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Asymmetric hydrogenation of aromatic ketones catalyzed by (1*S*,2*S*)-DPEN-modified Ru-PPh_3/γ-Al_2O_3 catalyst

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ABSTRACT

The asymmetric hydrogenations of acetophenone and its derivatives over the (1*S*,2*S*)-DPEN-modified Ru-PPh_3/γ-Al_2O_3 were investigated. The effects of reaction conditions on the asymmetric hydrogenation of acetophenone are discussed in detail. The results showed that this catalyst had high activity and moderate enantioselectivity for the asymmetric hydrogenation of acetophenone and its derivatives. Under the optimum conditions, the conversion of acetophenone was up to 100%, and the enantioselectivity for the formation of (*R*)-phenyl ethanol was 77.7% ee. The chiral alcohol products could be easily separated by centrifugation, while the catalyst could be reused several times.

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1. Introduction

The asymmetric catalytic hydrogenation of simple ketones is an useful method for the preparation of chiral alcohols. It had been a challenging problem[1,2] until 1995 when Noyori et al.[3–6] discovered the Ru(II)-BINAP-diamine–KOH [BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthalene] catalyst. Although these homogeneous catalysts show distinguished activities and enantioselectivities for the asymmetric hydrogenation of simple ketones, the separation and recycling of the catalysts remain difficult.[7] One method to resolve the problem involves the immobilization of a Ru-phosphine-diamine complex on a polymer.[8–10] However, the preparation of the polymer materials, to which the chiral ligand is bonded, is tedious. Furthermore, the phosphine bonded onto a polymer is easily oxidized in solution, while the metal is easily leached from the polymer because of its weak coordination ability. Another method is to immobilize the metal modified by a chiral ligand on an inorganic support. The latter type of catalyst can be easily prepared and reused; however, its enantioselectivity for the asymmetric hydrogenation of acetophenone is not high. Baiker et al.[11,12] first reported that a supported metal catalyst catalyzes the asymmetric hydrogenation of acetophenone, and the enantioselectivity for α-phenyl ethanol was about 30% ee. Recently, Zhao et al.[13] reported the asymmetric hydrogenation of acetophenone catalyzed by (*R*,*R*)-DPEN-modified Ru/γ-Al_2O_3 in the presence of PPh_3 with 60.5% ee. However, the ligand PPh_3 must be added again during recycling.

Here, a Ru-PPh_3/γ-Al_2O_3 catalyst was prepared, and further modified by (1*S*,2*S*)-DPEN in situ for asymmetric hydrogenations of acetophenone and its derivatives. The catalyst exhibits high activity and mediated enantioselectivity for the hydrogenation of acetophenone. The ee value of α-phenyl ethanol exceeds 75.0%. Furthermore, the Ru-PPh_3/γ-Al_2O_3 catalyst can be reused several times without additional PPh_3.

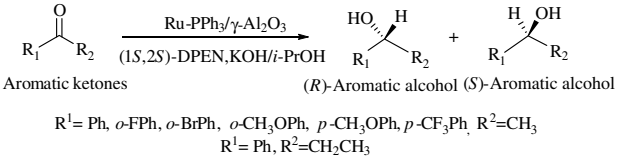

Figure 1. Asymmetric hydrogenation of aromatic ketones.

2. Results and discussion

2.1. Determination of Ru-PPh_3/γ-Al_2O_3

The morphology of Ru-PPh_3/γ-Al_2O_3 was investigated with a transmission electron microscope (JEM-2010) at an accelerating voltage of 200 kV. It can be seen that the size of Ru-PPh_3/γ-Al_2O_3 is about 5 nm (see Fig. 2).

The X-ray photoelectron spectroscopy (XPS) spectrum of Ru-PPh_3/γ-Al_2O_3 showed the Ru 3d binding energies at 280.0 eV and 284.8 eV, indicating that Ru(III) on γ-Al_2O_3 had been completely reduced into Ru(0).

