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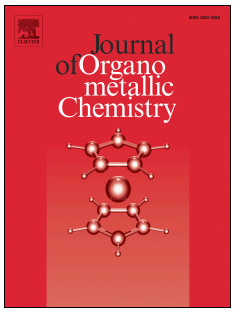

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A New Class of Well-Defined Ruthenium Catalysts for Enantioselective Transfer Hydrogenation of Various Ketones

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ABSTRACT

A pair of novel optically pure phosphinite ligands were synthesized by ring opening reaction of chiral amines with (*R*)-styrene oxide or (*S*)-glycidyl phenyl ether oxide using a straightforward method in high yields and their ruthenium complexes were described in detail. The ruthenium complexes proved to be highly efficient catalysts for the enenatioselective hydrogenation of ketones, affording products up to 99% ee. The results showed that the corresponding chiral alcohols could be obtained with high activity and excellent enantioselectivities at the desired temperature. (2*S*)-1-{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino}-3-phenoxypropan-2-yl diphenylphosphinito[dichloro(η^6-benzene)ruthenium (II)] acts an excellent catalyst in the reduction of ketones, giving the corresponding alcohol up to 99% ee.

Keywords: Asymmetric Transfer Hydrogenation; Chiral Ruthenium Complexes; Phosphinites; Epoxide Ring opening; Homogeneous Catalysis.

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1. INTRODUCTION

An increasing number of chiral compounds and enantiomerically pure drugs are prepared through transition metal-catalyzed asymmetric reactions [1]. Since the reactivity and stereoselectivity of an asymmetric transformation are highly dependent on the structure of the chiral ligand coordinated to the transition metal, the design and synthesis of efficient chiral ligands are important in this area and have attracted a great deal of attention both from academia and industry [2]. For many years, a large number of chiral monodendate and bidendate phosphorus containing ligands (P,P') were widely studied [3,4]. Among the recently developed transition-metal-based chiral reduction catalysts, the C_2-symmetric ferrocenyl phosphines were notably reported [5,6,7,8]. Because of its great success in catalytic asymmetric reactions [9], chiral ferrocenyl-phosphine ligands have attracted considerable attention in recent years [10,11]. These ligands are very efficient for a wide range of reactions, such as hydrogenation [12], hydrosilylation [13], allylic alkylation [14], palladium catalyzed cross-coupling reactions [15,16,17] and cyclopropanation [18]. Although ferrocenyl phosphine ligands have found widespread applications in transition metal catalyzed asymmetric transfer hydrogenation [19,20,21], the analogous phosphinites have scarcely been reported, which have different chemical, electronic and structural advantages in comparison with phosphines. For instance, the metal-phosphorus bond is often stronger in phosphinites compared to the related phosphine due to the presence of electron-withdrawing P-OR group. In addition, the empty σ*-orbital of the phosphinite $P(OR)R_2$ is stabilized, making the phosphinite a better acceptor [22]. The most important advantage of chiral phosphinite ligands over the corresponding *P*-based ligands is their facile preparation, which leads to a substantial interest to design highly effective chiral phosphinite ligands for asymmetric catalysis [23,24,25].

Catalytic asymmetric transfer hydrogenation (ATH) of ketones has recently emerged as a viable means of synthesizing chiral alcohols [26]. Due to operational simplicity, the easy availability of reductants, and the high enantioselectivity, the catalytic enantioselective reduction of ketones has been extensively studied during the last decades [27]. Particularly, asymmetric transfer hydrogenation of ketones has recently developed as an alternative method to asymmetric hydrogenation for the production of chiral alcohols [28,29,30]. Because hydrogen transfer reactions are mild techniques for reduction of ketones in which a substrate-selective catalyst transfers hydrogen between the substrate and a hydrogen donor or acceptor, respectively. Additionally, the donor (*e.g.* 2-propanol) and the acceptor (*e.g.* a ketone) are environmentally friendly and also easy to handle [31,32].

Chiral *β*-amino alcohols are useful building blocks for biologically active compounds [33] as well as important auxiliaries and ligands in asymmetric synthesis [34]. Also, amino alcohols continue to be of importance in modern synthetic chemistry, not only because of their biological properties, but also due to their wide range of synthetic applications [35]. Hence, the asymmetric synthesis of enantiomerically enriched amino alcohols has been extensively studied. Especially, amino alcohol derivative catalysts have received much attention and used in many asymmetric catalysis reactions, and they have shown powerful utilities in the asymmetric reduction of prochiral ketones [36,37]. In recent years, we have reported the synthesis and applications of a number of modified Ru(II) catalysts for ATH which contain well designed groups formed by the reaction of between the chiral ligand component and the η^6-arene ring [38,39,40,41]. We report here the synthesis of two novel phosphinite ligands and their application in the Ru(II)-catalyzed Asymmetric Transfer Hydrogenation of various ketones [42,43,44]. A comparison of the results obtained with the newly synthesized ligands and those of the corresponding Ru(II) complexes is

also discussed. The comparison concerns the structural features of ligands, four of their ruthenium complexes, and the hydrogenation results.

2. RESULTS AND DISCUSSION

2.1. Synthesis and characterization of the amino alcohols and phosphinite ligands

First of all, the precursor chiral secondary amine, *N*-benzyl-*N*-[(*S*)-1-[α-naphthylethyl]amine (**2**) was readily synthesized by the reaction of (*S*)-(-)-1-[naphthalen-1-yl-ethy]amine with benzaldehyde with procedures previously described, as shown in Scheme 1 [45,46]. It is well-known that the regioselective ring opening of epoxides by amines is an important way for the preparation of *β*-aminoalcohols [47]. Thus, two novel chiral amino alcohols, **3** and **4**, were synthesized by the ring opening reaction of *N*-benzyl-*N*-(*S*)-1-[α-naphthylethyl]amine **2** with (*R*)-styrene oxide or (*S*)-glycidyl phenyl ether, respectively (Scheme 1) [48]. The products were fully characterized by several spectroscopic methods: LC-ESI-IT-TOF MS, ^{1}H NMR, ^{13}C NMR and IR as well as elemental analysis. The assignment of the ^{1}H chemical shifts was derived from 2D HH-COSY spectra and the appropriate assignment of the ^{13}C chemical shifts from APT and 2D HMQC spectra. The results were given in experimental section with full details. Furthermore, ^{1}H NMR, ^{13}C NMR, IR and LC-ESI-IT-TOF MS spectra of amino alcohols also given in Supporting Information (SI).

Insert Scheme 1 Here

The synthetic procedure for the preparation of the phosphinite ligands [49] is shown in Scheme 1. Chiral monodendate C_1-symmetric ligands **5** and **6** were synthesized by hydrogen abstraction from the described chiral amino alcohols by Et_3N and the subsequent reaction with one equivalent of Ph_2PCl in anhydrous CH_2Cl_2 under inert argon atmosphere with the hydrolysis

reaction [50]. Typical spectra of these ligands are illustrated in supporting information (SI) and for details see experimental Section.

Insert Scheme 2 Here

It is well-known that the phosphinite ligands are mostly unstable and decompose gradually to give oxide and the hydrolysis product diphenylphosphinous acid, $Ph_2P(O)H$ [51]. Furthermore, the ^{31}P-{^{1}H} NMR spectrum displays formation of PPh_2PPh_2 and $P(O)Ph_2PPh_2$, as indicated by signals at about δ -15.4 ppm as singlet and δ 35.0 ppm and at δ -21.6 ppm as doublets with $^{1}J_{(PP)}$ 226 Hz, respectively [52]. These two compounds are very stable in ambient atmosphere up to 24 h because of the well-designed structures. The progress of preparation reactions of the ligands was conveniently monitored by ^{31}P-{^{1}H} NMR spectroscopy. The signals of the starting material PPh_2Cl at δ=81.0 ppm disappeared and new singlets appeared downfield due to the phosphinite ligands. The ^{31}P-{^{1}H} NMR spectra of the free ligands are in line with the values previously observed for similar compounds [53,54]. Typical spectra of these ligands are illustrated in Figure 1. The ^{1}H and ^{13}C NMR spectra of these ligands are also conclusive. The resonance assignments were made on the basis of ^{1}H-^{1}H COSY, NOESY, and ^{1}H-^{13}C COSY experiments. Typical spectra of these ligands are illustrated in supporting information (SI) and for details see experimental Section.

