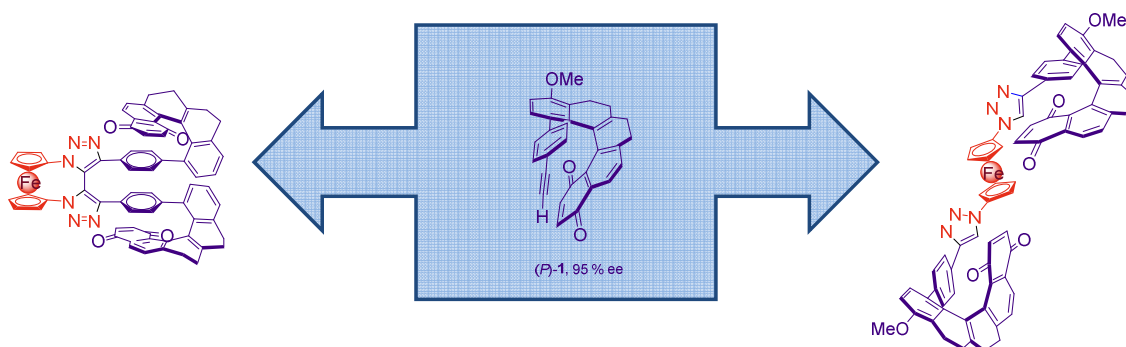


# Synthesis of enantiopure (*P*)-[5]- and (*P,P*)-Bis-[5]-Helicenequinones Joined by Aryl or Ferrocenyl Linkers Via Click Chemistry

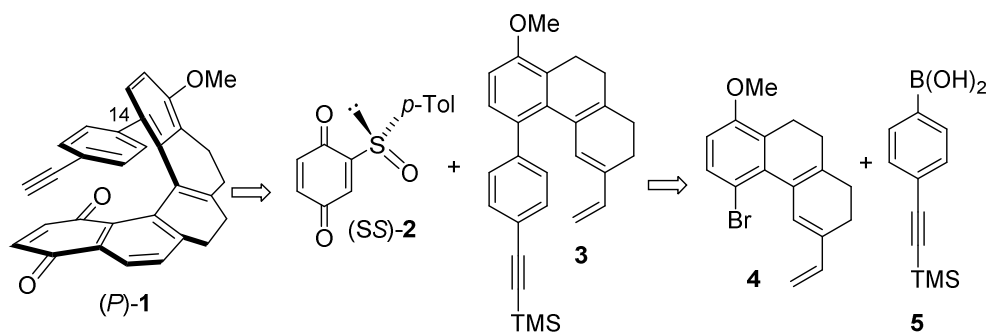
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The target *Bis*-[5]-Helicenequinones were synthesized by a double Cu-catalyzed Huisgen 1,3-dipolar cycloaddition<sup>1</sup> between the enantiopure arylalkyne substituted tetrahydro-[5]-helicenequinone (*P*)-**1** and aryldiazides. A detailed study of the click reactions revealed an essential role of the copper source (CuSO<sub>4</sub>/NaAscorbate or CuI) in controlling the formation of the triazole-ferrocenyl adducts.

Compound (*P*)-**1** was easily available through a Diels-Alder reaction/pyrolytic sulfoxide elimination/oxidation sequence<sup>2</sup> when an excess of (*SS*)-2-*p*-tolylsulfinyl-*p*-benzoquinone **2**<sup>3</sup> reacted with an adequately substituted diene **3**. The diene **3** was synthesized from bromo derivative **4** and boronic acid **5** by a Suzuki coupling.



SCHEME 1.

<sup>1</sup> (a) C.W. Tornøe, C. Christensen, M. Meldal, *J. Org. Chem.*, 2002, **67**, 3057; (b) V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless, *Angew. Chem. Int. Ed.*, 2002, **41**, 2596.

<sup>2</sup> (a) Feature article: M. C. Carreño, G. Hernández-Torres, M. Ribagorda, A. Urbano, *Chem. Commun.*, 2009, 6105. (b) A. Latorre, A. Urbano, M. C. Carreño, *Chem. Commun.*, 2011, **47**, 1283; (c) A. Latorre, A. Urbano, M. C. Carreño, *Chem. Commun.*, 2009, **45**, 6652; (d) M. C. Carreño, Á. Enríquez, S. García-Cerrada, M. J. Sanz-Cuesta, A. Urbano, F. Maseras, A. Nonell-Canals, *Chem. Eur. J.*, 2008, **14**, 603; (e) M. C. Carreño, M. González-López, A. Urbano, *Chem. Commun.*, 2005, 611; (f) M. C. Carreño, S. García-Cerrada, A. Urbano, *Chem. Eur. J.*, 2003, **9**, 4118.

<sup>3</sup> M. C. Carreño, J. L. García Ruano, A. Urbano, *Synthesis*, 1992, 651.