Supplementary

Manganese Catalyzed Epoxidations of Alkenes in Bicarbonate Solutions

Benjamin S. Lane, Matthew Vogt, Victoria J. DeRose, and Kevin Burgess*

Contribution from Department of Chemistry, Texas A & M University, PO Box 30012, College Station, TX 77842-3012

Figure S1. Spectra for the saturation transfer experiments.

Figure S2. Control spectra for the EPR experiments.

Figure S3. Parallel mode EPR spectra.

Figure S4. Overlay of $g = 2$ region.

Figure S5. Initial screens of additives in ^tBuOH.

Figure S6. Initial screens of additives in DMF.

Table S1a-b. Screening results for the optimization of the additive loading in both ^tBuOH (a) and DMF (b).

Experimental Section

Figure S1. Bicarbonate/peroxydicarbonate saturation transfer experiments. All experiments were performed with a Varian 500 MHz NMR utilizing standard ^{13}C parameters with the addition of a presaturation pulse sequence during the appropriate experiment. The solvents $\text{D}_2\text{O}:\text{tBuOH}$ (1 : 2) were utilized in all cases. a. $\text{NaH}^{13}\text{CO}_3$. b. $\text{NaH}^{13}\text{CO}_3 : \text{H}_2\text{O}_2$ (1 : 10) c. $\text{NaH}^{13}\text{CO}_3 : \text{H}_2\text{O}_2$ (1 : 10) with a presaturation pulse set to the peroxydicarbonate peak (158.8 ppm). d. $\text{NaH}^{13}\text{CO}_3 : \text{H}_2\text{O}_2$ (1 : 10) with a presaturation pulse set to the bicarbonate peak (160.4 ppm).

Figure S2. EPR spectra of MnSO_4 in control experiments. Each sample contains 0.2 mM MnSO_4 and (a) H_2O , (b) 100 mM bicarbonate in 1:2 $t\text{-BuOH}:\text{H}_2\text{O}$; (c) solution in (b) plus 20 mM 4-vinylbenzoic acid; (d) solution in (b) plus 10 equivalents H_2O_2 . EPR spectra obtained at a microwave frequency of 9.4 GHz, 2 mW power, 7K.

Figure S3. Parallel-mode EPR spectra of (a) 1 mM Mn(III) (salen); (b) 0.5 mM Mn(III) (OAc)₃; (c) and (d) Reaction mixtures (see Figure 5) at 1 and 60 min; (e) blank cavity. EPR obtained at 9.4 GHz, 1 mW microwave power, 7K, 10 G MA, in a Bruker ER 4116 DM cavity operating with $B_{\text{ext}} \parallel B_{\text{microwave}}$.

Figure S4. Overlay of $g = 2$ region. EPR spectra of the reaction mixture prior to addition of H_2O_2 (top two) and at times following addition. Conditions: 0.2 mM MnSO_4 , 20 mM 4-vinylbenzoic acid, 100 mM carbonate in 1:2 $\text{tBuOH}:\text{H}_2\text{O}$, 30 eq H_2O_2 . EPR spectra: 9.4 GHz, 7K, 2mW microwave power.

Figure S5. Initial screens of additives in ^tBuOH. Additives that: **a** enhanced the epoxide yield in the initial screen; and **b** decreased it. Relative yields are in terms of the process without additive that gave 85 % of the epoxide when 6 eq of hydrogen peroxide were used. All yields were measured by HPLC relative to benzoic acid as an internal standard.

a

b

Figure S6. Initial screens of additives in DMF that: **a** enhanced epoxide yield in the initial screen; and **b** decreased it. Yields relative yields to the process without additive that gave 50 % of the epoxide when 6 eq of hydrogen peroxide were used.

a

b

Table S1a-b. Screening results for the optimization of the additive loading in both ^tBuOH (a) and DMF (b). The values shown are the average and standard deviation over three trials.

