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Homometathesis and cross-metathesis coupling of phosphine-borane templates with electron-rich and electron-poor olefins

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Abstract

Ruthenium-catalysed olefin cross-metathesis can be used to synthesise structurally diverse acyclic phosphines protected as their borane complexes. Homodimerisations have been investigated and proved successful only for the allyl-substituted borane-protected phosphines. In the presence of various olefinic partners, allyl-substituted P templates reacted in cross-couplings to give predominantly the *E* products but traces of the *Z* isomers were always detected in the crude reaction mixtures. In contrast, cross-metathesis of vinyl-substituted phosphine boranes took place with exclusive *E*-selectivity. Although the conversions were consistently very good to excellent, the yields of purified products were often significantly lower suggesting that some of the newly formed compounds are prone to decompose upon purification.

Keywords: Homometathesis; Cross-metathesis; Phosphine borane complexes

1. Introduction

Chiral phosphines are key compounds for the discovery of new catalytic asymmetric transformations but their preparation remains a bottleneck in the search for new ligands in transition metal catalysis [1]. This is particularly true for the synthesis of P-stereogenic phosphines [2]. The demand for innovative synthetic routes towards known and novel free phosphines or diphosphines has prompted us to take advantage of the versatility and synthetic applicability of the metathesis reaction for this purpose [3]. Although free phosphines are required for transition metal mediated transformations, data reported in the literature revealed that these compounds required P-protection prior to the metathesis reaction when using ruthenium-based catalysts. Indeed, it was found that unprotected diallylphenylphosphine did not react in the presence of Ru-based catalysts **1**–**3** but underwent smooth ring closing metathesis in the presence of 5 mol% of the aryloxide(neopentylidene)tungsten catalyst **4** or 8 mol% of Schrock's Mo-based catalyst **5** with up to 95% conversion (Scheme 1) [4,5].

The scope and limitation of this transformation have not been investigated probably due to the difficulties associated with the synthesis of the starting free phosphines required for the metathesis reaction. It is therefore preferable and more practical to use protected phosphines such as phosphine oxides or phosphine boranes in metathesis reactions as these substrates are easier to handle and compatible with both Mo- and Ru-based catalysts. Ring closing metathesis as well as cross-metathesis reactions have already emerged as powerful transformations for the rapid construction of highly functionalised phosphine oxides including more recently novel P-stereogenic dienophiles [6], cyclic phosphinates and trialkenylphosphine oxides difficult to access by other routes [7]. In contrast, only limited information is available in the literature on the reactivity of phosphine-boranes in metathesis reactions. Borane complexes of phosphines are ideal precursors of

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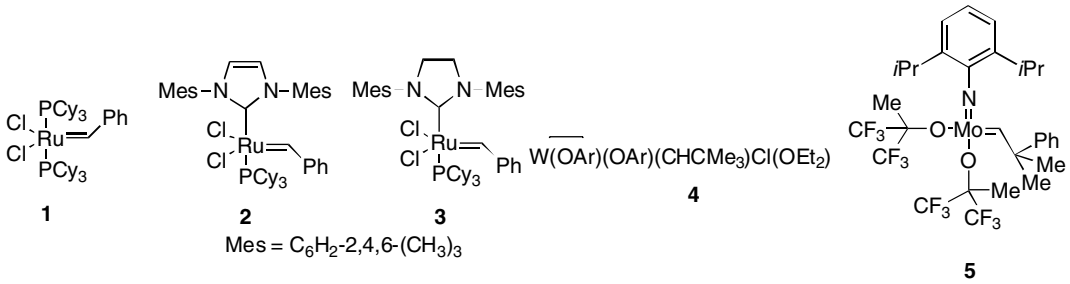
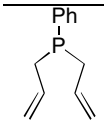


Substrate	Product	cat. **1** (%mol) reaction time conversion[a]	cat. **2** (%mol) reaction time conversion[a]	cat.**3** (%mol) reaction time conversion[a]	cat. **4** (%mol) reaction time conversion[a]	cat. **5** (%mol) reaction time conversion[a]
		4% 20h 0%	8% 72h 0%	8% 72h 0%	20% 5h 95%	12.5% 84h 95%

a: conversion determined by ^{1}H NMR

Scheme 1. RCM of diallylphenylphosphine.

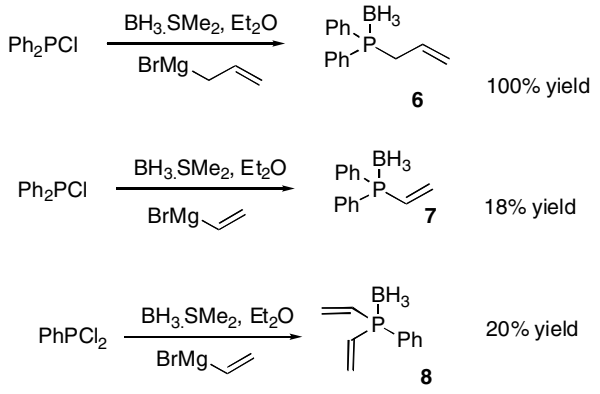
free phosphines and consequently, these compounds are particularly suitable for pioneering studies aimed at developing novel synthetic transformations based on the metathesis reaction for the preparation of new phosphine ligands to be used in transition metal mediated processes. In 2000, we reported the first examples of ring closing metathesis of bis(alkenyl)phosphine boranes for the preparation of differently substituted five, six and seven-membered P–BH_3 heterocycles, all featuring an endocyclic double bond, which can be used for further functional group manipulations. The reaction was also compatible with a P–BH_3 containing tetraene leading to the exclusive formation of the desired borane-protected bisphosphine [8]. These reactions were carried out in the presence of the first generation Grubbs catalyst **1** [9]. Further studies revealed that in the presence of catalyst **2** [10], **3** [11] or **5** [12], the reaction was broader in scope although none of these catalysts mediated the formation of P-containing heterocycles featuring an endocyclic tetrasubstituted double bond [5]. Studies carried out by Gladysz et al. further demonstrated the synthetic value of this reaction with the synthesis of architecturally complex topologically novel bisphosphine ligands [13]. Additional ring closing metathesis of phosphorus borane templates derived from bis(diisopropylamino)ethynylphosphine were carried out by van Boom et al. and led to the formation of unusual dienic mono- and bicyclic phosphorus heterocycles [14]. In contrast to ring closing metathesis, no data are available on the reactivity of phosphino-boranes in homo- and cross-metathesis reactions with the exception of five reactions on allyldiphenylphosphine borane and allyldicyclohexylphosphine borane reported by Grubbs et al. in 2002 [15]. Herein, we wish to report the scope and limitation of these reactions by studying the reactivity of five representative borane protected monoalkenylphosphines under homo- or cross-metathesis reaction conditions.

2. Results and discussion

2.1. Choices and synthesis of substrates

For this study, we selected three achiral and two chiral substrates, namely the borane complexes of allyldiphenyl, diphenylvinyl, phenyldivinyl, allylmethoxy(phenyl) and methoxy(phenyl)vinyl phosphines **6**–**10**. Compounds **6** and **7** were prepared in two steps from chlorodiphenylphosphine. The protection was carried out first using $BH_3 \cdot SMe_2$ followed by addition of allylmagnesium bromide or vinylmagnesium bromide. This procedure afforded compound **6** in quantitative yield. In contrast, compound **7** could be isolated in only 18% yield. Attempts to improve the yield by changing the order of steps or by modifying the purification procedure were unsuccessful. Similarly, compound **8** was prepared from dichlorophenylphosphine in low yield because of the propensity of this phosphine-borane complex to decompose upon purification. Although a large amount of material was lost upon purification of **7** and **8**, subsequent metathesis reactions were carried out only on purified compounds (Scheme 2).

The chiral substrates **9** and **10** were synthesised from the known oxazaphospholidine-borane **11** following a protocol developed by Genêt and Jugé [16]. The diastereomerically pure complex **11** was obtained in one step from bis(diethylamino)phenylphosphine, (±)-ephedrine and $BH_3 \cdot SMe_2$ with a chemical yield of 80%. The reaction of **11** with allyllithium proceeded with exclusive P–O bond cleavage when carried out at low temperature and afforded the desired aminophosphane-borane **12** with a diastereomeric ratio of 4:1 and a chemical yield of 77% [8]. Methanolysis of this key intermediate under acidic conditions afforded **9** in 79% yield [17]. A similar reaction sequence was followed for the preparation of compound **10**. For this substrate, the ring opening was carried out with vinyllithium leading to the

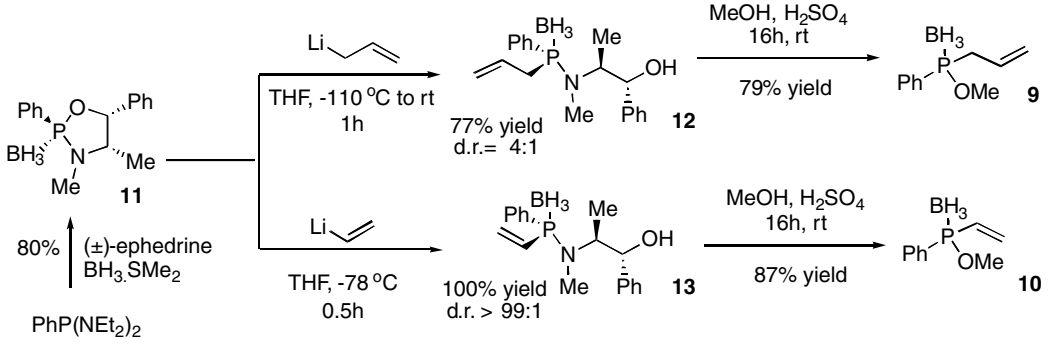


Scheme 2. Synthesis of compounds **6**–**8**.

vinyl-substituted aminophosphane-borane **13** in quantitative yield and with a diastereomeric excess superior to 98% corroborating literature data [18]. This compound was subsequently converted into **10** upon treatment with methanol in the presence of sulfuric acid. Notably, compounds **9** and **10** were prepared with good to excellent overall yield from **11** with no sign of decomposition observed upon purification (Scheme 3).

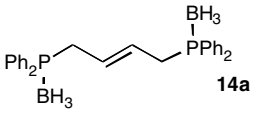
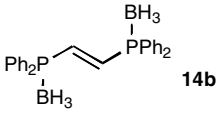
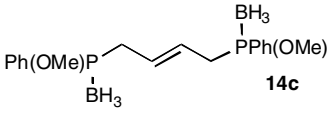
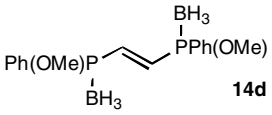
2.2. Homometathesis reactions

All homometathesis reactions were performed under argon at reflux in dichloromethane using a 0.3 M concentration of the substrate and up to 8 mol% of catalyst **3**. For compound **6**, the crude mixture revealed the presence of the major *E*-isomer **14a** with only traces of the *Z* stereoisomer. After purification, the dimeric *E*-product was isolated in 57% yield (Table 1, entry 1) [19]. No product **14b** resulting from a homometathesis could be detected after 24 h when compound **7** was submitted to our standard conditions suggesting that this α,β-unsaturated substrate bear-



Scheme 3. Synthesis of phosphine-boranes **9**–**10**.

