Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting information

Selectivity-tunable Amines Aerobic Oxidation Catalysed by Metal-free N, O-doped Carbons

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Materials

All starting materials and solvents were obtained from commercial suppliers and used without further purification.

Synthesis of m-NOC-x

The typical m-NOC-x catalysts were prepared as follows: 270 mg bidppz ligand (11,11'-bis(dipyrido[3,2-a:2,3-c]phenazinyl)) was added into 40 mL DMF under vigorous stirring. The mixture was refluxed at 130 ^oC for 0.5h. Then 1200 mg 40% dispersion of 12-nm SiO_2 particles (Ludox HS-40) in water was added into the mixture under vigorous stirring. After evaporation of DMF at 180 ^oC, the obtained bidppz/SiO_2 composites were then pyrolyzed under flowing N_2 with a heating ramp rate of 1 ^oC/min to desired temperatures (600-900 ^oC) and the temperature was kept for 5 h. Finally, m-NOC-*x* catalysts, where x indicated the pyrolysis temperature, were obtained after removal of templates by 0.5 M NaOH etching for 5 h at 100 ^oC.

Synthesis of NOC and m-OC

270mg bidppz ligand was directly pyrolyzed under flowing N_2 with a heating ramp rate of 1 ^oC/min to 800 ^oC and the temperature was kept for 5 h. The as-obtained black powder was denoted as NOC. The synthesis procedure for m-OC was quite similar to m-NOC-x, except that sucrose and H_2O replaced bidppz and DMF.

Table S1 The heterogeneous catalytic systems for amine aerobic oxidation to nitriles.

Entry	Catalyst	Reaction conditions	Yield (%)		Ref.
			benzonitrile	N-benzylidene benzylamine	
1	Ru /Al_2O_3	$PhCF_3$ (5mL), 110 °C, 1 bar O_2, 1h	81.2	-	5a
2	$Ru(OH)_x/Al_2O_3$	$PhCF_3$ (5 mL), 100 °C , 1 bar O_2, 1h	82.0	-	5b
3	Ru@PMO-IL	Anhydrous toluene (2 mL), 85 °C, 1 bar O_2, 6h	93.1	-	5c
4	Co_3O_4/NGr@C	*t*-amyl alcohol (4 mL), 110 °C, 3bar O_2, 200 µL aq. NH_3 (28–30% NH_3 basis)	96.0	-	5g
5	Fe_2O_3/NGr@C	*t*-amyl alcohol (4 mL). 110 °C, 3 bar O_2, 200 µL aq. NH_3 (28–30% NH_3 basis), 15-20h	97.0	-	5h
6	MnO_x	CH_3CN (5mL), 90 °C, 3 bar O_2, 14h	86.5	-	5i
7	GO	5 bar O_2, 100 °C, 4h	-	98.0	9a
8	BNHG1000	CH_3CN (5 mL), 85 °C, 1 bar O_2, 4h	-	90	9b
9	NBG/CNTs	CH_3CN (5 mL), 85 °C, 1 bar O_2, 3h	-	91.1	9c
10	B-C	O_2 balloon, 100 °C, 14h	-	90	9d
11	GO	0.59 mmol NaClO, CH_3CN (5 mL), 75 °C, 5h	54	40	10
12	m-NOC-800	*t*-amyl alcohol (0.5 mL), 110 °C, 2bar O_2, 200 µL aq. NH_3 (28–30% NH_3 basis)	83.6	-	***This work***

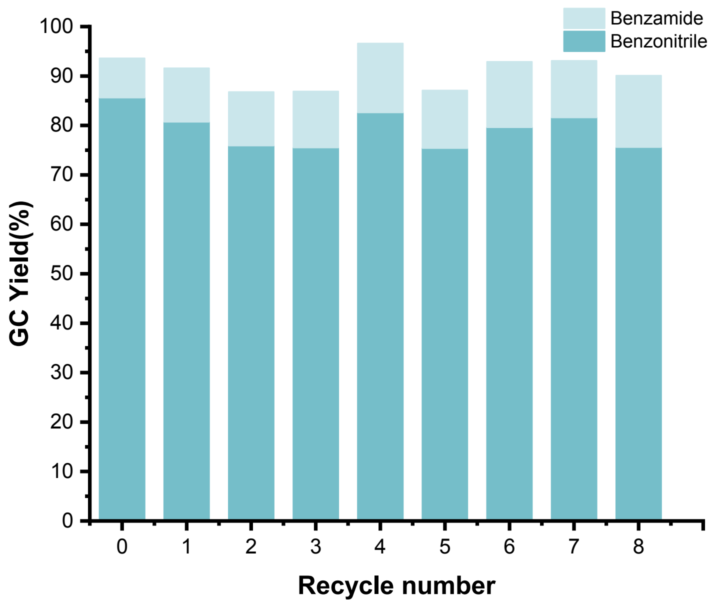


Fig. S1 Recycle experiment of m-NOC-800 catalysts.

