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ARTICLE TYPE

Enantioselective Cyanosilylation of Aldehydes Catalyzed by Multistereogenic Salen-Mn(III) Complex With Rotatable Benzylic Group As a Helping Hand

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A multistereogenic salen-Mn(III) complex bearing aromatic pocket and two benzylic groups as helping hands was found to be efficiently in the catalytic asymmetric cyanosilylation, in which the salen-Mn catalyst mimics partially the functions of biocatalysts by reasonable utilization of steric and electronic properties of catalytic center to interact with substrate.

In the past decades, nature occurring enzymatic systems have been revealed in some certain that effective stereochemical communication between catalyst and substrate is essential for attaining enantioselective control in catalytic asymmetric reactions.[1] The enantioselective transformations catalyzed by enzymes, in fact, take place with a rapid speed under mild conditions because of the existence of activated complex that is responsible for stereo- or enantioselectivity.[2] As a family of biocatalysts containing metal ion, it was characterized by a metallic site that hosted flexible structure and inside channels originated from the assembly of proteic macromolecules.[3] This is one of the reasons why chemists active in the area of biomimetic catalysis have attempted to design nonenzymatic or chemical catalyst systems according to the principle of enzymatic catalysis, including the reasonable utilization of right steric properties to catalytic center and the right electronic properties to interact with substrate inside channel/space of catalyst.[4] Inspired by the lesson derived from simplified biocatalysis to efficient enzyme mimic, it is now acceptable that an ideal enantioselective catalysts need to possess a metal complex/catalytic center, sophisticated and tunable structure with suitable size.[5] Especially, according to the concepts reported by Zecchina and coworkers,[6] nanoscale selective catalysts (1-1.5 nm range) can be considered as nanoreactors designed to promote organic transformations with high activity and selectivity. However, the design and synthesis of chiral ligands for metal-based catalysts with highly efficient, inexpensive, and selective with a wide range of substrates remain a challenging goal in asymmetric catalysis. Over the past decades, salen-type C_2-symmetric *N,O*-ligands have hogged the limelight as privileged chiral ligands in catalytic asymmetric reactions. Such ligands are very flexible molecules to modify and easy-to-prepare with fulfilling criteria, such as cost-effective synthesis and ease of derivatization.[7] Many groups have devoted their efforts to developing highly reactive salen-metal catalyst by modification of salen ligands (Figure 1).[7] In this context, Katsuki[8] and Jacobsen[9] have developed various privileged salen-metal complexes by multistereogenic salen ligands containing steric bulky groups for the versatile organic reactions. For example, the Katsuki salen ligands and corresponding metal complexes can adopt a square planar geometry that the stereomeric configuration as well as steric repulsion were beneficial to the achievement of high enantioselectivity, and following dissociation for the next catalytic cycle of metal complex.[8a] Previous works on the salen-metal based asymmetric catalysis showed that the rigid geometry of salen-metal complex could be manipulated by substituted phenyl group on axial chiral BINOL backbone,[7-9] in which the crowded salen ligand around the metal center has the ability to change the Lewis acid character of the metal and therefore could be effectively used to increase the reactivity of the resulting salen-metal complex.

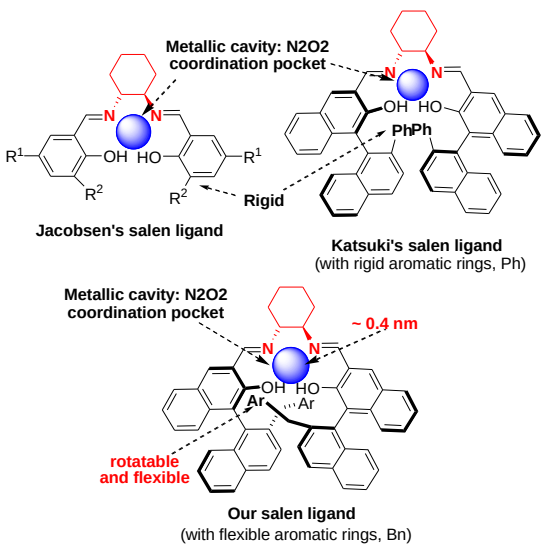
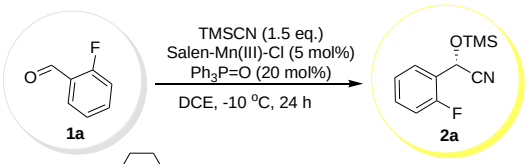
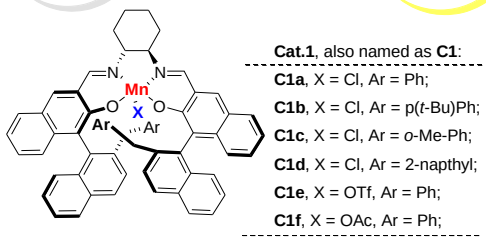


Figure 1. The structures of a chiral diamine derived symmetrical salen ligand.

