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Electronic Supplementary Information

Ru/Al_2O_3 catalyzed N-oxidation of tertiary amines by using H_2O_2

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S1.*Materials and reagents*

Pyridine, *N,N'*-dimethyl aniline (DMA), *para*-substituted N,N-dimethyl anilines (*p*-methyl, *p*-cyano, *p*-bromo and *p*-carboxy), quinoline, phenazine, quinoxaline, pyrazine, morpholine, triphenylamine, 2,2'-bipyridine (2,2''-Bipy) and 4,4'-bipyridine (4,4'-Bipy) were purchased from Aldrich and used as such. Dichloromethane (Merck), HPLC grade acetonitrile and 30% H_2O_2 were used as received.

S2.*Synthesis of Catalyst I*

The synthetic procedure for the catalyst **I** is briefly given here and more details can be found in our earlier report **[1]**. Briefly, $RuCl_3$ (0.1434 g, 5.25×10^{-4} M), and PVP (0.5828 g, 5.25×10^{-3} M, as monomeric unit) were dissolved in 1,2-propanediol (100 mL) under stirring to form a dark red solution and refluxed. The color of the solution changed from dark red to yellow and then turned to deep green and finally to dark brown. The dark brown colored (RuNPs) solution was then left to cool to room temperature. After impregnation of the RuNPs onto the alumina nano surface, a black solid (Catalyst **I**) was collected and dried under vacuum at room temperature and calcinated at 500 ^{o}C for 8 h and stored in a closed container.

S3. A larger-scale (100 mmol scale) preparation of N-Oxides

Into a glass reactor were successively placed catalyst **I** (5.0 mol %) with respect to amine and H_2O_2), amine (100 mmol), 30% aqueous H_2O_2 (100 mmol), and CH_3CN (50 mL). The reaction mixture was stirred at 293 K depending upon the reaction time. Then, acetonitrile was removed by evaporation. Into the resulting solution, the aqueous solution saturated with brine was added followed by the extraction of the products with 30: 40 ratio of dichloromethane:methanol (3×20 mL). The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. n-hexane/ethyl acetate (50 mL, 60/40, v/v) was added to the concentrated solution. The isolation of N-oxides was carried out by column chromatography on silica gel (60-120 mesh) using n-Hexane/ethyl acetate (60/40, v/v) as an eluent, giving of pure N-oxide as a product.

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S4. Additional HRTEM images of catalyst I

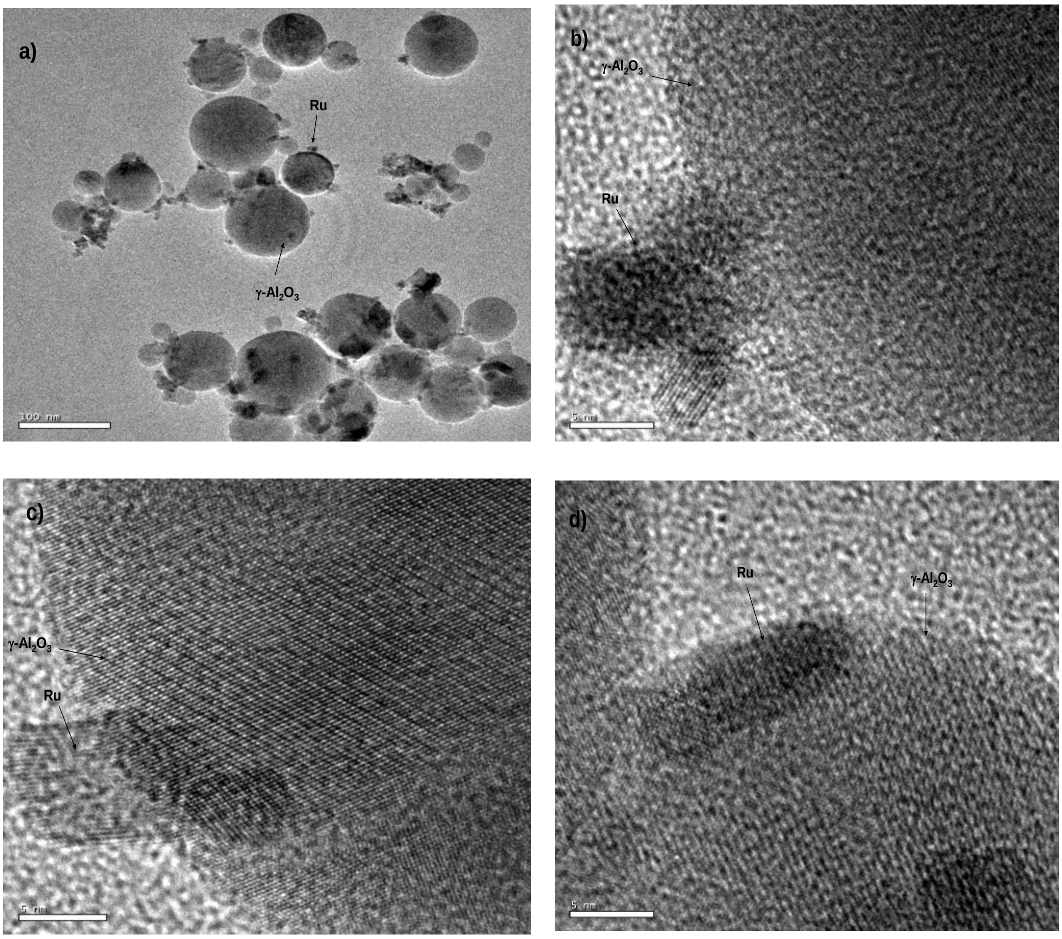

Figure 1. Additional HRTEM micrographs of the ruthenium nanocatalyst **I (**a-d).