Table S2 BET analysis results of m-NOC-x

Entry	NOC-900	m-NOC			
		-600	-700	-800	-900
S_{BET}(m^2·g^{-1})	32.6	655.8	656.1	689.3	780.4
S_{Micro}(m^2·g^{-1})	2.5	113.5	130.6	127.0	155.6
S_{Meso}(m^2·g^{-1})	-	542.2	525.4	562.3	624.9
V_{Total}(cc·g^{-1})	0.17	2.24	2.21	2.32	2.26
D_{Pore}[a](nm)	-	12.3	12.0	12.2	12.0

[a] Calculated using the BJH method.

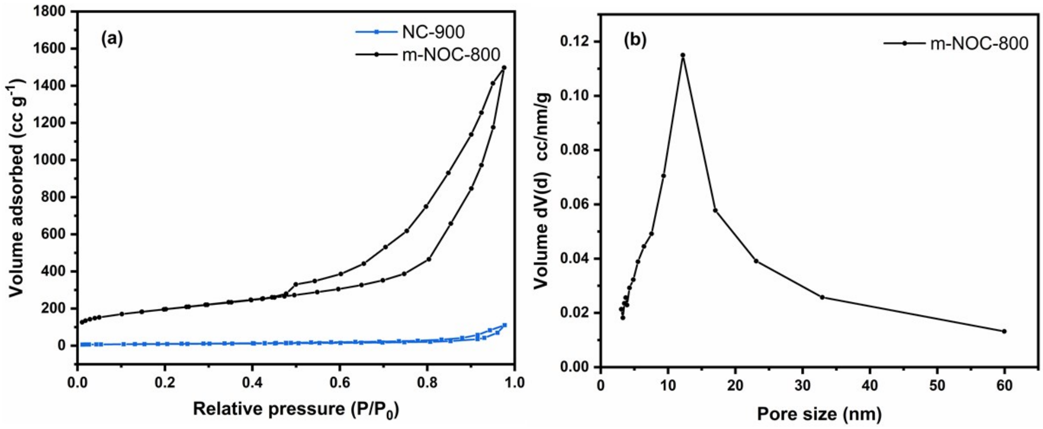


Fig. S2 (a) N_2 adsorption-desorption isotherms of m-NOC-800 and NOC-900. (b) Mesoporous size distribution curve of m-NOC-800.

