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Editorial

Foreword

The field of catalytic aromatic C–H activation has undergone explosive growth in the last few years, developing from a curiosity to a powerful set of synthetic tools. The interest generated is not least due to the fact that exploiting catalytic C–H activation can substantially reduce the number of steps required for a transformation. This appeals not only because of the simplification of the synthetic pathway but also because of the attendant reduction in waste. The aim of this 'symposium in print' is to draw together articles from many of the leading research teams in the field in order to give a balanced overview of the state of the art in the subject.

The first articles in this symposium in print focus on reactions that proceed via the insertion of unsaturated substrates into metallated aromatic and heteroaromatic intermediates. Kuninobu, Takai and co-workers report the insertion of acetylenes, acrylates and isocyanates into C–H bonds of heterocycles directed by imine functionalities. Satoh and Miura's group describe the oxidative insertion of alkenes into the C–H bonds of thiophenes and furans under weakly basic conditions, whilst Stoltz and co-workers exploit oxidative conditions for a range of annulations. Lautens and co-workers rely on the reversibility of insertion of norbornene into C–H bonds to trigger threefold domino reactions leading to tetracyclic fused pyrroles.

The second group of papers describes transformations that rely on the direct intramolecular arylation of tethered substrates. Fagnou's group have screened a range of ligands for ring-closing reactions leading to 6*H*-benzo[*c*]chromenes and find that an electron-deficient phosphine gives the best performance, consistent with the C–H activation step proceeding via a base-assisted deprotonation. This mechanism is further explored in the paper contributed by Echavarren and co-workers in a combined synthetic and computation study, based on palladium catalysts with chelating bisphosphines. As in many areas of catalysis, microwave irradiation is proving to be a convenient method of heating in aromatic C–H activation chemistry as exemplified here by the work of Maes and co-workers on the synthesis of a range of heterocycles and of our group on the synthesis of fluorinated carbazoles.

Inter-molecular arylation can also be achieved using aryl halide substrates as exemplified by the group of Oi and Inoue who report the arylation of aromatics directed by 2-pyridine or 2-oxazoline moiety. Bellina, Rossi and co-workers report the selective mono- and diarylation of benzylated imidazole whilst Itami and co-workers present the use of a rhodium catalyst with a highly electron-withdrawing phosphite ligand in the arylation of heterocycles and electron-rich aromatics. The aryl halide coupling partner can be replaced by diaryliodonium salts under oxidative conditions and Spencer and co-workers have exploited this in the arylation of benzodiazepines.

Catalytic coupling reactions that proceed via C–H activation are not limited to the formation of C–C bonds. This is illustrated by Kesharwani and Larock who exploit 1,4-migration of palladium from an aromatic sp^2 carbon to a benzylic sp^3 group in the production of a range of benzyl ethers and esters. Meanwhile Smith and co-workers present the iridium-catalysed borylation of thiophenes.

The simplification of catalysts for aromatic C–H activation will almost certainly feature heavily in the near future in order to increase their general usability and to allow easy scale-up of reactions. This area is represented by the submissions of the groups of Ackermann and Fairlamb, who use simple catalysts based on ruthenium chloride and palladium nanoparticles, respectively, in inter-molecular arylation reactions.

In summary, the papers presented in this 'symposium in print' paint a picture of a vibrant, rapidly expanding field. In particular some give important mechanistic insight into the reactions whilst others outline some of the first attempts to address issues of catalyst design emerging in the field; both areas will have a substantial impact on the future development of new catalysts and reactions.

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