Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Enhanced Catalase-like Activity of Manganese Salen Complexes in Water: Effect of Three-dimensionally Fixed Auxiliary

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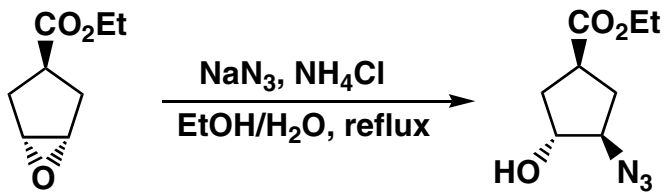
General Information. All reagents and solvents were of the highest commercial quality and were used without further purification unless otherwise noted. THF and diethyl ether were distilled from sodium/benzophenone ketyl immediately prior to use. Dichloromethane was distilled from CaH_2 immediately prior to use. MeOH and EtOH were distilled from Mg/I_2. Thin layer chromatography (TLC) was performed on Merck precoated plates (silica gel 60 F254, 0.25mm) and were visualised by fluorescence quenching. In addition, TLC plates were stained using potassium permanganate stain. Melting point (mp) determinations were performed using a Yanaco Micro Melting Point Apparatus and are uncorrected. ^{1}H-NMR spectra were recorded on a JEOL GSX-400 at 400 MHz. ^{13}C-NMR spectra were recorded on either a JEOL JNM-LA 500 or a Bruker AVANCE 600 at 125 MHz or 150 MHz, respectively. Chemical shifts are expressed as parts per million (ppm) using solvent as the internal standard. Data are reported as follows: (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet; coupling constants in Hz). Fast atom bombardment mass spectroscopy (FAB-MS) was measured with a JEOL JMS-LCMATE or JEOL JMS-700 mass spectrometer using 3-nitrobenzyl alcohol as the matrix. Column chromatography was performed on BW-200 or BW-300 (Fuji Silysia Chemical Ltd.).

Compound **3** was synthesised according to the procedure by Martinez et al.[s-1] *cis-syn*-1,2-Diazidocyclopentane (**11**) was synthesised from *cis*-1,2-cyclopentanediol according to the literature procedure.[s-2]

Ethyl 4-azido-3-hydroxycyclopentanecarboxylate (4).

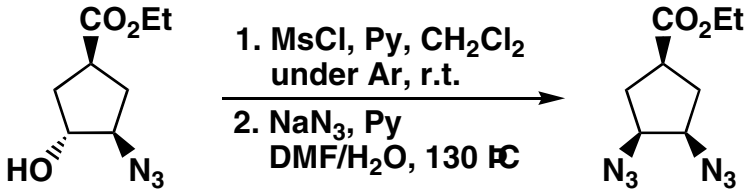


3 **4**

To the solution of **3** (9.8 g, 63 mmol) in ethanol/water (2:1, v/v, 300 mL), sodium azide (15.0 g,

230 mmol) and ammonium chloride (12.4 g, 230 mmol) were added and refluxed for 12 h. The mixture was cooled to room temperature and evaporated to remove ethanol. Additional water was added and extracted with ether. The organic layer was washed with brine and dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography (silica gel, 1:3 EtOAc/hexane) to give **4** (12.2 g, 97%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.16 (q, J = 7.1 Hz, 2H), 3.76 (m, 2H), 3.04 (m, 1H), 2.40 (m, 1H), 2.30 (m, 1H), 1.94 (m, 1H), 1.76 (d, J = 3.6 Hz, 1H), 1.27 (t, J = 7.1Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 175.0, 76.6, 67.8, 61.0, 39.3, 35.3, 32.1, 14.2; MS (FAB) 200 (M+1): Anal. Calcd for $C_8H_{13}N_3O_3$: C, 48.23; H, 6.58; N, 21.09. Found: C, 48.25; H, 6.60; N, 20.87.

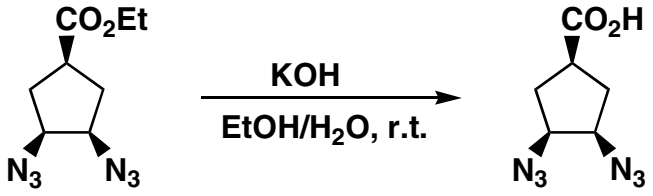
Ethyl *cis-syn*-3,4-diazidocyclopentanecarboxylate (5).



4 **5**

Mesyl chloride (3.3 mL, 43 mmol) was introduced into a mixture of **4** (6.1 g, 30 mmol) in dichloromethane (100 mL) and pyridine (3.3 mL, 40 mmol) at room temperature under Ar. After stirring for 14 h at room temperature, saturated $NaHCO_3$ was added. The mixture was extracted with dichloromethane, and organic layer was washed with 1N HCl and brine, dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure and the residue was dissolved in DMF (100 mL) and water (60 mL). Pyridine (10 mL, 120 mmol) and sodium azide (3.9 g, 60 mmol) were added and the reaction mixture was heated at 130 ˚C for 12 h. After being cooled, the reaction mixture was concentrated and extracted with ether. The organic solvent was removed under reduced pressure to give crude product, which was purified by column chromatography (silica gel, 1:4 EtOAc/hexane). Purified **5** (4.9 g, 73%) was obtained as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.19 (q, J = 7.2 Hz, 2H), 3.87 (m, 2H), 2.88 (m, 1H), 2.24 (m, 4H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 173.7, 63.6, 61.2, 39.0, 31.4, 14.2; MS (FAB) 225 (M+1); Anal. Calcd for $C_8H_{12}N_6O_2$: C, 42.85; H, 5.39; N, 37.48. Found: C, 43.05; H, 5.41; N, 37.30.

