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N-Functionalised TsDPEN catalysts for asymmetric transfer hydrogenation; synthesis and applications

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ABSTRACT

A series of Ru(II)/arene complexes containing *N*-alkylated derivatives of TsDPEN were prepared and tested in the asymmetric transfer hydrogenation (ATH) of ketones. The results demonstrated that a wide variety of functionality were tolerated on the basic amine of the TsDPEN ligand, without significantly disrupting the ability of the catalyst to catalyse hydrogen transfer reactions.

Introduction

The application of [(arene)Ru(TsDPEN)Cl] (TsDPEN = *N*-Tosyl-1,2-diphenylethyl-1,2-diamine) complexes of type **1** to asymmetric transfer hydrogenation (ATH) and asymmetric hydrogenation (AH) of ketones and imines is now well-established.[1–4] These catalysts have been widely applied in synthetic chemistry[5] and their mechanisms of action have been studied in detail.[6]

The majority of applications of this class of catalysts involve the use of **1**, or close derivatives, which contain a ligand with a primary amine group, and a *p*-cymene arene group.[7] However complexes derived from TsDPEN ligands containing secondary amine groups, for example, complexes **2a**–**2g**, are also viable, although less well studied despite the obvious scope for the attachment of functionality at this position. Ikariya and Kioke[8] have described the process of hydride transfer from formate to the Ru atom within *N*-methylated complex **2a**, whilst we have reported the preparation and applications to ketone and imine reduction of a series of *N*-alkylated complexes **2a**–**2g**.[9] Scheme 1 illustrates some examples of ketone reduction using formic acid/triethylamine 5:2 azeotrope (FA/TEA) as the reducing agent, however isopropanol and molecular hydrogen have also been employed.[1–6] Li et al. reported the use of catalyst **3**, and close derivatives containing an *N*-PEG chain to afford improved aqueous solubility and activity in the reduction of ketones in water.[10] Applications of *N*′-alkylated derivatives of *N*-tosyl-1,2-diaminocyclohexane to ATH have been reported,[11a,b] as have secondary amine ligands derived from proline.[11c,d] The ATH of some (electron poor) alkene bonds using *N*-alkylated TsDPEN derivatives has also been reported.[12]

In our work, we have found that it was important to use benzene as the arene for best results,[9] however others have found that *p*-cymene may be used.[10,11] *N*-Alkylated complexes of type **2** still work effectively because in the active hydride species **4**, the 'R' group can occupy a position in which it is proximal to the η^6-arene ring.[9a] This allows the remaining N-H bond to form a productive interaction with the ketone substrate (as illustrated by structure **5**), which is essential for the hydrogen transfer step. Tethered complexes such as **6** and **7**[9c,13] also contain an *N*-alkylated group although this is conformationally locked in a position which permits the N–H of the hydride form to operate in the required manner for reduction.

The ability to *N*-functionalise the basic nitrogen atom of the ligand in TsDPEN/Ru/arene complexes provides a valuable route for productive functionalisation, as illustrated by **3**,[10] and also provides a means to introduce groups which could allow the catalyst to be attached to other groups such as polymeric supports. Linking through this position appears to have found limited application to form solid-supported reagents[14] which is in contrast to the many examples of linking through the sulfonamide function of the ligand.[15] In this Letter we describe the synthesis of a number of

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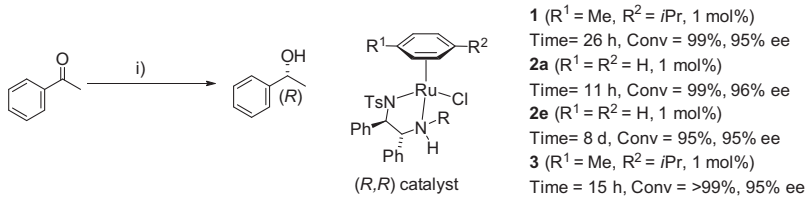


Scheme 1. ATH of acetophenone using *N*-alkylated Ru complexes. Reagents and conditions: (i) catalyst, FA/TEA, 28 °C.

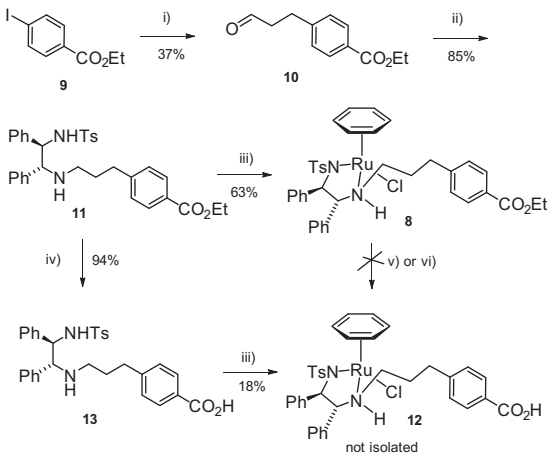
N-alkylated complexes and demonstrate their viability as catalysts for ketone reduction.

