Supplementary Information

For

Merrifield resin supported peroxomolybdenum(VI) compounds: recoverable heterogeneous catalysts for efficient, selective and mild oxidation of organic sulfides with H_2O_2

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Table S1 ^{13}C NMR Chemical Shift for polymer support, amino acid-anchored Merrifield resin and polymer-bound peroxomolybdates

Compound	Chemical Shift (ppm)								
	Merrifield Resin				Amino acid				
	Quaternary Aromatic Carbons	Protonated Aromatic Carbons	Aliphatic Methine Carbons	CH_2Cl	CH_3	CH_2/CH	C-NH	Carboxylate	
								Free	Complexed
MR	145.18	128.36	41.04	46.17	---	---	---	---	---
MRV	145.14	129.05	41.66	46.10	19.42	31.08	61.48	176.35	---
MRVMo	145.25	128.90	41.81	46.18	18.89	31.00	61.21	176.50	206.11
MRA	145.23	128.74	42.00	46.14	---	17.01	53.09	176.02	---
MRAMo	145.01	127.67	41.89	46.14	---	17.09	53.10	176.13	205.16

Table S2 Thermogravimetric data for **MRV**, **MRA**, **MRVMo** and **MRAMo**

Compound	Temperature range (°C)	Observed weight loss (%)	Final residue (%)
MRV	89-99	0.72	2.56
	199-255	17.61	
	283-480	50.88	
	480-700	28.23	
MRA	91-99	0.67	1.23
	221-274	12.08	
	280-482	56.90	
	482-700	29.12	
MRVMo	70-100	1.04	9.06
	103-181	1.59	
	205-259	15.89	
	286-488	46.15	
	488-700	26.31	
MRAMo	69-100	1.14	6.58
	103-177	1.19	
	216-271	11.89	
	280-488	50.48	
	488-700	28.72	

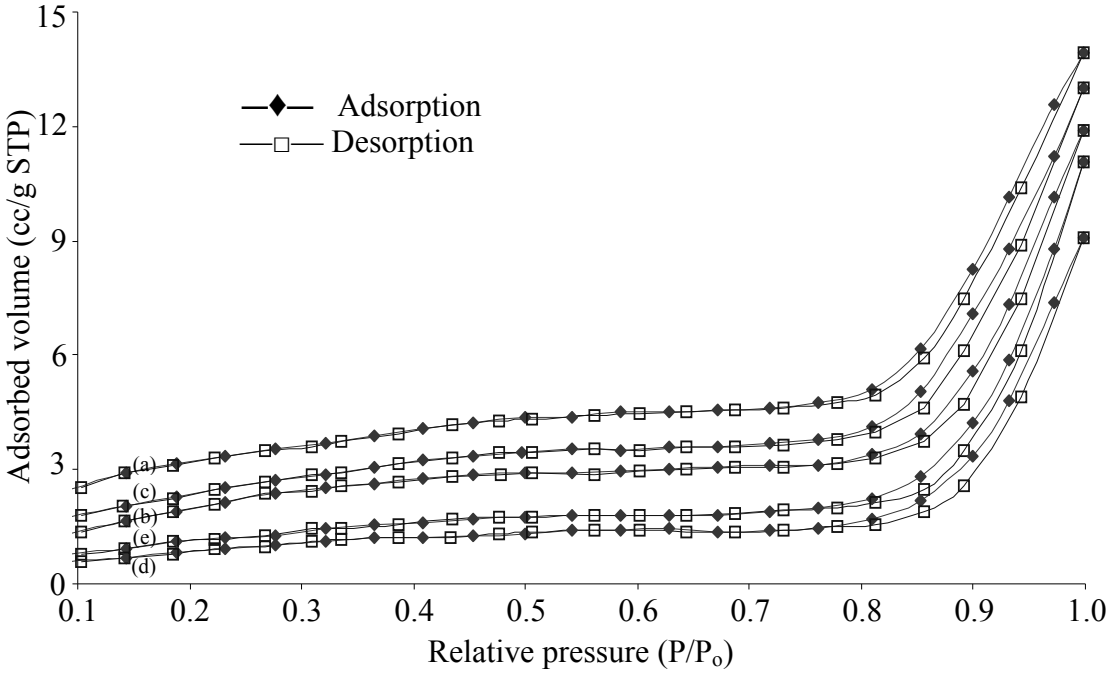


Fig. S1 The N_2 adsorption/desorption isotherm of (a) **MR**, (b) **MRV**, (c) **MRA**, (d) **MRVMo** and (e) **MRAMo**.