(a) Screens in ^tBuOH

3,5-dibromobenzoic acid				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
1a1	0.1	44.1	4.9	-2.5
1b1	0.5	61.2	3.2	14.5
1c1	1.0	66.9	0.9	20.3
1d1	2.0	67.8	1.8	21.1
1e1	4.0	68.7	2.0	22.1
1f1	6.0	66.0	5.2	19.4
1g1	10.0	63.3	1.3	16.7
1h1	30.0	62.6	1.1	15.9
4-nitrobenzoic acid				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
2a1	0.1	53.8	0.4	7.2
2b1	0.5	57.6	2.3	11.0
2c1	1.0	60.2	1.5	13.5
2d1	2.0	62.3	2.4	15.7
2e1	4.0	60.5	0.4	13.8
2f1	6.0	58.9	3.3	12.2
2g1	10.0	59.1	0.9	12.5
2h1	30.0	58.0	2.7	11.4
adipic acid				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
3a1	0.1	54.5	1.9	7.8
3b1	0.5	58.7	0.8	12.0
3c1	1.0	62.4	2.3	15.7
3d1	2.0	60.2	2.1	13.6
3e1	4.0	55.9	0.3	9.3
3f1	6.0	54.1	4.2	7.5
3g1	10.0	47.3	2.7	0.7
3h1	30.0	39.2	0.6	-7.4
3,5-dinitrobenzoic acid				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
4a1	0.1	50.7	4.8	4.1
4b1	0.5	54.0	3.0	7.4
4c1	1.0	60.3	3.5	13.7
4d1	2.0	60.8	3.0	14.2
4e1	4.0	55.9	2.7	9.3
4f1	6.0	58.5	1.8	11.9
4g1	10.0	57.1	1.5	10.4
4h1	30.0	50.3	1.5	3.7

sodium acetate				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
5a1	0.1	55.7	1.3	9.1
5b1	0.5	57.8	1.2	11.2
5c1	1.0	60.3	0.9	13.7
5d1	2.0	61.8	2.0	15.2
5e1	4.0	67.5	2.4	20.9
5f1	6.0	71.2	1.6	24.6
5g1	10.0	67.6	5.8	21.0
5h1	30.0	66.7	4.7	20.0
2,4-dinitrobenzoic acid				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
6a1	0.1	54.9	0.7	8.3
6b1	0.5	55.6	1.7	8.9
6c1	1.0	56.9	4.0	10.3
6d1	2.0	57.7	1.4	11.1
6e1	4.0	63.4	2.7	16.8
6f1	6.0	60.2	2.3	13.6
6g1	10.0	58.9	1.4	12.3
6h1	30.0	51.6	0.4	5.0
4-chloro-3,5-dinitrobenzoic acid				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
7a1	0.1	57.9	1.0	11.2
7b1	0.5	57.0	1.8	10.4
7c1	1.0	59.0	2.7	12.3
7d1	2.0	59.8	4.9	13.2
7e1	4.0	59.0	2.3	12.4
7f1	6.0	57.8	2.1	11.1
7g1	10.0	54.6	0.7	8.0
7h1	30.0	51.8	0.9	5.2
1,1'-binaphthyl-2,2'-hydrogenphosphate				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
8a1	0.1	51.5	3.5	4.9
8b1	0.5	54.8	3.0	8.2
8c1	1.0	58.1	4.0	11.5
8d1	2.0	57.7	2.3	11.1
8e1	4.0	59.4	2.9	12.8
8f1	6.0	55.4	2.1	8.7
8g1	10.0	54.3	2.1	7.7
8h1	30.0	47.6	2.0	1.0

trichloroacetic acid				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
9a1	0.1	52.8	1.5	6.1
9b1	0.5	54.0	2.1	7.4
9c1	1.0	61.5	3.2	14.9
9d1	2.0	71.4	6.7	24.7
9e1	4.0	62.0	4.0	15.3
9f1	6.0	62.8	1.1	16.2
9g1	10.0	61.4	4.3	14.8
9h1	30.0	62.2	5.2	15.6
sodium chloride				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
10a1	0.1	53.6	3.9	7.0
10b1	0.5	55.3	0.6	8.7
10c1	1.0	58.7	2.5	12.1
10d1	2.0	60.1	3.3	13.5
10e1	4.0	58.6	3.2	12.0
10f1	6.0	55.6	4.4	8.9
10g1	10.0	61.2	0.8	14.6
10h1	30.0	58.9	2.3	12.3
benzotriazole				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
11a1	0.1	55.1	3.5	8.5
11b1	0.5	55.8	3.5	9.2
11c1	1.0	62.7	2.3	16.1
11d1	2.0	60.3	5.8	13.7
11e1	4.0	59.5	1.7	12.9
11f1	6.0	59.8	3.9	13.1
11g1	10.0	59.8	0.9	13.1
11h1	30.0	56.7	5.7	10.1
phenylphosphonic acid				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
12a1	0.1	54.6	1.3	8.0
12b1	0.5	54.8	1.2	8.2
12c1	1.0	60.1	6.6	13.4
12d1	2.0	55.8	1.7	9.2
12e1	4.0	60.3	4.8	13.7
12f1	6.0	64.3	7.0	17.6
12g1	10.0	60.1	6.8	13.4
12h1	30.0	59.3	4.0	12.7

