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Supporting Information for:

Highly Enantiomerically Enriched Chlorophosphine Boranes: Synthesis and Applications as P-Chirogenic Electrophilic blocks

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Preparation of aminophosphine boranes 11a-h.

Preparation of aryllithium reagents by metal-halide exchange: In a two necked-flask equipped with a magnetic stirrer, 1 equiv of *sec*-butyllithium is added. The mixture is allowed to cool to 0°C and 1 equiv of 1-bromoanisole (1-bromonaphthalene or bromobenzene) is slowly added with a syringe while stirring. After formation of a white precipitate, the mixture is stirred for 1 h at 0°C. The organolithium reagent is dissolved with a minimum of dry THF before use.

In the case of the solid 2-bromonaphthalene, 1 equiv of aryl halide is introduced in a flask, and 1 equiv of *sec*-butyllithium is slowly added with a syringe while stirring at 0°C. The rest of the procedure is similar to that described above.

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Preparation of the cyclohexyllithium reagent from cyclohexyl chloride: In a three necked flask, equipped with a condenser and an addition funnel, under a dry atmosphere, 50 mL of petroleum ether (40-60°C) and metallic lithium (cut in small portions) (1.74 g, 5 equiv) were added. A solution of cyclohexyl chloride (5.9 mL, 1 equiv) in 10 mL of petroleum ether were added dropwise over a 4 h period under a vigorous stirring. The reaction was started by warming with a hot water bath. At the end of the addition, the reflux was continued for one more hour. The mixture reaction changed to a violet color. After filtration through a bed of Celite, the collected yellow solution was used without further purification and was titrated using classical techniques.

General procedure. In a 100 mL three-necked flask, equipped with a magnetic stirrer and an argon inlet, 15 mmol of the oxazaphospholidine borane complex **10** were dissolved in 15 mL of anhydrous THF. The mixture was cooled at -78°C and 2 equiv (30 mmol) of the organolithium reagent previously prepared were slowly added. The resulting mixture was stirred and warmed to 0°C until the starting material had completely reacted. The reaction was monitored by TLC over silica (toluene as eluent), and was finally hydrolyzed at 0°C with 5 mL of water. The THF was removed under reduced pressure and the aqueous layer was extracted several times with dichloromethane. The combined organic phases were dried over magnesium sulfate and the solvent was removed. The residue was purified on a short column of silica gel, using a mixture of toluene/AcOEt 95:5 as eluent, to afford the aminophosphine boranes **11** in excellent yields of up to 95%. The aminophosphine boranes can be recrystallized using a mixture hexane/isopropanol 7:3.

(*S_p*)-(+) -N-Methyl-N-[(1*S*,2*R*)(1-hydroxy-1-phenyl-prop-2-yl)]aminomethyl phenylphosphine borane **11a.**^{18a,20} Yield= 95%; White crystals: mp= 67°C (*i*PrOH/Hexane 1:1); R_f = 0.45 (toluene/AcOEt 9:1); $[\alpha]_{\text{D}}^{25}$ = $+12.8$ (c 1.0, CH_2Cl_2); IR (KBr, ν cm^{-1}): 3354, 3057-2873, 2376, 1437, 1136, 1116, 1066, 1049, 906;

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^1H NMR (CDCl_3): $\delta(\text{ppm})$ 0.00-1.60 (3H, br), 1.22 (3H, d, $^3J_{\text{H-H}} = 6.7$), 1.50 (3H, d, $^2J_{\text{P-H}} = 9.0$), 2.15 (1H, br), 2.45 (3H, d, $^3J_{\text{P-H}} = 8.6$), 4.00 (1H, m), 4.70 (1H, d, $^3J_{\text{H-H}} = 6.3$), 7.04-7.11 (3H, m), 7.21-7.42 (7H, m); ^{13}C NMR (CDCl_3): $\delta(\text{ppm})$ 11.2 (d, $^1J_{\text{P-C}} = 41.7$), 13.8, 28.9, 59.0 (d, $^2J_{\text{P-C}} = 7.6$), 77.6 (d, $^3J_{\text{P-C}} = 5.9$), 126.7, 128.1 (d, $J_{\text{P-C}} = 27.7$), 128.4, 128.5, 130.2 (d, $J_{\text{P-C}} = 10.0$), 130.5 (d, $J_{\text{P-C}} = 2.3$), 132.8 (d, $J_{\text{P-C}} = 65.4$), 142.6; ^{31}P NMR (CDCl_3): $\delta(\text{ppm})$ +66.5 (q, $^1J_{\text{P-B}} = 83$); MS (EI, 70 eV): m/z 272 ($\text{M}^+ - \text{BH}_3 - \text{CH}_3$; 1), 180 (100), 132 (21), 155 (54), 123 (54); Anal. calcd for $\text{C}_{17}\text{H}_{25}\text{BNO}_2\text{P}$ (301.1713): C 67.80, H 8.37, N 4.65; Found: C 67.75, H 8.56, N 4.64

(Rp)-(-)-N-Methyl[(1R,2S)(2-hydroxy-1-phenyl)ethyl]amino-o-anisylphenyl phosphine borane 11b.²⁰ Yield= 95%; White crystals (*i*PrOH/Hexane); mp= 111-112°C; $R_f = 0.45$ (toluene/AcOEt 9:1); $[\alpha]_{\text{D}}^{25} = -38.3$ (c 1.0, CH_2Cl_2); IR (KBr, $\nu \text{ cm}^{-1}$): 3500, 2950-2900, 2381, 1589, 1574, 1477, 1462, 1431, 1276, 1251, 1044; ^1H NMR (CDCl_3): $\delta(\text{ppm})$ 0.20-2.00 (3H, sl), 1.20 (3H, d, $^3J_{\text{H-H}} = 7.8$), 2.09 (1H, sl), 2.52 (3H, d, $^3J_{\text{P-H}} = 8.1$), 3.53 (3H, s), 4.31 (1H, m), 4.85 (1H, d, $^3J_{\text{H-H}} = 5.6$), 6.86-6.91 (1H, m), 6.96-7.02 (1H, m), 7.02-7.15 (1H, m), 7.15-7.36 (7H, m), 7.36-7.45 (3H, m), 7.45-7.60 (1H, m); ^{13}C NMR (CDCl_3): $\delta(\text{ppm})$ 12.5 (d, $J_{\text{P-C}} = 2.1$), 30.9 (d, $J_{\text{P-C}} = 3.8$), 55.0, 58.1 (d, $^2J_{\text{P-C}} = 10.4$), 78.8 (d, $^3J_{\text{P-C}} = 5.0$), 111.5 (d, $J_{\text{P-C}} = 4.7$), 118.5 (d, $J_{\text{P-C}} = 56.9$), 120.8 (d, $J_{\text{P-C}} = 10.5$), 126.5, 127.7 (d, $J_{\text{P-C}} = 16.9$), 128.0, 128.3, 129.9 (d, $J_{\text{P-C}} = 2.3$), 130.8 (d, $J_{\text{P-C}} = 10.4$), 132.2 (d, $J_{\text{P-C}} = 71.3$), 133.2 (d, $J_{\text{P-C}} = 1.6$), 134.9 (d, $J_{\text{P-C}} = 10.8$), 142.5, 161.0 (d, $J_{\text{P-C}} = 2.5$); ^{31}P NMR (CDCl_3): $\delta(\text{ppm})$ +69.5 (br); MS (EI, 70 eV): m/z 286 ($\text{M}^+ - o\text{An}$; 13), 272 ($\text{M}^+ - o\text{An} - \text{BH}_3$; 53), 232 (37), 216 (65), 146 (50), 91 (93), 58 (100); Anal. calcd for $\text{C}_{23}\text{H}_{29}\text{BNO}_2\text{P}$ (393.2667): C 70.24, H 7.43, N 3.56; Found: C 70.12, H 7.15, N 3.50.

