Supporting information

Highly Practical Sodium( I )/ Azobenzene Catalyst System for
Aerobic Oxidation of benzylic Alcohols

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1, General Remarks

Reagents and solvents: Commercially available reagents were used without any further purification. All organic solvents were of reagent grade quality without any further purification.

Chromatography: Flash column chromatography was performed using Silicycle silica gel (200-300 mesh). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm coated silica gel plates (HSGF 254) and visualized using a UV lamp (254 nm or 365 nm).

Nuclear Magnetic Resonance Spectroscopy: $^1$H NMR was recorded on magnet system 400'54 ascend purchased from Bruker Biospin AG. $^1$H NMR spectra chemical shifts (δ) are reported in parts per million (ppm) referenced to TMS (0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddt = doublet of doublet of triplets, dtd = doublet of triplet of doublets, m = multiplet, br = broad), coupling constant (J) in Hertz (Hz), and integration.

2, Table S1: The equivalent of NaBr screening

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (mol%)</th>
<th>Co-catalyst (equiv.)</th>
<th>T (°C)</th>
<th>Solvent</th>
<th>T(h)</th>
<th>Yield (%)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Azobenzene(5)</td>
<td>NaBr(0.2)</td>
<td>80</td>
<td>1,4-Dioxane</td>
<td>48</td>
<td>trace</td>
</tr>
<tr>
<td>2</td>
<td>Azobenzene(5)</td>
<td>NaBr(0.5)</td>
<td>80</td>
<td>1,4-Dioxane</td>
<td>48</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
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<td>NaBr(1)</td>
<td>80</td>
<td>1,4-Dioxane</td>
<td>48</td>
<td>38</td>
</tr>
<tr>
<td>4</td>
<td>Azobenzene(5)</td>
<td>NaBr(2)</td>
<td>80</td>
<td>1,4-Dioxane</td>
<td>48</td>
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<td>NaBr(3)</td>
<td>80</td>
<td>1,4-Dioxane</td>
<td>48</td>
<td>92</td>
</tr>
</tbody>
</table>

3, General procedure for the oxidation of benzylic alcohols to ketones and aldehydes

The specific benzylic alcohols (1 mmol, 1.0 eq) and sodium bromide (2 mmol, 2 eq) were dissolved in dioxane (3 mL), then azobenzene (0.05 mmol, 0.05 eq) was added to the reaction mixture and stirred for a certain time in a preheated oil bath at 80 °C under O₂ atmosphere (O₂ balloon). The reaction mixtures were diluted with ethyl acetate and washed with brine and water. The separated organic layers were dried over anhydrous Na₂SO₄ and filtered. The filtrate was concentrated under reduced pressure and the residue was chromatographed on silica gel using hexane/ethyl acetate to afford the desired product.
4, General procedure for the oxidation of benzylic 1<sup>°</sup> alcohols to acids

The specific benzylic 1<sup>°</sup> alcohols (1 mmol, 1.0 eq) and sodium hydroxide (2 mmol, 2 eq) were dissolved in dioxane (3 mL). Then, azobenzene (0.05 mmol, 0.05 eq) was added to the reaction mixture and stirred for a certain time in a preheated oil batch at 80 °C under O<sub>2</sub> atmosphere (O<sub>2</sub> balloon). The reaction mixtures were diluted with H<sub>2</sub>O and regulated the pH to 1-2 by hydrochloric acid (10%, aq). The product was extracted by ethyl acetate or dichloromethane from the solution before. The separated organic layers were dried over by anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. The filtrate was concentrated under reduced pressure and the residue was chromatographed on silica gel using hexane/ethyl acetate or dichloromethane/methanol to afford the desired product.

Benzoic acid (3a), p-toluic acid (3e), 2-furoic acid (3f), 2-thiophenecarboxylic acid (3g)

The specific benzylic 1<sup>°</sup> alcohols (1 mmol, 1.0 eq) and sodium hydroxide (2 mmol, 2 eq) were dissolved in dioxane (3 mL). Then, azobenzene (0.05 mmol, 0.05 eq) was added to the reaction mixture and stirred for a certain time in a preheated oil batch at 80 °C under O<sub>2</sub> atmosphere (O<sub>2</sub> balloon). The reaction mixtures were diluted with H<sub>2</sub>O and regulated the pH to 1-2 by hydrochloric acid (10%, aq). The product was extracted by ethyl acetate from the solution before. The separated organic layers were dried over by anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. The filtrate was concentrated under reduced pressure and the residue was chromatographed on silica gel using hexane/ethyl acetate (2:1) to afford the desired product.

p-Nitrobenzoic acid (3b), 4-Chlorobenzoic acid (3c), 4-Bromobenzoic acid (3d)

The specific benzylic 1<sup>°</sup> alcohols (1 mmol, 1.0 eq) and sodium hydroxide (2 mmol, 2 eq) were dissolved in dioxane (3 mL). Then, azobenzene (0.05 mmol, 0.05 eq) was added to the reaction mixture and stirred for a certain time in a preheated oil batch at 80 °C under O<sub>2</sub> atmosphere (O<sub>2</sub> balloon). The reaction mixtures were diluted with H<sub>2</sub>O and regulated the pH to 1-2 by hydrochloric acid (10%, aq). The product was extracted by dichloromethane from the solution before. The separated organic layers were dried over by anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. The filtrate was concentrated under reduced pressure and the residue was chromatographed on silica gel using dichloromethane/methanol (30:1) to afford the desired product.