sodium fluoride				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
13a1	0.1	47.7	3.8	1.1
13b1	0.5	55.6	6.3	8.9
13c1	1.0	65.6	12.2	19.0
13d1	2.0	58.1	3.0	11.4
13e1	4.0	55.2	12.1	8.6
13f1	6.0	57.2	1.3	10.5
13g1	10.0	64.0	4.8	17.4
13h1	30.0	59.1	3.0	12.4
trifluoromethylsulfonic acid				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
14a1	0.1	53.9	2.0	7.3
14b1	0.5	56.1	2.3	9.5
14c1	1.0	52.5	1.2	5.8
14d1	2.0	54.6	1.0	8.0
14e1	4.0	53.7	3.0	7.1
14f1	6.0	50.8	3.3	4.2
14g1	10.0	51.6	1.4	5.0
14h1	30.0	51.7	1.8	5.1
3,5-di-<i>tert</i>-butylbenzoic acid				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
15a1	0.1	53.9	1.0	7.2
15b1	0.5	54.1	2.5	7.4
15c1	1.0	56.4	3.3	9.8
15d1	2.0	56.0	5.1	9.4
15e1	4.0	50.7	0.8	4.1
15f1	6.0	55.8	5.0	9.2
15g1	10.0	52.4	3.1	5.8
15h1	30.0	52.9	5.5	6.3
pentafluorobenzoic acid				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
16a1	0.1	52.3	2.3	5.7
16b1	0.5	51.7	1.5	5.0
16c1	1.0	57.7	1.8	11.0
16d1	2.0	53.1	0.5	6.4
16e1	4.0	53.0	1.4	6.4
16f1	6.0	51.2	0.5	4.6
16g1	10.0	50.8	0.3	4.2
16h1	30.0	49.5	3.8	2.9

sodium thiocyanate				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
17a1	0.1	49.8	1.5	3.2
17b1	0.5	54.2	3.5	7.5
17c1	1.0	56.1	4.0	9.5
17d1	2.0	58.7	1.4	12.1
17e1	4.0	58.8	1.6	12.1
17f1	6.0	55.3	4.4	8.7
17g1	10.0	53.9	3.6	7.3
17h1	30.0	51.0	2.3	4.3
2-hydroxy-5-nitrobenzoic acid				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
18a1	0.1	44.1	3.0	-2.5
18b1	0.5	48.5	1.4	1.8
18c1	1.0	48.7	2.1	2.1
18d1	2.0	54.0	1.4	7.4
18e1	4.0	49.9	0.9	3.3
18f1	6.0	46.8	0.6	0.2
18g1	10.0	43.9	0.7	-2.7
18h1	30.0	29.1	0.5	-17.5

(b) Screens in DMF

salicylic acid				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
1a1	0.1	23.5	6.7	2.0
1b1	0.5	24.0	1.9	2.4
1c1	1.0	28.5	4.0	6.9
1d1	2.0	33.0	1.6	11.5
1e1	4.0	38.0	2.5	16.4
1f1	6.0	33.1	2.8	11.6
1g1	10.0	35.0	2.4	13.4
1h1	30.0	34.0	0.8	12.5
sodium chloride				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
2a1	0.1	22.4	7.2	0.8
2b1	0.5	28.6	4.4	7.0
2c1	1.0	29.0	5.5	7.5
2d1	2.0	34.9	0.9	13.3
2e1	4.0	31.8	3.0	10.2
2f1	6.0	29.2	3.7	7.6
2g1	10.0	32.5	0.2	11.0
2h1	30.0	31.5	3.0	9.9

