Supporting Information

for

**Stereospecific S\textsubscript{N}2@P Reactions: Novel Access to Bulky P-Stereogenic Ligands**

Contribution by

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EXPERIMENTAL SECTION

General Methods. All reactions were carried out under nitrogen atmosphere in dried solvents. THF, Et₂O and CH₂Cl₂ were dried in a PureSolv purification system from Innovative Technology, Inc. Other commercially available reagents and solvents were used with no further purification. Thin layer chromatography was carried out using TLC-aluminum sheets with silica gel (Merk 60 F₂₅₄). Silica gel chromatography was performed by using 35-70 mm silica or an automated chromatography system (Combiflash®, Teledyne Isco) with hexanes/ethyl acetate gradients as eluent unless noted otherwise. NMR spectra were recorded at 23°C on a Inova 300, Varian Mercury 400, Varian 500 or Bruker 600 apparatus. ¹H NMR and ¹³C NMR spectra were referenced either to relative internal TMS or to residual solvent peaks. ³¹P NMR spectra were referenced to phosphoric acid. Optical rotations were measured at room temperature (25°C) using a Jasco P-2000 iRM-800 polarimeter. Concentration is expressed in g/100 mL. The cell sized 10 cm long and had 1 mL of capacity, measuring λ was 589 nm, which corresponds to a sodium lamp. Melting points were determined using a Büchi melting point apparatus and were not corrected. IR spectra were recorded in a Thermo Nicolet Nexus FT-IR apparatus. HRMS were recorded in a LTQ-FT Ultra (Thermo Scientific) using Nanoelectrospray technique. HPLC chromatography was performed on an Agilent Technologies Series 1100 chromatograph with UV detector. Elemental analysis were done in a EA-1108 CE Instuments (Thermo Fisher). Synthesis of aminophosphine boranes 1a/b and 5a/b was performed as previously described by us.¹

Acidic hydrolysis of aminophosphines 1a/b and 5a/b

GM1. The corresponding aminophosphine borane 1a/b was dissolved in a mixture of methanol and water. Sulfuric acid (96 wt. % in H₂O) (4 eq) was slowly added drop wise and the solution was warmed up to 50 °C and stirred for the specified period of time. Most of the methanol was removed in vacuo and CH₂Cl₂ and H₂O were added. The phases were separated and the aqueous phase was extracted with CH₂Cl₂. The combined organic phases were washed with brine and dried over MgSO₄. The crude was then purified by column chromatography on silica gel when purification was required.

GM2. The corresponding aminophosphine borane 5a/b was dissolved in a mixture of methanol and water. Sulfuric acid (96 wt. % in H₂O) (8 eq) was slowly added drop wise and the solution was stirred 16 h at 80 °C. Most of the methanol was removed in vacuo and CH₂Cl₂ and H₂O were added. The phases were separated and the aqueous phase was extracted with CH₂Cl₂. The combined organic phases were washed with brine and dried over MgSO₄. The crude was then purified by column chromatography on silica gel when purification was required.
(–)-(R)-tert-butyl(methyl)phosphinous acid borane, (–)-3a

Following GM1, (S)-tert-butyl(methyl)aminophosphine borane, (+)-1a (1.00 g, 7.5 mmol), was dissolved in a mixture of methanol (40 mL) and water (2 mL). Sulfuric acid (96 wt. % in H2O) (1.7 mL, 30.0 mmol) was slowly added. The solution was stirred 2 h at 50 ºC. Solvent removal under vacuum yielded 0.97 g (97 %) of (–)-3a as a semisolid which did not require further purification (ee of the methylated product > 99.9% (CG)).

Following GM2, (1S,2R)-1-(tert-butyl(methyl)phosphinoamino)-2,3-dihydro-1H-inden-2-ol borane, (–)-5a (7.00 g, 26.4 mmol) was dissolved in a mixture of methanol (140 mL) and water (70 mL). Sulfuric acid (96 wt. % in H2O) (11.2 mL, 211.2 mmol) was slowly added drop wise. The solution was stirred at 80 ºC overnight. Solvent removal under vacuum yielded 3.45 g (98 %) of (–)-3a as a semisolid which did not require further purification (ee of the methylated product > 99.9% (CG)).

[α]D: - 4.8 (c 1.50, CHCl3). IR (KBr) νmax: 3361, 2971, 2376, 1476, 921 cm⁻¹. 1H NMR (400 MHz, CDCl3) δ; 0.53 (qd, J = 94, 15 Hz, 3H BH3), 1.17 (d, Jp = 14 Hz, 9H), 1.45 (d, Jp = 9 Hz, 3H) ppm. 13C NMR (101 MHz, CDCl3) δ; 11.1 (d, Jp = 38 Hz, CH3), 24.0 (d, Jp = 4 Hz, 3xCH3), 30.8 (d, Jp = 41 Hz, C) ppm. 31P NMR (121 MHz, CDCl3) δ; 121.1 (q, Jβ = 68 Hz, P-BH3) ppm. HRMS (ESI): calc for [C16H16PO–BH3+ H]+: 121.0777, found 121.0777.

(–)-(S)-tert-butyl(phenyl)phosphinous acid borane, (–)-3b

Following GM1, (R)-tert-butyl(phenyl)aminophosphine borane (–)-1b, (20 mg, 0.10 mmol), was dissolved in a mixture of methanol (0.66 mL) and water (0.33 mL) and sulfuric acid (96 wt. % in H2O) (21 µL, 0.41 mmol) was slowly added. The solution was stirred 7 h at 50 ºC. After the aqueous work up and extractions with CH2Cl2, the crude was purified by column chromatography (SiO2, CH2Cl2, 100%) to yield 12 mg (63 %) of (–)-3b as a white solid (ee of the methylated product > 99.9% (HPLC)).

Following GM2, (1S,2R)-1-(tert-butyl(phenyl)phosphinoamino)-2,3-dihydro-1H-inden-2-ol borane, (–)-5b (200 mg, 0.61 mmol) was dissolved in a mixture of methanol (5.5 mL) and water (1.5 mL) and sulfuric acid (96 wt. % in H2O) (0.26 mL, 4.89 mmol) was slowly added drop wise. The solution was stirred at 80 ºC overnight. After the aqueous work up and extractions with CH2Cl2, the crude was purified by column chromatography (SiO2, CH2Cl2, 100 %) to yield 77 mg (66 %) of (–)-3b as a white solid (ee of the methylated product > 99.9% (HPLC)).

1H NMR (400 MHz, CDCl3) δ; 0.35-1.17 (br m, 3H-BH3), 1.12 (d, Jp = 15 Hz, 9H), 7.40-7.56 (m, 3H), 7.68-7.79 (m, 2H) ppm.
Determination of the optical purity of phosphinous acid boranes 3a and 3b

Phosphinous acid boranes were transformed to the corresponding methyl phosphininate boranes by reaction with trimethylsilyldiazomethane and analyzed by either chiral GC or HPLC.

(−)-(R)-methyl tert-butyl(methyl)phosphinite borane.

