EurJOC European Journal of Organic Chemistry

FULL PAPER

DOI: 10.1002/ejoc.201200096

In Situ Dearomatisation/Alkylation of Arylphosphane Derivatives

Marek Stankevič,*[a] Karolina Wójcik,[a] Magdalena Jaklińska,[a] and K. Michał Pietrusiewicz[a]

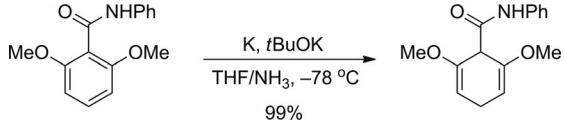
Keywords: Phosphanes / Boranes / Reduction / Alkylation

The dearomatisation of aryldialkylphosphane–boranes and aryldialkylphosphane oxides under Birch reduction conditions, followed by treatment with reactive alkyl halides, provides the corresponding α-functionalised (cyclohexa-1,4-dien-3-yl)phosphane derivatives. This reaction offers a method of choice for the synthesis of bulky (cyclohexadienyl)phosphanes.

Introduction

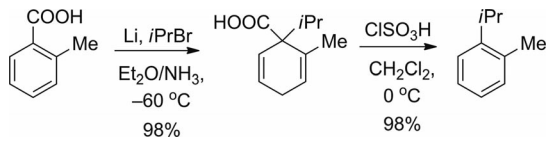
Many research groups have devoted intense attention to the synthesis of phosphanes because of their importance in organic synthesis and as ligands in transition-metal-catalysed transformations. Standard synthetic methods include 1) nucleophilic substitutions at electrophilic phosphorus atoms,[1] 2) nucleophilic substitutions with phosphorus nucleophiles,[2] 3) transition-metal-catalysed coupling reactions,[3] 4) addition of organophosphorus reagents to multiple bonds,[4] or 5) reduction of the corresponding phosphane oxides.[5] The common feature of these methods is their focus on the phosphorus centre as the source of reactivity, and quite strict constraints are imposed upon the synthetic pathway in order to allow the phosphane to be the final product. This means that any preparation of a modified phosphane by an analogous pathway is likely to be tedious, because the synthesis usually has to be reproduced in its totality. In cases in which the structural differences between two desired product phosphanes are small, as will often be the case in optimisation of a catalytic process, this problem would ideally be resolved by post-synthetic modification of the phosphane itself. Such an approach, which treats phosphanes as the starting point in the synthetic pathway, can obviously provide a step-economical synthesis of new compounds through a wide range of transformations. Any phosphanes already possessing a range of classical functional groups can obviously be modified through functional group interconversions (FGIs),[6] but those that lack functional groups require modification of the carbon skeleton.[7] For arylphosphanes and their derivatives, modification of the arene fragment can be achieved through electrophilic aromatic substitution, although this method is in practice limited to the (very important) introduction of sulfonyl groups.[8] Directed *ortho*-metallation reactions, very popular methods for the functionalisation of arenes in classical organic chemistry,[9] have to date found little use in organophosphorus chemistry.[10]

One particular arene group modification stands out through its very specific transformation of the aryl fragment. Birch reduction can be used to convert an aryl unit into the corresponding cyclohexa-1,4-dienyl fragment through the action of solutions of alkali metals in liquid ammonia (Scheme 1)[11] and is of general applicability. Many aromatic compounds such as unsubstituted arenes,[12] aryl ethers[13] or arenecarboxylic acid derivatives[14] are successfully dearomatised under Birch reduction conditions. This transformation has also been found to be useful in dearomatisations of heteroaromatic compounds such as furans,[15] indoles,[16] pyrroles[17] or pyridines[18] into the corresponding non-aromatic unsaturated heterocycles.



Scheme 1. Birch reduction of an arylamide.

The Birch reduction of an arene proceeds through the formation of a carbanionic intermediate, and this raises the possibility of coupling an initial Birch reduction step to an in situ reaction with an electrophile to generate a substituted cyclohexa-1,4-diene (Scheme 2).[19]



Scheme 2. In situ reduction/alkylation of an arene.

[a] Department of Organic Chemistry, Faculty of Chemistry, Maria Curie-Skłodowska University,
Gliniana 33, 20-614 Lublin, Poland
Fax: +48-81-524-22-51 ext. 136
E-mail: marek.stankevic@poczta.umcs.lublin.pl

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201200096.

Given that the both functionalised arenes and electrophiles are, in principle, likely to be tolerated, such a Birch reduction/alkylation might be usable to create very reactive structures well-adapted to further modification. More classical Birch reduction products have found use in syntheses of, for example, bicyclic[20] and polycyclic compounds,[21] as well as of natural products.[22]

Unlike in classic organic chemistry, where it is ubiquitous, the use of Birch reduction in organophosphorus chemistry has little precedent. The first report of Birch reductions of a few very electron-rich arylphosphanes appeared towards the end of the last century,[23] and as part of this research project, directed towards the application of Birch reductions in organophosphorus chemistry, we have already reported the efficient dearomatisations of the much more classical aryldialkylphosphane–boranes[24] and aryldialkylphosphane oxides.[25] More recently, the area has also been explored by Verdaguer et al., through the dearomatisation of *tert*-butylphenylphosphinous acid–borane amide.[26]

This very easy access to (cyclohexadienyl)phosphane derivatives that the Birch reduction provides has led us to publish a preliminary investigation of their utility in organic synthesis and it is already clear that these compounds can be used in Michael-type additions with secondary phosphane oxides to give diphosphane dioxides containing cyclohexenyl or cyclohexyl linkers;[27] similar reactivity has also recently been observed by Salem and colleagues.[28]

Here we wish to demonstrate the utility of Birch reduction reactions in the synthesis of structurally new α-substituted (cyclohexa-1,4-dien-3-yl)phosphane derivatives through in situ Birch reduction/alkylation of aryldialkylphosphane derivatives.

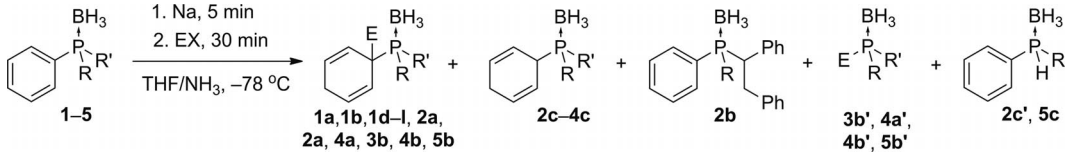
Results and Discussion

For the first set of in situ Birch reduction/alkylation experiments we chose five model arylphosphane–boranes (Scheme 3). Four of them – namely *tert*-butylmethylphenylphosphane–borane (**1**), benzyl-*tert*-butylphenylphosphane–borane (**2**), dimethylphenylphosphane–borane (**3**) and 1-phenylphospholane–borane (**4**) – possessed two alkyl substituents on their phosphorus atoms, whereas methyldiphenylphosphane–borane (**5**) had only one. All model phosphane–boranes were treated with the appropriate amount of alkali metal dissolved in liquid ammonia at –78 °C followed by treatment with an excess of an alkyl halide. The results of the screening are presented below.

The outcome is that treatment of substrates with alkali metals in liquid ammonia and subsequent addition of electrophiles generally provides the corresponding α-alkylated (cyclohexa-1,4-dien-3-yl)phosphane–boranes in modest to good yields. When methyl iodide was used, the corresponding α-alkylated phosphane–borane products shown in Table 1 were isolated in 21–91% yields (Table 1, Entries 1, 2, 4, and 5), except in the case of the diarylalkylphosphane–borane **5**. This underwent phenyl group cleavage and subsequent alkylation of the intermediate phosphane–borane anion rather than Birch reduction/alkylation (Table 1, Entry 6). It was found that phosphane–borane **2** is quite susceptible to benzyl group cleavage when sodium is used (Table 1, Entry 2) and that this process dominates massively when sodium is replaced by potassium (Table 1, Entry 3). Similar trends were observed when benzyl chloride replaced methyl iodide as the electrophile (Table 1, Entries 7–11). The corresponding α-alkylated Birch reduction products were obtained in good yields except in the case of **5**, which again predominantly underwent phenyl group cleavage and subsequent benzylation (Table 1, Entry 11). The unanticipated product **2b** was obtained in the system in which benzylphosphane–borane **2** was used with benzyl chloride as the electrophile (Table 1, Entry 8); it was probably formed through a reaction sequence involving debenzylation in the first step followed by alkylation, then deprotonation at the benzylic position and further benzylation. This assumption was based on the reaction between **2** and MeI, which yielded mainly **1** under the reaction conditions.

When the electrophile was the more hindered cyclohexyl bromide, the desired α-alkylated Birch reduction products were not obtained (Table 1, Entries 12–16). In these cases, the main products isolated from the reaction mixtures were either non-alkylated Birch reduction products (for **2**–**4**) or secondary phosphane–boranes resulting from P–Ph bond cleavage (for **2** and **5**). This lack of reactivity with the secondary alkyl halide can reasonably be ascribed to the small volume of unoccupied space about the contiguous quaternary centres; this obviously precludes the approach of the bulkier electrophile.

When performing the preliminary dearomatization/alkylation experiments we observed an interesting feature in dialkylphenylphosphane–boranes **3** and **4**; these formed significant amounts of trialkylphosphane–boranes **3b′**–**5b′** (Table 1, Entries 5, 9 and 10). These products could only have been formed if the phenyl-phosphorus bond had been cleaved prior to alkylation. The difference between these phosphane–boranes and **1** is that they each have two small alkyl substituents at phosphorus, so it seems that the natu-



Scheme 3. Products obtained upon in situ Birch reduction/alkylation of model phosphane–boranes.

Table 1. Screening of in situ Birch reduction/alkylation of model phosphane–boranes.

Entry		Substrate R	R′	Electrophile (equiv.)	Yields of the products[a]	
1[b]	**1**	*t*Bu	Me	MeI (**a**, 2.5)	**1a** (91%)	
2	**2**	*t*Bu	$PhCH_2$	MeI (**a**, 2.5)	**2a** (21%)[c]	**1** (45%)[c]
3[b]	**2**	*t*Bu	$PhCH_2$	MeI (**a**, 2.5)	**1** (86%)	
4	**3**	Me	Me	MeI (**a**, 2.5)	**3a** (49%)	
5	**4**		$-(CH_2)_4-$	MeI (**a**) (2.5)	**4a** (42%)	**4a′** (46%)
6	**5**	Ph	Me	MeI (**a**, 2.5)	**3** (86%)	
7[b]	**1**	*t*Bu	Me	$PhCH_2Cl$ (**b**, 2)	**1b** (74%)	
8	**2**	*t*Bu	$PhCH_2$	$PhCH_2Cl$ (**b**, 2)	**2b** (51%)	
9	**3**	Me	Me	$PhCH_2Cl$ (**b**, 2)	**3b** (67%)	**3b′** (30%)[d]
10	**4**		$-(CH_2)_4-$	$PhCH_2Cl$ (**b**) (2)	**4b** (62%)	**4b′** (30%)[d]
11	**5**	Ph	Me	$PhCH_2Cl$ (**b**, 2)	**5b** (25%)[e]	**5b′** (60%)[e]
12[b]	**1**	*t*Bu	Me	*c*HexBr (**c**, 2)	no reaction	
13	**2**	*t*Bu	$PhCH_2$	*c*HexBr (**c**, 2)	**2c** (21%)	**2c′** (35%)
14	**3**	Me	Me	*c*HexBr (**c**, 2)	**3c** (51%)	
15	**4**		$-(CH_2)_4-$	*c*HexBr (**c**, 2)	**4c** (47%)	
16	**5**	Ph	Me	*c*HexBr (**c**, 2)	**5c** (45%)[c]	
17[b]	**1**	*t*Bu	Me	chloroacetonitrile (**d**, 2)	**1d** (67%)	
18[b]	**1**	*t*Bu	Me	2-phenylethyl bromide (**e**, 2)	**1e** (75%)	
19[b]	**1**	*t*Bu	Me	propargyl bromide (**f**, 2)	**1f** (75%)[d]	
20[b]	**1**	*t*Bu	Me	ethyl bromoacetate (**g**, 2)	**1g** (56%)	
21[b]	**1**	*t*Bu	Me	allyl chloride (**h**, 2)	**1h** (35%)[d]	
22[b]	**1**	*t*Bu	Me	4-bromobut-1-ene (**i**, 2)	**1i** (57%)	
23[b]	**1**	*t*Bu	Me	2-bromobenzyl bromide (**j**, 2)	**1j** (38%)	
24[b]	**1**	*t*Bu	Me	1,2-dibromoethane (**k**, 4)	**1k** (48%)	
25[b]	**1**	*t*Bu	Me	1,3-dibromopropane (**l**, 2)	**1l** (72%)	

[a] Yields of pure compounds, unless otherwise noted. [b] The reaction was performed with potassium (2.5 equiv.). [c] Yields based on the NMR spectra of the mixture of **2a** and **1**. [d] Yields based on the NMR spectra of the mixtures with substrate. [e] Yields based on the NMR spectra of the mixture of **5b** and **5b′**.

res of the alkyl substituents might strongly influence the course of the reaction through an as yet unknown mechanism.

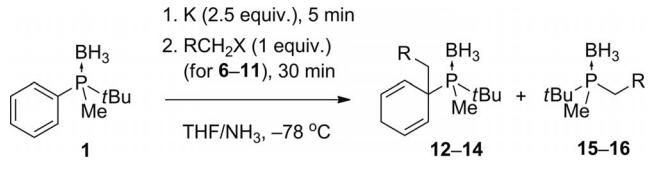
Given that the in situ Birch reduction/alkylation appeared to work for the reactions between most of the phenylphosphane–boranes tested and simple primary alkyl halides, we were curious to see whether or not other activated halides possessing additional functionalities could react similarly under the reaction conditions. Irrespective of the functionalised alkyl halides under investigation (all of them primary or benzylic), we observed the formation of the corresponding α-alkylated Birch reduction products of **1** in reasonable yields (Table 1, Entries 17–25). Functionalities such as double or triple bonds and cyano or carboxy groups are compatible with the reaction conditions. Even dihaloalkanes such as 1,2-dibromoethane and 1,3-dibromopropane (Table 1, Entries 24 and 25) can be used to generate monosubstituted products in good yields, although this was not the case for dihalomethanes, which failed to give the corresponding (α-halomethyl)cyclohexadienylphosphane–boranes (data not shown).

The successful use of functionalised haloalkanes to introduce an additional reactive centre such as cyano or carboxylate one carbon atom away remote from the cyclohexadienyl fragment gives a green light for the introduction of a second phosphorus group into the molecule by means of a phosphorus-functionalised halide. The phosphane–borane **1** was therefore subjected to the studied reaction sequence with a series of phosphorus-containing alkyl halides (Table 2 and Scheme 4).

Table 2. Birch reduction/alkylation with phosphorus-containing alkyl halides.

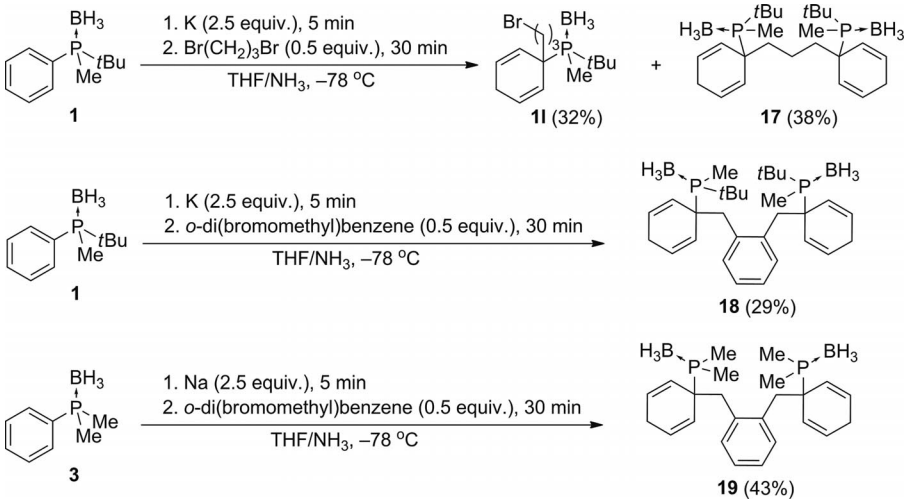
Entry	Substrate	Alkylated products	
1	$Ph_2P(O)CH_2I$ (**6**)	no alkylated product	
2	$Ph_2P(BH_3)CH_2CH_2Cl$ (**7**)	no alkylated product	
3	$(EtO)_2P(O)CH_2CH_2Br$ (**8**)	no alkylated product	
4	$Ph_2P(BH_3)(CH_2)_3Br$ (**9**)	**12** (47%)	**15** (23%)
5	$Ph_2P(BH_3)(CH_2)_4Br$ (**10**)	**13** (39%)	**16** (16%)
6	*t*BuPhP$(BH_3)(CH_2)_4Br$ (**11**)	**14** (31%)[a]	

[a] A mixture of two diastereoisomers.



Scheme 4. Birch reduction/alkylation with phosphorus-containing alkyl halides.