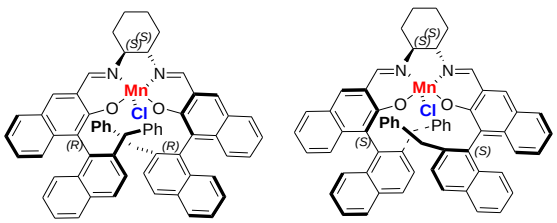
We recently reported a new nanoscale salan-Cu(II) and salen-Co(III) complex having distinguishing feature of enzyme for the asymmetric Henry reaction of aromatic aldehydes and asymmetric fluorination.[10] For the salan-copper complex, it was found that good catalytic performance for benzaldehyde and halogen-substituted aromatic aldehydes in term of conversion and

enantioselectivity (90-99% yields and up to 91% *ee*).[10a] We speculated that such unique salan ligand with two benzylic groups as helping hands would be a possible supramolecular catalyst system bearing large aromatic π-wall. Beside the inherent deficiency of catalytic copper center, the remarkable discrimination of different aldehydes in catalytic Henry reaction might be due to the considerable catalyst-substrate interaction, such as noncovalent interactions between copper ligand and aldehydes. Very recently, on the basis of salan-Cu catalysis, a new type of chiral salen-Co(III) catalyst that features multisetereogenic center and larger molecular space has been developed for highly enantioselective Henry/nitroaldol reactions (up to 93% and up to 98%*ee*).[10c] Given the potential importance of cyanosilylation reactions[11] and the privileged role of salen-Mn complex in biomimetic catalysis[12], the continued investigation of Ar-BINMOL-derived salen-Mn complex in cyanosilylation reactions would be highly desirable. Such a synthetic method could be of great value for both synthesis of optically pure cyanohydrins that are versatile synthetic intermediates, and structural-activity relationship (SAR) studies of metal catalysts. Notably, previous study has been suggested that the salen-Mn(III) play a critical role in the asymmetric Mn-catalyzed cyanosilylation reactions,[13] whereas it gave the desired products in only moderate to good yields with low to moderate enantiomeric excess (*ee*). Thus in this report, we present a preliminary study of multistereogenic salen-Mn(III) complex - catalyzed cyanosilylation of aldehydes, in which the well-established active center impacted by salen ligands were combined with a nanoscale cavity. Good to excellent enantioselective cyanosilylation reactions were achieved (up to 90% *ee*) in the addition of cyanide to aldehydes, the success of which relied exclusively on the special structure of Ar-BINMOL-derived backbone with chirality matching of multistereogenic centers.





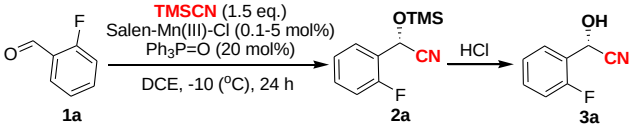
Salen-Mn(III) Catalyst from (*R*)-BINOL and (*R, R*)-diamine



C2: from (*S*)-BINOL and (*R, R*)-diamine **C3:** from (*R*)-BINOL and (*S, S*)-diamine

Scheme 1. Various Ar-BINMOL-derived salen-Mn(III) complexes for catalytic cyanosilylation of aldehyde **1a**

Table 1. Ar-BINMOL-derived Salen-Mn catalyzed cyanosilylation reaction of aldehyde **1a**



Entry[a]	Catalyst	Yield (%)[b]	Ee (%)[c]
1	**C1a**	94	88
2	**C1b**	80	59
3	**C1c**	85	73
4	**C1d**	<30	-
5	**C1e**	30	37
6	**C1f**	NR	-
7	**C2**	80	-31
8	**C3**	92	-59
9[d]	**C1a**	93	82
10[e]	**C1a**	86	78
11[f]	**C1a**	84	80
12[g]	**C1a**	<40	-
13[h]	**C1a**	93	88
14[i]	**C1a**	trace	-