benzotriazole				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
3a1	0.1	27.3	2.6	5.8
3b1	0.5	30.0	0.8	8.5
3c1	1.0	29.5	1.2	7.9
3d1	2.0	34.0	2.9	12.5
3e1	4.0	36.1	3.8	14.6
3f1	6.0	33.1	2.0	11.6
3g1	10.0	32.1	1.7	10.5
3h1	30.0	32.1	0.9	10.6
3,5-di-<i>tert</i>-butylbenzoic acid				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
4a1	0.1	25.3	1.5	3.8
4b1	0.5	26.8	1.7	5.2
4c1	1.0	27.3	0.2	5.8
4d1	2.0	28.4	1.2	6.8
4e1	4.0	33.9	3.8	12.3
4f1	6.0	29.2	1.9	7.7
4g1	10.0	30.2	1.4	8.6
4h1	30.0	22.8	5.5	1.3
4-hydroxypyridine				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
5a1	0.1	26.6	3.1	5.1
5b1	0.5	28.7	1.9	7.1
5c1	1.0	29.1	1.5	7.6
5d1	2.0	29.8	1.9	8.3
5e1	4.0	29.6	1.5	8.0
5f1	6.0	29.7	1.6	8.1
5g1	10.0	31.5	0.9	10.0
5h1	30.0	30.3	1.5	8.7
pyridine				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
6a1	0.1	25.5	0.9	4.0
6b1	0.5	26.3	0.9	4.7
6c1	1.0	27.1	1.1	5.5
6d1	2.0	27.2	1.0	5.7
6e1	4.0	28.6	2.4	7.0
6f1	6.0	27.7	1.2	6.1
6g1	10.0	29.5	2.1	8.0
6h1	30.0	27.9	0.7	6.3
trichloroacetic acid				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
7a1	0.1	26.6	2.2	5.0
7b1	0.5	27.6	0.7	6.0
7c1	1.0	27.9	0.3	6.4
7d1	2.0	27.7	0.6	6.1
7e1	4.0	30.0	0.6	8.5
7f1	6.0	28.8	0.5	7.2
7g1	10.0	28.9	0.3	7.4
7h1	30.0	28.3	0.7	6.8

phenylphosphonic acid				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
8a1	0.1	27.6	0.7	6.0
8b1	0.5	25.2	3.8	3.7
8c1	1.0	28.9	1.6	7.3
8d1	2.0	30.5	3.1	9.0
8e1	4.0	28.5	1.4	6.9
8f1	6.0	30.0	0.6	8.5
8g1	10.0	29.6	0.6	8.0
8h1	30.0	27.5	0.7	6.0
sodium thiocyanate				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
9a1	0.1	23.5	0.4	2.0
9b1	0.5	24.5	1.6	3.0
9c1	1.0	26.3	0.6	4.8
9d1	2.0	25.7	0.8	4.1
9e1	4.0	24.6	1.5	3.0
9f1	6.0	27.2	0.6	5.7
9g1	10.0	27.9	1.3	6.3
9h1	30.0	24.6	1.3	3.0
sodium nitrate				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
10a1	0.1	29.6	1.0	8.0
10b1	0.5	30.7	0.1	9.1
10c1	1.0	30.5	0.2	8.9
10d1	2.0	31.7	2.0	10.1
10e1	4.0	32.8	0.2	11.3
10f1	6.0	33.0	2.1	11.4
10g1	10.0	32.2	2.8	10.7
10h1	30.0	31.8	0.6	10.2
N,N'-ethylenebis(p-toluenesulfonamide)				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
11a1	0.1	27.1	0.3	5.5
11b1	0.5	26.7	1.4	5.2
11c1	1.0	26.2	1.1	4.6
11d1	2.0	26.6	4.0	5.1
11e1	4.0	32.4	6.1	10.8
11f1	6.0	27.0	0.5	5.5
11g1	10.0	26.4	1.5	4.8
11h1	30.0	26.9	2.4	5.4

**hydroquinidine-4-
chlorobenzoate**

Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
12a1	0.1	28.2	0.6	6.6
12b1	0.5	28.5	1.1	7.0
12c1	1.0	29.0	1.2	7.5
12d1	2.0	29.3	1.7	7.7
12e1	4.0	30.6	0.9	9.1
12f1	6.0	29.4	1.4	7.9
12g1	10.0	30.9	4.2	9.4
12h1	30.0	29.0	2.5	7.4

adipic acid

Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
13a1	0.1	24.6	1.4	3.0
13b1	0.5	26.6	0.9	5.1
13c1	1.0	28.4	2.2	6.8
13d1	2.0	29.6	1.3	8.0
13e1	4.0	28.4	2.0	6.8
13f1	6.0	26.5	1.9	5.0
13g1	10.0	24.8	0.8	3.3
13h1	30.0	19.5	0.8	-2.1

