SYNFACTS

Highlights in Current
Synthetic Organic
Chemistry

REPRINT

Thieme

Category

Metal-Mediated Synthesis

Key words

boronic esters

carbamates

lithium

boron

propargylic alcohols

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Enantioselective Synthesis and Cross-Coupling of Tertiary Propargylic Boronic Esters Using Lithiation-Borylation of Propargylic Carbamates

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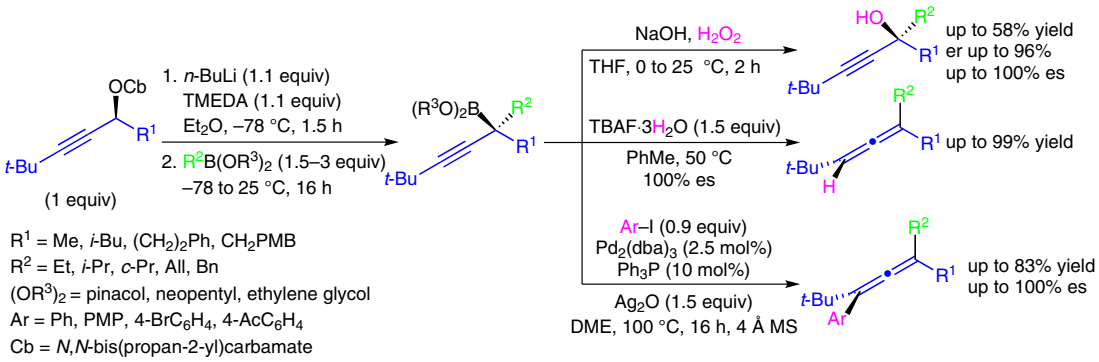
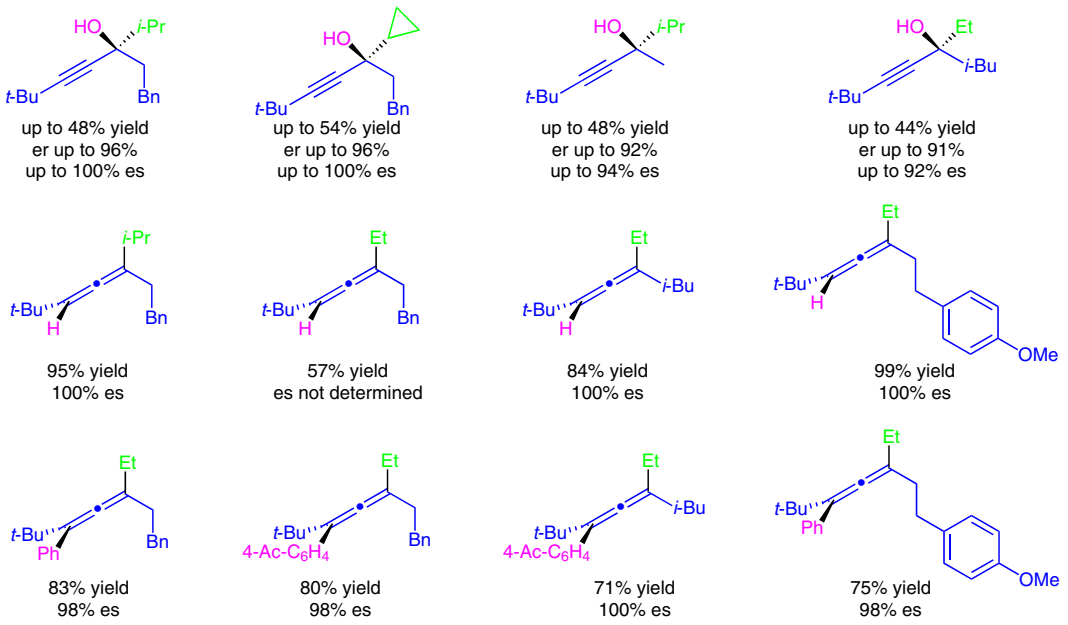
Enantioselective Synthesis of Tertiary Propargylic Boronic Esters



R^1 = Me, *i*-Bu, $(CH_2)_2$Ph, CH_2PMB
R^2 = Et, *i*-Pr, *c*-Pr, All, Bn
$(OR^3)_2$ = pinacol, neopentyl, ethylene glycol
Ar = Ph, PMP, 4-BrC_6H_4, 4-AcC_6H_4
Cb = *N,N*-bis(propan-2-yl)carbamate

Selected examples:



Significance: Tertiary propargylic boronic esters have been synthesized via lithiation–borylation of propargylic carbamates with very high enantioselectivity. These versatile intermediates can readily be converted into the corresponding alcohols, tertiary allenes, and tetrasubstituted allenes with high enantiospecificity (es).

Comment: Tertiary allenes can be obtained in excellent yield and enantioselectivity by a simple protodeboronation of the tertiary propargylic boronic esters with TBAF. Tetrasubstituted allenes have been provided in high enantiospecificity by Suzuki–Miyaura cross-couplings of the tertiary boron species with aryl iodides.

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