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(Rp)-(-)-N-Methyl[(1R,2S)(2-hydroxy-1-phenyl)ethyl]aminophenyl-*o*-tolyl phosphine borane 11c. Yield= 92%; White crystals (*i*PrOH/Hexane); R_f = 0.40 (toluene/AcOEt 9:1); mp= 105°C; $[\alpha]_D^{25}$ = -76.0 (c 2.0, CH₂Cl₂); IR (KBr, ν cm⁻¹): 3613, 2979, 2403, 1588, 1455, 1434; ¹H NMR (CDCl₃): δ (ppm) 0.20-2.00 (3H, br), 1.17 (3H, d, ³*J*_{H-H}= 6.9), 2.24 (3H, s), 2.64 (3H, d, ³*J*_{P-H}= 8.0), 4.38 (1H, m), 4.96 (1H, d, ³*J*_{H-H}= 4.0), 7.10-7.45 (11H, m), 7.49-7.65 (3H, m); ¹³C NMR (CDCl₃): δ (ppm) 11.4 (d, *J*_{P-C}= 4.6), 22.0 (d, *J*_{P-C}= 3.7), 31.3 (d, *J*_{P-C}= 3.6), 58.0 (d, ²*J*_{P-C}= 10.3), 79.0 (d, ³*J*_{P-C}= 2.0), 125.6 (d, *J*_{P-C}= 9.5), 125.9, 127.4, 128.3, 128.4 (d, *J*_{P-C}= 10.0), 128.7 (d, *J*_{P-C}= 64.1), 130.8 (d, *J*_{P-C}= 2.1), 130.9 (d, *J*_{P-C}= 2.3), 131.9 (d, *J*_{P-C}= 9.9), 132.1 (d, *J*_{P-C}= 60.9), 132.2 (d, *J*_{P-C}= 9.2), 132.7 (d, *J*_{P-C}= 8.1), 142.2 (d, *J*_{P-C}= 12.2), 142.5; ³¹P NMR (CDCl₃): δ (ppm) +71.5 (br); MS (EI, 70 eV): *m/z* 376 (M⁺-H; 20), 270 (10); 256 (60), 216 (15), 199 (60), 148 (35), 91 (27), 58 (100); Anal. calcd for C₂₃H₂₉BNOP (377.2673): C 73.22, H 7.75; Found: C 73.10, H 7.73.

(Rp)-(-)-N-Methyl[(1R,2S)(2-hydroxy-1-phenyl)ethyl]-amino-1-naphthylphenyl phosphine borane 11d.³¹ Yield= 87%; White crystals (*i*PrOH/Hexane); R_f = 0.55 (toluene/AcOEt 9:1); mp= 112-113°C; $[\alpha]_D^{25}$ = -84.5 (c 1.1, CH₂Cl₂); IR (KBr, ν cm⁻¹): 3415, 3055-2975, 2387-2348, 1638, 1618, 1450, 1435, 1105, 1068, 1024; ¹H NMR (CDCl₃): δ (ppm) 0.50-2.70 (3H, br), 1.28 (3H, d, ³*J*_{H-H}= 6.9), 1.83 (1H, d, *J* = 4.0), 2.61 (3H, d, ³*J*_{P-H}= 7.4), 4.47 (1H, m), 4.98 (1H, d, ³*J*_{H-H}= 5.6), 7.00-7.75 (14H, m), 7.86 (1H, d, *J*_{H-H}= 8.1), 7.95 (1H, d, *J*_{H-H}= 7.9), 8.23 (1H, d, *J*_{H-H}= 8.4); ¹³C NMR (CDCl₃): δ (ppm) 11.6 (d, ³*J*_{P-C}= 4.3), 31.4 (d, ²*J*_{P-C}= 3.4), 58.1 (d, ²*J*_{P-C}= 10.5), 79.1 (d, ³*J*_{P-C}= 2.0), 124.6 (d, *J*_{P-C}= 10.6), 126.0-126.5, 127.1-129.0, 130.9, 131.8-132.3, 132.2 (d, *J*_{P-C}= 10.2), 132.7 (d, *J*_{P-C}= 7.6), 133.3 (d, *J*_{P-C}= 11.4), 134.0 (d, *J*_{P-C}= 7.9), 142.5; ³¹P NMR (CDCl₃): δ (ppm) +72.1 (br).

(Rp)-(-)-N-Methyl[(1R,2S)(2-hydroxy-1-phenyl)ethyl]amino-2-naphthylphenyl phosphine borane 11e.^{20a,31} Yield= 89%; White crystals (*i*PrOH/Hexane); R_f = 0.55 (toluene/AcOEt 9:1); mp= 136°C; $[\alpha]_D^{25}$ = -64.7 (c 1.1, CH₂Cl₂). IR (KBr, ν cm⁻¹): 3523, 3052-2955, 2374, 1455, 1436, 1108, 1062, 1022; ¹H NMR (CDCl₃): δ (ppm) 0.00-2.00 (3H, br), 1.27 (3H, d, ³ J_{H-H} = 6.9), 1.85 (1H, br), 2.52 (3H, d, ³ J_{P-H} = 7.8), 4.35 (1H, m), 4.84 (1H, d, ³ J_{H-H} = 5.6), 7.10-7.65 (13H, m), 7.80-7.90 (3H, m), 8.10 (1H, d, J_{H-H} = 12); ¹³C NMR (CDCl₃): δ (ppm) 13.5, 30.5 (d, ² J_{P-C} = 3.8), 58.2 (d, ² J_{P-C} = 10.3), 78.7 (d, ³ J_{P-C} = 5.7), 126.7, 127.6-129.0, 130.6 (d, J_{P-C} = 68.3), 130.7 (d, J_{P-C} = 2.3), 132.0 (d, J_{P-C} = 10.3), 132.6 (d, J_{P-C} = 11.5), 133.8 (d, J_{P-C} = 10.7), 134.3, 142.4; ³¹P NMR (CDCl₃): δ (ppm) +71.7 (br); HRMS (EI, 70 eV): calcd for C₂₆H₂₉BNOP [M⁺]: 413.2080; Found: 413.2076; Anal. calcd for C₂₆H₂₉BNOP (413.2994): C 75.56, H 7.07, N 3.39; Found: C 75.77, H 7.09, N 3.29.

(Rp)-(-)-N-methyl[(1R,2S)(2-hydroxy-1-phenyl)ethyl]amino-*o*-biphenylphenyl phosphine borane 11f.^{31a} Yield= 81%; White crystals (*i*PrOH/Hexane); R_f = 0.30 (toluene); mp= 101°C; $[\alpha]_D^{20}$ = -43.4 (c 1.2, CHCl₃); IR (KBr, ν cm⁻¹): 3547, 3058-2880, 2422-2327, 1451, 1435, 1163, 1101, 1008, 914, 868, 773, 757, 707; ¹H NMR (CDCl₃): δ (ppm) 0.10-1.60 (3H, br), 0.70 (3H, d, ³ J_{H-H} = 6.9), 1.44 (1H, br), 2.48 (3H, d, ³ J_{P-H} = 7.2), 3.90 (1H, m), 4.78 (1H, d, ³ J_{H-H} = 2.8), 7.00-7.80 (17H, m), 7.45-7.65 (2H, m); ¹³C NMR (CDCl₃): δ (ppm) 9.9 (d, ³ J_{P-C} = 6.6), 31.7 (d, ² J_{P-C} = 4.1), 58.0 (d, ² J_{P-C} = 10.3), 78.8, 125.6, 126.8 (d, J_{P-C} = 9.8), 127.2 (d, J_{P-C} = 11.5), 127.4, 128.1, 128.1 (d, J_{P-C} = 10.1), 128.9 (d, ¹ J_{P-C} = 66.5), 129.7, 130.4-130.6, 132.2 (d, J_{P-C} = 9.8), 132.7 (d, J_{P-C} = 8.4), 133.4 (d, ¹ J_{P-C} = 57.9), 134.1 (d, J_{P-C} = 10.0), 141.4 (d, J_{P-C} = 3.0), 142.5, 147.4 (d, J_{P-C} = 9.9); ³¹P NMR (CDCl₃): δ (ppm) +71.6 (br, ¹ J_{P-B} = 74.1); MS (DCI, CH₄) m/z (relative intensity): 440 (M⁺+H; 10), 438 (M⁺-H; 25), 426 (M⁺+H-

