ChemPubSoc Europe

DOI: 10.1002/cctc.201402373

Asymmetric Hydrocyanation of Nitroolefins Catalyzed by an Aluminum(III) Salen Complex

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Chiral Al^{III} salen complexes were synthesized and used as catalysts for the asymmetric hydrocyanation of nitroolefins using 4-phenylpyridine *N*-oxide as an additive and trimethylsilyl cyanide (TMSCN) as a source of cyanide. An excellent yield of β-nitronitrile (87%) and enantioselectivity (90%) were achieved if (2-nitrovinyl)cyclohexane was used as a substrate at −15 °C in 16 h. To understand the interaction of the Al^{III} salen complex and additive, NMR and IR spectroscopic studies revealed that 4-phenylpyridine *N*-oxide acts both as an axial ligand and helps to activate the cyanide source TMSCN, which thereby increases the reactivity. A catalytic cycle was proposed based on the spectroscopic studies.

Introduction

The asymmetric hydrocyanation of nitroolefins (Michael acceptors) is an important protocol for the synthesis of bifunctional compounds. These bifunctional compounds play a key role in the synthesis of chiral building blocks such as β-amino acids,[1] 1,3-amino alcohols,[2] and 1,3-diamines and have a wider application in the pharmaceutical industry, which places them among the most versatile intermediates in organic chemistry.[3] The asymmetric cyanation of activated olefins such as α,β-unsaturated ketones[4] α,β-unsaturated imides,[5] α,β-unsaturated *N*-acylpyrroles,[6] α,β-unsaturated esters,[7] carbohydrate-derived nitroolefins,[8] and nitroalkenes are little studied compared to the asymmetric cyanation of C=O and C=N[9] bonds. Moreover, β-nitronitriles can also be synthesized from hydrazone-derived substrates[10] and conjugated nitroalkenes.[11] As a result of the strong tendency of nitroalkenes to polymerize in a basic medium, there are only four examples of asymmetric cyanide addition to nitroolefins in the literature to date.[1,12–14] The chiral hydrocyanation of nitroolefins was introduced for the first time by Ricci et al.[12] who used chiral quaternary ammonium salts, which were obtained from cinchona alkaloids, as phase-transfer catalysts with acetone cyanohydrin as a cyanide source to give a yield of β-nitronitrile up to 75% and an enantiomeric excess (*ee*) up to 72%. Later Lassaletta and co-workers[13] developed a thiourea-based cinchona quaternary ammonium salt as an organocatalyst with a cyanide counterion for the asymmetric addition of trimethylsilyl cyanide (TMSCN) to nitroolefins with excellent yields up to 98% with 86% *ee*. The first metal-based catalyst for asymmetric β-nitronitrile synthesis was reported by Wang et al. in 2012.[1] It was observed that a Ti salen complex generated in situ catalyzed the asymmetric addition of TMSCN to nitroolefins to give products with *ee* values up to 84% and yields up to 90% using 20 mol% of the catalyst at −40 to −15 °C. Recently, North and Watson[14] reported a vanadium(V) salen complex (2–3 mol%) for the hydrocyanation of nitroolefins to β-nitronitrile using TMSCN as a source of cyanide and obtained up to 89% *ee* of β-nitronitrile at 0 °C. The synthetic importance of the product explains the significant effort required to develop more catalytic systems for this versatile reaction. In view of our ongoing interest in the development of catalytic systems for asymmetric cyanation reactions, we have reported chiral transition-metal complexes for the cyanation of carbonyl compounds and imines.[15] Herein, we have explored the use of an Al^{III} salen complex as an effective catalytic system for the asymmetric cyanation of activated alkenes using 4-phenylpyridine *N*-oxide (4-PPNO) as an additive. Excellent yields (up to 93%) with high *ee* values (up to 90%) were achieved.

Results and Discussion

In our quest to develop a simple catalytic system to enhance enantioselectivity, we started searching for different metal sources and used a salen ligand reported previously by Wang et al.[1] and North and Watson.[14] To assess the viability, we initiated our systematic study by taking (2-nitrovinyl)cyclohexane as a model substrate with TMSCN as a source of cyanide. Subsequently, we scanned various metal sources for the hydrocya-

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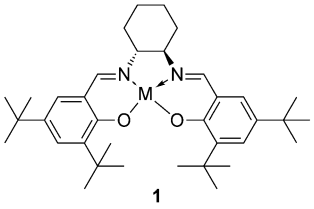
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.201402373.



