T. WAKAMATSU, K. NAGAO, H. OHMIYA,* M. SAWAMURA* (HOKKAIDO UNIVERSITY, SAPPORO, JAPAN)

Synthesis of Trisubstituted Alkenylstannanes through Copper-Catalyzed Three-Component Coupling of Alkylboranes, Alkynoates and Tributyltin Methoxide

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### Significance:
The authors report a highly regio-selective copper-catalyzed synthesis of trisubstituted alkenylstannanes. Through a three-component coupling of alkylboranes, alkynoates and tributyltin methoxide, these trisubstituted alkenylstannanes are obtained in good yields and with high syn selectivity. The appropriate alkylboranes are easily accessible by hydroboration of the corresponding alkenes with the 9-borabicyclo[3.3.1]nonane (9-BBN-H) dimer.

### Comment:
Standard methods for the synthesis of alkenylstannanes described by Shirakawa and Hiyama include the palladium- or nickel-catalyzed carbostaking of internal alkynes with organostannanes which are somewhat difficult to prepare.

**Equation:**

\[
\begin{align*}
&\text{R}^1-\equiv-\text{CO}_2\text{Et} \\
&\text{CuOAc/}^{t}\text{BuOK} (10 \text{ or } 20 \text{ mol%}) \\
&\text{Bu}_3\text{SnOMe} (2.0 \text{ or } 4.0 \text{ equiv}) \\
&\text{dioxane, } 60 ^\circ \text{C} \\
&\text{R}^1\text{SnBu}_3 \text{CO}_2\text{Et} \quad \text{up to 88% yield syn/anti up to >99:1}
\end{align*}
\]

\[
\begin{align*}
&\text{E}^+ (1.2–2.0 \text{ equiv}) \\
&\text{R}^1\text{E} \text{CO}_2\text{Et} \quad \text{up to 80% yield}
\end{align*}
\]

\[
\begin{align*}
\text{R}^1 &= \text{Ph, } n\text{-Bu, } n\text{-Pent, } (\text{CH}_2)_3\text{phthalimide, } (\text{CH}_2)_3\text{OTHP, } C(\text{Me})_2\text{CH}_2\text{CO}_2\text{Me, } 4\text{-BrC}_6\text{H}_4, (\text{CH}_2)_3\text{OTIPS} \\
\text{R}^2 &= \text{Ph, } 4\text{-MeOC}_6\text{H}_4, 4\text{-MeOC}_2\text{C}_6\text{H}_4, 2\text{-MeC}_6\text{H}_4, \text{Me, } \text{CH}_2\text{OTHP, } \text{CH}_2\text{OBn, } 4\text{-FC}_6\text{H}_4, 2\text{-thienyl derivative}
\end{align*}
\]

Selected examples:

- **61% yield syn/anti = 91:9**
- **49% yield syn/anti > 99:1**
- **74% yield syn/anti > 99:1**
- **49% yield syn/anti > 99:1**
- **77% yield syn/anti = 96:4**
- **63% yield syn/anti = 93:7**
- **80% yield**
- **77% yield**