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Enantioselective intramolecular amidation of sulfamate esters catalyzed by chiral manganese(III) Schiff-base complexes

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Abstract—Enantioselective intramolecular amidation of sulfamate esters catalyzed by chiral manganese(III) Schiff-base complexes under mild conditions ($PhI(OAc)_2$, Al_2O_3, C_6H_6, 5 °C) was achieved in moderate to good yields (up to 92%), substrate conversions (up to 99%), with virtually complete cis-selectivity and with ee values up to 79% ee.

Nitrogen atom insertion to saturated C–H bonds catalyzed by transition metal complexes provide a convenient synthetic route to amines and amine derivatives.[1] Seminal works by Jacobsen[2] and Katsuki[3] showed that chiral Schiff-base complexes of Cu(II), Ru(II), and Mn(III) are effective catalysts for enantioselective intermolecular amidation of saturated C–H bonds and aziridination of alkenes with PhI=NTs as nitrogen source. The asymmetric amidation and aziridination of alkenes by nitridomanganese(V) Schiff-base complexes were first reported by Carreira[4] and subsequently by Komatsu,[5] and Jørgensen.[6] Studies in our laboratory demonstrated that highly enantioselective intermolecular amidation of silyl enol ethers and intramolecular aziridination of C=C bonds can be accomplished by chiral ruthenium(II) Schiff-base and dirhodium(II,II) catalysts, respectively.[7] Despite these advances, examples on asymmetric intramolecular amidation of saturated C–H bonds using chiral metal catalysts remain sparse. A recent notable achievement by Du Bois and co-workers showed that dirhodium(II,II) catalysts can effect stereospecific intramolecular amidation of sulfamate esters and carbamates, allowing the synthesis of enantiomerically pure synthetically useful amidation products from enantiomerically pure sulfamate esters or carbamates.[8] We and others subsequently demonstrated that intramolecular amidation of sulfamate esters and carbamates can be achieved in the presence of chiral Ru(II),[9] Rh_2(II,II)[10] or achiral Ag(I)[11] catalyst. Using the chiral ruthenium(II) D_4-symmetric porphyrin catalyst, high enantioselectivity with ee value up to 88% ee was found.[9] However, to further improve ee values through structural modification of the metalloporphyrin catalyst, a drawback to the protocol remains the need to prepare the expensive chiral porphyrin ligands, which can be arduous and time consuming. The chiral Rh_2(II,II)-catalyzed intramolecular amidation of sulfamate esters were shown by Müller and Fruit to give low to moderate product yields and ee values.[10] In this context and considering the lower cost of Mn versus Ru or Rh, we envisioned that Mn(III) catalysts containing inexpensive chiral Schiff-base ligands could hold promising prospects for asymmetric intramolecular C–N bond formation reactions. Herein, we describe enantioselective amidation of sulfamate esters using chiral manganese(III) Schiff-base complexes as catalysts and with $PhI(OAc)_2$ as oxidant.

At the outset, we examined the effect of several chiral manganese(III) Schiff-base catalysts on the intramolecular amidation reactions studied in this work (Fig. 1). Chiral manganese(III) catalysts **1**–**7** and **9**–**12** were prepared following literature methods;[12] treatment of $[Mn(OAc)_2]\cdot 4H_2O$ (0.5 mmol) with the chiral H_2-(Schiff-base) ligand (1 mmol) in refluxing EtOH (10 mL) gave Mn(III) complexes **1**–**7** and **9**–**12** in 70–85% yield. The chiral Mn(III) salt **8** used in this work was prepared from reaction of **3** with AgOTf in 95% yield and structurally characterized by X-ray crystal analysis.[13] With **13a** as probe substrate, a survey of

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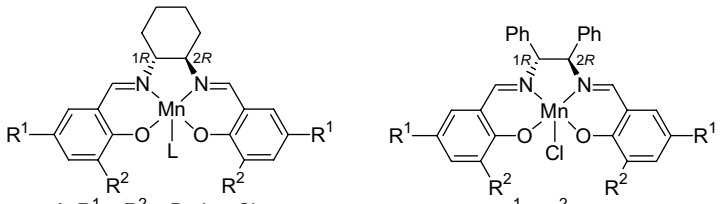


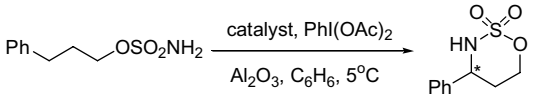
1: $R^1 = R^2$ = Br, L = Cl;
2: $R^1 = R^2$ = H, L = Cl;
3: $R^1 = R^2$ = L = Cl;
4: $R^1 = R^2$ = I, L = Cl;
5: $R^1 = R^2 = {}^t$Bu, L = Cl;
6: R^1 = H, R^2 = Br, L = Cl;
7: R^1 = Br, R^2 = H, L = Cl;
8: $R^1 = R^2$ = Br, L = OTf.

