



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



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## ABSTRACT

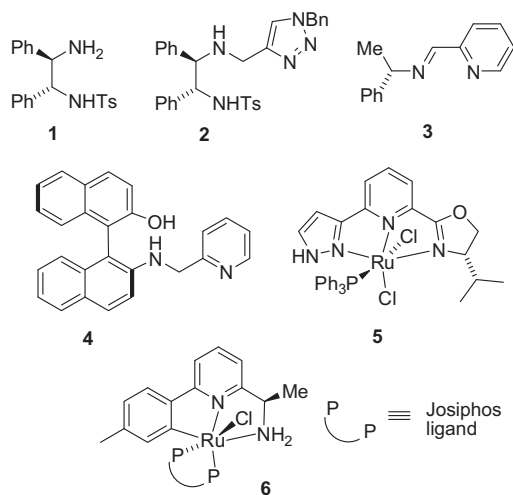
A series of enantiomerically pure tridentate ligands based on the 1,2-diphenylethane-1,2-diamine structure, containing additional pyridine groups, was prepared and tested in asymmetric transfer hydrogenation of ketones using  $\text{Ru}_3(\text{CO})_{12}$  as a metal source. Alcohols were formed in up to 93% ee in the best cases, and good results were obtained with *ortho*-haloarylketones.

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Asymmetric transfer hydrogenation (ATH) of ketones is a valuable method for the synthesis of enantiomerically pure alcohols.<sup>1–3</sup> 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-diphenylethane-1,2-diamine **1** in combination with a Ru/arene or Rh or Ir/pentamethylcyclopentadiene have been particularly successful.<sup>2</sup> Recently, we found<sup>4</sup> that an *N*-tosyl-1,2-diphenylethane-1,2-diamine (TsDPEN) modified with a triazole donor,<sup>5</sup> that is, **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.<sup>1,6–17</sup> Early examples include Schiff base **3** (the Ir complex of which reduced acetophenone in up to 84% ee),<sup>8</sup> 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),<sup>10</sup> as well as 2-(2'-pyridyl)pyridines,<sup>6</sup> phenanthrolines<sup>7</sup> and pyridines combined with phosphines in tridentate donor ligands.<sup>9</sup> 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),<sup>11a</sup> reported by Yu and co-workers.<sup>11</sup> 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.<sup>12</sup> Also containing a chiral diphosphine, **6** gave ketone reduction products of up to 99% ee in ATH

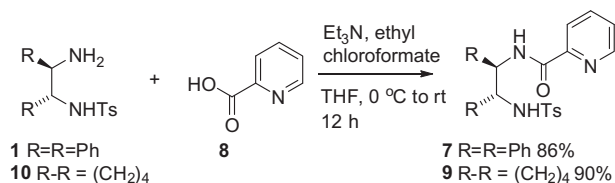
reactions in isopropanol, and is also active in ketone hydrogenation.<sup>12a</sup>



Pyridine-containing ligands have also been used extensively in non-asymmetric hydrogen-transfer processes, and for hydrogen generation from organic molecules.<sup>13</sup> Other applications of pyridine-containing ligands have been reported,<sup>14</sup> as have their applications in highly active non-asymmetric hydrogenations of

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Scheme 1. Synthesis of ligands 7 and 9.

ketones.<sup>15</sup> In some cases, ATH catalysts have been reported which contain a pyridine ring, but as one of a series of tosylated diamine (complex with  $Ru/\eta^6\text{-arene}$ )<sup>16</sup> or amino acid (complex with  $RhCp^*$ )<sup>17</sup> 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  $Ru_3(CO)_{12}$ .<sup>4</sup> 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 (1*R*,2*R*)-TsDPEN 1 using ethyl chloroformate.