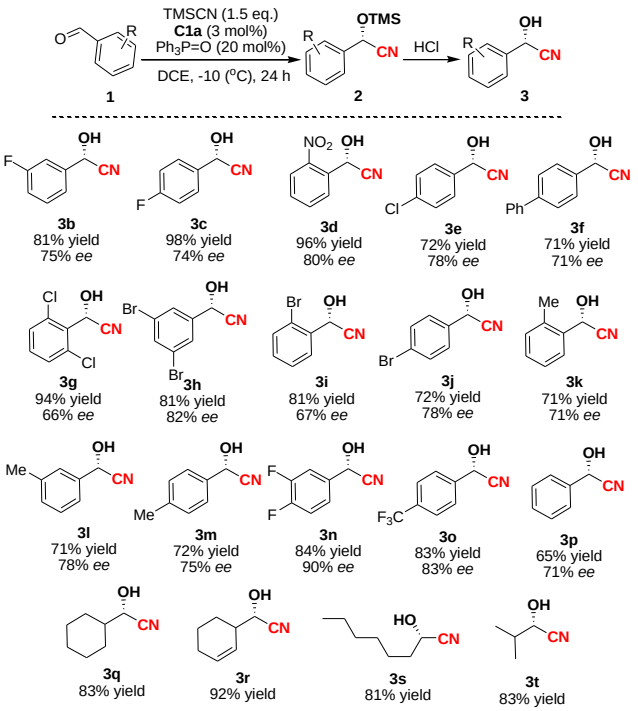
[a] Reaction conditions: Aldehyde (0.5 mmol), Salen-Mn(III) catalyst (5 mol%), TMSCN (1.5 eq.), triphenylphosphine oxide (20 mol%), at -10 °C, in DCE. [b] Yield of isolated product **3a** was calculated based on stating material **1a** (two step). [c] Determined by chiral HPLC, and the absolute configuration was confirmed in compassion to that of previous reports[11]. [d] 2 mol% of salen-Mn (**C1a**) was used in this case. [e] 1 mol% of salen-Mn (**C1a**) was used in this case. [f] 0.5 mol% of salen-Mn (**C1a**) was used in this case. [g] 0.1 mol% of salen-Mn (**C1a**) was used in this case. [h] 3 mol% of salen-Mn (**C1a**) was used in this case. [i] 0.01 mol% of salen-Mn (**C1a**) was used in this case, and almost no desired product was obtained.

Various Ar-BINMOL-derived salen ligands and related salen-Mn (III) complexes were easily prepared according to previous methods, in which the key step is neighboring lithium-assisted [1,2]-Wittig rearrangement (NLAWR).[10,14] And exploratory studies were then conducted with 2-fluorobenzaldehyde (**1a**) and were guided initially by previous reports that cyanosilylation of aldehydes in the presence of both catalytic amount of salen-Mn(III) complex and triphenylphosphine oxide gave the desired products.[13] The effect of solvent on the salen-Mn(III) complex (**C1a**) catalyzed cyanosilylation of 2-fluorobenzaldehyde (**1a**) with TMSCN was revealed in Table S1 (*see* Supporting Information). It was found that DCE was better than other solvents, such as DCM, toluene, Et_2O, THF, and other solvents evaluated in Table S1. In this case, good yield and promising enantiomeric excess could be achieved at room temperature (79% *ee* and 91% yield). And then we found this cyanosilylation was impacted largely by temperature, in which the better enantioselectivity and yield of the desired product could be obtained at -10 °C (Table S2, 88% *ee* and 94% yield). Higher and lower temperature led to inferior enantioselectivity and yield in the presence of the same salen-Mn(III) catalyst. Encouraged by

