Supplementary Material

A Metal-free and Ionic Liquid-catalyzed Aerobic Oxidative Bromination in Water

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**Experimental methods**

**General methods:**

Gas Chromatography (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. Identification of the constituents was based on comparison of the retention times with those of authentic samples. \(^1\)H NMR spectra were recorded on a Bruker Avance III 500 MHz Spectrometer. Chemical shifts (δ) are given in ppm. All substrates and authentic samples (for GC analysis) were commercial products.

**Preparation of the catalyst (1a-1q):**

In a 250 mL flask, amine (100 mmol) was dissolved in 50 mL ethanol, then nitric acid (105 mmol) was dropped into the solution. During the addition the temperature should be maintained lower than 10 °C (maybe ice bath is needed). The mixture should be stirred at room temperature for an extra hour after the addition. Evaporation of the solvents under reduced pressure gave the nitrate catalyst.

**Typical procedure:**

Substrate (5 mmol), HBr (5.5 mmol, 40% aqueous solution) and catalyst were vigorously stirred in a reaction tube which is exposed to air at certain temperature with condenser equipped. The reaction was carried out for a specific time.

**Analytical procedure:**

During the process of the reaction, a small part of the mixture was sampled and added into 1 mL saturated NaHSO₃ aqueous solution. After extraction by ethyl acetate (EA), a trace of the organic layer was injected into the GC instrument (oven temperature: from 70 °C to 170 °C in the rate of 25°C / min; injector temperature: 250 °C; detector temperature: 250 °C) to monitor conversion and yield of the reaction in comparison with authentic samples.

**Purification and identification of the product (3a-3l):**

For 3a, 3b, 3c, 3d, 3e, 3k, 3l:
After completion of the reaction (time was defined by GC), the mixture was quenched with 15 mL saturated NaHSO₃ aqueous solution. Then the mixture was extracted by EA (20 mL × 3). The combined organic layer was washed with brine and dried over MgSO₄, then concentrated under reduced pressure. The product was isolated by column chromatography (Petroleum ether (PE) : EA from 100:1 to 10:1) and characterized by ¹H NMR spectroscopy.

For 3f, 3g, 3h, 3i, 3j:

After completion of the reaction (time was defined by GC), the mixture was quenched with 15 mL saturated NaHSO₃ aqueous solution and 15 mL EA. After stirring for 15 min, the mixture was filtered. Then the filtrate was separated and the aqueous layer was extracted by EA (20 mL × 3), after which the combined organic layer was washed with brine and dried over MgSO₄ and concentrated under reduced pressure. The product was isolated by column chromatography (PE : EA from 7:1 to 1:1) and characterized by ¹H NMR spectroscopy.

Catalyst recycling:

After completion of the reaction (time was defined by GC), 15 mL water was added to the mixture, which was then washed by ethyl acetate (20 mL × 3). The aqueous layer was separated and concentrated in the reduced pressure until water was completely removed, after which fresh anisole (5 mmol) and HBr (5.5 mmol, 40% aqueous solution) were added to restart the reaction.

Catalyst recovering:

After completion of the reaction (time was defined by GC), 15 mL water was added to the mixture, which was then washed by ethyl acetate (20 mL × 3). After that, 0.05 mmol nitric acid was added to the aqueous layer and the solution was stirred in the room temperature for one hour. Then the solution was condensed in the reduced pressure until water was completely removed, after which fresh anisole (5 mmol) and HBr (5.5 mmol, 40% aqueous solution) were added to restart the reaction.
**1H NMR data of products:**

3a: $^1\text{H NMR (500 MHz, CDCl}_3/$TMS$): \delta$ 7.40 (d, $J = 9$ Hz, 2H), 6.80 (d, $J = 9$ Hz, 2H), 3.79 (s, 3H).

3b: $^1\text{H NMR (500 MHz, CDCl}_3/$TMS$): \delta$ 7.28-7.30 (m, 2H), 6.69-6.71 (m, 1H), 3.83 (s, 3H), 2.23 (s, 3H).

3c: $^1\text{H NMR (500 MHz, CDCl}_3/$TMS$): \delta$ 7.21 (d, $J = 2$ Hz, 1H), 6.90 (dd, $J = 8$ Hz, 2 Hz, 1H), 6.63 (d, $J = 8$ Hz, 1H), 3.69 (s, 3H), 2.12 (s, 3H).

3d: $^1\text{H NMR (500 MHz, CDCl}_3/$TMS$): \delta$ 7.42 (d, $J = 9$ Hz, 1H), 6.81 (d, $J = 3$ Hz, 1H), 6.64 (dd, $J = 9$ Hz, 3 Hz, 1H), 3.79 (s, 3H), 2.39 (s, 3H).

3e: $^1\text{H NMR (500 MHz, CDCl}_3/$TMS$): \delta$ 6.94-6.97 (m, 2H), 6.69 (d, $J = 8$ Hz, 1H), 5.97 (s, 2H).

3f: $^1\text{H NMR (500 MHz, CDCl}_3/$TMS$): \delta$ 7.34 (dd, $J = 6.5$ Hz, 2 Hz, 2H), 6.75 (dd, $J = 6.5$ Hz, 2 Hz, 2H), 6.22 (br, 1H).

3g: $^1\text{H NMR (500 MHz, CDCl}_3/$TMS$): \delta$ 7.25 (d, $J = 2.5$ Hz, 1H), 7.18 (dd, $J = 8.5$ Hz, 2.5 Hz, 1H), 6.66 (d, $J = 8.5$ Hz, 1H), 4.90 (s, 1H), 2.23 (s, 3H).

3h: $^1\text{H NMR (500 MHz, CDCl}_3/$TMS$): \delta$ 7.36 (d, $J = 9$ Hz, 1H), 6.75 (d, $J = 3$ Hz, 1H), 6.57 (dd, $J = 9$ Hz, 3 Hz, 1H), 5.01 (br, 1H), 2.35 (s, 3H).

3i: $^1\text{H NMR (500 MHz, CDCl}_3/$TMS$): \delta$ 6.94-7.30 (m, 3H), 5.53 (br, 1H), 2.30 (s, 3H).

3j: $^1\text{H NMR (500 MHz, CDCl}_3/$TMS$): \delta$ 7.01 (d, $J = 3$ Hz, 1H), 6.91 (d, $J = 9$ Hz, 1H), 6.74 (dd, $J = 9$ Hz, 3 Hz, 1H), 5.15 (br, 1H), 4.71 (br, 1H).

3k: $^1\text{H NMR (500 MHz, CDCl}_3/$TMS$): \delta$ 7.41 (d, $J = 8$ Hz, 2H), 7.08 (d, $J = 8$ Hz, 2H), 2.34 (s, 3H).

3l: $^1\text{H NMR (500 MHz, CDCl}_3/$TMS$): \delta$ 7.43 (d, $J = 8$ Hz, 1H), 7.08 (s, 1H), 6.89 (d, $J = 8$ Hz, 1H), 2.40 (s, 3H), 2.31 (s, 3H).
$^1$HNMR spectra of products:

3a:

3b: