

Editorial

Highlights of the Most Cited Papers in the Section “Catalysis in Organic and Polymer Chemistry”

Victorio Cadierno 

Laboratorio de Compuestos Organometálicos y Catálisis (Unidad Asociada al CSIC), Departamento de Química Orgánica e Inorgánica, Facultad de Química, Universidad de Oviedo, Julián Clavería 8, E-33006 Oviedo, Spain; vcm@uniovi.es

Received: 8 December 2020; Accepted: 14 December 2020; Published: 16 December 2020



The aim of this editorial is to highlight the most cited papers published during 2018–2019 in the section “Catalysis in Organic and Polymer Chemistry” of the journal *Catalysts*. The top 10 list is composed of five reviews, three regular papers, and two communications dealing with the following topics: metal-catalyzed cross-coupling reactions, C–H bond functionalization processes, catalytic oxidation, epoxidation and hydroisomerization reactions, and dearomatization processes.

The paper collecting the highest number of citations is a review article by Buchspies and Szostak covering recent advances in acylative Suzuki–Miyaura cross-coupling reactions, i.e., the catalytic coupling of organoboron reagents with acyl electrophiles, which have emerged in recent years as an appealing alternative to the classical stoichiometric nucleophilic additions or Friedel–Crafts reactions for the synthesis of aromatic ketones [1]. The use of different types of acyl electrophiles (acyl halides, anhydrides, carboxylic acids, esters, and amides) is discussed in depth, presenting from each of them the catalytic systems (both homogeneous and heterogeneous) described so far in the literature, mainly Pd- and Ni-based systems, as well as the range of organoboron reagents that can participate in the process. Additional evidence of the enormous interest in this topic is the fact that a preliminary communication published later by Szostak and co-workers is also among the most cited papers of 2018–2019 [2]. *N*-Acylphthalimides are therein introduced as new bench-stable acyl electrophiles for Suzuki–Miyaura cross-coupling reactions. In particular, employing a Pd-PEPPSI-type precatalyst, containing the sterically demanding *N*-heterocyclic carbene ligand IPr (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), a number of biaryl ketones were accessed in high yields by coupling with arylboronic acids. This work clearly sets the stage for an array of synthetic transformations in which readily available *N*-acylphthalimides can be employed as amide-based precursors for highly reactive acyl-metal intermediates.

Two other highly cited articles also encompass palladium-catalyzed Suzuki–Miyaura cross-coupling reactions. In one of them, Rocard and Hudhomme review recent discoveries in the use of nitroarenes as the electrophilic partners in these carbon–carbon bond forming processes [3]. Compared to the commonly employed aryl halides and triflates, nitroarenes are more accessible and their use could therefore result in the reduction of steps and cost in the synthesis of important chemicals. Although the field remains poorly explored, the examples discussed in the review show that nitroarenes are well tolerated in classical Suzuki–Miyaura couplings with boronic acids, although their activation is not so easy than that of halogenated analogues. Given the significance of the field, further developments are expected in the coming years. Regarding the second article, it presents the preparation and characterization of a new hybrid catalyst, consisting of PdCl₄²⁻ supported on a periodic mesoporous organosilica functionalized with a bipyridinium ionic liquid, featuring an outstanding efficiency for Suzuki–Miyaura reactions between aryl halides and aryl boronic acids in water [4]. The use of a cheap and environmentally friendly solvent, along with the effective catalyst recovery and reuse (up to six

times without loss of activity), makes the protocol presented in this article of valuable interest from a Green Chemistry perspective.

The catalytic functionalization of carbon–hydrogen bonds is an important issue in current chemistry research due to its enormous applications in organic synthesis. These processes avoid pre-functionalization strategies, prevent the formation of undesired waste, and thus provide greener and more economical pathways to access high-value products. Among the different strategies, the one based on the directing-group-assisted C–H bond metalation has tremendously contributed to the discovery of new carbon–carbon and carbon–heteroatom bond forming reactions. Recent advances in the field employing cost-effective ruthenium-based catalysts were reviewed by Singh [5]. A wide range of arylation, alkenylation, alkylation, allylation, and annulation processes were covered and a timely discussion of the most relevant mechanistic aspects presented.

Another review paper dealing with the dearomatization of pyridines received great attention due to the relevance of the resulting dihydropyridine products, which are key structural units present in numerous natural products and organic molecules with pharmacological interest [6]. This review complements well the previous contributions covering the chemistry of pyridines, summarizing the different strategies developed during the last decade for the activation of the pyridinic ring via *N*-functionalization. Such strategies render highly reactive pyridinium ions and ylides capable of reacting with a large variety of nucleophilic species, even in an asymmetric manner, or to undergo dipolar cycloaddition reactions for the construction of elaborated polycyclic frameworks containing dihydropyridine units. Researchers involved in heterocyclic chemistry will undoubtedly find this review article a source of inspiration for future work.

A review by Murzin and co-workers on the catalytic hydroisomerization of paraffins has also sparked interest [7]. The field is of paramount importance for petrochemical industries since increasingly available long-chain waxy alkanes can be upgraded into branched isomers with improved fuel properties. Different bifunctional catalysts (hierarchical and nano-shaped zeolites and nanocomposites), their stability and mechanism of action towards model compounds, such as octane, *n*-decane, *n*-dodecane or *n*-hexadecane, are analyzed along with the main factors affecting their activity and selectivity.

