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Enantioselective Conjugate Addition of Aromatic Amines to *N*-Alkenoyloxazolidinones Catalyzed by Iodido(binaphtholato)samarium

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Iodido(binaphtholato)samarium catalyzes the Michael addition of aromatic amines to *N*-alkenoyloxazolidinones affording β-amino acid derivatives with enantiomeric excesses of up to 88 %. A study of the effect of temperature on the asymmetric induction revealed an isoinversion in two reactions. The observation of a non-linear effect suggests an equilibrium between several active species including dimers.

Introduction

The enantioselective formation of carbon–nitrogen bonds by the addition of amines to double bonds is an atom-economic reaction giving access to molecules of pharmaceutical interest.[1] Several reviews concerning activated or non-activated double bonds have been devoted to this topic.[2] Most enantioselective hydroamination reactions involving the addition of amines to unactivated double bonds (1,2-addition) are intramolecular and allow the synthesis of enantioenriched nitrogen heterocycles. The enantioselective catalysts reported for these hydroamination/cyclization reactions are for the major part based on lanthanides,[3–6] although some examples of chiral zirconium complexes and a chiral lithium bis-amide have recently been described.[7–9] With regard to intermolecular enantioselective hydroamination reactions, only the Ir-catalyzed addition of aniline to norbornene and the Pd-BINAP-catalyzed addition of aniline to vinylstyrene or vinylnaphthalene have been reported.[10] Such intermolecular additions of amines generally require the use of activated olefins and are referred to as aza-Michael reactions. Nickel complexes coordinated to chiral tridendate ferrocenylphosphanes catalyze the addition of various amines to α,β-unsaturated nitriles with enantiomeric excesses of up to 69 %.[11] However, most of the studies on enantioselective aza-Michael reactions concern the reactions of various amino derivatives with α,β-unsaturated acyl derivatives which are efficient methodologies for the synthesis of β-amino acids.[12] Different catalytic systems have been successfully used for the conjugated addition of *O*-benzylhydroxylamine to *N*-alkenoyl substrates (oxazolidinones, imides, pyrazolidinones), for example, $TiCl_2$-BINOL,[13] magnesium salts or rare-earth triflates coordinated by chiral bis-oxazoline ligands.[14] Rare-earth catalysts coordinated by BINOL-type ligands such as yttrium-lithiumtris(binaphthoxide) (YLB) and $Sc(BNP)_3$ are highly enantioselective in the 1,4-addition of *O*-alkylhydroxylamine to enones.[15,16] Other nitrogen-containing substrates such as hydroxylamine or carbamates have been employed in enantioselective conjugate addition reactions using $Cu(OTf)_2$ with bis-oxazoline ligands.[17,18] Aldoximes have been employed in aza-Michael reactions catalyzed with $Zn(ClO_4)_2$ coordinated by bis-oxazoline.[19] The addition of N–H-containing heterocycles to α,β-unsaturated imides or ketones catalyzed by Al–salen complexes gave very high enantiomeric excesses (up to 99 %).[20]

Enantioselective catalyzed aza-Michael reactions involving amines have been less studied and only a few catalytic systems have been described. Nickel perchlorate coordinated by DBFOx-Ph catalyzes the addition of secondary aromatic amines to α,β-unsaturated *N*-acyloxazolidinones with moderate-to-high enantiomeric excesses.[21] Hii et al. described the first use of cationic palladium complexes coordinated by BINAP for the addition of aromatic amines to *N*-alkenoyloxazolidinones or *N*-alkenoylcarbamates.[22] High enantiomeric excesses were obtained with both substrates but the enantioselectivity was lower with electron-rich amines in the former case. In contrast, the enantioselectivity did not depend upon the electronegativity of the amine in the case of α,β-unsaturated imides. Sodeoka and co-workers improved the yield and enantioselectivity of this catalytic system for reactions involving *N*-alkenoyloxazolidinones by using aromatic amine trifluoromethanesulfonate salts as substrates and a cationic dimeric palladium complex coordinated by BINAP as a precatalyst.[23] Several chiral diphosphanes affording aza-Michael products with enantiomeric excesses of over 90 % were selected by parallel screening of various chiral ligands and recently a synthetic application and mechanistic studies were reported.[24]

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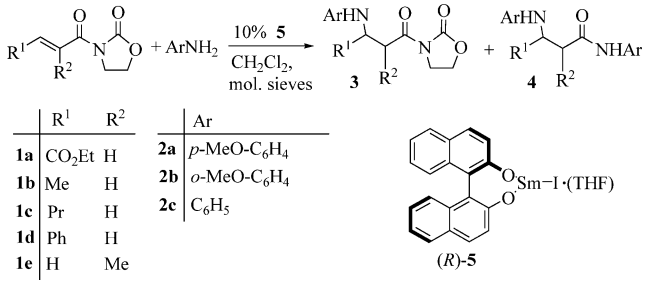
During the course of our previous investigations we studied the use of $SmI_2(THF)_2$ in dichloromethane as an efficient Lewis acid catalyst for carbon–carbon and carbon–nitrogen bond-forming reactions.[25] Samarium diiodide catalyzes Mukaiyama–Michael reactions of α,β-unsaturated ketones,[25b,25c] as well as aza-Michael reactions involving the addition of aromatic amines to α,β-unsaturated acyloxazolidinones to form β-amino acid derivatives.[26] Aza-Michael reactions can be followed by an amidation reaction by cleavage of oxazolidinone to give the corresponding β-amino amides. With the aim of developing new enantioselective catalysts we prepared lanthanide complexes with binaphthylamine or binaphthol-type ligands. A new family of lanthanide ionic complexes derived from chiral substituted (*R*)-binaphthylamine ligands, $[Li(THF)_4][Ln\{(R)\text{-}C_{20}H_{12}(NR)_2\}_2]$, proved indeed to be efficient enantioselective catalysts for intramolecular hydroamination reactions.[27] Iodido(binaphtholato)lanthanides have been employed as efficient Lewis acid catalysts for Diels–Alder reactions with moderate enantioselectivity,[28] while iodido(binaphtholato)samarium afforded high activity and enantioselectivity in iminoaldol reactions involving a glyoxylic imine.[29] This latter samarium complex catalyzes the ring-opening of *meso*-epoxides by aromatic amines to give β-amino alcohols with high enantiomeric excesses.[30] We wish now to report the use of this catalyst in the enantioselective conjugate addition of aromatic amines to *N*-alkenoyloxazolidinones and the effect of various parameters on these reactions. The results of aza-Michael reactions with *N*-fumaroyloxazolidinones have already been reported.[31]