Insert Figure 1 Here

Following a similar procedure described by Sawamura, Regadec et al. [55], ruthenium(II) complexes of the phosphinite ligands, (1*R*)-2-{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino}-1-

phenylethyl diphenylphosphite, **5** and (2*S*)-1-{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino}-3-phenoxypropan-2-yldiphenyl phosphinite, **6** were readily prepared in quantitative yields by reacting the appropriate ligands with either $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ or $[Ru(\eta^6\text{-benzene})(\mu\text{-Cl})Cl]_2$ precursor as outlined in Scheme 1. The ability of dimers $\{[Ru(arene)(\mu\text{-Cl})Cl]_2\}$ to form mono- or binuclear complexes of general formula $[Ru(\eta^6\text{-arene})Cl_2L]$ is well-known [56]. For synthesis of ruthenium(II) complexes **7** and **9**, $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ was initially chosen as a starting material, which was prepared from the reaction of the commercially available α-phellandrene(5-isoprophyl-2-methylcyclohexa-1,3-diene) with $RuCl_3$ [57]. The *p*-cymene ligand is particularly informative with respect to the symmetry of the three legged fragment [58]. One of the most available arene ligands in ruthenium chemistry is *p*-cymene, whose NMR signals are very sensitive to the symmetry of organometallic compound [59]. Thus, when it is η^6-coordinated to a ML_2L' metal fragment (C*s* symmetry), the ^1H and ^{13}C NMR spectra are very different from that of η^6-coordinated to a $ML_1L_2L_3$ fragment (C_1 symmetry) [60]. In this case, the steric hindrance of amino alcohol phosphinite ligands seems to prevent free rotation of *p*-cymene ligand around the arene-Ru axis [61]. In addition, the detailed analysis of NOE interaction between *p*-cymene and other ligands can give valuable information about the relative orientation of different groups in the molecule and thus establish the stereochemistry of the complex (**for details see experimental section**). After the preparation of the second precursor $[Ru(\eta^6\text{-benzene})(\mu\text{-Cl})Cl]_2$ by the reaction cyclo-1.3-hexadiene with $RuCl_3$ in aqueous solution, we synthesized (2*S*)-1-{[(1*R*)-1-phenylethyl]amino}propan-2-yldiphenylphosphinito [dichloro(η^6-benzene) ruthenium (II)], **8** and (2*S*)-1-{[(2*S*)-2-[(diphenylphosphanyl)oxy]propyl][(1*R*)-1-phenylethyl]amino} propan-2-yldiphenylphosphinitobis[dichloro(η^6-benzene) ruthenium (II)], **10** complexes with high yields **Scheme 1**. The poor solubility of the starting benzene derivative causes a decrease in the yields of the complexes (**8** and **10**), which are more conveniently

prepared by the reaction of the phosphinites with the monomeric adduct $[RuCl_2(C_6H_6)(NCCH_3)]$ [62]. Analysis of complexes **8** and **10** by ^1H NMR exhibits multiplet signals corresponding to the aromatic rings for at 8.06-7.58 and 7.94-7.09 ppm and the C_6H_6 protons as singlets at 4.95 and 5.47 ppm, respectively. The Ru-arene complexes were isolated as indicated by singlets in their ^{31}P-{^1H} NMR spectra at approximately δ 104-111 ppm, in line with the values previously observed for similar compounds (**Figure 1**) [63,64]. ^1H NMR spectra of these compounds clearly exhibit signals corresponding to the aromatic rings. The arene resonances are well resolved, as in the previously reported for mononuclear arene complexes [59]. In the ^{13}C-{^1H} NMR spectra of complexes, $J(^{31}P\text{-}^{13}C)$ coupling constants of the carbons of the phenyl rings were observed, which are in agreement with the literature (for details see experimental Section) [65]. The structure of Ru(II)-complexes were further confirmed by IR spectroscopy as well as microanalysis, and found to be consistent to expected structures.

2.2. Catalytic transfer hydrogenation of ketones

The admirable catalytic performance and the advanced structural permutability of phosphinite based transition metal complexes prompted us to improve new Ru(II) complexes with well-shaped ligands [66,67]. We paid particular attention to arene ligands [68], because (*i*) the spectator ligands automatically occupy three adjacent coordination sites of ruthenium in an octahedral coordination environment, leaving three facial sites for other functions, (*ii*) arene ligands that are relatively weak electron donors may provide a unique reactivity on the metallic center, and (*iii*) the substitution pattern on the ring is flexible. To take account of these advantages, complexes **7-10** were tested as catalysts in transfer hydrogenation of aromatic ketones in a ^{i}PrOH solution. First of all, compounds **7-10** were used as precatalysts, ^{i}PrOH/KOH as a reducing system, and acetophenone as a model substrate.

To evaluate the efficiency of our Ru(II) complexes, we deeply investigated the optimal conditions starting with acetophenone as a standard test reaction. Results for the asymmetric transfer hydrogenation of ketones with catalysts, **7-10** are collected in Table 1. Catalytic experiments were carried out under argon using standard Schlenk-line techniques. To an ^{i}PrOH solution of each complex, appropriate amounts of acetophenone and KOH/^{i}PrOH solution were added at room temperature. The solution was stirred, and the reaction was monitored by GC. The reactions proceeded to give (*R*) or (*S*)-1-phenyl ethanol in 12-28% conversion with 72-91% *ee's* after stirring at room temperature for 96 h. An increase in the reaction time to 144 h resulted in 22-53% conversion with 65-87% *ee*'s. Due to the reversibility at room temperature, prolonging the reaction time led to a slight decrease in enantioselectivity. However, when the reactions were carried out at 82 °C, all complexes showed satisfactory catalytic activity (up to 196 TOF values) and enantioselectivity (up to 96% *ee*) since almost quantitative conversions were observed (Table 1, entries 9-12). These results clearly indicate that the reaction temperature plays an important role on the catalytic activity and enantioselectivity.

The ruthenium(II) complexes were very active catalysts, leading to quantitative conversions of (*R*) or (*S*)-1-phenyl ethanol with a catalyst/base ratio of 1:5 (Table 1, entries 13-16). A control experiment in the absence of base did not lead to significant conversion (Entries 5-8). Furthermore, replacing KOH with NaOH slightly decreased both the reaction rate and enantioselectivity (Table 1, entries 9-12[e]). Increase or decrease of the base:Cat ratio from 5:1 to 9:1 or 3:1 slightly decrease the reaction with a slight loss of enantiomeric purity of the product (Table 1, entries 13-16).

Insert Table 1 Here

From the results, it can be obviously seen that generally complex **9** and **10**, which include -CH_2OPh instead of –Ph moiety on the phosphinite skeleton showed higher catalytic activity than complexes, **7** and **8**. Furthermore, the complexes (1*R*)-2-{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino}-1-phenylethyl diphenylphosphinito[dichloro(η^6-benzene)ruthenium (II)], **8** and (2*S*)-1-{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino}-3-phenoxypropan-2-yl diphenylphosphinito [dichloro(η^6-benzene) ruthenium (II)], **10** which have benzene fragment are more active than the complexes, **7** and **9** which include more commonly used *p*-cymene fragment. The good enantioselectivity obtained for initial reduction of acetophenone led us to keep employing Ru-benzene complexes. These results clearly indicate that the skeleton of the phosphinite ligands and the fragment attached to the ruthenium center are responsible for the high conversion (up to 99 %) and enantioselectivity (up to 96 ee %), whatever the exact reaction mechanism. The best results were obtained in the (2*S*)-1-{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino}-3-phenoxypropan-2-yldiphenylphosphinito [dichloro(η^6-benzene)ruthenium (II)], **10** catalytic system with up to 96% ee and 98% conversion.

Under optimized conditions, aromatic ketones were hydrogenated with high enantioselectivity and the same mode face selection. Table 2 illustrates conversions of the reduction performed in a 0.1 M of *iso*PrOH solution containing **7**-**10** and KOH (Ketone:Cat:KOH = 100:1:5). One can easily see from the results that a range of acetophenone derivatives can be hydrogenated with high enantioselectivities. Electronic properties (the nature as well as position) of the substituents on the phenyl ring of the ketone caused the changes in the reduction rate and enantioselectivity. It is well-known that the introduction of electron withdrawing substituents to the aryl ring of the ketone decreases the electron density of the C=O bond so that the activity was improved resulting in easier hydrogenation [69,70,71]. Therefore, the introduction of electron-withdrawing substituents, such as CF_3 or NO_2, to the aryl ring of the

ketone, led to improved activity with good enantioselectivity (Table 2, entries 1-16). On the contrary, the introduction of an electron-donating group such as methyl or methoxy group decelerates the reaction with similar enantioselectivity, whatever the position of substitution (Table 2, entries 17-36). It can be seen from Table 2, *ortho*-substituted acetophenones can dramatically increase the enantioselectivity, while *meta*- and *para*- substitution to ring of the ketone caused the changes in the reduction rate and enantioselectivity. As expected, the lowest enantioselectivity was observed in transfer hydrogenation of *p*-methoxyacetophenone, whereas the highest one was found in that of *m*-methoxyacetophenone (96% ee). Overall, the chiral efficiency attains a very high level in the asymmetric reduction of aromatic ketones and compares well with the recently discovered catalyst systems [72,73].

