

Mechanism of the Enantioselective Oxidation of Racemic Secondary Alcohols Catalyzed by Chiral Mn(III)-Salen Complexes

M. Kevin Brown, Megan M. Blewett, James R. Colombe and E. J. Corey*

*Department of Chemistry and Chemical Biology,
12 Oxford St., Cambridge, MA 02138*

SUPPORTING INFORMATION

General. Infrared (IR) spectra were recorded on a Bruker Tensor 27, ν_{\max} in cm^{-1} . Bands are characterized as broad (br), strong (s), medium (m), and weak (w). ^1H NMR spectra were recorded on a Varian Unity INOVA 500 (500 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl_3 : δ 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on a Varian Unity INOVA 500 (125 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl_3 : δ 77.16 ppm). Enantiomer ratios were determined by chiral HPLC analysis (Chiralcel OD-H and OJ columns) in comparison with authentic racemic materials. Optical rotations were measured on a Perkin Elmer 241 Polarimeter.

Unless otherwise noted, all reactions have been carried out with distilled and degassed solvents under an atmosphere of dry N_2 in oven- (135 °C) and flame-dried glassware with standard vacuum-line techniques. Diethyl ether, tetrahydrofuran and toluene were purified under a positive pressure of dry argon by passage through two columns of activated alumina. Dichloromethane was purified by distillation from calcium hydride immediately prior to use. All work-up and purification procedures were carried out with reagent grade solvents (purchased from VWR) in air.

■ Reagents and Catalysts:

Mn-Cl Complex 2a was purchased from Strem and was used as received.

Mn-Cl Complexes 2b-2f were prepared in accordance with literature procedures and purified by silica gel column chromatography (CH₂Cl₂ to 10% MeOH/CH₂Cl₂, gradient).¹

Mn-Br Complex 12 was prepared in accordance with literature procedures and purified by silica gel column chromatography (CH₂Cl₂ to 10% MeOH/CH₂Cl₂, gradient).²

Bromine was purchased from Aldrich and used as received.

tert-Butylhypobromite was prepared in accordance with literature procedures.³

Diacetoxyiodobenzene was purchased from Aldrich and used as received.

(±)-1-Indanol was purchased from Aldrich and purified by silica gel column chromatography (10% Et₂O/pet ether to 80% Et₂O/pet ether, gradient).

(S)-1-Indanol and (R)-1-Indanol (>99% ee) was prepared by oxidative kinetic resolution of (±)-1-indanol according to the general procedure shown below.

(±)-1-D(1)-Indanol was prepared by reduction of 1-indanone with NaBD₄ (MeOH/CH₂Cl₂, 0 °C to 23 °C, 30 min, quenched with NH₄Cl and extracted with EtOAc) and purified by silica gel column chromatography (10% Et₂O/pet ether to 80% Et₂O/pet ether, gradient).

(S)-1-D(1)-Indanol and (R)-1-D(1)-Indanol (>99% ee) was prepared by oxidative kinetic resolution of (±)-1-D(1)-indanol according to the general procedure shown below.

1-Indanone was purchased from Aldrich and used as received.

Indene was purchased from Aldrich and distilled under N₂ prior to use.

Iodosylbenzene was prepared in accordance with literature procedures.⁴

4-Methoxy-1-phenylethanol was purchased from Alfa and used as received.

1-Phenylethanol was purchased from Alfa and used as received.

1-Phenylpropanol was purchased from Alfa and used as received.

Potassium Acetate was purchased from Fisher and used as received.

Potassium Bromide was purchased from Fisher and used as received.

Potassium Chloride was purchased from Fisher and used as received.

Potassium Iodide was purchased from Fisher and used as received.

Sodium Bicarbonate was purchased from Fisher and used as received.

Tetrabutylammonium Acetate was azeotroped with THF/toluene (1:1) three times prior to use.

Tetraethylammonium Bromide was purchased from Aldrich and used as received.

4-Trifluoromethyl-1-phenylethanol was purchased from Alfa and used as received.

(1) (a) Pospisil, P. J.; Carsten, D. H.; Jacobsen, E. N. *Chem. Eur. J.* **1996**, 2, 974-980. (b) Palucki, M.; Finney, N. S.; Pospisil, P. J.; Guler, M. L.; Ishida, T.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1998**, 120, 948-954.

(2) Adam, W.; Roschmann, K. J.; Saha-Möller, C. R. *Eur. J. Org. Chem.* **2000**, 3519-3521.

(3) Walling, C.; McGuinness, J. A. *J. Am. Chem. Soc.* **1969**, 91, 2053-2058

(4) Saltzman, H.; Sharefkin, J. G. *Org. Syn., Coll. Vol. 5*, **1973**, 658.

■ Procedures:

•Preparation of Hypobromous Acid:

To a tared 100 mL round-bottom flask equipped with stir bar and septum was added a small quantity of red HgO (Caution: TOXIC) in a fume hood. The flask was reweighed to determine the exact quantity of red HgO (454 mg, 2.09 mmol) present. The round-bottom flask was then covered in foil and H₂O (21 mL) was added followed by the dropwise addition of Br₂ (108 μ L, 2.09 mmol). The pale yellow mixture with orange precipitate was allowed to stir for 10 min prior to use. We have found that solution of HOBr prepared in this manner should be used within 30 min of use.

•Representative Experimental Procedure for Enantioselective Oxidation:

(Note: all operations carried out in air).⁵ To a 5 mL round-bottom flask charged with (\pm)-1-indanol (33.5 mg, 0.250 mmol) and (*S,S*)-Mn-complex **2a** (3.2 mg, 0.0050 mmol) was added an aqueous solution of KBr (2.38 mg/mL H₂O, 1.00 mL, 0.0200 mmol) and CH₂Cl₂ (500 μ L). The biphasic mixture was allowed to stir for five minutes before PhI(OAc)₂ (56.4 mg, 0.175 mmol) was added. After 30 minutes the reaction was quenched upon addition of a saturated aqueous solution of Na₂S₂O₃. The mixture was then extracted with Et₂O (3 x 2 mL) and the combined organic extracts were passed through a short plug of silica gel (3 x 6 cm) eluted with Et₂O (40 mL). The filtrate was concentrated and the residue purified by silica gel column chromatography (5% EtOAc/hexanes to 50% EtOAc/hexanes, gradient) to afford (*S*)-1-indanol (10.1 mg, 0.0750 mmol, 30.0% yield) as a white solid. **Optical Rotation:** $[\alpha]_D^{22} +29.3$ (*c* 0.967, CHCl₃) for an enantiomerically enriched sample of >99% ee. Lit.⁶ $[\alpha]_D^{22} +25.4$ (*c* 1.03, CHCl₃) for the (*S*)-enantiomer. The enantiomeric purity was determined by HPLC analysis with a chiral column (Chiralpak OD-H column, 1.0 mL/min, 95:5 hexanes:isopropanol, 220 nm, $t_{\text{major}} = 8.770$ min, $t_{\text{minor}} = 9.800$ min).

(S)-4-Methoxy-1-phenylethanol.⁷ Obtained by oxidative kinetic resolution according to the general procedure with (*S,S*)-**2a**. **Optical Rotation:** $[\alpha]_D^{22} -44.2$ (*c* 0.450, CHCl₃) for an enantiomerically enriched sample of 91.0% ee. Lit.⁷ $[\alpha]_D^{22} -48.6$ (*c* 1, CHCl₃) for the (*S*)-enantiomer. The enantiomeric purity was determined by HPLC analysis with a chiral column (Chiralpak OD-H column, 1.0 mL/min, 98:2 hexanes:isopropanol, 220 nm, $t_{\text{minor}} = 22.282$ min, $t_{\text{major}} = 24.232$ min).

(S)-4-Trifluoromethyl-1-phenylethanol.⁷ Obtained by oxidative kinetic resolution according to the general procedure with (*S,S*)-**2a**. **Optical Rotation:** $[\alpha]_D^{22} -32.1$ (*c* 0.993, CHCl₃) for an enantiomerically enriched sample of >99% ee. Lit.⁷ $[\alpha]_D^{22} -30.2$ (*c* 1.00, CHCl₃) for the (*S*)-enantiomer. The enantiomeric purity was determined by HPLC analysis with a chiral column

(5) Control experiments carried out under N₂ provide identical results to those carried out in air.

(6) Suzuki, T.; Ghazati, K.; Katoh, T.; Sasai, H. *Org. Lett.* **2009**, *11*, 4286-4288.

(7) Li, W.; Ding, K.; Sandoval, C. A. *Org. Lett.* **2009**, *11*, 907-910

(Chiralpak OJ column, 0.5 mL/min, 99:1 hexanes:isopropanol, 220 nm, $t_{\text{major}} = 13.1791$ min, $t_{\text{minor}} = 14.423$ min).

• **Experimental Procedure for Confirmation that Bromide Ion is Oxidized by $\text{PhI}(\text{OAc})_2$:**

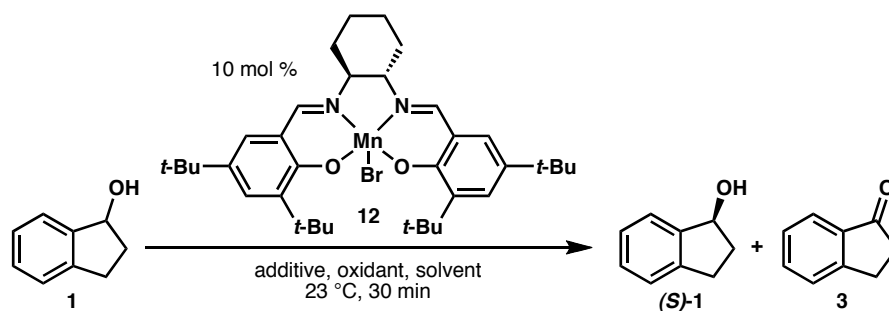
To a test tube containing potassium bromide (29 mg, 0.25 mmol) and $\text{PhI}(\text{OAc})_2$ (81 mg, 0.25 mmol) was added CH_2Cl_2 (500 μL) and H_2O (1.0 mL). The mixture turned light brown immediately and darkened to deep orange/brown over a couple minutes indicating the formation of Br_2 . The mixture was then extracted with CH_2Cl_2 (3 x 1 mL) and the volatiles removed under reduced pressure. ^1H NMR analysis of the residue indicated a 1:1 mixture of $\text{PhI}(\text{OAc})_2$ and PhI .

• **Experimental Procedure for Enantioselective Oxidation with HOBr (Table 2, entry 5):**

(Note: all operations carried out in air). To a 5 mL round-bottom flask charged with (\pm)-1-indanol (33.5 mg, 0.250 mmol), (*S,S*)-Mn-complex **12** (17.0 mg, 0.0250 mmol) and potassium acetate (31.9 mg, 0.325 mmol) was added CH_2Cl_2 (500 μL) and H_2O (400 μL). The biphasic mixture was allowed to stir for one minute before a solution of HOBr (1.12 mL, 0.225 mmol, 0.200 M in H_2O) was added over 30 min via syringe pump. After 15 minutes the reaction was quenched upon addition of a saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$. The mixture was then extracted with Et_2O (3 x 2 mL) and the combined organic extracts were passed through a short plug of silica gel (3 x 6 cm) eluted with Et_2O (40 mL). The filtrate was concentrated and the residue purified by silica gel column chromatography (5% EtOAc /hexanes to 50% EtOAc /hexanes, gradient) to afford (*S*)-1-indanol. The enantiomeric purity was determined by HPLC analysis with a chiral column (Chiralpak OD-H column, 1.0 mL/min, 95:5 hexanes:isopropanol, 220 nm, $t_{\text{minor}} = 8.770$ min, $t_{\text{major}} = 9.800$ min).

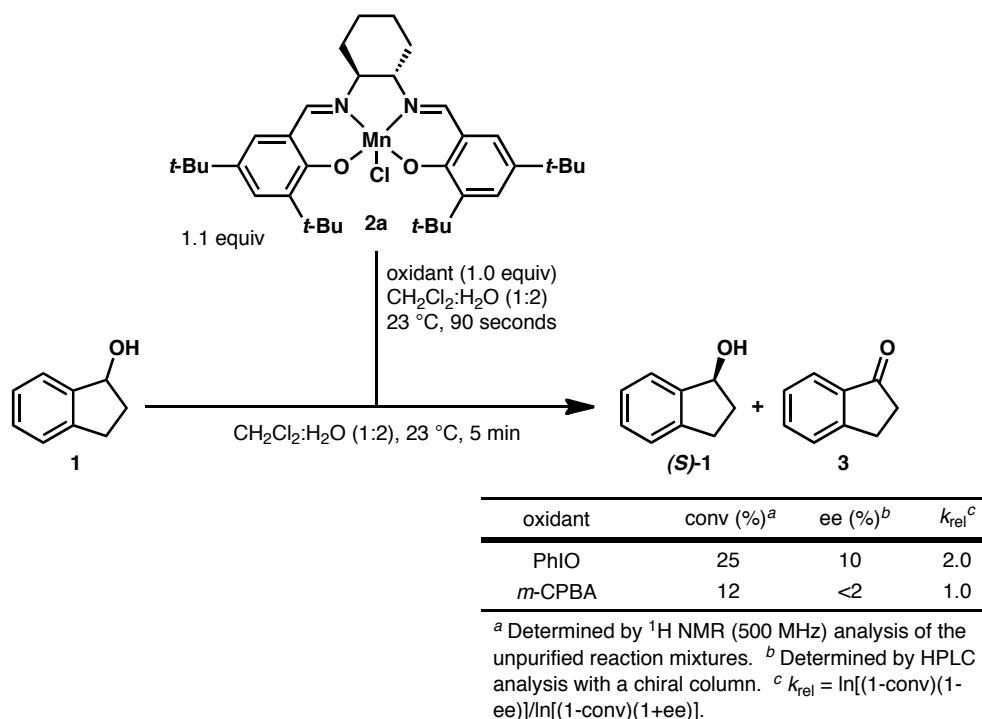
• **Experimental Procedure for Enantioselective Oxidation with Br_2 or *t*-BuOBr (Table 2, entries 3 and 6):**

(Note: all operations carried out in air). To a 5 mL round-bottom flask charged with (\pm)-1-indanol (33.4 mg, 0.250 mmol), (*S,S*)-Mn-complex **12** (17.0 mg, 0.0250 mmol) and potassium acetate (49.0 mg, 0.500 mmol) (24.5 mg, 0.250 mmol for *t*-BuOBr) was added CH_2Cl_2 (300 μL) and H_2O (1.0 mL). The biphasic mixture was allowed to stir for one minute before a solution of Br_2 (9.60 μL , 0.188 mmol) in CH_2Cl_2 (200 μL) (or *t*-BuOBr (23.0 μL , 0.200 mmol) in CH_2Cl_2 (200 μL)) was added over 30 min via syringe pump. After 15 minutes the reaction was quenched upon addition of a saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$. The mixture was then extracted with Et_2O (3 x 2 mL) and the combined organic extracts were passed through a short plug of silica gel (3 x 6 cm) eluted with Et_2O (40 mL). The filtrate was concentrated and the residue purified by silica gel column chromatography (5% EtOAc /hexanes to 50% EtOAc /hexanes, gradient) to afford (*S*)-1-indanol. The enantiomeric purity was determined by HPLC analysis with a chiral column (Chiralpak OD-H column, 1.0 mL/min, 95:5 hexanes:isopropanol, 220 nm, $t_{\text{minor}} = 8.770$ min, $t_{\text{major}} = 9.800$ min).