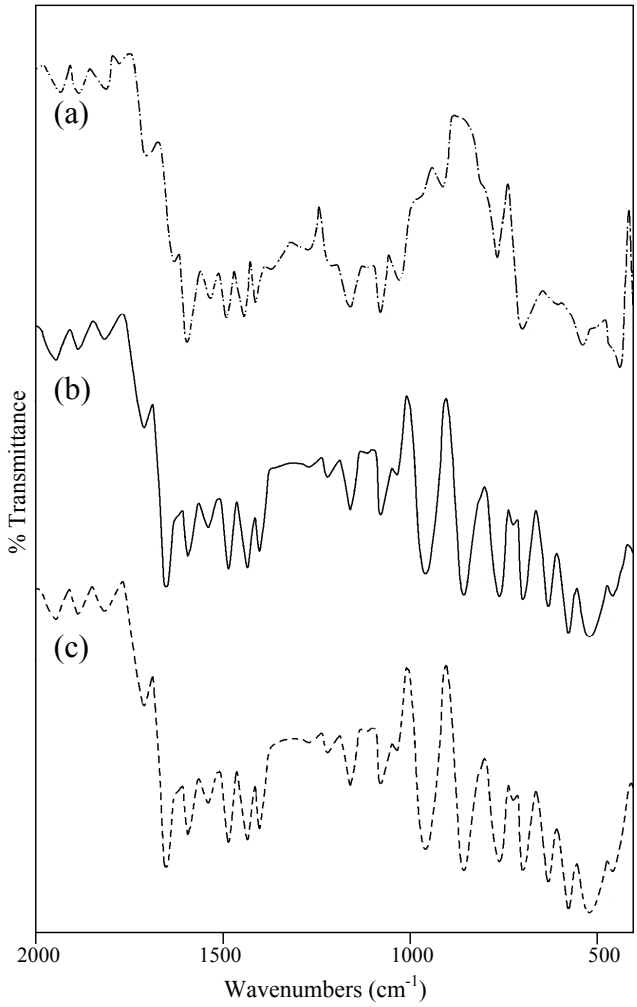
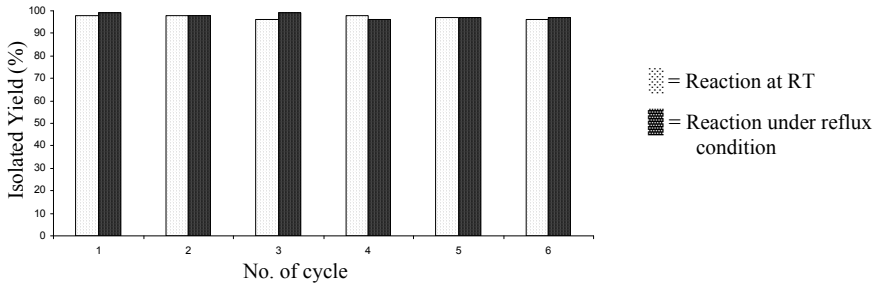
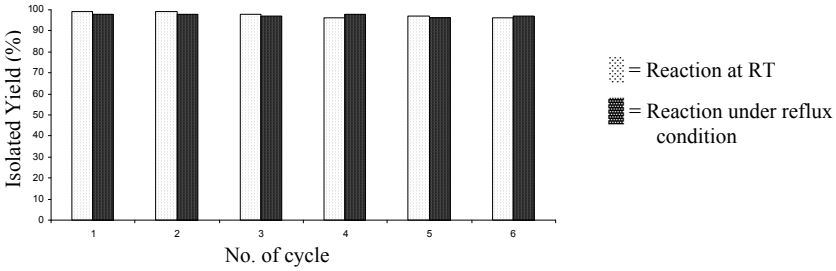


Fig. S2 FTIR spectra of (a) **MRA**, (b) **MRAMo** and (c) **MRAMo** after 6th cycle of reaction.



