Supporting Information

Manganese Protoporphyrin IX Reconstituted Myoglobin Capable of Epoxidation of C=C Bond with Oxone®

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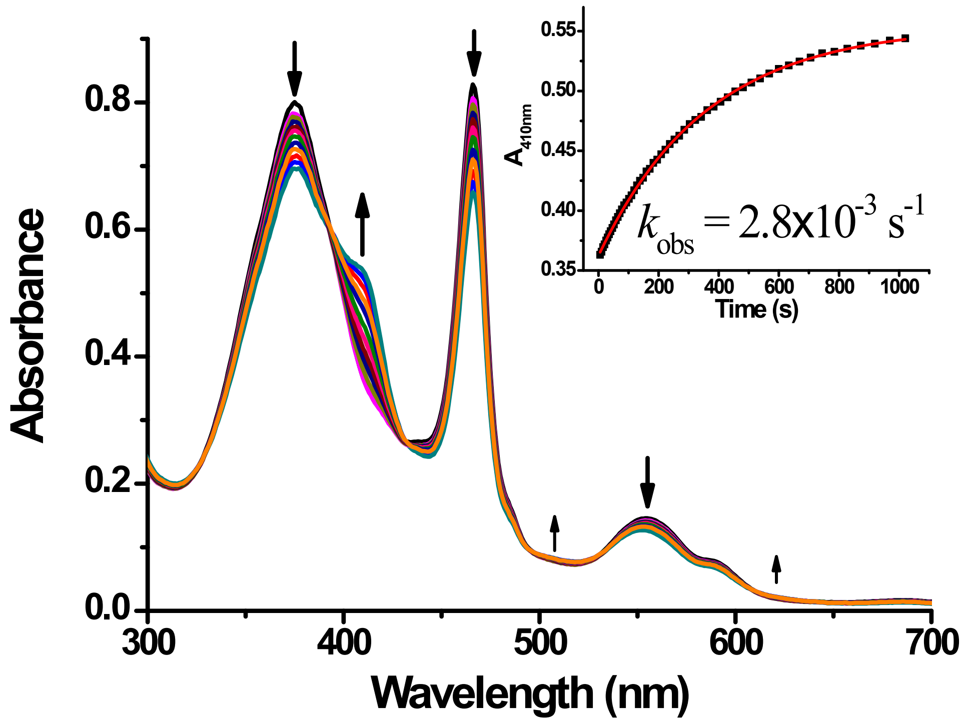


Figure S1 Kinetic studies of 30 μM His3 Mn^{III}Mb reacted with 20 equiv $KHSO_5$ in PBS buffer (pH=7.4). Inset: Time course plots of absorbance at 410 nm, and corresponding rate constants of Mn=O formation.

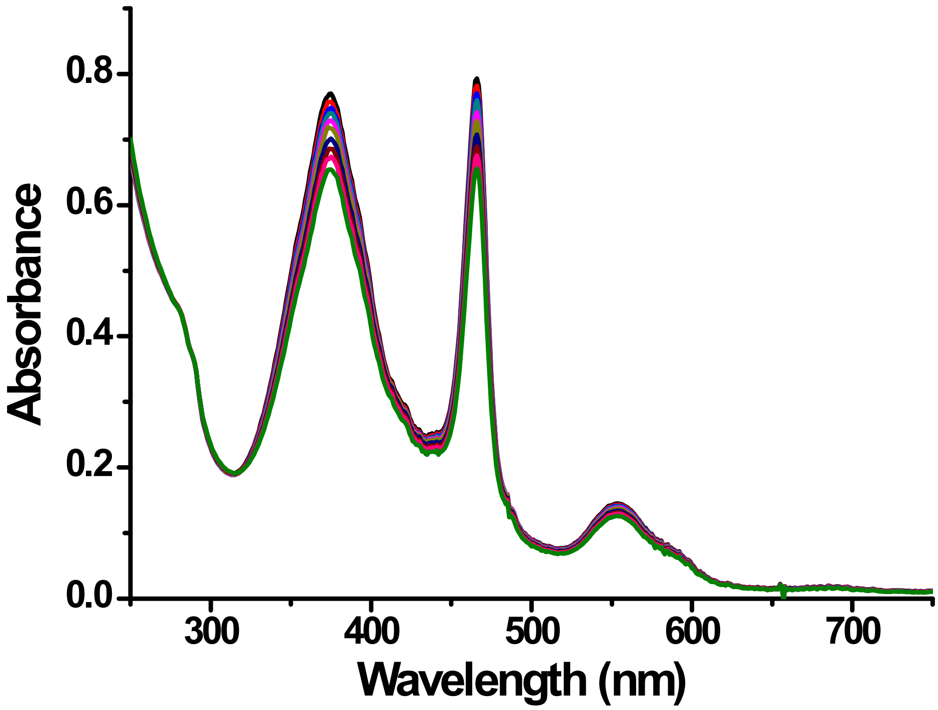


Figure S2 Kinetic studies of 30 μM F43H Mn^{III}Mb reacted with 200 equiv $KHSO_5$ in PBS buffer (pH=7.4).

