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# Asymmetric hydrogenation of pro-chiral ketones catalyzed by chiral Ru(II)-benzene organometallic compounds containing amino acid based aroylthiourea ligands

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ABSTRACT

A series of Ru(II)-benzene organometallic compounds (**1**–**6**) constructed from $[RuCl_2(\eta^6\text{-benzene})]_2$ and chiral aroylthiourea ligands (L1-L6) obtained from D/L-phenylalanine, was fully characterized. The chiral complexes along with 2-propanol and NaOH effected the asymmetric hydrogenation of aromatic ketones at 82 °C within 8–10 h. The reduction reactions proceeded with excellent conversions and enantiomeric excesses (up to 99%).



## 1. Introduction

Asymmetric synthesis affords enantiomerically enriched products which are important intermediates for the industrial synthesis of pharmaceuticals, agrochemicals, flavors and fragrances [1]. Asymmetric catalysis is one of the greatest methods for the synthesis of optically active products, and the structure of enantiopure metal complexes is the crucial factor in defining the asymmetric induction process. The asymmetric transfer hydrogenation (ATH) of pro-chiral ketones catalyzed by chiral Ru complexes has been considered as an effective and easy method for the production of optically pure secondary alcohols [2]. Ru(II)-arene half-sandwich complexes are essential due to their potential applications in the various arena of chemistry [3]. The reports on Ru-arene catalysts expose the role of the spectator arene ligand in catalysis [4]. A large number of novel, useful reactions has been developed using catalytic amounts of ruthenium complexes [5]. The Ru-metal is inexpensive compared to other metals known for asymmetric hydrogenation such as Rh, Ir and Os.

Transition metal complexes containing aroylthiourea ligands have been intensively studied over the past one decade [6]. Aroylthiourea ligands are well known in coordination chemistry due to its wide range of coordination possibilities towards transition metal atoms. The aroylthiourea complexes were successfully applied in the field of catalysis and also they exhibit a variety of biological applications. Density functional theory calculations suggested that thiourea itself can be used as a bifunctional organocatalyst for chiral and achiral catalytic transformations [7]. Variations in steric, geometric, and electronic properties of chiral ligands permit the fine-tuning of the coordinated species, thus allowing changes in reactivity and enantioselectivity of the complexes [8]. Ru(II)-arene complexes bearing amino acid based ligands are rare. Amino acids are important chiral auxiliaries for the preparation of optically active compounds [9]. Lately, α-amino acids/α-amino acids derived amides are used as chiral ligands for ATH of ketones [10]. To our surprise, there is no report available on the Ru-benzene complexes containing amino acid based ligands for the asymmetric hydrogenation of ketones even though the complexes are expected to be water soluble and would make the catalytic system green. Herein, we describe the synthesis and characterization of new chiral Ru(II)-benzene complexes (**1**–**6**) containing D/L-phenylalanine based aroylthiourea ligands. The

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organometallic compounds (**1**–**6**) were fruitfully applied for the asymmetric hydrogenation of aromatic ketones to give the respective enantiopure secondary alcohols.

## 2. Experimental

### 2.1. Synthesis of complexes **1**–**6**

$[RuCl_2(\eta^6\text{-benzene})]_2$ (101 mg, 0.2 mmol) and the chiral ligand (127–133 mg, 0.4 mmol) were dissolved in 20 mL of toluene and stirred for 20 h at 27 °C. The solution was concentrated to 5 mL under reduced pressure, and addition of hexane (25 mL) gave an orange solid. The product was collected by filtration, washed with hexane and dried in *vacuo*.