these findings, we continued to investigate the possible enhancement of additives in enantioselectivity. As shown in Table S3 (see Supporting Information), the use of various phosphine oxides and chiral Lewis bases could not improve the enantioselectivity in this reaction. Most of additives evaluated in this work resulted in low enantioselectivity and yield. Examination of additive effects on the cyanosilylation of 2-fluorobenzaldehyde (**1a**) in the presence of salen-Mn(III) complex (**C1a**) showed a strong dependence of the product yield and transformation on the additive type, with triphenylphosphine oxide giving the best results. In addition, the suitable amount of triphenylphosphine oxide has been further confirmed as 20 mol% for the activation of TMSCN. After considering options to improve the catalytic performance, especially as enantioselectivity, in the cyanosilylation of 2-fluorobenzaldehyde (**1a**), we continued to modify the multistereogenic Ar-BINMOL-derived salen ligand and corresponding salen-Mn(III) complex by changing the anionic group on salen-Mn(III) complex and increasing the steric bulk around the benzylic moiety of binaphthyl backbone. As shown in Scheme 1, except **C1a**, seven Ar-BINMOL-derived salen-Mn(III) complexes were synthesized for the investigation of steric repulsion of ligand (nano cavity), chirality matching or mismatching, and electronic effect of Salen-Mn(III) induced by anionic groups.

Upon screening a number of various Ar-BINMOL-derived salen-Mn complexes (Entries 1-8, Table 1), we found that the salen-Mn (**C1a**) catalyst, derived from (*R*)-BINOL and (1*R*,2*R*)-cyclohexane-1,2-diamine, did favor the efficient formation of the desired product, (*S*)-3-(2-fluorophenyl)-3-(trimethylsilyloxy)propanenitrile, in excellent yield (>94% yield) and high enantioselectivity (88% *ee*). Unfortunately, the introduction of substituted groups, such as *tert*-Butyl, methyl, and naphthyl group, on the benzylic moiety of salen ligand led to inferior conversion and enantioselectivity in this reaction (Entries 2-4). These results showed that the bulky benzylic groups with possible aromatic interaction and steric repulsion gave large impact on the capacity of metallic center (Mn). Similarly, the change of anion ion on salen-Mn complex from Cl to OAc or OTf was also disfavor the cyanosilylation reaction of aldehyde (Entries 5 and 6), in which the electronic effect of anion ion was suggested to be important for the catalytic performance of Mn. In addition, the configuration of salen ligand was proved to be crucial to the enantioselectivity. For example, both the salen-Mn complexes **C2** and **C3** that prepared from (*S*)-BINOL and two isomers of cyclohexane-1,2-diamine respectively resulted in low enantioselectivities (Entries 7 and 8, 31-59% *ee*). The experimental results also supported that the cavity of Ar-BINMOL-derived salen ligand that derived from (*S*)-BINOL and (1*R*,2*R*)-cyclohexane-1,2-diamine was smaller than that of obtaining from (*R*)-BINOL with (1*R*,2*R*)-cyclohexane-1,2-diamine or (1*S*,2*S*)-cyclohexane-1,2-diamine.[15] And interestingly, even though the chiral cyclohexane-1,2-diamine impacted the enantioselectivity largely on this cyanosilylation reaction, it was discovered that the chirality of BINOL governed the absolute configuration of reaction product **2a**/**3a** because chiral salen-Mn complexes **C2** and **C3** gave (*R*)-3-(2-fluorophenyl)-3-(trimethylsilyloxy)propanenitrile and salen-Mn complex **C1a** gave (*S*)-3-(2-fluorophenyl)-3-(trimethylsilyloxy)propanenitrile.

Thus the salen-Mn complex **C1** was selected as promising catalyst for further optimizing the catalyst load. As shown in Table 1 (Entries 9-12), the use of 3 mol%, 1 mol%, 0.5 mol%, and 0.1 mol% of salen-Mn was evaluated in this reaction and the corresponding yield was 93%, 86%, 83%, and <40% respectively. Notably, 0.5 mol% of salen-Mn complex **C1** gave promising yield and good enantioselectivity (80% *ee*), in which the salen-Mn catalyst was proved to be quite effective in this reaction. However, the salen-Mn(III) catalyst is still difficult to be recycled and reused for the cyanosilylation reaction. In comparison to previous work that reported by Kim and coworkers,[13] our salen-Mn catalyst system could be better than previous salen-Mn complex including Katsuki-like salen-Mn complex[13a] and Jacobsen salen-Mn complex[13c] in term of enantioselectivity for the cyanosilylation reaction of aldehydes.