Table 1
Homometathesis of **6**, **7**, (±)-**9** and (±)-**10** using catalyst **3**

Entry	Phosphine-borane (1 equiv.)	Product	Mol% cat. **3**	Conversion[a] (%)	*E*/*Z*[a]	Yield (%)
1	**6**	 **14a**	4	100	9/1	57[b] *E*/*Z*
2	**7**	 **14b**	4	0	–	–
3	±-**9**	 **14c**	2	100	5/1	85[c] *E*
4	±-**10**	 **14d**	8	0	–	–

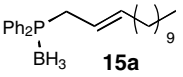
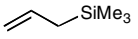
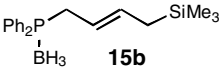
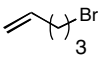
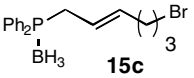
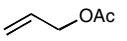
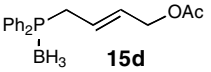
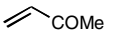
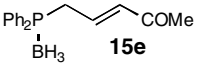
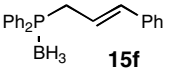
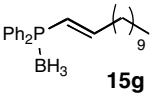
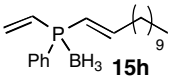
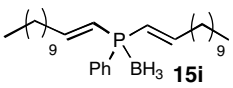
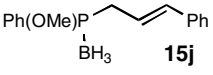
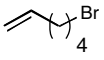
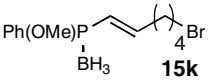
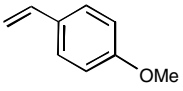
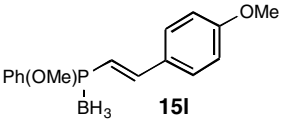
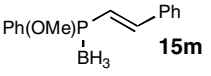
[a] Determined from ^{1}H NMR of crude mixture.
[b] Recrystallisation from MeOH gave 17% of the pure *E*-isomer.
[c] 1/1 mixture of *meso* and *dl* stereoisomers.

ing two phenyl groups is too sterically hindered to react (Table 1, entry 2). The NMR of the crude reaction mixture revealed only the presence of starting material. Subsequent studies focused on the reactivity of the chiral phosphine boranes (±)-**9** and (±)-**10**. Using 2 mol% of catalyst **3**, compound (±)-**9** underwent a highly successful homometathesis (100% conversion) after 12 h affording the desired product (±)-**14c** in 85% isolated yield (Table 1, entry 3). As expected, this reaction delivered several products, both *dl* and *meso* products are obtained with the possibility to be formed as *E* or *Z* isomers. After purification, careful analysis of the ^{1}H NMR spectrum of the purified product revealed that the *meso* and *dl* stereoisomers are formed in a 1/1 ratio. The *E*/*Z* ratio was found to be 5/1 [20]. In contrast, product **14d** resulting from a homometathesis process was not observed when the vinyl-substituted phosphine-borane (±)-**10** was left reacting for 48 h with up to 8 mol% of catalyst **3**. Only the starting material was recovered (Table 1, entry 4) [21].

2.3. Cross-metathesis reactions

We then attempted cross-metathesis reactions with phosphine boranes **6**–**10** (Table 2). A preliminary study revealed that the cross-metathesis couplings were best performed in dichloromethane at reflux combining 1 equiv. of the phosphine substrate (0.3 M) with 3 equiv. of various electron-rich and electron-deficient olefinic partners and in the presence of 2–8 mol% of the second generation Grubbs catalyst **3**. Under these conditions, the borane-protected diphenylallylphosphine **6** participated in cross-metathesis with terminal dodecene to generate after 24 h the disubstituted unsaturated phosphine-borane complex **15a** in moderate isolated yield (60%) and excellent *E* stereoselectivity with only trace amount of the minor *Z*-stereoisomer being formed (Table 1, entry 1). Notably, the isolated yield was significantly lower than the conversion, which was superior to 95% according to the ^{1}H NMR spectrum of the crude mixture. No trace of dimeric compound **14a** resulting from a homometathesis reaction of **6** could be detected in the crude reaction mixture. The only product formed in addition to **15a** was the disubstituted alkene resulting from the self-metathesis of dodecene. This positive result led us to examine the cross-metathesis reaction of **6** with other olefinic partners. Allyltrimethylsilane proved to be a suitable reaction partner affording the silylated phosphine-borane **15b** in 85% yield as a 5/1 mixture of *E*/*Z* stereoisomers (Table 1, entry 2). This reaction was repeated and left stirring under refluxing DCM for 96 h in an attempt to increase the *E*/*Z* ratio but no improvement was observed. 5-Bromopentene also reacted with **6** to afford the single *E* brominated product **15c** in 41% yield after silica gel chromatography. With diagnostic peaks overlapping, the *E*/*Z* ratio could not be assigned unambiguously based on the NMR data of the crude reaction mixture (Table 1, entry 3). For these two cross-metathesis reactions (entries 2–3), **6** was totally consumed and converted solely into the desired products along with the dimeric product resulting from a homometathesis of the olefinic partner used in excess. No trace of **14a** could be detected in the crude reaction mixtures. We also attempted a cross-metathesis using allylacetate as olefinic partner using our standard reaction conditions but this reaction was not successful. Only the starting material **6** and the product resulting from the homodimerisation of allylacetate were present in the crude reaction mixture after 96 h under reflux (Table 1, entry 4). Interestingly, the cross-metathesis with the electron-poor olefin methylvinylketone (MVK) led to the desired product **15e** but required up to 8 mol% of the catalyst to reach 70% conversion. This transformation was highly selective in favour of the *E*-isomer. After purification, the product *E*-**15e** was recovered in 60% yield suggesting that this compound was not prone to decompose upon purification (Table 1, entry 5). The cross-metathesis of **6** with styrene did reach completion after 36 h to give **15f** along with stilbene. This reaction was highly selective in favour of the *E*-isomer. The resulting product **15f** was isolated pure in 40% yield (Table 1, entry 6). A representative cross-metathesis was carried out with diphenylvinylphosphine borane **7**. With dodecene, this substrate underwent cross-metathesis with exclusive *E*-selectivity. However, a low coupling yield of 35% was obtained after purification for compound **15g** (Table 1, entry 7). The reluctance of compound **7** to homodimerise suggested that the structurally related prochiral diene **8** might be a suitable candidate for desymmetrisation [7]. We therefore investigated the reactivity of diene **8** with dodecene, a representative type I olefin [22]. In the light of related studies on the desymmetrisation of the corresponding phosphine oxides [7], this transformation was carried out using 1 equivalence of the olefinic partner and 3 equiv. of **8** in DCM at reflux in the presence of 8 mol% of catalyst **3**. This reaction produced a mixture of several products. The two major compounds were the desired P-stereogenic desymmetrised diene (±)-**15h** and the achiral diene **15i** resulting from a double cross-metathesis process. Traces of reduced compounds were also detectable in the crude mixture [23]. Upon purification, pure samples of **15h** and **15i** were isolated in 17% and 22% yield respectively, allowing for full characterisation. Both products were formed with exclusive *E*-selectivity (Table 2, entry 8). We then turned our attention on the cross-metathesis of the racemic chiral substrates (±)-**9** and (±)-**10**. For the reaction of (±)-**9** with styrene, two products were detected in the crude mixture, the desired phenyl-substituted product (±)-**15j** (*E*:*Z* ratio = 10:1) and compound (±)-**14c** resulting from a competitive homodimerisation process. These two compounds formed in a 88/12 ratio were separable upon purification (Table 2, entry 9). Finally, three cross-metathesis reactions were attempted with (±)-**10**. 6-Bromohexene, *para*-methoxystyrene and styrene were all suitable olefinic partners for the cross-metathesis affording the desired products in 55%, 46% and 66% respectively (Table 2,

Table 2
Cross-metathesis of **6**–**10** with electron-rich and electron-poor olefinic partners using catalyst **3**

Entry	Phosphine-borane (1 equiv.)	Cross-metathesis partner (3 equiv.)	Product	Mol% cat. **3**	Time (h)	Conversion[a] (%)	*E*/*Z*[a]	Yield (%)
1	**6**		 **15a**	4	24	>95	9/1	60 *E*/*Z*
2	**6**		 **15b**	4	24	100	5/1	85 *E*/*Z*
3	**6**		 **15c**	8	48	100	–[b]	41[c] *E*
4	**6**		 **15d**	8	96	0	–	–
5	**6**		 **15e**	8	48	70	9/1	63[c] *E*
6	**6**		 **15f**	6	36	100	9/1	40 *E*
7	**7**		 **15g**	8	48	74	*E* only	35 *E*
8[d]	**8**		 **15h**	8	48	85	*E* only	17
			 **15i**				*E* only	22
9	±-**9**		 **15j**	2	12	100[e]	10/1	43 *E*/*Z*
10	±-**10**		 **15k**	6	36	100	*E* only	55 *E*
11	±-**10**		 **15l**	6	36	68	*E* only	46 *E*
12	±-**10**		 **15m**	8	48	85	*E* only	66 *E*

[a] Determined from ^{1}H NMR of crude mixture.
[b] Conversion/ratio could not be determined due to overlapping NMR signals.
[c] *Z* isomer could not be isolated.
[d] This reaction was carried out with 3 equiv. of diene **8** and 1 equiv. of dodecene.
[e] **15j** and **14c** were formed in a ratio of 88:12. These two compounds are separable upon purification.

entries 10–12). Notably, all reactions led to the formation of the *E*-isomer only.

The results compiled in Tables 1 and 2 highlight important differences in reactivity for the allyl-substituted phosphines **6** and **9** in comparison with substrates **7**, **8** and **10** all featuring one or two vinyl groups. For homodimerisation, the coupling of the borane-protected vinylphosphines **7** and **10** bearing one or two phenyl groups were unsuccessful

with starting material recovered. These results corroborate literature data suggesting a similar trend of reactivity for diaryl phosphine oxides such as diphenylvinylphosphine oxide, which did not react using catalyst **3** or alternative Hoveyda–Grubbs catalysts. It is also noteworthy that alkyl–aryl or dialkyl vinylphosphine oxides could be coupled in only moderate yields with **3** but yields up to 80% using the more reactive nitro-substituted Hoveyda–Grubbs catalyst [6,7]. We found that in contrast to borane-protected vinyl-substituted phosphines, compounds **6** and **9** both homodimerised successfully leading to the desired borane-protected 1,4-bisphosphines in moderate to good yields. In cross-metathesis reactions, phosphine-boranes **6** and **9** are highly reactive templates leading more often to the formation of a major *E*-isomer although trace amount of the *Z* isomer are always present. Extended reaction times did not affect the *E*/*Z* ratio. This is not the case for the corresponding vinyl-substituted phosphine boranes, which are less reactive but present the advantage of leading exclusively to the formation of the *E*-isomer.

3. Conclusion

In summary, we have studied the reactivity of five borane-protected P-templates **6**–**10** under metathesis conditions. Homodimerisation of substrates **6**, **7**, **9** and **10** have been investigated and proved successful only for the allyl-substituted borane-protected phosphines. In contrast, all five borane-protected P-templates **6**–**10** are suitable starting materials for diverse cross-metathesis coupling with electron-rich and electron-poor olefinic partners. Although all reactions proceeded with excellent conversions, the resulting products are often prone to decompose upon purification and could be isolated only in moderate to good yields. Compounds **14c** and **15j**–**m** are the precursors of novel chiral phosphines and should be accessible enantioenriched from (+)- or (−)-ephedrine. These compounds are amenable to interesting functional group manipulation such as substitution around the phosphorus atom or various reactions involving the double bond. This chemistry is currently under investigation and will be reported in due course.

4. Experimental

4.1. General experimental methods

Solvents were purified prior to use by passing through a column of activated alumina under inert atmosphere [24]. All reactions were carried out under inert atmosphere using flame-dried glassware. Flash chromatography was carried out using silica gel (0.040–0.063 mm) and eluents as indicated. TLC was carried out on Merck aluminium-backed silica gel sheets and visualised with a UV lamp or by staining with I_2 and/or $KMnO_4$. ^{13}C and ^{31}P NMR spectra are proton-decoupled. Where required, structural assignments are supported by ^{13}C-DEPT and 2D-COSY, HMQC and HMBC spectra.

4.2. Allyldiphenylphosphine borane 6 [15]

Borane–methylsulfide complex (15.5 ml of a 0.8 M solution in diethyl ether, 12.4 mmol) was added dropwise to a solution of chlorodiphenylphosphine (2 ml, 11.1 mmol) in diethyl ether (20 ml) at 0 °C. The mixture was stirred at 0 °C for 2 h then allowed to warm to room temperature. A round-bottomed flask was charged with dried magnesium turnings (2.72 g, 112 mmol) and diethyl ether (20 ml). Several crystals of iodine were added in order to initiate the reaction, followed by dropwise addition of a solution of allyl bromide (2.9 ml, 34 mmol) in diethyl ether (25 ml). A gentle reflux was maintained, without external heating. After the addition was complete the Grignard solution was allowed to cool to room temperature then transferred to another flask via cannula, leaving behind excess magnesium. The Grignard reagent was cooled to 0 °C and the freshly prepared phosphine borane solution added dropwise. The mixture was stirred for 3 h whilst warming to room temperature then quenched by the addition of saturated aqueous ammonium chloride. The aqueous layer was extracted with diethyl ether. The combined organics were washed with water and saturated aqueous ammonium chloride, dried over $MgSO_4$ and solvents removed in vacuo. Purification by flash chromatography (hexane/toluene 2:3) afforded the product as a cloudy oil. Yield: 2.8 g (quantitative); R_f 0.4 (hexane/toluene 2:3); ^1H NMR (400 MHz, $CDCl_3$): δ 7.65–7.70 (m, 4H; Ph–H), 7.43–7.51 (m, 6H; Ph–H), 5.79 (m, 1H; PCH_2CH), 5.04–5.13 (m, 2H; $=CH_2$), 3.06 (dd, $^2J_{(H,P)}$ 12.5, $^3J_{(H,H)}$ 7.5 Hz, 2H; PCH_2), 1.00 ppm (brq, $^1J_{(H,B)}$ 89 Hz, 3H; BH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.4 (d, $^2J_{(C,P)}$ 8.9 Hz, Ph–C_{ortho}), 131.2 (d, $^4J_{(C,P)}$ 2.4 Hz, Ph–C_{para}), 128.8 (d, $^1J_{(C,P)}$ 54.6 Hz, Ph–C_{ipso}), 128.7 (d, $^3J_{(C,P)}$ 9.8 Hz, Ph–C_{meta}), 128.2 (d, $^2J_{(C,P)}$ 7.3 Hz, PCH_2CH), 120.4 (d, $^3J_{(C,P)}$ 11.0 Hz, $=CH_2$), 31.9 ppm (d, $^1J_{(C,P)}$ 35.8 Hz, PCH_2); ^{31}P NMR (162 MHz, $CDCl_3$): δ 15.7 ppm (q, $^1J_{(P,B)}$ 60 Hz); IR (film): ν 2383 (B − H), 1637 cm^{-1} (C=C); MS (CI): m/z 227 $[M-BH_2]^+$.

