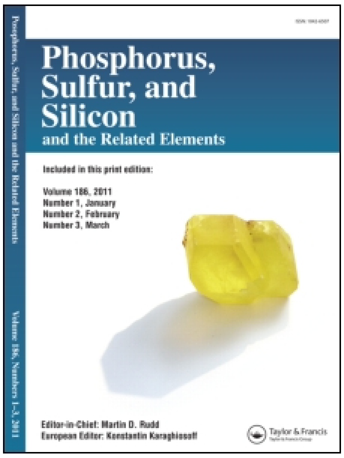

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First Examples of CP Cross-Coupling Reaction of Vinyl Tosylates with Diphenylphosphine Derivative: New Access to Vinylphosphine-boranes

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First Examples of C—P Cross-Coupling Reaction of Vinyl Tosylates with Diphenylphosphine Derivative: New Access to Vinylphosphine-boranes

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Vinylphosphine-borane complexes are efficiently synthesized by palladium-catalyzed C—P cross-coupling of vinyl tosylates with diphenylphosphine-borane. Both activated and unactivated vinyl tosylates are successfully used. The vinylphosphine derivatives are purified by chromatography on silica gel.

Keywords C—P cross-coupling reaction; phosphine-borane; vinylphosphine; vinyl tosylate

INTRODUCTION

The synthesis of vinylphosphines is of great interest for organic chemists. They are important synthetic intermediates, especially for the preparation of polyphosphines and ligands for organometallic catalysis.[1] For example, they can lead to new valuable bidentate ligands after functionalization of the carbon–carbon double bond. A survey of the literature reveals that only a few methods using carbon–phosphorus (C—P) bond formation have been developed to access vinylphosphines.[2] Such C—P connections can be made by the

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Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

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reaction between halophosphines and vinylic organometallic species. However, this method shows a lack of tolerance toward various functional groups. Alternative approaches are hydrophosphination of alkynes (addition of a *P—H* bond to a C—C triple bond) and catalytic carbon–phosphorus cross-coupling reaction. Hydrophosphination is the most attractive methodology from both the economic and ecological points of view and also for its tolerance toward functional groups.[1a,3] However, this method cannot lead to the formation of vinylphosphine containing cycles due to the lack of five- or six-membered ring alkynes. Moreover, hydrophosphination is sensitive, like various addition reactions, to steric factors. As our research program aims at developing uncatalyzed[4] or transition metal catalyzed[5] transformations for the construction of C—P bonds, a part of our work deals with the synthesis of various vinylphosphines by hydrophosphination using the convenient phosphine-borane derivatives.[6] However, we also experienced difficulty in synthesizing bulky derivatives starting from hindered alkynes. In order to overcome this problem and to provide a general and efficient access to vinylphosphine derivatives, we turned our attention to the C—P cross-coupling reaction of vinylic derivatives. Different vinylic coupling partners may be used as the electrophilic source: vinylic halides[7] and vinylic derivatives derived from the widely available ketones, i.e., vinyl triflates[8] or tosylates. Vinyl iodides are not widely available, and chloride and bromide derivatives show a low reactivity in the first step, i.e., the oxidative addition. We recently showed that acyclic and cyclic vinyl triflates could be efficiently coupled under mild conditions with phosphine-boranes having various electronic and steric properties.[5a] Indeed, using this methodology, we were able to synthesize various hindered vinylphosphines. The reaction was extended to the synthesis of enantiopure derivatives starting from ketones derived from the chiral pool.

We sought to extend this methodology to other enol sulfonates, readily available from the corresponding ketones: vinyl tosylates. Although vinyl tosylates are less reactive electrophiles than the corresponding vinyl triflates, they offer two important advantages. First, they are generally less expensive than the corresponding vinyl triflates. Second, vinyl tosylates are stable crystalline solids, which do not hydrolyze in the presence of residual water as observed with triflates. Furthermore, they are, unlike triflates, easily purified by silica gel chromatography. To the best of our knowledge, no such example involving the C—P cross-coupling reaction between vinyl tosylates and phosphine derivatives has ever been reported.

