Appendix A
Substrates and products
Suppliers of commercially available compounds. All reagents are of commercial grade (Aldrich, Acros, Fluka, Merck, NovaBiochem) and used as received unless stated otherwise. Hydrogen peroxide: 50 w/w % (Acros) or 30 v/v % (Merck, medical grade) solution in water. D$_2$O (Icon Isotopes): 30 % solution in D$_2$O, 99 atom% D. D$_2$O (Aldrich): 99.9 atom% D. H$_2^{18}$O (Icon Isotopes): 2 % solution in H$_2^{18}$O, 90 atom% $^{18}$O. H$_2^{18}$O (Icon Isotopes): 97 atom% $^{18}$O. mCPBA (Acros): 70-75% in 3-chlorobenzoic acid and water. Peracetic acid (Fluka): 39% in acetic acid (45%) and contains up to 6% H$_2$O$_2$. tBuOOH (Aldrich): 70% in water. CH$_3$CN (Acros, extra pure). Cyclooctene: 95 % stabilized with 100-200 ppm irganox 1076 FD (Acros), or 95% (Aldrich) remainder cyclooctane; alternatively, cyclooctene (Acros) was triple distilled to remove the stabilizer. Mn(OAc)$_3$.2H$_2$O (Aldrich). Mn(ClO$_4$)$_2$.6H$_2$O (Acros).

TLC staining. UV-Vis: 254 and/or 366 nm. Iodine: A few crystals of iodine were mixed with silica (20 g). Potassium permanganate: KMnO$_4$ (6 g) and anhydrous Na$_2$CO$_3$ (6 g) were dissolved in H$_2$O (1 litre) and the solution was kept in the dark. Cerium molybdate stain: Phosphomolybdic acid (25 g) and cerium(IV) sulfate (7.5 g) were dissolved in H$_2$O (500 ml) and conc. H$_2$SO$_4$ (25 ml) was added. Ninhydrin: Ninhydrin (5 g) was dissolved in EtOH (100 ml). Vanillin: Vanillin (15 g) was dissolved in EtOH (250 ml) and conc. H$_2$SO$_4$ was added (2.5 ml).

Cis- and trans-2,3-epoxyheptane were prepared by stereospecific epoxidation of the corresponding alkene using m-chloroperoxybenzoic acid according to a modified literature procedure.\(^1\)

**Cis-2,3-epoxyheptane.** A solution of m-chloroperoxybenzoic acid (5.0 g, 20.3 mmol) in CH$_2$Cl$_2$ (50 ml) was added slowly to a cooled mixture of cis-2,3-heptene (2.00 g, 20.4 mmol) in CH$_2$Cl$_2$ (50 ml) maintaining the temperature below 5°C. The reaction mixture was allowed to reach room temperature and was stirred overnight. m-Chlorobenzoic acid was removed by filtration and the organic layer was washed with saturated NaHCO$_3$ (3x50 ml) and brine (1x50 ml), was dried over Na$_2$SO$_4$ and the solvent was evaporated in vacuo, yielding a colorless oil (1.58 g, 13.8 mmol, 68%). $^1$H NMR (300 MHz, CDCl$_3$): δ 0.92 (t, $J$ = 6.8 Hz, 3H), 1.26 (d, $J$ = 5.5 Hz, 3H), 1.37-1.60 (m, 6H), 2.86-2.91 (m, 1H), 3.00-3.07 (m, 1H). $^{13}$C NMR (75.4 MHz, CDCl$_3$): δ 13.2, 14.0, 22.6, 27.2, 28.6, 52.6, 57.1. Both $^1$H and $^{13}$C NMR spectra are in accordance with ref. [1].

**Trans-2,3-epoxyheptane.** As for cis-2,3-epoxyheptane, except trans-2,3-heptene (4.00 g, 40.7 mmol) was used, yielding a colorless oil (3.38 g, 29.6 mmol, 73%). $^1$H NMR (300 MHz, CDCl$_3$): δ 0.91 (t, $J$ = 7.0 Hz, 3H), 1.29 (d, $J$ = 5.1 Hz, 3H), 1.34-1.53 (m, 6H), 2.60-2.64 (m, 1H), 2.71-2.76 (m, 1H). $^{13}$C NMR (75.4 MHz, CDCl$_3$): δ 14.0, 17.7, 22.5, 28.1, 31.7, 54.6, 59.8. Both $^1$H and $^{13}$C NMR spectra are in accordance with ref. [1].

**Threo-2,3-heptanediol** and **erythro-2,3-heptanediol** were obtained by hydrolysis of the corresponding epoxide according to a modified literature procedure.\(^1\)

**Threo-2,3-heptanediol.** A mixture of cis-2,3-epoxyheptane (2.00 g, 17.5 mmol), THF (24 ml) and 0.05 M HClO$_4$ (aq.) (16 ml) was stirred overnight at room temperature. Extraction with CH$_2$Cl$_2$ (3x20 ml), followed by drying of the combined organic layers with brine (30 ml) and Na$_2$SO$_4$, afforded the crude diol which was purified by column chromatography (silica, Et$_2$O/pentane 1:1), yielding a colorless oil (1.04 g, 7.9 mmol, 45%). $^1$H NMR (300 MHz, CDCl$_3$): δ 0.91 (t, $J$ = 6.6 Hz, 3H), 1.19 (d, $J$ = 6.2 Hz, 3H), 1.32-1.50 (m, 6H), 2.17 (bs, 2H), 3.32-3.36 (m, 1H), 3.55-3.63 (m, 1H). $^{13}$C NMR (75.4 MHz,
Substrates and products

CDCl₃): δ 14.0, 19.5, 22.7, 27.7, 33.0, 70.9, 76.2. Both ¹H and ¹³C NMR spectra are in accordance with ref. [1].

Erythro-2,3-heptanediol. As for threo-2,3-heptanediol, except trans-2,3-epoxyheptane was used, yielding a colorless solid (1.49 g, 11.3 mmol, 64%). ¹H NMR (300 MHz, CDCl₃): δ 0.90 (t, J = 7.0 Hz, 3H), 1.12 (d, J = 6.6 Hz, 3H), 1.23-1.50 (m, 6H), 2.43 (bs, 2H), 3.57-3.62 (m, 1H), 3.73-3.81 (m, 1H). ¹³C NMR (75.4 MHz, CDCl₃): δ 14.0, 16.5, 22.7, 28.2, 31.5, 70.4, 74.9. Both ¹H and ¹³C NMR spectra are in accordance with that reported in ref. [1].

Dimethyl cis-2,3-oxiranedicarboxylate. Cis-epoxysuccinic acid was prepared according to the literature procedure, except maleic acid (11.6 g, 100 mmol) was used, yielding the diacid as a colorless solid (8.42 g, 63.8 mmol, 64%). m.p. 145-148 °C (lit.: 148-149 °C). ¹H NMR (400 MHz, D₂O): δ 3.94 (s, 2H). The dimethylester was prepared according to the literature procedure, except using cis-epoxysuccinic acid (2.00 g, 15.1 mmol). Purification by column chromatography (neutral alox, CH₂Cl₂/pentane 2:1) yielded the title compound as a colorless oil (0.35 g, 2.2 mmol, 15%). ¹H NMR (400 MHz, CDCl₃): δ 3.71 (s, 2H), 3.79 (s, 6H), in accordance with that reported in ref. [3]. ¹³C NMR (50.3 MHz, CDCl₃): δ 52.5, 52.7, 166.1.

Dimethyl trans-2,3-oxiranedicarboxylate. Trans-epoxysuccinic acid was prepared according to the literature procedure, except fumaric acid (11.6 g, 100 mmol) was used, yielding the diacid as a colorless solid (6.2 g, 47 mmol, 47%). ¹H NMR (400 MHz, D₂O): δ 3.72 (s, 2H). The dimethylester was prepared according to the literature procedure, except using trans-epoxysuccinic acid (2.00 g, 15.1 mmol). Recrystallisation from CH₂Cl₂/pentane yielded a colorless solid (0.76 g, 4.7 mmol, 31%). m.p. 75.2-75.5 °C (lit.: m.p. 75-76 °C). ¹H NMR (300 MHz, CDCl₃): δ 3.69 (s, 2H), 3.82 (s, 6H). ¹³C NMR (50.3 MHz, CDCl₃): δ 51.9, 53.0, 167.0.

Dimethyl-meso-tartrate. Dimethyl-meso-tartrate was prepared by refluxing a mixture of meso-tartaric acid and excess SOCl₂ in MeOH according to the literature procedure for the synthesis of dimethyl D-tartrate. Dimethyl-meso-tartrate was obtained as a colorless solid (0.49 g, 2.8 mmol, 21%). ¹H NMR (400 MHz, CDCl₃): δ 3.25 (d, J = 5.9 Hz, 2H), 3.81 (s, 6H), 4.58 (d, J = 5.9 Hz, 2H). ¹H NMR (300 MHz, acetone-δ₆): δ 3.70 (s, 6H), 4.48 (s, 4H). ¹³C NMR (50.3 MHz, CDCl₃): δ 53.0, 72.9, 171.4. Both ¹H and ¹³C NMR spectra are in accordance with that reported in ref. [6].

Isolation of cis-cyclooctane diol from the reaction mixture (see Chapter 3, Table 3.8). The catalytic oxidation of cyclooctene (10 mmol) was performed according to general procedure C (see Appendix C). Subsequently, CH₂Cl₂ (10 ml) and saturated aq. NaHCO₃ (10 ml) were added and the organic layer was separated. The aqueous layer was extracted with CH₂Cl₂ (3x10 ml). The combined organic layers were washed with brine (15 ml) and dried on Na₂SO₄. The solvents were evaporated in vacuo. Pentane (5 ml) was added to the residue and the mixture was sonicated for a few minutes. The pentane was decanted and the resulting colorless precipitate was washed with pentane (2x5 ml) yielding cis-cyclooctane diol as a colorless solid (0.66 g, 4.6 mmol, 46%, average of 2 runs). ¹H NMR (400 MHz, CDCl₃) δ 1.48-1.56 (m, 6H), 1.64-1.69 (m, 4H), 1.86-1.96 (m, 2H), 2.06 (br s, 2H), 3.91 (d, 2H). ¹³C NMR (100.6 MHz, CDCl₃) δ 23.72, 26.18, 30.09, 73.10.
Appendix A

Preparation and isolation of suberic acid using cis-1,2-cyclooctanediol as substrate.
H$_2$O$_2$ (30 µl, 0.53 mmol) was added to a mixture of 1 (8.1 mg, 10 µmol) and 2,6-dichlorobenzoic acid (57.3 mg, 0.30 mmol) in CH$_3$CN (7 ml) at room temperature. The mixture was stirred for 20 min at room temperature followed by addition of cis-1,2-cyclooctanediol (0.72 g, 5 mmol) and CH$_3$CN (3 ml). The mixture was cooled to 0°C. H$_2$O$_2$ (50%, 1.13 ml, 20 mmol) was added via syringe pump (0.14 ml/h). The reaction mixture was stirred at 0°C for 1 h after the addition of H$_2$O$_2$ was completed. Water (10 ml) was added and the mixture was adjusted to pH 12 by adding 2 M aq. NaOH. The basic aqueous layer was washed with Et$_2$O (3x15 ml) and was subsequently acidified to pH 1 with 4 M aq. HCl. The acidic aqueous layer was extracted with Et$_2$O (5x15 ml) and the combined organic extracts were washed with brine (20 ml). After drying on anhydrous Na$_2$SO$_4$ the solvents were evaporated in vacuo yielding a colorless solid (367 mg, 42%).

$^1$H NMR (400 MHz, acetone-d$_6$) δ 1.31-1.35 (m, 4H), 1.55-1.58 (m, 4H), 2.25 (t, $J$ = 7.3 Hz, 4H). CI-MS m/z 192 [M+NH$_4$]$^+$.  

2,2-dimethylchromene (7.1). The synthesis was analogous to the preparation of precocene 1 as described in ref. [7]. Molecular sieves (3 Å) were heated at 160°C for 2 h under several vacuum/N$_2$ cycles. After cooling to room temperature, xylene (200 ml) was added, together with phenol (4.28 g, 45.5 mmol), phenylboronic acid (8.9 g, 73.0 mmol), 3-methyl-2-butenal (8.8 ml, 91.2 mmol) and propionic acid (2 ml, 27 mmol). The mixture was heated at reflux under Dean-Stark conditions for 3 days. After cooling to r.t., 20% NH$_4$OAc (150 ml) was added. The organic phase was separated and the aqueous layer was extracted with EtOAc (3x100 ml). The combined organic layers were washed with 0.5 M aq. NaHCO$_3$ (3x75 ml) and brine (100 ml). After drying on anhydrous Na$_2$SO$_4$ the solvents were evaporated in vacuo yielding a dark brown oil. Purification by column chromatography (silica, pentane) yielded 7.1 as a clear, pale yellow oil (2.95 g, 18.4 mmol, 40%). $^1$H NMR (400 MHz, CDCl$_3$) δ 1.43 (s, 6H), 5.60 (d, $J$ = 9.9 Hz, 1H), 6.32 (d, $J$ = 9.9 Hz, 1H), 6.76-6.85 (m, 2H), 6.96-6.98 (m, 1H), 7.08-7.12 (m, 1H), in accordance with that reported in ref. [9]. $^{13}$C NMR (50.3 MHz, CDCl$_3$) δ 27.97, 76.07, 116.27, 120.65, 121.23, 122.27, 126.24, 129.00, 130.67, 152.86. EI-MS m/z 160 [M$^+$]. HRMS (calc. for C$_{11}$H$_{12}$O: 160.089) found: 160.089.

Alternatively, this compound was prepared according to another modified literature procedure. MeMgBr (68 ml, 205 mmol, 3 M in Et$_2$O) was added dropwise using a dropping funnel to a vigorously stirred solution of 1-benzopyran-2-one (10 g, 68.4 mmol) in toluene (500 ml) at 0°C. After the addition was complete, the reaction mixture was stirred for an additional 2 h at the same temperature. The reaction mixture was then poured onto a cold solution of 20% aq. NH$_4$Cl. The organic phase was concentrated in vacuo to remove Et$_2$O and MeOH. The residue (still containing toluene) was heated at reflux overnight under Dean-Stark conditions in the presence of 60 g of silica gel (activated immediately before use at 120°C). The hot reaction mixture was filtered and the residue of silica gel was washed several times with EtOAc. The combined filtrates were concentrated in vacuo. Purification by flash column chromatography (silica, pentane) yielded 2,2-dimethylchromene as a clear oil (7.2 g, 44.9 mmol, 66%).

Cis-2,2-dimethylchromane-3,4-diol (cis-7.3) and trans-2,2-dimethylchromane-3,4-diol (trans-7.5). A mixture of 2a (5.4 mg, 5 µmol), CCl$_3$CO$_2$H (500 µl of a 0.1 mM stock in CH$_3$CN, i.e. 50 µmol), H$_2$O (110 µl) and 2,2'-dimethylchromene (400 µl, 2.5 mmol) in CH$_3$CN (4.5 ml) was cooled to 0°C. H$_2$O$_2$ (50% aq., 240 µl, 4.2 mmol) was added via
Syringe pump over 4 h (60 µl/h) and the reaction mixture was stirred for an additional 1 h after the addition of H₂O₂ was completed. CH₂Cl₂ (10 ml) and 0.5 M aq. NaHCO₃ (10 ml) were added. The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (3x10 ml). The combined organic layers were washed with brine (15 ml). After drying on anhydrous Na₂SO₄ the solvents were evaporated in vacuo. Purification by column chromatography (silica, CH₂Cl₂/MeOH 97.5:2.5) afforded racemic cis-7.3 (Rf 0.30) and racemic trans-7.5 (Rf 0.27).

Cis-7.3 (rac): 152 mg (0.78 mmol, 31%) of a very viscous, almost colorless oil which solidified upon standing. ¹H NMR (400 MHz, CDCl₃) δ 1.29 (s, 3H), 1.49 (s, 3H), 2.03 (d, J = 8.8 Hz, 1H), 2.61 (d, J = 9.9 Hz, 1H), 3.72 (dd, J = 8.4 and 4.4 Hz, 1H), 4.81 (dd, J = 9.5 and 4.0 Hz, 1H), 6.80-6.83 (m, 1H), 6.97-7.01 (m, 1H), 7.18-7.23 (m, 1H), 7.52-7.54 (m, 1H), in accordance with that reported in ref. [9]. ¹³C NMR (50.3 MHz, CDCl₃) δ 23.30, 24.79, 65.24, 71.61, 77.70, 116.89, 121.29, 122.25, 128.83, 129.40, 151.93. EI-MS m/z 194 [M]+. HRMS (calc. for C₁₁H₁₄O₃: 194.094) found: 194.094.

Trans-7.5 (rac): 8 mg (0.04 mmol, 2%) of a very viscous, almost colorless oil which solidified upon standing. ¹H NMR (400 MHz, CDCl₃) δ 1.17 (s, 3H), 1.43 (s, 3H), 3.57 (d, J = 8.8 Hz, 1H), 3.84 (br s, 1H), 4.00 (br s, 1H), 4.54 (d, J = 8.8 Hz), 6.75-6.77 (m, 1H), 6.89-6.92 (m, 1H), 7.14-7.18 (m, 1H), 7.37-7.39 (m, 1H), in accordance with that reported in ref. [9]. ¹³C NMR (50.3 MHz, CDCl₃) δ 18.64, 26.63, 69.61, 76.29, 78.38, 116.78, 120.69, 123.15, 127.34, 129.39, 152.16. EI-MS m/z 194 [M]+. HRMS (calc. for C₁₁H₁₄O₃: 194.094) found: 194.094.

3,4-Epoxy-2,2-dimethylchromane (7.4). A mixture of 2,2-dimethylchromene (200 mg, 1.25 mmol) in CH₂Cl₂ (12 ml) and 0.5 M aq. NaHCO₃ (5 ml) was cooled to 0°C and mCPBA (242 mg, 1.05 mmol) was added in small portions. After the addition was complete, the reaction mixture was stirred for an additional 30 min at 0°C and was subsequently allowed to reach room temperature. The organic layer was separated and washed with 0.5 M NaHCO₃ (5x10 ml), H₂O (10 ml) and brine (10 ml). After drying on anhydrous Na₂SO₄, the solvents were evaporated in vacuo, yielding a mixture of unreacted alkene and epoxide (215 mg, epoxide/alkene ratio: 1.7 as judged from ¹H NMR). For spectroscopic data of the epoxide see e.g. ref. [9] and [10].

2,2-dimethylchroman-3-one (7.7). was prepared according to the literature procedure¹¹ by heating cis-2,2-dimethylchromane-3,4-diol at reflux in the presence of a catalytic amount of p-toluenesulfonic acid in benzene. ¹H NMR (400 MHz, CDCl₃) δ 1.41 (s, 6H), 3.60 (s, 2H), 6.98-7.24 (m, 4H), in accordance with that reported in ref. [11]. For the isomer 2,2-dimethylchroman-4-one, the signal due to the -CH₂- protons are observed at 2.72 ppm, as reported in ref. [12].

**References**

Appendix B

Ligands and complexes
All reagents are of commercial grade (Aldrich, Acros, Fluka, NovaBiochem, Bachem) and used as received unless stated otherwise. Unilever R&D (Vlaardingen, the Netherlands) is acknowledged for the generous gift of the complexes $[\text{Mn}^{	ext{IV}}_2(\mu-\text{O})_3(\text{tmtacn})_2](\text{PF}_6)_2\cdot\text{H}_2\text{O}$, $[\text{Mn}^{	ext{III}}_2(\mu-\text{O})(\mu-\text{CH}_3\text{CO}_2)_2(\text{tmtacn-d}_9)_2](\text{PF}_6)_2\cdot\text{d}_{18,2}$, $[\text{Mn}^{	ext{III,IV}}_2(\mu-\text{O})_2(\text{Me}_4\text{dtne})](\text{PF}_6)_2$ and the ligand tmtacn. The synthesis and characterization of the complex $[\text{Mn}^{	ext{III}}_2(\mu-\text{O})(\mu-\text{CH}_3\text{CO}_2)_2(\text{tmtacn})_2](\text{PF}_6)_2$ $3\text{a}$ has been reported previously.\textsuperscript{1}

Caution! Perchlorate salts of metal complexes incorporating organic ligands are potentially explosive. These compounds should be prepared in small quantities and handled with suitable protective safety guards.

B.1 Ligands

2,3,6-Trichlorobenzoic acid. This compound was prepared according to a reported procedure.\textsuperscript{5} 2,3,6-Trichlorobenzaldehyde (2.00 g, 9.55 mmol) was added to a solution of KMnO$_4$ (1.58 g, 10.0 mmol) in H$_2$O (100 ml) and mixture was stirred at 90°C until the purple permanganate solution was decolorised and a brown suspension was obtained (1 h). The hot suspension was filtered on a glasfilter P4 and was rinsed with hot H$_2$O (3 x 40 ml). The filtrate was acidified with conc. HCl to pH 1 and a colorless precipitate formed. The solvent was evaporated in vacuo and the colorless solid was suspended in 0.1 M aq. HCl (25 ml). After filtration on a glasfilter P4, the colorless residue was dissolved in CHCl$_3$ (50 ml) and this solution was filtered to remove some insoluble material. The solvent was evaporated in vacuo and the title compound was obtained as a colorless solid (1.28 g, 5.68 mmol, 59%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.32 (d, J = 8.6 Hz, 1H), 7.49 (d, J = 8.6 Hz, 1H), 10.13 (br s, 1 H). $^{13}$C NMR (50.3 MHz, CDCl$_3$) $\delta$ 128.74, 129.72, 130.28, 130.35, 132.21, 134.06, 169.31. EI-MS $m/z$ 224 [M]+. HRMS (calc. for C$_7$H$_3$O$_2$Cl$_3$: 223.920) found: 223.921. m.p. 128.3-129.0 °C (lit.\textsuperscript{5} 124-126°C). Elemental analysis (calc. for C$_7$H$_3$O$_2$Cl$_3$) C 37.3% (37.29%), H 1.20 (1.34%).