Table S1. Additional Data

entry	solvent	additive	oxidant	addition time	conv (%) ^a	ee (%) ^b	<i>k</i> _{rel} ^c
1	CH ₂ Cl ₂ :H ₂ O (1:2)	--	Br ₂ (0.75 equiv)	1 min	-- ^d	<5	1.0
2	CH ₂ Cl ₂ :H ₂ O (1:2)	2.0 equiv KOAc	Br ₂ (0.75 equiv)	5 min	71	75	3.9
3	CH ₂ Cl ₂ :H ₂ O (1:2)	2.0 equiv KOAc	Br ₂ (0.75 equiv)	30 min	65	98	14
4	CH ₂ Cl ₂ :H ₂ O (1:2)	10.0 equiv KOAc	Br ₂ (0.75 equiv)	30 min	54	72	8.8
5	CH ₂ Cl ₂	2.0 equiv <i>n</i> -Bu ₄ NOAc	Br ₂ (0.75 equiv)	30 min	27	<5	1.0
6	CH ₂ Cl ₂ :H ₂ O (1:2)	--	HOBr (0.70 equiv)	5 min	-- ^d	<5	1.0
7	CH ₂ Cl ₂ :H ₂ O (1:2)	1.3 equiv KOAc	HOBr (0.90 equiv)	30 min	69	97	9.5
8	CH ₂ Cl ₂ :H ₂ O (1:2)	1.0 equiv KOAc	<i>t</i> -BuOBr (0.80 equiv)	5 min	71	98	9.2
9	CH ₂ Cl ₂ :H ₂ O (1:2)	1.0 equiv KOAc	<i>t</i> -BuOBr (0.80 equiv)	30 min	66	98	13
10	CH ₂ Cl ₂	10.0 equiv KOAc	<i>t</i> -BuOBr (0.80 equiv)	30 min	59	32	2.1
11	CH ₂ Cl ₂ :H ₂ O (1:2)	1.0 equiv <i>n</i> -Bu ₄ NOAc	<i>t</i> -BuOBr (0.80 equiv)	30 min	45	43	4.8

^a Determined by ¹H NMR (500 MHz) analysis of the unpurified reaction mixtures. ^b Determined by HPLC analysis with a chiral column. ^c *k*_{rel} = ln[(1-conv)(1-ee)]/ln[(1-conv)(1+ee)]. ^d Unpurified reaction mixture is complex as judged by ¹H NMR (500 MHz) analysis.

Scheme S1. Reactions with PhIO and *m*-CPBA**•Experimental Procedure for Enantioselective Oxidation with Stoichiometric Quantities of Mn-Cl Complex 2a and PhIO (Scheme S1).**

(Note: all operations carried out in air). To a 5 mL round-bottom flask charged with PhIO (11 mg, 0.050 mmol) and CH₂Cl₂ (400 μL) and H₂O (1.0 mL) was added (*S,S*)-Mn-complex **2a** (35 mg, 0.055 mmol). The black, biphasic mixture was allowed to stir for 90 seconds before (±)-1-indanol (6.7 mg, 0.050 mmol) was added as a solution in CH₂Cl₂ (100 μL). The mixture remained dark black throughout the reaction. After the mixture was allowed to stir for five minutes the reaction was quenched upon addition of a saturated aqueous solution of Na₂S₂O₃. The mixture was then extracted with Et₂O (3 x 2 mL) and the combined organic extracts were passed through a short plug of silica gel (3 x 6 cm) eluted with Et₂O (40 mL). The filtrate was concentrated and the residue purified by silica gel column chromatography (5% EtOAc/hexanes to 50% EtOAc/hexanes, gradient) to afford 1-indanol. The enantiomeric purity was determined by HPLC analysis with a chiral column (Chiralpak OD-H column, 1.0 mL/min, 95:5 hexanes:isopropanol, 220 nm, *t*_{minor} = 8.770 min, *t*_{major} = 9.800 min).

•Experimental Procedure for Enantioselective Oxidation with Stoichiometric Quantities of Mn-Cl Complex 2a and *m*-CPBA (Scheme S1).

(Note: all operations carried out in air). To a 5 mL round-bottom flask charged with (*S,S*)-Mn-complex **2a** (35 mg, 0.055 mmol) and CH₂Cl₂ (300 μL) and H₂O (1.0 mL) was added *m*-CPBA (8.6 mg, 0.050 mmol) as a solution in CH₂Cl₂ (100 μL). The dark green/brown, biphasic mixture was allowed to stir for 90 seconds before (±)-1-indanol (6.7 mg, 0.050 mmol) was added as a

solution in CH_2Cl_2 (100 μL). The mixture remained dark green/brown throughout the reaction. After the mixture was allowed to stir for five minutes the reaction was quenched upon addition of a saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$. The mixture was then extracted with Et_2O (3 x 2 mL) and the combined organic extracts were passed through a short plug of silica gel (3 x 6 cm) eluted with Et_2O (40 mL). The filtrate was concentrated and the residue purified by silica gel column chromatography (5% EtOAc /hexanes to 50% EtOAc /hexanes, gradient) to afford 1-indanol. The enantiomeric purity was determined by HPLC analysis with a chiral column (Chiralpak OD-H column, 1.0 mL/min, 95:5 hexanes:isopropanol, 220 nm, $t_{\text{minor}} = 8.770$ min, $t_{\text{major}} = 9.800$ min).

•Experimental Procedures for Determination of the Kinetic Isotope Effect:

Rate analysis of the kinetic resolution of 1-indanol and 1-D(1)-indanol reported by Xia and coworkers is complicated by the fact that k_{rel} changes as a function of time for the oxidation of (\pm)-1-indanol (Figure S1). This complicates the measurements for determining $k_{\text{H}}/k_{\text{D}}$ by using the method of initial rates as the reaction in the initial stages is not descriptive of the entire reaction, even if enantiomerically pure substrate is used.

The data presented in Figure S1 was acquired by analysis of small aliquots removed over the course of a reaction. The reaction (7.5 mmol of (\pm)-1-indanol) was carried out under conditions analogous to those described in the general procedure for oxidative kinetic resolution (see above). The aliquots, once removed, were quenched immediately upon addition to a test tube containing sodium thiosulfate (aq) (1 mL), sodium bicarbonate (aq) (1 mL), diethyl ether (1 mL) and dimethyl sulfide (100 μL). The mixture was then extracted with Et_2O (3 x 1 mL) and the combined organic phases were passed through a short plug of silica gel (3 x 0.5 cm) eluted with Et_2O (~8 mL). The volatiles were removed under reduced pressure and the conversion measured by ^1H NMR (500 MHz) analysis and the enantiomeric excess determined by HPLC analysis with a chiral column.

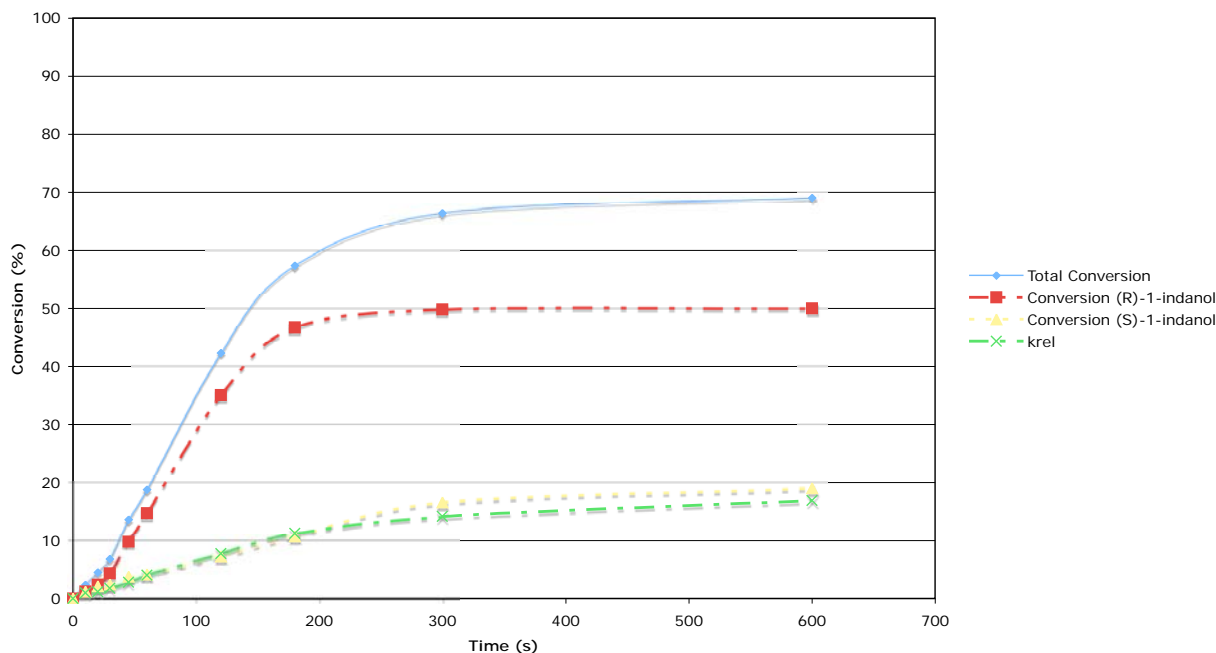
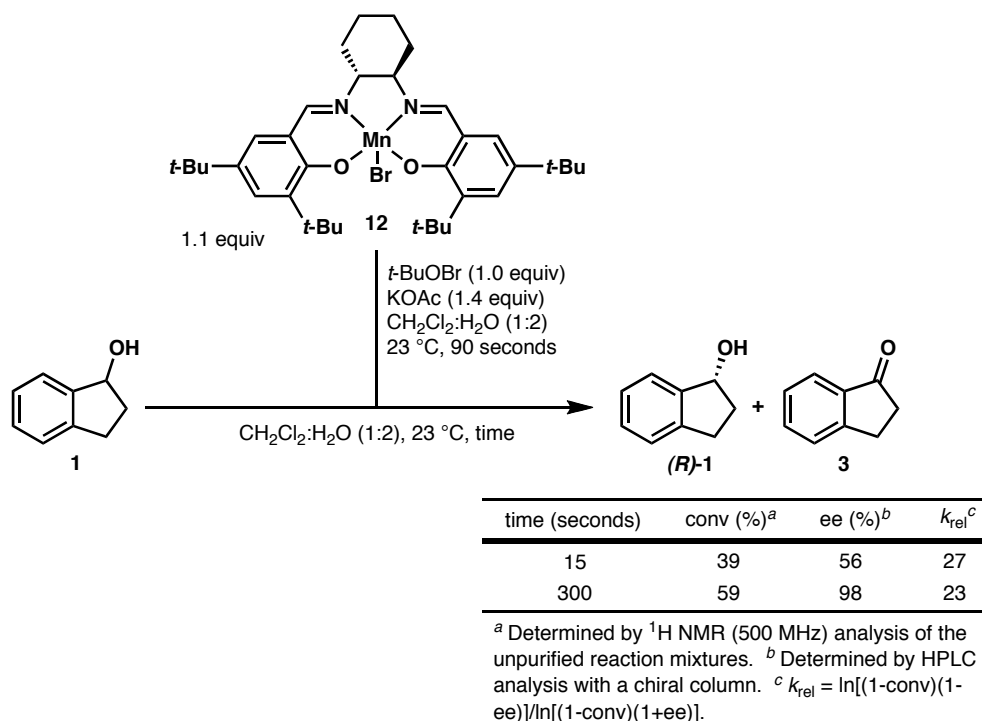


Figure S1. Conversion vs. Time

Reactions in which Mn-salen complex **12** (1.1 equiv) is first oxidized with *t*-BuOBr (1.0 equiv) followed by the addition of (±)-1-indanol (1.0 equiv), however, have a constant selectivity factor (k_{rel}) over time (Scheme S2). The kinetic isotope effect for this reaction was determined by initial rate analysis of an internal competition reaction between (*S*)-1-indanol and (*S*)-(D1)-1-indanol with (*R,R*)-salen-Mn complex **12** (run in triplicate). Enantiomerically pure substrates were used to simplify analysis and to gain greater insight into the nature of the transition state that predominates the catalytic cycle (i.e. the enantiomer of alcohol that undergoes reaction more readily). The conversions for each run were as follows: Run 1. (*S*)-(D1)-1-indanol: 8.5% conv, (*S*)-1-indanol 28.5% conv: $k_{\text{H}}/k_{\text{D}} = 3.3$. Run 2. (*S*)-(D1)-1-indanol: 13.5% conv, (*S*)-1-indanol 28.5% conv: $k_{\text{H}}/k_{\text{D}} = 2.1$. Run 3. (*S*)-(D1)-1-indanol: 8.0% conv, (*S*)-1-indanol 22.5% conv: $k_{\text{H}}/k_{\text{D}} = 2.8$. Average of the three runs is 2.7 ± 0.6

The reactions were carried out according to the general procedure with stoichiometric quantities of Mn-complex **12** (see below) with several adjustments: (1) before 1-indanol was added, the mixtures were allowed to cool to 0 °C, (2) the reactions were quenched upon addition of dimethyl sulfide (100 µL) and a saturated aqueous solution of sodium thiosulfate (1 mL), (3) after the addition of 1-indanol the reactions were quenched after 15 seconds. Conversions were determined by ¹H NMR (600 MHz) analysis against an internal standard of the unpurified reaction mixtures.

