Transition Metal- & Solvent-Free Double Hydroboration of Nitriles

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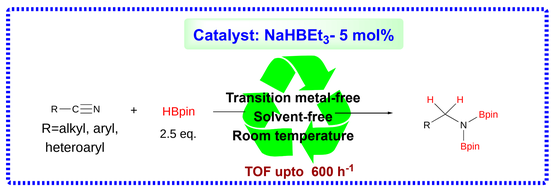
Abstract

Herein, we report a highly efficient, room temperature double hydroboration of nitriles under transition metal-free and solvent-free conditions using sodium triethyl borohydride as a catalyst. Up to 99 % yield of diborylated amine product could be obtained. Preliminary mechanistic studies reveal that the reaction proceeds in a step-wise manner; initial formation of a boryl-imine which then undergoes a second hydroboration to afford diborylated amine product.

Introduction

Hydroboration is the addition of hydrogen and boron bonds to unsaturated species, providing access to a wide range of organoborates. Organoborates act as versatile reagents in organic synthesis.

Amines have widespread utility in chemistry, ranging from the building blocks of proteins and many drug molecules to ligands for metals in synthetic and catalytic applications.

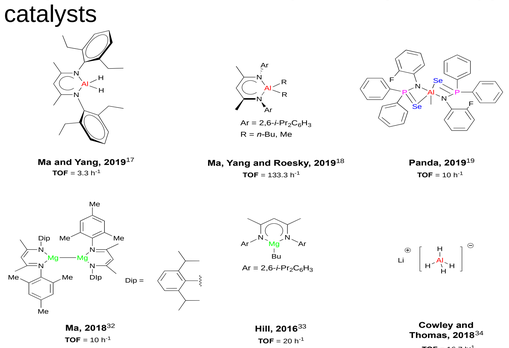


Conventional approaches: Reductive amination of aldehyde / ketones, N-alkylation of nitriles / ammonia

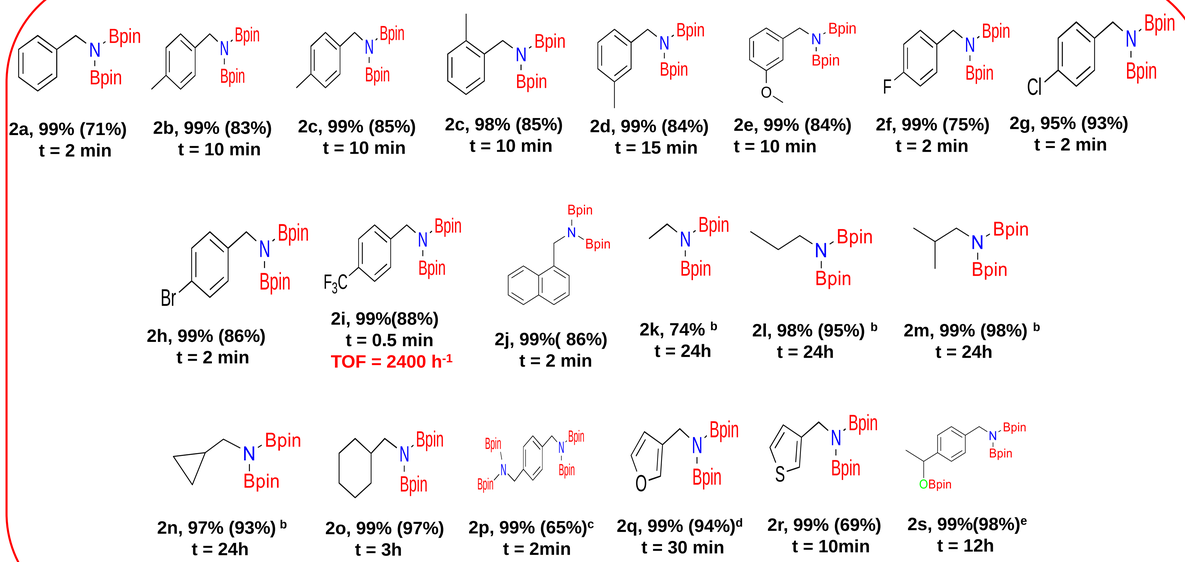
Disadvantages: Generate large amounts of waste, use of strong reductants incompatible with other groups.

