Synthesis of Novel Peripherally Fused Corannulenes via Quintuple Amination Reactions and Their Structural and Electronic Perturbations

(*Graduate School of Science, Kyoto University*) ○Koki Kise, Shota Ooi, Takayuki Tanaka, Atsuhiro Osuka

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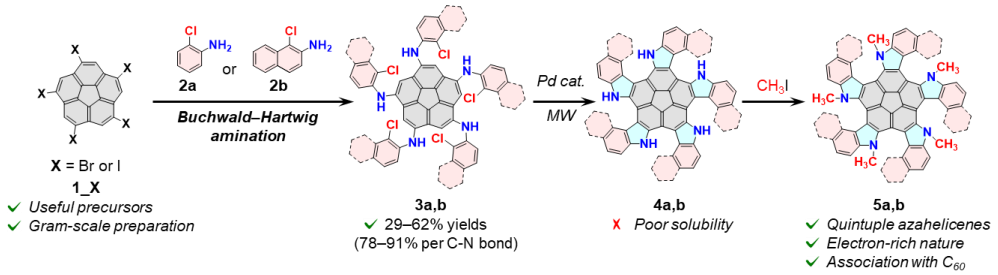
Structural and electronic properties of polycyclic aromatic hydrocarbons (PAHs) can be controlled by incorporation of heteroatoms at the periphery of the PAHs. Especially, corannulene, that is a fragment of fullerene, is an attractive research target due to its bowl-shaped structure and electron-deficient nature. Recent reports on nitrogen-embedded corannulenes have been attracting great attention due to the unique stereochemistry and effective electronic perturbation.[1] In this work, we first prepared *sym*-pentabromocorannulene **1_Br** and *sym*-pentaiodocorannulene **1_I** as promising substrates for palladium-catalyzed amination reaction. Then, we synthesized pentaaminocorannulenes **3a**,**b** in which five nitrogen atoms are peripherally incorporated. Subsequently, we synthesized pentaindolocorannulene **4a** and pentakis(benzoindolo)corannulene **4b** via intramolecular cyclization reactions under palladium catalysis, and subsequent *N*-methylation reaction afforded **5a**,**b** which possess quintuple azahelicene scaffolds.[2] Owing to the electron-rich nature, fused aminocorannulenes **5a**,**b** showed multi-step oxidations by cyclic voltammetry and larger association constants with fullerene C_{60} compared with previously reported corranulene-based PAHs.[3]



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