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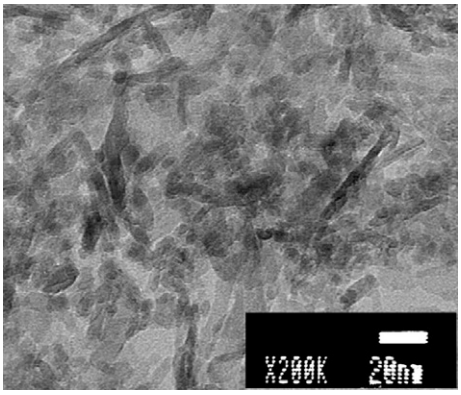

Figure 2. TEM photography of Ru-PPh_3/γ-Al_2O_3.

2.2. Influence of stabilizers on asymmetric hydrogenation of acetophenone

The effect of different stabilizers on the asymmetric hydrogenation of acetophenone was examined and the results are summarized in Table 1. The action of the stabilizer is to prevent metal in the catalyst from aggregating. The data show that catalyst Ru/γ-Al_2O_3 gave low enantioselectivity for the asymmetric hydrogenation of acetophenone without stabilizer. Furthermore, when OTPP (oxygenated triphenylphosphine) was used as the stabilizer, the catalytic activity and enantioselectivity were also low. However, when the catalyst Ru/γ-Al_2O_3 was stabilized by phosphine ligands, the catalytic activity and enantioselectivity increased. It can be seen that phosphine ligands act not only as stabilizers, but also as reducers. Using TPP(PPh_3, triphenylphosphine) as a stabilizer meant high activity and enantioselectivity were obtained. The substituent in the phenyl ring of the triphenylphosphine derivatives, whether it is an electron-withdrawing group or electron-donating group, markedly influences the activity and enantioselectivity. Moreover, when the substituent is electron-withdrawing group, the conversion of acetophenone and the enantioselectivity for (*R*)-phenyl ethanol are higher. With respect to TPPTS (sodium salt of sulfonated triphenylphosphine), the activity and enantioselectivity were lower than the results obtained by TPP because of the lower solubility of TPPTS in *i*-PrOH solvent. Using double phosphine ligands (*S*)-BINAP and BISBI instead of TPP, only moderate activities and enantioselectivities were obtained.

Table 1
Effect of different stabilizers on the asymmetric hydrogenation of acetophenone

Stabilizer	Conversion (%)	ee (%)	*R*/*S*
No [a]	92.9	5.6	(*R*)
TPP	100	77.7	(*R*)
OTPP	2.4	20.2	(*R*)
TDMOPP	27.0	26.0	(*R*)
TFMTPP	99.4	38.0	(*R*)
TPPTS	72.4	59.7	(*R*)
BISBI	79.4	51.6	(*R*)
(*S*)-BINAP	78.5	64.3	(*R*)

Reaction conditions: acetophenone: 0.85 mmol, Ru/acetophenone/(1*S*,2*S*)-DPEN = 1:444:4 (molar ratio), [KOH] = 0.18 mol/L, *i*-PrOH: 2.0 mL, P_{H2} = 5 MPa, Temp: 40 °C, reaction time: 3 h. except the different stabilizers.
[a] Reaction time: 16.0 h.

2.3. Influence of chiral modifiers on the asymmetric hydrogenation of acetophenone

The results seen in Table 2 show the effect of different chiral modifiers on the asymmetric hydrogenation of acetophenone. The data indicate that (*S*,*S*)-DPEN is the best modifier: the conversion of acetophenone and the enantioselectivity for (*R*)-phenyl ethanol could be up to 100% and 77.7%, respectively. The substituent in the amine group of DPEN derivatives, whether it is a methyl group or methylphenyl sulfonyl group, markedly influences the enantioselectivity. The activity and enantioselectivity were very low, although (*R*)-BNDN is also a diamine derivative.