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BH₃; 25), 410 (M⁺-H-CH₃; 5), 318 (10), 307 (5), 279 (40), 263 (20), 176 (20), 160 (40), 148 (100), 133 (15); Anal. calcd for C₂₈H₃₁BNOP (439.3366): C, 76.55; H, 7.11; N, 3.19; Found: C, 76.36; H, 7.22; N, 3.01.

(Sp)-(-)-N-Methyl[(1R,2S)(2-hydroxy-1-phenyl)ethyl]aminocyclohexylphenyl phosphine borane 11g. Yield= 87%; White crystals (iPrOH/Hexane); R_f= 0.26 (toluene); mp= 98°C; [α]_D²⁵= -28.5 (c 0.7, CHCl₃); IR (KBr, ν cm⁻¹): 3538, 3029-2857, 2369, 1492, 1452, 1436, 1368, 1257, 1221, 1159, 1109, 1086, 1000, 961, 887, 758, 742, 695; ¹H NMR (CDCl₃): δ(ppm) 0.10-1.60 (3H, br), 1.15 (3H, d, ³J_{H-H}= 6.9), 1.20-1.90 (10H, m), 2.27-2.34 (1H, m), 2.63 (3H, d, ³J_{P-H}= 7.2), 4.02-4.20 (1H, m), 4.80 (1H, d, ³J_{H-H}= 4.8), 7.10-7.65 (10H, m); ¹³C NMR (CDCl₃): δ(ppm) 12.2 (d, ³J_{P-C}= 3.8), 25.9, 26.6-27.0, 29.3 (d, ²J_{P-C}= 3.3), 32.6 (d, ¹J_{P-C}= 43.7), 58.3 (d, ²J_{P-C}= 8.1), 78.6 (d, ³J_{P-C}= 2.3), 126.0, 127.4, 128.2, 128.3 (d, J_{P-C}= 9.4), 130.5 (d, J_{P-C}= 2.1), 130.8 (d, ¹J_{P-C}= 55.7), 131.2 (d, J_{P-C}= 9.1), 142.5; ³¹P NMR (CDCl₃): δ(ppm) +73.7 (br.d, ¹J_{P-B}= 86.0); MS (DCI, CH₄) m/z (relative intensity): 368 (M⁺-H; 100), 356 (M⁺+H-BH₃; 25), 312 (10), 262 (15), 248 (15), 209 (10), 193 (25), 166 (10), 148 (20); HRMS (DCI, CH₄): calcd for C₂₂H₃₂BNOP [M⁺-H]: 368.2315; Found: 368.2319; Anal. calcd for C₂₂H₃₃BNOP (369.2883): C, 71.55; H, 9.01; N, 3.79; Found: C, 71.71; H, 9.13; N, 3.67.

(Sp)-(+)-N-Methyl[(1R,2S)(2-hydroxy-1-phenyl)ethyl]amino-*tert*-butylphenyl phosphine borane 11h.³² Yield= 82%; White crystals (iPrOH/Hexane); R_f= 0.10 (toluene); mp= 92°C; [α]_D²⁵= +3.8 (c 1.0, CHCl₃); IR (KBr, ν cm⁻¹): 3581, 3050-2984, 2380, 1449, 1433, 1384, 1180, 1102, 1071, 1028, 981, 948, 763, 742, 719, 699; ¹H NMR (CDCl₃): δ(ppm) 0.00-1.60 (3H, br), 1.08 (3H, d, ³J_{H-H}= 7.0), 1.22 (9H, d, ³J_{P-H}= 13.8), 1.82 (1H, br), 2.78 (3H, d, ³J_{P-H}= 6.4), 4.05 (1H, m), 5.09 (1H, d, ³J_{H-H}=

Structure and crystal data for the aminophosphine borane **11h**

Formula	C₂₀H₃₁B₁N₁O₁P₁
Fw =	346.26
Crystal System	Orthorhombic
a (Å) =	7.194 (5)

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b (Å) =	11.967 (2)
c (Å) =	23.749 (5)
α (deg.) =	90.
β (deg.) =	90.
γ (deg.) =	90.
V (Å³) =	2044 (2)
Z =	4
Space group	P 2₁ 2₁ 2₁
Crystal shape	Parallelepiped
Crystal colour	colorless
Linear absorption coefficient μ (cm⁻¹)	1.355
Density ρ(g cm⁻³)	1.115
Diffractometer	MACH 3-Enraf Nonius
Radiation	MoKα (λ = 0.71069 Å)
Scan type	ω/2θ
Scan range (°)	0.8 + 0.345 tgθ
θ Limits (°)	1 - 30
Temperature of measurement	Room temperature
Octants collected	0, 10 ; 0, 16 ; 0, 33
Nb of data collected	3409
Nb of unique data used for refinement	2504 (Fo)² > 3σ(Fo)²
Decay of standards reflections %	3.6
R = Σ Fo - Fc / Σ Fo	0.0495
Rw* = [Σw(Fo - Fc)² / ΣwFo²]^{1/2}	0.0585
Absorption correction	Psiscan (min=1.00 , max=1.14)
Secondary extinction coefficient	321.6
Goodness of fit	0.942
Nb of variables	219
Δρmin (e/ Å³)	-0.21
Δρmax (e/ Å³)	0.39

*** Weighting scheme of the form $w=w'[1-(\|Fo|-|Fc\|)/6\sigma(Fo)]^2$ with $w'=1/\Sigma_r A_r T_r(X)$ with coefficients 10.7, 1.23 and 8.22 for a Chebyshev serie for which $X=Fo/Fo(max)$**

Table S2 : Anisotropic thermal parameters for C₂₀H₃₁B₁N₁O₁P₁

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
P(1)	0.0438(3)	0.0334(2)	0.0406(3)	-0.0002(2)	-0.0000(2)	0.0054(2)
N(1)	0.045(1)	0.0368(9)	0.051(1)	0.0004(8)	-0.0093(9)	0.0066(9)
O(1)	0.096(2)	0.061(1)	0.049(1)	0.0091(9)	0.003(1)	0.002(1)
C(1)	0.073(2)	0.046(1)	0.057(1)	-0.010(1)	0.016(1)	0.001(1)
C(2)	0.133(4)	0.076(2)	0.052(2)	-0.017(1)	0.007(2)	0.001(3)
C(3)	0.081(2)	0.059(2)	0.102(3)	-0.020(2)	0.014(2)	0.021(2)
C(4)	0.106(3)	0.089(3)	0.103(3)	-0.028(2)	0.058(3)	-0.026(3)
C(5)	0.046(1)	0.036(1)	0.050(1)	0.0010(9)	0.002(1)	0.005(1)
C(6)	0.055(1)	0.048(1)	0.059(2)	-0.001(1)	-0.004(1)	0.001(1)
C(7)	0.054(2)	0.045(1)	0.093(2)	0.000(1)	-0.003(2)	-0.003(1)

