

## Synthesis of benzodithiophene systems by a ligand-free Suzuki-Miyaura coupling reaction in Deep Eutectic Solvents

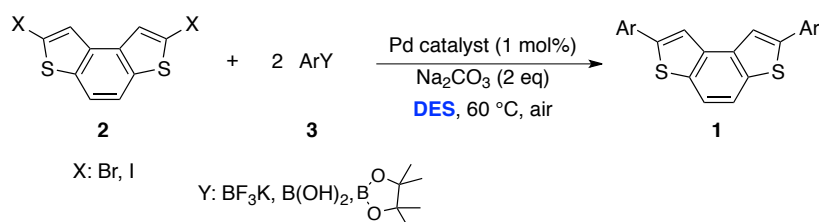
Valentina Pelliccioli<sup>a</sup> Silvia Cauteruccio,<sup>a,\*</sup> Giuseppe Dilauro,<sup>b</sup> Filippo Perna,<sup>b</sup> Vito Capriati,<sup>b</sup> Emanuela Licandro<sup>a,\*</sup>

<sup>a</sup> *Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19 I-20133, Milan, Italy*

<sup>b</sup> *Dipartimento di Farmacia–Scienze del Farmaco, Università degli Studi di Bari “Aldo Moro”, Consorzio C.I.N.M.P.I.S., I-70125, Bari, Italy*

valentina.pelliccioli@unimi.it

Benzo[1,2-b:4,3-b']dithiophene (**BDT**) and its derivatives belong to an interesting class of thiophene-based aromatic  $\pi$ -conjugated compounds that are widely studied as functional organic materials inserted, for instance, as units in mono and polydisperse oligomers, or as  $\pi$ -spacers in push-pull organic chromophores for photovoltaic applications<sup>1</sup>. Moreover, **BDTs** are key intermediates for the synthesis of inherent chiral tetrathia[7]helicenes, which are an attractive class of heterohelicenes with unique physicochemical and chiroptical properties due to their helix-like structure<sup>2</sup>. Thus, **BDT** is a key starting molecule which can allow access to more complex and interesting systems through a selective and judicious functionalization of the  $\alpha$  and  $\beta$ -positions of the terminal thiophene rings. Building on our recent studies on the synthesis and functionalization of **BDTs**<sup>3</sup>, we questioned whether a novel class of 2,7-diarylsubstituted **BDTs** **1** (**Figure 1**) could be synthesized via a palladium-catalysed Suzuki-Miyaura reaction between heteroaryl halides **2** and organoboron derivatives **3** in *Deep Eutectic Solvents* (**DESs**), which have proven to be effective as sustainable and environmentally responsible reaction media in several transition-metal-catalyzed reactions<sup>4</sup>.



**Figure 1.** General scheme for the synthesis of 2,7-diarylsubstituted **BDTs** **1**

In this communication, we report our preliminary results on the preparation of diarylsubstituted **BDTs** **1**, and discuss the substrate scope of the proposed protocol. Some of the compounds so far obtained display interesting photophysical properties, which are currently under investigation.

### References

1. Bossi, A.; Maiorana, S.; Baldoli, C.; Licandro, E. *et al. Eur. J. Org. Chem.*, **2013**, 84.
2. Licandro, E.; Cauteruccio, S.; Dova, D. *Adv. Het. Chem.*, **2016**, 118, 1.
3. Cauteruccio, S.; Dova, D.; Licandro, E. *New J. Chem.*, **2014**, 38, 2241.
4. Capriati, V. *et al. Chem. Commun.*, **2018**, 54, 8100; Capriati, V. *et al. ChemSusChem*, **2018**, 11, 3495.