Carbohydrate Research 344 (2009) 61–66

Contents lists available at ScienceDirect

Carbohydrate Research

journal homepage: www.elsevier.com/locate/carres

Asymmetric epoxidation of unfunctionalized alkenes catalyzed by sugar moiety-modified chiral salen–Mn(III) complexes

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ARTICLE INFO

Article history:
Received 24 July 2008
Received in revised form 5 September 2008
Accepted 7 October 2008
Available online 14 October 2008

Keywords:
Salen–Mn(III) complex
1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose
1,2:3,4-Di-*O*-isopropylidene-α-D-galactopyranose
3:5,6-Di-*O*-isopropylidede-α-D-mannofuranose
Asymmetric epoxidation

ABSTRACT

Several chiral Schiff-base ligands with sugar moieties at C-3 (3′) or C-5 (5′) of salicylaldehyde were synthesized from reaction of salicylaldehyde derivatives with diamine. These ligands coordinated with Mn(III) to afford the corresponding chiral salen–Mn(III) complexes characterized by FT-IR, MS, and elementary analysis. These complexes were used as catalysts for the asymmetric epoxidation of unfunctionalized alkenes. Only weak enantioselectivity is induced by the chiral sugar moieties at C-3 (3′) or C-5 (5′) in the case of absence of chirality in the diimine bridge moiety. It was also shown that the sugars at C-5 (5′) having the same rotation direction of polarized light as the diimine bridge in the catalyst could enhance the chiral induction in the asymmetric epoxidation, but the sugars with the opposite rotation direction would reduce the chiral induction.

1. Introduction

Salen–Mn(III) catalyzed asymmetric epoxidation, known as the Jacobsen–Katsuki epoxidation, has been extensively investigated since 1990.[1,2] Much attention has been focused on the design of the salen ligand and steric and electronic effects of the catalyst structure on stereoselectivity. The pathway and orientation of the approaching alkene to the active oxidant (the coordination atmosphere around the metal center of the catalyst) are crucial factors in asymmetric epoxidation of unfunctionalized alkenes.[3,4] As is known, the attainment of high enantioselectivity relies on the steric and electronic properties of the substituent in the salen complex, in addition to the presence of chiral diimine moiety.[5] The first generation Jacobsen catalysts had the chiral centers located at the diimine bridge. Later, Katsuki et al. developed a series of salen–Mn(III) complexes with four stereogenic centers, two at the diimne bridge and two at C-8 (8′). The epoxidation enantioselectivity was improved, and the conformation of the chiral substituents attached to C-8 (8′) had considerable influence on asymmetric induction.[6–8] Tang synthesized two Mn(III)–Schiff-base complexes assembled with L-amino acid ethyl esters at the C-3 (3′) positions. The catalysts were found to be highly effective catalysts for the enantioselective epoxidation of conjugated olefins.[5] All these results show that the chiral centers of the C-3 (3′) groups on the salen structure play an very important role on chiral induction. The presence and properties of substituents on the C-5 (5′) positions of the ligand also have a significant, although generally less important, influence on epoxidation enantioselectivity.[9]

Carbohydrates are natural products with chiral centers making them ideal precursors for the introduction of chiral building blocks into catalysts. Recently, Yan and Klemm reported the first carbohydrated-derived chiral salen–Mn(III) complex by incorporating a chiral carbohydrate into the diamine moiety.[10] Ruffo and co-workers also reported new chiral salen ligands derived from α-D-glucose and α-D-mannose by introducing appropriate functional groups at the C-2 and C-3 of the sugar ring.[11] High enantiomeric excesses for epoxidation reactions were received with the ligands-based complexes as catalysts. In another work, Ruffo and co-workers prepared a supported salen–Mn(III) catalyst derived from D-glucose, and the catalytic results showed that the complex had good reactivity and enantioselectivity.[12] These efforts have strengthened the prospects of utilizing natural products as templates for asymmetric epoxidative catalysts. We also reported sugar-based ligands by incorporating a glucofuranose moiety into the C-5 (5′) position of the salen structure and found that the carbohydrate moiety has an asymmetric inducing effect in the epoxidation reaction.[13] The interesting results encourage us to synthesize more sugar-based