Ac-D-Phg-OH. Ac-D-Phg-OH was prepared according to a reported procedure.\textsuperscript{6} D-(+)-α-phenylglycine (2.00 g, 13.2 mmol) was suspended in H$_2$O (30 ml) and the resulting suspension was cooled to 0-5°C with ice-water. Subsequently, NaOH (0.53 g, 13.2 mmol) was added and a clear solution was obtained. Acetic anhydride (2.5 ml, 26.4 mmol) was added, immediately followed by a solution of NaOH (1.59 g, 39.8 mmol) in H$_2$O (8 ml) (giving pH 5) and the mixture was stirred at 0-5°C for an additional 15 min. The reaction mixture was then acidified to pH 1 with conc. HCl (aq.). The colorless solid was collected on a glasfilter P4 and was subsequently washed with H$_2$O (3 x 20 ml). After recrystallisation from EtOH/H$_2$O (1:1) colorless needles were obtained (812 mg, 4.20 mmol, 32%). $^1$H NMR (200 MHz, dmso-d$_6$) $\delta$ 1.89 (s, 3H), 5.32 (d, J = 7.7 Hz, 1H), 7.27-7.39 (m, 5H), 8.60 (d, J = 7.7 Hz, 1H), in accordance with literature\textsuperscript{7}. $^{13}$C NMR (50.3 MHz, dmso-d$_6$) $\delta$ 22.24, 56.24, 127.63, 127.89, 128.99, 137.22, 169.07, 171.99. EI-MS $m/z$ 193 [M]$^+$. HRMS (calc. for C$_{10}$H$_{11}$NO$_3$: 193.074) found: 193.073.

Boc-Pro-Pro-OMe. Boc-Pro-OH (10.0 g, 46.4 mmol) was activated in CH$_2$Cl$_2$ (300 ml, freshly distilled from CaH$_2$) under N$_2$ with N-ethyl-N’-(3-dimethylaminopropyl)-carbodiimide (EDC) (9.76 g, 50.9 mmol) and 1-hydroxybenzotriazole hydrate (HOBt)
Ligands and complexes

(6.88 g, 50.9 mmol) and this mixture was stirred at r.t. for 1 h giving a clear, colorless solution (solution A).
H-Pro-OMe.HCl (7.69 g, 46.4 mmol) and N,N-diisopropylethylamine (24.2 ml, 139 mmol) were dissolved in CH₂Cl₂ (400 ml, freshly distilled from CaH₂) under N₂ in a three-necked flask equipped with a dropping funnel, giving a clear, colorless solution (solution B).
Solution A was transferred (under N₂) to the dropping funnel and was subsequently added slowly to solution B (ca. 90 min.) at r.t. with the reaction mixture being cooled in a waterbath. When the addition was complete, the reaction mixture was heated at reflux overnight. After cooling to r.t. the organic layer was washed with brine (1x150 ml), 4 M NaHCO₃ (4x100 ml), 1 M NaHSO₄ (4x100 ml) and brine (1x200 ml) and was dried over anhydrous Na₂SO₄. Evaporation of the solvents in vacuo yielded a very pale yellow oil. Purification by column chromatography (silica, CH₂Cl₂/MeOH 98:2; TLC visualised with ninhydrin dip) yielded Boc-Pro-Pro-OMe as a pale yellow oil (13.7 g, 42.0 mmol, 91%).

1H NMR (400 MHz, CDCl₃) δ 1.39 and 1.44 (2 × s, (C₃H₇)₃, 9H), 1.81-2.23 (m, 8H), 3.35-3.80 (m, 7H), 4.37-4.60 (m, 2H), mixture of rotamers (the Boc-group shows coalescence at 60 °C in dmso-d₆). 13C NMR (100.6 MHz, CDCl₃) δ 23.40, 23.89, 24.82, 24.88, 28.19, 28.35, 28.55, 28.67, 28.89, 29.83, 46.30, 46.34, 46.49, 46.68, 51.90, 51.96, 52.06, 57.53, 58.50, 79.23, 79.26, 153.56, 154.42, 170.95, 171.44, 172.49, 172.77, mixture of rotamers. EI-MS m/z 326 [M]+. HRMS (calc. for C₁₆H₂₆N₂O₅: 326.184) found: 326.185.

Boc-Pro-Pro-OMe (13.7 g, 42.0 mmol) was added to 2 M aq. NaOH (250 ml) and the resulting biphasic mixture was stirred at r.t. for 2 h until all oil had dissolved and TLC (silica, CH₂Cl₂/MeOH 98:2, ninhydrin-dip) showed complete conversion. The basic aqueous layer (pH 14) was washed with CH₂Cl₂ (3x100 ml) and was then acidified (to pH 1) with concentrated HCl (30% aq.). The resulting colorless suspension was extracted with EtOAc (5x75 ml). The combined EtOAc layers were washed with brine (1x100 ml) and dried on anhydrous Na₂SO₄. The solvents were evaporated in vacuo yielding a very sticky foam which was dissolved in a minimum amount of CH₂Cl₂ (40 ml). Pentane (200 ml) was added and the mixture was sonicated for a few minutes until a colorless suspension was obtained. Evaporation of the solvents in vacuo yielded Boc-Pro-Pro-OH as a white solid (10.2 g, 32.7 mmol, 78%). 1H NMR (300 MHz, CD₃CN) δ 1.39 and 1.45 (2 × s, 9H), 1.85-2.41 (m, 8H), 3.38-3.80 (m, 4H), 4.37-4.68 (m, 2H), mixture of rotamers. 13C NMR (50.3 MHz, CD₃CN) δ 23.65, 24.25, 25.04, 27.02, 27.24, 28.37, 28.44, 29.37, 30.20, 46.68, 46.92, 47.33, 57.57, 57.70, 59.91, 59.97, 79.79, 79.94, 153.48, 154.58, 172.16, 172.46, 174.38, 174.66, mixture of rotamers. EI-MS m/z 312 [M]⁺. HRMS (calc. for C₁₅H₂₄N₂O₅: 312.168) found: 312.170.

B.2 Complexes

[ MnIII²⁺(µ-O)(µ-CCl₃CO₂)₂(tmtacn)](PF₆)₂ (2a). Complex 2a was prepared by modification of the general procedure reported by Hage et al.⁸. L-Ascorbic acid (19 mg, 0.105 mmol) in H₂O (1 ml) was added to a solution of 1 (81 mg, 0.10 mmol) and CCl₃CO₂H (35 mg, 0.22 mmol) in H₂O (20 ml) with rapid stirring. The purple precipitate was isolated by filtration and rinsed with Et₂O (3x5 ml). Recrystallisation from CH₃CN by slow diffusion of Et₂O yielded purple crystals (75 mg, 0.07 mmol, 70%). ¹H NMR (400 MHz, CD₃CN) δ 66, 35, 32, 15, -74, -87, -108. ESI-MS m/z 935.0 [2a(PF₆)]⁺, 395.0 [2a]²⁺.
isotope pattern in agreement with the predicted pattern for 6xCl. Elemental analysis (calc. for Mn₂C₂H₂N₆Cl₂O₅PF₆): C 24.8 % (24.4%), H 4.01% (3.87 %), N 7.76 % (7.76 %). FT-IR (in KBr powder): 1720, 1659 cm⁻¹ (-CO₂-). X-band EPR silent, 10 mM in CH₃CN at 77 K. 

\[\text{[C}_{22}\text{H}_{42}\text{Cl}_6\text{Mn}_2\text{N}_6\text{O}_5\]_2+}_2\text{PF}_6^-\ (CP929), M_r = 1083.13, monoclinic, \(P2_1/n\), \(a = 12.2400\) Å, \(b = 15.5582\) Å, \(c = 21.494\) Å, \(\beta = 97.405\) °, \(V = 4059.0\) Å³, \(Z = 4\), \(D_v = 1.772\) g cm⁻³, \(F(000) = 2184\), \(\mu = 11.93\) cm⁻¹, \(\lambda(\text{MoK}α) = 0.71073\) Å, \(T = 100\) K. 29469 reflections measured, \(GooF = 1.030\), \(wR(F) = 0.0791\) for 9313 unique reflections and 664 parameters and \(R(F) = 0.0326\) for 7837 reflections obeying \(F_o \geq 4.0\) \(\sigma(F_o)\) criterion of observability. The asymmetric unit consists of three moieties: a cationic dinuclear Mn-complex and two PF₆⁻ anions.

\[[\text{Mn}^{II}_2(\mu-\text{OH})(\mu-\text{CCl}_3\text{CO}_2)(\text{tmtacn})_2](\text{ClO}_4)\ (2b).\] Complex 2b was prepared by modification of the general procedure reported by Wieghardt et al. Mn(ClO₄)₂·6H₂O (250 mg, 0.69 mmol) was added to a N₂ purged solution of tmtacn (200 mg, 1.16 mmol). After 10 min, CCl₃CO₂Na (278 mg, 1.5 mmol) was added in one portion with rapid stirring. After 1 h, the volume was reduced (by N₂ flow) to half its volume and kept at 6°C to yield white crystals (175 mg, 0.195 mmol, 28%) suitable for single crystal X-ray analysis. \(1^H\) NMR (400 MHz, CD₃CN) only signals observed between -120 and 100 ppm. ESI-MS m/z 791.0 \([2b]^-\), isotope pattern in agreement with predicted pattern for 6xCl. Elemental analysis (calc. for Mn₂C₂H₄N₆Cl₂O₅Na) C 29.7 % (29.6 %), H 4.90% (4.81%), N 9.43 % (9.40%). FT-IR (in KBr powder): 1692 cm⁻¹ (-CO₂-). \[\text{[C}_{22}\text{H}_{43}\text{Cl}_6\text{Mn}_2\text{N}_6\text{O}_5\]_2}^+ \cdot \text{ClO}_4^- \ (CP921), M_r = 893.66, monoclinic, \(Cm\), \(a = 15.695\) Å, \(b = 15.918\) Å, \(c = 15.594\) Å, \(\beta = 104.801\) °, \(V = 3766.6\) Å³, \(Z = 4\), \(D_v = 1.576\) g cm⁻³, \(F(000) = 1832\), \(\mu = 12.19\) cm⁻¹, \(\lambda(\text{MoK}α) = 0.71073\) Å, \(T = 100\) K, 10049 reflections measured, \(GooF = 1.052\), \(wR(F) = 0.1499\) for 5496 unique reflections and 447 parameters, 2 restraints and \(R(F) = 0.0567\) for 4828 reflections obeying \(F_o \geq 4.0\) \(\sigma(F_o)\) criterion of observability. The asymmetric unit consists of four half moieties: two cationic dinuclear Mn-complexes, and two disordered \text{ClO}_4^- anions; all moieties have a crystallographic imposed mirror plane.

\[[\text{Mn}^{II}_2(\mu-\text{OH})(\mu-\text{CCl}_3\text{CO}_2)(\text{tmtacn})_2](\text{PF}_6)\ (2c).\] Hydrazine hydrate (20 µl, 0.2 mmol) was added to a stirred solution of 1 (81 mg, 0.10 mmol) and CCl₃CO₂H (35 mg, 0.22 mmol) in CH₃CN (20 ml). The solution changed from red to light purple to colorless over 30 min. The solvent was evaporated to near dryness and the white precipitate washed with Et₂O yielding 2c as a white solid (84 mg, 0.088 mmol, 88%). ESI-MS m/z 809.0 \([2c]^-\), isotope pattern in agreement with predicted pattern for 6xCl. Elemental analysis (calc. for Mn₂C₂H₄N₆Cl₂O₅PF₆): C 26.5% (27.6%), H 4.23% (4.74%), N 8.79 % (8.78%). FT-IR (in KBr powder): 1695 cm⁻¹ (-CO₂-).
Ligands and complexes

\([\text{Mn}^\text{III} \cdot \text{II}(\mu-\text{O})(\mu-\text{CD}_3\text{CO}_2)(\text{tmtacn})_2](\text{PF}_6)_2\) (3a-d6). As for 2a except \(\text{CD}_3\text{CO}_2\text{D}\) (13.5 mg, 0.21 mmol) was employed, yielding 3a-d6 (43 mg, 0.049 mmol, 49%). \(^1\)H NMR (400 MHz, CD3CN) \(\delta\) 72, 68, 37, 22, -80, -93, -98, in accordance with that reported in ref. [2]. ESI-MS \(m/z\) 737.4 [3a-d6(\text{PF}_6)]\(^+\), 296.2 [3a-d6]\(^2+\). Elemental analysis (calc. for Mn\(_2\)C\(_{22}\)H\(_{42}\)D\(_6\)N\(_6\)O\(_5\)P\(_2\)F\(_{12}\): C 30.07% (29.94%), H 4.47% (5.48%), N 9.47% (9.52%).