Scheme S2. Oxidation with Stoichiometric Quantities of Mn-Complex **12****•Representative Experimental Procedure for Enantioselective Oxidation with Stoichiometric Quantities of Mn-Br Complex **12** and *t*-BuOBr (Scheme S2).**

(Note: all operations carried out in air). To a 5 mL round-bottom flask charged with (*R,R*)-Mn-complex **12** (37.3 mg, 0.0550 mmol) was added CH_2Cl_2 (500 μL), H_2O (1.0 mL) and potassium acetate (2.50 M aq, 20.0 μL , 0.0500 mmol). The biphasic mixture was allowed to stir for one minute before *t*-BuOBr (5.7 μL , 0.050 mmol) as a solution in CH_2Cl_2 (200 μL) was added. Immediately after the addition of oxidant the mixture turned from deep brown to dark black. After 90 seconds, (\pm)-1-indanol (6.7 mg, 0.050 mmol) was added as a solution in CH_2Cl_2 (100 μL). Within a couple minutes after the addition of 1-indanol the mixture turned from dark black to deep brown. After the mixture was allowed to stir for five minutes the reaction was quenched upon addition of a saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$. The mixture was then extracted with Et_2O (3 x 2 mL) and the combined organic extracts were passed through a short plug of silica gel (3 x 6 cm) eluted with Et_2O (40 mL). The filtrate was concentrated and the residue purified by silica gel column chromatography (5% EtOAc /hexanes to 50% EtOAc /hexanes, gradient) to afford (*R*)-1-indanol. The enantiomeric purity was determined by HPLC analysis with a chiral column (Chiralpak OD-H column, 1.0 mL/min, 95:5 hexanes:isopropanol, 220 nm, $t_{\text{minor}} = 8.770$ min, $t_{\text{major}} = 9.800$ min).

•Determination of the amount of acetate or bicarbonate present in CH_2Cl_2 :

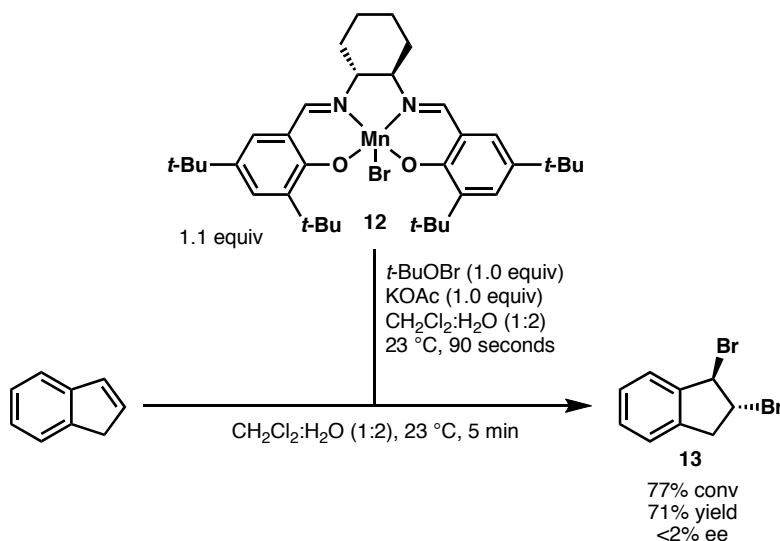
1) A mixture of KOAc (1.47g, 15.0 mmol) and AcOH (858 μL , 15.0 mmol), H_2O (60 mL) and CH_2Cl_2 (30 mL) was allowed to stir for 15 min. The organic layer was separated and filtered.

An infrared spectrum was taken of the organic phase, which showed no acetate to be present and a small peak corresponding to acetic acid. The mixture was concentrated under reduced pressure to reveal no residue (<1 mg).

2) A mixture of KOAc (1.47g, 15.0 mmol), H₂O (60 mL) and CH₂Cl₂ (30 mL) was allowed to stir for 15 min. The organic layer was separated and filtered. An infrared spectrum was taken of the organic phase, which showed no acetate to be present. The mixture was concentrated under reduced pressure to reveal no residue (<1 mg).

3) A mixture of NaHCO₃ (1.26g, 15.0 mmol), H₂O (60 mL) and CH₂Cl₂ (30 mL) was allowed to stir for 15 min. The organic layer was separated and filtered. The mixture was concentrated under reduced pressure to reveal no residue (<1 mg).

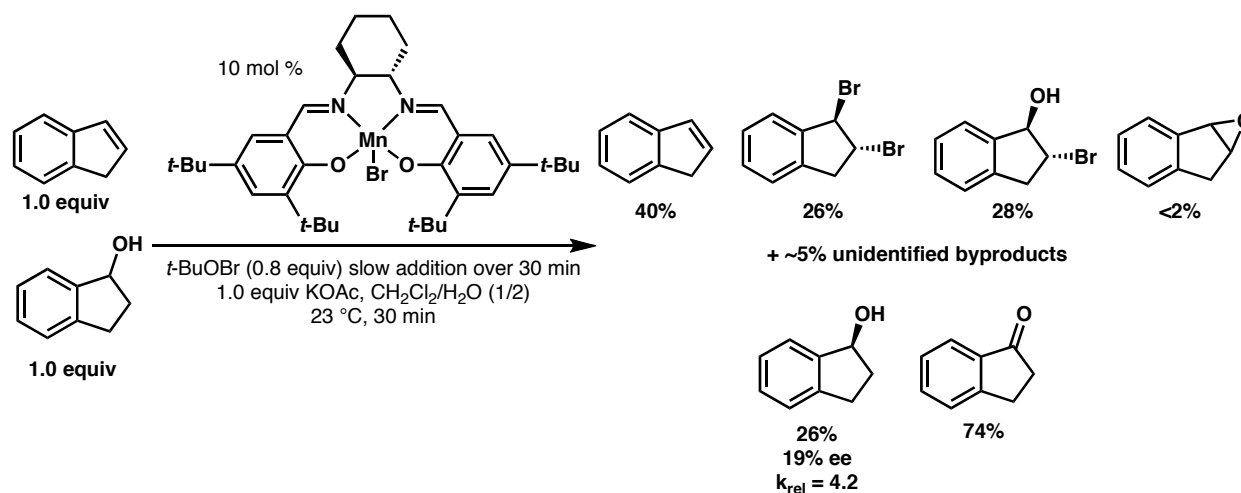
Scheme S3. Reaction of Indene with Stoichiometric Quantities of Mn-Complex **12** and *t*-BuOBr



• **Experimental Procedure for Reaction of Indene with Stoichiometric Quantities of Mn-Br Complex **12** and *t*-BuOBr (Scheme S3).** (Note: all operations carried out in air). To a 5 mL round-bottom flask charged with (*R,R*)-Mn-complex **12** (37.3 mg, 0.0550 mmol) was added CH₂Cl₂ (500 μL), H₂O (1.0 mL) and potassium acetate (2.50 M aq, 20.0 μL, 0.0500 mmol). The biphasic mixture was allowed to stir for one minute before *t*-BuOBr (5.7 μL, 0.050 mmol) as a solution in CH₂Cl₂ (200 μL) was added. Immediately after the addition of oxidant the mixture turned from deep brown to dark black. After 90 seconds, indene (5.8 mg, 0.050 mmol) was added as a solution in CH₂Cl₂ (100 μL). Within one minute after the addition of indene the mixture turned from dark black to deep brown. After the mixture was allowed to stir for five minutes the reaction was quenched upon addition of a saturated aqueous solution of Na₂S₂O₃. The mixture was then extracted with Et₂O (3 x 2 mL) and the combined organic extracts were passed through a short plug of silica gel (3 x 6 cm) eluted with Et₂O (40 mL). The filtrate was

concentrated and the residue purified by silica gel column chromatography (hexanes to 10% EtOAc/hexanes, gradient) to afford *trans*-1,2-dibromoindane⁸ (9.9 mg, 0.036 mmol, 71% yield). The enantiomeric purity was determined to be racemic by HPLC analysis with a chiral column (Chiralpak OD-H column, 1.0 mL/min, 99:1 hexanes:isopropanol, 220 nm, $t_{\text{minor}} = 5.026$ min, $t_{\text{major}} = 5.532$ min). (Note: <2% epoxide was detected in the crude reaction mixture by ¹H NMR (500 MHz) analysis.)

Scheme S4

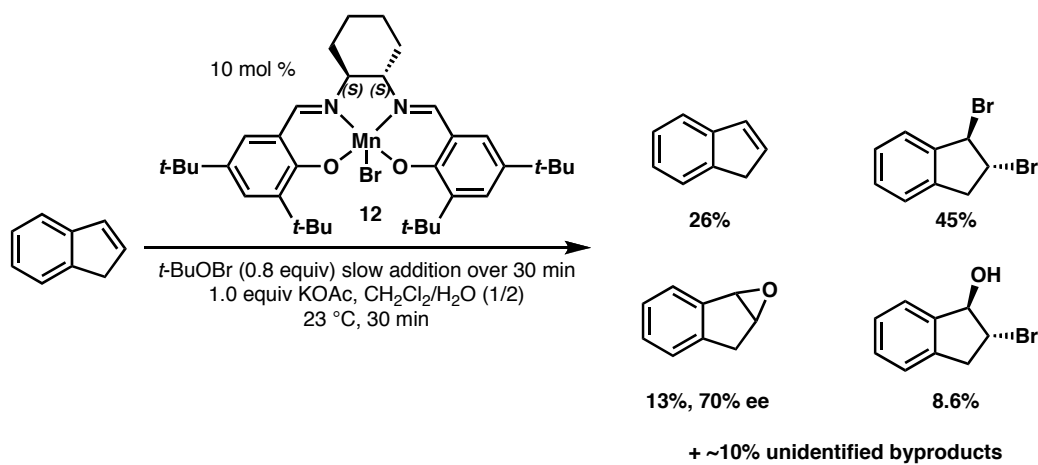


• **Experimental Procedure for Reaction of Indene and Indanol with Catalytic Quantities of Mn-Br Complex **12** and *t*-BuOBr (Scheme S4).** (Note: all operations carried out in air). To a 25 mL round-bottom flask charged with (±)-1-indanol (134 mg, 1.00 mmol), indene (117 μg, 1.00 mmol), (*S,S*)-Mn-complex **12** (67.8 mg, 0.100 mmol) and potassium acetate (98.2 mg, 1.00 mmol) was added CH₂Cl₂ (2.0 mL) and H₂O (2.0 mL). The biphasic mixture was allowed to stir for one minute before a solution of *t*-BuOBr (92.0 μL, 0.800 mmol) in H₂O (2.0 mL) was added over 30 min via syringe pump. After 15 minutes the reaction was quenched upon addition of a saturated aqueous solution of Na₂S₂O₃. The mixture was then extracted with Et₂O (3 x 2 mL) and the combined organic extracts were passed through a short plug of silica gel (3 x 6 cm) eluted with Et₂O (100 mL). The filtrate was carefully concentrated and the unpurified reaction mixture analyzed by ¹H NMR (500 MHz) spectroscopy to determine the relative amounts of the reaction products (NMR yields presented, determined by analysis with an internal standard).

(8) Tutar, A.; Cakmak, O.; Balci, M. *J. Chem. Res.* **2006**, 507-511. We have found that the ¹H NMR chemical shifts of *trans*-1,2-dibromoindane are slightly different to those reported. In all cases the chemical shifts are ~0.1 ppm downfield from the reported values. ¹H NMR (500 MHz, CDCl₃): 7.50-7.49 (1H, m), 7.38-7.32 (3H, m), 5.65 (1H, s), 4.90 (1H, d, $J = 5.0$ Hz), 3.84 (1H, dd, $J = 17.5, 5.5$ Hz), 3.29 (1H, d, $J = 17.5$ Hz). ¹³C NMR data is in good agreement with the reported values.

The residue was purified by silica gel column chromatography (5% Et₂O/hexanes to 50% Et₂O/hexanes, gradient) to isolate *trans*-1,2-dibromoindane,⁸ *trans*-2-bromoindan-1-ol,⁹ 1-indanol, indene and 1-indanone. The enantiomeric purity of (*S*)-1-indanol was determined by HPLC analysis with a chiral column (Chiralpak OD-H column, 1.0 mL/min, 95:5 hexanes:isopropanol, 220 nm, $t_{\text{minor}} = 8.770$ min, $t_{\text{major}} = 9.800$ min). (Note: <2% epoxide was detected in the crude reaction mixture by ¹H NMR (500 MHz) analysis.)

Scheme S5

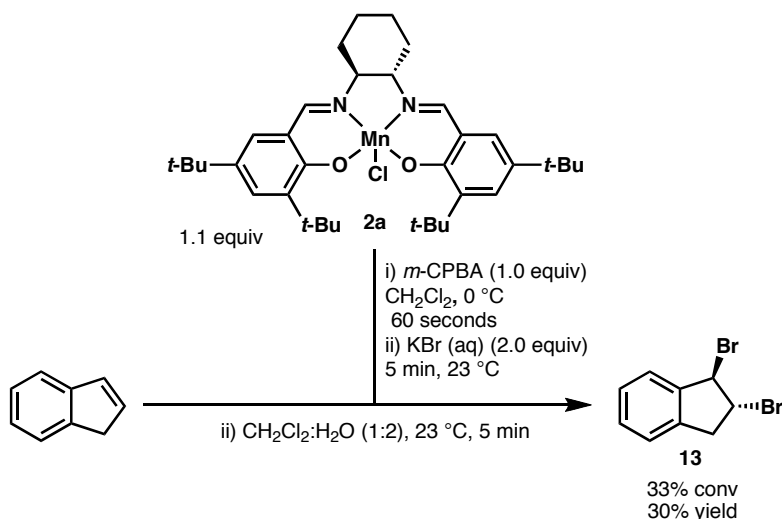


• **Experimental Procedure for Reaction of Indene with Catalytic Quantities of Mn-Br Complex **12** and *t*-BuOBr (Scheme S5).** (Note: all operations carried out in air). To a 25 mL round-bottom flask charged with indene (117 μg, 1.00 mmol), (*S,S*)-Mn-complex **12** (67.8 mg, 0.100 mmol) and potassium acetate (98.2 mg, 1.00 mmol) was added CH₂Cl₂ (2.0 mL) and H₂O (2.0 mL). The biphasic mixture was allowed to stir for one minute before a solution of *t*-BuOBr (92.0 μL, 0.800 mmol) in H₂O (2.0 mL) was added over 30 min via syringe pump. After 15 minutes the reaction was quenched upon addition of a saturated aqueous solution of Na₂S₂O₃. The mixture was then extracted with Et₂O (3 x 2 mL) and the combined organic extracts were passed through a short plug of silica gel (3 x 6 cm) eluted with Et₂O (100 mL). The filtrate was carefully concentrated and the unpurified reaction mixture analyzed by ¹H NMR (500 MHz) spectroscopy to determine the relative amounts of the reaction products (NMR yields presented, determined by analysis with an internal standard). The residue was purified by silica gel column chromatography (5% Et₂O/hexanes to 50% Et₂O/hexanes, gradient) to isolate *trans*-1,2-dibromoindane,⁸ *trans*-2-bromoindan-1-ol,⁹ indene oxide⁹ and indene. The enantiomeric purity

