Bicymantrenyl chemistry
4.* Resolution to enantiomers and determination of the absolute configuration of bicymantrenylcarbaldehydes

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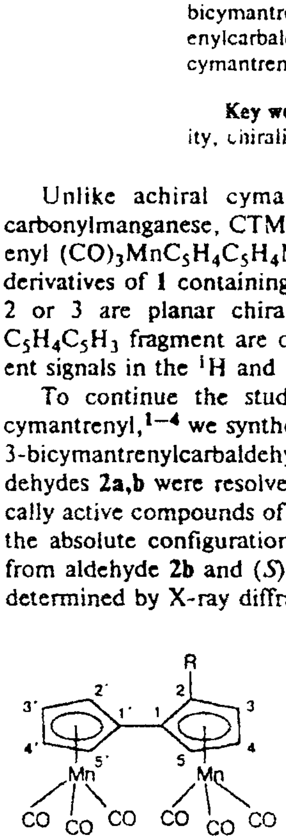
Planar chiral 2- and 3-bicymantrenylcarbaldehydes can be resolved to enantiomers through Schiff's bases with (S)-(−)-α-phenylethylamine. Optically active derivatives of bicymantrenyl with Me and CH_2OH substituents were synthesized from (−)-3-bicymantrenylcarbaldehyde. The absolute configuration of Schiff's base obtained from (+)-3-bicymantrenylcarbaldehyde was determined by X-ray diffraction analysis.

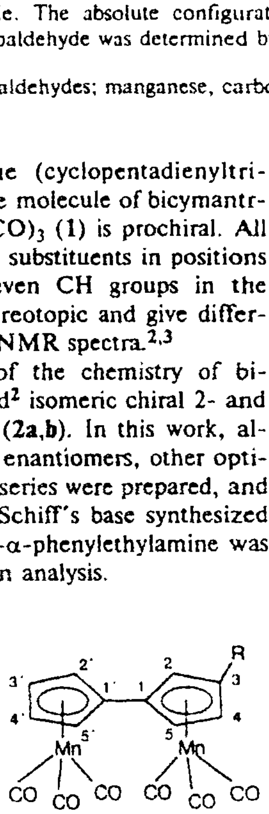
Key words: aldehydes; manganese, carbonyl, cyclopentadienyl, complexes; optical activity, chirality.

Unlike achiral cymantrene (cyclopentadienyltricarbonylmanganese, CTM), the molecule of bicymantrenyl $(CO)_3MnC_5H_4C_5H_4Mn(CO)_3$ (**1**) is prochiral. All derivatives of **1** containing any substituents in positions 2 or 3 are planar chiral. Seven CH groups in the $C_5H_4C_5H_3$ fragment are diastereotopic and give different signals in the ^1H and ^{13}C NMR spectra.[2,3]

To continue the studies of the chemistry of bicymantrenyl,[1–4] we synthesized[2] isomeric chiral 2- and 3-bicymantrenylcarbaldehydes (**2a,b**). In this work, aldehydes **2a,b** were resolved to enantiomers, other optically active compounds of this series were prepared, and the absolute configuration of Schiff's base synthesized from aldehyde **2b** and (*S*)-(−)-α-phenylethylamine was determined by X-ray diffraction analysis.



2a, 3a



2b—5b

2a: R = CHO
3a: R = CH=NCH(Me)Ph
(two diastereomers)

2b: R = CHO
3b: R = CH=NCH(Me)Ph
4b: R = CH_2OH
5b: R = Me

Aldehydes **2a,b** readily react with (*S*)-(−)-α-phenylethylamine in benzene to form the corresponding Schiff's bases **3a,b**, which are mixtures of two diastereomers. In the case of aldehyde **2a**, recrystallization of the reaction mixture from hexane gives a crystalline residue containing >97% of one diastereomer **3a** and no more than 1—2% of another diastereomer. The composition of the precipitate was monitored by the ^1H NMR spectra, in which the signals of three protons of the C_5H_3 fragment with the aldimine substituent and protons of CH=N and CHMe are fairly well distinguished (Table 1), while the signals of protons of C_5H_4 in both diastereomers almost coincide. After acidic hydrolysis of the precipitate under the action of 20% H_3PO_4 (brief boiling in MeOH), optically pure enantiomer (−)-**2a** was obtained with $[\alpha]_D$ −49° and *ee* ≥ 97%.

