Expanded \([n]\)Radialenes: Unusual Carbon-Rich Molecules

**Significance:** Conjugated macrocycles belong to a class of carbon-rich molecules that exhibit unusual structures and fascinating electronic and optical properties. Here, Tykwinski and co-workers report synthetic approaches to extended \([4]\)radialenes 1 and \([3]\)radialenes 2.

**Comment:** Synthesis of the extended radialenes 1 and 2 is accomplished by a one-pot deprotection and palladium-catalyzed cross-coupling reaction of common intermediates 3 and 4, respectively. Increased bond-angle strain appears to reduce yields in the synthesis of 2 compared to 1. A modified synthesis that leads to \(C_2\)-symmetric expanded \([4]\)radialenes is also presented in this work.

**Synthesis of extended \([4]\)radialenes:**

\[
\begin{align*}
\text{TBDMS} & \quad \text{TBDMS} \\
\text{1. TBAF, THF} \\
\text{2. Pd(PPh_3)_4, CuI, i-Pr_2NH, THF, \(\Delta\)} \\
\end{align*}
\]

Synthesis of extended \([3]\)radialenes:

\[
\begin{align*}
\text{TBDMS} & \quad \text{TBDMS} \\
\text{1. TBAF, THF} \\
\text{2. Pd(PPh_3)_4, CuI, i-Pr_2NH, THF, \(\Delta\)} \\
\end{align*}
\]

68% yield 79% yield 64% yield 77% yield

10% yield 45% yield 40% yield 33% yield

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