**A clean and facile method for deprotection of phosphines from borane complexes**

***(electronic supplementary information)***

Oleg M. Demchuk,\*,a Radomir Jasinski,b Dorota Strzelecka,a Kamil Dziuba,a Karolina Kula,b Jacek Chrzanowski,c Dorota Krasowskac

*a Department of Organic Chemistry, Maria Curie-Sklodowska University, 33 Gliniana St., 20614 Lublin, Poland. E-mail address: Oleh.Demchuk@UMCS.Lublin.pl; b Institute of Organic Chemistry and Technology, Cracow University of Technology, Warszawska 24, Cracow 31155, Poland; c Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland.*

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9. **General**

All reagents were purchased from Sigma-Aldrich, Strem, TCI, and Alfa Aesar chemical companies and used without further purification. Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F254 precoated plates (0.25 mm thickness) with a fluorescent indicator. Visualisation of TLC plates was performed by means of UV light and either KMnO4 or I2 stains. NMR spectra were recorded on Bruker Avance 500 MHz spectrometers, and chemical shifts are reported in ppm, and calibrated to residual solvent peaks at 7.27 ppm and 77.00 ppm for 1H and 13C in CDCl3 or internal reference compounds (H3PO4 capillary). The following abbreviations are used in reporting the NMR data: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). Coupling constants (*J*) are in Hz. Spectra are reported as follows: chemical shift (d, ppm), multiplicity, integration, coupling constants (Hz). Products were purified by flash chromatography on silica gel 60 (230-400 mesh) using a BUCHI MPLC chromatograph. MS spectra were recorded on a Shimadzu LCMS ITTOF spectrometer. Commercially unavailable compounds were obtained by known literature procedures.

1. ***General procedure for synthesis of phosphine borane complexes****.*

1.0 M solution of borane in THF (2.0 mL or 4.0 mL for diphosphines) was added to an evacuation-degassed and argon-refilled solution of phosphine (1 mmol) in dry THF (2 mL). The mixture was heated to 40 oC and stirred for 0.5 or 1 h. After that time, the reaction was cooled down to rt and the solvent was removed in vacuum to afford a crude product. The solid products were simply washed with a minimal amount of dry degassed cyclohexane. The liquid and hexane-soluble boranes were purified by flash column chromatography.

1. ***General procedure for deprotection of phosphine borane complexes with trimethylphosphine****.*

The phosphine borane complex (0.5 mmol) and 2 mL of CPME (cyclopenthyl methyl ether) were placed in a Schlenk tube. Then an amount of chromatographic silica gel 60 equal to borane mass was added, and the reactor was evacuated and refilled with argon. The 1.0 M solution of trimethylphosphine in toluene (1.5 mL and 3 mL for diphosphine borane complexes) was added under an argon atmosphere, and the mixture was heated at 100 oC for 12 h. The mixture was cooled down to r. t. After that, the 31P NMR analysis of the reaction mixture indicated the complete conversion of the starting complexes. The solvents were removed by a rotary evaporator. The trace amounts of volatile impurities were removed during an additional 16 h evacuation of the obtained crude products under 5 torr pressure. The resulting products did not need further purification.

1. ***Kinetic measurements****.*

The starting reaction mixtures were prepared in a Schlenk-type reactor charged with a dicyclohexylphenylphosphine borane complex (576 mg, 2 mmol) and 5.5 mL of toluene; the reactor was evacuated and refilled with argon and 2 mL of a 1M solution of trimethylphosphine in toluene was added. 1 mL of the obtained solution was introduced into an argon-filled NMR tube, which contained an internal standard capillary. The tube was next sealed with a teflon screw and placed into oil bath preheated up to the required temperature (80, 95, 110 oC). Progress of the reactions was monitored by means of 31P NMR spectroscopy. The conversion of Cy2PhPBH3 was determined at 1h periods. Since the initial concentrations of the reactants were known, the areas of NMR signals were correlated to the instantaneous concentration (c) of the reactants. Next, on the basis of plots 1/c vs reaction time, second order rate constants were calculated using standard equations. [1] Finally, on the basis of the rate constants measured at different temperatures, the activation enthalpy (ΔH≠) and activation entropy (ΔS≠) were calculated using the Eyring equation in the form:

k = (kB∙T / h) ∙ exp (∆S≠ / R) ∙ exp (- ∆H≠ / R∙T) = (kB∙T / h) ∙ exp (∆G≠ / R∙T)

*where ΔG≠ is the Gibbs energy of activation, kB is Boltzmann's constant, h is Planck's constant, ΔS≠ is the entropy of activation, and ΔH≠ is the enthalpy of activation.*

1. ***Quantumchemical calculations****.*

The calculations reported in this paper were performed both on the “Prometheus” cluster in the CYFRONET regional computational centre in Cracow and on a personal desktop PC (Intel® Core™ I7 – 3930K CPU @ 3.20 GHz, 16GB RAM). Hybrid functional B3LYP with the 6-31+G(d) basis set included in the GAUSSIAN 09[2] package and Spartan 10[3] were used. In particular, optimizations of the stable structures were performed with the Berny algorithm, whereas the transition states were calculated using the QST2 procedure followed by the TS method. Stationary points were characterised by frequency calculations. All reactants and products had positive Hessian matrices. All transition states showed only one negative eigenvalue in their diagonalized Hessian matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration. For all reactions, intrinsic reaction coordinate (IRC) calculations were performed to connect previously computed transition structures (**TS**s) with suitable minima. For the calculations of the solvent effect (GAUSSIAN 09 package) on the reaction paths, the polarizable continuum model (PCM)[4] in which the cavity is created via a series of overlapping spheres was used.

