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Diastereoselective desymmetrization of diarylphosphinous acid-borane amides under Birch reduction†

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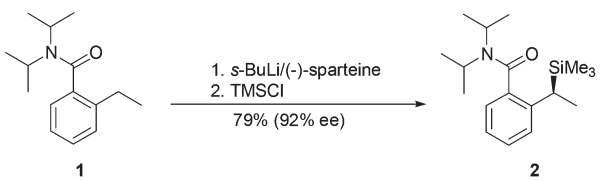
Treatment of diarylphosphinous acid-borane amides possessing chiral amido functionality with an alkali metal solution in liquid ammonia induced a preferential dearomatization of one aryl substituent at phosphorus leading to the formation of non-equimolar amounts of diastereomers. Diastereoselectivity of dearomatization depends strongly on the structure of a chiral auxiliary.

Introduction

Desymmetrization of non-chiral symmetrical substrates is one of the most convenient methods for the synthesis of chiral molecules. This process is based on the stereoselective transformation of a symmetrical fragment by a chiral reagent. The prominent example of such a reagent is a combination of a organolithium reagent and (−)-sparteine which is used for stereoselective deprotonation of prochiral groups or hydrogen atoms (Scheme 1).[1]

In organophosphorus chemistry this approach has found some applications, especially for the synthesis of *P*-stereogenic compounds in a non-racemic form. Deprotonation of one of the methyl groups in dimethylphenyl-phosphine-borane with a chiral base followed by the addition of an electrophile led to the formation of **4** with good yield and enantioselectivity (Scheme 2).[2]

This methodology was applied for the synthesis of many *P*-chiral organophosphorus compounds, including secondary phosphine-boranes,[3] MiniPHOS ligands,[4] proline analogues,[5] 1-phenyl-phosphol-2-ene-borane[6] or PHOX-type ligands.[7]



1 **2**

Scheme 1 Desymmetrization of amide **1**.

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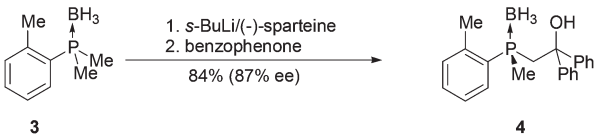
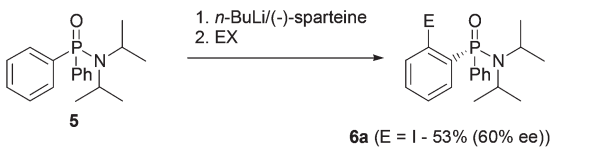


3 **4**

Scheme 2 Desymmetrization of phosphine-borane **3**.

The main feature of all the examples discussed above is that desymmetrization of organophosphorus compounds is affected through the transformation of alkyl groups. But, when considering the applications of organophosphorus compounds in the synthesis and catalysis a lot of examples of $Ph_2P(X)$-substituted compounds (X = lone pair, BH_3, O, S) could be found in the literature. Regarding all the above, these compounds could serve as excellent precursors for the preparation of *P*-stereogenic organophosphorus compounds through selective functionalization of one aryl moiety.

Desymmetrization of the $Ph_2P(X)$ fragment was a topic of several studies. Williams and coworkers used desymmetrization of diphenylphosphinic amides through the Directed *ortho*-Metallation (D*o*M) strategy in the synthesis of *P*,*P*-ligands.[8] A good example of the stereoselective desymmetrization of the $Ph_2P(O)$ moiety in phosphinic amides using the same approach was presented by Lopez Ortiz and coworkers (Scheme 3).[9]



5

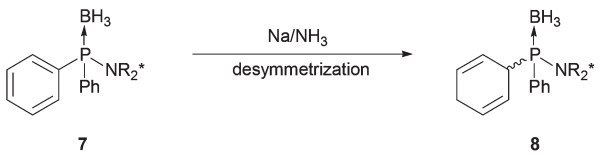
6a (E = I - 53% (60% ee))
6b (R = Me - 83% (59% ee))
6c (R = PPh_2 - 75% (55% ee))

Scheme 3 Desymmetrization of diphenylphosphinic amide **5** using (−)-sparteine.

The same authors attempted the desymmetrization of the $Ph_2P(O)$ fragment in diphenylphosphinic amides with chiral amido functionality using the Directed *ortho*-Metallation (D*o*M) methodology.[10] The diastereoselectivity level reached the highest 5 : 1 ratio when triphenyltin chloride was used as an electrophile. All this lead to the conclusion that despite the limited number of precedences the synthesis of *P*-stereogenic organophosphorus compounds through desymmetrization of the $Ar_2P(X)$ moiety seems to have high synthetic potential.

In the course of our studies on the use of Birch reduction in organophosphorus chemistry[11] we attempted the dearomatization of phosphinic acid amides and phosphinous acid-borane amides.[12] Whereas diarylphosphinic amides tend to undergo double Birch reduction of two arenes, dearomatization of diarylphosphinous acid-borane amides led preferentially to the formation of products with only one reduced aryl substituent.

Our observations lead to the conclusion that Birch reduction could be successfully applied for the synthesis of *P*-stereogenic organophosphorus compounds as dearomatization of symmetrically substituted diarylphosphinous acid-borane amides should lead to the formation of a new compound with a chirality centre at the phosphorus atom (Scheme 4).



Scheme 4 Desymmetrization of diphenylphosphorus acid amides **7**.

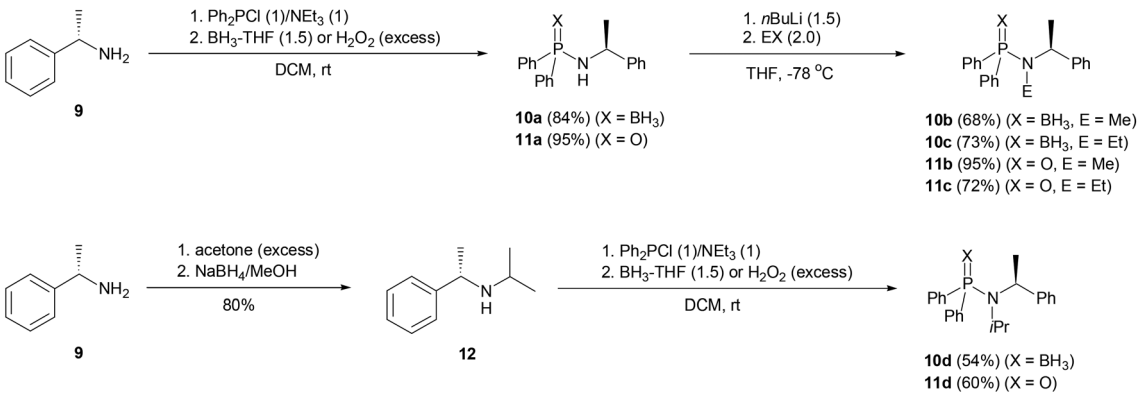
However, to achieve the transformation in a stereoselective manner an additional source of chirality is needed and the easiest way to fulfill this requirement is to use chiral amido functionality. Regarding the size of the reagent (an electron) the formation of an equimolar mixture of diastereomers is expected and a careful separation of both isomers is needed to get access to pure *P*-stereogenic compounds.

Results and discussion

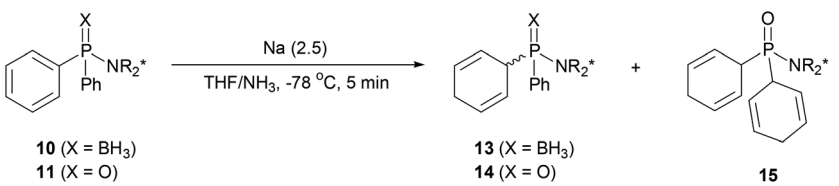
For initial screening, (*S*)-α-methylbenzylamine **9** was chosen as a chiral amine (Scheme 5).

Treatment of **9** with the Ph_2PCl–NEt_3 mixture followed by the addition of either the BH_3 complex or H_2O_2 led to the formation of **10a** and **11a** in good yields. These compounds were then used as substrates for the synthesis of *N*-methyl and *N*-ethyl derivatives **10b,c** and **11b,c** by treatment with a strong base followed by the addition of the corresponding alkyl halide. *N*-Isopropyl substituted amides **10d** and **11d** were obtained by a slightly different method. Treatment of **9** with an excess of acetone led to the formation of the corresponding imine which was *in situ* treated with $NaBH_4$ yielding a secondary amine **12** in good yield. Furthermore, a treatment of **12** with the Ph_2PCl–NEt_3 mixture followed by the addition of either the BH_3 complex or H_2O_2 led to **10d** and **11d**, respectively.

To get insight into the desymmetrization process Birch reduction of the obtained compounds was performed (Scheme 6, Table 1).



Scheme 5 The synthesis of (*S*)-α-phenylethylamine-derived diphenylphosphorus amides.

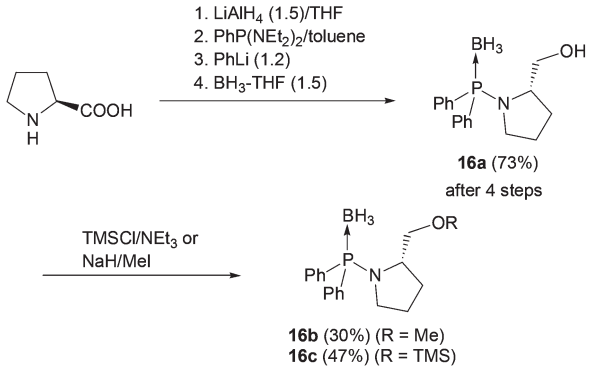


Scheme 6 Initial desymmetrization experiments.

Table 1 Dearomatization of **10** and **11**

Nr	Compound	NR_2*	Products (de)
1	**10a**	(*S*)-NHCHMePh	No reaction
2	**10b**	(*S*)-N(Me)CHMePh	**13b** (71%, 52% de)
3[a]	**10b**	(*S*)-N(Me)CHMePh	**13b** (76%, 72% de)
4[b]	**10b**	(*S*)-N(Me)CHMePh	**13b** (20%, 60% de)
5	**10c**	(*S*)-N(Et)CHMePh	**13c** (77%, 42% de)
6	**10d**	(*S*)-N(iPr)CHMePh	**13d** (21%, 10% de)
7	**11a**	(*S*)-NHCHMePh	No reaction
8[c]	**11b**	(*S*)-N(Me)CHMePh	**14b** (20%, 0% de)/**15b** (50%)
9[c]	**11c**	(*S*)-N(Et)CHMePh	**14c** (18%, 0% de)/**15c** (24%)
10[c]	**11d**	(*S*)-N(iPr)CHMePh	**14d** (14%, 9% de)/**15d** (24%)

[a] The reaction was performed at −97 °C. [b] The reaction was performed at −115 °C. [c] The yields of the products were assigned based on NMR analysis.



Scheme 7 The synthesis of L-prolinol-derived phosphorus acid amides.

It was found that amides **10a** and **11a** remained intact under the reaction conditions which could be attributed to the presence of an acidic amide proton in both substrates. The use of higher excess of an alkali metal led to the decomposition of the starting material. On the other hand, *N*-alkyl-substituted amides **10b–d** smoothly underwent Birch reduction of only one phenyl substituent yielding mixtures of two diastereomers. Regarding the size of the reagent (an electron) we rather expected the formation of an equimolar mixture of two diastereomers but to our surprise the obtained products were enriched in one diastereomer (Table 1, entries 2–6). In the case of *N*-methyl substituted amide **10b** Birch reduction led to the formation of a product with the highest diastereoselectivity (52% de) under the standard reaction conditions. The diastereoselectivity of the reaction could be additionally improved by lowering the temperature (Table 1, entry 3) but further cooling led to solidification of ammonia which impeded the reaction rate and diastereoselectivity (Table 1, entry 4). A further increase in the steric crowd at nitrogen by replacing the methyl group with ethyl or *i*-propyl groups dropped the diastereoselectivity of dearomatization down to 10% de in the case of **10d** (Table 1, entry 6).

In contrast to phosphinous acid-borane amides **10b–d**, attempted Birch reduction of phosphinic amides **11b–d** led predominantly to the formation of double Birch reduction products **15b–d**. This observation is in accordance with previous results obtained with racemic diarylphosphinic amides.[12] The minor single Birch reduction products obtained from **11b–d** were generally equimolar mixtures of diastereomers. Such a striking difference in the behavior of phosphinous acid-borane amides **10b–d** and phosphinic amides **11b–d** must evolve from different organizations of two phenyl substituents in **10** and in **11**. In **10**, there must be an interaction between the chiral amido group and two phenyls which lead to differentiation of SOMO+1 orbitals of both phenyl groups. Interestingly, there is no such differentiation in phosphinic amides **11**, which means that the presence of the P═O bond perturbs the interaction between the amido group and the aryl substituent.

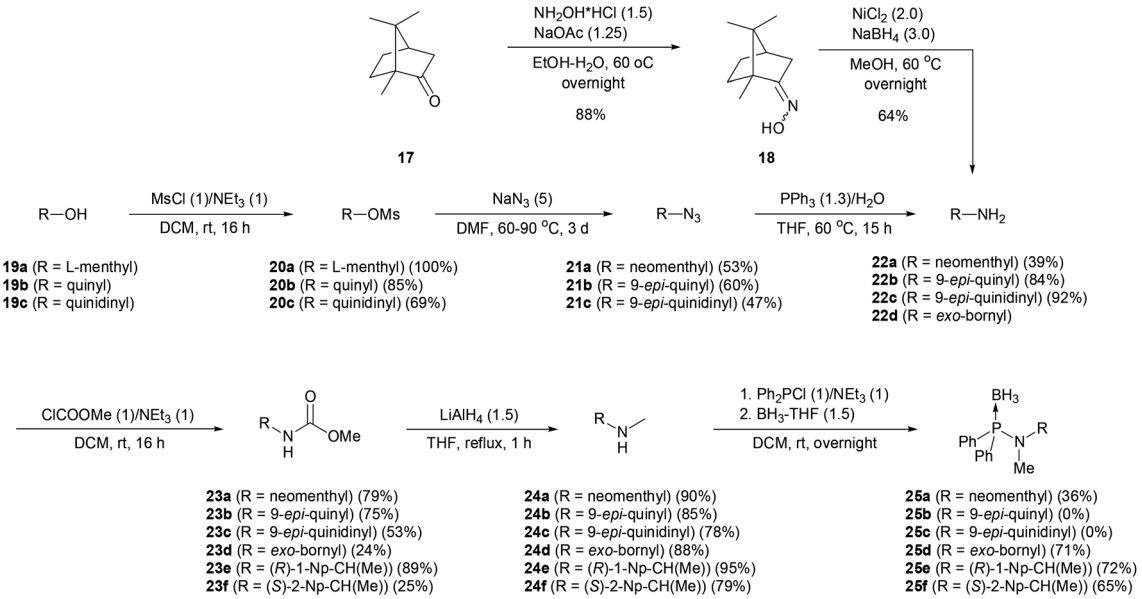
The diastereoselectivity of this desymmetrization could be possibly raised by the modification of a chiral auxiliary at nitrogen. Regarding this, we attempted to prepare a set of diphenylphosphinous acid-borane amides possessing different amido functions.

L-Prolinol-derived phosphinous acid-borane amides have been prepared in a few step synthesis starting from L-proline (Scheme 7).

A reduction of this amino acid with $LiAlH_4$ led to a corresponding aminoalcohol which upon treatment with $PhP(NEt_2)_2$ yielded a bicyclic oxazaphospholane as a single diastereomer. Its reaction with phenyllithium followed by the addition of the BH_3 complex led to the formation of **16a** in 73% yield after 4 steps. The free OH group in **16a** was further protected either with methyl (**16b**) or trimethylsilyl (**16c**) groups yielding new *C*-chiral phosphinous acid-borane amides.

Other compounds have been prepared in a common synthetic pathway which included the preparation of primary *C*-chiral amines in the first step (Scheme 8).

An amine **22d** has been prepared in a two-step synthesis from camphor **17**. First, ketone was treated with hydroxylamine hydrochloride and the obtained oxime **18** was further treated with $NaBH_4$ in the presence of $NiCl_2$. The product was obtained as a mixture of two isomers in a 1 : 0.2 ratio in favor of an *exo* isomer. Amines **22a–c** derived from L-menthol **19a**, quinine **19b** and quinidine **19c** were obtained in a three-step synthesis. First, three alcohols were transformed into the corresponding mesylates which were further treated with sodium azide yielding azides **21a–c**. Azide–amine group transformation was achieved using the Staudinger reaction. A prepared set of four amines plus two commercially available α-(1-naphthyl)ethylamine and α-(2-naphthyl)ethylamine were further subjected to the reaction with methyl chloroformate and the products were treated with $LiAlH_4$ yielding the corresponding secondary *N*-methylamines **24a–f**. In the final step amines have been reacted with the Ph_2PCl–NEt_3 mixture followed by the addition of the BH_3 complex leading to the formation of the desired diphenylphosphinous acid-borane amides **25a,d–f**. In the case of **25b** and **25c** the formation of a complex mixture of products was observed. Amide **25d** was prepared from a 1 : 0.2 mixture of *exo*-/*endo*-bornylamine as a 1 : 0.4 mixture of isomers. An attempted separation of diaster-



Scheme 8 Preparation of phosphinous acid-borane amides.

eomers yielded only a partially enriched mixture (dr = 1 : 0.1) which was used in the desymmetrization reaction.

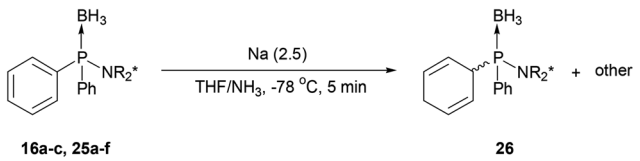
A prepared set of diphenylphosphinous acid-borane amides has been subjected to dearomatization reaction (Scheme 9, Table 2).

First, L-prolinol-derived phosphinous acid amides **16a–c** have been subjected to a reaction with sodium in liquid ammonia. Similar to the previous observations, an attempted Birch reduction of **16a** possessing an acidic hydrogen atom failed to produce the desired product. Protected amides **16b,c** underwent Birch reduction yielding the desired products in both low yields and diastereoselectivities (Table 2, entries 2 and 3). The diastereoselectivity of reduction of **16b** and **16c** was markedly lower than that for **10b**, probably due to the small difference in both substituents at nitrogen. Additionally, in the case of **16c** the formation of secondary phosphine-borane **27** was observed. Similarly, *N*-neomenthyl-derived amide **25a** poorly underwent Birch reduction under the standard reaction conditions (Table 2, entry 4) but the use of a higher excess of sodium improved the conversion remarkably (Table 2, entry 5). In the latter example the formation of *H*-phosphinous acid-borane amide **28** was observed as well. This compound could be formed through competitive P-aryl bond cleavage reaction. The diastereoselectivity of desymmetrization of **25a** was moderate (22–23% de) and surprisingly there was no selectivity in the formation of *H*-phosphinous acid-borane derivative **28**. Similarly, a treatment of *N*-bornyl-substituted amide **25d** with an excess of sodium in liquid ammonia led to the formation of *H*-phosphinous acid-borane amide **29** as the main product and the Birch reduction product **26d** as the minor compound (Table 2, entry 6). Both products were obtained with moderate diastereoselectivities but the diastereomeric excess of **29** was slightly higher.

A much more complex reaction was Birch reduction of amides **25e** and **25f** possessing naphthyl moieties in the amide fragment (Table 2, entries 7–10). In both cases the reaction with sodium in liquid ammonia led to the formation of complex reaction mixtures. The naphthalene unit present in the substrates undergoes most probably Birch reduction along with dearomatization of one of the phenyl groups at phosphorus. This process generates two additional chirality centers (at phosphorus and at carbon atoms) leading to a complex mixture of compounds. The use of higher excess of sodium led to decomposition of substrates and the formation of P–H-type compounds ($Ph_2P(BH_3)H$ for **25e** and P–H amides (58.90 ppm and 59.68 ppm) for **25f**).

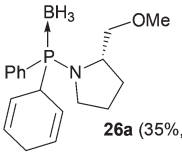
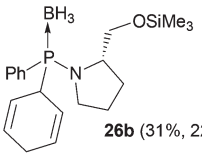
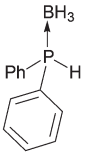
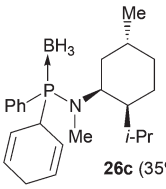
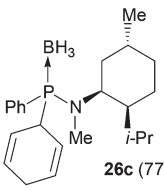
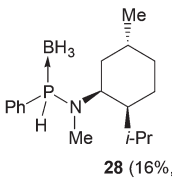
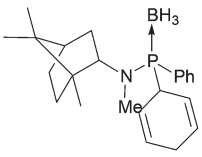
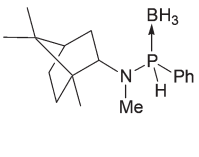
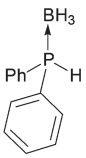
Unfortunately, despite many attempts, α-methylbenzylamine remained the best chiral auxiliary for desymmetrization of diphenylphosphinous acid-borane amides through Birch reduction. A replacement of this functionality with those derived from prolinol, L-menthol or camphor failed to improve the diastereoselectivity of the desymmetrization reaction.

