



**HAL**  
open science

## **P-Chirogenic Triazole-Based Phosphine: Synthesis, Coordination Chemistry, and Asymmetric Catalysis**

Jérôme Bayardon, Benjamin Rousselle, Yoann Rousselin, Quentin Bonnin, Raluca Malacea-Kabbara

### ► To cite this version:

Jérôme Bayardon, Benjamin Rousselle, Yoann Rousselin, Quentin Bonnin, Raluca Malacea-Kabbara. P-Chirogenic Triazole-Based Phosphine: Synthesis, Coordination Chemistry, and Asymmetric Catalysis. *European Journal of Organic Chemistry*, 2020, 2020, pp.4723-4729. <10.1002/ejoc.202000723>. <hal-02992577>

**HAL Id: hal-02992577**

**<https://hal.science/hal-02992577v1>**

Submitted on 18 Nov 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

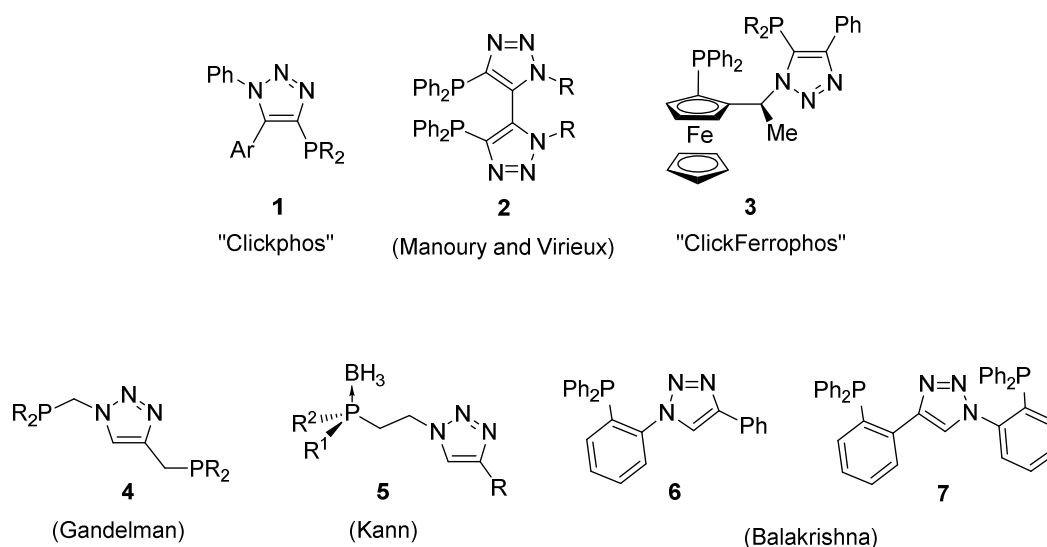
## P-chirogenic triazole-based phosphine: synthesis, coordination chemistry and asymmetric catalysis

Jérôme Bayardon,\*<sup>[a]</sup> Benjamin Rousselle,<sup>[a]</sup> Yoann Rousselin,<sup>[a]</sup> Quentin Bonnin,<sup>[a]</sup> and Raluca Malacea-Kabbara\*<sup>[a]</sup>

**Abstract:** Herein we report the synthesis of a new P-chirogenic triazole-based phosphine according to the ephedrine methodology. Upon reaction with late transition-metal derivatives, Rh(I) and Pd(II), phosphine-triazole forms complexes with bidentate P,N coordination, as demonstrated by spectroscopic and X-ray crystallographic analyses. First experiments in asymmetric catalysis showed the catalytic potential of this new chiral P,N-type ligand.

### Introduction

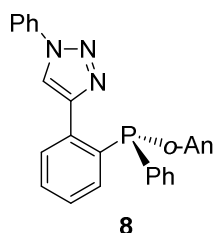
1,2,3-triazole-based phosphines are new class of compounds which have found many applications, especially in coordination chemistry as well as in catalysis[1]. The phosphine moiety can be incorporated either directly on the triazole ring such as in compounds 1-3 (Figure 1) or into the fragments attached to the nitrogen ring as for 4-6 (Figure 1). As examples in the first case, Zhang developed ca. 10 phosphine ligands 1 named "Clickphos" on a 1,2,3-triazole backbone for Pd-catalyzed amination or Suzuki-Miyaura coupling reaction[2]. In parallel, extensions of their synthesis and luminescent properties were studied by Bräse and co-workers[3]. Diphosphines supported by bis(triazole) backbone 2 were recently synthesized by Manoury and Virieux in order to study their coordination chemistry toward transition metals[4]. Chiral planar triazolylphosphines were also synthesized using click-chemistry such as Clickferrophos 3 which was able to induce high enantioselectivities in asymmetric rhodium- and ruthenium-catalyzed hydrogenation of alkenes or ketones as well as in copper-catalyzed synthesis of pyrrolidines[5]. In the second case, different linkers were used to attach phosphine moiety to the triazole unit. Alkyl ligating groups such as methylene or ethylene were employed, respectively for the synthesis of bis-phosphinotriazoles 4 used in the preparation of PCP pincer complexes, and the modular synthesis of more than twenty P-chirogenic BH<sub>3</sub>-protected monophosphines 5, as described by Gandelman[6] and Kann[7]. On the other hand, mono- and diphosphines such as 6-7 bearing phosphino group on the aromatic ring linked to the triazole backbone were also synthesized by Balakrishna[8] for their studies in coordination chemistry with various transition metals.



**Figure 1.** Examples of 1,2,3-triazole-based phosphines.

The triazole itself has already shown its good metal-coordination properties[9] but surprisingly, the use of triazoles as nitrogen donors in P,N ligands has been only few described to date[1g, 1n-o, 8]. Moreover, chiral P,N ligands containing a triazole backbone and their coordination chemistry have, as far as we know, not been reported yet [10].

As a part of our ongoing research concerned with the stereoselective synthesis of P-chirogenic ortho-functionalized arylphosphine and their application in asymmetric catalysis[11], we will report herein the preparation of a P-chirogenic 1,2,3-triazole-based phosphine, in which the nitrogen ring is located in ortho-position of the phosphorus center (Figure 2), its coordination chemistry toward transition metal, Rh(I) and Pd(II), and some preliminary results in Rh- and Pd-catalyzed asymmetric reactions.

