Inherently chiral cavitands through ionic catalyst-controlled cross-coupling

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Cavitands have emerged as privileged architectures in supramolecular chemistry. Nonetheless, achieving structural diversity and tunability through heterofunctionalization along the rims of macrocycles has remained a formidable challenge. As a rudimental example, stepwise conversion of C_{4v}-symmetric scaffolds to inherently chiral ABCD patterns is synthetically impractical owing to the low theoretical yields (0.8%) and the need for chromatographic enantioseparation. We have developed a catalytic desymmetrization strategy to access inherently chiral cavitands. Through engineering ionic chiral palladium catalysts, diverse functionalities, including aryl, alkenyl, alkynyl, and amino groups, can be installed on the large rims with high site- and stereoselectivity. An adaptable stepwise protocol has been established to furnish designer ABCD-type cavitands in accordance with the choreography of coupling partners. Experimental and computational studies reveal synergistic electrostatic steering and electrostatic catalysis by the ionic catalyst–substrate interactions.

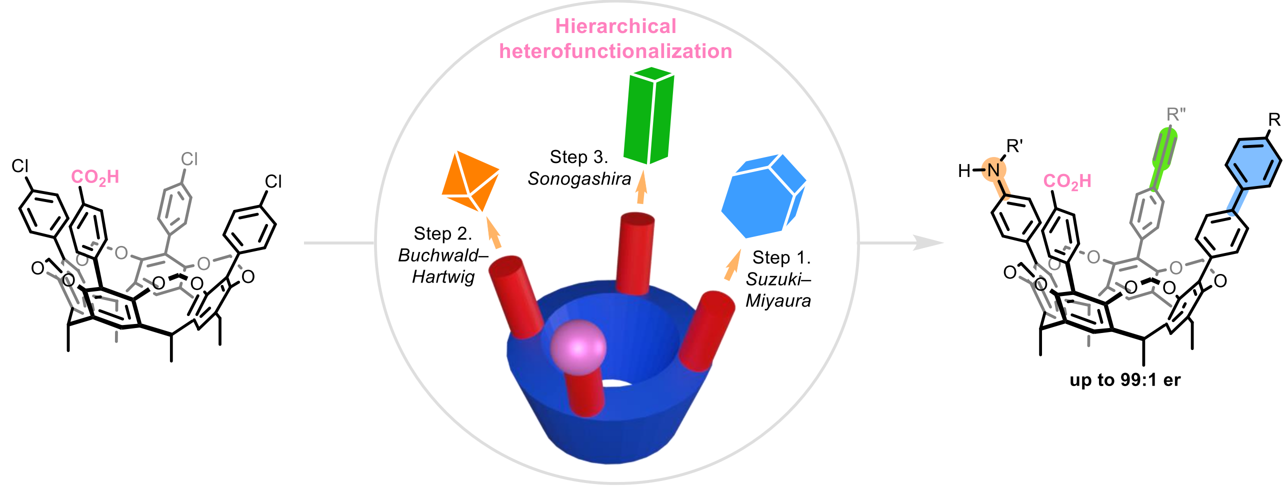

Figure 1. Catalyst-controlled stepwise cross-coupling reactions to access inherently chiral cavitands

Reference
[1] Li, M.; Ho, C. K. S.; On, I. K. W.; Gandon, V., Zhu, Y. *Chem* **2024**, DOI:10.1016/j.chempr.2024.06.012

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