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# Synthesis of aminomethyl quinazoline based ruthenium (II) complex and its application in asymmetric transfer hydrogenation under mild conditions

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# 1. Introduction

The enantioselective hydrogenation of ketones is crucial for synthesis of chiral secondary alcohols which are important motifs in the preparation of the pharmaceuticals and fine chemicals. As a result, tremendous efforts in recent years have been centered around identifying better catalytic systems with transition metal complexes for asymmetric transfer hydrogenation (ATH) reactions [1–6]. Among the various transition metals, Rh [7–9], Ir [10,11], Os [12–14] and Ru [15–21] have attracted the most attention. Novori and co-workers, in particular, have pioneered the use of Ru-NH catalyst systems for accelerating reaction rate and efficiency [22]. Since this seminal contribution, considerable effort has been dedicated to the design of more efficient catalysts which contain NH functionality [23,24]. Due to their phenomenal rigidity in coordination chemistry, N-heterocyclic framework compounds have been frequently applied as ligands. The Yu group has previously reported the highly stereoselective ATH reaction of ketones using pyridyl NNN-type coordinated ruthenium catalysts 1 [25]. Similarly,

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# ABSTRACT

The new chiral aminomethyl quinazoline (amq) type ligand derived from L-phenylalanine was synthesized and coordinated with [RuCl<sub>2</sub>(PPh<sub>3</sub>)dppb] to obtain ruthenium(II) complex. This catalyst displayed considerable reactivity (up to 97% ee and 99% conversion) in the asymmetric transfer hydrogenation of ketones using 2-propanol as a hydrogen source in the presence of NaO<sup>i</sup>Pr.

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excellent selectivities and reactivities for the asymmetric reduction of ketones have been attained through ruthenium complexes containing amino pyridyl (ampy) **2** donor groups by Baratta and coworkers [13,26,27]. Furthermore, our own research group has previously developed quinazoline based ruthenium complexes **6a** for transfer hydrogenation of acetophenone derivatives, obtaining excellent conversions (up to 99%) and high TOF values (up to 118800 h<sup>-1</sup>) [28]. More recently, we have also reported ATH reaction of ketones using ruthenium complexes **6b-d** based on the chiral quinazolines **3b-d** which were synthesized from optically pure amino acids, which resulted in very good enantioselectivities and conversions (Scheme 1) [29]. In the light of these results, we reported the preparation of new ruthenium catalytic system bearing another chiral quinazoline ligand **3e** derived from Lphenylalanine and tested as a catalyst in ATH reaction of ketones.

## 2. Results and discussion

As the chiral center  $\alpha$  to the 2 position of quinazoline ring can be modified [30–35] quickly by employing readily available optically pure amino acids under basic conditions, quinazoline structure **3be** was chosen as an ideal modular chiral ligand scaffold. We synthesized chiral chloroquinazoline **4e** according to our reported







Scheme 1. N-Heterocyclic chiral ligands for Ruthenium (II) complexes.

procedure with very good yield by choosing L-phenylalanine as a precursor [33]. The target optically pure amino methyl quinazoline type ligand (amq) **3e** was then achieved in a two-step reaction sequence involving first cross-coupling reaction of phenyl boronic acid and subsequent deprotection of the Boc group with TFA (Scheme 2).

Finally, the new guinazoline-based ruthenium complex 6e was prepared by treating ligand **3e** with RuCl<sub>2</sub>(PPh<sub>3</sub>)dppb in the presence of Et<sub>3</sub>N and <sup>i</sup>PrOH as a solvent at reflux for 3 h (Scheme 3). As described in our previous report [28], the amino quinazoline based ruthenium (II) complex can generate two isomeric forms 6a1-6a11 coordinating metal with ligand due to the position of nitrogen atoms on the guinazoline ring. It was found that the major complex **6a**<sup>1</sup> was energetically more stable than the minor complex **6a**<sup>11</sup> in accordance with the density functional theory (DFT) calculations. Furthermore, we obtained complex **6b<sup>1</sup>** as a single isomer for X-ray diffraction analysis. These results indicated that the possibility of complex formation  $6a^{1}-d^{1}$  which coordinated with N atom at 1position of quinazoline ring was higher than complex **6a<sup>n</sup>-d<sup>n</sup>** at 3 position of guinazoline ring [29]. Similarly, in this study, the new ruthenium complex 6e was acquired as a mixture of two isomers **6e<sup>1</sup>-6e<sup>11</sup>** in a ratio of 6.5:1 characterized by <sup>1</sup>H and <sup>31</sup>P NMR analyses. In spite of several attempts to provide recrystallization, major complex **6e<sup>1</sup>** could not be obtained as a single isomer. Consequently, in later attempts to investigate its catalytic activity, complex 6e was used as a mixture in ATH reactions.

