Supporting information

Synthesis, crystal structure and catalytic activity of Guanidinium cation directed Nickel (II)-containing open Wells – Dawson 19-tungstodiarsenate (III) $[\{Ni(H_2O)_4\}_2\{Na(H_2O)\}As_2W_{19}O_{67}(H_2O)]^{9-}$

Contents-

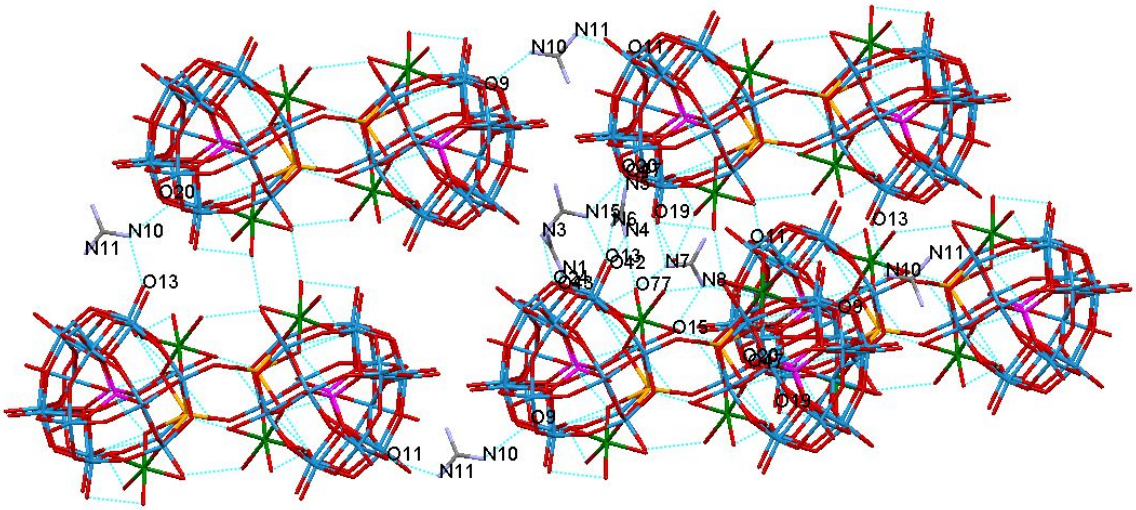


Fig. S1 Hydrogen bonding network along the b-axis between N-H atoms of guanidinium cations and oxygen atoms of the polyanion **1a**.

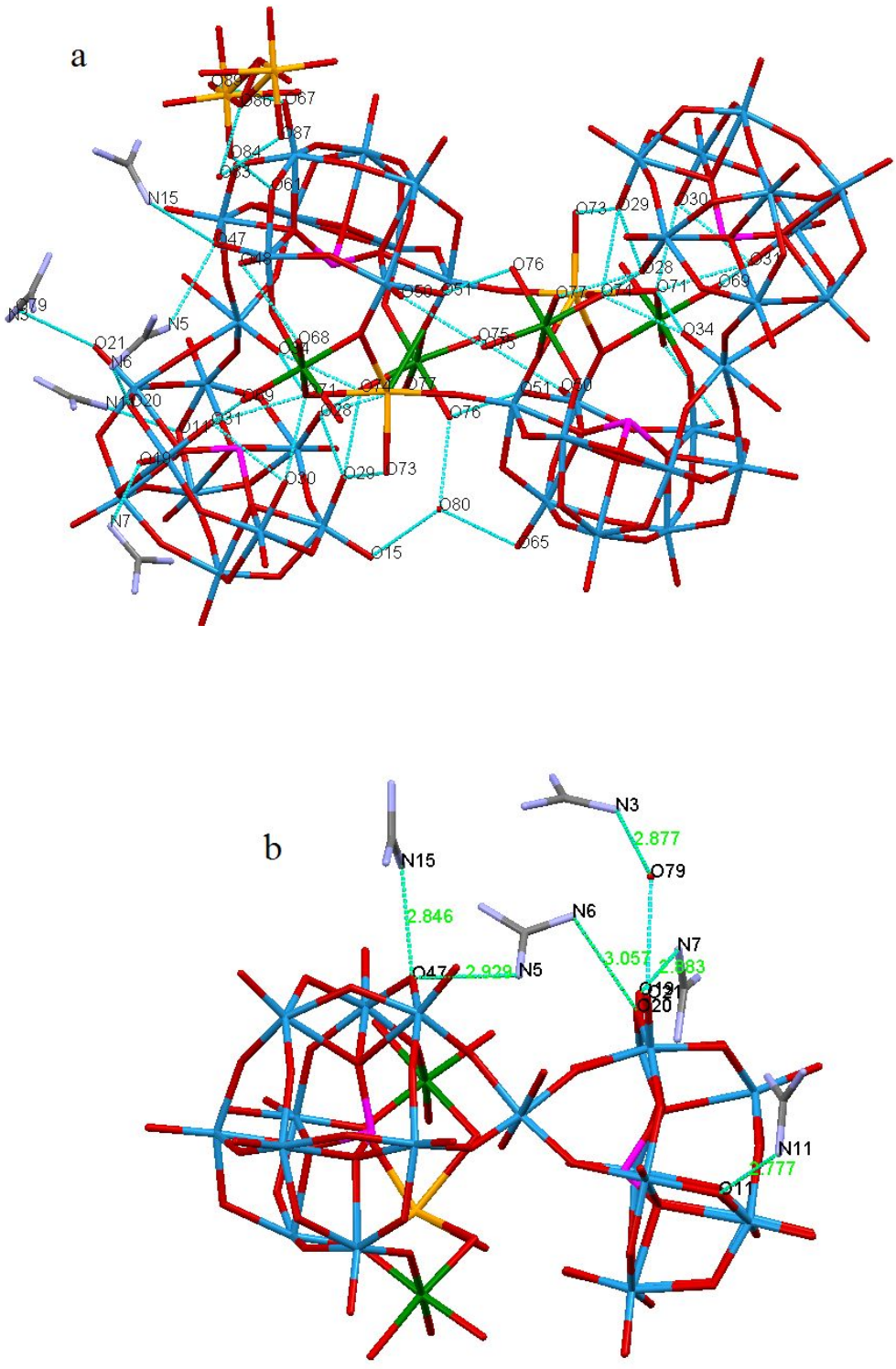


Fig. S2 Hydrogen bonding network in one unit of the polyanion **1a** (a) and N-H···O_{POM} distances between donor and acceptor atoms (b) in the polyanion **1a**.