Results and discussion

We first investigated the synthesis of an ester-functionalised catalyst **8**, in order to establish a synthetic route and the compatibility of an ester-containing group with the ATH conditions (Scheme 2). Using a literature procedure, allyl alcohol was coupled to 4-iodo ethylbenzoate **9** to form aldehyde **10**.[16] A side reaction also occurred to form an unsaturated 3-carbon chain as a side product (ca. 6–20%, see ESI).

The reductive amination of **10** with (*R*,*R*)-TsDPEN, was achieved using sodium cyanoborohydride as reductant to give the product amine **11** as a crystalline and air stable solid. Complexation with $[(benzene)RuCl_2]_2$ was achieved by treating **11** at reflux in IPA with triethylamine;[2d] formation of **8** was straightforward and the product was purified on silica gel. Suitable single crystals for X-ray analysis were obtained by recrystallisation and the resulting crystal structure confirmed the assigned stereochemistry (Fig. 2).[17] As expected for complexes of this type, the (*R*,*R*) carbon backbone led to an (*S*) configuration at the ruthenium atom.[2d]

It was hoped that the ethyl ester in **8** could be directly hydrolysed to generate the carboxylic acid complex **12**. However, although hydrolysis with both $KOH/DCM/H_2O$ and $LiOH/THF/H_2O$ generated the known 16 electron species through elimination of HCl,[2d] as characterised by a colour change from orange to bright purple, ESI MS and NMR showed no effect on the ester functionality. Acidic workup with HCl resulted in recovery of the 18 electron chloride complex **8**. However, treatment of **11** with KOH in refluxing $MeOH/H_2O$ gave **13** in high yield. Complexation of **13** with $[(benzene)RuCl_2]_2$ was attempted and a catalytically



Scheme 2. Reagents and conditions: (i) allyl alcohol, $Pd(OAc)_2$ (6 mol %), TBAB, $NaHCO_3$, 3 Å MS, DMF, 70 °C, sealed tube; (ii) (*R*,*R*)-TsDPEN, AcOH, 4 Å MS, MeOH, then $NaBH_3CN$, rt; (iii) $[(C_6H_6)RuCl_2]_2$, NEt_3, *i*PrOH, 80 °C, reflux; (iv) KOH, MeOH/H_2O, 70 °C, 1 h; (v) $KOH/DCM/H_2O$; (vi) $LiOH/THF/H_2O$.

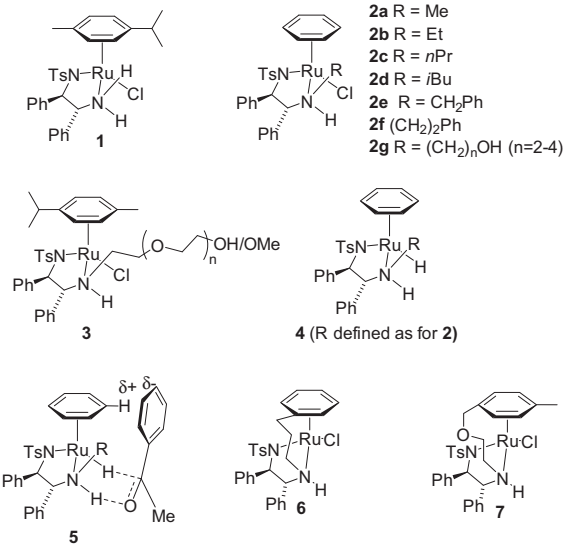


Figure 1. TsDPEN/Ru(II) complexes (**1**–**4**, **6**, **7**) for the ATH of ketones and imines, and the proposed mode of hydrogen transfer to ketone substrates (**5**).

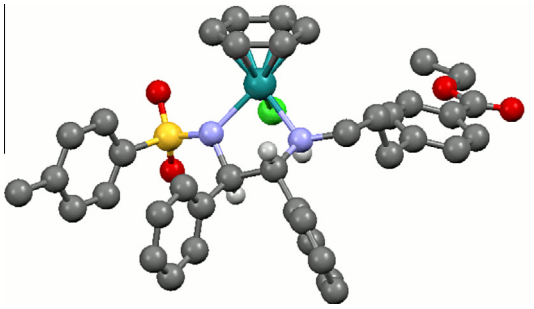


Figure 2. Single crystal X-ray structure of **8**; hydrogen atoms have been omitted for clarity, except at stereocentres.

