# Enantioselective α-amination of ketones mediated by chiral nitridomanganese(V) complexes using ammonia as the terminal nitrogen source

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A series of chiral nitridomanganese(V)salen complexes have been prepared, characterized and investigated as the source of the nitrogen fragment for chiral α-amination of ketones. The chiral nitridomanganese(V)salen complexes are formed by treatment of manganese(III)salen complexes with ammonia under oxidative reaction conditions, and these nitridomanganese(V) complexes have been characterized by spectroscopic methods and X-ray analysis. The structures of the different complexes are discussed and the ability of the chiral nitridomanganese(V)salen complexes to act as chiral nitrogen sources activated by trifluoroacetic anhydride for α-amination of silyl enol ethers has been investigated. The yield and enantiomeric excess of the α-amino ketones are very dependent on the nature of the chiral nitridomanganese(V)salen complex and the silyl enol ether, and the reaction has been investigated under various reaction conditions. The α-amino ketones can be formed in up to 83% yield and with up to 75% ee and the ee can be improved to 93% by a single recrystallization. The perspectives and mechanism for the α-amination of the silyl enol ethers by chiral nitridomanganese(V)salen complexes are discussed.

## Introduction

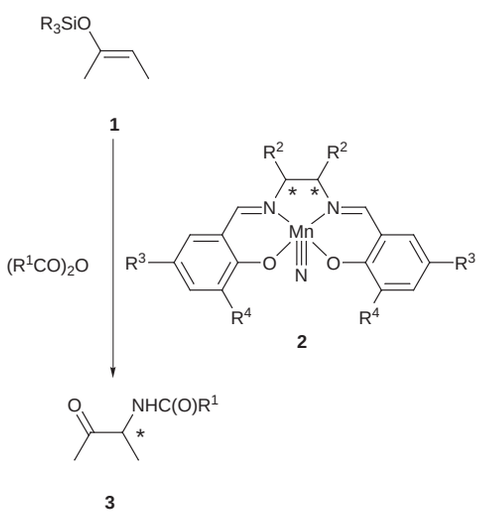
Nitrogen containing compounds are ubiquitous and of immense importance in biological systems, as medicinal drugs, and as metabolites.[1] The vast majority of the biologically active nitrogen containing compounds possess a chiral center. Thus, it is desirable to be able to synthesize enantiomerically pure nitrogen containing compounds.

Many methods exist that allow the making and breaking of bonds in nitrogen containing molecules from the chiral pool without affecting the chirality on existing chiral centers. However, only in recent years have the first methodologies for preparing chiral nitrogen containing molecules from non-chiral molecules been developed. The synthesis of chiral amino-containing molecules can be divided into two different types according to whether the nitrogen atom is already present in the molecule before the chiral induction—Type I—generally performed by addition to imines, enamines or enamides, or if the carbon–nitrogen bond is formed in the actual chiral transformation itself—Type II—most commonly performed by enantioselective addition of an amine fragment to an organic substrate. Representative examples of enantioselective Type I reactions leading to chiral amines include hydrogenation of cyclic enamides catalyzed by $Ru(OAc)_2$–BINAP,[2] hydrogenation of 2-acetamidocinnamic acids and other enamides catalyzed by rhodium complexes,[3] Mannich type addition of silyl ketene acetals to imines[4] and Strecker reactions of aldimines with tributyl cyanide catalyzed by zirconium complexes[5] and finally the recently published Alder-ene reactions[4,6] or addition of silyl enol ethers[7] to α-imino esters catalyzed by copper(I)–BINAP-complexes.

Prominent examples of asymmetric Type II reactions include aziridination of various alkenes using [*N*-(*p*-tolylsulfonyl)-imino]phenyliodane (PhI=NTs) in reactions catalyzed by chiral copper(I) complexes,[8] the nucleophilic ring opening of *meso*-acylaziridines with trimethylsilyl azide catalyzed by ytterbium, titanium, and zirconium complexes,[9] catalytic asymmetric aminohydroxylation of alkenes,[10] enantioselective Michael addition of *O*-alkyl hydroxylamines to α,β-unsaturated carboxylic acid derivatives catalyzed by copper,[11a] as well as magnesium, yttrium and ytterbium,[11b] and amination of silyl enol ethers to give α-amino ketones catalyzed by osmium complexes.[12] A variety of methods for enantioselective allylation of amines catalyzed by palladium complexes have also demonstrated their synthetic utility.[13]

However, we are interested in developing synthetic methods for incorporation of even simpler nitrogen-containing fragments into larger molecular assemblies in a diastereo- and enantioselective fashion, and have decided to turn our attention towards chiral activation of ammonia, which is the primary source of nitrogen for biosynthesis in nature. Ammonia has many advantages to the synthetic chemist, including its low price, ease of handling and low molecular weight, and a straightforward synthesis of chiral amines based on ammonia could therefore be of great use.

In this paper we would like to present a method for enantioselective α-amination of ketones *via* their trimethylsilyl enol ethers **1** in a reaction mediated by chiral nitridomanganese(V) complexes **2** [eqn. (1)]. The resulting α-amino ketones **3** repre-

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sent a group of highly functionalised organic compounds, which are potentially useful starting materials for the synthesis of natural products and medicinal drug candidates.

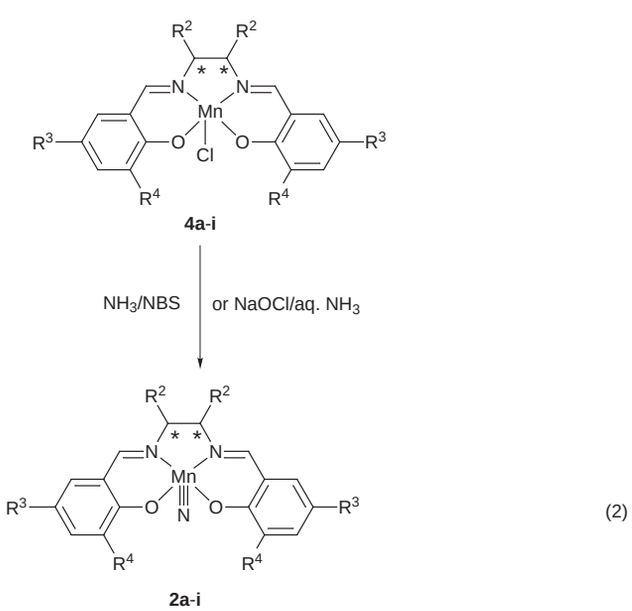
Nitrido complexes of several late transition metals have been known for years, amongst these the very stable N≡Cr(v) and N≡Mn(v) complexes with porphyrin ligands which are isolable and air-stable solids, generally prepared by extrusion of $N_2$ from the corresponding azidometal(III) complexes upon irradiation. It has been demonstrated that the addition of carboxylic anhydrides, such as trifluoroacetic anhydride (TFAA), to solutions of N≡Mn(v)TPP[14] and N≡Cr(v)TPP[15] (TPP = *meso*-tetraphenylporphyrin) produces the corresponding nitrenoid acylimido complexes *in situ* by acylation of the nitrido ligand. In the manganese series, the transfer of the nitrenoid fragment to nucleophilic alkenes leads to aziridines.[14]

Recently, Carreira *et al.*[16] demonstrated that substituted N≡Mn(v) salen (salen = *N*,*N*′-bis(salicylidene)-1,2-diaminoethane) complexes can be prepared by treatment of Mn(III)salen–Cl complexes with an oxidizing agent (NaOCl or NBS) in the presence of ammonia to give the corresponding nitrido complexes in reasonable to good yield as green solids. Treatment of these N≡Mn(v)salen complexes with TFAA in the presence of electron-rich alkenes effected nitrogen transfer.[16] Chiral N≡Mn(v) salen complexes have more recently been prepared and characterized.[17,18]

## Results and discussion

### Preparation, structure and electronic structure of chiral N≡Mn(v)salen complexes

A series of chiral Mn(v)salen complexes **2a**–**i** has been prepared from the appropriate chiral Mn(III)salen–Cl complex **4a**–**i** by treatment with ammonia and *N*-bromosuccinimide [eqn. (2)]

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or with aqueous sodium hypochlorite and saturated aqueous ammonia as described in detail in the Experimental section.

The chiral N≡Mn(v)salen complexes **2a**–**i** are formed in reasonable to good yields (Table 1) and have been characterized by NMR spectroscopy and, for the complexes **2e**,**f** and **i**, by single crystal X-ray structure analysis. The X-ray data are given in the Experimental section, and in the following only the general structural features of **2e**,**f** and **i** will be discussed. The X-ray structures of **2e**,**f** and **i** are presented in Fig. 1.

The X-ray structure of the chiral N≡Mn(v)[*N*,*N*′-bis(6-*tert*-butyl-4-methylsalicylidene)-1,2-diphenylethane-1,2-diaminato] complex **2e** has been briefly discussed earlier[17a] and is very similar to the structure of **2a** which has been characterized by Gray

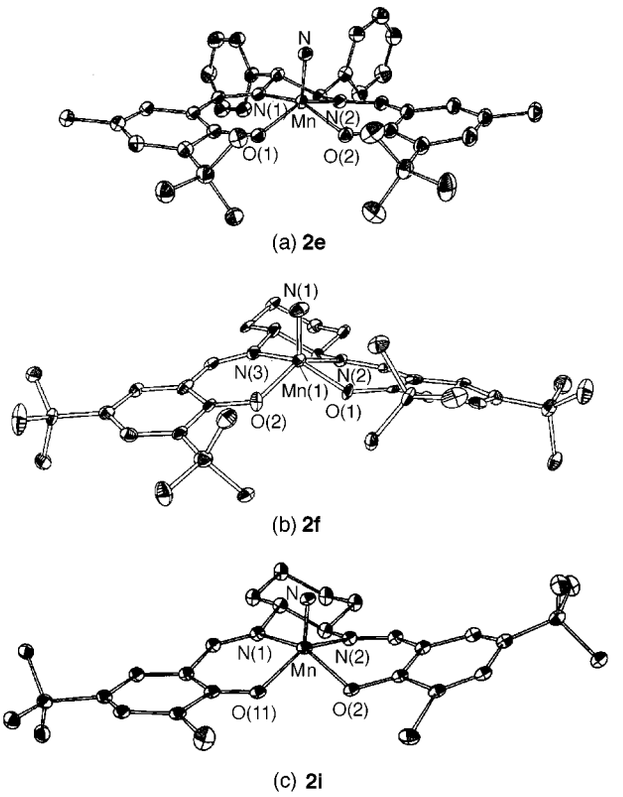
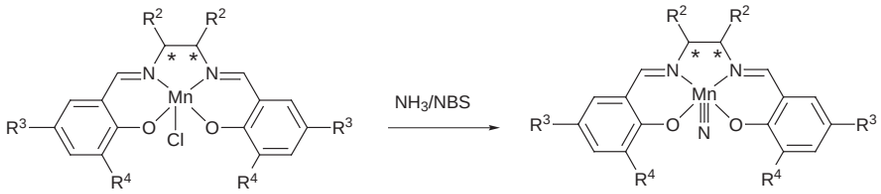



**Fig. 1** (a) Molecular structure of **2e**. C–H hydrogen atoms are not shown. Selected average distances (Å) and angles (°) for **2e**: Mn–N 1.537(6), Mn–N(1) 1.949(6), Mn–N(2) 1.968(6), Mn–O(1) 1.903(6), Mn–O(2) 1.915(6), O(1)–Mn–N 109.8(3), O(2)–Mn–N 103.2(3), N(1)–Mn–N 101.6(3), N(2)–Mn–N 104.0(3), O(1)–Mn–O(2) 85.1(2), O(1)–Mn–N(1) 90.2(2), O(1)–Mn–N(2) 146.2(2), O(2)–Mn–N(1) 155.0(2), O(2)–Mn–N(2) 89.3(2), N(1)–Mn–N(2) 81.2(2).

(b) Molecular structure of **2f**. C–H hydrogen atoms are not shown. Selected average distances (Å) and angles (°) for **2f**: Mn–N(1) 1.526(6), Mn–N(2) 1.972(7), Mn–N(3) 1.966(7), Mn–O(1) 1.916(5), Mn–O(2) 1.897(6), N(1)–Mn–O(1) 105.7(3), N(1)–Mn–O(2) 109.4(3), N(1)–Mn–N(2) 105.2(3), N(1)–Mn–N(3) 100.6(3), O(1)–Mn–O(2) 82.8(2), O(1)–Mn–N(2) 89.8(2), O(1)–Mn–N(3) 153.7(2), O(2)–Mn–N(2) 145.5(2), O(2)–Mn–N(3) 90.3(2), N(2)–Mn–N(3) 82.0(2).

(c) Molecular structure of **2i**. C–H hydrogen atoms are not shown. Selected average distances (Å) and angles (°) for **2i**: Mn–N 1.507(18), Mn–N(1) 1.969(19), Mn–N(2) 1.966(24), Mn–O(1) 1.910(20), Mn–O(2) 1.921(20), O(1)–Mn–N 107.3(9), O(2)–Mn–N 108.1(3), N(1)–Mn–N 103.5(8), N(2)–Mn–N 101.2(9), O(1)–Mn–O(2) 83.4(8), O(1)–Mn–N(1) 90.5(8), O(1)–Mn–N(2) 151.4(8), O(2)–Mn–N(1) 148.4(7), O(2)–Mn–N(2) 89.7(8), N(1)–Mn–N(2) 81.5(8).

