Taming Functionality: Easy-to-Handle Chiral Phosphiranes

Supporting Information

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Table of Contents

1 General Considerations and Chemical Analysis

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. Flash chromatography was performed on silica gel from Fluorochem (silica gel, 40-63u, 60A, LC301). (*S*)-[1,1'-Binaphthalen]-2-ylphosphine ((*S*)-**1a**) and (*R*)-(2'-methoxy-[1,1'-binaphthalen]-2-yl)phosphine ((*R*)-**1b**) were prepared according to literature procedures.[1]

Melting points were determined in open glass capillary tubes on a Stuart SMP3 melting point apparatus. ^{1}H, ^{13}C {^{1}H}, ^{19}F, 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. The labelling scheme is given in Fig. **1**; if necessary, the assignment of signals was carried out by using two-dimensional NMR experiments (COSY, NOESY, HSQC, HMBC). The absolute assignments of the 1"/2"-signals of the phosphirane heterocycle were performed in accordance with the predicted NMR shifts as generated by the quantum chemical calculations. Infrared spectra were recorded on a Varian 800 FT-IR spectrometer. Mass spectrometry was carried out by the EPSRC National Mass Spectrometry Service Centre, Swansea. Optical rotation values were determined on an Optical Activity Polaar 2001 device. Thin layer chromatography was performed on Merck aluminum-based plates with silica gel and fluorescent indicator (254 nm). For indicating, UV light (λ = 254 nm/366 nm) 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. Analytical high performance liquid chromatography (HPLC) was performed on a Varian Pro Star HPLC equipped with a variable wavelength detector using a Daicel Chiralcel OD-H column.

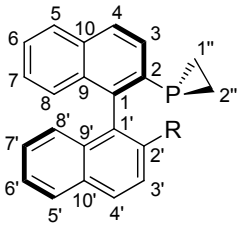


Fig. 1 Labelling scheme for binaphthyl compounds.

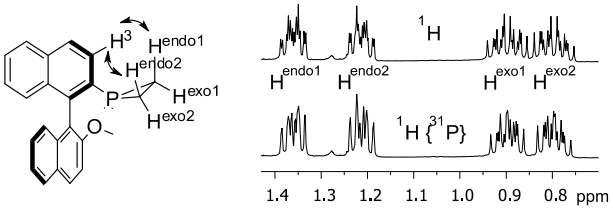
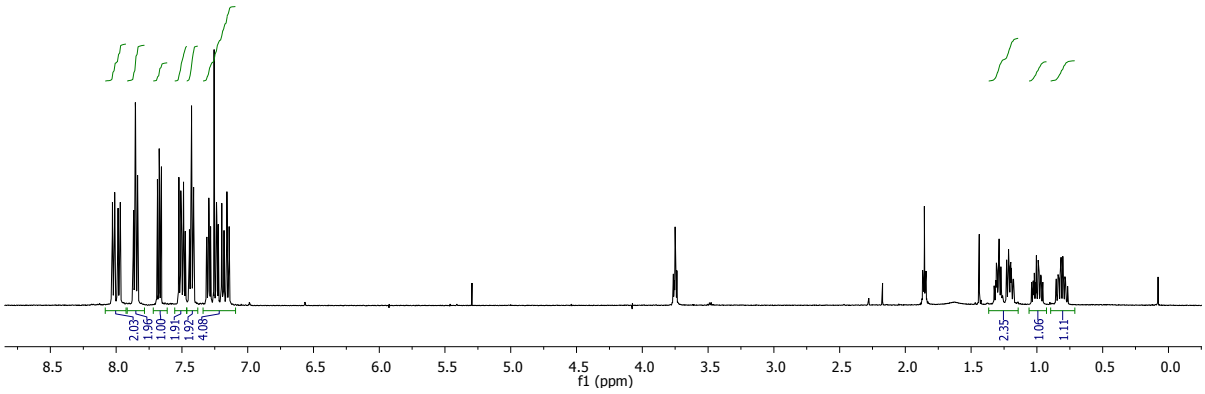


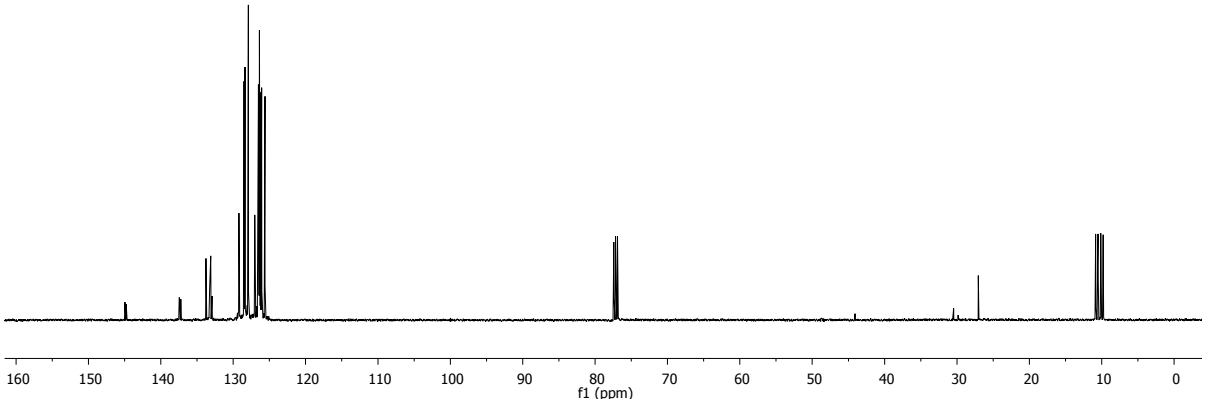
Fig. 2 Observed NOE correlations (arrows) and aliphatic sections of the ^{1}H and ^{1}H {^{31}P} NMR spectra of (*R*)-**2b**. Comparable NOE contacts are also found for (*S*)-**2a**.

2 Experimental Procedures

2.1 (*S*)-1-([1,1'-Binaphthalen]-2-yl)phosphirane ((*S*)-**2a**)

