Tetrahedron 69 (2013) 8360–8367

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Cyclodextrin–[$RuCl_2$(Arene)]$_2$ conjugates: another way to enhance the enantioselectivity of aromatic ketones reduction by aromatic ligands' volume

Hai-Min Shen, Hong-Bing Ji *

School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, China

ARTICLE INFO

Article history:
Received 18 April 2013
Received in revised form 14 July 2013
Accepted 22 July 2013
Available online 31 July 2013

Keywords:
Cyclodextrin
Artificial metalloenzyme
Asymmetric hydrogenation
Enantioselectivity
Ligand's volume

ABSTRACT

Eight amino alcohol-modified β-CDs CD-1–CD-8 have been synthesized in acceptable yields and were employed to form artificial metalloenzymes with [$RuCl_2$(Benzene)]$_2$ and [$RuCl_2$(Mesitylene)]$_2$, respectively. All the conformations of CD-1–CD-8, the complexes between CD-1–CD-8 and [$RuCl_2$(Arene)]$_2$, and the inclusion complexes between CD-1–CD-8 and acetophenone were characterized by UV, ^{1}H NMR, ^{1}H ROESY NMR, and quantum calculation. The catalytic activity of the formed artificial metalloenzymes in the asymmetric hydrogenation of aromatic ketones, especially the effect of the aromatic ligands' volume on the enantioselectivity were investigated in detail, in which it was obvious that the enantioselectivity increased as the increase in the aromatic ligands' volume. For the best artificial metalloenzyme constructed from the complex between CD-8 and [$RuCl_2$(Mesitylene)]$_2$, which not only exhibits a good tolerance to a wide range of substrates but also demonstrates some substrate selectivity, 76.39% ee was obtained for acetophenone and 79.67% ee for 2-acetylnaphthalene. A strategy to improve the enantioselectivity in the asymmetric reactions catalyzed by the artificial metalloenzymes based on CDs has been provided.

1. Introduction

Cyclodextrins (CDs) obtained from enzymatic degradation of starch, are a family of water-soluble macrocyclic oligomers of D-(+)-glucopyranosyl units linked by α-1,4-glycosidic bonds, which possess a hydrophilic exterior and a hydrophobic cavity. Among them, three main members are known widely as α-CD, β-CD (Fig. 1), and γ-CD with six, seven, and eight glucose units, respectively.[1–4] Because of their hydrophilic exteriors and hydrophobic cavities, CDs can form inclusion complexes with a wide range of guest molecules possessing suitable shape and size in water like the hydrophobic pockets in enzymes, and catalyze or promote organic reactions through weak interactions between CDs and substrate molecules.[5–9] CDs have become important catalysts and additives in aqueous organic reactions. Modification of CDs expands the application of CDs in aqueous organic reactions, and a lot of artificial enzymes and artificial metalloenzymes were constructed based on CDs, especially β-CD for its ready availability in commerce.[10–14] In the artificial enzymes and artificial metalloenzymes based on CDs, the CDs units can function as the hydrophobic pockets in enzymes and form inclusion complex with the substrate molecule, thus the substrate molecule would be immobilized near the modifying groups of CDs, which play the role of catalytic active center. Hence, enhanced catalytic activity, obvious acceleration in reaction rate, and excellent regioselectivity can usually be achieved in the organic reaction catalyzed by the artificial enzymes and artificial metalloenzymes based on CDs, such as the cytochrome P-450 oxidase mimics reported by Breslow and co-workers,[15–18] the carotene dioxygenases mimics reported by French and co-workers,[19,20] the glutathione peroxidase mimics reported by Liu and Jin[21–25] and the hydrolase mimics reported by Mao.[26–30]

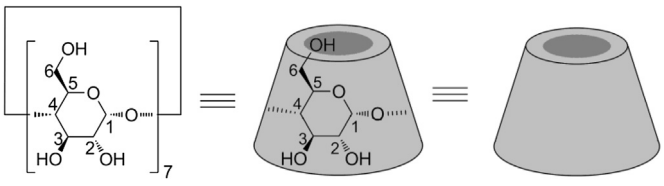


Fig. 1. Schematic structure of β-cyclodextrin (β-CD).

However, when applied in the asymmetric organic reaction, the artificial enzymes and artificial metalloenzymes based on CDs usually could not give so satisfactory results, such as the artificial

* Corresponding author. Tel.: +86 20 8411 3658; fax: +86 20 8411 3654; e-mail address: jihb@mail.sysu.edu.cn (H.-B. Ji).

0040-4020/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2013.07.077

metalloenzymes in the asymmetric oxidation of thioanisole reported by Bonchio and Sakuraba,[31,32] the ee just being 50–60%. We also have reported the asymmetric oxidation of thioanisole catalyzed by the artificial metalloenzymes formed by the complexation of β-CD derivatives CD-1–CD-7 (Fig. 2) and Na_2MoO_4 and just moderate ee (56%) was achieved.[33] With the aid of quantum calculation, the moderate enantioselectivity was ascribed to the two different binding models of CDs and thioanisole (Fig. 3), which existed concurrently. In model A, thioanisole conducted intramolecular catalytic oxidation giving the chiral product and in model B thioanisole conducted intermolecular catalytic oxidation giving the racemic product, resulting in the moderate ee. Thus in the asymmetric oxidation of thioanisole catalyzed by the complex of CD-5 and Na_2MoO_4, the ee just being 53% is rational.[33] But Schlatter had reported the complex of $[RuCl_2(Benzene)]_2$ and β-CD derivative CD-5 as artificial metalloenzyme to catalyze the asymmetric hydrogenation of prochiral aromatic and aliphatic ketones, higher ee were achieved, up to 77% for the substrate acetophenone,[34] which inspired us that besides CD-5, the existence of aromatic ligands of the metal ion might play a favorable role in the enhancement of the ee, because in the complex of CD-5 and Na_2MoO_4, the ligand of the metal ion was just CD-5. The existence of the aromatic ligands might increase the steric hindrance around the metal ion and prevent substrate from conducting intermolecular catalytic oxidation in model B.

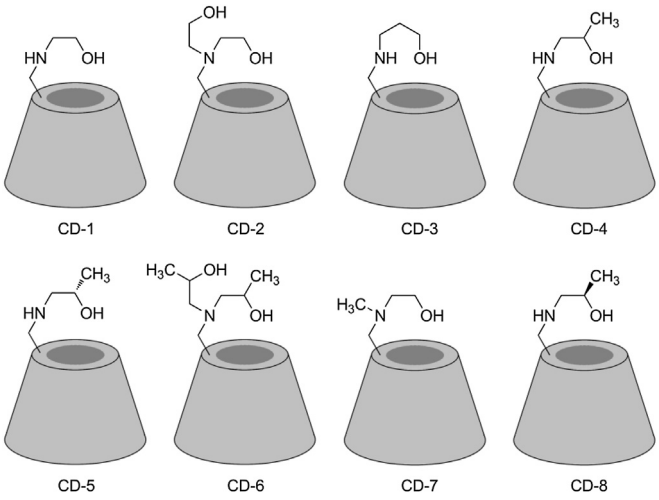


Fig. 2. Schematic structures of the amino alcohol-modified β-cyclodextrins (β-CDs).