Insert Table 2 Here

Complexes **7-10** were further investigated in transfer hydrogenation of a variety of ketones to be converted to the corresponding chiral alcohols under the optimum conditions. The reaction of methyl/alkyl or methyl/aryl ketones gave the corresponding chiral alcoholic products in an acceptable chemical yield and enantiomeric purity. Firstly, we carried out further experiments to study the influence of bulkiness of the alkyl groups on the catalytic activity and selectivity (Table 3, entries 1-16). For this aim, a variety of simple aryl/alkyl ketones were transformed to the corresponding secondary alcohols, and it was found that the activity and selectivity are extremely dependent on the steric hindrance of the alkyl group. Reaction of methyl/alkyl ketones possessing a bulky alkyl substituent proceeded rather sluggish and led a decrease in enantioselectivity. As the bulkiness of the alkyl group increases from ethyl to *sec*-butyl, the level of enantioselectivity lowers. Indeed, lower activity and enantioselectivity were obtained in case

of methyl *sec*-butyl ketone (Entries 13-16, 61-80% ee) [74,75,76,77]. Furthermore, as seen in Table 3, the best result in terms of enantioselectivity was observed with 1-naphtyl methyl ketone (up to 97% ee, entries 17-20). In that case, the highest enantioselectivity, up to 98% ee, were obtained for catalyst (2*S*)-1-{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino}-3-phenoxypropan-2-yldiphenylphosphinito[dichloro(η^6-benzene) ruthenium(II)] **(10)**. Furthermore, the hydrogenation of ketones including cyclohexyl group was very slow and the enantioselectivities were remarkable lower (Table 3, entries 25-32).

Insert Table 3 Here

3. Conclusion and Perspectives

This work presents new chiral phosphinite ligands which form highly efficient and practical catalysts with ruthenium precursor for asymmetric transfer hydrogenation of aryl/alkyl ketones. High conversion and enantioselectivity were obtained in the catalytic reaction. The high catalytic activity and enantioselectivity for this kind of ligands show great potential for further exploring similar system and achieving outstanding stereoselectivity for a wider scope of ketone substrates. Furthermore, the simplicity and efficiency clearly make it an excellent choice of catalyst for the practical preparation of highly valued alcohols via catalytic asymmetric transfer hydrogenation of ketones.

4. Materials and Methods

All manipulations were carried out under an atmosphere of argon using conventional Schlenk glassware. Solvents were dried using established procedures and distilled under argon immediately prior to use. Analytical grade and deuterated solvents were purchased from Merck. The starting materials D-glycine, D-alanine, PPh_2Cl and Et_3N are purchased from Fluka and

were used as received. [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ [78], and [Ru(η^6-benzene)(μ-Cl)Cl]$_2$ [79] were prepared according to the literature procedures. The IR spectra were recorded on a Mattson 1000 ATI UNICAM FT-IR spectrometer as KBr pellets. ^{1}H (400.1 MHz), ^{13}C NMR (100.6 MHz) and ^{31}P-{^{1}H} NMR (162.0 MHz) spectra were recorded on a Bruker AV400 spectrometer, with δ referenced to external TMS and 85% H_3PO_4 respectively. Elemental analysis was carried out on a Fisons EA 1108 CHNS-O instrument. Melting points were recorded by a Gallenkamp Model apparatus with open capillaries.

GC analyses were performed on a Shimadzu GC 2010 Plus Gas Chromatograph equipped with cyclodex B (Agilent) capillary column (30 m x 0.32 mm I.D. x 0.25 μm film thickness). The GC parameters for asymmetric transfer hydrogenation of ketones were as follows; initial temperature, 50 ºC; initial time 1.1 min; solvent delay, 4.48 min; temperature ramp 1.3 ºC/min; final temperature, 150 ºC; initial time 2.2 min; temperature ramp 2.15 ºC/min; final temperature, 250 ºC; initial time 3.3 min; final time, 44.33 min; injector port temperature, 200 ºC; detector temperature, 200 ºC, injection volume, 2.0 μL.

4.1 General procedure for the transfer hydrogenation of ketones

Typical procedure for the catalytic hydrogen-transfer reaction: a solution of the ruthenium complexes (**5-8**) (0.005 mmol), KOH (0.025 mmol) and the corresponding ketone (0.5 mmol) in degassed *iso*PrOH (5 mL) was refluxed until the reaction completed. A sample of the reaction mixture was taken off, diluted with acetone and analyzed immediately by GC, the conversions obtained are related to the residual unreacted ketone. Furthermore, ^{1}H NMR spectral data for the resultant products were consistent with previously reported results.

4.2. Synthesis and Characterization of Amino Alcohols

4.2.1. N-benzyl-N-[(S)-1-[α-naphthylethyl]amine (2)

(*S*)-(-)-1-[Naphthalen-1-yl-ethy]amine **1** (1.00 g, 5.84 mmol) was dissolved in anhydrous MeOH (5 mL) and heated to reflux. Benzaldehyde (0.62 g, 5.84 mmol) was added dropwise over a period of 2 min and the mixture was stirred at reflux temperature for 3 h. The solution was allowed to cool to room temperature and sodium borohydride (0.24 g, 6.13 mmol) was added portionwise. The mixture was stirred for further 2 h at room temperature and then heated to reflux temperature for 30 min. The reaction was then quenched by the addition of water (5 mL) and the aqueous phase extracted with DCM (3×10 mL). The separated organics were dried over $MgSO_4$ and filtered. The solution was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (n-hexane/EtOAc = 2/1), to afford product (1.01 g, 66 %) as an oil. $[\alpha]_D^{20}$ = +21.3^o (c 1, CH_2Cl_2).^{1}H NMR ($CDCI_3$, ppm): δ 8.22 (d, 1H, *J* =6.7 Hz, Ar-**H**), 7.93-7.95 (m, 1H, Ar-H), 7.82-7.84 (m, 2H, Ar-**H**), 7.54-7.59 (m, 3H, Ar-**H**), 7.30-7.39 (m, 5H, Ar-**H**), 4.76 (q, 1H, *J* = 6.6 Hz -C**H**CH_3), 3.75-3.86 (m, 2H, -C**H**$_2$Ph), 1.81 (br, 1H, -N**H**), 1.59 (d, 3H, *J* = 6.6 Hz, -C**H**$_3$); ^{13}C NMR ($CDCI_3$, ppm): δ 23.69 (-**C**H_3), 51.92 (-**C**H_2Ph), 53.06 (-**C**HCH_3), 122.94, 123.04, 125.33, 125.74, 125.79, 126.94, 127.27, 128.24, 128.42, 128.98, 131.41, 134.04, 140.67, 140.99 (Ar-**C**), assignment was based on the ^{1}H-^{13}C HETCOR and ^{1}H-^{1}H COSY spectra; IR (cm^{-1}): υ 3051, 3028 (aromatic C-H), 2964, 2925 (aliphatic C-H) cm^{-1}; Anal. Calc. for $C_{19}H_{19}N$ (261.37 g/mol): C 87.31, H 7.33, N 5.36; found C 87.19, H 7.28, N 5.29. IT-TOF MS ($[M+H]^+$): 262.15 g/mol.

4.2.2. (1R)-2-{benzyl[(1S)-1-(naphthalen-1-yl)ethyl]amino}-1-phenylethan-1-ol, (3)

(*R*)-Styrene oxide (0.51 g, 4.21 mmol) was added to the solution of *N*-benzyl-*N*-(*S*)-1-[α-naphthylethyl]amine **2** (1.00 g, 3.83 mmol) in methanol (5 ml). The solution was heated to 70^{o}C and the reaction was followed by TLC (n-hexane/EtOAc/TEA = 80/10/1). After 24 h, the reaction finished, the solvent was removed. The crude product was purified by silica-gel column chromatography (n-hexane//EtOAc / TEA = 80/10/1) to afford **3** (1.02 g, 70 %) as a white solid.

M.p = 104-106 °C. $[\alpha]_D^{20}$ = +16.4° (c 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, ppm): δ 8.16 (d, *J* = 9.3 Hz, 1H, Ar-**H**), 7.90 (d, *J* = 9.5 Hz, 1H, Ar-**H**), 7.83 (d, *J* = 8.1 Hz, 1H, Ar-**H**), 7.48-7.60 (m, 4H, Ar-**H**), 7.15-7.30 (m, 10H, Ar-**H**), 4.88 (q, *J* = 6.8 Hz, 1H, -C**H**CH_3), 4.03-4.06 (m, 1H, -C**H**Ph), 3.76 (s, 2H, -C**H**$_2$Ph), 3.37 (s, 1H, O**H**), 2.95-3.00 (m, 1H, -C**H**$_2$N, (a)), 2.79-2.85 (m, 1H, -C**H**$_2$N, (b)), 1.66 (d, *J* = 6.8 Hz, 3H, -C**H**$_3$); ^{13}C NMR ($CDCl_3$, ppm): δ 14.76 (-CH**C**H_3), 56.57, 56.59 (-**C**H_2Ph, -**C**HCH_3), 61.31 (-**C**H_2N), 70.99 (-**C**HPh), 124.03, 124.53, 125.06, 125.70, 125.82, 126.11, 127.30, 127.36, 128.25, 128.55, 128.93, 128.97, 132.25, 134.10, 138.70, 139.92, 142.55 (Ar-**C**), assignment was based on the ^{1}H-^{13}C HETCOR and ^{1}H-^{1}H COSY spectra; IR (cm^{-1}): υ 3394 (O-H), 3058, 3030 (aromatic C-H), 2965, 2940, 2906 (aliphatic C-H) cm^{-1}; Anal. Calc. for $C_{27}H_{27}NO$ (381.52 g/mol): C 85.00, H 7.13, N 3.67; found C 84.90, H 7.05, N 3.60; IT-TOF MS ($[M+H]^+$): 382.22 g/mol.

