

Enantioselective Desymmetrization of Diphenylphosphinamides via (–)-Sparteine-Mediated *Ortho*-Lithiation. Synthesis of *P*-Chiral Ligands

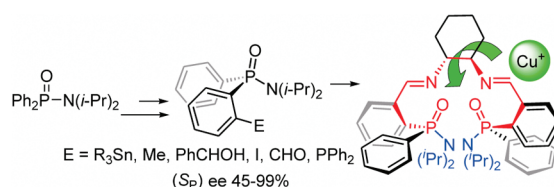
Cristinel Popovici,[†] Pascual Oña-Burgos,[†] Ignacio Fernández,[†] Laura Roces,[‡] Santiago García-Granda,[‡] María José Iglesias,[†] and Fernando López Ortiz^{*†}

Área de Química Orgánica, Universidad de Almería, Carretera de Sacramento s/n, 04120 Almería, Spain, and Departamento de Química Física y Analítica, Universidad de Oviedo, C/ Julián Clavería 8, 33006 Oviedo, Spain

flortiz@ual.es

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ABSTRACT



Asymmetric *ortho*-lithiation of *N*-dialkyl-*P,P*-diphenylphosphinamides using [*n*-BuLi(–)-sparteine] is described as an efficient method for the synthesis of *P*-chiral *ortho*-functionalized derivatives in high yields and ee's from 45 to >99%. The method allows access to new enantiomerically pure *P*-chiral phosphine and diimine ligands.

Ortho-directed metalation has become one of the most employed strategies in organic synthesis for derivatizing arenes.¹ Although a broad range of functional groups promote *ortho*-deprotonation, *P*-containing derivatives have been less exploited.² *P=X*-Directed (*X* = O, S) *ortho*-dilithiation strategies have been also described.³ To the best of our knowledge, there are no precedents on asymmetric *ortho*-deprotonation of aryl systems using chiral reagents (third-generation method).^{4,5} Recently, we have achieved the diastereoselective desymmetrization of the *P*(O)Ph₂ (Pop) group of chiral diphenylphosphinamides.⁶ As part of our ongoing project on selective phosphinamide-directed lithia-

tions⁷ we report herein (1) an efficient method for the enantioselective lithiation of diisopropylphosphinamide **1a** using (–)-sparteine as source of chirality, (2) the extension of the procedure to other Pop derivatives such as **1b–1f**, (3)

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[†] Universidad de Almería.

[‡] Universidad de Oviedo.

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