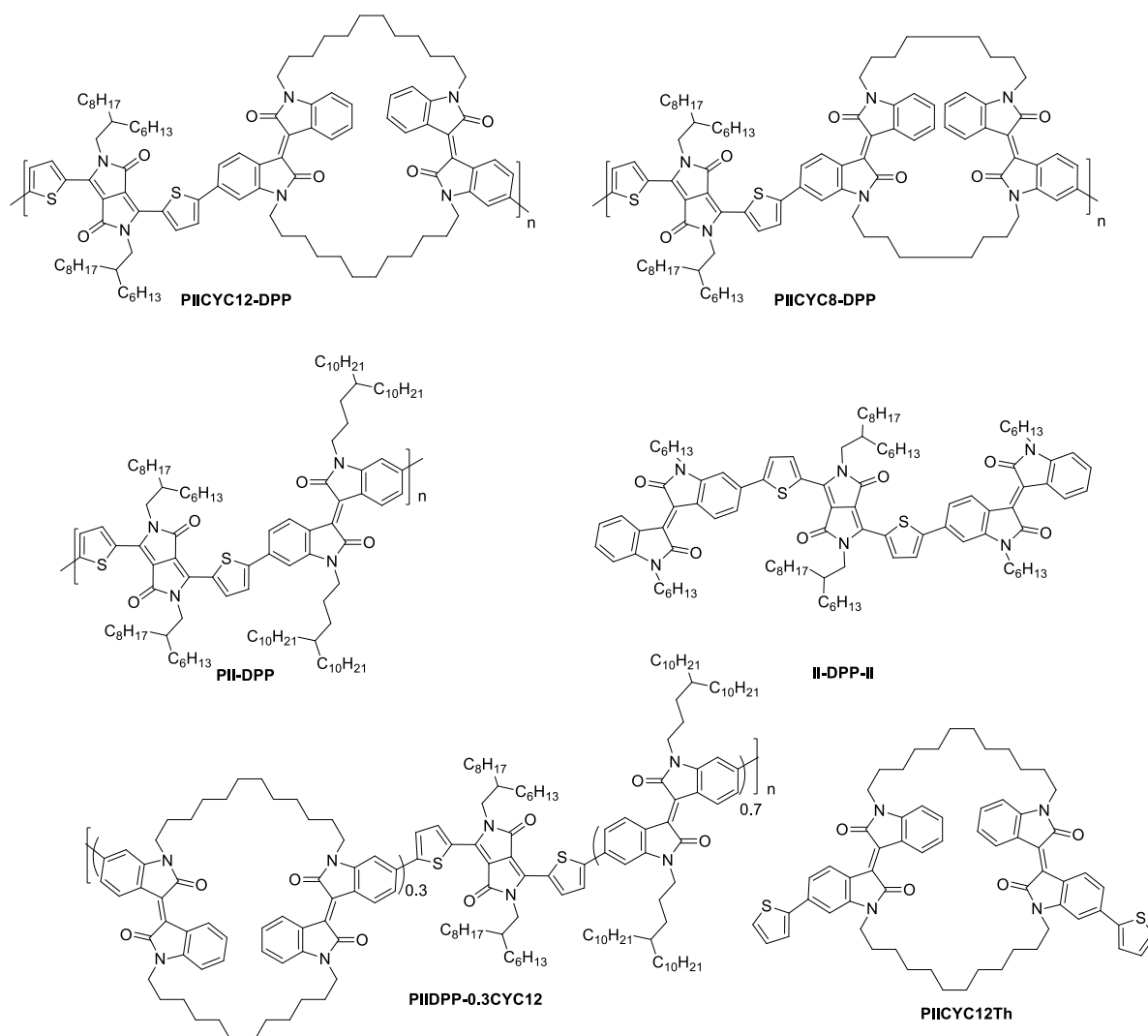
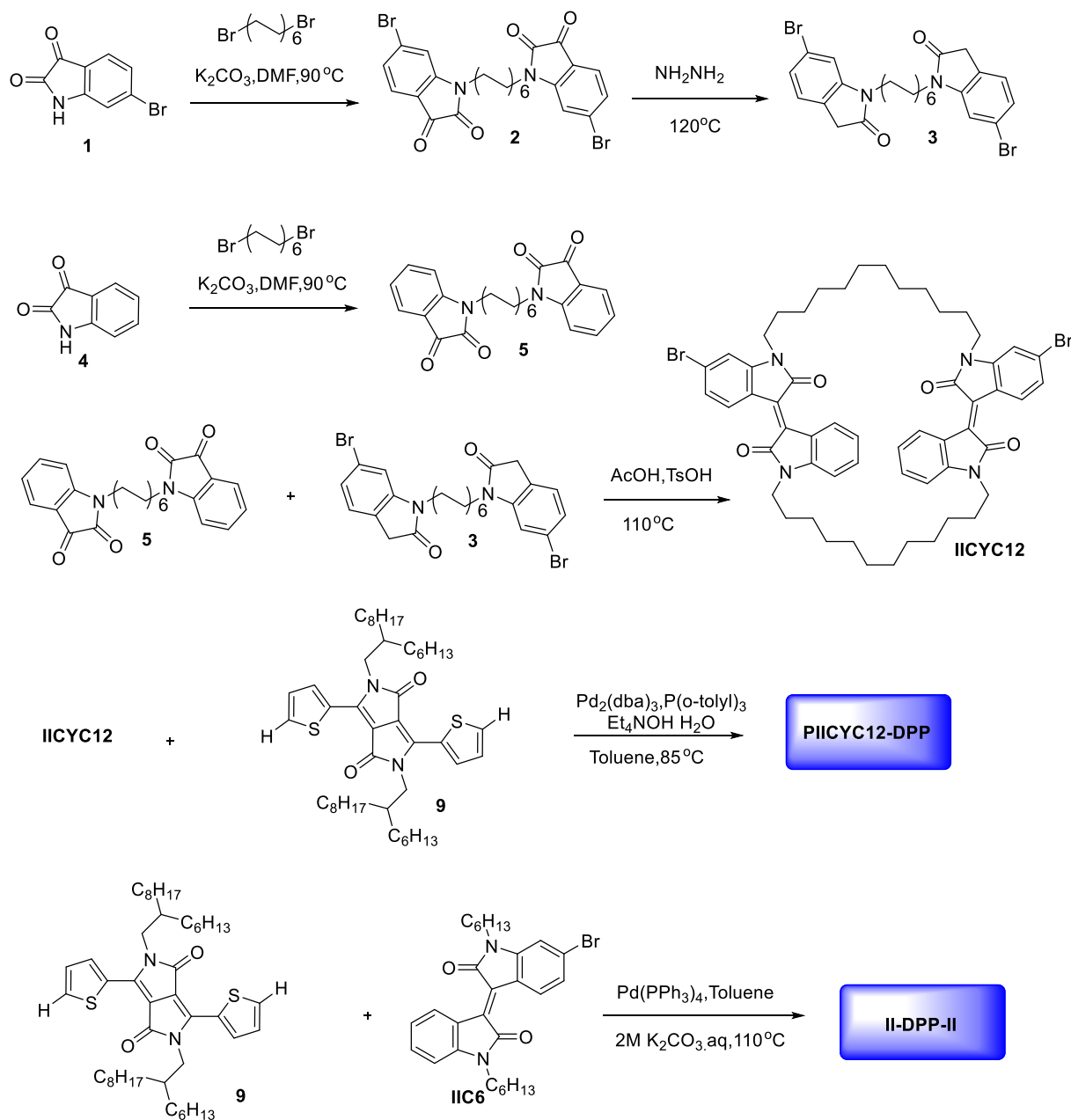