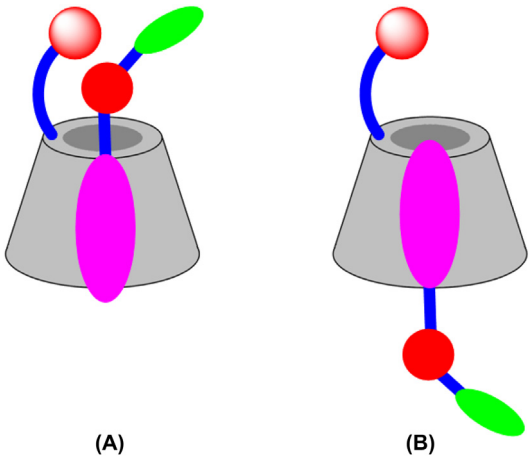


Fig. 3. Two schematic binding models for CD-1–CD-7 and thioanisole.

Thus, in order to investigate the effect of the aromatic ligands on the enantioselectivity in the asymmetric organic reaction, herein we employed the asymmetric hydrogenation of aromatic ketones as model reaction, used $[RuCl_2(Benzene)]_2$ and $[RuCl_2(Mesitylene)]_2$ (Fig. 4), which had different volume in aromatic ligands as precursor metal ion forming complex with CD-1–CD-8 to construct artificial metalloenzymes and investigated the effect of the aromatic ligands' volume on the enantioselectivity in the model reaction systematically. The formation of the complex between $[RuCl_2(Arene)]_2$ and CDs, the inclusion complex of aromatic ketones and CDs, and the reaction mechanism were also studied in detail, in which UV, ^1H NMR, ^1H ROESY NMR, and quantum calculation were employed. In addition, a practicable strategy to improve the enantioselectivity in the asymmetric reactions catalyzed by the artificial metalloenzymes based on CDs has been provided in this study, in which, besides the induction effect of the CDs, the enantioselectivity could also be enhanced through providing a secondary ligand for the metal ion and increasing its molecular volume, because of the increase in the steric hindrance around the metal ion.

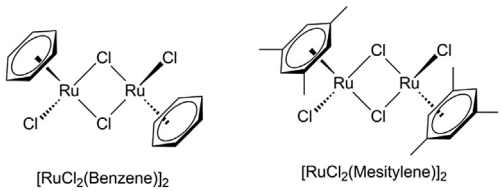
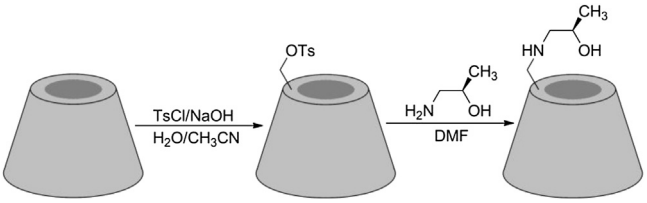


Fig. 4. Schematic structures of $[RuCl_2(Benzene)]_2$ and $[RuCl_2(Mesitylene)]_2$.

2. Results and discussion

2.1. Synthesis of CD-1–CD-8 and $[RuCl_2(Arene)]_2$

The synthesis of CD-1–CD-7 has been illustrated in our previous report,[33] and CD-8 was synthesized following the similar procedure illustrated in Scheme 1. Mono(6-*O*-*p*-tolylsulfonyl)-β-CD was synthesized by tosylation of β-CD with *p*-toluenesulfonyl chloride in basic aqueous solution according to literature procedure, which could be obtained in a large scale after filtration and washing with acetone and water.[35] Then CD-8 was smoothly synthesized by nucleophilic substitution of mono(6-*O*-*p*-tolylsulfonyl)-β-CD with an excess of (*R*)-1-amino-2-propanol at 80 °C in DMF. All of CD-1–CD-8 were characterized by ^1H NMR, ^{13}C NMR, ESIMS, and quantum calculation. When the conformation of CD-8 in aqueous solution was optimized by Gaussian 03 program at the level of B3LYP/6-31G(d)(Fig. 5),[36] the result is in good consistency with the conformations of CD-1–CD-7 as the modifying group pointing to the outside of the parent β-CD in their optimized conformations, which were due to the high solubility of the modifying groups in water.[33] To a certain extent, it could be concluded that when CD-8 combines with a metal ion without secondary ligand to form artificial metalloenzyme, the substrate might conduct intermolecular catalytic



Scheme 1. Schematic synthesis of the CD-8.

transformation in model B giving the racemic product, resulting in the moderate ee, because the modifying group pointing to the outside of the parent β-CD was the main origin for the intermolecular catalytic transformation of substrate in model B as reported in our previous study.[33]

H atoms in the modifying group of CD-8. In the ^{1}H NMR spectrum of the complex between CD-8 and $[RuCl_2(Benzene)]_2$, the chemical-shift of the H atoms in the modifying group shifted downfield by 0.43 ppm because of the effect of metal ion Ru and benzene. But at the same time, no obvious chemical-shift change was observed

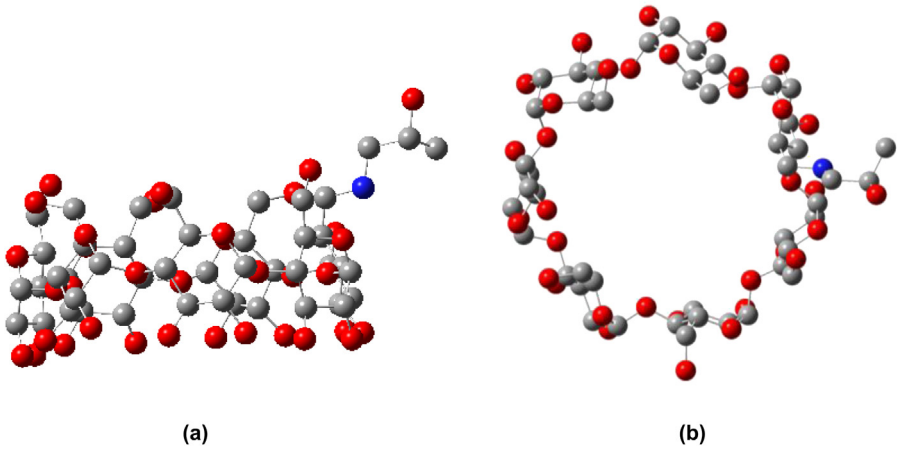


Fig. 5. Optimized conformation of CD-8 in aqueous solution (a, side view; b, vertical view) obtained at the level of B3LYP/6-31G(d).

$[RuCl_2(Benzene)]_2$ and $[RuCl_2(Mesitylene)]_2$ were synthesized according to literature procedure through refluxing the mixture of hydrated ruthenium(III) trichloride and 1,4-cyclohexadiene or 1,3,5-trimethylcyclohexa-1,4-diene in ethanol.[37] The brown precipitate was filtered off, washed with methanol, and dried in vacuum to give the target product in high purity.

2.2. Preparation and characterization of complexes between CD-1–CD-8 and $[RuCl_2$ -(Arene)$]_2$

With CD-1–CD-8 in hand, we prepared the complexes of CD-1–CD-8 and $[RuCl_2(Arene)]_2$ in situ prior to catalytic experiments by stirring CD-1–CD-8 and $[RuCl_2(Arene)]_2$ in the mixture of H_2O and DMF at 25 °C. The complexes of CD-1–CD-8 and $[RuCl_2(Arene)]_2$ were characterized by ^{1}H NMR studies (400 MHz, D_2O) and UV spectrum. The ^{1}H NMR spectra of CD-8 and its complex with $[RuCl_2(Benzene)]_2$ were shown in Fig. 6. Compared the two ^{1}H NMR spectra, significant chemical-shift changes were observed from the

from the H atoms belonged to the parent β-CD, which nearly remained at the same chemical-shift. Thus, it could be concluded that CD-8 formed complex with $[RuCl_2(Benzene)]_2$ mainly through its modifying group, the hydroxyls in the parent β-CD did not participate in the complexation with $[RuCl_2(Benzene)]_2$.