#### 2.1.1. $[RuCl_2(\eta^6\text{-}C_6H_6)L1]$ (**1**)

Yield: 96 mg, 83%. Mp.: 160 °C. $[\alpha]_D^{27}$: −162°. Anal. Calcd. for $C_{23}H_{22}Cl_2N_2O_3RuS$: C, 47.75; H, 3.83; N, 4.84; S, 5.54. Found: C, 47.54; H, 3.63; N, 4.69; S, 5.38. $^1$H NMR: δ 3.16–3.37 (m, 2H, $CH_2$), 5.14 (q, 1H, $J$ = 5 Hz, C*H), 5.96 (s, 6H, $C_6H_6$), 7.20–7.92 (m, 10H, aromatic), 11.21 (d, 1H, $J$ = 5 Hz, thiourea N–H), 11.51 (s, 1H, amide N–H), 13.30 (bs, 1H, carboxylic H). $^{13}$C NMR: δ 36.0 ($CH_2$), 58.6 (asymmetric carbon), 87.6 ($C_6H_6$), 126.8, 128.3, 128.4, 128.5, 129.2, 131.9, 133.0, 136.1 (aromatic), 168.3 (C=O), 171.3 (C=S), 180.2 (carboxylic C). FT-IR: 3221 (m; ν(amide N–H)), 3165 (s; ν(thiourea N–H)), 1673 (s; ν(C=O)), 1745 (s; ν(COOH)), 1185 (s; ν(C=S)) $cm^{-1}$. UV–vis [$CHCl_3$; λ, nm (ε, $dm^3mol^{-1}cm^{-1}$)]: 441 (6734), 326 (28639), 287 (85648), 251 (71240).

#### 2.1.2. $[RuCl_2(\eta^6\text{-}C_6H_6)L2]$ (**2**)

Yield: 93 mg, 80%. Mp.: 159 °C. $[\alpha]_D^{27}$: +159°. Anal. Calcd. for $C_{23}H_{22}Cl_2N_2O_3RuS$: C, 47.75; H, 3.83; N, 4.84; S, 5.54. Found: C, 47.57; H, 3.68; N, 4.71; S, 5.39. $^1$H NMR: δ 3.16–3.37 (m, 2H, $CH_2$), 5.14 (q, 1H, $J$ = 5 Hz, C*H), 5.96 (s, 6H, $C_6H_6$), 7.20–7.92 (m, 10H, aromatic), 11.21 (d, 1H, $J$ = 5 Hz, thiourea N–H), 11.51 (s, 1H, amide N–H), 13.30 (bs, 1H, carboxylic H). $^{13}$C NMR: δ 36.0 ($CH_2$), 58.5 (asymmetric carbon), 87.6 ($C_6H_6$), 126.8, 128.3, 128.3, 128.5, 129.1, 131.9, 133.0, 136.1 (aromatic), 168.3 (C=O), 171.3 (C=S), 180.2 (carboxylic C). FT-IR: 3220 (m; ν(amide N–H)), 3165 (s; ν(thiourea N–H)), 1672 (s; ν(C=O)), 1745 (s; ν(COOH)), 1185 (s; ν(C=S)) $cm^{-1}$. UV–vis [$CHCl_3$ λ, nm (ε, $dm^3mol^{-1}cm^{-1}$)]: 441 (6884), 326 (29627), 286 (86958), 252 (72342).

#### 2.1.3. $[RuCl_2(\eta^6\text{-}C_6H_6)L3]$ (**3**)

Yield: 98.0 mg, 84%. Mp.: 190 °C. $[\alpha]_D^{27}$: −120°. Anal. Calcd. for $C_{21}H_{20}Cl_2N_2O_3RuS_2$: C, 43.15; H, 3.45; N, 4.79; S, 10.97. Found: C, 43.04; H, 3.27; N, 4.63; S, 10.84. HR-MS: ($m/z$) calcd for $C_{21}H_{20}Cl_2N_2O_3RuS_2$: 583.49; found: 512.9889 ($M-2Cl^-$). $^1$H NMR: δ 3.15–3.37 (m, 2H, $CH_2$), 5.13 (q, 1H, $J$ = 5 Hz, C*H), 5.97 (s, 6H, $C_6H_6$), 7.19–8.34 (m, 8H, aromatic), 11.08 (d, 1H, $J$ = 10 Hz, thiourea N–H), 11.58 (s, 1H, amide N–H), 13.29 (bs, 1H, carboxylic H). $^{13}$C NMR: δ 36.0 ($CH_2$), 58.6 (asymmetric carbon), 87.6 ($C_6H_6$), 126.8, 128.3, 128.6, 129.1, 132.6, 135.2, 136.1, 136.4 (aromatic), 162.1 (C=O), 171.3 (C=S), 179.9 (carboxylic C). FT-IR: 3225 (m; ν(amide N–H)), 3172 (s; ν(thiourea N–H)), 1655 (s; ν(C=O)), 1759 (s; ν(COOH)), 1187 (s; ν(C=S)) $cm^{-1}$. UV–vis [$CHCl_3$; λ, nm (ε, $dm^3mol^{-1}cm^{-1}$)]: 441 (7182), 333 (34467), 295 (76048), 252 (99140).