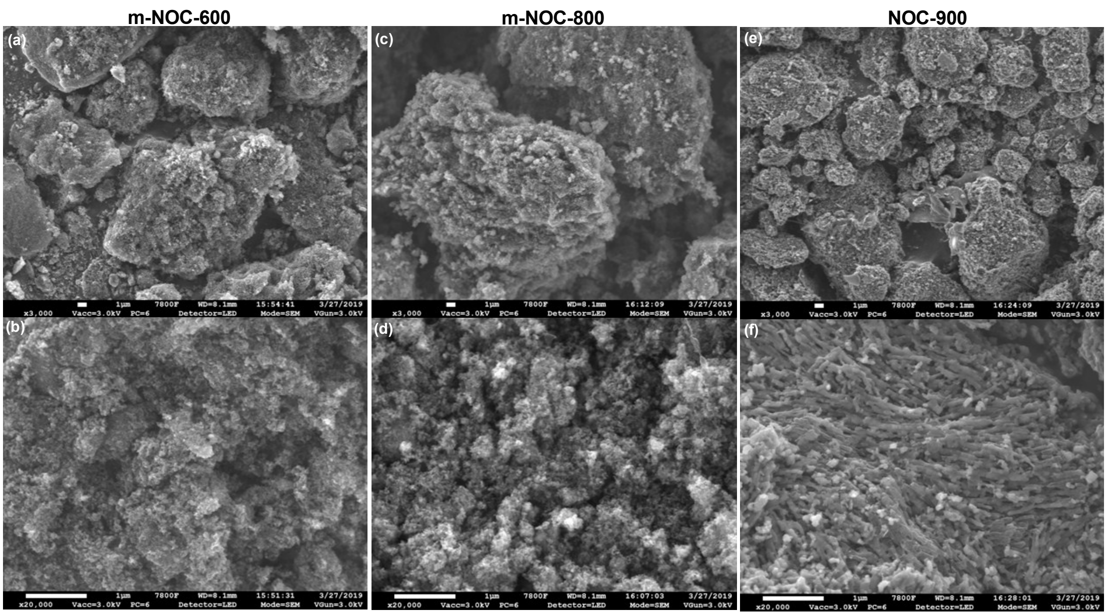


Fig. S3 (a, b) m-NOC-600; (c, d) m-NOC-800 and (e, f) NOC-900.

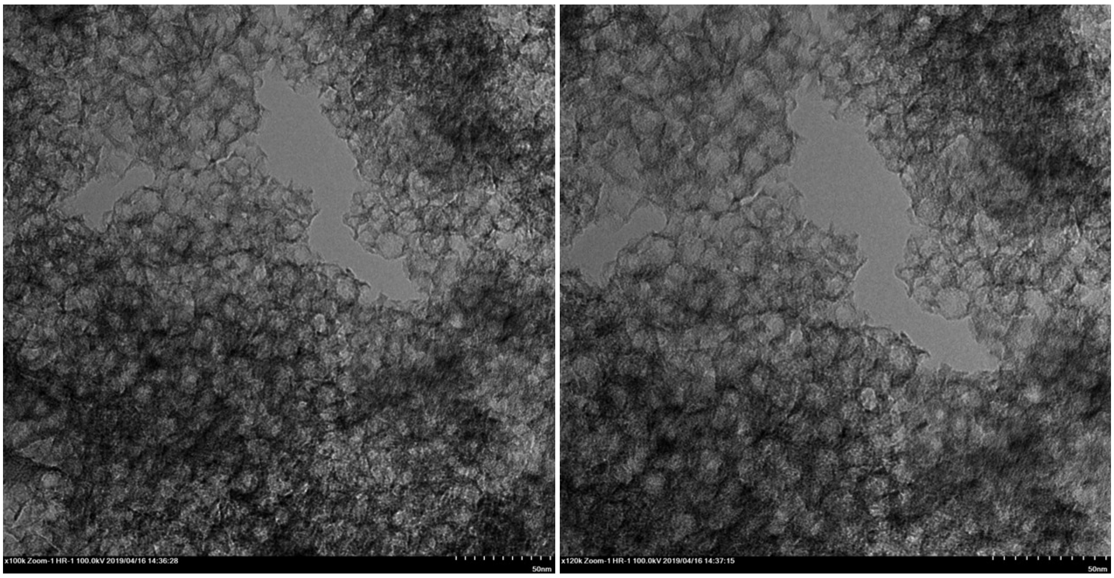


Fig. S4 TEM at high magnification of (a) m-NOC-600 and (b) m-NOC-800.

Table S3 C1s, N 1s and O 1s of m-NOC-*x* over XPS spectra.

m-NOC	Total C (at%)	C=C	C-N	C-O	O-C=O	Total N (at%)	Pyridinic N	Pyrrolic N	Graphitic N	Pyridinic N-O	Total O (at%)	C-OH	O-C=O	C=O	adsorbed O
-600	78.9	45.7	25.9	-	7.3	15.7	8.9	2.8	3.2	0.8	4.8	1.3	1.3	1.2	1.0
-700	82.8	39.3	24.3	14.0	5.2	11.5	4.5	1.8	3.9	1.3	5.6	1.6	1.5	1.3	1.2
-800	85.3	35.1	26.3	18.3	5.6	9.4	3.3	1.5	3.3	1.3	5.3	1.5	1.4	1.2	1.1
-900	86.8	45.9	28.8	7.1	5.0	7.8	2.4	1.2	2.8	1.3	5.4	1.6	1.4	1.3	1.1
m-OC	89.0	61.0	-	18.7	9.2	-	-	-	-	-	9.5	3.8	2.4	1.8	1.5