Table 1
Optimisation of conditions for the reduction of acetophenone using **8**[a]

Entry	*T* (°C)	S/C	Time (h)	Conv (%)	ee (%)
1	60	1000	48	65	97 (*R*,*R*)
2	45	500	48	92	95 (*R*,*R*)
3	45	100	6	99	95 (*R*,*R*)
4	28	100	21	100	96 (*R*,*R*)

[a] Conversion and ee were determined by chiral GC.

active complex was formed by combining the reagents in situ. A product was isolated which gave a ^1H NMR spectrum of what appeared to be the triethylammonium adduct of **12**, however in a DCM solution the complex decomposed over ~24 h, forming a

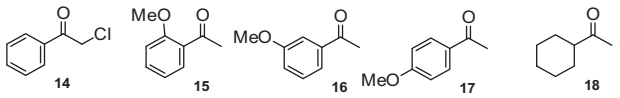


Figure 3. Substrates for ATH by complex **8**.

Table 2
Ketone reduction using catalysts **8** and **12**[a]

Entry	Ketone	Catalyst	Time (h)	Conv[b] (%)	ee[b] (%)
1	Acetophenone	**8**	6	99	95 (*R*)
2[c]	Acetophenone	**12**	20	99	95 (*R*)
3	**14**	**8**	1.5	100	88 (*S*)
4	**14**	**12**	1.5	100	89 (*S*)
5	**15**	**8**	5.5	98	79 (*R*)
6	**15**	**12**	5.5	97	79 (*R*)
7	**16**	**8**	5	92	95 (*R*)
8	**16**	**12**	5	95	96 (*R*)
9	**17**	**8**	23.5	88	92 (*R*)
10	**17**	**12**	23.5	89	95 (*R*)
11	**18**	**8**	22	99	42[d] (*S*)
12	**18**	**12**	22	96	42[d] (*S*)

[a] Reaction conditions: Ru-Catalyst (1 mol %), FA/TEA (5/2 azeotrope), 45 °C.
[b] Conversion and ee determined by chiral GC.
[c] Reduction performed at 28 °C.
[d] ee determined by chiral GC after acetylation of the alcohol product.

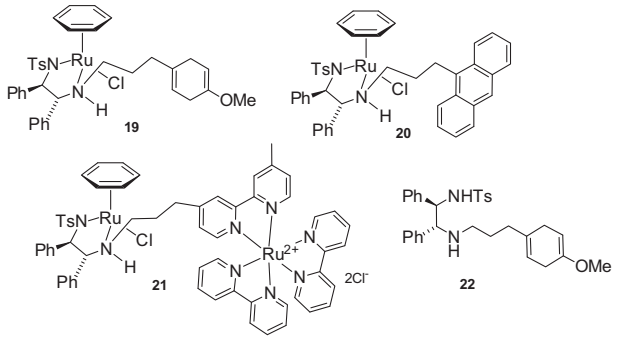


Figure 4. *N*-Alkylated catalysts for ATH.

black solution from the original bright orange. Hence **12** was used in its crude form.

Reduction of acetophenone to 1-phenylethanol (Scheme 1) is the standard benchmark to evaluate the performance of ATH catalysts, hence this reaction was used for the optimisation of reduction conditions. Using the (*R*,*R*) catalyst it was expected that the (*R*) enantiomer would be the major product. Using a standard substrate concentration of 2M in FA/TEA (5:2 azeotrope), the temperature and substrate to catalyst ratio were varied as shown in Table 1.

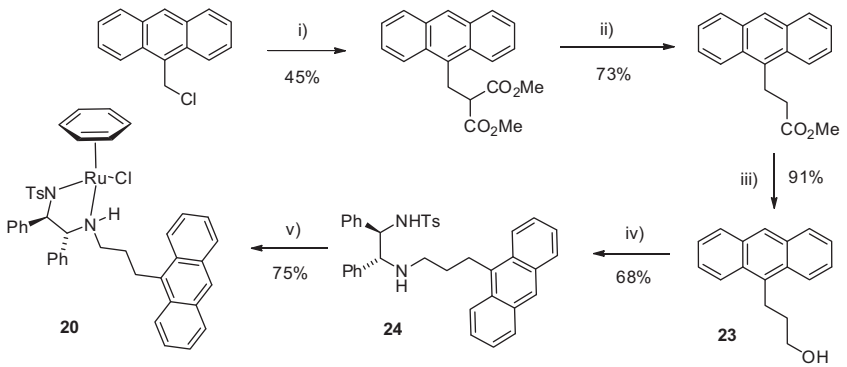
Initial attempts focused on the use of high temperature and low catalyst loading. However this required long reaction times and gave incomplete conversion. Increasing the loading to 1 mol % gave almost complete conversion after 6 h at 45 °C and 21 h at 28 °C, with almost no loss of enantioselectivity. Hence the conditions in entry 3 were selected for further applications. Under the optimised conditions, the new ester catalyst **8**, along with its acid analogue **12** were tested in the ATH of a series of ketones **14**–**18** (Fig. 3).

