CARBOCYANATION REACTION OF UNSATURATED BONDS

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Cleavage of C–C σ bonds followed by insertion of unsaturated bonds would allow an ultimate transformation involving simultaneous formation of two C–C bonds without any byproduct formation. While successful examples of such reactions have relied totally on the activation of strained C–C σ bonds in small rings such as cyclopropanes and cyclobutanes, we have focused our attention on the activation of C–CN bonds of nitriles and achieved their addition reactions across unsaturated bonds, namely carbocyanation reaction. We have found that the nickel/Lewis acid catalysis significantly promotes the carbocyanation reactions of alkynes, allowing addition reactions of acetonitrile (Eq. 1). The gram-scale addition reaction of α-siloxyallyl cyanide across alkynes proceeds exclusively at the γ-position of the cyano group with excellent stereo- and regioselectivity to give a highly substituted acrylonitrile, which serves as a synthetic precursor of plaunotol (Scheme 1). The intramolecular carbocyanation of alkenes has also been achieved by the nickel/Lewis acid catalyst to allow an enantioselective construction of quaternary carbon stereocenter often found in pyrroloindoline alkaloids such as (−)-esermethole (Scheme 2).
Dr Yoshiaki Nakao (born in 1976) was educated in chemistry at Kyoto University (Ph. D. with Profs. Tamejiro Hiyama and Eiji Shirakawa), Yale University (visiting student with Prof. John F. Hartwig), and Max-Planck-Institut für Kohlenforschung (visiting scholar with Prof. Manfred T. Reetz). Since 2010, he has been a senior lecturer at Kyoto University. His research interest includes development of new synthetic reactions by metal catalysis for selective synthesis.
SULFOXIMINE: A REUSABLE DIRECTING GROUP FOR SP² & SP³ C-H OXIDATION

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Directing group assisted transitional-metal-catalyzed C–H bond functionalizations delivers carbon-carbon and carbon-heteroatom bonds with high level of regio-, chemo- and stereoselectivity. Recently, we have achieved highly selective regio- and chemoselective ortho-C–H acyloxylation of N-benzoylated sulfoximines. This methodology has the following unique features: 1) the robust sulfoximine directing group is easily attachable and detachable from the substrates with ease and most importantly it is reusable, 2) the catalytic condition is amenable for the gram scale preparation of the ortho-acyloxylation products, 3) stereointegrity of the chiral sulfoximine moiety is preserved in the reaction, 4) this directing group efficiently activates the relatively more challenging unactivated sp³ C–H bond with ease and yielded the corresponding acyloxylation products in moderate to good yields.

Acknowledgment: The author thanks the DST (SR/S1/OC-34/2009) and University of Hyderabad for financial support. M. Ramu Yadav and Raja K. Rit thank CSIR, INDIA for the research fellowship.
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