Following GM3. Phosphinous acid borane (−)-3a (400 mg, 2.98 mmol) was dissolved in a mixture of CH₂Cl₂ and MeOH (6:1, 12 mL) and the solution was cooled down to 0 °C. Trimethylsilyldiazomethane (2 M in hexanes) (3 mL, 5.96 mmol) was added dropwise and the solution was stirred 1 h at rt. Filtration through a SiO₂ plug eluting with CH₂Cl₂ yielded the crude phosphinite as a yellow oil (69%). \([ee > 99.9\%\ \text{(GC)}]\)

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\text{Mp: 88-89 °C.} \quad [\alpha]_D: \quad -8.1 \ (c \ 1.00, \ \text{CHCl}_3).
\]

IR (KBr) \(\nu_{\text{max}}\): 3340, 2962, 1655, 1559 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\): 0.47 (qd, \(J = 96, 16 \ \text{Hz}, 3\text{H BH}_3\)), 1.15 (d, \(J_P = 14 \ \text{Hz}, 9\text{H}\)), 1.37 (d, \(J_P = 8 \ \text{Hz}, 3\text{H}\)), 3.66 (d, \(J_P = 11 \ \text{Hz}, 3\text{H}\)) ppm. \(^13\)C NMR (101 MHz, CDCl₃) \(\delta\): 9.9 (d, \(J_P = 37 \ \text{Hz}, \text{CH}_3\)), 24.3 (d, \(J_P = 3 \ \text{Hz}, 3\text{xCH}_3\)), 31.5 (d, \(J_P = 42 \ \text{Hz}, \text{C}\)), 55.0 (d, \(J_P = 3 \ \text{Hz}, \text{CH}_3\)) ppm. \(^31\)P NMR (121 MHz, CDCl₃) \(\delta\): 133.6 (q, \(J_B = 68 \ \text{Hz}, \text{P-BH}_3\)) ppm. HRMS (ESI): calcd for \([\text{C}_6\text{H}_{18}\text{BOP- BH}_3+\text{H}]^+\): 135.0933, found 135.0933.

GC: \(\beta\)-DEX (30 m), 90 °C, 1 mL/min \(t_k(+) = 17.9 \ \text{min}, \ t_k(-) = 18.5 \ \text{min}\).

(−)-(S)-methyl tert-butyl(phenyl)phosphinite borane.

Phosphinous acid borane (−)-3b (12 mg, 0.06 mmol) was dissolved in a mixture of CH₂Cl₂ and MeOH (6:1, 1 mL) and the solution was cooled down to 0 °C. Trimethylsilyldiazomethane (0.6 M in hexanes) (0.2 mL, 0.12 mmol) was added dropwise and the solution was stirred for 1 h at rt. Filtration through a SiO₂ plug eluting with CH₂Cl₂ yielded 10 mg (83%) of methyl phosphininate as a white solid (\(ee > 99.9\%\) (HPLC)).

\(^1\)H NMR (400 MHz, CDCl₃) \(\delta\): 0.31-1.19 (br m, 3H-BH₃), 1.10 (d, \(J_P = 15 \ \text{Hz}, 9\text{H}\)), 3.69 (d, \(J_P = 11 \ \text{Hz}, 3\text{H}\)), 7.42-7.57 (m, 3H), 7.64-7.74 (m, 2H) ppm. HPLC: Chiralcel OJ, Heptane/EtOH - 0.2% DEA 70:30, 0.50 mL/min, \(\lambda = 210 \ \text{nm}, \ t_k(+) = 15.7 \ \text{min}, \ t_k(-) = 22.6 \ \text{min}\).
Mixed anhydride between 3a and benzoic acid.

To a suspension of NaH (33 mg, 0.83 mmol, 60 % in mineral oil) in THF (6 mL) at 0 ºC was added a solution of phosphinous acid borane (–)-3a (100 mg, 0.75 mmol) in THF (2 ml). The resulting mixture was allowed to warm up to room temperature and stirred 1 h. The solution was then cooled down to 0 ºC and benzoyl chloride (0.10 mL, 0.89 mmol) was added drop wise. The resulting mixture was stirred 3 h at room temperature. Treatment with saturated aqueous solution of NaHCO$_3$ (3 mL) and extractions with EtOAc (2x10 mL) gave the crude which was concentrated. Purification by column chromatography (SiO$_2$, hexane:EtOAc; 9:1) afforded 120 mg (67 %) of the mixed anhydride as a white solid. Single crystals for X-ray analysis (vide infra) were obtained by slow evaporation of a CH$_2$Cl$_2$ solution.

Mp: 98-100 ºC. [α]$_D$: - 4.3 (c 1.05, CHCl$_3$).

IR (KBr) $\nu_{max}$: 2981, 2412, 1731, 1251, 1053, 887 cm$^{-1}$.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 0.27-1.14 (m, 3H BH$_3$), 1.34 (d, $J_P$ = 15 Hz, 9H), 1.85 (s, 9H), 1.71 (d, $J_P$ = 8 Hz, 3H), 7.48 (t, $J_P$ = 8 Hz, 2H), 7.60-7.66 (m, 1H), 7.98-8.04 (m, 2H) ppm.

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$: 10.2 (d, $J_P$ = 28 Hz, CH$_3$), 24.5 (d, $J_P$ = 3.1 Hz, 3xCH$_3$), 31.6 (d, $J_P$ = 37 Hz, C), 128.9 (s, 2xCH), 129.3 (d, $J_P$ = 3 Hz, C), 130.5 (s, 2xCH), 134.3(s, CH), 163.3 (d, $J_P$ = 8 Hz, C=O) ppm. $^{31}$P NMR (121 MHz, CDCl$_3$) $\delta$: 138.5 (q, $J_B$ = 48 Hz, P-BH$_3$) ppm.

HRMS (ESI): calc for [C$_{12}$H$_{20}$BO$_2$P + NH$_4^+$]: 256.1632, found 256.1631. E.A: calc for C$_{12}$H$_{20}$BO$_2$P: C, 60.54; H, 8.47. found C, 60.44; H, 8.77.

Synthesis of optically pure aminophosphanes, (–)-1a and (–)-1b

GM3. Phosphinous acid borane (+)-3a or (+)-3b (1 eq) and methanesulfonic anhydride (1.5 eq) were dissolved in anhydrous CH$_2$Cl$_2$. The reaction was cooled down to -20 ºC and anhydrous NEt$_3$ (2.5 eq) was slowly added drop wise. The reaction was stirred for 1 h at -20 ºC. NH$_3$ (g) was bubbled through the solution for 10 min at -20 ºC (formation of a white precipitate was observed) and the solution was stirred at -20 ºC for 30 min. The solution was allowed to warm up to room temperature and water was added. NH$_3$ was left to evaporate from the solution by stirring at room temperature in an open flask for 1 h. The phases were separated and the aqueous layer was extracted twice with CH$_2$Cl$_2$. The combined organic layers were dried over MgSO$_4$ and concentrated to provide the desired products as white solids.

