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Prolinol as a Chiral Auxiliary in Organophosphorus Chemistry

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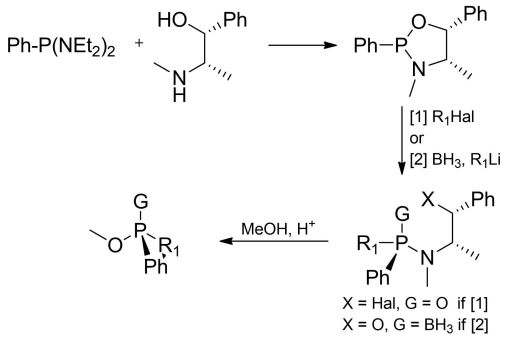
Several strategies for the development of the synthesis of P-chiral organophosphorus compounds with (L)-prolinol as a source of chirality have been examined. A reaction of *L*-prolinol with a set of different alkyl/arylphosphonous acid diamides led in most of the cases to the quantitative formation of the appropriate bicyclic oxazaphospholidines with complete diastereo and enantioselectivity. The latter were reacted with BH_3 complex and the formed borane analogues were submitted to structural modifications leading to tertiary phosphine-boranes. Additionally, the effectiveness of oxazaphospholidines as ligands in transition metal asymmetric catalysis has been tested in hydrogenation of dehydroaminoacid esters and imine.

Introduction

A constant search for novel and more efficient catalytic systems (especially for asymmetric catalysis) lead to the development of more and more sophisticated ligands what takes generally a lot of time and efforts.[1] Constructing new scaffolds is usually associated with the development of new strategies and the use of new building blocks. On the other hand some obsolete methods and molecules may still hide an interesting synthetic potential.[2] Among them, numerous naturally occurring compounds being excellent starting materials are still tested in diastereodivergent processes.

Easy access to P-stereogenic organophosphorus compounds is a key point in a broad range of chemical transformations. Although there are several well-known synthetic methodologies leading to these compounds, there is a constant interest in the development of a new synthetic methods and new precursors leading to the target molecules. In the end of 1980's, Jugé and co-workers have published a method of the synthesis of P-stereogenic phosphines using ephedrine as a chiral auxiliary (Scheme 1).[3]

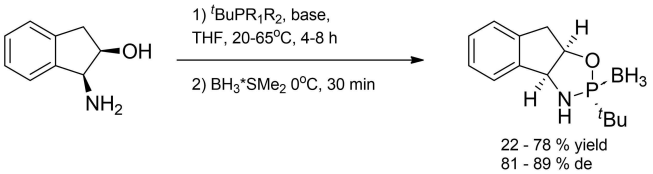
More importantly, the process was run under dynamic thermodynamic epimerization at the phosphorus atom what allowed to obtain one diastereomer exclusively. The amino-alcohol scaffold used in this transformation had few advantages



Scheme 1. Method for the synthesis of chiral phosphine derivatives developed by Jugé et al.

so the other research groups quickly adopted this methodology for the synthesis of other structural motifs possessing P-stereogenic phosphorus atom. One more important improvement was introduced later on followed papers by Jugé and co-workers: borane as protective group for phosphorous stereocenter became an integral part of this methodology.[4] Riera and Verdaguer have recently reported several papers describing attempted construction of chiral phosphines starting from chiral aminoalcohol attached via nitrogen atom (Scheme 2).[5]

Richter has reported that (L)-prolinol is an effective chiral auxiliary able to differentiate P-epimers of organophosphorous compounds. Despite its great utility,[6] prolinol was scarcely used for chiral resolution of racemic mixtures of compounds with stereogenic center located at phosphorous atom.[7] Even though that the synthesis of P-chiral scaffolds raised on prolinol



Scheme 2. Condensation of (1S,2R)-cis-1-amino-2-indanol with *tert*-butyl-phosphine derivatives.

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is easy, only a few more reports form Buono and Jugé research groups were published in past.[8]

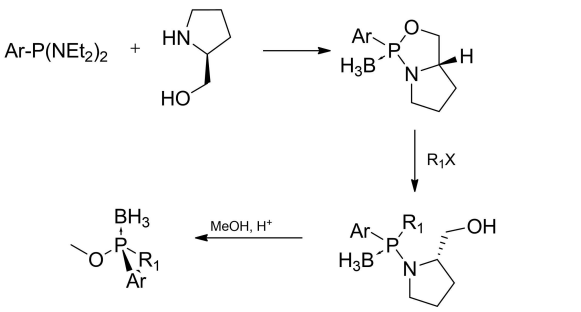
Discussed literature records strongly rely on the formation of rigid oxazaphospholidine scaffold. The conformational stability of formed 5-membered heterocyclic structure is beneficial for forecoming ring opening with a nucleophile, determining the direction of nucleophile attack. The chemoselectivity of P–O vs P–N bond cleavage is also a very useful advantage of this type compounds comparing them to eg. chiral diol-based phosponates. An ease access to prolinol, obtained from cheap and abundant proline, makes this approach even more attractive because of formation of fused 5-membered rings. Therefore, we decided to determine the effectiveness of this chiral auxiliary in the synthesis of P-stereogenic phosphines and their derivatives.

Herein, we would like to present our results concerning the synthesis of P-stereogenic oxazaphospholidines and their borane derivatives along with their applications in the synthesis and catalysis.

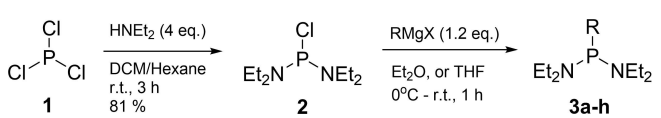
Results and Discussion

The basic concept of this research topic was the usage of easily accessible reagents, available in large amounts, allowing to obtain preparative quantities of P-chiral compounds (Scheme 3). Here the designed synthetic path starts from PCl_3, and leads through phosphonous acid amide, which in an exchange reaction with (*L*)-Prolinol defines a space orientation of substituents. Intended complexation of electron lone pair located at phosphorous atom, with borane, prevents the oxidation as well as locks the stereogenic center in defined configuration.

Afore mentioned phosphorous trichloride was a precursor which should undergo double P–N bond formation prior to the reaction with organometallic compound (Scheme 4).



Scheme 3. General concept for possessing P-stereogenic compounds derived from (L)-Prolinol.



Scheme 4. Synthesis of a starting material.

Reaction of PCl_3 with excess of secondary amine should lead to the appropriate diamidophosphorous acid chloride which upon treatment with a Grignard reagent afforded the corresponding (aryl/alkyl)phosphonous acid diamide. The latter should undergo transamidation reaction with L-proline leading to desired bicyclic oxazaphospholidines. A simple reaction of PCl_3 with organometallic species could be an alternative to the proposed pathway although it is generally difficult to avoid the formation of R_2PCl species in a reaction between organometallic reagent and PCl_3. Separation of $RPCl_2$ and R_2PCl usually is a complicated process due to high reactivity of products and similar properties.

According to the scheme discussed above, PCl_3 was subjected to a reaction with 4-fold excess of diethylamine which led to the formation of bis(*N,N*-diethylamino) chlorophosphine **2** in good yield. Compound **2** has been subjected in the next step to a reaction with a set of different organometallic compounds (Table 1).

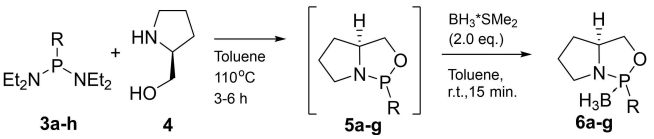
Generally, a reaction of Grignard reagents with 2 proceeded efficiently affording the appropriate (aryl/alkyl)phosphonous acid diamides in fair to good yields. The lower yields of **3b**, **3e** and **3f** may be associated with steric hindrance induced by incoming nucleophile. Best proof for that hypothesis is observed with a failed formation of mesityl-substituted **3g**.

In the next step, transamidation reaction between (*L*)-prolinol and a set of phosphonous diamides was attempted (Scheme 5, Table 2).

It appeared that in most of cases the formation of desired product occurred quantitatively, as judged by ^{31}P NMR analysis of the reaction mixture (Figure 1). Only in a case of mesityl derivative there was no reaction at all, probably due to a high steric hindrance caused by two *ortho*-methyl substituents. A consistent observation was noted by Mezetti and co-workers, where the bulky *ortho*-substituted lithiated arenes were non-reactive towards the oxazaphospholidine-boranes derived from ephedrine, modification of synthetic route resulted successful transformation in their case.[9] Unfortunately in our instance this procedure was not effective. Once the transamidation reaction was completed, BH_3*SMe_2 complex was added in order to fix

Table 1. Yields of isolated phosphonous diamides.

Compound	R=	Yield
3a	*p*-Tol	98
3b	*o*-An	43
3c	1-Nph	83
3d	*t*-Bu	99
3e	*c*-Hex	37
3f	*c*-Pent	67
3g	Mesityl	47



Scheme 5. Synthesis of oxazaphospholidine boranes.

Table 2. Yields of isolated oxazaphospholidine-boranes (**6a**–**g**).