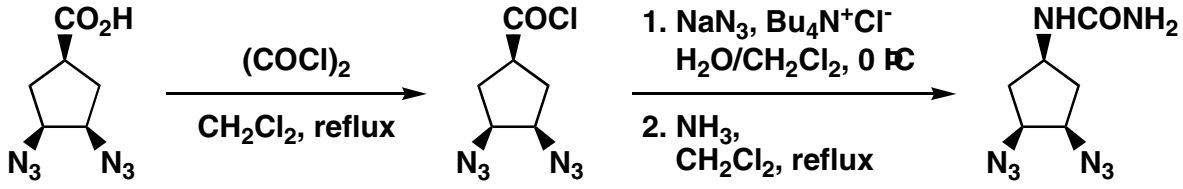
***cis-syn*-3,4-Diazidocyclopentanecarboxylic acid (6).**



5 **6**

To the mixture of **5** (2.2 g, 10 mmol) in ethanol (5 mL), 3N aqueous KOH solution (5 mL, 15 mmol) was added and stirred at room temperature for 8 h. The mixture was concentrated under reduced pressure and saturated $NaHCO_3$ was added. The aqueous solution was then washed with dichloromethane. The aqueous layer was added 1N HCl and extracted with dichloromethane. The organic layer was dried over $MgSO_4$, filtered, and concentrated to give **6** (1.92 g, 98%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.89 (m, 2H), 2.96 (m, 1H), 2.27 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.9, 63.6, 38.8, 31.2; MS (FAB) 197 (M+1); Anal. Calcd for $C_6H_8N_6O_2$: C, 36.74; H, 4.11; N, 42.84. Found: C, 37.00; H, 4.33; N, 42.61.

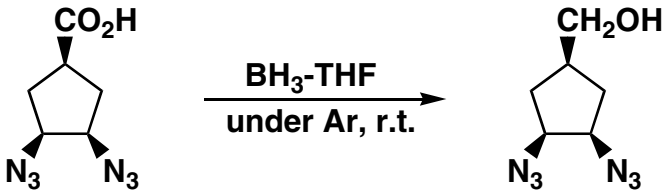
***cis-syn*-3,4-Diazidocyclopentylurea (7).**



6 **7**

To the solution of **6** (4.0 g, 20 mmol) in dichloromethane (40 mL), oxalyl chloride (3 mL, 33 mmol) was added at room temperature. The reaction mixture was refluxed for 4 h. After being cooled, the organic solvent was removed under reduced pressure to give a colorless oil (4.4 g, 98%). A portion of the oil thus obtained (1.1 g, 5 mmol) and tetrabutylammonium chloride (10 mg, 0.04 mmol) in dichloromethane (10 mL) was cooled in an ice bath. Sodium azide (460 mg, 7 mmol) in water (2 mL) was added and the reaction mixture was stirred at 0˚C for 4 h. The organic layer was separated, and washed with water, dried over $MgSO_4$ and filtered. NH_3 gas was bubbled into the filtrate and the reaction mixture was refluxed for 2 h. After being cooled, the precipitate was filtered and recrystallised from chloroform to give **7** (848 mg, 80%) as colorless needles. Mp 139-140 ˚C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 6.14 (d, J = 8.3 Hz, 1H), 5.41 (s, 2H), 4.05 (m, 2H), 3.96 (m, 1H), 2.26 (m, 2H), 1.44 (m, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 158.0, 62.5, 45.6, 36.1; MS (FAB) 211 (M+1); Anal. Calcd for $C_6H_{10}N_8O$: C, 34.28; H, 4.80; N, 53.26. Found: C, 34.53; H, 4.75; N, 53.26.

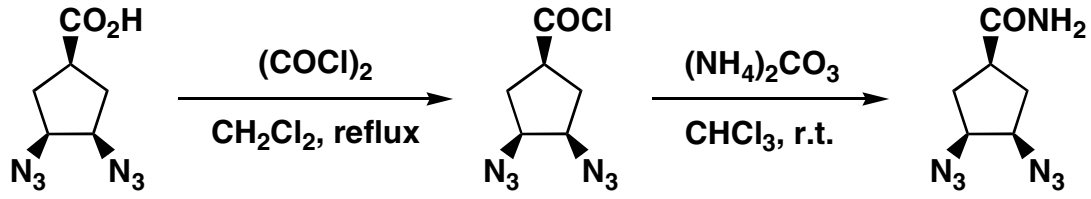
***cis-syn*-3,4-Diazidocyclopentanemethanol (9).**



6 **9**

To the cooled (0 ˚C) solution of **6** (460 mg, 2 mmol) in THF (6 mL), 1.0 M borane-THF (4.0 mL, 4 mmol) was added. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. Saturated K_2CO_3 was added and the reaction mixture was extracted with ether. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 2:1 EtOAc/hexane) to give **9** (406 mg, 97%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.88 (m, 2H), 3.62 (t, J = 6.0 Hz, 2H), 2.27 (m, 1H), 2.13 (m, 2H), 1.67 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 66.6, 64.1, 36.9, 31.4; MS (FAB) 183 (M+1); HRMS (FAB): $[M+H]^+$ calcd for $C_6H_{11}N_6O$, 113.0994; found, 113.0994.

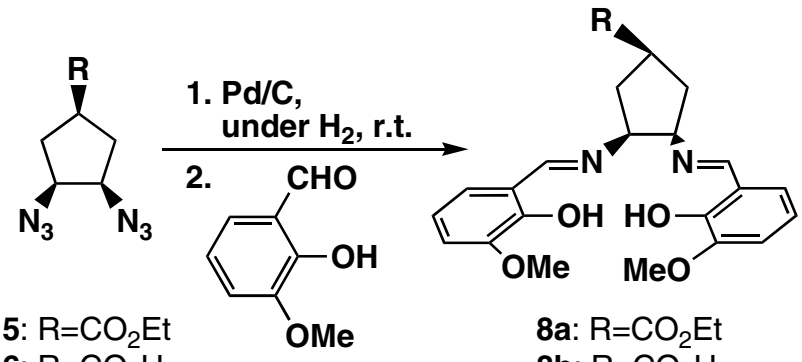
***cis-syn*-3,4-Diazidocyclopentanecarboxamide (10).**



6 **10**

To the solution of **6** (4.0 g, 20 mmol) in dichloromethane (40 mL), oxalyl chloride (3 mL, 33 mmol) was added at room temperature. The reaction mixture was refluxed for 4 h. After being cooled, the organic solvent was removed under reduced pressure to give a colorless oil (4.4 g, 98%). A portion of the oil thus obtained (800 mg, 4 mmol) was dissolved in chloroform (15 mL), ammonium carbonate (1.1 g, 10 mmol) was added and stirred for 20 h at room temperature. The mixture was filtrated, and the filtrate was concentrated under reduced pressure. The residue was dissolved in dichloromethane, and the organic layer was washed with saturated $NaHCO_3$, dried over $MgSO_4$, filtered, and concentrated. Crystallisation from dichloromethane/hexane provided **10** (480 mg, 61%) as colorless needles. Mp 76-77 ˚C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.76 (s, 1H), 5.27 (s, 1H), 3.93 (m, 2H), 2.80 (m, 1H), 2.27 (m, 2H), 2.16 (m, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 176.2, 64.0, 40.5, 32.4; MS (FAB) 197 (M+1); Anal. Calcd for $C_6H_9N_7O$: C, 36.92; H, 4.65; N, 50.23. Found: C, 37.13; H, 4.62; N, 50.28.

