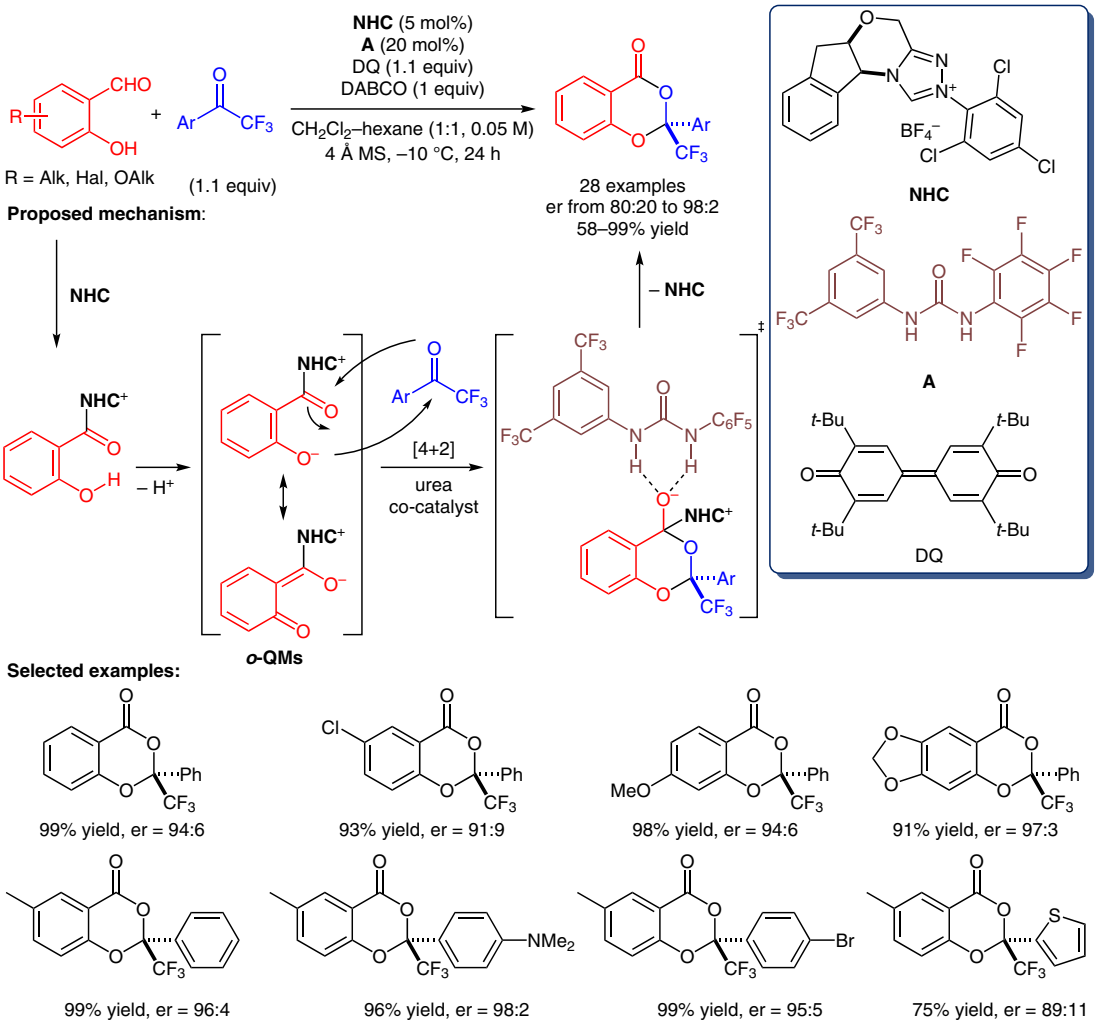
X. CHEN, H. WANG, K. DOITOMI, C. Y. OOI, P. ZHENG, W. LIU, H. GUO, S. YANG, B.-A. SONG, H. HIRAO*, Y. R. CHI* (NANYONG TECHNOLOGICAL UNIVERSITY, SINGAPORE; GUIZHOU UNIVERSITY, GUIYANG, CITY UNIVERSITY OF HONG KONG, AND FUDAN UNIVERSITY, SHANGHAI, P. R. OF CHINA)

A Reaction Mode of Carbene-Catalyzed Aryl Aldehyde Activation and Induced Phenol OH Functionalization
Nat. Commun. **2017**, *8*, 15598.

NHC-Catalyzed Oxidative [4+2] Annulation of 2-Hydroxybenzaldehydes and Ketones



Selected examples:

Significance: Chi and Hirao report an oxidative NHC-catalyzed [4+2] annulation of 2-hydroxybenzaldehydes with trifluoromethyl aryl ketones. This synthetic approach furnishes benzo[1,3]dioxin-4-one derivatives in good to excellent yields and enantioselectivites. Several of these reported compounds show antifungal activities.

Comment: The azolium-bound *ortho*-quinone methide intermediate (***o*-QMs**), obtained from the 2-hydroxybenzaldehyde by NHC catalysis in the presence of a weak oxidant (DQ), undergoes the oxidative [4+2] annulation with ketones. The enantioselectivities were increased by the addition of a urea co-catalyst (**A**). DFT calculations support the proposed mechanism.

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Key words
heterocycles
[4+2] annulation
N-heterocyclic carbenes
hydroxybenz-aldehydes
aryl trifluoromethyl ketones
benzodioxinones