#### 2.1.4. $[RuCl_2(\eta^6\text{-}C_6H_6)L4]$ (**4**)

Yield: 101 mg, 86%. Mp.: 189 °C. $[\alpha]_D^{27}$: +116°. Anal. Calcd. for $C_{21}H_{20}Cl_2N_2O_3RuS_2$: C, 43.15; H, 3.45; N, 4.79; S, 10.97. Found: C, 43.03; H, 3.37; N, 4.69; S, 10.89. $^1$H NMR: δ 3.15–3.37 (m, 2H, $CH_2$), 5.14 (q, 1H, $J$ = 5 Hz, C*H), 5.97 (s, 6H, $C_6H_6$), 7.19–8.34 (m, 8H, aromatic), 11.08 (d, 1H, $J$ = 10 Hz, thiourea N–H), 11.58 (s, 1H, amide N–H), 13.31 (bs, 1H, carboxylic H). $^{13}$C NMR: δ 36.0 ($CH_2$), 58.6 (asymmetric carbon), 87.6 ($C_6H_6$), 126.8, 128.3, 128.6, 129.1, 132.6, 135.2, 136.1, 136.4 (aromatic), 162.2 (C=O), 171.3 (C=S), 179.9 (carboxylic C). FT-IR (KBr, $cm^{-1}$): 3226 (m; ν(amide N–H)), 3173 (s; ν(thiourea N–H)), 1654 (s; ν(C=O)), 1759 (s; ν(COOH)), 1187 (s; ν(C=S)) $cm^{-1}$. UV–vis [$CHCl_3$; λ, nm ε, ($dm^3mol^{-1}cm^{-1}$)]: 438 (6128), 333 (30761), 295 (68467), 252 (92754).

#### 2.1.5. $[RuCl_2(\eta^6\text{-}C_6H_6)L5]$ (**5**)

Yield: 95 mg, 83%. Mp.: 187 °C. $[\alpha]_D^{27}$: −79°. Anal. Calcd. for $C_{21}H_{20}Cl_2N_2O_4RuS$: C, 44.37; H, 3.55; N, 4.93; S, 5.64. Found: C, 44.28; H, 3.46; N, 4.47; S, 5.51. $^1$H NMR: δ 3.14–3.35 (m, 2H, $CH_2$), 5.11 (q, 1H, $J$ = 5 Hz, C*H), 5.96 (s, 6H, $C_6H_6$), 6.72–8.04 (m, 8H, aromatic), 10.97 (d, 1H, $J$ = 5 Hz, thiourea N–H), 11.25 (s, 1H, amide N–H), 13.29 (bs, 1H, carboxylic H). $^{13}$C NMR: δ 36.0 ($CH_2$), 58.6 (asymmetric carbon), 87.6 ($C_6H_6$), 112.5, 118.5, 126.8, 128.3, 129.1, 136.1, 144.4, 148.3 (aromatic), 157.7 (C=O), 171.2 (C=S), 179.8 (carboxylic C). FT-IR: 3222 (m; ν(amide N–H)), 3121 (s; ν(thiourea N–H)), 1678 (s; ν(C=O)), 1744 (s; ν(COOH)), 1197 (s; ν(C=S)) $cm^{-1}$. UV–vis [$CHCl_3$; λ, nm (ε, $dm^3mol^{-1}cm^{-1}$)]: 444 (6506), 328 (30005), 286 (86202), 255 (71554).

