

Effective regioselective protection of amino groups of lysine achieved by a supramolecular enzyme-mimic
approach

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Supporting information

Table of Contents

EXPERIMENTAL SECTION	2
N- ϵ -Benzyloxycarbonyl-L-lysine.....	2
NMR.....	3
Liquid Chromatography/Mass Spectrometry.....	3
Cbz reacted with lysine in the present of β -CD derivatives	6
Other protective groups reacted with lysine in the present of β -CD.....	7
DFT calculations.....	8
FT-IR.....	34
Reference	35

EXPERIMENTAL SECTION

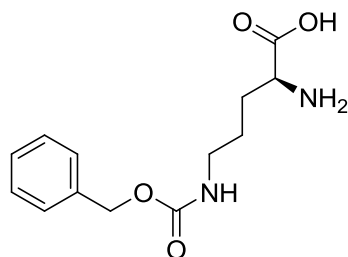
Materials

β -CD and derivatives were purchased from ShangdongZiyuan Chemical Reagent Co. Ltd, China. Standard sample N- ϵ -Benzyloxycarbonyl-L-lysine was purchased from Acros. Other reagents were all commercially available from Country Medicine Reagent Co. Ltd, Shanghai, China.

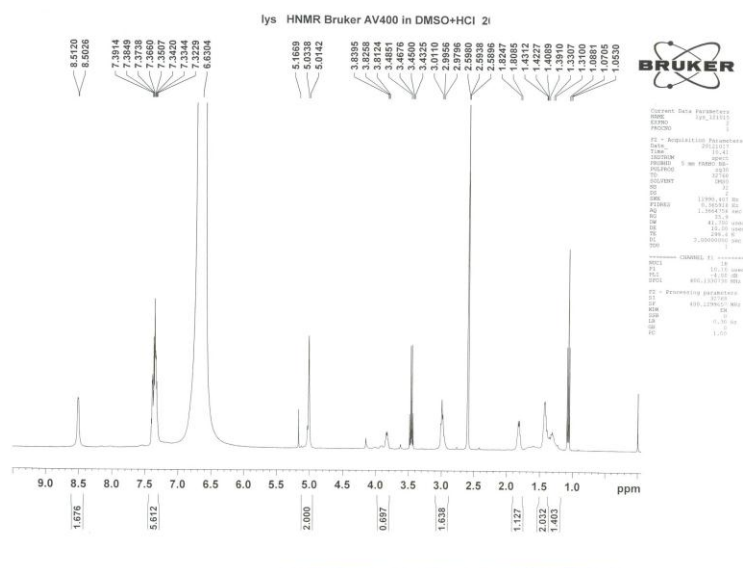
General Procedure for the Preparation of L-lysine Protection Derivatives

β -Cyclodextrin(0.1 mmol) was dissolved in 0.1 M carbonate buffer (pH = 8) (10 mL) at room temperature, then the L-lysine (1 mmol) was added and the reaction mixture was stirred for 5 min. Cbz-Cl (1 mmol) was added and stirring was continued at room temperature until the reaction was complete. The reaction mixture was extracted with ethyl acetate. The solvent was removed under vacuum and obtained the products.

N- ϵ -Benzyloxycarbonyl-L-lysine



m.p. 250-251 °C (Lit.¹ 252-254 °C) ¹H NMR (400 MHz, d₆-DMSO and one drop of HCl) δ 1.31 –1.43 (4H, m, CH₂CH₂); 1.80 –1.82 (2H, m, CH₂); 2.97 –3.01 (2H, m, CH₂⁶); 5.03 (2H, s, CH₂Ar); 7.32 –7.39 (5H, m, Ar); 8.50 (2H, s, NH₂)²



NMR

2D ^1H - ^1H NOESY experiments were recorded using an INOVA-600 (600 MHz) spectrometer at ambient temperature. A mixing time of 0.200 s, a relaxation delay time of 1.000 s, and an acquisition time of 0.228 s were used. All plus sequences were set according to the manufacturer's standards. TMS was used as internal standard.

Liquid Chromatography/Mass Spectrometry

Liquid Chromatography was recorded on an Agilent 1200 series. The separation was performed using mobile phase consisting of MeOH, H₂O (50: 50 v/v) with 0.1% TEA. The column used was a waters C₁₈ column (250 × 4.6 mm internal diameter with 5- μm particle size). The flow rate was 1.0 ml/min. Mass spectra were recorded on an Agilent 6510 Q-TOF, equipped with an electrospray ionization source (ESI). The capillary temperature was 350°C, drying gas is 12 L/min, and the spray voltage was 4.0 kV for all applications. Standard sample are purchased from Acros. Co. Limit.

Table S1 Retention time and ion mass

Target compound	R_t (min)	Ion
N- α -Benzyloxycarbonyl-L-lysine	2.265	281
N- ϵ -Benzyloxycarbonyl-L-lysine	4.736	281

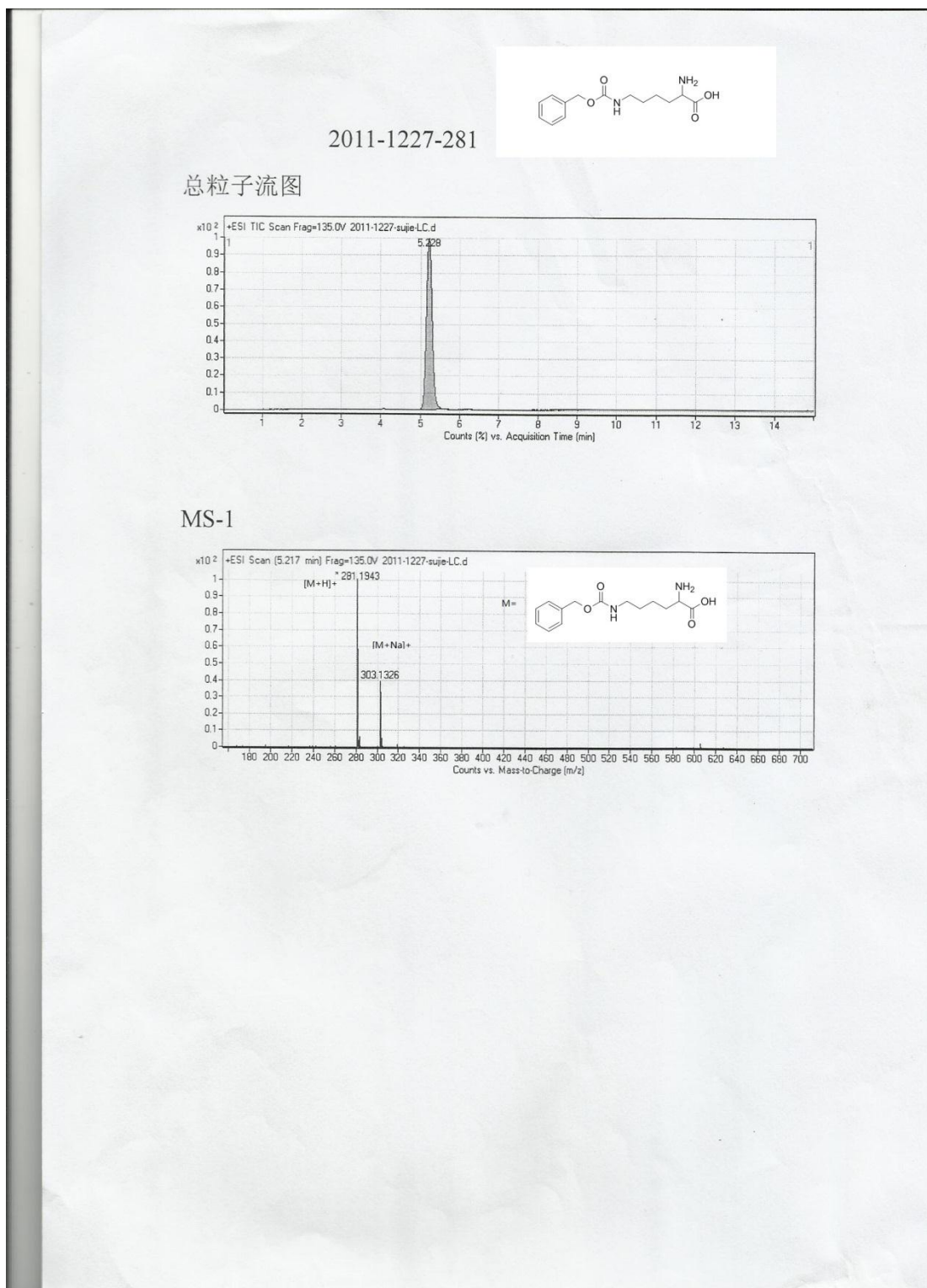
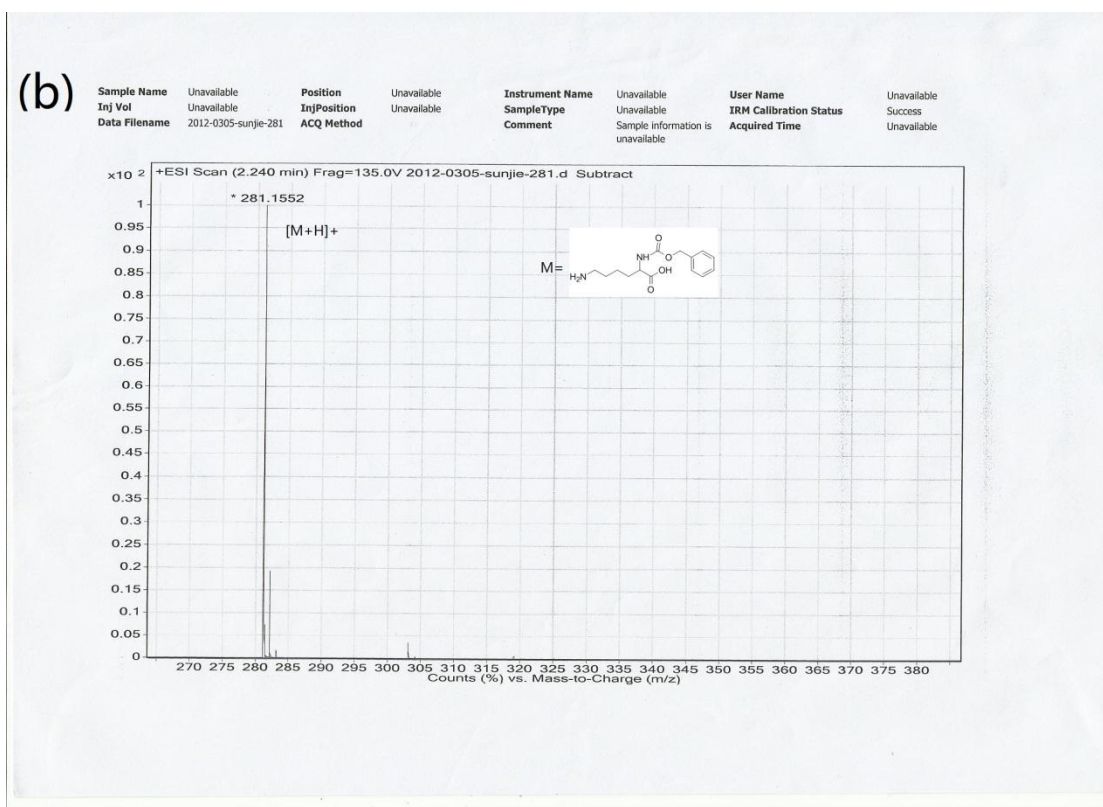
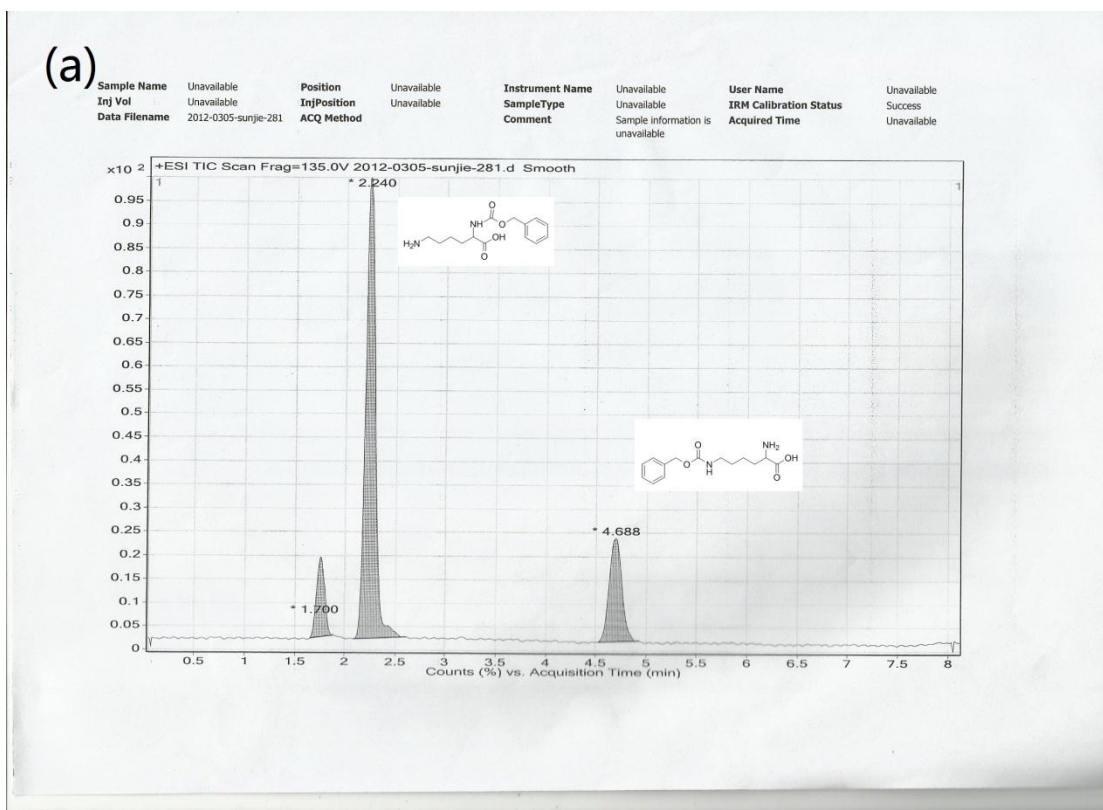


