

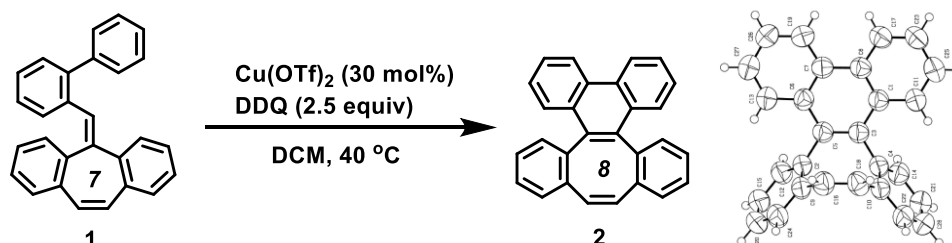


Oxidative Ring Expansion for Synthesis of 8-Membered Ring-fused π -Conjugated Polycycles

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π -Conjugated polycycles embedding with an eight-membered cyclooctatetraene (COT) moiety, such as various tetraphenylenes and dibenzocyclooctatetraenes are interesting molecules from both synthetic and theoretical viewpoints due to the nonplanar tub-shaped geometry of COT.¹ Importantly, those polycycles can act as new COT ligands for transition metal complexes and host molecules for dynamic molecular recognition. Although a few synthetic methods such as double Wittig reaction and Ni-catalyzed [2+2+2+2] cycloaddition of diynes for constructing benzo-annulated COT-polycycles have been reported,² new synthetic methods for the construction of novel π -extended COT-polycycles are still highly desirable. Recently, we have developed a new oxidative ring expansion reaction to generate dibenzo[*g,p*]chrysenes (DBC), which provided an efficient strategy for the construction of highly π -extended polycyclic aromatic hydrocarbons (PAHs).³

Herein, we report a highly efficient single electron oxidative ring expansion for a new series of dibenzocyclooctaphenanthrenes (DBCOPs) embedding with eight- and six-membered ring.⁴ The biphenyl-tethered 5-methylene-5*H*-dibenzo[*a,d*][7]annulene (**1**) underwent a single electron oxidative ring expansion in the presence of Cu(OTf)₂ and DDQ, affording the corresponding eight-membered ring-fused π -extended polycycle DBCOP (**2**) in 65% yield. The saddle-shaped structure of **2** was determined by X-ray crystallography analysis. Synthesis of various functional DBCOPs and their derivatization as well as the proposed reaction mechanism will be presented.



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