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Enantioselective Strecker reaction of aldimines using potassium cyanide catalyzed by recyclable macrocyclic V(V) salen complex

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Chiral dimeric macrocyclic V(V) salen complex based on chiral macrocyclic salen ligand derived from 1*R*, 2*R*-(-) diaminocyclohexane with trigol bisaldehyde was synthesized and evaluated as efficient catalyst (5 mol%) for asymmetric addition of potassium cyanide and trimethylsilyl cyanide to various *N*-benzylimines at -20 °C. The dimeric chiral macrocyclic salen complex was found to be an effecient recyclable catalyst to give high yield (91%) of α-aminonitrile with and high chiral induction (*ee* up to 99%) in case of 2-methoxy substituted *N*-benzylimines in 16 h. The catalytic system worked well with both organic and inorganic cyanide sources and the catalyst was recycled up to five cycles with retention of enantioselectivity. Based on the NMR investigation and kinetics a probable mechanism was proposed for the catalytic enantioselective Strecker reaction.

Introduction

The catalytic asymmetric Strecker reaction represents one of the most direct and viable methods for efficient asymmetric synthesis of naturally occurring and non-proteinogenic α-amino acid,[1] nucleic acids, various nitrogen and sulphur containing heterocycles,[2] chiral building blocks for organic synthesis and pharmaceuticals.[3] The classical Strecker reaction reported in 1850 comprises of three component reaction for the synthesis of α-amino nitrile,[1a] which after hydrolysis yield α-amino acids[4] in racemic form. Enormous efforts have been devoted to the development of non-recyclable chiral catalysts to effect the enantioselective Strecker reaction, which includes Schiff base complexes,[5] organocatalysts,[6] bi-functional catalysts[7] and various metal based catalysts.[8] Notable amongst these catalysts was Jacobsen's metal based salen complexes under homogeneous catalytic system in terms of enantio-induction and yield.[5] Recently we have developed efficient recyclable catalytic systems for different enantioselective transformations[9] including asymmetric Strecker reaction. Nevertheless, there are only very few systems which work efficiently with different cyanide sources.[8b, 8v] This prompted us to develop a recyclable catalytic system which can handle both the organic, easy to handle and safe cyanide source like TMSCN and also the cost effective inorganic cyanide source like potassium cyanide; that display high enantioselectivity and substrate generality over a broad spectrum of reactions. Due to the high cost of chiral ligands we have also taken care of issue of catalyst recovery and reuse while designing the chiral ligands for asymmetric Strecker reaction. In the present work we wish to report the use of chiral macrocyclic V(V) salen complex as efficient recyclable catalyst for the asymmetric addition of cyanide to various aldimines which delivers excellent enantioselectivity (ee up to 99%) of α-aminonitrile in 16h with over all good yield and added advantage of catalyst recyclability. These catalysts however, required an additive like water as a promoter in order to show high catalytic performance.

Results and Discussion

The synthesis of macrocyclic complexes was implemented in three step sequence, as illustrated in **Scheme 1**. The reaction of 3-*t*-Bu -5-chloromethyl-2-hydroxy benzaldehyde with trigol was carried out in dry THF containing sodium hydride to give trigol bis aldehyde **1**.[10] The interaction of **1** with diamines in 1:1 and 1: 2 molar ratio in dry MeOH and THF respectively gave macrocyclic chiral Schiff base ligands **2'-5'**. The complexation of chiral macrocyclic ligands with vanadyl sulphate hydrate was done followed by auto-oxidation to get V(V) macrocyclic complex **2-5**.[10]

