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Chiral nitrogen–metal complexes for the asymmetric reduction of ketones

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Abstract: Chiral cobalt–diamine complexes have been prepared and tested in catalytic reduction of β-ketoesters and ketones with molecular hydrogen or hydride transfer reduction (HTR). Modest to high conversions, but low e.e.s were obtained in the first case, whereas encouraging e.e.s (up to 58%) but low conversions were observed in the reduction of acetophenone by HTR. Synthesis of chiral nitrogen tetradentate ligands for Co, Ir and Rh are described. Furthermore, (1R,2R)-(−)-N-tosyl-1,2-ethanediamine proved to be a particularly efficient ligand for iridium in the hydride transfer reduction of acetophenone (87% conversion, 92% e.e.). © 1997 Elsevier Science Ltd

Introduction

Asymmetric catalytic reduction of ketones has been extensively studied since two decades. However few practical industrial applications have been developed, mainly due to the problem of recycling the catalytic system for minimizing its cost (chiral ligands and metals). In order to avoid these constraints, the first approach consists of using nitrogen-containing ligands easily available and less toxic than phosphine compounds. We have already developed the use of chiral diamines complexed to rhodium to perform efficient asymmetric hydrogenation or hydride transfer reduction.[1,2]

A similar way is using cheaper metals, such as cobalt, which already were efficient catalysts for asymmetric reduction of olefins or ketones with $NaBH_4$ to reach e.e.s of up to 99%.[3,4] Reasonable activities were observed for hydrogenation of C=C bonds but low e.e.s (<20%) using phosphine ligands.[5,6] More recently, Corma modified proline to synthesize an efficient ligand for cobalt-catalysed reduction of dehydroaminoacids. The corresponding substituted phenylalanine was obtained with 73% e.e. after complete conversion.[7] Ketones have been hydrogenated as well with the aid of cobalt complexes: benzil was reduced quantitatively to benzoin with 71% e.e.[8] Although more expensive than rhodium, iridium has been used with interesting results in the HTR with oxazoles as ligands. E.e.s of up to 91% were achieved for isopropyl phenyl ketone.[9] Also with 2-pyridinal-1-phenylethyl-imine high e.e.s (up to 84%) were obtained.[10]

Considering these results, we present in this paper the synthesis and the use of chiral diamine-complexed cobalt catalysts for reduction of aryl ketones and β-ketoesters with molecular hydrogen or isopropanol as hydride source. Synthesis of non commercially available chiral nitrogen compounds and their use as ligands for Co, Ir and Rh will also be discussed.

Cobalt catalysed hydrogenation with molecular hydrogen

Different cobalt precursors are available for the preparation of complexes. Based on previous work where Co(II) was commonly used, we studied the effect of preparation of the catalyst on the hydrogenation of ketones with molecular hydrogen.

$Co(acac)_2$ and $CoCl_2$ were allowed to complex (1R,2R)-cyclohexyldiamine **1** (Figure 1) as ligand. In the latter case, the complex was prepared *in situ* and no physical data are available. When

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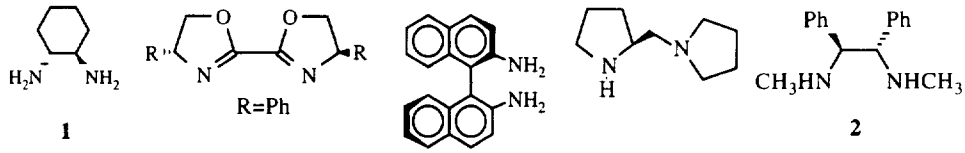


Figure 1. Tested chiral nitrogen containing ligands.

