PATHWAYS IN PERMANGANATE OXIDATION OF MANDELIC ACID: REACTIVITY AND SELECTIVITY OF INTERMEDIATE MANGANESE SPECIES.

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Supplementary Information

Mass Spectra of α-Deuteromandelic Acid(Mol. Wt. 153) at an
Electron Beam Energy of 8.2 eV.[a]

| m/e 152 | 153 | 154 |
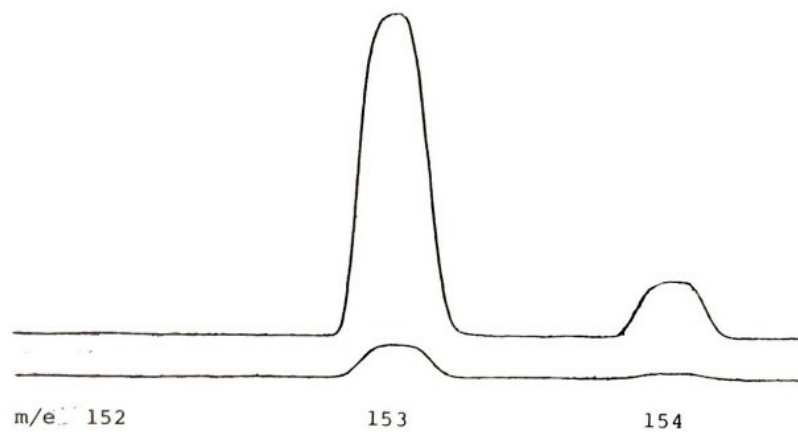
[a]Size of spectrum reproduced here has been reduced to
approximately 4/9 of the original.

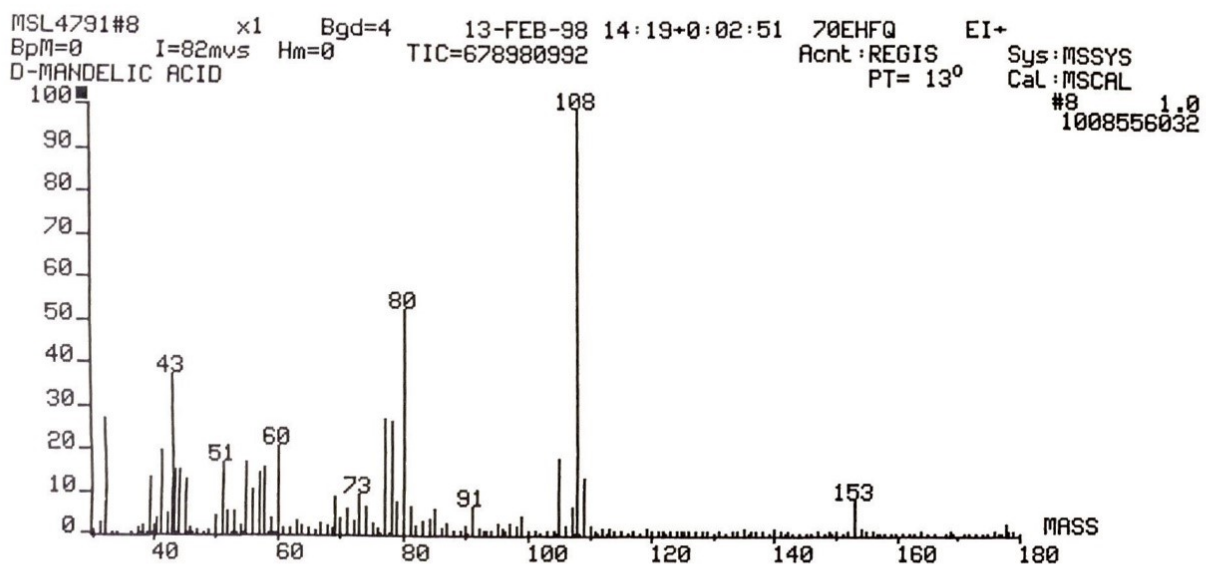**Figure S1. Mass spectra of α-deuteromandelic acid**

Figure S2. Mass Spectrum of **α-deuteromandelic acid**

Molecular ion, m/z = 153, base peak m/z = 108. The deuterium content was determined by mass spectrometry to be ≥98 % and by NMR

α-Deutero-mandelic acid

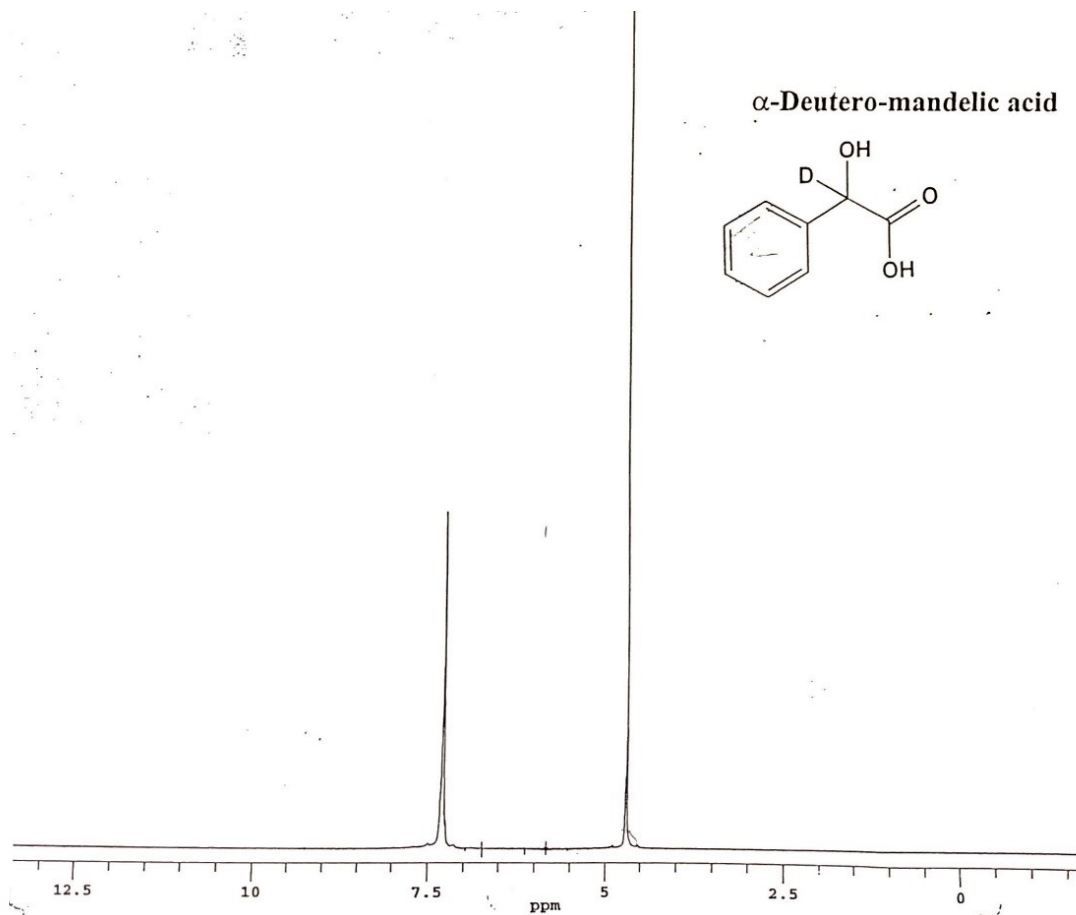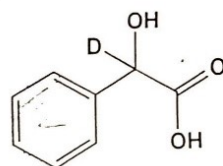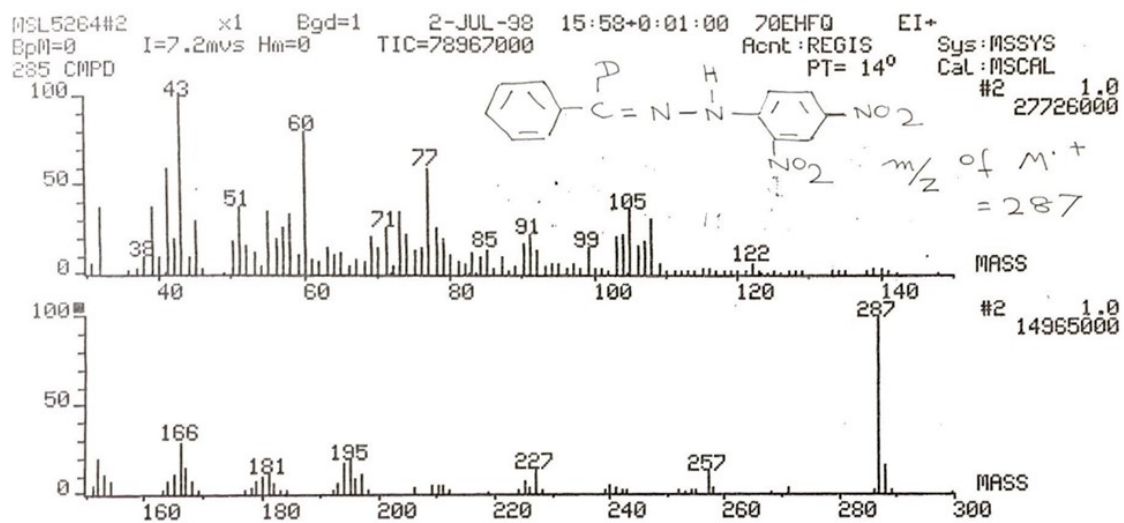**Figure S3.** ¹H-NMR of α-deutero-mandelic acid in D₂O. Peak at 4.6 is due to HOD

Figure S4A. EI-MS of 2,4-dinitrophenylhydrozone derivative of benzaldehyde

Average of 2.000 to 14.000 min.: SNM-35.D

Average of 2.000 to 14.000 min.: SNM-35.D
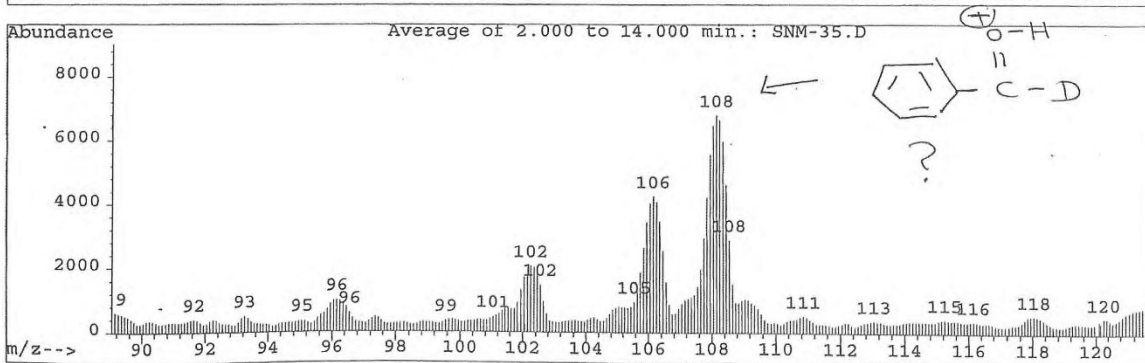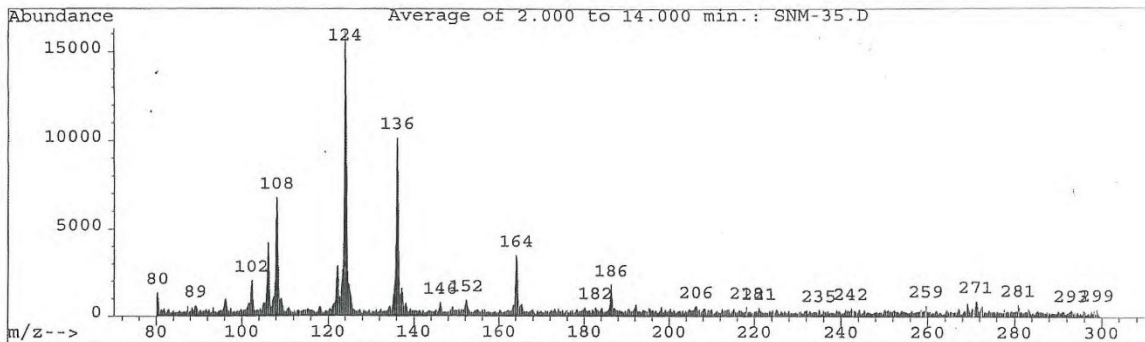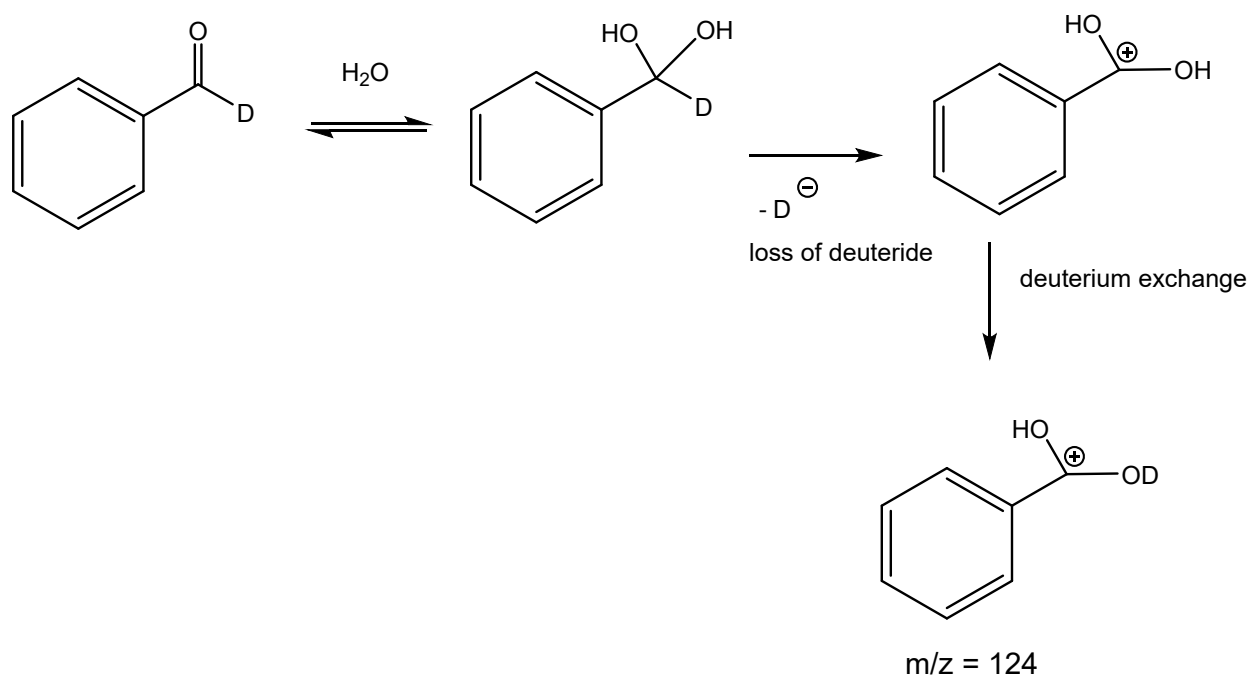
Figure S4B. (Top) ESI-MS of Benzaldehyde-D. (Bottom) Proposed ion at m/z = 124.