Results and Discussion

We previously found that the reaction of aromatic amines with *N*-alkenoyloxazolidinones **1** catalyzed by samarium diiodide in dichloromethane either selectively affords the aza-Michael addition product **3** or the amide **4** formed by the consecutive reaction of **3** with the aromatic amine.[26] The ratio **3/4** depends not only on the quantity of aromatic amine, but also on the reagents (*N*-alkenoyloxazolidinone and aromatic amine). The rate of amidation is higher for electron-enriched amines and a higher ratio of amide **4** has been found in reactions involving *p*-anisidine.

In order to evaluate the activity and selectivity of iodido(binaphtholato)samarium (**5**) as a catalyst for aza-Michael reactions we performed the reactions of various *N*-alkenoyloxazolidinones **1** with 1.2 equiv. of *p*-anisidine in dichloromethane at room temperature in the presence of 10 mol-% of complex **5** (Scheme 1). The results are shown in Table 1. Under these conditions fumaroyloxazolidinone selectively yielded the Michael addition product (entry 1), as was observed with samarium diiodide. The substrates substituted by alkyl or phenyl groups on the terminal carbon of the double bond afforded mixtures of Michael addition product **3** and amide **4** (entries 2–4). Use of substrate **1e** with a methyl substituent at the α-position to the carbonyl selectively led to the Michael adduct (entry 5). In the case of *N*-crotonoyloxazolidinone, comparison of the ratio **3ba/4ba** (80:20, entry 2) with that obtained in the similar samarium diiodide catalyzed reaction (10:90) showed that the rate of the amidation reaction is lower with iodido(binaphtholato)-samarium. This asymmetric catalyst also exhibited higher activity than samarium diiodide for aza-Michael additions: the reaction of substrate **1d** with *p*-anisidine in the presence of a catalytic amount of $SmI_2(THF)_2$ did not provide the product **3da**.[32] At room temperature only moderate enantiomeric excesses were observed for aza-Michael reactions catalyzed by samarium complex **5**.



Scheme 1. Aza-Michael reaction of aromatic amines with *N*-alkenoyloxazolidinones catalyzed by iodido(binaphtholato)samarium.

Table 1. Addition of *p*-anisidine (**2a**) to *N*-alkenoyloxazolidinones catalyzed by iodido(binaphtholato)samarium (**5**).

Entry	Substrate[a]	*t* [h]	Product	**3/4**[b]	% *ee* **3**[c]
1	**1a**	16	**3aa**	100:0	25
2	**1b**	48	**3ba** + **4ba**	80:20	22[d]
3	**1c**	48	**3ca** + **4ca**	63:37	4[e]
4	**1d**	48	**3da** + **4da**	87:13	19[e]
5	**1e**	48	**3ea**	100:0	18

[a] Reactions were performed at room temperature in CH_2Cl_2 using 10 mol-% **5** and a **2a/1** ratio of 1.2:1. [b] The ratio **3/4** was measured by ^1H NMR of the crude product. [c] Enantiomeric excesses were determined by HPLC. [d] –19% *ee* for **4ba**. The minus sign indicates a change in the major peak in the HPLC analysis. [e] The enantiomeric excesses for **4ca** and **4da** could not be determined by HPLC.

We previously found that the enantioselectivities of iodido(binaphtholato)samarium-catalyzed reactions are dramatically influenced by temperature. For iminoaldolization an increase in enantiomeric excess with temperature was observed,[29] while an isoinversion effect was recorded for the ring-opening of cyclohexene oxide by *o*-anisidine with the highest enantiomeric excess obtained at the inversion temperature of –40 °C.[30] To improve the enantioselectivity of this process, aza-Michael reactions were performed at various temperatures. The results are shown in Table 2. A high enantiomeric excess (88%) was obtained at –40 °C for the addition of *p*-anisidine to *N*-fumaroyloxazolidinone (entry 2). Other aza-Michael reactions were thus studied at this temperature under the conditions described above [1.2 equiv. of amine **2** and 10 mol-% iodido(binaphtholato)-samarium (**5**)]. A decrease in temperature selectively provided the Michael product **3ba** in the reaction of *p*-anisidine with *N*-crotonoyloxazolidinone (**1b**) (entries 3–6), but with a lower enantiomeric excess (**3ba** is nearly racemic at 0 and