Table 1. Selected data of different cobalt complexes

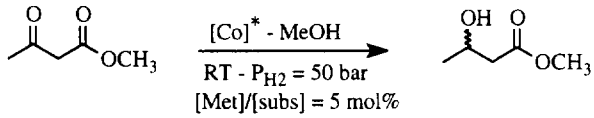
Entry	Co source	Counter-ion	$\delta\ ^{59}Co$ (ppm)[a]	$[\alpha]_D^{20}$ [b]
1	$Co(acac)_2$	$LiClO_4$	6561	+130 (c= 0.02)
2	$Co(acac)_2$	none	6561	+33 (c = 0.1)
3	$Co(acac)_3$	$LiClO_4$	6561	+260 (c= 0.02)

(a) NMR performed with Bruker AM 300 in d^6-DMSO using $Co(CN)_6$ as internal reference ; (b) specific rotation mesured in MeOH

acetylacetonate cobalt(II) was used as precursor, Co(III) was obtained as shown by NMR analyses of the resulting complex (Table 1). So $Co(acac)_3$ has also been used as cobalt source.

Whatever the cobalt precursor used and even without lithium perchlorate, Co(III) was always obtained as shown by NMR analyses; however the exact environment around the metal still remains unknown. Nevertheless, the different values obtained for specific rotation prove that the complex structures are different. The reversed sign observed between the free ($[\alpha]_D^{20}$(R,R)=−122 (c=0.02; MeOH)) and the chelated amine indicates that a chiral complex has been formed.

Hydrogenation of ketones was tested with these catalysts. Whereas no conversion was obtained for reduction of acetophenone, the cobalt catalysts were efficient for hydrogenation of methyl acetoacetate (Scheme 1).



Scheme 1. Hydrogenation of methyl acetoacetate.

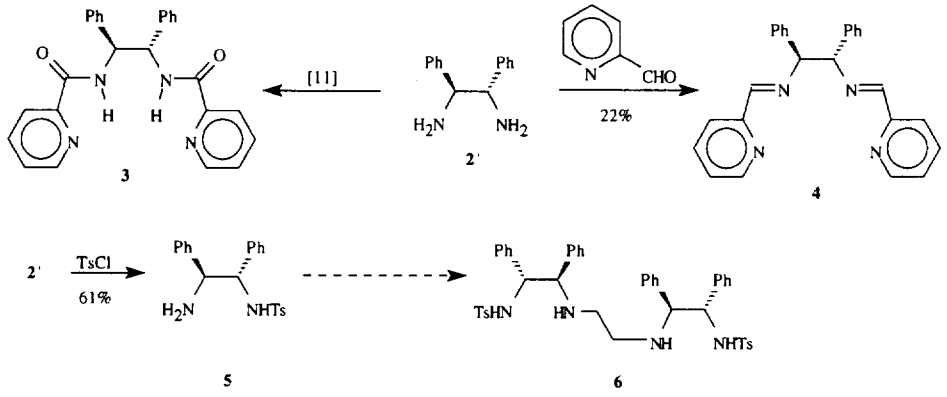
Modest to high conversions (17–77%) but no significant e.e.s (<5%) were obtained. In the case of the hydrogenation of α-ketoesters with diamine-complexed transition metals we observed that the e.e. was raised by increasing the diamine/metal ratio from 1 to 2.[2] In the case of β-ketoester, increasing the ratio of diamine/cobalt only affected the rate of the reaction by decreasing it dramatically.

We tested other commercially available diamines, either with *in situ* ($CoCl_2$ precursor) or isolated ($Co(acac)_3$ precursor) complexes. In each case the resulting complexes were stable upon hydrogenation conditions and moderated to high conversions (20–100%) but unsignificant e.e.s (<5%) were observed. As no enantioselectivity was obtained by using chiral cobalt complexes in hydrogenation with molecular hydrogen, we tested hydride transfer reduction as an alternative.[1]

Cobalt catalysed hydride transfer reduction (HTR)

The asymmetric hydride transfer reaction has been tested on the reduction of acetophenone in order to afford enantiomerically enriched phenylethanol. This type of reaction is not applicable to the transformation of methyl acetoacetate, which is not stable under the basic conditions. As already mentioned, this reaction on acetophenone has been succesfully performed with numerous metals, complexed to various chiral ligands: for example, Gladiali *et al.*[11] have carried out the transformation with a catalyst consisting of Rh^+ and a chiral alkylphenanthroline and achieved e.e.s of up to 65%. We

reported a similar result (67% e.e.) by using chiral Rh–diamine complexes, principally with (1R,2R)-(−)-N,N′-dimethyl-1,2-diphenyl-1,2-ethane **2** as ligand.[1] This C-2 symmetric ligand proved to be able of competing successfully with other widely used phosphine based ligands, which are less stable toward oxidation. A great improvement on the catalytic activity and enantioselectivity was made by Noyori *et al.*[12] who reached 97% e.e. by using the monotosylated diamine (1R,2R)-(−)-N-tosyl-1,2-diphenyl-1,2-ethanediamine **5** (Scheme 2) as ligand in the ruthenium catalysed hydride transfer reaction.



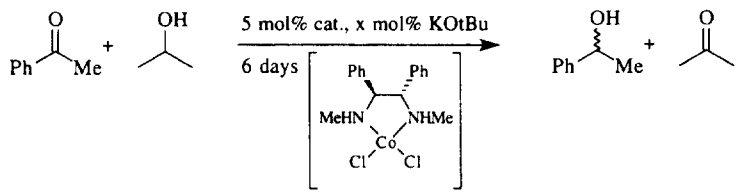
Scheme 2. Preparation of new diamine-based tetradentate ligands.

Although the results achieved so far in the HTR are very encouraging, the use of precious metals like Rh or Ru and expensive ligands limits the possibility for industrial application. We therefore tested cobalt as active metal for performing the HTR on acetophenone using **2** as ligand under conditions previously described with rhodium complexes as catalysts.[1] However a 1:1 complex, instead of 1:2 complex, was prepared *ex situ* by precipitation of the chiral diamine **2** and anhydrous $CoCl_2$.

Based on the obtained results (encouraging e.e. but low conversion, Table 2, entry 1), we tried to improve the catalytic activity by modifying the conditions of the reaction, principally the quantities of base and chiral ligand. Considering the mechanism proposed by Gladiali[11] for the HTR, the role of the base is the deprotonation of the inactive metal–isopropanol complex to the active metal–isopropoxide complex, the base being inefficient in the catalytic cycle itself. Therefore we increased the quantity of base, all other parameters remaining unmodified, in order to shift the equilibrium towards the formation of the active complex, thus obtaining higher conversions and e.e.s.

The conversion rose with increasing amount of base while the e.e. decreased (Table 2, entries 1–3). This result can be explained by a possible competitive reaction, occurring at the same time as

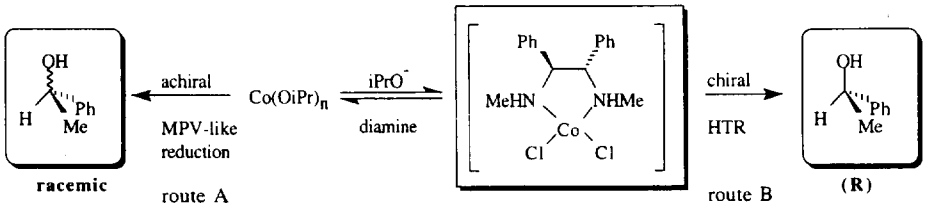
Table 2. Influence of the amount of base on conversion and e.e. for the HTR of acetophenone



Entry	x (mol%)[a] KO*t*Bu	conversion (%)	e.e. (%) (conf)
1	20	8	58 (R)
2	40	15	15 (R)
3	60	30	7 (R)

a) mol% relative to acetophenone.

the enantioselective HTR. We can assume that, with increasing amount of base, an active $Co(OiPr)_n$ complex is formed for a non enantioselective Meerwein–Pondorf–Verley like reaction, leading to a considerable decrease of e.e. We propose in Scheme 3 the supposed active species involved in the transformation of acetophenone: the $Co(OiPr)_n$ complex giving a racemic MPV-like reaction (route A), and a diamine–cobalt complex leading to the enantioselective formation of the (R)-enantiomer (route B). Even in the case where equimolar quantities of metal and chiral ligand are reacting, the above described equilibria between the complexes exist, leading to a lost of enantioselectivity. In order to achieve a good conversion together with an interesting e.e., the equilibrium governing the complex formation must be shifted towards the Co–diamine complex.



