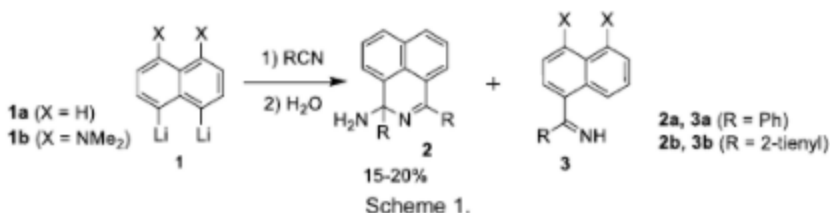
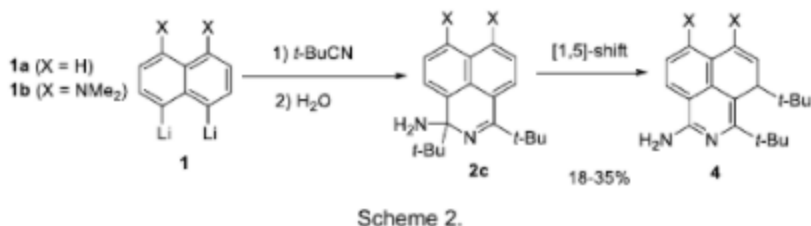


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We have demonstrated that the interaction between 1,8-dilithionaphthalene **1a** and arylcyanides surprisingly leads to the formation of benzo[de]isoquinolines **2a,b** together with small admixture of monoimines **3a,b**. At the same time the treatment of 4,5-dilithio-1,8-bis(dimethylamino)naphthalene **1b** with the same arylcyanides leads to the formation of monoimines **3** exclusively (Scheme 1). We believe that the formation of monoimines originates from high basicity of dilithionaphthalene facilitating deprotonation of C-H bonds of used arylcyanides instead of nucleophilic attack to cyano group. This unfortunate outcome becomes the major result of the reaction in the case of extremely basic **1b**.



Transition to the less acidic *tert*-butylcyanide excludes the formation of monoimines. However instead of the **2c** the isomeric **4** were formed due to [1,5]-sigmatropic shift of *tert*-butyl group (Scheme 2).



The most reasonable explanation of this unexpected cyclisation is the proximity of imino groups in the naphthalene core, which sterically facilitates nucleophilic attack. We believe that reaction starts with the formation of *peri*-diimides **5**, which upon hydrolysis to diimines **6** undergo spontaneous intramolecular nucleophilic cyclisation into **7** (Scheme 3). We have demonstrated that treatment of the reaction mixture with dimethylsulfate prior to quenching with water results in the formation of Schiff bases **8** exclusively. Thus, it was proven that the cyclisation occurs only after formation of neutral imines **6**.