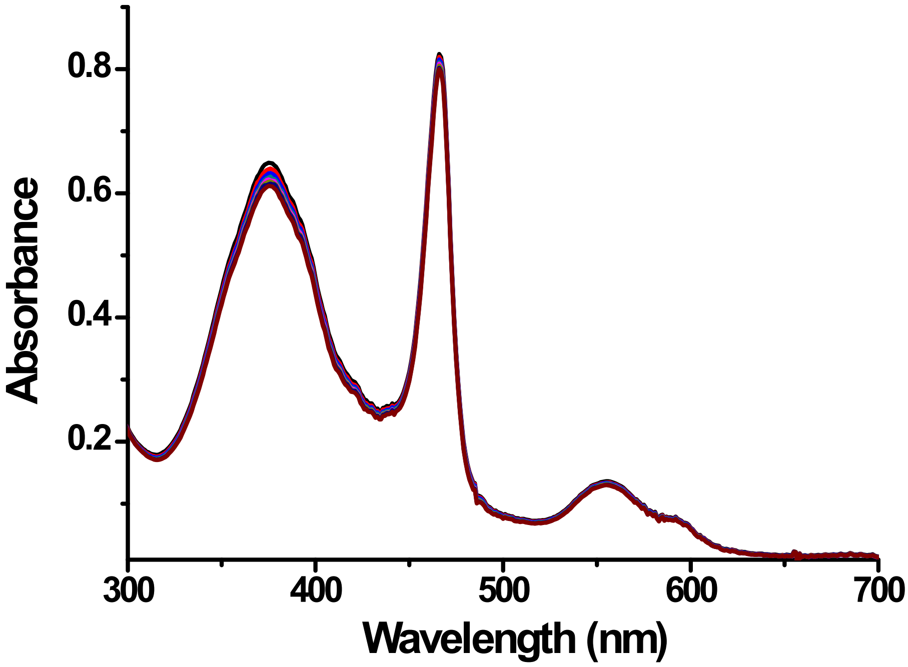


Figure S3 Kinetic studies of 30 μM L29H Mn^{III}Mb reacted with 200 equiv $KHSO_5$ in PBS buffer (pH=7.4).

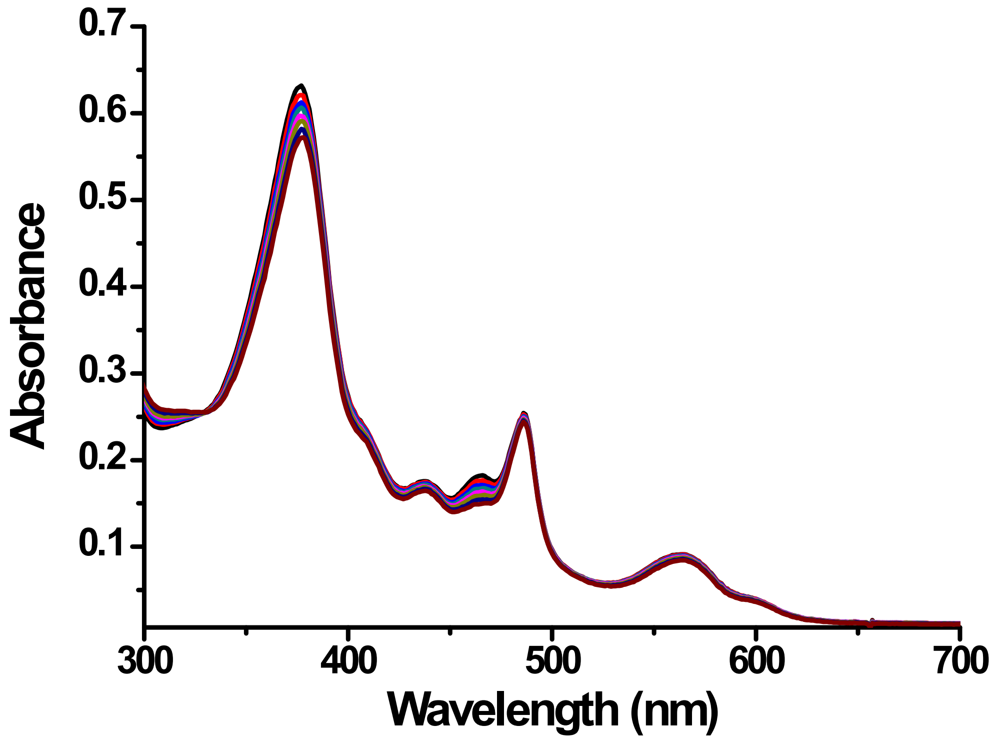


Figure S4 Kinetic studies of 30 μM H64F Mn^{III}Mb reacted with 200 equiv $KHSO_5$ in PBS buffer (pH=7.4).