1. **Phosphine borane complexes**

**Dicyclohexylphenylphosphine borane complex (1)**

According to the general procedure. Obtained product was purified by flash chromatography on column with silica gel using hexane : acetone (18 : 1) as eluent to give dicyclohexylphenylphosphine borane complexas a white crystals (208 mg, 75% yield). Mp = 168 - 170 °C. 1H NMR(500.13 MHz, CDCl3): *δ* = 7.71-7.66 (m, 2H, Ar), 7.52-7.42 (m, 3H, Ar), 2.12-1.94 (m, 4H, Cy-H), 1.83-1.59 (m, 8H, Cy-H), 1.35-1.13 (m, 10H, Cy-H), 0.98-0.23 (br, 3H, BH3); 13C NMR(DEPT 135, 125.75 MHz, CDCl3): *δ* = 25.9, 25.9 (CH2), 26.2 (CH2), 26.2 (CH2), 26.5 (CH2), 26.7 (CH2), 26.7 (CH2), 26.8 (CH2), 26.8 (CH2), 26.8 (CH2), 31.1 (CH), 31.3 (CH), 128.4 (CH), 128.4 (CH), 131.0 (CH), 131.0 (CH), 133.4 (CH), 133.4 (CH), 11B NMR(128 MHz, CDCl3) *δ* = −43.5 (br d, 1*J*B-P 61 Hz); 31P NMR(202.45 MHz, CDCl3) *δ* = 26.2 (bs). Data are in accordance with that previously reported.[5]

**Triphenylphosphine borane complex (7)**

According to the general procedure in 3.00 mmol scale. Crude product was washed with cyclohexane (15 mL) to give triphenylphosphine borane complexas a white crystals (760 mg, 92% yield). Mp = 183-184 oC dec. 1H NMR(500.13 MHz, CDCl3): *δ* = 7.61-7.34 (m, 15H, Ar), 1.67-0.88 (m, 3H, BH3); 13C NMR(DEPT 135, 125.75 MHz, CDCl3): *δ* = 128.7 (CH), 128.8 (CH), 131.2 (CH), 131.3 (CH), 133.2 (CH), 133.2 (CH); 11B NMR(128 MHz, CDCl3) *δ* = −37.9 (bd, 1*J*B-P 52 Hz); 31P NMR(202.45 MHz, CDCl3) *δ* = 20.7 (bs). Data are in accordance with that previously reported.[6], [7], [8]

**Tris(*o*-tolyl)phosphine borane complex (9)**

According to the general procedure. The crude product was washed with cyclohexane (15 mL) to give tris(*o*-tolyl)phosphine borane complexin 31% yield. Due to the dissolution of the desired product in cyclohexane the filtrate was evaporated and the obtained residue was purified by flash chromatography on column with silica gel using hexane : acetone (98 : 2) as eluent. The purified product contained 6% of tris(*o*-tolyl)phosphine therefore, additional oxidation of the initial phosphine was required. H2O2 (5 mL, 3%) and NaHCO3 were added into solution of previously purified product dissolved in CH2Cl2 (20 mL). The mixture was left on stirrer for 12 h and then dried over MgSO4. Further purification was done by flash column chromatography using hexane : acetone (98 : 2) as eluent to give tri*o*-tolylphosphine borane complexas a white solid (267 mg, 85% yield). Mp = 153-154 oC dec. 1H NMR(500.13 MHz, CDCl3): *δ* = 7.45-7.42 (m, 3H, Ar-H), 7.36-7.33 (m, 3H, Ar-H), 7.17-7.14 (m, 3H, Ar-H), 7.02-6.98 (m, 3H, Ar-H), 2.43 (s, H, ArCH3), 1.67-0.88 (br, 3H, BH3); 13C NMR(DEPT 135, 125.75 MHz, CDCl3): *δ* = 133.4 (d, *J* = 7.4 Hz, CH), 132.1 (d, *J* = 9.2 Hz, CH), 131.3 (d, *J* = 2.5 Hz, CH), 125.9 (d, *J* = 9.2 Hz, CH), 23.1 (d, *J* = 4.3 Hz, CH); 11B NMR(128 MHz, CDCl3) *δ* = −31.0 (bd, 1*J*B-P 57 Hz); 31P NMR(202.45 MHz, CDCl3) *δ* = 23.0 (bs). Data are in accordance with that previously reported.[9]

**Tris(2-methoxyphenyl)phospine borane complex (6)**

According to the general procedure. The crude product was washed with cyclohexane (15 mL) to give tris(2-methoxyphenyl)phospine borane complexas a white crystals which contained 2% of initial phospine (347 mg, 82% yield). Mp = 206 – 208 o C dec. 1H NMR(500.13 MHz, CDCl3): *δ* = 7.48 -7.42 (m, 6H, Ar-H), 6.98-6.95 (m, 3H, Ar-H), 6.91-6.89 (m, 3H, Ar-H), 3.58 (s, 9H, OCH3), 1.60-0.83 (bs, 3H, BH3); 13C NMR(DEPT 135, 125.75 MHz, CDCl3): *δ* = 135.1 (d, *J* = 8.0 Hz, CH), 132.3 (d, *J* = 1.9 Hz, CH), 120.5 (d, *J* = 10.5 Hz, CH), 111.6 (d, *J* = 4.9 Hz, CH); 11B NMR(128 MHz, CDCl3) *δ* = −35.2 (bd, 1*J*B-P 64 Hz); 31P NMR(202.45 MHz, CDCl3) *δ* = 27.0 (s), 13.6 (bs).

