SYNLETT Best Paper Award 2017: Synthesis of Tetraarylmethanes by the Triflic Acid-Promoted Formal Cross-Dehydrogenative Coupling of Triarylmethanes with Arenes

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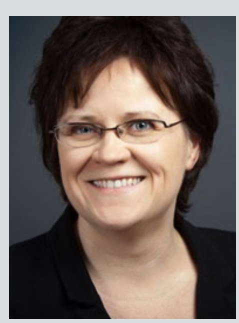
Background. Thieme Chemistry and the Editors of SYNTHESIS and SYNLETT present the 'SYNTHESIS/SYNLETT Best Paper Awards'. These annual awards honor the authors of the best original research papers in each of the journals, considering their immediate impact on the field of chemical synthesis.
Cathleen Crudden, Masakazu Nambo and their co-workers are the recipients of the SYNLETT Best Paper Award 2017. The work was a collaboration between Nagoya University in Japan and Queen's University in Canada. The authors are recognized for their work on the synthesis of tetraarylmethanes through a formal cross-dehydrogenative coupling of triarylmethanes with arenes, promoted by triflic acid. Benjamin List, Editor-in-Chief of SYNLETT, commented: "Nambo, Yim, Fowler, and Crudden have developed an elegant synthesis of tetraarylmethanes that involves an acid-catalyzed oxidative coupling of an arene with triarylmethanes, which became readily accessible in previous studies by the authors. The reaction proceeds via trityl-type cations and enables the formation of fascinating products, in which four different arenes are connected via a single stereogenic carbon atom."
SYNFORM spoke with Masakazu Nambo and Cathleen Crudden, who were happy to share some background information regarding the prize-winning paper as well as current research activities ongoing in their groups.

Biographical Sketches

Prof. M. Nambo

Masakazu Nambo was born in Fukui (Japan) and studied at Nagoya University (Japan). He obtained his BSc (2006), MSc (2008) and PhD (2011) degrees under the tutelage of Professors Ryoji Noyori and Susumu Saito, Professors Ryoji Noyori and Kenichiro Itami, and Professor Kenichiro Itami, respectively. In 2008, he also spent some time in Germany at the University of Münster, where he was supervised by Professor Bernhard Wünsch. Since his PhD, Professor Nambo has worked as a Research Scientist (Asahi-Kasei E-Materials Corporation, Japan, 2011–2013) and then moved back to Nagoya University to work with Professor Cathleen Crudden, firstly as a Designated Assistant Professor (2013–2018) and now as a Designated Lecturer. His current research interests include the development of new transformations of organosulfur compounds, establishment of new synthetic strategies for modular and straightforward synthesis, and discovery of new biologically activity of multiply-arylated structures. Outside the lab, he enjoys playing outside with his two sons.



Prof. C. M. Crudden

Cathleen Crudden is Full Professor and Canada Research Chair (Tier 1) at Queen's University (Canada), and also holds a cross appointment as a Research Professor at the Institute of Transformative Bio-Molecules (ITbM) in Nagoya (Japan). She is one of only four international faculty at ITbM, where she runs a satellite lab funded by the Japanese government. She has won numerous research awards including the 2018 Canadian Catalysis Society Award, the 2018 IPMI Carol Taylor Award, the 2017 R. U. Lemieux Award and the 2011 Clara Benson Award. She is a

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fellow of the Chemical Institute of Canada (2014) and the Royal Society of Chemistry (UK, 2017). She held a Killam Research Fellowship from 2015–2016. Cathleen has been a visiting professor in the labs of Professor Ryoji Noyori, was awarded a Global Center of Excellence Professorship at Kyoto University and a Visiting Professorship in Tarragona, Spain.

Cathleen was President of the Canadian Society for Chemistry in 2012/2013 and served on the Board of Directors for two terms representing the Catalysis Division. She also served on the Editorial Advisory Board for ACCN for ten years, and has been one of two Canadian members of the organizing committee of Pacifichem for the past 10 years. She is chair of the NSERC–Chemistry Liaison Panel. Cathleen is Associate Editor for *ACS Catalysis* and sits on the editorial advisory boards of *Chemical Record* (Japan), *Synthesis*, *Organometallics*, *ACSOmega* and *Chemical and Engineering News*. Her work in catalysis and materials has received significant acclaim, with recent work identifying a new class of carbon-based SAMs being called "game changing" and "the new gold standard" by international experts in the area.