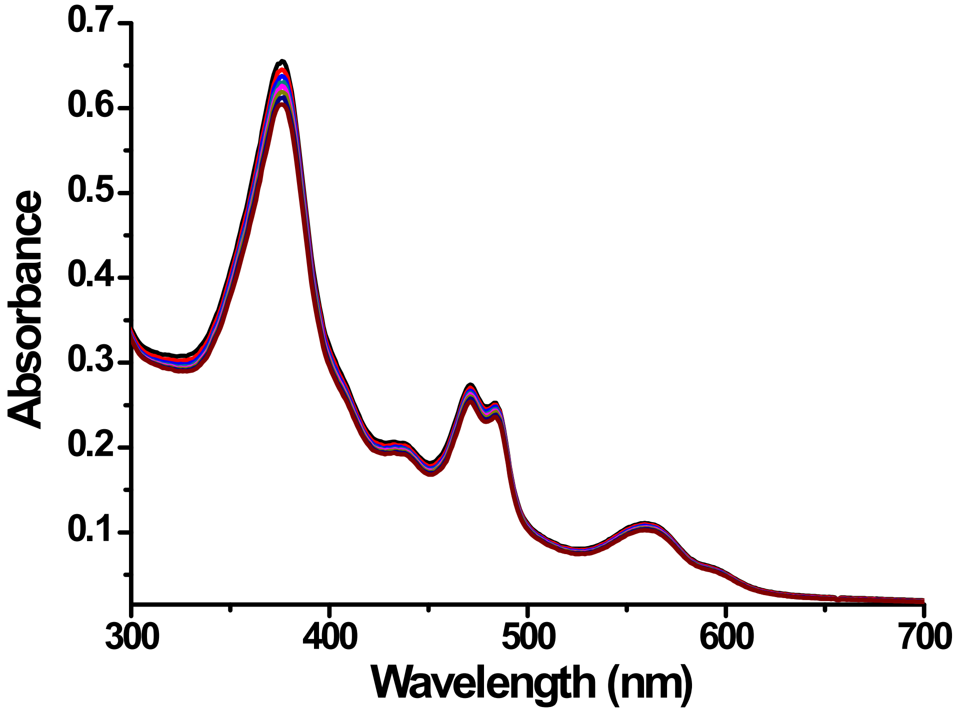


Figure S5 Kinetic studies of 30 μM F43H/H64F $Mn^{III}Mb$ reacted with 200 equiv $KHSO_5$ in PBS buffer (pH=7.4).

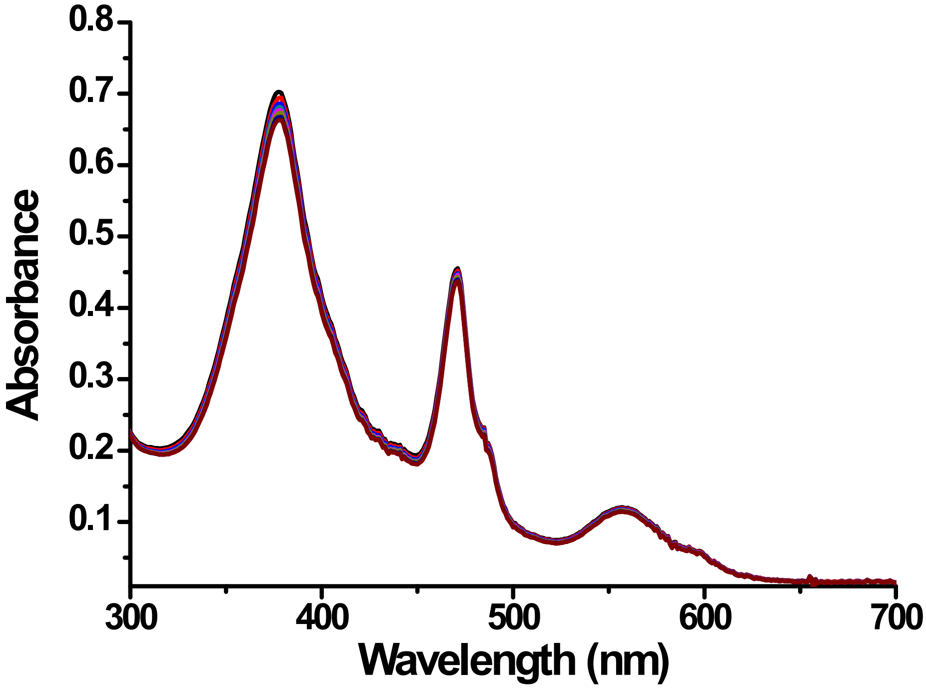


Figure S6 Kinetic studies of 30 μM L29H/H64F Mn^{III}Mb reacted with 200 equiv $KHSO_5$ in PBS buffer (pH=7.4).