(9) For characterization data of indene oxide and *trans*-2-bromoindan-1-ol, see: Palmer, M. J.; Kenny, J. A.; Walsgrove, T.; Kawamoto, A. M.; Willis, M. J. *Chem. Soc., Perkin. Trans. 1*, **2002**, 416-427.

of indene oxide was determined by HPLC analysis with a chiral column (Chiralpak OJ column, 1.0 mL/min, 98:2 hexanes:isopropanol, 220 nm, $t_{\text{minor}} = 14.420$ min, $t_{\text{major}} = 16.853$ min).¹⁰

Scheme S6



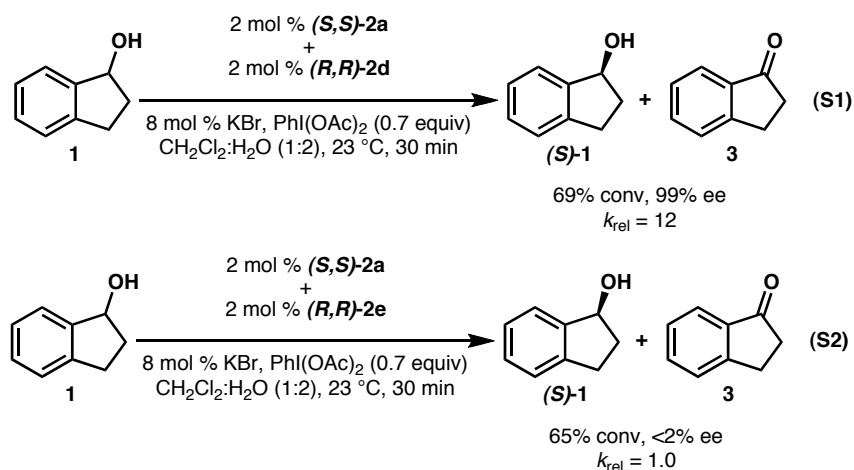
• **Experimental Procedure for the reaction shown in Scheme S6.** (Note: all operations carried out in air). To a 5 mL round-bottom flask charged with (*S,S*)-Mn-complex **2a** (34.7 mg, 0.0550 mmol) was added CH₂Cl₂ (300 μ L). The mixture was allowed to cool to 0 °C before *m*-CPBA (8.60 mg, 0.0500 mmol) was added as a solution in CH₂Cl₂ (100 μ L). The mixture turns from deep brown to deep green upon addition of *m*-CPBA. After 90 seconds potassium bromide (11.9 mg, 0.100 mmol) was added as a solution in H₂O (1.0 mL). The biphasic mixture was allowed to warm to 23 °C and stir for five minutes before indene (5.8 mg, 0.050 mmol) was added as a solution in CH₂Cl₂ (100 μ L). After the mixture was allowed to stir for five minutes the reaction was quenched upon addition of a saturated aqueous solution of Na₂S₂O₃. The mixture was then extracted with Et₂O (3 x 2 mL) and the combined organic extracts were passed through a short plug of silica gel (3 x 6 cm) eluted with Et₂O (40 mL). The filtrate was concentrated and the residue purified by silica gel column chromatography (hexanes to 10% EtOAc/hexanes, gradient) to afford *trans*-1,2-dibromoindane⁸ (4.1 mg, 0.015 mmol, 30% yield). (Note: <2% epoxide was detected in the crude reaction mixture by ¹H NMR (500 MHz) analysis.)

(10) The slight discrepancy observed in that the total amount of oxidation products exceeds the total amount of *t*-BuOBr added is likely due to small quantities of Br₂ present in the *t*-BuOBr mixture.

Table S2. Additional Data

entry	R_1	R_2	catalyst	conv (%) ^a	ee (%) ^b	k_{rel} ^c
1	<i>t</i> -Bu	<i>t</i> -Bu	2a	68	>99	>13
2	<i>t</i> -Bu	CH ₃	2b	65	34	1.9
3	<i>t</i> -Bu	H	2c	67	50	2.6
4	NO ₂	<i>t</i> -Bu	2d	68	26	1.6
5	OMe	<i>t</i> -Bu	2e	61	81	7.5
6	Me	<i>t</i> -Bu	2f	63	94	11

^a Determined by ¹H NMR (500 MHz) analysis of the unpurified reaction mixtures. ^b Determined by HPLC analysis with a chiral column. ^c $k_{rel} = \ln[(1-\text{conv})(1-\text{ee})]/\ln[(1-\text{conv})(1+\text{ee})]$.

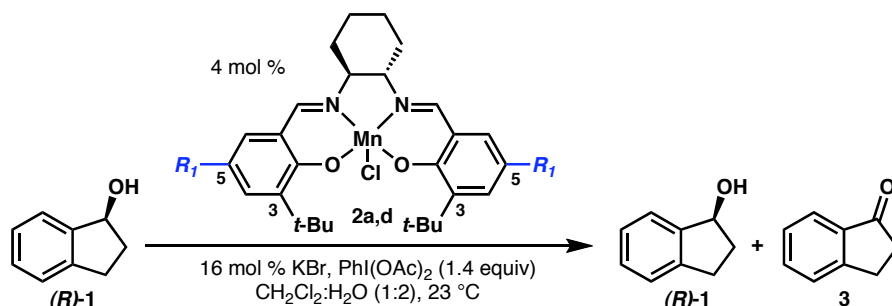


• The reactions illustrated in eqns (S1) and (S2) were carried out according to the general procedure for enantioselective oxidation with the exception that two different Mn-complexes were employed in the same reaction flask.

• To confirm that the result presented in eqn (S1) is valid, independent rate measurements for both catalysts (*S,S*)-**2a** and (*S,S*)-**2d** with (*R*)-1-indanol were carried out (Table 3). The conclusions derived from this data are in full accord with the results presented in eqn (S1). The data presented in Table 3 was acquired by analysis of small aliquots removed over the course of a reaction. The reaction was carried out under conditions analogous to those described in the general procedure for oxidative kinetic resolution (see above). The aliquots, once removed, were quenched immediately upon addition to a test tube containing sodium thiosulfate (aq) (1 mL),

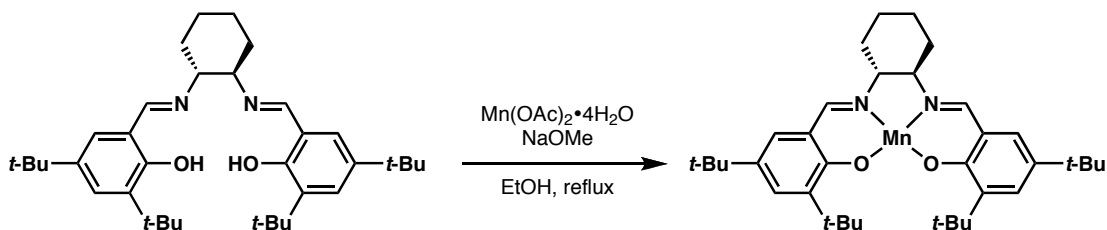
sodium bicarbonate (aq) (1 mL), diethyl ether (1 mL) and dimethyl sulfide (100 μ L). The mixture was then extracted with Et₂O (3 x 1 mL) and the combined organic phases were passed through a short plug of silica gel (3 x 0.5 cm) eluted with Et₂O (~8 mL). The volatiles were removed under reduced pressure and the conversion measured by ¹H NMR (500 MHz) analysis.

Table 3. Comparison of Rates for Catalyst **2a** and **2d**



entry	R ₁	catalyst	time (min)	conv (%) ^a
1	<i>t</i> -Bu	2a	1.0	46
2	<i>t</i> -Bu	2a	2.0	93
3	<i>t</i> -Bu	2a	3.0	>98
4	NO ₂	2d	1.0	27
5	NO ₂	2d	2.0	55
6	NO ₂	2d	3.0	71
7	NO ₂	2d	5.0	98

^a Determined by ¹H NMR (500 MHz) analysis of the unpurified reaction mixtures.

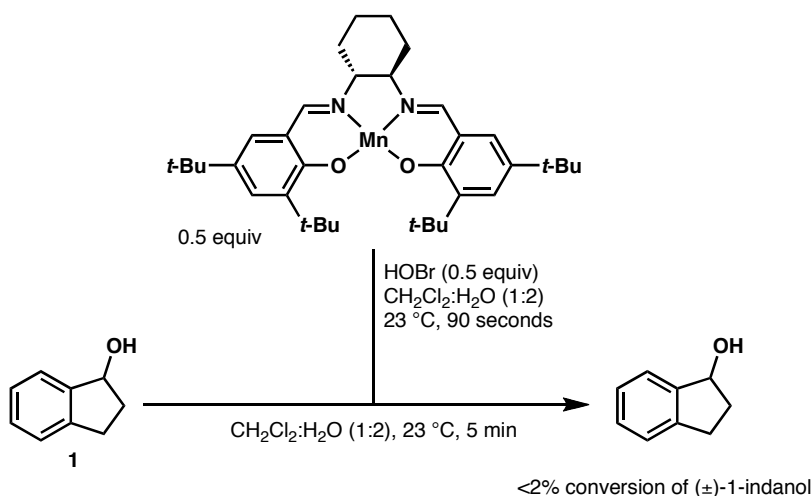


• Experimental Procedure for Synthesis of Mn(II)-Salen complex:

(Note: All operations carried out to *exclude* air.¹¹) To a three-neck flask equipped with stir-bar and reflux condenser was added the salen ligand (409 mg, 0.750 mmol). The whole apparatus was evacuated and backfilled with argon 3x. Degassed EtOH (60 mL) followed by NaOMe in degassed MeOH (3.0 mL, 1.5 mmol, 0.50 M in MeOH) were then added and the suspension heated to reflux. Once the solids had dissolved, a solution of Mn(OAc)₂•4H₂O (735 mg, 3.00

(11) Water, EtOH and MeOH were deoxygenated by bubbling argon through the liquid for several hours prior to use.

mmol) in H₂O/EtOH (5 mL) was added (the mixture turned from yellow to red). The mixture was allowed to reflux for 90 minutes. At this time the mixture was allowed to cool to 22 °C (the mixture turns from red to brown). The volatiles were removed under reduced pressure (~0.1 mmHg) to afford a brown solid. Dichloromethane (20 mL) was added to the residue and the suspension filtered. The mother liquor was concentrated under reduced pressure (~0.1 mmHg) to provide the Mn(II)-salen complex as a light yellow/brown solid (300 mg, 0.50 mmol, 66% yield).



• **Experimental Procedure for Attempted Oxidation with Mn(II)-Salen complex:**

(Note: All operations carried out to exclude air.) To a round-bottom flask equipped with a stir bar under argon was added the Mn(II)-salen complex (15 mg, 0.025 mmol) as a solution in CH₂Cl₂ (400 µL). Deoxygenated H₂O (750 µL) was added followed by an aqueous solution of hypobromous acid (250 µL, 0.025 mmol, 0.10 M in deoxygenated H₂O). The brown mixture was allowed to stir for 90 seconds before (±)-1-indanol (6.7 mg, 0.050 mmol) was added as a solution in CH₂Cl₂ (100 µL). After the mixture was allowed to stir for five minutes the reaction was quenched upon addition of a saturated aqueous solution of Na₂S₂O₃. The mixture was then extracted with Et₂O (3 x 2 mL) and the combined organic extracts were passed through a short plug of silica gel (3 x 6 cm) eluted with Et₂O (40 mL). The filtrate was then concentrated to afford a clear oil. ¹H NMR analysis of the unpurified reaction mixture indicates <2% conversion to 1-indanone.

X-ray Crystallographic Laboratory

Harvard University

Structure Report

Shao-Liang Zheng

Project Name: Brown101

Date: 01-27-2010

Prof. Corey

X-Ray Crystallography: A crystal mounted on a diffractometer was collected data at 100 K. The intensities of the reflections were collected by means of a Bruker APEX II CCD diffractometer ($\text{Mo}_{\text{K}\alpha}$ radiation, $\lambda=0.71073 \text{ \AA}$), and equipped with an Oxford Cryosystems nitrogen flow apparatus. The collection method involved 0.5° scans in ω at 28° in 2θ . Data integration down to 0.77 \AA resolution was carried out using SAINT V7.46 A (Bruker diffractometer, 2009) with reflection spot size optimization. Absorption corrections were made with the program SADABS (Bruker diffractometer, 2009). The structure was solved by the direct methods procedure and refined by least-squares methods against F^2 using SHELXS-97 and SHELXL-97 (Sheldrick, 2008). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. Crystal data as well as details of data collection and refinement are summarized in Table 1, geometric parameters are shown in Table 2, and hydrogen-bond parameters are listed in Table 3. The Ortep plots produced with SHELXL-97 program, and the other drawings were produced with Accelrys DS Visualizer 2.0 (Accelrys, 2007).

NOTE: C8/C13 and C58/C63 in the cyclohexane rings should be ONLY in S configuration. In that case, we use P1 space group to refine the structure rather than using the disorder model and refine it as a higher symmetry space group: P-1.

Table 1. Experimental details

	Brown101
Crystal data	
Chemical formula	$\text{C}_{101}\text{H}_{180}\text{F}_{12}\text{Mn}_2\text{N}_4\text{O}_{12}\text{Sb}_2$
M_r	2223.87
Crystal system, space group	Triclinic, $P1$
Temperature (K)	100
a, b, c (\AA)	9.7378 (12), 16.160 (2), 19.357 (2)
α, β, γ ($^\circ$)	74.762 (4), 78.464 (4), 87.099 (4)
V (\AA^3)	2879.5 (6)
Z	1

Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.75
Crystal size (mm)	0.36 × 0.18 × 0.05
Data collection	
Diffractometer	CCD area detector diffractometer
Absorption correction	Multi-scan <i>SADABS</i> (Sheldrick, 2009)
T_{\min} , T_{\max}	0.774, 0.963
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	68548, 26061, 24149
R_{int}	0.026
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.034, 0.072, 1.10
No. of reflections	26061
No. of parameters	1324
No. of restraints	272
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	1.06, -0.64
Absolute structure	Flack H D (1983), <i>Acta Cryst.</i> A39, 876-881
Flack parameter	-0.016 (10)

Computer programs: *APEX2* v2009.3.0 (Bruker-AXS, 2009), *SAINT* 7.46A (Bruker-AXS, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), Bruker *SHELXTL*.

