

Arenophile-Mediated Dearomative Reductions

Mikiko Okumura and David Sarlah

Dearomative functionalizations of simple aromatic compounds provide a rapid access to complex small molecules that are common motifs in many pharmaceuticals, agrochemicals, and natural products. However, due to the high resonance stability of arenes, such transformations are intrinsically challenging and have only seen limited developments, employing harsh conditions. Using a visible-light-mediated [4+2] cycloaddition of arenes and arenophiles as a dearomative platform, we have developed a novel dearomative reduction protocol of simple arenes with diimide as the reductant. Through the cycloreversion or fragmentation of the arenophile moiety, this methodology enables rapid access to a diverse set of structures including 1,3-cyclohexadienes, 1,4-diaminocyclohex-2-enes, and 1-aminocyclohex-3-enes that are not synthetically accessible through existing dearomatizations. Additionally, this methodology was applicable to polynuclear arenes as well as substrates containing sensitive functional groups, such as benzylic heteroatoms and halogens, which have proven particularly difficult under known dearomative reductions.

