Palladium-Catalyzed One-Pot Stereospecific Synthesis of 2-Deoxy Aryl C-Glycosides from Glycals and Anilines in the Presence of tert-Butyl Nitrite

Highlighted article by A. K. Singh, R. Venkatesh, J. Kandasamy
Dear Readers,

It’s already that time of the year when there is not a single TV advertisement without some snow falling in the background and wherever you go – even right in the middle of the Gobi desert – you will hear that “all I want...” song by the superstar singer with a piercing voice that apparently can shatter glass (well, certainly it can shatter other things...). No escape from that, I am afraid... so, why not immerse yourself in some good reading for a virtual change of landscape? And what could possibly be better for that purpose than SYNFORM? Amazing coincidence, the first article of this last issue of the year will take you very far away from both that pervasive lady in red and the cold weather, straight into the warmth of San Sebastian (Spain) where the Thieme Chemistry family gathered back in June for the Editorial Board Meeting. What about the second article then? Well, that will take you to the magic of Shanghai (P.R. of China), where S.-L. You presents a very special example of axial stereocontrol in the synthesis of heterobiaryls. Speaking of a magical atmosphere, what about the winter charm of Brussels (Belgium): U. Hennecke reports on an organocatalytic enantioselective dichlorination of unfunctionalized alkenes. The final chapter could not be happier – in line with the period – nor more exotic as it comes from India, and specifically from the group of J. Kandasamy and his SYNTHESIS paper on the stereospecific synthesis of a special class of C-glycosides.

Can you still hear that song now? Hopefully not...

Let me finish by wishing you all a fantastic New Year and a Very Happy Festive Season, extended to all your families.

Enjoy your reading!!!

Mattia Zanda
The Editors of SYNTHESIS, SYNLETT, SYNFACS, SynOpen and SYNFORM, together with over 20 members of the Thieme Chemistry team from all over the world, gathered on June 21st until the 24th in the beautiful coastal city of San Sebastian/Donostia, in the Basque Country (Spain).

A number of new editorial board members – namely Franziska Schoenebeck and Hideki Yorimitsu (SYNTHESIS), Ang Li (SYNLETT), Dirk Trauner (SYNFACS), Francoise Colobert, Philippa Cranwell and Daniel Seidel (SynOpen) as well as the new Chinese editorial office member Juan Zhang – were warmly welcomed by the “more experienced” Thieme Chemistry crew members.

A number of important editorial topics were discussed – such as new features for the journals, future Editorial Board changes and our very own Select Crowd Review, spearheaded by the SYNLETT Editor-in-Chief Ben List, which is emerging as an extremely effective new way to review manuscripts. After a very careful and successful test in SYNLETT, coordinated by the “Crowd Review Editor” Manuel van Gemmeren, Select Crowd Review – which features shorter turnaround times and often improved accuracy relative to the traditional peer-review process – is now being extended to SynOpen and will be used more systematically for SYNLETT, with SYNTHESIS also considering its future implementation as an option available to authors.

Concerning SYNFORM, which continues to increase its popularity and the number of downloads from all over the chemistry world, the data presented showed that it has clearly benefited from the greater integration with social media – such as Twitter and LinkedIn – and by the further expansion of its dynamic web dimension.

As a result of the toughest decision taken by the Editorial Board, the next meeting will take place in 2020 in the beautiful and sunny island of Sardinia (Italy).

P.S. The tone of this Editorial Board Meeting account is not as cheerful and upbeat as it normally is. It cannot be, because one week after the meeting in San Sebastian we received the incredibly sad and unexpected news that Professor Dieter Enders – former Editor-in-Chief of SYNTHESIS, a giant of organic chemistry and a beloved member of the Thieme Chemistry family – had passed away. We will always be grateful to Dieter, for his deep humanity, his friendship, his clever ideas and his love for organic chemistry, and he will be in our hearts forever.
Rhodium-Catalyzed Atroposelective C–H Arylation: Efficient Synthesis of Axially Chiral Heterobiaryls