S5.HRTEM images of catalyst I after the third cycle

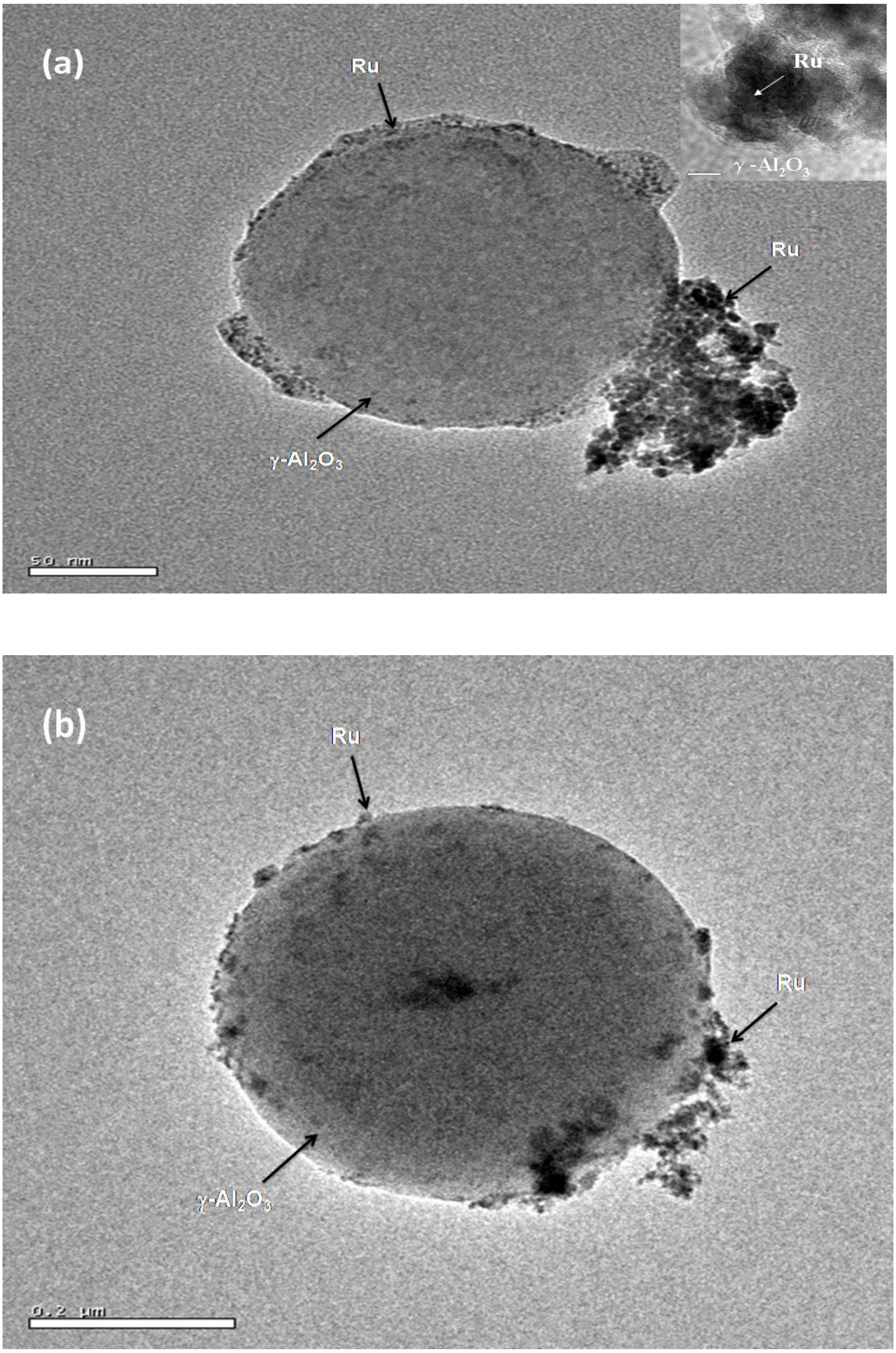

***Figure 2*. HRTEM images (a) and (b) after the third cycle.**

S6. Physicochemical and textual properties of the γ-Al_2O_3 and catalyst I.

Measurements	**γ-Al_2O_3**	**Catalyst I**
Surface area		
Single point surface area at P/Po = 0.300	25.7369 m^2/g	22.7390 m^2/g
BET Surface Area	26.5489 m^2/g	24.1558 m^2/g
Langmuir Surface Area	42.4125 m^2/g	40.0367 m^2/g
t-Plot External Surface Area	29.2283 m^2/g	26.3543 m^2/g
t-Plot Micropore area	0.1946 m^2/g	0.1456 m^2/g
BJH Adsorption cumulative surface area of pores between 17.000 Å and 3000.000 Å diameter	26.119 m^2/g	23.737 m^2/g
BJH Desorption cumulative surface area of pores between 17.000 Å and 3000.000 Å diameter	26.0178 m^2/g	21.0252 m^2/g
Pore Volume		
Single point adsorption total pore volume of pores less than 689.174 Å diameter at P/Po = 0.97	0.132667 cm^3/g	0.054809 cm^3/g
t-Plot micropore volume	0.000073 cm^3/g	-0.002794 cm^3/g
BJH Adsorption cumulative volume of pores between 17.000 Å and 3000.000 Å diameter	0.216778 cm^3/g	0.121114 cm^3/g
BJH Desorption cumulative volume of pores between 17.000 Å and 3000.000 Å diameter	0.216482 cm^3/g	0.119332 cm^3/g
Pore Size		
Adsorption average pore width (4V/A by BET)	219.6848 Å	182.5783 Å
BJH Adsorption average pore diameter (4V/A)	331.987 Å	204.091 Å
BJH Desorption average pore diameter (4V/A)	332.820 Å	227.027 Å

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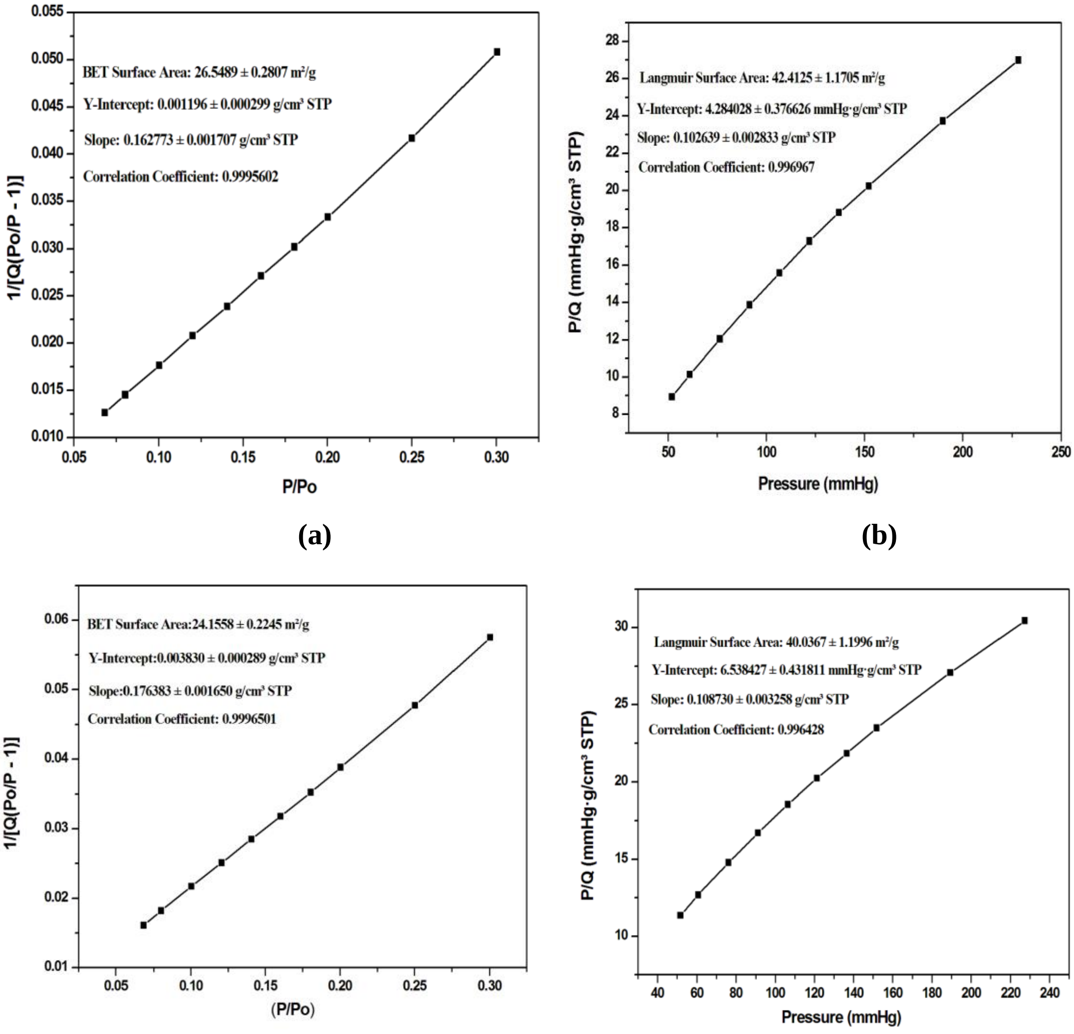
S7. Hydrogen chemisorption data of catalyst I