4.3. Diphenylvinylphosphine borane 7 [25]

Borane–methylsulfide complex (15.5 ml of a 0.8 M solution in diethyl ether, 12.4 mmol) was added dropwise to a solution of chlorodiphenylphosphine (2 ml, 11.1 mmol) in diethyl ether (20 ml) at 0 °C. The mixture was stirred at 0 °C for 2 h then allowed to warm to room temperature. Vinylmagnesium bromide (13.4 ml of a 1.0 M solution in THF, 13.4 mmol) was added at 0 °C and the mixture was stirred for 1.5 h whilst warming to room temperature. The reaction was quenched by the addition of saturated aqueous ammonium chloride. The aqueous layer was extracted with diethyl ether. The combined organics were washed with water and saturated aqueous ammonium chloride, dried over $MgSO_4$ and solvents removed in vacuo. Purification by flash chromatography (hexane/toluene 1:1) afforded the product as a cloudy oil. Yield: 460 mg

(18%); R_f 0.5 (hexane/toluene 2:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62–7.68 (m, 4H; Ph–H), 7.43–7.53 (m, 6H; Ph–H), 6.59 (ddd, $^3J_{(H,H)}$ 12.0, $^3J_{(H,H)}$ 14.3, $^2J_{(H,P)}$ 26.3 Hz, 1H; PCH), 6.29 (ddd, $^2J_{(H,H)}$ 1.4, $^3J_{(H,H)}$ 12.0, $^3J_{(H,P)}$ 39.7 Hz, 1H; $=CH_{trans}$), 6.13 (ddd, $^2J_{(H,H)}$ 1.4, $^3J_{(H,H)}$ 18.2, $^3J_{(H,P)}$ 20.0 Hz, 1H; $=CH_{cis}$), 1.04 ppm (brq, $^1J_{(H,B)}$ 70 Hz, 3H; BH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.2 (d, $^2J_{(C,P)}$ 4.7 Hz, $=CH_2$), 132.6 (d, $^2J_{(C,P)}$ 9.6 Hz, Ph–C_{ortho}), 131.3 (d, $^4J_{(C,P)}$ 2.4 Hz, Ph–C_{para}), 128.9 (d, $^1J_{(C,P)}$ 59.0 Hz, Ph–C_{ipso}), 128.8 (d, $^2J_{(C,P)}$ 10.2 Hz, Ph–C_{meta}), 128.3 ppm (d, $^1J_{(C,P)}$ 54.3 Hz, PCH); ^{31}P NMR (162 MHz, $CDCl_3$): δ 15.5 ppm (q, $^1J_{(P,B)}$ 65 Hz); IR (film): ν 2384 (B – H), 1437 cm^{-1} (P–Ph); MS (EI): m/z 213 $[M-BH_2]^+$.

4.4. Phenyldivinylphosphine borane **8**

Borane–methylsulfide complex (20 ml of a 0.8 M solution in diethyl ether, 16.0 mmol) was added dropwise to a solution of dichlorophenylphosphine (2 ml, 14.6 mmol) in diethyl ether (20 ml) at 0 °C. The mixture was stirred at 0 °C for 2 h then allowed to warm to room temperature. Vinylmagnesium bromide (35 ml of a 1.0 M solution in THF, 35.0 mmol) was added at 0 °C and the mixture was stirred for 1.5 h whilst warming to room temperature. The reaction was quenched by the addition of icy 2 M hydrochloric acid (200 ml). The aqueous layer was extracted with diethyl ether. The combined organics were washed with brine, dried over $MgSO_4$ and solvents removed in vacuo. Purification by flash chromatography (cyclohexane/toluene 1:1) afforded the product as a colourless oil. Yield: 520 mg (20%); R_f 0.2 (cyclohexane/toluene 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65–7.70 (m, 2H; Ph–H), 7.44–7.51 (m, 3H; Ph–H), 6.38 (ddd, $^3J_{(H,H)}$ 12.0, $^3J_{(H,H)}$ 14.8, $^2J_{(H,P)}$ 26.9 Hz, 1H; PCH), 6.21 (ddd, $^2J_{(H,H)}$ 1.7, $^3J_{(H,H)}$ 12.0, $^3J_{(H,P)}$ 39.3 Hz, 1H; $=CH_{trans}$), 6.15 (ddd, $^2J_{(H,H)}$ 1.6, $^3J_{(H,H)}$ 18.4, $^3J_{(H,P)}$ 20.0 Hz, 1H; $=CH_{cis}$), 1.04 ppm (brq, $^1J_{(H,B)}$ 70 Hz, 3H; BH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.5 (d, $^2J_{(C,P)}$ 4.3 Hz, $=CH_2$), 132.0 (d, $^3J_{(C,P)}$ 9.5 Hz, Ph–C_{meta}), 131.3 (d, $^4J_{(C,P)}$ 2.4 Hz, Ph–C_{para}), 128.8 (d, $^2J_{(C,P)}$ 10.1 Hz, Ph–C_{ortho}), 128.1 (d, $^1J_{(C,P)}$ 59.6 Hz, Ph–C_{ipso}), 127.8 ppm (d, $^1J_{(C,P)}$ 54.7 Hz, PCH); ^{31}P NMR (162 MHz, $CDCl_3$): δ 11.1 ppm (q, $^1J_{(P,B)}$ 54 Hz); IR (film): ν 2383 (B – H), 1643 cm^{-1} (C=C); HRMS (ESI): m/z calcd for $C_{10}H_{14}BNaP$ $[M+Na]^+$: 199.0824; found: 199.0818.

4.5. Bis(diethylamino)phenyl phosphine [26]

To a solution of dichlorophenylphosphine (24 ml, 176 mmol) in diethyl ether (300 ml) was added solution of diethylamine (80 ml, 773 mmol) in diethyl ether (50 ml) dropwise at 0 °C. The mixture was stirred for 1 h then allowed to warm to room temperature. The solution was filtered to remove precipitated diethylamine hydrochloride and the solvent and excess diethylamine were removed in vacuo. The residue was distilled under reduced pressure (130 °C/0.3 mbar) to afford the product as a colourless oil. Yield: 39.6 g (89%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45–7.48 (m, 2H; Ph–H_{ortho}), 7.34–7.38 (m, 2H; Ph–H_{meta}), 7.24–7.28 (m, 1H; Ph–H_{para}), 3.08–3.16 (m, 8H; CH_2), 1.14 ppm (t, $^3J_{(H,H)}$ 7.1 Hz, 12H; CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) d 142.0 (d, $^2J_{(C,P)}$ 4.0 Hz, Ph–C_{ortho}), 130.9 (d, $^1J_{(C,P)}$ 15.18, Ph–C_{ipso}), 128.1 (d, $^3J_{(C,P)}$ 3.2, Ph–C_{meta}), 127.2 (d, $^4J_{(C,P)}$ 1.6, Ph–C_{para}), 42.8 (d, $^2J_{(C,P)}$ 16.8, CH_2), 14.6 ppm (d, $^3J_{(C,P)}$ 3.2, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): d 97.2 ppm; IR (film): n 1434 cm^{-1} (P–Ph); MS (ESI): m/z 253 $[M+H]^+$.

4.6. (2RS,4SR,5RS)-2,5-Diphenyl-3,4-dimethyl-1,3,2-oxazaphospholidine-2-borane **11** [16]

A solution of bis(diethylamino)phenyl phosphine (7.6 g, 30.26 mmol) in toluene (25 ml) and a solution of (±)-ephedrine (5 g, 30.26 mmol) in toluene (25 ml) were added simultaneously and dropwise to refluxing toluene (100 ml) and the mixture refluxed for 16 h. The solution was allowed to cool to room temperature before borane–dimethylsulfide (22.7 ml of a 2.0 M solution in toluene, 45.39 mmol) was added dropwise and the mixture stirred for 2 h. The solvent was removed in vacuo leaving a yellow oil, which began to crystallise after several hours. Recrystallisation from propan-2-ol gave a crop of fine white needle crystals of the product as a single diastereomer. Yield: 6.03 g (70%); m.p. 98–100 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84–7.86 (m, 2H; Ph–H), 7.45–7.59 (m, 3H; Ph–H), 7.31–7.41 (m, 5H; Ph–H), 5.61 (dd, $^3J_{(H,H)}$ 6.0, $^3J_{(H,P)}$ 2.7 Hz, 1H; C*H*Ph), 3.69 (ddq, $^3J_{(H,H)}$ 6.5, $^3J_{(H,P)}$ 8.5 Hz, 1H; C*H*CH_3), 2.69 (d, $^3J_{(H,P)}$ 10.9 Hz, 3H; NCH_3), 0.98 (brq, $^1J_{(H,B)}$ 90 Hz, 3H; BH_3), 0.84 ppm (d, $^3J_{(H,H)}$ 6.5 Hz, 3H; CHCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.2 (d, $^3J_{(C,P)}$ 5.4 Hz, CPh–C_{ipso}), 132.9 (d, $^1J_{(C,P)}$ 54.7 Hz, PPh–C_{ipso}), 132.3 (d, $^4J_{(C,P)}$ 2.0 Hz, PPh–C_{para}), 130.9 (d, $^2J_{(C,P)}$ 12.1 Hz, PPh–C_{ortho}), 128.6 (d, $^3J_{(C,P)}$ 9.7 PPh–C_{meta}), 128.31 (s, CPh–C), 128.28 (s, CPh–C_{para}), 126.6 (s, CPh–C), 84.1 (d, $^2J_{(C,P)}$ 8.1 Hz, *C*HPh), 59.0 (d, $^2J_{(C,P)}$ 2.4 Hz, *C*HCH$_3$), 29.4 (d, $^2J_{(C,P)}$ 8.1 Hz, NCH_3), 13.5 ppm (d, $^3J_{(C,P)}$ 3.3 Hz, CH*C*H$_3$); ^{31}P NMR (162 MHz, $CDCl_3$): δ 133.0 ppm (q, $^1J_{(P,B)}$ 75 Hz); IR (KBr): ν 2385 (B–H), 1435 cm^{-1} (P–Ph); MS (CI): m/z 286 (30%) $[M+H]^+$, 272 (100%) $[M-BH_2]^+$.

4.7. Tetraallyl tin [27]

A large round-bottomed flask was charged with dried magnesium turnings (18.5 g, 770 mmol) and diethyl ether (500 ml). Several crystals of iodine were added in order to initiate the reaction, followed by dropwise addition of a solution of allyl bromide (53 ml, 616 mmol) in diethyl ether (300 ml). A gentle reflux was maintained, without external heating. After the addition was complete the Grignard solution was allowed to cool to room temperature then transferred to another flask via cannula, leaving behind excess magnesium. The Grignard solution was

cooled to −10 °C and tin (IV) chloride (9 ml, 77 mmol) added dropwise. After the addition was complete the mixture was refluxed for 16 h then cooled to −10 °C and quenched by dropwise addition of water (150 ml). Remaining solids were dissolved by the dropwise addition 3.5% HCl (300 ml). The aqueous phase was extracted with diethyl ether. The combined organics were washed repeatedly with 5% aqueous potassium fluoride (w/w solution), and filtered, until no more solids precipitated. After stirring over $MgSO_4$ for 1 h, solvent was removed in vacuo to leave a cloudy oil which was distilled under vacuum (65 °C/0.3 mbar) to yield the product as a colourless oil. Yield: 13.54 g (66%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.94 (m, 1H; $SnCH_2CH$), 4.88 (m, 1H; $=CH_AH_B$), 4.76 (m, 1H; $=CH_AH_B$), 1.93 ppm (d, $^3J_{(H,H)}$ 8.6 Hz, 2H; $SnCH_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.6 ($SnCH_2CH$), 111.1 ($=CH_2$), 16.1 ppm ($SnCH_2$); IR (film): ν 1623 cm^{-1} (C=C); MS (FI): m/z 239 (19%, $C_9H_{15}{}^{116}Sn$), 241 (56%, $C_9H_{15}{}^{118}Sn$), 243 (100%, $C_9H_{15}{}^{120}Sn$) $[M-C_3H_5]^{+\cdot}$.