Besides ^{1}H NMR study, the formation of the complex between CD-8 and $[RuCl_2(Benzene)]_2$ has also been characterized by UV spectrum (Fig. 7). At the same concentration of $[RuCl_2(Benzene)]_2$ in the mixture of H_2O and DMF, when CD-8 was added, which had no obvious UV absorption to form complex with $[RuCl_2(Benzene)]_2$, an enhancement in UV absorption was observed, different from the UV absorption of $[RuCl_2(Benzene)]_2$. UV spectrum also provided an evidence for the formation of the complex between CD-8 and $[RuCl_2(Benzene)]_2$ to some extent. Based on the ^{1}H NMR study, UV spectrum and related literature,[34] the structure of complexes formed by CD-8 and $[RuCl_2(Benzene)]_2$ was surmised as shown in Fig. 8. CD-8 coordinated to the $[RuCl_2(Benzene)]_2$ through its modifying group, combining the catalytic active center and modified β-CD together, forming artificial metalloenzyme.

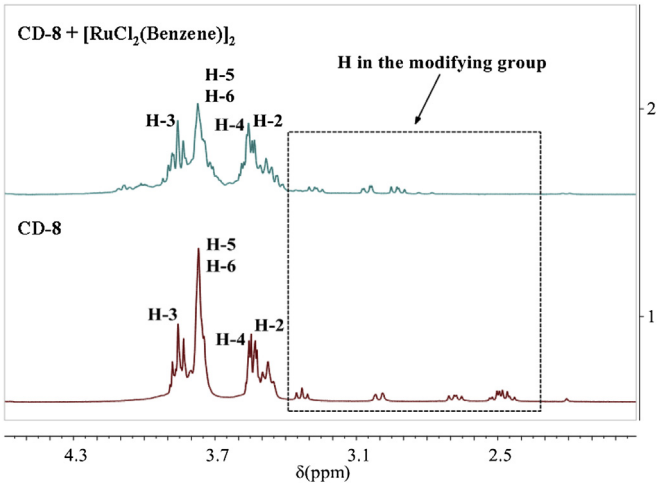


Fig. 6. ^{1}H NMR spectra of CD-8 and CD-8+$[RuCl_2(Benzene)]_2$ in D_2O.

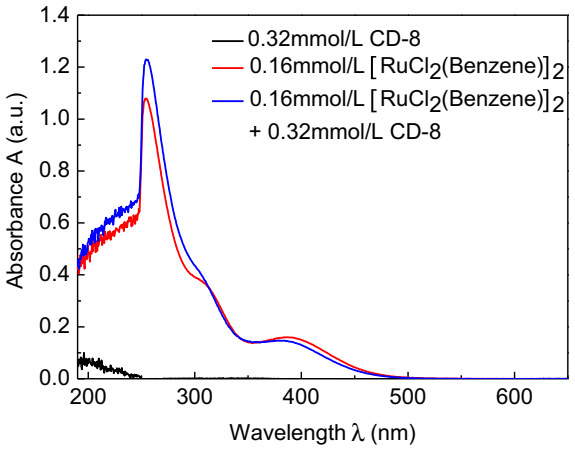


Fig. 7. UV absorption spectra of CD-8, $[RuCl_2(Benzene)]_2$, and CD-8+$[RuCl_2(Benzene)]_2$ in v_{H_2O}/v_{DMF} = 3 : 1.

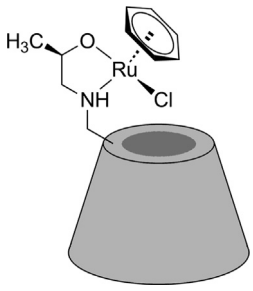


Fig. 8. Schematic structure of the complex between CD-8 and $[RuCl_2(Benzene)]_2$.

2.3. Preparation and characterization of the inclusion complexes between CD-1–CD-8 and aromatic ketones

The formation of inclusion complex is the critical step in the biomimetic catalysis based on artificial metalloenzyme constructed from CDs. In this study, the inclusion complexes between CD-1–CD-8 and aromatic ketones were prepared by stirring the mixture of CD-1–CD-8 and aromatic ketones in water and characterized by ^{1}H ROESY NMR and quantum calculation. Set CD-8 as example, the ^{1}H ROESY NMR spectrum of the inclusion complex between CD-8 and acetophenone was illustrated in Fig. 9. In Fig. 9, obvious correlation peaks between the H atoms located in the phenyl ring of acetophenone and the H-3, H-5 in the cavity of the parent β-CD could be observed, which illustrated the formation of inclusion complex between CD-8 and acetophenone. Meanwhile, there is no correlation peak observed between the H atoms located in the phenyl ring of acetophenone and the H-2, H-4 in the outside of the parent β-CD. Thus, in the inclusion complex of CD-8 and acetophenone, almost all the acetophenone molecules are included into the cavity of the parent β-CD, no acetophenone absorbed on the outside of the parent β-CD. But whether the inclusion complex between CD-8 and acetophenone had two binding models as shown in Fig. 3 could not be determined, for what the quantum calculation was employed to calculate the binding energy of CD-8 and acetophenone in model A and model B. The geometry of the inclusion complex between CD-8 and acetophenone was firstly optimized by Gaussian 03 program at the level of PM3, and then the output files were employed as input files for optimization at the level of ONIOM(B3LYP/6-31G(d):PM3), in which CD-8 and acetophenone were optimized at the level of PM3 and B3LYP/6-31G(d), respectively. And then the binding energy (*BE*) at the level of ONIOM(B3LYP/6-31G(d):PM3) was obtained according to Eq. 1:

$$BE = E[C]^{OPT}_{ONIOM} - E[H]^{OPT}_{PM3} - E[G]^{OPT}_{B3LYP/6-31G(d)} \quad (1)$$

where $E[C]^{OPT}_{ONIOM}$, $E[H]^{OPT}_{PM3}$, and $E[G]^{OPT}_{B3LYP/6-31G(d)}$ represented the total optimized energy of the inclusion complex at the level of ONIOM(B3LYP/6-31G(d):PM3), the free CD-8 at the level of PM3, and the free acetophenone at the level of B3LYP/6-31G(d).

The optimized geometry of the inclusion complex between CD-8 and acetophenone in model A and model B is shown in Fig. 10, and the binding energies in model A and B are −40.9452 kJ/mol and −45.0176 kJ/mol, respectively. The negative binding energy indicated the formation of inclusion complex between CD-8 and acetophenone is thermodynamically favorable and spontaneous. In addition, we also obtained that the difference in the binding energies between model A and B was just 4.0724 kJ/mol, a very low energy barrier. Two binding models exist in the inclusion complex of CD-8 and acetophenone simultaneously and can transform to each other freely. Thus, as reported in our previous study,[33] when CD-8 combines with a metal ion without secondary ligand to form artificial metalloenzyme, the substrate might conduct intermolecular catalytic transformation in model B giving the racemic product, just resulting in the moderate ee, because the modifying group of CD-8 pointing to the outside of the parent β-CD has been proved in the optimization of the conformation of CD-8 in aqueous solution employing quantum calculation.