Nicotinic acid (3h)

3-Pyridinemethanol (1 mmol, 1.0 eq) and sodium hydroxide (2 mmol, 2 eq) were dissolved in dioxane (3 mL). Then, azobenzene (0.05 mmol, 0.05 eq) was added to the reaction mixture and stirred for a certain time in a preheated oil batch at 80 °C under O<sub>2</sub> atmosphere (O<sub>2</sub> balloon). The reaction mixtures were diluted with H<sub>2</sub>O and regulated the pH to 3-4 by hydrochloric acid (10%, aq). The product was extracted by dichloromethane from the solution before. The separated organic layers were dried over by anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. The filtrate was concentrated under reduced pressure and the residue was chromatographed on silica gel using dichloromethane/methanol (10:1) to afford the desired product.

5, Characterization Data of the products
All the products were characterized by $^1$H NMR spectroscopy and compared with literature reported data.

Anisic aldehyde

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.79 (s, 1H), 7.77 – 7.72 (m, 2H), 6.94 – 6.89 (m, 2H), 3.79 (s, 3H). Spectral data are in accordance with the literature report.$^{[1-2]}$

4-Chlorobenzaldehyde

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.91 (s, 1H), 7.78 – 7.76 (m, 1H), 7.75 – 7.74 (m, 1H), 7.47 – 7.45 (m, 1H), 7.45 – 7.43 (m, 1H). Spectral data are in accordance with the literature report.$^{[1]}$

4'-Chloroacetophenone

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84 – 7.82 (m, 1H), 7.81 – 7.80 (m, 1H), 7.35 – 7.34 (m, 1H), 2.51 (s, 3H).

4-Bromobenzaldehyde

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.91 (s, 1H), 7.68 (d, $J$ = 8.3 Hz, 2H), 7.62 (d, $J$ = 8.3 Hz, 2H).

Benzophenone

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84 – 7.78 (m, 4H), 7.62 – 7.56 (m, 2H), 7.52 – 7.46 (m, 4H). Spectral data are in accordance with the literature report.$^{[2]}$

2, 6-Dichlorobenzaldehyde.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.43 (s, 1H), 7.33 (s, 3H). Spectral data are in accordance with the literature report.$^{[1]}$

Furfural

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.59 (s, 1H), 7.64 – 7.62 (m, 1H), 7.19 (dd, $J$ = 3.6, 0.5 Hz, 1H), 6.54 (dd, $J$ = 3.6, 2 Hz, 1H). Spectral data are in accordance with the literature report.$^{[3]}$

2-Acetylthiophene

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.63 (dd, $J$ = 3.8, 1.1 Hz, 1H), 7.57 (dd, $J$ = 5.0, 1.1 Hz, 1H), 7.06 (dd, $J$ = 4.9, 3.8 Hz, 1H), 2.50 (s, 3H). Spectral data are in accordance with the literature report.$^{[3]}$

3-Acetylpyridine

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.09 (d, $J$ = 2.1 Hz, 1H), 8.71 (dd, $J$ = 4.8, 1.6 Hz, 1H), 8.16 (dt, $J$ = 8.0, 2.0 Hz, 1H), 7.36 (dd, $J$ = 8.0, 4.8 Hz, 1H), 2.57 (s, 3H). Spectral data are in accordance with the literature report.$^{[4]}$
Benzaldehyde

\( ^1H \text{ NMR (400 MHz, CDCl}_3 \delta 9.94 \text{ (s, 1H), 7.83 - 7.78 (m, 2H), 7.58 - 7.53 (m, 1H), 7.45 (t, } J = 7.6 \text{ Hz, 2H). Spectral data are in accordance with the literature report}}^{[1]} \)

2-Chlorobenzaldehyde

\( ^1H \text{ NMR (400 MHz, CDCl}_3 \delta 10.41 \text{ (s, 1H), 7.84 (dd, } J = 7.7, 1.7 \text{ Hz, 1H), 7.48 - 7.43 (m, 1H), 7.37 (dd, } J = 8.0, 0.9 \text{ Hz, 1H), 7.31 (t, } J = 7.5 \text{ Hz, 1H).} \)

m-Tolualdehyde

\( ^1H \text{ NMR (400 MHz, CDCl}_3 \delta 9.89 \text{ (s, 1H), 7.58 (m, 2H), 7.37 - 7.30 (m, 2H), 2.33 (s, 3H).} \)