A crystalline precipitate and mother liquor form in the reaction of aldehyde **2b** with (*S*)-(−)-α-phenylethylamine in benzene. According to the data from ^1H NMR, the precipitate consists of one, virtually pure diastereomer **3b**, whose crystal structure was established by the X-ray diffraction method. Acid hydrolysis of this diastereomer gives optically active aldehyde (+)—**2b** with $[\alpha]_D$ +59° and *ee* ≥95%. Triple fractional crystallization of the mother liquor gave another diastereomer **3b**, and acid hydrolysis of the latter resulted in enantiomer (−)-**2b** with $[\alpha]_D$ −60° and *ee* 95%. Unlike isomers **3a**, in the ^1H NMR spectra of two diastereomers **3b**, only two of three protons in the C_5H_3 fragment differ, and the signals of all other protons almost coincide (see Table 1).

Optically active (−)-3-hydroxymethyldicymantrenyl (−)-**4b** and (+)-3-methyldicymantrenyl (+)-**5b** were synthesized from compound (−)-**2b** in *ee* 68%.

$$(-)\text{-}\mathbf{2b} \xrightarrow{NaBH_4/EtON} (-)\text{-}\mathbf{4b} \xrightarrow{CF_3COOH/HSiEt_3} (+)\text{-}\mathbf{5b}$$

The crystal structure and absolute configuration of less soluble diastereomer **3b** obtained from racemic **2b**

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* For Part 3, see Ref. 1.

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Table 1. ^{1}H NMR spectra (ppm from $SiMe_4$) of bicymantrenyls

Compound	C_5H_3 ring	C_5H_4 ring H(2′), H(5′)[a] (1 H)	C_5H_4 ring H(3′), H(4′)[a] (1 H)	Other protons
2a	5.546, 5.153 (both dd, 1 H, H(3), H(5)); 4.882 (t, 1 H, H(4))	5.571, 5.063	4.810, 4.782	9.772 (s, 1 H, CHO)
2b	5.622 (t, 1 H, H(2)); 5.090, 5.493 (both dd, 1 H, H(4), H(5))	5.038, 5.026	4.812, 4.802	9.597 (s, 1 H, CHO)
3a[b]	5.393, 4.932 (both dd, 1 H, H(3), H(5)); 4.806 (t, 1 H, H(4))	5.097, 4.998	4.722, 4.770	8.202 (s, 1 H, CH=N); 4.469 (q, 1 H, CH); 1.535 (d, 3 H, CH_3)
3a[b]	5.363, 4.963 (both dd, 1 H, H(3), H(5)); 4.770 (t, 1 H, H(4))	5.147, 4.998	4.722, 4.770	8.187 (s, 1 H, CH=N); 4.510 (q, 1 H, CH); 1.508 (d, 3 H, CH_3)
3b (S_c,R_p)	5.488 (t, 1 H, H(2)); 5.302, 4.980 (both dd, 1 H, H(4), H(5))	5.006, 4.933	4.773, 4.722	7.899 (s, 1 H, CH=N); 4.420 (q, 1 H, CH); 1.537 (d, 3 H, CH_3)
3b (S_c,S_p)	5.535 (t, 1 H, H(2)); 5.249 (dd, 1 H, H(4) or H(5)[c])	5.006, 4.933	4.773, 4.722	7.899 (s, 1 H, CH=N); 4.420 (q, 1 H, CH); 1.537 (d, 3 H, CH_3)
4b	4.958 (t, 1 H, H(2)); 4.724, 4.817 (both dd, 1 H, H(4), H(5))	4.863, 4.846	4.665, 4.642	4.254 (d, 2 H, CH_2); 1.705 (t, 1 H, OH)
5b	4.820 (t, 1 H, H(2)); 4.577, 4.862 (both dd, 1 H, H(4), H(5))	4.944, 4.909	4.740 (m, 2 H)	1.999 (s, 3 H, CH_3)

[a] Protons H(2′) and H(5′) give two multiplets of five lines, H(3′) and H(4′) give two multiplets of six lines.

[b] Two diastereomers of **3a**.