**Tris(2,6-dimethoxyphenyl)phospine borane complex (8)**

According to the typical procedure. The crude product was washed with cyclohexane (15 mL) to give tris(2,6-dimethoxyphenyl)phospine borane complexas a white crystals (368 mg, 80% yield). Mp = 149-152 o C dec. 1H NMR(500.13 MHz, CDCl3): *δ* = 7.25 (t, 3H, *J* = 8.2 Hz, Ar-H), 6.52 (dd, *J1* = 8.2 Hz, *J2* = 3.5 Hz, Ar-H), 3.50 (s, 18H, OCH3), 1.53-0.75 (bs, 3H, BH3); 13C NMR(DEPT 135, 125.75 MHz, CDCl3): *δ* = 130.6 (CH), 130.1 (CH), 130.1 (CH), 56.2 (OCH3); 11B NMR(128 MHz, CDCl3) *δ* = −25.3 (bd, 1*J*B-P 60 Hz); 31P NMR(202.45 MHz, CDCl3) *δ* = 14.5 (bs).

**Tris(2,4,6-trimethoxyphenyl)phospine borane complex (10)**

According to the typical procedure. The crude product was washed with cyclohexane (15 mL) to give tris(2,4,6-trimethoxyphenyl)phospine borane complexas a white crystals (470 mg, 85% yield). Mp = 164 – 166 o C dec. 1H NMR(500.13 MHz, CDCl3): *δ* = 6.08 (d, 6H, *J* = 3.2 Hz, Ar-H), 3.81 (s, 9H, OCH3), 3.52 (s, 18H, OCH3), 1.50-0.92 (bs, 3H, BH3); 13C NMR(DEPT 135, 125.75 MHz, CDCl3): *δ* = 91.8 (CH), 91.8 (CH), 56.2 (OCH3), 55.2 (OCH3); 11B NMR(128 MHz, CDCl3) *δ* = −25.8 (bd, 1*J*B-P 61 Hz); 31P NMR(202.45 MHz, CDCl3) *δ* = 15.4 (bs).

**1,2-Bis(diphenylphosphino)ethane borane complex (16)**

According to the typical procedure. The crude product was washed with cyclohexane (15 mL) to give 1,2-bis(diphenylphosphino)ethaneborane complexas a white crystalline solid (400 mg, 97% yield).

Mp = 166 - 170 oC dec. 1H NMR(500.13 MHz, CDCl3): *δ* = 7.66-7.62 (m, 8H, Ph), 7.55-7.49 (m, 4H, Ph), 7.46-7.43 (m, 8H, Ph), 2.39 (d, *J =* 3.5 Hz, 4H, CH2), 1.45-0.60 (m, 6H, BH3). Data are in accordance with that previously reported.[5], [10], [11]

**1,2-Bis(diphenylphosphino)butane borane complex (15)**

According to the typical procedure. The crude product was washed with cyclohexane (15 mL) to give 1,2-bis(diphenylphosphino)buthane borane complexas a white crystalline solid (359 mg, 81% yield). Mp = 185-190 oC dec. 1H NMR(500.13 MHz, CDCl3): *δ* = 7.65-7.61 (m, 8H, Ar), 7.51-7.47 (m, 4H, Ar), 7.45-7.41 (m, 8H, Ar), 2.20-2.15 (m, 4H, CH2), 1.62-1.58 (m, 4H, CH2), 1.27-0.57 (bs, 6H, BH3); 13C NMR(DEPT 135, 125.75 MHz, CDCl3): *δ* = 132.1 (CH), 132.0 (CH), 131.2 (d, *J* = 2.5 Hz, CH), 128.9 (CH), 128.8 (CH), 25.6 (CH2), 25.3 (CH2), 24.7 (CH2), 24.6 (CH2); 11B NMR(128 MHz, CDCl3) *δ* = −39.9 (bd, 1*J*B-P 52 Hz); 31P NMR(202.45 MHz, CDCl3) *δ* = 15.7 (bs). Data are in accordance with that previously reported.[12]

**(−)-2,3-O-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane borane complex (14)**

According to the typical procedure. The crude product was washed with cyclohexane (15 mL) to give (−)-2,3-O-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane borane complexas a white crystals (205 mg, 39% yield). Mp = 167 – 167 o C dec. [α]D= -7.8 (c 1, CH2Cl2). 1H NMR(500.13 MHz, CDCl3): *δ* = 7.72-7.67 (m, 4H, Ar), 7.65-7.61 (m, 4H, Ar), 7.48-7.38 (m, 12H, Ar), 4.1 (qt, *J =* 7.5, 3.6 Hz, 2H, CH), 2.63-2.54 (m, 2H, CH2), 2.23 (ddd, *J =* 14.8, 10.1, 3.2 Hz, 2H, CH2), 1.13 (s, 6H, CH3), 1.14-1.05 (m, 6H, BH3). 13C NMR(DEPT 135, 125.75 MHz, CDCl3): *δ* = 132.59 (d, *J =* 9.84 Hz), 132.07 (d, *J =* 9.23 Hz), 131.07 (d, *J =* 9.84 Hz), 131.30 (d, *J =* 2.46 Hz), 131.11 (d, *J =* 1.84 Hz), 128.88 (d, *J =* 9.84 Hz), 128.43 (d, *J =* 10.46 Hz), 77.36, 77.29, 77.22 , 29.31 (d, *J =* 37.53 Hz, CH2), 26.77. 11B NMR(128 MHz, CDCl3) *δ* = - 39.5 (bs). 31P NMR(202.45 MHz, CDCl3) *δ* = 14.53 (m).

