

Highly Active Polymer-Supported (Salen)Al Catalysts for the Enantioselective Addition of Cyanide to α,β -Unsaturated Imides

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Abstract: In this contribution, we describe polymer-supported (*R,R*)-(salen)AlCl complexes that were immobilized on poly(norbornene)s and display excellent activities and enantioselectivities as catalysts for the 1,4-conjugate addition of cyanide to α,β -unsaturated imides. These supported catalysts could be recycled up to 5 times without compromising catalyst activities or selectivities. Furthermore, the catalyst loadings could be reduced from 10–15 mol%, the common catalyst loadings for non-supported (salen)Al catalysts, to 5 mol%, a decrease of metal con-

tent by 50–66%, without lowering product yields or enantioselectivities. Kinetic studies indicated that the polymer-supported catalysts are significantly more active than their corresponding unsupported analogues, which makes this catalyst system key to a successful implementation of this catalytic transformation into the fine chemical and pharmaceutical industries.

Keywords: aluminum; asymmetric catalysis; conjugated addition; salen; supported catalysis

Introduction

Catalysis plays a key role in the efficient and facile synthesis of chiral organic compounds and biomolecules in the pharmaceutical and fine chemical industry. Metallated salen catalysts, first reported by Jacobsen and Katsuki,^[1–6] are among the most versatile catalysts for the enantioselective synthesis of organic compounds catalyzing a diverse set of organic transformations ranging from 1,4-conjugate additions^[7–11] and 1,2-additions^[12–14] to environmentally benign ones such as the CO₂ addition to epoxides^[15–18] and the formation of polylactide from renewable resources.^[19–21] The enantioselective 1,4-addition reaction is of particular interest because it is a key transformation in the syntheses of high therapeutic value compounds in the pharmaceutical industry. Furthermore, to obtain high selectivities for this transformation is often not a trivial task. Jacobsen and co-workers have reported the employment of (salen)Al complexes that catalyze the addition of cyanides to α,β -unsaturated imides in high yields and outstanding enantioselectivities, often higher than 95% *ee*.^[22] One major drawback of the employment of (salen)Al complexes is the catalyst loading since the CN addition reaction requires catalyst loadings of 10 to 15 mol%. The CN conjugate ad-

dition reaction is hypothesized to follow a bimetallic pathway^[22] – a cooperative dual catalysis approach employing a combination of (salen)Al and (pybox)-lanthanide complexes has been shown to allow for lower catalyst loadings of 7 mol% and to improve reaction rates.^[23] We rationalize that another approach, the attachment of the (salen)Al complexes onto a support might bring the individual catalytic sites into close proximity of each other allowing for interactions with each other and therefore higher activities and lower catalyst loadings. This strategy would circumvent the use of a second metal while having the additional advantage of easy catalyst removal and recycling. Herein, we present such a strategy and describe a fully recyclable and polymeric (salen)Al system that is highly active and selective for the addition of cyanides to α,β -unsaturated imides while allowing for significantly (up to 50%) lower catalyst loadings.

Metallosalen catalysts have been immobilized on inorganic, polymeric, and dendritic supports in order to facilitate easy recovery and reusability.^[24–33] In addition, for reactions involving a bimetallic pathway the increased local concentration of the catalysts on the support facilitates faster reactions with lower catalyst loadings.^[31,34–36] Our research group has previously demonstrated that the selectivity and activity of sa-

len(Co) and salen(Mn) catalysts for the hydrolytic kinetic resolution (HKR) and asymmetric epoxidation reactions can be improved significantly in a modular fashion by varying their catalyst site density along a polymeric backbone.^[37,38] In all cases, the polymer-supported catalysts could be precipitated easily after completion of the reaction and in some cases reused up to four times. For example, we have reported macrocyclic oligomeric salen(Co) catalysts with excellent activities for the HKR reaction of epoxides that allow for the reduction of catalyst loadings to 0.01 mol% for a wide variety of substrates without reducing the yields or enantioselectivities of the reaction.^[34] This example illustrates that soluble supports can be employed not only to remove the metal species after the reaction and/or to recycle the catalyst but also to engineer catalysts with higher efficiencies and selectivities than their corresponding non-supported analogues. Herein, we translate our findings with the salen(Co) system to salen(Al) catalysts and report the first example of a supported salen(Al)Cl catalyst for the conjugate addition of cyanide to unsaturated imides using poly(norbornene) as the polymeric support.

