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**Supporting Information**

(11 pages)

*cis*-Stilbene and (1 $\alpha$ ,2 $\beta$ ,3 $\alpha$ )-(2-ethenyl-3-methoxy-cyclopropyl)benzene as Mechanistic Probes in the Mn<sup>III</sup>(salen)-Catalyzed Epoxidation: Influence of the Oxygen Source and the Counterion on the Diastereoselectivity of the Competitive Concerted and Radical-Type Oxygen Transfer.

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## Experimental Section

**General Aspects.**  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were recorded in  $\text{CDCl}_3$  on a Bruker AC 200 or AC 250 ( $^1\text{H}$ : 200 or 250 MHz;  $^{13}\text{C}$ : 50 or 63 MHz) spectrometer. IR spectra were determined on a Perkin-Elmer 1600 series FTIR spectrophotometer. Mass spectra were carried out on a Finnigan MAT8200, exact mass on a Finnigan MAT90. HPLC analyses were run on a Bischoff 2200 equipment, furnished with a UV spectrophotometer SpectraFlow 600 from SunChrom (detection wavelength 220 nm). As stationary phase, an Eurosper-100 C18 (7  $\mu\text{m}$ ) from Knauer was employed, the mobile phase was a mixture of  $\text{H}_2\text{O}/\text{MeCN}$  (2:1 or 3:1) at a flow rate of 1.0 mL/min.

**Manganese-Catalyzed Epoxidation of *cis*-Stilbene (1):** A solution of 37.5  $\mu\text{mol}$  (10 mol%) of the particular  $\text{Mn}(\text{salen})\text{X}$  **3** in 3.75 mL of  $\text{CH}_2\text{Cl}_2$  was stirred for 3 min at ca. 20  $^\circ\text{C}$ . After addition of 375  $\mu\text{mol}$  of *cis*-stilbene (**1**), the mixture was stirred for another 2 min and 375  $\mu\text{mol}$  of the respective oxygen donor (OxD) was administered in small portions during 2 min. After stirring of the mixture for up to 16 h, the solvent was removed (20  $^\circ\text{C}$ , 400 mbar), the residue was transferred onto a short column of silica gel (ca. 10 g) and eluted with 200 mL of a petroleum ether/ $\text{Et}_2\text{O}$  mixture (1:1). The solvent was evaporated (30  $^\circ\text{C}$ , 10 mbar) and conversion, mass balance and the *cis/trans*-epoxide ratio for the resulting colorless oil was determined by  $^1\text{H}$ -NMR spectroscopy (1,1,2,2-tetrachlorethane as internal standard). The results are summarized in Table 1 (see main text).

**Manganese-Catalyzed Epoxidation of *cis*-Stilbene (1) with Ozone as OxD:** A solution of 37.5  $\mu\text{mol}$  (10 mol%) of the particular  $\text{Mn}(\text{salen})\text{X}$  **3** in 3.75 mL of  $\text{CH}_2\text{Cl}_2$  was stirred for 3 min at  $-78$   $^\circ\text{C}$ . After addition of 375  $\mu\text{mol}$  of *cis*-stilbene (**1**), the mixture was stirred for another 2 min and a gentle stream of  $\text{O}_3/\text{O}_2$  was allowed to pass through the solution for 5 to 15 min. Subsequently, aqueous

Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (5 mL) was added, the organic phase separated, the solvent removed (20 °C, 400 mbar), and the workup was continued as described above.

**Control Experiments on the Oxidation of the Chloride Ion by the Oxygen Donors PhIO, C<sub>6</sub>F<sub>5</sub>IO and TBA<sup>⊕</sup>HSO<sub>5</sub><sup>⊖</sup>:** A mixture of 32.0 mg (140 μmol) of triethylbenzylammonium chloride (TEBA<sup>⊕</sup>Cl<sup>⊖</sup>) and 15.4 mg (70 μmol) of PhIO or 21.7 mg (70 μmol) of C<sub>6</sub>F<sub>5</sub>IO or 43.0 mg (70 μmol) of KHSO<sub>5</sub> in 0.7 mL of CH<sub>2</sub>Cl<sub>2</sub> was shaken for about 2 min. The solid oxygen sources PhIO and KHSO<sub>5</sub> were not consumed, as witnessed by their lack of dissolution. Only in the case of C<sub>6</sub>F<sub>5</sub>IO, a pale green solution emerged immediately, which on standing at ca. 20 °C evolved chlorine gas and the green color was bleached.

