

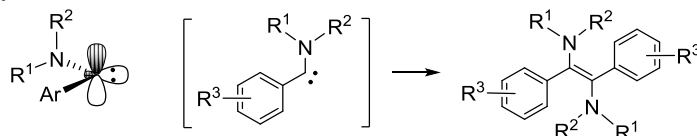
# STABLE AND REACTIVE HALOGEN STABILIZED ACYCLIC AMINO(ARYL)CARBENES



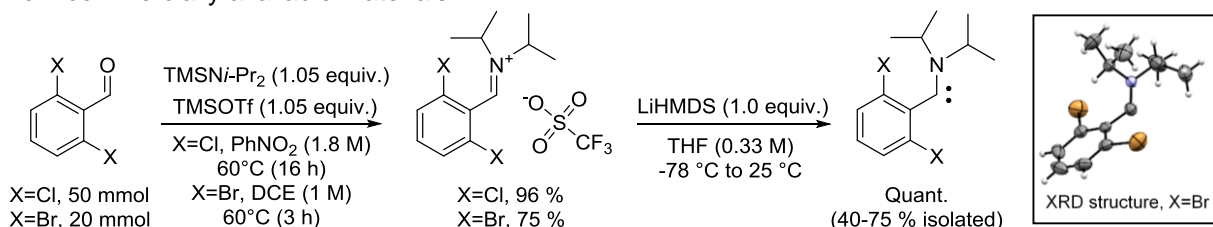
**Damien Magis**,<sup>1</sup> **Karinne Miqueu**,<sup>3</sup> **Jean-Marc Sotiropoulos**,<sup>3</sup> **Joan Vignolle**,<sup>2</sup> **Daniel Taton**<sup>2</sup> & **Yannick Landais**<sup>1</sup>

<sup>1</sup> Université de Bordeaux, ISM, UMR 5255, 33400 Talence, France. <sup>2</sup> Laboratoire de Chimie des Polymères Organiques, INP-ENSCP, Pessac Cedex, France. <sup>3</sup> Université de Pau & Pays de l'Adour, IPREM UMR 5254, Hélioparc, Pau cedex 09, France.

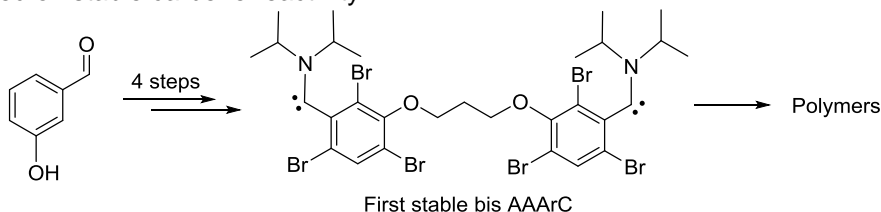
Acyclic amino(aryl)carbenes (AAArC) have been discovered in 2001.<sup>1</sup> They are singlet carbenes bearing a spectator aryl group. These carbenes have been underexplored due to their high reactivity and a strong tendency to dimerize.<sup>2,3</sup>



The selective dimerization of mono- and bis-AAArC has been exploited to access diaminoalkenes and amino-containing poly(p-phenylene vinylene)s.<sup>4</sup> In the present study, we describe a new class of AArC stabilized by two halogens in *ortho* position relative to the carbene. The stability of these carbenes thus increases going from fluorine to bromine. The less stable difluorinated carbene dimerizes, while the other two are stable. The dibrominated carbene is currently the most stable AArC known. Yet, these stable AArC show high reactivity in insertion reactions (C-H, Si-H, B-H or B-allyl), cyclopropanation and display general nucleophilic reactivity. The synthesis of these carbenes has been optimized and opens an access to a broad range of carbene structures in only three steps from commercially available materials.



The various reactivities observed experimentally were rationalized through DFT calculations and supported with XRD structures. This methodology finally allowed the synthesis of the first stable bis-AAArC using the same halogen stabilizing effect. This paves the way to the synthesis of new organic polymers based on stable carbene reactivity.<sup>4</sup>



## References

- <sup>1</sup> (a) G. Bertrand *et al.*, *Science*, **2001**, 292, 1901-1903; (b) G. Bertrand *et al.*, *J. Org. Chem.*, **2003**, 68, 911-914; (c) G. Bertrand *et al.*, *J. Am. Chem. Soc.*, **2004**, 126, 1342-1343.
- <sup>2</sup> G. Bertrand *et al.*, *New J. Chem.*, **2011**, 35, 2037-2042.
- <sup>3</sup> H. V. Huynh *et al.*, *Organometallics*, **2021**, 40, 1699-1705.
- <sup>4</sup> D. Taton *et al.*, *Nat. Commun.*, **2021**, 12, 4093-4100.