Our catalyst-support system is based on three key components: (i) the catalytically active moiety, (ii) the polymer backbone and (iii) the linker connecting them (Figure 1). We employ an asymmetrically modi-

ed catalysts can be isolated readily from reaction mixtures and reused upto 3 cycles.^[38] Since the addition reaction follows a bimetallic pathway, a crucial component in the research design is the linker. A flexible linker is desirable for the attachment of the salen to the polymer backbone in order to facilitate interactions between two metal centers as well as access of reagents to the catalysts.^[42] Furthermore, we mimic the optimal Jacobsen catalyst as close as possible and employ a tertiary carbon as the point of attachment between the linker and the catalyst. The supported catalyst system that incorporates all these desirable design elements is **1**. To our knowledge this is the closest supported analogue of the Jacobsen catalyst at the catalytic site due to the incorporation of the tertiary carbon atom in the linker.

Results and Discussion

The synthesis of the supported salen **1** can be envisaged by two pathways; either *via* the polymerization of a fully metallated monomer or by the polymerization of a non-metallated salen monomer followed by the metallation step. Since synthetic post-polymerization manipulations do not always go to completion, we pursued the synthesis of the metallated salen monomer **8**. The synthesis of **8** is described in Scheme 1. The first step involved a one-pot synthesis of unsymmetrical salen ligands.^[43,44] Salicaldehyde **3** was reacted with (*R,R*)-diaminocyclohexane monohydrogen chloride **2** to afford the monoammonium imine **4**, which was directly converted to the corresponding amine using triethylamine. Subsequently, aldehyde **5** which was synthesized in 3 steps from 2-*tert*-butylphenol as described in the literature^[43] was added affording the unsymmetrical salen ligand **6** in 47% yield. Coupling of **6** with the norbornene *exo*-acid under DCC/DMAP conditions gave the unmetallated monomer **7** in 76% yield. Metallation of **7** with diethylaluminum chloride afforded monomer **8** in 91% yield. Monomer **8** was then subjected to ROMP at room temperature using chloroform as the solvent and Grubbs' 3rd generation initiator (a 50:1 monomer to initiator ratio was employed) to afford catalyst **1** in 87% isolated yield. The polydispersity index of **1** was 1.32 as determined by gel-permeation chromatography.

With the polymeric catalyst **1** in hand, we investigated its activity for the enantioselective 1,4-addition reaction. All reactions were carried out at 45 °C by adding TMSCN and isopropyl alcohol to the imide derivative in the presence of **1**.^[45] To screen the initial catalyst activity as well as the substrate scope, 15 mol% of the catalyst was used. The reactions could not be monitored by thin layer chromatography or NMR spectroscopy as the flask was sealed after the