In the next step, desymmetrization of other symmetrically substituted diarylphosphinous acid-borane amides has been attempted. Two types of symmetrical secondary phosphine oxides were chosen. The first type (oTol$_2$P(O)H, pTol$_2$P(O)H, pAn$_2$P(O)H) constitutes the molecules possessing either unsymmetrically substituted arene substituents or arene substituents possessing *para*-substituted aryls. Birch reduction of amides derived from these substrates should lead to the for-



Scheme 9 Desymmetrization of **16a–c** and **25a–f**.

Table 2 Desymmetrization of **16a–c** and **25a–f**

Nr	Substrate	Products
1	**16a**	No reaction
2	**16b**	 **26a** (35%, 54% de)
3	**16c**	 **26b** (31%, 22% de)[a]  **27** (13%)[a]
4	**25a**	 **26c** (35%, 22% de)
5[b]	**25a**	 **26c** (77%, 23% de)[a]  **28** (16%, 0% de)[a]
6[b]	**25d**	 **26d** (33%, 38% de)[a]  **29** (42%, 42% de)[a]
7	**25e**	A mixture of products (69.15 ppm, 70.94 ppm, 72.66 ppm and 73.16 ppm)
8[c]	**25e**	 **27** (36%)[a] and other products
9	**25f**	A mixture of products (71.41 ppm, 72.45 ppm and 74.69 ppm)
10[c]	**25f**	A mixture of products (58.90 ppm, 59.68 ppm, 71.41 ppm, 72.45 ppm and 74.69 ppm)

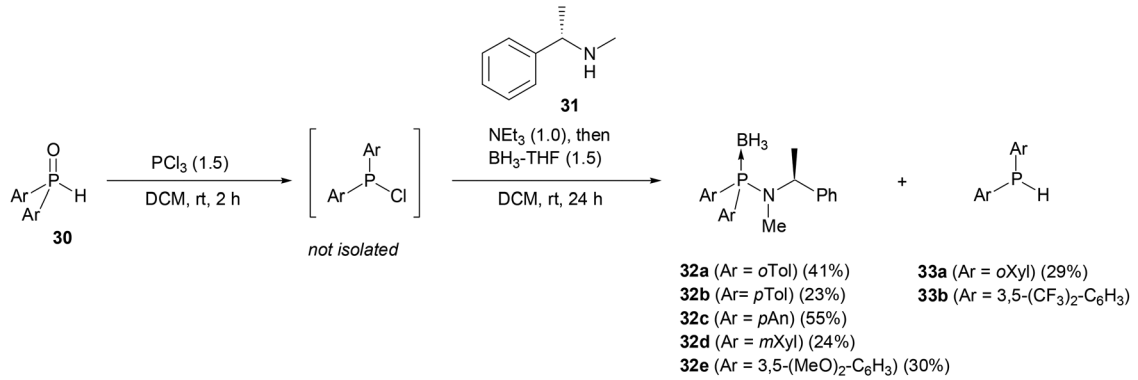
[a] Isolated as a mixture of products. [b] 4.0 equiv. of sodium was used. [c] 5.0 equiv. of sodium was used.

mation of up to 8 isomers. The second type (*m*Xyl$_2$P(O)H, (3,5-(MeO)$_2$-C$_6$H$_3$)$_2$P(O)H, *o*Xyl$_2$P(O)H, (3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_2$P(O)H) constitutes the molecules with symmetrical aryl substituents. Birch reduction of amides derived from these oxides should yield mixtures of two diastereomers only.

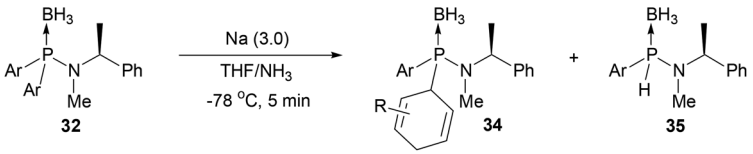
The substrates for test reactions were prepared from secondary phosphine oxides by treatment with PCl_3, followed by the addition of a chiral amine–NEt_3 mixture and then the BH_3–THF complex (Scheme 10).

Generally, products **32** were obtained in moderate yields which could be attributed to the difficulties with the preparation of chlorophosphines. Additionally, *o*Xyl$_2$P(O)H and (3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_2$P(O)H failed to produce the corresponding amides **32**. Instead, secondary phosphines **33** were observed which could arise from P–Cl bond reduction by borane. In the case of *o*Xyl$_2$P(O)H lack of the reactivity might arise from the steric crowd around phosphorus generated by four methyl groups at the *ortho* position. Compound **33a** appeared to be sufficiently stable to resist oxidation during chromatographic purification.

The obtained set of symmetrically substituted diarylphosphinous acid-borane amides has been subjected to the reaction with sodium in liquid ammonia (Scheme 11, Table 3).



Scheme 10 Synthesis of diarylphosphinous acid-borane amides.



Scheme 11 Desymmetrization of **32**.

Table 3 Desymmetrization of **32**

Nr	Compound	Products[a]
1	**32a**	**34a** (21%) 4 isomers (30:11:40:19)
2	**32b**	**34b** (76%) *trans*:*cis* = 53:47 de_{trans} = 44% de_{cis} = 44%
3	**32c**	**34c** (38%) de = 58%
4	**32d**	**34d** (43%) de = 37% **35a** (15%) de = 30%
5	**32e**	**34e** (11%) de = 50% **35b** (17%) de = 30%

[a] In brackets, yields based on NMR analysis are presented.

Scheme 12 Rearomatization of **34c**.

An attempted desymmetrization of **32a** with 3 equiv. of sodium led to the formation of the expected product **34a** albeit in low yields. The product has been obtained as a mixture of four isomers in a 30 : 11 : 40 : 19 ratio. Under identical reaction conditions amide **32b** afforded the corresponding product which appeared to be an almost an equimolar mixture of *trans* and *cis* isomers. The diastereomeric excesses of both isomers were identical and reached 44% de. In the case of **32c** Birch reduction of one aryl substituents proceeded with a cleavage of the carbon–oxygen bond. Compound **34c** was obtained as a mixture of diastereomers with a moderate selectivity (58% de). The structure of this compound was additionally confirmed by rearomatization of the cyclohexadienyl substituent which afforded **36** (Scheme 12).

Dearomatization of **32d** and **32e** in both cases led to Birch reduction products **34d** and **34e** as well as *H*-phosphinous acid-borane amides **35a** and **35b**. The latter compounds arose most probably through *P*-aryl bond cleavage and subsequential protonation of the formed P-anion. In each case, both Birch reduction products and *H*-phosphinous acid-borane amides were formed as mixtures of diastereomers in moderate excess.

A brief look at Table 3 led to the conclusion that *para* and *meta*-diarylphosphinous acid-borane amides undergo Birch desymmetrization with a diastereoselectivity comparable with the diastereoselectivity obtained for parent amide **10b** (Table 3, entries 2–5 and Table 1, entry 2). For *ortho*-substituted amide **32a** the diastereoselectivity of the desymmetrization is difficult to establish due to the presence of an additional chirality centre.

Conclusions

The main goal of this work was to develop a method for the synthesis of *P*-chiral organophosphorus compounds by desymmetrization through Birch reduction of symmetrically substituted diarylphosphorus amides possessing chiral amido functionality.

It has been found that:

- phosphinous acid-borane amides undergo preferentially Birch reduction of only one aryl substituent whereas phosphinic acid amides undergo preferential double Birch reduction,

- the substitution pattern at nitrogen influences the reaction course; the presence of a hydrogen atom at nitrogen or the presence of any acidic hydrogen atom in the molecule stops the dearomatization reaction,

- the size of the non-chiral substituent at nitrogen influences the reaction course; an increase of steric bulk of this group decreases the selectivity of desymmetrization,

- selectivity of reaction can be controlled by the reaction temperature – the lower the temperature the higher the selectivity,

- an increase in the amount of alkali metal shifts the selectivity of the reaction towards *P*-aryl bond cleavage; diastereoselectivity of this process strongly depends on the structure of the amido group,

- among tested chiral auxiliaries, the one derived from commercially available α-phenylethylamine appeared to give the best selectivities,

- selectivity of Birch reduction of diarylphosphinous acid-borane amides is partially influenced by the structure of the aryl substituent,

- Birch reduction of **32c** led to both dearomatization of the arene group and cleavage of the C–OMe bond in the *para* position of the aryl group.

Despite the fact that desymmetrization of phosphinous acid-borane amides by the developed method is underdeveloped it offers an operationally simple way for the synthesis of *P*-stereogenic compounds. The development of more effective chiral auxiliaries would make this approach more reliable for practical applications.

Experimental section

All reactions were performed under an argon atmosphere by using Schlenk techniques. Only dry solvents were used and the glassware was heated under vacuum prior to use. All chemicals were used as received unless otherwise noted. Solvents for chromatography and crystallization were distilled once before use and the solvents for extraction were used as received. Tetrahydrofuran was dried over sodium/benzophenone ketyl and dichloromethane was dried over P_2O_5. Secondary phosphine oxides **31** were prepared according to the literature procedure.[13]

NMR spectra were recorded with Bruker Ascend (500 MHz) and Varian Mercury (400 MHz) and Bruker Avance (300 MHz) spectrometers in $CDCl_3$ as a solvent at room temperature unless otherwise noted. Chemical shifts (δ) are reported in ppm relative to residual solvent peak. Mass spectra were recorded on a Shimadzu GC-MS QP2010S spectrometer working in electron ionization (EI) mode using a Phenomenex Zebron ZB-35HT INFERNO column (pressure – 65 kPa, total flow – 23.9 mL min^{-1}, column flow – 1.2 mL min^{-1}, linear velocity – 36.8 cm s^{-1}, split – 20, temperature program (80 °C – hold 3 min, 80–250 °C/10 °C min^{-1} – hold 5 min, 250–280 °C/10 °C min^{-1} – hold 4.67 min, 280–340 °C/10 °C min^{-1} – hold 4 min – total 35 min)). Thin-Layer Chromatography (TLC) was performed with precoated silica gel plates and visualized by UV light or $KMnO_4$ solution. The reaction mixtures were purified by column chromatography over silica gel (60–240 mesh).

The synthesis of 10a and 11a

In a flame-dried, two-neck, round-bottom 100 mL flask equipped with a magnetic stirrer and an inert gas inlet were

placed (*S*)-α-methylbenzylamine **9** (1.212 g, 1.289 mL, 0.01 mol) and triethylamine (1.012 g, 1.394 mL, 0.01 mol) in dichloromethane (20 mL). Then, diphenylchlorophosphine (2.206 g, 1.795 mL, 0.01 mol) was added slowly dropwise. The reaction was stirred overnight and then 1 M BH_3–THF (15 mL, 0.015 mol) or 30% H_2O_2 (20 mL) was added to the reaction mixture. After stirring for 1 h, the reaction mixture was quenched by the addition of water (30 mL), the mixture was extracted with DCM (3 × 20 mL), an organic phase was dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography using hexane–EtOAc = 6 : 1 (for **10a**) or $CHCl_3$–MeOH = 15 : 1 (for **11a**) as the eluent.

Diphenylphosphinous acid-borane (*S*)-α-methylbenzylamide (10a). Yield 2.681 g (84%). White solid, mp 76.1–77.8 °C. R_F 0.53 (hexane–EtOAc 6 : 1). $[\alpha]_D$ −39.8 (*c* 1.21, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.57–1.55 (3 H, bm), 1.41 (3 H, d, *J* = 7.0 Hz), 2.48 (1 H, bs), 4.36–4.48 (1 H, m), 7.13–7.27 (5 H, m), 7.30–7.51 (6 H, m), 7.53–7.62 (4 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 25.9 (d, *J* = 4.9 Hz), 53.0 (d, *J* = 2.30 H), 125.8, 126.9, 128.3 (d, *J* = 8.3 Hz), 128.4, 128.5 (d, *J* = 8.1 Hz), 131.1 (d, *J* = 2.6 Hz), 131.8 (d, *J* = 6.0 Hz), 131.9 (d, *J* = 6.3 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz) δ 54.35 (bm); GC (Phenomenex Zebron ZB-35 HT) R_T 21.85 min; GC–MS (EI, 70 eV) *m*/*z* (%) 304 (5), 262 (16), 200 (42), 122 (33), 104 (100), 78 (57), 77 (49); $C_{20}H_{23}BNP$ (319.19): calcd C 75.26, H 7.26, N 4.39; found C 75.44, H 7.30, N 4.55.

Diphenylphosphinic acid (*S*)-α-methylbenzylamide (11a). Yield 3.053 g (95%). White solid, mp 179.1–180.6 °C (lit. 178–179 °C).[14] R_F 0.85 ($CHCl_3$–MeOH 15 : 1). $[\alpha]_D$ −29.3 (*c* 1.07, $CHCl_3$) (lit.[14] −35.5 (*c* 0.78, methanol). ^{1}H NMR ($CDCl_3$, 500 MHz,) δ 1.58 (3 H, d, *J* = 6.9 Hz), 3.19–3.25 (1 H, m), 4.35–4.45 (1 H, m), 7.23–7.34 (5 H, m), 7.35–7.40 (2 H, m), 7.42–7.47 (3 H, m), 7.47–7.52 (1 H, m), 7.80–7.86 (2 H, m), 7.89–7.94 (2 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 26.0 (d, *J* = 2.7 Hz), 51.0, 125.9, 127.1, 128.4 (d, *J* = 12.7 Hz), 128.5 (d, *J* = 12.7 Hz), 128.5, 131.7 (d, *J* = 2.7 Hz), 131.8 (d, *J* = 2.7 Hz), 131.9 (d, *J* = 10.0 Hz), 132.3 (d, *J* = 10.0 Hz), 132.4 (d, *J* = 10.0 Hz), 132.1 (d, *J* = 135.3 Hz), 133.1 (d, *J* = 132.6 Hz), 145.0 (d, *J* = 6.4 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz) δ 68.88 (bm); GC (Phenomenex Zebron ZB-35 HT) R_T 17.17 min; GC–MS (EI, 70 eV) *m*/*z* (%) 306 (18), 202 (7), 201 (39), 121 (9), 120 (100); $C_{20}H_{20}NOP$ (321.35): calcd C 74.75, H 6.47, N 4.36; found C 74.88, H 6.70, N 4.58. Spectral data are in accordance with those reported in the literature.[14]

The synthesis of 10b, 10c, 11b and 11c

In a flame-dried Schlenk tube (50 mL) equipped with a magnetic stirrer and an inert gas inlet amide **10a** or **11a** (0.5 mmol) was dissolved in THF (5 mL). The solution was cooled to −78 °C and *n*BuLi (0.46 mL, 1.6 M solution in hexane, 0.75 mmol) was added dropwise *via* a syringe. After stirring for 1 h at −78 °C an electrophile (2.0 mmol) was added and the mixture was allowed to warm to rt overnight. The reaction was quenched by the addition of aqueous NH_4Cl (5 mL), the mixture was extracted with DCM (3 × 10 mL), the combined organic phases were dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography using hexane–EtOAc = 6 : 1 (for **10b** and **10c**) or $CHCl_3$–MeOH = 15 : 1 (for **11b** and **11c**) as the eluent.

Diphenylphosphinous acid-borane *N*-methyl-(*S*)-α-methylbenzylamide (10b). Prepared from **10a** (0.160 g, 0.0005 mol) and MeI (0.062 mL, 0.142 g, 0.001 mol). Yield 0.113 g (68%). White solid, mp 105.3–106.9 °C. R_F 0.60 (hexane–EtOAc 6 : 1). $[\alpha]_D$ 35.7 (*c* 1.1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz,) δ 0.74–1.50 (3 H, bm), 1.51 (3 H, d, *J* = 6.9 Hz), 2.24 (3 H, d, *J* = 7.9 Hz), 5.31–5.41 (1 H, m), 7.26–7.29 (1 H, m), 7.32–7.37 (2 H, m), 7.39–7.44 (4 H, m), 7.44–7.55 (6 H, m), 7.65–7.71 (2 H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.5 (d, *J* = 1.7 Hz), 28.9 (d, *J* = 4.0 Hz), 55.4 (d, *J* = 11.2 Hz), 127.1, 127.9, 128.2, 128.4 (d, *J* = 10.4 Hz), 128.5 (d, *J* = 10.4 Hz), 130.8 (d, *J* = 50.8 Hz), 130.9 (d, *J* = 2.6 Hz), 131.1 (d, *J* = 2.6 Hz), 131.6 (d, *J* = 42.8 Hz), 132.2 (d, *J* = 10.4 Hz), 132.4 (d, *J* = 10.6 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz) δ 54.35 (bm); GC (Phenomenex Zebron ZB-35 HT) R_T 22.63 min; GC–MS (EI, 70 eV) *m*/*z* (%) 319 (M − BH_3) (8), 318 (12), 263 (18), 262 (93), 214 (45), 185 (14), 183 (36), 152 (10), 134 (28), 122 (14), 109 (100), 108 (27), 105 (25), 104 (17), 91 (11); $C_{21}H_{25}BNP$ (333.21): calcd C 75.69, H 7.56, N 4.20; found C 75.50, H 7.49, N 4.45.

Diphenylphosphinous acid-borane *N*-ethyl-(*S*)-α-methylbenzylamide (10c). Prepared from **10a** (0.160 g, 0.0005 mol) and EtBr (0.075 mL, 0.109 g, 0.001 mol). Yield 0.127 g (73%). Colorless thick oil. R_F 0.67 (hexane–EtOAc 2 : 1). $[\alpha]_D$ 9.8 (*c* 1.055, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.55–1.26 (3 H, bm), 0.45 (3 H, t, *J* = 7.3 Hz), 0.71–1.72 (3 H, bm), 1.64 (3 H, d, *J* = 7.3 Hz), 2.91–3.14 (2 H, m), 5.23–5.32 (1 H, m), 7.24–7.29 (1 H, m), 7.30–7.35 (2 H, m), 7.39–7.47 (6 H, m), 7.47–7.52 (2 H, m), 7.57–7.63 (2 H, m), 7.66–7.72 (2 H, m); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 16.6, 19.4 (d, *J* = 1.8 Hz), 39.4 (d, *J* = 1.8 Hz), 56.1 (d, *J* = 10.0 Hz), 127.1, 128.0, 128.1, 128.33 (d, *J* = 10.0 Hz), 128.34 (d, *J* = 10.0 Hz), 130.8 (d, *J* = 2.7 Hz), 130.9 (d, *J* = 2.7 Hz), 131.7 (d, *J* = 52.7 Hz), 132.2 (d, *J* = 52.7 Hz), 132.3 (d, *J* = 6.4 Hz), 132.4 (d, *J* = 6.4 Hz), 142.2 (d, *J* = 5.5 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz) δ 69.22 (bm); GC (Phenomenex Zebron ZB-35 HT) R_T 15.37 min; GC–MS (EI, 70 eV) *m*/*z* (%) 333 (M − BH_3) (6), 332 (8), 263 (19), 262 (100), 229 (6), 228 (37), 214 (9), 185 (24), 184 (9), 183 (55), 152 (10), 148 (19), 122 (8), 118 (12), 109 (44), 108 (24), 107 (11), 105 (25); $C_{22}H_{27}BNP$ (347.24): calcd C 76.10, H 7.84, N 4.03; found C 75.99, H 7.77, N 4.05.

Diphenylphosphinic acid *N*-methyl-(*S*)-α-methylbenzylamide (11b). Prepared from **11a** (0.161 g, 0.0005 mmol) and MeI (0.062 mL, 0.142 g, 0.001 mol). Yield 0.159 g (95%). Colorless thick oil. R_F 0.32 ($CHCl_3$). $[\alpha]_D$ −51.3 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.57 (3 H, d, *J* = 6.9 Hz), 2.35 (3 H, d, *J* = 10.7 Hz), 4.68–4.78 (1 H, m), 7.21–7.26 (1 H, m), 7.32–7.37 (2 H, m), 7.39–7.49 (8 H, m), 7.86–7.94 (4 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 16.9 (d, *J* = 2.7 Hz), 27.7 (d, *J* = 3.6 Hz), 53.1 (d, *J* = 2.7 Hz), 126.9, 127.5, 128.1, 128.4 (d, *J* = 11.8 Hz), 131.5 (d, *J* = 3.6 Hz), 131.5 (d, *J* = 2.7 Hz), 131.8 (d, *J* = 129.0 Hz), 132.0 (d, *J* = 128.1 Hz), 132.2 (d, *J* = 9.1 Hz), 132.2 (d, *J* = 10.0 Hz), 140.9 (d, *J* = 5.5 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz) δ 30.74; GC (Phenomenex Zebron ZB-35 HT) R_T 17.44 min; GC–MS (EI, 70 eV) *m*/*z* (%) 320 (4), 202 (6), 201 (35), 135 (10),

134 (100), 105 (6); $C_{21}H_{22}NOP$ (335.38): calcd C 75.21, H 6.61, N 4.18; found C 75.44, H 6.79, N 4.22.

