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Aerobic oxidative kinetic resolution of racemic alcohols with bidentate ligand-binding Ru(salen) complex as catalyst

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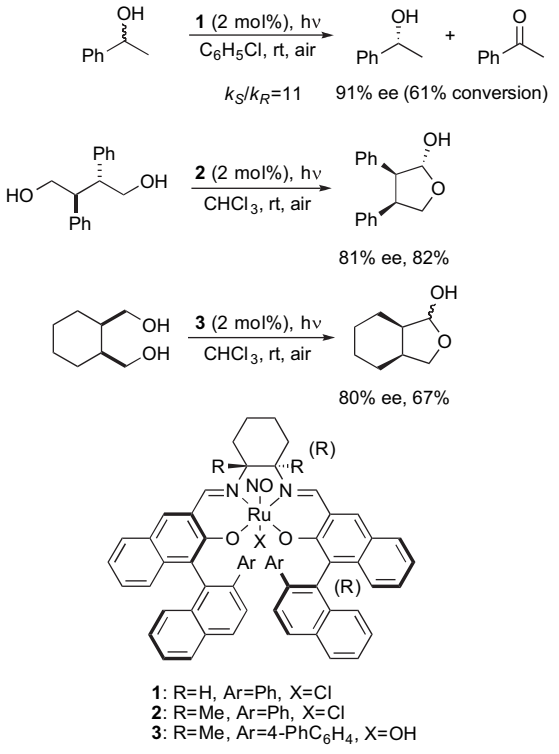
Abstract—Chiral Ru(salen)(nitrosyl) complex **1** is a useful catalyst for asymmetric aerobic oxidation of alcohols under photo-irradiation. In this study, it was found that addition of β-hydroxy ketone or 1,3-diketone had a significant influence on its asymmetric catalysis. For example, the addition of 1,3-bis(*p*-bromophenyl)propane-1,3-dione **9** improved the relative reaction ratio in kinetic resolution of simple racemic secondary alcohols up to 30, while the addition gave an adverse effect on desymmetrization of an acyclic *meso*-1,3-diol. This additive effect was considered to be attributable to the chelate formation of the β-hydroxy ketone or 1,3-diketone with a Ru(salen) complex.

1. Introduction

Oxidation of alcohols is of tremendous importance for organic synthesis and numerous methods have been developed. Although various oxidants have also been introduced, most of them are unsatisfactory from the viewpoint of atom economy and ecological sustainability, because their use produces waste co-products. Of various oxidants, molecular oxygen is the oxidant of choice, since the co-product is water.[1] Moreover, molecular oxygen in ambient air is ubiquitous and abundant. Thus, aerobic oxidation has been extensively studied but there is still a big room for improvement in aerobic oxidation of alcohols. In particular, the asymmetric version of aerobic oxidation is still immature and only a few examples of asymmetric aerobic oxidation have been reported to date.[2] We for the first time achieved aerobic oxidative kinetic resolution by using chiral (ON)-Ru(salen) complex **1** as the catalyst (Scheme 1).[2a] Subsequently, (ON)Ru(salen) complexes (**2** and **3**) bearing axial methyl groups at the cyclohexane moiety were found to serve as efficient catalysts for oxidative desymmetrization of *meso*-1,4-primary diols.[3] The following aspects of the reactions are unique: the oxidation is promoted by irradiation of visible light under ambient condition in the absence of any auxiliary activator such as a base or mediator. On the other hand, oxidative kinetic resolution has been well effected by using a Pd/sparteine/base system.[2d–h] Recently, efficient oxidative kinetic resolution of racemic α-hydroxy esters using molecular oxygen under atmospheric pressure has been achieved by using a vanadium–Schiff base complex as catalyst.[2i]



Scheme 1. Ru(salen) complexes used as catalyst for aerobic asymmetric oxidation.

Oxidative desymmetrization of *meso*-1,3-diols is a useful method for synthesizing β-hydroxy ketones that are a sub-unit seen in various natural products such as acetogenins. Sigman and co-workers have reported that

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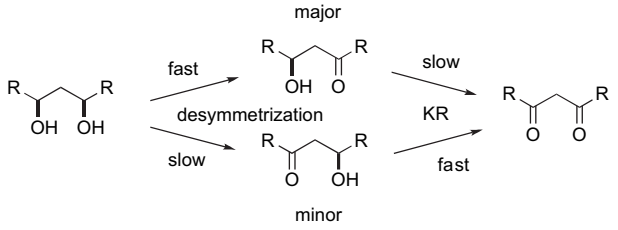
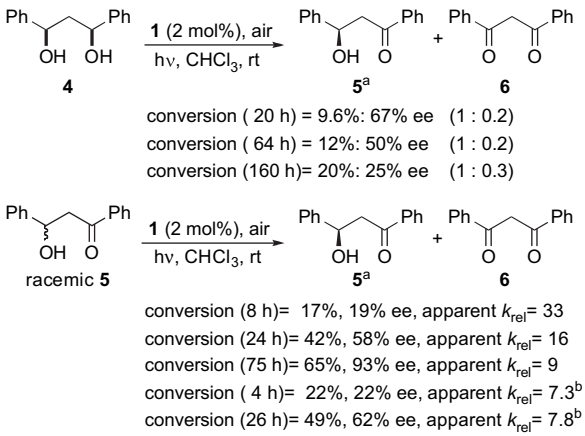
desymmetrization of *meso*-1,3-diols can be effected with good enantioselectivity by using the Pd/sparteine/base/molecular oxygen system.[2d,f] Our recent study indicated that complex **1** is not the best catalyst for oxidative desymmetrization of *meso*-diols.[3c] However, we expected that desymmetrization of *meso*-1,3-diols using complex **1** as catalyst would give the corresponding β-hydroxy ketones with high enantiomeric excess, if the minor enantiomer of the resultant β-hydroxy ketones is consumed in preference to the major isomer in the second oxidation (Scheme 2).[4] Contrary to our expectation, the desymmetrization gave a disappointing result, but it led us to a new oxidation system. In this paper, we describe improvement of a Ru(salen) catalyst based on the unexpected result and aerobic oxidative kinetic resolution of racemic secondary alcohols with the improved catalyst.



Scheme 2. An expected reaction pathway of aerobic oxidation of *meso*-1,3-diols: *meso*-trick strategy.

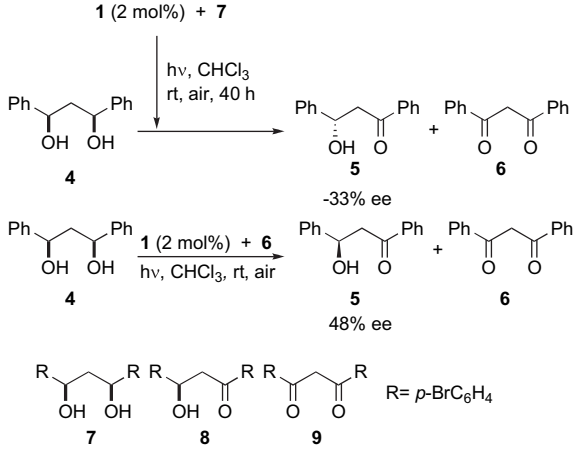
2. Results and discussion

We examined oxidative desymmetrization of *meso*-1,3-diphenylpropane-1,3-diol **4** using 2 mol % of **1** in anticipation of the so-called '*meso*-trick'. Contrary to our expectation, the enantiomeric excess of the resultant β-hydroxy ketone **5** diminished over the reaction time (Scheme 3). In addition, the reaction was much slower than the oxidation of simple secondary alcohols.[2a] These results seemed explicable, given that the hydroxy ketone yielded in the first step remains coordinated to the ruthenium ion and the major enantiomer can be oxidized to the 1,3-diketone preferentially in the second step. We next examined the oxidative kinetic resolution of the racemic **5**, and it was observed that the enantiomer corresponding to the minor isomer of the oxidative desymmetrization was oxidized preferentially. However, the relative reaction ratio (k_{rel}) also diminished, as the reaction proceeded. On the other hand, alteration in k_{rel} and enantioselectivity has not been observed in both oxidative kinetic resolution of simple racemic secondary alcohols[2a] and oxidative desymmetrization of *meso*-1,4-diols,[3] in which the products are mono-dentate ketones and lactols, respectively. Thus, the decrease of the stereoselectivity observed in the present desymmetrization and kinetic resolution was considered to be attributable not only to a slow exchange of the hydroxy ketone but also to the bidentate nature of the products. Since both desymmetrization of **4** and kinetic resolution of racemic **5** produced bidentate 1,3-diketone **6**, we examined kinetic resolution of racemic **5** using **1** pre-treated with **6**, as catalyst. Although both **1** and the pre-treated **1** showed the same sense of enantiomer differentiation, the oxidation with the pre-treated **1** was ca. twice as fast as that with **1**. Moreover, the k_{rel} value in the reaction using the pre-treated **1** as the catalyst scarcely changed, while the value was much smaller than that observed with **1** at the early stage of the kinetic resolution. This result suggested that, in the kinetic resolution of **5**, complex **1** gradually changed to a new catalyst that might be equal to the pre-treated **1**. We also examined a consecutive oxidation of 1,3-di(*p*-bromophenyl)propane-1,3-diol **7** and **4** in one pot (Scheme 4). At first, **7** was oxidized under the standard condition for 40 h to give a mixture containing **7** (61%), hydroxy ketone **8** [32% (43% ee)], and diketone **9** (7%), followed by the addition of **4** to the reaction mixture. After being stirred for another 1 h, the mixture was worked up and the ee of **5** was determined to be −33% ee. On the other hand, the oxidation of **4** using the **1** pre-treated with diketone **6** showed 48% ee at 8% conversion. This result meant that the resultant β-hydroxy ketone also affected the stereochemistry of the oxidative desymmetrization. If the coordination of bidentate product(s) is responsible for the unusual stereochemistry observed in the oxidative desymmetrization of **4** as described above, the oxidative desymmetrization of *meso*-indan-1,3-diol **10** that gives the corresponding mono-dentate β-hydroxy ketone **11** and diketone **12** was considered to show the stereochemistry as

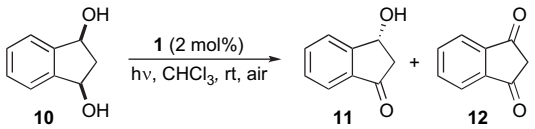


a) The ee of **5** was determined by HPLC analysis using Daicel Chiralcel OD-H .
b) The reaction was carried out with **1** pre-treated with **6**.

Scheme 3. Oxidative desymmetrization of **4** and kinetic resolution of racemic **5** using **1** or the pre-treated **1**.



Scheme 4. Consecutive oxidation of **7** and **4** using **1** as catalyst, and oxidative kinetic resolution of **4** using the pre-treated **1** as catalyst.



Scheme 5. Oxidative desymmetrization of *meso*-indan-1,3-diol **10**.

exhibited in Scheme 2. Indeed, the ee of the resultant **11** increased as the reaction proceeded: 71% ee at 43% conversion (**11**:**12**=1:0.13) and 77% ee at 69% conversion (**11**:**12**=1:0.19) (Scheme 5).

It is well known that a metallosalen complex adopts a cis-β configuration, on chelation of a bidentate ligand.[5,6] Moreover, recent studies by us and others have revealed that *cis*-β metallosalen complexes show unique asymmetric catalysis.[6] In particular, *cis*-β metallosalen complexes bearing the same salen ligand as complex **1** showed high enantioselectivity in the oxidation of simple sulfides and ketones.[7] From the above described results, we expected that complex **1** pre-treated with a suitable bidentate ligand might serve as an efficient catalyst for oxidative kinetic resolution of simple racemic alcohols. Thus, we examined the kinetic resolution of racemic 1-phenylethanol **13** using **1** pre-treated with a 1,3-diketone or a β-hydroxy ketone, as catalyst (Table 1).[8] The k_{rel} value of the kinetic resolution using complex **1** is 11 (entry 1).[2a] The k_{rel} was enhanced to 15 by using the complex **1** pre-treated with 1,3-diketones **6**, without reducing the reaction rate (entry 2).[9] Although the kinetic resolution using **1** as catalyst was well effected in chlorobenzene,[2a] it was found that kinetic resolution using the pre-treated **1** was better performed in chloroform. Consequently, the following reactions were performed in chloroform. Pre-treatment with (*S*)- or (*R*)-**5** resulted in further enhancement of the k_{rel} values to 33 or 21 at the early stages of the reactions, respectively (entries 3–6). However, both the values diminished to 14, as the reactions proceeded. Therefore, we examined the pre-treatment with various 1,3-diketones and the best value of 19 was attained when 1,3-bis(*p*-bromophenyl)propane-1,3-dione **9** was added (entry 7). It should be noted that the reduction of k_{rel} values was not observed during the reactions, when **1** was pre-treated with a 1,3-diketone.

Oxidative kinetic resolution of various racemic secondary alcohols was also examined with complex **1** pre-treated with **9** and the improvement (up to 30) of the k_{rel} values was observed (Table 2).

Our recent kinetic study on the aerobic oxidation of alcohols with a Ru(salen) complex under irradiation disclosed that oxidation of mono-ols includes three steps, a single electron transfer (SET), an intramolecular hydrogen-atom transfer (HAT) from the α-carbon of the alkoxide to the phenolic oxygen atom of the ligand, and ligand exchange (Scheme 6).[3c] The present results suggested that pre-treatment of **1** with a β-hydroxy ketone or a 1,3-diketone under irradiation gives an addition product **A**.[10] It is known that metal alkoxide makes a hydrogen-bond with alcohol, and it is likely that the irradiation of **A** in the presence of alcohol gives a cation radical species (**B**) carrying the alcohol, which undergoes an

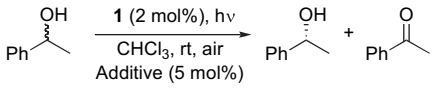
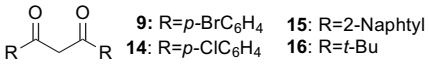


Table 1. Aerobic oxidative KR of racemic 1-phenylethanol **13**

Entry	Additive	Time (h)	Conv. (%)[a]	ee (%)[b]	k_{rel}
1	—	7	41	50	11 (±1)[c]
2	**6**	10	62	97	15 (±1)
3	(*S*)-**5**[d]	8	37	53	33 (±1)
4	(*S*)-**5**[d]	14	59	93	14 (±1)
5	(*R*)-**5**[d]	5	28	34	21 (±1)
6	(*R*)-**5**[d]	13	53	80	14.5 (±1)
7	**9**	12	61	98	19 (±1)
8	**14**	10	60	95	16 (±1)
9	**15**	12	62	97	15 (±1)
10	**16**	10	62	97	15 (±1)

[a] Determined by GLC analysis using optically active column (SPELCO BETA-DEX-325).
[b] Determined by HPLC analysis using chiral stationary phase column (Daicel Chiralcel OB-H; hexane/*i*PrOH=49:1).
[c] The reaction was carried out in chlorobenzene (Ref. 2a).
[d] Both the enantiomeric excesses of (*R*)- and (*S*)-**5**s are 97.5% ee.



intramolecular hydrogen-atom transfer and subsequently dissociates the resultant carbonyl compound (Scheme 7). Further coordination of substrate alcohol to the sterically crowded ruthenium complex (**A**) is unlikely and, moreover, the coordination giving (**C**) formally violates the 18-electron rule. Although the participation of a trans- or cis-β[11] species **D** (Fig. 1), in which the bidentate ligand partially dissociates, cannot be completely ruled out, it is also considered unlikely by the present experimental results (cf. Schemes 3 and 5). However, further study is required to conclude the mechanism of the present oxidation.

In conclusion, we have disclosed that addition of an acyclic β-hydroxy ketone or 1,3-diketone to Ru(salen) complexes changed their catalytic performance for asymmetric aerobic

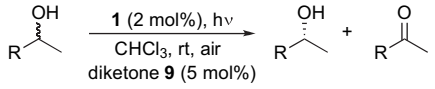
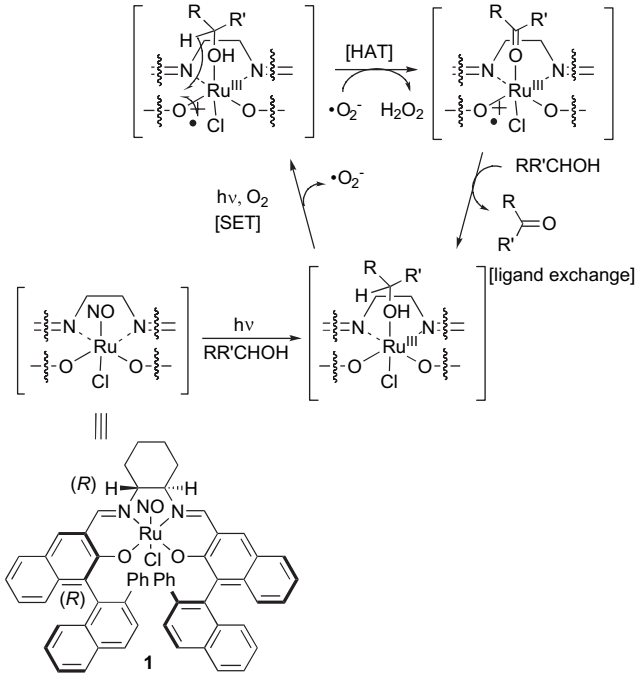


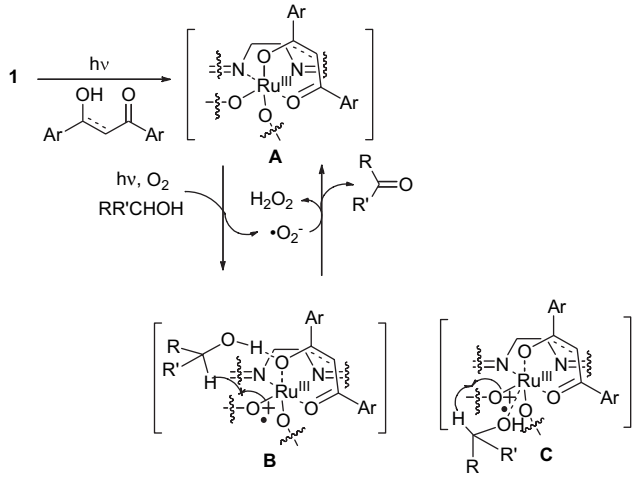
Table 2. Aerobic oxidative KR of simple racemic secondary alcohol in the presence of diketone **9**

Entry	Substrate R=		Time (h)	Conv. (%)[a]	ee (%)	k_{rel}[b]
1	PhC≡C	**17**	10	58	99[c]	30 (±2) [20]
2	(*E*)-PhCH=CH	**18**	9	54	82[c]	14 (±1) [11]
3	4-ClC$_6$H$_4$	**19**	9	57	95[d]	23 (±1)
4	4-BrC$_6$H$_4$	**20**	9	54	90[d]	22 (±1)
5	PhCH$_2$	**21**	11	41	55[e]	15 (±1) [11]

[a] Determined by GLC analysis using optically active column (SPELCO BETA-DEX-325).
[b] The value observed in the absence of diketone **9** was taken from Ref. 3a and is shown in parentheses.
[c] Determined by HPLC analysis using chiral stationary phase column (Daicel Chiralcel OD-H; hexane/*i*PrOH=19:1).
[d] Determined by HPLC analysis using chiral stationary phase column (Daicel Chiralcel OB-H; hexane/*i*PrOH=24:1).
[e] Determined by HPLC analysis using chiral stationary phase column (Daicel Chiralpak IA; hexane/*i*PrOH=99:1).



