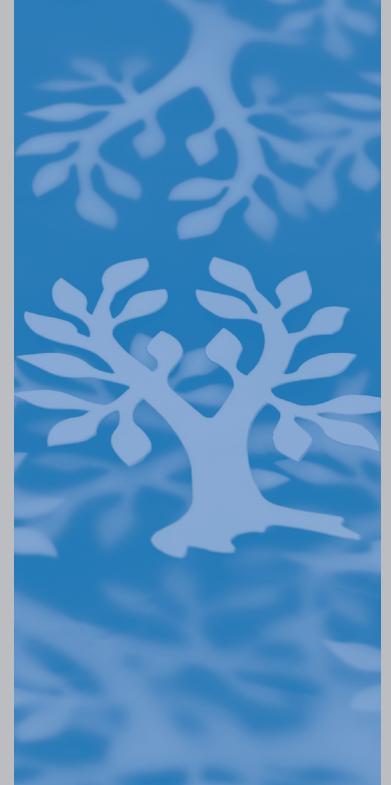
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# SYNFACTS Highlights in Current Synthetic Organic Chemistry

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#### Category

Metal-Mediated Synthesis

#### Key words

alkynylation

boron

enantiospecificity

Y. WANG, A. NOBLE, E. L. MYERS, V. K. AGGARWAL\* (UNIVERSITY OF BRISTOL, UK) Enantiospecific Alkynylation of Alkylboronic Esters *Angew. Chem. Int. Ed.* **2016**, *55*, 4270–4274.

### **Alkynylation of Alkylboronic Esters**

$$\begin{array}{c} \text{Bpin} \\ \text{R}^{1} \\ \text{R}^{2} \end{array} + \\ \text{Br} \\ \begin{array}{c} 1. \text{ LDA, Et}_{2}\text{O} \\ -95 \, ^{\circ}\text{C, 1 h} \\ -95 \, ^{\circ}\text{C to r.t., 1 h} \end{array} \\ \begin{array}{c} 1. \text{ work-up} \\ 2. \text{ TBAF, DMF} \\ 60 \, ^{\circ}\text{C, 1 h} \\ \end{array} \\ \begin{array}{c} \text{R}^{3} \\ \text{Bpin} \\ \text{R}^{2} \end{array} + \\ \begin{array}{c} \text{OCb} \\ \hline \\ 2. \text{ I}_{2}, \text{ MeOH} \\ -95 \, ^{\circ}\text{C, 1 h} \\ \end{array} \\ \begin{array}{c} 1. \text{ work-up} \\ \hline \\ 2. \text{ f-BuLi, 0 } ^{\circ}\text{C} \end{array} \\ \begin{array}{c} \text{R}^{3} \\ \text{R}^{1} \end{array} \\ \begin{array}{c} \text{R}^{3} \\ \text{R}^{2} \end{array} \\ \begin{array}{c} \text{R}^{3} \\ \text{R}^{3} \end{array} \\ \begin{array}{c} \text{H, Alk, Ar, All} \\ \end{array} \\ \begin{array}{c} \text{R}^{3} \\ \text{R}^{3} \end{array} \\ \begin{array}{c} \text{H, Alk, Ar, All} \\ \end{array}$$

#### Selected examples:

**Significance:** The authors report an enantiospecific deborylative alkynylation of secondary and tertiary alkyl pinacolboronic esters through a Zweifel-type alkenylation followed by a 1,2-elimination reaction in high yields and with excellent levels of enantioselectivity.

**Comment:** Internal and silyl-protected alkynes can be obtained by introducing suitable carbonor silicon-based electrophiles after the base-mediated 1,2-elimination reaction.

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