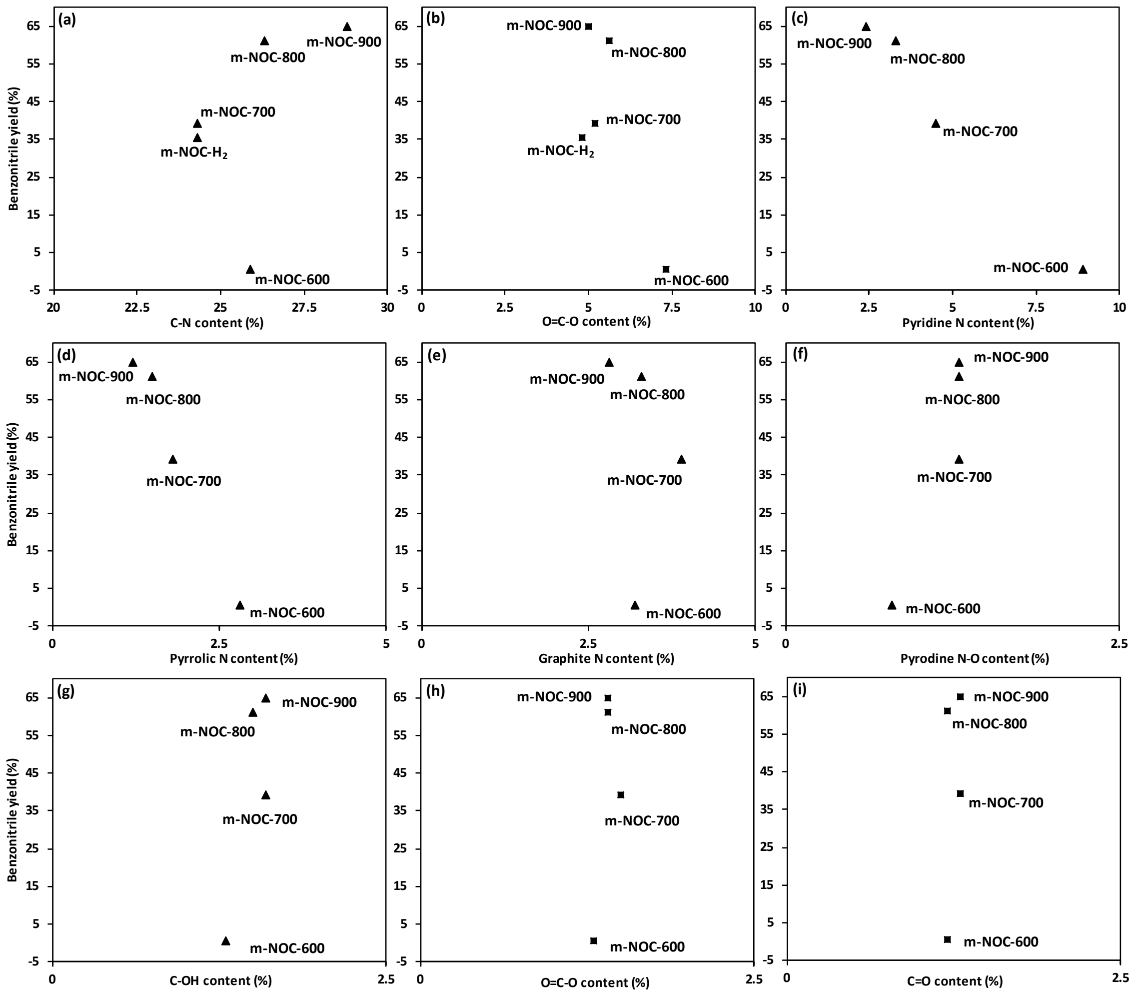


Fig. S5 Plots of benzonitrile yield in aerobic oxidation of benzylamine against the amount of (a, b) C configuration; (c-f) N configuration; (g-i) O configuration group listed in Table S3.