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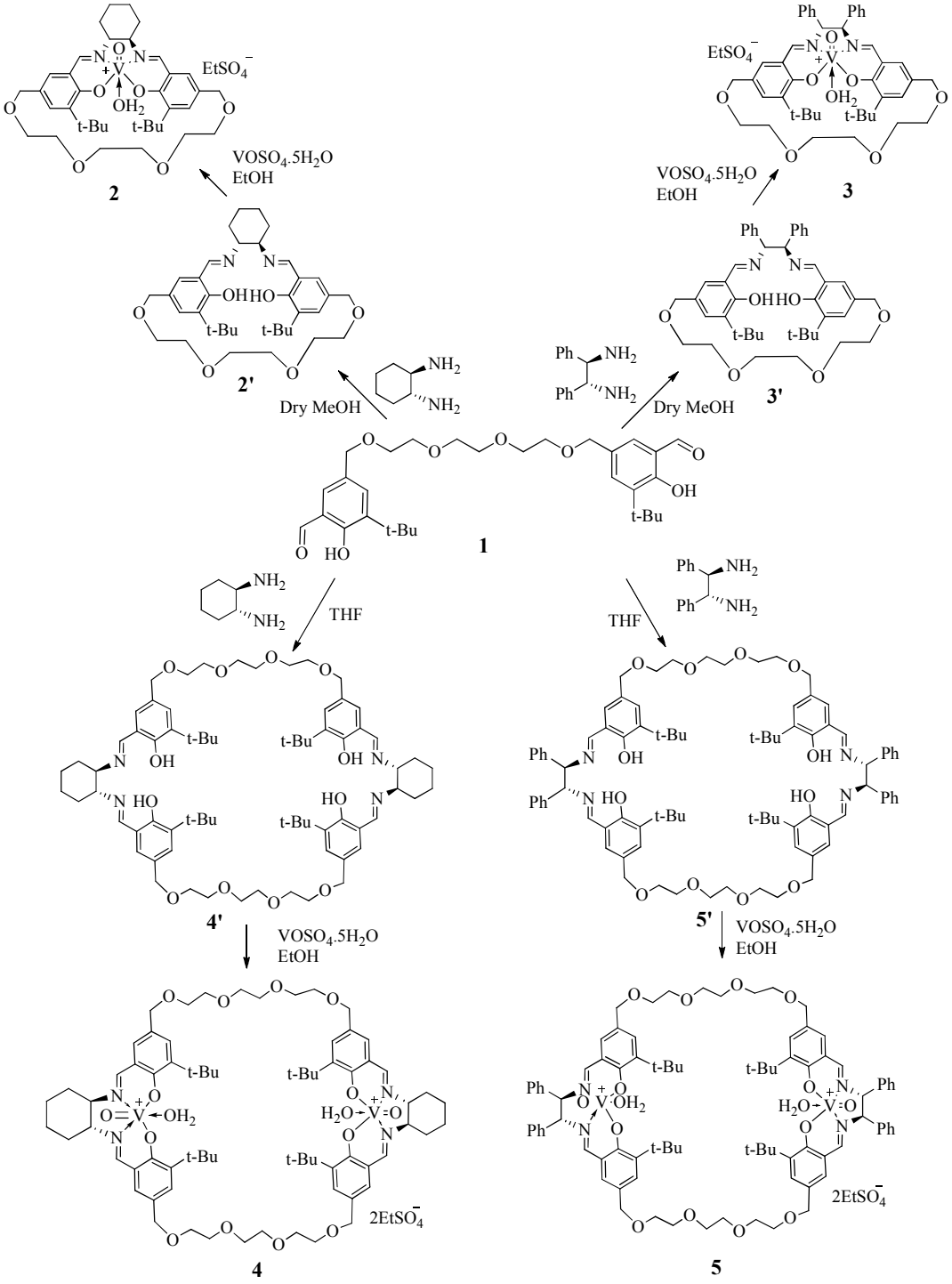

Scheme 1: Synthesis of V(V) macrocyclic complex **2-5**

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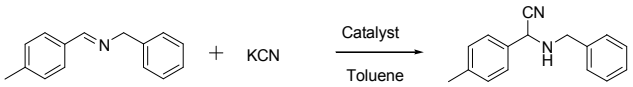
Table1: Screening of V(V) macrocyclic salen complex for asymmetric Strecker reaction[a]



Entry	Catalyst	Yield (%)[b]	ee (%)[c]	TON[d]	TOF (min^{-1})[e]
1	**2**	66	56	13.2	$9.16x10^{-3}$
2	**3**	62	50	12.4	$8.61x10^{-3}$
3	**4**	76	79	15.2	$10.56x10^{-3}$
4	**5**	73	69	14.6	$10.14x10^{-3}$

[a] Reaction condition: catalyst (5 mol%), substrate (0.2 mmol), in toluene (1 mL) with 1.5 equiv. KCN at -20 °C for 24 h.
[b] Isolated yield
[c] ee were determined using chiral OD column
[d] TON is calculated by the expression [product]/[catalyst]
[e] TOF is calculated by the expression TON/reaction time (min^{-1})

