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The Reactivity of Arylphosphorus Acid Amides Under Birch Reduction Conditions

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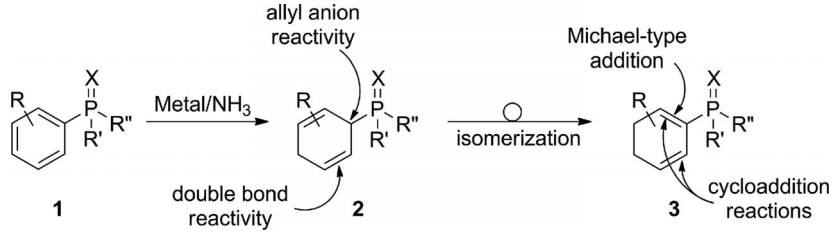
Several classes of arylphosphorus acid amides have been tested in reactions with alkali metal solutions in liquid ammonia. The outcomes of such reactions depend on the structures of the starting materials. Generally, two processes – Birch reduction or cleavage of the P–aryl bond – can be operative. Diarylphosphinic amides tend to undergo double Birch reduction to afford bis(cyclohexadienyl)phosphinic amides.

Introduction

A brief look into organophosphorus chemistry immediately shows how the extraordinary richness of this part of organic chemistry arises from the special features of the central phosphorus atom.[1] Like nitrogen, phosphorus can form stable trivalent and tetravalent compounds, such as phosphanes or phosphonium salts. Unlike nitrogen, however, phosphorus can also form stable tetravalent phosphorus(V) compounds such as phosphane oxides, phosphane sulfides etc. If it is borne in mind that phosphorus can also form many stable P–X bonds (X = O, N, S, halogen) the potential for variation both of the valency at phosphorus and of the groups bound to it provides an enormous number of different organophosphorus compounds that, logically, should give rise to a rich reactivity. In practice, the functionalisation of organophosphorus compounds usually occurs at reactive bonds such as P–H or P–heteroatom through a number of broad reaction classes including nucleophilic substitution at an electrophilic phosphorus atom,[2] nucleophilic substitution with a phosphorus nucleophile,[3] transition-metal-catalyzed coupling,[4] addition of an organophosphorus reagent to a multiple bond[5] or a Friedel–Crafts reaction.[6] All of the reactions listed take place at phosphorus: the only important class of transformations that does not is functionalisation at the α-carbon atom.[7]

One of the less widely used transformations in organophosphorus chemistry is the Birch reduction, which is based on the dearomatisation of arenes with alkali metal solutions in liquid ammonia and would seem to have great synthetic potential in the preparation of structurally new organophosphorus compounds. In principle, the dearomatisation of a phosphorus-substituted arene of type **1** should provide a reactive (cyclohexa-1,4-dien-3-yl)-substituted organophosphorus compound of type **2** (Scheme 1).

The two isolated double bonds present in a compound of type **2** could then be further engaged in electrophilic or radical addition reactions, or the deprotonation of the carbon atom adjacent to phosphorus could provide a reactive allylic anion. Additionally, the isomerisation of one of the double bonds in **2**, to provide a conjugated system of type **3**, should allow reactivity either as a Michael acceptor in 1,4-conjugated additions with nucleophiles or as a dienophile in cycloaddition reactions.



Scheme 1. Dearomatisation of an arylphosphorus compound and potential further transformations.

Despite the potential of the Birch reduction, its use in organophosphorus chemistry is rare; this is mainly because

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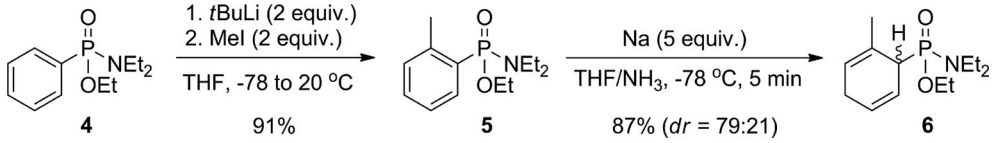


Scheme 2. Dearomatisation of a monophosphonate monoamide.

treatment of arylphosphorus compounds with alkali metals in liquid ammonia often leads to P–aryl bond cleavage and the formation of phosphide anions.[8] The first mention of dearomatisation of the aryl substituents in some electron-rich tertiary phosphanes appeared in the late 1980s,[9] but thereafter the topic was left underdeveloped.

In the course of our research program directed towards the "activation" of a phenyl substituent at phosphorus through its transformation into a more reactive fragment we have found that the treatment of aryldialkylphosphane–boranes with alkali metals in liquid ammonia generally provides the corresponding (cyclohexa-1,4-dien-3-yl)phosphane–boranes,[10] and similar behaviour has also been observed for arylphosphane oxides.[11] In situ Birch reduction/alkylation of tertiary phosphane–boranes and phosphane oxides has also been shown to provide the corresponding α-functionalised (cyclohexa-1,4-dien-3-yl)phosphane derivatives, even when the electrophile employed possesses a reactive functional group (or groups) in its carbon chain.[12] We have also found that treatment of (cyclohexa-1,4-dien-3-yl)phosphane oxides with secondary phosphane oxides under basic conditions provokes an in situ double bond migration/Michael addition sequence to yield bis(phosphorus-substituted)cyclohexenes.[13] This last transformation seems to have particularly interesting potential for the synthesis of diphosphane ligands containing cyclohexane-1,2-diyl linkers between the two phosphorus atoms.

The next obvious step in the development of Birch reduction methodologies for organophosphorus chemistry would be to employ *P*-heteroatom-substituted compounds such as amides or esters. An initial study carried out with monophosphonate monoamides demonstrated that the arene ring could undergo dearomatisation quite efficiently (Scheme 2).[14]

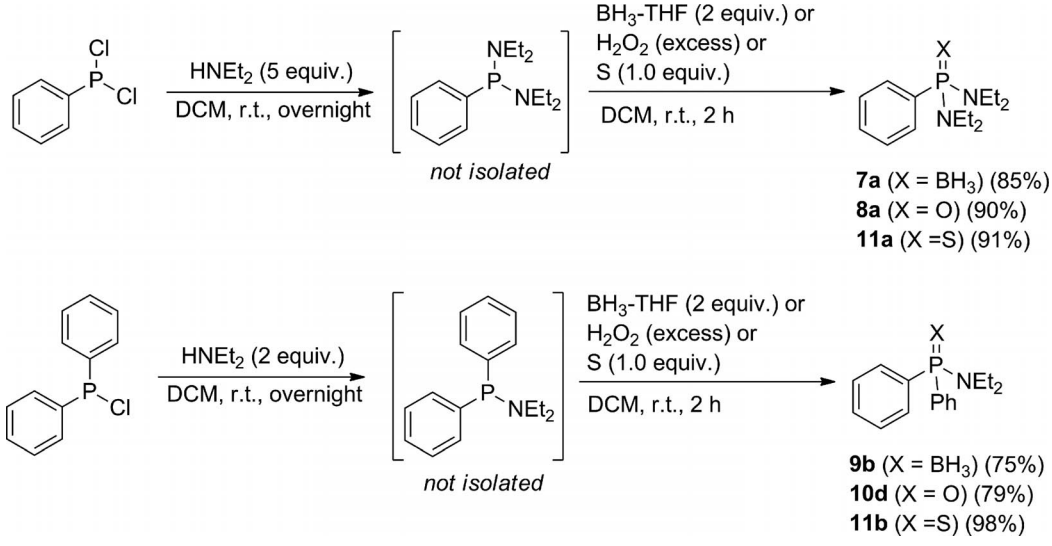
As a further step in our research project, we have therefore attempted to delineate a general reactivity scheme for several classes of phosphorus acid amides towards alkali metal solutions in liquid ammonia.

Results and Discussion

The reactivity of phosphorus acid amides under Birch reduction conditions is practically unknown. The only observation is that provided by Riera, Verdaguer et al., who isolated *tert*-butyl(cyclohexa-1,4-dien-3-yl)phosphinous acid–borane amide as the main product after debenzylation of the corresponding *N*-benzyl amide with lithium in liquid ammonia.[15]

Because of the versatility of the phosphorus atom in forming different classes of compounds, the representatives of at least six classes of arylphosphorus acid amides would need to be screened in any thorough test of reactivity. These are: phosphonous acid–borane diamides, phosphonic acid diamides, thiophosphonic acid diamides, phosphinous acid–borane amides, phosphinic acid amides and thiophosphinic acid amides. Model compounds for Birch reduction were therefore made by several different pathways.

Compounds **7a**, **8a** and **11a** (Scheme 3) were prepared from dichlorophenylphosphane and diethylamine, followed by addition of BH_3·THF, H_2O_2 or sulfur, respectively,



Scheme 3. The synthesis of **7a**, **8a**, **11a**, **9b**, **10d** and **11b**.

whereas compounds **9b**, **10d** and **11b** were prepared analogously by starting from diphenylchlorophosphane.

The yields of diamides **7a**, **8a** and **11a** varied between 85% and 91%, whereas those of amides **9b**, **10d** and **11b** were 75%, 79% and 98%, respectively.

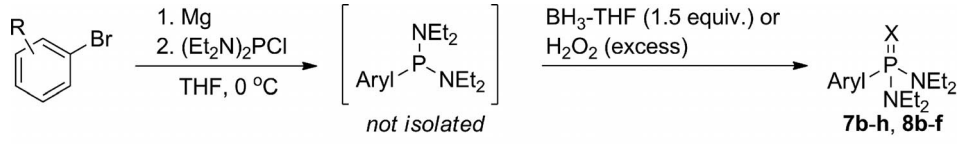
Amides **7b**–**h** and **8b**–**f** (Scheme 4) were prepared by treatment of $(Et_2N)_2PCl$ with the corresponding Grignard reagent, followed by treatment of the intermediate $RP(NEt_2)_2$ with either BH_3·THF or H_2O_2.

This reaction sequence seems to be of general applicability, because all of the aryl Grignard reagents afforded the corresponding phosphonous acid–borane diamides and phosphonic acid diamides in good yields.

Phosphinous acid–borane amides **9d**–**f** and phosphinic acid amides **10e**–**h** (Scheme 5) were prepared from Et_2NPCl_2 through sequential addition of two different Grignard reagents, followed by treatment either with the BH_3·THF complex or with excess H_2O_2.

The yields of compounds **9d**–**g** and **10e**–**h** were significantly lower than for compounds **7** and **8**, probably because of the difficulty in controlling the reaction course. Both halides could be replaced by the same Grignard reagent, thus yielding symmetrically substituted compounds.

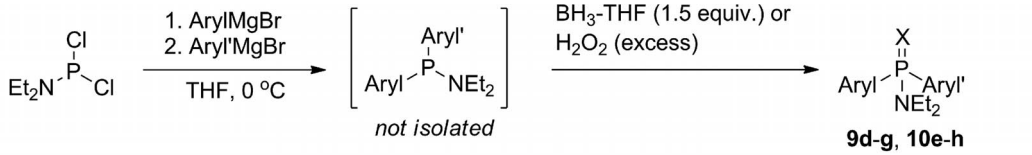
Amides **9a**, **9c** and **10b** (Scheme 6) were prepared from the corresponding secondary phosphane oxides by treatment with PCl_3, followed by treatment of the formed



7b (X = BH_3, Aryl = 2-Me-1-Np) (65%)
7c (X = BH_3, Aryl = 1-Np) (65%)
7d (X = BH_3, Aryl = Mes) (95%)
7e (X = BH_3, Aryl = *o*Tol) (68%)
7f (X = BH_3, Aryl = *o*An) (58%)
7g (X = BH_3, Aryl = *p*Tol) (57%)
7h (X = BH_3, Aryl = 2-Np) (68%)

8b (X = O, Aryl = *o*An) (54%)
8c (X = O, Aryl = *p*Tol) (57%)
8d (X = O, Aryl = *o*Tol) (42%)
8e (X = O, Aryl = 2-Np) (89%)
8f (X = O, Aryl = Mes) (63%)

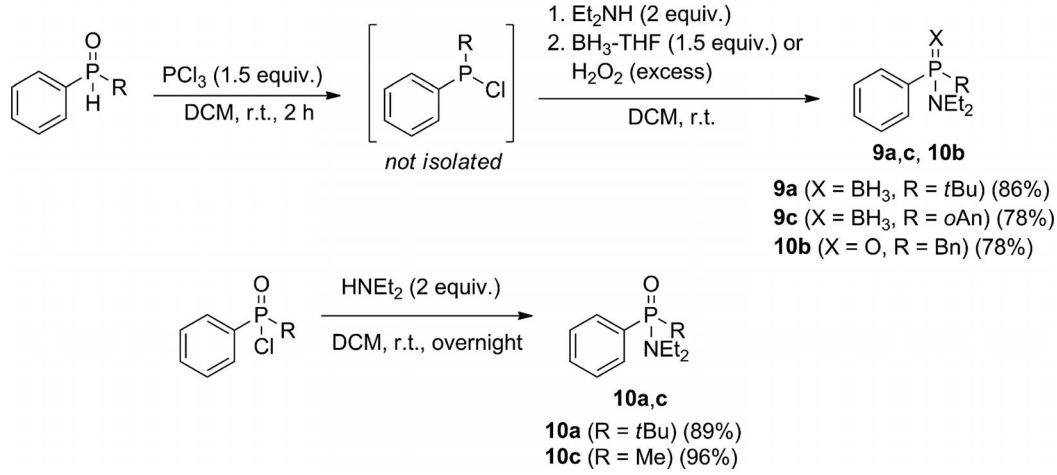
Scheme 4. The synthesis of **7b**–**h** and **8b**–**f**.



9d (X = BH_3, Aryl = *p*Tol, Aryl' = *o*An) (34%)
9e (X = BH_3, Aryl = 2-Me-1-Np, Aryl' = *o*An) (28%)
9f (X = BH_3, Aryl = *o*Tol, Aryl' = Mes) (27%)

10e (X = O, Aryl = *o*An, Aryl' = *p*Tol) (44%)
10f (X = O, Aryl = 2-Me-1-Np, Aryl' = *p*Tol) (36%)
10g (X = O, Aryl = 2-Me-1-Np, Aryl' = *o*An) (43%)
10h (X = O, Aryl = 2-Me-1-Np, Aryl' = *o*Tol) (33%)

Scheme 5. The synthesis of **9d**–**f** and **10e**–**h**.



9a (X = BH_3, R = *t*Bu) (86%)
9c (X = BH_3, R = *o*An) (78%)
10b (X = O, R = Bn) (78%)

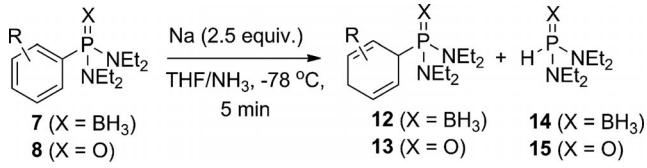
10a (R = *t*Bu) (89%)
10c (R = Me) (96%)

Scheme 6. The synthesis of **9a**, **9c** and **10a**–**c**.

chlorophosphane product with $HNEt_2$ and either BH_3·THF complex or H_2O_2.

Finally, amides **10a** and **10c** (Scheme 6) were prepared by treatment of the corresponding phosphinic acid chlorides with $HNEt_2$ (excess).

Once the synthesis of the substrates was completed, we turned our attention to evaluation of their behaviour with alkali metal solutions in liquid ammonia. Firstly, the reactivity of phosphonous acid–borane diamides **7a**–**h** and phosphonic acid diamides **8a**–**f** under Birch reduction conditions was tested (Scheme 7, Table 1).



Scheme 7. Birch reduction of **7** and **8**.

Table 1. Birch reduction of **7** and **8**.

Entry	Comp.	X	Aryl	Yields [%] **12/13**	**14/15**
1	**7a**	BH_3	Ph	**12a** (87)	–
2	**7b**	BH_3	2-Me-1-Np	**12b** (45)	**14** (25)[a]
3	**7c**	BH_3	1-Np	**12c** (74)[b]	–
4	**7d**	BH_3	Mes	**12d** (69)[c]	**14** (9)[a]
5	**7e**	BH_3	*o*Tol	**12e** (87)	–
6	**7f**	BH_3	*o*An	**12f** (75)	–
7	**7g**	BH_3	*p*Tol	**12g** (90)[d]	–
8	**8a**	O	Ph	**13a** (91)	–
9	**8b**	O	*o*An	**13b** (60)	**15** (13)
10	**8c**	O	*p*Tol	**13c** (69)[e],[f]	–
11	**8d**	O	*o*Tol	**13d** (60)[e],[g]	–
12	**8f**	O	Mes	**13e** (83)[c]	–

[a] NMR yields. [b] An isomerised product **12c′** was isolated in 9% yield. [c] Only the *trans* isomer was observed. [d] A *trans*/*cis* mixture of isomers in 1.48:1 ratio was observed. [e] 5 equiv. of sodium were used. [f] A *trans*/*cis* mixture of isomers in 51:49 ratio was observed. [g] With 2.5 equiv. of sodium, the yield of **13d** was only 24%.

Consideration of the data collected in Table 1 shows that phosphonous acid–borane diamides **7a**–**g** underwent smooth dearomatisation of their aryl fragments to yield the corresponding cyclohexadienyl-substituted organophosphorus compounds in fair to good yields. In the case of the 1-naphthyl-substituted compound **7c** we observed the formation of (3,4-dihydronaphth-1-yl)phosphonous acid–borane diamide in 9% yield (Table 1, Entry 3), which suggests that isomerisation of the primary Birch reduction product is possible under the reaction conditions. Interestingly, compound **7b**, an *ortho*-methyl-substituted analogue of **7c**, was resistant to isomerisation under the same reaction conditions.

Because of their specific substitution patterns, compounds **7d** and **7g** should theoretically each produce two isomers under Birch reduction conditions. Whereas mesityl-substituted diamide **7d** underwent stereoselective dearomatisation to yield only the *trans* isomer, as deduced from 2D NMR analysis (Table 1, Entry 4), the *p*-tolyl-substituted diamide **7g** afforded a mixture of *trans* and *cis* isomers in 1.48:1 ratio (Table 1, Entry 7).

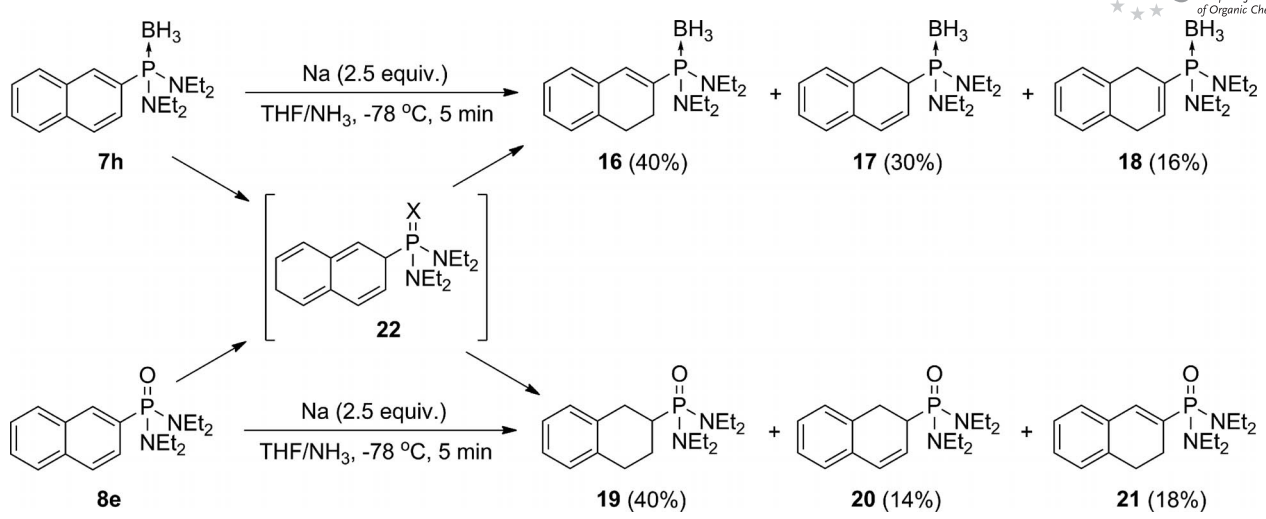
In the cases of the compounds **7b** and **7d** we also observed the presence of phosphonous acid–borane bis(diethylamide) **14** in the reaction mixture, in 25% and 9% yields, respectively. This product arose from P–aryl bond cleavage, most probably at the radical anion stage.

Similar observations were made for phosphonic acid diamides **8a**, **8b** and **8f** (Table 1, Entries 8–12), although the *p*-tolyl-substituted phosphonic diamide **8c** and the *o*-tolyl-substituted phosphonic diamide **8d** each required 5 equiv. of sodium for efficient conversion into the products. Compounds **8c** and **8f** were again expected to generate isomers, and their reactivity showed parallels with their borane analogues: *p*-tolyl-substituted phosphonic diamide **8c** afforded a nearly equimolar mixture of *trans* and *cis* isomers (Table 1, Entry 10), whereas dearomatisation of mesityl-substituted phosphonic diamide **8f** yielded only the *trans* isomer.

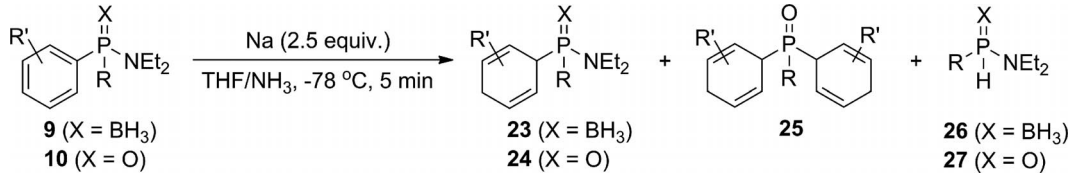
In the phosphonic diamide series the formation of phosphonic acid bis(diethylamide) **15** was observed during the dearomatisation of *o*-anisyl-substituted amide **8b**, but the yield was again low (Table 1, Entry 9). However, it is reasonable to assume that both **14** and **15** should have potential as starting materials once practical and preparative methods for their synthesis are fully established.

The reactivity of arylphosphonous acid–borane mono ester monoamides[16] and arylphosphonic acid mono ester monoamides[14] under Birch reduction conditions is already known, and a comparison with the reactivity of arylphosphonous acid–borane diamides **7** and arylphosphonic acid diamides **8** is interesting. In the case of arylphosphonous acid–boranes the introduction of one alkoxy functionality shifts the reaction selectivity completely away from Birch reduction towards P–O bond cleavage. This is not the case when the reactivities of phosphonic acid diamides and monoamide mono esters are compared. In these cases both classes of arylphosphonic acid derivatives undergo clean Birch reduction of their arene fragments. The reason for such behaviour most probably lies in the ability of the P=O group to stabilise the intermediate radical anion and thus favour the dearomatisation process.

