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Oxidative kinetic resolution of 1-phenylethanol catalyzed by sugar-based salen–Mn(III) complexes

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Abstract—Three new chiral salen–Mn(III) complexes with sugars at the C-5(5′) positions of the salicylaldehyde moieties of the salen ligand were synthesized. Their structures were characterized by FTIR, MS, and elemental analysis. The complexes together with two previously reported ones were successfully used as chiral catalysts for the oxidative kinetic resolution (OKR) of 1-phenylethanol using $PhI(OAc)_2$ as an oxidant and KBr as an additive. Excellent enantiomeric excess (up to 89%) of the product was achieved in 0.5 h at 20 °C. The results showed that the sugars at C-5(5′) of salicylaldehyde moieties in the ligand had influences on the catalytic performances of the complexes. It was concluded that the sugars with the same rotation direction of polarized light as the diimine bridge within the complex could enhance the chiral induction of the complex in the OKR of 1-phenylethanol, but the sugars with the opposite one would reduce that of the corresponding complex.

Keywords: Salen–Mn(III) complex; α-D-Glucofuranose; α-D-Mannofuranose; Oxidative kinetic resolution; 1-Phenylethanol

1. Introduction

Optically active alcohols are useful chiral auxiliaries and key synthetic intermediates in pharmaceutical, agrochemical, and fine chemical industries.[1] The oxidative kinetic resolution (OKR) of racemic alcohols is a potentially attractive method to obtain optically active alcohols together with corresponding carbonyl compounds.[2]

To the best of our knowledge, there are several representative nonenzymatic catalytic systems that are active in the OKR of racemic alcohols. One is the sparteine–Pd(II) complex reported by Stoltz and Sigman in 2001, which can catalyze the aerobic OKR of secondary alcohols with high enantioselectivities (ee's).[3] However, the method required a long reaction time and high loading of catalyst when this catalyst was employed in the OKR of racemic alcohols. Furthermore, the sparteine is not easily available and very expensive. The second one is the optically active nitroso salen ruthenium(II) chloride founded by Katasuki and co-workers, which also displayed high enantioselectivities in the OKR of racemic secondary alcohols.[4] Besides, Nishibayashi and co-workers employed [$RuCl_2(PPh_3)$(ferrocenyloxazolinylphosphine)] to catalyze the oxidative kinetic resolution of racemic 1-indanol, obtaining an optically active 1-indanol in good yield (turnover frequency exceeds 80,000 h^{-1}) with high enantioselectivity (up to 94% ee).[5] Inspired by the outstanding performance of the salen ruthenium(II) complex in the OKR of secondary alcohols and high enantioselectivities and activities of chiral salen–Mn(III) complexes on the asymmetric epoxidation of nonfunctionalized olefins,[6–11] subsequently, some salen–Mn(III) complexes were also used as catalysts in the OKR of racemic alcohols and gave good results.[2,12–16] For example, an excellent enantioselectivity (up to 98% ee) was received when 4-chloro-α-phenylethanol was resolved using $PhI(OAc)_2$ as an oxidant catalyzed by the traditional chiral salen–Mn(III) complex.[16]

As is known, the attainment of a high enantioselectivity in the asymmetric epoxidation catalyzed by chiral salen–Mn(III) complex relies on the steric and electronic

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properties of the substituents on the salicylaldehyde moieties of the salen complexes, in addition to the presence of a chiral diimine bridge.[17,18] The presence and properties of substituents on the C-5(5′) positions of the salicylaldehyde moieties of the ligand also have a significant, although generally less important, influence on enantioselectivity.[19] Recent work showed that both the chiral Mn(III) complexes of the ligands from the introduction of sugar moieties into the diimine bridge[20] and the one derived directly from the sugar-based ligand[21] had moderate ee induction in the asymmetric epoxidation of unfunctional olefins. Inspired by the above results, we much lately reported a facile synthesis of several sugar-based chiral salen–Mn(III) complexes and their application in the asymmetric epoxidation of unfunctional olefins.[22] It was found that the carbohydrate groups at the C-5(5′) positions had an enhancement on the asymmetric induction of the epoxides. Based on the previous results, it is expected that the Mn(salen) complexes with sugar moieties at C-5(5′) positions will also have some influences on the OKR of racemic alcohols. Therefore, we report here the synthesis of several new salen–Mn(III) complexes bearing sugar groups using the reported method.[22] The new complexes, together with the previously reported ones, were employed in the OKR of 1-phenylethanol, and some helpful results were obtained.

2. Experimental

2.1. Methods and materials

^{1}H NMR spectra were obtained in $CDCl_3$ using a Bruker AC 400 spectrometer. IR spectra in KBr pellets were recorded on a Bruker Vector-22 spectrophotometer. Melting points were determined on a Perkin XT-4 microscopic analyzer. Optical rotations were measured on a Shanghai WZZ-2S/2SS digital rotation analyzer, at ambient temperature using a 100-mm sample tube. Fast-atom-bombardment mass spectrometry was performed on a VG ZAB-HS mass spectrometer. Electrospray-ionization mass spectrometry was performed on a LCQ Advantage mass spectrometer. Reaction 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. 1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose, 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose, and 1-phenylethanol were purchased from Acros. (1*S*,2*S*)-1,2-Diphenylethylenediamine (99%) was purchased from Zhejiang Dongyang Lingxing Biochemistry Co., Ltd $PhI(OAc)_2$ was prepared using the procedure reported in the literature[23] (mp 160.2–160.5 °C). (1*S*,2*S*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylaldehyde)-1,2-diphenylethylenediamine Mn(III) chloride (complex **4N**) was prepared as reported by Katsuki.[24] Solvents were redistilled prior to use. Other chemicals were purchased from commercial sources and used as received.

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

2.2.1. Synthesis of 1,2:5,6-Di-*O*-isopropylidene-3-*O*-methylene-[5-(3-*tert*-butyl-2-hydroxybenzaldehyde)]-α-D-glucofuranose (2G). Compound **2G** was prepared by the procedure reported in the literature.[25] Light-yellow solid: yield 67%; mp 96–98 °C; $[\alpha]_D^{20}$ −34.1 (*c* 0.80, EtOH); ^{1}H 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; FTIR (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}; FABMS: *m*/*z* 450 $[M]^+$. Anal. Calcd for $C_{24}H_{34}O_8$: C, 63.98; H, 7.61. Found: C, 63.71; H, 7.83.

2.2.2. Synthesis of 2,3:5,6-di-*O*-isopropylidene-1-*O*-methylene-[3-(5-*tert*-butyl-2-hydroxybenzaldehyde)]-α-D-mannofuranose (2M). Compound **2M** was prepared by the procedure reported in the literature.[26] Light-yellow liquid: yield 79%; $[\alpha]_D^{20}$ +112.0 (*c* 1.10, EtOH); ^{1}H 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); ^{13}C NMR($CDCl_3$): δ 192.5, 156.5, 134.0, 129.9, 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; FTIR (Film) *v*: 3446, 2957, 2872, 1652, 1620, 1457, 1440, 1372, 1324, 1267, 1212, 1187, 1157, 1118, 1069, 886, 846, 773, 755 cm^{-1}; FABMS: *m*/*z* 450 $[M]^+$. Anal. Calcd for $C_{24}H_{34}O_8$: C, 63.98; H, 7.61. Found: C, 63.78; H, 7.55.

2.2.3. Synthesis of Schiff-base ligand 3Ga. A solution of compound **2G** (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 a nitrogen atmosphere. EtOH was removed under reduced pressure. The residue was purified by chromatography (1:2 EtOAc–petroleum ether) to afford, after removal of the solvent under reduced pressure, the Schiff-base **3 Ga** as yellow solid (0.65 g, yield 60%): mp 81–83 °C; $[\alpha]_D^{20}$ −56.0 (*c* 0.20, EtOH); ^{1}H 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; FTIR (KBr) *v*: 3442, 2987, 2932, 1633, 1444, 1373, 1341, 1268, 1215, 1164, 1077, 1026, 848, 798, 776 cm^{-1}; FABMS: *m/z* 925 $[M+H]^+$. Anal. Calcd for $C_{50}H_{72}N_2O_{14}$: C, 64.92; H, 7.84; N, 3.03. Found: C, 64.89; H, 8.04; N, 3.10.

2.2.4. Synthesis of Schiff-base ligand 3Gb. Ligand **3Gb** was prepared by the procedure reported in the literature.[27] Light-yellow solid: yield 86.4%; mp 202–203 °C; $[\alpha]_D^{20}$ −66.3 (*c* 0.12, EtOH); ^1H NMR (300 MHz, $CDCl_3$): δ 13.83 (s, 1H), 8.34 (s, 1H), 7.18–7.23 (m, 6H), 7.00 (d, $J = 2.4$ Hz, 1H), 5.84 (d, $J = 3.9$ Hz, 1H), 4.74 (s, 1H), 3.95–4.53 (m, 8H), 1.44 (s, 12H), 1.28 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.9, 160.4, 139.7, 137.7, 129.8, 129.7, 128.6, 128.2, 127.9, 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; FTIR (KBr) *v*: 3439, 2986, 2930, 1633, 1440, 1370, 1340, 1263, 1214, 1160, 1076, 1025, 848, 798, 776 cm^{-1}; FABMS: *m/z* 925 $[M+H]^+$. Anal. Calcd for $C_{62}H_{80}N_2O_{14}$: C, 69.12; H, 7.48; N, 2.60. Found: C, 69.36; H, 7.24; N, 2.39.

2.2.5. Synthesis of salen–Mn(III) complex 4Ga. A mixture of **3Ga** (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 in an 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 under reduced pressure, and the residue was extracted with CH_2Cl_2. The extract was washed with brine, dried over Na_2SO_4, and concentrated to obtain a dark-brown powder **4Ga** (0.22 g, 65%): mp 135–137 °C; $[\alpha]_D^{20}$ −156.3 (*c* 0.02, CH_2Cl_2); FTIR (KBr) *v*: 2957, 1615, 1544, 1440, 1383, 1339, 1302, 1264, 1210, 1165, 1076, 1026, 848, 823, 584, 537 cm^{-1}. ESIMS: *m/z* 978 $[M-Cl]^+$. Anal. Calcd for $C_{50}H_{70}ClMnN_2O_{14}$: C, 59.25; H, 6.96; N, 2.76. Found: C, 59.46; H, 7.10; N, 2.47.

2.2.6. Synthesis of salen–Mn(III) complex 4Gb. Compound **4Gb** was synthesized according to our previous procedure.[27] Dark-brown powder: yield 86.8%; mp 68–69 °C; $[\alpha]_D^{20}$ −480.4 (*c* 0.08, CH_2Cl_2); FTIR (KBr) *v*: 2926, 1613, 1543, 1435, 1382, 1344, 1309, 1258, 1209, 1165, 1070, 1026, 853, 825, 566, 553 cm^{-1}; ESIMS: *m/z* 1130 $[M-Cl]^+$. Anal. Calcd for $C_{62}H_{78}ClMnN_2O_{14}$: C, 63.88; H, 6.74; N, 2.40. Found: C, 63.70; H, 6.84; N, 2.35.

2.2.7. Synthesis of salen–Mn(III) complex 4M. A solution of compound **2M** (0.8 g, 1.78 mmol) and (1*S*,2*S*)-1,2-diphenylethylenediamine (0.19 g, 0.89 mmol) in dry EtOH (30 mL) was refluxed for 2 h under a nitrogen atmosphere. $Mn(OAc)_2{\cdot}4H_2O$ (0.44 g, 1.78 mmol) was added, and the mixture was refluxed further for 4 h. Then solid LiCl (0.11 g, 2.65 mmol) was added, and the mixture was further heated for 3 h while exposed to air. The solvent was removed under reduced pressure, and the residue was extracted with CH_2Cl_2. The extract was washed with brine, dried over Na_2SO_4, and concentrated to obtain a dark-brown powder **4M**: (0.65 g, 63%); mp 77–78 °C; $[\alpha]_D^{20}$ −495 (*c* 0.02, CH_2Cl_2); FTIR (KBr) *v*: 2925, 1614, 1543, 1435, 1382, 1344, 1309, 1258, 1209, 1169, 1071, 1025, 853, 825, 577, 556 cm^{-1}; ESIMS: *m/z* 1130 $[M-Cl]^+$. Anal. Calcd for $C_{62}H_{78}ClMnN_2O_{14}$: C, 63.88; H, 6.74; N, 2.40. Found: C, 63.90; H, 6.59; N, 2.48.

2.3. General procedure for OKR of (±)-1-phenylethanol

A mixture of (±)-1-phenylethanol (0.122 g, 1 mmol), salen–Mn(III) complex (0.023 g, 2 mol %), KBr (0.009 g, 8 mol %), CH_2Cl_2 (2.0 mL), and water (4.0 mL) was stirred in a 25-mL round-bottomed flask for a few min at 20 °C. The oxidant $PhI(OAc)_2$ (0.224 g, 0.7 mmol) was then added and the reaction mixture was magnetically stirred for needed time at 20 °C. The reaction was monitored by a GC equipped with a suitable chiral column. After the desired oxidation level was achieved, the CH_2Cl_2 layer was separated, and the water layer was re-extracted again with CH_2Cl_2. The CH_2Cl_2 was combined, dried over sodium sulfate, and then concentrated under vacuum. The alcohol in the reaction mixture was separated by column chromatography.

