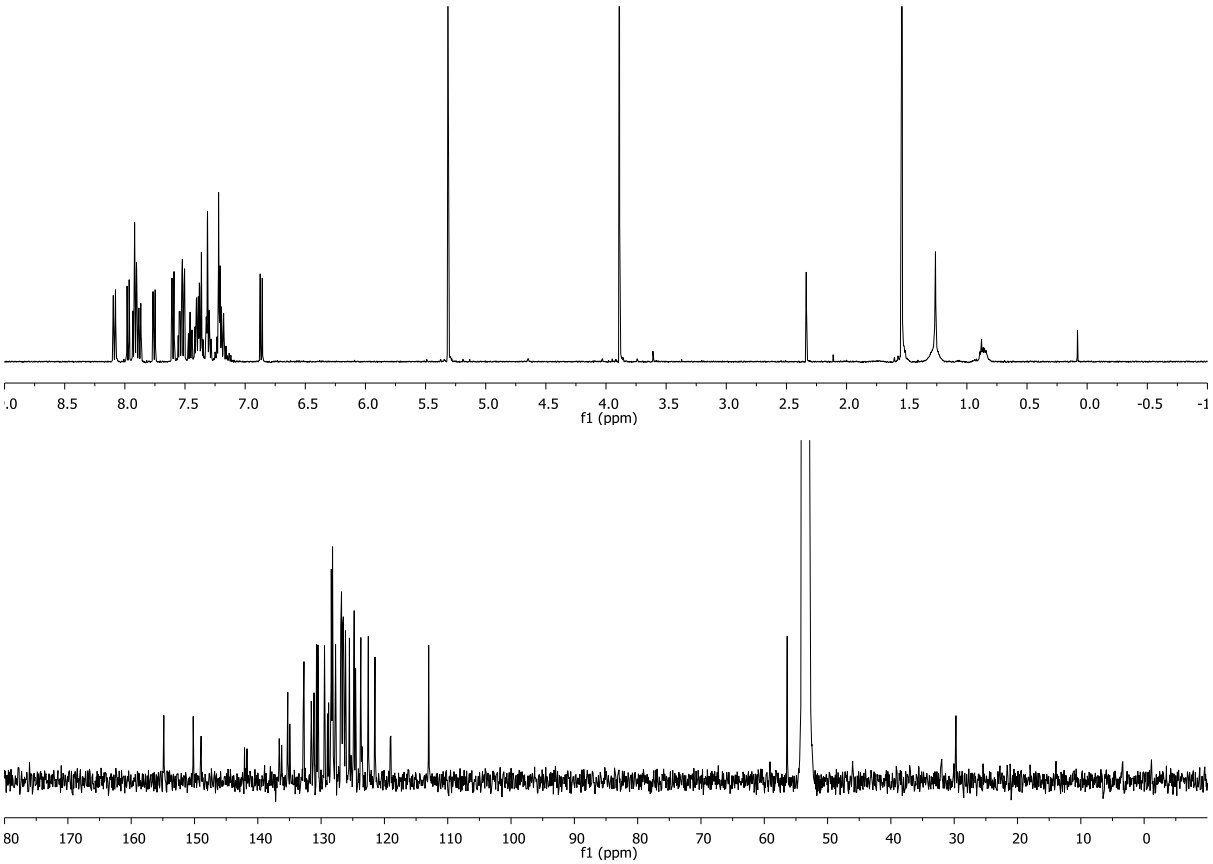
2.3 (R,R_b)-[1,1'-binaphthalene]-2,2'-diyl (2'-methoxy-[1,1'-binaphthalen]-2-yl)phosphonite (**6a**)

Phosphorus pentachloride (458 mg, 2.20 mmol) was dissolved in toluene (8 mL). (*R*)-**2** (316 mg, 1.00 mmol) was added and the reaction mixture was left to stir for 45 minutes. The volatiles were removed *in vacuo* to give (*R*)-**4** (^{31}P {^{1}H} NMR, $CDCl_3$): δ = 159.1 ppm) as yellow solid. Tetrahydrofuran (8 mL), triethylamine (448 mg, 0.64 mL, 4.40 mmol) and (*R*)-BINOL (286 mg, 1.00 mmol) were added subsequently and the solution was left to stir overnight. The volatiles were removed *in vacuo* and the crude product was dissolved in toluene and filtered through a plug of silica. The title product was obtained after removal of the solvent as a white solid. Yield: 523 mg, (87%). **MP**: >270 °C. **OR** (c = 1.0 mg/ml, $CHCl_3$: $[\alpha]_D^{20}$ = +444°. **IR** (neat): ν 2981.2, 1619.8, 1590.0, 1507.0, 1461.8, 1431.0, 1327.7, 1228.2, 1149.5, 1078.1, 947.3, 866.6, 820.5, 799.5, 746.7, 686.7, 630.3 cm^{-1}. **^{1}H NMR** (CD_2Cl_2, 500 MHz): δ (ppm) 8.09 (d, $^3J_{HH}$ = 9.1 Hz, 1H, *H*4'), 7.94-7.90 (m, 4H, *H*5'/*H*14/*H*15'/ Ar*H*), 7.89 (d, $^3J_{HH}$ = 8.2 Hz, 1H, *H*5), 7.72 (d, $^3J_{HH}$ = 8.8 Hz, 1H, *H*14'), 7.59 (d, $^3J_{HH}$ = 8.5 Hz, 1H, *H*4), 7.55 (ddd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 5.7 Hz, $^4J_{HH}$ = 2.1 Hz, 1H, *H*6), 7.53 (d, $^3J_{HH}$ = 9.1 Hz, 1H, *H*3'), 7.47 (ddd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, Ar*H*), 7.44-7.40 (m, 3H, *H*13/Ar*H*), 7.38 (ddd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, Ar*H*), 7.36-7.24 (m, 6H, Ar*H*), 7.23 (dd, $^3J_{HH}$ = 8.5 Hz, $^3J_{HP}$ = 1.4 Hz, 1H, *H*3), 7.02 (d, $^3J_{HH}$ = 8.5 Hz, 1H, Ar*H*), 6.93 (d, $^3J_{HH}$ = 8.8 Hz, 1H, *H*13'), 3.99 (s, 3H, O*CH*$_3$). **^{13}C {^{1}H} NMR** (CD_2Cl_2, 126 MHz): δ (ppm) 156.6 (d, $^4J_{CP}$ = 3.5 Hz, *C*2'), 150.3 (d, $^2J_{CP}$ = 2.5 Hz, *C*12), 154.9 (d, $^2J_{CP}$ = 5.8 Hz, *C*12'), 141.8 (d, $^2J_{CP}$ = 37.5 Hz, *C*1), 136.3 (d, $^1J_{CP}$ = 37.7 Hz, *C*2), 135.3, 134.5 (d, $^4J_{CP}$ = 2.9 Hz, *C*9'), 132.9, 132.8, 132.7 (d, J_{CP} = 1.0 Hz), 131.6 (d, J_{CP} = 0.9 Hz), 131.4, 131.2, 130.8 (*C*4'), 130.5 (*C*5'), 129.5 (*C*14'), 128.7, 128.5, 128.5, 128.3 (*C*5), 128.2 (*C*10'), 128.1, 127.7, 127.1, 126.8, 126.7 (*C*4), 126.6, 126.5, 126.4 (d, J_{CP} = 2.6 Hz), 126.2, 126.1, 125.2, 124.9, 124.8, 124.5 (d, $^2J_{CP}$ = 2.0 Hz, *C*3), 123.8, 122.7 (*C*13), 121.6 (*C*13'), 118.9 (d, $^3J_{CP}$ = 10.2 Hz, *C*1'), 112.8 (*C*3'), 56.2 (s, O*C*H$_3$). **^{31}P {^{1}H} NMR** (CD_2Cl_2, 202 MHz): δ (ppm) 177.8. **HRMS** (m/z, ESI^+, CH_2Cl_2): found 599.1767, calcd for $[M + H]^+$ 599.1771.



