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Oxidative kinetic resolution of racemic secondary alcohols catalyzed by recyclable chiral dimeric Mn(III) salen catalysts

Kavita Pathak, Irshad Ahmad, Sayed H.R. Abdi *, Rukhsana I. Kureshy, Noor-ul H. Khan, Raksh V. Jasra

Discipline of Inorganic Materials and Catalysis, Central Salt and Marine Chemicals Research Institute (CSMCRI), Bhavnagar 364 002, Gujarat, India

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Abstract

The oxidative kinetic resolution of racemic secondary alcohols was efficiently catalyzed by chiral dimeric Mn(III) salen complexes using $PhI(OAc)_2$ as an oxidant in the presence of various additives in water/organic solvent mixture. Excellent ee (up to 99%) of chiral secondary alcohols was achieved in 0.5 h. The catalyst **1A** was recovered easily and reused five times with retention of enantioselectivity.

Keywords: Oxidative kinetic resolution; Racemic secondary alcohols; Recyclable; Dimeric Mn(III) salen

1. Introduction

The oxidation of alcohols to carbonyl compounds is one of the most fundamental organic transformations with significant biological and mechanistic interest [1]. With readily available efficient methods for the oxidation of alcohols [2,3], oxidative kinetic resolution (OKR) of racemic alcohols is potentially attractive method to achieve optically active alcohols together with corresponding carbonyl compounds. Optically active alcohols are extremely important starting materials and key intermediates in the production of chiral building blocks for the synthesis of pharmaceutically important and biologically active compounds [4]. Toward this goal, enzyme catalysts were extensively used for kinetic resolution through selective oxidation of one of the enantiomers [5,6]. Recently, several effective non-enzymatic catalysts for the OKR of racemic alcohols have been studied [7]. Katsuki and co-workers have reported the use of BINOL-derived Ru(salen) complexes as catalysts in the photo-induced aerobic oxidation of racemic secondary alcohols. In this system though alcohols with high enantioselectivity was achieved, the reaction time was too long [8a]. Later, the same group reported enantioselective oxidation of racemic alcohols using BINOL-derived Mn(salen) complexes as catalysts with PhIO as an oxidant, however, only low yields and moderate enantioselectivity were achieved [8b].

Recently, Xia and co-workers have reported OKR of racemic secondary alcohols with chiral Mn(salen) catalysts with excellent enantioselectivity [9]. However, the catalyst stability, product and catalyst separation remained difficult for this homogeneous system. As chiral catalysts are expensive, their reusability is highly advantageous. The use of chiral dimeric Mn salen complexes have been extensively used as recyclable catalysts in asymmetric epoxidation reaction in the literature [10,11]. As a part of our ongoing research to develop recyclable chiral catalysts for various asymmetric organic transformations using chiral salen complexes as catalysts [12], herein, we are extending the application of chiral dimeric Mn(III) salen complexes in the OKR of racemic secondary alcohols using iodobenzene diacetate ($PhI(OAc)_2$) as an oxidant with various additives. Under the present OKR protocol one of the enantiomer of the racemic alcohol was selectively oxidized to respective ketone leaving behind the other enantiomer in high chiral purity (ee, up to 99%) in 0.5 h. Besides, the dimeric Mn(III) salen complex **1A** was effectively recycled five times.

* Corresponding author. Fax: +91 278 2566970.
E-mail address: shrabdi@csmcri.org (S.H.R. Abdi).

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2. Experimental

2.1. Materials and methods

Reagents and solvents were of analytical grade and were used as received. $PhI(OAc)_2$, tetraethtylammonium bromide, tetrabutylammonium bromide, KBr, LiBr and NaBr were purchased from Across Organics, Belgium. Hexylpyridinium bromide was prepared according to the known procedure [13]. 1-Phenyl-2-propanol and (±)-menthol was purchased from Aldrich, while other alcohols used in the present study were prepared by the reduction of corresponding ketones with $NaBH_4$. Precursors of complexes and complex **1A** were synthesized according to the reported procedure [10a].

