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

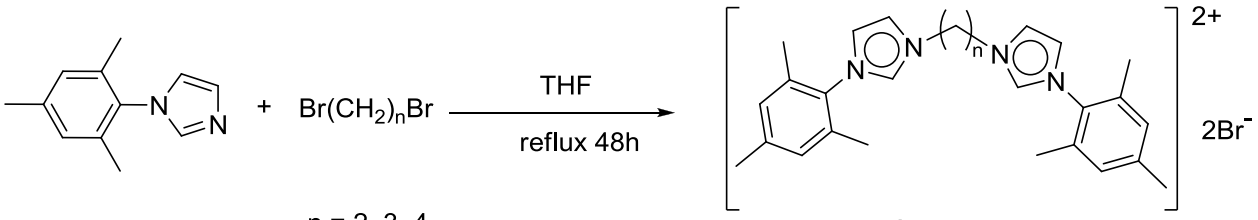
E-mail: fuwf@mail.ipc.ac.cn

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.[1,2] Column chromatography was carried out with silica gel (200-300 mesh). Thin layer chromatography was carried out using Merck silica gel GF_{254} 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_3OD: 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).[3] 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



1-(2,4,6-Trimethylphenyl)-1*H*-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_3OD): 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_3OD): 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

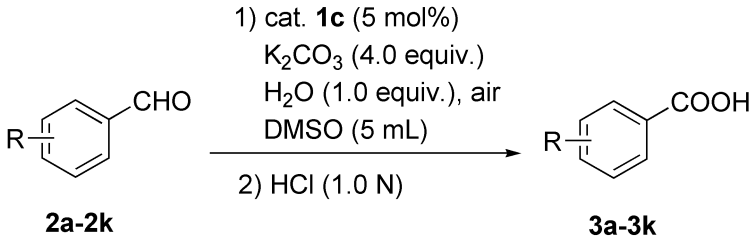
1-(2,4,6-trimethylphenyl)-1*H*-imidazole with 1,3-dibromoprothane and 1,4-dibromobutane, respectively. **1b**: Yield 83%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.96 (s, 2H), 8.67 (s, 2H), 7.11 (s, 2H), 6.98 (s, 4H), 4.97–4.90 (m, 4H), 3.17–3.08 (m, 2H), 2.32 (s, 6H), 2.05 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) 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_3OD) 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_3OD) *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**.

compounds	**1a**	**1b•H_2O**	**1c**
formula	$C_{26}H_{32}Br_2N_4$	$C_{27}H_{36}Br_2N_4O$	$C_{28}H_{36}Br_2N_4$
fw	560.38	592.42	588.43
space group	Pna2(1)	P2(1)/c	P2(1)/c
cryst syst	Orthorhombic	Monoclinic	Monoclinic
a(Å)	18.050(4)	6.859(1)	14.276(3)
b(Å)	6.754(1)	18.823(4)	9.121(2)
c(Å)	21.429(4)	22.137(4)	13.007(3)
α(deg)	90	90	90
β(deg)	90	93.85(3)	113.75(3)
γ(deg)	90	90	90
V(Å^3)	2612.5(9)	2581.5(10)	1550.2(5)
Z	4	4	2
T (K)	293(2)	293(2)	293(2)
ρ_{calcd} (g cm^{-3})	1.425	1.380	1.261
θ rang (deg)	3.16 to 27.46	3.17 to 27.48	3.12 to 25.00
μ (mm^{-1})	3.123	2.868	2.635
crystal size (mm)	0.22 × 0.18 × 0.16	0.24 × 0.20 × 0.18	0.14 × 0.10 × 0.10
GOF	1.064	1.066	1.113
no. of unique data	5850	6459	2708
no. of parameters	295	320	158
R_{int}	0.0760	0.0561	0.1139
$R_1{}^a$	0.0553	0.0401	0.1107
w$R_2{}^b$	0.1322	0.0851	0.3370
max, min peaks (e Å^{-3})	1.240 and -0.988	0.544 and -0.594	1.561 and -0.558

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $Rw = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Representative procedure for catalyst reaction

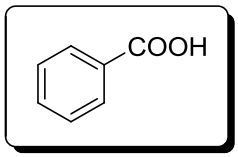


2a-2k **3a-3k**

Bis-NHC **1c** (0.05 mmol), K_2CO_3 (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 H_2O (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 Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography to give the pure acid.