The effect of varying the substrate substitution pattern was explored by the use of α-chloro acetophenone **14**, as well as *ortho*, *meta* and *para* (**15**, **16**, **17**) isomers of methoxyacetophenone. Cyclohexylmethylketone **18** was also chosen to investigate how the selectivity changed when reducing di-alkyl ketones (Table 2). As expected, an α-chloro substituent on the ketone increases the rate of reaction due to the increased electrophilicity of the carbonyl carbon. This increased rate came at the penalty of selectivity, with reduced enantiomeric excess when compared to those for acetophenone. Upon introducing a methoxy substituent onto the aromatic ring at the *meta* position there was little effect other than reducing the reaction rate; which was due to the increased electron density on the aromatic ring making the carbonyl less electrophilic.[13g] This effect was strongly increased at the *para* position, where full conversions could not be achieved even after 24 h. Enantioselectivity was unaffected however and the obtained ee remained high. *Ortho* substitution appeared to have no additional effect on the rate, but significantly reduced the enantiomeric excess, as had been seen before,[2,13] possibly due to a steric clash with the catalyst.

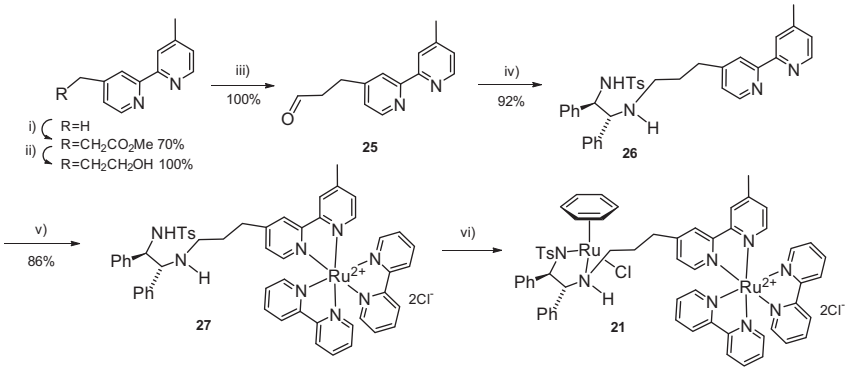
Reduction of cyclohexyl methyl ketone is challenging for most ATH catalysts, as the high enantioselectivities achieved in reduction of aryl alkyl ketones are generally dependent on the aromatic CH-π interaction with the ruthenium arene (**5**, Fig. 1). Without this interaction the two faces of the ketone are solely distinguished by the steric bulk of its substituents, hence the ee is frequently lower, and selectivity is reversed, as observed.[2–4]

The basic nitrogen atom of the TsDPEN ligand was also functionalised through the addition of a number of other groups with potential functionality including a cyclohexadiene (**19**), anthracene (**20**), and even a ruthenium complex (**21**) (Fig. 4).

Complex **19** was prepared by the reaction between **22** and $[(C_6H_6)RuCl_2]_2$. Complex **20** was synthesised through in situ formation of the triflate derived from 3-(1-anthracen-9-yl)propan-1-ol **23**,[18] followed by reaction with TsDPEN, and reaction of the resulting ligand **24** with $[(C_6H_6)RuCl_2]_2$ (Scheme 3). The BIPY–containing



Scheme 3. Reagents and conditions: (i) dimethyl malonate, NaOMe, MeOH, reflux, 30 h; (ii) LiCl, H_2O, DMSO, 130 °C, 18 h; (iii) $LiAlH_4$, THF, 0 °C–rt, 5 h; (iv) 2,6-lutidine, triflic anhydride, DCM, 0 °C, 30 min, rt, 60 min, then (*R*,*R*)-TsDPEN, TEA, DCM, 0 °C, 30 min, rt, 18 h; (v) $[(C_6H_6)RuCl_2]_2$, IPA, TEA, 80 °C, 1 h.



