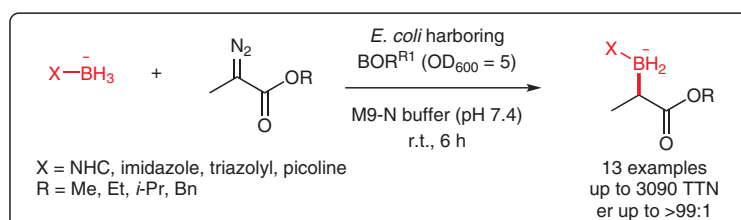
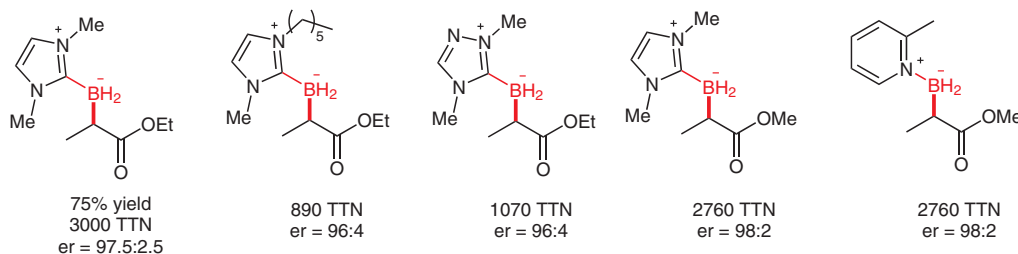


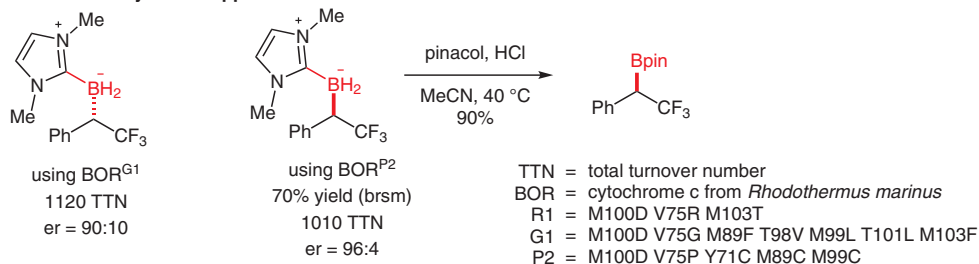
Whole-Cell-Catalyzed Carbenoid B–H Insertion



Selected examples:



Further modification and synthetic application:



Significance: The Arnold group reports a whole-cell-catalyzed organoboron synthesis through carbenoid B–H insertion. Identification of an appropriate boron reagent that is stable and active under physiological conditions and site-saturation mutagenesis of the wild-type cytochrome *c* from *Rodothermus marinus* to afford a series of *Escherichia coli* cells that catalyze the desired transformation permitted the synthesis to be performed with remarkable turnover numbers and enantioselectivities. Interestingly, lower turnover frequencies were obtained by using either purified protein or cell lysate. Turnover numbers could be increased up to 15300 TTN by portionwise addition of substrates.

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Comment: Chiral organoboron compounds are versatile synthetic intermediates, and therefore their asymmetric synthesis is of great interest. However, no organism is known to form the desired C–B bond. As a continuation of their previous work on enzyme-catalyzed carbenoid insertions (*Science* **2016**, 354, 1048), the authors again impressively demonstrate that selective DNA modification can produce microorganisms that are able to achieve this unnatural bond formation in high efficiency (up to 400 times more active than published metal-catalyzed systems) and with high selectivity.