2.4 (R,S_b)-[1,1'-binaphthalene]-2,2'-diyl (2'-methoxy-[1,1'-binaphthalen]-2-yl)phosphonite (**6b**)

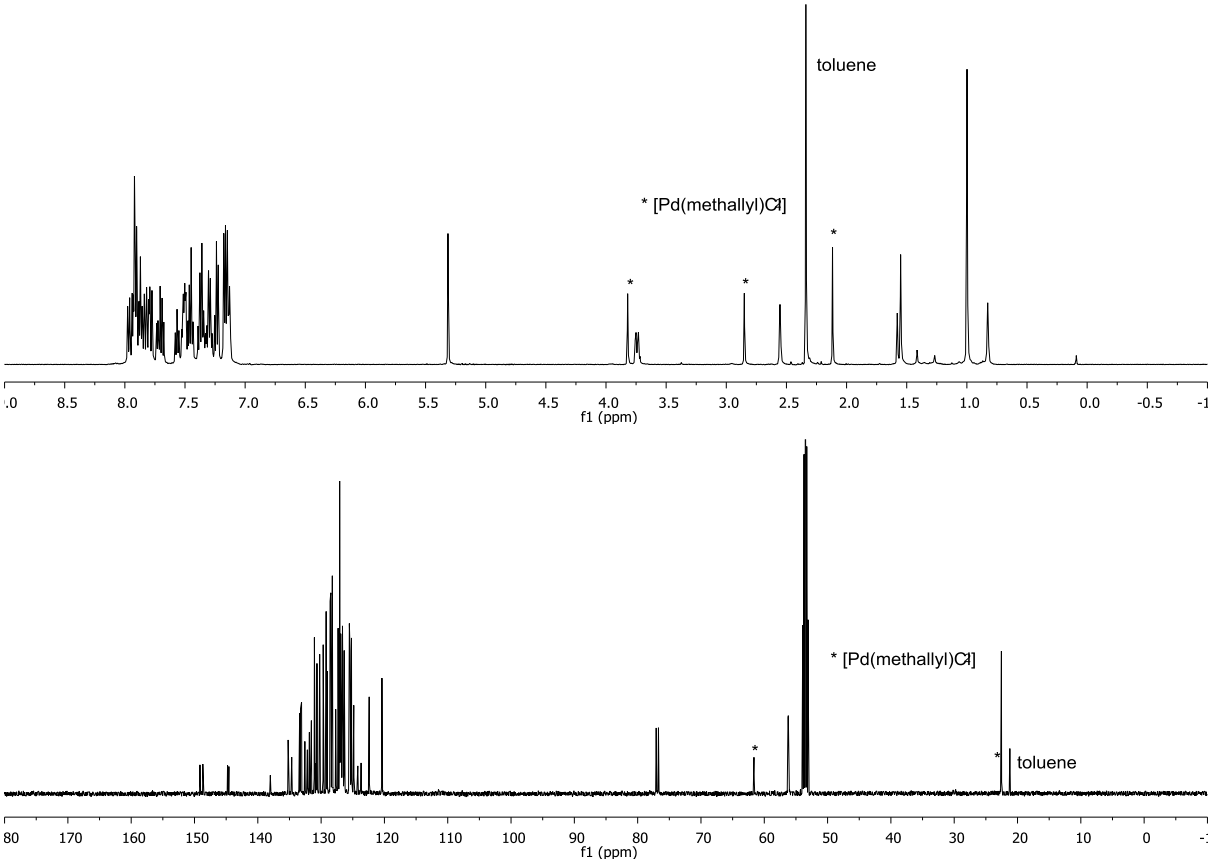
The same procedure was followed as for **6a**, except for using (*S*)-BINOL as the nucleophile. The title product was obtained as a white solid after removal of the solvent. Yield: 430 mg (72%). **MP**: 231 °C (decomposition). **OR** (*c* = 1.0 mg/ml, $CHCl_3$): $[\alpha]_D^{20}$ = –310°. **IR** (neat): *v* 2980.8, 1620.1, 1590.2, 1506.3, 1462.7, 1431.5, 1329.8, 1230.2, 1203.4, 1146.0, 1070.1, 949.5, 867.8, 820.8, 789.7, 747.2, 684.7, 628.8 cm^{-1}. **^{1}H NMR** (CD_2Cl_2, 500 MHz): δ (ppm) 8.09 (d, $^3J_{HH}$ = 9.1 Hz, 1H, *H*4'), 7.97 (d, $^3J_{HH}$ = 8.8 Hz, 1H, *H*14'), 7.93-7.90 (m, 3H, *H*15/*H*5'/*H*15'), 7.88 (d, $^3J_{HH}$ = 8.2 Hz, 1H, *H*5), 7.76 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *H*14), 7.60 (d, $^3J_{HH}$ = 8.6 Hz, 1H, *H*4), 7.54 (dd, $^3J_{HH}$ = 8.0 Hz, $^{3/4}J_{HH}$ = 4.0 Hz, 1H, *H*6'), 7.52 (d, $^3J_{HH}$ = 8.8 Hz, 1H, *H*13'), 7.51 (d, $^3J_{HH}$ = 9.1 Hz, 1H, *H*3'), 7.46 (ddd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, *H*16), 7.42-7.35 (m, 4H, *H*18/Ar*H*), 7.32 (d, $^3J_{HH}$ = 4.0 Hz, 2H, *H*7'/*H*8'), 7.30 (ddd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, *H*17), 7.23-7.18 (m, 4H, *H*3/Ar*H*), 6.87 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *H*13), 3.89 (s, 3H, OCH_3). **^{13}C {^{1}H} NMR** (CD_2Cl_2, 101 MHz): δ (ppm) 154.9 (d, $^4J_{CP}$ = 2.9 Hz, *C*2'), 150.2 (d, $^2J_{CP}$ = 2.3 Hz, *C*12'), 149.0 (d, $^2J_{CP}$ = 5.9 Hz, *C*12), 141.9 (d, $^2J_{CP}$ = 39.2 Hz, *C*1), 136.4 (d, $^1J_{CP}$ = 38.3 Hz, *C*2), 135.3, 135.0 (*C*9'), 132.8, 132.7, 132.7, 131.6, 131.1, 130.7 (*C*4'), 130.5 (*C*14'), 129.5 (*C*14), 128.8, 128.4 (*C*15), 128.4 (*C*15'), 128.3 (*C*5'), 128.3 (*C*10'), 128.2 (*C*5), 127.7, 126.9 (*C*4), 126.8, 126.7, 126.6, 126.5, 126.4 (d, J_{CP} = 2.1 Hz), 126.2, 126.1, 125.5, 124.9, 124.8 (*C*16), 124.6 (d, J_{CP} = 2.5 Hz), 123.7, 123.6 (d, J_{CP} = 2.5 Hz), 122.5 (*C*13), 121.5 (*C*13'), 119.0 (d, $^3J_{CP}$ = 10.3 Hz, *C*1'), 113.0 (*C*3'), 56.4 (s, OCH_3). **^{31}P {^{1}H} NMR** (CD_2Cl_2, 202 MHz): δ (ppm) 177.9. **HRMS** (*m*/*z*, ESI^+, CH_2Cl_2): found 599.1766, calcd for $[M + H]^+$ 599.1771.



2.5 [Pd(**5a**)(η^3-C_4H_7)Cl] (**7a**)

Methallylpalladium chloride dimer (7 mg, 18 µmol) and **5a** (20 mg, 35 µmol) were dissolved in dichloromethane (1 mL) and stirred for 10 minutes. The intended complex was formed quantitatively. Slow diffusion of diethyl ether into the reaction mixture yielded colorless crystals overnight, which were suitable for X-ray diffraction analysis. Yield: 25 mg (92%). **MP**: >270 °C. **IR** (neat): *v* 3052.0, 1587.6, 1505.8, 1460.0, 1432.9, 1360.3, 1322.4, 1220.7, 1067.8, 977.3, 942.2, 871.8, 838.4, 810.2, 759.4, 706.9, 677.2, 634.3, 596.8 cm^{-1}. **^{1}H NMR** (CD_2Cl_2, 500 MHz): δ (ppm) isomer A (97%), 7.97 (d, $^3J_{HH}$ = 8.1 Hz, 1H, *H*4'), 7.94-7.90 (m, 4H, *H*14/*H*5/*H*15/*H*15'), 7.89-7.85 (m, 2H, *H*2'/*H*5'), 7.84-7.80 (m, 2H, *H*13/*H*4), 7.78 (d, $^3J_{HH}$ = 8.9 Hz, 1H, *H*14'), 7.72 (dd, $^3J_{HH}$ = 8.6 Hz, $^3J_{HP}$ = 5.5 Hz, 1H, *H*3), 7.69 (dd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 7.2 Hz, 1H, *H*3'), 7.58-7.55 (m, 1H, Ar*H*), 7.53-7.43 (m, 5H, *H*6'/Ar*H*), 7.39-7.27 (m, 5H, Ar*H*), 7.18-7.13 (m, 2H, *H*13'/Ar*H*), 3.75 (dd, $^3J_{HP}$ = 9.9 Hz, $^4J_{HH}$ = 2.5 Hz, 1H, allyl-*H*t$_{syn}$), 2.56 (s, 1H, allyl-*H*c$_{syn}$), 1.57 (d, $^3J_{HP}$ = 14.1 Hz, 1H, allyl-*H*t$_{anti}$), 1.00 (s, 3H, allyl-C*H*$_3$), 0.83 (s, 1H, allyl-*H*c$_{anti}$); isomer B (3%), 8.00-6.99 (m, 23H, Ar*H*), 6.92 (m, 1H, Ar*H*), 6.87 (m, 1H, Ar*H*), 3.96 (d, $^3J_{HP}$ = 6.8 Hz, 1H, allyl-*H*t$_{syn}$), 2.96 (m, 1H, allyl-*H*c$_{syn}$), 2.64 (d, $^3J_{HP}$ = 12.3 Hz, 1H, allyl-*H*t$_{anti}$), 1.53 (m, 1H, allyl-*H*c$_{anti}$), 1.42 (s, 3H, allyl-C*H*$_3$). **^{13}C {^{1}H} NMR** (CD_2Cl_2, 126 MHz): δ (ppm) isomer A (97%), 149.1 (d, $^2J_{CP}$ = 5.3 Hz, *C*12), 148.6 (d, $^2J_{CP}$ = 13.2 Hz, *C*12'), 144.7 (d, $^2J_{CP}$ = 27.2 Hz, *C*1), 135.2, 134.7 (d, $^1J_{CP}$ = 9.3 Hz, *C*2), 133.5, 133.4, 133.3, 133.1, 132.6 (d, J_{CP} = 1.4 Hz), 132.2 (d, J_{CP} = 1.9 Hz), 131.9 (d, J_{CP} = 1.3 Hz), 131.5 (d, J_{CP} = 1.3 Hz), 131.1 (*C*2'), 131.0 (d, J_{CP} = 28.6 Hz, allyl-*C*), 130.7 (d, $^4J_{CP}$ = 1.1 Hz, *C*14), 130.2 (d, $^4J_{CP}$ = 1.4 Hz, *C*14'), 129.7, 129.2 (*C*4'), 128.6, 128.5, 128.3, 128.2, 128.2, 127.7 (d, $^3J_{CP}$ = 5.2 Hz, *C*4), 127.3, 127.1, 127.1, 127.0 (d, J_{CP} = 2.3 Hz), 126.9, 126.8, 126.7, 126.6, 126.4, 125.5, 125.4, 125.2 (*C*3'), 124.9 (d, $^2J_{CP}$ = 2.8 Hz, *C*3), 124.2 (d, $^3J_{CP}$ = 3.8 Hz, *C*11), 123.7 (d, $^3J_{CP}$ = 2.9 Hz, *C*11'),