Initial tests were carried out in refluxing <sup>i</sup>PrOH with acetophenone was chosen as a substrate. In our recently published report [29], we disclosed two different methods for these reactions differing in the reagent addition sequence and initial reaction temperature. According to the first method, the complex and base were added to the solution of acetophenone, heated to reflux temperature in <sup>i</sup>PrOH. Although this method resulted in good conversions, no significant enantiomeric excess could be observed. In contrast, when all of the reagents were added simultaneously at room temperature and then rapidly heated to reflux, good enantioselection was achieved although with diminished rates of conversion.

In order to determine efficient reaction parameters such as base, temperature, and substrate-catalyst ratio, a series of reactions were conducted according to the second method. The best enantiomeric excess and conversion were acquired via use of 1/500 substrate-complex ratio in the presence of NaO<sup>i</sup>Pr as a base. While 79% ee

could be obtained in good conversion in under 2 min, prolonged reaction times caused the ee to diminish. These results suggested that racemication might be responsible. Reducing the reaction temperature to 50 °C increased enantioselectivity (85% ee), however longer reaction times were required for good conversion. The similar results were obtained when the reaction was conducted at ambient temperature (92% conv., 85% ee). On the other hand complexes **6b-d** which are bearing Me, <sup>*i*</sup>Pr and <sup>*t*</sup>Bu groups on the chiral center, exhibited very low reactivity at room temperature (less than 10% conv.). These results showed that the benzyl group on the chiral center influenced the catalytic efficiency positively.

With suitable conditions in hand (1/500 substrate-complex ratio, 0.4 mL 1 M NaO<sup>i</sup>Pr, in 10 mL <sup>i</sup>PrOH at room temperature), a series of aromatic and aliphatic ketones were explored in ATH reaction and the results are shown in Table 1. In general, high conversions and enantioselectivities ranging between 82 and 94% were observed in reduction of acetophenone derivatives (entries 1-12) again indicative of a potential  $\pi$ -stacking interaction between the catalyst and substrate. Acetophenones bearing methyl and bromine in all positions of the phenyl ring showed almost the same reactivities (entries 2-4 and 8-10). While obtaining 94% ee for omethoxy substituted acetophenone, *m*- and *p*-substituted ones gave moderate ee values (entries 5–7). Chloroacetophenones furnished relatively better enantioinduction when compared with bromine counterparts (entries 11 and 12). Also, the modest ees and conversions were gained from reduction of  $\alpha$ - and  $\beta$ -acetyl naphthalenes (entries 13 and 14). But, when methyl group was displaced with ethyl or isopropyl in acetophenone, the enantioselectivity diminished significantly (entries 15 and 16). The similar ees were detected as a result of reduction of the tetralone at reflux temperature (entry 17). As a result of using heteroaryl ketones as substrates, 2-acetylpyridine gave the desired product in excellent ee and conversion (entry 18). On the contrary, 2-acetylthiophene and 2-acetylfuran were successively converted to the related alcohols with acceptable results (entries 19 and 20). But, the catalyst showed low reactivity in the reduction of aliphatic ketones at room temperature (entries 21 and 22). However, when the reactions were conducted under reflux conditions, very good conversions were detected with lower ee (entries 22 and 23). Similarly, ATH reaction of diaromatic ketones did not give a significant conversions at room temperature, but also great conversions were succeeded with poor ee at reflux as well (entries 24-26).

These results indicated that acetophenone derivatives showed



Scheme 2. Synthesis of amino methyl quinazoline 3e.



Scheme 3. Preparation of Ruthenium (II) complexes 6a-e.

able 1	
symmetric transfer hydrogenation of ketones catalyzed by complex <b>6e</b> .	

