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# First study on the enantioselective palladium-catalyzed C-P cross-coupling reaction between an alkenyltriflate and a phosphine-borane

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## ABSTRACT

In this article, we report the first example of a palladium-catalyzed asymmetric C-P cross-coupling reaction between a racemic secondary phosphine-borane, methylphenylphosphine-borane **1**, and an achiral triflate. The influence of various parameters such as the structure of the chiral ligand, the temperature and the nature of the solvent on the activity and the selectivity of the reaction is reported. Enantiomeric ratios up to 78:22 were obtained using (S,S)-Me-DUPHOSPdCl<sub>2</sub> as catalyst. A kinetic resolution process is proposed to account for this selectivity.

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## R É S U M É

Dans cet article, nous décrivons le premier exemple de couplage C-P asymétrique catalysé au palladium entre une phosphine-borane secondaire racémique, la méthylphénylphosphine-borane **1** et un triflate achiral. L'influence de différents paramètres tels que la structure du ligand chiral, la température, la nature du solvant et de la base, sur l'activité et la sélectivité de la réaction a été étudiée. Un rapport énantiomérique de 78:22 a été obtenu lorsque le catalyseur (S,S)-Me-DUPHOSPdCl<sub>2</sub> est utilisé. Un processus de dédoublement cinétique est proposé pour justifier cette sélectivité.

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## 1. Introduction

Alkenylphosphines are a class of compounds that undergo numerous useful synthetic transformations due to the carbon-carbon double bond, which is directly linked to the phosphorus atom [1–3]. For example, a large variety of nucleophiles can add to the double bond to provide bifunctional or polyfunctional adducts (polyphosphines, dendrimers, polymers). Alkenylphosphines can also be used as dienophiles in cycloaddition reactions [4,5]. Due to the presence of both phosphorus and carbon-carbon double bond, they are also of great interest in coordination

chemistry. Recently, they were successfully used as ligands in homogeneous catalysis. Various synthetic methods for accessing alkenylphosphine derivatives have been developed. The main methodologies are related to the preparation of racemic or achiral alkenylphosphines. They involve reaction between halophosphines and vinylic organometallic species, hydrophosphination of alkynes or C-P cross-coupling reactions [2]. Contrarily, enantiopure or enantioenriched derivatives are rare. If a few C-stereogenic derivatives have been prepared by C-P cross-coupling of enantiopure alkenyl-triflates [6–8] or halides [9], P-stereogenic derivatives are neglected and their synthesis requires resolution processes [5,10]. A more appealing route to P-chirogenic phosphines relies on the use of asymmetric catalysis. To the best of our knowledge, the only example dealing with the synthesis of an enantioenriched

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alkenylphosphine derivative by asymmetric catalysis was reported recently by some of us [11] in the course of our studies on the hydrophosphination reaction [12–16]. We report here the preliminary results dealing with the enantioselective coupling between an achiral alkenyltriflate and a racemic secondary phosphine-borane. Indeed, although examples of enantioselective Pd-catalyzed C–P cross-coupling reaction between an arylhalide and a secondary phosphine have recently appeared in the literature [17,18], no enantioselective variant of the coupling reaction involving alkenyl derivatives has ever been reported.

## 2. Experimental

### 2.1. General comments

All reactions were carried out under nitrogen atmosphere. All glassware was flamed before use. Cyclohex-1-en-1-yltrifluoromethanesulfonate, commercially available, was distilled under reduced pressure (Kugelrohr) before use. Methylphenylphosphine-borane was prepared according to literature procedure [19]. All commercially available ligands were used as purchased.

Dimethylsulfoxide (DMSO) was distilled from calcium hydride and degassed before use. DMF was stored on molecular sieves, freshly distilled and degassed before use. Toluene and THF were purified by an innovative technology Pure Solv. device (activated alumina column containing a copper catalyst and molecular sieves). Pentane was distilled from calcium hydride before use.

Column chromatography was performed on Merck silica gel Si 60 (40–63  $\mu\text{m}$ ). 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.

$^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectra were obtained on BRUKER DPX 250 or AC 400 spectrometers,  $^{11}\text{B}$  NMR spectra were recorded on a BRUKER AC 400 spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts are reported relative to  $\text{Me}_4\text{Si}$  used as an internal standard.  $^{31}\text{P}$ ,  $^{19}\text{F}$  and  $^{11}\text{B}$  NMR chemical shifts are reported relative to respectively  $\text{H}_3\text{PO}_4$  (85%),  $\text{CFCl}_3$  and  $\text{BF}_3\cdot\text{Et}_2\text{O}$  used as external references. Coupling constants are reported in Hertz (Hz).

