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Practical (Asymmetric) Transfer Hydrogenation of Ketones catalyzed by manganese with (chiral) diamines ligands

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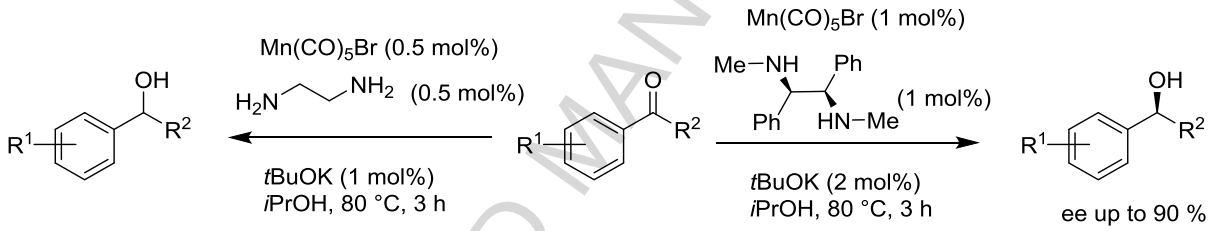
Abstract

The reduction of ketones with 2-propanol as reductant was achieved using an in-situ generated catalytic system based on manganese pentacarbonyl bromide, as metal precursor, and ethylenediamine as ligand. The reaction proceeds in high yield at 80 °C, in 3h, with 0.5 mol% of catalyst. In the presence of chiral (1*R*,2*R*)-*N*,*N*′-Dimethyl-1,2-diphenylethane-1,2-diamine, as the ligand, sterically hindered alcohols were produced with enantiomeric excess up to 90%.

Keywords

Manganese, reduction, asymmetric hydrogen transfer, ketones, chiral diamines, chiral alcohol, ethylenediamine, (1*R*,2*R*)-*N*,*N*′-Dimethyl-1,2-diphenylethane-1,2-diamine

Graphical abstract



Highlights

- **In-situ generated catalytic system based on manganese pentacarbonyl bromide and ethylenediamine promotes the reduction of ketones with low catalytic loading**
- **With (1*R*,2*R*)-*N*,*N*′-Dimethyl-1,2-diphenylethane-1,2-diamine as chiral ligand, asymmetric reduction of ketones was achieved with enantioselectivity up to 90% ee.**
- **Phosphine-free bidendate aliphatic diamines as ligand for hydrogen transfer reaction with manganese**

Acknowledgements

We thank the Centre National de la Recherche Scientifique (CNRS), the Université de Rennes 1, INCREASE FR-CNRS 3707, la Fondation Rennes 1 (grant to D.W.), the Institut Universitaire de France (IUF) and the Agence National de la Recherche (ANR agency, program JCJC ANR-15-CE07-0001 "Ferracycles").

Funding: This work was supported by the Agence National de la Recherche (ANR agency, program JCJC ANR-15-CE07-0001 "Ferracycles"), l'Université de Rennes 1, the Institut Universitaire de France (IUF) and the Centre National de la Recherche Scientifique (CNRS).

Introduction

Homogeneous catalysis plays an important role in the development of modern environmentally friendly and atom-economical chemistry. While noble transition metal complexes still remain the prominent actors in this area, the search for new alternatives based on their more abundant, inexpensive first row congeners clearly becomes one of the emerging trends of the present century.[1] Compared to iron,[2] manganese-based catalysis has remained in the shadow in spite of the natural abundance of this metal, third most abundant transition metal in the Earth's crust after iron and titanium, and its biocompatibility.[3]

The rise of manganese catalyzed reduction reactions started recently after the initial work of Beller[4] in hydrogenation and Milstein in hydrogen auto-transfer reaction.[5] The potential of manganese catalysts in such redox reactions was exemplified with various type of tridendate ligands, mainly phosphorus and nitrogen atoms.[6-19] Interestingly, in the case of hydrogen transfer reaction, using isopropanol as hydrogen donor, Beller has shown that tridentate nitrogen ligand, namely di(picolyl)amine, could promote the reduction of ketones, at 70°C, in 24 h, with a ratio substrate:catalyst of 100:1.[20] Asymmetric reduction of ketones with manganese is far less developed and the two first example were reported by Clarke[21] and Kirchner[22], using related chiral ferrocenyl based tridentate PNN or PNP' ligands.

