**Not-So-Triyne Route to Heteroarylene and Arylene Macrocycles**

**Representative reaction:**

\[
\text{TsN} \quad \text{TsN} \quad \text{TsN} \quad \text{TsN} \quad \text{TsN} \\
\text{DCE, r.t. to 60 °C} \\
45\% \text{ yield} \\
52\% \text{ ee}
\]

**Selected compounds:**

Significance: This is the first reported synthesis of macrocyclic \(\pi\)-conjugated structures featuring both benzene and heterocycle units. Isolated yields up to \(\sim 85\%\) and stereochemical purity up to \(\sim 95\%\) ee are reported, though it is difficult to achieve both simultaneously. Bis- and tri-thiophene substrates produce trimers. While absorbance maxima were red-shifted with increasing thiophene rings, fluorescence maxima were not, indicating poor conjugation through the benzene ring vertices. However, this resulted in large Stokes shifts (90–120 nm) for these structures.

Comment: Ligand selection was found to be crucial for stereoselectivity, with QuinoxP* overall performing well. In trimer-forming systems, preference for dimer or trimer can also be tuned by ligand choice. The proposed mechanism is two rounds of metallacyclopentadiene formation followed by [2+2+2] cyclization. Stereochemistry is determined by the second \([2+2+2]\) cyclization step. While thiophene-based systems performed well, attempts to use furans resulted in poor yields and stereoselectivity.