(–)-(R)-tert-butyl(methyl)phosphanamine borane, (–)-1a

Following GM3, (S)-tert-butyl(methyl)phosphinous acid borane (+)-3a (50 mg, 0.37 mmol) and methansulfonic anhydride (98 mg, 0.56 mmol) in CH$_2$Cl$_2$ (4 mL). Then NEt$_3$ (0.13 mL, 0.93 mmol) was added. NH$_3$ (g) was bubbled through
the solution. Water (2 mL) was added. The phases were separated and the aqueous layer was extracted twice with CH₂Cl₂ (2x5 mL). The combined organic layers were dried over MgSO₄ and were concentrated to provide 50 mg (99 %) of (–)-1a as a white solid (ee = 96 % (CG)).

**GC**: β-DEX (30 m), 130 ºC, 1 mL/min. tᵣ(+) = 15.2 min, tᵣ(–) = 15.6 min.

(–)-(S)-**tert**-butyl(phenyl)aminophosphine borane (–)-1b

Following **GM3**, (R)-**tert**-butyl(phenyl)phosphinous acid borane (+)-3b (20 mg, 0.10 mmol) and methansulfonic anhydride (26 mg, 0.15 mmol) in CH₂Cl₂ (1.5 mL). Then NEt₃ (35 µL, 0.26 mmol) was added. NH₃ (g) was bubbled through the solution. Water (2 mL) was added. The phases were separated and the aqueous layer was extracted twice with CH₂Cl₂ (2x3 mL). The combined organic layers were dried over MgSO₄ and concentrated to provide 20 mg (99 %) of (–)-1b as a white solid (ee = 99.6 % (HPLC)).

**HPLC**: CHIRALCEL OD-H. Heptane/i-PrOH 70:30, 0.5 mL/min, λ = 254 nm. tᵣ(+) = 10.1 min, tᵣ(–) = 13.7.

**Formation of optically pure aminophosphanes from phosphinous acid boranes 3a/b**

**GM4.** A solution of phosphinous acid borane (+)-3a or (+)-3b (1 eq) and methansulfonic anhydride (1.5 eq) in CH₂Cl₂ was cooled to -20 ºC. To this solution, anhydrous NEt₃ (2.5 eq) was slowly added, and the mixture was stirred 1 h at -20 ºC. The corresponding amine or thiol (3-4 eq) was then added and the solution was stirred overnight at -20 ºC. Water was added and the mixture was allowed to warm to room temperature. The organic layer was separated and the aqueous phase was extracted twice with CH₂Cl₂. The combined extracts were washed with brine and concentrated on a rotary evaporator under reduced pressure. Purification by column chromatography (SiO₂, hexane:EtOAc) yielded the corresponding compounds.

(–)-(R)-**N**-benzyl-1-(**tert**-butyl)-1-methylphosphinamine borane, (–)-6

Following **GM4**, (S)-**tert**-butyl(methyl)phosphinous acid borane (+)-3a (50 mg, 0.37 mmol), methansulfonic anhydride (98 mg, 0.56 mmol), NEt₃ (0.13 mL, 0.93 mmol) and benzylamine (0.12 mL, 1.11 mmol) in CH₂Cl₂ (4 mL). Purification by column chromatography (SiO₂, hexane:EtOAc; 85:15) yielded 50 mg (60 %) of (–)-6 as white solid (ee = 98.4 % (HPLC)).

**Mp**: 42-44 ºC. **IR(KBr)**: vₘₐₓ = 3347, 2956, 2373, 1457, 1073, 880, 701 cm⁻¹. **¹H NMR** (400 MHz, CDCl₃) δ: 0.14 – 0.96 (m, 3H-BH₃), 1.16 (d, Jₚ = 15 Hz, 9H), 1.36 (d, Jₚ = 9 Hz, 3H), 1.76 (br s, 1H-NH), 3.94 – 4.17 (m, 1H), 4.17 – 4.30 (m, 1H), 7.22 – 7.39 (m, 5H) ppm. **¹³C NMR**
(101 MHz, CDCl$_3$) δ; 9.2 (d, $J_P = 39$ Hz, CH$_3$), 24.8 (d, $J_P = 3$ Hz, 3xCH$_3$), 31.4 (d, $J_P = 39$ Hz, C), 47.5 (CH$_2$), 127.3 (CH), 127.4 (2xCH), 128.6 (2xCH), 140.6 (d, $J_P = 6$ Hz, C) ppm. $^{31}$P NMR (202 MHz, CDCl$_3$) δ; 70.2-71.3 (m) ppm. HRMS (ESI$^+$): Calc per [C$_{12}$H$_{23}$BNP + NH$_4^+$] 214.1999, found 214.2000. E.A: Calc for [C$_{12}$H$_{23}$BNP]: C, 64.60; H, 10.39; N, 6.28; found C, 64.44; H, 10.80; N, 6.12. HPLC: CHIRALCEL OJ 250 x 4.6 mm, Heptane/EtOH-0.2%DEA 80:20, 0.50 mL/min, λ= 210 nm. $t_R(-)$ = 12.3 min, $t_R(+)$ = 13.8 min.

(–)-(R)-1-tert-butyl-1-methyl-N-(prop-2-yn-1-yl)phosphanamine borane, (–)-7

Following GM4, (S)-tert-butyl(methyl)phosphinous acid borane (+)-3a (100 mg, 0.75 mmol), methansulfonic anhydride (195 mg, 1.12 mmol), NEt$_3$ (0.26 mL, 1.88 mmol) and propargylamine (0.15 mL, 2.25 mmol) in CH$_2$Cl$_2$ (6 mL). Purification by column chromatography (SiO$_2$, hexane:EtOAc; 9:1) yielded 82 mg (64 %) of (–)-7 as an oil.

[α]$_D$: -11.1 (c 1.00, CHCl$_3$). IR (KBr) $\nu_{max}$: 3293, 2963, 2379, 1413, 1099, 893 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) δ; 0.47 (dq, $J = 94$, 15 Hz, 3H, BH$_3$), 1.14 (d, $J_P = 14$ Hz, 9H), 1.34 (d, $J_P = 9$ Hz, 3H), 1.74 (br s, 1H), 2.27 (t, $J = 3$ Hz 1H), 3.62-3.94 (m, 2H) ppm.

$^{13}$C NMR (101 MHz, CDCl$_3$) δ; 9.5 (d, $J_P = 38$ Hz, CH$_3$), 24.5 (d, $J_P = 3$ Hz, 3xCH$_3$), 30.9 (d, $J_P = 40$, Hz, C), 31.4 (d, $J_P = 39$ Hz, C), 31.4 (d, $J_P = 39$ Hz, C), 31.4 (d, $J_P = 39$ Hz, C), 47.5 (d, $J_P = 1$ Hz, CH$_2$), 121.9 (CH) , 122.3 (CH) , 136.8 (CH), 149.1 (CH), 159.0 (d, $J_P = 5$ Hz, C) ppm. $^{31}$P NMR (202 MHz, CDCl$_3$) δ; 72.9-73.9 (m, P-BH$_3$) ppm. HRMS (ESI): calc for [C$_8$H$_{19}$BNP+H]$^+$: 172.1421, found 172.1421.