3. Instrumentation

^1H and ^{13}C NMR spectra were recorded using a Bruker, F113V (200 and 50 MHz) FT-NMR spectrometer. FTIR spectra were recorded on a Perkin-Elmer Spectrum GX spectrophotometer in a KBr/nujol mull. Microanalysis of the complex was done on CHNS analyzer, Perkin-Elmer model 2400. Optical rotations were measured with a Digipol 781 Automatic Polarimeter Rudolph instrument. Ee's of secondary alcohols were determined by HPLC (Shimadzu SCL-10AVP) using Chiralcel OD and OB columns with hexane/2-propanol as eluent. Conversion of the products was carried out by gas chromatography using Shimadzu GC 14B using dodecane as an internal standard.

3.1. Synthesis of 5,5-methylene di-[(R,R)-{N-(3-tert-butyl salicylidine)-N′-(3′,5′-di-tert-butyl salicylidene)}-1,2-cyclohexanediaminato(2-) manganese(III) acetate] 1B

5,5-Methylene di-[(*R,R*)-{*N*-(3-*tert*-butyl salicylidine)-*N*′-(3′,5′-di-*tert*-butyl salicylidene)}-1,2-cyclohexanediamine] (1 g, 0.001 mol) was dissolved in CH_2Cl_2 (15 ml) while manganese acetate (0.48 g, 0.002 mol) was taken in CH_3OH (5 ml) and the two solutions were mixed and refluxed under an inert atmosphere for 5–8 h. The reaction mixture was allowed to cool to room temperature and a slow stream of air was allowed to pass through the reaction mixture for 2 h. The mixture was filtered and the solvent was removed from the filtrate. The evaporation residue was extracted with dichloromethane (3× 15 ml), and the dichloromethane extracts were combined and washed with water (3× 10 ml) and the organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude product thus obtained was recrystallized with petroleum ether/CH_2Cl_2 to get the desired complex **1B** (0.95 g, yield 94%) as brown powder. IR (KBr): 3426 (br), 2951 (s), 2865 (s), 1612 (s), 1537 (s), 1477 (sh), 1432 (s), 1389 (m), 1341 (s), 1310 (s), 1271 (sh), 1252 (sh), 1201 (m), 1173 (m), 1102 (w), 1028 (m), 928 (w), 835 (m), 780 (w), 748 (w), 691 (w), 567 (s), 477 (w), 418 (w) cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} (ε) 242 (50,000), 264 (49,956), 323 (47,535), 418 (41,450), 436 (41,032), 512 (36,058). Anal. calcd. for $C_{69}H_{94}Mn_2N_4O_8$ (1216): C, 68.09; H, 7.73; N 4.60. Found: C, 67.98; H, 7.69; N, 4.58%. $[\alpha]_D^{25} = -174$ ($c = 0.12$, CH_2Cl_2). MS (ESI): $m/z = 1234$ $[M + H_2O]^+$

3.2. Synthesis of 5,5-methylene di-[(R,R)-{N-(3-tert-butyl salicylidine)-N′-(3′,5′-di-tert-butyl salicylidene)}-1,2-diphenylethylene diaminato(2-) manganese(III) chloride] 2

5,5-Methylene di-[(*R,R*)-{*N*-(3-*tert*-butyl salicylidine)-*N*′-(3′,5′-di-*tert*-butyl salicylidene)}-1,2-diphenylethylenediamine ligand (1.2 g, 0.001 mol) in CH_2Cl_2 (15 ml) was stirred under reflux with manganese acetate (0.48 g, 0.002 mol) in CH_3OH (5 ml) under an inert atmosphere for 8–10 h. The reaction mixture was cooled to room temperature. Lithium chloride (0.25 g, 0.006 mol) was added and the mixture was stirred for a further 4 h while exposed to air. The mixture was filtered and the solvent was removed from the filtrate. The evaporation residue was extracted with dichloromethane (3× 10 ml) and washed with water (2× 10 ml), brine and dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure and the crude product thus obtained was recrystallized with petroleum ether to get the desired complex **2** (1.0 g, yield 90%) as solid brown powder. IR (KBr): 3434 (br), 2954 (s), 2867 (s), 1608 (s), 1535 (s), 1456 (sh), 1428 (s), 1388, 1311 (s), 1250 (s), 1172 (m), 1026 (w), 918 (w), 850 (w), 698 (w), 554 (s) cm^{-1}. UV–vis: (CH_2Cl_2): λ_{max} (ε) 242 (5239), 323 (73,078), 440 (23,548), 508 (8265), 538 (6608). Anal. calcd. for $C_{81}H_{92}Cl_2Mn_2N_4O_4$ (1364.5): C, 71.21; H, 7.03; N 4.10. Found: C, 71.35; H, 6.90; N, 3.95%; $[\alpha]_D^{25} = -128$ ($c = 0.14$, CH_2Cl_2). MS (ESI): $m/z = 1382.5$ $[M + H_2O]^+$

3.3. Procedure for the oxidative kinetic resolution of racemic secondary alcohols catalyzed by chiral dimeric Mn(III) salen complexes

In a typical procedure, a mixture of the substrate (1 mmol), catalyst 1A/1B/2 (0.02 mmol, based on monomeric salen unit), additive (0.04 mmol, 4 mol%), CH_2Cl_2 (1 ml) and water (2 ml) was stirred in a 10 ml glass vial for 10 min at room temperature. The oxidant $PhI(OAc)_2$ (0.7 mmol) was then added and the system was magnetically stirred for mentioned time at room temperature. Progress of the reaction was monitored on GC/HPLC using suitable chiral columns. After the desired level of oxidation was achieved, the catalyst was precipitated out by the addition of *n*-hexane, which was removed by filtration. The recovered catalyst was washed with diethyl ether (3× 5 ml), dried under vacuum and kept in desiccator for recycling experiments. The filtrate and washings were combined, washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure.

3.4. Characterization of recycled catalyst 1A

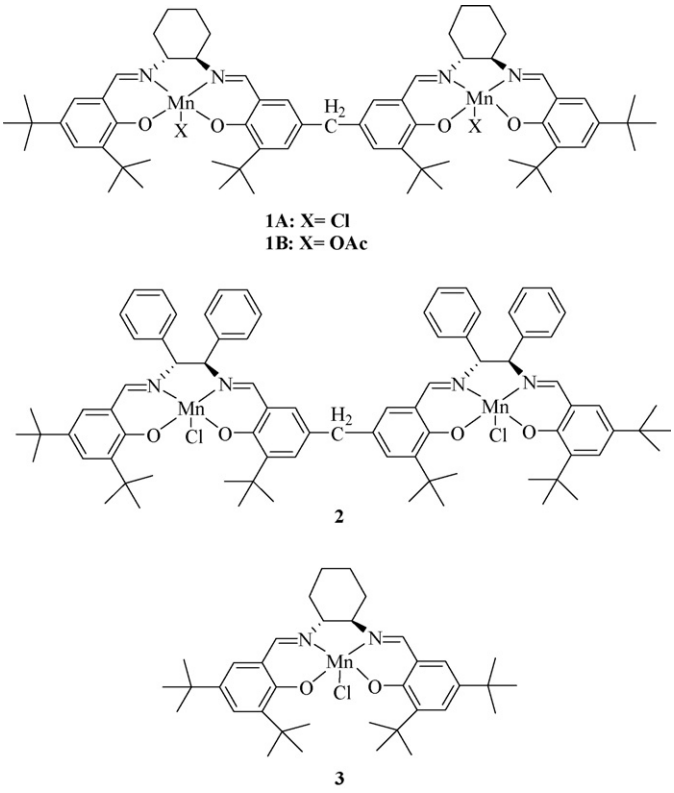
Dimeric Mn(III) salen complex **1A** was recovered after its 3rd consecutive reuse in OKR of 1-phenylethanol. The recovered catalyst was characterized by IR, elemental analysis, UV and ESI-MS analysis: IR (KBr): 3427 (br), 2952 (s), 2860 (s), 1611

(s), 1535 (s), 1470 (sh), 1432 (s), 1392 (m), 1336 (s), 1310 (s), 1283 (sh), 1242 (sh), 1200 (m), 1170 (m), 1100 (w), 1030 (m), 945 (w), 836 (m), 785 (w), 732 (w), 690 (w), 562 (s), 470 (w) cm^{-1}. Anal. calcd. for $C_{65}H_{88}Cl_2Mn_2N_4O_4$ (1169): C, 67.80; H, 8.05; N, 4.85. Found: C, 66.67; H, 7.85; N, 4.70%; UV–vis (CH_2Cl_2): λ_{max} (ε) 253 (50,000), 260 (49,960), 343 (47,540), 422 (41,460), 455 (41,040), 513 (36,060). MS (ESI): $m/z = 1187$ $[M + H_2O]^+$