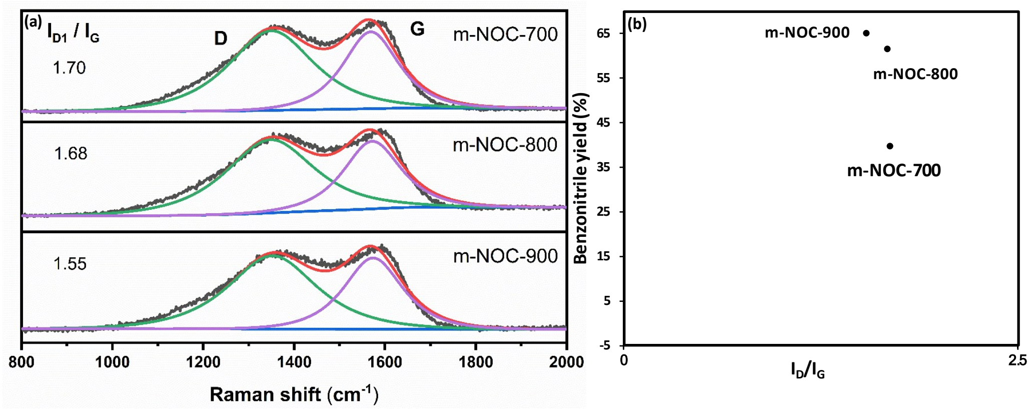


Fig. S6 (a) Raman spectrum of m-NOC-700, -800 and -900. (b) Plots of benzonitrile yield in aerobic oxidation of benzylamine against I_D/I_G value.

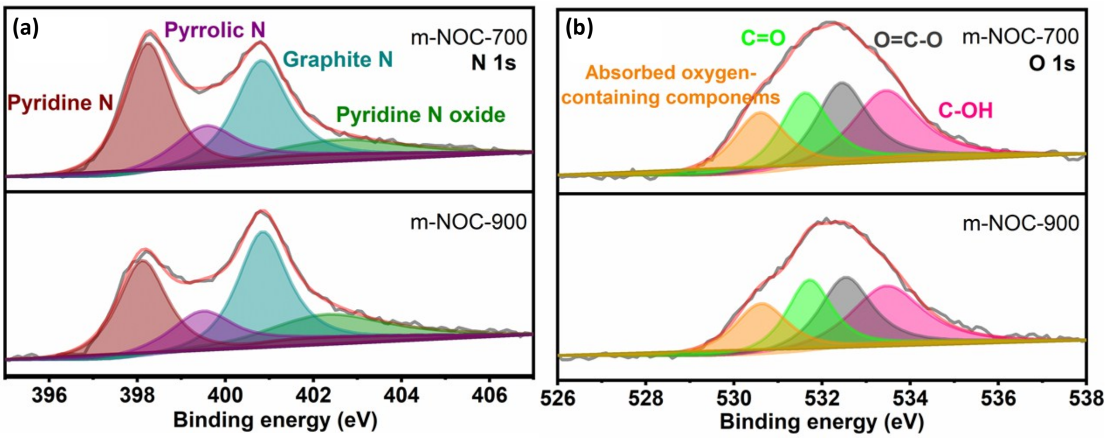


Fig. S7 (a) N 1s, (b) O 1s XPS spectra of m-NOC-700 and -900.

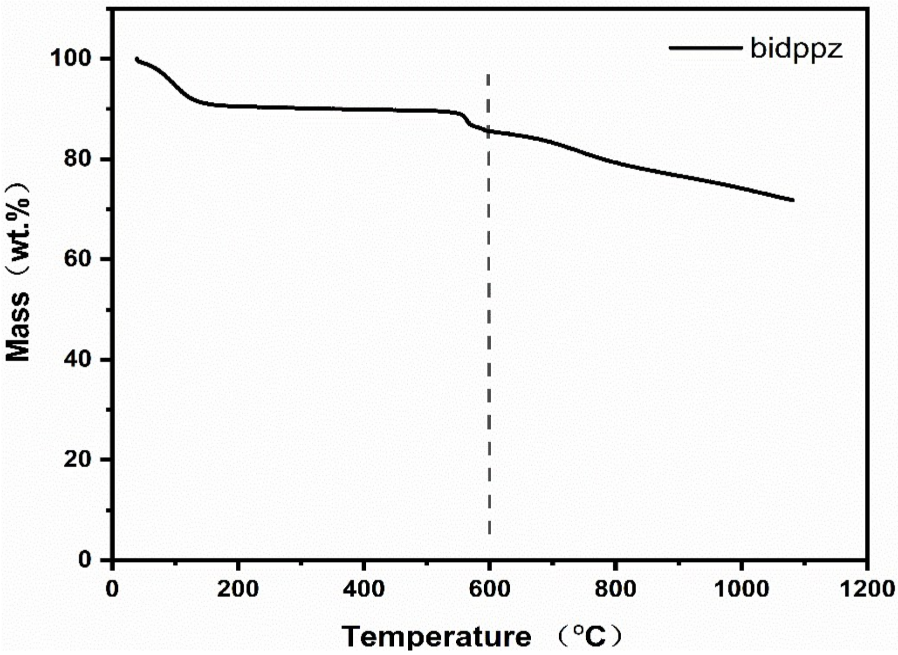


Fig. S8 TG of bidppz.