(–)-(R)-1-tert-butyl-1-methyl-N-(pyridin-2-ylmethyl)phosphinamine borane, (–)-8

Following GM4, (S)-tert-butyl(methyl)phosphinous acid borane (+)-3a (100 mg, 0.75 mmol), methansulfonic anhydride (195 mg, 1.12 mmol), NEt$_3$ (0.26 mL, 1.88 mmol) and 2-picolylamine (0.31 mL, 3.00 mmol) in CH$_2$Cl$_2$ (6 mL). Purification by column chromatography (SiO$_2$, hexane:EtOAc; 7:3) yielded 146 mg (87 %) of (–)-8 as white solid (ee = 99.3 % (HPLC)).

Mp: 75-76 °C. [α]$_D$: -18.2 (c 1.00, CHCl$_3$). IR (KBr) $\nu_{max}$: 3244, 2967, 2380, 1589, 1129, 893 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) δ; 0.95 – 0.11 (m, 3H, BH$_3$), 1.13 (d, $J_P = 14$ Hz, 9H), 1.32 (d, $J_P = 9$ Hz, 3H), 2.79 (br s, 1H-NH), 4.18 – 4.43 (m, 2H), 7.14 – 7.19 (m, 1H), 7.24 – 7.29 (m, 1H), 7.64 (td, $J = 8$ and 2 Hz, 1H), 8.44 – 8.59 (m, 1H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ; 9.8 (d, $J_P = 39$ Hz, CH$_3$), 24.8 (d, $J_P = 3$ Hz, 3xCH$_3$), 31.4 (d, $J_P = 39$ Hz, C), 48.3 (d, $J_P = 1$ Hz, CH$_2$), 121.9 (CH) , 122.3 (CH) , 136.8 (CH), 149.1 (CH), 159.0 (d, $J_P = 5$ Hz, C) ppm. $^{31}$P NMR (202 MHz, CDCl$_3$) δ; 70.4-71.4 (m, P-BH$_3$) ppm. HRMS (ESI): calc for [C$_{12}$H$_{23}$BNP+P + H]$^+$: 225.1686, found 225.1686. E.A: calc for C$_{12}$H$_{23}$BN$_2$P: C, 58.96; H, 9.90; N, 12.50. found C,
58.89; H, 10.32; N, 12.24. **HPLC:** CHIRALCEL OJ. Heptane:EtOH 90:10-0.2% DEA, 0.50 mL/min, \( \lambda = 210 \text{ nm} \). \( t_R(-) = 12.4 \text{ min} \), \( t_R(+) = 13.3 \text{ min} \).

\((-\text{-}(R)-1\text{-tert-butyl-1-methyl-N-(thiophen-2-ylmethyl)phosphinamine borane, (–)-9\n
\text{Following GM4, (S)-}\text{-}1\text{-tert-butyl(methyl)phosphinous acid (}+\text{-)3a (500 mg, 3.73 mmol), methansulfonic anhydride (974 mg, 5.59 mmol), NEt}_3 \text{ (1.30 mL, 9.33 mmol) and 2-thiophenemethylamine (1.15 mL, 11.2 mmol) in CH}_2\text{Cl}_2 \text{ (25 mL). Purification by column chromatography (SiO}_2\text{, hexane:EtOAc; 9:1) yielded 619 mg (73 %) of (–)-9 as white solid (}ee = 95.7 % \text{ (HPLC)}\text{).}\n
**Mp:** 46-47 ºC. [\( \alpha \)] \text{D: -4.1 (c 1.00, CHCl}_3\text{). IR (KBr) } \text{\( \nu_{\text{max}}\): 3346, 2971, 2376, 1475, 1410, 1066, 893, 701 cm}^{-1}. \text{\( ^1H \) NMR (400 MHz, CDCl}_3\text{) } \delta: 0.11 - 0.94 \text{ (m, 3H, BH}_3\text{)}, 1.15 \text{ (d, } J_P = 14 \text{ Hz, 9H)}, 1.36 \text{ (d, } J_P = 9 \text{ Hz, 3H)}, 1.87 \text{ (br s, 1H-NH)}, 4.26 - 4.48 \text{ (m, 2H)}, 6.91 - 6.96 \text{ (m, 2H)}, 7.19 - 7.23 \text{ (m, 1H) ppm. \( ^13C \) NMR (101 MHz, CDCl}_3\text{) } \delta: 9.6 \text{ (d, } J_P = 38 \text{ Hz, CH}_3\text{)}, 24.8 \text{ (d, } J_P = 3 \text{ Hz, 3xCH}_3\text{)}, 31.3 \text{ (d, } J_P = 40 \text{ Hz, C)}, 42.6 \text{ (CH}_2\text{)}, 124.9 \text{ (CH)}, 124.9 \text{ (CH)}, 126.9 \text{ (CH)}, 144.8 \text{ (d, } J_P = 6 \text{ Hz, C) ppm. \( ^31P \) NMR (243 MHz, CDCl}_3\text{) } \delta: 71.0 - 71.9 \text{ (m, P-BH}_3\text{) ppm. HRMS (ESI): calc for [C}_{10}H_{21}BNPS+NH}_4\text{]+: 247.1564, found 225.1565. E.A: calc for C}_{10}H_{21}BNPS: C, 52.42; H, 9.24; N, 6.11; S, 13.52. found C, 52.66; H, 9.65; N, 5.86; S, 13.38. HPLC: CHIRALCEL OJ. Heptane:EtOH 80:20-0.2% DEA, 0.50 mL/min, \( \lambda = 210 \text{ nm} \). \( t_R(-) = 14.2 \text{ min} \), \( t_R(+) = 15.5 \text{ min} \).\n
\((-\text{-}(R)-1\text{-tert-butyl-1-methyl-N-((S)-1-phenylethyl)phosphanamine borane, (–)-10\n
\text{Following GM4, (S)-}\text{-}1\text{-tert-butyl(methyl)phosphinous acid borane (}+\text{-)3a (100 mg, 0.75 mmol), methansulfonic anhydride (194 mg, 1.12 mmol), NEt}_3 \text{ (0.26 mL, 1.88 mmol) and (S)-}1\text{-phenylethylamine (0.30 mL, 2.25 mmol) in CH}_2\text{Cl}_2 \text{ (6 mL). Purification by column chromatography (SiO}_2\text{, hexane:EtOAc; 9:1) yielded 135 mg (76 %) of (–)-10 as white solid (}de = 98 % \text{ (NMR)}\text{).}\n
**Mp:** 94-95 ºC. [\( \alpha \)] \text{D: -54.7 (c 1.00, CHCl}_3\text{). IR (KBr) } \text{\( \nu_{\text{max}}\): 3344, 2975, 2373, 1065, 899 cm}^{-1}. \text{\( ^1H \) NMR (400 MHz, CDCl}_3\text{) } \delta: 0.12 - 0.96 \text{ (m, 3H, BH}_3\text{)}, 1.07 \text{ (d, } J_P = 14 \text{ Hz, 9H)}, 1.24 \text{ (d, } J_P = 9 \text{ Hz, 3H)}, 1.46 \text{ (d, } J = 7 \text{ Hz, 3H)}, 1.81 \text{ (br d, } J = 9 \text{ Hz, 1H-NH)}, 4.41-4.50 \text{ (m, 1H)}, 7.20 - 7.37 \text{ (m, 5H) ppm. \( ^13C \) NMR (101 MHz, CDCl}_3\text{) } \delta: 9.7 \text{ (d, } J_P = 38 \text{ Hz, CH}_3\text{)}, 24.7 \text{ (d, } J_P = 3 \text{ Hz, 3xCH}_3\text{)}, 26.8 \text{ (d, } J_P = 4 \text{ Hz, C)}, 31.3 \text{ (d, } J_P = 40 \text{ Hz, CH)}, 53.1 \text{ (CH)}, 125.7 \text{ (2xCH)}, 126.9 \text{ (CH)}, 128.6 \text{ (2xCH)}, 146.1 \text{ (d, } J = 4 \text{ Hz, C) ppm. \( ^31P \) NMR (202 MHz, CDCl}_3\text{) } \delta: 68.2-69.2 \text{ (m, P-BH}_3\text{) ppm. HRMS (ESI): calc for [C}_{13}H_{25}BNP+H]^+: 238.1890, found 238.1890. E.A: calc for C}_{13}H_{25}BNP: C, 68.85; H, 10.63; N, 5.91. Found C, 65.72; H, 11.03; N, 5.80.\n
8
(+)-(R)-1-tert-butyl-1-methyl-N-((R)-1-phenylethyl)phosphanamine borane, (+)-11