3-Chlorobenzaldehyde

\( ^1H \text{ NMR (400 MHz, CDCl}_3 \delta 9.90 \text{ (s, 1H), 7.77 (t, } J = 1.6 \text{ Hz, 1H), 7.69 (dt, } J = 7.6, 1.3 \text{ Hz, 1H), 7.52 (ddd, } J = 8.0, 2.4, 1.2 \text{ Hz, 1H), 7.41 (t, } J = 7.8 \text{ Hz, 1H).} \)

p-Tolualdehyde

\( ^1H \text{ NMR (400 MHz, CDCl}_3 \delta 9.88 \text{ (s, 1H), 7.69 (d, } J = 8.1 \text{ Hz, 2H), 7.25 (d, } J = 7.9 \text{ Hz, 2H), 2.36 (s, 3H). Spectral data are in accordance with the literature report}}^{[1]} \)

Acetophenone

\( ^1H \text{ NMR (400 MHz, CDCl}_3 \delta 7.88 \text{ (dt, } J = 8.5, 1.7 \text{ Hz, 2H), 7.51 - 7.45 (m, 1H), 7.41 - 7.35 (m, 2H), 2.52 (s, 3H). Spectral data are in accordance with the literature report}}^{[1]} \)

4-Fluoroacetophenone

\( ^1H \text{ NMR (400 MHz, CDCl}_3 \delta 7.93 - 7.87 \text{ (m, 2H), 7.04 (m, 2H), 2.51 (s, 3H).} \)

2-Acetylfuran

\( ^1H \text{ NMR (400 MHz, CDCl}_3 \delta 7.53 - 7.51 \text{ (m, 1H), 7.12 (dd, } J = 3.5, 0.8 \text{ Hz, 1H), 6.47 (dd, } J = 3.5, 1.7 \text{ Hz, 1H), 2.41 (s, 3H). Spectral data are in accordance with the literature report}}^{[3]} \)

2-Thenaldehyde

\( ^1H \text{ NMR (400 MHz, CDCl}_3 \delta 9.87 \text{ (d, } J = 1.2 \text{ Hz, 1H), 7.73 - 7.68 (m, 2H), 7.14 (dd, } J = 4.8, 3.8 \text{ Hz, 1H). Spectral data are in accordance with the literature report}}^{[2]} \)

3-Pyridinecarboxaldehyde

\( ^1H \text{ NMR (400 MHz, CDCl}_3 \delta 10.06 \text{ (s, 1H), 9.02 (dd, } J = 1.6 \text{ Hz,0.4 Hz,1H), 8.78 (dd, } J = 4.8, 1.6 \text{ Hz, 1H), 8.11 (dt, } J = 7.9, 2.0 \text{ Hz, 1H), 7.43 (dd, } J = 7.9, 4.8 \text{ Hz, 1H). Spectral data are in accordance with the literature report}}^{[1]} \)
1-Tetralone
\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \delta 7.95 (d, J = 7.6 Hz, 1H), 7.38 (td, J = 7.5, 1.3 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.17 (t, J = 6.4 Hz, 1H), 2.88 (t, J = 6.1 Hz, 2H), 2.61 - 2.53 (t, J = 6 Hz, 2H), 2.10 - 2.01 (m, 2H). \]

1-Acetyl-4-formylbenzene
\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \delta 10.04 (s, 1H), 8.04 (d, J = 8.3 Hz, 2H), 7.93 - 7.90 (m, 2H), 2.60 (s, 3H). \]

4-Bromobenzoic acid
\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \delta 7.91 - 7.87 (m, 2H), 7.57 - 7.53 (m, 2H). \]

Benzoic acid
\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \delta 8.06 (dd, J = 8.2, 1.1 Hz, 2H), 7.58 - 7.52 (m, 1H), 7.41 (t, J = 7.7 Hz, 2H). \]

2-Furoic acid
\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \delta 9.81 (s, 1H), 7.59 - 7.57 (m, 1H), 7.28 - 7.26 (m, 1H), 6.50 (dd, J = 3.5, 1.7 Hz, 1H). \]

4-Chlorobenzoic acid
\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \delta 7.97 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H). \]

p-Toluic acid
\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \delta 7.94 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 8.2 Hz, 2H), 2.36 (s, 3H). \]

p-Nitrobenzoic acid
\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \delta 8.26 (m 2H), 8.23 - 8.19 (m, 2H). \]
6, $^1$H spectra

Yu-1
Yu-1

Yu-2
Yu-2

Yu-3

Yu-4
7. References