Abbreviations are used as follows: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintuplet, sept = septuplet, oct = octuplet, m = multiplet and br = broad.

Mass spectroscopy was performed on a QTOF Micro WATERS.

High performance liquid chromatography (HPLC) separations were achieved using the following components:

- For flow up to 0.5 mL/min, the components are: a Waters 600 pump, a Waters 996 photodiode array detector (190–250 nm) and Millennium Software;
- For flow below 0.5 mL/min, the components are: a Waters Alliance 2695 pump, a Waters 2996 photodiode array detector (190–250 nm) and Empower Software.

Enantiomeric excess of compound **2** was measured by HPLC using two possible different conditions:

- Conditions A: Daicel Chiralpack OJ-H (250  $\times$  4.6 mm, L  $\times$  ID) column (*n*-heptane/isopropanol 90:10, 1 mL/min,  $t_{\text{R}1}$  = 9.34 min,  $t_{\text{R}2}$  = 10.95 min) at 20  $^\circ\text{C}$ ;
- Conditions B: Daicel Chiralpack AD-H (250  $\times$  4.6 mm, L  $\times$  ID) column (*n*-heptane/(MeOH/EtOH 50:50) 98:2, 0.2 mL/min,  $t_{\text{R}1}$  = 36.41 min,  $t_{\text{R}2}$  = 40.13 min) at 12  $^\circ\text{C}$ .

Given enantiomeric excesses of compound **2** are average of at least two experiments.

### 2.2. General procedures

Enantiopure catalytic systems, (*R*)-Tol-BINAPPdCl<sub>2</sub> [20], (*R,R*)-BDPPPdCl<sub>2</sub> [21], (*R*)-*i*-Pr-PHOXPdCl<sub>2</sub> [22] and (*S,S*)-Me-DUPHOSPdCl<sub>2</sub> [23] were synthesized according to modified literature procedures [24].

#### 2.2.1. General procedure for the preparation of $\text{L}_2\text{PdCl}_2$

In a two-necked round bottomed flask, containing a solution of  $(\text{CH}_3\text{CN})_2\text{PdCl}_2$  (0.077 M, 1 equiv.) in toluene, a solution of ligand  $\text{L}_2$  (0.077 M, 1 equiv.) in toluene is added. The mixture is stirred overnight at room temperature. The obtained precipitate is filtered, washed with freshly distilled pentane and dried under vacuum to give quantitatively the desired complex.

#### 2.2.2. Typical procedure for palladium-catalyzed asymmetric phosphination

In a schlenk tube, flushed under  $\text{N}_2$ ,  $\text{L}_2\text{PdCl}_2$  (0.01 mmol, 4.8 mol%) is dissolved under the solvent (0.3 mL). Cyclohex-1-en-1-yltrifluoromethanesulfonate (38  $\mu\text{L}$ , 0.22 mmol, 1 equiv.), the base (0.26 mmol, 1.2 equiv.) and methylphenylphosphine-borane **1** (30  $\mu\text{L}$ , 0.22 mmol, 1 equiv.) are then introduced. The mixture is stirred during a time *t* at the desired temperature *T*. The reaction is monitored by  $^{31}\text{P}$  NMR spectroscopy. When the expected conversion is reached, the medium is hydrolyzed with degassed water (0.5 mL). The aqueous layer is extracted with diethyl ether (3  $\times$  2 mL). The combined organic layers are dried over  $\text{MgSO}_4$  and concentrated under reduced pressure. The crude product is then purified by silica-gel column chromatography with pentane/AcOEt (95/5,  $R_f$  = 0.30) as eluent affording pure coupling product **2** as a yellow oil. All attempts to crystallize the oily product failed. Er values are measured by HPLC using conditions A or B.