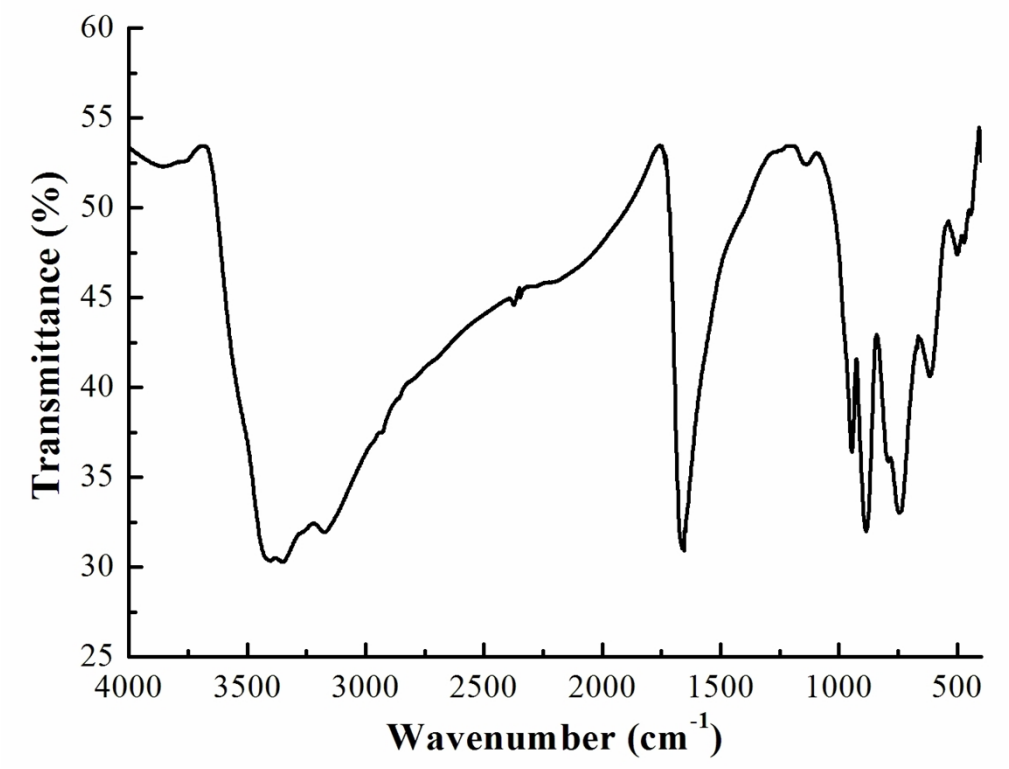


Fig. S1 FT-IR spectrum of **1a** recorded on KBr pellets.

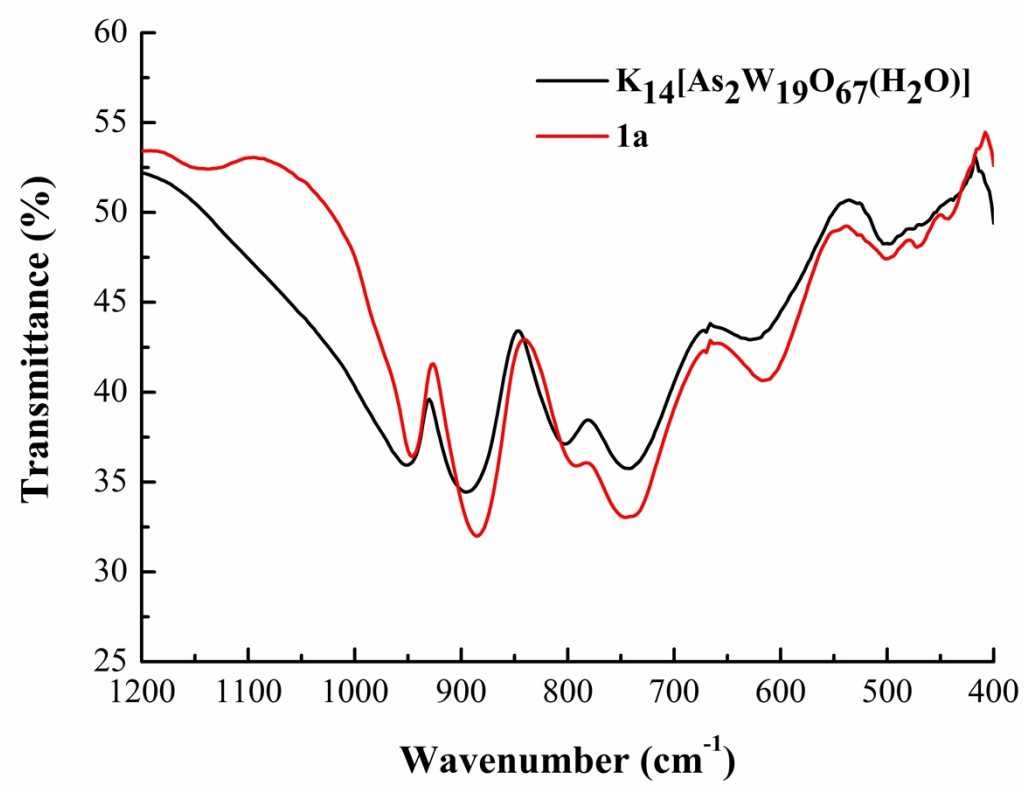


Fig. S2 Comparison of FT-IR spectra of compound **1a**, and $K_{14}[As_2W_{19}O_{67}(H_2O)]$ recorded on KBr pellets.