Table 2
Effect of different modifiers on the asymmetric hydrogenation of acetophenone

Modifier	Conversion (%)	ee (%)	R/*S*
(1*S*,2*S*)-DPEN	100	77.7	(*R*)
(1*R*,2*R*)-DPEN	100	72.9	(*S*)
(1*S*,2*S*)-T_SDPEN	86.3	41.0	(*S*)
(1*R*,2*R*)-DMTFM-DPEN	93.8	23.4	(*S*)
(1*R*,2*R*)-DMDPEN	87.2	43.2	(*S*)
(1*R*,2*R*)-DACH	98.7	46.0	(*S*)
(*R*)-BNDN	17.3	5.8	(*S*)
Cinchonidine	4.5	15.6	(*S*)
Cinchonidine[a]	8.3	21.8	(*S*)
L-Tartaric acid	14.5	43.6	(*S*)

The reaction conditions are the same as in Table 1, except the chiral modifiers.
[a] Reaction temperature: 20 °C, reaction time: 14 h.

According to the metal–ligand difunctional mechanism proposed by Noyori[14] and Morris[15–18] for the asymmetric hydrogenation of aromatic ketones in the homogeneous system, the nucleophilic hydride at the ruthenium center attacks the carbon atom of C=O in the substrate, and the acidic H on the nitrogen atom combines with the oxygen atom of C=O, so that a transition state of a six-membered ring is formed (Fig. 3). Except for (*R*)-BNDN, the other diamines could form a six-membered ring transition state with ruthenium–phosphine, which could not only enhance the enantioselectivity but also significantly accelerate the rate of the reaction. Using cinchonidine as a chiral modifier, low activity and enantioselectivity were obtained, although this result is higher than that reported by Baiker[11,12] in the asymmetric hydrogenation of acetophenone over a Pt-cinchonidine system. When catalyst Ru/γ-Al_2O_3 was modified by L-tartaric acid, a 43.6% ee was achieved.

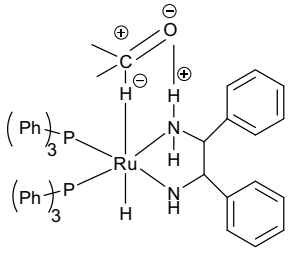

Figure 3. Six-membered transition state ring.

2.4. Influence of solvent on the asymmetric hydrogenation of acetophenone

There is a complex interactional process among a solvent–reactant–catalyst. Therefore, the effect of the solvent on the asymmetric hydrogenation of acetophenone is significant. As shown in Table 3, good catalytic activity and enantioselectivity were observed in alcohol solvents, such as CH_3OH, EtOH and *i*-PrOH. Higher enantioselectivity for (*R*)-phenyl ethanol was achieved in *i*-PrOH, which was consistent with that in the homogeneous system for the asym-

Table 3
Effect of different solvents on the asymmetric hydrogenation of acetophenone

Solvent	Conversion (%)	ee (%)	*R*/*S*
H_2O	76.2	65.2	(*R*)
CH_3OH	100	75.4	(*R*)
EtOH	100	75.2	(*R*)
i-PrOH	100	77.7	(*R*)
THF	90.7	64.1	(*R*)
Toluene	87.8	56.8	(*R*)

The reaction conditions are the same as in Table 1.

metric hydrogenation of aromatic ketones.[19–21] In non-polar solvents, the catalytic activity and enantioselectivity were lower than those in polar alcohol solvents. However, using water as a solvent resulted in lower catalytic activity and enantioselectivity.