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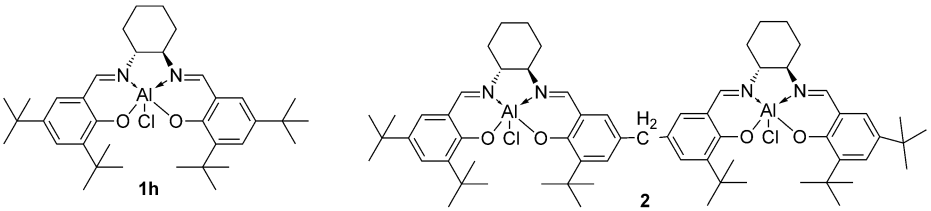
1a, M = Mn^{III}, 15 % yield, racemic
1b, M = Fe^{III}, no reaction
1c, M = Co^{III}, no reaction
1d, M = Cu^{II}, no reaction
1e, M = Pd^{II}, no reaction
1f, M = Cr^{III}, 20 % yield, racemic
1g, M = Ni^{II}, trace yield
1h, M = Al^{III}, 85 % yield, 71 % *ee*
1i, M = In^{III}, no reaction

Figure 1. Screening of metal sources.

nation of nitroolefins at room temperature in the presence of pyridine *N*-oxide (PNO), and the results are given in Figure 1. We found that no reaction occurred in the presence of Fe^{III},[16a] Co^{III},[16b] Cu^{II},[16c] Pd^{II},[16d] and In^{III}[16e] salen complexes (Figure 1).

In the presence of Mn^{III}[16f] and Cr^{III}[16g] salen complexes, racemic product was obtained with very low yields of 15 and 20%, respectively. In contrast, if we used Al^{III} as a metal source with a salen ligand (5 mol%), the reaction gave the corresponding nitrile of (2-nitrovinyl)cyclohexane with 71% *ee* in the presence of PNO (10 mol%) as an additive. A similar trend was observed



1h

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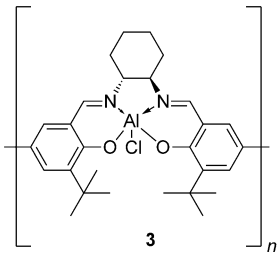

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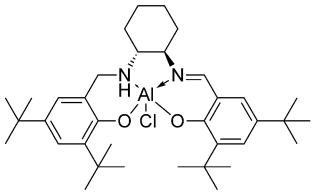

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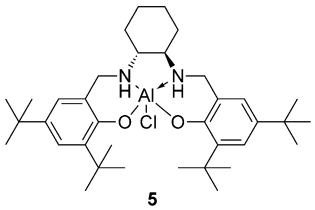

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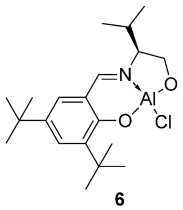

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Figure 2. Screening of Al complexes.

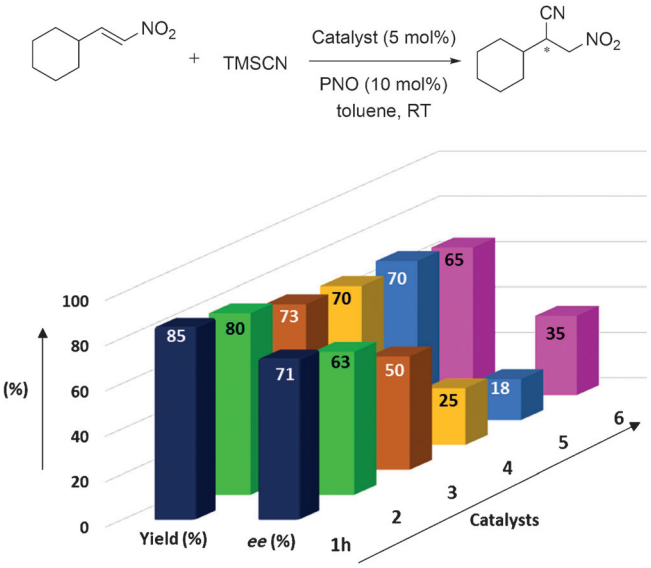


Figure 3. Screening of catalysts.