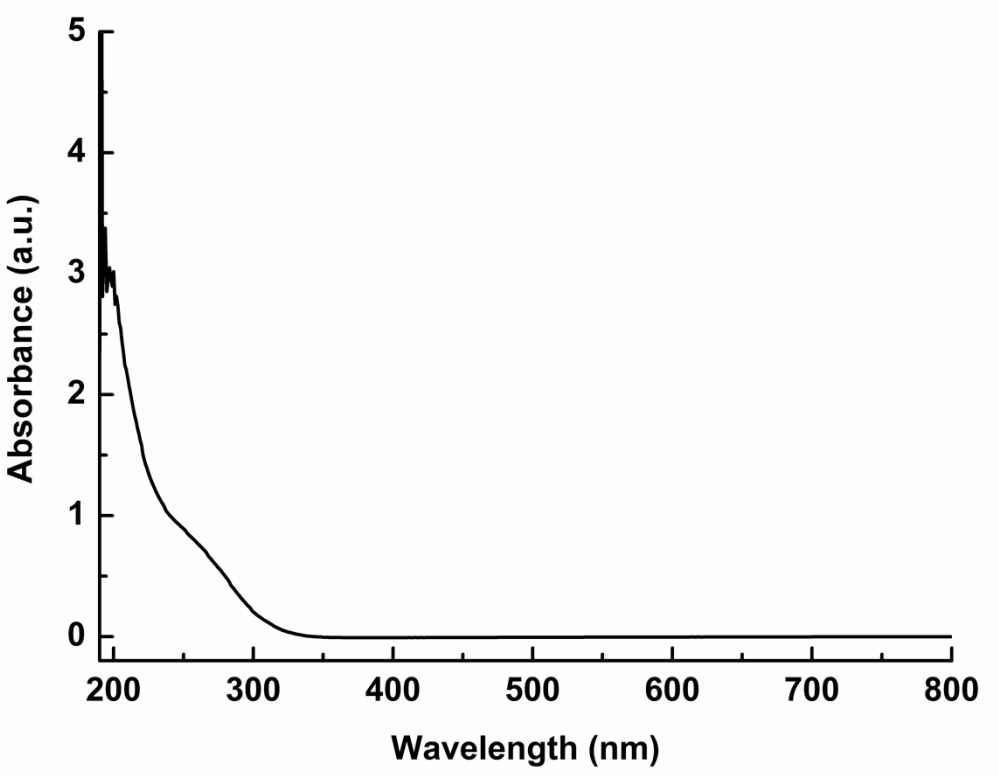


Fig. S5 UV/vis spectrum of **1a**.

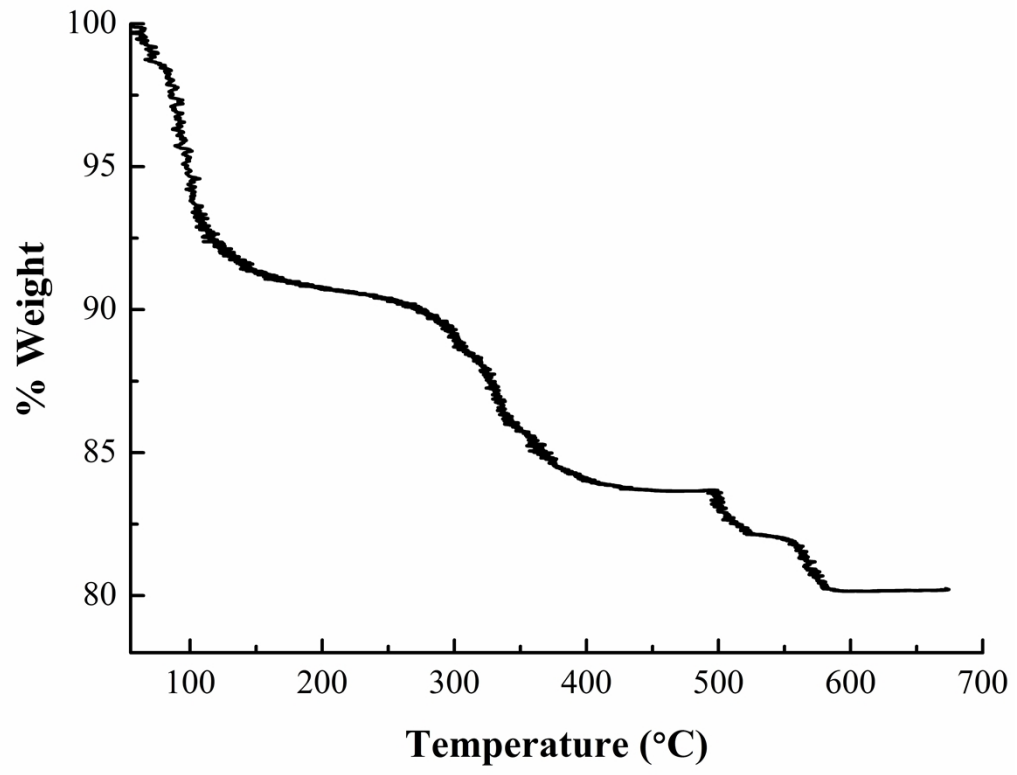


Fig. S6 Thermogram of **1a** from room temperature to 700 °C.

