

# IODANE-DIRECTED *ORTHO* C-H ALLYLATION AS GATEWAY TOWARDS ADDED VALUE CORES

Wei Wen Chen,<sup>a,b</sup> Sébastien Lethu<sup>c</sup>, Albert López de Moraga,<sup>a,b</sup> Ana B. Cuenca,<sup>b</sup>  
and Alexandr Shafir<sup>a</sup>

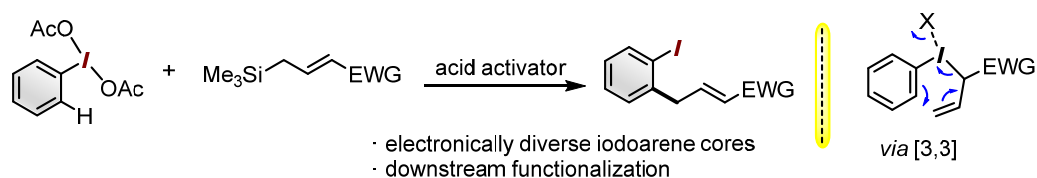
<sup>a</sup>IQAC-CSIC, c/Jordi Girona 20, 08034 Barcelona, Spain, weiqbl@cid.csic.es

<sup>b</sup>Institut Químic de Sarrià (IQS-URL), Via Augusta, 390, 08017 Barcelona, Spain

<sup>c</sup>ICIQ, Barcelona Institute of Science and Technology, 43007 Tarragona, Spain

Haloarenes represent a key class of organic reagents, mainly due to their potential as aryl-transfer agents. Also, the heavier iodo- and bromo derivatives proved to be interesting candidates as recognition elements in drug design. A renewed demand for diverse functionalized haloarenes has spurred the development of new synthetic methods to access this class of cores, including innovative metal-catalyzed *ortho* C-H halogenation. As a complementary strategy, a number of groups, including ours, have focused on the ability of the hypervalent organoiodine Ar-I(OAc)<sub>2</sub> to undergo iodane-directed *ortho* C-H functionalization [1,2] *via* iodonio-Claisen rearrangement, including the C-H allylation and propargylation reactions [3], albeit with the former limited to iodoarenes with electron-donating substituents [3].

In this context, we recently reported that the use of allylsilane bearing a 3-sulfone group allows to extend the allylation reaction to mildly electron-poor iodoarene cores [4]. We now show that this reactivity enhancement applies to a broader range of EWG-substituted allylsilanes, enabling expedient generation of a variety of *ortho*-allylated iodoarenes [5]. In addition, we describe the routes to access the requisite allylsilanes, and illustrate the synthetic potential of the newly formed allylated iodoarenes.



[1] a) M. Ochiai, T. Ito, Y. Takaoka, Y. Masaki, *J. Am. Chem. Soc.* **1991**, *113*, 1319-1323

[2] For a recent mini-review, see: A. Shafir, *Tetrahedron Lett.* **2016**, *57*, 2673–2682.

[3] For recent reports, see: a) H. R. Khatri, J. Zhu, *Chem. Eur. J.* **2012**, *18*, 12232–12236; b) S. Izquierdo, S. Bouvet, Y. Wu, S. Molina, A. Shafir, *Chem. Eur. J.* **2018**, *24*, 15517-15521.

[4] Y. Wu, S. Bouvet, S. Izquierdo, A. Shafir, *Angew. Chem. Int. Ed.* **2019**, *58*, 2617-2621.

[5] Manuscript in preparation.