[c] The signal of the second proton is disguised by an intense signal with δ 5.006.

and (*S*)-(−)-α-phenylethylamine were determined by X-ray diffraction analysis. The structure of the molecule of **3b** is presented in Fig. 1. It can be seen that this diastereomer has a (S_c,R_p)-configuration. Therefore, the enantiomer of aldehyde (+)-**2b** obtained from **3b** and its derivatives (+)-**4b** and (−)-**5b** also have an absolute (R_p)-configuration with respect to the plane of the cyclopentadienyl ligand. By contrast, enantiomer (−)-**2b**

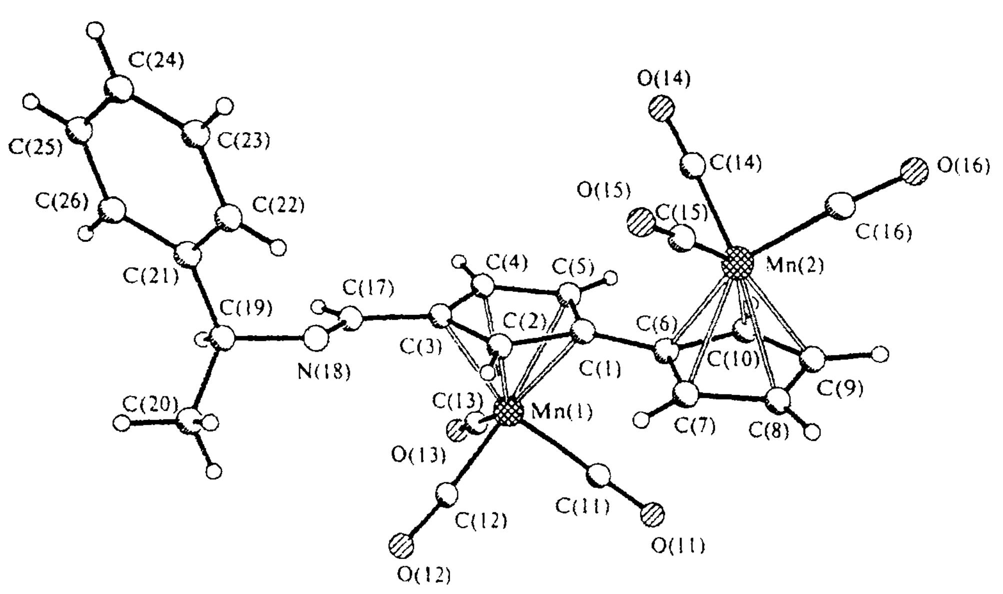

Fig. 1. Molecular structure of Schiff's base **3b**.

