Supporting Information for

Aerobic oxidative N-dealkylation of tertiary amines in aqueous solution catalyzed by rhodium porphyrins

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General considerations. D_2O, CD_3OD and $CDCl_3$ were purchased from Cambridge Isotope Laboratory Inc.; tetra p-sulfonatophenyl porphyrin from Tokyo Chemical Industry (TCI); $(Rh(CO)_2Cl)_2$ from Stream Chemical Inc.; and all other chemicals were purchased from Aldrich or Alfa Aesar unless otherwise noted and used as received. Room temperature ^1H NMR spectra were recorded on a Bruker AV-400 spectrometer and variant temperature ^1H NMR spectra on a Bruker AV-500. The chemical shifts were referenced to 3-trimethylsilyl-1-propanesulfonic acid sodium salt (DSS). GC-MS results were obtained by the Agilent 7980A/5975C GC/MSD system equipped with the DB-17MS (30 m, 0.25 mm, 0.25 μm) column, GC results were obtained by the Agilent 7980A system equipped with the DB-5MS UI (30 m, 0.25 mm, 0.50 μm) column.

Preparation of $Na_3[(TSPP)Rh^{III}(H_2O)_2]$: $Na_3[(TSPP)Rh^{III}(H_2O)_2]$ was synthesized by following literature methods of Ashley.[1] The equilibrium distribution of $[(TSPP)Rh^{III}(D_2O)_2]^{-3}$, $[(TSPP)Rh^{III}(D_2O)(OD)]^{-4}$ and $[(TSPP)Rh^{III}(OD)_2]^{-5}$ were reported in the previously published paper.[2] ^{1}HNMR (D_2O, 400 MHz) δ(ppm): 9.15 (s, 8H, pyrrole), 8.44 (d, 8H, o-phenyl, J_{H-H} =8 Hz), 8.25 (d, m-phenyl, J_{H-H}=8 Hz). The stock solution of $(TPPS)Rh^{III}$ was prepared in H_2O solution.

Oxidative N-dealkylation of triethylamine in the absence of dioxygen (pH=13). 0.4 mL $(TSPP)Rh^{III}$ solution (2.5 mM) and 0.4mL NaOH solution (0.1 M) were mixed in a 5 mL round bottom flask. After the solvent was removed under vacuum, the solid was dissolved in 0.4 mL D_2O solution of triethylamine (50 mM). The solution was transferred to a J. Young Valve NMR tube containing an external standard benzaldehyde dissolved in $CDCl_3$. Then the sample was subjected to three freeze-pump-thaw cycle. The kinetic ^1H NMR spectra were recorded on the Bruker AV-500 magnet at 308 K over at least three half-lives. Activation parameters were obtained by measuring rate constants at different temperatures at 303 K, 308 K, 313 K, 318K and 323 K respectively. Then kinetic ^1H NMR spectra at different concentration of triethylamine were recorded at 308K. The porphyrin pyrrole and phenyl ^1H NMR shifts were used in identifying the (TSPP)Rh species in D_2O. Trace amount of diethylamine and $(TSPP)Rh^I$ were already formed during NMR deuterium lock and shimming. (Figure 1S, A)