Scheme 6. The mechanism of the oxidation of alcohols using **1** as catalyst. The salen ligand is omitted for clarity, except for their donor atoms.



Scheme 7. Proposed mechanism for the oxidation of alcohols using **1** in the presence of a bidentate ligand. The salen ligand is omitted for clarity, except for their donor atoms.

oxidation of alcohols and the addition showed a significant positive effect on oxidative kinetic resolution of simple racemic secondary alcohols using complex **1** as catalyst.[12] The present study will open a new entry to further improvement of catalytic performances of Ru(salen) complexes.

3. Experimental

3.1. General

^{1}H and ^{13}C NMR spectra were recorded at 400 MHz on a JEOL JNM-AL 400 instrument. All signals were expressed as parts per million down field from tetramethylsilane used as an internal standard (δ value in $CDCl_3$). IR spectra were obtained with a SHIMADZU FTIR-8400 instrument. Optical rotations were measured with a JASCO P-1020 polarimeter. Column chromatography was conducted on silica gel 60N (spherical, neutral), 63–210 μm, available from Kanto Chemical Co., Inc. Preparative thin-layer chromatography was performed on 0.5 mm×20 cm×20 cm E. Merck silica gel plate (60 F-254). Conversions of alcohols were determined by GLC analysis using SHIMADZU GC-1700 and GC-17A with chiral capillary column chiral SUPELCO BET-DEX 325. Enantiomeric excesses were determined by HPLC analysis using SHIMADZU LC-10AT-VP with an appropriate optically active column, as described in the footnotes to the corresponding tables. Ru(salen) complex **1**,[13] *rac*-secondary alcohols, (3*R*)- and (3*S*)-1,3-diphenyl-3-hydroxypropan-1-one **5**,[14] and 1,3-diketone derivatives (**6**, **9**, and **14**–**16**)[15] were prepared according to the literature procedures. All the reagents and the solvents were carefully dried immediately before use.

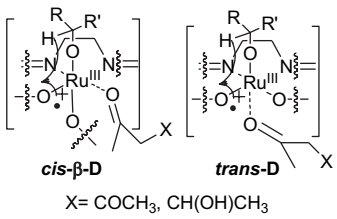


Figure 1. Non-chelated cation radical species.

3.2. General procedure for kinetic resolution of *rac*-secondary alcohols using Ru(salen) complex 1 pre-treated with 1,3-bis(*p*-bromophenyl)propane-1,3-dione 9

Ru(salen) complex **1** (2.0 mg, 2.0 μmol) and diketone **9** (1.9 mg, 5.0 μmol) were dissolved in 1.0 mL of $CHCl_3$ and stirred over 1 h under photo-irradiation with a halogen lamp. To this solution was added *rac*-secondary alcohol (0.1 mmol) and bicyclohexyl (19 μl, 0.10 mmol) as an internal standard for GLC analysis. An aliquot (80 μl) of this solution was taken out of the flask as a zero point and passed through a pad of silica gel (hexane/ethyl acetate=8:2). The filtrate was submitted to GLC analysis to adjust the molar ratio. The remnant solution was stirred at room temperature under irradiation in air and aliquots (100 μL) of the solution were then periodically taken via a syringe. After passing through a pad silica gel, the samples were then analyzed using a GC and HPLC equipped with a chiral column to determine the conversion of alcohol and the enantiomeric excesses of the unreacted alcohols, respectively. The k_{rel} was then calculated according to Kagan's equation.