Table 2. Bond lengths (*d*) and main bond angles (ω) in the molecule of **3b**

Bond	*d*/Å	Angle	ω/deg
Mn(1)—C(12)	1.791(6)	C(2)—C(1)—C(5)	107.8(4)
Mn(1)—C(13)	1.794(6)	C(2)—C(1)—C(6)	126.0(4)
Mn(1)—C(11)	1.801(5)	C(5)—C(1)—C(6)	126.3(4)
Mn(1)—C(4)	2.120(5)	C(1)—C(2)—C(3)	108.8(4)
Mn(1)—C(3)	2.133(4)	C(4)—C(3)—C(2)	106.7(4)
Mn(1)—C(5)	2.141(5)	C(4)—C(3)—C(17)	128.6(4)
Mn(1)—C(2)	2.143(4)	C(2)—C(3)—C(17)	124.7(4)
Mn(1)—C(1)	2.173(5)	C(5)—C(4)—C(3)	109.3(4)
Mn(2)—C(16)	1.793(6)	C(4)—C(5)—C(1)	107.3(4)
Mn(2)—C(15)	1.792(6)	C(7)—C(6)—C(10)	106.7(4)
Mn(2)—C(14)	1.792(6)	C(7)—C(6)—C(1)	127.2(4)
Mn(2)—C(7)	2.126(5)	C(10)—C(6)—C(1)	126.1(4)
Mn(2)—C(9)	2.128(6)	C(8)—C(7)—C(6)	109.3(5)
Mn(2)—C(8)	2.129(5)	C(7)—C(8)—C(9)	107.8(5)
Mn(2)—C(10)	2.138(5)	C(10)—C(9)—C(8)	108.4(5)
Mn(2)—C(6)	2.147(5)	C(9)—C(10)—C(6)	107.9(5)
O(11)—C(11)	1.135(6)	O(11)—C(11)—Mn(1)	178.6(5)
O(12)—C(12)	1.145(7)	O(12)—C(12)—Mn(1)	176.1(6)
O(13)—C(13)	1.138(7)	O(13)—C(13)—Mn(1)	179.6(6)
O(14)—C(14)	1.140(7)	O(14)—C(14)—Mn(2)	176.4(7)
O(15)—C(15)	1.136(7)	O(15)—C(15)—Mn(2)	178.0(6)
O(16)—C(16)	1.139(7)	O(16)—C(16)—Mn(2)	177.8(6)
N(18)—C(17)	1.259(6)	C(17)—N(18)—C(19)	117.5(4)
N(18)—C(19)	1.472(7)	N(18)—C(17)—C(3)	120.4(5)
C(1)—C(2)	1.398(7)	N(18)—C(19)—C(21)	109.4(4)
C(1)—C(5)	1.441(7)	N(18)—C(19)—C(20)	108.1(5)
C(1)—C(6)	1.466(6)	C(21)—C(19)—C(20)	112.1(5)
C(2)—C(3)	1.433(7)	C(22)—C(21)—C(26)	118.0(5)
C(3)—C(4)	1.415(7)	C(22)—C(21)—C(19)	120.9(5)
C(3)—C(17)	1.467(7)	C(26)—C(21)—C(19)	121.1(5)
C(4)—C(5)	1.404(7)	C(23)—C(22)—C(21)	120.5(5)
C(6)—C(7)	1.412(7)	C(22)—C(23)—C(24)	120.5(6)
C(6)—C(10)	1.437(7)	C(25)—C(24)—C(23)	119.5(6)
C(7)—C(8)	1.399(8)	C(24)—C(25)—C(26)	121.4(6)
C(8)—C(9)	1.415(9)	C(25)—C(26)—C(21)	120.1(5)
C(9)—C(10)	1.406(7)		
C(19)—C(21)	1.500(7)		
C(19)—C(20)	1.519(9)		
C(21)—C(22)	1.395(7)		
C(21)—C(26)	1.403(7)		
C(22)—C(23)	1.378(8)		
C(23)—C(24)	1.384(9)		
C(24)—C(25)	1.355(10)		
C(25)—C(26)	1.379(8)		

and its derivatives (−)-**4b** and (+)-**5b** have an absolute (S_p)-configuration.

The bond lengths and main bond angles in the molecule of **3b** are presented in Table 2. The planes of Cp rings in the bicymantrenyl fragment are almost parallel (the dihedral angle between the C(1)C(2)C(3)C(4)C(5) and C(6)C(7)C(8)C(9)C(10) planes is equal to 4.8°). The N(18) atom is out of the C(1)C(2)C(3)C(4)C(5) plane and localized at a distance of 0.200 Å from this plane (the C(2)—C(3)—C(17)—N(18) torsion angle is equal to 10.6°). The bond lengths and bond angles in the molecule of **3b** are close to the standard values.

Table 3. CD spectra of bicymantrenyls

Enantiomer	Optical purity (%)	[θ] (heptane, c 5 · 10^{-4})	λ/nm	$[\alpha]_D$/deg (benzene)
(−)-**2a**	97	−660, 7920, −12280	413, 347, 294	−49
(+)-**2b**	95	7200, 528, 1060, −12670	387.5, 346.5, 331, 280	+59
(−)-**2b**	68	−3830, −378, −718, 7390, 10000	387.5, 346.5, 331, 280, 252.5	−45
(−)-**4b**	68	189, −1200	338.5, 270	−3.14
(+)-**5b**	68	7880, −13650	360, 263	+60

All compounds obtained were characterized by the ^{1}H NMR spectra, and the circular dichroism (CD) spectra were recorded for optically active substances.