Details of magnetic properties of the polyanion 1a

$\mu_{eff} = 2.828(\chi_m T)^{1/2}$ ……(**Eq.1**)

Where, χ_m is magnetic susceptibility and T = temperature in Kelvin

χ_m = M/H × Molecular weight of polyanion **1a** ……(**Eq.2**)

M = 0.00685 and H = 9002 from data and molecular weight of polyanion **1a** is 5823.98 g/mol

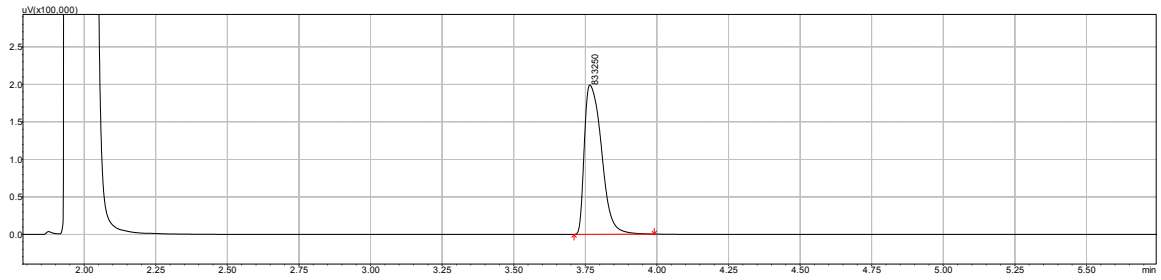
χ_m = 0.0044 and T = 294 K substitute these values in (**Eq.1**)

$\mu_{eff} = 3.23\ \mu_B$

Plots of Gas Chromatographic analysis

Gas chromatogram for standard styrene

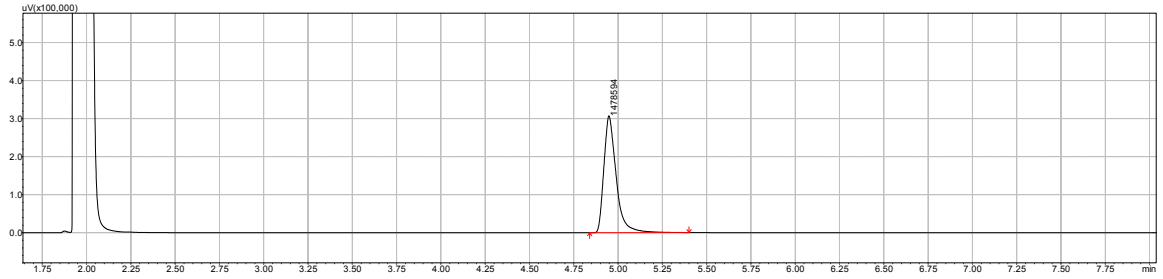
GC conditions for standard styrene. Column information Rtx-5, L = 30.0 m, 0.25 mm/ID, injector temperature 220 °C, column flow rate 1.00 ml/min, column temperature 90 – 160 °C, hold time 10 min, temperature program 3 °C/min, detector temperature 250 °C.



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	3.766	833250.3	197971.7	100.00000	100.0000	Styrene

Gas chromatogram for standard Benzaldehyde

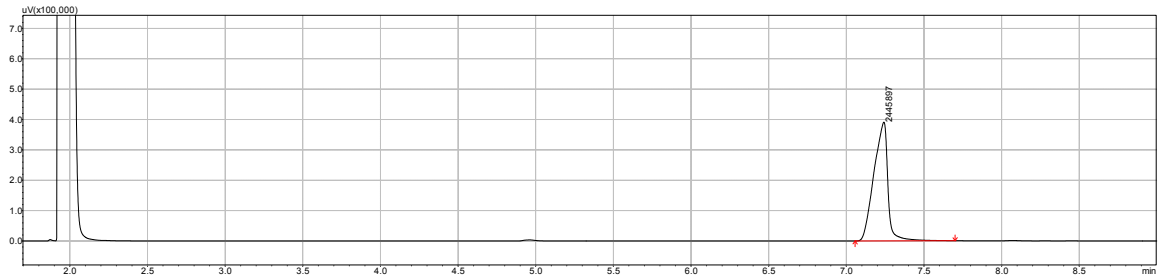
GC conditions are same as standard styrene.



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	4.949	1478594.3	306318.8	100.00000	100.0000	Benzaldehyde

Gas chromatogram for standard Phenyl acetaldehyde

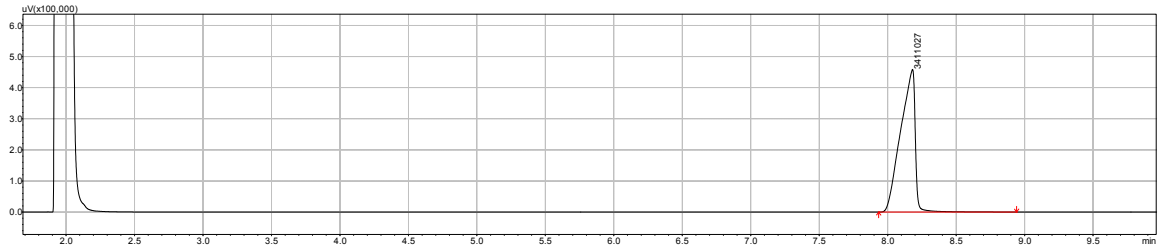
GC conditions are same as standard styrene.



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	7.241	2445897.3	387386.2	100.00000	100.0000	Phenyl acetaldehyde

Gas chromatogram for standard Acetophenone

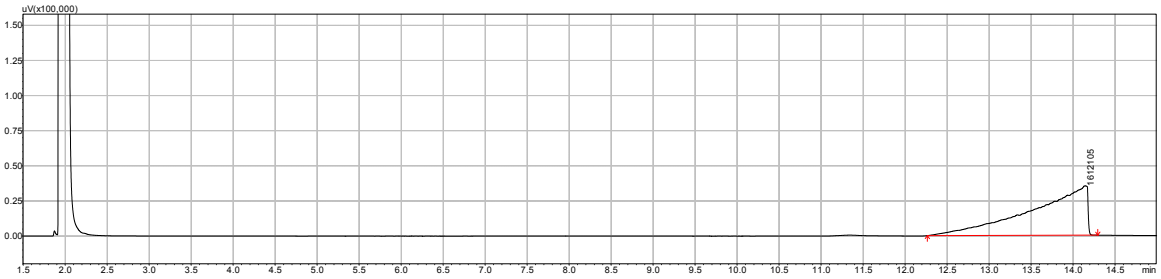
GC conditions are same as standard styrene.