**Control Experiments on the Ligation Ability of the IO<sub>3</sub><sup>⊖</sup> and Cl<sup>⊖</sup> Counterions:** A solution of 27.9 mg (37.5 μmol) of Mn(salen)PF<sub>6</sub> catalyst **3b** and 21.0 mg (41.3 μmol) of *n*-octadecylpyridinium iodate (PyR<sup>⊕</sup>IO<sub>3</sub><sup>⊖</sup>)<sup>24</sup> or 9.11 mg (40.0 μmol) of triethylbenzylammonium chloride (TEBA<sup>⊕</sup>Cl<sup>⊖</sup>) in 3.75 mL CH<sub>2</sub>Cl<sub>2</sub> was stirred for 3 min at ca. 20 °C. After addition of 66.3 μL (375 μmol) of *cis*-stilbene (**1**), the mixture was stirred for another 2 min and 82.5 mg (375 μmol) of PhIO was administered in small portions during 2 min. The resulting suspension was stirred for up to 16 h until a clear brown solution was obtained. After work-up as described above, the *cis/trans*-epoxide ratio for the resulting colorless oil was determined by <sup>1</sup>H-NMR spectroscopy (1,1,2,2-tetrachlorethane as internal standard) to be 37:63 for PyR<sup>⊕</sup>IO<sub>3</sub><sup>⊖</sup> and 23:77 for TEBA<sup>⊕</sup>Cl<sup>⊖</sup>.

**DMD Epoxidation of (1 $\alpha$ ,2 $\beta$ ,3 $\alpha$ )-(2-Ethenyl-3-methoxycyclopropyl)benzene (4):** To 61.0 mg (350  $\mu$ mol) of the vinylcyclopropane **4** was added 4.0 mL of a 0.09 M DMD solution, which prior to use was filtered over anhydrous Na<sub>2</sub>CO<sub>3</sub>. The reaction mixture was stirred for 15 h at RT (ca. 20 °C) and removal of the solvent (20 °C, 10 mbar) yielded the epoxide **5** quantitatively as a mixture of diastereomers (dr 54:46).

**(2-Methoxy-3-phenylcyclopropyl)oxirane (5)**

*Diastereomer 1:*

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  7.15-7.33 (m, 5 H, H<sub>Ar</sub>), 3.44 (dd,  $J = 6.7$  Hz, 3.4 Hz, 1 H, 2-H), 3.15 (s, 3 H, OMe), 2.98-3.04 (m, 1 H,  $\alpha$ -H), 2.74-2.84 (m, 1 H,  $\beta'$ -H), 2.67 (dd,  $J = 5.0$  Hz, 2.6 Hz, 1 H,  $\beta$ -H), 2.09 (t,  $J = 6.6$  Hz, 1 H, 3-H), 1.63-1.76 (m, 1 H, 1-H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>)  $\delta$  136.9, 128.3, 128.2, 126.2, 62.7, 58.1, 50.6, 46.5, 27.0, 25.9.

*Diastereomer 2:*

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  7.15-7.33 (m, 5 H, H<sub>Ar</sub>), 3.36 (dd,  $J = 6.7$  Hz, 3.4 Hz, 1 H, 2-H), 3.16 (s, 3 H, OMe), 3.13-3.19 (m, 1 H,  $\alpha$ -H), 2.74-2.84 (m, 1 H,  $\beta'$ -H), 2.52 (dd,  $J = 5.0$  Hz, 2.7 Hz, 1 H,  $\beta$ -H), 1.98 (t,  $J = 6.7$  Hz, 1 H, 3-H), 1.63-1.76 (m, 1 H, 1-H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>)  $\delta$  136.9, 128.3, 128.2, 126.2, 61.6, 58.1, 49.9, 45.5, 26.3, 24.8.

*For the Mixture of Diastereomers:*

HPLC (2:1 water/acetonitrile):  $t_r = 20.9$  min; IR (neat):  $\nu = 2988$  cm<sup>-1</sup>, 2934, 2825, 1604, 1498, 1447, 1389, 1353, 1218, 1033; HRMS (EI): Calcd. for C<sub>12</sub>H<sub>14</sub>O<sub>2</sub> 190.0994 (M<sup>+</sup>), found 190.0993.

