Take Et instead of Me: Preparation and Application of a Novel Class of Stable Arylboronic Esters

**Preparation of Ar–B(Epin):**

\[
\begin{align*}
\text{Ar}^1 & \quad \text{B(OH)}_2 \\
(1.0-1.1 \text{ equiv}) & \\
\text{Br} & \\
\text{n-BuLi (1.1-1.2 equiv)} & \\
\text{B(OH)}_3 & \\
(2.0-2.4 \text{ equiv}) & \\
& \text{then} \\
\text{Epin (1.0-2.0 equiv)} & \\
& \text{6 examples} \\
& \text{78-91% yield}
\end{align*}
\]

**Selected examples:**

\[
\begin{align*}
\text{92% yield} & \\
\text{94% yield} & \\
\text{95% yield} & \\
\text{96% yield} & \\
\text{92% yield}
\end{align*}
\]

**Significance:** The synthesis and application of arylboronic 1,1,2,2-tetraethylene glycol esters, Ar–B(Epin), is disclosed. These aryl boronates are readily accessible via dehydrative esterification of boronic acids, metalation of aryl bromides or Miyaura borylation. Substitution of the methyl units of the pinacol esters Ar–Bpin by ethyl groups leads to higher stability, and the corresponding arylboronic esters Ar–B(Epin) are easily purified by column chromatography on silica gel.

**Comment:** The novel arylboronic esters show enhanced reactivity in Suzuki–Miyaura cross-couplings, providing the coupling products in excellent yields. These organoboron compounds represent a viable alternative to the commonly used arylboronic acids or pinacol esters.

**SYNFACTS Contributors:** Martin Oestreich, Hendrik F. T. Klare, Lucie Finck

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