Category

Metal-Mediated Synthesis

Key words

allylsilanes

asymmetric lithiation

carbamates

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Asymmetric Synthesis of Tertiary and Quaternary Allyl- and Crotylsilanes via the Borylation of Lithiated Carbamates
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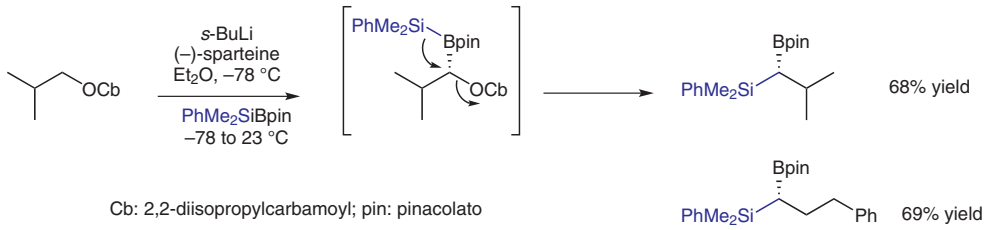
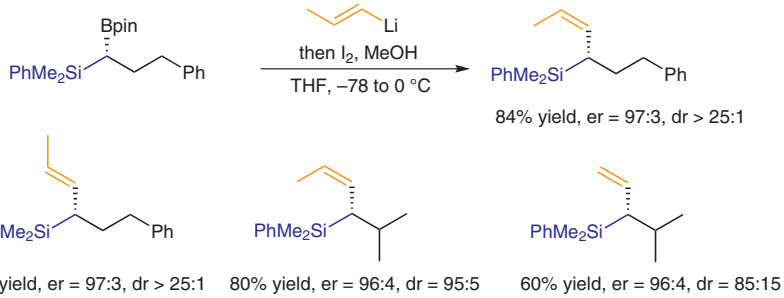
Synthesis of Tertiary and Quaternary Allyl- and Crotylsilanes

Silaboration of lithiated carbamates:

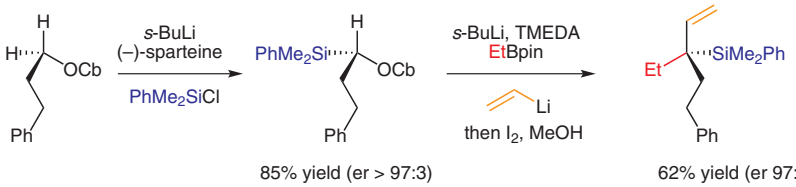


Cb: 2,2-diisopropylcarbamoyl; pin: pinacolato

Olefination of silaboronates:



Synthesis of quaternary allylsilanes:



Significance: The authors disclose synthetic methods for the preparation of tertiary and quaternary allyl- and crotylsilanes. A lithiation–borylation sequence of alkyl carbamates with silaboronates leads to tertiary silanes with high enantiomeric and diastereomeric ratios. The quaternary allylsilanes were obtained after a sequential lithiation–silylation and lithiation–borylation procedure with comparable enantiomeric ratios.

Comment: The lithiation–borylation pathway was chosen, since the primary silyl-substituted lithiated carbamate intermediate was configurationally unstable. However, the secondary silyl-substituted lithiated carbamates in the reaction sequence towards the quaternary products proved to be configurationally stable at low temperature. The absolute stereochemistry of the isolated products was determined by X-ray crystal structure analysis.

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