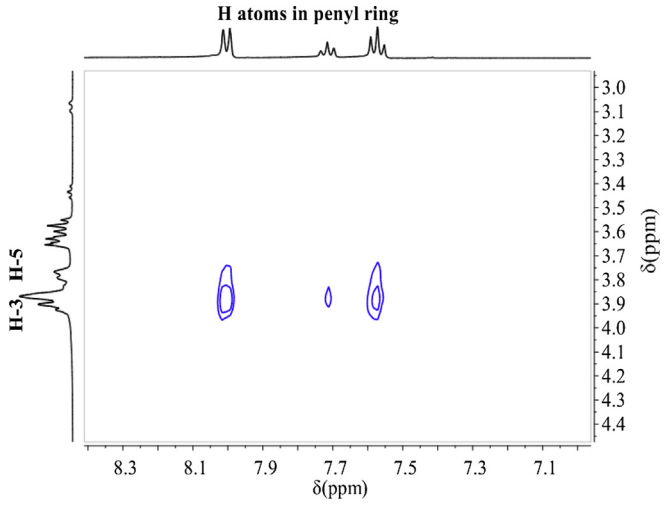


Fig. 9. Partial ^{1}H ROESY NMR spectrum of the inclusion complex formed by CD-8 and acetophenone in D_2O.

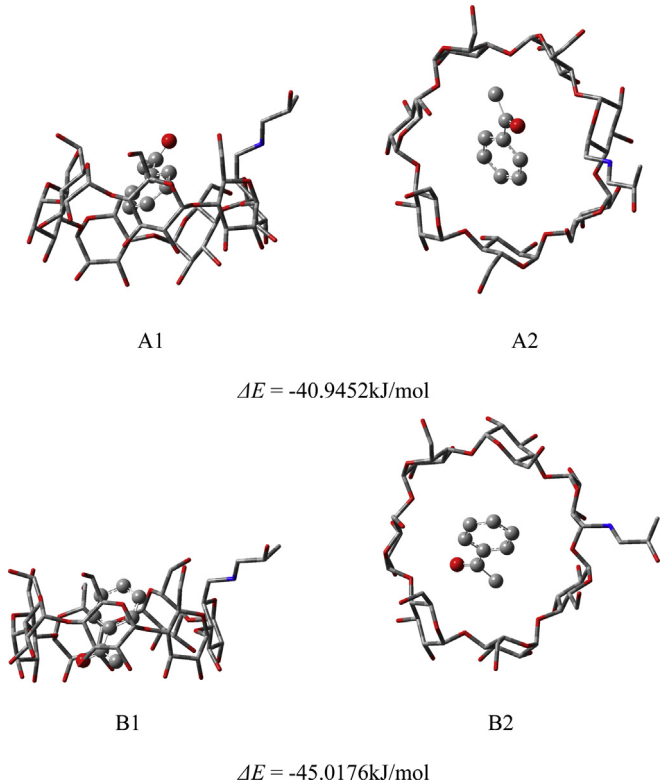


Fig. 10. Two optimized conformations of the inclusion complexes formed by CD-8 and acetophenone, and the binding energy (1: side view; 2: vertical view).

2.4. Asymmetric reduction of aromatic ketones

To evaluate the effect of the aromatic ligands on the enantioselectivity in the asymmetric organic reaction, the complexes between CD-1–CD-8 and $[RuCl_2(Benzene)]_2$ or $[RuCl_2(Mesitylene)]_2$ were applied to the asymmetric hydrogenation of aromatic ketones

as artificial metalloenzymes. And the effect of the aromatic ligands' volume on the enantioselectivity was our research focus. The results of the asymmetric hydrogenation of acetophenone were listed in Table 1. Obviously, the CDs play an important role in the catalytic property of the artificial metalloenzymes constructed from CD-1–CD-8 and $[RuCl_2(Benzene)]_2$ or $[RuCl_2(Mesitylene)]_2$. When CD-3, CD-6, and CD-7 were employed, the formed artificial metalloenzymes did not possess catalytic activity in the asymmetric hydrogenation of acetophenone. CD-2 being employed, the formed artificial metalloenzyme possessed catalytic activity, but no enantioselectivity being observed. Only when CD-1, CD-4, CD-5, and CD-8 were employed to form artificial metalloenzymes with $[RuCl_2(Benzene)]_2$ or $[RuCl_2(Mesitylene)]_2$, there were both expected catalytic activity and enantioselectivity being observed. Besides the effect of CDs on the catalytic activity and enantioselectivity, especially from the results of the artificial metalloenzymes based on CD-1, CD-4, CD-5, and CD-8, we also could observe the effect of the aromatic ligands' volume on the enantioselectivity in the asymmetric hydrogenation of acetophenone. The enantioselectivity increased as the aromatic ligands being changed from 'Benzene' to 'Mesitylene', which had larger molecular volume except for CD-5. Although it could not be applicable to all the CDs, for CD-1, CD-4, and CD-8, the enantioselectivity increased as the increase in the aromatic ligands' volume from 4.76% to 47.89%, 5.73% to 55.81%, and 30.26% to 76.39%, respectively, which could be attributed to the increase in the aromatic ligands' volume increased the steric hindrance around the metal ion and prevented substrate from conducting intermolecular catalytic hydrogenation in model B as shown in Fig. 11, which would give the racemic products. The experiment result about the relation between enantioselectivity and the aromatic ligands' volume is in good consistency with our speculation to some extent. Based on Table 1, the best artificial metalloenzyme in this study is the complex between CD-8 and $[RuCl_2(Mesitylene)]_2$, the ee being 76.39% for acetophenone.

Table 1
Effect of the aromatic ligands of Ru on the asymmetric reduction of acetophenone

Entry	CDs	Ru precursors	Conversion (%)	Yield (%)	ee (%)
1	CD-1	$[RuCl_2(Benzene)]_2$[a]	99.86	70.51	4.76[d]
		$[RuCl_2(Mesitylene)]_2$[b]	74.19	62.63	47.89[d]
2	CD-2	$[RuCl_2(Benzene)]_2$[a]	54.59	36.48	0.00
		$[RuCl_2(Mesitylene)]_2$[b]	54.51	46.36	0.00
3	CD-3	$[RuCl_2(Benzene)]_2$[a]	N.D.	<5	N.D.
		$[RuCl_2(Mesitylene)]_2$[b]	N.D.	<5	N.D.
4	CD-4	$[RuCl_2(Benzene)]_2$[a]	99.54	71.06	5.73[c]
		$[RuCl_2(Mesitylene)]_2$[b]	69.14	58.97	55.81[d]
5	CD-5	$[RuCl_2(Benzene)]_2$[a]	89.24	58.99	67.07[c]
		$[RuCl_2(Mesitylene)]_2$[b]	43.45	24.14	18.29[c]
6	CD-6	$[RuCl_2(Benzene)]_2$[a]	N.D,	<5	N.D.
		$[RuCl_2(Mesitylene)]_2$[b]	N.D.	<5	N.D.
7	CD-7	$[RuCl_2(Benzene)]_2$[a]	N.D.	<5	N.D.
		$[RuCl_2(Mesitylene)]_2$[b]	N.D.	<5	N.D.
8	CD-8	$[RuCl_2(Benzene)]_2$[a]	99.89	68.16	30.26[d]
		$[RuCl_2(Mesitylene)]_2$[b]	85.41	70.36	76.39[d]

Reaction conditions: acetophenone (0.2 mmol), modified CDs (0.02 mmol), Ru precursors (0.01 mmol), $HCOONa{\cdot}2H_2O$ (2.0 mmol) in the mixture of H_2O and DMF (v_{DMF}/v_{H_2O} = 1 : 1, 1.0 mL) at 25 °C.
The ee and absolute isomer were determined by HPLC analysis with a Chiralcel OD-H column and comparison of the eluting sequence of the enantiomers with the authentic sample.
[a] Reaction 24.0 h.
[b] Reaction 96.0 h.
[c] *S*-Isomer.
[d] *R*-Isomer.

