Electronic Supplementary Information

Molybdenum based metallomicellar catalyst for controlled and selective

sulfoxidation reactions in aqueous medium

R. D. Chakravarthy, V. Ramkumar and D. K.Chand

Department of Chemistry, Indian Institute of Technology Madras, Chennai, India.

E-mail: dillip@iitm.ac.in

CONTENTS

Figure S1: ¹ H-NMR spectrum of complex $(C_{19}H_{42}N)_2 [MoO(O_2)_2 (C_2O_4)] \cdot H_2O$	3
Figure S2: ¹³ C-NMR spectrum of complex $(C_{19}H_{42}N)_2[MoO(O_2)_2(C_2O_4)] \cdot H_2O$	4
Figure S3:ORTEP diagram of the complex $(C_{19}H_{42}N)_2 [MoO(O_2)_2 (C_2O_4)] \cdot H_2O$ with	5
50% thermal ellipsoids	
Table S1: Crystallographic data and parameters for complex $(C_{19}H_{42}N)_2$	5
$[MoO(O_2)_2(C_2O_4)] \cdot H_2O$	
Figure S4: Powder XRD pattern of the bulk complex $(C_{19}H_{42}N)_2 [MoO(O_2)_2 (C_2O_4)] \cdot H_2O$	6
compared with the simulated data	
Figure S5:ESI-MS of complex $(C_{19}H_{42}N)_2[MoO(O_2)_2(C_2O_4)] \cdot H_2O$	7
Figure S6: Critical micellar concentration (CMC) of metallo-micelle obtained from a plot	8
of specific conductance against concentration.	
Figure S7: Dynamic light scattering (DLS) histogram of CTAB	9
Figure S8: Dynamic light scattering (DLS) histogram of complex 1	9
Figure S9: Particle size distribution histogram from TEM image	9
Figure S10: ¹ H-NMR spectrum of 2-(4-(methylthio)phenyl)-1,3-dioxane	10
Figure S11: ¹³ C-NMR spectrum of 2-(4-(methylthio)phenyl)-1,3-dioxane	11

Figure S12:ESI-HRMS of 2-(4-(methylthio)phenyl)-1,3-dioxane	12
Figure S13: ¹ H-NMR spectrum of 2-(4-(methylsulfinyl)phenyl)-1,3-dioxane	13
Figure S14: ¹³ C-NMR spectrum of 2-(4-(methylsulfinyl)phenyl)-1,3-dioxane	14
Figure S15:ESI-HRMS of2-(4-(methylsulfinyl)phenyl)-1,3-dioxane	15
Figure S16: ¹ H-NMR spectrum of 2-(4-(methylsulfonyl)phenyl)-1,3-dioxane	16
Figure S17: ¹³ C-NMR spectrum of 2-(4-(methylsulfonyl)phenyl)-1,3-dioxane	17
Figure S18:ESI-HRMS of 2-(4-(methylsulfonyl)phenyl)-1,3-dioxane	18
Figure S19: ¹ H-NMR spectrum of N-(4-(methylthio)benzylidene)aniline	19
Figure S20: ¹³ C-NMR spectrum of N-(4-(methylthio)benzylidene)aniline	20
Figure S21:ESI-HRMS of N-(4-(methylthio)benzylidene)aniline	21
Figure S22: ¹ H-NMR spectrum of N-(4-(methylsulfinyl)benzylidene)aniline	22
Figure S23: ¹³ C-NMR spectrum of N-(4-methylsulfinyl)benzylidene)aniline	23
Figure S24:ESI-HRMS of N-(4-(methylsulfinyl)benzylidene)aniline	24
Determination of critical micelle concentration of $(C_{19}H_{42}N)_2 [MoO(O_2)_2 (C_2O_4)] \cdot H_2O$	25
Procedure for the recyclability of the catalyst	26



Figure S1:¹H-NMR spectrum of complex $(C_{19}H_{42}N)_2[MoO(O_2)_2(C_2O_4)] \cdot H_2O$



