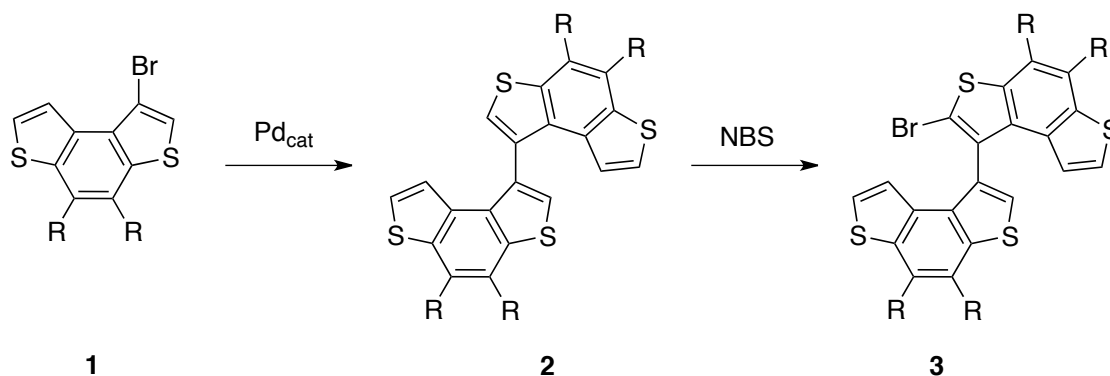


Chiral bis(benzo[1,2-*b*:4,3-*b'*]dithiophene)s: synthesis and stereochemical characterization*Valentina Pelliccioli^a, Silvia Cauteruccio^a, Clara Baldoli^b, Roberta Franzini^c, Claudio Villani^c, Emanuela Licandro^a*

^a Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano, Italia; ^b CNR-Istituto di Scienze e Tecnologie Molecolari, Via Golgi 19, 20133 Milano, Italia; ^c Dipartimento di Chimica e Tecnologie del Farmaco, Sapienza Università di Roma, Piazzale Aldo Moro 5, 00185 Roma 3, Italia; valentina.pelliccioli@unimi.it

Thiophene-containing fused aromatic compounds are 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 widely studied, for instance 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). Furthermore, **BDT** is a key intermediate for the synthesis of inherently chiral helical systems such as tetrathia[7]helicenes (4). Thus, **BDT** can be identified as a key starting molecule, which can allow access to more complex and interesting systems through a judicious functionalization of the α -positions of the thiophene rings. In our ongoing studies on the synthesis and functionalization of **BDT**s (5,6), we have developed a novel synthesis to prepare bis(benzo[1,2-*b*:4,3-*b'*]dithiophene) systems **2**, starting from bromides **1** (**Figure 1**).

**Figure 1**

Compounds **2** belong to an interesting class of chiral atropisomeric heterobiaryl derivatives with C_2 -symmetry, which can be selectively functionalized into bromides **3**. The chiroptical properties of both systems **2** and **3** have been fully elucidated by experimental and theoretical studies. On the other hand, enantiopure bromides **3** represent useful intermediates for the enantioselective synthesis of the corresponding tetrathiahelicene derivatives.

References: 1. Rieger, R.; Beckmann, D.; Mavrinskiy, A.; Kastler, M.; Müllen, K. *Chem. Mater.* **2010**, *22*, 5314. 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.; Doulcet, J.; Stephenson, G. R.; Licandro, E. *New J. Chem.* **2014**, *38*, 2241. 6. Stephenson, G. R.; Cauteruccio, S.; Doulcet, J. *Synlett* **2014**, 701.