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Trace Amount Cu (ppm)–Catalyzed Intramolecular Cyclization of 2-(*gem*-Dibromovinyl)phenols(thiophenols) to 2-Bromobenzofurans(thiophenes)

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1. General consideration

All reagents were purchased from commercial suppliers and used without further purification. 2-(*gem*-Dibromovinyl)phenols(thiophenols) were prepared according to the literature [(a) S. G. Newman, V. Aureggi, C. S. Bryan, M. Lautens, *Chem. Commun.* **2009**, 5236–5238; (b) S. Bhatt, S. K. Nayak, *Tetrahedron Lett.* **2009**, 50, 5823–5826]. All the intramolecular cyclization reactions of *gem*-dibromoolefins were carried out under an air atmosphere. ^1H NMR and ^{13}C NMR spectra were measured on a Bruker Avance NMR spectrometer (400 MHz or 100 MHz, respectively) with CDCl_3 as solvent and recorded in ppm relative to internal tetramethylsilane standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). High resolution mass spectroscopy data of the product were collected on a Waters Micromass GCT instrument.

2. Typical procedure for the synthesis of 2-bromobenzofuran (2a) through an intramolecular cyclization of 2-(*gem*-dibromovinyl)phenol (1a)

In air atmosphere, a sealable reaction tube with a Teflon-coated screw cap equipped with a magnetic stir bar was charged with 2-(*gem*-dibromovinyl)phenol (**1a**, 1.0 mmol), Cs_2CO_3 (0.50 mmol, 99.9%, Shanghai, China) and $\text{C}_2\text{H}_5\text{OH}$ (2.0 mL). The reaction vessel was placed in an oil bath at 80 °C and the mixture was stirred for 8 h, then it was cooled to room temperature, the solvent was concentrated under reduced pressure and the residue was washed with water, extracted with AcOEt until it was free of the product. Solvent was removed and the product was further purified by flash chromatography on silica gel (eluant: hexane/ethyl acetate) to give the desired product 2-bromobenzofuran (**2a**).

3. ^1H and ^{13}C NMR spectra of all products













