In the ^{1}H NMR spectra, seven individual signals correspond to seven protons of the $C_5H_4C_5H_3$ fragment. Three protons of C_5H_3 are manifested as three characteristic multiplets: a triplet with a broadened central line and two doublets of doublets. For compounds **2a** and **3a** with an electron-acceptor substituent in position 2, the H(4) proton gives a triplet in the upfield region with spin-spin coupling constant of $^1J_{3,4}$ = $^1J_{4,5}$ = 3.0 Hz, and the H(3) and H(5) protons give two doublets of doublets with the constants $^1J_{3,4}$ = $^1J_{5,4}$ = 3.0 Hz and $^2J_{3,5}$ = 1.8 Hz. In the spectra of compounds **2b**—**4b** with an electron-acceptor substituent in position 3, a triplet in the downfield region with the constant of $^2J_{2,4}$ = $^2J_{2,5}$ = 1.8 Hz corresponds to the H(2) proton, and two doublets of doublets with the constants equal to 3.0 and 1.8 Hz correspond to the H(3) and H(4) protons. Due to diastereotopic nonequivalence, four protons of the C_5H_4 ring form the ABCD system and give four individual signals with multiplicities that differ in pairs. The H(2) and H(5) protons give two signals in the form of a triplet of doublets, but due to partial overlapping only five of six lines appear in the spectrum. The H(3) and H(4) protons give two signals in the form of a doublet of triplets (six lines).

Since the planar chiral derivatives of **1** contain two nearly identical cymantrenyl chromophores, Cotton effect (CE)[5] exciton splitting could be expected in the region of electronic absorption of these compounds (300—400 nm) in their CD spectra (Table 3). However, no exciton interaction is observed in the CD spectra obtained for these compounds, in particular, for 3-methyldicymantrenyl (+)-**5b**. This is probably related to the fact that the vectors of the electric moments (μ) of the transitions of two cymantrenyl chromophores (linking the metal atom and centroid of the Cp ring) are located in almost the same plane, which agrees with the molecular structure of the dicymantrenyl fragment in the structures of **3b** and other compounds of this series.

The comparison of the CD spectra of bicymantrenyls (−)-**2b** and (+)-**5b** shows that the shape of the spectrum is mainly determined by the contribution of the conjugated Cp—CH=O chromophore, as mentioned previously for planar chiral cymantrene derivatives.[6] According to the rule suggested for determination of the conformation of the CHO group in formylcymantrenes,[6] the negative CE of this chromophore in the region of 350 nm in the case of aldehyde (−)-**2b** (or positive in the case of (+)-**2b**) corresponds to the conformation of a molecule, in which the O atom of the CHO group is directed toward the second substituent. This conclusion agrees with the X-ray diffraction data for compound **3b**, if it is assumed that the conformations of **2b** and **3b** in crystal are similar.

Unexpectedly it turned out that although the (+)-(R_p)-enantiomer of **5b** in heptane possesses the value of $[\theta] \approx +8000$ (λ = 360 nm), the CE for (−)-(R_p)-**4b** is substantially lower ($[\theta]$ = +189 for λ = 338 nm). Moreover, when heptane is replaced by benzene, the sign of CE of (−)-(R_p)-**4b** becomes negative, and the bathochromic shift of the CE maximum by 23 nm occurs simultaneously. In the case of the (+)-**5b** enantiomer, similar replacement of the solvent only results in a decrease in the value of $[\theta]$. Probably, the spectral changes observed are caused by changes in the conformational equilibrium of a molecule of **4b**.

As in the case of β-aldehyde (−)-**2b**, the CD spectrum of α-isomer (−)-**2a** has two opposite CE in the region of 300—400 nm, and a weakly pronounced negative long-wave effect of this isomer can be related by analogy to the Cp—CH=O chromophore. If it is assumed that in the predominant conformer (−)-**2a**, the O atom of the CHO group is directed to the side opposite the substituent for steric reasons, the absolute (R_p)-configuration can be assigned to this enantiomer according to the known rule.[6]

Experimental

^{1}H NMR spectra were recorded on a Bruker-WP-200-SY spectrometer (200.13 MHz), CD spectra were recorded on JASCO-720 and Dichrograph-III spectropolarimeters, and mass spectra were obtained on a Kratos MS-890 mass spectrometer (EI, 70 eV).

Schiff's bases 3a,b were obtained by the reactions of aldehydes **2a** or **2b** [2] (3—5 mmol) with a small excess of (*S*)-(−)-α-phenylethylamine in benzene (5—8 mL). The mixture of reagents was heated to boiling and left overnight at room temperature for slow crystallization. The precipitate formed (usually 20—25% of the theoretical amount) was separated, washed 2—3 times with hexane (portions of 0.5 mL), and dried *in vacuo*. When no precipitate formed, the solvent was slowly removed in a low vacuum until the beginning of crystallization. For preparation of a racemic mixture of diastereomers of Schiff's bases after the reaction was complete (controlled by the IR spectrum: the disappearance of the ν(C=O) absorption band of aldehydes at 1690—1710 cm^{-1} and the appearance of the ν(C=N) band at 1650 cm^{-1}), the benzene was removed *in vacuo*, and the residue was recrystallized from hexane.