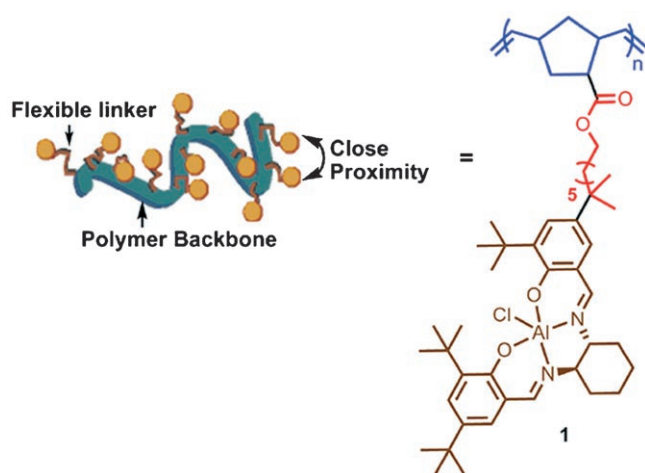
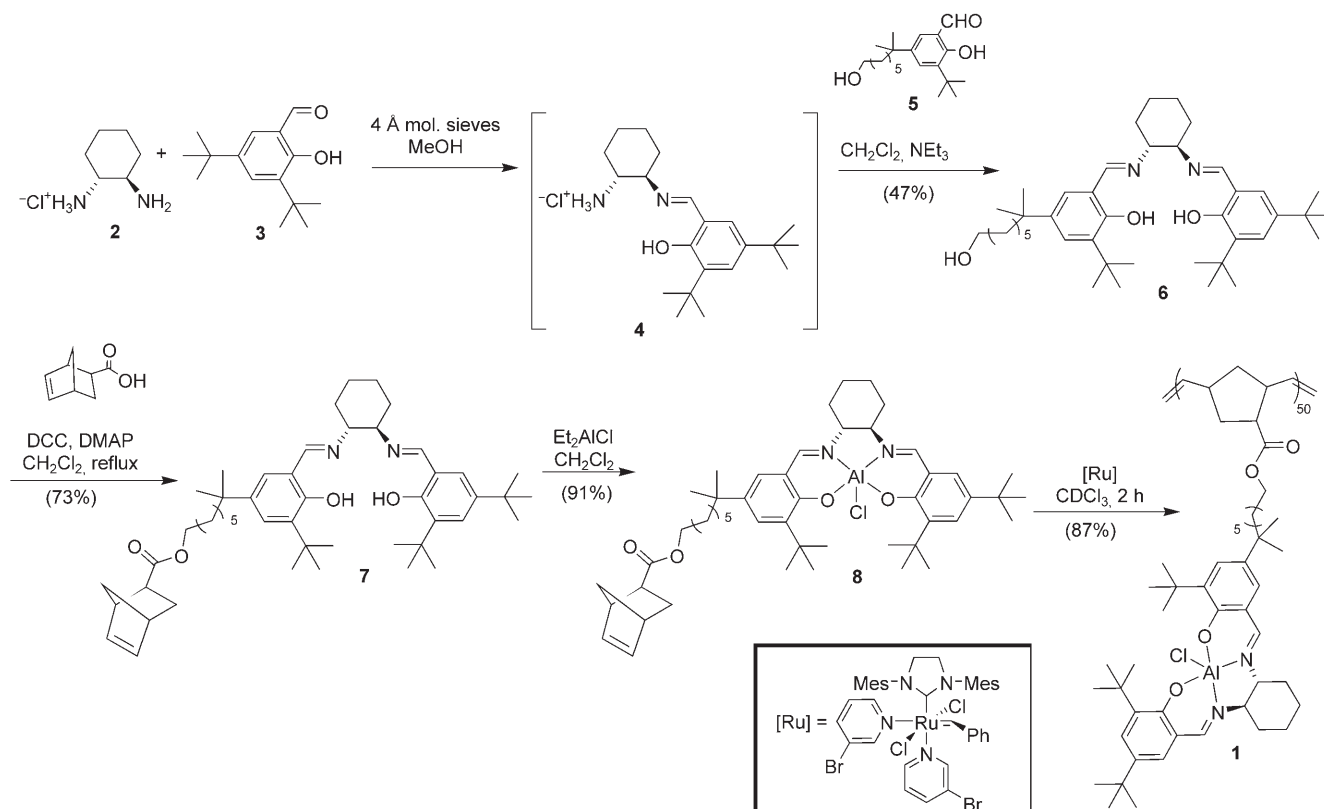


Figure 1. Schematic representation of the research design and catalyst **1** employed in this study.

fied (*R,R*)-salen(AlCl) complex as the catalyst for the 1,4-conjugate addition of cyanides to α,β -unsaturated imides. Poly(norbornene) is an attractive choice for the polymer backbone owing to the ease of its functionalization as well as synthesis *via* highly functional group tolerant and controlled ring-opening metathesis polymerization (ROMP).^[39–41] Furthermore, we have demonstrated before that poly(norbornene)-support-