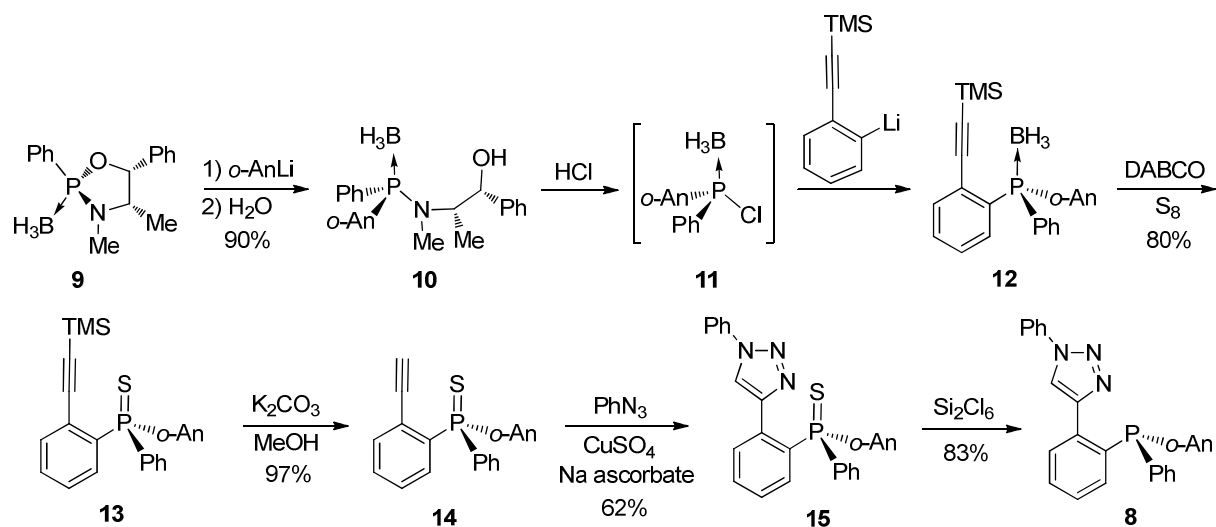


**Figure 2.** P-chirogenic phosphine 8.

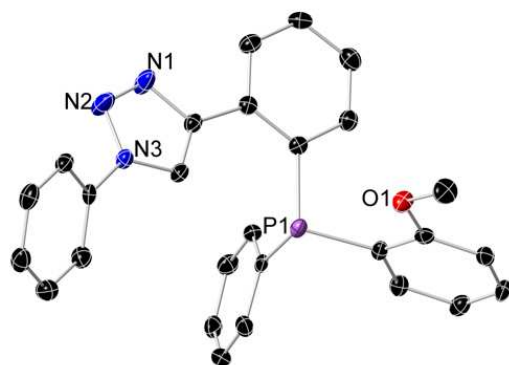
## Results and Discussion

The new P-chirogenic 1,2,3-triazole-based phosphine 8 has been synthesized according to ephedrine methodology starting from (+)-oxazaphospholidine borane complex 9, prepared from (-)-ephedrine[12], as illustrated in Scheme 1.

The reaction of the complex (+)-9 with o-anisyllithium[13] stereospecifically affords the aminophosphine-borane 10 in 90% yield, by a ring opening reaction upon P-O bond cleavage. After acidolysis of the aminophosphine-borane 10 with dry HCl[14], the resulting chlorophosphine-borane 11 reacted with 2-[2-(trimethylsilyl)ethynyl]phenyllithium[15] to provide the corresponding P-chirogenic phosphine-borane 12 in moderate yield because of the partial decomplexation of the borane due to the high steric hindrance around the phosphorus center[16]. To prevent this, the phosphine borane 12 is immediately transformed to phosphine-sulfide 13 by a tandem decomplexation-sulfidation reaction in presence of DABCO and elementary sulfur. The phosphine-sulfide 13 is obtained in 80% overall yield from 10 and its analysis by HPLC on chiral column (99% ee), proves that the two-step reaction sequence proceeds without racemization at the P-center. The desilylation of 13 was readily achieved at room temperature using K<sub>2</sub>CO<sub>3</sub> in methanol/THF. The resulting terminal alkyne 14 was isolated in 97% yield after silica gel chromatography. It was then subjected to the Cu(I)-catalyzed cycloaddition with phenyl azide under classical Click reaction conditions (CuSO<sub>4</sub>·5H<sub>2</sub>O (10 mol%)/sodium ascorbate (20 mol%) in t-BuOH-H<sub>2</sub>O (1:1))[17] to form the corresponding triazolylphosphine-sulfide 15 in 62% yield. Finally, desulfidation of 15 was performed by reaction with Si<sub>2</sub>Cl<sub>6</sub>[18] in toluene at 80°C during one hour to give, after recrystallization, P-chirogenic phosphine 8 in 83% yield (Scheme 1). The enantiomeric excess of phosphine-triazole 8 was determined by HPLC on a chiral column with 99% ee. Moreover, crystals of 8 suitable for X-ray analysis have been obtained and the X-ray structure is depicted in Figure 3. The compound 8 crystallizes in P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> chiral space group and the Flack parameter refinement allows the unambiguous determination of the R-absolute configuration at the phosphorus atom.[19]

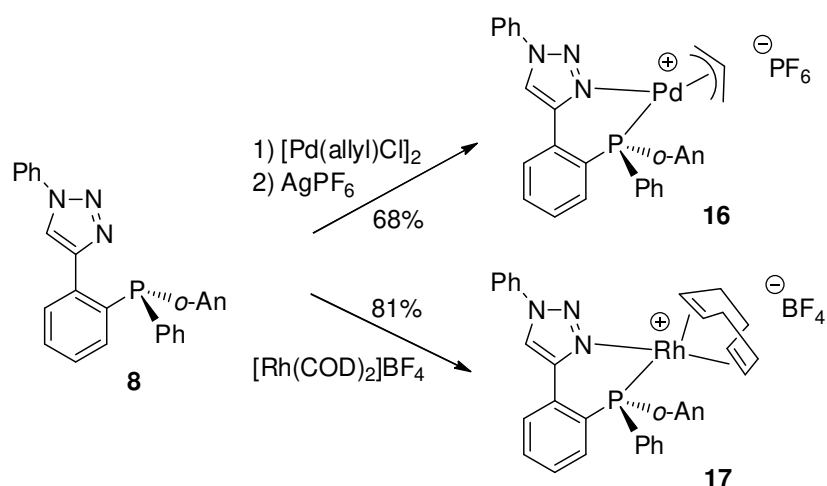


**Scheme 1.** Synthetic route to P-chirogenic phosphine-triazole **8**.



**Figure 3.** View of phosphine-triazole **8**. Thermal ellipsoids are drawn at 50% probability plot. Hydrogen atoms were omitted for clarity.

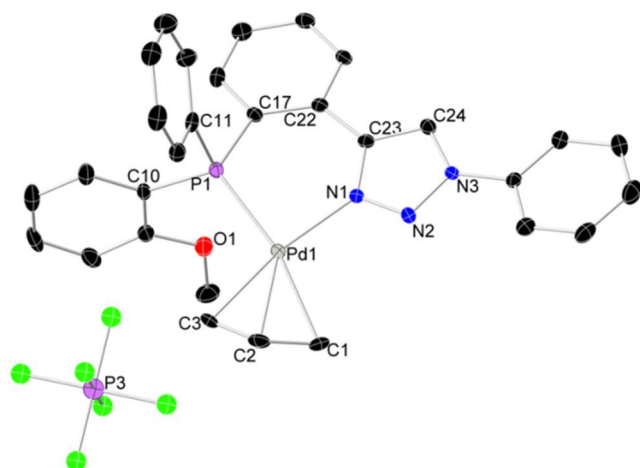
With new triazole-phosphine-containing P,N ligand in hands, we examined the complexation with Pd(II) and Rh(I) salts (Scheme 2). Phosphine **8** reacted with half equivalent of  $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}]_2$  and  $\text{AgPF}_6$  in  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  at room temperature to give the corresponding cationic palladium-allylic complex **16** in 68% yield. Spectroscopic and X-ray crystallographic analyses (*vide infra*) have elucidated that the phosphine-triazole subunit in **16** coordinates to the palladium(II) center as the P,N-bidentate ligand.



**Scheme 2.** Synthesis of Pd(II) and Rh(I) complexes with P-chirogenic phosphine-triazole 7.

In  $^{31}P\{^1H\}$  NMR spectroscopy, a clear shift of the phosphine signal with respect to the free ligand was observed (from -22.4 ppm for 8 to 11.4 ppm for 16). The  $^1H$  NMR signal of the triazole proton is shifted 0.63 ppm to lower field (from 8.19 to 8.82 ppm)[20]. In addition,  $^{15}N$  NMR spectroscopy of phosphine-triazole 8 and Pd(II)-complex 16 was recorded using  $^1H$ - $^{15}N$  HMBC correlation experiment (Table 1). For the phosphine-triazole 8, the  $^{15}N$  NMR chemical shifts are -25 and -126 ppm for N-1 and N-3 atom respectively[21] (entry 1). In the case of the Pd(II)-complex 16, a large upfield shift (-77 ppm) of N-1 atom was observed (entry 2), attesting the binding of the triazole ring to the metal center[22].