Scheme 3. Involved species for the Co catalyzed reduction of acetophenone.

Despite results obtained in hydrogenation of methylacetoacetate, we increased the amount of diamine ligand, in order to favour the route B. 20 mol% of base present in the reaction mixture were used to have the highest possible e.e. In this case *in situ* complexes were tested.

No significant difference was observed using *in situ* or *ex situ* cobalt catalysts (compare entries 1, Tables 2 and 3). Increasing the amount of diamine did not result into an increase of both the selectivity and the reactivity of the reduction. In the same way, our attempts with another Co(II) precursor ($Co(acac)_2$), a Co(III) source ($Co(acac)_3$) and Co(I) remained all unsuccessful.

Our results indicate that using a large excess of chiral bidentate ligands (Table 3, entry 2) does not modify the chiral environment of the metal as no improvement of the e.e. could be observed. These values are in contradiction with the conclusions of Gladiali[11] who claimed the necessity of two chiral phenanthroline-type ligands for an efficient enantioselectivity in the rhodium-catalysed HTR of acetophenone.

Suggesting that the binding ability of our diamine-containing ligand was not strong enough to create an efficient chiral system around the cobalt, we prepared diamine **2**-based tetradentate ligands in order to shift the equilibrium depicted in Scheme 3 towards the pure cobalt–nitrogen complex (Scheme 3, route B).

Our mechanistic proposition has however to be considered with reserves especially concerning the role of the base. Noyori published indeed very recently that KOH is only necessary for the generation of a reduced catalyst that further forms a metal hydride species, supposed to be the true catalyst rather than the metal alkoxides presumed for the Meerwein–Ponndorf–Verley type reaction.[13] These propositions are based on the synthesis, isolation and description (by X-ray crystallographic analyses) of the chiral ruthenium complexes involved in the asymmetric HTR of acetophenone. Nevertheless, in the case of cobalt catalysis, it is clear that the quantity of base influences not only the reaction rate, but also the e.e. (see Table 2).

Table 3. Influence of the amount of ligand on conversion and e.e. for the HTR of acetophenone[(a)]

Entry	chiral ligand **2** /Co	conversion (%)[(b)]	e.e. (%)(conf.)[(b)]
1	1	3	55 (R)
2	4	5	55 (R)

a) reaction conditions are similar to those described in table 2 ; b) after 4 days.

Preparation of diamine-based tetradentate ligands

Several diamine-based tetradentate ligands have then been synthetized and tested for the asymmetric reduction of ketones with molecular hydrogen or isopropanol. As the diamine moiety **2** proved to be a good ligand in the Rh-catalysed HTR, we modified this compound principally with pyridine units, because of their known strong binding ability to metals. We planed the synthesis of the compounds described in Scheme 2.

Amide **3** and imine **4** derivatives were chosen to test their own unique characteristics with regard to rigidity in their structure and strength of bonding towards the metal.

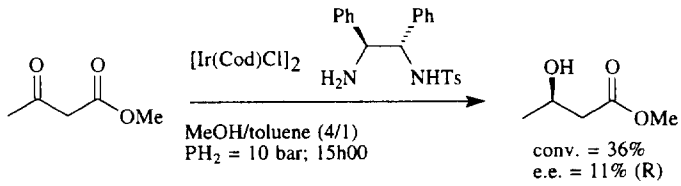
The ethylenediamide dipyridyl ligand **3** was prepared from (S,S)-1,2-diphenylethylene diamine **2′** and 2-pyridine carboxylic acid, via its acyl chloride derivative.[14] The synthesis of the diimine ligand **4** was achieved through reaction of **2′** and 2-pyridine carboxaldehyde in methanol with 22% yield. As described by Mangeney[15] for the synthesis of chiral dihydropyridines, we obtained an aminal compound as major by-product.

