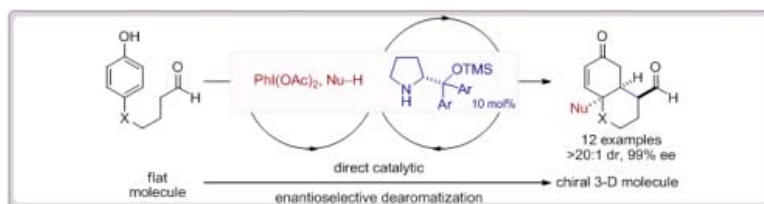


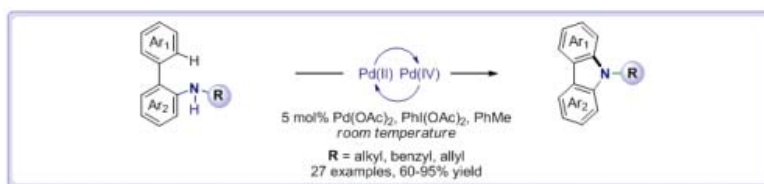
Dr M Gaunt, University of Cambridge
New Catalytic Reactivity Concepts in Organocatalysis

In the area of organocatalysis, Dr Gaunt has focussed on the development of new catalytic reactivity concepts and strategies that enable the rapid generation of molecular complexity to provide a novel approach to the synthesis of natural products and related architectures. In the last year the Gaunt group has focussed on harnessing the latent reactivity and functionality stored within aromatic systems. By combining dearomatization with desymmetrization, he developed a catalytic enantioselective dearomatization strategy that converts phenols directly to complex decalin structures containing three chiral centres, complex architecture and diverse functionality (*J. Am. Chem. Soc.* **2008**, *130*, 404). This work opens up numerous possibilities for the synthesis of natural products and complex molecules of structural and stereochemically diverse scaffolds.

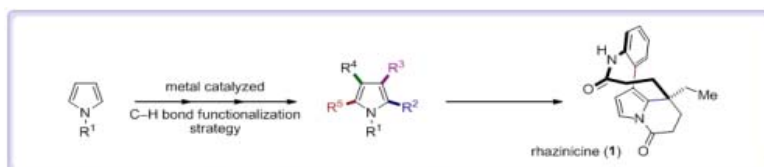


In relation to the second active area of Gaunt's research, the primary aim has been to develop a blueprint for chemical synthesis that enables the assembly of molecules without the reliance of functional groups. A key aspect of this metal catalyzed C–H bond functionalization programme has been the development of mild and selective new reactions. This reaction will provide the basis for a synthesis approach that enables the deployment of these tactics in structurally complex and functionally sensitive molecules, such as those found in natural products and active pharmaceutical agents. In general, many of the developments in this area relate to transformations that proceed under harsh conditions that may not be widely applicable. However, Gaunt's approach has focussed on developing reactions that will be amenable to applications in real systems that will have widespread application in academia and industry.

The general CH activation concept involves controlling electrophilic metalation using transition metal salts. A particularly key aspect of the research programme is the control of the site-selectivity of the C–H bond functionalization step in the new reaction. In many cases they have demonstrated that Pd(II)-catalyzed C–H functionalizations can be controlled and steered selectively to the site of choice, yielding a predictable and interchangeable product. We have also discovered a new C–H bond amination process that operates at room temperature, and proceeds through a novel Pd(II)-Pd(IV) mechanistic pathway for this class of reaction (*J. Am. Chem. Soc.* **2008**, *130*, 16184). Current studies have identified a catalytic intermolecular amination process that could have significant impact in synthesis.



In line with the original goals of impacting C–H bond functionalization methods into synthesis, Gaunt has completed the first synthesis of rhazinicine using an iterative C–H bond functionalization strategy. This synthesis sequenced Ir(I)-catalyzed C–H borylation and Pd(II)-catalyzed C–H alkenylation on a pyrrole nucleus to assemble the natural product in a remarkably short synthesis (*Angew. Chem. Int. Ed.* **2008**, *47*, 3004). This strategy highlights that CH bond functionalization can positively streamline synthesis, and provides the first demonstration of the groups efforts to install metal catalyzed C–H bond functionalization as an enabling strategy for chemical synthesis.



The EPSRC Mass Spectrometry service at Swansea provided an extremely rapid and efficient mechanism for us to characterise our compounds using the High Resolution techniques. This service certainly expedited our ability to publish our work quickly and continues to help us develop new synthetic chemistry.