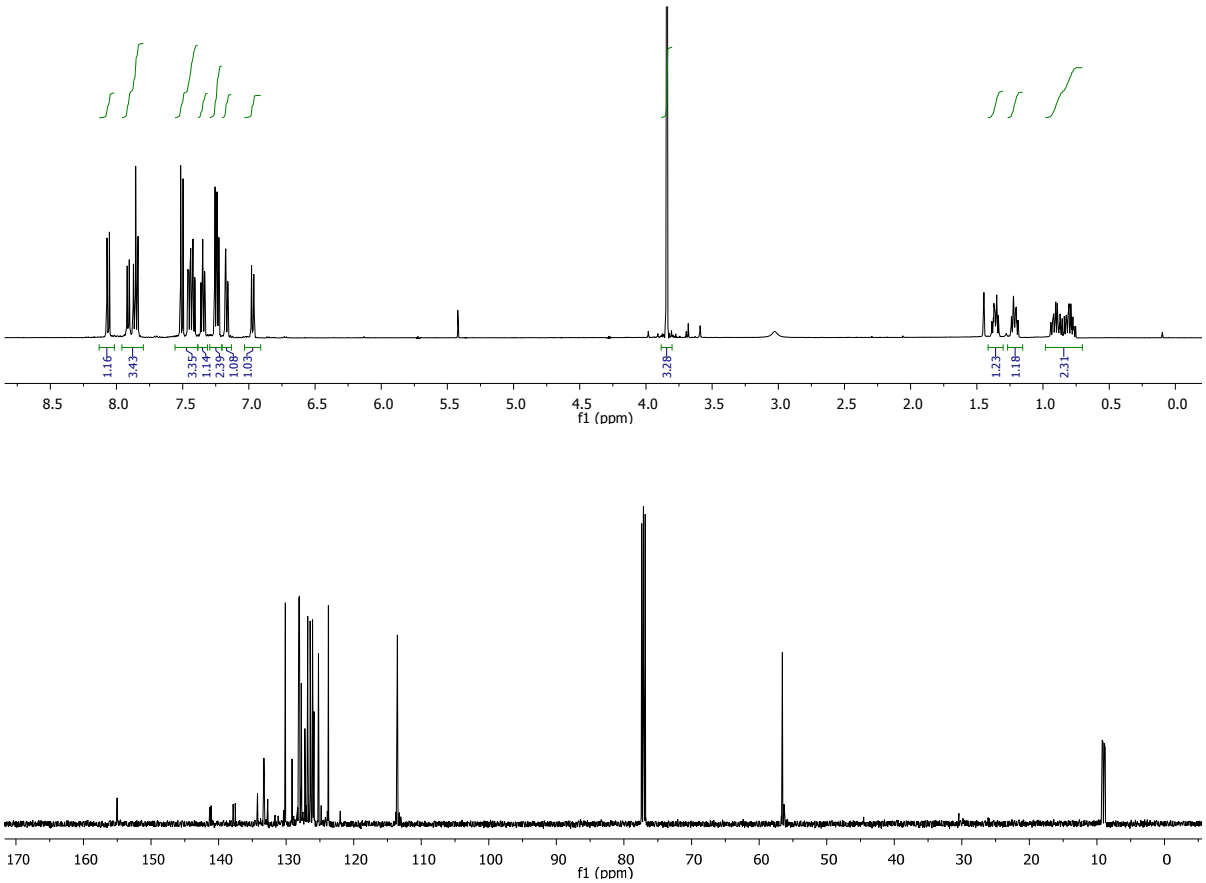
(*S*)-[1,1'-Binaphthalen]-2-ylphosphine (500 mg, 1.75 mmol) was dissolved in tetrahydrofuran (10 mL) and cooled to –78 °C. Methyllithium (2.40 mL, 1.6 M in diethyl ether, 3.84 mmol) was added and the orange-red solution was stirred at –78 °C for 30 minutes. 1,2-Dichloroethane (0.17 mL, 2.10 mmol) was added, and the solution was allowed to warm up to ambient temperature and stirred for 2 hours to give a yellow-brown solution. The reaction was slowly quenched with water (10 mL) and extracted with diethyl ether (2x 30 mL). The organic phase was dried over magnesium sulfate to give the fairly pure crude product as a pale-yellow solid (513 mg). Purification was performed by column chromatography (cyclohexane/dichloromethane, 1:1) on a silica media (w = 2 cm, h = 10 cm) to yield the intended product as a white solid (473 mg, 1.51 mmol, 87%). **MP** (uncorrected): 92 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.04 (d, $^3J_{HH}$ = 7.8 Hz, 1H, *H*4'), 8.00 (d, $^3J_{HH}$ = 7.8 Hz, 1H, *H*5'), 7.88 (d, $^3J_{HH}$ = 7.8 Hz, 1H, *H*5), 7.86 (d, $^3J_{HH}$ = 7.8 Hz, 1H, *H*4), 7.69 (m, $^3J_{HH}$ = 7.8 Hz, 1H, *H*3'), 7.54 (d, $^3J_{HH}$ = 7.8 Hz, 1H, *H*2'), 7.51 (m, 1H, *H*6'), 7.45 (m, 1H, *H*6), 7.44 (m, 1H, *H*3), 7.32 (dd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 8.7 Hz, 1H, *H*7'), 7.25 (dd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 8.7 Hz, 1H, *H*7), 7.22 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *H*8'), 7.18 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *H*8), 1.31 (m, 1H, *endo-H*1''), 1.22 (m, 1H, *endo-H*2''), 1.01 (m, 1H, *exo-H*1''), 0.82 (m, 1H, *exo-H*2'') ppm. **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 144.9 (d, $^2J_{CP}$ = 23.0 Hz, *C*1), 137.4 (d, $^3J_{CP}$ = 8.2 Hz, *C*1'), 137.4 (d, $^1J_{CP}$ = 40.1 Hz, *C*2), 133.8, 133.3, 133.1, 132.9, 129.2 (d, $^4J_{CP}$ = 1.9 Hz, *C*2'), 128.5 (*C*5'), 128.4 (*C*4'), 127.9 (*C*4/*C*5), 127.0 (d, $^2J_{CP}$ = 2.9 Hz, *C*3), 126.5 (*C*7), 126.5 (*C*8), 126.4 (*C*7'/*C*8'), 126.2 (*C*6), 126.1 (*C*6'), 125.6 (*C*3'), 10.7 (d, $^1J_{CP}$ = 40.3 Hz, *C*1''), 10.0 (d, $^1J_{CP}$ = 40.3 Hz, *C*2'') ppm. **^{31}P NMR** (202 MHz, $CDCl_3$): δ = –235.4 (pseudo-t, average $^2J_{PH}$ = 18.6 Hz) ppm. **IR** (neat): $\tilde{\nu}$ = 3048.3 (w), 2922.8 (w), 1587.2 (w), 1553.3 (w), 1501.5 (m), 1358.7 (m), 1255.9 (w), 1047.5 (w), 1014.9 (w), 968.6 (w), 867.5 (w), 801.6 (s), 779.5 (s), 744.9 (s), 686.5 (m), 628.3 (m), 561.2 (w) cm^{-1}. **HRMS** (ESI$^+$, acetone): Calc. for $[M + H]^+$ m/z = 313.1146, found: m/z = 313.1146 (0.0 ppm). **OR** ($CHCl_3$, c = 1.0 mg/ml): $[\alpha]_D^{20}$ = +74°. **TLC** (silica gel; cyclohexane/dichloromethane, 1:1): R_f = 0.7.