Scheme 4. Reagents and Conditions: (i) LDA, THF, −78 °C to rt then $BrCH_2CO_2Me$, −78 °C; (ii) DIBAL, −78 °C to rt, 18 h; (iii) $(COCl)_2$, DCM, DMSO, −78 °C, Et_3N; (iv) TsDPEN, MeOH, AcOH, rt, 4.5 h, then $NaBH_3CN$, 4A MS, rt, 18 h; (v) $[Ru(bipy)_2Cl_2]$, MeOH, water, 95 °C, 17 h; (vi) $[(C_6H_6)RuCl_2]_2$, *i*PrOH, Et_3N, 80 °C, 1 h, crude product used in reduction reactions.

Table 3
Acetophenone reduction using complexes **19–21**[a]

Entry	Catalyst	Temp (°C)	Time (h)	Conv[a] (%)	ee[a] (%)
1	**19**	28	20	99	96 (*R*)
2	**20**	28	4	70	97 (*R*)
3	**20**	28	8	93	97 (*R*)
4	**20**	28	23	100	97 (*R*)
5	**21**	28	15	68	93 (*R*)
6	**21**	28	22	81	93 (*R*)
7	**21**	28	39	89	93 (*R*)

[a] Reaction conditions: Ru-catalyst (1 mol %), FA/TEA (5:2 azeotrope).

ligand was prepared via aldehyde **25**[19] which was coupled by reductive amination with (*R*,*R*)-TsDPEN to give **26**, conversion to ter(BIPY) complex **27** and subsequently reaction with $[(C_6H_6)RuCl_2]_2$ to give **21** (Scheme 4). Complex **21** was not fully characterised but used directly as the in situ-formed material, although ^{1}H-NMR spectroscopy indicated the correct composition.

A summary of the results from the ATH studies on acetophenone using complexes **19–21** is given in Table 3. All of these worked as effective catalysts, including those formed and used in situ, and products of high ee were formed in each case. This highlights the versatility and functional group tolerance to substitution on the *N* atom of TsDPEN-derived Ru(II) catalysts.

In conclusion, complexes **8**, **12** and **19–21**, containing a range of functional groups on the basic nitrogen atom of the TsDPEN ligand, were synthesised and applied to the ATH of ketones using formic acid/trimethylamine (FA/TEA) as the reducing agent. All demonstrated good activity for the ATH of ketones under the conditions used. In principle it should be possible to utilise this linkage to combine the catalyst to other useful molecules, such as secondary catalysts, fluorescent tags or polymeric supports.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2015.09.135.