For decomposition to aldehyde, the corresponding Schiff's base (0.3—0.5 g) was boiled in MeOH (10—15 mL) with several drops of 20% H_3PO_4 for 15—20 min (controlled by the IR spectrum), then the solution was cooled, poured in water, and the aldehyde obtained was extracted with ether.

2-[(1-Phenylethyl)iminomethyl]bicymantrenyl (3a). Yellow crystals with m.p. 119—121 °C (from hexane). Found (%): C, 55.74; H, 3.14; N, 2.44. $C_{25}H_{17}NMn_2O_6$. Calculated (%): C, 55.87; H, 3.17; N, 2.61. MS, *m/z*: 537 [M$^+$], 453 [M−3CO], 369 [M−6CO], 314 [M−6CO−Mn], 259 [M−6CO−2Mn].

3-[(1-Phenylethyl)iminomethyl]bicymantrenyl (3b). Yellow crystals with m.p. 109—110 °C (from benzene). Found (%): C, 55.94; H, 3.18; N, 2.54. $C_{25}H_{17}NMn_2O_6$. Calculated (%): C, 55.87; H, 3.17; N, 2.61. The mass spectrum coincides with that of **3a**.

3-Hydroxymethylbicymantrenyl (4b). Racemic **4b** was obtained by reduction of compound **3b** under the action of $NaBH_4$ in EtOH. Aldehyde **2b** (1.39 g, 3.2 mmol) and $NaBH_4$ (0.12 g, 3 mmol) were stirred in EtOH (30 mL) for 1 h at 20 °C (controlled by TLC and the IR spectrum), then the reaction mixture was poured in water and extracted with ether. Racemic **4b** (1.27 g, 91%) was isolated from the ether layer. Light-yellow crystals with m.p. 73.5—75.5 °C (from toluene—hexane mixture). Found (%): C, 47.05; H, 2.15. $C_{17}H_{10}Mn_2O_7$. Calculated (%): C, 46.79; H, 2.29. MS, *m/z*: 436 [M$^+$], 434 [M−2H], 352 [M−3CO], 268 [M−6CO], 213 [M−6CO−Mn], 196 [M−6CO−Mn−OH], 141 [M−6CO−2Mn−OH].

Enantiomer (−)-4b. Aldehyde (−)-**2b** (0.13 g, *ee* 68%) and $NaBH_4$ (0.03 g) were stirred in EtOH (10 mL) for 1 h, then the reaction mixture was poured in water and extracted with ether. Enantiomer (−)-**4b** (0.13 g) was extracted from the ether layer. After recrystallization from hexane—toluene (3 : 1) mixture, (−)-**4b** was obtained with m.p. 105—107 °C, $[\alpha]_D$ −3.14 (*c* 0.4, benzene).

3-Methylbicymantrenyl (5b). Racemic 3-methylbicymantrenyl **5b** was obtained by ionic hydrogenation of compound **2b**. A mixture of aldehyde **2b** (0.10 g), Et_3SiH (0.11 mL, excess), and CF_3COOH (0.15 mL, twofold excess) in $CHCl_3$ (3 mL) was boiled for 10 h. Control by TLC showed that intermediate alcohol **4b** is transformed into compound **5b**. The mixture was poured in an aqueous solution of Na_2CO_3, and the reaction product was extracted with CH_2Cl_2. Raw product **5b** (0.11 g) was isolated from the extract, dissolved in benzene—heptane (1 : 3) mixture, and filtered through the Al_2O_3 layer (5 cm). After the solvent was removed, the residue was recrystallized from hexane. Racemic **5b** (0.07 g, 70%) was obtained as yellow crystals with m.p. 123—124 °C. Found (%): C, 48.39; H, 2.51. $C_{17}H_{10}Mn_2O_6$. Calculated (%): C, 48.57; H, 2.38.