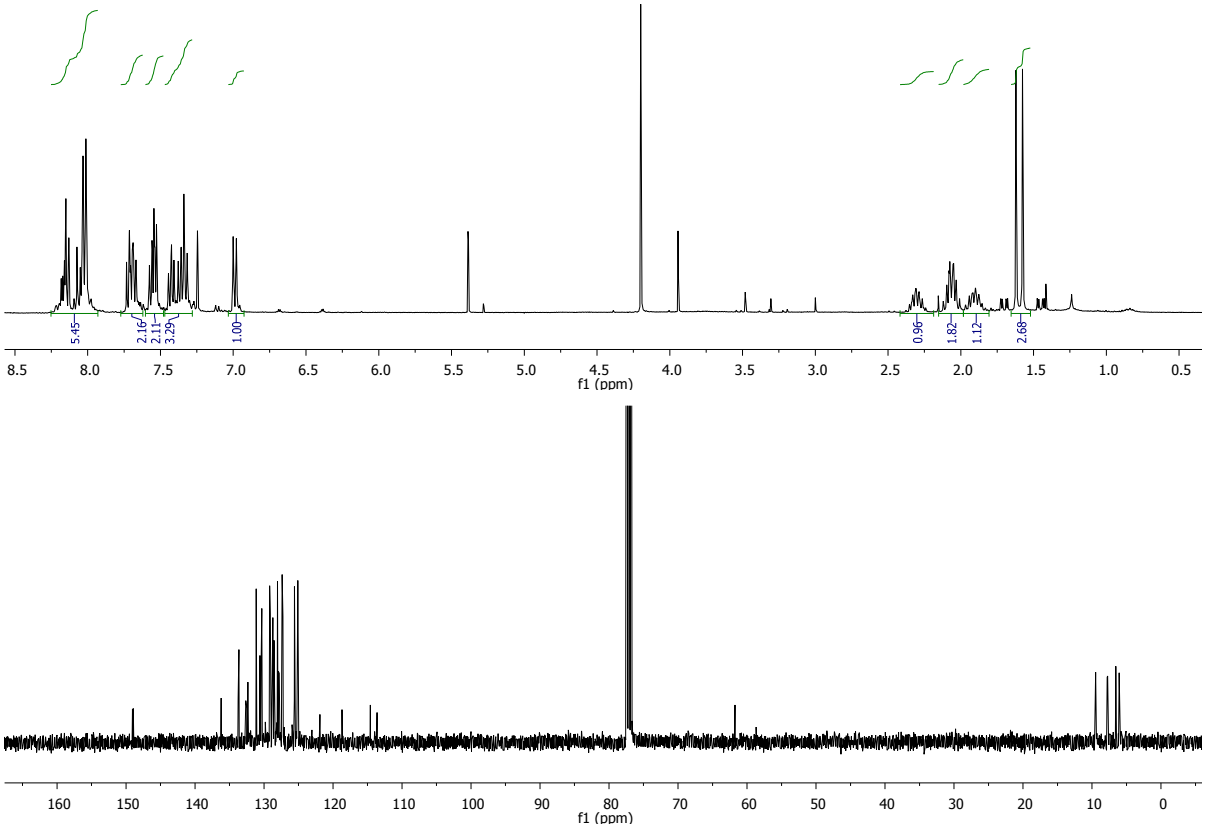
2.2 (*R*)-1-(2'-Methoxy-1,1'-binaphthyl-2-yl)phosphirane ((*R*)-**2b**)

(*R*)-(2'-Methoxy-[1,1'-binaphthalen]-2-yl)phosphine (500 mg, 1.58 mmol) was dissolved in tetrahydrofuran (10 mL) and cooled to –78 °C. Methyllithium (2.17 mL, 1.6 M in diethyl ether, 3.48 mmol) was added and the orange-red solution was stirred at –78 °C for 30 minutes. 1,2-Dichloroethane (0.15 mL, 1.90 mmol) was added and the solution was allowed to warm up to ambient temperature and stirred for 2 hours to give an orange solution. The reaction was slowly quenched with water (10 mL) and extracted with diethyl ether (2x 30 mL). The organic phase was dried over magnesium sulfate to give the fairly pure crude product (530 mg). Purification was performed by column chromatography (cyclohexane/dichloromethane, 1:1) on a silica media (w = 4 cm, h = 7 cm) to yield the intended product as a white solid (482 mg, 1.41 mmol, 89%). **MP** (uncorrected): 142 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.06 (d, $^3J_{HH}$ = 8.8 Hz, 1H, *H*4'), 7.91 (d, $^3J_{HH}$ = 8.2 Hz, 1H, *H*5'), 7.86 (d, $^3J_{HH}$ = 8.4 Hz, 1H, *H*4), 7.84 (d, $^3J_{HH}$ = 8.2 Hz, 1H, *H*5), 7.50 (d, $^3J_{HH}$ = 8.8 Hz, 1H, *H*3'), 7.44 (dd, $^3J_{HH}$ = 8.4 Hz, $^3J_{PH}$ = 3.6 Hz, 1H, *H*3), 7.42 (m, $^3J_{HH}$ = 8.2 Hz, 1H, *H*6), 7.34 (m, $^3J_{HH}$ = 8.2 Hz, 1H, *H*6'), 7.27 (m, $^3J_{HH}$ = 8.2 Hz, 1H, *H*7), 7.27 (m, $^3J_{HH}$ = 8.2 Hz, 1H, *H*7'), 7.16 (d, $^3J_{HH}$ = 8.2 Hz, 1H, *H*8'), 6.96 (d, $^3J_{HH}$ = 8.2 Hz, 1H, *H*8), 3.85 (s, 3H, OCH_3), 1.35 (m, 1H, *endo*-*H*1"), 1.21 (m, 1H, *endo*-*H*2"), 0.89 (m, 1H, *exo*-*H*1"), 0.79 (m, 1H, *exo*-*H*2") ppm. **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 155.0 (*C*2'), 141.2 (d, $^2J_{CP}$ = 24.5 Hz, *C*1), 137.7 (d, $^1J_{CP}$ = 38.8 Hz, *C*2), 134.1, 133.2, 132.6, 130.0 (*C*4'), 129.0, 128.0 (*C*5'), 127.9 (*C*4), 127.6 (*C*5), 127.1 (*C*3), 126.7 (*C*7'), 126.3 (*C*7), 126.0 (*C*6), 125.8 (*C*8), 125.1 (*C*8'), 123.6 (*C*6'), 122.0 (d, $^3J_{CP}$ = 6.7 Hz, *C*1'), 113.4 (*C*3'), 56.6 (s, OCH_3), 9.1 (d, $^1J_{CP}$ = 40.1 Hz, *C*2"), 8.7 (d, $^1J_{CP}$ = 40.1 Hz, *C*1") ppm. **^{31}P NMR** (202 MHz, $CDCl_3$): δ = –235.0 (pseudo-t, average $^2J_{PH}$ = 18.6 Hz) ppm. **IR** (neat): $\tilde{\nu}$ = 3051.6 (w), 2930.0 (w), 1620.7 (w), 1592.4 (m), 1507.5 (m), 1460.7 (w), 1338.9 (w), 1249.3 (s), 1147.1 (w), 1079.1 (m), 1050.6 (m), 1019.6 (w), 907.2 (w), 866.2 (w), 806.2 (s), 774.1 (w), 745.2 (s), 686.1 (w), 627.5 (w) cm^{-1}. **HRMS** (ESI^+, acetone): Calc. for $[M + H]^+$ *m*/*z* = 343.1252, found: *m*/*z* = 343.1246 (–1.7 ppm). **OR** ($CHCl_3$, *c* = 1.1 mg/ml): $[\alpha]_D^{20}$ = +60°. **TLC** (silica gel; cyclohexane/dichloromethane, 1:1): R_f = 0.5.