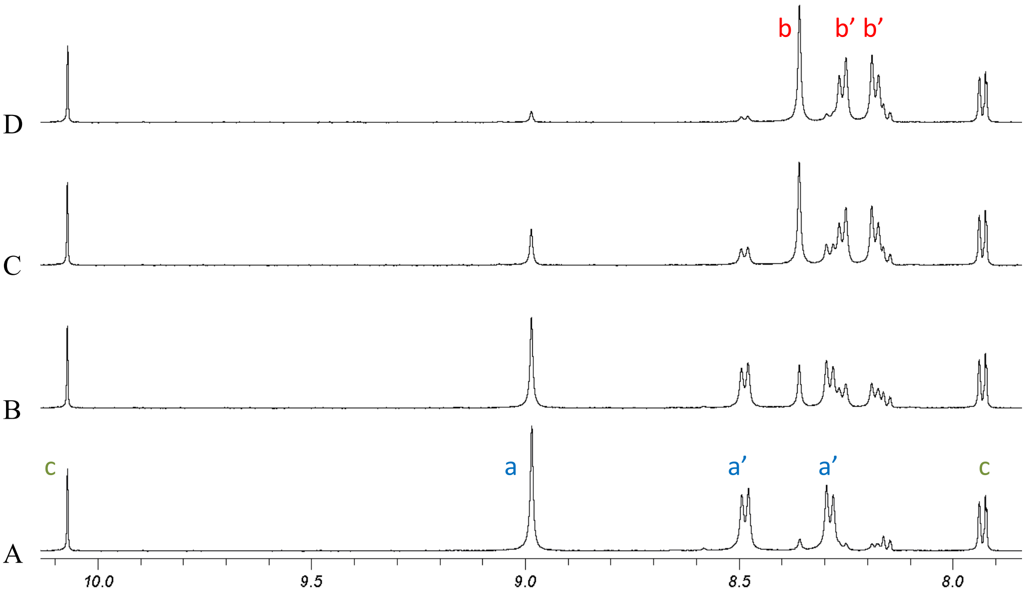


Figure 1S The kinetic ^{1}H NMR spectra of oxidative N-dealkylation of triethylamine catalyzed by $(TSPP)Rh^{III}$ at 308K. ($[(TSPP)Rh^{III}]_{initial}$=2.5 mM, $[NEt_3]$=50mM, [NaOH]=0.1 M). A: time=0 min; B: time=23 min; C: time=95 min; D: time=178min. a: Pyrrole ^{1}H NMR shift of $(TSPP)Rh^{III}$, a’: Phenyl ^{1}H NMR shift of $(TSPP)Rh^{III}$. b: Pyrrole ^{1}H NMR shift of formed $(TSPP)Rh^{I}$, b’: Phenyl ^{1}H NMR shift of formed $(TSPP)Rh^{I}$. c: ^{1}H NMR shift of external standard benzaldehyde.

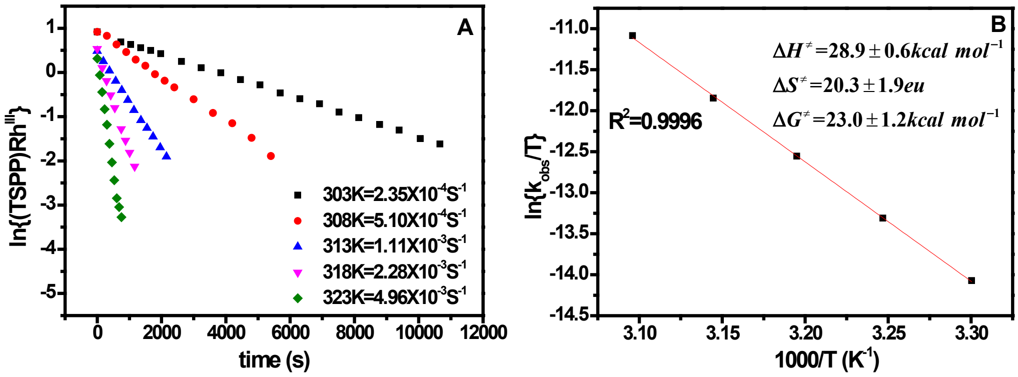


Figure 2S A: Rate constants dependence on temperature in the reaction of $(TSPP)Rh^{III}$ and triethylamine, [NEt3] = 50 mM, $[(TSPP)Rh^{III}]$ = 2.5mM, and B: Determination of activation parameters.

Table 1S Measurement of rate constant of oxidative N-dealkylation of triethylamine in the absence of dioxygen at 308K (pH=13).