Our initial study commenced with the screening of catalyst **2**-**5** for the enantioselective Strecker reaction using 4-methyl imine as representative substrate and toluene as solvent at -20 °C. For purposes of comparison, initially the chiral macrocyclic mononuclear complexes **2** and **3** with varied chiral collars were screened for its catalytic activity and found that the complex with 1*R*, 2*R*-(-) diaminocyclohexane as a collar results in better yield and enantioselectivity (Table 1, entries 1&2). Then among the dinculear variants **4** and **5**, the catalyst **4** fared better than this counterpart **5** in terms of yield (76%) and enantioselectivity (79%). The enhanced activity of the chiral dinuclear macrocyclic V(V) salen complex **4** may be attributed to the increase in the active reaction sites that are functioning in synergy.

With these initial results it was found that the catalyst **4** was distinctly better in terms of reactivity, then in order to find optimal reaction conditions such as catalyst loading, solvent variation, temperature, use of additives the Strecker reaction of 4-methyl *N*-benzylimine was carried out. The catalyst loading was screened ranging from 2.5 mol% -10 mol% for the asymmetric Strecker reaction using toluene as solvent at -20 °C. On conducting the Strecker reaction using 2.5 mol% catalyst loading gave 65% yield of α-aminonitrile with 69% ee within 16 h (Figure 1). On increasing the catalyst loading from 2.5 to 5 mol% there was an improvement in the yield (76%) and 79% ee of the corresponding product. However a further increase in the catalyst loading (10 mo%) does not enhance the results in term of yield and enantioselectivity (Figure 1). Hence 5 mol% catalyst was sufficient enough to progress the reaction smoothly.

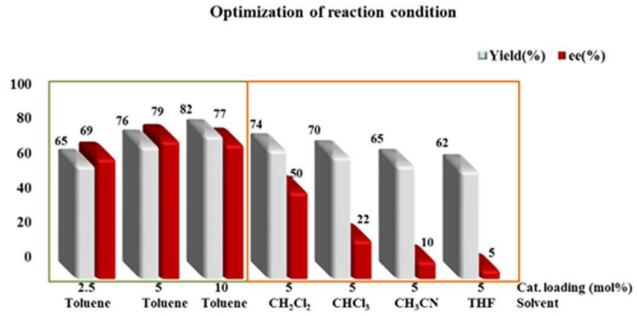


Figure 1: Asymmetric addition of KCN to 4-methyl-*N*-benzylimine using chiral macrocyclic V(V) salen complex 4 for optimizing the reaction condition by screening the loading of catalyst and solvent.

The reactivity and enatioselectivity of the asymmetric Strecker reaction is strongly dependent on the nature of solvent used. Thus asymmetric addition of KCN to 4-methyl imines was conducted in various solvents viz. toluene, chloroform, dichloromethane and THF, whereas toluene was found to be the solvent of choice (Figure 1). As temperature plays a crucial role in achieving high chiral induction of the desired product α-aminonitrile in asymmetric Strecker reaction, therefore, we have varied the reaction temperature from 0 to -30 °C. On increasing the reaction temperature from -20 to -10 and 0 °C, there is increase in yield with considerable loss in enantioselectivity (Figure 2). Whereas on further decreasing the temperature from -20 to -30 °C there is no significant change in the yield and enantioselectivity of the desired product. So, the best results in term of yield of α-aminonitrile with high chiral induction (ee, 84%) was achieved at -20 °C and was considered as the optimum reaction temperature (Figure 2).

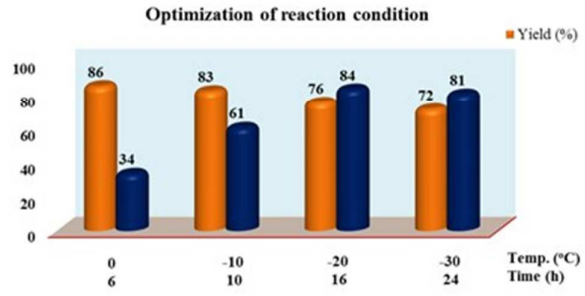


Figure 2: Asymmetric addition of KCN to 4-methyl-*N*-benzylimine using chiral macrocyclic V(V) salen complex 4 for optimization of reaction temperature

Use of additive play a crucial role in asymmetric Strecker reaction [7]. Therefore, different additives viz., H_2O, MeOH, EtOH, *i*PrOH, *t*-BuOH were screened in asymmetric addition of KCN to 4-methyl *N*-benzylimine as representative substrate in toluene at -20 ^{o}C. Although all the additive used (Figure 3) helped in improving the reactivity (time 16 h) and enantioselectivity (ee, 88%) of α-aminonitrile however, water was proved to be the best additive to give 82% yield of α-aminonitrile.

