Enantioselective [3+2] Annulation via C–H Activation Catalyzed by Iridium

**Significance:** The activation/functionallization of aromatic C–H bonds has become one of the main objectives of organometallic chemistry and catalysis. Specifically, the use of directing groups has allowed a vast array of carbon atom functionalization processes to proceed without the need to activate by halogenated or metalation at that carbon. One challenge in this field is the continued development of enantioselective variants which allow the installation of increased molecular complexity from simple and readily available starting materials.

**Comment:** The authors report the enantioselective iridium-catalyzed [3+2] annulation by way of C–H activation. The chiral diene ligand (S,S)-Me-tfb* gave the highest levels of enantioselectivity. A broad scope of diversely substituted nitrogen-substituted benzo-fused carbocycles can be obtained with excellent yields, regioselectivities, and diastereoselectivity. The authors also propose a mechanism involving an Ir–π-allyl intermediate.