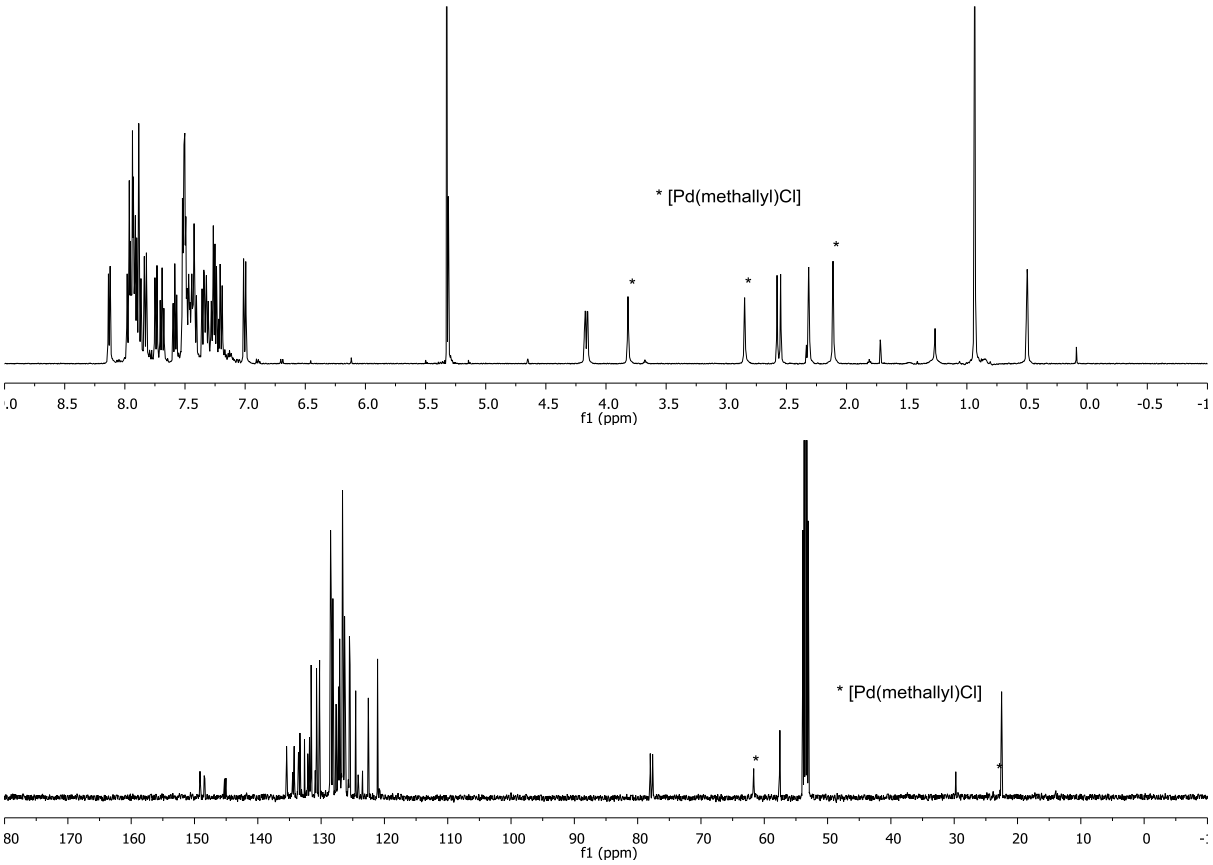
122.4 (d, $^{3}J_{CP}$ = 2.4 Hz, *C*13), 120.4 (*C*13'), 76.8 (d, $^{2}J_{CP}$ = 45.3 Hz, allyl-*C*t), 56.1 (d, $^{2}J_{CP}$ = 5.8 Hz, allyl-*C*c), 22.4 (allyl-*C*H$_3$); signals of isomer B could not be observed. **^{31}P {^{1}H} NMR** (CD_2Cl_2, 202 MHz): δ (ppm) isomer A (97%), 173.4; isomer B (3%), 175.7. **HRMS** (*m*/*z*, ESI$^+$, MeOH): found 727.1178, calcd for [M – Cl]$^+$ 727.1176.



2.6 [Pd(**5b**)(η^3-C$_4$H$_7$)Cl] (**7b**)

Methallylpalladium chloride dimer (7 mg, 18 µmol) and **5b** (20 mg, 35 µmol) were dissolved in dichloromethane (1 mL) and stirred for 10 minutes. The intended complex was formed quantitatively. Slow diffusion of diethyl ether into the reaction mixture yielded colorless crystals overnight which were suitable for X-ray diffraction analysis. Yield: 23 mg (83%). **MP**: >270 °C. **IR** (neat): *v* 3047.7, 1585.8, 1505.6, 1461.1, 1434.2, 1360.9, 1322.9, 1269.3, 1222.1, 1161.0, 1121.5, 1068.7, 1027.5, 977.3, 943.4, 877.1, 839.5, 803.3, 757.5, 729.6, 687.3, 634.8, 598.0, 557.6 cm^{-1}. **^{1}H NMR** (CD_2Cl_2, 500 MHz): δ (ppm) 8.13 (d, $^{3}J_{HH}$ = 7.0 Hz, 1H, *H*2'), 7.98-7.86 (m, 7H, *H*4'/*H*15/*H*5'/*H*14'/*H*5/*H*15'/*H*13'), 7.83 (d, $^{3}J_{HH}$ = 8.8 Hz, 1H, *H*14), 7.74 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H, *H*4), 7.69 (dd, $^{3}J_{HH}$ = 8.7 Hz, $^{3}J_{HH}$ = 7.0 Hz, 1H, *H*3'), 7.60-7.57 (m, 1H, Ar*H*), 7.53-7.40 (m, 7H, *H*3/Ar*H*), 7.36-7.23 (m, 5H, Ar*H*), 7.00 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H, *H*13), 4.16 (dd, $^{3}J_{HP}$ = 10.2 Hz, $^{4}J_{HH}$ = 2.8 Hz, 1H, allyl-*H*t$_{syn}$), 2.56 (d, $^{3}J_{HP}$ = 14.8 Hz, 1H, allyl-*H*t$_{anti}$), 2.31 (s, 1H, allyl-*H*c$_{syn}$), 0.93 (s, 3H, allyl-C*H*$_3$), 0.50 (s, 1H, allyl-*H*c$_{anti}$). **^{13}C {^{1}H} NMR** (CD_2Cl_2, 126 MHz,): δ (ppm) 149.1 (d, $^{2}J_{CP}$ = 5.3 Hz, *C*12'), 148.4 (d, $^{2}J_{CP}$ = 13.1 Hz, *C*12), 145.1 (d, $^{2}J_{CP}$ = 29.7 Hz, *C*1), 135.5, 134.5 (d, $^{1}J_{CP}$ = 9.4 Hz, *C*2), 134.3, 133.6 (d, J_{CP} = 4.7 Hz), 133.5 d, J_{CP} = 4.4 Hz), 133.3, 132.6 (d, J_{CP} = 1.4 Hz), 132.1, 131.8 (d, J_{CP} = 0.9 Hz), 131.6, 131.5 (d, $^{4}J_{CP}$ = 1.0 Hz, *C*2'), 130.8 (d, J_{CP} = 28.5 Hz, allyl-*C*), 130.7 (*C*14'), 130.2 (d, $^{4}J_{CP}$ = 1.4 Hz, *C*14), 128.6, 128.5, 128.5, 128.3, 128.1, 128.1 (*C*4'), 127.6 (d, $^{3}J_{CP}$ = 4.9 Hz, *C*4), 127.3, 127.2, 127.1, 127.0,