### 2.3. Experimental data

#### Coupling-product **2** [934338-23-5] [8]

Anal. calcd for  $\text{C}_{13}\text{H}_{20}\text{BP}$  (218.1): C 71.60, H 9.24. Found: C 71.08, H 9.79.  $^{31}\text{P}$  NMR (161.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.4 (q,  $^1J_{\text{PB}} = 64.6$  Hz).  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.70–7.62 (m, 2H), 7.52–7.43 (m, 3H), 6.57 (dm, 1H,  $^3J_{\text{HP}} = 18.8$  Hz), 2.28–2.18 (m, 2H), 2.11–1.93 (m, 2H), 1.67–1.63 (m, 4H), 1.63 (d, 3H,  $^2J_{\text{HP}} = 10.0$  Hz), 0.79 (q, 3H,  $^1J_{\text{HB}} = 92.0$  Hz).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.0 (d,  $^2J_{\text{CP}} = 10.2$  Hz), 131.5 (d,  $^2J_{\text{CP}} = 9.1$  Hz), 130.8 (d,  $^4J_{\text{CP}} = 2.4$  Hz), 129.9 (d,  $^1J_{\text{CP}} = 54.3$  Hz), 128.7 (d,  $^3J_{\text{CP}} = 9.9$  Hz), 128.5 (d,  $^1J_{\text{CP}} = 52.5$  Hz), 26.6 (d,  $^3J_{\text{CP}} = 12.8$  Hz), 24.7 (d,  $^2J_{\text{CP}} = 6.9$  Hz), 22.3 (d,  $^3J_{\text{CP}} = 6.4$  Hz), 21.4 (d,  $^4J_{\text{CP}} = 1.3$  Hz), 9.3 (d,  $^1J_{\text{CP}} = 40.5$  Hz).

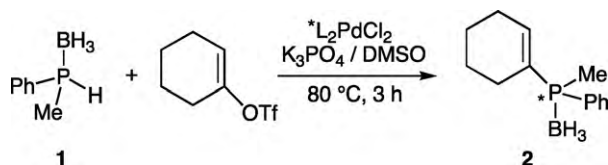
$^{11}\text{B}$  NMR (128.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  -35.6 (dq,  $^1J_{\text{BP}} = 64.6$  Hz,  $^1J_{\text{BH}} = 92.0$  Hz).

Side-product **3** was isolated as a pale yellow oil (eluent: pentane/AcOEt: 95/5,  $R_f = 0.41$ ).  $^{31}\text{P}$  NMR (161.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  109.4 (q,  $^1J_{\text{PB}} = 63.6$  Hz).  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.90–7.83 (m, 2H), 7.61–7.48 (m, 3H), 5.16–5.11 (m, 1H), 2.14–2.04 (m, 2H), 2.02–1.94 (m, 2H), 1.77 (d, 3H,  $^2J_{\text{HP}} = 8.8$  Hz), 1.70–1.61 (m, 2H), 1.53–1.44 (m, 2H), 0.90 (q, 3H,  $^1J_{\text{HB}} = 95.5$  Hz).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  149.4 (d,  $^3J_{\text{CP}} = 7.0$  Hz), 132.8 (d,  $^1J_{\text{CP}} = 56.0$  Hz), 132.1 (d,  $^4J_{\text{CP}} = 2.4$  Hz), 130.7 (d,  $^2J_{\text{CP}} = 11.5$  Hz), 128.6 (d,  $^3J_{\text{CP}} = 10.4$  Hz), 111.2 (d,  $^2J_{\text{CP}} = 6.3$  Hz), 28.7 (d,  $^4J_{\text{CP}} = 2.3$  Hz), 23.6 (s), 22.7 (s), 21.6 (s), 17.1 (d,  $^1J_{\text{CP}} = 46.6$  Hz).  $^{11}\text{B}$  NMR (128.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  -36.6 (dq,  $^1J_{\text{BP}} = 63.6$  Hz,  $^1J_{\text{BH}} = 95.5$  Hz). HRMS calcd for  $\text{C}_{13}\text{H}_{17}\text{OP}$  ( $[\text{M}-\text{BH}_3]^+$ ): 220.1017, found 220.1016.