9: $R^1 = R^2$ = Br;
10: $R^1 = R^2$ = I;
11: $R^1 = R^2 = {}^t$Bu;
12: R^1 = Br, R^2 = H.

Figure 1. Chiral manganese(III) Schiff-base catalysts used in this work.

different reaction conditions revealed amidation of **13a** would be best performed in the presence of 1.5 equiv of $PhI(OAc)_2$ and Al_2O_3 (2.5 equiv) in C_6H_6 at 5 °C for 10 h with **1** (10 mol %) as catalyst (Table 1, entry 1). Under these conditions, cyclic sulfamidate **14a** was furnished with an ee value of 55% in 68% yield based on 95% substrate conversion. Examination of other manganese(III) Schiff-base catalysts revealed the performances of **3**, **4**, **6**, and **8** similar to that of **1** in terms of product yields and substrate conversions but gave lower ee values of 45–53% (entries 3–5, 7, and 9). In addition, reaction with (1*S*,2*S*)-**3** as catalyst gave the epimer of **14a** in a comparable product yield and ee value to that obtained for the same reaction catalyzed by **3** (in (1*R*,2*R*) form) (cf. entries 3 and 4). In contrast, the analogous reactions catalyzed by either **2** or **7** were found to give markedly lower ee values (23–36% ee); the latter catalyst was found to be less reactive and afforded **14a** in 49% yield with 79% substrate conversion (entries 2 and 8).

Table 1. Enantioselective intramolecular amidation of **13a** catalyzed by manganese(III) Schiff-bases **1**–**12**[a]



13a **1** **14a**

Entry	Catalyst	Conversion (%)	Yield (%)	ee[b] (%)
1	**1**	95	68	55
2	**2**	93	66	23
3	**3**	95	71	51
4	***ent-3***	93	68	53[c]
5	**4**	94	68	45
6	**5**	—	—	—
7	**6**	81	51	52
8	**7**	79	49	36
9	**8**	70	66	49
10	**9**	96	67	20
11	**10**	95	63	22
12	**11**	—	—	—
13	**12**	82	39	6

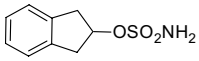
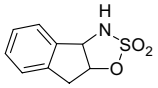
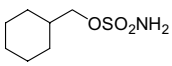
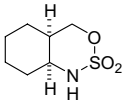
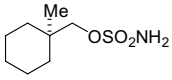
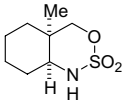
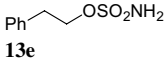
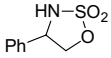
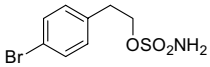
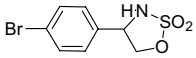
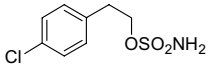
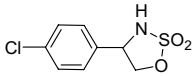
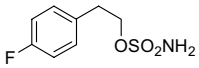
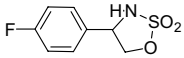
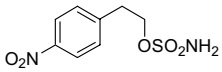
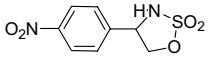
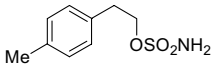
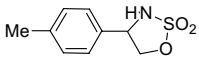
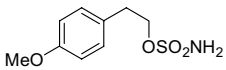
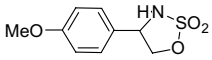
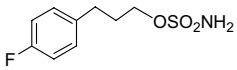
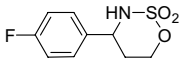
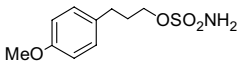
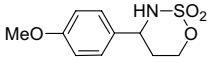
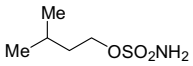
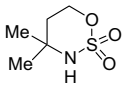
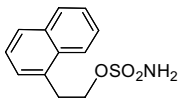
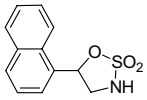
[a] All reactions were performed for 10 h with catalyst–**13a**–$PhI(OAc)_2$–Al_2O_3 molar ratio = 0.1:1:1.5:2.5 in C_6H_6 at 5 °C.
[b] Determined by HPLC analysis (Chiralcel OD column, hexane–^{i}PrOH = 4:1).
[c] Gave *epi*-**14a**.

