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

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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.