**Reaction of Epoxide 5 with Cr(salen)PF<sub>6</sub>:** To a solution of 66.6 mg (350 μmol) of epoxide **5** in 2 mL of CDCl<sub>3</sub> was added a catalytic amount (ca. 0.5 mg) of [{2,2'-[1,2-ethanediylbis(nitrilomethylidene)]bis(phenolato)}(2-)-N,N',O,O']chromium(1+)-hexafluorophosphate [Cr(salen)PF<sub>6</sub>], and the mixture was stirred for 15 h at RT (ca. 20 °C). After removal of the solvent (20 °C, 10 mbar), the crude product was purified by silica-gel chromatography to yield 7.3 mg (12%) of acetal **6a** (R<sub>f</sub> = 0.53, 10:1 mixture of petroleum ether and Et<sub>2</sub>O) and 46.9 mg (77%) of products **A-C** (R<sub>f</sub> = 0.16, 20:1 mixture of CH<sub>2</sub>Cl<sub>2</sub> and MeOH). The aldehyde **6b** was not detected by <sup>1</sup>H-NMR spectroscopy. The <sup>1</sup>H-NMR spectra and HPLC traces are given in Figure S1 for acetal **6a** and in Figure S2 for the mixture **A-C**.

### **3,6-Dihydro-2-methoxy-3-phenyl-2H-pyran (6a)**<sup>25</sup>

*(2R\*,3R\*) Diastereomer:*

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 7.23-7.29 (m, 5 H, H<sub>Ar</sub>), 5.75-6.00 (m, 2 H, 4-H, 5-H), 4.80 (d, *J* = 3.8 Hz, 1 H, 2-H), 4.15-4.41 (m, 2 H, 6-H), 3.69-3.74 (m, 1 H, 3-H), 3.35 (s, 3 H, OMe).