*et al.*[17b,18] The N≡Mn bond in **2e** is found to be 1.537 Å, while in **2a**, where there are also two molecules in the asymmetric unit, the approximate N≡Mn bond length is 1.52 Å (1.509(3) and 1.531(3) Å). In the complexes **2a** and **2e**, the manganese atom is situated 0.47 and 0.49 Å, respectively, above the least square plane defined by the coordinating atoms of the ligand. The X-ray structures of the two similar N≡Mn(v)[*N*,*N*′-bis(salicylidene)cyclohexane-1,2-diaminato] complexes **2f** and **i**, in which the N≡Mn bond length for the two complexes are 1.53 Å (1.526(6) Å and 1.525(6) Å; two molecules in the asymmetric unit) and 1.51 Å (1.505(18) Å and 1.510(10) Å; two molecules in the asymmetric unit), respectively, are also presented in Fig. 1. The manganese atom in these complexes also resides 0.507 Å (0.507(3) Å and 0.508(3) Å for the molecules in the asymmetric unit) in **2f** and 0.504 Å (0.494(7) Å and 0.511(7) Å for the molecules in the asymmetric unit) in **2i** above the least square plane defined by the four donor atoms of the ligand framework. From the structural data of these chiral N≡Mn(v)salen complexes no significant variation in the N≡Mn bond length is observed when changing the chiral and electronic properties of the ligand. The N≡Mn(v) bond lengths in the N≡Mn(v)salen




**2a-i**

**Table 1** Preparation of the chiral N≡Mn(v)salen complexes **2a**–**i**

| Entry | Compound | Abs. stereochemistry | $R^2$ | $R^3$ | $R^4$ | Method of synth.[a,b] | Yield (%) |
|---|---|---|---|---|---|---|---|
| 1 | **2a** | (*R*,*R*) | -Ph | -H | -H | A | 59 |
| 2 | **2b** | (*R*,*R*) | -$(CH_2)_4$- | -H | -H | A | 53 |
| 3 | **2c** | (*R*,*R*) | -Ph | -Bu$^t$ | -H | B | 56 |
| 4 | **2d** | (*R*,*R*) | -$(CH_2)_4$- | -Bu$^t$ | -H | B | 60 |
| 5 | **2e** | (*R*,*R*) | -Ph | -Me | -Bu$^t$ | B | 89 |
| 6 | **2f** | (*R*,*R*) | -$(CH_2)_4$- | -Bu$^t$ | -Bu$^t$ | B | 65 |
| 7 | **2g** | (*S*,*S*) | -Ph | -H | -H | A | 55 |
| 8 | **2h** | (*S*,*S*) | -Ph | -Bu$^t$ | -H | B | 61 |
| 9 | **2i** | (*R*,*R*) | -$(CH_2)_4$- | -Bu$^t$ | -Br | C | 45 |

[a] A: Treatment of a methanolic solution of the Mn(III)salen–Cl complex with aq. $NH_3$ and aq. NaOCl at 0 °C. B: Treatment of a $CH_2Cl_2$ solution of the Mn(III)salen–Cl complex with NBS and gaseous $NH_3$ at −50 °C. C: Treatment of the Mn(III)salen–Cl complex with NBS (excess) in $CH_2Cl_2$ at 0 °C overnight, followed by treatment with gaseous $NH_3$ at −50 °C. [b] The salen ligands were prepared from the corresponding enantiopure 1,2-diamines and the appropriate salicylaldehyde, and converted to the intermediary Mn(III)salen–Cl complex by standard methods.

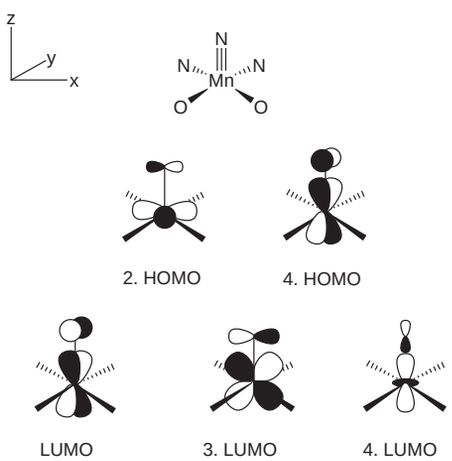


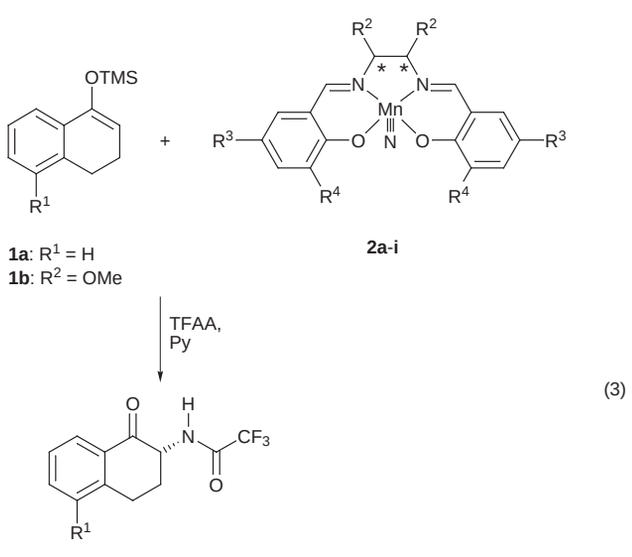

**Fig. 2** The frontier orbitals of the N≡Mn(v) bond.

complexes are very similar to the O=Mn(v) bond length of related types of complexes.[19] With regard to the structure of the chiral N≡Mn(v)salen complexes it should be pointed out that the chirality of the 1,2-diphenylethylenediamine and 1,2-diaminocyclohexane has influence on the orientation of the *tert*-butyl substituents of the salicylidene fragment as these are non-equivalent as demonstrated both by NMR spectroscopy and by X-ray single crystal structure analysis. It is particularly notable in the X-ray structure of **2f** (Fig. 1) that one *tert*-butyl substituent "points up" (the one to the right) while the other "points down" (the one to the left). It is interesting to note that for the other molecule in the unit cell the influence is the opposite for the substituents in the *ortho* positions to the phenoxy group. In short the chirality of the diamine "bridge" appears to be expressed also in the region of the ligand most distant from the origin of the chirality.

The electronic structure of the N≡Mn(v) bond in this type of complex has been studied from both experimental[17b] and theoretical[17a] points of view. In relation to the present investigations only the frontier orbitals of the N≡Mn(v) bond will be discussed. The frontier orbitals calculated for the N≡Mn bond using *ab initio* DFT calculations[20] applying a B3LYP/6-31G* basis set and a TZV basis set for manganese gives the HOMO at −5.71 eV and with only a minor contribution Mn-$d_{x^2-y^2}$, but this orbital is mainly located on the ligand (not shown). The second HOMO is at −6.00 eV and is mainly on the manganese atom as $d_{x^2-y^2}$; while the fourth HOMO at −7.62 eV is the bonding combination of N-$p_y$–Mn-$d_{yz}$. The LUMO and the third LUMO, at −1.60 eV and −0.95 eV, respectively, are the antibonding combination of N-$p_y$–Mn-$d_{yz}$ and N-$p_x$–Mn-$d_{xz}$ orbitals, respectively. The antibonding combination of N-$p_z$–Mn-$d_{z^2}$, the $\sigma^*_{N-Mn}$ orbital, is found at −0.20 eV. This calculated orbital picture corresponds well with the experimental one for the chiral N≡Mn(v)salen complex **2a**[17b] where the HOMO is a′($x^2 - y^2$), while the unfilled levels are dπ* a′($yz$) and a″($xz$) having N≡Mn antibonding character. The higher-lying unoccupied orbital is the a′($z^2$) antibonding $\sigma^*_{N-Mn}$ orbital. The frontier orbitals of the N≡Mn bond are schematically outlined in Fig. 2.