4. Results and discussion

4.1. Synthesis and catalysis of chiral dimeric Mn(III) salen complexes

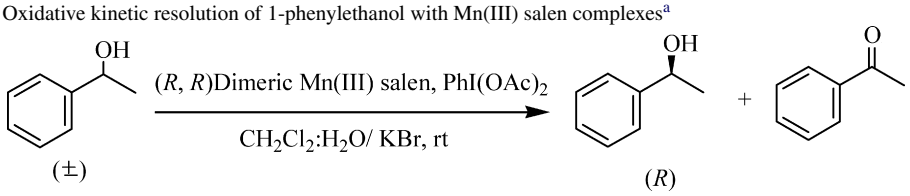
Chiral dimeric Mn(III) salen complex **1A** was synthesized according to our previously published procedure [10a], while complexes **1B** and **2** were obtained by the reaction of chiral salen ligands, viz., 5,5-Methylene di-[(*R,R*)-{*N*-(3-*tert*-butyl salicylidine)-*N*′-(3′,5′-di-*tert*-butyl salicylidene)}-1,2-cyclohexanediamine] and 5,5-methylene di-[(*R,R*)-{*N*-(3-*tert*-butyl salicylidine)-*N*′-(3′,5′-di-*tert*-butyl salicylidene)}-1,2-diphenylethylenediamine, respectively, with manganese(II) acetate followed by their air oxidation. In the case of complex **2** LiCl was added just before air oxidation (characterization data are given in Section 2) (Scheme 1). Dimeric Mn(III) salen complexes **1A**, **1B** and **2** were screened for their efficacy as catalysts in oxidative kinetic resolution of racemic secondary alcohols. The catalytic results are summarized in Table 1.



Scheme 1. Chiral monomeric and dimeric Mn(III) salen complexes.

It has been reported earlier that bromide salts play distinctive role for the activation of both PhIO [14] and $PhI(OAc)_2$ [9b] for the oxidation of various alcohols to give ketones whereas others halide ions were only marginally active. Therefore, these catalysts (5 mol%, based on monomeric salen unit) were examined for the OKR of racemic 1-phenylethanol as a representative substrate with KBr as an additive using $PhI(OAc)_2$ as an oxidant at room temperature. We observed that catalyst **1A** gave high enantioselectivity (ee, 95%) (Table 1, entry 1) and changing the counter ion from Cl with OAc (complex **1B**) did not alter conversion and ee significantly (Table 1, entry 2). Whereas complex **2** was less effective catalyst than complex **1A** as evidenced by low ee and k_{rel} values obtained for the alcohol (Table 1, entry 3). To check the efficiency of complex **1A** in the kinetic resolution of 1-phenylethanol, catalytic run was performed with 2 mol% catalyst. This low catalyst loading significantly improved enantioselectivity (ee, 99%). However, further reduction in the catalyst loading from 2 to 0.2 mol% (Table 1, entry 5) resulted in 48% conversion and 90% ee with longer reaction time (60 min).

Table 1
Oxidative kinetic resolution of 1-phenylethanol with Mn(III) salen complexes[a]



Entry	Catalyst	Catalyst loading (mol%)	Time (min)	Conversion (%)[b]	ee (%)[c]	k_{rel}[d]
1	**1A**	5	30	58	95	19
2	**1B**	5	30	55	91	21
3	**2**	5	30	60	78	7
4	**1A**	2	30	62	99	20
5	**1A**	0.2	60	48	90	59
6	**3**	2	30	60	97	18

[a] Reactions were carried out at room temperature in mentioned time.
[b] Determined by GC analysis using dodecane as an internal standard.
[c] Determined by HPLC using Chiralcel OD column.
[d] Selectivity factor k_{rel} represents an average of at least two experiments.

