Supporting Information

Abnormal Bis–NHC Mediated Aerial Oxidation of Arylaldehyde: Transformation of Highly Efficient Arylaldehydes to Corresponding Carboxylic Acids Catalyzed by Organic Catalysts

Wei Yang, a Gao-Zhang Gou, a Yi Wang, a* and Wen-Fu Fu a,b*

a W. Yang, G. –Z. Gou, Dr. Y. Wang, Prof. Dr. W.-F. Fu

College of Chemistry and Engineering, Yunnan Normal University, Kunming 650092, P.R. China

Fax: (+86) 871-5516-199

E-mail: fuwf@mail.ipc.ac.cn

b Prof. Dr. W.-F. Fu

Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry

Chinese Academy of Sciences, Beijing 100190, P.R. China

Fax: (+86) 10-6255-4670

E-mail: fuwf@mail.ipc.ac.cn
General information

All reagents were purchased from commercial sources and used without further purification. Water was deionized. Compounds 1a–c were prepared according to the reported methods. Column chromatography was carried out with silica gel (200-300 mesh). Thin layer chromatography was carried out using Merck silica gel GF254 plates. $^1$H NMR and $^{13}$C NMR (500 MHz and 126 MHz, respectively) spectra were recorded on a Bruker MR-500 spectrometer. Chemical shifts are reported in ppm from TMS with the solvent resonance as an internal standard (CDCl$_3$: δ 7.26 ppm, CD$_3$OD: δ 3.31 ppm, DMSO-d$_6$: δ 2.54 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet) and coupling constants (Hz).

X-ray Diffraction. Diffraction data were collected on a Rigaku RAXIS RAPID IP X-Ray diffractometer using a graphite monochromator with Mo Kα radiation (λ = 0.071073 nm) at 293(2) K. The structures were solved by direct methods and refined by full-matrix least-squares methods on all $F^2$ data (SHELX-97). Non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated and refined isotropically. Despite numerous attempts at collecting better data for 1c, its good crystals were easy changed to powder during measurement, the diffraction records remain poor, which are indicated by the high R$_{int}$.

Preparation for Catalysts

\[
\begin{align*}
\text{Ph} = 1,2, & \quad \text{Br(CH$_2$)$_n$Br} \\
\text{THF} = 48h & \text{ reflux} & \\
1a: n = 2 & \quad 1b: n = 3 & \quad 1c: n = 4
\end{align*}
\]

1-(2,4,6-Trimethylphenyl)-1H-imidazole$^{[1]}$ (2.1 g, 8.6 mmol) and 1,2-dibromoethane (0.34 mL, 4.3 mmol) in fresh THF (15 mL) were stirred and refluxed for 48 h. The mixture was concentrated in vacuum after the reaction completed. The residue was filtered and dried under vacuum to afford a white solid 1,1'-di(mesityl)-3,3'-alkyenediimidazolium dibromide 1a.$^{[2]}$ Yield 32%. $^1$H NMR (500 MHz, CD$_3$OD): δ 9.54 (s, 2H), 8.14 (t, $J = 1.7$ Hz, 2H), 7.89 (d, $J = 1.8$ Hz, 2H), 7.17 (s, 4H), 5.19 (s, 4H), 2.39 (s, 6H), 2.11 (s, 12H). $^{13}$C NMR (126 MHz, CD$_3$OD): δ 141.46, 137.98, 134.28, 130.85, 129.43, 125.00, 123.46, 48.62, 19.72, 16.25. ESI: m/z: 200.13.

Catalysts 1,1'-di(mesityl)-3,3'-propyenediimidazolium dibromide 1b and 1,1'-di(mesityl)-3,3'-butyenediimidazolium dibromide 1c were obtained by reacting
1-(2,4,6-trimethylphenyl)-1H-imidazole with 1,3-dibromopropane and 1,4-dibromobutane, respectively. **1b**: Yield 83%. $^1$H NMR (500 MHz, CDCl$_3$) δ 9.96 (s, 2H), 8.67 (s, 2H), 7.11 (s, 2H), 6.98 (s, 4H), 4.97–4.90 (m, 4H), 3.17–3.08 (m, 2H), 2.32 (s, 6H), 2.05 (s, 12H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 141.27, 137.17, 134.22, 130.66, 129.82, 124.86, 122.96, 47.03, 32.11, 21.06, 17.65. ESI: m/z: 207.14. **1c**: Yield 64%. $^1$H NMR (500 MHz, CD$_3$OD) δ 9.42 (s, 2H), 8.08 (s, 2H), 7.79 (t, $J = 1.6$ Hz, 2H), 7.17 (s, 4H), 4.57 (s, 4H), 2.39 (s, 6H), 2.17 (s, 4H), 2.13 (s, 12H). $^{13}$C NMR (126 MHz, CD$_3$OD) δ 141.23, 137.23, 134.42, 131.09, 129.36, 124.39, 123.21, 49.11, 26.66, 19.74, 16.09. ESI: m/z: 214.14.

