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Per-6-amino-β-cyclodextrin catalyzed asymmetric Michael addition of nitromethane and thiols to chalcones in water

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ABSTRACT

An environmentally benign and enantioselective Michael addition of nitromethane/thiols to *trans*-chalcone catalyzed by per-6-amino-β-cyclodextrin (per-6-ABCD) is carried out in water at room temperature with good yield and enantiomeric excess. The catalyst is recovered and reused without loss in its activity.

1. Introduction

Catalytic asymmetric addition of stabilized carbanions to α,β-unsaturated enones (Michael reaction) is one of the fundamental C–C bond-forming reactions and useful method for remote functionalization in organic synthesis.[1–8] In the case of nitroalkanes, conjugate addition to α,β-unsaturated carbonyl substrates[9–13] is a meaningful tool for further transformation of masked functionalities. The nitro group, described as a 'synthetic chameleon',[14] can undergo Nef reaction,[15] nucleophilic displacements,[16] reduction to an amino group[17] and conversion into a nitrile oxide.[18] Several attempts have been made towards achieving asymmetric conjugate addition of nitromethane to chalcones in the presence of lanthanum tris-binaphthoxide,[19–21] L-proline,[22] natural cinchona alkaloids,[23] cinchona alkaloids-derived thiourea,[24] polymer-anchored chiral catalyst LiAl-poly2A,[25] chiral quaternary ammonium salts,[26] Ni(II) complexes[27] and chiral imidazoline catalysts.[28] On the other hand, the conjugate addition of thiols to α,β-unsaturated carbonyls[29–34] provides useful route for the synthesis of chiral sulfur compounds, which have versatile applications in chemistry and biology.[35–37] However, the asymmetric Michael addition of thiols to α,β-unsaturated carbonyl compounds is still a challenging process.[29–34] Catalysts such as heterobimetallic asymmetric complexes,[38–40] LaN_3-tris(binaphthoxide), $SmNa_3$tris(binaphthoxide), chiral hafnium catalyst,[41] cinchona alkaloids,[42,43] proline and its derivatives[44–46] are employed to achieve good asymmetric induction. Although different catalysts have been used for the asymmetric synthesis of sulfides from arenethiols, chiral catalysts have not been utilized so far for the conjugate addition of aliphatic thiols to chalcones. Considerable efforts have been expended in recent years to develop methods towards the recovery and reuse of the chiral catalysts, which will make asymmetric synthesis more economically usable and environmentally friendly. In the search to remove harmful organic solvents, water has emerged as a versatile solvent for organic reactions.[47,48]

Cyclodextrins (CDs) are cyclic oligosaccharides possessing hydrophobic cavities to bind substrates selectively and to catalyze chemical reactions through the formation of reversible host–guest complexes via non-covalent interactions.[49–51] In asymmetric catalysis, the chemical modification of cyclodextrins may improve the enantioselectivity of most of the reactions.[52] Aminocyclodextrins and carboxymethylated cyclodextrins are employed as chiral discriminating agents in enantioseparation in capillary electrophoresis,[53] high performance liquid chromatography[54] and chiral NMR analysis.[55] Peramino-CDs are homogeneous CD derivatives modified by persubstitution at the primary face with amino pendant groups, which display combined hydrophobic and electrostatic bindings of guest molecules relative to their native CDs. They are employed as biomimetic catalysts for Kemp elimination,[56] deprotonation[57] and chiral recognition processes.[58,59] They are also widely employed as chiral selectors for the enantioseparation of different anionic analytes such as amino acids.[53] Aminocatalysts are also receiving greater attention in asymmetric Michael addition.[60–62] Native β-CD has been employed as a catalyst for thiol[63,64] and aza-Michael addition[65] in water medium with poor chiral induction. In the present work, we have successfully employed as aminomodified cyclodextrin namely, heptakis(6-amino-6-deoxy)-β-cyclodextrin (per-6-ABCD) **1** as a chiral base catalyst and a host for conjugate addition of nitromethane **3** and thiols to *trans*-chalcones in an aqueous medium at room temperature.

2. Results and discussion

Table 1 shows the results of our preliminary studies with per-6-ABCD **1** to mediate asymmetric 1,4-addition with different Michael acceptors and donors in water. Compound **1** fails in the conjugate addition of diethyl malonate and malononitrile with

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Table 1
Per-6-ABCD **1** catalyzed asymmetric Michael addition with different Michael acceptors and donors[a]

Entry	Michael acceptor	Michael donor	Yield[b] (%)	% ee[c]
1	Chalcone	Diethyl malonate	8	—
2	Chalcone	Malononitrile	Nil	—
3	Benzylideneacetone	Nitromethane	100	2.80
4	Chalcone	Nitromethane	100	68.5 (*S*)[d]
5	Chalcone[e]	Nitromethane	Nil	—
6	Chalcone[f]	Nitromethane	98	−2.4

[a] All reactions are carried out in water for 24 h at room temperature.
[b] Analyzed by GC.
[c] Analyzed by HPLC using Chiralcel AD-H column.
[d] Absolute configuration is determined by comparing the specific rotation with that of the literature data.[27]
[e] With native β-cyclodextrin.
[f] With native β-cyclodextrin and triethylamine as an external base.

trans-chalcone **2**; although the conjugate addition of **3** to benzylideneacetone is effectively catalyzed, very poor enantioselectivity was obtained. On the other hand, **1** turns out to be a very good catalyst for the conjugate addition of **3** to **2**, resulting in good conversion as well as enantiomeric excess up to 68.5%. The absolute configuration is determined as (*S*) by comparison with the reported specific rotation values.[27] When the reaction is carried out with the native β-cyclodextrin in water, it completely fails to catalyze the addition. When triethylamine is employed as an external base along with native β-CD, good conversion is noticed, but with very poor enantiomeric excess (−2.4%). These preliminary results clearly show that **1** acts as a useful catalyst for the addition of **3** to **2** in aqueous medium.