Side-product **4** was isolated as a pale yellow oil (eluent: methanol,  $R_f = 1$ ).  $^{31}\text{P}$  NMR (161.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  25.1 (q,  $^1J_{\text{PB}} = 66.0$  Hz).  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.73–7.65 (m, 2H), 7.51–7.36 (m, 3H), 2.55 (s, 1H), 1.78–1.69 (m, 2H), 1.66–1.52 (m, 3H), 1.55 (d, 3H,  $^2J_{\text{HP}} = 10.0$  Hz), 1.52–1.48 (m, 1H), 1.48–1.38 (m, 2H), 1.12–0.18 (m, 5H).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  133.1 (d,  $^2J_{\text{CP}} = 8.2$  Hz), 131.5 (s), 128.6 (d,  $^3J_{\text{CP}} = 9.7$  Hz), 126.5 (d,  $^1J_{\text{CP}} = 50.1$  Hz), 71.2 (d,  $^2J_{\text{CP}} = 39.9$  Hz), 41.0 (s), 31.5 (d,  $^2J_{\text{CP}} = 21.4$  Hz), 31.4 (d,  $^1J_{\text{CP}} = 23.1$  Hz), 25.0 (s), 20.4 (s), 4.4 (d,  $^1J_{\text{CP}} = 38.6$  Hz).  $^{11}\text{B}$  NMR (128.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  -35.5 to -40.0 (m). HRMS calcd for  $\text{C}_{13}\text{H}_{19}\text{O}^{11}\text{BP}$   $[\text{M}-3\text{H}]^+$ : 233.1267. Found: 233.1267. HRMS calcd for  $\text{C}_{13}\text{H}_{19}\text{OP}$   $[\text{M}-\text{BH}_3]^+$ : 222.1173. Found: 222.1186.

### 3. Results and discussion

To investigate the enantioselective version, racemic methylphenylphosphine-borane **1** and achiral cyclohexenyl triflate were selected as model reaction partners. Phosphine-boranes were selected as phosphine precursors in order to ensure an easy handling of the phosphine derivatives and also to activate the *P-H* bond of the phosphine [25–27]. Very bulky groups on phosphorus such as isityl ((2,4,6-*i*-Pr) $_3$ C $_6$ H $_2$ ) or mesityl groups were prohibited since they are not representative substituents. A preliminary study in the racemic version having shown that catalysis could take place under certain conditions by using  $\text{Pd}(\text{OAc})_2$  and phosphine-borane **1**, we decided to use



Scheme 1. Asymmetric C-P coupling of cyclohexenyl triflate and phosphine-borane **1**.

only pre-formed complexes  $\text{L}_2\text{PdCl}_2$  in the enantioselective version in order to avoid a possible catalysis by the substrate. Indeed, chiral bidentate ligands tightly bind to the metal and no displacement of the chiral ligand from the metal either by the precursor **1** or the product **2** was observed, whatever the conditions [28]. It is worthy of note that no reaction occurred in the absence of the palladium catalyst. Coupling conditions were based on those developed for the racemic coupling: 1:1 ratio of precursors (phosphine **1** and triflate), 1.2 equiv. of  $\text{K}_3\text{PO}_4$  as a base,  $\text{L}_2$  chelating ligand-PdCl $_2$  complex (4.8 mol%) as catalyst in DMSO at 80 °C (Scheme 1) [8].

The procedure is quite simple: the pre-formed catalyst  $\text{L}_2\text{PdCl}_2$  is dissolved in DMSO. Then cyclohexenyl triflate,  $\text{K}_3\text{PO}_4$  and phosphine-borane **1** are added. The mixture is then heated to 80 °C and monitored by  $^{31}\text{P}$  NMR spectroscopy. After completion, the reaction is hydrolysed, the product is extracted and purified on silica gel chromatography under the air (allowed by the presence of the borane group) [25]. Conditions for the separation of the two enantiomers were defined by HPLC on the racemic compound, which was previously obtained by C-P cross-coupling between racemic **1** and cyclohexenyltriflate, catalyzed by  $\text{dpppPdCl}_2$  [8]. The ability of ligands **L1-L4** to promote asymmetry was then evaluated (Fig. 1, Table 1).

After 3 h at 80 °C, excellent conversions were obtained whatever the ligand. Whereas most of the ligands afforded racemic **2**, (*S,S*)-Me-DUPHOS **L4**, an electron-rich and rigid ligand, induced a promising level of enantioselectivity. (Table 1, entry 4). Hence, a 64:36 enantiomeric ratio was determined by HPLC. Consequently, [(*S,S*)-Me-DUPHOS] PdCl $_2$  was kept for the rest of the study. A survey of reaction conditions (temperature, time) was next performed using **L4**PdCl $_2$  as catalyst. Following the reaction by  $^{31}\text{P}$  NMR, we observed that with **L4**, an almost complete conversion (86%)