in the asymmetric cyanation of imines reported by Sigman and Jacobsen.[17] We took Al as our best metal source and screened various chiral ligands (Figure 2). The results are given in Figure 3. In our initial screening of Al^{III} catalysts, we have used monomer,[17] dimer,[18a] polymer,[18b] salalen (half reduced salen),[18c] salan (reduced salen),[18d] and amino alcohol based ligands.[18e] We observed that the chiral monomeric Al^{III} salen complex is an effective catalyst in terms of reactivity and enantioinduction (Figure 3). Next, with Al as our best metal source and by using a simple salen ligand as the active catalyst (**1h**), we checked the other parameters to optimize the reaction conditions to improve the results, particularly enantioselectivity, using (2-nitrovinyl)cyclohexane as a model substrate and TMSCN as a cyanide source. The role of additives in asymmetric cyanation is well documented.[19] Therefore, we first explored the effect of other additives, which are used widely in cyanation reactions, and we kept the other parameters constant. Initially, we checked isopropyl alcohol (10 mol%) and triphenylphosphine (10 mol%; Figure 4) as additives, but only a trace amount of product was detected. We next used triphenylphosphine oxide as an additive and observed 73% *ee* with a moderate yield of 51% at room tempera-

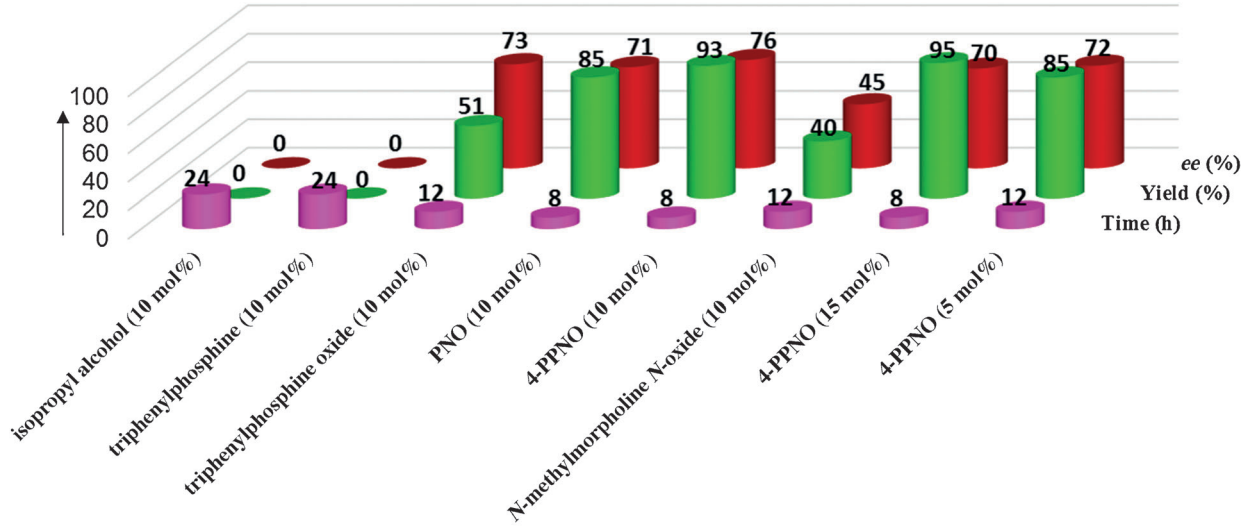
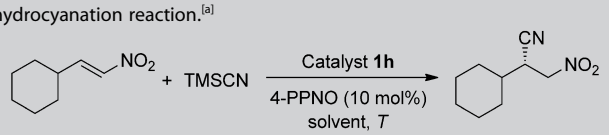


Figure 4. Effect of additives on the asymmetric hydrocyanation reaction catalyzed by **1 h**.

ture in 12 h. We conducted the hydrocyanation reaction in the presence of other *N*-oxides such as 4-PPNO and *N*-methylmorpholine *N*-oxide as additives, however, a better result in terms of yield (93%) and *ee* (76%) was achieved with 4-PPNO (Figure 4). Then we optimized the amount of 4-PPNO. If we lowered the 4-PPNO loading (5 mol%), there was a decrease in the product *ee* (72%) and yield (85%), whereas an increased amount of 4-PPNO (15 mol%) led to a slightly increased reactivity (95%) but a decreased enantioselectivity[20] (70%). Therefore, 10 mol% of additive loading was taken as an optimum (Figure 4).