4.8. (RS_P)-Allyl{N-methyl-[(1RS,2SR)-(1-hydroxy-1-phenylprop-2-yl)]amino}phenyl-phosphine borane **12** [8]

To a solution of tetraallyl tin (5 g, 18.67 mmol) in diethyl ether (120 ml) was added *n*-butyllithium (32 ml of a 2.3 M solution in hexane, 74.68 mmol) dropwise over 20 min at −10 °C. The resulting solution was stirred for 40 min at −10 °C then allowed to warm to room temperature. Dry 1,4-dioxane (60 ml) was added slowly, causing the formation of a fine white precipitate. The supernatant was removed via cannula and the remaining solids washed three times with pentane. The solid was dissolved in THF (50 ml) to give an orange solution of allyllithium, which was titrated (0.74 M, ~50%) by standard techniques. The freshly prepared allyllithium solution (12 ml, 8.88 mmol) was added dropwise over 20 min to a vigorously stirred solution of (2*RS*,4*SR*,5*RS*)-2,5-diphenyl-3,4-dimethyl-1,3,2-oxazaphospholidine-2-borane (3 g, 8.77 mmol) in THF (20 ml) at −110 °C (ethanol/liquid nitrogen slush bath). After addition was complete the mixture was stirred for 10 min at −110 °C then removed from the cold-bath and stirred for a further 1 h. The reaction was quenched by the addition of water. The aqueous phase was extracted with dichloromethane and the combined organics washed with brine dried over $MgSO_4$ and the solvents removed in vacuo. Purification by flash chromatography (toluene/EtOAc 24:1) afforded the product as a colourless oil which crystallised over several days to give a white crystalline solid (de = 60%). Yield: 2.21 g (77%); R_f 0.2 (toluene/EtOAc 24:1); m.p. 78–80 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15–7.45 (m, 10H; Ph–H), 5.94 (m, 1H; PCH_2CH), 5.83 (m, 1H; $PCH_2CH)^{minor}$, 5.13–5.25 (m, 2H; PCH_2CHCH_2), 4.88 (d, $^3J_{(H,H)}$ 4.7 Hz, 1H; $CHOH)^{minor}$, 4.83 (dd, $^3J_{(H,H)}$ 6.1, $^3J_{(H,H)}$ 2.8 Hz, 1H; CHOH), 4.05 (ddq, 1H; $CHCH_3$), 2.91 (ddd, $^3J_{(H,H)}$ 8.8, $^2J_{(H,H)}$ 14.7, $^2J_{(H,P)}$ 14.7 Hz, 1H; PCH_AH_B), 2.77 (m, 1H; PCH_AH_B), 2.55 (d, $^3J_{(H,P)}$ 7.7 Hz, 3H; NCH_3), 2.52 (d, $^3J_{(H,P)}$ 7.6 Hz, 3H; NCH_3), 1.87 (d, $^3J_{(H,H)}$ 3.3 Hz, 1H; OH), 1.21 (d, $^3J_{(H,H)}$ 6.8 Hz, 3H; CCH_3), 1.16 (d, $^3J_{(H,H)}$ 6.9 Hz, 3H; $CCH_3)^{minor}$, 0.77 ppm (brq, $^1J_{(H,B)}$ 109 Hz, 3H; BH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5 (s, CPh–$C_{ipso})^{minor}$, 142.4 (s, CPh–C_{ipso}), 132.5 (d, $^1J_{(C,P)}$ 63.9 Hz, PPh–C_{ipso}), 132.1 (d, $^1J_{(C,P)}$ 58.5 Hz, PPh–$C_{ipso})^{minor}$, 130.8 (d, $^4J_{(C,P)}$ 2.2 Hz, PPh–C_{para}), 130.5 (d, $^4J_{(C,P)}$ 2.4 Hz, PPh–C_{para}), 130.6 (d, $^2J_{(C,P)}$ 9.4 Hz, $PCH_2CH)^{minor}$, 130.4 (d, $^2J_{(C,P)}$ 9.5 Hz, PCH_2CH), 129.6 (d, $^3J_{(C,P)}$ 5.0 Hz, PPh–$C_{meta})^{minor}$, 129.5 (d, $^3J_{(C,P)}$ 4.7 Hz, PPh–C_{meta}), 128.6 (d, $^2J_{(C,P)}$ 9.2 Hz, PPh–$C_{ortho})^{minor}$, 128.5 (d, $^2J_{(C,P)}$ 9.2 Hz, PPh–C_{ortho}), 128.5 (s, CPh–C), 128.3 (s, CPh–C)^{minor}, 127.5 (s, PPh–$C_{para})^{minor}$, 127.0 (s, PPh–C_{para}), 126.7 (s, PPh–C), 126.1 (s, PPh–C)^{minor}, 119.7 (d, $^3J_{(C,P)}$ 11.2 Hz, PCH_2CHCH_2), 119.5 (d, $^3J_{(C,P)}$ 11.2 Hz, $PCH_2CHCH_2)^{minor}$, 78.8 (d, $^3J_{(C,P)}$ 4.8 Hz, CHOH), 78.8 (d, $^3J_{(C,P)}$ 4.8 Hz, $CHOH)^{minor}$, 58.1 (d, $^2J_{(C,P)}$ 9.3 Hz, $CCH_3)^{minor}$, 57.9 (d, $^2J_{(C,P)}$ 9.8 Hz, CCH_3), 31.8 (d, $^1J_{(C,P)}$ 38.0 Hz, PCH_2), 31.7 (d, $^1J_{(C,P)}$ 41.5 Hz, $PCH_2)^{minor}$, 29.8 (d, $^2J_{(C,P)}$ 3.3 Hz, $NCH_3)^{minor}$, 29.4 (d, $^2J_{(C,P)}$ 3.8 Hz, NCH_3), 13.4 (d, $^3J_{(C,P)}$ 2.4 Hz, CCH_3), 12.2 ppm (d, $^3J_{(C,P)}$ 2.9 Hz, $CCH_3)^{minor}$; ^{31}P NMR (162 MHz, $CDCl_3$): δ 70.4 ppm (q, $^1J_{(P,B)}$ 79 Hz); IR (film): ν 3453 (O–H), 2381 (B–H), 1636 (C=C), 1436 cm^{-1} (P–Ph); MS (CI): m/z 314 $[M-BH_2]^+$.

4.9. (RS_P)-{N-Methyl-[(1RS,2SR)-(1-hydroxy-1-phenylprop-2-yl)]amino}phenyl-(vinyl) phosphine borane **13** [18]

n-Butyllithium (14.4 ml of a 2.3 M solution in hexanes, 33.06 mmol) was added dropwise to tetravinyl tin (3 ml, 16.53 mmol) in a schlenk tube. A white precipitate formed rapidly and after being allowed to settle, the liquid was removed via cannula. The solid was washed four times with dry pentane. Dissolution of the solid in degassed THF (10 ml) produced an orange solution which was titrated (2.8 M, ~85%) by standard techniques. The freshly prepared vinyllithium solution (3.25 ml, 9.10 mmol) was added dropwise to a solution of (2*RS*,4*SR*,5*RS*)-2,5-diphenyl-3,4-dimethyl-1,3,2-oxazaphospholidine-2-borane (2 g, 7.01 mmol) in degassed THF (18 ml) at −78 °C, under argon. The mixture was stirred for 30 min at −78 °C then allowed to warm to room temperature and quenched with water. THF was removed in vacuo and the product extracted with dichloromethane, dried over $MgSO_4$ and solvents evaporated. Purification by flash chromatography (toluene/EtOAc 9:1) afforded the product as a white crystalline solid. Yield: 2.20 g (100%); R_f 0.4 (toluene/EtOAc 9:1); m.p. 90–95 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46–7.50 (m, 2H; Ph–H), 7.34–7.42 (m, 4 H; Ph–H), 7.24–7.30 (m, 2H; Ph–H), 7.03–7.09 (m, 2H; Ph–H), 6.35–6.43 (m, 1H; PCH), 6.13–6.27 (m, 2H; $PCHCH_2$), 4.80 (dd, $^3J_{(H,H)}$ 6.8, $^3J_{(H,H)}$ 3.8 Hz, 1H; CHOH), 4.16 (ddq, $^3J_{(H,H)}$ 6.6, $^3J_{(H,H)}$ 6.6, $^3J_{(HP)}$ 11.4 Hz, 1H; $CHCH_3$), 2.49 (d, 3H, $^3J_{(HP)}$ 8.1 Hz, NCH_3), 1.86 (d, $^3J_{(H,H)}$ 3.8 Hz, 1H; OH), 1.29 (d, $^3J_{(H,H)}$ 6.6 Hz, 3H; CCH_3), 0.80 ppm (brq, $^1J_{(H,B)}$ 86 Hz, 3H; BH_3); ^{13}C NMR (101 MHz,

$CDCl_3$) δ 142.5 (s, CPh–C_{ipso}), 133.8 (d, $^2J_{(C,P)}$ 7.0 Hz, PCH*C*H_2), 131.0 (PPh–C), 130.9 (d, $J_{(C,P)}$ 10.2 Hz PPh–C), 129.0 (d, $^1J_{(C,P)}$ 54.0 Hz, PCH), 128.5 (s, CPh–C), 128.3 (d, $J_{(C,P)}$ 10.2 Hz, PPh–C), 127.8 (s, CPh–C), 126.8 (s, CPh–C), 78.4 (d, $^3J_{(C,P)}$ 7.2 Hz, CHOH), 57.9 (d, $^2J_{(C,P)}$ 9.6 Hz, *C*CH_3), 29.6 (d, $^2J_{(C,P)}$ 4.0, NCH_3), 13.7 ppm (s, C*C*H_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 66.5 ppm (q, $^1J_{(P,B)}$ 87 Hz); IR (film): ν 3423 (O–H), 2382 (B–H), 1436 cm^{-1} (P–Ph); MS (CI): m/z 300 $[M-BH_2]^+$.

4.10. Allyl(methoxy)phenylphosphine borane (±)-9

Concentrated sulfuric acid (34 μl, 0.64 mmol) was added to a solution of (RS_P)-allyl{*N*-methyl-[(1*RS*,2*SR*)-(1-hydroxy-1-phenyl-prop-2-yl)]amino}phenylphosphine borane (1.85 g, 5.65 mmol) in methanol (45 ml) and stirred at room temperature overnight. The methanol was removed in vacuo and the remaining solids stirred in diethyl ether for several minutes to dissolve the product. The solution was filtered to remove insoluble ephedrine hydrochloride and the ether removed in vacuo. Purification by flash chromatography (hexane/EtOAc 4:1) to afforded the product as a colourless oil. Yield: 868 mg (79%); R_f 0.4 (hexane/EtOAc 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71–7.76 (m, 2H; Ph–H), 7.46–7.55 (m, 3H; Ph–H), 5.69 (m, 1H; PCH_2CH), 5.69 (m, 1H; $=CH_{trans}$), 5.14 (m, 1H; $=CH_{cis}$), 3.64 (d, $^3J_{(H,P)}$ 11.9 Hz, 3H; OCH_3), 2.79 (m, 2H; PCH_2), 0.77 ppm (brdq, $^1J_{(H,B)}$ 96, $^2J_{(H,P)}$ 14.3 Hz, 3H; BH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.1 (d, $^4J_{(C,P)}$ 2.4 Hz, Ph–C_{para}), 131.1 (d, $^2J_{(C,P)}$ 10.7 Hz, Ph–C_{ortho}), 130.4 (d, $^1J_{(C,P)}$ 54.5 Hz, Ph–C_{ipso}), 128.6 (d, $^3J_{(C,P)}$ 10.2 Hz, Ph–C_{meta}), 127.2 (d, $^2J_{(C,P)}$ 6.2 Hz, PCH_2CH), 120.5 (d, $^3J_{(C,P)}$ 7.7 Hz, $=CH_2$), 54.2 (d, $^2J_{(C,P)}$ 3.1 Hz, OCH_3), 36.5 ppm (d, $^1J_{(C,P)}$ 42.6 Hz, PCH_2); ^{31}P NMR (162 MHz, $CDCl_3$): δ 114.1 ppm (q, $^1J_{(P,B)}$ 63 Hz); IR (film): ν 2385 (B–H), 1638 (C=C), 1438 cm^{-1} (P–Ph); HRMS (FI): m/z calcd for $C_{10}H_{16}BOP$ $M^{+\cdot}$: 194.1032; found: 194.1195.