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C(8)	0.063(2)	0.052(1)	0.093(2)	0.022(2)	0.015(2)	-0.000(1)
C(9)	0.079(2)	0.059(2)	0.063(2)	0.011(1)	0.014(2)	-0.000(2)
C(10)	0.065(2)	0.047(1)	0.055(1)	0.004(1)	0.001(1)	-0.002(1)
C(11)	0.057(2)	0.051(1)	0.080(2)	0.008(1)	-0.017(2)	0.014(1)
C(12)	0.045(1)	0.039(1)	0.044(1)	0.0003(9)	0.0008(9)	-0.002(1)
C(13)	0.045(1)	0.065(2)	0.082(2)	0.002(2)	0.007(1)	-0.010(1)
C(14)	0.053(1)	0.043(1)	0.049(1)	-0.0024(9)	0.003(1)	-0.001(1)
C(15)	0.056(1)	0.044(1)	0.053(1)	-0.009(1)	0.001(1)	0.004(1)
C(16)	0.104(3)	0.058(2)	0.089(3)	-0.010(2)	-0.040(2)	-0.004(2)
C(17)	0.129(4)	0.055(2)	0.120(4)	-0.023(2)	-0.049(3)	-0.007(2)
C(18)	0.100(3)	0.045(1)	0.121(3)	-0.014(2)	-0.015(3)	0.010(2)
C(19)	0.124(4)	0.050(2)	0.113(3)	-0.011(2)	-0.045(3)	0.026(2)
C(20)	0.098(3)	0.051(2)	0.091(2)	-0.018(2)	-0.038(2)	0.016(2)
B(1)	0.054(2)	0.047(1)	0.062(2)	0.007(1)	-0.014(1)	0.009(1)

Table S3 : Hydrogen atoms fractional atomic coordinates for

C ₂₀ H ₃₁ B ₁ N ₁ O ₁ P ₁				
Atom	x/a	y/b	z/c	U(iso)
H(21)	0.2813	0.7972	0.6869	0.098(3)
H(22)	0.0994	0.7962	0.7280	0.098(3)
H(23)	0.1818	0.9146	0.7047	0.098(3)
H(31)	0.4735	0.6928	0.7521	0.098(3)
H(32)	0.3008	0.6804	0.7963	0.098(3)
H(33)	0.4983	0.7330	0.8174	0.098(3)
H(41)	0.5862	0.8816	0.7245	0.098(3)
H(42)	0.4723	0.9937	0.7431	0.098(3)
H(43)	0.5929	0.9244	0.7898	0.098(3)
H(61)	-0.0182	0.7282	0.7969	0.098(3)
H(71)	-0.2133	0.6067	0.8513	0.098(3)
H(81)	-0.2330	0.6257	0.9492	0.098(3)
H(91)	-0.0678	0.7718	0.9955	0.098(3)
H(101)	0.1280	0.8944	0.9420	0.098(3)
H(111)	0.5752	0.9312	0.9302	0.098(3)
H(112)	0.4179	0.8333	0.9251	0.098(3)
H(113)	0.5738	0.8480	0.8757	0.098(3)
H(121)	0.3571	1.1236	0.8465	0.098(3)
H(131)	0.6251	1.1968	0.8927	0.098(3)
H(132)	0.6758	1.0905	0.8524	0.098(3)
H(133)	0.6621	1.0740	0.9205	0.098(3)
H(141)	0.1550	1.1034	0.9284	0.098(3)
H(161)	0.4504	1.2835	0.9998	0.098(3)
H(171)	0.4539	1.4851	0.9937	0.098(3)
H(181)	0.2704	1.5733	0.9268	0.098(3)
H(191)	0.1088	1.4717	0.8571	0.098(3)
H(201)	0.1062	1.2700	0.8637	0.098(3)

Table S4 : Fractional atomic coordinates for C₂₀H₃₁B₁N₁O₁P₁

Atom	x/a	y/b	z/c	U(eqv)
P(1)	0.21862(9)	0.92082(5)	0.82643(2)	0.0387
N(1)	0.3721(3)	0.9660(2)	0.87380(9)	0.0429
O(1)	0.3445(4)	1.0853(2)	0.98352(9)	0.0654
C(1)	0.3426(5)	0.8452(2)	0.7691(1)	0.0557
C(2)	0.2164(9)	0.8372(4)	0.7171(1)	0.0784
C(3)	0.4076(6)	0.7269(3)	0.7851(2)	0.0726
C(4)	0.5126(8)	0.9173(4)	0.7547(2)	0.0844
C(5)	0.0743(4)	0.8215(2)	0.8652(1)	0.0436
C(6)	-0.0282(4)	0.7375(2)	0.8389(1)	0.0536
C(7)	-0.1402(5)	0.6669(2)	0.8697(2)	0.0606
C(8)	-0.1537(5)	0.6788(3)	0.9270(2)	0.0638
C(9)	-0.0576(6)	0.7626(3)	0.9537(1)	0.0648
C(10)	0.0568(5)	0.8337(2)	0.9226(1)	0.0553
C(11)	0.4922(5)	0.8890(3)	0.9040(2)	0.0579
C(12)	0.4030(4)	1.0873(2)	0.8821(1)	0.0424
C(13)	0.6090(4)	1.1154(3)	0.8881(2)	0.0613
C(14)	0.2867(5)	1.1320(2)	0.9310(1)	0.0481
C(15)	0.2836(5)	1.2590(2)	0.9316(1)	0.0497
C(16)	0.3796(7)	1.3221(3)	0.9694(2)	0.0757
C(17)	0.3764(9)	1.4386(3)	0.9669(2)	0.0854
C(18)	0.2756(8)	1.4915(3)	0.9261(2)	0.0795
C(19)	0.1790(8)	1.4308(3)	0.8882(2)	0.0812
C(20)	0.1797(6)	1.3147(3)	0.8912(2)	0.0703
B(1)	0.0676(5)	1.0399(3)	0.7965(1)	0.0521

Table S5 : Interatomic distances () for C₂₀H₃₁B₁N₁O₁P₁

P(1) - N(1)	1.666(2)	P(1) - C(1)	1.863(3)
P(1) - C(5)	1.827(3)	P(1) - B(1)	1.927(3)
N(1) - C(11)	1.452(3)	N(1) - C(12)	1.481(3)
O(1) - C(14)	1.428(3)	C(1) - C(2)	1.535(6)
C(1) - C(3)	1.539(5)	C(1) - C(4)	1.535(6)
C(5) - C(6)	1.395(4)	C(5) - C(10)	1.378(4)
C(6) - C(7)	1.378(5)	C(7) - C(8)	1.371(5)
C(8) - C(9)	1.373(5)	C(9) - C(10)	1.395(4)
C(12) - C(13)	1.526(4)	C(12) - C(14)	1.529(4)
C(14) - C(15)	1.520(4)	C(15) - C(16)	1.361(4)
C(15) - C(20)	1.387(5)	C(16) - C(17)	1.396(5)
C(17) - C(18)	1.365(6)	C(18) - C(19)	1.349(6)
C(19) - C(20)	1.391(5)		

Table S6 : Bond angles (°) for C₂₀H₃₁B₁N₁O₁P₁

N(1) - P(1) - C(1)	109.5(1)	N(1) - P(1) - C(5)	104.3(1)
C(1) - P(1) - C(5)	108.9(1)	N(1) - P(1) - B(1)	112.5(1)