RESULTS AND DISCUSSION

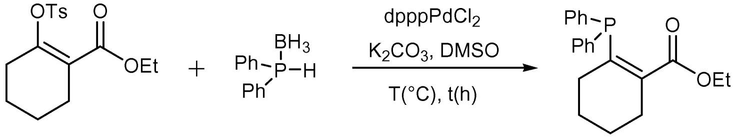
We report here the preliminary results of our investigation on the palladium-catalyzed C—P cross-coupling of vinyl tosylates with phosphine derivatives. Knowing that vinyl tosylates are less reactive than the corresponding vinyl triflates, the reactions were performed with diphenylphosphine-borane **1**, which is a well-known reactive phosphine derivative.[9] Indeed, both phenyl and borane groups are able to activate the *P—H* bond of the phosphine.

In a preliminary test, we selected the activated vinyl tosylate **2** featuring an electron-withdrawing group in the β-position of the enol tosylate in order to offset the lack of reactivity of these substrates. 2-(Ethoxycarbonyl)cyclohex-1-en-1-yl-*p*-toluenesulfonate **2** was prepared using the method of Klapars et al.[10] Conditions for the coupling are inspired by our work on the C—P cross-coupling of vinyl triflates.[5a] Thus, we selected dpppPdCl$_2$ as the source of palladium, K$_2$CO$_3$ as base, and DMSO as solvent. The reactions were carried out with a stoichiometric amount of phosphine **1** and tosylate, unlike with triflate, where a slight excess of triflate was used to circumvent its partial hydrolysis.[5a,11]

After 3 h at 60°C, the crude mixture was analyzed by ^{31}P NMR spectroscopy (Table I, entry 1). Although an almost complete conversion (89%) was observed, only a moderate amount of the expected coupling product **3** (52%) was obtained together with various unindentified side products. This result is not so surprising, since we have already observed in a previous work[5a] that when the coupling conditions are not optimized, an oxidation–degradation of phosphine-borane **1** takes place, leading to the formation of side products. To improve the conversion, a higher temperature (80°C) was tested. Under these conditions, the reaction was completed in only 3 h affording **3** in 83% (percentages given always correspond, unless otherwise noted, to ^{31}P NMR proportion) (Table I, entry 2). The same reaction was also carried out without any catalyst. After 3 h, the expected product **3** was obtained in significantly lower amount (33%) together with various unindentified side products (Table I, entry 3). Using palladium acetate in the absence of a bidentate phosphine ligand also afforded a low amount of the expected phosphine **3** (61%) together with various unidentified derivatives (Table I, entry 4). These experiments demonstrate that the use of a palladium catalyst bearing a bidentate phosphine is required to promote a clean coupling reaction and thus avoid side reactions.

In order to improve the amount of the expected product **3**, reaction time was decreased to 2 h, then to 1 h, and to 0.5 h (Table I, entries 5–7). In the first two cases (2 h and 1 h), both good conversion (95%) and amount of the coupling product (83%–85%) were obtained (Table I,

TABLE I C–P Cross-Coupling Reaction of Activated Vinyltosylate 2



2 **1** **3**

Entry	T (°C)	t	Conversion^a (%)	Coupling product 3^a (%)
1	60	3 h	89	52
2	80	3 h	100	83
3	80	3 h	72	33^b
4	80^c	3 h	99	61
5	80	2 h	95	85
6	80	1 h	95	83
7	80	0.5 h	71	47
8	80^d	5 min	28	7
9	80^d	15 min	29	18
10	90^d	15 min	66	21
11	80^e	1 h	58	41

[a] Conversion and proportion were determined by ^{31}P NMR spectroscopy, [b] reaction without catalyst, [c] reaction without ligand using $Pd(OAc)_2$as catalyst, [d] under microwave irradiation, [e] reaction with Ph_2PH instead of borane derivative.

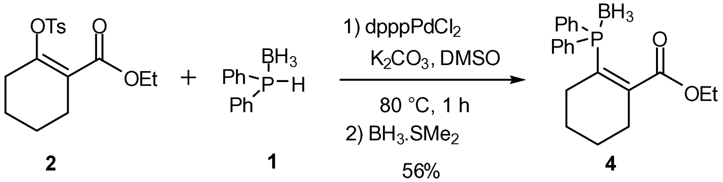
entries 4 and 5), while after only half an hour of reaction, incomplete conversion was observed (Table I, entry 6).