2.5. Influence of (1*S*,2*S*)-DPEN and KOH concentrations on the asymmetric hydrogenation of acetophenone

As shown in Figures 4 and 5, the influence of (1*S*,2*S*)-DPEN and KOH on the asymmetric hydrogenation of acetophenone was investigated and can be seen that it is significant. The modifier could not only enhance the enantioselectivity but also significantly accelerate the rate of the reaction in the asymmetric hydrogenation of ethyl pyruvate over Pt/γ-Al_2O_3, Rh/γ-Al_2O_3 or Ir/γ-Al_2O_3 catalyst modified by cinchona.[22] A similar phenomenon was observed in the asymmetric hydrogenation of acetophenone over Ru/γ-Al_2O_3 catalyst modified by (1*S*,2*S*)-DPEN. The conversion was only 15.8% and no ee value in the absence of (1*S*,2*S*)-DPEN. Adding (1*S*,2*S*)-DPEN apparently heightened the catalytic activity and enantioselectivity. When the concentration of (1*S*,2*S*)-DPEN was 4×10^{-3} mol/L, conversion of acetophenone and the ee value of (*R*)-phenyl ethanol could reach up to 100% and 77.7%, respectively. However, if the concentration of (1*S*,2*S*)-DPEN in the reaction solution was increased, the conversions and ee values did not increase.

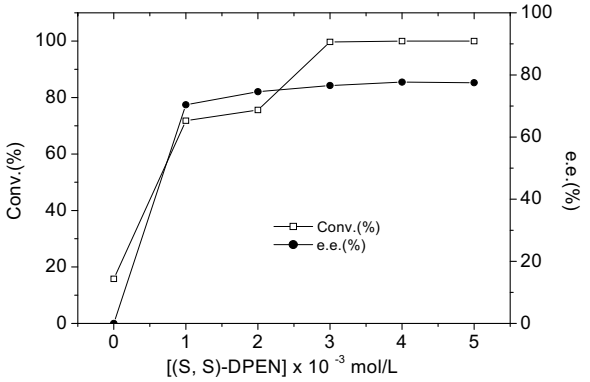

Figure 4. Influence of the (1*S*,2*S*)-DPEN concentration on the asymmetric hydrogenation of acetophenone. Reaction conditions are the same as those listed in Table 1.

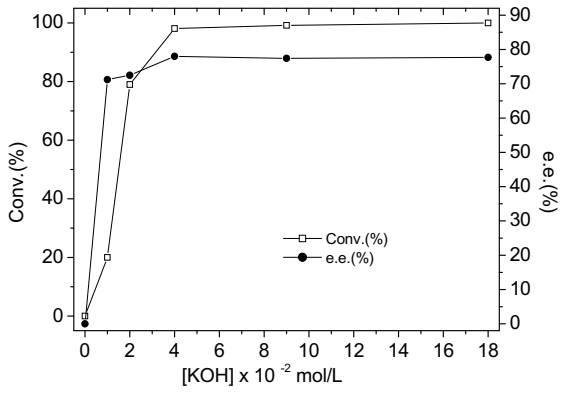

Figure 5. Influence of the KOH concentration on asymmetric hydrogenation of acetophenone. Reaction conditions are the same as those listed in Table 1 except for the change of KOH concentration.

Similarly, if there was no addition of KOH, no hydrogenation of the carbonyl group took place even in the presence of (1*S*,2*S*)-DPEN. With an increase in KOH concentration, the conversion and ee value also increased. When the concentration of KOH increased from 1×10^{-2} mol/L to 4×10^{-2} mol/L, the conversion increased from 20% to 98.1%. When the concentration of KOH was 18×10^{-2} mol/L, the conversion could reach up to 100%. However, after the concentration of KOH was 18×10^{-2} mol/L, again adding KOH into the reaction solution, the conversions and ee values did not increase. The results shown in Figures 4 and 5 indicate that there has a synergistic effect between (1*S*,2*S*)-DPEN and KOH.