In general, tridentate ligands were used in manganese catalyzed reduction, except in one recent case in which bidentate amino-phosphine ligand was efficient for the hydrogenation of esters.[23] In the meantime, most of the ligands used to date, except the dipicolylamine, were phosphine-based ligands. Following our previous contributions on manganese catalyzed hydrosilylation [24-26], hydrogenation and hydrogen borrowing reactions [15, 27, 28], we were looking for simple, sustainable and practical catalytic systems to promote hydrogen transfer reactions. We found that well-defined nitrogen-based bidendate manganese catalysts, featuring a picolylamine ligand, were highly efficient for the reduction of ketones and aldehydes by hydrogen transfer reactions.[29] Inspired by the breakthrough of Noyori, introducing chiral diamines as ligands in ruthenium catalyzed asymmetric reduction of ketones,[30, 31] we envisioned that simple diamines could be suitable for manganese-

catalyzed reduction of ketones using isopropanol as the hydrogen donor, and that eventually asymmetric reduction of ketones could be achieved with chiral diamines.

In the present contribution, we demonstrate that diamines, as simple as ethylenediamine, can promote hydrogen transfer reaction with manganese, and that the catalytic system can be generated *in-situ*. Besides, we have extended the reactivity to asymmetric hydrogen transfer reaction, with ee up to 90%, employing symmetrical chiral diamines as ligands.

Experimental

Representative procedure for transfer hydrogenation reaction of acetophenone: To a solution of acetophenone (58 µL, 0.5 mmol) in 2-propanol (0.5 mL) was added a stock solution of manganese pentacarbonyl bromide (0.5 mL, 0.005 $mol.L^{-1}$; 2.7 mg, 0.010 mmol, in 2 mL 2-propanol) followed, in this order, by a stock solution of ethylenediamine (0.5 mL, 0.005 $mol.L^{-1}$; 1.0 µL, 0.0125 mmol, in 2.5 mL 2-propanol) and *t*BuOK (0.5 mL, 0.010 $mol.L^{-1}$; 2.4 mg, 0.020 mmol, in 2 mL 2-propanol). The reaction mixture was stirred for 3 hours at 80°C in an oil bath. The solution was then filtered through a small pad of silica (2 cm in a Pasteur pipette). The silica was washed with ethyl acetate. The filtrate was evaporated and the conversion was determined by ^1H NMR. The crude residue was then purified by column chromatography (SiO_2, mixture of petroleum ether/ethyl acetate or dietyl ether as eluent**.**

Enantiomeric excesses were determined by GC analyses performed on GC-2014 (Shimadzu) 2010 apparatus equipped with Supelco beta-DEX 120 column (30 m x 0.25 mm). The determination of the absolute configuration was done by comparison with (*S*)-alcohol obtained by kinetic resolution of racemic alcohols with Novozym 435 (Candida Antarctica Lipase B) and by comparison of the retention times with the literature.[32-34]