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	8.181	3411026.9	457024.0	100.00000	100.0000	Acetophenone

Gas chromatogram for standard Benzoic acid

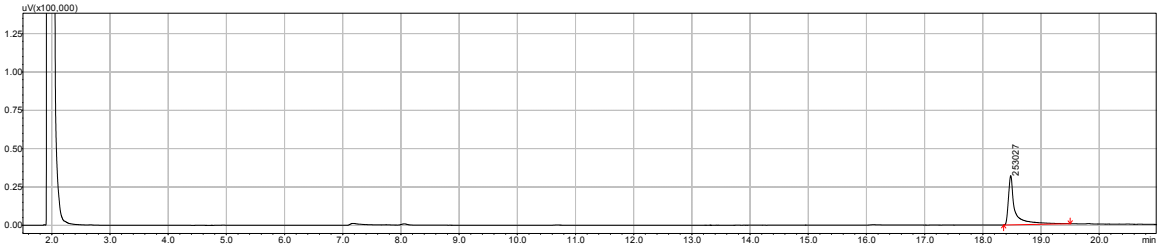
GC conditions are same as standard styrene.



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	14.150	1612105.3	35075.4	100.00000	100.0000	Benzoic acid

Gas chromatogram for standard 1-phenylethane-1, 2-diol

GC conditions are same as standard styrene.

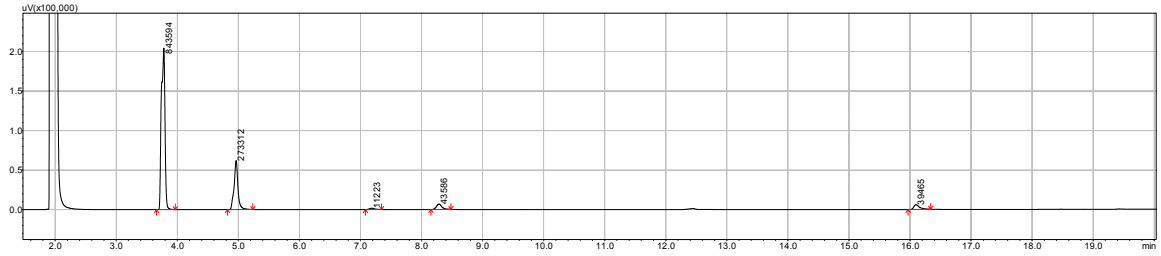


Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	18.480	253026.5	32026.6	100.00000	100.0000	1-phenylethane1, 2-diol

Gas chromatogram for styrene oxidation reactions

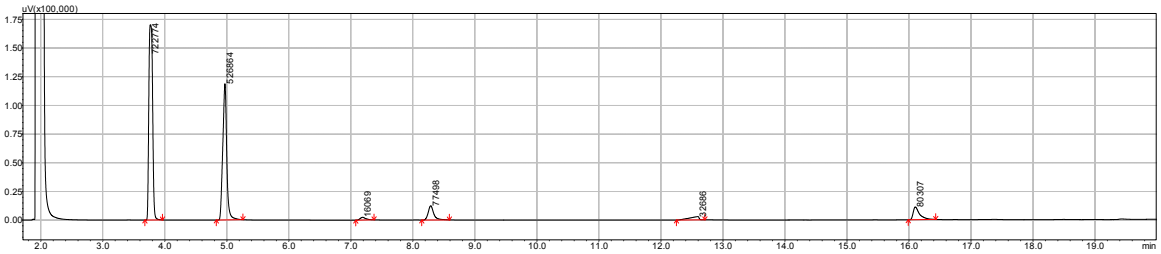
GC plot for the reaction at 60 °C temperature and 4:1 (H_2O_2/substrate) ratio for 6h

GC conditions are same as standard styrene.



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	3.779	843593.8	199801.2	69.65059	69.6506	Styrene
2	4.963	273311.7	61916.7	22.56574	22.5657	Benzaldehyde
3	7.185	11223.2	1816.4	0.92663	0.9266	Phenylacetaldehyde
4	8.286	43585.7	6892.8	3.59862	3.5986	Acetophenone
5	16.100	39465.4	5923.2	3.25843	3.2584	2-hydroxy-1-phenylethanone

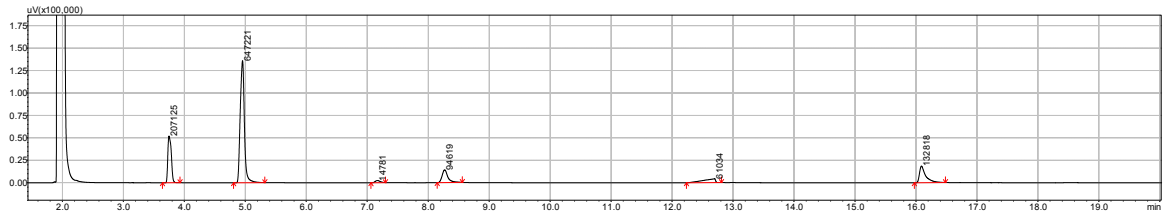
GC plot for the reaction at 70 °C temperature and 4:1 (H_2O_2/substrate) ratio for 6h GC conditions are same as standard styrene.



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	3.767	722773.9	169953.4	49.63433	49.6343	Styrene
2	4.970	526864.3	117415.3	36.18083	36.1808	Benzaldehyde
3	7.191	16068.8	2484.5	1.10348	1.1035	Phenylacetaldehyde
4	8.289	77497.5	12445.6	5.32191	5.3219	Acetophenone
5	12.597	32686.1	2950.0	2.24462	2.2446	Benzoic acid
6	16.102	80306.6	11181.9	5.51482	5.5148	2-hydroxy-1-phenylethanone

GC plot for the reaction at 80 °C temperature and 4:1 (H_2O_2/substrate) ratio for 6h

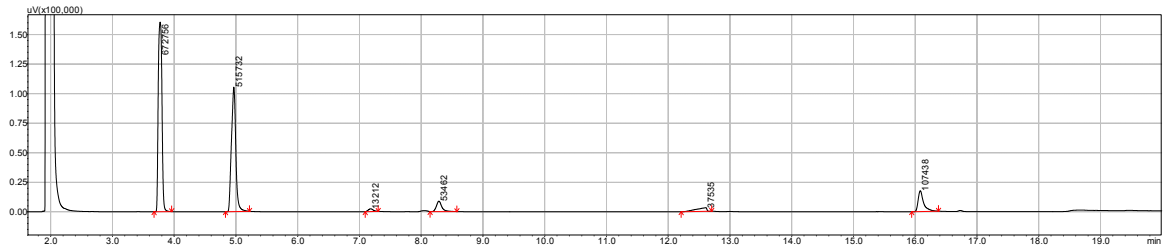
GC conditions are same as standard styrene.