The cases of 2-naphthyl-substituted diamides **7h** and **8e** were slightly different (Scheme 8). Treatment of borane adduct **7h** with sodium in liquid ammonia afforded a mixture of **16**, **17** and **18** in 40%, 30% and 18% yields, respectively. Treatment of **8e** under the same reaction conditions afforded **19**, **20** and **21** in 40%, 14% and 18% yields, respectively. In view of the electron-accepting properties of phosphorus groups the initial reduction products should have the structures **22**, in which both aromatic rings are dearomatised to afford highly reactive conjugated systems. These intermediates should rearrange rapidly into the more stable compounds **17** or **20**, which can undergo further double bond migration. The presence of compound **19** suggests that reduction of the conjugated compound **21** is also possible under the reaction conditions.



Scheme 8. Birch reduction of **7h** and **8e**.



Scheme 9. Birch reduction of **9** and **10**.

In another set of experiments, Birch reduction of arylphosphinous acid–borane amides **9a**–**g** and arylphosphinic acid amides **10a**–**b** was attempted (Scheme 9, Table 2).

With sodium in liquid ammonia, phosphinous acid–borane amides **9a**–**e** each efficiently underwent Birch reduction of an aryl substituent. In the case of compounds possessing two different aryl substituents at phosphorus, the one yielding the more stabilised radical anion underwent the dearomatisation (Table 2, Entries 3–5). Diarylphosphinous acid–borane amides therefore appear to be the first class of organophosphorus compounds containing two P–aryl bonds to be capable of undergoing Birch reduction almost exclusively. Attempted Birch reductions either of diarylphosphanealkyl–boranes[17] or of diarylalkylphosphane oxides[11] have been described previously, and these resulted only in P–aryl bond cleavage with the formation of P–H-type compounds.

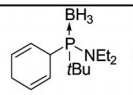
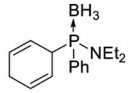
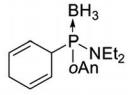
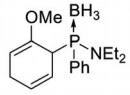
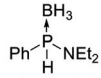
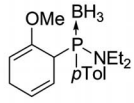
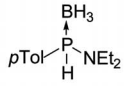
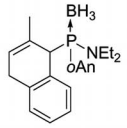
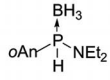
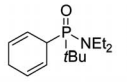
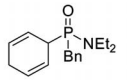
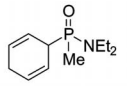
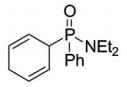
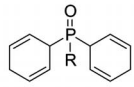
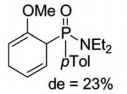
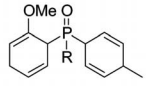
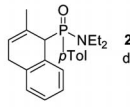
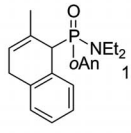
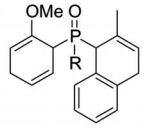
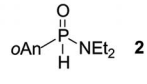
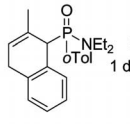
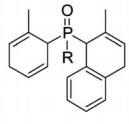
The dearomatisation of an unsymmetrically substituted aryl substituent causes the formation of a new chiral centre at what was formerly the *ipso* carbon atom. If an unsymmetrically substituted arylphosphinous acid–borane is used, the inherent chirality at the phosphorus atom means that the Birch reduction should then produce a mixture of diastereomers. We have already observed preferential formation of one of the diastereomers in the Birch reduction of *ortho*-substituted arylphosphonic acid mono ester monoamides.[14] Here we made similar observations. Dearomatisation of the *o*-anisyl group in **9c** led to a mixture of two diastereomers in 66% *de* (Table 2, Entry 3), and a similar outcome was found with compound **9d**, which showed only a slightly lower diastereomeric ratio (Table 2, Entry 4). Dearomatisation of the naphthyl fragment in **9e** led to even better diastereoselectivity than obtained with **9c**; this might be attributable to the significant steric crowding around phosphorus created by the two *ortho*-substituted arenes (Table 2, Entry 5).

Despite quite clean reactivity of compounds **9**, cleavage of the phosphorus–aryl bond was sometimes observed and the formation of P–H-type compounds **26** was detected. In all cases the cleaved arene was the one that had undergone dearomatisation.

Compound **9f** behaved differently from the other members of the class (Scheme 10). The only products isolated from the reaction mixture were P–H-type compounds **26f**, **26f′** and **28**–**30**, which suggests that the intermediate radical anion is too reactive to undergo significant phosphorus–nitrogen or phosphorus–carbon bond cleavage.

The reactivity of phosphinic acid amides under Birch reduction conditions is slightly different. Compounds **10a**–**c**, each possessing only one aryl substituent, underwent clean dearomatisation to yield the corresponding cyclohexadienyl-substituted phosphinic amides (Table 2, Entries 6–8). Here, it is again useful to underline the influence of the phosphoryl group (P=O) on the course of the reaction between a phosphorus acid amide and an alkali metal solution in liquid ammonia. Amides **10b** and **10c** underwent Birch reduction exclusively, whereas the borane analogues of **10b** and **10c** had exclusively undergone phosphorus-ni-

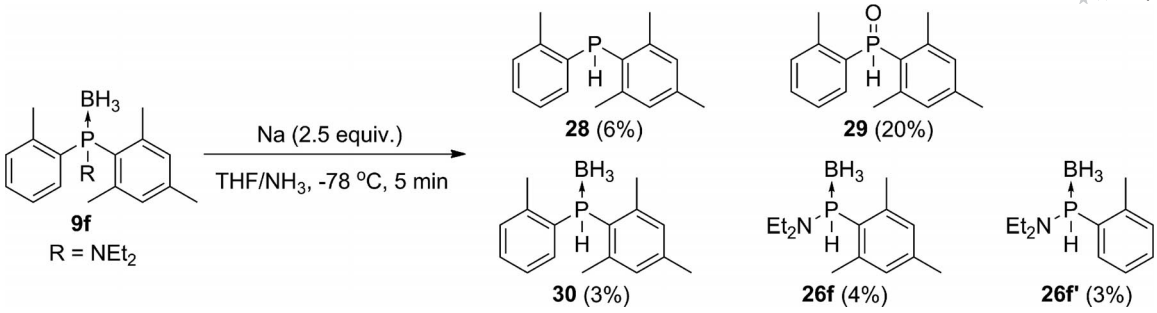
Table 2. Birch reduction of **9** and **10**.

Entry	Compound	Aryl	R	X	Products
1	**9a**	Ph	*t*Bu	BH_3	 **23a** (89%)
2	**9b**	Ph	Ph	BH_3	 **23b** (62%)
3	**9c**	Ph	*o*An	BH_3	 **23c** (32%)[a]  **23c'** (26%) de = 66%  **26c** (3%)[a]
4	**9d**	*o*An	*p*Tol	BH_3	 **23d** (41%)[a] de = 54%  **26d** (12%)[a]
5	**9e**	2-Me-1-Np	*o*An	BH_3	 **23e** (72%)[a] de = 70%  **26e** (6%)[a]
6	**10a**	Ph	*t*Bu	O	 **24a** (95%)
7	**10b**	Ph	Bn	O	 **24b** (86%)
8	**10c**	Ph	Me	O	 **24c** (90%)
9	**10d**	Ph	Ph	O	 **24d** (30%)[a]  **25d** (36%)[a] R = NEt_2
10	**10e**	*o*An	*p*Tol	O	 **24e** (17%)[a] de = 23%  **25e** (13%)[a] R = NEt_2 4 isomers
11	**10f**	2-Me-1-Np	*p*Tol	O	 **24f** (43%)[a] de = 12%
12	**10g**	2-Me-1-Np	*o*An	O	 **24g** (18%)[a] 1 diastereomer  **25g** (10%)[a] R = NEt_2 2 isomers de = 45%  **2**
13	**10h**	2-Me-1-Np	*o*Tol	O	 **24h** (13%)[a] 1 diastereomer  **25h** (60%)[a] R = NEt_2 3 isomers

[a] NMR yields.

trogen bond cleavage.[16] This is not the case for **9a** and **10a**, but here the steric influence of the *tert*-butyl group seems likely to have played a significant role.

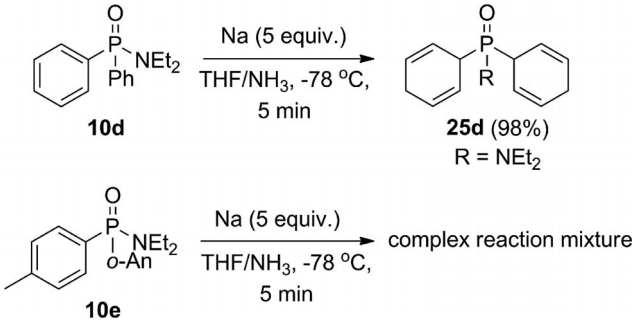
Unlike diarylphosphinous acid–borane amides, diarylphosphinic amides tended to undergo double dearomatisation, even if only 2.5 equiv. of sodium were used. On



Scheme 10. Birch reduction of **9f**.

treatment with the standard amount of sodium, diphenylphosphinic *N*,*N*-diethylamide afforded a mixture of starting material (25%), the single Birch reduction product **24d** in 30% yield, and the double Birch reduction product **25d** in 36% yield (Table 2, Entry 9). In the case of its borane analogue **9b**, the double Birch reduction product had not been detectable. Similar results were observed with other diarylphosphinic amides (Table 2, Entries 10, 12, 13). The use of phosphinic amides containing unsymmetrically substituted arenes would again be expected to produce diastereomers and in the case of double dearomatisation this could produce up to four pairs of diastereomers; this was observed for **10e**.

Bearing in mind the ease of the double dearomatisation of diarylphosphinic acid amides we treated phosphinic amides **10d** and **10e** with excess sodium in liquid ammonia (Scheme 11).



Scheme 11. Attempted double dearomatisation of **10d** and **10e**.

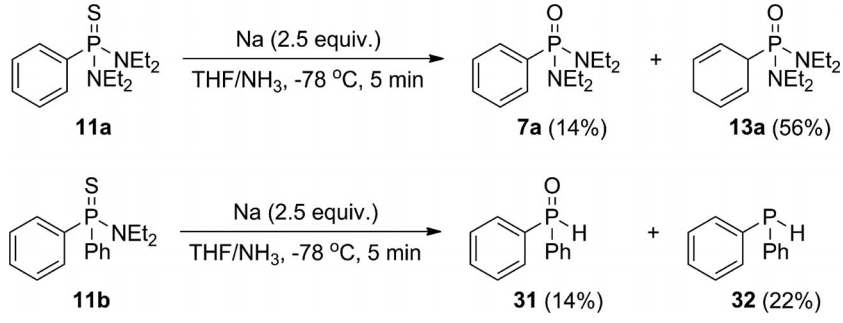
Treatment of **10d** with 5 equiv. of sodium in liquid ammonia cleanly afforded the double Birch reduction product **25d** in almost quantitative yield. On the other hand, treatment of the unsymmetrically substituted **10e** with the same amount of sodium afforded a mixture of at least eight compounds, which indicates that **10e** probably undergoes a sequence of transformations under the reaction conditions. Nevertheless, it seems that double Birch reduction is a general process for this class of compounds.

An attempt was also made to subject phenylthiophosphonic acid diamide **11a** and diphenylthiophosphinic acid amide **11b** to Birch reduction with sodium in liquid ammonia (Scheme 12).

Thiophosphonic acid diamide **11a** underwent two processes: Birch reduction and cleavage of the P=S bond. From this reaction alone, it is not possible to deduce which process took place first. However, thiophosphinic acid amide **11b** also underwent two processes: P–N and P=S bond cleavage. The cleavage of P=S bonds in solutions of alkali metals in liquid ammonia has been observed previously[18] and it seems to be a general phenomenon with P=S-type compounds. The outcomes of the two reactions show that the use of thio analogues of organophosphorus compounds in Birch reduction is likely to give unpredictable results.

Conclusions

The aim of this paper is to describe the reactivity of arylphosphorus acid amides towards alkali metal solutions in liquid ammonia. Most of the compounds under evaluation follow the reactivity profiles described earlier for arylphosphonic acid mono ester monoamides: they undergo Birch reduction of the arene fragment of the organophosphorus



Scheme 12. Treatment of **11a** and **11b** with sodium in liquid ammonia.

compound. Differences start to appear when diarylphosphorus acid amides are used in the Birch reduction protocol. Diarylphosphinous acid–borane amides predominantly undergo Birch reduction of only one arene fragment, and this kind of reactivity has no precedent. Diarylphosphinic amides, on the other hand, tend to undergo double Birch reduction to afford bis(cyclohexa-1,4-dien-3-yl)phosphinic amides.

Experimental Section

General: All reactions were performed under argon by use of 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 crystallisation were distilled once before use, and solvents for extraction were used as received. Tetrahydrofuran was dried with sodium/benzophenone ketyl.

The NMR spectra were recorded with Bruker Ascend (500 MHz), 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 the residual solvent peak. Mass spectra were recorded with a Shimadzu GC–MS QP2010S spectrometer working in electron ionisation (EI) mode with a Phenomenex Zebron ZB-35HT INFERNO column [pressure – 97.9 kPa, total flow – 19.5 mL min^{-1}, column flow – 1.5 mL min^{-1}, linear velocity – 44.9 cm sec^{-1}, split – 10, temperature program (70 °C – hold 3 min, 70–340 °C/12 °C min^{-1} – hold 9.5 min – total 35 min)] or Phenomenex Zebron ZB-5MSi column [pressure – 65 kPa, total flow – 23.9 mL min^{-1}, column flow – 1.2 mL min^{-1}, linear velocity – 36.8 cm sec^{-1}, split – 20, temperature program (80 °C – hold 3 min, 80–250 °C/20 °C min^{-1} – hold 5 min – 250–300 °C/10 °C min^{-1} – hold 30.5 min total 50 min)]. TLC was performed with precoated silica gel plates with visualisation by use of UV light or $KMnO_4$ solution. The reaction mixtures were purified by column chromatography over silica gel (60–240 mesh).

Synthesis of PhP(X)(NEt$_2$)$_2$-Type Compounds 7a, 8a and 11a: $PhPCl_2$ (5 mL, 0.037 mol) in diethyl ether (200 mL) was placed in a flame-dried two-necked flask (500 mL) containing a magnetic stirrer and fitted with an inert gas inlet. The mixture was placed in cold water bath, and diethylamine (19 mL, 0.184 mol) was added dropwise by syringe. After the addition was complete, the mixture was left under argon overnight. It was then filtered (funnel) with careful extrusion of oxygen and moisture. The solids were washed with diethyl ether (3× 50 mL), and the filtrate was concentrated under reduced pressure. For compound **7a**, the obtained intermediate was dissolved in THF (20 mL), BH_3·THF complex (74 mL, 0.074 mol) was added, and the mixture was allowed to stir for an additional hour. For compound **8a**, the obtained intermediate was dissolved in $CHCl_3$ (50 mL), H_2O_2 (20 mL) was added, and the mixture was allowed to stir for an additional hour. For compound **11a**, the obtained intermediate was dissolved in $CHCl_3$ (50 mL), sulfur (1.179 g, 0.037 mol) was added, and the mixture was allowed to stir for an additional hour. After the reaction was complete in each case, NH_4Cl solution (30 mL) was added, the organic phase was removed, and the aqueous phase was extracted with $CHCl_3$ (3× 25 mL). The collected organic phases were dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography with hexane/EtOAc (6:1, v/v) for **7a** and **11a** or $CHCl_3$/MeOH (15:1, v/v) for **8a** as eluents.

Phenylphosphonous Acid–Borane Bis(*N*,*N*-diethylamide) (7a): Yield 8.330 g (85%). Colourless liquid. R_F = 0.51 (hexane/EtOAc 6:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.13–1.20 (br. m, 3 H), 1.11 (t, $J_{H,H}$ = 7.0 Hz, 12 H), 3.15 (dq, $J_{H,H}$ = 7.0, $J_{P,H}$ = 10.15 Hz, 8 H), 7.40–7.45 (m, 3 H), 7.59–7.67 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.87 (d, $J_{P,C}$ = 2.6 Hz), 40.19 (d, $J_{P,C}$ = 4.4 Hz), 128.39 (d, $J_{P,C}$ = 10.6 Hz), 130.52 (d, $J_{P,C}$ = 2.3 Hz), 131.75 (d, $J_{P,C}$ = 10.4 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 92.72 (br. m) ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 9.27 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 252 (18) [M – BH_3], 181 (12), 180 (91), 175 (5), 166 (6), 161 (14), 120 (6), 110 (7), 109 (100), 107 (8), 104 (22), 91 (8), 83 (7). $C_{14}H_{28}BN_2P$ (266.17): calcd. C 63.17, H 10.60, N 10.52; found C 63.44, H 10.35, N 10.50.

Phenylphosphonic Acid Bis(*N*,*N*-diethylamide) (8a): Yield 8.887 g (90%). Pale yellow oil. R_F = 0.55 ($CHCl_3$/MeOH 15:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.03 (t, $J_{H,H}$ = 7.2 Hz, 12 H), 3.07 (dq, $J_{H,H}$ = 7.2, $J_{P,H}$ = 10.9 Hz, 8 H), 7.35–7.47 (m, 3 H), 7.72–7.80 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.62 (d, $J_{P,C}$ = 3.5 Hz), 38.30 (d, $J_{P,C}$ = 4.3 Hz), 128.15 (d, $J_{P,C}$ = 12.9 Hz), 130.82 (d, $J_{P,C}$ = 2.6 Hz), 131.85 (d, $J_{P,C}$ = 8.6 Hz), 133.33 (d, $J_{P,C}$ = 154.0 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 28.37 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 11.29 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 268 (10) [M], 253 (4), 197 (18), 196 (100), 195 (9), 182 (18), 168 (8), 154 (7), 152 (11), 140 (21), 125 (14), 122 (11), 120 (17), 119 (6), 106 (28), 104 (8), 95 (9), 93 (8). $C_{14}H_{25}N_2OP$ (268.33): calcd. C 62.66, H 9.39, N 10.44; found C 62.80, H 9.35, N 10.52.

Phenylthiophosphonous Acid Bis(*N*,*N*-diethylamide) (11a): Yield 9.522 g (91%). Yellow oil. R_F = 0.81 (hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.04 (t, $J_{H,H}$ = 6.9 Hz, 12 H), 3.05–3.22 (m, 8 H), 7.39–7.48 (m, 3 H), 7.93–8.00 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.29 (d, $J_{P,C}$ = 4.5 Hz), 39.15 (d, $J_{P,C}$ = 4.5 Hz), 128.00 (d, $J_{P,C}$ = 12.7 Hz), 130.79 (d, $J_{P,C}$ = 3.6 Hz), 131.42 (d, $J_{P,C}$ = 10.0 Hz), 135.41 (d, $J_{P,C}$ = 124.4 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 77.59 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 14.88 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 284 (5) [M], 212 (14), 181 (12), 180 (100), 141 (8), 109 (37), 107 (6). $C_{14}H_{25}N_2PS$ (284.40): calcd. C 59.12, H 8.86, N 9.85; found C 59.44, H 9.02, N 10.00.

Synthesis of Ph$_2$P(X)(NEt$_2$)-Type Compounds 9b, 10d and 11b: Ph_2PCl (5 mL, 0.028 mol) in diethyl ether (200 mL) was placed in a flame-dried two-necked flask (500 mL) containing a magnetic stirrer and fitted with an inert gas inlet. The mixture was placed in cold water bath, and diethylamine (5.76 mL, 0.056 mol) was added dropwise by syringe. After the addition was complete, the mixture was left under argon overnight. It was then filtered (funnel) with careful extrusion of oxygen and moisture. The solids were washed with diethyl ether (3× 50 mL), and the filtrate was concentrated under reduced pressure. For compound **7a**, the obtained intermediate was dissolved in THF (20 mL), BH_3·THF complex (56 mL, 0.056 mol) was added, and the mixture was allowed to stir for an additional hour. For compound **8a**, the obtained intermediate was dissolved in $CHCl_3$ (50 mL), H_2O_2 (20 mL) was added, and the mixture was allowed to stir for an additional hour. For compound **11a**, the obtained intermediate was dissolved in $CHCl_3$ (50 mL), sulfur (0.892 g, 0.028 mol) was added, and the mixture was allowed to stir for an additional hour. After the reaction was complete in each case, NH_4Cl solution (30 mL) was added, the organic phase was removed, and the aqueous phase was extracted with $CHCl_3$ (3× 25 mL). The collected organic phases were dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography with hexane/EtOAc (6:1 v/v) for **9b** and **11b** or $CHCl_3$/MeOH (15:1 v/v) for **10d** as eluents.

Diphenylphosphinous Acid–Borane *N*,*N*-Diethylamide (9b): Yield 5.664 g (75%). Colourless waxy solid. R_F = 0.61 (hexane/EtOAc

6:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.39–1.61 (br. m, 3 H), 0.97 (t, $J_{H,H}$ = 7.1 Hz, 6 H), 3.20 (dq, $J_{H,H}$ = 7.0, $J_{P,H}$ = 10.6 Hz, 4 H), 7.39–7.53 (m, 6 H), 7.58–7.66 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.82, 40.96 (d, $J_{P,C}$ = 3.9 Hz), 128.36 (d, $J_{P,C}$ = 9.7 Hz), 130.84, 131.39 (d, $J_{P,C}$ = 43.9 Hz), 132.05 (d, $J_{P,C}$ = 10.3 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 67.84 (br. m) ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 11.18 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 258 (7), 257 (38) [M – BH_3], 242 (7), 228 (7), 214 (44), 186 (17), 185 (90), 184 (13), 183 (90), 180 (10), 167 (10), 166 (100), 152 (18), 133 (6), 115 (7), 109 (71), 108 (55), 107 (28), 91 (8), 83 (9). $C_{16}H_{23}BNP$ (271.15): calcd. C 70.87, H 8.55, N 5.17; found C 70.98, H 8.31, N 5.00.