4.2.3. (2S)-1-{benzyl [(1S)-1-(naphthalen-1-yl)ethyl]amino}-3-phenoxypropan-2-ol, (4)

(*S*)-Glycidyl phenyl ether (0.63 g, 4.21 mmol) was added to the solution of *N*-benzyl-*N*-(*S*)-1-[α-naphthylethyl]amine **2** (1.00 g, 3.83 mmol) in methanol (5 ml). The solution was heated to 70°C and the reaction was followed by TLC (n-hexane/EtOAc/TEA = 40/8/3). After 24 h, the reaction finished, the solvent was removed. The crude product was purified by silica-gel column chromatography (n-hexane/EtOAc / TEA = 40/8/3) to afford **4** (1.44 g, 91 %) as a viscous product. $[\alpha]_D^{20}$ = +80.4° (c 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, ppm): δ 7.99 (d, *J* = 8.6 Hz, 1H, Ar-**H**), 7.93 (d, *J* = 8.1 Hz, 1H, Ar-**H**), 7.83 (d, *J* = 8.2 Hz, 1H, Ar-**H**), 7.22-7.62 (m, 11H, Ar-**H**), 6.97 (t, *J* = 7.3 Hz, 1H, Ar-**H**), 6.45 (d, *J* = 8.1 Hz, 2H, Ar-**H**), 4.83 (q, *J* = 6.7 Hz, 1H, -C**H**CH_3), 3.90 (s, 2H, C**H**$_2$Ph), 3.73-3.75 (m, 1H, C**H**CH_2), 3.55 (m, 1H, C**H**$_2$OPh a)), 3.02 (m, 1H, C**H**$_2$OPh b)), 2.82-2.89 (m, AB system, 2H, C**H**$_2$N), 2.68 (s, 1H, OH), 1.68 (d, *J* = 6.7 Hz, 3H, -CHC**H**$_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 12.03 (-CH**C**H_3), 53.29 (-**C**H_2N), 55.23 (-**C**HCH_3), 57.59 (-**C**H_2Ph), 68.02 (-**C**HCH_2), 70.46 (-**C**H_2OPh), 114.35, 120.70, 124.72, 124.83, 125.07, 125.60,

125.88, 127.55, 128.23, 128.50, 128.77, 129.30, 129.58, 132.30, 134.14, 138.72, 139.51, 158.55 (Ar-**C**), assignment was based on the ^{1}H-^{13}C HETCOR and ^{1}H-^{1}H COSY spectra; IR (cm^{-1}): υ 3445 (O-H), 3050, 3029 (aromatic C-H), 2968, 2923, 2834 (aliphatic C-H) cm^{-1}; Anal. Calc. for $C_{28}H_{29}NO_2$ (411.54 g/mol): C 81.72, H 7.10, N 3.40; found C 81.66, H 7.01, N 3.32; IT-TOF MS ([M+H]$^{+}$): 412.23 g/mol.

4.3. Synthesis of chiral ruthenium(II) phosphinite ligands and their complexes

4.3.1.(1R)-2-{benzyl[(1S)-1-(naphthalen-1-yl)ethyl]amino}-1-phenylethyldiphenylphosphite, (5)

(1*R*)-2-{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino}-1-phenylethan-1-ol, **(3)** (0.100 gr, 0.26 mmol) and Et_3N (0.027 gr, 0.26 mmol) were dissolved in dry CH_2Cl_2 (30 mL) under an argon atmosphere. Next, Ph_2PCl (0.059 gr, 0.26 mmol) was added dropwise with a syringe to this solution. The mixture was stirred at 0 ^{o}C for 30 min, and the solvent was removed under reduced pressure. After addition of dry thf, the white precipitate (triethylammonium chloride) was filtered off under argon and dried in vacuo to produce a white viscous oily compound **5** (Yield: 0.14 g, 94.7 %). $[\alpha]_D^{20}$= +34.3 (c 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, ppm): δ 8.16 (d, *J* = 9.1 Hz, 1H, Ar-**H**), 7.17-7.92 (m, 24 H, Ar-**H**), 7.01 (m, 1H, Ar-**H**), 6.90 (d, *J* = 7.6 Hz, 1H, Ar-**H**), 4.88 (q, *J* = 6.9 Hz, 1H, -C**H**CH_3), 4.04-4.06 (m, 1H, C**H**Ph), 3.77 (s, 2H, -C**H**$_2$Ph), 2.98 (m, 1H, -C**H**$_2$N (a)), 2.83 (m, 1H, -C**H**$_2$N (b)), 1.66 (d, *J* = 6.9 Hz, 3H, -CHC**H**$_3$); ^{13}C NMR ($CDCl_3$, ppm): δ 14.72 (CH**C**H_3), 56.53, 56.62 (**C**H_2Ph, **C**HCH_3), 61.28 (**C**H_2N), 70.91 (**C**HPh), 123.96, 124.47, 125.00, 125.75, 126.05, 127.03, 127.69, 128.04, 128.18, 128.48, 128.86, 129.48, 132.02, 134.03, 138.65, 139.87, 142.50 (aromatic carbons), 125.16 (d, *J* = 4.0 Hz, *m*-carbons of $OPPh_2$), 125.63 (s, *p*-carbons of PPh_2), 127.26 (d, *J* = 6.0 Hz, *o*-carbons of $OPPh_2$), 135.38 (d, *J* = 19.1 Hz, *i*-carbons of $OPPh_2$); ^{31}P-{^{1}H} NMR ($CDCl_3$, ppm): δ 108.80 (s, O-PPh_2) assignment was based on the ^{1}H-^{13}C HETCOR and ^{1}H-^{1}H COSY spectra; IR (cm^{-1}): υ 3054 (aromatic C-H), 2967

(aliphatic C-H), 1437 (P-Ph), 971 (O-P); Anal. Calc. for $C_{39}H_{36}NOP$ (565.69 g/mol): C 82.81, H 6.41, N 2.48; found C 82.69, H 6.35, N 2.43.

4.3.2. (2S)-1-{benzyl[(1S)-1-(naphthalen-1-yl)ethyl]amino}-3-phenoxypropan-2-yl diphenylphosphinite, (6)

(2*S*)-1-{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino}-3-phenoxy propan-2-ol, **(4)** (0.100 gr, 0.24 mmol) and Et_3N (0.025 gr, 0.24 mmol) were dissolved in dry CH_2Cl_2 (30 mL) under an argon atmosphere. Next, Ph_2PCl (0.055 gr, 0.24 mmol) was added dropwise with a syringe to this solution. The mixture was stirred at room temperature for 30 min, and the solvent was removed under reduced pressure. After addition of dry thf, the white precipitate (triethylammonium chloride) was filtered off under argon and dried in vacuo to produce a white viscous oily compound **6** (Yield: 0.14 g, 96.8 %). $[\alpha]_D^{20}$= +83.0 (c 1, CH_2Cl_2). ^{1}H NMR ($CDCI_3$, ppm): δ 7.23-7.86 (m, 22H, Ar-**H**), 7.05 (t, *J* = 7.8 Hz, 2H, Ar-**H**), 6.82 (t, *J* = 7.3 Hz, 1H, Ar-**H**), 5.90 (d, *J* = 8.2 Hz, 2H, Ar-**H**), 4.68 (q, *J* = 6.6 Hz, 1H, C**H**CH_3), 4.10-4.12 (m, 1H, C**H**CH_2), 3.89 (s, 2H, C**H**$_2$Ph), 3.35 (m, 1H, C**H**$_2$OPh a)), 2.70-2.74 (m, AB system, 1H, C**H**$_2$N a)), 2.79-2.85 (m, AB system, 1H, C**H**$_2$N b)), 2.64 (m, 1H, C**H**$_2$OPh b)), 1.55 (d, *J* = 6.6 Hz, 3H, -CHC**H**$_3$); ^{13}C NMR ($CDCl_3$): δ 10.34 (-CH**C**H_3), 50.89 (d, *J* = 5.0 Hz, -**C**H_2N), 53.36 (**C**HCH_3), 57.84 (**C**H_2Ph), 69.66 (-**C**H_2OPh), 78.32 (d, *J* = 19.1Hz, -**C**HCH_2), 114.11, 119.99, 124.87, 125.42, 127.55, 128.20, 128.30, 128.78, 128.84, 129.23, 130.07, 130.49, 130.71, 132.13, 133.95, 138.47, 138.76, 158.33 (aromatic carbons), 128.04 (d, *J* = 7.0 Hz, *m*-carbons of $OPPh_2$), 128.41 (s, *p*-carbons of $OPPh_2$), 130.08 (d, *J* = 21.2 Hz, *o*-carbons of $OPPh_2$), 142.51 (d, *J* = 25.2 Hz, *i*-carbons of $OPPh_2$) assignment was based on the ^{1}H-^{13}C HETCOR and ^{1}H-^{1}H COSY spectra; ^{31}P-{^{1}H} NMR ($CDCl_3$, ppm): δ 113.60 (s, O-PPh_2); IR (cm^{-1}): υ 3055 (aromatic C-H), 2965 (aliphatic C-H), 1438 (P-Ph), 971 (O-P); Anal. Calc. for $C_{40}H_{38}NO_2P$ (595.72 g/mol): C 80.65, H 6.43, N 2.35; found C 80.55, H 6.37, N 2.29.