#### 2.1.6. $[RuCl_2(\eta^6\text{-}C_6H_6)L6]$ (**6**)

Yield: 93 mg, 82%. Mp.: 186 °C. $[\alpha]_D^{27}$: +75°. Anal. Calcd. for $C_{21}H_{20}Cl_2N_2O_4RuS$: C, 44.37; H, 3.55; N, 4.93; S, 5.64. Found: C, 44.23; H, 3.43; N, 4.85; S, 5.53. $^1$H NMR: δ 3.15–3.37 (m, 2H, $CH_2$), 5.12 (q, 1H, $J$ = 10 Hz, C*H), 5.97 (s, 6H, $C_6H_6$), 6.73–8.04 (m, 8H, aromatic), 10.98 (d, 1H, $J$ = 10 Hz, thiourea N–H), 11.26 (s, 1H, amide N–H), 13.30 (bs, 1H, carboxylic H). $^{13}$C NMR: δ 36.0 ($CH_2$), 58.6 (asymmetric carbon), 87.6 ($C_6H_6$), 112.6, 118.5, 126.8, 128.3, 129.1, 136.1, 144.4, 148.3 (aromatic), 157.7 (C=O), 171.2 (C=S), 179.9 (carboxylic C). FT-IR: 3220 (m; ν(amide N–H)), 3124 (s; ν(thiourea N–H)), 1679 (s; ν(C=O)), 1748 (s; ν(COOH)), 1180 (s; ν(C=S)) $cm^{-1}$. UV–vis [$CHCl_3$; λ, nm (ε, $dm^3mol^{-1}cm^{-1}$)]: 437 (7293), 326 (29596), 284 (86580), 253 (71964).

### 2.2. General protocol for the asymmetric hydrogenation of ketones

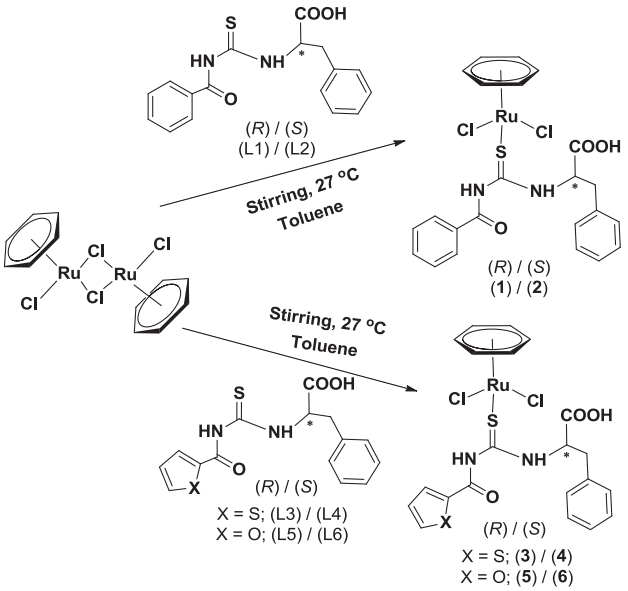
The 2-propanol (5 mL) solution containing Ru(II)-benzene catalyst (**1**–**6**) (0.005 mmol) and NaOH (1 mmol) was stirred at 82 °C for 10 min. Then ketone (1 mmol) was added and stirring persisted at 82 °C for another 8–10 h. Then the reaction mixture was cooled to room temperature and passed through a short silica gel column with *n*-hexane/ethyl acetate (1/1) eluent to remove the Ru catalyst. Conversions were monitored by GC-MS, and the enantiomeric excesses were determined using HPLC with a Chiralcel OB-H column.

## 3. Results and discussion

### 3.1. Synthesis and characterization of the complexes

The chiral aroylthiourea ligands (L1–L6) were synthesized and characterized as reported in our previous publication [11]. The half-sandwich Ru(II)-benzene compounds (**1**–**6**) were synthesized from $[RuCl_2(\eta^6\text{-benzene})]_2$ and chiral ligands (L1–L6) (Scheme 1). The complexes were only partially soluble in water, which unfortunately made catalysis experiments difficult in water medium.

Initially the complex formation was recognized by UV–visible and FT–IR spectra. A new band observed in the spectra of the complexes at 438–444 nm was assigned to d–d transition. The charge transfer transition was observed in the region 326–333 nm, and the n–π* and π–π* transitions were observed in the regions 286–295 and 251–255 nm respectively. The FT–IR spectra of the free ligands exhibited bands in the regions 3205–3272 $cm^{-1}$ for amide N–H, 3162–3196 $cm^{-1}$ for thiourea N–H, 1651–1665 $cm^{-1}$