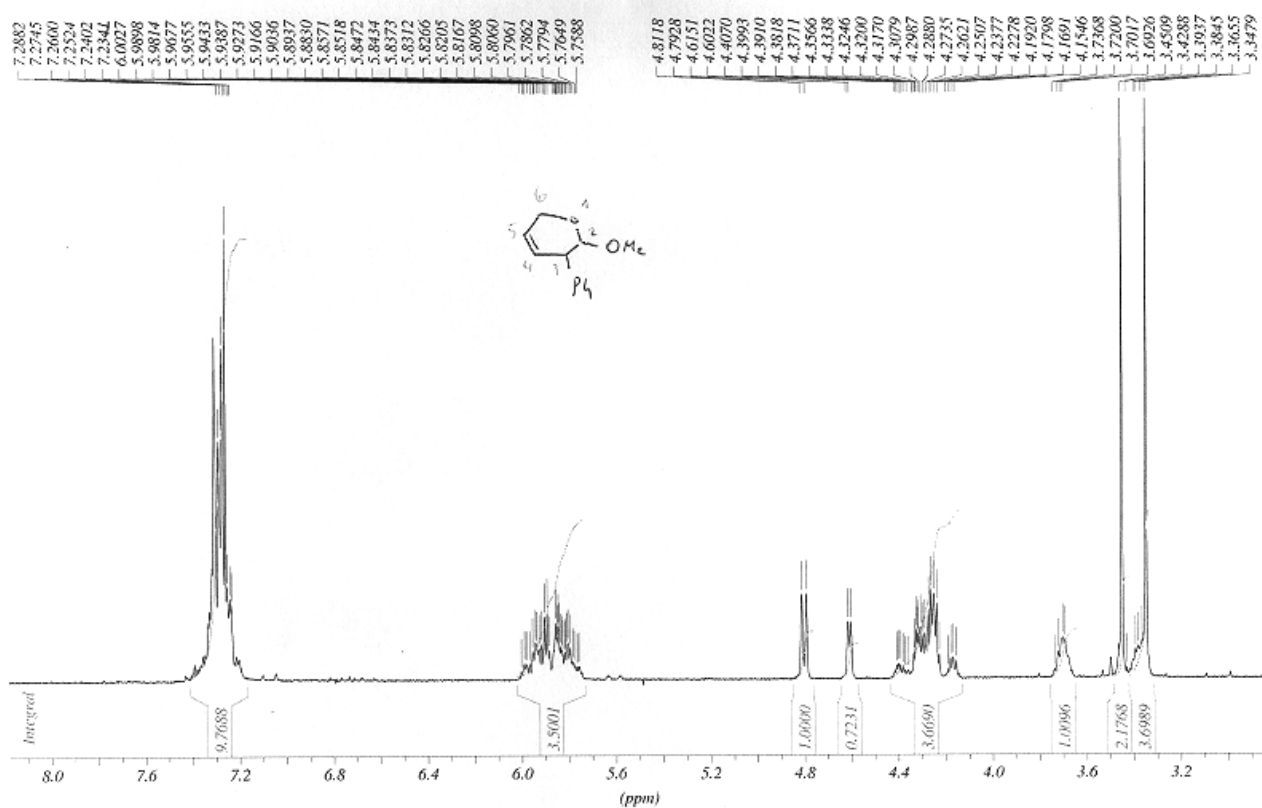
*(2R\*,3S\*) Diastereomer:*

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 7.23-7.29 (m, 5 H, H<sub>Ar</sub>), 5.75-6.00 (m, 2 H, 4-H, 5-H), 4.61 (d, *J* = 