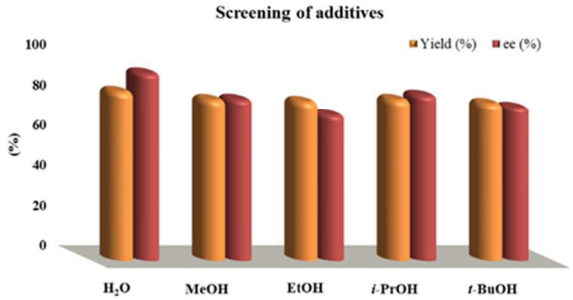


Figure 3: Asymmetric addition of KCN to 4-Me-*N*-Benzylimine using chiral macrocyclic V(V) salen complex **4** for the choice of additive.

Thus, with the promising results under optimized reaction conditions, the catalytic protocol was explored for various N-benzylimines in order to see the generality of the catalytic system and the results are summarized in Table 2. Both the electron donating and electron withdrawing substituent present on imine demonstrated the effectiveness of this protocol on the asymmetric Strecker reaction. The electron donating (-Me, -OMe) groups at 4- positions of N-benzylimines gave higher yields as well as ee (Table 2, entries 1 and 4) than in the cases where these substituents were on 2- and 3-position (Table 2, entries 2, 3, 5, 6). The presence of electron withdrawing group on the aromatic ring of imines gave moderate yield and ee (Table 2, entries 7, 8).

Furthermore, on increasing the bulkiness on *N*-benzylimines viz., *N*-benzylidene-1,1-diphenylmethanamine, *N*-(4-methylbenzylidene)-1,1-diphenylmethanamine, *N*-(2-methoxybenzylidene)-1,1-diphenylmethanamine, *N*-(4-bromobenzylidene)-1,1-diphenylmethanamine for asymmetric Strecker reaction with KCN excellent enantio-induction (ee, >99%) in α-aminonitrile was achieved in case of *N*-(2-methoxybenzylidene)-1,1-diphenylmethanamine with excellent yield. This protocol also worked well with trimethyl acetaldehyde in term of yield (71%) and enantioselectivity (91%) in their respective α-aminonitrile. To the best of our knowledge, the chiral macrocyclic V(V) salen complex 4 is the efficient recyclable catalyst for the asymmetric Strecker reaction of various *N*-benzylimines with KCN as cyanide source in presence of water as additive giving good yields of chiral α-aminonitrile with excellent enantioselectivity. Further to compare the activity of the V(V) dinuclear complex **4** with an organic cyanide source like TMSCN, the obtained results (Table 2, in parenthesis) showed that the catalyst is efficient to work with both inorganic and organic cyanide sources. In all catalytic runs the 1*R*,2*R* chiral macrocyclic dimeric V(V) salen complex gave the *S*-form of corresponding α-aminonitriles.

Table 2: Substrate scope of catalytic asymmetric Strecker reaction of *N*-benzylimines using catalyst **4**[a]

