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Efficient catalytic synthesis of optically pure 1,2-azido alcohols through enantioselective epoxide ring opening with HN_3

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Abstract

Chiral binuclear Co(salen) complexes bearing Lewis acid of group 13 metal chlorides show very high catalytic activity and enantioselectivity for the ring opening of epoxides using HN_3 as azide source. It provides a facile and practical synthetic route to a wide range of chiral nonracemic 1,2-azido alcohols and related compounds in one-pot synthesis with excellent selectivity (92.0–99.6% e.e.) under mild conditions. The presence of Lewis acid of group 13 shows a strong synergistic effect.

Keywords: Asymmetric catalysis; Heterometallic chiral salen complexes; 1,2-Azido alcohols; 1,2-Amino alcohols

1. Introduction

1,2-Azido alcohols are compounds of interest in organic synthesis as either precursors of vicinal amino alcohols or in the chemistry of carbohydrates and nucleosides [1,2]. A common method for the synthesis of enantiomerically enriched 1,2-azido alcohol is ring opening of the corresponding epoxide with the combined use of $TMSN_3$ or sodium azide in the presence of chiral catalyst zirconium alkoxides linked with chiral trialkanolamines [3].

Actually, Jacobsen's chiral (salen) metal complexes of Zn, Ni, Fe, Cu, and Co were found to be inactive and the chiral (salen) chromium(III) complex catalyze a limited extent for the enantioselective ring opening of mesoaziridines with $TMSN_3$ [4]. Co(Salen) complex [5] was proved unreactive for the kinetic resolution of 2,2-disubstituted epoxides with $TMSN_3$ [6]. Our recent research found that binuclear chiral Co(salen), bearing Lewis acids of group 13 elements, very efficient for the hydrolytic kinetic resolution (HKR) of terminal epoxides [7]. We became interested to broaden the application range of binuclear catalyst (**1a**–**2c**, Scheme 1) for direct synthesis of optically active 1,2-azido alcohols and 1,2-amino alcohols. We report herein rapid enantioselective epoxide ring opening with HN_3 catalyzed by binuclear chiral Co(salen) complexes bearing Lewis acids of group 13 metal chlorides (Scheme 1).

2. Experimental

2.1. General

All ^1H NMR, ^{13}C NMR data were recorded using a 400 MHz FT-NMR spectrophotometer (VARIAN UNITY NOVA 400) at the ambient temperature. Optical rotation measurements were conducted using a JASCO DIP 370 digital polarimeter. Gas chromatographic analyses were performed on Hewlett-Packard 5890 Series II instruments equipped with FID detectors using chiral columns (CHIRALDEX G-TA and A-TA, 20 m × 0.25 mm i.d. Astec) and HP 3396 integrators with HP Chem Station software for data analysis. Chiral HPLC analyses were performed on a YOUNGLIN instrument using a Chiralcel® OD column (24 cm × 0.46 cm i.d.; Chiral Technologies, Inc.) and Regis (*S*,*S*)Whelk-O1 at 254 nm. UV spectra were recorded on UV–vis spectrophotometer (Optizen 2120 UV) interfaced with PC using Optizen view 3.1 software for data analysis. Vibrational circular dichroism (VCD) and IR were measured in Chiral*ir*™ (ABB Bomem Inc.) using Bomem GRAMS-32 software. Solvents were used after distillation *tert*-butyl methyl

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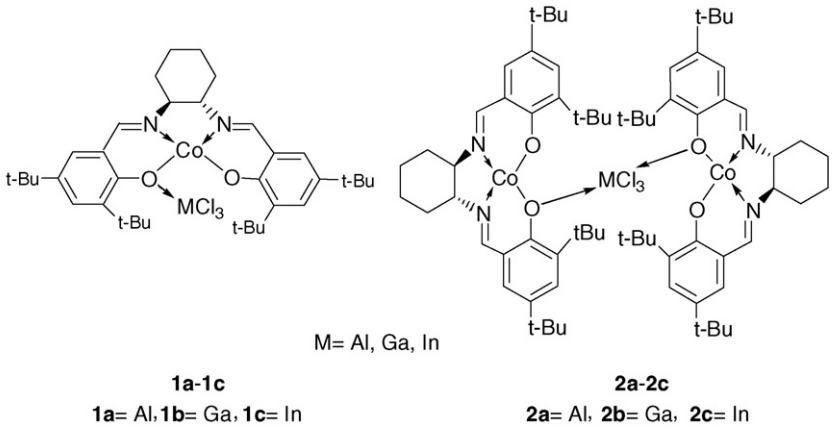


Scheme 1. Schematic diagram of chiral Co(salen) monomers and dimmers linked through Lewis acids.

ether (TBME) was used without purification as obtained from Aldrich.