2.6 Hz, 1 H, 2-H), 4.15-4.41 (m, 2 H, 6-H), 3.45 (s, 3 H, OMe), 3.35-3.39 (m, 1 H, 3-H).

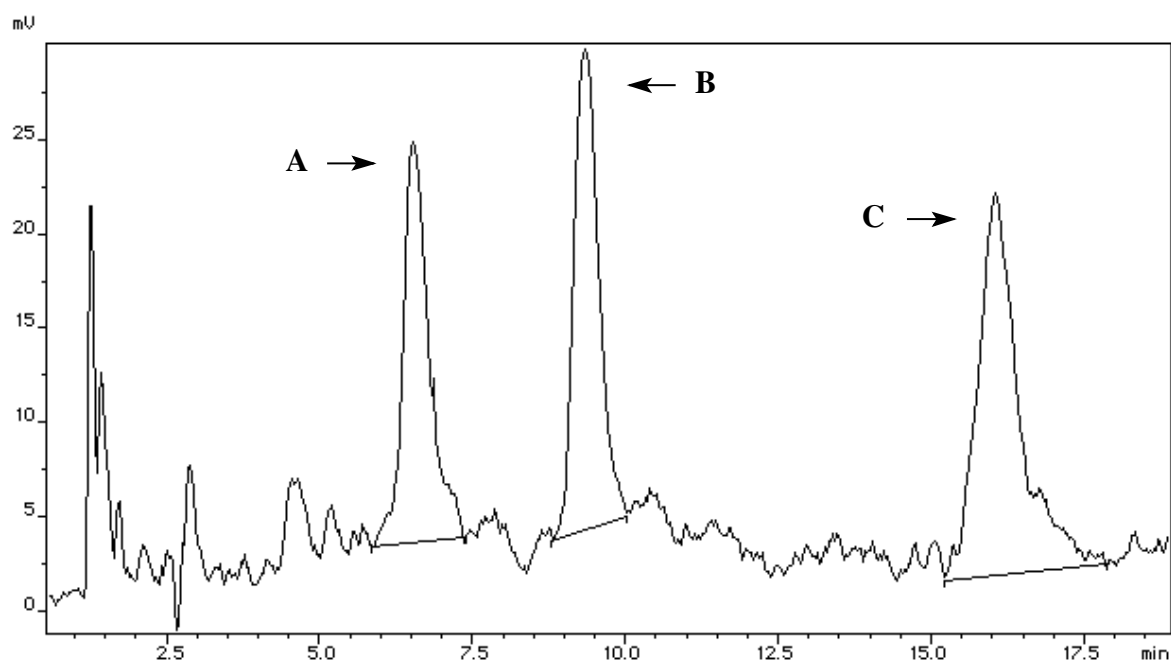
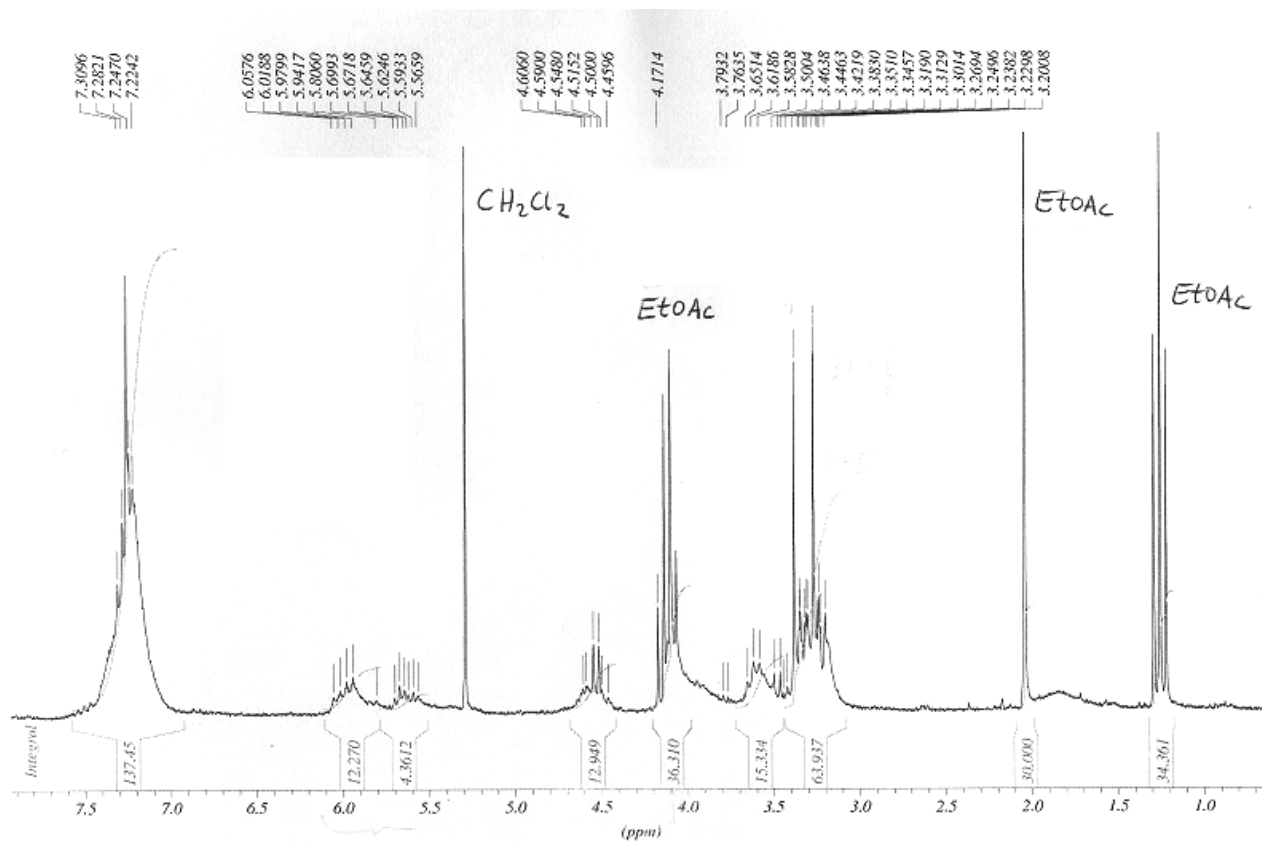
*For the Mixture of Diastereomers:*

<sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ 141.1, 139.8, 129.7, 128.8, 128.8, 128.3, 127.2, 127.0, 126.2, 126.0, 125.8, 125.4, 102.7, 100.5, 61.3, 60.2, 56.0, 55.6, 45.8, 45.0; HPLC (2:1 water/acetonitrile) t<sub>R</sub> = 27.3, 29.5 min; MS (EI, 70 eV) m/e 158 (18, M<sup>+</sup> - MeOH), 130 (100, M<sup>+</sup> - HC(O)OMe); MS [CI (NH<sub>3</sub>)] m/e 208 (100, M + NH<sub>4</sub><sup>+</sup>).

**Figure S1.**  $^1\text{H-NMR}$  (200 MHz) spectrum and HPLC trace (2:1  $\text{H}_2\text{O}/\text{MeCN}$ ) of the isolated cationic ring-opened product **6a** (diastereomeric mixture)

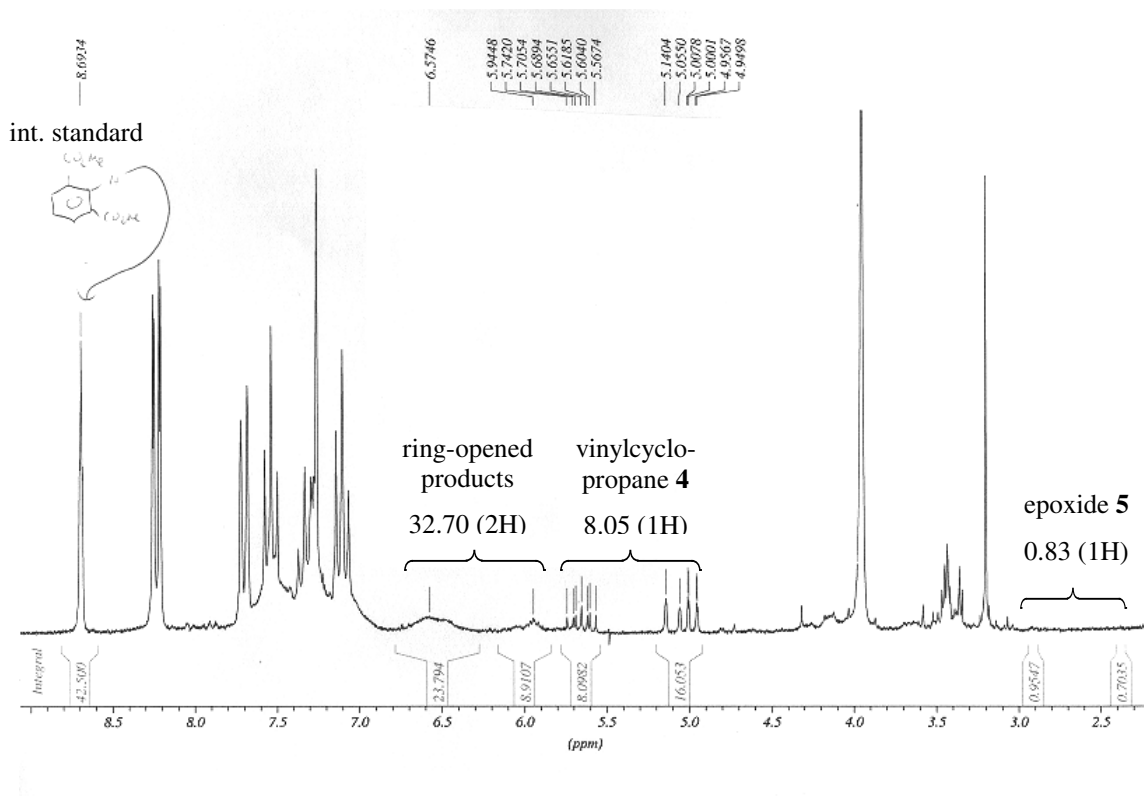


**Figure S2.** <sup>1</sup>H-NMR (200 MHz) spectrum and HPLC trace (2:1 H<sub>2</sub>O/MeCN) of the isolated mixture of cationic ring-opened products **A-C**

