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Regio-and stereoselective chlorocyanation of alkynes

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Substituted acrylonitriles are highly valuable precursors for the synthesis of fine chemicals in the pharmaceutical and agrochemical industry. Recently our research group reported the syntheses of imidazolium thiocyanates and their reactivities as CN+ synthons were successfully evaluated. To extend the scope of this versatile reagent, a new methodology for the regio- and stereoselective chlorocyanation of internal and terminal alkynes is described. The selected substrates are treated with BCl3 in the presence of stoichiometric amounts of imidazolium thiocyanates, obtaining (Z)-3-chloroacrylo-nitriles as main products. These products could be further functionalized demonstrating the synthetic value of the method. Mechanistic studies indicate initial activation of the cationic thiocyanate by the Lewis acid, followed by electrophilic attack of the alkyne. The syn addition of a chloride moiety to the vinyl cation intermediate and final elimination of the thiourea unit, afford the desired chloroacrylonitriles.

Recent Publications

1. G. Talavera, J. Pena, M. Alcarazo, J. Am. Chem. Soc. 2015, 137 (27), 8704-8707.
2. A. G. Barrado, A. Zieliński, R. Goddard, M. Alcarazo, Angew. Chem. Int. Ed. 2017, 56, 13401-13405.

Biography

Alejandro García Barrado initially started getting involved with Chemistry and Laboratory Techniques in Universidad de Salamanca, Spain where he obtained his Chemistry Licenciatura Degree, and later moved to Germany for his Masters in Chemistry at the Max-Planck-Institut für Kohlenforschung in Mülheim and der Ruhr, focusing in the development of organocatalysts based on dicationic phosphonium salts. He is now finishing his PhD in Organic Chemistry at Georg-August-Universität Göttingen on electrophilic cyanation of alkynes.

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