Axially chiral biaryls are important scaffolds that exist widely in natural products and pharmaceuticals, and are also utilized as privileged ligands and catalysts in asymmetric synthesis. Thus, the development of novel methods for the efficient asymmetric synthesis of axially chiral biaryls, enabled by transition-metal catalysis or organocatalysis, has attracted enormous interest in the chemical community. The group of Professor Shu-Li You from the Shanghai Institute of Organic Chemistry (SIOC, P.R. of China) has been interested in the synthesis of axially or planar chiral molecules through transition-metal-catalyzed asymmetric C–H functionalization reactions for some time. “Recently, transition-metal catalyzed asymmetric C–H functionalization reactions have received much attention for their great potential in efficient and straightforward synthesis of axially chiral biaryls. As there are numerous applications of axially chiral pyridine-derived ligands/catalysts in asymmetric catalysis, it is highly desirable to develop efficient methods for their asymmetric synthesis,” said Professor You. “Although palladium-catalyzed asymmetric Suzuki coupling, reported recently by Fernández, Lasaletta and co-workers, represents a powerful strategy for the asymmetric synthesis of axially chiral aryl pyridines(isoquinolines)* (J. Am. Chem. Soc. **2013**, *135*, 15730–15733), catalytic asymmetric synthesis with high enantioselectivity and efficiency via atroposelective C–H functionalization strategy* (Tetrahedron: Asymmetry **2000**, *11*, 2647; *J. Am. Chem. Soc. **2016**, *138*, 5242–5245) remains a challenging topic (Scheme 1).”

Recently, Professor You and his group developed an efficient method for facile synthesis of axially chiral heterobiaryls with high enantioselectivities via atroposelective C–H arylation reactions.

Professor You explained: “Five years ago, we reported the direct asymmetric C–H olefination of aryl benzo[**h**]isoquinolines using the Cramer catalyst* (Angew. Chem. Int. Ed. **2014**, *53*, 13244–13247), but moderate enantioselectivities were obtained with aryl pyridines (isoquinolines). At the same time, we also developed the Pd(II)-catalyzed asymmetric C–H iodonation of aryl-substituted pyridine N-oxides via kinetic resolution, but only moderate s-values were afforded* (ACS Catal. **2014**, *4*, 2741–2745). Later on, we introduced the SCP ligand in Rh(III)-catalyzed asymmetric C–H olefination* (J. Am. Chem. Soc. **2016**, *138*, 5242–5245) and the enantioselectivities could be significantly improved. However, the substrate scope was relatively narrow, and low enantioselectivities were observed for 1-(naphthalen-1-yl)isoquinoline. It has been a long-standing problem to synthesize axially chiral pyridine(isoquinoline) by C–H functionalization reaction in a highly enantioselective manner.”

Professor You further explained: “Dr. Zhong-Jian Cai, a former postdoc in our lab, found that rhodium(I)/TADDOL-derived monodentate phosphonite catalytic system, introduced by the Glorius group* (Angew. Chem. Int. Ed. **2018**, *57*, 9950–9954), worked well in the asymmetric C(sp2)–H arylation of ferrocenes. Encouraged by these results, Dr. Qiang Wang, another talented postdoc working in the same fume hood, investigated the Rh-catalyzed C–H arylation of 1-(naphthalen-1-yl)isoquinoline.” Dr. Qiang Wang remarked: “Initially, the reaction under Glorius’ conditions using aryl iodides as arylating reagents only gave low yields (10–15%) in this transformation. Later on, Dr. Zhong-Jian Cai and Mr. Chen-Xu Liu, a graduate student in Professor You’s lab, synthesized many different types of ligands. These ligands were found inefficient in the Rh-catalyzed C–H arylation of 1-(naphthalen-1-yl)isoquinoline despite several months of optimization work.” Professor You continued: “Considering the halide effect in transition-metal catalysis* (Angew. Chem. Int. Ed. **2002**, *41*, 26–47), we tried to revisit this reaction using aryl bromides as arylating reagents.”
Scheme 2 Selected substrate scope, a gram-scale reaction and application of chiral $N$-oxide as a catalyst in the allylation of aldehyde
ating reagents. To our delight, the efficiency of Rh-catalyzed C–H arylation of 1-(naphthalen-1-yl)isoquinoline was dramatically improved. Then Dr. Qiang Wang quickly identified the optimal conditions for this reaction.

Professor You continued: “One of the most exciting parts of this methodology is that the reaction is extremely efficient. The reaction conditions are mild and the starting materials are readily available (Scheme 2). Heteroaryl bromides, such as pyridine, thiophene, benzofuran are well tolerated. Good to excellent yields and enantioselectivities are obtained. Moreover, 2-aryl pyridines, quinazolines and benzofuranisoquinolines are efficient coupling partners. What’s more, the gram-scale reaction with relatively low catalyst loading further highlights the potential utility of this method. In addition, a chiral N-oxide from one-step oxidation of the product could act as an efficient catalyst for asymmetric allylation of benzaldehyde with allyltrichlorosilane.”