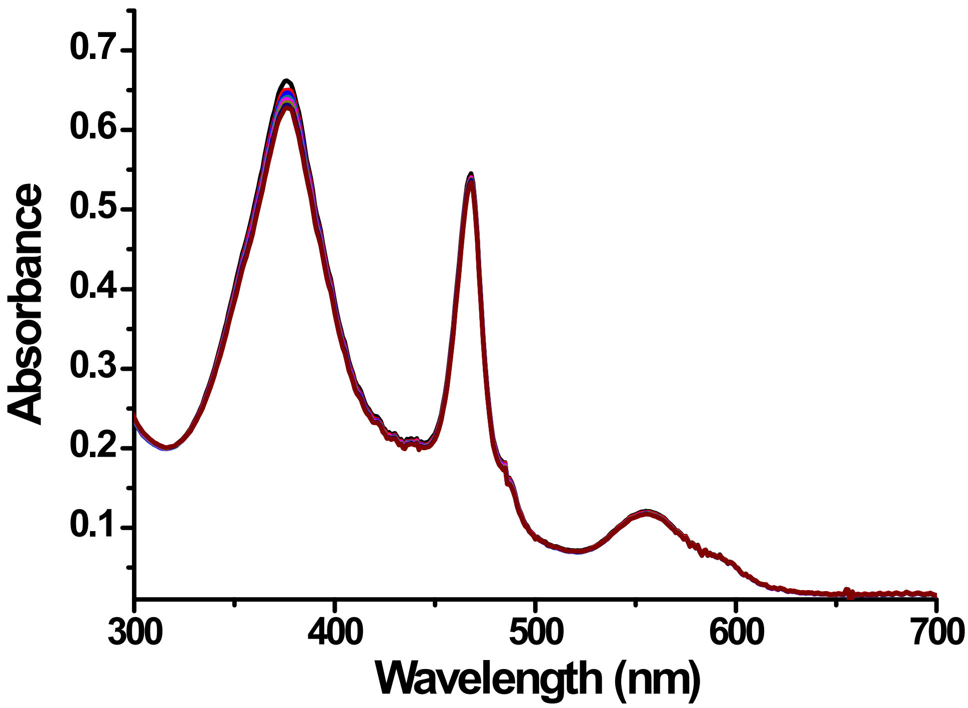
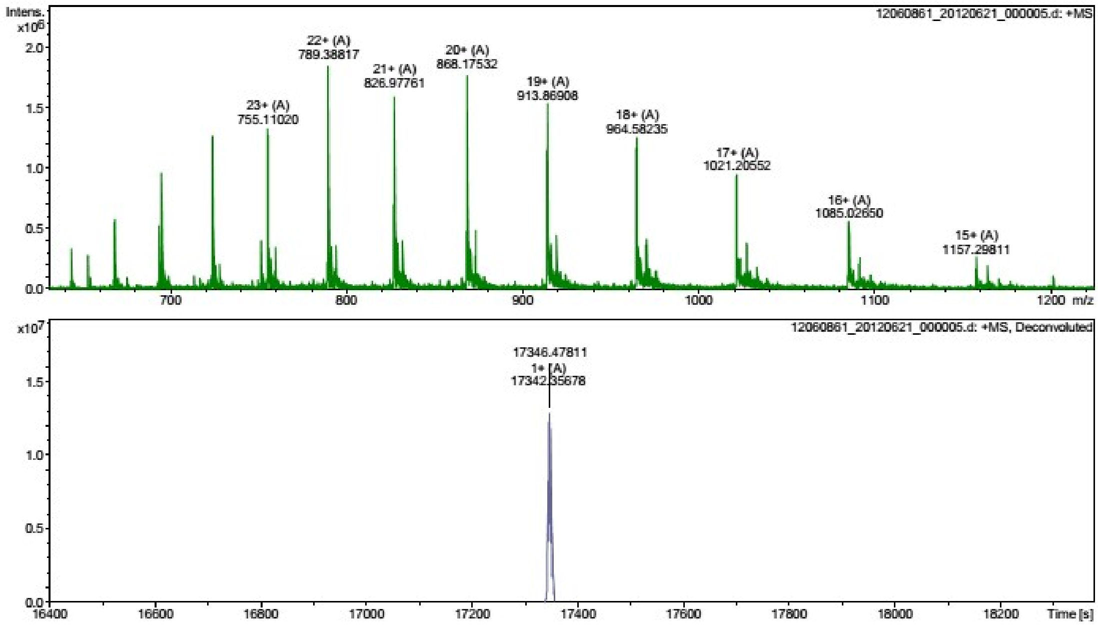