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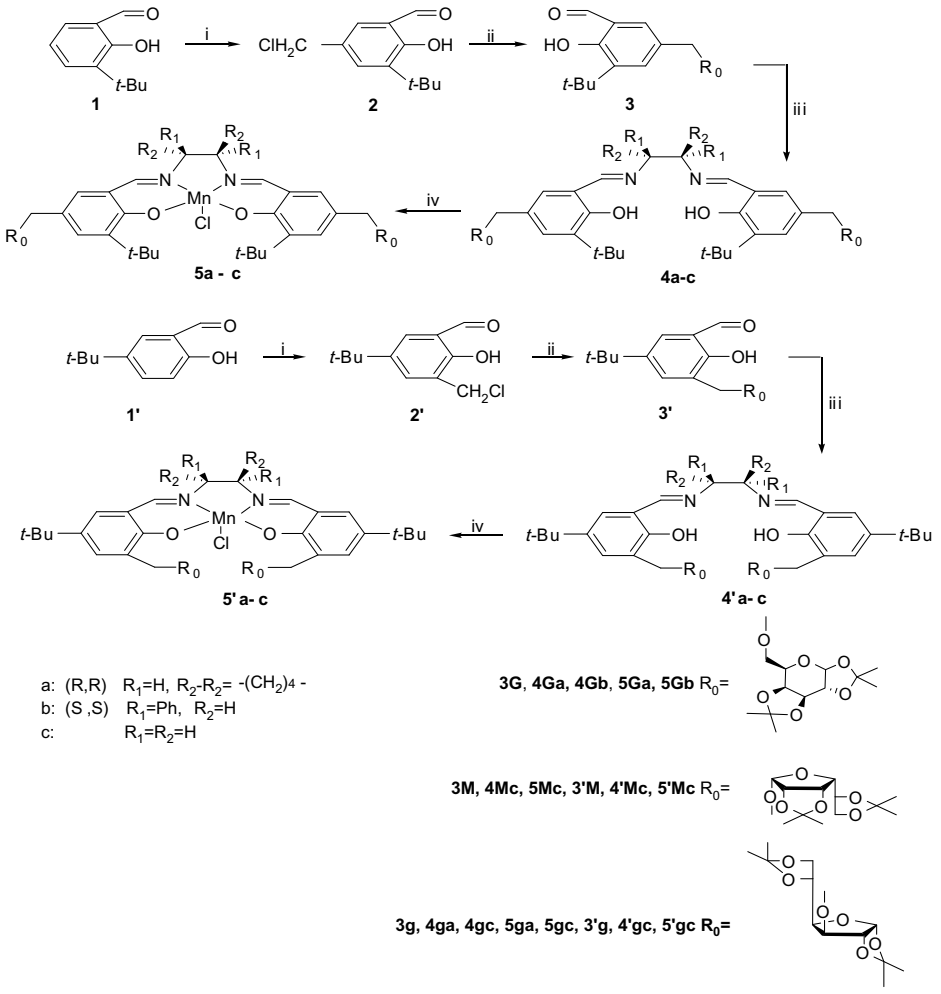
0008-6215/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carres.2008.10.005



Scheme 1. Preparation of salen–Mn(III) complexes with carbohydrate moiety.

salen–Mn(III) complexes to elucidate the asymmetric induction effects (Scheme 1).

2. Experimental

2.1. Materials and methods

^{1}H NMR and ^{13}C NMR spectra were recorded with an AC 400 Bruker spectrometer operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C measurements. IR spectra were obtained on a Bruker Vector-22 FT-IR spectrometer. Melting points were determined on a Perkin XT-4 microscopic analyzer. Electrospray ionization mass spectra were performed on a Finnigan LCQ Advanced instrument. Elemental analyses were performed on an Elementar Vario EL instrument. Optical rotations were measured on a Shanghai WZZ-2S/2SS digital rotation analyzer, at 20 °C at 589 nm (Na) using a 10 cm sample tube. The asymmetric epoxidation products were analyzed on a Shandong Lunan Ruihong Gas Chromatograph, SP-6800A, equipped with a Cyclodex-β capillary column (30 m × 250 μm i.d.) using an FID detector. 1,2-Dihydronapthalene, α-methylstyrene, *cis*-β-methylstyrene, *N*-methylmorpholine *N*-oxide (NMO), 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose, 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose, and 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose were purchased from Acros. Other chemicals were obtained from local suppliers or prepared in our laboratory. All solvents used were purified by standard procedures.

2.2. Synthesis of the chiral Schiff bases and salen–Mn(III) complexes

2.2.1. Synthesis of 3-*tert*-butyl-5-(chloro-methyl)-2-hydroxy benzaldehyde (2)

Compound **2** was prepared by the procedure reported in the literature.[14] Light yellow crystalline solid. Yield 87%, mp 61–63 °C. (Lit. mp 63–65 °C[14]). ^{1}H NMR (DMSO): δ 1.39 (s, 9H), 4.81 (s, 2H), 7.63 (d, J = 2.2 Hz, 1H), 7.75 (d, J = 2.2 Hz, 1H), 9.98 (s, 1H), 11.91 (s, 1H).

2.2.2. Synthesis of 5-*tert*-butyl-3-(chloro-methyl)-2-hydroxy benzaldehyde (2′)

Compound **2′** was prepared by the procedure reported in the literature.[14] Light yellow liquid. Yield 90%. ^{1}H NMR ($CDCl_3$): δ 1.34 (s, 9H), 4.70 (s, 2H), 7.53 (d, J = 2.7 Hz, 1H), 7.67 (d, J = 2.4 Hz, 1H), 9.91 (s, 1H), 11.29 (s, 1H). IR (film) ν: 2986, 2730, 1656, 1460, 1370, 910, 830, 700.

2.2.3. Synthesis of 1,2:3,4-di-*O*-isopropylidene-3-*O*-methylene-[5-(3-*tert*-butyl-2-hydroxy benzaldehyde)]-α-D-galactopyranose (3G)

Compound **3G** was prepared by the procedure reported in the literature.[15] Light yellow solid. Yield 60%, mp 31–32 °C. $[\alpha]_D^{20}$ −32.1 (*c* 0.80, EtOH). ^{1}H NMR($CDCl_3$): δ 1.39 (s, 9H), 1.42 (s, 12H), 3.62–3.72 (d, J = 46 Hz, 2H), 4.00–4.62 (m, 4H), 4.63 (s, 2H), 5.56 (d, J = 4.8 Hz, 1H), 7.41 (s, 1H), 7.49 (s, 1H), 9.86 (s, 1H)

11.80 (s, 1H). IR (KBr) *v*: 2982, 2959, 2925, 2870, 1653, 1620, 1458, 1440, 1383, 1374, 1325, 1259, 1212, 1168, 1151, 1071, 1006, 865 773, 757 cm^{-1}. Anal. Calcd for $C_{24}H_{34}O_8$: C, 63.98; H, 7.61. Found: C, 63.71; H, 7.83.