Table 1. Effect of catalyst loading and temperature on the asymmetric hydrocyanation reaction.[a]



Entry	Catalyst [mol%]	Solvent	*T* [°C]	*t* [h]	Yield[b] [%]	*ee*[c] [%]
1	5	toluene	RT	8	93	76
2	10	toluene	RT	8	96	73
3	2	toluene	RT	12	83	70
4	5	CH_2Cl_2	RT	6	93	45
5	5	$CHCl_3$	RT	6	85	68
6	5	THF	RT	24	70	61
7	5	acetonitrile	RT	36	40	38
8	5	toluene	10	8	93	81
9	5	toluene	0	12	90	83
10	5	toluene	−15	16	87	90
11	5	toluene	−25	24	70	91

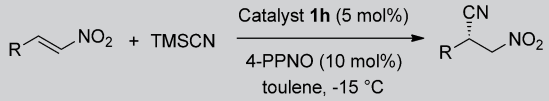
[a] The enantioselective hydrocyanation reaction of (2-nitrovinyl)cyclohexane (0.16 mmol) was performed with catalyst **1 h** and 4-PPNO (10 mol%) in toluene using TMSCN (0.25 mmol) as a source of cyanide. [b] Isolated yield. [c] *ee* Values were determined by chiral HPLC using an OD-H column.

Furthermore, the catalyst loading of 5 mol%, which was used in the preceding experiments was found to be optimum (Table 1, entry 1) as it was observed that by decreasing the catalyst loading (2 mol%) the product yield (83%) and *ee* (70%) decreased (Table 1, entry 3). However, an increased catalyst loading (10 mol%) results in a faster reaction with a marginal decrease in *ee* (73%), and the product yield was increased slightly (Table 1, entry 2).

For the solvent variation, toluene, CH_2Cl_2, THF, and acetonitrile were used to perform the asymmetric cyanation reaction under the conditions optimized above (Table 1, entries 1, 4–7). However, toluene remained the solvent of choice (Table 1, entry 1). Furthermore, variation in reaction temperature (Table 1, entries 1, 8–11) revealed that a decreased temperature of −15 °C had a beneficial effect on the product *ee* (from 74% at room temperature to 90%) though the reaction took longer (from 8 h at room temperature to 16 h) to reach completion. A further decrease of the temperature (−25 °C) did not have a positive impact on the product *ee* as the reaction became very sluggish (24 h). Therefore, −15 °C (Table 1, entry10) was taken as the optimum for further studies.

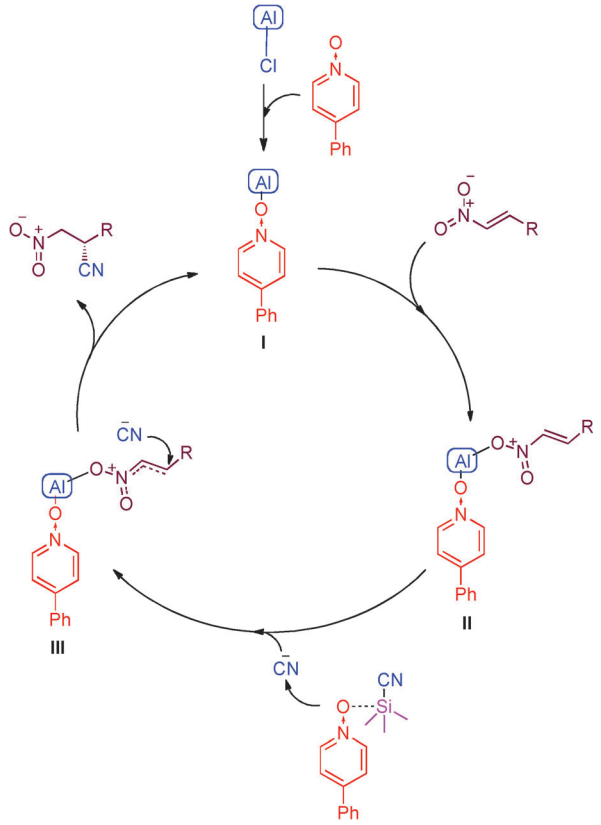
After we established the reaction parameters for the use of catalyst **1 h** in the asymmetric cyanation reaction with the substrate (2-nitrovinyl)cyclohexane and TMSCN at −15 °C, we extended this protocol to various substituents derived from other aliphatic aldehydes to check the generality of our system, and the results are summarized in Table 2. The results of these studies do not suggest a trend to indicate the effect of the electronic and steric properties of the substrates used. We found that the catalytic system works well (*ee* up to 90% and yield up to 93%) with various nitroolefins irrespective of their structure or chain length.