Linear: y = 3.452e+06*x + 185.7
R^2 = 0.9972
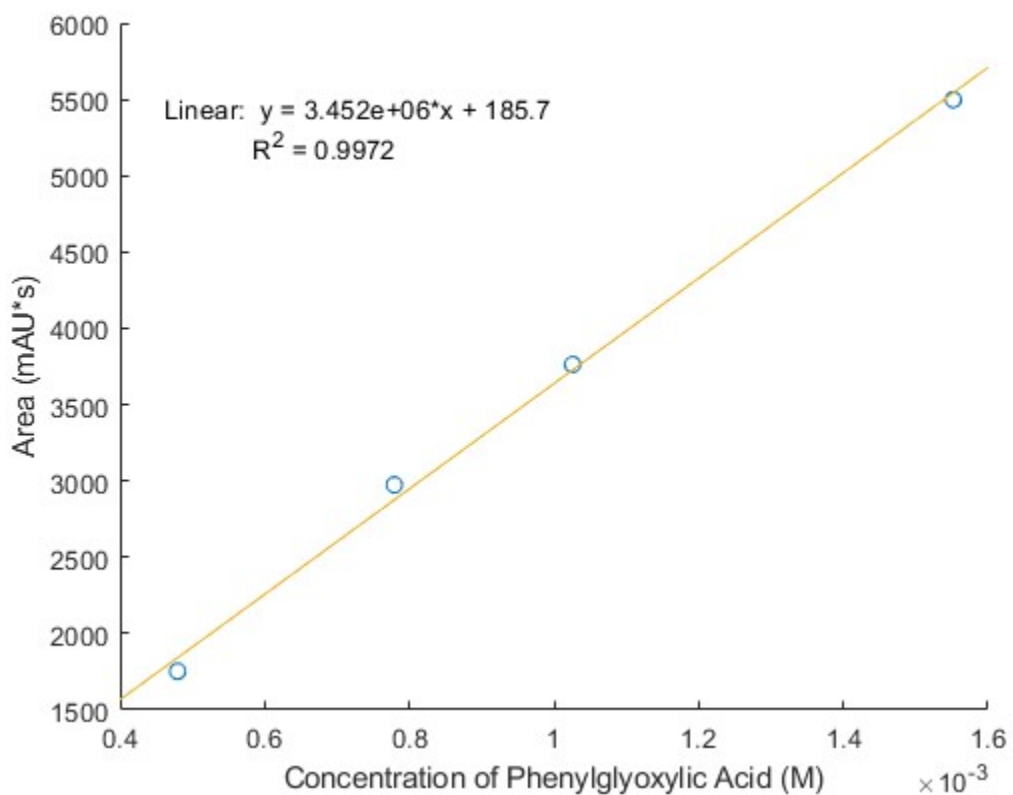
Figure S5. Standard curve for phenylglyoxylic acid (PGA). 264 nm detection.

Linear: $y = 3.382e{+}06{*}x + 165.2$
$R^2 = 0.9999$

Figure S6. Standard curve for benzaldehyde (BZ). 254 nm detection

Figure S7. Standard curve for benzoic acid (BA). 254 nm detection.