Inspection of entries 10–13 in Table 1 reveals intramolecular amidation of **13a** with catalysts **9**–**12** containing a chiral 1,2-diphenylethylenediamine backbone structure exhibited similar reactivities but are much less enantioselective. Under the conditions: $PhI(OAc)_2$ (1.5 equiv) and Al_2O_3 (2.5 equiv) in C_6H_6 at 5 °C for 10 h, intramolecular amidation of **13a** using either **9**, **10**, or **12** as catalyst (10 mol %) gave **14a** in 39–67% yield with 82–96% substrate conversions and ee values of 6–22% ee (entries 10–11, and 13). Reactions of **13a** with either **5** or **11** as catalyst are the only instances where no product formation could be detected (entries 6 and 12).

To explore the scope of these chiral manganese(III) Schiff-base catalysts in intramolecular amidation reactions, we examined the similar reactions of other sulfamate esters **13b**–**p**. The results are summarized in Table 2.

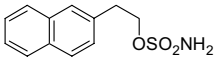
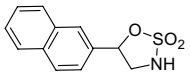
It is evident that sulfamate esters **13b**–**n** are good substrates for **1**-catalyzed intramolecular amidation, as the corresponding cyclic sulfamidates **14b**–**n** were obtained in reasonable to good yields (48–92%) and with ee values up to 79% ee (entries 1–18). The highest enantioselectivity of 79% ee attained in this work is for the intramolecular amidation of **13i**, which, to our knowledge, is also the highest enantiocontrol so far achieved for intramolecular amidation of saturated C–H bonds using a nonporphyrin based metal catalyst (entry 13). More notably, intramolecular amidation of **13b** with **1** (10 mol %), $PhI(OAc)_2$ (1.5 equiv) and Al_2O_3 (2.5 equiv) in CH_2Cl_2 at 5 °C for 10 h, was found to proceed with virtually complete cis-selectivity (entry 1). Likewise, intramolecular amidation of **13c** and **13d** gave the cis-diastereomers of **14c** and **14d** as the sole products based on ^{1}H and ^{13}C NMR measurements, and chiral GC analysis[14] (entries 4 and 5). In this work, the analogous reaction of **13c** with $[Rh_2(CH_3CO_2)_4]$ (5 mol %) as catalyst gave **14c** as a 1:1.9 cis:trans mixture of

Table 2. Enantioselective intramolecular amidation of sulfamate esters **13b–p** catalyzed by manganese(III) Schiff-base catalyst **1**[a]

Entry	Substrate	Product	% Yield (conversion)	% ee[b]
1	 **13b**	 **14b**	48 (82)	52
2[c]			60 (94)	35
3[d]			68 (98)	42
4	 **13c**	 **14c**	55 (92)	—[e]
5	 **13d**	 **14d**	92 (99)	—[e]
6	 **13e**	 **14e**	57 (84)	54
7	 **13f**	 **14f**	67 (85)	61
8	 **13g**	 **14g**	64 (91)	71
9[c]			60 (89)	72
10[d]			59 (87)	45
11[f]			76 (42)	69
12	 **13h**	 **14h**	58 (81)	52
13	 **13i**	 **14i**	63 (90)	79
14	 **13j**	 **14j**	62 (93)	27
15	 **13k**	 **14k**	64 (97)	23[g]
16	 **13l**	 **14l**	68 (74)	47
17	 **13m**	 **14m**	69 (94)	36
18	 **13n**	 **14n**	58 (87)	—[e]
19	 **13o**	 **14o**	40 (72)	35[g]

(*continued on next page*)

Table 2 (*continued*)

Entry	Substrate	Product	% Yield (conversion)	% ee[b]
20	 **13p**	 **14p**	19 (83)	45

