Synthesis of 2,5-Diarylated Thiophene 1,1-Dioxides

**Significance:** The authors disclose the palladium-catalyzed diarylation of distannylated thiophene 1,1-dioxide (electron-poor aryl coupling partners) and diiodo thiophene 1,1-dioxide (electron-rich aryl coupling partners) by Stille cross-coupling reactions to synthesize various 2,5-bis(aryl)thiophene 1,1-dioxides in moderate yields. Furthermore, the electrochemical and photophysical properties of these diarylated thiophene dioxides were investigated using cyclic voltammetry and fluorescence spectroscopy.

**Comment:** The corresponding distannylated thiophene 1,1-dioxides are obtained by treatment of 2,5-bis(trimethylsilyl)thiophene 1,1-dioxide with tetrabutylammonium fluoride (TBAF) and bis(tributyltin) oxide. A wide range of these diarylated thiophene dioxides show significant quantum yields, and their appropriate reduction and oxidation potentials may easily be tuned by the use of electron-donating and -withdrawing aryl groups.

\[
\begin{align*}
\text{method A:} & \quad \text{ArSnMe}_3 (2.5 \text{ equiv}) \\
& \quad \text{Pd}_2(\text{dba})_3 (5 \text{ mol\%}), \text{Ph}_3\text{As} (40 \text{ mol\%}) \\
& \quad \text{or Pd(PPh}_3)_4 (10 \text{ mol\%}) \\
& \quad \text{dioxane or PhMe, 100 °C} \\
\text{method B:} & \quad \text{ArBr (2.5 equiv)} \\
& \quad \text{Pd}_2(\text{dba})_3 (2.5 \text{ mol\%}), \text{Ph}_3\text{As} (20 \text{ mol\%}) \\
& \quad \text{dioxane, 100 °C} \\
& \quad \text{up to 58\% yield}
\end{align*}
\]