Then the complex between CD-8 and $[RuCl_2(Mesitylene)]_2$ was employed as the best artificial metalloenzyme to catalyze the asymmetric hydrogenation of a variety of typical aromatic ketones

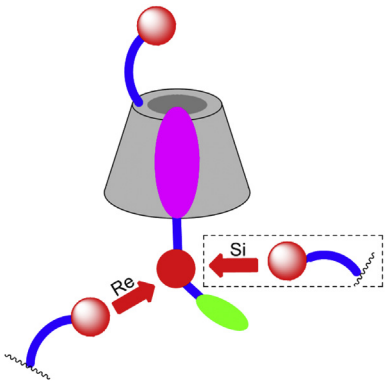
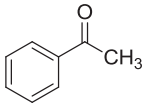
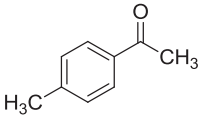
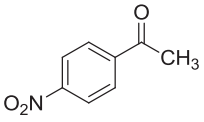
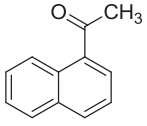
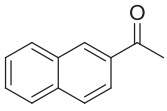
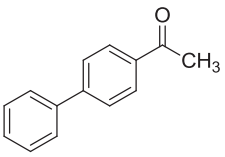


Fig. 11. Schematic intermolecular catalytic transformation of substrate in model B.

as shown in Table 2. The constructed artificial metalloenzyme not only exhibits a good tolerance to a wide range of substrates but also demonstrates some substrate selectivity. For 2-acetylnaphthalene, which has most suitable molecular shape and size, the highest ee in this study was obtained, 79.67%. The complex between CD-8 and $[RuCl_2(Mesitylene)]_2$ can be accounted as an effective artificial metalloenzyme in the asymmetric hydrogenation of aromatic ketones. In order to investigate the reaction mechanism, the control experiments were conducted as shown in Table 3. From Table 3, we

Table 2
The asymmetric reduction of typical aromatic ketones catalyzed by CD-8+$[RuCl_2(Mesitylene)]_2$

Entry	Ketones	Conversion (%)	Yield (%)	ee (%)	Configuration
1		85.41	70.36	76.39	*R*
2		76.25	67.33	75.51	*R*
3		72.44	53.39	60.94	*R*
4		47.71	39.21	73.69	*S*
5		75.79	63.68	79.67	*R*
6		49.88	28.49	76.61	*R*

Reaction conditions: aromatic ketones (0.2 mmol), CD-8 (0.02 mmol), $[RuCl_2(Mesitylene)]_2$ (0.01 mmol), $HCOONa{\cdot}2H_2O$ (2.0 mmol) in the mixture of H_2O and DMF (v_{DMF}/v_{H_2O} = 1 : 1, 1.0 mL) at 25 °C for 96.0 h. The ee and absolute isomer were determined by HPLC analysis with a Chiralcel OD-H or AS-H column and comparison of the eluting sequence of the enantiomers with the authentic sample.

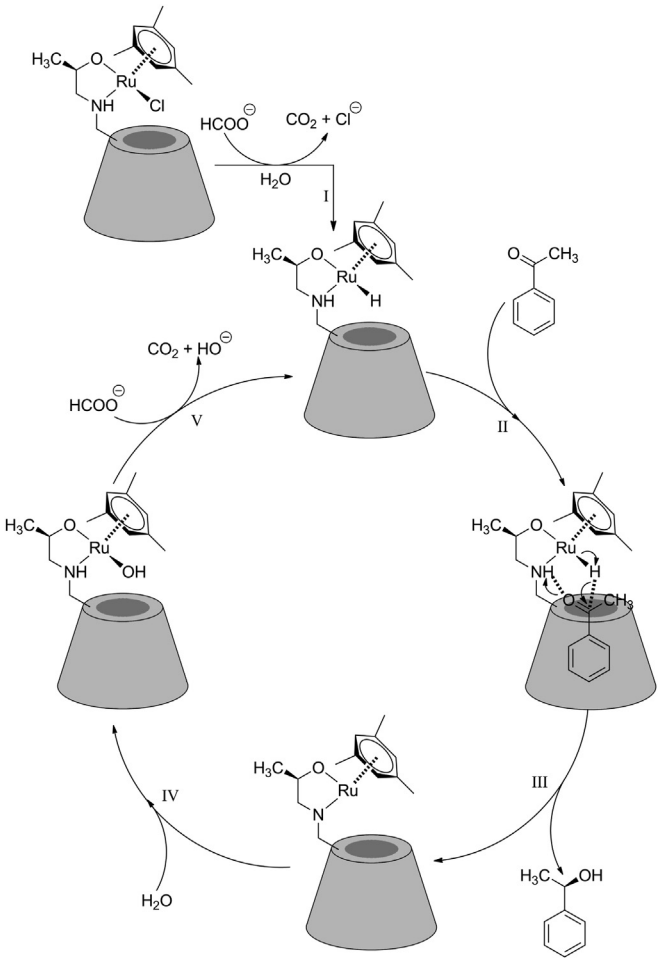
could see that it was necessary to attach (*R*)-1-amino-2-propanol to parent β-CD covalently, and then to form complex with [$RuCl_2$(-Mesitylene)]$_2$ to construct the effective artificial metalloenzyme in this study. Any one of [$RuCl_2$(Mesitylene)]$_2$, CD-8, the mixture of β-CD and [$RuCl_2$(Mesitylene)]$_2$, the mixture of (*R*)-1-amino-2-propanol and [$RuCl_2$(Mesitylene)], the mixture of β-CD, (*R*)-1-amino-2-propanol, and [$RuCl_2$(Mesitylene)]$_2$ could not catalyze the asymmetric hydrogenation of aromatic ketones effectively. The delicate cooperation between the modifying groups in CD-8, metal ion Ru, the aromatic ligand of Ru, and the hydrophobic cavity of the parent β-CD is the origin of the catalytic activity and the enantioselectivity in our constructed artificial metalloenzyme.

Table 3
Control experiments

Entry	Catalysts	Conversion (%)	Yield (%)	ee (%)
1	[$RuCl_2$(Mesitylene)]$_2$	N.D.	<2	N.D.
2	CD-8	N.D.	<0.2	N.D.
3	CD-8+[$RuCl_2$(Mesitylene)]$_2$	85.41	70.36	76.39[a]
4	β-CD+[$RuCl_2$(Mesitylene)]$_2$	N.D.	<2	N.D.
5	(*R*)-1-Amino-2-propanol+[$RuCl_2$(Mesitylene)]$_2$	50.46	38.01	39.56[a]
6	β-CD+(*R*)-1-Amino-2-propanol+[$RuCl_2$(Mesitylene)]$_2$	55.10	37.26	38.69[a]

Reaction conditions: acetophenone (0.2 mmol), catalyst (0.02 mmol), HCOONa·2H_2O (2.0 mmol) in the mixture of H_2O and DMF (v_{DMF}/v_{H_2O} = 1 : 1, 1.0 mL) at 25 °C for 96.0 h.
The ee and absolute isomer were determined by HPLC analysis with a Chiralcel OD-H column and comparison of the eluting sequence of the enantiomers with the authentic sample.
[a] *R*-Isomer.

At last, on the basis of our study and related literature,[34,38,39] the catalytic cycle in the asymmetric hydrogenation of aromatic ketones catalyzed by the complex between CD-8 and [$RuCl_2$(Mesitylene)]$_2$ was proposed as illustrated in Scheme 2: (1) activation and complexation of H from formate (I); (2) formation of inclusion complex between formed artificial metalloenzyme and substrate acetophenone in model A (II); (3) hydrogenation of substrate acetophenone and liberation of the generated product (III); (4) recovery of the coordination number for metal ion Ru (IV); (5) activation and complexation of H from formate (V). This is also the reaction mechanism and the origin of the catalytic activity and enantioselectivity in our study.