4.11. Methoxy(phenyl)vinylphosphine borane (±)-10

Concentrated sulfuric acid (34 μl, 0.64 mmol) was added to a solution of (RS_P)-{*N*-methyl-[(1*RS*,2*SR*)-(1-hydroxy-1-phenylprop-2-yl)]amino}phenyl(vinyl)phosphine borane (200 mg, 0.64 mmol) in methanol (5 ml) and stirred at room temperature overnight. The methanol was removed in vacuo and the remaining solids stirred in diethyl ether for several minutes to dissolve the product. The solution was filtered to remove insoluble ephedrine hydrochloride and the ether removed in vacuo. Purification by flash chromatography (hexane/EtOAc 19:1) afforded the product as a colourless oil. Yield: 100 mg (87%); R_f 0.2 (hexane/EtOAc 19:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74–7.80 (m, 2H; Ph–H), 7.46–7.57 (m, 3H; Ph–H), 6.12–6.45 (m, 3H; $PCHCH_2$), 3.65 (d, $^3J_{(H,P)}$ 12.6 Hz, 3H; OCH_3), 0.83 ppm (3H, brdq, $^1J_{(H,B)}$ 97, $^2J_{(H,P)}$ 15.0 Hz; BH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.3 (d, $^2J_{(C,P)}$ 7.2 Hz, $PCHCH_2$), 132.1 (d, $^4J_{(C,P)}$ 2.4 Hz, Ph–C_{para}), 131.1 (d, $^2J_{(C,P)}$ 11.2 Hz, Ph–C_{ortho}), 130.5 (d, $^1J_{(C,P)}$ 60.7 Hz, PCH), 128.7 (d, $^3J_{(C,P)}$ 10.4 Hz, Ph–C_{meta}), 53.7 ppm (s, OCH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 105.5 ppm (q, $^1J_{(P,B)}$ 67 Hz); IR (film): ν 2252 (B–H), 1438 cm^{-1} (P–Ph); HRMS (FI): m/z calcd for $C_9H_{14}BOP$ $M^{+\cdot}$: 180.0875; found: 180.0874.

4.12. Procedure A: cross-metathesis

A solution of phosphine borane (1 equiv.) and olefinic partner (3 equiv.) in dichloromethane (0.3 M in phosphine borane) was heated to reflux. Grubbs' 2nd generation catalyst (0.02 equiv.) was then added as a solid and the mixture stirred at reflux. The reaction was followed by TLC and further portions of catalyst added as required. The solvent was then removed in vacuo.

4.13. Procedure B: self-metathesis

A solution of the starting material (1 equiv.) in dichloromethane (0.3 M) was heated to reflux. Grubbs' 2nd generation catalyst (0.02 equiv.) was then added as a solid and the mixture stirred at reflux. The reaction was followed by TLC and further portions of catalyst added as required. The solvent was then removed in vacuo.

4.14. 2-Butenyl-1,4-bis(diphenylphosphine borane) 14a [15]

Procedure B from allyldiphenyl-phosphine borane (100 mg, 0.44 mmol) in dichloromethane (1.5 ml) using 0.04 equiv. Grubbs' 2nd generation catalyst (15 mg, 0.016 mmol) over 24 h. The residue was purified by flash chromatography (toluene/hexane 1:1) to yield the product as a white solid (*E*:*Z* = 9:1). Yield: 54 mg (57%). Recrystallisation from methanol gave the pure *E*-isomer. R_f 0.4 (toluene/hexane: 3/2); m.p. 160–163 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (m, 8H; Ph–H), 7.45 (m, 4H; Ph–H), 7.38 (m, 8H; Ph–H), 5.34 (m, 2H; PCH_2CH), 2.97 (m, 4H; PCH_2), 0.90 ppm (brq, 6H, $^1J_{(H,B)}$ 100 Hz, BH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.2 (d, $^3J_{(C,P)}$ 9.0 Hz, Ph–C_{meta}), 131.2 (d, $^4J_{(C,P)}$ 1.4 Hz, Ph–C_{para}), 128.8 (d, $^2J_{(C,P)}$ 9.7 Hz, Ph–C_{ortho}), 128.7 (d, $^1J_{(C,P)}$ 54.3 Hz, Ph–C_{ipso}), 125.7 (dd, $^3J_{(C,P)}$ 4.7, $^2J_{(C,P)}$ 11.5 Hz, PCH_2CH), 30.9 ppm (d, $^1J_{(C,P)}$ 34.4 Hz, PCH_2); ^{31}P NMR (162 MHz, $CDCl_3$): δ 16.5 ppm (q, $^1J_{(P,B)}$ 68 Hz); IR (film): ν 2383 (B–H), 1436 cm^{-1} (P–Ph); MS (EI): m/z 439 $[M-BH_2]^+$.

4.15. 2-Butenyl-1,4-bis(methoxy(phenyl)phosphine borane) (±)-14c

Procedure B from allyl(methoxy)-phenylphosphine borane (100 mg, 0.52 mmol) in dichloromethane (1.7 ml) using 0.02 equiv. Grubbs' 2nd generation catalyst (9 mg, 0.011 mmol) over 12 h. The residue was purified by flash chromatography (cyclohexane/EtOAc 4:1) to yield the

product as a cloudy oil (E:Z = 5:1). Yield: 80 mg (85%); R_f 0.3 (cyclohexane/EtOAc 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63–7.70 (m, 4H; Ph–H), 7.51–7.55 (m, 2H; Ph–H), 7.43–7.47 (m, 4H; Ph–H), 5.36 (m, 2H; PCH_2CH), 3.58 (d, $^3J_{(H,P)}$ 11.9 Hz, 6H; OCH_3), 2.71 (m, 4H; PCH_2), 0.72 ppm (brq, 6H, $^1J_{(H,B)}$ 80 Hz, BH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.0 (d, $^4J_{(C,P)}$ 1.8 Hz, Ph–C_{para}), 130.9 (d, $^2J_{(C,P)}$ 10.7 Hz, Ph–C_{ortho}), 130.1 (d, $^1J_{(C,P)}$ 54.6 Hz, Ph–C_{ipso}), 128.5 (d, $^3J_{(C,P)}$ 10.0 Hz, Ph–C_{meta}), 124.5 (dd, $^3J_{(C,P)}$ 6.1, $^2J_{(C,P)}$ 11.1 Hz, PCH_2CH), 53.95 (d, $^2J_{(C,P)}$ 1.9 Hz, OCH_3), 35.1 (d, $^1J_{(C,P)}$ 40.7 Hz, PCH_2)^E; ^{31}P NMR (162 MHz, $CDCl_3$): δ 113.6 ppm (q, $^1J_{(P,B)}$ 75 Hz); IR (film): ν 2385 (B–H), 1438 cm^{-1} (P–Ph); HRMS (FI): m/z calcd for $C_{18}H_{25}BO_2P_2$ $[M-BH_3]^{+\cdot}$: 346.1423; found: 346.1362. Signals overlapping on the ^{1}H NMR for *dl* and *meso* isomers except for the OMe group: ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.58 (d, $^3J_{(H,P)}$ 11.9 Hz, OCH_3) for *dl* or *meso*, 3.56 (d, $^3J_{(H,P)}$ 11.8 Hz, OCH_3) for *dl* or *meso*.

4.16. Diphenyltridec-2-enylphosphine borane **15a**

Procedure A from allyldiphenylphosphine borane (100 mg, 0.44 mmol) and 1-dodecene (0.28 ml, 1.26 mmol) in dichloromethane (1.5 ml) using 0.04 equiv. Grubbs' 2nd generation catalyst (15 mg, 0.018 mmol) over 24 h. The residue was purified by flash chromatography (hexane/EtOAc 19:1) to afford the product as a colourless oil (E:Z = 9:1). Yield: 100 mg (60%); R_f 0.5 (hexane/EtOAc 19:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65–7.71 (m, 4H; Ph–H)$^{E+Z}$, 7.42–7.51 (m, 6H; Ph–H)$^{E+Z}$, 5.54 (m, 2H; $PCH_2CHCH)^Z$, 5.40 (m, 2H; $PCH_2CHCH)^E$, 3.05 (dd, $^3J_{(H,H)}$ 7.9, $^2J_{(H,P)}$ 12.5 Hz, 2H; $PCH_2)^Z$; 3.00 (dd, $^3J_{(H,H)}$ 6.5, $^2J_{(H,P)}$ 12.2 Hz, 2H; $PCH_2)^E$, 1.92 (m, 2H; $PCH_2(CH)_2CH_2)^E$, 1.85 (m, 2H; $PCH_2(CH)_2CH_2)^Z$, 1.33–1.12 (m, 16H; $(CH_2)_8)^{E+Z}$, ~1.0 (brq, obscured, 3H; $BH_3)^{E+Z}$, 0.90 ppm (t, $^3J_{(H,H)}$ 7.0 Hz, 3H; $CH_3)^{E+Z}$; ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.9 (d, $^2J_{(C,P)}$ 11.1 Hz, $PCH_2CH)^E$, 135.1 (d, $^2J_{(C,P)}$ 11.1 Hz, $PCH_2CH)^Z$, 132.4 (d, $^3J_{(C,P)}$ 9.0 Hz, Ph–$C_{meta})^E$, 132.3 (d, $^3J_{(C,P)}$ 8.9 Hz, Ph–$C_{meta})^Z$, 131.0 (d, $^4J_{(C,P)}$ 2.0 Hz, Ph–$C_{para})^Z$, 131.0 (d, $^4J_{(C,P)}$ 2.0 Hz, Ph–$C_{para})^E$, 129.9 (d, $^1J_{(C,P)}$ 52.9 Hz, Ph–$C_{ipso})^Z$, 129.1 (d, $^1J_{(C,P)}$ 54.2 Hz, Ph–$C_{ipso})^E$, 128.6 (d, $^2J_{(C,P)}$ 9.9 Hz, Ph–$C_{ortho})^Z$, 128.5 (d, $^2J_{(C,P)}$ 9.5, Ph–$C_{ortho})^E$, 119.0 (d, $^3J_{(C,P)}$ 5.4 Hz, $PCH_2CHCH)^E$, 118.3 (d, $^3J_{(C,P)}$ 5.0 Hz, $PCH_2CHCH)^Z$, 32.4 (d, $^4J_{(C,P)}$ 1.5 Hz, $PCH_2(CH)_2CH_2)^E$, 31.8 (s, $CH_2)^E$, 30.5 (d, $^1J_{(C,P)}$ 35.8 Hz, $PCH_2)^E$, 29.53 (s, $CH_2)^E$, 29.50 (s, $CH_2)^Z$, 29.48 (s, $CH_2)^E$, 29.44 (s, $CH_2)^Z$, 29.38 (s, $CH_2)^Z$, 29.34 (s, $CH_2)^E$, 29.30 (s, $CH_2)^Z$, 29.24 (s, $CH_2)^E$, 29.21 (s, $CH_2)^Z$, 29.04 (s, $CH_2)^Z$, 29.01 (s, $CH_2)^E$, 28.99 (s, $CH_2)^E$, 28.9 (s, $CH_2)^Z$, 28.8 (s, $CH_2)^E$, 27.4 (d, $^4J_{(C,P)}$ 1.4 Hz, $PCH_2(CH)_2CH_2)^Z$, 25.6 (d, $^1J_{(C,P)}$ 35.5 Hz, $PCH_2)^Z$, 22.6 (s, $CH_2)^{E+Z}$, 14.0 ppm (s, $CH_3)^{E+Z}$; ^{31}P NMR (162 MHz, $CDCl_3$): δ 16.0 ppm (q, $^1J_{(P,B)}$ 60 Hz)$^{E+Z}$; IR (film): ν 2384 (B–H), 1437 cm^{-1} (P–Ph); HRMS (FI): m/z calcd for $C_{25}H_{38}BP$ $M^{+\cdot}$: 380.2804; found: 380.2804.

