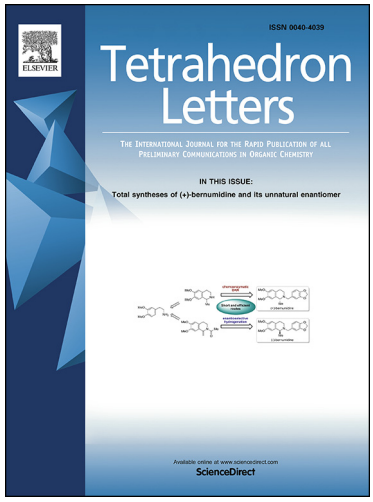

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PII: S0040-4039(18)31134-1
DOI: https://doi.org/10.1016/j.tetlet.2018.09.044
Reference: TETL 50283

To appear in: *Tetrahedron Letters*

Received Date: 23 July 2018
Revised Date: 14 September 2018
Accepted Date: 17 September 2018

Please cite this article as: Gao, Y., Qiu, Z., Sun, R., Gao, N., Cao, G., Teng, D., New spiro phosphinooxazolines for palladium-catalyzed asymmetric allylic amination, *Tetrahedron Letters* (2018), doi: https://doi.org/10.1016/j.tetlet.2018.09.044

Tetrahedron Letters
journal homepage: www.elsevier.com

New spiro phosphinooxazolines for palladium-catalyzed asymmetric allylic amination

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
spiro-phosphine oxazoline
asymmetric synthesis
allyl amination
1,3-diphenylallyl acetate

ABSTRACT

The new conformational rigid spiro phosphinooxazolines **1** were synthesized from 7-bromo-1-indanone. The asymmetric catalytic potential of them was demonstrated in the asymmetric palladium catalyzed allylic amination. High yields and enantioselectivities were obtained with alkylamines.

Introduction

Transition metal-catalyzed asymmetric allylic substitution has become a powerful method in the formation of carbon-carbon and carbon-heteroatom bond[1-3]. The enantioselective allylic amination is an important reaction for the synthesis of chiral allylamines which are ubiquitous in biologically active motifs and natural products[4-8]. Many efforts have been devoted to the design and synthesis of the chiral ligands. The rigid conformation of chiral ligand is an important factor for high enantioselectivity in asymmetric catalysis. The ligands with rigid backbone could reduce the conformation obscurity of catalyst and create an effective asymmetric environment around the central metal, which could lead to high enantioselectivities in asymmetric reactions[9]. However, there are only a few investigations on the catalyst's rigidity of backbones[10]. The phosphinooxazolines such as PHOX have proven to be efficient ligands in asymmetric allylic substitution[11-13]. Bidentate ligands with a more rigid linker between the two coordinating sites can form more rigid metallocycle with fewer available conformations and thus enhance the enantiofacial differentiation[14-15]. Herein, we report a new spiro phosphinooxazolines and their asymmetric catalytic potential in palladium catalyzed asymmetric allylic amination.

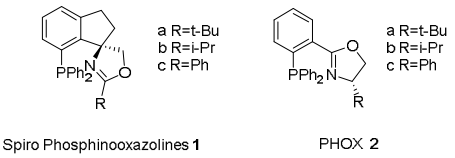
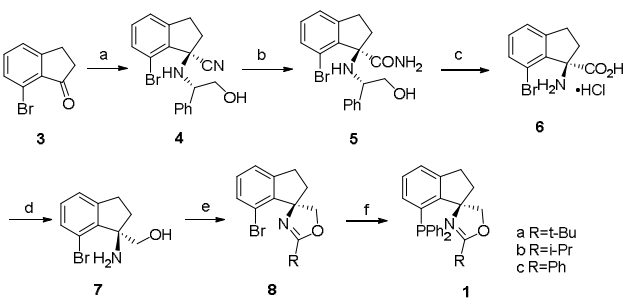


Figure 1. The phosphinooxazoline ligands.

Results and discussion

The synthetic route of the ligands was outlined in Scheme 1. The (R)-aminoacid **6** was synthesized by a modified Warmuth method[16]. Asymmetric Strecker reaction of 7-bromoindanone **3** with (*S*)-phenylglycinol and trimethylsilyl cyanide catalyzed by *p*-toluenesulfonic acid gave amino carbonitrile **4**, which was directly subjected to hydrolysis with sulfuric acid to afford (*R*)-aminocarboxamide **5** in 81% yield.



Scheme 1. Synthesis of spiro phosphinooxazolines

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