Professor You concluded: “We have developed an efficient and highly enantioselective synthesis of axially chiral heterobiaryls, which is enabled by rhodium(I)-catalyzed atroposelective C–H arylation of heterobiaryls. We expect that our study will provide a straightforward method for the synthesis of axially chiral pyridine(isoquinoline)-derived ligands and catalysts. The products obtained herein provide an excellent platform for this purpose.”

### About the authors

**Qiang Wang** was born in Hubei (P. R. of China), in 1990. He received his BSc from Central China Normal University (CCNU, P. R. of China). He subsequently carried out his doctoral studies at the same university under the supervision of Prof. Wen-Jing Xiao and Prof. Liang-Qiu Lu, receiving his PhD in 2018. During his graduate studies, he joined the group of André M. Beauchemin (University of Ottawa, Canada) as a visiting PhD student for 18 months. In July 2018, he joined Prof. Shu-Li You’s group for his postdoctoral studies after being awarded the Initiative Postdocs Supporting Program. His current research interests are transition-metal-catalyzed asymmetric C–H bond functionalization.

**Zhong-Jian Cai** was born and raised in Ganzhou, Jiangxi (P. R. of China). He received a B.A. in chemistry from Nanchang University (P. R. of China), where he worked in the research group of Prof. Sen Lin. He obtained his Ph.D. from Soochow University (P. R. of China), working under the direction of Prof. Shun-Jun Ji. Following his doctoral work, he joined the laboratory of Prof. Shu-Li You at the Shanghai Institute of Organic Chemistry (SIOC, P. R. of China) as a postdoctoral fellow studying transition-metal-catalyzed asymmetric C–H bond functionalization reactions. Zhong-jian is currently a postdoctoral scholar at Purdue University, IN (USA), working in the research group of Prof. Mingji Dai.

**Chen-Xu Liu** was born and grew up in Xuzhou, Jiangsu Province (P. R. of China). He received his bachelor’s degree (2017) in applied chemistry from Donghua University (P. R. of China) under the supervision of Prof. Yong-Fen Xu and now he is a PhD candidate in the group of Prof. Shu-Li You. His research interests focus on the construction of new chiral skeletons via asymmetric C–H bond functionalization.

**Qing Gu** received his BSc in chemistry from East China University of Science and Technology (ECUST, P. R. of China) in 2001. He obtained his Master’s degree and PhD in organic chemistry from ECUST in 2005 and 2008 under the co-supervision of Prof. Qi-Lin Zhou and Prof. Xin-Yan Wu. He carried out his postdoctoral studies at the Shanghai Institute of Organic Chemistry (SIOC, P. R. of China) with Prof. Shu-Li You from 2009 to 2011 and at Georg-August-University of Göttingen (Germany) with Prof. Lutz Ackermann from 2012 to 2013. In 2011, he joined SIOC as an associate professor. His current research interests include asymmetric catalysis and C–H bond functionalization.
Shu-Li You was born in Henan (P. R. of China) and received his BSc in chemistry from Nankai University (P. R. of China) in 1996. He obtained his PhD from the Shanghai Institute of Organic Chemistry (SIOC, P. R. of China) in 2001 under the supervision of Prof. Li-Xin Dai before conducting postdoctoral studies with Prof. Jeffrey Kelly at The Scripps Research Institute (USA). From 2004, he worked at the Genomics Institute of the Novartis Research Foundation (USA) as a PI before returning to SIOC as a Professor in 2006. He is currently the director of the State Key Laboratory of Organometallic Chemistry. His research interests mainly focus on asymmetric C–H functionalization and catalytic asymmetric dearomatization (CADA) reactions.
Organocatalytic, Enantioselective Dichlorination of Unfunctionalized Alkenes


The dihalogenation of alkenes is a very old reaction, one of the fundamental processes of organic chemistry that is usually taught to undergraduates in an introductory organic chemistry course. “Since the suggestion of Robert and Kimball in 1937\(^1\) that these reactions could proceed via cyclic halonium ions (following IUPAC rules, it is better to call them ‘haliranium ions’ to indicate the three-membered ring), one might argue that the mechanism is well understood. Indeed, the mechanism involving the haliranium ion is found in most organic chemistry textbooks! It is the prime example of an electrophilic addition reaction supposed to proceed via a cyclic halonium ion, explaining the usually observed anti-addition of the two halogen atoms,” explained Professor Ulrich Hennecke, previously of the University of Münster (Germany) and now at Vrije Universiteit Brussel (VUB, Belgium). However, things are not always as straightforward as originally thought, and a group of researchers led by Professor Hennecke has been investigating the reaction from a novel angle.