General procedure for the preparation of cyclopetane-fused Salen ligand.



5: R=CO_2Et
6: R=CO_2H
7: R=$NHCONH_2$
9: R=CH_2OH
10: R=$CONH_2$
11: R=H

8a: R=CO_2Et
8b: R=CO_2H
8c: R=CH_2OH
8d: R=$NHCONH_2$
8e: R=$CONH_2$
8f: R=H

To the solution of diazide (**5**, **6**, **7**, **9, 10** or **11**) in methanol (0.2-1.0 M), 10% palladium on carbon (10 % w/w) was added and stirred under hydrogen at room temperature. When the reduction was completed, the reaction mixture was filtered and the filtrate was concentrated under reduced pressure to give desired diamine, which was used for the next reaction without further purification. A mixture of diamine (1 eq.) and *o*-vanillin (2 eq.) in methanol (0.05-0.2 M) was stirred at room temperature. The precipitate formed during the reaction was filtered, washed with methanol and recrystallised from methanol to give desired cyclopentane-fused Salen lignad.

8a (R = CO_2Et) (57%): mp 195-196 ˚C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 13.12 (s, 2H), 8.32 (s, 2H), 6.86 (m, 4H), 6.76 (t, *J* = 7.8 Hz, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 4.02 (m, 2H), 3.85 (s, 6H), 3.14 (m, 1H), 2.43 (m, 4H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 174.5, 164.8, 151.4, 148.3, 123.4, 118.6, 118.0, 114.4, 71.9, 61.1, 56.1, 40.3, 33.9, 14.2; MS (FAB) 441 (M+1); Anal. Calcd for $C_{24}H_{28}N_2O_6$: C, 65.44; H, 6.41; N, 6.36. Found: C, 65.28; H, 6.34; N, 6.17.

8b (R = CO_2H) (47%): mp 112-113 ˚C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 13.27 (s, 2H), 12.27 (s, 1H), 8.53 (s, 2H), 6.99 (m, 4H), 6.79 (t, *J* = 8.0 Hz, 2H), 4.01 (m, 2H), 3.73 (s, 6H), 3.05 (m, 1H), 2.37 (m, 2H), 2.21 (m, 2H) ; ^{13}C NMR (DMSO-d_6, 125 MHz): δ 176.1, 165.4, 150.9, 147.8, 123.1, 118.3, 117.8, 114.6, 71.5, 55.5, 34.6; MS (FAB) 413 (M+1); Anal. Calcd for $C_{22}H_{24}N_2O_6$: C, 64.07; H, 5.87; N, 6.79. Found: C, 64.32; H, 6.06; N, 6.63.

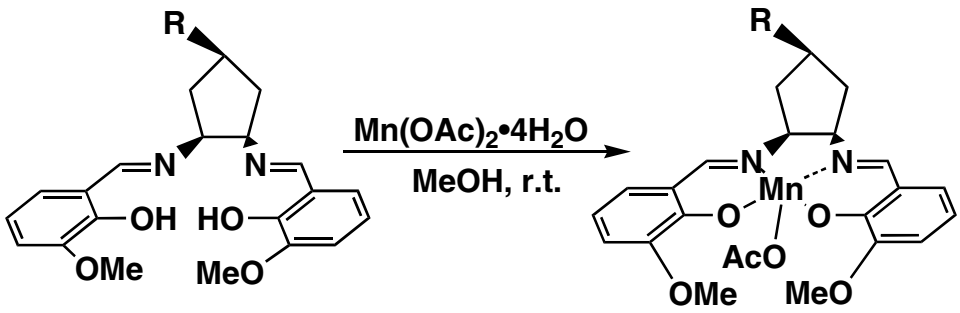
8c (R = CH_2OH) (60%): mp 179-180 ˚C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 13.52 (s, 2H), 8.32 (s, 2H), 7.27 (m, 4H), 6.77 (t, *J* = 7.8 Hz, 2H), 4.02 (m, 2H), 3.86 (s, 6H), 3.76 (d, *J* = 6.4 Hz, 2H), 2.54 (m, 1H), 2.30 (m, 2H), 1.86 (m, 2H) ; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 164.5, 151.6, 148.3, 123.2, 118.5, 118.0, 114.1, 72.3, 67.9, 56.1, 38.0, 34.2; MS (FAB) 399 (M+1); Anal. Calcd for $C_{22}H_{26}N_2O_5$: C, 66.32; H, 6.58; N, 7.03. Found: C, 66.43; H, 6.61; N, 7.01.

8d (R = $NHCONH_2$) (72%): mp 213-214 ˚C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 13.53 (s, 2H), 8.35 (s, 2H), 6.91 (d, *J* = 7.8 Hz, 2H), 6.87 (d, *J* = 7.8 Hz, 2H), 6.81 (t, *J* = 7.8 Hz, 2H), 4.80 (d, *J* = 7.8 Hz, 1H), 4.61 (m, 1H), 4.34 (s, 2H), 3.93 (m, 2H), 3.87 (s, 6H), 2.62 (m, 2H), 1.92 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.1, 157.7, 151.4, 148.3, 123.3, 118.5, 118.3, 114.3, 71.8, 56.1, 48.1, 39.8; MS (FAB) 427 (M+1); Anal. Calcd for $C_{22}H_{26}N_4O_5$: C, 61.96; H, 6.15; N, 13.14. Found: C, 61.70; H, 6.12; N, 13.08.

8e (R = $CONH_2$) (70%): mp 198-199 ˚C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 13.03 (s, 2H), 8.35 (s, 2H), 6.85 (m, 4H), 6.76 (t, *J*=7.8 Hz, 2H), 5.69 (s, 1H), 5.34 (s, 1H), 4.03 (m, 2H), 3.85 (s, 6H), 3.11 (m, 1H), 2.47 (m, 2H), 2.37 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 176.3, 165.0, 151.3, 148.3, 123.4, 118.5, 118.1, 114.4, 72.3, 56.1, 41.7, 34.8; MS (FAB) 412 (M+1); Anal. Calcd for $C_{22}H_{25}N_3O_5$: C, 64.22; H, 6.12; N, 10.21. Found: C, 64.26; H, 6.14; N, 10.23.