References and notes

1. Reviews (a) Gladiali, S.; Alberico, E. *Chem. Soc. Rev.* **2006**, *35*, 226–236; (b) Ikariya, T.; Murata, K.; Noyori, R. *Org. Biomol. Chem.* **2006**, *4*, 393–406; (c) Ikariya, T.; Blacker, A. J. *Acc. Chem. Res.* **2007**, *40*, 1300–1308; (d) Wang, C.; Wu, X.; Xiao, J. *Chem. Asian J.* **2008**, *3*, 1750–1770; (e) Zhao, B.; Han, Z.; Ding, K. *Angew. Chem., Int. Ed.* **2013**, *52*, 4744–4788; (f) Vaclavik, J.; Sot, P.; Vilhanova, B.; Pechacek, J.; Kuzma, M.; Kacer, P. *Molecules* **2013**, *18*, 6804–6828; (g) Wu, X. F.; Xiao, J. L. *Chem. Commun.* **2007**, 2449–2466.
2. (a) Hashiguchi, S.; Fujii, A.; Takehara, J.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1995**, *117*, 7562–7563; (b) Fujii, A.; Hashiguchi, S.; Uematsu, N.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 2521–2522; (c) Matsumura, K.; Hashiguchi, S.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1997**, *119*, 8738–8739; (d) Haack, K. J.; Hashiguchi, S.; Fujii, A.; Ikariya, T.; Noyori, R. *Angew. Chem.* **1997**, *109*, 297–300. *Angew. Chem., Int. Ed.*, **1997**, *36*, 285–288.
3. (a) Liu, J.; Zhou, D.; Jia, X.; Huang, L.; Li, X.; Chan, A. S. C. *Tetrahedron: Asymmetry* **2008**, *19*, 1824–1828; (b) Li, X.; Wu, X.; Chen, W.; Hancock, F. E.; King, F.; Xiao, J. *Org. Lett.* **2004**, *6*, 3321–3324; (c) Geldbach, T. J.; Dyson, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 8114–8115; (d) Ward, T. R. *Acc. Chem. Res.* **2011**, *44*, 47–57; (e) Wu, X.; Liu, J.; di Tommaso, D.; Iggo, J. A.; Catlow, C. R. A.; Bacsa, J.; Xiao, J. *Chem. Eur. J.* **2008**, *14*, 7699–7715; (f) Mohar, B.; Valleix, A.; Desmurs, J. R.; Felemez, M.; Wagner, A.; Mioskowski, C. *Chem. Commun.* **2001**, 2572–2573; (g) Limanto, J.; Krska, S. W.; Dorner, B. T.; Vazquez, E.; Yoshikawa, N.; Tan, L. *Org. Lett.* **2010**, *12*, 512–515; (h) Cartigny, D.; Püntener, K.; Ayad, T.; Scalone, M.; Ratovelomanana-Vidal, V. *Org. Lett.* **2010**, *12*, 3788–3791.
4. (a) Wills, M. In *Modern Reduction Methods*; Andersson, P. G., Munslow, I. J., Eds.; Wiley-VCH: Weinheim, 2008; pp 271–296. Chapter 11; (b) Uematsu, N.; Fujii, A.; Hashiguchi, S.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 4916–4917; (c) Wang, C.; Li, C.; Wu, X.; Pettman, A.; Xiao, J. *Angew. Chem., Int. Ed.* **2009**, *48*, 6524–6528; (d) Strotman, N. A.; Baxter, C. A.; Brands, K. M. J.; Cleator, E.; Krska, S. W.; Reamer, R. A.; Wallace, D. J.; Wright, T. J. *J. Am. Chem. Soc.* **2011**, *133*, 8362–8371; (e) Mangion, I. K.; Chen, C.-Y.; Li, H.; Maligres, P.; Chen, Y.; Christensen, M.; Cohen, R.; Jeon, I.; Klapars, A.; Krska, S.; Nguyen, H.; Reamer, R. A.; Sherry, B. D.; Zavialov, I. *Org. Lett.* **2014**, *16*, 2310–2313; (f) Sun, X.; Manos, G.; Blacker, J.; Martin, J.; Gavriilidis, A. *Org. Proc. Res. Dev.* **2004**, *8*, 909–914; (g) Åberg, J. B.; Samec, A. M.; Bäckvall, J.-E. *Chem. Commun.* **2006**, 2771–2773; (h) Kuzma, M.; Vaclavik, J.; Novak, P.; Prech, J.; Januscak, J.; Cerveny, J.; Pechacek, J.; Sot, P.; Vilhanova, B.; Matousek, V.; Goncharova, I. I.; Urbanova, M.; Kacer, P. *Dalton Trans.* **2013**, *42*, 5174–5182.
5. (a) Bradley, P. A.; Carroll, R. L.; Lecouturier, Y. C.; Moore, R.; Noeureuil, P.; Patel, B.; Snow, J.; Wheeler, S. *Org. Proc. Res. Dev.* **2010**, *14*, 1326–1336; (b) Bai, J.; Miao, S.; Wu, Y.; Zhang, Y. *Chin. J. Chem.* **2011**, *29*, 2476–2480; (c) Slungård, S. V.; Krakeli, T.-A.; Thvedt, T. H. K.; Fuglseth, E.; Sundby, E.; Hoff, B. H. *Tetrahedron* **2011**, *67*, 5642–5650; (d) Nakayama, A.; Kogure, N.; Kitajima, M.; Takayama, H. *Angew. Chem., Int. Ed.* **2011**, *50*, 8025–8028; (e) Dias, L. C.; Ferreira, M. A. B. *J. Org. Chem.* **2012**, *77*, 4046–4062; (f) Hems, W. P.; Jackson, W. P.; Nightingale, P.; Bryant, R. *Org. Proc. Res. Dev.* **2012**, *16*, 461–463; (g) Lemke, M.-K.; Schwab, P.; Fischer, P.; Tischer, S.; Witt, M.; Noehringer, L.; Rogachev, V.; Jäger, A.; Kataeva, O.; Fröhlich, R.; Metz, P. *Angew. Chem., Int. Ed.* **2013**, *52*, 11651–11655; (h) Cortez, N. A.; Aguirre, G.; Parrra-Hake, M.; Somanathan, R. *Tetrahedron: Asymmetry* **2013**, *24*, 1297–1302; (i) Bligh, C. M.; Anzalone, L.; Jung, Y. C.; Zhang, Y.; Nugent, W. A. *J. Org. Chem.* **2014**, *79*, 3238–3243.
6. (a) Alonso, D. A.; Brandt, P.; Nordin, S. J. M.; Andersson, P. G. *J. Am. Chem. Soc.* **1999**, *121*, 9580–9588; (b) Yamakawa, M.; Ito, H.; Noyori, R. *J. Am. Chem. Soc.* **2000**, *122*, 1466–1478; (c) Noyori, R.; Yamakawa, M.; Hashiguchi, S. *J. Org. Chem.* **2001**, *66*, 7931–7944; (d) Yamakawa, M.; Yamada, I.; Noyori, R. *Angew. Chem., Int. Ed.* **2001**, *40*, 2818–2821; (e) Casey, C. P.; Johnson, J. B. *J. Org. Chem.* **2003**, *68*, 1998–2001; (f) Brandt, P.; Roth, P.; Andersson, P. G. *J. Org. Chem.* **2004**, *69*, 4885–4890; (g) Handgraaf, J.-W.; Meijer, E. J. *J. Am. Chem. Soc.* **2007**, *129*, 3099–3103; (h) Dub, P. A.; Ikariya, T. *J. Am. Chem. Soc.* **2013**, *135*, 2604–2619.
7. Matsuoka, A.; Sandoval, C. A.; Uchiyama, M.; Noyori, R.; Naka, H. *Chem.-Asian J.* **2015**, *10*, 112–115.