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$\mathbb{R}^{1} \xrightarrow{\text{OH}} \mathbb{R}^{2} \xrightarrow{\text{NaO'Pr}, \mathbf{6e}} \mathbb{R}^{1} \xrightarrow{\text{OH}} \mathbb{R}^{2} \xrightarrow{\text{OH}} \mathbb{R}^{1} \xrightarrow{\text{OH}} \mathbb{R}^{2} \xrightarrow{\text{OH}} \mathbb{R}^{1} \xrightarrow{\text{OH}} \mathbb{R}^{2} \xrightarrow{\text{OH}} \mathbb{R}^{1} \xrightarrow{\text{OH}}$												
Entry	Ketone	Time	Conv. % <sup>a</sup>	ee % <sup>b</sup>	Config. <sup>c</sup>	Entry	Ketone	Time	Conv. % <sup>a</sup>	ee % <sup>b</sup>	Config. <sup>c</sup>	
1		1 h	92	85	R [36]	14		2 h	95	83 <sup>b</sup>	R [36]	
2		24 h	70	87	R [36]	15		0.2 h	97	65	R [36]	
3	Me 0	1.5 h	90	86	R [36]	16		5 h <sup>d</sup>	64	63	R [36]	
4		1.5 h	85	85	R [36]	17	XXX C	2 h <sup>d</sup>	80	54	R [37]	
5	Me	3 h	95	94	R [36]	18		2 h	96	97	R [38]	
6	MoMe 0	1 h	93	84	R [36]	19	XXXVO	1 h	78	70	R [39]	
7		1 h	65	82	R [36]	20		0.5 h	81	70	R [38]	
8	MeOT	1 h	95	85	R [40]	21	L's j	4 h	70	20	nd	
9	K → Br	1 h	96	85	R [41]	22	Ϋ́Ύ`	0.5 h <sup>d</sup>	37	27	nd	
	Ý o						~ ``		96	3		
10	Br	1 h	97	85	R [41]	23		6 h <sup>d</sup>	96	6	R [36]	
11	Br C	0.5 h	83	89	R [36]	24		0.15 h <sup>d,e</sup>	93	14	R [42]	
12		1 h	96	89	R [36]	25	Me	0.15 h <sup>d,e</sup>	95	15	R [43]	
13	pr K	3 h	85	77	R [36]	26		0.15 h <sup>d,e</sup>	99	5	nd	

<sup>a</sup> Determined by GC.

<sup>b</sup> Determined by GC or HPLC (see supplementary content).

<sup>c</sup> The absolute configurations of adducts were assigned in accordance with literature.

<sup>d</sup> Under reflux temperature.

<sup>e</sup> 1.2 mL NaO<sup>i</sup>Pr was used.

considerably higher catalytic activity when compared to the diaromatic and dialiphatic ketones. We assumed that the increase in the enantioselectivity of catalyst stemmed from the interaction between phenyl ring of benzyl group on the complex **6e** and aryl group on the ketones. Probably, the lack of aromatic structure on the aliphatic ketones did not allow for the interaction with benzyl group on complex **6e**. Nevertheless, the competitive reaction proceeded due to the presence of two aromatic structures on diaryl ketone. Unfortunately, a good selectivity could not be obtained from these substrates further suggesting that arene coordination is important for stereoinduction as differentiation between two nearly identical aryl substituents gives minimal enantioselectivity. In the light of these results, a possible transition state structure was proposed (Fig. 1).



Fig. 1. Proposed mechanism and transition state geometry for ATH reaction of ketones.

