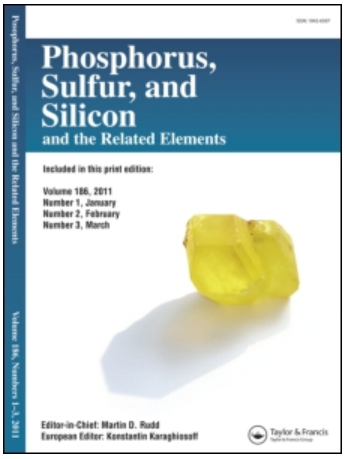


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Copper(I) Complexes of Fesulphos Ligands: Highly Efficient Chiral Lewis Acids for the Formal Aza Diels-Alder Reaction of *N*-Sulfonyl Imines

Juan C. Carretero[a]; Olga García Mancheño[a]; Ramón Gómez Arrayás[a]
[a] Departamento de Química Orgánica, Universidad Autónoma de Madrid, Madrid, Spain

To cite this Article Carretero, Juan C. , Mancheño, Olga García and Arrayás, Ramón Gómez(2005) 'Copper(I) Complexes of Fesulphos Ligands: Highly Efficient Chiral Lewis Acids for the Formal Aza Diels-Alder Reaction of *N*-Sulfonyl Imines', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 5, 1515 — 1516
To link to this Article: DOI: 10.1080/10426500590913483
URL: http://dx.doi.org/10.1080/10426500590913483

Phosphorus, Sulfur, and Silicon, 180:1515–1516, 2005

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500590913483

Taylor & Francis
Taylor & Francis Group

Copper(I) Complexes of Fesulphos Ligands: Highly Efficient Chiral Lewis Acids for the Formal Aza Diels–Alder Reaction of *N*-Sulfonyl Imines

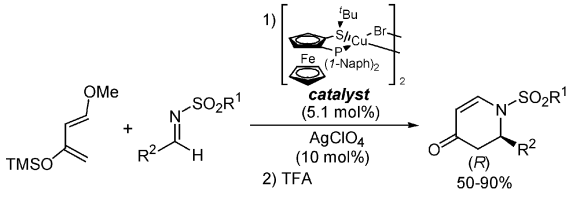
Olga García Mancheño
Ramón Gómez Arrayás
Juan C. Carretero
Departamento de Química Orgánica, Universidad Autónoma de Madrid, Madrid, Spain

Keywords Aza Diels-Alder; copper-catalyzed; N-sulfonyl imines; planar chirality; sulfur ligand

INTRODUCTION

Enantiopure dihydropyridones are intermediates of great interest in alkaloid synthesis.[1] The enantioselective Aza Diels–Alder reaction (ADAR) of electron-rich dienes with aldimines is one of the most powerful strategies for the construction of such nitrogen heterocycles.

Herein we describe how copper(I) complexes of planar chiral Fesulphos ligands[2] act as highly efficient catalysts in enantioselective ADAR of *N*-sulfonyl imines with Danishefsky diene.[3] The application of this methodology to the synthesis of alkaloids is also presented.



SCHEME 1 Enantioselective Aza Diels–Alder reaction of *N*-sulfonyl imines.

Received July 9, 2004; accepted October 5, 2004.

Address correspondence to Juan C. Carretero, Departamento de Química Orgánica, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain. E-mail: juancarlos.carretero@uam.es

TABLE I Scope of the ADAR in the Presence of Fesulphos-Copper Catalyst

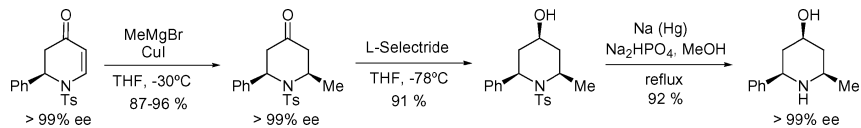
R^1	R^2	ee (%)[a]
2-Thiophen	Ph	93[b]
(p-NO_2)C_6H_4	Ph	90[b]
(p-OMe)C_8H_4	Ph	94[b]
(p-Me)C_6H_4	Ph	93[b](97)[c]
(p-Me)C_6H_4	(p-F)C_6H_4	88[b](93)[c]
(p-Me)C_6H_4	(p-OMe)C_6H_4	91[b]
(p-Me)C_6H_4	2-Naph	86[b](93)[c]
(p-Me)C_6H_4	PhCH=CH	83[b](96)[c]
(p-Me)C_6H_4	n-Pr	82[b]

[a]Determined by HPLC. [b]At rt. [c]At −20°C. [d]At −78°C.

RESULTS

High enantioselectivities (ee = 82–97%, in CH_2Cl_2) were achieved with a number of *N*-aryl sulfonyl imines derived from both aliphatic and aromatic aldehydes (Scheme 1 and Table I). Interestingly, the enantioselectivity is high, regardless of the substitution at the arylsulfonyl group.

Ready access to (2*R*, 4*S*, 6*R*)-4-hydroxy-2-phenyl-6-methylpiperidine[4] from the phenyl cycloadduct (R^2 = Ph), which was obtained in enantiopure form upon a single recrystallization, has been accomplished by simple functional group transformations (Scheme 2).



SCHEME 2 Synthesis of (2*R*, 4*S*, 6*R*)-4-hydroxy-2-phenyl-6-methylpiperidine.

REFERENCES

[1] D. O'Hagan, *Nat. Prod. Rep.*, **17,** 435 (2000); D. L. Comins, S. Huang, C. L. McArdle, and C. L. Ingalls, *Org. Lett.*, **3,** 469 (2001) and references cited therein.
[2] O. García Mancheño, J. Priego, S. Cabrera, R. Gómez Arrayás, T. Llamas, and J. C. Carretero, *J. Org. Chem.*, **68,** 3679 (2003).
[3] For a previous communication, see O. García Mancheño, R. Gómez Arrayás, and J. C. Carretero, *J. Am. Chem. Soc.*, **126,** 456 (2004).
[4] F. A. Davis, A. Rao, and P. J. Caroll, *Org. Lett.*, **5,** 3855 (2003), and references cited therein.