Scheme 1. Synthesis of polymeric catalyst **1**.

addition of all reagents to prevent hydrogen cyanide leakage. Therefore, the sealed reaction was allowed to stir for 36 h in order to ensure complete conversions of all starting materials. We investigated a variety of α,β -unsaturated imide substrates such as primary, secondary, tertiary alkyl and phenyl terminated substituents (Table 1).^[46] Similar compounds have been studied as substrates for the addition of nucleophiles to α,β -unsaturated imides with the non-supported analogue of **1** providing an excellent platform to compare the activity and selectivity of **1** to the original salen(Al) Jacobsen catalyst.^[22]

In all cases, the (*S*)-adduct was selectively formed with enantiomeric excesses (*ees*) of 98–99% (but for the use of substrate **9e**) and high conversions (88–96%) (entries 1–4) indicating that **1** is a highly active catalyst. Similar yields (90–92%) and *ees* (94–98%) were obtained for entries 1–3 with the 10 mol% of the original Jacobsen catalyst analogue of **1** under similar reaction conditions.^[22,47] Only the catalysis of *tert*-butyl-substituted imide (**9e**) as substrate resulted in lower yields (entry 5) than that for the Jacobsen catalyst (90%). However, the *ee* for the adduct **10e** still remained high (89%). We rationalize that the lower conversions in this case may be attributed to the steric congestion caused at the catalytic site by the bulky *tert*-butyl groups.

After establishing that **1** is as active and selective as its non-supported analogue, we targeted one of the primary objectives of our study, the recycling and reuse of the supported (salen)Al catalysts. For all re-

Table 1. The addition of cyanide to various α,β -unsaturated imides catalyzed by **1**.

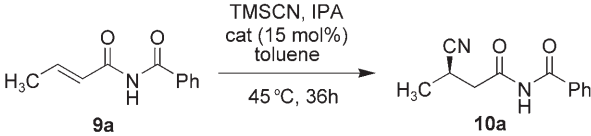
$\text{R}-\text{CH}=\text{CH}-\text{C}(=\text{O})\text{NH}-\text{C}(=\text{O})\text{Ph} \xrightarrow[\text{45 } ^\circ\text{C, 36 h}]{\text{TMSCN, IPA cat (15 mol\%), toluene}} \text{R}-\text{CH}(\text{CN})-\text{CH}_2-\text{C}(=\text{O})\text{NH}-\text{C}(=\text{O})\text{Ph}$			
No.		R	Yield ^[a] (<i>ee</i>) ^[b]
1	9a	CH ₃	10a 96% (98%)
2	9b		10b 89% (99%)
3	9c		10c 88% (99%)
4	9d		10d 93% (98%)
5	9e		10e 22% (89%)

^[a] Isolated yield.

^[b] Enantiomeric excess determined by HPLC analysis using a chiral Pirkle-L-leucine column

cycling studies, we employed **9a** as the substrate of choice. Again, all recycling reactions were carried out at 45 °C and stopped after 36 h. After complete reaction, we were able to separate the polymer easily from the reaction mixture by simply adding ethyl acetate. The polymer quantitatively precipitated out of the solution and the remainder of the reaction mixture was isolated by decantation. We then tested the activity of the precipitated and recycled polymer under identical reaction conditions for subsequent catalytic cycles. Table 2 describes the use of one supported catalyst **1** in five catalytic cycles.

Table 2. Studies demonstrating the reusability of catalyst **1**.

		
No.	Catalyst	Yield ^[a] (ee) ^[b]
1	Polymer 1	96% (98%)
2	Cycle 2	95% (98%)
3	Cycle 3	90% (98%)
4	Cycle 4	90% (98%)
5	Cycle 5	95% (96%)

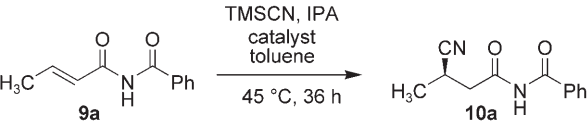
^[a] Isolated yield.