# 3. Conclusion

In conclusion, ruthenium (II) complex **6e** was obtained from the reaction [RuCl<sub>2</sub>(PPh<sub>3</sub>)dppb] with optically pure amino methyl 4phenyl quinazoline **3e** synthesized in a few steps starting from Lphenylalanine, and the catalytic performance of the complex 6e was tested in ATH reaction of the ketones. In general, the alkyl-(hetero)aryl ketones were converted to the related secondary alcohols with good enantioselectivities and conversions. Unfortunately, poor selectivities were obtained for the reduction of dialiphatic and diaromatic ketones. In this study, we investigated the efficiency of different groups on the chiral center by comparing the selectivity with our previous report. Interestingly, while previous reactions gave less than 10% conversion after 24 h at room temperature in the presence of **6b-d** catalysts, considerable reactivity was accomplished when the new catalyst 6e containing benzyl group in the chiral center was employed. While Ru-NH moiety is known to have a positive effect on the catalytic activity [22,44-46], we believe that the quinazoline ring makes an additional contribution to the reactivity as well. Moving forward, these ligands are exciting because the chiral environment of quinazoline structure can be easily modified by employing the range of commercially available optically pure  $\alpha$ -amino acids [30–32]. To explore these effects in the ATH reaction, further modifications are ongoing modifying the substituents on the 4-position of quinazoline with more electron-donating and electron-withdrawing groups.

## 4. Experimental

### 4.1. General remarks

Reagents and solvents were purchased from chemical suppliers and purified to match the reported physical and spectroscopic data. The solvents were carefully dried using standard methods. Melting points were determined with an Electro thermal IA9100 apparatus. IR spectra were obtained on KBr pellets with a Perkin Elmer apparatus. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker (300 MHz, 400 MHz and 600 MHz) spectrometers in CDCl<sub>3</sub>. The conversions and enantioselectivity ratios were determined by GC analysis with YL6500 Instrument and by HPLC analysis with Hitachi 7000 series. All column chromatography was performed on silica gel (230-400mesh).

## 4.1.1. Synthesis of t-butyl (S)-(2-phenyl-1-(4-phenylquinazolin-2yl)ethyl)carbamate 5e

t-butyl (S)-(1-(4-chloroquinazolin-2-yl)-2-phenylethyl)carbamate 4e (5.1 g, 13,28 mmol), phenylboronic acid (2.73 g, 22.39 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (307 mg, 026 mmol) and Na<sub>2</sub>CO<sub>3</sub> (29 mL, 1 M in water) were dissolved in dimethoxyethane (45 mL) and ethanol (45 mL) and the resulting mixture was then refluxed for 4 h. The solution was cooled to ambient temperature, after the addition of water (100 mL), the organic material was extracted with ethyl acetate (3  $\times$  100 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, hexane/ EtOAc, 6:1) to give t-butyl (S)-(2-phenyl-1-(4-phenylquinazolin-2yl)ethyl)carbamate **5e** as a colourless oil (4.64 g, 82%).  $[a]_D^{20} - 45 (c = 1.6 \text{ CHCl}_3);$  ee: 99.9%; retention time 9.7 min, Chiralcel OD-H, 95:5 *n*-hexane-<sup>*i*</sup>PrOH, flow rate of 0.5 mL/min, 254 nm; IR (KBr, cm<sup>-1</sup>) 3423, 2925, 2856, 1710, 1610, 1557, 1492, 1385, 1248, 1168, 1054, 1025, 774, 700; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  8.02 (1H, d, J = 8.2 Hz), 7.96 (1H, d, J = 8.0 Hz), 7.80 (1H, t, J = 7.3 Hz), 7.63(2H, dd, J = 6.5, 2.8 Hz), 7.56–7.46 (4H, m), 7.07 (4H, bs), 6.92 (1H, bs), 5.91 (1H, d, J = 6.7 Hz), 5.38 (1H, d, J = 6.7 CHCH<sub>2</sub>PhHz), 3.41 (1H, dd, J = 13.4, 5.9 Hz,  $CH_2Ph$ ), 3.29 (1H, dd, J = 13.4, 5.9 Hz, CH<sub>2</sub>Ph), 1.38 (9H, s); <sup>13</sup>C NMR (151 MHz, DMSO, ppm)) δ 168.4, 165.9, 156.0, 151.1, 138.9, 137.1, 134.8, 130.6, 130.4, 129.7, 129.0, 128.6, 128.5, 128.3, 127.2, 126.6, 121.4, 78.4, 59.1, 28.6, 28.2; HRMS (ESI) *m*/*z* calc. for C<sub>27</sub>H<sub>28</sub>N<sub>3</sub>O<sub>2</sub> [M+H] 426,2182, found 426.2179.

