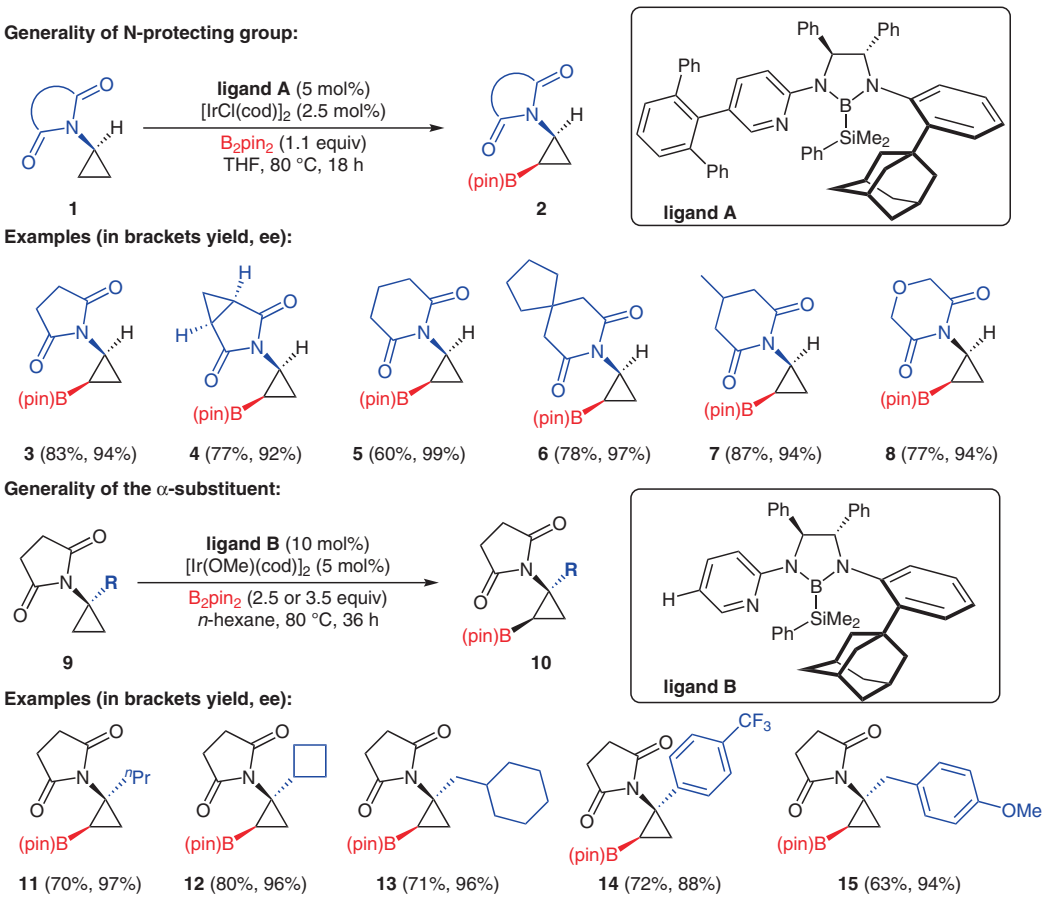
Y. SHI, Y. YANG, S. XU* (LANZHOU INSTITUTE OF CHEMICAL PHYSICS, UNIVERSITY OF CHINESE ACADEMY OF SCIENCES, BEIJING, AND HANGZHOU NORMAL UNIVERSITY, P. R. OF CHINA)

Iridium-Catalyzed Enantioselective C(sp^3)–H Borylation of Aminocyclopropanes
Angew. Chem. Int. Ed. **2022**, *61*, e202201463 DOI: 10.1002/anie.202201463.

Efficient Functionalization of Aminocyclopropanes



Significance: A judicious choice of both ligand and directing group (DG) plays an important role in the reactivity, regioselectivity, and stereoselectivity of a C–H functionalization reaction, with the cyclometalation typically dictating the observed regioselectivity. Whereas five-membered metallacycles are common, examples of asymmetric C–H functionalizations involving four- or six-membered rings are rare. The current report describes a method for the C–H borylation of aminocyclopropanes **1** and the identification of a suitable DG for achieving selective C–H borylation while avoiding competing σ-bond hydroboration.

Comment: Several potential DGs were evaluated with the succinimide **3** leading to selective borylation of the vicinal C(sp^3)–H bond under iridium-catalyzed conditions, albeit with only 9% ee. Optimization of the ligand by increasing the steric bulk of the *ortho* substituent on the *N*-aryl ring led to significantly enhanced enantioselectivities, whereas tuning of the pyridine C5 substituent permitted a range of both N-protecting groups (**3–8**) and α-substituents (**11–15**) to be tolerated in the process. A gram-scale preparation and several synthetic applications of the products are demonstrated through both manipulation of the DG and cross-coupling of the BPin moiety.

SYNFACTS Contributors: Paul Richardson, Carmen Irizarry-Garcia (Pfizer)
Synfacts 2022, 18(08), 0839 Published online: 19.07.2022
DOI: 10.1055/s-0041-1738409; **Reg-No.:** V08222SF