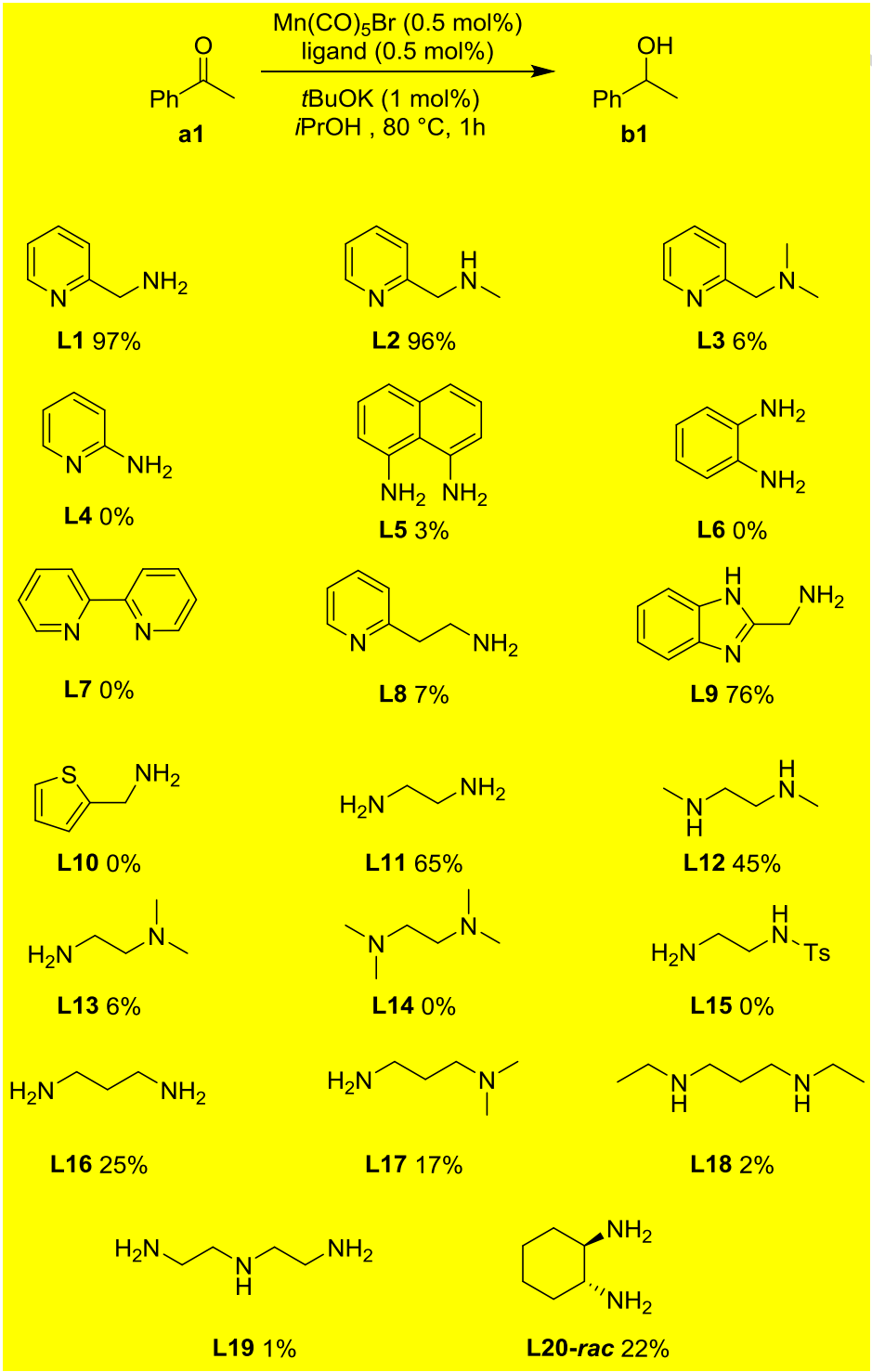
Results and Discussion

To start our investigation, based our optimized conditions for well-defined picolylamine manganese complexes,[29] we have screened a series of diamines as ligands (0.5 mol%), using $Mn(CO)_5Br$ as metal precursor (0.5 mol%) and *t*BuOK as the base (1 mol%) for the reduction of acetophenone at 80 °C in 1 h. The results are summarized in Scheme 1. First, several amines were found inactive for this transformation, demonstrating that the base-catalyzed reaction was limited under these conditions.[35] Second, the reduction of