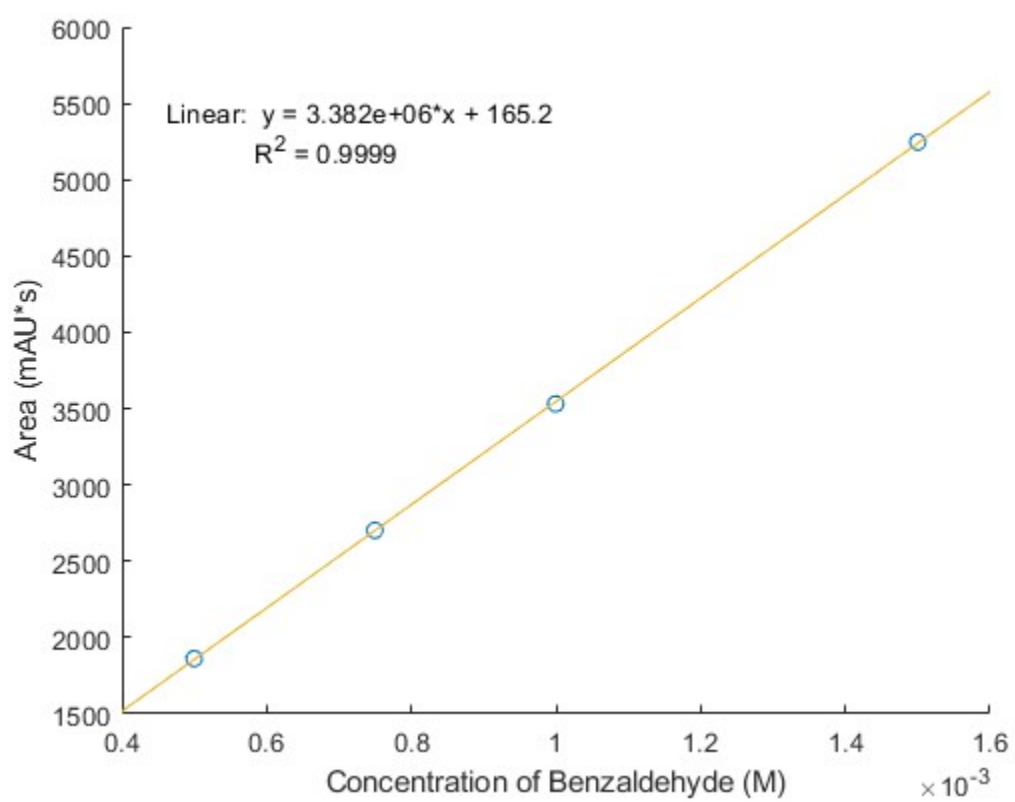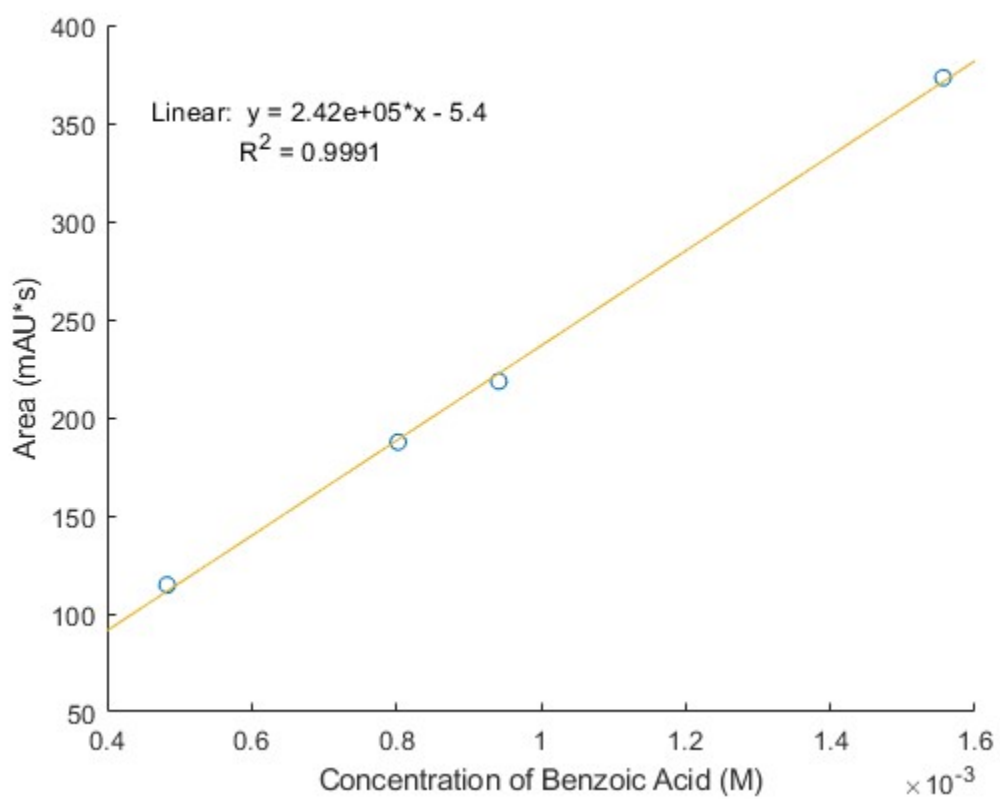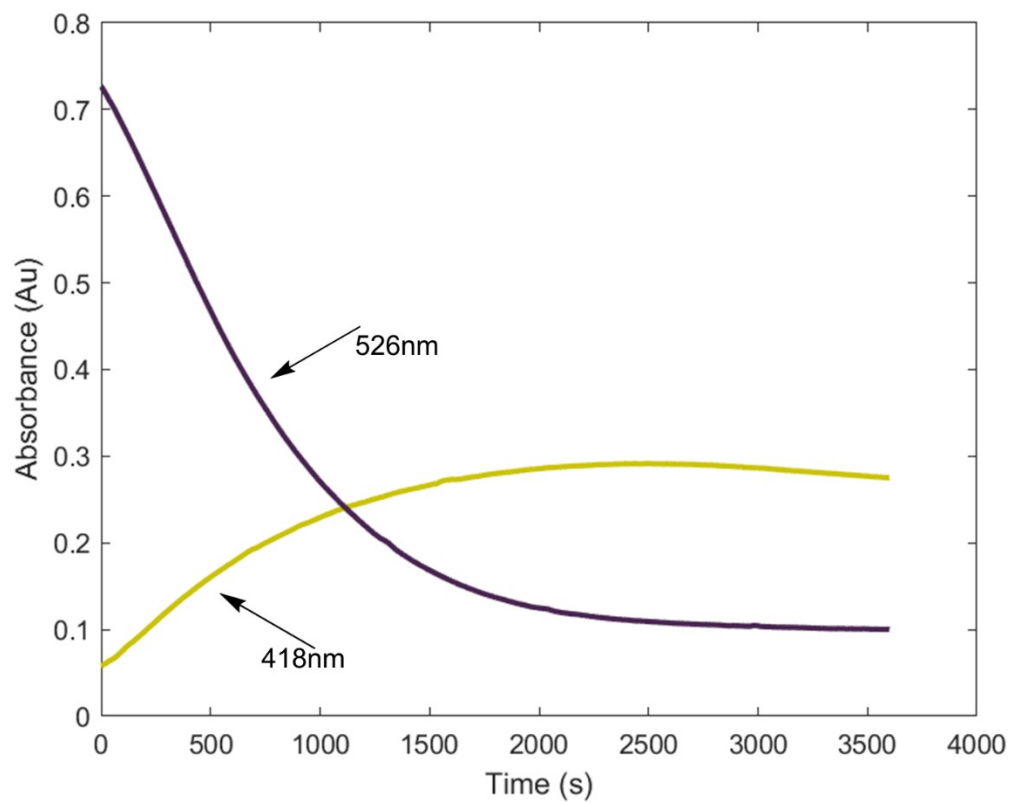**Figure S8**. The growth of a soluble Mn(IV) species is observed at neutral pH in the oxidation of mandelic acid by permanganate. Conditions: mandelate = 0.05 M, MnO_4^- = 3.0×10^{-4} M, pH = 7 (0.1 M phosphate buffer)

Figure S9. Determination of oxidation of the intermediate manganese species by Iodometric titrations Oxidation of mandelic acid by permanganate. Conditions: mandelate = 0.05 M, MnO_4^- = 1.0×10^{-3} M, pH = 13; 22 °C.

Thiosulfate = 1 mM. Total reaction volume 50 ml. Five mL aliquots were quenched with NaI in acidic medium and titrated with 1 mM thiosulfate