Table 2. Geometric parameters (Å, °)

Mn1—O2	1.879 (3)	C60—H60B	0.9900
Mn1—O1	1.879 (2)	C61—C62	1.526 (5)
Mn1—N1	1.981 (3)	C61—H61A	0.9900
Mn1—N2	1.982 (3)	C61—H61B	0.9900
Mn1—O4	2.248 (3)	C62—C63	1.515 (5)
Mn1—O3	2.284 (2)	C62—H62A	0.9900
O1—C1	1.323 (4)	C62—H62B	0.9900
O2—C20	1.327 (4)	C63—H63A	1.0000
O3—C37	1.440 (4)	C64—C65	1.447 (5)
O3—H3O	0.8295	C64—H64A	0.9500
O4—C40	1.452 (5)	C65—C66	1.404 (5)

O4—H4O	0.9668	C65—C70	1.430 (5)
N1—C7	1.289 (4)	C66—C67	1.379 (5)
N1—C8	1.480 (4)	C66—H66A	0.9500
N2—C14	1.284 (4)	C67—C68	1.408 (5)
N2—C13	1.484 (4)	C67—C79	1.534 (4)
C1—C6	1.408 (5)	C68—C69	1.384 (5)
C1—C2	1.425 (5)	C68—H68A	0.9500
C2—C3	1.398 (5)	C69—C70	1.421 (5)
C2—C21	1.533 (6)	C69—C83	1.542 (5)
C3—C4	1.409 (5)	C71—C73	1.527 (6)
C3—H3A	0.9500	C71—C74	1.537 (6)
C4—C5	1.363 (5)	C71—C72	1.543 (5)
C4—C25	1.529 (4)	C72—H72A	0.9800
C5—C6	1.419 (5)	C72—H72B	0.9800
C5—H5A	0.9500	C72—H72C	0.9800
C6—C7	1.435 (5)	C73—H73A	0.9800
C7—H7A	0.9500	C73—H73B	0.9800
C8—C13	1.520 (4)	C73—H73C	0.9800
C8—C9	1.523 (5)	C74—H74A	0.9800
C8—H8A	1.0000	C74—H74B	0.9800
C9—C10	1.516 (5)	C74—H74C	0.9800
C9—H9A	0.9900	C75—C78	1.523 (5)
C9—H9B	0.9900	C75—C77	1.531 (5)
C10—C11	1.514 (4)	C75—C76	1.541 (6)
C10—H10A	0.9900	C76—H76A	0.9800
C10—H10B	0.9900	C76—H76B	0.9800
C11—C12	1.532 (5)	C76—H76C	0.9800
C11—H11A	0.9900	C77—H77A	0.9800
C11—H11B	0.9900	C77—H77B	0.9800
C12—C13	1.528 (4)	C77—H77C	0.9800
C12—H12A	0.9900	C78—H78A	0.9800
C12—H12B	0.9900	C78—H78B	0.9800
C13—H13A	1.0000	C78—H78C	0.9800
C14—C15	1.446 (5)	C79—C82	1.523 (6)
C14—H14A	0.9500	C79—C80	1.536 (6)
C15—C16	1.410 (5)	C79—C81	1.537 (5)
C15—C20	1.424 (5)	C80—H80A	0.9800

C16—C17	1.376 (6)	C80—H80B	0.9800
C16—H16A	0.9500	C80—H80C	0.9800
C17—C18	1.391 (6)	C81—H81A	0.9800
C17—C29	1.542 (5)	C81—H81B	0.9800
C18—C19	1.386 (5)	C81—H81C	0.9800
C18—H18A	0.9500	C82—H82A	0.9800
C19—C20	1.418 (5)	C82—H82B	0.9800
C19—C33	1.542 (6)	C82—H82C	0.9800
C21—C24	1.527 (5)	C83—C85	1.537 (5)
C21—C23	1.541 (5)	C83—C86	1.540 (5)
C21—C22	1.548 (5)	C83—C84	1.541 (5)
C22—H22A	0.9800	C84—H84A	0.9800
C22—H22B	0.9800	C84—H84B	0.9800
C22—H22C	0.9800	C84—H84C	0.9800
C23—H23A	0.9800	C85—H85A	0.9800
C23—H23B	0.9800	C85—H85B	0.9800
C23—H23C	0.9800	C85—H85C	0.9800
C24—H24A	0.9800	C86—H86A	0.9800
C24—H24B	0.9800	C86—H86B	0.9800
C24—H24C	0.9800	C86—H86C	0.9800
C25—C28	1.519 (6)	C87—C88	1.488 (8)
C25—C26	1.538 (5)	C87—C89	1.495 (9)
C25—C27	1.543 (5)	C87—H87A	1.0000
C26—H26A	0.9800	C88—H88A	0.9800
C26—H26B	0.9800	C88—H88B	0.9800
C26—H26C	0.9800	C88—H88C	0.9800
C27—H27A	0.9800	C89—H89A	0.9800
C27—H27B	0.9800	C89—H89B	0.9800
C27—H27C	0.9800	C89—H89C	0.9800
C28—H28A	0.9800	C88B—H88D	0.9800
C28—H28B	0.9800	C88B—H88E	0.9800
C28—H28C	0.9800	C88B—H88F	0.9800
C29—C32B	1.450 (8)	C89B—H89D	0.9800
C29—C31	1.513 (9)	C89B—H89E	0.9800
C29—C30	1.527 (9)	C89B—H89F	0.9800
C29—C31B	1.528 (9)	C90—C92	1.498 (6)
C29—C32	1.567 (10)	C90—C91	1.516 (6)

C29—C30B	1.654 (8)	C90—H90A	1.0000
C30—H30A	0.9800	C91—H91A	0.9800
C30—H30B	0.9800	C91—H91B	0.9800
C30—H30C	0.9800	C91—H91C	0.9800
C31—H31A	0.9800	C92—H92A	0.9800
C31—H31B	0.9800	C92—H92B	0.9800
C31—H31C	0.9800	C92—H92C	0.9800
C32—H32A	0.9800	Sb1—F4	1.857 (3)
C32—H32B	0.9800	Sb1—F2	1.867 (3)
C32—H32C	0.9800	Sb1—F6	1.870 (3)
C30B—H30D	0.9800	Sb1—F3	1.877 (3)
C30B—H30E	0.9800	Sb1—F5	1.879 (3)
C30B—H30F	0.9800	Sb1—F1	1.879 (3)
C31B—H31D	0.9800	Sb2—F12B	1.849 (15)
C31B—H31E	0.9800	Sb2—F11	1.868 (5)
C31B—H31F	0.9800	Sb2—F8	1.870 (3)
C32B—H32D	0.9800	Sb2—F10	1.873 (3)
C32B—H32E	0.9800	Sb2—F7	1.876 (3)
C32B—H32F	0.9800	Sb2—F12	1.877 (5)
C33—C34	1.529 (6)	Sb2—F9	1.883 (3)
C33—C35	1.542 (6)	Sb2—F11B	1.900 (13)
C33—C36	1.546 (6)	O1S—C1S	1.414 (5)
C34—H34A	0.9800	O1S—H1S	0.9238
C34—H34B	0.9800	C1S—C3S	1.502 (7)
C34—H34C	0.9800	C1S—C2S	1.508 (7)
C35—H35A	0.9800	C1S—H1SA	1.0000
C35—H35B	0.9800	C2S—H2SA	0.9800
C35—H35C	0.9800	C2S—H2SB	0.9800
C36—H36A	0.9800	C2S—H2SC	0.9800
C36—H36B	0.9800	C3S—H3SA	0.9800
C36—H36C	0.9800	C3S—H3SB	0.9800
C37—C38	1.514 (5)	C3S—H3SC	0.9800
C37—C39	1.514 (5)	O2S—C4S	1.453 (5)
C37—H37A	1.0000	O2S—H2S	0.9420
C38—H38A	0.9800	C4S—C6S	1.509 (5)
C38—H38B	0.9800	C4S—C5S	1.512 (6)
C38—H38C	0.9800	C4S—H4SA	1.0000

C39—H39A	0.9800	C5S—H5SA	0.9800
C39—H39B	0.9800	C5S—H5SB	0.9800
C39—H39C	0.9800	C5S—H5SC	0.9800
C40—C42	1.507 (6)	C6S—H6SA	0.9800
C40—C41	1.519 (6)	C6S—H6SB	0.9800
C40—H40A	1.0000	C6S—H6SC	0.9800
C41—H41A	0.9800	O3S—C7S	1.439 (5)
C41—H41B	0.9800	O3S—H3S	0.9166
C41—H41C	0.9800	C7S—C9S	1.481 (7)
C42—H42A	0.9800	C7S—C8S	1.514 (7)
C42—H42B	0.9800	C7S—H7SA	1.0000
C42—H42C	0.9800	C8S—H8SA	0.9800
Mn2—O5	1.872 (3)	C8S—H8SB	0.9800
Mn2—O6	1.873 (2)	C8S—H8SC	0.9800
Mn2—N4	1.981 (3)	C9S—H9SA	0.9800
Mn2—N3	1.984 (3)	C9S—H9SB	0.9800
Mn2—O8	2.259 (2)	C9S—H9SC	0.9800
Mn2—O7	2.292 (2)	O4S—C10S	1.430 (5)
O5—C51	1.317 (4)	O4S—H4S	0.9141
O6—C70	1.322 (4)	C10S—C12S	1.511 (5)
O7—C87	1.448 (4)	C10S—C11S	1.518 (6)
O7—H7O	0.9743	C10S—H10C	1.0000
O8—C90	1.447 (4)	C11S—H11C	0.9800
O8—H8O	0.8558	C11S—H11D	0.9800
N3—C57	1.287 (4)	C11S—H11E	0.9800
N3—C58	1.489 (4)	C12S—H12C	0.9800
N4—C64	1.283 (4)	C12S—H12D	0.9800
N4—C63	1.493 (4)	C12S—H12E	0.9800
C51—C56	1.413 (5)	C1P—C2P	1.516 (9)
C51—C52	1.432 (5)	C1P—H1PA	0.9800
C52—C53	1.395 (5)	C1P—H1PB	0.9800
C52—C71	1.536 (5)	C1P—H1PC	0.9800
C53—C54	1.416 (5)	C2P—C3P	1.424 (9)
C53—H53A	0.9500	C2P—H2PA	0.9900
C54—C55	1.377 (6)	C2P—H2PB	0.9900
C54—C75	1.529 (5)	C3P—C4P	1.441 (9)
C55—C56	1.405 (5)	C3P—H3PA	0.9900

C55—H55A	0.9500	C3P—H3PB	0.9900
C56—C57	1.439 (5)	C4P—C5P	1.435 (9)
C57—H57A	0.9500	C4P—H4PA	0.9900
C58—C63	1.522 (4)	C4P—H4PB	0.9900
C58—C59	1.532 (4)	C5P—H5PA	0.9800
C58—H58A	1.0000	C5P—H5PB	0.9800
C59—C60	1.521 (5)	C5P—H5PC	0.9800
C59—H59A	0.9900	C2Q—H2QA	0.9900
C59—H59B	0.9900	C2Q—H2QB	0.9900
C60—C61	1.531 (5)	C4Q—H4QA	0.9900
C60—H60A	0.9900	C4Q—H4QB	0.9900
O2—Mn1—O1	95.08 (11)	C59—C60—C61	111.9 (3)
O2—Mn1—N1	172.94 (12)	C59—C60—H60A	109.2
O1—Mn1—N1	91.45 (12)	C61—C60—H60A	109.2
O2—Mn1—N2	91.34 (11)	C59—C60—H60B	109.2
O1—Mn1—N2	173.53 (11)	C61—C60—H60B	109.2
N1—Mn1—N2	82.17 (12)	H60A—C60—H60B	107.9
O2—Mn1—O4	93.43 (11)	C62—C61—C60	112.0 (3)
O1—Mn1—O4	90.28 (10)	C62—C61—H61A	109.2
N1—Mn1—O4	89.22 (11)	C60—C61—H61A	109.2
N2—Mn1—O4	88.60 (10)	C62—C61—H61B	109.2
O2—Mn1—O3	89.01 (10)	C60—C61—H61B	109.2
O1—Mn1—O3	93.16 (10)	H61A—C61—H61B	107.9
N1—Mn1—O3	87.94 (11)	C63—C62—C61	110.3 (3)
N2—Mn1—O3	87.67 (10)	C63—C62—H62A	109.6
O4—Mn1—O3	175.59 (10)	C61—C62—H62A	109.6
C1—O1—Mn1	129.2 (2)	C63—C62—H62B	109.6
C20—O2—Mn1	130.4 (2)	C61—C62—H62B	109.6
C37—O3—Mn1	126.1 (2)	H62A—C62—H62B	108.1
C37—O3—H3O	109.1	N4—C63—C62	115.9 (3)
Mn1—O3—H3O	124.4	N4—C63—C58	106.5 (2)
C40—O4—Mn1	126.9 (2)	C62—C63—C58	111.0 (3)
C40—O4—H4O	106.3	N4—C63—H63A	107.7
Mn1—O4—H4O	126.6	C62—C63—H63A	107.7
C7—N1—C8	122.3 (3)	C58—C63—H63A	107.7
C7—N1—Mn1	124.3 (3)	N4—C64—C65	126.0 (3)