\([\text{Mn}^\text{III} \cdot \text{II}(\mu-\text{CD}_3\text{CO}_2)(\text{tmtacn})_2](\text{PF}_6)_2\) (6). As for 2a except \(\text{CD}_3\text{CO}_2\text{D}\) (24 mg, 0.22 mmol) was employed, yielding 6 (75 mg, 0.075 mmol, 75%). \(^1\)H NMR (400 MHz, CD3CN) \(\delta\) 72, 35, 21, 14, 6, -80, -92, -96. ESI-MS \(m/z\) 855.4 [6(\text{PF}_6)]\(^+\), 355.2 [6]\(^2+\). Elemental analysis (calc. for Mn\(_2\)C\(_{32}\)H\(_{52}\)N\(_6\)O\(_5\)P\(_2\)F\(_{12}\): C 36.7% (38.41%), H 5.22% (5.24%), N 8.67% (8.40%). \[\text{C}_{32}\text{H}_{52}\text{Mn}_{2}\text{N}_{6}\text{O}_{5}\]\(^2+\) \((\text{PF}_6)^-\) \((\text{CP904})\), \(M_r = 1088.71\), triclinic, \(P\)-1, \(a = 11.4974(5)\), \(b = 13.7430(6)\), \(c = 16.3508(7)\) Å, \(\alpha = 76.826(1)^\circ\), \(\beta = 76.090(1)^\circ\), \(\gamma = 69.359(1)^\circ\), \(V = 2317.49(17)\) Å\(^3\), \(Z = 2\), \(D_x = 1.560\) g/cm\(^3\), \(F(000) = 1124\), \(\mu = 7.14\) cm\(^{-1}\), \(\lambda(\text{MoK}\_\alpha) = 0.71073\) Å, 22101 reflections measured, \(\text{GooF} = 1.025\), \(wR(\text{F}) = 0.1078\) for 11061 unique reflections and 538 parameters and \(R(F) = 0.0384\) for 10023 reflections obeying \(F_o \geq 4.0\) \(\sigma(F_o)\) criterion of observability. The asymmetric unit consists of five moieties: a cationic dinuclear Mn-complex, two \(\text{PF}_6^-\) anions and two disordered, half ethylacetate solvent molecules.

\([\text{Mn}^\text{III} \cdot \text{II}(\mu-\text{O})(\mu-\text{4-bromobenzoato})(\text{tmtacn})_2](\text{PF}_6)_2\) (7). As for 9 except 4-bromobenzoic acid (44.2 mg, 0.22 mmol) was employed, yielding 7 (90 mg, 0.078 mmol, 78%). \(^1\)H NMR (400 MHz, CD3CN) \(\delta\) 71, 34, 20, 14, 6, -81, -92, -98. ESI-MS \(m/z\) 1011.1 [7(\text{PF}_6)]\(^+\), 433.2 [7]\(^2+\). Isotope pattern in agreement with predicted pattern for 2xBr. Elemental analysis (calc. for Mn\(_2\)C\(_{32}\)H\(_{50}\)Br\(_2\)N\(_6\)O\(_5\)Br\(_2\)P\(_2\)F\(_{12}\): C 33.5% (33.22%), H 4.54% (4.36%), N 7.08% (7.27%). \[\text{C}_{32}\text{H}_{50}\text{Br}_{2}\text{Mn}_{2}\text{N}_{6}\text{O}_{5}\]\(^2+\) \((\text{PF}_6)^-\) \((\text{CP983})\), \(M_r = 1158.40\), monoclinic, \(P_2_1/\text{n}\), \(a = 17.329(2)\), \(b = 19.586(2)\), \(c = 33.522(4)\) Å, \(\beta = 104.403(2)^\circ\), \(V = 11020(2)\) Å\(^3\), \(Z = 8\), \(D_x = 1.396\) g/cm\(^3\), \(F(000) = 4656\), \(\mu = 20.44\) cm\(^{-1}\), \(\lambda(\text{MoK}\_\alpha) = 0.71073\) Å, \(T = 100(1)\) K, 84406 reflections measured, \(\text{GooF} = 1.067\), \(wR(\text{F}) = 0.2365\) for 21538 unique reflections and 1111 parameters and \(R(F) = 0.0803\) for 12278 reflections obeying \(F_o \geq 4.0\) \(\sigma(F_o)\) criterion of observability. The asymmetric unit consists of six moieties: two cationic dinuclear Mn-complexes and four disordered \(\text{PF}_6^-\) anions.

\([\text{Mn}^\text{III} \cdot \text{II}(\mu-\text{4-nitrobenzoato})(\text{tmtacn})_2](\text{PF}_6)_2\) (8). As for 2a except 4-nitrobenzoic acid (36.8 mg, 0.22 mmol) was employed, yielding 8 (30 mg, 0.028 mmol, 28%). \(^1\)H NMR (400 MHz, CD3CN) \(\delta\) 71, 34, 19, 15, 7, -81, -92, -98. ESI-MS \(m/z\) 945.3 [8(\text{PF}_6)]\(^+\), 400.2 [8]\(^2+\). Elemental analysis (calc. for Mn\(_2\)C\(_{32}\)H\(_{50}\)Br\(_2\)N\(_6\)O\(_9\)Br\(_2\)P\(_2\)F\(_{12}\)): C 35.3% (35.22%), H 4.72% (4.62%), N 9.11% (10.28%). \[\text{C}_{32}\text{H}_{50}\text{Mn}_{2}\text{N}_{8}\text{O}_{9}\]\(^2+\) \((\text{PF}_6)^-\) \((\text{CP982})\), \(M_r = 1090.60\), monoclinic, \(C_2/c\), \(a = 33.528(2)\), \(b = 20.104(1)\), \(c = 16.215(1)\) Å, \(\beta = 107.300(1)^\circ\), \(V = 10435.2(10)\) Å\(^3\), \(Z = 8\), \(D_x = 1.388\) g/cm\(^3\), \(F(000) = 4464\), \(\mu = 6.38\) cm\(^{-1}\), \(\lambda(\text{MoK}\_\alpha) = 0.71073\) Å, \(T = 100(1)\) K, 40157 reflections measured, \(\text{GooF} = 1.074\), \(wR(\text{F}) = 0.1532\) for 10248 unique

\(^1\)The measured values for several elemental analyses are not close enough to the calculated values by acceptable standards (+/- 3%). This is due to the presence of fluor in these compounds (PF\(_6^-\) is used as anion in most cases) which makes the elemental analysis measured in our laboratory too inaccurate. Elemental analyses of the same samples by Kolbe - Mikroanalytisches Laboratorium (Mülheim an der Ruhr, Germany) afforded values considerably closer to the calculated ones, indicating that the method used is the problem and not the purity of the samples. Due to cost considerations, however, not all samples were sent for analyses to Kolbe.

185
reflections and 592 parameters and $R(F) = 0.0545$ for 7605 reflections obeying $F_o > 4.0 \sigma(F_o)$ criterion of observability. The asymmetric unit consists of three moieties: a cationic dinuclear Mn-complex and two PF$_6^-$ anions.

$[\text{Mn}^{III}_2(\mu-O)(\mu-\text{BuCO}_2)_2(\text{tmtacn})_2]\text{(PF}_6\text{)}_2$ (9). Hydrazine hydrate (20 µl, 0.2 mmol) was added to a solution of 1 (81 mg, 0.10 mmol) and pivalic acid (22.5 mg, 0.22 mmol) in CH$_3$CN (20 ml) with stirring. The solution was evaporated to dryness, washed with Et$_2$O and recrystallised from CH$_3$CN by slow infusion of Et$_2$O. 9 was obtained as red/purple crystals (85 mg, 0.088 mmol, 88%). $^1$H NMR (400 MHz, CD$_3$CN) $\delta$ 75, 68, 39, 21, 10, -82, -95, -102. ESI-MS $m/z$ 815.3 [9(PF$_6$)]$^+$, 335.3 [9]$^2+$. Elemental analysis (calc. for Mn$_2$C$_{28}$H$_{60}$N$_6$O$_5$P$_2$F$_{12}$): C 35.0% (35.01%), H 6.79% (6.30%), N 8.66% (8.75%).

$[\text{Mn}^{III}_2(\mu-O)(\mu-4$-iodobenzoato)(tmtacn)$_2]\text{(PF}_6\text{)}_2$ (10). As for 2a except 4-iodobenzoic acid (54.6 mg, 0.22 mmol) was employed, yielding 10 (15 mg, 0.012 mmol, 12%). $^1$H NMR (400 MHz, CD$_3$CN) $\delta$ 71, 34, 20, 14, 6, -81, -92, -98. ESI-MS $m/z$ 1107.2 [10(PF$_6$)]$^+$, 481.2 [10]$^2+$. Elemental analysis (calc. for Mn$_2$C$_{32}$H$_{50}$N$_6$O$_5$I$_2$P$_2$F$_{12}$): C 30.8% (30.67%), H 4.33% (4.02%), N 6.84% (6.71%).

$[\text{Mn}_2(\mu-O)(\mu-3$-chlorobenzoato)(tmtacn)$_2]\text{(PF}_6\text{)}_2$ (11). As for 2a except 3-chlorobenzoic acid (34 mg, 0.22 mmol) was employed, yielding 11 (30 mg, 0.028 mmol, 25%). $^1$H NMR (400 MHz, CD$_3$CN) $\delta$ 66, 35, 32, 15, -74, -87, -108. ESI-MS $m/z$ 923.3 [11(PF$_6$)]$^+$, 389.3 [11]$^2+$. Isotope pattern in agreement with predicted pattern for 2xCl. Elemental analysis (calc. for Mn$_2$C$_{32}$H$_{50}$N$_6$Cl$_2$O$_5$P$_2$F$_{12}$): C 36.0% (35.9%), H 4.98% (4.68%), N 7.80% (7.86%).