Another topic of relevance is the oxidation of organic molecules: in particular, in two highly cited articles, Gushchin, Bilyachenko, Shul'pin, and coworkers presented efficient procedures for the conversion of alkanes and alcohols into alcohols and ketones, respectively, employing peroxides as oxidants (H_2O_2 or $^t\text{BuOOH}$). The catalytic systems employed were composed of new polymeric oxovanadium(IV) complexes of general composition $[\text{VO}(\text{L})\text{X}_2]_n$ ($\text{X} = \text{Cl}$ or Br ; $\text{L} = 2,2'$ -bipyridine or 1,10-phenanthroline) [8] and the unusual heterometallic cage-like silsesquioxane derivative $[(\text{PhSiO}_{1.5})_6]_2[\text{CuO}]_4[\text{NaO}_{0.5}]_4[\text{dppmO}_2]_2$ ($\text{dppmO}_2 = \text{bis}(\text{diphenylphosphino})\text{methanedioxide}$) [9]. In both works, complete details on the structure and mechanism of action of these new catalysts are given.

The list of the most cited papers is completed by a preliminary communication dealing with the epoxidation of olefins, including polymeric systems such as polybutadiene and polyisoprene [10]. Remarkable results in terms of activity and stereoselectivity were achieved under mild conditions (r.t.) employing a supramolecular manganese porphyrin cage complex as catalyst, molecular oxygen as the oxidant, and isobutyraldehyde as a sacrificial co-reductant.

I encourage *Catalysts* readers to turn their attention to the excellent papers summarized here as they all deal with front-line aspects of current chemistry research.

Funding: This research received no external funding.

Conflicts of Interest: The author declares no conflict of interest.

References

1. Buchspies, J.; Szostak, M. Recent advances in acyl Suzuki cross-coupling. *Catalysts* **2019**, *9*, 53. [[CrossRef](#)]
2. Rahman, M.M.; Buchspies, J.; Szostak, M. *N*-Acylphthalimides: Efficient acyl coupling reagents in Suzuki-Miyaura cross-coupling by N-C cleavage catalyzed by Pd-PEPSI precatalysts. *Catalysts* **2019**, *9*, 129. [[CrossRef](#)]
3. Rocard, L.; Hudhomme, P. Recent developments in the Suzuki-Miyaura reaction using nitroarenes as electrophilic coupling reagents. *Catalysts* **2019**, *9*, 213. [[CrossRef](#)]
4. Ahadi, A.; Rostamnia, S.; Panahi, P.; Wilson, L.D.; Kong, Q.; An, Z.; Shokouhimehr, M. Palladium comprising dicationic bipyridinium supported periodic mesoporous organosilica (MPO): Pd@Bipy-PMO as an efficient hybrid catalyst for Suzuki-Miyaura cross-coupling reaction in water. *Catalysts* **2019**, *9*, 140. [[CrossRef](#)]
5. Singh, K.S. Recent advances in C-H bond functionalization with ruthenium-based catalysts. *Catalysts* **2019**, *9*, 173. [[CrossRef](#)]
6. Bertuzzi, G.; Bernardi, L.; Fochi, M. Nucleophilic dearomatization of activated pyridines. *Catalysts* **2018**, *8*, 632. [[CrossRef](#)]
7. Mäki-Arvela, P.; Kaka khel, T.A.; Azkaar, M.; Engblom, S.; Murzin, D.Y. Catalytic hydroisomerization of long-chain hydrocarbons for the production of fuels. *Catalysts* **2018**, *8*, 534. [[CrossRef](#)]
8. Fomenko, I.S.; Gushchin, A.L.; Abramov, P.A.; Sokolov, M.N.; Shul'pina, L.; Ikonnikov, N.S.; Kuznetsov, M.L.; Pombeiro, A.J.L.; Kozlov, Y.N.; Shul'pin, G.B. New oxidovanadium(IV) complexes with 2,2'-bipyridine and 1,10-phenanthroline ligands: Synthesis, structure and high catalytic activity in oxidations of alkanes and alcohols with peroxides. *Catalysts* **2019**, *9*, 217. [[CrossRef](#)]
9. Kulakova, A.N.; Khrustalev, V.N.; Zubavichus, Y.V.; Shul'pina, L.S.; Shubina, E.S.; Levitsky, M.M.; Ikonnikov, N.S.; Bilyachenko, A.N.; Kozlov, Y.N.; Shul'pin, G.B. Palanquin-like Cu₄Na₄ silsesquioxane synthesis (via oxidation of 1,1-bis(diphenylphosphino)methane), structure and catalytic activity in alkane or alcohol oxidation with peroxides. *Catalysts* **2019**, *9*, 154. [[CrossRef](#)]
10. Bernar, I.; Rutjes, F.P.J.T.; Elemans, J.A.A.W.; Nolte, R.J.M. Aerobic epoxidation of low-molecular-weight and polymeric olefins by a supramolecular manganese porphyrin catalyst. *Catalysts* **2019**, *9*, 195. [[CrossRef](#)]

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



© 2020 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).