Following GM4, (S)-tert-butyl(methyl)phosphinous acid borane (+)-3a (100 mg, 0.75 mmol), methansulfonic anhydride (194 mg, 1.12 mmol), NEt₃ (0.26 mL, 1.88 mmol) and (R)-(1)-phenylethylamine (0.30 mL, 2.25 mmol) in CH₂Cl₂ (6 mL). Purification by column chromatography (SiO₂, hexane:EtOAc; 9:1) yielded 125 mg (71 %) of (+)-11 as white solid (de = 95%(NMR)).

Mp: 102-103 ºC. [α]D: + 13.1 (c 1.00, CHCl₃). IR (KBr) ʋₘₐₓ: 3335, 2943, 2354, 1450, 889 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ; 0.92-0.11 (m, 3H, BH₃), 1.11 (d, Jₚ = 14 Hz, 9H), 1.20 (d, Jₚ = 9 Hz, 3H), 1.44 (d, J = 7 Hz, 3H), 1.74 (br d, J = 10 Hz, 1H), 4.38 – 4.53 (m, 1H), 7.14-7.48 ppm. ¹³C NMR (101 MHz, CDCl₃) δ; 9.9 (d, Jₚ = 36 Hz, CH₂), 24.6 (d, Jₚ = 3 Hz, 3xCH₃), 26.6 (d, Jₚ = 5 Hz, CH₃), 30.5 (d, Jₚ = 42 Hz, C), 52.6 (CH), 125.8 (2xCH), 126.9 (CH), 128.5 (2xCH), 146.2 (d, Jₚ = 3 Hz, C) ppm. ³¹P NMR (243 MHz, CDCl₃) δ; 68.7-69.7 (m, P-BH₃) ppm. HRMS (ESI): calc for [C₁₃H₂₅BNP+H]⁺: 238.1890, found 238.1895. E.A: calc for C₁₃H₂₅BNP: C, 68.85; H, 10.63; N, 5.91. Found C, 65.45; H, 10.85; N, 5.70.

(--)-(2R)-2-[((R)-tert-butyl(methyl)phosphinoamino]-2-phenyl acetamide borane, (--)-12

Following GM4, (S)-tert-butyl(methyl)phosphinous acid borane (+)-3a (100 mg, 0.75 mmol), methansulfonic anhydride (194 mg, 1.12 mmol), NEt₃ (0.26 mL, 1.88 mmol) and (R)-2-phenylglycine amide (338 mg, 2.25 mmol) in CH₂Cl₂ (6 mL). Purification by column chromatography (SiO₂, hexane:EtOAc; 7:3) yielded 125 mg (63 %) of (--)-12 as white solid (de = 97 % (NMR)).

Mp: 158-159 ºC. [α]D: - 112.2 (c 1.00, CHCl₃). IR (KBr) ʋₘₐₓ: 3403, 2359, 1671, 1365, 931, 697cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ; 0.91-0.87 (m, 3H, BH₃), 0.98 (d, Jₚ = 14 Hz, 9H), 1.39 (d, Jₚ = 9 Hz, 3H), 3.00 (br d, J = 9 Hz, NH), 4.99 (t, J = 9 Hz, 1H), 5.49 (br d, J = 32 Hz, NH₂), 7.28 – 7.34 (m, 2H), 7.34 – 7.38 (m, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ; 10.4 (d, Jₚ = 37 Hz, CH₃), 24.2 (d, Jₚ = 3 Hz, 3xCH₃), 30.6 (d, Jₚ = 43 Hz, C), 60.0 (CH), 127.2, (2xCH), 129.0 (CH), 128.2 (2xCH), 140.3 (C), 174.0 (C=O) ppm. ³¹P NMR (243 MHz, CDCl₃) δ; 72.9-73.9 (m, P-BH₃) ppm. HRMS (ESI): calc for [C₂₆H₄₈B₂N₄O₂P₂ (2M) + H]⁺: 533.3511, found 533.3518.
(–)-(R)-1-(tert-butyl(methyl)phosphanyl)pyrrolidine, (–)-13

Following GM4, (S)-tert-butyl(methyl)phosphinous acid borane, (+)-3a (200 mg, 1.49 mmol), methansulfonic anhydride (390 mg, 2.24 mmol), NEt₃ (0.52 mL, 3.73 mmol) and freshly distilled pyrrolidine (0.62 mL, 7.45 mmol) in CH₂Cl₂ (8 mL). Purification by column chromatography (SiO₂, isocratic CH₂Cl₂) yielded 180 mg (65 %) of (–)-13 as oil (ee = 97.8 % (HPLC)).

[α]D: -13.1 (c 1.00, CHCl₃). IR (KBr) ʋ max: 2971, 2377, 1475, 1363, 1291, 1068, 1012, 889, 781 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ: 0.51 (br q, J_B = 94 Hz, 3H, BH₃), 1.13 (d, J_P = 14 Hz, 9H), 1.36 (d, J_P = 9 Hz, 3H), 1.72-1.83 (m, 4H), 3.05-3.17 (m, 2H), 3.21-3.31 (m, 2H) ppm.

¹³C NMR (101 MHz, CDCl₃) δ: 6.7 (d, J_P = 41 Hz, CH₃), 25.7 (d, J_P = 3 Hz, 3xCH₂), 26.4 (d, J_P = 6 Hz, 2xCH₂), 34.0 (d, J_P = 37 Hz, C), 114.4 (2xCH), 134.7 (d, J_P = 4 Hz, C), 155.6 (C) ppm.

³¹P NMR (202 MHz, CDCl₃) δ: 68.9 – 70.0 (m, P-BH₃) ppm.

HRMS (ESI): calc for [C₉H₂₃BNOP + H]⁺: 188.1734, found 188.1735.