8f (R = H) (62%): mp 160-162 ˚C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 13.70 (s, 2H), 8.34 (s, 2H), 6.86 (m, 4H), 6.76 (t, *J*=7.8 Hz, 2H), 3.96 (m, 2H), 3.86 (s, 6H), 2.05 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 164.4, 151.7, 148.4, 123.1, 118.6, 117.8, 114.0, 72.7, 56.1, 30.6, 20.9; MS (FAB) 369 (M+1); Anal. Calcd for $C_{21}H_{24}N_2O_4$: C, 68.46; H, 6.57; N, 7.60. Found: C, 68.55; H, 6.77; N, 7.67.

General procedure for the preparation of cyclopentane-fused Mn(Salen) complexes.



8a: R=CO_2Et **2a**: R=CO_2Et
8b: R=CO_2H **2b**: R=CO_2H
8c: R=CH_2OH **2c**: R=CH_2OH
8d: R=$NHCONH_2$ **2d**: R=$NHCONH_2$
8e: R=$CONH_2$ **2e**: R=$CONH_2$
8f: R=H **2f**: R=H

To a stirred suspension of the ligand **8a-f** (1 eq.) in methanol (0.02-0.05 M), manganese(Ⅱ) acetate tetrahydrate (1 eq.) was added at room temperature. The reaction mixture was stirred at room temperature for 1-2 h, the solvent was then removed under reduced pressure. The resulting dark brown solid was thoroughly washed with acetone to give cyclopentane-fused Mn(Salen) complexes.

2a (R = CO_2Et) (88%): MS (FAB) 493 [$(M\text{-}OAc)^+$]; Anal. Calcd for $C_{26}H_{29}MnN_2O_8$•$2H_2O$: C,

53.06; H, 5.65; N, 4.76. Found: C, 53.18; H, 5.57; N, 4.76.

2b (R = CO_2H) (91%): MS (FAB) 465 [(M-OAc)$^+$]; Anal. Calcd for $C_{24}H_{25}MnN_2O_8$•2/3H_2O: C, 53.74; H, 4.95; N, 5.22. Found: C, 53.52; H, 4.66; N, 5.41.

2c (R = CH_2OH) (87%): MS (FAB) 451 [(M-OAc)$^+$]; Anal. Calcd for $C_{24}H_{27}MnN_2O_7$•4H_2O: C, 49.49; H, 6.06; N, 4.81. Found: C, 49.63; H, 5.89; N, 4.77.

2d (R = $NHCONH_2$) (91%): MS (FAB) 479 [(M-OAc)$^+$]; Anal. Calcd for $C_{24}H_{27}MnN_4O_7$•1/2AcOH•2H_2O: C, 49.67; H, 5.50; N, 9.27. Found: C, 49.61; H, 5.43; N, 9.17.

2e (R = $CONH_2$) (69%): MS (FAB) 464 [(M-OAc)$^+$]; Anal. Calcd for $C_{24}H_{26}MnN_3O_7$•AcOH•2H_2O: C, 50.41; H, 5.53; N, 6.78. Found: C, 50.41; H, 5.32; N, 6.96.

2f (R = H) (61%): MS (FAB) 421 [(M-OAc)$^+$]; Anal. Calcd for $C_{23}H_{25}MnN_2O_6$•AcOH•2/3H_2O: C, 54.35; H, 5.53; N, 5.07. Found: C, 54.57; H, 5.62; N, 4.99.

Measurement of catalase-like activity.

Catalase-like activity was examined by monitoring the concentration of O_2, which was generated from the conversion of hydrogen peroxide, using a Clark type polarographic oxygen electrode.[s-3] To the solution of Mn(Salen) complex (**2a**-**2f**; 10 μM) in 50 mM sodium phosphate buffer at pH 7.4, 10 mM (final concentration) H_2O_2 was added. The reaction mixture was maintained at 25±0.2 ˚C under Ar. Initial rates were calculated by linear regression using the data from 0-5 sec of the reaction.

Michaelis-Menten plot for the reaction of 2d

Catalase-like activity was examined according to the protocol described above. Initial rates were measured at four different substrate (H_2O_2) concentrations (5, 10, 15, and 20 mM) and the initial rate data were fitted to the Michaelis-Menten equation $V_0 = V_{max}[H_2O_2]/(K_m + [H_2O_2])$ using KaleidaGraph® (Synergy Software). R = 0.99. A plot of initial rate of O_2 formation versus H_2O_2 concentration for compound **2d** is shown in Table S1 and Figure S1.

Table s-1 Initial rate of O_2 formation by compound **2d**

$[H_2O_2]$ (mM)	Initial Rate (μM O_2/min)
0	0
5	290
10	606
15	752
20	776

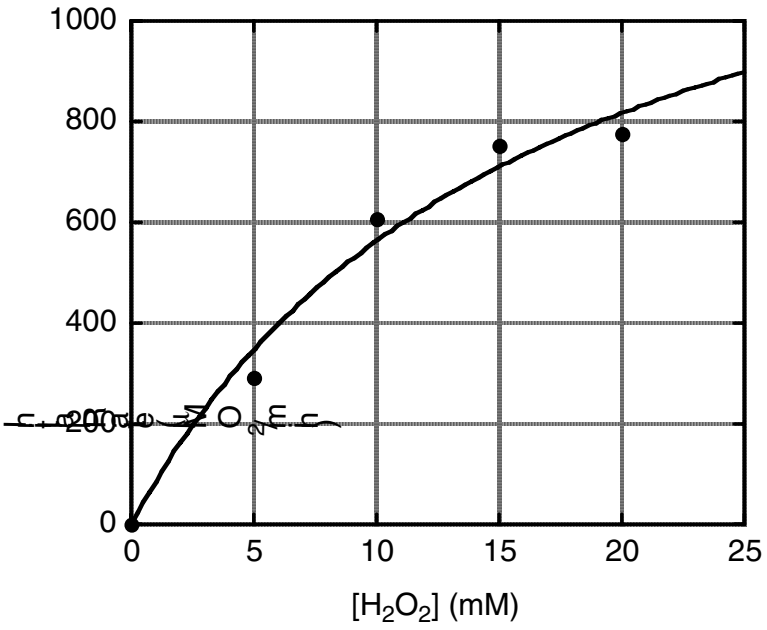


Fig. s-1 Initial rate of O_2 formation versus substrate concentration at constant concentration of 2d (10 μM); • indicates data points, - indicates curve fit.