Single crystals of Pd(II)-complex 16 suitable for X-ray diffraction analysis were obtained by recrystallization in  $CH_2Cl_2/MeOH$ . The structure of the complex 16 is shown in Figure 4.

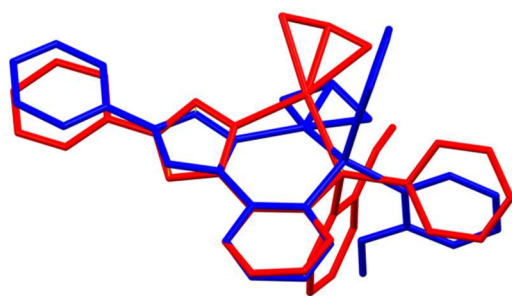


**Figure 4.** View of complex 16. Thermal ellipsoids are drawn at 50% probability plot. Hydrogen atoms, disordered part and other complex presents in asymmetric unit are omitted for clarity.

The compound 16 crystallizes with two complexes in asymmetric unit. “endo/exo” isomers of 16 can be defined when the central C-atom of the allyl group points in opposite direction or toward the *o*-anisyl substituent. In one of them, the allyl ligand was found to be disordered and was refined with the

central C-atom in two positions. Refining the occupancy factors afforded an "endo/exo" ratio of 50%. The other complex is the "endo" form as depicted in Figure 4.

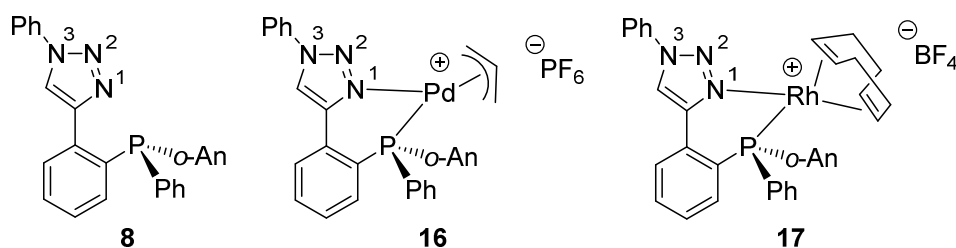
This structure confirms that ligand 8 binds palladium through phosphorus and nitrogen atoms to form a six-membered ring chelate. The conformations of the six-membered rings of the bound ligand were assessed by ring-puckering analysis [23] ( $Q=0.407$ ,  $\tau_1=120^\circ$ ,  $\tau_2=215^\circ$  for Pd1 complex,  $Q=0.589$ ,  $\tau_1=66.8^\circ$ ,  $\tau_2=49^\circ$  for Pd1A complex), and reveal a half-boat conformation where the phosphorus atom is farthest from the mean plane of six-membered ring ( $P1 = 0.257 \text{ \AA}$  from Pd1, N1, C23, C22, C17, P1 mean plane and  $P1A = 0.378 \text{ \AA}$  from Pd1A, N1A, C23A, C22A, C17A, P1A mean plane). Both complexes have a sinister conformation of phosphorus atom, but differ by the different orientation of the o-anisyl group as shown the superposition in Figure 5.



**Figure 5.** Superposition of both Pd coordination complex present in asymmetric unit.

The coordination geometry is pseudo square-planar. The four coordination sites are occupied by the P- and N-atom of the phosphine-triazole ligand and the allylic termini. Bond lengths and bond angles are within the expected range for  $[\text{Pd}(\eta^3\text{-allyl})]$  complexes with a soft and a hard donor atom[24].

**Table 1.**  $^{15}\text{N}$  NMR chemical shift in ppm[a] for the compound 8, 16 and 17[b], [c].

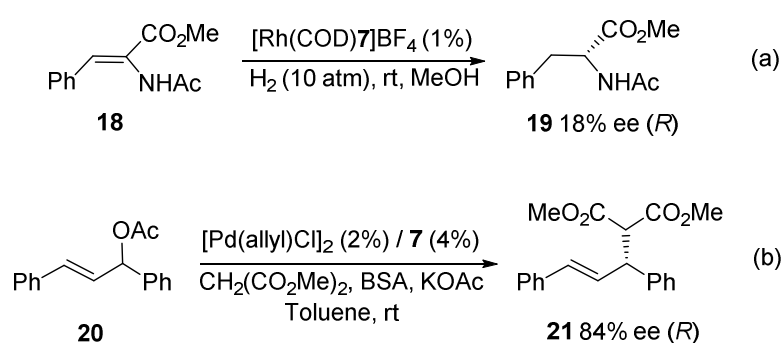


| Entry | Compound | $\delta\text{N-1}$ | $\delta\text{N-2}$ | $\delta\text{N-3}$ |
|-------|----------|--------------------|--------------------|--------------------|
| 1     | 8        | -25                | - [d]              | -126               |
| 2     | 16       | -102               | - [d]              | -122               |
| 3     | 17       | -106               | - [d]              | -123               |

[a] Referenced to neat  $\text{CH}_3\text{NO}_2$ . [b] N-1, N-2 and N-3 for compounds 8, 16 and 17 represented above. [c] In  $\text{CD}_2\text{Cl}_2$ . [d] not determined.

Rhodium complex 17 was also synthesized in 81% yield by mixing phosphine-triazole 8 and [Rh(COD)2]BF4 in CH2Cl2 at room temperature (Scheme 2). Analysis of this complex by 31P-{1H} NMR spectroscopy shows the presence of a doublet at  $\delta$  23.4 ppm ( $1J_{\text{Rh-P}}$  148.7 Hz).[25] As previously observed for Pd-complex 16, the 1H NMR peak of the triazole proton is clearly shifted (from 8.19 ppm for 8 to 8.69 ppm for 17) and 15N NMR indicates also a shift of ca. -81 ppm toward lower frequency for N-1 atom (from -25 ppm for 8 to -106 ppm for 17; table 1, entries 1 and 3). These data all point to the formation of a rhodium-complex in which the phosphine-triazole 8 shows bidentate P,N coordination.

In the next step, we evaluated the catalytic performance of the new P-chirogenic phosphine-triazole 8 as chiral ligand in asymmetric catalysis. The Rh-catalyzed asymmetric hydrogenation of methyl  $\alpha$ -acetamidocinnamate 18 and Pd-catalyzed asymmetric allylic alkylation of (E)-1,3-diphenylprop-2-en-1-yl acetate 20 served as test reactions[26] (Scheme 3).



Scheme 3. Asymmetric transition-metal-catalyzed reactions studied using P-chirogenic phosphine-triazole 8.

Hydrogenation of methyl  $\alpha$ -acetamidocinnamate 18 was carried out using 1 mol% of [Rh(COD)8]BF4 in methanol at room temperature during 18 hours under hydrogen (10 bar). In these conditions, hydrogenated product 19 was obtained in full conversion and with low enantioselectivity (18% ee) (Scheme 3a).

