
ortho-Selective Dearomative [2+2+2] Photocycloadditions of Bicyclic Aza-Arenes

**Significance:** Dearomatization of (hetero)arene molecules is an ongoing goal in medicinal chemistry, as the increased three-dimensionality of the resulting molecules may have improved drug-like qualities. Glorius, Houk and co-workers report highly ortho-selective photocycloadditions of bicyclic heteroarenes, leveraging the strained bicyclo[1.1.0]butanes as reactive partners to generate highly functionalized, medicinally-relevant molecular scaffolds.

**Comment:** The authors ruled out thermal background reactivity by performing the reaction in MeCN at 100 °C. DFT studies are in support of an EnT mechanism; however, additional studies are underway to elucidate other productive pathways which may be operative.

**Selected examples:**

- 89% yield
- 2 mmol scale: 79% yield
- 44% yield
- 45% yield
- 67% yield
- 80% yield

- 68% yield
- 45% yield
- 56% yield
- 66% yield

**ortho-Cycloaddition of a naphthalene derivative:**

- 33% yield

**Selected synthetic modification:**

- 85% yield