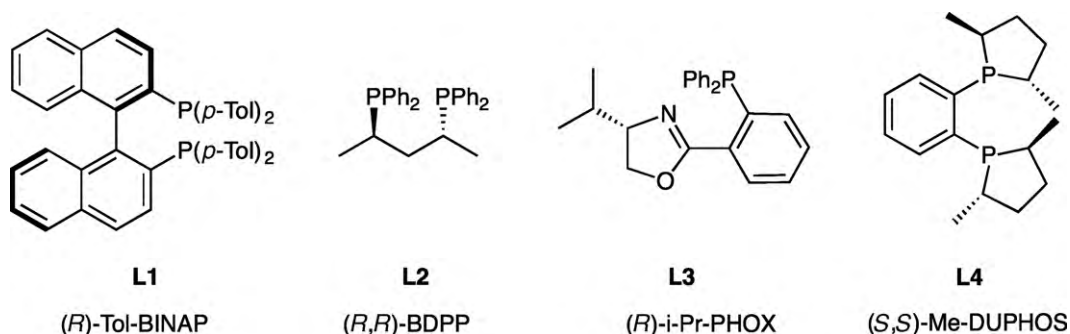


Fig. 1. Enantiopure ligands used in the C-P coupling reactions.

**Table 1**  
Screening of ligands.

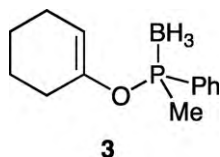
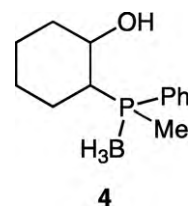
Entry	Ligand	Conversion of <i>rac</i> - <b>1</b> (%) <sup>a</sup>	er of <b>2</b> (%) <sup>b,c</sup>
1	<b>L1</b>	89	50:50
2	<b>L2</b>	94	50:50
3	<b>L3</b>	93	50:50
4	<b>L4</b>	97	64:36

<sup>a</sup> Determined by <sup>31</sup>P NMR integration.<sup>b</sup> Enantiomeric ratio measured by chiral HPLC (average of at least two experiments).<sup>c</sup> Conditions used: **L2**PdCl<sub>2</sub> (4.8 mol%) as precatalyst, K<sub>3</sub>PO<sub>4</sub> (1.2 equiv.) with a 1:1 ratio of phosphine **1** and triflate, in DMSO (3 h, 80 °C).**Table 2**  
Asymmetric C-P coupling of cyclohexenyl triflate and phosphine-borane **1**<sup>a</sup>.

Entry	Temperature (°C)	Solvent	Time (h)	Conversion of <i>rac</i> - <b>1</b> (%) <sup>b</sup>	er of <b>2</b> (%) <sup>c</sup>
1	80	DMSO	3	97	64:36
2	80	DMSO	0.5	86	64:36
3	60	DMSO	3	93	64:36
4	20	DMSO	86	94	67:33
5	80	DMSO	0.08	23	66:34
6	60	DMSO	0.5	32	69:31
7	40	DMSO	2	24	74:26
8	20	DMSO	14.5	23	78:22
9 <sup>d</sup>	20	DMSO	14.5	17	75:25
10 <sup>e</sup>	20	DMSO	14.5	35	74:26
11	20	THF	14.5	23	68:32
12	20	DMF	14.5	20	75:25

<sup>a</sup> Catalyst: [(*S,S*)-Me-DUPHOS]PdCl<sub>2</sub> (4.8 mol%), base: K<sub>3</sub>PO<sub>4</sub> (1.2 equiv.).<sup>b</sup> Determined by <sup>31</sup>P NMR integration.<sup>c</sup> Enantiomeric ratio measured by chiral HPLC (average of at least two experiments); the major enantiomer is **e**<sub>1</sub>.<sup>d</sup> One equivalent of KI was added.<sup>e</sup> One equivalent of *n*-Bu<sub>4</sub>NI was added.

with a similar er of 64:36 was obtained after only 30 minutes of reaction, (Table 2, entry 2) demonstrating the great efficiency of **L4** compared to the achiral dppp [8], for which at least 6 h were required for a complete conversion at the same temperature (80 °C). Decrease of the temperature, from 80 to 60 then 20 °C (Table 2, entries 2–4) has only little effect on the enantiomeric ratio (er=67:33 at 20 °C compared to 64:36 at 80 °C). However, the kinetic of the reaction was markedly lowered (86 h for a 94% conversion at 20 °C compared to 3 h for a 97% conversion at 80 °C). Furthermore, at 20 °C, together with the expected product **2**, a small amount (13%) of a side-product was detected by NMR. Isolation of this product by chromatography and full characterization allowed to identify it as product **3** (Fig. 2) having an oxygen inserted in the newly created C-P bond ( $\delta$  (<sup>31</sup>P)=109 ppm) [29]. This product results from a non-catalytic process as confirmed by its formation in the absence of the palladium catalyst.

