

Young Career Focus: Dr. Akkattu T. Biju (CSIR-National Chemical Laboratory, Pune, India)

Background and Purpose. From time to time SYNFORM 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. Akkattu T. Biju (CSIR-National Chemical Laboratory, Pune, India).

Biographical Sketch



Dr. A. T. Biju

Akkattu T. Biju was born and raised in Cochin, Kerala (India). He received his B.Sc. and M.Sc. degrees from Mahatma Gandhi University, Kerala (India) and his Ph.D. under the guidance of Dr. Vijay Nair at the CSIR-NIIST, Trivandrum (India). Subsequently, he has been a postdoctoral fellow with Professor Tien-Yau Luh at the National Taiwan University, Taipei (Taiwan) and an Alexander von Humboldt fellow with Professor Frank Glorius at the Westfälische Wilhelms-Universität Münster (Germany). In June 2011, he began his independent research career at the CSIR-National Chemical Laboratory, Pune (India). His research focuses on the development of transition-metal-free carbon–carbon and carbon–heteroatom bond-forming reactions using aryne chemistry and N-heterocyclic carbene (NHC) organocatalysis, and their application in organic synthesis. He is the recipient of the CRSI Young Scientist Award (2015), NCL-Research Foundation Scientist of the Year Award (2014), ISCB Young Scientist Award (2014), Thieme Chemistry Journals Award (2014), OPPI Young Scientist Award (2012), Alexander von Humboldt Fellowship (2009), and is a member of the National Academy of Sciences, India (NASI), Allahabad (2012).

INTERVIEW

SYNFORM *What is the focus of your current research activity?*

Dr. A. T. Biju Our present research focuses on the development of transition-metal-free carbon–carbon and carbon–heteroatom bond-forming reactions, and their implementation in organic synthesis. Specifically, we employ aryne chemistry for the rapid synthesis of various 1,2-disubstituted arenes. We also use N-heterocyclic carbene (NHC) based organocatalysis for the enantioselective construction of heterocycles and carbocycles. In addition to the synthesis of benzo-fused compounds and chiral heterocycles, evaluation of the biological activity of these molecules forms part of our research.

SYNFORM *When did you get interested in synthesis?*

Dr. A. T. Biju I have been very fortunate to be taught by talented chemistry teachers throughout my studies. During my college days, I was fascinated by the remarkable properties of carbon, and the concepts of isomerism and catenation. This interest in organic chemistry persisted through all my studies and was transformed to synthetic chemistry during my Ph.D. studies, where I was introduced to the enchanting world of organic synthesis. All my mentors (Dr. V. Nair, Professor T.-Y. Luh and Professor F. Glorius) have had a tremendous influence on my academic development over the years, and they very much inspired me to pursue a career in synthetic organic chemistry.

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

Dr. A. T. Biju Over the years, organic synthesis has played a pivotal role in human wellbeing. The recent developments in synthetic chemistry include the invention of mild and effi-

cient concepts for C–H bond activation, advances in asymmetric organocatalysis, synthesis of complex molecular architectures using multicomponent reactions, and the application of these methods to the synthesis of natural and unnatural compounds of biological importance. These methods are vital for the pharmaceutical, petrochemical and agrochemical industries. Also the fundamental understanding of organic synthesis is essential for the growth of materials chemistry, nanotechnology and other interdisciplinary areas. I strongly believe that organic synthesis will continue to flourish and lead to surprising developments in the years to come.

SYNFORM Your research group is active in the areas of catalysis and development of new methodologies. Could you tell us more about your research and its aims?