**Scheme 1.** Formation of complexes (**1**–**6**).

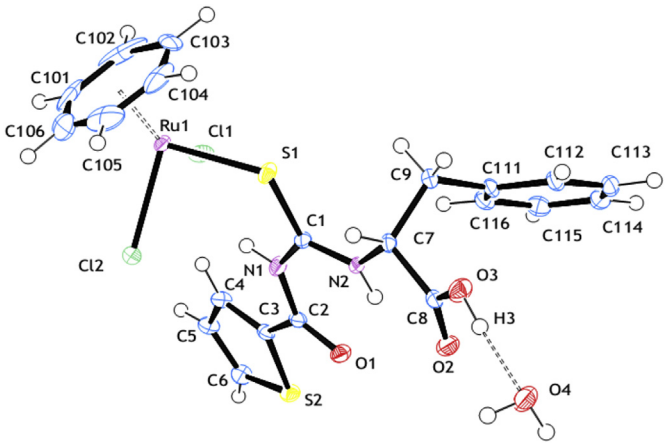



**Fig. 1.** Molecular structure of **4** [Important bond lengths (Å) and angles (°): Ru(1)–S(1) 2.3939(12), Ru(1)–Cl(1) 2.4327(12), Ru(1)–Cl(2) 2.4297(12), S(1)–Ru(1)–Cl(1) 92.02(4), S(1)–Ru(1)–Cl(2) 90.27(4), Cl(2)–Ru(1)–Cl(1) 87.61(4), C(1)–S(1)–Ru(1) 117.32(16)].

for amide C═O, 1705–1718 $cm^{-1}$ for acid C═O and 1240–1246 $cm^{-1}$ for C═S. On complexation, the $\nu$(C═S) of the ligands diminished to 1164–1195 $cm^{-1}$ and all other frequencies remained the same, which confirmed the sulfur only coordination mode of the thiourea ligands [11]. In the $^1$H NMR spectra of **1**–**6**, signals at 10.97–11.21 (doublet) and 11.25–11.58 (singlet) ppm were assigned to amide and thiourea N–H protons respectively. A broad singlet detected at 13.29–13.31 ppm confirmed the presence of COOH. The signal appeared at 5.97 ppm corresponded to the protons of benzene moiety [12]. Chemical shift values of all other aliphatic and aromatic protons were observed in the anticipated regions. The $^{13}$C NMR spectra of L1-L6 displayed signals due to the methylene and asymmetric carbons at 36.0 and 58.6 ppm respectively. The signals characteristic of aromatic carbons were appeared at 112.5–148.3 ppm. The resonances due to the amide C═O, C═S and acid C═O were observed around 157.7–168.3, 171.2–171.3 and 179.8–180.2 ppm respectively. The $^{13}$C NMR chemical shift values did not change significantly upon coordination of the ligand to Ru. The new signal at 87.6 ppm confirmed the linkage of Ru with benzene in all the complexes.

Complex **4** crystallized in the chiral monoclinic space group $P2_1$ and the absolute configuration was explicitly determined directly from the XRD data. The Ru atom adopted a 3-legged piano-stool coordination geometry. The monodentate coordination of the ligand *via* S was evident from the structure (Fig. 1). Not many reports deal with this type of coordination of aroylthiourea ligand with Ru. The experimental details for the X-ray diffraction study of complex **4** is given in Table 1.

**Table 1**
Crystal data and structure refinement for complex **4**.

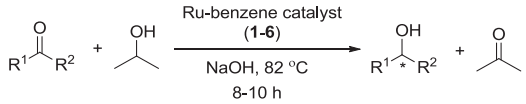
| Compound formula | $C_{21}H_{22}Cl_2N_2O_4RuS_2$ |
|---|---|
| Formula weight | 602.49 |
| Space group | $P2_1$ |
| Crystal system | Monoclinic |
| $a$/Å | 6.8959(2) |
| $b$/Å | 14.2448(3) |
| $c$/Å | 12.2951(3) |
| β/deg | 101.597(1) |
| $V$/Å$^{-3}$ | 1183.10(5) |
| $Z$ | 2 |
| $D_{calc}$/g cm$^{-3}$ | 1.691 |
| λ/Å | 0.71073 |
| μ/mm$^{-1}$ | 1.096 |
| Temperature/K | 100(2) |
| Crystal size/mm | 0.45 × 0.14 × 0.08 |
| θ range/deg | 2.214–29.826 |
| No. of data used for merging | 45532 |
| No. of unique data | 6803 |
| *hkl* range | $-9 \le h \le 9$<br>$-19 \le k \le 19$<br>$-17 \le l \le 17$ |
| $R_{int}$ | 0.053 |
| $R_\sigma$ | 0.040 |
| Refinement | |
| No. of data in refinement | 6803 |
| No. of refined parameters | 293 |
| Final $R$ [$I > 2\sigma(I)$] (all data) | 0.042(0.043) |
| $R_w^2$ [$I > 2\sigma(I)$] (all data) | 0.105(0.105) |
| Goodness of fit $S$ | 1.125 |
| Extrema in residual map/e Å$^{-3}$ | 3.87 → −0.86 |