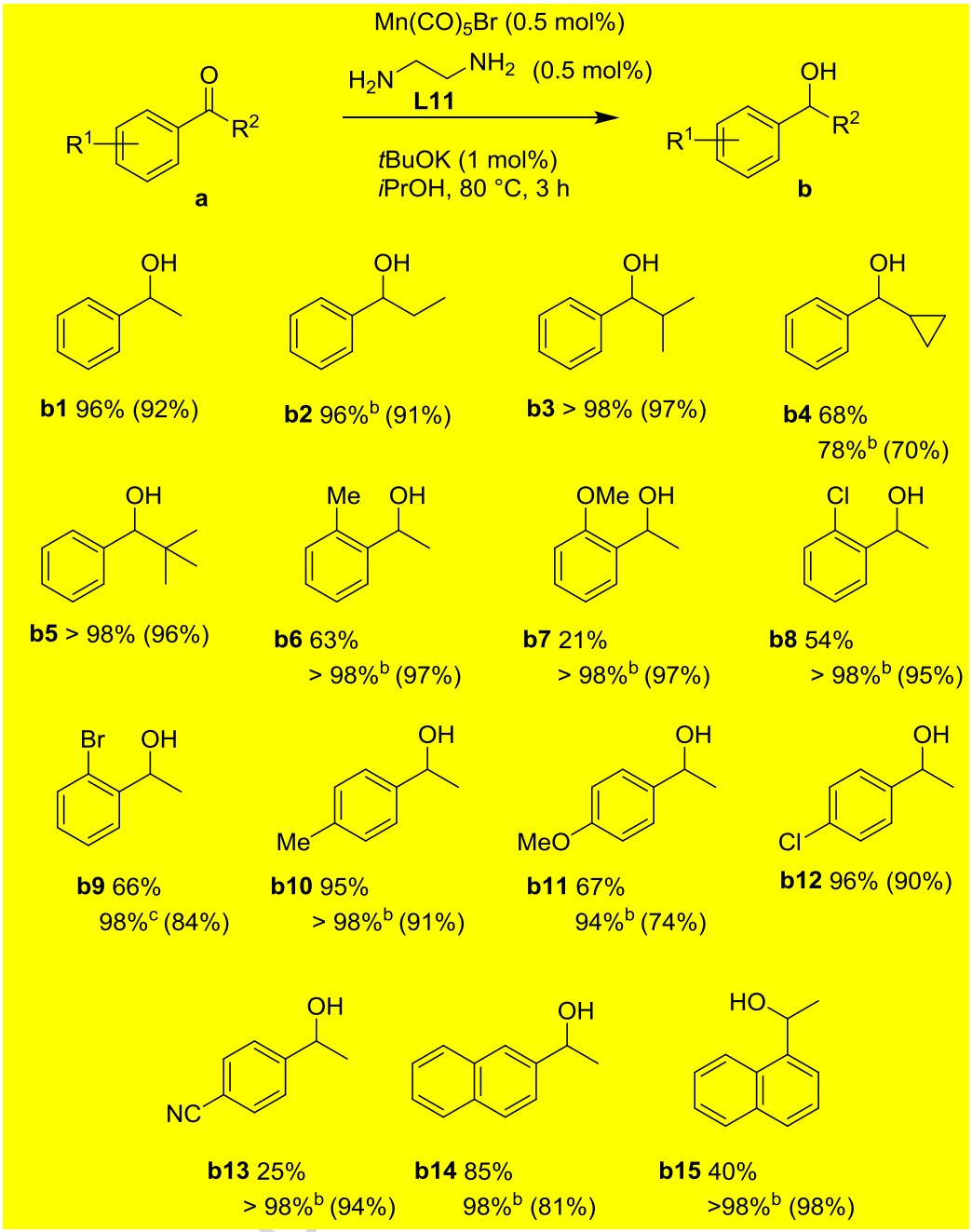
acetophenone proceeded well with *in-situ* generated catalysts based on aminomethylpyridine ligand **L1**, as a full conversion of acetophenone into 1-phenylethanol was observed after 1 h. *N*-methylaminomethylpyridine ligand **L2,** featuring one NH moieties, led also to a full conversion in 1 h but *N*,*N*-dimethylaminomethylpyridine **L3** was almost inactive. These results are in line with those obtained previously with well-defined complexes based on picolylamine ligands.[29] Due to the simplicity of the system, we then explored different parameters to optimize the design of the ligand. Aromatic amines, such as 2-amino-pyridine **L4**, 1,8-diaminonaphtalene **L5** and 1,2-diaminobenzene **L6,** did not promote the hydrogen transfer. 2,2'-bipyidine **L7** was completely inactive.[11] The length of the linker in between the pyridinyl unit and the amine moieties was also found to be crucial as 2-pyridin-2-ylethanamine **L8** was inactive, as **L4**. Interestingly, benzimidazolyl analogue of **L1**, namely 1*H*-benzimidazole-2-methanamine **L9**, gave a good conversion (76%), but 2-aminomethylthiophene **L10** was inactive. In order to develop the simplest and the less expensive catalytic system as possible, we have tested the simplest diamine, namely, ethylenediamine **L11**: to our delight, a very encouraging conversion was obtained under standard conditions (65%). Several diamines were also tested: the presence of at least two NH moieties was found to be crucial to detect some activity (**L11**, **L12** versus **L13**, **L14**). The presence of a tosyl group on one nitrogen atom inhibited the reduction, probably due to a slow coordination of the ligand to the manganese precursor. An ethylene bridge, leading to a five-membered metallacycle, was more favorable than a propylene one (**L16**, **L17**, **L18**) (65 % conversion with **L11** versus 25% with **L16**). Finally, racemic ligand **L20-*rac*,** (±)-*trans*-1,2-diaminocyclohexane, gave moderate (22%) conversion, opening the gate to asymmetric reduction of acetophenone (*vide infra*).

