

Research Topic for the ParisTech/CSC PhD Program

Field: Chemistry, Physical Chemistry and Chemical Engineering

Subfield: Chemistry

ParisTech School: LSO, Ecole Polytechnique

Title: New Routes to Organoboron Derivatives and to Functional Polymers

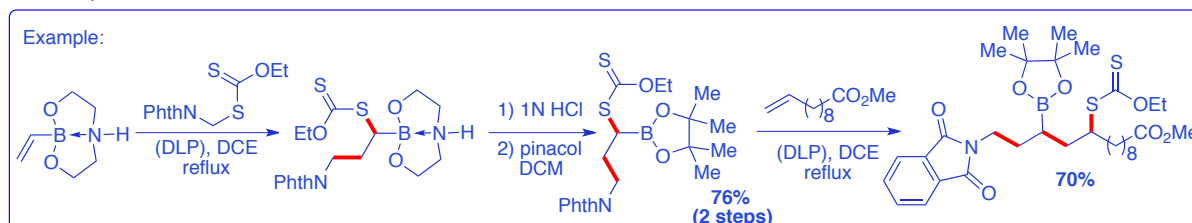
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Short description of possible research topics for a PhD:

The reversible transfer of dithiocarbonates (xanthates) is a uniquely powerful tool for the creation of carbon-carbon bonds. Xanthates reversibly store reactive radicals in a dormant form, thus significantly extending their lifetime while at the same time regulating their absolute and relative concentrations. This allows *intermolecular* radical additions even to unactivated alkenes (see example below). We propose to exploit the properties of xanthates to construct novel medicinally relevant boron heterocycles and study at the same time the little-known chemistry of α -boryl radicals. Organoboron compounds have recently acquired a dramatic importance in medicinal chemistry (e. g. Tavorole or Kerydin[®]; Bortezomib or Velcade[®]). This chemistry will also be applied to create a new family of boron containing polyamides that mimic natural hair in their ability to form disulfide bridges reversibly and to generate double and treble pronged self-healing polymeric hydrogels by modifying existing polymers. Practical applications include adhesives, hair care, surface treatment, modification of cellulose fibres, anticorrosion and anti-graffiti paints, heavy metal recovery, slow release of actives, etc.



Required background of the student: General Organic Chemistry

A list of representative publications of the group:

1. *A Highly Stereoselective, Modular Route to (E)-Vinylsulfones and to (Z)- and (E)-Alkenes.* Braun, M.-G.; Quiclet-Sire, B.; Zard, S. Z. *J. Am. Chem. Soc.* **2011**, *133*, 15954-15957.
2. *From a Remarkable Manifestation of Polar Effects in a Radical Fragmentation to the Convergent Synthesis of Highly Functionalized Ketones.* Debien, L.; Zard, S. Z. *J. Am. Chem. Soc.* **2013**, *135*, 3808-3811.
3. *Radical Instability in Aid of Efficiency. A Powerful Route to Highly Functional MIDA Boronates.* Quiclet-Sire, B.; Zard, S. Z. *J. Am. Chem. Soc.* **2015**, *137*, 6762-6765.
6. *A Radical Bidirectional Fragment Coupling Route to Unsymmetrical Ketones.* Anthore-Dalion, L.; Liu, Q.; Zard, S. Z. *J. Am. Chem. Soc.* **2016**, *138*, 8404-8407.
5. *The Xanthate Route to Ketones. When the Radical is Better than the Enolate.* Zard, S. Z. *Acc. Chem. Res.* **2018**, *51*, 1722-1733.