TEMPLATE-DIRECTED SYNTHESIS

Running rings around rings

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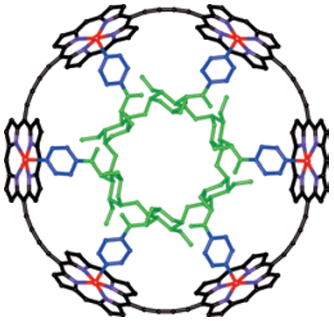

The use of metal ions or small molecules to template the synthesis of other compounds is a well-established principle of host–guest chemistry. The templating entity gathers together the required building blocks and organizes them into a specific arrangement such that their covalent attachment to one another results in the formation of a favoured target structure — one that is often difficult to make in the absence of the template. For example, templates are quite useful when it comes to the synthesis of large cyclic compounds — the final ring-closing step is much more likely to occur if the ends of a long linear precursor are held in close proximity on a template rather than waiting for a chance meeting in an untemplated reaction.

Led by Harry Anderson, a team of researchers at the University of Oxford in the UK and Aix Marseille Université in France and have now shown how cyclodextrins decorated with pyridyl groups can be used to template the synthesis of zinc-porphyrin nanorings. Cyclodextrins are naturally occurring macrocyclic compounds made up of six (α), seven (β) or eight (γ) repeating glucose residues. Anderson and co-workers demonstrate that the relatively flexible α-cyclodextrin-based template is almost as effective at orchestrating the synthesis of a hexameric zinc-porphyrin ring around its outer rim (pictured) as a rigid radial oligopyridyl template used in previous studies. A β-cyclodextrin analogue — with its seven repeating glucose units — was found to template the formation of a nanoring made up of seven porphyrins, albeit with a lower yield.

The availability of a molecular scaffold that can present a prime number of coordination sites in a symmetrical arrangement should enable very large porphyrin rings to be made through so-called Vernier templating approaches, in which different building blocks with mismatched numbers of binding sites are combined. Moreover, the use of cyclodextrin-based templates means that the cavities of these well-known macrocyclic molecular hosts could be filled with guest species to modulate the properties of the porphyrin-nanoring–cyclodextrin assemblies. *SC*

CARBON DIOXIDE CAPTURE

Natural gas scrubs up well

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Natural gas is not only more abundant than coal and oil, but also produces less CO_2 per unit of energy obtained when it is burned. Although both of these factors make it an attractive fossil fuel, natural gas fields can themselves contain high concentrations of CO_2. Because the CO_2 is often then vented into the atmosphere at the point of natural gas extraction, any reduced emissions during combustion are therefore offset. To circumvent this problem, cheap aqueous amine scrubbers are commonly used as a CO_2 capture method in natural-gas wells.

C–H ACTIVATION

Additional directions

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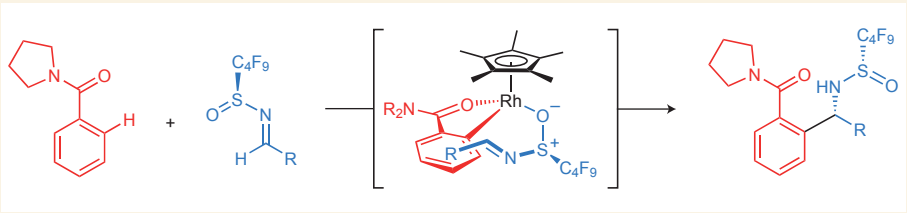
Nucleophilic additions to imines are one of the most convenient ways to prepare chiral α-branched amines — a class of compounds that are widely found in natural products and drugs. Aryl lithiums and other organometallic reagents have been widely used in conjunction with chiral ligands in these transformations, but the high reactivity of such nucleophiles can limit the reaction scope. Approaches in which a metal-coordinating group directs a metal centre to activate a nearby C–H bond and form a reactive organometallic intermediate *insitu* have also been explored but, so far, have not been successful for asymmetric reactions.

Now Jonathan Ellman and co-workers from Yale University and the University of California, Berkeley have reported a Rh(III)-catalysed addition of aryl nucleophiles to imines bearing a perfluorobutanesulfinyl auxiliary (pictured). Initial experiments used an amide to direct C–H activation, and showed that addition occurred with high diastereoselectivity to a variety of aryl imines. Electron-donating substituents on the aryl ring of the amide were well tolerated, as were electron-withdrawing groups in the imine component. Inverting this electron demand, however, resulted in poorer yields. Additions to alkyl imines were not successful, but the methodology was extended to an imino ester, which could ultimately provide access to amino acids with aryl side chains. The sulfinyl chiral auxiliary could be removed easily under acidic conditions to give the chiral amines without any loss of stereochemical purity.



Synthetically useful C–H activation reactions often rely, as here, on the use of directing groups to control regioselectivity. Ellman and co-workers also report, as part of this work, that azo groups are effective directing groups for Rh-catalysed C–H activation — further adding to the 'toolbox' of potential directing groups available for this type of methodology. These reactions also provided insight into the mechanistic aspects of the reaction: an unsymmetrical azobenzene with a single dimethylphenyl substituent reacted solely at the unsubstituted ring. This reveals the strong steric bias exerted by the substituents on such reactions. *SD*

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