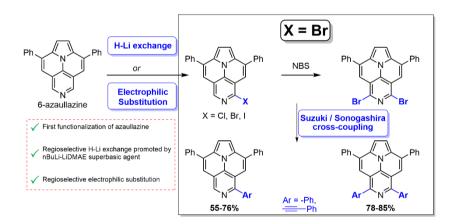
## Regioselective Functionalization of 6-Azaullazine by H-Li exchange and Electrophilic Substitution

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Ullazine synthesis has been reported for the first time in 1983 by Balli and Zeller. [1] That planar nitrogen-containing polycyclic aromatic hydrocarbon (PAH), isoelectronic to pyrene, has been the basis of many studies related to dye-sensitized solar cells and organic field-effect transistors (OFET). More recently, the synthesis of 6-azaullazine has been reported concomitantly by Langer *et al.* and our group. <sup>[2,3]</sup> In comparison with parent ullazine, the presence of an additional nitrogen atom at a peripheral position gives the opportunity to set up regioselective functionalization to enable rational tuning of the optoelectronic properties. In that context, we developed regioselective H-Li exchange and electrophilic substitutions allowing to introduce valuable halogen atoms at the alpha position of the peripheral nitrogen, the latter being subsequently engaged in Suzuki or Sonogashira arylation through efficient Pd-based cross-coupling reactions. <sup>[4]</sup>



## References:

[1] H. Balli, M. Zeller *Helv. Chim. Acta* **1983**, *66*, 2135–2139, [10.1002/hlca.19830660724]. [2] S. Boldt, S. Parpart, A. Villinger, P. Ehlers, P. Langer, *Angew. Chem. Int. Ed.* **2017**, *56*, 4575–4578. [10.1002/anie.201701347]. [3] P. Pierrat, S. Hesse, C. Cebrián, P. C. Gros, *Org. Biomol. Chem.* **2017**, *15*, 8568–8575, [10.1039/C7OB02149F]. [4] D. Ibrahim, P. Boulet, P. C. Gros, P. Pierrat *Eur. J. Org. Chem.* **2021**, *22*, 3331-3339, [10.1002/ejoc.202100333].