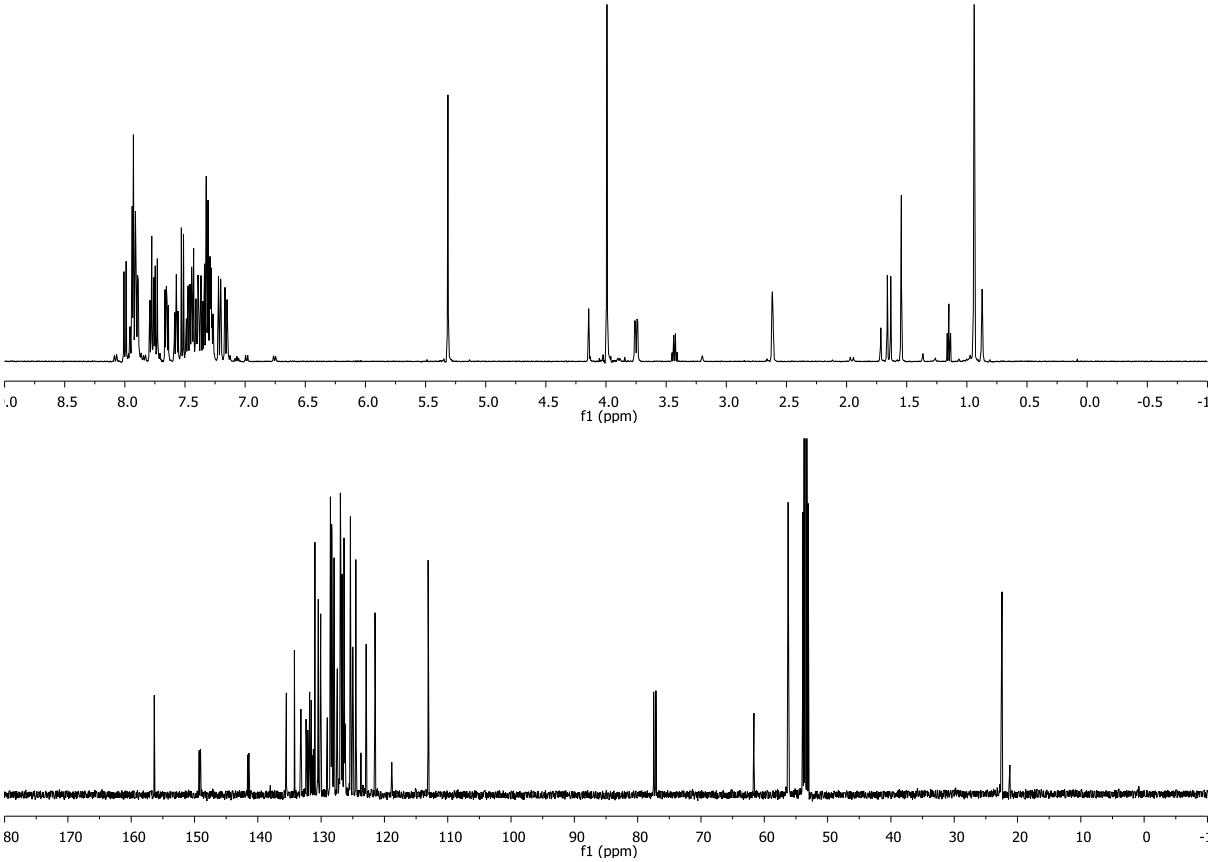
126.6, 126.6, 126.5, 126.3, 126.3, 126.2 (*C*3'), 125.5, 125.4, 124.5 (*C*3), 124.1 (d, $^{3}J_{CP}$ = 4.2 Hz, *C*11'), 123.5 (d, $^{3}J_{CP}$ = 2.6 Hz, *C*11), 122.5 (d, $^{3}J_{CP}$ = 2.3 Hz, *C*13'), 121.1 (d, $^{3}J_{CP}$ = 0.8 Hz, *C*13), 77.8 (d, $^{2}J_{CP}$ = 46.5 Hz, allyl-*C*t), 57.6 (d, $^{2}J_{CP}$ = 5.3 Hz, allyl-*C*c), 22.5 (allyl-*C*H$_3$). **^{31}P {^{1}H} NMR** (CD_2Cl_2, 202 MHz): δ (ppm) 172.1. **HRMS** (*m*/*z*, ESI$^+$, MeOH): found 725.1177, calcd for $[M - Cl]^+$ 725.1176.



2.7 [Pd(**6a**)(η^3-C_4H_7)Cl] (**8a**)

Methallylpalladium chloride dimer (7 mg, 18 µmol) and **6a** (21 mg, 35 µmol) were dissolved in dichloromethane (1 mL) and stirred for 10 minutes. The intended complex was formed quantitatively. Slow diffusion of diethyl ether into the reaction mixture yielded colorless crystals overnight, which were suitable for X-ray diffraction analysis. Yield: 26 mg (91%). **MP**: >270 °C. **IR** (neat): ν 3065.2, 1620.2, 1589.0, 1507.6, 1463.0, 1431.3, 1327.7, 1247.8, 1223.0, 1194.2, 1151.8, 1068.9, 1021.8, 943.5, 873.9, 839.0, 807.0, 743.7, 677.2, 637.2, 597.2, 597.8, 560.2 cm^{-1}. **^{1}H NMR** (CD_2Cl_2, 500 MHz,): δ (ppm) isomer A (93%), 7.98 (d, $^{3}J_{HH}$ = 9.1 Hz, 1H, *H*4'), 7.93 (dd, $^{3}J_{HH}$ = 8.9 Hz, $^{4}J_{HP}$ = 0.9 Hz, 1H, *H*13), 7.91-7.86 (m, 4H, *H*14/*H*5/*H*15/*H*15'), 7.78-7.73 (m, 2H, *H*5'/*H*4), 7.72 (d, $^{3}J_{HH}$ = 8.9 Hz, 1H, *H*14'), 7.63 (dd, $^{3}J_{HH}$ = 8.6 Hz, $^{3}J_{HP}$ = 5.4 Hz, 1H, *H*3), 7.55 (ddd, $^{3}J_{HH}$ = 8.1 Hz, $^{3}J_{HH}$ = 6.8 Hz, $^{4}J_{HH}$ = 1.1 Hz, 1H, Ar*H*), 7.50 (d, $^{3}J_{HH}$ = 9.1 Hz, 1H, *H*3'), 7.47-7.24 (m, 10H, Ar*H*/*H*6'), 7.19 (d, $^{3}J_{HH}$ = 8.9 Hz, $^{4}J_{HP}$ = 1.0 Hz, 1H, *H*13'), 7.14 (d, $^{3}J_{HH}$ = 8.4 Hz, 1H, Ar*H*), 3.97 (s, 3H, OC*H*$_3$), 3.73 (dd, $^{3}J_{HP}$ = 10.0 Hz, $^{4}J_{HH}$ = 3.0 Hz, 1H, allyl-*H*t$_{syn}$), 2.60 (m, 1H, allyl-*H*c$_{syn}$), 1.63 (d, $^{3}J_{HP}$ = 14.1 Hz, 1H, allyl-*H*t$_{anti}$), 0.92 (s, 3H, allyl-C*H*$_3$), 0.85 (m, 1H, allyl-*H*c$_{anti}$); isomer B (7%), 8.05 (d, $^{3}J_{HH}$ = 9.1 Hz, 1H, *H*4'), 7.99-7.10 (m, 20H, Ar*H*), 7.07-7.02 (m, 1H, Ar*H*), 6.97 (d, $^{3}J_{HH}$ = 8.9 Hz, 1H, *H*13'), 6.74 (d, $^{3}J_{HH}$ = 8.5 Hz, 1H, Ar*H*), 4.12 (s, 3H, OC*H*$_3$), 3.87 (m, 1H, allyl-*H*t$_{syn}$), 3.18 (m, 1H, allyl-*H*c$_{syn}$), 1.94 (d, $^{3}J_{HP}$ = 13.0 Hz, 1H, allyl-*H*t$_{anti}$), 1.70 (s, 3H, allyl-C*H*$_3$), 1.35 (m, 1H, allyl-*H*c$_{anti}$).