H_2 - Adsorption		H_2 - Desorption	
Weight % H_2	Absolute Pressure (mmHg)	Weight % H_2	Absolute Pressure (mmHg)
0.001557	1.430162	0.049726	850.0068
0.009012	11.03804	0.047442	785.4033
0.016974	30.45373	0.045872	735.3377
0.021255	59.95316	0.044121	685.443
0.023083	80.08102	0.042983	650.1025
0.024107	100.5238	0.04121	600.3011
0.025484	140.6532	0.039494	550.2545
0.026668	180.461	0.037599	500.1969
0.027196	200.4984	0.035651	450.1777
0.028777	250.2491	0.03383	400.2013
0.030226	300.2715	0.032019	350.343
0.031572	350.4329	0.03032	300.3363
0.033353	400.2528	0.0285	250.4271
0.035143	450.3754	0.026591	200.2562
0.036798	500.2924	0.024067	140.3327
0.038481	550.2508	0.022164	100.6373
0.040183	600.1837	0.020766	80.70963
0.042033	650.1796	0.019049	51.1592
0.043926	700.0977	0.017538	31.02545
0.045852	750.1765	0.015032	9.85792
0.047703	800.0555	0.012546	0.999295
0.049726	850.0068		

S8. BET and Langmuir linear plots of the γ-Al_2O_3 and catalyst I



(a) **(b)**

(c) **(d)**

Figure 3. BET and Langmuir linear plots of the γ-Al_2O_3 (a,b) and catalyst **I** (c,d) at 77K.

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S9. SEM-EDX observation of catalyst I

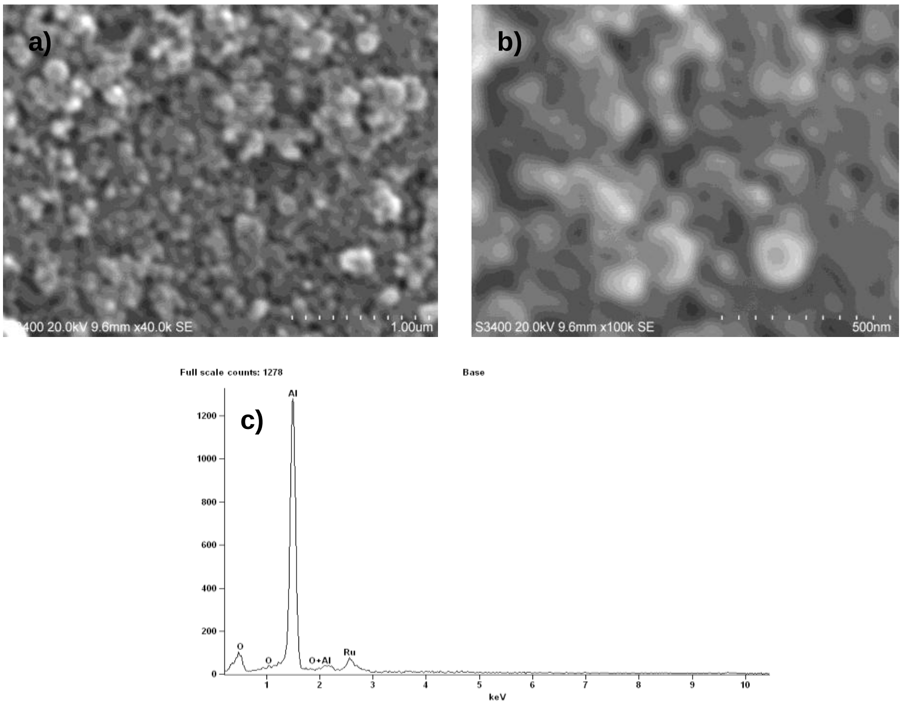
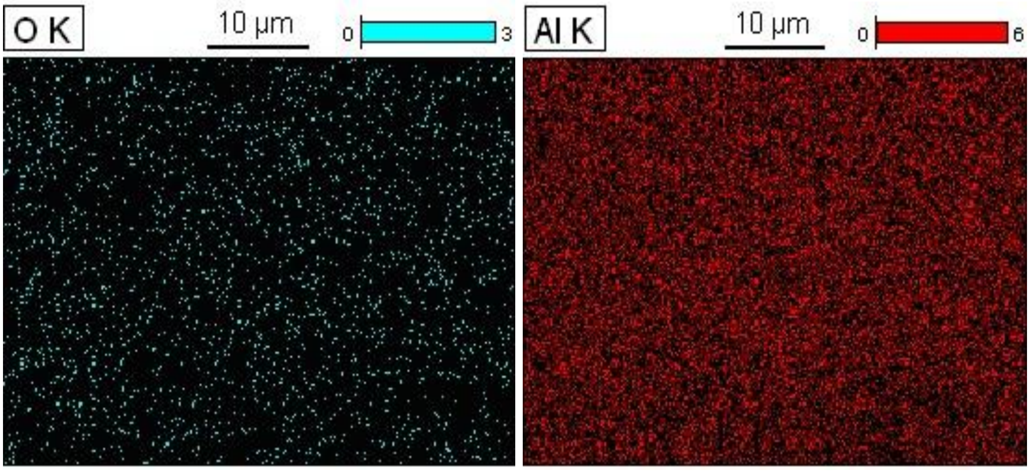
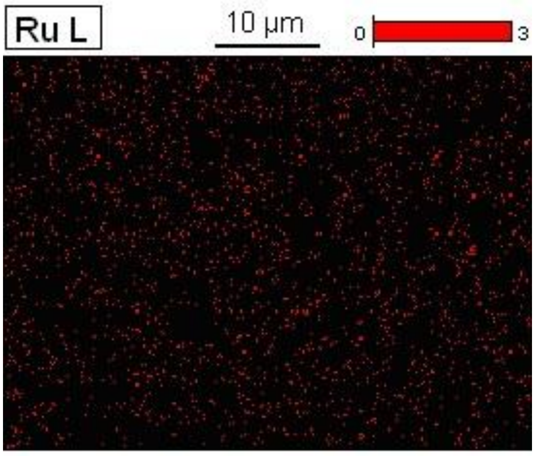


Figure 4. SEM pictures of catalyst **I**: (a) 40 K× magnification, (b) 100 K× magnification and (c) EDX analysis of catalyst **I**.