(a)



(b)

Fig. S3 Recyclability of **MRAMo** (used as representative) for the selective oxidation of MPS to (a) sulfoxide or (b) sulfone.

Text S1: Determination of H_2O_2 efficiency or effective use of H_2O_2 in the sulfoxidation reaction

The calculations are shown with oxidation of methyl phenyl sulfide (MPS) to methyl phenyl sulfoxide as a representative example.

H_2O_2 efficiency (%) = 100 × [mole of H_2O_2 consumed in the formation of oxyfunctionalized products / mole of H_2O_2 converted]

(a) Assuming that one mole of oxidant reacts with one mole of substrate, H_2O_2 (mole) consumed in the formation of sulfoxide (yield: 98%) from 5 mmol sulfides = **4.9 mmol**

(b) In order to determine the H_2O_2 (mole) converted, the spent catalyst was separated by centrifugation and the left H_2O_2 was estimated by titration with standard Cerium (IV) solution. The value was found to be : **4.8 mmol**

Since 10 mmol H_2O_2 has been originally used for the reaction,

therefore, total mole of H_2O_2 converted = (10.0 - 4.8) mmol = **5.2 mmol**

Thus, **H_2O_2 efficiency = 100 × [4.9 / 5.2]**

= 94.2 %

Text S2: Characterization of Sulfoxides and Sulfones

(a) Methylphenylsulfoxide: Isolated as light yellow solid; mp 28-29^{o}C; ν (KBr)/cm^{-1} 1046;

^{1}H NMR (400MHz; $CDCl_3$, δ): 2.73(s, 3H); 7.30-7.36(m, 1H); 7.41-7.50(m, 2H); 7.62-7.69(m, 2H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 43.93; 123.54; 128.63; 130.95; 145.42

(b) Methylphenylsulfone: Isolated as white solid; mp 85-86^{o}C; ν (KBr)/cm^{-1} 1321, 1165;

^{1}H NMR (400MHz; $CDCl_3$, δ): 3.02(s, 3H); 7.52-7.59(m, 1H); 7.61-7.71(m, 2H); 7.89-7.95(m, 2H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 44.83; 126.23; 128.54; 133.21; 137.44

(c) Dimethylsulfoxide: Isolated as liquid; ν (KBr)/cm^{-1} 1053;

^{1}H NMR (400MHz; $CDCl_3$, δ): 2.63(s, 6H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 40.53

(d) Dimethylsulfone: Isolated as white solid; mp 236-237^{o}C; ν (KBr)/cm^{-1} 1314, 1136;

^{1}H NMR (400MHz; $CDCl_3$, δ): 3.27(s, 6H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 44.63

(e) Dibutylsulfoxide: Isolated as white solid; mp 32-33^{o}C; ν (KBr)/cm^{-1} 1063;

^{1}H NMR (400MHz; $CDCl_3$, δ): 0.96(t, 6H, J=7.41Hz); 1.37-1.49(m, 4H); 1.68-1.78(m, 4H); 2.61-2.69(m, 4H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 13.74; 22.13; 24.52; 51.91

(f) Dibutylsulfone: Isolated as white solid; mp 42-43^{o}C; ν (KBr)/cm^{-1} 1342, 1135;

^{1}H NMR (400MHz; $CDCl_3$, δ): 0.96 (t, 6H, J=7.41Hz); 1.39-1.51(m, 4H); 1.79-1.88(m, 4H); 2.87-2.94(m, 4H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 13.54; 21.72; 23.98; 52.53

(g) Butylpropylsulfoxide: Isolated as liquid; ν (KBr)/cm^{-1} 1057;

^{1}H NMR (400MHz; $CDCl_3$, δ): 0.92-0.99(m, 6H); 1.28-1.39(m, 2H); 1.71-1.79(m, 4H); 2.54-2.62 (m, 4H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 13.76; 22.14; 24.51; 51.97

(h) Butylpropylsulfone: Isolated as white solid; mp 81-82^{o}C; ν (KBr)/cm^{-1} 1342, 1132;