Figure S2:¹³C-NMR spectrum of complex $(C_{19}H_{42}N)_2[MoO(O_2)_2(C_2O_4)] \cdot H_2O$



Figure S3 : ORTEP diagram of the complex ($C_{19}H_{42}N$)₂[MoO(O₂)₂(C_2O_4)]·H₂O with 50% thermal ellipsoids

Table S1: Crystallographi	c data and parameters	s for complex ($C_{19}H_{42}N)_2[N$	$MoO(O_2)_2(C_2O_4)] \cdot H_2O$
---------------------------	-----------------------	-----------------	----------------------	----------------------------------

Compound reference	1
Chemical formula	$C_{40}H_{86}MoN_2O_{10}$
Formula mass	851.05
Crystal system	Triclinic
a/Å	9.7003(3)
b/Å	10.0807(4)
c/Å	26.1807(10)
$\alpha/^{\circ}$	88.397(2)
β/°	82.0730(10)
γ/°	69.8550(10)
Unit cell volume/Å ³	2379.99(15)
Temperature/ K	298(2)
Space group	P-1
No. of formula unit per cell/ Z	2
Radiation type	Mo Ka
Absorption coefficient, $m/$ mm ⁻¹	0.326
No. of reflections measured	31760
No. of independent reflections	11050
R _{int}	0.025
Final R_I values $[I > 2\sigma(I)]$	0.0396
Final $wR(F^2)$ values $[I > 2\sigma(I)]$	0.1233
Final R_1 values (all data)	0.0551
Final $wR(F^2)$ values (all data)	0.1433
Goodness of fit on F^2	1.046
CCDC number	CCDC 918215



Figure S4: Powder XRD pattern of the bulk complex $(C_{19}H_{42}N)_2[MoO(O_2)_2(C_2O_4)] \cdot H_2O$ compared with the simulated data.



Figure S5:ESI-MS of complex $(C_{19}H_{42}N)_2[MoO(O_2)_2(C_2O_4)] \cdot H_2O$



Figure S6: Critical micellar concentration (CMC) of metallo-micelle obtained from a plot of specific conductance against concentration. (Standard Deviation = 0.23)



Figure S7: Dynamic light scattering (DLS) histogram of CTAB



Figure S8: Dynamic light scattering (DLS) histogram of complex 1



Figure S9: Particle size distribution histogram from TEM image



Figure S10:¹H-NMR spectrum of 2-(4-(methylthio)phenyl)-1,3-dioxane



Figure S11:¹³C-NMR spectrum of 2-(4-(methylthio)phenyl)-1,3-dioxane

Elemental	Compos	ition Report						Page 1
Single Ma Tolerance Isotope clu	ss Analy = 200.0 n uster para	sis nDa / DBE: meters: Sepa	min = - ration =	1.5, max = 1.0 Abu	= 50.0 ndance = 1	.0%		
Monoisotopi 5 formula(e)	c Mass, Odo evaluated v	d and Even Elect vith 1 results with	tron lons	(all results (up to 1000) fo	or each mass)		
QTOF MICRO DKC-PH-ACE-	S 2 (0.037) AN	I (Cen,2, 80.00, Ht,5	DEPAF 000.0,0.00,	RTMENT OF CI 1.00); Sm (Mn, 2	HEMISTRY IITM , 2x4.00); Cm (1: 11.0792	2)	15	5-Apr-201314:37:02 TOF MS ES+ 1,16e3
210.6658	210.	8029						211.4273
210.700	210	800 210.90	00	211.000	211.100	211.200	211.300	211.400
Minimum: Maximum:		200.0	5.0	-1.5 50.0				
Mass	Calc. Mas	s mDa	PPM	DBE	Score	Formula		
211.0792	211.0793	-0.1	-0.5	4.5	1	C11 H15	02 S	