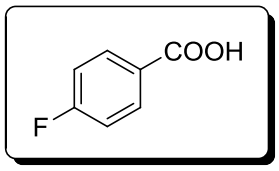
Experimental data for products

Benzoic acid **3a**[4]



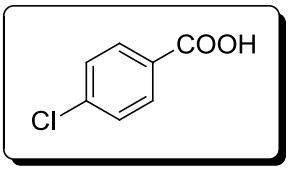
White solid in 91% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.74 (s, 1H), 8.18 (d, J = 7.3 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.57, 133.83, 130.25, 129.41, 128.51. ESI-MS: m/z: 122.04.

4-Fluorobenzoic acid **3b**



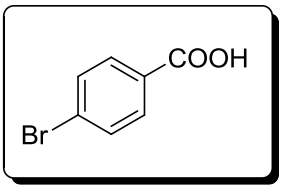
White solid in 90% yield. ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.06 (s, 1H), 8.11–7.92 (m, 2H), 7.40–7.21 (m, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 166.84, 166.37, 164.38, 132.59, 127.83, 116.14. ESI: m/z: 140.03.

4-Chlorobenzoic acid **3c**[5]



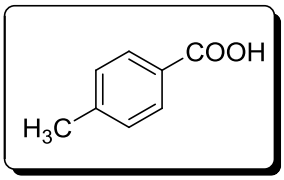
White solid in 94% yield. ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.20 (s, 1H), 7.87 (d, J = 8.4 Hz, 2H), 7.72 (dd, J = 8.4, 2.6 Hz, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 166.92, 138.26, 131.60 , 130.10, 129.19. ESI: m/z: 156.00.

4-Bromobenzoic acid **3d**[5]



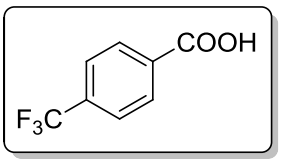
White solid in 92% yield. ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.20 (s, 1H), 7.87 (d, J = 8.4 Hz, 2H), 7.72 (dd, J = 8.4, 2.6 Hz, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 166.93, 138.26, 131.60, 130.10, 129.19. ESI: m/z:199.95.

4-Methylbenzoic acid **3e**



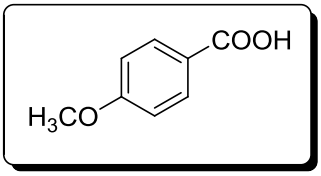
White solid in 85% yield. ^{1}H NMR (500 MHz, CD_3OD) δ 7.92 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (126 MHz,CD_3OD) δ 168.62, 143.56, 129.42, 128.69, 127.71, 20.20. ESI: m/z: 136.05.

4-(trifluoromethyl)benzoic acid **3f**[5]



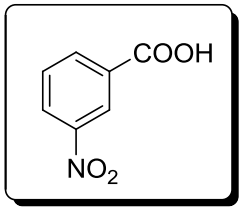
White solid in 93% yield. ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.46 (s, 1H), 8.13 (d, J = 8.1 Hz, 2H), 7.85 (d, J = 8.3 Hz, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 166.66, 135.05, 132.82, 130.53, 125.98, 123.16. ESI: m/z:190.02.