R=	Yield (conv.)	$[\alpha]_D$= (c = in $CHCl_3$) [de]
p-Tol (**6a**)	100(100) [32%[a]]I	+123,1; (1,0) [100%de]
o-An (**6b**)	32(100)	+87,1; (1,145) [100%de]
1-Nph (**6c**)	14(100)	+49,5; (1,0) [100%de]
t-Bu (**6d**)	7(100)	+76,6; (1,325) [100%de]
c-Hex (**6e**)	36(100)	+66,9; (1,925) [100%de]
c-Pent (**6f**)	51(100)	+73,9; (0,955) [100%de]
Mesityl (**6g**)	0(0)	–[b]

[a] Yield of collected crystal. [b] No new signals in ^{31}P NMR was observed, substrate remained unreacted.

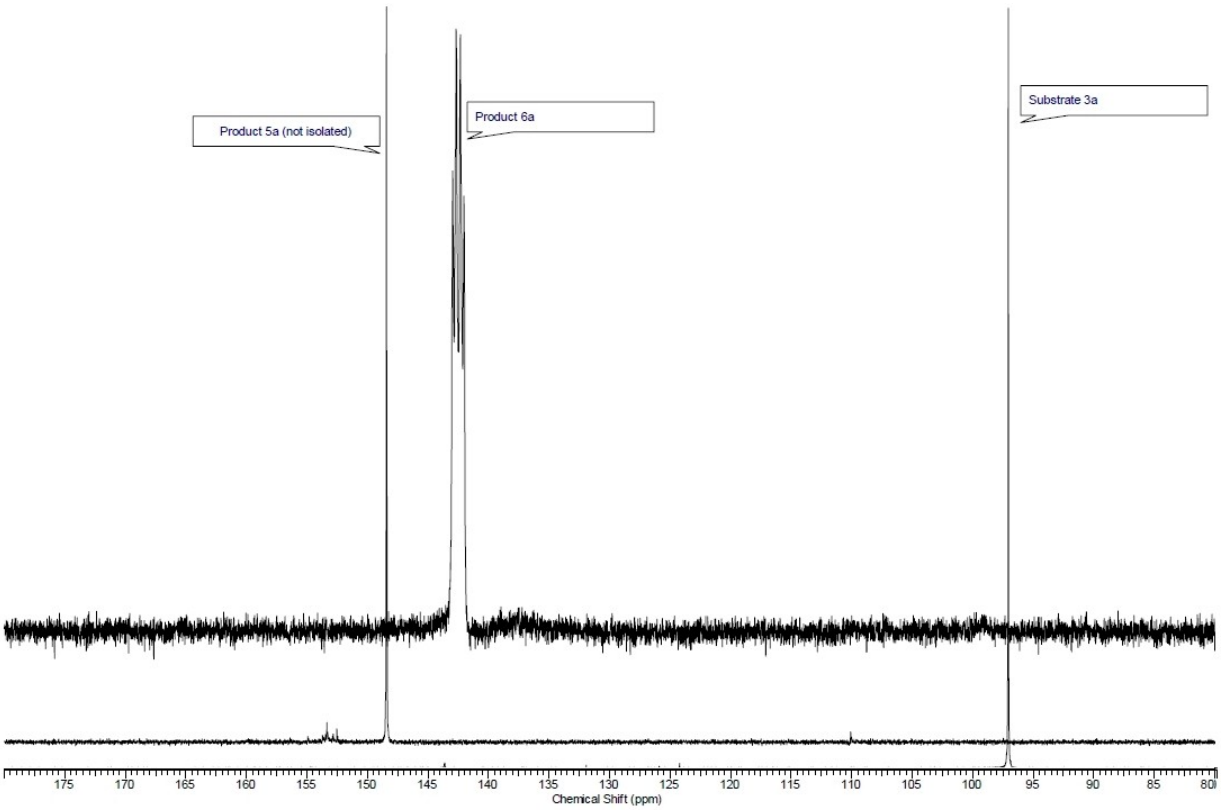


Figure 1. ^{31}P NMR signals of respective compounds leading to formation of compound **6a**.

the configuration at phosphorus but also to prevent the oxidation of phosphorous atom. Final products were isolated from the reaction mixtures with moderate yields, probably due to partial decomposition during chromatographic purification. Only one of them (**6a**) formed crystals suitable for an X-ray structure analysis which allowed to determine the absolute configuration at phosphorus atom as R_P (Figure 2).

Preparation of oxazaphospholidine-borane with confirmed configuration allowed us to perform a quick look at the P–O bond cleavage with strong carbon nucleophiles.(Scheme 6) This would allow to obtain the appropriate P-stereogenic phosphinous acid-borane amides in a non-racemic form provided by the S_N2 mechanism. Already published reports are ambiguous in their claims about obtained optical purity. Most of authors declare that the phosphorus stereogenic center sustains its

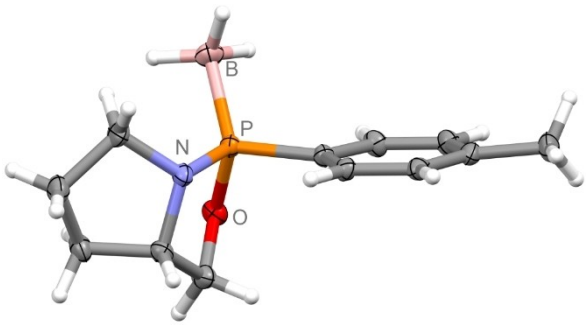
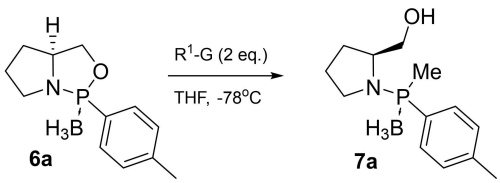


Figure 2. Perspective view of molecular structure of $(R)_P$-**6a**. Elipsoids are at 50% probability level.

optical purity during the nucleophilic substitution reaction, however in few reports partial racemization was noticed.[10] First, a short screen over different organometallic reagents was run in order to find the most effective nucleophile for this transformation. León, Riera and Verdaguer reported an opening of hindered oxazaphospholidine rings by nucleophilic substitution of P–O bond with several organometallic reagents. In most cases they observed a loss of diastereomeric excess to ca. 92% de. The ephedrine-derived oxazaphospholidine-borane undergoes organolithium compounds substitution in a diastereoselective manner preserving optical purity, thus we have decided to try this procedure with our substrates.[8,10] In many literature reports describing P–O bond cleavage via nucleophilic substitution of chiral oxazaphospholidines boranes only a slight drop of optical purity was recorded.[8] (Table 3).

From a set of tested organometallic reagents organolithium compounds provided the most satisfying results (Table 3, **7a** and **7aa**). With methyllithium, the yield of **7a** was found to be 78% and the reaction appeared to proceed with complete stereospecificity. With phenyllithium the stereospecificity was preserved albeit with lower yield of the product. Organozinc compounds failed to give the desired substitution products, same as Grignard reagents. On the other hand, treatment of **6a** with methylmagnesium bromide in toluene afforded the corresponding **7a** albeit in low yield and with a significant loss of stereochemical information at phosphorus atom. Further experiments showed that the reaction with phenyllithium was possible only with **6a** and other analogues were completely non-reactive. The same situation was observed with *t*-butyllithium as nucleophile but, here, the steric crowd created by alkyl group may play a crucial role.

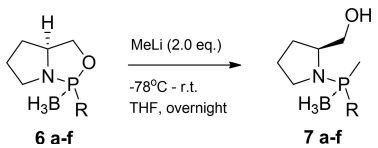


Scheme 6. Cleavage of P–O bond with various organometallic reagents.

Table 3. Yields of P–O bond cleaving products.

Product	R=	Yield
7a	$Zn(Me)_2$	0
7a	$Zn(Et)_2$	0
7a	*i*-PrMgCl*LiCl	0
7a	MeMgBr	0
7a	MeMgBr[a]	37 (dr 5:2)
7a	MeLi	78
7aa	PhLi	60
7ab	*t*-BuLi	0

[a] Reaction was run in toluene in 100 °C.



Scheme 7. Cleavage of P–O bond with methyllithium in **6**.

The optimized conditions for P–Me bond formation were applied for a set of previously obtained oxazaphospholidine-boranes **6a–g** (Scheme 7, Table 4).

It appeared that only a substrate possessing *p*-tolyl substituent (**7a**) underwent a reaction with methyllithium stereospecifically and with good yield (Table 4). Other substrates underwent substitution reaction less efficiently or failed to provide a product at all. This was the case for **6d** with bulky *t*-butyl substituent at phosphorus. This substituent most probably create too high steric crowd around the electrophilic phosphorus center thus the substrate becomes unreactive under these conditions. For compounds possessing less bulky *c*-hexyl and *c*-pentyl substituents attached to phosphorus (**6f** and **6g**, respectively) the reaction proceeds with modest effectiveness and the stereospecificity of the reaction is not complete. Interestingly, a compound possessing smaller *c*-pentyl substituent (**6g**) afforded the product with lower stereospecificity than the compound with larger c-hexyl group (**6f**). Compounds with o-anisyl substituent (**6b**) afforded product with modest yields and remarkable erosion of enantiomeric purity at phosphorus center. Only in case of oxazaphospholidine-boranes possessing *p*-tolyl and 1-naphtyl substituents at phosphorus products were obtained with acceptable yields and with almost complete retention of configuration at phosphorus.