2.2.4. Synthesis of 1,2:5,6-di-*O*-isopropylidene-3-*O*-methylene-[5-(3-*tert*-butyl-2-hydroxy benzaldehyde)]-α-D-glucofuranose (3g)

Compound **3g** was prepared by the procedure reported in the literature.[15] Light yellow solid. Yield 67%, mp 96–98 °C. $[\alpha]_D^{20}$ −34.1 (*c* 0.80, EtOH). ^1H NMR ($CDCl_3$): δ 1.38 (s, 9H), 1.42 (s, 12H), 4.01–4.68 (m, 8H), 5.90 (d, *J* = 3.9 Hz, 1H), 7.41 (d, *J* = 2.4 Hz, 1H), 7.48 (d, *J* = 1.8 Hz, 1H), 9.87 (s, 1H), 11.80 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 197.0, 161.0, 138.6, 133.9, 131.0, 128.3, 120.3, 111.9, 109.1, 105.3, 82.6, 81.6, 81.3, 77.7, 76.7, 72.4, 71.8, 67.5, 34.9, 29.1, 26.9, 26.8, 26.7, 26.2. IR (KBr) *v*: 3423, 2992, 2969, 2936, 2862, 1655, 1617, 1456, 1440, 1384, 1374, 1321, 1265, 1226, 1212, 1167, 1152, 1081, 1024, 847, 771, 759 cm^{-1}. Anal. Calcd for $C_{24}H_{34}O_8$: C, 63.98; H, 7.61. Found: C, 63.71; H, 7.83.

2.2.5. Synthesis of 1,2:5,6-di-*O*-isopropylidene-3-*O*-methylene-[3-(5-*tert*-butyl-2-hydroxy benzaldehyde)]-α-D-glucofuranose (3′g)

Compound **3′g** was prepared by the procedure reported in the literature.[16] Light yellow liquid. Yield 45%. $[\alpha]_D^{20}$ −95.8 (*c* 1.30, EtOH). ^1H NMR ($CDCl_3$): δ 1.34 (s, 9H), 1.44 (s, 12H), 3.71 (s, 1H), 4.04–4.85 (m, 7H), 5.91 (d, *J* = 6.0 Hz, 1H), 7.47 (d, *J* = 2.7 Hz, 1H), 7.69 (s, *J* = 2.4 Hz, 1H), 9.90 (s, 1H), 11.13 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 192.5, 156.5, 134.0, 130.0, 127.0, 123.4, 115.7, 109.3, 104.8, 97.1, 75.2, 74.6, 72.1, 68.8, 66.6, 62.3, 30.4, 24.7, 22.5, 21.2, 20.7, 20.6, 20.0. IR (film) *v*: 2960, 2872, 1655, 1619, 1459, 1381, 1321, 1268, 1216, 1165, 1076, 1022, 847, 746, 729 cm^{-1}. Anal. Calcd for $C_{24}H_{34}O_8$: C, 63.98; H, 7.61. Found: C, 63.95; H, 7.82.

2.2.6. Synthesis of 2,3:5,6-di-*O*-isopropylidene-1-*O*-methylene-[5-(3-*tert*-butyl-2-hydroxy benzaldehyde)]-α-D-mannofuranose (3M)

Compound **3M** was prepared by the procedure reported in the literature.[15] Light yellow liquid. Yield 79%. $[\alpha]_D^{20}$ +112.0 (*c* 1.10, EtOH). ^1H NMR ($CDCl_3$): δ 1.39 (s, 9H), 1.42 (s, 12H), 3.61 (q, *J* = 3.9, 3.6, 3.9 Hz, 1H), 4.10 (d, *J* = 5.4 Hz, 2H), 4.47–4.89 (m, 6H), 7.43 (d, *J* = 2.1 Hz, 1H), 7.54 (d, *J* = 2.1 Hz, 1H), 9.87 (s, 1H), 11.81 (s, 1H). IR (film) *v*: 3446, 2957, 2872, 1652, 1620, 1457, 1440, 1372, 1324, 1267, 1212, 1187, 1157, 1118, 1069, 886, 846, 773, 755 cm^{-1}. Anal. Calcd for $C_{24}H_{34}O_8$: C, 63.98; H, 7.61. Found: C, 63.78; H, 7.55.

2.2.7. Synthesis of 2,3:5,6-di-*O*-isopropylidene-1-*O*-methylene-[3-(5-*tert*-butyl-2-hydroxy benzaldehyde)]-α-D-mannofuranose (3′M)

Compound **3′M** was prepared by the procedure reported in the literature.[16] White solid. Yield 60%, mp 78–80 °C. $[\alpha]_D^{20}$ +85.0 (*c* 0.90, EtOH). ^1H NMR ($CDCl_3$): δ 1.33 (s, 9H), 1.44 (s, 12H), 3.61 (q, *J* = 3.6, 4.2, 3.9 Hz, 1H), 4.06 (d, *J* = 5.4 Hz, 2H), 4.46–4.90 (m, 6H), 7.46 (d, *J* = 2.7 Hz, 1H), 7.79 (d, *J* = 2.4 Hz, 1H), 9.90 (s, 1H), 11.09 (s, 1H). IR (KBr) *v*: 3423, 2971, 2870, 1666, 1620, 1461, 1379, 1275, 1258, 1246, 1215, 1146, 1119, 1070, 1005, 901, 847, 802 cm^{-1}. Anal. Calcd for $C_{24}H_{34}O_8$: C, 63.98; H, 7.61. Found: C, 63.77; H, 7.79.