Taking in account both the simplicity and the low cost of ethylenediamine **L11** compared to 2-aminomethylpyridine **L1**, the scope of the reaction was then explored using **L11** as ligand (0.5 mol%), $Mn(CO)_5Br$ (0.5 mol%) and *t*BuOK as base (1 mol%) in isopropanol at 80 °C for 3 h (Scheme 2). In most cases, ketones were fully reduced, and the corresponding alcohols were isolated in high yields. Increasing the length and the branching of the alkyl chains from methyl (**a1)** to tertbutyl (**a5**) has little influence on the reaction. On the opposite, for *ortho*-substituted acetophenones (**b6-b9** and **b15**), a higher catalyst loading (1 mol%) was required to afford the alcohol in quantitative yield.

Scheme 1: Screening of bidentate nitrogen based ligands for the reduction of acetophenone in the presence of $Mn(CO)_5Br$ and *t*BuOK in 2-propanol.[a] [[a] Typical conditions : acetophenone **a1** (2 mmol), 2-propanol (8 mL). Conversions were determined by ^1H NMR.]



Scheme 2: Generality of the reduction of ketones with the *in-situ* prepared Manganese-ethylenediamine catalytic system.[a] [[a] Typical conditions: Ketone (0.5 mmol), 2-propanol (2 mL). Conversion determined by ^{1}H NMR, isolated yield given in parentheses. [b] $Mn(CO)_5Br$ (1 mol%), ethylenediamine (1 mol%), *t*BuOK (2 mol%), 80 °C, 3 h. [c] $Mn(CO)_5Br$ (1 mol%), ethylenediamine (1 mol%), *t*BuOK (2 mol%), 80 °C, 6 h.]



Encouraged by these results, especially by the activity of **L20**-*rac*, we submitted a series of commercial chiral diamines featuring an ethylenediamine motif for the reduction of acetophenone (Scheme 3, Table 1) using one equivalent of ligand (1 mol%) per $Mn(CO)_5Br$ (1 mol%) and two equivalents of *t*BuOK (2 mol%) at 80 °C for 3 h.

With (1*R*, 2*R*)-(+)-1,2-diphenyl-1,2-ethanediamine (DPEN) **L21**, a promising enantiomeric excess of 36 % was obtained (entry 1). Using (1*R*, 2*R*)-(-)-1,2-diaminocyclohexane **L22**, under the same conditions, the selectivity increased to 43% ee (entry 2). The enantiomeric