# 1,1′-Bis(di-*tert*-butylphosphino)ferrocene borane complex (13)

According to general procedure. The crude product was purified by flash chromatography to give 1,1′-bis(di-tert-butylphosphino)ferrocene borane complexas an orange amorphous solid (295 mg, 59% yield). 31P NMR (202.45 MHz, CDCl3): δ = 44.96 (m). 1H NMR(500.13 MHz, CDCl3): *δ* = 4.78-4.77 (m, 4H, Cp), 4.47(q, J = 1.6 Hz, 4H, Cp), 1.30 (d, *J =* 12.6, 36H, *t*Bu), 1.10-0.25 (m, 6H, BH3). 13C NMR (dept-135, 125.75 MHz, CDCl3): δ = 74.46 (d, *J =* 6.8 Hz), 73.91 (d, *J =* 6.2 Hz), 28.67 (d, *J =* 1.2 Hz). 11B NMR(128 MHz, CDCl3) *δ* = - 40.6 (m).

**Trihydrido{(1R,2S,5R)-5-methyl-2-(propan-2-yl)cyclohexyl [(R)-methyl(phenyl)phosphanyl-*κ*P]acetate}boron (11)**

According to the general procedure from corresponding phosphine.[13] The crude product was purification was done by flash column chromatography using hexane : acetone (90 : 10) as eluent to give white semisolid borane complex (90% yield). The data are in accordance with that previously reported.[14]

31P NMR (202.45 MHz, CDCl3): δ = 14.20 ppm. Major diastereomer: 1H NMR (500.13 MHz, CDCl3): δ = 7.89 (ddd, *J* = 14.4, 7.6, 1.7 Hz, 1H), 7.71 – 7.64 (m, 2H), 7.55 – 7.49 (m, 1H), 7.46 – 7.36 (m, 3H), 7.09 – 7.04 (m, 1H), 6.93 – 6.89 (m, 1H), 4.55 (td, *J* = 10.8, 4.4 Hz, 1H), 3.75 (s, 3H), 3.72 – 3.59 (m, 1H), 3.38 (dd, *J* = 13.7, 9.6 Hz, 1H), 1.88 – 1.82 (m, 1H), 1.63 – 1.53 (m, 3H), 1.38 – 1.25 (m, 1H), 1.09 – 1.01 (m, 1H), 0.98 – 0.87 (m, 1H), 0.82 (d, *J* = 6.5 Hz, 3H), 0.76 (d, *J* = 7.1 Hz, 3H), 0.73 – 0.65 (m, 1H), 0.63 (d, *J* = 6.9 Hz, 3H). 13C NMR (125.75 MHz, CDCl3): δ = 166.65 (d, *J* = 2.2 Hz), 161.31 (d, *J* = 1.8 Hz), 136.37 (d, *J* = 15.8 Hz), 134.06 (d, *J* = 2.3 Hz), 131.64 (d, *J* = 9.9 Hz), 130.81 (d, *J* = 2.5 Hz), 129.44 (d, *J* = 58.8 Hz), 128.39 (d, *J* = 10.5 Hz), 121.17 (d, *J* = 13.0 Hz), 115.46 (d, *J* = 54.0 Hz), 111.01 (d, *J* = 4.1 Hz), 75.50 , 55.42 , 46.64 , 40.29 , 34.10 , 32.42 (d, *J* = 32.3 Hz), 31.28 , 25.76 , 23.07 , 21.96 , 20.86, 16.01.

The diastereomeric excess calculated based on 1H NMR signals at 3.38 ppm (major diastereomer), and 3.45 ppm (minor diastereomer) as well as 3.75 ppm (major), and 3.76 (minor) was 48% de.



**{2-[(R)-tert-Butyl(phenyl)phosphanyl-*κ*P]ethanol} (trihydrido)boron *ee*= 99%**

Was obtained according to the literature procedure, the data are in accordance with that previously reported.[15]

The solution of (*R*)-tert-butyl(2-hydroxyethyl)phenylphosphine oxide (0,25g, 1.1 mmol, {[α]D = +35 (CHCl3)} in THF (30 mL) was cooled to 0 °C and treated dropwise with borane tetrahydrofuran complex solution (1M in THF, 6.6 mL, 6 equiv) with continuous stirring, under an argon atmosphere. Once the dropping was complete the reaction mixture was warmed to room temperature and heated at 50 °C for 7 days. The aqueous saturated solution of NaHCO3 was added slowly to the reaction mixture at 0 °C. Diethyl ether (30 mL) was added and the mixture was poured into the separatory funnel. Ether extract was separated, and an inorganic layer was washed with CH2Cl2 (2 x 20 mL). The combined organic layers were dried over MgSO4, filtered and concentrated in vacuo. The purification of the resulting slurry by column chromatography (SiO2, EtOAc: hexane 1:3) gave 0,1872 g (76%) of the product as a white solid. *ee*= 99% HPLC (Chiralcel AS-H, 4.6 x 250 mm, 5 µm, *i*-PrOH/*n*-hexane 5/95, flow: 1 mL/min, k = 254 nm): tR = 28.45 min (major), tR = 44,38 min (minor)). Mp = 74-75 °C (Boetius).[α]D20= +22.14 (0.86; CHCl3).