Diphenylphosphinic acid *N*-ethyl-(*S*)-α-methylbenzylamide (11c). Prepared from **11a** (0.161 g, 0.0005 mmol) and EtBr (0.075 mL, 0.109 g, 0.001 mol). Yield 0.126 g (72%). Colorless thick oil. R_F 0.26 ($CHCl_3$). $[\alpha]_D$ −47.2 (*c* 0.835, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.73 (3 H, t, *J* = 7.3 Hz), 1.63 (3 H, d, *J* = 6.9 Hz), 2.83–3.06 (2 H, m), 4.69–4.78 (1 H, m), 7.22–7.28 (1 H, m), 7.31–7.36 (2 H, m), 7.41–7.52 (8 H, m), 7.90–7.99 (4 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 17.0 (d, *J* = 2.7 Hz), 19.3 (d, *J* = 2.7 Hz), 37.9 (d, *J* = 3.6 Hz), 54.0 (d, *J* = 3.6 Hz), 127.0, 127.9, 128.3 (d, *J* = 12.7 Hz), 128.3 (d, *J* = 12.7 Hz), 131.5 (d, *J* = 2.7 Hz), 131.5 (d, *J* = 2.7 Hz), 132.4 (d, *J* = 10.0 Hz), 132.5 (d, *J* = 128.1 Hz), 132.6 (d, *J* = 128.1 Hz), 141.9 (d, *J* = 4.5 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz,) δ 30.05; GC (Phenomenex Zebron ZB-35 HT) R_T 17.48 min; GC–MS (EI, 70 eV) *m*/*z* (%) 334 (3), 320 (8), 230 (5), 202 (9), 201 (54), 149 (11), 148 (100), 105 (13); $C_{22}H_{24}NOP$ (349.41): calcd C 75.62, H 6.92, N 4.01; found C 75.90, H 6.88, N 4.14.

The synthesis of 10d and 11d

Compound **12** was prepared according to the literature procedure.[15]

In a flame-dried, two-neck, round-bottom 100 mL flask equipped with a magnetic stirrer and an inert gas inlet were placed **12** (0.163 g, 0.001 mol) and triethylamine (0.101 g, 0.139 mL, 0.001 mol) in dichloromethane (5 mL). Then, diphenylchlorophosphine (0.221 g, 0.180 mL, 0.001 mol) was added slowly dropwise. The reaction was stirred overnight and then 1 M BH_3–THF (1.5 mL, 0.0015 mol) or 30% H_2O_2 (2 mL) was added to the reaction mixture. After stirring for 1 h, the reaction mixture was quenched by the addition of water (10 mL), the mixture was extracted with DCM (3 × 10 mL), an organic phase was dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography using hexane–EtOAc = 2 : 1 (for **10d**) or $CHCl_3$ (for **11d**) as the eluent.

Diphenylphosphinous acid-borane *N*-i-propyl-(*S*)-α-methylbenzylamide (10d). Yield 0.195 g (54%). Colorless thick oil. R_F 0.69 (hexane–EtOAc 2 : 1). $[\alpha]_D$ −23.3 (*c* 0.98, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz,) δ 0.32–1.20 (3 H, bm), 0.74 (3 H, d, *J* = 6.9 Hz), 1.06 (3 H, d, *J* = 6.6 Hz), 1.73 (3 H, d, *J* = 7.3 Hz), 3.61–3.71 (1 H, m), 5.08–5.18 (1 H, m), 7.21–7.26 (1 H, m), 7.27–7.31 (2 H, m), 7.40–7.53 (8 H, m), 7.70–7.76 (2 H, m), 7.76–7.81 (2 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz,) δ 20.8 (d, *J* = 1.8 Hz), 23.4 (d, *J* = 1.8 Hz), 23.6 (d, *J* = 1.8 Hz), 55.3 (d, *J* = 10.0 Hz), 126.9, 127.9, 128.2, 128.3 (d, *J* = 10.0 Hz), 128.3 (d, *J* = 10.0 Hz), 130.8 (d, *J* = 1.8 Hz), 130.8 (d, *J* = 1.8 Hz), 132.4 (d, *J* = 63.6 Hz), 132.6 (d, *J* = 10.9 Hz), 143.3 (d, *J* = 4.5 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz) δ 67.93 (bm); GC (Phenomenex Zebron ZB-35 HT) R_T 15.05 min; GC–MS (EI, 70 eV) *m*/*z* (%) 347 (M − BH_3) (3), 346 (4), 304 (7), 263 (20), 262 (100), 242 (22), 228 (6), 185 (34), 184 (9), 183 (50), 162 (8), 152 (9), 122 (18), 109 (17), 108 (21), 107 (10), 105 (25); $C_{23}H_{29}BNP$ (361.27): calcd C 76.47, H 8.09, N 3.88; found C 76.50, H 7.99, N 3.81.

Diphenylphosphinic acid *N*-i-propyl-(*S*)-α-methylbenzylamide (11d). Yield 0.218 g (60%). Colorless thick oil. R_F 0.25 ($CHCl_3$). $[\alpha]_D$ −15.3 (*c* 1.025, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.14 (3 H, d, *J* = 6.9 Hz), 1.22 (3 H, d, *J* = 6.9 Hz), 1.71 (3 H, d, *J* = 7.3 Hz), 3.52–3.62 (1 H, m), 4.52–4.61 (1 H, m), 7.16–7.20 (1 H, m), 7.21–7.25 (2 H, m), 7.25–7.30 (2 H, m), 7.35–7.49 (6 H, m), 7.70–7.76 (2 H, m), 7.88–7.94 (2 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 20.6 (d, *J* = 3.6 Hz), 23.4 (d, *J* = 4.5 Hz), 23.7 (d, *J* = 1.8 Hz), 48.8 (d, *J* = 4.5 Hz), 53.1 (d, *J* = 3.6 Hz), 126.6, 127.7, 127.9 (d, *J* = 12.7 Hz), 128.1 (d, *J* = 11.8 Hz), 131.0 (d, *J* = 2.7 Hz), 131.2 (d, *J* = 2.7 Hz), 132.4 (d, *J* = 9.1 Hz), 132.5 (d, *J* = 9.1 Hz), 133.43 (d, *J* = 126.2 Hz), 134.13 (d, *J* = 127.2 Hz), 143.26 (d, *J* = 1.8 Hz); ^{31}P NMR ($CDCl_3$ 202 MHz,) δ 28.19; GC (Phenomenex Zebron ZB-35 HT) R_T 17.50 min; GC–MS (EI, 70 eV) *m*/*z* (%) 363 (M) (1), 321 (15), 320 (66), 306 (8), 258 (8), 244 (33), 202 (15), 201 (100), 162 (26), 120 (5), 105 (32), 103 (7); $C_{23}H_{26}NOP$ (363.43): calcd C 76.01, H 7.21, N 3.85; found C 76.15, H 7.17, N 3.99.

The synthesis of 16a

L-Prolinol was obtained according to the literature procedure.[16]

In a flame-dried Schlenk tube (100 mL) equipped with a magnetic stirrer and an inert gas inlet was placed. L-prolinol (0.427 mL, 0.438 g, 0.004 mol) and $PhP(NEt_2)_2$ (1.093 g, 0.004 mol) (prepared from $PhPCl_2$ and $HNEt_2$)[17] were dissolved in toluene (20 mL) and refluxed for 4 h. The mixture was cooled to rt and evaporated to dryness. NMR analysis of the residue showed the presence of the corresponding bicyclic oxazaphospholane as a single diastereomer (^{31}P NMR 147.74 ppm). The intermediate was dissolved in THF (20 mL) under an inert atmosphere and cooled to −78 °C. Then, PhLi (2.89 mL, 1.8 M in dibutyl ether, 0.005 mol) was added *via* a syringe and the mixture was allowed to warm to rt overnight. BH_3–THF (6.5 mL, 1 M in THF, 0.0065 mol) was added and the mixture was stirred for an additional 1 h. The reaction was quenched by the addition of aqueous NH_4Cl (20 mL), the mixture was extracted with DCM (3 × 20 mL), dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography using hexane–EtOAc = 2 : 1 as the eluent.

Diphenylphosphinous acid-borane (2*S*)-2-(hydroxymethyl)-pyrolidinamide (16a). Yield 0.944 g (73%, after 4 steps). Colorless thick oil. R_F 0.33 (hexane–EtOAc 2 : 1). $[\alpha]_D$ −24.5 (*c* 0.935, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.71–1.41 (3 H, bm), 1.63–1.76 (2 H, m), 1.84–2.00 (3 H, m), 2.86–2.96 (1 H, m), 3.05–3.14 (1 H, m), 3.51 (1 H, dd, *J* = 6.3 Hz, 11.0 Hz), 3.60 (1 H, dd, *J* = 4.7 Hz, 11.0 Hz), 4.05–4.11 (1 H, m), 7.42–7.54 (6 H, m), 7.56–7.61 (2 H, m), 7.64–7.70 (2 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 25.3 (d, *J* = 4.5 Hz), 28.9 (d, *J* = 4.5 Hz), 48.5 (d, *J* = 2.7 Hz), 61.4 (d, *J* = 7.3 Hz), 65.78, 128.5 (d, *J* = 10.0 Hz), 128.5 (d, *J* = 10.0 Hz), 130.7 (d, *J* = 69.0 Hz), 131.1 (d, *J* = 1.8 Hz), 131.2 (d, *J* = 1.8 Hz), 131.2 (d, *J* = 76.3 Hz), 131.9 (d, *J* = 10.0 Hz), 132.3 (d, *J* = 10.0 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz,) δ 60.18 (bm); GC (Phenomenex Zebron ZB-35 HT) R_T 13.43 min; GC–MS (EI, 70 eV) *m*/*z* (%) 299 (M) (3), 255 (13), 254 (69), 186 (14), 185 (100), 184 (10), 183 (70), 178 (9), 152 (13), 109 (11), 108 (11), 107 (13); $C_{17}H_{23}BNOP$ (299.16): calcd C 68.24, H 7.75, N 4.68; found C 68.50, H 7.82, N 4.50.

The synthesis of 16b

In a flame-dried Schlenk tube (50 mL) equipped with a magnetic stirrer and an inert gas inlet amide **16a** (0.150 g, 0.5 mmol) was dissolved in THF (5 mL). The solution was cooled to −78 °C and NaH (0.020 g, 60% in mineral oil, 0.55 mmol) was added. After stirring for 30 min at −78 °C MeI (0.047 mL, 0.106 g, 0.75 mmol) was added and the mixture was allowed to warm to rt overnight. The reaction was quenched by the addition of aqueous NH_4Cl (5 mL), the mixture was extracted with DCM (3 × 10 mL), the combined organic phases were dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography using hexane–EtOAc = 2 : 1 as the eluent.

Diphenylphosphinous acid-borane (2*S*)-2-(methoxymethyl)-pyrolidinamide (16b). Yield 0.047 g (30%). White thick oil. R_F 0.65 (hexane–EtOAc 2 : 1). $[\alpha]_D$ −37.3 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz,) δ 0.69–1.42 (3 H, bm), 1.67–1.74 (1 H, m), 1.87–2.00 (3 H, m), 2.81–2.89 (1 H, m), 3.06–3.13 (1 H, m), 3.28 (3 H, s), 3.29–3.33 (1 H, m), 3.36–3.41 (1 H, m), 4.06–4.14 (1 H, m), 7.39–7.54 (6 H, m), 7.55–7.62 (2 H, m), 7.63–7.70 (2 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 25.3 (d, J = 4.5 Hz), 29.1 (d, J = 6.4 Hz), 48.4 (d, J = 1.8 Hz), 58.7, 58.9 (d, J = 7.3 Hz), 75.6, 128.4 (d, J = 10.0 Hz), 128.4 (d, J = 10.9 Hz), 130.8 (d, J = 2.7 Hz), 130.9 (d, J = 62.7 Hz), 131.0 (d, J = 2.7 Hz), 131.7 (d, J = 65.4 Hz), 131.8 (d, J = 10.9 Hz), 132.3 (d, J = 10.0 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 58.99 (bm); GC (Phenomenex Zebron ZB-35 HT) R_T 13.43 min; GC–MS (EI, 70 eV) *m*/*z* (%) 299 (M − BH_3) (3), 255 (13), 254 (68), 186 (13), 185 (100), 184 (10), 183 (71), 178 (8), 152 (13), 109 (10), 108 (11), 107 (13); $C_{18}H_{25}BNOP$ (313.18): calcd C 69.03, H 8.05, N 4.47; found C 69.27, H 7.98, N 4.40.

The synthesis of 16c

In a flame-dried Schlenk tube (50 mL) equipped with a magnetic stirrer and an inert gas inlet amide **16a** (0.150 g, 0.5 mmol) was dissolved in DCM (5 mL). Then, NEt_3 (0.209 mL, 0.125 g, 1.5 mmol) was added followed by TMSCl (0.095 mL, 0.081 g, 0.75 mmol). The mixture was allowed to stir overnight at rt and then quenched by the addition of aqueous NH_4Cl (10 mL). The mixture was extracted with DCM (3 × 10 mL), the organic phase was dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography using hexane–EtOAc = 2 : 1 as the eluent.

Diphenylphosphinous acid-borane (2*S*)-2-(trimethylsililoxymethyl)-pyrolidinamide (16c). Yield 0.087 g (47%) (isolated as a mixture of rotamers). Colorless oil. R_F 0.73 (hexane–EtOAc 2 : 1). ^{1}H NMR ($CDCl_3$, 500 MHz) (major rotamer) δ 0.08 (9 H, s), 0.65–1.45 (3 H, bm), 1.67–1.75 (1 H, m), 1.83–1.98 (2 H, m), 1.98–2.05 (1 H, m), 2.81–2.89 (1 H, m), 3.06–3.13 (1 H, m), 3.37–3.44 (1 H, m), 3.57–3.63 (1 H, m), 3.96–4.04 (1 H, m), 7.40–7.53 (6 H, m), 7.56–7.62 (2 H, m), 7.63–7.71 (1 H, m); (minor rotamer) δ 0.17 (9 H, s), 0.65–1.45 (3 H, bm), 1.67–1.75 (1 H, m), 1.83–1.98 (3 H, m), 2.89–2.96 (1 H, m), 3.06–3.13 (1 H, m), 3.49–3.54 (1 H, m), 3.57–3.63 (1 H, m), 4.05–4.13 (1 H, m), 7.40–7.53 (6 H, m), 7.56–7.62 (2 H, m), 7.63–7.71 (2 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) (major rotamer) δ −0.5, 25.0 (J = 5.5 Hz), 28.6 (d, J = 5.5 Hz), 28.4 (d, J = 2.7 Hz), 61.0 (d, J = 7.3 Hz), 65.1, 128.4 (d, J = 10.0 Hz), 130.8 (d, J = 1.8 Hz), 131.0 (d, J = 2.7 Hz), 131.03 (d, J = 70.8 Hz), 131.5 (d, J = 72.7 Hz), 131.9 (d, J = 10.0 Hz), 132.3 (d, J = 10.0 Hz); (minor rotamer) δ 1.3, 25.3 (J = 4.5 Hz), 28.9 (d, J = 5.5 Hz), 28.5 (d, J = 2.7 Hz), 61.4 (d, J = 7.3 Hz), 65.7, 128.5 (d, J = 10.9 Hz), 128.5 (d, J = 10.0 Hz), 130.7 (d, J = 76.3 Hz), 131.0 (d, J = 1.8 Hz), 131.2 (d, J = 1.8 Hz), 131.2 (d, J = 76.3 Hz), 131.9 (d, J = 10.0 Hz), 132.2 (d, J = 10.9 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz) (major rotamer) δ 59.01 (bm); (minor rotamer) δ 60.17 (bm); GC (Phenomenex Zebron ZB-35 HT) R_T 13.73 min; GC–MS (EI, 70 eV) *m*/*z* (%) 203 (16), 201 (11), 183 (9), 125 (7), 108 (7), 84 (68), 83 (100), 82 (15); $C_{20}H_{31}BNOPSi$ (371.34): calcd C 64.69, H 8.41, N 3.77; found C 64.85, H 8.13, N 3.52.

D-Camphor oxime (18). This compound was prepared according to the literature procedure.[17] Data are in accordance with those reported in the literature.[17]

***exo*-Bornylamine (22d).** This compound was prepared according to the literature procedure.[17] Data are in accordance with those reported in the literature.[17]

L-Menthyl methanesulfonate (20a). This compound was prepared according to the literature procedure.[18] Data are in accordance with those reported in the literature.

9-Mesyl-quinine (20b). This compound was prepared according to the literature procedure.[19] Data are in accordance with those reported in the literature.[19]

9-Mesyl-quinidine (20c). This compound was prepared according to the literature procedure.[19] Data are in accordance with those reported in the literature.[19]

Neomenthyl azide (21a). This compound was prepared according to the literature procedure.[20] Data are in accordance with those reported in the literature.[20]

9-*epi*-9-Azidoquinine (21b). This compound was prepared according to the literature procedure.[21] Data are in accordance with those reported in the literature.[21]

9-*epi*-9-Azidoquinidine (21c). This compound was prepared according to the literature procedure.[21] Data are in accordance with those reported in the literature.[21]

Neomenthylamine (22a). This compound was prepared according to the literature procedure.[22] Data are in accordance with those reported in the literature.[17]

9-*epi*-9-Aminoquinine (22b). This compound was prepared according to the literature procedure.[23] Data are in accordance with those reported in the literature.[23]

9-*epi*-9-Aminoquinidine (22c). This compound was prepared according to the literature procedure.[24] Data are in accordance with those reported in the literature.[24]

The synthesis of 23a–f

In a flame-dried Schlenk tube (25 mL) equipped with a magnetic stirrer and an inert gas inlet was placed amine (1 equiv.) in DCM (10 mL). Then, NEt_3 (1 equiv.) was added followed by ClCOOMe (1 equiv.). The mixture was allowed to stir at rt for 16 h, then water (10 mL) was added. The mixture was extracted with DCM (3 × 20 mL), combined organic phases were dried over Na_2SO_4 and evaporated. The residue was purified by flash

chromatography using hexane–EtOAc = 6 : 1 or $CHCl_3$–MeOH = 15 : 1 as the eluent.

***N*-Neomenthyl methyl carbamate (23a).** Prepared from neomenthylamine (**22a**) (0.276 g, 0.0018 mol), ClCOOMe (0.137 mL, 0.168 g, 0.0018 mol) and NEt_3 (0.248 mL, 0.180 g, 0.0018 mol). Yield 0.302 g (79%). White solid, mp 92.6–93.4 °C. R_F 0.50 (hexane–EtOAc 6 : 1). $[\alpha]_D$ 50.0 (*c* 0.87, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.87 (3 H, d, J = 6.6 Hz), 0.89 (3 H, d, J = 6.9 Hz), 0.91 (3 H, d, J = 6.6 Hz), 0.86–0.95 (2 H, m), 0.98–1.08 (2 H, m), 1.33–1.451 (1 H, m), 1.41–1.51 (1 H, m), 1.69–1.74 (1 H, m), 1.78–1.84 (1 H, m), 1.84–1.90 (1 H, m), 3.66 (3 H, s), 4.05–4.10 (1 H, m), 4.72–4.78 (1 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz,) δ 20.8, 20.9, 22.2, 25.2, 26.6, 29.4, 34.7, 40.4, 46.4, 47.8, 51.9, 156.4; $C_{12}H_{23}NO_2$ (213.32): calcd C 67.57, H 10.87, N 6.57; found C 67.44, H 10.99, N 6.59.

9-*epi*-9-((Methoxycarbonyl)amino)quinine (23b). Prepared from 9-*epi*-9-aminoquinine (**22b**) (0.504 g, 0.0016 mol), ClCOOMe (0.120 mL, 0.147 g, 0.0016 mol) and NEt_3 (0.217 mL, 0.158 g, 0.0016 mol). Yield 0.444 g (75%). Pale yellow foam. R_F 0.39 ($CHCl_3$–MeOH 15 : 1). $[\alpha]_D$ −3.4 (*c* 1.03, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.89–0.96 (1 H, m), 1.34–1.44 (1 H, m), 1.58–1.64 (2 H, m), 1.64–1.69 (1 H, m), 2.26–2.33 (1 H, m), 2.67–2.81 (2 H, m), 3.01–3.22 (2 H, m), 3.23–3.30 (1 H, m), 3.56 (3 H, bs), 3.97 (3 H, s), 4.92–5.01 (2 H, m), 5.04–5.19 (1 H, bm), 5.67–5.76 (1 H, m), 6.19 (1 H, bs), 7.36–7.42 (2 H, m), 7.63 (1 H, bs), 8.03 (1 H, d, J = 9.1 Hz), 8.74 (1 H, d, J = 4.4 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 26.0, 27.3, 27.9, 39.5, 40.8, 52.1, 55.6, 55.9, 60.0 (bs), 101.7, 114.6, 119.4 (bs), 121.5, 128.2, 131.8, 141.2, 144.8, 147.6, 156.8, 157.7; GC (Phenomenex Zebron ZB-35 HT) R_T 18.40 min; GC–MS (EI, 70 eV) *m*/*z* (%) 137 (11), 136 (100), 95 (5), 82 (5), 81 (11); $C_{22}H_{27}N_3O_3$ (381.47): calcd C 69.27, H 7.13, N 11.02; found C 69.44, H 7.01, N 11.00.

