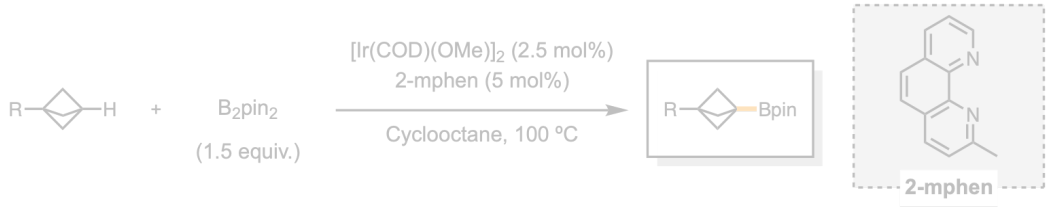
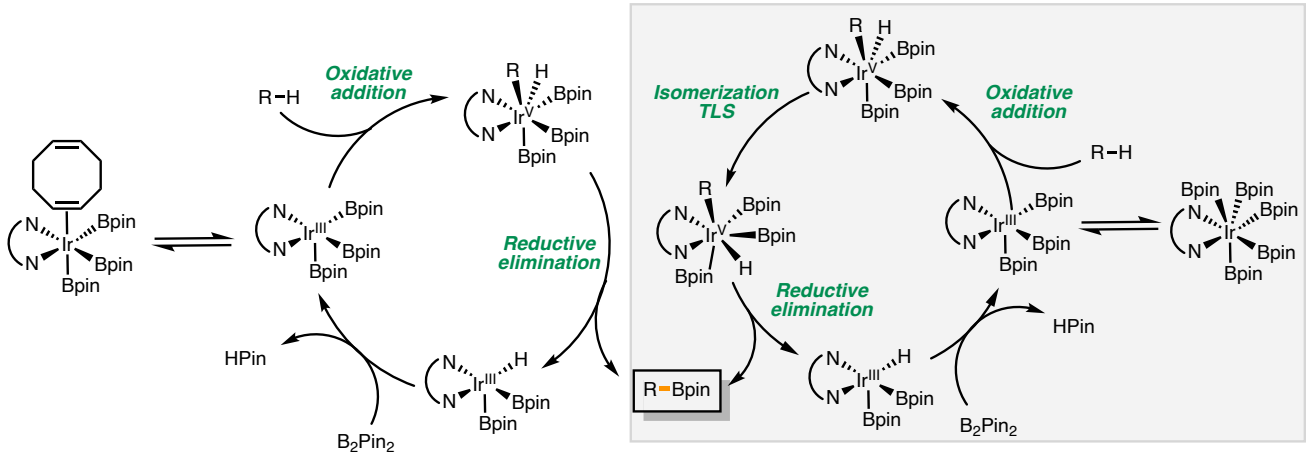
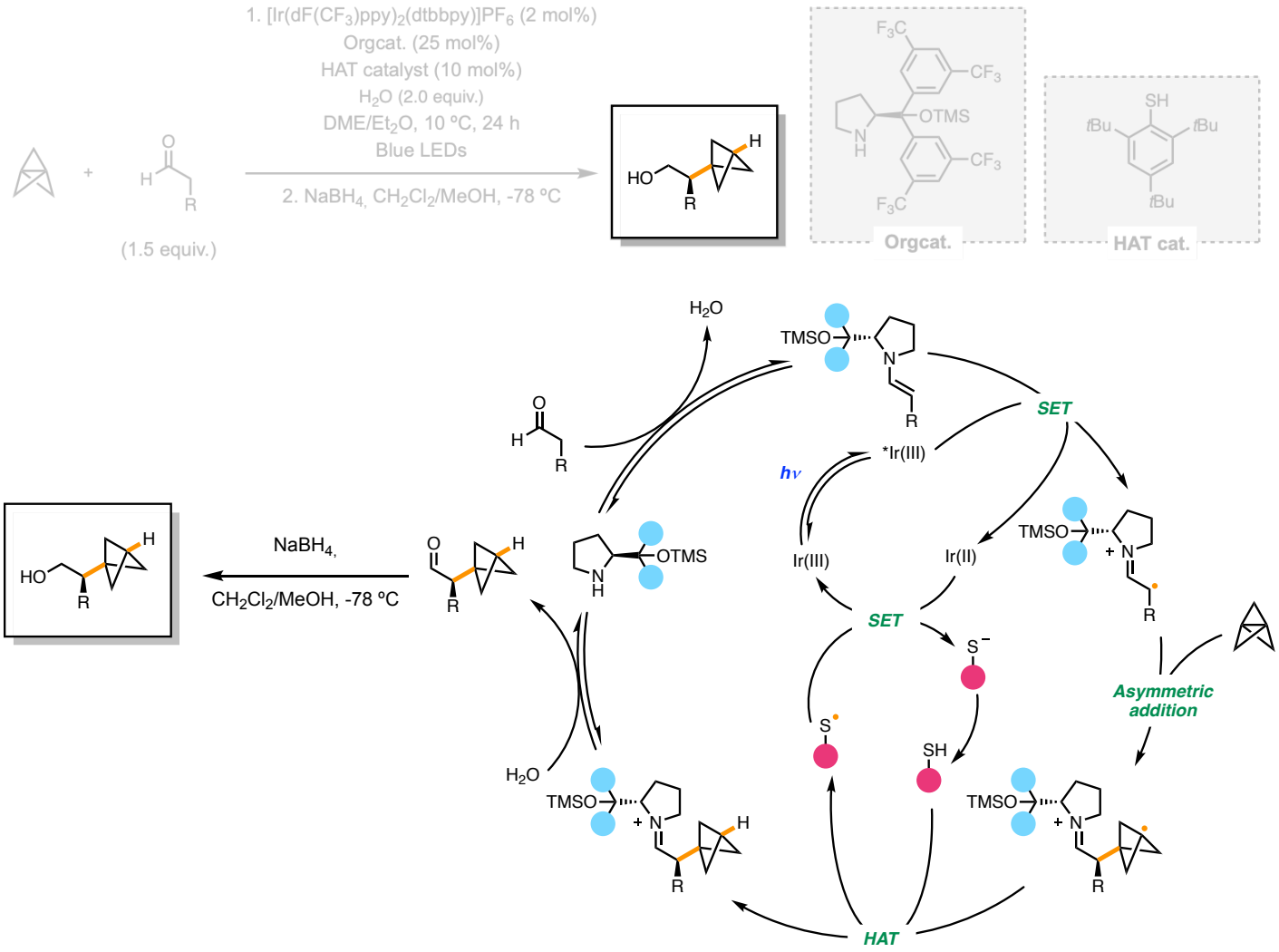
1. Draw the mechanism proposed by the authors and spot the differences with the general established C-H borylation mechanism (*Nat. Chem.* **2023**, *15*, 685-693). [★★]