^{1}H NMR (400MHz; $CDCl_3$, δ): 0.94-0.99(m, 6H); 1.29-1.39(m, 2H); 1.82-1.89(m, 4H); 2.85-2.95(m, 4H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 13.51; 21.75; 23.99; 52.53

(i) Dibenzothiophene sulfoxide: Isolated as white solid; mp 188-189^{o}C; ν (KBr)/cm^{-1} 1043;

^{1}H NMR (400MHz; $CDCl_3$, δ): 7.52-7.59(m, 2H); 7.71-7.75(m, 2H); 7.91-7.98(m, 4H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 123.45; 124.16; 126.37; 129.83; 132.67; 143.33

(j) Dibenzothiophene sulfone: Isolated as white solid; mp 231-232°C; ν (KBr)/cm^{-1} 1363, 1165;

^{1}H NMR (400MHz; $CDCl_3$, δ): 7.51-7.55(m, 2H); 7.61-7.66(m, 2H); 7.77-7.85(m, 4H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 121.54; 121.97; 130.16; 131.53; 133.77; 137.62

(k) Phenylvinylsulfoxide: Isolated as pale yellow liquid; ν (KBr)/cm^{-1} 1054;

^{1}H NMR (400MHz; $CDCl_3$, δ): 5.94(d, 1H, J=10.13Hz); 6.26(d, 1H, J=15.89Hz); 6.55-6.69(m, 1H); 7.27-7.37(m, 1H); 7.44-7.53(m, 2H); 7.62-7.68(m, 2H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 120.55; 124.52; 129.38; 131.13; 142.95; 143.41

(l) Phenylvinylsulfone: Isolated as white solid; mp 63-64°C; ν (KBr)/cm^{-1} 1364, 1161;

^{1}H NMR (400MHz; $CDCl_3$, δ): 6.11(d, 1H, J=9.60Hz); 6.43(d, 1H, J=16.42Hz); 6.64-6.78(m, 1H); 7.44-7.51(m, 1H); 7.56-7.68(m, 2H); 7.87-7.93(m, 2H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 127.85; 129.33; 133.77; 138.51; 139.70

(m) 2-(Phenylsulfinyl)ethanol: Isolated as light brown solid; mp 42-43°C; ν (KBr)/cm^{-1} 1040;

^{1}H NMR (400MHz; $CDCl_3$, δ): 2.43(s, 1H); 3.12(t, 2H, J=5.31Hz); 3.87(t, 2H, J=5.26Hz); 7.26-7.39(m, 1H); 7.48-7.57(m, 2H); 7.61-7.68(m, 2H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 56.15; 60.91; 125.47; 129.98; 131.23; 144.55

(n) Dihexylsulfoxide: Isolated as pale yellow liquid; ν (KBr)/cm^{-1} 1042;

^{1}H NMR (400MHz; $CDCl_3$, δ): 0.95 (t, 6H, J= 7.65 Hz), 1.21-1.37 (m, 12H), 1.68 (m, 4H), 2.71 (t, 4H, J=6.71Hz)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 13.54, 21.91, 32.85, 27.64, 28.53, 52.64

(o) Dihexylsulfone: Isolated as pale yellow liquid; ν (KBr)/cm^{-1} 1323, 1161;

^{1}H NMR (400MHz; $CDCl_3$, δ): 0.95 (t, 6H, J= 7.66 Hz), 1.21-1.38 (m, 12H), 1.91 (m, 4H), 3.36 (t, 4H, J=6.71Hz)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 13.48, 21.78, 32.64, 27.91, 26.45, 53.72

(p) Allylphenylsulfone: Isolated as pale yellow liquid; ν (KBr)/cm^{-1} 1318, 1144;

^{1}H NMR (400MHz; $CDCl_3$, δ): 3.91(dt, 2H, J= 7.19, 1.22Hz); 5.02(dq, 1H, J= 1.48, 17.21Hz); 5.18(dq,1H, J= 1.22, 10.31Hz); 5.63(ddt, 1H, J= 7.19, 10.31, 17.21Hz); 7.37-7.44(m, 1H); 7.62-7.69(m, 2H); 7.91-7.95(m, 2H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 60.67; 117.51; 124.63; 128.88; 129.02; 133.74; 138.27