Figure S12:ESI-HRMS of 2-(4-(methylthio)phenyl)-1,3-dioxane



Figure S13:¹H-NMR spectrum of 2-(4-(methylsulfinyl)phenyl)-1,3-dioxane



Figure S14:¹³C-NMR spectrum of 2-(4-(methylsulfinyl)phenyl)-1,3-dioxane

Liementa	an oompoornor								
Single M Tolerance Isotope c	ass Analysis e = 200.0 mDa luster paramete	/ DBE: n ers: Separa	min = -1. ation = 1	.5, max .0 Abu	= 50.0 Indance = 1.	0%			
Monoisotor 7 formula(e	bic Mass, Odd and e) evaluated with 1	Even Electro results within	on lons n limits (al	ll results (up to 1000) for	each mass)		
QTOF MICRO DKC-PHE-AC	D ET-SULFO 3 (0.056) /	AM (Cen,2, 80.0	DEPARTM 00, Ht,5000.0	MENT OF C 0,0.00,1.00) 227.	HEMISTRY IITM ; Sm (Mn, 2x4.00) 0743			20	-May-201316:38: TOF MS ES 1
%									
%	226.900		227.000	• • • • •	227,100	227.	200	· · ·	227.324 227.300
% 226.802 0 Minimum: Maximum:	226.900	200.0	227.000 5.0	-1.5 50.0	227.100	227.	200		227.32 227.300
% 226.802 0 Minimum: Maximum: Mass	226.900 Calc. Mass	200.0 mDa	227.000 5.0 PPM	-1.5 50.0 DBE	227.100 Score	227. Formula	200		227.32 227.300

Figure S15:ESI-HRMS of 2-(4-(methylsulfinyl)phenyl)-1,3-dioxane



Figure S16:¹H-NMR spectrum of 2-(4-(methylsulfonyl)phenyl)-1,3-dioxane



Figure S17:¹³C-NMR spectrum of 2-(4-(methylsulfonyl)phenyl)-1,3-dioxane

Liementa	al Composit	ion Report	:					Page 1
Single M Tolerance Isotope c	ass Analysi e = 200.0 mE luster param	s Da / DBE eters: Sepa	: min = -1 aration = 1	.5, max = 1.0 Abun	50.0 dance = 1.0	%		
Monoisotor 9 formula(e	oic Mass, Odd a e) evaluated with	and Even Elec h 1 results wit	ctron lons thin limits (a	all results (up	to 1000) for e	each mass)		
QTOF MICRO DKC-PHE-ME	D E-ACE-AULFONE	1 (0.019) AM (Ce	DEPART en,2, 80.00, Ht 2	MENT OF CHE ,5000.0,0.00,1. 243.0693	MISTRY IITM 00); Sm (Mn, 2x4	.00); Cm (1)	02-Jul-20 TC	1314:26:49 F MS ES+ 215
%- -242.717	⁷² 242.7994_242.82	244						243.4994
%- -242.717 0	⁷² 242.7994 242.82 242.800	244 242.900	243.000	243.100	243.200	243.300	243.400	243.4994
%- 242.717 0 Minimum: Maximum:	7 ² 242.7994.242.82 242.800	244 242.900 200.0	243.000 5.0	243.100 -1.5 50.0	243.200	243.300	243.400	_243.4994 m/;
%- 242.717 0 Minimum: Maximum: Mass	72 _{242,7994,242.82} 242.800 Calc. Mass	244 242.900 200.0 mDa	243.000 5.0 PPM	243.100 -1.5 50.0 DBE	243.200 Score	243.300 Formula	243.400	243.4994 m/2

