Supporting information

Aerobic oxidation of primary benzylic amines to amides and nitriles catalyzed by ruthenium carbonyl clusters carrying *N,O*-bidentate ligands

Xinlong Yan,[a]‡ Qing Dong,[a]‡ Ying Li,[a] Lizhen Meng,[a] Zhiqiang Hao,*[a] Zhangang Han,[a] Guo-Liang Lu[b] and Jin Lin*[a]

[a] Hebei Key Laboratory of Organic Functional Molecules, The College of Chemistry and Material Science, Hebei Normal University, Shijiazhuang 050024, People's Republic of China

[b]Auckland Cancer Society Research Centre, Faculty of Medical and Health Sciences, The University of Auckland, Private Bag 92019, Auckland 1142, New Zealand

‡ Both authors contributed equally to this work.

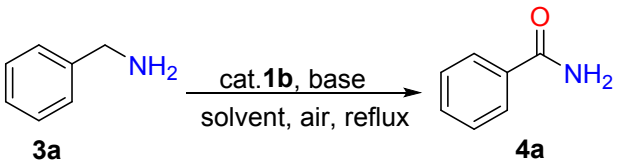
Correspondence to: Zhiqiang Hao and Jin Lin, College of Chemistry and Material Science, Hebei Normal University, Shijiazhuang 050024, China

E-mail: haozhiqiang1001@163.com; linjin64@126.com

Table of Contents

1. The screening of bases and solvents

Table S1. Screening of bases and solvents for oxygenation of bezylamine to benzamide catalyzed by **1b**[a]



3a **4a**

Run	Solvent	Base	Conversion[b] (%)	Yield[b] (%)
1	*i*-PrOH	*t*-BuOK	76	60
2	CH_3CH_2OH	*t*-BuOK	79	18
3	CH_3OH	*t*-BuOK	72	12
4	THF	*t*-BuOK	42	11
5	Toluene	*t*-BuOK	trace	trace
6	1,4-dioxide	*t*-BuOK	56	32
7	*t*-BuOH	*t*-BuOK	90	77
8	*t*-BuOH	KOH	86	70
9	*t*-BuOH	NaOH	68	43
10	*t*-BuOH	Na_2CO_3	60	22
11	*t*-BuOH	$NaHCO_3$	48	17
12	*t*-BuOH	DABCO	35	trace
13	*t*-BuOH	Cs_2CO_3	28	trace

[a] Reaction conditions: benzyl amine (1.0 mmol), Cat. **1b** (3.0 mol%), *t*-BuOK (1.0 mmol), *t*-BuOH (4.0 mL), t = 12 h. [b] determined by GC.

2. Crystal data for 1b, 2a and 2b.

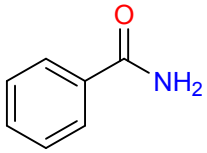
Table S2. Crystal data and structure refinements of ruthenium complexes

Complex	**1b**	**2a**	**2b**
formula	$C_{32}H_{16}Br_4N_2O_{10}Ru_3$	$C_{36}H_{24}N_2O_{12}Ru_3$	$C_{34}H_{18}Br_2N_2O_{10}Ru_3$
Fw	1211.32	979.78	1077.52
T, K	298(2)	298(2) K	296(2) K
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic
space group	*C2/c*	*P*-1	*P*-1
a (Å)	11.6950(9)	11.4233(11)	9.9227(5)
b (Å)	16.5574(16)	12.1695(12)	12.4570(6)
c (Å)	19.8654(18)	15.1533(14)	16.0614(8)
a (°)	90	70.4830(10)	80.5840(10)
β (°)	103.851(3)	87.865(2)	74.3200(10)
γ (°)	90	78.5920(10)	67.5180(10)
Volume ($Å^3$)	3720.7(5)	1945.3(3)	1762.10(15)
Z	4	2	2
D_{calc} (mg/m^3)	2.162	1.673	2.031
μ (mm^{-1})	5.554	1.211	3.596
F (000)	2296	964	1036
Crystal size (mm)	0.27×0.23×0.12	0.43 x 0.32 x 0.30	0.28 x 0.26 x 0.19 mm
θ range (°)	2.47-25.02	2.28-25.02	2.281-28.315
Reflections collected	9115/3259	9720/6722	2.281 to 28.315
R (int)	0.0437	0.0414	0.0329
Completeness to *θ*	99.70%	97.9%	98.7 %
Max. and min. transmission	0.5554/0.3155	0.7127/0.6240	0.5636/ 0.3812
Data/restraints/ parameters	3259/0/231	6722 / 0 / 480	8654 / 0 / 461
Goodness-of-fit on F^2	1.044	1.046	1.023

