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Original citation:

Darwish, Moftah O., Wallace, Alistair, Clarkson, Guy J. and Wills, Martin. (2013) Use of tridentate TsDPEN/pyridine ligands in ruthenium-catalysed asymmetric reduction of ketones. *Tetrahedron Letters*, Volume 54 (Number 32). pp. 4250-4253.

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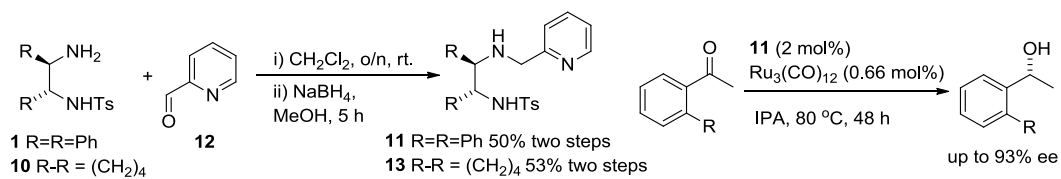
Graphical Abstract

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Use of tridentate TsDPEN/pyridine ligands in ruthenium-catalysed asymmetric reduction of ketones

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Moftah O. Darwish, Alistair Wallace, Guy J. Clarkson, Martin Wills





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Use of tridentate TsDPEN/pyridine ligands in ruthenium-catalysed asymmetric reduction of ketones

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Abstract— A series of enantiomerically pure tridentate ligands based on the 1,2-diphenyl-ethane-1,2-diamine structure, containing additional pyridine groups, was prepared and tested in asymmetric transfer hydrogenation of ketones using $\text{Ru}_3(\text{CO})_{12}$ as a metal source. Alcohols were formed in up to 93% ee in the best cases, and good results were obtained for substrates containing halides at the *ortho*-position. © 2015 Elsevier Science. All rights reserved

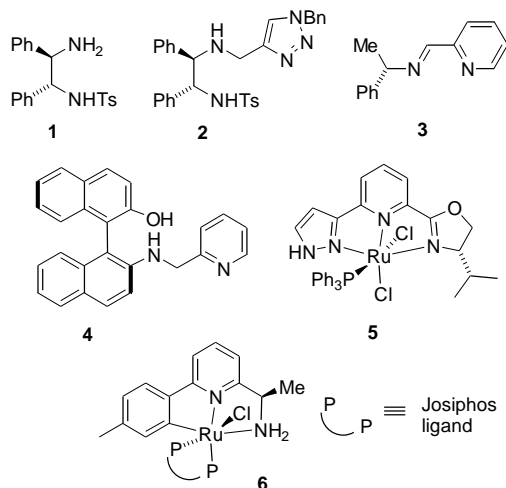
Keywords

Asymmetric catalysis
Reduction
Transfer hydrogenation
Ruthenium
Alcohol

Asymmetric transfer hydrogenation (ATH) of ketones is a valuable method for the synthesis of enantiomerically pure alcohols.^{1–3} A large number of catalysts have been reported for this application in recent years, of which those based on enantiomerically-pure *N*-tosyl-1,2-diphenyl-ethane-1,2-diamine **1** in combination with a Ru/arene or Rh or Ir/pentamethylcyclopentadiene have been particularly successful.² Recently, we found⁴ that an *N*-tosyl-1,2-diphenyl-ethane-1,2-diamine (TsDPEN) modified with a triazole donor,⁵ i.e. **2**, gave good results in the reduction of ketones when used in conjunction with $\text{Ru}_3(\text{CO})_{12}$. The results of the use of the triazole made us consider pyridine as an alternative donor, and the results of our study are described below.