References:

s-1 L. E. Martinez, W. A. Nugent, E. N. Jacobsen, *J. Org. Chem.* 1996, **61**, 7963-7966

s-2 S. G. Gouin, J.-F. Gestin, K. Joly, A. Loussouarn, A. Reliquet, J. C. Meslin, D. Deniaud, *Tetrahedron* 2002, **58**, 1131-1136.

s-3 (a) P. K. Gonzalez, J. Zhuang, S. R. Doctrow, B. Malfroy, P. F. Benson, M. J. Menconi, M. P. Fink, *J. Pharmacol. Exp. Ther.* 1995, **275**, 798-806. (b) S. R. Doctrow, K. Huffman, C. B. Marcus, G. Tocco, E. Malfroy, C. A. Adinolfi, H. Kruk, K. Baker, N. Lazarowych, J. Mascarenhas, B. Malfroy, *J. Med. Chem.* 2002, **45**, 4549-4558.

Single-crystal X-ray Diffraction Analysis of 2d

Crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent (acetonitrile-methanol) solution. Data collections were made on an Bruker APEX II diffractometer with a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Diffracted intensities were reduced to a set of relative structure factors by the application of the standard Lorentz and polarization factors.

Table s-2. Crystal data and structure refinement for **2d**.

Identification code	Mn-Salen	
Empirical formula	C24 H31 Mn N4 O9	
Formula weight	573.46	
Temperature	90 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 13.8291(11) Å	α= 90°.
	b = 9.3189(8) Å	β= 108.220(1)°.
	c = 21.4664(18) Å	γ = 90°.
Volume	2627.7(4) Å ^{3}	
Z	4	
Density (calculated)	1.450 Mg/m^3	
Absorption coefficient	0.561 mm^{-1}	
F(000)	1196	
Crystal size	0.25 x 0.20 x 0.05 mm^3	
Theta range for data collection	1.56 to 28.25°.	
Index ranges	-15<=h<=18, -12<=k<=6, -28<=l<=25	
Reflections collected	12381	
Independent reflections	5866 [R(int) = 0.0273]	
Completeness to theta = 25.00∞	99.6 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9725 and 0.8725	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5866 / 0 / 370	
Goodness-of-fit on F^2	1.066	

Final R indices [I>2sigma(I)]	R1 = 0.0813, wR2 = 0.2530
R indices (all data)	R1 = 0.1025, wR2 = 0.2742
Largest diff. peak and hole	3.595 and -0.583 e. Å $^{-3}$

Table s-3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å ^{2}x 10^3) for **2d**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	4879(3)	7071(5)	7952(2)	21(1)
C(2)	3730(3)	6741(5)	7700(2)	24(1)
C(3)	3614(4)	5851(6)	7073(2)	29(1)
C(4)	4427(4)	6429(6)	6782(2)	27(1)
C(5)	5118(4)	7414(5)	7319(2)	25(1)
C(6)	4961(3)	5099(5)	5961(2)	20(1)
C(7)	6316(3)	5443(5)	8364(2)	20(1)
C(8)	6911(3)	4328(5)	8782(2)	19(1)
C(9)	6592(3)	3652(5)	9269(2)	18(1)
C(10)	7261(3)	2643(5)	9684(2)	20(1)
C(11)	8187(3)	2318(5)	9604(2)	22(1)
C(12)	8501(3)	3025(5)	9122(2)	22(1)
C(13)	7876(3)	4024(5)	8724(2)	21(1)
C(14)	7565(4)	1164(5)	10635(2)	28(1)
C(15)	2524(3)	6030(5)	8243(2)	24(1)
C(16)	2148(3)	5322(5)	8711(2)	23(1)
C(17)	2759(3)	4353(5)	9184(2)	23(1)
C(18)	2333(3)	3759(5)	9650(2)	25(1)
C(19)	1364(4)	4092(5)	9645(2)	26(1)
C(20)	767(4)	5053(5)	9166(3)	28(1)
C(21)	1148(3)	5655(5)	8710(2)	27(1)
C(22)	2609(4)	2089(5)	10544(2)	27(1)
C(23)	6403(4)	2065(6)	7385(2)	34(1)
C(24)	6706(5)	871(7)	7896(3)	45(1)
Mn(1)	4564(1)	4786(1)	8800(1)	20(1)
N(1)	5391(3)	5780(4)	8322(2)	21(1)
N(2)	3435(3)	5922(4)	8202(2)	23(1)
N(3)	4986(3)	5272(5)	6593(2)	26(1)
N(4)	5475(3)	3960(5)	5848(2)	24(1)
O(1)	4492(2)	5924(4)	5514(1)	22(1)

O(2)	5722(2)	3913(3)	9385(1)	21(1)
O(3)	6889(2)	2080(4)	10155(2)	24(1)
O(4)	3693(2)	3962(4)	9221(2)	27(1)
O(5)	2998(2)	2866(4)	10094(2)	27(1)
O(6)	5617(3)	2836(5)	7392(2)	40(1)
O(7)	6864(3)	2288(5)	6995(2)	45(1)
O(8)	4376(3)	2924(4)	8114(2)	37(1)
O(9)	4837(3)	6737(4)	9473(2)	24(1)

Table s-4. Bond lengths [Å] and angles [°] for **2d**.

C(2)-C(1)	1.541(6)
C(3)-C(2)	1.546(6)
C(3)-C(4)	1.543(7)
C(5)-C(1)	1.530(6)
C(5)-C(4)	1.548(7)
C(7)-C(8)	1.450(6)
C(8)-C(13)	1.407(6)
C(9)-C(8)	1.404(6)
C(9)-C(10)	1.421(6)
C(10)-C(11)	1.378(6)
C(12)-C(11)	1.405(6)
C(13)-C(12)	1.372(6)
C(16)-C(15)	1.429(7)
C(16)-C(21)	1.416(6)
C(17)-C(16)	1.423(7)
C(17)-C(18)	1.422(7)
C(18)-C(19)	1.373(6)
C(19)-C(20)	1.418(7)
C(21)-C(20)	1.368(7)
C(23)-C(24)	1.526(8)
Mn(1)-N(1)	1.988(4)
Mn(1)-N(2)	1.988(4)
Mn(1)-O(2)	1.883(3)
Mn(1)-O(4)	1.881(3)
Mn(1)-O(8)	2.237(4)
Mn(1)-O(9)	2.279(3)
N(1)-C(1)	1.492(6)
N(1)-C(7)	1.292(6)
N(2)-C(2)	1.479(6)
N(2)-C(15)	1.293(6)
N(3)-C(4)	1.456(6)
N(3)-C(6)	1.357(6)
N(4)-C(6)	1.340(6)