The outcomes of such in situ alkylations of the intermediate carbanion of **1** with phosphorus-containing alkyl halides seemed to be quite sensitive to the structures of the electrophiles. Functionalised alkyl halides with short linkers between the two functionalities, as in **6**–**8**, failed to react with the carbanion formed in situ (Table 2, Entries 1–3) but



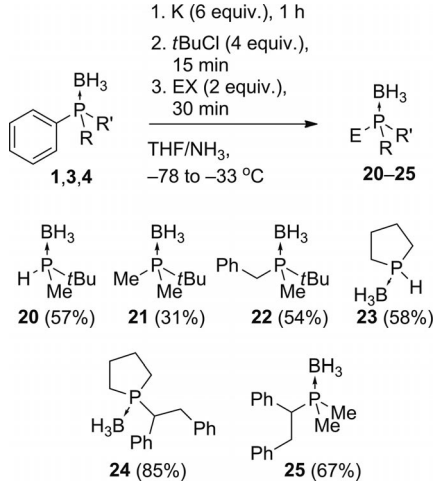
Scheme 5. Double alkylation of carbanions formed in situ .

those with longer linkers such as **9**–**11** afforded the desired products in fair yields (Table 2, Entries 4–6). In view of the crowded nature of the intermediate tertiary carbanion, the lack of the reactivity of **6**–**8** is probably again associated with strong steric interactions with the incoming proximal quaternary phosphorus centre. In the cases of **9** and **10** we also observed the formation of the side products **15** and **16** (Table 2, Entries 4 and 5), which are formally the alkylation products of the corresponding secondary phosphane–borane anion. This indicates that cleavage of the phosphorus-phenyl bond in **1** can also occur to some extent under the reaction conditions.

Because in situ alkylation of the intermediate carbanion with an excess of a dihaloalkane provides an α-alkylated Birch reduction product possessing an easily substituted halide group in the side chain, adjustment of the amount of dihaloalkane might give rise to a double alkylation process and thus to new diphosphane derivatives containing very special linkers (Scheme 5).

We anticipated that use of 1,3-dibromopropane (0.5 equiv.) should drive the reaction towards double alkylation, but obtained the monoalkylation product **1l** in 32% yield together with the desired bis-alkylation product **17** in 38% yield (Scheme 5). However, *o*-bis(bromomethyl)benzene underwent reaction with **1** under Birch reduction conditions to give the disubstituted compound **18** as the only observable product, isolated in 29% yield (see Scheme 5). The sterically less demanding organophosphorus substrate **3** gave an increased yield (43%) of the bis(phosphane)–bis(borane) **19**, which again emphasises the influence of the steric crowding in the substrate on the reaction yield.

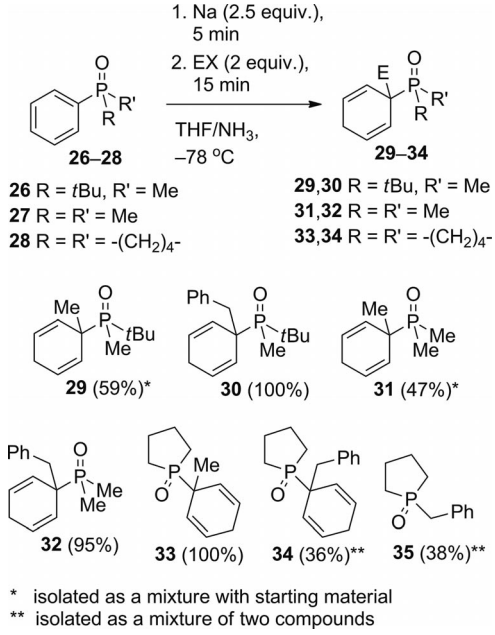
Above we discussed the formation of compounds **4a′**, **3b′**, **4b′**, **15** and **16** during the Birch reduction/alkylation of **1**. It is postulated that these products arise through initial phosphorus-phenyl bond cleavage and formation of the secondary phosphane–borane anion, which subsequently undergoes alkylation with an added electrophile. It seemed reasonable to assume that this methodology might represent a valuable method for replacing a phosphane aryl fragment by an alkyl group, which was successfully applied by another research group in the case of diarylalkylphosphane–boranes.[29] The replacement of the phenyl substituents in phenyldialkylphosphane–boranes in the presence of large excesses of alkali metal was thus attempted (Scheme 6).



Scheme 6. In situ P–Ph bond cleavage/alkylation of **1**, **3** and **4**.

This treatment of model phosphane–boranes **1**, **3** and **4** with large excesses of alkali metal, although preferentially at –33 °C, indeed caused phosphorus-phenyl bond cleavage in the phenyldialkylphosphane–boranes. Treatment of the obtained secondary phosphane–borane anions with methyl iodide or benzyl chloride in situ yielded the corresponding trialkylphosphane–boranes in moderate to good yields. The phosphane–borane anions derived from **3** and **4** afforded chain homologated products **24** and **25** upon treatment with benzyl chloride. Again, the initial products seem to undergo benzyl group deprotonation under the reaction conditions and subsequent alkylation with excess benzyl chloride. When ammonium chloride was used as the electrophile, the corresponding secondary phosphane–boranes **20** and **23** were formed.

Given that dearomatization/alkylation of the phenyl substituent in phenyldialkylphosphane–boranes appears to have quite general utility, we also attempted similar Birch reduction/alkylation sequences with the corresponding phosphane oxides (Scheme 7).



Scheme 7. In situ Birch reduction/alkylation of phosphane oxides **26**–**28**.

It appears that phenyldialkylphosphane oxides cleanly undergo analogous reaction sequences under the same conditions to yield the corresponding α-alkylated (cyclohexadienyl)phosphane oxides in fair to excellent yields. The only exception here was the reaction between 1-phenylphospholane oxide (**28**) and benzyl chloride, which afforded a mixture of **34** and benzylphospholane oxide (**35**).

Conclusions

The application of Birch reduction methodology to organophosphorus chemistry is still in its infancy, but the results obtained so far show the potential of this reaction as a tool for transforming the relatively stable *P*-phenyl substituent into a reactive cyclohexadienyl fragment without affecting the phosphorus functionality. The formation of an intermediate cyclohexadienyl carbanion during the dearomatisation process allows the preparation of new organophosphorus compounds featuring bulky cyclohexadienyl *P*-substituents by simple alkylation of this carbanion with reactive primary alkyl halides. The presence of other functionalities in alkyl halides is tolerated in this reaction, which means that it can be applied to the synthesis of diphosphorus compounds containing complex carbon linkers. The flexibility of the chemistry available with phosphane–borane complexes is nicely illustrated by the easy shift of the reaction outcome from Birch reduction/alkylation to P–Ph bond cleavage/alkylation through a simple change in the quantity of the alkali metal.

Experimental Section

General: All the reactions were performed under argon by 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 the solvents for extraction were used as received. Ammonia was passed through solid NaOH before condensation.

The NMR spectra were recorded with Bruker Ascend (500 MHz), Varian Mercury 400BB or Bruker Avance (300 MHz) spectrometers in $CDCl_3$ as a solvent at room temperature unless otherwise noted. Chemical shifts (δ) are reported in ppm relative to residual solvent peak. Mass spectra were recorded with a Shimadzu GC-MSQP2010S spectrometer in electron ionisation (EI) mode and 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)]. Thin-layer chromatography (TLC) was performed with precoated silica gel plates and visualised with UV light or $KMnO_4$ solution. The reaction mixtures were purified by column chromatography over silica gel (60–240 mesh).

tert-Butylmethylphenylphosphane–borane (**1**),[30] benzyl-*tert*-butylphenylphosphane–borane (**2**),[31] dimethylphenylphosphane–borane (**3**),[27] diphenyl(iodomethyl)phosphane oxide (**6**),[32] diethyl 2-bromoethylphosphonate (**8**),[33] *tert*-butylmethylphenylphosphane oxide (**26**)[34] and dimethylphenylphosphane oxide (**27**)[26] were prepared as reported in the literature.

1-Phenylphospholane–Borane (4): A solution of 1-phenylphospholane oxide[35] (1.246 g, 7.0 mmol) in methanol (15 mL) was placed in a flame-dried Schlenk tube (100 mL). Pd/C (10%, 0.125 g) was then added, the reaction vessel was evacuated three times and filled with hydrogen, and the reaction mixture was stirred under hydrogen (1 atm) at room temperature for 24 h. The reaction mixture was then filtered through Celite, which was washed with CH_2Cl_2 (2 × 20 mL), and the organic phase was evaporated under reduced pressure to yield chemically and spectroscopically pure 1-phenylphospholane oxide (**28**, 1.26 g, 100%) as a colourless liquid. R_F = 0.59 (EtOAc/MeOH 20:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.78–2.23 (m, 8 H), 7.39–7.51 (m, 3 H), 7.63–7.72 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.23 (d, $J_{P,C}$ = 8.3 Hz), 29.58 (d, $J_{P,C}$ = 67.5 Hz), 128.58 (d, $J_{P,C}$ = 11.2 Hz), 129.81 (d, $J_{P,C}$ = 9.5 Hz), 131.56 (d, $J_{P,C}$ = 2.9 Hz), 134.20 (d, $J_{P,C}$ = 90.2 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 60.98 ppm. GC (Phenomenex Zebron ZB-5MSi): R_T = 12.92 min. GC-MS (EI, 70 eV): *m*/*z* (%) = 180 (100) $[M]^{+\cdot}$, 179 (65), 152 (65), 151 (24), 134 (42), 125 (21), 124 (32), 105 (73), 91 (26), 79 (17), 78 (13), 77 (68). $C_{10}H_{13}OP$ (180.18): calcd. C 66.66, H 7.27; found C 66.80, H 7.32.

A solution of 1-phenylphospholane oxide (1.26 g, 7.0 mmol) was dissolved in toluene (10 mL) and trichlorosilane (2.10 mL, 21 mmol) was added, followed by triethylamine (2.92 mL, 21 mmol). The reaction mixture was heated to 100 °C for 24 h and, after cooling, BH_3·THF (10.5 mL, 1 M in THF, 10.5 mmol) was added and the stirring was continued for 2 h at room temperature. The reaction mixture was quenched by slow addition of NaOH solution (5 M, 10 mL), water (10 mL) was then added, and the reaction mixture was extracted with $CHCl_3$ (5 × 20 mL). The organic

phase was washed with water (2 × 10 mL), dried with $MgSO_4$ and concentrated to dryness. The residue was purified by column chromatography on silica gel with hexane/EtOAc (6:1) to yield 1-phenylphospholane–borane (**4**, 0.90 g, 72%). The analytical data are in accordance with those reported in the literature.[36]

Methyldiphenylphosphane–Borane (5): A solution of diphenylphosphane–borane[37] (1.00 g, 4.95 mmol) in THF (10 mL) was placed in a flame-dried Schlenk vessel (100 mL) under argon. The solution was cooled to –78 °C and *n*-butyllithium (3.41 mL, 1.6 M in hexanes, 5.44 mmol) was added over 5 min. After the mixture had been kept for 30 min at –78 °C, methyl iodide (0.46 mL, 7.42 mmol) was added in one portion and the reaction mixture was allowed to warm to room temperature over 2 h. Saturated NH_4Cl solution (5 mL) was then added, the mixture was extracted with CH_2Cl_2 (3 × 15 mL), and collected organic fractions were dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified with column chromatography on silica gel with hexane/EtOAc (6:1) as eluent to yield **5** as a colourless pasty solid (0.96 g, 90%). The spectroscopic data are in accordance with those reported in the literature.[38]

(2-Chloroethyl)diphenylphosphane–Borane (7): Triphenylphosphane–borane (2.76 g, 10 mmol) in THF (10 mL) was placed under argon in a flame-dried two-necked flask (100 mL). Sodium (0.506 g, 22 mmol) was then added in several pieces and the reaction mixture was allowed to stir at room temperature for 24 h. During the reaction time, the colour of the reaction mixture changed from colourless to deep maroon. After 24 h, excess sodium was removed, *tert*-butyl chloride (1.196 mL, 11 mmol) was added, and the reaction mixture was stirred for another hour. The reaction mixture was cooled to –70 °C, 1,2-dichloroethane (0.788 mL, 10 mmol) was added, and the reaction mixture was allowed to warm to room temperature over 3 h. The reaction was quenched by addition of aqueous HCl (1 M, 5 mL), the mixture was extracted with dichloromethane (3 × 20 mL), the collected organic fraction was dried with $MgSO_4$, the solvent was evaporated under reduced pressure, and the residue was purified by column chromatography with hexane/ethyl acetate (6:1) as eluent to yield **7** (1.103 g, 42%) as a white solid; m.p. 68.8–69.6 °C. R_F = 0.70 (hexane/EtOAc 6:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.39–1.58 (m, 3 H), 2.69–2.82 (m, 2 H), 3.62–3.72 (m, 2 H), 7.39–7.63 (m, 6 H), 7.64–7.74 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.14 (d, $J_{P,C}$ = 39.0 Hz), 45.51 (d, $J_{P,C}$ = 16.1 Hz), 128.84 (d, $J_{P,C}$ = 55.6 Hz), 128.89 (d, $J_{P,C}$ = 9.8 Hz), 131.33, 132.04 (d, $J_{P,C}$ = 9.3 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 29.99 (d, $J_{P,C}$ = 32.7 Hz), 38.51 (d, $J_{P,C}$ = 8.2 Hz), 128.03 (d, $J_{P,C}$ = 55.4 Hz), 129.07 (d, $J_{P,C}$ = 10.0 Hz), 131.67 (d, $J_{P,C}$ = 2.7 Hz), 131.99 [d, J(P,C) = 10.0 Hz] ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 13.83 ppm. GC (Phenomenex Zebron ZB-35HT INFERNO): R_T = 19.01 min. GC-MS (EI, 70 eV): *m*/*z* (%) = 262 (16) $[M]^{+\cdot}$, 233 (11), 200 (25), 199 (100), 183 (52), 158 (15), 121 (15), 107 (22), 91 (31). $C_{14}H_{17}BClP$ (262.52): calcd. C 64.05, H 6.53; found C 65.30, H 6.35.

(3-Bromopropyl)diphenylphosphane–Borane (9): This compound was prepared as described for compound **7** with triphenylphosphane–borane (2.76 g, 10 mmol), sodium (0.506, 22 mmol) and 1,3-dibromopropane (1.614 mL, 10 mmol). Yield 1.573 g (49%). Pale orange pasty solid. R_F = 0.40 (hexane/EtOAc 6:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.39–1.63 (m, 3 H), 1.98–2.19 (m, 2 H), 2.33–2.47 (m, 2 H), 3.46 (t, $J_{H,H}$ = 6.22 Hz, 2 H) 7.41–7.54 (m, 6 H), 7.67–7.76 (m, 4 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.42 (d, $J_{P,C}$ = 37.5 Hz), 26.28 (d, $J_{P,C}$ = 1.8 Hz), 34.27 (d, $J_{P,C}$ = 15.4 Hz), 128.85 (d, $J_{P,C}$ = 55.4 Hz), 128.90 (d, $J_{P,C}$ = 10.0 Hz), 131.34 (d, $J_{P,C}$ = 2.7 Hz), 132.05 (d, $J_{P,C}$ = 9.1 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 15.92 ppm. GC (Phenomenex Zebron ZB-35HT INFERNO): R_T = 20.28 min. GC-MS (EI, 70 eV): *m*/*z* (%) = 307 (14), 305 (15), 280 (12), 279 (28), 278 (11), 277 (28), 227 (13), 226 (16), 204 (15), 202 (17), 200 (18), 199 (100), 185 (26), 184 (13), 183 (91), 152 (18), 123 (18), 121 (49), 109 (18), 108 (23), 107 (39), 78 (16), 77 (24), 54 (91). $C_{15}H_{19}BBrP$ (321.00): calcd. C 56.12, H 5.97; found C 56.33, H 6.29.

(4-Bromobutyl)diphenylphosphane–Borane (10): This compound was prepared as described for compound **7** with triphenylphosphane–borane (2.76 g, 10 mmol), sodium (0.506, 22 mmol) and 1,4-dibromobutane (1.195 mL, 10 mmol). Yield 1.809 g (54%). White oily solid. R_F = 0.42 (hexane/EtOAc 6:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.21–1.42 (m, 3 H), 1.61–1.77 (m, 2 H), 1.87–2.01 (m, 2 H), 2.16–2.29 (m, 2 H), 3.36 (t, $J_{H,H}$ = 6.68 Hz, 2 H) 7.39–7.52 (m, 6 H), 7.62–7.72 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.69, 24.80 (d, $J_{P,C}$ = 40.0 Hz), 32.43, 33.62 (d, $J_{P,C}$ = 13.7 Hz), 128.81 (d, $J_{P,C}$ = 9.8 Hz), 131.19, 132.01 (d, $J_{P,C}$ = 9.3 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 16.30 ppm. GC (Phenomenex Zebron ZB-35HT INFERNO): R_T = 16.26 min. GC-MS (EI, 70 eV): *m*/*z* (%) = 242 (21), 200 (36), 199 (100), 183 (36), 120 (10), 109 (14), 108 (35), 107 (18), 91 (22). $C_{16}H_{21}BBrP$ (335.03): calcd. C 57.36, H 6.32; found C 57.33, H 6.55.

