**The Power of Light in Hexadehydro-Diels–Alder Chemistry**

Significance: The authors demonstrate the efficient formation of reactive benzyne intermediates through photochemically initiated hexadehydro-Diels–Alder (HDDA) cycloisomerization reaction of multi-yne precursors. The reported photochemical transformation occurs at lower temperatures than the thermal version of the HDDA.

Comment: The authors also report that the resulting benzyne intermediates behave identically to those obtained through thermal HDDA reactions. The subsequent, highly efficient trapping reactions with π-donors and nucleophilic agents demonstrate the application of this method to access more elaborate structures.