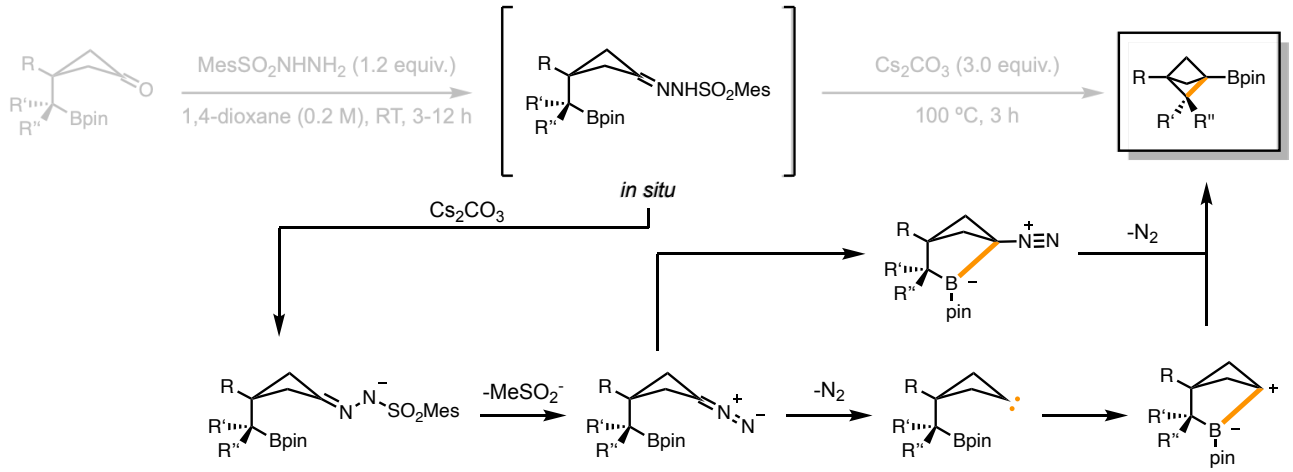
Through mechanistic studies and DFT calculations, the authors proposed that the turnover limiting step consists in an isomerization of the seven coordinate Ir(V) species, which brings the BCP and boron fragment together the BCP and reduces the energy barrier, facilitating the reductive elimination of the final alkyl boronic ester product (see **Figure 5b** of the manuscript). The high s-character of the bridgehead position is proposed as the main hypothesis of why this tertiary center can undergo facile oxidative addition with the iridium center.

2. Identify the product and propose a plausible mechanism for this transformation reported by Anderson and co-workers (*Nat. Commun.* **2021**, *12*, 1644-1653). [★★]



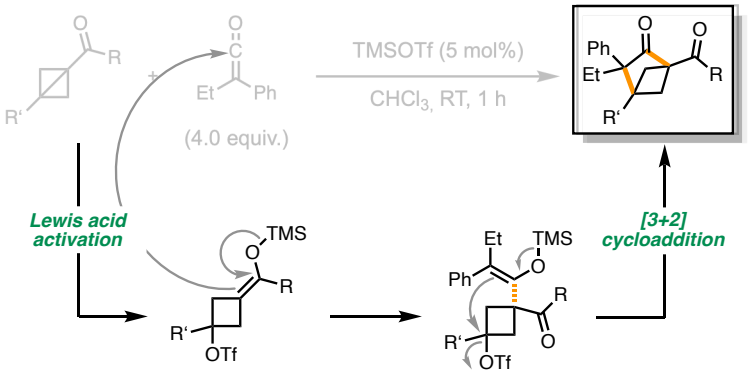
By combining photoredox catalysis and organocatalysis, the authors were able to produce α-chiral bicyclo[1.1.1]pentanes (BCPs) in high yield and enantioselectivity. The condensation between the Jørgenson-type organocatalyst and the aldehyde moiety forms the corresponding enamine. The latter then enters the photocatalytic cycle to generate the corresponding α-alkyl radical, which attacks bicyclobutane (BCB) in an enantioselective manner thanks to the organocatalyst. After a reductive hydrogen atom transfer (HAT) event and hydrolysis of the iminium ion, the corresponding coupling product is released. Final reduction conditions afford the desired alcohol product.