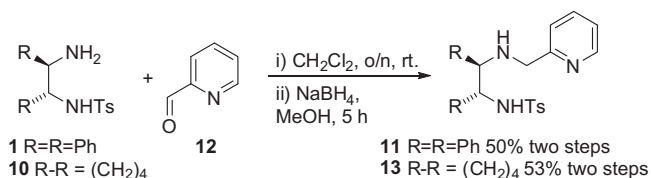
In addition, the known (*R,R*)-[2-(toluene-4-sulfonylamino)-cyclohexyl]-amide 9<sup>18</sup> was prepared from pyridine-2-carboxylic acid 8 and (*R,R*)-(-)-*N*-(4-toluenesulfonyl)-1,2-diaminocyclohexane 10 (90% yield, Scheme 1). The synthesis of the reduced analogues of compounds 7 and 9 was completed by reductive amination. (*R,R*)-*N*-[1,2-Diphenyl-2-[(pyridin-2-ylmethyl)amino]-ethyl]-4-methylbenzenesulfonamide (11) was prepared by reacting (1*R*,2*R*)-TsDPEN 1 in  $CH_2Cl_2$  with 2-pyridinecarboxaldehyde (12). The mixture was stirred overnight at rt to obtain the known imine (*R,R*)-*N*-[1,2-diphenyl-2-[(pyridin-2-ylmethylene)amino]-ethyl]-4-methylbenzenesulfonamide (81%).<sup>19,20</sup> This was reduced using  $NaBH_4$  to afford 11 (62% yield, Scheme 2).

Compound 11 was found to be stable over a period of weeks and its structure was confirmed by X-ray crystallography (Fig. 1).<sup>21</sup>

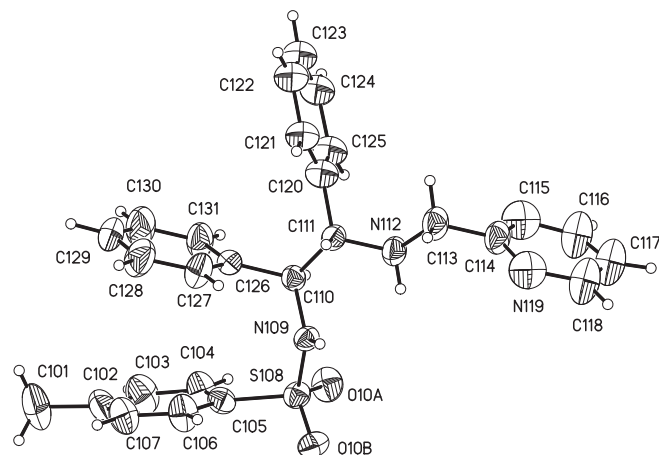
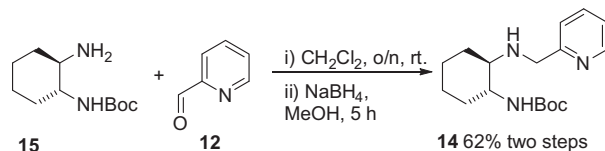
The synthesis of (*R,R*)-4-methyl-*N*-{2-[(pyridin-2-ylmethyl)amino]cyclohexyl}benzenesulfonamide (13)<sup>16</sup> was likewise achieved via the corresponding imine<sup>20</sup> from (1*R*,2*R*)-(-)-*N*-*p*-tosyl-1,2-cyclohexanediamine (10) (Scheme 2). The synthesis of (*R,R*)-{2-[(pyridin-2-ylmethyl)amino]cyclohexyl}carbamic acid *tert*-butyl ester (14) was completed by treatment of mono-Boc diamine 15<sup>22</sup> with 2-pyridinecarboxaldehyde (12) in  $CH_2Cl_2$  to give the intermediate imine, which was reduced by  $NaBH_4$  (Scheme 3).

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  $Ru_3(CO)_{12}$ , that is a 1:1 ratio of  $Ru$ :ligand. Experiments were carried out using varying concentrations and catalyst loadings for 72 h (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).

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 h, therefore the



Scheme 2. Synthesis of ligands 11 and 13.

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

Scheme 3. Synthesis of ligand 14.

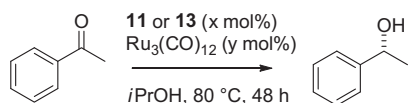
reaction was repeated using ligand 13 (Table 1), which gave a similar trend in the results. The supplementary data shows graphical comparisons of the ATH of acetophenone at different concentrations using ligand 11, and of the ee for ATH of acetophenone at different concentrations using ligand 13. The 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% to 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.<sup>4</sup> Initial decomposition of  $Ru_3(CO)_{12}$  with CO release, then ligation by 11 and proton transfer form 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.