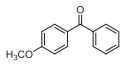
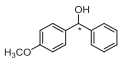
### 3.2. Asymmetric hydrogenation of aromatic ketones

In the beginning, the reaction conditions were optimized using acetophenone as a model substrate. We have chosen 2-propanol as a hydrogen donor as well as solvent. ATH of acetophenone catalyzed by **1** was carried out in different bases [$NEt_3$, NaOH, KOH, $K_2CO_3$, and $(CH_3)_3COK$]. NaOH was found to be a better one as the conversion was 99%. Further, the optimum amount of base was found to be 1 mmol and 0.005 mmol of catalyst **1** was sufficient for the efficient conversion of acetophenone to 1-phenyl ethanol. It was noted that the temperature had significant effect on the efficiency of the present catalytic system. Product was obtained in good yield (99%) only at 82 °C after 8 h.

The Ru(II)-benzene complexes (**1**–**6**) functioned as catalysts for the asymmetric hydrogenation of aromatic ketones to generate enantiopure secondary alcohols at 82 °C. NaOH and 2-propanol were used as base and hydrogen donor respectively. The ratio of substrate:NaOH:catalyst for better catalytic performance was found to be 200:200:1. The acetophenone was converted (99%) into chiral 1-phenylethanol (99% ee) in 8 h (Table 2, entries 1–6). Catalysts **1** and **2** offered (*S*)-1-phenylethanol, **3** and **4** provided *R* isomer, and **5** and **6** gave *S* isomer. Compared to our previous Ru-benzene system [12] which afforded chiral 1-phenylethanol (up to 99% *R* alcohol and 86% *S* alcohol) after 14 h, the present one required less time

**Table 2**
Asymmetric hydrogenation of ketones catalyzed by **1**–**6**.[a]




| Entry | Catalyst | Substrate | Product | Conversion[b] (%) | ee[c] (%)/Configuration[d] | TON[e] | TOF[f] ($h^{-1}$) |
|---|---|---|---|---|---|---|---|
| 1 | **1** |  |  | 99 | 99/*S* | 198 | 24.8 |
| 2 | **2** | | | 99 | 99/*S* | 198 | 24.8 |
| 3 | **3** | | | 99 | 84/*R* | 198 | 24.8 |
| 4 | **4** | | | 99 | 83/*R* | 198 | 24.8 |
| 5 | **5** | | | 99 | 70/*S* | 198 | 24.8 |
| 6 | **6** | | | 99 | 92/*S* | 198 | 24.8 |
| 7 | **1** |  |  | 61 | 62/*R* | 122 | 12.2 |
| 8 | **2** | | | 98 | 66/*S* | 196 | 19.6 |
| 9 | **3** | | | 78 | 94/*R* | 156 | 15.6 |
| 10 | **4** | | | 98 | 62/*S* | 196 | 19.6 |
| 11 | **5** | | | 64 | 96/*R* | 128 | 12.8 |
| 12 | **6** | | | 84 | 99/*S* | 168 | 16.8 |
| 13 | **1** |  |  | 98 | 99/*R* | 196 | 19.6 |
| 14 | **2** | | | 98 | 99/*R* | 196 | 19.6 |
| 15 | **3** | | | 97 | 99/*R* | 194 | 19.4 |
| 16 | **4** | | | 97 | 99/*R* | 194 | 19.4 |
| 17 | **5** | | | 90 | 96/*R* | 180 | 18.0 |
| 18 | **6** | | | 95 | 97/*R* | 190 | 19.0 |
| 19 | **1** |  |  | 99 | 96/*R* | 198 | 19.8 |
| 20 | **2** | | | 97 | 90/*R* | 194 | 19.4 |
| 21 | **3** | | | 98 | 96/*R* | 196 | 19.6 |
| 22 | **4** | | | 99 | 95/*R* | 198 | 19.8 |
| 23 | **5** | | | 96 | 89/*R* | 192 | 19.2 |
| 24 | **6** | | | 97 | 90/*R* | 194 | 19.4 |
| 25 | **1** |  |  | 84 | 98/*S* | 168 | 16.8 |
| 26 | **2** | | | 73 | 99/*S* | 146 | 14.6 |
| 27 | **3** | | | 54 | 96/*S* | 108 | 10.8 |
| 28 | **4** | | | 90 | 99/*S* | 180 | 18.0 |
| 29 | **5** | | | 76 | 99/*S* | 152 | 15.2 |
| 30 | **6** | | | 85 | 93/*S* | 170 | 17.0 |