A number of pyridine-containing ligands have been employed in ATH reactions.^{1,6–17} Early examples include Schiff base **3** (the Ir complex of which reduced acetophenone in up to 84% ee),⁸ the BINOL-derived **4** (the complex with $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ gave up to 97% ee in ATH in *i*PrOH),¹⁰ as well as 2-(2'-pyridyl)pyridines,⁶ phenanthrolines⁷ and pyridines combined with phosphines in tridentate donor ligands.⁹ More recent examples include a series of Ru(II) complexes of pyridine/phosphine tridentate ligands together with phosphines, for example **5** (gave an alcohol of 93% ee from acetophenone reduction in *i*PrOH),^{11a} reported by Yu and co-workers.¹¹ The pyridine-containing catalysts, for example **6**, reported by Baratta, are

highly active and give products of high ee in ketone reductions in ATH using *i*PrOH.¹² Also containing a chiral diphosphine, **6** gave ketone reduction products of up to 99% ee in ATH reactions in isopropanol, and is also active in ketone hydrogenation.^{12a}

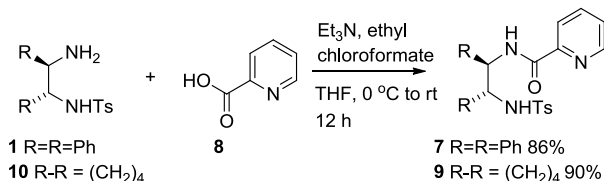


Pyridine-containing ligands have also been used extensively in non-asymmetric hydrogen-transfer processes, and for hydrogen-generation from organic molecules.¹³ Other applications of pyridine-containing ligands have been reported,¹⁴ as have their applications in highly active non-asymmetric hydrogenations of ketones.¹⁵ In some cases, ATH catalysts have been reported which contain a pyridine ring, but as one of a series of tosylated

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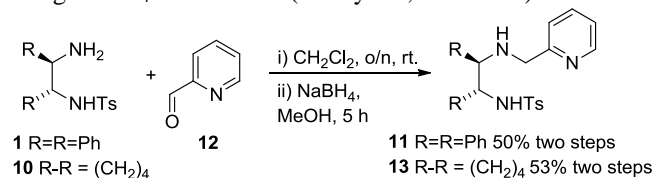
diamine (complex with Ru/ η^6 -arene)¹⁶ or amino acid (complex with RhCp*)¹⁷ derivatives.

In view of the encouraging precedents, we elected to study tridentate ligands containing pyridine groups, with regard to their efficiency when used in a novel complex with Ru₃(CO)₁₂.⁴ Towards this end we first prepared (*R,R*)-pyridine-2-carboxylic acid [2-(toluene-4-sulfonylamino)-1,2-diphenyl-1,2-ethylenediamine]-amide **7** in 86% yield (Scheme 1) by the reaction between pyridine-2-carboxylic acid **8** and (*1R,2R*)-TsDPEN **1** using ethyl chloroformate.



Scheme 1. Synthesis of ligands **7** and **9**.

In addition, the known (*R,R*)-[2-(toluene-4-sulfonylamino)-cyclohexyl]-amide **9**¹⁸ was prepared from pyridine-2-carboxylic acid **8** and (*R,R*)-(-)-*N*-(4-toluenesulfonyl)-1,2-diaminocyclohexane **10** (90% yield, Scheme 1). The synthesis of the reduced analogues of compounds **7** and **9** was completed by reductive amination. (*R,R*)-*N*-{1,2-Diphenyl-2-[(pyridin-2-ylmethyl)-amino]-ethyl}-4-methyl-benzenesulfonamide (**11**) was prepared by reacting (*1R,2R*)-TsDPEN **1** in CH₂Cl₂ with 2-pyridinecarboxaldehyde (**12**). The mixture was stirred overnight at r.t. to obtain the known imine (*R,R*)-*N*-{1,2-diphenyl-2-[(pyridin-2-ylmethylene)-amino]-ethyl}-4-methyl-benzenesulfonamide (81%).^{19,20} This was reduced using NaBH₄ to afford **11** (62% yield, Scheme 2).



Scheme 2. Synthesis of ligands **11** and **13**.

Compound **11** was found to be stable over a period of weeks and its structure was confirmed by X-ray crystallography (Figure 1).²¹