C8—N1—Mn1	113.40 (19)	N4—C64—H64A	117.0
C14—N2—C13	122.0 (3)	C65—C64—H64A	117.0
C14—N2—Mn1	124.8 (2)	C66—C65—C70	120.6 (3)
C13—N2—Mn1	113.16 (18)	C66—C65—C64	116.1 (3)
O1—C1—C6	122.0 (3)	C70—C65—C64	123.0 (3)
O1—C1—C2	119.2 (3)	C67—C66—C65	121.5 (3)
C6—C1—C2	118.8 (3)	C67—C66—H66A	119.2
C3—C2—C1	117.3 (4)	C65—C66—H66A	119.2
C3—C2—C21	121.4 (3)	C66—C67—C68	116.8 (3)
C1—C2—C21	121.3 (3)	C66—C67—C79	122.7 (3)
C2—C3—C4	124.7 (3)	C68—C67—C79	120.4 (3)
C2—C3—H3A	117.7	C69—C68—C67	124.7 (3)
C4—C3—H3A	117.7	C69—C68—H68A	117.6
C5—C4—C3	116.8 (3)	C67—C68—H68A	117.6
C5—C4—C25	123.2 (3)	C68—C69—C70	117.9 (3)
C3—C4—C25	120.0 (3)	C68—C69—C83	121.6 (3)
C4—C5—C6	121.7 (4)	C70—C69—C83	120.4 (3)
C4—C5—H5A	119.1	O6—C70—C69	120.2 (3)
C6—C5—H5A	119.1	O6—C70—C65	121.5 (3)
C1—C6—C5	120.7 (3)	C69—C70—C65	118.3 (3)
C1—C6—C7	123.3 (3)	C73—C71—C52	110.9 (3)
C5—C6—C7	116.1 (3)	C73—C71—C74	107.2 (4)
N1—C7—C6	126.1 (4)	C52—C71—C74	111.9 (3)
N1—C7—H7A	116.9	C73—C71—C72	110.7 (3)
C6—C7—H7A	116.9	C52—C71—C72	109.0 (3)
N1—C8—C13	106.3 (2)	C74—C71—C72	107.1 (4)
N1—C8—C9	116.6 (3)	C71—C72—H72A	109.5
C13—C8—C9	111.2 (3)	C71—C72—H72B	109.5
N1—C8—H8A	107.5	H72A—C72—H72B	109.5
C13—C8—H8A	107.5	C71—C72—H72C	109.5
C9—C8—H8A	107.5	H72A—C72—H72C	109.5
C10—C9—C8	110.1 (3)	H72B—C72—H72C	109.5
C10—C9—H9A	109.6	C71—C73—H73A	109.5
C8—C9—H9A	109.6	C71—C73—H73B	109.5
C10—C9—H9B	109.6	H73A—C73—H73B	109.5
C8—C9—H9B	109.6	C71—C73—H73C	109.5
H9A—C9—H9B	108.2	H73A—C73—H73C	109.5

C11—C10—C9	112.7 (3)	H73B—C73—H73C	109.5
C11—C10—H10A	109.0	C71—C74—H74A	109.5
C9—C10—H10A	109.0	C71—C74—H74B	109.5
C11—C10—H10B	109.0	H74A—C74—H74B	109.5
C9—C10—H10B	109.0	C71—C74—H74C	109.5
H10A—C10—H10B	107.8	H74A—C74—H74C	109.5
C10—C11—C12	110.9 (3)	H74B—C74—H74C	109.5
C10—C11—H11A	109.5	C78—C75—C54	109.5 (3)
C12—C11—H11A	109.5	C78—C75—C77	109.9 (3)
C10—C11—H11B	109.5	C54—C75—C77	108.4 (3)
C12—C11—H11B	109.5	C78—C75—C76	108.6 (3)
H11A—C11—H11B	108.0	C54—C75—C76	111.5 (3)
C13—C12—C11	109.2 (3)	C77—C75—C76	108.9 (3)
C13—C12—H12A	109.8	C75—C76—H76A	109.5
C11—C12—H12A	109.8	C75—C76—H76B	109.5
C13—C12—H12B	109.8	H76A—C76—H76B	109.5
C11—C12—H12B	109.8	C75—C76—H76C	109.5
H12A—C12—H12B	108.3	H76A—C76—H76C	109.5
N2—C13—C8	106.8 (2)	H76B—C76—H76C	109.5
N2—C13—C12	116.8 (2)	C75—C77—H77A	109.5
C8—C13—C12	110.5 (2)	C75—C77—H77B	109.5
N2—C13—H13A	107.5	H77A—C77—H77B	109.5
C8—C13—H13A	107.5	C75—C77—H77C	109.5
C12—C13—H13A	107.5	H77A—C77—H77C	109.5
N2—C14—C15	126.1 (3)	H77B—C77—H77C	109.5
N2—C14—H14A	116.9	C75—C78—H78A	109.5
C15—C14—H14A	116.9	C75—C78—H78B	109.5
C16—C15—C20	120.3 (3)	H78A—C78—H78B	109.5
C16—C15—C14	116.6 (3)	C75—C78—H78C	109.5
C20—C15—C14	123.0 (3)	H78A—C78—H78C	109.5
C17—C16—C15	121.5 (4)	H78B—C78—H78C	109.5
C17—C16—H16A	119.3	C82—C79—C67	110.4 (3)
C15—C16—H16A	119.3	C82—C79—C80	109.1 (4)
C16—C17—C18	116.8 (3)	C67—C79—C80	111.4 (3)
C16—C17—C29	121.2 (4)	C82—C79—C81	108.7 (3)
C18—C17—C29	122.0 (4)	C67—C79—C81	108.4 (3)
C19—C18—C17	125.2 (4)	C80—C79—C81	108.8 (4)

C19—C18—H18A	117.4	C79—C80—H80A	109.5
C17—C18—H18A	117.4	C79—C80—H80B	109.5
C18—C19—C20	117.6 (4)	H80A—C80—H80B	109.5
C18—C19—C33	122.0 (4)	C79—C80—H80C	109.5
C20—C19—C33	120.4 (3)	H80A—C80—H80C	109.5
O2—C20—C19	120.2 (3)	H80B—C80—H80C	109.5
O2—C20—C15	121.3 (3)	C79—C81—H81A	109.5
C19—C20—C15	118.5 (3)	C79—C81—H81B	109.5
C24—C21—C2	112.4 (3)	H81A—C81—H81B	109.5
C24—C21—C23	107.9 (3)	C79—C81—H81C	109.5
C2—C21—C23	110.5 (3)	H81A—C81—H81C	109.5
C24—C21—C22	107.6 (3)	H81B—C81—H81C	109.5
C2—C21—C22	109.6 (3)	C79—C82—H82A	109.5
C23—C21—C22	108.8 (3)	C79—C82—H82B	109.5
C21—C22—H22A	109.5	H82A—C82—H82B	109.5
C21—C22—H22B	109.5	C79—C82—H82C	109.5
H22A—C22—H22B	109.5	H82A—C82—H82C	109.5
C21—C22—H22C	109.5	H82B—C82—H82C	109.5
H22A—C22—H22C	109.5	C85—C83—C86	111.1 (3)
H22B—C22—H22C	109.5	C85—C83—C84	107.5 (3)
C21—C23—H23A	109.5	C86—C83—C84	107.3 (3)
C21—C23—H23B	109.5	C85—C83—C69	109.9 (3)
H23A—C23—H23B	109.5	C86—C83—C69	109.6 (3)
C21—C23—H23C	109.5	C84—C83—C69	111.4 (3)
H23A—C23—H23C	109.5	C83—C84—H84A	109.5
H23B—C23—H23C	109.5	C83—C84—H84B	109.5
C21—C24—H24A	109.5	H84A—C84—H84B	109.5
C21—C24—H24B	109.5	C83—C84—H84C	109.5
H24A—C24—H24B	109.5	H84A—C84—H84C	109.5
C21—C24—H24C	109.5	H84B—C84—H84C	109.5
H24A—C24—H24C	109.5	C83—C85—H85A	109.5
H24B—C24—H24C	109.5	C83—C85—H85B	109.5
C28—C25—C4	112.1 (3)	H85A—C85—H85B	109.5
C28—C25—C26	108.6 (3)	C83—C85—H85C	109.5
C4—C25—C26	109.9 (3)	H85A—C85—H85C	109.5
C28—C25—C27	108.1 (4)	H85B—C85—H85C	109.5
C4—C25—C27	109.4 (3)	C83—C86—H86A	109.5

C26—C25—C27	108.7 (3)	C83—C86—H86B	109.5
C25—C26—H26A	109.5	H86A—C86—H86B	109.5
C25—C26—H26B	109.5	C83—C86—H86C	109.5
H26A—C26—H26B	109.5	H86A—C86—H86C	109.5
C25—C26—H26C	109.5	H86B—C86—H86C	109.5
H26A—C26—H26C	109.5	O7—C87—C88	115.2 (4)
H26B—C26—H26C	109.5	O7—C87—C89	114.8 (5)
C25—C27—H27A	109.5	C88—C87—C89	96.9 (5)
C25—C27—H27B	109.5	O7—C87—H87A	109.8
H27A—C27—H27B	109.5	C88—C87—H87A	109.8
C25—C27—H27C	109.5	C89—C87—H87A	109.8
H27A—C27—H27C	109.5	H88D—C88B—H88E	109.5
H27B—C27—H27C	109.5	H88D—C88B—H88F	109.5
C25—C28—H28A	109.5	H88E—C88B—H88F	109.5
C25—C28—H28B	109.5	H89D—C89B—H89E	109.5
H28A—C28—H28B	109.5	H89D—C89B—H89F	109.5
C25—C28—H28C	109.5	H89E—C89B—H89F	109.5
H28A—C28—H28C	109.5	O8—C90—C92	110.3 (3)
H28B—C28—H28C	109.5	O8—C90—C91	109.7 (3)
C32B—C29—C31	132.0 (6)	C92—C90—C91	112.6 (3)
C32B—C29—C30	75.5 (6)	O8—C90—H90A	108.0
C31—C29—C30	111.9 (6)	C92—C90—H90A	108.0
C32B—C29—C31B	113.7 (6)	C91—C90—H90A	108.0
C30—C29—C31B	128.7 (6)	C90—C91—H91A	109.5
C32B—C29—C17	114.7 (4)	C90—C91—H91B	109.5
C31—C29—C17	107.2 (5)	H91A—C91—H91B	109.5
C30—C29—C17	109.4 (4)	C90—C91—H91C	109.5
C31B—C29—C17	110.6 (5)	H91A—C91—H91C	109.5
C31—C29—C32	110.3 (6)	H91B—C91—H91C	109.5
C30—C29—C32	108.2 (6)	C90—C92—H92A	109.5
C17—C29—C32	109.9 (4)	C90—C92—H92B	109.5
C32B—C29—C30B	106.8 (5)	H92A—C92—H92B	109.5
C31B—C29—C30B	98.7 (5)	C90—C92—H92C	109.5
C17—C29—C30B	111.1 (4)	H92A—C92—H92C	109.5
C29—C30—H30A	109.5	H92B—C92—H92C	109.5
C29—C30—H30B	109.5	F4—Sb1—F2	178.83 (17)
C29—C30—H30C	109.5	F4—Sb1—F6	90.59 (16)

C29—C31—H31A	109.5	F2—Sb1—F6	90.50 (14)
C29—C31—H31B	109.5	F4—Sb1—F3	90.20 (13)
C29—C31—H31C	109.5	F2—Sb1—F3	89.34 (13)
C29—C32—H32A	109.5	F6—Sb1—F3	90.97 (14)
C29—C32—H32B	109.5	F4—Sb1—F5	90.00 (15)
C29—C32—H32C	109.5	F2—Sb1—F5	88.93 (13)
C29—C30B—H30D	109.5	F6—Sb1—F5	178.63 (14)
C29—C30B—H30E	109.5	F3—Sb1—F5	90.26 (13)
H30D—C30B—H30E	109.5	F4—Sb1—F1	90.57 (13)
C29—C30B—H30F	109.5	F2—Sb1—F1	89.86 (14)
H30D—C30B—H30F	109.5	F6—Sb1—F1	90.45 (14)
H30E—C30B—H30F	109.5	F3—Sb1—F1	178.37 (15)
C29—C31B—H31D	109.5	F5—Sb1—F1	88.30 (13)
C29—C31B—H31E	109.5	F12B—Sb2—F11	169.2 (10)
H31D—C31B—H31E	109.5	F12B—Sb2—F8	83.7 (14)
C29—C31B—H31F	109.5	F11—Sb2—F8	87.73 (19)
H31D—C31B—H31F	109.5	F12B—Sb2—F10	95.0 (14)
H31E—C31B—H31F	109.5	F11—Sb2—F10	93.51 (18)
C29—C32B—H32D	109.5	F8—Sb2—F10	178.29 (18)
C29—C32B—H32E	109.5	F12B—Sb2—F7	83.7 (9)
H32D—C32B—H32E	109.5	F11—Sb2—F7	89.8 (2)
C29—C32B—H32F	109.5	F8—Sb2—F7	90.63 (16)
H32D—C32B—H32F	109.5	F10—Sb2—F7	88.19 (14)
H32E—C32B—H32F	109.5	F11—Sb2—F12	177.3 (5)
C34—C33—C19	109.6 (3)	F8—Sb2—F12	90.4 (4)
C34—C33—C35	108.0 (4)	F10—Sb2—F12	88.4 (4)
C19—C33—C35	112.2 (3)	F7—Sb2—F12	92.2 (3)
C34—C33—C36	109.5 (3)	F12B—Sb2—F9	94.3 (9)
C19—C33—C36	110.2 (4)	F11—Sb2—F9	92.4 (2)
C35—C33—C36	107.3 (4)	F8—Sb2—F9	90.92 (16)
C33—C34—H34A	109.5	F10—Sb2—F9	90.21 (15)
C33—C34—H34B	109.5	F7—Sb2—F9	177.36 (16)
H34A—C34—H34B	109.5	F12—Sb2—F9	85.7 (3)
C33—C34—H34C	109.5	F12B—Sb2—F11B	174.9 (15)
H34A—C34—H34C	109.5	F8—Sb2—F11B	101.5 (5)
H34B—C34—H34C	109.5	F10—Sb2—F11B	79.9 (5)
C33—C35—H35A	109.5	F7—Sb2—F11B	96.0 (7)