8. (a) Koike, T.; Ikariya, T. *Adv. Synth. Catal.* **2014**, *346*, 37–41; (b) Koike, T.; Ikariya, T. *J. Organomet. Chem.* **2007**, *692*, 408–419.
9. (a) Martins, J. E. D.; Clarkson, G. J.; Wills, M. *Org. Lett.* **2009**, *11*, 847–850; (b) Martins, J. E. D.; Contreras Redondo, M. A.; Wills, M. *Tetrahedron: Asymmetry* **2010**, *21*, 2258–2264; (c) Parekh, V.; Ramsden, J. A.; Wills, M. *Catal. Sci. Technol.* **2012**, *2*, 406–414; (d) Zammit, C. M.; Wills, M. *Tetrahedron: Asymmetry* **2013**, *24*, 844–852.
10. (a) Shan, W.; Meng, F.; Wu, Y.; Mao, F.; Li, X. *J. Organomet. Chem.* **2011**, *696*, 1687–1690; (b) Luo, Z.; Qin, F.; Yan, S.; Li, S. *Tetrahedron: Asymmetry* **2012**, *23*, 333–338.
11. (a) Cortez, N. A.; Rodriguez-Apodaca, R.; Aguirre, G.; Parra-Hake, M.; Cole, T.; Somanathan, R. *Tetrahedron Lett.* **2006**, *47*, 8515–8518; (b) Cortez, N. A.; Flores-Lopez, C. Z.; Rodriguez-Apodaca, R.; Flores-Lopez, L. Z.; Parra-Hake, M.; Somanathan, R. *ARKIVOC* **2005**, *6*, 162; (c) Canivet, J.; Süss-Fink, G. *Green Chem.* **2007**, *9*, 391–397; (d) Dahlin, N.; Bøgevig, A.; Adolfsson, H. *Adv. Synth. Catal.* **2004**, *346*, 1101.
12. Xue, D.; Chen, Y.-C.; Cui, X.; Wang, Q.-W.; Zhu, J.; Deng, J.-G. *J. Org. Chem.* **2005**, *70*, 3584–3591.
13. (a) Hayes, A. M.; Morris, D. J.; Clarkson, G. J.; Wills, M. *J. Am. Chem. Soc.* **2005**, *127*, 7318–7319; (b) Cheung, F. K.; Lin, C.; Minissi, F.; Lorente Crivillé, A.; Graham, M. A.; Fox, D. J.; Wills, M. *Org. Lett.* **2007**, *9*, 4659–4662; (c) Soni, R.; Cheung, F. K.; Clarkson, G. C.; Martins, J. E. D.; Graham, M. A.; Wills, M. *Org. Biomol. Chem.* **2011**, *9*, 3290–3294; (d) Soni, R.; Jolley, K. E.; Clarkson, G. J.; Wills, M. *Org. Lett.* **2013**, *15*, 5110–5113; (e) Perryman, M. S.; Harris, M. E.; Foster, J. L.; Joshi, A.; Clarkson, G. J.; Fox, D. J. *Chem. Commun.* **2013**, 10022–10024; (f) Touge, T.; Hakamata, T.; Nara, H.; Kobayashi, T.; Sayo, N.; Saito, T.; Kayaki, Y.; Ikariya, T. *J. Am. Chem. Soc.* **2011**, *133*, 14960–14963; (g) Soni, R.; Hall, T. H.; Mitchell, B. P.; Owen, M. R.; Wills, M. *J. Org. Chem.* **2015**, *80*, 6784–6793; (h) Hodgkinson, R.; Jurčík, V.; Zanotti-Gerosa, A.; Nedden, H. G.; Blackaby, A.; Clarkson, G. J.; Wills, M. *Organometallics* **2014**, *33*, 5517–5524; (i) Kišić, A.; Stephan, M.; Mohar, B. *Org. Lett.* **2013**, *15*, 1614–1617.
14. Wang, R.; Wan, J.; Ma, X.; Liu, L. *Dalton Trans.* **2013**, *42*, 6513–6522.