Diphenylphosphinic Acid *N*,*N*-Diethylamide (10d): Yield 6.010 g (79%). Colourless solid, m.p. 134.3–135.9 °C (ref.[19] 135–138 °C). R_F = 0.81 ($CHCl_3$/MeOH 15:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.09 (t, $J_{H,H}$ = 7.0 Hz, 6 H), 3.06 (dq, $J_{H,H}$ = 6.9, $J_{P,H}$ = 11.1 Hz, 4 H), 7.40–7.51 (m, 6 H), 7.82–7.88 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.06 (d, $J_{P,C}$ = 3.7 Hz), 39.31 (d, $J_{P,C}$ = 3.7 Hz), 128.38 (d, $J_{P,C}$ = 12.6 Hz), 131.51 (d, $J_{P,C}$ = 2.3 Hz), 132.29 (d, $J_{P,C}$ = 8.6 Hz), 132.55 (d, $J_{P,C}$ = 129.0 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 30.00 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 13.56 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 273 (2) [M], 258 (13), 202 (19), 201 (100), 183 (4), 173 (4), 171 (4), 155 (8), 154 (5), 153 (5), 152 (5), 125 (5), 95 (6). $C_{16}H_{20}NOP$ (273.31): calcd. C 70.31, H 7.38, N 5.12; found C 70.22, H 7.51, N 5.01. Spectral data are in accordance with those reported in the literature.[19]

Diphenylthiophosphinic Acid *N*,*N*-Diethylamide (11b): Yield 7.893 g (98%). Pale yellow liquid. R_F = 0.71 (hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.10 (t, $J_{H,H}$ = 7.3 Hz, 6 H), 3.01–3.10 (m, 4 H), 7.41–7.51 (m, 6 H), 7.97–8.04 (m, 4 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.63 (d, $J_{P,C}$ = 5.5 Hz), 40.39 (d, $J_{P,C}$ = 2.7 Hz), 128.25 (d, $J_{P,C}$ = 12.7 Hz), 131.38 (d, $J_{P,C}$ = 3.6 Hz), 132.00 (d, $J_{P,C}$ = 10.9 Hz), 133.74 (d, $J_{P,C}$ = 102.6 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 68.46 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 17.10 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 289 (3) [M], 219 (8), 218 (50), 217 (32), 185 (65), 184 (11), 183 (66), 166 (10), 152 (17), 141 (16), 140 (93), 139 (100), 109 (35), 108 (17), 107 (31). $C_{16}H_{20}NPS$ (289.37): calcd. C 66.41, H 6.97, N 4.84; found C 66.55, H 6.88, N 5.05.

General Procedure for the Preparation of Arylphosphonous Acid Diamide Derivatives: $(Et_2N)_2PCl$ (0.628 mL, 3 mmol) was placed in dry THF (20 mL) in a flame-dried two-necked round-bottomed flask (100 mL) containing a magnetic stirrer and fitted with an argon inlet, and the flask was cooled in a cold water bath. An ethereal solution of the relevant Grignard reagent [prepared earlier from magnesium (0.072 g, 3 mmol) and aryl bromide (3 mmol) in Et_2O (20 mL)] was then added by cannula over a 5 min period. After addition of the Grignard reagent, the mixture was left for 2 h. For compounds **7b**–**h**, BH_3·THF complex in THF (4.5 mL, 4.5 mmol) was then added. For compounds **8b**–**f**, H_2O_2 (10 mL) was added. After the addition of the reagent the mixture was left overnight at room temperature. The reaction was quenched by addition of saturated solution of NH_4Cl (10 mL), the formed mixture was extracted with CH_2Cl_2 (3 × 30 mL), the collected organic fractions were dried with $MgSO_4$ and concentrated in vacuo, and the residue was purified with column chromatography on silica gel either with hexane/EtOAc (100:1 v/v, compounds **7b**–**h**) or with hexane/EtOAc (2:1 v/v, compounds **8b**–**f**).

2-Methyl-1-naphthylphosphonous Acid–Borane Bis(*N*,*N*-diethylamide) (7b): This compound was prepared from 1-bromo-2-methylnaphthalene (0.663 g, 3 mmol), magnesium (0.072 g, 3 mmol), $(Et_2N)_2PCl$ (0.628 mL, 3 mmol) and BH_3·THF (4.5 mL, 4.5 mmol), yield 0.644 g (65%). White solid, m.p. 87.9–89.7 °C. R_F = 0.31 (hexane/EtOAc 50:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.65–1.41 (br. m, 3 H), 1.19 (t, $J_{H,H}$ = 7.1 Hz, 12 H), 2.67 (d, $J_{H,H}$ = 1.0 Hz, 3 H), 3.02–3.21 (m, 8 H), 7.25 (dd, $J_{H,H}$ = 3.8, $J_{H,H}$ = 8.5 Hz, 1 H), 7.38–7.45 (m, 2 H), 7.73–7.78 (m, 2 H), 8.74–8.77 (m, 1 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.64 (d, $J_{P,C}$ = 2.7 Hz), 22.84 (d, $J_{P,C}$ = 4.5 Hz), 42.36 (d, $J_{P,C}$ = 3.6 Hz), 124.88, 125.32, 125.83 (d, $J_{P,C}$ = 73.6 Hz), 127.56 (d, $J_{P,C}$ = 3.6 Hz), 127.99, 130.67 (d, $J_{P,C}$ = 10.0 Hz), 131.09 (d, $J_{P,C}$ = 1.8 Hz), 132.47 (d, $J_{P,C}$ = 7.3 Hz), 134.64 (d, $J_{P,C}$ = 9.1 Hz), 142.90 (d, $J_{P,C}$ = 9.1 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 86.97 (br. m) ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 15.55 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 316 (14) [M – BH_3], 245 (10), 244 (52), 175 (6), 174 (12), 173 (100), 172 (7), 171 (33), 170 (8), 161 (14), 147 (7), 141 (8), 132 (9), 129 (8), 128 (16), 115 (7), 104 (28), 74 (12), 72 (12), 70 (11), 46 (9), 42 (8), 29 (8), 28 (6). $C_{19}H_{32}BN_2P$ (330.26): calcd. C 69.10, H 9.77, N 8.48; found C 69.37, H 9.50, N 8.21.

1-Naphthylphosphonous Acid–Borane Bis(*N*,*N*-diethylamide) (7c): This compound was prepared from 1-bromonaphthalene (0.420 mL, 3 mmol), magnesium (0.072 g, 3 mmol), $(Et_2N)_2PCl$ (0.628 mL, 3 mmol) and BH_3·THF (4.5 mL, 4.5 mmol), yield 0.616 g (65%). Colourless solid, m.p. 124.8–125.3 °C. R_F = 0.30 (hexane/EtOAc 50:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.57–1.32 (br. m, 3 H), 1.18 (t, $J_{H,H}$ = 7.1 Hz, 12 H), 3.14–3.33 (m, 8 H), 7.48–7.57 (m, 3 H), 7.69–7.74 (m, 1 H), 7.84–7.88 (m, 1 H), 7.92–7.96 (m, 1 H), 8.67–8.70 (m, 1 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.18 (d, $J_{P,C}$ = 2.7 Hz), 41.14 (d, $J_{P,C}$ = 2.7 Hz), 124.58 (d, $J_{P,C}$ = 10.9 Hz), 126.07 (d, $J_{P,C}$ = 4.5 Hz), 127.75 (d, $J_{P,C}$ = 3.6 Hz), 128.54, 129.18 (d, $J_{P,C}$ = 76.3 Hz), 131.84 (d, $J_{P,C}$ = 8.2 Hz), 132.03 (d, $J_{P,C}$ = 2.7 Hz), 133.06 (d, $J_{P,C}$ = 11.8 Hz), 134.19 (d, $J_{P,C}$ = 8.2 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 89.19 (br. m) ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 15.55 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 302 (14) [M – BH_3], 231 (8), 230 (48), 161 (18), 160 (11), 159 (100), 157 (12), 155 (5), 133 (38), 115 (13), 104 (23), 74 (9), 72 (8), 70 (14), 46 (8), 42 (9), 29 (6). $C_{18}H_{30}BN_2P$ (316.23): calcd. C 68.37, H 9.56, N 8.86; found C 68.12, H 9.51, N 9.12.

Mesitylphosphonous Acid–Borane Bis(*N*,*N*-diethylamide) (7d): This compound was prepared from mesityl bromide (0.459 mL, 3 mmol), magnesium (0.072 g, 3 mmol), $(Et_2N)_2PCl$ (0.628 mL, 3 mmol) and BH_3·THF (4.5 mL, 4.5 mmol), yield 0.878 g (95%). White solid, m.p. 51.3–52.6 °C. R_F = 0.77 (hexane/EtOAc 10:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.50–1.15 (br. m, 3 H), 1.20 (t, $J_{H,H}$ = 7.1 Hz, 12 H), 2.25 (s, 3 H), 2.51 (s, 6 H), 3.00–3.20 (m, 8 H), 6.85 (dd, $J_{H,H}$ = 0.6, $J_{H,H}$ = 3.5 Hz, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.81 (d, $J_{P,C}$ = 2.7 Hz), 20.64, 22.66 (d, $J_{P,C}$ = 2.7 Hz), 42.19 (d, $J_{P,C}$ = 3.6 Hz), 126.83 (d, $J_{P,C}$ = 74.5 Hz), 131.15 (d, $J_{P,C}$ = 9.1 Hz), 139.47 (d, $J_{P,C}$ = 2.7 Hz), 142.78 (d, $J_{P,C}$ = 10.0 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 88.06 (br. m) ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 13.22 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 294 (9) [M – BH_3], 223 (9), 222 (42), 221 (6), 175 (5), 152 (10), 151 (100), 149 (12), 147 (7), 105 (26), 104 (22), 91 (8), 74 (9), 72 (14), 70 (10), 46 (5), 42 (6), 29 (5). $C_{17}H_{34}BN_2P$ (308.25): calcd. C 66.24, H 11.12, N 9.09; found C 66.22, H 11.01, N 9.30.

***o*-Tolylphosphonous Acid–Borane Bis(*N*,*N*-diethylamide) (7e):** This compound was prepared from 2-bromotoluene (0.361 mL, 3 mmol), magnesium (0.072 g, 3 mmol), $(Et_2N)_2PCl$ (0.628 mL, 3 mmol) and BH_3·THF (4.5 mL, 4.5 mmol), yield 0.571 g (68%). Colourless solid, m.p. 54.2–55.6 °C. R_F = 0.44 (hexane/EtOAc 50:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.30–1.20 (br. m, 3 H),

1.15 (t, $J_{H,H}$ = 7.1 Hz, 12 H), 2.59 (s, 3 H), 3.07–3.26 (m, 8 H), 7.20–7.26 (m, 2 H), 7.31–7.37 (m, 1 H), 7.42–7.49 (m, 1 H) ppm. ^{13}C NMR (76 MHz, $CDCl_3$): δ = 14.08 (d, $J_{P,C}$ = 2.3 Hz), 21.51 (d, $J_{P,C}$ = 2.3 Hz), 40.83 (d, $J_{P,C}$ = 3.5 Hz), 125.38 (d, $J_{P,C}$ = 9.2 Hz), 130.54 (d, $J_{P,C}$ = 2.3 Hz), 131.09 (d, $J_{P,C}$ = 77.6 Hz), 132.20 (d, $J_{P,C}$ = 4.0 Hz), 132.32 (d, $J_{P,C}$ = 2.9 Hz), 142.18 (d, $J_{P,C}$ = 12.6 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 88.63 (br. m) ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 11.56 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 266 (22) [M – BH_3], 195 (16), 194 (94), 175 (8), 166 (6), 161 (8), 136 (6), 124 (7), 123 (100), 122 (5), 121 (47), 119 (7), 104 (32), 91 (8), 79 (13), 78 (15), 77 (9), 74 (14), 72 (25), 70 (44), 56 (6), 46 (12), 44 (8), 42 (22), 29 (11), 28 (8). $C_{15}H_{30}BN_2P$ (280.20): calcd. C 64.30, H 10.79, N 10.00; found C 64.50, H 10.50, N 9.92.

***o*-Anisylphosphonous Acid–Borane Bis(*N*,*N*-diethylamide) (7f):** This compound was prepared from 2-bromoanisole (0.374 mL, 3 mmol), magnesium (0.072 g, 3 mmol), $(Et_2N)_2PCl$ (0.628 mL, 3 mmol) and BH_3·THF (4.5 mL, 4.5 mmol), yield 0.515 g (58%). Colourless solid, m.p. 89.2–90.7 °C. R_F = 0.25 (hexane/EtOAc 25:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.40–1.05 (br. m, 3 H), 1.11 (t, $J_{H,H}$ = 7.1 Hz, 12 H), 3.07–3.20 (m, 8 H), 3.83 (s, 3 H), 6.88–6.92 (m, 1 H), 6.96–7.01 (m, 1 H), 7.39–7.45 (m, 1 H), 7.47–7.53 (m, 1 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.91 (d, $J_{P,C}$ = 1.8 Hz), 40.26 (d, $J_{P,C}$ = 4.5 Hz), 55.02, 111.19 (d, $J_{P,C}$ = 5.5 Hz), 120.31 (d, $J_{P,C}$ = 10.0 Hz), 120.99 (d, $J_{P,C}$ = 75.4 Hz), 132.47 (d, $J_{P,C}$ = 1.8 Hz), 133.91 (d, $J_{P,C}$ = 8.2 Hz), 161.07 (d, $J_{P,C}$ = 5.5 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 88.60 (br. m) ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 12.55 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 282 (17) [M – BH_3], 211 (10), 210 (72), 161 (11), 140 (8), 139 (100), 137 (15), 109 (22), 104 (15), 95 (20), 91 (10), 83 (5), 77 (7), 74 (11), 72 (11), 70 (23), 65 (5), 58 (5), 56 (5), 46 (9), 44 (6), 42 (14), 29 (9), 28 (7). $C_{15}H_{30}BN_2OP$ (296.20): calcd. C 60.82, H 10.21, N 9.46; found C 60.89, H 10.11, N 9.19.

***p*-Tolylphosphonous Acid–Borane Bis(*N*,*N*-diethylamide) (7g):** This compound was prepared from 4-bromotoluene (0.369 mL, 3 mmol), magnesium (0.072 g, 3 mmol), $(Et_2N)_2PCl$ (0.628 mL, 3 mmol) and BH_3·THF (4.5 mL, 4.5 mmol), yield 0.479 g (57%). White solid, m.p. 50.3–52.7 °C. R_f = 0.58 (hexane/EtOAc 25:1). ^{1}H NMR (400 MHz $CDCl_3$): δ = 0.26–1.17 (br. m, 3 H), 1.12 (t, $J_{H,H}$ = 7.2 Hz, 12 H), 2.39 (s, 3 H), 3.11–3.19 (m, 8 H), 7.22–7.26 (m, 2 H), 7.49–7.55 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.85 (d, $J_{P,C}$ = 2.7 Hz), 21.36, 40.07 (d, $J_{P,C}$ = 3.6 Hz), 129.21 (d, $J_{P,C}$ = 10.9 Hz), 129.81 (d, $J_{P,C}$ = 89.0 Hz), 131.75 (d, $J_{P,C}$ = 10.9 Hz), 140.78 (d, $J_{P,C}$ = 1.8 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 89.26 (br. m) ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 11.98 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 266 (16) [M – BH_3], 195 (10), 194 (69), 161 (9), 124 (7), 123 (100), 122 (5), 121 (24), 104 (13), 91 (5), 79 (11), 78 (9), 74 (8), 72 (14), 70 (28), 46 (8), 42 (13), 29 (7), 28 (5). $C_{15}H_{30}BN_2P$ (280.20): calcd. C 64.30, H 10.79, N 10.00; found C 64.41, H 10.59, N 9.99.

2-Naphthylphosphonous Acid–Borane Bis(*N*,*N*-diethylamide) (7h): This compound was prepared from 2-bromonaphthalene (0.621 g, 3 mmol), magnesium (0.072 g, 3 mmol), $(Et_2N)_2PCl$ (0.628 mL, 3 mmol) and BH_3·THF (4.5 mL, 4.5 mmol), yield 0.645 g (68%). Colourless solid, m.p. 68.5–69.9 °C. R_f = 0.29 (hexane/EtOAc 50:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.40–1.21 (br. m, 3 H), 1.17 (t, $J_{H,H}$ = 7.2 Hz, 12 H), 3.17–3.27 (m, 8 H), 7.52–7.59 (m, 2 H), 7.66–7.71 (m, 1 H), 7.86–7.92 (m, 3 H), 8.16 (m, 1 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.91 (d, $J_{P,C}$ = 2.7 Hz), 40.23 (d, $J_{P,C}$ = 3.6 Hz), 126.40, 127.43 (d, $J_{P,C}$ = 10.9 Hz), 127.44, 127.65, 128.09 (d, $J_{P,C}$ = 10.0 Hz), 128.60, 130.69 (d, $J_{P,C}$ = 86.3 Hz), 132.80 (d, $J_{P,C}$ = 11.8 Hz), 132.96 (d, $J_{P,C}$ = 10.9 Hz), 134.24 (d, $J_{P,C}$ = 1.8 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 90.43 (br. m) ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 16.13 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 302 (15) [M – BH_3], 231 (10), 230 (58), 161 (12), 160 (11), 159 (100), 157 (12), 133 (41), 128 (5), 115 (15), 104 (15), 74 (10), 72 (11), 70 (18), 46 (9), 42 (10), 29 (7), 28 (5). $C_{18}H_{30}BN_2P$ (316.23): calcd. C 68.37, H 9.56, N 8.86; found C 68.55, H 9.72, N 9.03.

***o*-Anisylphosphonic Acid Bis(*N*,*N*-diethylamide) (8b):** This compound was prepared from 2-bromoanisole (0.374 mL, 3 mmol), magnesium (0.072 g, 3 mmol), $(Et_2N)_2PCl$ (0.628 mL, 3 mmol) and H_2O_2 (10 mL), yield 0.483 g (54%). Pale yellow oil. R_F = 0.33 (EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.98 (t, $J_{H,H}$ = 7.0 Hz, 12 H), 2.98–3.24 (m, 8 H), 3.75 (s, 3 H), 6.79–6.86 (m, 1 H), 6.91–6.98 (m, 1 H), 7.35–7.43 (m, 1 H), 7.81–7.91 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.54 (d, $J_{P,C}$ = 2.3 Hz), 38.32 (d, $J_{P,C}$ = 5.8 Hz), 54.66, 110.02 (d, $J_{P,C}$ = 7.5 Hz), 121.07 (d, $J_{P,C}$ = 148.3 Hz), 120.23 (d, $J_{P,C}$ = 12.6 Hz), 132.75 (d, $J_{P,C}$ = 2.3 Hz), 135.95 (d, $J_{P,C}$ = 6.9 Hz), 160.26 (d, $J_{P,C}$ = 2.9 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 26.41 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 15.17 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 298 (3) [M], 267 (8), 227 (20), 226 (41), 196 (11), 155 (26), 148 (5), 108 (5), 106 (13), 91 (8), 86 (6), 77 (19), 74 (6), 73 (9), 72 (100), 71 (8), 70 (5), 58 (42), 56 (10), 47 (9), 44 (14), 42 (12), 30 (5), 29 (10), 28 (7). $C_{15}H_{27}N_2O_2P$ (298.18): calcd. C 60.38, H 9.12, N 9.39; found C 60.55, H 8.88, N 9.45.

***p*-Tolylphosphonic Acid Bis(*N*,*N*-diethylamide) (8c):** This compound was prepared from 4-bromotoluene (0.369 mL, 3 mmol), magnesium (0.072 g, 3 mmol), $(Et_2N)_2PCl$ (0.628 mL, 3 mmol) and H_2O_2 (10 mL), yield 0.482 g (57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.01 (t, $J_{H,H}$ = 7.2 Hz, 12 H), 2.36 (s, 3 H), 2.98–3.12 (m, 4 H), 7.17–7.23 (m, 4 H), 7.59–7.67 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 3.58 (d, $J_{P,C}$ = 2.9 Hz), 21.37 (d, $J_{P,C}$ = 1.7 Hz), 38.27 (d, $J_{P,C}$ = 4.6 Hz), 129.77 (d, $J_{P,C}$ = 156.3 Hz), 128.88 (d, $J_{P,C}$ = 13.2 Hz), 131.83 (d, $J_{P,C}$ = 9.2 Hz), 141.06 (d, $J_{P,C}$ = 2.9 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 28.17 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 14.59 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 282 (5) [M], 211 (10), 210 (38), 154 (6), 139. (6), 106 (13), 91 (14), 73 (8), 72 (100), 71 (15), 58 (22), 56 (6), 47 (6), 44 (11), 42 (6), 29 (8). $C_{15}H_{27}N_2OP$ (282.19): calcd. C 63.80, H 9.64, N 9.92; found C 63.95, H 9.40, N 9.81.

***o*-Tolylphosphonic Acid Bis(*N*,*N*-diethylamide) (8d):** This compound was prepared from 2-bromotoluene (0.361 mL, 3 mmol), magnesium (0.072 g, 3 mmol), $(Et_2N)_2PCl$ (0.628 mL, 3 mmol) and H_2O_2 (10 mL), yield 0.355 g (42%). Pale yellow oil. R_F = 0.28 (EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04–1.10 (m, 3 H), 2.64 (d, $J_{P,H}$ = 1.5 Hz, 3 H), 3.01–3.12 (m, 8 H), 7.13–7.19 (m, 1 H), 7.19–7.24 (m, 1 H), 7.29–7.35 (m, 1 H), 7.40–7.47 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.90 (d, $J_{P,C}$ = 2.3 Hz), 21.31 (d, $J_{P,C}$ = 4.0 Hz), 38.97 (d, $J_{P,C}$ = 4.6 Hz), 124.85 (d, $J_{P,C}$ = 13.2 Hz), 130.89 (d, $J_{P,C}$ = 155.2 Hz), 130.91 (d, $J_{P,C}$ = 2.3 Hz), 131.64 (d, $J_{P,C}$ = 13.2 Hz), 132.23 (d, $J_{P,C}$ = 10.4 Hz), 143.42 (d, $J_{P,C}$ = 9.8 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 30.01 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 14.06 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 282 (3) [M], 211 (6), 210 (27), 194 (5), 137 (7), 106 (6), 91 (11), 74 (6), 73 (8), 72 (100), 65 (5), 58 (13), 44 (11), (5), 29 (6). $C_{15}H_{27}N_2OP$ (282.19): calcd. C 63.80, H 9.64, N 9.92; found C 63.77, H 9.38, N 9.99.

2-Naphthylphosphonic Acid Bis(*N*,*N*-diethylamide) (8e): This compound was prepared from 2-bromonaphthalene (0.621 g, 3 mmol), magnesium (0.072 g, 3 mmol), $(Et_2N)_2PCl$ (0.628 mL, 3 mmol) and H_2O_2 (10 mL), yield 0.849 g (89%). Pale yellow oil. R_F = 0.20 (EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.06 (t, $J_{H,H}$ = 7.1 Hz, 12 H), 3.08–3.18 (m, 8 H), 7.50–7.59 (m, 2 H), 7.69–7.76 (m, 1 H),

7.84–7.89 (m, 2 H), 7.91–7.95 (m, 1 H), 8.37–8.44 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.65 (d, $J_{P,C}$ = 2.9 Hz), 38.36 (d, $J_{P,C}$ = 4.0 Hz), 127.10 (d, $J_{P,C}$ = 9.2 Hz), 127.54 (d, $J_{P,C}$ = 7.5 Hz), 127.64 (d, $J_{P,C}$ = 5.2 Hz), 127.83, 128.83, 130.54 (d, $J_{P,C}$ = 154.0 Hz), 132.72 (d, $J_{P,C}$ = 14.4 Hz), 133.70 (d, $J_{P,C}$ = 8.6 Hz), 134.32 (d, $J_{P,C}$ = 2.3 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 27.69 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 18.36 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 318 (7) [M], 247 (9), 246 (32), 128 (19), 127 (15), 106 (15), 73 (8), 72 (100), 71 (11), 58 (21), 44 (11), 42 (6), 29 (6). $C_{18}H_{27}N_2OP$ (318.19): calcd. C 67.90, H 8.55, N 8.80; found C 68.12, H 8.80, N 8.91.