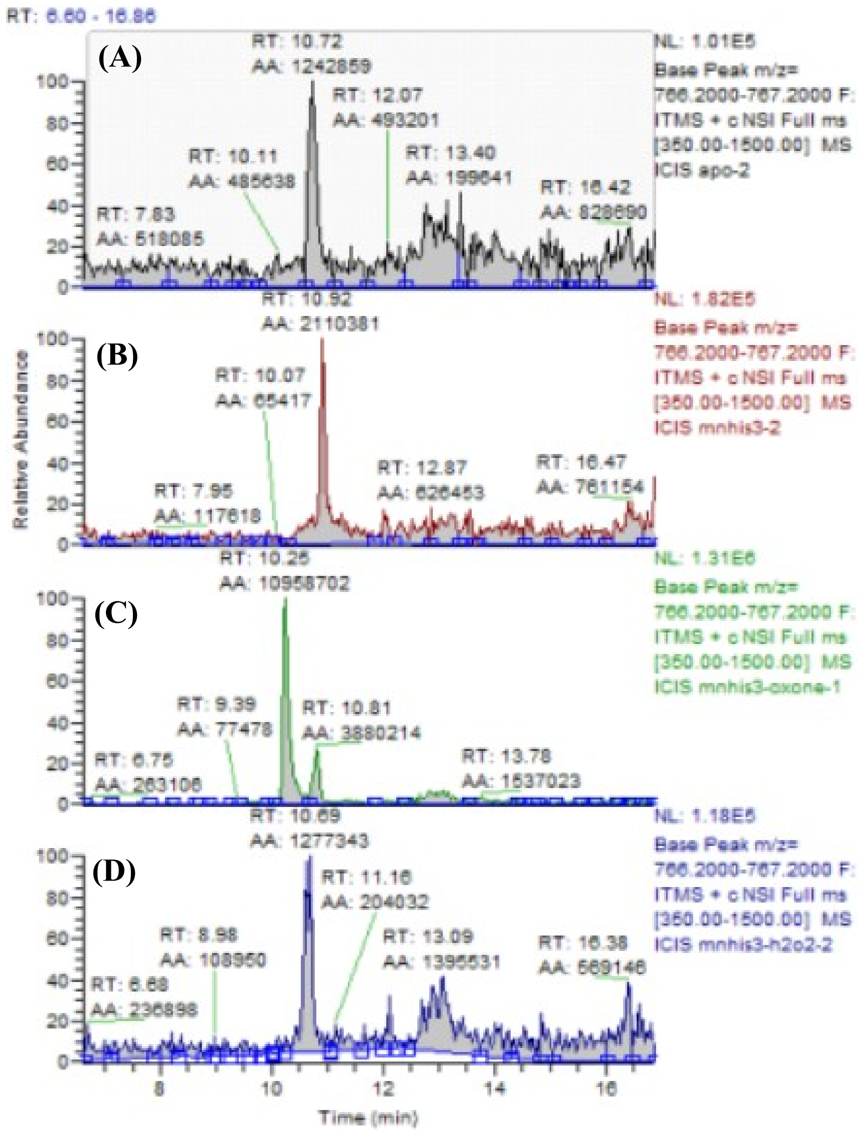