**Table S1.** Summary of X-ray crystallographic data for catalysts **1a–c**.

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<tr>
<th>compounds</th>
<th><strong>1a</strong></th>
<th><strong>1b•H$_2$O</strong></th>
<th><strong>1c</strong></th>
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<td>formula</td>
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<td>C$<em>{27}$H$</em>{36}$Br$_2$N$_4$O</td>
<td>C$<em>{28}$H$</em>{36}$Br$_2$N$_4$O</td>
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<td>592.42</td>
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<td>P2(1)/c</td>
<td>P2(1)/c</td>
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<tr>
<td>cryst syst</td>
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<td>Monoclinic</td>
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<td>a(Å)</td>
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<td>6.859(1)</td>
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<td>c(Å)</td>
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<td>90</td>
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<td>$\gamma$(deg)</td>
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<td>90</td>
<td>90</td>
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<td>V(Å$^3$)</td>
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<td>2581.5(10)</td>
<td>1550.2(5)</td>
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<tr>
<td>Z</td>
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<td>4</td>
<td>2</td>
</tr>
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<td>293(2)</td>
<td>293(2)</td>
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<tr>
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<td>$R_{1}$a</td>
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<td>0.0401</td>
<td>0.1107</td>
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<td>0.0851</td>
<td>0.3370</td>
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<tr>
<td>max, min peaks (e Å$^{-3}$)</td>
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<td>0.544 and -0.594</td>
<td>1.561 and -0.558</td>
</tr>
</tbody>
</table>
Representative procedure for catalyst reaction

Bis-NHC 1c (0.05 mmol), K₂CO₃ (392 mg, 4.0 mmol) were added in a tube with DMSO (2 mL). After stirred 15 min at room temperature, aldehyde substrate (1.0 mmol) in 3 mL DMSO and H₂O (1.0 mmol) were added. The mixture was stirred under open-air in 60°C. After completion of the reaction, the solution was then quenched by the addition of 1N HCl (25 mL), extracted with ethyl acetate (25 mL × 3). The organic layer was washed with aqueous NaCl, dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by flash column chromatography to give the pure acid.

Experimental data for products

Benzoic acid 3a

White solid in 91% yield. \(^1\)H NMR (500 MHz, CDCl₃) δ 11.74 (s, 1H), 8.18 (d, \(J = 7.3\) Hz, 2H), 7.65 (t, \(J = 7.4\) Hz, 1H), 7.52 (t, \(J = 7.8\) Hz, 2H). \(^1\)C NMR (126 MHz, CDCl₃) δ 172.57, 133.83, 130.25, 129.41, 128.51. ESI-MS: m/z: 122.04.

4-Fluorobenzoic acid 3b

White solid in 90% yield. \(^1\)H NMR (500 MHz, DMSO-d₆) δ 13.06 (s, 1H), 8.11–7.92 (m, 2H), 7.40–7.21 (m, 2H). \(^1\)C NMR (126 MHz, DMSO-d₆) δ 166.84, 166.37, 164.38, 132.59, 127.83, 116.14. ESI: m/z: 140.03.

4-Chlorobenzoic acid 3c

Electronic Supplementary Material (ESI) for RSC Advances
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White solid in 94% yield. $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 13.20 (s, 1H), 7.87 (d, $J = 8.4$ Hz, 2H), 7.72 (dd, $J = 8.4$, 2.6 Hz, 2H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$ 166.92, 138.26, 131.60, 130.10, 129.19. ESI: m/z: 156.00.

4-Bromobenzoic acid 3d$^{[5]}$

White solid in 92% yield. $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 13.20 (s, 1H), 7.87 (d, $J = 8.4$ Hz, 2H), 7.72 (dd, $J = 8.4$, 2.6 Hz, 2H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$ 166.93, 138.26, 131.60, 130.10, 129.19. ESI: m/z:199.95.