These preliminary results show that the coupling between diphenylphosphine-borane **1** and tosylate **2** can be performed under reasonably mild conditions (1 h at 80°C). In order to lower the consumed energy, we envisioned performing the cross-coupling reaction under microwave irradiation (Table I, entries 8–10). Our previous work on the C—P cross-coupling reaction has shown that the microwave activation was efficient with triflates, phosphine-boranes, and palladium catalyst allowing a decrease of the reaction time.

However, after both 5 min and 15 min of irradiation at 80°C, only a low conversion of 30% was obtained (Table I, entries 8 and 9). Temperature was then increased to 90°C (Table I, entry 10). After 15 min of irradiation, a higher conversion of 66% was measured, but a lot of side products were observed. As no improvement was observed in these preliminary tests, the microwave activation was abandoned.

It is worth noting that in each previous experiment, the coupling product was always recovered as the free phosphine, indicating that deboronation has occurred during the reaction. In order to check if the borane activation was required for this coupling, diphenylphosphine-borane **1** was replaced by diphenylphosphine in the coupling reaction using the optimized conditions (dpppPdCl$_2$, K$_2$CO$_3$, DMSO, 80°C, 1 h). As anticipated, a lower conversion (58%) was observed compared to the one obtained with phosphine-borane (95%) (Table I, entry 11 vs. entry 6). Hence, the cross-coupling reaction of vinyl tosylate must be performed with phosphine-borane complexes to avoid long reaction time and to limit decomposition.

Finally, the cross-coupling reaction of vinyltosylate **2** with diphenylphosphine-borane **1** was repeated using the best defined conditions (Scheme 1). After boration, an easy purification by silica gel flash chromatography in air afforded coupling product **4** in 56% yield.

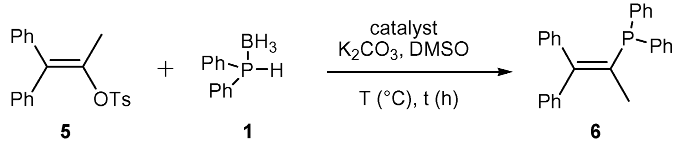


SCHEME 1

We then turned our attention to the cross-coupling of unactivated and consequently less reactive vinyl tosylates. We first used 1,1-diphenylprop-1-en-2-yl-*p*-toluenesulfonate **5**, which is easily prepared using the method of Klapars et al.[10] This tosylate was coupled with phosphine-borane **1** using the conditions previously defined for cross-coupling of tosylate **2**: dpppPdCl$_2$ as catalyst, K$_2$CO$_3$ as base, and DMSO as solvent. As anticipated, due to the poor reactivity of **5**, only 16% of coupling product **6** was observed after 3 h of reaction at 80°C together with a high proportion of side products (Table II, entry 1). Various conditions were then tested by modifying the reaction parameters such as the temperature, the reaction time, the catalytic system, the solvent, and by adding salts. First, the reaction was carried out under the conditions described above, and potassium iodide (3 equiv.) was added to the mixture (Table II, entry 2). Previous work in our laboratory on the C—P cross-coupling reaction of triflates had shown that the addition of iodide salt facilitated sluggish reactions.[5a] However with tosylates, no benefit in the conversion was observed.

Reaction temperature was then increased to 90°C, 110°C, and 120°C keeping the other parameters as previously defined: dpppPdCl$_2$, K$_2$CO$_3$, DMSO, 3 h (Table II, entries 3–5). At 90°C, a high conversion (95%) was observed, but with a low coupling product proportion, showing a degradation of the starting material. At increased

TABLE II C–P Cross-Coupling Reaction of Vinyltosylate 5



Entry	T (°C)	t	Catalyst	Conversion[a] (%)	Coupling Product 6[a] (%)
1	80	3 h	dpppPdCl$_2$	88	16
2	80	3 h	dpppPdCl$_2^b$	61	9
3	90	3 h	dpppPdCl$_2$	95	21
4	110	3 h	dpppPdCl$_2$	95	76
5	120	3 h	dpppPdCl$_2$	96	54
6	110	2 h	dpppPdCl$_2$	100	77
7	110	1 h	dpppPdCl$_2$	74	54
8	110	2 h	dppfPdCl$_2$	100	27
9	110	2 h	Pd(OAc)$_2$/(*t*-Bu)$_3$P	71	26
10	110	2 h	Pd(OAc)$_2$/Biph(*t*-Bu)$_2$P	100	63
11	110	2 h	Pd(OAc)$_2$/Biph(Cy)$_2$P	97	37
12	90	2 h	Pd(OAc)$_2$/Biph(*t*-Bu)$_2$P	65	11
13	110[d]	2 h	dpppPdCl$_2$	100	61
14	110[e]	2 h	dpppPdCl$_2$	100	55
15	90[e]	2 h	dpppPdCl$_2$	95	27
16	110[e]	2 h	Pd(OAc)$_2$/Biph(*t*-Bu)$_2$P	100	—
17	110[f]	2 h	dpppPdCl$_2$	94	59