Figure. S1 LC/MS spectra of lysine Cbz reaction in the present β -CD



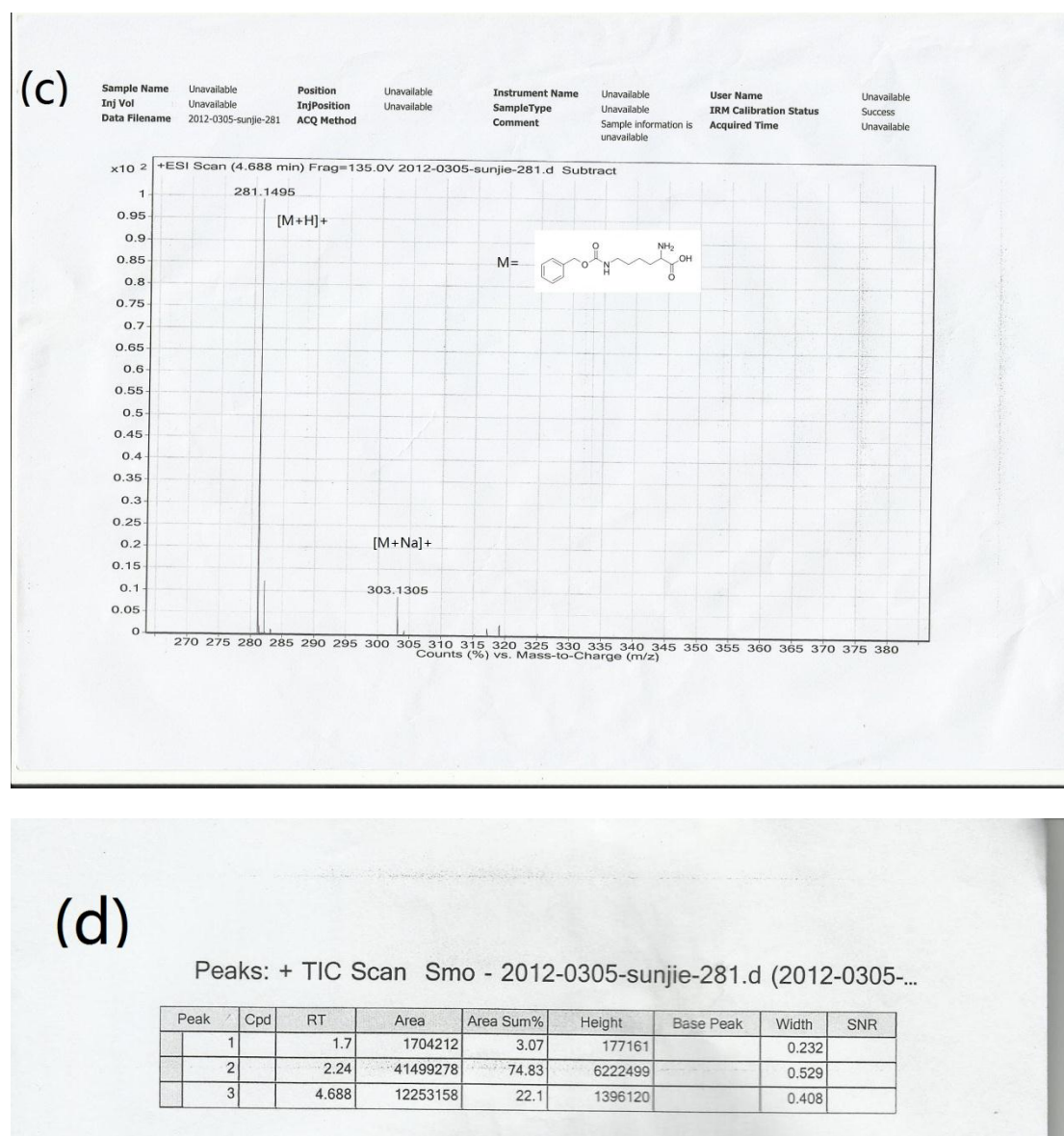


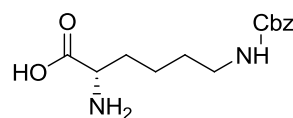
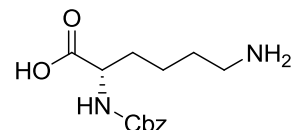
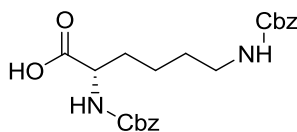
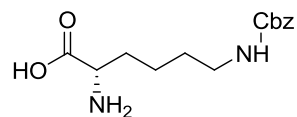
Figure. S2 LC/MS spectra of lysine Cbz reaction in the present of EDA- β -CD (a) HPLC spectrum of reaction product (b) mass spectrum of peak 2.2 min (c) mass spectrum of peak 4.7 min (d) analysis result of product.

Cbz reacted with lysine in the present of β -CD derivatives

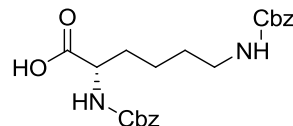
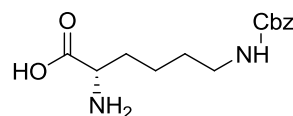
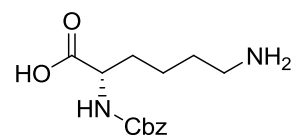
Table S2. Cbz reacted with lysine in the present of β -CD derivative

β -CD derivative	Product
hydroxypropyl- β -CD	

sulfydryl- β -CD



methyl- β -CD



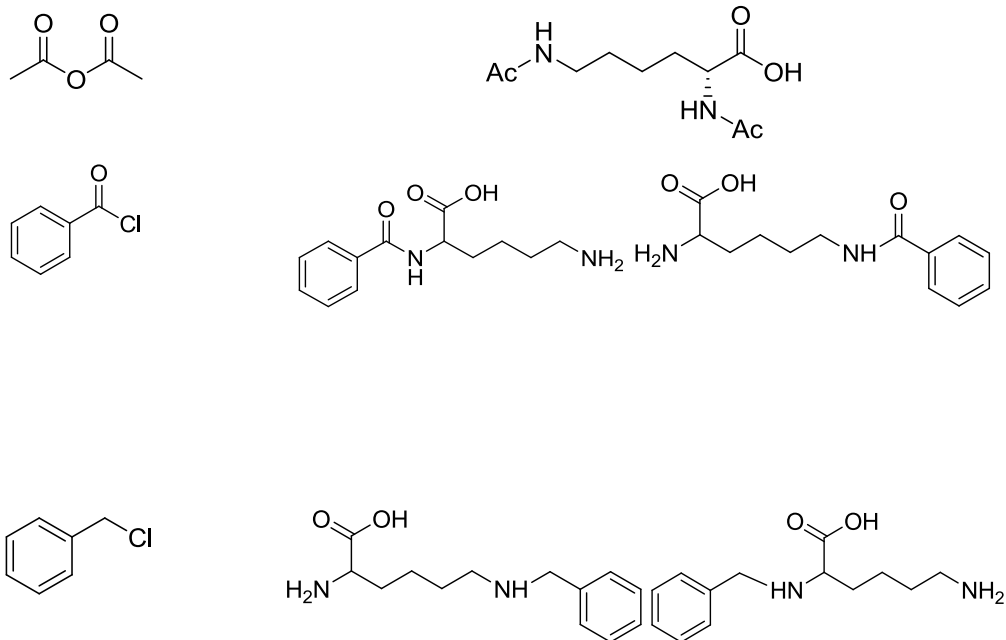
sulfobutylether- β -CD

Not detective

Other protective groups reacted with lysine in the present of β -CD

Table S3 Other protective groups reacted with lysine in the present of β -CD

Protective group	Product



DFT calculations

Geometry optimizations and single point calculations were performed with B3LYP at 6-31G(d,p) level, which includes double polarization functions on each atom and can describe the nonbonding interaction, such as hydrogen bonding and steric effects, among CD units and guest molecules reliably. Frequency calculations were performed with the 6-31G (d,p) basis set to obtain zero-point vibrational energies (ZPE) and to confirm the energies of all stationary points. No negative eigenvalues for all optimized structures. In order to provide realistic pictures of the interaction between lysine and β -CD, we calculated the energies of four types of β -CD/lysine inclusion in solvent phase using polarizable-continuum model ($\epsilon=80$)³⁻⁵.