In situ generated phosphineoxazoline (**5a**) was selected as model substrate to perform reactions at tri-coordinated phosphorus atom. Michaelis-Arbusov was chosed as a test reaction. Publications form Jugé and co-workers reports that analogous compounds derived from ephedrine afforded good yields but with loss of optical purity at phosphorous.[6] Additional experiments, performed with compound **5a**, mostly afforded complex mixtures of undefined products, which after isolation and purification were obtained in trace amounts. Although the Michaelis-Arbusov reaction was described by Buono and co-worker with similar structures,[7,11] many attempts performed in our case gave poor results with complex reaction mixtures or with traces amounts of products

This situation was observed in Michaelis-Arbusov reaction with methyl iodide. (Scheme 8) Also, reactions of tricoordinated oxazaphospholidine with organometallic reagent such as methyl lithium and methyl magnesium bromide afforded the same effects.

Table 4. Yields of products of P–O bond substitution with methyllithium.

Product R=	Yield (de)	$[\alpha]_D$ (c, $CHCl_3$)
p-Tol (**7a**)	78 (100%de)	−16,5 (1,075)
o-An (**7b**)	31 (62%de)	−1,01 (1,05)
1-Nph (**7c**)	56 (98%de)	−3,35 (1,105)
t-Bu (**7d**)	0[a]	–
c-Hex (**7e**)	34 (98%de)	−6,15 (1,3)
c-Pent (**7f**)	47 (85%de)	+1,44 (1,45)

[a] No product was observed

Replacement of alkoxy group by an alkyl group can be also accomplished via a sequence of P–O bond cleavage with alkali metals in liquid ammonia[12] followed by an alkylation with an alkyl halide. The same set of substrates was therefore submitted to a reaction with lithium in liquid ammonia followed by a reaction with methyl iodide as an electrophile (Scheme 9, Table 5). Products were obtained with poor yields and, even more sadly, almost complete racemization was detected.

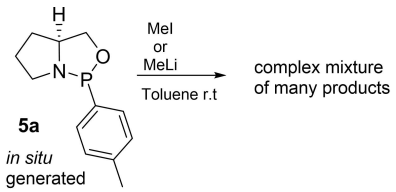
It was surprising to conclude that P–O bond cleavage by methyllithium led to diastereomerically pure compounds in only two cases. These results are quite interesting as usually a cleavage of P–O bond proceeds with high degree of stereospecificity.[12,13] It is difficult to conclude now, what is the reason of such a behavior as the structure of the substrate seems to lack any special interactions in the molecule.

Compounds obtained in the above sequence were transformed into phosphinous acid-borane methyl esters by a reaction with methanol in the presence of sulfuric acid (Scheme 10, Table 6).

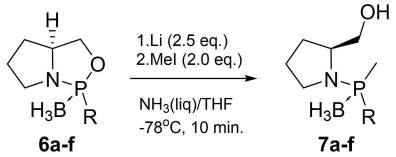
Attempted synthesis of methyl esters **8** has been performed as these compounds are convenient precursors for the synthesis of chiral phosphine-boranes. Some loss of optical purity was detected for compounds **8a** and **8c** whereas for **8e** and **8f** the determination of enantiomeric excess was impossible by chromatographic methods. All this caused that only one proved experiment revealing the effectiveness of complete transformation from oxazaphosphoborolidine to chiral phosphine-borane has been successfully completed (Scheme 11).

Albeit prolinol proved high effectiveness in differentiating P-epimers, utility in further processes was much lower than expected. A set of in situ prepared single diastereomers of phoshinooxazolines were applied as ligands for asymmetric hydrogenation of α-acetamidocinnamic acid methyl ester (Scheme 12) and imine hydrogenation (Scheme 13).

Catalytic asymmetric hydrogenation reactions performed with several ligands (**5a–f**) showed mostly good selectivity



Scheme 8. Attempts for P-3 coordinated **5a** and methyl reagents.

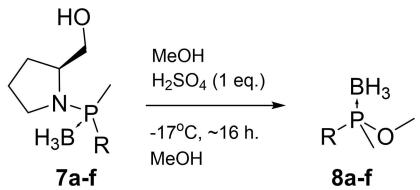


Scheme 9. Sequence of reduction of P–O bond with alkaline metal in liquid ammonia, followed by alkylation.

Table 5. Yields of reduction-alkylation sequence products.

Product	R=	Yield (de)
7a	*p*-Tol	46 (26% de)
7b	*o*-An	14 (100% de)
7c	1-Nph	12 (10% de)
7d	*t*-Bu	13 (12% de)[a]
7e	*c*-Hex	12 (44% de)
7f	*c*-Pent	21 (50% de)

[a] O-Methylated product was yielded.

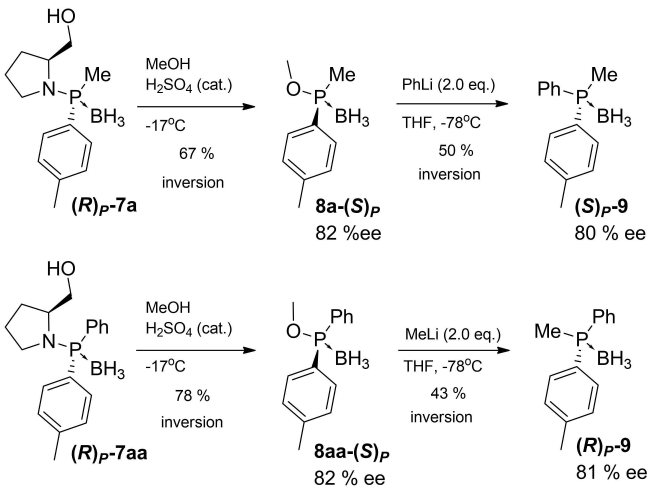


Scheme 10. Synthesis of methylphosphinite boranes (**8a–f**).

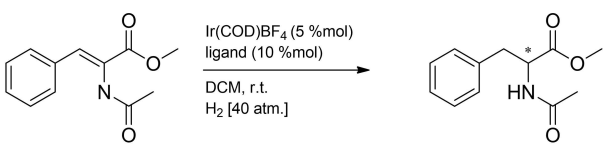
Table 6. Isolated yields of **8a**, **8c**, **8e**, and **8f**.

Product	R=	Yield [%] ee
8a	*p*-Tol	67 (82% ee)
8c	1-Nph	25 (89% ee)
8e	*c*-Hex	25 (unknown)[a]
8f	*c*-Pent	33 (unknown)[a]

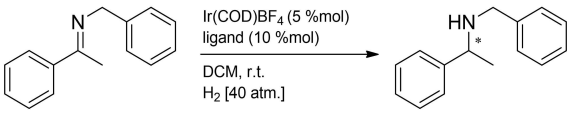
[a] Compounds do not absorb an UV-Vis spectrum, no signals were detected on HPLC with UV-Vis detector.



Scheme 11. Synthesis of both enantiomers of methylphenyl(p-tolyl) phosphine-borane (**9**).



Scheme 12. Catalytic asymmetric hydrogenation of α,β-unsaturated ester.



Scheme 13. Imine catalytic asymmetric hydrogenation with various ligands.

Table 7. α,β-Unsaturated ester catalytic asymmetric hydrogenation with various ligands.

Ligand	R=	Conversion	*ee* [%][a]
5a	*p*-Tol	100	86 (*S*)
5b	*o*-An	100	83 (*S*)
5c	1-Nph	100	85 (*S*)
5e	*c*-Hex	100	79 (*S*)
5f	*c*-Pent	100	86 (*S*)
(*R*)$_P$-9	*p*-TolPhPMe	100	3(*R*)

[a] Absolute configuration was assigned with chiral stationary phase HPLC Daicell OJ-H column.

leading to individual enantiomers of hydrogenated products with moderate to high *ee* values (Table 7). Considering that the reaction conditions were adopted strictly from literature without optimization, these results are optimistic towards further trials. A narrow distribution of ee values suggest that the asymmetric outcome of the reaction depends in major from the structure of the ligand. In case of asymmetric hydrogenation of imine (Scheme 13, Table 8) the enantiomers differentiation was highly dependent from substituent at phosphorus atom. Bulky substituents gave higher ee's of the appropriate amine. We omitted obvious experiments with ligands cluched with *t*-butyl substituent, because after many unsuccessful attempts, we decided to give up and summarize our efforts without this representative.

Conclusion

We have proved that the L-prolinol is an easily avialable chiral auxiliary with a great efficiency for diastereoselective differentiation of organophosphorus compounds. Difficult processing of P–O and P–N bond cleavage were observed forcing us to explore a field of catalysis with oxazaphospholidines as chiral ligands. The results of test reactions were not outstanding but did not discouraged us from applying those ligands to better fitted reactions. Also, protection of phosphorous atom with BH_3 group is not the best solution in here, thus essential modifications of presented methodology are necessary and will be described in further reports.

Experimental Section

General Remarks: All reactions were carried out under an argon atmosphere using Schlenk techniques. Only dry solvents were used, and glassware was heated under vacuum before use. All chemicals were used as received unless otherwise noted. Solvents for chromatography and crystallization were distilled once before use,

Table 8. Imine catalytic asymmetric hydrogenation with various ligands.

Ligand	R=	Conversion	*ee* [%][a]
5a	*p*-Tol	100	2 (*R*)
5b	*o*-An	100	8 (*S*)
5c	1-Nph	100	79 (*S*)
5e	*c*-Hex	100	83 (*S*)
5f	*c*-Pent	100	3 (*S*)
(*R*)$_P$-9	*p*-TolPhPMe	100	2(*R*)

[a] Absolute configuration was assigned with chiral stationary phase HPLC.

and solvents for extraction were used as received. Tetrahydrofuran and diethyl ether were dried by distillation from sodium/benzophenone ketyl.