Progress I: Direct arylation polymerization (DAP) has emerged as a greener polymerization method for donor–acceptor (D–A) type conjugated polymers. DAP, in contrast to Stille or Suzuki polymerization, does not involve organometallic compounds as nucleophiles. This feature makes it feasible to directly use asymmetric aryl halides as monomers for preparing D–A polymers. **In this project, incorporation of macrocycles into semiconducting polymers is reported.** Two isoindigo macrocycles with different alky chain length (IICYC12 and IICYC8) were prepared and incorporated to make PIICYC12-DPP and PIICYC8-DPP. Fully conjugated polymer (PII-DPP) and a model compound (II-DPP-II) were prepared for a comparison, as displayed in Scheme 1.



Scheme 1. Structure of isoindigo macrocycle polymer PIICYC12-DPP and PIICYC8-DPP, fully conjugated polymer PII-DPP, trimer II-DPP-II, random polymer PIIDPP-0.3CYC12 and isoindigo macrocycle PIICYC12Th.

Starting with 1,12-dibromododecane, use excess equivalents of 6-bromoisatin or isatin to install on both side of the alkane chain to get the di-isatin (compound 2&5). Reduction of di-isatin with hydrazine hydrate to get the di-2-oxyindole (compound 3). The same equivalent of di-2-oxyindole (compound 3) and di-isatin (compound 5) reacted in acetic acid with TsOH as catalyst to afford the isoindigo macrocycle IICYC12. The relative polymer is got by Suzuki polymerization of isoindigo macrocycle and diketopyrrolopyrrole pinacolatoboron. PIICYC8-DPP is got by the similar method. The fully conjugated polymer PII-DPP, random polymer PIIDPP-0.3CYC12 and trimer II-DPP-II is also synthesized by direct arylation polymerization.



Scheme 2. Synthetic route to PIICYC12-DPP and IIDPP-II