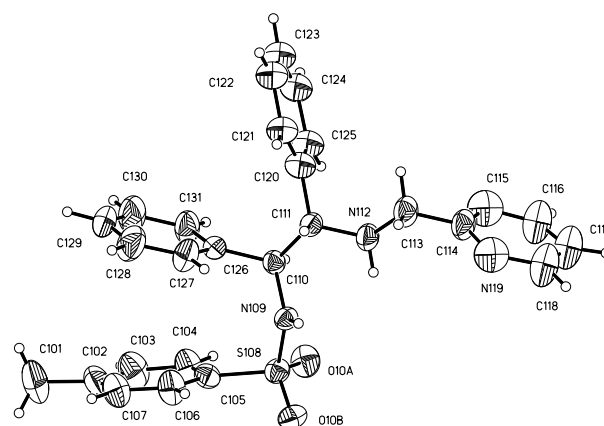
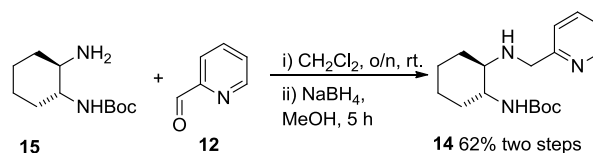


Figure 1. X-ray crystallographic structure of (*R,R*)-**11** with thermal ellipsoids drawn at 50% probability (ORTEP).

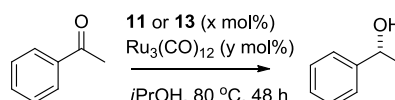
The synthesis of (*R,R*)-4-methyl-*N*-{2-[(pyridin-2-ylmethyl)-amino]-cyclohexyl}-benzenesulfonamide (**13**).¹⁶ was likewise achieved via the corresponding imine²⁰ from (*1R,2R*)-(-)-*N*-*p*-tosyl-1,2-cyclohexanediamine (**10**) (Scheme 2). The synthesis of (*R,R*)-{2-[(pyridin-2-ylmethyl)-amino]-cyclohexyl}-carbamic acid *tert*-butyl ester (**14**) was completed by treatment of mono-Boc diamine **15**²² with 2-pyridinecarboxaldehyde (**12**) in CH₂Cl₂ to give the intermediate imine, which was reduced by NaBH₄ (Scheme 3).



Scheme 3. Synthesis of ligand **14**.

To carry out the ATH of ketone substrates, the reaction was first optimised with respect to reaction time, concentration and catalyst loading using compound **11** and acetophenone as a representative ketone (Table 1). An optimum ratio of 1:3 Ru₃(CO)₁₂, i.e. a 1:1 ratio of Ru: ligand. Experiments were carried out using varying concentrations and catalyst loadings for 72 hours (Table 1). In all cases, the enantiomeric excesses decreased slightly with respect to time, possibly due to slow racemisation of the products (see supplementary data for full tables of conversion and ee with respect to reaction time).

Table 1. A summary of initial ATH of acetophenone with ligands **11** and **13**.^a



Entry	Ligand	[Substrate]	x:y	Conv (%) ^b	Ee (%) ^{b,c}
1	11	0.1 M	1 : 0.33	90	93 (<i>R</i>)
2	11	0.2 M	1 : 0.33	97	86 (<i>R</i>)
3	11	0.5 M	1 : 0.33	97	84 (<i>R</i>)
4	11	0.1 M	2 : 0.66	97	92 (<i>R</i>)
5	13	0.1 M	1 : 0.33	62	91 (<i>R</i>)
6	13	0.2 M	1 : 0.33	96	88 (<i>R</i>)
7	13	0.5 M	1 : 0.33	94	87 (<i>R</i>)
8	13	0.1 M	2 : 0.66	97	90 (<i>R</i>)
9	14	0.1 M	2 : 0.66	96	88 (<i>R</i>)

^a The reaction was carried out at 80 °C using acetophenone (1 mmol). ^b Enantiomeric excess and conversion determined by chiral GC. ^c Configuration determined by the sign of the optical rotation of the isolated product.

It was found that a reaction concentration of 0.1 M combined with a catalyst loading of 2 mol% returned optimal results (Table 1 entry 4). The reaction reached completion after 48 hours, therefore the reaction was repeated using ligand **13** (Table 1), which gave a similar trend in the results. The supplementary data shows graphical comparisons of the ATH of acetophenone at different concentrations using ligand **11**, and of the ee for ATH of acetophenone at different concentrations using ligand **13**. The reduction of acetophenone using ligand **14** for 48 h (0.1 M concentration, 2 mol% catalyst loading) gave almost the same conversion and ee compared to compounds **11** and **13** (Table 1 entry 9).