Scheme 2. Ar-BINMOL-derived Salen-Mn catalyzed cyanosilylation of aldehydes

With the optimized reaction conditions in hand, we investigated the scope of this cyanosilylation protocol. As shown in Scheme 2, the salen-Mn **C1a** exhibited excellent activity and high functional-group tolerance. Aromatic aldehydes containing methyl, halide, trifluoromethyl, phenyl, and nitro groups, were reacted with TMSCN efficiently to give the corresponding products **2** and subsequent desilylated product **3** in high yields (The yields showed in Scheme 2 were calculated based on stating material **1** for the two-step transformations) and good enantioselectivities (Determined by chiral HPLC for product **3**). The fact that up to 90% *ee* of cyanohydrin could be obtained by salen-Mn complex **C1a** is of interest, because there are no previous reports on salen-Mn(III) complex -catalyzed cyanosilylation of aldehydes with such high enantioselectivity. Although the true reason could not be concluded completely at present, we suggested the substituted benzyl group on the multistereogenic salen ligand played considerable role in the

enantioselective induction of salen-Mn(III) catalyst system. Under the optimized reaction conditions, the Ar-BINMOL-derived salen-Mn(III) complex **C1a** were also effective for the cyanosilylation of alkyl aldehydes (**1q-t**), in which high yields of the desired product were achieved (81-92% yields). Unfortunately, the *ee* values of these products could not be determined by chiral HPLC.

On the basis of the experimental results that showed in the text as well as the Supporting Information, the proposed transition state was provided in Figure 2 that featured with dual-activation catalysis. Similarly to previous Ar-BINMOL-derived salen-metal complex,[10] the salen-Mn complex acted as chiral Lewis acid to activate aldehyde by binding the oxygen atom of carbonyl group while triphenylphosphine oxide worked as a Lewis base for activation of TMSCN through the formation of pentacoordination intermdiate and subsequent transferring to hexacoordination intermediate with substrate. The attack of cyanide (CN) would prefer *Re* face of the carbonyl group of aldehyde to afford *R*-cyanohydrin, and the *Si* face is blocked by the steric repulsion of salen-Mn complex.

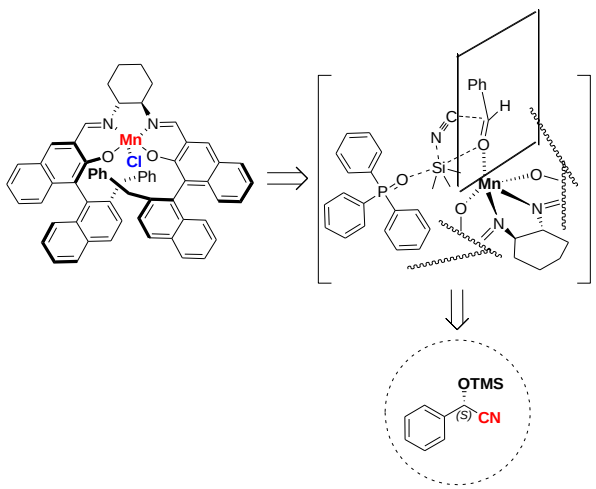


Figure 2. Proposed transition state involved in the enantioselective cyanosilylation of aldehyde by dual-activation catalysis in the cage of salen-Mn complex **C1a**

In summary, inspired by the lesson of nanoscale enzyme mimic, we have developed an efficient enantioselective salen-Mn(III) complex catalyzed cyanosilylation of aldehydes with TMSCN. In comparison to previous efforts in this area, it was found firstly that the construction of macromolecular Ar-BINMOL-derived salen-Mn(III) catalyst bearing aromatic pocket and two benzylic groups as helping hands exhibited excellent yields and good enantioselectivties in this reaction (up to 94% yield and 90% *ee*), in which our Ar-BINMOL-derived salen-Mn complex exhibited superior activity than other salen-Mn catalysts in term of yields and enantioselectivity. In addition, the multisetereogenic salen-Mn complex with multifunctional groups mimics partially the functions of biocatalysts in term of reasonable utilization of steric properties to catalytic center and the electronic properties to interact with substrate inside channel/space of catalyst.

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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15 It was found that the salen-Mn(III) complex **C2** and **C3** were difficult to be obtained under the same reaction conditions in comparison to that of salen-Mn(III) complex **C1a**. On the basis of this finding, we can conclude that the cavity of the Ar-BINMOL derived salen ligand was largely impacted by the multistereogenic configuration of two chiral sources. Considering the critical phenomenon of coordination between Mn(II) salt and salen ligand, we suggested that the estimated cavity might be about 3.6-4.0 Å (Ionic radius of Mn^{2+} is 0.9 or 0.96 Å) for these Ar-BINMOL derived salen ligands.