Another way of obtaining tetradentate ligands is the preparation of a dimer of two diamine units, **6**, linked together using an alkyl spacer, as shown in Scheme 2. This type of ligands have an advantage: all the coordinating moieties are directly linked to the chiral backbone. In the first step, the diamine was monoprotected using the tosyl group giving (1R,2R)-(−)-N-tosyl-1,2-diphenyl-1,2-ethanediamine **5** as already described by Noyori[12] in 61% yield. However, the coupling of this monoprotected diamine to afford **6** proved to be difficult and is still under investigations. As Noyori reported high enantioselectivity with the monotosylated diamine **5**, we tested its catalytic activity for the reduction of prochiral ketones with various metals.

Use of Ir, Rh and Co complexes for the enantioselective reduction of ketones with 3, 4 and 5

Hydrogenation as well as hydride transfer reduction were performed with these ligands.No significant results were obtained for the hydrogenation of methyl acetoacetate, neither with tetradentate nitrogen (**3,4**)-based cobalt complexes as catalysts, nor with monotosylated diamine **5**–cobalt complex.

Iridium was also tested as catalyst with these ligands. The non-racemic β-hydroxyester was obtained with a low enantiomeric excess using **5**–iridium complex prepared *in situ* (Scheme 4).[2]



Scheme 4. Hydrogenation of methyl acetoacetate with an iridium complex.

Hydride transfer reduction of acetophenone was then studied with the tetradentate ligands **3** and **4** and with the monotosylated diamine **5** complexed with Co, Ir and Rh. The results are summarized in Table 4.

Whatever metal used the results achieved with the tetradentate ligands were disappointing: only a modest e.e. (22%) was obtained with the diamide **3**–rhodium complex but with a low conversion (entry 3). It is possible that the distance between each liganding function is not optimized and the desired 1:1 complex is not formed as expected.

More successful results were observed with the dissymmetric ligand **5** especially when iridium was tested: using 2 equivalents of ligand per metal (in order to have 4 nitrogens around the metal as for the tetradentate ligands) led to good conversion and enantioselectivity (entry 9). These performances were improved when only one equivalent of ligand was used (entry 8): higher conversion and enantioselectivity were achieved showing that this ligand is active with other metals than ruthenium.[12]

Table 4. HTR of acetophenone catalysed by nitrogen ligands based complexes[a]

Entry	Metal precursor	Ligand	conversion (%)	e.e. (%)
1	$CoCl_2$	**3**	3[b]	17 (R)
2	$[Ir(Cod)Cl]_2$	**3**	73[c]	< 5
3	$[Rh(Cod)Cl]_2$	**3**	5[c]	22 (R)
4	$CoCl_2$	**4**	0[b]	-
5	$[Ir(Cod)Cl]_2$	**4**	97[c]	< 5
6	$[Rh(Cod)Cl]_2$	**4**	29[c]	< 5
7	$CoCl_2$	**5**	1[d]	-
8	$[Ir(Cod)Cl]_2$	**5**	87[d]	92 (S)
9	$[Ir(Cod)Cl]_2$	**5**[e]	72[d]	80 (S)
10	$[Rh(Cod)Cl]_2$	**5**	4[d]	60 (S)

(a) Reaction conditions otherwise mentionned : 5% ligand/metal (1/1) complex, 20% tBuOK, RT, iPrOH ; (b) after 2 days ; (c) after 6 days ; (d) after 1 day ; (e) ligand/metal = 2/1.

Furthermore this high selectivity requires only one ligand as described by Noyori in the case of ruthenium. This result is showing the highest e.e. obtained so far with iridium in HTR of acetophenone.

Obviously the higher selectivity obtained with iridium with regard to rhodium in case of ligand **5**, which is in contrast with the result obtained with ligand **3**, emphasises the need for tuning the metal for each ligand. Current research is in progress to optimize the obtained results.