Entry	t_1/s	t_2/min	Integration values of pyrrole ^{1}H NMR of $(TSPP)Rh^{III}$	$[(TSPP)Rh^{III}]$/mM	$\ln\{[(TSPP)Rh^{III}]\}$
1	0	0	4.215	2.5	0.916291
2	733	12.22	3.356	1.99051	0.688391
3	1043	17.38	3.1688	1.879478	0.630994

4	1354	22.57	2.9431	1.745611	0.557105
5	1665	27.75	2.7741	1.645374	0.497968
6	1975	32.92	2.5708	1.524792	0.421858
7	2624	43.74	2.1631	1.282977	0.249184
8	3234	53.90	1.8754	1.112337	0.106463
9	3845	64.09	1.6738	0.992764	-0.00726
10	4455	74.25	1.4292	0.847687	-0.16524
11	5066	84.44	1.2733	0.755219	-0.28075
12	5693	94.89	1.0606	0.629063	-0.46352
13	6303	105.05	0.929	0.551008	-0.59601
14	6914	115.24	0.8294	0.491934	-0.70941
15	7524	125.40	0.6868	0.407355	-0.89807
16	8135	135.59	0.605	0.358837	-1.02489
17	8782	146.37	0.5193	0.308007	-1.17763
18	9392	156.54	0.4567	0.270878	-1.30609
19	10049	167.49	0.3773	0.223784	-1.49707
20	10659	177.65	0.3335	0.197805	-1.62047

Table 2S Rate constant of oxidative N-dealkylation of triethylamine in the absence of dioxygen at different temperatures.

Entry	T/K	k_{obs}/s^{-1}
1	303	2.35E-4
2	308	5.10E-4
3	313	1.11E-3
4	318	2.28E-3
5	323	4.96E-3

The cyanation of N,N-diethylaniline catalyzed by (TSPP)Rh^{III}: *N,N*-diethylaniline, TMSCN, a certain amount of acid and (TSPP)Rh^{III} were mixed. After the completion of the reaction, the mixture was poured into NaOH aqueous solution and extracted with diethyl ether. The organic layer was collected and washed with deionized water. The resulting cyanated compound was detected by GC-MS and the conversion was determined by GC.

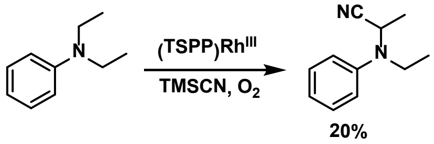


Figure 3S The cyanation of *N,N*-diethylaniline catalyzed by (TSPP)Rh^{III}.

Table 3S Rate constant of oxidative N-dealkylation of triethylamine in the absence of dioxygen at different concentrations of triethylamine at 308K.

Entry	[NEt$_3$]/mM	k$_{obs}$/s^{-1}
1	23	2.13E-4
2	50	5.10E-4
3	66	7.88E-3
4	94	1.20E-3
5	123	1.53E-3

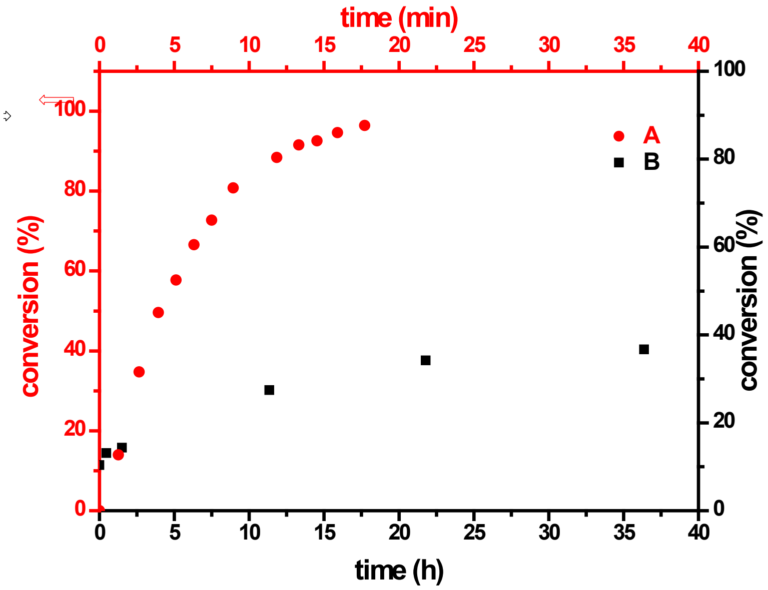


Figure 4S Stoichiometric oxidative N-dealkylation of triethylamine in the absence of dioxygen. A: Concentration changes of (TSPP)Rh^{III} upon reaction with triethylamine ([NEt$_3$] = 50 mM) at room temperature (red plots). B: Conversion of (TSPP)Rh^{III} upon reaction with triethylamine in the presence of diethylamine ([NEt$_3$] = [NHEt$_2$] = 50 mM) (black plots).