2.2.8. Synthesis of Schiff-base ligands (4Ga, 4Gb, 4Mc, 4′Mc, 4ga, 4gc, 4′gc)

Compound **4Ga**: A solution of compound **3G** (1.00 g, 2.2 mmol) and (*R*,*R*)-1,2-cyclohexanediamine (0.125 g, 1.1 mmol) in dry EtOH (25 mL) was refluxed for 2 h under nitrogen atmosphere. Ethanol was removed under reduced pressure, the residue was purified by chromatography (EtOAc–petroleum ether 1:2) to afford, after removal of the solvent, the Schiff-base **4Ga** as yellow foam solid (1.02 g, yield 86.4%), mp 83–84 °C, $[\alpha]_D^{20}$ −443.7 (*c* 0.20, EtOH). ^1H NMR ($CDCl_3$): δ 1.25 (s, 12H), 1.31 (s, 18H), 1.42 (s, 12H), 1.56–1.94 (m, 8H), 3.31 (m, 2H), 3.54–3.65 (m, 4H), 4.23–4.47 (m, 8H), 4.56 (d, *J* = 2.4 Hz 4H), 5.51 (d, *J* = 3.6 Hz 2H), 6.98 (s, 2H), 7.22 (s, 2H), 8.27 (s, 2H), 13.82 (s, 2H). IR (KBr) *v*: 3444, 2989, 2934, 1630, 1443, 1381, 1373, 1340, 1257, 1212, 1167, 1071, 1005, 865, 802, 775 cm^{-1}. Anal. Calcd for $C_{54}H_{78}O_{14}N_2$: C, 66.26; H, 7.98; N, 2.86. Found: C, 66.54; H, 8.00; N, 2.61.

Compound **4Gb**: Ligand **4Gb** was synthesized from compound **3G** and (1*S*,2*S*)-1,2-diphenylethylenediamine as yellow foam solid. Yield 97%, mp 86–88 °C, $[\alpha]_D^{20}$ −122 (*c* 0.1, EtOH). ^1H NMR ($CDCl_3$): δ 1.25 (s, 12H), 1.34 (s, 18H) 1.41 (s, 12H), 3.56–3.58 (m, 4H), 4.22–4.56 (m, 8H), 4.58 (d, *J* = 2.4 Hz 4H), 4.72 (s, 2H), 5.51 (d, *J* = 4.2 Hz, 2H), 7.17 (s, 2H), 7.18–7.22 (m, 10H), 7.24 (s, 2H), 8.32 (s, 2H), 13.77 (s, 2H). IR (KBr) *v*: 3443, 2957, 2871, 1628, 1464, 1373, 1263, 1214, 1163, 1076, 1027, 848, 800, 776 cm^{-1}. Anal. Calcd for $C_{62}H_{80}O_{14}N_2$: C, 69.12; H, 7.48; N, 2.60. Found: C, 69.42; H, 7.67; N, 2.53.

Compound **4Mc**: Ligand **4Mc** was synthesized from compound **3M** and ethylenediamine as yellow foam solid. Yield 73%, mp 81–83 °C, $[\alpha]_D^{20}$ +69 (*c* 0.32, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 1.35 (s, 18H), 1.41 (s, 24H), 4.10 (s, 4H), 4.12–4.86 (m, 18H), 7.11 (d, *J* = 1.8 Hz, 2H), 7.32 (d, *J* = 1.8 Hz, 2H), 8.39 (s, 2H), 13.89 (s, 2H). IR (KBr) *v*: 3447, 2958, 2871, 1633, 1464, 1372, 1257, 1217, 1165, 1076, 1022, 848, 826, 750 cm^{-1}. Anal. Calcd for $C_{50}H_{72}O_{14}N_2$: C, 64.92; H, 7.84; N, 3.03. Found: C, 64.91; H, 7.88; N, 3.12.

Compound **4′Mc**: Ligand **4′Mc** was synthesized from compound **3M** and ethylenediamine as yellow foam solid. Yield 90%, mp 109–110 °C, $[\alpha]_D^{20}$ +178 (*c* 0.40, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 1.32 (s, 18H), 1.44 (s, 24H), 3.92 (s, 4H), 4.44–4.90 (m, 18H), 7.15 (s, 2H), 7.46 (d, *J* = 2.4 Hz, 2H), 8.37 (s, 2H), 13.33 (s, 2H). IR (KBr) *v*: 3423, 2959, 2869, 1635, 1466, 1371, 1341, 1271, 1217, 1157, 1070, 1046, 859, 846, 750 cm^{-1}. Anal. Calcd for $C_{50}H_{72}O_{14}N_2$: C, 64.92; H, 7.84; N, 3.03. Found: C, 64.99; H, 8.06; N, 3.13.