[a]Conversion and proportion were determined by ^{31}P NMR spectroscopy, [b]additive added: KI (3 equiv.), [c]additive added: KI (1 equiv.), [d]additive added: n-Bu$_4$NI (1 equiv.), [e]using DMF as solvent.

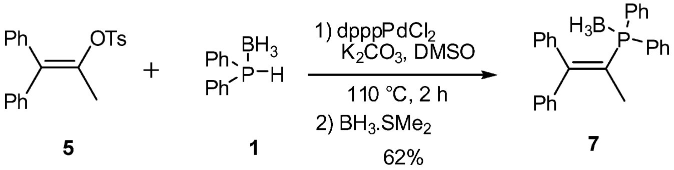
temperatures (110–120°C), an almost total conversion was obtained, with a higher proportion of **6** at 110°C rather than at 120°C, indicating a probable decomposition of **6** at high temperature. Consequently, temperature of 110°C was kept, and reaction time was decreased to 2 h and 1 h. After 2 h, a complete conversion and a good coupling product proportion (77%) were obtained (Table II, entry 6), while after 1 h, conversion was incomplete (Table II, entry 7).

At the sight of these first results, best conditions are a temperature of 110°C for a reaction time of 2 h using conventional oil bath activation (Table II, entry 6). In order to improve this catalytic system, various metal/phosphine ligand couples were examined. Electron-poor ligands such as dppf (dppfPdCl$_2$ complex) provided a lower amount of the expected coupling product presumably because electron-poor ligands do not favor the oxidative addition step (Table II, entry 8).[12] Hence, electron-rich phosphine ligands were tested (Table II, entries 9–12). Unfortunately, a lower proportion of coupling product **6** was also measured. The best result in this C—P coupling reaction is consequently obtained with the simple and inexpensive diphosphine ligand dppp (Table II, entry 6).

Screening of additives was then conducted. Salts such as KI and *n*-Bu_4NI were added in the mixture, but whatever the conditions used, no improvement in the formation of **6** was observed (Table II, entries 13–16). These results confirm that the addition of iodide salts had no benefit for the cross-coupling reaction of vinyl tosylates.

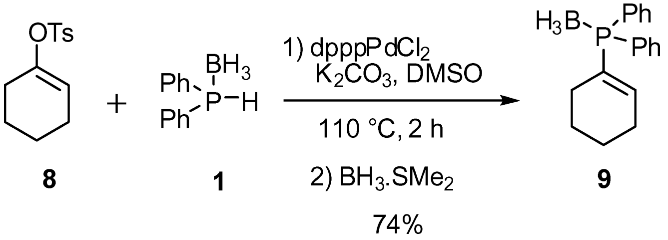
The influence of the nature of the solvent was then examined. By analogy with vinyl triflates, the oxidative addition of vinyl tosylates should lead to cationic palladium species. Our previous work on C—P cross-coupling of vinyl triflates had shown that use of a polar solvent was necessary to ensure fast oxidative addition of vinyl triflate to Pd(0).[5a,13] Consequently, using the previously defined conditions (dpppPdCl_2, K_2CO_3, 110°C, 2 h), DMSO was replaced by DMF (Table II, entry 17). No improvement was noted.

Finally, cross-coupling reaction between vinyl tosylate **5** and diphenylphosphine-borane **1** was repeated under optimized conditions (Scheme 2). After boration and purification, coupling product **7** was isolated in 62% yield.



SCHEME 2

The coupling reaction was extended to the unactivated cyclohex-1-en-1-yl-*p*-toluenesulfonate **8**. Reaction was carried out using optimized conditions developed for the cross-coupling of vinyl tosylate **5**. After boration and purification, coupling product **9** was isolated in 74% yield (Scheme 3).