S. No.	Imine	Yield (%)[b,d]	ee (%)[c,d]
1	$C_6H_5CH{=}NCH_2Ph$	89 (92)	84 (80)
2	4-$MeC_6H_4CH{=}NCH_2Ph$	91 (93)	93 (83)
3	3-$MeC_6H_4CH{=}NCH_2Ph$	84 (86)	79 (73)
4	2-$MeC_6H_4CH{=}NCH_2Ph$	88 (85)	90 (76)
5	4-$MeOC_6H_4CH{=}NCH_2Ph$	90 (91)	91 (89)
6	3-$MeOC_6H_4CH{=}NCH_2Ph$	86 (82)	80 (75)
7	2-$MeOC_6H_4CH{=}NCH_2Ph$	90 (84)	89 (85)
8	4-$FC_6H_4CH{=}NCH_2Ph$	87 (89)	92 (80)
9	4-$ClC_6H_4CH{=}NCH_2Ph$	83 (80)	91 (76)
10	$C_6H_5CH{=}NCH(Ph)_2$	92 (94)	96 (92)
11	4-$MeC_6H_4CH{=}NCH(Ph)_2$	90 (95)	93 (90)
12	2-$MeOC_6H_4CH{=}NCH(Ph)_2$	89 (91)	99 (83)
13	4-$BrC_6H_4CH{=}NCH(Ph)_2$	86 (90)	87 (80)
14	$C_{10}H_8CH{=}NCH(Ph)_2$	84 (89)	90 (85)
15	$(CH_3)_3CCH{=}NCH(Ph)_2$	71 (83)	91 (88)

[a] Reaction conditions: catalyst **4** (5mol%), *N*-benzylimines as substrates using KCN (1.5 equiv.), H_2O as an additive using toluene (1mL) at -20 ^{o}C.
[b] Isolated yield
[c] ee were determined using Chiral OD, ADH and ODH column

[d] Results in parenthesis were obtained using TMSCN (1.5 equiv) as a source of cyanide.

Next we extended the study for its applicability in one pot three component reaction using catalyst **4** with 4-methyl benzaldehyde, benzyl amine as model substrates and KCN as a source of cyanide to examine its effect under this optimized condition, it results in good yield (90%) with loss of enantioselectivity (55%). This is possibly due to the rapid release of HCN, thereby increasing the rate of the non-enantioselective background reaction. We also tried with ketimine substrate derived from acetophenone and benzyl amine using catalyst **4** under the optimized condition, we found that the reaction is relatively sluggish and gave low yield because of the low reactivity of ketone derived substrates.[4b]

Kinetic Studies

In order to understand the mechanism of hydrocyanation of imine, kinetic experiments were done using catalyst **4** with 4-methyl *N*-benzyl benzylimine as a model substrate and KCN as source of cyanide. During the kinetic run, the plot for the product formation with time was found to be increasing linearly in the initial period and saturation point was obtained during the later stage of the reaction[9a] (Figure 4). Based on this observation, the initial rate constants k_{obs} were determined by the amount of product formed with respect to time.

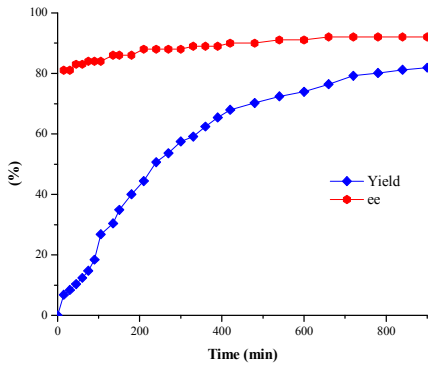


Figure 4: Time dependent plot of the formation of α-aminonitrile at -20 °C, [catalyst] = 0.003M, [benzylimine] = 0.06M, [KCN] = 0.09M.

Effect of catalyst concentration on rate of the reaction

To find out the dependence of catalyst concentration on the reaction rate, we have carried out Strecker reaction of 4-methyl *N*-benzylimine with different concentration of the catalyst **4** [0.001 M-0.0057 M] at constant concentration of benzylimine [0.06M] and KCN [0.09M]. From the kinetic data a linear plot of formation of product, α-aminonitrile (k_{obs}) versus log[catalyst] with unit slopes (d log k_{obs}/d log[catalyst] ~1) was obtained which passes through the origin, indicating that the Strecker reaction is of first order with respect to the concentration of the catalyst (Figure 5).

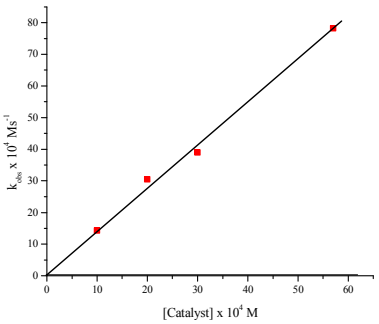


Figure 5: Plot of catalyst **4** concentration versus k_{obs} at -20 °C, [4-methyl *N*- benzylimine] = 0.06M, [KCN] = 0.09M.