(4-Bromobutyl)-*tert*-butylphenylphosphane–Borane (11): *tert*-Butylphenylphosphane–borane (1.80 g, 10 mmol) in THF (10 mL) was placed under argon in a flame-dried three-necked flask (100 mL) and the mixture was cooled to –70 °C. *n*BuLi (6.88 mL, 1.6 M in hexanes, 11 mmol) was added dropwise by syringe over 5 min and the mixture was stirred at –78 °C for 30 min. 1,4-Dibromobutane (1.195 mL, 10 mmol) was added in one portion and the mixture was allowed to warm to room temperature over 5 h. The reaction was quenched by addition of aqueous HCl (1 M, 5 mL), the mixture was extracted with dichloromethane (3 × 20 mL), the collected organic fraction was dried with $MgSO_4$, the solvent was evaporated under reduced pressure, and the residue was purified by column chromatography with hexane/ethyl acetate (6:1) as eluent to yield **11** (2.394 g, 76%). Pale yellow solid; m.p. 65.3–66.4 °C. R_F = 0.77 (hexane/EtOAc 6:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.21–1.12 (br. m, 3 H), 1.09 (d, $J_{P,H}$ = 13.6 Hz, 9 H), 1.72–1.86 (m, 2 H), 1.87–1.99 (m, 2 H), 1.99–2.07 (m, 1 H), 2.09–2.23 (m, 1 H), 3.30–3.41 (m, 2 H), 7.43–7.54 (m, 3 H), 7.66–7.72 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.92 (d, $J_{P,C}$ = 33.6 Hz), 21.88, 25.43 (d, $J_{P,C}$ = 2.6 Hz), 29.05 (d, $J_{P,C}$ = 33.1 Hz), 30.93, 34.13 (d, $J_{P,C}$ = 12.4 Hz), 125.78 (d, $J_{P,C}$ = 48.0 Hz), 128.35 (d, $J_{P,C}$ = 9.8 Hz), 131.18 (d, $J_{P,C}$ = 2.6 Hz), 133.35 (d, $J_{P,C}$ = 8.3 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 30.90 ppm. $C_{14}H_{25}BBrP$ (315.04): calcd. C 53.37, H 8.00; found C 53.30, H 7.88.

General Procedure for in situ Birch Reduction/Alkylation of Arylphosphane-Boranes: Gaseous ammonia was passed through a flame-dried three-necked flask (100 mL) fitted with inert gas inlet, dry-ice condenser and cooling bath (–78 °C) until 15 mL of it was condensed. The alkali metal (2.5 equiv.) was added and the mixture was stirred for 15 min. The phosphane–borane (1 equiv.) was then added, followed after 5 min by the electrophile (2–2.5 equiv.), and the mixture was allowed to stir at –78 °C for 30 min. The reaction was quenched by addition of solid NH_4Cl (0.5 g), ammonia was evaporated off, the residue was filtered, the solid was washed with CH_2Cl_2 (3 × 15 mL), and the collected organic phases were concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/EtOAc (6:1) as an eluent.

***tert*-Butylmethyl(3-methylcyclohexa-1,4-dien-3-yl)phosphane–Borane (1a):** This compound was prepared by the General Procedure from **1** (0.097 g, 0.5 mmol), potassium (0.049 g, 1.25 mmol)

and methyl iodide (0.078 mL, 1.25 mmol). Yield 0.096 g (91%). Colourless oil. R_F = 0.65 (hexane/EtOAc 6:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.15 to 0.93 (br. m, 3 H, BH_3), 1.18 (d, $J_{P,H}$ = 8.3 Hz, 3 H), 1.21 (d, $J_{P,H}$ = 13.0 Hz, 9 H), 1.39 (d, $J_{P,H}$ = 13.9 Hz, 3 H), 2.54–2.65 (m, 2 H), 5.62–5.83 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 3.05 (d, $J_{P,C}$ = 33.9 Hz), 26.07 (d, $J_{P,C}$ = 3.7 Hz), 26.24 (d, $J_{P,C}$ = 2.3 Hz), 127.13 (d, $J_{P,C}$ = 1.2 Hz), 31.21 (d, $J_{P,C}$ = 26.7 Hz), 37.28 (d, $J_{P,C}$ = 28.7 Hz), 124.69 (d, $J_{P,C}$ = 7.8 Hz), 124.79 (d, $J_{P,C}$ = 6.6 Hz), 129.00 (d, $J_{P,C}$ = 3.7 Hz), 129.04 (d, $J_{P,C}$ = 5.8 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 39.86 ppm. GC (Phenomenex Zebron ZB-35 HT Inferno): R_T = 7.07 min. GC-MS (EI, 70 eV): *m*/*z* (%) = 104 (31), 93 (73), 92 (14), 91 (52), 77 (30), 65 (10), 57 (100). $C_{12}H_{24}BP$ (210.10): calcd. C 68.60, H 11.51; found C 68.84, H 11.80.

Benzyl-*tert*-butyl-(3-methylcyclohexa-1,4-dien-3-yl)phosphane–Borane (2a): This compound was prepared by the General Procedure from **2** (0.135 g, 0.5 mmol), sodium (0.029 g, 1.25 mmol) and methyl iodide (0.078 mL, 1.25 mmol). It was isolated as a mixture with **1**, yield 21% (based on NMR). R_F = 0.67 (hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.16 to 1.21 (br. m, 3 H), 1.20 (d, $J_{P,H}$ = 12.5 Hz, 9 H), 1.37 (d, $J_{P,H}$ = 13.6 Hz), 2.65–2.76 (m, 2 H), 2.99–3.10 (m, 1 H), 3.23–3.37 (m, 1 H), 5.78–5.96 (m, 4 H), 7.20–7.30 (m, 3 H), 7.39–7.45 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 26.27 (d, $J_{P,C}$ = 1.8 Hz), 26.95 (d, $J_{P,C}$ = 1.8 Hz), 27.93, 29.94 (d, $J_{P,C}$ = 30.9 Hz), 33.16 (d, $J_{P,C}$ = 22.7 Hz), 39.05 (d, $J_{P,C}$ = 26.3 Hz), 124.63 (d, $J_{P,C}$ = 7.3 Hz), 125.00 (d, $J_{P,C}$ = 6.4 Hz), 126.53 (d, $J_{P,C}$ = 1.8 Hz), 128.04 (d, $J_{P,C}$ = 1.8 Hz), 129.53 (d, $J_{P,C}$ = 3.6 Hz), 129.58 (d, $J_{P,C}$ = 3.6 Hz), 130.60 (d, $J_{P,C}$ = 3.6 Hz), 132.97 (d, $J_{P,C}$ = 5.5 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 46.94 ppm. GC (Phenomenex Zebron ZB-35 HT Inferno): R_T = 14.15 min. GC-MS (EI, 70 eV): *m*/*z* (%) = 272 (11) [M – BH_3], 258 (3), 216 (4), 215 (4), 125 (49), 123 (12), 122 (12), 109 (8), 105 (9), 93 (34), 92 (10), 91 (100).

***tert*-Butylmethylphenylphosphane–Borane (1):** This compound was prepared by the General Procedure from **2** (0.135 g, 0.5 mmol), sodium (0.029 g, 1.25 mmol) and methyl iodide (0.078 mL, 1.25 mmol). It was isolated as a mixture with **2a**, yield 45% (based on NMR). The analytical data are in accordance with those reported in the literature.[30]

Dimethyl(3-methylcyclohexa-1,4-dien-3-yl)phosphane–Borane (3a): This compound was prepared by the General Procedure from **3** (0.076 g, 0.5 mmol), sodium (0.029 g, 1.25 mmol) and methyl iodide (0.078 mL, 1.25 mmol). Yield 0.041 g (49%). Colourless solid; m.p. 48.8–50.1 °C. R_F = 0.60 (hexane/EtOAc 6:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.12 to 1.06 (br. m, 3 H), 1.12 (d, $J_{P,H}$ = 9.9 Hz, 6 H), 1.26 (d, $J_{P,H}$ = 15.6 Hz, 3 H), 2.51–2.72 (m, 2 H), 5.48–5.57 (m, 2 H), 5.79–5.88 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 7.04 (d, $J_{P,C}$ = 36.3 Hz), 22.84 (d, $J_{P,C}$ = 3.6 Hz), 26.40 (d, $J_{P,C}$ = 4.5 Hz), 34.83 (d, $J_{P,C}$ = 34.5 Hz), 126.45 (d, $J_{P,C}$ = 7.3 Hz), 126.85 (d, $J_{P,C}$ = 3.6 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 22.48 ppm. GC (Phenomenex Zebron ZB-35 HT Inferno): R_T = 10.63 min. GC-MS (EI, 70 eV): *m*/*z* (%) = 167 (2) [M – 1], 153 (5), 140 (7), 139 (8), 126 (4), 93 (100), 92 (30), 91 (78), 89 (15). $C_9H_{18}BP$ (168.02): calcd. C 64.33, H 10.80; found C 64.44, H 10.64.

1-(3-Methylcyclohexa-1,4-dien-3-yl)phospholane–Borane (4a): This compound was prepared by the General Procedure from **4** (0.089 g, 0.5 mmol), sodium (0.029 g, 1.25 mmol) and methyl iodide (0.078 mL, 1.25 mmol). Yield 0.041 g (42%). Colourless solid; m.p. 41.4–42.2 °C. R_F = 0.58 (hexane/EtOAc 6:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.10 to 1.10 (br. m, 3 H), 1.29 (d, $J_{H,P}$ = 15.4 Hz, 3 H), 1.71–1.89 (m, 4 H), 1.96–2.16 (m, 4 H), 2.66–2.78 (m, 2 H), 5.58–5.67 (m, 2 H), 5.84–5.93 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.49 (d, $J_{P,C}$ = 33.3 Hz), 23.97 (d, $J_{P,C}$ = 3.7 Hz), 26.51 (d, $J_{P,C}$ = 4.3 Hz), 27.33, 35.01 (d, $J_{P,C}$ = 28.2 Hz), 126.15 (d, $J_{P,C}$ = 7.5 Hz), 127.40 (d, $J_{P,C}$ = 3.7 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 51.20 ppm. GC (Phenomenex Zebron ZB-35 HT Inferno): R_T = 10.63 min. GC-MS (EI, 70 eV): *m*/*z* (%) = 93 (100), 92 (23), 91 (91), 89 (22), 88 (94), 87 (15). $C_{11}H_{20}BP$ (194.06): calcd. C 68.08, H 10.39; found C 67.84, H 10.10.

1-Methylphospholane–Borane (4a′): This compound was prepared by the General Procedure from **4** (0.089 g, 0.5 mmol), sodium (0.029 g, 1.25 mmol) and methyl iodide (0.078 mL, 1.25 mmol). Yield 0.027 g (46%). Colourless oil. R_F = 0.54 (hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.23–0.92 (br. m, 3 H), 1.33 (d, $J_{P,H}$ = 10.7 Hz), 1.64–1.77 (m, 2 H), 1.79–1.95 (m, 6 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.75 (d, $J_{P,C}$ = 31.8 Hz), 25.60 (d, $J_{P,C}$ = 36.3 Hz), 26.81 ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 23.56 ppm. GC (Phenomenex Zebron ZB-35 HT Inferno): R_T = 8.07 min. GC-MS (EI, 70 eV): *m*/*z* (%) = 115 (17) [M], 113 (16), 102 (100), 101 (30), 99 (21), 85 (10). $C_5H_{14}BP$ (115.95): calcd. C 51.79, H 12.17; found C 51.94, H 12.00.

Dimethylphenylphosphane–Borane (3): This compound was prepared by the General Procedure from **5** (0.107 g, 0.5 mmol), sodium (0.029 g, 1.25 mmol) and methyl iodide (0.078 mL, 1.25 mmol). Yield 0.065 g (86%). The analytical data are in accordance with those reported in the literature.[27]

(3-Benzylcyclohexa-1,4-dien-3-yl)-*tert*-butylmethylphosphane–Borane (1b): This compound was prepared by the General Procedure from **1** (0.097 g, 0.5 mmol), potassium (0.049 g, 1.25 mmol) and benzyl chloride (0.126 mL, 1 mmol). Yield 0.106 g (74%). Colourless pasty solid. R_F = 0.54 (hexane/EtOAc 6:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.19 to 0.89 (br. m, 3 H), 1.20 (d, $J_{P,H}$ = 12.9 Hz, 9 H), 1.21 (d, $J_{P,H}$ = 10.1 Hz, 3 H), 2.00–2.43 (m, 2 H), 2.86–3.17 (dd, $J_{H,H}$ = 5.8 Hz, $J_{P,H}$ = 13.0 Hz, 2 H), 5.60–5.69 (m, 3 H), 5.77–5.85 (m, 1 H), 7.06–7.14 (m, 3 H), 7.15–7.26 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 3.28 (d, $J_{P,C}$ = 33.9 Hz), 25.83 (d, $J_{P,C}$ = 4.6 Hz), 27.35 (d, $J_{P,C}$ = 1.7 Hz), 31.70 (d, $J_{P,C}$ = 26.4 Hz), 42.39 (d, $J_{P,C}$ = 5.2 Hz), 42.80 (d, $J_{P,C}$ = 27.6 Hz), 126.56, 126.66 (d, $J_{P,C}$ = 6.9 Hz), 126.91 (d, $J_{P,C}$ = 7.5 Hz), 128.16 (d, $J_{P,C}$ = 9.8 Hz), 128.27 (d, $J_{P,C}$ = 2.3 Hz), 129.97 (d, $J_{P,C}$ = 4.0 Hz), 132.76 (d, $J_{P,C}$ = 8.6 Hz), 132.89 (d, $J_{P,C}$ = 5.2 Hz) ppm. ^{31}P NMR (161.5 MHz, $CDCl_3$): δ = 40.28 ppm. GC (Phenomenex Zebron ZB-35 HT Inferno): R_T = 11.74 min. GC-MS (EI, 70 eV): *m*/*z* (%) = 169 (13), 168 (97), 167 (100), 153 (28), 152 (28), 141 (4), 139 (4), 128 (4), 115 (8), 91 (28), 89 (10), 83 (14), 65 (16), 63 (11). $C_{18}H_{28}BP$ (286.20): calcd. C 75.54, H 9.86; found C 75.50, H 9.99.

***tert*-Butyl(1,2-diphenylethyl)phenylphosphane–Borane (2b):** This compound was prepared by the General Procedure from **2** (0.135 g, 0.5 mmol), sodium (0.029 g, 1.25 mmol) and benzyl chloride (0.126 mL, 1 mmol). Yield 0.092 g (51%). White solid; m.p. 109.4–110.8 °C. R_F = 0.86 (hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.33–1.05 (m, 3 H), 0.87 (d, $J_{P,H}$ = 13.6 Hz, 9 H), 2.76–2.83 (m, 1 H), 3.12–3.19 (m, 1 H), 3.79–3.87 (m, 1 H), 6.64–6.68 (m, 2 H), 7.05–7.09 (m, 3 H), 7.10–7.38 (m, 5 H), 7.58–7.62 (m, 3 H), 8.06–8.11 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 26.01 (d, $J_{P,C}$ = 1.8 Hz), 30.96 (d, $J_{P,C}$ = 28.2 Hz), 39.21 (d, $J_{P,C}$ = 4.5 Hz), 42.31 (d, $J_{P,C}$ = 26.3 Hz), 126.08, 127.42 (d, $J_{P,C}$ = 9.2 Hz), 127.43 (d, $J_{P,C}$ = 1.7 Hz), 127.50 (d, $J_{P,C}$ = 46.6 Hz), 127.97, 128.10 (d, $J_{P,C}$ = 9.5 Hz), 128.55 (d, $J_{P,C}$ = 9.2 Hz), 128.56, 131.29 (d, $J_{P,C}$ = 2.9 Hz), 136.86, 139.40 (d, $J_{P,C}$ = 12.9 Hz) ppm. ^{31}P NMR (161.5 MHz, $CDCl_3$): δ = 39.73 ppm. GC (Phenomenex Zebron ZB-35 HT Inferno): R_T = 12.55 min. GC-MS (EI, 70 eV): *m*/*z* (%) = 346 (12) [M – BH_3], 345 (10), 290 (6), 255 (7), 199 (13),

182 (15), 181 (100), 180 (24), 179 (11), 167 (17), 166 (32), 165 (25), 121 (17), 110 (14), 109 (29), 103 (34), 91 (24). $C_{24}H_{30}BP$ (360.28): calcd. C 80.01, H 8.39; found C 79.75, H 8.50.