As hydrogen bonds play a crucial role in the inclusion structures, we have analyzed all hydrogen bonds in those proposed configurations. In this paper, hydrogen bond defined by geometry criteria: a hydrogen bond exists when the distance between N or O atom of donor and N or O atom of acceptor is less than 3.8 Å and the angle formed by N (or O)-H bond of donor and N or O atom of acceptor is in the range from 120 to 180°. From the structures of four β -CD lysine inclusion, five hydrogen bonds were found in α -NH₂ secondary face, including one by O-H of lysine and ether oxygen atom of β -CD, one by O-H of β -CD and nitrogen of ϵ -NH₂, one by N-H of ϵ -NH₂ and hydroxyl oxygen atom of β -CD and two by N-H of α -NH₂ and ether oxygen atom of β -CD (corresponding bond distances 2.74, 2.62, 2.82, 3.39 and 3.38 Å and angles 171.6, 173.1, 145.5, 134.0 and 146.8°, respectively). Hydrogen bonds also can be observed in the other three inclusion structures, but only three, three and one hydrogen bonds were formed in α -NH₂ primary face, ϵ -NH₂ secondary face and ϵ -NH₂ primary face respectively. Thus, we can conclude that the hydrogen bonds directed determined the binding mode of β -CD lysine inclusion. Simultaneously, we observed that hydrogen bonds were formed and two of them formed by N-H of lysine and ether oxygen atom of β -CD in both EDA- β -CD lysine inclusion configurations from the optimized structures. But the donor of hydrogen bond between EDA and lysine was the O-H of lysine in ϵ -NH₂ primary face

while N-H of ϵ -NH₂ of lysine in α -NH₂ primary face (corresponding bond distances 2.58 and 3.18 Å and angles 164.3 and 160.4°, respectively). Since energy of N...H-O is higher than that of N...H-N, ϵ -NH₂ primary face is stable than α -NH₂ primary face and take relatively major proportion.

Figure. S3 The proposed initial geometry models for β -CD lysine inclusions

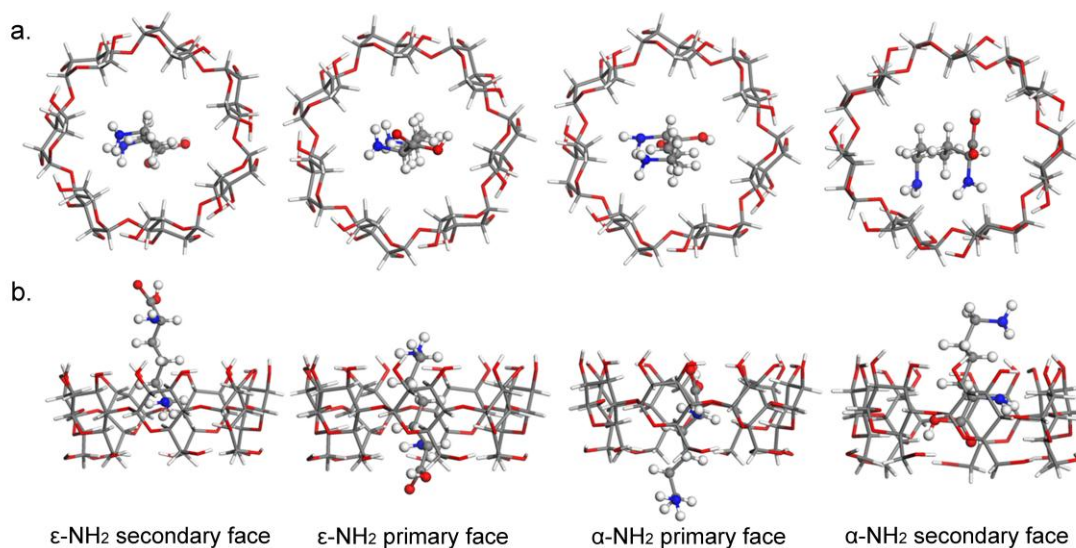


Figure. S4 The proposed initial geometry models for EDA- β -CD lysine inclusions

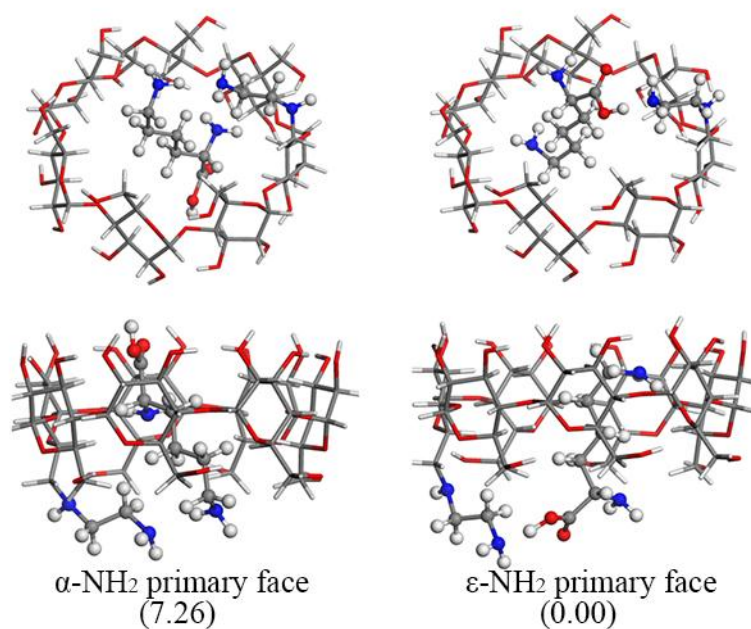


Table S4. Relative Energies (kcal/mol) of the Conformers of all Inclusion Complexes

Inclusion configuration	Relative Energies $\Delta E(\text{KJ/mol})$
β -CD lysineinclusion	ϵ -NH ₂ secondary face 11.28
	ϵ -NH ₂ primary face 8.39
	α -NH ₂ primary face 7.05
	α -NH ₂ secondary face 0.00
EDA- β -CD lysineinclusion	α -NH ₂ primary face 7.26
	ϵ -NH ₂ primary face 0.00

Table S5 Final coordinates of the B3LYP/6-31G(d,p) ϵ -NH₂ primary face geometry optimized model

C	2.61767400	-5.50480900	-0.11157200
C	1.92288200	-5.98321900	-1.38203200
C	0.57751400	-5.30263500	-1.58492000
C	-0.28147300	-5.48266900	-0.33903900
C	0.42801600	-4.96700300	0.91386500
C	-0.35997800	-5.20400700	2.21670900
C	6.25043800	-1.49330300	0.04065900
C	6.17417800	-2.41876700	-1.16901300
C	4.79289200	-3.03554700	-1.33693400
C	4.35434600	-3.71366500	-0.04394900
C	4.42332200	-2.75234000	1.14392300
C	4.11241800	-3.41008100	2.50612000
C	5.02596400	3.78345800	-0.35129500
C	5.64795200	3.09671800	-1.56013800
C	5.44498700	1.59118600	-1.51273100
C	5.95708600	0.99692800	-0.20125700
C	5.44368500	1.75008500	1.03638800
C	6.24050500	1.45039700	2.32641600
C	0.15359000	6.05338500	-0.08083400
C	1.04436000	6.21375900	-1.30958500
C	1.97722600	5.02177300	-1.48187700
C	2.76857100	4.81348000	-0.19659800
C	1.84222800	4.61004900	1.00157100
C	2.58970600	4.45325800	2.33401300
C	-4.83712200	3.97998800	-0.07864400

C	-4.33878600	4.81030700	-1.25824300
C	-2.82525300	4.75661000	-1.40664500
C	-2.16111400	5.13221200	-0.08823400
C	-2.64378000	4.23156900	1.04867300
C	-2.06257100	4.59662100	2.42592300
C	-6.21269900	-1.24594700	-0.64123500
C	-6.40765200	-0.31154200	-1.82772100
C	-5.50808500	0.90835800	-1.72445500
C	-5.71510200	1.64375100	-0.40223300
C	-5.62835100	0.69951600	0.80713100
C	-6.18058100	1.29779400	2.12092200
C	-2.75688700	-5.39565300	-0.56515400
C	-3.51715400	-5.03852700	-1.83634200
C	-3.90343700	-3.56702600	-1.86650200
C	-4.67780100	-3.20739300	-0.60313500
C	-3.89938600	-3.56920500	0.66455900
C	-4.69620000	-3.36266600	1.97155100
O	-1.50215700	-4.70231600	-0.54335000
O	1.73108200	-5.68501500	1.02811000
O	2.95860900	-4.11791700	-0.23724400
O	5.80979900	-2.20881700	1.22469000
O	5.39326300	-0.35709700	-0.15775500
O	5.58349200	3.22165400	0.86371300
O	3.60157900	3.61453200	-0.37141500
O	0.98046800	5.82373800	1.09616800
O	-0.72317800	4.94237500	-0.27850700
O	-4.12968000	4.36990100	1.12766600
O	-4.59405700	2.58564900	-0.32264700
O	-6.46649400	-0.51194300	0.58570500
O	-4.87451300	-1.75520900	-0.63101300
O	-3.54537500	-5.01945000	0.59565100
H	3.50042800	-6.10359600	0.11782600
H	1.75621000	-7.06387300	-1.29466800
H	0.73695700	-4.22800200	-1.74853600
H	-0.53585000	-6.53731500	-0.19640700
H	0.65311800	-3.90130600	0.79619800
H	-0.79950500	-4.25504000	2.54736900
H	7.26983000	-1.17706000	0.26009100
H	6.90234600	-3.22667700	-1.02841700
H	4.07102000	-2.24063800	-1.57140500
H	4.97113700	-4.59431000	0.15829400
H	3.75297300	-1.90689800	0.96210700
H	3.16614100	-3.01136800	2.89319100
H	5.28514800	4.84310500	-0.31451200