Data Type: Counts Mag: 2500 Acc. Voltage: 20.0 kV

S10. UV-visible spectroscopy

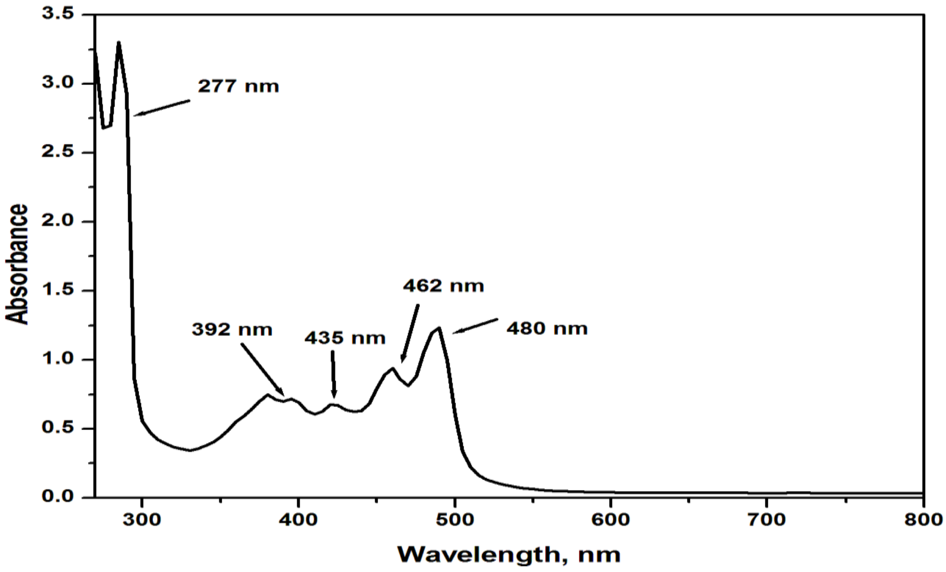


Figure 5. **The absorption spectrum of PDO in CH_2Cl_2 solvent.**

S11. Oxygen transfer reactions of N-oxides

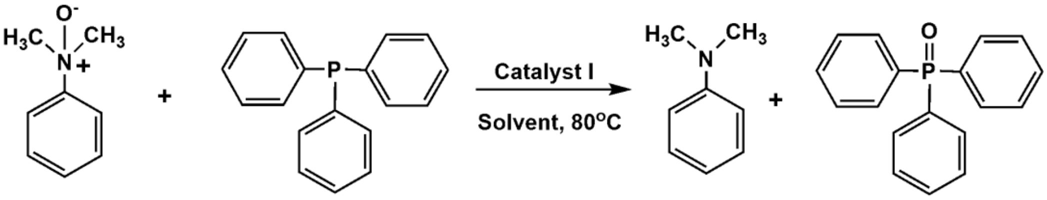
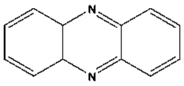
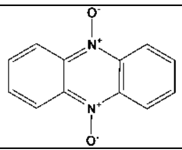
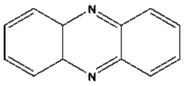
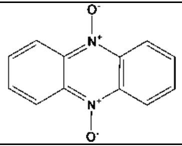
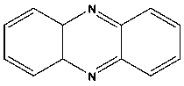
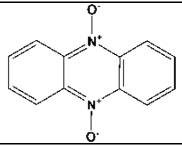
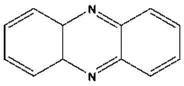
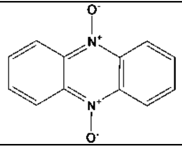


***Figure 6*. Oxygen transfer reactions of N-oxides.**

S12. Catalyst I reuse

Oxidation of phenazine catalyzed by catalyst **I** for different cycles[a]

Catalyst I	**Substrate**	**Product**	**Yield (%)**
Fresh			98
Cycle 1			95
Cycle 2			90
Cycle 3			87

[a] Reaction conditions: Phenazine (2.0 mmol), solvent (3.0 mL), H_2O_2 (6.0 mmol), and catalyst **I** (0.25 mol%).

[b] Determined by TLC and NMR method.

[c] Yield = No. of moles of *N*-oxide / No. of moles of amine.

RT= Room temperature.

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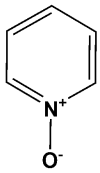
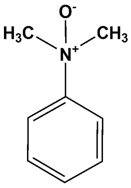
S13. NMR data of N-oxides

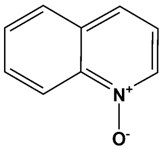


Pyridine N-oxide (Table 1 entry 1)**:** Colorless solid [2]; ^{1}H-NMR (300 Hz, $CDCl_3$): δ 7.32-7.45 (m, 3H), 8.23-8.36 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 125.9, 125.9, 139.0

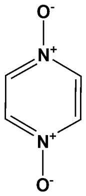
4-Picoline N-oxide (Table 1 entry 2): White solid [2]; ^{1}H-NMR (300 MHz, D_2O): δ 2.31 (s, 3H), 7.44 (d, *J* = 6.9Hz, 2H), 8.14 (d, *J* = 6.9Hz, 2H); FT-IR (KBr, cm^{-1}) 2941, 1432-1490, 1180-1248, 1046, 859, 758.



N,N-Dimethyl aniline N-oxide (Table 1 entry 3): Yellow colored hygroscopic solid**[78]**; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.32 (s, 6H), 7.18-7.21 (m, 3H), 7.55-7.59 (m, 2H); FT-IR (KBr, cm^{-1}) 2941, 1587, 1492, 1351, 1219, 1190, 1162, 1063, 1030, 1000, 943, 746, 689.



Quinoline N-oxide (Table 1 entry 4): Colorless solid [2]; ^{1}H-NMR (300 MHz, D_2O): δ 7.12-7.83 (m, 4H), 8.11-8.15 (m, 2H), 8.5 (d, *J* = 7.2Hz, 1H); FT-IR (KBr, cm^{-1}) 3448, 3030, 1492, 1428, 1388, 1298, 1265, 1219, 1204, 1176, 1136, 1086, 1052, 1010, 877, 826, 763,722.



Pyrazine N,N-dioxide. (Table 1 entry 5): Colorless solid [2]; ^{1}H-NMR (300MHz, D_2O): δ 8.52 (s, 4H); FT-IR (KBr, cm^{-1}) 3028, 1652, 1599, 1441, 1391, 1315, 1221, 1042, 1002, 864, 801.

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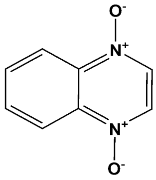
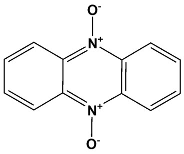
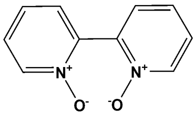


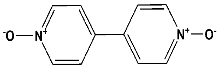
Quinoxaline N-oxide (Table 1, entry 6**)**: Yellow crystals ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.74-7.87 (m, 2H), 8.12 (d, *J* = 6.9Hz, 1H), 8.87 (s, 2H), ^{13}C-NMR (75 MHz, $CDCl_3$): δ 118.9, 130.2, 137.4, 145.9.



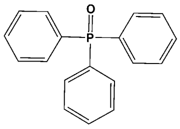
Phenazine-5,10-dioxide (Table 1, entry 8**)**: Red orange crystals **[3]**; ^{1}H-NMR (300 MHz, $CDCl_3$): δ ppm 7.82-7.87 (m, 4H), 8.70 (d, *J* = 7.2Hz, 4H) ^{13}C-NMR (75 MHz, $CDCl_3$): δ 120.1, 131.1, 136.0.



2,2'-bipyridine N-dioxide (Table 1, entry 9**)**: Light grey white solid **[4]**; FT-IR (KBr, cm^{-1}): 1250.



4,4'-bipyridine N-dioxide (Table 1, entry10**)**: Grey white solid **[4]**; ^{1}H-NMR (300 MHz, D_2O): δ 7.60 (d, *J* = 7.8Hz, 4H). 8.52 (d, *J* = 7.8Hz, 4H).