(3-Benzylcyclohexa-1,4-dien-3-yl)dimethylphosphane–Borane (3b): This compound was prepared by the General Procedure from **3** (0.076 g, 0.5 mmol), sodium (0.029 g, 1.25 mmol) and benzyl chloride (0.126 mL, 1 mmol). Yield 0.082 g (67%). Colourless solid; m.p. 83.9–85.5 °C. R_F = 0.43 (hexane/EtOAc 6:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.03 to 1.21 (br. m, 3 H), 1.29 (d, $J_{P,H}$ = 9.5 Hz, 6 H), 2.91 (d, $J_{P,H}$ = 7.6 Hz, 2 H), 5.52–5.61 (m, 1 H), 5.71–5.80 (m, 1 H), 7.01–7.12 (m, 3 H), 7.15–7.26 (m, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 7.42 (d, $J_{P,C}$ = 36.3 Hz), 26.21 (d, $J_{P,C}$ = 4.5 Hz), 40.23 (d, $J_{P,C}$ = 33.6 Hz), 40.69 (d, $J_{P,C}$ = 5.5 Hz), 124.95 (d, $J_{P,C}$ = 3.6 Hz), 126.28, 127.60, 128.04 (d, $J_{P,C}$ = 8.2 Hz), 130.28, 136.92 (d, $J_{P,C}$ = 12.7 Hz) ppm. ^{31}P NMR (161.5 MHz, $CDCl_3$): δ = 22.94 ppm. GC (Phenomenex Zebron ZB-35 HT Inferno): R_T = 8.78 min. GC-MS (EI, 70 eV): *m*/*z* (%) = 168 (10), 167 (12), 153 (5), 152 (5), 91 (100), 65 (17). $C_{15}H_{22}BP$ (244.12): calcd. C 73.80, H 9.08; found C 73.52, H 8.81.

Benzyldimethylphosphane–Borane (3b′): This compound was prepared by the General Procedure from **3** (0.076 g, 0.5 mmol), sodium (0.029 g, 1.25 mmol) and benzyl chloride (0.126 mL, 1 mmol). It was isolated as a mixture with **3**, yield 30% (based on NMR). R_F = 0.47 (hexane/EtOAc 6:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.11 to 1.06 (br. m, 3 H), 1.13 (d, $J_{P,H}$ = 10.4 Hz, 6 H), 2.95 (d, $J_{P,H}$ = 10.5 Hz, 2 H), 7.03–7.10 (m, 2 H), 7.15–7.29 (m, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.14 (d, $J_{P,C}$ = 37.6 Hz), 34.29 (d, $J_{P,C}$ = 31.0 Hz), 126.99 (d, $J_{P,C}$ = 2.9 Hz), 128.59 (d, $J_{P,C}$ = 2.6 Hz), 129.38 (d, $J_{P,C}$ = 4.0 Hz), 132.51 (d, $J_{P,C}$ = 8.1 Hz) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 5.86 ppm. GC (Phenomenex Zebron ZB-35 HT Inferno): R_T = 11.74 min. GC-MS (EI, 70 eV): *m*/*z* (%) = 152 (25) [M – BH_3], 109 (5), 91 (100), 65 (20).

1-(3-Benzylcyclohexa-1,4-dien-3-yl)phospholane–Borane (4b): This compound was prepared by the General Procedure from **4** (0.089 g, 0.5 mmol), sodium (0.029 g, 1.25 mmol) and benzyl chloride (0.126 mL, 1 mmol). Yield 0.124 g (92%). Colourless solid; m.p. 87.4–88.7 °C. R_F = 0.67 (hexane/EtOAc 6:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.03–1.24 (br. m, 3 H), 1.54–1.82 (m, 6 H), 1.87–2.07 (m, 2 H), 2.31–2.58 (m, 2 H), 2.97 (d, $J_{P,H}$ = 9.1 Hz, 2 H), 5.56–5.63 (m, 2 H), 5.71–5.79 (m, 2 H), 7.04–7.19 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.88 (d, $J_{P,C}$ = 33.3 Hz), 26.32 (d, $J_{P,C}$ = 4.6 Hz), 27.21 (d, $J_{P,C}$ = 0.9 Hz), 40.43 (d, $J_{P,C}$ = 26.4 Hz), 42.20 (d, $J_{P,C}$ = 5.8 Hz), 125.55 (d, $J_{P,C}$ = 4.3 Hz), 126.33, 127.51 (d, $J_{P,C}$ = 7.8 Hz), 127.64, 130.35, 136.70 (d, $J_{P,C}$ = 11.2 Hz) ppm. ^{31}P NMR (161.5 MHz, $CDCl_3$): δ = 51.15 ppm. $C_{17}H_{24}BP$ (270.16): calcd. C 75.58, H 8.95; found C 75.75, H 8.96.

1-Benzylphospholane–Borane (4b′): This compound was prepared by the General Procedure from **4** (0.089 g, 0.5 mmol), sodium (0.029 g, 1.25 mmol) and benzyl chloride (0.126 mL, 1 mmol). It was isolated as a mixture with starting material, yield 30% (based on NMR). R_F = 0.60 (hexane/EtOAc 6:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.03 to 1.21 (br. m, 3 H), 1.55–1.84 (m, 8 H), 3.00 (d, $J_{P,H}$ = 10.70 Hz, 2 H), 7.04–7.14 (m, 3 H), 7.23–7.32 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.20 (d, $J_{P,C}$ = 37.4 Hz), 27.49 (d, $J_{P,C}$ = 1.4 Hz), 33.06 (d, $J_{P,C}$ = 24.7 Hz), 126.95 (d, $J_{P,C}$ = 2.9 Hz), 128.65 (d, $J_{P,C}$ = 2.6 Hz), 129.38 (d, $J_{P,C}$ = 4.0 Hz), 131.33 (d, $J_{P,C}$ = 8.9 Hz) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 32.92 ppm. GC (Phenomenex Zebron ZB-35HT INFERNO): R_T = 7.25 min. GC-MS (EI, 70 eV): *m*/*z* (%) = 178 (18) [M – BH_3], 150 (16), 92 (11), 91 (100), 65 (23).

(3-Benzylcyclohexa-1,4-dien-3-yl)methylphenylphosphane–Borane (5b): This compound was prepared by the General Procedure from **5** (0.107 g, 0.5 mmol), sodium (0.029 g, 1.25 mmol) and benzyl chloride (0.126 mL, 1 mmol). It was isolated as a mixture with **5b′**, yield 25% (based on NMR). R_F = 0.61 (hexane/EtOAc 6:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.23–1.41 (br. m, 3 H), 1.60 (d, $J_{P,H}$ = 9.5 Hz, 3 H), 2.23–2.34 (m, 2 H), 3.18–3.29 (m, 2 H), 5.31–5.40 (m, 1 H), 5.77–5.86 (m, 3 H), 6.96–7. 03 (m, 2 H), 7.12–7.19 (m, 3 H), 7.42–7.59 (m, 3 H), 7.74–7.82 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 5.84 (d, $J_{P,C}$ = 40.2 Hz), 26.14 (d, $J_{P,C}$ = 4.9 Hz), 35.90 (d, $J_{P,C}$ = 31.0 Hz), 40.85 (d, $J_{P,C}$ = 6.6 Hz), 125.32 (d, $J_{P,C}$ = 8.6 Hz), 125.36 (d, $J_{P,C}$ = 4.3 Hz), 126.16, 126.71 (d, $J_{P,C}$ = 48.0 Hz), 127.50, 128.16 (d, $J_{P,C}$ = 9.5 Hz), 129.69 (d, $J_{P,C}$ = 4.3 Hz), 130.23, 131.79 (d, $J_{P,C}$ = 2.6 Hz), 133.40 (d, $J_{P,C}$ = 8.1 Hz) ppm. ^{31}P NMR (161.5 MHz, $CDCl_3$): δ = 25.52 ppm.

Benzylmethylphenylphosphane–Borane (5b′): This compound was prepared by the General Procedure from **5** (0.107 g, 0.5 mmol), sodium (0.029 g, 1.25 mmol) and benzyl chloride (0.126 mL, 1 mmol). It was isolated as a mixture with **5b**, yield 60% (based on NMR). R_F = 0.55 (hexane/EtOAc 6:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.23–1.41 (br. m, 3 H), 1.52 (d, $J_{P,H}$ = 9.8 Hz, 3 H), 2.59–2.68 (m, 2 H), 6.90–6.95 (m, 2 H), 7.21–7.26 (m, 3 H), 7.39–7.60 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.89 (d, $J_{P,C}$ = 39.1 Hz), 41.99 (d, $J_{P,C}$ = 31.0 Hz), 126.55 (d, $J_{P,C}$ = 2.9 Hz), 128.19 (d, $J_{P,C}$ = 8.9 Hz), 128.24 (d, $J_{P,C}$ = 2.0 Hz), 128.32 (d, $J_{P,C}$ = 4.9 Hz), 128.55 (d, $J_{P,C}$ = 10.1 Hz), 131.34 (d, $J_{P,C}$ = 2.6 Hz), 131.74 (d, $J_{P,C}$ = 9.2 Hz), 131.95 (d, $J_{P,C}$ = 46.3 Hz) ppm. ^{31}P NMR (161.5 MHz, $CDCl_3$): δ = 10.69 ppm. GC (Phenomenex Zebron ZB-5MSI): R_T = 8.85 min. GC-MS (EI, 70 eV): *m*/*z* (%) = 214 (26) [M – BH_3], 213 (30), 167 (4), 123 (37), 121 (34), 107 (9), 91 (100), 79 (11), 77 (21).

Benzyl-*tert*-butyl(cyclohexa-1,4-dien-3-yl)phosphane–Borane (2c): This compound was prepared by the General Procedure from **2** (0.135 g, 0.5 mmol), sodium (0.029 g, 1.25 mmol) and cyclohexyl bromide (0.123 mL, 1 mmol). Yield 0.029 g (21%). The data are in accordance with those reported in the literature.[25]

***tert*-Butylphenylphosphane–Borane (2c′):** This compound was prepared by the General Procedure from **2** (0.135 g, 0.5 mmol), sodium (0.029 g, 1.25 mmol) and cyclohexyl bromide (0.123 mL, 1 mmol). Yield 0.032 g (35%). The data are in accordance with those reported in the literature.[39]

(Cyclohexa-1,4-dien-3-yl)dimethylphosphane–Borane (3c): This compound was prepared by the General Procedure from **3** (0.076 g, 0.5 mmol), sodium (0.029 g, 1.25 mmol) and cyclohexyl bromide (0.123 mL, 1 mmol). Yield 0.039 g (51%). The data are in accordance with those reported in the literature.[25]

1-(Cyclohexa-1,4-dien-3-yl)phospholane–Borane (4c): This compound was prepared by the General Procedure from **4** (0.089 g, 0.5 mmol), sodium (0.029 g, 1.25 mmol) and cyclohexyl bromide (0.123 mL, 1 mmol). Yield 0.042 g (47%). The data are in accordance with those reported in the literature.[25]

Methylphenylphosphane–Borane (5c): This compound was prepared by the General Procedure from **5** (0.107 g, 0.5 mmol), sodium (0.029 g, 1.25 mmol) and cyclohexyl bromide (0.123 mL, 1 mmol). It was isolated as a mixture with starting material, yield 45% (based on NMR). R_F = 0.65 (hexane/EtOAc 6:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.15–1.29 (br. m, 3 H), 1.53 (dd, $J_{H,H}$ = 6.0 Hz, $J_{P,H}$ = 11.2 Hz), 5.48 (dm, $J_{P,H}$ = 371.3 Hz, 1 H), 7.31–7.48 (m, 3 H), 7.55–7.67 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.03 (d, $J_{P,C}$ = 38.8 Hz), 126.29 (d, $J_{P,C}$ = 56.9 Hz), 128.90 (d, $J_{P,C}$ = 10.4 Hz), 131.51 (d, $J_{P,C}$ = 2.9 Hz), 132.13 (d, $J_{P,C}$ =

9.2 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –15.47 ppm. GC (Phenomenex Zebron ZB-35HT INFERNO): R_T = 5.99 min. GC-MS (EI, 70 eV): *m*/*z* (%) = 124 (100) [M – BH_3], 121 (12), 109 (80), 108 (59), 107 (31), 91 (9), 83 (12), 81 (10.).

***tert*-Butyl(3-cyanomethyl-cyclohexa-1,4-dien-3-yl)methylphosphane–Borane (1d):** This compound was prepared by the General Procedure from **1** (0.097 g, 0.5 mmol), potassium (0.049 g, 1.25 mmol) and chloroacetonitrile (0.063 mL, 1 mmol). Yield 0.079 g (67%). White solid; m.p. 93–94 °C. R_F = 0.27 (hexane/EtOAc 6:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –0.04 to 0.89 (br. m, 3 H), 1.21 (d, $J_{P,H}$ = 13.7 Hz, 9 H), 1.25 (d, $J_{P,H}$ = 9.0 Hz, 3 H), 2.62–2.72 (m, 1 H), 2.74–2.81 (m, 1 H), 2.84–2.90 (m, 1 H), 2.91–2.98 (m, 1 H), 5.66–5.72 (m, 1 H), 5.79–5.85 (m, 1 H), 6.07–6.14 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 3.39 (d, $J_{P,C}$ = 33.9 Hz), 26.29 (d, $J_{P,C}$ = 3.2 Hz), 26.94 (d, $J_{P,C}$ = 1.4 Hz), 28.35 (d, $J_{P,C}$ = 10.4 Hz), 31.59 (d, $J_{P,C}$ = 27.0 Hz), 38.98 (d, $J_{P,C}$ = 28.5 Hz), 116.51 (d, $J_{P,C}$ = 16.4 Hz), 124.07 (d, $J_{P,C}$ = 4.6 Hz), 124.26 (d, $J_{P,C}$ = 2.3 Hz), 129.11 (d, $J_{P,C}$ = 7.2 Hz), 129.58 (d, $J_{P,C}$ = 6.0 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 41.13 ppm. GC (Phenomenex Zebron ZB-35HT INFERNO): R_T = 9.43 min. GC-MS (EI, 70 eV): *m*/*z* (%) = 117 (100), 116 (42), 90 (58), 89 (32), 63 (15), 51 (17). $C_{13}H_{23}BNP$ (235.11): calcd. C 66.41, H 9.86; found C 66.53, H 9.91.

***tert*-Butylmethyl[3-(2-phenylethyl)cyclohexa-1,4-dien-3-yl]phosphane–Borane (1e):** This compound was prepared by the General Procedure from **1** (0.097 g, 0.5 mmol), potassium (0.049 g, 1.25 mmol) and 2-phenylethyl bromide (0.137 mL, 1 mmol). Yield 0.113 g (75%). Colourless oil. R_F = 0.75 (hexane/EtOAc 6:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.06–1.03 (br. m, 3 H), 1.20 (d, $J_{P,H}$ = 9.3 Hz, 3 H), 1.23 (d, $J_{P,H}$ = 12.8 Hz, 9 H), 1.93–2.03 (m, 1 H), 2.12–2.22 (m, 1 H), 2.43–2.56 (m, 2 H), 2.68–2.81 (m, 2 H), 5.68–5.74 (m, 1 H), 5.80–5.86 (m, 1 H), 5.95–6.01 (m, 2 H), 7.13–7.18 (m, 3 H), 7.18–7.25 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 3.14 (d, $J_{P,C}$ = 34.0 Hz), 26.41 (d, $J_{P,C}$ = 4.2 Hz), 27.36, 31.19 (d, $J_{P,C}$ = 8.8 Hz), 31.63 (d, $J_{P,C}$ = 26.3 Hz), 37.60 (d, $J_{P,C}$ = 3.4 Hz), 41.85 (d, $J_{P,C}$ = 28.2 Hz), 125.75, 127.04 (d, $J_{P,C}$ = 3.1 Hz), 127.13, 127.20 (d, $J_{P,C}$ = 8.0 Hz), 128.31, 128.38 ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 38.93 ppm. GC (Phenomenex Zebron ZB-5MSI): R_T = 11.13 min. GC-MS (EI, 70 eV): *m*/*z* (%) = 182 (15), 165 (15), 91 (100). $C_{19}H_{30}BP$ (300.23): calcd. C 76.01, H 10.07; found C 76.12, H 9.98.

***tert*-Butylmethyl[3-(prop-2-ynyl)cyclohexa-1,4-dien-3-yl]phosphane–Borane (1f):** This compound was prepared by the General Procedure from **1** (0.097 g, 0.5 mmol), potassium (0.049 g, 1.25 mmol) and propargyl bromide (0.108 mL, 80% in toluene, 1 mmol). It was isolated as a mixture with starting material, yield 75% (based on NMR). R_F = 0.63 (hexane/EtOAc 6:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –0.14–1.01 (br. m, 3 H), 1.21 (d, $J_{P,H}$ = 13.3 Hz, 9 H), 1.23 (d, $J_{P,H}$ = 9.1 Hz, 3 H), 1.95 (t, $J_{H,H}$ = 2.7 Hz, 1 H), 2.28–2.33 (m, 2 H), 2.70–2.75 (m, 2 H), 5.66–5.73 (m, 1 H), 5.74–5.81 (m, 1 H), 5.94–6.01 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 3.53 (d, $J_{P,C}$ = 33.6 Hz), 26.30 (d, $J_{P,C}$ = 3.6 Hz), 27.12 (d, $J_{P,C}$ = 1.8 Hz), 28.44 (d, $J_{P,C}$ = 8.2 Hz), 31.52 (d, $J_{P,C}$ = 27.3 Hz), 40.56 (d, $J_{P,C}$ = 28.2 Hz), 70.88 (d, $J_{P,C}$ = 2.7 Hz), 80.22 (d, $J_{P,C}$ = 15.4 Hz), 125.89 (d, $J_{P,C}$ = 4.5 Hz), 127.34 (d, $J_{P,C}$ = 7.3 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 41.26 ppm. GC (Phenomenex Zebron ZB-5MSI): R_T = 7.59 min. GC-MS (EI, 70 eV): *m*/*z* (%) = 220 (30) [M – BH_3], 219 (6), 164 (42), 163 (52), 162 (12), 149 (17), 147 (17), 133 (13), 124 (10), 117 (37), 116 (61), 115 (100), 91 (37).

