

7th World Congress on Chemistry

November 13-15, 2017 Athens, Greece

Xi-Yang Cui et al., J Biotech and Phyto 2017

Copper-guanidine catalyzed asymmetric allylic alkynylation under phase transfer conditions

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Forging a more intense link between transition metal catalysis and asymmetric ion-pairing catalysis are recently purchased by us. Enantiopure skipped 1, 4-enynes are useful building blocks due to its transformability. In this work, enantioselective alkynylation of cyclic allylic bromides was achieved due to an in situ-generated guanidinium cuprate ion pair. Thus, enantiopure cyclic 1,4-enynes were obtained by the first time through a proposed distinct dynamic kinetic pathway, not common SN2' pathway. In the presence of catalytic amount of copper(I) salt and cyclic-guanidinium(CG), the asymmetric Csp–Csp3 bonds were formed via alkynylation of racemic cyclic bromides with aid of K₂CO₃ as a base at room temperature. Various terminal alkynes with different substituents on an aryl group and different functional groups such as ester, amide, silyl, amine, hydroxyl, and thioether are all suitable under the standard reaction condition. The enantiospecific derivatization of products demonstrated the practicability of this methodology. The mechanism study revealed that alkynide in this Cu-catalyzed reaction behaves as 'hard' nucleophile; a model ion-pairing catalysis which was characterized by X-ray analysis and 1H-NMR and; meanwhile, in situ CSI-MS and 1H-NMR spectra recognized several guanidinium cuprates ion-pairs and copper-alkynide complex which is a complementary to the current Cu-catalyzed asymmetric allylic alkylation mechanistic study.

Biography

Xi-Yang Cui is working as a assistant professor at Nanyang Technological University at Singapore .He belongs to chemistry department

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