Initial titer at zero-time = 25 mL

Assuming that the intermediate stabilized at Mn(VI) the final titer should be ≈20 mL.
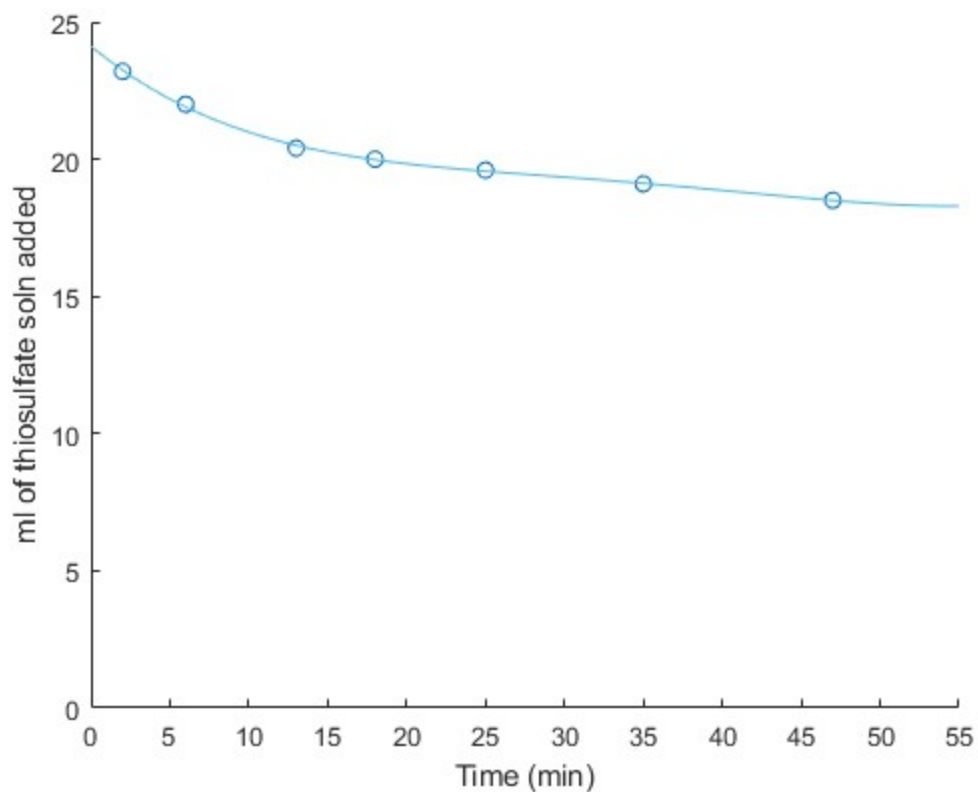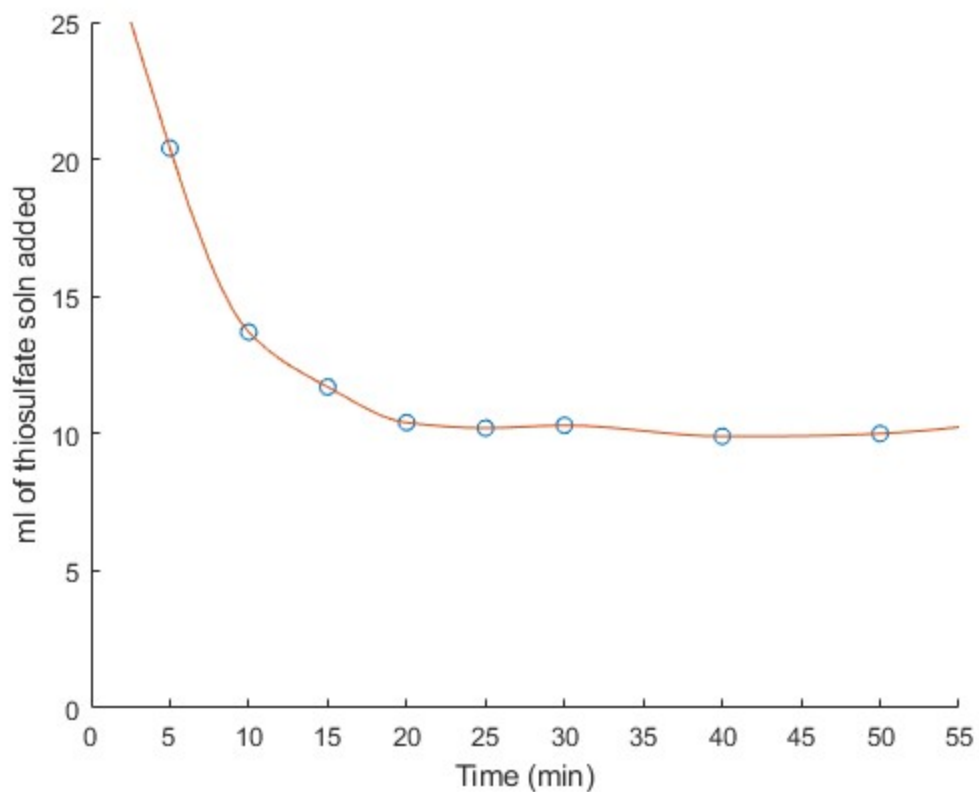
Figure S10. Determination of oxidation of the intermediate manganese species by Iodometric titrations in the oxidation of mandelic acid by permanganate. Conditions: mandelate = 0.05 M, MnO_4^- = 1.0 x10^{-3} M, pH = 7 (0.1 M phosphate buffer); 22 ^{o}C.

Thiosulfate = 1 mM

Assuming that the intermediate stabilized at Mn(IV) the titer should be ≈10 mL.
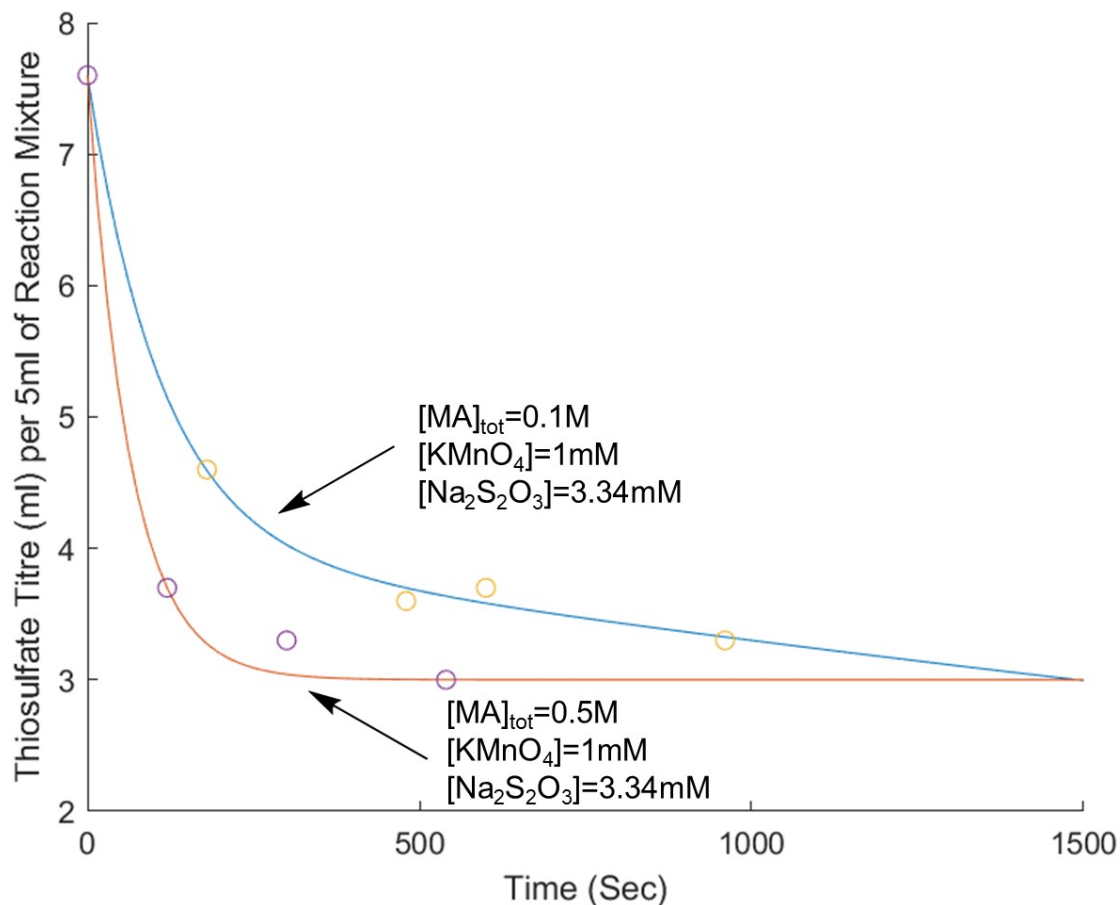
Figure S11. Determination of oxidation of the intermediate manganese species by Iodometric titrations (pH 4.2)

Calculations for the iodometry titrations (determination of oxidation state).