4.17. Diphenyl(4-trimethylsilylbut-2-enyl)phosphine borane **15b**

Procedure A from allyldiphenylphosphine borane (100 mg, 0.44 mmol) and allyltrimethylsilane (0.21 ml, 1.32 mmol) in dichloromethane (1.5 ml) using 0.04 equiv. Grubbs' 2nd generation catalyst (15 mg, 0.018 mmol) over 24 h. The residue was purified by flash chromatography (cyclohexane/EtOAc 19:1) to afford the product as a white solid (E:Z = 5:1). Yield: 122 mg (85%); R_f 0.3 (cyclohexane/EtOAc 19:1); m.p. 46–50 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65–7.70 (m, 4H; Ph–H)$^{E+Z}$, 7.40–7.49 (m, 6H; Ph–H)$^{E+Z}$, 5.60 (m, 1H; $PCH_2CHCH)^Z$, 5.48 (m, 1H; $PCH_2CHCH)^E$, 5.31 (m, 1H; $PCH_2CHCH)^Z$, 5.23 (m, 1H; $PCH_2CHCH)^E$, 3.03 (dd, $^3J_{(H,H)}$ 7.7, $^2J_{(H,P)}$ 12.4 Hz, 2H; $PCH_2)^{E/Z}$, 3.01 (dd, $^3J_{(H,H)}$ 7.8, $^2J_{(H,P)}$ 12.0 Hz, 2H; $PCH_2)^{E/Z}$, 1.39 (dd, $^3J_{(H,H)}$ 7.9, $^4J_{(H,H)}$ 3.5 Hz, 2H; $CH_2SiMe_3)^{E+Z}$, 1.01 (brq, $^1J_{(H,B)}$ 80 Hz, 3H; $BH_3)^{E+Z}$, −0.02 (s, 9H; $Si(CH_3)_3)^Z$, −0.16 ppm (s, 9H; $Si(CH_3)_3)^E$; ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.9 (d, $^2J_{(C,P)}$ 11.3 Hz, $PCH_2CHCH)^E$, 132.5 (d, $^2J_{(C,P)}$ 9.1 Hz, $PCH_2CHCH)^Z$, 132.3 (d, $^3J_{(C,P)}$ 8.7 Hz, Ph–$C_{meta})^E$, 132.0 (d, $^3J_{(C,P)}$ 9.0 Hz, Ph–$C_{meta})^Z$, 131.1 (d, $^4J_{(C,P)}$ 2.4 Hz, Ph–$C_{para})^Z$, 131.0 (d, $^4J_{(C,P)}$ 2.3 Hz, Ph–$C_{para})^E$, 129.2 (d, $^1J_{(C,P)}$ 53.9 Hz, Ph–$C_{ipso})^E$, 129.1 (d, $^1J_{(C,P)}$ 54.2 Hz, Ph–$C_{ipso})^Z$, 128.6 (d, $^2J_{(C,P)}$ 9.8 Hz, Ph–$C_{ortho})^{E+Z}$, 117.0 (d, $^3J_{(C,P)}$ 5.4 Hz, $PCH_2CH)^E$, 116.2 (d, $^3J_{(C,P)}$ 4.6 Hz, $PCH_2CH)^Z$, 30.7 (d, $^1J_{(C,P)}$ 36.2 Hz, $PCH_2)^E$, 25.1 (d, $^1J_{(C,P)}$ 36.7 Hz, $PCH_2)^Z$, 23.2 (d, $^4J_{(C,P)}$ 1.9 Hz, $CH_2SiMe_3)^E$, 18.8 (d, $^4J_{(C,P)}$ 1.6 Hz, $CH_2SiMe_3)^Z$, −1.8 (s, $Si(CH_3)_3)^Z$, −2.2 ppm (s, $Si(CH_3)_3)^E$; ^{31}P NMR (162 MHz, $CDCl_3$): δ 16.6 (q, $^1J_{(P,B)}$ 70 Hz)^Z, 15.5 ppm (q, $^1J_{(P,B)}$ 70 Hz)^E; IR (film): ν 2382 (B–H), 1437 cm^{-1} (P–Ph); HRMS (FI): m/z calcd for $C_{19}H_{28}BPSi$ $M^{+\cdot}$: 326.1795; found: 326.1791.

4.18. 6-Bromohex-2-enyldiphenylphosphine borane **15c**

Procedure A from allyldiphenyl-phosphine borane (100 mg, 0.44 mmol) and 5-bromopent-1-ene (0.16 ml, 1.32 mmol) in dichloromethane (1.5 ml) using 0.08 equiv. Grubbs' 2nd generation catalyst (30 mg, 0.036 mmol) over 48 h. The residue was purified by flash chromatography (cyclohexane/EtOAc 9:1) to afford the E-isomer of the product as a colourless oil. Yield: 65 mg (41%); R_f 0.3 (cyclohexane/EtOAc 9:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62–7.67 (m, 4H; Ph–H), 7.41–7.49 (m, 6H; Ph–H), 5.39 (m, 2H; PCH_2CHCH), 3.17 (t, $^3J_{(H,H)}$ 6.7 Hz, 2H; $BrCH_2$), 2.99 (dd, $^3J_{(H,H)}$ 7.0, $^2J_{(H,P)}$ 12.4 Hz, 2H; PCH_2), 2.07 (m, 2H; $BrCH_2CH_2CH_2$), 1.74 (tt, $^3J_{(H,H)}$ 6.9, $^3J_{(H,H)}$ 6.9 Hz, 2H; $BrCH_2CH_2$), 0.94 ppm (brq, $^1J_{(H,B)}$ 100 Hz, 3H; BH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.4 (d, $^2J_{(C,P)}$ 11.1 Hz, PCH_2CHCH), 132.3 (d, $^3J_{(C,P)}$ 8.9 Hz, Ph–C_{meta}), 131.2 (d, $^4J_{(C,P)}$ 2.4 Hz, Ph–C_{para}), 128.8 (d, $^1J_{(C,P)}$ 54.3 Hz, Ph–C_{ipso}), 128.7 (d, $^2J_{(C,P)}$ 9.8 Hz, Ph–C_{ortho}), 121.0 (d, $^3J_{(C,P)}$ 5.5 Hz, PCH_2CH), 32.8 (s, $BrCH_2$), 31.8 (d, $^5J_{(C,P)}$ 3.3 Hz, $BrCH_2CH_2$), 30.6 (d, $^4J_{(C,P)}$ 2.2 Hz, $BrCH_2CH_2CH_2$), 30.5 ppm (d, $^1J_{(C,P)}$ 35.6 Hz, PCH_2); ^{31}P

NMR (162 MHz, $CDCl_3$): δ 16.2 ppm (q, $^1J_{(P,B)}$ 69 Hz); IR (film): ν 2382 (B–H), 1436 cm^{-1} (P–Ph); HRMS (FI): m/z calcd for $C_{18}H_{20}BrP$ $[M-BH_3]^{+\cdot}$: 346.0486; found: 346.0492.

4.19. 4-Ketopent-2-enyldiphenylphosphine borane **15e**

Procedure A from allyldiphenylphosphine borane (100 mg, 0.44 mmol) and methylvinylketone (0.11 ml, 1.32 mmol) in dichloromethane (1.5 ml) using 0.08 equiv. Grubbs' 2nd generation catalyst (30 mg, 0.036 mmol) over 48 h. The residue was purified by flash chromatography (cyclohexane/EtOAc 7:3) to afford the *E*-isomer of the product as a colourless oil. Yield: 74 mg (63%); R_f 0.2 (cyclohexane/EtOAc 7:3); ^1H NMR (400 MHz, $CDCl_3$): δ 7.62–7.67 (m, 4H; Ph–H), 7.43–7.53 (m, 6H; Ph–H), 6.73 (ddt, $^3J_{(H,P)}$ 5.4, $^3J_{(H,H)}$ 7.8, $^3J_{(H,H)}$ 15.8 Hz, 1H; PCH_2CH), 5.95 (dd,$^3J_{(H,H)}$ 16.0, $^4J_{(H,P)}$ 4.0 Hz, 1H; PCH_2CHCH), 3.18 (dd, $^3J_{(H,H)}$ 7.9, $^2J_{(H,P)}$ 13.3 Hz, 2H; PCH_2), 2.16 (s, 3H; CH_3), 1.02 ppm (brq, $^1J_{(H,B)}$ 120 Hz, 3H; BH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5 (d, $J_{(C,P)}$ 2.3 Hz, COMe), 137.6 (d, $^2J_{(C,P)}$ 4.9 Hz, PCH_2CH), 135.3 (d, $^3J_{(C,P)}$ 9.9 Hz, PCH_2CHCH), 132.1 (d, $^3J_{(C,P)}$ 9.2 Hz, Ph–C_{meta}), 131.7 (d, $^4J_{(C,P)}$ 2.4 Hz, Ph–C_{para}), 128.9 (d, $^2J_{(C,P)}$ 10.1 Hz, Ph–C_{ortho}), 127.9 (d, $^1J_{(C,P)}$ 54.7 Hz, Ph–C_{ipso}), 31.0 (d, $^1J_{(C,P)}$ 33.7 Hz, PCH_2), 26.7 ppm (s, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.3 ppm (q, $^1J_{(P,B)}$ 68 Hz); IR (film): ν 2383 (B–H), 1674 (C=O), 1626 (C=C), 1437 cm^{-1} (P–Ph); HRMS (FI): m/z calcd for $C_{17}H_{17}OP$ $[M-BH_3]^{+\cdot}$: 268.1017; found: 268.0968.

4.20. Diphenyl-(3-phenylallyl)phosphine borane **15f**

Synthesised using procedure A from allyldiphenylphosphine borane (100 mg, 0.44 mmol) and styrene (0.15 ml, 1.32 mmol) in dichloromethane (1.5 ml) using 0.06 equiv. Grubbs' 2nd generation catalyst (22 mg, 0.026 mmol) over 36 h. The residue was purified by flash chromatography (cyclohexane/EtOAc 9:1) to afford the *E*-isomer of the product as a white solid. Yield: 56 mg (40%); R_f 0.3 (cyclohexane/EtOAc 9:1); ^1H NMR (400 MHz, $CDCl_3$): δ 7.68–7.73 (m, 4H; PPh–H), 7.44–7.55 (m, 6H; PPh–H), 7.20–7.30 (m, 5H; CPh–H), 6.34 (dd, $^4J_{(H,P)}$ 4.3, $^3J_{(H,H)}$ 15.8 Hz, 1H; PCH_2CHCH), 5.95 (ddt, $^3J_{(H,P)}$ 5.4, $^3J_{(H,H)}$ 7.5, $^3J_{(H,H)}$ 15.6 Hz, 1H; PCH_2CH), 3.22 (ddd, $^4J_{(H,H)}$ 1.0, $^3J_{(H,H)}$ 7.6, $^2J_{(H,P)}$ 12.7 Hz, 2H; PCH_2), 1.05 ppm (brq, $^1J_{(H,B)}$ 120 Hz, 3H; BH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.7 (d, $J_{(C,P)}$ 3.0 Hz, CPh–C_{ipso}), 135.0 (d, $^3J_{(C,P)}$ 11.2 Hz, PCH_2CHCH), 132.4 (d, $^3J_{(C,P)}$ 8.9 Hz, PPh–C_{meta}), 131.3 (d, $^4J_{(C,P)}$ 2.4 Hz, PPh–C_{para}), 128.8 (d, $^1J_{(C,P)}$ 54.1 Hz, PPh–C_{ipso}), 128.7 (d, $^2J_{(C,P)}$ 9.9 Hz, PPh–C_{ortho}), 128.5 (s, CPh–C_{meta}), 127.5 (s, CPh–C_{para}), 126.2 (d, $^5J_{(C,P)}$ 1.6 Hz, CPh–C_{ortho}), 119.7 (d, $^2J_{(C,P)}$ 6.1 Hz, PCH_2CH), 31.3 ppm (d, $^1J_{(C,P)}$ 35.2 Hz, PCH_2); ^{31}P NMR (162 MHz, $CDCl_3$): δ 16.7 ppm (q, $^1J_{(P,B)}$ 69 Hz); IR (film): ν 2373 (B–H), 1437 cm^{-1} (P–Ph); HRMS (FI): m/z calcd for $C_{21}H_{22}BP$ $M^{+\cdot}$: 316.1552; found: 316.1454.