3. Draw the structures of the intermediate and the final product of the following reaction reported by Quin and co-workers. What is the name of this transformation? Propose and explain a plausible mechanism (*Nat. Chem.* **2021**, *13*, 950-955). [★★]



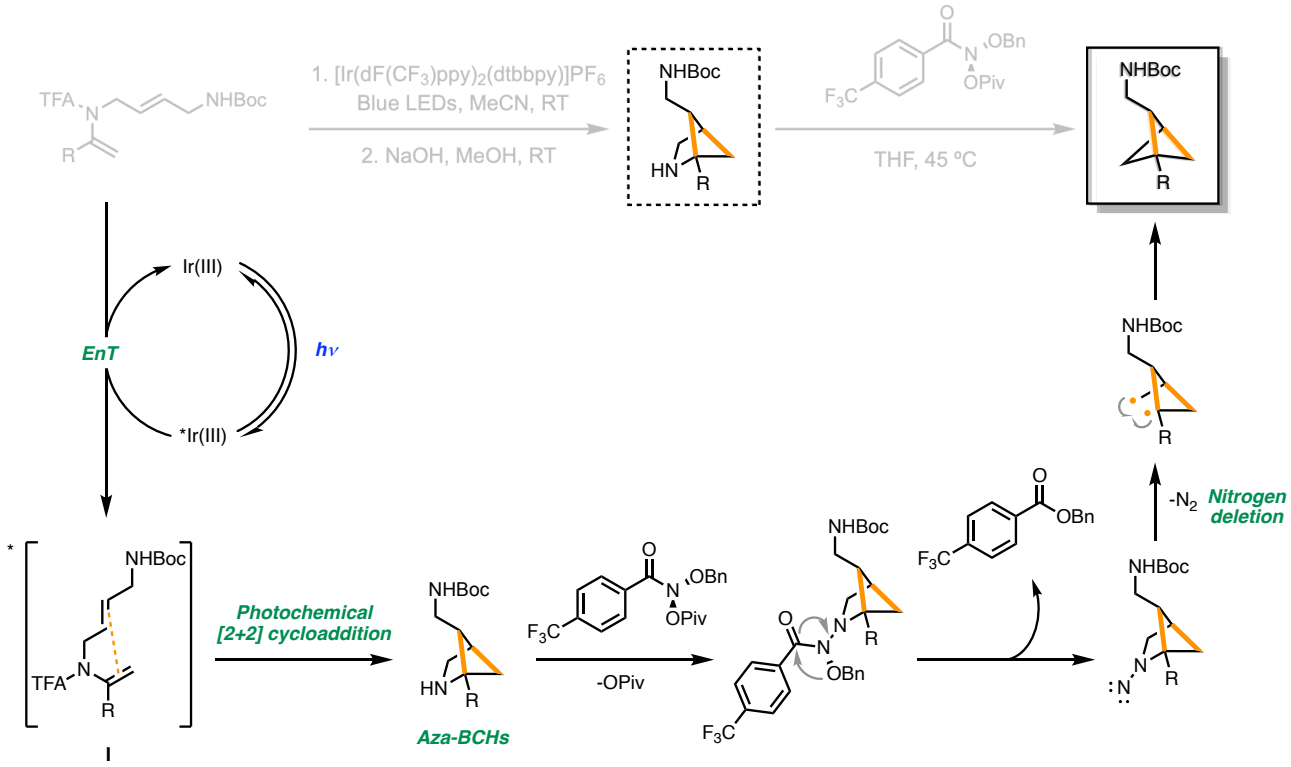
Mesitylene sulfonyl hydrazide acts as the activator reagent to promote the *in situ* hydrazone condensation and subsequent formation of the diazo intermediate, which is crucial for the Barluenga–Valdés coupling (see *Nat. Chem.* **2009**, *1*, 494-499).

4. Identifying the product of the following transformation and propose a plausible mechanism for this transformation reported by Studer and co-workers. What is the role of TMSOTf? (*ACIE* **2023**, *62*, e20230477). [★★]