Pd-catalyzed asymmetric allylic alkylation of (E)-1,3-diphenylprop-2-en-1-yl acetate 20 was carried out at room temperature for 5h in toluene using 2 mol% of [Pd( $\eta^3$ -C3H5)Cl]2 and 4 mol% of ligand 8 in the presence of N,O-bis(trimethylsilyl)acetamide (BSA) and a catalytic amount of potassium acetate as bases. The complex with 8 gave the product 21 in full conversion with 84% ee (Scheme 3b).

## Conclusions

New P-chirogenic triazole-based phosphine could be stereoselectively synthesized by using ephedrine methodology and Click-type chemistry. The ability of this phosphine to coordinate with metal centers was also studied and a Rh(I) complex and a Pd(II) complex could be synthesized. Spectroscopic and X-ray crystallographic analyses have elucidated the structures of both complexes in which phosphine-triazole shows bidentate P,N coordination. Preliminary studies in asymmetric catalysis have demonstrated the usefulness of this ligand, especially in Pd-catalyzed asymmetric allylic alkylation for which ee up to 84% was achieved. The synthesis of further P-chirogenic phosphine-triazoles such as 8 and their application as ligand in different asymmetric transformations is under investigation.

## Experimental Section

General: All reactions were carried out using standard Schlenk techniques under an inert gas. Solvents were dried using a MBRAUN SPS 800. Methylene chloride, diethyl ether, ethyl acetate, pentane, petroleum ether, tetrahydrofuran (THF), toluene and methanol were purchased in anhydrous form. Hexane and 2-propanol for HPLC were of chromatographic grade and used without purification. The reagents 2-[2-(trimethylsilyl)ethynyl]-bromobenzene, n-BuLi (2.5 M in hexane), DABCO, sulfur, potassium carbonate, t-butanol, sodium ascorbate, copper sulfate pentahydrate, hexachlorodisilane, allylpalladium(II) chloride dimer and bis(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate were purchased from commercial suppliers. (2R,4S,5R)-(+)-2,4-dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine-2-borane **9** and (Sp)-(-)-N-methyl-N-[(1R,2S)(1-hydroxy-2-methyl-1-phenyl-2-propyl)]amino-o-anisylphenyl-phosphine-borane **10** were prepared according to published procedure[14, 27]. Phenyl azide was prepared from aniline according to procedure described by Mangione et al.[28]. Flash chromatography was carried out with the indicated solvents using silica gel 60 (60AAC, 35-70 $\mu$ m; SDS). <sup>1</sup>H (and <sup>1</sup>H decoupled), <sup>13</sup>C, <sup>31</sup>P and <sup>15</sup>N NMR spectra were recorded with Bruker 600 Avance III-HD or Bruker 500 Avance III spectrometers at 25°C, using tetramethylsilane as internal reference for <sup>1</sup>H and <sup>13</sup>C spectra, 85% phosphoric acid as external reference for <sup>31</sup>P NMR and a neat solution of nitromethane as external reference for <sup>15</sup>N NMR. Sweep width for spectra recorded at 600MHz were 20,240, 396 and 13-400 ppm for <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P and <sup>15</sup>N NMR respectively and for spectra recorded at 500 MHz 20, 237 and 405 ppm for <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P NMR respectively. The signals of <sup>13</sup>C NMR spectra were allocated by the J-mod technology. Data are reported in ppm as follows: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br.s = broad signal), coupling constant(s), integration. HPLC analyses were performed on a Shimadzu chromatograph equipped with a UV detector at  $\lambda$  = 210 and 254 nm. Mass spectrometry and accurate mass measurements (HRMS) were recorded on a Thermo LTQ Orbitrap XL ESI-MS (ElectroSpray Ionization Mass Spectrometry). Melting points were measured with a Kofler melting points apparatus and are uncorrected. Optical rotation values were measured at 20°C with a Perkin-Elmer 241 polarimeter at 589 nm (sodium lamp). Elemental analyses were measured with a precision superior to 0.4% on a CHNS/-O Thermo Electron Flash EA 1112 Series instrument apparatus.

X-Ray experimental procedure: All experimental data procedure and refinement are detailed in Supplementary Information. Data CCDC-1953272 and 1953273 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)

(Sp)-o-Anisyl-phenyl-{2-[2-(trimethylsilyl)ethynyl]phenyl}phosphine-sulfide (**13**): A freshly titrated toluene solution of dry HCl (40 mL, 12 mmol) was added to (Sp)-(-)-N-methyl-N-[(1R,2S)(1-hydroxy-2-methyl-1-phenyl-2-propyl)]amino-o-anisylphenylphosphine-borane **10** (0.786g, 2 mmol) and the reaction was stirred under argon at room temperature during two hours. The ephedrine hydrochloride was filtered off using a Millipore 4  $\mu$ m filter. The resulting solution of o-anisyl-chloro-phenylphosphine-borane **11** was collected and cooled to -78°C. Under argon, 2-[2-(trimethylsilyl)ethynyl]phenyllithium (4 mmol), previously prepared by reaction between 2-[2-(trimethylsilyl)ethynyl]-bromobenzene (1.01 g, 4 mmol) and n-BuLi (2.5M in hexane) (1.8 mL, 4.4 mmol) in THF (5 mL) at -78°C during one hour, was added and the resulting mixture was stirred until room temperature during 5 hours. After hydrolysis with water (20 mL), the mixture was extracted with methylene chloride (3x20 mL) and the combined organic phases were dried over MgSO<sub>4</sub>. The solvent was removed under vacuum and the resulting crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate 3:1 as eluent. The corresponding phosphine borane **12**, obtained partially decomplexed was dissolved under argon in dry toluene (10 mL) and DABCO (0.450 g, 4 mmol) and sulfur (0.128 g, 4 mmol)

were successively added. The reaction mixture was stirred at 50 °C during 3 hours and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate 3:1 as eluent to give compound 13 as a white solid (0.673 g, 80%). Rf 0.44 (petroleum ether/ethyl acetate 3:1); m.p. 50-52°C (dec.); Enantiomeric excess: 99% by HPLC analysis (Chiralpak IA, 1 mL.min<sup>-1</sup>, hexane/2-propanol 90:10, tR (R) 6.9 min, tR (S) 9.4 min); [α]<sub>D</sub> -48.3 (c 0.5, CHCl<sub>3</sub>). <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 0.01 (s, 9H), 3.52 (s, 3H), 6.95 (dd, J = 5.3, 8.0 Hz, 1H), 7.16-7.19 (m, 1H), 7.35-7.38 (m, 1H), 7.44-7.61 (m, 7H), 8.02-8.05 (m, 2H), 8.17 (ddd, J = 2.0, 8.0, 16.7 Hz, 1H); {<sup>1</sup>H}<sup>13</sup>C NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ -0.9, 55.2, 102.7 (d, JC-P = 6.4 Hz), 103.5, 111.5 (d, JC-P = 5.1 Hz), 120.5 (d, JC-P = 85.7 Hz), 121.1 (d, JC-P = 13.7 Hz), 125.2 (d, JC-P = 6.9 Hz), 127.7 (d, JC-P = 13.7 Hz), 128.0 (d, JC-P = 13.7 Hz), 130.3 (d, JC-P = 2.1 Hz), 131.0 (d, JC-P = 3.0 Hz), 131.8 (d, JC-P = 12.0 Hz), 132.5 (d, JC-P = 10.3 Hz), 133.2, 134.0 (d, JC-P = 1.9 Hz), 134.8 (d, JC-P = 6.9 Hz), 135.4 (d, JC-P = 10.3 Hz), 136.0, 160.3; {<sup>1</sup>H}<sup>31</sup>P NMR (243 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 40.5 (s). HRMS calcd for C<sub>24</sub>H<sub>26</sub>OPSSi [M+H]<sup>+</sup> m/z 421.12058, found m/z 421.11908. Anal. Calcd for C<sub>24</sub>H<sub>25</sub>OPSSi: C, 68.54; H, 5.99. Found C, 68.40; H, 6.32.