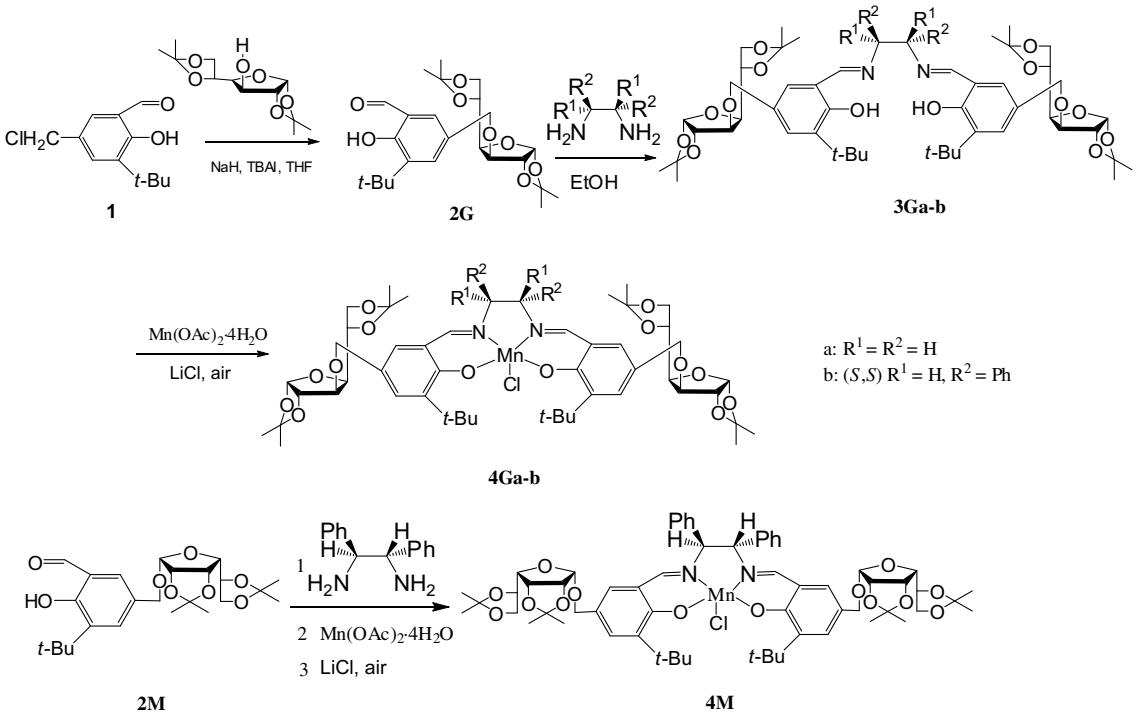
3. Results and discussion

3.1. Synthesis of chiral salen–Mn(III) complexes

The synthetic route for the chiral complexes **4Ga**, **4Gb**, and **4M** is shown in Scheme 1. First, ligand **3Ga** and complexes **4Ga**, **4Gb** were prepared according to our previously published procedure.[22] Chiral complex **4M** is directly synthesized from condensation product of **2M** and (1*S*,2*S*)-1,2-diphenylethylenediamine in situ due to decomposition of the ligand in the purification process. The complexes were characterized by optical rotation, IR spectroscopy, elementary analysis, and MS.

3.2. Catalysis of salen chiral Mn(III) complexes

In order to get an insight of the effect of the sugar moieties at C-5(5′) of salen–Mn(III) complexes on the chiral induction of OKR, complexes **4Ga**, **4Gb**, **4M**, and **4N** were employed in the OKR of 1-phenylethanol with $PhI(OAc)_2$ as an oxidant at 20 °C. Potassium bromide was used as an additive because bromide salts play a distinctive role for the activation of both PhIO[17] and $PhI(OAc)_2$[18] for the oxidation of various alcohols to



Scheme 1. Synthesis route for the complexes.

give ketones.[12] The results are shown in Table 1. For comparison, some results from the literature[2,15,16] are also listed in Table 1. In Table 1, $k_{rel} = k_{fast}/k_{slow}$, which represent the relative rates of enantiomers of racemic substrates to form a product.[28] It can be calculated by using equation

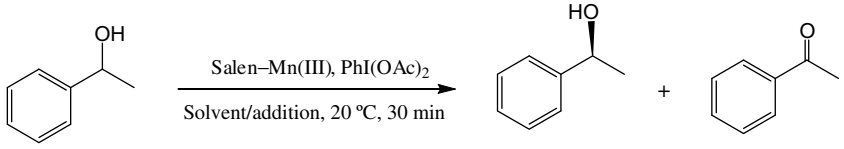
$$k_{rel} = \frac{\ln(1-c)(1-ee)}{\ln(1-c)(1+ee)}$$

where ee is the enantiomeric excess of the secondary alcohol and c is the conversion of the secondary alcohol.

The k_{rel} values are generally considered to be more useful for the evaluation and especially comparison of the efficacy of kinetic resolution catalysts.[12]

It was observed that when catalyst was absent in the reaction mixture, no enantioselectivity was achieved (entry 1). In the case of **4Ga** with an absence of chirality in the diimine bridge moiety, an ee of 27% and a k_{rel}

Table 1. OKR of 1-phenylethanol using different salen–Mn(III)complexes as catalysts[a]



Entry	Catalyst	Conversion (%)	ee (%)	k_{rel}
1	—	53	0	—
2	**4Ga**	55	27	1.98
3	**4Gb**	60	89	11.2
4	**4M**	65	77	5.14
5	**4N**	65	79	5.63
	A[b]	69	98	10.0
	B[c]	61	55	3.50
	C[d]	63	88	8.90

[a] Reaction conditions: (±)1-phenylethanol (1 mmol), salen–Mn(III) complex (2 mol %), $PhI(OAc)_2$ (0.7 mmol), KBr (8 mol %), CH_2Cl_2 (2 mL), H_20 (4 mL), 30 min, and reaction temperature 20 °C.

[b] Results are from Table 2 in Ref. 15; for the structure of the catalyst and the reaction conditions see the reference.