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C(1) - P(1) - B(1)	111.1(2)	C(5) - P(1) - B(1)	110.3(1)
P(1) - N(1) - C(11)	121.5(2)	P(1) - N(1) - C(12)	120.5(2)
C(11) - N(1) - C(12)	117.8(2)	P(1) - C(1) - C(2)	109.5(3)
P(1) - C(1) - C(3)	114.3(2)	C(2) - C(1) - C(3)	108.7(3)
P(1) - C(1) - C(4)	105.7(2)	C(2) - C(1) - C(4)	109.1(3)
C(3) - C(1) - C(4)	109.3(4)	P(1) - C(5) - C(6)	123.0(2)
P(1) - C(5) - C(10)	118.8(2)	C(6) - C(5) - C(10)	118.1(3)
C(5) - C(6) - C(7)	120.9(3)	C(6) - C(7) - C(8)	120.4(3)
C(7) - C(8) - C(9)	119.9(3)	C(8) - C(9) - C(10)	119.9(3)
C(5) - C(10) - C(9)	120.9(3)	N(1) - C(12) - C(13)	112.0(2)
N(1) - C(12) - C(14)	111.2(2)	C(13) - C(12) - C(14)	112.6(2)
O(1) - C(14) - C(12)	111.5(2)	O(1) - C(14) - C(15)	112.8(2)
C(12) - C(14) - C(15)	111.4(2)	C(14) - C(15) - C(16)	123.6(3)
C(14) - C(15) - C(20)	118.8(3)	C(16) - C(15) - C(20)	117.6(3)
C(15) - C(16) - C(17)	121.2(4)	C(16) - C(17) - C(18)	120.1(4)
C(17) - C(18) - C(19)	119.8(3)	C(18) - C(19) - C(20)	120.1(4)
C(15) - C(20) - C(19)	121.1(3)		

Structure and crystal data for the (*R*)-*o*-anisylphenyl-*o*-tolylphosphine 14.

Figure S2

Table S7

CRYSTAL DATA for	C ₂₀ H ₁₉ OP
Fw =	306.34
a (Å) =	7.809(1)
b (Å) =	7.910(1)
c (Å) =	13.990(2)
α (°) =	90
β (°) =	94.30 (1)
γ (°) =	90.
V (Å ³) =	861.8(2)
Z =	2
Crystal system	Monoclinic
Space group	P 2 ₁
Crystal shape	Parallelepiped
Crystal colour	Colourless
Crystal size	0.2, 0.2, 0.4
Linear absorption coefficient μ (cm ⁻¹)	1.2
Density ρ(g cm ⁻³)	1.53
Diffractometer	CAD4 - Enraf-Nonius
Radiation	MoKα (λ = 0.71069 Å)
Scan type	ω/2θ
Scan range (°)	0.8 + 0.345 tgθ
θ Limits (°)	1 - 28
Temperature of measurement	Room temperature
Octants collected	0, 10 ; 0, 10 ; -18, 18
Nb of data collected	2396
Nb of unique data collected	2234
Nb of unique data used for refinement	1198 (Fo) ² > 3σ(Fo) ²
R (int)	.020
Decay of standards reflexions %	4
R = Σ Fo - Fc / Σ Fo	0.046
Rw = [Σw(Fo - Fc) ² / ΣwFo ²] ^{1/2}	0.054
Absorption correction	Psiscan
Extinction parameter	519
Goodness of fit	1.0
Δρmin (e/Å ³)	-0.17
Δρmax (e/Å ³)	0.17

* Weighting scheme of the form $w=w'[1-(|| Fo | - | Fc ||) / 6\sigma(Fo)]^2$ with $w'=1/\Sigma_r A_r T_r(X)$ with coefficients 8.12, -4.17 and 5.45 for a Chebyshev serie for which $X=Fo/Fo(max)$

Table S8: Fractional atomic coordinates for: (compound 14)

Atom	x/a	y/b	z/c	U(eqv)
P(1)	0.2607(2)	0.2911(4)	0.1975(1)	0.0511
O(1)	0.1865(7)	0.0329(9)	0.0598(4)	0.0723

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C(1)	0.3969(9)	0.425(1)	0.2787(5)	0.0514
C(2)	0.461(1)	0.574(1)	0.2419(6)	0.0643
C(3)	0.558(1)	0.683(1)	0.3001(8)	0.0704
C(4)	0.590(1)	0.650(1)	0.3944(7)	0.0694
C(5)	0.531(1)	0.505(1)	0.4327(6)	0.0772
C(6)	0.433(1)	0.393(1)	0.3746(5)	0.0612
C(7)	0.1503(9)	0.163(1)	0.2824(5)	0.0506
C(8)	0.190(1)	-0.003(1)	0.3020(6)	0.0625
C(9)	0.100(1)	-0.097(1)	0.3645(7)	0.0821
C(10)	-0.031(1)	-0.025(2)	0.4111(7)	0.0775
C(11)	-0.074(1)	0.144(2)	0.3917(6)	0.0742
C(12)	0.015(1)	0.239(1)	0.3286(6)	0.0595
C(13)	-0.036(1)	0.421(1)	0.3114(7)	0.0813
C(14)	0.4178(9)	0.142(1)	0.1556(4)	0.0499
C(15)	0.5923(9)	0.144(1)	0.1826(5)	0.0563
C(16)	0.7050(9)	0.038(1)	0.1398(5)	0.0622
C(17)	0.647(1)	-0.072(1)	0.0715(6)	0.0639
C(18)	0.476(1)	-0.078(1)	0.0429(5)	0.0678
C(19)	0.358(1)	0.029(1)	0.0844(5)	0.0590
C(20)	0.117(1)	-0.069(2)	-0.0148(9)	0.1047

Table S9: anisotropic thermal parameters for: (compound 14)

Table : Anisotropic thermal parameters for :

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
P(1)	0.060(1)	0.051(1)	0.0440(8)	0.003(1)	-0.0015(7)	0.003(1)
O(1)	0.058(3)	0.108(5)	0.075(4)	-0.039(4)	-0.005(3)	-0.004(4)
C(1)	0.055(4)	0.047(5)	0.053(4)	-0.004(4)	0.004(3)	0.003(4)
C(2)	0.083(6)	0.047(5)	0.072(5)	0.008(4)	0.014(4)	0.001(5)
C(3)	0.087(6)	0.043(5)	0.110(7)	-0.006(5)	0.037(5)	-0.007(5)
C(4)	0.073(6)	0.071(6)	0.094(7)	-0.035(6)	0.022(5)	-0.028(5)
C(5)	0.086(6)	0.101(8)	0.062(5)	-0.022(5)	0.008(4)	-0.027(6)
C(6)	0.078(5)	0.061(5)	0.055(4)	-0.000(4)	0.008(4)	-0.022(5)
C(7)	0.047(4)	0.059(5)	0.048(4)	-0.007(4)	-0.006(3)	-0.002(4)
C(8)	0.073(5)	0.056(5)	0.061(5)	0.001(4)	0.006(4)	-0.007(4)
C(9)	0.113(8)	0.065(6)	0.085(7)	0.010(6)	0.010(6)	-0.026(6)
C(10)	0.090(7)	0.100(9)	0.070(6)	0.000(6)	0.008(5)	-0.049(7)
C(11)	0.064(5)	0.114(9)	0.068(5)	-0.026(6)	0.018(4)	-0.022(6)
C(12)	0.051(4)	0.078(7)	0.056(4)	-0.015(4)	0.004(4)	-0.007(4)
C(13)	0.074(6)	0.083(8)	0.097(7)	-0.006(6)	0.018(5)	0.017(6)
C(14)	0.064(5)	0.055(5)	0.036(3)	-0.000(3)	0.002(3)	-0.006(4)
C(15)	0.065(5)	0.058(5)	0.047(4)	-0.001(4)	-0.001(3)	-0.007(4)
C(16)	0.050(4)	0.072(6)	0.067(5)	-0.004(5)	0.001(4)	0.004(4)
C(17)	0.060(5)	0.075(6)	0.068(5)	-0.017(5)	0.016(4)	0.008(5)
C(18)	0.084(6)	0.073(6)	0.060(5)	-0.023(5)	0.015(4)	-0.011(5)
C(19)	0.061(5)	0.078(6)	0.045(4)	-0.011(4)	0.006(3)	-0.005(5)
C(20)	0.082(7)	0.18(1)	0.140(9)	-0.10(1)	-0.006(6)	-0.023(8)

