# Supporting Information

## Effect of Additives on the Chemoselectivity and Diastereoselectivity in the Catalytic Epoxidation of Chiral Allylic Alcohols with Hydrogen Peroxide and Binuclear Manganese Complexes

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**General Aspects and Product Identification.** $^1H$ and $^{13}C$ NMR spectra were recorded on 200, 250 (50, 62.5) MHz NMR spectrometers and are reported in δ units with chloroform as internal standard. The carbonyl compounds **4a** is commercially available and was identified by comparison with authentic sample. The ketones **4b**,[8] *E*-**4c**,[9] *Z*-**4c**,[10] *E*-**4d**,[11] *Z*-**4d**[12] and **4e**[13] and the epoxy alcohols *threo/erythro*-**3a**-**f**[1-7] were identified by comparison with the literature known NMR data.

**1-(Oxiran-2-yl)ethanol (3a)**[1]

*threo*-**3a**: $^1H$ NMR (250 MHz, $CDCl_3$): δ= 1.25 (d, *J* = 6.4 Hz, 3 H), 2.60 - 3.00 (m, 4 H), 3.55 (dq, *J* = 6.4 Hz, 5.5 Hz, 1 H). $^{13}C$ NMR (63 MHz, $CDCl_3$): δ = 19.4, 45.0, 55.3, 68.1.

*erythro*-**3a**: $^1H$ NMR (250 MHz, $CDCl_3$): δ = 1.21 (d, *J* = 6.4 Hz, 3 H), 2.60 - 3.00 (m, 4 H), 3.94 (dq, *J* = 6.4, 5.5 Hz, 1 H). $^{13}C$ NMR (63 MHz, $CDCl_3$): δ = 18.5, 43.5, 56.3, 64.2.

**1-(2-Methyloxiran-2-yl)ethanol (3b)**[2]

*threo*-**3b**: $^1H$ NMR (200 MHz, $CDCl_3$): δ = 1.20 (d, *J*= 6.6 Hz, 3 H), 1.29 (s, 3 H,), 2.10 (br s, 1 H, OH), 2.60 (d, *J* = 4.8 Hz, 1 H), 2.75 (d, *J*= 4.8 Hz, 1H), 3.50 (q, *J*= 6.6 Hz, 1 H). $^{13}C$ NMR (50 MHz, $CDCl_3$): δ = 15.5, 18.8, 52.3, 60.2, 70.6.

*erythro*-**3b**: $^1H$ NMR (200 MHz, $CDCl_3$): δ = 1.19 (d, *J*= 6.6 Hz, 3 H), 1.28 (s, 3 H), 2.10 (br s, 1 H, OH), 2.56 (d, *J* = 4.8 Hz, 1 H), 2.86 (d, *J* = 4.8Hz, 1 H), 3.73 (q, *J* = 6.6 Hz, 1 H). $^{13}C$ NMR (50 MHz, $CDCl_3$): δ = 17.8, 18.4, 50.0, 59.9, 67.6.

**1-(3-Methyloxiran-2-yl)ethanol (3c)**[3,4] *threo-E*-**3c**: $^1$H NMR (200 MHz, $CDC1_3$): δ = 1.25 (d, *J* = 6.5 Hz, 3 H), 1.30 (d, *J* = 5.2 Hz, 3 H), 2.11 (br s, 1 H, OH), 2.69 (dd, *J* = 5.2, 2.3 Hz), 2.98 (dq, *J*= 5.2, 2.3 Hz, 1 H), 3.60 (dq, *J* = 6.5, 5.2 Hz). $^{13}$C NMR (50 MHz, $CDC1_3$): δ = 17.0, 19.3, 52.7, 63.6, 67.5.

*erythro-E*-**3c**: $^1$H NMR (200 MHz, $CDC1_3$): δ = 1.22 (d, *J*= 6.4 Hz, 3 H), 1.31 (d, *J* = 5.5 Hz, 3 H), 2.11 (br s, 1 H, OH), 2.72 (dd, *J* = 3.2, 2.7 Hz, 1 H), 3.06 (dq, 7= 5.5, 2.7 Hz, 1 H), 3.90 (dq, 7= 6.4, 3.2 Hz, 1 H). $^{13}$C NMR (50 MHz, $CDC1_3$): δ = 17.1, 18.7, 51.4, 62.6, 65.1.