In kinetic resolutions, enantiomers of racemic substrate react at different rates to form a product and these relative rates of reaction is typically expressed as $k_{rel} = k_{fast}/k_{slow}$. The k_{rel} values are generally considered to be more useful for the evaluation and especially comparison of the efficacy of kinetic resolution catalysts [15]. Accordingly, selectivity factor k_{rel} was 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 secondary alcohol.

In order to compare the reactivity of dimeric Mn(III) salen complex **1A** with its monomeric counterpart, we have conducted the OKR of 1-phenylethanol as a representative substrate with monomeric Mn(III) salen complex using KBr as an additive (Table 1, entry 6). It has also been observed from the kinetic profile that the formation of the corresponding ketone increased linearly up to 5 min, after which a significant increase is not observed (Fig. 1). Therefore, the initial rate constants K_{obs} were determined from the data in this time range for the complex **1A** and monomeric Mn(III) salen complex **3** that gives K_{obs} values 46×10^{-2} and 30×10^{-2} M/h, respectively.

The scope of OKR of various other racemic secondary alcohols was investigated with catalyst **1A** (2 mol%) by using KBr (4 mol%) as an additive (Table 2). In general racemic 1-phenylethanol with substituents at the *para*-position were enantioselectively oxidized to the respective ketones (conversion, 59–67%) to yield remaining alcohol in high chiral purity (ee, 95–97%) in 30 min (Table 2, entries 7–9) and these results are comparable with earlier reported procedure with monomeric complex **3** [9]. The k_{rel} values are very sensitive towards the conversion for a given ee, however, a selectivity factor as low as 11 allows the isolation of unreacted alcohol in 97% ee with quite reasonable 31% recovery (Table 2, entry 8). However, substituents at the *o*-position of the phenyl group (Table 2, entry 10) or extension of alkyl chain (from R′=CH_3 to R′=CH_2CH_3) (Table 2, entries 11 and 12) severely effected ee's and k_{rel} values presumably due to the steric hindrance caused by the substituted group which, does not allow close contact of the substrate with chiral centers bearing catalytically active metal center of the complex **1A**. On the other hand, 1-phenyl-2-propanol gave good results in terms of enantioselectivity (ee, 89%) (Table 2, entry 13). Other bulkier secondary alcohols like 1-naphthylethanol and 2-naphthylethanol gave good enantioselectivity (73–85%) but the reaction was slower (Table 2, entries 14 and 15). Remarkably, (±)-menthol exhibited high k_{rel} value with very good enantioselectivity (ee, 92%) (entry 16). Here it is worth mentioning that (*R*,*R*) form of the catalyst selectively oxidized *S* form of the alcohols to produce respective ketones leaving behind remaining alcohol enriched with *R* configuration.

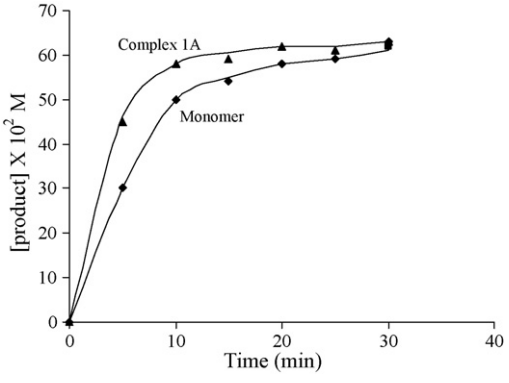


Fig. 1. Time-dependent plot of OKR of 1-phenylethanol at rt: [catalyst **1A**] = 0.66×10^{-2} M, [1-phenylethanol] = 33.0×10^{-2} M, [KBr] = 1.3×10^{-2} M, [oxidant] = 23.0×10^{-2} M.

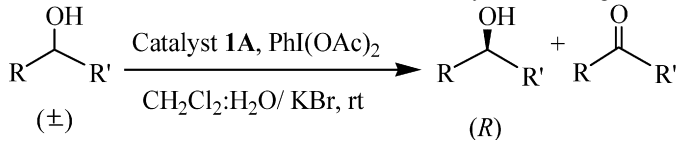
Solvent plays critical role in the OKR of secondary alcohols [9b]. In view of this, the effect of solvents was carried out using catalyst **1A** for the OKR of 1-phenylethanol as a representative substrate and the results are summarized in Table 3. In the case of H_2O alone as a solvent (Table 3, entry 17) and KBr as an additive a conversion of 47% with 36% ee for 1-phenylethanol was obtained, possibly due to only partial solubility of the catalyst **1A** in the alcoholic substrate. Solvents like toluene, 1,2-dichloroethane and chloroform when mixed with water, gave high enantioselectivity (82–98%) in the case of 1-phenylethanol (Table 3, entries 18–20), while ethyl acetate gave poor results (entry 22). Out of all the solvent systems studied, the CH_2Cl_2:water::1:2 was found to be the solvent of choice (Table 3, entry 21).