2.3 (*S*)-1-([1,1'-Binaphthalen]-2-yl)-1-methylphosphiranium triflate ((*S*)-**3a**)

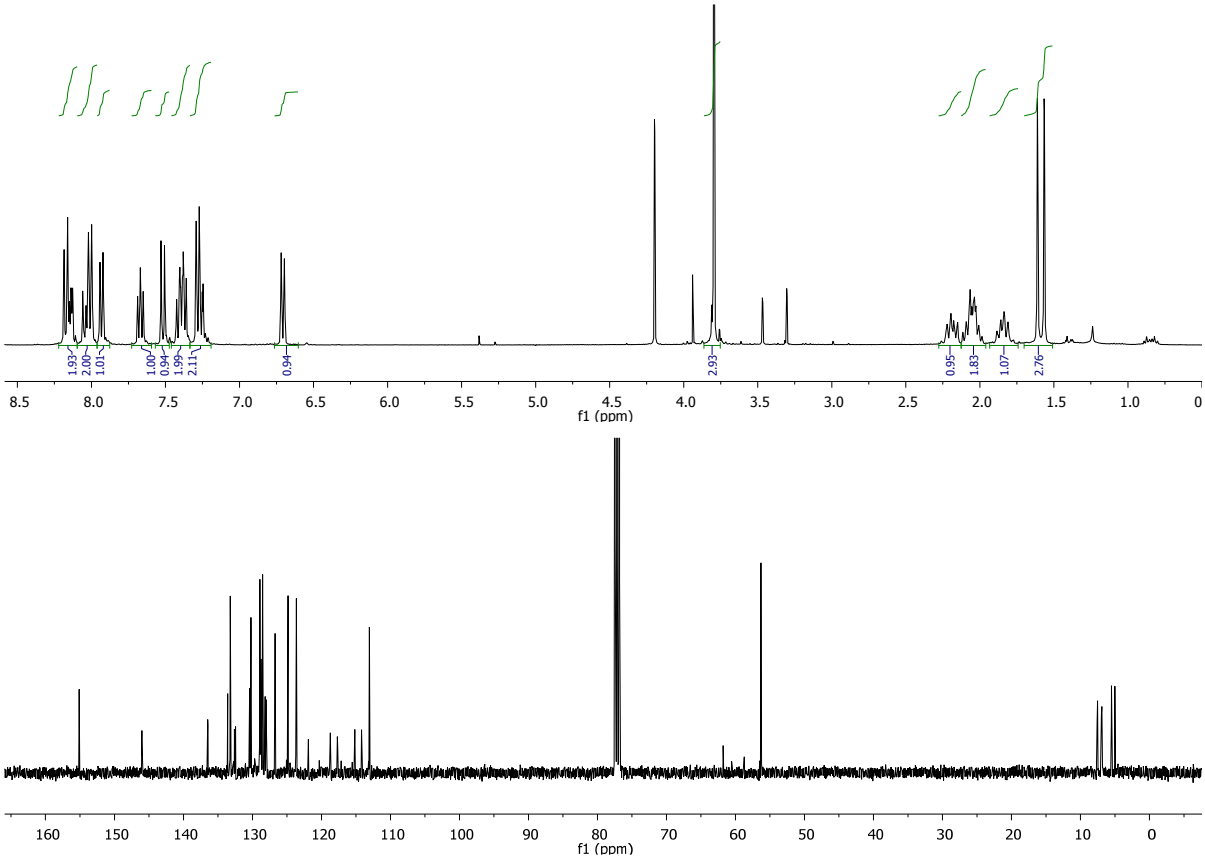
(*S*)-1-([1,1'-Binaphthalen]-2-yl)phosphirane (31.2 mg, 0.10 mmol) was dissolved in dichloromethane (7 mL) and methyl trifluoromethanesulfonate (32.8 mg, 0.02 mL, 0.20 mmol) was added. The reaction mixture was stirred at room temperature for 2 hours. The volatiles were removed *in vacuo* to give the intended product as a colourless solid (quantitative conversion). **^{1}H NMR** (400 MHz, $CDCl_3$): $\delta = 8.18$ (dd, $^{4}J_{HP} = 4.0$ Hz, $^{3}J_{HH} = 8.7$ Hz, 1H, *H*4), 8.15 (d, $^{3}J_{HH} = 8.7$ Hz, 1H, *H*4'), 8.06 (dd, $^{3}J_{HH} = 8.7$ Hz, $^{3}J_{HP} = 13.9$ Hz, 1H, *H*3), 8.03 (m, $^{3}J_{HH} = 8.7$ Hz, 2H, *H*5/*H*5'), 7.72 (dd, $^{3}J_{HH} = 7.8$ Hz, $^{3}J_{HH} = 8.7$ Hz, 1H, *H*3'), 7.70 (m, $^{3}J_{HH} = 8.7$ Hz, 1H, *H*6), 7.57 (d, $^{3}J_{HH} = 8.7$ Hz, 1H, *H*6'), 7.55 (d, $^{3}J_{HH} = 7.8$ Hz, 1H, *H*2'), 7.44 (m, $^{3}J_{HH} = 8.7$ Hz, 1H, *H*7), 7.37 (m, $^{3}J_{HH} = 8.7$ Hz, 1H, *H*7'), 7.34 (d, $^{3}J_{HH} = 8.7$ Hz, 1H, *H*8), 7.00 (d, $^{3}J_{HH} = 8.7$ Hz, 1H, *H*8'), 2.31 (m, 1H, *endo*-*H*1"), 2.06 (m, 2H, *endo*-*H*2"/*exo*-*H*1"), 1.91 (m, 1H, *exo*-*H*2"), 1.60 (d, $^{2}J_{HP} = 17.9$ Hz, 3H, CH_3) ppm.
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): $\delta = 149.0$ (d, $^{2}J_{CP} = 10.1$ Hz, *C*1), 136.2, 133.8, 133.6, 132.7, 132.5, 132.3, 131.1 (*C*4'), 130.6, 130.4, 130.3, 129.2, 129.1, 128.7, 128.6, 128.0, 127.9, 127.8, 127.4 (*C*6'), 127.3 (*C*8), 125.6 (*C*3'), 125.1 (*C*8'), 9.5 (d, $^{1}J_{CP} = 5.5$ Hz, *C*1"), 7.8 (d, $^{1}J_{CP} = 5.5$ Hz, *C*2"), 6.3 (d, $^{1}J_{CP} = 50.5$ Hz, CH_3) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -78.3$ ppm. **^{31}P {^{1}H} NMR** (202 MHz, $CDCl_3$): $\delta = -101.2$ ppm. **IR** (neat): $\tilde{\nu}$ = 3062.0 (w), 3001.7 (w), 2921.4 (w), 1586.9 (w), 1558.1 (w), 1506.0 (w), 1370.0 (w), 1275.8 (m), 1222.7 (s), 1162.8 (s), 1027.2 (m), 969.8 (m), 911.1 (m), 806.8 (m), 782.9 (m), 728.9 (s), 688.8 (w), 634.3 (s) cm^{-1}.
HRMS (ESI^+, MeCN): Calc. for $[M - CF_3SO_3]^+$ $m/z = 327.1297$, found: $m/z = 327.1301$ (+1.2 ppm).