O(1)-C(6)	1.242(5)
O(2)-C(9)	1.325(5)
O(3)-C(10)	1.374(5)
O(3)-C(14)	1.437(5)
O(4)-C(17)	1.320(5)
O(5)-C(18)	1.378(6)
O(5)-C(22)	1.439(5)
O(6)-C(23)	1.306(7)
O(7)-C(23)	1.217(7)
C(1)-H(1)	1.0000
C(2)-H(2)	1.0000
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-H(4)	1.0000
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(7)-H(7)	0.9500
C(11)-H(11)	0.9500
C(12)-H(12)	0.9500
C(13)-H(13)	0.9500
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-H(15)	0.9500
C(19)-H(19)	0.9500
C(20)-H(20)	0.9500
C(21)-H(21)	0.9500
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
N(3)-H(25)	0.98(6)
N(4)-H(27)	0.78(7)

N(4)-H(26)	0.88(7)
O(8)-H(28)	0.98(6)
O(9)-H(29)	0.89(6)
O(9)-H(30)	0.97(9)

C(1)-C(2)-C(3)	103.1(4)
C(1)-C(5)-C(4)	106.4(4)
C(1)-N(1)-Mn(1)	113.4(3)
C(2)-N(2)-Mn(1)	113.9(3)
C(3)-C(4)-C(5)	105.3(3)
C(4)-C(3)-C(2)	106.0(4)
C(5)-C(1)-C(2)	102.5(3)
C(6)-N(3)-C(4)	121.1(4)
C(7)-N(1)-C(1)	121.8(4)
C(7)-N(1)-Mn(1)	124.5(3)
C(8)-C(9)-C(10)	117.9(4)
C(9)-C(8)-C(7)	122.2(4)
C(9)-O(2)-Mn(1)	125.9(3)
C(10)-C(11)-C(12)	120.1(4)
C(10)-O(3)-C(14)	116.5(3)
C(11)-C(10)-O(3)	125.8(4)
C(11)-C(10)-C(9)	121.1(4)
C(12)-C(13)-C(8)	120.8(4)
C(13)-C(8)-C(7)	117.4(4)
C(13)-C(8)-C(9)	120.2(4)
C(13)-C(12)-C(11)	119.8(4)
C(15)-C(16)-C(17)	121.9(4)
C(15)-C(16)-C(21)	117.9(4)
C(15)-N(2)-C(2)	120.4(4)
C(15)-N(2)-Mn(1)	125.6(3)
C(17)-C(16)-C(21)	120.1(4)
C(17)-O(4)-Mn(1)	128.3(3)
C(18)-C(17)-C(16)	117.7(4)
C(18)-C(19)-C(20)	119.6(5)
C(18)-O(5)-C(22)	117.3(4)

C(19)-C(18)-C(17)	121.7(5)
C(19)-C(18)-O(5)	125.4(4)
C(20)-C(21)-C(16)	120.3(5)
C(21)-C(20)-C(19)	120.7(5)
N(1)-C(1)-C(2)	106.9(4)
N(1)-C(1)-C(5)	116.3(4)
N(1)-C(7)-C(8)	125.1(4)
N(1)-Mn(1)-O(8)	89.39(15)
N(1)-Mn(1)-O(9)	86.97(14)
N(2)-C(2)-C(1)	109.7(3)
N(2)-C(2)-C(3)	112.4(4)
N(2)-C(15)-C(16)	126.0(4)
N(2)-Mn(1)-O(8)	94.72(15)
N(2)-Mn(1)-O(9)	85.71(14)
N(2)-Mn(1)-N(1)	83.17(15)
N(3)-C(4)-C(3)	111.8(4)
N(3)-C(4)-C(5)	112.8(4)
N(4)-C(6)-N(3)	115.2(4)
O(1)-C(6)-N(3)	122.9(4)
O(1)-C(6)-N(4)	122.0(4)
O(2)-C(9)-C(8)	125.0(4)
O(2)-C(9)-C(10)	117.1(4)
O(2)-Mn(1)-N(1)	92.25(14)
O(2)-Mn(1)-N(2)	173.23(16)
O(2)-Mn(1)-O(8)	90.20(14)
O(2)-Mn(1)-O(9)	89.08(13)
O(3)-C(10)-C(9)	113.2(4)
O(4)-C(17)-C(16)	124.7(4)
O(4)-C(17)-C(18)	117.6(4)
O(4)-Mn(1)-N(1)	175.04(15)
O(4)-Mn(1)-N(2)	92.03(15)
O(4)-Mn(1)-O(2)	92.42(14)
O(4)-Mn(1)-O(8)	92.27(16)
O(4)-Mn(1)-O(9)	91.43(14)
O(5)-C(18)-C(17)	112.9(4)

O(6)-C(23)-C(24)	115.9(5)
O(7)-C(23)-C(24)	122.2(5)
O(7)-C(23)-O(6)	122.0(5)
O(8)-Mn(1)-O(9)	176.26(14)
C(1)-C(2)-H(2)	110.5
C(1)-C(5)-H(5A)	110.5
C(1)-C(5)-H(5B)	110.5
C(2)-C(1)-H(1)	110.2
C(2)-C(3)-H(3A)	110.5
C(2)-C(3)-H(3B)	110.5
C(3)-C(2)-H(2)	110.5
C(3)-C(4)-H(4)	108.9
C(4)-C(3)-H(3A)	110.5
C(4)-C(3)-H(3B)	110.5
C(4)-C(5)-H(5A)	110.5
C(4)-C(5)-H(5B)	110.5
C(4)-N(3)-H(25)	118(3)
C(5)-C(1)-H(1)	110.2
C(5)-C(4)-H(4)	108.9
C(6)-N(3)-H(25)	118(3)
C(6)-N(4)-H(26)	124(4)
C(6)-N(4)-H(27)	110(5)
C(8)-C(7)-H(7)	117.4
C(8)-C(13)-H(13)	119.6
C(10)-C(11)-H(11)	120.0
C(11)-C(12)-H(12)	120.1
C(12)-C(11)-H(11)	120.0
C(12)-C(13)-H(13)	119.6
C(13)-C(12)-H(12)	120.1
C(16)-C(15)-H(15)	117.0
C(16)-C(21)-H(21)	119.9
C(18)-C(19)-H(19)	120.2
C(19)-C(20)-H(20)	119.7
C(20)-C(19)-H(19)	120.2
C(20)-C(21)-H(21)	119.9

