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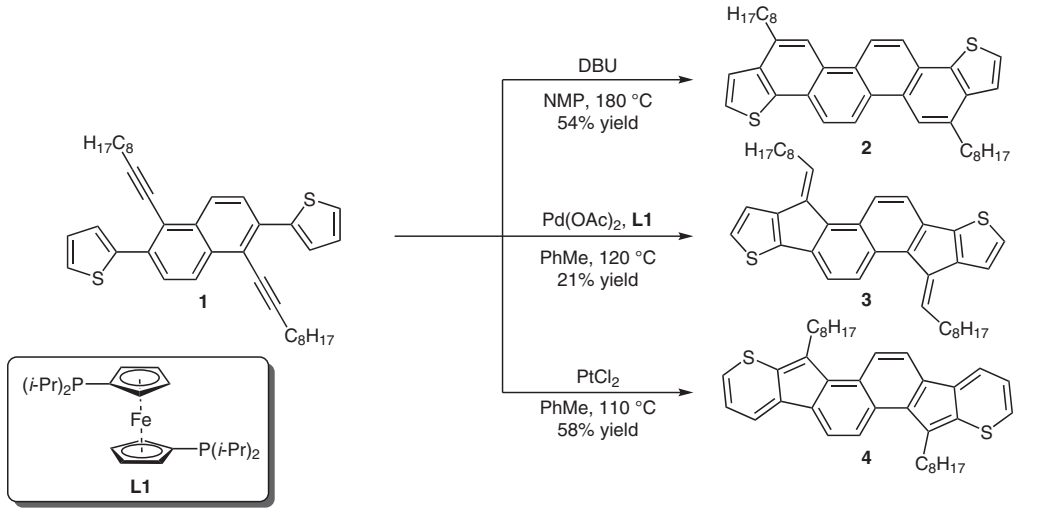
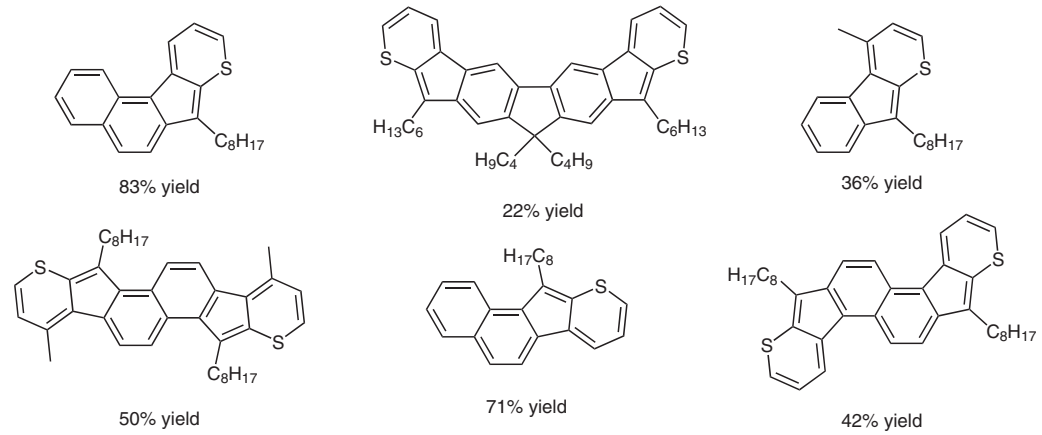
From Colorless to Near-Infrared *S*-Heteroarene Isomers: Unexpected Cycloaromatization of Cyclopenta[*b*]thiopyran Catalyzed by $PtCl_2$

Org. Lett. **2018**, *20*, 6632–6635.

Endo, Exo, and What?



Selected thiopyrans:



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.

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Category

Synthesis of Materials and Unnatural Products

Key words

thiopyrans
polycycles
cycloaromatization

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