## 4.1.2. Synthesis of (S)-2-phenyl-1-(4-phenylquinazolin-2-yl)ethan-1-amine 3e

t-butyl (S)-(2-phenyl-1-(4-phenylquinazolin-2-yl)ethyl)carbamate 5e (3.98 g, 9.35 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) and triflouroacetic acid (10.64 g, 93.35 mmol) was added slowly at 0 °C. After stirring 24 h at room temperature, the reaction was quenched with saturated NaHCO<sub>3</sub> (100 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub>  $(2 \times 100 \text{ mL})$ . The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>/methanol, 12:1) to give (S)-2-phenyl-1-(4-phenylquinazolin-2-yl)ethan-1amine **3e** as a colourless oil (2.99 g, 98%).  $[a]_{D}^{20} + 20 (c = 0.7, c)$ EtOH); ee: 99%; retention time 6.3 min, Chiralcel AD-H, 90:10 nhexane-<sup>*i*</sup>PrOH, flow rate of 1 mL/min, 254 nm; IR (KBr, cm<sup>-1</sup>) 3455, 3009, 2970, 1738, 1435, 1365; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  8.00 (2H, t, J = 9.2 Hz), 7.80 (1H, ddd, J = 8.4, 6.9, 1.1 Hz), 7.70–7.66 (2H, m), 7.51-7.46 (4H, m), 7.21-7.16 (4H, m), 7.14-7.10 (1H, m), 4.54 (1H, dd, *J* = 8.8, 5.0 Hz, CHCH<sub>2</sub>Ph), 3.41 (1H, dd, *J* = 13.6, 5.0 Hz, CHCH<sub>2</sub>Ph), 2.99 (1H, dd, J = 13.6, 8.8 Hz, CHCH<sub>2</sub>Ph), 2.51 (2H, bs, NH<sub>2</sub>); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  166.6, 165.5, 149.3, 136.8, 135.4, 131.7, 128.1, 128.0, 127.6, 126.7, 126.6, 126.4, 125.2, 125.1, 124.4, 119.7, 57.4, 42.1; HRMS (ESI) *m*/*z* calc. for C<sub>22</sub>H<sub>20</sub>N<sub>3</sub> [M+H] 326.1656,

#### found 326.1657.

#### 4.1.3. Preparation of ruthenium complex 6e

Ru(PPh<sub>3</sub>)dppbCl<sub>2</sub> (1.1 g, 1.27 mmol) was suspended in <sup>i</sup>PrOH (6 mL) and (S)-2-phenyl-1-(4-phenylquinazolin-2-yl)ethan-1amine **3e** (0.5 g, 1.5 mmol) and Et<sub>3</sub>N (1.3 g, 12.9 mmol) were added. The resulting mixture was then refluxed for 6 h at nitrogen atmosphere. The precipitate was filtered and washed petroleum ether (20 mL) and diethyl ether (2  $\times$  20 mL). The ruthenium complex **6e** was obtained as an orange solid (0.78 g, 67%). mp: 224-226 °C; IR (KBr, cm-1) 3457, 3027, 2970, 1738, 1564, 1526, 1431, 1365, 696, 515, 505.; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  10.50 (d, J = 8.7 Hz, 1H), 8.41 (t, J = 8.6 Hz, 2H), 8.03 (t, J = 7.6 Hz, 1H), 7.87–6.87 (m, 30H), 6.76 (d, I = 7.0 Hz, 2H), 6.45 (t, I = 6.8 Hz, 2H), 4.21 (t, I = 13.3 Hz, 1H), 4.11-3.82 (m, 3H), 3.69 (t, I = 11.9 Hz, 1H), 2.90 (d, I = 13.2 Hz, 1H), 2.76–2.25 (m, 3H), 2.14–1.78 (m, 2H); <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>)  $\delta$  54.40 (d, I = 39.2 Hz), 52.68 (d, I = 39.2 Hz), 41.54 (d, I = 39.0 Hz), 39.89 (d, J = 39.0 Hz); HRMS (ESI) m/z calc. for  $C_{52}H_{50}CIN_4P_2Ru$ [M-Cl + CH<sub>3</sub>CN] 929.2243, found 929.2248; Anal. calc. for C<sub>50</sub>H<sub>47</sub>Cl<sub>2</sub>N<sub>3</sub>P<sub>2</sub>Ru (%): C, 65.00; H, 5.13; Cl, 7.67; N, 4.55; found: C, 64.29, H, 5.23, N, 4.35.