–20 °C). At –40 °C the sense of the enantioselectivity is reversed. Such unusual behaviour was observed by Sibi et al. for the enantioselective conjugate amine addition catalyzed by magnesium bromide coordinated by bis-oxazolines.[14c] The addition of *o*-anisidine to *N*-crotonoyloxazolidinone (**1b**) selectively afforded the aza-Michael product **3bb** in all cases (entries 7–9). For aza-Michael reactions catalyzed by samarium diiodide it has already been observed that amidation does not occur with *o*-anisidine probably due to steric hindrance.[26] The *ee* for **3bb** was slightly higher at lower temperatures, but was still low. Similarly, the addition of aniline (**2c**) to *N*-crotonoyloxazolidinone (**1b**) selectively provided the Michael adduct **3bc** with very low asymmetric induction even at low temperatures (entries 10–12). The reactions of *N*-hexenoyloxazolidinone (**1c**) with *p*-anisidine (**2a**) and *o*-anisidine (**2b**) showed the same trends as the reactions with **1b**. At room temperature with **2a** a mixture of aza-Michael product **3ca** and amidation product **4ca** was formed (entry 13), while at –40 °C **3ca** was selectively obtained with 45% *ee* (entry 15). Reactions with **2b** led to the selective formation of **3cb**, but with low conversions and enantioselectivities (entries 16 and 17). Addition of **2a** to *N*-cinnamoyloxazolidinone (**1d**) furnished mixtures of adducts at room temperature, but selectively gave adduct **3da** at –40 °C with low *ee* values in both cases (entries 18 and 19). In the selective aza-Michael addition of *p*-anisidine to the substrate **1e** with two substituents in the α-position to the carbonyl, a decrease in temperature led to an improvement in the enantiomeric excess (76%, entries 20 and 21). Iodido(binaphtholato)samarium (**5**) appears to be an efficient catalyst for the reaction of aromatic amines with *N*-alkenoyloxazolidinones. Aza-Michael adducts are selectively obtained with *o*-anisidine and aniline, and with *p*-anisidine at a low temperature. Conjugate addition of amines to *N*-alkenoyloxazolidinones **1a** and **1e** provided new β-amino acid derivatives. Since reactions involving *p*-anisidine (**2a**) afforded higher enantiomeric excesses than those with *o*-anisidine or aniline, further studies of the aza-Michael additions of this amine on substrates **1a** and **1e** have been performed.

In our first studies of the aza-Michael reaction catalyzed by iodido(binaphtholato)samarium we examined the effect of temperature on the addition of *p*-anisidine (**2a**) to substrate **1a**.[31] We found that the enantiomeric excesses did not show a monotonous variation with temperature. The enantiomeric excess first increased upon decreasing the temperature to reach a maximum value of 88% at –40 °C. Reactions performed at still lower temperatures resulted in lower asymmetric inductions. Such variations in enantioselectivity with an isoinversion effect have already been reported.[33] The corresponding Eyring plot is presented in Figure 1 and shows non-linear behaviour; it shows two linear regions intersecting at the inversion temperature (T_{inv}). This intersection corresponds to a value of –39 °C in Figure 1. A study of the effect of temperature on the enantiomeric excess of the adduct **3ea** obtained by the addition of *p*-anisidine to substrate **1e** showed a similar non-monotonous variation, as can be seen in Table 3. For this reaction only small variations in the enantiomeric excess were observed between –20 and –50 °C. The corresponding Eyring plot in Figure 2 also exhibits two linear regions. The graphically determined inversion temperature is identical to that observed for **3aa** (–39 °C). Previously we described similar

Table 2. Effect of temperature on the enantiomeric excess of aza-Michael reactions catalyzed by iodido(binaphtholato)samarium (**5**).

Entry	Substrate	Amine	Temp. [°C][a]	*t* [h]	Products	**3/4**	% Conv. (% isolated yield of **3**)	% *ee* of **3**[b]
1	**1a**	**2a**	25	18	**3aa**	100:0	100	25[c]
2	**1a**	**2a**	–40	18	**3aa**	100:0	100 (65)	88
3	**1b**	**2a**	25	48	**3ba** + **4ba**	80:20	100 (30)	22[d]
4	**1b**	**2a**	0	48	**3ba** + **4ba**	80:20	100	5
5	**1b**	**2a**	–20	48	**3ba** + **4ba**	85:15	100	4
6	**1b**	**2a**	–40	48	**3ba**	>95:5	100 (66)	–8[e]
7	**1b**	**2b**	25	48	**3bb**	100:0	100 (64)	17
8	**1b**	**2b**	0	48	**3bb**	100:0	98 (75)	28
9	**1b**	**2b**	–40	48	**3bb**	100:0	47 (20)	29
10	**1b**	**2c**	25	48	**3bc**	100:0	100 (67)	5
11	**1b**	**2c**	0	48	**3bc**	100:0	98 (55)	11[d]
12	**1b**	**2c**	–40	48	**3bc**	100:0	88 (60)	12[d]
13	**1c**	**2a**	25	48	**3ca** + **4ca**[e]	63:37	100	4
14	**1c**	**2a**	0	48	**3ca** + **4ca**[f]	93:7	97	20
15	**1c**	**2a**	–40	48	**3ca**	100:0	100	45
16	**1c**	**2b**	0	48	**3cb**	100:0	71 (38)	7
17	**1c**	**2b**	–40	48	**3cb**	100:0	25 (10)	18
18	**1d**	**2a**	25	48	**3da** + **4da**[g]	87:13	100	19
19	**1d**	**2a**	–40	48	**3da**	100:0	100 (7)[h]	28
20	**1e**	**2a**	25	48	**3ea**	100:0	100 (80)	18
21	**1e**	**2a**	–40	48	**3ea**	100:0	75 (50)	76

[a] Reactions were performed in CH_2Cl_2 using 10 mol-% **5** and a **2/1** ratio of 1.2:1. [b] Enantiomeric excesses were determined by HPLC. [c] Catalyst **5** prepared from (*R*)-binaphthol afforded (*S*)-**3aa**; see ref.[31] for the determination of the configuration. [d] Catalyst **5** prepared from (*R*)-binaphthol afforded (*R*)-**3ba** and (*R*)-**3bc**: the configurations were determined by comparison of the sign of the optical rotations with those described in the literature (see ref.[23]). [e] The minus sign indicates a change in the major peak on HPLC analysis. [f] The enantiomeric excess of **4ca** could not be determined by HPLC. [g] The enantiomeric excess of **4da** could not be determined by HPLC. [h] Compound **3da** decomposed on silica.

behaviour for the ring-opening of cyclohexene oxide by *o*-anisidine catalyzed by iodido(binaphtholato)samarium which also has an inversion temperature of –39 °C.[30]