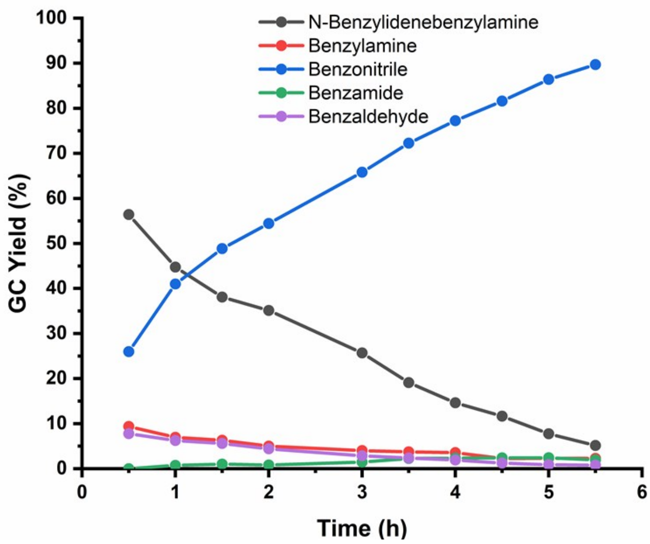
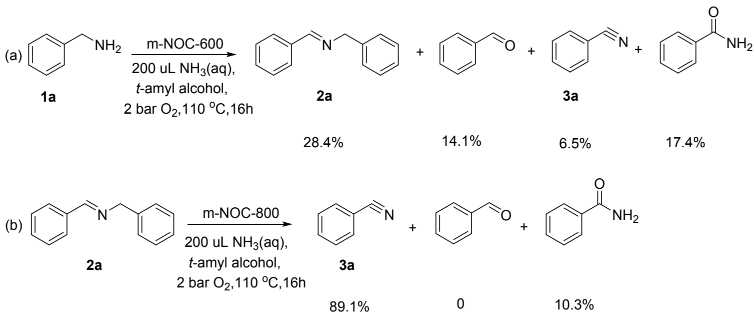


Fig. S9 Reaction time course with imine as substrate catalysed by m-NOC-800.

Scheme S1. Control experiments.



Scheme S2. Possible Reaction Pathway.

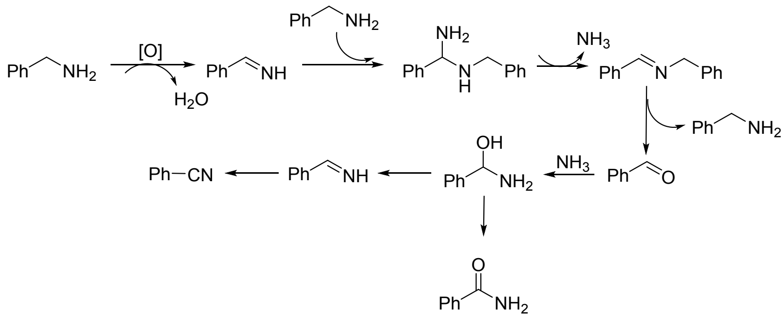
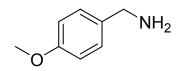
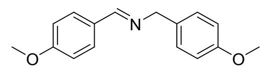
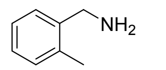
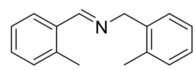
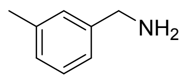
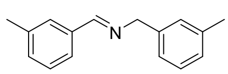
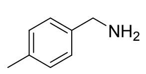
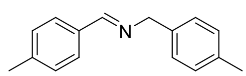
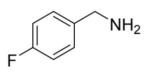
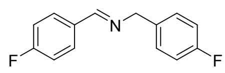
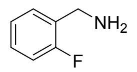
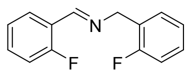
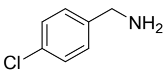
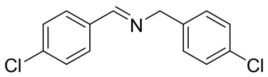
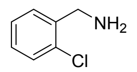
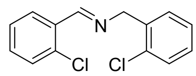
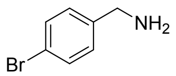
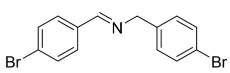
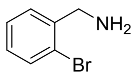
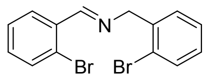
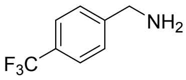
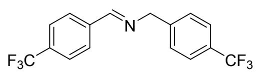
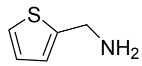
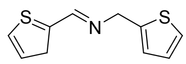
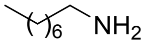
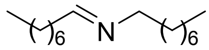