## 4.1.4. General procedure for the asymmetric transfer hydrogenation reaction

Ruthenium complex (3.7 mg, 0.004 mmol), ketone (2 mmol) and NaO<sup>1</sup>Pr (0.4 mL, 0.1 M) were dissolved in degassed <sup>1</sup>PrOH (10 mL) and the mixture was stirred under nitrogen atmosphere at appropriate temperature. A small volume of sample was taken from reaction mixture and diluted with diethyl ether (1:1), and rapidly filtered using a short silica pad. The conversion and enantiomeric excess were determined by GC using Agilent HP-Chiral 20B column (30 m, 0.25 mm, 0.25  $\mu m)$  and by HPLC using Supelco AD-H, OD-H chiral columns.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.jorganchem.2016.07.001.

#### References

- [1] D. Wang, D. Astruc, Chem. Rev. 115 (2015) 6621–6686.
- [2] R. Noyori, T. Ohkuma, Angew. Chem. Int. Ed. 40 (2001) 40-73.
- [3] W.P. Liu, M.L. Yuan, X.H. Yang, K. Li, J.H. Xie, Q.L. Zhou, Chem. Commun. 51 (2015) 6123-6125.
- J. Canivet, G. Suss-Fink, Green Chem. 9 (2007) 391-397.
- X. Xu, R. Wang, J.W. Wan, X.B. Ma, J.D. Peng, Rsc. Adv. 3 (2013) 6747–6751.
- [6] P.N. Liu, J.G. Deng, Y.Q. Tu, S.H. Wang, Chem. Commun. (2004) 2070–2071.
   [7] S. Kang, J. Han, E.S. Lee, E.B. Choi, H.K. Lee, Org. Lett. 12 (2010) 4184–4187. [8] P.G. Echeverria, C. Ferard, P. Phansavath, V. Ratovelomanana-Vidal, Catal.
- Commun. 62 (2015) 95-99.
- [9] J.H. Li, Y.F. Tang, Q.W. Wang, X.F. Li, L.F. Cun, X.M. Zhang, J. Zhu, L.C. Li, J.G. Deng, J. Am. Chem. Soc. 134 (2012) 18522-18525.
- [10] H. Vazquez-Villa, S. Reber, M.A. Ariger, E.M. Carreira, Angew. Chem. Int. Ed. 50 (2011) 8979-8981.
- [11] H. Chiyojima, S. Sakaguchi, Tetrahedron Lett. 52 (2011) 6788-6791.
- [12] E. Vega, E. Lastra, M.P. Gamasa, Inorg. Chem. 52 (2013) 6193-6198.
- [13] W. Baratta, M. Bosco, G. Chelucci, A. Del Zotto, K. Siega, M. Toniutti, E. Zangrando, P. Rigo, Organometallics 25 (2006) 4611-4620.
- [14] D. Carmona, F.J. Lahoz, P. Garcia-Orduna, L.A. Oro, M.P. Lamata, F. Viguri, Organometallics 31 (2012) 3333-3345.
- T. Touge, T. Hakamata, H. Nara, T. Kobayashi, N. Sayo, T. Saito, Y. Kayaki, [15] T. Ikariya, J. Am. Chem. Soc. 133 (2011) 14960-14963.