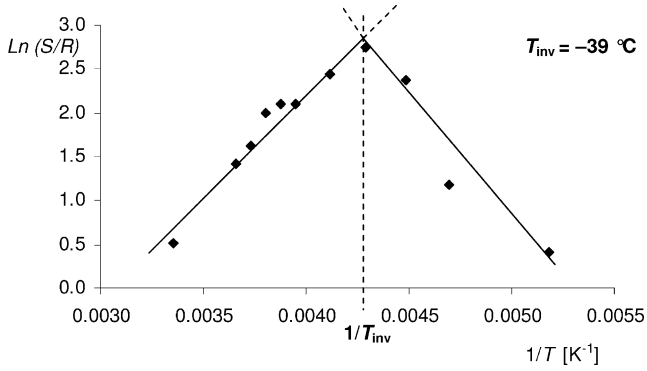


Figure 1. Eyring plot for the aza-Michael addition of *p*-anisidine (**2a**) to *N*-acyloxazolidinone (**1a**) catalyzed by samarium complex **5**.

Table 3. Effect of temperature on the enantiomeric excess of product **3ea**.

Temp. [°C]	–60	–50	–40	–35	–30	–25	–20	0	25
% Conversion[a]	26	68	75	80	89	90	89	100	100
% *ee*	58	69	76	68	71	68	74	49	18

[a] After a reaction time of 48 h.

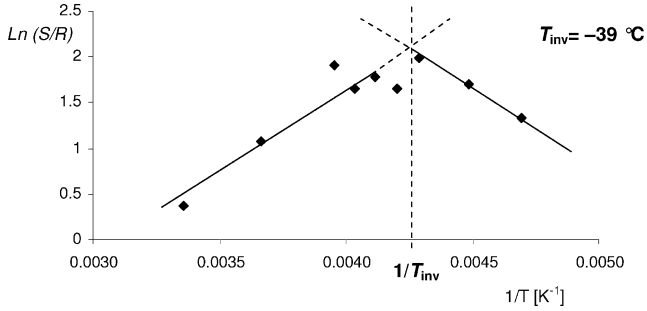


Figure 2. Eyring plot for the aza-Michael addition of *p*-anisidine (**2a**) to *N*-acyloxazolidinone (**1e**) catalyzed by samarium complex **5**.

The inversion temperatures can be explained by a reaction pathway with at least two enantioselective steps weighted differently according to the temperature. Observation of the same values for the inversion temperatures of two different reactions, aza-Michael reaction and aminolysis of epoxides, suggests the involvement of different catalytic species rather than different reaction mechanisms as an explanation of the isoinversion. Cainelli and co-workers proposed T_{inv} to be the temperature for the interconversion between two different solvation clusters that behave like two different molecules.[33e,33f] For the aza-Michael reaction as well as for the aminolysis of *meso*-epoxides catalyzed by iodido(binaphtholato)samarium, the inversion temperature could be explained similarly. Several catalytic species with variable numbers of coordinated THF molecules and/or amines can be envisaged. Numerous attempts to prepare crystals of iodido(binaphtholato)samarium (**5**) suitable for X-ray diffraction were unsuccessful. The preparation of catalyst **5** using Ph_2CHK to generate the BINOL potassium salt involves treatment with hexane to eliminate diphenylmethane.[30] The ^{1}H NMR spectra of iodido(binaphtholato)-samarium (**5**) thus prepared show only one molecule of THF coordinated to samarium which has a formal coordination number of four.[26,34] The formation of a dimer or oligomers can be anticipated and these could also be the origin of the isoinversion phenomena. The observation of a non-linear correlation between the enantiomeric excesses of products and catalysts has been recognised as a tool for detecting association in catalytic active species.[35] Examples of asymmetric amplification in various chiral lanthanide-catalyzed reactions have been the topic of a review.[36] We thus investigated the possible involvement of a non-linear effect in the reaction leading to **3ea** catalyzed by iodido-(binaphtholato)samarium (**5**).

The study of the effect of enantiomeric purity of binaphthol on the enantiomeric excess of the Michael product **3ea** requires the preparation of several iodido(binaphtholato)-samarium complexes (**5**) with different enantiomeric purities. Two methods can be envisaged for the synthesis of such catalysts and both of them were examined. In the first series of experiments different complexes were prepared by the usual method with binaphthol samples having different enantiomeric purities (8, 24, 40, 67% *ee*). The aza-Michael reaction involving **1e** and *p*-anisidine catalyzed by these complexes was studied at three temperatures: room temperature and 0 and –40 °C (the temperature affording the highest enantiomeric excess). The results indicated in Figure 3 show a non-linear relationship between the enantiomeric excess of the Michael adduct **3ea** and the enantiomeric excess of binaphthol. A negative non-linear effect is observed for the three different temperatures. As an alternative, two scalemic catalysts were prepared by mixing iodido-(binaphtholato)samarium complexes prepared separately with enantiomerically pure (*R*)- and (*S*)-binaphthol (giving catalysts with 32 and 47% *ee*, respectively). The Michael addition reaction involving **1e** and *p*-anisidine was performed with both catalysts at the inversion temperature of –40 °C and the enantiomeric excesses were compared with those calculated for a linear correlation between the enantiomeric excesses of the catalyst and the product (Scheme 2). The values of the enantiomeric excesses of **3ea** produced by reactions catalyzed by the mixtures of (*R*)- and (*S*)-**5** are higher than the calculated values. These results indicate asymmetric amplification in these cases.