^[b] Enantiomeric excess determined by HPLC analysis using a chiral Pirkle-L-leucine column.

As can be seen in Table 2, catalyst **1** could be recycled up to 5 times with no significant loss in yield or enantioselectivity of the product (entries 1–5). This presents the first example of a (salen)Al catalyst that can be recycled and reused 5 times with no appreciable loss in conversions demonstrating the superiority of the supported version of the salen (Al) catalyst in comparison to its non-supported analogue.

Recycling the catalyst is one strategy to maximize product formation while minimizing the amount of needed Al. The second strategy for lowering the Al content and the main objective of our study was to determine whether the catalytic activity of **1** was retained at lower catalyst loadings due to an increase in local catalyst concentration facilitating the bimetallic pathway. To determine if our bimetallic enhancement hypothesis holds true in this system, we investigated whether we can lower the catalyst loading in the reaction mixture while keeping the activity and selectivity of the catalytic transformation high. Table 3 describes

Table 3. The effect of catalyst loading on yield and enantioselectivity of CN addition.

		
No.	Catalyst loading	Yield ^[a] (ee) ^[b]
1	15 mol%	96% (98%)
2	10 mol%	96% (98%)
3	5 mol%	96% (98%)
4	3.8 mol%	90% (98%)
5	1 mol%	17% (98%)

^[a] Isolated yield.

^[b] Enantiomeric excess determined by HPLC analysis using a chiral Pirkle-L-leucine column.

our results of varying the catalyst concentration for the transformation. We were able to lower the catalyst loading for the transformation of **9a** to **10a** from 10 mol% to 5 mol% without changing the yields or enantioselectivities of product formation. Even a catalyst loading of 3.8 mol% resulted in high yields and outstanding selectivities. Only when reducing the catalyst concentration below 3.8 mol% did we observe significantly lower yields. However, even in these cases we observed outstanding selectivities. This result clearly demonstrates the positive enhancement effect of the support on the catalytic activity of the transformation.

In order to gain a better understanding of the activity of **1** and to compare it to its non-supported analogue, we measured the kinetics for the reaction of **9a** with TMSCN using 15 mol% and 5 mol% of **1** and the non-supported Jacobsen catalyst using ¹H NMR spectroscopy. Since the reaction flask had to be sealed during the progress of the reaction, the kinetics studies were performed by splitting the reaction into 5–6 NMR tubes and quenching the reaction in each NMR tube at different time intervals to determine product conversions.^[22] The reaction progressed significantly faster with the supported catalyst when compared to its small-molecule analogue.^[48] The catalytic transformation using 15 mol% of **1** is complete within 6 h while the same catalyst loading for the non-supported analogue resulted in less than 50% conversions. Furthermore, the differences in reaction rates between the catalyst loadings of 15 and 5 mol% are small for the polymer-supported catalyst **1** (both reactions are complete within 6–8 h) and not as significant as that for the homogenous analogue. The use of 5 mol% of the non-supported catalyst resulted in no significant

catalytic transformation and product formation during the time-scales investigated. Again, these results clearly demonstrate the superiority of the supported catalyst system.

Conclusions

We have developed a highly active poly(norbornene)-supported (salen)AlCl catalyst for the enantioselective addition of cyanide to α,β -unsaturated imides. The catalyst is versatile and possesses the ability to catalyze the conjugate addition to a variety of substrates in excellent yields. We were able to successfully recycle the catalyst 5 times with no appreciable loss in activity. High yields (95%) and selectivities (96%) were obtained even for the 5th cycle of the catalyst. In addition, we were able to lower the catalyst loadings for the reaction from 10–15 mol%, the common catalyst loadings for all non-supported catalyst analogues, to 5 mol% with identical yields and enantioselectivities. Furthermore, kinetic studies indicated that the activity of the polymeric catalyst is significantly higher than that of the unsupported analogue suggesting an enhancement effect of the bimetallic pathway due the close proximity of the catalytic sites to each other. As a result of its excellent selectivities and activities, as well as recyclability and low catalyst loadings, the catalyst system described herein is an excellent candidate for applications in the synthesis of chiral fine chemicals and pharmaceuticals.