The group was surprised when they conducted their first experiments on indene and realised that the dihalogenation was not stereospecific for the anti-addition as it also provided the syn-addition product, something that cannot be explained by the formation of a haliranium ion (Scheme 1). However, they quickly learned that this fact was well known\(^2\) and that the standard mechanism does not explain the experimental findings under all conditions.

Professor Hennecke remarked on the curious coincidence of his new location: “One thing that I find very interesting/remarkable is that we are now, after our move to VUB, studying the stereochemical aspects of the dihalogenation in Brussels, just around the corner from Ghent University, where August Kekulé started all of this. As far as I know, Kekulé was the first to study stereochemical aspects of alkene dibromination...”
when he realised that bromination of maleic acid and fumaric acid resulted in isomeric 2,3-dibromo succinic acids. This discovery is even more remarkable when considering that Kekulé was carrying out these experiments around 1860, when the modern bonding theory of carbon was just in its infancy,” concluded Prof Hennecke.

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Literature Coverage

About the authors

Constantin G. Daniliuc obtained his Diploma at the ‘Alexandru Ioan Cuza’ University of Iaşi (Romania) in 2002. As a beneficiary of an Erasmus Scholarship, he completed in 2003 his Master’s thesis at the Technical University of Braunschweig, Institute of Inorganic and Analytical Chemistry (Germany) and received his Ph.D. from the same university in 2008 under the supervision of Professor W.-W. du Mont. Since 2012, he has been Head of the Crystallographic Laboratory at University of Münster, Organic Chemistry Institute (Germany), sustaining numerous collaboration projects with research groups from all over the world.

Frank De Proft (1969) obtained his PhD in sciences from the Vrije Universiteit Brussel (VUB) in 1995 and is currently full professor at this institution. His main research interests involve the development, implementation and use of chemical concepts from quantum mechanics, with special attention to the concepts introduced within the framework of the so-called “Conceptual Density Functional Theory”. Applications he has investigated concern the reactivity of organic, inorganic, biochemical and solid-state compounds, catalysis and the in silico design of new compounds with optimal chemical properties and reactivity.

Ruben Van Lommel obtained his Master’s degree in chemistry at the KU Leuven (Belgium) in 2018. During his Master’s studies he worked on the topic of supramolecular gels in the group of Prof. Wim De Borggraeyeve. His PhD continues this work and is a combination of experiments and computational chemistry, co-supervised by Prof. Frank De Proft and Prof. Mercedes Alonso at the Vrije Universiteit Brussel (VUB, Belgium). Besides supramolecular gels, his current research interests lie in the study of reaction mechanisms by means of density functional theory and ab initio molecular dynamics.

Volker Wedek received his BSc (2013) and MSc degrees (2015) in organic chemistry from The University of Münster (Germany) working on the synthesis of polychlorinated natural products. For his PhD studies he has stayed in the Hennecke group, where his research focuses on the development of new organocatalytic methods for the enantioselective dihalogenation of alkenes.

Ulrich Hennecke studied chemistry at the University of Marburg (Germany) before joining the group of Prof. Thomas Carell for his PhD studies on nucleic acid chemistry (PhD 2007, LMU Munich, Germany). After a postdoctoral stay with Prof. Jonathan Clayden (University of Manchester, UK), he joined the Organic Chemistry Institute of the University of Münster as junior group leader (2008). In 2018, he moved to the Vrije Universiteit Brussel (Belgium). His research interests involve synthetic organic as well as bioorganic chemistry with a special focus on halogenated organic compounds and their synthesis by new catalytic, enantioselective methods.