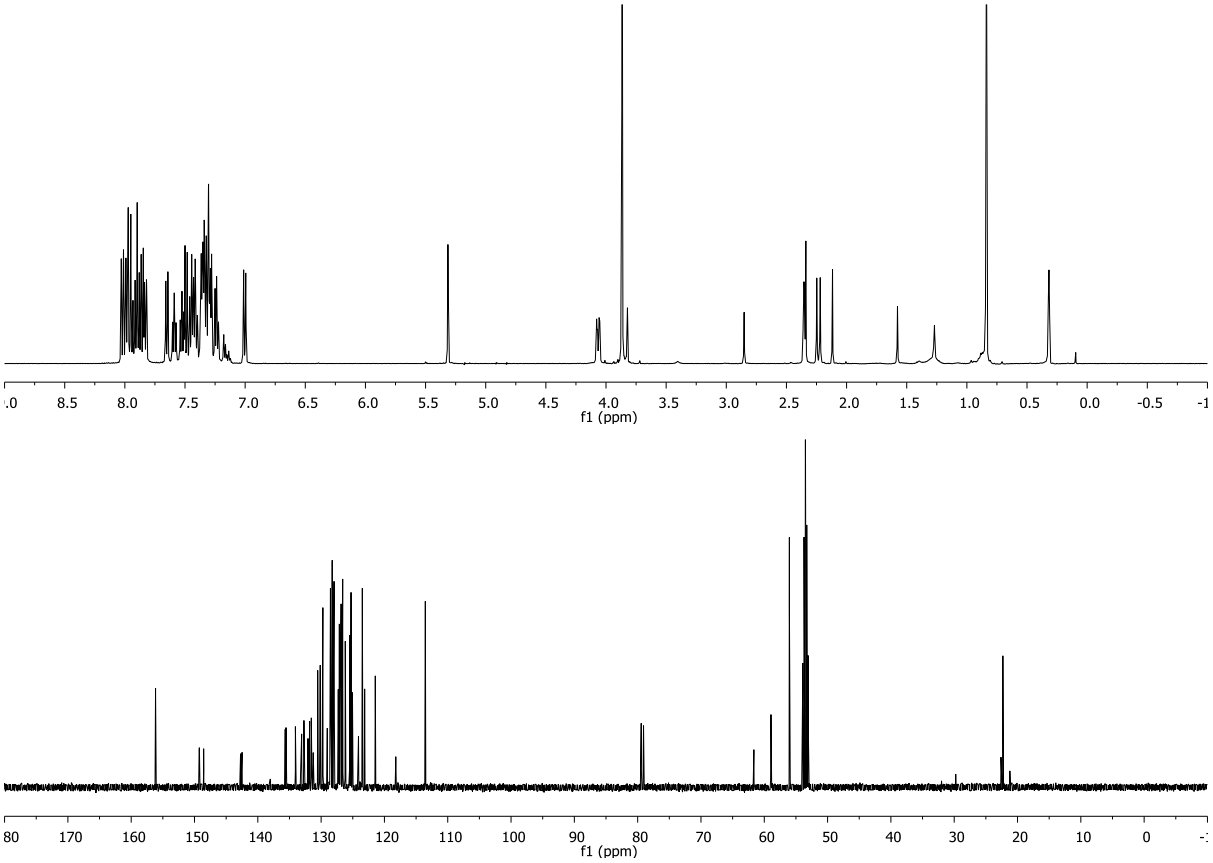
^{13}C {^{1}H} NMR (CD_2Cl_2, 126 MHz): δ (ppm) isomer A (93%), 156.4 (*C*2'), 149.3 (d, $^{2}J_{CP}$ = 5.3 Hz, *C*12), 149.1 (d, $^{2}J_{CP}$ = 12.9 Hz, *C*12'), 141.5 (d, $^{2}J_{CP}$ = 27.0 Hz, *C*1), 135.5 (d, $^{1}J_{CP}$ = 1.4 Hz, *C*2), 134.2 (*C*9'), 133.2 (d, J_{CP} = 7.1 Hz), 133.2 (d, J_{CP} = 8.1 Hz), 132.4 (d, J_{CP} = 1.3 Hz), 132.1 (d, J_{CP} = 1.4 Hz), 131.8 (d, J_{CP} = 8.1 Hz), 131.6 (d, J_{CP} = 1.1 Hz), 131.3 (d, $^{2}J_{CP}$ = 28.8 Hz, allyl-C), 131.0 (*C*4'), 130.5 (d, $^{4}J_{CP}$ = 1.1 Hz, *C*14), 130.1 (d, $^{4}J_{CP}$ = 1.3 Hz, *C*14'), 128.6, 128.5, 128.4, 128.4, 128.3, 128.2 (*C*6), 128.0, 127.5 (d, $^{3}J_{CP}$ = 5.3 Hz, *C*4), 127.0 (*C*10'), 127.0, 126.9 (*C*5'), 126.7, 126.4, 126.3 (d, J_{CP} = 2.3 Hz), 126.2 (*C*8), 125.4, 125.3, 125.0 (d, $^{2}J_{CP}$ = 2.7 Hz, *C*3), 124.5 (*C*6'), 124.4 (d, $^{3}J_{CP}$ = 3.8 Hz, *C*11), 123.7 (d, $^{3}J_{CP}$ = 3.0 Hz, *C*11'), 122.9 (d, $^{3}J_{CP}$ = 2.4 Hz, *C*13), 121.5 (*C*13'), 118.8 (d, $^{3}J_{CP}$ = 9.5 Hz, *C*1'), 113.1 (*C*3'), 77.3 (d, $^{2}J_{CP}$ = 44.9 Hz, allyl-*C*t), 56.2 (O*C*H$_3$), 56.1 (d, $^{2}J_{CP}$ = 5.3 Hz, allyl-*C*c), 22.5 (allyl-*C*H$_3$); signals of isomer B could not be observed. **^{31}P {^{1}H} NMR** (CD_2Cl_2, 202 MHz): δ (ppm) isomer A (93%), 173.6; isomer B (7%) 175.6. **HRMS** (*m*/*z*, ESI$^+$, MeOH): found 755.1301, calcd for $[M - Cl]^+$ 755.1296.



2.8 [Pd(**6b**)(η^3-C$_4$H$_7$)Cl] (**8b**)

Methallylpalladium chloride dimer (7 mg, 18 µmol) and **6b** (21 mg, 35 µmol) were dissolved in dichloromethane (1 mL) and stirred for 10 minutes. The intended complex was formed quantitatively. Slow diffusion of diethyl ether into the reaction mixture yielded colorless crystals overnight, which were suitable for X-ray diffraction analysis. Yield: 23 mg (80%). **MP**: >270 °C. **IR** (neat): ν 3066.0, 1619.1, 1587.6, 1506.6, 1463.6, 1429.5, 1323.0, 1276.0, 1226.1, 1199.8, 1155.9, 1117.7, 1070.1, 1028.0, 946.1, 867.4, 833.3, 814.2, 751.9, 706.2, 686.6, 634.8, 606.6, 560.1 cm^{-1}. **^{1}H NMR** (CD_2Cl_2, 500 MHz,): δ (ppm) 8.02 (d, $^{3}J_{HH}$ = 9.1 Hz, 1H, *H*4'), 8.00-7.97 (m, 2H, *H*15/*H*13'), 7.94 (d, $^{3}J_{HH}$ = 8.9 Hz, 1H, *H*14'), 7.91 (d, $^{3}J_{HH}$ = 8.1 Hz, 1H, *H*5), 7.89 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H, *H*15'), 7.86 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H, *H*14), 7.83 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H, *H*5'), 7.65 (d,