***tert*-Butyl[3-(ethoxycarbonylmethyl)cyclohexa-1,4-dien-3-yl]-methylphosphane–Borane (1g):** This compound was prepared by the General Procedure from **1** (0.097 g, 0.5 mmol), potassium (0.049 g, 1.25 mmol) and ethyl bromoacetate (0.111 mL, 1 mmol). Yield 0.079 g (56%). Colourless oil. R_F = 0.31 (hexane/EtOAc 6:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.02–1.05 (m, 3 H), 1.18 (t, $J_{H,H}$ = 7.0 Hz, 3 H), 1.21 (d, $J_{P,H}$ = 9.1 Hz, 3 H), 1.24 (d, $J_{P,H}$ = 13.1 Hz, 9 H), 2.61–2.75 (m, 2 H), 2.77–2.82 (m, 2 H), 4.05 (q, $J_{H,H}$ = 7.0 Hz, 3 H), 5.75–5.81 (m, 1 H), 5.88–5.96 (m, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 3.22 (d, $J_{P,C}$ = 34.8 Hz), 14.21, 26.27 (d, $J_{P,C}$ = 4.6 Hz), 27.37 (d, $J_{P,C}$ = 1.4 Hz), 31.82 (d, $J_{P,C}$ = 24.7 Hz), 40.71 (d, $J_{P,C}$ = 27.9 Hz), 42.16 (d, $J_{P,C}$ = 6.0 Hz), 60.34, 126.11 (d, $J_{P,C}$ = 4.6 Hz), 126.17 (d, $J_{P,C}$ = 4.3 Hz), 126.74 (d, $J_{P,C}$ = 7.2 Hz), 127.09 (d, $J_{P,C}$ = 7.5 Hz), 169.84 (d, $J_{P,C}$ = 18.1 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 42.67 ppm. $C_{15}H_{28}BO_2P$ (282.17): calcd. C 63.85, H 10.00; found C 63.75, H 9.82.

***tert*-Butylmethyl[3-(prop-2-enyl)cyclohexa-1,4-dien-3-yl]phosphane–Borane (1h):** This compound was prepared by the General Procedure from **1** (0.097 g, 0.5 mmol), potassium (0.049 g, 1.25 mmol) and allyl chloride (0.082 mL, 1 mmol). It was isolated as a mixture with starting material, yield 35% (based on NMR). R_F = 0.65 (hexane/EtOAc 6:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.16 to 0.92 (br. m, BH_3), 1.17 (d, J = 12.9 Hz, 9 H), 1.25 (d, $J_{P,H}$ = 9.7 Hz, 3 H), 1.88–2.03 (m, 2 H), 2.04–2.27 (m, 2 H), 4.99–5.03 (m, 2 H), 5.47–6.05 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 3.24 (d, $J_{P,C}$ = 34.5 Hz), 25.50 (d, $J_{P,C}$ = 2.7 Hz), 26.35 (d, $J_{P,C}$ = 3.6 Hz), 31.64 (d, $J_{P,C}$ = 26.3 Hz), 33.79 (d, $J_{P,C}$ = 10.0 Hz), 41.50 (d, $J_{P,C}$ = 28.2 Hz), 117.01, 123.21 (d, $J_{P,C}$ = 5.5 Hz), 123.65 (d, $J_{P,C}$ = 8.2 Hz), 126.54 (d, $J_{P,C}$ = 8.2 Hz), 126.71 (d, $J_{P,C}$ = 4.5 Hz), 133.93 (d, $J_{P,C}$ = 11.8 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 40.12 ppm. GC (Phenomenex Zebron ZB-5MSI): R_T = 8.44 min. GC-MS (EI, 70 eV): *m*/*z* (%) = 222 (8) [M – BH_3], 221 (7), 125 (42), 123 (10), 109 (14), 103 (100), 91 (10), 79 (13), 77 (12).

***tert*-Butylmethyl[3-(but-3-enyl)-cyclohexa-1,4-dien-3-yl]phosphane–Borane (1i):** This compound was prepared by the General Procedure from **1** (0.097 g, 0.5 mmol), potassium (0.049 g, 1.25 mmol) and 4-bromobut-1-ene (0.051 mL, 1 mmol). Yield 0.072 g (57%). Colourless oil. R_F = 0.79 (hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.09–0.82 (br. m, 3 H), 1.19 (d, $J_{P,H}$ = 9.1 Hz, 3 H), 1.22 (d, $J_{P,H}$ = 12.9 Hz, 9 H), 1.72–1.80 (m, 1 H), 188–1.97 (m, 3 H), 2.64–2.73 (m, 2 H), 4.91–5.01 (m, 2 H), 5.59–5.63 (m, 1 H), 5.71–5.75 (m, 1 H), 5.77–5.84 (m, 1 H), 5.87–5.94 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 3.13 (d, $J_{P,C}$ = 34.5 Hz), 26.34 (d, $J_{P,C}$ = 4.5 Hz), 27.37 (d, $J_{P,C}$ = 1.8 Hz), 29.18 (d, $J_{P,C}$ = 10.0 Hz), 31.59 (d, $J_{P,C}$ = 25.4 Hz), 34.99 (d, $J_{P,C}$ = 3.6 Hz), 41.69 (d, $J_{P,C}$ = 28.2 Hz), 114.59, 126.93 (d, $J_{P,C}$ = 8.2 Hz), 127.03 (d, $J_{P,C}$ = 1.8 Hz), 138.35 ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 39.35 ppm. $C_{15}H_{28}BP$ (250.17): calcd. C 72.02, H 11.28; found C 72.30, H 11.50.

{3-[(2-Bromophenyl)methyl]cyclohexa-1,4-dien-3-yl}-*tert*-butylmethylphosphane–Borane (1j): This compound was prepared by the General Procedure from **1** (0.097 g, 0.5 mmol), potassium (0.049 g, 1.25 mmol) and 2-bromobenzyl bromide (0.250 g, 1 mmol). Yield 0.069 g (38%). Colourless crystals; m.p. 95.3–97.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.10–1.03 (br. m, 3 H), 1.28 (d, $J_{P,H}$ = 12.9 Hz, 9 H), 1.35 (d, $J_{P,H}$ = 9.1 Hz, 3 H), 2.08–2.21 (m, 1 H), 2.35–2.49 (m, 1 H), 3.24–3.37 (m, 2 H), 5.64–5.70 (m, 1 H), 5.74–5.81 (m, 1 H), 5.86–5.93 (m, 1 H), 6.01–6.08 (m, 1 H), 6.99–7.04 (m, 1 H), 7.09–7.17 (m, 2 H), 7.44–7.49 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 3.31 (d, $J_{P,C}$ = 33.9 Hz), 25.78 (d, $J_{P,C}$ = 4.0 Hz), 27.32 (d, $J_{P,C}$ = 1.2 Hz), 31.78 (d, $J_{P,C}$ = 26.4 Hz), 41.32 (d, $J_{P,C}$ = 6.3 Hz), 43.57 (d, $J_{P,C}$ = 28.2 Hz), 125.80 (d, $J_{P,C}$ = 5.2 Hz), 126.18, 126.40 (d, $J_{P,C}$ = 2.9 Hz), 127.00 (d, $J_{P,C}$ = 2.3 Hz), 127.11 (d, $J_{P,C}$ = 1.2 Hz), 127.84, 128.19 (d, JP,C = 9.2 Hz), 132.39, 132.63, 136.26 ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 40.13 ppm. GC (Phenomenex Zebron ZB-35HT INFERNO): R_T = 14.59 min.

GC-MS (EI, 70 eV): *m*/*z* (%) = 228 (25), 227 (100), 197 (8), 196 (5), 166 (5), 165 (19), 133 (5), 113 (6), 91 (14). $C_{18}H_{27}BBrP$ (365.10): calcd. C 59.22, H 7.45; found C 59.40, H 7.70.

[3-(2-Bromoethyl)cyclohexa-1,4-dien-3-yl]-*tert*-butylmethylphosphane–Borane (1k): This compound was prepared by the General Procedure from **1** (0.097 g, 0.5 mmol), potassium (0.049 g, 1.25 mmol) and 1,2-dibromoethane (0.172 mL, 2 mmol). Yield 0.073 g (48%). Colourless oil. R_F = 0.56 (hexane/EtOAc 6:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –0.16 to 0.90 (br. m, 3 H), 1.19 (d, $J_{P,H}$ = 9.0 Hz, 3 H), 1.22 (d, $J_{P,H}$ = 13.2 Hz, 9 H), 2.8–2.31 (m, 1 H), 2.35–2.48 (m, 1 H), 2.62–2.73 (m, 2 H), 3.19–3.26 (m, 2 H), 5.59–5.61 (m, 1 H), 5.72–5.80 (m, 1 H), 5.91–6.00 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 5.69 (d, $J_{P,C}$ = 37.9 Hz), 26.76 (d, $J_{P,C}$ = 4.6 Hz), 27.78 (d, $J_{P,C}$ = 1.4 Hz), 29.17 (d, $J_{P,C}$ = 11.8 Hz), 32.21 (d, $J_{P,C}$ = 25.9 Hz), 39.48 (d, $J_{P,C}$ = 5.2 Hz), 42.74 (d, $J_{P,C}$ = 27.3 Hz), 126.23 (d, $J_{P,C}$ = 4.3 Hz), 126.28 (d, $J_{P,C}$ = 3.2 Hz), 128.24 (d, $J_{P,C}$ = 7.8 Hz), 128.40 (d, $J_{P,C}$ = 7.2 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 40.85 ppm. $C_{13}H_{25}BBrP$ (303.03): calcd. C 51.53, H 8.32; found C 51.74, H 8.65.

[3-(3-Bromopropyl)cyclohexa-1,4-dien-3-yl]-*tert*-butylmethylphosphane–Borane (1l): This compound was prepared by the General Procedure from **1** (0.097 g, 0.5 mmol), potassium (0.049 g, 1.25 mmol) and 1,3-dibromopropane (0.102 mL, 1 mmol). Yield 0.114 g (72%). Colourless solid; m.p. 57.6–59.1 °C. R_F = 0.59 (hexane/EtOAc 6:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –0.12 to 0.54 (br. m, 3 H), 1.13 (d, $J_{P,H}$ = 8.8 Hz, 3 H), 1.16 (d, $J_{P,H}$ = 12.9 Hz, 9 H), 1.64–1.98 (m, 4 H), 2.57–2.68 (m, 2 H), 3.32 (t, $J_{H,H}$ = 6.5 Hz, 2 H), 5.50–5.59 (m, 1 H), 5.62–5.70 (m, 1 H), 5.80–5.90 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 3.15 (d, $J_{P,C}$ = 34.5 Hz), 26.29 (d, $J_{P,C}$ = 4.0 Hz), 27.36 (d, $J_{P,C}$ = 1.4 Hz), 28.44 (d, $J_{P,C}$ = 9.5 Hz), 31.60 (d, $J_{P,C}$ = 25.9 Hz), 33.78, 34.33 (d, $J_{P,C}$ = 4.0 Hz), 41.40 (d, $J_{P,C}$ = 28.4 Hz), 126.80 (d, $J_{P,C}$ = 4.3 Hz), 126.82 (d, $J_{P,C}$ = 3.4 Hz), 127.18 (d, $J_{P,C}$ = 7.5 Hz), 127.28 (d, $J_{P,C}$ = 7.2 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 40.07 ppm. GC (Phenomenex Zebron ZB-5MSI): R_T = 7.57 min. GC-MS (EI, 70 eV): *m*/*z* (%) = 222 (8), 221 (6), 180 (14), 166 (39), 165 (10), 138 (41), 124 (20), 118 (73), 117 (19), 115 (13), 103 (11), 91 (100). $C_{14}H_{27}BBrP$ (317.05): calcd. C 53.04, H 8.58; found C 53.30, H 8.80.

***tert*-Butyl{3-[3-(diphenylboranatophosphanyl)propyl]cyclohexa-1,4-dien-3-yl}methylphosphane–Borane (12):** This compound was prepared by the General Procedure from **1** (0.097 g, 0.5 mmol), potassium (0.049 g, 1.25 mmol) and 3-bromopropyldiphenylphosphane–borane (**9**, 0.161 g, 0.5 mmol). Yield 0.103 g (47%). Colourless oil. R_F = 0.40 (hexane/EtOAc 6:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –0.06 to 1.81 (br. m, 6 H), 1.11 (d, $J_{P,H}$ = 9.2 Hz, 3 H), 1.16 (d, $J_{P,H}$ = 13.0 Hz, 9 H), 1.44–1.55 (m, 2 H), 1.66–1.76 (m, 1 H), 1.82–1.92 (m, 1 H), 2,17–2.26 (m, 2 H), 2.55–2.63 (m, 2 H), 5.46–5.54 (m, 1 H), 5.61–5.68 (m, 1 H), 5.79–5.88 (m, 2 H), 7.39–7.51 (m, 6 H), 7.59–7.67 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 3.07 (d, $J_{P,C}$ = 34.5 Hz), 18.64 (d, $J_{P,C}$ = 10.1 Hz), 25.72 (d, $J_{P,C}$ = 36.8 Hz), 26.25 (d, $J_{P,C}$ = 4.0 Hz), 27.33 (d, $J_{P,C}$ = 1.4 Hz), 29.43 (d, $J_{P,C}$ = 37.1 Hz), 31.57 (d, $J_{P,C}$ = 25.9 Hz), 36.86 (d, $J_{P,C}$ = 3.5 Hz), 126.53 (d, $J_{P,C}$ = 4.6 Hz), 126.58 (d, $J_{P,C}$ = 3.7 Hz), 127.21 (d, $J_{P,C}$ = 7.8 Hz), 127.36 (d, $J_{P,C}$ = 7.5 Hz), 128.77 (d, $J_{P,C}$ = 9.8 Hz), 129.61 (d, $J_{P,C}$ = 54.6 Hz), 129.69 (d, $J_{P,C}$ = 54.9 Hz), 131.08 (d, $J_{P,C}$ = 2.6 Hz), 132.03 (d, $J_{P,C}$ = 8.9 Hz), 132.04 (d, $J_{P,C}$ = 8.9 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 15.20, 38.68 ppm. GC (Phenomenex Zebron ZB-35HT INFERNO): R_T = 13.07 min. GC-MS (EI, 70 eV): *m*/*z* (%) = 304 (12), 303 (20), 275 (8), 262 (6), 200 (38), 199 (100), 185 (8), 183 (36), 152 (8), 121 (8), 108 (15), 107 (14), 91 (44). $C_{26}H_{40}B_2P_2$ (436.17): calcd. C 71.60, H 9.24; found C 71.91, H 9.50.

***tert*-Butyl{3-[4-(diphenylboranatophosphanyl)butyl]cyclohexa-1,4-dien-3-yl}methylphosphane–Borane (13):** This compound was prepared by the General Procedure from **1** (0.097 g, 0.5 mmol), potassium (0.049 g, 1.25 mmol) and 4-bromobutyldiphenylphosphane–borane (**10**, 0.168 g, 0.5 mmol). Yield 0.092 g (39%). White waxy solid. R_F = 0.40 (hexane/EtOAc 6:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.00–1.00 (br. m, 6 H), 1.15 (d, $J_{P,H}$ = 8.8 Hz, 3 H), 1.19 (d, $J_{P,H}$ = 12.9 Hz, 9 H), 1.46–1.50 (m, 2 H), 1.50–1.59 (m, 2 H), 1.60–1.66 (m, 1 H), 1.73–1.83 (m, 1 H), 2.13–2.21 (m, 2 H), 2.59–2.67 (m, 2 H), 5.50–5.55 (m, 1 H), 5.63–5.67 (m, 1 H), 5.83–5.87 (m, 2 H), 7.40–7.50 (m, 6 H), 7.61–7.67 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 3.10 (d, $J_{P,C}$ = 35.1 Hz), 23.21, 25.73 (d, $J_{P,C}$ = 37.1 Hz), 26.29 (d, $J_{P,C}$ = 4.3 Hz), 26.35 (d, $J_{P,C}$ = 9.2 Hz), 27.34 (d, $J_{P,C}$ = 1.2 Hz), 31.58 (d, $J_{P,C}$ = 26.2 Hz), 35.17 (d, $J_{P,C}$ = 3.5 Hz), 41.67 (d, $J_{P,C}$ = 28.2 Hz), 126.76 (d, $J_{P,C}$ = 8.1 Hz), 126.86 (d, $J_{P,C}$ = 7.5 Hz), 127.03 (d, $J_{P,C}$ = 4.6 Hz), 127.08 (d, $J_{P,C}$ = 3.5 Hz), 128.75 (d, $J_{P,C}$ = 10.1 Hz), 127.47 (d, $J_{P,C}$ = 54.9 Hz), 129.52 (d, $J_{P,C}$ = 54.9 Hz), 131.06 (d, $J_{P,C}$ = 2.3 Hz), 132.06 (d, $J_{P,C}$ = 8.9 Hz), 132.07 (d, $J_{P,C}$ = 9.2 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 25.00, 38.60 ppm. GC (Phenomenex Zebron ZB-35HT INFERNO): R_T = 13.78 min. GC-MS (EI, 70 eV): *m*/*z* (%) = 318 (13), 289 (24), 262 (8), 213 (12), 200 (16), 199 (46), 187 (9), 186 (67), 183 (34), 152 (8), 121 (14), 109 (16), 108 (100), 107 (20), 91 (47). $C_{27}H_{42}B_2P_2$ (450.19): calcd. C 72.03, H 9.40; found C 72.22, H 9.72.