2.6. Asymmetric hydrogenation of different aromatic ketones

Various aromatic ketones were asymmetrically hydrogenated with Ru-PPh_3/γ-Al_2O_3–(1*S*,2*S*)-DPEN–KOH catalyst system and the results are reported in Table 4. The results indicate that this supported catalyst modified by chiral diamine shows high catalytic activities in the asymmetric hydrogenation of acetophenone and its derivatives. Moreover, good enantioselectivities were obtained for the asymmetric hydrogenation of acetophenone, propiophenone 4′-(trifluoromethyl) acetopheone and 4′-methoxyacetopheone. The substituent in the phenyl ring, whether it was an electron-withdrawing group or an electron-donating group, obviously influences the enantioselectivity of aromatic ketones. Furthermore, the steric effect, which influences the reactant-modifier interaction, also markedly effects the activity and enantioselectivity.

Table 4
Asymmetric hydrogenation of aromatic ketones

Substrate	Conversion (%)	ee (%)	*R*/*S*
Acetophenone	100	77.7	(*R*)
Propiophenone	100	78.0	(*R*)
2′-Fluoroacetophenone	100	44.3	(*R*)
2′-Bromoacetophenone	100	43.7	(*R*)
2′-Methoxyacetophenone	82.8	33.4	(*S*)
4′(Trifluoromethyl)acetophenone	100	73.6	(*R*)
4′-Methoxyacetophenone	100	74.6	(*R*)

The reaction conditions are the same as in Table 1.

Table 5
Recyclability of the catalyst in the asymmetric hydrogenation of acetophenone

Run	Conversion (%)	ee (%)	*R*/*S*
1	100	77.7	(*R*)
2	85.3	76.6	(*R*)
3	46.6	75.9	(*R*)
4	25.5	75.6	(*R*)

Reaction conditions are the same as in Table 1, except 8.0×10^{-6} mol (*S*,*S*)-DPEN is added at each recycle.

2.7. Catalyst recycling

The results in Table 5 show that the reuse of the catalyst in the asymmetric hydrogenation of acetophenone over Ru-PPh_3/γ-Al_2O_3. For the catalyst, we have also demonstrated that the chiral alcohol products could be easily separated by centrifugation, while the catalyst could be recycled and reused several times. As shown in Table 5, although the reactivities of the Ru-PPh_3/γ-Al_2O_3 catalyst started to drop after the first run, the ee value could be maintained at above 75%. The reactivity decreased probably owing to the loss of Ru-PPh_3/γ-Al_2O_3 catalyst in the process of separation and the partial oxidation of the stabilizer TPP in the reaction solution. However, the catalyst exhibited a steady catalytic performance when saved at normal temperature and dry conditions.

The reaction was performed heterogeneously on the surface of the supported catalyst. The catalyst was separated from the reaction mixture by centrifugation after the first run, and the filtrate was mixed with fresh substrate to examine the asymmetric hydrogenation of acetophenone; however, no reaction occurred under the same reaction conditions. Furthermore, the filtrate was determined by ICP, and it is worth noting that the leaching of Ru is not obvious; only 0.02% Ru is leached to the organic solvent. From above observations, it can be determined that the homogeneous catalytic active species [$RuCl_2(PPh_3)_3$(1*S*,2*S*)-DPEN] does not form in situ in reaction processes.