9-*epi*-9-((Methoxycarbonyl)amino)quinidine (23c). Prepared from 9-*epi*-9-aminoquinidine (**22c**) (0.387 g, 0.0012 mol), ClCOOMe (0.092 mL, 0.113 g, 0.0012 mol) and NEt_3 (0.167 mL, 0.121 g, 0.0012 mol). Yield 0.241 g (53%). Pale yellow foam. R_F 0.29 ($CHCl_3$–MeOH 15 : 1). $[\alpha]_D$ 160.2 (*c* 0.84, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.90–1.02 (1 H, m), 1.24–1.34 (1 H, m), 1.44–1.62 (2 H, m), 1.62–1.70 (1 H, m), 2.26–2.36 (1 H, m), 2.85–3.05 (5 H, m), 3.56 (3 H, bs), 3.97 (3 H, s), 5.07–5.19 (3 H, m), 5.87–5.97 (1 H, m), 6.21–6.34 (1 H, m), 7.34–7.44 (2 H, m), 7.50–7.61 (1 H, m), 7.98–8.05 (1 H, m), 8.71–8.76 (1 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 25.2, 26.5, 27.2, 39.0, 46.9, 49.2, 52.1, 55.4, 60.3 (bs), 101.1, 114.7, 119.1 (bs), 121.9, 128.2 (bs), 131.8, 140.4, 144.7, 147.6, 156.9, 157.7; GC (Phenomenex Zebron ZB-35 HT) R_T 18.44 min; GC–MS (EI, 70 eV) *m*/*z* (%) 349 (5), 308 (6), 294 (5), 214 (3), 159 (6), 137 (19), 136 (100), 108 (5), 95 (12), 94 (8), 82 (11), 81 (26); $C_{22}H_{27}N_3O_3$ (381.47): calcd C 69.27, H 7.13, N 11.02; found C 69.11, H 6.92, N 11.15.

***N*-Bornyl methyl carbamate (23d).** Prepared from bornylamine (**22d**) (3.400 g, 0.022 mol), ClCOOMe (1.714 mL, 2.096 g, 0.022 mol) and NEt_3 (3.092 mL, 2.245 g, 0.022 mol). Yield 1.128 g (24%). Isolated as a mixture of two diastereomers in a 1 : 0.3 ratio. White solid. R_F 0.44 (hexane–EtOAc 6 : 1). ^{1}H NMR ($CDCl_3$, 500 MHz,) (major isomer) δ 0.82 (3 H, s), 0.85 (3 H, s), 0.87 (3 H, s), 1.10–1.17 (1 H, m), 1.20–1.28 (1 H, m), 1.52–1.60 (2 H, m), 1.66–1.74 (2 H, m), 1.82–1.89 (1 H, m), 3.60–3.68 (1 H, m), 3.64 (3 H, s), 4.59–4.66 (1 H, m); (minor diastereomer) δ 0.82 (3 H, s), 0.87 (3 H, s), 0.93 (3 H, s), 1.26–1.32 (1 H, m), 1.32–1.40 (1 H, m), 1.43–1.50 (1 H, m), 1.52–1.61 (1 H, m), 1.63–1.72 (2 H, m), 2.31–2.39 (1 H, m), 3.66 (3 H, s), 3.92–3.98 (1 H, m), 4.69–4.76 (1 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) (major diastereomer) δ 11.6, 13.5, 20.2, 26.9, 35.9, 39.3, 44.7, 46.9, 48.4, 51.9, 58.6, 156.7; (minor diastereomer) δ 14.1, 19.8, 18.6, 22.7, 27.7, 28.3, 31.9, 37.8, 47.9, 49.2, 55.7, 157.1; GC (Phenomenex Zebron ZB-35 HT) R_T 8.45 min; (major diastereomer); R_T 8.51 min (minor diastereomer); GC–MS (EI, 70 eV) *m*/*z* (%) (major diastereomer) 211 (M) (4), 196 (4), 136 (14), 121 (37), 110 (10), 109 (12), 102 (23), 101 (10), 96 (11), 95 (100), 93 (14); (minor diastereomer) 211 (M) (4), 196 (4), 136 (14), 121 (37), 110 (10), 109 (12), 102 (23), 101 (10), 96 (11), 95 (100), 93 (14); $C_{12}H_{21}NO_2$ (211.30): calcd C 68.21, H 10.02, N 6.63; found C 68.00, H 10.16, N 6.70.

***N*-(*R*)-1-(1-Naphthyl)ethyl methyl carbamate (23e).** Prepared from (*R*)-1-(1-naphthyl)ethylamine (0.937 mL, 1.000 g, 0.0058 mol), ClCOOMe (0.451 mL, 0.552 g, 0.0058 mol) and NEt_3 (0.814 mL, 0.591 g, 0.0058 mol). Yield 1.194 g (89%). White solid, mp 87.8–88.5 °C. R_F 0.45 (hexane–EtOAc 6 : 1). $[\alpha]_D$ 92.4 (*c* 0.99, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.66 (3 H, d, J = 6.6 Hz), 3.69 (3 H, s), 5.03–5.12 (1 H, m), 5.64–5.71 (1 H, m), 7.44–7.48 (1 H, m), 7.49–7.53 (2 H, m), 7.55–7.59 (2 H, m), 7.78–7.82 (1 H, m), 7.87–7.90 (1 H, m), 8.13–8.17 (1 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.6, 46.6, 52.1, 122.2, 123.2, 125.2, 125.7, 126.4, 128.2, 128.8, 130.8, 133.9, 138.7, 156.1; GC (Phenomenex Zebron ZB-35 HT) R_T 12.10 min; GC–MS (EI, 70 eV) *m*/*z* (%) 229 (M) (30), 215 (15), 214 (100), 182 (16), 171 (30), 170 (13), 155 (35), 154 (40), 153 (35), 152 (19), 143 (17), 129 (28), 128 (45), 127 (42), 126 (11), 115 (12); $C_{14}H_{15}NO_2$ (229.27): calcd C 73.34, H 6.59, N 6.11; found C 73.55, H 6.71, N 6.12. Data are in accordance with those reported in the literature.[25]

***N*-(*S*)-1-(2-Naphthyl)ethyl methyl carbamate (23f).** Prepared from (*S*)-1-(2-naphthyl)ethylammonium sulfonate (1.034 g, 0.0038 mol), ClCOOMe (0.297 mL, 0.363 g, 0.0038 mol) and NEt_3 (0.535 mL, 0.388 g, 0.0038 mol). Yield 0.215 g (25%). White solid mp 70.1–71.7 °C. R_F 0.46 (hexane–EtOAc 6 : 1). $[\alpha]_D$ −93.2 (*c* 1.02, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz,) δ 1.56 (3 H, d, J = 6.6 Hz), 3.69 (3 H, s), 5.00–5.11 (1 H, m), 5.42–5.52 (1 H, m), 7.42–7.53 (3 H, m), 7.75–7.80 (1 H, m), 7.80–7.86 (3 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 22.1, 50.5, 51.9, 124.2, 124.3, 125.6, 126.0, 127.4, 127.7, 128.2, 132.5, 133.2, 140.9, 156.2; GC (Phenomenex Zebron ZB-35 HT) R_T 12.31 min; GC–MS (EI, 70 eV) *m*/*z* (%) 229 (M) (39), 215 (15), 214 (100), 182 (17), 171 (42), 170 (19), 155 (41), 154 (38), 153 (24), 152 (15), 143 (13), 129 (32), 128 (52), 127 (45), 126 (12), 115 (13), 102 (8); $C_{14}H_{15}NO_2$ (229.27): calcd C 73.34, H 6.59, N 6.11; found C 73.17, H 6.41, N 6.09.

The synthesis of 24a–f

In a flame-dried, two-neck, round-bottom 100 mL flask equipped with a magnetic stirrer and an inert gas inlet substrate (1 equiv.) was mixed with THF (20 mL). The mixture was

cooled to 0 °C and $LiAlH_4$ (1.5 equiv.) was slowly added by portions (CAUTION: a violent gas evolution was observed). After all of the $LiAlH_4$ was added, the mixture was refluxed for 1 h and then cooled again to 0 °C. Aqueous KOH (20% m/m) was added dropwise until the slurry changed colour from grey to white. The obtained mixture was filtered through silica gel, the solid was washed with Et_2O (3 × 30 mL), the filtrate was dried over Na_2SO_4 and evaporated yielding a crude product. NMR analysis of the sample showed essentially no impurities so it was decided to use the amine without further purification.

***N*-Methylneomenthylamine (24a).** Prepared from *N*-neomenthyl methyl carbamate (**23a**) (0.302 g, 0.0014 mol) and $LiAlH_4$ (0.081 g, 0.0021 mol). Yield 0.216 g (90%). Colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz,) δ 0.85 (3 H, d, J = 6.6 Hz), 0.90 (3 H, d, J = 6.6 Hz), 0.91 (3 H, d, J = 6.3 Hz), 0.82–0.96 (2 H, m), 1.15–1.27 (1 H, m), 1.43–1.52 (1 H, m), 1.56–1.77 (4 H, m), 1.93–1.99 (1 H, m), 2.39 (3 H, s), 2.76–2.79 (1 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 20.6, 21.6, 22.5, 25.0, 25.5, 28.9, 34.4, 35.4, 37.3, 48.4, 55.9; GC (Phenomenex Zebron ZB-35 HT) R_T 4.66 min; GC–MS (EI, 70 eV) *m*/*z* (%) 169 (M) (5), 154 (4), 112 (6), 85 (6), 84 (100).

9-*epi*-9-(Methylamino)quinine (24b). Prepared from 9-*epi*-9-((methoxycarbonyl)amino)quinine (**23b**) (0.444 g, 0.0012 mol) and $LiAlH_4$ (0.066 g, 0.0017 mol). Yield 0.333 g (85%) (contained some impurities). Pale yellow waxy solid. ^{1}H NMR ($CDCl_3$, 500 MHz) (some peaks are very broad, probably due to the restricted rotation) δ 0.76–0.88 (1 H, m), 1.46–1.71 (4 H, m), 2.13–2.41 (4 H, m), 2.61–2.85 (2 H, m), 2.89–3.10 (1 H, m), 3.13–3.30 (2 H, m), 3.67–3.81 (1 H, m), 3.97 (3 H, bs), 4.85–5.04 (2 H, m), 5.64–5.83 (2 H, m), 7.33–7.43 (1 H, m), 7.48–7.74 (1 H, m), 7.99–8.11 (1 H, m), 8.52–8.87 (2 H, m); GC (Phenomenex Zebron ZB-35 HT) R_T 16.62 min; GC–MS (EI, 70 eV) *m*/*z* (%) 337 (M) (2), 308 (19), 202 (16), 201 (100), 199 (8), 186 (7), 173 (11), 160 (15), 157 (7), 137 (28), 136 (50), 122 (11), 117 (5), 108 (38), 95 (10), 94 (10), 82 (45), 81 (22), 80 (24).

9-*epi*-9-(Methylamino)quinidine (24c). Prepared from 9-*epi*-9-((methoxycarbonyl)amino)quinidine (**23c**) (0.241 g, 0.006 mol) and $LiAlH_4$ (0.036 g, 0.009 mol). Yield 0.166 g (78%) (contained some impurities). Pale yellow waxy solid. ^{1}H NMR ($CDCl_3$, 500 MHz) (some peaks are very broad, probably due to the restricted rotation) δ 0.67–0.88 (1 H, m), 1.10–1.24 (1 H, m), 1.37–1.60 (3 H, m), 2.16 (3 H, s), 2.13–2.31 (1 H, m), 2.70–3.06 (6 H, m), 3.93 (3 H, s), 4.23–4.41 (1 H, m), 4.97–5.13 (2 H, m), 5.82–5.94 (1 H, m), 7.30–7.40 (1 H, m), 7.39–7.54 (1 H, m), 7.58–7.72 (1 H, m), 7.95–8.05 (1 H, m), 8.62–8.81 (1 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz,) (some peaks are very broad, probably due to the restricted rotation) δ 24.5, 26.5, 27.4, 34.2, 39.4, 47.5, 49.3, 55.3, 59.1, 62.3, 100.5, 114.3, 119.6, 121.3, 129.9, 131.6, 140.6, 144.3, 146.8, 147.9, 157.5; GC (Phenomenex Zebron ZB-35 HT) R_T 16.62 min; GC–MS (EI, 70 eV) *m*/*z* (%) 337 (M) (2), 308 (17), 202 (15), 201 (100), 199 (8), 186 (6), 173 (10), 160 (14), 157 (6), 137 (29), 136 (15), 122 (10), 108 (37), 95 (9), 94 (9), 82 (45), 81 (19), 80 (23). Data are in accordance with those reported in the literature.[26]

***N*-Methylbornylamine (24d).** Prepared from *N*-bornyl methyl carbamate (**23d**) (1.128 g, 0.0053 mol) and $LiAlH_4$ (0.304 g, 0.0080 mol). Yield 0.782 g (88%). Isolated as a mixture of two diastereomers in a 1 : 0.3 ratio.

***N*-Methyl-(*R*)-1-(1-naphthyl)ethylamine (24e).** Prepared from *N*-(*R*)-1-(1-naphthyl)ethyl methyl carbamate (**23e**) (1.194 g, 0.0028 mol) and $LiAlH_4$ (0.297 g, 0.0078 mol). Yield 0.911 g (94%). Colorless oil. $[\alpha]_D$ 63.4 (*c* 1.14, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz,) δ 1.52 (3 H, d, J = 6.6 Hz), 1.71 (1 H, bs), 2.43 (3 H, s), 4.54 (1 H, q, J = 6.6 Hz), 7.47–7.55 (3 H, m), 7.63–7.66 (1 H, m), 7.75–7.78 (1 H, m), 7.87–7.91 (1 H, m), 8.18–8.22 (1 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 23.1, 34.7, 55.4, 122.5, 122.9, 125.3, 125. 7, 125.8, 127.2, 128.9, 131.3, 133.9, 140.8; GC (Phenomenex Zebron ZB-35 HT) R_T 9.40 min; GC–MS (EI, 70 eV) *m*/*z* (%) 185 (M) (5), 171 (14), 170 (100), 155 (13), 154 (11), 153 (17), 152 (12), 129 (10), 128 (15), 127 (17). Data are in accordance with those reported in the literature.[25]

***N*-Methyl-(*S*)-1-(2-naphthyl)ethylamine (24f).** Prepared from *N*-(*S*)-1-(2-naphthyl)ethyl methyl carbamate (**23f**) (0.215 g, 0.0009 mol) and $LiAlH_4$ (0.053 g, 0.0014 mol). Yield 0.138 g (79%). Colorless oil. $[\alpha]_D$ 63.7 (*c* 1.04, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.46 (3 H, d, J = 6.6 Hz), 1.81 (1 H, bs), 2.36 (3 H, s), 3.84 (1 H, q, J = 6.6 Hz), 7.44–7.51 (3 H, m), 7.74–7.77 (1 H, m), 7.82–7.86 (3 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 23.9, 34.5, 60.3, 124.8, 125.3, 125.4, 125.9, 127.6, 127.7, 128.2, 132.8, 133.4, 142.6; GC (Phenomenex Zebron ZB-35 HT) R_T 9.44 min; GC–MS (EI, 70 eV) *m*/*z* (%) 185 (M) (3), 171 (14), 170 (100), 155 (13), 154 (10), 153 (12), 152 (8), 129 (9), 128 (15), 127 (15), 115 (7), 85 (11).

The synthesis of 25a,d–f

In a flame-dried Schlenk tube (25 mL) equipped with a magnetic stirrer and an inert gas inlet was placed amine (1 equiv.) in DCM (10 mL). Then, NEt_3 (1 equiv.) was added followed by Ph_2PCl (1 equiv.). The mixture was allowed to stir at rt for 16 h, then BH_3–THF (1.5 equiv., 1 M in THF) was added and the mixture was allowed to stir for an additional hour. Then, water (10 mL) was added to the reaction mixture. The mixture was extracted with DCM (3 × 20 mL), combined organic phases were dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography using hexane–EtOAc = 6 : 1 or $CHCl_3$–MeOH = 15 : 1 as the eluent.

Diphenylphosphinous acid-borane *N*-methylneomenthylamide (25a). Prepared from *N*-methylneomenthylamine (**24a**) (0.211 g, 0.0012 mol), Ph_2PCl (0.224 mL, 0.275 g, 0.0012 mol), NEt_3 (0.174 mL, 0.126 g, 0.0012 mol) and BH_3–THF (1.87 mL, 0.0019 mol). Yield 0.163 g (36%). Colorless oil. R_F 0.56 (hexane–EtOAc 6 : 1). $[\alpha]_D$ −15.7 (*c* 0.825, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.66–1.37 (bm, 3 H), 0.80 (d, J_{H-H} = 6.3 Hz, 3 H), 0.86–0.98 (m, 1 H), 0.95 (d, J_{H-H} = 6.6 Hz, 3 H), 1.09 (d, J_{H-H} = 6.3 Hz, 3 H), 1.19–1.29 (m, 1 H), 1.27–1.36 (m, 1 H), 1.42–1.53 (m, 1 H), 1.62–1.78 (m, 2 H), 1.79–1.86 (m, 2 H), 1.98–2.04 (m, 1 H), 2.76 (d, J_{P-H} = 7.9 Hz, 3 H), 4.18–4.25 (m, 1 H), 7.41–7.53 (m, 6 H), 7.58–7.63 (m, 2 H), 7.65–7.71 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.2 22.82, 23.1, 26.6, 28.7, 29.0, 34.8, 36.6 (d, J_{P-C} = 4.5 Hz), 43.4, 47.5 (d, J_{P-C} = 8.2 Hz), 53.5 (d, J_{P-C} = 10.9 Hz), 128.2 (d, J_{P-C} = 10.0 Hz), 128.3 (d, J_{P-C} = 10.0 Hz), 130.7 (d, J_{P-C} = 2.7 Hz), 130.8 (d, J_{P-C} = 1.8

Hz), 131.4 (d, J_{P-C} = 69.0 Hz), 131.7 (d, J_{P-C} = 57.2 Hz), 132.1 (d, J_{P-C} = 10.9 Hz), 132.5 (d, J_{P-C} = 10.0 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 72.33 ppm (bm). GC (Phenomenex Zebron ZB-35 HT): R_T = 14.65 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 353 (M − BH_3) (6), 268 (13), 215 (24), 214 (23), 186 (24), 185 (27), 183 (37), 169 (13), 168 (100), 109 (20), 108 (37), 107 (9), 84 (7). $C_{23}H_{35}BNP$ (367.32): calcd C 75.21, H 9.60, N 3.81; found C 75.02, H 9.59, N 4.03.

Diphenylphosphinous acid-borane *N*-methyl-bornylamide (25d). Prepared from *N*-methylbornylamine (**24d**) (0.782 g, 0.0047 mol), Ph_2PCl (0.840 mL, 1.032 g, 0.0047 mol), NEt_3 (0.652 mL, 0.473 g, 0.0047 mol) and BH_3–THF (7.01 mL, 0.0070 mol). Isolated as a mixture of *exo*–*endo* isomers in a 1 : 0.4 ratio. Crystallization of this mixture afforded a product in a 1 : 0.1 ratio. Yield 1.205 g (71%). White sticky oil. R_F 0.77 (hexane–EtOAc 6 : 1). ^{1}H NMR ($CDCl_3$, 500 MHz) (*exo* isomer) δ 0.41–1.29 (3 H, bm), 0.85 (3 H, s), 0.94 (3 H, s), 0.95 (3 H, s), 1.19–1.29 (2 H, m), 1.37–1.45 (1 H, m), 1.47–1.56 (1 H, m), 1.63–1.72 (4 H, m), 1.93–2.02 (1 H, m), 2.70 (3 H, d, *J* = 10.1 Hz), 2.73–2.83 (1 H, m), 3.78–3.86 (1 H, m), 5.64–5.71 (1 H, m), 5.79–5.94 (3 H, m), 7.42–7.52 (3 H, m), 7.61–7.66 (2 H, m); (*endo* isomer) δ 0.41–1.29 (3 H, bm), 0.76 (3 H, s), 0.83 (3 H, s), 0.90 (3 H, s), 1.19–1.29 (2 H, m), 1.37–1.45 (1 H, m), 1.47–1.56 (1 H, m), 1.63–1.72 (4 H, m), 1.93–2.02 (1 H, m), 2.72 (3 H, d, *J* = 10.7 Hz), 2.73–2.83 (1 H, m), 3.42–3.49 (1 H, m), 3.92–4.01 (1 H, m), 5.74–5.79 (1 H, m), 5.79–5.94 (3 H, m), 7.42–7.52 (3 H, m), 7.71–7.76 (2 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz,) (only some peaks are described due to overlapping of signals) (*exo* isomer) δ 50.6 (d, *J* = 3.6 Hz), 67.4 (d, *J* = 5.5 Hz), 121.6 (d, *J* = 2.7 Hz), 121.8 (d, *J* = 5.5 Hz), 127.6 (d, *J* = 10.0 Hz), 127.7 (d, *J* = 8.2 Hz), 128.8 (d, *J* = 10.0 Hz), 130.8 (d, *J* = 10.0 Hz), 131.2 (d, *J* = 1.8 Hz), 132.1 (d, *J* = 74.5 Hz); (*endo* isomer) δ 50.4 (d, *J* = 3.6 Hz), 68.5 (d, *J* = 5.5 Hz), 121.6 (d, *J* = 2.7 Hz), 122.0 (d, *J* = 6.4 Hz), 127.3 (d, *J* = 7.3 Hz), 127.5 (d, *J* = 10.0 Hz), 128.8 (d, *J* = 10.0 Hz), 131.2 (d, *J* = 9.1 Hz), 131.3 (d, *J* = 1.8 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz) (*exo* isomer) δ 79.95 (bm); (*endo* isomer) δ 81.78 (bm); $C_{23}H_{33}BNP$ (365.30): calcd C 75.62, H 9.11, N 3.83; found C 75.70, H 9.30, N 3.88.