Table S10: Angles for 14

axis 1 atom C(1) C(2)

axis 2 atom P(1) C(14)

axis 4 atom C(12) C(13)

axis 5 atom C(7) P(1)

axis 6 atom C(20) O(1)

axis 7 atom C(19) C(14)

axis 8 atom C(1) P(1)

axis 9 atom C(14) C(15)

plane 10 atom C(7) C(8) C(9) C(10) C(11) C(12) C(13)

plane 11 atom C(1) C(2) C(3) C(4) C(5) C(6)

plane 12 atom C(14) C(15) C(16) C(17) C(18) C(19)

Angle between axis 1 and axis 2 is 80.80 Degrees

Angle between axis 4 and axis 5 is 59.94 Degrees

Angle between axis 6 and axis 7 is 174.93 Degrees

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Angle between axis 8 and axis 9 is 46.61 Degrees
 Angle between axis 10 and axis 11 is 77.73 Degrees
 Angle between axis 10 and axis 12 is 77.49 Degrees
 Angle between axis 11 and axis 12 is 88.28 Degrees

Table S11: interatomic distances (Å) and bond angles (°) for: (compound **14**)

P(1) -C(1)	1.836(7)
P(1) -C(7)	1.826(8)
P(1) -C(14)	1.830(8)
P(1) -O(1)	2.837 (6)
O(1) -C(19)	1.359(8)
O(1) -C(20)	1.39(1)
C(1) -C(2)	1.39(1)
C(1) -C(6)	1.374(9)
C(2) -C(3)	1.37(1)
C(3) -C(4)	1.35(1)
C(4) -C(5)	1.36(1)
C(5) -C(6)	1.39(1)
C(7) -C(8)	1.37(1)
C(7) -C(12)	1.42(1)
C(8) -C(9)	1.38(1)
C(9) -C(10)	1.37(1)
C(10) -C(11)	1.40(2)
C(11) -C(12)	1.39(1)
C(12) -C(13)	1.51(1)
C(14) -C(15)	1.387(9)
C(14) -C(19)	1.39(1)
C(15) -C(16)	1.38(1)
C(16) -C(17)	1.34(1)
C(17) -C(18)	1.36(1)
C(18) -C(19)	1.41(1)
C(1) -P(1) -C(7)	101.4(3)
C(1) -P(1) -C(14)	101.6(3)
C(7) -P(1) -C(14)	102.2(4)
C(19) -O(1) -C(20)	119.8(7)
P(1) -C(1) -C(2)	117.9(6)
P(1) -C(1) -C(6)	124.3(6)
C(2) -C(1) -C(6)	117.7(7)
C(1) -C(2) -C(3)	120.5(8)
C(2) -C(3) -C(4)	121.0(8)
C(3) -C(4) -C(5)	120.1(8)
C(4) -C(5) -C(6)	119.6(8)
C(1) -C(6) -C(5)	121.1(8)
P(1) -C(7) -C(8)	123.5(6)
P(1) -C(7) -C(12)	117.8(6)
C(8) -C(7) -C(12)	118.7(8)
C(7) -C(8) -C(9)	121.5(9)
C(8) -C(9) -C(10)	120.7(10)
C(9) -C(10) -C(11)	118.9(9)
C(10) -C(11) -C(12)	120.9(9)
C(7) -C(12) -C(11)	119.2(9)
C(7) -C(12) -C(13)	122.1(8)
C(11) -C(12) -C(13)	118.7(9)
P(1) -C(14) -C(15)	125.0(6)
P(1) -C(14) -C(19)	116.5(5)
C(15) -C(14) -C(19)	118.2(7)
C(14) -C(15) -C(16)	121.3(7)
C(15) -C(16) -C(17)	120.5(7)
C(16) -C(17) -C(18)	120.0(7)
C(17) -C(18) -C(19)	121.0(7)
O(1) -C(19) -C(14)	116.0(7)
O(1) -C(19) -C(18)	124.9(7)
C(14) -C(19) -C(18)	119.0(7)
P(1) -C(14) - C(19) - O(1)	52.77

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P(1) -C(14) - C(1) - C(2) 80.80
P(1) -C(7) - C(12) - C(13) 59.94

Table S12: Hydrogen atoms fractional atomic coordinates for the compound **14** :

Atom	x/a	y/b	z/b	U(iso)
H(2)	0.4221	0.5871	0.1682	0.098(7)
H(3)	0.5867	0.7833	0.2675	0.098(7)
H(4)	0.6813	0.7071	0.4391	0.098(7)
H(5)	0.5375	0.4817	0.4964	0.098(7)
H(6)	0.3971	0.3038	0.4066	0.098(7)
H(8)	0.2900	-0.0467	0.2709	0.098(7)
H(9)	0.1088	-0.1954	0.3811	0.098(7)
H(10)	-0.0941	-0.0911	0.4603	0.098(7)
H(11)	-0.1683	0.1679	0.4384	0.098(7)
H(15)	0.6383	0.2242	0.2318	0.098(7)
H(16)	0.8075	0.0533	0.1686	0.098(7)
H(17)	0.7242	-0.1354	0.0359	0.098(7)
H(18)	0.4446	-0.1613	-0.0018	0.098(7)
H(131)	-0.0421	0.4908	0.3759	0.098(7)
H(132)	-0.1578	0.4231	0.2770	0.098(7)
H(133)	0.0431	0.4751	0.2693	0.098(7)
H(201)	-0.0179	-0.0471	-0.0241	0.098(7)
H(202)	0.1394	-0.1900	-0.0019	0.098(7)
H(203)	0.1675	-0.0372	-0.0777	0.098(7)

Table S13: Hydrogen atoms interatomic distances (Å) and bond angles (°) for the compound **14**

C(2) -H(2)	1.058(8)		
C(3) -H(3)	0.953(9)		
C(4) -H(4)	1.016(8)	C(5) -H(5)	0.907(9)
C(6) -H(6)	0.892(8)	C(8) -H(8)	0.985(8)
C(9) -H(9)	0.82(1)	C(10) -H(10)	1.025(9)
C(11) -H(11)	1.036(9)	C(13) -H(131)	1.06(1)
C(13) -H(132)	1.031(9)	C(13) -H(133)	0.98(1)
C(15) -H(15)	0.984(7)	C(16) -H(16)	0.877(7)
C(17) -H(17)	0.952(7)	C(18) -H(18)	0.930(8)
C(20) -H(201)	1.07(1)n	C(20) -H(202)	0.99(2)
C(20) -H(203)	1.02(1)		
C(1) -C(2) -H(2)	110.9(8)	C(3) -C(2) -H(2)	128.6(8)
C(2) -C(3) -H(3)	112.2(10)	C(4) -C(3) -H(3)	126.4(10)
C(3) -C(4) -H(4)	126.0(10)	C(5) -C(4) -H(4)	112.0(10)
C(4) -C(5) -H(5)	124.1(10)	C(6) -C(5) -H(5)	115.6(10)
C(1) -C(6) -H(6)	126.0(8)	C(5) -C(6) -H(6)	113.0(8)
C(7) -C(8) -H(8)	114.7(8)	C(9) -C(8) -H(8)	123.7(9)
C(8) -C(9) -H(9)	131.1(12)	C(10) -C(9) -H(9)	108.2(11)
C(9) -C(10) -H(10)	121.3(13)	C(11) -C(10) -H(10)	119.8(12)
C(10) -C(11) -H(11)	102.9(11)	C(12) -C(11) -H(11)	135.9(12)
C(12) -C(13) -H(131)	112.8(9)	C(12) -C(13) -H(132)	108.1(9)
H(131) -C(13) -H(132)	107.1(8)	C(12) -C(13) -H(133)	109.7(8)
H(131) -C(13) -H(133)	110.7(10)	H(132) -C(13) -H(133)	108.3(9)
C(14) -C(15) -H(15)	119.8(8)	C(16) -C(15) -H(15)	118.8(7)
C(15) -C(16) -H(16)	107.8(8)	C(17) -C(16) -H(16)	131.5(9)
C(16) -C(17) -H(17)	121.4(8)	C(18) -C(17) -H(17)	118.1(8)
C(17) -C(18) -H(18)	115.2(9)	C(19) -C(18) -H(18)	123.6(8)
O(1) -C(20) -H(201)	108.9(9)	O(1) -C(20) -H(202)	111.7(11)
H(201) -C(20) -H(202)	109.4(11)	O(1) -C(20) -H(203)	110.7(10)
H(201) -C(20) -H(203)	107.3(12)	H(202) -C(20) -H(203)	108.7(10)

S16

Structure and crystal data for the (*S,S*)-(-)-1,2-bis(methylphenylphosphinito borane) benzene 18.

Figure S3

Table S14 CRYSTAL DATA

Formula	$C_{20}H_{26}B_2O_2P_2$
Fw =	382.00
Crystal System	Tetragonal
a (Å) =	6.830 (2)
b (Å) =	6.830 (3)
c (Å) =	46.829 (14)
α (deg.) =	90.
β (deg.) =	90.
γ (deg.) =	90.
V (Å ³) =	2185 (1)
Z =	4
Space group	$P 4_1 2_1 2$
Crystal shape	Parallelepiped
Crystal colour	colorless
Linear absorption coefficient μ (cm ⁻¹)	4.08
Density ρ (g cm ⁻³)	1.16
Diffractometer	MACH 3-Enraf Nonius
Radiation	MoK α ($\lambda = 0.71069$ Å)
Scan type	$\omega/2\theta$
Scan range (°)	$0.8 + 0.345 \tan \theta$
θ Limits (°)	1 - 25
Temperature of measurement	Room temperature
Octants collected	0, 8 ; 0, 8 ; 0, 55
Nb of data collected	2318
Nb of unique data collected	1253
Nb of unique data used for refinement	$776 (F_o)^2 > 2\sigma(F_o)^2$

Merging R	S17 0.052
Decay of standards reflections %	9.9
$R = \sum F_o - F_c / \sum F_o$	0.082
$Rw^* = [\sum w(F_o - F_c)^2 / \sum w F_o^2]^{1/2}$	0.087
Secondary extinction coefficient	none
Goodness of fit	0.945
Nb of variables	119
$\Delta\rho_{min}$ (e/Å³)	-0.41
$\Delta\rho_{max}$ (e/Å³)	0.42

* Weighting scheme of the form $w=w'[1-(||F_o|-|F_c||)/6\sigma(F_o)]^2$ with $w'=1/\sum_r A_r T_r(X)$ with coefficients 4.70, 1.94 and 3.47 for a Chebyshev serie for which $X=F_c/F_c(max)$

Table S15 : Anisotropic thermal parameters for C₂₀H₂₆B₂O₂P₂

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
P(1)	0.043(2)	0.052(2)	0.049(2)	0.005(1)	-0.006(1)	-0.008(1)
B(1)	0.06(1)	0.09(1)	0.065(9)	-0.008(9)	0.011(8)	0.02(1)
O(1)	0.048(5)	0.062(5)	0.047(4)	0.000(4)	-0.004(4)	-0.007(4)
C(1)	0.058(8)	0.048(7)	0.039(6)	0.005(6)	-0.011(5)	-0.010(7)
C(2)	0.09(1)	0.08(1)	0.058(7)	0.006(8)	0.006(8)	-0.013(9)
C(3)	0.14(2)	0.09(1)	0.08(1)	0.021(9)	0.03(1)	-0.02(1)
C(4)	0.17(2)	0.06(1)	0.08(1)	0.015(9)	-0.05(1)	-0.01(1)
C(5)	0.11(1)	0.08(1)	0.09(1)	-0.01(1)	-0.02(1)	0.02(1)
C(6)	0.07(1)	0.060(9)	0.058(7)	-0.011(7)	-0.015(7)	0.008(7)
C(7)	0.071(9)	0.07(1)	0.094(9)	0.018(8)	-0.009(8)	-0.025(7)
C(8)	0.043(7)	0.051(7)	0.050(7)	0.012(5)	-0.004(5)	-0.003(6)
C(9)	0.06(1)	0.053(8)	0.062(7)	-0.000(7)	0.004(7)	-0.000(6)
C(10)	0.09(1)	0.058(9)	0.07(1)	-0.000(6)	0.011(8)	-0.020(8)

Table S16: Hydrogen atoms fractional atomic coordinates for C₂₀H₂₆B₂O₂P₂

Atom	x/a	y/b	z/c	U(iso)
H(21)	0.1917	0.3769	-0.0957	0.10(2)
H(31)	0.0628	0.6464	-0.1266	0.10(2)
H(41)	-0.2541	0.7574	-0.1210	0.10(2)
H(51)	-0.4574	0.6230	-0.0868	0.10(2)
H(61)	-0.3535	0.3614	-0.0553	0.10(2)
H(71)	-0.2909	0.0822	-0.0344	0.10(2)
H(72)	-0.2218	-0.0612	-0.0604	0.10(2)
H(73)	-0.1404	-0.0985	-0.0281	0.10(2)
H(91)	0.2109	0.6051	-0.0329	0.10(2)
H(101)	0.5308	0.7094	-0.0170	0.10(2)

S18Table S17 : Fractional atomic coordinates for C₂₀H₂₆B₂O₂P₂

Atom	x/a	y/b	z/c	U(eqv)
P(1)	0.0259(5)	0.1638(5)	-0.04942(6)	0.0469
B(1)	0.255(3)	0.038(3)	-0.0643(3)	0.0675
O(1)	0.048(1)	0.269(1)	-0.0182(2)	0.0518
C(1)	-0.071(2)	0.353(2)	-0.0723(2)	0.0460
C(2)	0.050(2)	0.431(2)	-0.0928(3)	0.0734
C(3)	-0.022(3)	0.578(3)	-0.1110(3)	0.0903
C(4)	-0.208(3)	0.642(2)	-0.1074(4)	0.0827
C(5)	-0.321(3)	0.568(3)	-0.0874(4)	0.0885
C(6)	-0.258(2)	0.421(2)	-0.0701(3)	0.0608
C(7)	-0.172(2)	0.002(2)	-0.0422(3)	0.0720
C(8)	0.231(2)	0.339(2)	-0.0093(2)	0.0469
C(9)	0.294(2)	0.519(2)	-0.0190(3)	0.0596
C(10)	0.474(2)	0.584(2)	-0.0097(3)	0.0682

Table S18 : Interatomic distances () for C₂₀H₂₆B₂O₂P₂

P(1) - B(1)	1.92(2)	P(1) - O(1)	1.636(8)
P(1) - C(1)	1.80(1)	P(1) - C(7)	1.78(1)
O(1) - C(8)	1.40(1)	C(1) - C(2)	1.37(2)
C(1) - C(6)	1.36(2)	C(2) - C(3)	1.40(2)
C(3) - C(4)	1.35(3)	C(4) - C(5)	1.31(2)
C(5) - C(6)	1.36(2)	C(8) - C(8)'	1.35(2)
C(8) - C(9)	1.38(2)	C(9) - C(10)	1.37(2)
C(10) - C(10)'	1.40(3)		

Table S19 : Bond angles (°) for C₂₀H₂₆B₂O₂P₂

B(1) - P(1) - O(1)	116.5(6)	B(1) - P(1) - C(1)	113.8(7)
O(1) - P(1) - C(1)	104.6(5)	B(1) - P(1) - C(7)	114.3(8)
O(1) - P(1) - C(7)	99.9(6)	C(1) - P(1) - C(7)	106.2(7)
P(1) - O(1) - C(8)	119.9(7)	P(1) - C(1) - C(2)	118.4(12)
P(1) - C(1) - C(6)	122.8(10)	C(2) - C(1) - C(6)	118.8(13)
C(1) - C(2) - C(3)	119.6(16)	C(2) - C(3) - C(4)	119.0(15)
C(3) - C(4) - C(5)	120.9(16)	C(4) - C(5) - C(6)	121.5(17)
C(1) - C(6) - C(5)	120.2(15)	O(1) - C(8) - C(8)'	119.3(6)
O(1) - C(8) - C(9)	119.0(10)	C(8)' - C(8) - C(9)	121.7(7)
C(8) - C(9) - C(10)	117.4(12)	C(9) - C(10) - C(10)'	120.9(8)

Symmetry code : y,x,-z

S19

Crystal structure and data of the (+)-N,N'-bis[(*R*)-*o*-anisylphenylphosphino borane] ethylenediamine 20.

Figure S4

Table S20:

Formula: C₂₈H₃₆B₂N₂O₂P₂; M: 516.15; T, K: 110(2)

Crystal system: Orthorhombic

Space group P2₁ 2₁ 2₁

a: Å 8.7003(2)

b: Å 12.3994(4)

c: Å 27.423(1)

V: Å³ 2958.35 (16)

Z: 4

F(000): 1096

D_{calc}: g/cm³ 1.159

Diffractometer: Enraf-Nonius KappaCCD

Scan type: mixture of Φ rotations and ω scans

λ : Å 0.71073

μ : mm⁻¹ 0.173

Crystal size: mm³ 0.25 x 0.15 x 0.08

sin(θ)/ λ max: Å⁻¹ 0.65

Index ranges h: -11 ; 7
k: -15 ; 16
l: -24 ; 35

Absorption correction SCALEPACK

RC = Refl. Collected 11947

IRC = independent RC 6279 [R(int) = 0.0646]

IRCGT = IRC and [I > 2 σ (I)] 5060

Refinement method: Full-matrix least-squares on F²

S20

Data / restraints / parameters 6279 / 0 / 333

R for IRCGT R1^a = 0.0548, wR2^b = 0.1162R for IRC R1^a = 0.0764, wR2^b = 0.1272Goodness-of-fit^c 1.044Largest diff. peak and hole; e.Å⁻³ 0.294 and -0.268^a R1 = $\Sigma(|F_o| - |F_c|) / \Sigma |F_o|$.^b wR2 = $[\Sigma w(F_o^2 - F_c^2)^2 / \Sigma [w(F_o^2)^2]]^{1/2}$ where $w = 1 / [\sigma^2(F_o^2) + 1.06 * P + (0.0470 * P)^2]$ where $P = (\text{Max}(F_o^2, 0) + 2 * F_c^2) / 3$ ^c Goodness of fit = $[\Sigma w(F_o^2 - F_c^2)^2 / (N_o - N_v)]^{1/2}$.

Table S21:

Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³) for:
(compound **20**)

	x	y	z
P(1)	4372(1)	4251(1)	8257(1)
P(2)	3209(1)	4307(1)	6253(1)
B(1)	5043(4)	5696(3)	8141(1)
B(2)	2982(4)	5718(3)	6527(2)
N(1)	5349(2)	3357(2)	7928(1)
N(2)	4241(2)	3481(2)	6596(1)
O(1)	2614(2)	2250(2)	8357(1)
O(2)	4158(2)	2430(2)	5660(1)
C(27)	4003(3)	3424(3)	7125(1)
C(28)	5513(3)	3532(3)	7399(1)

Table S22: Bond lengths [Å] and angles [deg] for: (compound **20**)

P(1) -N(1)	1.6642 (19)	P(2) -N(2)	1.6546(18)
P(1) -B(1)	1.911(4)	P(2) -B(2)	1.914(4)
N(2) -C(27)	1.468(4)	N(1) -C(28)	1.473 (3)
O(1) -C(6)	1.367(4)	O(1) -C(7)	1.415(4)
O(2) -C(20)	1.432(4)	O(2) -C(19)	1.368(4)
P(1) -C(1)	1.812 (3)	P(1) -C(8)	1.808(3)
P(2) -C(14)	1.810(3)	P(2) -C(21)	1.827(3)
N(1) -P(1) -C(1)	110.31(12)	N(1) -P(1) -C(8)	104.24(11)
N(2) -P(2) -C(14)	104.95(11)	N(2) -P(2) -C(21)	109.95(12)
N(1) -P(1) -B(1)	112.22(13)	N(2) -P(2) -B(2)	113.51(15)
C(8) -P(1) -B(1)	111.51(15)	C(1) -P(1) -B(1)	112.82(16)
C(21) -P(2) -B(2)	109.26(14)	C(14) -P(2) -B(2)	112.95(17)
C(8) -P(1) -C(1)	105.18(13)	C(14) -P(2) -C(21)	105.89(13)
C(28) -N(1) -P(1)	119.04(16)	C(27) -N(2) -P(2)	120.98(16)
O(1) -C(6) -C(5)	125.0(4)	O(1) -C(6) -C(1)	115.5(2)

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O(2) -C(19) -C(18)	123.8(3)	O(2) -C(19) -C(14)	115.3{3}
C(6) -O(1) -C(7)	118.8(3)	C(19) -O(2) -C(20)	118.4(2)
C(9)-C(8) -P(1)	120.0(2)	C(13) -C(8) -P(1)	121.1(2)
C(2)-C(1) -P(1)	119.3(3)	C(6)-C(1) -P(1)	120.6(2)
C(15) -C(14) -P(2)	119.2(2)	C(19) -C(14) -P(2)	121.9(2)
C(22) -C(21) -P(2)	119.7(2)	C(26) -C(21) -P(2)	121.3 (2)

N(1)-H..H-B(1)	2.27 Å
N(2)-H..H-B(2)	2.26 Å
N(1)-H..O(1)C(7)	2.43 Å
N(2)-H..O(2)C(20)	2.31 Å

Diedral angles (°)

N(2) -P(2) -C(21) -C(26)	1.5
P(1) -B(1) -P(2) -B(2)	30.1
P(1) -C(1) - C(6) -O(1)	1
C(1) -C(6) -O(1) - C(7)	179
B(1) -P(1) -C(1) - C(6)	178
N(1) -P(1) -C(8) -C(9)	36.2
C(13) -C(8) -P(1) -C(1)	32.8
N(1) -C(28) -C(27) -N(2)	173.5
N(1) -P(1) -N(2) -P(2)	10
P(2) -C(14) -C(19) -O(2)	2.7
C(14) -C(19) -O(2) -C(20)	176.5
B(2) -P(2) -C(14) -C(19)	176.3