Triphenylphosphine oxide. Colorless solid **[5]**; ^{1}H-NMR (300 MHz, $CDC1_3$): δ 7.43- 7.68 (m, 15H).

S14. NMR spectra of some N-oxides

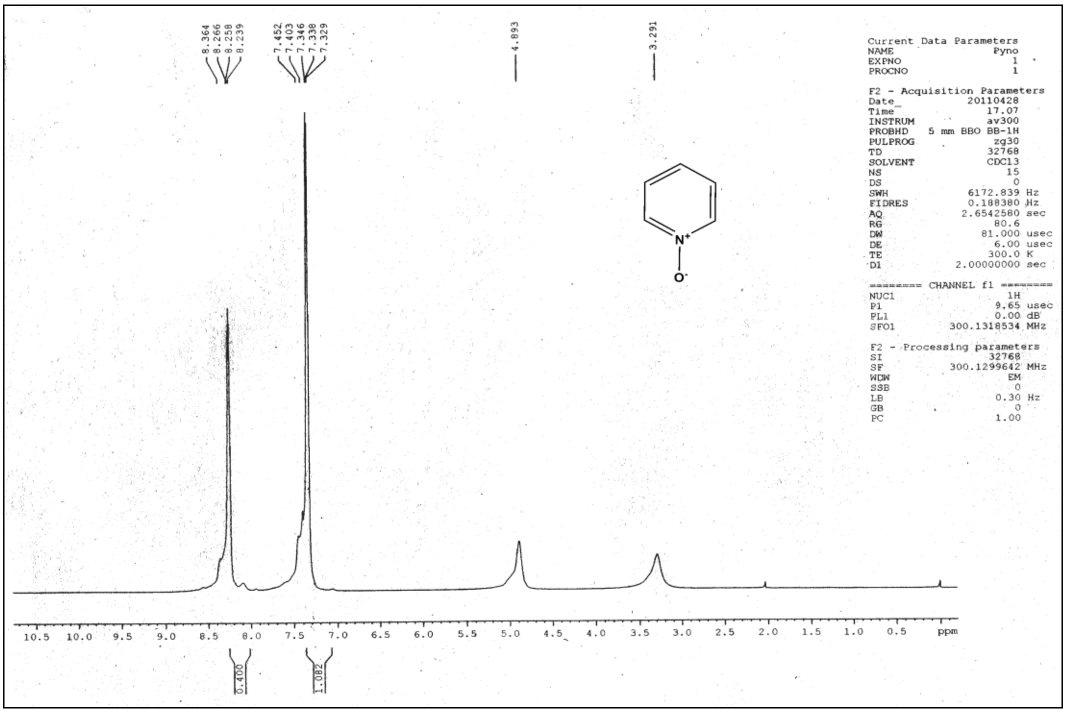


Figure 7. **^{1}H-NMR spectrum of pyridine N-oxide (Table 3.1, entry 1).**

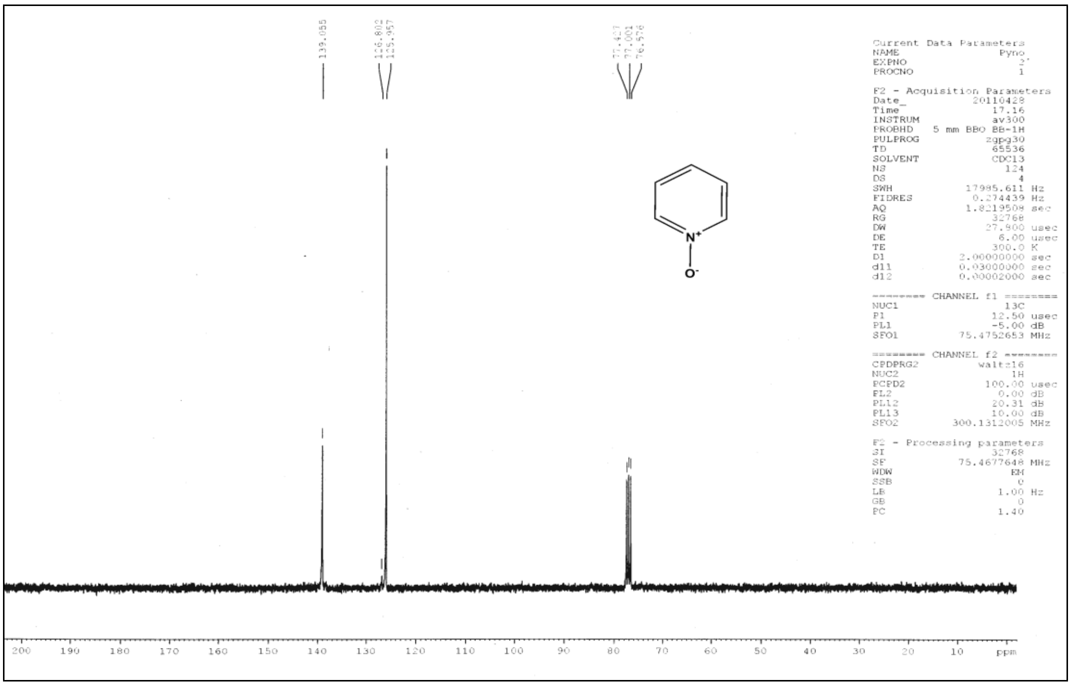


Figure 8. **^{13}C-NMR spectrum of pyridine N-oxide (Table 1, entry 1).**

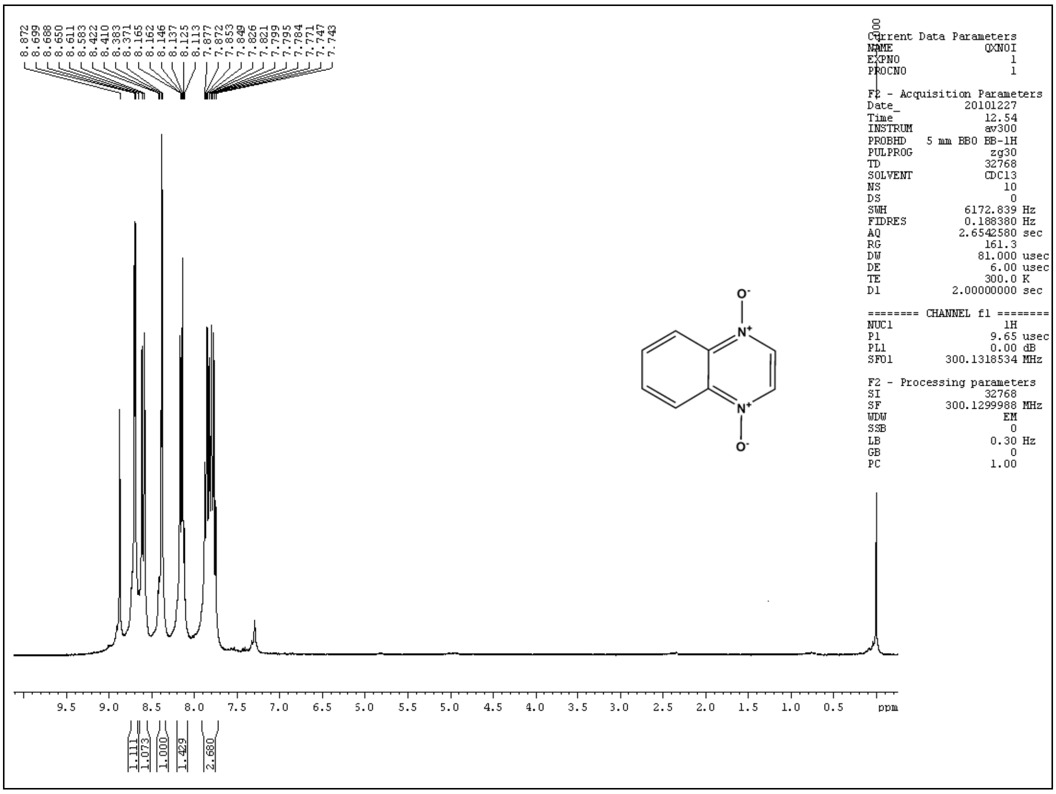


Figure 9. ***^{1}H-NMR spectrum of quinoxaline N-oxide (Table 1, entry 6).***

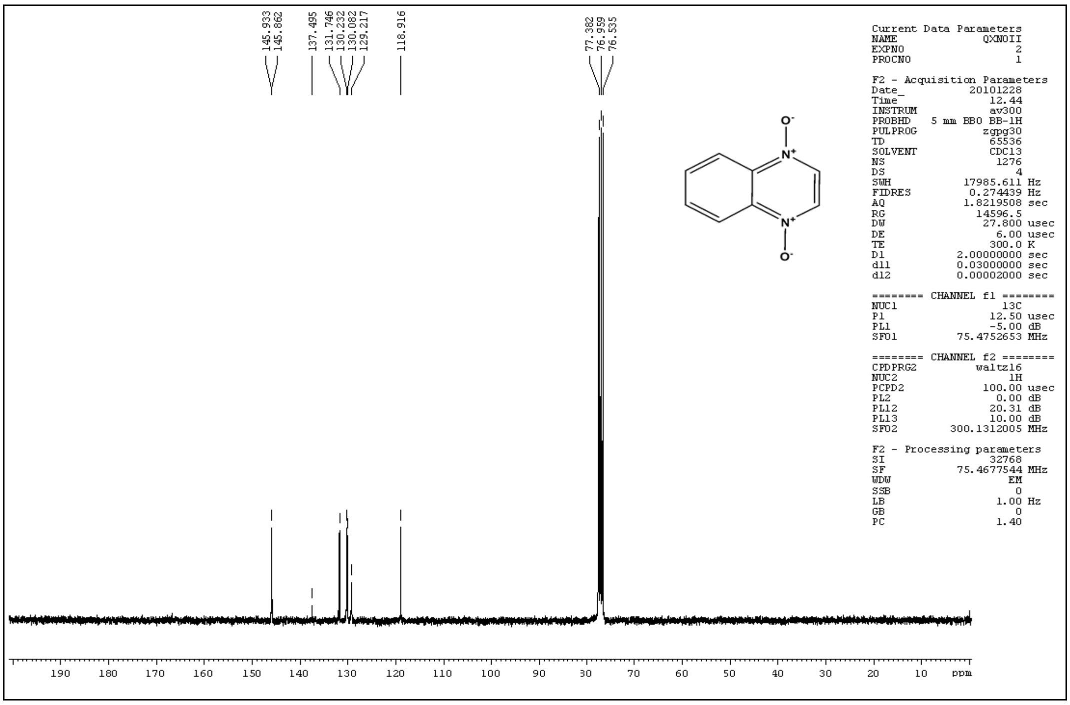


Figure 10. ***^{13}C-NMR spectrum of quinoxaline N-oxide (Table 1, entry 6).***