Diphenylphosphinous acid-borane *N*-methyl-(*R*)-1-(1-naphthyl)ethylamide (25e). Prepared from *N*-methyl-(*R*)-1-(1-naphthyl)ethylamine (**24e**) (0.910 g, 0.0049 mol), Ph_2PCl (0.881 mL, 1.083 g, 0.0049 mol), NEt_3 (0.684 mL, 0.497 g, 0.0049 mol) and BH_3–THF (7.37 mL, 0.0074 mol). Yield 1.357 g (72%). White solid, mp 144.2–145.8 °C. R_F 0.63 (hexane–EtOAc 6 : 1). $[\alpha]_D$ −172.7 (*c* 1.24, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.05–1.88 (3 H, bm), 1.67 (3 H, d, *J* = 6.9 Hz), 2.11 (3 H, d, *J* = 7.3 Hz), 5.99–6.06 (3 H, m), 7.28–7.34 (2 H, m), 7.40–7.57 (10 H, m), 7.74–7.80 (2 H, m), 7.82–7.86 (1 H, m), 7.88–7.91 (1 H, m), 8.66–8.69 (1 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz,) δ 17.2, 29.6 (d, *J* = 4.5 Hz), 53.0 (d, *J* = 10.9 Hz), 124.6, 125.3 (d, *J* = 1.8 Hz), 125.4, 125.8, 126.1, 128.2 (d, *J* = 10.9 Hz), 128.3, 128.4 (d, *J* = 10.0 Hz), 128.5, 130.5 (d, *J* = 64.5 Hz), 130.7 (d, *J* = 2.7 Hz), 131.2 (d, *J* = 1.8 Hz), 131.4 (d, *J* = 53.6 Hz), 131.9, 132.0 (d, *J* = 10.9 Hz), 132.8 (d, *J* = 10.0 Hz), 134.0, 136.6 (d, *J* = 9.1 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz) δ 68.05 (bm); GC (Phenomenex Zebron ZB-35 HT) R_T 19.37 min; GC–MS (EI, 70 eV) *m*/*z* (%) 369 (M − BH_3) (12), 368 (10), 313 (12), 312 (52), 311 (30), 215 (9), 214 (52), 185 (7), 184 (7), 183 (25), 155 (15), 153 (15), 152 (10), 128 (9), 127 (8), 122 (13), 115 (9), 109 (100), 108 (10), 107 (8), 104 (12); $C_{25}H_{27}BNP$ (383.27): calcd C 78.34, H 7.10, N 3.65; found C 78.55, H 7.00, N 3.49.

Diphenylphosphinous acid-borane *N*-methyl-(*S*)-1-(2-naphthyl)ethylamide (25f). Prepared from *N*-methyl-(*S*)-1-(2-naphthyl)ethylamine (**24f**) (0.138 g, 0.0007 mol), Ph_2PCl (0.133 mL, 0.164 g, 0.0007 mol), NEt_3 (0.104 mL, 0.075 g, 0.0007 mol) and BH_3–THF (1.12 mL, 0.0011 mol). Yield 0.185 g (65%). White solid, mp 145.0 °C (dec.). R_F 0.63 (hexane–EtOAc 6 : 1). $[\alpha]_D$ −15.0 (*c* 1.045, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.82–1.72 (3 H, bm), 1.64 (3 H, d, *J* = 6.6 Hz), 2.26 (3 H, d, *J* = 7.3 Hz), 5.50–5.58 (1 H, m), 7.40–7.45 (2 H, m), 7.47–7.52 (5 H, m), 7.53–7.60 (3 H, m), 7.61–7.64 (1 H, m), 7.70–7.75 (2 H, m), 7.77 (1 H, bs), 7.81–7.88 (3 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 16.5, 28.9 (d, *J* = 4.5 Hz), 55.6 (d, *J* = 11.8 Hz), 125.8, 125.9, 126.0, 127.0, 127.5, 127.9, 127.9, 128.4 (d, *J* = 10.9 Hz), 128.5 (d, *J* = 10.0 Hz), 130.8 (d, *J* = 68.1 Hz), 130.9 (d, *J* = 1.8 Hz), 131.1 (d, *J* = 2.7 Hz), 131.4 (d, *J* = 60.0 Hz), 132.2 (d, *J* = 10.9 Hz), 132.4 (d, *J* = 10.0 Hz), 132.6, 133.0, 139.1 (d, *J* = 5.5 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz) δ 69.59 (bm); GC (Phenomenex Zebron ZB-35 HT) R_T 19.77 min; GC–MS (EI, 70 eV) *m*/*z* (%) 369 (M − BH_3) (11), 368 (9), 313 (16), 312 (65), 215 (11), 214 (58), 184 (11), 183 (25), 155 (19), 154 (9), 153 (15), 152 (10), 128 (10), 127 (10), 122 (13), 115 (10), 110 (7), 109 (100), 108 (16), 107 (9), 104 (12); $C_{25}H_{27}BNP$ (383.27): calcd C 78.34, H 7.10, N 3.65; found C 78.33, H 7.12, N 3.88.

***N*-Methyl-(*S*)-1-phenylethylamine (31).** This compound was prepared according to the literature procedure.[27] Data are in accordance with those reported in the literature.[28]

The synthesis of 32a–e and 33a,b

In a flame-dried Schlenk tube (25 mL), equipped with a magnetic stirrer and inert gas inlet was placed secondary phosphine oxide (1 equiv.) in DCM (10 mL). Then, PCl_3 (1.5 equiv.) was added and the mixture was allowed to stir at rt for 2 h. Then, the solution was transferred to a flame-dried, round-bottom, inert gas-flushed flask (25 mL) and evaporated under reduced pressure. The residue was dissolved in DCM (5 mL). In a separate flame-dried Schlenk tube (25 mL), equipped with a magnetic stirrer and an inert gas inlet were placed *N*-methyl-(*S*)-1-phenylethylamine (**31**) (1 equiv.) and NEt_3 (1 equiv.) in DCM (5 mL). A solution of chlorophosphine in DCM, prepared in a separate flask, was transferred to the amine solution using a syringe. After complete addition of chlorophosphine, the mixture was allowed to stir at rt for 23 h. Then, BH_3–THF (1.5 equiv.) was added and the mixture was stirred for an additional hour. Then, water (10 mL) was added to the reaction mixture. The mixture was extracted with DCM (3 × 20 mL), combined organic phases were dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography using hexane–EtOAc = 6 : 1 as the eluent.

Di(*o*-tolyl)phosphinous acid-borane *N*-methyl-(*S*)-α-methylbenzylamide (32a). Prepared from di(*o*-tolyl)phosphine oxide (0.401 g, 0.0017 mol), PCl_3 (0.228 mL, 0.359 g, 0.0026 mol), **31**

(0.236 g, 0.0017 mol), NEt_3 (0.243 mL, 0.176 g, 0.0017 mol) and BH_3–THF (2.61 mL, 0.0026 mol). Yield 0.261 g (41%). Colorless thick oil. R_F 0.69 (hexane–EtOAc 6 : 1). $[\alpha]_D$ −71.0 (*c* 1.135, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz) δ 1.04–1.77 (3 H, bm), 1.64 (3 H, d, J = 6.9 Hz), 2.34 (3 H, s), 2.35 (3 H, s), 5.46–5.56 (1 H, m), 7.01–7.12 (2 H, m), 7.17–7.23 (1 H, m), 7.23–7.27 (1 H, m), 7.28–7.45 (9 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 17.1 (d, J = 1.8 Hz), 22.2 (d, J = 3.6 Hz), 22.5 (d, J = 2.7 Hz), 29.0 (d, J = 2.7 Hz), 55.6 (d, J = 10.0 Hz), 125.4 (d, J = 9.1 Hz), 125.6 (d, J = 9.1 Hz), 127.3, 128.0, 128.4, 129.8 (d, J = 61.8 Hz), 130.7 (d, J = 1.8 Hz), 130.7 (d, J = 60.4 Hz), 131.0 (d, J = 1.8 Hz), 131.8 (d, J = 9.1 Hz), 132.0 (d, J = 9.1 Hz), 132.3 (d, J = 7.3 Hz), 132.8 (d, J = 8.2 Hz), 141.2 (d, J = 3.6 Hz), 141.5 (d, J = 12.7 Hz), 142.3 (d, J = 12.7 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz,) δ 70.92 (bm); GC (Phenomenex Zebron ZB-35 HT) R_T 15.29 min; GC–MS (EI, 70 eV) *m*/*z* (%) 347 (M − BH_3) (26), 346 (4), 290 (13), 275 (11), 243 (17), 242 (100), 214 (8), 213 (24), 212 (12), 211 (29), 197 (10), 196 (22), 179 (12), 165 (18), 152 (11), 150 (52), 136 (16), 135 (43), 134 (76), 133 (10), 123 (19), 122 (23), 121 (32), 105 (40), 103 (9), 91 (25); $C_{23}H_{29}BNP$ (361.27): calcd C 76.47, H 8.09, N 3.88; found C 76.43, H 8.30, N 4.00.

Di(*p*-tolyl)phosphinous acid-borane *N*-methyl-(*S*)-α-methylbenzylamide (32b). Prepared from di(*p*-tolyl)phosphine oxide (0.419 g, 0.0018 mol), PCl_3 (0.238 mL, 0.375 g, 0.0027 mol), **31** (0.246 g, 0.0018 mol), NEt_3 (0.254 mL, 0.184 g, 0.0018 mol) and BH_3–THF (2.73 mL, 0.0027 mol). Yield 0.154 g (23%). Colorless thick oil. R_F 0.58 (hexane–EtOAc 6 : 1). $[\alpha]_D$ −31.4 (*c* 0.81, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz) δ 0.74–1.63 (3 H, bm), 1.49 (3 H, d, J = 6.9 Hz), 2.22 (3 H, d, J = 7.3 Hz), 2.39 (3 H, s), 2.42 (3 H, s), 7.20–7.24 (2 H, m), 7.25–7.30 (3 H, m), 7.32–7.37 (2 H, m), 7.38–7.44 (4 H, m), 7.54–7.60 (2 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz,) δ 16.4, 21.4, 21.4, 28.7 (d, J = 3.6 Hz), 55.2 (d, J = 11.8 Hz), 127.0, 127.6 (d, J = 71.8 Hz), 127.9, 128.0, 128.2 (d, J = 61.8 Hz), 129.1 (d, J = 10.9 Hz), 129.1 (d, J = 10.9 Hz), 132.1 (d, J = 10.0 Hz), 132.3 (d, J = 10.9 Hz), 141.0 (d, J = 1.8 Hz), 141.3 (d, J = 1.8 Hz), 141.7 (d, J = 5.5 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz) δ 68.45 (bm); GC (Phenomenex Zebron ZB-35 HT) R_T 15.92 min; GC–MS (EI, 70 eV) *m*/*z* (%) 347 (M − BH_3) (9), 346 (16), 291 (22), 290 (100), 243 (9), 242 (52), 213 (14), 211 (14), 197 (6), 183 (10), 165 (11), 136 (20), 135 (9), 134 (30), 123 (90), 122 (37), 121 (29), 118 (15), 105 (27), 91 (20); $C_{23}H_{29}BNP$ (361.27): calcd C 76.47, H 8.09, N 3.88; found C 76.70, H 8.19, N 3.77.

Di(*p*-anisyl)phosphinous acid-borane *N*-methyl-(*S*)-α-methylbenzylamide (32c). Prepared from di(*p*-anisyl)phosphine oxide (0.461 g, 0.0018 mol), PCl_3 (0.230 mL, 0.362 g, 0.0026 mol), **31** (0.238 g, 0.0017 mol), NEt_3 (0.245 mL, 0.178 g, 0.0017 mol) and BH_3–THF (2.64 mL, 0.0026 mol). Yield 0.380 g (55%). Colorless thick oil. R_F 0.44 (hexane–EtOAc 6 : 1). $[\alpha]_D$ 27.6 (*c* 0.87, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz) δ 0.83–1.54 (3 H, bm), 1.50 (3 H, d, J = 6.9 Hz), 2.24 (3 H, d, J = 7.6 Hz), 3.84 (3 H, s), 3.86 (3 H, s), 5.29–5.39 (1 H, m), 6.92–6.96 (2 H, m), 6.98–7.02 (2 H, m), 7.25–7.29 (1 H, m), 7.32–7.37 (2 H, m), 7.40–7.44 (2 H, m), 7.45–7.50 (2 H, m), 7.61–7.67 (2 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz,) δ 16.3, 28.5 (d, J = 3.6 Hz), 55.2, 55.2, 113.95 (d, J = 10.9 Hz), 113.98 (d, J = 11.8 Hz), 122.0 (d, J = 73.6 Hz), 122.7 (d, J = 64.5 Hz), 126.9, 127.8, 128.1, 133.8 (d, J = 10.9 Hz), 134.0 (d, J = 11.8 Hz), 141.7 (d, J = 6.4 Hz), 161.6 (d, J = 2.7 Hz), 161.7 (d, J = 2.7 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz) δ 67.07 (bm); GC (Phenomenex Zebron ZB-35 HT) R_T 19.14 min; GC–MS (EI, 70 eV) *m*/*z* (%) 379 (M − BH_3) (9), 378 (13), 323 (18), 322 (83), 274 (43), 245 (19), 214 (9), 152 (9), 139 (100), 138 (54), 134 (24), 113 (10), 105 (20), 95 (10); $C_{23}H_{29}BNO_2P$ (393.27): calcd C 70.24, H 7.43, N 3.56; found C 70.38, H 7.33, N 3.70.

Di(3,5-dimethylphenyl)phosphinous acid-borane *N*-methyl-(*S*)-α-methylbenzylamide (32d). Prepared from di(3,5-dimethylphenyl)phosphine oxide (0.384 g, 0.0015 mol), PCl_3 (0.195 mL, 0.306 g, 0.0022 mol), **31** (0.201 g, 0.0015 mol), NEt_3 (0.207 mL, 0.150 g, 0.0015 mol) and BH_3–THF (2.23 mL, 0.0023 mol). Yield 0.136 g (24%). Colorless thick oil. R_F 0.67 (hexane–EtOAc 6 : 1). $[\alpha]_D$ 32.3 (*c* 0.95, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz,) δ 0.75–1.60 (3 H, bm), 1.53 (3 H, d, J = 6.9 Hz), 2.27 (3 H, d, J = 7.3 Hz), 2.31 (6 H, s), 2.38 (6 H, s), 7.11 (2 H, bs), 7.14 (1 H, bs), 7.16 (1 H, bs), 7.28–7.33 (3 H, m), 7.34–7.39 (2 H, m), 7.43–7.47 (2 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 16.5 (d, J = 1.8 Hz), 21.3, 21.4, 28.9 (d, J = 3.6 Hz), 55.3 (d, J = 10.9 Hz), 127.0, 127.97, 127.99, 129.7 (d, J = 10.0 Hz), 129.9 (d, J = 10.0 Hz), 130.7 (d, J = 67.2 Hz), 131.2 (d, J = 60.9 Hz), 132.5 (d, J = 1.8 Hz), 132.8 (d, J = 2.7 Hz), 137.9 (d, J = 10.9 Hz), 137.9 (d, J = 10.9 Hz), 141.7 (d, J = 5.5 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz,) δ 69.57 (bm); GC (Phenomenex Zebron ZB-35 HT) R_T 15.60 min; GC–MS (EI, 70 eV) *m*/*z* (%) 375 (M − BH_3) (8), 374 (12), 319 (22), 318 (100), 271 (8), 270 (44), 241 (15), 211 (9), 193 (8), 149 (15), 137 (58), 136 (32), 135 (15), 134 (40), 133 (16), 119 (16), 109 (12), 105 (40), 103 (10), 92 (18), 91 (41); $C_{25}H_{33}BNP$ (389.32): calcd C 77.13, H 8.54, N 3.60; found C 77.30, H 8.55, N 3.55.

Di(3,5-dimethoxyphenyl)phosphinous acid-borane *N*-methyl-(*S*)-α-methylbenzylamide (32e). Prepared from di(3,5-dimethoxyphenyl)phosphine oxide (0.458 g, 0.0014 mol), PCl_3 (0.186 mL, 0.293 g, 0.0021 mol), **31** (0.192 g, 0.0014 mol), NEt_3 (0.198 mL, 0.144 g, 0.0014 mol) and BH_3–THF (2.13 mL, 0.0021 mol). Yield 0.191 g (30%). Colorless thick oil. R_F 0.42 (hexane–EtOAc 6 : 1). $[\alpha]_D$ 45.2 (*c* 0.75, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz) δ 0.91–1.74 (3 H, bm), 1.55 (3 H, d, J = 7.3 Hz), 2.28 (3 H, d, J = 7.3 Hz), 3.71 (6 H, s), 3.80 (6 H, s), 5.28–5.39 (1 H, m), 6.54 (1 H, t, J = 2.2 Hz), 6.59 (1 H, t, J = 2.2 Hz), 6.66 (2 H, dd, J = 2.5 Hz, 12.0 Hz), 6.84 (2 H, dd, J = 2.2 Hz, 11.7 Hz), 7.25–7.29 (1 H, m), 7.33–7.37 (2 H, m), 7.44–7.47 (2 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 16.5, 29.0 (d, J = 3.6 Hz), 55.30, 55.38, 55.37 (d, J = 11.8 Hz), 102.8, 103.2, 109.6 (d, J = 11.8 Hz), 110.1 (d, J = 11.8 Hz), 127.1, 127.9, 128.1, 132.7 (d, J = 67.2 Hz), 133.3 (d, J = 60.9 Hz), 141.4 (d, J = 6.4 Hz), 160.5 (d, J = 5.5 Hz), 160.7 (d, J = 4.5 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz) δ 72.17 (bm); GC (Phenomenex Zebron ZB-35 HT) R_T 20.81 min; GC–MS (EI, 70 eV) *m*/*z* (%) 439 (9), 438 (M − BH_3) (14), 383 (24), 382 (100), 334 (31), 305 (8), 196 (11), 182 (17), 181 (10), 169 (16), 168 (14), 167 (18), 151 (12), 139 (9), 137 (9), 134 (40), 121 (9), 105 (36), 95 (11); $C_{25}H_{33}BNO_4P$ (453.22): calcd C 66.24, H 7.34, N 3.09; found C 66.50, H 7.45, N 3.00.

Di(2,6-dimethylphenyl)phosphine (33a). Prepared from di(2,6-dimethylphenyl)phosphine oxide (0.517 g, 0.002 mol), PCl_3 (0.262 mL, 0.412 g, 0.003 mol), **31** (0.271 g, 0.002 mol), NEt_3 (0.279 mL, 0.202 g, 0.002 mol) and BH_3–THF (3.00 mL, 0.003 mol). Yield 0.140 g (29%) (the product partially oxidized to the corresponding phosphine oxide during analysis). R_F 0.95 (hexane–EtOAc 6 : 1). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.34 (12 H, s), 5.35 (1 H, d, J = 232.7 Hz), 7.01–7.06 (4 H, m), 7.12–7.17 (2 H, m); ^{31}P NMR ($CDCl_3$, 202 MHz) δ −91.57. Data are in accordance with those reported in the literature.[29]

Di(3,5-bis(trifluoromethyl)phenyl)phosphine (33b). Obtained from di(2,6-dimethylphenyl)phosphine oxide (0.474 g, 0.001 mol), PCl_3 (0.131 mL, 0.206 g, 0.0015 mol), **31** (0.135 g, 0.001 mol), NEt_3 (0.139 mL, 0.101 g, 0.001 mol) and BH_3–THF (1.50 mL, 0.0015 mol) as a mixture with other compounds. ^{31}P NMR (202 MHz, $CDCl_3$) δ −40.59. Data are in accordance with those reported in the literature.[13a]

A general procedure of Birch reduction of arylphosphorus acid amides

A flame-dried, two-neck, round-bottom flask (100 mL), equipped with a dry-ice condenser, a magnetic stirring bar and an inert gas inlet was cooled to −78 °C. Gaseous ammonia was passed through the system until 10 mL was collected. Then, sodium (2.5–5 equiv.) was added and the mixture was allowed to stir at −78 °C for 5 min. Then, amide (1 equiv.) in THF (5 mL) was added and the mixture was stirred for 5 min. Solid NH_4Cl (0.5 g) was added to quench the reaction, ammonia was evaporated under reduced pressure, the inorganic solid was filtered off and the filtrate was evaporated. The residue was purified by flash chromatography using hexane–EtOAc = 6 : 1, hexane–EtOAc = 2 : 1 or $CHCl_3$–MeOH = 15 : 1 as eluents.