SCHEME 3

CONCLUSION

To conclude, we have shown that vinyl tosylate can be efficiently coupled with diphenylphosphine-borane using a simple and inexpensive catalytic system such as dpppPdCl_2. The best-defined conditions involved a weak base, K_2CO_3, a polar solvent (DMSO), and a temperature between 80°C and 110°C. Vinyl tosylate bearing an electron-withdrawing group can be coupled under conditions quite similar to vinyl triflates. Less reactive vinyl tosylates were also successfully coupled, although a higher temperature was required (110°C). It is worth noting that this methodology allows us, for the first time, to generate vinylphosphine derivatives from easily accessible enol tosylates, which are known to be rather poor electrophiles.

EXPERIMENTAL

All reactions were carried out under nitrogen atmosphere, and all glassware was flame dried before use. Vinyl tosylates[10] **2** and **5** and phosphine-borane **1**[14] precursors were prepared according to literature procedures. Dimethylsulfoxide was distilled from calcium hydride and degassed before use.

The microwave oven used was a CEM Discover with a power up to 300 W. The software used was ChemDriver. Reactions were carried out by setting temperature and a power threshold of 30 W.

Column chromatography was performed on Merck silica gel Si 60 (40–63 μm). Solvents were used as purchased. Thin layer chromatography (TLC) was performed on silica gel 60 F-254 plates (0.1 mm) with iodine or UV detection.

^1H and ^{13}C NMR chemical shifts are reported relative to Me_4Si as an internal standard. ^{31}P and ^{11}B NMR chemical shifts are reported relative to H_3PO_4 (85%) and $BF_3.Et_2O$ as external references, respectively. Coupling constants are reported in Hertz (Hz). Abbreviations are used as follows: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, oct = octet, and m = multiplet.

Melting points were measured with an Electrotherma IA 9200 apparatus and are given without correction.

Mass spectroscopy was performed with a Waters QTOF APCI instrument.

Cyclohex-1-en-1-yl-p-toluenesulfonate 8[15]

In a two-necked round-bottomed flask equipped with a thermometer and a nitrogen inlet, HMDS (2.25 mL, 10.6 mmol, 1.1 equiv.) is dissolved in anhydrous THF (15 mL). The solution is cooled to –50°C, and *n*-BuLi (4.24 mL, 2.5 M in hexane, 10.6 mmol, 1.1 equiv.) is slowly added. After 15 min, a solution of cyclohexanone (1 mL, 9.6 mmol) in anhydrous THF (15 mL) is added, and the mixture is stirred at –50°C for 2 h. A solution of *p*-tolylsulfonic anhydride (3.46 g, 10.6 mmol, 1.1 equiv.) in anhydrous THF (15 mL) is added. The mixture is stirred for 15 min at –50°C and for 2 h at 0°C. The mixture is then concentrated under reduced pressure, and MTBE (50 mL) is added. The organic layer is washed with aqueous 2M $NaHCO_3$ (50 mL) and water (3 × 50 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product is purified by silica-gel column chromatography with pentane:AcOEt (95:5, $R_f = 0.24$) as eluent giving a white solid (1.6 g, 65 %), mp = 24°C. ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 7.73$ (d, $^3J_{HH} =$ 8.3 Hz, 2H), 7.26 (d, $^3J_{HH} = 8.3$ Hz, 2H), 5.31–5.24 (m, 1H), 2.38 (s, 3H), 2.05–1.88 (m, 4H), 1.61–1.49 (m, 2H), 1.48–1.36 (m, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 148.2$, 144.8, 133.7, 129.6, 128.2, 117.2, 27.6, 23.8, 22.7, 21.7, 21.3. HRMS Calcd. for $C_{13}H_{16}O_3S$ $[M+H]^+$: 253.0898. Found: 253.0901.