NMR spectra were recorded with Bruker Ascend (500 MHz) spectrometer at room temperature using $CDCl_3$ as a solvent. Chemical shifts (δ) are reported in ppm, and spectra were calibrated using residual solvent peaks. High Resolution Mass spectra were recorded with a Shimadzu IT-TOF spectrometer in electrospray ionization (ESI). Optical rotations were masured with Perkin-Elmer Polarimeter with sodium lamp (λ = 589 nm). Thin-layer chromatography (TLC) was carried out with precoated silica gel plates, which were visualized using UV light or $KMnO_4$ solution. Reaction mixtures were purified by column chromatography on silica gel (60–240 mesh). The intensities of X-ray diffraction reflections for **6a** were measured at 120(2) K with a SuperNova diffractometer equipped with a microfocus X-ray source (Cu-Kα, λ = 1.54184 Å) and a CCD (charge-coupled device) detector. The CRYSALIS program system was used for data collection, cell refinement, and data reduction. The data were corrected for Lorentz and polarization effects. A multi-scan absorption correction was applied. The structure was solved by direct methods implemented in the SHELXS-97 program, and refined with SHELXL-97.

Chlorophosphonic acid bis(N,N)-diethylamide (**2**) prepared according to Gilson B. H. et al. *Canad. J. Chem.* **2007**, 1045–1052, and Qin L. et al. *Angew. Chem Int. Ed.* **2012**, 5915–5919. Analytical data were in accordance with previously reported.

(*L*)-Prolinol (**4**) was prepared from (*L*)-Proline according to patent WO 2006/025920. Analytical data are in accordance with previously reported in literature.

General procedure for synthesis of phosphonic acid bis(*N,N*)-diethylamides:

In a flame dried, argon filled 2 neck 250 mL flask equipped with a stirring bar, 50 mL of dry THF was placed. Chlorophosphonic acid bis(*N,N*)-diethylamide (**2**) was added to the solvent and flask was chilled in acetone/CO_2 bath. Previously prepared Grignard reagent (2.0 equivalent) was added via canula to stirred solution in a period of ca. 5 minutes. After the addition was complete flask was left to stir in a room temperature overnight. The solution was filtered under inert atmosphere through glass frit, solvent was evaporated and the resulting oli was distilled on a short path apparatus under reduced pressure.

p-Tollylphosphonic acid bis(N,N)-diethylamide (**3a**). Prepared according to general procedure from *p*-TollylMgBr (30 mmol), and 2 (25 mmol) after distillation (120-125 °C @ 2mmHg) yielded 6,52 g (98 % 24,5 mmol) as bright yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 1.13 (t, J = 7.1 Hz, 12 H), 2.37 (s, 3 H), 3.06–3.16 (m, 8 H), 7.15–7.21 (m, 2 H), 7.32–7.37 (m, 2 H) ppm. **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 97.24 ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 14.57 (d, J = 3.6 Hz), 21.14, 42.67 (d, J = 17.3 Hz), 128.91 (d, J = 3.6 Hz), 130.95 (d, J =

16.3 Hz), 136.91, 138.44 (d, J=4.5 Hz) ppm. Other data are in accordance with reported in literature.[14]

o-Anisylphosphonic acid bis(N,N)-diethylamide (**3b**). Prepared according to general procedure from *o*-AnisylMgBr (30 mmol), and 2 (25 mmol) after distillation (143 °C @ 2mmHg) yielded 3.03 g (43% 10.7 mmol) as colourless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 1.07–1.14 (m, 12 H), 2.99–3.13 (m, 8 H), 3.82 (s, 3 H), 6.79–6.86 (m, 1 H), 6.93–7.00 (m, 1 H), 7.25–7.32 (m, 1 H), 7.35–7.40 (m, 1 H) ppm. **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 89.54 ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 14.66 (d, J = 2.7 Hz), 43.22 (d, J = 18.2 Hz), 54.79, 109.68, 120.17, 129.10 (d, J = 1.8 Hz), 129.62 (d, J = 9.1 Hz), 131.70 (d, J = 5.4 Hz), 160.04 (d, J = 16.4 Hz) ppm. Other data are in accordance with reported in literature.[14]

1-Naphtylphosphonic acid bis(N,N)-diethylamide (**3c**). Prepared according to general procedure from 1-NphMgBr (30 mmol), and **2** (25 mmol) after distillation (157-161 °C @ 2mmHg) yielded 6.27 g (83% 20.7 mmol) as colourless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 1.10 (t, J = 7.1 Hz, 12 H), 3.10–3.19 (m, 8 H), 7.43–7.50 (m, 3 H), 7.65 (s, 1 H), 7.76–7.80 (m, 1 H), 7.81–7.87 (m, 1 H), 8.37–8.43 (m, 1 H) ppm. **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 93.86 ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 14.76 (d, J = 2.7 Hz), 43.62 (d, J = 17.3 Hz), 125.07, 125.42, 126.42, 126.53, 126.85 (d, J = 50.0 Hz), 128.37 (d, J = 1.8 Hz), 128.58 (d, J = 1.8 Hz), 129.00 (d, J = 7.3 Hz), 133.60, 133.77 (d, J = 2.7 Hz). Other data are in accordance with reported in literature.[14]

t-Buthylphosphonic acid bis(N,N)-diethylamide (**3d**). Prepared according to general procedure from *t*-BuMgCl (30 mmol), and **2** (25 mmol) after distillation (90-95 °C @ 2mmHg) yielded 5.75 g (99% 24 mmol) as colourless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 1.05 (t, J = 7.3 Hz, 12 H), 1.08–1.12 (m, 9 H), 3.04–3.12 (m, 8 H) ppm. **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 110.56 ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 14.78 (d, J = 2.7 Hz), 28.56 (d, J = 20.0 Hz), 38.78 (d, J = 20.0 Hz), 44.60 (d, J = 18.2 Hz) ppm. Other data are in accordance with reported in literature.[15]

c-Hexylphosphonic acid bis(N,N)-diethylamide (**3e**). Prepared according to general procedure from *c*-HexMgBr (30 mmol), and **2** (25 mmol) after distillation (120 °C @ 2mmHg) yielded 2,39 g (37% 9 mmol) as colourless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 1.03 (t, J = 7.1 Hz, 12 H), 1.09–1.18 (m, 2 H), 1.19–1.31 (m, 3 H), 1.62–1.75 (m, 3 H), 1.75–1.88 (m, 3 H), 2.93–3.06 (m, 8 H) ppm. **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 98.50 ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 14.51 (d, J = 2.7 Hz), 26.22 (d, J = 13.6 Hz), 26.93 (d, J = 12.7 Hz), 28.58 (d, J = 20.9 Hz), 37.67 (d, J = 6.4 Hz), 42.51 (d, J = 14.5 Hz) ppm. Other data are in accordance with reported in literature.[15]

c-Pentylphosphonic acid bis(N,N)-diethylamide (**3f**). Prepared according to general procedure from *c*-PentMgBr (30 mmol), and **2** (25 mmol) after distillation (105 °C @ 2mmHg) yielded 2.26 g (37% 9.25 mmol) as colourless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 1.01 (t, J = 6.9 Hz, 12 H), 1.39–1.50 (m, 2 H), 1.52–1.60 (m, 2 H), 1.61–1.74 (m, 4 H), 2.36–2.45 (m, 1 H), 2.92–3.06 (m, 8 H) ppm. **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 97.26 ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 14.74 (d, J = 2.7 Hz), 26.82 (d, J = 8.2 Hz), 29.14 (d, J = 26.3 Hz), 34.51 (d, J = 1.8 Hz), 42.54 (d, J = 13.6 Hz) ppm. Other data are in accordance with reported in literature.[11]

General procedure for preparation of oxazaphosphole boranes. In flame dried, argon filled, 10 mL screw cap tube, equipped with stirrer, 1 mmol of various acid bis(N,N)-diethylamide was palced, 1 mmol of (L)-Prolinol and 3–5 mL of toluene were added. After completion of reaction (monitored on NMR) mixture was chilled to room temperature and BH_3*SMe_2 (3 mmol) was slowly added. After about 5 minutes mixture was transferred to separatory funnel and was washed with 2% HCl, next with 5% $NaHCO_3$, and twice with water. Organic phase was separated, dried with $MgSO_4$ and condensed with rotary evaporator to give viscous oil as a product (1R,3aS)-1-(*p*-tolyl)hexahydropyrrolo[1,-2c][1, 3, 2]oxazaphosphole borane (**6a**). Prepared according to general procedure from **3a** (1 mmol), and **4** (1 mmol) after workup yielded 0.2350 g (100% 0.1 mmol) as colourless oil. Resulting oil was dissolved in a mixture of: 4 mL diethyl ether, 4 mL MTBE, 8 mL hexane. Crystallization gave 0.075 g (0.32 mmol) of transparent crystals. **MP** t = 95.2–96.7 °C. **TLC** R_f = 0.34 (hexane-ethyl acetate 10–1). **ORP** $[\alpha]_D$ = + 123.1° (c = 1.0 in $CHCl_3$) **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 0.46–1.13 (m, 3 H), 1.70–1.77 (m, 1 H), 1.91–2.00 (m, 2 H), 2.05–2.13 (m, 1 H), 2.41 (s, 3 H), 3.12–3.20 (m, 1 H), 3.76–3.85 (m, 2 H), 3.88–3.94 (m, 1 H), 4.23–4.29 (m, 1 H), 7.25–7.28 (m, 2 H), 7.63–7.68 (m, 2 H) ppm. **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 141.51 ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 21.55, 26.39 (d, J = 1.82 Hz), 30.51 (d, J = 2.72 Hz), 48.36 (d, J = 6.36 Hz), 62.50 (d, J = 1.82 Hz), 72.08 (d, J = 5.45 Hz), 129.16 (d, J = 10.90 Hz), 130.29 (d, J = 11.81 Hz), 131.21 (d, J = 69.94 Hz), 142.31 (d, J = 1.82 Hz) ppm. **HRMS** [M + MeOH + H] predicted 268.1634 found 268.1629.