(q) Ethylphenylsulfoxide: Isolated as pale yellow liquid; ν (KBr)/cm^{-1} 1054;

^{1}H NMR (400MHz; $CDCl_3$, δ): 1.23(t, 3H, J=6.61Hz); 2.69-2.78(q, 1H, J=6.61Hz); 2.91(q, 1H, J=6.61Hz) 7.13-7.48(m, 3H); 7.49-7.84(m, 2H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 10.39, 47.19, 125.42, 129.85, 131.47, 145.69

(r) Ethylphenylsulfone: Isolated as white solid; mp > 261 ^{o}C; ν (KBr)/cm^{-1} 1322, 1153;

^{1}H NMR (400MHz; $CDCl_3$, δ): 1.30(t, 3H, J=7.11Hz); 3.09(q, 2H, J=7.11Hz); 7.59(m, 3H); 7.99(m, 2H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 7.34, 50.28, 127.86, 128.92, 133.47, 138.31

(s) Diphenyl sulfoxide: Isolated as white solid; mp 70 ^{o}C; ν (KBr)/cm^{-1} 1043;

^{1}H NMR(400MHz; $CDCl_3$, δ): 7.63-7.68(m, 4H), 7.43-7.51(m, 6H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 144.71, 129.87, 128.23, 123.71

(t) Diphenyl sulfone: Isolated as pale yellow solid; mp 127^{o}C; ν (KBr)/cm^{-1} 1322, 1155;

^{1}H NMR(400MHz; $CDCl_3$, δ): 7.91-7.99(m, 4H),7.44-7.53(m, 6H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 141.77, 133.20, 129.32, 127.69

(u) Benzylphenylsulfoxide: Isolated as white solid; mp 120 ^{o}C; ν (KBr)/cm^{-1} 1033;

^{1}H NMR (400MHz; $CDCl_3$, δ): 3.98(s, 2H), 6.93-7.11(m, 5H), 7.17-7.36(m, 3H), 7.42-7.55(m, 2H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 63.44, 124.21, 128.15, 128.24, 128.57, 128.87, 130.26, 130.83, 142.59

(v) Benzylphenylsulfone: Isolated as white solid; mp 143 ^{o}C; ν (KBr)/cm^{-1} 1328, 1159;

^{1}H NMR (400MHz; $CDCl_3$, δ): 4.41(s, 2H), 7.06-7.14(m, 5H), 7.32-7.41(m, 3H), 7.65-7.74(m, 2H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 62.53, 128.31, 128.39, 128.47, 128.61, 130.53, 133.44, 137.49

(w) 2-(Phenylsulfonyl)ethanol: Isolated as white solid; mp 96-97^{o}C; ν (KBr)/cm^{-1} 1334, 1152;

^{1}H NMR (400MHz; $CDCl_3$, δ): 2.47(s, 1H); 3.33(t, 2H, J=5.46Hz); 3.95(t, 2H, J=5.26Hz); 7.44-7.53(m, 1H); 7.57-7.68(m, 2H); 7.89-7.97(m, 2H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 57.35; 61.56; 128.92; 129.58; 134.06; 140.71

(x) Allylphenylsulfoxide: Isolated as pale yellow liquid; ν (KBr)/cm^{-1} 1043;

^{1}H NMR (400MHz; $CDCl_3$, δ): 3.43(dt, 2H, J=7.11, 1.12Hz); 5.01(dq, 1H, J=1.42, 17.10Hz); 5.16(dq, 1H, J=1.12, 10.22Hz); 5.44(ddt, 1H, J=7.11, 10.22, 17.10 Hz); 7.26-7.31(m, 1H); 7.36-7.39(m, 2H); 7.60-7.64(m, 2H)

^{13}C NMR (100.5MHz; $CDCl_3$, δ): 60.36; 117.93; 124.71; 125.09; 129.06; 131.24; 142.13

Splitting patterns are designated as s (singlet), d (dublet), t (triplet), dt (double triplet), ddt (double-double triplet), q (quartet), dq (double quartet), m (multiplet).