Scheme 2. Proposed catalytic cycle for complex between CD-8 and [$RuCl_2$(Mesitylene)]$_2$ in asymmetric hydrogenation of acetophenone.

3. Conclusion

In summary, eight amino alcohol-modified β-CDs CD-1–CD-8 have been synthesized to form artificial metalloenzymes with [$RuCl_2$(Benzene)]$_2$ and [$RuCl_2$(Mesitylene)]$_2$, respectively. And the formed artificial metalloenzymes being applied in the asymmetric hydrogenation of aromatic ketones, it was found that the enantioselectivity increased as the increase in the aromatic ligands' volume because the increase in the aromatic ligands' volume increased the steric hindrance around the metal ion and prevented substrate from conducting intermolecular catalytic hydrogenation in model B, which would give the racemic products. Among the constructed artificial metalloenzymes, the best one was the combination of CD-8 and [$RuCl_2$(Mesitylene)]$_2$, which not only exhibits a good tolerance to a wide range of substrates but also demonstrates some substrate selectivity, 76.39% ee being obtained for acetophenone and 79.67% ee for 2-acetylnaphthalene. A successful artificial metalloenzyme in the asymmetric hydrogenation of aromatic ketones was reported in our study. More importantly, a strategy to improve the enantioselectivity in the asymmetric reactions catalyzed by the artificial metalloenzymes based on CDs has been provided in this study too, which is, in addition to the CDs, providing a secondary ligand for the metal ion and increasing its molecular volume, because of the increase in the steric hindrance around the metal ion. Additionally, a strategy in the construction of artificial metalloenzymes also has been illustrated in our study through employing CDs to simulate the hydrophobic pockets in enzymes. At last, quantum calculation has been proved to be a powerful tool in the investigation of the supramolecular catalysts' conformation and their complexes with substrate.

4. Experimental

4.1. Materials and methods

β-CD in 99% purity was purchased from Shanghai Boao Biological Technology Co. Ltd., China. *p*-Toluenesulfonyl chloride, 3-amino-1-propanol, (*R*,*S*)-1-amino-2-propanol, (*S*)-1-amino-2-propanol, (*R*)-1-amino-2-propanol, 1,1′-iminodi-2-propanol, 2-methylamino-1-ethanol, and acetophenone in 98% purity were purchased from Aladdin. 2-Amino-1-ethanol and 2,2′-iminodiethanol of analytical grade were purchased from Tianjin Damao Chemical Reagent factory, China. (*R*)-1-Phenyethanol was obtained from Alfa Aesar. All the other common reagents were analytical grade. All of the reagents were used as received without further purification unless otherwise noted. NMR spectra were recorded on a Bruker Avance^{III} 400 spectrometer in DMSO-d_6 or D_2O. The quantum calculation was carried out by using Gaussian 03 program at the level of PM3 and B3LYP/6-31G(d). The ee value was determined by HPLC analysis (SHIMADZU

LC-20AT chromatography, UV–vis detector, 254 nm, Chiralcel OD-H or AS-H column, eluted with the mixture of *n*-hexane and isopropyl alcohol). The absolute configuration was determined by comparison of the eluting sequence of the enantiomers with the authentic sample.

4.2. Synthesis of mono[6-*O*-(*p*-toluenesulfonyl)]-β-CD

A solution of sodium hydroxide (6.0000 g, 150 mmol) in water (20 mL) was added dropwise to a solution of β-CD (56.7490 g, 50 mmol) in water (500 mL) with magnetic stirring at 10–15 °C over about 15 min. The solution became homogeneous, and then a solution of *p*-toluenesulfonyl chloride (11.4384 g, 60 mmol) in acetonitrile (30 mL) was added dropwise at 10–15 °C over about 45 min forming white precipitate immediately. The resultant solution was kept stirring for 3.0 h, and rose to room temperature. The precipitate formed was collected by suction filtration and then suspended in water (300 mL) with magnetic stirring at room temperature for 3.0 h. The precipitate collected by suction filtration was washed successively with acetone (100 mL) and water (160 mL), and then dried in vacuum at 80 °C for 8.0 h to afford white solid powder 8.1746 g in 12.68% yield.

$[\alpha]_D^{25}$ +124.15 (*c* 0.8044, DMF); mp>160 °C (decomp.); ^{1}H NMR (400 MHz, DMSO-d_6): δ=7.76 (d, *J*=8.3 Hz, 2H), 7.44 (d, *J*=8.2 Hz, 2H), 5.83–5.63 (m, 14H), 4.85–4.76 (m, 7H), 4.50–4.44 (m, 5H), 4.37–4.32 (m, 2H), 4.21–4.17 (m, 1H), 3.70–3.43 (m, 26H), 3.40–3.19 (m, 14H, overlaps with H_2O), 2.43 ppm (s, 3H); ^{13}C NMR (400 MHz, DMSO-d_6): δ=144.67, 132.53, 129.75, 127.44, 102.09–101.14 (m), 81.51–80.63 (m), 72.88–71.69 (m), 69.56, 68.76, 59.74–59.04 (m), 21.06 ppm; MS (ESI): *m*/*z*: 1311.3 $[M+Na]^+$, 1289.0 $[M+H]^+$.

4.3. Typical procedure for the synthesis of CD-1 to CD-8

A solution of mono[6-*O*-(*p*-toluenesulfonyl)]-β-CD (6.4459 g, 5 mmol) in amino alcohol (375 mmol) was stirred at 70 °C or 80 °C for 12.0 h, and then cooled to room temperature. Water (20 mL) was added to dilute the mixture, and resultant solution was poured into a mixture of acetone (200 mL) and ethanol (200 mL) slowly forming white precipitate immediately. The white precipitate was collected by suction filtration and recrystallized two times in water (2×10 mL), dried in vacuum at 80 °C for 8.0 h to afford white crystal.

CD-1: Yield: 60.15%; $[\alpha]_D^{25}$ +150.54 (*c* 0.8020, H_2O); mp>250 °C (decomp.); ^{1}H NMR (400 MHz, D_2O): δ=5.11–5.09 (dd, *J*=6.9, 3.4 Hz, 7H), 4.02–3.88 (m, 26H), 3.76–3.58 (m, 14H), 3.49–3.44 (m, 1H), 3.12–3.09 (m, 1H), 2.90–2.75 ppm (m, 4H); ^{13}C NMR (400 MHz, D_2O): δ=101.80, 101.40, 83.58, 81.11, 80.73, 73.06–72.90 (m), 72.05–71.77 (m), 70.47, 60.29–60.11 (m), 50.21, 49.25, 41.96 ppm; MS (ESI): *m*/*z*: 1200.5 $[M+Na]^+$, 1178.4 $[M+H]^+$.

CD-2: Yield: 42.68%; $[\alpha]_D^{25}$ +140.90 (*c* 0.8060, H_2O); mp>260 °C (decomp.); ^{1}H NMR (400 MHz, D_2O): δ=5.15–5.06 (m, 7H), 4.04–3.87 (m, 26H), 3.74–3.58 (m, 14H), 3.42 (t, *J*=9.3 Hz, 1H), 3.09–3.05 (m, 1H), 2.86–2.69 ppm (m, 8H); ^{13}C NMR (400 MHz, D_2O): δ=101.78, 100.95, 83.42, 81.11–80.87 (m), 80.27, 73.19–72.75 (m), 72.10–71.69 (m), 70.07, 60.37–60.09 (m), 59.57, 58.94, 55.96, 55.58, 49.62 ppm; MS (ESI): *m*/*z*: 1244.5 $[M+Na]^+$, 1222.4 $[[M+H]^+$.