**{2-[(R)-*tert*-Butyl(phenyl)phosphanyl-*κ*P]ethanol} (trihydrido)boron with *ee*= 75%**

The stirred solution of (*R*)-tert-butyl(2-hydroxyethyl)phenylphosphine oxide (0,2196 g, 0.97 mmol, {[α]D = +35 (CHCl3), *ee* = 99%} in toluene (30 mL) was treated dropwise, under an argon atmosphere, with borane tetrahydrofuran complex solution (1M in THF, 9.7 mL, 10 equiv). Once the dropping was complete the reaction mixture was heated at 100 °C for 5 days. The aqueous saturated solution of NaHCO3 was added slowly to the reaction mixture at 0 °C. Toluene (20 mL) was added and the mixture was poured into the separatory funnel. Organic extract was separated, and an inorganic layer was washed with CH2Cl2 (2 x 20 mL). The combined organic layers were dried over MgSO4, filtered and concentrated in vacuo. The purification of the resulting slurry by column chromatography (SiO2, EtOAc: hexane 1:2, Rf = 0.18) gave 0,1383 g (64%) of the product as a colourless oil). [*ee* = 75% HPLC (Chiralcel AS-H, 4.6x250 mm, 5µm, *i*-PrOH/*n*-hexane 5/95, flow: 1 mL/min, k = 254 nm): tR = 28.45 min (major), tR = 44,38 min (minor), [α]D = +17.43 (1.19; CHCl3).

31P NMR(202.45 MHz, CDCl3) *δ* = 26.53 (m). 1H NMR(500.13 MHz, CDCl3): *δ* = 7.67-7.77 (m, 2H), 7.41-7.53 (m, 3H), 3.77-3.92 (m, 2H), 2.39-2.59 (m, 1H,), 2.24 (brs, 1H, OH), 2.12 – 2.20 (m, 1H), 1.09 (d, J = 14.0 Hz, 9H), 0.74 (m, 3H, BH3).

13C NMR (125.75 MHz, CDCl3) δ 133.26 (d, JP-C = 8.18 Hz), 131.37 (d, JP-C = 1.77 Hz), 128.41 (d, JP-C = 9.20 Hz), 125.65 (d, JP-C = 49.42 Hz), 57.78 (s, CH2OH), 29.03 (d, JP-C = 33.60 Hz), 25.21 (s), 22.34 (d, JP-C = 32.80 Hz).

13C NMR(DEPT 135, 125.75 MHz, CDCl3): *δ* = 133.33 (d, J = 8.1 Hz), 131.62 (d, J = 2.9 Hz), 128.48 (d, J = 9.6 Hz), 57.88 (d, J = 1.4 Hz), 25.28 (d, J = 2.2 Hz), 22.40 (d, J = 32.3 Hz).

**(*R*P)-[tert-Butyl(methyl)phenylphosphine](trihydrido)boron**

Was obtained according to the literature procedures starting from (*tert*-butyl)phenyl phosphine oxide,[16] which was converted to (*tert*-butyl)phenylphosphine-borane, [17] following to (*R*P)-tert-Butylmethylphenylphosphine-borane, [18] the data are in accordance with that previously reported.

Step 1, (*tert*-butyl)phenylphosphine borane. In flame-dried Schlenk tube racemic (*tert-*butyl)phenyl phosphine oxide (0.8152 g, 4.5 mmol) was placed and dissolved in dry toluene (5 mL). Cooled to 0°C and oxalyl chloride (387 µl, 4.5 mmol) was added dropwise under a argon atmosphere. 31P-NMR spectra of the reaction mixture shows full conversion to chlorophosphosphonium salt. Then, sodium borohydride (4.95 mL, 2.2 eq.) (C = 2M in tetraglyme) was added dropwise to the reaction mixture. After 3h, 31P NMR spectra showed full conversion of chlorophosphosphonium salt to (*tert*-butyl)phenylphosphine-borane. Deionised water (5 mL) was added slowly and reaction mixture was transferred to the separatory funnel. Water phase was extracted (3 x 10 mL) with Et2O. The combined organic layers was dried over anhydrous Na2SO4, filtered and solvents were removed in vacuo to give colourless oil. Crude product was purified through column chromatography in gradient (Et2O:Hex 1:5 -> 1:1). After purification pure (*tert*-butyl)phenylphosphine borane was obtained as colourless oil (0.6808 g, 84%). Data are in accordance with that previously reported.[17]

Step 2, (*RP*)-[*tert*-butyl(methyl)phenylphosphine](trihydrido)boron. In flame-dried Schlenk tube, under argon atmosphere, racemic (*tert*-butyl)phenylphosphine-borane (0.2770 g, 1.54 mmol) and (-)-sparteine (0.4688 g, 2.0 mmol) were dissolved in dry Et2O (9 mL). The solution was cooled to -78 °C and stirred for 20 minutes. Then, *n*-BuLi solution (616 µl, 1.54 mmol, 2.5 M in heptane) was added slowly to the reaction mixture. After stirring for 15 minutes in -78 °C, the solution was allowed to warm to room temperature (white precipitate formed). After 1h, the reaction mixture was cooled to -78 °C and iodomethane (125 µl, 2.0 mmol) was dropped. Reaction mixture was stirred for 24 h with slowly warm to room temperature. A solution of 5% H2SO4 (5 mL) was added, the layers were separated and the aqueous layer was extracted with Et2O (3 x 5 mL). The combined organic layers were washed with water (3 mL) and brine (3 mL), dried over anhydrous Na2SO4, filtered and evaporated under reduced pressure. The residue was purified by column chromatography (2% Et2O in hexane) to furnish product in 93% (0.2767 g) yield. Spectroscopic data of (*R*P)-[*tert*-butyl(methyl)phenylphosphane](trihydrido)boron in agreement with literature. The enantiomeric excess (92% ee) was determined by chiral HPLC (Chiralcel AS-H, 4.6 x 250 mm, 5 µm, *i*-PrOH/*n*-hexane 1/99, flow: 0.5 mL/min, k = 254 nm): tR = 22.5 min (major), tR = 28.8 min (minor). Mp = 71-72 oC. [α]D = -13.9 (c 0.3, CHCl3). 1H NMR(500.13 MHz, CDCl3): *δ* = 7.74-7.69 (m, 2H), 7.53-7.44 (m, 3H), 1.58 (d, *J* = 9.5 Hz, 3H), 1.11 (d, *J* = 13.9 Hz, 9H), 1.00-0.44 (m, 3H, BH3). 31P NMR(202.45 MHz, CDCl3) *δ* = 25.43-24.55 (m). 13C NMR(DEPT 135, 125.75 MHz, CDCl3): *δ* = 132.90 (d, *J =* 7.38), 131.10 (d, *J =* 2.50), 128.29 (d, *J =* 9.23), 25.17 (d, *J =* 3.10), 5.25 (d, *J =* 37.50). 11B NMR(128 MHz, CDCl3) *δ* = - 40.47 (m).

