Transition Metal-Catalyzed Cyclization of Enediynes to Benzopyranones, Carbazoles and Benzothiophenes

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Recently, we found that treatment of *N*,*N*-dimethyl 2-[(2-(2-alkynylphenyl)ethynyl)anilines **1** with ten mol% of PdCl₂ and two equivalents of CuCl₂ at refluxing THF for one hour gave the chlorinated benzo[a]carbazoles **2** in excellent yields. The chloroindoles **3** was proposed as the key intermediate and can be prepared separately by reaction of **1** with two equivalents of CuCl₂ at refluxing THF. Treatment of **3** with various electrophilic transition metals, such as PdCl₂, Pd(OAc)₂ and PtCl₂, gave carbazoles **2** in good yields. Under the similar reaction conditions, methyl 2-[6-substituted 3(*Z*)-hexen-1,5-diynyl]benzoates and 2-(2-(2-(2-substituted ethynyl)phenyl)ethynyl)thioanisoles were converted to dibenzo[*b*,*d*]pyran-6-ones and benzo[*b*]naphtho[2,1-*d*]thiophenes, respectively.



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