Significance: The instability of aryne has prevented its polymerization to form poly(o-arylene)s. Only few examples of oligomeric o-arylenes through iterative coupling reactions are reported. Ito, Takahashi, and Nozaki report the synthesis of poly(o-arylene)s via polymerization of [2.2.1]oxabicyclic alkenes, followed by acid-catalyzed dehydration.

Comment: In this chain-growth polymerization, the co-solvent and the additive 2,6-lutidine play key roles. Toluene may stabilize the cationic palladium catalyst species and may hinder β-oxygen elimination (the termination step). Dichloroethane (DCE) solubilizes the palladium catalyst in toluene. 2,6-Lutidine produces polymer 2 with high yields and a low polydispersity index.