**Endo, Exo, and What?**

**Significance:** The properties of cyclopenta[b]thiopyran and derivatives thereof are largely unexplored, due in part to their challenging synthesis. This methodology, however, provides rapid access to many thiopyran derivatives. Thiopyran 4, being isoelectronic to azulene, exhibits many interesting properties, such as strong near-IR absorption and exceptional electrochemical stability, as observed by cyclic voltammetry studies.

**Comment:** The ability to transform a single compound into a multitude of products with unique properties is particularly useful for the synthesis of functional materials. In this report, the authors cyclize diyne 1 to form 2 via a 6-endo cyclization, 3 via a 5-exo cyclization, and 4 via an unexpected skeletal rearrangement.