4.3.3.(1R)-2-{benzyl[(1S)-1-(naphthalen-1-yl)ethyl]amino}-1-phenylethyldiphenyl phosphinito[dichloro(η^6-p-cymene) ruthenium(II)] (7)

[Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ (0.05 g, 0.09 mmol) and (1*R*)-2-{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino}-1-phenylethyl diphenylphosphinite, **(5)** (0.10 g, 0.18 mmol) were dissolved in 30 mL of dry CH_2Cl_2 under an argon atmosphere and stirred for 30 min at room temperature. The volume was concentrated to ca. 1-2 mL under reduced pressure and addition of petroleum ether (25 mL) gave **7** as a red solid. The product was collected by filtration and dried in vacuo (yield: 0.13 g, 85.8 %; mp: 123-124 ^{0}C); $[\alpha]_D^{25}$ = + 27^o (c 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, ppm): δ 7.88 (t, *J* = 7.8 Hz, 4H, Ar-H), 7.57 (t, *J* = 8.3 Hz, 3H, Ar-H), 7.29-7.37 (m, 12 H, Ar-H), 6.65-7.07 (m, 8H, Ar-H), 5.41 (m, 1H, C**H**Ph), 5.17 (d, *J* = 5.8 Hz, 1H, aromatic proton of *p*-cymene), 4.96 (d, *J* = 6.0 Hz, 1H, aromatic proton of *p*-cymene), 4.84 (d, *J* = 6.0 Hz, 1H, aromatic proton of *p*-cymene), 4.47 (d, *J* = 5.8 Hz, 1H, aromatic proton of *p*-cymene), 4.25 (q, *J* = 6.5 Hz, 1H, -C**H**CH$_3$), 3.38 (d, *J* = 13.2 Hz, 1H, -C**H$_2$**Ph, (a)), 3.20 (d, *J* = 13.3 Hz, 1H, -C**H$_2$**Ph, (b)), 2.87 (dd (pseudo t), *J* = 11.6 Hz, *J* = 11.5 Hz 1H, -C**H**$_2$N (a)), 2.59 (m, 1H, -C**H**$_2$N (b)), 2.37 (m, 1H, –C**H**- of *p*-cymene), 1.49 (s, 3H, C**H**$_3$Ph of *p*-cymene), 1.20 (d, *J* = 7.9 Hz, 3H, -CHC**H**$_3$), 1.05 (m, 6H, C**H**$_3$)$_2$CHPh of *p*-cymene); ^{13}C NMR ($CDCl_3$, ppm): δ 10.51 (CH**C**H$_3$), 17.01 (**C**H$_3$Ph of *p*-cymene), 21.99 ((**C**H$_3$)$_2$CHPh of *p*-cymene), 29.80 (–**C**H- of *p*-cymene), 52.22 (**C**HCH$_3$), 54.54, 55.39 (**C**H$_2$Ph, **C**H$_2$N), 77.24 (**C**HPh), 87.16, 88.23, 88.56, 89.00 (aromatic carbons of *p*-cymene), 99.54, 111.76 (quaternary carbons of *p*-cymene), 124.63, 124.78, 126.91, 126.97, 127.09, 127.72, 127.82, 130.00, 130.73, 130.83, 132.13, 132.38, 132.49, 133.67, 138.47, 138.97, 140.13 (aromatic carbons), 124.18 (d, *J* = 4.0 Hz, *m*-carbons of OPPh$_2$), 125.19 (s, *p*-carbons of PPh$_2$), 127.36 (d, *J* = 6.0 Hz, *o*-carbons of OPPh$_2$), 134.25 (d, *J* = 11.1 Hz, *i*-carbons of OPPh$_2$); assignment was based on the ^{1}H-^{13}C HETCOR and ^{1}H-^{1}H COSY spectra; ^{31}P-{^{1}H} NMR ($CDCl_3$, ppm): δ 109.70 (s, O-PPh$_2$); IR (cm^{-1}): υ 3057 (aromatic C-H), 2963 (aliphatic C-H),

1435 (P-Ph), 970 (O-P), 531 (Ru-P); Anal. Calc. for $C_{49}H_{50}NOPRuCl_2$ (871.89 g/mol): C 67.50, H 5.78, N 1.61; found C 67.41, H 5.70, N 1.52.

4.3.4. (1R)-2-{benzyl[(1S)-1-(naphthalen-1-yl)ethyl]amino}-1-phenylethyldiphenyl phosphinito [dichloro(η^6-benzene)ruthenium (II)] (8)

[Ru(η^6-benzene)(μ-Cl)Cl]$_2$ (0.04 g, 0.09 mmol) and (1*R*)-2-{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino}-1-phenylethyl diphenylphosphinite, **(5)** (0.10 g, 0.18 mmol) were dissolved in 30 mL of dry CH_2Cl_2 under an argon atmosphere and stirred for 30 min at room temperature. The volume was concentrated to ca. 1–2 mL under reduced pressure and addition of petroleum ether (25 mL) gave **8** as a red solid. The product was collected by filtration and dried in vacuo (yield: 0.12 g, 83.9 %; mp: 191-193 ^{0}C); $[\alpha]_D^{25}$ = + 113^o (c 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, ppm): δ 8.06 (t, *J* = 8.9 Hz, 2H, Ar-H), 7.96 (t, *J* = 8.5 Hz, 2H, Ar-H), 6.73-7.58 (m, 23H, Ar-H), 5.63-5.70 (m, 1H, C**H**Ph), 4.95 (s, 6H, aromatic protons of benzene), 4.27 (q, *J* = 6.6 Hz, 1H, -C**H**CH_3), 3.39 (d, *J* = 13.2 Hz, 1H, -C**H**$_2$Ph, (a)), 3.14 (d, *J* = 13.2 Hz, 1H, -C**H**$_2$Ph, (b)), 2.88 (dd (pseudo t), *J* = 11.5 Hz, *J* = 11.3 Hz, 1H, -C**H**$_2$N (a)), 2.32 (d, *J* = 10.0 Hz, 1H, -C**H**$_2$N (b)), 1.17 (d, *J* = 6.6 Hz, 3H, -CHC**H**$_3$); ^{13}C NMR ($CDCl_3$, ppm): δ 10.61 (CH**C**H_3), 51.99 (**C**HCH_3), 54.98, 55.44 (**C**H_2Ph, **C**H_2N), 77.23 (**C**HPh), 90.13 (d, *J* = 4.0 Hz, aromatic carbons of benzene), 124.71, 124.82, 126.85, 126.99, 127.16, 127.59, 127.79, 127.92, 128.12, 130.06, 130.42, 130.70, 131.48, 133.68, 138.37, 138.72, 140.44 (aromatic carbons), 124.07 (d, *J* = 7.0 Hz, *m*-carbons of $OPPh_2$), 125.13 (s, *p*-carbons of PPh_2), 127.46 (d, *J* = 6.0 Hz, *o*-carbons of $OPPh_2$), 135.42 (d, *J* = 13.1 Hz, *i*-carbons of $OPPh_2$); assignment was based on the ^{1}H-^{13}C HETCOR and ^{1}H-^{1}H COSY spectra; ^{31}P-{^{1}H} NMR ($CDCl_3$, ppm): δ 104.76 (s, O-PPh_2); IR (cm^{-1}): υ 3049 (aromatic C-H), 2966, 2935, 2888, 2841, 2806 (aliphatic C-H), 1436 (P-Ph), 992 (O-P), 524 (Ru-P); Anal. Calc. for $C_{45}H_{42}NOPRuCl_2$ (815.78 g/mol): C 66.26, H 5.19, N 1.72; found C 66.18, H 5.10, N 1.67.

4.3.5. (2S)-1-{benzyl[(1S)-1-(naphthalen-1-yl)ethyl]amino}-3-phenoxypropan-2-yldiphenyl phosphinito[dichloro(η^6-p-cymene) ruthenium (II)] (9)

[Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ (0.05 g, 0.08 mmol) and (2*S*)-1-{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino}-3-phenoxypropan-2-yl diphenylphosphinite, **(6)** (0.10 g, 0.17 mmol) were dissolved in 30 mL of dry CH_2Cl_2 under an argon atmosphere and stirred for 30 min at room temperature. The volume was concentrated to ca. 1-2 mL under reduced pressure and addition of petroleum ether (25 mL) gave **9** as a red solid. The product was collected by filtration and dried in vacuo (yield: 0.13 g, 85.9 %; mp: 168-170 ^{0}C); $[\alpha]_D^{25}$ = + 56^o (c 1, CH_2Cl_2). ^{1}H NMR ($CDCI_3$, ppm): δ 7.99 (t, *J* = 8.7 Hz, 2H, Ar-H), 7.11-7.82 (m, 22H, Ar-H), 6.91 (t, *J* = 7.3 Hz, 1H, Ar-H), 5.98 (d, *J* = 8.0 Hz, 2H, Ar-H), 5.48 (q, *J* = 5.8 Hz, 2H, aromatic protons of *p*-cymene), 5.35 (d, *J* = 5.8 Hz, 1H, aromatic proton of *p*-cymene), 5.22 (d, *J* = 5.8 Hz, 1H, aromatic proton of *p*-cymene), 4.75 (br, 1H, C**H**CH_2), 4.47 (q, *J* = 6.6 Hz, 1H, C**H**CH_3), 3.71 (d, *J* = 13.4 Hz, 1H, C**H**$_2$Ph, (a)), 3.60 (d, *J* = 10.4 Hz, 1H, C**H**$_2$OPh (a)), 3.41 (d, *J* = 13.4 Hz, 1H, C**H**$_2$Ph, (b)), 2.61 (t, *J* = 9.3 Hz, 1H, C**H**$_2$OPh (b)), 2.50 (m, 1H, –C**H**- of *p*-cymene), 2.30 (m, 2H, C**H**$_2$N), 1.70 (s, 3H, C**H**$_3$Ph of *p*-cymene), 1.26 (d, *J* = 6.7 Hz, 3H, -CHC**H**$_3$), 1.09 (d, *J* = 6.9 Hz, 3H, C**H**$_3$)$_2$CHPh of *p*-cymene), 0.93 (d, *J* = 6.9 Hz, 3H, C**H**$_3$)$_2$CHPh of *p*-cymene); ^{13}C NMR ($CDCl_3$): δ 8.79 (-CH**C**H_3), 17.00 (**C**H_3Ph of *p*-cymene), 21.60, 22.14 ((**C**H_3)$_2$CHPh of *p*-cymene), 29.98 (–**C**H- of *p*-cymene), 49.20 (**C**H_2N), 51.90 (**C**HCH_3), 56.14 (**C**H_2Ph), 69.29 (-**C**H_2OPh), 75.91 (d, *J* = 6.0 Hz, -**C**HCH_2), 86.19 (d, *J* = 6.0 Hz, aromatic carbon of *p*-cymene), 87.94 (d, *J* = 5.0 Hz, aromatic carbon of *p*-cymene), 89.64 (s, aromatic carbon of *p*-cymene), 92.29 (d, *J* = 5.0 Hz, aromatic carbon of *p*-cymene), 97.51, 111.20 (quaternary carbons of *p*-cymene), 113.75, 120.38, 124.73, 125.01, 125.20, 125.41, 127.22, 127.33, 127.90, 129.20, 130.27, 131.96, 132.12, 133.88, 134.17, 138.51, 139.13, 158.26 (aromatic carbons), 127.82 (d, *J* = 10.1 Hz, *m*-karbons of $OPPh_2$), 128.07 (s, *p*-carbons of $OPPh_2$), 130.65 (d, *J* = 15.1 Hz, *o*-

carbons of $OPPh_2$), (*i*-carbons of $OPPh_2$ were not observed); assignment was based on the ^{1}H-^{13}C HETCOR and ^{1}H-^{1}H COSY spectra; ^{31}P-{^{1}H} NMR ($CDCl_3$, ppm): δ 111.15 (s, O-PPh_2); IR (cm^{-1}): υ 3051 (aromatic C-H), 2963, 2925, 2871 (aliphatic C-H), 1435 (P-Ph), 1019 (O-P), 537 (Ru-P); Anal. Calc. for $C_{50}H_{52}NO_2PRuCl_2$ (901.92 g/mol): C 66.59, H 5.81, N 1.55; found C 66.42, H 5.75, N 1.49.

4.3.6. (2S)-1-{benzyl[(1S)-1-(naphthalen-1-yl)ethyl]amino}-3-phenoxypropan-2-yldiphenyl phosphinito[dichloro(η^6-benzene) ruthenium (II)] (10)

[Ru(η^6-benzene)(μ-Cl)Cl]$_2$ (0.04 g, 0.08 mmol) and (2*S*)-1-{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino}-3-phenoxypropan-2-yl diphenylphosphinite, **(6)** (0.10 g, 0.17 mmol) were dissolved in 30 mL of dry CH_2Cl_2 under an argon atmosphere and stirred for 30 min at room temperature. The volume was concentrated to ca. 1-2 mL under reduced pressure and addition of petroleum ether (25 mL) gave **10** as a red solid. The product was collected by filtration and dried in vacuo (yield: 0.12 g, 85.6 %; mp: 147-149 ^{0}C); $[\alpha]_D^{25}$ = + 90^{o} (c 1, CH_2Cl_2). ^{1}H NMR ($CDCI_3$, ppm): δ 7.09-7.94 (m, 24H, Ar-H), 6.90 (t, *J* = 7.2 Hz, 1H, Ar-H), 5.98 (d, *J* = 8.0 Hz, 2H, Ar-H), 5.47 (s, 6H, aromatic protons of benzene), 4.94 (m, 1H, C**H**CH_2), 4.56 (q, *J* = 6.3 Hz, 1H, C**H**CH_3), 3.92 (d, *J* = 13.4 Hz, 1H, C**H**$_2$Ph, (a)), 3.65 (d, *J* = 9.6 Hz, 1H, C**H**$_2$OPh (a)), 3.49 (d, *J* = 13.4 Hz, 1H, C**H**$_2$Ph, (b)), 2.68 (t, *J* = 9.1 Hz, 1H, C**H**$_2$OPh (b)), 2.39 (dd (pseudo t), *J* = 11.8 Hz, *J* = 11.7 Hz 1H, C**H**$_2$N (a)), 2.26 (d, *J* = 9.5 Hz, 1H, C**H**$_2$N (b)), 1.27 (d, *J* = 6.6 Hz, 3H, -CHC**H**$_3$); ^{13}C NMR ($CDCl_3$): δ 9.09 (-CH**C**H_3), 49.19 (**C**H_2N), 52.47 (**C**HCH_3), 56.40 (**C**H_2Ph), 69.04 (-**C**H_2OPh), 76.74 (d, *J* = 3.0 Hz, -**C**HCH_2), 90.32 (d, *J* = 4.0 Hz, aromatic carbons of benzene), 113.82, 120.52, 124.71, 125.00, 125.24, 125.44, 127.22, 127.98, 129.21, 130.30, 130.64, 131.18, 132.15, 133.92, 134.62, 138.45, 139.25, 158.18 (aromatic carbons), 127.46 (d, *J* = 10.1 Hz, *m*-carbons of $OPPh_2$), 128.10 (s, *p*-carbons of $OPPh_2$), 128.28 (d, *J* = 22.1 Hz, *o*-carbons of $OPPh_2$), 140.19 (d, *J* = 58.4 Hz, *i*-carbons of $OPPh_2$); assignment was based on the

^{1}H-^{13}C HETCOR and ^{1}H-^{1}H COSY spectra; ^{31}P-{^{1}H} NMR ($CDCl_3$, ppm): δ 109.59 (s, O-PPh_2); IR (cm^{-1}): υ 3058 (aromatic C-H), 2966, 2935 (aliphatic C-H), 1435 (P-Ph), 967 (O-P), 537 (Ru-P); Anal. Calc. for $C_{46}H_{44}NO_2PRuCl_2$ (845.81 g/mol): C 65.32, H 5.24, N 1.66; found C 65.18, H 5.17, N 1.60.

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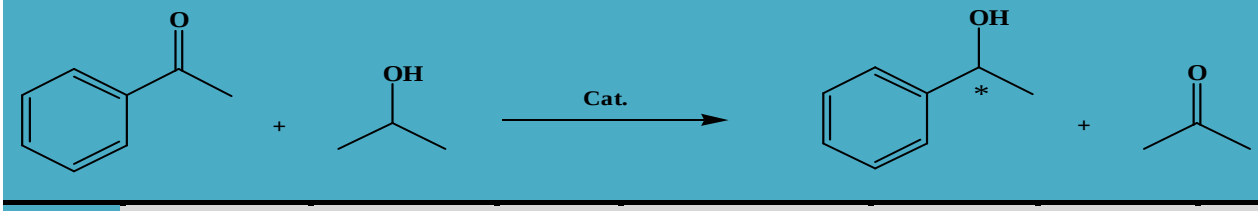
Captions

Scheme 1 Synthesis of aminoalcohols and phosphinites. (*i*) a) PhCHO, MeOH, (reflux); b) $NaBH_4$, (reflux); MeOH equiv. (*ii*) (*R*)-Styrene oxide, MeOH; (*iii*) (*S*)-Glycidyl phenyl ether, MeOH; (*iv* and *v*) 1/2 equiv. Ph_2PCl, 1/2 equiv. Et_3N, thf.

Scheme 2 Synthesis of aminoalcohols, phosphinites and their corresponding Ru(II)-arene complexes. (*i* and *iii*) 1/2 equiv. $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$, thf; (*ii* and *iv*) 1/2 equiv. $[Ru(\eta^6\text{-benzene})(\mu\text{-Cl})Cl]_2$, thf.

Figure 1 The $^{31}P\text{-}\{^1H\}$ NMR spectra of phosphinites (**3, 4**) and their Ru(II)-complexes (**5-8**).