$[\text{Mn}_2(\mu-O)(\mu-4$-chlorobenzoato)(tmtacn)$_2]\text{(PF}_6\text{)}_2$ (12). As for 2a except 4-chlorobenzoic acid (42 mg, 0.22 mmol) was employed, yielding 12 (75 mg, 0.062 mmol, 62%). $^1$H NMR (400 MHz, CD$_3$CN) $\delta$ 65, 42, 36, 15, -80, -93, -100. ESI-MS $m/z$ 991.3 [12(PF$_6$)]$^+$, 424.3 [12]$^2+$. Isotope pattern in agreement with predicted pattern for 4xCl. Elemental analysis (calc. for Mn$_2$C$_{32}$H$_{48}$N$_6$Cl$_4$O$_5$P$_2$F$_{12}$): C 33.6% (33.7%), H 4.27% (4.22%), N 7.30% (7.38%).

$[\text{Mn}_2(\mu-O)(\mu-2$,6$-dichlorobenzoato)(tmtacn)$_2]\text{(PF}_6\text{)}_2$ (13). As for 2a except 2,6-dichlorobenzoic acid (42 mg, 0.22 mmol) was employed, yielding 13 (50 mg, 0.044 mmol, 40%). $^1$H NMR (400 MHz, CD$_3$CN) $\delta$ 65, 42, 36, 15, -80, -93, -100. ESI-MS $m/z$ 991.3 [13(PF$_6$)]$^+$, 424 [13]$^2+$. Isotope pattern in agreement with predicted pattern for 4xCl. Elemental analysis (calc. for Mn$_2$C$_{32}$H$_{48}$N$_6$Cl$_4$O$_5$P$_2$F$_{12}$): C 33.6% (33.7%), H 4.47% (4.22%), N 7.51% (7.38%).

$[\text{Mn}_2(\mu-O)(\mu-2$,4$-dichlorobenzoato)(tmtacn)$_2]\text{(PF}_6\text{)}_2$ (14). As for 2a except 2,4-dichlorobenzoic acid (42 mg, 0.22 mmol) was employed, yielding 14 (75 mg, 0.062 mmol, 62%). $^1$H NMR (400 MHz, CD$_3$CN) $\delta$ 65, 42, 36, 15, -80, -93, -100. ESI-MS $m/z$ 991.3 [14(PF$_6$)]$^+$, 424.3 [14]$^2+$. Isotope pattern in agreement with predicted pattern for 4xCl. Elemental analysis (calc. for Mn$_2$C$_{32}$H$_{48}$N$_6$Cl$_4$O$_5$P$_2$F$_{12}$): C 33.6% (33.7%), H 4.47% (4.22%), N 7.51% (7.38%).

$[\text{Mn}_2(\mu-O)(\mu-2$,4$,6$-trichlorobenzoato)(tmtacn)$_2]\text{(PF}_6\text{)}_2$ (15). As for 2a except 2,4,6-trichlorobenzoic acid (46 mg, 0.22 mmol) was employed, yielding 15 (75 mg, 0.062 mmol, 62%). $^1$H NMR (400 MHz, CD$_3$CN) $\delta$ 66, 35, 32, 15, -74, -87, -108. ESI-MS $m/z$ 1059.0 [15(PF$_6$)]$^+$, 457.3 [15]$^2+$. Isotope pattern in agreement with predicted pattern for
Ligands and complexes

6xCl. Elemental analysis (calc. for Mn$_2$C$_3$H$_{40}$N$_6$O$_7$P$_2$F$_{12}$) C 31.4 % (31.8 %), H 4.05% (3.81 %), N 7.08 % (6.96 %).

[Mn$^{III}_2$(µ-O)(µ-4-fluorobenzoato)$_2$(tmtacn)$_2$](PF$_6$)$_2$ (16). As for 2a except 4-fluorobenzoic acid (29.4 mg, 0.21 mmol) was employed, yielding (54 mg, 0.052 mmol, 52%). $^1$H NMR (400 MHz, CD$_3$CN) δ 72, 35, 20, 13, 6, -80, -92, -97. ESI-MS m/z 891.3 [16(PF$_6$)$_2$]$^+$, 373.2 [16]$^2+$. Elemental analysis (calc. for Mn$_2$C$_3$H$_{40}$N$_6$O$_7$P$_2$F$_{12}$): C 37.0% (37.06%), H 4.39% (4.48%), N 7.75 % (7.84%).

[Mn$^{III}_2$(µ-O)(µ-2,4-difluorobenzoato)$_2$(tmtacn)$_2$](PF$_6$)$_2$ (17). As for 2a except 2,4-difluorobenzoic acid (70 mg, 0.44 mmol) and 1 (162 mg, 0.20 mmol) were employed, yielding (17) (100 mg, 0.093 mmol, 47 %). $^1$H NMR (400 MHz, CD$_3$CN) δ 66, 35, 32, 15, -74, -87, -108. $^{19}$F NMR (121.5 MHz) δ -55, -84. ESI-MS m/z 927.3 [17(PF$_6$)$_2$]$^+$, 391.3 [17]$^2+$. Elemental analysis (calc. for Mn$_2$C$_3$H$_{40}$N$_6$O$_7$P$_2$F$_{16}$): C 35.9 % (35.8%), H 4.39% (4.48%), N 7.10 % (7.84%).

[Mn$^{III}_2$(µ-O)(µ-2,6-difluorobenzoato)$_2$(tmtacn)$_2$](PF$_6$)$_2$ (18). As for 2a except 2,6-difluorobenzoic acid (35 mg, 0.22 mmol) was employed, yielding (18) (85 mg, 0.079 mmol, 72 %). $^1$H NMR (400 MHz, CD$_3$CN) δ 70, 34, 19, 7, -79, -90, -100. $^{19}$F NMR (121.5 MHz) δ -58. ESI-MS m/z 927.3 [18(PF$_6$)$_2$]$^+$, 391.2 [18]$^2+$. Elemental analysis (calc. for Mn$_2$C$_3$H$_{40}$N$_6$O$_7$P$_2$F$_{16}$): C 37.3% (35.8%), H 5.27% (4.48%), N 7.10 % (7.84%).

[Mn$^{III}_2$(µ-O)(µ-3,4-difluorobenzoato)$_2$(tmtacn)$_2$](PF$_6$)$_2$ (19). As for 2a except 3,4-difluorobenzoic acid (35 mg, 0.22 mmol) was employed, yielding (19) (75 mg, 0.07 mmol, 63%). $^1$H NMR (400 MHz, CD$_3$CN) δ 70, 35, 34, 18, 7.5, 5.5, -79, -90, -96. $^{19}$F NMR (121.5 MHz) δ -127.5, -104.5. ESI-MS m/z 927.3 [19(PF$_6$)$_2$]$^+$, 390.6 [19]$^2+$. Elemental analysis (calc. for Mn$_2$C$_3$H$_{40}$N$_6$O$_7$P$_2$F$_{16}$): C 36.3% (35.8%), H 4.52% (4.48%), N 7.50% (7.84%).

[Mn$^{III}_2$(µ-O)(µ-3,5-difluorobenzoato)$_2$(tmtacn)$_2$](PF$_6$)$_2$ (20). As for 2a except 3,5-difluorobenzoic acid (70 mg, 0.44 mmol) and 1 (162 mg, 0.20 mmol) were employed, yielding (20) (125 mg, 0.12 mmol, 60%). $^1$H NMR (400 MHz, CD$_3$CN) δ 70, 35, 34, 18, 7, 5.5, -79, -90, -96. $^{19}$F NMR (121.5 MHz) δ -127.5, -104.5. ESI-MS m/z 927.3 [20(PF$_6$)$_2$]$^+$, 390.6 [20]$^2+$. Elemental analysis (calc. for Mn$_2$C$_3$H$_{40}$N$_6$O$_7$P$_2$F$_{16}$): C 36.0% (35.8%), H 4.52% (4.48%), N 7.95% (7.84%).

[Mn$^{III}_2$(µ-O)(µ-3-hydroxybenzoato)$_2$(tmtacn)$_2$](PF$_6$)$_2$ (21). As for 2a except 3-hydroxybenzonic acid (31 mg, 0.22 mmol) was employed, yielding (21) (70 mg, 0.068 mmol, 68 %). $^1$H NMR (400 MHz, CD$_3$CN) δ 70, 35, 20, 14, 7, 5, 3, -1, -80, -92, -96. ESI-MS m/z 887.3 [21(PF$_6$)$_2$]$^+$, 371.1 [21]$^2+$. Elemental analysis (calc. for Mn$_2$C$_3$H$_{40}$N$_6$O$_7$P$_2$F$_{12}$): C 37.31% (37.22%), H 5.14% (5.08%), N 8.06% (8.14%).

[Mn$^{III}_2$(µ-O)(µ-4-hydroxybenzoato)$_2$(tmtacn)$_2$](PF$_6$)$_2$ (22). As for 2a except 4-hydroxybenzonic acid (31 mg, 0.22 mmol) was employed, yielding (22) (72 mg, 0.07 mmol, 63 %). $^1$H NMR (400 MHz, CD$_3$CN) δ 72, 35, 19, 13.5, 8, -1, -80, -95. ESI-MS m/z 887.3 [22(PF$_6$)$_2$]$^+$, 371.3 [22]$^2+$. Elemental analysis (calc. for Mn$_2$C$_3$H$_{40}$N$_6$O$_7$P$_2$F$_{12}$): C 34.5% (37.2%), H 5.18% (5.04%), N 7.56 % (8.14%).

[Mn$^{III}_2$(µ-O)(µ-2-methoxybenzoato)$_2$(tmtacn)$_2$](PF$_6$)$_2$ (23). As for 9 except 2-methoxybenzonic acid (33.5 mg, 0.22 mmol) was employed, yielding (23) (75 mg, 0.07 mmol, 63%). $^1$H NMR (400 MHz, CD$_3$CN) δ 72, 35, 34, 18, 7, 5.5, -79, -90, -96. $^{19}$F NMR (121.5 MHz) δ -127.5, -104.5. ESI-MS m/z 927.3 [23(PF$_6$)$_2$]$^+$, 390.6 [23]$^2+$. Elemental analysis (calc. for Mn$_2$C$_3$H$_{40}$N$_6$O$_7$P$_2$F$_{16}$): C 36.0% (35.8%), H 4.52% (4.48%), N 7.50% (7.84%).

187
Appendix B

0.071 mmol, 71%). $^1$H NMR (400 MHz, CD$_3$CN) $\delta$ 71, 35, 21, 15, 13, 6, 0, -80, -94. ESI-MS m/z 915.4 $^{[23]}$[(PF$_6$)$_2$], 385.3 $^{[23]}$[(PF$_6$)$_2$]. Elemental analysis (calc. for Mn$_2$C$_3$H$_{36}$N$_6$O$_7$P$_2$F$_{12}$): C 38.8% (38.48%), H 5.49% (5.32%), N 8.06% (7.92%).

[Mn$^{III}_2$(µ-O)(µ-4-methoxybenzoato)$_2$(tmtacn)$_2$][PF$_6$]$_2$ (24). As for 2a except 4-methoxybenzoic acid (33.5 mg, 0.22 mmol) was employed, yielding 24 (36 mg, 0.034 mmol, 34%). $^1$H NMR (400 MHz, CD$_3$CN) $\delta$ 72, 36, 21, 13, 6, -80, -92, -95. ESI-MS m/z 915.4 $^{[24]}$[(PF$_6$)$_2$], 385.3 $^{[24]}$[(PF$_6$)$_2$]. Elemental analysis (calc. for Mn$_2$C$_3$H$_{36}$N$_6$O$_7$P$_2$F$_{12}$): C 38.8% (38.48%), H 5.64% (5.32%), N 7.84% (7.92%).