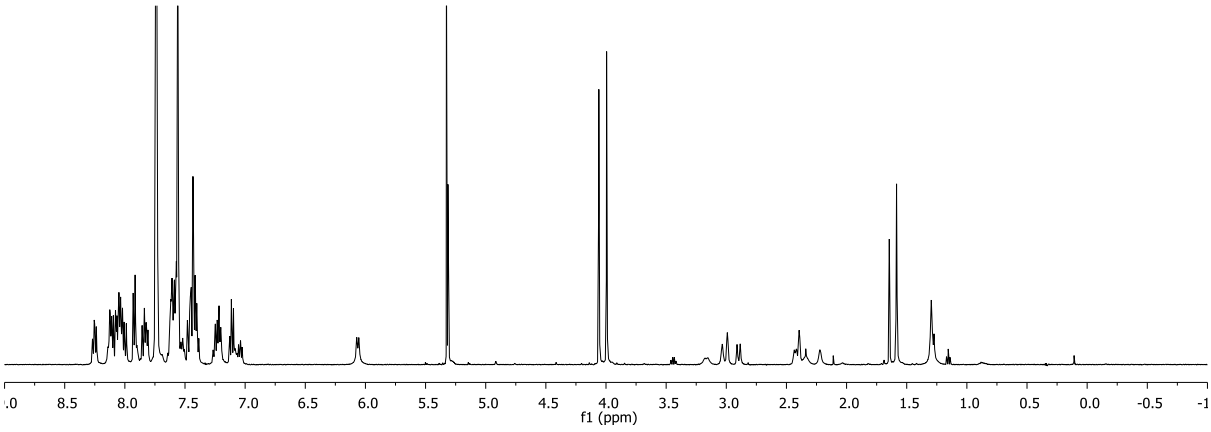
$^3J_{HH}$ = 8.7 Hz, 1H, *H*4), 7.59 (ddd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, *H*6), 7.54-7.51 (m, 1H, *H*16), 7.49 (d, $^3J_{HH}$ = 9.1 Hz, 1H, *H*3'), 7.46-7.39 (m, 3H, ArH/H16'), 7.37-7.27 (m, 7H, Ar*H*/*H*17/*H*7'/*H*6'/*H*3/*H*7/*H*18'), 7.25-7.22 (m, 1H, *H*17'), 7.00 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *H*13), 4.07 (dd, $^3J_{HP}$ = 9.9 Hz, $^4J_{HH}$ = 3.8 Hz, 1H, allyl-*H*t$_{syn}$), 3.87 (s, 3H, OC*H*$_3$), 2.35 (s, 1H, allyl-*H*c$_{syn}$), 2.24 (d, $^3J_{HP}$ = 13.6 Hz, 1H, allyl-*H*t$_{anti}$), 0.84 (s, 3H, allyl-C*H*$_3$), 0.32 (s, 1H, allyl-*H*c$_{anti}$). **^{13}C {^{1}H} NMR** (CD_2Cl_2, 126 MHz): δ (ppm) 156.2 (*C*2'), 149.2 (d, $^2J_{CP}$ = 5.3 Hz, *C*12'), 148.5 (d, $^2J_{CP}$ = 12.4 Hz, *C*12), 142.6 (d, $^2J_{CP}$ = 29.8 Hz, *C*1), 135.6 (d, $^1J_{CP}$ = 1.3 Hz, *C*2), 135.5 (d, $^4J_{CP}$ = 0.9 Hz, *C*9'), 134.0 (d, J_{CP} = 9.2 Hz), 133.1 (d, J_{CP} = 9.8 Hz), 132.7 (d, J_{CP} = 1.5 Hz), 132.1 (d, J_{CP} = 1.9 Hz), 131.8 (d, J_{CP} = 1.3 Hz), 131.6 (d, J_{CP} = 1.3 Hz), 131.3 (d, $^2J_{CP}$ = 26.3 Hz, allyl-C), 130.5 (d, $^4J_{CP}$ = 0.9 Hz, *C*14'), 130.1 (d, $^4J_{CP}$ = 1.3 Hz, *C*14), 129.7 (*C*4'), 128.5 (*C*15), 128.5 (*C*15'), 128.5 (*C*6), 128.3 (*C*5), 128.2 (*C*10'), 128.0 (*C*5'), 127.3 (d, $^3J_{CP}$ = 4.7 Hz, *C*4), 127.0, 127.0, 126.9, 126.8, 126.6, 126.6, 126.2 (*C*17'), 125.5 (*C*16), 125.3 (*C*16'), 125.3, 125.1 (d, $^2J_{CP}$ = 1.4 Hz, *C*3), 124.1 (d, $^3J_{CP}$ = 3.8 Hz, *C*11'), 123.5, 123.4 (d, $^3J_{CP}$ = 2.8 Hz, *C*11), 123.1 (d, $^3J_{CP}$ = 2.4 Hz, *C*13'), 121.4 (*C*13), 118.2 (d, $^3J_{CP}$ = 10.5 Hz, *C*1'), 113.5 (*C*3'), 79.3 (d, $^2J_{CP}$ = 46.1 Hz, allyl-*C*t), 59.0 (d, $^2J_{CP}$ = 4.5 Hz, allyl-*C*c), 56.0 (O*C*H$_3$), 22.3 (allyl-*C*H$_3$). **^{31}P {^{1}H} NMR** (CD_2Cl_2, 202 MHz): δ (ppm) 174.4. **HRMS** (*m*/*z*, ESI$^+$, MeOH): found 755.1280, calcd for [M – Cl]$^+$ 755.1296.

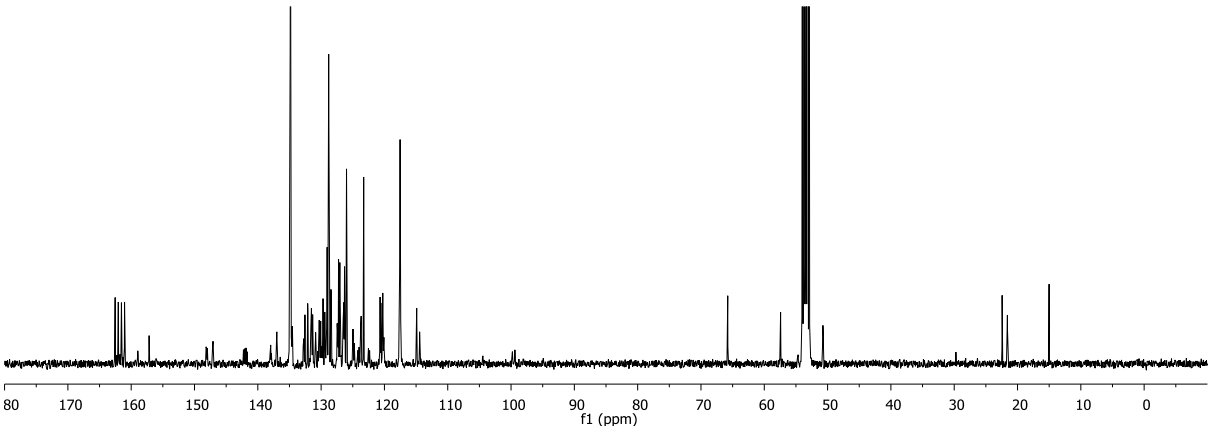


2.9 [Pd(**6a**)(η^3-C$_4$H$_7$)]BArF (**9a**)

8a (30.0 mg, 37.7 μmol) and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (33.4 mg, 37.7 μmol) were dissolved in dichloromethane (2 mL) and stirred for 30 minutes. The reaction mixture was filtered through a layer of celite and the solvent removed in vacuo; the intended product was obtained as a yellow solid. Yield: 48.9 mg (80%). **IR** (neat): *v* 1612.4, 1588.2, 1506.9, 1464.1, 1353.8, 1273.2, 1220.7, 1116.5, 953.5, 882.6,