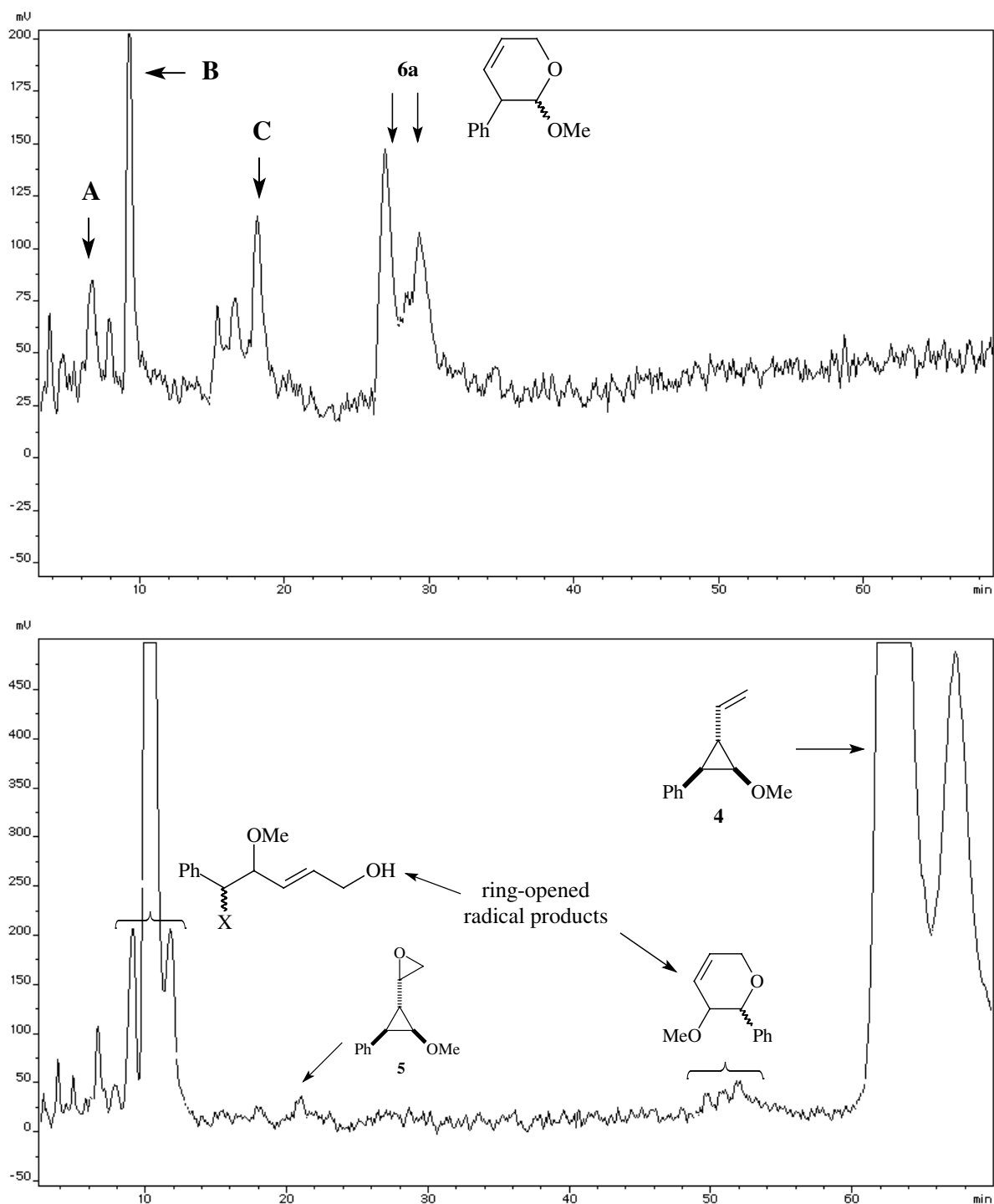


**Manganese-Catalyzed Epoxidation of (1 $\alpha$ ,2 $\beta$ ,3 $\alpha$ )-(2-Ethenyl-3-methoxycyclopropyl)benzene (4) with Polymer-Bound Salen:** To a solution of 8.7 mg (50  $\mu$ mol) of the vinylcyclopropane **4** and 3.4 mg (20  $\mu$ mol) of 4-phenylpyridine *N*-oxide (PPNO) in 1.5 mL of CH<sub>2</sub>Cl<sub>2</sub> was added 50.0 mg (10  $\mu$ mol) of the **p-MnCl** catalyst, the suspension was stirred for ca. 2 min and 22.0 mg (100  $\mu$ mol) of iodosyl benzene (PhIO) was administered in small portions during 1 min. After stirring of the mixture for 16 h at RT (ca. 20 °C), the catalyst was removed by filtration, the solvent evaporated (20 °C, 10 mbar), and the crude product was submitted to <sup>1</sup>H-NMR spectroscopy (Figure S3) and RP-HPLC analysis. At 83% conversion of the vinylcyclopropane **4** (dimethyl isophthalate as internal standard), 2% of the epoxide **5** and 33% of ring-opened products were obtained (mass balance 51%). By comparison of the retention times with that of coinjected authentic samples of **6a** and **A-C** (Figures S4 and S5), the formation of cationic ring-opened products was ruled out. Since in the crude product mixture of the **p-MnCl**-catalyzed epoxidation of vinylcyclopropane **4** (Figure S4, lower chromatogram) the possible cationic ring-opened products **A** and **B** were strongly overlapped with the observed ring-opened radical products (see 5-15 min region), this region was run at a better separation (Figure S5).