2.4 (*R*)-1-(2'-Methoxy-[1,1'-binaphthalen]-2-yl)-1-methylphosphiranium triflate ((*R*)-**3b**)

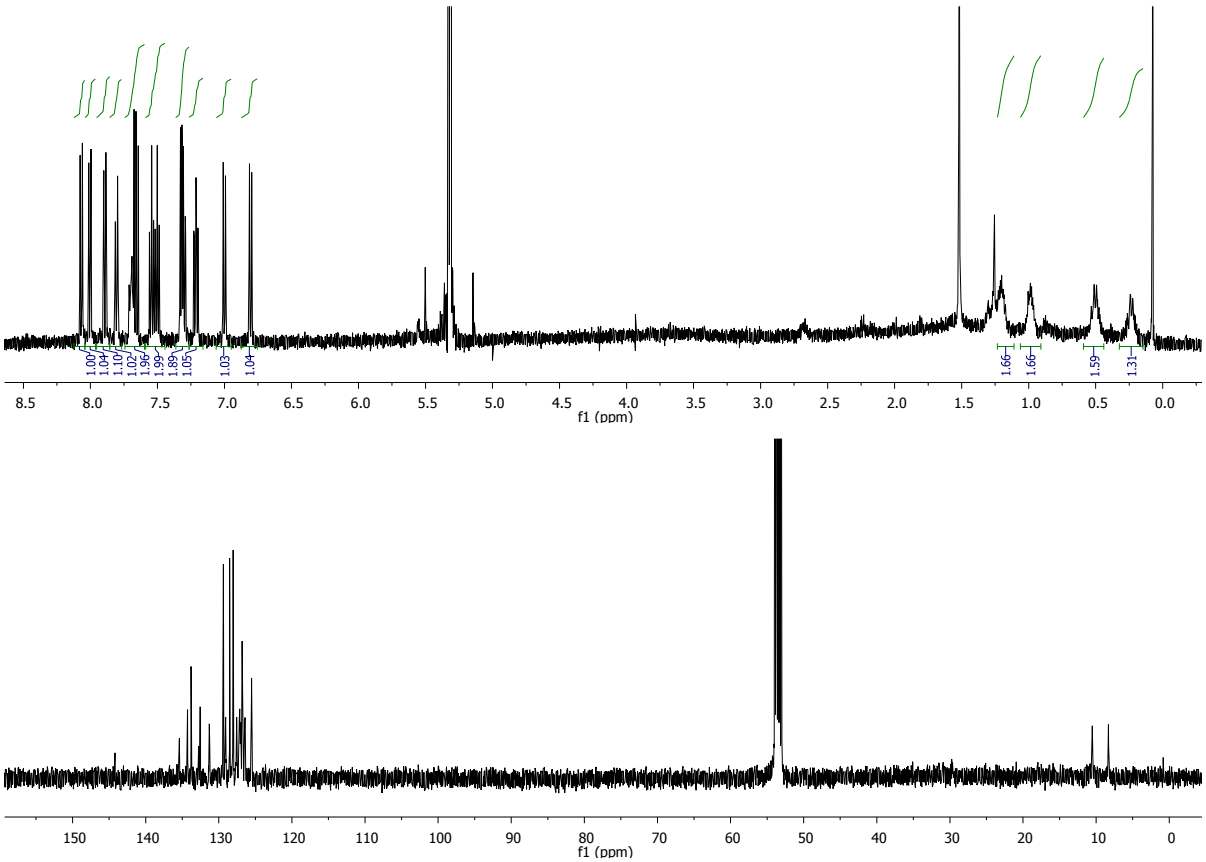
(*R*)-1-(2'-Methoxy-[1,1'-binaphthalen]-2-yl)phosphirane (34.2 mg, 0.10 mmol) was dissolved in dichloromethane (7 mL) and methyl trifluoromethanesulfonate (32.8 mg, 0.02 mL, 0.20 mmol) was added. The reaction mixture was stirred at room temperature for 2 hours. The volatiles were removed *in vacuo* to give the intended product as a colourless solid (quantitative conversion). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.18 (d, $^{3}J_{HH}$ = 9.2 Hz, 1H, *H*4'), 8.15 (dd, $^{3}J_{HH}$ = 8.2 Hz, $^{4}J_{HP}$ = 4.1 Hz, 1H, *H*4), 8.05 (dd, $^{3}J_{HH}$ = 8.7 Hz, $^{3}J_{HP}$ = 13.7 Hz, 1H, *H*3), 8.02 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H, *H*5), 7.94 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H, *H*5'), 7.68 (m, $^{3}J_{HH}$ = 8.2 Hz, 1H, *H*6), 7.52 (d, $^{3}J_{HH}$ = 9.2 Hz, 1H, *H*3'), 7.41 (m, $^{3}J_{HH}$ = 8.2 Hz, 1H, *H*7), 7.39 (m, $^{3}J_{HH}$ = 8.7 Hz, 1H, *H*6'), 7.29 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H, *H*8), 7.28 (m, $^{3}J_{HH}$ = 8.7 Hz, 1H, *H*7'), 6.71 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H, *H*8'), 3.81 (s, 3H, OCH_3), 2.28 (m, 1H, *endo*-*H*1''), 2.16 (m, 1H, *endo*-*H*2''), 2.03 (m, 1H, *exo*-*H*1''), 1.84 (m, 1H, *exo*-*H*2''), 1.63 (d, $^{2}J_{HP}$ = 18.3 Hz, 3H, CH_3) ppm. **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 154.9 (*C*2'), 146.1 (d, $^{2}J_{CP}$ = 10.5 Hz, *C*1), 136.5, 133.2 (*C*4'), 132.5 (d, $^{1}J_{CP}$ = 15.3 Hz, *C*2), 128.0 (d, $^{4}J_{CP}$ = 14.4 Hz, *C*4), 130.2 (*C*6), 128.9, 128.8 (*C*5/*C*5'), 128.5 (*C*7/*C*7'), 128.1 (d, $^{3}J_{CP}$ = 13.4 Hz, *C*3), 126.7 (*C*8), 124.9 (*C*6'), 123.6 (*C*8'), 117.7 (d, $^{3}J_{CP}$ = 6.7 Hz, *C*1'), 113.0 (*C*3'), 56.3 (s, O*C*H_3), 7.6 (d, $^{1}J_{CP}$ = 4.8 Hz, *C*1''), 7.0 (d, $^{1}J_{CP}$ = 4.8 Hz, *C*2''), 5.3 (d, $^{1}J_{CP}$ = 50.8 Hz, *C*H_3) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = –78.3 ppm. **^{31}P {^{1}H} NMR** (202 MHz, $CDCl_3$): δ = –102.0 ppm. **IR** (neat): $\tilde{\nu}$ = 3087.4 (w), 3002.5 (w), 2922.1 (w), 2846.5 (w), 1621.5 (w), 1592.9 (w), 1508.8 (w), 1464.6 (w), 1251.3 (s), 1223.0 (s), 1026.9 (s), 969.2 (w), 906.2 (m), 872.7 (w), 813.1 (m), 775.3 (w), 728.8 (s),

688.2 (w), 634.9 (s), 572.6 (w) cm^{-1}. **HRMS** (ESI^+, MeCN): Calc. for $[M - CF_3SO_3]^+$ m/z = 357.1403, found: m/z = 357.1408 (+1.4 ppm).