3.2.1. (*R*)-1-Phenylethanol (13). Colorless oil; conversion=47%, 71% ee; $[\alpha]_D^{21}$ +35.9 (*c* 0.367, $CHCl_3$) [lit.[16] $[\alpha]_D^{23}$ +48.6 (*c* 1.0, CH_2Cl_2), (*R*)-configuration, 96% ee]; ^{1}H NMR ($CDCl_3$): δ 7.38–7.24 (m, 5H), 4.95–4.87 (m, 1H), 1.50 (d, 3H, *J*=6.4 Hz).

3.2.2. (2*R*,3*E*)-4-Phenylbut-3-en-2-ol (17). Colorless solid; conversion=57%, 87% ee; $[\alpha]_D^{21}$ +26.0 (*c* 0.267, $CHCl_3$) [lit.[17] $[\alpha]_D^{20}$ +31.4 (*c* 1.38, $CHCl_3$), (*R*)-configuration, 98% ee]; ^{1}H NMR ($CDCl_3$): δ 7.43–7.16 (m, 5H), 6.57 (d, 1H, *J*=15.9 Hz), 6.26 (dd, 1H, *J*=6.6, 15.9), 4.55–4.45 (m, 1H), 1.38 (d, 3H, *J*=6.4 Hz).

3.2.3. (*R*)-4-Phenylbut-3-yn-2-ol (18). Colorless oil; conversion=54%, 94% ee; $[\alpha]_D^{22}$ +34.8 (*c* 0.40, $CHCl_3$) [lit.[18] $[\alpha]_D^{21}$ 36.68 (*c* 0.81, $CHCl_3$), (*R*)-configuration, >99% ee]; ^1H NMR ($CDCl_3$): δ 7.46–7.40 (m, 2H), 7.34–7.29 (m, 3H), 4.76 (quintet, 1H, *J*=6.6 Hz), 1.56 (d, 3H, *J*=6.6 Hz).

3.2.4. (*R*)-1-(*p*-Bromophenyl)ethanol (19). Colorless oil; conversion=59%, 98% ee; $[\alpha]_D^{22}$ +39.8 (*c* 0.375, $CHCl_3$) [lit.[19] $[\alpha]_D^{25}$ −37.9 (*c* 1.13, $CHCl_3$), (*S*)-configuration, >99% ee]; ^1H NMR ($CDCl_3$): δ 7.47 (d, 2H, *J*=8.8 Hz), 7.25 (d, 2H, *J*=8.8 Hz), 4.92–4.83 (m, 1H), 1.47 (d, 3H, *J*=6.4 Hz).

3.2.5. (*R*)-1-(*p*-Chlorophenyl)ethanol (20). Colorless oil; conversion=61%, 99% ee; $[\alpha]_D^{21}$ +47.6 (*c* 0.125, $CHCl_3$) [lit.[20] $[\alpha]_D^{20}$ −48.8 (*c* 3.13, $CHCl_3$), (*S*)-configuration, 99% ee]; ^1H NMR ($CDCl_3$): δ 7.38–7.19 (m, 4H), 4.93–4.85 (m, 1H), 1.48 (d, 3H, *J*=6.6 Hz).

3.2.6. (*R*)-3-Phenyl-propan-2-ol (21). Colorless oil; conversion=46%, 65% ee; $[\alpha]_D^{22}$ −24.3 (*c* 0.292, $CHCl_3$) [lit.[21] $[\alpha]_D^{15}$ +39.7 (*c* 0.515, $CHCl_3$), (*S*)-configuration, >99.9% ee]; ^1H NMR ($CDCl_3$): δ 7.35–7.19 (m, 5H), 4.08–3.98 (m, 1H), 2.80 (dd, 1H, *J*=4.7, 13.6 Hz), 2.69 (dd, 1H, *J*=8.2, 13.6 Hz), 1.26 (d, 3H, *J*=6.1).

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