C33—C35—H35B	109.5	F9—Sb2—F11B	85.8 (7)
H35A—C35—H35B	109.5	C1S—O1S—H1S	113.0
C33—C35—H35C	109.5	O1S—C1S—C3S	106.9 (4)
H35A—C35—H35C	109.5	O1S—C1S—C2S	111.1 (4)
H35B—C35—H35C	109.5	C3S—C1S—C2S	113.5 (4)
C33—C36—H36A	109.5	O1S—C1S—H1SA	108.4
C33—C36—H36B	109.5	C3S—C1S—H1SA	108.4
H36A—C36—H36B	109.5	C2S—C1S—H1SA	108.4
C33—C36—H36C	109.5	C1S—C2S—H2SA	109.5
H36A—C36—H36C	109.5	C1S—C2S—H2SB	109.5
H36B—C36—H36C	109.5	H2SA—C2S—H2SB	109.5
O3—C37—C38	110.6 (3)	C1S—C2S—H2SC	109.5
O3—C37—C39	109.8 (3)	H2SA—C2S—H2SC	109.5
C38—C37—C39	111.8 (3)	H2SB—C2S—H2SC	109.5
O3—C37—H37A	108.2	C1S—C3S—H3SA	109.5
C38—C37—H37A	108.2	C1S—C3S—H3SB	109.5
C39—C37—H37A	108.2	H3SA—C3S—H3SB	109.5
C37—C38—H38A	109.5	C1S—C3S—H3SC	109.5
C37—C38—H38B	109.5	H3SA—C3S—H3SC	109.5
H38A—C38—H38B	109.5	H3SB—C3S—H3SC	109.5
C37—C38—H38C	109.5	C4S—O2S—H2S	111.8
H38A—C38—H38C	109.5	O2S—C4S—C6S	109.9 (4)
H38B—C38—H38C	109.5	O2S—C4S—C5S	106.3 (3)
C37—C39—H39A	109.5	C6S—C4S—C5S	113.4 (3)
C37—C39—H39B	109.5	O2S—C4S—H4SA	109.0
H39A—C39—H39B	109.5	C6S—C4S—H4SA	109.0
C37—C39—H39C	109.5	C5S—C4S—H4SA	109.0
H39A—C39—H39C	109.5	C4S—C5S—H5SA	109.5
H39B—C39—H39C	109.5	C4S—C5S—H5SB	109.5
O4—C40—C42	110.6 (3)	H5SA—C5S—H5SB	109.5
O4—C40—C41	109.3 (4)	C4S—C5S—H5SC	109.5
C42—C40—C41	113.5 (4)	H5SA—C5S—H5SC	109.5
O4—C40—H40A	107.7	H5SB—C5S—H5SC	109.5
C42—C40—H40A	107.7	C4S—C6S—H6SA	109.5
C41—C40—H40A	107.7	C4S—C6S—H6SB	109.5
C40—C41—H41A	109.5	H6SA—C6S—H6SB	109.5
C40—C41—H41B	109.5	C4S—C6S—H6SC	109.5

H41A—C41—H41B	109.5	H6SA—C6S—H6SC	109.5
C40—C41—H41C	109.5	H6SB—C6S—H6SC	109.5
H41A—C41—H41C	109.5	C7S—O3S—H3S	109.1
H41B—C41—H41C	109.5	O3S—C7S—C9S	111.1 (4)
C40—C42—H42A	109.5	O3S—C7S—C8S	106.1 (4)
C40—C42—H42B	109.5	C9S—C7S—C8S	114.0 (4)
H42A—C42—H42B	109.5	O3S—C7S—H7SA	108.5
C40—C42—H42C	109.5	C9S—C7S—H7SA	108.5
H42A—C42—H42C	109.5	C8S—C7S—H7SA	108.5
H42B—C42—H42C	109.5	C7S—C8S—H8SA	109.5
O5—Mn2—O6	94.70 (11)	C7S—C8S—H8SB	109.5
O5—Mn2—N4	169.35 (12)	H8SA—C8S—H8SB	109.5
O6—Mn2—N4	91.84 (12)	C7S—C8S—H8SC	109.5
O5—Mn2—N3	91.76 (11)	H8SA—C8S—H8SC	109.5
O6—Mn2—N3	169.93 (11)	H8SB—C8S—H8SC	109.5
N4—Mn2—N3	82.97 (12)	C7S—C9S—H9SA	109.5
O5—Mn2—O8	94.90 (11)	C7S—C9S—H9SB	109.5
O6—Mn2—O8	88.70 (10)	H9SA—C9S—H9SB	109.5
N4—Mn2—O8	93.63 (11)	C7S—C9S—H9SC	109.5
N3—Mn2—O8	83.05 (10)	H9SA—C9S—H9SC	109.5
O5—Mn2—O7	88.51 (10)	H9SB—C9S—H9SC	109.5
O6—Mn2—O7	92.93 (10)	C10S—O4S—H4S	102.8
N4—Mn2—O7	82.77 (11)	O4S—C10S—C12S	110.7 (4)
N3—Mn2—O7	94.96 (10)	O4S—C10S—C11S	106.9 (3)
O8—Mn2—O7	176.09 (10)	C12S—C10S—C11S	112.3 (3)
C51—O5—Mn2	131.0 (2)	O4S—C10S—H10C	109.0
C70—O6—Mn2	131.2 (2)	C12S—C10S—H10C	109.0
C87—O7—Mn2	128.4 (2)	C11S—C10S—H10C	109.0
C87—O7—H7O	110.8	C10S—C11S—H11C	109.5
Mn2—O7—H7O	120.1	C10S—C11S—H11D	109.5
C90—O8—Mn2	128.5 (2)	H11C—C11S—H11D	109.5
C90—O8—H8O	109.0	C10S—C11S—H11E	109.5
Mn2—O8—H8O	121.1	H11C—C11S—H11E	109.5
C57—N3—C58	121.5 (3)	H11D—C11S—H11E	109.5
C57—N3—Mn2	125.4 (2)	C10S—C12S—H12C	109.5
C58—N3—Mn2	112.52 (18)	C10S—C12S—H12D	109.5
C64—N4—C63	121.3 (3)	H12C—C12S—H12D	109.5

C64—N4—Mn2	125.6 (3)	C10S—C12S—H12E	109.5
C63—N4—Mn2	112.3 (2)	H12C—C12S—H12E	109.5
O5—C51—C56	122.5 (3)	H12D—C12S—H12E	109.5
O5—C51—C52	118.9 (3)	C2P—C1P—H1PA	109.5
C56—C51—C52	118.6 (3)	C2P—C1P—H1PB	109.5
C53—C52—C51	117.5 (3)	H1PA—C1P—H1PB	109.5
C53—C52—C71	121.5 (3)	C2P—C1P—H1PC	109.5
C51—C52—C71	120.9 (3)	H1PA—C1P—H1PC	109.5
C52—C53—C54	124.5 (4)	H1PB—C1P—H1PC	109.5
C52—C53—H53A	117.8	C3P—C2P—C1P	122.8 (12)
C54—C53—H53A	117.8	C3P—C2P—H2PA	106.6
C55—C54—C53	116.4 (3)	C1P—C2P—H2PA	106.6
C55—C54—C75	121.4 (3)	C3P—C2P—H2PB	106.6
C53—C54—C75	122.2 (3)	C1P—C2P—H2PB	106.6
C54—C55—C56	122.1 (3)	H2PA—C2P—H2PB	106.6
C54—C55—H55A	119.0	C2P—C3P—C4P	99.8 (8)
C56—C55—H55A	119.0	C2P—C3P—H3PA	111.8
C55—C56—C51	120.7 (3)	C4P—C3P—H3PA	111.8
C55—C56—C57	116.2 (3)	C2P—C3P—H3PB	111.8
C51—C56—C57	123.1 (3)	C4P—C3P—H3PB	111.8
N3—C57—C56	126.0 (3)	H3PA—C3P—H3PB	109.5
N3—C57—H57A	117.0	C5P—C4P—C3P	115.6 (11)
C56—C57—H57A	117.0	C5P—C4P—H4PA	108.4
N3—C58—C63	106.5 (2)	C3P—C4P—H4PA	108.4
N3—C58—C59	116.1 (2)	C5P—C4P—H4PB	108.4
C63—C58—C59	110.7 (2)	C3P—C4P—H4PB	108.4
N3—C58—H58A	107.7	H4PA—C4P—H4PB	107.5
C63—C58—H58A	107.7	C4P—C5P—H5PA	109.5
C59—C58—H58A	107.7	C4P—C5P—H5PB	109.5
C60—C59—C58	109.9 (3)	H5PA—C5P—H5PB	109.5
C60—C59—H59A	109.7	C4P—C5P—H5PC	109.5
C58—C59—H59A	109.7	H5PA—C5P—H5PC	109.5
C60—C59—H59B	109.7	H5PB—C5P—H5PC	109.5
C58—C59—H59B	109.7	H2QA—C2Q—H2QB	106.3
H59A—C59—H59B	108.2	H4QA—C4Q—H4QB	107.3
O2—Mn1—O1—C1	155.9 (3)	N4—Mn2—O5—C51	65.7 (7)

N1—Mn1—O1—C1	-21.4 (3)	N3—Mn2—O5—C51	5.7 (3)
O4—Mn1—O1—C1	-110.6 (3)	O8—Mn2—O5—C51	-77.5 (3)
O3—Mn1—O1—C1	66.6 (3)	O7—Mn2—O5—C51	100.6 (3)
O1—Mn1—O2—C20	160.6 (3)	O5—Mn2—O6—C70	-161.8 (3)
N2—Mn1—O2—C20	-18.7 (3)	N4—Mn2—O6—C70	9.8 (3)
O4—Mn1—O2—C20	70.0 (3)	N3—Mn2—O6—C70	68.5 (7)
O3—Mn1—O2—C20	-106.3 (3)	O8—Mn2—O6—C70	103.4 (3)
O2—Mn1—O3—C37	22.8 (3)	O7—Mn2—O6—C70	-73.1 (3)
O1—Mn1—O3—C37	117.8 (3)	O5—Mn2—O7—C87	-33.4 (3)
N1—Mn1—O3—C37	-150.8 (3)	O6—Mn2—O7—C87	-128.1 (3)
N2—Mn1—O3—C37	-68.6 (3)	N4—Mn2—O7—C87	140.4 (3)
O2—Mn1—O4—C40	98.2 (3)	N3—Mn2—O7—C87	58.2 (3)
O1—Mn1—O4—C40	3.1 (3)	O5—Mn2—O8—C90	-90.6 (3)
N1—Mn1—O4—C40	-88.4 (3)	O6—Mn2—O8—C90	4.1 (3)
N2—Mn1—O4—C40	-170.5 (3)	N4—Mn2—O8—C90	95.8 (3)
O1—Mn1—N1—C7	15.0 (3)	N3—Mn2—O8—C90	178.3 (3)
N2—Mn1—N1—C7	-166.1 (3)	O5—Mn2—N3—C57	-5.0 (3)
O4—Mn1—N1—C7	105.2 (3)	O6—Mn2—N3—C57	124.9 (6)
O3—Mn1—N1—C7	-78.1 (3)	N4—Mn2—N3—C57	-175.7 (3)
O1—Mn1—N1—C8	-164.7 (2)	O8—Mn2—N3—C57	89.8 (3)
N2—Mn1—N1—C8	14.2 (2)	O7—Mn2—N3—C57	-93.6 (3)
O4—Mn1—N1—C8	-74.5 (2)	O5—Mn2—N3—C58	-175.97 (19)
O3—Mn1—N1—C8	102.2 (2)	O6—Mn2—N3—C58	-46.1 (7)
O2—Mn1—N2—C14	14.5 (3)	N4—Mn2—N3—C58	13.31 (19)
N1—Mn1—N2—C14	-168.3 (3)	O8—Mn2—N3—C58	-81.24 (19)
O4—Mn1—N2—C14	-78.9 (3)	O7—Mn2—N3—C58	95.38 (19)
O3—Mn1—N2—C14	103.5 (3)	O5—Mn2—N4—C64	123.3 (6)
O2—Mn1—N2—C13	-164.32 (19)	O6—Mn2—N4—C64	-4.6 (3)
N1—Mn1—N2—C13	12.88 (19)	N3—Mn2—N4—C64	-175.9 (3)
O4—Mn1—N2—C13	102.29 (19)	O8—Mn2—N4—C64	-93.4 (3)
O3—Mn1—N2—C13	-75.36 (19)	O7—Mn2—N4—C64	88.2 (3)
Mn1—O1—C1—C6	16.5 (5)	O5—Mn2—N4—C63	-46.6 (7)
Mn1—O1—C1—C2	-164.3 (2)	O6—Mn2—N4—C63	-174.5 (2)
O1—C1—C2—C3	178.9 (3)	N3—Mn2—N4—C63	14.2 (2)
C6—C1—C2—C3	-1.9 (5)	O8—Mn2—N4—C63	96.7 (2)
O1—C1—C2—C21	-1.4 (5)	O7—Mn2—N4—C63	-81.8 (2)
C6—C1—C2—C21	177.8 (3)	Mn2—O5—C51—C56	-3.5 (5)

C1—C2—C3—C4	0.3 (5)	Mn2—O5—C51—C52	177.9 (2)
C21—C2—C3—C4	-179.5 (3)	O5—C51—C52—C53	-176.1 (3)
C2—C3—C4—C5	1.7 (5)	C56—C51—C52—C53	5.2 (5)
C2—C3—C4—C25	-177.1 (3)	O5—C51—C52—C71	5.2 (5)
C3—C4—C5—C6	-2.0 (5)	C56—C51—C52—C71	-173.4 (3)
C25—C4—C5—C6	176.7 (3)	C51—C52—C53—C54	-2.4 (6)
O1—C1—C6—C5	-179.2 (3)	C71—C52—C53—C54	176.3 (3)
C2—C1—C6—C5	1.7 (5)	C52—C53—C54—C55	-1.6 (6)
O1—C1—C6—C7	1.6 (5)	C52—C53—C54—C75	176.2 (3)
C2—C1—C6—C7	-177.6 (3)	C53—C54—C55—C56	2.8 (5)
C4—C5—C6—C1	0.4 (5)	C75—C54—C55—C56	-175.1 (3)
C4—C5—C6—C7	179.7 (3)	C54—C55—C56—C51	0.2 (5)
C8—N1—C7—C6	175.0 (3)	C54—C55—C56—C57	178.8 (3)
Mn1—N1—C7—C6	-4.6 (5)	O5—C51—C56—C55	177.1 (3)
C1—C6—C7—N1	-7.2 (6)	C52—C51—C56—C55	-4.3 (5)
C5—C6—C7—N1	173.6 (3)	O5—C51—C56—C57	-1.5 (5)
C7—N1—C8—C13	143.4 (3)	C52—C51—C56—C57	177.1 (3)
Mn1—N1—C8—C13	-36.9 (3)	C58—N3—C57—C56	172.6 (3)
C7—N1—C8—C9	18.9 (5)	Mn2—N3—C57—C56	2.3 (4)
Mn1—N1—C8—C9	-161.4 (2)	C55—C56—C57—N3	-176.8 (3)
N1—C8—C9—C10	177.6 (3)	C51—C56—C57—N3	1.9 (5)
C13—C8—C9—C10	55.6 (4)	C57—N3—C58—C63	151.8 (3)
C8—C9—C10—C11	-54.3 (4)	Mn2—N3—C58—C63	-36.8 (3)
C9—C10—C11—C12	55.7 (4)	C57—N3—C58—C59	28.0 (4)
C10—C11—C12—C13	-56.8 (4)	Mn2—N3—C58—C59	-160.6 (2)
C14—N2—C13—C8	145.2 (3)	N3—C58—C59—C60	179.0 (3)
Mn1—N2—C13—C8	-35.9 (3)	C63—C58—C59—C60	57.4 (4)
C14—N2—C13—C12	21.0 (4)	C58—C59—C60—C61	-54.8 (4)
Mn1—N2—C13—C12	-160.1 (2)	C59—C60—C61—C62	54.0 (4)
N1—C8—C13—N2	45.3 (3)	C60—C61—C62—C63	-54.3 (4)
C9—C8—C13—N2	173.2 (2)	C64—N4—C63—C62	28.1 (4)
N1—C8—C13—C12	173.2 (3)	Mn2—N4—C63—C62	-161.5 (2)
C9—C8—C13—C12	-58.9 (3)	C64—N4—C63—C58	152.1 (3)
C11—C12—C13—N2	-179.1 (3)	Mn2—N4—C63—C58	-37.5 (3)
C11—C12—C13—C8	58.7 (3)	C61—C62—C63—N4	178.7 (3)
C13—N2—C14—C15	173.6 (3)	C61—C62—C63—C58	57.0 (4)
Mn1—N2—C14—C15	-5.1 (5)	N3—C58—C63—N4	46.6 (3)