**Dicyclohexyl[4-methoxy-3-(2,4,6-trimethoxyphenyl)-naphthalen-2-yl]phosphine borane**

According to general procedure from corresponding phosphine.[19] The crude product was washed with cyclohexane (15 mL) to give ***Sym*-PhosBH3** as a white powder (500 mg, 94% yield). Mp = 209.7-212.5 o C dec. 31P NMR(202.45 MHz, CDCl3) *δ* = 34.16 (bs). 1H NMR(500.13 MHz, CDCl3): *δ* = 8.35 (d, *J =* 13.56 Hz, 1H), 8.10 (bd, *J =* 8.20 Hz, 1H), 7.98 (bd, *J =* 8.83 Hz, 1H), 7.60-7.53 (m, 2H), 6.26 (s, 2H), 3.93 (s, 3H), 3.68 (s, 6H), 3.62 (s, 3H), 1.95-1.85 (m, 2H), 1.75-1.72 (m, 4H), 1.66-1.55 (m, 4H), 1.54-1.45 (m, 4H), 1.38-1.29 (m, 2H), 1.20-1.04 (m, 6H), 0.89-0.14 (m, 3H, BH3). 13C NMR(DEPT 135, 125.75 MHz, CDCl3): *δ* = 133.78 (d, *J =* 11.70 Hz), 128.97, 127.39, 126.41, 122.54, 90.39, 61.26, 55.50, 55.43, 33.53 (d, *J =* 33.22 Hz), 28.14 (CH2), 27.51 (CH2), 27.19 (CH2), 27.09 (CH2), 27.05 (CH2), 26.96 (CH2), 25.90(CH2). 11B NMR(128 MHz, CDCl3) *δ* = - 41.98 (bs).

1. **Deprotection of phosphine borane complexes with trimethylphosphine**

**Dicyclohexylphenylphosphine (3)**

According to general procedure. Yield = 117.8 mg (86%). 31P NMR (202.45 MHz, CDCl3): δ = 3.15 ppm. 13C NMR (125.75 MHz, CDCl3): δ = 134.79 (CH), 134.63 (CH), 127.83 (CH), 127.77 (CH), 32.45 (CH), 32.36 (CH), 30.05 (CH2), 29.92 (CH2), 28.78 (CH2), 28.73 (CH2), 27.27 (CH2), 27.18 (CH2), 27.02 (CH2), 26.96 (CH2), 26.40 (CH2) ppm. Product is consistent with commercially available samples (H26992, Alfa Aesar).

**Triphenylphosphine (18)**

According to general procedure. Yield = 102.0 mg (96%). 1H NMR (500.13 MHz, CDCl3): δ = 7.31 (m, 15H, CH) ppm; 13C NMR (DEPT 135*,* 125.75 MHz, CDCl3): δ = 133.82 (CH), 133.67 (CH), 128.72 (CH), 128.53 (CH), 128.47 (CH) ppm; 31P NMR (202.45 MHz, CDCl3): δ = -5.41 ppm. Product is consistent with commercially available samples (**T84409, Sigma-Aldrich** ).

**Tris(*o*-tolyl)phosphine (20)**

According to general procedure. Yield = 136.3 mg (96%). 1H NMR (500.13 MHz, CDCl3): δ = 2.40 (s, 9H, CH3), 6.73 (ddd, *J* = 7.57, 4.14, 1.26 Hz, 3H, CH), 7.10 (dt, *J* = 7.57, 1.58 Hz, 3H, CH), 7.23-7.29 (m, 6H, CH) ppm; 13C NMR (DEPT 135*,* 125.75 MHz, CDCl3): δ = 21.12 (CH3), 21.29 (CH3), 126.15 (CH), 128.67 (CH), 130.04 (CH), 133.05 (CH) ppm; 31P NMR (202.45 MHz, CDCl3): δ = -29.62 ppm. Product is consistent with commercially available samples (**287822, Aldrich** ).

**Tris(o-methoxyphenyl)phospine (17)**

According to general procedure. Yield = 170.7 mg (99%). 1H NMR (500.13 MHz, CDCl3): δ = 7.37 -7.33 (m, 3H, CH), 6.92 (ddd, *J* = 8.20, 4.73, 0.95 Hz; 3H, CH), 6.86 (dt, *J* = 7.57, 0.63 Hz, 3H, CH), 6.74-6.71 (m, 3H, CH), 3.58 (s, 9H, OCH3) ppm; 13C NMR (125.75 MHz, CDCl3): δ = 161.64 (CH), 161.51 (CH), 133.83 (CH), 129.93 (CH), 124.76 (CH), 124.65 (CH), 120.87 (CH)110.21 (CH), 55.73 (CH3) ppm; 31P NMR (202.45 MHz, CDCl3): δ = -39.70 ppm. Product is consistent with commercially available samples (**710563, Aldrich** ).

