Dearomative Functionalization with Arenophiles

Emma H. Southgate and David Sarlah

Dearomatization of aromatic compounds is a fundamental synthetic strategy that provides direct and efficient access to a wide range of valuable natural products, pharmaceuticals, and materials, using simple and abundant sources of hydrocarbons. Despite substantial achievements and developments in this area, dearomative alkene-like functionalizations, such as hydroboration, dihydroxylation, and epoxidation, are still virtually nonexistent. We have developed a new dearomative platform using small organic molecules, defined herein as *arenophiles*, which can engage arenes in *para*-photocycloaddition and enable chemoselective *in-situ* transformations of the resulting adducts. Based on the desired level of functionalization, these cycloadducts can undergo subsequent cycloreversion to deliver a diene or fragmentation to give tetra- or hexafunctionalized carbocycles. This synthetic strategy bridges the gap between limited dearomative options and the vast area of olefin functionalization chemistry. As a first foray into dearomative functionalization processes, we have developed a formal dihydroxylation and diaminodihydroxylation of benzene and naphthalene derivatives.