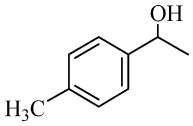
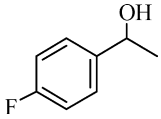
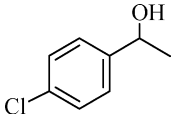
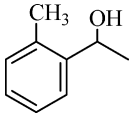
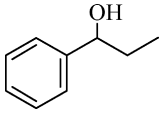
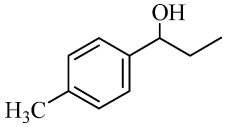
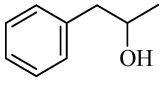
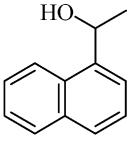
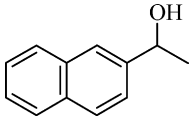
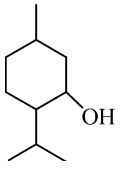
Further, we studied the effect of various additives on the efficacy of OKR of 1-phenylethanol using complex **1A** as a catalyst (Table 4). The phase transfer catalysts like tetraethyl ammonium bromide and tetrabutyl ammonium bromide as additives gave moderate to high enantioselectivity (ee, 59–95%) with conversions (50–64%) (Table 4, entries 23 and 24). While bromine salts like hexylpyridinium bromide, NaBr and LiBr exhibited better enantioselectivity (ee, 92–97%) (Table 4, entries 25–27). Surprisingly Cetyl trimethylammonium bromide (CTAB) as phase transfer catalyst gave very poor results (entry 28). On carrying out OKR of 1-phenylethanol in the absence of an additive the enantioselectivity of the reaction dropped considerably (Table 4, entry 29), inferring that presence of bromide ion is required for the activation of $PhI(OAc)_2$ to carry out the oxidative kinetic resolution of alcohols in the presence of water–organic solvent system. These observations are in consonance with earlier report [9b].

4.2. Recovery and recycling of complex *1A*

Dimeric Mn(III) salen complex has inherent tendency to get precipitated out in non-polar solvents like *n*-hexane due to its higher molecular weights. Therefore, after the completion of catalytic run the catalyst **1A** was recovered by the addition of *n*-hexane to the reaction mixture. The recovered catalyst was washed thoroughly with *n*-hexane and diethyl ether, dried and reused for the subsequent OKR runs of 1-phenylethanol as a representative substrate by adding fresh reactants. Table 5 represented the recycling of complex **1A** for oxidative kinetic resolution of 1-phenylethanol. From the data presented in Table 5 it is evident that the catalyst **1A** worked well for five cycles with

Table 2
Oxidative kinetic resolution (OKR) of various secondary alcohols using chiral dimeric Mn(III) salen catalyst **1A**[a]



Entry	Substrate	Time (min)	Conversion (%)[b]	ee (%)[c]	k_{rel}[d]
7		30	59	95	19
8		30	67 (31)[e]	97	11
9		30	60	96	17
10		60	15	9	4
11		30	57	25	2
12		30	49	14	2
13		30	64	89	9
14		80	50	73	15
15		60	52	85	22
16		30	51	92	53

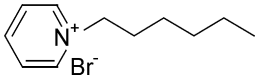
[a] Reactions were carried out using 2 mol% dimeric Mn(III) salen complex-**1A**, KBr (4 mol%), racemic secondary alcohols (1 mmol), $PhI(OAc)_2$ (0.7 mmol) in 1 ml CH_2Cl_2 + 2 ml H_2O at room temperature in mentioned time.
[b] Determined by GC analysis using dodecane as an internal standard.
[c] Determined by HPLC using Chiralcel OD/OB column.
[d] Selectivity factor k_{rel} represents an average of at least two experiments.
[e] Isolated yield of enantioenriched secondary alcohol.