4.21. (E)-Dodec-1-enyldiphenylphosphine borane **15g**

Procedure A from diphenylvinylphosphine borane (100 mg, 0.47 mmol) and 1-dodecene (0.31 ml, 1.26 mmol) in dichloromethane (1.6 ml) using 0.08 equiv. Grubbs' 2nd generation catalyst (32 mg, 0.038 mmol) over 48 h. The residue was purified by flash chromatography (cyclohexane/EtOAc 19:1) to afford the product as a colourless oil. Yield: 60 mg (35%); R_f 0.3 (hexane/EtOAc 19:1); ^1H NMR (400 MHz, $CDCl_3$): δ 7.59–7.67 (m, 4H; Ph–H), 7.41–7.48 (m, 6H; Ph–H), 6.65 (ddt, $^3J_{(H,H)}$ 6.6, $^3J_{(H,H)}$ 16.7, $^3J_{(H,P)}$ 18.6 Hz, 1H; $PCHCH$), 6.12 (ddt, $^4J_{(H,H)}$ 1.5, $^2J_{(H,P)}$ 11.9, $^3J_{(H,H)}$ 16.7 Hz, 1H; PCH), 2.28 (ddt, $^3J_{(H,H)}$ 6.9, $^3J_{(H,H)}$ 6.9, $^4J_{(H,H)}$ 1.5 Hz, 2H; $PCHCHCH_2$), 1.47 (tt, $^3J_{(H,H)}$ 7.2, $^3J_{(H,H)}$ 7.2 Hz, 2H; $PCHCHCH_2CH_2$), 1.26–1.30 (m, 14H; $(CH_2)_7$), ~1.0 (brq, obscured, 3H; BH_3), 0.88 ppm (t, $^3J_{(H,H)}$ 6.7 Hz, 3H; CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6 (d, $^2J_{(C,P)}$ 7.3 Hz, $PCHCH$), 132.4 (d, $^3J_{(C,P)}$ 9.5 Hz, Ph–C_{meta}), 130.9 (d, $^4J_{(C,P)}$ 2.3 Hz, Ph–C_{para}), 130.2 (d, $^1J_{(C,P)}$ 59.1 Hz, Ph–C_{ipso}), 128.7 (d, $^2J_{(C,P)}$ 10.0 Hz, Ph–C_{ortho}), 118.0 (d, $^1J_{(C,P)}$ 58.5 Hz, PCH), 34.9 (d, $^3J_{(C,P)}$ 15.2 Hz, $PCHCHCH_2$), 31.9 (s, CH_2), 29.6 (s, CH_2), 29.5 (s, CH_2), 29.34 (s, CH_2), 29.31 (s, CH_2), 29.1 (s, CH_2), 28.0 (s, $PCHCHCH_2CH_2$), 22.7 (s, CH_2), 14.1 ppm (s, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 13.0 ppm (q, $^1J_{(P,B)}$ 60 Hz); IR (film): ν 2375 (B–H), 1640 cm^{-1} (C=C); HRMS (ESI): m/z calcd for $C_{24}H_{36}BNaP$ $[M+Na]^+$: 389.2545; found: 389.2535.

4.22. Procedure for the cross-metathesis of **8** with dodecene

Procedure A using phenyldivinylphosphine borane (200 mg, 1.14 mmol) and 1-dodecene (94 μl, 0.36 mmol) in dichloromethane (1.2 ml). 0.08 equiv. Grubbs' 2nd generation catalyst (24 mg, 0.028 mmol) added over 48 h. At this point 86% consumption of 1-dodecene and 70% consumption of phenyldivinylphosphine borane had occurred. The two cross-metathesis products were separated by flash chromatography (cyclohexane/toluene 4:1). The desymmetrised product (*E*)-dodec-1-enyl(phenyl)vinylphosphine borane was found to be contaminated with traces of (*E*)-dodec-1-enyl(ethyl)phenylphosphine borane, ethyl(phenyl)vinylphosphine borane and diethyl(phenyl)phosphine borane, which resulted from reduction of the vinyl double bonds.

4.23. (E)-Dodec-1-enyl(phenyl)vinylphosphine borane (±)-**15h**

Yield: 18 mg (17%); R_f 0.2 (cyclohexane/toluene 4:1); ^1H NMR (400 MHz, $CDCl_3$): δ 7.63–7.70 (m, 2H; Ph–H), 7.41–7.46 (m, 3H; Ph–H), 6.57 (ddt, $^3J_{(H,H)}$ 6.6, $^3J_{(H,H)}$ 16.7, $^3J_{(H,P)}$ 18.5 Hz, 1H; $PCHCH$), 6.38 (ddd, $^3J_{(H,H)}$ 12.0, $^3J_{(H,H)}$ 14.8, $^2J_{(H,P)}$ 26.9 Hz, 1H; $PCHCH_2$), 6.21 (ddd, $^2J_{(H,H)}$ 1.7, $^3J_{(H,H)}$ 12.0, $^3J_{(H,P)}$39.3 Hz, 1H; $=CH_{trans}$), 6.15 (ddd, $^2J_{(H,H)}$ 1.6, $^3J_{(H,H)}$ 18.4, $^3J_{(H,P)}$ 20.0 Hz, 1H; $=CH_{cis}$), 5.88 (ddt, $^4J_{(H,H)}$ 1.4, $^2J_{(H,P)}$ 13.0,

$^{3}J_{(H,H)}$ 16.7 Hz, 1H; PC*H*CH), 2.28 (ddt, $^{3}J_{(H,H)}$ 6.8, $^{3}J_{(H,H)}$ 6.8, $^{4}J_{(H,H)}$ 1.5 Hz, 2H; PCHCHC*H*$_2$), 1.46 (tt, $^{3}J_{(H,H)}$ 7.1, $^{3}J_{(H,H)}$ 7.1 Hz, 2H; PCHCHCH$_2$C*H*$_2$), 1.26–1.32 (m, 14H; (CH$_2$)$_7$), ~1.0 (brq, obscured, 3H; BH$_3$), 0.88 ppm (t, $^{3}J_{(H,H)}$ 6.7 Hz, 3H; CH$_3$); ^{13}C NMR (101 MHz, CDCl$_3$) δ 153.1 (d, $^{2}J_{(C,P)}$ 6.9 Hz, PCH*C*H), 133.4 (d, $^{2}J_{(C,P)}$ 3.8 Hz, =CH$_2$), 131.9 (d, $^{3}J_{(C,P)}$ 9.4 Hz, Ph–C$_{meta}$), 131.0 (d, $^{4}J_{(C,P)}$ 2.3 Hz, Ph–C$_{para}$), 129.4 (d, $^{1}J_{(C,P)}$ 59.8 Hz, Ph–C$_{ipso}$), 128.7 (d, $^{2}J_{(C,P)}$ 10.0 Hz, Ph–C$_{ortho}$), 128.9 ppm (d, $^{1}J_{(C,P)}$ 56.5 Hz, P*C*HCH$_2$); 117.4 (d, $^{1}J_{(C,P)}$ 58.9 Hz, PCH), 34.9 (d, $^{3}J_{(C,P)}$ 15.2 Hz, PCHCH*C*H$_2$), 31.9 (s, CH$_2$), 29.6 (s, CH$_2$), 29.5 (s, CH$_2$), 29.33 (s, CH$_2$), 29.29 (s, CH$_2$), 29.1 (s, CH$_2$), 28.0 (s, PCHCHCH$_2$*C*H$_2$), 22.7 (s, CH$_2$), 14.1 ppm (s, CH$_3$); ^{31}P NMR (162 MHz, CDCl$_3$): δ 8.9 ppm (q, $^{1}J_{(P,B)}$ 70 Hz); IR (film): ν 2342 (B–H), 1467 cm^{-1} (P–Ph); HRMS (ESI): *m/z* calcd for $C_{20}H_{34}BNaP$ [M+Na]$^{+}$: 339.2387; found: 339.2383.

4.24. Di-(*E*)-dodec-1-enyl(phenyl)phosphine borane **15i**

Yield: 16 mg (22%); R_f 0.3 (cyclohexane/toluene 4:1); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.61–7.66 (m, 2H; Ph–H), 7.41–7.46 (m, 3H; Ph–H), 6.57 (ddt, $^{3}J_{(H,H)}$ 6.6, $^{3}J_{(H,H)}$ 16.7, $^{3}J_{(H,P)}$ 18.5 Hz, 2H; PCHC*H*), 5.88 (ddt, $^{4}J_{(H,H)}$ 1.4, $^{2}J_{(H,P)}$ 13.0, $^{3}J_{(H,H)}$ 16.7 Hz, 2H; PCH), 2.28 (ddt, $^{3}J_{(H,H)}$ 6.8, $^{3}J_{(H,H)}$ 6.8, $^{4}J_{(H,H)}$ 1.5 Hz, 4H; PCHCHC*H*$_2$), 1.46 (tt, $^{3}J_{(H,H)}$ 7.1, $^{3}J_{(H,H)}$ 7.1 Hz, 4H; PCHCHCH$_2$C*H*$_2$), 1.26–1.32 (m, 28H; (CH$_2$)$_7$), ~1.0 (brq, obscured, 3H; BH$_3$), 0.88 ppm (t, $^{3}J_{(H,H)}$ 6.7 Hz, 6H; CH$_3$); ^{13}C NMR (101 MHz, CDCl$_3$) δ 151.9 (d, $^{2}J_{(C,P)}$ 6.4 Hz, PCH*C*H), 131.7 (d, $^{3}J_{(C,P)}$ 9.4 Hz, Ph–C$_{meta}$), 130.69 (d, $^{1}J_{(C,P)}$ 59.7 Hz, Ph–C$_{ipso}$), 130.67 (d, $^{4}J_{(C,P)}$ 2.3 Hz, Ph–C$_{para}$), 128.6 (d, $^{2}J_{(C,P)}$ 10.0 Hz, Ph–C$_{ortho}$), 118.6 (d, $^{1}J_{(C,P)}$ 59.2 Hz, PCH), 34.8 (d, $^{3}J_{(C,P)}$ 15.0 Hz, PCHCH*C*H$_2$), 31.9 (s, CH$_2$), 29.6 (s, CH$_2$), 29.5 (s, CH$_2$), 29.4 (s, CH$_2$), 29.3 (s, CH$_2$), 29.1 (s, CH$_2$), 28.0 (s, PCHCHCH$_2$*C*H$_2$), 22.7 (s, CH$_2$), 14.1 ppm (s, CH$_3$); ^{31}P NMR (162 MHz, CDCl$_3$): δ 6.6 ppm (q, $^{1}J_{(P,B)}$ 50 Hz); IR (film): ν 2348 (B–H), 1437 cm^{-1} (P–Ph); HRMS (ESI): *m/z* calcd for $C_{30}H_{54}BNaP$ [M+Na]$^{+}$: 479.3954; found: 479.3948.

4.25. (*E*)-Dodec-1-enyl(ethyl)phenylphosphine borane

R_f 0.2 (cyclohexane/toluene 4:1); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.61–7.66 (m, 2H; Ph–H), 7.41–7.46 (m, 3H; Ph–H), 6.57 (ddt, $^{3}J_{(H,H)}$ 6.6, $^{3}J_{(H,H)}$ 16.7, $^{3}J_{(H,P)}$ 18.5 Hz, 2H; PCHC*H*), 5.88 (ddt, $^{4}J_{(H,H)}$ 1.4, $^{2}J_{(H,P)}$ 13.0, $^{3}J_{(H,H)}$ 16.7 Hz, 1H; PCH), 2.28 (ddt, $^{3}J_{(H,H)}$ 6.8, $^{3}J_{(H,H)}$ 6.8, $^{4}J_{(H,H)}$ 1.5 Hz, 2H; PCHCHC*H*$_2$), 1.91 (dq, $^{3}J_{(H,H)}$ 7.6, $^{2}J_{(H,P)}$ 10.6 Hz, 2H; PCH$_2$), 1.46 (tt, $^{3}J_{(H,H)}$ 7.1, $^{3}J_{(H,H)}$ 7.1 Hz, 2H; PCHCHCH$_2$C*H*$_2$), 1.26–1.32 (m, 14H; (CH$_2$)$_7$), 1.08 (dt, $^{3}J_{(H,H)}$ 7.6, $^{3}J_{(H,P)}$ 17.0 Hz, 3H; PCH$_2$C*H*$_3$), ~1.0 (brq, obscured, 3H; BH$_3$), 0.88 ppm (t, $^{3}J_{(H,H)}$ 6.7 Hz, 3H; CH$_3$); HRMS (ESI): *m/z* calcd for $C_{20}H_{36}BNaP$ [M+Na]$^{+}$: 341.2545; found: 341.2480.