Other solvents were used after distillation. All reagents were purchased from Aldrich, Fluka and TCI. Catalysts were synthesized by the earlier reported method [7]. A similar method [7c] has been adopted for kinetic measurements.

2.2. General procedure for the asymmetric ring opening of terminal epoxides

An oven dried 25 mL flask equipped with a magnetic stirring bar cooled to 0 °C in an ice bath is charged with 0.5% equiv. of catalyst followed by 1.0 equiv. of epoxides. Then 0.5 equiv. of HN_3 in TBME (2.0 mol/L) was added dropwise slowly via a syringe pump. The reaction was mildly exothermic and the reaction mixture was stirred continuously until GC or HPLC analysis showed the occurrence of optically pure azido alcohol. Then the crude reaction mixture was flushed through a plug of silica. Solvent and unreacted highly volatile epoxides were removed by rotary evaporation and the residue was isolated by vacuum distillation or purified by flash chromatography to give the azidoalcohols in the enantioenriched form. The enantiomeric excess % (e.e.%) of the products was determined by chiral GC or HPLC. The products were identified by ^{1}H and ^{13}C NMR.

2.2.1. Characterization of azidoalcohols (Table 3)

2.2.1.1. (S)-1-Azido-propan-2-ol (entry 1). ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 1.18$ (d, 3H, HOCHC**H**$_3$), 2.42 (s(br), 1H, CHO**H**), 3.19 (dd, 1H, C**H**$_2$N$_3$), 3.32 (dd, 1H, C**H**$_2$N$_3$), 3.91–3.95 ppm (m, 1H, C**H**OH); ^{13}C NMR ($CDCl_3$): $\delta = 19.9$ (CH_3), 57.8 (CH_2), 66.5 ppm (**C**HOH). Elemental anal. calcd for $C_3H_7N_3O$: C, 35.64; H, 6.98. Found: C, 35.67; H, 6.99.

2.2.1.2. (S)-1-Azido-butan-2-ol (entry 2). ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 0.86$ (t, 3H, C**H**$_3$), 1.51 (m, 2H, C**H**$_2$CH$_3$), 2.30 (s(br), 1H, CHO**H**), 3.25 (dd, 1H, C**H**$_2$N$_3$), 3.36 (dd, 1H, C**H**$_2$N$_3$), 3.68 ppm (m, 1H, C**H**OH); ^{13}C NMR ($CDCl_3$): $\delta = 9.7$ (**C**H$_3$), 27.2 (**C**H$_2$CH$_3$), 56.6 (**C**H$_2$N$_3$), 72.1 ppm (**C**HOH). Elemental anal. calcd for $C_4H_9N_3O$: C, 41.73; H, 7.88. Found: C, 35.70; H, 7.90.

2.2.1.3. (R)-1-Azido-3-chloro-propan-2-ol (entry 3). ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 2.15$ (s(br), 1H, O**H**), 3.42 (d, 2H, C**H**$_2$N$_3$), 3.58 (d, 2H, C**H**$_2$Cl), 3.97 ppm (m, 1H, C**H**OH); ^{13}C NMR ($CDCl_3$): $\delta = 45.5$ (**C**H$_2$N$_3$), 52.9 (**C**H$_2$Cl), 69.8 ppm (**C**HOH). Elemental anal. calcd for $C_3H_6ClN_3O$: C, 26.58; H, 4.46. Found: C, 26.60; H, 4.45.