***tert*-Butyl{3-[4-(*tert*-butylphenylboranatophosphanyl)butyl]cyclohexa-1,4-dien-3-yl}methylphosphane–Borane (14):** This compound was prepared as a mixture of diastereoisomers by the General Procedure from **1** (0.097 g, 0.5 mmol), potassium (0.049 g, 1.25 mmol) and *tert*-butyl(4-bromobutyl)phenylphosphane–borane (**11**, 0.158 g, 0.5 mmol). It was isolated as a mixture of diastereoisomers, yield 0.067 g (31%). Colourless oil. R_F = 0.44 (hexane/EtOAc 6:1). Major diastereoisomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.01–1.01 (br. m, 6 H), 1.06 (d, $J_{P,H}$ = 13.6 Hz, 9 H), 1.14 (d, $J_{P,H}$ = 9.1 Hz, 3 H), 1.18 (d, $J_{P,H}$ = 12.9 Hz, 9 H), 1.19–1.29 (m, 2 H), 1.53–1.70 (m, 2 H), 1.71–1.83 (m, 3 H), 2.04–2.15 (m, 1 H), 2.59–2.68 (m, 2 H), 5.50–5.59 (m, 1 H), 5.61–5.71 (m, 1 H), 5.82–5.90 (m, 2 H), 7.42–7.52 (m, 3 H), 7.63–7.69 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 3.11 (d, $J_{P,C}$ = 34.5 Hz), 18.70 (d, $J_{P,C}$ = 33.6 Hz), 23.26, 25.36 (d, $J_{P,C}$ = 1.8 Hz), 26.26 (d, $J_{P,C}$ = 4.5 Hz), 26.65 (dd, $J_{P,C}$ = 9.1, $J_{P,C}$ = 13.6 Hz), 27.25 (d, $J_{P,C}$ = 1.8 Hz), 28.90 (d, $J_{P,C}$ = 32.7 Hz), 31.52 (d, $J_{P,C}$ = 25.4 Hz), 35.22 (d, $J_{P,C}$ = 2.7 Hz), 41.45 (d, $J_{P,C}$ = 28.2 Hz), 125.94 (d, $J_{P,C}$ = 48.1 Hz), 126.61 (d, $J_{P,C}$ = 8.2 Hz), 126.78 (d, $J_{P,C}$ = 7.3 Hz), 126.96 (d, $J_{P,C}$ = 4.5 Hz), 127.07 (d, $J_{P,C}$ = 2.7 Hz), 128.22 (d, $J_{P,C}$ = 9.1 Hz), 130.98 (d, $J_{P,C}$ = 3.6 Hz), 133.27 (d, $J_{P,C}$ = 8.2 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 31.17, 39.10 ppm. Minor diastereoisomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.01–1.01 (br. m, 6 H), 1.06 (d, $J_{P,H}$ = 13.6 Hz, 9 H), 1.14 (d, $J_{P,H}$ = 9.1 Hz, 3 H), 1.18 (d, $J_{P,H}$ = 12.9 Hz, 9 H), 1.19–1.29 (m, 2 H), 1.53–1.70 (m, 2 H), 1.71–1.83 (m, 3 H), 2.04–2.15 (m, 1 H), 2.59–2.68 (m, 2 H), 5.50–5.59 (m, 1 H), 5.61–5.71 (m, 1 H), 5.82–5.90 (m, 2 H), 7.42–7.52 (m, 3 H), 7.63–7.69 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 2.97 (d, $J_{P,C}$ = 33.6 Hz), 18.56 (d, $J_{P,C}$ = 33.6 Hz), 23.33, 25.36 (d, $J_{P,C}$ = 1.8 Hz), 26.23 (d, $J_{P,C}$ = 4.5 Hz), 26.90 (dd, $J_{P,C}$ = 10.0, $J_{P,C}$ = 12.7 Hz), 27.37, 28.90 (d, $J_{P,C}$ = 32.7 Hz), 31.52 (d, $J_{P,C}$ = 25.4 Hz), 35.19 (d, $J_{P,C}$ = 4.5 Hz), 41.90 (d, $J_{P,C}$ = 28.2 Hz), 125.92 (d, $J_{P,C}$ = 48.1 Hz), 126.90 (d, $J_{P,C}$ = 8.2 Hz), 127.07 (d, $J_{P,C}$ = 2.7 Hz), 127.11 (d, $J_{P,C}$ = 7.3 Hz), 127.12 (d, $J_{P,C}$ = 4.5 Hz), 128.23 (d, $J_{P,C}$ = 9.1 Hz), 130.98 (d, $J_{P,C}$ = 3.6 H), 133.27 (d, $J_{P,C}$ = 8.2 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 31.17, 39.10 ppm. GC (Phenomenex Zebron ZB-5MSI): R_T = 16.78 min. GC-MS (EI, 70 eV): *m*/*z* (%) = 298 (17), 200 (15), 199 (26), 166 (39), 124 (100), 110 (76),

109 (58), 108 (24), 91 (57). $C_{25}H_{46}B_2P_2$ (430.20): calcd. C 69.80, H 10.78; found C 70.03, H 11.03.

***tert*-Butyl[3-(diphenylboranatophosphanyl)propyl]methylphosphane–Borane (15):** This compound was prepared by the General Procedure from **1** (0.097 g, 0.5 mmol), potassium (0.049 g, 1.25 mmol) and 3-bromopropyldiphenylphosphane–borane (**9**, 0.161 g, 0.5 mmol). Yield 0.048 g (23%). Pasty white solid. R_F = 0.23 (hexane/EtOAc 6:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –0.09 to 0.80 (br. m, 6 H), 1.08 (d, $J_{P,H}$ = 13.5 Hz, 9 H), 1.11 (d, $J_{P,H}$ = 9.4 Hz, 3 H), 1.55–1.72 (m, 2 H), 1.74–1.94 (m, 2 H), 2.22–2.34 (m, 2 H), 2.42–2.54 (m, 2 H), 7.41–7.53 (m, 6 H), 7.65–7.73 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 4.97 (d, $J_{P,C}$ = 34.5 Hz), 17.56 (d, $J_{P,C}$ = 1.2 Hz), 22.27 (dd, $J_{P,C}$ = 10.9 Hz, $J_{P,C}$ = 31.0 Hz), 24.92 (d, $J_{P,C}$ = 2.3 Hz), 27.06 (dd, $J_{P,C}$ = 10.9 Hz, $J_{P,C}$ = 36.2 Hz), 27.24 (d, $J_{P,C}$ = 34.5 Hz), 128.75 (d, $J_{P,C}$ = 55.2 Hz), 128.86 (d, $J_{P,C}$ = 9.8 Hz), 128.91 (d, $J_{P,C}$ = 10.4 Hz), 129.48 (d, $J_{P,C}$ = 55.2 Hz), 131.26 (d, $J_{P,C}$ = 2.3 Hz), 131.35 (d, $J_{P,C}$ = 2.3 Hz), 132.02 (d, $J_{P,C}$ = 9.2 Hz), 132.18 (d, $J_{P,C}$ = 9.2 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 14.96, 25.24 ppm. GC (Phenomenex Zebron ZB-35HT INFERNO): R_T = 18.11 min. GC-MS (EI, 70 eV): *m*/*z* (%) = 274 (17), 273 (100), 258 (5), 185 (6), 183 (13), 139 (5), 121 (8), 91 (5), 57 (12). $C_{20}H_{34}B_2P_2$ (358.05): calcd. C 67.09, H 9.57; found C 67.01, H 9.90.

***tert*-Butyl[4-(diphenylboranatophosphanyl)butyl]methylphosphane–Borane (16):** This compound was prepared by the General Procedure from **1** (0.097 g, 0.5 mmol), potassium (0.049 g, 1.25 mmol) and 4-bromobutyldiphenylphosphane–borane (**10**, 0.161 g, 0.5 mmol). Yield 0.035 g (16%). White solid; m.p. 126.7–128.3 °C. R_F = 0.37 (hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.09–1.09 (br. m, 6 H), 1.13 (d, $J_{P,H}$ = 13.5 Hz, 9 H), 1.14 (d, $J_{P,H}$ = 9.7 Hz, 3 H), 1.43–1.78 (m, 6 H), 2.11–2.35 (m, 2 H), 7.14–7.51 (m, 6 H), 7.61–7.70 (m, 4 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 5.09 (d, $J_{P,C}$ = 33.6 Hz), 20.93 (d, $J_{P,C}$ = 32.7 Hz), 24.94 (d, $J_{P,C}$ = 6.4 Hz), 25.01 (d, $J_{P,C}$ = 1.8 Hz), 25.05 (d, $J_{P,C}$ = 4.5 Hz), 25.43 (dd, $J_{P,C}$ = 5.5 Hz, $J_{P,C}$ = 36.3 Hz), 27.21 (d, $J_{P,C}$ = 34.5 Hz), 128.83 (d, $J_{P,C}$ = 10.0 Hz), 128.87 (d, $J_{P,C}$ = 10.0 Hz), 129.19 (d, $J_{P,C}$ = 55.2 Hz), 129.42 (d, $J_{P,C}$ = 55.2 Hz), 131.21 (d, $J_{P,C}$ = 2.7 Hz), 131.26 (d, $J_{P,C}$ = 2.7 Hz), 132.00 (d, $J_{P,C}$ = 8.1 Hz), 132.12 (d, $J_{P,C}$ = 7.8 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 15.54, 25.74 ppm. GC (Phenomenex Zebron ZB-35HT INFERNO): R_T = 13.10 min. GC-MS (EI, 70 eV): *m*/*z* (%) = 288 (18), 287 (100), 185 (7), 183 (15), 121 (5), 108 (11). $C_{21}H_{36}B_2P_2$ (372.08): calcd. C 67.79, H 9.75; found C 67.85, H 9.90.

1,3-Bis[3-(*tert*-butylmethylboranatophosphanyl)cyclohexa-1,4-dien-3-yl]propane (17): This compound was prepared by the General Procedure from **1** (0.097 g, 0.5 mmol), potassium (0.049 g, 1.25 mmol) and 1,3-dibromopropane (0.025 mL, 0.25 mmol) as a mixture of two diastereoisomers. Yield 0.041 g (38%). Colourless oil. R_F = 0.78 (hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.08–0.76 (br. m, 6 H), 1.16 (d, $J_{P,H}$ = 9.1 Hz, 6 H), 1.20 (d, $J_{P,H}$ = 12.9 Hz 18 H), 1.24–1.32 (m 2 H), 1.61–1.73 (m, 2 H), 1.74–1.86 (m, 2 H), 2.59–2.68 (m, 4 H), 5.52–5.59 (m, 2 H), 5.64–5.71 (m, 2 H), 5.83–5.90 (m, 4 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 3.07 (d, $J_{P,C}$ = 33.6 Hz), 3.09 (d, $J_{P,C}$ = 34.5 Hz), 20.17 (q, $J_{P,C}$ = 9.1 Hz), 26.31 (d, $J_{P,C}$ = 5.5 Hz), 27.37 (d, $J_{P,C}$ = 1.8 Hz), 31.58 (d, $J_{P,C}$ = 26.3 Hz), 35.56 (d, $J_{P,C}$ = 3.6 Hz), 35.58 (d, $J_{P,C}$ = 3.5 Hz), 41.94 (d, $J_{P,C}$ = 28.2 Hz), 42.00 (d, $J_{P,C}$ = 28.2 Hz), 126.58 (d, $J_{P,C}$ = 8.2 Hz), 126.61 (d, $J_{P,C}$ = 8.2 Hz), 126.69 (d, $J_{P,C}$ = 9.1 Hz), 127.16 (d, $J_{P,C}$ = 4.5 Hz), 127.22 (d, $J_{P,C}$ = 3.6 Hz), 127.26 (d, $J_{P,C}$ = 3.6 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 39.09 ppm.

1,2-Bis{[3-(*tert*-butylmethylboranatophosphanyl)cyclohexa-1,4-dien-3-yl]methyl}benzene (18): This compound was prepared by the General Procedure from **1** (0.097 g, 0.5 mmol), potassium (0.049 g, 1.25 mmol) and *o*-bis(bromomethyl)benzene (0.066 g, 0.25 mmol) as a mixture of two diastereoisomers. Yield 0.036 g (29%). White solid; m.p. 159.7–160.8 °C. R_F = 0.58 (hexane/EtOAc 6:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.14–1.41 (br. m, 6 H), 1.23 (d, $J_{P,H}$ = 12.8 Hz, 18 H), 1.43 (d, $J_{P,H}$ = 9.1 Hz, 6 H), 1.81–1.94 (m, 2 H), 2.23–2.36 (m, 2 H), 2.82–2.90 (m, 2 H), 3.28–3.36 (m, 2 H), 5.58–5.66 (m, 4 H), 5.72–5.80 (m, 2 H), 5.88–5.95 (m, 2 H), 6.89–6.99 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 3.34 (d, $J_{P,C}$ = 33.6 Hz), 25.79 (d, $J_{P,C}$ = 4.3 Hz), 27.32 (d, $J_{P,C}$ = 1.4 Hz), 31.78 (d, $J_{P,C}$ = 26.2 Hz), 41.31 (d, $J_{P,C}$ = 6.3 Hz), 43.59 (d, $J_{P,C}$ = 27.9 Hz), 125.79 (d, $J_{P,C}$ = 5.2 Hz), 126.18, 126.40 (d, $J_{P,C}$ = 2.9 Hz), 127.00 (d, $J_{P,C}$ = 2.3 Hz), 127.11 (d, $J_{P,C}$ = 1.2 Hz), 127.84, 128.20 (d, $J_{P,C}$ = 9.2 Hz), 132.39, 132.63, 136.26 ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 38.48 ppm. GC (Phenomenex Zebron ZB-35HT INFERNO): R_T = 16.79 min. GC-MS (EI, 70 eV): *m*/*z* (%) = 259 (6), 258 (29), 181 (14), 180 (100), 179 (88), 178 (32); 168 (6), 167 (47), 166 (14), 165 (59), 152 (24), 115 (10), 91 (19), 89 (13).

1,2-Bis{[3-(dimethylboranatophosphanyl)cyclohexa-1,4-dien-3-yl]methyl}benzene (19): This compound was prepared by the General Procedure from **3** (0.076 g, 0.5 mmol), sodium (0.029 g, 1.25 mmol) and *o*-bis(bromomethyl)benzene (0.066 g, 0.25 mmol). Yield 0.044 g (43%). Colourless oil. R_F = 0.27 (hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.19–0.93 (br. m, 6 H), 1.31 (d, $J_{P,H}$ = 9.5 Hz, 12 H), 2.22–2.33 (m, 2 H), 2.38–2.49 (m, 2 H), 3.10 (d, $J_{P,H}$ = 7.3 Hz, 4 H), 5.66–5.71 (m, 4 H), 5.79–5.85 (m, 4 H), 7.01–7.05 (m, 2 H), 7.05–7.09 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 7.62 (d, $J_{P,C}$ = 36.2 Hz), 26.05 (d, $J_{P,C}$ = 4.5 Hz), 36.96 (d, $J_{P,C}$ = 7.3 Hz), 40.92 (d, $J_{P,C}$ = 33.6 Hz), 124.66 (d, $J_{P,C}$ = 4.5 Hz), 125.49, 128.23 (d, $J_{P,C}$ = 9.1 Hz), 131.35, 135.77 (d, $J_{P,C}$ = 13.6 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 22.59 ppm. $C_{24}H_{38}B_2P_2$ (410.26): calcd. C 70.28, H 9.34; found C 70.60, H 9.55.

General Procedure for in situ P–Ph Bond Cleavage/Alkylation of Arylphosphane-Boranes: Gaseous ammonia was passed through a flame-dried three-necked flask (100 mL) fitted with inert gas inlet, dry-ice condenser and cooling bath (–78 °C) until 15 mL of it was condensed. Potassium (6 equiv.) was added and the mixture was stirred for 15 min. Phosphane–borane (1 equiv.) was then added, followed after 1 h at –33 °C by *t*BuCl (4 equiv.) and the mixture was cooled again and allowed to stir at –78 °C for 15 min. An electrophile (2 equiv.) was added and the mixture was stirred at the same temperature for 30 min. The reaction was quenched by addition of solid NH_4Cl (0.5 g), ammonia was evaporated, the residue was filtered, the solid was washed with CH_2Cl_2 (3 × 15 mL), and the collected organic phases were concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/EtOAc (6:1) as an eluent.