(Sp)-o-Anisyl-[2-(ethynyl)phenyl]-phenylphosphine-sulfide (14): To a solution of compound 13 (0.430 g, 1.02 mmol) in a mixture of MeOH/THF (2:1) (7.5 mL) was added K<sub>2</sub>CO<sub>3</sub> (0.141 g, 1.02 mmol). The mixture was stirred at room temperature during two hours and the solvent was evaporated. Water (5 mL) and CH<sub>2</sub>Cl<sub>2</sub> (15 mL) were added and organic phase was separated then washed with water (5 mL) and finally dried over MgSO<sub>4</sub>. After filtration and evaporation of the solvent, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate 3:1 as eluent to give compound 14 as a white solid (0.345 g, 97%). Rf 0.39 (petroleum ether/ethyl acetate 3:1); m.p. < 50°C; [α]<sub>D</sub> +2.5 (c 0.3, CHCl<sub>3</sub>). <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 2.95 (s, 1H), 3.53 (s, 3H), 6.95 (dd, J = 5.5, 7.7 Hz, 1H), 7.16-7.18 (m, 1H), 7.38-7.41 (m, 1H), 7.46-7.62 (m, 7H), 8.03-8.07 (m, 2H), 8.19 (ddd, J = 1.7, 7.7, 17.1 Hz, 1H); {<sup>1</sup>H}<sup>13</sup>C NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 55.2, 81.3 (d, JC-P = 6.6 Hz), 85.0, 111.3 (d, JC-P = 5.6 Hz), 120.3 (d, JC-P = 85.4 Hz), 121.0 (d, JC-P = 14.0 Hz), 123.8 (d, JC-P = 5.6 Hz), 127.8 (d, JC-P = 12.9 Hz), 128.5 (d, JC-P = 11.8 Hz), 130.3 (d, JC-P = 2.4 Hz), 131.2 (d, JC-P = 3.5 Hz), 131.6 (d, JC-P = 11.8 Hz), 132.5 (d, JC-P = 89.4 Hz), 132.7 (d, JC-P = 11.8 Hz), 134.1 (d, JC-P = 2.4 Hz), 135.0 (d, JC-P = 9.4 Hz), 135.5 (d, JC-P = 10.6 Hz), 136.7 (d, JC-P = 88.2 Hz), 160.4; {<sup>1</sup>H}<sup>31</sup>P NMR (243 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 40.6 (s). HRMS calcd for C<sub>21</sub>H<sub>18</sub>OPS [M+H]<sup>+</sup> m/z 349.08105, found m/z 349.08151. Anal. Calcd for C<sub>21</sub>H<sub>17</sub>OPS: C, 72.40; H, 4.92. Found C, 72.08; H, 5.07.

(Sp)-4-[2-(o-anisylphenylthiophosphinyl)phenyl]-1-phenyl-1H-1,2,3-triazole (15): To a solution of phosphine-alkyne 14 (0.399 g, 1.15 mmol) in t-BuOH (2 mL) were successively added phenyl azide (0.136 g, 1.15 mmol) then a solution of CuSO<sub>4</sub>·5H<sub>2</sub>O (5.5 mg, 0.034 mmol) and sodium ascorbate (13.6 mg, 0.068 mmol) in water (2 mL). The resulting mixture was stirred at 40°C during 16 hours. After cooling to room temperature, a solution of NH<sub>4</sub>OH (30% in water) (2 mL) was added followed by 5 mL of water. The mixture was extracted with methylene chloride (3x10 mL) and the combined organic phases were dried over MgSO<sub>4</sub>. After filtration and evaporation of the solvent, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate 1:1 as eluent to give the titled compound 15 as a pale yellow solid (0.333 g, 62%). Rf 0.40 (petroleum ether/ethyl acetate 1:1); m.p. 88-90°C; [α]<sub>D</sub> -32.0 (c 0.4, CHCl<sub>3</sub>). <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 3.54 (s, 3H), 6.76 (br. t, J = 7.1 Hz, 1H), 6.98 (br. t, J = 7.1 Hz, 1H), 7.35-7.55 (m, 11H), 7.64 (t, J = 7.1 Hz, 1H), 7.87-7.89 (m, 1H), 8.06 (dd, J = 8.0, 14.2 Hz, 2H), 8.37 (dd, J = 7.6, 17.0 Hz, 1H), 8.92 (s, 1H); {<sup>1</sup>H}<sup>13</sup>C NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 55.0, 111.2 (d, JC-P = 6.3 Hz), 119.3 (d, JC-P = 83.5 Hz), 120.5, 120.7 (d, JC-P = 12.7 Hz), 124.3, 127.7 (d, JC-P = 13.0 Hz), 127.9 (d, JC-P = 13.0 Hz), 128.4, 129.5, 130.8 (d, JC-P = 2.0 Hz), 131.2, 131.2 (d, JC-P = 15.0 Hz), 131.5 (d, JC-P = 9.0 Hz), 132.1 (d, JC-P = 86.8 Hz), 132.5 (d, JC-P = 12.0 Hz), 133.1 (d, JC-P = 8.0 Hz), 133.4, 133.9 (d, JC-P = 2.0 Hz), 135.2 (d, JC-P = 9.0 Hz), 136.8, 145.1 (d, JC-P = 4.6 Hz), 159.4; {<sup>1</sup>H}<sup>31</sup>P NMR (243 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 41.1 (s). HRMS calcd for C<sub>27</sub>H<sub>22</sub>N<sub>3</sub>OPSSiNa

[M+Na]<sup>+</sup> m/z 490.11134, found m/z 490.11154. Anal. Calcd for C<sub>27</sub>H<sub>22</sub>N<sub>3</sub>O<sub>3</sub>PS: C, 69.36; H, 4.74. Found C, 69.02; H, 4.87.