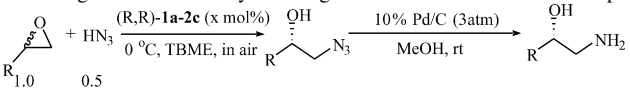
2.2.1.4. (R)-1-Azido-3-methoxy-propan-2-ol (entry 4). ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 2.12$ (s(br), 1H, O**H**), 3.21 (d, 2H, C**H**$_2$N$_3$), 3.28 (S, 3H, OC**H**$_3$), 3.40 (d, 2H, C**H**$_2$OCH$_3$), 3.84 (m, 1H, C**H**OH); ^{13}C NMR ($CDCl_3$): $\delta = 53.1$ (**C**H$_2$N$_3$), 58.8 (O**C**H$_3$), 69.1 (**C**HOH), 73.6 (**C**H$_2$OCH$_3$). Elemental anal. calcd for $C_4H_9N_3O_2$: C, 36.64; H, 6.92. Found: C, 36.65; H, 6.90.

2.2.1.5. (R)-1-Azido-3-isopropoxy-propan-2-ol (entry 5). ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 1.14$ (d, 6H, 2C**H**$_3$), 2.15 (s, 1H, O**H**), 3.19 (d, 2H, C**H**$_2$N$_3$), 3.34 (q, 1H, C**H**(CH$_3$)$_2$), 3.42 (d, 2H, C**H**$_2$O), 3.60 (m, 1H, C**H**OH); ^{13}C NMR ($CDCl_3$): $\delta = 21.9$ (2**C**H$_3$), 53.4 (**C**H$_2$N$_3$), 66.7 (**C**H(CH$_3$)$_2$), 69.3 (**C**HOH), 72.3 (**C**H$_2$OCH(CH$_3$)$_2$). Elemental anal. calcd for $C_6H_{13}N_3O_2$: C, 45.27; H, 8.23. Found: C, 45.23; H, 8.21.

2.2.1.6. (S)-2-Azido-2-phenyl-ethanol (entry 6). ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 2.52$ (s(br), 1H, CH$_2$O**H**), 3.73 (d, 2H, C**H**$_2$OH), 4.65 (t, 1H, C**H**N$_3$), 7.31–7.42 (m, 5H, Ar-**H**); ^{13}C NMR ($CDCl_3$): $\delta = 53.4$ (**C**HN$_3$), 69.1 (**C**H$_2$OH), 125.4 (**C**H), 127.07 (2**C**H), 128.6 (2**C**H), 136.2 (**C**). Elemental anal. calcd for $C_8H_9N_3O$: C, 58.88; H, 5.56. Found: C, 58.86; H, 5.61.

2.2.1.7. (R)-1-Azido-3-phenoxy-propan-2-ol (entry 7). ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 2.10$ (s(br), 1H, CHO**H**), 3.50 (dd, 1H, C**H**$_2$OAr), 3.66 (dd, 1H, C**H**$_2$OAr), 4.02 (d, 2H, C**H**$_2$N$_3$), 4.18–4.20 (m, 1H, C**H**OH), 6.85 (m, 2H, Ar-**H**), 7.04 (t, 1H, Ar-**H**), 7.32 (m, 2H, Ar-**H**); ^{13}C NMR ($CDCl_3$): $\delta = 53.24$ (**C**H$_2$N$_3$), 69.04 (**C**HOH), 77.00 (**C**H$_2$O), 114.3 (2**C**H), 121.0 (**C**H), 129.3 (2**C**H), 158.0 (**C**). Elemental anal. calcd for $C_9H_{11}N_3O_2$: C, 55.95; H, 5.74. Found: C, 58.91; H, 5.76.

Table 1
Screening and effect of catalyst loading amount on the ARO of terminal epoxides

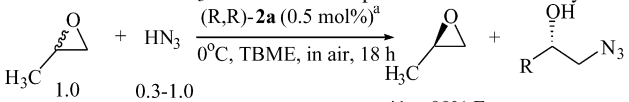


Entry	*R*	Catalyst	Catalyst[a] amount, *x*	Time (h)	Yield[b] (%)	e.e.[c] (%)
1	CH_2Cl	**1a**	0.5	11	41.0	90.8
2	CH_2Cl	**1b**	0.5	10	42.4	92.0
3	CH_2Cl	**1c**	0.5	10	44.7	91.3
4	CH_2Cl	**2a**	0.5	3	49.5	99.5
5	CH_2Cl	**2b**	0.5	6	49.1	99.2
6	CH_2Cl	**2c**	0.5	8	49.0	99.2
7	CH_3	**2a**	0.2	3	35.3	99.2
8	CH_3	**2a**	0.5	3	49.6	99.6
9	CH_3	**2a**	1.0	2	49.7	99.7
10	CH_3	**2a**	5.0	2	49.5	95.2

[a] The catalyst loading based on per [Co] unit relative to racemic epoxide.
[b] Yield of isolated azido alcohol product based on racemic epoxides (theoretical maximum = 50%).
[c] Determined by chiral GC analysis of the corresponding azido alcohol.

