Facial selectivity in the bis(oxazoline)-copper mediated Michael addition of indoles to benzylidene malonates can be dramatically influenced either by modifying the transition state with additives or having a nontraditional excess of metal in relation to ligand. The paradigm followed in many asymmetric catalytic systems, that an excess of chiral ligand with respect to the metal should improve enantioselectivity because a background reaction by free metal is suppressed, is not applicable here. The use of electron richaza-bis(oxazoline) ligands was found to accelerate the Pd-catalyzed Tsuji-Trost allylation of malonates with allylic acetate. Improved enantioselectivity was achieved through accelerated oxidative addition, allowing effective equilibration of the meso intermediate to take place. Simple monosulfonated cyclohexane-1,2-diamines are highly enantioselective organocatalysts for the conjugate addition of ketones to nitro olefins. Moreover the irreversible formation of pyrrolderived has been recognized as a reaction pathway for catalyst deactivation.

![Scheme 1](image)

**Scheme 1.** Complex molecules of interest a. Traceless lithiation–borylation–protodeboronation strategy. b. Structure of hydroxyphthioceranic acid, and recent previous syntheses. Cb, N,N-diisopropyl carbamate; pin, Pinacol; LB, lithiation–borylation; LLS, longest linear sequence; TS, total number of steps.

The use of boronic esters as a removable group in organic synthesis allows the traceless synthesis of stereochemical arrays using a one-pot lithiation–borylation–protodeboronation sequence. To realize this strategy, a methodology for the protodeboronation of alkyl pinacol boronic esters was developed (Scheme 1). Formation of a boronate complex 1 with a nucleophile followed by oxidation with Mn(OAc)₃ which leads to radical intermediate 2 which can yield protodeboronated product in the presence of the hydrogen-atom donor 4-tert-butilcatechol (TBC). Iterative lithiation–borylation–protodeboronation (LBP) allows the coupling of smaller fragments to build-up long alkyl chains. This strategy was employed in the synthesis of hydroxyphthioceranic acid 3, a key component lipid of the cell-wall of the virulent mycobacterium tuberculosis, in just 14 steps (longest linear sequence) with full stereocontrol.

**Selected references**

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