(Rp)-4-[2-(*o*-anisylphenylphosphinyl)phenyl]-1-phenyl-1*H*-1,2,3-triazole (8): To a solution of compound 15 (0.31 g, 0.663 mmol) in toluene (14 mL) was added Si<sub>2</sub>Cl<sub>6</sub> (0.23 mL, 1.326 mmol). The resulting mixture was stirred under argon at 80 °C during one hour. After cooling to 0 °C, a solution of NaOH (30% in water) (20 mL) was added dropwise followed by water (10 mL) and methylene chloride (20 mL). The two phases were separated then aqueous phase was extracted with methylene chloride (2 x 20 mL). The combined organic phases were dried over MgSO<sub>4</sub>, filtered and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate 1:1 as eluent and recrystallization in hexane/CH<sub>2</sub>Cl<sub>2</sub> to give the phosphine-triazole 8 as a white crystalline solid (0.24 g, 83%). R<sub>f</sub> 0.65 (petroleum ether/ethyl acetate 1:1); m.p. 134-136 °C; Enantiomeric excess: 99% by HPLC analysis (Chiralpak IA, 1.0 mL.min<sup>-1</sup>, hexane/2-propanol 90:10, t<sub>R</sub> (R) 32.6 min, t<sub>R</sub> (S) 35.2 min); [α]<sub>D</sub> +49.0 (c 0.3, CHCl<sub>3</sub>). <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 3.76 (s, 3H), 6.78-6.80 (m, 1H), 6.92 (t, J = 7.2 Hz, 1H), 6.98 (dd, J = 4.6, 7.9 Hz, 1H), 7.07-7.09 (m, 1H), 7.31-7.58 (m, 11H), 7.69 (d, J = 7.9 Hz, 2H), 8.05-8.07 (m, 1H), 8.19 (s, 1H); {<sup>1</sup>H}<sup>13</sup>C NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 55.7, 110.5, 120.3, 121.2, 121.6 (d, J<sub>C-P</sub> = 17.8 Hz), 125.1 (d, J<sub>C-P</sub> = 11.5 Hz), 128.2, 128.5, 128.7 (d, J<sub>C-P</sub> = 7.6 Hz), 128.8, 128.9, 129.6 (d, J<sub>C-P</sub> = 5.1 Hz), 129.7, 130.6, 134.0, 134.1, 134.2 (d, J<sub>C-P</sub> = 2.6 Hz), 135.2 (d, J<sub>C-P</sub> = 17.4 Hz), 135.5 (d, J<sub>C-P</sub> = 27.6 Hz), 136.4 (d, J<sub>C-P</sub> = 11.6 Hz), 137.1, 146.7 (d, J<sub>C-P</sub> = 4.9 Hz), 161.2 (d, J<sub>C-P</sub> = 14.1 Hz); {<sup>1</sup>H}<sup>31</sup>P NMR (243 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ -22.4 (s). HRMS calcd for C<sub>27</sub>H<sub>22</sub>N<sub>3</sub>O<sub>3</sub>Na [M+Na]<sup>+</sup> m/z 458.13927, found m/z 458.13979. Anal. Calcd for C<sub>27</sub>H<sub>22</sub>N<sub>3</sub>O<sub>3</sub>P: C, 74.47; H, 5.09. Found C, 74.57; H, 4.99.

Palladium complex (16): To a solution of phosphine-triazole 8 (0.050 g, 0.115 mmol) and [Pd(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)Cl]<sub>2</sub> (0.019 g, 0.052 mmol) in methylene chloride (1 mL) was added a solution of AgPF<sub>6</sub> (0.026 g, 0.104 mmol) in methanol (0.3 mL). The mixture was stirred at room temperature in the dark during one hour and the finely divided precipitate was filtered off using a Millipore 4 μm filter. Slow addition of diethyl ether to the filtrate induced the formation of a powder which was filtered and washed with diethyl ether. Crystallization in CH<sub>2</sub>Cl<sub>2</sub>/MeOH gave the palladium complex 16 as a white crystalline solid (0.051 g, 68%). M.p. 202-204 °C; [α]<sub>D</sub> -27.8 (c 0.3, CHCl<sub>3</sub>). <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 3.05 (br.s, 1H), 3.28 (br.s, 1H), 3.65 (s, 3H), 3.89-3.92 (m, 1H), 4.95 (br.s, 1H), 5.79 (t, J = 8.2 Hz, 1H), 6.61-6.64 (m, 1H), 6.86-6.89 (m, 1H), 6.95-6.98 (m, 1H), 7.04-7.07 (m, 1H), 7.28-7.54 (m, 10H), 7.62-7.64 (m, 1H), 7.79-7.80 (m, 2H), 7.94-7.96 (m, 1H), 8.82 (s, 1H); {<sup>1</sup>H}<sup>13</sup>C NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 55.8, 57.0, 79.5 (d, J<sub>C-P</sub> = 29.4 Hz), 111.5 (d, J<sub>C-P</sub> = 3.9 Hz), 116.5 (d, J<sub>C-P</sub> = 48.6 Hz), 120.8, 121.5 (d, J<sub>C-P</sub> = 7.8 Hz), 121.9 (d, J<sub>C-P</sub> = 5.8 Hz), 122.5, 123.3 (d, J<sub>C-P</sub> = 40.8 Hz), 128.1 (d, J<sub>C-P</sub> = 48.8 Hz), 129.3 (d, J<sub>C-P</sub> = 10.9 Hz), 130.1, 130.3 (d, J<sub>C-P</sub> = 6.5 Hz), 130.5, 130.8 (d, J<sub>C-P</sub> = 8.7 Hz), 131.7 (d, J<sub>C-P</sub> = 2.2 Hz), 131.9 (d, J<sub>C-P</sub> = 16.3 Hz), 132.5, 133.4 (d, J<sub>C-P</sub> = 4.3 Hz), 133.9 (d, J<sub>C-P</sub> = 8.7 Hz), 134.0, 135.7, 146.3 (d, J<sub>C-P</sub> = 5.3 Hz), 160.3 (d, J<sub>C-P</sub> = 7.0 Hz), one C missing; {<sup>1</sup>H}<sup>31</sup>P NMR (243 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 11.4 (s), -144.4 (hept, J<sub>F-P</sub> = 710.5 Hz). HRMS calcd for C<sub>30</sub>H<sub>27</sub>N<sub>3</sub>O<sub>3</sub>PPd [M-PF<sub>6</sub>]<sup>+</sup> m/z 582.09211, found m/z 582.09182.

Rhodium complex (17): A solution of phosphine-triazole 8 (0.050 g, 0.115 mmol) in methylene chloride (3.5 mL) was slowly added to a suspension of [Rh(COD)<sub>2</sub>]BF<sub>4</sub> (0.045 g, 0.110 mmol) in methylene chloride (2.5 mL). The resulting mixture was stirred at room temperature during one hour then half of the solvent was removed under vacuum. Addition of diethyl ether induced the formation of an orange powder which was filtered, washed with diethyl ether and dried under vacuum. The rhodium complex was obtained as an orange solid (0.069 g, 81%). M.p. 214-216 °C (dec.). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 2.9-2.30 (m, 2H), 2.39-2.42 (m, 3H), 2.52-2.69 (m, 3H), 3.62 (br. s, 1H), 3.76 (br. s, 1H), 3.78 (s, 3H), 5.77-5.80 (m, 1H), 6.18-6.20 (m, 1H), 7.01-7.10 (m, 3H), 7.42-7.53 (m, 5H), 7.60-7.78 (m, 7H), 7.84-7.86 (m, 2H), 7.92-7.93 (m, 1H), 8.69 (s, 1H); {<sup>1</sup>H}<sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 28.1, 29.1, 31.4, 33.3, 55.4,

79.5 (d, J = 11.9 Hz), 80.4 (d, J = 11.9 Hz), 105.4 (dd, J = 6.3, 10.0 Hz), 107.2 (dd, J = 6.9, 9.0 Hz), 111.6 (d, JC-P = 3.5 Hz), 114.0 (d, JC-P = 48.3 Hz), 120.6, 121.4 (d, JC-P = 9.4 Hz), 122.6, 123.4 (d, JC-P = 43.5 Hz), 128.6 (d, JC-P = 47.5 Hz), 129.1 (d, JC-P = 11.1 Hz), 129.6 (d, JC-P = 7.1 Hz), 130.0, 130.1, 130.5, 130.9 (d, JC-P = 16.6 Hz), 131.5 (d, JC-P = 2.4 Hz), 131.8, 132.4, 134.0, 131.9 (d, JC-P = 12.7 Hz), 135.6 (d, JC-P = 8.7 Hz), 135.7, 160.3, two C missing;  $\{^1\text{H}\}^31\text{P}$  NMR (203 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  23.4 (d, JRh-P = 148.7 Hz). HRMS calcd for  $\text{C}_{35}\text{H}_{34}\text{N}_3\text{OPRh} [\text{M-BF}_4]^+$  m/z 646.14890, found m/z 646.14781.