2.2.1.8. (R)-3-Azido-1-(1-naphthyloxy)-propan-2-ol (entry 8). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.14 (s(br), 1H, CHO**H**), 3.43 (dd, 1H, C**H**$_2$OAr), 3.52 (dd, 1H, C**H**$_2$OAr), 4.12 (m, 2H, C**H**$_2$N$_3$), 4.34–4.40 (m, 1H, C**H**OH), 6.78 (dd, 1H, Ar-**H**), 7.4 (t, 1H, Ar-**H**), 7.42–7.49 (m, 3H, Ar-**H**), 7.83 (dd, 1H, Ar-**H**), 8.22 ppm (dd, 1H, Ar-**H**); ^{13}C NMR ($CDCl_3$): δ = 53.5 (**C**H$_2$N$_3$), 69.0 (**C**HOH), 77.3 (**C**H$_2$O), 104.9 (**C**H), 120.8 (**C**H), 121.44 (**C**H), 125.2 (**C**H), 125.3 (**C**), 125.6 (**C**H), 126.4 (**C**H), 127.5 (**C**H), 134.3 (**C**), 153.7 ppm (**C**). Elemental anal. calcd for $C_{13}H_{13}N_3O_2$: C, 64.19; H, 5.39. Found: C, 64.21; H, 5.40.

Table 2
Effect of substrate:HN_3 mole ratio on the product enantioselectivity



Entry	P.O:HN_3 mole ratio	Recovered epoxide[a] e.e. (%)	Product[b] e.e. (%)
1	1:0.3	41.8	99.8
2	1:0.5	99.9	99.6
3	1:0.7	99.9	79.7
4	1:1.0	99.9	77.2

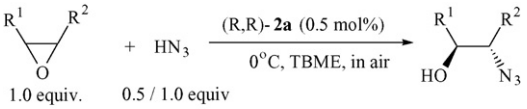
[a] The catalyst loading based on per [Co] unit relative to racemic epoxide.
[b] Determined by chiral GC.

3. Results and discussion

A series of chiral Co(salen) complexes (Scheme 1) were screened in order to identify the most enantioselective and reactive catalyst for the asymmetric ring opening (ARO) of epichlorohydrin (ECH) with HN_3 [8]. The dimeric catalysts (**2a**–**2c**) exhibited not only enhanced reactivity, but also higher enantioselectivity relative to monomeric catalysts (**1a**–**1b**).

Furthermore, catalyst **2a** was identified as the most effective one among those evaluated, and it was selected for further study (Table 1). It is evident from Table 1 (entry 8) that 0.5 mol% of catalyst loading amount can induce the reaction efficiently. Organic solvent profoundly affected the reaction rate. Interestingly, the use of TBME as a solvent dramatically increased the activity, reaching completion within 3 h (Table 3, entry 1). The use of other solvents such as CH_2Cl_2, $CHCl_3$, THF led to 18%, 21% and 33% yield, respectively, under the same conditions. The HN_3 can be generated from NaN_3 and H_2SO_4 [8] or by com-

Table 3
Asymmetric ring opening of epoxides with HN_3 catalyzed by **2a**



Entry	R^1	R^2	Time (h)	Yield[a] (%)	e.e.[b] (%)
Terminal epoxides					
1	CH_3	H	3	49.6	99.6
2	CH_2CH_3	H	4	49.3	99.0
3	CH_2Cl	H	3	49.5	99.5
4	CH_2OCH_3	H	4	49.6	99.2
5	$CH_2OCH(CH_3)_2$	H	4	49.5	99.0
6[c]	C_6H_5	H	8	49.6	92.0
7[c]	$CH_2OC_6H_5$	H	6	49.2	98.1
8[c]	CH_2O(1-naphthyl)	H	6	49.6	93.0
Meso-epoxides					
9	CH_3	CH_3	24	23.4	5.7
10	$-(CH_2)_3-$	$-(CH_2)_3-$	24	35.0	60.8
11	$-(CH_2)_4-$	$-(CH_2)_3-$	24	31.0	54.1

[a] Yield of isolated product based on racemic epoxides.
[b] Determined by chiral GC or HPLC analysis of the corresponding azido alcohol.
[c] 1.0 mol% of **2a** was used.

bining equimolar amounts of $TMSN_3$ and 2-propanol in TBME [6].