Mesitylphosphonic Acid Bis(*N*,*N*-diethylamide) (8f): This compound was prepared from mesityl bromide (0.459 mL, 3 mmol), magnesium (0.072 g, 3 mmol), $(Et_2N)_2PCl$ (0.628 mL, 3 mmol) and H_2O_2 (10 mL), yield 0.586 g (63%). Pale yellow oil. R_F = 0.30 (EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.09 (t, $J_{H,H}$ = 7.0 Hz, 12 H), 2.21 (s, 3 H), 2.50 (d, $J_{P,H}$ = 1.3 Hz, 6 H), 2.90–3.12 (m, 8 H), 6.81 (d, $J_{H,H}$ = 3.9 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.26 (d, $J_{P,C}$ = 2.3 Hz), 20.72 (d, $J_{P,C}$ = 1.2 Hz), 23.16 (d, $J_{P,C}$ = 4.0 Hz), 39.68 (d, $J_{P,C}$ = 5.2 Hz), 127.02 (d, $J_{P,C}$ = 153.5 Hz), 130.56 (d, $J_{P,C}$ = 12.6 Hz), 140.01 (d, $J_{P,C}$ = 2.9 Hz), 143.21 (d, $J_{P,C}$ = 10.4 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 28.63 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 15.66 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 310 (2) [M], 295 (6), 239 (11), 238 (28), 222 (14), 165 (13), 120 (9), 119 (9), 91 (8), 74 (18), 73 (6), 72 (100), 58 (11), 44 (8), 29 (5). $C_{17}H_{31}N_2OP$ (310.22): calcd. C 65.78, H 10.07, N 9.02; found C 65.99, H 9.93, N 9.15.

General Procedure for the Preparation of Diarylphosphinous Acid Amide Derivatives: $(Et_2N)PCl_2$ (0.443 mL, 3 mmol) was placed in dry THF (20 mL) in a flame-dried two-necked round-bottomed flask (100 mL) containing a magnetic stirrer and fitted with an argon inlet, and the flask was cooled in a cold water bath. An ethereal solution of the relevant bulkier Grignard reagent [prepared earlier from magnesium (0.072 g, 3 mmol) and aryl bromide (3 mmol) in Et_2O (20 mL)] was then added by cannula over a 5 min period. After addition of this Grignard reagent, the mixture was left for 2 h. An ethereal solution of the relevant less bulky Grignard reagent [prepared earlier from magnesium (0.072 g, 3 mmol) and aryl bromide (3 mmol) in Et_2O (20 mL)] was then added by cannula over a 5 min period. After addition of this Grignard reagent, the mixture was left for 2 h. For compounds **9d**–**f**, BH_3·THF complex in THF (4.5 mL, 4.5 mmol) was then added, whereas for compounds **10e**–**h**, H_2O_2 (10 mL) was added. After addition of the appropriate reagent the mixture was left overnight at room temperature. The reaction was quenched by addition of saturated solution of NH_4Cl (10 mL), the formed mixture was extracted with CH_2Cl_2 (3 × 30 mL), the collected organic fractions were dried with $MgSO_4$ and concentrated in vacuo, and the residue was purified by column chromatography on silica gel either with hexane/EtOAc (100:1 v/v, compounds **9d**–**f**) or with hexane/EtOAc (2:1 v/v, compounds **10e**–**h**).

***o*-Anisyl(*p*-tolyl)phosphinous Acid–Borane *N*,*N*-Diethylamide (9d):** This compound was prepared from 2-bromoanisole (0.374 mL, 3 mmol), 4-bromotoluene (0.369 mL, 3 mmol), magnesium (0.144 g, 6 mmol), $(Et_2N)PCl_2$ (0.443 mL, 3 mmol) and BH_3·THF (4.5 mL, 4.5 mmol), yield 0.321 g (34%). White solid, m.p. 65.8–67.7 °C. R_F = 0.39 (hexane/EtOAc 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.46–1.47 (br. m, 3 H), 0.96 (t, $J_{H,H}$ = 6.9 Hz, 6 H), 2.38 (s, 3 H), 3.14–3.25 (m, 4 H), 3.63 (s, 3 H), 6.93 (m, 1 H), 7.01–7.08 (m, 1 H), 7.17–7.22 (m, 2 H), 7.43–7.52 (m, 3 H), 7.60–7.66 (m, 1 H) ppm. ^{13}C NMR (76 MHz, $CDCl_3$): δ = 14.01 (d, $J_{P,C}$ = 2.3 Hz), 21.41 (d, $J_{P,C}$ = 1.2 Hz), 41.34 (d, $J_{P,C}$ = 3.5 Hz), 55.14, 111.44 (d, $J_{P,C}$ = 4.6 Hz), 119.97 (d, $J_{P,C}$ = 56.9 Hz), 120.68 (d, $J_{P,C}$ = 10.3 Hz), 128.77 (d, $J_{P,C}$ = 10.9 Hz), 129.28 (d, $J_{P,C}$ = 71.3 Hz), 131.21 (d, $J_{P,C}$ = 10.9 Hz), 132.91 (d, $J_{P,C}$ = 2.3 Hz), 134.51 (d, $J_{P,C}$ = 9.8 Hz), 140.33 (d, $J_{P,C}$ = 2.3 Hz), 161.10 (d, $J_{P,C}$ = 3.5 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 64.61 (br. m) ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 15.84 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 302 (6), 301 (33) [M – BH_3], 258 (14), 230 (9), 229 (45), 199 (5), 197 (7), 196 (33), 183 (6), 181 (6), 180 (45), 166 (6), 165 (10), 152 (7), 139 (26), 138 (19), 137 (41), 136 (5), 133 (6), 123 (38), 122 (11), 121 (21), 109 (17), 107 (7), 106 (9), 105 (100), 95 (10), 91 (34), 79 (12), 78 (12), 77 (12), 74 (9), 72 (49), 70 (7), 65 (8), 58 (7), 56 (6), 46 (5), 44 (7), 42 (10), 29 (9), 28 (7). $C_{18}H_{27}BNOP$ (315.20): calcd. C 68.59, H 8.63, N 4.44; found C 68.61, H 8.51, N 4.19.

***o*-Anisyl(2-methyl-1-naphthyl)phosphinous Acid–Borane *N*,*N*-Diethylamide (9e):** This compound was prepared from 2-bromoanisole (0.374 mL, 3 mmol), 1-bromo-2-methylnaphthalene (0.663 g, 3 mmol), magnesium (0.144 g, 6 mmol), $(Et_2N)PCl_2$ (0.443 mL, 3 mmol) and BH_3·THF (4.5 mL, 4.5 mmol), yield 0.307 g (28%). White solid, m.p. 114.3–116.7 °C. R_F = 0.32 (hexane/EtOAc 25:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.82–1.48 (br. m, 3 H), 0.98 (t, $J_{H,H}$ = 7.09 Hz, 6 H), 2.49 (s, 3 H), 3.06 (s, 3 H), 3.14–3.25 (m, 2 H), 3.27–3.37 (m, 2 H), 6.68–6.72 (m, 1 H), 7.11–7.18 (m, 2 H), 7.25 (m, 1 H), 7.31–7.35 (m, 1 H), 7.42–7.47 (m, 1 H), 7.73–7.79 (m, 2 H), 8.03–8.10 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.53 (d, $J_{P,C}$ = 1.8 Hz), 23.21 (d, $J_{P,C}$ = 6.4 Hz), 43.29 (d, $J_{P,C}$ = 3.6 Hz), 54.75, 110.95 (d, $J_{P,C}$ = 4.5 Hz), 121.47 (d, $J_{P,C}$ = 11.8 Hz), 124.63, 124.78, 125.59 (d, $J_{P,C}$ = 95.4 Hz), 126.14 (d, $J_{P,C}$ = 65.4 Hz), 126.02, 128.02, 130.24 (d, $J_{P,C}$ = 10.0 Hz), 130.46 (d, $J_{P,C}$ = 2.7 Hz), 132.06 (d, $J_{P,C}$ = 7.3 Hz), 132.40, 132.51 (d, $J_{P,C}$ = 1.8 Hz), 134.23 (d, $J_{P,C}$ = 9.1 Hz), 141.12 (d, $J_{P,C}$ = 9.1 Hz), 159.66 ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 62.53 (br. m) ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 19.09 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 352 (11), 351 (47) [M – BH_3], 322 (7), 321 (14), 320 (62), 280 (6), 279 (26), 278 (53), 277 (9), 264 (7), 263 (36), 249 (8), 248 (7), 247 (36), 246 (38), 245 (17), 244 (6), 233 (7), 231 (7), 216 (15), 215 (21), 210 (19), 202 (9), 197 (5), 196 (42), 186 (12), 185 (12), 173 (24), 172 (16), 171 (33), 170 (21), 156 (6), 155 (41), 153 (5), 152 (6), 142 (11), 141 (33), 140 (9), 139 (100), 138 (16), 137 (40), 133 (6), 129 (8), 128 (21), 123 (6), 121 (8), 115 (27), 109 (32), 108 (5), 107 (9), 95 (24), 94 (7), 91 (41), 83 (5), 77 (12), 74 (18), 72 (57), 70 (17), 65 (8), 58 (6), 56 (8), 47 (5), 46 (8), 44 (8), 42 (18), 29 (16), 28 (8). $C_{22}H_{29}BNOP$ (365.26): calcd. C 72.34, H 8.00, N 3.83; found C 72.55, H 8.22, N 3.87.

Mesityl(*o*-Tolyl)Phosphinous Acid–Borane *N*,*N*-Diethylamide (9f): This compound was prepared from 2-bromotoluene (0.361 mL, 3 mmol), mesityl bromide (0.459 mL, 3 mmol), magnesium (0.144 g, 6 mmol), $(Et_2N)PCl_2$ (0.443 mL, 3 mmol) and BH_3·THF (4.5 mL, 4.5 mmol), yield 0.265 g (27%). White solid, m.p. 133.5–134.8 °C. R_F = 0.49 (hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.79–1.56 (br. m, 3 H), 1.03 (t, $J_{H,H}$ = 7.1 Hz, 6 H), 2.24 (s, 3 H), 2.29 (d, $J_{P,H}$ = 3.4 Hz, 6 H), 3.21–3.36 (m, 4 H), 6.85–6.88 (m, 2 H), 7.17–7.21 (m, 1 H), 7.22–7.26 (m, 1 H), 7.30–7.35 (m, 1 H), 7.41–7.46 (m, 1 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.94 (d, $J_{P,C}$ = 1.8 Hz), 20.88 (s), 22.12 (d, $J_{P,C}$ = 3.6 Hz), 23.83 (d, $J_{P,C}$ = 4.5 Hz), 43.38 (d, $J_{P,C}$ = 2.7 Hz), 125.04 (d, $J_{P,C}$ = 61.8 Hz), 125.75 (d, $J_{P,C}$ = 8.2 Hz), 129.65 (d, $J_{P,C}$ = 6.4 Hz), 129.95 (d, $J_{P,C}$ = 2.7 Hz), 131.04 (d, $J_{P,C}$ = 9.1 Hz), 131.88 (d, $J_{P,C}$ = 9.1 Hz), 137.41 (d, $J_{P,C}$ = 52.7 Hz), 140.11 (d, $J_{P,C}$ = 12.7 Hz), 140.63 (d, $J_{P,C}$ = 1.8 Hz), 143.22 (d, $J_{P,C}$ = 8.2 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 65.23 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 15.77 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 314 (8) [M – BH_3], 313 (38), 299 (8), 298 (39), 284 (8), 242 (9), 241 (38), 240 (100), 239 (14), 227 (17), 226 (13), 225 (76), 224 (18), 222 (5),

211 (7), 210 (15), 209 (11), 208 (52), 207 (50), 194 (18), 193 (19), 192 (11), 180 (11), 179 (7), 178 (12), 165 (6), 164 (7), 152 (7), 151 (46), 150 (24), 149 (20), 148 (6), 147 (16), 136 (7), 135 (21), 134 (8), 133 (21), 123 (50), 122. (34), 121 (42), 120 (6), 119 (29), 117 (5), 116 (5), 115 (11), 109 (6), 107 (6), 106 (12), 105 (50), 103 (7), 95 (6), 92 (5), 91 (40), 79 (20), 78 (43), 77 (25), 74 (25), 73 (5), 72 (80), 70 (23), 65 (11), 58 (5), 56 (7), 53 (5), 46 (10), 44 (10), 42 (20), 41 (10), 39 (7), 29 (18), 28 (11), 27 (8). $C_{20}H_{31}BNP$ (327.25): calcd. C 73.70, H 9.55, N 4.28; found C 73.61, H 9.29, N 4.37.

***o*-Anisyl(*p*-tolyl)phosphinic Acid *N*,*N*-Diethylamide (10e):** This compound was prepared from 2-bromoanisole (0.374 mL, 3 mmol), 4-bromotoluene (0.369 mL, 3 mmol), magnesium (0.144 g, 6 mmol), $(Et_2N)PCl_2$ (0.443 mL, 3 mmol) and H_2O_2 (10 mL), yield 0.419 g (44%). Orange oil. R_F = 0.56 (EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.01 (t, $J_{H,H}$ = 7.0 Hz, 6 H), 2.31 (s, 3 H), 2.93–3.13 (m, 4 H), 3.71 (s, 3 H), 6.78–6.85 (m, 1 H), 6.95–7.02 (m, 1 H), 7.13–7.19 (m, 2 H), 7.38–7.45 (m, 1 H), 7.67–7.74 (m, 2 H), 7.91–7.99 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.76 (d, $J_{P,C}$ = 3.5 Hz), 21.29 (d, $J_{P,C}$ = 1.2 Hz), 38.80 (d, $J_{P,C}$ = 4.6 Hz), 54.72, 110.45 (d, $J_{P,C}$ = 7.5 Hz), 120.21 (d, $J_{P,C}$ = 123.0 Hz), 120.46 (d, $J_{P,C}$ = 11.5 Hz), 128.43 (d, $J_{P,C}$ = 13.8 Hz), 129.57 (d, $J_{P,C}$ = 136.2 Hz), 132.37 (d, $J_{P,C}$ = 10.3 Hz), 133.47 (d, $J_{P,C}$ = 2.3 Hz), 135.73 (d, $J_{P,C}$ = 6.9 Hz), 141.33 (d, $J_{P,C}$ = 2.9 Hz), 160.18 (d, $J_{P,C}$ = 2.9 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 29.14 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 18.77 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 317 (3) [M], 246 (13), 245 (33), 215 (5), 213 (22), 166 (5), 165 (7), 141 (6), 106 (8), 105 (40), 91 (12), 77 (6), 72 (100), 65 (6), 47 (5). $C_{18}H_{24}NO_2P$ (317.15): calcd. C 68.12, H 7.62, N 4.41; found C 68.10, H 7.81, N 4.32.

(2-Methyl-1-naphthyl)(*p*-tolyl)phosphinic Acid *N*,*N*-Diethylamide (10f): This compound was prepared from 4-bromotoluene (0.369 mL, 3 mmol), 1-bromo-2-methylnaphthalene (0.663 g, 3 mmol), magnesium (0.144 g, 6 mmol), $(Et_2N)PCl_2$ (0.443 mL, 3 mmol) and H_2O_2 (10 mL), yield 0.379 g (36%). Yellow oil. R_F = 0.44 (EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.16 (t, $J_{H,H}$ = 7.1 Hz, 6 H), 2.36 (s, 3 H), 2.62 (d, $J_{P,H}$ = 1.9 Hz, 3 H), 3.12–3.28 (m, 4 H), 7.18–7.22 (m, 2 H), 7.26–7.29 (m, 1 H), 7.39–7.46 (m, 2 H), 7.64–7.70 (m, 2 H), 7.76–7.80 (m, 1 H), 7.83 (d, $J_{H,H}$ = 8.5 Hz, 1 H), 8.94–8.98 (m, 1 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.16 (d, $J_{P,C}$ = 3.6 Hz), 21.50, 24.37 (d, $J_{P,C}$ = 4.5 Hz), 39.78 (d, $J_{P,C}$ = 3.6 Hz), 124.99, 125.66 (d, $J_{P,C}$ = 120.8 Hz), 126.32, 127.21 (d, $J_{P,C}$ = 4.5 Hz), 128.43, 129.08 (d, $J_{P,C}$ = 12.7 Hz), 130.67 (d, $J_{P,C}$ = 13.6 Hz), 131.77 (d, $J_{P,C}$ = 10.0 Hz), 132.28 (d, $J_{P,C}$ = 119.0 Hz), 132.25 (d, $J_{P,C}$ = 2.7 Hz), 132.31 (d, $J_{P,C}$ = 10.0 Hz), 134.83 (d, $J_{P,C}$ = 10.0 Hz), 141.49 (d, $J_{P,C}$ = 2.7 Hz), 144.31 (d, $J_{P,C}$ = 10.0 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 33.58 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 21.87 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 351 (6) [M], 280 (7), 279 (26), 277 (8), 261 (6), 260 (11), 231 (5), 230 (6), 229 (5), 215 (8), 186 (6), 141 (9), 139 (7), 115 (15), 91 (6), 74 (57), 73 (5), 72 (100), 58 (8). $C_{22}H_{26}NOP$ (351.18): calcd. C 75.19, H 7.46, N 3.99; found C 75.36, H 7.70, N 4.09.

***o*-Anisyl(2-methyl-1-naphthyl)phosphinic Acid *N*,*N*-Diethylamide (10g):** This compound was prepared from 2-bromoanisole (0.374 mL, 3 mmol), 1-bromo-2-methylnaphthalene (0.663 g, 3 mmol), magnesium (0.144 g, 6 mmol), $(Et_2N)PCl_2$ (0.443 mL, 3 mmol) and H_2O_2 (10 mL), yield 0.474 g (43%). Light brown solid, m.p. 129.2–131.3 °C. R_F = 0.10 (EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.12 (t, $J_{H,H}$ = 7.0 Hz, 6 H), 2.61 (d, $J_{P,H}$ = 1.9 Hz, 3 H), 3.18–3.27 (m, 4 H), 3.37 (s, 3 H), 6.75–6.80 (m, 1 H), 7.02–7.07 (m, 1 H), 7.22–7.26 (m, 1 H), 7.29–7.37 (m, 2 H), 7.39–7.44 (m, 1 H), 7.71–7.75 (m, 1 H), 7.76–7.85 (m, 2 H), 8.69–8.74 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.11 (d, $J_{P,C}$ = 2.3 Hz), 23.47 (d, $J_{P,C}$ = 4.6 Hz), 39.75 (d, $J_{P,C}$ = 4.6 Hz), 55.14, 111.44 (d, $J_{P,C}$ = 6.9 Hz), 120.47 (d, $J_{P,C}$ = 12.1 Hz), 124.44 (d, $J_{P,C}$ = 123.0 Hz), 124.58, 125.67, 126.89 (d, $J_{P,C}$ = 125.9 Hz), 126.89 (d, $J_{P,C}$ = 4.6 Hz), 128.13 (d, $J_{P,C}$ = 1.2 Hz), 130.33 (d, $J_{P,C}$ = 13.8 Hz), 131.52 (d, $J_{P,C}$ = 3.5 Hz), 131.99 (d, $J_{P,C}$ = 9.8 Hz), 132.87 (d, $J_{P,C}$ = 6.9 Hz), 133.07 (d, $J_{P,C}$ = 2.3 Hz), 134.48 (d, $J_{P,C}$ = 10.9 Hz), 143.16 (d, $J_{P,C}$ = 9.8 Hz), 160.98 (d, $J_{P,C}$ = 3.5 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 29.90 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 22.06 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 338 (4), 337 (10), 336 (79), 295 (13), 292 (6), 278 (5), 275 (6), 266 (6), 265 (36), 264 (20), 263 (100), 262 (14), 247 (7), 233 (5), 231 (5), 217 (6), 216 (17), 215 (27), 202 (9), 187 (11), 156 (5), 155 (35), 154 (5), 153 (5), 142 (12), 141 (40), 140 (5), 139 (18), 137 (3), 133 (6), 115 (31), 91 (9), 77 (11), 74 (44), 73 (5), 72 (99), 58 (14), 56 (6), 47 (8), 44 (11), 42 (8), 29 (9), 28 (6). $C_{22}H_{26}NO_2P$ (367.17): calcd. C 71.92, H 7.13, N 3.81; found C 71.80, H 6.99, N 4.07.

(2-Methyl-1-naphthyl)(*o*-tolyl)phosphinic Acid *N*,*N*-Diethylamide (10h): This compound was prepared from 2-bromotoluene (0.361 mL, 3 mmol), 1-bromo-2-methylnaphthalene (0.663 g, 3 mmol), magnesium (0.144 g, 6 mmol), $(Et_2N)PCl_2$ (0.443 mL, 3 mmol) and H_2O_2 (10 mL), yield 0.348 g (33%). White solid, m.p. 125.6–126.6 °C. R_F = 0.18 (hexane/EtOAc 2:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.18 (t, $J_{H,H}$ = 7.1 Hz, 6 H), 2.22 (s, 3 H), 2.48 (br. s, 3 H), 3.23–3.37 (m, 4 H), 7.13–7.16 (m, 1 H), 7.24–7.29 (m, 2 H), 7.32–7.41 (m, 3 H), 7.63–7.68 (m, 1 H), 7.76–7.79 (m, 1 H), 7.84 (d, $J_{H,H}$ = 8.5 Hz, 1 H), 8.74 (d, $J_{H,H}$ = 8.5 Hz, 1 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.25 (d, $J_{P,C}$ = 1.8 Hz), 21.23 (d, $J_{P,C}$ = 4.5 Hz), 23.92 (d, $J_{P,C}$ = 5.5 Hz), 39.67 (d, $J_{P,C}$ = 4.5 Hz), 125.12 (d, $J_{P,C}$ = 51.8 Hz), 125.09 (d, $J_{P,C}$ = 10.0 Hz), 125.23, 126.31, 126.83 (d, $J_{P,C}$ = 4.5 Hz), 128.34, 130.25 (d, $J_{P,C}$ = 12.7 Hz), 130.69 (d, $J_{P,C}$ = 10.0 Hz), 130.95 (d, $J_{P,C}$ = 2.7 Hz), 131.79 (d, $J_{P,C}$ = 11.8 Hz), 132.14, 132.20 (d, $J_{P,C}$ = 2.7 Hz), 134.58 (d, $J_{P,C}$ = 10.0 Hz), 135.77 (d, $J_{P,C}$ = 126.2 Hz), 142.58 (d, $J_{P,C}$ = 10.9 Hz), 143.15 (d, $J_{P,C}$ = 9.1 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 34.65 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 20.82 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 351 (4) [M], 337 (8), 336 (38), 279 (16), 278 (7), 265 (18), 264 (7), 263 (36), 261 (5), 256 (9), 246 (6), 230 (7), 229 (8), 216 (10), 215 (16), 187 (8), 142 (6), 141 (16), 139 (10), 137 (5), 133 (6), 120 (6), 115 (22), 104 (5), 91 (12), 74 (67), 73 (5), 72 (100), 65 (6), 58 (10), 44 (8), 42 (5). $C_{22}H_{26}NOP$ (351.42): calcd. C 75.19, H 7.46, N 3.99; found C 75.25, H 7.55, N 4.12.