***tert*-Butylmethylphosphane–Borane (20):** This compound was prepared by the General Procedure from **1** (0.097 g, 0.5 mmol), potassium (0.117 g, 3 mmol), *tert*-butyl chloride (0.217 mL, 2 mmol) and ammonium chloride (0.5 g). Yield 0.034 g (57%). Colourless oil. R_F = 0.73 (hexane/EtOAc 6:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.09 to 1.03 (br. m, 3 H), 1.19 (d, $J_{P,H}$ = 14.6 Hz, 9 H), 1.30 (dd, $J_{H,H}$ = 6.1 Hz, $J_{P,H}$ = 10.8 Hz, 3 H), 4.39 (dm, $J_{P,H}$ = 355.1 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 2.13 (d, $J_{P,C}$ = 35.1 Hz), 25.96 (d, $J_{P,C}$ = 35.1 Hz), 26.21 (d, $J_{P,C}$ = 2.9 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 11.89 ppm. GC (Phenomenex Zebron ZB-35HT INFERNO): R_T = 8.12 min. GC-MS (EI, 70 eV): *m*/*z* (%) = 117 (7) [M – 1], 105 (7), 104 (100), 89 (13). $C_5H_{16}BP$ (117.97): calcd. C 50.91, H 13.67; found C 51.22, H 14.01.

***tert*-Butyldimethylphosphane–Borane (21):** This compound was prepared by the General Procedure from **1** (0.097 g, 0.5 mmol), potas-

sium (0.117 g, 3 mmol), *tert*-butyl chloride (0.217 mL, 2 mmol) and methyl iodide (0.062 mL, 1 mmol). Yield 0.021 g (31%). Colourless solid; m.p. 74.5–77.1 °C (subl.). R_F = 0.84 (hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.11–0.77 (br. m, 3 H), 1.16 (d, $J_{P,H}$ = 13.6 Hz, 9 H), 1.23 (d, $J_{P,H}$ = 9.8 Hz, 6 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 7.32 (d, $J_{P,C}$ = 35.4 Hz), 24.78 (d, $J_{P,C}$ = 2.7 Hz), 26.67 (d, $J_{P,C}$ = 35.4 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 20.25 ppm. GC (Phenomenex Zebron ZB-35HT INFERNO): R_T = 4.11 min. GC-MS (EI, 70 eV): *m/z* (%) = 118 (79) [M – BH_3], 88 (16), 74 (23), 73 (13), 63 (17), 62 (100), 61 (14), 59 (15), 57 (78). $C_6H_{18}BP$ (131.99): calcd. C 54.60, H 13.75; found C 54.92, H 13.77.

Benzyl-*tert*-butylmethylphosphane–Borane (22): This compound was prepared by the General Procedure from **1** (0.097 g, 0.5 mmol), potassium (0.117 g, 3 mmol), *tert*-butyl chloride (0.217 mL, 2 mmol) and benzyl chloride (0.126 mL, 1 mmol). Yield 0.056 g (54%). Colourless solid; m.p. 83.1–84.7 °C. R_F = 0.79 (hexane/EtOAc 6:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.22 to 0.98 (br. m, 3 H), 0.95 (d, $J_{P,H}$ = 9.4 Hz, 3 H), 1.13 (d, $J_{P,H}$ = 13.7 Hz, 9 H), 2.82–3.04 (m, 2 H), 7.11–7.27 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 4.58 (d, $J_{P,C}$ = 35.3 Hz), 25.16 (d, $J_{P,C}$ = 2.0 Hz), 27.75 (d, $J_{P,C}$ = 31.9 Hz), 28.96 (d, $J_{P,C}$ = 28.2 Hz), 126.81 (d, $J_{P,C}$ = 2.9 Hz), 128.56 (d, $J_{P,C}$ = 2.6 Hz), 130.00 (d, $J_{P,C}$ = 3.7 Hz), 132.93 (d, $J_{P,C}$ = 5.5 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 27.94 ppm. GC (Phenomenex Zebron ZB-35HT INFERNO): R_T = 11.02 min. GC-MS (EI, 70 eV): *m/z* (%) = 194 (15) [M – BH_3], 138 (33), 91 (100), 57 (33). $C_{12}H_{22}BP$ (208.09): calcd. C 69.26, H 10.66; found C 69.55, H 10.99.

Phospholane–Borane (23): This compound was prepared by the General Procedure from **4** (0.089 g, 0.5 mmol), potassium (0.117 g, 3 mmol), *tert*-butyl chloride (0.217 mL, 2 mmol) and ammonium chloride (0.5 g). Yield 0.030 g (58%). Colourless oil. R_F = 0.42 (hexane/EtOAc 6:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.01 to 1.23 (br. m, 3 H), 1.56–1.94 (m, 6 H), 1.98–2.17 (m, 2 H), 4.72 (dm, $J_{P,C}$ = 353.4 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.88 (d, $J_{P,C}$ = 36.8 Hz), 27.44 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –3.84 ppm. GC (Phenomenex Zebron ZB-35HT INFERNO): R_T = 3.25 min. GC-MS (EI, 70 eV): *m/z* (%) = 88 (100) [M – BH_3], 87 (26). $C_4H_{12}BP$ (101.92): calcd. C 47.14, H 11.87; found C 47.50, H 12.20.

1-(1,2-Diphenylethyl)phospholane–Borane (24): This compound was prepared by the General Procedure from **4** (0.089 g, 0.5 mmol), potassium (0.117 g, 3 mmol), *tert*-butyl chloride (0.217 mL, 2 mmol) and benzyl chloride (0.126 mL, 1 mmol). Yield 0.120 g (85%). White solid; m.p. 91.9–93.5 °C. R_F = 0.54 (hexane/EtOAc 6:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.08–1.23 (br. m, 3 H), 1.35–1.61 (m, 6 H), 1.61–1.78 (m, 2 H), 2.98–3.23 (m, 2 H), 3.26–3.37 (m, 1 H), 6.94–7.02 (m, 2 H), 7.02–7.10 (m, 3 H), 7.10–7.26 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.36 (d, $J_{P,C}$ = 35.3 Hz), 25.06 (d, $J_{P,C}$ = 34.2 Hz), 26.49, 26.86, 37.10 (d, $J_{P,C}$ = 5.2 Hz), 45.29 (d, $J_{P,C}$ = 23.6 Hz), 126.31, 127.27 (d, $J_{P,C}$ = 2.0 Hz), 128.23, 128.50 (d, $J_{P,C}$ = 1.7 Hz), 128.73, 128.86 (d, $J_{P,C}$ = 4.3 Hz), 136.96 (d, $J_{P,C}$ = 3.5 Hz), 139.07 (d, $J_{P,C}$ = 11.2 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 41.19 ppm. GC (Phenomenex Zebron ZB-35HT INFERNO): R_T = 18.61 min. GC-MS (EI, 70 eV): *m/z* (%) = 268 (27) [M – BH_3], 267 (72), 181 (100), 180 (61), 177 (41), 166 (46), 165 (67), 141 (9), 115 (14), 103 (94), 77 (66). $C_{18}H_{24}BP$ (282.17): calcd. C 76.62, H 8.57; found C 76.70, H 8.90.

(1,2-Diphenylethyl)dimethylphosphane–Borane (25): This compound was prepared by the General Procedure from **3** (0.076 g, 0.5 mmol), potassium (0.117 g, 3 mmol), *tert*-butyl chloride (0.217 mL, 2 mmol) and benzyl chloride (0.126 mL, 1 mmol). Yield 0.086 g (67%). White solid; m.p. 126.3–128.0 °C. R_F = 0.55 (hexane/EtOAc 6:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.03 to 1.21 (br. m, 3 H), 1.02 (d, $J_{P,H}$ = 10.0 Hz, 3 H), 1.10 (d, $J_{P,H}$ = 10.1 Hz, 3 H), 3.00–3.15 (m, 2 H), 3.27–3.40 (m, 1 H), 6.99–7.11 (m, 6 H), 7.12–7.23 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 9.08 (d, $J_{P,C}$ = 36.2 Hz), 11.21 (d, $J_{P,C}$ = 37.1 Hz), 35.63 (d, $J_{P,C}$ = 5.2 Hz), 45.95 (d, $J_{P,C}$ = 29.3 Hz), 126.23, 128.19, 128.64, 127.29 (d, $J_{P,C}$ = 2.0 Hz), 128.47 (d, $J_{P,C}$ = 1.7 Hz), 128.80 (d, $J_{P,C}$ = 4.3 Hz), 136.15 (d, $J_{P,C}$ = 4.9 Hz), 139.13 (d, $J_{P,C}$ = 12.6 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 13.41 ppm. GC (Phenomenex Zebron ZB-35HT INFERNO): R_T = 9.18 min. GC-MS (EI, 70 eV): *m/z* (%) = 242 (27) [M – BH_3], 241 (87), 182 (10), 181 (69), 180 (45), 179 (38), 178 (28), 167 (10), 166 (56), 165 (58), 153 (12), 152 (21), 151 (84), 139 (12), 138 (100), 123 (26), 121 (10), 115 (11), 109 (38), 104 (15), 103 (93), 102 (13), 91 (81), 89 (10). $C_{16}H_{22}BP$ (256.13): calcd. C 75.03, H 8.66; found C 75.32, H 8.70.

General Procedure for in situ Birch Reduction/Alkylation of Arylphosphane Oxides: Gaseous ammonia was passed through a flame-dried three-necked flask (100 mL) fitted with inert gas inlet, dry-ice condenser and cooling bath (–78 °C) until 15 mL of it was condensed. Sodium (2.5 equiv.) was added and the mixture was stirred for 15 min. Phosphane oxide (1 equiv.) was then added, followed after 5 min by an electrophile (2–2.5 equiv.), and the mixture was allowed to stir at –78 °C for 15 min. The reaction was quenched by addition of solid NH_4Cl (0.5 g), ammonia was evaporated off, the residue was filtered, the solid was washed with CH_2Cl_2 (3 × 15 mL), and the collected organic phases were concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$/MeOH (15:1) as an eluent.

***tert*-Butylmethyl(3-methylcyclohexa-1,4-dien-3-yl)phosphane Oxide (29):** This compound was prepared by the General Procedure from **26** (0.098 g, 0.5 mmol), sodium (0.029 g, 1.25 mmol) and methyl iodide (0.078 mL, 1.25 mmol). It was isolated as a mixture with starting material, yield 59% (based on NMR). R_F = 0.36 (EtOAc/MeOH 20:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.16 (d, $J_{P,H}$ = 13.8 Hz, 9 H), 1.31 (d, $J_{P,H}$ = 10.9 Hz, 3 H), 1.37 (d, $J_{P,H}$ = 13.1 Hz, 3 H), 2.58–2.71 (m, 2 H), 5.55–5.61 (m, 1 H), 5.67–5.82 (m, 3 H) ppm. ^{13}C NMR (125 MHz, CDC13): δ = 7.49 (d, $J_{P,C}$ = 60.0 Hz), 24.17, 24.83 (d, $J_{P,C}$ = 4.5 Hz), 26.20, 35.33 (d, $J_{P,C}$ = 60.9 Hz), 42.15 (d, $J_{P,C}$ = 60.9 Hz), 124.40 (d, $J_{P,C}$ = 8.2 Hz), 124.99 (d, $J_{P,C}$ = 9.1 Hz), 128.66 (d, $J_{P,C}$ = 3.6 Hz), 128.96 (d, $J_{P,C}$ = 3.6 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 58.22 ppm. GC (Phenomenex Zebron ZB-35HT INFERNO): R_T = 12.79 min. GC-MS (EI, 70 eV): *m/z* (%) = 211 (1) [M – 1], 121 (7), 120 (100), 93 (47), 92 (27), 91 (83).

(3-Benzylcyclohexa-1,4-dien-3-yl)-*tert*-butyl-methylphosphane Oxide (30): This compound was prepared by the General Procedure from **26** (0.098 g, 0.5 mmol), sodium (0.029 g, 1.25 mmol) and benzyl chloride (0.126 mL, 1 mmol). Yield 0.144 g (100%). White solid; m.p. 102.6–103.3 °C. R_F = 0.74 ($CHCl_3$/MeOH 15:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.29 (d, $J_{P,H}$ = 13.6 Hz, 9 H), 1.45 (d, $J_{P,H}$ = 11.0 Hz), 2.18–2.30 (m, 1 H), 2.38–2.52 (m, 1 H), 3.05–3.13 (m, 1 H), 3.23–3.31 (m, 1 H), 5.63–5.78 (m, 3 H), 5.88–5.95 (m, 1 H), 7.07–7.12 (m, 2 H), 7.13–7.24 (m, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 7.83 (d, $J_{P,C}$ = 60.0 Hz), 25.95 (d, $J_{P,C}$ = 4.5 Hz), 26.41, 35.85 (d, $J_{P,C}$ = 60.9 Hz), 41.11 (d, $J_{P,C}$ = 1.9 Hz), 47.71 (d, $J_{P,C}$ = 60.0 Hz), 126.07, 126.44 (d, $J_{P,C}$ = 9.1 Hz), 126.56 (d, $J_{P,C}$ = 6.4 Hz), 126.57 (d, $J_{P,C}$ = 5.5 Hz), 127.21 (d, $J_{P,C}$ = 9.1 Hz), 127.31, 130.89, 136.69 (d, $J_{P,C}$ = 11.8 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 57.42 ppm. GC (Phenomenex Zebron ZB-35HT INFERNO): R_T = 17.30 min. GC-MS (EI, 70 eV): *m/z* (%) = 288 (17) [M], 287 (20), 231 (10), 197 (58), 167 (14), 165 (12), 152

(10), 141 (83), 140 (30), 125 (13), 120 (13), 119 (25), 92 (20), 91 (100), 57 (72). $C_{18}H_{25}OP$ (288.36): calcd. C 74.97, H 8.74; found C 75.15, H 8.89.

Dimethyl(3-methylcyclohexa-1,4-dien-3-yl)phosphane Oxide (31): This compound was prepared by the General Procedure from **27** (0.077 g, 0.5 mmol), sodium (0.029 g, 1.25 mmol) and methyl iodide (0.078 mL, 1.25 mmol). It was isolated as a mixture with starting material, yield 47% (based on NMR). R_F = 0.56 (EtOAc/MeOH 20:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.37 (d, $J_{P,H}$ = 12.3 Hz, 6 H), 1.70 (d, $J_{P,H}$ = 13.2 Hz, 3 H), 2.53–2.80 (m, 2 H), 5.55–5.61 (m, 2 H), 5.83–5.88 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.72 (d, $J_{P,C}$ = 67.2 Hz), 21.25 (d, $J_{P,C}$ = 3.6 Hz), 26.27 (d, $J_{P,C}$ = 5.5 Hz), 40.65 (d, $J_{P,C}$ = 69.0 Hz), 126.36 (d, $J_{P,C}$ = 9.1 Hz), 127.19 (d, $J_{P,C}$ = 4.5 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 51.40 ppm. GC (Phenomenex Zebron ZB-35HT INFERNO): R_T = 17.30 min. GC-MS (EI, 70 eV): *m/z* (%) = 169 (1) [M – 1], 93 (57), 92 (19), 91 (100).

(3-Benzylcyclohexa-1,4-dien-3-yl)dimethylphosphane Oxide (32): This compound was prepared by the General Procedure from **27** (0.077 g, 0.5 mmol), sodium (0.029 g, 1.25 mmol) and benzyl chloride (0.126 mL, 1 mmol). Yield 0.117 g (95%). Colourless solid; m.p. 76.6–78.1 °C. R_F = 0.56 ($CHCl_3$/MeOH 15:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.45 (d, $J_{P,H}$ = 12.0 Hz, 6 H), 2.35–2.55 (m, 2 H), 3.10 (d, $J_{P,H}$ = 6.9 Hz, 2 H), 5.62–5.69 (m, 2 H), 5.76–5.84 (m, 2 H), 7.08–7.13 (m, 2 H), 7.13–7.23 (m, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.15 (d, $J_{P,C}$ = 67.2 Hz), 26.05 (d, $J_{P,C}$ = 5.5 Hz), 38.93 (d, $J_{P,C}$ = 2.7 Hz), 46.08 (d, $J_{P,C}$ = 68.1 Hz), 125.33 (d, $J_{P,C}$ = 5.5 Hz), 126.16, 127.53, 127.88 (d, $J_{P,C}$ = 10.0 Hz), 130.24, 136.79 (d, $J_{P,C}$ = 12.7 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 50.86 ppm. GC (Phenomenex Zebron ZB-35HT INFERNO): R_T = 16.41 min. GC-MS (EI, 70 eV): *m/z* (%) = 246 (2) [M], 245 (3), 168 (10), 167 (14), 165 (9), 155 (19), 153 (6), 152 (7), 92 (11), 91 (100). $C_{15}H_{19}OP$ (246.28): calcd. C 73.15, H 7.78; found C 73.10, H 8.11.