R_1, wR_2 [I>2σ(I)]	0.0354, 0.0731	0.0400, 0.1000	0.0381, 0.1040
R_1, wR_2 (all data)	0.0592, 0.0797	0.0531, 0.1100	0.0473, 0.1211
Max.peak/(e.Å^{-3})	0.856	0.924	2.251
Mini.peak/(e.Å^{-3})	-0.783	-1.033	-1.380
CCDC	1559100	1558722	1504156

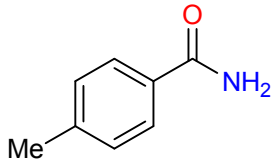
3. NMR data of the primary amides

1. benzamide (**4a**)



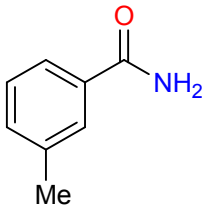
^{1}H NMR (DMSO-d_6, 400 MHz, 298 K): δ 7.99 (s, 1H, NH_2), 7.89 (d, J = 7.0 Hz, 2H, Ph-H), 7.51 (t, J = 7.3 Hz, 1H, Ph-H), 7.45 (t, J = 7.3 Hz, 2H, Ph-H), 7.38 (s, 1H, NH_2) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 298 K): δ 167.9, 134.3, 131.2, 128.2, 127.5 ppm.

2. 4-methylbenzamide (**4b**)



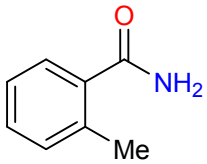
^{1}H NMR (DMSO-d_6, 400 MHz, 298 K): δ 7.87 (s, 1H, NH_2), 7.77 (d, J = 8.1 Hz, 2H, C$_6H_4$), 7.23-7.25 (m, 3H, C$_6H_4$, NH_2), 2.34 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 298 K): δ 167.7, 141.1, 131.5, 128.7, 127.5, 20.9 ppm.

3. 3-methylbenzamide (**4c**)



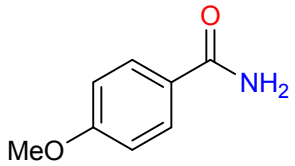
^{1}H NMR (DMSO-d_6, 400 MHz, 298 K): δ 7.93 (s, 1H, NH_2), 7.67-7.71 (m, 2H, C$_6H_4$), 7.31-7.34 (m, 3H, C$_6H_4$, NH_2), 2.34 (s, 3H, CH_3) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz, 298 K): δ 168.1, 137.4, 134.3, 131.8, 128.1, 124.6, 20.9 ppm.

4. 2-methylbenzamide (**4d**)



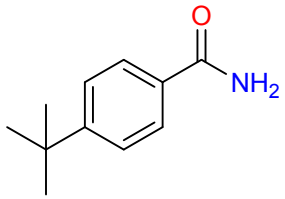
^{1}H NMR (DMSO-d_6, 400 MHz, 298 K): δ 7.68 (s, 1H, NH_2), 7.28-7.36 (m, 3H, C$_6H_4$, NH_2), 7.18-7.23 (m, 2H, C$_6H_4$), 2.36 (s, 2H, CH_3) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz, 298 K): δ 171.1, 137.0, 135.2, 130.5, 129.1, 127.0, 125.3, 19.7 ppm.

5. 4-methoxybenzamide (**4e**)



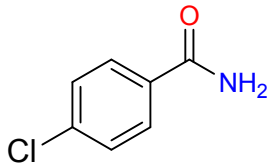
^{1}H NMR (DMSO-d_6, 400 MHz, 298 K): δ 7.85 (m, 3H, C_6H_4, NH_2), 7.17 (s, 1H, NH_2), 6.97 (d, J = 8.9 Hz, 2H, C_6H_4), 3.80 (s, 3H, OCH_3) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz, 298 K): δ 167.4, 161.6, 129.3, 126.5, 113.4, 55.3 ppm.

