Young Career Focus: Dr. Sandip Murarka (Indian Institute of Technology Jodhpur, India)

Background and Purpose. SYNFORM regularly meets young up-and-coming researchers who are performing exceptionally well in the arena of organic chemistry and related fields of research, in order to introduce them to the readership. This Young Career Focus presents Dr. Sandip Murarka (Indian Institute of Technology Jodhpur, India).

Interview

SYNFORM What is the focus of your current research activity?

Dr. S. Murarka The motivation of our research in organic synthesis and catalysis comes from the tremendous societal impact it holds on today’s global problems of health, food, energy, and the environment. We are primarily focused on unraveling new activation modes of unsaturated π-bonds and unreactive C–H bonds, enabling us to forge chemical bonds in an unprecedented fashion. We utilize a chemical tool-box consisting of transition-metal catalysis, photocatalysis and radical chemistry to synthesize interesting molecular architectures, and perform late-stage functionalizations. All this is expected to facilitate drug discovery, materials science and agrochemical research.

SYNFORM When did you get interested in synthesis?

Dr. S. Murarka My initial interest in organic synthesis grew during my high school days. I was fascinated by the concept of chemical reactions and making new molecules. Organic chemistry seemed most exciting, logical and natural to me as I was able to understand the bond-breaking and bond-making phenomena. I must acknowledge the role of my chemistry instructor in igniting my interest in organic synthesis. I took no time to decide that I should pursue my undergraduate education in chemistry. Although I was studying different branches of chemistry along with mathematics and physics, I took a deep interest in organic chemistry and finally decided to pursue an M.Sc. with a major in organic chemistry. The courses in organic chemistry and the laboratory project on the synthesis and application of Morita–Baylis–Hillman (MBH) adducts during my M.Sc. further excited me, to the point where I decided to pursue doctoral research in organic and organo-metallic chemistry with Prof. Armido Studer at the Universi-
ty of Münster (Germany). Following my PhD, I did post-doc research with Prof. Herbert Waldmann at Max-Planck Dortmund (Germany), where I was involved in a highly interdisciplinary and collaborative research program focusing on the development of novel chemotypes to suppress oncogenic RAS signaling for the treatment of cancer. My PhD and post-doc research made me realize the potential of organic synthesis, which is not limited to making molecules, but has widespread utility in allied field of sciences.

**SYNFORM** What do you think about the modern role and prospects of organic synthesis?

**Dr. S. Murarka** In principle, organic synthesis is about making novel and interesting molecules through an innovative disconnection approach. Hence, development of efficient, green and sustainable synthetic methods will remain as the most sought-after area of research. The molecules that are being made by organic chemists have huge implications in the discovery and manufacturing of products that we encounter in our day-to-day lives, like medicines, materials, energy storage, agrochemicals, perfumes, polymers, food, etc. Accordingly, the true potential of organic chemistry will be unfolded through endorsing interdisciplinary research and blurring cross-disciplinary boundaries. Discoveries and advances in research and development are more likely to happen at the borders between multiple scientific fields, which necessitates reinventing ourselves and engaging with researchers across the disciplines and sectors.

**SYNFORM** Could you tell us more about your group’s areas of research and your aims?

**Dr. S. Murarka** I started my independent career with a vision to develop a research program on cascade/domino/tandem annulations and direct C–H functionalizations utilizing base metal-catalyzed cross-couplings and photocatalysis as sustainable chemical tools (Figure 1). Cascade annulations allow rapid increment of molecular complexity leading to the synthesis of interesting molecular frameworks in an efficient fashion, and direct C–H functionalizations enable late-stage diversification of molecular scaffolds. In both these cases, our primary focus lies in the synthesis and late-stage functionalization of bioactive molecules, therapeutics and agrochemicals. On a mechanistic level, we are interested in the generation and study of reactive organic intermediates (car-

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**Figure 1** Ongoing research program
bocations, radicals, and carbenes) and electron-transfer processes in organic molecules through unique approaches. Since we aim to develop sustainable synthetic methods that work under amenable conditions, we utilized the synthetic potential of photoredox catalysis to generate structurally and electronically diverse alkyl radicals from N-(acyloxy)phthalimides (NHPI esters) under mild conditions and trigger those to forge a variety of carbon–carbon bonds through cascade annihilations, leading to a plethora of highly substituted heterocyclic architectures. NHPI esters have emerged as a surrogate of alkyl halides and can easily be synthesized from carboxylic acid feedstock. They are predisposed to participate in single electron transfer (SET) processes, ultimately leading to the generation of alkyl radicals through reductive fragmentation and concomitant decarboxylation. We wrote the first concise (Adv. Synth. Catal. 2018, 360, 1735; Chem. Asian J. 2021, 16, 879) and comprehensive (ACS Catal. 2021, 11, 1640) reviews on the diverse reactivity of NHPI esters and successfully synthesized alkylated chroman-4-ones (Chem. Asian J. 2020, 15, 568), not so easily accessible Z-alkoxy-alkylidene succinimides (Org. Chem. Front. 2021, 8, 2256), and alkylated indoles (Chem. Commun. 2021, 57, 13130) through innovative radical cascade annihilations involving NHPI esters under photoredox catalyzed conditions. Lately, we have also become interested in the chemistry of diaryl iodonium reagents (DIARs) due to their ready availability, bench stability and low cost. We have successfully utilized DIARs as aryl cation equivalents under metal-free conditions to synthesize S-aryl dithiocarbamates (Org. Lett. 2021, 23, 6401), and as aryl radical synthons under photoredox conditions to perform late-stage functionalization of quinoxalinones (J. Org. Chem. 2022, 87, 10947). Currently, we are engaged in unraveling further applications of NHPI esters and DIARs in a diverse range of (non)photoinduced processes leading to the construction and functionalization of densely functionalized molecular frameworks.

**SYNFORM** What is your most important scientific achievement to date and why?

**Dr. S. Murarka** At this early stage of my independent career, I feel that the ‘most awaited important scientific achievement’ is yet to arrive. Currently, I believe that the most impactful aspect of our research is about the approach we have adopted, which is basically about the development of sustainable methods with mechanistic rationale, and the synthesis of molecules of medicinal importance. In this way, we are able to amalgamate the fundamental understanding of a chemical transformation with potential applications. However, if I am pressed to pick one from my early career, that would be the development of a metal-free multi-component annulation between diaryliodonium salts, aliphatic amines, and carbon disulfide enabling access to S-aryl dithiocarbamates (Org. Lett. 2021, 23, 6401). This methodology is scalable, exhibits broad scope, and most importantly, allows access to some of hitherto inaccessible dithiocarbamates (Figure 2). Gratifyingly, one of the S-aryl dithiocarbamates exhibited antiproliferative activity in cancer cells and affected tubulin dynamics by inducing microtubule bundling, which makes this class of compounds a promising scaffold for designing new anticancer drugs (Bioorg. Med. Chem. 2022, 68, 116874).

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