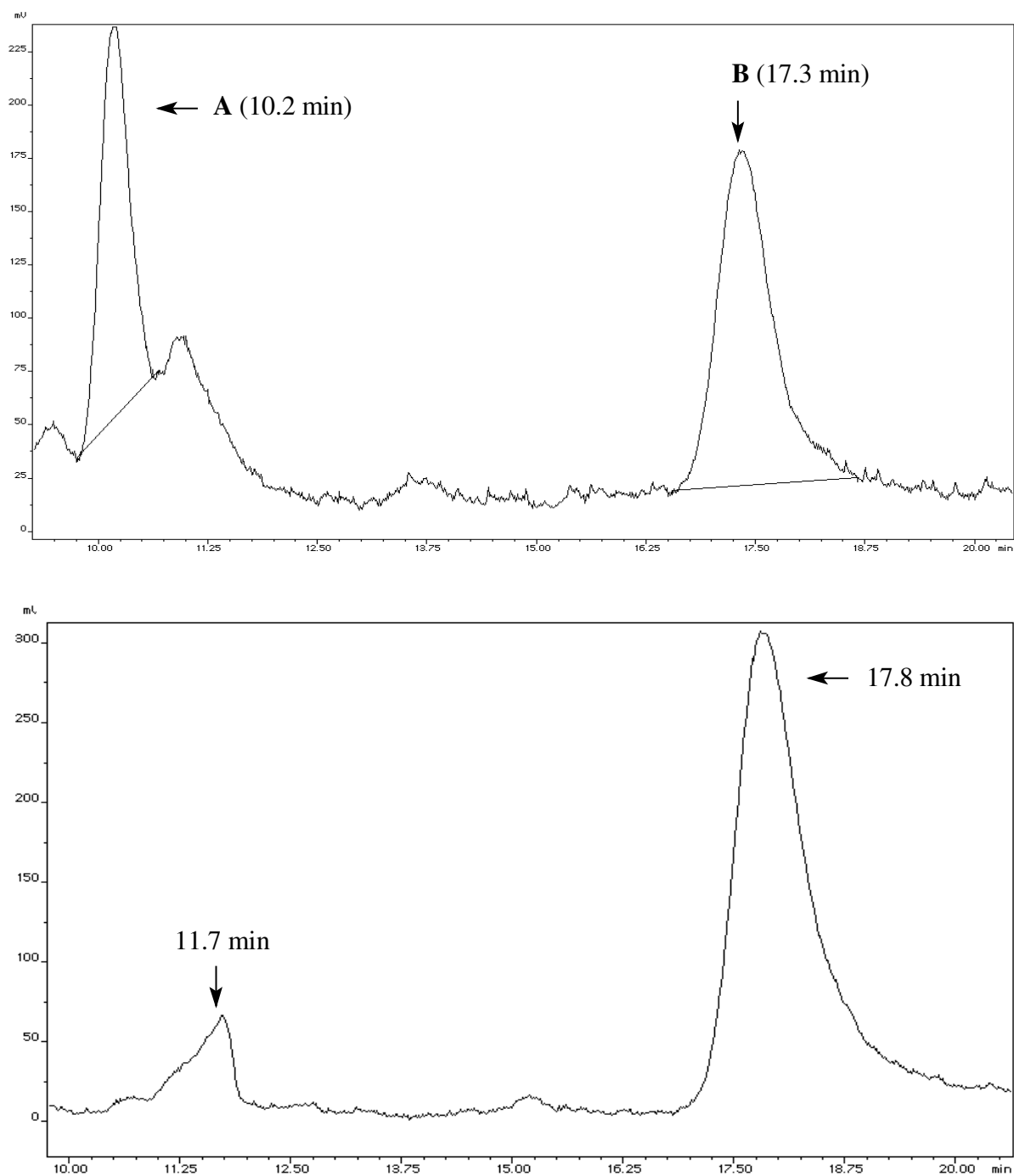
**Figure S3.** <sup>1</sup>H-NMR (200 MHz) spectrum of the crude product mixture in CDCl<sub>3</sub> for the **p-MnCl**-catalyzed epoxidation of vinylcyclopropane **4**



**Figure S4.** HPLC traces (2:1 H<sub>2</sub>O/MeCN) of the crude product mixtures for the authentic cationic ring-opened products **6a** and **A-C**, prepared by Cr(salen)-catalyzed reaction of epoxide **5** (upper chromatogram), and of the *p*-MnCl-catalyzed epoxidation of vinylcyclopropane **4** (lower chromatogram);  $t_r$  (**A**) = 6.5,  $t_r$  (**B**) = 9.3,  $t_r$  (**C**) = 16.0,  $t_r$  (**6a**) = 27.3 and 29.5 min.



**Figure S5.** HPLC traces (3:1 H<sub>2</sub>O/MeCN) of the isolated cationic ring-opened products **A** and **B** (upper chromatogram) and of the crude product mixture for the **p-MnCl**-catalyzed epoxidation of vinylcyclopropane **4** (lower chromatogram).



## Additional References

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(24) (a) Knight, G. A.; Shaw, B. D. *J. Chem. Soc.* **1938**, 682-683. (b) Brown, G. L.; Grieger, P. F.; Kraus, C. A. *J. Am. Chem. Soc.* **1949**, *71*, 95-99.

(25) Brescia, M.-R.; DeShong, P. *J. Org. Chem.* **1998**, *63*, 3156-3157.