Effect of substrate concentration on rate of the reaction

To study the influence of substrate concentration on reaction rate, kinetic experiments were carried out at different initial concentration of benzylimine ranging from (0.03 M–0.08M) by keeping all parameter constant from which the rate was calculated and the plot of rate constant (k_{obs}) versus the concentration of substrate (d log k_{obs}/d log[substrate] ~1) showed the first order dependence of the reaction on the substrate concentration (Figure 6).

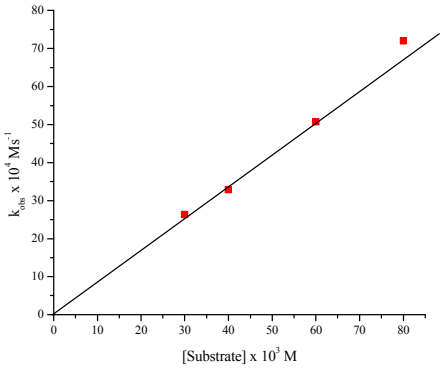


Figure 6: Plot of substrate concentration versus k_{obs} at -20 °C, [catalyst] = 0.003M, [KCN] = 0.09M.

Effect of cyanide concentration on rate of the reaction

To evaluate the effect of concentration of the KCN (0.01M - 0.15M) on the rate of Strecker reaction of the 4-methyl *N*-benzyl benzylimine were studied, under similar condition (catalyst [0.003M] and benzylimine [0.06M]) which also indicates the first order dependence (d log k_{obs}/d log[KCN] ~1) in terms of the concentration of KCN (Figure 7). Overall the

kinetic data revealed a first order dependence of rate on KCN, substrate and catalyst **4**.

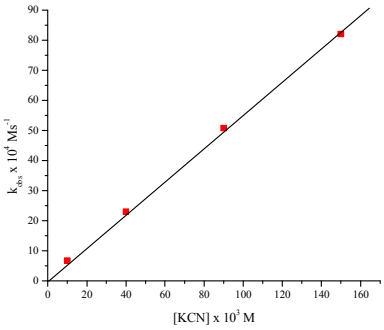


Figure 7: Plot of KCN versus K_{obs} at -20 ^{o}C, [catalyst 4] = 0.003M, [4-methyl *N*-benzylimine] = 0.06M.

To understand the mechanism a series of experiments were carried out. We have already disclosed the role of trigol (ether linkage) which helps in attracting alkali metals and hence activate the cyanide source, KCN for the cyanation reaction.[10] With this backdrop, a probable catalytic cycle for the enantioselective Strecker reaction is shown in Scheme 2. In the catalytic cycle, the imine was polarized by the weak interaction through its lone pair of electrons with metal centre of the catalyst **4** and it was also observed in the ^{51}V NMR by the downfield shift (Figure 8). To this intermediate A, upon addition of the cyanide source, KCN there was a significant downfield shift which in terms confirm the interaction with the catalyst and the generated cyanide ion attacks the polarized carbon of imines (intermediate B), resulting in formation of the product and the catalyst was resumed back almost to its original ppm which indicates the catalyst is free to takes part in another catalytic cycle. Based on the kinetics data and from the NMR studies, a probable mechanism is proposed here (Scheme 2).

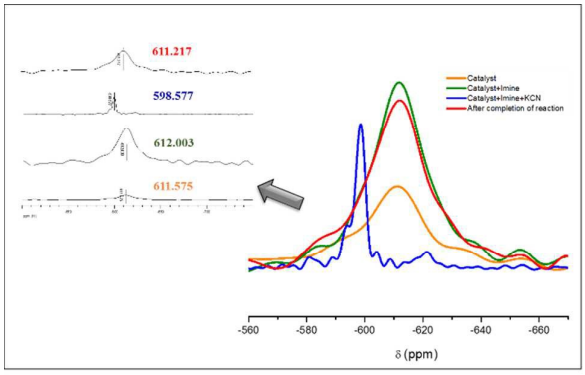
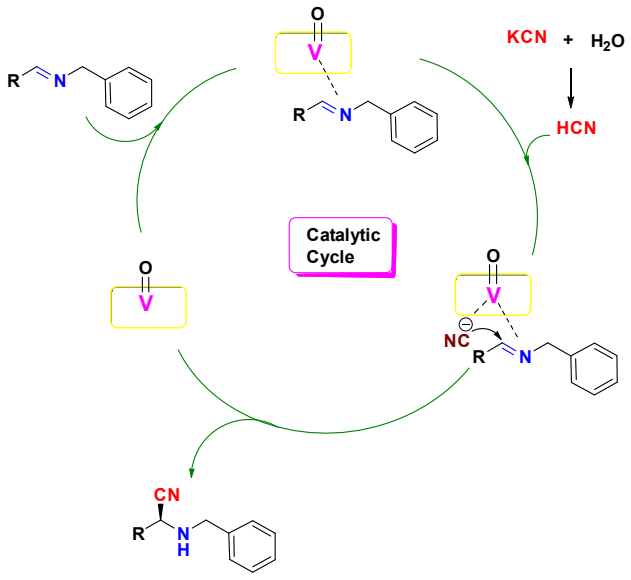