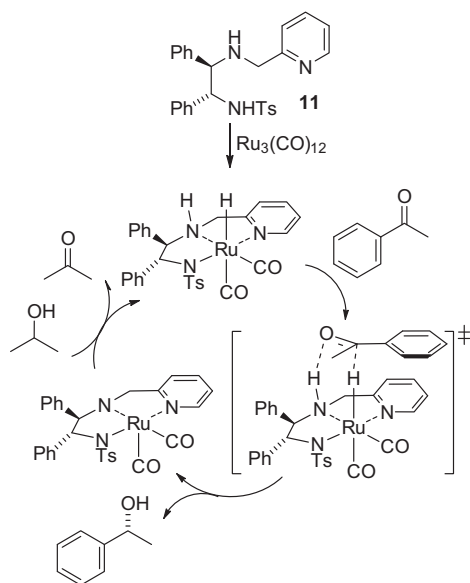
The orientation of approach may be influenced by a favourable  $\pi$ - $\pi$  interaction between the pyridine group in the ligand and the aromatic substituent on the respective ketone. Finally, hydrogen donation by the *i*PrOH solvent regenerates 18 to complete the catalytic cycle.

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

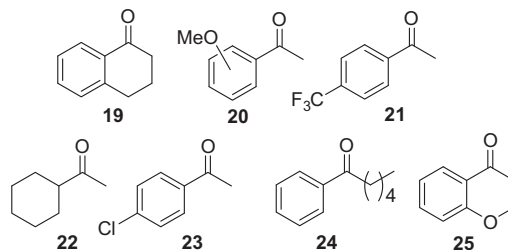
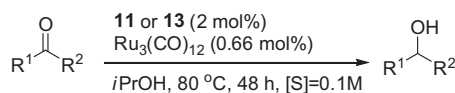
**Table 1**A summary of initial ATH of acetophenone with ligands **11** and **13**<sup>a</sup>

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

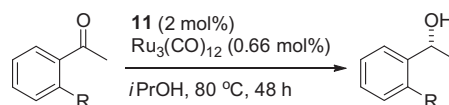
<sup>a</sup> The reaction was carried out at 80 °C using acetophenone (1 mmol).<sup>b</sup> Enantiomeric excess and conversion determined by chiral GC.<sup>c</sup> Configuration determined by the sign of the optical rotation of the isolated product.**Figure 2.** Proposed mechanism of action of the catalyst derived from tridentate ligand **11**.

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.

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 a lower rate compared to aryl ketones, and additionally 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.

**Table 2**ATH of ketones with ligands **11** and **13** in conjunction with Ru<sub>3</sub>(CO)<sub>12</sub><sup>a</sup>

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

<sup>a</sup> The reaction was carried out at 80 °C using acetophenone (1 mmol), *i*PrOH (10 cm<sup>3</sup>).<sup>b</sup> Enantiomeric excess and conversion determined by chiral GC.<sup>c</sup> Determined by the sign of optical rotation of isolated product.**Table 3**ATH of aryl ketones containing a substituent at the *ortho* position<sup>a</sup>

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

<sup>a</sup> The reaction was carried out using substrate (1 mmol) in *i*PrOH (10 cm<sup>3</sup>), 48 h.<sup>b</sup> Enantiomeric excess and conversion determined by chiral GC.<sup>c</sup> Determined by the sign of the optical rotation of the isolated product.

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  $\pi$ - $\pi$  interaction (Fig. 2). Among the substrates reduced, 2'-methylacetophenone yielded optimal results

after 48 h, achieving almost quantitative conversion and an ee of 93.8%. The electron-donating effect of the methyl substituent may encourage more favourable  $\pi$ – $\pi$  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.

In conclusion, we have described the synthesis of an effective tridentate ligand for incorporation into an active asymmetric transfer hydrogenation catalyst upon combination with  $\text{Ru}_3(\text{CO})_{12}$ . We are currently investigating further applications of this system.

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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.2013.05.141>.