HPLC: Chiralcel OD-H. Heptane: i-PrOH = 99:1, 0.50 mL/min, λ = 210 nm. tₘ(+) = 22.3 min, tₙ(–) = 24.2 min.

(+)-(R)-1-tert-butyl-N-(4-methoxyphenyl)-1-methylphosphanamine borane, (+)-14

Following GM4, (S)-tert-butyl(methyl)phosphinous acid borane (+)-3a (200 mg, 1.49 mmol), methansulfonic anhydride (390 mg, 2.24 mmol), NEt₃ (0.52 mL, 3.73 mmol) and 4-methoxyaniline (550 mg, 4.47 mmol) in CH₂Cl₂ (6 mL). Purification by column chromatography (SiO₂, isocratic CH₂Cl₂) yielded 150 mg (42 %) of (+)-14 as a yellow solid (ee = 91.0 % (HPLC)).

Mp: 124-125 ºC. [α]D: +5.7 (c 1.00, CHCl₃). IR (KBr) ʋ max: 3308, 2403, 1511, 1246, 1037, 934, 826 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ: 1.01 – 0.22 (m, 3H, BH₃), 1.17 (d, J_P = 14 Hz, 9H), 1.50 (d, J_P = 9 Hz, 3H), 3.74 (br s, 1H, NH), 3.76 (s, 3H), 6.78 (d, J = 9 Hz, 2H), 7.00 (d, J = 8 Hz, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ: 69.5 (d, J_P = 40 Hz, CH₃), 25.1 (d, J_P = 3 Hz, 3xCH₂), 32.1 (d, J_P = 35 Hz, C), 55.5 (CH₃), 114.4 (2xCH), 123.2 (d, J_P = 3 Hz, 2xCH), 134.7 (d, J_P = 4 Hz, C), 155.6 (C) ppm. ³¹P NMR (162 MHz, CDCl₃) δ: 69.5 – 70.3 (m, P-BH₃) ppm.

HRMS (ESI): calc for [C₁₂H₂₅BNOP – BH₃ + H⁺]: 226.1355, found 226.1351. E.A: calc for C₁₂H₂₅BNOP: C, 60.28; H, 9.82; N, 5.80; found C, 60.11; H, 9.70; N, 5.86. HPLC: Chiralpak IA. Heptane:i-PrOH = 90:10, 0.50 mL/min, λ = 210 nm. tₘ(+) = 14.7 min, tₙ(–) = 18.5 min.

(–)-(benzylthio)(tert-butyl)(methyl)phosphine borane, (–)-17

Following GM4, (S)-tert-butyl(methyl)phosphinous acid borane (+)-3a (100 mg, 0.75 mmol), methansulfonic anhydride (195 mg, 1.12 mmol),
NEt₃ (0.26 mL, 1.86 mmol) and benzylthiol (0.26 mL, 2.25 mmol) in CH₂Cl₂ (6 mL). The solution was stirred 16 h at -20 °C. Purification by preparative HPLC (SiO₂, hexane:Et₂O; 96:4) yielded 64 mg (22 %) of (–)-17 as yellow oil.

[α]₀D: -23.5 (c 1.00, CHCl₃). IR (KBr) v_max: 2962, 2392, 1454, 1059, 699 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ: 0.39-1.21 (m, 3H BH₃), 1.21 (d, J_P = 15 Hz, 9H), 1.47 (d, J_P = 9 Hz, 3H), 4.05 (dd, J_P = 13, 8 Hz, 1H), 4.17 (dd, J_P = 13, 8 Hz, 1H), 7.39 – 7.20 (m, 5H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ: 11.3 (d, J_P = 30 Hz, CH₃), 25.1 (d, J_P = 3 Hz, 3xCH₃), 31.9 (d, J_P = 27 Hz, C), 34.9 (CH₂), 127.7 (CH), 128.8 (2xCH), 129.2 (2xCH), 138.0 (C) ppm. ³¹P NMR (202 MHz, CDCl₃) δ: 70.4-71.3 (m, P-BH₃) ppm. HRMS (ESI): calc for [C₁₂H₂₂BPS-BH₃+O+H⁺]: 243.0972, found 243.0988.

(–)-tert-butyl(methyl)(phenylthio)phosphine borane, (–)-18

Following GM₄, (S)-tert-butyl(methyl)phosphinous acid borane (+)-3a (50 mg, 0.37 mmol), methansulfonic anhydride (98 mg, 0.56 mmol), NEt₃ (0.13 mL, 0.93 mmol) and phenylthiol (0.12 mL, 1.11 mmol) in CH₂Cl₂ (4 mL). The solution was stirred 16 h at -10 °C. Purification by column chromatography (SiO₂, hexane:CH₂Cl₂; 6:4) yielded 32 mg (36 %) of (–)-18 as a yellow oil.

[α]₀D: -2.1 (c 1.49, CHCl₃). IR(KBr): v_max = 2962, 2384, 1473, 1057, 747 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ: 0.12-0.94 (m, 3H BH₃), 1.27 (d, J_P = 15 Hz, 9H), 1.50 (d, J_P = 8 Hz, 3H), 7.30-7.41 (m, 3H), 7.54-7.60 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ: 10.8 (d, J_P = 26 Hz, CH₃), 25.6 (d, J_P = 3 Hz, 3xCH₃), 32.2 (d, J_P = 24 Hz, C), 126.8 (d, J_P = 4 Hz, C), 129.1 (d, J_P = 2 Hz, 2xCH), 129.6 (d, J_P = 2 Hz, CH), 137.0 (d, J_P = 3 Hz, 2xCH) ppm. ³¹P NMR (202 MHz, CDCl₃) δ: 75.1-75.7 (m, P-BH₃) ppm. HRMS (ESI⁺): Calc per [C₁₁H₂₀BPS–BH₃–O⁺H⁺]: 229.0811, found 229.0809.

(–)-(S)-1-tert-butyl-1-phenyl-N-((R)-1-phenylethyl)phosphanamine borane, (–)-19

Following GM₄, (R)-1-tert-butyl(phenyl)phosphinous acid (±)-3b (100 mg, 0.51 mmol), methansulfonic anhydride (134 mg, 0.77 mmol), NEt₃ (0.18 mL, 1.28 mmol) and (R)-(1)-phenylethylamine (0.33 mL, 2.55 mmol) in CH₂Cl₂ (4 mL). Purification by column chromatography (SiO₂, hexane:EtOAc; 95:5) yielded 110 mg (72 %) of (–)-19 as white solid (de = 96 % (NMR)).

