## List of nominee's 10 most significant publications

**1. Dattatraya H. Dethe\***, Rohan D. Erande, Alok Ranjan, Biomimetic total syntheses of flinderoles B and C. *J. Am. Chem. Soc.*, **2011**, *133*, 2864-2867.

A highly stereo- and regioselective formal [3 + 2] cycloaddition reaction between a tertiary alcohol and an olefin has been developed for use in the synthesis of pyrrolo[1,2-a] indoles. The potential of this methodology has been amply demonstrated in the first total synthesis of the isomeric flinderoles B and C, which involves 11 steps in the longest linear sequence and gave an overall yield of 17.2%. The strategy is fairly general and is amenable to the synthesis of other natural products of this class as well as their analogues.

**2. Dattatraya H. Dethe\***, G. Murhade. FeCl<sub>3</sub> Catalyzed Prins-Type Cyclization for the Synthesis of Highly Substituted Indenes: Application to the Total Synthesis of (±)-Jungianol and epi-Jungianol. *Org. Lett.*, **2013**, *15*, 429-431.

Syntheses of various highly substituted indenes were achieved using FeCl<sub>3</sub> catalyzed Prinstype cyclization, which was further applied in the total synthesis of natural product jungianol, (8.15% overall yield), and its epimer, (18.75% overall yield); in the process, known Hg(OAc)<sub>2</sub> mediated aromatization of carvone was exploited for the development of regioselective synthesis of highly substituted aromatic rings.

**3. Dattatraya H. Dethe,\*** Rohan D. Erande, and Balu D. Dherange. Remarkable Switch of Regioselectivity in Diels–Alder Reaction: Divergent Total Synthesis of Borreverine, Caulindoles, and Flinderoles. *Org. Lett.*, **2014**, *16*, 2764.

Switchable reaction patterns of dimerization of indole substituted butadienes via a Lewis acid and thermal activation are reported. While under acidic conditions dimerization occurred around the internal double bond of the dienophile, a complete switch of regioselectivity was observed under thermal conditions, where dimerization occurred around the terminal double bond of the dienophile. This switch of regioselectivity was further exploited for the divergent total synthesis of structurally diverse indole alkaloid natural products. The biomimetic divergent total syntheses of structurally diverse indole alkaloid natural products (caulindoles A–D, borreverine, flinderole A–C, and their analogues) have been achieved. We also discovered a switch of regioselectivity in the Diels–Alder reaction by fine-tuning the reaction conditions.

**4. Dattatraya H. Dethe,\*** Rohan D. Erande, S. Mahapatra, S. Das, B. VijayKumar. Protecting group free enantiospecific total syntheses of structurally diverse natural products of the tetrahydrocannabinoid family. *Chem. Commun.*, **2015**, 51, 2871-2873.

A simple, highly diastereoselective, Lewis acid catalyzed Friedel–Crafts coupling of a cyclic allylic alcohol with resorcinol derivatives has been developed. The method was applied for the enantiospecific total syntheses of structurally diverse natural products such as machaeriol-D,  $\Delta^8$ -THC,  $\Delta^9$ -THC, *epi*-perrottetinene and their analogues. Synthesis of both natural products and their enantiomers has been achieved with high atom economy, in a protecting group free manner and in less than 6 steps, the longest linear sequence, in a very good overall yield starting from R-(+) and S-(-)-limonene.

**5. Dattatraya H. Dethe\***, S. K. Sau, S. Mahapatra. Biomimetic Enantioselective Total Synthesis of (–)-Mycoleptodiscin A. *Org. Lett.*, **2016**, *18*, 6392-6395.

Biomimetic total synthesis of (-)-mycoleptodiscin A (1) was achieved starting from the enantiopure key intermediate, which was prepared by Friedel-Crafts reaction between 7-methoxyindole and chiral primary allylic alcohol. The crucial step in this synthesis was an intramolecular Friedel-Crafts reaction at C-4 of the indole derivative driven by the EDG/ EWG within a compound that was rationally designed to prevent the cyclization reaction at the C-2 positon of indole, thereby successfully providing the complete carbon framework of 1. This intramolecular Friedel-Crafts reaction at C-4 of indole derivative could be applied for the synthesis of other C-4-substituted indole alkaloid natural products.

**6. Dattatraya H. Dethe\***, S. Mahapatra, S. K. Sau. Enantioselective Total Synthesis and Assignment of the Absolute Configuration of the Meroterpenoid (+)-Taondiol. *Org. Lett.*, **2018**, *20*, 2766-2769.