Compound **4ga**: Ligand **4ga** was synthesized as described in the literature.[13]

Compound **4gc**: A solution of compound **3g** (1.00 g, 2.2 mmol) and ethylenediamine (0.07 g, 1.1 mmol) in dry EtOH (25 mL) was refluxed for 2 h under nitrogen atmosphere. Ethanol was removed under reduced pressure, the residue was purified by chromatography (EtOAc–petroleum ether 1:2) to afford, after removal of the solvent, the Schiff-base **4g** as yellow foam solid (0.65 g, yield 60%), mp 81–83 °C, $[\alpha]_D^{20}$ −56.0 (*c* 0.20, EtOH). ^1H NMR ($CDCl_3$): δ 1.31 (s, 9H), 1.42 (s, 12H), 3.95 (s, 2H), 4.00–4.34 (m, 5H), 4.55–4.58 (m, 3H), 5.87 (d, *J* = 3.6 Hz, 1H), 7.10 (s, 1H), 7.26 (s, 1H), 8.38 (s, 1H), 13.87 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 202.8, 167.2, 160.5, 137.9, 129.8, 129.5, 126.9, 118.4, 112.0, 109.2, 105.5, 83.0, 81.7, 77.6, 76.8, 72.7, 67.6, 60.8, 59.8, 48.9, 35.1, 29.5, 27.1, 26.5, 25.7. IR (KBr) *v*: 3442, 2987, 2932, 1633, 1444, 1373, 1341, 1268, 1215, 1164, 1077, 1026, 848, 798, 776 cm^{-1}. Anal. Calcd for $C_{50}H_{72}O_{14}N_2$: C, 64.92; H, 7.84; N, 3.03. Found: C, 64.89; H, 8.04; N, 3.10.

Compound **4′gc**: Ligand **4′gc** was synthesized from compound **3′g** and ethylenediamine as yellow liquid. Yield 68%, $[\alpha]_D^{20}$ −128 (*c* 0.50, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 1.28 (s, 9H), 1.44 (s, 12H), 3.95 (s, 2H), 3.95–4.53 (m, 8H), 5.84 (d, *J* = 3.9 Hz, 1H), 7.17 (s, 1H), 7.23 (s, 1H), 8.34 (s, 1H), 13.83 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 166.9, 160.4, 139.7, 137.7, 126.9, 118.4, 112.0, 109.2, 105.5, 82.9, 81.6, 81.5, 80.2, 76.0, 72.7, 72.5, 67.5, 67.3, 35.0, 29.5, 27.1, 26.5, 25.7; IR (film) *v*: 3446, 2958, 2871, 1631, 1459, 1372, 1268, 1216, 1165, 1126, 1076, 1022, 885, 847 cm^{-1}. Anal. Calcd for $C_{50}H_{72}O_{14}N_2$: C, 64.92; H, 7.84; N, 3.03. Found: C, 64.85; H, 7.91; N, 3.22.

2.2.9. Synthesis of salen–Mn(III) complexes (5Ga, 5Gb, 5Mc, 5′Mc, 5ga, 5gc, 5′gc)

Compound **5Ga**: A mixture of **4Ga** (0.33 g, 0.34 mmol) and $Mn(OAc)_2{\cdot}4H_2O$ (0.17 g, 0.68 mmol) in EtOH (30 mL) was stirred under reflux at the atmosphere of nitrogen for 4 h. Solid LiCl (0.04 g, 1.02 mmol) was added and the mixture was further heated for 3 h while exposed to air. The solvent was removed and the residue was extracted with CH_2Cl_2. The extract was washed with brine, dried over Na_2SO_4, and concentrated to obtain dark brown powder **5Ga** (0.31 g, yield 86%). Mp 139–141 °C $[\alpha]_D^{20}$ −480.5 (*c* 0.80, CH_2Cl_2). IR (KBr) *v*: 2957, 1614, 1543, 1440, 1382, 1342, 1310, 1260, 1210, 1169, 1072, 1072, 865, 820, 566, 512 cm^{-1}. ESIMS: *m/z* 1032 $[M-Cl]^+$ Anal. Calcd for $C_{54}H_{76}O_{14}N_2MnCl$: C, 60.73; H, 7.12; N, 2.62. Found: C, 60.06; H, 7.67; N, 2.36.

Compound **5Gb**: For complex **5Gb**, similar procedures were followed as above by use of ligand **4Gb**. Dark brown powder, yield 97.5%, $[\alpha]_D^{20}$ −163 (*c* 0.08, EtOH). IR (KBr) *v*: 2957, 2875, 1614, 1435, 1382, 1344, 1309, 1258, 1209, 1169, 1071, 939, 853, 825, 805, 556, 513 cm^{-1}. ESIMS: *m/z* 1130 $[M-Cl]^+$. Anal. Calcd for $C_{62}H_{78}O_{14}N_2MnCl$: C, 63.88; H, 6.74; N, 2.40. Found: C, 63.92; H, 6.50; N, 2.35.

Compound **5Mc**: For complex **5Mc**, similar procedures were followed as above by use of ligands **4Mc** and **4′Mc**. Dark brown powder, yield 93%, $[\alpha]_D^{20}$ +209.0 (*c* 0.02, CH_2Cl_2). IR (KBr) *v*: 2960, 2872, 1616, 1440, 1381, 1339, 1302, 1262, 1210, 1165, 1069, 932, 844, 822, 803, 551, 474 cm^{-1}. ESIMS: *m/z* 978 $[M-Cl]^+$. Anal. Calcd for $C_{50}H_{70}O_{14}N_2MnCl$: C, 59.25; H, 6.96; N, 2.76. Found: C, 59.40; H, 7.13; N, 2.50.