Procedure for asymmetric hydrogenation: A solution of  $[\text{Rh}(\text{COD})_8]\text{BF}_4$  (3.7 mg, 0.005 mmol, 1 mol %) and methyl  $\alpha$ -acetamidocinnamate 18 (109.5 mg, 0.5 mmol) in dry methanol (7.5 mL) was introduced in a stainless steel autoclave. The autoclave was closed, purged with hydrogen and then pressurized with 10 bar of hydrogen. After 16h of stirring at room temperature, the pressure was released to atmospheric pressure and the solution was transferred to a round bottom flask. The solvent was removed to give a residue, which was purified by column chromatography on silica gel to afford the hydrogenated product 19. Enantiomeric excess was determined by HPLC analysis (Chiralcel OD-H, 1 mL.min<sup>-1</sup>, hexane/2-propanol 95:5, tR (R) 21.4 min, tR (S) 34.7 min).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.97 (s, 3H), 3.06-3.07 (m, 2H), 3.64 (s, 3H), 4.85-4.87 (m, 1H), 6.11 (br. s, 1H), 7.18-7.20 (m, 5H).

Procedure for asymmetric allylic alkylation: A solution of  $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}]_2$  (3.6 mg, 0.010 mmol), phosphine-triazole 8 (8.8 mg, 0.020 mmol) and (E)-1,3-diphenylprop-2-en-1-yl acetate 20 (126 mg, 0.5 mmol) in 2 mL of toluene was stirred one hour at room temperature. Dimethylmalonate (0.12 mL, 1.0 mmol) was added followed by BSA (0.24 mL, 1.0 mmol) and KOAc (5.0 mg, 0.05 mmol). The reaction was stirred at room temperature during 5 hours (full conversion). The reaction mixture was diluted with Et<sub>2</sub>O and saturated aqueous NH<sub>4</sub>Cl solution was added. The mixture was extracted with Et<sub>2</sub>O, and the organic phases were dried over MgSO<sub>4</sub>. After filtration, the solvent was removed to give a residue, which was purified by column chromatography on silica gel to afford the product 21. Enantiomeric excess was determined by HPLC analysis (Chiralpak IA, 1 mL.min<sup>-1</sup>, hexane/2-propanol 90:10, tR (R) 8.5 min, tR (S) 10.4 min).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.56 (s, 3H), 3.75 (s, 3H), 4.02 (d, J = 10.9 Hz, 1H), 4.27 (dd, J = 8.8, 10.8 Hz, 1H), 6.40 (dd, J = 8.6, 15.7 Hz, 1H), 6.54 (d, J = 15.7 Hz, 1H), 7.10-7.40 (m, 10H).

## Acknowledgments

The authors are grateful for the financial support provided by the CNRS, Ministère de l'Éducation Nationale et de la Recherche, Université de Bourgogne, Conseil Régional de Bourgogne through the Plan d'Actions Régional pour l'Innovation (PARI) and the Fonds Européen de Développement Régional (FEDER) programs. It is also a pleasure to thank M. J. Penouilh and M. Picquet at the Sayens/Pôle Chimie Moléculaire for the NMR and mass spectrometry analyses, and M. J. Eymin for her skilled technical assistance.

**Keywords:** P-Chirogenic phosphine • Stereoselective synthesis • Coordination chemistry • Transition metals • Asymmetric catalysis

[1] a) Y. Zhao, M. G. Wakeling, F. Meloni, T. J. Sum, H. van Nguyen, B. R. Buckley, P.W. Davies, J. S. Fossey, *Eur. J. Org. Chem.* 2019, 5540-5548; b) Y. Zhao, M. G. Wakeling, F. Meloni, T. J. Sum, H. van Nguyen, B. R. Buckley, P.W. Davies, J. S. Fossey, *ChemRxiv* 2019, 1-17; c) T. P. Seifert, S. Bestgen, T. J. Feuerstein, S. Lebedkin, F. Krämer, C. Fengler, M. T. Gamer, M. M. Kappes, P. W. Roesky, *Dalton Trans.* 2019, 48, 15427-15434; d) Y. Zhao, H. van Nguyen, L. Male, P. Craven, B. R. Buckley, J. S. Fossey, *Organometallics* 2018, 37, 4224-4241; e) L. Cao, S. Huang, W. Liu, X. Yan, *Organometallics* 2018, 37, 2010-2013; f) Y. Zhao, H. van Nguyen, L. Male, P. Craven, B. R. Buckley, J. S. Fossey, *ChemRxiv* 2018, 1-30; g) C. Zeng, N. Wang, T. Peng, S. Wang, *Inorg. Chem.* 2017, 56, 1616-1625; h) R. Veillard, E. Bernoud, I. Abdellah, J.-F. Lohier, C. Alayrac, A.-C. Gaumont, *Org. Biomol. Chem.* 2014, 12, 3635-3640; i) N. V.

Dubrovina, L. Domke, I. A. Shuklov, A. Spannenberg, R. Franke, A. Villinger, A. Börner, *Tetrahedron* 2013, 69, 8809-8817; j) J. E. Glover, D. J. Martin, P. G. Plieger, G. J. Rowlands, *Eur. J. Org. Chem.* 2013, 1671-1675; k) M. Austeri, M. Enders, M. Nieger, S. Bräse, *Eur. J. Org. Chem.* 2013, 1667-1670; l) T. Konno, K. Shimizu, K. Ogata, S.-i. Fukuzawa, *J. Org. Chem.* 2012, 77, 3318-3324; m) E. A. Slutsky Smith, G. Molev, M. Botoshansky, M. Gandelman, *Chem. Commun.* 2011, 47, 319-321; n) Y. Matano, M. Nakashima, A. Saito, H. Imahori, *Org. Lett.* 2009, 11, 3338-3341; o) R. J. Detz, S. Arévalo Heras, R. de Gelder, P. W. N. M. van Leeuwen, H. Hiemstra, J. N. H. Reek, J. H. van Maarseveen, *Org. Lett.* 2006, 8, 3227-3230; p) S. Trofimenko, A. L. Rheingold, C. D. Incarvito, *Angew. Chem. Int. Ed.* 2003, 42, 3506-3509.

[2] a) D. Liu, W. Gao, Q. Dai, X. Zhang, *Org. Lett.* 2005, 7, 4907-4910; b) Q. Dai, W. Gao, D. Liu, L. M. Kapes, X. Zhang, *J. Org. Chem.* 2006, 71, 3928-3934.

[3] a) D. M. Zink, T. Grab, T. Baumann, M. Nieger, E. C. Barnes, W. Koppler, S. Bräse, *Organometallics* 2011, 30, 3275-3283; b) D. M. Zink, T. Baumann, M. Nieger, S. Bräse, *Eur. J. Org. Chem.* 2011, 1432-1437.

[4] C. Laborde, M.-M. Wei, A. van der Lee, E. Deydier, J.-C. Daran, J.-N. Volle, R. Poli, J.-L. Pirat, E. Manoury, D. Virieux, *Dalton Trans.* 2015, 44, 12539-12545.

[5] a) S.-i. Fukuzawa, H. Oki, M. Hosaka, J. Sugazawa, S. Kikuchi, *Org. Lett.* 2007, 9, 5557-5560; b) S.-i. Fukuzawa, H. Oki, *Org. Lett.* 2008, 10, 1747-1750; c) H. Oki, I. Oura, T. Nakamura, K. Ogata, S.-i. Fukuzawa, *Tetrahedron: Asymmetry* 2009, 20, 2185-2191.