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	3.749	207124.8	51938.2	17.89264	17.8926	Styrene
2	4.955	647220.9	135031.2	55.91069	55.9107	Benzaldehyde
3	7.167	14780.7	2498.0	1.27684	1.2768	Phenylacetaldehyde
4	8.270	94619.4	14268.9	8.17377	8.1738	Acetophenone
5	12.698	61033.5	4271.0	5.27243	5.2724	Benzoic acid
6	16.090	132818.5	18650.5	11.47363	11.4736	2-hydroxy-1-phenylethanone

GC plot for the reaction at 80 °C temperature and 2:1 (H_2O_2/substrate) ratio for 6h

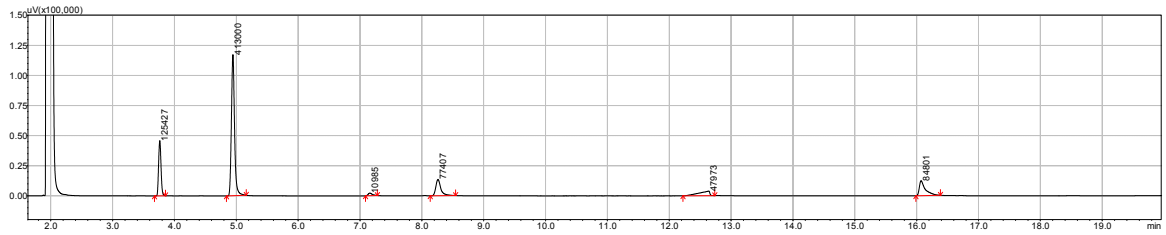
GC conditions are same as standard styrene.



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	3.772	672755.5	160315.9	48.04940	48.0494	Styrene
2	4.966	515731.8	104842.1	36.83448	36.8345	Benzaldehyde
3	7.182	13212.0	2355.8	0.94363	0.9436	Phenylacetaldehyde
4	8.285	53461.6	8790.3	3.81832	3.8183	Acetophenone
5	12.610	37534.7	3048.0	2.68079	2.6808	Benzoic acid
6	16.083	107437.6	17553.0	7.67338	7.6734	2-hydroxy-1-phenylethanone

GC plot for the reaction at 80 °C temperature and 3:1 (H_2O_2/substrate) ratio for 6h

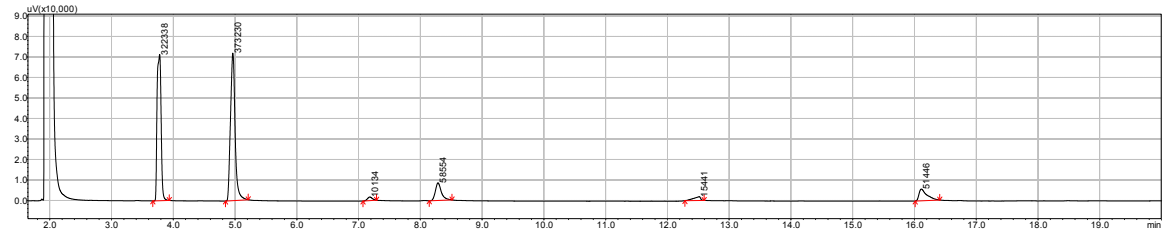
GC conditions are same as standard styrene.



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	3.763	125427.4	45634.0	16.51245	16.5124	Styrene
2	4.945	413000.1	117100.3	54.37125	54.3712	Benzaldehyde
3	7.160	10985.2	2275.7	1.44619	1.4462	Phenylacetaldehyde
4	8.261	77406.6	13629.4	10.19053	10.1905	Acetophenone
5	12.639	47972.9	3830.4	6.31560	6.3156	Benzoic acid
6	16.072	84800.8	12458.4	11.16398	11.1640	2-hydroxy-1-phenylethanone

GC plot for the reaction at 80 °C temperature and 3:1 (H_2O_2/substrate) ratio for 3h

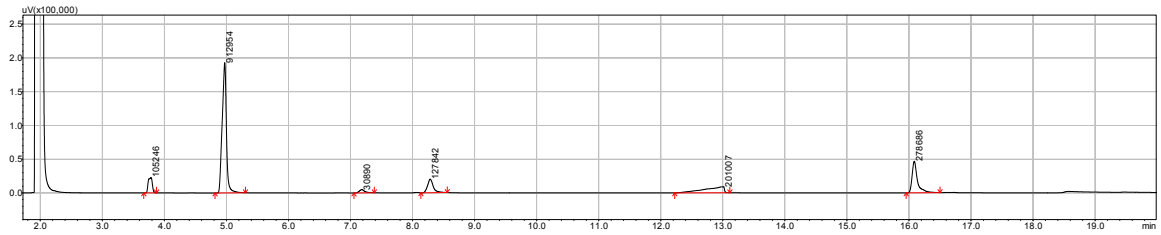
GC conditions are same as standard styrene.