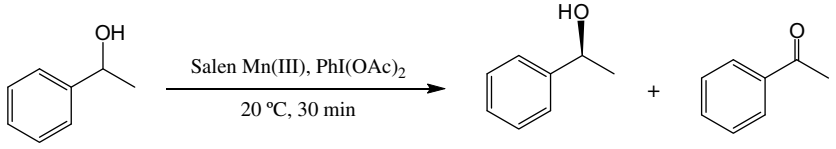
[c] Results are from Table 3 in Ref. 2; for the structure of the catalyst and the reaction conditions see the reference.

[d] Results are from Table 2 in Ref. 16; for the structure of the catalyst and the reaction conditions see the reference.

value of 1.98 were obtained (entry 2). This enantioselectivity is undoubtedly induced by the chiral sugar groups at C-5(5′). Thus, it can be concluded that the chiral centers attached on C-5 of the salicylaldehyde moiety have an influence on the OKR of 1-phenylethanol in a weak manner. The highest ee and k_{rel} were on **4Gb**. An ee of 89% and k_{rel} value of 11 were obtained (entry 3). For **4N** the ee and k_{rel} were 79% and 5.63, respectively. The results indicated that α-D-glucofuranose moities at C-5 of the salicylaldehyde in the complex enhanced the OKR of 1-phenylethanol. However, not all sugars at C-5 had the same effect as α-D-glucofuranose. When the sugar moiety was α-D-mannofuranose as in **4M**, a slight decrease of enantioselectivity for the OKR of 1-phenylethanol was observed in comparison with that for **4N**. The ee and k_{rel} were 77% and 5.14, respectively (entry 4). Perhaps the sugars having the same rotation direction of polarized light as the (1*S*,2*S*)-diimine bridge in the complex could enhance the chiral induction of the complex in the OKR of 1-phenylethanol, but the sugars with the opposite one would reduce that of the corresponding complex. The results indicate that complex **4Gb** has better performance than the metal complexes in the literature listed in Table 1 from the point of view of k_{rel}.

Generally, solvent plays a critical role in the OKR of secondary alcohols.[12] Therefore, the effects of solvents were carried out using **4Gb** as a catalyst for the OKR of 1-phenylethanol, and the results are summarized in Table 2. In the case of H_2O alone as a solvent (Table 2, entry 6) and KBr as an additive, a conversion of 51% with 20% of ee for 1-phenylethanol was obtained, possibly due to only partial solubility of the catalyst **4Gb** in the mixture of alcoholic substrate and water. CH_2Cl_2 alone as a solvent showed the poorest conversion (36%), ee (6%) and k_{rel} (Table 2, entry 7), which may be attributed to the fact that KBr is insoluble in CH_2Cl_2. Solvents like toluene and CH_2Cl_2 when mixed with water gave high enantioselectivity (80–89%) in the case of OKR of 1-phenylethanol (entries 10 and 11), while cyclohexane and CH_3CN, gave poor results (entries 8 and 9). Out of all the solvent systems studied,

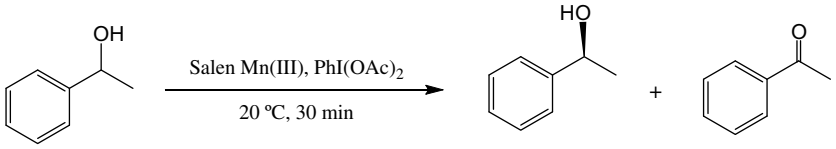
Table 2. OKR of 1-phenylethanol using **4Gb** as catalyst in various solvent systems[a]



Entry	Solvents	Conversion (%)	ee (%)	k_{rel}
6	H_2O	51	20	1.76
7	CH_2Cl_2	36	6	1.31
8	$CH_3CN + H_2O$	37	24	2.91
9	Cyclohexane + H_2O	42	37	4.38
10	Toluene + H_2O	68	80	4.99
11	$CH_2Cl_2 + H_2O$	60	89	11.17

[a] Reaction conditions: (±)1-phenylethanol (1 mmol), salen–Mn(III) (2 mol %), $PhI(OAc)_2$ (0.7 mmol), KBr (8 mol %), organic solvent (2 mL), H_2O (4 mL), 30 min, and 20 °C.