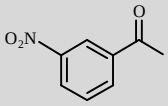
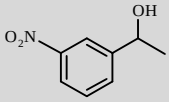
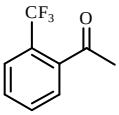
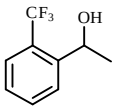
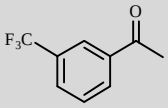
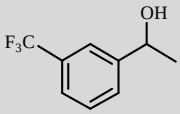
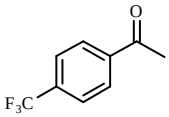
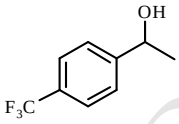
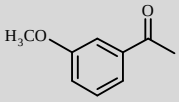
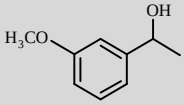
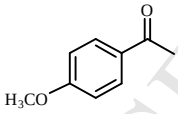
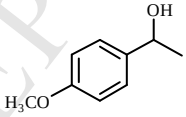
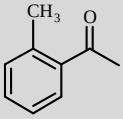
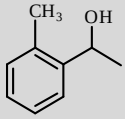
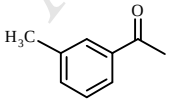
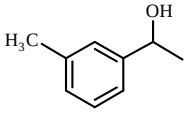
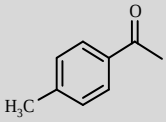
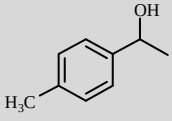
Table 1 Transfer hydrogenation of acetophenone with 2-propanol catalyzed by (1*R*)-2-{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino}-1-phenylethyl diphenylphosphinito[dichloro(η^6-*p*-cymene)ruthenium(II)] **(7)**, (1*R*)-2-{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino}-1-phenylethyl diphenylphosphinito[dichloro(η^6-benzene) ruthenium (II)] **(8)**, (2*S*)-1-{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino}-3-phenoxypropan-2-yl diphenyl-phosphinito[dichloro(η^6-*p*-cymene)ruthenium (II)] **(9)** and **(**2*S*)-1-{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino}-3-phenoxypropan-2-yl diphenylphosphinito [dichloro(η^6-benzene) ruthenium (II)] **(10).**



Entry	*Complex*	*S/C/KOH*	*Time*	*Conversion(%)[f]*	*% ee[g]*	*Conf.[h]*	*TOF(h^{-1})[i]*
1	7 [a]	100:1:5	96h	12 (22) [d]	72 (65) [d]	*S*	<5
2	8 [a]	100:1:5	96h	16 (28) [d]	81 (77) [d]	*S*	<5
3	9 [a]	100:1:5	96h	21 (34) [d]	86 (81) [d]	*R*	<5
4	10 [a]	100:1:5	96h	28 (53) [d]	91 (87) [d]	*R*	<5
5	7 [b]	100:1	1h	trace	....	....	....
6	8 [b]	100:1	1h	trace	....	....	....
7	9 [b]	100:1	1h	trace	....	....	....
8	10 [b]	100:1	1h	trace	....	....	....
9	7 [c]	100:1:5	2 h	97 (91) [e]	78 (70) [e]	*S*	48
10	8 [c]	100:1:5	1 h	98 (93) [e]	87 (79) [e]	*S*	98
11	9 [c]	100:1:5	1 h	99 (93) [e]	91 (86) [e]	*R*	99
12	10 [c]	100:1:5	1/2 h	98 (92) [e]	96 (91) [e]	*R*	196
13	10	100:1:3 [k]	1/2 h	94	89	*S*	188
14	10	100:1:5 [k]	1/2 h	98	96	*S*	196
15	10	100:1:7 [k]	1/2 h	90	90	*R*	180
16	10	100:1:9 [k]	1/2 h	87	91	*R*	174

Reaction conditions:[a] At room temperature; acetophenone/Cat./KOH, 100:1:5; [b] Refluxing in 2-propanol; acetophenone/Cat., 100:1, in the absence of base; [c] Refluxing in 2-propanol; acetophenone/Cat./KOH, 100:1:5; [d] At room temperature; acetophenone/Cat./KOH, 100:1:5, (120 h); [e] Refluxing in 2-propanol; acetophenone/Cat./NaOH, 100:1:5; [f] Determined by GC (three independent catalytic experiments); [g] Determined by capillary GC analysis using a chiral cyclodex B (Agilent) capillary column (30 m x 0.32 mm I.D. x 0.25 µm film thickness); [h] Determined by comparison of the retention times of the enantiomers on the GC traces with the literature values, (S) or (R) configuration was obtained in all experiments; [i] TOF = (mol product/mol Cat.) x h^{-1}; [k] Refluxing in 2-propanol; acetophenone/Cat.,100:1.

Table 2 Transfer hydrogenation results for substituted acetophenones with the catalyst systems prepared from (1*R*)-2-{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino}-1-phenylethyl diphenylphosphinito[dichloro(η^6-*p*-cymene)ruthenium(II)] **(7)**, (1*R*)-2-{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino}-1-phenylethyl diphenylphosphinito[dichloro(η^6-benzene) ruthenium (II)] **(8)**, (2*S*)-1-{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino}-3-phenoxypropan-2-yl diphenyl- phosphinito[dichloro(η^6-*p*-cymene)ruthenium (II)] **(9)** and **(**2*S*)-1-{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino}-3-phenoxypropan-2-yl diphenylphosphinito [dichloro(η^6-benzene) ruthenium (II)] **(10).**[a]

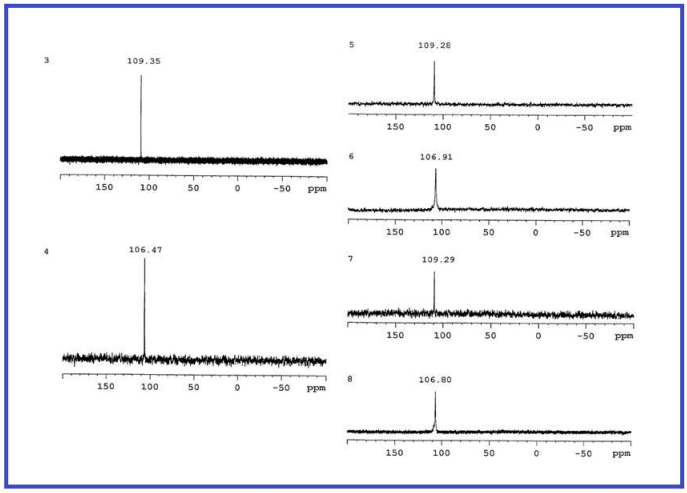
Entry	*Cat.*	*Substrate*	***Product***	***Time***	***Conv.(%)***[b]	***% ee***[c]	***Config.***[d]
1	**7**			45 min	98	77	*S*
2	**8**			20 min	97	85	*S*
3	**9**			20 min	99	90	*R*
4	**10**			10 min	99	94	*R*
5	**7**			1 h	97	79	*S*
6	**8**			30 min	98	87	*S*
7	**9**			30 min	98	92	*R*
8	**10**			20 min	97	96	*R*
9	**7**			45 min	99	76	*R*
10	**8**			20 min	98	85	*R*
11	**9**			20 min	98	90	*R*
12	**10**			10 min	99	94	*R*
13	**7**			30 min	99	74	*S*
14	**8**			15 min	99	84	*S*
15	**9**			15 min	97	86	*R*
16	**10**			5 min	98	90	*R*
17	**7**			13 h	97	81	*S*
18	**8**			8 h	99	89	*S*
19	**9**			8 h	98	92	*R*
20	**10**			5 h	98	98	*R*
21	**7**			8 h	99	66	*S*
22	**8**			5 h	99	73	*S*
23	**9**			5 h	97	81	*R*
24	**10**			3 h	99	87	*R*
25	**7**			12 h	97	70	*S*
26	**8**			7 h	99	74	*S*
27	**9**			7 h	98	85	*R*
28	**10**			4 h	99	93	*R*
29	**7**			9 h	97	67	*S*
30	**8**			5 h	98	71	*S*
31	**9**			5 h	98	81	*R*
32	**10**			3 h	99	90	*R*
33	**7**			6 h	98	64	*S*
34	**8**			3 h	99	68	*S*
35	**9**			3 h	97	79	*R*
36	**10**			2 h	99	84	*R*