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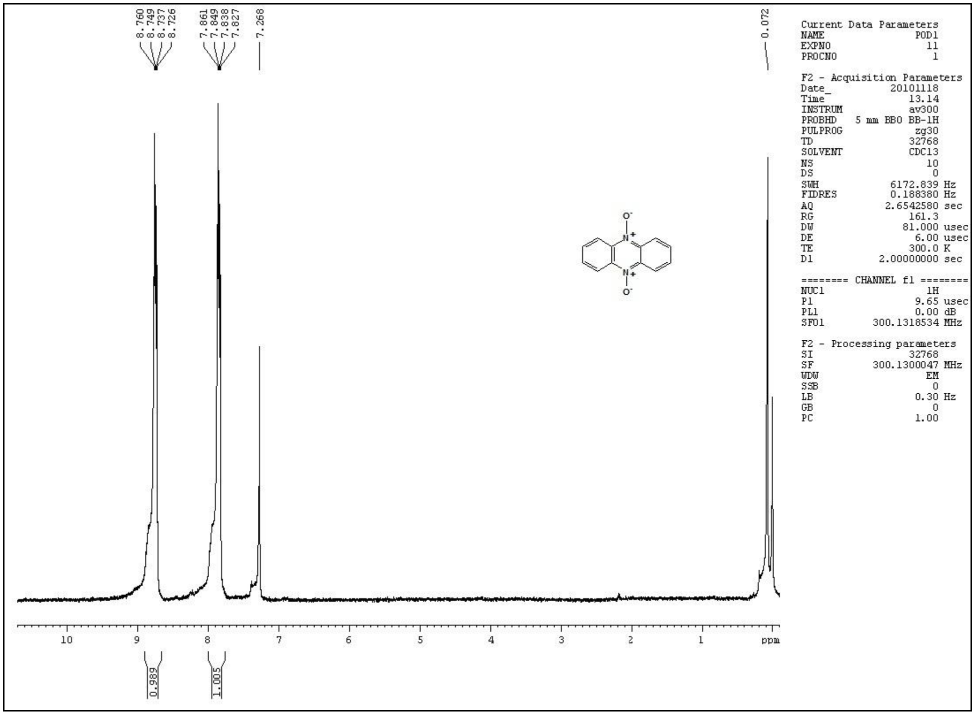

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PROCNO                 1

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DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec

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PL1                 0.00 dB
SFO1         300.1318534 MHz

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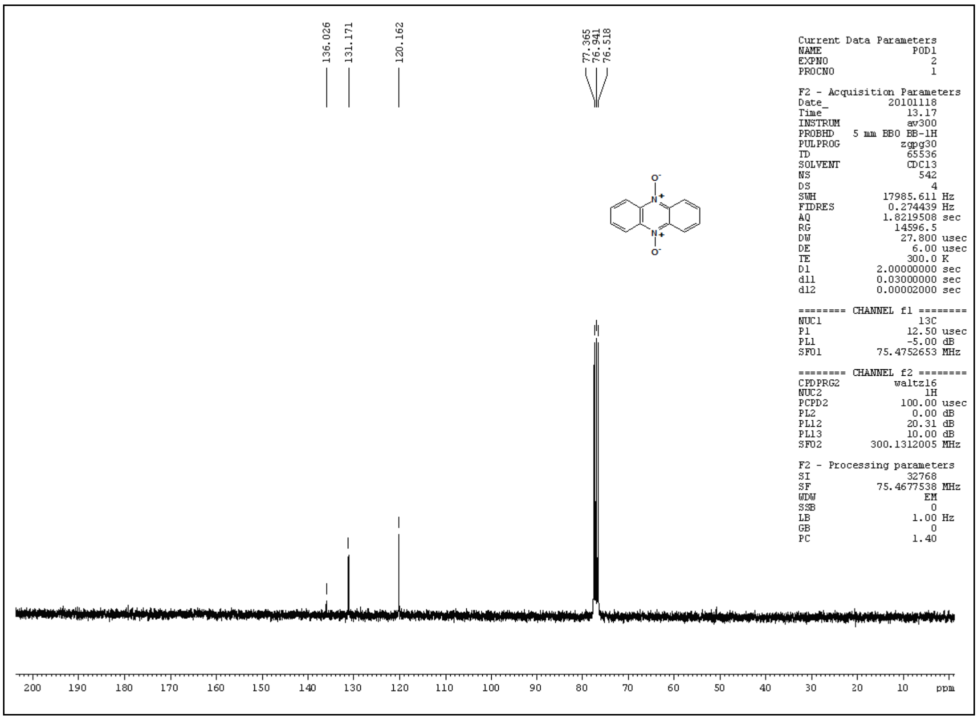
Figure 11. ***^{1}H-NMR spectrum of phenazine-5,10- dioxide (Table 1, entry 8).***