The reduction of azido alcohols in the presence of 10% Pd/C and three atmospheric pressure of hydrogen gas (Table 1) underwent quantitatively to yield optically pure corresponding amino alcohols at ambient temperature within 24 h.

In a typical example of propylene oxide ring opening, the effect of the HN_3 concentration has been observed and the results are summarized in Table 2. The asymmetric ring opening (ARO) of diverse epoxides with HN_3 were conducted under the optimized reaction conditions and the results are outlined in Table 3. Alkyl-substituted epoxides underwent ring opening with very high levels of enantioselectivity (entries 1–5), while aryl-substituted substrates (entries 6–8) were slightly less effective. These might be due to the conflicting steric and electronic factors that affect the regio- and enantioselectivity in the ring opening of terminal epoxides.

In all the cases studied, conversion of various epoxides to the corresponding azido alcohols (entries 1–8) was performed in one-pot. The products were obtained in excellent yields with very high optical purity. The kinetic resolution of racemic epoxides catalyzed by **2a** was extended to ARO of meso-epoxides. Catalyst **2a** was found to catalyze the ARO of 2,3-epoxybutane (entry 9); however, the product showed low enantioselectivity. Similarly, the reaction of cyclopentene and cyclohexene oxides with HN_3 afforded the products in 60.8% e.e., 35.0% yield (entry 10) and 54.1% e.e., 31.0% yield (entry 11), respectively, within 24 h.

Table 4
Kinetic data for the asymmetric ring opening of racemic ECH with HN_3 catalyzed by **1a–2c**

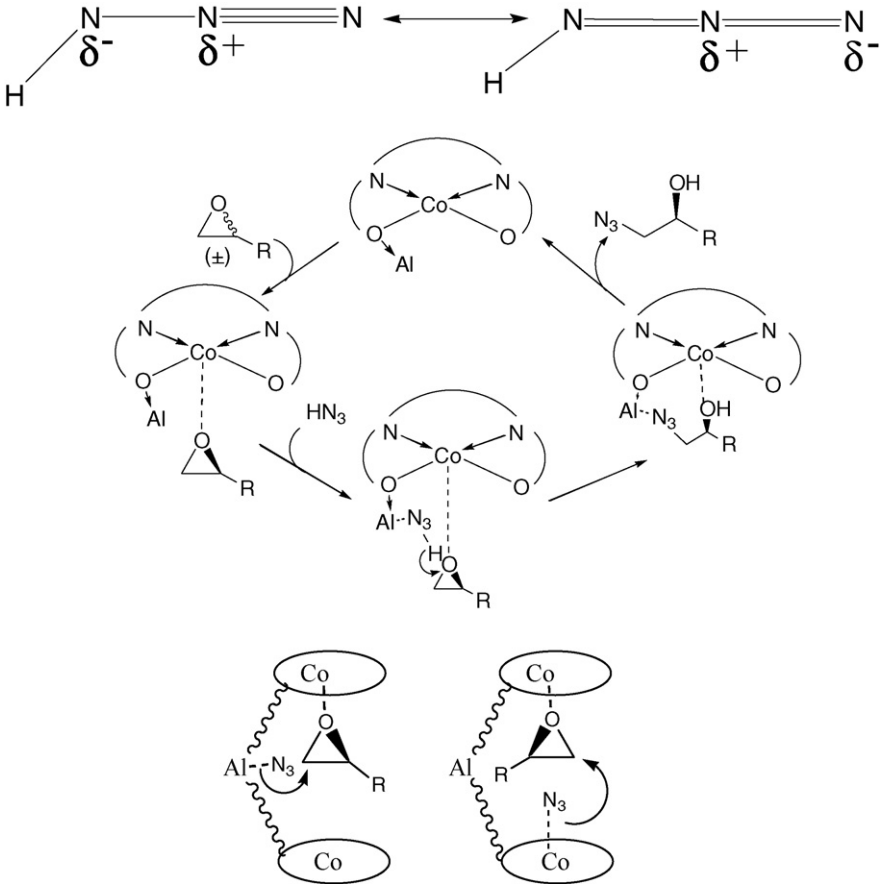
Catalyst	No. of (salen) Co unit	k_{intra}[a] ($\times 10^{-2}$ min^{-1})	k_{inter}[a] (M^{-1} min^{-1})
1a	1	32.6	11.2
2a	2	66.0	22.5
1b	1	30.3	10.1
2b	2	61.7	20.3
1c	1	25.4	8.7
2c	2	52.2	17.4