Crystal data: crystal system orthorhombic, space group $P2_12_12_1$, unit cell dimensions a = 7.6840(2) Å, b = 11.0636(3) Å, c = 14.9848(3) Å, V = 1273.90(5) Å^3, Z = 4. Independent reflections 2602 [R(int) = 0.0434], parameters 221, Goodness-of-fit on F^2 1.106; final R indices [I > 2σ (I)] R1 = 0.0290, wR2 = 0.0721; R indices (all data) R1 = 0.0341, wR2 = 0.0809. Absolute structure parameter −0.015(12).

(1R,3aS)-1-(*o*-anisyl)hexahydropyrrolo[1,-2c][1,3,2]oxazaphosphole borane (**6b**). Prepared according to general procedure from **3b** (1 mmol), and **4** (1 mmol) after workup yielded 0.0803 g (32% 0.32 mmol) as colourless oil. **TLC** R_f = 0.35(hexane-ethyl acetate 10-1). **ORP** $[\alpha]_D$ = + 87.1° (c = 1.145 in $CHCl_3$) **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 0.45–1.12 (m, 3 H), 1.26 (t, J = 7.3 Hz, 2 H), 1.69 (td, J = 11.7, 6.0 Hz, 1 H), 1.88–1.97 (m, 2 H), 2.01–2.09 (m, 1 H), 2.78–2.90 (m, 1 H), 3.08–3.18 (m, 1 H), 3.78 (dd, J = 14.5, 7.6 Hz, 1 H), 3.85 (td, J = 11.3, 5.4 Hz, 1 H), 3.91 (s, 2 H), 4.30 (dd, J = 14.9, 8.7 Hz, 1 H), 6.93 (dd, J = 8.2, 4.7 Hz, 1 H), 6.99 (t, J = 7.4 Hz, 1 H), 7.46 (t, J = 7.9 Hz, 1 H), 7.65 (dd, J = 12.3, 7.6 Hz, 1 H) ppm. **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 140.22 ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 11.81, 26.44 (d, J = 1.8 Hz), 30.50 (d, J = 2.7 Hz), 48.03 (d, J = 7.3 Hz), 49.09, 55.90, 62.36 (d, J = 1.8 Hz), 72.58 (d, J = 5.4 Hz), 111.44 (d, J = 5.4 Hz), 120.41, 120.50, 122.39 (d, J = 65.4 Hz), 132.32 (d, J = 10.9 Hz), 133.69 (d, J = 1.8 Hz), 160.85 (d, J = 5.4 Hz) ppm. **HRMS** [M + MeOH + H] predicted 284.1573 found 284.1579.

(1R,3aS)-1-(1-naphtyl)hexahydropyrrolo[1,-2c][1,3,2]oxazaphosphole borane (**6c**). Prepared according to general procedure from **3c** (1 mmol), and **4** (1 mmol) after workup yielded 0.0352 g (14% 0.13 mmol) as colourless oil. **TLC** R_f = 0.34(hexane-ethyl acetate 10–1). **ORP** $[\alpha]_D$ = + 49.5° (c = 1.0 in $CHCl_3$) **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 0.61–1.36 (m, 3 H), 1.69–1.76 (m, 1 H), 1.97–2.04 (m, 2 H), 2.06–2.14 (m, 1 H), 3.34 (ddt, J = 12.5, 10.3, 7.2, 7.2 Hz, 1 H), 3.74–3.81 (m, 1 H), 3.87 (ddd, J = 10.4, 8.8, 6.0 Hz, 1 H), 4.00 (ddt, J = 12.1, 10.5, 6.0, 6.0 Hz, 1 H), 4.12–4.18 (m, 1 H), 7.47–7.63 (m, 3 H), 7.87–7.98 (m, 3 H), 8.54 (d, J = 8.5 Hz, 1 H) ppm. **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 141.23 ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 26.45 (d, J = 2.7 Hz), 30.94 (d, J = 2.7 Hz), 48.29 (d, J = 6.4 Hz), 61.96, 72.23 (d, J = 7.3 Hz), 124.51 (d, J = 10.0 Hz), 126.26, 126.51 (d, J = 6.4 Hz), 126.72, 128.70, 130.19 (d, J = 7.3 Hz), 130.39–131.04 (m), 132.40 (d, J = 13.6 Hz), 132.54 (d, J = 1.8 Hz), 133.70 (d, J = 8.2 Hz) ppm. **HRMS** [M-BH_3 + H] predicted 258.1041 found 258.1042

(1R,3aS)-1-(*t*-butyl)hexahydropyrrolo[1,-2c][1,3,2]oxazaphosphole borane (**6d**). Prepared according to general procedure from **3d** (1 mmol), and **4** (1 mmol) after workup yielded 0.014 g (7% 0.07 mmol) as colourless oil. **TLC** R_f = 0.375(hexane-ethyl acetate 10-1). **ORP** $[\alpha]_D$ = + 76.6° (c = 1.325 in $CHCl_3$)**^{1}H NMR (500 MHz, $CDCl_3$)** δ = 0.10–0.88 (m, 3 H), 1.10 (d, J = 14.8 Hz, 9 H), 1.65–1.71 (m, 1 H), 1.74–1.84 (m, 1 H), 1.88 (s, 1 H), 1.94–2.02 (m, 1 H), 2.91–3.00 (m, 1 H), 3.50 (td, J = 8.7, 2.4 Hz, 1 H), 3.61–3.69 (m, 1 H), 3.80–3.86 (m,

1 H), 4.33 (ddd, J = 15.1, 8.7, 6.5 Hz, 1 H) ppm. **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 167.80 ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 23.71 (d, J = 3.6 Hz), 26.22, 29.33 (d, J = 3.6 Hz), 34.97 (d, J = 40.9 Hz), 48.64 (d, J = 5.4 Hz), 62.83 (d, J = 1.8 Hz), 73.06 (d, J = 4.5 Hz) ppm. **HRMS** [M-BH_3 + H] predicted 188.1197 found 188.1199

(1R,3aS)-1-(*c*-hexyl)hexahydropyrrolo[1,-2c][1,3,2]oxazaphosphole borane(**6e**). Prepared according to general procedure from **3e** (1 mmol), and **4** (1 mmol) after workup yielded 0.0817 g (36% 0.36 mmol) as colourless oil. **TLC** R_f = 0.50(hexane-ethyl acetate 10–1). **ORP** $[\alpha]_D$ = +66.9° (c = 1.952 in $CHCl_3$) **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 0.11–0.78 (m, 3 H), 1.16–1.33 (m, 5 H), 1.54–1.64 (m, 1 H), 1.65–1.73 (m, 2 H), 1.74–1.83 (m, 3 H), 1.84–1.95 (m, 3 H), 1.96–2.04 (m, 1 H), 2.97 (dddd, J = 13.95, 10.64, 9.14, 5.99 Hz, 1 H), 3.52 (td, J = 8.51, 4.10 Hz, 1 H), 3.62 (tdd, J = 11.11, 11.11, 7.41, 3.15 Hz, 1 H), 3.78–3.84 (m, 1 H), 4.28 (ddd, J = 13.24, 8.67, 6.46 Hz, 1 H) ppm. **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 160.89 ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 25.16 (d, J = 12.72 Hz), 25.86 (d, J = 1.82 Hz), 26.06, 26.17 (d, J = 2.72 Hz), 29.59 (d, J = 2.72 Hz), 41.42 (d, J = 43.60 Hz), 48.47 (d, J = 5.45 Hz), 62.44, 72.45 (d, J = 4.54 Hz) ppm. **HRMS** [M + MeOH + H] predicted 260.1952 found 260.1942

(1R,3aS)-1-(*c*-Pentyl)hexahydropyrrolo[1,-2c][1,3,2]oxazaphosphole borane(**6f**). Prepared according to general procedure from **3f** (1 mmol), and **4** (1 mmol) after workup yielded 0.1086 g (51% 0.51 mmol) as colourless oil. **TLC** R_f = 0.34(hexane-ethyl acetate 10-1). **ORP** $[\alpha]_D$ = +73.9° (c = 1.145 in $CHCl_3$) **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 0.14–0.79 (m, 3 H) 1.53–1.60 (m, 2 H) 1.61–1.72 (m, 5 H) 1.75–1.91 (m, 4 H) 2.00 (ddt, J = 12.45, 9.62, 6.94, 6.94 Hz, 1 H) 2.04–2.12 (m, 1 H) 2.97 (dddd, J = 13.95, 10.56, 8.91, 5.99 Hz, 1 H) 3.51–3.57 (m, 1 H) 3.65 (tdd, J = 11.11, 11.11, 7.41, 3.15 Hz, 1 H) 3.80–3.88 (m, 1 H) 4.30 (ddd, J = 13.08, 8.83, 6.46 Hz, 1 H) ppm. **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 162.26 ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 26.07 (d, J = 1.82 Hz) 26.26 (d, J = 6.36 Hz) 26.33 (d, J = 6.36 Hz) 26.57, 26.71 (d, J = 2.72 Hz) 29.65 (d, J = 2.72 Hz) 41.23 (d, J = 45.41 Hz) 48.51 (d, J = 5.45 Hz) 62.48 (d, J = 1.82 Hz) 72.38 (d, J = 5.45 Hz) ppm. **HRMS** [2M + H2O + H] predicted 463.3196 found 463.3186

