Modified Flavins Permit Catalytic Reductive Cyclization

**Significance:** Storch and co-workers report a novel class of reduced air-stable flavin photocatalysts that, upon photoexcitation, permit the catalytic reductive cyclization of barbituric acid derivatives and, therefore, replace the rare-earth reductant SmI\(_2\) previously used to achieve this transformation. By using a catalytic system consisting of the flavin photocatalyst, triethylamine, and cysteine as a hydrogen-atom donor, along with \(\alpha\)-terpinene as a superstoichiometric reductant, the bicyclic products could be obtained in poor to excellent yields.

**Comment:** Whereas reductive transformations are well known for DNA photolyase enzymes, molecular flavins have not been used previously to achieve this reactivity. By introducing an additional substituent in the 6-position, the authors found the corresponding flavins to be air-stable in their reduced form, opening up a plethora of possibilities for catalytic reductive transformations. We look forward to the synthetic potential of this novel concept being revealed, especially in the context of asymmetric catalysis.

**Proposed Mechanism**

**Selected Examples**

8 examples
25–90% yield