**Tris(2,6-dimethoxyphenyl)phospine (19)**

According to general procedure. Yield = 205.5 mg (96%). 1H NMR (500.13 MHz, CDCl3): δ = 7.15 (t, *J* = 8.20 Hz, 3H, CH), 6.46 (dd, *J* = 8.20, 3.15 Hz, 6H, CH); 3.49 (s, 18H, CH3) ppm; 13C NMR (125.75 MHz, CDCl3): δ = 162.39 (CH), 162.32 (CH), 128.378 (CH), 104.30 (CH), 55.97 (CH3) ppm; 31P NMR (202.45 MHz, CDCl3): δ = -67.16 ppm. Product is consistent with commercially available samples (**393436, Aldrich** ).

**Tris(2,4,6-trimethoxyphenyl)phospine (21)**

According to general procedure. Yield = 256.8 mg (91%). 1H NMR (500.13 MHz, CDCl3): δ = 6.01 (s, 1H, CH), 6.01 (s, 1H, CH), 3.75 (s, 3H, OCH3), 3.47 (s, 6H, OCH3) ppm; 13C NMR (DEPT 135*,* 125.75 MHz, CDCl3): δ = 91.15 (CH), 56.02 (CH3), 55.06 (CH3) ppm; 31P NMR (202.45 MHz, CDCl3): δ = -66.18 ppm. Product is consistent with commercially available samples (**392081, Aldrich** ).

**Ethane-1,2-diylbis(diphenylphosphine) (22)**

According to general procedure. Yield = 184.7 mg (93%). 1H NMR (500.13 MHz, CDCl3): δ = 7.37-7.32 (m, 20H, CH), 2.11 (t, *J* = 4.10 Hz, 4H, CH2) ppm; 13C NMR (DEPT 135*,* 125.75 MHz, CDCl3): δ = 132.78 (CH), 132.70 (CH), 132.64 (CH), 128.63 (CH), 128.42 (CH), 23.86 (CH), 23.83 (CH) ppm; 31P NMR (202.45 MHz, CDCl3): δ = -12.61 ppm. Product is consistent with commercially available samples (**376728, Aldrich** ).

**Butane-1,4-diylbis(diphenylphosphine) (24)**

According to general procedure. Yield = 211.9 mg (98%). 1H NMR (500.13 MHz, CDCl3): δ = 7.44-7.34 (m, 20H, CH), 2.06 (t, *J* = 7.57 Hz, 4H, CH2), 1.61-1.58 (m, 4H, CH2); 13C NMR (125.75 MHz, CDCl3): δ = 132.81 (CH), 132.66 (CH), 125.88 (CH), 128.45 (CH), 128.39 (CH) ppm; 31P NMR (202.45 MHz, CDCl3): δ = -16.02 ppm. Product is consistent with commercially available samples (**261947, Aldrich**).

**(−)-(*R*,*R*)-2,3-*O*-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (29)**

According to general procedure. Yield = 99%, 99% de. 1H NMR (500.13 MHz, CDCl3): δ = 7.51-7.44 (m, 8H, CH), 7.37-7.34 (m, 12H, CH), 4.01-3.95 (m, 2H, CH), 2.50 (d, *J* = 4.10 Hz, 1H, CH2), 2.47 (d, *J* = 3.78 Hz, 1H, CH2), 2.41 (d, *J* = 5.67 Hz, 1H, CH2), 2.38 (d, *J* = 5.67 Hz, 1H, CH), 1.41 (s, 6H, CH); 13C NMR (125.75 MHz, CDCl3): δ = 138.66 (CH), 138.56 (CH), 138.37 (CH), 138.27 (CH), 133.14 (CH),132.99 (CH),132.79 (CH),132.63 (CH),128.84 (CH), 128.61 (CH), 128.56 (CH), 128.50 (CH), 128.48 (CH), 128.43 (CH), 108.85 (CH), 79.72 (CH), 79.66 (CH), 79.61 (CH), 79.55 (CH), 32.38 (d, *J* = 2.72 Hz, CH), 32.26 (d, *J* = 2.73 Hz, CH), 27.31 (CH2), 13.11 (CH3), 12.81 (CH3) ppm; 31P NMR (202.45 MHz, CDCl3): δ = -23.35 ppm. Product is consistent with commercially available samples (**237655, Aldrich** ).

**1,1′-Bis(di-*tert*-butylphosphino)ferrocene (23)**

According to general procedure. Yield = 86%. 1H NMR (500.13 MHz, CDCl3): δ = 4.76-4.75 (m, 4H, CH), 4.51-4.50 (m, 4H, CH), 1.30 (s, 18H, CH3), 1.27 (s, 18H, CH3) ppm; 13C NMR (DEPT 135*,* 125.75 MHz, CDCl3): δ = 77.24 (CH), 73.68 (CH), 73.58 (CH), 71.74 (CH), 30.89 (CH), 30.78 (CH), 27.44 (CH) ppm; 31P NMR (202.45 MHz, CDCl3): δ = 27.35 ppm. Product is consistent with commercially available samples (**695149, Aldrich** ).