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© Georg Thieme Verlag Stuttgart • New York – Synform 2019/12, A191–A193 • Published online: November 18, 2019 • DOI: 10.1055/s-0037-1612211
Palladium-Catalyzed One-Pot Stereospecific Synthesis of 2-Deoxy Aryl C-Glycosides from Glycals and Anilines in the Presence of tert-Butyl Nitrite

*Synthesis* 2019, 51, 4215–4230

The lay person generally understands carbohydrates as a source of energy, but these compounds are also an important class of biomolecules which have been investigated as drugs, vaccines, drug targets, diagnostic tools, and more.¹ Unlike other biomolecules, such as proteins and nucleic acids, carbohydrates are complex in nature not only because of their structure and stereochemistry, but also because of their manifold biological functions.² Complex carbohydrates such as polysaccharides are known as glycans, which can be broadly classified as O- and C-glycosides depending on their anomeric linkages. The group of Dr. Jeyakumar Kandasamy at the Indian Institute of Technology (Varanasi, India) has been studying these classes of molecules and recently published the title paper on the one-pot synthesis of 2-deoxy aryl C-glycosides.

Aryl C-glycosides are compounds having direct C–C bonds between the sugar anomeric carbon and the aryl moiety, which are incorporated in various biologically active molecules and natural products.³ Dr. Kandasamy said: “Due to their potential bioactivity and medicinal significance, synthesis of aryl C-glycosides has attracted remarkable interest in synthetic organic chemistry.” He continued: “There are two types of aryl C-glycosides widely found in bioactive molecules, namely 2-hydroxy aryl C-glycosides and 2-deoxy aryl C-glycosides. Canagliflozin, dapagliflozin, bergenin, papulacandin, aspalathin, puercarin, mangiferin, cassialoin and ipragliflozin are some examples of bioactive molecules possessing 2-hydroxy aryl C-glycoside units.⁴ Angucyclines, marmycin A–B, urdamycinones A–D, kidamycin, pluramycin A, medermycin, saptomycin B and vineomycinone B, methyl ester are among the natural products having 2-deoxy aryl C-glycoside units.⁵”

Importantly, the stereochemistry at the sugar anomeric carbon plays a key role in the biological activity. “It has been widely noted that most of the bioactive aryl C-glycosides (both natural and synthetic) exist as a β-anomer. However, creation of stereocentre at the anomeric centre is a challenging task which requires special care in terms of selection of substrate, protecting groups, reagents, reaction conditions, and so on,” Dr. Kandasamy explained. He continued: “2-Hydroxy aryl β-C-glycosides are typically obtained by Friedel–Crafts alkylation of electron-rich arenes with different glycosyl donors or by the treatment of organometallic reagents such as aryllithium or aryl Grignard reagents to protected aldono lactones."⁶"

On the other hand, transition-metal-catalyzed cross-coupling reactions are well-established tools for the construction of 2-deoxy aryl C-glycosides. Dr. Kandasamy pointed out that Heck-type arylation of glycals with different aryl donors including aryl halides, arylboronic acids, arylzinc reagents, aryldiazirines, arylsulphinates, aryl carboxylic acids, etc. have been developed for the easy preparation of 2-deoxy aryl C-glycosides.⁴ “However, most of these methods have drawbacks, such as limited substrate scope, low yield, prolonged reaction time, etc.” remarked Dr. Kandasamy. He continued: “Moreover, these reactions failed to generate 2-deoxy-β-C-aryl glycosides. Therefore, the development of a high-yielding stereochemical protocol for the preparation of 2-deoxy aryl C-glycosides remains a challenge in synthetic carbohydrate chemistry.”

Aryldiazonium salts are important synthetic intermediates that have been explored in different palladium-catalyzed cross-coupling reactions.⁷ In particular, as explained by the authors of this paper, aryl diazonium salt mediated Heck couplings of allyl alcohols, allyl ethers and vinyl ethers have received significant attention in organic synthesis, because such reactions take place under ligand-free conditions at room temperature. In this context, Dr. Kandasamy’s team has recently explored the synthesis of 2-deoxy α-aryl C-glycosides from aryl diazonium salts and glycals.⁸ “The reactions proceeded at room temperature without any additives and gave excellent yields of the desired products,” said Dr. Kandasamy. He continued: “However, to some extent, the extensive use of aryl diazonium salts has been limited in organic synthesis due to their instability and even explosive nature. Considering this fact, here we have developed a one-pot method to access both α and β anomers of 2-deoxy aryl C-glycosides stereospecifically from glycals and anilines in the presence of palladium acetate and tert-butyl nitrite (TBN) (Schemes 1 and 2). TBN has been used as an in situ diazotization reagent when isolation of the unstable aryl diazonium salt intermediate is not required.”
Basically, this one-pot method was optimized very carefully by changing the different reaction parameters including solvent, catalyst, acid additives, etc. to identify the best conditions that can provide a high yield,” explained Dr. Kandasamy. The team found that under optimized conditions, the glycols such as β-glucal, β-galactal, β-rhamnal, and 1-rhamnal provided 2,3-deoxy 3-keto α-aryl C-glycosides stereospecifically in high yields. “From the proposed mechanism (Scheme 3), it is clear that the configuration at the C-3 position in the glycal dictates the α-anomeric selectivity through the β-syn-elimination process,” said Dr. Kandasamy. He explained: “One can easily achieve β-anomers of aryl C-glycosides stereospecifically by inverting the configuration at the C-3 position in the glycols. In order to prove that we have synthesized anti-glycols (i.e. C-3 inverted glycols) from β-glucal and 1-rhamnal, these products were subjected to the Heck coupling reaction with anilines under optimized conditions. As expected, to our delight, the reactions provided 2,3-deoxy-3-keto β-aryl C-glycosides in good to excellent yields.”