Table 2
Per-6-ABCD **1** catalyzed asymmetric Michael addition in various solvents and with different amounts of catalyst[a]

Entry	Solvent	Per-6-ABCD:chalcone[b]	Yield[c] (%)	% ee[d]
1	ACN	1:1	Nil	—
2	Toluene	1:1	Nil	—
3	Methanol	1:1	100	34.6
4	DMF	1:1	Nil	—
5	Water	1:1	100	68.5
6	Water	1:0.25	100	66.0
7	Water	1:0.50	100	66.8
8	Water	1:2	100	67.2
9	Water[e]	1:1	100	63.6

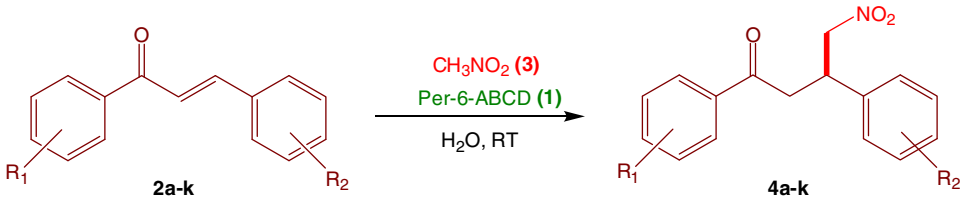
[a] All reactions are carried out at room temperature for 24 h. 10 mL of solvent is used for each reaction. After completion of the reaction, solvents are evaporated in vacuum and products are extracted with ethyl acetate.
[b] Mole ratio.
[c] Analyzed by GC.
[d] Analyzed by HPLC using Chiralcel AD-H column.
[e] Carried out at 4 °C.

Influences of other experimental parameters such as solvent, catalyst amount and temperature were also optimized using **1**. Conjugate addition of **3** to **2** is studied separately in water and in four different organic solvents (Table 2). In ACN, toluene and DMF, catalyst **1** is inactive. In methanol, a better yield but with low ee is observed. In water in addition to complete conversion, better enantiomeric excess is achieved under this reaction condition. Equimolar amounts of catalyst and substrate are employed in all the reactions as these form a 1:1 complex, which gives good chemical yield and ee. When the reaction is carried out at low temperature (4 °C), no significant improvement in ee is noticed.

This procedure thus avoids environmentally hazardous organic solvents. Use of aqueous medium also has several other advantages: the reaction proceeds under simpler experimental conditions at ambient temperature with no metals and other harmful external acids or bases. The reaction is also studied with various substituted chalcones as substrates. As shown in Table 3, addition of **3** to substituted chalcones **2a–k** containing electron-withdrawing and electron-donating groups on the phenyl ring was studied. In most cases, the corresponding Michael adducts are obtained in good yields and also with better enantiomeric excess, suggesting that electronic factors have only a limited role to play. The highest ee is observed with **2k**, which contains a 3-nitro group (which may ensure a stronger binding into the CD cavity). Chiral HPLC traces showing the ee in the case of a representative reaction are given in Figure 1.

The reusability of per-6-ABCD **1** as a catalyst is also examined. Even after three consecutive reactions, it retained its catalytic activity, resulting in 100% yield; however, the enantiomeric excess decreased considerably in the third run (Table 4).

Table 3
Per-6-ABCD **1** catalyzed asymmetric Michael addition of nitromethane **3** to chalcones **2a–k**[a]



Entry	Chalcones				Yield[b] (%)	% ee[c]
		R_1	R_2			
1	**2a**	H	H	**4a**	100	68.5
2	**2b**	H	4-Cl	**4b**	100	55.4
3	**2c**	H	2,3-Cl	**4c**	94	57.4
4	**2d**	4′-CH_3	4-Cl	**4d**	45	70.0
5	**2e**	H	4-F	**4e**	85	72.8
6	**2f**	4′-Br	H	**4f**	92	22.4
7	**2g**	H	4-OCH_3	**4g**	100	62.6
8	**2h**	H	3-OCH_3	**4h**	90.0	54.0
9	**2i**	4′-OH	H	**4i**	100	71.4
10	**2j**	2′-OH	H	**4j**	57	25.0
11	**2k**	H	3-NO_2	**4k**	100	87.0

[a] All reactions are carried out in water at room temperature for 24 h. All the products are characterized by ^{1}H and ^{13}C NMR.
[b] Isolated yield.
[c] Analyzed by HPLC using Chiralcel AD-H column.

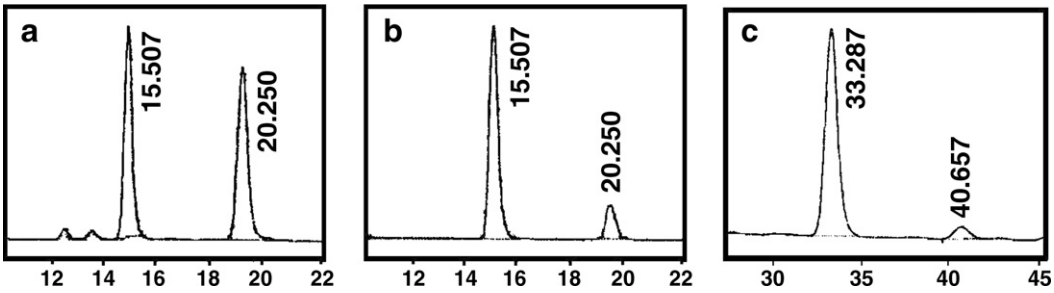


Figure 1. HPLC traces of Michael adducts of (a) **4a** with native β-CD + triethylamine, (b) **4a** with per-6-ABCD and (c) **4k** with per-6-ABCD.