Table 3
Oxidative kinetic resolution (OKR) of 1-phenylethanol using catalyst **1A** in various solvent systems[a]

Entry	Solvent system	Time (min)	Conversion (%)[b]	ee (%)[c]	k_{rel}[d]
17	H_2O	30	47	36	3
18	H_2O + toluene	30	63	98	16
19	H_2O + DCE	30	60	96	17
20	H_2O + $CHCl_3$	30	64	82	7
21	H_2O + CH_2Cl_2	30	62	99	20
22	H_2O + ethyl acetate	30	43	17	2

[a] Reactions were carried out using 2 mol% complex-**1A**, KBr (4 mol%), 1-phenylethanol (1 mmol), $PhI(OAc)_2$ (0.7 mmol) in 1 ml organic solvent + 2 ml H_2O at rt in mentioned time.
[b] Determined by GC analysis using dodecane as an internal standard.
[c] Determined by HPLC using Chiralcel OD column.
[d] Selectivity factor k_{rel} represents an average of at least two experiments.

Table 4
Oxidative kinetic resolution (OKR) of 1-phenylethanol using catalyst **1A** in presence of various additives[a]

Entry	Additives	Time (min)	Conversion (%)[b]	ee (%)[c]	k_{rel}[d]
23	$N(C_2H_5)_4Br$	30	64	95	11
24	$N(C_4H_9)_4Br$	30	50	59	7
25		30	61	92	12
26	NaBr	30	56	93	9
27	LiBr	30	64	97	13
28	CTAB	60	39	16	2
29[e]	–	60	5	<1	1
30	KCl	60	8	1	1

[a] Reactions were carried out using 2 mol% complex-**1A**, additive (4 mol%), 1-phenylethanol (1 mmol), $PhI(OAc)_2$ (0.7 mmol) in 1 ml CH_2Cl_2 + 2 ml H_2O at rt in mentioned time.
[b] Determined by GC analysis using dodecane as an internal standard.
[c] Determined by HPLC using Chiralcel OD column.
[d] Selectivity factor k_{rel} represents an average of at least two experiments.
[e] Reaction was carried out in absence of additive.

Table 5
OKR of 1-phenylethanol with recycled complex **1A**[a]

Catalytic run	Time (min)	Conversion (%)[b]	ee (%)[c]
1	30	62	99
2	30	60	98
3	30	58	99
4	30	57	99
5	30	55	98

[a] 2 mol% complex-**1A**, KBr (4 mol%), 1-phenylethanol (1 mmol), $PhI(OAc)_2$ (0.7 mmol) in 1 ml CH_2Cl_2 + 2 ml H_2O at rt.
[b] Determined by GC analysis using dodecane as an internal standard.
[c] Determined by HPLC using Chiralcel OD column.

retention of enantioselecitivity.[1] To check the stability of the catalyst during the OKR we characterized the recovered catalyst (after third reuse) by IR, UV and ESI-MS analysis and the data are given in Section 2. It is evident from these data that the catalyst remained unchanged during the course of OKR of 1-phenylethanol used as model substrate.

5. Conclusions

In conclusion, we have demonstrated that chiral dimeric Mn(III) salen complexes can be successfully used as recyclable chiral catalysts for the oxidative kinetic resolution of racemic secondary alcohols using $PhI(OAc)_2$ as an oxidant. Excellent ee (up to 99%) of chiral secondary alcohols was achieved in 0.5 h. Catalyst **1A** was recovered easily and reused up to five times with the retention of enantioselecitivity.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2007.04.036.

[1] While revising this manuscript, a paper appeared on Merrifield's resin supported sulfonato-Mn(salen) complex on OKR of racemic secondary alcohols "M.L. Kantam, T. Ramani, L. Chakrapani, B.M. Choudary, Oxidative kinetic resolution of racemic secondary alcohols catalyzed by resin supported sulfonato-Mn(salen) complex in water, Journal of Molecular Catalysis A: Chemical 274 (2007) 11" where the catalyst was recycled three times but showed only moderate to good enantioselectivity for most of the substrates.

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