An investigation into the possibility of non-linear chirality transfer from ligand **11** to the product was carried out using ligand samples of varying ee from 0-100%. This did not indicate any significant effect (see supplementary data for full details), indicating a 1:1 ligand:metal ratio in the active species. A suggested mechanism of action for the ATH of an aryl ketone using compound **11** as the ligand is illustrated in Figure 2.⁴ Initial decomposition of Ru₃(CO)₁₂ with CO release, then ligation by **11** and proton transfer forms the coordinatively saturated active species **16**. Aryl ketones can be reduced by **16** via an outer sphere, concerted mechanism as shown in transition state **17**.

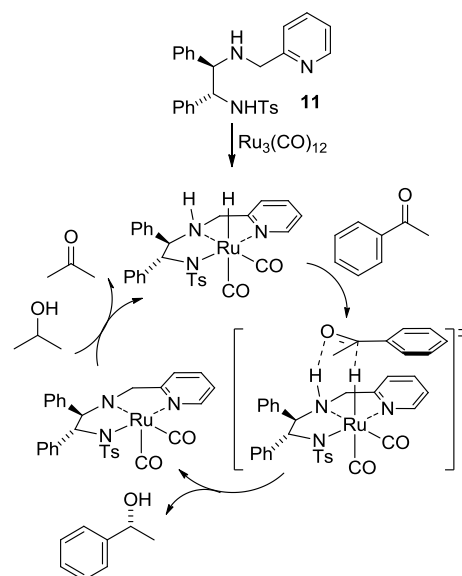


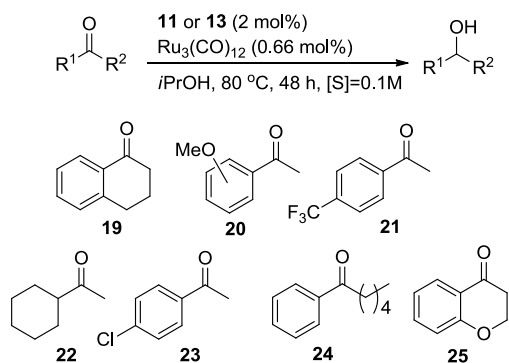
Figure 2. Proposed mechanism of action of the catalyst derived from tridentate ligand **11**.

The orientation of approach may be influenced by a favourable π - π interaction between the pyridine group in the ligand and the aromatic substituent on the respective ketone. Finally, hydrogen donation by the *i*PrOH solvent regenerates **18** to complete the catalytic cycle.

Compound **7** was employed as a ligand in the ATH of acetophenone, however no reduction product was observed after two days, as might be predicted in light of the anticipated requirement for a basic amine in the catalyst. The amide bond functionality may prevent the coordination of the corresponding nitrogen to ruthenium to form the active catalyst, as the lone pair is not available due to conjugation.

A series of ketone derivatives were then reduced by ATH using ligands **11** and **13**, (Table 2). Clearly, substituted aryl ketones are highly compatible with this methodology. Near quantitative conversion and high enantioselectivity were achieved for the majority of the substrates tested. Most of the substituted aryl ketones gave high conversions and good enantioselectivities (Table 2). Among the substituted aryl ketones tested, it was found that the presence of a *meta*-methoxy substituent on the aromatic ring yielded optimal results under the ATH conditions employed (48 h, 98% conv., 94% ee). Acetophenone was reduced completely with only 88% ee compared to other substituted aryl ketones, which may indicate the effect of substitution on enhancing the ee. Trifluoromethyl- and chloro- substituted acetophenone were reduced completely with 91% ee.

Table 2. ATH of ketones with ligands **11** and **13** in conjunction with Ru₃(CO)₁₂.^a



Entry	Ketone	Ligand	Conv (%) ^b	Ee (%) ^{b,c}
1	19	13	26	86 (<i>R</i>)
2	<i>p</i> - 20	13	68	88 (<i>R</i>)
3	21	13	100	86 (<i>R</i>)
4	22	13	86	17 (<i>S</i>)
5	19	11	84	93 (<i>R</i>)
6	<i>o</i> - 20	11	99	89 (<i>R</i>)
7	<i>m</i> - 20	11	98	94 (<i>R</i>)
8	<i>p</i> - 20	11	90	92 (<i>R</i>)
9	23	11	99	91 (<i>R</i>)
11	21	11	99	91 (<i>R</i>)
12	24	11	85	90 (<i>R</i>)
13	25	11	95	91 (<i>R</i>)
14	22	11	88	19 (<i>S</i>)