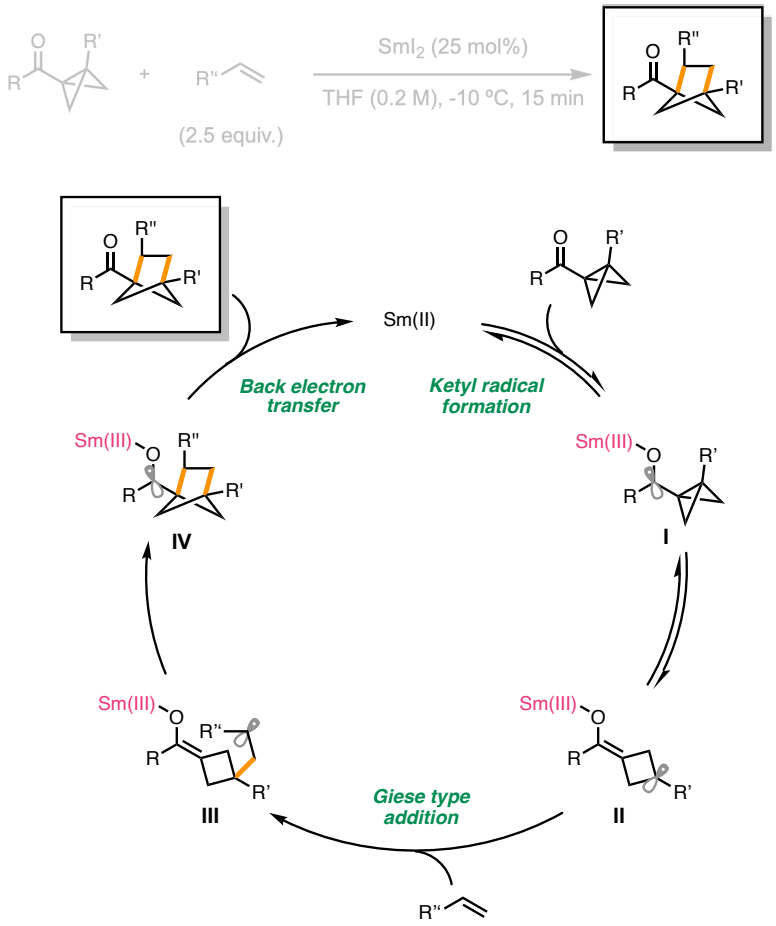
In this methodology, the authors were able to synthesize substituted bicyclo[2.1.1]hexan-2-ones in a metal-free fashion, using TMSOTf as Lewis acid catalyst. The activated BCB ketone reacts with the ketene counterpart to form a TMS-enolether, which undergoes [3+2]-cycloaddition ring closure to afford the desired BCH product.

5. A collaboration between Sarpong and Janssen reported a two-step route towards the synthesis of bridge-functionalized BCPs. Draw the structure of the product resulted of the first step. Propose and explain a plausible mechanism for the entire route (*J. Am. Chem. Soc.* **2023**, *145*, 10960-10966). [★★★]



The *N*-allyl enamide starting material interacts with the excited Ir photocatalyst in an energy transfer (EnT) event, resulting in the formation of the triplet-excited state intermediate **I**. **I** then reacts via intramolecular [2+2] addition, resulting in the formation of an aza-BCH framework. Using conditions previously reported by Levin (see *Nature* **2021**, 593, 223–227), the authors transformed these aza-BCHs structures into the final BCPs cores through nitrogen deletion mechanism.

6. Identify the product and propose a plausible mechanism for this samarium-catalyzed methodology reported by Procter and co-workers. (*Nat. Chem.* **2023**, *15*, 535-541). [★★★]



Samarium iodide (SmI_2), a well-stablished stoichiometric reagent, is employed in catalytic manner in this transformation where the authors were able to synthesize bicyclo[2.1.1]hexan-2-enones via electron-deficient alkene insertion into BCB ketones. Single electron transfer (SET) reduction of the BCB starting material with SmI_2 results in the formation of the ketyl radical species **I.** After ring opening, planar cyclobutyl radical **II** is formed, which attacks the alkene moiety in a Giese-type fashion to form radical species **III.** Radical rebound of **III** on to the Sm-enolate affords radical **IV,** which after a final back electron event leads to the formation of BCHs final product and the regeneration of the Sm(II) catalyst.