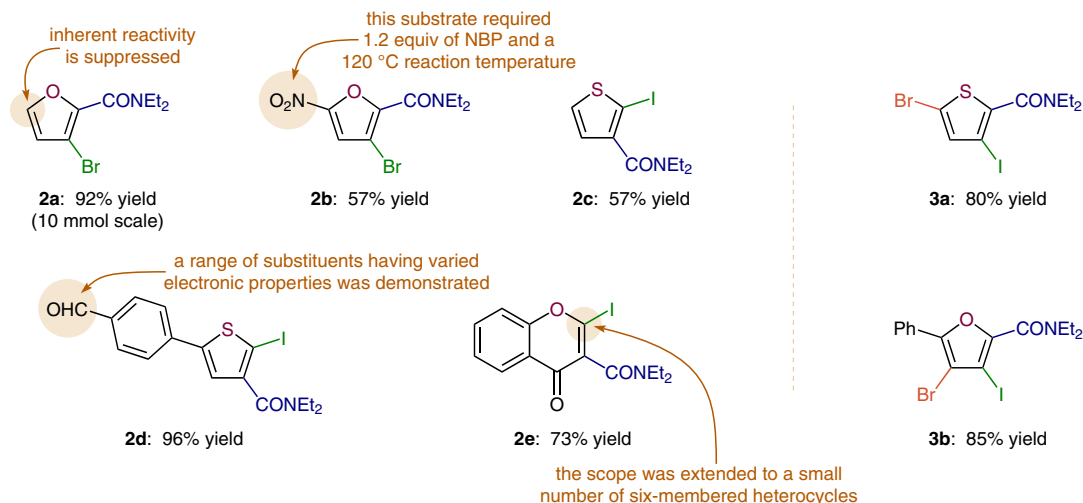
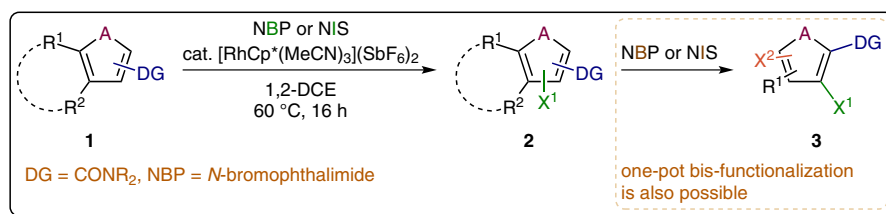


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Dual Role of Rh(III) Catalyst Enables Regioselective Halogenation of (Electron-Rich) Heterocycles  
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## Rhodium-Catalyzed Directed Halogenation of $\pi$ -Excessive Heterocycles



**Significance:** The bromination and iodination of  $\pi$ -excessive heterocycles **1** under directed rhodium(III) catalysis is reported. The reaction provides an orthogonal approach to electrophilic halogenation, overriding the inherent reactivity of the starting materials. Additionally, the method is complementary to directed *ortho* metalation, which can afford similar products (**2** and **3**) without the need for a heavy metal catalyst, but under strongly basic conditions (e.g., see: E. G. Doadt, V. Snieckus *Tetrahedron Lett.* **1985**, *26*, 1149). Bis-halogenated products **3** were also obtained from compounds **2** in a one-pot process by addition of a second equivalent of the electrophile. The reaction was reported to proceed efficiently under air and without special precautions to exclude moisture.

**Comment:** The scope and functional group tolerance of the reported reaction were demonstrated to be broad, with a range of substituted five- and six-membered heterocycles being demonstrated. However, the viability of directing groups other than dialkyl amides would have provided welcome generality. Kinetic studies demonstrated a dual role for the rhodium(III) catalyst, whereby it additionally functions to suppress the inherent reactivity of the heterocycle. AgSbF<sub>6</sub> was also observed to suppress the innate reactivity, and in its presence, the catalyst loading could be decreased to 0.1%. Additional mechanistic evidence showed that C–H bond activation is turnover limiting but electrophilic aromatic substitution and concerted metalation–deprotonation mechanisms could not be distinguished.

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