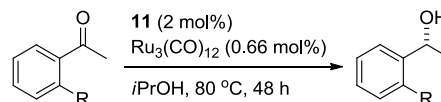
^a The reaction was carried out at 80 °C using acetophenone (1 mmol), *i*PrOH (10 cm³). ^b Enantiomeric excess and conversion determined by chiral GC. ^c Determined by the sign of optical rotation of isolated product.

The bicyclic compounds **19** and **25** were reduced in 84 and 95% conversion with 93 and 91% ees respectively. Also the long chain high molecular weight compound **24** was reduced in 85% conversion with 90% ee. Acetylcyclohexane was reduced at lower rates compared to aryl ketones, however the enantiomeric excess was significantly lower. The reversed enantioselectivity for acetylcyclohexane reduction, relative to acetophenone derivatives, suggest that weaker steric factors were directing the reaction, rather than electronic ones. The supplementary data contains tables and graphs of the observed conversion and ee for ketone reduction.

An investigation was carried out into the reduction of *ortho*-substituted aryl ketones (Table 3). Most of the substrates were reduced with near quantitative conversion and high enantioselectivity and are highly compatible with this methodology. Conversion improved with smaller electron-withdrawing groups (fluorine and chlorine) compared to unsubstituted acetophenone. Among the reduced substituents, lower conversion was obtained for large substituents such as iodide and trifluoromethyl groups. In these cases, it is likely that the substituents cause an unfavourable orthogonal orientation of the arene group, which will subsequently disrupt the proposed π - π interaction (Figure 2). Among the substrates reduced, 2'-methylacetophenone yielded optimal results after 48 hours,

achieving almost quantitative conversion and an ee of 93.8%. The electron-donating effect of the methyl substituent may encourage more favourable π - π interactions in the transition state, whilst sterically it appears to be of optimum size to encourage high conversion without preventing approach to the catalyst. The supplementary data features further information on conversion and ee against time for these reductions.

Table 3: ATH of aryl ketones containing a substituent at the *ortho* position.^a



Entry	R	Conv (%) ^b	Ee (%) ^{b,c}
1	F	>99	83.7 (<i>R</i>)
2	Cl	>99	87.6 (<i>R</i>)
3	Br	99.0	86.2 (<i>R</i>)
4	I	3.1	9.1 (<i>R</i>)
5	CF ₃	33.3	17.6 (<i>R</i>)
6	Me	>99	93.8 (<i>R</i>)

^a The reaction was carried out using substrate (1 mmol) in *i*PrOH (10 cm³), 48 h. ^b Enantiomeric excess and conversion determined by chiral GC. ^c Determined by the sign of the optical rotation of the isolated product.

In conclusion, we have described the synthesis of an effective tridentate ligand for incorporation into an active asymmetric transfer hydrogenation catalyst upon combination with Ru₃(CO)₁₂. We are currently investigating further applications of this system.

Acknowledgments

We thank the Libyan Ministry for Higher Education and Scientific Research for financial support (to M.O.D.), and Warwick University for support of A.W. The X-ray diffractometer was funded through the Advantage West Midlands Science City Advanced Materials project and ERDF support.

Supplementary data

General experimental details, graphs of experimental results, ¹H and ¹³C-NMR spectra of all new compounds and chiral GC/HPLC spectra.

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21. Compound **11** CCDC 929339; C₂₇H₂₇N₃O₂S, M = 457.58, monoclinic, space group P2(1)2(1)2(1), a = 11.9961(2), b = 18.3565(3), c = 22.6663(3) Å, α = 90°, β = 90°, γ = 90°, U = 4991.26(13) Å³ (by least squares refinement on 14229 reflection positions), T = 150(2)K, λ = 0.71073 Å, Z = 8, D(cal) = 1.218 Mg/m³, F(000) = 1936. μ(MoK-α) = 0.158 mm⁻¹. Crystal character: colourless block. Crystal dimensions 0.45 x 0.45 x 0.40 mm.
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