6. 4-(tert-butyl)benzamide (**4f**)



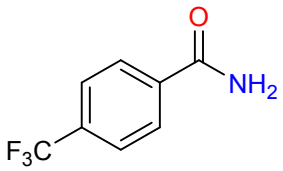
^{1}H NMR (DMSO-d_6, 400 MHz, 298 K): δ 7.88 (s, 1H, NH_2), 7.80 (d, J = 8.5 Hz, 2H, C_6H_4), 7.45 (d, J = 8.5 Hz, 2H, C_6H_4), 7.25 (s, 1H, NH_2), 1.29 (s, 9H, CH_3) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz, 298 K): δ 167.8, 153.9, 131.5, 127.3, 124.9, 34.6, 30.9 ppm.

7. 4-chlorobenzamide (**4g**)



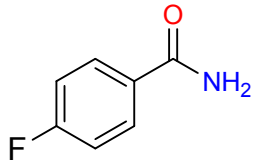
^{1}H NMR (DMSO-d_6, 400 MHz, 298 K): δ 8.04 (s, 1H, NH_2), 7.89 (d, J = 8.5 Hz, 1H, C_6H_4), 7.52 (d, J = 8.5 Hz, 1H, C_6H_4), 7.45 (s, 1H, NH_2) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz, 298 K): δ 166.8, 136.1, 133.0, 129.4, 128.3 ppm.

8. 4-(trifluoromethyl)benzamide (**4h**)



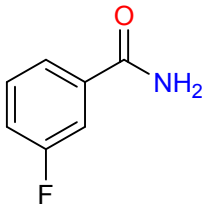
^{1}H NMR (DMSO-d_6, 400 MHz, 298 K): δ 8.19 (s, 1H, NH_2), 8.06 (d, J = 8.0 Hz, 2H, C_6H_4), 7.84 (d, J = 8.2 Hz, 2H, C_6H_4), 7.61 (s, 1H, NH_2) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz, 298 K): δ 166.7, 138.1, 131.3 (q, $J_{C\text{-}F}$ = 31.7 Hz), 128.3, 125.3. (q, $J_{C\text{-}F}$ = 5.1 Hz), 122.6 (q, $J_{C\text{-}F}$ = 270.7 Hz) ppm.

9. 4-fluorobenzamide (**4i**)



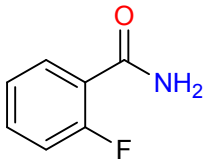
^{1}H NMR (DMSO-d_6, 400 MHz, 298 K): δ 7.99 (s, 1H, NH_2), 7.92-7.96 (m, 2H, C$_6H_4$), 7.39 (s, 1H, NH_2), 7.24-7.29 (m, 2H, C$_6H_4$) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz, 298 K): δ 166.8, 165.2, 130.8, 130.1, 115.2 ppm.

10. 3-fluorobenzamide (**4j**)



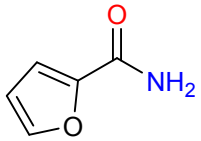
^{1}H NMR (DMSO-d_6, 400 MHz, 298 K): δ 8.05 (s, 1H, NH_2), 7.72 (d, J = 7.7 Hz, 1H, C$_6H_4$), 7.67 (d, J = 9.2 Hz, 1H, C$_6H_4$), 7.48-7.53 (m, 2H, C$_6H_4$, NH_2), 7.37 (t, J = 8.3 Hz, 1H, C$_6H_4$) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz, 298 K): δ 166.5, 163.2, 136.8, 130.3, 123.6, 118.0, 114.1 ppm.

11. 2-fluorobenzamide (**4k**)



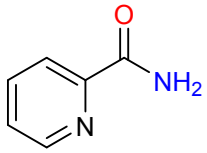
^{1}H NMR (DMSO-d_6, 400 MHz, 298 K): δ 7.61-7.69 (m, 3H, C$_6H_4$, NH_2), 7.49-7.55 (m, 1H, C$_6H_4$), 7.24-7.29 (m, 2H, C$_6H_4$) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz, 298 K): δ 165.2, 160.5, 132.4, 130.2, 124.4, 123.8, 116.2 ppm.