Figure S7 Kinetic studies of 30 μM L29H/F43H/H64F $Mn^{III}Mb$ reacted with 200 equiv $KHSO_5$ in PBS buffer (pH=7.4).

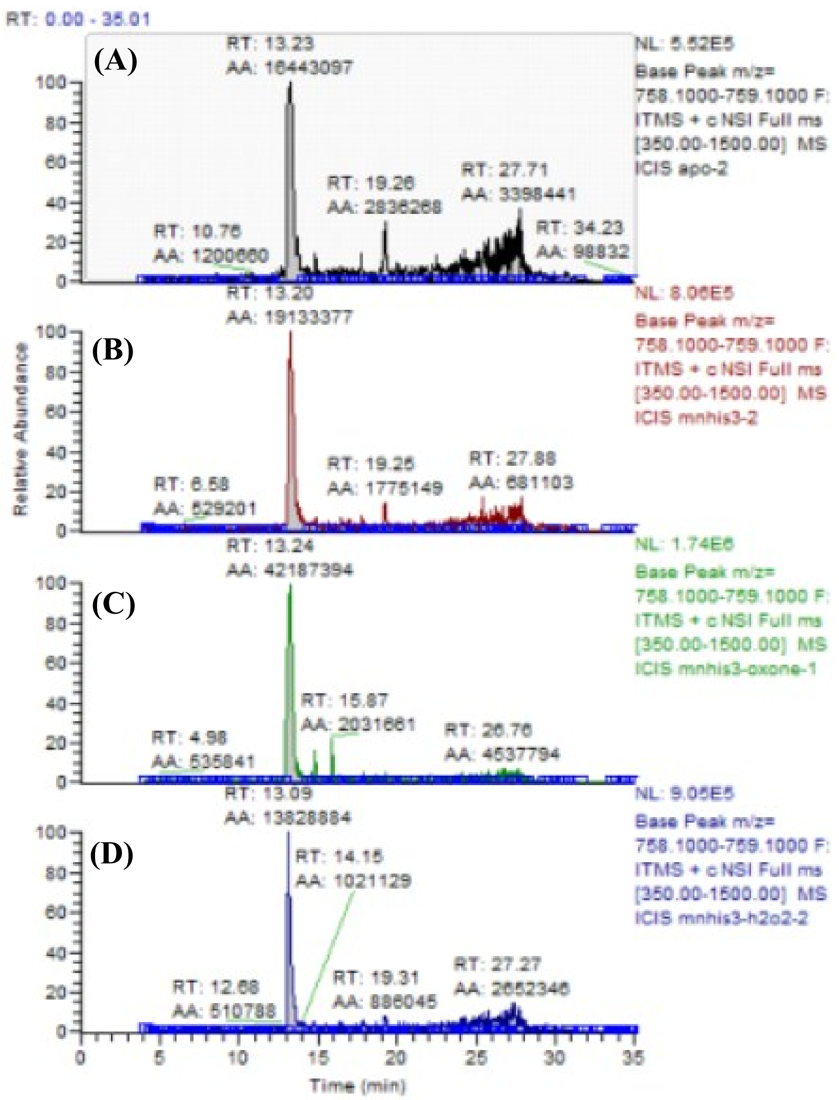


(b)

Figure S8 ESI-MS of apo His3 Mb with 20 equiv $KHSO_5$ after reacting for 3 min.