phenol

Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
14a1	0.1	31.4	0.3	9.9
14b1	0.5	32.3	0.3	10.8
14c1	1.0	34.4	0.8	12.8
14d1	2.0	35.7	1.1	14.2
14e1	4.0	34.2	0.6	12.7
14f1	6.0	33.2	1.3	11.6
14g1	10.0	25.6	2.9	4.1
14h1	30.0	20.7	3.5	-0.8

quinuclidine

Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
15a1	0.1	26.7	1.9	5.1
15b1	0.5	29.4	0.8	7.8
15c1	1.0	32.4	0.7	10.8
15d1	2.0	31.8	1.5	10.2
15e1	4.0	33.5	1.7	11.9
15f1	6.0	31.6	0.6	10.0
15g1	10.0	28.0	0.1	6.4
15h1	30.0	27.9	0.8	6.3

tartaric acid				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
16a1	0.1	27.4	4.5	5.8
16b1	0.5	31.7	1.9	10.2
16c1	1.0	28.8	0.3	7.2
16d1	2.0	28.0	0.6	6.4
16e1	4.0	28.4	1.0	6.8
16f1	6.0	28.3	0.8	6.7
16g1	10.0	25.9	1.0	4.4
16h1	30.0	21.3	3.6	-0.2
2-hydroxypyridine				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
17a1	0.1	27.2	0.7	5.7
17b1	0.5	27.1	0.7	5.5
17c1	1.0	28.1	0.2	6.5
17d1	2.0	27.9	1.2	6.4
17e1	4.0	28.8	0.6	7.2
17f1	6.0	28.8	0.1	7.3
17g1	10.0	27.1	1.9	5.6
17h1	30.0	27.4	0.3	5.8
hydroquinidine				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
18a1	0.1	22.7	1.1	1.1
18b1	0.5	24.9	1.3	3.4
18c1	1.0	27.3	1.0	5.7
18d1	2.0	29.0	0.5	7.5
18e1	4.0	30.7	1.2	9.1
18f1	6.0	31.5	0.4	10.0
18g1	10.0	26.3	0.0	4.8
18h1	30.0	25.3	0.6	3.7
hydroquinidine-4-methyl-2-quinolyether				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
19a1	0.1	23.8	0.8	2.2
19b1	0.5	25.5	0.4	4.0
19c1	1.0	27.1	0.2	5.6
19d1	2.0	28.8	1.1	7.2
19e1	4.0	29.0	0.9	7.5
19f1	6.0	29.3	1.9	7.8
19g1	10.0	25.3	0.5	3.8
19h1	30.0	22.9	2.0	1.3

ascorbic acid				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
20a1	0.1	21.8	0.7	0.2
20b1	0.5	22.3	0.7	0.7
20c1	1.0	21.9	0.5	0.3
20d1	2.0	23.4	2.1	1.8
20e1	4.0	27.4	0.3	5.8
20f1	6.0	27.5	1.6	6.0
20g1	10.0	24.8	0.6	3.3
20h1	30.0	21.2	0.7	-0.4
ninhydrin				
Vial #	additive Mol%	average epoxide yield %	Std Dev epoxide yield %	relative yield %
21a1	0.1	22.3	0.1	0.7
21b1	0.5	22.3	0.3	0.7
21c1	1.0	22.0	0.5	0.4
21d1	2.0	23.0	2.2	1.4
21e1	4.0	23.3	0.7	1.8
21f1	6.0	25.5	0.9	3.9
21g1	10.0	30.4	0.8	8.8
21h1	30.0	25.9	1.8	4.4

Experimental Section

General Procedures. HPLC analyses were done using a Vydac C₁₈ column (218TP54, 300 Å, 5 µm, 4.6 mm i.d. x 250 mm) using CH₃CN and 0.1 % TFA in water as eluant at a flow rate of 1 mL/min. A gradient was used from 10 % to 40% CH₃CN in 20 min, followed by 40% to 90 % CH₃CN in 3 min then 90 % to 10% CH₃CN in 3 min.