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DE                  6.00 usec
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d11           0.03000000 sec
d12           0.00002000 sec

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PL1                -5.00 dB
SFO1          75.4752653 MHz

======== CHANNEL f2 ========
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PL2                 0.00 dB
PL12               20.31 dB
PL13               10.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
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WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
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Figure 12. ***^{13}C-NMR spectrum of phenazine-5, 10- dioxide (Table 1, entry 8).***

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S15. FT-IR spectra of some N-oxide products

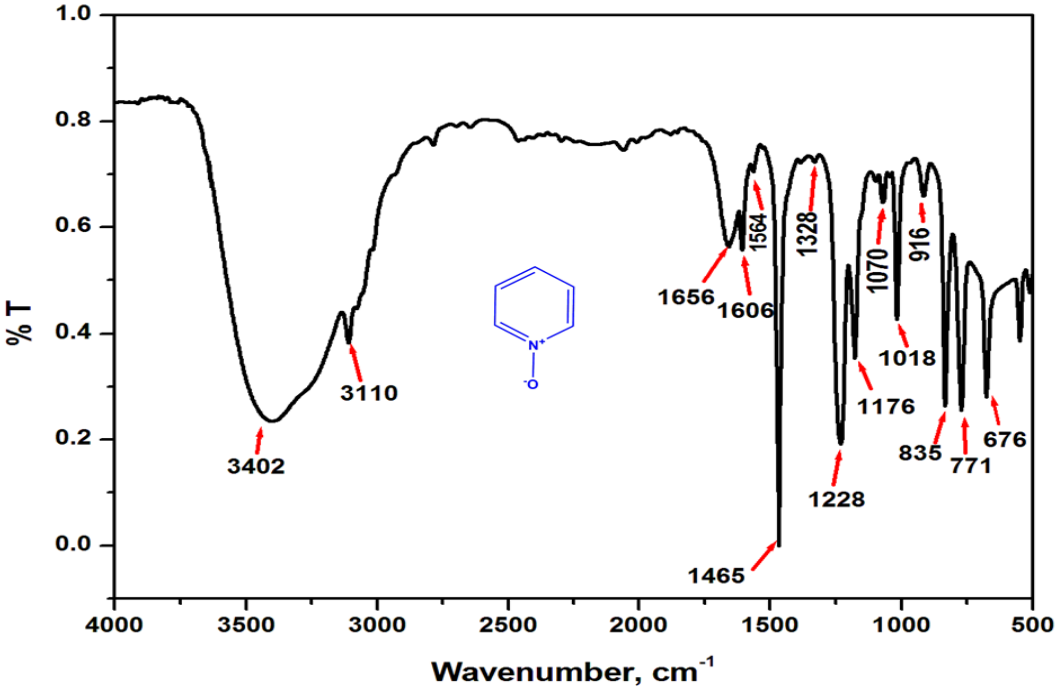

Figure 13. ***FT-IR spectrum of pyridine-N-oxide (Table 1, entry 1).***

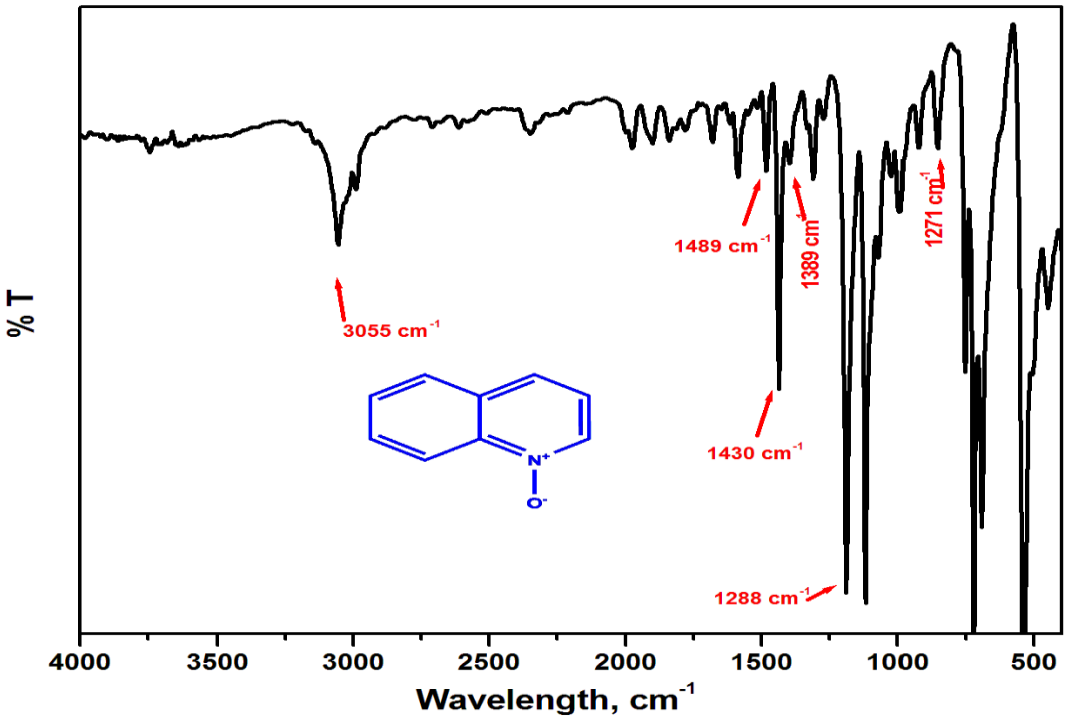