Figure S18:ESI-HRMS of 2-(4-(methylsulfonyl)phenyl)-1,3-dioxane



Figure S19:¹H-NMR spectrum of N-(4-(methylthio)benzylidene)aniline



Figure S20:¹³C-NMR spectrum of N-(4-(methylthio)benzylidene)aniline

Elemental Composi	tion Report					Page 1
Single Mass Analys Tolerance = 200.0 m Isotope cluster paran Monoisotopic Mass, Odd	is Da / DBE: mi neters: Separat and Even Electron	in = -1.5, max = ion = 1.0 Abur lons	= 50.0 ndance = 1.0	%		
3 formula(e) evaluated wi QTOF MICRO DKC-PHE-ME-THIO-IMI 77 (1.	th 1 results within 1 435) AM (Cen,2, 80.00	limits (all results (u DEPARTMENT OF CH Ht,5000.0,0.00,1.00); 228.0856	ip to 1000) for e IEMISTRY IITM Sm (Mn, 2x4.00); (ach mass) Cm (76:77)	1	9-Apr-201316:56:15 TOF MS ES+ 6.28
%- 227.9025						228.3739 m/z
227.950 2	28.000 228.050	228.100 228	.150 228.200	228.250	228.300	228.350
Minimum: Maximum:	200.0 5	-1.5 50.0				
Mass Calc. Mass	s mDa I	PPM DBE	Score	Formula		
228.0856 228.0847	1.0 4	.2 8.5	1	C14 H14	N S	

Figure S21:ESI-HRMS of N-(4-(methylthio)benzylidene)aniline



Figure S22:¹H-NMR spectrum of N-(4-(methylsulfinyl)benzylidene)aniline



Figure S23:¹³C-NMR spectrum of N-(4-(methylsulfinyl)benzylidene)aniline



Figure S24:ESI-HRMS of N-(4-(methylsulfinyl)benzylidene)aniline

Determination of critical micelle concentration of (C₁₉H₄₂N)₂[MoO(O₂)₂(C₂O₄)]·H₂O

Electrical conductivity method was employed to determine the critical micelle concentration (CMC) of the complex($C_{19}H_{42}N$)₂[MoO(O₂)₂(C_2O_4)]·H₂O. The conductivity experiments were carried out in a double-jacket flask. The temperature of the flask was maintained at 25 °C by circulating water with Julabo FP50 Refrigerated - Heating Circulators. A SYSTRONICS digital bench top conductivity meter (Model 306) was usedfor the measurements. Solutions were prepared in deionised water which was first filtered with a Millipore Milli-Q system. A step-by-step dilution-extraction method was adopted for the measurements of specific conductance of the complex at various concentrations in order to avoid dilution error.¹The conductance was plotted as a function of molar concentration and the inflection point gives the value of CMC which is indicated in the **figure S6**.

(a) A. Jover, F. Meijide, V. Mosquera and J. V. Tato, J. Chem. Educ. 1990, 67, 530. (b) A. Domínguez, A. Fernández, N. González, E. Iglesias, and L. Montenegro, J. Chem. Educ. 1997, 74, 1227.

Procedure for the recyclability of the catalyst

In a centrifuge tube, molybdenum complex (0.032g, 2.5 mol%) and thioanisole (0.186g, 1.5 mmol) in 2.5 ml of water were taken and stirred at room temperature. Then 40% (w/v) hydrogen peroxide (0.128ml, 1.5 mmol) was added slowly into the reaction mixture.Stirring was continued for 10 min. Reaction progress was monitored by TLC. After completion, ethyl acetate was added to it and the reaction mixture was centrifuged and decanted to separate molybdenum compound. The residual compound obtained was dried and used for second run. The aqueous phase is extracted with ethyl acetate 3-4 times. Then the combined organic extracts were dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The crude product thus obtained was purified by column chromatography with Hexane: Ethyl acetate as an eluent.

For the second run: To the residual catalyst in the centrifuge tube, 2.5 ml of water and hydrogen peroxide (0.128ml, 1.5 mmol) was added. The mixture was stirred for 30 min to activate the catalyst. Then thioanisole (0.186g, 1.5 mmol) was added and stirring was continued for 45 min. Reaction progress was monitored by TLC. After completion, ethyl acetate was added to it and the reaction mixture was centrifuged and decanted to separate molybdenum compound. The residual compound was dried and used for the subsequent cycle.

After 4 run, 0.013g of catalyst was recovered. So in each run, on an average of 81 % catalysts can be recovered.