Screening Conditions For Epoxidation Reactions Using ^tBuOH as a Co-Solvent. Glass vials (15 x 45 mm, 1 dram) were placed in a multi-well aluminum block. The catalyst was added to the vials (20 µL of a 0.0169 M_(aq) solution, typically MnSO₄), then NaHCO₃ (808 µL of a 0.2 M_(aq), pH 8.0 solution), ^tBuOH (515 µL), and 4-vinylbenzoic acid (193 µL of a 0.17 M_(aq), pH 7 solution) in that order. The vials were shaken for 5 min using a Glass-Col pulse vortex shaker apparatus, then 30% H₂O₂ (35.6 µL) was added. After the addition of H₂O₂, the vials were shaken for 1 h. An internal standard, sodium benzoate (20 µL of a 1.685 M solution), was then added to the reactions and mixed thoroughly. A portion of the reaction (200 µL) was diluted with water to 1.5 mL, and the solution was analyzed by HPLC.

Additive Screens For The Reactions Using ^tBuOH as a Co-Solvent. Glass vials (15 x 45 mm, 1 dram) were placed in an aluminum block. To the vials were added MnSO₄ (20 µL of a 0.0169 M_(aq) solution) and the additive (20 µL of a 0.169 M DMF solution; except for the inorganic salts like NaCl that were added in water). To this mixture was added NaHCO₃ (808 µL of a 0.2 M_(aq), pH 8.0 solution), ^tBuOH (515 µL), and 4-vinylbenzoic acid (193 µL of a 0.17 M_(aq), pH 7 solution). The vials were then shaken for 5 min, 30% H₂O₂ (21.4 µL for 6 eq; 7.1 µL for 2 eq) was added, then the vials were shaken for an additional 1 h. An internal standard, sodium benzoate (20 µL of a 1.685 M solution), was then added to the reactions and mixed thoroughly. A portion of the reaction (200 µL) was diluted with water to 1.5 mL, and the solution was analyzed by HPLC.

Additive Screens For The Reactions Using DMF As A Co-Solvent. Glass vials (15 x 45 mm, 1 dram) were placed in an aluminum block. To the vials were added MnSO₄ (20 µL of a 0.0169 M_(aq) solution) the additive (20 µL of a 0.169 M DMF solution; except for the inorganic salts like NaCl that were added in water). To this mixture was added NaHCO₃ (551 µL of a 0.2 M_(aq), pH 8.0 solution), DMF (772 µL), and 4-vinylbenzoic acid (193 µL of a 0.17 M_(aq), pH 7 solution). The vials were then shaken for 5 min, then 30% H₂O₂ (21.4 µL for 6 eq; 7.1 µL for 2 eq) was added, and the vials were shaken for an additional 1 h. An

internal standard, sodium benzoate (20 μ L of a 1.685 M solution), was then added to the reactions and mixed thoroughly. A portion of the reaction (200 μ L) was diluted with water to 1.5 mL, and the solution was analyzed by HPLC.

Screens for Optimum Additive Loading. The procedure used was based on the ones reported above except the volume of the additive stock solution used was adjusted according to the equivalents of additive desired in each reaction.

Large Scale Synthesis of Cyclooctene Oxide. DMF (1.68 L) and MnSO_4 (1.69g, 0.01 mol) were placed in a 12 L 3-neck flask, equipped with a mechanical stirrer and a vent to an oil bubbler. Cyclooctene (110 g, 1.00 mol) was added all at once. The flask was then placed in a water bath at 20 $^{\circ}\text{C}$ (cryocooler). A 3 L 2-neck flask equipped with a magnetic stirrer, was charged with 20.6 g of NaHCO_3 , 0.123 g of Na_2CO_3 , and 1.2 L of H_2O , and the pH of the resulting solution was adjusted to 8.0 with 1 M HCl. The flask was then placed into a water bath maintained at 1 $^{\circ}\text{C}$, then 1.1 L of 30% H_2O_2 was added all at once. The aqueous solution of buffer/peroxide was then added dropwise to the DMF solution over a period of 36 h via a cannula. **CAUTION!** *The reaction exotherms if the buffer/peroxide solution is added too quickly, or if heat transfer from the receiving flask is inadequate to maintain the desired temperature.* The reaction mixture was extracted into Et_2O (900 mL x 4), washed with brine (900 mL), and dried (Na_2SO_4). The organic fraction was concentrated, and residual DMF was fractionally distilled from it at 5 mmHg. The final product was purified via bulb-to-bulb distillation at 5 mmHg using 57 $^{\circ}\text{C}$ oven temperature. The product epoxide was collected as a colorless liquid that solidified at room temperature, 84.5 g, 67 %, mp = 53 - 55 $^{\circ}\text{C}$.