Preparation of Compounds 9a, 9c and 10b: The appropriate secondary phosphane oxide (5 mmol) in CH_2Cl_2 (15 mL) was placed under argon in a flame-dried Schlenk tube (25 mL) containing a magnetic stirrer. PCl_3 (0.655 mL, 7.5 mmol) was then added at room temp., and the mixture was allowed to stir for 1.5 h. The solution was then transferred from the reaction vessel to a carefully argon-flushed standard round-bottomed flask, and the solvents were evaporated to dryness. The residue was dissolved in CH_2Cl_2 again (20 mL), and a sample was taken to check the complete transformation of the substrate. Diethylamine (1.033 mL, 10 mmol) was then added, and the mixture was left for 2 h at room temperature. For compounds **9a** and **9c**, BH_3·THF (7.5 mL, 7.5 mmol) was next added, and the mixture was left overnight, whereas for compound **10b**, H_2O_2 (10 mL) was added, and the mixture was left overnight. After each reaction was complete, NH_4Cl solution (30 mL) was added, the organic phase was removed, and the aqueous phase was extracted with CH_2Cl_2 (3 × 25 mL). The collected organic phases were dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography either with hexane/EtOAc (6:1 v/v) for **9a** and **9c** or with $CHCl_3$/MeOH (15:1 v/v) for **10d** as eluents.

***tert*-Butylphenylphosphinous Acid–Borane *N,N*-Diethylamide (9a):** This compound was prepared from *t*BuPhP(O)H (0.910 g, 5 mmol), PCl_3 (0.655 mL, 7.5 mmol), Et_2NH (1.033 mL, 10 mmol) and BH_3·THF (7.5 mL, 7.5 mmol), yield 1.079 g (86%). Colourless liquid. R_F = 0.52 (hexane/EtOAc 6:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 0.41–1.15 (br. m, 3 H), 1.11 (t, $J_{H,H}$ = 6.9 Hz, 6 H), 1.35 (d, $J_{P,H}$ = 13.9 Hz, 9 H), 3.11–3.17 (m, 4 H), 7.40–7.46 (m, 3 H), 7.76–7.81 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.83 (d, $J_{P,C}$ = 1.8 Hz), 27.35 (d, $J_{P,C}$ = 2.7 Hz), 34.38 (d, $J_{P,C}$ = 35.4 Hz), 42.12 (d, $J_{P,C}$ = 1.8 Hz), 128.25 (d, $J_{P,C}$ = 10.0 Hz), 130.26 (d, $J_{P,C}$ = 1.8 Hz), 132.09 (d, $J_{P,C}$ = 9.1 Hz), 131.18 (d, $J_{P,C}$ = 55.4 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 84.11 (br. m) ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 8.50 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 237 (5) [M – BH_3], 181 (17), 180 (98), 166 (8), 110 (7), 109 (100), 107 (8), 83 (7). $C_{14}H_{27}BNP$ (251.16): calcd. C 66.95, H 10.84, N 5.58; found C 66.80, H 10.99, N 5.81.

***o*-Anisylphenylphosphinous Acid–Borane *N,N*-Diethylamide (9c):** This compound was prepared from *o*AnPhP(O)H (1.160 g, 5 mmol), PCl_3 (0.655 mL, 7.5 mmol), Et_2NH (1.033 mL, 10 mmol) and BH_3·THF (7.5 mL, 7.5 mmol), yield 1.174 g (78%). White solid, m.p. 72.0–74.2 °C. R_F = 0.27 (hexane/EtOAc 6:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 0.64–1.37 (br. m, 3 H), 0.96 (t, $J_{H,H}$ = 6.9 Hz, 6 H), 3.17–3.25 (m, 4 H), 3.61 (s, 3 H), 6.91–6.94 (m, 1 H), 7.04–7.08 (m, 1 H), 7.36–7.46 (m, 3 H), 7.47–7.52 (m, 1 H), 7.54–7.59 (m, 2 H), 7.63–7.68 (m, 1 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.01 (d, $J_{P,C}$ = 1.8 Hz), 41.39 (d, $J_{P,C}$ = 3.6 Hz), 55.13, 111.48 (d, $J_{P,C}$ = 4.5 Hz), 119.75 (d, $J_{P,C}$ = 57.2 Hz), 120.80 (d, $J_{P,C}$ = 10.0 Hz), 128.00 (d, $J_{P,C}$ = 10.9 Hz), 130.15 (d, $J_{P,C}$ = 1.8 Hz), 131.12 (d, $J_{P,C}$ = 10.0 Hz), 132.90 (d, $J_{P,C}$ = 69.9 Hz), 133.04 (d, $J_{P,C}$ = 1.8 Hz), 134.58 (d, $J_{P,C}$ = 10.0 Hz), 161.07 (d, $J_{P,C}$ = 2.7 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 65.61 (br. m) ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 12.32 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 288 (7), 287 (39) [M – BH_3], 258 (5), 244 (16), 216 (11), 215 (60), 199 (7), 196 (36), 183 (19), 167 (8), 166 (62), 165 (6), 152 (14), 139 (36), 138 (23), 137 (54), 121 (18), 109 (65), 108 (17), 107 (16), 95 (12), 91 (100), 83 (8). $C_{17}H_{25}BNOP$ (301.17): calcd. C 67.80, H 8.37, N 4.65; found C 67.97, H 8.55, N 4.72.

Benzylphenylphosphinic Acid *N,N*-Diethylamide (10b): This compound was prepared from BnPhP(O)H (1.080 g, 5 mmol), PCl_3 (0.655 mL, 7.5 mmol), Et_2NH (1.033 mL, 10 mmol) and H_2O_2 (10 mL), yield 1.119 g (78%). White solid, m.p. 97.4–99.2 °C. R_F = 0.56 ($CHCl_3$/MeOH 15:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.04 (t, $J_{H,H}$ = 7.3 Hz, 6 H), 2.99–3.15 (m, 4 H), 3.31–3.50 (m, 2 H), 7.10–7.22 (m, 5 H), 7.34–7.42 (m, 2 H), 7.42–7.48 (m, 1 H), 7.59–7.68 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.30 (d, $J_{P,C}$ = 3.6 Hz), 36.14 (d, $J_{P,C}$ = 85.4 Hz), 39.28 (d, $J_{P,C}$ = 2.7 Hz), 126.40 (d, $J_{P,C}$ = 2.7 Hz), 128.12 (d, $J_{P,C}$ = 7.3 Hz), 128.18 (d, $J_{P,C}$ = 1.8 Hz), 135.03 (d, $J_{P,C}$ = 5.5 Hz), 131.38 (d, $J_{P,C}$ = 2.7 Hz), 131.63 (d, $J_{P,C}$ = 9.1 Hz), 132.13 (d, $J_{P,C}$ = 10.0 Hz), 132.65 (d, $J_{P,C}$ = 105.4 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 35.35 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 14.10 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 287 (2) [M], 272 (4), 215 (4), 197 (12), 196 (100), 168 (6), 140 (12), 125 (9), 120 (6), 92 (6), 91 (67). $C_{17}H_{22}NOP$ (287.34): calcd. C 71.06, H 7.72, N 4.87; found C 71.30, H 7.93, N 4.88.

Preparation of Compounds 10a and 10c: Phosphinic acid chloride (5 mmol) was placed in CH_2Cl_2 (20 mL) in a flame-dried two-necked round-bottomed flask (100 mL) containing a magnetic stirrer and fitted with an argon inlet. Diethylamine (1.033 mL, 10 mL) was then added dropwise and the mixture was left overnight. After the reaction was complete, NH_4Cl solution (30 mL) was added, the organic phase was removed, and the aqueous phase was extracted with CH_2Cl_2 (3 × 25 mL). The collected organic phases were dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography with $CHCl_3$/MeOH (15:1 v/v) as eluent.

***tert*-Butylphenylphosphinic Acid *N,N*-Diethylamide (10a):** This compound was prepared from *t*BuPhP(O)Cl (1.083 g, 5 mmol), and Et_2NH (1.033 mL, 10 mmol), yield 1.126 g (89%). Yellow oil. R_F = 0.76 ($CHCl_3$/MeOH 15:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.09 (d, $J_{H,H}$ = 7.0 Hz, 6 H), 1.21 (d, $J_{P,H}$ = 14.5 Hz, 9 H), 3.12 (dq, $J_{H,H}$ = 6.9, $J_{P,H}$ = 9.3 Hz, 4 H), 7.39–7.50 (m, 3 H), 7.78–7.87 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.64 (d, $J_{P,C}$ = 3.7 Hz), 26.34, 34.03 (d, $J_{P,C}$ = 89.1 Hz), 39.55 (d, $J_{P,C}$ = 1.7 Hz), 127.96 (d, $J_{P,C}$ = 11.2 Hz), 131.14 (d, $J_{P,C}$ = 2.9 Hz), 131.53 (d, $J_{P,C}$ = 113.8 Hz), 132.64 (d, $J_{P,C}$ = 8.6 Hz) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 47.21 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 10.97 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 253 (2) [M], 238 (3), 197 (15), 196 (100), 168 (6), 154 (5), 140 (11), 125 (34), 120 (12), 106 (16). $C_{14}H_{24}NOP$ (253.32): calcd. C 66.38, H 9.55, N 5.53; found C 66.59, H 9.83, N 5.80. This compound had been prepared earlier, and the analytical data are in accordance with those reported in the literature.[20]

Methylphenylphosphinic Acid *N,N*-Diethylamide (10c): This compound was prepared from MePhP(O)Cl (0.873 g, 5 mmol), and Et_2NH (1.033 mL, 10 mmol), yield 1.013 g (96%). Pale yellow oil. R_F = 0.52 ($CHCl_3$/MeOH 15:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.09 (t, $J_{H,H}$ = 7.3 Hz, 6 H), 1.69 (d, $J_{P,H}$ = 13.6 Hz, 3 H), 2.97–3.12 (m, 4 H), 7.40–7.52 (m, 3 H), 7.72–7.78 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.46 (d, $J_{P,C}$ = 3.6 Hz), 15.92 (d, $J_{P,C}$ = 93.6 Hz), 39.24 (d, $J_{P,C}$ = 3.6 Hz), 128.35 (d, $J_{P,C}$ = 11.8 Hz), 131.22 (d, $J_{P,C}$ = 10.0 Hz), 131.37 (d, $J_{P,C}$ = 2.7 Hz), 133.92 (d, $J_{P,C}$ = 126.3 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 35.69 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 10.42 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 211 (1) [M], 196 (18), 140 (12), 139 (100), 125 (8), 91 (8). $C_{11}H_{28}NOP$ (211.24): calcd. C 62.54, H 8.59, N 6.63; found C 62.50, H 8.43, N 6.88.

General Procedure for the Treatment of Organophosphorus Compounds Under Birch Reduction Conditions: Gaseous ammonia was passed through a flame-dried three-necked 100 mL round-bottomed flask, cooled with an acetone/dry ice bath, containing a magnetic stirrer and fitted with inert gas inlet and coldfinger containing a dry ice/acetone mixture until 15 mL of it was condensed. Sodium (0.029 g, 1.25 mmol) was then added, and the mixture was allowed to stir at –78 °C for 15 min. Once all the sodium had dissolved, a solution of the appropriate organophosphorus compound (0.5 mmol) in THF (5 mL) was added in one portion, and the mixture was allowed to stir at –78 °C for 5 min. The reaction was quenched by addition of solid NH_4Cl (0.5 g), ammonia was removed from the reaction mixture with the aid of a water pump, the residue was filtered, the solids were washed with CH_2Cl_2 (2 × 10 mL), and the filtrate was concentrated by rotary evaporator. The residue was purified by flash column chromatography with either hexane/EtOAc (6:1) or $CHCl_3$/MeOH (15:1) as eluents.

(Cyclohexa-1,4-dien-3-yl)phosphonous Acid–Borane Bis(*N,N*-diethylamide) (12a): This compound was prepared from **7a** (0.136 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol), yield 0.119 g (87%). Colourless oil. R_F = 0.75 (hexane/EtOAc 6:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 0.15–1.08 (br. m, 3 H), 1.11 (t, $J_{H,H}$ = 7.1 Hz, 12 H), 2.67–2.88 (m, 2 H), 3.05–3.17 (m, 8 H), 3.62–3.74 (m, 1 H), 5.63–5.70 (m, 2 H), 5.85–5.91 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.83 (d, $J_{P,C}$ = 2.7 Hz), 26.35 (d, $J_{P,C}$ = 5.5 Hz), 35.97

(d, $J_{P,C}$ = 53.6 Hz), 39.91 (d, $J_{P,C}$ = 1.8 Hz), 121.91 (d, $J_{P,C}$ = 2.7 Hz), 126.90 (d, $J_{P,C}$ = 10.0 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 94.25 (br. m) ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 11.26 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 176 (6), 175 (62), 105 (6), 104 (100), 103 (8). $C_{14}H_{30}BN_2P$ (268.19): calcd. C 62.70, H 11.28, N 10.45; found C 62.51, H 11.50, N 10.49.

(2-Methyl-1,4-dihydronaphth-1-yl)phosphonous Acid–Borane Bis(*N*,*N*-diethylamide) (12b): This compound was obtained by the General Procedure from **7b** (0.165 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol) as a mixture with **14**, yield 45% (based on NMR analysis). Colourless oil. R_F = 0.63 (hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.16–0.96 (br. m, 3 H), 0.88 (t, $J_{H,H}$ = 6.9 Hz, 6 H), 1.10 (t, $J_{H,H}$ = 6.9 Hz, 6 H), 1.96–1.99 (m, 3 H), 2.90–3.02 (m, 4 H), 3.12–3.21 (m, 4 H), 3.22–3.30 (m, 1 H), 3.68–3.80 (m, 1 H), 4.25–4.33 (m, 1 H), 5.84–5.88 (m, 1 H), 7.10–7.18 (m, 4 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.87 (d, $J_{P,C}$ = 2.7 Hz), 14.10 (d, $J_{P,C}$ = 2.7 Hz), 31.95 (d, $J_{P,C}$ = 4.5 Hz), 41.43 (d, $J_{P,C}$ = 6.4 Hz), 47.70 (d, $J_{P,C}$ = 44.5 Hz), 124.38 (d, $J_{P,C}$ = 9.1 Hz), 125.12 (d, $J_{P,C}$ = 2.7 Hz), 126.24 (d, $J_{P,C}$ = 2.7 Hz), 127.91 (d, $J_{P,C}$ = 2.7 Hz), 129.40 (d, $J_{P,C}$ = 2.7 Hz), 132.05 (d, $J_{P,C}$ = 1.8 Hz), 133.81 (d, $J_{P,C}$ = 1.8 Hz), 136.85 (d, $J_{P,C}$ = 4.5 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 99.38 (br. m) ppm.

(1,4-Dihydronaphth-1-yl)phosphonous Acid–Borane Bis(*N*,*N*-diethylamide) (12c): This compound was obtained by the General Procedure from **7c** (0.153 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol) as a mixture with **12c′**, yield 74% (based on NMR analysis). R_F = 0.56 (hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.11 to 0.67 (br. m, 3 H), 1.03 (t, $J_{H,H}$ = 6.9 Hz, 6 H), 1.13 (t, $J_{H,H}$ = 6.9 Hz, 6 H), 3.02–3.26 (m, 8 H), 3.26–3.35 (m, 1 H), 3.71–3.83 (m, 1 H), 4.31–4.40 (m, 1 H), 5.78–5.84 (m, 1 H), 6.10–6.16 (m, 1 H), 7.04–7.09 (m, 1 H), 7.10–7.17 (m, 2 H), 7.17–7.22 (m, 1 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.01 (d, $J_{P,C}$ = 2.7 Hz), 14.06 (d, $J_{P,C}$ = 2.7 Hz), 31.29 (d, $J_{P,C}$ = 4.5 Hz), 39.95 (d, $J_{P,C}$ = 50.0 Hz), 40.73, 41.17, 122.38 (d, $J_{P,C}$ = 3.6 Hz), 125.06 (d, $J_{P,C}$ = 2.7 Hz), 126.45 (d, $J_{P,C}$ = 3.6 Hz), 128.15 (d, $J_{P,C}$ = 2.7 Hz), 128.62 (d, $J_{P,C}$ = 9.1 Hz), 129.00 (d, $J_{P,C}$ = 3.6 Hz), 131.98, 136.84 (d, $J_{P,C}$ = 4.5 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 98.04 (br. m) ppm.

(3,4-Dihydronaphth-1-yl)phosphonous Acid–Borane Bis(*N*,*N*-diethylamide) (12c′): This compound was obtained by the General Procedure from **7c** (0.153 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol) as a mixture with **12c**, yield 9% (based on NMR analysis). R_F = 0.56 (hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.11 to 0.67 (br. m, 3 H), 1.07 (t, $J_{H,H}$ = 6.9 Hz, 12 H), 2.36–2.42 (m, 2 H), 2.73–2.77 (m, 2 H), 3.02–3.23 (m, 8 H), 6.66 (dt, $J_{H,H}$ = 4.7, $J_{P,H}$ = 16.1 Hz, 1 H), 7.13–7.22 (m, 3 H), 7.89–7.91 (m, 1 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, some arene signals could not be assigned, due to overlapping with the signals of the major compound): δ = 13.95 (d, $J_{P,C}$ = 2.7 Hz), 24.55 (d, $J_{P,C}$ = 10.0 Hz), 27.93 (d, $J_{P,C}$ = 1.8 Hz), 40.66 (d, $J_{P,C}$ = 2.7 Hz), 126.07, 137.12 (d, $J_{P,C}$ = 6.4 Hz), 141.60 (d, $J_{P,C}$ = 7.3 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 87.70 (br. m) ppm.

(*trans*-2,4,6-Trimethylcyclohexa-1,4-dien-3-yl)phosphonous Acid–Borane Bis(*N*,*N*-diethylamide) (12d): This compound was prepared from **7d** (0.154 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol), yield 0.107 g (69%). Colourless oil. R_F = 0.71 (hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.26–0.98 (m, 3 H), 1.07 (d, $J_{H,H}$ = 7.6 Hz, 3 H), 1.11 (t, $J_{H,H}$ = 6.9 Hz, 12 H), 1.85–1.88 (m, 6 H), 2.82–2.94 (m, 1 H), 3.07–3.21 (m, 8 H), 3.44–3.50 (m, 1 H), 5.43–5.46 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.15 (d, $J_{P,C}$ = 2.7 Hz), 21.62 (d, $J_{P,C}$ = 6.4 Hz), 24.12, 31.94 (d, $J_{P,C}$ = 5.5 Hz), 41.57 (d, $J_{P,C}$ = 1.8 Hz), 48.91 (d, $J_{P,C}$ = 47.2 Hz), 130.64 (d, $J_{P,C}$ = 8.2 Hz), 130.93 (d, $J_{P,C}$ = 4.5 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 98.17 (br. m) ppm. $C_{17}H_{36}BN_2P$ (310.27): calcd. C 65.81, H 11.70, N 9.03; found C 65.99, H 11.87, N 9.29.

2-Methylcyclohexa-1,4-dien-3-ylphosphonous Acid–Borane Bis(*N*,*N*-diethylamide) (12e): This compound was prepared from **7e** (0.140 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol), yield 0.123 g (87%). Colourless oil. R_F = 0.70 (hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.16–0.86 (br. m, 3 H), 1.10 (t, $J_{H,H}$ = 6.9 Hz, 6 H), 1.11 (t, $J_{H,H}$ = 6.9 Hz, 6 H), 1.83 (br. s, 3 H), 2.58–2.71 (m, 1 H), 2.76–2.91 (m, 1 H), 3.08–3.25 (m, 8 H), 3.63–3.72 (m, 1 H), 5.52–5.58 (m, 1 H), 5.59–5.63 (m, 1 H), 5.87–5.93 (m, 1 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.82 (d, $J_{P,C}$ = 2.7 Hz), 13.96 (d, $J_{P,C}$ = 1.8 Hz), 24.08, 27.40 (d, $J_{P,C}$ = 5.5 Hz), 40.43 (d, $J_{P,C}$ = 51.8 Hz), 40.68, 40.87, 122.87 (d, $J_{P,C}$ = 3.6 Hz), 123.78 (d, $J_{P,C}$ = 9.1 Hz), 127.65 (d, $J_{P,C}$ = 9.1 Hz), 129.8 ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 94.77 (br. m) ppm. $C_{15}H_{32}BN_2P$ (282.21): calcd. C 63.84, H 11.43, N 9.93; found C 63.78, H 11.59, N 10.12.

2-Methoxycyclohexa-1,4-dien-3-ylphosphonous Acid–Borane Bis(*N*,*N*-diethylamide) (12f): This compound was prepared from **7f** (0.148 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol), yield 0.112 g (75%). Colourless oil. R_F = 0.48 (hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.10–0.84 (br. m, 3 H), 1.06 (t, $J_{H,H}$ = 6.9 Hz, 6 H), 1.10 (t, $J_{H,H}$ = 6.9 Hz, 6 H), 2.70–2.81 (m, 1 H), 2.91–3.00 (m, 1 H), 3.04–3.20 (m, 8 H), 3.51 (s, 3 H), 3.71–3.80 (m, 1 H), 4.75–3.79 (m, 1 H), 5.51–5.56 (m, 1 H), 5.86–5.91 (m, 1 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.92 (d, $J_{P,C}$ = 2.7 Hz), 14.09 (d, $J_{P,C}$ = 2.7 Hz), 26.66 (d, $J_{P,C}$ = 5.5 Hz), 38.50 (d, $J_{P,C}$ = 50.0 Hz), 40.41, 40.95 (d, $J_{P,C}$ = 2.7 Hz), 53.90, 93.96 (d, $J_{P,C}$ = 7.3 Hz), 121.92 (d, $J_{P,C}$ = 2.7 Hz), 128.06 (d, $J_{P,C}$ = 9.1 Hz), 151.39 (d, $J_{P,C}$ = 3.6 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 94.42 (br. m) ppm. $C_{15}H_{32}BN_2OP$ (298.21): calcd. C 60.41, H 10.82, N 9.39; found C 60.70, H 10.55, N 9.66.