H	6.72331600	3.31317700	-1.56281500
H	4.36996900	1.37836100	-1.58050100
H	7.05087600	0.95115500	-0.20785600
H	4.37809300	1.52129900	1.14658100
H	5.59305200	1.57283400	3.20466800
H	7.04150300	2.18919400	2.39061200
H	-0.40507600	6.96497900	0.13810400
H	1.65038800	7.11927600	-1.18341800
H	1.37283100	4.12627600	-1.67331300
H	3.41617000	5.67312600	0.00100200
H	1.18594000	3.75065000	0.82575300
H	2.66766900	3.38381100	2.56761000
H	-5.89066300	4.15780800	0.13606600
H	-4.63312900	5.85336400	-1.08962500
H	-2.52048100	3.73391800	-1.66793000
H	-2.36637300	6.17639400	0.16680700
H	-2.42451700	3.18461300	0.81394000
H	-2.87390900	4.53809500	3.15709600
H	-1.30235200	3.85256500	2.68923900
H	-6.93977600	-2.05978400	-0.63882300
H	-7.45523300	0.01277000	-1.84370000
H	-4.46140200	0.57813700	-1.76027200
H	-6.66602500	2.18650300	-0.40994200
H	-4.58585600	0.37646500	0.90223400
H	-7.22893900	1.00237900	2.19345600
H	-5.64718100	0.86856800	2.98018800
H	-2.60833800	-6.47297300	-0.47165900
H	-4.43315000	-5.64095000	-1.86932600
H	-2.99188400	-2.95507800	-1.90194200
H	-5.64858300	-3.71175400	-0.59080300
H	-2.96013200	-3.00715200	0.68835300
H	-4.23348500	-2.55951900	2.55512600
H	-4.62474600	-4.28766100	2.54856200
H	0.34767700	-5.54123900	2.97849900
H	4.91036800	-3.13031100	3.19795200
H	1.99530800	4.93128000	3.11676000
O	4.08320500	-4.85779800	2.47897700
H	3.17731700	-5.18259400	2.26527600
O	6.90784300	0.16902500	2.33154800
H	6.28986200	-0.59686700	2.34636300
O	3.89447700	5.08225500	2.35592000
H	4.58652600	4.43986300	2.07431700
O	-1.52815900	5.94197400	2.50761400
H	-0.56540600	5.93436400	2.29654400

O	-6.19158700	2.74085000	2.16993300
H	-5.29290800	3.14428400	2.17526000
O	-6.11072300	-3.11592600	1.77463500
H	-6.28227700	-2.15292000	1.65469400
O	-1.37989500	-6.22835500	2.11586900
H	-2.23778700	-5.82786200	1.84020100
O	0.00929700	-5.92318400	-2.75438100
H	-0.93158300	-5.63718200	-2.90514400
O	4.91860600	-3.95475400	-2.43963900
H	4.10864400	-4.52358600	-2.53873200
O	6.13850600	1.06655000	-2.66134800
H	6.20192500	0.07391600	-2.62059400
O	2.81482500	5.34401700	-2.61191000
H	3.53809100	4.67610800	-2.74086500
O	-2.51304900	5.67387400	-2.47502700
H	-1.53466700	5.83130700	-2.54813200
O	-5.82815800	1.72434200	-2.86808700
H	-5.43432200	2.63481200	-2.78552200
O	-4.68087900	-3.40433900	-3.06863400
H	-5.11058900	-2.50825200	-3.11575100
O	-2.69195900	-5.36004500	-2.99020800
H	-3.13653100	-4.98290000	-3.77901600
O	2.78755000	-5.72508300	-2.52328600
H	2.26441200	-5.91542000	-3.33100200
O	6.52325300	-1.66911600	-2.36963000
H	6.36483700	-2.26522600	-3.13289700
O	5.04179600	3.64150400	-2.76464800
H	5.33722800	3.08899400	-3.51899700
O	0.19897700	6.36281200	-2.48408900
H	0.78286400	6.33052200	-3.27115200
O	-4.97122600	4.33293600	-2.48194300
H	-4.55574400	4.82010300	-3.22548300
O	-6.11172100	-1.03355300	-3.05625100
H	-6.08055100	-0.37094000	-3.77935800
N	-1.04360300	1.32467300	3.56285800
C	-1.26067200	-0.05964300	3.15410400
C	-1.49508200	-0.98033400	4.34926800
O	-1.26512200	-0.70958700	5.52833200
C	-0.06947300	-0.58552400	2.31181800
C	0.01947100	0.04024000	0.91055200
C	1.25757200	-0.45308300	0.14352100
C	1.34189900	0.03223500	-1.31187900
N	1.46848200	1.48910400	-1.39651500
O	-2.00662000	-2.21158500	3.96603300

H	-0.23458900	1.43153200	4.16994500
H	-1.85656300	1.75542600	3.99331600
H	-2.16307400	-0.10324500	2.53148100
H	-0.15781400	-1.67545700	2.22055400
H	0.85659000	-0.38830600	2.87417300
H	0.03599000	1.13146900	0.98245800
H	-0.88575700	-0.22311700	0.34193500
H	1.28088300	-1.55327900	0.13311000
H	2.16896300	-0.13300100	0.67459300
H	0.42437700	-0.25686900	-1.84062600
H	2.17185500	-0.50880900	-1.80532700
H	1.28975000	1.87670000	-2.31504100
H	2.29827700	1.89208100	-0.97225800
H	-2.13987800	-2.78942400	4.75010900

Table S3 Final coordinates of the B3LYP/6-31G(d,p) ϵ -NH₂ secondary face geometry optimized model

C	-0.64895400	5.83150100	0.29069900
C	-1.49568800	5.59807900	1.53934700
C	-2.38227300	4.36626800	1.41942800
C	-3.21790200	4.47303400	0.14940700
C	-2.32830300	4.62302400	-1.08441400
C	-3.11246000	4.79676900	-2.39809200
C	4.52786400	4.45965200	-0.25139800
C	3.99972000	5.08789700	1.03436500
C	2.52013100	4.78805000	1.22972100
C	1.74527900	5.23765100	-0.00190400
C	2.28713900	4.61043600	-1.28689600
C	1.60096700	5.14232400	-2.56027700
C	6.65045800	-0.51681200	-0.43765700
C	6.92686600	0.39501900	0.75266800
C	5.84240600	1.44602100	0.92986600
C	5.62153600	2.21385500	-0.36793400
C	5.35686900	1.27408900	-1.54605600
C	5.28366000	1.99299700	-2.91279100
C	3.55796400	-4.94969600	0.13357400
C	4.30426600	-4.44338300	1.35947400
C	4.68292900	-2.97956300	1.21725300
C	5.46409300	-2.71559300	-0.06963600
C	4.78078300	-3.32448000	-1.30526900
C	5.69048100	-3.42594200	-2.54621800
C	-1.76153000	-5.29523800	-0.54869300
C	-1.14956900	-5.45081300	0.84960000

C	0.15746400	-4.67591500	0.98781400
C	1.09444700	-5.06289500	-0.15396000
C	0.45455700	-4.78377700	-1.51358800
C	1.33329900	-5.16362600	-2.71570800
C	-5.83055400	-1.91782500	-1.48041200
C	-5.85931100	-2.97495200	-0.38428800
C	-4.45307900	-3.34227000	0.05888200
C	-3.63283400	-3.78377700	-1.14435600
C	-3.63948900	-2.74033100	-2.26011100
C	-2.94656100	-3.24084200	-3.54280900
C	-5.40174700	3.27991900	0.04201600
C	-5.92541600	2.29193600	1.07594500
C	-5.48185700	0.87782000	0.73154500
C	-5.93538000	0.48343200	-0.67597700
C	-5.55087900	1.54469100	-1.72424000
C	-6.28538100	1.40606600	-3.06863100
O	-3.97387400	3.22965900	0.02885500
O	-1.48790400	5.84165600	-0.89362400
O	0.35280300	4.80803500	0.17166400
O	3.73949600	4.93270400	-1.38064500
O	4.42332100	3.03451100	-0.16574100
O	6.47490200	0.29186100	-1.62987700
O	5.43857900	-1.25646500	-0.21490600
O	4.38008200	-4.73301200	-1.04431600
O	2.31040800	-4.25927800	-0.00169300
O	-0.79068900	-5.59711600	-1.58562200
O	-2.23848800	-3.95316100	-0.72470400
O	-5.05402300	-2.41029800	-2.59779700
O	-5.17816700	-0.72893800	-0.98711400
O	-5.91490300	2.91100100	-1.26717700
H	-0.18107600	6.81739000	0.31035000
H	-2.14559800	6.47231300	1.67252800
H	-1.76364500	3.46102700	1.35403300
H	-3.90570900	5.32251900	0.20523200
H	-1.65779000	3.75899700	-1.15105600
H	-3.09258700	3.84884200	-2.95028800
H	5.55165700	4.76880700	-0.46789500
H	4.13449200	6.17436300	0.96897900
H	2.39019400	3.70477300	1.35836400
H	1.78147500	6.32688300	-0.09720000
H	2.19469500	3.52045900	-1.23335300
H	0.89238700	4.38605600	-2.92251600
H	7.48185800	-1.18506100	-0.65881000
H	7.88578400	0.89990300	0.58559100

H	4.90128400	0.94504600	1.19432800
H	6.47897400	2.85558800	-0.58993200
H	4.44006700	0.70718900	-1.35195900
H	4.27207400	1.89073200	-3.32557900
H	5.98151000	1.49071100	-3.58633700
H	3.40253800	-6.02932100	0.17244400
H	5.21638800	-5.04066200	1.47914800
H	3.76152400	-2.38333400	1.16968100
H	6.49548500	-3.07038300	0.02855600
H	3.87410700	-2.74250400	-1.50230300
H	5.07736300	-3.46133900	-3.45657600
H	-2.56897500	-6.01383200	-0.70343100
H	-0.92997700	-6.51375500	1.01140300
H	-0.04773700	-3.59892500	0.91847400
H	1.35042100	-6.12542100	-0.09710800
H	0.16307700	-3.72879600	-1.58043500
H	0.68101900	-5.56205700	-3.49721700
H	1.81508000	-4.25585000	-3.10028800
H	-6.81609600	-1.68613300	-1.88171700
H	-6.36591900	-3.86732500	-0.76943300
H	-3.97731800	-2.45329900	0.49219100
H	-4.01455600	-4.72999600	-1.54125500
H	-3.16508400	-1.81942300	-1.90604300
H	-3.53506700	-2.90472800	-4.39928900
H	-1.94982100	-2.78604300	-3.60662500
H	-5.76521600	4.29418200	0.21794400
H	-7.02086300	2.34614300	1.09091100
H	-4.38787300	0.83501900	0.76404800
H	-7.01228800	0.27941000	-0.69542000
H	-4.46311300	1.50041400	-1.84182800
H	-5.75298400	1.97797900	-3.84025800
H	-7.28144000	1.83821900	-2.95519900
H	-2.60229900	5.55338900	-2.99951000
H	2.36943000	5.28354600	-3.32421300
H	6.24239400	-4.36495500	-2.47325300
O	0.94331000	6.42001900	-2.39045000
H	0.00846000	6.29100300	-2.10382900
O	5.68462000	3.38484800	-2.88042700
H	4.92477700	3.96500300	-2.64058200
O	6.70504100	-2.39930000	-2.62818500
H	6.33913600	-1.49092700	-2.71590800
O	2.32033500	-6.18236100	-2.42416100
H	3.17757800	-5.75753900	-2.18736700
O	-2.86022900	-4.68263600	-3.65392400

