

Arylene Ethynylene Macrocycles Prepared by Precipitation-Driven Alkyne Metathesis

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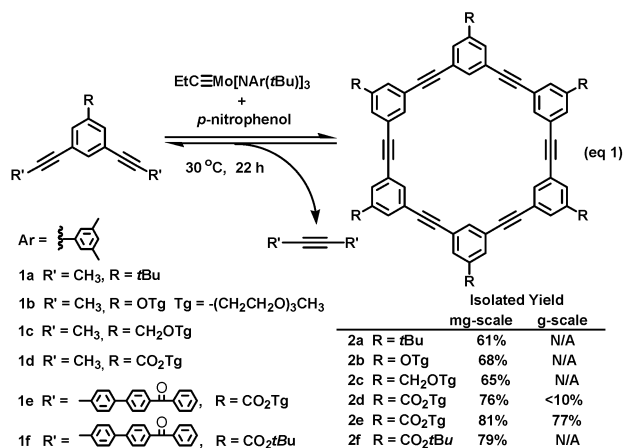
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Here we outline a convenient, multigram synthesis of arylene ethynylene macrocycles near room temperature through reversible alkyne metathesis. Driven by the precipitation of a diarylacetylene byproduct, the desired macrocycles are obtained in one step from monomers in high yields.

Shape-persistent arylene ethynylene macrocycles have attracted attention in the fields of supramolecular chemistry and materials science over the past decade due to their novel properties and potential applications.¹ Considerable efforts have been devoted to the development of methodologies allowing selectively functionalized structures to be obtained in high yields. The reversibility of the alkyne metathesis reaction is envisioned as a potentially powerful tool for preparing phenylene ethynylene macrocycles.^{2,3} The availability of highly active Mo(VI) alkylidyne catalysts synthesized by a reductive recycle strategy⁴ prompted us to reinvestigate this idea.

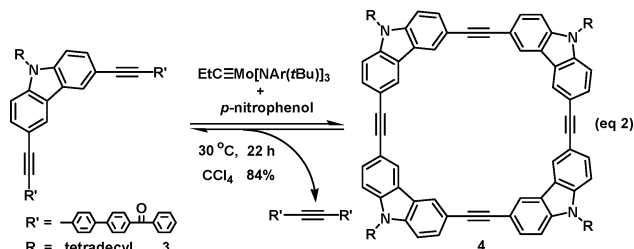
In our initial attempts, alkyne metatheses were performed under open, driven conditions (1 mmHg) to facilitate complete removal of the 2-butyne byproduct. We chose 1,2,4-trichlorobenzene as a high-boiling solvent for these reactions. Phenylene ethynylene macrocycles **2a–d** were obtained in good yields on a small scale (15–33 mg, 61–76%) from monomers **1a–d** at a concentration of 0.13 M (eq 1).⁵ However, several attempts to increase the scale



of the procedure using the vacuum-driven strategy resulted in poor macrocycle yields, low conversions, and considerable amounts of oligomeric products. Failure may be due to the introduction of air into the reaction vessel, leading to catalyst decomposition, or the consumption of catalyst by polymerization of the 2-butyne byproduct, which cannot be removed fast enough in gram-scale batches.^{4b} We imagined that a poorly soluble, less reactive byproduct would allow the desired metathesis reaction to be performed in a closed system. Precipitation rather than evaporation thus serves as the driving force to shift the metathesis equilibrium. Numerous arylethynyl-substituted monomers were tested in various solvents;

the metathesis of benzoylbiphenyl-substituted monomers **1e,f** in CCl₄ provided the highest yields of macrocycles **2e,f**. Multigram synthesis of **2e** was accomplished in one-step using the precipitation-driven strategy under optimized conditions (5.68 g, 77%).^{5,6}

To demonstrate the generality of the precipitation-driven strategy, we next applied the approach to the synthesis of square-shaped macrocycle **4** from monomer **3**. The only product observed was tetracycle **4** isolated in 84% yield (eq 2). The predominant formation



of macrocycles **2a–f** and **4** presumably reflects the thermodynamic stability of these products.⁷ The scope and mechanism of this precipitation-driven macrocycle synthesis are being investigated and will be reported in due course.

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Supporting Information Available: Experimental procedures, characterization data for **1–4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (3) Bunz previously reported the synthesis of macrocycles via alkyne metathesis. Under their conditions, which required high temperature (150 °C), the desired products were only obtained in 0.5–6% yields. Ge, P.-H.; Fu, W.; Herrmann, W. A.; Herdtweck, E.; Campana, C.; Adams, R. D.; Bunz, U. H. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3607–3610.
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- (5) A small amount of pentameric macrocycle is present in the isolated macrocyclic product. For the large-scale synthesis of **2e**, the macrocyclic product was a 9:1 hexacycle/pentacycle mixture. The pentacycle could be separated from the hexacycle by column chromatography.
- (6) Initial monomer concentration was 0.038 M in CCl₄; 10 mol % catalyst.
- (7) Preliminary studies have shown the reversibility of macrocycle formation in the case of **2e** and **2f**. The macrocyclic products appear to be thermodynamically favored over larger macrocycles and open-chain oligomer and polymer, analogous to the molecular architectures prepared via coordination reactions. See: Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853–908.

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