excess of the product dropped to 38% after 24 h of reaction (entry 3), probably due to racemization of the product under hydrogen transfer conditions. The activity dramatically decreased if the reaction was performed at 30 °C (entry 4). *N*-tosyl substituted ligand **L23** displayed no activity, as **L15**, even if a preactivation step at 100 °C in toluene was accomplished (entries 5-6). Disappointingly, more sterically demanding diamine **L24** or less bulky (1*S*,2*S*)-*trans*-1,2-cyclopentanediamine **L25** gave both a lower activity and selectivity (entries 7-8). (1*S*,2*S*)-1,2-di-1-naphthyl-ethylenediamine **L26**, as the achiral aniline derivatives **L4**-**L6**, gave almost no conversion and no enantiomeric excess (entry 9). Gratifyingly, *N*,*N*'-dimethylated ligands **L27** and **L28** displayed a significant higher selectivity than their analogues **L21** and **L22** (64% and 52% ee respectively, entries 10-11), (1*R*, 2*R*)-(+)-*N*,*N*'-dimethyl-1,2-diphenyl-1,2-ethane diamine **L27** giving the highest ee.

Scheme 3: Chiral diamines screened for the asymmetric reduction of ketones.

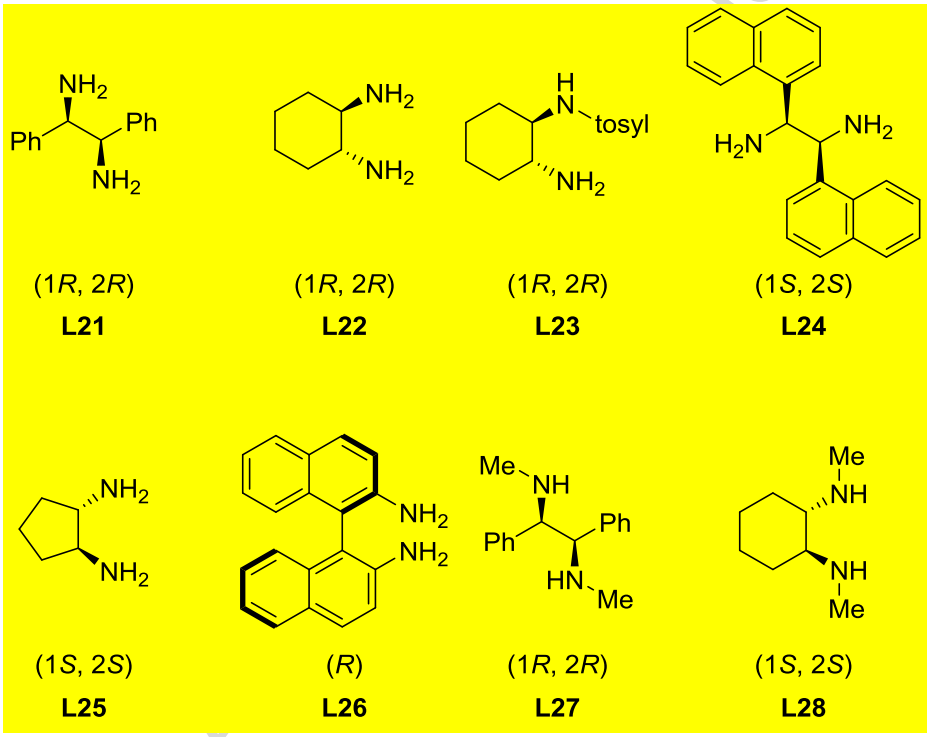