N2—C14—C15—C16	176.5 (3)	C59—C58—C63—N4	173.7 (3)
N2—C14—C15—C20	-7.6 (5)	N3—C58—C63—C62	173.6 (3)
C20—C15—C16—C17	0.8 (5)	C59—C58—C63—C62	-59.3 (3)
C14—C15—C16—C17	176.8 (3)	C63—N4—C64—C65	169.6 (3)
C15—C16—C17—C18	-2.9 (5)	Mn2—N4—C64—C65	0.6 (5)
C15—C16—C17—C29	177.1 (3)	N4—C64—C65—C66	-172.6 (3)
C16—C17—C18—C19	2.0 (6)	N4—C64—C65—C70	1.4 (5)
C29—C17—C18—C19	-178.1 (3)	C70—C65—C66—C67	-0.8 (5)
C17—C18—C19—C20	1.2 (6)	C64—C65—C66—C67	173.3 (3)
C17—C18—C19—C33	-176.5 (4)	C65—C66—C67—C68	2.1 (5)
Mn1—O2—C20—C19	-170.0 (2)	C65—C66—C67—C79	-174.6 (3)
Mn1—O2—C20—C15	12.2 (5)	C66—C67—C68—C69	-0.7 (5)
C18—C19—C20—O2	178.8 (3)	C79—C67—C68—C69	176.0 (3)
C33—C19—C20—O2	-3.5 (5)	C67—C68—C69—C70	-1.9 (5)
C18—C19—C20—C15	-3.4 (5)	C67—C68—C69—C83	-179.8 (3)
C33—C19—C20—C15	174.4 (3)	Mn2—O6—C70—C69	168.5 (2)
C16—C15—C20—O2	-179.8 (3)	Mn2—O6—C70—C65	-10.4 (5)
C14—C15—C20—O2	4.5 (5)	C68—C69—C70—O6	-175.8 (3)
C16—C15—C20—C19	2.4 (5)	C83—C69—C70—O6	2.0 (5)
C14—C15—C20—C19	-173.3 (3)	C68—C69—C70—C65	3.1 (5)
C3—C2—C21—C24	-1.7 (5)	C83—C69—C70—C65	-179.0 (3)
C1—C2—C21—C24	178.5 (3)	C66—C65—C70—O6	177.1 (3)
C3—C2—C21—C23	118.8 (4)	C64—C65—C70—O6	3.4 (5)
C1—C2—C21—C23	-60.9 (4)	C66—C65—C70—C69	-1.9 (5)
C3—C2—C21—C22	-121.3 (4)	C64—C65—C70—C69	-175.6 (3)
C1—C2—C21—C22	59.0 (4)	C53—C52—C71—C73	119.0 (4)
C5—C4—C25—C28	7.1 (5)	C51—C52—C71—C73	-62.3 (4)
C3—C4—C25—C28	-174.2 (3)	C53—C52—C71—C74	-0.6 (5)
C5—C4—C25—C26	-113.7 (4)	C51—C52—C71—C74	178.0 (4)
C3—C4—C25—C26	65.0 (4)	C53—C52—C71—C72	-118.9 (4)
C5—C4—C25—C27	127.0 (4)	C51—C52—C71—C72	59.7 (5)
C3—C4—C25—C27	-54.3 (4)	C55—C54—C75—C78	-52.7 (5)
C16—C17—C29—C32B	132.2 (5)	C53—C54—C75—C78	129.6 (4)
C18—C17—C29—C32B	-47.8 (6)	C55—C54—C75—C77	67.2 (5)
C16—C17—C29—C31	-71.8 (6)	C53—C54—C75—C77	-110.5 (4)
C18—C17—C29—C31	108.2 (6)	C55—C54—C75—C76	-173.0 (3)
C16—C17—C29—C30	49.6 (6)	C53—C54—C75—C76	9.4 (5)

C18—C17—C29—C30	-130.3 (6)	C66—C67—C79—C82	-133.1 (4)
C16—C17—C29—C31B	-97.6 (5)	C68—C67—C79—C82	50.3 (5)
C18—C17—C29—C31B	82.5 (5)	C66—C67—C79—C80	-11.8 (5)
C16—C17—C29—C32	168.3 (5)	C68—C67—C79—C80	171.7 (4)
C18—C17—C29—C32	-11.7 (6)	C66—C67—C79—C81	107.9 (4)
C16—C17—C29—C30B	11.0 (6)	C68—C67—C79—C81	-68.6 (4)
C18—C17—C29—C30B	-168.9 (4)	C68—C69—C83—C85	-119.4 (3)
C18—C19—C33—C34	117.9 (4)	C70—C69—C83—C85	62.8 (4)
C20—C19—C33—C34	-59.7 (5)	C68—C69—C83—C86	118.2 (3)
C18—C19—C33—C35	-2.0 (6)	C70—C69—C83—C86	-59.6 (4)
C20—C19—C33—C35	-179.6 (4)	C68—C69—C83—C84	-0.5 (5)
C18—C19—C33—C36	-121.4 (4)	C70—C69—C83—C84	-178.3 (3)
C20—C19—C33—C36	60.9 (5)	Mn2—O7—C87—C88	136.1 (4)
Mn1—O3—C37—C38	119.2 (3)	Mn2—O7—C87—C89	-112.6 (5)
Mn1—O3—C37—C39	-117.0 (3)	Mn2—O8—C90—C92	99.8 (3)
Mn1—O4—C40—C42	129.1 (3)	Mn2—O8—C90—C91	-135.7 (3)
Mn1—O4—C40—C41	-105.3 (3)	C1P—C2P—C3P—C4P	168.8 (12)
O6—Mn2—O5—C51	-166.5 (3)	C2P—C3P—C4P—C5P	-174.6 (12)

Table 3. Hydrogen-bond parameters

$D-H\cdots A$	$D-H$ (Å)	$H\cdots A$ (Å)	$D\cdots A$ (Å)	$D-H\cdots A$ (°)
O3—H3O \cdots O2S ⁱ	0.83	1.93	2.757 (4)	177.9
O4—H4O \cdots O3S	0.97	1.75	2.712 (4)	172.8
O7—H7O \cdots O4S	0.97	1.82	2.787 (4)	171.9
O8—H8O \cdots O1S ⁱⁱ	0.86	1.92	2.756 (4)	166.7
O1S—H1S \cdots F3	0.92	1.87	2.791 (4)	173.8
O2S—H2S \cdots F1	0.94	1.98	2.875 (4)	158.6
O3S—H3S \cdots F7 ⁱⁱⁱ	0.92	1.88	2.780 (5)	165.1
O4S—H4S \cdots F9	0.91	2.00	2.898 (4)	167.5

Symmetry code(s): (i) $x, y-1, z$; (ii) $x+1, y, z$; (iii) $x-1, y-1, z$.

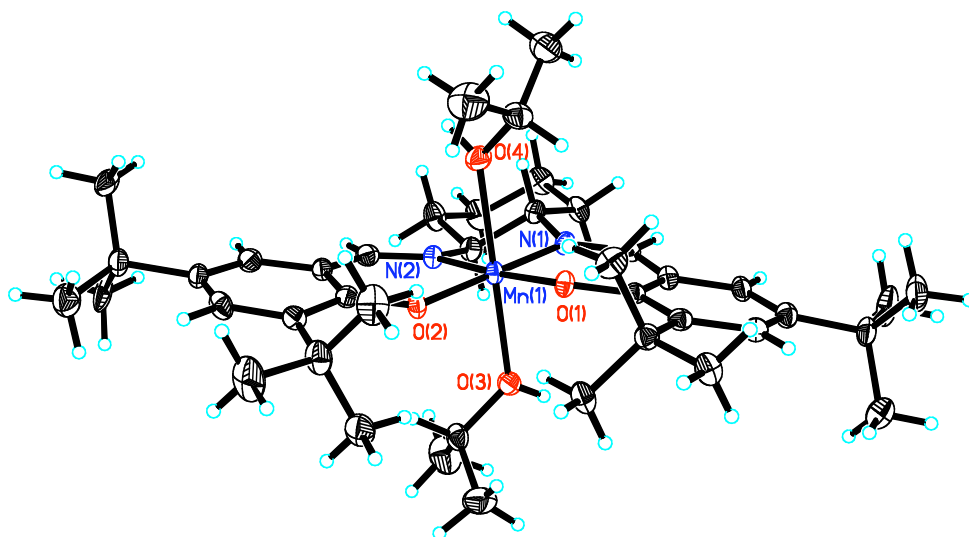


Figure 1a

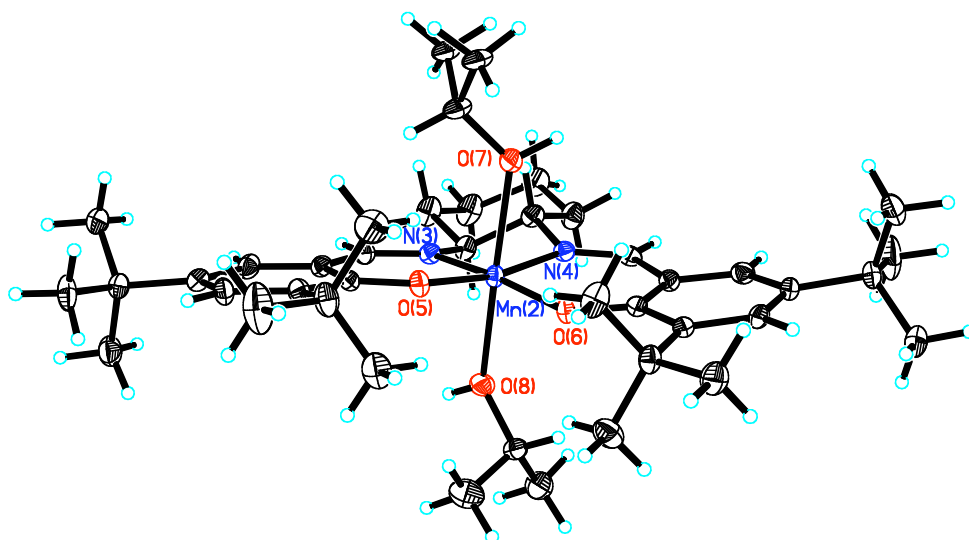


Figure 1b

Figure 1. Perspective views showing 50% probability for two independent cations (disorder part has been omitted).

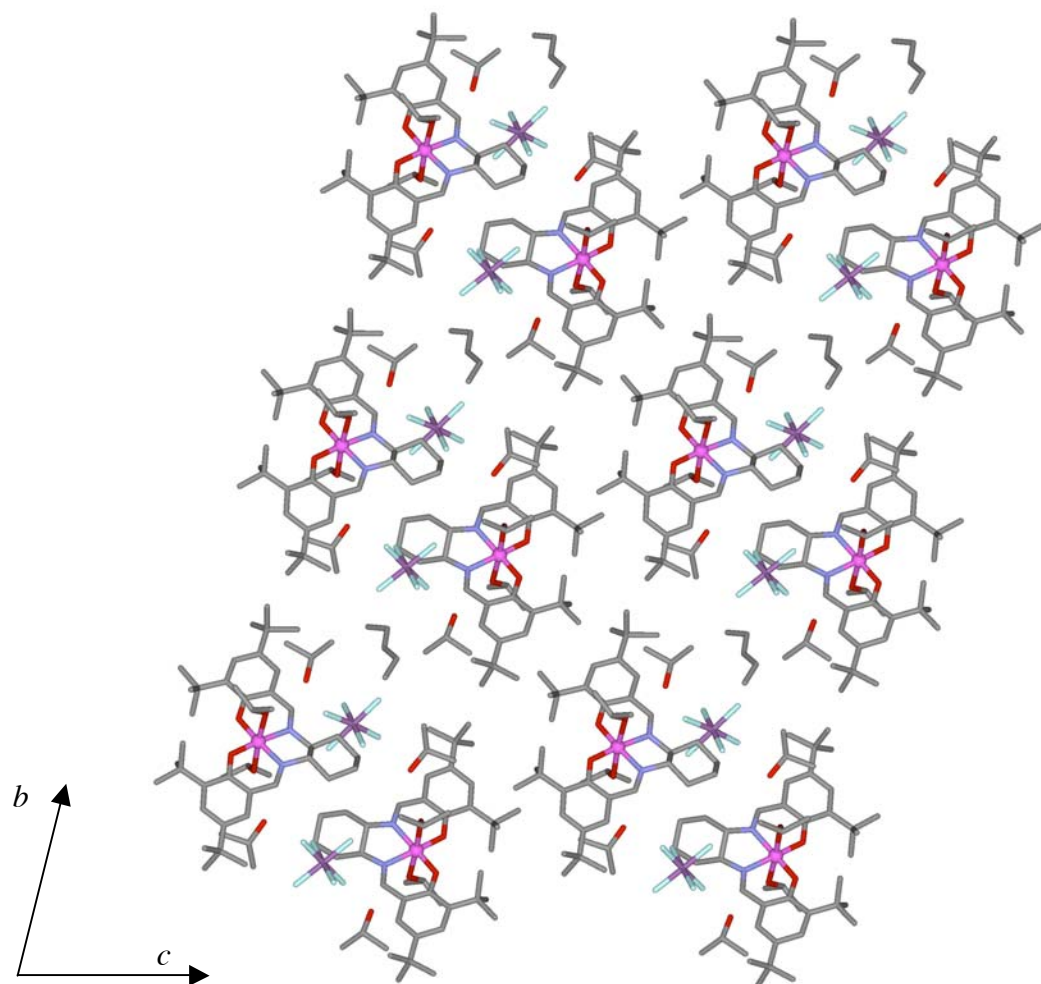


Figure 2. Three-dimensional supramolecular architecture viewed along the *a*-axis direction (disorder part has been omitted).