[α]₀D: -7.6 (c 1.00, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ: 0.41-1.24 (m, 3H, BH₃), 1.09 (d, J_P = 14 Hz, 9H), 1.58 (d, J = 7 Hz, 3H), 2.09 (br d, J = 10 Hz, 1H), 4.47 – 4.65 (m, 1H), 7.14-7.24 (m, 4H), 7.22-7.31 (m, 3H), 7.40-7.47 (m, 2H) ppm.
(R)-2-Methyl-1-(\((S)\)-4-phenyl-4,5-dihydrooxazol-2-yl)propan-1-amine, 20

Compound 20 was obtained following procedures described in the literature.\(^4\)

\(
\text{\(1H\) NMR (400 MHz, CDCl}_3\): \(\delta; \) 1.01 (d, \(J = 7\) Hz, 3H), 1.05 (d, \(J = 7\) Hz, 3H), 1.58 (br s, 2H), 2.00-2.14 (m, 1H), 3.45 (dd, \(J = 5, 1\) Hz, 1H), 4.12 (t, \(J = 9\) Hz, 1H), 4.67 (dd, \(J = 10, 9\) Hz, 1H), 5.21 (t, \(J = 9\) Hz, 1H), 7.22-7.33 (m, 3H), 7.31-7.40 (m, 2H) ppm.}

(R)-(+)-1-tert-butyl-1-methyl-N-(\((R)\)-2-methyl-1-(\((S)\)-4-phenyl-4,5-dihydrooxazol-2-yl)propyl)phosphanamine borane, (+)-21

Following GM4, (S)-tert-butyl(methyl)phosphinous acid borane, (+)-3a (250 mg, 1.86 mmol), methansulfonic anhydride (390 mg, 2.24 mmol), NEt\(_3\) (0.65 mL, 4.65 mmol) and amine 20 (756 mg, 3.47 mmol) in CH\(_2\)Cl\(_2\) (15 mL). Water (10 mL) was added and the mixture was allowed to warm to room temperature. The organic layer was separated and the aqueous phase was extracted twice with CH\(_2\)Cl\(_2\) (2x15mL). The combined organic layers were washed twice with NaOH\(_{aq}\) (1 M) (2x10 mL). The organic layer was dried over MgSO\(_4\) and concentrated on a rotary evaporator under reduced pressure. Purification by column chromatography (SiO\(_2\), hexane:EtOAc; 85:15) yielded 269 mg (43%) of (+)-21 as a white solid (\(\text{de} = 98.5\%\) (NMR)).

\(\text{Mp}: 66-67^\circ\text{C}. [\alpha]_D: +14.8\) (c 1.00, CHCl\(_3\)). IR (KBr) \(\nu_{max};\) 2964, 2380, 1660, 1466, 1137, 916 cm\(^{-1}\). \(\text{\(1H\) NMR (400 MHz, CDCl}_3\): \(\delta;\) 0.88-0.09 (m, 3H), 1.00 (d, \(J = 7\) Hz, 3H), 1.05 (d, \(J = 7\) Hz, 3H), 1.15 (d, \(J_P = 14\) Hz, 9H), 1.36 (d, \(J_P = 9\) Hz, 3H), 2.02-2.14 (m, 1H), 2.14-2.23 (m, 1H), 3.91-4.02 (m, 1H), 4.11 (t, \(J = 9\) Hz, 1H), 5.17-5.24 (m, 1H), 7.22-7.31 (m, 3H), 7.33-7.39 (m, 2H) ppm. \(\text{\(13C\) NMR (101 MHz, CDCl}_3\): \(\delta;\) 10.4 (d, \(J_P = 33\) Hz, CH\(_3\)), 18.0 (CH\(_3\)), 19.5 (CH\(_3\)), 24.7 (d, \(J_P = 3\) Hz, 3xCH\(_3\)), 30.8 (d, \(J_P = 45\) Hz, C), 33.3 (d, \(J_P = 6\) Hz, CH), 56.7 (CH), 69.5 (CH), 75.5 (CH), 126.9 (2xCH), 127.9 (CH), 129.0 (2xCH), 142.0 (C), 171.0 (C) ppm. \(\text{\(31P\) NMR (162 MHz, CDCl}_3\): \(\delta;\) 71.8-73.0 (m, P-BH\(_3\)) ppm. HRMS (ESI): \text{calc for [C}_{18}H_{32}BN_2OP+H]^+: 335.2416, found 335.2416.}

[Ir(26)(COD)]BAr\(_F\), (+)-22

Borane protected phosphine-oxazoline (+)-21 (200 mg, 0.60 mmol) was dissolved in freshly distilled pyrrolidine (10 mL) and
the solution was stirred 16 h at 90 ºC. After this period of time, pyrrolidine was removed in vacuo. When all the pyrrolidine was removed, the crude was left under vacuum at 50 ºC for 30 min, keeping always the crude under N₂. A solution of [Ir(COD)(Cl)]₂ (200 mg, 0.30 mmol) in CH₂Cl₂ (8 mL) was added to the free ligand via cannula or syringe. The resulting mixture was left to stir 40 min at room temperature. NaBAr₅ (531 mg, 0.60 mmol) was then added and the solution was stirred 1 h at room temperature. The formation of an apolar product was observed by TLC; Rf = 0.9 (100% CH₂Cl₂). The crude was then filtered through a small plug of silica gel (washed first with Et₂O) eluting with hexane:CH₂Cl₂ (50-100%) mixtures. The orange fraction was collected and concentrated in vacuo to yield 800 mg (89 %) of [Ir(25)(COD)]BAr₅, (+)-22 as an orange solid.

Mp: 190-191 ºC. [α]D: + 57.9 (c 0.50, CHCl₃). IR (KBr) νmax: 2925, 1612, 1354, 1276, 1134, 886, 701 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ; 1.06 (d, J = 7 Hz, 3H), 1.11 (d, Jp = 15 Hz, 9H), 1.15 (d, J = 7 Hz, 3H), 1.30 (d, Jp = 8 Hz, 3H), 1.46-1.62 (m, 2H), 1.84-2.04 (m, 4H), 2.05-2.15 (m, 1H), 2.15-2.26 (m, 1H), 2.38 (br d, J = 7 Hz, 1H), 2.85-3.05 (m, 1H), 3.38-3.54 (m, 3H), 4.13-4.19 (m, 1H), 4.43 (dd, J = 9, 5 Hz, 1H), 4.63-4.82 (m, 2H), 5.03 (dd, J = 10, 5 Hz, 1H), 7.21-7.28 (m, 2H), 7.35-7.46 (m, 3H), 7.53 (br s, 4H), 7.71 (br s, 8H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ; 7.9 (d, Jp = 35 Hz, CH₃), 18.6 (CH₃), 19.2 (CH₃), 25.6 (d, Jp = 5 Hz, 3xCH₃), 28.3 (d, Jp = 1 Hz, CH₂), 30.4 (d, Jp = 3 Hz, CH₂), 30.5 (d, Jp = 3 Hz, CH₂), 33.4 (d, Jp = 3 Hz, CH₂), 36.6 (d, Jp = 38 Hz, C), 36.9 (d, Jp = 5 Hz, CH), 58.3 (CH), 60.8 (d, J = 5 Hz, CH), 63.6 (CH), 71.3 (CH), 78.4 (CH₂), 89.3 (d, Jp = 13 Hz, CH), 94.5 (d, Jp = 10 Hz, CH), 117.5 (hept, Jp = 4 Hz, 4xCH), 124.5 (q, Jp = 273 Hz, 8xCF₃), 126.6 (2xCCH), 128.9 (qq, ³Jp = 31, ⁴Jp = 3 Hz, 8xC), 129.8 (2xC), 130.4 (CH), 134.8 (8xC), 138.5 (C), 161.7 (q, Jp = 50 Hz, 4xC), 177.8 (d, Jp = 5 Hz, C) ppm. ³¹P NMR (162 MHz, CDCl₃) δ; 57.4 ppm. ¹⁹F NMR (376 MHz, CDCl₃) δ; -62.38 ppm. HRMS (ESI): calc for [C₂₆H₄₁IrN₂OP]⁺: 621.2580, found 621.2573. Calc for [C₃₂H₁₂BF₂₄]⁻: 863.0654, found 863.0627.