Dissolved 0.4206 g of sodium thiosulfate pentahydrate (molar mass = 248.18 g/mol) in 500 mL of water giving a concentration of thiosulfate of 3.4×10^{-3} M (3.4 mM).

Thiosulfate titer for initial permanganate solution at zero time (no reaction)

0.005 L x 0.001 M Permanganate x (2.5 I_2/permanganate) x (2 Thiosulfate/I_2) (L/0.003389mol) = 7.4 mL of thiosulfate.

If the intermediate stabilizes as Mn(IV)

0.005 L x 0.001 permanganate x (Mn(IV)/permanganate) x (I_2/Mn(IV) x (2 thiosulfate/I_2) X L/0.003389 mol thiosulfate = 3 mL of thiosulfate.

If the intermediate stabilizes as Mn(III)

0.005 L x 0.001 permanganate x (Mn(III)/permanganate) x (I_2/ 2Mn(III) x (2 thiosulfate/I_2) X L/0.003389 mol thiosulfate = 1.47ml of thiosulfate.

the iodometric titration data for two concentrations of mandelic acid/mandelate anion (0.1 M and 0.5 M), the thiosulfate titer stabilized around 3-3.2 mL.
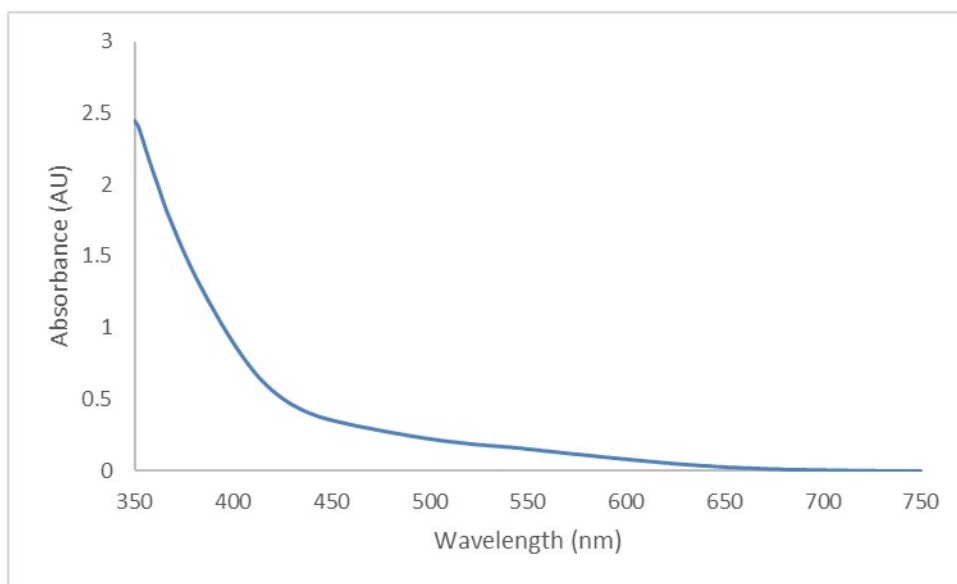
Figure S12. shows the final spectra the manganese species at the end of successive sans in Figure 3. Conditions same as in Figure 3.
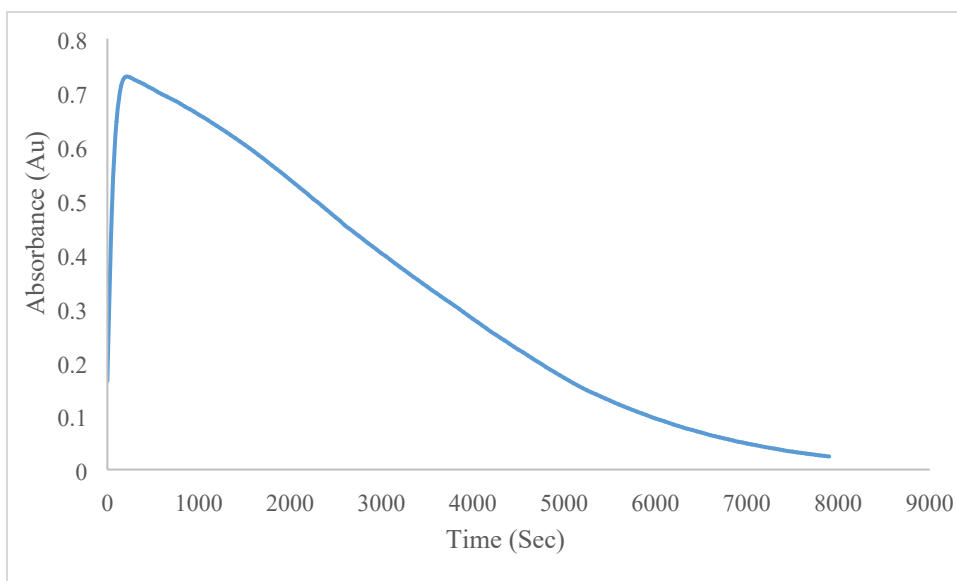
Figure S13. Decay of 418 nm intermediate. Conditions same as in Figure 3

Linear: y = - 2.701*x + 0.894
$R^2 = 0.9993$
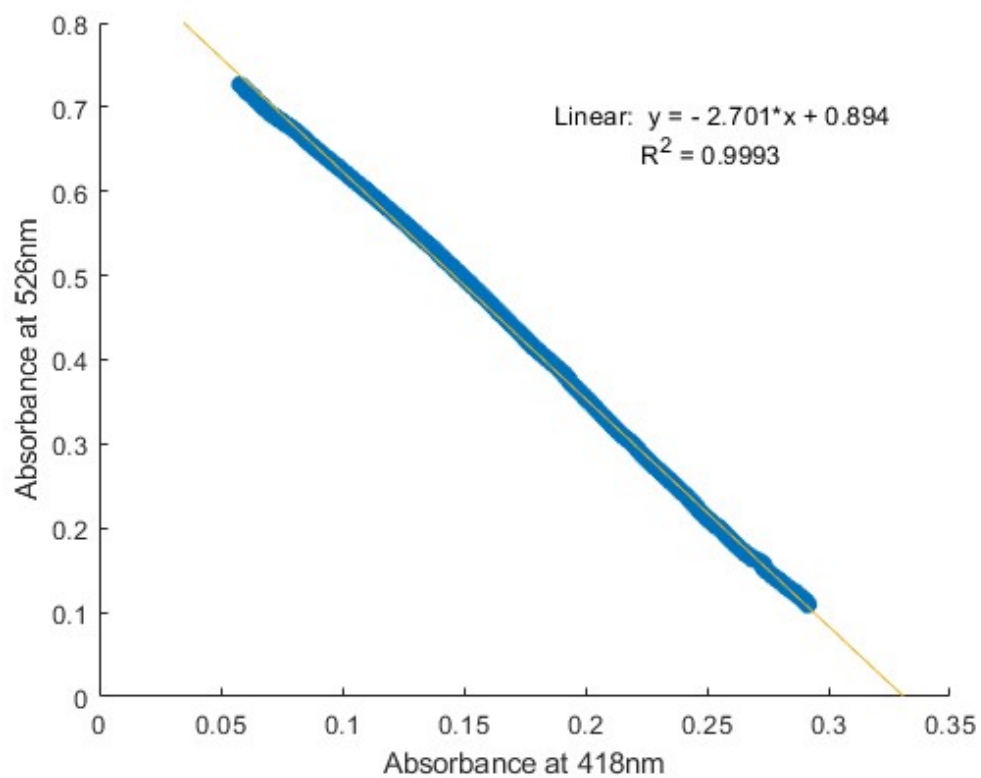
Figure S14. Plot of A_{526nm} versus A_{418nm}. Soluble (colloidal) manganese(IV) intermediate; the end-product of oxidation at neutral pH (phosphate buffer, pH 6.8-7.40).