General procedure for Phosphineoxazolodine ring opening with methyllithium: In a flame dried, argon filled schlenck flask equipped with a magnetic stirrer, the substrate was placed and the flask was deaired with triple vaccum/argon flushing sequence. Next, about 5–10 mL of THF was added and flask was left for several minutes to let the substrate dissolve. Flask was then cooled in dry ice acetone mixture and when it was cold, appropriate volume of MeLi (2 equivalents) solution was added and left to stir overnight (ca. 16 h) and let to warm to room temperature. On a next day, a pinch (about 200 mg) of solid NH_4Cl was added to quench the reaction and was let to stir for about 5 minutes. Solution was then transferred to funnel with celite plug and was filtered from solid residues. Supernatant was then condensed with rotary evaporator and resulted oil was purified with column chromatography with chloroform:methanol 50 : 1 (vol.) as eluent.

P-(S)-((S)-2-(hydroxymethyl)pyrrolidin-1-yl)quinolin-2-ol-*P*-(methyl)-*P*-(4-methylphenyl) Phosphine borane(**7a**). Prepared according to general procedure from **6a** (0.309 mmol), after workup yielded 0.0605 g (78%) as colourless oil. **TLC** R_f = 0.28 (chloroform-methanol 50–1). **ORP** $[\alpha]_D$ = −16.5° (c = 1.075 in $CHCl_3$) **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 0.24–0.93 (m, 3 H) 1.39–1.48 (m, 1 H) 1.52 (d, J = 9.46 Hz, 3 H) 1.54–1.63 (m, 3 H) 1.68–1.95 (m, 1 H) 2.17 (s, 3 H) 2.63–2.71 (m, 1 H) 2.80–2.86 (m, 1 H) 3.21–3.30 (m, 2 H) 3.62–3.70 (m, 1 H) 7.01–7.07 (m, 3 H) 7.29–7.35 (m, 2 H) ppm. **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 55.15 ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 12.04 (d, J = 49.05 Hz) 21.44 (s) 25.06 (d, J = 4.54 Hz) 29.01 (d, J = 4.54 Hz) 47.33 (d, J = 2.72 Hz) 61.13 (d, J = 5.45 Hz) 65.54, 128.43 (d, J = 59.90 Hz) 129.43 (d, J = 9.08 Hz) 130.48 (d, J = 9.99 Hz) 141.53 (d, J = 2.72 Hz) ppm. **HRMS** [M-BH_3 + O + H] predicted 254.1304 found 254.1302

P-(S)-((S)-2-(hydroxymethyl)pyrrolidin-1-yl)quinolin-2-ol-*P*-(phenyl)-*P*-(4-methylphenyl) Phosphine borane(**7aa**). Prepared according to general procedure from **6a** (0.385 mmol), and Phenyllithium (0.769 mmol) after workup yielded 0.0715 g (60%) as colourless oil. **TLC** R_f = 0.41 (chloroform-methanol 50–1). **ORP** $[\alpha]_D$ = −31.6 (c = 0.99 in $CHCl_3$) **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 0.69–1.42 (m, 3 H), 1.61–1.75 (m, 1 H), 1.84–2.00 (m, 3 H), 2.38–2.46 (m, 3 H), 2.88–2.98 (m, 1 H), 3.06–3.15 (m, 1 H), 3.52 (dd, J = 10.9, 6.5 Hz, 1 H), 3.58–3.64 (m, 1 H), 4.04–4.12 (m, 1 H), 7.21–7.32 (m, 3 H), 7.41–7.55 (m, 5 H), 7.55–7.63 (m, 1 H), 7.64–7.71 (m, 2 H) ppm. **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 59.83 ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 21.47, 25.31 (d, J = 4.5 Hz), 28.91 (d, J = 5.4 Hz), 48.45 (d, J = 2.7 Hz), 61.27 (d, J = 6.4 Hz), 65.68–65.82 (m), 115.27, 120.39, 127.13 (d, J = 62.7 Hz), 128.51 (d, J = 10.0 Hz), 128.49 (d, J = 10.0 Hz), 129.27 (d, J = 10.0 Hz), 130.94 (d, J = 2.7 Hz), 131.82 (d, J = 10.9 Hz), 131.94 (d, J = 10.0 Hz), 132.17 (d, J = 10.9 Hz), 132.34 (d, J = 10.0 Hz), 141.66 (d, J = 2.7 Hz) ppm. **HRMS** [M + Na] predicted 336.1656 found 336.1661

P-(S)-((S)-2-(hydroxymethyl)pyrrolidin-1-yl)quinolin-2-ol-*P*-(methyl)-*P*-(1-Naphtyl) Phosphine borane(**7c**). Prepared according to general procedure from **6c** (1.834 mmol), after workup yielded 0.3041 g (56%) as colourless oil. **TLC** R_f = 0.36(hexane-ethyl acetate 2-1). **ORP** $[\alpha]_D$ = −3.35 (c = 1.105 in $CHCl_3$) **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 0.71–1.34 (m, 3 H), 1.58–1.66 (m, 1 H), 1.76–1.91 (m, 4 H), 1.94 (s, 2 H), 2.68–2.75 (m, 1 H), 3.01–3.06 (m, 1 H), 3.37–3.50 (m, 2 H), 4.01–4.07 (m, 1 H), 7.48–7.64 (m, 3 H), 7.75 (ddd, J = 12.7, 7.2, 1.3 Hz, 1 H), 7.89–7.93 (m, 1 H), 7.97–8.01 (m, 1 H), 8.48 (dd, J = 7.4, 0.8 Hz, 1 H) ppm. **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 56.25 (major dia), 59.21 (minor dia) ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 14.08 (d, J = 46.3 Hz), 24.96 (d, J = 5.4 Hz), 28.64 (d, J = 5.4 Hz), 47.23, 61.33 (d, J = 5.4 Hz), 65.52, 124.71 (d, J = 10.9 Hz), 125.82 (d, J = 6.4 Hz), 126.46, 126.88, 128.34 (d, J = 59.9 Hz), 129.11–129.33 (m), 130.87 (d, J = 9.1 Hz), 132.54 (d, J = 1.8 Hz), 133.15 (d, J = 9.1 Hz), 133.77 (d, J = 7.3 Hz) ppm. **HRMS** [M + Na] predicted 310.1500 found 310.1500

P-(S)-((S)-2-(hydroxymethyl)pyrrolidin-1-yl)quinolin-2-ol-*P*-(methyl)-*P*-(*cyclo*-hexyl) Phosphine borane(**7e**). Prepared according to general procedure from **6e** (1.725 mmol), after workup yielded 0.1426 g (34% 0.5868 mmol) as colourless oil. **TLC** R_f = 0.32(toluene-ethyl acetate 9-1). **ORP** $[\alpha]_D$ = −6.15° (c = 1,3 in $CHCl_3$) **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 0.16–0.85 (m, 3 H), 1.17–1.30 (m, 3 H), 1.39 (d, J = 9.5 Hz, 3 H), 1.41–1.50 (m, 2 H), 1.59–1.66 (m, 1 H), 1.67–1.75 (m, 2 H), 1.80–1.97 (m, 8 H), 3.04–3.16 (m, 2 H), 3.40–3.45 (m, 1 H), 3.51–3.56 (m, 1 H), 3.78 (br. s., 1 H) ppm. **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 63.28 ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 11.07 (d, J = 42.7 Hz), 24.93 (d, J = 3.6 Hz), 25.92 (d, J = 13.6 Hz), 26.58 (d, J = 11.9 Hz), 26.63 (d, J = 27.2 Hz), 28.82 (d, J = 4.5 Hz), 35.69 (d, J = 38.1 Hz), 46.04 (d, J = 1.8 Hz), 61.58 (d, J = 4.5 Hz), 65.58 ppm. **HRMS** [M–H] predicted 242.1837 found 242.1849

P-(S)-((S)-2-(hydroxymethyl)pyrrolidin-1-yl)quinolin-2-ol-*P*-(methyl)-*P*-(*cyclo*-pentyl) Phosphine borane(**7f**). Prepared according to general procedure from **6f** (2.375 mmol), and **4** (1 mmol) after workup yielded 0.2558 g (47% 1.116 mmol) as colourless oil. **TLC** R_f = 0.39(hexane-ethyl acetate 2-1). **ORP** $[\alpha]_D$ = +1.44° (c = 1.455 in $CHCl_3$) **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 0.15–0.80 (m, 3 H), 1.39 (d, J = 9.1 Hz, 3 H) major dia, 1.46 (d, J = 9.1 Hz, 3 H) minor dia, 1.53–1.62 (m, 2 H), 1.62–1.68 (m, 1 H), 1.68–1.79 (m, 6 H), 1.79–1.96 (m, 5 H), 2.29–2.43 (m, 1 H), 3.06–3.18 (m, 2 H), 3.41–3.48 (m, 1 H), 3.49–3.54 (m, 1 H), 3.77–3.85 (m, 1 H) ppm. **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 65.8 ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 12.39 (d, J = 42.7 Hz), 24.98 (d, J = 3.6 Hz), 26.54 (d, J = 7.3 Hz), 26.64, 27.13 (d, J = 2.7 Hz), 27.69 (d, J = 4.5 Hz), 28.84 (d, J = 4.5 Hz), 35.05 (d, J = 40.0 Hz), 46.32, 61.36, 65.51 ppm. **HRMS** [M–H] predicted 228.1680 found 228.1684

