



PALLADIUM-CATALYZED FUNCTIONALIZATION OF 2-iodoiminoglycals AS VERSATILE SUBSTRATES TO ACCESS 1,2-UNSATURATED IMINOSUGARS WITH STRUCTURAL DIVERSITY AT C2 POSITION

Quentin Joachim,^{1,2,3} Delphine Carry,¹ Mattéo di Pasquale,^{2,3} Jérôme Marrot,⁴ Jacques Uziel,^{2,3} Atsushi Kato,⁵ Nadège Lubin-Germain,^{2,3} Jérôme Désiré,¹ Yves Blériot¹ and Angélique Ferry^{2,3,6}

¹ Université de Poitiers, Organic Synthesis Team, IC2MP, UMR CNRS 7285, 86073 Poitiers Cedex 9, France.

² Université Paris-Saclay, BioCIS, UMR CNRS 8076, 91400 Orsay, France.

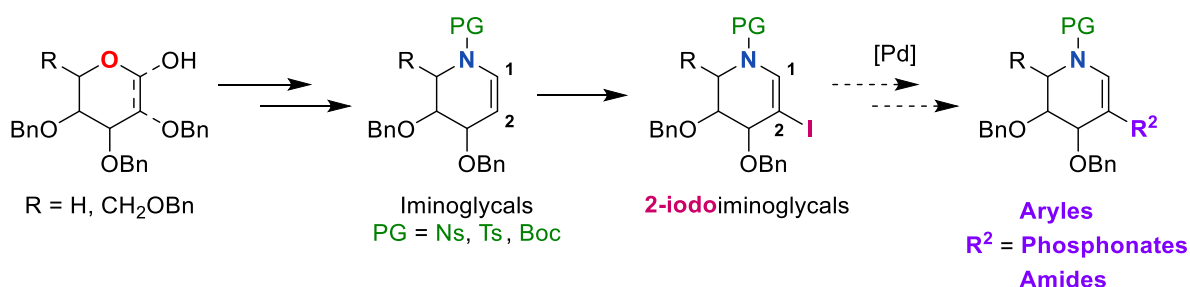
³ CY Cergy-Paris Université, BioCIS, CNRS, 95000 Cergy-Pontoise Cedex, France.

⁴ Université de Versailles, Institut Lavoisier de Versailles, UMR CNRS 8180, 78035 Versailles Cedex, France.

⁵ University of Toyama, Department of Hospital Pharmacy, 930-0194 Toyama, Japan.

⁶ Institut Universitaire de France (IUF).

Iminoglycals¹ are limited in literature, even if they have been used in Ferrier rearrangement,² and scarcely in Heck and Stille reactions.³ Although the synthetic potential of the enamide moiety in these iminosugar derivatives is underexplored, cyclic enamides have emerged as a powerful functional group that has been involved in a variety of new synthetic transformations, providing key intermediates for the synthesis of natural products and/or bioactive molecules.⁴ The π -donating ability of the nitrogen atom renders enamides more electron-rich than simple alkenes and they afford a means of activating carbon-carbon double bonds, giving them both nucleophilic and electrophilic properties. Importantly, the electronic bias can be controlled by adjusting the nitrogen-protecting group, suggesting sugar-derived enamides as a powerful platform to access iminosugars and analogs with unprecedented structural diversity. The direct and selective functionalization of iminoglycals being an attractive challenge, we will present the synthesis of a range of iminoglycals and 2-iodoiminoglycals, with different protecting groups on the nitrogen and their use in metal-catalyzed cross-coupling reactions.



Références:

¹ a) Désiré, J.; Dransfield, P. J.; Gore, P. M.; Shipman, M. *Synlett*. **2001**, 2001, 1329; b) Désiré, J.; Shipman, M. *Synlett*. **2001**, 2001, 1332.

² Di Bussola, V.; Fiasella, A.; Romano, M. R.; Favero, L.; Pineschi, M.; Crotti, P. *Org. Lett.* **2007**, 9, 4479.

³ a) Dransfield, P. J.; Gore, P. M.; Prokes, I.; Shipman, M.; Slawin, A. M. Z. *Org. Biomol. Chem.* **2003**, 1, 2723; b) Oliveira, D. F.; Severino, E. A.; Correia, C. R. D. *Tetrahedron Lett.* **1999**, 40, 2083; c) Häberli, A.; Leumann, C. J. *Org. Lett.* **2001**, 3, 489.

⁴ a) Beltran, F.; Miesch, L. *Synthesis* **2020**, 52, 2497; b) Gigant, N.; Chausset-Boissarie, L.; Gillaizeau, I. *Chem. Eur. J.* **2014**, 20, 7548.