Linear: $y = -1.509 \cdot x + 0.825$
$R^2 = 0.9992$
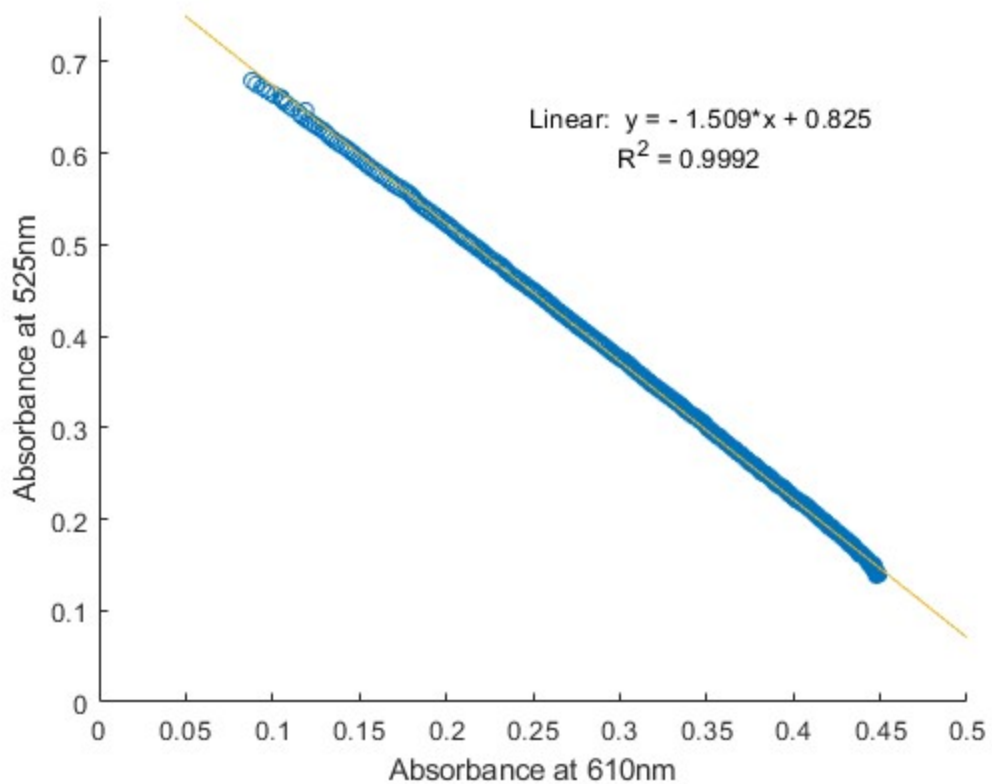
Figure S15. The plot of log A_{526nm} versus A_{606nm} is linear ($R^2 = 0.999$). Conditions same as in Figure 5.

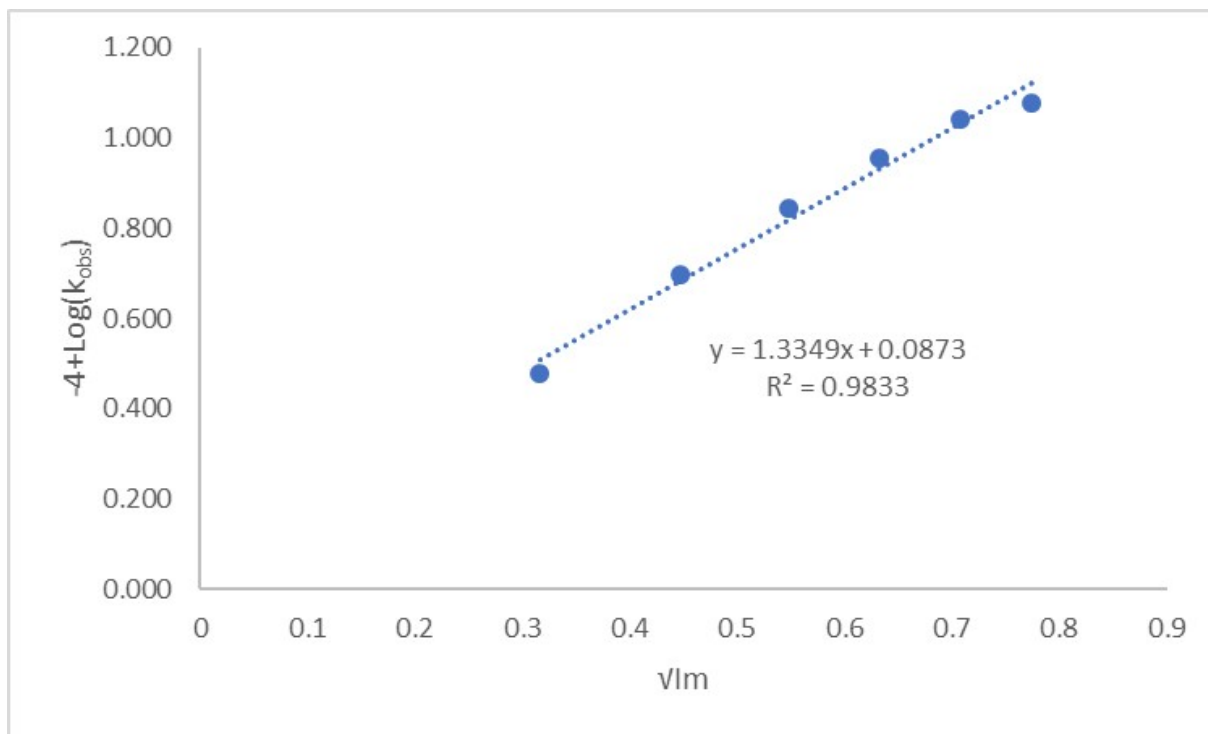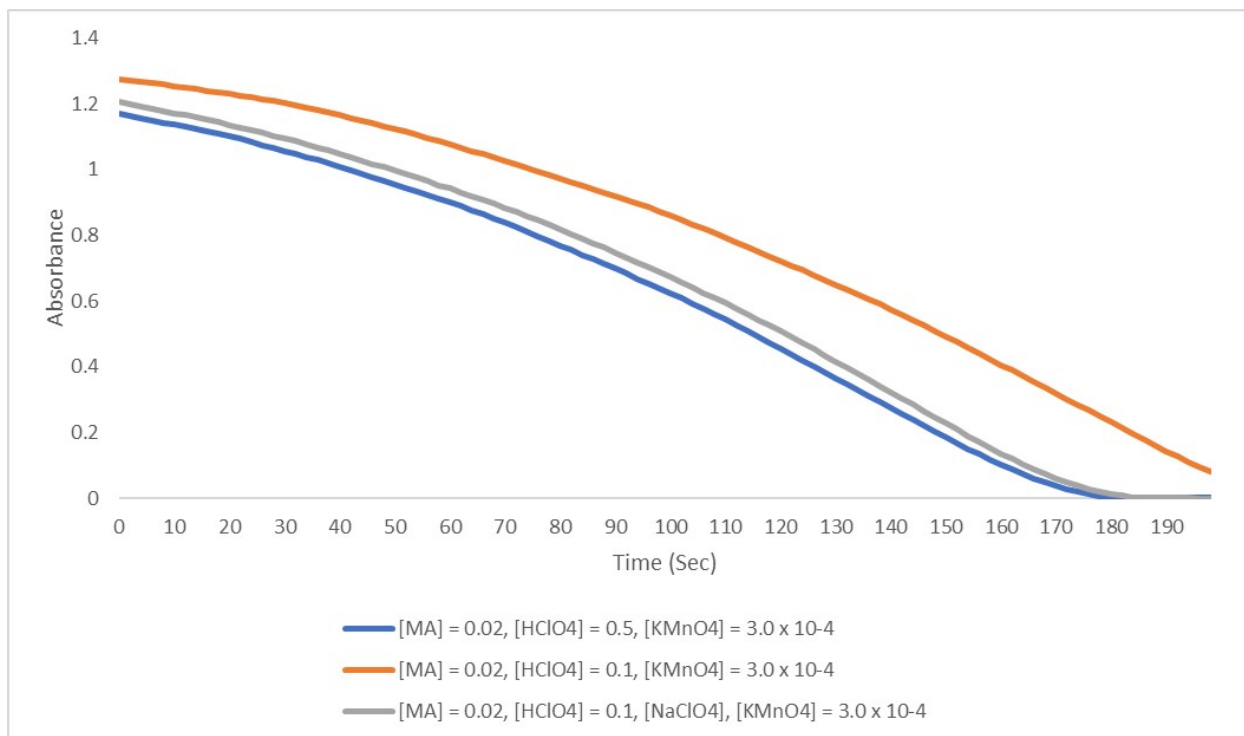**Figure S16.** Effect of ionic strength (I) in the permanganate oxidation of mandelic acid[a]

