Category

Synthesis of Materials and Unnatural Products

Key words

annulation

hypervalent iodine

metal-free reaction

quinoxalines

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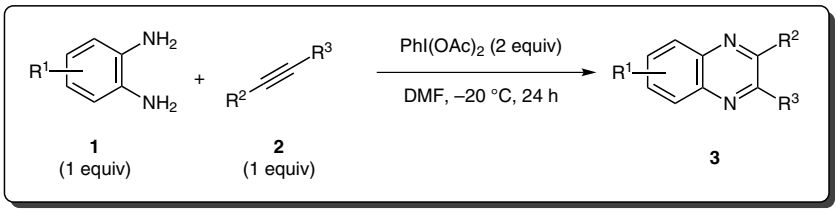
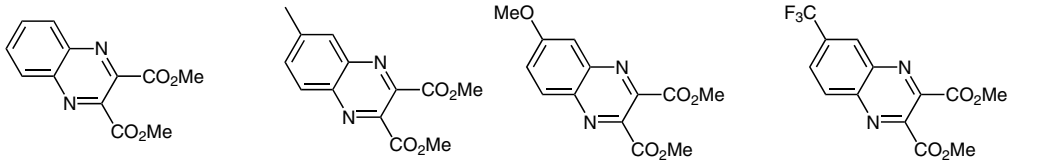
Hypervalent Iodine(III)-Induced Oxidative [4+2] Annulation of *o*-Phenylenediamines and Electron-Deficient Alkynes: Direct Synthesis of Quinoxalines from Alkyne Substrates under Metal-Free Conditions
Chem. Commun. **2013**, *49*, 9266–9268.

Quinoxalines Directly from Electron-Deficient Alkynes

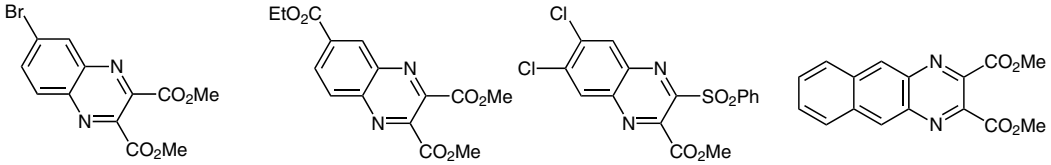


1 (1 equiv) + **2** (1 equiv) → **3**

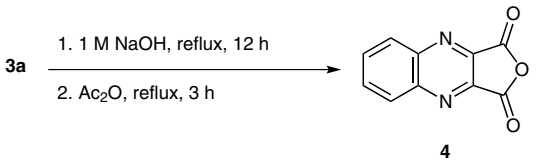
Selected examples:



3a, 92% yield; **3b**, 85% yield; **3c**, 97% yield; **3d**, 91% yield



3e, 85% yield; **3f**, 95% yield; **3g**, 65% yield; **3h**, 56% yield



4

Significance: The authors report the metal-free oxidative [4+2] annulation of electron-deficient alkynes and *ortho*-phenylenediamines to synthesize quinoxalines, which are most commonly prepared by condensing diamines with α-diketones. The reactions with electron-rich, -neutral, and -poor substrates all proceed with high yield. The synthesis of anhydride **4** demonstrates the utility of this method, as such electron-deficient quinoxalines are challenging to prepare by traditional methods.

Comment: Initial results with *tert*-butyl hypoiodite predominately yielded the dearomatized *cis*,*cis*-muconontrile. Phenyliodine diacetate (PIDA) proved to be crucial, despite attempts with several other hypervalent iodine reagents. The reaction is also highly solvent-dependent, proceeding more effectively with increasing solvent polarity.

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