[a] All reactions were performed in C_6H_6 at 5 °C for 10 h with **1**–substrate–$PhI(OAc)_2$–Al_2O_3 molar ratio = 0.1:1.0:1.5:2.5.
[b] Determined by HPLC analysis using a Chiralcel OD column unless specially noted.
[c] Reaction conducted with **3** as catalyst.
[d] Reaction conducted with **4** as catalyst.
[e] Not determined.
[f] Reaction conducted in toluene at −20 °C.
[g] Determined by HPLC analysis using a Chiralcel OJ column.

diastereomers in 87% yield based on 99% conversion. The **1**-catalyzed intramolecular amidations of **13b** and **13d** also compare favorably to the same reactions of **13b** and **13d** using either ruthenium(II) porphyrin[9] or dirhodium(II,II) catalysts,[8b] which were reported to proceed with either only cis-selectivity or 8:1 cis:trans selectivity in the case of the Rh_2(II,II)-catalyzed intramolecular cyclization of **13d**.

Inspection of entries 6–8 and 12–17 in Table 2 reveals that the electron-withdrawing or -donating capability of the substituent on the acyclic sulfamate ester can affect the enantioselectivity of the intramolecular amidation process. With the exception of **13h**, on going from **13f** → **13g** → **13i**, the ee values of the resultant cyclic sulfamidates increased from 61% to 79% ee as the substituent on the substrate becomes more electron-withdrawing (cf. entries 7–8, and 13). For sulfamate esters with electron-donating substituents as in **13j** and **13k**, a significant drop in enantioselectivity was observed (cf. entries 14 and 15). A similar trend can be found on comparing the ee values obtained for amidation of **13l** and **13m** catalyzed by **1**, which afforded cyclic sulfamidates **14l** and **14m** in 47% and 36% ee, respectively (entries 16 and 17).

A comparison of isolated product yields shows the position of the substituent on the substrate can also affect the efficiency of the intramolecular amidation process. Under the conditions: 10 mol % of **1**, $PhI(OAc)_2$ (1.5 equiv), Al_2O_3 (2.5 equiv), 5 °C, 10 h, reaction of **13o** and **13p** afforded **14o** and **14p** in 40% and 19% yield, respectively (entries 19 and 20). The analogous reactions of **13a**–**n** under these conditions gave product yields of 48–92%.

We attempt to rationalize the virtually complete cis-selectivity observed for the intramolecular amidation of **13b**–**d** with a putative manganese(V)-imido species having a conformation depicted in Figure 2. This shows the cis-hydrogen atom of **13b** is able to interact with the imido-nitrogen atom to form a three-atom centered transition state. In contrast, the trans-hydrogen atom of **13b** always points away during any combinations of the internal rotations. For sulfamate esters **13o** and **13p**, the unfavorable steric interactions between the naphthyl ring of the substrate and cyclohexane ring of **1** rendering it difficult for the benzylic C–H bonds to approach the imido-nitrogen atom. The observed trend in ee values found for the amidation products **14e**–**k** suggests that through-space electrostatic interactions, that is, the field effects,[15] in addition to steric effects could be operative.

To shed more information on the rate-limiting step, we performed competition experiments on the intramolecular amidations of *p*-X–$C_6H_4(CH_2)_2OSO_2NH_2$ [X = H (**13e**), Br (**13f**), Cl (**13g**), F (**13h**) and NO_2 (**13i**),

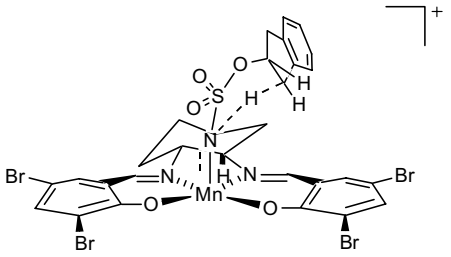


Figure 2. Proposed transition state for intramolecular amidation of **13b** catalyzed by **1**.

