Synthetic Versatility in C—H Oxidation: A Rapid Approach to Differentiated Diols and Pyrans from Simple Olefins

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Conventionally, C—H oxidation reactions are used to install functional groups onto preformed carbon skeletons. The use of C—H oxidation to transform simple starting materials into highly versatile intermediates, which enable rapid access to a range of complex target structures is a new area with tremendous potential in synthesis. To this end, we have developed a Pd(II)/sulfoxide-catalyzed allylic C—H oxidation to form *anti*-1,4-dioxan-2-ones homoallylic oxygenates. These versatile building blocks are rapidly elaborated to differentiated *syn*-1,2-diols, stereodefined amino polyols, and *syn*-pyrans, structures ubiquitous in medicinally important complex molecules found in Nature. We also demonstrate that a C—H oxidation approach to the synthesis of these motifs is orthogonal and complementary to other state-of-the-art methods.