Figure S17.Oxidation of mandelic acid in acid medium. Reaction followed at 526nm 22.5±0.5°C
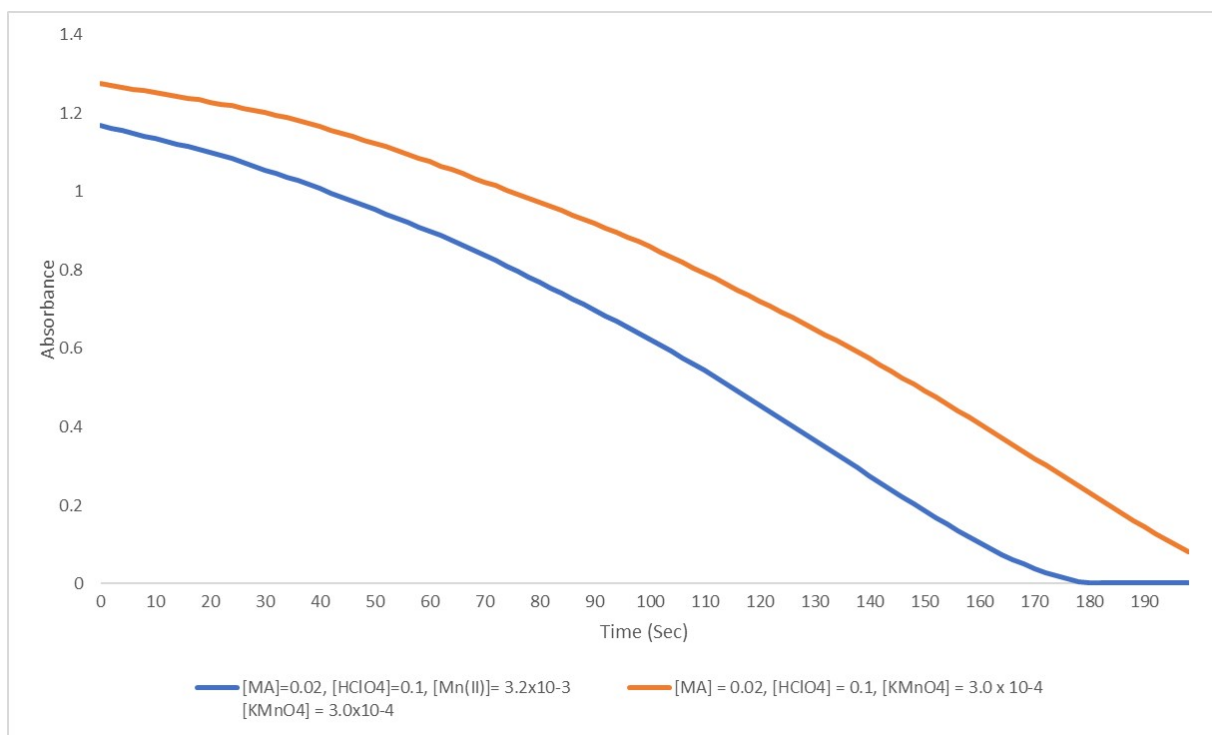
Figure S18. Effect of added Mn(II) on the oxidation of mandelic acid in acid medium . Reaction followed at 526nm 22.5±0.5°C

Table S1. Dependence on mandelate anion in the oxidation of mandelic acid by permanganate

[MA], M	$10^4 k_1$, sec^{-1} (525 nm)	$10^4 k_1$, sec^{-1} (616 nm)	k_2 (M^{-1}sec^{-1})
0.005	3.0	4.1	0.071
0.02	10.1	12.1	0.055
0.05	27.2	33	0.060
0.10	62	74	0.068

pH= 13, [MnO$_4^-$] = 3 x 10^{-4} M, 25 °C; in replicate measurements rate constants are reproducible to ± 7%

Table S2. Effect of ionic strength (I) in the permanganate oxidation of mandelic acid[a]

[OH$^-$], M	[LiClO$_4$], M	Ionic strength	$10^4 k$ s^{-1} (525 nm)
0.10		0.1	3.0
0.10	0.10	0.2	5.0
0.10	0.20	0.3	7.0
0.10	0.30	0.4	9.0
0.10	0.40	0.5	11
0.10	0.50	0.6	12
0.20	0.20	0.4	12
0.20		0.2	6.0
0.40		0.4	12
0.10	0.90	1.0	18
0.20	0.80	1.0	39
0.30	0.70	1.0	75

[a]Conditions: [MA] = 0.005 M, [MnO$_4^-$] = 3.0 x 10^{-4} M, T = 25 ^{o}C

Table S3. Effect of ionic strength (I) in the permanganate oxidation of mandelic acid[a]

Effect of Ionic Strength					
OH	LiClO$_4$	I_m	10^4 k_{obs} S^{-1}	$\sqrt{I_m}$	-4+Log(k_{obs})
0.1	0	0.1	3.0±0.2	0.316	0.477
0.1	0.1	0.2	5.0±0.4	0.447	0.699
0.1	0.2	0.3	7.0±0.5	0.548	0.845
0.1	0.3	0.4	9.0±0.6	0.632	0.954
0.1	0.4	0.5	11.0±0.8	0.707	1.041
0.1	0.5	0.6	12.0±0.8	0.775	1.079