Experimental Section^[49]

Salen Ligand 6

(*R,R*)-1,2-Diaminocyclohexane monohydrochloride **2** (441 mg, 2.93 mmol, 1 equiv.), methanol (24 mL) and some 4 Å molecular sieves were added to a flame-dried 100-mL Schlenk flask equipped with a stir bar under an atmosphere of Ar. Subsequently, 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde **3** (687 mg, 2.93 mmol, 1 equiv.) was added. The solution was allowed to stir for 3 h followed by the addition of salicylaldehyde **5**^[43] (940 mg, 2.93 mmol, 1 equiv.) as a solution in CH₂Cl₂ (24 mL) and NEt₃ (817 μ L, 5.86 mmol, 2 equiv.). The reaction mixture was stirred for an additional 3 h and then concentrated under vacuum to afford a brown residue. The residue was dissolved in CH₂Cl₂ (200 mL) and aqueous HCl (200 mL, 1 M). The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (2 $\times$ 100 mL). The combined organic layers were washed with water and saturated NaCl solution, dried over anhydrous magnesium sulfate, filtered and concentrated under vacuum to afford a brown solid. The crude product was subjected to flash column chromatography (Gradient elution. 10:1 $\rightarrow$ 3:1 hexane/EtOAc) to afford the salen **6** as a yellow solid; yield: 870 mg (47%).

Salen-Norbornene Ester 7

Salen **6** (867 mg, 1.37 mmol, 1 equiv.) and CH₂Cl₂ (25 mL) were added to a flame-dried round-bottomed flask (100 mL) equipped with a magnetic stir bar and a reflux condenser. To the solution, DCC (311 mg, 1.51 mmol, 1.1 equiv.), norbornene *exo*-acid (189 mg, 1.37 mmol, 1 equiv.), and DMAP (catalytic) were added. The reaction mixture was heated under reflux for 12 h under an atmosphere of Ar, following which the reaction mixture was diluted with CH₂Cl₂ (20 mL) and filtered. The filtrate was dried over magnesium sulfate, filtered and concentrated under vacuum to afford a yellow solid. The crude mixture was subjected to flash column chromatography (20:1 hexane/EtOAc) to afford the ester **7** as a yellow solid; yield: 785 mg (76%).

Al-Salen Monomer 8

Salen-norbornene **7** (776 mg, 1.03 mmol, 1 equiv.) and CH₂Cl₂ (7.6 mL) were added to a flame-dried Schlenk flask (50 mL) equipped with a magnetic stir bar in an atmosphere of argon. To the solution diethylaluminum chloride (573 μ L, 1.03 mmol, 1 equiv.) was added slowly. The reaction mixture was allowed to stir for 3 h, following which the solvents were removed under vacuum to afford a yellow solid. The solid was rinsed with cold hexane at 0 °C and concentrated under vacuum to afford the Al-salen **8** as a yellow solid; yield: 760 mg (91%).

Al-Salen 50-mer 1

Monomer **8** (46.0 mg, 56.6 μ mol, 50 equiv.), 3rd generation Grubbs' catalyst (1.0 mg, 1.1 μ mol, 1 equiv.) and deoxygenated CDCl₃ (3.7 mL) were added to a scintillation vial equipped with a magnetic stir bar. The polymerization was complete in 10 min as indicated by ¹H NMR spectroscopy. The reaction mixture was stirred for an additional hour following which the polymer was precipitated out of Et₂O (20 mL) and isolated *via* centrifugation as a yellow solid. The crude polymer was subjected to washings with Et₂O (2 $\times$ 20 mL) and centrifugation to afford the 50-mer **1** as a yellow solid; yield: 40 mg (87%).

General Procedure for the Cyanide Addition to α,β -Unsaturated Imides

Caution: Trimethylsilyl cyanide and hydrogen cyanide are highly toxic and should be handled extremely carefully in a fume hood as per the experimental protocol mentioned below.