## References and notes

- (a) Gladiali, S.; Alberrico, 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) Clapham, S. E.; Hadzovic, A.; Morris, R. H. *Coord. Chem. Rev.* **2004**, 248, 2201–2237; (e) Hashiguchi, S.; Noyori, R. *Acc. Chem. Res.* **1997**, 30, 97–102.
- (a) Fujii, A.; Hashiguchi, S.; Uematsu, N.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, 118, 2521–2522; (b) Murata, K.; Okano, K.; Miyagi, M.; Iwane, H.; Noyori, R.; Ikariya, T. *Org. Lett.* **1999**, 1, 1119–1121; (c) Haack, K. J.; Hashiguchi, S.; Fujii, A.; Ikariya, T.; Noyori, R. *Angew. Chem., Int. Ed.* **1997**, 36, 285–288; (d) Alonso, D. A.; Brandt, P.; Nordin, S. J. M.; Andersson, P. G. *J. Am. Chem. Soc.* **1999**, 121, 9580–9588; (e) Handgraaf, J.-W.; Meijer, E. J. *J. Am. Chem. Soc.* **2007**, 129, 3099–3103; (f) Soni, R.; Cheung, F. K.; Clarkson, G. C.; Martins, J. E. D.; Graham, M. A.; Wills, M. *Org. Biomol. Chem.* **2011**, 9, 3290–3294; (g) Steward, K. M.; Gentry, E. C.; Johnson, J. S. *J. Am. Chem. Soc.* **2012**, 134, 7329–7332.
- (a) Mashima, K.; Abe, T.; Tani, K. *Chem. Lett.* **1998**, 1199–1200; (b) Murata, K.; Ikariya, T.; Noyori, R. *J. Org. Chem.* **1999**, 64, 2186–2187; (c) Hamada, T.; Torii, T.; Izawa, K.; Noyori, R.; Ikariya, T. *Org. Lett.* **2002**, 4, 4373–4376; (d) Hamada, T.; Torii, T.; Izawa, K.; Ikariya, T. *Tetrahedron* **2004**, 60, 7411–7417; (e) Hamada, T.; Torii, T.; Onishi, T.; Izawa, K.; Ikariya, T. *J. Org. Chem.* **2004**, 69, 7391–7394; (f) Thorpe, T.; Blacker, J.; Brown, S. M.; Bubert, C.; Crosby, J.; Fitzjohn, S.; Muxworthy, J. P.; William, J. M. *J. Tetrahedron Lett.* **2001**, 42, 4041–4143; (g) Sterk, D.; Stephan, M. S.; Mohar, B. *Tetrahedron: Asymmetry* **2002**, 13, 2605–2608; (h) Wu, X.; Vinci, D.; Ikariya, T.; Xiao, J. *Chem. Commun.* **2005**, 4447–4449.
- Johnson, T. C.; Totty, W. G.; Wills, M. *Org. Lett.* **2012**, 14, 5230–5233.
- (a) Timmis, F.; Adolfsson, H. *Org. Biomol. Chem.* **2010**, 8, 4536–4539; (b) Cambreiro, X. C.; Pericas, M. A. *Adv. Synth. Catal.* **2011**, 353, 113–124.
- Botteghi, C.; Chelucci, G.; Chessa, G.; Delogu, G.; Gladiali, S.; Soccolini, F. *J. Organomet. Chem.* **1986**, 304, 217–225.
- Gladiali, S.; Pinna, L.; Delogu, G.; De-Martin, S.; Zassinovich, G.; Mestroni, G. *Tetrahedron: Asymmetry* **1990**, 1, 635–648.
- Zassinovich, G.; Bettella, R.; Mestroni, G.; Bresciani-Pahor, N.; Geremia, S.; Randaccio, L. *J. Organomet. Chem.* **1989**, 370, 187–202.
- Jiang, Q.; Van Plew, D.; Murtuza, S.; Zhang, X. *Tetrahedron Lett.* **1996**, 37, 797–800.
- Brunner, H.; HenningWeber, F.; Weber, M. *Tetrahedron: Asymmetry* **2002**, 13, 37–42.
- (a) Ye, W.; Zhao, M.; Yu, A. *Chem. Eur. J.* **2012**, 18, 10843–10846; (b) Du, W.; Wang, L.; Wu, P.; Yu, Z. *Chem. Eur. J.* **2012**, 18, 11550–11554; (c) Zeng, F.; Yu, Z. *Organometallics* **2008**, 27, 2898–2901; (d) Ye, W.; Zhao, M.; Du, W.; Jiang, Q.; Wu, K.; Wu, P.; Yu, Z. *Chem. Eur. J.* **2011**, 17, 4737–4741.