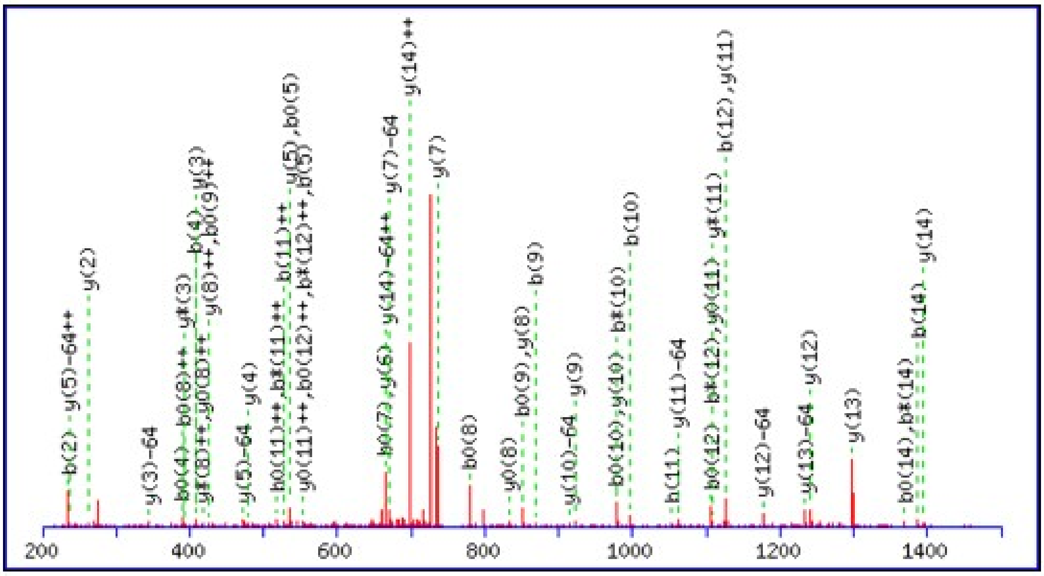

RT: 6.60 - 16.86
(A)
RT: 10.72
AA: 1242859
RT: 12.07
AA: 493201
RT: 10.11
AA: 485638
RT: 13.40
AA: 199641
RT: 16.42
AA: 828690
RT: 7.83
AA: 518085
NL: 1.01E5
Base Peak m/z= 766.2000-767.2000 F: ITMS + c NSI Full ms [350.00-1500.00] MS ICIS apo-2
(B)
RT: 10.92
AA: 2110381
RT: 10.07
AA: 65417
RT: 12.87
AA: 626453
RT: 16.47
AA: 761154
RT: 7.95
AA: 117618
NL: 1.82E5
Base Peak m/z= 766.2000-767.2000 F: ITMS + c NSI Full ms [350.00-1500.00] MS ICIS mnhis3-2
(C)
RT: 10.25
AA: 10958702
RT: 9.39
AA: 77478
RT: 10.81
AA: 3880214
RT: 6.75
AA: 263106
RT: 13.78
AA: 1537023
NL: 1.31E6
Base Peak m/z= 766.2000-767.2000 F: ITMS + c NSI Full ms [350.00-1500.00] MS ICIS mnhis3-oxone-1
(D)
RT: 10.69
AA: 1277343
RT: 11.16
AA: 204032
RT: 8.98
AA: 108950
RT: 13.09
AA: 1395531
RT: 16.38
AA: 569146
RT: 6.68
AA: 236898
NL: 1.18E5
Base Peak m/z= 766.2000-767.2000 F: ITMS + c NSI Full ms [350.00-1500.00] MS ICIS mnhis3-h2o2-2
Relative Abundance
Time (min)

(a)



(b)

Figure S9. Retention times and peak areas of (a) oxidized and (b) unoxidized peptide HPGDFGADAQGAMNK in LC/MS. In each graph, A-D represent apo-His3 Mb with Oxone®, His3 Mn^{III}Mb without any oxidants, His3 Mn^{III}Mb with Oxone®, and His3 Mn^{III}Mb with H_2O_2, respectively.