Dr. A. T. Biju Our research aims at developing transition-metal-free carbon–carbon and carbon–heteroatom bond-forming reactions using aryne chemistry and NHC-organocatalysis. In the area of aryne chemistry, we have recently developed a mild, efficient and scalable Diels–Alder reaction of arynes with challenging diene systems such

as pentafulvenes, 1,2-benzoquinones, styrenes, indenenes/benzofurans, and tropones. Moreover, the synthetic utility of N-heterocycles such as pyridine, and (iso)quinoline in aryne multicomponent reactions (MCRs) has been demonstrated for the synthesis of various heterocycles. In addition, we recently developed aryne MCRs triggered by phosphines for the synthesis of functionalized benzooxaphospholes, and the use of CO₂ as a one-carbon synthon in aryne MCRs has been developed. Furthermore, a transition-metal-free protocol for the N-arylation of tertiary amines has been developed. The results are summarized in Figure 1.

In another phase of the work using NHC catalysis, we have developed an efficient and facile Stetter reaction using vinyl sulfones, and vinyl phosphonates as Michael acceptors. Moreover, an efficient homoenolate annulation reaction with hydroxy chalcones for the synthesis of cyclopentane-fused coumarins has been realized. We are also working on asymmetric catalysis using NHCs. We recently demonstrated a facile method for the enantioselective synthesis of functionalized dihydropyranones and dihydropyridinones by the reaction of modified enals with β -dicarbonyl compounds or enamines, enolizable aldehydes, and heterocyclic C–H acids.