Compound **5′Mc**: For complex **5′Mc**, similar procedures were followed as above by use of ligand **4′M**. Dark brown powder, yield 63%, $[\alpha]_D^{20}$ +257 (*c* 0.02, CH_2Cl_2). IR (KBr) *v*: 2955, 2927, 1620, 1553, 1458, 1444, 1380, 1371, 1264, 1217, 1116, 1069, 1047, 888, 845, 540, 475 cm^{-1}. ESIMS: *m/z* 978 $[M-Cl]^+$. Anal. Calcd for $C_{50}H_{70}O_{14}N_2MnCl$: C, 59.25; H, 6.96; N, 2.76. Found: C, 59.16; H, 6.90; N, 2.57.

Compound **5ga**: For complex **5ga**, see literature.[13]

Compound **5gc**: For complex **5gc**, see literature.[13]

Compound **5′gc**: For complex **5′gc**, similar procedures were followed as above by use of ligand **4′gc**. Dark brown powder, yield 88%, $[\alpha]_D^{20}$ −190.0 (*c* 0.02, CH_2Cl_2). IR (KBr) *v*: 2957, 2926, 1620, 1553, 1444, 1381, 1262, 1217, 1165, 1074, 1022, 847, 833, 803, 537, 469 cm^{-1}. ESIMS: *m/z* 978 $[M-Cl]^+$. Anal. Calcd for $C_{50}H_{70}O_{14}N_2MnCl$: C, 59.25; H, 6.96; N, 2.76. Found: C, 59.45; H, 7.19; N, 2.86.

2.3. General procedure for asymmetric epoxidation of alkenes

2.3.1. For NaClO/PyNO oxidant system

The solution of alkene (1 mmol), PyNO (20 mg, 0.20 mmol), and salen–Mn(III) complex (0.02 mmol) in CH_2Cl_2 (5.0 mL) was cooled to 0 °C. A precooled NaClO aqueous solution (2 mmol, pH 11.3, 0 °C) was added. The mixture was stirred at 0 °C, and the reaction was monitored by gas chromatography.

2.3.2. For *m*-CPBA/NMO oxidant system

A solution of alkene (0.5 mmol), NMO (0.30 g, 2.5 mmol), and salen–Mn(III) complex (0.01 mmol) in CH_2Cl_2 (2.5 mL) was cooled to the desired temperature. Solid *m*-CPBA (0.20 g, 1.0 mmol) was added in one time. The reaction was monitored by GC.

3. Results and discussion

3.1. Synthesis of complexes

For synthesis of the ligands, 3-*tert*-butyl-5-(chloro-methyl)-2-hydroxy benzaldehyde (**2**) and 5-*tert*-butyl-3-(chloro-methyl)-2-hydroxy benzaldehyde (**2′**) were synthesized as described in the literature[11] in high yields. Compounds **2** and **2′** reacted, respectively, with 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose, 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose, and 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose readily to give the correspondent intermediates **3G**, **3M**, **3g**, and **3′M**, **3′g** in the presence of NaH and tetrabutylammonium iodide (TBAI) in THF under reflux. The synthesis of the ligands **4Ga**, **4Gb**, **4Mc**, **4gc**, **4′gc**, and **4′Mc** is straightforward, which involves the direct reaction of ethylenediamine with the intermediate **3G**, **3M**, and **3′M** in 1:2 molar ratio with ethanol as solvent. The correspondent complexes were prepared by the reaction of ligands with $Mn(OAc)_2{\cdot}4H_2O$, followed by the treatment of the mixture with LiCl, same as the preparation of Jacobsen catalyst.[1]

3.2. Characterization of ligands and complexes

The ligands and complexes were characterized by ^1H NMR, IR, and Elemental analysis. The data are in accordance with the proposed structures. The IR spectra of all complexes, compared with the spectra of the corresponding ligands, indicate that *v*C=N band at 1628–1635 cm^{-1} is shifted to lower energy by 14–17 cm^{-1}, indicating the ligands are coordinated to the metal ion Mn(III) through the nitrogen atoms of the ligands. The disappearance of the band around 3423–3447 cm^{-1} of ligands after coordination indicates the −OH is transferred to –O–, which is coordinated to Mn directly (Fig. 1).

3.3. Asymmetric epoxidation catalyzed by complexes

The catalytic activity and enantioselectivity of complexes were explored for the asymmetric epoxidation of *cis*-β-methyl-styrene, 1,2-dihydronaphthalene, styrene, and α-methyl-styrene using NaClO/PyNO or *m*-CPBA/NMO as an oxidant system, respectively. The results are summarized in Table 1.

It could be seen that the epoxidation of *cis*-β-methyl-styrene and 1,2-dihydronaphthalene in the *m*-CPBA/NMO system was much faster than that in the NaClO/PyNO biphasic system and afforded higher ee values (entries 1–27). For example, complex **5Gb** gave 82% ee for the epoxidation of 1,2-dihydronaphthalene in the *m*-CPBA/NMO system within 0.17 h (10 min) (entry 19), whereas the same reaction in NaClO/PyNO system was completed in 5 h with 72% ee (entry 18). Furthermore, some reactions did not take place in NaClO/PyNO system (entries 7 and 13). All the complexes showed low ee values in the epoxidation of α-methylstyrene (entries 37–43). The kind of sugar moiety obviously has influence on the yields and ee values of epoxides. Though **5Ga** and **5ga** have the same diimine bridge structure, the **5ga** showed higher ee than **5Ga** for the asymmetric epoxidation of the *cis*-substituted alkenes (entries 1, 2, 9, 10; 15, 16, 24, 25).