[Mn$^{III}_2$(µ-O)(µ-3-cyanobenzoato)$_2$(tmtacn)$_2$][PF$_6$]$_2$ (25). As for 2a except 3-cyanobenzoic acid (32.4 mg, 0.22 mmol) was employed, yielding 25 (40 mg, 0.038 mmol, 38%). $^1$H NMR (400 MHz, CD$_3$CN) $\delta$ 71, 35, 33, 18, 14, 7, -80, -92, -99. ESI-MS m/z 905.3 $^{[25]}$[(PF$_6$)$_2$], 380.3 $^{[25]}$[(PF$_6$)$_2$]. Elemental analysis (calc. for Mn$_2$C$_3$H$_{30}$N$_8$O$_5$P$_2$F$_{12}$): C 38.5% (38.85%), H 5.26% (4.80%), N 10.19% (10.67%).

[Mn$^{III}_2$(µ-O)(µ-2,4,6-trimethylbenzoato)$_2$(tmtacn)$_2$][PF$_6$]$_2$ (26). As for 2a except 2,4,6-trimethylbenzoic acid (36.1 mg, 0.22 mmol) was employed, yielding 26 (80 mg, 0.074 mmol, 74%). $^1$H NMR (400 MHz, CD$_3$CN) $\delta$ 73, 68, 34, 26, 20, 14, 11, -82, -87, -95. ESI-MS m/z 939.6 $^{[26]}$[(PF$_6$)$_2$], 397.4 $^{[26]}$[(PF$_6$)$_2$]. Elemental analysis (calc. for Mn$_2$C$_3$H$_{44}$N$_6$O$_5$P$_2$F$_{12}$): C 43.1% (42.05%), H 6.32% (5.95%), N 8.17% (7.75%).

[Mn$^{III}_2$(µ-O)(µ-O$_2$C(CH$_2$)$_3$CO$_2$)(tmtacn)$_2$][PF$_6$]$_2$ (27). As for 2a except glutaric acid (14 mg, 0.106 mmol) was employed, yielding 27 (40 mg, 0.045 mmol, 45%). $^1$H NMR (400 MHz, CD$_3$CN) $\delta$ 74, 70, 40, 19, 10, -76, -88, -102. ESI-MS m/z 743.5 $^{[27]}$[(PF$_6$)$_2$], 447.3 $^{[27]}$[(PF$_6$)$_2$], 299.4 $^{[27]}$[(PF$_6$)$_2$]. Elemental analysis (calc. for Mn$_2$C$_3$H$_{26}$N$_6$O$_5$P$_2$F$_{12}$): Mn 12.35% (12.32%), C 31.2% (31.0%), H 5.54% (5.39%), N 9.35% (9.44%).

[Mn$^{III}_2$(µ-O)(µ-2-hydroxybenzoato)(tmtacn)$_2$][PF$_6$]$_2$ (28). As for 2a except 2-hydroxybenzoic acid (31 mg, 0.22 mmol) was employed and the mauve precipitate was removed from water very quickly, yielding 28 (11 mg, 0.011 mmol, 11%). UV-Vis: 483 nm, 525 nm, 725 nm (shoulder) (see also Figure 6.4 and 6.5, Chapter 6). ESI-MS m/z 887.3 $^{[28]}$[(PF$_6$)$_2$], 371.2 $^{[28]}$[(PF$_6$)$_2$], 362.2 $^{[28]}$[(PF$_6$)$_2$]. Elemental analysis (calc. for Mn$_2$C$_{16}$H$_{26}$N$_3$O$_3$PF$_6$): Mn 10.72% (10.85%), C 37.7% (37.8%), H 5.23% (4.93%), N 8.22% (8.28%).

[Mn$^{III}_2$(µ-O)(µ-BrCH$_2$CO$_2$)(tmtacn)$_2$][PF$_6$] (30). As for 2a except bromoacetic acid (30.6 mg, 0.22 mmol) was employed, yielding 30 (70 mg, 0.068 mmol, 68%). $^1$H NMR (400 MHz, CD$_3$CN) $\delta$ 70, 68, 37, 35, 19, -79, -92, -104. ESI-MS m/z 887.0 $^{[30]}$[(PF$_6$)$_2$], 371.2 $^{[30]}$[(PF$_6$)$_2$]. Elemental analysis (calc. for Mn$_2$C$_{22}$H$_{46}$N$_6$O$_5$Br$_2$P$_2$F$_{12}$): C 25.8% (25.55%), H 4.43% (4.48%), N 8.14% (8.13%).
Ligands and complexes

\[ \text{[Mn}^{III}(\mu-O)(\mu-Boc-\text{Phg})_2(\text{tmtacn})_2](\text{PF}_6)_2 \] (31). As for 2a except 1 (160 mg, 0.20 mmol) and Boc-Phg-OH (100.6 mg, 0.40 mmol) were employed, yielding 31 (86.1 mg, 0.068 mmol, 34%). \(^1^H\) NMR (400 MHz, CD\(_{3}\)CN) \(\delta\) 75, 72, 68, 66, 61, 44, 40, 31, 24, 15, 10, 9, 7, -78, -80, -91, -93, -103. ESI-MS \(m/z\) 1113.6 \([31(\text{PF}_6)]^+\), 484.5 \([31]^2+\). Elemental analysis (calc. for Mn\(_2\)C\(_{44}\)H\(_{74}\)N\(_8\)O\(_9\)P\(_2\)F\(_{12}\)): C 41.64% (41.98%), H 6.05% (5.92%), N 8.80% (8.90%).

\[ \text{[Mn}^{III}(\mu-O)(\mu-Boc-\text{Phe})_2(\text{tmtacn})_2](\text{PF}_6)_2 \] (32). As for 2a except Boc-Phe-OH (106.1 mg, 0.40 mmol) and 1 (162 mg, 0.20 mmol) were employed, yielding 32 (64 mg, 0.050 mmol, 25%). \(^1^H\) NMR (400 MHz, CD\(_3\)CN) \(\delta\) 81, 75, 69, 58, 41, 37, 33, 22, 20, 9, 8, 7.5, 7.3, 7.2, -73, -82, -90, -104. ESI-MS \(m/z\) 1141.6 \([32(\text{PF}_6)]^+\), 498.3 \([32]^2+\). Elemental analysis (calc. for Mn\(_2\)C\(_{46}\)H\(_{78}\)N\(_8\)O\(_9\)P\(_2\)F\(_{12}\)): C 43.41% (42.93%), H 6.01% (6.11%), N 8.45% (8.71%).

\[ \text{[Mn}^{III}(\mu-O)(\mu-Boc-\text{D-Pro})_2(\text{tmtacn})_2](\text{PF}_6)_2 \] (33). As for 2a except Boc-D-Pro-OH (86.1 mg, 0.40 mmol) and 1 (162 mg, 0.20 mmol) were employed, yielding 33 (98 mg, 0.084 mmol, 42%). \(^1^H\) NMR (400 MHz, CD\(_3\)CN) \(\delta\) 88, 84, 76, 61, 50, 44, 29, 26, 12, 9, 6, 5, 4.2, 4.1, -80, -87, -98, -104. ESI-MS \(m/z\) 1041.6 \([33(\text{PF}_6)]^+\), 448.5 \([33]^2+\). Elemental analysis (calc. for Mn\(_2\)C\(_{38}\)H\(_{74}\)N\(_8\)O\(_9\)P\(_2\)F\(_{12}\)): C 36.99% (38.46%), H 6.34% (6.28%), N 9.47% (9.44%).

\[ \text{[Mn}^{III}(\mu-O)(\mu-Boc-\text{Ala})_2(\text{tmtacn})_2](\text{PF}_6)_2 \] (34). As for 2a except Boc-Ala-OH (75.7 mg, 0.40 mmol) and 1 (162 mg, 0.20 mmol) were employed, yielding 34 (41 mg, 0.036 mmol, 18%). \(^1^H\) NMR (400 MHz, CD\(_3\)CN) \(\delta\) 79, 72, 61, 59, 44, 36, 22, 12, -72, -83, -87, -104. ESI-MS \(m/z\) 989.5 \([34(\text{PF}_6)]^+\), 422.5 \([34]^2+\). Elemental analysis (calc. for Mn\(_2\)C\(_{34}\)H\(_{70}\)N\(_8\)O\(_9\)P\(_2\)F\(_{12}\)): C 34.93% (35.99%), H 6.38% (6.22%), N 9.60% (9.87%).

\[ \text{[Mn}^{III}(\mu-O)(\mu-\text{Ac-D-Phg})_2(\text{tmtacn})_2](\text{PF}_6)_2 \] (35). As for 2a except 1 (160 mg, 0.20 mmol) and Ac-D-Phg-OH (77.3 mg, 0.40 mmol) were employed, yielding 35 (109.2 mg, 0.096 mmol, 48%). \(^1^H\) NMR (400 MHz, CD\(_3\)CN) \(\delta\) 76, 68, 66, 45, 40, 32, 30, 23, 15, 11, 9, -79, -87, -96, -104. ESI-MS \(m/z\) 997.5 \([35(\text{PF}_6)]^+\), 426.4 \([35]^2+\). Elemental analysis (calc. for Mn\(_2\)C\(_{38}\)H\(_{62}\)N\(_8\)O\(_7\)P\(_2\)F\(_{12}\)): C 39.68% (39.94%), H 5.53% (5.47%), N 9.59% (9.81%).

B.3 References

Appendix B

Appendix C
Measurements
Although the catalytic oxidation reactions were performed typically at 0 °C, spectroscopic investigations were performed typically at 20 °C for practical reasons. Several cross-checks and controls were performed to take this temperature difference into account. At higher temperatures (i.e. 20 °C) a decreased lag period is observed (30-45 min), however, overall conversion and turnover numbers are not affected significantly, although the amount of cis-diol is somewhat reduced due to increased overoxidation. Similar to the results obtained at 0 °C, the lag period for both initiation of the reaction and formation of, e.g., 2a coincide.

C.1 Catalysis experiments

All catalytic oxidation reactions were performed *in duplo*.

**General procedure (A).** The alkene (10 mmol), 1,2-dichlorobenzene (internal standard, 735 mg, 5.0 mmol), the appropriate Mn₂-dimer (10 µmol) and co-catalyst (typically 0.10 mmol) in CH₃CN (10 ml) was cooled to 0°C. H₂O₂ (50%, 0.74 ml, 13 mmol) was added via syringe pump over 6 h (0.12 ml/h). The reaction mixture was stirred at 0°C for 1 h after the addition of H₂O₂ was completed, prior to sampling by GC.

**General procedure (B) for catalyst pretreatment (employing carboxylic acids in general).** H₂O₂ (30 µl, 0.53 mmol) was added to a mixture of 1,2-dichlorobenzene (735 mg, 5.0 mmol), 1 (8.1 mg, 10 µmol) and carboxylic acid (0.10 mmol) in CH₃CN (7 ml) at room temperature. The mixture was stirred for 20 min, after which the alkene (10 mmol) was added together with CH₃CN (3 ml) and the mixture was cooled to 0°C. H₂O₂ (0.71 ml, 12.5 mmol) was added via syringe pump (0.12 ml/h). The reaction mixture was stirred at 0°C for 1 h after the addition of H₂O₂ was completed, prior to sampling by GC.