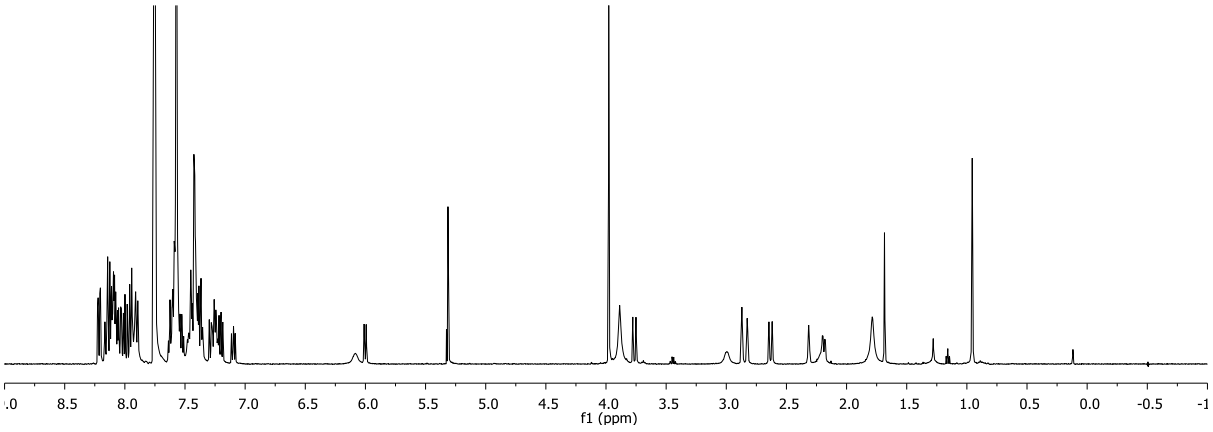
836.8, 813.3, 746.2, 711.9, 681.4, 638.0, 599.2 cm^{-1}. **^{1}H NMR** (CD_2Cl_2, 500 MHz): δ (ppm) isomer A,B, 8.27-7.23 (m, 2H, *H*4'^{B}/*H*4'^{A}), 8.14-7.98 (m, 10H, *H*5'/ *H*14/*H*15'/*H*15/*H*14'), 7.93-7.89 (m, 3H, *H*5'/*H*3'^{B}), 7.86-7.80 (m, 3H, *H*3'^{A}/*H*4), 7.74 (br s, 16H, *o*-BArF), 7.63-7.51 (m, 18H, *H*6'/*H*16/*H*16'/*H*6/Ar*H*/*p*-BArF), 7.48-7.38 (m, 10H, *H*13/Ar*H*), 7.26-7.19 (m, 4H, *H*7/Ar*H*), 7.13-7.02 (m, 4H, *H*13'/*H*3), 6.06 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H, *H*8), 4.06 (s, OCH_3^{B}), 4.00 (s, OCH_3^{A}), 3.16 (br d, $^{3}J_{HP}$ = 10.7 Hz, allyl-*H*t$_{anti}^{B}$), 3.03 (s, allyl-*H*c$_{syn}^{B}$), 2.99 (s, allyl-*H*c$_{syn}^{A}$), 2.90 (d, $^{3}J_{HP}$ = 13.2 Hz, allyl-*H*t$_{anti}^{A}$), 2.43 (br d, $^{3}J_{HP}$ = 8.2 Hz, allyl-*H*t$_{syn}^{A}$), 2.39 (s, allyl-*H*c$_{anti}^{A}$), 2.34 (br s, allyl-*H*t$_{syn}^{B}$), 2.22 (s, allyl-*H*c$_{anti}^{B}$), 1.58 (s, allyl-CH_3^{A}), 1.30 (s, allyl-CH_3^{B}); A:B ratio from integration of CH_3 signals: 52:48. **^{11}B NMR** (CD_2Cl_2, 160 MHz): δ (ppm) –7.6. **^{13}C {^{1}H} NMR** (CD_2Cl_2, 101 MHz): δ (ppm) isomer A,B, 161.8 (q, $^{1}J_{CB}$ = 40.8 Hz, *ipso*-BArF), 159.0 (*C*2'^{B}), 157.2 (*C*2'^{A}), 148.1 (d, $^{2}J_{CP}$ = 10.1 Hz, *C*12'^{B}), 148.0 (d, $^{2}J_{CP}$ = 11.0 Hz, *C*12'^{A}), 147.1 (d, $^{2}J_{CP}$ = 7.7 Hz, *C*12), 142.1 (d, $^{2}J_{CP}$ = 41.7 Hz, *C*1^{B}), 141.9 (d, $^{2}J_{CP}$ = 41.7 Hz, *C*1^{A}), 137.9 (d, $^{2}J_{CP}$ = 9.5 Hz, allyl-*C*^{A}), 137.0 (*C*2), 134.8 (*o*-BArF), 134.6 (*C*4'), 132.8, 132.5, 132.1, 132.0, 131.7, 131.6 (*C*14), 131.5 (*C*9'^{A}), 131.4 (*C*9'^{B}), 131.4 (*C*14'), 130.9, 130.8, 130.4, 130.3 (*C*4), 130.1 (*C*5'), 130.0, 129.8, 129.4, 128.9 (qq, $^{2}J_{CF}$ = 31.2 Hz, $^{4}J_{CF}$ = 2.8 Hz, *m*-BArF), 128.8, 128.4 (*C*10'), 127.5, 127.4, 127.3, 127.1, 127.0, 126.9, 126.5, 126.4, 126.3, 126.0, 125.0, 124.8, 124.7 (q, $^{1}J_{CF}$ = 273.2 Hz, *C*F_3), 124.1, 124.0 (d, J_{CP} = 3.4 Hz), 123.8, 123.7, 123.3, 122.5, 122.3, 120.7 (*C*3), 120.6 (*C*13'), 120.3 (*C*13), 120.1, 117.5 (septet, $^{3}J_{CF}$ = 4.0 Hz, *p*-BArF), 114.9 (*C*3'^{A}), 114.5 (*C*3'^{B}), 104.6 (*C*1'^{A}), 99.6 (d, $^{2}J_{CP}$ = 40.1 Hz, allyl-*C*t^{A}), 57.5 (O*C*H$_3^{B}$), 57.4 (O*C*H$_3^{A}$), 53.2 (allyl-*C*c^{A}), 22.4 (allyl-*C*H$_3^{A}$), 21.6 (allyl-*C*H$_3^{B}$); not all signals could be observed due to peak broadening and overlap. **^{19}F NMR** (CD_2Cl_2, 471 MHz): δ (ppm) –62.7. **^{31}P {^{1}H} NMR** (CD_2Cl_2, 202 MHz): δ (ppm) isomer **A** 177.5; isomer **B** 178.0. **HRMS** (*m*/*z*, ESI^{+}, MeCN): found 757.1287, calcd for $[M]^{+}$ 757.1281.

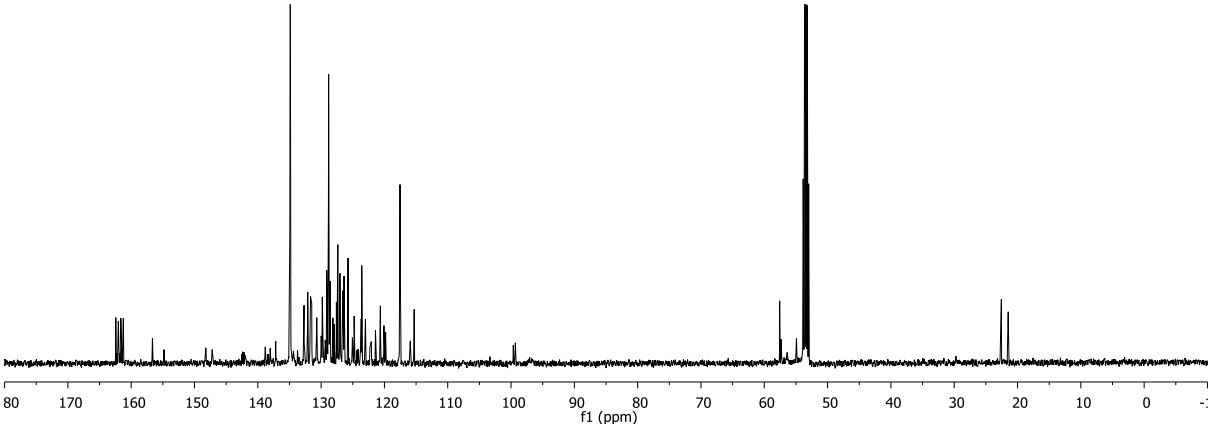




2.10 [Pd(**6b**)(η^3-C_4H_7)]BArF (**9b**)