Literature reports

s- and p-block elements have previously been applied as catalysts



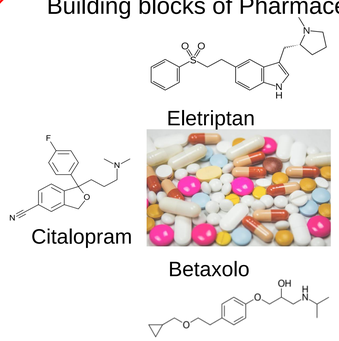
Results and Discussion



[a] Yields based on ^{1}H NMR; [b] Reaction mixture heated at 80^{o}C; [c] 4 eq. of HBpin was used; [d] 3.5 eq of HBPin was used; [e] 3.5 eq of Hbpin was used reaction mixture heated at 80^{o}C. Yields in the parentheses are the isolated yields when reaction carried out on a 0.5 mmol scale.

Applications of Amines

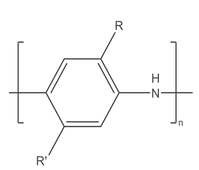
Building blocks of Pharmaceuticals



Agrochemicals

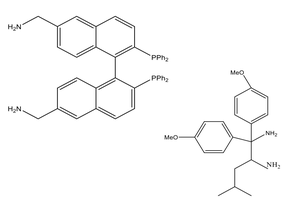
Dyes

Electroconducting Polymers

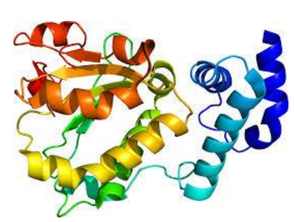


R =OCH_3; R'= H (PMOA)
R =OC_2H_5; R'= H(PEOA)
R =OC_4H_9; R'= H(PBOA)
R =OC_6H_{13}; R'= H(PHOA)
R = R'= OCH_3 (PDMOA)
R = R' =OC_2H_5 (PDEOA)
R = R' =OC_4H_9 (PDBOA)
R = R' =OC_6H_{13} (PDHOA)

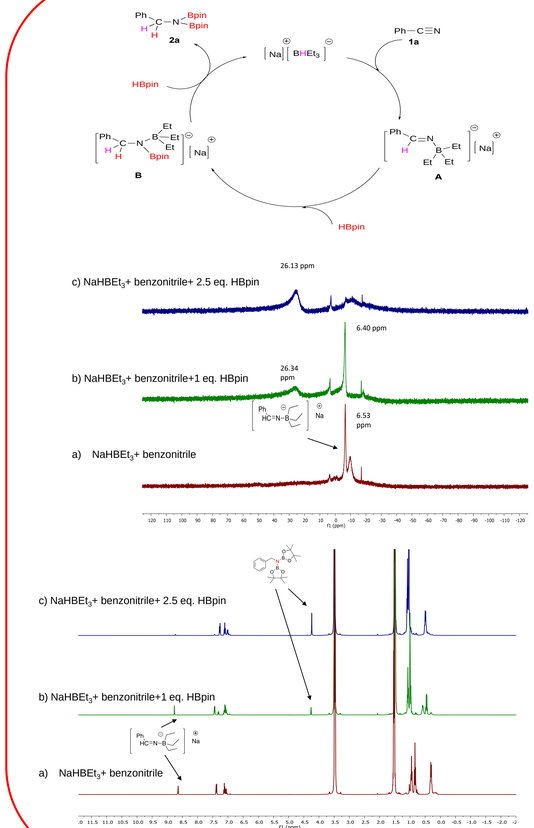
Amine based ligands



Building blocks of Protiens



Plausible Mechanism



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