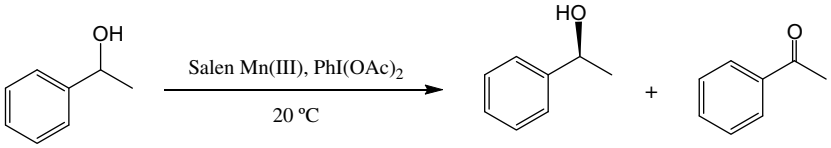
Table 3. OKR of 1-phenylethanol using **4Gb** as catalyst in the presence of various additives[a]



Entry	Additives	Conversion (%)	ee (%)	k_{rel}
12	—	56	6	1.15
13	KCl	55	6	1.16
14	KI	25	6	1.52
15	KBr	60	89	11.17
16	NaBr	57	78	4.17
17	$N(C_2H_5)_4Br$	58	72	6.58
18	$N(n\text{-}C_4H_9)_4Br$	60	77	6.90

[a] Reaction conditions: (±)1-phenylethanol (1 mmol), salen–Mn(III) (2 mol %), $PhI(OAc)_2$ (0.7 mmol), additive (8 mol %), CH_2Cl_2 (2 mL), H_2O (4 mL), 30 min, and 20 °C.

Table 4. OKR of 1-phenylethanol using **4Gb** as catalyst in different reaction times[a]



Entry	Time (min)	Conversion (%)	ee (%)	k_{rel}
14	5	53	54	4.74
15	10	54	62	5.93
16	15	56	66	6.05
17	20	57	71	6.77
18	25	59	74	6.63
19	30	60	89	11.17
20	35	63	73	5.16

[a] Reaction conditions: (±)1-phenylethanol (1 mmol), salen–Mn(III) (2 mol %), $PhI(OAc)_2$ (0.7 mmol), KBr (8 mol %), CH_2Cl_2 (2 mL), H_2O (4 mL), and 20 °C.

the 1:2 CH_2Cl_2–water was found to be the best one. The same result was also observed in the literature[12] with other complexes as catalysts.

We also studied the effect of various additives on the OKR of 1-phenylethanol using complex **4Gb** as a catalyst. The results are shown in Table 3. Phase-transfer catalysts such as tetraethylammonium bromide and tetrabutylammonium bromide as additives gave moderate to high enantioselectivity (ee, 72–77%) with conversions (58–60%) (Table 3, entries 17 and 18), which were not as good as we expected. Meanwhile, KCl and KI as additives gave very poor results (Table 3, entries 13 and 14). However, NaBr and KBr exhibited good enantioselectivity (Table 3, entries 15 and 16). In the case of the absence of an additive, the enantioselectivity of the reaction dropped considerably (entry 12), which indicated that the presence of bromide ion is essential for the activation of $PhI(OAc)_2$ to carry out the OKR of alcohols in the biphasic system. The results are in accord with those reported in the literature.[2,12]

In the OKR process, reaction time can influence the resolution effect, because long reaction times can increase the conversion of a substrate, but excess time can reduce the ee. Table 4 gives the results of the OKR of 1-phenylethanol at different times. It can be seen that the optimal reaction time for the OKR of 1-phenylethanol is 30 min when the reaction was run at 20 °C in the CH_2Cl_2–H_2O biphasic system in the presence of KBr. At this stage a high ee of 89% and a k_{rel} value of 11 were reached (Table 4, entry 19).

4. Conclusions

In conclusion, three new chiral Salen–Mn(III) complexes with sugar moieties were synthesized. These complexes, together with our previously reported ones, were successfully used as chiral catalysts for the OKR of 1-phenylethanol using $PhI(OAc)_2$ as an oxidant. An ee of 89% of the chiral secondary alcohol was achieved in 0.5 h. The study revealed that the sugars at the C-5(5′) moiety of salicylaldehyde parts had some influence on the enantioselectivity of OKR of 1-phenylethanol. The sugars with the same rotation direction of polarized light as the diimine bridge in the complex could enhance the chiral induction, but the sugars with the opposite one would reduce that of the corresponding complex.

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