(1,4-Cyclohexadien-3-yl)phenylphosphinous acid-borane *N*-methyl-(*S*)-α-methylbenzylamide (13b). Prepared from **10b** (0.094 g, 0.0003 mol) and sodium (0.016 g, 0.0007 mol). Isolated as a mixture with unreacted starting material. Yield 71% (a mixture of two diastereomers in 52% de) (based on NMR analysis). R_F 0.69 (hexane–EtOAc 2 : 1). ^{1}H NMR ($CDCl_3$, 500 MHz,) (major diastereomer) δ 0.55–1.28 (3 H, bm), 1.48 (3 H, d, J = 6.9 Hz), 2.37 (3 H, dd, J = 1.0 Hz, 6.9 Hz), 2.60–2.74 (2 H, m), 3.87–3.97 (1 H, m), 5.09–5.19 (1 H, m), 5.59–5.65 (1 H, m), 5.73–5.85 (3 H, m), 7.24–7.30 (2 H, m), 7.39–7.45 (3 H, m), 7.46–7.56 (3 H, m), 7.72–7.79 (2 H, m); (minor diastereomer) δ 0.55–1.28 (3 H, bm), 1.56 (3 H, d, J = 6.9 Hz), 2.39 (3 H, dd, J = 0.6 Hz, 6.3 Hz), 2.70–2.85 (2 H, m), 3.82–3.91 (1 H, m), 5.32–5.41 (1 H, m), 5.63–5.68 (1 H, m), 5.78–5.88 (3 H, m), 7.31–7.38 (2 H, m), 7.39–7.45 (3 H, m), 7.46–7.56 (3 H, m), 7.66–7.72 (2 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz,) (major diastereomer) δ = 16.4, 26.4 (d, J = 5.5 Hz), 29.0 (d, J = 4.5 Hz), 36.7 (d, J = 40.9 Hz), 55.9 (d, J = 9.1 Hz), 121.2 (d, J = 2.7 Hz), 121.6 (d, J = 6.4 Hz), 127.1, 127.9, 128.1 (d, J = 6.4 Hz), 128.1 (d, J = 5.5 Hz), 128.1, 128.7 (d, J = 10.0 Hz), 130.7 (d, J = 2.7 Hz), 131.2 (d, J = 9.1 Hz), 131.7 (d, J = 51.8 Hz); (minor diastereomer) δ 16.5, 26.5 (d, J = 5.5 Hz), 28.8 (d, J = 4.5 Hz), 38.1 (d, J = 36.3 Hz), 55.9 (d, J = 10.0 Hz), 121.8 (d, J = 2.7 Hz), 122.2 (d, J = 7.3 Hz), 127.1, 127.7, 128.0, 128.1 (d, J = 10.0 Hz), 128.4 (d, J = 6.4 Hz), 128.5 (d, J = 5.5 Hz), 130.5 (d, J = 2.7 Hz), 131.1 (d, J = 9.1 Hz), 131.4 (d, J = 51.1 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz) (major diastereomer) δ 72.85 (bm); (minor diastereomer) δ 75.09 (bm).

(1,4-Cyclohexadien-3-yl)phenylphosphinous acid-borane *N*-ethyl-(*S*)-α-methylbenzylamide (13c). Prepared from **10c** (0.093 g, 0.0003 mol) and sodium (0.015 g, 0.0007 mol). Isolated as a mixture with a substrate. Yield 77% (a mixture of two diastereomers in 42% de) (based on NMR analysis). R_F 0.67 (hexane–EtOAc 2 : 1). ^{1}H NMR ($CDCl_3$, 500 MHz,) (major diastereomer) δ 0.55–1.35 (3 H, bm), 0.64 (3 H, t, J = 7.3 Hz), 1.57 (3 H, d, J = 6.9 Hz), 2.77–2.85 (2 H, m), 2.89–2.97 (1 H, m), 3.05–3.13 (1 H, m), 4.00–4.10 (1 H, m), 5.06–5.17 (1 H, m), 5.67–5.73 (1 H, m), 5.77–5.82 (1 H, m), 5.87–5.93 (1 H, m), 5.96–6.02 (1 H, m), 7.30–7.35 (2 H, m), 7.45–7.54 (6 H, m), 7.83–7.89 (2 H, m); (minor diastereomer) δ 0.55–1.35 (3 H, bm), 0.78 (3 H, t, J = 7.3 Hz), 1.56 (3 H, d, J = 6.9 Hz), 2.83–2.88 (2 H, m), 2.95–3.03 (1 H, m), 3.05–3.13 (1 H, m), 3.97–4.07 (1 H, m), 5.24–5.33 (1 H, m), 5.72–5.77 (1 H, m), 5.84–5.89 (1 H, m), 5.91–5.99 (2 H, m), 7.30–7.35 (2 H, m), 7.45–7.54 (6 H, m), 7.73–7.77 (2 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz,) (major diastereomer) δ 17.2, 18.8, 26.6 (d, J = 5.5 Hz), 36.1 (d, J = 40.9 Hz), 38.8, 56.0 (d, J = 7.3 Hz), 121.4 (d, J = 4.5 Hz), 121.4 (d, J = 1.8 Hz), 127.1, 128.0, 127.98, 128.00 (d, J = 4.5 Hz), 128.1 (d, J = 3.6 Hz), 128.6 (d, J = 9.1 Hz), 130.9 (d, J = 1.8 Hz), 131.4 (d, J = 52.7 Hz), 131.7 (d, J = 9.1 Hz); (minor diastereomer) δ 17.6, 19.4, 26.6 (d, J = 5.5 Hz), 37.2 (d, J = 38.2 Hz), 39.6, 56.4 (d, J = 8.2 Hz), 121.5 (d, J = 5.5 Hz), 121.7 (d, J = 1.8 Hz), 127.1, 127.96, 127.98, 128.3 (d, J = 4.5 Hz), 128.4 (d, J = 3.6 Hz), 128.6 (d, J = 9.1 Hz), 130.7 (d, J = 1.8 Hz), 131.5 (d, J = 9.1 Hz), 131.7 (d, J = 51.8 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz,) (major diastereomer) δ 72.54 (bm); (minor diastereomer) δ 74.49 (bm).

(1,4-Cyclohexadien-3-yl)phenylphosphinous acid-borane *N*-isopropyl-(*S*)-α-methylbenzylamide (13d). Prepared from **10d** (0.129 g, 0.0004 mol) and sodium (0.021 g, 0.0009 mol). Isolated as a mixture with a substrate. Yield 21% (a mixture of two diastereomers in 10% de) (based on NMR analysis). R_F 0.69 (hexane–EtOAc 2 : 1). ^{1}H NMR ($CDCl_3$, 500 MHz) (major diastereomer) δ 0.56–1.48 (3 H, bm), 1.01 (3 H, d, J = 6.9 Hz), 1.05 (3 H, d, J = 6.9 Hz), 1.59 (3 H, d, J = 6.9 Hz), 2.69–2.86 (2 H, m), 3.50–3.60 (1 H, m), 3.95–4.06 (1 H, m), 4.85–4.97 (1 H, m), 5.63–5.72 (2 H, m), 5.83–5.90 (2 H, m), 7.20–7.26 (2 H, m), 7.41–7.53 (6 H, m), 7.83–7.88 (2 H, m); (minor diastereomer) δ 0.56–1.48 (3 H, bm), 0.85 (3 H, d, J = 6.9 Hz), 1.02 (3 H, d, J = 6.9 Hz), 1.46 (3 H, d, J = 6.9 Hz), 2.80–2.94 (2 H, m), 3.61–3.70 (1 H, m), 4.12–4.22 (1 H, m), 4.98–5.06 (1 H, m), 5.88–5.95 (2 H, m), 5.96–6.06 (2 H, m), 7.20–7.26 (2 H, m), 7.41–7.53 (6 H, m), 7.91–7.96 (2 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) (some peaks were overlapped) (major diastereomer) δ 20.4, 23.5 (d, J = 1.8 Hz), 24.5, 26.7 (d, J = 5.5 Hz), 35.5 (d, J = 40.0 Hz), 50.0, 55.2 (d, J = 5.5 Hz), 121.4 (d, J = 3.6 Hz), 121.8, 127.1, 127.8, 128.1, 128.6 (d, J = 9.1 Hz), 130.8, 132.0 (d, J = 9.1 Hz); (minor diastereomer) δ 19.6, 23.6 (d, J = 1.8 Hz), 24.3, 26.6 (d, J = 5.5 Hz), 35.7 (d, J = 40.9 Hz), 50.2, 55.9 (d, J = 5.5 Hz), 121.4 (d, J = 3.6 Hz), 121.7, 127.0, 128.0, 128.1, 128.6 (d, J = 9.1 Hz), 130.8,

131.8 (d, J = 9.1 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz) (major diastereomer) δ 69.12 (bm); (minor diastereomer) δ 69.36 (bm).

(1,4-Cyclohexadien-3-yl)phenylphosphinic acid *N*-methyl-(*S*)-α-methylbenzylamide (14b). Prepared from **11b** (0.095 g, 0.0003 mol) and sodium (0.016 g, 0.0007 mol). Isolated as a mixture with a substrate and **15b**. Yield 20% (a mixture of two diastereomers in 0% de) (based on NMR analysis). R_F 0.77 ($CHCl_3$–MeOH 15 : 1). ^{1}H NMR ($CDCl_3$, 500 MHz) (first diastereomer) δ 1.57 (3 H, d, J = 6.3 Hz), 2.41 (3 H, d, J = 9.2 Hz), 2.67–2.84 (2 H, m), 3.76–3.86 (1 H, m), 4.81–4.87 (1 H, m), 5.61–5.67 (2 H, m), 5.69–5.75 (1 H, m), 5.76–5.85 (1 H, m), 7.21–7.27 (3 H, m), 7.39–7.54 (5 H, m), 7.78–7.83 (2 H, m); (second diastereomer) δ 1.61 (3 H, d, J = 6.9 Hz), 2.47 (3 H, d, J = 10.4 Hz), 2.67–2.84 (2 H, m), 3.82–3.92 (1 H, m), 4.87–4.93 (1 H, m), 5.61–5.67 (2 H, m), 5.69–5.75 (1 H, m), 5.76–5.85 (1 H, m), 7.21–7.27 (3 H, m), 7.39–7.54 (5 H, m), 7.83–7.89 (2 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) (first diastereomer) δ 17.0 (d, J = 1.8 Hz), 26.0 (d, J = 5.5 Hz), 27.6 (d, J = 1.8 Hz), 39.2 (d, J = 89.0 Hz), 53.1 (d, J = 1.8 Hz), 120.9 (d, J = 7.3 Hz), 121.1 (d, J = 6.4 Hz), 126.9, 127.3, 127.5, 128.0 (d, J = 11.8 Hz), 129.9 (d, J = 120.8 Hz), 131.6 (d, J = 2.7 Hz), 132.7 (d, J = 9.1 Hz), 141.0 (d, J = 5.5 Hz); (second diastereomer) δ 17.3 (d, J = 1.8 Hz), 26.0 (d, J = 5.5 Hz), 27.7 (d, J = 1.8 Hz), 39.4 (d, J = 88.1 Hz), 53.1 (d, J = 1.8 Hz), 121.0 (d, J = 5.5 Hz), 121.1 (d, J = 7.3 Hz), 127.39, 127.44, 127.7, 128.0 (d, J = 11.8 Hz), 130.3 (d, J = 120.8 Hz), 131.6 (d, J = 2,7 Hz), 132.7 (d, J = 8.2 Hz), 141.2 (d, J = 5.5 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz) (first diastereomer) δ 36.07; (second diastereomer) δ 36.83; GC (Phenomenex Zebron ZB-35 HT) (first diastereomer) R_T 17.54 min; (second diastereomer) R_T 17.60 min; GC–MS (EI, 70 eV) (first diastereomer) m/z (%) 337 (M) (2), 259 (7), 258 (32), 203 (3), 201 (5), 154 (47), 134 (28), 118 (6), 106 (13), 105 (100); (second diastereomer) m/z (%) 337 (M) (2), 259 (7), 258 (32), 203 (3), 201 (5), 154 (47), 134 (28), 118 (6), 106 (13), 105 (100).

Bis(1,4-cyclohexadien-3-yl)phosphinic acid *N*-methyl-(*S*)-α-methylbenzylamide (15b). Prepared from **11b** (0.095 g, 0.0003 mol) and sodium (0.016 g, 0.0007 mol). Isolated as a mixture with a substrate and **14b**. Yield 50% (based on NMR analysis). R_F 0.77 ($CHCl_3$–MeOH 15 : 1). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.51 (3 H, d, J = 6.9 Hz), 2.41 (3 H, d, J = 9.1 Hz), 2.67–2.84 (4 H, m), 3.58–3.70 (2 H, m), 5.05–5.13 (1 H, m), 5.77–5.97 (8 H, m), 7.33–7.38 (3 H, m), 7.45–7.53 (2 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 17.0 (d, J = 1.8 Hz), 26.3 (d, J = 5.5 Hz), 26.4 (d, J = 5.5 Hz), 27.4 (d, J = 2.7 Hz), 38.8 (d, J = 77.2 Hz), 39.7 (d, J = 76.3 Hz), 51.2 (d, J = 1.8 Hz), 120.5 (d, J = 7.3 Hz), 120.9 (d, J = 7.3 Hz), 120.9 (d, J = 8.2 Hz), 121.1 (d, J = 7.3 Hz), 126.8, 127.8, 128.1, 141.3 (d, J = 3.6 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz) δ 41.71.

(1,4-Cyclohexadien-3-yl)phenylphosphinic acid *N*-ethyl-(*S*)-α-methylbenzylamide (14c). Prepared from **11c** (0.094 g, 0.0003 mol) and sodium (0.015 g, 0.0007 mol). Isolated as a mixture with a substrate and **15c**. Yield 20% (a mixture of two diastereomers in 0% de) (based on NMR analysis). R_F 0.67 ($CHCl_3$–MeOH 15 : 1). ^{1}H NMR ($CDCl_3$, 500 MHz) (first diastereomer) δ 0.83 (3 H, t, J = 6.9 Hz), 1.65 (3 H, d, J = 6.9 Hz), 2.21–2.39 (1 H, m), 2.54–2.68 (1 H, m), 2.85–3.15 (2 H, m), 3.76–3.89 (1 H, m), 4.84–4.95 (1 H, m), 5.72–5.78 (1 H, m), 5.80–5.96 (3 H, m), 7.30–7.38 (3 H, m), 7.43–7.53 (5 H, m), 7.87–7.95 (2 H, m); (second diastereomer) δ 0.87 (3 H, t, J = 7.3 Hz), 1.66 (3 H, d, J = 6.9 Hz), 2.21–2.39 (1 H, m), 2.54–2.68 (1 H, m), 2.85–3.15 (2 H, m), 3.76–3.89 (1 H, m), 4.84–4.95 (1 H, m), 5.72–5.78 (1 H, m), 5.80–5.96 (3 H, m), 7.30–7.38 (3 H, m), 7.43–7.53 (5 H, m), 7.87–7.95 (2 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) (first diastereomer) δ 17.3 (d, J = 2.7 Hz), 19.3 (d, J = 2.7 Hz), 26.0 (d, J = 5.5 Hz), 37.6 (d, J = 1.8 Hz), 39.7 (d, J = 89.0 Hz), 40.0 (d, J = 88.1 Hz), 53.7 (d, J = 1.8 Hz), 121.2 (d, J = 6.4 Hz), 121.5 (d, J = 7.3 Hz), 127.0, 127.8, 130.6 (d, J = 118.1 Hz), 132.7 (d, J = 11.8 Hz), 141.8 (d, J = 5.5 Hz); (second diastereomer) δ 17.3 (d, J = 2.7 Hz), 19.5 (d, J = 2.7 Hz), 26.1 (d, J = 6.4 Hz), 37.7 (d, J = 2.7 Hz), 53.9 (d, J = 1.8 Hz), 121.3 (d, J = 6.4 Hz), 121.6 (d, J = 7.3 Hz), 127.0, 127.9, 130.7 (d, J = 119.0 Hz), 132.7 (d, J = 11.8 Hz), 142.0 (d, J = 3.6 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz) (first diastereomer) δ 35.56; (second diastereomer) δ 35.65; GC (Phenomenex Zebron ZB-35 HT) R_T 17.60 min; GC–MS (EI, 70 eV) m/z (%) 351 (1), 327 (1), 273 (7), 272 (30), 203 (5), 201 (5), 168 (42), 148 (19), 140 (6), 106 (9), 105 (100), 104 (6), 103 (8).

Bis(1,4-cyclohexadien-3-yl)phosphinic acid *N*-ethyl-(*S*)-α-methylbenzylamide (15c). Prepared from **11c** (0.094 g, 0.0003 mol) and sodium (0.015 g, 0.0007 mol). Isolated as a mixture with a substrate and **14c**. Yield 24% (based on NMR analysis). R_F 0.77 ($CHCl_3$–MeOH 15 : 1). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.87 (3 H, t, J = 6.9 Hz), 1.61 (3 H, d, J = 6.9 Hz), 2.74–2.83 (4 H, m), 2.87–3.14 (2 H, m), 3.57–3.72 (2 H, m), 5.01–5.07 (1 H, m), 5.80–5.96 (8 H, m), 7.30–7.38 (3 H, m), 7.43–7.53 (2 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 17.3 (d, J = 1.8 Hz), 19.3 (d, J = 3.6 Hz), 26.3 (d, J = 5.5 Hz), 26.3 (d, J = 5.5 Hz), 37.1 (d, J = 2.7 Hz), 39.4 (d, J = 77.2 Hz), 40.0 (d, J = 76.3 Hz), 52.2 (d, J = 1.8 Hz), 121.0 (d, J = 7.3 Hz), 121.1 (d, J = 8.2 Hz), 121.3 (d, J = 7.3 Hz), 121.5 (d, J = 7.3 Hz), 126.8, 127.2 (d, J = 7.3 Hz), 127.2 (d, J = 7.3 Hz), 127.3 (d, J = 6.4 Hz), 127.9, 128.0, 142.5 (d, J = 3.6 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz) δ 42.27.

(1,4-Cyclohexadien-3-yl)phenylphosphinic acid *N*-isopropyl-(*S*)-α-methylbenzylamide (14d). Prepared from **11d** (0.100 g, 0.0003 mol) and sodium (0.016 g, 0.0007 mol). Isolated as a mixture with a substrate and **15c**. Yield 14% (a mixture of two diastereomers in 9% de) (based on NMR analysis). R_F 0.67 ($CHCl_3$–MeOH 15 : 1). ^{1}H NMR ($CDCl_3$, 500 MHz) (major diastereomer) δ 1.16 (3 H, d, J = 6.6 Hz), 1.18 (3 H, d, J = 6.6 Hz), 1.61 (3 H, d, J = 6.9 Hz), 2.52–2.67 (2 H, m), 3.51–3.63 (1 H, m), 3.67–3.78 (1 H, m), 4.47–4.68 (1 H, m), 5.60–5.66 (3 H, m), 5.68–5.73 (1 H, m), 7.15–7.31 (3 H, m), 7.34–7.48 (5 H, m), 7.84–7.91 (2 H, m); (minor diastereomer) δ 1.07 (3 H, d, J = 6.9 Hz), 1.34 (3 H, d, J = 6.9 Hz), 1.71 (3 H, d, J = 6.9 Hz), 2.27–2.41 (2 H, m), 3.51–3.63 (1 H, m), 3.78–3.89 (1 H, m), 4.47–4.68 (1 H, m), 5.43–5.50 (1 H, m), 5.54–5.60 (3 H, m), 7.15–7.31 (3 H, m), 7.34–7.48 (5 H, m), 7.84–7.91 (2 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) (major diastereomer) δ 20.2 (d, J = 2.7 Hz), 23.8 (d, J = 3.6 Hz), 23.5, 26.1 (d, J = 5.5 Hz), 40.0 (d, J = 87.2 Hz), 48.6 (d, J = 2.7 Hz), 53.2 (d, J = 3.6 Hz), 121.2 (d, J = 8.2 Hz), 121.3 (d, J = 6.4 Hz), 126.8, 131.0 (d, J = 2.7 Hz), 132.0 (d, J = 8.2 Hz),

143.0 (d, J = 2.7 Hz); (minor diastereomer) δ 20.3 (d, J = 1.8 Hz), 23.5 (d, J = 1.8 Hz), 24.5, 26.2 (d, J = 6.4 Hz), 39.9 (d, J = 87.2 Hz), 48.2 (d, J = 2.7 Hz), 53.1 (d, J = 2.7 Hz), 121.3 (d, J = 7.3 Hz), 121.5 (d, J = 6.4 Hz), 126.8, 131.0 (d, J = 2.7 Hz), 132.0 (d, J = 9.1 Hz), 142.5 (d, J = 2.7 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz) (major diastereomer) δ 34.75; (minor diastereomer) δ 34.16; GC (Phenomenex Zebron ZB-35 HT) R_T 17.56 min; GC–MS (EI, 70 eV) m/z (%) 322 (M − iPr) (3), 320 (2), 286 (24), 244 (7), 201 (8), 182 (35), 140 (17), 125 (6), 106 (10), 105 (100), 103 (7), 86 (13).