### Amination mediated by the chiral N≡Mn(v)salen complexes 2a–i

The ability of the various chiral N≡Mn(v)salen complexes **2a**–**i** to transfer the chiral nitrogen atom to an organic molecule was tested by reaction with 3,4-dihydro-1-(trimethylsilyloxy)-naphthalene **1a** and trifluoroacetic anhydride (TFAA) at low temperature in the presence of pyridine [eqn. (3)]. In a typical

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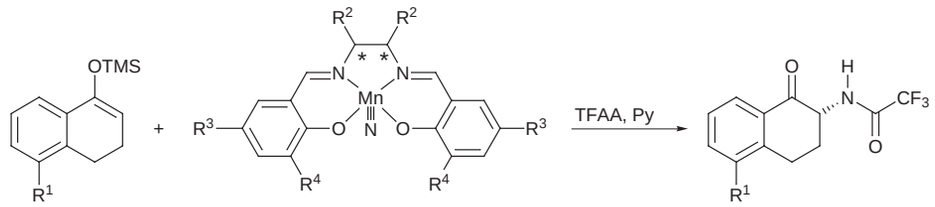


**1a,b** **2a-i** **3a,b**

**Table 2** Enantioselective nitrogen transfer to 3,4-dihydro-1-(trimethylsilyloxy)naphthalenes[5] **1a**,**b** by the chiral N≡Mn(v)salen complexes **2a**–**i**

| Entry | $R^1$ | Complex | Product | Isolated yield (%) | Ee (%)[a] |
|---|---|---|---|---|---|
| 1 | -H | **2a** | **3a** | 79 | 49 |
| 2 | -H | **2b** | **3a** | 83 | 75 |
| 3 | -H | **2c** | **3a** | 75 | 65 |
| 4 | -H | **2d** | **3a** | 62 | 20 |
| 5 | -H | **2e** | **3a** | <5 | — |
| 6 | -H | **2f** | **3a** | <5 | — |
| 7 | -H | **2g** | **3a** | 76 | −49[b] |
| 8 | -H | **2h** | **3a** | 74 | −65[b] |
| 9 | -H | **2i** | **3a** | <5 | — |
| 10 | -OMe | **2g** | **3b** | 55 | −41[b] |
| 11 | -OMe | **2b** | **3b** | 58 | 62 |

[a] Ee of the product was determined by HPLC using a Daicel Chiralcel OD column eluting with hexane–propan-2-ol 98 : 2. [b] Negative values indicate the opposite enantiomer.

experiment, the appropriate chiral N≡Mn(v)salen complex **2a**–**i** was dissolved in dry dichloromethane under $N_2$ and cooled to −78 °C. Pyridine and the silyl enol ether **1a** in dry dichloromethane was added, followed by the dropwise addition of TFAA over a period of 5 min. After stirring for 6 hours at −78 °C the reaction was allowed to warm up to room temperature over a period of 2 hours (increasing the reaction times gave no increase in enantiomeric excess, and resulted in slightly lower chemical yields). The yields and ee's of **3a** for the reactions of **2a**–**i** are summarized in Table 2.

From the results in Table 2, it appears that the α-amination reaction of 3,4-dihydro-1-(trimethylsilyloxy)naphthalene **1a** is very dependent on the chiral ligand. The 1,2-diphenylethylenediamine derived N≡Mn(v)salen complex **2a** reacts with **1a** to give 3,4-dihydro-2-(2,2,2-trifluoroacetamido)naphthalen-1(2*H*)-one **3a** in 79% isolated yield and with 49% ee (entry 1). Changing the chiral fragment of the ligand from 1,2-diphenylethylenediamine to cyclohexane-1,2-diamine (entry 2) leads to an increase in both yield and ee of **3a** to 83% and 75%, respectively. The ee of the product could be improved from 75% to 93% by a single recrystallization from hexane. An introduction of a *tert*-butyl substituent in the 4-position of the salicylidene fragment leads to an increase of the ee when complex **2c** is applied (compared to **2a**), whereas for complex **2d** a decrease in ee is observed (Table 2, entries 3 and 4). Surprisingly, attempted amination reactions with the chiral N≡Mn(v)-salen complexes **2e**,**f** which have the *tert*-butyl substituent in the 6-position (*ortho* to the phenoxy substituents) in the salicylidene ring in close proximity to the manganese center, leads only to very low yields of the α-aminated product **3a** (entries 5, 6). Changing the absolute stereochemistry in the chiral ligand leads to the opposite enantiomer of product **3a** (entries 7, 8). We have also tried to introduce other substituents *ortho* to the phenoxy substituents and in the case of bromine, complex **2i**, also very low yield of **3a** was obtained (entry 9).

The yield and ee of 3,4-dihydro-2-(2,2,2-trifluoroacetamido)-naphthalen-1(2*H*)-one **3a** in the α-amination reaction of 3,4-dihydro-1-(trimethylsilyloxy)naphthalene **1a** using the chiral N≡Mn(v)salen complex **2b** as the nitrogen source and TFAA has also been investigated in different solvents. In $CH_2Cl_2$ 82% yield and 75% ee are obtained while in toluene 54% yield and 55% ee, in hexane 21% yield and 51% ee and in ether 38% yield and 50% ee are obtained. The ee of **3a** is also dependent on the nitrogen base added—in all the previous examples pyridine has been used. The use of other pyridines, such as 4-dimethylaminopyridine leads to nearly the same yield of **3a** (73%) while the ee drops to 52%.

The reaction of 3,4-dihydro-5-methoxy-1-(trimethylsilyloxy)-naphthalene **1b** with **2g** (the (*S*,*S*)-isomer of **2a**) under conditions similar to those employed for the amination of **1a** (pyridine, TFAA, −78 °C for 6 hours) provided the product **3b** in 55% and 41% ee (Table 2, entry 10). This result could be improved both in terms of conversion and optical yield by the use of **2b** as the nitrogen donor instead of **2g** to give **3b** in 58% yield and 62% ee (Table 2, entry 11).

The absolute stereochemistry of the α-aminated product **3a**, obtained by reaction of the silyl enol ether **1a** with the chiral N≡Mn(v)salen complex **2b** which has (*R*,*R*) as the absolute stereochemistry has tentatively been assigned to be (*R*) by comparison of the optical rotation for **3a** with the optical rotation of the corresponding *N*-methoxycarbonyl protected aminotetralone formed from chiral homophenylalanine.[21] The absolute stereochemistry of **3a** indicates that it is the *Re*-face of the alkene fragment of the silyl enol ether that approaches the TFA-activated nitrogen atom in the chiral N≡Mn(v)[*N*,*N*′-bis(salicylidene)cyclohexane-1,2-diaminato] complex. A model for the proposed approach of **1a** to the TFA-activated chiral N≡Mn(v)[*N*,*N*′-bis(salicylidene)cyclohexane-1,2-diaminato] complex (*R*,*R*-stereochemistry) is outlined in Fig. 3.