General procedure for P–O bond cleavage with alkali metals in liquid ammonia: 50 mL 2-neck flask equipped with a stirrer was flame dried and argon filled and was left with argon overpressure (ballon or manifold). Next the dry ice coldfinger condenser was placed on one neck, and flask was placed in cooling bath with dry ice CO2 mixture. Coldfinger was loaded with CO_2/acetone mixture and gaseous ammonia hose was attached to condenser. After 5–10 mL of liquid ammonia was collected, Ammonia source was disconnected and vessel was sealed. Next alkali metal was put into a liquid ammonia and was left to stir for 5 minutes to form deep blue colour of solution. After that time, substrate dissolved in 5 mL of dry THF was added via syringe and was left to react for 5 minutes. After 5 minutes MeI (ca. 10 equiv.) was added with syringe and mixture was left for stir for 10 minutes. Addition of a pinch (ca 0.2 g) of NH_4Cl quenched the residual anion and then solution was transferred on a rotary evaporator to get rid of NH_3. Product was then dissolved in DCM and filtered through a plug of celite and again condensated in vacuo. The resulting oil was analysed and if necessary purified on collumn chromatography on silica gel with hexanes-ethyl acetate 2-1 as an eluent.

P-(S)-(2-(hydroxymethyl)pyrrolidin-1-yl)quinolin-2-ol-*P*-(methyl)-*P*-(2-methoxyphenyl) Phosphine borane(**7b**). Prepared according to general procedure from **6b** (0.5 mmol), after workup yielded 0.0187 g (14% 0.07 mmol) as colourless oil. **TLC** R_f = 0.19(hexane-ethyl acetate 2-1). **ORP** $[\alpha]_D = -1.90°$ (c = 1.05 in CHCl3) **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 0.49–1.14 (3 H, m), 1.69–1.78 (2 H, m), 1.81 (3 H, d, J = 9.5 Hz), 1.82–1.91 (2 H, m), 1.91–2.04 (1 H, bm), 3.08–3.14 (1 H, m), 3.15–3.22 (1 H, m), 3.36–3.41 (1 H, m), 3.46–3.50 (1 H, m), 3.80–3.87 (1 H, m), 3.90 (3 H, s), 6.94–6.97 (1 H, m), 7.02–7.06 (1 H, m), 7.45–7.49 (1 H, m), 7.69–7.74 (1 H, m) ppm. **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 55.77 ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 12.36 (d, J = 47.2 Hz), 25.49 (d, J = 4.5 Hz), 29.28 (d, J = 4.5 Hz), 48.29, 55.50, 60.79 (d, J = 3.6 Hz), 65.31 (d, J = 1.8 Hz), 111.17 (d, J = 4.5 Hz), 120.42 (d, J = 55.4 Hz), 121.00 (d, J = 10.9 Hz), 133.24 (d, J = 1.8 Hz), 133.88 (d, J = 11.8 Hz), 160.79 ppm. **HRMS** [M + Na] predicted 290.1449 found 290.1446

P-(S)-(2-(methoxymethyl)pyrrolidin-1-yl)quinolin-2-ol-*P*-(methyl)-*P*-(1-*t*-Butyl) Phosphine borane(**7d**). Prepared according to general procedure from **6d** (0.9529 mmol), after workup yielded 0.0271 g (13%) as colourless oil. **TLC** R_f = 0.72(hexane-*i*-PrOH-chloroform 10-1-1). **ORP** $[\alpha]_D = -41.46$ (c = 1.365 in $CHCl_3$) **^{1}H NMR (500 MHz, $CDCl_3$)** δ = ppm 0.21–0.90 (m, 3 H), 1.16 (d, J = 13.9 Hz, 3 H) (major dia), 1.17 (d, J = 13.9 Hz, 3 H) (minor dia), 1.36 (d, J = 8.5 Hz, 1 H) (major dia), 1.43 (d, J = 8.8 Hz, 1 H) (minor dia), 1.68–1.75 (m, 1 H) (mixed), 1.79–1.93 (m, 4 H) (mixed), 3.05–3.15 (m,1 H) (mixed), 3.18 (dd, J = 9.3, 8.4 Hz, 1 H) (minor dia), 3.24 (dd, J = 9.5, 7.6 Hz, 1 H) (major dia), 3.35 (s, 1 H) (major dia), 3.35 (s, 1 H) (minor dia), 3.39 (dd, J = 9.5, 3.8 Hz, 1 H) (major dia), 3.51 (dd, J = 9.3, 4.3 Hz, 1 H) (minor dia), 3.79–3.85 (m, 1 H) (minor dia), 4.00–4.07 (m, 1 H) (major dia). **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 72.4 (major dia),72.3 (minor dia) ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 6.80 (d, J = 38.1 Hz) (minor dia), 7.94 (d, J = 42.7 Hz) (major dia), 23.71 (d, J = 3.6 Hz) (major dia), 24.72 (d, J = 3.6 Hz) (minor dia), 25.71 (d, J = 2.7 Hz) (major dia), 26.00 (d, J = 2.7 Hz) (minor dia), 26.16 (d, J = 3.6 Hz) (major dia), 28.08 (d, J = 1.8 Hz) (major dia), 28.30 (d, J = 5.4 Hz), 28.87 (d, J = 4.5 Hz) (minor dia), 32.79 (d, J = 42.7 Hz), 33.93 (d, J = 32.7 Hz) (minor dia), 48.36 (s), 48.80 (d, J = 3.6 Hz) (minor dia), 58.82 (d, J = 7.3 Hz) (mixed), 59.15 (d, J = 6.4 Hz), 59.48 (d, J = 4.5 Hz) (minor dia), 75.00 (minor dia), 76.15 (major dia) ppm. **HRMS** [M–H] predicted 230.1837 found 230.1836

General procedure for the synthesis of methylphosphinite boranes amide (**8a–h**): In a flame dried, argon filled flask substrate (0.1 mmol) was placed, 5 mL of dry methanol was added to vessel, and next concentrated sulfuric acid (0.1 mmol) was added with micropipete. Flask was closed with a glass stopper and was placed in a freezer (−17 °C) for 48 hours. After that time, small amount of K_2CO_3 was added to quench the reaction. Supernatant was filtered through plug of cellite filtrate was concentrated on rotary evaporator and purified on chromatography column with hexane: chloroform:methanol 50:50:1 as an eluent.

(*S*)-*p*-Tollylmethyl boranephosphinous acid methyl ester (**8a**). Prepared according to general procedure from **7b** (1 mmol), after workup yielded 0.1219 g (67% 0.670 mmol) as colourless oil. **TLC** R_f = 0.52(hexane-ethyl acetate 10-1). **HPLC** 82%ee Daicell OJ–H (4.5 × 250 mm); 99:1 hexane:*i*-PrOH; 1 mL/min t_R = 12.5 min and t_R = 14.2 min. **ORP** $[\alpha]_D = +83.3°$ (c = 1.64 in $CHCl_3$) (82%ee). **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 0.44–1.13 (m, 3 H), 1.70 (d, J = 9.1 Hz, 3 H), 2.42 (s, 3 H), 3.55 (d, J = 12.3 Hz, 3 H), 7.32 (d, J = 7.6 Hz, 2 H), 7.64–7.74 (m, 2 H) ppm. **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 112.40(m) ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 16.02 (d, J = 47.2 Hz), 21.61, 53.48 (d, J = 2.7 Hz), 128.63 (d, J = 41.8 Hz), 129.51 (d, J = 10.0 Hz), 130.80 (d, J = 11.8 Hz), 142.81 (d, J = 1.8 Hz) ppm. **HRMS** [M-BH_3 + O + Na] predicted 207.0545 found 207.0545

(*S*)-Phenyl-*p*-Tollyll boranephosphinous acid methyl ester (**8aa**). Prepared according to general procedure from **7aa** (1.478 mmol), after workup yielded 0.2813 g (78%) as colourless oil. **TLC** R_f = 0.58(hexane-ethyl acetate 10-1). **HPLC** 82%ee Daicell AS–H (4.5 × 250 mm); hexane:MeOH:*i*-PrOH 98:1:1; 0.25 mL/min t_R = 23.2 min and t_R = 23.9 min **ORP** $[\alpha]_D = +8.3°$ (c = 0.965 in $CHCl_3$) **^{1}H NMR (500 MHz, $CDCl_3$)** δ = ppm 0.67–1.42 (m, 3 H), 2.40 (s, 3 H), 3.73 (d, J = 12.0 Hz, 3 H), 7.28 (d, J = 8.5 Hz, 2 H), 7.42–7.48 (m, 2 H), 7.48–7.55 (m, 1 H), 7.64 (dd, J = 10.4, 8.2 Hz, 2 H), 7.73 (dd, J = 9.9, 8.7 Hz, 2 H) ppm. **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 107.21 ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 21.57 (s), 53.94 (d, J = 2.7 Hz), 128.10 (d, J = 64.5 Hz), 128.58 (d, J = 10.9 Hz), 129.41 (d, J = 10.9 Hz), 131.17 (d, J = 11.8 Hz), 131.38 (d, J = 10.9 Hz), 131.74 (d, J = 2.7 Hz), 131.81 (d, J = 64.5 Hz), 142.52 (d, J = 1.8 Hz) ppm. H**RMS** [2M-BH3 + O + Na] predicted 515.1512 found 515.1518 Other data are in accordance with reported in literature.[16]

