

Axially chiral benzo[1,2-*b*:4,3-*b'*]dithiophene derivatives: a new route to tetrathiahelicenes

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Thiophene-containing fused aromatic compounds represent an interesting class of π -conjugated systems in functional organic materials [1]. Among them, benzo[1,2-*b*:4,3-*b'*]dithiophene (BDT) and its derivatives are by far the most widely studied, especially as units in mono and polydisperse oligomers in the field of the materials science [2], and as π -spacers in push-pull organic chromophores for photovoltaic applications [3]. Moreover, BDT is a key intermediate for the synthesis of inherently chiral helical systems such as tetrathia[7]helicenes **3** [4]. For all these reasons, BDT can be identified as a key starting molecule that, through a judicious functionalization of the α -positions of the thiophene rings, can allow access to more complex and interesting systems. Exploiting the experience acquired in our laboratories on the synthesis and functionalization of BDT derivatives [5,6], we have studied a novel and simple synthetic route to prepare bis(benzo[1,2-*b*:4,3-*b'*]dithiophene) systems **2**, through Pd-catalyzed cross coupling reactions, starting from bromides **1** (Figure 1).

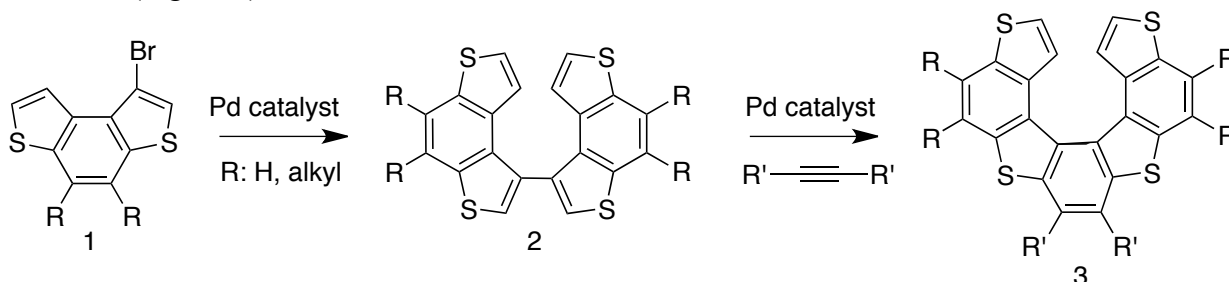


Figure 1

This strategy provides a convenient route to an interesting class of chiral atropisomeric heterobiaryl derivatives **2** with C_2 -symmetry, which can be used as starting reagents for an innovative non-photochemical synthesis of tetrathiahelicenes exploiting a Suzuki-Miyaura cross coupling and a Pd-catalyzed annulation with internal alkynes as key steps. Asymmetric versions of this synthesis is under study.

References: 1. Roncali, J. *Acc. Chem. Res.* **2009**, *42*, 1719. 2. Nishide, Y.; Osuga, H.; Saito, M.; Aiba, T.; Inagaki, Y.; Doge, Y.; Tanaka, K. *J. Org. Chem.* **2007**, *72*, 9141. 3. Longhi, E.; Bossi, A.; Di Carlo, G.; Maiorana, S.; De Angelis, F.; Salvatori, P.; Petrozza, A.; Binda, M.; Roiati, V.; Mussini, P. R.; Baldoli, C.; Licandro, E. *Eur. J. Org. Chem.* **2013**, 84. 4. Licandro, E.; Rigamonti, C.; Ticozzelli, M. T.; Monteforte, M.; Baldoli, C.; Giannini, C.; Maiorana, S. *Synthesis* **2006**, 3670. 5. Cauteruccio, S.; Dova, D.; Graiff, C.; Carrara, C.; Doucet, J.; Stephenson, G. R.; Licandro, E. *New J. Chem.* **2014**, *38*, 2241. 6. Stephenson, G. R.; Cauteruccio, S.; Doucet, J. *Synlett* **2014**, 701.