[6] a) E. M. Schuster, M. Botoshansky, M. Gandelman, *Angew. Chem. Int. Ed.* 2008, 47, 4555-4558; b) E. M. Schuster, M. Botoshansky, M. Gandelman, *Organometallics* 2009, 28, 7001-7005; c) E. M. Schuster, G. Nisnevich, M. Botoshansky, M. Gandelman, *Organometallics* 2009, 28, 5025-5031.

[7] F. Dolhem, M. J. Johansson, T. Antonsson, N. Kann, *J. Comb. Chem.* 2007, 9, 477-486.

[8] a) B. Choubey, L. Radhakrishna, J. T. Mague, M. S. Balakrishna, *Inorg. Chem.* 2016, 55, 8514-8526. b) L. Radhakrishna, M. K. Pandey, M. S. Balakrishna, *RSC Adv.* 2018, 8, 25704. c) L. Radhakrishna, H. S. Kunchur, P. K. Namdeo, R. J. Butcher, M. S. Balakrishna, *Dalton Trans.* 2020, 49, 3434-3449.

[9] J. D. Crowley, D. A. McMorran, *Top Heterocycl. Chem.* 2012, 28, 31-84.

[10] Fukuzawa and Kann reported, respectively, the use of a planar chiral and P-chirogenic triazole-based P,N ligand in Pd-catalyzed asymmetric allylic alkylation (see ref 5b and 7) but no study of its coordination mode toward Pd was reported.

[11] a) J. Bayardon, H. Lauréano, V. Diemer, M. Dutartre, U. Das, Y. Rousselin, J.-C. Henry, F. Colobert, F. R. Leroux, S. Jugé, *J. Org. Chem.* 2012, 77, 5759-5769; b) E. Rémond, J. Bayardon, S. Takizawa, Y. Rousselin, H. Sasai, S. Jugé, *Org. Lett.* 2013, 15, 1870-1873; c) J. Bayardon, J. Bernard, E. Rémond, Y. Rousselin, R. Malacea-Kabbara, S. Jugé, *Org. Lett.* 2015, 17, 1216-1219; d) J. Bayardon, S. Jugé, *Phosphorus, Sulfur, and Silicon* 2015, 190, 700-705; e) J. Bayardon, M. Maronnat, A. Langlois, Y. Rousselin, P. D. Harvey, S. Jugé, *Organometallics* 2015, 34, 4340-4358; f) J. Bayardon, Y. Rousselin, S. Jugé, *Org. Lett.* 2016, 18, 2930-2933.

[12] F. Chaux, S. Frynas, H. Lauréano, C. Salomon, G. Morata, M.-L. Auclair, M. Stephan, R. Merdès, P. Richard, M.-J. Ondel-Eymin, J.-C. Henry, J. Bayardon, C. Darcel, S. Jugé, *C. R. Chim.* 2010, 12, 1213-1226.

- [13] *o*-anisyllithium was prepared by metal-halide exchange from 2-bromoanisole, using *sec*-butyllithium, as reported in ref 12.
- [14] C. Bauduin, D. Moulin, E. B. Kaloun, C. Darcel, S. Jugé, *J. Org. Chem.* 2003, 68, 4293-4301.
- [15] Y. Xu, Z. Wang, Z. Gan, Q. Xi, Z. Duan, F. Mathey, *Org. Lett.* 2015, 17, 1732-1734.
- [16] Partial decomplexation of sterically hindered phosphine borane has been already observed in our group (see ref 11a and 14).
- [17] V. V. Rostotsev, L. G. Green, V. V. Fokin, K. B. Sharpless, *Angew. Chem. Int. Ed.* 2002, 41, 2596-2599.
- [18] G. Zon, K. E. DeBruin, K. Naumann, K. Mislow, *J. Am. Chem. Soc.* 1969, 91, 7023-7027.
- [19] The RP configuration of phosphine-triazole 8 as well as the configuration of the P-center of each intermediate 10, 12, 13, 14 and 15 are in good agreement with the stereochemistry previously reported for the ephedrine methodology (see for example ref 14) and for the desulfidation with Si<sub>2</sub>Cl<sub>6</sub> (see ref 18).
- [20] Shifting of the triazole methine-proton in palladium complexes indicates a bidentate P,N coordination mode, see ref 1n and 1o.
- [21] In some cases, <sup>15</sup>N NMR chemical shift of N-2 central atom on the triazole ring was not determined. See for example: A. Bolje, D. Urankar, J. Kosmrlj, *Eur. J. Org. Chem.* 2014, 8167-8181.
- [22] Similar coordination shifts of <sup>15</sup>N resonances were already reported for nitrogen containing ligand and palladium and rhodium complexes. See for example: a) V. Rosar, D. Dedeic, T. Nobile, F. Fini, G. Balducci, E. Alessio, C. Carfagna, B. Milani, *Dalton Trans.* 2016, 45, 14609-14619; b) M. Teresa Pereira, J. M. Antelo, L. A. Adrio, J. Martinez, J. M. Ortigueira, M. Lopez-torres, J. M. Vila, *Organometallics* 2014, 33, 3265-3274; c) A. Satake, H. Koshino, T. Nakata, *J. Organomet. Chem.* 2000, 595, 208-214; d) E. Szlyk, A. Grodzicki, L. Pazderski, A. Wojtczak, J. Chatlas, G. Wrzeszcz, J. Sitkowski, B. Kamienski, *J. Chem. Soc., Dalton Trans.* 2000, 867-872.
- [23] D. Cremer, J. A. Pople, *J. Am. Chem. Soc.* 1975, 97, 1354-1358.
- [24] a) M. Kollmar, B. Goldfuss, M. Reggelin, F. Rominger, G. Helmchen, *Chem. A Eur. J.* 2001, 7, 4913-4927; b) L. B. Schenkel, J. A. Ellman, *Org. Lett.* 2003, 5, 545-548; c) N. Baltzer, L. Macko, S. Schaffner, M. Zehnder, *Helv. Chim. Acta* 1996, 79, 803-812.
- [25] Similar coupling constant was already observed for triazole-phosphine rhodium complex (see ref 8c).
- [26] For reviews of P,N-ligands in Rh- and Pd-catalyzed asymmetric reactions, see: a) B. V. Rokade, P. J. Guiry, *ACS Catal.* 2018, 8, 624-643; b) I. D. Kostas, *Curr. Org. Chem.* 2008, 5, 227-249; c) P. J. Guiry, C. P. Saunders, *Adv. Synth. Catal.* 2004, 346, 497-537; d) G. Chelucci, G. Orrù, G. A. Pinna, *Tetrahedron* 2003, 59, 9471-9515; e) K. N. Gavrilov, A. I. Polosukhin, *Russ. Chem. Rev.* 2000, 69, 661-682; f) G. Helmchen, A. Pfaltz, *Acc. Chem. Res.* 2000, 33, 336-345.
- [27] E. B. Kaloun, R. Merdès, J.-P. Genêt, J. Uziel, S. Jugé, *J. Organomet. Chem.* 1997, 529, 455-463.
- [28] M. I. Mangione, R. A. Spanevello, M. B. Anzardi, *RSC Adv.* 2017, 7, 47681-47688.

## **FULL PAPER**

The stereoselective synthesis of a novel P-chirogenic triazole-based phosphine was achieved. Its coordination to transition-metals was explored, and a P,N-chelation mode was demonstrated. Application to this chiral phosphine as ligand in asymmetric catalysis is also reported.

P-Chirogenic Phosphine\*

Jérôme Bayardon,\* Benjamin Rousselle, Yoann Rousselin, Quentin Bonnin, Raluca Malacea-Kabbara\*

Page No. – Page No.

P-chirogenic triazole-based phosphine: synthesis, coordination chemistry and asymmetric catalysis