The positive and negative non-linear effects can be explained by the formation of dimers. The use of scalemic binaphthol for the preparation of the catalysts would lead to the formation of heterochiral [(*R*)-**5**–(*S*)-**5**] and homochiral dimers [(*R*)-**5**–(*R*)-**5**] and [(*S*)-**5**–(*S*)-**5**]. The negative non-linear effect suggests that the homochiral dimers are less active than the heterochiral dimer. The positive non-linear effect obtained with the mixtures of complexes indicates that the homochiral dimers [(*R*)-**5**–(*R*)-**5**] and [(*S*)-**5**–(*S*)-**5**] are not completely dissociated to monomers under the conditions of the reaction. Complete dissociation would

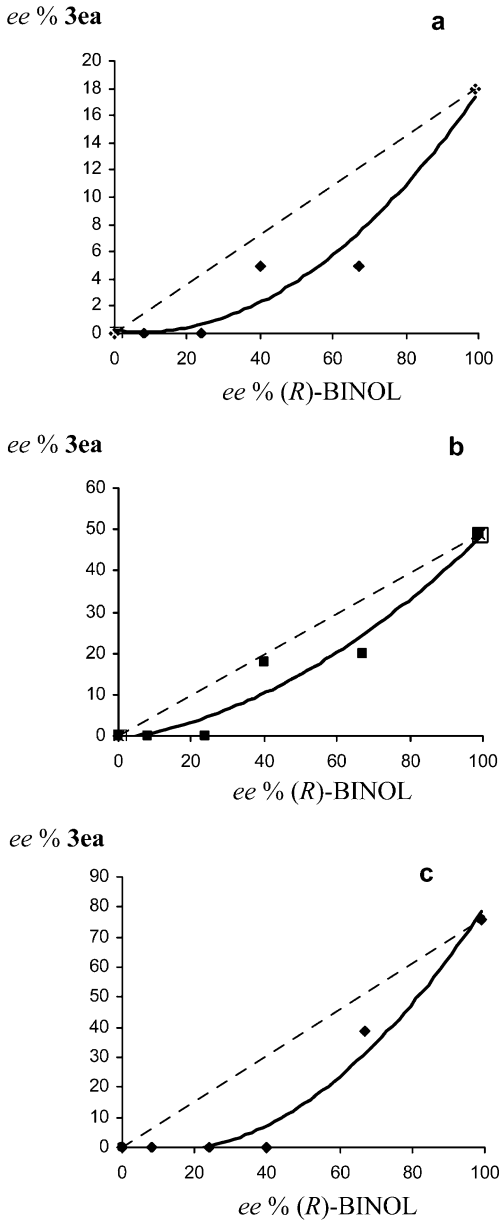
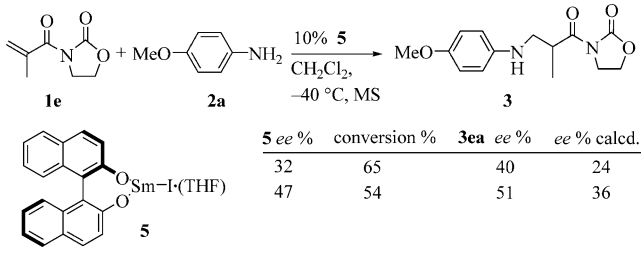


Figure 3. Correlation between the enantiomeric excess of binaphthol and the enantiomeric excess of aza-Michael adduct **3ea** at a) 20, b) 0 and c) –40 °C.

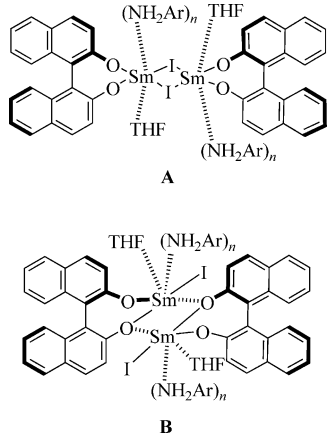


5 *ee* %	conversion %	3ea *ee* %	*ee* % calcd.
32	65	40	24
47	54	51	36

Scheme 2. Aza-Michael reaction catalyzed by mixtures of (*R*)- and (*S*)-**5**.

either give a linear correlation or lead to the formation of the heterochiral dimer together with a negative non-linear effect. To study the possibility of the dissociation of homochiral dimers we examined the effect of concentration on the reaction affording **3ea** catalyzed by (*R*)-**5** at –40 °C. The reaction was performed by using 20 mL of CH_2Cl_2 instead of 5 mL which afforded a lower conversion (38% instead of 75%) and a lower enantiomeric excess (64% instead of 76%). Since dilution should favour the dissociation of dimers and increase the monomer ratio, this result suggests that the homochiral dimer [(*R*)-**5**–(*R*)-**5**] is more active and enantioselective than the monomer (*R*)-**5**. As a possible explanation we propose that iodido(binaphtholato)samarium (**5**) is isolated as a dimeric species that can dissociate to a small extent under the conditions of the reaction. Both monomer and dimer species should be active for the aza-Michael reaction with the heterochiral dimer more active than the homochiral complex and the monomer species. Kinetic constants for the aza-Michael reaction are expected to decrease in the following order: $k_{[(R)\text{-}5\text{–}(S)\text{-}5]} > k_{[(R)\text{-}5\text{–}(R)\text{-}5]} > k_{[(R)\text{-}5]}$.

Non-linear effects have previously been observed in different asymmetric reactions involving bidentate binaphthol ligands and different metals, for example, titanium[35e,35f] or lanthanum.[36,37] In several cases the non-linear correlation was explained by the formation of dimers with metal–oxygen bonds. For the iodido(binaphtholato)samarium-catalyzed reactions species such as dimer **A** (Scheme 3) with samarium–iodine bridges and THF and/or amines as ligands can be proposed. Dimeric structures with metal–halogen bridges are frequently found in lanthanide complexes and X-ray structures of dimeric samarium aryloxide/halide complexes have been reported.[38] As an alternative, a dimeric structure such as **B** (Scheme 3) with samarium atoms coordinated to two different binaphthol ligands can be suggested. Such structures were found for alkyl(biphenolato)-lanthanums employed as intramolecular hydroamination catalysts.[39] An equilibrium between the monomeric and dimeric forms of yttrium alkoxides has been described, the dimer being favoured by a non-coordinating solvent.[40] Thus, iodido(binaphtholato)samarium could be present in the catalytic medium as a dimer or as an equilibrium between monomer, dimer and oligomers. The coexistence of



Scheme 3. Proposed dimeric structures for the catalytic species in the aza-Michael reactions.

several catalytic species may explain the non-linear behaviour as well as the isoinversion observed for the aza-Michael reactions. However, further studies are needed to determine the structure of the active species involved in the catalytic process.