Bis(1,4-cyclohexadien-3-yl)phosphinic acid *N*-isopropyl-(*S*)-α-methylbenzylamide (15d). Prepared from **11d** (0.100 g, 0.0003 mol) and sodium (0.016 g, 0.0007 mol). Isolated as a mixture with a substrate and **14d**. Yield 24% (based on NMR analysis). R_F 0.67 ($CHCl_3$–MeOH 15 : 1). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.22 (3 H, d, J = 6.6 Hz), 1.27 (3 H, d, J = 6.9 Hz), 1.67 (3 H, d, J = 6.9 Hz), 2.64–2.75 (2 H, m), 2.77–2.87 (2 H, m), 3.42–3.62 (2 H, m), 4.47–4.68 (1 H, m), 5.67–5.82 (4 H, m), 5.87–6.02 (4 H, m), 7.21–7.30 (3 H, m), 7.35–7.48 (2 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 21.9 (d, J = 1.8 Hz), 23.82 (d, J = 1.8 Hz), 23.84 (d, J = 2.7 Hz), 26.4 (d, J = 5.5 Hz), 26.5 (d, J = 5.5 Hz), 40.1 (d, J = 76.3 Hz), 40.2 (d, J = 73.6 Hz), 47.9 (d, J = 2.7 Hz), 53.6 (d, J = 2.7 Hz), 120.9 (d, J = 7.3 Hz), 121.1 (d, J = 7.3 Hz), 121.6 (d, J = 9.1 Hz), 121.7 (d, J = 6.4 Hz), 126.7, 127.1 (d, J = 10.0 Hz), 127.4 (d, J = 10.0 Hz), 127.8, 128.1, 143.6 (d, J = 1.8 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz) δ 43.15.

(1,4-Cyclohexadien-3-yl)phenylphosphinous acid-borane (2*S*)-2-(methoxymethyl)pyrolidinamide (26a). Prepared from **16b** (0.070 g, 0.0002 mol) and sodium (0.013 g, 0.0006 mol). Isolated as a mixture with a substrate. Yield 35% (a mixture of two diastereomers in 54% de) (based on NMR analysis). R_F 0.59 (hexane–EtOAc 6 : 1). ^{1}H NMR ($CDCl_3$, 500 MHz) (major diastereomer) δ 0.39–1.40 (3 H, bm), 1.68–1.78 (1 H, m), 1.79–2.00 (3 H, m), 2.70–2.79 (2 H, m), 2.92–2.99 (1 H, m), 3.12–3.19 (1 H, m), 3.20–3.25 (1 H, m), 3.34 (3 H, s), 3.39–3.43 (1 H, m), 3.82–3.92 (1 H, m), 3.99–4.06 (1 H, m), 5.72–5.81 (2 H, m), 5.82–5.88 (1 H, m), 5.88–5.94 (1 H, m), 7.41–7.53 (3 H, m), 7.65–7.73 (2 H, m); (minor diastereomer) δ 0.39–1.40 (3 H, bm), 1.68–1.78 (1 H, m), 1.79–2.00 (3 H, m), 2.70–2.79 (2 H, m), 3.02–3.08 (1 H, m), 3.12–3.19 (1 H, m), 3.20–3.25 (1 H, m), 3.27 (3 H, s), 3.39–3.43 (1 H, m), 3.82–3.92 (1 H, m), 3.92–3.97 (1 H, m), 5.60–5.66 (1 H, m), 5.72–5.81 (1 H, m), 5.82–5.88 (1 H, m), 5.88–5.94 (1 H, m), 7.41–7.53 (3 H, m), 7.65–7.73 (2 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) (major diastereomer) δ 25.2 (d, J = 4.5 Hz), 26.5 (d, J = 5.5 Hz), 28.6 (d, J = 5.5 Hz), 36.7 (d, J = 42.7 Hz), 47.9 (d, J = 3.6 Hz), 58.8, 58.9 (d, J = 6.4 Hz), 75.6, 121.2 (d, J = 2.7 Hz), 121.5 (d, J = 6.4 Hz), 127.8 (d, J = 9.1 Hz), 127.9 (d, J = 10.0 Hz), 128.6 (d, J = 9.1 Hz), 130.3 (d, J = 52.7 Hz), 130.8 (d, J = 1.8 Hz), 131.4 (d, J = 9.1 Hz); (minor diastereomer) δ 25.5 (d, J = 4.5 Hz), 26.5 (d, J = 5.5 Hz), 28.7 (d, J = 5.5 Hz), 37.2 (d, J = 38.2 Hz), 47.9 (d, J = 3.6 Hz), 58.8, 59.6 (d, J = 5.5 Hz), 75.5, 121.2 (d, J = 3.6 Hz), 121.7 (d, J = 6.4 Hz), 127.4 (d, J = 8.2 Hz), 127.7 (d, J = 10.9 Hz), 128.5 (d, J = 10.0 Hz), 130.7 (d, J = 1.8 Hz), 131.2 (d, J = 9.1 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz) (major diastereomer) δ 64.68 (bm); (minor diastereomer) δ 62.95 (bm).

(1,4-Cyclohexadien-3-yl)phenylphosphinous acid-borane (2*S*)-2-(trimethylsilyloxymethyl)pyrolidinamide (26b). Prepared from **16c** (0.110 g, 0.0003 mol) and sodium (0.017 g, 0.0007 mol). Isolated as a mixture with a substrate and **27**. Yield 31% (a mixture of two diastereomers in 22% de) (based on NMR analysis). R_F 0.69 (hexane–EtOAc 6 : 1). ^{1}H NMR ($CDCl_3$, 500 MHz) (major diastereomer) δ 0.12 (9 H, s), 0.38–1.40 (3 H, bm), 1.67–2.05 (4 H, m), 2.68–2.79 (2 H, m), 2.92–2.99 (1 H, m), 3.12–3.19 (1 H, m), 3.27 (1 H, dd, J = 8.8 Hz, 10.1 Hz), 3.63 (1 H, dd, J = 4.1 Hz, 9.8 Hz), 3.81–3.93 (2 H, m), 5.73–5.81 (2 H, m), 5.82–5.87 (1 H, m), 5.87–5.94 (1 H, m), 7.40–7.52 (3 H, m), 7.67–7.74 (2 H, m); (minor diastereomer) δ 0.07 (9 H, s), 0.38–1.40 (3 H, b), 1.67–2.05 (4 H, m), 2.68–2.79 (2 H, m), 3.12–3.19 (1 H, m), 3.33 (1 H, dd, J = 7.9 Hz, 10.1 Hz), 3.33–3.39 (1 H, m), 3.59 (1 H, dd, J = 3.8 Hz, 9.8 Hz), 3.81–3.93 (2 H, m), 5.61–5.67 (1 H, m), 5.73–5.81 (3 H, m), 7.40–7.52 (3 H, m), 7.67–7.74 (2 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) (major diastereomer) δ −0.4, 25.0 (d, J = 4.5 Hz), 26.5 (d, J = 5.5 Hz), 28.1 (d, J = 5.5 Hz), 36.6 (d, J = 41.8 Hz), 47.9 (d, J = 3.6 Hz), 61.0 (d, J = 5.5 Hz), 65.1, 121.2 (d, J = 2.7 Hz), 121.6 (d, J = 5.5 Hz), 127.7 (d, J = 8.2 Hz), 127.8 (d, J = 9.1 Hz), 128.4 (d, J = 10.9 Hz), 130.8 (d, J = 2.7 Hz), 131.4 (d, J = 8.2 Hz); (minor diastereomer) δ = −0.5, 24.9 (d, J = 3.6 Hz), 26.5 (d, J = 5.5 Hz), 28.3 (d, J = 5.5 Hz), 37.1 (d, J = 37.2 Hz), 47.9 (d, J = 3.6 Hz), 61.7 (d, J = 5.5 Hz), 64.9, 121.2 (d, J = 2.7 Hz), 121.7 (d, J = 6.4 Hz), 127.3 (d, J = 8.2 Hz), 127.7 (d, J = 10.0 Hz), 128.5 (d, J = 10.0 Hz), 130.7 (d, J = 2.7 Hz), 131.3 (d, J = 9.1 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz) (major diastereomer) δ 64.50 (bm); (minor diastereomer) δ 63.10 (bm); GC (Phenomenex Zebron ZB-35 HT) R_T 13.45 min; GC–MS (EI, 70 eV) m/z (%) 357 (2), 342 (2), 255 (16), 254 (88), 186 (14), 185 (100), 184 (8), 183 (57), 178 (10), 152 (9), 108 (9), 107 (7).

Diphenylphosphine-borane (27). Prepared from **16c** (0.110 g, 0.0003 mol) and sodium (0.017 g, 0.0007 mol). Isolated as a mixture with a substrate and **26b**. Yield 13% (based on NMR analysis). Analytical data are identical with those reported in the literature.[30]

(1,4-Cyclohexadien-3-yl)phenylphosphinous acid-borane *N*-methylneomenthylamide (26c). Prepared from **25a** (0.084 g, 0.0002 mol) and sodium (0.021 g, 0.0009 mol). Isolated as a mixture with a substrate and **28**. Yield 77% (a mixture of two diastereomers in 23% de) (based on NMR analysis). R_F 0.77 (hexane–EtOAc 6 : 1). ^{1}H NMR ($CDCl_3$, 500 MHz) (major diastereomer) δ 0.41–1.35 (3 H, bm), 0.77 (3 H, d, J = 6.6 Hz), 0.94 (3 H, d, J = 6.9 Hz), 1.06 (3 H, d, J = 6.3 Hz), 1.13–1.25 (1 H, m), 1.44–1.56 (1 H, m), 1.61–1.92 (9 H, m), 2.73–2.84 (1 H, m), 2.90 (3 H, d, J = 7.6 Hz), 3.88–4.02 (1 H, m), 5.59–5.68 (2 H, m), 5.79–5.89 (2 H, m), 7.43–7.52 (3 H, m), 7.71–7.77 (2 H, m); (minor diastereomer) δ 0.41–1.35 (3 H, bm), 0.89 (3 H, d, J = 6.3 Hz), 0.92 (3 H, d, J = 6.6 Hz), 0.97 (3 H, d, J = 6.6 Hz), 1.13–1.25 (1 H, m), 1.44–1.56 (1 H, m), 1.61–1.92 (9 H, m), 2.73–2.84 (1 H, m), 2.94 (3 H, d, J = 6.6 Hz), 3.88–4.02 (1 H, m), 5.70–5.77 (2 H, m), 5.92–6.02 (2 H, m), 7.43–7.52 (3 H, m), 7.64–7.69 (2 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) (major diastereomer) δ 21.0, 23.0, 23.3, 26.3, 26.5 (d, J = 5.5 Hz), 28.5, 28.8, 34.9, 36.4 (d, J = 4.5 Hz), 37.0 (d, J = 43.6 Hz), 43.4, 47.6 (d, J =

8.2 Hz), 54.0 (d, J = 7.3 Hz), 121.5 (d, J = 2.7 Hz), 122.1 (d, J = 6.4 Hz), 127.3 (d, J = 8.2 Hz), 127.6 (d, J = 9.1 Hz), 128.5 (d, J = 9.1 Hz), 130.6 (d, J = 1.8 Hz), 131.4 (d, J = 8.2 Hz); (minor diastereomer) δ 21.2, 22.9, 23.2, 26.5 (d, J = 5.5 Hz), 26.6, 28.4, 29.1, 34.9, 36.8 (d, J = 4.5 Hz), 38.6 (d, J = 35.4 Hz), 44.2, 47.6 (d, J = 8.2 Hz), 53.8 (d, J = 9.1 Hz), 122.5 (d, J = 2.7 Hz), 122.8 (d, J = 7.3 Hz), 126.9 (d, J = 6.4 Hz), 127.2 (d, J = 10.0 Hz), 128.6 (d, J = 10.0 Hz), 130.3 (d, J = 2.7 Hz), 131.0 (d, J = 8.2 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz) (major diastereomer) δ 74.31 (bm); (minor diastereomer) δ 76.35 (bm); GC (Phenomenex Zebron ZB-35 HT) R_T 14.55 min; GC–MS (EI, 70 eV) m/z (%) 355 (M – BH_3) (8), 283 (16), 282 (67), 268 (10), 267 (36), 266 (13), 265 (26), 263 (10), 252 (23), 217 (11), 187 (15), 169 (12), 168 (100), 141 (12), 138 (16), 133 (31), 131 (20), 126 (36), 124 (13), 115 (12), 110 (26), 109 (55), 108 (62), 107 (14), 91 (15), 84 (22), 83 (16), 82 (13), 81 (11).

Phenylphosphinous acid-borane *N*-methylneomenthylamide (28). Prepared from **25a** (0.084 g, 0.0002 mol) and sodium (0.021 g, 0.0009 mol). Isolated as a mixture with a substrate and **26c**. Yield 16% (a mixture of two diastereomers in 0% de) (based on NMR analysis). R_F 0.77 (hexane–EtOAc 6 : 1). ^{1}H NMR ($CDCl_3$, 500 MHz) (only few peaks could be ascribed due to overlapping) (major diastereomer) δ 1.10 (3 H, d, J = 6.6 Hz), 6.55 (1 H, dm, J = 380.8 Hz); (minor diastereomer) δ 1.11 (3 H, d, J = 6.6 Hz), 6.69 (1 H, dm, J = 392.5 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) (only few peaks could be ascribed due to overlapping) (major diastereomer) δ 20.53, 22.49, 23.07, 28.33, 28.95; (minor diastereomer) δ 20.69, 22.65, 23.11, 28.73, 29.02; ^{31}P NMR ($CDCl_3$, 202 MHz) (major diastereomer) δ 64.48 (bm); (minor diastereomer) δ 66.34(bm); GC (Phenomenex Zebron ZB-35 HT) R_T 11.37 min; GC–MS (EI, 70 eV) m/z (%) 277 (M – BH_3) (12), 262 (6), 234 (4), 193 (16), 192 (87), 168 (22), 165 (15), 164 (28), 152 (31), 151 (21), 140 (13), 139 (41), 138 (37), 125 (19), 124 (17), 114 (30), 110 (48), 109 (84), 108 (15), 107 (12), 97 (16), 96 (12), 95 (13), 91 (11), 84 (100), 83 (35), 82 (40), 81 (19).

(1,4-Cyclohexadien-3-yl)phenylphosphinous acid-borane *N*-methylbornylamide (26d). Prepared from **25d** (0.094 g, 0.0003 mol) (1 : 0.1 mixture of diastereomers) and sodium (0.024 g, 0.0010 mol). Isolated as a mixture with **29**. Yield 33% (a mixture of two diastereomers in 38% de) (based on NMR analysis). R_F 0.77 (hexane–EtOAc 6 : 1). ^{1}H NMR ($CDCl_3$, 500 MHz) (major diastereomer) δ 0.41–1.29 (3 H, bm), 0.85 (3 H, s), 0.94 (3 H, s), 0.95 (3 H, s), 1.19–1.29 (2 H, m), 1.37–1.45 (1 H, m), 1.47–1.56 (1 H, m), 1.63–1.72 (4 H, m), 1.93–2.02 (1 H, m), 2.70 (3 H, d, J = 10.1 Hz), 2.73–2.83 (1 H, m), 3.78–3.86 (1 H, m), 5.64–5.71 (1 H, m), 5.79–5.94 (3 H, m), 7.42–7.52 (3 H, m), 7.61–7.66 (2 H, m); (minor diastereomer) δ 0.41–1.29 (3 H, bm), 0.76 (3 H, s), 0.83 (3 H, s), 0.90 (3 H, s), 1.19–1.29 (2 H, m), 1.37–1.45 (1 H, m), 1.47–1.56 (1 H, m), 1.63–1.72 (4 H, m), 1.93–2.02 (1 H, m), 2.72 (3 H, d, J = 10.7 Hz), 2.73–2.83 (1 H, m), 3.42–3.49 (1 H, m), 3.92–4.01 (1 H, m), 5.74–5.79 (1 H, m), 5.79–5.94 (3 H, m), 7.42–7.52 (3 H, m), 7.71–7.76 (2 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) (only a few peaks could be ascribed due to overlapping) (major diastereomer) δ 50.6 (d, J = 3.6 Hz), 67.4 (d, J = 5.5 Hz), 121.6 (d, J = 2.7 Hz), 121.8 (d, J = 5.5 Hz), 127.6 (d, J = 10.0 Hz), 127.7 (d, J = 8.2 Hz), 128.8 (d, J = 10.0 Hz), 130.8 (d, J = 10.0 Hz), 131.2 (d, J = 1.8 Hz), 132.1 (d, J = 74.5 Hz); (minor diastereomer) δ = 50.4 (d, J = 3.6 Hz), 68.5 (d, J = 5.5 Hz), 121.60 (d, J = 2.7 Hz), 122.0 (d, J = 6.4 Hz), 127.3 (d, J = 7.3 Hz), 127.5 (d, J = 10.0 Hz), 128.8 (d, J = 10.0 Hz), 131.2 (d, J = 9.1 Hz), 131.3 (d, J = 1.8 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz) (major diastereomer) δ 79.95 (bm); (minor diastereomer) δ 81.78 (bm).

Phenylphosphinous acid-borane *N*-methylbornylamide (29). Prepared from **25d** (0.094 g, 0.0003 mol) (1 : 0.1 mixture of diastereomers) and sodium (0.024 g, 0.0010 mol). Isolated as a mixture with **26d**. Yield 42% (a mixture of two diastereomers in 42% de) (based on NMR analysis). R_F 0.77 (hexane–EtOAc 6 : 1). ^{1}H NMR ($CDCl_3$, 500 MHz) (major diastereomer) δ 0.41–1.29 (3 H, bm), 0.85 (3 H, s), 0.94 (3 H, s), 0.95 (3 H, s), 1.19–1.29 (2 H, m), 1.37–1.45 (1 H, m), 1.47–1.56 (1 H, m), 1.63–1.72 (2 H, m), 1.93–2.02 (1 H, m), 2.69 (3 H, d, J = 8.2 Hz), 3.58–3.65 (1 H, m), 6.72 (1 H, dm, J = 396.3 Hz), 7.42–7.52 (3 H, m), 7.53–7.59 (2 H, m); (minor diastereomer) δ 0.41–1.29 (3 H, bm), 0.83 (3 H, s), 0.87 (3 H, s), 0.93 (3 H, s), 1.19–1.29 (2 H, m), 1.37–1.45 (1 H, m), 1.47–1.56 (1 H, m), 1.63–1.72 (2 H, m), 1.93–2.02 (1 H, m), 2.61 (3 H, d, J = 7.3 Hz), 3.42–3.49 (1 H, m), 6.68 (1 H, dm, J = 394.1 Hz), 7.42–7.52 (3 H, m), 7.60–7.67 (2 H, m); ^{13}C NMR (126 MHz, $CDCl_3$) (only a few peaks could be ascribed due to overlapping) (major diastereomer) δ 50.0 (d, J = 4.5 Hz), 67.8 (d, J = 6.4 Hz), 128.6 (d, J = 9.1 Hz), 130.6 (d, J = 1.8 Hz), 131.3 (d, J = 8.2 Hz), 131.7 (d, J = 75.4 Hz); (minor diastereomer) δ 50.3 (d, J = 4.5 Hz), 66.0 (d, J = 10.9 Hz), 128.6 (d, J = 9.1 Hz), 130.5 (d, J = 1.8 Hz), 131.3 (d, J = 8.2 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz) (major diastereomer) δ 61.13 (bm); (minor diastereomer) δ 67.72 (bm).