*threo-Z*-**3c**: $^1$H NMR (250 MHz, $CDC1_3$): δ = 1.25 (d, *J*= 6.5 Hz, 3 H), 1.30 (d, *J* = 5.2 Hz, 3 H), 2.11 (br s, 1 H, OH), 2.69 (dd, *J* = 5.2, 2.3 Hz, 1 H), 2.98 (dq, *J* = 5.2, 2.3 Hz, 1 H), 3.60 (dq, *J* = 6.5, 5,2 Hz, 1 H). 13C NMR (63 MHz, $CDC1_3$): δ = 13.4, 18.9, 53.1, 61.4, 66.1.

*erythro-Z*-**3c**: $^1$H NMR (250 MHz, $CDC1_3$): δ = 1.32 (d, 7 = 6.4 Hz, 3 H), 1.33 (d, 7 = 5.8 Hz, 3 H), 2.15 (br s, 1 H, OH), 2.77 (dd, *J* = 7.6, 4.3 Hz, 1 H), 3.11 (dq, *J* = 5.8, 4.3 Hz, 1 H), 3.70 (dq, *J* = 7.6, 6.4 Hz, 1 H). $^{13}$C NMR (63 MHz, $CDC1_3$): δ = 13.1, 20.7, 53.3, 59.9, 64.7.

**1-(2,3-Dimethyloxiran-2-yl)ethanol (3d)**[5]

*threo-E*-**3d**: $^1$H NMR (250 MHz, $CDC1_3$): δ = 1.17 (d, *J* = 6.6 Hz, 3 H), 1.22 (s, 3 H), 1.26 (d, *J* = 5.6 Hz, 3 H), 2.48 (br s, 1 H, OH), 2.99 (q, *J* = 5.6 Hz, 1 H), 3.42 (q, *J* = 6.6 Hz, 1 H).$^{13}$C NMR (50 MHz, $CDC1_3$): δ = 11.0, 13.5, 18.7, 57.2, 64.1, 72.0.

*erythro-E*-**3d**: $^1$H NMR (250 MHz, $CDC1_3$): δ = 1.17 (d, *J*= 6.4 Hz, 3 H), 1.23 (s, H), 1.28 (d, *J* = 5.5 Hz, 3 H), 2.48 (br s, 1 H, OH), 3.14 (q, *J* = 5.5 Hz, 1 H), 3.73 (q, 7= 6.4 Hz, 1 H). $^{13}$C NMR (50 MHz, $CDC1_3$): δ = 13.6, 13.8, 18.2, 54.7, 63.5, 68.6.

*threo-Z*-**3d**: $^1$H NMR (250 MHz, $CDC1_3$): δ = 1.20 (d, *J* = 6.7 Hz, 3 H), 1.29 (s, 3 H), 1.30 (d, *J* = 5.7 Hz, 3 H), 2.15 (br s, 1 H, OH), 2.96 (q, *J* = 5.7 Hz, 1 H), 3.69 (q, *J* = 6.7 Hz, 1 H). $^{13}$C NMR (63 MHz, $CDC1_3$): δ = 13.7, 15.8, 19.0, 60.8, 64.4, 69.0.

*erythro-Z*-**3d**: $^1$H NMR (250 MHz, $CDCl_3$): δ = 1.26 (s, 3 H), 1.27 (d, *J* = 6.5 Hz, 3 H), 1.42 (d, *J* = 5.8 Hz, 3 H), 2.15 (br s, 1 H, OH), 2.95 (q, *J* = 5.8 Hz, 1 H), 3.77 (q, *J* = 6.5 Hz, 1 H). $^{13}$C NMR (63 MHz, $CDCl_3$): δ = 13.5, 17.7, 18.6, 61.3, 62.8, 67.8.

**1-(3,3-Dimethyloxiran-2-yl)ethanol (3e)**[6]

*threo*-**3e**: $^1$H NMR (200 MHz, $CDCl_3$): δ = 1.22 (d, *J*= 6.5 Hz, 3 H), 1.28 (s, 3 H), 1.30 (s, 3 H), 2.53 (br s, 1 H, OH), 2.69 (d, *J* = 8.0 Hz, 1 H), 3.61 (dq, *J* = 8.0, 6.5 Hz, 1 H). $^{13}$C NMR (50 MHz, $CDCl_3$): δ = 19.0, 19.1, 24.8, 59.3, 66.9, 68.5.