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Average mass of neutral peptide Mr(calc): 1531.6057
Variable modifications:
M13    : Oxidation (M), with neutral losses 0.0000(shown in table), 64.1069
Ions Score: 112  Expect: 6.3e-012
Matches : 57/204 fragment ions using 74 most intense peaks   (help)
```

#	b	b++	b*	b*++	b0	b0++	Seq.	y	y++	y*	y*++	y0	y0++	#
1	138.1467	69.5770					H							15
2	**235.2619**	118.1346					P	***1395.4738***	698.2406	1378.4433	689.7253	1377.4585	689.2329	14
3	292.3132	146.6603					G	***1298.3586***	649.6830	1281.3281	641.1677	1280.3433	640.6753	13
4	**407.4006**	204.2040			389.3853	195.1964	D	***1241.3073***	621.1573	1224.2768	612.6421	1223.2920	612.1497	12
5	**554.5745**	277.7909			536.5592	268.7833	F	***1126.2199***	563.6136	1109.1894	555.0984	1108.2046	554.6060	11
6	611.6258	306.3166			593.6105	297.3090	G	***979.0460***	490.0267	962.0155	481.5114	961.0307	481.0190	10
7	682.7037	341.8555			664.6884	332.8479	A	***921.9947***	461.5010	904.9642	452.9858	903.9794	452.4934	9
8	797.7911	399.3992			779.7758	390.3916	D	***850.9168***	425.9621	833.8863	417.4468	832.9015	416.9544	8
9	**868.8690**	434.9382			850.8537	425.9306	A	***735.8294***	368.4184	718.7989	359.9031			7
10	**996.9982**	499.0028	979.9677	490.4875	978.9829	489.9952	Q	***664.7515***	332.8794	647.7210	324.3642			6
11	**1054.0495**	527.5284	1037.0190	519.0132	1036.0342	518.5208	G	***536.6223***	268.8148	519.5918	260.2996			5
12	**1125.1274**	563.0674	1108.0969	554.5521	1107.1121	554.0598	A	***479.5710***	240.2892	462.5405	231.7739			4
13	1272.3229	636.6651	1255.2924	628.1499	1254.3076	627.6575	M	***408.4931***	204.7502	391.4626	196.2350			3
14	**1386.4255**	693.7164	1369.3950	685.2012	1368.4102	684.7088	N	***261.2976***	131.1525	244.2671	122.6372			2
15							K	147.1950	74.1012	130.1645	65.5859			1

Figure S10. Fragmentation patterns of peptide from HPGDFGADAQGAM(Ox)NK the digestion of His3 Mn^{III}Mb reacted with $KHSO_5$.

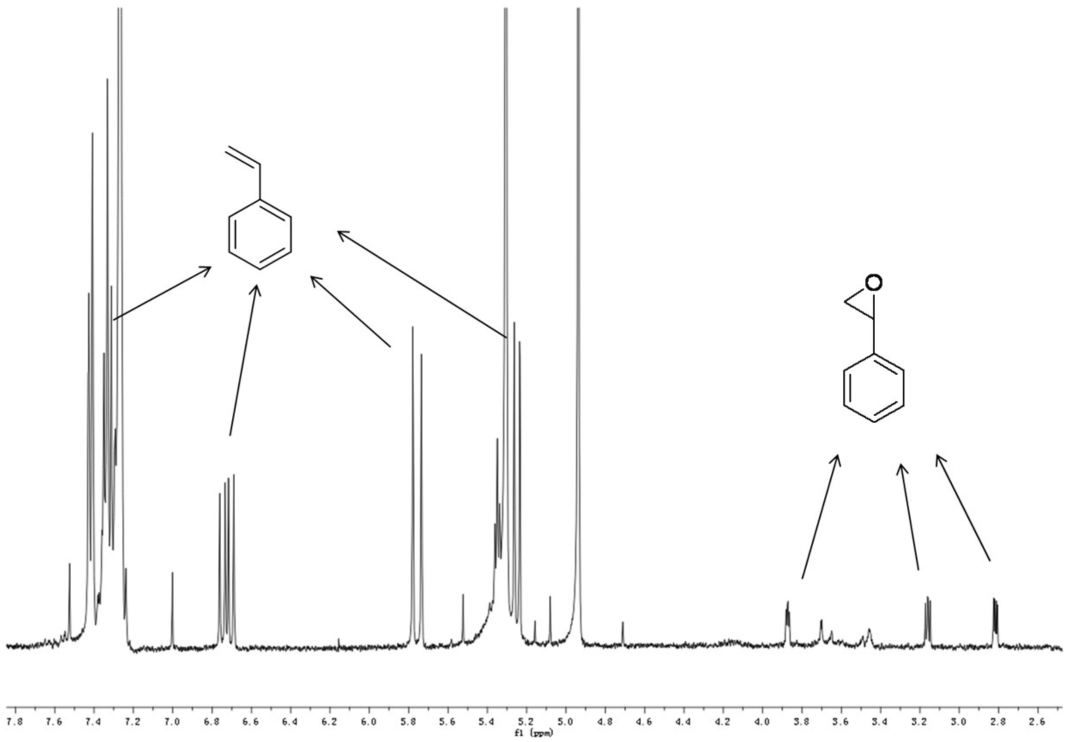

Figure S11. ^{1}H NMR after the reaction of styrene and Oxone® catalyzed by His3 $Mn^{III}Mb$.

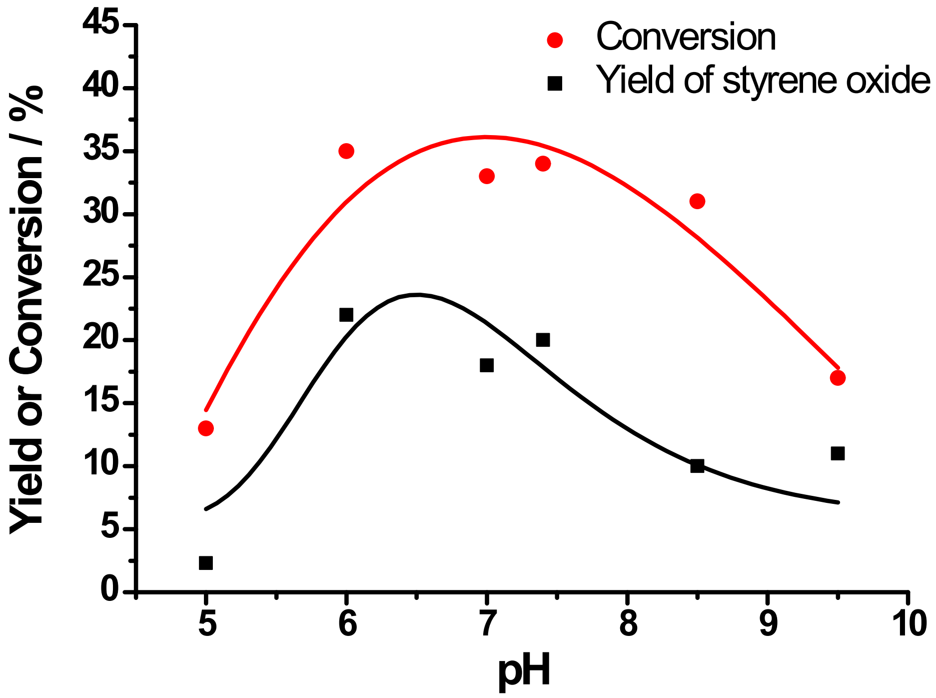

Figure S12. Conversion of epoxidation (red) and yield of styrene oxide (black) at different pHs. Conversion was calculated by 1-(unreacted styrene/total added styrene). Yield was based on styrene oxide generated/total added styrene.