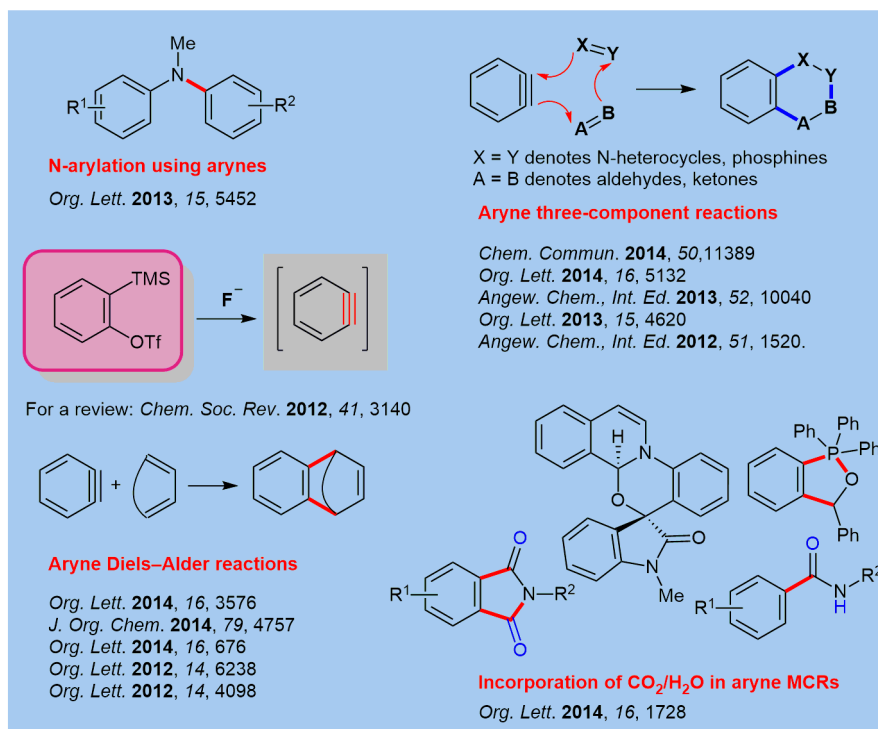
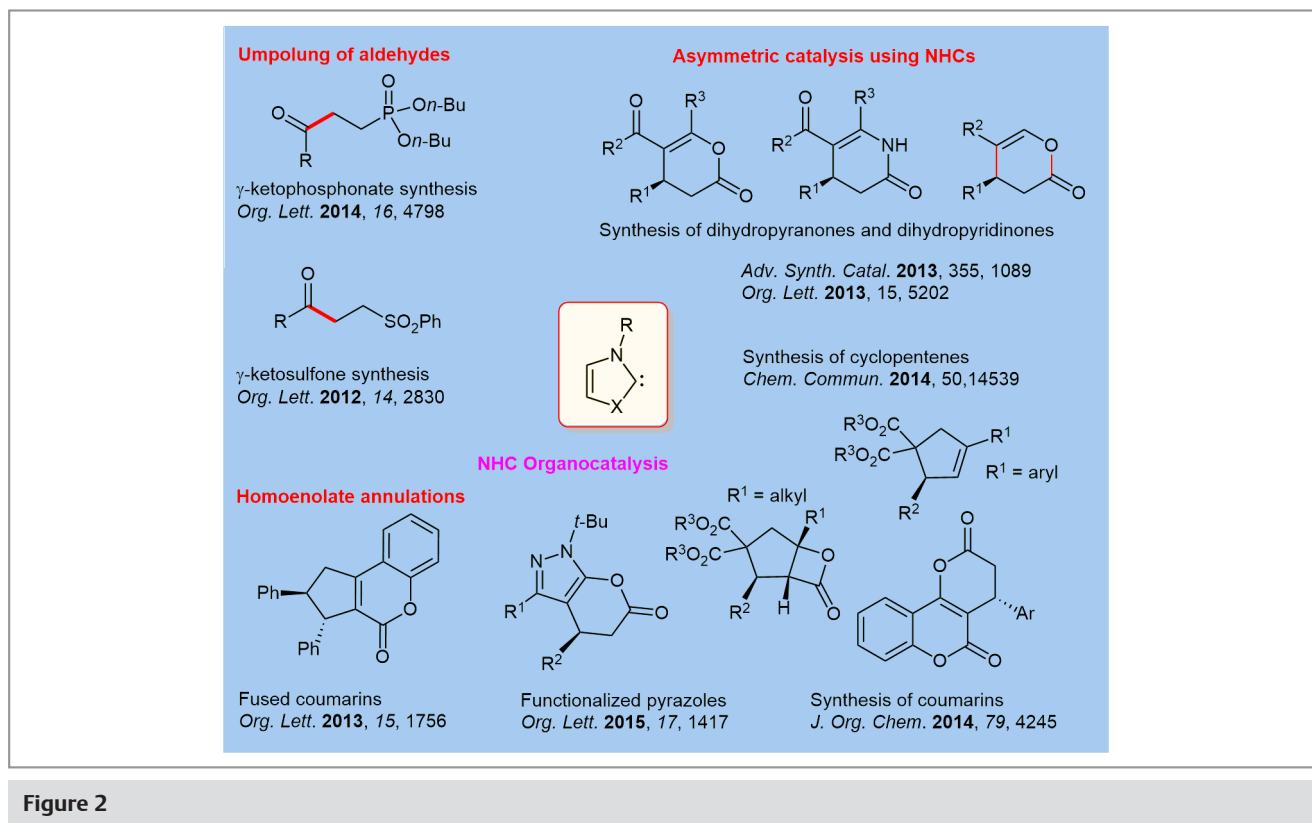


Figure 1



Furthermore, we have disclosed the enantioselective synthesis of functionalized cyclopentenones, β -lactone-fused cyclopentanes, and functionalized pyrazoles by the NHC-catalyzed reaction proceeding via the α,β -unsaturated acyl azolium intermediates. The results are summarized in Figure 2.

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

Dr. A. T. Biju Being at the beginning of my independent research career, my greatest scientific achievements lie ahead of me (I hope!). However, one of our recent results that I am proud of is the generation of a highly nucleophilic pyridyli-dene intermediate in the aryne MCRs triggered by pyridine using N-substituted isatins as the third component (*Angew. Chem. Int. Ed.* **2013**, *52*, 10040). These reactions resulted in the formation of indolin 2-one derivatives in good yields. This is the first time that NHCs have been found to be intermediates in aryne MCRs.

Annette Fenske