4-Methoxybenzoic acid **3g**[5]



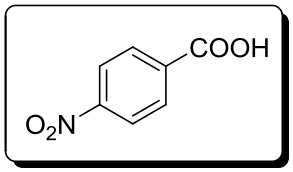
White solid in 70% yield. ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.63 (s, 1H), 7.90 (d, J = 8.8 Hz, 2H), 7.02 (dd, J = 7.8, 2.4 Hz, 2H), 3.84–3.81 (m, 3H). ^{13}C NMR (126 MHz, DMSO-*d6*) δ 167.48, 163.30, 131.81, 123.46, 114.26, 55.88. ESI: m/z: 152.05.

3-Nitrobenzoic acid **3h**



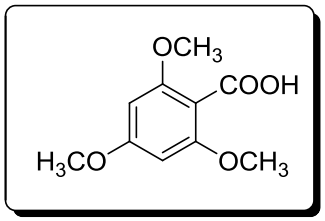
White solid in 60% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.37 (s, 1H), 9.08–8.88 (m, 1H), 8.51 (ddd, J = 8.2, 2.3, 1.1 Hz, 1H), 8.50 – 8.45 (m, 1H), 7.75 (dd, J = 10.0, 6.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.06, 148.39, 135.79, 130.96, 129.92, 128.37, 125.25. ESI: m/z: 167.02.

4-Nitrobenzoic acid **3i**



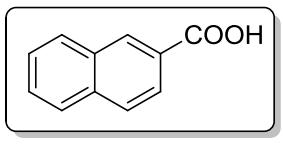
Yellow solid in 95% yield. ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.64 (s, 1H), 8.33–8.30 (m, 2H), 8.20–8.13 (m, 2H). ^{13}C NMR13C NMR (126 MHz, DMSO-d_6) δ 166.27, 150.47, 136.89, 131.15, 124.16. .ESI: m/z: 167.02.

2,4,6-Trimethoxybenzoic acid **3j**



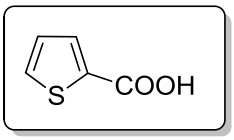
White solid in 72% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.78 (s, 1H), 7.60 (s, 1H), 6.57 (s, 1H), 4.07 (s, 3H), 3.97 (s, 3H), 3.89 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.38, 154.38, 153.68, 144.03, 114.47, 108.88, 96.34, 57.34, 56.34. ESI: m/z: 212.07.

2-Naphthoic acid **3k**



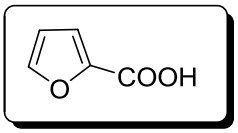
White solid in 91% yield. ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.12 (s, 1H), 8.63 (s, 1H), 8.12 (d, J = 8.0 Hz, 1H), 8.05–7.95 (m, 3H), 7.63 (dt, J = 15.0, 6.9 Hz, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 167.93, 135.40, 132.61, 130.99, 129.75, 128.79, 128.63, 128.54, 128.12, 127.27, 125.63. ESI: m/z: 172.05.

Thiophene-2-carboxylic acid **3l**



White solid in 83% yield. 1H NMR (500 MHz, DMSO) δ 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) δ 163.40, 135.12, 133.70, 133.68, 128.68. ESI: m/z: 127.99.

Furan-2-carboxylic acid **3m**



White solid in 68% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 163.64, 147.43, 143.85, 120.09, 112.27. ESI: m/z: 112.02.

References

1 J. Liu, J. Cheng, J. Zhao, Y. Zhao, L. Li, H. Zhang, *Synthesis*, 2003, 2661–2666.

2 H. M. Lee, C. Y. Lu, C. Y. Chen, W. L. Chen, H. C. Ling, P. L. Chiu, P. Y. Cheng, *Tetrahedron*, 2004**, 60**, 5807–5825.

3 G. M. Sheldrich, *SHELX-97, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, 1997.

4 P. Chiang, J. W. Bode, *Org. Lett*. 2011, **13**, 2422–2425.

5 L. Gu, Y. Zhang, *J. Am. Chem. Soc*. 2010, **132**, 914–915.

^{1}H and ^{13}C NMR spectra for catalysts and products