(6-Methylcyclohexa-1,4-dien-3-yl)phosphonous Acid–Borane Bis(*N*,*N*-diethylamide) (12g): This compound was prepared from **7g** (0.140 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol), yield 0.127 g (90%). Isolated as a mixture of *trans* and *cis* compounds (1.48:1).

***trans* Isomer:** R_F = 0.70 (hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.12–0.84 (br. m, 3 H), 1.09 (t, $J_{H,H}$ = 6.9 Hz, 12 H), 1.15 (d, $J_{H,H}$ = 7.3 Hz, 3 H), 2.77–2.87 (m, 1 H), 3.04–3.18 (m, 8 H), 3.60–3.68 (m, 1 H), 5.56–5.65 (m, 2 H), 5.72–5.78 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.90 (d, $J_{P,C}$ = 1.8 Hz), 21.05 (d, $J_{P,C}$ = 11.8 Hz), 30.66 (d, $J_{P,C}$ = 4.5 Hz), 35.65 (d, $J_{P,C}$ = 54.5 Hz), 40.01 (d, $J_{P,C}$ = 1.8 Hz), 120.47 (d, $J_{P,C}$ = 1.8 Hz), 132.55 (d, $J_{P,C}$ = 10.9 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 92.04 (br. m) ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 11.45 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 281 (1), 176 (7), 175 (69), 125 (2), 105 (9), 104 (100), 103 (5), 90 (7).

***cis* Isomer:** R_F = 0.70 (hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.12–0.84 (br. m, 3 H), 1.09 (t, $J_{H,H}$ = 6.9 Hz, 12 H), 1.09 (d, $J_{H,H}$ = 7.3 Hz, 3 H), 2.85–2.93 (m, 1 H), 3.04–3.18 (m, 8 H), 3.55–3.64 (m, 1 H), 5.56–5.65 (m, 2 H), 5.72–5.78 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.88 (d, $J_{P,C}$ = 2.7 Hz), 21.80 (d, $J_{P,C}$ = 7.3 Hz), 30.47 (d, $J_{P,C}$ = 4.5 Hz), 36.37 (d, $J_{P,C}$ = 52.7 Hz), 39.98 (d, $J_{P,C}$ = 2.7 Hz), 120.66 (d, $J_{P,C}$ = 2.7 Hz), 133.13 (d, $J_{P,C}$ = 9.1 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 94.48 (br. m) ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 11.49 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 281 (1), 176 (7), 175 (72), 125 (2), 105 (7), 104 (100), 103 (7), 91 (5). $C_{15}H_{32}BN_2P$ (282.21): calcd. C 63.84, H 11.43, N 9.93; found C 63.99, H 11.70, N 10.01.

(Cyclohexa-1,4-dien-3-yl)phosphonic Acid Bis(*N*,*N*-diethylamide) (13a): This compound was prepared from **8a** (0.134 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol), yield 0.123 g (91%). Colourless oil. R_F = 0.58 ($CHCl_3$/MeOH 15:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.03 (t, $J_{H,H}$ = 7.2 Hz, 12 H), 2.61–2.72 (m, 2 H), 2.97–3.06 (m, 8 H), 3.40–3.54 (m, 1 H), 5.69–5.78 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.67 (d, $J_{P,C}$ = 2.9 Hz), 26.06 (d, $J_{P,C}$ = 5.8 Hz), 38.20 (d, $J_{P,C}$ = 2.9 Hz), 38.40 (d, $J_{P,C}$ = 114.1 Hz), 122.15 (d, $J_{P,C}$ = 7.8 Hz), 125.67 (d, $J_{P,C}$ = 10.9 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 32.90 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 11.75 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 192 (11), 191 (100), 163 (9), 135 (8), 120 (9), 118 (5), 107 (7), 104 (5). $C_{14}H_{27}N_2OP$ (270.35): calcd. C 62.20, H 10.07, N 10.36; found C 62.33, H 10.13, N 10.45.

2-Methoxycyclohexa-1,4-dien-3-ylphosphonic Acid Bis(*N*,*N*-diethylamide) (13b): This compound was obtained by the General Procedure from **8b** (0.149 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol) as a mixture with **15**, yield 60% (based on NMR analysis). R_F = 0.73 ($CHCl_3$/MeOH 15:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.05 (t, $J_{H,H}$ = 7.3 Hz, 6 H), 1.10 (t, $J_{H,H}$ = 7.3 Hz, 6 H), 2.78–2.88 (m, 2 H), 2.99–3.15 (m, 8 H), 3.52 (s, 3 H), 3.55–3.65 (m, 1 H), 4.68–4.71 (m, 1 H), 5.80–5.89 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.77 (d, $J_{P,C}$ = 3.6 Hz), 14.19 (d, $J_{P,C}$ = 2.7 Hz), 26.54 (d, $J_{P,C}$ = 5.5 Hz), 38.50 (d, $J_{P,C}$ = 3.6 Hz), 38.82 (d, $J_{P,C}$ = 3.6 Hz), 40.69 (d, $J_{P,C}$ = 109.0 Hz), 53.74, 92.91 (d, $J_{P,C}$ = 7.3 Hz), 122.87 (d, $J_{P,C}$ = 9.1 Hz), 125.87 (d, $J_{P,C}$ = 10.0 Hz), 151.18 (d, $J_{P,C}$ = 9.1 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 32.35 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 12.54 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 300 (0.1) [M], 192 (19), 191 (100), 163 (8), 135 (7), 120 (10), 109 (7), 108 (5), 107 (7), 94 (9). $C_{15}H_{29}N_2O_2P$ (300.38): calcd. C 59.98, H 9.73, N 9.33; found C 59.96, H 10.00, N 9.50.

(6-Methylcyclohexa-1,4-dien-3-yl)phosphonic Acid Bis(*N*,*N*-diethylamide) (13c): This compound was prepared from **8c** (0.141 g, 0.5 mmol) and sodium (0.058 g, 2.5 mmol), yield 0.084 g (69%). Isolated as a mixture of *trans* and *cis* compounds (51:49).

***trans* Isomer:** R_F = 0.60 ($CHCl_3$/MeOH 15:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.09 (t, $J_{H,H}$ = 6.9 Hz, 12 H), 1.10 (d, $J_{H,H}$ = 6.9 Hz, 3 H), 2.78–2.88 (m, 1 H), 3.03–3.11 (m, 8 H), 3.42–3.54 (m, 1 H), 5.66–5.72 (m, 2 H), 5.75–5.81 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.81 (d, $J_{P,C}$ = 2.7 Hz), 21.30 (d, $J_{P,C}$ = 10.9 Hz), 30.33 (d, $J_{P,C}$ = 5.5 Hz), 38.34 (d, $J_{P,C}$ = 2.7 Hz), 38.78 (d, $J_{P,C}$ = 118.1 Hz), 120.93 (d, $J_{P,C}$ = 8.2 Hz), 131.79 (d, $J_{P,C}$ = 11.8 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 33.34 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 11.74 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 192 (11), 191 (100), 163 (8), 135 (7), 120 (8), 118 (4), 107 (6), 91 (12).

***cis* Isomer:** R_F = 0.60 ($CHCl_3$/MeOH 15:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.10 (t, $J_{H,H}$ = 6.9 Hz, 12 H), 1.11 (d, $J_{H,H}$ = 6.9 Hz, 3 H), 2.74–2.82 (m, 1 H), 3.01–3.08 (m, 8 H), 3.42–3.54 (m, 1 H), 5.66–5.72 (m, 2 H), 5.75–5.81 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.90 (d, $J_{P,C}$ = 2.7 Hz), 21.99 (d, $J_{P,C}$ = 8.2 Hz), 30.40 (d, $J_{P,C}$ = 4.5 Hz), 38.41 (d, $J_{P,C}$ = 2.7 Hz), 38.73 (d, $J_{P,C}$ = 113.5 Hz), 120.97 (d, $J_{P,C}$ = 7.3 Hz), 132.05 (d, $J_{P,C}$ = 10.0 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 33.34 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 11.88 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 192 (11), 191 (100), 163 (7), 135 (6), 120 (7), 118 (4), 107 (6), 91 (12). $C_{15}H_{29}N_2OP$ (284.38): calcd. C 63.35, H 10.28, N 9.85; found C 63.51, H 10.50, N 9.77.

2-Methylcyclohexa-1,4-dien-3-ylphosphonic Acid Bis(*N*,*N*-Diethylamide) (13d): This compound was prepared from **8d** (0.141 g, 0.5 mmol) and sodium (0.058 g, 2.5 mmol), yield 0.085 g (60%). Colourless oil. R_F = 0.75 ($CHCl_3$/MeOH 15:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.07 (d, $J_{H,H}$ = 7.3 Hz, 6 H), 1.12 (t, $J_{H,H}$ = 7.3 Hz, 6 H), 1.98 (br. s, 3 H), 2.60–2.77 (m, 2 H), 3.01–3.14 (m, 8 H), 3.40–3.52 (m, 1 H), 5.51–5.55 (m, 1 H), 5.69–5.79 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.90 (d, $J_{P,C}$ = 2.7 Hz), 14.01 (d, $J_{P,C}$ = 2.7 Hz), 21.99, 27.21 (d, $J_{P,C}$ = 5.5 Hz), 38.56 (d, $J_{P,C}$ = 2.7 Hz), 38.82 (d, $J_{P,C}$ = 2.7 Hz), 43.63 (d, $J_{P,C}$ = 111.7 Hz), 121.71 (d, $J_{P,C}$ = 10.0 Hz), 123.51 (d, $J_{P,C}$ = 8.2 Hz), 130.35 (d, $J_{P,C}$ = 11.8 Hz), 143.46 (d, $J_{P,C}$ = 10.0 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 32.83 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 11.34 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 282 (3), 254 (4), 245 (4), 239 (14), 211 (5), 210 (6), 183 (16), 182 (100), 154 (14), 138 (6), 137 (25), 136 (15), 112 (7), 109 (8), 92 (16), 91 (39). $C_{15}H_{29}N_2OP$ (284.38): calcd. C 63.35, H 10.28, N 9.85; found C 63.33, H 10.40, N 9.99.

(*trans*-2,4,6-Trimethylcyclohexa-1,4-dien-3-yl)phosphonic Acid Bis(*N*,*N*-diethylamide) (13f): This compound was prepared from **7d** (0.155 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol), yield 0.129 g (83%). Colourless oil. R_F = 0.64 ($CHCl_3$/MeOH 15:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.04 (d, $J_{H,H}$ = 7.3 Hz, 3 H), 1.11 (t, $J_{H,H}$ = 7.3 Hz, 12 H), 1.93 (br. s, 6 H), 2.69–2.81 (m, 1 H), 2.95–3.18 (m, 8 H), 3.22–3.36 (m, 1 H), 5.38–5.42 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.30 (d, $J_{P,C}$ = 2.7 Hz), 21.18, 21.91 (d, $J_{P,C}$ = 7.3 Hz), 31.59 (d, $J_{P,C}$ = 6.4 Hz), 39.80 (d, $J_{P,C}$ = 2.7 Hz), 47.16 (d, $J_{P,C}$ = 109.0 Hz), 130.04 (d, $J_{P,C}$ = 10.0 Hz), 130.37 (d, $J_{P,C}$ = 9.1 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 33.64 ppm. $C_{17}H_{33}N_2OP$ (312.43): calcd. C 65.35, H 10.65, N 8.97; found C 65.48, H 10.90, N 8.70.

Phosphonous Acid–Borane Bis(*N*,*N*-diethylamide) (14): This compound was obtained by the General Procedure as a mixture with **12b** or **7d**. R_F = 0.71 (hexane/EtOAc 6:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 0.26–0.98 (m, 3 H), 1.07 (t, $J_{H,H}$ = 6.9 Hz, 12 H), 2.98–3.15 (m, 8 H), 6.42 (dm, $J_{P,H}$ = 429.4 Hz, 1 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.20 (d, $J_{P,C}$ = 1.8 Hz), 41.56 ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 78.02 (br. m) ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 4.11 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 176 (11) [M – BH_3], 161 (3), 105 (6), 104 (100), 103 (11), 90 (5).

Phosphonic Acid Bis(*N*,*N*-diethylamide) (15): This compound was obtained by the General Procedure as a mixture with **13b**, yield 13% (based on NMR analysis). R_F = 0.73 ($CHCl_3$/MeOH 15:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.10 (t, $J_{H,H}$ = 6.9 Hz, 12 H), 2.98–3.18 (m, 8 H), 6.75 (d, $J_{P,H}$ = 570.9 Hz, 1 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.21 (d, $J_{P,C}$ = 2.7 Hz), 37.68 (d, $J_{P,C}$ = 6.4 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 20.40 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 9.29 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 192 (12), 191 (100) [M], 177 (8), 163 (10), 161 (7), 147 (7), 135 (9), 120 (13), 118 (10), 107 (11), 104 (7), 92 (6).

(3,4-Dihydronaphth-2-yl)phosphonous Acid–Borane Bis(*N*,*N*-diethylamide) (16): This compound was obtained by the General Procedure from **7h** (0.158 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol) as a mixture with **17** and **18**, yield 40% (based on NMR analysis). R_F = 0.63 (hexane/EtOAc 6:1). ^1H NMR (500 MHz, $CDCl_3$): δ = 0.21–1.05 (br. m, 3 H), 1.13 (t, $J_{H,H}$ = 7.3 Hz, 12 H), 3.08–3.19 (m, 8 H), 3.45–3.49 (m, 2 H), 3.52–3.57 (m, 2 H), 6.53–6.60 (m, 1 H), 7.15–7.22 (m, 4 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.05 (d, $J_{P,C}$ = 2.7 Hz), 30.62 (d, $J_{P,C}$ = 11.8 Hz), 31.85 (d, $J_{P,C}$ = 10.9 Hz), 40.14 (d, $J_{P,C}$ = 2.7 Hz), 126.14, 126.25, 127.70, 128.01, 131.29 (d, $J_{P,C}$ = 79.9 Hz), 133.44 (d, $J_{P,C}$ = 2.7 Hz), 134.43, 136.65 (d, $J_{P,C}$ = 8.2 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 90.13 (br. m) ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 12.64 min. GC–MS (EI, 70 eV): *m*/*z* (%) =

304 (20) [M – BH_3], 233 (17), 232 (62), 231 (12), 202 (7), 175 (14), 162 (6), 161 (49), 160 (13), 159 (80), 157 (15), 133 (42), 129 (19), 128 (57), 127 (7), 115 (24), 104 (100), 103 (9), 102 (10), 91 (6), 90 (8).

(1,2-Dihydronaphth-2-yl)phosphonous Acid–Borane Bis(*N*,*N*-diethylamide) (17): This compound was obtained by the General Procedure from **7h** (0.158 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol) as a mixture with **16** and **18**, yield 30% (based on NMR analysis). R_F = 0.63 (hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.21–1.05 (br. m, 3 H), 1.16 (t, $J_{H,H}$ = 6.9 Hz, 6 H), 1.18 (t, $J_{H,H}$ = 6.9 Hz, 6 H), 2.70–2.77 (m, 1 H), 3.08–3.27 (m, 9 H), 3.31–3.41 (m, 1 H), 5.89–5.95 (m, 1 H), 6.60–6.65 (m, 1 H), 7.06–7.09 (m, 1 H), 7.12–7.16 (m, 1 H), 7.53–7.61 (m, 1 H), 7.90–7.93 (m, 1 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.94 (d, $J_{P,C}$ = 2.7 Hz), 14.09 (d, $J_{P,C}$ = 2.7 Hz), 28.78 (d, $J_{P,C}$ = 3.6 Hz), 30.66 (d, $J_{P,C}$ = 63.6 Hz), 40.20 (d, $J_{P,C}$ = 3.6 Hz), 40.27 (d, $J_{P,C}$ = 3.6 Hz), 125.71 (d, $J_{P,C}$ = 17.3 Hz), 126.06, 126.74, 127.44, 128.87 (d, $J_{P,C}$ = 9.1 Hz), 129.38 (d, $J_{P,C}$ = 10.9 Hz), 134.26 (d, $J_{P,C}$ = 1.8 Hz), 134.55 ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 93.76 (br. m) ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 12.09 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 304 (2) [M – BH_3], 303 (3), 302 (15), 232 (7), 231 (11), 230 (56), 161 (19), 160 (10), 159 (100), 157 (13), 141 (6), 133 (43), 128 (12), 115 (17), 104 (24).

(1,4-Dihydronaphth-2-yl)phosphonous Acid–Borane Bis(*N*,*N*-diethylamide) (18): This compound was obtained by the General Procedure from **7h** (0.158 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol) as a mixture with **16** and **17**, yield 16% (based on NMR analysis). R_F = 0.63 (hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.21–1.05 (br. m, 3 H), 1.13 (t, $J_{H,H}$ = 6.9 Hz, 12 H), 3.08–3.27 (m, 10 H), 3.42–3.45 (m, 2 H), 5.93–5.97 (m, 1 H), 7.38–7.44 (m, 1 H), 7.67–7.73 (m, 1 H), 7.87–7.90 (m, 1 H), 8.15–8.20 (m, 1 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.86 (d, $J_{P,C}$ = 2.7 Hz), 24.27 (d, $J_{P,C}$ = 3.6 Hz), 29.79 (d, $J_{P,C}$ = 10.0 Hz), 39.75 (d, $J_{P,C}$ = 2.7 Hz), 124.54 (d, $J_{P,C}$ = 40.0 Hz), 127.43 (d, $J_{P,C}$ = 10.9 Hz), 127.67, 130.74 (d, $J_{P,C}$ = 85.4 Hz), 131.99 (d, $J_{P,C}$ = 10.9 Hz), 132.83 (d, $J_{P,C}$ = 10.9 Hz), 132.96 (d, $J_{P,C}$ = 10.9 Hz), 134.49 ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 90.60 (br. m) ppm.

(1,2,3,4-Tetrahydronaphth-2-yl)phosphonic Acid Bis(*N*,*N*-diethylamide) (19): This compound was obtained by the General Procedure from **8e** (0.159 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol) as a mixture with **20** and **21**, yield 40% (based on NMR analysis). R_F = 0.65 ($CHCl_3$/MeOH 15:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.08 (t, $J_{H,H}$ = 7.3 Hz, 6 H), 1.12 (t, $J_{H,H}$ = 7.3 Hz, 6 H), 1.78–1.89 (m, 1 H), 2.13–2.21 (m, 1 H), 2.22–2.33 (m, 1 H), 2.78–2.88 (m, 1 H), 2.88–2.96 (m, 2 H), 2.97–3.08 (m, 1 H), 3.06–3.22 (m, 8 H), 7.09–7.14 (m, 4 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.09 (d, $J_{P,C}$ = 1.8 Hz), 23.66 (d, $J_{P,C}$ = 3.6 Hz), 29.45 (d, $J_{P,C}$ = 13.6 Hz), 29.67 (d, $J_{P,C}$ = 1.8 Hz), 32.74 (d, $J_{P,C}$ = 119.0 Hz), 38.50 (d, $J_{P,C}$ = 3.6 Hz), 125.68, 125.81, 128.83, 128.95, 134.30 (d, $J_{P,C}$ = 1.8 Hz), 136.04 ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 38.64 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 14.75 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 322 (4) [M], 318 (11), 247 (15), 246 (50), 232 (4), 192 (42), 191 (77), 175 (6), 172 (6), 163 (7), 132 (6), 131 (54), 130 (38), 129 (43), 128 (57), 127 (32), 121 (10), 120 (100), 118 (13), 116 (15), 115 (21), 107 (7), 106 (26), 104 (10), 92 (8), 91 (37).

(1,2-Dihydronaphth-2-yl)phosphonic Acid Bis(*N*,*N*-diethylamide) (20): This compound was obtained by the General Procedure from **8e** (0.159 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol) as a mixture with **19** and **21**, yield 14% (based on NMR analysis). R_F = 0.65 ($CHCl_3$/MeOH 15:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.11 (t, $J_{H,H}$ = 7.3 Hz, 6 H), 1.16 (t, $J_{H,H}$ = 7.3 Hz, 6 H), 3.05–3.27 (m, 11 H), 5.95–6.01 (m, 1 H), 6.55–6.59 (m, 1 H), 7.18–7.20 (m, 4 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.75 (d, $J_{P,C}$ = 2.7 Hz), 14.03 (d, $J_{P,C}$ = 2.7 Hz), 31.31 (d, $J_{P,C}$ = 14.5 Hz), 33.87 (d, $J_{P,C}$ = 119.9 Hz), 38.11 (d, $J_{P,C}$ = 2.7 Hz), 38.73 (d, $J_{P,C}$ = 2.7 Hz), 125.10 (d, $J_{P,C}$ = 6.4 Hz), 126.26, 126.66, 127.77, 128.11, 129.54 (d, $J_{P,C}$ = 10.9 Hz), 133.12 (d, $J_{P,C}$ = 2.7 Hz), 135.97 ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 37.89 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 14.64 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 320 (14) [M], 250 (8), 249 (42), 248 (100), 247 (11), 234 (8), 177 (9), 172 (8), 130 (8), 129 (31), 128 (50), 127 (18), 120 (8), 106 (36).

(3,4-Dihydronaphth-2-yl)phosphonic Acid Bis(*N*,*N*-diethylamide) (21): This compound was obtained by the General Procedure from **8e** (0.159 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol) as a mixture with **19** and **20**, yield 18% (based on NMR analysis). R_F = 0.65 ($CHCl_3$/MeOH 15:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.16 (t, $J_{H,H}$ = 7.3 Hz, 12 H), 3.07–3.21 (m, 8 H), 3.50–3.56 (m, 4 H), 6.78–6.85 (m, 1 H), 7.14–7.18 (m, 4 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.66 (d, $J_{P,C}$ = 2.7 Hz), 27.77 (d, $J_{P,C}$ = 3.6 Hz), 30.40 (d, $J_{P,C}$ = 10.9 Hz), 38.34 (d, $J_{P,C}$ = 4.5 Hz), 126.03, 126.22, 127.49, 127.88, 130.65 (d, $J_{P,C}$ = 154.4 Hz), 133.13 (d, $J_{P,C}$ = 1.8 Hz), 133.94 (d, $J_{P,C}$ = 10.0 Hz), 138.15 (d, $J_{P,C}$ = 8.2 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 29.46 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 14.58 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 320 (23) [M], 319 (9), 248 (30), 247 (10), 246 (24), 163 (5), 130 (14), 129 (100), 128 (72), 127 (22), 120 (10), 106 (34).