In Fig. 3, top, four possible modes **A**–**D** for the side-on approach of the silyl enol ether to the TFA-activated nitrogen atom in the chiral N≡Mn(v)salen complex **2b** are presented. These four approaches have also been discussed for the mechanism of the epoxidation reaction of alkenes catalyzed by chiral O=Mn(v)salen complexes.[22] The results in Table 1 allow one to begin to understand how the silyl enol ether approaches the chiral nitrogen atom in the N≡Mn(v) nitrido complex; the *tert*-butyl and bromine substituents *ortho* to the phenoxy substituents have a detrimental effect on the course of the reaction and only very low yield of α-amination product **3a** was obtained when the chiral N≡Mn(v)salen complexes **2e**,**f** and **i** were used as the nitrogen donor system, while for the chiral N≡Mn(v)salen complexes **2a**–**d** good yield of **3a** was obtained, however only the complexes **2a**–**c** induced reasonable ee in the α-aminated product. The effect of the *tert*-butyl and bromine substituents on the reaction course indicates that the

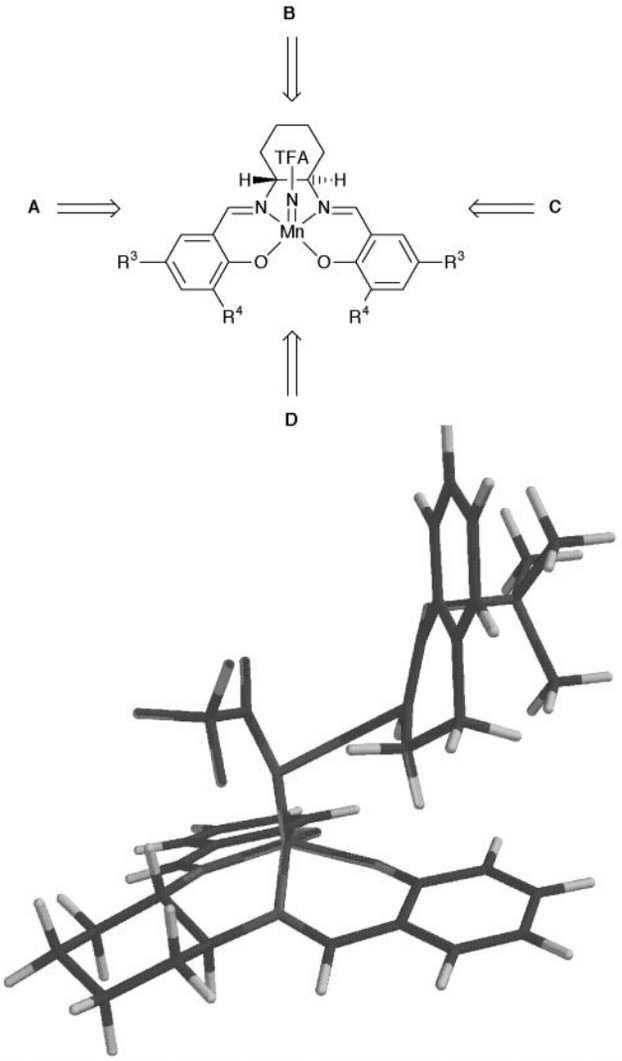


**Fig. 3** (Top) The four different side-on approaches to the chiral N≡Mn(v)salen complex. (Bottom) A model for the approach of the silyl enol ether **1a** to the chiral N≡Mn(v)salen complex (*R*,*R* stereochemistry) **2b** viewed from the **A** site.

space occupied by these two substituents (corresponding to the **D** region in Fig. 3) of the N≡Mn(v)salen complex is of importance for the reaction as very low yield of **3a** is obtained when these two substituents are present in the complex. Different approaches of the silyl enol ether **1a** to the chiral N≡Mn(v)-salen complex **2b** (*R*,*R* stereochemistry) have been investigated using PM3 calculations. The approach of **1a** which accounts for the substituent effects in the complex and the absolute stereochemistry of the α-aminated product **3a** is also shown in Fig. 3. The preferred approach of the silyl enol ether to the TFA activated chiral N≡Mn(v)salen complex is thus probably taking place in the **A**–**D** region of the N≡Mn(v)salen complex.

## Conclusion

A series of chiral nitridomanganese(v)salen complexes has been prepared by reaction of manganese(III)salen complexes with ammonia under oxidative reaction conditions and have been characterized by spectroscopic methods and X-ray analysis. The chiral nitridomanganese(v)salen complexes can act as a chiral nitrogen source activated by trifluoroacetic anhydride for α-amination of aromatic silyl enol ethers and give the α-amino ketones in up to 83% yield and with up to 75% ee and the ee of the product can be improved to be 93% by a single recrystallization. The mechanism for the α-amination of the silyl enol ethers by chiral nitridomanganese(v)salen complexes probably takes place by a side-on approach of the silyl enol ether to the trifluoroacetic acid activated nitrogen atom in the chiral nitridomanganese(v)salen complex.

## Experimental

### General methods

The $^1$H NMR and $^{13}$C NMR spectra were recorded in $CDCl_3$ at 300 MHz and 75 MHz, respectively on a Varian Gemini 300. Chemical shifts for $^1$H NMR and $^{13}$C NMR are reported in ppm downfield from tetramethylsilane (TMS). HPLC analysis was performed using a 4.6 mm × 25 cm DAICEL CHIRALCEL OD column. Optical rotation was measured on a Perkin-Elmer 241 polarimeter. Flash chromatography was performed using silica gel 60 (particle size 0.040–0.063 mm, Merck). Solvents were dried using standard procedures. The starting silyl enol ethers **1a**,**b** were prepared by the standard method[23] and purified by distillation before use.

### General N≡Mn(v)salen syntheses

The substituted N≡Mn(v)salen complexes were prepared by either of the two known methods,[16a,b] depending on solubility of the starting materials. The methods described below were representative examples of these protocols.

**Method A. Nitrido[(*R*,*R*)-*N*,*N*′-bis(salicylidene)cyclohexane-1,2-diaminato]manganese(v) 2b.** (*R*,*R*)-*N*,*N*′-Bis(salicylidene)-cyclohexane-1,2-diamine[24] (6.70 g, 21.6 mmol) was dissolved in MeOH (125 mL) and heated to 55 °C on an oil bath, whereupon $Mn(OAc)_2{\cdot}4H_2O$ (5.56 g, 22.7 mmol) was added over a period of 5 min. The resulting brown solution was refluxed for 1 h, after which it was allowed to cool to rt with stirrring over a period of 45 min. Conc. aq. $NH_3$ (25 ml, 0.37 mol) was added dropwise over 5 min, followed by dropwise addition of aqueous NaOCl (12% by weight, 81 mL, 6 equiv.) with vigorous stirring over 40 min, after which the reaction was stirred for 15 min. $CH_2Cl_2$ (150 mL) was carefully added, followed by water (100 mL). The phases were separated, and the aqueous phase was extracted with $CH_2Cl_2$ (4 × 75 mL). The combined $CH_2Cl_2$ phases were washed with water (3 × 100 mL) and brine (100 mL), the solvent was removed *in vacuo*, and the resulting green residue was filtered through a short column of deactivated basic alumina (Brockman III, eluent: $CH_2Cl_2$). Evaporation of the solvent gave **2b** as a dark green microcrystalline solid, yield 4.43 g (11.4 mmol, 53%).