(*S*)-1-Naphtylmethyl boranephosphinous acid methyl ester (**8c**). Prepared according to general procedure from **7b** (1 mmol), after workup yielded 0,057 g (25% 0.2614 mmol) as colourless oil. **TLC** R_f = 0.70 (hexane-chloroform-methanol 50-50-1). **ORP** $[\alpha]_D = +36.08$ (c = 1.02 in $CHCl_3$) **HPLC** 89%ee Daicell OJ–H (4.5 × 250 mm); 95:5 hexane:*i*-PrOH; 0.5 mL/min t_R = 24.4 min and t_R = 25.3 min **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 0.65–1.33 (m, 3 H), 1.94 (d, J = 9.1 Hz, 3 H), 3.57–3.65 (m, 3 H), 7.52–7.68 (m, 3 H), 7.96 (d, J = 8.2 Hz, 1 H), 8.03–8.08 (m, 1 H), 8.22 (ddd, J = 15.9, 7.1, 0.9 Hz, 1 H), 8.51 (dd, J = 8.4, 1.1 Hz, 1 H) ppm. **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 116.67 ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 15.81 (d, J = 51.8 Hz), 53.59 (d, J = 3.6 Hz), 124.85 (d, J = 14.5 Hz), 125.26 (d, J = 4.5 Hz), 126.32–126.49 (m), 127.02 (d, J = 48.1 Hz), 127.56, 129.38–129.52 (m), 132.67 (d, J = 2.7 Hz), 133.62, 133.65 (d, J = 2.7 Hz), 134.86 (d, J = 20.0 Hz) ppm. **HRMS** [2M-BH3 + O + Na] predicted 463.1199 found 463.1187

(*S*)-cyclo-Hexylmethyl boranephosphinous acid methyl ester (**8e**). Prepared according to general procedure from **7e** (1 mmol), after workup yielded 0,057 g (25% 0,2614 mmol) as colourless oil. **TLC** R_f = 0.85(toluene-ethyl acetate 10-1). **ORP** $[\alpha]_D = -2.3°$ (c = 0.95 in $CHCl_3$) **HPLC** enatiomeric excess was not determinated, compound does not absorb an UV-Vis radiation **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 0.14–0.77 (m, 3 H), 1.19–1.36 (m, 5 H), 1.40 (d, J = 8.8 Hz, 3 H), 1.69–1.77 (m, 2 H), 1.85 (d, J = 4.7 Hz, 2 H), 1.88–1.96 (m, 2 H), 3.63 (d, J = 11.3 Hz, 3 H) ppm. **^{31}P NMR (202 MHz, $CDCl_3$)** δ = 126.36 ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 11.05 (d, J = 39.1 Hz), 25.24, 25.32, 25.84, 26.29 (d, J = 15.4 Hz), 26.29 (d, J = 9.1 Hz), 37.97 (d, J = 41.8 Hz), 54.10 (d, J = 3.6 Hz) ppm. **HRMS** [2M-BH3 + O + Na] predicted 463.1199 found 463.1187(*S*)-cyclo-Pentylmethyl boranephosphinous acid methyl ester (**8f**). Prepared according to general procedure from **7f** (1 mmol), after workup yielded 0.0528 g (33%,

0.33 mol) as colourless oil. **TLC** $R_f = 0.49$(hexane:ethyl acetate 10:1). **ORP** $[\alpha]_D = +2{,}6$ (c = 1 in $CHCl_3$) **HPLC** enatiomeric excess was not determinated, compound does not absorb an UV-Vis radiation **^{1}H NMR (500 MHz, $CDCl_3$)** $\delta = 0.13$–0.77 (m, 3 H), 1.42 (d, J = 8.8 Hz, 3 H), 1.57–1.79 (m, 6 H), 1.83–1.91 (m, 2 H), 2.10–2.19 (m, 1 H), 3.63 (d, J = 11.3 Hz, 3 H) ppm. **^{31}P NMR (202 MHz, $CDCl_3$)** $\delta =$ 127.22 ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** $\delta = 12.39$ (d, J = 39.06 Hz), 26.43 (d, J = 20.89 Hz), 26.76 (d, J = 2.72 Hz), 37.94 (d, J = 43.60 Hz), 54.01 (d, J = 3.63 Hz) ppm. **EA** calculated: C 55.52 H 11.34 O 10.00 found: C 55.49 H 11.36 O 10.05.

General procedure for the synthesis of tertiary Phosphineboranes

In a flame dried, argon filled schlenck flask equipped with a magnetic stirrer, the substrate was placed and the flask was deaired with triple vaccum/argon flushing sequence. Next, about 5 mL of THF was added and flask was left for several minutes to let the substrate dissolve. Flask was then cooled in dry ice acetone mixture and when it was cold, appropriate volume of organolithium reagent (2 equivalents) solution was added and left to stir overnight (ca. 16 h) and let to warm to room temperature. On a next day, a pinch (about 200 mg) of solid NH_4Cl was added to quench the reaction and was let to stir for about 5 minutes. Solution was then transferred to funnel with celite plug and was filtered from solid residues. Supernatant was then condensed with rotary evaporator and resulted oil was purified with column chromatography with chloroform:methanol 50:1 (vol.) as eluent.

Methylphenyl-*p*-tollyl phosphine borane (**9**). Prepared according to general procedure from **8aa** (1.478 mmol), after workup yielded 0.1449 g (43%) as colourless oil. **TLC** $R_f = 0.58$(hexane-ethyl acetate 10–1). **HPLC** Daicell OJ-H (4.5×250 mm); 99:1 hexane:*i*-PrOH; 1 mL/min $t_R = 37.0$ min and $t_R = 40.0$ min. Daicell OD–H (4.5×250 mm); 99:1 hexane:iPrOH; 1 mL/min $t_R = 8.16$ min and $t_R = 8.61$ min **^{1}H NMR (500 MHz, $CDCl_3$)** $\delta = 0.64$–1.33 (m, 3 H), 1.85 (d, J = 10.1 Hz, 3 H), 2.39 (s, 3 H), 7.24–7.29 (m, 2 H), 7.41–7.51 (m, 3 H), 7.56 (dd, J = 10.6, 8.0 Hz, 2 H), 7.62–7.68 (m, 2 H) ppm. **^{31}P NMR (202 MHz, $CDCl_3$)** $\delta = 9.21$(m) ppm. **^{13}C NMR (126 MHz, $CDCl_3$)** $\delta = 12.02$ (d, J = 41.8 Hz), 21.47, 126.88 (d, J = 58.1 Hz), 128.77 (d, J = 10.0 Hz), 129.61 (d, J = 10.9 Hz), 130.94 (d, J = 56.3 Hz), 131.00 (d, J = 2.7 Hz), 131.64 (d, J = 9.1 Hz), 131.78 (d, J = 10.0 Hz), 141.62 (d, J = 1.8 Hz) ppm. **HRMS** [2M-BH3 + O + Na] predicted 483.1613 found 483.1605 Other data are in accordance with reported in literature.[17]

General procedure for catalytic hydrogenation : In a flame dried argon filled, equipped with a stirrer Schlenck flask 0.1 mmol of proper phosphonic acid bis(*N,N*)-diethylamide (**3a–f**) was placed with proline (**4**) (0.1 mmol) and 5 mL of toluene. Flask was heated at 110 °C for about 16 hours to complete exchange of diamide (monitored with ^{31}P NMR). Next the reaction was evaporated till dryness with vacuum pump to dispose of toluene and amine, and residual oil was dissolved in 10 mL of dry and degassed dichloromethane. In a second flame dried argon filled Schlenck flask 0.025 mmol (0.0167 g) of $[Ir(COD)Cl]_2$ was placed and 5 mL of dry and degassed dichloromethane was added to flask, then vessel was cooled in acetone/dry ice bath. To cold mixture (0.05 mmol, 0.010 g) of $AgBF_4$ was added and mixture was stirred for 30 minutes in −78 °C. From first flask 5 mL of solution was taken with syringe and was added to second Schlenck flask and was left to stir for additional 30 minutes in −78 °C. 10 mL volume of second flask contains 0.05 mmol of catalyst as a solution in dichloromethane, necessary amount of catalyst can be easily calculated. In a glass vial α-Acetamidocinnamic acid methyl ester(0.2 mmol, 0.044 g) or 1-phenyl-N-(1-phenylethylidene)methanamine (0.2 mmol, 0.042 g) was placed and vial was flushed with argon. From second Schlenck flask 2 mL of solution of catalyst was transferred with a syringe to vial, and vial was placed in autoclave and was pressurized with 40 bar of Hydrogen. After 24 hours solution from vial was filtered through a plug of celite evaporated and analyzed with chiral stationary phase HPLC to determinate enantiomeric excess.

Deposition Number 2038641 (for **6a**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Chiral phosphorous · Phosphine boranes · Phosphineoxazolines · Prolinol

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