

An Efficient Copper-Catalysed Aerobic Oxybromination of Arenes in Water

Jian Wang, Wei Wang, Jing-Hua Li*

College of Pharmaceutical Sciences, Zhejiang University of Technology, 310032, Hangzhou, China

E-mail: lijh@zjut.edu.cn.

Supporting Information

List of Contents

1	General information -----	S1
2	General procedure for the Aerobic Oxybromination of Arenes -----	S1
3	¹H NMR spectra of bromoarenes -----	S2

1. General Information

All experiments were carried out in standard round bottom flask with three necks. GC analysis was performed with a Techcomp 7890II instrument fitted with a SE-54 30m×0.32mm×0.25µm capillary column and a FID detector (analytical conditions: oven temperature: 170 °C; injector temperature: 250 °C; detector temperature: 250 °C). Identification of the constituents was based on comparison of the retention times with those of authentic samples. ¹H NMR spectra were recorded on a Bruker Avance III 500 MHz Spectrometer. Chemical shifts (δ) are given in ppm and are referenced to residual solvent peaks. All substrates and authentic samples (for GC analysis) were commercial products.

2. General procedure for the Aerobic Oxybromination of Arenes

In a typical run, a mixture of the aromatic compound (5.0 mmol), Cu(NO₃)₂·3H₂O (0.05 mmol, 12 mg), and HBr (5.5 mmol, 0.69 mL 8 mol/L aq.) was vigorously stirred, air was pumped into the reactor by an air compressor. The reaction was carried out at 80 °C for a specified time, and then analysed by gas chromatography (GC). After the conversion of substrate come up to certain level, the reaction was quenched with 10 mL saturated aq. NaHSO₃. Then the mixture was extracted by ethyl acetate. The organic layer was concentrated under reduced pressure. Product was isolated by thin layer chromatography (TLC) (PE : CH₂Cl₂ = 1 : 1) and characterized by ¹H NMR spectroscopy.

¹H NMR:

2-Methyl-4-bromophenol (**2a**): δ (500 MHz, CDCl₃): 2.21 (s, 3H, C⁷H), 4.98 (br, 1H, OH), 6.64 (d, 1H, C⁶H, $J = 8.5$ Hz), 7.16 (dd, 1H, C⁵H, $J = 8.5$ Hz, 2.5 Hz), 7.23 (d, 1H, C³H, $J = 2.5$ Hz).

3-Methyl-4-bromophenol (**3a**): δ (500 MHz, CDCl₃): 2.34 (s, 3H, C⁷H), 4.89 (br, 1H, OH), 6.55 (dd, 1H, C⁶H, $J = 9$ Hz, 3 Hz), 6.73 (d, 1H, C²H, $J = 3$ Hz), 7.35 (d, 1H, C⁵H, $J = 9$ Hz).

4-Methyl-2-bromophenol (**4a**): δ (500 MHz, DMSO-*d*₆): 2.18 (s, 3H, C⁷H), 6.84 (d, 1H, C⁶H, $J = 8$ Hz), 6.96 (dd, 1H, C⁵H, $J = 8$ Hz, 2 Hz), 7.28 (d, 1H, C³H, $J = 2$ Hz), 10.03 (br, 1H, OH).

4-Chloro-2-bromophenol (**5a**): δ (500 MHz, DMSO-*d*₆): 6.96 (d, 1H, C⁶H, $J = 9$ Hz), 7.22 (dd, 1H, C⁵H, $J = 9$ Hz, 2.5 Hz), 7.52 (d, 1H, C³H, $J = 2.5$ Hz), 10.54 (s, 1H, OH).

2-Bromohydroquinone (**6a**): δ (500 MHz, DMSO-*d*₆): 6.63 (dd, 1H, C⁵H, $J = 9$ Hz, 2.5 Hz), 6.79 (d, 1H, C⁶H, $J = 9$ Hz), 6.90 (d, H, C³H, $J = 2.5$ Hz), 9.08 (s, 1H, OH), 9.37 (s, 1H, OH).

3. ^1H NMR spectra of bromoarenes