H	-2.08962000	-5.02686400	-3.14615200
O	-6.51336900	0.03883200	-3.48275700
H	-5.68478400	-0.47655400	-3.59011500
O	-4.47383600	5.25607700	-2.21744500
H	-5.08414900	4.48638400	-2.13611600
O	-3.18253700	4.35799300	2.61842500
H	-3.89522800	3.66620400	2.58049000
O	2.13497900	5.49824300	2.42270200
H	1.16025700	5.41361200	2.60204900
O	6.29848300	2.28638400	2.00884400
H	5.69879000	3.06843700	2.14107700
O	5.44063000	-2.65738100	2.39991600
H	5.93106600	-1.79817400	2.29324600
O	0.68960100	-5.01282000	2.28235100
H	1.64094900	-4.74291100	2.37765500
O	-4.61555200	-4.37486600	1.05133800
H	-3.72957500	-4.64134100	1.43213600
O	-6.02307400	0.01094500	1.76225700
H	-6.23545100	-0.89747600	1.40482100
O	-5.40771300	2.67802700	2.38044100
H	-5.62022500	1.95781000	3.00996100
O	-0.61699300	5.47850300	2.69113600
H	-1.16580500	5.18650800	3.44938300
O	4.76054200	4.57923900	2.16457500
H	4.30367700	4.87889800	2.97937600
O	7.01995100	-0.41299700	1.96351200
H	7.11286100	0.21229400	2.71445000
O	3.45380100	-4.62118400	2.52572400
H	3.88442700	-4.15885600	3.27596300
O	-2.13555800	-5.01290600	1.81356500
H	-1.74333300	-4.72868500	2.67325400
O	-6.60599500	-2.47134800	0.76646700
H	-6.51180100	-3.15033900	1.47093200
N	-3.20452000	-0.42993300	3.10203700
C	-2.35249400	-1.60321200	3.06938200
C	-2.37997700	-2.37864100	4.38323600
O	-2.71198200	-1.94322400	5.48469600
C	-0.87452800	-1.22484200	2.75076400
C	-0.71695500	-0.61264400	1.34952800
C	0.72209000	-0.14480000	1.07565000
C	0.94205500	0.43688100	-0.33087200
N	0.15666900	1.65284100	-0.56655800
O	-1.92221400	-3.69067800	4.23911100
H	-3.07585100	0.15442600	3.91989800

H	-4.17974200	-0.54809300	2.84392600
H	-2.70404700	-2.27955900	2.28376200
H	-0.24409500	-2.11845000	2.85328900
H	-0.53875600	-0.50479500	3.51214800
H	-1.40763600	0.22831600	1.24129600
H	-1.00821900	-1.36003300	0.59410100
H	1.42025000	-0.98625800	1.20319500
H	1.01190900	0.60963000	1.82424900
H	0.63104100	-0.30794200	-1.07583600
H	2.02941800	0.59010600	-0.47227800
H	0.05228500	1.91908100	-1.53743500
H	0.35403600	2.44861500	0.02995300
H	-1.87538900	-4.14045300	5.11082200

Table S4 Final coordinates of the B3LYP/6-31G(d,p) α -NH₂ primary face geometry optimized model

C	5.09974100	-3.73059600	0.13447500
C	4.71066700	-4.49166300	-1.12909800
C	3.21215400	-4.42993000	-1.39273900
C	2.45858000	-4.91961500	-0.16450800
C	2.85165900	-4.13352700	1.08689100
C	2.19481400	-4.65639900	2.37962000
C	6.05188100	1.61947400	-0.18056700
C	6.39181400	0.74297100	-1.37698000
C	5.63777700	-0.57410100	-1.36405800
C	5.83822400	-1.31975300	-0.04471300
C	5.60644100	-0.42811300	1.18687600
C	6.19380500	-1.01052000	2.48971900
C	2.53019100	5.71502300	-0.22989000
C	3.36872400	5.39816100	-1.46184500
C	3.76544700	3.92672400	-1.51270300
C	4.43271900	3.53214800	-0.19998500
C	3.55916400	3.85457800	1.01570900
C	4.24049000	3.54775200	2.36051000
C	-2.86168700	5.55558400	-0.07351600
C	-2.13998100	6.11802600	-1.29351700
C	-0.74535800	5.52757600	-1.43717000
C	0.03783600	5.72467600	-0.14425700
C	-0.70378200	5.14954000	1.06317500
C	-0.00644700	5.42403600	2.41155800
C	-6.19837300	1.30838800	-0.12445400
C	-6.17487900	2.29953800	-1.28498900
C	-4.82763100	2.99608900	-1.41903500

C	-4.43153300	3.62255900	-0.08790300
C	-4.42955900	2.58824700	1.03737400
C	-4.11215900	3.17847700	2.42480100
C	-4.82313300	-3.90479900	-0.72630200
C	-5.43995900	-3.17786100	-1.91335600
C	-5.26293400	-1.67234300	-1.79407300
C	-5.77921000	-1.14863500	-0.45350200
C	-5.19498600	-1.93172200	0.73001400
C	-5.86419900	-1.65135900	2.09559400
C	0.18473500	-5.88814100	-0.44108600
C	-0.60647600	-5.95075600	-1.74541500
C	-1.63995500	-4.83934700	-1.84333000
C	-2.52664700	-4.85142500	-0.60444700
C	-1.70636900	-4.73196200	0.68083200
C	-2.54414700	-4.83606600	1.96726700
O	1.02658500	-4.72135200	-0.42251700
O	4.33071600	-4.24158900	1.25676100
O	4.78864400	-2.33833700	-0.01758800
O	6.28019500	0.89548400	1.04368400
O	4.67543600	2.07420600	-0.24741900
O	3.25782000	5.31499000	0.96704700
O	1.29635900	4.99532500	-0.30372400
O	-2.05462900	5.77928000	1.11725500
O	-3.07540300	4.15052900	-0.25020000
O	-5.79117400	1.98862300	1.09714500
O	-5.28702000	0.23395800	-0.38262800
O	-5.40377900	-3.39167100	0.50086000
O	-3.40965300	-3.69137800	-0.72326000
O	-0.72153000	-5.86146900	0.68918200
H	6.14526000	-3.87364700	0.40848500
H	5.00207400	-5.54110600	-1.00005600
H	2.91868500	-3.39226600	-1.59942200
H	2.65262800	-5.98259300	0.00668300
H	2.62162200	-3.07315200	0.94080700
H	1.39894500	-3.96279900	2.68044500
H	6.70635300	2.48949000	-0.12258400
H	7.46814100	0.53260700	-1.33801100
H	4.56222200	-0.39413800	-1.48404900
H	6.82841500	-1.78667800	-0.01532800
H	4.52947900	-0.25030600	1.27039900
H	5.64710100	-0.61607400	3.35634900
H	2.35805800	6.78675400	-0.11759300
H	4.28288700	6.00279400	-1.42384400
H	2.86077100	3.31822100	-1.64852100

H	5.39381900	4.04062900	-0.08983900
H	2.60449300	3.32568900	0.94704000
H	3.82302900	2.61602300	2.76048700
H	4.00220900	4.35800300	3.05426700
H	-3.80231100	6.07513300	0.11727700
H	-2.05195200	7.20455300	-1.17199900
H	-0.83074100	4.45001400	-1.63172700
H	0.24200200	6.78596200	0.02595700
H	-0.85212400	4.07393100	0.91901300
H	0.43071000	4.48988800	2.78562300
H	-7.20071600	0.93238600	0.07975400
H	-6.94296900	3.06069500	-1.10160700
H	-4.06542600	2.25459000	-1.69567400
H	-5.11581100	4.43537800	0.17354800
H	-3.72838800	1.78053800	0.79963800
H	-4.79188800	2.72020100	3.14740600
H	-3.08462800	2.90688900	2.69942900
H	-5.06069500	-4.97014200	-0.73196900
H	-6.51117800	-3.41038800	-1.94620700
H	-4.19006300	-1.44216600	-1.84707600
H	-6.87330100	-1.15963500	-0.42952400
H	-4.11586200	-1.75161900	0.76180800
H	-6.53196900	-2.48924700	2.30575300
H	-5.09220600	-1.61368200	2.87370800
H	0.78555500	-6.78854200	-0.30206700
H	-1.13368700	-6.91269400	-1.77207500
H	-1.12538200	-3.87048400	-1.89907100
H	-3.12400200	-5.76776300	-0.56866800
H	-1.14397100	-3.79286900	0.67295100
H	-2.65243200	-3.83760100	2.40734800
H	-1.99721200	-5.46995200	2.67104300
H	2.95773700	-4.66388800	3.16200500
H	7.23073800	-0.67651700	2.56151000
H	-0.76874100	5.75355800	3.12166800
O	6.26053600	-2.45411900	2.51273100
H	5.37891700	-2.88897000	2.47770800
O	5.68674600	3.46917000	2.28332500
H	5.97078700	2.53357900	2.16779600
O	0.99228900	6.47176200	2.36074200
H	1.87667100	6.09212400	2.14731300
O	-4.30591900	4.61004400	2.52192200
H	-3.47135800	5.08407600	2.29639300
O	-6.71079300	-0.47704200	2.12625800
H	-6.19578000	0.36214600	2.12718400

O	-3.84653300	-5.44930500	1.77973500
H	-4.51813800	-4.74956100	1.60254100
O	1.68307600	-6.00719700	2.28558100
H	0.74648200	-5.99917300	1.97522000
O	3.00194800	-5.26889300	-2.54875300
H	2.03493500	-5.39189300	-2.74211100
O	6.15586200	-1.30573900	-2.49475500
H	5.82166800	-2.24426000	-2.49425100
O	4.64390000	3.81299100	-2.64757300
H	5.07736900	2.91903700	-2.70086000
O	-0.14852700	6.20778100	-2.55896500
H	0.80870100	5.96387300	-2.66730200
O	-5.00222700	3.96994100	-2.46740000
H	-4.21295400	4.56859700	-2.54885000
O	-5.96413900	-1.10773100	-2.91927400
H	-6.06436300	-0.12252000	-2.82790700
O	-2.37445100	-5.09589800	-3.05755100
H	-3.17264900	-4.50898900	-3.13521400
O	0.31681400	-5.88191100	-2.86668600
H	-0.21874500	-5.78551800	-3.68223100
O	5.42541500	-3.94463400	-2.27627500
H	5.04517300	-4.37870200	-3.07106700
O	6.09186100	1.46824400	-2.60098400
H	6.16077400	0.82431000	-3.33858100
O	2.60793700	5.74980100	-2.64986100
H	3.10924100	5.42564800	-3.42774600
O	-2.92933100	5.83037800	-2.48078100
H	-2.38317300	6.06758200	-3.25998000
O	-6.48907900	1.59426500	-2.51998300
H	-6.36842900	2.23296000	-3.25484900
O	-4.80392500	-3.65809000	-3.13207100
H	-5.10326300	-3.08084700	-3.86602300
N	-0.33277700	-1.55959700	-0.12334900
C	0.31478200	-0.40526700	0.48619200
C	1.66365200	-0.09597100	-0.16659500
O	2.16439900	-0.74567600	-1.09386500
C	0.46966800	-0.58178900	2.02168100
C	-0.88423100	-0.61042200	2.74790200
C	-0.74864500	-0.89765500	4.25246000
C	-2.08478400	-0.94107000	5.01247200
N	-2.93217200	-2.06128100	4.56698500
O	2.28788200	0.98388700	0.39624600
H	0.29918900	-2.32180800	-0.35437400
H	-0.95493100	-1.34952100	-0.89399600

H	-0.31874400	0.47741900	0.32158000
H	1.09750500	0.22684500	2.41350100
H	1.00521200	-1.52578700	2.20370200
H	-1.52884300	-1.36210400	2.28307200
H	-1.38570200	0.36260200	2.61317500
H	-0.11303400	-0.13294000	4.72294000
H	-0.22621300	-1.85714800	4.39765000
H	-2.63889500	-0.01215000	4.82661300
H	-1.87045400	-0.96946400	6.09615000
H	-3.87921800	-2.03301100	4.93151700
H	-2.51490600	-2.97465700	4.72462500
H	3.17864300	1.20881700	-0.00369900

Table S5 Final coordinates of the B3LYP/6-31G(d,p) α -NH2 secondary face geometry optimized model

C	2.68909500	5.50589500	-0.15475300
C	2.01149900	5.92516200	1.14844200
C	0.68582100	5.20297600	1.35358700
C	-0.18133900	5.37329600	0.11090300
C	0.52225000	4.88731300	-1.15574600
C	-0.29597400	5.08441800	-2.43812000
C	6.38953500	1.62054300	-0.71134400
C	6.40144300	2.52294500	0.52042300
C	5.01936100	3.08161300	0.82454700
C	4.44391500	3.75973600	-0.41138300
C	4.42796300	2.81882400	-1.61615100
C	3.94923400	3.48134400	-2.92215900
C	5.15423700	-3.64121900	-0.25989500
C	5.87790600	-2.98252800	0.90585900
C	5.70268900	-1.47551500	0.87455300
C	6.14033000	-0.88040400	-0.46164700
C	5.54945800	-1.62969400	-1.66833400
C	6.27574400	-1.33587200	-2.99725700
C	0.10140900	-5.51610400	-0.24703900
C	0.83055200	-5.39407800	1.10425700
C	1.94605300	-4.34055100	1.06776800
C	2.80762800	-4.49691400	-0.18672200
C	1.96531300	-4.46425600	-1.45908700
C	2.76118600	-4.61082300	-2.76736900
C	-4.88258700	-3.70512300	-1.03478400
C	-4.48143200	-4.60723500	0.12718400
C	-3.00822900	-4.46749500	0.47446900
C	-2.16918400	-4.69825700	-0.77397800

C	-2.57908500	-3.80664100	-1.94365600
C	-1.83219400	-4.15537000	-3.24615600
C	-6.38788200	1.41926300	-0.12222300
C	-6.72201500	0.39262700	0.94928800
C	-5.83319800	-0.83454400	0.81927700
C	-5.88064000	-1.42852800	-0.59044800
C	-5.71068300	-0.37561100	-1.69703200
C	-6.16377200	-0.85791400	-3.09173800
C	-2.67436100	5.30742000	0.27496100
C	-3.53564700	4.95648800	1.48656700
C	-4.08962800	3.53887100	1.42831900
C	-4.72267500	3.26486000	0.06685300
C	-3.77587700	3.56914400	-1.09237500
C	-4.41900400	3.39891600	-2.48082000
O	-1.41081800	4.59594100	0.33986700
O	1.77348000	5.68869300	-1.27214900
O	3.06874300	4.13111900	-0.06974500
O	5.82395700	2.34422800	-1.83681500
O	5.56993400	0.47084800	-0.45684600
O	5.68356300	-3.10258700	-1.49968800
O	3.74975500	-3.37140200	-0.16748200
O	1.02767300	-5.61353800	-1.36449800
O	-0.76438400	-4.39216000	-0.46920700
O	-4.03894100	-3.98226600	-2.18302100
O	-4.71570300	-2.32055500	-0.66706500
O	-6.56158700	0.81784100	-1.43222000
O	-5.03045500	1.83651100	0.04525800
O	-3.35834700	4.99993700	-0.95382900
H	3.54754200	6.13989400	-0.38278100
H	1.81457000	7.00332500	1.10297400
H	0.88508400	4.13511300	1.51608000
H	-0.45104700	6.42395900	-0.02497200
H	0.80912400	3.83450300	-1.05633400
H	-0.83136000	4.15107600	-2.65033300
H	7.39052400	1.32880700	-1.02800700
H	7.08664100	3.35777800	0.33075700
H	4.35353700	2.25552800	1.10860600
H	5.01726200	4.65696600	-0.66272500
H	3.81590700	1.93950000	-1.38891600
H	2.93078600	3.13798700	-3.14274700
H	5.34419500	-4.71433600	-0.31008300
H	6.94360300	-3.23197300	0.84338100
H	4.63595600	-1.24786800	0.99904500
H	7.23249200	-0.83210700	-0.52084100

H	4.48222900	-1.39064200	-1.71488200
H	5.59556400	-1.50342000	-3.84264600
H	7.10331400	-2.04276800	-3.08236600
H	-0.47085700	-6.44494500	-0.27635400
H	1.31728700	-6.36295600	1.29193100
H	1.49769500	-3.33803300	1.05774800
H	3.36221500	-5.43947400	-0.15328600
H	1.36455500	-3.54749400	-1.48853700
H	2.84240600	-3.62748700	-3.24680100
H	-5.90070000	-3.88916600	-1.37661800
H	-4.68359500	-5.64577900	-0.16291100
H	-2.80980300	-3.46001300	0.85768500
H	-2.24932300	-5.74294500	-1.09235100
H	-2.41328100	-2.75283400	-1.69684800
H	-2.53092300	-4.05249200	-4.07942200
H	-1.01821000	-3.43234800	-3.38587100
H	-7.06971900	2.27151900	-0.10373200
H	-7.77205700	0.09668100	0.83980600
H	-4.79794300	-0.52662700	1.01448100
H	-6.80338300	-2.00098100	-0.72829800
H	-4.66478500	-0.05192500	-1.68880200
H	-7.22451800	-0.61985200	-3.19178500
H	-5.61676400	-0.31252300	-3.87224900
H	-2.47461700	6.37867200	0.23627300
H	-4.38514600	5.65119600	1.50017400
H	-3.27420800	2.82518500	1.58544200
H	-5.64043800	3.84793400	-0.05537400
H	-2.87425000	2.95139000	-1.02197300
H	-4.04878100	2.46738000	-2.92552800
H	-4.09317000	4.23049600	-3.11117900
H	0.39940500	5.27621700	-3.26004100
H	4.60614200	3.14506600	-3.72814000
H	2.19302800	-5.26823700	-3.43054500
O	4.00937200	4.92826800	-2.90923000
H	3.14850500	5.29860500	-2.60291800
O	6.88988100	-0.02816400	-3.05878700
H	6.24228400	0.71178200	-3.03251000
O	4.07331900	-5.20421700	-2.60079700
H	4.75145400	-4.49398800	-2.52488100
O	-1.33000200	-5.51165100	-3.30654300
H	-0.47674300	-5.58865500	-2.82002000
O	-6.07978000	-2.28806300	-3.28451800
H	-5.15928900	-2.63503500	-3.26309800
O	-5.86701000	3.42289300	-2.47010200

H	-6.21677300	2.50552000	-2.37770400
O	-1.21094000	6.20419200	-2.37591000
H	-2.10959700	5.88114800	-2.13013000
O	0.08451800	5.79829000	2.52275200
H	-0.84011500	5.47054000	2.66613700
O	5.19840000	3.99633500	1.92589400
H	4.36305800	4.49621700	2.12013700
O	6.46816100	-0.96698900	1.98525300
H	6.55177000	0.02354200	1.93900300
O	2.76593800	-4.51419300	2.25365500
H	3.64988600	-4.06201600	2.17166400
O	-2.74988700	-5.45857800	1.49390800
H	-1.81112300	-5.35199200	1.83489400
O	-6.28893000	-1.75992900	1.82393200
H	-5.86491900	-2.65435300	1.70761200
O	-5.04938600	3.44236900	2.50276500
H	-5.49769200	2.55578500	2.49923500
O	-2.72484900	5.15590700	2.67825700
H	-3.23919500	4.84300100	3.45092200
O	2.92182800	5.64541800	2.24724400
H	2.44619600	5.82079300	3.08572500
O	6.88619900	1.76224300	1.66655600
H	6.79462200	2.34100400	2.45346000
O	5.33278600	-3.50790700	2.14954100
H	5.69027900	-2.95658100	2.87830400
O	-0.16849300	-5.13157900	2.10519000
H	0.20815800	-4.85910800	3.04986700
O	-5.28689000	-4.28294700	1.30042800
H	-4.88778100	-4.78139000	2.04723000
O	-6.52450600	1.01161200	2.25332700
H	-6.58155800	0.29944400	2.92529600
N	-1.77365900	-1.37601000	0.71119600
C	-1.38201000	-0.23570500	1.50658500
C	-1.21657600	1.04820700	0.68713900
O	-1.32774800	1.13683400	-0.54586300
C	-0.12315200	-0.55438300	2.35053700
C	-0.33898000	-1.75443000	3.29287000
C	0.86734400	-2.01103200	4.21495800
C	0.71209300	-3.24021000	5.12959200
N	0.93631700	-4.51763200	4.39956400
O	-1.02146100	2.14199100	1.48684200
H	-1.03332900	-1.90054900	0.26239900
H	-2.60467600	-1.27598400	0.14255000
H	-2.19342100	-0.00551900	2.21506200

H	0.14549600	0.34096000	2.92304200
H	0.71788300	-0.76146500	1.66978500
H	-0.56085000	-2.64897600	2.70367500
H	-1.22799700	-1.56307500	3.91307300
H	1.03019100	-1.12982400	4.85197900
H	1.78200700	-2.13216000	3.61575400
H	-0.29850000	-3.26250000	5.55511700
H	1.41502000	-3.15039200	5.97269900
H	0.81394200	-5.32740300	5.00573400
H	1.85241200	-4.54656600	3.93233800
H	-1.10510800	3.01319400	0.99995600

Table S6 Final coordinates of the B3LYP/6-31G(d,p) α -NH₂ primary face geometry optimized model

C	-5.56435300	3.36890000	0.11817900
C	-5.19199000	4.22241100	-1.08943700
C	-3.68658100	4.29221700	-1.29901500
C	-2.99661300	4.73845900	-0.01566700
C	-3.36901100	3.83768100	1.16227900
C	-2.77693300	4.28403600	2.51243600
C	-6.27246800	-1.99273600	-0.34598500
C	-6.62111200	-1.12169500	-1.54552700
C	-5.90010700	0.21317400	-1.47885700
C	-6.18258500	0.93923900	-0.16529200
C	-5.96549700	0.04061300	1.06282500
C	-6.59881800	0.58399800	2.36149200
C	-2.26690800	-5.59724000	-0.19942300
C	-3.11034000	-5.41623200	-1.45634100
C	-3.68968500	-4.01133400	-1.54655900
C	-4.45713800	-3.69236900	-0.26811800
C	-3.58382900	-3.86688700	0.97540000
C	-4.33760100	-3.65072500	2.30258400
C	3.08817100	-5.05187100	0.11285700
C	2.41487300	-5.68100000	-1.10837700
C	1.00156600	-5.15805300	-1.32897300
C	0.19819800	-5.33950200	-0.04851000
C	0.87837200	-4.64873500	1.13276100
C	0.14943100	-4.85421100	2.47232600
C	6.41869400	-0.77320900	-0.31335500
C	6.29116400	-1.72497900	-1.50070600
C	4.98000300	-2.51030300	-1.46628200
C	4.72739800	-3.16317000	-0.10004100
C	4.89866800	-2.13658500	1.02379000

C	4.84378700	-2.65389600	2.45569300
C	4.35138500	4.24740000	-0.55113000
C	5.06068500	3.68292600	-1.77472700
C	5.12221500	2.16730700	-1.73308700
C	5.73071700	1.65874600	-0.42161600
C	5.12160600	2.31572600	0.82982800
C	5.97852800	2.17556300	2.10200100
C	-0.76252700	5.82238900	-0.14053500
C	0.04996600	6.03376200	-1.41640700
C	1.12016000	4.96560900	-1.60524300
C	1.97205900	4.89297300	-0.34448100
C	1.12025100	4.59152500	0.88885100
C	1.92529000	4.52946900	2.19359300
O	-1.55475300	4.63708600	-0.26185400
O	-4.85855300	3.85146000	1.29010300
O	-5.17856800	2.00538800	-0.11742400
O	-6.61755700	-1.28573200	0.87395600
O	-4.87134100	-2.29101600	-0.35556800
O	-3.05949200	-5.26366500	0.97479000
O	-1.11939800	-4.74286500	-0.26401600
O	2.24256400	-5.22211800	1.26901100
O	3.34283400	-3.65222600	-0.12112100
O	6.24945800	-1.56063100	0.88210500
O	5.39311700	0.23020200	-0.39162800
O	5.01890300	3.78989500	0.64927000
O	2.97356900	3.84049700	-0.53890000
O	0.13316400	5.70263700	1.00039900
H	-6.62298500	3.43733400	0.36742600
H	-5.56991200	5.23826700	-0.92282700
H	-3.31460900	3.29237500	-1.56165400
H	-3.25733600	5.77341500	0.22460200
H	-3.07407500	2.80728800	0.94241000
H	-1.97838600	3.58895500	2.79929700
H	-6.86652600	-2.90813500	-0.32006500
H	-7.70440500	-0.95055700	-1.54756200
H	-4.81887500	0.02969000	-1.52840000
H	-7.19141700	1.36495300	-0.17290000
H	-4.88760100	-0.12164900	1.16358700
H	-6.05056100	0.19997300	3.23258300
H	-1.97316200	-6.63904500	-0.05733600
H	-3.93962100	-6.13345700	-1.42046600
H	-2.86987400	-3.28836600	-1.65513600
H	-5.33951900	-4.33358100	-0.18066100
H	-2.71942400	-3.19720900	0.91211700

H	-4.03281800	-2.68894800	2.73376700
H	-4.03728500	-4.44417100	2.99143700
H	4.01891000	-5.56859600	0.35966600
H	2.35334400	-6.76227900	-0.93231500
H	1.02961100	-4.09173100	-1.58861500
H	0.08540600	-6.40319000	0.18376000
H	0.98632500	-3.57751900	0.92810100
H	-0.42319200	-3.94721400	2.70623100
H	7.40417700	-0.31500800	-0.23368600
H	7.12317200	-2.43774900	-1.45282200
H	4.15559400	-1.80949500	-1.65699500
H	5.41622800	-4.00655400	0.04013300
H	4.15835000	-1.34004300	0.91018600
H	5.63437700	-3.40416000	2.59219000
H	3.88204200	-3.15659400	2.61742400
H	4.42637500	5.33588800	-0.51610600
H	6.08170800	4.08426900	-1.79175100
H	4.10393300	1.77054100	-1.82125000
H	6.81882100	1.78390300	-0.44050200
H	4.11320500	1.91398500	0.97390900
H	6.78582500	2.90908500	2.03815800
H	5.36354700	2.42824100	2.97822500
H	-1.38810500	6.68781500	0.08396900
H	0.55195400	7.00649900	-1.34209400
H	0.63989800	3.99136200	-1.77268400
H	2.48166500	5.84709400	-0.17717900
H	0.55462700	3.66190000	0.75834800
H	2.16981200	3.47981400	2.39880600
H	1.29006600	4.89593000	3.00394200
H	-3.57293200	4.22122900	3.25936900
H	-7.62072200	0.20291200	2.41049700
H	0.90995900	-4.99215200	3.24470500
O	-6.72994300	2.02170400	2.40739400
H	-5.86833200	2.49853600	2.40596400
O	-5.77890700	-3.72630400	2.18609000
H	-6.15465600	-2.83487800	1.99501300
O	-0.70510600	-6.02269700	2.51248300
H	-1.61665100	-5.78900900	2.21760900
O	6.62217600	0.89672100	2.23806400
H	5.98989100	0.15376100	2.40054400
O	3.11859900	5.34997500	2.18668800
H	3.89082700	4.82297300	1.87347100
O	-2.30885900	5.65817600	2.52395000
H	-1.35463500	5.69239300	2.28070400

O	-3.49570900	5.21320100	-2.39209800
H	-2.53469800	5.43142200	-2.52346900
O	-6.34748900	0.95883400	-2.62832400
H	-6.07921100	1.91530400	-2.56356900
O	-4.53052600	-4.01775200	-2.71737600
H	-5.06393000	-3.18187100	-2.79456700
O	0.48244100	-5.93363500	-2.43144600
H	-0.48524900	-5.75887600	-2.57801000
O	5.08909200	-3.46666900	-2.53746500
H	4.34583300	-4.12855900	-2.51548400
O	5.90973600	1.77555600	-2.87769800
H	5.99361200	0.78611900	-2.92442300
O	1.86768800	5.37850900	-2.76609200
H	2.68314600	4.82644700	-2.90287300
O	-0.85203700	6.04979500	-2.55682700
H	-0.29909300	6.05576900	-3.36660400
O	-5.82607300	3.67054800	-2.28179000
H	-5.48096800	4.18043400	-3.04612300
O	-6.24377200	-1.82378700	-2.76367000
H	-6.30883100	-1.17928100	-3.50056800
O	-2.28635300	-5.69690600	-2.62192300
H	-2.79968900	-5.42587600	-3.41234400
O	3.21936700	-5.44625100	-2.29793700
H	2.69204700	-5.76151500	-3.06310600
O	6.37405800	-0.97577200	-2.74630100
H	6.15657400	-1.59491400	-3.47503000
O	4.35149600	4.12020900	-2.96655300
H	4.68618600	3.58712900	-3.71887000
N	5.01497300	-1.54699200	3.41963000
C	3.91823900	-1.26877900	4.36184000
C	2.84031500	-0.34491400	3.75737700
N	1.69058400	-0.09513100	4.64321400
H	5.92980800	-1.55017400	3.85516100
H	3.43574000	-2.20112300	4.70948900
H	4.34534800	-0.78344400	5.24875300
H	3.29725600	0.61772700	3.50366900
H	2.46697900	-0.76130200	2.81599300
H	1.91558900	0.44767300	5.47225800
H	1.17041400	-0.93257300	4.89039700
N	2.27350300	0.40260700	-0.20932400
C	1.34564300	-0.56736900	-0.77196700
C	1.43744400	-0.64594600	-2.29482400
O	2.13023900	0.07014200	-3.02360900
C	-0.11150400	-0.28309900	-0.33015200

C	-0.28479800	-0.31143000	1.19619200
C	-1.72342100	0.00320000	1.63423700
C	-1.89614200	0.08667400	3.16078100
N	-1.08929400	1.16224100	3.75080900
O	0.65337500	-1.66261800	-2.80874100
H	2.06823900	1.36838700	-0.45463100
H	3.25315700	0.19112600	-0.37993400
H	1.62968800	-1.56286400	-0.40432100
H	-0.77128200	-1.01829000	-0.80507800
H	-0.40846300	0.70608300	-0.71198900
H	0.40362600	0.41111300	1.64509800
H	0.00759800	-1.30455700	1.57648300
H	-2.41101500	-0.75732700	1.23149500
H	-2.02542700	0.96682500	1.20448300
H	-1.67222000	-0.90896200	3.59650400
H	-2.95130000	0.28913200	3.38633600
H	-0.10467100	0.92260900	3.89240800
H	-1.49553700	1.56992200	4.58567300
H	0.74162800	-1.70537100	-3.78633800

Table S7 Final coordinates of the B3LYP/6-31G(d,p) ϵ -NH₂ primary face geometry optimized model

C	-6.50454200	0.94963800	0.24348900
C	-6.64336500	1.95707300	-0.89402800
C	-5.35472800	2.72570200	-1.14378400
C	-4.80789900	3.30884200	0.15619100
C	-4.68535700	2.26696300	1.26751300
C	-4.27533700	2.84396700	2.63831700
C	-4.75103800	-4.12343700	-0.56729100
C	-5.49698300	-3.44608800	-1.71024000
C	-5.47023400	-1.93349700	-1.57579500
C	-5.97403800	-1.47812000	-0.20616000
C	-5.31892900	-2.23720300	0.95837300
C	-6.06628700	-2.10382100	2.30339200
C	0.34781300	-5.83631100	-0.58461900
C	-0.54863200	-5.96707600	-1.81372500
C	-1.61290300	-4.87872900	-1.86461100
C	-2.39305300	-4.88470500	-0.55721600
C	-1.47137100	-4.69414400	0.64773000
C	-2.20248700	-4.75524700	1.99858800
C	5.16982900	-3.40706500	-0.56104000
C	4.70613800	-4.23527900	-1.75771300
C	3.18831000	-4.27398500	-1.86537900

C	2.58817900	-4.75816000	-0.55196200
C	3.06266300	-3.90764800	0.62862200
C	2.59782400	-4.43613800	2.00197800
C	6.04257100	1.92150500	-1.11972400
C	6.24950200	1.03629300	-2.33939700
C	5.48669800	-0.27404100	-2.20669900
C	5.81443700	-0.98846600	-0.89380200
C	5.70979300	-0.05498900	0.32166400
C	6.28905900	-0.63517400	1.60739200
C	2.13931200	5.59717100	-0.55889600
C	2.90547000	5.44730200	-1.86989100
C	3.44808200	4.03692200	-2.04570800
C	4.27230600	3.64821800	-0.82340900
C	3.46339700	3.77587700	0.46856500
C	4.26854000	3.46609700	1.74613500
C	-3.20262800	5.20967200	0.04143300
C	-2.60515500	5.80591100	-1.22924400
C	-1.21323900	5.25888000	-1.52280300
C	-0.32622300	5.42509100	-0.29308800
C	-0.94331300	4.75906600	0.93699300
C	-0.11959500	4.93933800	2.22371600
O	-3.46451800	3.81620500	-0.15434100
O	-6.01901000	1.61882500	1.43396900
O	-5.55860800	-0.07349300	-0.11772900
O	-5.32138100	-3.70246800	0.69826600
O	-3.35863900	-3.78473400	-0.61621500
O	-0.46934700	-5.79807600	0.61786100
O	1.13199600	-4.64031900	-0.67548900
O	4.55571700	-3.92301100	0.63678200
O	4.79383800	-2.02884000	-0.74289200
O	6.47501000	1.19441300	0.06335800
O	4.65585400	2.24869600	-1.00422300
O	2.98233500	5.18616400	0.55423100
O	0.95682500	4.78822000	-0.59807600
O	-2.27758300	5.38745900	1.15103000
H	-7.45908100	0.50729100	0.52553500
H	-7.43267600	2.66914700	-0.62405600
H	-4.61490500	2.03947900	-1.57225500
H	-5.44040100	4.13204900	0.50068000
H	-3.97837100	1.48971900	0.96357700
H	-3.25570400	2.51442400	2.87173100
H	-4.88553200	-5.20667000	-0.58841900
H	-6.53860300	-3.78937900	-1.69116000
H	-4.43541300	-1.58793300	-1.68994900

H	-7.06545800	-1.55168700	-0.16161800
H	-4.27763300	-1.90533200	1.02905900
H	-5.36343100	-2.24729800	3.13506000
H	0.98772100	-6.71162100	-0.46084300
H	-1.05399800	-6.93951000	-1.76318100
H	-1.12823700	-3.90041300	-1.98818500
H	-2.92753000	-5.83232200	-0.43838200
H	-0.92071100	-3.75094600	0.55882000
H	-2.38431800	-3.73011700	2.34575900
H	-1.54444100	-5.24705700	2.71923300
H	6.24795000	-3.49690800	-0.40374300
H	5.07172900	-5.26041800	-1.62261100
H	2.81255100	-3.26196100	-2.06926500
H	2.85706500	-5.80292400	-0.36994800
H	2.74718100	-2.86837600	0.48643000
H	1.84923500	-3.75951700	2.42976500
H	6.66208800	2.81977700	-1.15163300
H	7.32031300	0.82001200	-2.43555900
H	4.41129100	-0.05316100	-2.19741400
H	6.81253800	-1.44245800	-0.95805600
H	4.66041000	0.20950200	0.47476000
H	7.36928100	-0.80639400	1.46058600
H	5.82253500	-1.61321500	1.76768400
H	1.89133300	6.64043100	-0.35574800
H	3.75061800	6.14661200	-1.85532200
H	2.60825800	3.33508500	-2.13868400
H	5.16886300	4.27129000	-0.74755400
H	2.57693300	3.13422700	0.41411600
H	4.00838900	4.21431200	2.49864800
H	3.98338000	2.47741600	2.12375700
H	-4.10943000	5.73580100	0.34357400
H	-2.52152200	6.89093500	-1.08936500
H	-1.28545600	4.18835600	-1.76124800
H	-0.16692800	6.48585900	-0.07693800
H	-1.11063700	3.69328300	0.74506800
H	0.43412400	4.01262100	2.41932600
H	-0.81556600	5.10208300	3.05064700
H	-4.95151900	2.42436300	3.38759100
H	-6.80606000	-2.90565800	2.34391100
H	3.47080500	-4.43789500	2.65946200
O	-6.82424400	-0.88398200	2.45132500
H	-6.26867000	-0.07088500	2.47031900
O	-3.43548900	-5.51330000	1.96623100
H	-4.19516800	-4.91635800	1.77056600

O	2.10634300	-5.80087500	1.97210300
H	1.13702800	-5.81503500	1.79594700
O	5.70704300	3.53364900	1.57407300
H	6.04201300	2.66229300	1.25537000
O	0.77716800	6.07625400	2.19634200
H	1.66948100	5.79431000	1.88639400
O	-4.39915500	4.28521000	2.73754600
H	-3.55898300	4.72021300	2.46108900
O	-5.69126500	3.75690800	-2.10037700
H	-4.90326600	4.32816300	-2.29453400
O	-6.29200100	-1.42617900	-2.64685300
H	-6.45114800	-0.45088400	-2.53943600
O	-2.43113100	-5.19740100	-3.00763100
H	-3.24174500	-4.62398200	-3.05786400
O	2.91612200	-5.15615900	-2.97276400
H	1.94452500	-5.35327600	-3.05820400
O	5.84787800	-1.04304800	-3.36925500
H	5.54830100	-1.98918800	-3.28738200
O	4.23008200	4.06869100	-3.25660300
H	4.69533600	3.20529800	-3.41650900
O	-0.73983200	6.00527800	-2.66051500
H	0.22241400	5.83286000	-2.84057000
O	-3.50303500	5.53247500	-2.34002700
H	-3.04621300	5.80725800	-3.16269300
O	-7.03561900	1.24335300	-2.10471800
H	-7.02771800	1.89475900	-2.83798200
O	-4.88053800	-3.84576300	-2.96644200
H	-5.25081100	-3.27430800	-3.67207600
O	0.27171900	-5.91987300	-3.01337000
H	-0.33670100	-5.85785300	-3.78006600
O	5.26593600	-3.69567200	-2.98945800
H	4.83749900	-4.18345100	-3.72657400
O	5.79467800	1.75528300	-3.51994300
H	5.78272400	1.11860800	-4.26574200
O	2.02104100	5.78932100	-2.97255400
H	2.48393500	5.55296300	-3.80400800
N	6.00430400	0.21651800	2.76296500
C	5.65143300	-0.42483700	4.03244400
C	4.18156100	-0.87209600	4.00006900
N	3.69507800	-1.58966800	5.20835200
H	6.61071400	1.02204700	2.84784400
H	6.29917500	-1.29141200	4.26651700
H	5.79393100	0.30610000	4.83688600
H	3.54629700	0.00710400	3.86958700

H	4.01484000	-1.53133500	3.14133200
H	3.61849500	-0.98025200	6.02132600
H	4.23162400	-2.42548400	5.43322100
N	-1.28239900	0.72392700	3.78820100
C	-0.45948000	-0.43775100	3.42854800
C	0.72457000	-0.61901600	4.37511400
O	1.18139000	0.31795300	5.06444500
C	0.10913400	-0.29695600	1.99060900
C	-0.95639300	-0.38569300	0.89318700
C	-0.38629800	-0.12579100	-0.51077300
C	-1.43917700	-0.24209200	-1.63636300
N	-2.59423900	0.64562600	-1.51234500
O	1.28566500	-1.84212600	4.31812700
H	-0.69467700	1.49566000	4.10104600
H	-1.97258100	0.51463300	4.50440700
H	-1.07598000	-1.34242100	3.47391000
H	0.87030500	-1.07265400	1.83642700
H	0.62318900	0.67433700	1.92863600
H	-1.74854500	0.33866900	1.11415500
H	-1.42276200	-1.38460600	0.91550500
H	0.43306900	-0.83176700	-0.71826700
H	0.05662100	0.88285900	-0.54015200
H	-1.81815100	-1.27220400	-1.67346900
H	-0.94872500	-0.05549200	-2.60128900
H	-3.32971000	0.34168900	-0.88707000
H	-2.39103300	1.63515200	-1.43039600
H	2.24124300	-1.85996100	4.80000400

FT-IR

FT-IR could provide useful information for the supramolecular inclusion phenomenon. All the data are acquired in solid samples. The inclusion sample was prepared by dissolving the L-lysine and CDs (1:1, mol:mol) in water and then evaporating the solvent. Physical mixture sample was prepared by just mixing the L-lysine and CDs together at solid states. There are three characteristic bands of lysine: (1) at 1690 cm^{-1} (a strong band attributed to C=O), (2) at 2885 cm^{-1} (a broad band attributed to N-H and O-H), (3) at 1550 cm^{-1} (a band attributed to CO_2^-). There are four characteristic bands of β -CD: (1) at 1250 cm^{-1} (a band attributed to C-O-H), (2) at 950 cm^{-1} (a band attributed to C-C), (3) at 1080 cm^{-1} (a band attributed to C-O), (4) at 3485 cm^{-1} (attributed to O-H). The interaction between β -CD and lysine will affect the band of C=O. By comparing the physical mixture and inclusion spectrum of β -CD/lysine, the band of 1550 cm^{-1} become weaker in inclusion but remained the same in the physical mixture. That could be the proof that the cavity of β -CD affected the CO_2^- group and make only the ϵ -amino group have the advantage to react with the Cbz-Cl. By comparing the physical mixture and inclusion spectrum of EDA- β -CD/lysine, the band of 1550 cm^{-1} become stronger in inclusion but remain the same in physical mixture. This is opposite phenomenon in β -CD/lysine inclusion. Those observations could be the proof the orientations of lysine in the β -CD are different in EDA- β -CD.

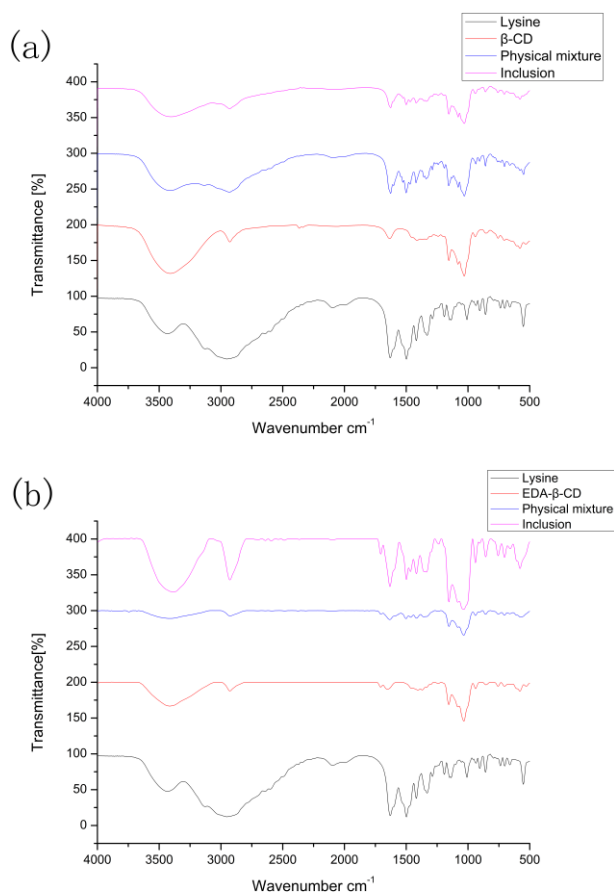


Figure. S5 FT-IR spectra of (a) lysine, β -CD, physical mixture, inclusion and (b) lysine, EDA- β -CD, physical mixture, inclusion

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