(4-Methyl-1,4-cyclohexadien-3-yl)(*o*-tolyl)phosphinous acid-borane *N*-methyl-(*S*)-α-methylbenzylamide (34a). Prepared from **32a** (0.097 g, 0.0003 mol) and sodium (0.019 g, 0.0008 mol). Isolated as a mixture with a substrate. Yield 21% (a mixture of isomers in a 30 : 11 : 40 : 19 ratio) (based on NMR analysis). R_F 0.67 (hexane–EtOAc 6 : 1). ^{1}H NMR ($CDCl_3$, 500 MHz) (only selected peaks were ascribed due to signal overlapping) (first isomer) δ 1.51 (3 H, d, J = 6.9 Hz), 1.98 (3 H, bs), 2.45 (3 H, d, J = 6.3 Hz), 2.76 (3 H, s), 3.89–4.02 (1 H, m), 5.30–5.42 (2 H, m), 5.61–5.70 (1 H, m), 5.85–5.92 (1 H, m); (second isomer) δ 1.57 (3 H, d, J = 6.9 Hz), 2.14 (3 H, bs), 2.46 (3 H, d, J = 6.3 Hz), 2.71 (3 H, s), 3.89–4.02 (1 H, m), 5.30–5.42 (2 H, m), 5.61–5.70 (1 H, m), 5.85–5.92 (1 H, m); (third isomer) δ 1.55 (3 H, d, J = 6.9 Hz), 1.95 (3 H, bs), 2.47 (3 H, d, J = 6.3 Hz), 2.66 (3 H, s), 3.89–4.02 (1 H, m), 5.30–5.42 (2 H, m), 5.61–5.70 (1 H, m), 5.85–5.92 (1 H, m); (fourth isomer) δ 1.57 (3 H, d, J = 6.9 Hz), 2.27 (3 H, bs), 2.49 (3 H, d, J = 6.3 Hz), 2.73 (3 H, s), 3.89–4.02 (1 H, m), 5.30–5.42 (2 H, m), 5.61–5.70 (1 H, m), 5.85–5.92 (1 H, m); ^{31}P NMR ($CDCl_3$, 202 MHz) (first isomer) δ 73.67 (bm); (second isomer) δ 75.38 (bm); (third isomer) δ 77.77 (bm); (fourth isomer) δ 75.05; GC (Phenomenex Zebron ZB-35 HT) R_T 15.44 min; GC–MS (EI, 70 eV) m/z (%) 364 (29), 363 (M) (48), 307 (12), 306 (22), 278 (8), 259 (57), 258 (100), 256 (12), 231 (14), 230 (34), 229 (16), 216 (12), 215 (16), 203 (11), 202 (21), 201 (27), 200 (12), 187 (14), 169 (24), 155 (12), 154 (16), 152 (21), 147 (18), 142 (13), 141

(11), 138 (12), 137 (11), 129 (10), 125 (11), 124 (10), 108 (16), 107 (26), 92 (20), 81 (11), 80 (28).

(6-Methyl-1,4-cyclohexadien-3-yl)(*p*-tolyl)phosphinous acid-borane *N*-methyl-(*S*)-α-methylbenzylamide (34b). Prepared from **32b** (0.085 g, 0.0002 mol) and sodium (0.016 g, 0.0007 mol). Isolated as a mixture of *cis*/*trans* isomers. Yield 76% (*cis*/*trans* 47 : 53, de_{cis} 44%, de_{trans} 44% de) (based on NMR analysis). R_F 0.73 (hexane–EtOAc 6 : 1). ^{1}H NMR ($CDCl_3$, 500 MHz) (*trans* isomer, major diastereomer) δ 0.57–1.37 (3 H, bm), 1.01 (3 H, d, J = 7.3 Hz), 1.48 (3 H, d, J = 6.9 Hz), 2.35 (3 H, d, J = 6.9 Hz), 2.42 (3 H, s), 2.66–2.95 (1 H, m), 3.76–3.92 (1 H, m), 5.09–5.18 (1 H, m), 5.57–5.79 (4 H, m), 7.21–7.44 (7 H, m), 7.61–7.66 (2 H, m); (*trans* isomer, minor diastereomer) δ 0.57–1.37 (3 H, bm), 1.17 (3 H, d, J = 7.3 Hz), 1.58 (3 H, d, J = 6.9 Hz), 2.37 (3 H, d, J = 6.3 Hz), 2.38 (3 H, s), 2.66–2.95 (1 H, m), 3.76–3.92 (1 H, m), 5.09–5.18 (1 H, m), 5.57–5.79 (3 H, m), 5.86–5.92 (1 H, m), 7.21–7.44 (7 H, m), 7.56–7.60 (2 H, m); (*cis* isomer, major diastereomer) δ 0.57–1.37 (3 H, bm), 1.09 (3 H, d, J = 7.6 Hz), 1.48 (3 H, d, J = 6.9 Hz), 2.34 (3 H, d, J = 6.6 Hz), 2.42 (3 H, s), 2.66–2.95 (1 H, m), 3.76–3.92 (1 H, m), 5.09–5.18 (1 H, m), 5.57–5.79 (4 H, m), 7.21–7.44 (7 H, m), 7.61–7.66 (2 H, m); (*cis* isomer, minor diastereomer) δ 0.57–1.37 (3 H, bm), 1.15 (3 H, d, J = 7.6 Hz), 1.57 (3 H, d, J = 7.3 Hz), 2.36 (3 H, d, J = 6.3 Hz), 2.38 (3 H, s), 2.66–2.95 (1 H, m), 3.76–3.92 (1 H, m), 5.09–5.18 (1 H, m), 5.57–5.79 (3 H, m), 5.94–5.99 (1 H, m), 7.21–7.44 (7 H, m), 7.56–7.60 (2 H, m); ^{31}P NMR ($CDCl_3$, 202 MHz) (*trans* isomer, major diastereomer) δ 71.59 (bm); (*trans* isomer, minor diastereomer) δ 75.20 (bm); (*cis* isomer, major diastereomer) δ 72.37 (bm); (*cis* isomer, minor diastereomer) δ 74.84.

(1,4-Cyclohexadien-3-yl)(*p*-anisyl)phosphinous acid-borane *N*-methyl-(*S*)-α-methylbenzylamide (34c). Prepared from **32c** (0.087 g, 0.0002 mol) and sodium (0.015 g, 0.0007 mol). Isolated as a mixture with a substrate. Yield 38% (a mixture of two diastereomers in 58% de) (based on NMR analysis). R_F 0.58 (hexane–EtOAc 6 : 1). ^{1}H NMR ($CDCl_3$, 500 MHz) (major diastereomer) δ 0.49–1.36 (3 H, bm), 1.44 (3 H, d, J = 6.9 Hz), 2.34 (3 H, d, J = 6.9 Hz), 2.64–2.74 (1 H, m), 3.81–3.95 (1 H, m), 3.87 (3 H, s), 5.07–5.17 (1 H, m), 5.61–5.72 (2 H, m), 5.81–5.87 (2 H, m), 6.99–7.03 (2 H, m), 7.31–7.36 (2 H, m), 7.39–7.44 (3 H, m), 7.67–7.72 (2 H, m); (minor diastereomer) δ 0.49–1.36 (3 H, bm), 1.55 (3 H, d, J = 6.9 Hz), 2.37 (3 H, d, J = 6.6 Hz), 2.74–2.84 (1 H, m), 3.81–3.95 (1 H, m), 3.87 (3 H, s), 5.07–5.17 (1 H, m), 5.61–5.72 (1 H, m), 5.75–5.81 (1 H, m), 5.94–5.98 (2 H, m), 6.92–6.96 (2 H, m), 7.31–7.36 (2 H, m), 7.39–7.44 (3 H, m), 7.61–7.66 (2 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) (major diastereomer) δ 16.4, 26.4 (d, J = 5.5 Hz), 28.7 (d, J = 3.6 Hz), 36.4 (d, J = 41.8 Hz), 55.3, 55.8 (d, J = 9.1 Hz), 114.3 (d, J = 10.0 Hz), 121.3 (d, J = 1.8 Hz), 121.6 (d, J = 5.5 Hz), 122.3 (d, J = 55.4 Hz), 127.0, 127.7 (d, J = 8.2 Hz), 127.9, 128.0 (d, J = 7.3 Hz), 128.0, 133.1 (d, J = 10.0 Hz), 141.4 (d, J = 6.4 Hz), 161.6 (d, J = 2.7 Hz); (minor diastereomer) δ 16.5, 26.5 (d, J = 5.5 Hz), 28.7 (d, J = 3.6 Hz), 38.0 (d, J = 37.2 Hz), 55.3, 55.3 (d, J = 8.2 Hz), 114.3 (d, J = 9.1 Hz), 121.9 (d, J = 2.7 Hz), 122.2 (d, J = 7.3 Hz), 127.0, 127.2 (d, J = 7.3 Hz), 127.9 (d, J = 6.4 Hz), 128.96, 127.98, 132.9 (d, J = 10.0 Hz), 141.5 (d, J = 6.4 Hz), 161.4 (d, J = 2.7 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz) (major diastereomer) δ 71.31 (bm); (minor diastereomer) δ 74.11 (bm).

(1,5-Dimethyl-1,4-cyclohexadien-3-yl)(*m*-xylyl)phosphinous acid-borane *N*-methyl-(*S*)-α-methylbenzylamide (34d). Prepared from **32d** (0.071 g, 0.0002 mol) and sodium (0.013 g, 0.0005 mol). Isolated as a mixture with a substrate and **35a**. Yield 43% (a mixture of two diastereomers in 37% de) (based on NMR analysis). R_F 0.67 (hexane–EtOAc 6 : 1). ^{1}H NMR ($CDCl_3$, 500 MHz) (major diastereomer) δ 0.49–1.21 (3 H, bm), 1.49 (3 H, d, J = 6.9 Hz), 1.64–1.67 (3 H, m), 1.71–1.74 (3 H, m), 2.28 (3 H, d, J = 6.6 Hz), 2.39 (6 H, s), 2.41–2.48 (2 H, m), 3.80–3.93 (1 H, m), 5.07–5.16 (1 H, m), 5.26–5.30 (1 H, m), 5.52–5.57 (1 H, m), 7.03–7.17 (2 H, m), 7.24–7.31 (2 H, m), 7.32–7.36 (2 H, m), 7.39–7.45 (2 H, m); (minor diastereomer) δ 0.49–1.21 (3 H, bm), 1.49 (3 H, d, J = 6.9 Hz), 1.62–1.64 (3 H, m), 1.81–1.84 (3 H, m), 2.25 (3 H, d, J = 6.3 Hz), 2.30 (6 H, s), 2.52–2.59 (2 H, m), 3.80–3.93 (1 H, m), 5.07–5.16 (1 H, m), 5.35–5.39 (1 H, m), 5.74–5.78 (1 H, m), 7.03–7.17 (2 H, m), 7.24–7.31 (2 H, m), 7.32–7.36 (2 H, m), 7.39–7.45 (2 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) (major diastereomer) δ 16.5, 21.5, 23.1 (d, J = 2.7 Hz), 23.3 (d, J = 2.7 Hz), 28.9 (d, J = 4.5 Hz), 36.2 (d, J = 5.5 Hz), 38.5 (d, J = 40.9 Hz), 55.9 (d, J = 9.1 Hz), 115.2 (d, J = 2.7 Hz), 115.7 (d, J = 7.3 Hz), 126.9, 127.9, 128.1, 128.7 (d, J = 8.2 Hz), 131.9 (d, J = 51.8 Hz), 132.3 (d, J = 1.8 Hz), 134.9 (d, J = 8.2 Hz), 135.3 (d, J = 10.0 Hz), 138.1 (d, J = 10.0 Hz), 141.7 (d, J = 5.5 Hz); (minor diastereomer) δ 16.0, 21.4, 23.1 (d, J = 2.7 Hz), 23.3 (d, J = 2.7 Hz), 28.8 (d, J = 4.5 Hz), 36.3 (d, J = 5.5 Hz), 39.8 (d, J = 36.3 Hz), 55.9 (d, J = 10.0 Hz), 115.9 (d, J = 2.7 Hz), 116.2 (d, J = 8.2 Hz), 127.1, 127.9, 128.2, 128.7 (d, J = 8.2 Hz), 129.8 (d, J = 10.0 Hz), 130.0 (d, J = 10.9 Hz), 131.5 (d, J = 57.2 Hz), 132.1 (d, J = 1.8 Hz), 138.2 (d, J = 10.0 Hz), 141.5 (d, J = 4.5 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz) (major diastereomer) δ 73.21 (bm); (minor diastereomer) δ 75.23 (bm); GC (Phenomenex Zebron ZB-35 HT) R_T 15.01 min; GC–MS (EI, 70 eV) m/z (%) 377 (M − BH_3) (16), 376 (7), 321 (9), 320 (46), 318 (7), 272 (17), 270 (70), 246 (23), 214 (9), 213 (22), 211 (14), 166 (48), 138 (11), 137 (48), 136 (19), 135 (17), 134 (41), 133 (16), 120 (20), 119 (29), 118 (14), 109 (14), 107 (37), 106 (15), 105 (100), 104 (7), 103 (13), 93 (9), 92 (16), 91 (64), 79 (34), 78 (11), 77 (34), 60 (30), 56 (10), 51 (10).

***m*-Xylylphosphinous acid-borane *N*-methyl-(*S*)-α-methylbenzylamide (35a).** Prepared from **32d** (0.071 g, 0.0002 mol) and sodium (0.013 g, 0.0005 mol). Isolated as a mixture with a substrate and **34d**. Yield 15% (a mixture of two diastereomers in 30% de) (based on NMR analysis). R_F 0.67 (hexane–EtOAc 6 : 1). ^{1}H NMR ($CDCl_3$, 500 MHz) (major diastereomer) δ 0.47–1.20 (3 H, bm), 1.51 (3 H, d, J = 6.9 Hz), 2.35 (3 H, d, J = 9.1 Hz), 2.38 (6 H, s), 4.87–4.95 (1 H, m), 6.58 (1 H, dm, J = 388.4 Hz), 7.07–7.17 (2 H, m), 7.24–7.44 (6 H, m); (minor diastereomer) δ 0.47–1.20 (3 H, bm), 1.48 (3 H, d, J = 6.9 Hz), 2.34 (6 H, s), 2.35 (3 H, d, J = 7.3 Hz), 4.80–4.87 (1 H, m), 6.58 (1 H, dm, J = 388.7 Hz), 7.07–7.17 (2 H, m), 7.24–7.44 (6 H, m); ^{31}P NMR ($CDCl_3$, 202 MHz) (major diastereomer) δ 59.33 (bm); (minor diastereomer) δ 59.90 (bm).

(1,5-Dimethoxy-1,4-cyclohexadien-3-yl)(3,5-dimethoxyphenyl)-phosphinous acid-borane *N*-methyl-(*S*)-α-methylbenzylamide

(34e). Prepared from **32e** (0.080 g, 0.0002 mol) and sodium (0.012 g, 0.0005 mol). Isolated as a mixture with a substrate and **35b**. Yield 11% (a mixture of two diastereomers in 50% de) (based on NMR analysis). R_F 0.35 (hexane–EtOAc 6 : 1). ^{1}H NMR ($CDCl_3$, 500 MHz) (major diastereomer) δ 0.45–1.33 (3 H, bm), 1.69 (3 H, d, J = 6.6 Hz), 2.35 (3 H, d, J = 6.3 Hz), 2.66–2.73 (2 H, m), 3.46 (3 H, s), 3.59 (3 H, s), 3.66–3.75 (1 H, m), 3.84 (6 H, s), 4.55–4.59 (1 H, m), 4.76–4.80 (1 H, m), 5.08–5.18 (1 H, m), 6.57 (1 H, t, J = 2.2 Hz), 6.85 (2 H, dd, J = 2.2 Hz, 10.1 Hz), 7.23–7.47 (5 H, m); (minor diastereomer) δ 0.45–1.33 (3 H, bm), 1.50 (3 H, d, J = 6.9 Hz), 2.33 (3 H, d, J = 6.0 Hz), 2.81–2.87 (2 H, m), 3.43 (3 H, s), 3.66–3.75 (1 H, m), 3.68 (6 H, s), 3.69 (3 H, s), 4.60–4.64 (1 H, m), 5.01–5.05 (1 H, m), 5.08–5.18 (1 H, m), 6.50 (1 H, t, J = 2.2 Hz), 6.64 (2 H, dd, J = 2.2 Hz, 10.4 Hz), 7.23–7.47 (5 H, m); ^{31}P NMR ($CDCl_3$, 202 MHz) (major diastereomer) δ 75.01 (bm); (minor diastereomer) δ 77.42 (bm).

3,5-Dimethoxyphenylphosphinous acid-borane *N*-methyl-(*S*)-α-methylbenzylamide (35b). Prepared from **32e** (0.080 g, 0.0002 mol) and sodium (0.012 g, 0.0005 mol). Isolated as a mixture with a substrate and **34e**. Yield 17% (a mixture of two diastereomers in 30% de) (based on NMR analysis). R_F 0.44 (hexane–EtOAc 6 : 1). ^{1}H NMR ($CDCl_3$, 500 MHz) (major diastereomer) δ 0.54–1.51 (3 H, bm), 1.52 (3 H, d, J = 6.9 Hz), 2.38 (3 H, d, J = 8.8 Hz), 3.84 (6 H, s), 4.89–4.96 (1 H, m), 6.58 (1 H, t, J = 2.2 Hz), 6.60 (1 H, dm, J = 392.2 Hz), 6.77 (2 H, dd, J = 2.2 Hz, 12.6 Hz), 7.29–7.38 (5 H, m); (minor diastereomer) δ 0.54–1.51 (3 H, bm), 1.50 (3 H, d, J = 7.3 Hz), 2.46 (3 H, d, J = 9.1 Hz), 3.77 (6 H, s), 4.82–4.89 (1 H, m), 6.54 (1 H, t, J = 1.9 Hz), 6.60 (1 H, dm, J = 392.2 Hz), 6.66 (2 H, dd, J = 2.2 Hz, J = 12.9 Hz), 7.29–7.38 (5 H, m); ^{13}C NMR (126 MHz, $CDCl_3$) (major diastereomer) δ 16.8 (d, J = 1.8 Hz), 31.3, 55.5, 103.6, 108.8 (d, J = 11.8 Hz), 127.3, 127.4, 128.3, 132.6 (d, J = 62.7 Hz), 140.9 (d, J = 4.5 Hz), 161.1 (d, J = 14.5 Hz); (minor diastereomer) δ 17.0 (d, J = 1.8 Hz), 30.8, 55.5, 103.7, 108.5 (d, J = 11.8 Hz), 127.4, 127.5, 128.4, 132.4 (d, J = 64.5 Hz), 141.2 (d, J = 4.5 Hz), 161.1 (d, J = 15.4 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz) (major diastereomer) δ 60.72 (bm); (minor diastereomer) δ 61.38 (bm).

(*p*-Anisyl)phenylphosphinous acid-borane *N*-methyl-(*S*)-α-methylbenzylamide (36). Compound **34c** was left for 2 months after which this compound was found to rearomatize into **36**. A mixture of two diastereomers in 58% de ratio (based on NMR analysis). R_F 0.50 (hexane–EtOAc 6 : 1). ^{1}H NMR ($CDCl_3$, 500 MHz) (major diastereomer) δ 0.76–1.56 (3 H, bm), 1.48 (3 H, d, J = 6.9 Hz), 2.23 (3 H, d, J = 7.6 Hz), 3.87 (3 H, s), 5.29–5.38 (1 H, m), 6.96–7.01 (2 H, m), 7.24–7.31 (2 H, m), 7.31–7.38 (3 H, m), 7.38–7.44 (3 H, m), 7.44–7.54 (2 H, m), 7.60–7.66 (2 H, m); (minor diastereomer) δ 0.76–1.56 (3 H, bm), 1.53 (3 H, d, J = 6.9 Hz), 2.34 (3 H, d, J = 7.6 Hz), 3.87 (3 H, s), 5.08–5.16 (1 H, m), 6.92–6.96 (2 H, m), 7.24–7.31 (2 H, m), 7.31–7.38 (3 H, m), 7.38–7.44 (3 H, m), 7.44–7.54 (2 H, m), 7.64–7.70 (2 H, m); ^{13}C NMR ($CDCl_3$, 126 MHz) (major diastereomer) δ 16.3, 28.7 (d, J = 3.6 Hz), 55.3, 55.3 (d, J = 9.1 Hz), 114.0 (d, J = 10.9 Hz), 122.3 (d, J = 63.6 Hz), 127.1, 128.0, 128.1, 128.4 (d, J = 10.9 Hz), 130.7 (d, J = 2.7 Hz), 131.3 (d, J = 69.0 Hz), 132.1 (d, J = 10.0 Hz), 134.3 (d, J = 11.8 Hz), 141.7 (d, J = 6.4 Hz), 161.8 (d, J = 2.7 Hz); (minor diastereomer) δ 16.5, 28.8 (d, J = 3.6 Hz), 114.1 (d, J = 11.8 Hz), 127.0, 127.9, 128.1, 128.4 (d, J = 10.9 Hz), 130.9 (d, J = 1.8 Hz), 132.2 (d, J = 10.9 Hz), 134.0 (d, J = 11.8 Hz), 141.7 (d, J = 6.4 Hz), 161.7 (d, J = 2.7 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz) (major diastereomer) δ 67.94 (bm); (minor diastereomer) δ 71.30 (bm); GC (Phenomenex Zebron ZB-35 HT) R_T 16.60 min; GC–MS (EI, 70 eV) m/z (%) 349 (M – BH_3) (9), 248 (15), 293 (21), 292 (100), 245 (9), 244 (52), 215 (19), 213 (12), 184 (8), 183 (14), 170 (8), 152 (18), 139 (42), 138 (16), 135 (24), 134 (43), 120 (9), 109 (40), 108 (17), 107 (11), 105 (22), 91 (11).

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Notes and references

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