C(21)-C(20)-H(20)	119.7
C(23)-C(24)-H(24A)	109.5
C(23)-C(24)-H(24B)	109.5
C(23)-C(24)-H(24C)	109.5
Mn(1)-O(8)-H(28)	111(4)
Mn(1)-O(9)-H(29)	107(4)
Mn(1)-O(9)-H(30)	91(5)
N(1)-C(1)-H(1)	110.2
N(1)-C(7)-H(7)	117.4
N(2)-C(2)-H(2)	110.5
N(2)-C(15)-H(15)	117.0
N(3)-C(4)-H(4)	108.9
O(3)-C(14)-H(14A)	109.5
O(3)-C(14)-H(14B)	109.5
O(3)-C(14)-H(14C)	109.5
O(5)-C(22)-H(22A)	109.5
O(5)-C(22)-H(22B)	109.5
O(5)-C(22)-H(22C)	109.5
H(3A)-C(3)-H(3B)	108.7
H(5A)-C(5)-H(5B)	108.6
H(14A)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
H(22A)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
H(24A)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
H(27)-N(4)-H(26)	123(6)
H(29)-O(9)-H(30)	120(7)

Symmetry transformations used to generate equivalent atoms:

Table s-5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **2d**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	21(2)	29(2)	12(2)	-1(2)	3(2)	6(2)
C(2)	22(2)	38(3)	12(2)	2(2)	3(2)	9(2)
C(3)	22(2)	48(3)	13(2)	-5(2)	3(2)	4(2)
C(4)	30(2)	39(3)	12(2)	0(2)	4(2)	10(2)
C(5)	29(2)	32(2)	13(2)	3(2)	5(2)	6(2)
C(6)	13(2)	30(2)	16(2)	0(2)	3(2)	-5(2)
C(7)	18(2)	29(2)	14(2)	-3(2)	5(2)	0(2)
C(8)	17(2)	26(2)	14(2)	-4(2)	4(2)	3(2)
C(9)	12(2)	25(2)	15(2)	-6(2)	3(2)	2(2)
C(10)	17(2)	27(2)	14(2)	-1(2)	4(2)	2(2)
C(11)	15(2)	28(2)	19(2)	0(2)	1(2)	7(2)
C(12)	13(2)	30(2)	25(2)	-5(2)	7(2)	-1(2)
C(13)	17(2)	24(2)	24(2)	-4(2)	9(2)	-1(2)
C(14)	31(2)	34(3)	19(2)	5(2)	8(2)	12(2)
C(15)	15(2)	36(3)	16(2)	-1(2)	-1(2)	8(2)
C(16)	14(2)	34(2)	21(2)	-8(2)	3(2)	-2(2)
C(17)	13(2)	35(2)	20(2)	-5(2)	4(2)	1(2)
C(18)	16(2)	29(2)	28(2)	-7(2)	6(2)	-2(2)
C(19)	20(2)	29(2)	33(2)	-9(2)	12(2)	-7(2)
C(20)	16(2)	30(2)	39(3)	-10(2)	9(2)	-2(2)
C(21)	17(2)	32(2)	29(2)	-10(2)	4(2)	2(2)
C(22)	25(2)	31(2)	26(2)	-2(2)	10(2)	-7(2)
C(23)	41(3)	38(3)	24(2)	-12(2)	10(2)	-8(2)
C(24)	59(4)	39(3)	34(3)	-10(2)	10(3)	-2(3)
Mn(1)	14(1)	33(1)	12(1)	1(1)	3(1)	5(1)
N(1)	19(2)	29(2)	12(2)	-1(1)	2(1)	4(2)
N(2)	18(2)	37(2)	13(2)	0(2)	3(1)	5(2)
N(3)	28(2)	36(2)	14(2)	2(2)	7(2)	10(2)
N(4)	25(2)	34(2)	16(2)	0(2)	8(2)	5(2)
O(1)	21(2)	31(2)	14(1)	3(1)	4(1)	2(1)

O(2)	16(1)	35(2)	14(1)	4(1)	6(1)	6(1)
O(3)	23(2)	35(2)	16(1)	8(1)	7(1)	11(1)
O(4)	13(2)	42(2)	26(2)	6(1)	6(1)	5(1)
O(5)	21(2)	35(2)	26(2)	4(1)	9(1)	-4(1)
O(6)	36(2)	52(2)	30(2)	4(2)	7(2)	5(2)
O(7)	52(2)	50(2)	33(2)	5(2)	15(2)	16(2)
O(8)	26(2)	50(2)	32(2)	-12(2)	6(2)	-2(2)
O(9)	18(2)	37(2)	16(2)	1(1)	5(1)	6(1)

Table s-6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **2d**.

	x	y	z	U(eq)
H(1)	5011	7929	8246	25
H(2)	3329	7650	7590	29
H(3A)	3728	4820	7181	34
H(3B)	2924	5973	6757	34
H(4)	4083	7021	6386	33
H(5A)	5844	7223	7373	30
H(5B)	4973	8436	7199	30
H(7)	6630	5967	8100	24
H(11)	8614	1615	9875	26
H(12)	9144	2811	9071	27
H(13)	8098	4517	8406	25
H(14A)	7719	307	10419	34
H(14B)	7240	879	10962	34
H(14C)	8197	1682	10853	34
H(15)	2063	6636	7933	28
H(19)	1094	3681	9961	32
H(20)	95	5281	9161	34
H(21)	741	6298	8392	32
H(22A)	2400	2770	10826	32
H(22B)	3140	1456	10815	32
H(22C)	2020	1515	10297	32
H(24A)	6836	1281	8335	54
H(24B)	7324	398	7868	54
H(24C)	6154	168	7813	54
H(25)	5220(40)	4470(60)	6900(30)	28(14)
H(26)	5900(50)	3440(70)	6160(30)	35(15)
H(27)	5480(50)	3970(70)	5480(30)	36(17)
H(28)	4870(40)	2960(60)	7880(30)	31(15)
H(29)	5490(50)	6720(60)	9720(30)	35(16)

H(30)	4310(70)	6430(100)	9660(40)	90(30)

Table s-7. Torsion angles [°] for **2d**.