*erythro*-**3e**: $^1$H NMR (200 MHz, $CDCl_3$): δ = 1.33 (s, 3 H), 1.34 (d, *J*= 6.3 Hz, 3 H), 1.36 (s, 3 H), 2.53 (br s, 1 H, OH), 2.62 (d, *J* = 7.9 Hz, 1 H), 3.52 (dq, *J* = 7.9, 6.3 Hz, 1 H). $^{13}$C NMR (50 MHz, $CDCl_3$): δ = 18.6, 20.9, 24.8, 59.3, 66.2, 67.1.

**1-(2,3,3-trimethyloxiran-2-yl)ethanol (3f)**[7]

*threo*-**3f**: $^1$H NMR (250 MHz, $CDCl_3$): δ = 1.16 (d, *J*= 6.7 Hz, 3 H), 1.30 (s, 3 H), 1.32 (s, 6 H), 1.93 (br s, 1 H, OH), 3.76 (q, *J* = 6.7 Hz, 1 H). $^{13}$C NMR (63 MHz, $CDCl_3$): δ = 11.3, 18.5, 20.3, 21.5, 63.0, 64.8, 69.6.

*erythro*-**3f**: $^1$H NMR (250 MHz, $CDCl_3$): δ = 1.21 (d, *J*= 6.7 Hz, 3 H), 1.26 (s, 3 H), 1.28 (s, 6 H), 3.84 (q, *J* = 6.7 Hz, 1 H). $^{13}$C NMR (63 MHz, $CDCl_3$): δ = 13.4, 18.2, 20.0, 22.2, 63.3, 66.0, 67.9.

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# Structure Matrix

| Allylic alcohols | *threo*-epoxy alcohols | *erythro*-epoxy alcohols | Ketones |
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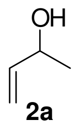
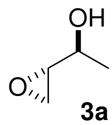
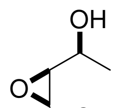
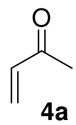
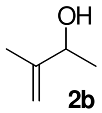
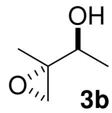
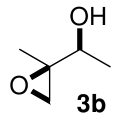
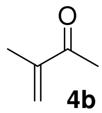
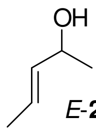
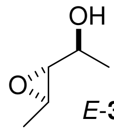
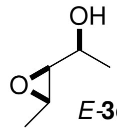
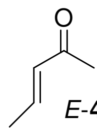
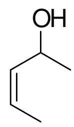
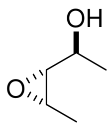
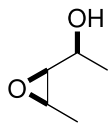
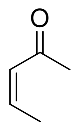
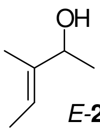
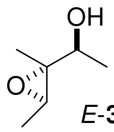
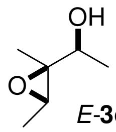
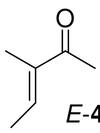
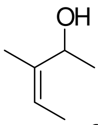
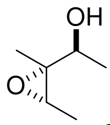
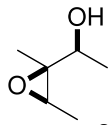
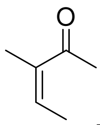
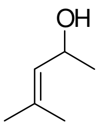
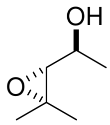
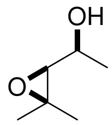
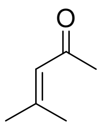
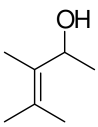
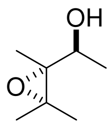
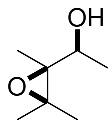
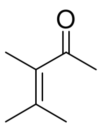
|  **2a** |  **3a** |  **3a** |  **4a** |
|  **2b** |  **3b** |  **3b** |  **4b** |
|  *E*-**2c** |  *E*-**3c** |  *E*-**3c** |  *E*-**4c** |
|  *Z*-**2c** |  *Z*-**3c** |  *Z*-**3c** |  *Z*-**4c** |
|  *E*-**2d** |  *E*-**3d** |  *E*-**3d** |  *E*-**4d** |
|  *Z*-**2d** |  *Z*-**3d** |  *Z*-**3d** |  *Z*-**4d** |
|  **2e** |  **3e** |  **3e** |  **4e** |
|  **2f** |  **3f** |  **3f** |  **4f** |