**Method B. [(*R*,*R*)-*N*,*N*′-Bis(4,6-bis(*tert*-butyl)salicylidene)-cyclohexane-1,2-diaminato]nitridomanganese(v) 2f.** [(*R*,*R*)-*N*,*N*′-Bis(4,6-bis(*tert*-butyl)salicylidene)cyclohexane-1,2-diaminato]chloromanganese(III) **4f**[25] (1.10 g, 1.74 mmol) was dissolved in dry $CH_2Cl_2$ (200 mL) and cooled to −50 °C on a solid $CO_2$–ethanol cooling bath, and NBS (1.55 g, 8.74 mmol) was added in one portion. The resulting brown solution was stirred, while gaseous $NH_3$ was bubbled through the reaction for 25 minutes, causing the reaction to turn green. The cooling bath was removed, and the reaction was allowed to warm to room temperature over a period of 2 h with stirring. Finally the reaction mixture was poured into water (100 mL), the phases were separated, and the aqueous phase was extracted with $CH_2Cl_2$ (100 mL). The combined organic extracts were washed with water (3 × 100 mL) and dried ($MgSO_4$). Removal of the solvent gave the product as a dark green solid, which could be recrystallized from MeCN to give **2f** as dark green needles, yield 690 mg (1.12 mmol, 65%). Crystals suitable for X-ray crystallography were prepared by slow cooling (48 h) of a dilute MeCN solution of **2f** in a Dewar flask.

**Nitrido[*N*,*N*′-bis(salicylidene)-1,2-diphenylethylene-1,2-diaminato]manganese(v) 2a.** $^1$H NMR ($CDCl_3$) $\delta$ 7.81 (s, 2H),

7.64 (s, 1H), 7.54 (s, 1H), 7.43–7.29 (m, 8H), 7.18–7.00 (m, 8H), 5.07 (m, 1H), 4.89 (m, 1H). $\nu_{max}$/cm$^{-1}$ 1050 (Mn≡N).

**Nitrido[*N*,*N*′-bis(salicylidene)cyclohexane-1,2-diaminato]-manganese(v) 2b.** $^1$H NMR ($CDCl_3$) $\delta$ 8.00 (d, $J$ = 7.6 Hz, 2H), 7.37 (dd, $J$ = 13.2, 6.7 Hz, 2H), 7.20 (m, 2H), 7.16 (m, 2H), 6.69 (dd, $J$ = 6.8, 17.0 Hz, 2H), 3.43 (m, 1H), 3.19 (m, 1H), 2.67 (m, 1H), 2.55 (m, 1H), 2.05 (br s, 2H), 1.59–1.35 (br m, 4H). $\nu_{max}$/cm$^{-1}$ 1052 (Mn≡N).

**[*N*,*N*′-Bis(4-*tert*-butylsalicylidene)-1,2-diphenylethylene-1,2-diaminato]nitridomanganese(v) 2c.** $^1$H NMR ($CDCl_3$) $\delta$ 7.78 (br s, 2H), 7.65 (s, 1H), 7.41 (br s, 1H), 7.39–7.28 (m, 6H), 7.16 (br s, 6H), 6.85 (s, 2H), 5.00–4.80 (m, 2H), 1.09 (s, 18H). $^{13}$C NMR ($CDCl_3$) $\delta$ 167.68, 166.80, 138.83, 138.75, 136.55, 134.81, 134.77, 129.51, 129.38, 129.24, 129.15, 129.13, 128.93, 128.50, 122.38, 122.28, 118.84, 118.60, 81.70, 81.13, 33.75, 31.19. $\nu_{max}$/cm$^{-1}$ 1051 (Mn≡N).

**[*N*,*N*′-Bis(4-*tert*-butylsalicylidene)cyclohexane-1,2-diaminato]nitridomanganese(v) 2d.** $^1$H NMR ($CDCl_3$) $\delta$ 8.00 (d, $J$ = 11.5, 2H), 7.43 (m, 2H), 7.08 (m, 4H), 3.37 (br m, 1H), 3.17 (br m, 1H), 2.68 (br m, 1H), 2.53 (br m, 1H), 2.05 (m, 2H), 1.57–1.13 (br m, 4H), 1.28 (s, 9H), 1.27 (s, 9H). $^{13}$C NMR ($CDCl_3$) $\delta$ 167.23, 165.06, 162.49, 161.90, 138.75, 138.56, 134.13, 134.02, 129.50, 129.15, 122.43, 121.95, 119.50, 117.80, 73.21, 71.81, 33.76, 31.15, 28.85, 28.41, 24.51, 24.13. $\nu_{max}$/cm$^{-1}$ 1050 (Mn≡N).

**[*N*,*N*′-Bis(4-methyl-6-*tert*-butylsalicylidene)-1,2-diphenylethylene-1,2-diaminato]nitridomanganese(v) 2e.** Previously reported.[17a]

**[*N*,*N*′-Bis(4,6-bis(*tert*-butyl)salicylidene)cyclohexane-1,2-diaminato]nitridomanganese(v) 2f.** $^1$H NMR ($CDCl_3$) $\delta$ 7.96 (d, $J$ = 18.2 Hz, 2H), 7.46 (d, 7.1 Hz, 2H), 6.97 (d, $J$ = 16.5 Hz, 2H), 3.45 (br s, 1H), 3.03 (br m, 1H), 2.68 (br s, 1H), 2.53 (m, 1H), 2.02 (br s, 2H), 1.50–1.33 (br m, 4H), 1.49 (s, 9H), 1.45 (s, 9H), 1.29 (s, 9H), 1.28 (s, 9H).$^{13}$C NMR ($CDCl_3$) $\delta$ 168.02, 167.51, 162.52, 161.88, 140.64, 137.35, 130.94, 130.62, 127.85, 127.43, 120.46, 118.35, 73.29, 71.50, 35.85, 33.93, 31.32, 29.70, 28.88, 28.44, 24.58, 24.19. $\nu_{max}$/cm$^{-1}$ 1050 (Mn≡N).

**[*N*,*N*′-Bis(6-bromo-4-*tert*-butylsalicylidene)cyclohexane-1,2-diaminato]nitridomanganese(v) 2i.** Prepared by a modification of Method B by stirring [(*R*,*R*)-*N*,*N*′-bis(4-*tert*-butylsalicylidene)cyclohexane-1,2-diaminato]chloromanganese(III) **4d** with a 10-fold excess of NBS in $CH_2Cl_2$ for 24 h before the addition of ammonia at −50 °C. $^1$H NMR ($CDCl_3$) $\delta$ 7.99 (d, $J$ = 7.9 Hz, 2H), 7.78 (dd, $J$ = 2.2, 5.0 Hz, 2H), 7.09 (dd, $J$ = 2.8, 12.1 Hz, 2H), 3.34 (m, 1H), 3.22 (m, 1H), 2.68 (m, 1H), 2.52 (m, 1H), 2.07 (m, 2H), 1.58–1.31 (m, 4H), 1.27 (s, 9H), 1.26 (s, 9H). $^{13}$C NMR ($CDCl_3$) $\delta$ 162.57, 162.00, 160.85, 139.55, 139.37, 137.12, 136.81, 129.50, 129.13, 119.74, 118.13, 117.62, 117.18, 73.28, 72.23, 33.85, 31.25, 28.79, 28.29, 24.43, 24.07. $\nu_{max}$/cm$^{-1}$ 1052 (Mn≡N).

