
Doctoral position – Autumn 2018

“Chiral Iodanes for Asymmetric Carbon–Carbon Bond Construction”

Laboratory: Institut des Sciences Moléculaires (ISM), CNRS–UMR 5255,
Building A12, 351 cours de la Libération, 33405 Talence Cedex, France.

Research team: SASN team (www.squideau-lab.fr) in the ORGA group.

Funding: Agence Nationale de la Recherche (ANR – IODOCHEM project) for 36 months.

Application (CV + cover letter + Master degree marks + 2 recommendation letters) has to be sent before September 7th, 2018 to Prof. Laurent Pouységu laurent.pouysegu@u-bordeaux.fr
Prof. Stéphane Quideau stephane.quideau@u-bordeaux.fr

Student profile: With a Master degree (or equivalent) in Organic Chemistry, he/she is expected to possess good experimental skills in organic synthesis and in chromatography purification techniques, as well as good knowledge in characterization techniques, such as NMR and mass spectrometry. An experience in asymmetric synthesis and chiral HPLC techniques will be appreciated.

Context and aims of the study: Hypervalent organoiodine compounds, also referred to as iodanes, are increasingly used in organic synthesis not only for their useful oxidizing properties and their capacity to replace toxic heavy metal-based (*e.g.*, thallium, lead, mercury, as well as chromium) reagents in oxygenative reactions, but also for the similarities that exist with transition metal chemistry.^[1] Over the last decade, our research team has been developing new chiral iodanes and has been investigating their applications in metal-free asymmetric reactions. In the continuation of our excellent results reported for oxygenative transformations,^[2] we are now interested in chiral iodanes bearing transferable carbon-based ligands for the asymmetric construction, ideally catalytic, of carbon–carbon (C–C) bonds. Following our most recent results on the asymmetric alkynylation of β -ketoesters and naphthols,^[3] the work of the doctoral student will aim at *i*) the synthesis of new chiral iodoarenes and iodanes on which diverse carbon-based ligands will be installed, *ii*) the evaluation of the capacity of these new iodanes to transfer these carbon-based ligands in a stereoselective manner in (organoiodo-catalyzed) transformations, such as trifluoromethylation, arylation, allylation or vinylation reactions, *iii*) the implementation of the best iodoarene/iodane systems in the synthesis of natural products.

References

- [1] a) *Hypervalent iodine chemistry*, in *Topics Curr. Chem.*, Vol. 373 (Ed.: T. Wirth), Springer, Switzerland, **2016**;
b) Yoshimura, A.; Zhdankin, V. V. “Advances in synthetic applications of hypervalent iodine compounds”. *Chem. Rev.* **2016**, *116*, 3328–3435.
- [2] a) Bosset, C.; Coffinier, R.; Peixoto, P. A.; El Assal, M.; Miqueu, K.; Sotiropoulos, J.-M.; Pouységu, L.; Quideau, S. “Asymmetric hydroxylative phenol dearomatization promoted by chiral binaphthyl and biphenyl iodanes”. *Angew. Chem. Int. Ed.* **2014**, *53*, 9860–9864; b) Coffinier, R.; El Assal, M.; Peixoto, P. A.; Bosset, C.; Miqueu, K.; Sotiropoulos, J.-M.; Pouységu, L.; Quideau, S. “Total synthesis of (–)-bacchopetiolone via an asymmetric hydroxylative phenol dearomatization/[4+2]-dimerization cascade promoted by a novel Salen-type chiral iodane”. *Org. Lett.* **2016**, *18*, 1120–1123; c) El Assal, M.; Peixoto, P. A.; Coffinier, R.; Garnier, T.; Deffieux, D.; Miqueu, K.; Sotiropoulos, J.-M.; Pouységu, L.; Quideau, S. “Synthesis of scyphostatin analogues through hypervalent iodine-mediated phenol dearomatization”. *J. Org. Chem.* **2017**, *82*, 11816–11828.
- [3] Companys, S.; Peixoto, P. A.; Bosset, C.; Chassaing, S.; Miqueu, K.; Sotiropoulos, J.-M.; Pouységu, L.; Quideau, S. “Asymmetric alkynylation of β -ketoesters and naphthols promoted by new chiral biphenyl iodanes”. *Chem. Eur. J.* **2017**, *23*, 13309–13313.