Supporting Information

Palladium-Catalyzed Oxidative Annulation of Pyrrolyl-alkyl-1H-azoles: Towards the Synthesis of Poly-heterocyclic Arenes

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Preparation of starting materials:

The following starting materials were either purchased or used as it is or they were synthesized using known literature procedure. Compounds I (a-d), II (a-c) and III were purchased from Sigma- Aldrich and Alfa aesar, used without further purification. Compound IV (a, b) were prepared in two steps from pyrrole following literature procedure.

![Chemical structures of I, II, III, and IV](image)

General procedure A for N-alkylation of pyrrols:

To a suspension of NaH (1.0 equivalent) in dry DMF at 0 °C, was drop wise added a solution of 5,6 disubstituted benzimidazoles, I (a-d), 4,5 disubstituted imidazoles II (a-c), and triazole (III) (1.0 equivalent) in dry DMF and the reaction mixture was allowed to stir at rt for 30 min. A solution of 2-(1H-pyrrol-1-yl) alkyl 4-methylbenzenesulfonate derivatives VI (a,b) (1.2 equiv.) in DMF was added to it and the resulting solution was heated at 80 °C for 16 h. The completion of reaction was monitored by TLC. Once the reaction completed, saturated brine solution was added to the reaction mixture and it was extracted with EtOAc (three times). The combined organic layers were washed with brine and dried over Na₂SO₄. Further, it was filtered and concentrated under reduced pressure to provide an organic residue. The residue was purified by silica gel column chromatography to provide the desired product.
**Scheme S1:** Coupling of 2-(1H-pyrrol-1-yl) alkyl 4-methylbenzenesulfonate derivatives with substituted azoles

**General procedure B for intramolecular dehydrogenative cross coupling of Pyrrolyl-alkyl-1H-azoles:**

To a sealed tube with screw cap was loaded N-alkylated pyrrole (0.2 mmol, 1 equiv), Palladium acetate (0.1 equiv), silver acetate (2 equiv) and Acetic acid (5 equiv) in DMF (1 ml). The reaction mixture was stirred in a preheated silicon oil bath at 120°C for 24h. Once the reaction is completed, mixture was allowed to cool and saturated brine solution was added to the reaction mixture and it was extracted with EtOAc (three times). The combined organic layers were washed with brine and dried over Na₂SO₄. The residue was purified by silica gel column chromatography to provide the desired product.

**References:**

NMR spectra

1a

S4
Crystal structure of compound 2a: