Carbohydrate Research 354 (2012) 49–58

Contents lists available at SciVerse ScienceDirect

Carbohydrate Research

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

Amino alcohol-modified β-cyclodextrin inducing biomimetic asymmetric oxidation of thioanisole in water

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ARTICLE INFO

Article history:
Received 8 November 2011
Received in revised form 31 January 2012
Accepted 27 March 2012
Available online 2 April 2012

Keywords:
β-Cyclodextrin
Modification
Oxidation
Enantioselectivity
Quantum calculation

ABSTRACT

Inspired by β-CD, a macrocyclic oligomers of D-(+)-glucopyranose and a renewable material, which could be obtained from starch, that can promote a lot of organic reactions in water, a green solvent, several amino alcohol-modified β-CDs CD-1 to CD-7 were synthesized in the yields of 36–61%. Their conformations in vacuum and in aqueous solution were optimized by quantum calculation. Their complexes with sodium molybdate prepared in situ were characterized by ^{1}H NMR and were applied in the asymmetric oxidation of thioanisole. Their performance in inducing enantioselectivity was investigated in detail. For the optimal one, CD-1, moderate enantioselectivity (56% ee) was achieved in aqueous CH_3COONa–HCl buffer solution (pH 7.0). The abilities of CD-1 to CD-7 to induce asymmetry are highly dependent on the pH value of the reaction medium and the structure of the modifying group. The origin of the moderate enantioselectivity and the reaction mechanism were investigated with the aid of ^{1}H ROESY NMR studies and quantum calculation. The moderate enantioselectivity was attributed to the two different binding models between CD-1 and thioanisole, which could be defined as intramolecular catalysis and intermolecular catalysis, in which intramolecular catalysis gave (*S*)-methyl phenyl sulfoxide and intermolecular catalysis gave (*R*,*S*)-methyl phenyl sulfoxide.

1. Introduction

Cyclodextrins (CDs), possessing a hydrophilic exterior and a hydrophobic cavity, are a family of water-soluble macrocyclic oligomers of D-(+)-glucopyranosyl units linked by α-1,4-glycosidic bonds, which can form inclusion complexes with a wide range of guest molecules possessing suitable shape and size. In the cyclodextrin family, there are three main members known as α-CD, β-CD (Fig. 1), and γ-CD with six, seven, and eight glucose units, respectively.[1–3] Among them, β-CD is most readily available in commerce, thus it is employed widely as drug carriers, microvessel reactors, enzyme mimics, and so on.[4–7] The ability of β-CD to accommodate hydrophobic guest molecules in its hydrophobic cavity in aqueous solution makes it an attractive component in the construction of artificial enzymes, in which β-CD acts as host to hydrophobic guest molecules and its hydrophobic cavity mimics the hydrophobic pockets in enzymes. The driving forces in the formation of host–guest inclusion complexes between β-CD and guest molecules in aqueous medium could be attributed to several factors, but the primary driving force is the hydrophobic interactions between the guest molecules and water.[8,9]

Besides, β-CD can also provide an asymmetric environment for the guest molecules bound in its cavity and induce asymmetric reaction to them.[10,11] However, the utility of native β-CD in organic synthesis is rather limited, especially in asymmetric organic reaction for the native β-CD is a rigid molecule because of the intramolecular hydrogen network, which makes β-CD difficult to be subjected to topological changes. Moreover, hydroxyl is the only functional group in β-CD.[12] Through modification of native β-CD, the utility of β-CD in organic synthesis expands obviously. Appropriate modification permits β-CD derivatives performing as artificial enzymes directly or ligands in metal catalysis mimicking the hydrophobic pockets in metalloenzymes.[13,14] β-CD derivatives coordinating to metal ions forms artificial metalloenzymes, combining molecular recognition, phase transfer catalysis, and metal catalysis in one same water-soluble catalyst, in which β-CD derivatives play the role of substrate transportation, immobilization, and asymmetric induction, and metal ions act as catalytic active site.[8] In biomimetic reactions catalyzed by artificial metalloenzymes based on β-CD derivatives, β-CD derivatives transfer water-insoluble substrates to aqueous phase where the catalytic metal center exists, and immobilize substrates near the catalytic metal center by forming inclusion complexes as molecular scaffolds.[15] In the inclusion complexes, weak interactions between substrates and the hydrophobic cavity of β-CD offer substrates a beneficial orientation and conformation. Hence, enhanced catalytic activity, obvious acceleration in reaction rate, excellent substrate selectivity, regioselectivity, and enantioselectivity can usually be achieved. One of successful artificial metalloenzymes based on

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http://dx.doi.org/10.1016/j.carres.2012.03.034

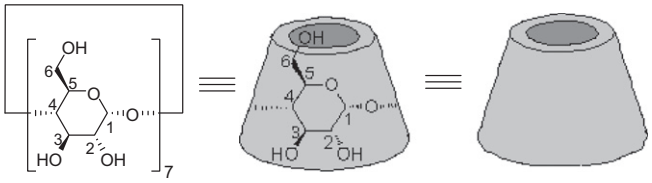
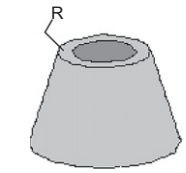


Figure 1. Schematic structure of β-cyclodextrin (β-CD).

β-CD derivatives is the cytochrome P-450 mimics reported by Breslow and co-workers. Their work demonstrated that metalloporphyrins possessing two or four β-CD units could oxidize and hydroxylate substrates bound in the cavity of β-CD with excellent regioselectivity in the presence of more reactive functional groups.[16–21] French et al.[22,23] also reported metalloporphyrins with two β-CD units mimicking the carotene dioxygenases, catalyzed the central cleavage of carotenoids in 15,15′ double bond regioselectively. The origin of these excellent regioselectivity should be attributed to that β-CD units immobilize substrates in a reactive conformation, in which reaction is directed to certain substrate atoms. Application of artificial metalloenzymes based on β-CD derivatives in catalytic hydrolysis of esters has been investigated extensively too, because of their remarkable acceleration in reaction rate by up to more than four orders of magnitude.[24–28] In asymmetric organic reaction, Bonchio and Sakuraba[29,30] reported the asymmetric oxidation of thioanisole catalyzed by the complexes of β-CD derivatives and metal ions, respectively, with moderate enantiomeric excesses (ee). Wong and Schlatter[31–33] attached rhodium and ruthenium complexes to β-CD derivatives forming artificial metalloenzymes and applied them in asymmetric hydrogenation of prochiral olefins, aromatic, and aliphatic ketones. High enantiomeric excesses (ee) have been achieved, up to 98%, although the origin of enantioselectivity is still in speculation to some extent. But to my best knowledge, the application of artificial metalloenzymes based on β-CD derivatives in asymmetric organic reaction is rather limited, despite there are a large number of reports on remarkable acceleration in reaction rate and obvious enhancement of regioselectivity.

We have reported β-CD catalyzed the deprotection of acetals and ketals, oxidation of alcohols and hydrolysis of cinnamaldehyde in aqueous medium, and remarkable rate acceleration and substrate selectivity were observed.[34–36] We also found that weak interactions between hydroxyls of β-CD and substrates played a crucial role in the catalytic reaction. Herein, we report the synthesis of several amino alcohol-modified β-CDs (Fig. 2) and the characterization of their complexes with sodium molybdate. The catalytic performances of these complexes in the asymmetric oxidation of thioanisole were investigated in detail. Their inclusion complexes between amino alcohol-modified β-CDs and thioanisole were characterized by ^{1}H ROESY NMR spectrum and quantum calculation, respectively. To illustrate the moderate enantioselectivity and reaction mechanism in the asymmetric oxidation of thioanisole, quantum calculation was employed.



CD-1: R = $NHCH_2CH_2OH$

CD-2 :R = $N(CH_2CH_2OH)_2$

CD-3: R = $NHCH_2CH_2CH_2OH$

CD-4: R = $NHCH_2CH(CH_3)OH$

CD-5: R = (*S*)-$NHCH_2CH(CH_3)OH$

CD-6: R = $N[CH_2CH(CH_3)OH]_2$

CD-7: R = $N(CH_3)CH_2CH_2OH$

CD-8: R = $NHCH_2CH_2NH_2$

Figure 2. Schematic structures of the amino alcohol-modified β-cyclodextrins (β-CDs) and CD-8.

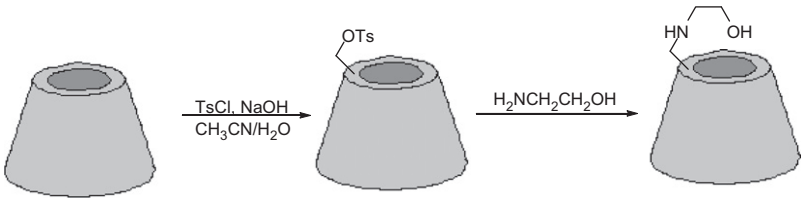
2. Results and discussion

2.1. Design and synthesis of amino alcohol-modified β-CDs

β-CD has become a universal structure unit in the design of artificial enzymes and artificial metalloenzymes for its unique properties to accommodate hydrophobic molecules in aqueous medium, and be soluble in water, readily available from starch by enzymatic degradation and possible to modify selectively. Appropriate modification enhances its ability to bind metal ions and improves its potential applications in organic synthesis. Wong and Schlatter[31–33] reported the application of rhodium and ruthenium complexes coordinating to amino alcohol-modified β-CDs in the asymmetric hydrogenation of olefins, aromatic, and aliphatic ketones with high enantioselectivity. Bonchio[29] applied the complex of sodium molybdate and ethylenediamine-modified β-CD in the asymmetric oxidation of thioanisole. Inspired by their works, a series of amino alcohol-modified β-CDs CD-1 to CD-7 were synthesized and applied in the asymmetric oxidation of thioanisole to evaluate their catalytic performance. It should be mentioned that this research might give some information about sulfur metabolism in life cycle during medication, since amino acids widely exist in body and many medicines use β-CD as drug carrier.

The amino alcohol-modified β-CDs (setting CD-1 as an example) were synthesized as illustrated in Scheme 1. Firstly, 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.[37] Then the amino alcohol-modified β-CDs, CD-1 to CD-7, were readily synthesized by nucleophilic substitution of mono(6-*O*-*p*-tolylsulfonyl)-β-CD with an excess of the corresponding amino alcohol at 70 °C or 90 °C. After precipitation in a large quantity of acetone–ethanol mixture and recrystallization in water, pure amino alcohol-modified β-CD in a gram scale could be obtained. 2-Amino-1-ethanol, 2,2′-iminodiethanol, 3-amino-1-propanol, *(R,S)*-1-amino-2-propanol, (*S*)-1-amino-2-propanol, 1,1′-iminodi-2-propanol, and 2-methylamino-1-ethanol were selected as modifying groups on the purpose of illustrating the effect of modifying groups' structure on the catalytic performance in the asymmetric oxidation of thioanisole. To our best knowledge, these amino alcohol-modified β-CDs had not yet been employed as ligands in organic synthesis except for 2-amino-1-ethanol and (*S*)-1-amino-2-propanol-modified β-CDs employed in the asymmetric hydrogenation of olefins, aromatic, and aliphatic ketones. Ethylenediamine-modified β-CD (CD-8) was also synthesized as comparison accordingly. All of the modified β-CDs were characterized by ^{1}H NMR, ^{13}C NMR and ESI-MS. Interestingly, compared with native β-CD, the heterogeneous aqueous solution of the modified β-CDs mentioned above might become homogeneous when guest molecule thioanisole was added, which could not be observed from the native β-CD.

The conformation of CD-1 in vacuum and in aqueous solution was optimized by GAUSSIAN 03 program at the level of PM3 and B3LYP/6-31G(d), respectively (Fig. 3).[38] The optimized conformation of CD-1 in aqueous solution is nearly the same as in vacuum



Scheme 1. Schematic synthesis of the modified β-cyclodextrin (CD-1).

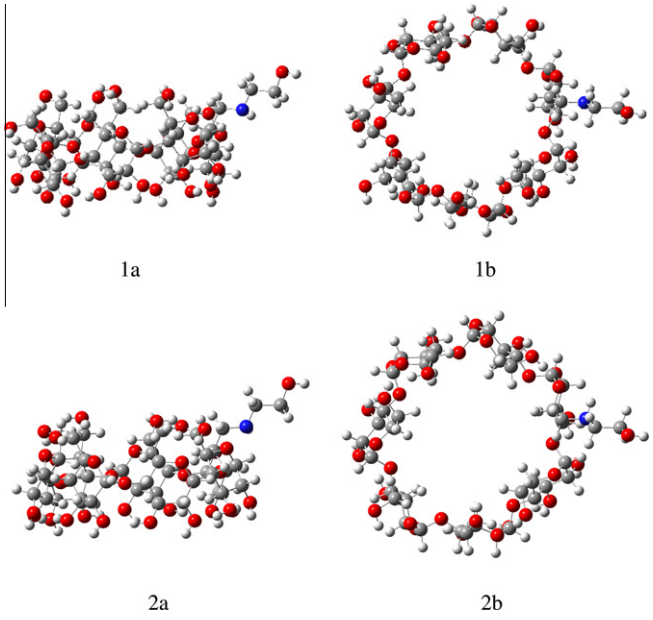


Figure 3. Optimized conformations of CD-1 in vacuum (1a, side view; 1b, vertical view) and in aqueous solution (2a, side view; 2b, vertical view) obtained at the level of PM3 and B3LYP/6-31G(d), respectively.

with the modifying group pointing to the outside of the parent β-CD because of the high solubility of the modifying group in water. The result is in good consistency with the ^{1}H ROESY NMR studies for CD-1, no obvious correlation peak between the H atoms in the modifying group and the H-3, H-5 in the cavity of the parent β-CD observed from the ^{1}H ROESY NMR spectrum of CD-1. Similar optimized conformations were also observed from the other modified β-CDs, CD-2 to CD-8. No obvious self-inclusion occurred because all modifying groups are soluble in water, and no hydrophobic interaction exists. Therefore, as mentioned above, hydrophobic interaction is the key driving force in the formation of inclusion complexes based on β-CD.

2.2. Preparation and characterization of complexes between amino alcohol-modified β-CD and sodium molybdate

With amino alcohol-modified β-CDs in hand, we prepared the complexes of amino alcohol-modified β-CDs and sodium molybdate in situ prior to catalytic experiments by stirring modified β-CDs and sodium molybdate in aqueous CH_3COONa–HCl buffer solution at room temperature. The complexes of amino alcohol-modified β-CDs and sodium molybdate were characterized by ^{1}H NMR studies (400 MHz, D_2O). For example, significant chemical-shift changes were observed from the H atoms at C-1 in the 2-amino-1-ethanol-modified β-CD (CD-1) when sodium molybdate was added (Fig. 4). The multiplets assigned to the H atoms at C-1 linking to the hydroxyl in the modifying group (–NH–CH_2–CH_2–OH) shifted downfield by 0.017 ppm, however the triplets assigned to the H atoms at C-2 linking to the amino in the modifying group (–NH–CH_2–CH_2–OH) nearly remained at the same chemical-shift. Meanwhile, no obvious chemical-shift changes were observed from the H atoms belonged to the parent β-CD too. For 3-amino-1-propanol-modified β-CD (CD-3), the triplets assigned to the H atoms at C-1′ linking to the hydroxyl in the modifying group (–NH–CH_2–CH_2–CH_2–OH) shifted downfield by 0.018 ppm, and the other H atoms belonged to the modifying group and parent β-CD nearly remained at the same chemical-shift as shown in CD-1. Similar changes in chemical-shift occurred in all the other modified β-CDs. This indicates that the amino alcohol-modified β-CDs formed complexes with molybdate by means of coordination of the oxygen atoms in the amino alcohols with the molybdenum. The oxygen atoms in the hydroxyls of the parent β-CD and the nitrogen atoms in the modifying groups may not be involved in the formation of the catalytic complexes, which is consistent with that the parent β-CD possesses low coordinating ability to metal ions commented by Bellia.[14] But unfortunately, we could not obtain the crystals suitable for X-ray crystallographic analysis of these complexes, hence the precise structure of these complexes still remained in speculation.

Based on the ^{1}H NMR studies, the structure of complexes formed by amino alcohol-modified β-CDs (setting CD-1 as an example) and molybdate were surmised as shown in Figure 5. The modified β-CDs coordinated to the Mo atom through the oxygen atom in the modifying group, forming catalytic metal complexes and combining the catalytic active center molybdate and modified β-CDs together.

2.3. Asymmetric oxidation of thioanisole

To evaluate the catalytic properties of the amino alcohol-modified β-CDs, asymmetric oxidation of thioanisole was conducted as a model reaction employing the complexes of amino alcohol-modified β-CDs and molybdate as catalysts. The asymmetric oxidation was carried out in aqueous CH_3COONa–HCl buffer solution (1 mol/L) at 0 °C with the catalyst/substrate ratio of 1:10 and H_2O_2 as oxidant. After 8.0 h, the corresponding oxidized product sulfoxide was obtained with *S*-configuration as the favorable isomer. The performances of CD-1 to CD-8 in the reaction were studied in detail. Surprisingly, the enantioselectivity is very sensitive to the pH value of the reaction medium and the structure of the modifying groups in the modified β-CDs. For example, when CD-1 was employed as ligand, the ee value increased from 9% to 56% as the pH value of the reaction medium rose from 5.5 to 7.0 (Table 1). Further increase in the pH value of the reaction medium from 7.0 to 8.0 led to no rise in the enantioselectivity, but a sharp decrease in the ee value from 56% to 37%. This might be due to the effect of the pH value on the structure of CD-1. The pH value of the medium exerts high influence on the conformation of native β-CD and modified β-CDs being illustrated in the literature.[39,40] As for CD-3, the ee value increased from 7% to 11% as the pH value of the reaction medium from 5.5 to 8.0 (Table 1), exhibiting a different pH-enantioselectivity profile. Furthermore, the enantioselectivity of CD-3 was much poorer compared with CD-1. Comprehensive studies were conducted to investigate the pH-enantioselectivity

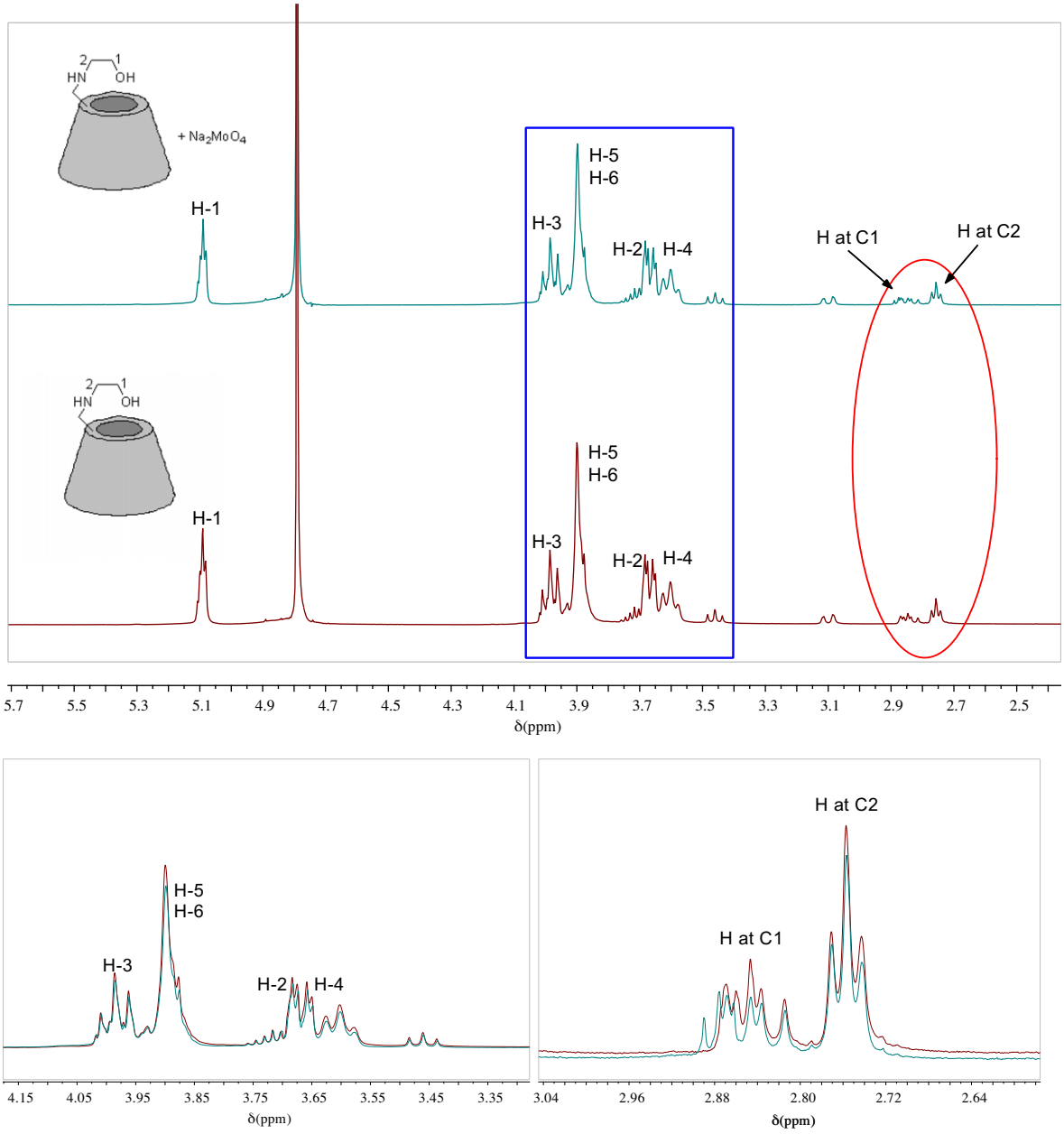


Figure 4. ^{1}H NMR spectra of CD-1 and CD-1 + Na_2MoO_4 in D_2O.

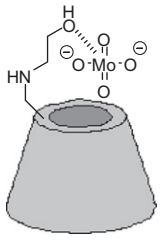


Figure 5. Proposed structure of the complex between CD-1 and molybdate.

profiles of CD-1 to CD-8. In general, the pH-enantioselectivity profiles could be divided into two types. In the first type, containing CD-1, CD-4, CD-5, and CD-8, the enantioselectivity increased as the rise in the pH value. When reaching a maximum, a moderate enantioselectivity could be achieved, and then decreased as further increase in the pH value of the reaction medium. The second type contained CD-2, CD-3, CD-6, and CD-7, in which the enantioselectivity increased as the rise in the pH value from 5.5 to 8.0 to some extent, but lower ee values. The optimal pH values of the reaction medium and maximal ee values for CD-1 to CD-8 were listed in

Table 1
Effect of pH value and modifying groups' structure on the enantioselectivity in the asymmetric oxidation of thioanisole[a]

Entry	Ligand	pH	Conversion[b] (%)	Yield[b] (%)	ee[c] (%)	Configuration[d]
1	CD-1	5.5	100	86	9	*S*
2	CD-1	6.0	100	87	19	*S*
3	CD-1	6.5	100	86	42	*S*
4	CD-1	7.0	100	84	56	*S*
5	CD-1	7.5	100	78	51	*S*
6	CD-1	8.0	90	76	37	*S*
7	CD-2	5.5	100	86	8	*S*
8	CD-2	6.0	100	88	10	*S*
9	CD-2	6.5	94	83	11	*S*
10	CD-2	7.0	92	83	12	*S*
11	CD-2	7.5	87	75	16	*S*
12	CD-2	8.0	85	70	18	*S*
13	CD-3	5.5	100	83	7	*S*
14	CD-3	6.0	100	84	8	*S*
15	CD-3	6.5	100	87	8	*S*
16	CD-3	7.0	96	83	8	*S*
17	CD-3	7.5	87	71	11	*S*
18	CD-3	8.0	89	72	11	*S*
19	CD-4	5.5	100	89	12	*S*
20	CD-4	6.0	99	86	22	*S*
21	CD-4	6.5	100	84	43	*S*
22	CD-4	7.0	100	85	51	*S*
23	CD-4	7.5	98	83	35	*S*
24	CD-4	8.0	95	79	28	*S*
25	CD-5	5.5	100	88	14	*S*
26	CD-5	6.0	100	86	25	*S*
27	CD-5	6.5	100	86	43	*S*
28	CD-5	7.0	100	82	53	*S*
29	CD-5	7.5	100	85	35	*S*
30	CD-5	8.0	100	88	27	*S*
31	CD-6	5.5	100	85	11	*S*
32	CD-6	6.0	100	86	14	*S*
33	CD-6	6.5	97	85	17	*S*
34	CD-6	7.0	87	78	17	*S*
35	CD-6	7.5	86	73	19	*S*
36	CD-6	8.0	87	72	18	*S*
37	CD-7	5.5	100	89	6	*S*
38	CD-7	6.0	100	89	8	*S*
39	CD-7	6.5	100	89	10	*S*
40	CD-7	7.0	91	81	12	*S*
41	CD-7	7.5	89	77	15	*S*
42	CD-7	8.0	86	71	15	*S*
43	CD-8	5.5	100	87	22	*S*
44	CD-8	6.0	100	84	42	*S*
45	CD-8	6.5	94	80	55	*S*
46	CD-8	7.0	84	67	25	*S*
47	CD-8	7.5	83	64	15	*S*
48	CD-8	8.0	83	63	12	*S*

[a] Reaction conditions: thioanisole (0.5 mmol), modified CDs (0.05 mmol), $Na_2MoO_4{\cdot}2H_2O$ (0.05 mmol) and 30% H_2O_2 (0.05 mL) in aqueous CH_3COONa–HCl buffer solution (10 mL, 1 mol/L) for 8.0 h at 0 °C.
[b] Determined by HPLC analysis employing toluene as internal standard.
[c] Determined by HPLC analysis with a Chiralcel OD-H column.
[d] Determined by comparison of the eluting sequence of the enantiomers with the authentic sample and literature.

Table 1, from which we could conclude that the modified β-CDs in the first type exhibited higher performance in the asymmetric oxidation of thioanisole than those in the second type.

Besides the pH value, the enantioselectivity in the asymmetric oxidation of thioanisole is also heavily dependent on the structure of the modifying groups (Table 1). The ability of β-CD to induce asymmetry in the oxidation of thioanisole depends on its modifying groups deeply. Compared with CD-1, CD-3 just has one more CH_2 unit, but the ee value decreased sharply from 56% to 11% at their optimal pH values, respectively. One CH_2 unit difference not only affects the pH-enantioselectivity profile, but also induces sharp decrease in the optimal ee value. CD-2 has two hydroxyethyls compared with CD-1 having one, the ee value also

Table 2
Control experiments of CD-1 in the asymmetric oxidation of thioanisole[a]

Entry	Catalyst	Conversion[b] (%)	Yield[b] (%)	ee[c] (%)	Configuration[d]
1	CD-1	trace	trace		
2	Na_2MoO_4	100	92	0	
3	β-CD + $H_2NCH_2CH_2OH$ + Na_2MoO_4	90	74	1	*S*
4	CD-1 + Na_2MoO_4	100	84	56	*S*
5[e]	CD-1 + Na_2MoO_4	100	91	8	*S*

[a] Reaction conditions: thioanisole (0.5 mmol), catalyst (0.05 mmol) and 30% H_2O_2 (0.05 mL) in aqueous CH_3COONa–HCl buffer solution (10 mL, 1 mol/L, pH 7.0) for 8.0 h at 0 °C.
[b] Determined by HPLC analysis employing toluene as internal standard.
[c] Determined by HPLC analysis with a Chiralcel OD-H column.
[d] Determined by comparison of the eluting sequence of the enantiomers with the authentic sample and literature.
[e] 1-Adamantanecarboxylic acid (0.05 mmol) was added.

decreased sharply from 56% to 18%. However, compared with CD-1, CD-4, and CD-5 having one more CH_3 unit linking to the carbon atom next to the hydroxyl in the modifying groups, their enantioselectivity in the asymmetric oxidation of thioanisole did not decrease so much (51% and 53%), nearly remained at the same level. However, when a CH_3 unit was linked to the nitrogen atom in the modifying group (CD-7), the ee value decreased sharply from 56% to 15%. From the results of CD-4 and CD-5, we could learn that the effect of the absolute configuration of the modifying group on the enantioselectivity could be ignored. As for CD-6, the difference in the enantioselectivity between CD-4 and CD-6 is similar to that between CD-1 and CD-2. The hydrogen atom linking to the nitrogen atom may be indispensable in inducing enantioselectivity in the asymmetric oxidation of thioanisole. CD-8 was applied in the asymmetric oxidation of thioanisole as comparison, and moderate enantioselectivity (55%) was achieved. Therefore, in the asymmetric oxidation of thioanisole catalyzed by the complexes of amino alcohol-modified β-CDs and molybdate, 2-amino-1-ethanol modified β-CD (CD-1) exhibited the optimal performance in inducing enantioselectivity, a moderate ee value being achieved. The structures of the modifying groups in CD-1 to CD-8 exert a heavy influence on their performance in the asymmetric oxidation of thioanisole. When there are two carbon atoms between the hydroxyl and the nitrogen atom in the modifying groups, and one hydrogen atom in the corresponding nitrogen atom, better enantioselectivity can be achieved. Both a longer alkyl chain between the hydroxyl and the nitrogen atom, and trisubstitution of ammonia can reduce the enantioselectivity in the asymmetric oxidation of thioanisole. The delicate cooperation between the parent β-CD and the modified groups in CD-1 to CD-8 determines the enantioselectivity in the model reaction.

Control experiments were carried out next to gain more comprehension to the asymmetric oxidation induced by amino alcohol-modified β-CDs (Table 2). When CD-1 was utilized as the catalyst alone, no reaction occurred under the standard reaction conditions. This means that CD-1 could not promote the oxidation of thioanisole with H_2O_2 herein. Sodium molybdate could do it when employed as the only catalyst, but unfortunately there was no enantioselectivity observed. As illustrated in Table 2, the metal complex formed by CD-1 and sodium molybdate, not only promotes the oxidation of thioanisole but also induces moderate enantioselectivity, from which we can learn that in this catalytic system, sodium molybdate is the catalytic active center and CD-1 plays the role of asymmetric induction. In addition, the enantioselectivity induced by CD-1 could be inhibited by addition of 1-adamantanecarboxylic acid which is known as a good guest molecule for the cavity of β-CD, the ee value sharply dropping from 56% to 8%. Thus the cavity in the parent β-CD is indispensable in inducing

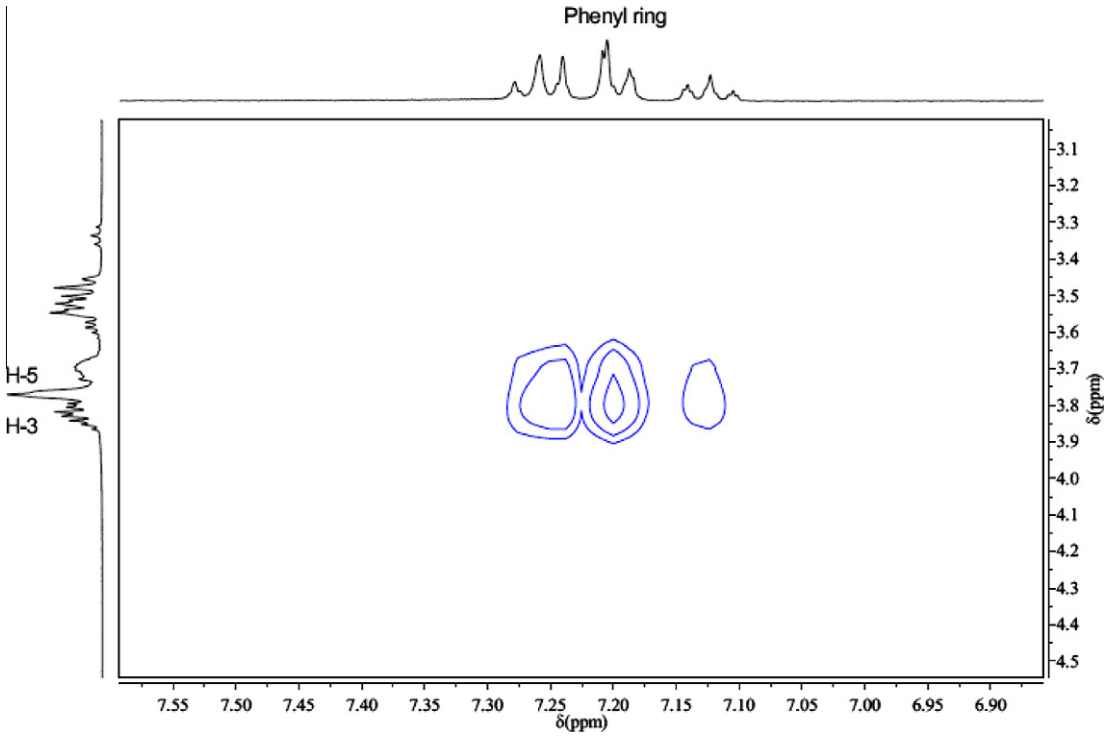


Figure 6. Partial ^{1}H ROESY NMR spectrum of the inclusion complex between CD-1 and thioanisole.

enantioselectivity in the asymmetric oxidation of thioanisole. To get more detail about this catalytic reaction, the physical mixture of native β-CD, 2-amino-1-ethanol, and sodium molybdate was employed as catalyst, applied in the model reaction under the standard reaction conditions. The oxidation occurred, but the ee value was nearly zero, no enantioselectivity induced. Therefore it must be necessary to attach 2-amino-1-ethanol to the parent β-CD and the ability of native β-CD to induce enantioselectivity in this catalytic system is extremely poor. Consequently, we can get the conclusion that the enantioselectivity induced by amino alcohol-modified β-CDs in the oxidation of thioanisole is controlled by the delicate structure of the modified β-CDs, and the exquisite cooperation between the modified groups and the parent β-CD, especially the cavity in the parent β-CD, playing a decisive role in inducing enantioselectivity, which are similar to the enzymatic catalysis practiced in nature.

2.4. Mechanism studies

As illustrated in Table 2, the formation of inclusion complex played an essential role in the asymmetric oxidation of thioanisole, therefore the inclusion complex of CD-1 and thioanisole was probed with the aid of ^{1}H ROESY NMR study. Obvious correlation peaks between the H atoms located in the phenyl ring of thioanisole and the H-3, H-5 in the cavity of the parent β-CD can be observed (Fig. 6). Obviously, there is no correlation peak observed between the H atoms located in the phenyl ring of thioanisole and the H-2, H-4 in the outside of the parent β-CD. Thus, in the complex of CD-1 and thioanisole, almost all the thioanisole molecules are included into the cavity of the parent β-CD, no thioanisole absorbed on the outside of the parent β-CD. Similar correlation peaks were also observed from the ^{1}H ROESY NMR spectra of the inclusion complexes formed by CD-2 to CD-8 and thioanisole except for CD-6 for its low solubility in water. All the modified β-CDs, CD-1 to CD-8, can form stable inclusion complexes with thioanisole in aqueous medium, giving obvious correlation peaks, although their abilities to induce enantioselectivity in the asymmetric oxidation of thioanisole differ from each other.

The 2-amino-1-ethanol modified β-CD (CD-1) exhibits the optimal performance in inducing enantioselectivity in present work, yet we must acknowledge that the enantioselectivity achieved is moderate, 56% ee. To gain more details about this intriguing asymmetric oxidation, we firstly speculated the moderate ee value might be ascribed to the oxidation proceeding in aqueous solution, in which racemic oxidation products were obtained, as illustrated in Table 2 when 1-adamantanecarboxylic acid was added or sodium molybdate was employed as catalyst alone, the ee value almost was zero, not in the cavity of the parent β-CD, in which enantioselectivity could be achieved. To verify our speculation, we increased the amount of catalyst and ligand, respectively, in the asymmetric oxidation of thioanisole on the purpose to reduce the oxidation proceeding in the aqueous solution and to reduce the amount of free sodium molybdate in the aqueous solution. The results are presented in Tables 3 and 4. Unexpected to us, both increase in the amount of catalyst and ligand did not lead to any increase in the ee value, but a slightly decrease. The enantioselectivity maintained in a moderate level. Therefore the nonenantioselective oxidation of thioanisole proceeding in aqueous solution could not account for the moderate ee value in our present work. Similar phenomenon was also observed from CD-4, CD-5 and CD-8. When the amount of catalyst increased, all of them gave moderate ee values, about 50%, a meaningful figure.

Inspired by the figure 50% ee, we presumed the moderate ee values induced by CD-1, CD-4, CD-5, and CD-8 might be ascribed to the two different binding models between the modified β-CD and thioanisole as shown in Figure 7 (setting CD-1 as an example). In model a (intramolecular catalysis), the sulfur atom in thioanisole is located in the same rim of CD-1 with the modifying group. When the oxidation takes place, there may be a favorable face attack, leading to chiral sulfoxide. In model b (intermolecular catalysis), the sulfur atom in thioanisole and the modifying group in CD-1 are located in two different rims of CD-1. When the oxidation

Table 3
Effect of the amount of catalyst on enantioselectivity of CD-1 in the asymmetric oxidation of thioanisole[a]

Entry	Catalyst (mmol)	Conversion[b] (%)	Yield[b] (%)	ee[c] (%)	Configuration[d]
1	0.05	100	84	56	*S*
2	0.10	100	87	54	*S*
3	0.15	100	87	49	*S*
4	0.20	100	88	51	*S*
5	0.25	100	88	52	*S*

[a] Reaction conditions: thioanisole (0.5 mmol), catalyst (CD-1 + $Na_2MoO_4{\cdot}2H_2O$) and 30% H_2O_2 (0.05 mL) in aqueous CH_3COONa–HCl buffer solution (10 mL, 1 mol/L, pH 7.0) for 8.0 h at 0 °C.
[b] Determined by HPLC analysis employing toluene as internal standard.
[c] Determined by HPLC analysis with a Chiralcel OD-H column.
[d] Determined by comparison of the eluting sequence of the enantiomers with the authentic sample and literature.

Table 4
Effect of the amount of ligand (CD-1) on the enantioselectivity in the asymmetric oxidation of thioanisole[a]

Entry	CD-1 (mmol)	Conversion[b] (%)	Yield[b] (%)	ee[c] (%)	Configuration[d]
1	0.05	100	84	56	*S*
2	0.15	100	89	53	*S*
3	0.25	100	88	50	*S*

[a] Reaction conditions: thioanisole (0.5 mmol), $Na_2MoO_4{\cdot}2H_2O$ (0.05 mmol) and 30% H_2O_2 (0.05 mL) in aqueous CH_3COONa–HCl buffer solution (10 mL, 1 mol/L, pH 7.0) for 8.0 h at 0 °C.
[b] Determined by HPLC analysis employing toluene as internal standard.
[c] Determined by HPLC analysis with a Chiralcel OD-H column.
[d] Determined by comparison of the eluting sequence of the enantiomers with the authentic sample and literature.

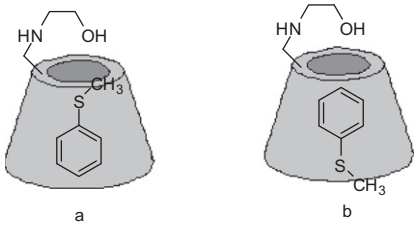


Figure 7. Two proposed binding models for CD-1 and thioanisole.

happens, both the *Re*-face and the *Si*-face of the sulfur atom are accessible, leading to racemic sulfoxide. Since the probabilities of thioanisole to be oxidized in model a and model b are nearly the same, moderate enantioselectivity is achieved. To verify our speculation, the quantum calculation was employed to calculate the binding energy of CD-1 and thioanisole in model a and model b. The geometries of the inclusion complexes between CD-1 and thioanisole were 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),[38] in which CD-1 and thioanisole were optimized at the level of PM3 and B3LYP/6-31G(d), respectively, and the binding energy (*BE*) at the level of ONIOM(B3LYP/6-31G(d):PM3) was obtained according to Eq. 1:

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

where $E[\mathrm{C}]^{\mathrm{OPT}}_{\mathrm{ONIOM}}$, $E[\mathrm{H}]^{\mathrm{OPT}}_{\mathrm{PM3}}$ and $E[\mathrm{G}]^{\mathrm{OPT}}_{\mathrm{B3LYP/6\text{-}31G(d)}}$ represent the total optimized energy of the inclusion complex at the level of ONIOM(B3LYP/6-31G(d):PM3), the free CD-1 at the level of PM3 and the free thioanisole at the level of B3LYP/6-31G(d).[41]

The optimized geometries of the inclusion complexes between CD-1 and thioanisole in model a and model b are shown in Figure 8, and the binding energies in model a and b are −30.1773 kJ/mol and −33.3004 kJ/mol, respectively. The negative binding energy indicated the formation of inclusion complex of CD-1 and thioanisole is thermodynamically favorable and spontaneous. In addition, we also obtained that the difference in the binding energies between model a and b is just 3.1231 kJ/mol, a very low energy barrier. As a comparison, the energy required to pass the barrier to rotation around the C–C bond in ethane is about 12.0499 kJ/mol.[42] Thus, the *BE* difference between models a and b can be ignored. The intramolecular catalysis and intermolecular catalysis exist in the oxidation of thioanisole concurrently which is in good consistency with our hypothesis and can account for the moderate ee value. In intramolecular catalysis, the sulfur atom in thioanisole is located in the same rim of CD-1 with the modifying group which has coordinated to the catalytic center molybdate. When the modifying group coordinates to the molybate rotates to point toward the cavity of CD-1, the oxidation occurs with a favorable face attack, giving *S*-configuration isomer. In intermolecular catalysis, the sulfur atom in thioanisole and the modifying group of CD-1 coordinating to the molybate are located in two different rims in which the oxidation takes place with the aid of another molecular complex whose modifying group coordinating to the molybate points to the outside of CD-1, both the *Re*-face and the *Si*-face of the sulfur atom being accessible and giving racemic products. Herein, the quantum calculation also provides a useful access to predict the outcome of organic reaction. In the model reaction employed here, if the binding energy between the substrate and CD-1 in model a was lower than in model b, the inclusion complex would exist in model a more than in model b. Therefore, the intramolecular catalysis based on the inclusion complex in model a would have advantage over the intermolecular catalysis based on the inclusion complex in model b, better enantioselectivity might be obtained.

On the basis of data analysis and quantum calculation, we proposed the catalytic cycle for CD-1 as illustrated in Scheme 2: (1) coordination of CD-1 to molybdate (I); (2) formation of inclusion complexes of CD-1 and thioanisole in models a and b (II and II′); (3) oxidation of thioanisole in models a and b (III and III′); (4) liberation of the generated sulfoxide from the cavity of CD-1 and regeneration of the catalyst (IV and IV′). This is also the origin of the moderate enantioselectivity.

The binding energies (*BE*) for CD-2 to CD-8 with thioanisole in model a and model b have also been calculated at the level of ONIOM(B3LYP/6-31G(d):PM3). The results are listed in Table 5. All the binding energies (*BE*) for CD-1 to CD-8 are negative, indicating that all of them can form thermodynamically favorable inclusion complexes with thioanisole spontaneously, which is consistent with the ^{1}H ROESY NMR studies in which obvious correlation peaks between the H atoms located in the phenyl ring of thioanisole and the H-3, H-5 in the cavity of the parent β-CD are observed. However, we must acknowledge that, as shown in Table 5, the differences of the binding energies in model a and model b stay at the same level for CD-1 to CD-8, but CD-2, CD-3, CD-6, and CD-7 exhibit low enantioselectivity compared with CD-1, CD-4, CD-5, and CD-8. This may be caused by the difference in the modifying groups' structure. When the inclusion complexes are formed in model a, the modifying groups' structure of CD-2, CD-3, CD-6, and CD-7 disfavor the enantioselective oxidation of the sulfur atom in thioanisole from the *Si*-face exclusively. The oxidation may take place to both the *Re*-face and *Si*-face of the sulfur atom producing some racemic sulfoxide. In model b, racemic sulfoxide is produced for all of CD-1 to CD-8, thus resulting in the low enantiomeric excesses (ee). Hence, the delicate cooperation between the modifying groups and the parent β-CD plays the decisive role in inducing

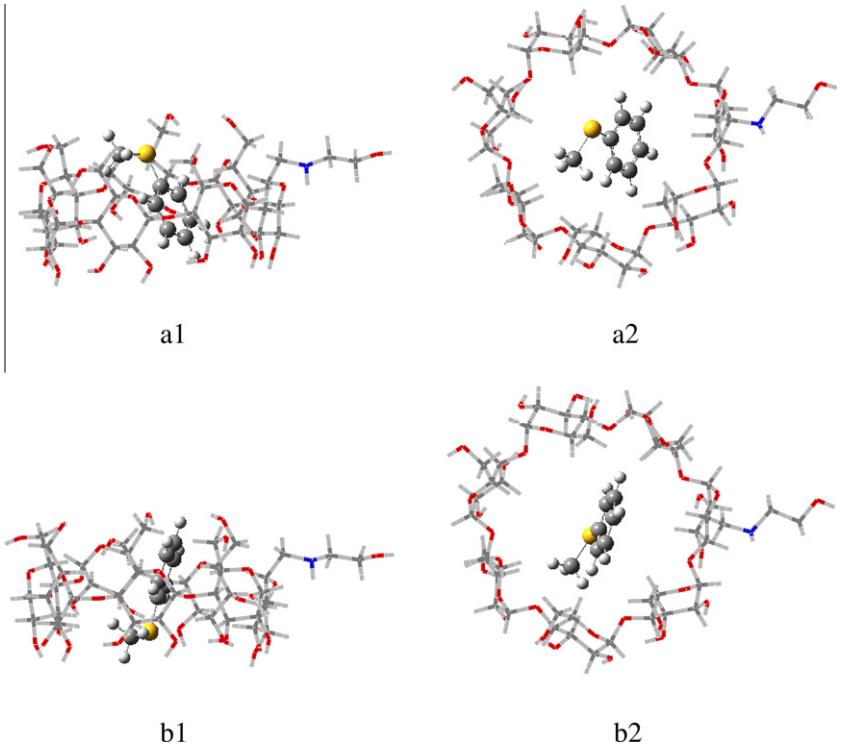


Figure 8. Optimized geometries of the inclusion complex between CD-1 and thioanisole in model a (a1, side view; a2, vertical view) and in model b (b1, side view; b2, vertical view) obtained at the level of ONIOM(B3LYP/6-31G(d):PM3).

enantioselectivity in the asymmetric oxidation of thioanisole catalyzed by the complexes of CD-1 to CD-8 and sodium molybdate.

3. Experimental

3.1. 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, 1,1′-iminodi-2-propanol, 2-methylamino-1-ethanol, and thioanisole in 98% purity were purchased from Aladdin. 2-Amino-1-ethanol, 2,2′-iminodiethanol and ethylenediamine of analytical grade were purchased from Tianjin Damao Chemical Reagent factory, China. Methyl phenyl sulfoxide was obtained from Alfa Aesar. All the other common reagents were of 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. Tetramethylsilane was used as the internal standard (0.00 ppm) in DMSO-d_6 and H_2O was used as the internal standard (4.79 ppm) in 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 column, eluted with *n*-hexane/isopropyl alcohol = 4:1, 0.9 mL/min). The absolute configuration was determined by comparison of the eluting sequence of the enantiomers with the authentic sample and literature.[43]

