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Stereo- and Regiocontrolled Methylboration of Terminal Alkynes

**Zirconium-Catalyzed Carboalumination–Transmetalation**

**Significance:** The authors report a zirconium-catalyzed carboalumination of terminal alkynes followed by in situ transmetalation with $i$-PrOBpin to form trisubstituted alkenyl boronic esters in good to excellent regioselectivities.

**Comment:** Interestingly, no reaction was observed for substrates bearing Lewis basic functional groups (i.e., an ester). To overcome this problem, the authors enhanced the reactivity of these substrates by the addition of modified methylaluminoxane (MMAO-12). Furthermore, the utility of the methodology is presented by performing gram-scale reactions with significant improvements compared to reported procedures.

**Selected examples:**

- 70% yield, $rr = 98.2$
  - 82% yield, $rr = 97.3$

- 75% yield, $rr = 96.4$

- 68% yield, $rr = 97.3$
  - 78% yield, $rr > 98.2$

- 85% yield, $rr = 95.5$

- 80% yield, $rr > 98.2$

- 61% yield, $rr > 98.2$
  - 74% yield, $rr = 97.3$

**Modified methylaluminoxane (MMAO-12, 1.0 equiv):**

- 88% yield, $rr = 98.2$

- 69% yield, $rr = 95.5$

- 33% yield, $rr = 98.2$

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SYNFACTS 2018, 14(08), 0854 Published online: 18.07.2018 DOI: 10.1055/s-0037-1609598; Reg-No.: P08718SF