- [16] F.K. Cheung, A.M. Hayes, J. Hannedouche, A.S.Y. Yim, M. Wills, J. Org. Chem. 70 (2005) 3188-3197.
- [17] T. Ohkuma, N. Utsumi, K. Tsutsumi, K. Murata, C. Sandoval, R. Noyori, J. Am. Chem. Soc. 128 (2006) 8724-8725.
- [18] B. Yigit, M. Yigit, I. Ozdemir, E. Cetinkaya, Transit. Metal. Chem. 37 (2012) 297–302.
- [19] O. Dayan, B. Cetinkaya, J. Mol. Catal. A Chem. 271 (2007) 134–141.
- [20] L. Gok, H. Turkmen, Tetrahedron 69 (2013) 10669–10674.
- [21] S. Yasar, S. Cekirdek, N. Akkus Tas, S. Yildirim, I. Ozdemir, Turk. J. Chem. 37 (2013) 292-298.
- [22] M. Yamakawa, I. Yamada, R. Noyori, Angew. Chem. Int. Ed. 40 (2001) 2818-2821.
- [23] B.G. Zhao, Z.B. Han, K.L. Ding, Angew. Chem. Int. Ed. 52 (2013) 4744–4788.
- [24] B. Zhang, H. Wang, G.Q. Lin, M.H. Xu, Eur. J. Org. Chem. (2011) 4205-4211.
- [25] W.J. Ye, M. Zhao, Z.K. Yu, Chem-Eur, J. 18 (2012) 10843–10846.
   [26] W. Baratta, E. Herdtweck, K. Siega, M. Toniutti, P. Rigo, Organometallics 24 (2005) 1660-1669
- [27] G. Chelucci, S. Baldino, R. Solinas, W. Baratta, Tetrahedron Lett. 46 (2005) 5555-5558
- [28] S. Karabuga, S. Bars, I. Karakaya, S. Gumus, Tetrahedron Lett. 56 (2015) 101 - 104
- [29] C. Kucukturkmen, A. Agac, A. Eren, I. Karakaya, M. Aslantas, O. Celik, S. Ulukanli, S. Karabuga, Catal. Commun. 74 (2016) 122–125.
- [30] I. Karakaya, S. Karabuga, R. Altundas, S. Ulukanli, Tetrahedron 70 (2014) 8385-8388
- [31] M. Cakici, M. Catir, S. Karabuga, H. Kilic, S. Ulukanli, M. Gulluce, F. Orhan,

- Tetrahedron-Asymmetry 21 (2010) 2027-2031.
- [32] M. Cakici, M. Catir, S. Karabuga, S. Ulukanli, H. Kilic, Tetrahedron-Asymmetry 22 (2011) 300-308.
- [33] M. Catir, M. Cakici, S. Karabuga, S. Ulukanli, E. Sahin, H. Kilic, Tetrahedron-Asymmetry 20 (2009) 2845–2853.
- [34] T. Fekner, H. Muller-Bunz, P.J. Guiry, Org. Lett. 8 (2006) 5109-5112.
- [35] U.A. Kshirsagar, N.P. Argade, Org. Lett. 12 (2010) 3716–3719.
  [36] W. Li, G.H. Hou, C.J. Wang, Y.T. Jiang, X.M. Zhang, Chem. Commun. 46 (2010) 3979-3981.
- [37] H.M. Huang, T. Okuno, K. Tsuda, M. Yoshimura, M. Kitamura, J. Am. Chem. Soc. 128 (2006) 8716-8717.
- [38] L.T. Chai, W.W. Wang, Q.R. Wang, F.G. Tao, J. Mol. Catal. A-Chem. 270 (2007) 83-88.
- [39] F.S. Bie, Y.H. Li, W.G. Cao, C.A. Sanboval, Chin. J. Chem. 27 (2009) 2309-2315. [40] C. Guyon, E. Metay, N. Duguet, M. Lemaire, Eur. J. Org. Chem. 2013 (2013)
- 5439-5444. [41] X.S. Gao, R. Liu, D.C. Zhang, M. Wu, T.Y. Cheng, G.H. Liu, Chem-Eur. J. 20 (2014)
- 1515-1519. [42] K.H. Wu, H.M. Gau, J. Am. Chem. Soc. 128 (2006) 14808–14809.
- [43] Y. Muramatsu, S. Kanehira, M. Tanigawa, Y. Miyawaki, T. Harada, B. Chem. Soc.
- Jpn. 83 (2010) 19-32. [44] P.A. Dub, N.J. Henson, R.L. Martin, J.C. Gordon, J. Am. Chem. Soc. 136 (2014)
- 3505-3521.
- [45] W. Baratta, M. Ballico, G. Esposito, P. Rigo, Chem-Eur. J. 14 (2008) 5588-5595.
- [46] J.X. Gao, T. Ikariya, R. Noyori, Organometallics 15 (1996) 1087-1089.