***(R)-tert*-Butylphenylmethylphosphine (27)**

According to general procedure. To prevent the thermal racemisation the deprotection was performed at 60 oC for 72 h. Yield = 97%, 92% *ee*. The *ee* of the product was determined after the conversion to a corresponding phosphine oxide. A 5 mg sample of phosphine oxide and 50 mg of Naproxene were dissolved in 0.6 mL of CDCl3 next 1H and 31P NMR spectra were recorded.[20] The signals corresponded to Me-P group were integrated. For comparison the H and 31P NMR spectra of racemic tert-butylphenylmethylphosphine oxide in presence of Naproxene were recorded.[20]

1H NMR(500.13 MHz, C6D6): *δ* = 7.66-7-63 (m, 2H), 7.12-7.09 (m, 3H), 7.66-7-63 (m, 2H), 1.25 (d, *J* = 12 Hz, 3H), 0.93 (d, *J* = 14.5 Hz, 9H). 31P NMR(202.45 MHz, C6D6) *δ* = 47.5. For comparison, the racemic phosphine was analysed in a similar way. The measurement of optical rotation power proved that the studied reductions processes run with retention of configuration at phosphorus atom.[21] Data are in accordance with that previously reported.[22], [23], [24]

**(1*R*,2*S*,5*R*)-5-Methyl-2-(propan-2-yl)cyclohexyl [(*R*)-methyl(phenyl) phosphanyl]acetate (28)**

According to general procedure. To prevent the thermal racemisation the deprotection was performed at 60 oC for 16 h. Yield 97%, 46% de.  31P NMR (202.45 MHz, C6D6): δ = -23.30 (minor diastereomer), -23.37 (major diastereomer). 1H NMR (500.13 MHz, C6D6): δ = 7.61 – 7.52 (m, 2H), 7.29 (ddd, *J* = 7.5, 5.9, 1.7 Hz, 1H), 7.13 – 7.03 (m, 4H), 6.80 – 6.72 (m, 1H), 6.42 (ddd, *J* = 8.3, 3.8, 1.1 Hz, 1H), 4.81 – 4.73 (m, 1H), 3.37 (dd, *J* = 13.5, 0.9 Hz, 1H), 3.18 (s, 3H), 3.10 (d, *J* = 13.5 Hz, 1H), 1.96 – 1.81 (m, 2H), 1.45 – 1.35 (m, 2H), 1.30 – 1.22 (m, 1H), 1.14 – 1.05 (m, 1H), 0.85 – 0.76 (m, 4H), 0.72 – 0.68 (m, 6H), 0.66 – 0.55 (m, 1H). 13C NMR (125.75 MHz, C6D6): δ = 169.69 (d, *J* = 8.6 Hz), 161.07 (d, *J* = 12.0 Hz), 137.54 (d, *J* = 15.8 Hz), 133.18 (d, *J* = 21.2 Hz), 132.95 (d, *J* = 9.6 Hz), 130.21 , 128.64 , 128.22 (d, *J* = 4.7 Hz), 126.30 (d, *J* = 19.5 Hz), 120.79 , 110.29 , 73.89 , 54.73 , 46.91 , 40.76 , 34.10 , 33.78 (d, *J* = 21.8 Hz), 31.08 , 25.82 , 23.09 , 21.81 , 20.74 , 15.95 .

The diastereomeric excess calculated based on 1H NMR signals at 3.10 ppm (major diastereomer), and 3.11 ppm (minor diastereomer) as well as 7.29 (major), and 7.21 (minor) was 46% de. The absolute configuration was assigned after the conversion of phosphine to borane and comparison 1H, 13P NMR spectra.

**(*R*)**-**2-[*tert*-Butyl(phenyl)phosphanyl]ethanol (26)**

According to general procedure. Yield 95%, 71% ee.

31P NMR(202.45 MHz, C6D6) *δ* = -6.05. 1H NMR(500.13 MHz, C6D6): *δ* = 7.51 – 7.45 (m, 2H), 7.15 – 7.10 (m, 3H), 3.81 – 3.74 (m, 1H), 3.70 – 3.63 (m, 1H), 2.30 – 2.24 (m, 1H), 1.96 – 1.90 (m, 1H), 0.92 (d, *J* = 12.0 Hz, 9H). 13C NMR(DEPT 135, 125.75 MHz, C6D6): *δ* = 134.88 (d, *J* = 20.0), 129.52 (s), 128.54 (d, *J* = 6.8), 61.07 (d, *J* = 27.69, CH2~~2~~), 27.88 1(d, *J* = 14.2), 25.94 (d, *J* = 17.2, CH2).

The *ee* of the product was determined by HPLC-MS (Phenomenex Kinetex Core-Shell Biphenyl HPLC/UHPLC columns 2.1x150 mm, 5µm,, CH3CN/H2O 40/60, flow: 0.3 mL/min, k = 254 nm): tR = 7.9 min (major), tR = 12.6 min (minor), after the conversion to a corresponding diasteriomeric complexes [13],[25] in reaction with bis(acetonitrile) [(*S*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*]palladium(II) chloride.[26] For comparison, the racemic phosphine was analysed in a similar way.

**Dicyclohexyl[4-methoxy-3-(2,4,6-trimethoxyphenyl)-naphthalen-2-yl]phosphane (25)**

According to general procedure. Yield = 505 mg (97%). Mp = 186 - 188 °C. 31P NMR(202.45 MHz, CDCl3) *δ* = -8.87. 1H NMR(500.13 MHz, CDCl3): *δ* = 8.18-8.16 (m, 1H), 7.93-7.91 (m, 1H), 7.84 (bs, 1H), 7.53-7.49 (m, 2H), 6.24 (s, 2H), 3.90 (s, 3H), 3.68 (s, 3H), 3.62 (s, 3H), 1.89-1.84 (m, 2H), 1.74-1.64 (m, 10H), 1.32-1.07 (m, 10H). Data are in accordance with that previously reported.[19]

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