(3-Methylcyclohexa-1,4-dien-3-yl)phospholane Oxide (33): This compound was prepared by the General Procedure from **28** (0.090 g, 0.5 mmol), sodium (0.029 g, 1.25 mmol) and methyl iodide (0.078 mL, 1.25 mmol). Yield 0.098 g (100%). Colourless solid; m.p. 81.4–83.1 °C. R_F = 0.60 ($CHCl_3$/MeOH 15:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.41 (d, $J_{P,H}$ = 13.9 Hz, 3 H), 1.54–1.72 (m, 4 H), 1.73–1.85 (m, 2 H), 1.88–2.01 (m, 2 H), 2.59–2.82 (m, 2 H), 5.56–5.63 (m, 2 H), 5.80–5.88 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.11 (d, $J_{P,C}$ = 3.6 Hz), 24.11 (d, $J_{P,C}$ = 62.7 Hz), 25.12 (d, $J_{P,C}$ = 7.3 Hz), 26.39 (d, $J_{P,C}$ = 5.5 Hz), 40.54 (d, $J_{P,C}$ = 60.9 Hz), 126.31 (d, $J_{P,C}$ = 9.1 Hz), 127.19 (d, $J_{P,C}$ = 4.5 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 79.87 ppm. GC (Phenomenex Zebron ZB-35HT INFERNO): R_T = 13.90 min. GC-MS (EI, 70 eV): *m/z* (%) = 195 (0.25) [M – 1], 105 (10), 104 (100), 103 (34), 93 (30), 92 (11), 91 (44). $C_{11}H_{17}OP$ (196.23): calcd. C 67.33, H 8.73; found C 67.34, H 8.95.

(3-Benzylcyclohexa-1,4-dien-3-yl)phospholane Oxide (34): This compound was prepared by the General Procedure from **28** (0.090 g, 0.5 mmol), sodium (0.029 g, 1.25 mmol) and benzyl chloride (0.126 mL, 1 mmol). It was isolated as a mixture with **35**, yield 36% (based on NMR). R_F = 0.73 ($CHCl_3$/MeOH 15:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.44–1.56 (m, 2 H), 1.57–1.68 (m, 4 H), 1.78–1.87 (m,2 H), 2.52–2.61 (m, 2 H), 3.16 (d, $J_{P,H}$ = 8.8 Hz, 2 H), 5.66–5.73 (m, 2 H), 5.80–5.88 (m, 2 H), 7.17–7.28 (m, 5 H) ppm. ^{13}C NMR (125 MHz, CDCl3): δ = 25.03 (d, $J_{P,C}$ = 6.4 Hz), 26.05 (d, $J_{P,C}$ = 65.4 Hz), 26.33 (d, $J_{P,C}$ = 5.5 Hz), 38.55 (d, $J_{P,C}$ = 55.4 Hz), 40.58 (d, $J_{P,C}$ = 2.7 Hz), 126.36, 127.65 (d, $J_{P,C}$ = 10.0 Hz), 127.72, 129.41 (d, $J_{P,C}$ = 5.5 Hz), 130.48, 136.67 (d, $J_{P,C}$ = 10.0 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 78.72 ppm. GC (Phenomenex Zebron ZB-35HT INFERNO): R_T = 18.12 min. GC-MS (EI, 70 eV): *m/z* (%) = 271 (2) [M – 1], 181 (9), 168 (10), 167 (14), 165 (8), 153 (6), 152 (7), 105 (25), 104 (100), 103 (27), 91 (81).

1-Benzylphospholane Oxide (35): This compound was prepared by the General Procedure from **28** (0.090 g, 0.5 mmol), sodium (0.029 g, 1.25 mmol) and benzyl chloride (0.126 mL, 1 mmol). It was isolated as a mixture with **34**, yield 38% (based on NMR). R_F = 0.64 ($CHCl_3$/MeOH 15:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.68–1.78 (m, 4 H), 1.86–1.98 (m, 4 H), 3.26 (d, $J_{P,H}$ = 14.8 Hz, 2 H), 7.17–7.28 (m, 3 H), 7.30–7.34 (m, 2 H) ppm. ^{13}C NMR (125 MHz, CDCl3): δ = 24.31 (d, $J_{P,C}$ = 8.2 Hz), 24.81 (d, $J_{P,C}$ = 74.5 Hz), 46.02 (d, $J_{P,C}$ = 59.9 Hz), 125.54 (d, $J_{P,C}$ = 3.6 Hz), 126.91 (d, $J_{P,C}$ = 2.7 Hz), 128.82 (d, $J_{P,C}$ = 2.7 Hz), 132.19 (d, $J_{P,C}$ = 7.3 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 69.40 ppm. GC (Phenomenex Zebron ZB-35HT INFERNO): R_T = 15.06 min. GC-MS (EI, 70 eV): *m/z* (%) = 194 (31) [M], 193 (19), 166 (10), 148 (7), 117 (20), 103 (19), 92 (13), 91 (100), 85 (14).

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

Acknowledgments

Financial support from the Polish Ministry of Science and Higher Education (grant number N204 2328 34) is gratefully acknowledged. The authors are grateful to Dr. Duncan Carmichael for his guidance during the preparation of manuscript.

[1] a) K. Tamura, M. Sugiya, K. Yoshida, A. Yanagisawa, T. Imamoto, *Org. Lett.* **2010**, *12*, 4400–4403; b) R. Garcia-Álvarez, J. Diez, P. Crochet, V. Cadierno, *Organometallics* **2010**, *29*, 3955–3965; c) M. P. Castaldi, S. E. Gibson, M. Rudd, A. J. P. White, *Angew. Chem.* **2005**, *117*, 3498; *Angew. Chem. Int. Ed.* **2005**, *44*, 3432–3435; d) W. Zhang, X. Zhang, *Angew. Chem.* **2006**, *118*, 5641; *Angew. Chem. Int. Ed.* **2006**, *45*, 5515–5518; e) Y. Takemura, H. Takenada, T. Nakajima, T. Tanase, *Angew. Chem.* **2009**, *121*, 2191; *Angew. Chem. Int. Ed.* **2009**, *48*, 2157–2161.

[2] a) D.-R. Hou, J. H. Reibenspies, K. Burgess, *J. Org. Chem.* **2001**, *66*, 206–215; b) X. Hao, M. Kuriyama, Q. Chen, Y. Yamamoto, K. Yamada, K. Tomioka, *Org. Lett.* **2009**, *11*, 4470–4473; c) P. Nandi, J. L. Dye, P. Bentley, J. E. Jackson, *Org. Lett.* **2009**, *11*, 1689–1692; d) M. Lotz, R. Schuecker, K. Mereiter, P. Knochel, *Organometallics* **2010**, *29*, 6503–6508; e) A. K. Brisdon, C. J. Herbert, *Chem. Commun.* **2009**, 6658–6660.

[3] a) D. J. Brauer, M. Hingst, K. W. Kottsieper, K. Liek, T. Nickel, M. Tepper, O. Stelzer, W. S. Sheldrick, *J. Organomet. Chem.* **2002**, *645*, 14–26; b) T. Senda, M. Ogasawara, T. Hayashi, *J. Org. Chem.* **2001**, *66*, 6852–6856; c) D. Gelman, L. Jiang, S. L. Buchwald, *Org. Lett.* **2003**, *5*, 2315–2318.

[4] a) M. V. Jiménez, J. J. Pérez-Torrente, M. I. Bartolomé, L. A. Oro, *Synthesis* **2009**, 1916–1922; b) A. Sato, H. Yorimitsu, K. Oshima, *Angew. Chem.* **2005**, *117*, 1722; *Angew. Chem. Int. Ed.* **2005**, *44*, 1694–1696; c) M. Hayashi, Y. Matsuura, Y. Watanabe, *J. Org. Chem.* **2006**, *71*, 9248–9251; d) I. Ibrahem, P. Hammar, J. Vesely, R. Rios, L. Eriksson, A. Córdova, *Adv. Synth. Catal.* **2008**, *350*, 1875–1884; e) K. Bourumeau, A.-C. Gaumont, J.-M. Denis, *J. Organomet. Chem.* **1997**, *529*, 205–213.

[5] a) E. Bergin, C. T. O'Connor, S. B. Robinson, E. M. McGarrigle, C. P. O'Mahony, D. G. Gilheany, *J. Am. Chem. Soc.* **2007**, *129*, 9566–9567; b) P. Barbaro, C. Bianchini, G. Giambastani, A. Togni, *Chem. Commun.* **2002**, 2672–2673; c) M. Berthod, A. Favre-Réguillon, J. Mohamad, G. Mignani, G. Doherty, M. Lemaire, *Synlett* **2007**, 1545–1548; d) G. Keglevich, M. Fekete,

T. Chuluunbaatar, A. Dobó, V. Harmat, L. Tőke, *J. Chem. Soc. Perkin Trans. 1* **2000**, 4451–4455.
[6] a) Y. K. Kim, S. J. Lee, K. H. Ahn, *J. Org. Chem.* **2000**, *65*, 7807–7813; b) E. Saxon, J. I. Armstrong, C. R. Bertozzi, *Org. Lett.* **2000**, *2*, 2141–2143; c) A. Kless, C. Lefeber, A. Spannenberg, R. Kempe, W. Baumann, J. Holz, A. Börner, *Tetrahedron* **1996**, *52*, 14599–14606; d) F. Lam, J. X. Xu, K. S. Chan, *J. Org. Chem.* **1996**, *61*, 8414–8418; e) E. P. Kyba, C. N. Clubb, S. B. Larson, V. J. Schueler, R. E. Davis, *J. Am. Chem. Soc.* **1985**, *107*, 2141–2148.
[7] a) H. Gulyás, Z. Bacsik, Á. Szöllősy, J. Bakos, *Adv. Synth. Catal.* **2006**, *348*, 1306–1310; b) F. Piestert, R. Fetouaki, M. Bogza, T. Oeser, J. Blümel, *Chem. Commun.* **2005**, 1481–1483; c) C. E. Anderson, D. C. Apperley, A. S. Batsanov, P. W. Dyer, J. A. K. Howard, *Dalton Trans.* **2006**, 4134–4145; d) S. Chatterjee, R. Doyle, D. C. R. Hockless, G. Salem, A. C. Willis, *J. Chem. Soc., Dalton Trans.* **2000**, 1829–1830.
[8] M. Ferreira, H. Bricout, N. Azaroual, C. Gaillard, D. Landy, S. Tilloy, E. Monflier, *Adv. Synth. Catal.* **2010**, *352*, 1193–1203.
[9] a) J. Blanchet, T. Macklin, P. Ang, C. Metallinos, V. Snieckus, *J. Org. Chem.* **2007**, *72*, 3199–3206; b) T.-H. Nguyen, N. T. T. Chau, A.-S. Castanet, K. P. P. Nguyen, J. Mortier, *J. Org. Chem.* **2007**, *72*, 3419–3429.
[10] a) M. Gray, B. J. Chapell, J. Felding, N. J. Taylor, V. Snieckus, *Synlett* **1998**, 422–424; b) C. Baillie, J. Xiao, *Tetrahedron* **2004**, *60*, 4159–4168; c) B. Schaub, T. Jenny, M. Schlosser, *Tetrahedron Lett.* **1984**, *25*, 4997–5000; d) D. B. G. Williams, S. J. Evans, H. de Bod, M. S. Mokhadinyana, T. Hughes, *Synthesis* **2009**, 3106–3112.
[11] M. C. Elliott, M. J. Gist, F. Binns, R. C. Jones, *Tetrahedron Lett.* **2004**, *45*, 2899–2901.
[12] R. J. Graham, L. A. Paquette, *J. Org. Chem.* **1995**, *60*, 5770–5777.
[13] J. J. Venit, M. DiPierro, P. Magnus, *J. Org. Chem.* **1989**, *54*, 4298–4301.
[14] a) M. Toyota, M. Yokota, M. Ihara, *J. Am. Chem. Soc.* **2001**, *123*, 1856–1861; b) R. Mazitschek, A. Huwe, A. Giannis, *Org. Biomol. Chem.* **2005**, *3*, 2150–2154; c) A. G. Schultz, J. P. Dittami, F. P. Lavieri, C. Salowey, P. Sundaraman, M. B. Szymula, *J. Org. Chem.* **1984**, *49*, 4429–4440.
[15] R. L. Beddoes, M. L. Lewis, P. Gilbert, P. Quayle, S. P. Thompson, S. Wang, K. Mills, *Tetrahedron Lett.* **1996**, *37*, 9119–9122.
[16] C. C. McComas, D. L. van Vranken, *Tetrahedron Lett.* **1999**, *40*, 8039–8043.
[17] T. J. Donohoe, H. O. Sintim, *Org. Lett.* **2004**, *6*, 2003–2006.
[18] D. N. Kumar, B. V. Rao, *Tetrahedron Lett.* **2004**, *45*, 2227–2229.
[19] K. Vorndran, T. Linker, *Angew. Chem.* **2003**, *115*, 2593; *Angew. Chem. Int. Ed.* **2003**, *42*, 2489–2491.
[20] a) I. Usui, K. Nomura, B. Breit, *Org. Lett.* **2011**, *13*, 612–615; b) R. Lebeuf, F. Robert, K. Schenk, Y. Landais, *Org. Lett.* **2006**, *8*, 4755–4758; c) D. L. J. Clive, R. Sunasee, *Org. Lett.* **2007**, *9*, 2677–2680.
[21] a) B. A. Mendelsohn, S. Lee, S. Kim, F. Teyssier, V. A. Aulakh, M. A. Ciufolini, *Org. Lett.* **2009**, *11*, 1539–1542; b) D. Bland, G. Chambournier, V. Dragan, D. J. Hart, *Tetrahedron* **1999**, *55*, 8953–8966; c) A. G. Schultz, W. Geiss, *J. Am. Chem. Soc.* **1991**, *113*, 3490–3494; d) A. L. J. Beckwith, D. H. Roberts, *J. Am. Chem. Soc.* **1986**, *108*, 5893–5901.
[22] a) S. Hirai, M. Nakada, *Tetrahedron Lett.* **2010**, *51*, 5076–5079; b) M. Inai, T. Goto, T. Furuta, T. Wakimoto, T. Kan, *Tetrahedron: Asymmetry* **2008**, *19*, 2771–2773; c) R. Lebeuf, F. Robert, Y. Landais, *Org. Lett.* **2005**, *7*, 4557–4560.
[23] J. A. van Doorn, N. Meijboom, *J. Chem. Soc., Chem. Commun.* **1987**, 1700–1701.
[24] M. Stankevič, K. M. Pietrusiewicz, *Tetrahedron Lett.* **2009**, *50*, 7093–7095.
[25] M. Stankevič, A. Włodarczyk, M. Jaklińska, R. Parcheta, K. M. Pietrusiewicz, *Tetrahedron* **2011**, *67*, 8671–8678.
[26] a) M. Revés, C. Ferrer, T. Léon, S. Doran, P. Etayo, A. Vidal-Ferran, A. Riera, X. Verdaguer, *Angew. Chem. Int. Ed.* **2010**, *49*, 9452–9455; b) T. Léon, A. Riera, X. Verdaguer, *J. Am. Chem. Soc.* **2011**, *133*, 5740–5743.
[27] M. Stankevič, M. Jaklińska, K. M. Pietrusiewicz, *J. Org. Chem.* **2012**, *77*, 1991–2000.
[28] M. Bulbrook, M. Chu, K. Deane, R. J. Doyle, J. Hinc, C. Peterson, G. Salem, N. Thorman, A. C. Willis, *Dalton Trans.* **2010**, *39*, 8878–8881.
[29] P. Pellon, C. Le Goaster, G. Marchand, B. Martin, *Heteroat. Chem.* **1997**, *8*, 123–128.
[30] M. Stankevič, K. M. Pietrusiewicz, *J. Org. Chem.* **2007**, *72*, 816–822.
[31] D. Gatineau, L. Giordano, G. Buono, *J. Am. Chem. Soc.* **2011**, *133*, 10728–10731.
[32] K. Kiyokawa, I. Suzuki, M. Yasuda, A. Baba, *Eur. J. Org. Chem.* **2011**, 2163–2171.
[33] K. Ohashi, S. Kosai, M. Arizuka, T. Watanabe, Y. Yamagiwa, T. Kamikawa, M. Kates, *Tetrahedron* **1989**, *45*, 2557–2570.
[34] R. K. Haynes, T.-L. Au-Yeung, W.-K. Chan, W.-L. Lam, Z.-Y. Li, L.-L. Yeung, A. S. C. Chan, P. Li, M. Koen, C. R. Mitchell, S. C. Vonwiller, *Eur. J. Org. Chem.* **2000**, 3205–3216.
[35] W. B. McCormack, *US Patent*, 2663737 (**1953**).
[36] X.-M. Sun, K. Manabe, W. W.-L. Lam, N. Shiraishi, J. Kobayashi, M. Shiro, H. Utsumi, S. Kobayashi, *Chem. Eur. J.* **2005**, *11*, 361–368.
[37] M. Stankevič, M. Siek, K. M. Pietrusiewicz, *ARKIVOC* **2011**, *5*, 102–126.
[38] C. A. Busacca, R. Raju, N. Grinberg, N. Haddad, P. James-Jones, H. Lee, J. C. Lorenz, A. Saha, C. H. Senanayake, *J. Org. Chem.* **2008**, *73*, 1524–1531.
[39] T. Imamoto, T. Oshiki, T. Onozawa, T. Kusumoto, K. Sato, *J. Am. Chem. Soc.* **1990**, *112*, 5244–5252.

Received: January 27, 2012
Published Online: March 27, 2012