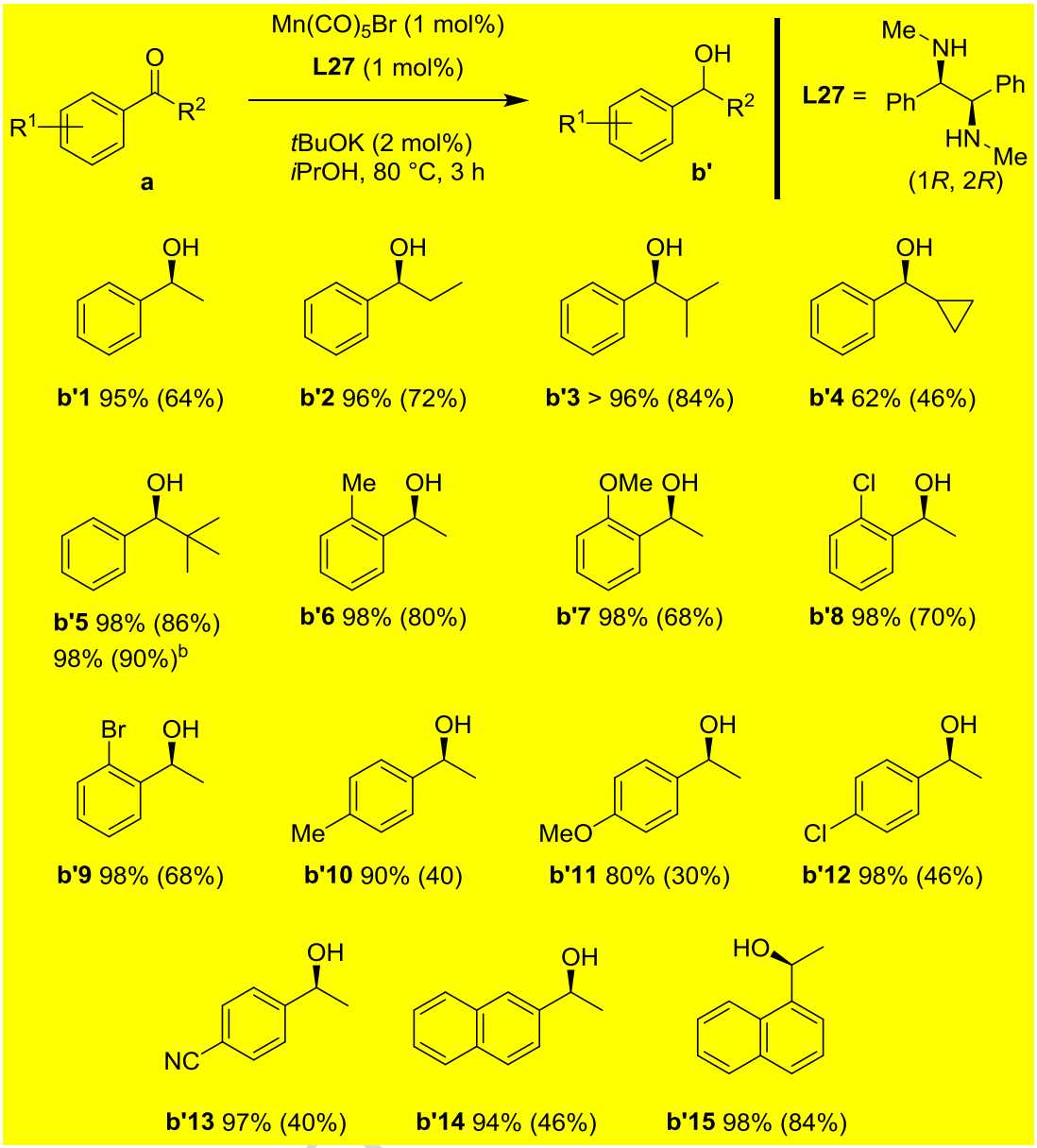
Table 1. Asymmetric reduction of acetophenone with chiral diamines ligands and $Mn(CO)_5Br$[a]

Entry	Ligand	Temp. (°C)	Time (h)	ee[b] (%)	Conv.[c] (%)
1	**L21**	80	3	36 (*S*)	> 97
2	**L22**	80	3	43 (*S*)	87

3	**L22**	80	24	38 (*S*)	> 97
4	**L22**	30	24	42 (*S*)	8
5	**L23**	80	3	0	0
6	**L23**[d]	80	3	46 (*S*)	4
7	**L24**[e]	80	3	16 (*R*)	7
8	**L25**[e]	80	3	0	16
9	**L26**	80	3	6 (*S*)	13
10	**L27**	80	3	64 (*S*)	95
11	**L28**	80	3	52 (*R*)	94

[a] Typical conditions : To a solution of acetophenone in 2-propanol were added in this order the diamine (1 mol%), $Mn(CO)_5Br$ (1 mol%) and finally *t*BuOK (2 mol%). [b] Enantiomeric excess values were determined by chiral GC. [c] Conversions were determined by ^1H NMR. [d] Preactivation step was operated: $Mn(CO)_5Br$ (0.02 mmol) and **L23** (0.02 mmol) were stirred in refluxing toluene (1 mL) for 1 hour, then 2-propanol (8 mL), acetophenone (2 mmol) and base (0.04 mmol) were added. [e] Commercial **L24**.2 HCl and **L25.** 2HCl were first neutralized with *t*BuOK (5 mol%) in 2-propanol for 30 min prior to reaction.