Figure 14. ***FT-IR spectrum of quinoline-N-oxide (Table 1, entry 4).***

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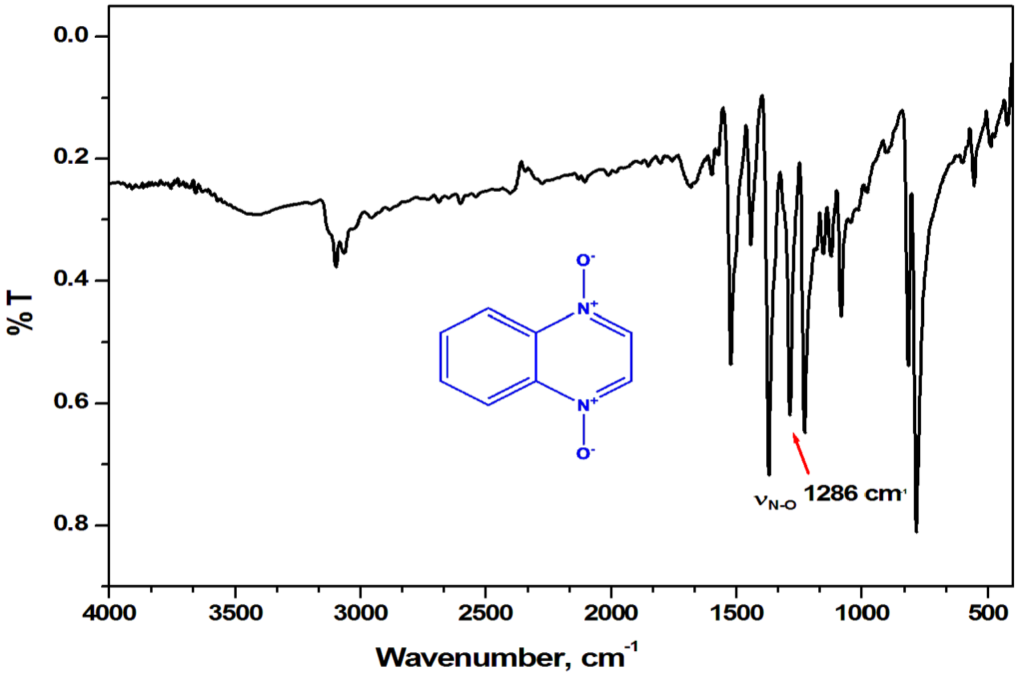

Figure 15. ***FT-IR spectrum of quinoxaline-1,4-dioxide (Table 1, entry 6).***

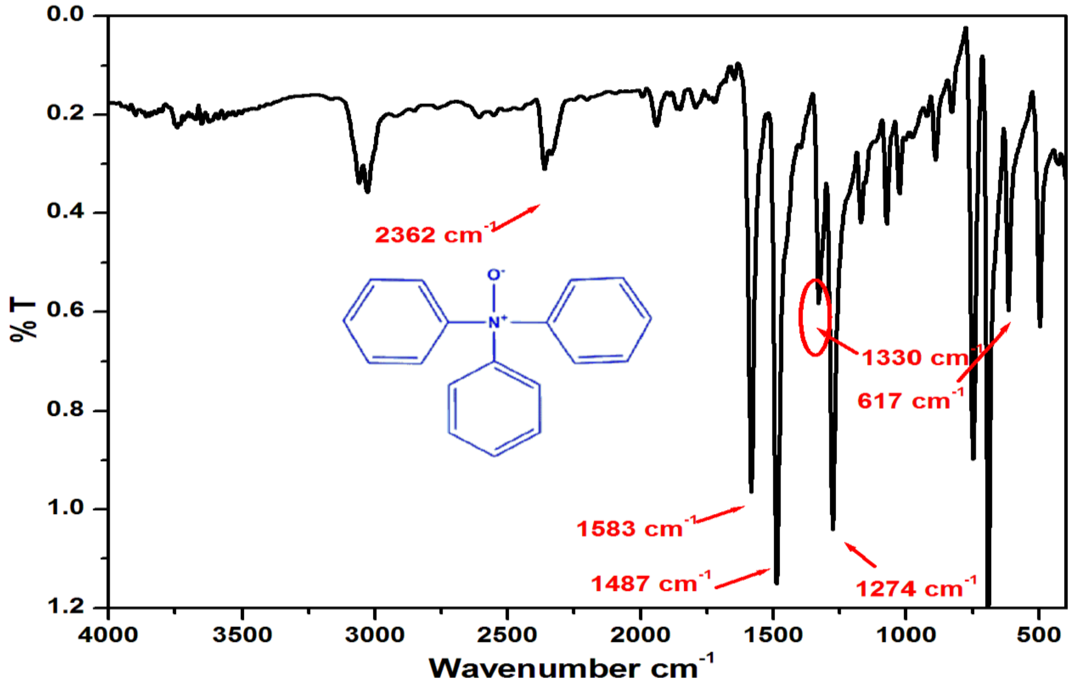

Figure 16. ***FT-IR spectrum of triphenyl amine-N-oxide (Table 1, entry7).***

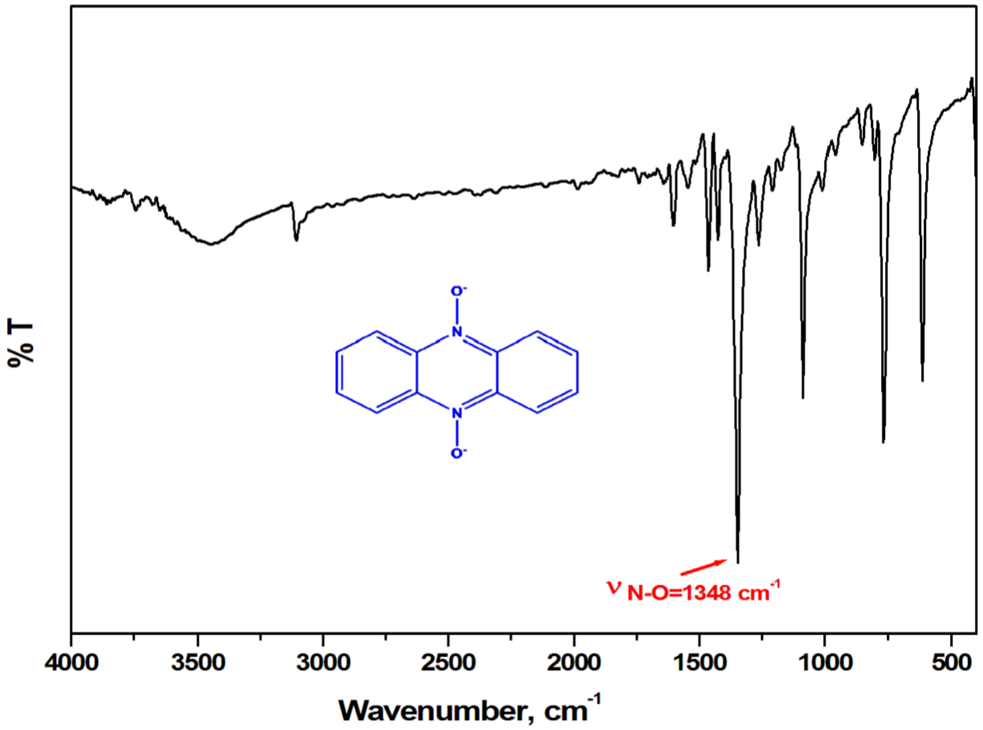

Figure 17. ***FT-IR spectrum of phenazine 5,10-dioxide (Table 1, entry 8).***

S16. References

[1] P. Veerakumar, Zong-Zhan Lu, M. Velayudham, Kuang-Lieh Lu, S. Rajagopal *J. Mol. Catal. A: Chem.* 332 (2010) 128-137.

[2] M. Ramakrishna Prasad, G. Kamalakar, G. Madhavi, S. J. Kulkarni, K. V. Raghavan, *J. Mol. Catal. A: Chem.* 186 (2002) 109.

[3] A. Nansathit, S. Apipattarakul, C. Phaosiri, P. Pongdontri, S. Chanthai, C. Ruangviriyachai, *Walailak J. Sci.Tech* 6 (2009) 79.

[4] D. J. Hoffart, N. C. Habermeh, S. J. Loe, *Dalton Trans.*, (2007) 2870.

[5] Z. Zhu, J. H. Espenson, *J. Mol. Catal. A: Chem.* 103 (1995) 87.