The first enantioselective total synthesis of (+)-taondiol, a pentacyclic marine meroterpenoid, has been achieved, which in addition to confirming the structure also established the absolute configuration of the natural product. The notable points in the synthetic route are synthesis of a highly functionalized tricyclic diterpenoid moiety starting from an enantiopure Wieland–Miescher ketone derivative in concise manner via Robinson-type annulation and an elegant hydrogen atom transfer olefin reduction followed by Lewis acid-catalyzed Friedel–Crafts reaction for one-pot C–C and C–O bond formations resulting in construction of the pentacyclic meroterpenoid skeleton.

**7. Dattatraya H. Dethe\***, Balu D. Dherange, S. Das, Biomimetic Total Syntheses of Callistrilones A, B, and D. *Org. Lett.*, **2018**, *20*, 680-683.

A biomimetic total syntheses of antibacterial natural products ( $\pm$ )-callistrilones A, B, and D, the first triketone– phloroglucinol–monoterpene hybrids with an unprecedented [1]benzofuro[2,3-a]xanthene and [1]benzofuro[3,2-b]xanthene pentacyclic ring system along with the postulated biosynthetic intermediate, isolated from the leaves of Callistemon rigidus, were achieved. The total synthesis features highly regio- and diastereoselective catalytic Friedel–Crafts alkylation, palladium-catalyzed Wacker-type oxidative cyclization, Michael addition, and late-stage diastereoselective epoxide formation from the extremely hindered  $\beta$  face as key steps. This method is fairly general to the synthesis of other natural products of this class as well as their analogues.

**8. Dattatraya H. Dethe\***, S. K. Sau. Total Synthesis of (+)-Strongylophorines 2 and 9. *Org. Lett.*, **2019**, *21*, 3799-3803.

The first enantioselective total syntheses of strongylophorine-9 and strongylophorine-2 have been achieved in 27 and 29 steps, respectively, as the longest linear sequences, which in addition to confirming the structure of the molecule also established their absolute configurations. The notable points of the synthesis include application of the Robinson-type annulation for attaining the diterpene moiety in a concise manner from an enantiopure Wieland-Miescher ketone derivative and highly fascinating sp<sup>3</sup> C–H activation on axial methyl to install the lactone moiety. It is presumed that the overall synthetic sequence can provide a useful guide for the synthesis of the other congeners of the strongylophorine family and their analogues.

**9. Dattatraya H. Dethe\***, and C. B. Nagabhushana. Ruthenium-Catalyzed Direct Dehydrogenative Cross-Coupling of Allyl Alcohols and Acrylates: Application to Total Synthesis of Hydroxy β-Sanshool, ZP-Amide I, and Chondrillin. *Org. Lett.* **2020**, 22, 1618–1623.

Ru-catalyzed oxidative coupling of allyl alcohols and activated olefins has been developed by C(allyl)–H activation of allyl alcohols providing efficient and direct access to synthetically useful  $\alpha,\beta$ -unsaturated enone intermediates. Synthetic utility of this method was demonstrated by its application to synthesis of bioactive natural products such as Hydroxy- $\beta$ -sanshool, ZP-amide I, Chondrillin, Plakorin, and (+)-cis-Solamin A.

**10. Dattatraya H. Dethe\***, C. B. Nagabhushana, S. Das, A. K. Nirpal. Ruthenium-catalyzed formal sp<sup>3</sup> C-H activation of allylsilanes/esters with olefins and Ruthenium-Catalyzed Oxidative Cross-Coupling Reaction of Activated Olefins with Vinyl Boronates. *Chem. Sci.*, **2021**, *12*, 4367-4372.

Ru-catalysed oxidative coupling of allylsilanes and allyl esters with activated olefins has been developed via isomerization followed by C(allyl)–H activation providing efficient access to stereodefined 1,3-dienes in excellent yields. It is likely that this reaction occurs by the formation allyl ruthenium complex which is highly favorable due to the  $\alpha$ -silyl effect which stabilizes the carbanion forming *in situ* in the reaction. Next, the regioselective C–H insertion of vinyl silanes could be controlled by stabilization of the carbon– metal (C–M) bond in the  $\alpha$ -position to silicon. Mild reaction conditions, less expensive catalysts, and excellent regio- and diastereoselectivity ensure universality of the reaction. In addition, the unique power of this reaction was illustrated by performing the Diels–Alder reaction and enantioselective synthesis of highly functionalized cyclohexenone and piperidine and finally synthetic utility was further demonstrated by the efficient synthesis of norpyrenophorin, an antifungal agent.