[a] Ketone (1 mmol), Ru(II) catalyst (0.005 mmol), 2-propanol (5 mL) and NaOH (1 mmol).
[b] Analyzed by GC-MS.
[c] Analyzed by chiral HPLC.
[d] Based on optical rotation values.
[e] TON = moles of the product formed/moles of the catalyst used.
[f] TOF = TON/h.

(8 h) under almost identical conditions. The activity of the catalysts (**1**–**6**) was also better than analogues Ru(II)-*p*-cymene catalysts which took 12 h for providing good yield and enantioselectivity [11]. These facts attested the superior action of the present catalysts toward ATH. The same trend was seen in other investigated substrates.

The substituted ketones were converted (99%) into corresponding alcohols with excellent optical purity after 10 h. 2-methylacetophenone was converted to 2-methyl-1-phenylethanol with up to 98% conversion and 99% ee (Table 2, entries 7–12). Catalysts **2**, **4** and **6** gave *S* alcohol (up to 99% ee) and the other catalysts yielded *R* alcohol (up to 96% ee). Enantiopure fluorine compounds are biologically and pharmacologically active [13]. The piano-stool Ru(II) complexes were used as catalysts for the production of enantiopure *R* alcohol from 4-fluoro acetophenone. Conversions and ee were up to 98% and 99% respectively after 10 h (Table 2, entries 13–18). Though many catalytic systems are available for the enantioselective reduction of ketones, catalysts for the reduction of heterocyclic ketones are rare. Interestingly, reduction of 2-acetylfuran provided corresponding *R* alcohol (96% ee) (Table 2, entries 19–24). Chiral benzhydrol is a valuable starting material for many pharmaceuticals [14]. Our present catalytic system is very effective for the transformation of 4-methoxy benzophenone to corresponding *S* benzhydrol with excellent optical purity (96–99%) (Table 2, entries 25–30). All the substrate ketones were selectively (100%) converted into their corresponding chiral alcohols. In the reduction of some ketones we have observed only *R* alcohol or *S* alcohol, which indicates that the chirality of the product alcohols is not only based on the chiral catalyst but also on the CH–π interactions between the catalyst and the substrate [15,16]. This is clarified in our previous report by theoretical studies, where we have also discussed the mechanism of transfer hydrogenation of ketones catalyzed by similar Ru-arene complexes in detail [12,17].

## 4. Conclusion

Chiral half-sandwich Ru(II)-benzene complexes were synthesized from the reaction between $[RuCl_2(\eta^6\text{-benzene})]_2$ and chiral amino acid derived aroylthiourea ligands, and characterized. In all the complexes, the unusual neutral monodentate coordination behaviour (*via* S atom) was observed for the ligands. The complexes efficiently catalyzed the asymmetric hydrogenation of aromatic ketones to the respective alcohols with excellent conversion (up to 99%) and ee (up to 99%) within 8–10 h. This might be the first report on Ru(II)-benzene complexes bearing aminoacid or amino-acid based ligands for the ATH reaction. Hence the present catalytic system will pave the way for exploring Ru(II)-benzene complexes

containing amino acid based ligands for ATH of ketones and other asymmetric reactions.

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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.2016.12.016.

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