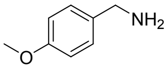
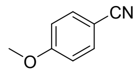
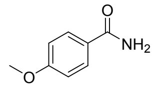
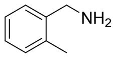
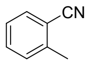
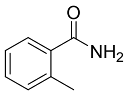
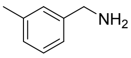
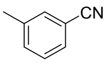
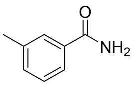
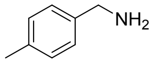
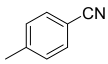
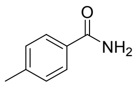
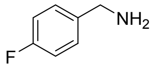
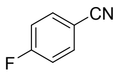
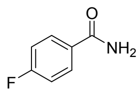
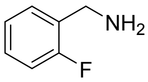
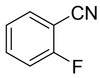
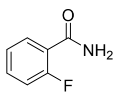
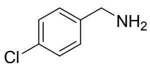
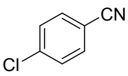
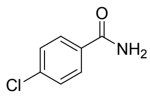
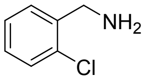
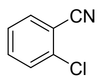
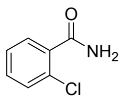
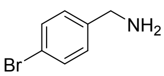
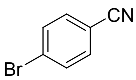
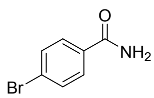
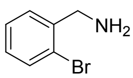
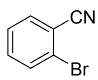
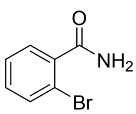
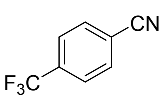
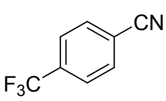
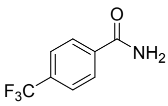
Table S4 Aerobic oxidation of various substituted benzylamines under aqueous ammonia catalysed by m-NOC-600[a]

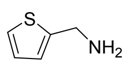
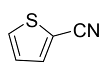
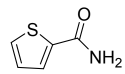
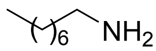
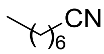
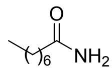
Entry	Substrate	Product	Y (%)
1			80.3[b]
2			86
3			86.2
4			80[c]
5			81
6			79.8
7			71.2(80)[d]
8			88.9
9			73.7
10			85.2
11			76.7

12			87
13			-

[a] Reaction conditions: 60mg m-NOC-600, 0.5mmol benzylamine, 200μL aq. NH_3, 1ml tert-amyl alcohol, 2 bar O_2, T=110^{o}C, t=5h. [b] T=100^{o}C, t=3.5h. [c] T=100^{o}C, t=4h. [d] T=100^{o}C, t=5h.

Table S5 Aerobic oxidation of various substituted benzylamines under aqueous ammonia catalysed by m-NOC-800[a]

Entry	Substrate	Product	Product	Y(%) (nitrile, amide)
1				(79.3, 13.6)
2				(82.8, 10.4)
3				(65.9, 19.2)
4				(67.2, 16.2), (72.1, 12.6)[b]
5				(77.2, 13.2)
6				(60.8, 23)
7				(61.7, 22)
8				(65.9, 29.6)
9				(64.6, 15.9)
10				(64.1, 28.1)
11				(54.8, 31.6)

12				(83.3, 8.3)
13				-

[a] Reaction conditions: 60mg m-NOC-800, 0.5mmol benzylamine, 200μL aq. NH_3, 1ml t-amyl alcohol, 2 bar O_2, T=110^{o}C, t=16h, [b] T=120^{o}C, t=12h