In general, the complexes with no chiral centers on the diimine bridge such as **5Mc**, **5′Mc**, **5gc**, and **5′gc** showed low activity and ee values, which indicated that the chiral induction of chiral salen–Mn(III) complexes is mainly derived from the chiral diimine, and only poor induction effect is received from the sugar moieties at C-3 (3′) or C-5 (5′) positions. In other words the chiral diimine bridge is necessary in the salen–Mn(III) complexes as asymmetric epoxidation catalysts.

Meanwhile, complexes **5′Mc** and **5′gc** bearing sugar moieties at C-3 (3′) positions showed very low activity. In extreme circumstances no reaction took place (entries 7 and 13). The reason is that the sugar moieties that are much more hindered than *tert*-butyl are more close to the Mn, which blocks the alkene from approaching the salen–Mn-oxo species according to side-on approach theory.[17]

Although the chiral effect of sugar moieties at C-3 (3′) or C-5 (5′) positions is weak, it is indeed present in the epoxidation reaction

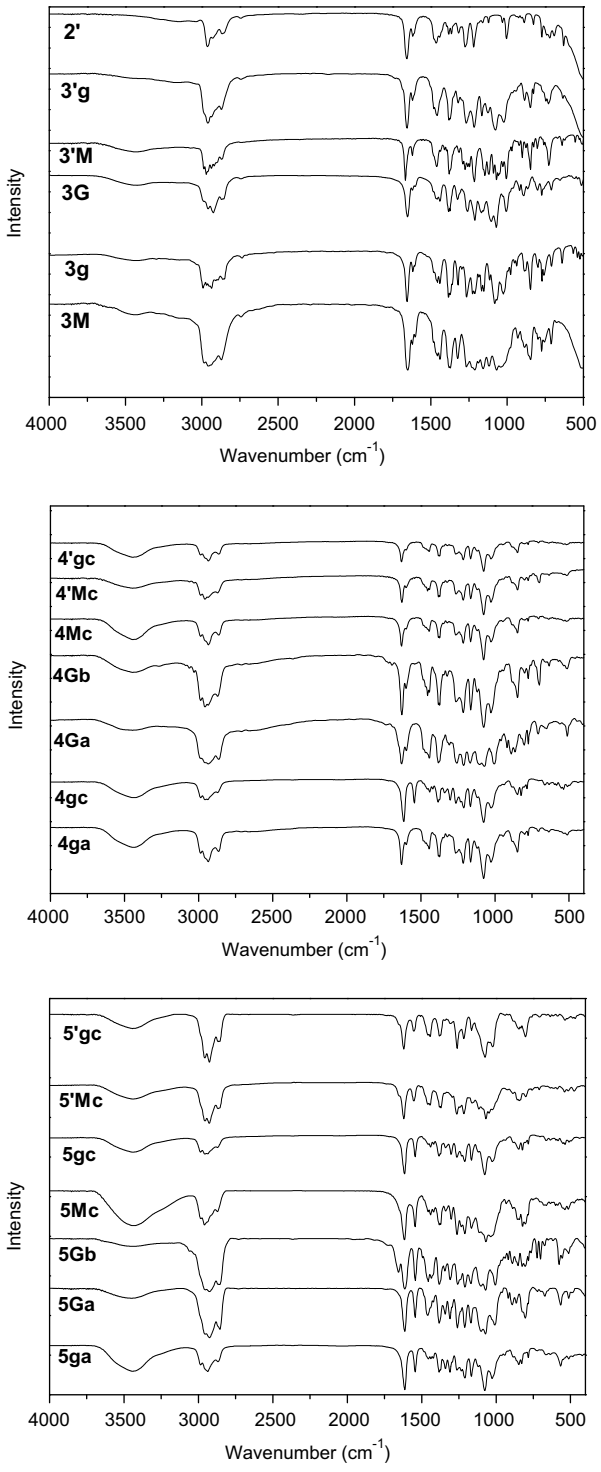


Figure 1. The FT-IR spectra of the ligands and complexes.

(entries 27, 28, 29, and 36). For further elucidating the chiral induction of sugar moieties of salen–Mn(III) complexes on epoxidation reaction, the catalysis of complexes **5Ga** and **5Gb** was studied thoroughly. They showed good activity and moderate to good enantioselectivities in *m*-CPBA/NMO system (entries 2, 4, 17, 19, 30, and 31) except for the α-methylstyrene which afforded low to moderate ee value (entries 36 and 37). The catalytic properties of **5Ga** and **5Gb** were compared with that of the Jacobsen's catalyst in the literatures.[18,19] It was found that **5Ga afforded** ee value of 62% in the epoxidation of 1,2-dihydronaphthalene in NaClO system

Table 1
Epoxidation of *cis*-β-methyl-styrene, 1,2-dihydronaphthalene, styrene and α-methylstyrene and using catalysts **5Ga**,**b**