Table 2. Substrate scope in the synthesis of β-nitronitriles catalyzed by **1 h**.



Entry	R	*t* [h]	Yield [%][b]	*ee* [%][c]
1	cyclohexyl (**2 a**)	16	87	90 (*S*)[d,e]
2	$CH_3CH_2CH_2$– (**2 b**)	18	85	80
3	$CH_3(CH_2)_4$– (**2 c**)	12	87	82
4	$CH_3(CH_2)_5$– (**2 d**)	16	85	80
5	$(CH_3)_2CH$– (**2 e**)	14	82	82
6	$(CH_3)_2CHCH_2$– (**2 f**)	12	93	68
7	$(CH_3)_3C$– (**2 g**)	16	90	88
8	$(CH_3CH_2)_2CH$– (**2 h**)	16	81	86
9	$C_6H_5CH_2CH_2$– (**2 i**)	20	88	76

[a] The enantioselective hydrocyanation reaction of (2-nitrovinyl)cyclohexane (0.16 mmol) was performed with catalyst **1 h** (5 mol%) and 4-PPNO (10 mol%) in toluene using TMSCN (0.25 mmol) as a source of cyanide. [b] Isolated yield. [c] *ee* Values were determined by chiral HPLC using OD-H, AD-H and IC columns. [d] The absolute configuration was determined by comparison of the optical rotation values with those in the literature.[1,14] [e] Reaction performed on 10 mmol scale.



Scheme 1. Proposed catalytic cycle for the asymmetric cyanation of nitroolefins.

Mechanism

To understand the interaction of additives, substrate, and cyanide source with complex **1 h** and to explain the outcome of these interactions, a series of experiments were performed. Based on the experimental results and analysis, a suitable mechanism is proposed (Scheme 1). It is well known in the literature that the *N*-oxide plays a significant dual role in asymmetric cyanation reactions, it acts as an axial ligand and also activates the cyanide source (TMSCN).[21] There has been no mechanistic investigation on the interaction of *N*-oxide with **1 h** in asymmetric cyanation reactions. To address this issue and to study the effect of this combination in the asymmetric cyanation of nitroolefins, we have used spectroscopic studies as an effective tool to correlate the results. In our initial studies, to confirm the interaction of 4-PPNO with **1 h**, both ^{27}Al and ^{1}H NMR spectra were recorded in $CDCl_3$. The ^{27}Al NMR spectrum shows a significant upfield shift ($\delta = 68.66$ to 66.88 ppm; Figure 5) of Al after interaction with 4-phenylpyridine *N*-oxide, which is attributed to a five-coordinate Al complex (**I**; Scheme 1). This effect is also observed in the ^{1}H NMR spectrum; the –C*H*=N– proton of **1 h** was shifted slightly downfield ($\delta = 8.284$ to 8.306 ppm; Figure 6). A similar phenomenon was observed by LC–MS, which indicated the molecular ion peak (742) of 4-PPNO coordinated to **1 h** clearly. This is further supported by IR spectroscopy (the C=N- > M band shifts from $\tilde{\nu} = 1619$ to 1635 cm^{-1} (Supporting Information). UV/Vis spectra recorded for **1 h** and 4-PPNO in acetonitrile showed a redshift of the metal-to-ligand charge transfer

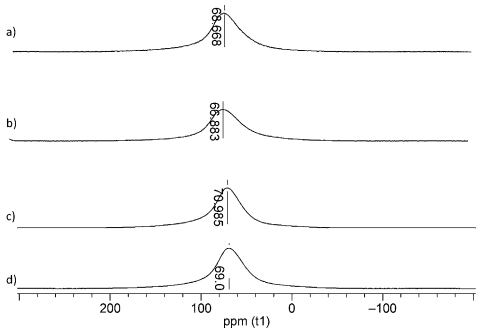


Figure 5. ^{27}Al NMR spectra in $CDCl_3$ of a) complex **1 h**, b) complex **1 h** with 4-PPNO, c) complex **1 h** with 4-PPNO followed by the addition of substrate, and d) reaction mixture containing complex **1 h**, 4-PPNO, substrate, and TMSCN.