### Representative N-transfer reaction

Nitrido[*N*,*N*′-bis(salicylidene)cyclohexane-1,2-diaminato]-manganese(v) **2b** (128 mg, 0.50 mmol) was dissolved in dry $CH_2Cl_2$ (4.0 mL) in a 10 mL Schlenck flask under an atmosphere of dry $N_2$, and the resulting green solution was stirred magnetically and cooled to −78 °C. After 5 min of stirring, dry pyridine (70 μL, 68 mg, 0.87 mmol) was added by means of a syringe through a septum, followed by 3,4-dihydro-1-(trimethylsilyloxy)naphthalene **1a** (50 mg, 0.23 mmol) dissolved in dry $CH_2Cl_2$ (1.0 mL). Dry TFAA (0.10 mL, 0.71 mmol) was added dropwise from a syringe over a period of 5 min, the resulting reaction mixture was stirred for 6 h while maintaining the temperature at −78 °C, after which the reaction mixture was allowed to warm to rt over a period of two hours. The reaction was quenched and hydrolyzed by addition of Celite (800 mg) and silica gel (800 mg) and stirred for 30 minutes. After filtration through a plug of Celite, the solvent was removed *in vacuo*, and the resulting residue was chromatographed on silica gel (gradient elution: $CH_2Cl_2$–hexane 1:2 to $CH_2Cl_2$). Evaporation of the solvent gave 3,4-dihydro-2-(2,2,2-trifluoroacetamido)naphthalen-1(2*H*)-one **3a** as a colorless crystalline solid, yield 49 mg (0.19 mmol, 83%), mp 152–154 °C (subl.).

**(*R*)-3,4-Dihydro-2-(2,2,2-trifluoroacetamido)naphthalen-1(2*H*)-one 3a.** $^1$H NMR ($CDCl_3$) $\delta$ 8.03 (dd, $J$ = 7.7, 1.1 Hz, 1H), 7.57 (dt, $J$ = 7.7, 1.6 Hz, 1H) overlaid with 7.58 (br s, 1H; NH), 7.36 (t, $J$ = 7.6 Hz, 1H), 7.30 (d, $J$ = 7.7 Hz, 1H), 4.64 (dt, $J$ = 13.7, 5.0 Hz, 1H), 3.30 (ddd, $J$ = 5.0, 13.2, 17.0 Hz, 1H), 3.07 (ddd, $J$ = 17.6, 4.4, 2.7 Hz, 1H), 2.92–2.84 (m, 1H), 1.99 (m, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$ 193.92, 157.21 (q, $^2J$(F,C) = 37.6 Hz), 143.56, 134.66, 130.74, 129.02, 127.81, 115.64 (q, $^1J$(F,C) = 286.9 Hz), 56.77, 29.45, 27.98. MS (EI) *m*/*z* 257 ($M^+$, 15%). HPLC (Daicel Chiralcel OD, hexane–Pr$^i$OH 98:2, flow rate 0.7 mL min$^{-1}$, UV-detection at 248 nm) $t_r$ = 13.2 min (major), $t_r$ = 19.3 min (minor). $[\alpha]_D^{25}$ = −58.8 ($c$ = 1.0, $CHCl_3$).

**(*R*)-3,4-Dihydro-5-methoxy-2-(2,2,2-trifluoroacetamido)-naphthalen-1(2*H*)-one 3b.** $^1$H NMR ($CDCl_3$) $\delta$ 7.61 (dd, $J$ = 7.7, 1.1 Hz, 1H), overlaid with 7.56 (br s, 1H), 7.33 (t, $J$ = 7.7 Hz, 1H), 7.09 (d, $J$ = 7.7 Hz, 1H), 4.62 (dt, $J$ = 14.3, 4.4 Hz, 1H), 3.88 (s, 3H), 3.22 (dd, $J$ = 5.0, 17.6 Hz, 1H), 2.96–2.84 (m, 2H), 1.96–1.81 (m, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$ 194.21, 157.13 (q, $^2J$(F,C) = 37.6 Hz), 156.82, 132.50, 131.74, 127.61, 119.06, 115.65 (q, $^1J$(F,C) = 288.0 Hz), 115.29, 56.31, 55.71, 28.58, 21.91. MS (EI) *m*/*z* 287 ($M^+$, 10%). HPLC (Daicel Chiralcel OD, hexane–Pr$^i$OH 98:2, flow rate 0.7 mL min$^{-1}$, UV-detection at 248 nm) $t_r$ = 11.7 min (minor), $t_r$ = 13.3 min (minor). $[\alpha]_D^{25}$ = −37.0 ($c$ = 0.7, $CHCl_3$).

### Crystallographic data †

**2e.** $C_{38}H_{42}N_3O_2Mn$; MW 627.72; triclinic, space group $P\bar{1}$, $a$ = 10.2919(8), $b$ = 12.0062(9), $c$ = 14.139(1) Å, $\alpha$ = 88.543(1)°, $\beta$ = 76.608(1)°, $\gamma$ = 77.637(1)°, $V$ = 1659.7(2) Å$^3$, $Z$ = 2. 6542 independent reflections measured at 120 K on a Siemens SMART CCD diffractometer. Mo-Kα. 4697 reflections with $I > 3\sigma(I)$ and 329 variables yields $R$ = 0.052, $R_w$ = 0.057. The structures of the two molecules are related by an approximate center of symmetry except for the chiral centers. This necessitated the use of severe constraints on the refinement.[26] One of the molecules shows disorder such that the manganese and nitride atoms are on the other side of the salen plane. In most of the crystals this develops into twinning. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC).

**2f.** $C_{36}H_{52}N_3O_2Mn$; MW 613.75; triclinic, space group $P\bar{1}$, $a$ = 9.9795(4), $b$ = 13.4234(6), $c$ = 14.6685(6) Å, $\alpha$ = 63.1440(10)°, $\beta$ = 78.5960(10)°, $\gamma$ = 71.5410(10)°, $V$ = 1659.37(12) Å$^3$, $Z$ = 2. 9514 independent reflections measured at 120 K on a Siemens SMART CCD diffractometer. Mo-Kα. 8212 reflections with $I > 3\sigma(I)$ and 757 variables yields $R$ = 0.068, $R_w$ = 0.119.[27]

**2i.** $C_{28}H_{34}N_3O_2MnBr_2$; MW 661.39; monoclinic, space group $P2_1$, $a$ = 12.2876(5), $b$ = 9.1876(4), $c$ = 24.399(1) Å, $\beta$ = 90.518(1)°, $V$ = 2754.3(2) Å$^3$, $Z$ = 4. 15788 independent reflections measured at 120 K on a Siemens SMART CCD dif-

† CCDC reference number 207/318. See http://www.rsc.org/suppdata/p1/1999/1559 for crystallographic files in .cif format.

fractometer. Mo-Kα. 3748 reflections with $I > 2\sigma(I)$ and 271 variables yields $R = 0.060$, $R_w = 0.060$.

## Note added in proof

After the submission of this paper Komatsu *et al.* have published a paper where it was shown that the nitridomanganese(v) complex **2b** reacts with 3,4-dihydro-1-(trimethylsilyloxy)naphthalene **1a** to the *N*-trifluoroacetylated α-aminoketone in 55% yield and 79% ee, results which are very similar to ours.[28]


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## References


1 For an introduction to the biological importance of nitrogen containing compounds, see for example, *Comprehensive Organic Chemistry, Vol. 5*, exec. eds. D. Barton and W. D. Ollis, ed. E. Haslam, Pergamon Press, Oxford, 1979, part 22, p. 21, part 23, p. 177, part 28, p. 867, part 30, p. 1043.