***tert*-Butyl(cyclohexa-1,4-dien-3-yl)phosphinous Acid–Borane *N*,*N*-Diethylamide (23a):** This compound was prepared from **9a** (0.125 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol), yield 0.113 g (89%). Colourless oil. R_F = 0.57 (hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.12–0.82 (br. m, 3 H), 1.09 (t, $J_{H,H}$ = 6.9 Hz, 6 H), 1.25 (d, $J_{P,H}$ = 13.2 Hz, 9 H), 2.66–2.89 (m, 2 H), 3.09–3.26 (m, 4 H), 3.62–3.72 (m, 1 H), 5.76–5.82 (m, 1 H), 5.83–5.92 (m, 3 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.98, 26.41 (d, $J_{P,C}$ = 4.5 Hz), 21.18 (d, $J_{P,C}$ = 1.8 Hz), 35.12 (d, $J_{P,C}$ = 29.1 Hz), 35.96 (d, $J_{P,C}$ = 32.7 Hz), 41.57, 122.72 (d, $J_{P,C}$ = 2.7 Hz), 122.81 (d, $J_{P,C}$ = 6.4 Hz), 127.45 (d, $J_{P,C}$ = 9.1 Hz), 127.50 (d, $J_{P,C}$ = 7.3 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 90.90 (br. m) ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 8.73 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 161 (6), 160 (20), 105 (9), 104 (100), 90 (4). $C_{14}H_{29}BNP$ (253.17): calcd. C 66.42, H 11.55, N 5.53; found C 66.70, H 11.73, N 5.70.

(Cyclohexa-1,4-dien-3-yl)phenylphosphinous Acid–Borane *N*,*N*-Diethylamide (23b). This compound was prepared from **9b** (0.136 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol), yield 0.085 g (62%). Colourless oil. R_F = 0.47 (hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.37–1.16 (br. m, 3 H), 1.06 (t, $J_{H,H}$ = 7.1 Hz, 6 H), 2.73–2.81 (m, 2 H), 3.12–3.24 (m, 4 H), 3.78–3.87 (m, 1 H), 5.68–5.73 (m, 1 H), 5.79–5.94 (m, 3 H), 7.43–7.48 (m, 2 H), 7.58–7.64 (m, 1 H), 7.65–7.70 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.22, 26.44 (d, $J_{P,C}$ = 4.5 Hz), 37.27 (d, $J_{P,C}$ = 38.2 Hz), 41.32 (d, $J_{P,C}$ = 1.8 Hz), 121.54, 121.57 (d, $J_{P,C}$ = 3.6 Hz), $J_{P,C}$ (d, $J_{P,C}$ = 7.3 Hz), 127.43 (d, $J_{P,C}$ = 10.0 Hz), 128.57 (d, $J_{P,C}$ = 10.0 Hz), 130.53 (d, $J_{P,C}$ = 1.8 Hz), 131.04 (d, $J_{P,C}$ = 9.1 Hz), 131.94 (d, $J_{P,C}$ = 56.3 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 72.82 (br. m) ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 11.13 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 260 (9), 259 (39) [M – BH_3], 216 (13), 187 (30), 166 (73), 159 (18), 155 (24), 141 (8), 133 (24), 129 (8), 128 (8), 111 (10), 110 (118), 109 (100), 108 (25), 107 (20), 103 (8), 91 (21), 83 (18). $C_{16}H_{25}BNP$ (273.16): calcd. C 70.35, H 9.22, N 5.13; found C 70.50, H 9.41, N 5.33.

***o*-Anisyl(cyclohexa-1,4-dien-3-yl)phosphinous Acid–Borane *N*,*N*-Diethylamide (23c):** This compound was prepared from **9c** (0.150 g,

0.5 mmol) and sodium (0.029 g, 1.25 mmol), yield 32% (based on NMR analysis). Isolated as a mixture with starting material and **26c**. R_F = 0.43 (hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.37–1.11 (br. m, 3 H), 1.08 (t, $J_{H,H}$ = 6.9 Hz, 6 H), 2.72–2.81 (m, 2 H), 3.16–3.25 (m, 4 H), 3.88 (s, 3 H), 4.15–4.25 (m, 1 H), 5.60–5.67 (m, 1 H), 5.73–5.78 (m, 1 H), 5.80–5.89 (m, 2 H), 6.93–6.97 (m, 1 H), 7.02–7.07 (m, 1 H), 7.43–7.46 (m, 1 H), 7.62–7.66 (m, 1 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.36 (d, $J_{P,C}$ = 1.8 Hz), 26.53 (d, $J_{P,C}$ = 5.5 Hz), 37.80 (d, $J_{P,C}$ = 40.9 Hz), 41.63 (d, $J_{P,C}$ = 1.8 Hz), 55.38, 111.17 (d, $J_{P,C}$ = 5.5 Hz), 120.07 (d, $J_{P,C}$ = 49.1 Hz), 121.08 (d, $J_{P,C}$ = 10.0 Hz), 123.01 (d, $J_{P,C}$ = 7.3 Hz), 126.35 (d, $J_{P,C}$ = 8.2 Hz), 132.52 (d, $J_{P,C}$ = 1.8 Hz), 133.99 (d, $J_{P,C}$ = 8.2 Hz), 160.21 (d, $J_{P,C}$ = 4.5 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 75.33 (br. m) ppm.

(2-Methoxycyclohexa-1,4-dien-3-yl)phenylphosphinous Acid–Borane *N*,*N*-Diethylamide (23c′): This compound was prepared from **9c** (0.150 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol), yield 0.039 g (26%). Isolated as a mixture of two diastereomers in 66% *de* ratio. Colourless oil. R_F = 0.38 (hexane/EtOAc 6:1).

Major Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.34–1.09 (br. m, 3 H), 0.98 (t, $J_{H,H}$ = 7.3 Hz, 6 H), 2.80–2.88 (m, 1 H), 2.91–2.99 (m, 1 H), 3.05–3.18 (m, 4 H), 3.46 (s, 3 H), 3.91–3.99 (m, 1 H), 4.79–4.82 (m, 1 H), 5.60–5.65 (m, 1 H), 5.86–5.91 (m, 1 H), 7.38–7.46 (m, 3 H), 7.75–7.80 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.54 (d, $J_{P,C}$ = 1.8 Hz), 26.74 (d, $J_{P,C}$ = 4.5 Hz), 38.75 (d, $J_{P,C}$ = 32.7 Hz), 41.70 (d, $J_{P,C}$ = 2.7 Hz), 53.84, 94.06 (d, $J_{P,C}$ = 6.4 Hz), 121.48 (d, $J_{P,C}$ = 1.8 Hz), 128.08 (d, $J_{P,C}$ = 9.1 Hz), 128.46 (d, $J_{P,C}$ = 10.0 Hz), 130.34 (d, $J_{P,C}$ = 1.8 Hz), 131.38 (d, $J_{P,C}$ = 9.1 Hz), 132.77 (d, $J_{P,C}$ = 60.0 Hz), 151.11 (d, $J_{P,C}$ = 6.4 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 73.40 (br. m) ppm.

Minor Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.34–1.09 (br. m, 3 H), 1.07 (t, $J_{H,H}$ = 6.9 Hz, 6 H), 2.76–2.83 (m, 1 H), 2.97–3.05 (m, 1 H), 3.05–3.18 (m, 4 H), 3.33 (s, 3 H), 3.95–4.03 (m, 1 H), 4.74–4.77 (m, 1 H), 5.63–5.68 (m, 1 H), 5.91–5.97 (m, 1 H), 7.44–7.52 (m, 3 H), 7.78–7.84 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.23 (d, $J_{P,C}$ = 1.8 Hz), 26.71 (d, $J_{P,C}$ = 4.5 Hz), 38.94 (d, $J_{P,C}$ = 32.7 Hz), 41.55 (d, $J_{P,C}$ = 2.7 Hz), 53.76, 93.73 (d, $J_{P,C}$ = 6.4 Hz), 121.36 (d, $J_{P,C}$ = 4.5 Hz), 127.76 (d, $J_{P,C}$ = 10.0 Hz), 128.32 (d, $J_{P,C}$ = 9.1 Hz), 130.27 (d, $J_{P,C}$ = 2.7 Hz), 131.49 (d, $J_{P,C}$ = 9.1 Hz), 133.32 (d, $J_{P,C}$ = 57.2 Hz), 150.77 (d, $J_{P,C}$ = 3.6 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 74.61 (br. m) ppm. $C_{17}H_{27}BNOP$ (303.19): calcd. C 67.35, H 8.98, N 4.62; found C 67.59, H 9.15, N 4.60.

(2-Methoxycyclohexa-1,4-dien-3-yl)(*o*-tolyl)phosphinous Acid–Borane *N*,*N*-Diethylamide (23d): This compound was obtained by the General Procedure from **9d** (0.158 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol) as a mixture with **26d**, yield 41% (based on NMR analysis) as a mixture of two diastereomers in 54% *de* ratio. R_F = 0.58 (hexane/EtOAc 6:1).

Major Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.30–1.05 (br. m, 3 H), 0.96 (t, $J_{H,H}$ = 7.1 Hz, 6 H), 2.39 (s, 3 H), 2.74–2.87 (m, 1 H), 2.88–3.03 (m, 1 H), 3.04–3.18 (m, 4 H), 3.48 (s, 3 H), 3.90–4.00 (m, 1 H), 4.79–4.83 (m, 1 H), 5.56–5.62 (m, 1 H), 5.83–5.89 (m, 1 H), 7.23–7.28 (m, 2 H), 7.64–7.69 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.59 (d, $J_{P,C}$ = 1.8 Hz), 21.41, 26.75 (d, $J_{P,C}$ = 4.5 Hz), 38.65 (d, $J_{P,C}$ = 32.7 Hz), 41.70 (d, $J_{P,C}$ = 2.7 Hz), 53.88, 94.03 (d, $J_{P,C}$ = 6.4 Hz), 121.60 (d, $J_{P,C}$ = 1.8 Hz), 127.55 (d, $J_{P,C}$ = 65.4 Hz), 128.91 (d, $J_{P,C}$ = 10.0 Hz), 129.52, 131.47 (d, $J_{P,C}$ = 9.1 Hz), 140.65 (d, $J_{P,C}$ = 2.7 Hz), 151.22 (d, $J_{P,C}$ = 6.4 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 72.86 (br. m) ppm.

Minor Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.06–1.5 (br. m, 3 H), 0.97 (t, $J_{H,H}$ = 7.1 Hz, 6 H), 2.39 (s, 3 H), 2.74–2.87 (m, 1 H), 2.88–3.03 (m, 1 H), 3.04–3.18 (m, 4 H), 3.35 (s, 3 H), 3.90–4.00 (m, 1 H), 4.73–4.77 (m, 1 H), 5.62–5.68 (m, 1 H), 5.89–5.95 (m, 1 H), 7.23–7.28 (m, 2 H), 7.67–7.72 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.28 (d, $J_{P,C}$ = 1.8 Hz), 21.49, 26.73 (d, $J_{P,C}$ = 4.5 Hz), 39.09 (d, $J_{P,C}$ = 32.7 Hz), 41.55 (d, $J_{P,C}$ = 1.8 Hz), 52.80, 93.64 (d, $J_{P,C}$ = 6.4 Hz), 121.55 (d, $J_{P,C}$ = 4.5 Hz), 128.41 (d, $J_{P,C}$ = 10.0 Hz), 129.61, 131.56 (d, $J_{P,C}$ = 9.1 Hz), 140.50 (d, $J_{P,C}$ = 1.8 Hz), 150.97 (d, $J_{P,C}$ = 3.6 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 74.08 (br. m) ppm.

***o*-Anisyl-(2-methyl-1,4-dihydronaphth-1-yl)phosphinous Acid–Borane *N*,*N*-Diethylamide (23e):** This compound was obtained by the General Procedure from **9e** (0.183 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol) as a mixture with **26e** and starting material, yield 72% (based on NMR analysis) as a mixture of two diastereomers in 70% *de* ratio. R_F = 0.44 (hexane/EtOAc 6:1).

Major Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.23–1.02 (br. m, 3 H), 0.73 (t, $J_{H,H}$ = 6.9 Hz, 6 H), 1.45–1.48 (m, 3 H), 2.84–2.93 (m, 2 H), 3.17–3.27 (m, 3 H), 3.87–3.99 (m, 1 H), 4.02 (s, 3 H), 5.11–5.19 (m, 1 H), 5.78–5.84 (m, 1 H), 6.94–7.00 (m, 1 H), 7.05–7.10 (m, 1 H), 7.12–7.22 (m, 4 H), 7.49–7.53 (m, 1 H), 8.11–8.17 (m, 1 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.19 (d, $J_{P,C}$ = 1.8 Hz), 22.87, 32.31 (d, $J_{P,C}$ = 3.6 Hz), 42.85 (d, $J_{P,C}$ = 1.8 Hz), 46.52 (d, $J_{P,C}$ = 30.9 Hz), 54.82, 110.42 (d, $J_{P,C}$ = 3.6 Hz), 121.30 (d, $J_{P,C}$ = 11.8 Hz), 124.90 (d, $J_{P,C}$ = 2.7 Hz), 125.95 (d, $J_{P,C}$ = 10.0 Hz), 126.31 (d, $J_{P,C}$ = 2.7 Hz), 127.97 (d, $J_{P,C}$ = 2.7 Hz), 129.44 (d, $J_{P,C}$ = 3.6 Hz), 130.62, 133.22 (d, $J_{P,C}$ = 1.8 Hz), 133.40 (d, $J_{P,C}$ = 2.7 Hz), 136.49 (d, $J_{P,C}$ = 16.4 Hz), 137.81 (d, $J_{P,C}$ = 4.5 Hz), 160.68 (d, $J_{P,C}$ = 1.8 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 77.41 (br. m) ppm.

Minor Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.23–1.02 (br. m, 3 H), 0.96 (t, $J_{H,H}$ = 6.9 Hz, 6 H), 2.00–2.02 (m, 3 H), 3.08–3.17 (m, 3 H), 3.29–3.36 (m, 1 H), 3.41–3.49 (m, 2 H), 4.05 (s, 3 H), 5.08–5.15 (m, 1 H), 5.98–6.02 (m, 1 H), 6.91–6.95 (m, 1 H), 6.99–7.04 (m, 1 H), 7.12–7.22 (m, 4 H), 7.42–7.49 (m, 1 H), 7.81–7.86 (m, 1 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.91 (d, $J_{P,C}$ = 1.8 Hz), 24.07, 32.40 (d, $J_{P,C}$ = 3.6 Hz), 42.56 (d, $J_{P,C}$ = 1.8 Hz), 45.40 (d, $J_{P,C}$ = 34.5 Hz), 54.84, 110.16 (d, $J_{P,C}$ = 4.5 Hz), 121.47 (d, $J_{P,C}$ = 12.7 Hz), 124.59 (d, $J_{P,C}$ = 3.6 Hz), 125.79 (d, $J_{P,C}$ = 9.1 Hz), 126.05 (d, $J_{P,C}$ = 3.6 Hz), 128.00 (d, $J_{P,C}$ = 2.7 Hz), 131.22 (d, $J_{P,C}$ = 4.5 Hz), 130.45, 132.97 (d, $J_{P,C}$ = 1.8 Hz), 132.75 (d, $J_{P,C}$ = 2.7 Hz), 136.68 (d, $J_{P,C}$ = 14.5 Hz), 137.80 (d, $J_{P,C}$ = 4.5 Hz), 160.21 (d, $J_{P,C}$ = 1.8 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 79.59 (br. m) ppm.

***tert*-Butyl(cyclohexa-1,4-dien-3-yl)phosphinic Acid *N*,*N*-Diethylamide (24a):** This compound was prepared from **10a** (0.127 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol), yield 0.121 g (95%). Colourless oil. R_F = 0.79 ($CHCl_3$/MeOH 15:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.99 (d, $J_{H,H}$ = 7.1 Hz, 6 H), 1.12 (d, $J_{P,H}$ = 14.7 Hz, 9 H), 2.60–2.71 (m, 2 H), 2.96–3.12 (m, 4 H), 3.45–3.58 (m, 1 H), 5.71–5.84 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.05 (d, $J_{P,C}$ = 1.72 Hz), 25.59 (d, $J_{P,C}$ = 92.53 Hz), 25.85, 38.40 (d, $J_{P,C}$ = 3.16 Hz), 39.34 (d, $J_{P,C}$ = 104.31 Hz), 39.57 (d, $J_{P,C}$ = 3.74 Hz), 121.69 (d, $J_{P,C}$ = 7.47 Hz), 122.02 (d, $J_{P,C}$ = 6.32 Hz), 126.71 (d, $J_{P,C}$ = 8.91 Hz), 126.93 (d, $J_{P,C}$ = 8.91 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 51.43 ppm. $C_{14}H_{26}NOP$ (255.34): calcd. C 65.85, H 10.26, N 5.49; found C 65.80, H 10.50, N 5.66.

Benzyl(cyclohexa-1,4-dien-3-yl)phosphinic Acid *N*,*N*-Diethylamide (24b): This compound was prepared from **10b** (0.144 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol), yield 0.125 g (86%). White solid, m.p. 89.3–91.1 °C. R_F = 0.48 ($CHCl_3$/MeOH 15:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.90 (t, $J_{H,H}$ = 6.9 Hz, 6 H), 2.73–2.83 (m, 2 H), 2.98–3.08 (m, 4 H), 3.12–3.20 (m, 1 H), 3.25–3.33 (m, 1 H),

3.25–3.38 (m, 1 H), 5.77–5.93 (m, 4 H), 7.19–7.25 (m, 1 H), 7.27–7.32 (m, 2 H), 7.34–7.39 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.05 (d, $J_{P,C}$ = 1.8 Hz), 26.40 (d, $J_{P,C}$ = 5.5 Hz), 32.50 (d, $J_{P,C}$ = 76.3 Hz), 38.25 (d, $J_{P,C}$ = 1.8 Hz), 41.64 (d, $J_{P,C}$ = 80.8 Hz), 121.14 (d, $J_{P,C}$ = 7.3 Hz), 121.70 (d, $J_{P,C}$ = 7.3 Hz), 126.51 (d, $J_{P,C}$ = 2.7 Hz), 126.85 (d, $J_{P,C}$ = 10.0 Hz), 127.14 (d, $J_{P,C}$ = 10.0 Hz), 128.41 (d, $J_{P,C}$ = 2.7 Hz), 129.97 (d, $J_{P,C}$ = 5.5 Hz), 132.30 (d, $J_{P,C}$ = 8.2 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 43.10 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 14.34 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 211 (2), 210 (8), 196 (3), 120 (29), 92 (10), 91 (100). $C_{17}H_{24}NOP$ (289.35): calcd. C 70.57, H 8.36, N 4.84; found C 70.81, H 8.60, N 4.66.

(Cyclohexa-1,4-dien-3-yl)methylphosphinic Acid *N*,*N*-Diethylamide (24c): This compound was prepared from **10c** (0.106 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol), yield 0.096 g (90%). Colourless oil. R_F = 0.46 ($CHCl_3$/MeOH 15:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.10 (t, $J_{H,H}$ = 6.9 Hz, 6 H), 1.40 (d, $J_{P,H}$ = 12.6 Hz, 3 H), 2.59–2.82 (m, 2 H), 2.97–3.19 (m, 4 H), 3.23–3.37 (m, 1 H), 5.62–5.69 (m, 1 H), 5.78–5.89 (m, 3 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 9.51 (d, $J_{P,C}$ = 88.1 Hz), 14.68 (d, $J_{P,C}$ = 1.8 Hz), 26.24 (d, $J_{P,C}$ = 5.5 Hz), 30.09 (d, $J_{P,C}$ = 2.7 Hz), 41.48 (d, $J_{P,C}$ = 84.5 Hz), 121.83 (d, $J_{P,C}$ = 6.4 Hz), 122.39 (d, $J_{P,C}$ = 7.3 Hz), 126.38 (d, $J_{P,C}$ = 10.0 Hz), 126.81 (d, $J_{P,C}$ = 10.0 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 45.25 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 10.70 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 139 (5), 134 (100), 121 (4), 120 (72), 106 (19), 92 (6). $C_{11}H_{20}NOP$ (213.26): calcd. C 61.95, H 9.45, N 6.57; found C 62.12, H 9.70, N 6.67.

(Cyclohexa-1,4-dien-3-yl)phenylphosphinic Acid *N*,*N*-Diethylamide (24d): This compound was obtained by the General Procedure from **10d** (0.137 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol) as a mixture with **25d** and starting material, yield 30% (based on NMR analysis). R_F = 0.79 ($CHCl_3$/MeOH 15:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.12 (t, $J_{H,H}$ = 7.1 Hz, 6 H), 2.04–2.17 (m, 1 H), 2.42–2.57 (m, 1 H), 3.06–3.12 (m, 4 H), 3.64–3.77 (m, 1 H), 5.59–5.82 (m, 4 H), 7.38–7.46 (m, 3 H), 7.78–7.85 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.76 (d, $J_{P,C}$ = 3.6 Hz), 25.92 (d, $J_{P,C}$ = 6.4 Hz), 38.89 (d, $J_{P,C}$ = 1.8 Hz), 39.14 (d, $J_{P,C}$ = 89.0 Hz), 121.23 (d, $J_{P,C}$ = 6.4 Hz), 121.30 (d, $J_{P,C}$ = 7.3 Hz), 126.87 (d, $J_{P,C}$ = 10.9 Hz), 127.41 (d, $J_{P,C}$ = 10.0 Hz), 127.67 (d, $J_{P,C}$ = 11.8 Hz), 130.02 (d, $J_{P,C}$ = 121.7 Hz), 131.44 (d, $J_{P,C}$ = 2.7 Hz), 132.78 (d, $J_{P,C}$ = 7.3 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 36.61 ppm.

(2-Methoxycyclohexa-1,4-dien-3-yl)(*p*-tolyl)phosphinic Acid *N*,*N*-Diethylamide (24e): This compound was obtained by the General Procedure from **10e** (0.159 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol) as a mixture of two diastereomers (23% *de*) in a mixture with double Birch reduction product **25e** (a mixture of four isomers) and starting material, yield 17% (based on NMR analysis).