Table 4
Reusability of per-6-ABCD **1** in asymmetric Michael addition of **3** with **2**[a]

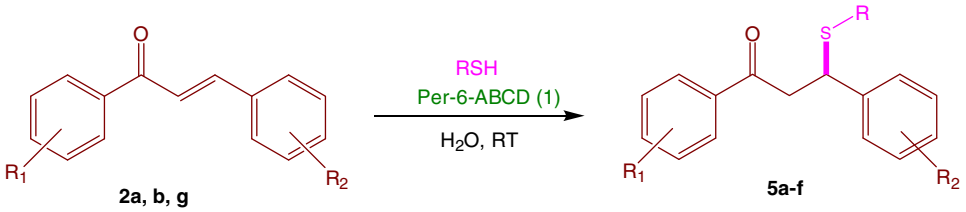
Entry	Substrate	Run[b]	Yield[c] (%)	% ee[d]
1	**2a**	First	100	68.5
2	**2a**	Second	100	66.8
3	**2a**	Third	100	58.0

[a] Reaction is carried out in water for 24 h at room temperature.
[b] After completion of the reaction **1** was filtered, washed with ethylacetate for three times, dried in vacuum and reused.
[c] Analyzed by GC.
[d] Analyzed by HPLC using Chiralcel AD-H.

Although various chiral catalysts are employed for the asymmetric conjugate addition between α,β-unsaturated ketone and arenethiols, studies are not extended to the addition of aliphatic thiols. To extend the scope of the present protocol further, per-6-ABCD **1** is also employed in enantioselective Michael addition of aliphatic thiols to *trans*-chalcones **2a**,**b**,**g** under the present conditions, and the observed results are given in Table 5. Butanethiol undergoes addition to **2a** with good yield and poor ee. With an increase in chain length as in octanethiol, although the yield has decreased, a marked improvement in ee is noticed. These results provide additional support that co-inclusion of the Michael donor and acceptor inside the CD cavity is necessary to achieve significant ee in the present study. On the other hand when compared with addition of nitromethane, the conversion is moderate and only marginal ee is observed. With thiophenol, although the yield is good, the ee is very low compared with aliphatic thiols. In all cases, no disulfide formation is observed in water medium.

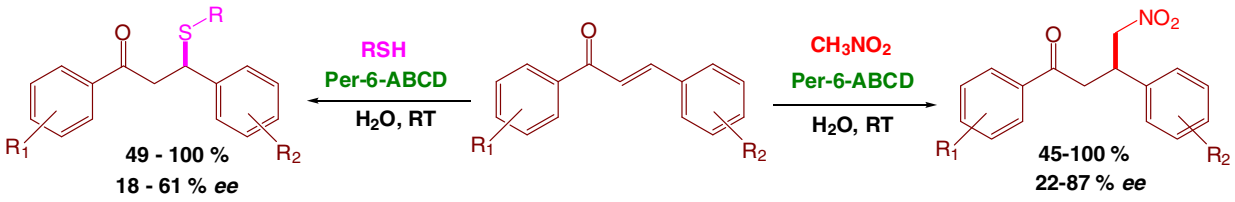
The observed reactivity and enantioselectivity in the presence of **1** are rationalized by proposing a suitable mechanism. Michael addition of **3** to **2** takes place inside the cavity of **1**, and the mode of inclusion is visualized as shown in Scheme 1. The phenyl ring along with olefinic double bond is deeply penetrated inside the cavity and the benzoyl part of **2** stays out of the wider rim of **1**. This type of inclusion is preferred more and is evident from energy minimization studies. This mode of inclusion (mode a, Fig. 2), has a lower complexation energy ($\Delta E = -38.00$ kcal M^{-1}) than the other mode (mode b, Fig. 2), in which the benzoyl moiety penetrates inside the cavity and the phenyl group with olefinic double bond stays outside ($\Delta E = -36.60$ kcal M^{-1}). This complexation is stabilized by hydrogen bonding between the carbonyl group of chalcone **2** and per-6-ABCD's **1** secondary hydroxyl groups (Fig. 2). During the addition of **3**, a ternary complex of **2** and **3** with **1** is formed, which has a higher binding constant (3674 M^{-1}). This ternary complex is more stable than a binary complex (1391 M^{-1}) of **1** and **2**, which is also supported by molecular modelling studies. Primary amino groups present in the narrow rim of **1** act as an internal base (pK_a 6.5–8.9),[66] activating the nitromethane by abstracting a proton followed by nucleophilic attack, which is favoured from the amino functionalized narrow rim side of **1**. This leads to the formation of the major (*S*)-isomer and was confirmed from the specific rotation[27] of the adduct. If the attack takes place from the wider rim of CD, it may lead to formation of the (*R*)-enantiomer, which is obtained as the major isomer in the β-CD triethylamine system (Table 1, entry 6) and not observed with **1**. Active participation and catalysis by the amino groups of **1** are also supported by the fact that per-6-amino-β-cyclodextrin hydrochloride fails to catalyze the addition of **3** to **2.** The complexation energies of two enantiomers

Table 5
Per-6-ABCD **1** catalyzed asymmetric Michael addition of thiols to chalcones **2a**,**b**,**g**[a]



Entry		Chalcones		Thiols (RSH)		Yield[b] (%)	% ee[c]
		R_1	R_2				
1	**2a**	H	H	*n*-Butanethiol	**5a**	100	23.0
2	**2a**	H	H	*n*-Octanethiol	**5b**	50	42.2
3	**2a**	H	H	Thiophenol	**5c**	75	4.00
4	**2b**	H	4-Cl	*n*-Butanethiol	**5d**	82	29.0
5	**2b**	H	4-Cl	*n*-Octanethiol	**5e**	50	60.6
6	**2g**	H	4-OCH_3	*n*-Octanethiol	**5f**	54	18.2

[a] All reactions are carried out in water at room temperature for 24 h, and the products are characterized by ^1H and ^{13}C NMR.
[b] Isolated yield.
[c] Analyzed by HPLC using Chiralcel OD-H column.



Scheme 1. Per-6-ABCD catalyzed asymmetric Michael addition of nitromethane and thiols to chalcones.

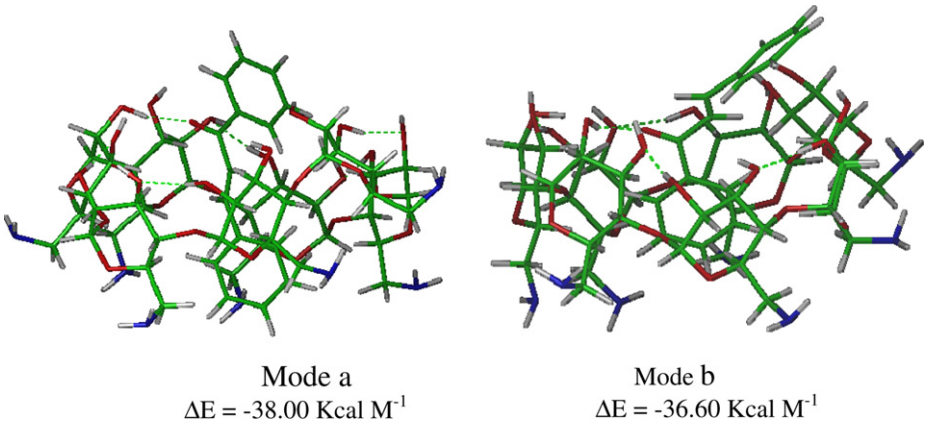


Figure 2. CVFF-optimized inclusion complex of per-6-ABCD **1** with *trans*-chalcone **2a**; In mode (a) the chalcone's olefinic double bond is inside the CD-cavity and benzoyl part is outside the cavity. In mode (b) olefinic double bond is outside the CD-cavity and benzoyl part is inside the cavity.

(*R*)- and (*S*)- of Michael adduct **4a** with CD are also calculated, and confirm that the (*S*)-enantiomer forms a more stable complex with ($\Delta E = -46.03$ kcal M^{-1}, mode c, Fig. 3) than the corresponding (*R*)-enantiomer ($\Delta E = -35.47$ kcal M^{-1}, mode d, Fig. 3).

3. Conclusions

In conclusion, per-6-ABCD is successfully employed for the first time as a chiral catalyst and as a base for the asymmetric Michael addition of nitromethane and aliphatic thiols to chalcones in aqueous medium. Per-6-ABCD **1** performs a dual role, acting both as a base to catalyze the reaction and as a chiral inductor by enhancing the enantiomeric excess. In the additions of both nitromethane and thiols, better enantioselectivities are observed and water is employed (without any cosolvent) as an eco-friendly solvent in this asymmetric Michael addition, and the catalyst is reused without any loss in its activity. The reaction takes place readily at room temperature and does not require lower temperature to achieve good ee. Other advantages include much more simpler experimental conditions, ease of recovery and reuse of catalyst, and the absence of hazardous external acids and bases (Scheme 2).

4. Experimental

4.1. Materials

Per-6-amino-β-cyclodextrin was synthesized and purified according to the procedure described in the literature.[67] The product was dried for 24 h in dryer under vacuum over phosphorus pentoxide at 60 °C and then stored in a vacuum desiccator. β-Cyclodextrin, *trans*-chalcone, nitromethane, diethyl malonate and malononitrile were purchased from Aldrich. *n*-Butanethiol,

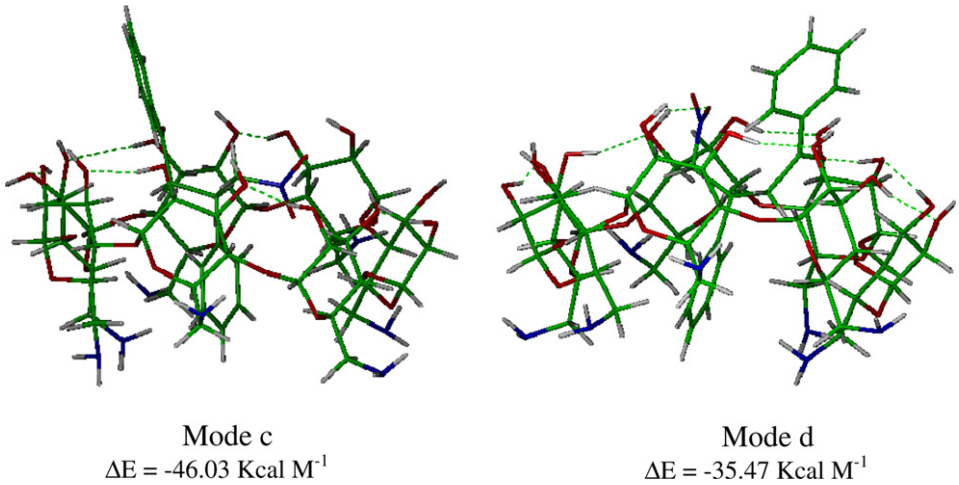
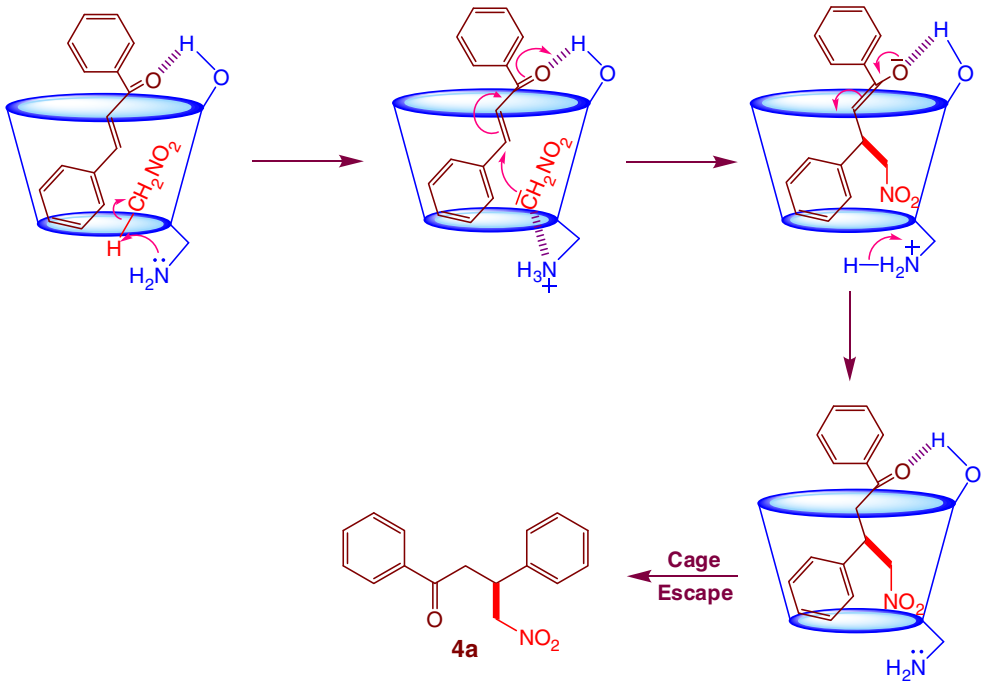


Figure 3. CVFF-optimized inclusion complex of per-6-ABCD **1** with (*S*)-enantiomer of Michael adduct **4a** (mode c) and (*R*)-enantiomer of Michael adduct **4a** (mode d).



Scheme 2. Proposed mechanism for asymmetric Michael addition catalyzed by per-6-ABCD **1**.

n-octanethiol and thiophenol were purchased from Merck. Substituted chalcones and benzylideneacetone were prepared as described in the literature.[68] Double distilled water was used for all reactions.

Nuclear magnetic resonance (NMR) spectra were acquired on a Bruker DRX-300 (300 MHz) instrument using TMS as an internal standard. Gas Chromatographic analysis was performed in Shimadzu 17A, using ZB-5, 30 m capillary column, FID detector and high purity nitrogen as carrier gas. For column chromatography, Merck Silica Gel 60–120 mesh is employed. Specific rotations were measured using a RUDOLPH Autopol® IV Polarimeter. Enantiomer ratios were determined by chiral HPLC analysis using a Shimadzu LC-10AT *VP* series and a Shimadzu LC-10A *VP* UV–vis detector with Chiralcel AD-H and OD-H columns using *n*-hexane and *i*-propanol as mobile phases. Binding constants were calculated by non-linear regression using prism software (trial version) in an IBM compatible personal computer with Microsoft Windows XP service pack 2 operating system.

4.2. Energy minimization studies

Energy minimized geometries of the complexes were obtained using Molecular Mechanics Calculations by INSIGHT II/DISCOVER program.[69–71] The initial structures of host and guest molecules were constructed by INSIGHT II/DISCOVER on Silicon Graphics IRIS workstation. We have adapted CVFF force field to express the MM energies of per-6-ABCD host, *trans*-chalcone, Michael adducts and their complexes. Structures were minimized using CVFF force field and RMS derivative 0.001 was achieved in each case. Complexation energies were calculated using the following equation: $\Delta E = \Delta E_{\text{Complex}} - \Delta E_{\text{Host}} - \Delta E_{\text{Guest}}$.

4.3. Procedure for asymmetric Michael addition of nitromethane 3 to chalcones 2

Per-β-ABCD **1** (0.112 g, 0.1 mmol) was dissolved in water (10 mL). *trans*-Chalcone **2** (0.02 g, 0.1 mmol) dissolved in acetone (1 mL) was added dropwise to **1** with constant stirring and continued for an hour to complete complexation. Then, nitromethane **3** (0.024 mL, 0.4 mmol) was added and allowed to stir at room temperature for 24 h. After completion of the reaction, the product was extracted with ethyl acetate, dried with sodium sulfate and concentrated under reduced pressure. The resulting crude product was purified by passing over a column of Silica Gel 60–120 mesh using pet-ether/ethyl acetate (8/2 ratio as an eluant) affording Michael adduct **4** as a pale yellow solid, which was analyzed by NMR spectroscopy (300 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm) and CSP (Chiral Stationary Phase)-HPLC. Percentage ee was determined by HPLC at 254 nm using chiralcel AD-H column, with *n*-hexane/*i*-propanol (90/10) mixture at a flow rate of 1.0 mL/min. After extraction of the product, per-6-ABCD was washed three times with ethyl acetate, filtered, dried in vacuum and reused.

4.4. Procedure for asymmetric Michael addition of thiols to chalcones 2

Per-β-ABCD **1** (0.112 g, 0.1 mmol) was dissolved in water (10 mL). *trans*-Chalcone **2** (0.02 g, 0.1 mmol) was dissolved in acetone (1 mL) and was added dropwise to **1** with constant stirring and continued for an hour to complete complexation. Then, *n*-butanethiol (0.01 mL, 0.1 mmol) was added and allowed to stir at room temperature for 24 h. After completion of the reaction, the product was extracted with ethyl acetate, dried with sodium sulfate and concentrated under reduced pressure, and resulting crude product was purified by passing over a column of Silica Gel 60–120 mesh using pet-ether/ethyl acetate (9/1 ratio as an eluant) affording Michael adduct **5** as a yellow oily liquid, which was analyzed by NMR spectroscopy (300 MHz, $CDCl_3$, T = 300 K, TMS = 0 ppm) and CSP-HPLC. Percentage ee was determined by HPLC at 254 nm using chiralcel OD-H column, with *n*-hexane/*i*-propanol (90/10) mixture at a flow rate of 1.0 mL/min.

4.4.1. 4-Nitro-1,3-diphenylbutan-1-one 4a[11]

The crude product was purified by column chromatography on silica gel (pet-ether/ethyl acetate = 9/1 as eluant). $[\alpha]_D^{25} = -11.1$, (*c* 1.00, CH_2Cl_2), ^{1}H NMR (300 MHz,$CDCl_3$): δ 7.91 (d, J = 8.4 Hz, 2H),

7.25–7.60 (m, 8H), 4.83 (ABX, J_{AB} = 12.3 Hz, J_{AX} = 6.6 Hz, J_{BX} = 7.8 Hz, 1H), 4.71 (ABX, J_{AB} = 12.3 Hz, J_{AX} = 6.6 Hz, J_{BX} = 7.8 Hz, 1H), 4.23 (br pseudo quintet, J = 7.2 Hz, 1H), 3.38–3.53 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.8, 139.0, 136.3, 133.5, 129.0, 128.7, 128.0, 127.8, 127.4, 79.5, 41.4, 39.2. HPLC: 68.5% ee, t_{major} 15.5 min, t_{minor} 20.2 min.

4.4.2. 3-(4-Chlorophenyl)-4-nitro-1-phenylbutan-1-one 4b

The crude product was purified by column chromatography on silica gel (pet-ether/ethyl acetate = 8/2 as eluant). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, J = 8.1 Hz, 2H), 7.59 (t, J = 7.2 Hz, 1H), 7.46 (t, J = 7.2 Hz, 2H), 7.31 (d, J = 8.7 Hz, 2H), 7.23 (d, J = 3.4 Hz, 2H), 4.82 (ABX, J_{AB} = 12.6 Hz, J_{AX} = 6.6 Hz, J_{BX} = 8.1Hz, 1H), 4.66 (ABX, J_{AB} = 12.6 Hz, J_{AX} = 6.6 Hz, J_{BX} = 8.1 Hz, 1H), 4.22 (br pseudo quintet, J = 7.2 Hz, 1H), 3.46 (ABX, J_{AB} = 18 Hz, J_{AX} = 6.6 Hz, J_{BX} = 7.2 Hz, 1H), 3.40 (ABX, J_{AB} = 18 Hz, J_{AX} = 6.6 Hz, J_{BX} = 7.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.4, 137.5, 136.1, 133.7, 132.2, 129.2, 128.8, 128.7, 127.9, 79.3, 41.3, 38.6. HPLC: 55.4% ee, t_{major} 17.7 min, t_{minor} 25.1 min.

4.4.3. 3-(2,3-Dichlorophenyl)-4-nitro-1-phenylbutan-1-one 4c

The crude product was purified by column chromatography on silica gel (pet-ether/ethyl acetate = 8/2 as eluant). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.92 (d, J = 8.1 Hz, 2H), 7.60 (t, J = 7.8 Hz, 1H), 7.40–7.50 (m. 4H), 7.15 (d, J = 8.1 Hz, 1H), 4.82 (ABX, J_{AB} = 12.7 Hz, J_{AX} = 6.3 Hz, J_{BX} = 8.1 Hz, 1H), 4.66 (ABX, J_{AB} = 12.7 Hz, J_{AX} = 6.3, J_{BX} = 8.1 Hz, 1H), 4.21 (br pseudo quintet, J = 6.9 Hz, 1H), 3.43 (d, J = 6.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.0, 139.3, 135.9, 133.8, 133.1, 132.0, 130.9, 129.5, 128.8, 127.9, 126.9, 78.9, 41.1, 38.3. HPLC: 57.4% ee, t_{major} 15.7 min, t_{minor} 19.7 min.

4.4.4. 3-(4-Chlorophenyl)-4-nitro-1-*p*-tolylbutan-1-one 4d

The crude product was purified by column chromatography on silica gel (pet-ether/ethyl acetate = 8/2 as eluant). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81 (d, J = 8.1 Hz, 2H), 7.21–7.37 (m, 6H), 4.82 (ABX, J_{AB} = 12.6 Hz, J_{BX} = 8.4 Hz, 1H), 4.65 (ABX, J_{AB} = 12.6 Hz, J_{BX} = 8.4 Hz, 1H) 4.21 (br pseudo quintet J = 6.9 Hz, 1H), 3.41 (ABX, J_{AB} = 17.7 Hz, J_{AX} = 6.9 Hz, J_{BX} = 8.1 Hz, 1H), 3.39 (ABX, J_{AB} = 17.7 Hz, J_{AX} = 6.9 Hz, J_{BX} = 8.1 Hz, 1H), 2.14 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.0, 144.6, 137.6, 133.6, 130.5, 129.4, 129.2, 128.8, 128.1, 79.3, 41.1, 38.6, 21.6. HPLC: 70.0% ee, t_{major} 19.7 min, t_{minor} 25.2 min.

4.4.5. 3-(4-Fluorophenyl)-4-nitro-1-phenylbutan-1-one 4e

The crude product was purified by column chromatography on silica gel (pet-ether/ethyl acetate = 8/2 as eluant). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, J = 7.2 Hz, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 7.8 Hz, 2H), 7.26 (t, J = 8.1 Hz, 2H), 7.02 (t, J = 8.1Hz, 2H), 4.82 (ABX, J_{AB} = 12.3 Hz, J_{AX} = 6.6 Hz, J_{BX} = 8.1 Hz, 1H), 4.65 (ABX, J_{AB} = 12.3 Hz, J_{AX} = 6.6 Hz, J_{BX} = 8.1 Hz,1H) 4.22 (br pseudo quintet J = 7.5 Hz, 1H), 3.43 (dd, J = 6.9 Hz, 1.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.5, 163.7, 136.2, 134.7, 133.6, 129.0 (d), 128.7, 127.6, 115.9 (d), 79.5, 41.4, 38.5. HPLC: 72.8% ee, t_{major} 16.9 min, t_{minor} 23.3 min.

4.4.6. 1-(4-Bromophenyl)-4-nitro-3-phenylbutan-1-one 4f

The crude product was purified by column chromatography on silica gel (pet-ether/ethyl acetate = 8/2 as eluant). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, J = 8.7 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.26–7.36 (m, 5H), 4. 81 (ABX, J_{AB} = 12.3 Hz, J_{AX} = 6.6 Hz, J_{BX} = 7.5 Hz, 1H), 4.68 (ABX, J_{AB} = 12.3 Hz, J_{AX} = 6.6 Hz, J_{BX} = 7.5 Hz, 1H), 4.20 (br pseudo quintet, J = 7.2 Hz, 1H), 3.42 (dd, J = 6.6, 2.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.8, 138.8, 134.9, 132.0, 129.5, 129.1, 128.8, 127.9, 127.4, 79.4, 41.4, 39.1. HPLC: 22.4% ee, t_{major} 23.1 min, t_{minor} 29.0 min.

