

# SESSION II: SPEAKER ABSTRACTS

## Palladium-catalyzed Dearomative 1,4-*syn*-aminofunctionalizations

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Aromatic compounds represent one of the most abundant classes of molecules, produced on hundred million ton scales annually. The dearomatization of arenes is a fundamental synthetic strategy, providing a direct connection between simple, feedstock sources of hydrocarbons and valuable products. Nevertheless, while exceptionally powerful synthetic transformations, most of the dearomatized products need to be subjected to further manipulations to reach the desired level of complexity. Furthermore, there are relatively few methods available for the site-selective introduction of heteroatom functionality. To overcome this shortcoming, we have developed a one-pot protocol for a dearomative 1,4-*syn*-aminofunctionalization using readily available naphthalene derivatives and benzene. Palladium-catalyzed formal allylic substitution of the arene-arenophile *para*-cycloadducts, formed *via* visible light-mediated [4+2] photocycloaddition, with lithium enolates of ketones or esters, Grignard reagents, and amines as nucleophiles provides direct access to 1,4-*syn*-carboaminated products and 1,4-*syn*-diaminated products. These methods not only deliver products with exclusive 1,4-*syn* selectivity, but are also capable of undergoing highly enantioselective transformations, thus demonstrating the power of these protocols as a means of enantioselective desymmetrization. Moreover, the resulting 1,4-*syn*-carboaminated/diaminated products are amenable for further derivatizations, which effectively installs various functionalities onto the dearomatized carbocycles. Overall, these novel dearomative 1,4-*syn*-aminofunctionalizations offer straightforward access to complex structures from simple arenes, enabling rapid formation of highly functionalized building blocks that are otherwise difficult or not possible to synthesize through existing dearomative strategies.