Moreover these results indicate that the active catalytic species remain still unclear, especially concerning the number of chiral ligands in report to the metal necessary for an effective enantioselectivity in the hydride transfer reduction of ketones.

Conclusion

We developed the use of cobalt complexes for asymmetric reduction of ketones. Unfortunately, we were not able to obtain simultaneously good conversions and high enantioselectivities. Only the hydride transfer reduction shows promising results: modest e.e. (58%) but low conversion was achieved using (1R,2R)-(−)-N,N′-dimethyl-1,2-diphenyl-1,2-ethanediamine **2**–cobalt complex. Cobalt complexes are not as efficient in these conditions as in the $NaBH_4$ reduction system. On the contrary, iridium is an adequate metal for this reaction and it can be a good alternative when the dissymmetric (1R, 2R)-(−)-N-tosyl-1,2-diphenyl-1,2-ethanediamine **5** is chosen as ligand.

Experimental part

Ethanol and isopropanol were purchased from Normapur, diethyl ether from Aldrich. All starting compounds were commercially available and used as received. Solvents were, if not denoted otherwise, of technical grade. Determination of the conversion and the e.e. was done on a Shimadzu GC-14A, using a flame-ionization detector and a chiral column: SGE Cydex B (acetophenone) or Lipodex A (methylaceto-acetate). Integrations were performed on a Shimadzu C-R6A integrator. ^1H NMR spectra were recorded on a Bruker AC 200 (200 MHz). ^{13}C NMR spectra were recorded on a Bruker AC 200 (50 MHz) and ^{59}Co on a Bruker AM 300 (71.2 MHz). The notation of the different types of peaks are s (singlet), d (doublet), m (multiplet), dd (double doublet), dt (double triplet), br (broad).

Co(diam)Cl₂

To a stirred solution of 123 mg (0.95 mmol) of $CoCl_2$ in absolute ethanol was added dropwise a solution of 250 mg (1.04 mmol) of (1R,2R)-(+)-N,N′-dimethyl-1,2-diphenylethylenediamine ((R,R)-DMPEDA) in 2 mL of ethanol. Stirring was continued for another hour, yielding a purple precipitate. After filtration and drying overnight in vacuo 0.22 g (0.61 mmol, 65% yield) of a purple solid was

obtained. The same procedure was used for the preparation of complexes with other cobalt precursors ($Co(acac)_2$ and $Co(acac)_3$).

[[(1R,2R)-N,N′-cyclohexyldiamine]-pentane-2,4-dionato] cobalt(II) perchlorate

Prepared according to Ref.[7] with slight modifications.

Standard procedure for hydrogenation using in situ *prepared complexes*

In a 10 ml Schlenck, previously purged with 3 vacuum/argon cycles, 20 mg of $CoCl_2$ and 1 equivalent of diamine were added in 4 ml degassed MeOH. The solution was stirred for 2h at room temperature, then it was introduced under argon in a 30 ml autoclave. Solution of 40 mg of methyl acetoacetate in 4 ml degassed MeOH was added. The autoclave was purged with argon then with hydrogen and pressurised under 50 atm hydrogen. The stirring was maintained for indicated time. The conversion and e.e. were determined on Lipodex A column and are reported in the Tables.

Standard procedure for the hydride transfer reduction, using ex situ *prepared complexes*

In a 5 ml Wheaton mini reactor, 6.10^{-3} mmol (5 mol%) of catalyst was dissolved in 2 ml of a 0.012 M solution of KO*t*Bu in isopropanol. After stirring for 15 min 14 mg (0.12 mmol) of acetophenone was added. The resulting suspensions were stirred for indicated time. The conversion and e.e. were determined on a chiral GC-column (Cydex B) and are reported in the general part.

Variation of the amount of base: The reactions were carried out in the same manner as described for the *ex situ* complexes. After dissolving the catalyst in pure isopropanol, the indicated amount of base was added to this solution.

Variation of the ligands: The reactions were carried out in the same manner as described for the *ex situ* complexes, except that after dissolving the catalyst in the KO*t*Bu/isopropanol solution, the extra ligands were added. Additional stirring for one hour was applied, before adding the acetophenone.