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

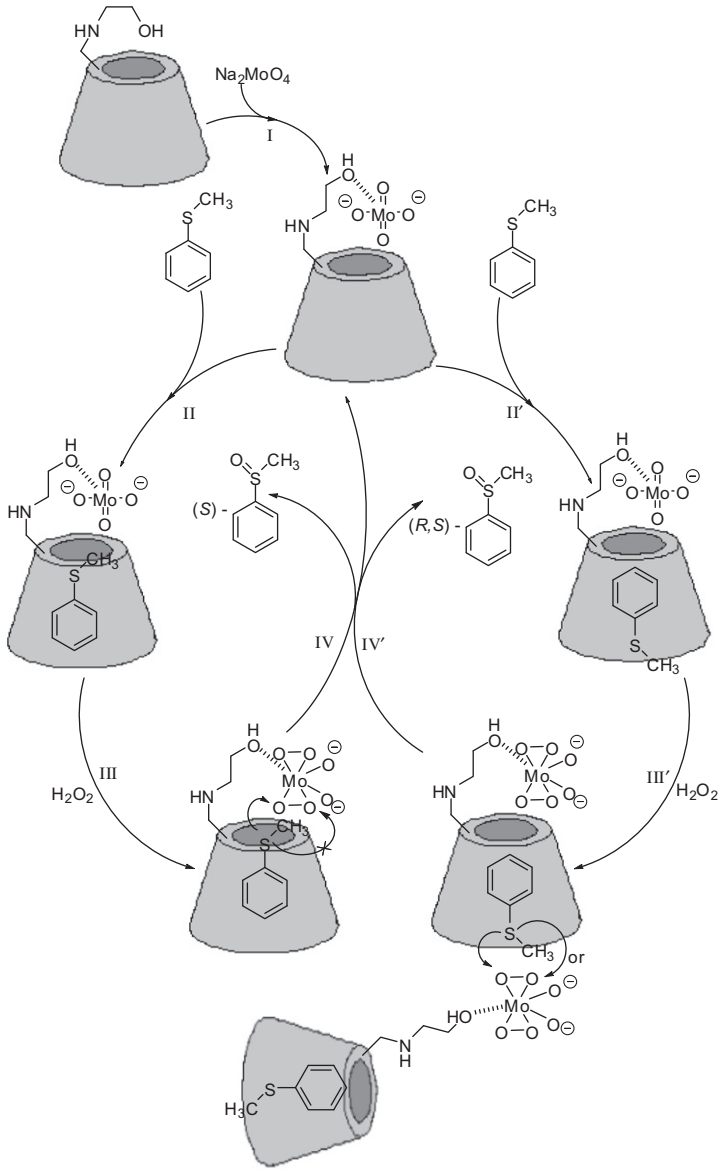
A solution of sodium hydroxide (6.0000 g, 150 mmol) in water (20 mL) was added dropwise to a solution of β-CD (56.7490 g, 50 mmol) in water (500 mL) with magnetic stirring at 10–15 °C over about 15 min. The solution became homogeneous, and then a solution of *p*-toluenesulfonyl chloride (11.4384 g, 60 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 13% yield.

3.3. Typical procedure for the synthesis of amino alcohol-modified β-CDs, CD-1 to CD-7

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 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.

3.4. Typical procedure for asymmetric oxidation of thioanisole to methyl phenyl sulfoxide

A solution of modified β-CD (0.05 mmol) and $Na_2MoO_4{\cdot}2H_2O$ (0.0121 g, 0.05 mmol) in aqueous CH_3COONa–HCl buffer solution (10 mL, 1 mol/L) was stirred at room temperature for 1.0 h, and then thioanisole (0.0621 g, 0.5 mmol) was added. After the resultant mixture was stirred at room temperature for another 1.0 h, the mixture was cooled to 0 °C and 30% H_2O_2 (0.05 mL) was added. After stirring at 0 °C for 8.0 h, 0.1 mol/L aqueous $Na_2S_2O_3$ (5 mL) was added to stop deep oxidation. The obtained solution was extracted with CH_2Cl_2 (3 × 10 mL), and the combined organic



Scheme 2. Proposed catalytic cycle for CD-1 in the asymmetric oxidation of thioanisole.

Table 5
Binding energies (*BE*) of D-1 to CD-8 with thioanisole in model a and model b[a]

Entry	CDs	BE_a (kJ/mol)	BE_b (kJ/mol)	ΔBE[b] (kJ/mol)
1	CD-1	−30.1773	−33.3004	3.1231
2	CD-2	−34.6727	−32.3497	−2.3231
3	CD-3	−35.8970	−36.2708	0.3738
4	CD-4	−40.6133	−43.9479	3.3347
5	CD-5	−30.8773	−34.9031	4.0257
6	CD-6	−39.4868	−29.4137	−10.0731
7	CD-7	−37.2553	−39.3855	2.1302
8	CD-8	−35.3275	−38.7153	3.3878

[a] All calculations were carried out by using the GAUSSIAN 03 program at the level of ONIOM (B3LYP/6-31G(d):PM3). See Section 3 for detail.
[b] $\Delta BE = BE_a - BE_b$.

phase was washed with saturated brine (10 mL), dried over anhydrous Na_2SO_4, and evaporated under reduced pressure to afford the crude product which was analyzed by HPLC to determine the yield and ee value.

3.5. 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).[38] The initial structure of β-CD was constructed with the aid of the available crystallographic data obtained from XRD without any optimization.[44] The initial structures of thioanisole 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 literatures.[41,45–48] 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. The C-6 hydroxyls were located pointing to the

positive *Z* axis. The coordinate of the guest molecule thioanisole 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 thioanisole was determined by the distance, angle and dihedral angle between the labeled carbon atom in thioanisole and the three dummy atoms. To facilitate the calculation, the carbon atom linking to the sulfur atom in the benzene ring of thioanisole was appointed to be the labeled carbon atom. All 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 energies.

4. Conclusion

In summary, seven amino alcohol-modified β-CDs have been synthesized in acceptable yields (36–61%), and their complexes with sodium molybdate were prepared in situ in aqueous CH_3COO-Na–HCl buffer solution at room temperature. Their performance to induce enantioselectivity was investigated with the asymmetric oxidation of thioanisole as model reaction, and moderate ee value (56%) was achieved for the optimal ligand CD-1. The moderate enantioselectivity can be ascribed to the two different binding models of CD-1 with thioanisole, which can be defined as intramolecular catalysis and intermolecular catalysis, and intramolecular catalysis gave (*S*)-methyl phenyl sulfoxide and intermolecular catalysis gave (*R*,*S*)-methyl phenyl sulfoxide. The delicate cooperation between the modifying groups and the parent β-CD plays a decisive role in inducing enantioselectivity in these modified β-CDs. To our best knowledge, this work provides an example to apply amino alcohol-modified β-CDs in the asymmetric oxidation of thioanisole and systematically investigate the effect of the reaction medium's pH value and the modifying group's structure on the enantioselectivity, providing a promising model in the design of artificial metalloenzymes based on β-CD. It also provides a method to employ quantum calculation to illustrate the enantioselectivity in the asymmetric oxidation of thioanisole catalyzed by β-CD derivatives, providing a good access to illustrate the origin of the enantioselectivity in the asymmetric organic reaction. To further investigate the origin of the enantioselectivity in this intriguing catalytic system, the synthesis of new β-CD derivative and its application in the asymmetric oxidation of thioanisole are in process.

Acknowledgements

The authors thank the National Natural Science Foundation of China (Nos. 21036009 and 21176268), higher-level talent project for Guangdong provincial universities and the Fundamental Research Funds for the Central Universities for providing financial support to this project.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carres.2012.03.034.

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