Figure 8: ^{51}V NMR in $CDCl_3$ for (a) Catalyst (b) Catalyst and imine (c) reaction mixture containing catalyst, imine and KCN (d) after the completion of reaction.



Scheme 2: Probable catalytic cycle for asymmetric Strecker reaction

In order to assess the reuse of chiral macrocyclic dinuclear V(V) salen complex **4**, 2-MeO substituted imine (Table 2, entry 11) was used for the catalytic runs. Consequently, after the first catalytic run, the catalyst was retrieved quantitatively by precipitating the catalyst by the addition of hexane. The recovered catalyst was then washed repeatedly with hexane, dried and reused for further catalytic runs. The recovered catalyst was reused five times with no loss in their performance (Figure 9) which indicates that there is no structural changes during the catalytic run as well as during post-catalytic work-up unit operation.

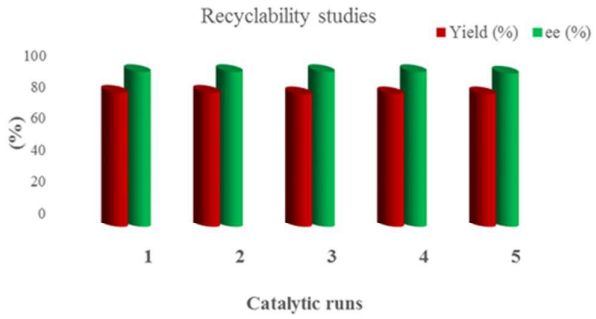


Figure 9: Recycling data for enantioselective Strecker reaction using *N*-(2-methoxybenzylidene)-1,1-diphenylmethanamine and KCN at -20 ^{o}C.

Conclusions

In conclusion chiral macrocyclic V(V) dimeric salen complex demonstrated the effectiveness in asymmetric Strecker protocol for various aldimines with KCN in presence of water

as additive at -20 °C in toluene with good yield and enantioselectivity of α-aminonitriles. The catalyst worked well with both organic and inorganic cyanide sources. The chiral macrocyclic V(V) dimeric salen complex used in the present study can be easily separated from the reaction system and re-used effectively. Based on the kinetic and NMR studies a probable catalytic cycle was proposed for the asymmetric Strecker reaction.

Acknowledgements

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Experimental Section

Synthesis of complex 2-5

The chiral macrocyclic dimeric and monomeric V(V) salen complexes **2-5** were synthesized by our reported procedure.[10]

Typical experimental procedure for addition of cyanide to *N*-benzylimines

The chiral V(V) dinuclear salen complex (5 mol%) was dissolved in toluene[11] (1 ml) and the solution was cooled to -20 °C under N_2 atmosphere. To the cooled solution *N*-benzylimine (0.2 mmol) was added which was followed by the addition of KCN (1.5 equiv) slowly over 30 min with stirring. To this stirred solution, H_2O (20 µl) was added and an over a period of 10 min. The reaction was monitored on TLC using hexane/ethyl acetate (90/10) as eluent. Then saturated NH_4Cl aqueous solution was added and the mixture was extracted with dichloromethane. The extracts were combined, dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The product was purified by flash column chromatography on silica gel (eluted with hexane/ethyl acetate = 90:10). The purified products were characterized by ^1H NMR and were in agreement with the reported values.[4, 8u]

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Graphical Abstract

Enantioselective Strecker reaction of aldimines using potassium cyanide catalyzed by recyclable macrocyclic V(V) salen complex

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