Entry	Substrate[a]	Catalyst[b]	Oxidant[c]	*T* (°C)	Time (h)	Yield[d] (%)	ee[e] (%)
1	A	**5Ga** (2.0)	NaClO	0	12	64	71
2	A	**5Ga** (2.0)	*m*-CPBA	−78	0.05	88	79
3	A	**5Gb** (2.0)	NaClO	0	4	63	83
4	A	**5Gb** (2.0)	*m*-CPBA	−78	0.167	69	85
5	A	**5Mc** (2.0)	NaClO	0	5	34	3
6	A	**5Mc** (2.0)	*m*-CPBA	−78	0.167	82	5
7	A	**5′Mc** (2.0)	NaClO	0	5	—	—
8	A	**5′Mc** (2.0)	*m*-CPBA	−78	0.167	8	7
9	A	**5ga** (1.0)	NaClO	0	10.5	41	82
10	A	**5ga** (1.0)	*m*-CPBA	−78	0.833	74	84
11	A	**5gc** (2.0)	NaClO	0	5	28	2
12	A	**5gc** (2.0)	*m*-CPBA	−78	0.25	80	2
13	A	**5′gc** (2.0)	NaClO	0	5	—	—
14	A	**5′gc** (4.0)	*m*-CPBA	−78	0.333	8	5
15	B	**5Ga** (2.0)	NaClO	0	7	49	64
16	B	**5Ga** (1.5)	NaClO	0	6	46	62
17	B	**5Ga** (2.0)	*m*-CPBA	−78	0.25	45	66
18	B	**5Gb** (2.0)	NaClO	0	5	65	72
19	B	**5Gb** (2.0)	*m*-CPBA	−78	0.167	74	82
20	B	**5Mc** (2.0)	NaClO	0	6.5	72	<1
21	B	**5Mc** (2.0)	*m*-CPBA	−78	1	54	8
22	B	**5′Mc** (2.0)	NaClO	0	7	34	2
23	B	**5′Mc** (2.0)	*m*-CPBA	−78	0.333	21	15
24	B	**5ga** (1.0)	NaClO	0	9.5	66	67
25	B	**5ga** (1.0)	*m*-CPBA	−78	1.25	44	78
26	B	**5gc** (2.0)	NaClO	0	5.5	57	4
27	B	**5gc** (2.0)	*m*-CPBA	−78	0.5	40	11
28	B	**5′gc** (2.0)	NaClO	0	9.5	19	19
29	B	**5′gc** (2.0)	*m*-CPBA	−78	0.197	7	7
30	C	**5Ga** (2.0)	*m*-CPBA	−78	0.25	93	72
31	C	**5Gb** (2.0)	*m*-CPBA	−78	0.25	93	87
32	C	**5Gb** (1.0)	*m*-CPBA	−78	2.0	80	70
33	C	**5Mc** (2.0)	*m*-CPBA	−78	0.167	>99	6
34	C	**5′Mc** (2.0)	*m*-CPBA	−78	0.333	9	9
35	C	**5ga** (1.0)	*m*-CPBA	−78	0.333	99	37
36	C	**5′gc** (4.0)	*m*-CPBA	−78	0.5	16	21
37	D	**5Ga** (2.0)	*m*-CPBA	−78	0.333	94	49
38	D	**5Gb** (2.0)	*m*-CPBA	−78	0.167	89	26
39	D	**5Mc** (2.0)	*m*-CPBA	−78	0.167	>99	4
40	D	**5′Mc** (2.0)	*m*-CPBA	−78	0.333	21	5
41	D	**5ga** (2.0)	*m*-CPBA	−78	0.333	93	51
42	D	**5gc** (2.0)	*m*-CPBA	−78	0.25	82	10
43	D	**5′gc** (4.0)	*m*-CPBA	−78	0.333	28	5

[a] A: *cis*-β-methyl-styrene; B: 1,2-dihydronaphthalene; C: styrene; D: α-methylstyrene.
[b] The number in parentheses is the molar percentage of catalyst used as compared to the amount of substrate.
[c] Reactions were carried out in CH_2Cl_2. For the *m*-CPBA oxidative system the substrate/oxidant/NMO molar ratios were 1:2:5. For the NaClO system the substrate/oxidant/PyNO molar ratios were 1:2:0.2.
[d] Determined by GC.
[e] Determined by GC with a chiral Cyclodex-β column.

(entry 16), worse than that of 72% displayed by Jacobsen's catalyst.[18] However, **5Gb** showed ee value of 70% in the epoxidation of styrene (entry 32) better than that of 64% displayed by Jacobsen's catalyst.[19] It can be concluded that the sugars with opposite rotation direction of polarized light as the diimine bridge in the complex could reduce the chiral induction of the complex in the asymmetry epoxidation, but the sugars with the same one would enhance the chiral induction. A same result was also observed in the oxidative kinetic resolution of 1-phenylethanol catalyzed by the sugar-based salen–Mn(III) complexes.[20]

4. Conclusion

Several salen–Mn(III) complexes bearing sugar moieties have been synthesized. These complexes have been used for the

asymmetric epoxidation of unfunctionalized alkenes. Weak enantioselectivity is induced by the chiral sugar groups at C-3 (3′) or C-5 (5′) in the case of absence of chirality in the diimine bridge moiety. It was also shown that the sugars at C-5 (5′) having the same rotation direction of polarized light as the diimine bridge in the catalyst could enhance the chiral induction in the asymmetry epoxidation, but the sugars with the opposite one would reduce the chiral induction.

Acknowledgment

This work was supported by NSFC of China (Grant Nos. 20376017 and 20776035).

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