Typical procedure for olefin hydrogenation

The alkene (0.5 mmol) and Ir complex (+)-22 (1 mol%) were dissolved in CH₂Cl₂ (1 mL) in a high-pressure autoclave. The autoclave was purged four times with hydrogen. Then, it was
pressurized at the desired pressure. After the desired reaction time, the autoclave was depressurized and the solvent evaporated off. The residue was dissolved in Et₂O (1 ml) and filtered through a short plug of celite. The conversions were determined by ¹H NMR or GC and enantiomeric excess was determined by chiral GC or chiral HPLC. All conversions were 100%.

(R)-Ethyl 3-phenylbutanoate⁵

¹H NMR (400 MHz, CDCl₃) δ; 1.16 (t, 3H, J= 7.2 Hz), 1.30 (d, 3H, J= 6.8 Hz), 2.54 (m, 2H), 3.28 (m, 1H), 4.08 (q, 2H, J= 7.2 Hz), 7.2-7.4 (m, 5H).

HPLC: Chiracel IB column (hexane/2-propanol=99.5/0.5, 1 mL/min, 254 nm). tᵣ(R) = 12.4 min; tᵣ(S) = 26.3 min. (ee = 94.7% (R) (HPLC))

(R)-Ethyl 4-methyl-3-phenylpentanoate.⁶

¹H NMR (400 MHz, CDCl₃) δ; 0.77 (d, 3H, J= 6.0 Hz), 0.97 (d, 3H, J= 6.0 Hz), 1.06 (t, 3H, J= 6.8 Hz), 1.86 (m, 1H), 2.60 (m, 1H), 2.80 (m, 1H), 2.88 (m, 1H), 3.96 (q, 2H, J= 6.8 Hz), 7.1-7.3 (m, 5H).

HPLC: Chiracel OD-H column (hexane/2-propanol=99/1, 0.5 mL/min, 254 nm). tᵣ(R) = 11.0 min; tᵣ(S) = 18.8 min. (ee = 97.1% (R) (HPLC))

(R)-Ethyl 3-cyclohexyl-3-phenylpropanoate⁷

¹H NMR (CDCl₃) δ: 0.90 (m, 1H), 0.93 (m, 1H), 1.06 (t, 3H, J= 7.2 Hz), 1.12 (m, 1H), 1.24 (m, 2H), 1.42 (m, 2H), 1.60 (m, 2H), 1.72 (m, 1H), 1.80 (m, 1H), 2.54 (m, 1H), 2.78 (m, 1H), 2.89 (m, 1H), 3.92 (q, 2H, J= 7.2 Hz), 7.1-7.3 (m, 5H).

HPLC: Chiracel OD-H column (hexane/2-propanol=99/1, 0.5 mL/min, 254 nm). tᵣ(R) = 10.3 min; tᵣ(S) = 17.0 min. (ee = 97.1% (R) (HPLC)).

(R)-Ethyl 3-(p-tolyl)butanoate.⁵

¹H NMR (CDCl₃) δ: 1.18 (t, 3H, J= 7.2 Hz), 1.28 (d, 3H, J= 6.0 Hz), 2.31 (s, 3H), 2.56 (m, 2H), 3.25 (m, 1H), 4.08 (q, 2H, J= 7.2 Hz), 7.12 (m, 4H) ppm. HPLC: Chiracel IB column (hexane/2-propanol=99.5/0.5, 0.5 mL/min, 254 nm). tᵣ(R) = 10.9 min; tᵣ(S) = 12.0 min. (ee = 99.9% (R) (HPLC)).
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
\[^1\text{H NMR (400 MHz, CDCl}_3\text{)}\]

\[^{13}\text{C NMR (101 MHz, CDCl}_3\text{)}\]
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
\(^1\)H NMR (400 MHz, CDCl\(_3\))

\(^{13}\)C NMR (101 MHz, CDCl\(_3\))
$^1$H NMR (400 MHz, CDCl$_3$)

$^13$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
\[ ^{1}H \text{ NMR (400 MHz, CDCl}_3) \]

\[ ^{13}C \text{ NMR (101 MHz, CDCl}_3) \]
$^1$H NMR (400 MHz, CDCl$_3$)

($^1$H NMR spectrum of compound (+)-21)

$^{13}$C NMR (101 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)

($^1$H NMR spectrum of compound (+)-22)
$^{13}$C NMR (101 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
HPLC, Racemic sample

Table 3, entry 1

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<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
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<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
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$^1$H NMR (400 MHz, CDCl$_3$)
HPLC, Racemic sample

Table 3, entry 2

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$^1$H NMR (400 MHz, CDCl$_3$)
HPLC, Racemic sample

Table 3, entry 3

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$^1$H NMR (400 MHz, CDCl$_3$)
HPLC, Racemic sample

Table 3, entry 4

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Crystal data and structure refinement for mixed anhydride between 3a and benzoic acid

Empirical formula  
C12 H20 B O2 P

Formula weight  
238.06

Temperature  
100(2) K

Wavelength  
0.71073 Å

Crystal system  
Orthorhombic

Space group  
P2(1)2(1)2(1)

Unit cell dimensions  
a = 10.5960(9) Å  \( \alpha = 90.00 \, ^\circ \).
b = 11.0390(9) Å  \( \beta = 90.00 \, ^\circ \).
c = 11.6053(9) Å  \( \gamma = 90.00 \, ^\circ \).

Volume  
1357.46(19) Å³

Z  
4

Density (calculated)  
1.165 Mg/m³

Absorption coefficient  
0.186 mm⁻¹

F(000)  
512

Crystal size  
0.15 x 0.02 x 0.02 mm³

Theta range for data collection  
2.55 to 33.10 °.

Index ranges  
-13 ≤ h ≤ 15, -15 ≤ k ≤ 16, -16 ≤ l ≤ 15

Reflections collected  
9755

Independent reflections  
4313 [R(int) = 0.0142]

Completeness to theta =33.10 °  
86.7%

Absorption correction  
Empirical

Max. and min. transmission  
0.9963 and 0.9726

Refinement method  
Full-matrix least-squares on F²

Data / restraints / parameters  
4313 / 0 / 150

Goodness-of-fit on F²  
1.264

Final R indices [I>2σ(I)]  
R1 = 0.0271, wR2 = 0.0795

R indices (all data)  
R1 = 0.0316, wR2 = 0.0955

Flack parameter  
x = -0.03(6)

Largest diff. peak and hole  
0.492 and -0.604 e.Å⁻³
References


