EFFICIENT METAL-FREE ARYLATION OF [2.2]PARACYCLOPHANES MEDIATED BY A SULFINYL GROUP

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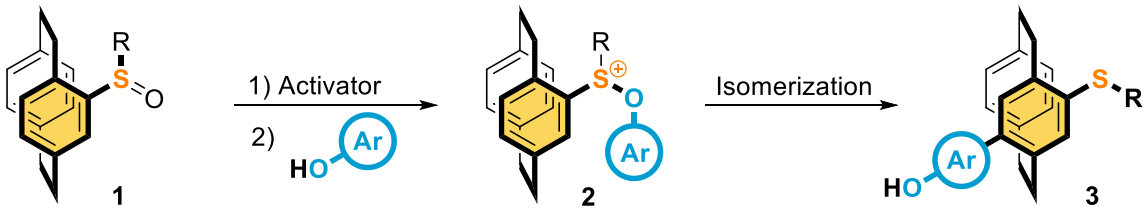
[2.2]paracyclophane ([2.2]PCP) is an original 3D carbon architecture consisting in two benzene rings opposite to each other and covalently linked at the *para* positions by CH_2–CH_2 groups.[1] [2.2]PCP derivatives are characterized by a high rigidity, strong π-π interactions and planar chirality (a single substituent is enough to generate enantiomers). In the last few years, [2.2]PCP chemistry has progressed tremendously, in terms of functionalization and applications (bio- and materials science). However, examples of sulfur-containing building blocks remain scarce.[2]

We aim to present in this communication a novel, metal-free strategy providing a highly regioselective functionalization of planar chiral sulfur-based [2.2]paracyclophanes. Our approach uses readily accessible [2.2]PCP sulfoxides **1**[3] and phenols as starting materials. Under the conditions of an interrupted Pummerer reaction, an intermediate aryloxy sulfonium salt **2** is formed, which then undergoes isomerization to generate the [2.2]PCP sulfide **3**, through the creation of a [2.2]PCP–aryl bond. This presentation will cover the optimization of reaction conditions and the exploration of the scope and limitations of the methodology. A reaction mechanism, supported by DFT calculations, will also be presented.[4]



Reference(s)

[1](a) Wu, S.; Felder, S.; Brom, J.; Pointillart, F.; Maury, O.; Micouin, L.; Benedetti, E. *Adv. Optical Mater.* **2024**, *12*, 2400934. (b) Hassan, Z.; Spuling, E.; Knoll, D. M.; S. Bräse, *Angew. Chem. Int. Ed.* **2020**, *59*, 2156–2170. (c) Weiland, K. J.; Gallego, A.; M. Mayor, *Eur. J. Org. Chem*. **2019**, *20*, 3073–3085.

[2] See for example: (a) Enders, M.; Friedmann, C. J.; Plessow, P. N.; Bihlmeier, A.; Nieger, M.; Klopper, W.; Bräse, S. *Chem. Commun.* **2015**, *51*, 4793–4795. (b) Rowlands, G.; Seacome, R. J. *Org. Biomol. Chem*. **2005**, *3*, 3873–3876.

[3] Lohier, J.-F.; Foucoin, F.; Jaffrès, P.-A.; Garcia, J. I.; Sopková−de Oliveira Santos, J.; Perrio, S.; Metzner, P. *Org. Lett.* **2008**, *10*, 1271–1274.

[4] For literature precedents of this type of approach: (a) Yanagi,T.; Yorimitsu, H. *Chem. Eur. J.* **2021**, *27*, 13450–13456. (b) Bisht, R.; Popescu, M. V.; He, Z.; Ibrahim, A. M.; Crisenza, G. E. M.; Paton, R. S.; Procter, D. J. *Angew. Chem. Int. Ed.* **2023**, e202302418.