AN ANION-DIRECTED APPROACH TO ENANTIOENRICHED α-TRIARYL AMINES

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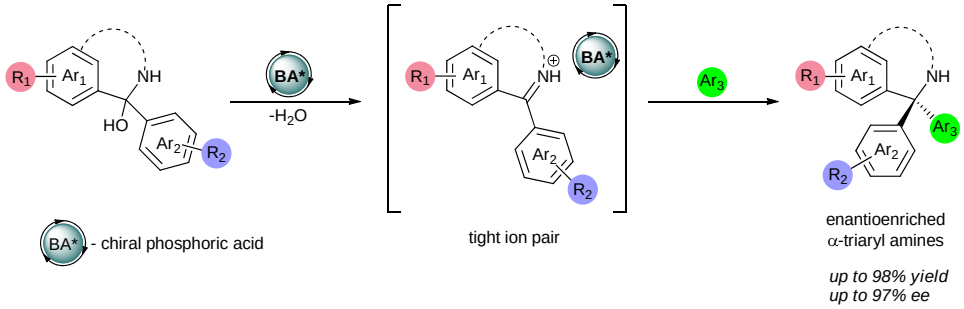
Chiral α-quaternary amines are important building blocks of naturally occuring and artificial biologically active molecules. Hence, much research has been directed towards the development of asymmetric protocols for their preparation. Although there are catalytic amination reactions to access these chiral building blocks, synthetically more efficient strategy is the catalytic asymmetric addition of carbon nucleophiles to ketones and ketimines, since it can simultaneously construct a carbon skeleton and a quaternary stereogenic center. In this regard, a well-developed methodology is a transition-metal-catalyzed asymmetric addition of organoboron reagents to ketimines, though only a handful of protocols report the generation of chiral α-triaryl amines [1]. On the other hand, asymmetric organocatalytic variants for the preparation of these valuable motifs are virtually non-existent.

We developed asymmetric counteranion-directed arylations of diaryl-ketimines to afford enantioenriched α-triaryl amines. These processes use chiral Brønsted acids to control enantioselectivities in the addition reactions of heteroaryls [2] and aryls [3] to *N*-Acyl diaryl-ketiminium species, generated *in situ* from *N*-hydroxymethyl amides.



[1] a) Nishimura, T.; Noishiki, A.; Tsui, G. C.; Hayashi, T. *J. Am. Chem. Soc.* **2012**, *134*, 5056–5059. b) Nishimura, T.; Noishiki, A.; Ebe, Y.; Hayashi, T. *Angew. Chem. Int. Ed.* **2013**, *52*, 1777–1780. c) Álvarez-Casao, Y.; Monge, D.; Álvarez, E.; Fernández, R.; Lassaletta, J. M. *Org. Lett.* **2015**, *17*, 5104–5107.

[2] Glavač, D.; Zheng, C.; Dokli, I.; You, S.-L.; Gredičak, M. *J. Org. Chem.* **2017**, *82*, 8752–8760.

[3] Glavač, D.; Gredičak, M. *manuscript submitted*