Typical Small Scale Epoxidation Procedure. Similar to above except that 23 mL of DMF and 17 mL of 0.2 M NaHCO_3 (aq) and 1 mL of 30 % H_2O_2 were used per 1 mmol of substrate. The aqueous mixture of H_2O_2 and NaHCO_3 was added dropwise over a period of 16 h via a syringe pump. After the reaction was complete, 10 ml of brine was added and the reaction was extracted with pentane (5 x 30mL). The organic layer was then washed with brine (2 x 10ml). The product was dried over sodium sulfate, filtered, and the pentane was removed by atmospheric distillation. The product was further purified by distillation under conditions appropriate for the product.

Variations Of The Small Scale Epoxidation Procedure Using Catalytic NaHCO_3 . DMF (168 mL) and MnSO_4 (0.169 g, 0.001 mol) were placed in a 1 L 3-neck flask, equipped with a magnetic stirrer and a vent to an oil bubbler. To this solution, the alkene (0.10 mol) was added all at once. The flask was then placed in a water bath at 20 °C (cryocooler). A 500 mL 2-neck flask equipped with a magnetic stirrer was placed into a water bath maintained at 1 °C, and charged with 124 mL of 0.2 M $\text{NaHCO}_{3(\text{aq})}$ pH 8.0 buffer and 105.7 mL of 30% H_2O_2 . The aqueous solution of buffer/peroxide was then added dropwise to the DMF solution over a period of 16 h via a cannula. After the reaction was complete, the product was extracted into pentane (90 mL x 4), washed with brine (90 mL), and dried (Na_2SO_4). The organic fraction was concentrated and the product purified via fractional distillation.

Epoxidation Procedure With Salicylic Acid as an Additive (DMF Co-solvent). Salicylic Acid (0.570 mg, 4.13 mmol) and MnSO_4 (174 mg, 1.03 mmol) were placed in a 1 L 3-neck flask, equipped with a magnetic stirrer and a vent to an oil bubbler. To this mixture, DMF (237 mL) and the alkene (103.3 mmol) was added all at once. The flask was then placed in a water bath at 20 °C (cryocooler). A 250 mL 2-neck flask, equipped with a magnetic stirrer, was placed into a water bath maintained at 1 °C and charged with 128 mL of 0.2 M $\text{NaHCO}_{3(\text{aq})}$ pH 8.0 buffer and 54.6 mL of 30% H_2O_2 . The aqueous solution of buffer/peroxide was then added dropwise to the DMF solution over a period of 16 h via a cannula. After the reaction was complete, the product was extracted into pentane (90 mL x 4), washed with brine (90 mL), and dried (Na_2SO_4). The organic fraction was concentrated and the product purified via fractional distillation.

Pseudo-first Order Kinetic Studies. A Hewlett Packard 8452A diode array UV spectrophotometer, equipped with a multiple sample holder, sample stirrers, and a cryocooler was used for all the kinetic studies. The temperature of each cuvet was maintained at 25 °C during each run. A cuvet containing the reaction mixture but without substrate was used as a control to compare the UV absorbance of the reactions with and without additive. These were monitored at 266 nm once every 60 seconds for 7200 seconds simultaneously. Each run was performed three times and the results averaged.

For the kinetics studies in $^t\text{BuOH}$. Each cuvet was charged with MnSO_4 (2.3 μL of a 0.590 $\text{mM}_{(\text{aq})}$ solution), while NaOAc (2.3 μL of a 3.52 $\text{mM}_{(\text{aq})}$ solution) was only added to the third. To each cuvet was then added NaHCO_3 (2.133 mL of a 0.2 $\text{M}_{(\text{aq})}$ Ph 8.0 solution) and $^t\text{BuOH}$ (1.167 mL). Next 4-vinylbenzoic

acid (0.2 mL of a 0.675 mM solution) was added to the second and third cuvetts. Finally, 30 % H₂O₂ (10.0 µL) was added to each cell, and the kinetic run was started.

For the kinetic studies in DMF The procedure was the same as the one reported above except a salicylic acid (2.3 µL of a 2.35 mM_(aq) solution) was used in place of the NaOAc as an additive, and DMF was used in place of ^tBuOH.

EPR. EPR spectroscopy was performed using a Bruker ESP-300 X-band spectrometer equipped with an Oxford liquid helium cryostat. Samples were placed in 3 mm quartz tubes and frozen in liquid N₂ before data collection. Typical spectrometer conditions were 9.4 GHz microwave frequency, 2 mW microwave power, 7K, 25 G modulation amplitude.