CD-3: Yield: 55.48%; $[\alpha]_D^{25}$ +149.66 (*c* 0.8116, H_2O); mp>250 °C (decomp.); ^{1}H NMR (400 MHz, D_2O): δ=5.10 (t, *J*=3.1 Hz, 7H), 4.01–3.88 (m, 26H), 3.69–3.59 (m, 14H), 3.45 (t, *J*=9.3 Hz, 1H), 3.08 (d, *J*=11.1 Hz, 1H), 2.89–2.78 (m, 2H), 2.68 (t, *J*=7.3 Hz, 2H), 1.82–1.72 ppm (m, 2H); ^{13}C NMR (400 MHz, D_2O): δ=101.84, 101.39, 83.64, 81.10, 80.71, 73.07–72.93 (m), 72.05–71.76 (m), 70.28, 60.24–60.03 (m), 59.27, 49.45, 45.91, 31.07 ppm; MS (ESI): *m*/*z*: 1192.5 $[M+H]^+$.

CD-4: Yield: 50.21%; $[\alpha]_D^{25}$ +147.81 (*c* 0.4860, H_2O); mp>250 °C (decomp.); ^{1}H NMR (400 MHz, D_2O): δ=5.09 (t, *J*=3.6 Hz, 7H), 4.02–3.88 (m, 26H), 3.69–3.58 (m, 14H), 3.46 (t, *J*=9.4 Hz, 1H), 3.14–3.06 (m, 1H), 2.89–2.77 (m, 1H), 2.67–2.55 (m, 2H), 1.21–1.17 ppm (m, 3H); ^{13}C NMR (400 MHz, D_2O): δ=101.85, 100.34, 83.58, 81.21–81.02 (m), 80.68, 73.10–72.89 (m), 72.04–71.78 (m), 70.51, 70.23, 66.40, 65.75, 60.29–60.07 (m), 55.88, 55.52, 20.33, 20.09 ppm; MS (ESI): *m*/*z*: 1214.5 $[M+Na]^+$, 1192.4 $[M+H]^+$.

CD-5: Yield: 59.75%; $[\alpha]_D^{25}$ +151.07 (*c* 0.3248, H_2O); mp>250 °C (decomp.); ^{1}H NMR (400 MHz, D_2O): δ=5.10 (d, *J*=3.4 Hz, 7H), 4.02–3.88 (m, 26H), 3.69–3.59 (m, 14H), 3.48 (dd, *J*=21.4, 12.1 Hz, 1H), 3.08 (d, *J*=12.3 Hz, 1H), 2.90–2.84 (m, 1H), 2.66–2.60 (m, 2H), 1.19 ppm (d, *J*=6.3 Hz, 3H); ^{13}C NMR (400 MHz, D_2O): δ=101.84, 101.32, 99.00, 82.79, 81.15–80.66 (m), 73.04–72.87 (m), 72.03–71.78 (m), 65.61, 60.24, 55.44, 20.07 ppm; MS (ESI): *m*/*z*: 1214.5 $[M+Na]^+$, 1192.4 $[M+H]^+$.

CD-6: Yield: 36.86%; $[\alpha]_D^{25}$ +140.75 (*c* 0.1132, H_2O); mp>260 °C (decomp.); ^{1}H NMR (400 MHz, D_2O): δ=5.21–5.08 (m, 7H), 4.01–3.85 (m, 26H), 3.71–3.64 (m, 14H), 3.42 (t, *J*=8.6 Hz, 1H), 3.13–2.99 (m, 1H), 2.86–2.77 (m, 2H), 2.67–2.53 (m, 4H), 1.17 ppm (d, *J*=5.9 Hz, 6H); ^{13}C NMR (400 MHz, DMSO-d_6): δ=102.09–100.72 (m), 84.37, 81.32–80.49 (m), 73.22–71.57 (m) 70.21, 69.56, 64.38–63.08 (m), 59.71–59.30 (m), 56.83–56.36 (m), 21.14–20.57 ppm (m); MS (ESI): *m*/*z*: 1272.5 $[M+Na]^+$, 1250.5 $[M+H]^+$.

CD-7: Yield: 61.13%; $[\alpha]_D^{25}$ +149.90 (*c* 0.4136, H_2O); mp>250 °C (decomp.); ^{1}H NMR (400 MHz, D_2O): δ=5.16–5.09 (m, 7H), 4.10–3.92 (m, 26H), 3.78–3.60 (m, 14H), 3.45 (t, *J*=9.2 Hz, 1H), 2.97–2.88 (m, 1H), 2.77–2.53 (m, 4H), 2.35 ppm (s, 3H); ^{13}C NMR (400 MHz, D_2O): δ=101.77, 100.91, 83.74, 81.14–80.94 (m), 80.13, 73.12–72.76 (m), 72.09–71.68 (m), 69.34, 60.28–60.16 (m), 58.50, 58.26, 57.98, 42.18 ppm (m); MS (ESI): *m*/*z*: 1214.5 $[M+Na]^+$, 1192.4 $[M+H]^+$.

CD-8: Yield: 34.07%; $[\alpha]_D^{17}$ +147.25 (*c* 0.5012, H_2O); mp>250 °C (decomp.); ^{1}H NMR(400 MHz, D_2O): δ=5.22–5.16 (m, 7H), 4.09–3.94 (m, 26H), 3.78–3.65 (m, 14H), 3.53 (t, 1H), 3.18 (d, 1H), 2.91–2.85 (m, 1H), 2.73–2.63 (m, 2H), 1.26 ppm (d, 3H); ^{13}C NMR (400 MHz, D_2O): δ=101.82, 101.33, 83.55, 81.17, 80.65, 73.02–72.86 (m), 71.99–71.73 (m), 70.42, 66.32, 60.24–60.03 (m), 55.82, 49.55, 20.30, 16.73 ppm; MS (ESI): *m*/*z*: 1214.5 $[M+Na]^+$, 1192.4 $[M+H]^+$.

4.4. Typical procedure for the asymmetric hydrogenation of aromatic ketones

A solution of modified β-CD (0.02 mmol) and $[RuCl_2(Arene)]_2$ (0.01 mmol) in the mixture of H_2O and DMF (1 mL) was stirred at 25 °C for 1.0 h, and then $HCOONa\cdot 2H_2O$ (2.0 mmol) was added. After the resultant mixture was stirred at 25 °C for another 1.0 h, aromatic ketone (0.2 mmol) was added. After stirring at 25 °C for 24.0 h or 96.0 h, the obtained solution was extracted with *n*-hexane (4×2 mL), and the combined organic phase was dried over anhydrous Na_2SO_4 and analyzed by HPLC to determine the yield and ee value.

4.5. Quantum calculation

All calculations were carried out by using Gaussian 03 program at the level of PM3, B3LYP, and ONIOM(B3LYP/6-31G(d):PM3). The initial structure of β-CD was constructed with the aid of the available crystallographic data obtained from XRD without any optimization.[40] The initial structures of acetophenone and amino alcohols were constructed with the aid of ChemBioOffice 3D Ultra (Version 12.0, Cambridge software) and were fully optimized at the level of B3LYP/6-31G(d). Then the optimized amino alcohols were attached to the C-6 of β-CD forming amino alcohol-modified β-CDs, which were fully optimized at the level of PM3 and B3LYP/6-31G(d) without any symmetrical restrictions. The coordinate system for describing the inclusion complexes between native β-CD and guest molecules has been reported in many literature.[41–44] In general, all

the glycosidic oxygen atoms in the parent β-CD were located onto the XY plane, and their center was defined as the origin of this coordinate system. And the C-6 hydroxyls were located pointing to the positive *Z* axis. The coordinate of the guest molecule acetophenone was determined with the aid of three dummy atoms, one in the *Z* axis and two in the XY plane. The relative position between the modified β-CDs and acetophenone was determined by the distance, angle, and dihedral angle between the labeled carbon atom in acetophenone and the three dummy atoms. The inclusion complexes were firstly optimized at the level of PM3, and then the output files were employed as input files for optimization at the level of ONIOM(B3LYP/6-31G(d):PM3) to obtain optimized energy.