An appropriate amount of catalyst **1** was added to a Schlenk tube (25 mL). The catalyst was dried azeotropically with toluene (2 $\times$ 50 μ L). Subsequently the imide **9** (0.26 mmol, 1 equiv.), toluene (80 μ L) and TMSCN (132 μ L, 1.06 mmol, 4 equiv.) were added to the flask. The reaction mixture was heated gently with a heat gun and immersed in an oil bath at 45 °C, following which 2-propanol (81 μ L, 1.06 mmol, 4 equiv.) was added. The flask was sealed and allowed to stir for 36 h. Upon completion of the reaction, the flask was vented into a FeSO₄ solution to quench unreacted HCN gas. After allowing the HCN to bubble out for 5–10 min, the solvent was removed under vacuum. To the residue EtOAc (15 mL) was added to solubilize the crude reac-

tion mixture while the polymer precipitated from the solution. The crude reaction mixture was separated from the polymer by decantation. The polymer was rinsed with EtOAc (4 × 15 mL) and the combined supernatant solutions were concentrated under vacuum to afford an off-white solid. The crude product was purified by flash column chromatography to afford the pure product.

N-[3-(S)-Cyanobutyl]benzamide 10a:^[22] Flash column chromatography with 3:1 hexane/EtOAc afforded the product **10a** as a white solid; yield: 55 mg (96%). The *ee* was found to be 98%, 254 nm, 5% ethanol in hexane, 0.7 mL min⁻¹, *t_r*(major) = 73.1 min, *t_r*(minor) = 80.0 min.

N-[3-(S)-Cyanohexanoyl]benzamide 10b:^[22] Flash column chromatography with 3:1 hexane/EtOAc afforded the product **10b** as a white solid; yield: 55 mg (96%). The *ee* was found to be 98%, 254 nm, 5% ethanol in hexane, 0.7 mL min⁻¹, *t_r*(major) = 73.1 min, *t_r*(minor) = 80.0 min.

N-[3-(S)-Cyano-4-methylpentanoyl]benzamide 10c:^[22] Flash column chromatography with 3:1 hexane/EtOAc afforded the product **10c** as a white solid; yield: 55 mg (96%). The *ee* was found to be 98%, 254 nm, 5% ethanol in hexane, 0.7 mL min⁻¹, *t_r*(major) = 54.2 min, *t_r*(minor) = 61.1 min.

N-[3-(S)-Cyano-5-phenylpentanoyl]benzamide 10d: Flash column chromatography with 3:1 hexane/EtOAc afforded the product **10d** as a white solid; yield: 55 mg (96%). The *ee* was found to be 98%, 254 nm, 5% ethanol in hexane, 0.7 mL min⁻¹, *t_r*(major) = 56.1 min, *t_r*(minor) = 59.3 min.

N-[3-(S)-Cyano-4,4-dimethylpentanoyl]benzamide 10e:^[22] Flash column chromatography with 3:1 hexane/EtOAc afforded the product **10e** as a white solid; yield: 55 mg (96%). The *ee* was found to be 89%, 254 nm, 5% ethanol in hexane, 0.7 mL min⁻¹, *t_r*(major) = 46.7 min, *t_r*(minor) = 52.1 min.

General Procedure for the Kinetic Studies using 1 and Jacobsen's Catalyst

The addition reaction was divided into 5–6 NMR tubes. In each tube the appropriate catalyst, imide substrate (7.6 mg, 0.04 mmol, 1 equiv.) and toluene (4 µL) were added. The NMR tube was sealed with a septum and TMSCN (20 µL, 0.16 mmol, 4 equiv.) and 2-propanol (12 µL, 0.16 mmol, 4 equiv.) were added. The reaction mixture was heated to 45 °C and quenched at the appropriate time by adding CDCl₃ (400 µL). The amount of product formation was calculated by adding a known amount of 1,1,2,2-tetrachloroethane (0.0075 mmol) in CDCl₃ (100 µL) to the NMR tube as an internal standard.

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