2 (*a*) M. Kitamura, Y. Hsiao, M. Ohta, M. Tsukamoto, T. Ohta, H. Takaya and R. Noyori, *J. Org. Chem.*, 1994, **59**, 297; (*b*) R. Noyori, M. Ohta, Y. Hsiao, M. Kitamura, T. Ohta and H. Takaya, *J. Am. Chem. Soc.*, 1986, **108**, 7117.

3 (*a*) G. Zhu and X. Zhang, *J. Org. Chem.*, 1998, **63**, 3133; (*b*) F.-Y. Zhang, C.-C. Pai and A. S. C. Chan, *J. Am. Chem. Soc.*, 1998, **120**, 5808.

4 W. J. Drury, III, D. Ferraris, C. Cox, B. Young and T. Lectka, *J. Am. Chem. Soc.*, 1998, **120**, 11006.

5 (*a*) M. S. Sigma and E. N. Jacobsen, *J. Am. Chem. Soc.*, 1998, **120**, 5315; (*b*) H. Ishitani, S. Kamiyama and S. Kobayashi, *Angew. Chem., Int. Ed.*, 1998, **37**, 3186.

6 S. Yao, X. Fang, K. A. Jørgensen, *Chem. Commun.*, 1998, 2547.

7 D. Ferraris, B. Young, C. Cox, W. J. Drury, III, T. Dudding and T. Lectka, *J. Org. Chem.*, 1998, **63**, 6090.

8 (*a*) D. A. Evans, K. A. Woerpel, M. M. Hinman and M. M. Faul, *J. Am. Chem. Soc.*, 1991, **113**, 726; (*b*) D. A. Evans, M. M. Faul, M. T. Bilodeau, B. A. Anderson and D. M. Barnes, *J. Am. Chem. Soc.*, 1993, **115**, 5328; (*c*) Z. Li, K. R. Conser and E. N. Jacobsen, *J. Am. Chem. Soc.*, 1993, **115**, 5326; (*d*) Z. Li, R. W. Quan and E. N. Jacobsen, *J. Am. Chem. Soc.*, 1995, **117**, 5889.

9 D. Ferraris and W. J. Drury, III, *J. Org. Chem.*, 1998, **63**, 4568.

10 (*a*) G. Li, H.-T. Chang and K. B. Sharpless, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 451; (*b*) K. L. Reddy and K. B. Sharpless, *J. Am. Chem. Soc.*, 1998, **120**, 1207.

11 (*a*) L. Falborg and K. A. Jørgensen, *J. Chem. Soc., Perkin Trans. 1*, 1996, 2823; (*b*) M. P. Sibi, J. J. Shay, M. Liu and C. P. Jasperse, *J. Am. Chem. Soc.*, 1998, **120**, 6615.

12 P. Phukan and A. Sudalai, *Tetrahedron: Asymmetry*, 1998, **9**, 1001.

13 M. Johannsen and K. A. Jørgensen, *Chem. Rev.*, 1998, **98**, 1689.

14 L. A. Bottomley and F. L. Neely, *J. Am. Chem. Soc.*, 1988, **110**, 6748.

15 L. A. Bottomley and F. L. Neely, *Inorg. Chem.*, 1990, **29**, 1860.

16 (*a*) J. Du Bois, J. Hong, E. M. Carreira and M. W. Day, *J. Am. Chem. Soc.*, 1996, **118**, 915; (*b*) J. Du Bois, C. S. Tomooka, J. Hong, E. M. Carreira and M. W. Day, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1645; (*c*) J. Du Bois, C. S. Tomooka, J. Hong and E. M. Carreira, *Acc. Chem. Res.*, 1997, **30**, 364; (*d*) J. Du Bois, C. S. Tomooka, J. Hong and E. M. Carreira, *J. Am. Chem. Soc.*, 1997, **119**, 3179.

17 (*a*) A. S. Jepsen, M. Roberson, R. G. Hazell and K. A. Jørgensen, *Chem. Commun.*, 1998, 1599; (*b*) C. J. Chang, W. B. Connick, D. W. Low, M. W. Day and H. B. Gray, *Inorg. Chem.*, 1998, **37**, 3107.

18 See also: C. J. Chang, D. W. Low, M. W. Day and H. B. Gray, *Inorg. Chem.*, 1997, **37**, 270 for a study of nitrogen-atom transfer between manganese(v) nitrido and manganese(iii) Schiff-base complexes.

19 (*a*) T. J. Collins and S. W. Gordon-Wylie, *J. Am. Chem. Soc.*, 1989, **111**, 4511; (*b*) F. M. MacDonnell, N. L. P. Fackler, C. Stern and T. V. O'Halloran, *J. Am. Chem. Soc.*, 1994, **116**, 7431; C. G. Miller, S. W. Gordon-Wylie, C. P. Horwitz, S. A. Strazisar, D. K. Peraino, G. R. Clark, S. T. Weintraub and T. R. Collins, *J. Am. Chem. Soc.*, 1998, **120**, 11540.

20 Gaussian 94, Revision E. 2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrezewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzales and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1995.

21 B. E. McClure, P. K. Lumma, B. H. Arison, J. H. Jones and J. J. Baldwin, *J. Org. Chem.*, 1983, **48**, 2675.

22 See *e.g.* (*a*) E. N. Jabobsen, in *Catalytic Asymmetric Synthesis*, ed. I. Ojima, VCH Publishers, New York, 1993, p. 159; (*b*) M. Palucki, N. S. Finney, P. J. Pospisil, M. L. Gueler, T. Ishida and E. N. Jacobsen, *J. Am. Chem. Soc.*, 1998, **120**, 948; (*c*) T. Linker, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2060.

23 H. C. Bell, J. T. Pinhey and S. Sternhell, *Austr. J. Chem.*, 1982, **35**, 2237.

24 Y. Belokon, N. Ikonnikov, M. Moscalenko, M. North, S. Orlova, V. Tararov and L. Yashkina, *Tetrahedron: Asymmetry*, 1996, 7; 851.

25 J. F. Larrow, E. N. Jacobsen, Y. Gao, Y. Hong, X. Nie and C. M. Zepp, *J. Org. Chem.*, 1994, **59**, 1939.

26 X-Ray programs: (*a*) SIR97, G. Cascarano, A. Altomare, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, D. Siliqi, M. C. Burla, G. Polidori and M. Camalli, *Acta Crystallogr., Sect. A*, 1996, **52**, C50; (*b*) G. S. Pawley, *Adv. Struct. Res. Diffr. Methods*, 1972, **4**, 1; (*c*) ORTEP III, M. N. Burnett and C. K. Johnson, Report ORNL-6895, Oak Ridge National Laboratory, Tennessee, USA, 1996.

27 Also for **2f** and **2i** pseudosymmetry necessitated the use of constraints in the refinement.

28 S. Minakata, T. Ando, M. Nishimura, I Ryu and M. Komatsu, *Angew. Chem., Int. Ed.*, 1998, **37**, 3392.



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