Acknowledgements

The authors thank the National Natural Science Foundation of China (Nos. 21176268 and 21036009) for providing financial support to this project.

Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.07.077.

References and notes

1. Szejtli, J. *Chem. Rev.* **1998**, *98*, 1743–1753.
2. Villalonga, R.; Cao, R.; Fragoso, A. *Chem. Rev.* **2007**, *107*, 3088–3116.
3. Sallas, F.; Darcy, R. *Eur. J. Org. Chem.* **2008**, 957–969.
4. Abdel-Naby, M. A.; El-Refai, H. A.; Abdel-Fattah, A. F. *J. Appl. Microbiol.* **2011**, *111*, 1129–1137.
5. Takahashi, K. *Chem. Rev.* **1998**, *98*, 2013–2033.
6. Johnson, A. E.; Perchyonok, V. T. *Curr. Org. Chem.* **2009**, *13*, 914–918.
7. Chen, H. Y.; Ji, H. B. *AIChE J.* **2010**, *56*, 466–476.
8. Prasantha, P. A.; Sandhya, N. C.; Kempegowda, B. K.; Bhadregowda, D. G.; Mantelingu, K.; Ananda, S.; Rangappa, K. K. S.; Kumara, M. N. *J. Mol. Catal. A: Chem.* **2012**, *353*, 111–116.
9. Zhao, W.; Zhong, Q. *J. Incl. Phenom. Macrocycl. Chem.* **2012**, *72*, 1–14.
10. Breslow, R.; Dong, S. D. *Chem. Rev.* **1998**, *98*, 1997–2011.
11. Marinescu, L.; Bols, M. *Curr. Org. Chem.* **2010**, *14*, 1380–1398.
12. Woggon, W. D. *Curr. Org. Chem.* **2010**, *14*, 1362–1379.
13. Marchetti, L.; Levine, M. *ACS Catal.* **2011**, *1*, 1090–1118.
14. Dong, Z. Y.; Luo, Q.; Liu, J. Q. *Chem. Soc. Rev.* **2012**, *41*, 7890–7908.
15. Breslow, R.; Zhang, X.; Xu, R.; Maletic, M.; Merger, R. *J. Am. Chem. Soc.* **1996**, *118*, 11678–11679.
16. Breslow, R.; Zhang, X.; Huang, Y. *J. Am. Chem. Soc.* **1997**, *119*, 4535–4536.
17. Yang, J.; Breslow, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 2692–2694.
18. Yang, J.; Gabriele, B.; Belvedere, S.; Huang, Y.; Breslow, R. *J. Org. Chem.* **2002**, *67*, 5057–5067.
19. French, R. R.; Holzer, P.; Leuenberger, M. G.; Woggon, W. D. *Angew. Chem., Int. Ed.* **2000**, *39*, 1267–1269.
20. French, R. R.; Holzer, P.; Leuenberger, M.; Nold, M. C.; Woggon, W. D. *J. Inorg. Biochem.* **2002**, *88*, 295–304.
21. Dong, Z. Y.; Liu, J. Q.; Mao, S. Z.; Huang, X.; Yang, B.; Ren, X. J.; Luo, G. M.; Shen, J. C. *J. Am. Chem. Soc.* **2004**, *126*, 16395–16404.
22. Dong, Z. Y.; Liu, J. Q.; Mao, S. Z.; Huang, X.; Luo, G. M.; Shen, J. C. *J. Incl. Phenom. Macrocycl. Chem.* **2006**, *56*, 179–182.
23. Dong, Z. Y.; Liang, K.; Wang, C. Y.; Huang, X.; Mao, S.; Li, X. Z.; Xu, J. Q.; Liu, J. Q.; Luo, G. M.; Shen, J. C. *J. Mol. Catal. A: Chem.* **2007**, *277*, 193–201.
24. Lin, T.; Ding, Z.; Li, N.; Xu, J.; Luo, G.; Liu, J.; Shen, J. *Carcinogenesis* **2011**, *32*, 154–167.
25. Jiao, A. Q.; Yang, N.; Wang, J. P.; Toure, A.; Xu, X. M.; Jin, Z. Y. *J. Incl. Phenom. Macrocycl. Chem.* **2012**, *74*, 335–341.
26. Zhou, Y. H.; Zhao, M.; Mao, Z. W.; Ji, L. N. *Chem.—Eur. J.* **2008**, *14*, 7193–7201.
27. Tang, S. P.; Zhou, Y. H.; Chen, H. Y.; Zhao, C. Y.; Mao, Z. W.; Ji, L. N. *Chem.—Asian J.* **2009**, *4*, 1354–1360.
28. Zhao, M.; Zhang, L.; Chen, H. Y.; Wang, H. L.; Ji, L. N.; Mao, Z. W. *Chem. Commun.* **2010**, 6497–6499.
29. Zhao, M.; Wang, H. L.; Zhang, L.; Zhao, C. Y.; Ji, L. N.; Mao, Z. W. *Chem. Commun.* **2011**, 7344–7346.
30. Hu, P.; Liu, G. F.; Ji, L. N.; Mao, Z. W. *Chem. Commun.* **2012**, 5515–5517.
31. Bonchio, M.; Carofiglio, T.; Di Furia, F.; Fornasier, R. *J. Org. Chem.* **1995**, *60*, 5986–5988.
32. Sakuraba, H.; Maekawa, H. *J. Incl. Phenom. Macrocycl. Chem.* **2006**, *54*, 41–45.
33. Shen, H. M.; Ji, H. B. *Carbohydr. Res.* **2012**, *354*, 49–58.
34. Schlatter, A.; Kundu, M. K.; Woggon, W. D. *Angew. Chem., Int. Ed.* **2004**, *43*, 6731–6734.
35. Petter, R. C.; Salek, J. S.; Sikorski, C. T.; Kumaravel, G.; Lin, F. T. *J. Am. Chem. Soc.* **1990**, *112*, 3860–3868.
36. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; R. Cheeseman, J.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision D.01*; Gaussian: Wallingford CT, 2004.
37. Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233–241.
38. Canivet, J.; Suss-Fink, G.; Stepnicka, P. *Eur. J. Inorg. Chem.* **2007**, 4736–4742.
39. Canivet, J.; Suss-Fink, G. *Green Chem.* **2007**, *9*, 391–397.
40. Betzel, C.; Saenger, W.; Hingerty, B. E.; Brown, G. M. *J. Am. Chem. Soc.* **1984**, *106*, 7545–7557.
41. Yang, E. C.; Zhao, X. J.; Hua, F.; Hao, J. K. *J. Mol. Struct.: THEOCHEM* **2004**, *712*, 75–79.
42. Cao, Y. J.; Xiao, X. H.; Ji, S. F.; Lu, R. H.; Guo, Q. X. *Spectrochim. Acta, Part A* **2004**, *60*, 815–820.
43. Cao, Y. J.; Lu, R. H. *Spectrochim. Acta, Part A* **2009**, *73*, 713–718.
44. Yahia, O. A.; Khatmi, D. E. *J. Mol. Struct.: THEOCHEM* **2009**, *912*, 38–43.