To further testify that this reaction is catalyzed by a heterogeneous catalyst, we investigated the differences between the Ru-PPh_3/γ-Al_2O_3 catalyst and $RuCl_2(PPh_3)_3$ in the asymmetric hydrogenation of acetophenone using L-proline as the modifier. The results are shown in Table 6. It can be seen that the effect of the heterogeneous and homogeneous catalyst on activities and enantioselectivies for the asymmetric hydrogenation of acetophenone is significant. Under the same reaction conditions, the conversion of acetophenone was only 7.2%, while the ee value of (*R*)-α-phenylethanol was also low, at only 29.2% when using $RuCl_2(PPh_3)_3$ as a catalyst precursor. However, in the case of Ru-PPh_3/γ-Al_2O_3 as a catalyst precursor, the conversion and enantioselectivity were markedly higher than the results obtained by $RuCl_2(PPh_3)_3$. The conversion and ee value can reach up to 61.5% and 59.5%, respectively. Moreover, the reverse absolute configuration of α-phenylethanol was obtained. In the heterogeneous system, substrate and modifier are anchored on the surface of the catalyst and form the different chiral induce microenvironments from the homogeneous system. Moreover, the valent state of metal active center changed energy difference between the transition states for two enantiomers. As a result, the absolute configurations of α-phenylethanol were different. This experiment indicated further that (1*S*,2*S*)-DPEN-modified Ru-PPh_3/γ-Al_2O_3 catalyzed the asymmetric hydrogenation reaction heterogeneously on the surface of catalyst, but not homogeneously in the liquid phase.

Table 6
Comparison of between $RuCl_2(PPh_3)_3$ and Ru-2TPP/γ-Al_2O_3 in the catalytic performance modified by L-proline

Catalyst	Conversion (%)	ee (%)	*R*/*S*
$RuCl_2(PPh_3)_3$	7.2	29.2	(*R*)
1% Ru/γ-Al_2O_3-2TPP	61.5	59.5	(*S*)

3. Conclusions

The Ru-PPh_3/γ-Al_2O_3 catalyst modified by a chiral modifier (1*S*,2*S*)-DPEN exhibited higher catalytic activity and good enantioselectivity for the asymmetric hydrogenations of acetophenone and its derivatives in basic solution of *i*-PrOH. The modifier could not only enhance the enantioselectivity but also accelerate significantly the rate of the reaction. Furthermore, there is a synergistic effect between (1*S*,2*S*)-DPEN and KOH. Moreover, the catalyst exhibited steady catalytic performance when saved in normal temperature and dry conditions. The chiral alcohol products could be easily separated by centrifugation, while the catalyst could be recycled and reused several times.

4. Experimental

4.1. Material

Aromatic ketones, (1*R*,2*R*)-DMTFM-DPEN {(1*R*,2*R*)-(+)-*N*,*N*′-dimethyl-1,2-bis[3-(trifluoromethyl)phenyl-1,2-ethanediamine (P98%, Acros)}, (*S*)-BINAP [(*S*)-2,2′-bis (diphenylphosphino)-1,1′-binaphthyl], cinchonidine (P98%, TCI), L-tartaric acid (P99%, Aldrich), (*R*)-BNDN [(*R*)-(+)-2,2′-diamino-1,1′-binaphthalene], (1*S*,2*S*)-DPEN [(1*S*,2*S*)-1,2-diphenyl-ethylene-1,2-diamine], (1*R*,2*R*)-DPEN, (*S*,*S*)-T_SDPEN[(*S*,*S*)-*N*-*p*-methylphenyl-sulfonyl-1,2-diphenyl-1,2-ethanediamine], (1*R*,2*R*)-DACH[(1*R*,2*R*)-(−)-1,2-diaminocyclohexane] (Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, China), and $RuCl_3{\cdot}3H_2O$ (Institute of Kunming Noble Metals, China) were used as received without further purification. Triphenylphosphine(PPh_3) and other reagents were of analytical grade. The purity of hydrogen was 99.99%. The surface area of γ-Al_2O_3 was 154 $m^2\ g^{-1}$. TPPTS [tris(*m*-sodium sulfonatophenyl) phosphine], TDMOPP [tri-(3,4-bismethoxy-phenyl) phenylphosphine], TFMTPP [tri-(4-trifluoromethyl-phenyl) phenylphosphine] BISBI [2,2′-bis (diphenylphosphinomethyl)-1,1′-biphenyl], and OTPP [oxygenated triphenylphosphine] were synthesized according to known methods in our laboratory.[23,24]