INTERVIEW

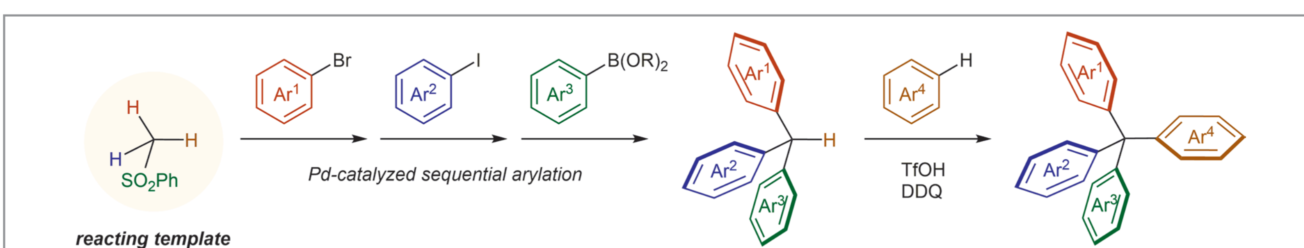
SYNFORM *Could you highlight the value of your award-winning paper with respect to the state-of-the-art, as well as the potential or actual applications?*

Prof. Masakazu Nambo and Prof. Cathleen Crudden Polyarylated methanes are valuable structures found in a variety of biologically active molecules and functional organic materials. Among arylated methanes, fully- or tetra-arylated methanes are structurally beautiful molecules that have unique chemical and physical properties and are challenging to prepare. Indeed, this rigid motif has been used as a ligand for metal–organic frameworks, *n*-type material for optoelectronic devices, and an agent for drug delivery. Very bulky tetraarylmethanes are also critical as 'stoppers' in rotaxane chemistry, subject of the Nobel Prize in 2016. Despite intense interest in tetraarylmethanes for these applications, most synthetic approaches rely on very classical methods, such that finding modular and straightforward syntheses of unsymmetrical tetraarylmethanes is still a challenge in synthetic organic chemistry.

In this paper, we have established a new synthetic route for the preparation of tetraarylmethanes from triarylmethanes and arenes by a formal cross-dehydrogenative coupling. Combined with our previous studies describing cross-coupling methods for the synthesis of triarylmethanes, the method described in our SYNLETT paper permitted the preparation of structurally diverse tetraarylmethanes in four steps from readily available materials. Thus, we believe this method will provide an opportunity to explore new tetraarylmethane-based materials and pharmaceuticals.

SYNFORM *Can you explain the origin, motivations and strategy used for conducting the award-winning research?*

Prof. Masakazu Nambo and Prof. Cathleen Crudden Previously, our group has developed the modular synthesis of di- and triarylmethanes employing Pd-catalyzed sequential arylations of alkyl sulfones followed by the use of the sulfone group as an electrophile in a Suzuki–Miyaura cross-coupling. However, introducing the fourth aryl ring was challenging due to the considerable steric bulk. Therefore, we attempted the preparation of tetraarylmethanes from triarylmethanes by arylating the remaining C(sp^3)–H bond. Inspired by recent progress of oxidative C–H/C–H coupling reactions, we discovered a new formal cross-dehydrogenative coupling promoted by TfOH and DDQ. This result is based on considerable efforts by



Scheme 1 Straightforward synthesis of tetraarylmethanes (total 4 steps)

postdoctoral fellows Dr. Jacky Yim and Dr. Kevin Fowler from our groups.

The invitation to submit an article for a Special Issue dedicated to Professor Victor Snieckus was another motivation to make sure the paper was of fitting quality to recognize the monumental contributions made by my colleague and friend to the chemistry of arenes. Having it selected as the Best Paper for 2017 was yet another honor, and we were very pleased to dedicate it to Vic!

SYNFORM *What is the focus of your current research activity, both related to the award paper and in general?*

Prof. Masakazu Nambo and Prof. Cathleen Crudden One of the key research goals of our group in Canada/Japan is to establish a new synthetic strategy that permits the construction of diverse molecules in a straightforward way, from simple starting materials. Minimizing the total number of synthetic steps, including those required for substrate preparation, is very important if synthetic schemes are to be viable and useful. We are also focused on employing the power of catalysis to enable high-value transformations such as enantioselective/specific reactions and inert bond activations. A key part of this strategy is to rely upon the unique properties of different main-group elements including boron, sulfur, and phosphorus, which we believe will lead to development of versatile transformations in synthetic organic chemistry.

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

Prof. Masakazu Nambo and Prof. Cathleen Crudden There is no doubt that organic synthesis has made an extremely great contribution to the development of science and society and it will continue to do so in the future. In our institute in Nagoya, Japan, we have the pleasure of collaborating with some of the world's best plant and animal biologists. This collaborative relationship has made it clear that the biologically active compounds available to biologists are very limited, constituting a huge barrier to biological research. Thus, we also believe in developing simple strategies that will empower researchers outside the synthetic organic community to assemble molecules in facile, predictable ways. It is really in this way that the power of organic chemistry will be translated to other fields, and significant discoveries will result from that.