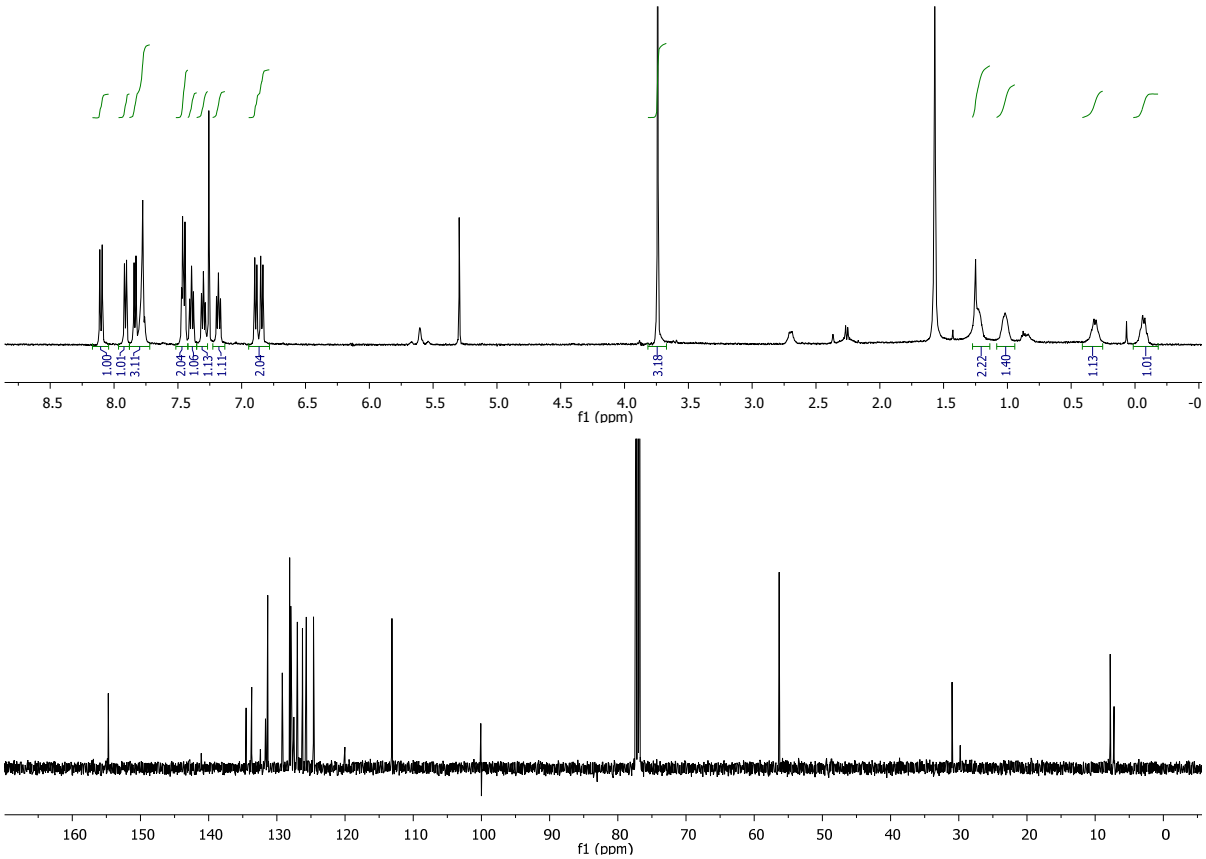
2.5 $[(S)$-**2a**$]_2PtCl_2$ (**4a**)

(*S*)-1-([1,1'-Binaphthalen]-2-yl)phosphirane (31.2 mg, 0.10 mmol) and dichloro(1,5-cyclooctadiene)platinum(II) (19.2 mg, 0.05 mmol) were dissolved in dichloromethane (7 mL) and stirred at room temperature for 2 hours. The volatiles were removed *in vacuo* to give the intended product as a colourless solid (quantitative conversion). Crystals suitable for X-ray analysis were obtained by slow evaporation of dichloromethane at ambient temperature. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ = 8.07 (d, $^3J_{HH}$ = 8.6 Hz, 2H, *H*4'), 8.00 (d, $^3J_{HH}$ = 8.6 Hz, 2H, *H*5), 7.89 (d, $^3J_{HH}$ = 8.6 Hz, 2H, *H*5'), 7.81 (d, $^3J_{HH}$ = 8.6 Hz, 2H, *H*4), 7.69 (m, 2H, *H*3), 7.66 (dd, $^3J_{HH}$ = 7.0 Hz, $^3J_{HH}$ = 8.6 Hz, 2H, *H*3'), 7.54 (m, $^3J_{HH}$ = 8.6 Hz, 2H, *H*6), 7.50 (m, $^3J_{HH}$ = 8.6 Hz, 2H, *H*6'), 7.32 (d, $^3J_{HH}$ = 7.0 Hz, 2H, *H*2'), 7.30 (m, $^3J_{HH}$ = 8.6 Hz, 2H, *H*7), 7.21 (m, $^3J_{HH}$ = 8.6 Hz, 2H, *H*7'), 7.00 (d, $^3J_{HH}$ = 8.6 Hz, 2H, *H*8), 6.80 (d, $^3J_{HH}$ = 8.6 Hz, 2H, *H*8'), 1.21 (m, 2H, *endo-H*), 0.99 (m, 2H, *endo-H*), 0.50 (m, 2H, *exo-H*), 0.23 (m, 2H, *exo-H*) ppm. **^{13}C {^{1}H} NMR** (125 MHz, CD_2Cl_2): δ = 144.2 (*C*1), 135.4, 134.3, 133.8, 132.8, 132.5, 131.3, 129.4, 129.1, 129.1, 128.5, 128.0, 127.6, 127.2, 127.0, 126.8, 126.5, 126.4, 125.5, 10.5 (*C*1"), 8.3 (*C*2") ppm. **^{31}P {^{1}H} NMR** (202 MHz, CD_2Cl_2): δ = –149.2 (s with ^{195}Pt satellites, $^1J_{PPt}$ = 4170 Hz) ppm. **IR** (neat): $\tilde{\nu}$ = 3060.3 (w), 2991.3 (w), 1586.0 (w), 1557.2 (w), 1501.3 (w), 1376.1 (w), 1313.6 (w), 1258.0 (w), 1013.5 (w), 946.7 (w), 913.6 (s), 782.3 (s), 739.2 (s), 707.4 (m), 672.6 (m) cm^{-1}. **HRMS** (ESI^+, MeCN): Calc. for $[M + Na]^+$ m/z = 913.1048, found: m/z = 913.1054 (+0.7 ppm).