**General procedure (C) for catalyst pretreatment (employing 2,6-dichlorobenzoic acid).** H₂O₂ (30 µl, 0.53 mmol) was added to a mixture of 1,2-dichlorobenzene (735 mg, 5.0 mmol), 1 (8.1 mg, 10 µmol) and 2,6-dichlorobenzoic acid (0.30 mmol) in CH₃CN (7 ml) at room temperature. The mixture was stirred for 20 min at room temperature followed by addition of the alkene (10 mmol) and CH₃CN (3 ml). The mixture was cooled to 0°C. H₂O₂ (1.00 ml, 17.6 mmol) was added via syringe pump (0.14 ml/h). The reaction mixture was stirred at 0°C for 1 h after the addition of H₂O₂ was completed, prior to sampling by GC.

**Procedure (D) for the catalytic oxidation of dimethylmaleate and dimethylfumarate.** H₂O₂ (30 µl, 0.53 mmol) was added to a mixture of 1,2-dichlorobenzene (0.368 mg, 2.5 mmol), 1 (8.1 mg, 10 µmol) and co-catalyst (salicylic acid and trichloroacetic acid: 0.10 mmol; 2,6-dichlorobenzoic acid: 0.30 mmol) in CH₃CN (7 ml) at room temperature. The mixture was stirred for 20 min, after which the alkene (5 mmol) was added together with CH₃CN (3 ml). H₂O₂ (0.34 ml, 6.0 mmol) was added via syringe pump (0.06 ml/h) at room temperature. The reaction mixture was stirred at r.t. for 1 h after the addition of H₂O₂ was completed, prior to sampling by GC.

Under these conditions, using CCl₃CO₂H as additive, cyclooctene gives: 79% conversion, 122 t.o.n. epoxide, 166 t.o.n. *cis*-diol (mass-balance: 78%).

**Procedure (E) for ¹⁸O isotopic labelling studies.** To CH₃CN (300 µl) was added 1,2-dichlorobenzene (100 µl of a 250 mM stock in CH₃CN, *i.e.* 25 µmol), the appropriate
Measurements

MnIII2-complex (50 µl of a 10 mM stock solution in CH3CN, i.e. 0.5 µmol), carboxylic acid (50 µl of a 100 mM stock solution in CH3CN, i.e. 5 µmol) and cyclooctene (65 µl, 500 µmol) and the reaction mixture was cooled to 0°C. H2O2 (2% in H2O, 4x45 µl, 106 µmol) was added at t = 0, 15, 30 and 45 min. Samples for both GC analysis (to determine t.o.n.) and GC-MS (CI) (to determine 18O isotopic composition of the products) were taken at t = 60 min.

Procedure (F) for 18O isotopic labelling studies (second phase 1/oxalic acid). To examine the 18O isotopic labelling of the cis-diol and epoxide products during the second phase of the 1/oxalic acid catalysed reaction, the reaction was first performed according to general procedure A employing cis-2-heptene (5 mmol) as substrate. H2O2 (50 w/w%, 4x30 µl, 2.1 mmol) was added every 15 min during one hour. The reaction mixture was then left overnight and the presence of a MnIII2 bis(carboxylato) complex was confirmed by UV-Vis spectroscopy. Part of this reaction volume (500 µl) was taken and subjected to procedure E using cyclooctene (250 µmol) as substrate.

Procedure (G) for the catalytic oxidation of 2,2-dimethylchromene. 2,2-Dimethylchromene (100 mg, 624 µmol), 1,2-dichlorobenzene (45.9 mg, 312 µmol), the appropriate Mn2-dimer (2.5 µmol) and chiral carboxylic acid (typically 25 µmol) were dissolved in a mixture of CH3CN (2.25 ml) and H2O (0.25 ml). This mixture was cooled (typically) to 0°C. A solution of H2O2 (50 w/w%) in CH3CN (250 µl of a 4.2 M solution, i.e. 1.7 equiv. H2O2 w.r.t. substrate) was added via syringe pump over 4 h (62.5 µl/h). The reaction mixture was stirred at 0°C for 1 h after the addition of H2O2 was completed, prior to sampling by GC and HPLC.

Procedure (H) for the screening of chiral carboxylic acids (in scintillation vials) for the enantioselective cis-dihydroxylation of 2,2-dimethylchromene. H2O2 (7.5 µl, 132 µmol) was added at room temperature to a mixture of 1,2-dichlorobenzene (1 ml of a 312 mM stock in CH3CN, i.e. 312 µmol), I (1 ml of a 2.5 mM stock in CH3CN, i.e. 2.5 µmol), CH3CN (0.25 ml) and chiral carboxylic acid (156 µmol). The mixture was stirred for 20 min, followed by addition of 2,2-dimethylchromene (100 µl, 100 mg, 625 µmol) and H2O (0.25 ml). H2O2 (50%, 4x15 µl, 1060 µmol) was added in four portions at t = 0, 1, 2 and 3 h at room temperature. The reaction mixture was stirred for 1 h after the addition of H2O2 was completed, prior to sampling by GC.

To determine the ee of both the cis- and trans-diol and the cis/trans-diol ratio by HPLC, a small sample of the diols was isolated via preparative TLC. A small sample of the reaction mixture (25 µl) was separated on a TLC plate (5x10 cm, silica, CH3Cl/MeOH 97.5 : 2.5). After drying in the air (10-15 min), 0.5 cm of the TLC plate was cut off and stained with Ce/Mo-dip (the diols turn blue, Rf ~ 0.25-0.3). The area containing the diols was scraped off from the undeveloped TLC plate and this silica (containing the diols) was suspended in n-heptane/IPA (96:4). The resulting suspension was filtered on a plug of anhydrous Na2SO4 (1 cm) and the filtrate was collected in a sample vial (equipped with 0.3 ml glass insert) and subjected to HPLC analysis.
C.2 Gas chromatography

GC analyses were performed on an Agilent 6890 Gas Chromatograph equipped with a HP-1 dimethyl polysiloxane column (30 m × 0.25 mm × 0.25 µm). Peak identification and calibration were performed using independent samples (either purchased from a commercial supplier or independently synthesized, see Appendix A). Conversion and turnover numbers were determined in duplo employing 1,2-dichlorobenzene or bromobenzene as internal standard. Before and after each series of catalytic runs the calibrations were checked in duplo with two known, independent samples (the values found were +/- 10% of their expected values).

**Benzylalcohol.** Column: HP-1 (30 m × 0.25 mm × 0.25 µm), oven temp.: 5 min at 100°C, 10°C/min to 200°C, 5 min at 200°C, 25°C/min to 100°C (inlet: 250°C, detector: 250°C). Benzaldehyde (2.93 min), benzylalcohol (3.70 min), 1,2-dichlorobenzene (internal standard, 3.92 min), benzoic acid (6.59 min).

**Cyclooctane.** Column: HP-1 (30 m × 0.25 mm × 0.25 µm), oven temp.: 5 min at 100°C, 10°C/min to 200°C, 5 min at 200°C, 25°C/min to 100°C (inlet: 250°C, detector: 250°C). Cyclooctane (2.82 min), 1,2-dichlorobenzene (internal standard, 3.94 min), cyclooctanone (5.34 min), cyclooctanol (5.95 min).

**Cyclooctene.** Column: HP-1 (30 m × 0.25 mm × 0.25 µm), oven temp.: 5 min at 100°C, 10°C/min to 200°C, 5 min at 200°C, 25°C/min to 100°C (inlet: 250°C, detector: 250°C). Cyclooctene (2.64 min), 1,2-dichlorobenzene (internal standard, 3.94 min), cyclooctene oxide (5.21 min), α-hydroxycyclooctanone (not calibrated, 7.32 min), trans-1,2-cyclooctanediol (not calibrated, 9.11 min), cis-1,2-cyclooctanediol (9.28 min).

**Cyclopentene.** Column: HP-1 (30 m × 0.25 mm × 0.25 µm), oven temp.: 5 min at 40°C, 5°C/min to 70°C, 2 min at 70°C, 25°C/min to 200°C, 2 min at 200°C, 25°C/min to 40°C (inlet: 250°C, detector: 250°C). Cyclopentene (not calibrated, same retention time as solvent peak), cyclopentene oxide (4.30 min), 2-cyclopenten-1-one (not calibrated, 6.72 min), cis-1,2-cyclopentanediol (12.68 min), trans-1,2-cyclopentanediol (not calibrated, 13.20 min), 1,2-dichlorobenzene (internal standard, 14.40 min).

**2,2-Dimethylchromene.** Column: HP-1 (30 m × 0.25 mm × 0.25 µm), oven temp.: 5 min at 100°C, 10°C/min to 250°C, 10 min at 250°C, 25°C/min to 100°C (inlet: 250°C, detector: 250°C). 1,2-Dichlorobenzene (internal standard, 3.93 min), 2,2-dimethylchromene (7.33 min), 2,2-dimethylchroman-3-one (not calibrated, 9.04 min), cis-2,2-dimethylchromane-3,4-diol (not calibrated, 12.47 min, partially decomposes to 2,2-dimethylchroman-3-one), trans-2,2-dimethylchromane-3,4-diol (not calibrated, 12.72 min, partially decomposes to 2,2-dimethylchroman-3-one), 3,4-epoxy-2,2-dimethylchromane (completely decomposes to 2,2-dimethylchroman-3-one).

**Dimethylmaleate and dimethylfumarate.** Column: HP-1 (30 m × 0.25 mm × 0.25 µm), oven temp.: 5 min at 85°C, 5°C/min to 100°C, 25°C/min to 200°C, 2 min at 200°C, 25°C/min to 85°C (inlet: 250°C, detector: 250°C). Dimethylmaleate (4.92 min), dimethylfumarate (5.19 min), 1,2-dichlorobenzene (internal standard, 5.72 min), dimethyl-
Measurements

cis-2,3-oxiranedicarboxylate (8.24 min), dimethyl-trans-2,3-oxiranedicarboxylate (8.49 min), dimethyl-meso-tartrate (9.49 min), dimethyl-D,L-tartrate (9.56 min).

Cis- and trans-2-heptene. Column: HP-1 (30 m × 0.25 mm × 0.25 µm), oven temp.: 7.5 min at 35°C, 10°C/min to 130°C, 25°C/min to 250°C, 5 min at 250°C, 25°C/min to 35°C (inlet: 200°C, detector: 250°C). Trans-2-heptene (4.58 min), cis-2-heptene (4.81 min), racemic trans-2,3-epoxyheptane (10.17 min), racemic cis-2,3-epoxyheptane (10.92 min), 1,2-dichlorobenzene (internal standard, 14.39 min), racemic threo-2,3-heptanediol (15.03 min), racemic erythro-2,3-heptanediol (15.22 min).

n-Octane. Column: HP-1 (30 m × 0.25 mm × 0.25 µm), oven temp.: 5 min at 100°C, 10°C/min to 200°C, 5 min at 200°C, 25°C/min to 100°C (inlet: 250°C, detector: 250°C). n-Octane (2.06 min), 1,2-dichlorobenzene (internal standard, 3.94 min).