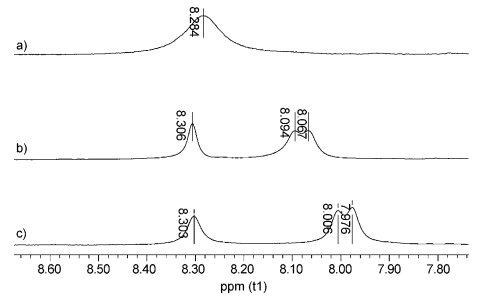


Figure 6. ^{1}H NMR spectra in $CDCl_3$ of a) complex **1 h**, b) complex **1 h** with 4-PPNO, and c) complex **1 h** with 4-PPNO followed by the addition of substrate.

(MLCT) band at $\lambda = 359$ nm with hyperchroism upon the generation of the five-coordinate complex (Supporting Information). Subsequently, the nitroolefin was added to the five-coordinate Al^{III} salen complex, and we presume that it occupies the vacant sixth position. This was confirmed by the downfield shift ($\delta = 66.88$ to 70.98 ppm) seen in the ^{27}Al NMR spectra. Then TMSCN was added, and the presence of excess 4-PPNO polarizes the cyanide source to generate the cyanide ion that attacks the stereochemically bound nitroolefin to result in the enantioenriched product. After the formation of the product, the upfield shift ($\delta = 70.98$ to 69.04 ppm) in the ^{27}Al NMR spectrum indicates the generation of the catalyst.

Conclusions

The present protocol was also applied successfully on a 10 mmol scale. This work has introduced Al^{III} as an alternative metal source for the synthesis of chiral β-nitronitriles by the reaction of nitroolefins and trimethylsilyl cyanide in the presence of 4-phenylpyridine *N*-oxide as an additive. The protocol was used to prepare a series of β-nitronitriles with moderate to high enantioselectivities up to 90% and yields up to 93%. A probable mechanism was proposed according to spectroscopic studies.

Experimental Section

Materials and characterization

Different aldehydes and reagents were used as received. All the solvents used in the present study were dried by known purification techniques.[22] NMR spectra were obtained by using a Bruker F113 V spectrometer (500/200 MHz) and are referenced internally with Me_4Si. Splitting patterns were reported as s, singlet; d, doublet; dd, doublet of doublet; t, triplet; m, multiplet. Enantiomeric excess (*ee*) values were determined by HPLC by using Daicel Chiralcel OD-H and AD-H and Daicel Chiralpak IC chiral columns with 2-propanol/hexane as the eluent. Optical rotations were determined by using an automatic polarimeter. For product purification, flash chromatography was performed with silica gel 100–200 mesh. The Al^{III} salen complexes was synthesized according to methods reported previously.[17,18e,23] Nitroalkenes were prepared according to the reported literature.[24]

Reaction procedure

To a solution of chiral Al complex (0.008 mmol) in dry toluene (0.7 mL), 4-PPNO (0.0161 mmol) was added, and the mixture was stirred under a N_2 atmosphere. Subsequently, nitroalkene (0.161 mmol) was added, and the resulting solution was cooled to $-15\,^{\circ}C$. To the cooled solution, TMSCN (0.25 mmol) was added dropwise over 30 min. The reaction was monitored by TLC. On completion, $NaHCO_3$ was added to quench the reaction, and the product was extracted into CH_2Cl_2 (3×10 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and the solvent was removed by using a rotary evaporator to obtain the desired product, which was further purified by column chromatography using hexane/ethyl acetate (90:10). The purified products were characterized by NMR spectroscopy, which was in agreement with the reported values.[1,14]

Acknowledgements

The authors are thankful to CSIR for a junior research fellowship, a senior research fellowship, and CSIR Network Project on Catalysis for financial assistance. A.J. is also thankful to AcSIR for Ph.D. registration and "Analytical Discipline and Centralized Instrumental Facilities" for providing instrumentation facilities. CSIR-CSMCRI communication no. DIMC-52/2014.

Keywords: aluminum · asymmetric catalysis · enantioselectivity · homogeneous catalysis · N,O ligands

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Received: May 23, 2014
Published online on August 1, 2014