Enantiomer (+)-5b. A mixture of compound (−)-**4b** (0.05 g) with an excess of CF_3COOH and Et_3SiH in $CHCl_3$ (2 mL) was boiled for 1.5 h. When reduction was complete (controlled by TLC), the reaction mixture was poured in an aqueous solution of Na_2CO_3 and extracted with CH_2Cl_2. Enantiomer (+)-**5b** (~0.05 g) was isolated from the extract, m.p. 116—117 °C (from hexane), $[\alpha]_D$ +60 (*c* 0.5, benzene).

Table 4. Coordinates of atoms ($\times 10^4$) and equivalent isotropic thermal parameters ($U_{eq} \times 10^3$) in the structure of **3b**

Atom	x	y	z	U_{eq}/Å^2
Mn(1)	−2085(1)	−1401(1)	−7011(1)	40(1)
Mn(2)	−4671(1)	−4236(1)	−7783(1)	44(1)
O(11)	−5880(5)	−1038(3)	−8032(5)	79(1)
O(12)	−2264(9)	−670(3)	−4251(6)	117(2)
O(13)	−708(7)	22(3)	−8212(7)	106(2)
O(14)	−1200(7)	−4464(4)	−9088(7)	122(2)
O(15)	−3236(10)	−5058(3)	−5256(5)	117(2)
O(16)	−6421(8)	−5624(3)	−9014(6)	98(2)
N(18)	1478(6)	−2171(2)	−3978(4)	49(1)
C(1)	−2568(7)	−2624(3)	−7351(5)	41(1)
C(2)	−1566(7)	−2506(2)	−6064(5)	41(1)
C(3)	137(6)	−2138(3)	−6315(5)	42(1)
C(4)	128(7)	−2023(3)	−7783(5)	47(1)
C(5)	−1521(7)	−2308(3)	−8437(5)	47(1)
C(6)	−4352(7)	−3012(3)	−7558(5)	42(1)
C(7)	−5432(7)	−3302(3)	−6508(6)	50(1)
C(8)	−7021(7)	−3641(4)	−7145(7)	61(2)
C(9)	−6949(7)	−3573(3)	−8618(7)	62(2)
C(10)	−5318(7)	−3188(3)	−8887(5)	48(1)
C(11)	−4411(7)	−1169(3)	−7630(6)	54(1)
C(12)	−2248(9)	−942(3)	−5343(7)	67(2)
C(13)	−1240(8)	−532(3)	−7749(7)	63(1)
C(14)	−2576(9)	−4392(3)	−8611(7)	73(2)
C(15)	−3810(9)	−4751(3)	−6244(7)	69(2)
C(16)	−5709(8)	−5090(3)	−8542(5)	59(1)
C(17)	1564(7)	−1930(3)	−5216(5)	48(1)
C(19)	2983(8)	−1958(3)	−2938(5)	52(1)
C(20)	2142(9)	−1722(4)	−1592(7)	75(2)
C(21)	4274(7)	−2626(3)	−2712(5)	46(1)
C(22)	3609(8)	−3377(3)	−2644(6)	55(1)
C(23)	4805(9)	−3989(4)	−2454(7)	72(2)
C(24)	6684(9)	−3867(4)	−2336(7)	72(2)
C(25)	7343(9)	−3139(4)	−2370(7)	67(2)
C(26)	6183(8)	−2515(4)	−2563(6)	59(1)

X-ray diffraction study of compound 3b. The crystals of **3b** are monoclinic, at 20 °C a = 7.297(2) Å, b = 17.365(4) Å, c = 9.540(2) Å, β = 94.25(3)°, V = 1205.5(4) Å^3, d_{calc} = 1.480 g cm^{-3}, Z = 2, space group $P2_1$. Unit cell parameters and intensities of 3257 independent reflections were measured on a CAD-4 Enraf-Nonius automated diffractomer (20 C, Mo-Kα radiation, graphite monochromator, θ/(5/3 θ)-scanning, θ < 30°).

The structure was solved by the direct method and refined by the full-matrix least-square method in the anisotropic approximation. The hydrogen atoms were arranged geometrically and included in the refinement of the "rider" model.

The absolute configuration was determined by refinement of the Flack parameter (x = 0.01(3)).[7] Final divergence factors: R_1 = 0.0358 (by F for 2148 observed reflections with $I > 2\sigma(I)$), wR_2 = 0.0979 (by F^2 for all 3257 independent reflections used in the refinement). All calculations were performed by SHELXTL PLUS 5 programs (gamma-version). The coordinates of the atoms are presented in Table 4.

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