

**Title:** High-valent iodine intermediates for new synthetic strategies

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The field of hypervalent iodine has grown rapidly in the last two decades. Hypervalent iodine reagents are now common in a wide range of synthetic applications, both as reagents, and, recently, as organocatalysts. Organoiodine(III) and (V) species exhibit attractive reactivity features, oftentimes similar to those of transition metals. In addition, the hypervalent Ar-I(III) fragment is considered a super-nucleofuge, and thus opens the door to new types of substitution patterns. In this project, two applications of iodine(III) chemistry were studied: the formation of iodonium ylides, conceived in the context of positron emission tomography (PET), and a new application of the so-called “iodine-guided” C-H functionalization of arenes.

Recently, arylodonium ylides have been used as precursors in the  $^{18}\text{F}$ -radiofluorination of aromatic substrates for PET applications. The synthesis of such ylides usually begins with the oxidation of a suitable iodoarene. Herein, we explored an alternative access to arylodonium ylides that would allow to circumvent this oxidation step which can be challenging for richly functionalized substrates. Therefore, we sought a new reagent that would allow an oxidation-free access to iodonium ylides. The synthesis of the corresponding iodinated  $\beta$ -dicarbonyl species was successfully accomplished. However, its instability, coupled with the time demands of the second research line, have led to an adjournment of this project to a future moment.

The second part of the project was based on exploring a new oxidative C-H functionalization reaction of arenes using functionalized pentadienylsilanes. This process is inspired by a related highly efficient *ortho* C-H allylation recently developed in the host research group. Surprisingly, the change from an allylsilane to its vinylogous (i.e. pentadienyl) analogue led to the selectivity switch from *ortho* to a *para*-selective C-H functionalization. Our initial foray into this process is discussed, as well as a mechanistic hypothesis based on the group's recent precedent with the *para*-selective C-H benzylation. Based on DFT evidence, our current proposal involves a two-step [5,5]-type rearrangement proceeding via an unusual  $\pi$ -stacked intermediate.

**Keywords:** hypervalent iodine, radiofluorination, C-H functionalization, iodine-directed coupling.