4.4.7. 3-(4-Methoxyphenyl)-4-nitro-1-phenylbutan-1-one 4g

The crude product was purified by column chromatography on silica gel (pet-ether/ethyl acetate = 8/2 as eluant). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.92 (d, J = 7.9 Hz, 2H), 7.58 (t, J = 7.8 Hz, 1H), 7.46 (t, J = 7.8 Hz, 2H), 7.20 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.7Hz, 2H), 4.80 (ABX, J_{AB} = 12.3 Hz, J_{AX} = 6.6 Hz, J_{BX} = 7.8 Hz, 1H), 4.64 (ABX, J_{AB} = 12.3 Hz, J_{AX} = 6.6 Hz, J_{BX} = 7.8 Hz, 1H), 4.18 (br pseudo quintet, J = 7.2 Hz, 1H), 3.77 (s, 3H), 3.42 (dd, J = 6.6, 2.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.3, 159.4, 136.7, 133.9, 131.3, 129.1, 128.9, 128.4, 114.8, 80.2, 55.6, 42.0, 39.0. HPLC: 62.6% ee, t_{major} 23.1 min, t_{minor} 29.0 min.

4.4.8. 3-(3-Methoxyphenyl)-4-nitro-1-phenylbutan-1-one 4h

The crude product was purified by column chromatography on silica gel (pet-ether/ethyl acetate = 8/2 as eluant). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29 (d, J = 7.8 Hz, 2H), 7.58 (t, J = 8.1 Hz, 1H), 7.46 (t, J = 7.5 Hz, 2H), 7.26 (s, 1H). 6.18 (m, 3H), 4.82 (ABX, J_{AB} = 12.3 Hz, J_{AX} = 6.6 Hz, J_{BX} = 7.9 Hz, 1H), 4.67 (ABX, J_{AB} = 12.3 Hz, J_{AX} = 6.6 Hz, J_{BX} = 7.9 Hz, 1H), 4.20 (br pseudo quintet, J = 7.2 Hz, 1H), 3.45 (m, 2H), 3.78 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.7, 159.8, 140.6, 136.2, 133.5, 130.0, 128.7, 127.9, 119.4, 113.6, 112.8, 79.4, 55.1, 41.4, 39.2. HPLC: 54.0% ee, t_{major} 18.9 min, t_{minor} 22.6 min.

4.4.9. 1-(4-Hydroxyphenyl)-4-nitro-3-phenylbutan-1-one 4i

The crude product was purified by column chromatography on silica gel (pet-ether/ethyl acetate = 7/3 as eluant). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85 (d, J = 8.7 Hz, 2H), 7.26–7.33 (m, 5H), 6.86 (d, J = 9 Hz, 2H), 6.23 (s, 1H), 4.83 (ABX, J_{AB} = 12.3 Hz, J_{AX} = 6.6 Hz, J_{BX} = 8.1 Hz, 1H) 4.68 (ABX, J_{AB} = 12.3 Hz, J_{AX} = 6.6 Hz, J_{BX} = 8.1 Hz, 1H), 4.21 (br pseudo quintet, J = 7.2 Hz, 1H), 3.40 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.6, 160.6, 139.1, 130.6, 129.0, 127.8, 127.4, 115.4, 79.6, 41.1, 39.4. HPLC: 71.4% ee, t_{major} 15.6 min, t_{minor} 20.2 min.

4.4.10. 1-(2-Hydroxyphenyl)-4-nitro-3-phenylbutan-1-one 4j

The crude product was purified by column chromatography on silica gel (pet-ether ethyl acetate = 7/3 as eluant). ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.01 (s, 1H), 8.22 (t, J = 2.1 Hz, 1H), 8.18 (d, J = 8.5 Hz, 2H), 7.95 (d, J = 8.1 Hz, 2H), 7.72 (d, J = 7.8 Hz, 2H), 7.52–7.66 (m, 1H), 7.50 (t, J = 7.8 Hz, 1H), 4.92 (ABX, J_{AB} = 12.9 Hz, J_{AX} = 6.3 Hz, J_{BX} = 8.4 Hz, 1H), 4.72 (ABX, J_{AB} = 12.9 Hz, J_{AX} = 6.3 Hz, J_{BX} = 8.4 Hz, 1H), 4.41 (br pseudo quintet J = 8.1 Hz, 1H), 3.55 (d, J = 6.9Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 202.6, 162.4, 138.6, 136.8, 129.1, 128.6, 128.2, 127.3, 127.0, 118.8, 79.4, 55.8, 41.0, 39.0. HPLC: 25.0% ee, t_{major} 13.0 min, t_{minor} 15.3 min.

4.4.11. 4-Nitro-3-(3-nitrophenyl)-1-phenylbutan-1-one 4k

The crude product was purified by column chromatography on silica gel (pet-ether/ethyl acetate = 8/2 as eluant). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.22 (t, J = 2.1 Hz, 1H), 8.18 (d, J = 8.5 Hz, 1H), 7.95 (d, J = 8.1 Hz, 2H), 7.72 (d, J = 7.8 Hz, 1H), 7.52–7.66 (m, 2H), 7.50 (t, J = 7.8 Hz, 2H), 4.92 (ABX, J_{AB} = 12.9 Hz, J_{AX} = 6.3 Hz, J_{BX} = 8.4 Hz, 1H), 4.72 (ABX, J_{AB} = 12.9 Hz, J_{AX} = 6.3 Hz, J_{BX} = 8.4 Hz, 1H), 4.41 (br pseudo quintet, J = 8.1 Hz, 1H), 3.55 (d, J = 6.9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.3, 148.9, 141.7, 136.3, 134.8, 134.3, 130.5, 129.2, 128.4, 123.4.122.6, 79.3, 41.5, 39.2. HPLC: 87.0% ee, t_{major} 33.2 min, t_{minor} 40.6 min.

4.4.12. 3-(Butylthio)-1,3-diphenylpropan-1-one 5a

The crude product was purified by column chromatography on silica gel (pet-ether/ethyl acetate = 9/1 as eluant). ^{1}H NMR (300 MHz,$CDCl_3$): δ 7.91 (d, J = 7.5 Hz, 2H), 7.54 (t, J = 7.5 Hz, 1H), 7.43 (t, J = 7.8 Hz, 4H), 7.30 (t, J = 7.2 Hz, 2H), 7.20 (t, J = 7.5 Hz, 1H), 4.55 (s, J = 6.9 Hz, 1H), 3.53 (d, J = 6.9 Hz, 2H), 2.33 (m, 2H), 1.46 (m, 2H), 1.31 (m, 2H), 0.83 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75

MHz, $CDCl_3$): δ 197.0, 142.2, 136.7, 133.2, 128.6, 128.0, 127.8, 127.1, 45.4, 44.2, 31.2, 31.1, 29.7, 21.9, 13.6. HPLC: 23.0% ee, t_{major} 5.0 min, t_{minor} 5.2 min.

4.4.13. 3-(Octylthio)-1,3-diphenylpropan-1-one 5b

The crude product was purified by column chromatography on silica gel (pet-ether/ethyl acetate = 9/1 as eluant). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7. 90 (d, J = 7.9 Hz, 2H), 7.52 (t, J = 7.2 Hz, 1H), 7.42 (dd, J = 6.9 Hz, 1.8 Hz, 4H), 7.29 (t, J = 7.2 Hz, 2H), 7.20 (t, J = 7.2 Hz, 1H), 4.55 (t, J = 6.9 Hz, 1H), 3.54 (d, J = 6.6 Hz, 2H), 1.48 (m, 2H), 1.32 (m, 2H), 1.25 (m, 10H), 0.865 (t, J = 6.6, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.9, 142.2, 136.7, 133.1, 128.5, 128.4, 128.0, 127.8, 127.1, 45.3, 44.2, 31.7, 31.4, 29.2, 29.1, 29.0, 28.8, 22.6, 14.1. HPLC: 42.2% ee, t_{major} 4.6 min, t_{minor} 4.8 min.

4.4.14. 1,3-Diphenyl-3-(phenylthio)propan-1-one 5c

The crude product was purified by column chromatography on silica gel (pet-ether/ethyl acetate = 9/1 as eluant). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, J = 7.2 Hz, 2H), 7.58 (t, J = 7.2 Hz, 1H), 7.46 (t, J = 7.8 Hz, 2H), 7.36 (m, 5H), 7.25 (m, 5H), 4.99 (t, J = 7.2 Hz, 1H), 3.65 (m, J = 17.4 Hz, 8.1 Hz, 5.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.4, 141.5, 137.1, 134.6, 133.6, 133.1, 129.4, 129.2, 128.8, 128.4, 128.2, 127.8, 127.7, 48.5, 47.0. HPLC: 4.00% ee, t_{major} 6.4 min, t_{minor} 6.8 min.

4.4.15. 3-(Butylthio)-3-(4-chlorophenyl)-1-phenylpropan-1-one 5d

The crude product was purified by column chromatography on silica gel (pet-ether/ethyl acetate = 9/1 as eluant). ^{1}H NMR (300 MHz,$CDCl_3$): δ 7.91 (d, J = 7.8 Hz, 2H), 7.54 (t, 2H, J = 6.9 Hz, 2H), 7.43 (t, J = 7.8 Hz, 1H), 7.33 (d, J = 8.4 Hz, 2H), 6.83 (d, J = 8.4 Hz, 2H), 4.52 (t, J = 7.2 Hz, 1H), 3.50 (dd, J = 7.8 Hz, 2.7 Hz, 2H), 2.31 (m, 2H), 1.48 (m, 2H), 1.30 (m, 2H), 0.83 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.1, 158.5, 136.8, 134.1, 133.1, 128.8, 128.5, 128.1, 113.8, 45.5, 43.6, 31.2, 31.0, 21.9, 13.6. HPLC: 29.0% ee, t_{major} 4.9 min, t_{minor} 5.0 min.

4.4.16. 3-(4-Chlorophenyl)-3-(octylthio)-1-phenylpropan-1-one 5e

The crude product was purified by column chromatography on silica gel (pet-ether/ethyl acetate = 9/1 as eluant). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (d, J = 7.2 Hz, 2H), 7.57 (t, J = 7.2 Hz, 1H), 7.46 (t, J = 7.8 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 4.56 (t, J = 7.2 Hz, 1H), 3.54 (d, J = 7.2 Hz, 2H), 2.35 (m, 2H), 1.53 (m, 2H), 1.29 (m, 10H), 0.91 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.0, 141.3, 137.0, 133.7, 133.1, 130.0, 129.6, 129.06, 129.05, 128.4, 45.7, 44.0, 32.2, 31.8, 29.55, 29.52, 29.2, 23.0. 14.5. HPLC: 60.6% ee, t_{major} 4.1 min, t_{minor} 4.5 min.

4.4.17. 3-(4-Methoxyphenyl)-3-(octylthio)-1-phenylpropan-1-one 5f

The crude product was purified by column chromatography on silica gel (pet-ether ethyl acetate = 9/1 as eluant). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20 (d, J = 7.2 Hz, 2H), 7.51 (t, J = 7.2 Hz, 1H), 7.40 (t, J = 7.2 Hz, 2H), 7.30 (d, J = 8.7 Hz, 2H), 6.80 (d, J = 8.7 Hz, 2H), 4.50 (t, J = 7.2 Hz, 1H), 3.74 (s, 3H), 3.48 (dd, J = 7.5 Hz and 3.0 Hz, 2H), 2.28 (m, 2H), 1.46 (m, 2H), 1.19 (m, 10H), 0.84 (t, J = 6.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.1, 158.5, 136.7, 134.1, 133.1, 128.8, 128.5, 128.0, 113.7, 55.1, 45.5, 43.6, 31.7, 31.3, 29.16, 29.13, 29.11, 28.8, 22.6, 14.1. HPLC: 18.2% ee, t_{major} 8.1 min, t_{minor} 8.4 min.

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