Table 4S The pKa values of amines[3]

Entry	amine	pKa
1	Triethylamine	10.65
2	Diethylamine	10.98
3	Tributylamine	10.89
4	dibutylamine	11.25
5	*N,N*-dimethylbenzylamine	8.93
6	*N*-methylbenzylamine	9.58
7	*N,N*-diethylbenzylamine	9.48
8	*N*-ethylbenzylamine	9.68
9	Triallylamine	8.31
10	Diallylamine	9.29

General procedure for aerobic Rh-Catalyzed oxidative N-dealkylation of tertiary aliphatic Amines in Water. In a 25 mL Schlenk flask sealed with a Teflon cap, 1 mL aqueous solution of

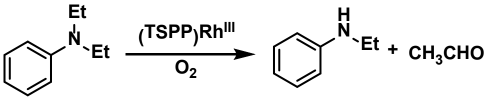
(TSPP)Rh^{III} (1 mM), 2.0 mmol tertiary aliphatic amines and 1.6 mmol CF_3COOH were added. The mixture was stirred at 100 °C for 2 hours after the flask was pressurized with molecular oxygen (1 atm). Then, the mixture was poured into NaOH aqueous solution and extracted with ether. The organic layer was washed with deionized water and diluted to 10 mL in a volumetric flask. The resulting secondary amines and aldehydes (or ketones) were detected by GC-MS and the conversion was determined by GC or ^{1}H NMR.

Table 5S The acid effect[a].

Entry	Substrate	TON[b]	TON[c]
1	triethylamine	134	698
2	tributylamine	18	887

[a] Reactions conditions: 2.0 mmol tertiary amines, 1.0 µmol (TSPP)Rh^{III} in 1 mL H_2O stirred for 2 h at 373K under 1 atm O_2. [b] no acid. [c] 1.6 mmol of CF_3COOH was added.

Table 6S Optimization of the oxidative N-alkylation of *N,N*-diethylaniline catalyzed by (TSPP)Rh^{IIIa}



entry	solvent	TON[b]
1	H_2O[c]	28
2	H_2O	52
3	DMF/H_2O=10/1	177
4	DMSO/H_2O=10/1	125
5	**CH_3OH/H_2O=10/1**	**219**

[a] A mixture of *N,N*-diethylaniline (2.0 mmol) and (TSPP)Rh^{III} (1 µmol) in solvent was stirred under O_2 (1 atm) at 90°C for 4h. [b] Determined by GC. [c] 0.8equivalent CF_3COOH was added.

General Procedure for Aerobic Rh-Catalyzed Oxidative N-dealkylation of Tertiary Aromatic Amines in mixed solvent. In a 25 mL Schlenk flask sealed with a Teflon cap, 1 mL CH_3OH/H_2O (10/1) solution of (TSPP)Rh^{III} (1 µmol/L), 2.0 mmol tertiary aromatic amines were added. The mixture was stirred at 90 °C for 4-22 hours after the flask was pressurized with molecular oxygen (1 atm). Then, the mixture was poured into aqueous solution and subsequently extracted with ether. The organic layer was washed with deionized water and dilute to 10 mL in a volumetric flask. The resulting secondary amines and aldehydes (or ketones) were detected by GC-MS and the conversion was determined by GC.

Reference

(1) K. R. Ashley, S. B. Shyu and J. G. Leipoldt, *Inorg. Chem.*, 1980, **19**, 1613;
(2) X. Fu, B. B. Wayland, *J. Am. Chem. Soc.*, 2004, **126**, 2623;
(3) H. K. Hall, Jr., *J. Am. Chem. Soc.*, 1957, **79**, 5441.