Conclusions

Iodido(binaphtholato)samarium (**5**) is an efficient enantioselective catalyst for aza-Michael additions involving *N*-alkenoyloxazolidinones and aromatic amines. Interestingly, higher enantiomeric excesses were obtained with *p*-anisidine than with *o*-anisidine or aniline. These reactions afforded β-amino acid derivatives with up to 88% enantiomeric excess. An isoinversion phenomenon was evidenced for two reactions with the highest enantioselectivities observed at the same temperature. A non-linear relationship between the enantiomeric excesses of the catalyst and the aza-Michael adducts led to the proposal that the catalyst is composed of dimeric structures. Further work in this area is ongoing to gain an insight into the structure of this family of catalysts and to extend their application to other enantioselective catalytic reactions.

Experimental Section

General Remarks: All manipulations were carried out under argon using standard Schlenk or glove-box techniques. THF was distilled from sodium benzophenone ketyl and degassed immediately prior to use. Hexane, benzene and dichloromethane were distilled from CaH_2 and degassed immediately prior to use. Iodido(binaphtholato)samarium (**5**) was prepared according to the procedure previously described.[30] α,β-Unsaturated *N*-acyloxazolidinones were prepared according to reported procedures.[41] All aromatic amines were recrystallized or distilled and degassed immediately prior to use. Thin-layer chromatographic plates were prepared from silica gel 60 PF_{254} for preparative thin-layer chromatography.

Bruker AM 250 and 400 spectrometers operating at 250 and 400 MHz for ^1H and 62.5 and 100 MHz for ^{13}C were used for recording the NMR spectra. Chemical shifts for the ^1H and ^{13}C NMR spectra were referenced internally according to the residual solvent resonances and are reported relative to tetramethylsilane. Infrared spectra were recorded in $CHCl_3$ or in KBr pellets with a Perkin–Elmer 1000 FT-IR spectrometer and are reported in cm^{-1}. HRMS were recorded with a Thermo-Finnigan-Mat 95 spectrometer. Optical rotations were measured with a Perkin–Elmer 341 Polarimeter and are reported as follows: $[a]_D^{rt}$ (*c* in g per 100 mL, solvent). The enantiomeric excesses of the products were determined by chiral stationary phase HPLC with Chiralcel OD-H, Whelk O1 or Chiralpak AD columns and compared with racemic **3bb** prepared with $SmI_2(THF)_2$ or $Cu(OTf)_2$. The method for the determination of enantiomeric excesses has been already reported for **3aa**,[31] **3ba**[23] and **3bc**.[23]

General Method for the Preparation of Enantiomeric-Enriched Aza-Michael Products 3: In an argon-filled glove-box, iodido(binaphtholato)samarium (35 mg, 0.05 mmol) and 4-Å molecular sieves (50 mg) were suspended in dichloromethane (4 mL) in a Schlenk flask equipped with a magnetic stirring bar. Amine **2** (0.6 mmol) was then added and the reaction mixture was stirred for 10 min at room temperature. The reaction mixture was then cooled to the required temperature outside the glove-box and a solution of *N*-alkenoyloxazolidinone **1** (0.5 mmol) in dichloromethane (1 mL) was introduced by syringe. The reaction mixture was stirred for 16 or 48 h at the same temperature, quenched with a solution of 0.1 N HCl (10 mL) and extracted with CH_2Cl_2. The crude product was purified by preparative chromatography (heptane/AcOEt, 75:25) to afford compound **3** (**3aa**, **3ba**, **3bb**, **3bc**, **3ca**, **3cb**, **3da** and **3ea**). The enantiomeric excesses were determined by chiral HPLC as described below.

(*R*)-3-[3-(2-Methoxyphenylamino)butyryl]oxazolidin-2-one (3bb): Oil, yield 104 mg, 75%. $[a]_D^{20}$ = –6.12 (*c* = 0.67, $CHCl_3$) for 28% *ee*. ^1H NMR (250 MHz, $CDCl_3$): δ = 6.60–6.90 (m, 4 H), 4.20–4.29 (m, 2 H), 4.10–4.13 (m, 1 H), 3.81–3.88 (m, 5 H), 3.31 (dd, J_1 = 15.7, J_2 = 6.2 Hz, 1 H), 3.03 (dd, J_1 = 15.7, J_2 = 6.2 Hz, 1 H), 1.30 (d, J = 5.0 Hz, 3 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 177.6, 153.5, 146.9, 136.7, 121.1, 116.5, 110.5, 109.6, 61.9, 55.3, 45.4, 42.4, 41.5, 21.1 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3394, 1781, 1697, 1602, 1387, 1364 cm^{-1}. HRMS (EI): calcd. for $C_{14}H_{18}N_2NaO_4$ 301.1159; found 301.1169. HPLC: Chiralcel OD-H, hexane/ethanol, 85:15, 0.7 mL/min, λ = 254 nm, $t_{1,minor}$ = 30.83 and $t_{2,major}$ = 33.73 min.