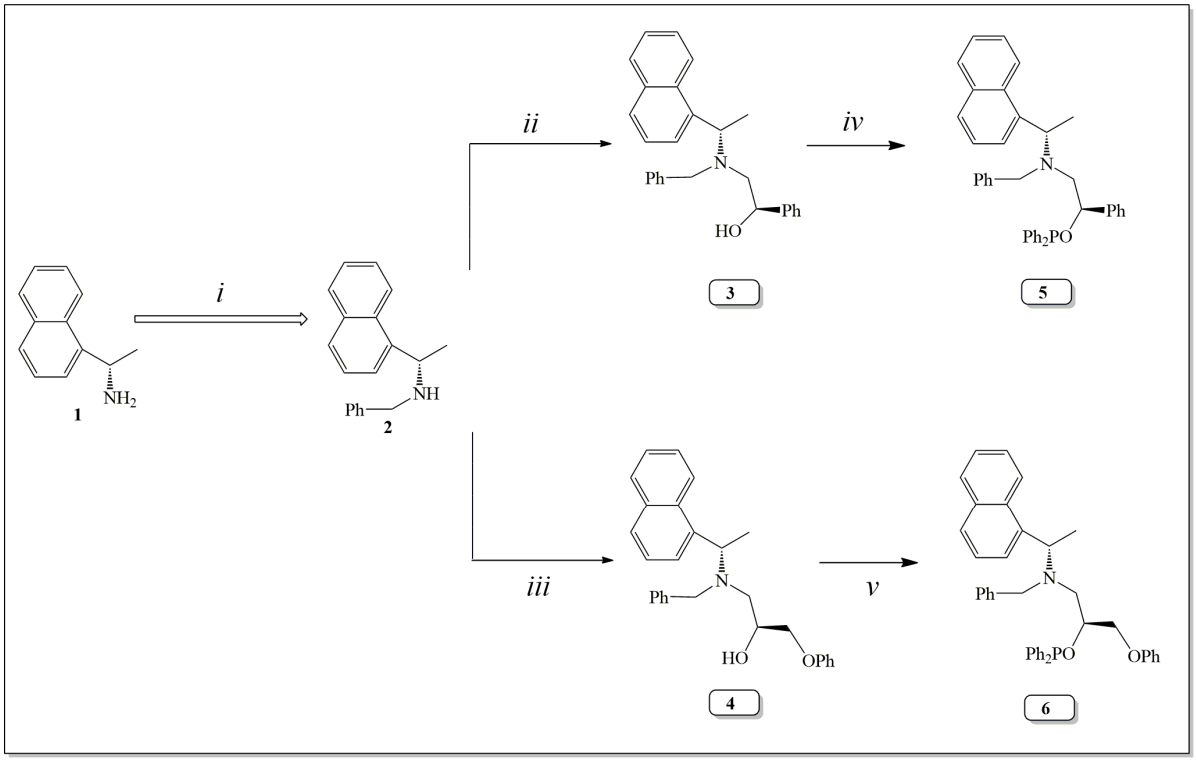
Reaction conditions: [a] Catalyst (0.005 mmol), substrate (0.5 mmol), 2-propanol (5 mL), KOH (0.025 mmol %), 82 ºC, the concentration of acetophenone derivatives are 0.1 M; [b] Purity of compounds is checked by NMR and GC (three independent catalytic experiments), yields are based on aryl ketone; [c] Determined by capillary GC analysis using a chiral cyclodex B (Agilent) capillary column (30 m x 0.32 mm I.D. x 0.25 μm film thickness); [d] Determined by comparison of the retention times of the enantiomers on the GC traces with literature values, *(S)* or *(R)* configuration was obtained in all experiments.

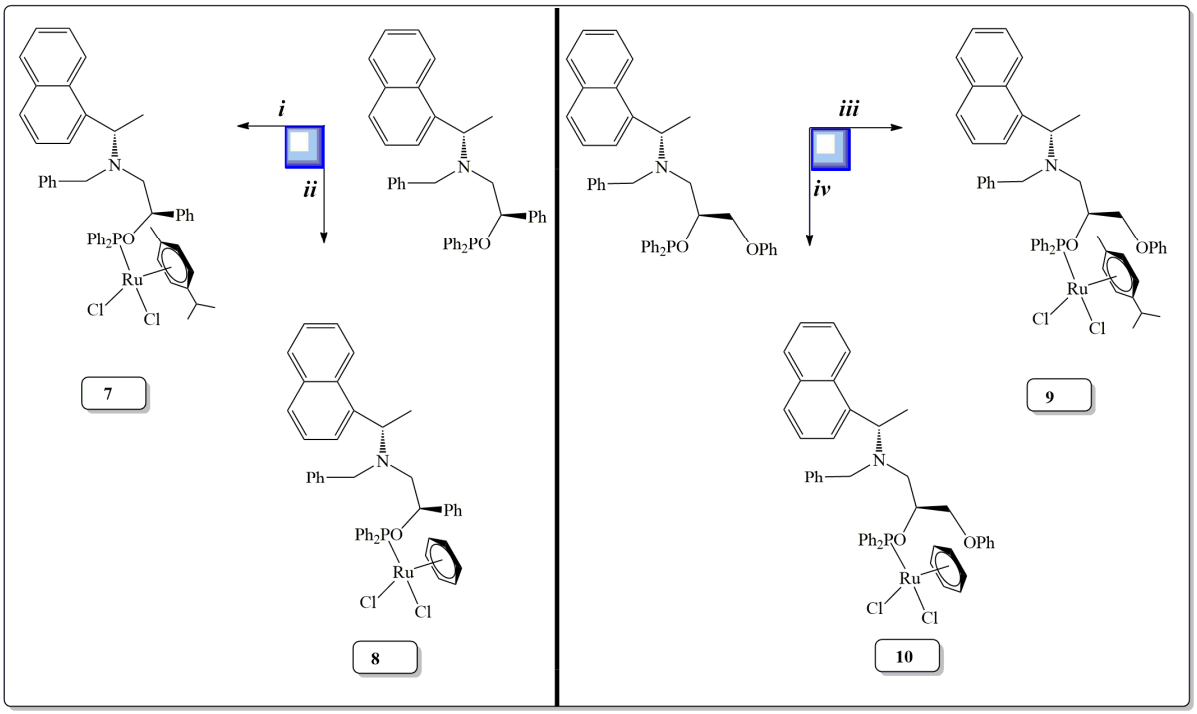
Table 3 Asymmetric Transfer Hydrogenation results for various ketones catalyzed by (1*R*)-2-{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino}-1-phenylethyl diphenylphosphinito[dichloro(η^6-*p*-cymene)ruthenium(II)] **(7)**, (1*R*)-2-{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino}-1-phenylethyl diphenylphosphinito[dichloro(η^6-benzene) ruthenium (II)] **(8)**, (2*S*)-1-{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino}-3-phenoxypropan-2-yl diphenyl-phosphinito[dichloro(η^6-*p*-cymene)ruthenium (II)] **(9)** and **(**2*S*)-1-{benzyl[(1*S*)-1-(naphthalen-1-yl)ethyl]amino}-3-phenoxypropan-2-yl diphenylphosphinito [dichloro(η^6-benzene) ruthenium (II)] **(10).**[a]

Entry	Cat.	R_1	R_2	Time	Conv.(%)[b]	ee(%)[c]	Conf.[d]
1	**7**	**CH_3**	**CH_2CH_3**	5/2 h	98	**76**	*S*
2	**8**			3/2 h	98	**87**	*S*
3	**9**			3/2 h	97	**90**	*R*
4	**10**			1/2 h	98	**93**	*R*
5	**7**	**CH_3**	**$CH_2CH_2C_6H_5$**	4 h	98	**73**	*S*
6	**8**			3 h	97	**83**	*S*
7	**9**			3 h	99	**88**	*R*
8	**10**			2 h	98	**91**	*R*
9	**7**	**CH_3**	**$CH(CH_3)_2$**	7 h	97	**66**	*S*
10	**8**			5 h	98	**77**	*S*
11	**9**			5 h	98	**81**	*R*
12	**10**			3 h	99	**87**	*R*
13	**7**	**CH_3**	**$CH_2CH(CH_3)_2$**	6 h	99	**67**	*S*
14	**8**			4 h	98	**75**	*S*
15	**9**			4 h	99	**82**	*R*
16	**10**			5/2 h	98	**86**	*R*
17	**7**	**CH_3**	**1-naphthyl**	2 h	99	**81**	*S*
18	**8**			1 h	98	**85**	*S*
19	**9**			1 h	98	**93**	*R*
20	**10**			1/2 h	99	**99**	*R*
21	**7**	**CH_3**	***n*-C_4H_9**	5 h	97	**66**	*S*
22	**8**			3 h	99	**74**	*S*
23	**9**			3 h	98	**80**	*R*
24	**10**			2 h	99	**85**	*R*
25	**7**	**CH_3**	**C_6H_{11}**	3 h	98	**56**	*S*
26	**8**			3/2 h	98	**62**	*S*
27	**9**			3/2 h	99	**68**	*R*
28	**10**			1 h	98	**74**	*R*
29	**5**	**C_6H_5**	**C_6H_{11}**	4 h	99	**60**	*S*
30	**6**			3 h	97	**64**	*S*
31	**7**			3 h	98	**71**	*R*
32	**8**			2 h	99	**78**	*R*

Reaction conditions:[a] Catalyst (0.005 mmol), substrate (0.5 mmol), 2-propanol (5 mL), KOH (0.025 mmol %), 82 ºC, the concentration of acetophenone derivatives are 0.1 M; [b] Purity of compounds is checked by NMR and GC (three independent catalytic experiments), yields are based on aryl ketone; [c] Determined by capillary GC analysis using a chiral cyclodex B (Agilent) capillary column (30 m x 0.32 mm I.D. x 0.25 μm film thickness); [d] Determined by comparison of the retention times of the enantiomers on the GC traces with literature values, (*S)* or (*R)* configuration was obtained in all experiments.







Highlights

- ***The first modified examples of chiral phosphinite ligands based on amino alcohol were synthesized.***
- ***We have shown, for the first time, preparing of four Ru(II)-phosphinite complexes.***
- ***They are superb catalyst for the transfer hydrogenation of various ketones.***
- ***Up to 99% ee was gained in 25 min (TOF≤ 396h^{-1}) for asymmetric transfer hydrogenation.***