**Fig. 2.** By-product **3**.**Fig. 3.** By-product **4**.

We next decided to perform the reaction under kinetic resolution conditions. Interestingly, an increase in the enantioselectivity was observed for a conversion below 50% (Table 2, entries 5–8). Hence at 60 °C, for a conversion of 32%, the enantiomeric ratio was 69:31. By lowering the temperature to 40 °C and 20 °C, enantiomeric ratios of 74:26 and 78:22 were obtained, respectively (Table 2, entries 7 and 8). Although, this enantioselectivity is not as high as might be desirable, it should be pointed out that an enantiomeric ratio of 78:22 is the best result obtained for the synthesis of P-chirogenic alkenylphosphines by asymmetric catalysis yet.<sup>1</sup>

With the aim to increase the enantiomeric ratio, various parameters were modified. First, several inorganic and organic bases were tested. The change of the base dramatically affected the rate of the coupling reaction and led to the formation of several side-products. Hence, upon replacing K<sub>3</sub>PO<sub>4</sub> by K<sub>2</sub>CO<sub>3</sub>, side-product **3** was mainly obtained. With Cs<sub>2</sub>CO<sub>3</sub> and Me<sub>3</sub>SiOK, **3** was formed together with another side-product **4**. Characterization by NMR and HRMS allowed the determination of the structure of **4** (Fig. 3), which results from the hydrophosphination of the carbon-carbon double bond of the starting vinyltriflate, followed by the hydrolysis of the triflate into the corresponding alcohol ( $\delta$  (<sup>31</sup>P)=24 ppm). As for **3**, by-product **4** results from a non-catalytic process and is formed in the absence of the catalyst. With sodium *tert*-pentoxide, only **4** was obtained. Moreover, whatever the base used, no improvement of the enantiomeric ratio was observed, so the preferred base was K<sub>3</sub>PO<sub>4</sub>.

As already reported in the literature, adjunction of a salt like KI could influence the transmetalation step and thus affect the efficiency and the selectivity of the reaction [30]. In our case, addition of 1 equiv. of KI or *n*-Bu<sub>4</sub>NI showed no benefit (Table 2, entries 9 and 10). Finally, influence of the solvent was evaluated. Replacement of DMSO ( $\epsilon$ =47) (Table 2, entry 8) by a weakly polar solvent (THF,  $\epsilon$ =7.5) (Table 2, entry 11) induced a strong decrease in the enantioselectivity (er=68:32). Interestingly, DMF ( $\epsilon$ =38) promoted a clean reaction. Hence, by-product **3**, formed at 20 °C in DMSO, was totally suppressed in DMF and a satisfactory enantiomeric ratio of 75:25 was obtained (Table 2, entry 12). Conversion versus enantioselectivity was then measured in DMF at 20 °C. As anticipated, the enantiomeric ratio decreased when conversion increased (Table 3) going down from 75:25 for a 20% conversion to 70:30 for a 45% conversion and 64:36 for a full conversion.

<sup>1</sup> Er up to 71:29 was obtained in ref. [11].

**Table 3**  
er versus conversion at 20 °C in DMF<sup>a</sup>.

Entry	Time (h)	Conversion of <i>rac</i> - <b>1</b> (%) <sup>b</sup>	er of <b>2</b> (%) <sup>c</sup>
1	14.5	20	75:25
2	24	26	73:27
3	48	45	70:30
4	96	98	64:36

<sup>a</sup> Catalyst: **L4**PdCl<sub>2</sub> (4.8 mol%), base: K<sub>3</sub>PO<sub>4</sub> (1.2 equiv.).

<sup>b</sup> Determined by <sup>31</sup>P NMR integration.

<sup>c</sup> Measured by chiral HPLC (average of at least 2 experiments); the major enantiomer is **e**<sub>1</sub>.

#### 4. Conclusion

In summary, we have demonstrated that an enantioenriched P-chirogenic alkenylphosphine could be formed by asymmetric C–P coupling reaction between an achiral alkenyltriflate and a racemic phosphine-borane. An enantiomeric ratio up to 78:22 was measured by HPLC. The evolution of the enantiomeric ratio versus the conversion seems to be in agreement with a kinetic resolution process. A mechanistic investigation to gain more information on the enantiodiscriminating step is currently underway and will be published in due course.

#### Acknowledgements

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