4-Methylbenzoic acid 3e

White solid in 85% yield. $^1$H NMR (500 MHz, CD$_3$OD) $\delta$ 7.92 (d, $J = 8.2$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 2.41 (s, 3H). $^{13}$C NMR (126 MHz, CD$_3$OD) $\delta$ 168.62, 143.56, 129.42, 128.69, 127.71, 20.20. ESI: m/z: 136.05.

4-(trifluoromethyl)benzoic acid 3f$^{[5]}$

White solid in 93% yield. $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 13.46 (s, 1H), 8.13 (d, $J = 8.1$ Hz, 2H), 7.85 (d, $J = 8.3$ Hz, 2H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$ 166.66, 135.05, 132.82, 130.53, 125.98, 123.16. ESI: m/z:190.02.

4-Methoxybenzoic acid 3g$^{[5]}$

White solid in 70% yield. $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 12.63 (s, 1H), 7.90 (d, $J = 8.8$ Hz, 2H), 7.02 (dd, $J = 7.8$, 2.4 Hz, 2H), 3.84–3.81 (m, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$ 167.48, 163.30, 131.81, 123.46, 114.26, 55.88. ESI: m/z: 152.05.
3-Nitrobenzoic acid 3h

![3h](image)

White solid in 60% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 10.37 (s, 1H), 9.08–8.88 (m, 1H), 8.51 (ddd, J = 8.2, 2.3, 1.1 Hz, 1H), 8.50 – 8.45 (m, 1H), 7.75 (dd, J = 10.0, 6.0 Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 170.06, 148.39, 135.79, 130.96, 129.92, 128.37, 125.25. ESI: m/z: 167.02.

4-Nitrobenzoic acid 3i

![3i](image)

Yellow solid in 95% yield. $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 13.64 (s, 1H), 8.33–8.30 (m, 2H), 8.20–8.13 (m, 2H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$ 166.27, 150.47, 136.89, 131.15, 124.16. ESI: m/z: 167.02.

2,4,6-Trimethoxybenzoic acid 3j

![3j](image)

White solid in 72% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 10.78 (s, 1H), 7.60 (s, 1H), 6.57 (s, 1H), 4.07 (s, 3H), 3.97 (s, 3H), 3.89 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 165.38, 154.38, 153.68, 144.03, 114.47, 108.88, 96.34, 57.34, 56.34. ESI: m/z: 212.07.

2-Naphthoic acid 3k

![3k](image)

White solid in 91% yield. $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 13.12 (s, 1H), 8.63 (s, 1H), 8.12 (d, J = 8.0 Hz, 1H), 8.05–7.95 (m, 3H), 7.63 (dt, J = 15.0, 6.9 Hz, 2H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$ 167.93, 135.40, 132.61, 130.99, 129.75, 128.79, 128.63, 128.54, 128.12, 127.27, 125.63. ESI: m/z: 172.05.
Thiophene-2-carboxylic acid 3I

\[
\text{\includegraphics[width=0.2\textwidth]{thiophene_carboxylic_acid_3i}}
\]

White solid in 83% yield. $^1$H NMR (500 MHz, DMSO) $\delta$ 13.05 (s, 1H), 7.87 (dd, $J = 5.0, 1.3$ Hz, 1H), 7.74 (dd, $J = 3.7, 1.3$ Hz, 1H), 7.18 (dd, $J = 5.0, 3.7$ Hz, 1H). $^{13}$C NMR (126 MHz, DMSO) $\delta$ 163.40, 135.12, 133.70, 133.68, 128.68. ESI: m/z: 127.99.

Furan-2-carboxylic acid 3m

\[
\text{\includegraphics[width=0.2\textwidth]{furan_carboxylic_acid_3m}}
\]

White solid in 68% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.71 (s, 1H), 7.67 (dd, $J = 1.6, 0.8$ Hz, 1H), 7.36 (dd, $J = 3.5, 0.7$ Hz, 1H), 6.59 (dd, $J = 3.5, 1.7$ Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 163.64, 147.43, 143.85, 120.09, 112.27. ESI: m/z: 112.02.

References
\( ^1\text{H} \) and \( ^13\text{C} \) NMR spectra for catalysts and products