8b (29.0 mg, 36.5 µmol) and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (32.3 mg, 36.5 µmol) were dissolved in dichloromethane (2 mL) and stirred for 30 minutes. The reaction mixture was filtered through a layer of celite and the solvent was removed in vacuo; the intended product was obtained as a yellow solid. Yield: 54.0 mg (91%). **IR** (neat): ν 1612.1, 1588.9, 1506.1, 1463.5, 1353.6, 1273.0, 1219.8, 1116.1, 952.9, 882.4, 836.7, 811.4, 745.5, 711.9, 669.8, 638.6, 602.7 cm^{-1}. **^{1}H NMR** (CD_2Cl_2, 500 MHz): δ (ppm) isomer A,B, 8.22 (d, $^3J_{HH}$ = 9.2 Hz, 1H, *H*4'^{A}), 8.21 (d, $^3J_{HH}$ = 9.2 Hz, 1H, *H*4'^{B}), 8.17-8.01 (m, 10H, *H*14/*H*14'/*H*5'/Ar*H*), 7.99 (d, $^3J_{HH}$ = 9.2 Hz, 1H, *H*3'^{A}), 7.96-7.89 (m, 5H, Ar*H*/*H*4/*H*3'^{B}), 7.76 (br s, 16H, *o*-BArF), 7.64-7.51 (m, 18H, Ar*H*/*p*-BArF), 7.49-7.35 (m, 12H, Ar*H*/*H*13^B/*H*13'^{A}/*H*13^A), 7.30-7.22 (m, 4H, Ar*H*/*H*7/*H*13'^{B}), 7.20 (dd, $^3J_{HH}$ = 8.5 Hz, $^3J_{HP}$ = 6.9 Hz, 1H, *H*3^A), 7.10 (dd, $^3J_{HH}$ = 8.5 Hz, $^3J_{HP}$ = 6.9 Hz, 1H, *H*3^B), 6.09 (br d, 1H, *H*8^B), 6.00 (d, $^3J_{HH}$ = 8.6 Hz, 1H, *H*8^A), 3.98 (s, OC*H*$_3^A$), 3.89 (s, OC*H*$_3^B$), 3.76 (d, $^3J_{HP}$ = 13.6 Hz, allyl-*H*t$_{anti}^A$), 3.00 (br d, allyl-*H*t$_{syn}^B$), 2.87 (s, allyl-*H*c$_{syn}^B$), 2.82 (s, allyl-*H*c$_{syn}^A$), 2.63 (d, $^3J_{HP}$ = 13.5 Hz, allyl-*H*t$_{anti}^B$), 2.32 (s, allyl-*H*c$_{anti}^A$), 2.20 (br s, allyl-*H*c$_{anti}^B$), 2.19 (d, allyl-*H*t$_{syn}^A$), 1.79 (br s, allyl-C*H*$_3^B$), 0.96 (s, allyl-C*H*$_3^A$); A:B ratio of 50:50 from integration of OMe resonances (signals of isomer B broadened). **^{11}B NMR** (CD_2Cl_2, 128 MHz): δ (ppm) –7.6. **^{13}C {^{1}H} NMR** (CD_2Cl_2, 126 MHz): δ (ppm) isomer A,B, 161.8 (q, $^1J_{CB}$ = 40.7 Hz, *ipso*-BArF), 156.6 (*C*2'^{A}), 154.8 (d, J_{CP} = 2.4 Hz, *C*2'^{B}), 148.3 (d, $^2J_{CP}$ = 13.5 Hz, *C*12^A), 148.3 (d, $^2J_{CP}$ = 13.3 Hz, *C*12^B), 147.2 (d, $^2J_{CP}$ = 7.1 Hz, *C*12'^{A}), 147.1 (d, $^2J_{CP}$ = 7.4 Hz, *C*12'^{B}), 142.4 (d, $^2J_{CP}$ = 43.5 Hz, *C*1^B), 142.2 (d, $^2J_{CP}$ = 41.3 Hz, *C*1^A), 138.9 (d, $^2J_{CP}$ = 10.4 Hz, allyl-*C*^{A}), 138.1 (d, J = 10.0 Hz, allyl-*C*^{B}), 137.1 (*C*2^B), 137.0 (*C*2^A), 134.9 (*C*4'^{A}), 134.9 (*o*-BArF), 134.3 (*C*4'^{B}), 133.7 (*C*9'^{B}), 132.8, 132.7 (*C*9'^{A}) 132.1, 131.8, 131.7, 131.6, 131.5, 130.7 (d, $^3J_{CP}$ = 4.7 Hz, *C*4), 130.0 (*C*10'^{B}), 129.8, 129.8, 129.7, 129.3 (*C*10'^{A}), 128.9 (qq, $^2J_{CF}$ = 31.6 Hz, $^4J_{CF}$ = 2.9 Hz, *m*-BArF), 128.7, 128.6, 128.0, 127.6, 127.4, 127.4, 127.0, 127.0, 126.6, 126.5, 126.4, 125.1, 124.8, 124.7 (q, $^1J_{CF}$ = 272.3 Hz, *C*F$_3$), 124.3, 124.1, 123.7 (d, $^2J_{CP}$ = 1.4 Hz, *C*3^B), 123.7 (d, $^2J_{CP}$ = 1.4 Hz, *C*3^A), 123.0, 122.3, 122.1, 120.7 (d, $^3J_{CP}$ = 1.0 Hz, *C*13^B), 120.6 (d, $^3J_{CP}$ = 1.0 Hz, *C*13^A), 120.1 (d, $^3J_{CP}$ = 2.1 Hz, *C*13'^{A}), 119.8 (*C*13'^{B}), 117.5 (septet, $^3J_{CF}$ = 4.0 Hz, *p*-BArF), 115.9 (*C*3'^{B}), 115.3 (*C*3'^{A}), 104.5 (*C*1'^{B}), 103.4 (*C*1'^{A}), 99.5 (d, $^2J_{CP}$ = 41.1 Hz, allyl-*C*t^A), 96.9 (br, allyl-*C*t^B), 57.6 (O*C*H$_3^A$), 57.3 (O*C*H$_3^B$), 56.4(allyl-*C*c^B), 54.9 (allyl-*C*c^A), 22.6 (allyl-*C*H$_3^B$), 21.5 (allyl-*C*H$_3^A$); not all signals could be observed due to peak broadening and overlap. **^{19}F NMR** (CD_2Cl_2, 471 MHz): δ (ppm) –62.7. **^{31}P {^{1}H} NMR** (CD_2Cl_2, 202 MHz): δ (ppm) isomer A 178.9; isomer B 179.1. **HRMS** (*m*/*z*, ESI$^+$, MeCN): found 757.1296, calcd for [M]$^+$ 757.1281.





2.11 Typical Procedure for the Asymmetric Palladium-Catalyzed Hydrosilylation of Styrene

Allylpalladium(II) chloride dimer (4.6 mg, 0.0125 mmol, 0.125 mol%), ligand (0.25 mol%) and styrene (1.2 mL, 1.0 g, 10.0 mmol) were stirred at room temperature for 20 minutes. Trichlorosilane (1.2 mL, 1.6 g, 12.0 mmol) was added and the reaction was stirred at room temperature for the appropriate time. The conversion of the reaction was followed by ^{1}H NMR spectroscopy. The product was purified by Kugelrohr distillation (reduced pressure, 150 °C).

Trichloro(1-phenylethyl)silane (400 mg, 1.67 mmol) was dissolved in methanol (30 mL) and tetrahydrofuran (30 mL). Potassium carbonate (1.40 g, 10.1 mmol), potassium fluoride (600 mg, 10.3 mmol) and 35% hydrogen peroxide (1.8mL) were added subsequently and left to stir overnight. The solution was filtered, water was added and the product was extracted with diethyl ether three times. The combined organic washings were dried over magnesium sulphate and the crude product was purified by column chromatography on silica (hexane/ethyl acetate, 4:1, R_f = 0.20). The enantiomeric excess was measured by chiral HPLC (Column Daicel Chiralcel OD; flow rate: 0.5 mL/min; hexane/2-propanol, 95:5; retention times: (*R*) t_1 = 19.3 min, (*S*) t_2 = 22.3 min). The absolute configuration was assigned by comparing the retention times to literature data.[5]

3 *Syn*/*Anti* Exchange in Allylpalladium Complexes 7a and 8a

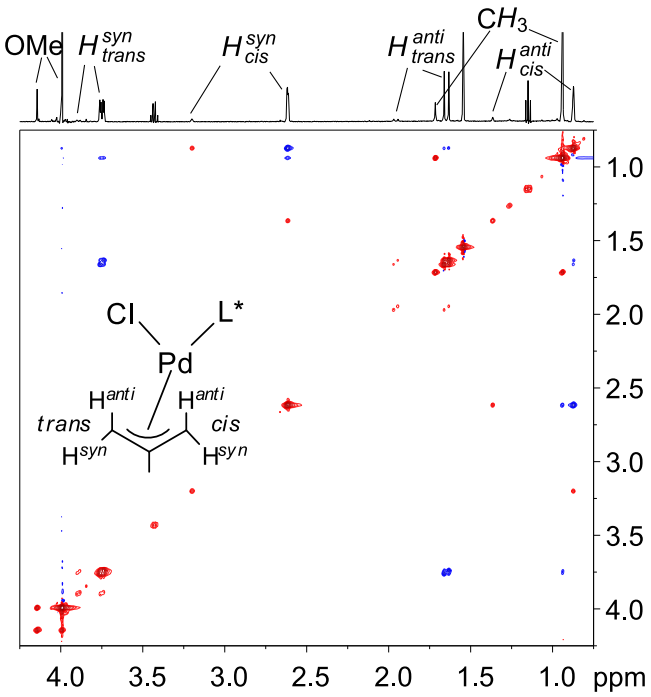


Fig. S2 Section of the ^{1}H-NOESY spectrum of **8a** in CD_2Cl_2; two isomers were observed. NOE correlations are shown in blue, exchange correlations are shown in red. The spectrum was acquired at 21 °C, using a 500 MHz spectrometer with a mixing time of 400 ms.

Table S2 ^{31}P and Selected ^{1}H NMR Data (δ in ppm) for Complexes **7a**, **7b**, **8a** and **8b**, and the Relative Ratio of Isomers Observed (CD_2Cl_2, 21 °C, 202 and 500 MHz).

Complex	P	H_t^{syn}	H_t^{anti}	H_c^{syn}	H_c^{anti}	CH_3	A/B
7a	173.4 (A)	3.75	1.57	2.56	0.83	1.00	97/3
	175.7 (B)	3.96	2.64	2.96	1.53	1.42	
8a	173.6 (A)	3.73	1.63	2.60	0.85	0.92	93/7
	175.6 (B)	3.87	1.94	3.18	1.35	1.70	
9a	177.5 (A)	2.43	2.90	2.99	2.34	1.58	52/48
	178.0 (B)	2.34	3.16	3.03	2.22	1.30	
7b	172.1	4.16	2.56	2.31	0.50	0.93	100/0
8b	174.4	4.07	2.24	2.35	0.32	0.84	100/0
9b	178.9 (A)	2.19	3.76	2.82	2.32	0.96	50/50
	179.1 (B)	3.00	2.63	2.87	2.20	1.79	

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Table S3 ^{13}C NMR Data (δ in ppm) with ^{31}P-Splitting in Parentheses (J_{CP} in Hz) for the Allyl-carbons in **7a**,**b**, **8a**,**b** and **9a**,**b**.

Carbon	**7a**	**8a**	**9a**	**7b**	**8b**	**9b**
allyl-CH_3	22.4	22.5	22.4 21.6	22.5	22.3	21.5 22.6
cis-C	56.1 (5.8)	56.1 (5.3)	53.2 n.d.	57.6 (5.3)	59.0 (4.5)	54.9 56.4
trans-C	76.8 (45.3)	77.3 (44.9)	99.6 (40.1) n.d.	77.8 (46.5)	79.3 (49.3)	99.5 (41.1) 96.9
quart.-C	131.0 (28.6)	131.3 (28.8)	137.9 (9.5) n.d.	130.8 (28.5)	131.3 (26.3)	138.9 (10.4) 138.1 (10.0)

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