15. (a) Deng, J.; Lu, C.; Yang, G.; Chen, Z. *React. Funct. Polym.* **2012**, *72*, 378–382; (b) Zoabi, A.; Omar, S.; Abu-Reziq, R. *Eur. J. Inorg. Chem.* **2015**, 2101–2109; (c) Wu, M.; Kong, L.; Wang, K.; Jin, R.; Cheng, T.; Liu, G. *Catal. Sci. Technol.* **2015**, *5*, 1750–1757; (d) Wang, W.-W.; Li, Z.-M.; Su, L.; Wang, Q.-R.; Wu, Y.-L. J. *Mol. Catal. A: Chem.* **2014**, *387*, 92–102; (e) Liu, R.; Jin, R. H.; Kong, L. Y.; Wang, J. Y.; Chen, C.; Cheng, T. Y.; Liu, G. H. *Chem.-Asian J.* **2013**, *8*, 3108–3115; (f) Gao, F.; Jin, R.; Zhang, D.; Liang, Q.; Ye, Q.; Liu, G. *Green Chem.* **2013**, *15*, 2208–2214; (g) Xia, D. Q.; Cheng, T. Y.; Xiao, W.; Liu, K. T.; Wang, Z. L.; Liu, G. H.; Li, H. X.; Wang, W. *ChemCatChem* **2013**, *5*, 1784–1789; (h) Sun, Y.; Liu, G.; Gu, H.; Hunag, T.; Zhang, Y.; Li, H. *Chem. Commun.* **2011**, 2583–2585; (i) Liu, G.; Wang, J.; Huang, T.; Liang, X.; Zhang, Y.; Li, H. *J. Mater. Chem.* **2010**, *20*, 1970–1975; (j) Jiang, D.; Gao, J.; Yang, Q.; Yang, J.; Li, C. *Chem. Mater.* **2006**, *18*, 6012–6018; (k) Jiang, D.; Yang, Q.; Yang, J.; Zhang, L.; Zhu, G.; Su, W.; Li, C. *Chem. Mater.* **2005**, *17*, 6154–6160; (l) Liu, P. N.; Gu, P. M.; Wang, F.; Tu, Y. Q. *Org. Lett.* **2004**, *6*, 169–172; (m) Huang, X.; Ying, J. Y. *Chem. Commun.* **2007**, 1825–1827; (n) Adima, A.; Moreau, J. J. E.; Man, M. W. C. *Chirality* **2000**, *12*, 411–420; (o) Liu, P.-N.; Gu, P.-M.; Deng, J.-G.; Tu, Y.-Q.; Ma, Y.-P. *Eur. J. Org. Chem.* **2005**, 3221–3227; (p) Jiang, D.; Yang, Q.; Wang, H.; Zhu, G.; Yang, J.; Li, C. *J. Catal.* **2006**, *239*, 65–73.
16. Gesinski, M. R.; Tadpetch, K.; Rychnovsky, S. D. *Org. Lett.* **2009**, *11*, 5342–5345.
17. CCDC 1411528. Crystal Data: $C_{39}H_{41}ClN_2O_4RuS$, $M = 770.32$, Orthorhombic, space group P2(1)2(1)2(1), $a = 6.9302(8)$, $b = 14.9635(18)$, $c = 34.894(3)$ A, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $U = 3618.5(7)$ Å^3 (by least squares refinement on 5908 reflection positions), $T = 150(2)$K, $\lambda = 1.54184$ Å, $Z = 4$, D(cal) = 1.414 Mg m^{-3}, $F(000) = 1592$. μ(MoK-α) = 5.063 mm^{-1}.
18. Bach, A.; Eildal, J. N. N.; Stuhr-Hansen, N.; Deeskamp, R.; Gottschalk, M.; Pedersen, S. W.; Kristensen, A. S.; Stromgaard, K. *J. Med. Chem.* **2011**, *54*, 1333–1346.
19. Terbrueggen, R. H.; Johann, T. W.; Barton, J. K. *Inorg. Chem.* **1998**, *37*, 6874–6883.