12. furan-2-carboxamide (**4l**)



^{1}H NMR (DMSO-d_6, 400 MHz, 298 K): δ 7.79 (s, 1H, furan-CH), 7.74 (s, 1H, NH_2), 7.35 (s, 1H, NH_2), 7.08 (d, J = 3.4 Hz, 1H, furan-CH), 6.59 (d, J = 3.3 Hz, 1H, furan-CH) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz, 298 K): δ 159.4, 147.9, 145.0, 113.6, 111.8 ppm.

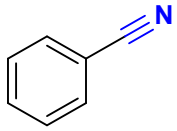
13. pyridin-2-ylmethanamine (**4m**)



^{1}H NMR (DMSO-d_6, 400 MHz, 298 K): δ 8.62 (d, J = 4.3 Hz, 1H, Py-H), 8.14 (s, 1H, NH_2), 8.02 (d, J = 8.9 Hz, 1H, Py-H), 7.98 (t, J = 7.7, 1H, Py-H), 7.65 (s, 1H, NH_2), 7.58 (t, J = 7.4 Hz, 1H, Py-H) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz, 298 K): δ 165.7, 150.0, 148.2, 137.4, 126.2, 121.6 ppm.

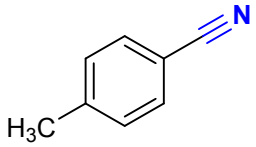
4. NMR data of the benzonitrile derivatives

1. benzonitrile (**5a**)



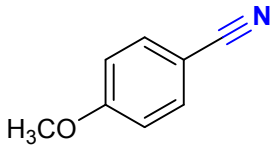
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.59-7.70 (m, 3H), 7.52-7.46 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 132.4, 131.6, 129.1, 118.8, 112.3 ppm.

2. 4-Methylbenzonitrile (**5b**)



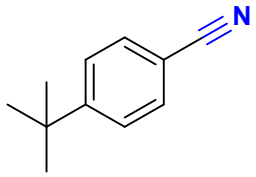
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.81 (d, *J* = 7.0 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 2H), 2.05 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 143.7, 132.0, 129.8, 119.2, 109.2, 21.8 ppm.

3. 4-Methoxybenzonitrile (**5d**)



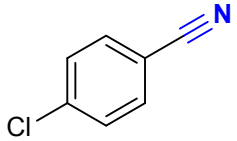
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.59 (d, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 3.86 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 163.0, 134.1, 119.3, 114.8, 104.0, 55.6 ppm.

4. 4-*tert*-Butylbenzonitrile (**5e**)



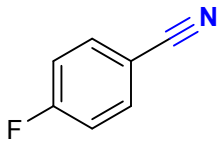
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.59 (d, *J* = 7.0 Hz, 2H), 7.48 (d, *J* = 7.1 Hz, 2H), 1.33 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 156.8, 131.9, 126.1, 119.1, 109.1, 35.2, 30.9 ppm.

5. 4-Chlorobenzonitrile (**5f**)



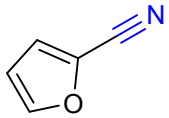
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.61 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 2.2 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 144.4, 131.0, 129.0, 115.7, 109.2 ppm.

6. 4-Fluorobenzonitrile (**5g**)



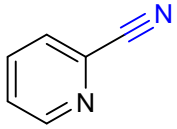
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.74-7.68 (m, 2H), 7.55-7.51 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 166.4, 132.3, 118.9, 116.4, 108.2 ppm.

7. 2-Furonitrile (**5i**)



^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.57 (s, 1H), 6.80 (s, 1H), 6.55 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 149.5,143.4, 137.1,112.2, 110.2 ppm.

8. 2-Pyridinecarbonitrile (**5j**)



^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.65 (s, 1H), 7.81 (s, 1H), 7.71 (s, 1H), 7.54 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 151.1, 137.1, 134.0,128.6, 127.0, 117.2 ppm.