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Ischia

New Catalytic Reactions Mediated by Organozincs

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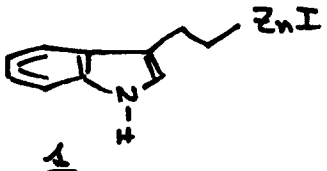
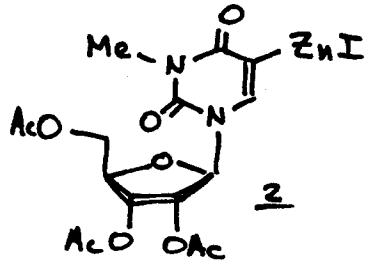
The carbon-zinc bond tolerates the presence of many organic functionalities and the preparation of polyfunctional organometallics such as 1 or 2 occurs in high yields

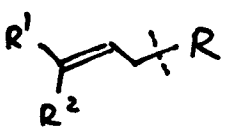


1

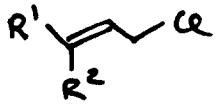


2

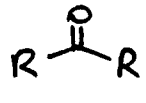
The low reactivity of R_2Zn or $RZnX$ can be greatly improved by transmetalations. The preparation of organocoppers by this method has been well studied in our group but the preparation of new stable (!) polyfunctional alkylcobalt(II) or alkyliron(III) species is also possible opening the door to many new synthetic applications.



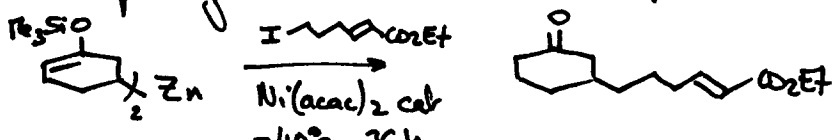
$\xleftarrow[S_N2 \text{ subst.}]{CoBr_2 \text{ cat.}}$



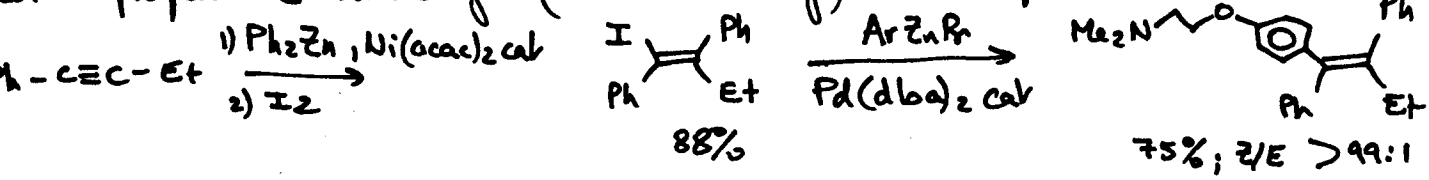
100% retention of the double bond stereochemistry

$RZnX \xrightarrow[CO\ (1atm)]{CoBr_2}$ 

Similarly new nickel(II) intermediates have been prepared and a new Csp^3-Csp^3 cross-coupling reaction has been developped. An extension of these reactions lead to



The development of a new stereoselective nickel catalyzed carbozincation which was used to prepare Z-tamoxifen (anticancer drug) in 2 steps:



Finally the first preparation of a non-stabilized chiral secondary organozinc reagent will be presented.