Major Diastereomer: R_F = 0.52 ($CHCl_3$/MeOH 15:1). ^{1}H NMR (500 MHz, $CDCl_3$, only selected signals are presented, due to overlapping of signals with the signals of other compounds): δ = 1.05 (t, $J_{H,H}$ = 7.3 Hz, 6 H), 2.40 (s, 3 H), 3.03–3.22 (m, 4 H), 3.45 (s, 3 H), 4.65–4.68 (m, 1 H), 7.18–7.24 (m, 2 H), 7.67–7.73 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, only selected signals are presented due to the overlapping of signals with the signals of other compounds): δ = 14.21 (d, $J_{P,C}$ = 3.6 Hz), 21.45, 26.42 (d, $J_{P,C}$ = 5.5 Hz), 39.03 (d, $J_{P,C}$ = 2.7 Hz), 41.89 (d, $J_{P,C}$ = 84.5 Hz), 54.02, 93.51 (d, $J_{P,C}$ = 7.3 Hz), 121.56 (d, $J_{P,C}$ = 8.2 Hz), 128.48 (d, $J_{P,C}$ = 11.8 Hz), 132.19 (d, $J_{P,C}$ = 9.1 Hz), 150.42 (d, $J_{P,C}$ = 9.1 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 36.18 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 14.68 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 226 (33), 212 (8), 211 (56), 210 (100), 196 (10), 182 (8), 168 (10), 155 (16), 154 (19), 139 (21), 136 (9), 120 (80), 110 (16), 109 (35), 108 (40), 107 (10), 106 (55), 105 (8), 94 (22), 93 (16), 92 (20), 91 (62).

Minor Diastereomer: R_F = 0.52 ($CHCl_3$/MeOH 15:1). ^{1}H NMR (500 MHz, $CDCl_3$, only selected signals are presented due to the overlapping of signals with the signals of other compounds): δ = 1.10 (t, $J_{H,H}$ = 6.9 Hz, 6 H), 2.39 (s, 3 H), 3.03–3.22 (m, 4 H), 3.49 (s, 3 H), 4.54–4.58 (m, 1 H), 7.14–7.18 (m, 2 H), 7.56–7.63 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, only selected signals are presented due to the overlapping of signals with the signals of other compounds): δ = 13.76 (d, $J_{P,C}$ = 3.6 Hz), 21.52, 25.88 (d, $J_{P,C}$ = 5.5 Hz), 39.17 (d, $J_{P,C}$ = 2.7 Hz), 41.55 (d, $J_{P,C}$ = 85.4 Hz), 53.88, 93.92 (d, $J_{P,C}$ = 8.2 Hz), 121.90 (d, $J_{P,C}$ = 7.3 Hz), 128.22 (d, $J_{P,C}$ = 12.7 Hz), 133.01 (d, $J_{P,C}$ = 8.2 Hz), 151.12 (d, $J_{P,C}$ = 8.2 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 37.08 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 14.95 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 212 (8), 211 (53), 210 (100), 196 (8), 192 (8), 168 (9), 154 (18), 139 (22), 136 (8), 120 (13), 109 (16), 108 (26), 107 (8), 106 (50), 105 (8), 94 (15), 93 (7), 92 (12), 91 (41).

(2-Methyl-1,4-dihydronaphth-1-yl)(*p*-tolyl)phosphinic Acid *N*,*N*-Diethylamide (24f): This compound was obtained by the General Procedure from **10f** (0.176 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol) as a mixture with starting material, yield 43% (a mixture of two diastereomers: 12% *de*, based on NMR analysis).

Major Diastereomer: R_F = 0.67 ($CHCl_3$/MeOH 15:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.13 (t, $J_{H,H}$ = 6.9 Hz, 6 H), 2.13 (br. s, 3 H), 2.33 (s, 3 H), 2.71–2.86 (m, 2 H), 3.12–3.27 (m, 4 H), 4.19–4.23 (m, 1 H), 5.59–5.64 (m, 1 H), 6.88–6.91 (m, 1 H), 6.95–7.03 (m, 3 H), 7.14–7.17 (m, 2 H), 7.25–7.29 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.65 (d, $J_{P,C}$ = 4.5 Hz), 21.49, 24.20, 30.44 (d, $J_{P,C}$ = 4.5 Hz), 39.27 (d, $J_{P,C}$ = 1.8 Hz), 47.60 (d, $J_{P,C}$ = 86.3 Hz), 125.17 (d, $J_{P,C}$ = 2.7 Hz), 125.67, 126.29 (d, $J_{P,C}$ = 3.6 Hz), 127.59 (d, $J_{P,C}$ = 3.6 Hz), 128.06 (d, $J_{P,C}$ = 11.8 Hz), 128.43 (d, $J_{P,C}$ = 3.6 Hz), 131.59 (d, $J_{P,C}$ = 7.3 Hz), 132.34 (d, $J_{P,C}$ = 5.5 Hz), 133.31 (d, $J_{P,C}$ = 8.2 Hz), 137.47 (d, $J_{P,C}$ = 5.5 Hz), 141.82 (d, $J_{P,C}$ = 2.7 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 38.14 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 15.91 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 212 (18), 211 (41), 210 (100), 196 (4), 182 (5), 168 (8), 154 (13), 143 (13), 142 (47), 141 (28), 139 (18), 128 (21), 120 (9), 115 (16), 106 (34), 91 (25).

Minor Diastereomer: R_F = 0.52 ($CHCl_3$/MeOH 15:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.98 (t, $J_{H,H}$ = 6.9 Hz, 6 H), 1.81 (br. s, 3 H), 2.39 (s, 3 H), 2.91–3.05 (m, 2 H), 2.98–3.08 (m, 4 H), 4.23–4.28 (m, 1 H), 5.74–5.79 (m, 1 H), 6.95–7.03 (m, 3 H), 7.11–7.17 (m, 3 H), 7.56–7.61 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.03 (d, $J_{P,C}$ = 3.6 Hz), 21.52, 23.65, 31.18 (d, $J_{P,C}$ = 4.5 Hz), 39.48 (d, $J_{P,C}$ = 1.8 Hz), 48.58 (d, $J_{P,C}$ = 82.7 Hz), 125.15 (d, $J_{P,C}$ = 2.7 Hz), 125.75, 126.20 (d, $J_{P,C}$ = 4.5 Hz), 127.34 (d, $J_{P,C}$ = 2.7 Hz), 128.45 (d, $J_{P,C}$ = 11.8 Hz), 129.73 (d, $J_{P,C}$ = 3.6 Hz), 130.66 (d, $J_{P,C}$ = 7.3 Hz), 132.41 (d, $J_{P,C}$ = 8.2 Hz), 133.51 (d, $J_{P,C}$ = 5.5 Hz), 136.70 (d, $J_{P,C}$ = 6.4 Hz), 141.87 (d, $J_{P,C}$ = 2.7 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 36.42 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 16.48 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 212 (18), 211 (41), 210 (100), 196 (4), 182 (5), 168 (8), 154 (13), 143 (13), 142 (47), 141 (28), 139 (18), 128 (21), 120 (9), 115 (16), 106 (34), 91 (25).

***o*-Anisyl(2-methyl-1,4-dihydronaphth-1-yl)phosphinic Acid *N*,*N*-Diethylamide (24g):** This compound was obtained by the General Procedure from **10g** (0.184 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol) as a mixture with **25g**, **27g** and starting material, yield 18% (based on NMR analysis). R_F = 0.81 ($CHCl_3$/MeOH 15:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84 (t, $J_{H,H}$ = 6.9 Hz, 6 H), 1.50

(br. s, 3 H), 2.73–2.99 (m, 4 H), 3.22–3.31 (m, 1 H), 3.81–3.92 (m, 1 H), 4.01 (s, 3 H), 4.51–4.56 (m, 1 H), 5.85–5.91 (m, 1 H), 6.95–6.99 (m, 1 H), 7.09–7.14 (m, 1 H), 7.16–7.23 (m, 4 H), 7.50–7.55 (m, 1 H), 8.02–8.08 (m, 1 H) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 36.47 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 17.09 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 228 (11), 227 (48), 226 (100), 196 (26), 184 (7), 156 (6), 155 (56), 143 (12), 142 (47), 141 (45), 139 (9), 128 (24), 120 (12), 115 (23), 108 (12), 107 (8), 106 (40), 91 (22), 86 (12).

(2-Methyl-1,4-dihydronaphth-1-yl)(*o*-tolyl)phosphinic Acid *N*,*N*-Diethylamide (24h): This compound was obtained by the General Procedure from **10h** (0.176 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol) as a mixture with three isomers of **25h** and other unidentified minor compounds, yield 18% (based on NMR analysis – the ^{1}H NMR spectrum of the mixture was too complicated to ascribe the signals to the structure). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 34.71 ppm.

Bis(cyclohexa-1,4-dien-3-yl)phosphinic Acid *N*,*N*-Diethylamide (25d): This compound was obtained by the General Procedure from **10d** (0.137 g, 0.5 mmol) and sodium (0.058 g, 2.5 mmol), yield 0.136 g (98%). Colourless oil. R_F = 0.79 ($CHCl_3$/MeOH 15:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.04 (t, $J_{H,H}$ = 7.3 Hz, 6 H), 2.69–2.81 (m, 4 H), 3.04–3.14 (m, 4 H), 3.48–3.60 (m, 2 H), 5.69–5.76 (m, 2 H), 5.76–5.82 (m, 2 H), 5.82–5.90 (m, 4 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.03 (d, $J_{P,C}$ = 1.8 Hz), 26.24 (d, $J_{P,C}$ = 5.5 Hz), 38.00 (d, $J_{P,C}$ = 1.8 Hz), 38.86 (d, $J_{P,C}$ = 77.2 Hz), 120.57 (d, $J_{P,C}$ = 8.2 Hz), 120.82 (d, $J_{P,C}$ = 7.3 Hz), 127.21 (d, $J_{P,C}$ = 10.0 Hz), 127.27 (d, $J_{P,C}$ = 10.0 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 41.79 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 13.99 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 277 (2) [M], 198 (3), 121 (13), 120 (100), 106 (5), 104 (6), 92 (4), 91 (3), 80 (18). $C_{16}H_{24}NOP$ (277.34): calcd. C 69.29, H 8.72, N 5.05; found C 69.51, H 9.00, N 5.01.

(2-Methoxycyclohexa-1,4-dien-3-yl)(6-methylcyclohexa-1,4-dien-3-yl)phosphinic Acid *N*,*N*-Diethylamide (25e): This compound was obtained by the General Procedure from **10e** (0.159 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol) as a mixture with single Birch reduction product **24e** (a mixture of two diastereomers), yield 13% (a mixture of four isomers; based on NMR analysis – the signals of the compounds in the ^{1}H NMR spectra were too overlapped with other signals and were not ascribed to the structure). ^{31}P NMR (202 MHz, $CDCl_3$): δ = 40.88, 42.71, 42.86, 42.98 ppm.

(2-Methoxycyclohexa-1,4-dien-3-yl)(2-methyl-1,4-dihydronaphth-1-yl)phosphinic Acid *N*,*N*-Diethylamide (25g): This compound was obtained by the General Procedure from **10g** (0.184 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol) as a mixture with **24g**, **27g** and starting material, yield 10% (a mixture of two diastereomers *de* = 45%, based on NMR analysis).

Major Diastereomer: R_F = 0.81 ($CHCl_3$/MeOH 15:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.04 (t, $J_{H,H}$ = 6.9 Hz, 3 H), 1.15 (t, $J_{H,H}$ = 6.9 Hz, 3 H), 2.07 (br. s, 3 H), 3.03–3.33 (m, 4 H), 3.21–3.39 (m, 1 H), 3.48 (s, 3 H), 3.56–3.72 (m, 1 H), 4.24–4.40 (m, 1 H), 4.79–4.82 (m, 1 H), 5.61–5.67 (m, 1 H), 5.76–5.81 (m, 1 H), 6.02–6.07 (m, 1 H), 7.22–7.30 (m, 4 H) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 46.03 ppm.

Minor Diastereomer: R_F = 0.81 ($CHCl_3$/MeOH 15:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.05 (t, $J_{H,H}$ = 6.9 Hz, 3 H), 1.13 (t, $J_{H,H}$ = 6.9 Hz, 3 H), 1.95 (br. s, 3 H), 3.03–3.33 (m, 4 H), 3.21–3.39 (m, 1 H), 3.56–3.72 (m, 1 H), 3.94 (s, 3 H), 4.18–4.23 (m, 1 H), 4.81–4.85 (m, 1 H), 5.61–5.67 (m, 1 H), 5.76–5.81 (m, 1 H), 6.05–6.10 (m, 1 H), 7.22–7.30 (m, 4 H) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 47.40 ppm.

(2-Methylcyclohexa-1,4-dien-3-yl)(2-methyl-1,4-dihydronaphth-1-yl)phosphinic Acid *N*,*N*-Diethylamide (25h): This compound was obtained by the General Procedure from **10h** (0.176 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol) as a mixture with **24h**, yield 60% (a mixture of three isomers; based on NMR analysis – the signals of the compounds in the ^{1}H NMR spectra were too overlapped with other signals and were not ascribed to the structure). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 40.40, 41.16, 43.67 ppm.

Phenylphosphinous Acid–Borane *N*,*N*-Diethylamide (26c): This compound was obtained by the General Procedure from **9c** (0.150 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol) as a mixture with **23c′** and **26c**, yield 3% (based on NMR analysis). R_F = 0.48 (hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.37–1.16 (br. m, 3 H), 1.07 (t, $J_{H,H}$ = 6.9 Hz, 6 H), 3.02–3.16 (m, 4 H), 6.61 (dm, $J_{P,H}$ = 388.1 Hz, 1 H), 7.44–7.53 (m, 5 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.88 (d, $J_{P,C}$ = 2.7 Hz), 42.42 (d, $J_{P,C}$ = 2.7 Hz), 128.80 (d, $J_{P,C}$ = 10.0 Hz), 130.41 (d, $J_{P,C}$ = 2.7 Hz), 130.95 (d, $J_{P,C}$ = 10.0 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 53.69 (br. m) ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 10.72 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 195 (28) [M], 181 (8), 120 (8), 119 (100), 105 (31), 91 (36).

***p*-Tolylphosphinous Acid–Borane *N*,*N*-Diethylamide (26d):** This compound was obtained by the General Procedure from **9d** (0.158 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol) as a mixture with **23d**, yield 12% (based on NMR analysis). R_F = 0.58 (hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.30–1.05 (br. m, 3 H), 1.06 (t, $J_{H,H}$ = 7.3 Hz, 6 H), 2.38 (s, 3 H), 2.98–3.14 (m, 4 H), 6.58 (dm, $J_{P,H}$ = 387.1 Hz, 1 H), 7.19–7.25 (m, 2 H), 7.47–7.53 (m, 2 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.88 (d, $J_{P,C}$ = 1.8 Hz), 22.66, 42.35 (d, $J_{P,C}$ = 2.7 Hz), 128.57 (d, $J_{P,C}$ = 10.0 Hz), 129.43, 129.80 (d, $J_{P,C}$ = 59.0 Hz), 131.07 (d, $J_{P,C}$ = 10.9 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 52.90 (br. m) ppm.

***o*-Anisylphosphinous Acid–Borane *N*,*N*-Diethylamide (26e):** This compound was obtained by the General Procedure from **9d** (0.183 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol) as a mixture with starting material and **23e**, yield 6% (based on NMR analysis). R_F = 0.44 (hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.23–1.02 (br. m, 3 H), 1.07 (t, $J_{H,H}$ = 6.9 Hz, 6 H), 3.12–3.23 (m, 4 H), 3.88 (s, 3 H), 6.59–6.63 (m, 1 H), 7.38–7.42 (m, 1 H), 7.77–7.85 (m, 1 H), 8.08–8.13 (m, 1 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.51 (d, $J_{P,C}$ = 1.8 Hz), 43.29 (d, $J_{P,C}$ = 3.6 Hz), 54.75, 110.96 (d, $J_{P,C}$ = 4.5 Hz), 120.95 (d, $J_{P,C}$ = 10.0 Hz), 125.26 (d, $J_{P,C}$ = 12.7 Hz), 127.60 (d, $J_{P,C}$ = 2.7 Hz), 159.68 (d, $J_{P,C}$ = 1.8 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 38.21 (br. m) ppm.

Mesitylphosphinous Acid–Borane *N*,*N*-Diethylamide (26f): This compound was obtained by the General Procedure from **9f** (0.165 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol) as a mixture with **26f′** and **30**, yield 4% (based on NMR analysis). R_F = 0.57 (hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.29–1.11 (br. m, 3 H), 1.09 (t, $J_{H,H}$ = 6.9 Hz, 6 H), 2.29 (s, 6 H), 2.52 (s, 3 H), 3.00–3.16 (m, 4 H), 6.73 (dm, $J_{P,H}$ = 385.9 Hz, 1 H), 6.87–6.89 (m, 2 H) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 51.33 (br. m) ppm.

***o*-Tolylphosphinous Acid–Borane *N*,*N*-Diethylamide (26f′):** This compound was obtained by the General Procedure from **9f** (0.165 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol) as a mixture with **26f** and **30**, yield 3% (based on NMR analysis). R_f = 0.57 (hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.29–1.11 (br. m, 3 H), 1.09 (t, $J_{H,H}$ = 6.9 Hz, 6 H), 1.89 (br. s, 3 H), 3.00–3.16 (m, 4 H), 6.56 (dm, $J_{P,H}$ = 383.4 Hz, 1 H), 7.19–7.22 (m, 1 H), 7.25–7.29 (m, 1 H), 7.33–7.36 (m, 1 H), 7.41–7.45 (m, 1 H) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 38.40 (br. m) ppm. GC (Phe-

nomenex Zebron ZB-35 HT): t_R = 10.71 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 196 (29), 181 (8), 120 (9), 119 (100), 105 (29), 91 (37).

***o*-Anisylphosphinic Acid *N*,*N*-Diethylamide (27g):** This compound was obtained by the General Procedure from **10g** (0.184 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol) as a mixture with **24g** and **25g**, yield 17% (based on NMR analysis). R_F = 0.73 ($CHCl_3$/MeOH 15:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.07 (t, $J_{H,H}$ = 7.3 Hz, 6 H), 3.03–3.14 (m, 4 H), 3.85 (s, 3 H), 6.89–6.93 (m, 1 H), 7.05–7.09 (m, 1 H), 7.48 (d, $J_{P,H}$ = 543.8 Hz, 1 H), 7.48–7.52 (m, 1 H), 7.82–7.86 (m, 1 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.32 (d, $J_{P,C}$ = 2.7 Hz), 39.33 (d, $J_{P,C}$ = 6.4 Hz), 55.28, 110.38 (d, $J_{P,C}$ = 6.4 Hz), 119.53 (d, $J_{P,C}$ = 121.7 Hz), 120.66 (d, $J_{P,C}$ = 11.8 Hz), 132.08 (d, $J_{P,C}$ = 10.0 Hz), 133.89 (d, $J_{P,C}$ = 6.4 Hz), 160.61 (d, $J_{P,C}$ = 3.6 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 17.27 ppm.

Mesityl(*o*-tolyl)phosphane (28): This compound was obtained by the General Procedure from **9f** (0.165 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol) as a mixture with **29** and starting material, yield 6% (based on NMR analysis). R_F = 0.86 (hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.32 (s, 6 H), 2.40 (s, 3 H), 2.45 (s, 3 H), 5.18 (d, $J_{P,H}$ = 225.1 Hz, 1 H), 6.76–6.80 (m, 1 H), 6.80–6.83 (m, 1 H), 6.97–6.98 (m, 2 H), 6.98–7.02 (m, 1 H), 7.14–7.16 (m, 1 H) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = –84.46 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 11.74 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 243 (16), 242 (95) [M], 228 (8), 227 (51), 210 (5), 193 (9), 179 (7), 178 (9), 150 (60), 149 (17), 147 (10), 135 (63), 133 (23), 123 (10), 122 (100), 121 (17), 120 (23), 119 (71), 115 (14), 107 (13), 106 (53), 105 (81), 103 (11), 92 (9), 91 (56).

Mesityl(*o*-tolyl)phosphane Oxide (29): This compound was obtained by the General Procedure from **9f** (0.165 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol) as a mixture with **28** and starting material, yield 20% (based on NMR analysis). R_F = 0.49 ($CHCl_3$/MeOH 15:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.36 (s, 3 H), 2.39 (s, 3 H), 2.44 (s, 6 H), 6.90–6.92 (m, 2 H), 7.21–7.25 (m, 1 H), 7.28–7.32 (m, 1 H), 7.41–7.46 (m, 1 H), 7.67–7.73 (m, 1 H), 8.51 (d, $J_{P,H}$ = 477.3 Hz, 1 H) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 8.29 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 14.49 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 258 (7) [M], 257 (11), 244 (17), 243 (100), 225 (5), 210 (4), 165 (4), 120 (5), 119 (16), 115 (6), 105 (18), 91 (30).

Mesityl(*o*-tolyl)phosphaneborane (30): This compound was obtained by the General Procedure from **9f** (0.165 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol) as a mixture with **26f** and **26f'**, yield 3% (based on NMR analysis). R_F = 0.86 (hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.29–1.11 (br. m, 3 H), 2.13 (s, 3 H), 2.28 (s, 3 H), 6.64 (dm, $J_{P,H}$ = 381.1 Hz, 1 H), 7.21–7.25 (m, 1 H), 7.36–7.41 (m, 1 H), 7.46–7.51 (m, 1 H), 8.04–8.10 (m, 1 H) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = –26.27 ppm. GC (Phenomenex Zebron ZB-35 HT): t_R = 11.76 min. GC–MS (EI, 70 eV): *m*/*z* (%) = 43 (16), 242 (96) [M – BH_3], 227 (51), 193 (8), 179 (9), 178 (10), 165 (7), 150 (59), 149 (18), 147 (10), 135 (63), 133 (24), 123 (11), 122 (100), 121 (19), 120 (23), 119 (70), 115 (15), 107 (13), 106 (54), 105 (81), 103 (11), 92 (10), 91 (58).

Diphenylphosphane Oxide (31): This compound was obtained by the General Procedure from **11b** (0.145 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol) as a mixture with **32** and starting material, yield 14% (based on NMR analysis). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44–7.54 (m, 6 H), 7,57–7.61 (m, 4 H), 8.11 (d, $J_{P,H}$ = 480.5 Hz, 1 H) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 21.44 ppm. Spectral data are in accordance with those reported in the literature.[11]

Diphenylphosphane (32): This compound was obtained by the General Procedure from **11b** (0.145 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol) as a mixture with **31** and starting material, yield 22% (based on NMR analysis). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.26 (d, $J_{P,H}$ = 219.1 Hz, 1 H), 7,34–7.44 (m, 6 H), 7,70–7.76 (m, 4 H) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 40.45 ppm. Spectral data are in accordance with those reported in the literature.[21]

Supporting Information (see footnote on the first page of this article): Copies of ^{1}H, ^{13}C and ^{31}P NMR spectra and GC-MS analyses of the compounds.

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