4.26. Ethyl(phenyl)vinylphosphine borane

R_f 0.2 (cyclohexane/toluene 4:1); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.61–7.66 (m, 2H; Ph–H), 7.41–7.46 (m, 3H; Ph–H), 6.38 (ddd, $^{3}J_{(H,H)}$ 12.0, $^{3}J_{(H,H)}$ 14.8, $^{2}J_{(H,P)}$ 26.9 Hz, 1H; PC*H*CH$_2$), 6.21 (ddd, $^{2}J_{(H,H)}$ 1.7, $^{3}J_{(H,H)}$ 12.0, $^{3}J_{(H,P)}$39.3 Hz, 1H; =CH$_{trans}$), 6.15 (ddd, $^{2}J_{(H,H)}$ 1.6, $^{3}J_{(H,H)}$ 18.4, $^{3}J_{(H,P)}$ 20.0 Hz, 1H; =CH$_{cis}$), 1.91 (dq, $^{3}J_{(H,H)}$ 7.6, $^{2}J_{(H,P)}$ 10.6 Hz, 2H; PCH$_2$), 1.08 (dt, $^{3}J_{(H,H)}$ 7.6, $^{3}J_{(H,P)}$ 17.0 Hz, 3H; PCH$_2$C*H*$_3$), ~1.0 ppm (brq, obscured, 3H; BH$_3$).

4.27. Diethyl(phenyl)phosphine borane

R_f 0.2 (cyclohexane/toluene 4:1); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.61–7.66 (m, 2H; Ph–H), 7.41–7.46 (m, 3H; Ph–H), 1.91 (dq, $^{3}J_{(H,H)}$ 7.6, $^{2}J_{(H,P)}$ 10.6 Hz, 4H; PCH$_2$), 1.08 (dt, $^{3}J_{(H,H)}$ 7.6, $^{3}J_{(H,P)}$ 17.0 Hz, 6H; PCH$_2$C*H*$_3$), ~1.0 ppm (brq, obscured, 3H; BH$_3$).

4.28. Methoxy(phenyl)-3-phenylprop-2-enylphosphine borane (±)-**15j**

Procedure A from allyl(methoxy)phenyl-phosphine borane (100 mg, 0.52 mmol) and styrene (0.18 ml, 1.56 mmol) in dichloromethane (1.7 ml) using 0.02 equiv. Grubbs' 2nd generation catalyst (9 mg, 0.011 mmol) over 12 h. The residue was purified by flash chromatography (cyclohexane/EtOAc 4:1) to afford the *E*-isomer of the product as a colourless oil. Yield: 60 mg (43%); R_f 0.4 (cyclohexane/EtOAc 4:1); ^{1}H NMR (400 MHz, CDCl$_3$): δ ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.71–7.76 (m, 2H; PPh–H), 7.44–7.50 (m, 3H; PPh–H), 7.18–7.29 (m, 5H; CPh–H), 6.31 (dd, $^{4}J_{(H,P)}$ 4.5, $^{3}J_{(H,H)}$ 15.8 Hz, 1H; PCH$_2$CHC*H*), 6.04 (ddt, $^{3}J_{(H,P)}$ 5.1, $^{3}J_{(H,H)}$ 7.7, $^{3}J_{(H,H)}$ 15.5 Hz, 1H; PCH$_2$C*H*), 3.64 (d, $^{3}J_{(H,H)}$ 11.9 Hz, 3H; OCH$_3$), 2.92 (dd, $^{3}J_{(H,H)}$ 7.7, $^{2}J_{(H,P)}$ 11.5 Hz, 2H; PCH$_2$), 0.81 ppm (brq, $^{1}J_{(H,B)}$ 88 Hz, 3H; BH$_3$); ^{13}C NMR (101 MHz, CDCl$_3$) δ 136.8 (d, $J_{(C,P)}$ 3.1 Hz, CPh–C$_{ipso}$), 132.0 (d, $^{3}J_{(C,P)}$ 11.1 Hz, PCH$_2$CH*C*H), 132.1 (d, $^{4}J_{(C,P)}$ 2.5 Hz, PPh–C$_{para}$), 131.1 (d, $^{3}J_{(C,P)}$ 10.7 Hz, PPh–C$_{meta}$), 130.4 (d, $^{1}J_{(C,P)}$ 54.3 Hz, PPh–C$_{ipso}$), 128.6 (d, $^{2}J_{(C,P)}$ 10.1 Hz, PPh–C$_{ortho}$), 128.5 (s, CPh–C$_{meta}$), 127.6 (s, CPh–C$_{para}$), 126.7 (d, $^{5}J_{(C,P)}$ 1.2 Hz, CPh–C$_{ortho}$), 118.5 (d, $^{2}J_{(C,P)}$ 7.2 Hz, PCH$_2$*C*H), 54.3 (d, $^{2}J_{(C,P)}$ 3.2 Hz, OCH$_3$), 35.8 ppm (d, $^{1}J_{(C,P)}$ 42.2 Hz, PCH$_2$); ^{31}P NMR (162 MHz, CDCl$_3$): δ 116.4 ppm (q, $^{1}J_{(P,B)}$ 74 Hz); IR (film): ν 2383 (B–H), 1598 (C=C), 1437 cm^{-1} (P–Ph); HRMS (FI): *m/z* calcd for $C_{16}H_{20}BOP$ M$^{+\cdot}$: 270.1345; found: 270.1351.

4.29. (*E*)-6-Bromohex-1-enylmethoxy(phenyl)phosphine borane (±)-**15k**

Procedure A from methoxy(phenyl)vinylphosphine borane (100 mg, 0.56 mmol) and 6-bromo-1-hexene (0.23 ml, 1.68 mmol) in dichloromethane (1.7 ml) using 0.06 equiv. Grubbs' 2nd generation catalyst (27 mg, 0.034 mmol) over

36 h. The residue was purified by flash chromatography (hexane/EtOAc: 19/1) to yield the product as a brown oil. Yield: 99 mg (55%); R_f 0.2 (hexane/EtOAc 9:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74–7.79 (m, 2H, Ph–H), 7.47–7.56 (m, 3H, Ph–H), 6.75 (ddt, $^3J_{(H,H)}$ 6.5, $^3J_{(H,H)}$ 17.0, $^3J_{(H,P)}$ 18.5 Hz, 1H; PCHC*H*), 6.02 (ddt, $^4J_{(H,H)}$ 1.3, $^2J_{(H,P)}$ 11.8, $^3J_{(H,H)}$ 16.9 Hz, 1H; PCH), 3.63 (d, $^3J_{(H,P)}$ 12.1 Hz, 3H; OCH_3), 3.42 (t, $^3J_{(H,H)}$ 6.6 Hz, 2H; $BrCH_2$), 2.30 (ddt, 2H, $^4J_{(H,H)}$ 1.4, $^3J_{(H,H)}$ 7.1, $^3J_{(H,H)}$ 14.5 Hz, PCHCHCH_2), 1.88 (m, 2H; $BrCH_2CH_2$), 1.65 (m, 2H; $Br(CH_2)_2CH_2$), 0.82 (brq, $^1J_{(H,B)}$ 90 Hz, 3H; BH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1 (d, $^2J_{(C,P)}$ 10.5 Hz, PCH*C*H), 131.9 (d, $^4J_{(C,P)}$ 2.1 Hz, Ph–C_{para}), 130.9 (d, $^3J_{(C,P)}$ 11.0 Hz, Ph–C_{ortho}), 128.7 (d, $^2J_{(C,P)}$ 10.3 Hz, Ph–C_{meta}), 122.0 (d, $^1J_{(C,P)}$ 63.9 Hz, PCH), 53.5 (d, $^2J_{(C,P)}$ 3.1 Hz, OCH_3), 33.6 (d, $^3J_{(C,P)}$ 15.9 Hz, PCHCH*C*H_2), 33.2 (s, Br*C*H_2), 32.0 (s, $BrCH_2CH_2$), 26.4 ppm (s, $Br(CH_2)_2CH_2$); ^{31}P NMR (162 MHz, $CDCl_3$): δ 104.3 ppm (q, $^1J_{(P,B)}$ 67 Hz); IR (film): ν 2384 (B–H), 1621 (C=C), 1437 cm^{-1} (P–Ph); HRMS (FI): m/z calcd for $C_{13}H_{18}BrOP$ $[M-BH_3]^{+\cdot}$: 300.0279; found: 300.0282.

4.30. (*E*)-Methoxy-4-methoxystyrylphenylphosphine borane (±)-15l

Procedure A from methoxy(phenyl)vinylphosphine borane (100 mg, 0.56 mmol) and 4-methoxystyrene (0.22 ml, 1.68 mmol) in dichloromethane (1.7 ml) using 0.06 equiv. Grubbs' 2nd generation catalyst (27 mg, 0.034 mmol) over 36 h. The residue was purified by flash chromatography (hexane/EtOAc 9:1) to yield the product as a colourless oil. Yield: 75 mg (46%); R_f 0.2 (hexane/EtOAc 9:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (m, 2H; PPh–H); 7.45–7.57 (m, 4H, PPh–H, PCHC*H*), 7.48 (d, $^3J_{(H,H)}$ 8.8 Hz, 2H; Ar–H), 6.91 (d, 3H, $^3J_{(H,H)}$ 8.8 Hz, Ar–H), 6.44 (dd, $^3J_{(H,H)}$ 17.3, $^2J_{(H,P)}$ 9.2 Hz, 1H; PCH), 3.84 (s, 3H; $ArOCH_3$), 3.69 (d, $^3J_{(H,P)}$ 12.4 Hz, 3H; $POCH_3$), 0.94 ppm (brq, $^1J_{(H,B)}$ 100 Hz, 3H; BH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3 (s, Ar–C_{para}), 147.9 (d, $^2J_{(C,P)}$ 13.2 Hz, PCH*C*H), 131.9 (d, $^4J_{(C,P)}$ 2.3 Hz, PPh–C_{para}), 131.8 (d, $^1J_{(C,P)}$ 66.3 Hz, PPh–C_{ipso}), 130.9 (d, $^2J_{(C,P)}$ 11.1 Hz, PPh–C_{ortho}), 129.5 (s, Ar–C), 128.7 (d, $^3J_{(C,P)}$ 10.4 Hz, PPh–C_{meta}), 127.9 (d, $^3J_{(C,P)}$ 17.9 Hz, Ar–C_{ipso}), 115.7 (d, $^1J_{(C,P)}$ 65.6 Hz, PCH), 114.2 (s, Ar–C), 55.4 (s, $ArOCH_3$), 53.6 ppm (d, $^2J_{(C,P)}$ 2.9 Hz, $POCH_3$); ^{31}P NMR (162 MHz, $CDCl_3$): δ 105.5 ppm (q, $^1J_{(P,B)}$ 60 Hz); IR (film): ν 2383 cm^{-1} (B–H); HRMS (FI): m/z calcd for $C_{16}H_{20}BO_2P$ $M^{+\cdot}$: 286.1294; found: 286.1289.

4.31. (*E*)-Methoxy(phenyl)styrylphosphine borane (±)-15m

Synthesised using procedure A from methoxy(phenyl)vinyl-phosphine borane (100 mg, 0.56 mmol) and styrene (0.19 ml, 1.68 mmol) in dichloromethane (1.7 ml) using 0.08 equiv. Grubbs' 2nd generation catalyst (38 mg, 0.045 mmol) over 48 h. The residue was purified by flash chromatography (cyclohexane/toluene 1:1) to yield the product as a colourless oil. Yield: 95 mg (66%); R_f 0.3 (cyclohexane/toluene 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (m, 2H; Ph–H); 7.48–7.55 (m, 6H; Ph–H, PCHC*H*), 7.37–7.39 (m, 3H; Ph–H), 6.59 (dd, $^3J_{(H,H)}$ 17.3, $^2J_{(H,P)}$ 10.3 Hz, 1H; PCH), 3.70 (d, $^3J_{(H,P)}$ 12.2 Hz, 3H; $POCH_3$), 0.92 ppm (brq, $^1J_{(H,B)}$ 90 Hz, 3H; BH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0 (d, $^2J_{(C,P)}$ 12.2 Hz, PCH*C*H), 132.0 (d, $^4J_{(C,P)}$ 2.9 Hz, PPh–C_{para}), 131.0 (d, $^2J_{(C,P)}$ 11.2 Hz, PPh–C_{ortho}), 130.2 (s, CPh–C), 128.8 (s, CPh–C), 128.7 (d, $^3J_{(C,P)}$ 10.5 Hz, PPh–C_{meta}), 127.8 (s, CPh–C), 118.8 (d, $^1J_{(C,P)}$ 64.7 Hz, PCH), 53.7 ppm (d, $^2J_{(C,P)}$ 2.8 Hz, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 105.6 ppm (q, $^1J_{(P,B)}$ 70 Hz); IR (film): ν 2385 (B–H), 1609 (C=C), 1438 cm^{-1} (P–Ph); HRMS (FI): m/z calcd for $C_{15}H_{15}OP$ $[M-BH_3]^{+\cdot}$: 242.0861; found: 242.0875.

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