“Overall, the developed protocol provides simple and easy access to α- and β-anomers of 2-deoxy aryl C-glycosides in good yields at room temperature with high stereospecificity,” said Dr. Kandasamy. He concluded: “The current methodology appears to be quite general from a synthetic viewpoint, therefore we hope it will find broad applications for the preparation of biologically relevant aryl-C-glycosides.”

Scheme 1 Stereospecific reaction of tri-O-benzyl β-glucal and tri-O-benzyl β-altral (C-3 inverted β-glucal) with different anilines
Scheme 2: Stereospecific reaction of di-O-benzyl L-rhamnal and di-O-benzyl 6-deoxy-L-allal (C-3 inverted L-rhamnal) with different anilines.

Scheme 3: Plausible mechanisms for the C-arylation of glycals and anti-glycals.
About the authors

Adesh Kumar Singh was born (1991) in Varanasi, Uttar Pradesh, India. He is currently pursuing Ph.D. in the Department of Chemistry, Indian Institute of Technology (BHU) Varanasi, India under the supervision of Dr. Jeyakumar Kandasamy. He obtained his B.Sc. in chemistry (2011) from V.B.S. Purvanchal University, Jaunpur (India) and M.Sc. in organic chemistry (2014) from Banaras Hindu University, Varanasi (India). He qualified for national level competition exams such as GATE (2015) and CSIR-JRF (2015) and was admitted to the PhD program at IIT (BHU) in 2015. His research interest is focused on carbohydrate synthesis and glycosylation methodology.

Rapelly Venkatesh was born (1993) in Mancherial, Telangana State, India. He is currently pursuing a Ph.D. in the Department of Chemistry, Indian Institute of Technology (BHU), Varanasi (India) under the supervision of Dr. Jeyakumar Kandasamy. He obtained his B.Sc. in chemistry (2014) from Osmania University (India) and M.Sc. in chemical science (2017) from Pondicherry University (India). He qualified for the national level competition exam GATE (2018) and was admitted to the PhD program at IIT (BHU) in 2018. His research interest is focused on synthetic applications of aryl diazonium salts.

Jeyakumar Kandasamy was born in Tamil Nadu, India. He obtained his B.Sc. and M.Sc. from the University of Madras (India) in 2000 and 2003, respectively. In 2008, he obtained his PhD from the Department of Chemistry, Indian Institute of Technology Madras (India) under the supervision of Prof. Dillip Kumar Chand. After his PhD, he worked with Prof. Timor Baasov in Technion-Israel (2008–2011) and Prof. Peter H. Seeberger in Max-Planck Institute of Colloids and Interfaces, Berlin, Germany (2012–2013) as a postdoctoral fellow. In June 2014, he joined the Department of Chemistry, Indian Institute of Technology Madras (BHU), Varanasi (India) as an Assistant Professor. In August 2019, he was promoted to Associate Professor in the same institute. His research focus is organic synthesis covering catalysis, synthetic methodology, and carbohydrate synthesis.

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Literature Coverage

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Young Career Focus

Dr. Bill C. Hawkins (University of Otago, New Zealand)

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**Synthesis**

Review: Recent Advances in Reactions of Propargylamines
(by D. Huang and co-workers)

**Synlett**

Account: Synthesis of Enantioenriched Tetra-ortho-3,3′-substituted Biaryls by Small-Molecule-Catalyzed Noncanonical Polyketide Cyclizations
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**Synfacts**

Synfact of the Month in category “Chemistry in Medicine and Biology”: Click Chemistry for the Synthesis of Azides