4.2. Preparation and determination of supported Ru catalyst

Ru-PPh_3/γ-Al_2O_3 was prepared according to the literature procedure:[25] A solution of $RuCl_3$ aqueous (3.0 mL, 0.1 mmol) was added to 30 mL of deoxygenated *i*-PrOH, and then 1.0 g γ-Al_2O_3 had been added. The resulting mixture was stirred for 15 h at room temperature. After 0.24 mmol of triphenylphosphine was added, the solution was refluxed at 110 °C for 5 h, and then the solid (Ru/γ-Al_2O_3) was filtered and dried under vacuum. The catalyst was abbreviated as 1.0% Ru-PPh_3/γ-Al_2O_3. The TEM of Ru-PPh_3/γ-Al_2O_3 was examined using a JEM-2010 microscope operating at an accelerating voltage of 200 kV. XPS spectra were recorded with a XSAM800 photoelectron spectrometer using monochromatic Mg Kα X-ray 1486.6 eV and binding energies were referred to C1s 284.8 eV.

4.3. Asymmetric hydrogenation of aromatic ketones

To a 60 mL stainless autoclave with a glass liner and magnetic stirrer were added the desired amount of catalyst, KOH, (1*S*,2*S*)-DPEN, isopropanol, and substrate. Hydrogen was introduced at the desired pressure after the reaction mixture had been purged with H_2 five times. The reaction was carried out under the designed conditions. At the end of the reaction, the catalyst was separated by means of centrifugation. The reaction equation is shown in Figure 1.

The products were analyzed by GC960 with a FID detector and a β-CD™ chiral capillary column (30 m × 0.25 mm, 0.15 μm, Supelco). With the exception of aromatic alcohol, no other products were detected. Enantiomeric excess (ee) was calculated according

to the following equation: ee (%) = 100[(C(R) − C(S))/(C(R) + C(S))], where C is the concentration of (R) or (S).

(R)-(+)-1-Phenylethanol: $[\alpha]_D^{24} = +38.5$ (c 1.12, CH_2Cl_2), 77.7% ee, (R); column temperature: 115 °C, $t_R(R)$ = 12.6 min, $t_R(S)$ = 13.3 min.

(R)-(+)-1-Phenylpropanol: $[\alpha]_D^{24} = +22.6$ (c 1.23, C_2H_5OH), 78.0% ee, (S); column temperature: 120 °C, $t_R(R)$ = 16.3 min, $t_R(S)$ = 16.8 min.

(R)-(+)-1-(2′-Fluorophenyl)ethanol: $[\alpha]_D^{24} = +21.7$ (c 1.36, $CHCl_3$), 44.3% ee, (R); column temperature: 110 °C, $t_R(R)$ = 15.7 min, $t_R(S)$ = 17.4 min.

(R)-(+)-1-(2′-Bromophenyl)ethanol: $[\alpha]_D^{24} = +29.3$ (c 1.24, $CHCl_3$), 43.7% ee, (R); column temperature: 140 °C, $t_R(R)$ = 21.2 min, $t_R(S)$ = 26.5 min.

(S)-(−)-1-(2′-Methoxyphenyl)ethanol: $[\alpha]_D^{24} = -10.3$ (c 1.65, $CHCl_3$), 33.4% ee, (S); column temperature: 135 °C, $t_R(R)$ = 15.9 min, $t_R(S)$ = 16.8 min.

(R)-(+)-1-(4′-Methoxyphenyl)ethanol: $[\alpha]_D^{24} = +38.6$ (c 1.13, $CHCl_3$), 74.6% ee, (R); column temperature: 115 °C, $t_R(R)$ = 20.6 min, $t_R(S)$ = 21.5 min.

(R)-(+)-1-(4′-Trifluoromethylphenyl)ethanol: $[\alpha]_D^{24} = +27.5$ (neat), 73.6% ee, (R); column temperature: 120 °C, $t_R(R)$ = 13.0 min, $t_R(S)$ = 14.6 min.

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