(S,S)-Dipyridine 1,2-diphenyl ethylene 1,2-diamide ***3***

Prepared according to Ref.[14] with modifications. $[\alpha]_D=-80$ (c=0.23, DMSO); m.p.=224°C; ^{1}H NMR ($CDCl_3$): δ 5.54 (2H, dd, CH); 7.1–7.3 (12H, m, 10 CH-arom., 2 CH-pyr); 7.66 (2H, dt, CH-pyr); 8.01 (2H, dd, CH-pyr); 8.44 (2H, dd, CH-pyr); 8.85 (2H, d, NH); ^{13}C NMR ($CDCl_3$): δ 58.8 (CH); 122.1 (CH); 126. 1 (CH); 127.7 (2×CH); 128.5 (CH); 137. 0 (Cq); 138.7 (CH); 148.1 (CH); 149.5 (Cq); 164.5 (CO).

(S,S)-Dipyridine 1,2-diphenyl ethylene 1,2-diimine ***4***

0.505 g (4.8 mmol) of 2-pyridine carboxaldehyde and 0.5 g (2.4 mmol) of (S,S)-diamine were dissolved in 5 mL of MeOH. After stirring overnight the brownish suspension was filtered off and washed with pentane. After crystallisation of the brown solid from $MeOH/CH_2Cl_2$, 109 mg of white needles were obtained. A second crystallisation yielded another 98 mg of white needles (0.053 mmol, 22% global yield). $[\alpha]_D$ −4.3 (c=0.46, $CHCl_3$); m.p.=139°C; ^{1}H NMR ($CDCl_3$): δ 4.72 (2H, s, CH); 7.08–7.32 (14H, m, 2 CH, 2 CH-pyr, 10 CH-arom.); 7.63 (2H, d, CH-pyr); 7.67 (2H, d, CH-pyr); 8.27 (2H, s, CH-pyr); ^{13}C NMR ($CDCl_3$): δ 81.5 (CH); 127.1 (CH); 128.0 (CH); 128.2 (CH); 128.3 (CH); 128.5 (CH); 128.6 (CH); 130.6 (CH); 136.6 (Cq); 141.3 (Cq); 161.9 (CN).

(1R,2R)-(−)-N-tosyl-N,N′-dimethyl-1,2-diphenyl-1,2-ethanediamine ***5***

1.00 g (4.7 mmol) **1** was dissolved in 15 mL of CH_2Cl_2 and 5 mL of Et_3N. After 0.90 g (4.7 mmol) of p-tosylchloride in 10 mL of CH_2Cl_2 was added at 0°C, the solution was stirred overnight. The solution was washed with 5% NaOH (aq), dried on $MgSO_4$ and the solvent was evaporated under reduced pressure. After dissolving the white solid in Et_2O, 3 mL of 37% HCl(aq) was added. The resulting white solid was treated with 5% NaOH and extracted with CH_2Cl_2. After drying on $MgSO_4$ and evaporating the solvent under reduced pressure, 1.05 g (2.9 mmol) of monotosylated diamine was obtained. $[\alpha]_D=-124$ (c=0.4, $CHCl_3$); m.p.=104°C; ^{1}H NMR ($CDCl_3$): δ 2.32 (3H, s, CH_3); 4.14 (1H, d, CH); 4.41 (1H, d, CH); 6.98 (2H, d, CH-tosyl); 7.15 (13H, s, br, 10 CH, NH_2, NH); 7.34

(2H, d, CH-tosyl); ^{13}C NMR ($CDCl_3$): δ 21.5 (CH_3); 60.6 (CH); 63.4 (CH); 126.7 (CH); 126.9 (CH); 127.1 (CH); 127.3 (CH); 127.4 (CH); 128.3 (CH); 128.4 (CH); 129.2 (CH); 137.2 (Cq); 139.4 (Cq); 141.5 (Cq);142.5 (Cq).

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