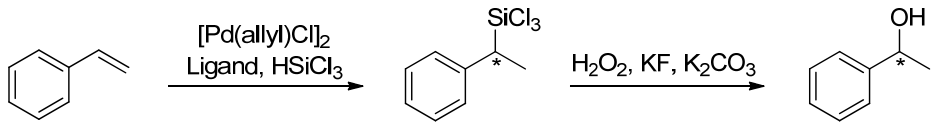


2.6 [(*R*)-**2b**]$_2$PtCl$_2$ (**4b**)

(*R*)-1-(2'-Methoxy-[1,1'-binaphthalen]-2-yl)phosphirane (34.2 mg, 0.10 mmol) and dichloro(1,5-cyclooctadiene)platinum(II) (19.2 mg, 0.05 mmol) were dissolved in dichloromethane (7 mL) and stirred at room temperature for 2 hours. The volatiles were removed *in vacuo* to give the intended product as a colourless solid (quantitative conversion). Crystals suitable for X-ray analysis were obtained by slow evaporation of chloroform at ambient temperature. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.10 (d, $^3J_{HH}$ = 9.2 Hz, 2H, *H*4'), 7.91 (d, $^3J_{HH}$ = 8.3 Hz, 2H, *H*5'), 7.84 (d, $^3J_{HH}$ = 8.3 Hz, 2H, *H*5), 7.78 (m, 4H, *H*3/*H*4), 7.45 (m, 4H, *H*3'/*H*6), 7.39 (t, $^3J_{HH}$ = 8.3 Hz, 2H, *H*6'), 7.30 (t, $^3J_{HH}$ = 8.3 Hz, 2H, *H*7'), 7.18 (t, $^3J_{HH}$ = 8.3 Hz, 2H, *H*7), 6.90 (t, $^3J_{HH}$ = 8.3 Hz, 2H, *H*8'), 6.84 (t, $^3J_{HH}$ = 8.3 Hz, 2H, 2H, *H*8), 3.74 (s, 6H, OCH_3), 1.22 (m, 2H, *endo*-*H*1''), 1.02 (m, 2H, *endo*-*H*2''), 0.32 (m, 2H, *exo*-*H*2''), –0.07 (m, 2H, *exo*-*H*1'') ppm. **^{13}C {^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 154.7 (*C*2'), 141.1 (*C*1), 134.5, 133.7, 132.5, 131.7 (*C*3), 131.3 (*C*4), 129.2, 128.1 (*C*5/*C*5'), 128.0 (*C*7'), 127.9 (*C*6), 127.5 (*C*4), 127.0 (*C*7), 126.3 (*C*8), 125.7 (*C*8'), 124.6 (*C*6'), 120.0 (*C*1'), 113.1 (*C*3'), 56.4 (s, OCH_3), 7.8 (*C*2''), 7.2 (*C*1'') ppm. **^{31}P {^{1}H} NMR** (202 MHz, $CDCl_3$): δ = –149.3 (s with ^{195}Pt satellites, $^1J_{PtP}$ = 4160 Hz) ppm. **IR** (neat): $\tilde{\nu}$ = 3058.4 (w), 2986.2 (w), 2937.1 (w), 1620.7 (w), 1592.3 (w), 1506.8 (m), 1473.8 (w), 1429.7 (w), 1383.6 (w), 1333.1 (w), 1271.5 (s), 1252.8 (s), 1215.8 (w), 1181.3 (w), 1149.6 (w), 1117.8 (w), 1076.9 (m), 1046.5 (m), 1018.8 (w), 951.0 (w), 916.3 (s), 871.4 (w), 808.1 (s), 774.6 (w), 738.3 (s), 708.9 (m), 680.7 (m), 628.8 (m) cm^{-1}. **HRMS** (ESI$^+$, MeCN): Calc. for [M + Na]$^+$ *m*/*z* = 971.1242, found: *m*/*z* = 971.1237 (–0.5 ppm).



3 Palladium-Catalysed Hydrosilylation of Styrene



Allylpalladium(II) chloride dimer (4.6 mg, 0.125 mol%), ligand (0.050 mmol, 0.50 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. 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 organic components were extracted with diethyl ether (3x). The combined organic washings were dried over magnesium sulfate. The crude product was purified by column chromatography (hexane/ethyl acetate, 4:1, R_f = 0.20) on silica media to obtain the desired product. 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.[2]

4 Quantum Chemical Calculations

4.1 General Considerations

All calculations were carried out using the Spartan 10 software.[3] Full geometry optimizations of the studied compounds were performed using density functional theory with a B3LYP/6-31G* basis set. A vibrational analysis was performed at the same level to characterize calculated structures as minima.

4.2 Relative Energy of Rotamers

To elucidate the likelihood of different rotamers, the torsion angle of the heterocycle relative to the binaphthyl backbone was constrained, and stepwise rotated to give the relative energy of the molecules. The conformer in which the heterocycle is pointing over the aromatic backbone is disfavored ($\tau \approx 150°$), being approximately 5.5 kcal/mol higher in energy than the lowest energy conformer. Both derivatives show the presence of three rotamers with relative energies of under 0.7 kcal/mol ($\tau \approx 50°$, 260°, 340°) which can interconvert via an activation barrier smaller than 1.5 kcal/mol.

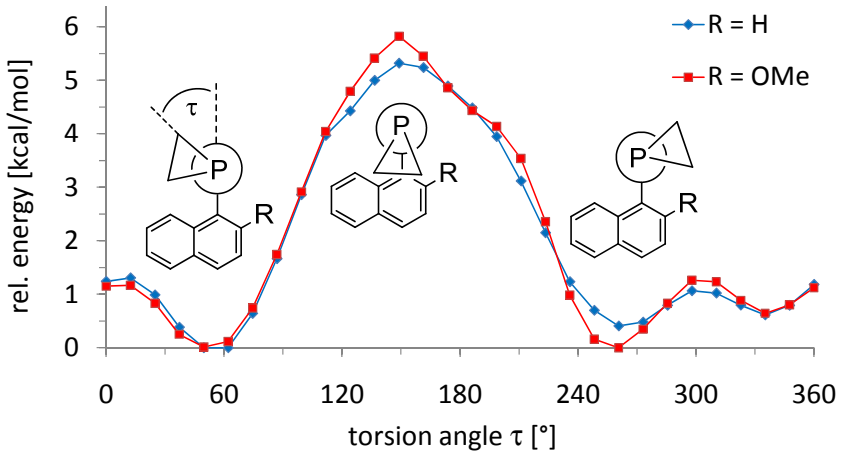
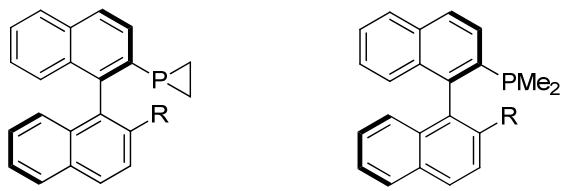


Fig. 3 The effect of changing the phosphirane torsion angle in (*S*)-**2a** and (*R*)-**2b** on the relative optimized energy of the molecules.