Preparation of Racemic 3bb Catalyzed by $Cu(OTf)_2$: $Cu(OTf)_2$ (72 mg, 0.2 mmol) was weighed in the glove-box and dichloromethane (4 mL) was added followed by a solution of *o*-anisidine (**2b**) (615 mg, 5 mmol) and *N*-acyloxazolidinone **1b** (144 mg, 1 mmol) in dichloromethane (1 mL). The reaction mixture was stirred at 35 °C during 16 h and treated as described above. The crude product was purified by preparative chromatography (hexane/AcOEt, 75:25) to afford **3bb** (conversion 81%, yield 166 mg, 60%).

3-[3-(4-Methoxyphenylamino)hexanoyl]oxazolidin-2-one (3ca): Oil, yield 84 mg, 55%. $[a]_D^{20}$ = +24.5 (*c* = 2.18, $CHCl_3$) for 45% *ee* {ref.[22c] $[a]_D^{20}$ = +0.69 (*c* = 0.026, $CHCl_3$) for 10% *ee*}. ^1H NMR (250 MHz, $CDCl_3$): δ = 6.76 (d, J = 8.7 Hz, 2 H), 6.60 (d, J = 8.7 Hz, 2 H), 4.22–4.37 (m, 2 H), 3.81–3.98 (m, 3 H), 3.75 (s, 3 H), 3.45 (br. s, 1 H), 3.31 (dd, J_1 = 15.0, J_2 = 7.9 Hz, 1 H), 3.01 (dd, J_1 = 15.0, J_2 = 4.6 Hz, 1 H), 1.37–1.66 (m, 4 H), 0.93 (t, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 172.2, 153.6, 152.1, 141.5, 114.9, 114.8, 61.8, 55.7, 51.7, 42.4, 39.9, 38.0, 19.3, 13.9 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3744, 1777, 1685, 1600, 1384 cm^{-1}. HRMS: calcd. for $C_{16}H_{22}N_2NaO_4$ 329.1472; found 329.1480. HPLC: Whelk O1, hexane/2-propanol, 90:10, 0.5 mL/min, λ = 254 nm, 15 °C, $t_{1,major}$ = 70.4 and $t_{2,minor}$ = 77.2 min.

Preparation of Racemic 3ca Using $Cu(OTf)_2$: In the glove-box, $Cu(OTf)_2$ (13 mg, 0.05 mmol) was suspended in dichloromethane (4 mL). Then a solution of *p*-anisidine (**2a**) (74 mg, 0.6 mmol) and *N*-acyloxazolidinone **1c** (92 mg, 0.5 mmol) in dichloromethane (1 mL) was added. The reaction mixture was stirred at room temperature during 48 h and treated as described previously. The crude product was purified by preparative thin-layer chromatography (hexane/AcOEt, 75:25). Yield 9 mg, 6%.

3-[3-(2-Methoxyphenylamino)hexanoyl]oxazolidin-2-one (3cb): Oil, yield 58 mg, 38%. ^1H NMR (250 MHz, $CDCl_3$): δ = 6.85–6.60 (m, 4 H), 4.50–4.06 (m, 4 H), 3.80–3.78 (m, 4 H), 3.22 (dd, J_1 = 15.2, J_2 = 7.6 Hz, 1 H), 3.03 (dd, J_1 = 15.2, J_2 = 5.7 Hz, 1 H), 1.60–1.30 (m, 4 H), 0.89 (t, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 171.9, 153.6, 146.8, 137.3, 121.2, 116.2, 110.2, 109.7, 61.9, 55.4, 49.7, 42.4, 40.2, 37.9, 19.2, 14.1 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3748, 1777, 1697, 1600, 1387, 1363 cm^{-1}. HRMS (EI): calcd. for $C_{16}H_{22}N_2NaO_4$ 329.1472; found 329.1485. HPLC: Whelk O1, hexane/2-propanol, 90:10, 0.5 mL/min, λ = 254 nm, 15 °C, $t_{1,minor}$ = 26.5 and $t_{2,major}$ = 32.1 min.

3-[3-(4-Methoxyphenylamino)-3-phenylpropionyl]oxazolidin-2-one (3da): Solid, m.p. 137–140 °C, yield 12 mg, 7%. $[\alpha]_D^{20}$ = –1.21 (*c* = 0.6, $CHCl_3$) for 28% *ee*. ^1H NMR (250 MHz, $CDCl_3$): δ = 7.44–7.23 (m, 5 H), 6.69 (d, *J* = 5.0 Hz, 2 H), 6.52 (d, *J* = 5.0 Hz, 2 H), 4.90 (t, *J* = 5.0 Hz, 1 H), 4.35 (t, *J* = 7.50 Hz, 2 H), 3.96 (t, *J* = 7.50 Hz, 2 H), 3.69 (s, 3 H), 3.44 (m, 2 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 171.0, 153.6, 152.2, 142.3, 140.8, 128.6, 127.3, 126.3, 115.1, 114.6, 62.0, 55.7, 55.6, 42.85, 42.4 ppm. IR (CaF_2, $CHCl_3$): $\tilde{\nu}$ = 3739, 1779, 1689, 1597, 1387, 1360 cm^{-1}. HRMS (ESI): calcd. for $C_{19}H_{20}N_2NaO_4$ 363.1315; found 329.1311. HPLC: Chiracel OD-H, hexane/2-propanol, 90:10, 0.5 mL/min, λ = 254 nm, $t_{1,minor}$ = 57.7 and $t_{2,major}$ = 59.4 min.