1-Octene. Column: HP-1 (30 m × 0.25 mm × 0.25 µm), oven temp.: 7.5 min at 40°C, 10°C/min to 130°C, 2 min at 130°C, 25°C/min to 225°C, 5 min at 225°C, 25°C/min to 40°C (inlet: 250°C, detector: 250°C). 1-Octene (6.74 min), 1,2-epoxyoctane (13.41 min), 1,2-dichlorobenzene (internal standard, 13.75 min), 1,2-octanediol (17.39 min).

Styrene. Column: HP-1 (30 m × 0.25 mm × 0.25 µm), oven temp.: 5 min at 50°C, 10°C/min to 150°C, 20°C/min to 200°C, 5 min at 200°C, 20°C/min to 50°C (inlet: 150°C, detector: 150°C). Styrene (7.19 min), bromobenzene (internal standard, 8.07 min), benzaldehyde (8.53 min), phenylacetaldehyde (10.27 min), (+)-styrene oxide (10.82 min, partly decomposes to phenylacetaldehyde), 2-hydroxyacetophenone (not calibrated, 13.59 min), (+)-1-phenyl-1,2-ethanediol (14.50 min).

C.3 HPLC

HPLC analyses were performed on a Shimadzu LC10Advp.

2,2-dimethylchromene. Column: Chiralcel OD-H (4.6 mm × 250 mm, particle size 5 µm), n-heptane/PrOH (96:4) at 0.5 ml/min for 45 min. Monitored between 190-400 nm, ee determined at 210 nm. Cis-2,2-dimethylchromane-3,4-diol (27.6 and 33.5 min), trans-2,2-dimethylchromane-3,4-diol (25.8 and 30.0 min).

C.4 Electrochemistry

Recommended reading: ref. [1], [2], [3] and [4].

C.4.1 Cyclic voltammetry

Electrochemical measurements were carried out on a Model CHI630B or Model CHI760B electrochemical workstation (CH Instruments). Analyte concentrations were typically between 0.5 and 1.0 mM in anhydrous CH₃CN containing either 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) or 0.1 M KPF₆. Unless stated otherwise, a Teflon shrouded glassy carbon working electrode (CH Instruments, partnumber CHI104), a Pt-wire counter electrode (partnumber CHI115) and a SCE.
reference electrode (partnumber CHI150) were employed (calibrated externally using a 0.1 mM solution of ferrocene in 0.1 M TBAPF₆/CH₃CN). Cyclic voltammograms were obtained at sweep rates of between 1 mV s⁻¹ to 10 V s⁻¹ (typically 0.1 V s⁻¹). For reversible processes the half-wave potential (E½) values are reported. For irreversible processes either the cathodic or anodic peak potential (E_p,c or E_p,a, respectively) is given. Redox potentials are reported +/- 10 mV.

The glassy carbon working electrode was always cleaned mechanically and by sonication: the electrode was polished on a polishing pad containing a slurry of alumina (0.05 micron) and water. After rinsing with water, the glassy carbon working electrode was sonicated in CH₃CN for 1-2 min. If needed, the glassy carbon working electrode was also cleaned electrochemically: 15 cycles in 0.2 M H₂SO₄ (aq.) between 1.1 and -0.3 V vs. SCE (at 0.1 V s⁻¹), followed by 30 sec at constant potential at 1.1, -0.3, 1.2 and finally 0.3 V, followed by rinsing thoroughly with water and then CH₃CN. The Pt-wire counter electrode was cleaned by rinsing with water, acetone and finally CH₃CN. The saturated calomel electrode (SCE) (Hg/Hg₂Cl₂) reference electrode was stored in sat. KCl (aq.). Before use, it was rinsed with water first, then with CH₃CN. After use, the SCE reference electrode was rinsed with CH₃CN, acetone and finally with water.

Before measurements, both the solvents, electrolyte and electrodes were checked for possible contaminants by scanning at 0.1 V s⁻¹ (typically 5-7 cycles) between -0.4 and 1.8 V, starting cathodically from the open circuit potential (OCP).

Cyclic voltammetry was generally performed in 2 ml CH₃CN solutions containing TBAPF₆ electrolyte (0.1 M) and Mn₂ complex (1 mM), carboxylic acid (1-250 mM), cyclooctene (1 M) and/or 1,2-dichlorobenzene (0.5 M). Scans were always started at the OCP. Both positive and negative initial scan directions were run for all samples and at least 5 sweep segments were recorded in order to check reproducibility and/or the occurrence of (electro)chemical changes/processes. Before each new experiment (i.e. before each scan with different scan rate, initial scan direction and/or potential window) the solution was shaken to allow for ‘fresh’ solution close to the working electrode surface. The electrodes were cleaned periodically as described above.

Table C.1 Relevant redox potentials in 0.1 M TBAPF₆/CH₃CN.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Potential (in V vs. SCE)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe⁵⁺(Cp)₂ / Fe⁴⁺(Cp)₂ + e⁻</td>
<td>Eᵥ,2 +0.45 V</td>
<td>ref. [1a]</td>
</tr>
<tr>
<td>O₂ + e⁻ / O₂⁻</td>
<td>Eᵥ,c -0.7 V, Eᵥ,a -0.5 V</td>
<td>ref. [1a]</td>
</tr>
<tr>
<td>H₂O</td>
<td>Eᵥ,a +1.1 V</td>
<td></td>
</tr>
<tr>
<td>SCE</td>
<td>+0.24 V vs. NHE</td>
<td>at 25°C, ref. [1a]</td>
</tr>
</tbody>
</table>

C.4.2 Thin-layer electrochemistry

The setup for thin-layer electrochemistry is identical to that for standard (diffusion limited) cyclic voltammetry, except that the working electrode is placed directly on top of the (flat) base of the beaker containing the solution of interest, thus limiting diffusion of the species generated electrochemically (Figure C.1).
Measurements

Figure C.1 Setup for standard (diffusion limited) cyclic voltammetry (left) and thin-layer electrochemistry (right).

C.4.3 Spectroelectrochemistry
UV-Vis spectroelectrochemistry was performed in a homemade Optically Transparent Thin Layer Electrochemical (OTTLE) cell, consisting of a 2 mm quartz cuvette, a Pt-gauze working electrode, Pt-wire counter electrode (separated from the main solution with a fritted glass tube) and a SCE reference electrode.

C.4.4 Bulk electrolysis
Bulk electrolysis was performed with a reticulated vitreous carbon working electrode, carbon rod counter electrode and a SCE reference electrode.

C.5 Electron paramagnetic resonance
Recommended reading: ref. [5].

EPR spectra (X-band, 9.46 GHz) were recorded in liquid nitrogen (77 K) on a Bruker ECS 106 instrument, equipped with a Bruker ECS 041 XK microwave bridge and a Bruker ECS 080 magnet. Samples for measurement (250 µl) were transferred from the reaction solution to an EPR tube, which was frozen in 77 K immediately.

Spectra were typically obtained with the following settings: conversion time (81 msec), time constant (81 msec), central field (3450 G), sweep width (6000 or 2000 G), number of scans (1), receiver gain (usually between 2x10^4 and 2x10^5).
C.6 Nuclear magnetic resonance

$^1$H (400, 300 or 200 MHz), $^{13}$C (100.6 or 50.3 MHz) and $^{19}$F NMR (376 MHz) spectra were recorded on a Varian Mercury Plus 400, Varian VXR-300, Varian Mercury Plus 200 or Varian Gemini-200. Chemical shifts are reported in ppm relative to the solvent residual peak:$^6$ $^1$H NMR: CDCl$_3$ (7.26 ppm), dmso-d$_6$ (2.50 ppm), CD$_2$CN (1.94 ppm), acetone-d$_6$ (2.05 ppm), D$_2$O (4.79 ppm). $^{13}$C NMR: CDCl$_3$ (77 ppm), dmso-d$_6$ (39.5 ppm), acetone-d$_6$ (29.8 ppm). $^{19}$F NMR: PF$_6$ ($^{19}$F NMR: CDCl$_3$ (74.3 ppm, $J_{PF} = 580$ Hz). The splitting patterns are designated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad).

$^1$H NMR spectra of the [Mn$^{III}$($\mu$-O)(µ-RCO$_2$)$_2$(tmtacn)$_2$]$^{2+}$ complexes were recorded on a Varian Mercury Plus (400 MHz) using the following settings: sw = 100000, alfa = 0 or -2, rof2 = 0. For processing of the data, to partly correct for 1st order phasing issues, the first 4 data points were recalculated using 32 prediction coefficients and 1024 data points (command blp) before setting line broading (lb = 2-10 Hz) and performing the weighted fourier transformation (wft).

C.7 UV-Vis

UV-Vis spectra were recorded on a Hewlett-Packard 8453 or Jasco V-570 UV/VIS/NIR spectrophotometer using either 2 or 10 mm pathlength quartz cuvettes. Unless noted otherwise, the concentrations used were the same as used for the standard catalysis experiments (section C.1).

C.8 FT-IR

FT-IR spectra were recorded (as intimate mixtures in KBr) in reflectance mode, using a Nicolet Nexus FT-IR spectrometer.

C.9 Mass spectrometry

ESI-MS. Electrospray ionization mass spectra were recorded on a Triple Quadrupole LC/MS/MS Mass spectrometer (API 3000, Perkin-Elmer Sciei Instruments) or API-365. Samples (2 µl) were taken from the reaction mixture at the indicated times and were diluted in CH$_3$CN (1 ml) before injection in the mass spectrometer (via syringe pump). Alternatively, spectra were recorded while injecting at standard catalytic concentrations of the analytes in the mass spectrometer, so without dilution (i.e. 1 mM Mn$_2$ complex in CH$_3$CN). Mass spectra were measured in positive mode (no manganese complexes were observed in negative mode) and in the range of m/z 100-1500. Typical settings: ion-spray voltage (5200 V), orifice (+15 V), ring (+150 V), Q0 (-10 V).

For kinetic measurements only a small portion of the spectrum was recorded to minimize measuring time between each subsequent data point, while monitoring the [Mn$^{III}$($\mu$-O)(µ-RCO$_2$)$_2$(tmtacn)$_2$]$^{2+}$ ion. The presence of cyclooctene (1 M) and/or
Measurements
carboxylic acid did not result in significant interference of the mass spectra and neither
cyclooctene nor the cis-diol and epoxide products gave rise to significant signals.
EI-MS. Electron impact ionisation mass spectrometry was performed on a Jeol JMS-600H
mass spectrometer.
CI-MS. Chemical ionisation mass spectrometry was performed on a Jeol JMS-600H mass
spectrometer using NH₃ as reacting gas.
GC-MS (CI). Samples to determine the isotopic composition of the products were taken at
t = 60 min and were analyzed by GC-MS using chemical ionisation (CI) employing NH₃ as
reacting gas. GC: Agilent 6890 Gas Chromatograph equipped with a HP-5 (5%-phenyl)-methyl
polysiloxane column (30 m × 0.32 mm × 0.25 µm), oven temp.: 5 min at 100°C, 10 °C/min to
200°C, 5 min at 200°C, 25 °C/min to 100°C (inlet: 250°C). Cyclooctene oxide (3.5 min) and
cis-cyclooctane diol (7.5 min) were detected as their [M+NH₄]⁺ ions. MS:
Jeol JMS-600H mass spectrometer.

C.10 References

1 Electrochemistry in general: a) Sawyer, D. T.; Sobkowiak, A.; Roberts, Jr., J. L. Electrochemistry
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