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

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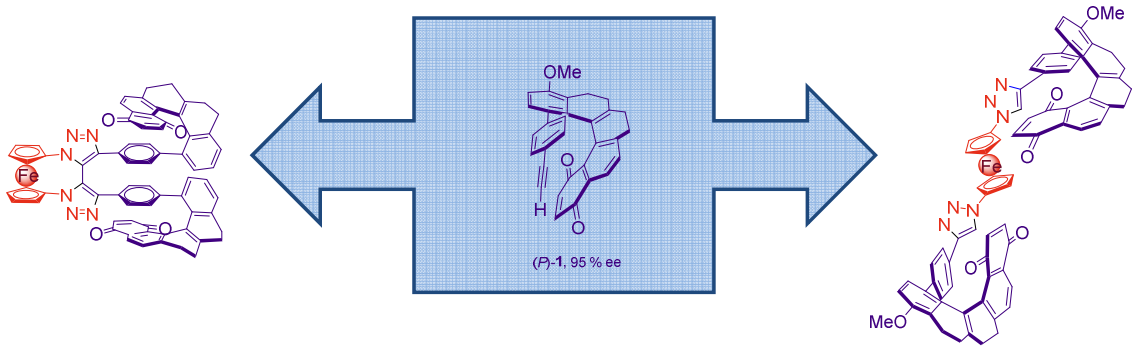
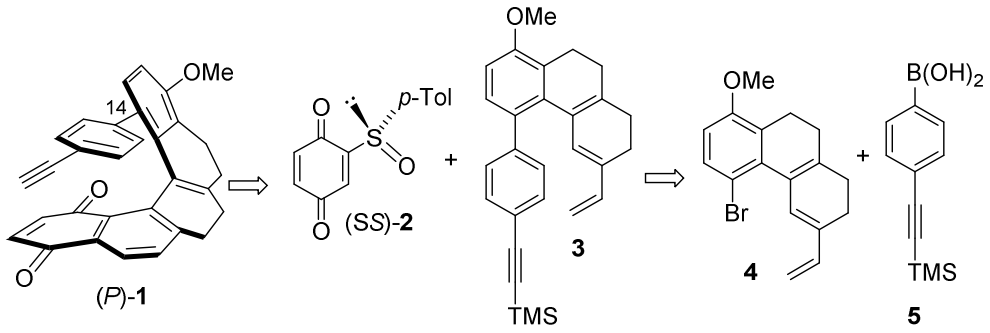


The target *Bis*-[5]-Helicenequinones were synthesized by a double Cu-catalyzed Huisgen 1,3-dipolar cycloaddition[1] between the enantiopure arylalkyne substituted tetrahydro-[5]-helicenequinone (*P*)-**1** and aryldiazides A detailed study of the click reactions revealed an essential role of the copper source ($CuSO_4$/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[2] when an excess of (*SS*)-2-*p*-tolylsulfinyl-*p*-benzoquinone **2**[3] 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.

[1] (*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.

[2] (*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.

[3] M. C. Carreño, J. L. García Ruano, A. Urbano, *Synthesis*, 1992, 651.