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	3.779	322337.7	70716.5	38.78247	38.7825	Styrene
2	4.964	373230.2	71914.1	44.90566	44.9057	Benzaldehyde
3	7.183	10133.6	1822.5	1.21924	1.2192	Phenylacetaldehyde
4	8.286	58554.2	8688.2	7.04502	7.0450	Acetophenone
5	12.517	15440.8	1866.3	1.85778	1.8578	Benzoic acid
6	16.112	51446.4	5776.6	6.18984	6.1898	2-hydroxy-1-phenylethanone

GC plot for the reaction at 80 °C temperature and 3:1 (H_2O_2/substrate) ratio for 9h

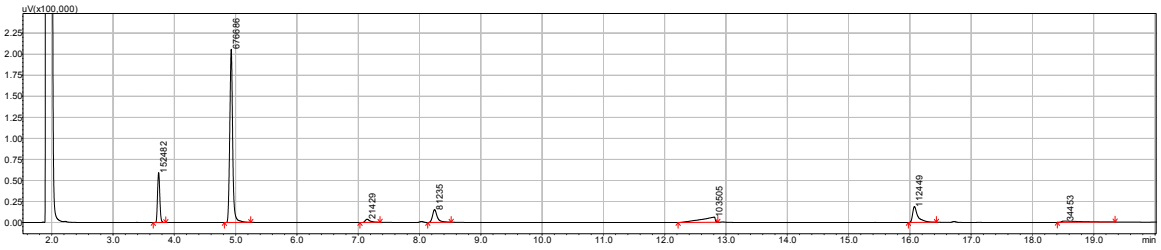
GC conditions are same as standard styrene.



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	3.786	105246.3	22909.0	6.35305	6.3531	Styrene
2	4.973	912954.3	192707.2	55.10927	55.1093	Benzaldehyde
3	7.182	30890.2	4933.5	1.86465	1.8646	Phenylacetaldehyde
4	8.285	127841.9	20093.6	7.71701	7.7170	Acetophenone
5	13.012	201006.7	8954.6	12.13350	12.1335	Benzoic acid
6	16.086	278686.3	46645.8	16.82253	16.8225	2-hydroxy-1-phenylethanone

GC plot for the reaction at 80 °C temperature and 3:1 (H_2O_2/substrate) ratio for 9h, catalyst used Ni-POM reported by Mialane et al.

GC conditions are same as standard styrene.

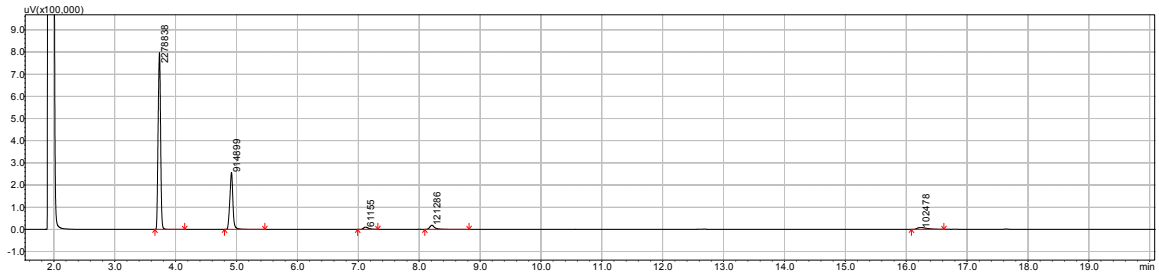


Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	3.744	152482.1	58961.2	12.89775	12.8977	Styrene
2	4.928	676686.5	202783.7	57.23773	57.2377	Benzaldehyde
3	7.146	21429.0	3843.2	1.81258	1.8126	Phenylacetaldehyde
4	8.246	81234.5	15126.4	6.87125	6.8712	Acetophenone
5	12.809	103504.7	6140.0	8.75497	8.7550	Benzoic acid
6	16.074	112448.8	18966.6	9.51151	9.5115	2-hydroxy-1-phenylethanone

7	18.538	34453.0	1552.1	2.91421	2.9142	1-Phenylethane-1, 2-diol

GC plot for the reaction at 80 °C temperature and 3:1 (H_2O_2/substrate) ratio for 6h, $K_{14}[As_2W_{19}O_{67}(H_2O)]$ used as catalyst

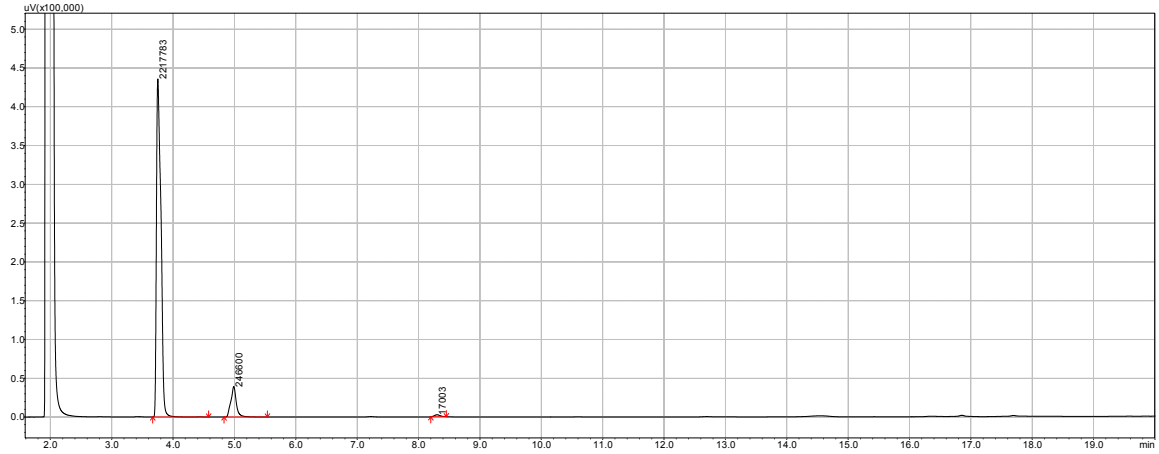
GC conditions are same as standard styrene.



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	3.734	2278837.9	789122.6	65.50915	65.5092	Styrene
2	4.917	914898.8	256250.8	26.30035	26.3004	Benzaldehyde
3	7.118	61155.4	10714.2	1.75802	1.7580	Phenylacetaldehyde
4	8.208	121286.1	19108.7	3.48658	3.4866	Acetophenone
5	16.242	102477.6	8432.0	2.94590	2.9459	2-hydroxy-1-phenylethanone

GC plot for the reaction at 80 °C temperature and 3:1 (H_2O_2/substrate) ratio for 6h, $NiCl_2 \cdot 6H_2O$ used as catalyst

GC conditions are same as standard styrene.

