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Synthesis of Macrocyclic Heteroarylenes by Consecutive Inter- and Intramolecular Cycloadditions of Thiophenylene-Tethered Triynes

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Category

Synthesis of Materials and Unnatural Products

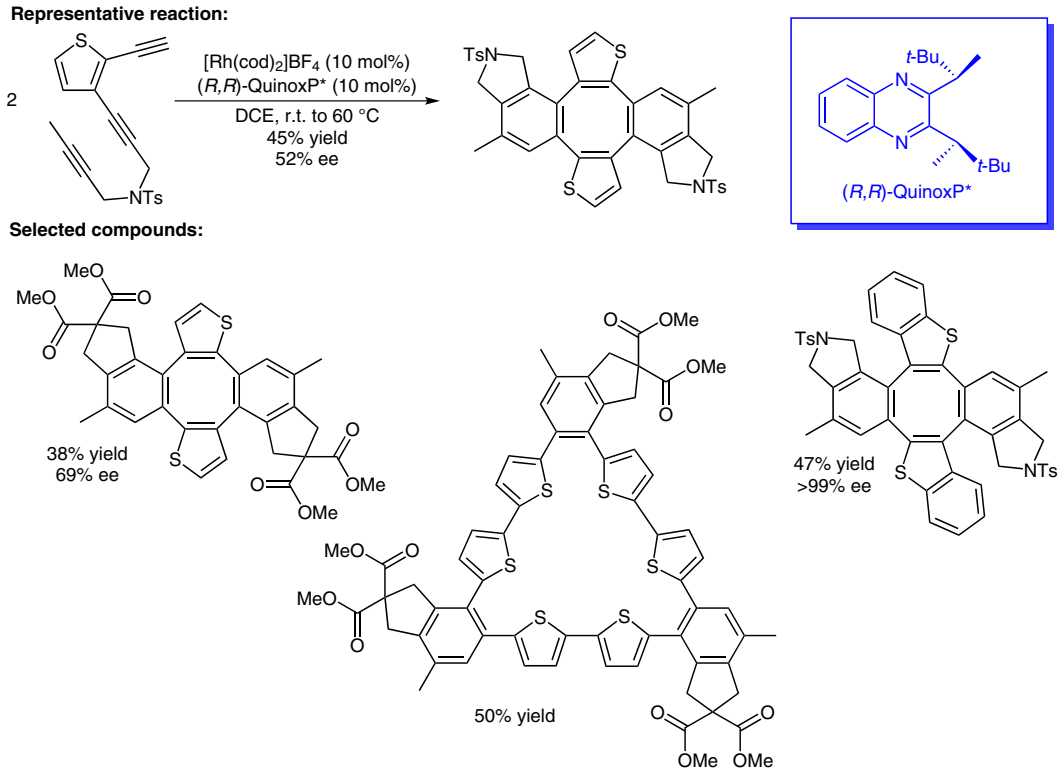
Key words

electronic materials

[2+2+2] cycloaddition

rhodium catalysis

Not-So-Triyne Route to Heteroarylene and Arylene Macrocycles



Significance: This is the first reported synthesis of macrocyclic π-conjugated structures featuring both benzene and heterocycle units. Isolated yields up to ~85% and stereochemical purity up to ~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.

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