(2-(Ethoxycarbonyl)cyclohex-1-en-1-yl)diphenylphosphine-borane 4

In a Schlenk tube, flushed under nitrogen, dpppPdCl_2 (16.5 mg, 0.03 mmol, 5.6 mol %) is dissolved in DMSO (1 mL). 2-(Ethoxycarbonyl)cyclohex-1-en-1-yl-*p*-toluenesulfonate **2** (162 mg, 0.50 mmol), K_2CO_3 (83 mg, 0.60 mmol, 1.2 equiv.), and phosphine-borane **1** (100 mg, 0.50 mmol) are introduced. The mixture is heated to 80°C for 3 h. After cooling to room temperature, $BH_3{\cdot}SMe_2$ is added up to complete boration of the product if a partial decomplexation has occurred during the reaction. The mixture is stirred for 30 min and hydrolyzed with 1 mL of degassed water. The aqueous layer is extracted with diethyl ether (3 × 2 mL). The combined organic layers are dried over $MgSO_4$ and concentrated under reduced pressure. The crude product is then purified by silica-gel column chromatography with toluene ($R_f = 0.27$) as eluent giving a red viscous oil (99 mg, 56%). ^{31}P NMR (161.9 MHz, $CDCl_3$): $\delta = 24.1$–21.3 (m). ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 7.65$–7.58 (m, 4H), 7.43–7.32 (m, 6H), 3.33 (q, $^3J_{HH} = 7.2$ Hz, 2H), 2.45–2.37 (m, 2H), 2.09–2.00 (m, 2H), 1.77–0.51 (m, 3H), 1.68–1.60 (m, 2H), 1.60–1.51 (m, 2H), 0.89 (t, $^3J_{HH} = 7.2$ Hz, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta =$ 168.2 (d, $^3J_{PC} = 6.9$ Hz), 144.2 (d, $^2J_{PC} = 1.9$ Hz), 133.2 (d, $^2J_{PC} = 9.6$ Hz), 131.0 (d, $^4J_{PC} = 2.4$ Hz), 129.3 (d, $^1J_{PC} = 46.2$ Hz), 128.5 (d, $^1J_{PC} =$ 57.5 Hz), 128.4 (d, $^3J_{PC} = 10.2$ Hz), 60.9, 29.7 (d, $^3J_{PC} = 8.2$ Hz), 29.1

(d, $^{2}J_{PC} = 10.7$ Hz), 22.2 (d, $^{3}J_{PC} = 7.4$ Hz), 21.1, 13.4. ^{11}B NMR (128.4 MHz, $CDCl_3$): $\delta = -31.6$ to -36.2 (m). HRMS Calcd. for $C_{21}H_{25}O_2BP$ $[M\text{-}H]^+$: 351.1685. Found: 351.1670.

Preparation of Vinylphosphine-Boranes from Unactivated Vinyl Tosylates: General Procedure

In a Schlenk tube, flushed under N_2, dpppPdCl_2 (5.6 mol %) is dissolved in DMSO. Vinyl tosylate (1 equiv.), K_2CO_3 (1.2 equiv.) and phosphine-borane **1** (1 equiv.) are introduced. The mixture is heated to 110°C for 2 h. After cooling to room temperature, $BH_3{\cdot}SMe_2$ is added up to complete boration of the product if a partial decomplexation has occurred during the reaction. The mixture is stirred for 30 min and hydrolyzed with degassed water. The aqueous layer is extracted with diethyl ether. The combined organic layers are dried over $MgSO_4$ and concentrated under reduced pressure. The crude product is then purified by silica-gel column chromatography.

(1,1-Diphenylprop-1-en-2-yl)diphenylphosphine-borane[16]

dpppPdCl_2 (14.9 mg, 0.025 mmol), DMSO (0.9 mL), 1,1-diphenylprop-1-en-2-yl-*p*-toluenesulfonate **5** (164.2 mg, 0.45 mmol), K_2CO_3 (74.7 mg, 0.54 mmol), diphenylphosphine-borane **1** (90 mg, 0.45 mmol), degassed water (1 mL), diethyl ether (3 × 2 mL). Eluent: toluene:pentane (60:40), $R_f = 0.50$, yield: 62% (110 mg), red powder, mp = 130°C.

(Cyclohex-1-en-1-yl)diphenylphosphine-borane 9[16]

dpppPdCl_2 (14.9 mg, 0.025 mmol), DMSO (0.9 mL), cyclohex-1-en-1-yl-*p*-toluenesulfonate **8** (113.7 mg, 0.45 mmol), K_2CO_3 (74.7 mg, 0.54 mmol), diphenylphosphine-borane **1** (90 mg, 0.45 mmol), degassed water (1 mL), diethyl ether (3 × 2 mL). Eluent: pentane:AcOEt (80:20), $R_f = 0.80$, yield: 74% (93 mg), red powder, mp = 95°C.

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