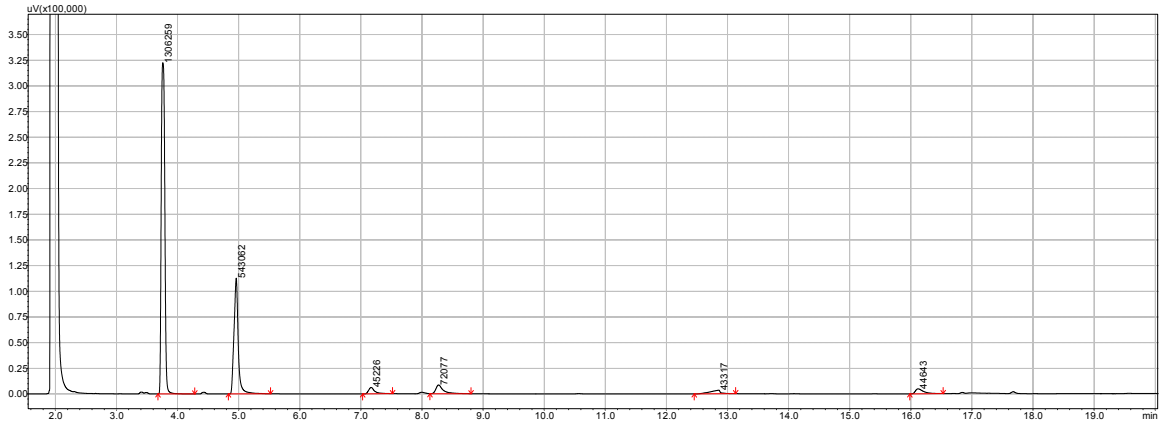


Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name

1	3.751	2217782.9	435323.2	89.37678	89.3768	Styrene
2	4.989	246600.1	39339.2	9.93800	9.9380	Benzaldehyde
3	8.302	17003.0	2521.5	0.68522	0.6852	Acetophenone

GC plot for the reaction at 80 °C temperature and 3:1 (H_2O_2/substrate) ratio for 6h, $NiCl_2 \cdot 6H_2O$ and $K_{14}[As_2W_{19}O_{67}(H_2O)]$ both used as catalyst in same reaction

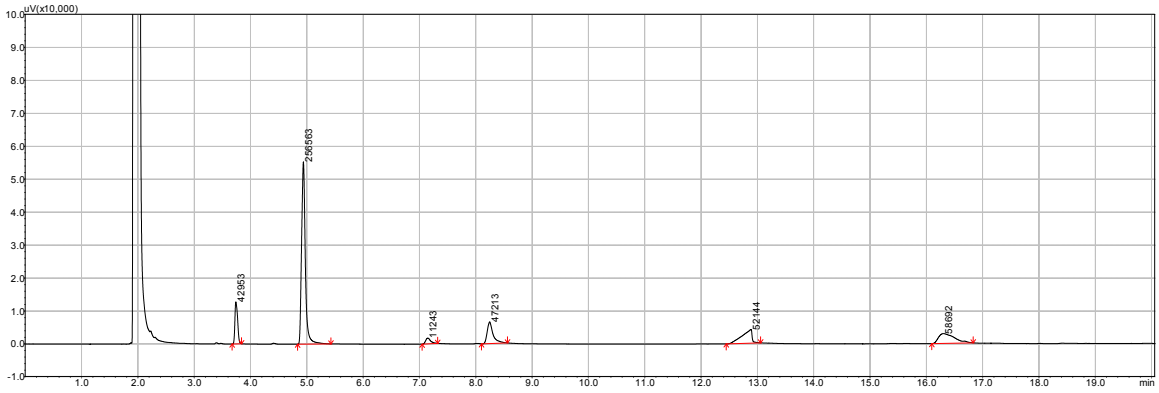
GC conditions are same as standard styrene.



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	3.759	1306258.8	322319.1	63.57780	63.5778	Styrene
2	4.960	543062.2	112627.3	26.43174	26.4317	Benzaldehyde
3	7.169	45225.9	6216.2	2.20122	2.2012	Phenylacetaldehyde
4	8.271	72076.8	8528.0	3.50810	3.5081	Acetophenone
5	12.856	43316.7	3547.2	2.10829	2.1083	Benzoic acid
6	16.120	44643.0	4799.7	2.17285	2.1728	2-hydroxy-1-phenylethanone

GC plot for the reaction at 80 °C temperature and 4:1 (H_2O_2/substrate) ratio for 6h

GC conditions are same as standard styrene.



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	3.740	42952.6	12755.9	9.16208	9.1621	Styrene
2	4.939	256563.2	55160.2	54.72669	54.7267	Benzaldehyde
3	7.146	11242.9	1788.9	2.39820	2.3982	Phenylacetaldehyde
4	8.246	47213.0	6558.2	10.07086	10.0709	Acetophenone
5	12.888	52144.1	4134.4	11.12270	11.1227	Benzoic acid
6	16.304	58692.3	2979.1	12.51947	12.5195	2-hydroxy-1-phenylethanone

Recycling and recovery of the catalyst

After completion of the catalytic reaction, acetonitrile solvent was removed by the evaporation followed by addition of ethyl acetate to the reaction mixture. Organic products were separated in ethyl acetate and the catalyst was precipitated out as solid. The solid recovered catalyst was collected and washed with ethanol and dried at ambient temperature. The dried recovered catalyst was reused for the next catalytic cycle.

Table S1 Recycling of the polyanion **1a** catalyst for the styrene oxidation reaction up to two cycles [a]

Sr. No.	Catalytic cycle	H_2O_2/sub	Temp. (°C)	Time (h)	Conversion (%)[b]	Selectivity for different products (%)					
						1a	1b	1c	1d	1e	1f
01	1st	3 : 1	80	6	57	66	4	8	7	15	-
02	2nd	3 : 1	80	6	44	68	4	13	4	11	-

[a]Reaction conditions: 2 mmol (styrene), 0.15 mol% **1a** catalyst, in 2 mL CH_3CN stirred for specified temperature and time. [b]Conversion was determined by GC.