Construction of Quaternary Stereogenic Centers from Tertiary Boronic Esters

**Significance:** The authors report on a lithiation–borylation reaction with subsequent one-carbon homologation or vinylation. The ready availability of the starting materials, broad range of substrates, bearing versatile functional groups with quaternary stereogenic centers, and very high enantioselectivities are noteworthy.

**Comment:** This methodology allows the formation of quaternary stereogenic centers with high enantioselectivity. It should be mentioned that products can be obtained exhibiting contiguous quaternary and tertiary stereogenic centers with high diastereoselectivities.

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**Bpin**

\[ \text{R}_1 \text{Bpin} \]

1) CH\(_2\)Br\(_2\), n-BuLi

THF, –78 °C to r.t.

2) H\(_2\)O\(_2\), NaOH

er up to >99:1

37–88% yield

**Bpin**

\[ \text{R}_1 \text{Bpin} \]

1) MgBr

THF, r.t.

2) I\(_2\), NaOMe

MeOH, –78 °C

er up to >99:1

58–92% yield

**Bpin**

\[ \text{R}_1 \text{Bpin} \]

1) LDA, –118 °C

THF–Et\(_2\)O–n-pentane (4:4:1)

\[ \text{LDA, –118 °C} \]

\[ \text{R}_1 \] (1 atm CI)

73–96% yield

dr up to 24:1

er > 99:1

**Synthesis of (+)-(S)-sporochnol:**

\[ \text{MeO} \]

\[ \text{Bpin} \]

2 steps

84% yield

er = 97:3

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