3-[3-(4-Methoxyphenylamino)-2-methylpropionyl]oxazolidin-2-one (3ea): Oil, yield 70 mg, 50%. $[\alpha]_D^{20}$ = –25.28 (*c* = 1.24, $CHCl_3$) for 76% *ee*. ^1H NMR (250 MHz, $CDCl_3$): δ = 6.79 (d, *J* = 8.8 Hz, 2 H), 6.61 (d, *J* = 8.8 Hz, 2 H), 4.40–4.26 (m, 2 H), 4.19–4.88 (m, 3 H), 3.76 (s, 3 H), 3.50 (dd, J_1 = 12.6, J_2 = 8.8 Hz, 1 H), 3.22 (dd, J_1 = 12.6, J_2 = 5.4 Hz, 1 H), 1.26 (d, *J* = 6.6 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.1, 153.4, 152.2, 141.9, 114.8, 114.2, 61.9, 55.7, 48.4, 42.7, 32.7, 15.1 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3432, 1773, 1673, 1388 cm^{-1}. HRMS (EI): calcd. $C_{14}H_{18}N_2NaO_4$ 301.1159; found 301.1169. HPLC: Chiralcel OD-H, hexane/2-propanol, 75:25, 0.7 mL/min, λ = 254 nm, $t_{1,major}$ = 35.8 and $t_{2,minor}$ = 55.0 min.

General Method for the Preparation of Mixtures of Enantiomeric-Enriched Aza-Michael and Amidation Products 3 and 4: The reactions were performed as described above. The crude product was purified by preparative thin-layer chromatography (hexane/AcOEt, 75:25) to afford a mixture of **3** and **4**.

***N*-(4-Methoxyphenyl)-3-(4-methoxyphenylamino)butanamide (4ba):** Amide **4ba** was separated from the mixture **3ba** + **4ba** by a second preparative thin-layer chromatography (hexane/AcOEt, 75:25). Amide **4ba** was alternatively prepared by the method described for the synthesis of compounds **3** using 2 equiv. of *p*-anisidine at room temperature. Amide **4ba** was isolated as a white solid (yield 79 mg, 50%). Solid, m.p. 95 °C. $[\alpha]_D^{20}$ = –61.9 (*c* = 1.9, $CHCl_3$) for 27% *ee*. ^1H NMR (250 MHz, $CDCl_3$): δ = 8.83 (br. s, 1 H), 7.39 (d, *J* = 9.2 Hz, 2 H), 6.84 (d, *J* = 8.8 Hz, 4 H), 6.74 (d, *J* = 9.2 Hz, 2 H), 3.75–3.91 (m, 1 H), 3.79 (s, 6 H), 2.53 (d, *J* = 6.3 Hz, 2 H), 1.28 (d, *J* = 6.0 Hz, 3 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 169.5, 156.2, 153.4, 140.2, 131.1, 121.6, 116.9, 114.9, 114.0, 55.6, 55.4, 48.9, 43.4, 21.0 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1779, 1671, 1600, 1335 cm^{-1}. HRMS (EI): calcd. for $C_{18}H_{22}N_2NaO_3$ 337.1523; found 337.1529. HPLC: Chiralpak AD, hexane/2-propanol, 75:25, 1.0 mL/min, λ = 254 nm, $t_{1,major}$ = 11.9 and $t_{2,minor}$ = 25.3 min.

***N*-(4-Methoxyphenyl)-3-(4-methoxyphenylamino)hexanamide (4ca):** Amide **4ca** was separated from the mixture **3ca** + **4ca** by a second preparative thin-layer chromatography (hexane/AcOEt, 75:25). It was also prepared by the method described for the synthesis of compounds **3** using 2 equiv. of *p*-anisidine at room temperature. Amide **4ca** was isolated as an oil. The enantiomeric excess of **4ca** could not be measured by HPLC. Oil, yield 86 mg, 50%. ^1H NMR (250 MHz, $CDCl_3$): δ = 8.59 (br. s, 1 H), 7.32–7.29 (m, 2 H), 6.80–6.67 (m, 6 H), 3.74–3.63 (m, 7 H), 2.55 (dd, J_1 = 15.1, J_2 = 3.9 Hz, 1 H), 2.42 (dd, J_1 = 15.1, J_2 = 7.6 Hz, 1 H), 1.63–1.47 (m, 2 H), 1.43–1.32 (m, 2 H), 0.88 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 169.8, 156.1, 153.0, 140.8, 131.2, 121.6, 116.2, 114.9, 113.9, 55.5, 55.3, 52.7, 41.4, 37.3, 19.2, 13.9 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3434, 1674, 1387 cm^{-1}. HRMS: calcd. for $C_{20}H_{26}N_2O_3Na$ 365.1836; found 365.1835.

Preparation of Racemic 4ca Catalyzed by $SmI_2(THF)_2$: Samarium diiodide (54 mg, 0.1 mmol) was weighed in the glove-box and dichloromethane (8 mL) was added followed by *p*-anisidine (615 mg, 5 mmol) and *N*-acyloxazolidinone **1c** (184 mg, 1 mmol). The reaction mixture was stirred at room temperature during 48 hours and treated as described previously. The crude product was purified by preparative thin-layer chromatography (hexane/AcOEt, 75:25) to afford **4ca** (yield 284 mg, 83%).

Study of Non-Linear Effects

Preparation of Catalyst 5 with Mixtures of (*R*)- and (*S*)-Binaphthol: In an argon-filled glove-box (*R*)- (32 mg, 0.11 mmol) and (*S*)-binaphthol (11 mg, 0.04 mmol) were dissolved in THF (3 mL). Potassium diphenylmethide (62 mg, 0.3 mmol), prepared as reported in the literature,[42] was added in portions and the reaction mixture was stirred for 2 hours. The white suspension of the potassium binaphtholate salt was then added to a suspension of $SmI_3(THF)_3$ (43 mg, 0.15 mmol) in THF (3 mL) and the reaction mixture was stirred for 18 h. The potassium iodide was separated by centrifugation and the solution concentrated in vacuo to afford a yellow solid. This product, which is a mixture of (*R*)- and (*S*)-**5** and diphenylmethane, was used after washing with hexane and dissolved in dichloromethane (3 mL) before performing the catalytic reactions as described above.

For reactions catalyzed by mixtures of complexes, (*R*)- and (*S*)-iodido(binaphtholato)samarium were weighed in the glove-box, dissolved in dichloromethane (3 mL) and the catalytic reactions were performed as described above.

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