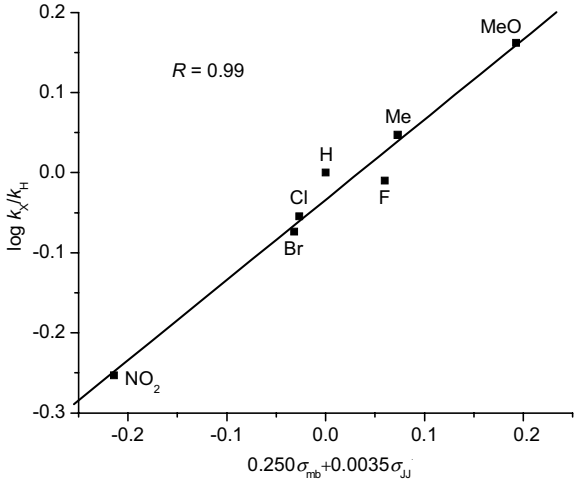
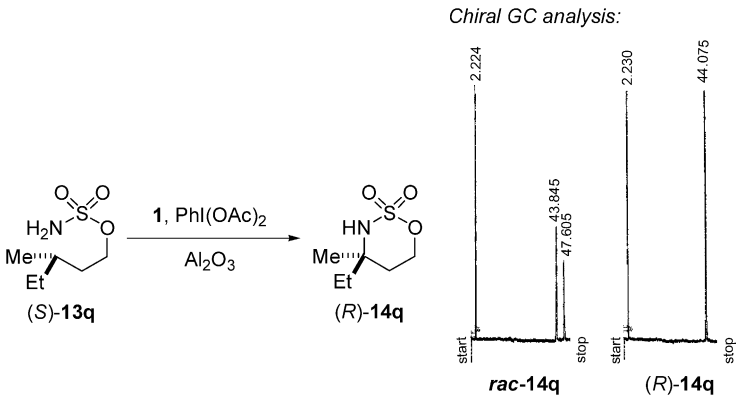


Figure 3. Linear free-energy correlation of $\log k_X/k_H$ versus (σ_{mb}, σ_{JJ}) plot for intramolecular amidation of *para*-substituted sulfamate esters *p*-X–$C_6H_4(CH_2)_2OSO_2NH_2$ **13e**–**k** catalyzed by **1** with $PhI(OAc)_2$.



Scheme 1. Intramolecular amidation of **13q** with $PhI(OAc)_2$ catalyzed by **1**. Gas chromatograms of cyclic sulfamidate **14q** furnished from racemic and optically pure **13q**.

Me (**13j**), OMe (**13k**)]. This gave $\log k_X/k_H$ values of 0.16 (**13k**), 0.047 (**13j**), −0.01 (**13h**), −0.055 (**13g**), −0.074 (**13f**), and −0.253 (**13i**), suggesting that electron-donating groups accelerate whereas electron-withdrawing groups retard the nitrogen atom insertion reaction. A dual-parameter ($\sigma_{mb}, \sigma_{JJ}^{\cdot}$) fitting of $\log k_X/k_H$, as established by Jiang,[16] through multiple regression gave rise to good linearity ($R = 0.99$) with ρ_{mb} and $\rho_{JJ}^{\cdot}$ values of −0.25 and 0.0035, respectively. The $\log k_X/k_H$ versus ($\sigma_{mb}, \sigma_{JJ}^{\cdot}$) plot is shown in Figure 3.

To gain further insight into the mechanism, we examined the reactions of racemic and enantiopure **13q** with **1** as catalyst under the same conditions as that for **13a**–**p**. Intramolecular cyclization of **13q** afforded **14q** in 60% yield with 95% substrate conversion (Scheme 1). For the amidation of (*S*)-**13q**, only a single isomer of **14q** was detected, whose absolute configuration is identical to that observed for the same reactions using either Rh_2(II,II),[8] Ru(II),[9] or Ag(I)[11] as catalyst, as determined by chiral GC[14] (see Scheme 1) and ^{1}H NMR (in the presence of (+)-Eu(hfc)$_3$) analyses of the products. This result indicates the Mn(III)-catalyzed intramolecular amidation reaction is stereospecific.

In summary, the first chiral metallosalen catalyzed enantioselective intramolecular amidation of sulfamate esters that proceeded in moderate to good yields, substrate conversions, with exclusive cis-selectivity and with moderate to good enantioselectivity is reported. The manganese(III) Schiff-base catalyzed reaction also represents the first step toward the development of a general catalytic system for asymmetric intramolecular C–N bond formation. Efforts are currently underway to examine the scope of the present Mn(III)-catalyzed intramolecular amidation protocol with respect to fine-tuning the ee values obtained through structural modification of the chiral Schiff-base ligand.

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13. CCDC 245227 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).
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