[a] Calculated from using Eq. (1).

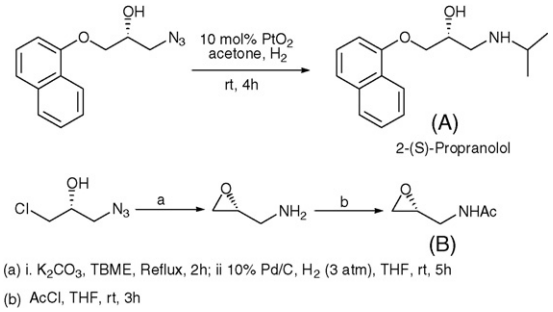
Kinetic data of the reaction of epichlorohydrin (ECH) with HN_3 catalyzed by **1a–1c** and **2a–2c** could be implemented to the two-term rate equation involving both intra- and inter-molecular components (Eq. (1)) [7,9]:

$$\text{rate} \propto k_{intra}[\text{catalyst}] + k_{inter}[\text{catalyst}]^2 \quad (1)$$

The result is consistent with participation of both inter- and intra-molecular pathway in the ARO of epoxide with HN_3 (Table 4). In contrast to the HKR of ECH with catalyst **2a** [7], even the monomer type Co–Al **1a** shows the intra-molecular pathway in the present study. It seems that Co–Al **1a** acts as



Scheme 2. Possible working model for the ARO of terminal epoxides with HN_3 catalyzed by Co–Al heterometallic complex.



Scheme 3. Practical utility of the present study.

heterometallic complexes exhibiting two different Lewis acid centers. Both Co and Al show the strong synergistic effect in the activation of epoxide and HN_3. However, dinuclear complex **2a** shows two-fold as active as corresponding monomeric analogue **1a**.

The central metal atom Co appears to activate and control the orientation of epoxide as well as nucleophile HN_3 by enabling an enantioselective ring opening of epoxides with nucleophiles. It has already been known that hydrazoic acid HN_3 exists in two resonance structures consisting of three unequivalent nitrogen atoms [10]. The nitrogen atom bearing a partially negative charge can be linked to the Al atom selectively through non-bonded interactions.

The proposed model for intra-molecular ARO of epoxides with HN_3 catalyzed by Co–Al complexes **1a** and **2a** is given in Scheme 2 which may be similar to the enantioselective ring opening of epoxides as reported by Shibasaki and coworkers [11]. The intermolecular reaction may follow the earlier reported pathway [9].

The results of the present study are feasible in the synthesis of enantiopure (*S*)-propanolol (Scheme 3A); a widely used anti-hypertensive agent (β-blocker) [12], and (*R*)-9-[2-(phosphonomethoxy)propyl]adenine (PMPA), a compound demonstrated to display prophylactic activity against SIV infection [13]. Compound B (Scheme 3) was obtained from azido alcohol by sequential ring closing, azide reduction and acetylation [14]. It is a very useful substrate for the synthesis of biological targets such as oxazolidinone U-100592; a highly promising antibacterial agent [15].

4. Conclusion

In summary, the inactive chiral Co(salen) complex for the asymmetric ring opening of epoxide with HN_3 is activated in the presence of Lewis acids of group 13 metal chlorides by forming monomeric and dimeric metal complexes. The presence of Al, Ga and In chlorides show strong a synergistic effect and the order of Lewis acidity falls $AlCl_3 > GaCl_3 > InCl_3$, in the present study. Potentially, these complexes may be useful for other valuable asymmetric catalytic reactions.

Acknowledgement

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