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 \(\pi\)-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 \(\pi\)-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 \(\alpha\)-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).

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.