- (a) Baratta, W.; Chelucci, G.; Magnolia, S.; Siega, K.; Rigo, P. *Chem. Eur. J.* **2009**, 15, 726–732; Baratta, W.; Benedetti, F.; Del Zotto, A.; Lidia, L.; Fulvia Felluga, F.; Magnolia, S.; Putignano, E.; Rigo, P. *Organometallics* **2010**, 29, 3563–3570; (c) Baratta, W.; Ballico, M.; Chelucci, G.; Siega, K.; Rigo, P. *Angew. Chem., Int. Ed.* **2008**, 47, 4362–4365; (d) Baratta, W.; Chelucci, G.; Gladiali, S.; Siega, K.; Toniutti, M.; Zanette, M.; Zangrando, E.; Rigo, P. *Angew. Chem., Int. Ed.* **2005**, 44, 6214–6219; (e) Putignano, E.; Bossi, G.; Rigo, P.; Baratta, W. *Organometallics* **2012**, 31, 1133–1142; (f) Baratta, W.; Ballico, M.; del Zotto, A.; Herdweck, E.; Magnolia, S.; Peloso, R.; Siega, K.; Toniutti, M.; Zangrando, E.; Rigo, P. *Organometallics* **2009**, 28, 4421–4430.
- (a) Langer, R.; Leitus, G.; Ben-David, Y.; Milstein, D. *Angew. Chem., Int. Ed.* **2011**, 50, 2120–2124; (b) Montag, M.; Zhang, J.; Milstein, D. *J. Am. Chem. Soc.* **2012**, 134, 10325–10328; (c) Gnanaprakasam, B.; Zhang, J.; Milstein, D. *Angew. Chem., Int. Ed.* **2010**, 49, 1468–1471; (d) Kohl, S. W.; Weiner, L.; Schwartzburd, L.; Konstantinovski, L.; Shimon, L. J. W.; Ben-David, Y.; Iron, M. A.; Milstein, D.; Kohl, S. W. *Nature* **2009**, 324, 74–77.
- Kwong, H.-L.; Yeung, H.-L.; Yeung, C.-T.; Lee, W.-S.; Lee, C.-S.; Wong, W.-L. *Coord. Chem. Rev.* **2007**, 251, 2188–2222.
- (a) Prakash, O.; Singh, P.; Mukherjee, G.; Singh, A. K. *Organometallics* **2012**, 31, 3379–3388; (b) Nieto, I.; Livings, M. S.; Sacchi, J. B., III; Reuther, L. E.; Zeller, M.; Papish, E. T. *Organometallics* **2011**, 30, 6339–6342; (c) Spasyuk, D.; Gusev, D. G. *Organometallics* **2012**, 31, 5239–5242.
- Cortez, N. A.; Flores-López, C. Z.; Rodríguez-Apodaca, R.; Flores-López, L. Z.; Parra-Hake, M.; Somanathan, R. *ARKIVOC* **2005**, vi, 162–171.
- Ahlford, K.; Livendahl, M.; Adolfsson, H. *Tetrahedron Lett.* **2009**, 50, 6321–6324.
- (a) Bisai, A.; Prasad, B.; Singh, V. *ARKIVOC* **2007**, v, 20–37; (b) Trost, B. M.; Zhang, Y. *Chem. Eur. J.* **2011**, 17, 2916–2922.
- Liu, B.; Zhong, Y.; Li, X. *Chirality* **2009**, 21, 595–599.
- Mei, W.; Wang, S.; Chungu, X.; Wei, S. *Chin. J. Chem.* **2010**, 28, 1424–1428.
- Compound 11 CCDC 929339;  $\text{C}_{27}\text{H}_{27}\text{N}_3\text{O}_2\text{S}$ ,  $M = 457.58$ , monoclinic, space group  $P2(1)2(1)2(1)$ ,  $a = 11.9961(2)$ ,  $b = 18.3565(3)$ ,  $c = 22.6663(3)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$ ,  $U = 4991.26(13)$  Å<sup>3</sup> (by least squares refinement on 14229 reflection positions),  $T = 150(2)$  K,  $\lambda = 0.71073$  Å,  $Z = 8$ ,  $D(\text{cal}) = 1.218$  Mg/m<sup>3</sup>,  $F(000) = 1936$ ,  $\mu(\text{MoK}\alpha) = 0.158$  mm<sup>−1</sup>. Crystal character: colourless block. Crystal dimensions  $0.45 \times 0.45 \times 0.40$  mm.
- Lee, D. W.; Ha, H. *Synth. Commun.* **2007**, 37, 737–742.