Based on the promising enantioselectivity obtained with **L27** for the reduction of acetophenone, we probed the scope of the reaction with several aromatic ketones (Scheme 4), under the optimized conditions. In most cases, good to excellent conversions were obtained in 3 h. Increasing the substitution on the methyl group of the acetophenone has a beneficial impact on the enantioselectivity, as 2,2-dimethyl-1-phenyl-1-propanol **b'5** was obtained with 86% ee from pivalophenone **a5**. The selectivity could even be improved further to 90% ee by lowering the temperature to 50 °C. On the other hand, in the case of *ortho*-substituted acetophenone, the substitution on the aromatic ring has also a positive effect on the enantioselectivity, leading to moderate to good ee up to 80% for **b'6** and 84 % for **b'15**. In the case of both electron donating (**a10**, **a11**) and electron withdrawing (**a12**, **a13**) substituents at the *para*-position, the selectivity was lower than for the reduction of acetephenone **a1**, with ee ranging from 30% to 46%



Scheme 4: Scope of the asymmetric reduction of ketones catalyzed by (1*R*, 2*R*)-(+)-*N*,*N*'-dimethyl-1,2-diphenyl-1,2-ethane diamine **L27** and $Mn(CO)_5Br$.[a] [[a] Typical conditions : To a solution of ketone in 2-propanol were added in this order the diamine (1 mol%), $Mn(CO)_5Br$ (1 mol%) and finally *t*BuOK (2 mol%). Conversion determined by ^1H NMR, ee determined by chiral GC given in parentheses. Each reaction has been repeated at least twice. [b] 50 °C, 24 h.]

Conclusions

We have developed a very simple and efficient catalytic system based on manganese pentacarbonyl bromide and ethylenediamine for the reduction of ketones by hydrogen transfer

using isopropanol as the donor. The low cost of both metal precursor and ligand, associated with the *in-situ* generation of the catalytic active species, make this system economically attractive as a sustainable alternative to sodium borohydride for the reduction of ketones. More importantly, the reactivity has been extended to asymmetric reaction of sterically hindered ketones with ee up to 90% using (1*R*,2*R*)-*N*,*N*′-Dimethyl-1,2-diphenylethane-1,2-diamine as chiral ligand. This first approach demonstrated that simple bidendate, phosphine-free ligand, can be used with manganese to promote enantioselective reactions with good selectivity. Further optimization of the design of the ligand to reach very high level of selectivity is currently under investigation in our laboratory.

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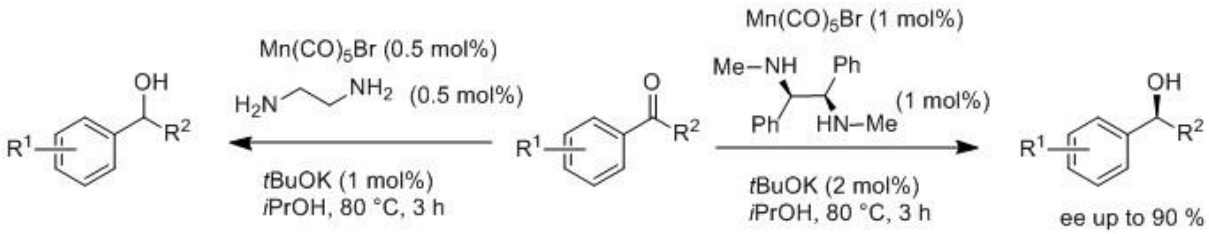

Highlights

- **Manganese pentacarbonyl bromide and ethylenediamine promotes hydrogen transfer**
- **Asymmetric reduction of ketones was achieved with enantioselectivity up to 90% ee**
- **Phosphine-free aliphatic diamines as ligand for transfer hydrogenation with manganese**