4.3 HOMO/LUMO Energy Levels



(*S*)-**2a** R = H
(*R*)-**2b** R = OMe

(*S*)-**5a** R = H
(*R*)-**5b** R = OMe

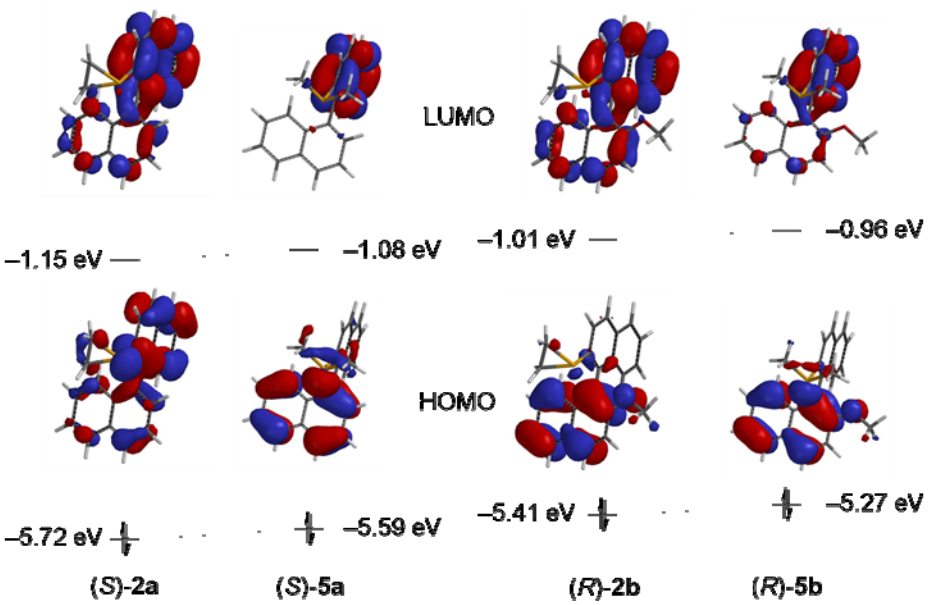
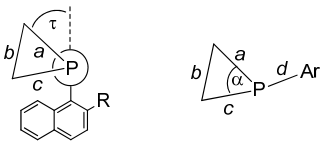


Fig. 4 HOMO and LUMO energies of (*S*)-**2a**, (*S*)-**5a** and (*R*)-**2b**, (*R*)-**5b** calculated at the B3LYP/6-31G* level of theory.

4.4 Selected Bond Lengths and Angles

Table 1 Selected bond lengths and angles for **2a**/**b**[a] and **4**/**b**[b].



	a [Å]	*b* [Å]	*c* [Å]	*d* [Å]	α [°]	τ [°]	Σ(P) [°]
(*S*)-**2a**[a]	1.88	1.50	1.87	1.86	47.1	59	250.0
4a[b]	1.80	1.53	1.80	1.81	50.4	251	268.0
(*R*)-**2b**[a]	1.88	1.50	1.88	1.86	47.0	49	251.4
4b[b]	1.80	1.55	1.81	1.80	50.8	252	267.4

[a] Calculated values of the lowest energy rotamer. [b] Experimental average values for both ligands in their platinum complexes (by X-ray crystallographic analysis).

5 X-ray Diffraction

Measurements were made at 150 K on an Oxford Diffraction Gemini A Ultra diffractometer using graphite-monochromated Mo-Kα radiation (l =0.71073 A˚). Cell parameters were refined from the observed positions of all strong reflections. Intensities were corrected semiempirically for absorption, based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and refined on F^2 values for all unique data. All non-hydrogen atoms were refined anisotropically, and C-bound H atoms were constrained with a riding model; U(H) was set at 1.2 (1.5 for methyl groups) times U_{eq} for the parent C atom.
Programs used were Oxford Diffraction CrysAlisPro[4] and SHELXTL[5] for structure solution and refinement.

Crystal data for ***4a***: $C_{44}H_{34}Cl_2P_2Pt{\cdot}0.75CH_2Cl_2$, M = 954.3, monoclinic, space group $P2_1$, a = 14.8961(3), b = 8.09268(12), c = 16.9803(3) Å, β = 105.640(2)°, V = 1971.17(6) Å^3, Z = 2, T = 150 K, 11728 reflections

collected, 6013 unique, R_{int} = 0.034, $R(F, F^2 > 2\sigma)$ = 0.033, $R_w(F^2$, all data) = 0.084, goodness of fit = 1.03, 469 refined parameters, difference map extremes +2.00 and –0.87 e Å^{-3}, absolute structure parameter = 0.006(7);[6] the site occupancy factor was initially refined for the solvent molecule before being fixed, and implies facile loss of solvent.

Crystal data for ***4b***: $C_{46}H_{38}Cl_2O_2P_2Pt{\cdot}CHCl_3$, M = 1070.1, monoclinic, space group $C2$, a = 19.9049(8), b = 8.3739(2), c = 14.7846(6) Å, β = 122.417(5)°, V = 2080.30(13) Å^3, Z = 2, T = 150 K, 8694 reflections collected, 3631 unique, R_{int} = 0.052, $R(F, F^2 > 2\sigma)$ = 0.034, $R_w(F^2$, all data) = 0.076, goodness of fit = 1.05, 241 refined parameters, difference map extremes +1.62 and –0.81 e Å^{-3}, absolute structure parameter = 0.009(9); disordered chloroform solvent was treated by the SQUEEZE procedure of PLATON.[7]

CCDC-816636 (**4a**) and 816637 (**4b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

6 References

1 R. M. Hiney, L. J. Higham, H. Müller-Bunz and D. G. Gilheany, *Angew. Chem.*, 2006, **118**, 7406; *Angew. Chem. Int. Ed.*, 2006, **45**, 7248.

2 M. Ito, Y. Endo, N. Tejima and T. Ikariya, *Organometallics*, 2010, **29**, 2397.

3 *Spartan 10*; Wavefunction Inc., Irvine, CA, 2011.

4 *CrysAlis^{Pro}*, Agilent Ltd., Abingdon, Oxfordshire, UK, 2008.

5 G. M. Sheldrick, *Acta Crystallogr., Sect. A*: *Found. Crystallogr.*, 2008, **64**, 112.

6 H. D. Flack, *Acta Crystallogr. Sect. A*, 1983, **39**, 876.

7 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.