C(1)-C(5)-C(4)-C(3)	14.9(5)
C(1)-C(5)-C(4)-N(3)	-107.4(4)
C(1)-N(1)-C(7)-C(8)	171.4(4)
C(2)-C(3)-C(4)-C(5)	10.8(5)
C(2)-C(3)-C(4)-N(3)	133.8(4)
C(2)-N(2)-C(15)-C(16)	-178.8(4)
C(3)-C(2)-C(1)-C(5)	41.0(5)
C(3)-C(2)-C(1)-N(1)	-81.9(4)
C(4)-C(3)-C(2)-C(1)	-32.2(5)
C(4)-C(3)-C(2)-N(2)	-150.3(4)
C(4)-C(5)-C(1)-C(2)	-34.8(5)
C(4)-C(5)-C(1)-N(1)	81.5(5)
C(4)-N(3)-C(6)-N(4)	-177.4(4)
C(4)-N(3)-C(6)-O(1)	2.0(7)
C(6)-N(3)-C(4)-C(3)	118.4(5)
C(6)-N(3)-C(4)-C(5)	-123.1(5)
C(7)-C(8)-C(13)-C(12)	177.3(4)
C(7)-N(1)-C(1)-C(2)	151.1(4)
C(7)-N(1)-C(1)-C(5)	37.4(6)
C(8)-C(9)-C(10)-C(11)	-1.2(6)
C(8)-C(9)-C(10)-O(3)	178.1(4)
C(8)-C(13)-C(12)-C(11)	-1.6(7)
C(9)-C(8)-C(13)-C(12)	2.7(7)
C(9)-C(10)-C(11)-C(12)	2.4(7)
C(10)-C(9)-C(8)-C(7)	-175.6(4)
C(10)-C(9)-C(8)-C(13)	-1.3(6)
C(13)-C(12)-C(11)-C(10)	-1.0(7)
C(14)-O(3)-C(10)-C(11)	5.4(6)
C(14)-O(3)-C(10)-C(9)	-173.9(4)
C(15)-C(16)-C(21)-C(20)	-177.3(4)
C(15)-N(2)-C(2)-C(1)	150.9(4)
C(15)-N(2)-C(2)-C(3)	-95.0(5)
C(16)-C(17)-C(18)-C(19)	0.5(7)

C(16)-C(17)-C(18)-O(5)	-178.4(4)
C(16)-C(21)-C(20)-C(19)	0.1(7)
C(17)-C(16)-C(15)-N(2)	-2.1(7)
C(17)-C(16)-C(21)-C(20)	0.3(7)
C(17)-C(18)-C(19)-C(20)	-0.1(7)
C(18)-C(17)-C(16)-C(15)	176.9(4)
C(18)-C(17)-C(16)-C(21)	-0.6(7)
C(18)-C(19)-C(20)-C(21)	-0.2(7)
C(22)-O(5)-C(18)-C(19)	7.5(7)
C(22)-O(5)-C(18)-C(17)	-173.6(4)
Mn(1)-N(1)-C(1)-C(2)	-34.4(4)
Mn(1)-N(1)-C(1)-C(5)	-148.2(3)
Mn(1)-N(1)-C(7)-C(8)	-2.5(6)
Mn(1)-N(2)-C(2)-C(1)	-26.2(5)
Mn(1)-N(2)-C(2)-C(3)	87.9(4)
Mn(1)-N(2)-C(15)-C(16)	-2.0(7)
Mn(1)-O(2)-C(9)-C(8)	19.4(6)
Mn(1)-O(2)-C(9)-C(10)	-162.8(3)
Mn(1)-O(4)-C(17)-C(16)	13.0(7)
Mn(1)-O(4)-C(17)-C(18)	-167.2(3)
N(1)-C(7)-C(8)-C(9)	-10.7(7)
N(1)-C(7)-C(8)-C(13)	174.8(4)
N(1)-Mn(1)-N(2)-C(2)	5.8(3)
N(1)-Mn(1)-N(2)-C(15)	-171.1(4)
N(1)-Mn(1)-O(2)-C(9)	-24.4(4)
N(2)-C(2)-C(1)-C(5)	160.9(4)
N(2)-C(2)-C(1)-N(1)	38.1(5)
N(2)-Mn(1)-N(1)-C(1)	17.0(3)
N(2)-Mn(1)-N(1)-C(7)	-168.8(4)
N(2)-Mn(1)-O(4)-C(17)	-13.0(4)
O(2)-C(9)-C(8)-C(7)	2.2(7)
O(2)-C(9)-C(8)-C(13)	176.6(4)
O(2)-C(9)-C(10)-C(11)	-179.2(4)
O(2)-C(9)-C(10)-O(3)	0.1(6)
O(2)-Mn(1)-N(1)-C(1)	-158.0(3)

O(2)-Mn(1)-N(1)-C(7)	16.2(4)
O(2)-Mn(1)-O(4)-C(17)	161.9(4)
O(3)-C(10)-C(11)-C(12)	-176.9(4)
O(4)-C(17)-C(16)-C(15)	-3.4(7)
O(4)-C(17)-C(16)-C(21)	179.2(4)
O(4)-C(17)-C(18)-C(19)	-179.3(4)
O(4)-C(17)-C(18)-O(5)	1.8(6)
O(4)-Mn(1)-N(2)-C(2)	-175.4(3)
O(4)-Mn(1)-N(2)-C(15)	7.6(4)
O(4)-Mn(1)-O(2)-C(9)	157.2(4)
O(5)-C(18)-C(19)-C(20)	178.7(4)
O(8)-Mn(1)-N(1)-C(1)	111.8(3)
O(8)-Mn(1)-N(1)-C(7)	-73.9(4)
O(8)-Mn(1)-N(2)-C(2)	-83.0(3)
O(8)-Mn(1)-N(2)-C(15)	100.1(4)
O(8)-Mn(1)-O(2)-C(9)	65.0(4)
O(8)-Mn(1)-O(4)-C(17)	-107.8(4)
O(9)-Mn(1)-N(1)-C(1)	-69.1(3)
O(9)-Mn(1)-N(1)-C(7)	105.2(4)
O(9)-Mn(1)-N(2)-C(2)	93.3(3)
O(9)-Mn(1)-N(2)-C(15)	-83.7(4)
O(9)-Mn(1)-O(2)-C(9)	-111.4(3)
O(9)-Mn(1)-O(4)-C(17)	72.7(4)

Symmetry transformations used to generate equivalent atoms: