Supporting information

A Highly Stereoselectivity and Recyclable Microgel-Supported Bifunctional Sulfonamide Organocatalyst for Asymmetric Alcoholysis of *meso*-Cyclic Anhydrides: A Thermo-responsive "Organic Nanoreactor"

Fei Xiong,[†,*,a] Chao Ma,[†,a] Yi-Ren Zhu,[†,a] Chen Sun,[a] Lu Chen,[a] Yan-Jun Zhang[a], Yuan-Jie Zhu[a] and Zhong-Hua Wang*[,b]

[a] Department of Chemistry, University of Shanghai for Science and Technology, Shanghai 200093, China.
Fax: (+86)-21-65710384-621; e-mail: fxiong@usst.edu.cn/feixiong09@fudan.edu.cn

[b] School of Chemical and Environmental and Engineering, Shanghai Institute of Technology, Shanghai 201400, China. E-mail: wzhsit@163.com

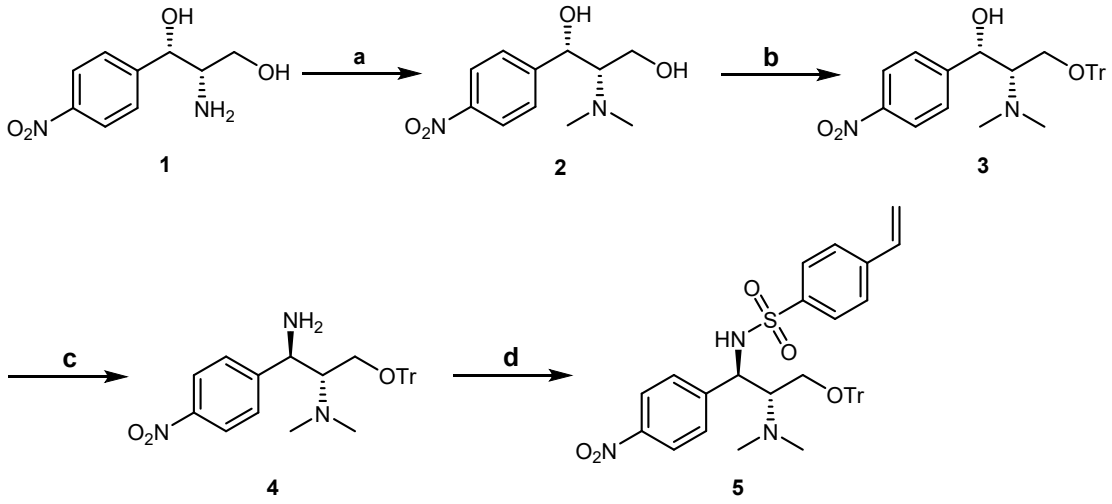
[†] These authors contributed equally: Fei Xiong, Chao Ma and Yi-Ren Zhu.

Table of Content

1. General Information

All alcohols were purified according to standard methods prior to use. Other reagents were obtained from commercial sources (Adamas-Beta) and used without further purification. All reactions were carried out in dried glassware with magnetic stirring. Reactions were performed in anhydrous solvents dried and distilled following standard procedures. Water for microgel synthesis was distilled water, for dialysis deionized water. Analytical thin-layer chromatography (TLC) was performed on GF-254 silica gel plates, visualized by UV irradiation 254 nm or $KMnO_4$ stain. Melting points were measured on *WRS*-1B digital melting-point apparatus. Optical rotations were measured by a Rudolph AUTOPOL I Automatic Polarimeter. Products were purified by flash column chromatography on silica gel purchased from Qingdao Haiyang Chemical Co. Ltd. HPLC analysis was performed using Daicel AD-H column (0.46 cm×25 cm×5 μm) or Chiralcel OD-H column (0.46 cm×25 cm×5 μm). ^1H (400 MHz) and ^{13}C (100 MHz) NMR were recorded on a Bruker Avance 400 spectrometer in $CDCl_3$/DMSO using tetramethylsilane (TMS) as internal standards. Dialysis membranes MD34 with molecular weight cutoff 8000-14000 were purchased from Adamas-Beta. Hydrodynamic radii (Rh) were measured by dynamic light scattering (DLS) at a wavelength of 410 nm with a Brookhaven NanoBrook 90Plus Zeta. TEM pictures were taken at a Transmission Electron Microscope JEOL JEM-F200 from Japan. The sedimentation velocities were determined with the stability analyzer LUMiSizer®651 at a rotation speed of 2000 rpm. Coupling constant (*J*) values are given in Hz. Multiplicities are designated by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; br, broad; m, multiplet. Mass spectra (MS-ESI) were conducted on Thermo Scientific Q Exactive Combined Quadrupole Orbitrap Mass Spectrometer. IR spectra were recorded on a Thermo FT-IR spectrometer (Nicolet IS5) and are reported in terms of frequency of transmittance (cm^{-1}).

2. General Procedure for the Synthesis of organocatalyst 5

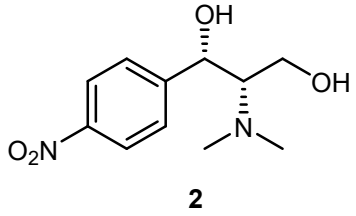


Conditions: a) HCOOH, HCHO, H_2O; b) TrCl, Et_3N, CH_2Cl_2; c) Ph_3P, DIAD, diphenyl phosphoryl azide, THF; d) *p*-styrenesulfonpl chloride, Et_3N, CH_2Cl_2.

Scheme S1 General synthesis procedure for chloramphenicol-based bifunctional sulfonamide catalyst **5**

Compound **5** was prepared from commercially available (1*S*, 2*S*)-2-amino-1-(*p*-nitrophenyl)-propane-1, 3-diol (**1**). The preparation procedure is referred to the following literatures: H. J. Yang, F. J. Xiong, J. Li, F. E. Chen, *Chinese Chem. Lett.* **2013**, *24*, 553-558; B. Vakulya, S. Varga, A. Csámpai, T. Soós, *Org. Lett.*, **2005**, *36*, 1967-1969.

(1*S*, 2*S*)-2-(*N*, *N*-dimethylamino)-1-(*p*-nitrophenyl)-propane-1, 3-diol (2)

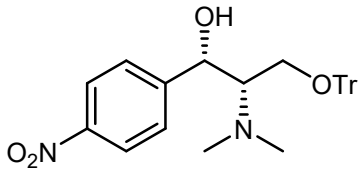


2

(1*S*, 2*S*)-2-amino-3-(*p*-nitrophenyl)-propane-1, 3-diol (10 g, 47.2 mmol), formaldehyde (37-40%, 12 mL) and formic acid (88%, 22 mL) were added to a 25 mL flask and heated at reflux for 8 h. After the solvents were removed under reduced pressure, the residue was neutralized with 1N sodium hydroxide (60 mL) and extracted with CH_2Cl_2 (3×30 mL). The combined organic solution was concentrated, and purified by flash chromatography (CH_2Cl_2/CH_3OH = 10:1) to give a yellow solid product (1*S*, 2*S*)-2-(*N*, *N*-dimethylamino)-1-(*p*-nitrophenyl)-propane-1, 3-diol (**2**) (8.9 g, 79% yield). m.p. 88.2-89.3 ℃; $[\alpha]_D^{25}$ = +24.2 (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz,

$CDCl_3$): δ 8.20 (d, J = 7.9 Hz, 2H), 7.59 (d, J = 8.0 Hz, 2H), 4.58 (d, J = 9.6 Hz, 1H), 3.60 (d, J = 4.5 Hz, 2H), 2.60 (m, 1H), 2.50 (s, 6H).^{13}C NMR (100 MHz, $CDCl_3$): δ 149.98, 147.53, 128.02, 123.64, 71.28, 69.87, 57.81, 41.61.

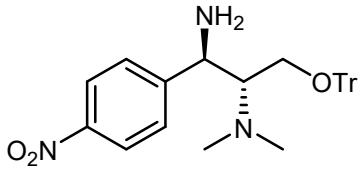
(1*S*, 2*S*)-2-(*N*, *N*-dimethylamino)-3-trityl-1-(*p*-nitrophenyl)-propane-1-ol (3)



3

Trityl chloride (11.1 g, 40 mmol) and triethylamine (6.6 g, 66.6 mmol) were sequentially added to a solution of **2** (8 g, 33.3mmol) in CH_2Cl_2 (50 mL) at 0 °C. The reaction was allowed to proceed at room temperature for 10 h and then washed by water (3×30 mL). The organic phase was dried over anhydrous sodium sulfate, filtered and concentrated. The residues were recrystallized from ether to give **3** (2.7 g, 70% yield) as a white solid. m.p. 155.6-156.9 ℃; $[\alpha]_D^{25}$ = -18.3 (*c* 0.5, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 7.4 Hz, 2H), 7.40 (d, J = 7.3 Hz, 2H), 7.21 (s, 15H), 4.46 (d, J = 9.7 Hz, 1H), 3.31-2.90 (m, 3H), 2.55 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.09, 147.56, 142.94, 128.43, 128.30, 127.88, 127.34, 123.63, 87.71, 70.33, 57.93, 41.15.

(1*R*, 2*R*)-2-(*N*, *N*-dimethylamino)-1-(4-nitrophenyl)-3-triphenylmethoxy-1, 2 propane-diamine (4)

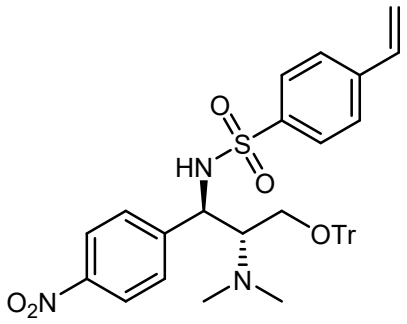


4

3 (5.0 g, 10 mmol) and Ph_3P (3.28 g, 12.5 mmol) were placed under vacuum and purged with N_2 three times, anhydrous THF (30 mL) was added and the solution was cooled to 0 °C. Diisopropyl azodicarboxylate (2.53 g, 12.5 mmol) was added followed by the dropwise addition of a solution of diphenyl phosphoryl azide (3.45 g mL, 12.5 mmol) in anhydrous THF (10 mL). The mixture was then allowed to warm to room temperature and stir for 10 h, at which point the mixture was heated at 50 °C for 2 h. Ph_3P (3.28 g, 12.5 mmol) was then added and the mixture was stirred for a further 2 h at 50 °C. The solution was allowed to cool to room temperature before

H_2O (0.7 mL) was added and then stirred for a further 2 h. The mixture was then concentrated in vacuo and the crude residue was dissolved in CH_2Cl_2 (30 mL). The mixture was washed three times with water. The combined organic phases were dried over Na_2SO_4, filtered and concentrated in vacuo. Purification by column chromatography (CH_2Cl_2 : Et_3N = 100 : 1) afforded **4** as a brown oily. (2.94 g, 59%). $[\alpha]_D^{25}$ = -11.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400MHz, $CDCl_3$): δ 2.02 (s, 2H), 2.41 (s, 6H), 2.76-2.81 (m, 1H), 2.87 (dd, *J* = 3.6Hz, 10.0Hz, 1H), 3.12 (dd, *J* = 6.0 Hz, 10.0 Hz, 1H), 3.89 (d, *J* = 10.0 Hz, 1H), 7.18 (s, 15H), 7.37 (d, *J* = 8.8 Hz, 2H), 8.02 (d, *J* = 8.8 Hz, 2H) ppm;^{13}C NMR (100 MHz, $CDCl_3$): δ 41.44, 55.45, 59.19, 69.57, 87.30, 123.53, 126.89, 127.61, 128.58, 128.71, 143.52, 147.03, 151.93 ppm.

***N*-((1*R*, 2*R*)-2-(dimethylamino)-1-(4-nitrophenyl)-3-(trityloxy)propyl)-4-vinyl benzenesulfonyl chloride (5)**



5

To a solution of chloramphenicol base **4** (1 g, 2 mmol) in CH_2Cl_2 (20 mL) was added the solution of Et_3N (1.15 mL, 8 mmol) in CH_2Cl_2 (10 mL) under N_2 atmosphere. After cooling to 0 °C, 4-vinyl benzenesulfonyl chloride (3 mmol) was added dropwise over 10 min. After addition, the reaction mixture was stirred for 3 h at room temperature and then quenched by water (10 mL). The organic phase was washed with H_2O (20 mL), brine (20 mL), dried over Na_2SO_4 and concentrated under reduced pressure to give a white solid. The crude product was purified by flash chromatography using PE : EA = 2 : 1 to give product **5** (2.7 g, 70% yield). m.p. 188.5-189.5 °C; $[\alpha]_D^{25}$ = +73.6 (*c* 0.05, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.76 (m, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.24-6.97 (m, 17H), 6.68 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.83 (d, *J* = 17.6 Hz, 1H), 5.42 (d, *J* = 10.9 Hz, 1H), 3.93 (d, *J* = 10.6 Hz, 1H), 3.08 (dd, *J* = 10.6, 6.1 Hz, 1H), 2.93 (dd, *J* = 10.6, 3.4 Hz, 1H), 2.70 (ddd, *J* = 9.9, 6.1, 3.3 Hz, 1H), 2.25 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.14, 135.25, 129.15, 128.53, 127.82, 127.26, 126.39, 123.44, 117.73, 87.66, 68.03,

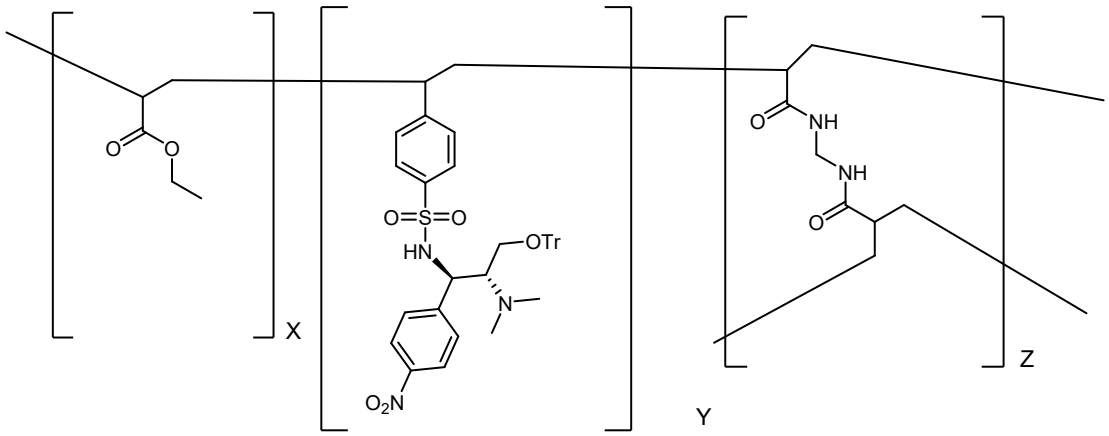
58.05, 56.51, 40.95. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{38}H_{37}N_3O_5S$ 648.25138, found 648.25140.

3. Synthesis and characterization of the microgel

3.1 Synthetic procedure

First, we synthesized catalyst **5**, a chloramphenicol-based sulfonamide containing a polymerizable styryl group. Polymeric catalyst **6a-c** was prepared by reacting chiral monomer **5** with ethyl acrylate (EA) and *N*, *N*-methylenebis(acrylamide) (BIS) in the presence of 2, 2-azobis(2-methylpropionamidine) dihydrochloride (AMPA) as a radical initiator in water (Scheme S2). A series of microgels with 3 mol % cross-linker and organocatalyst contents of 1, 4, and 20 mol % was synthesized (polymeric catalysts **6a**, **6b**, and **6c**, respectively). The chemical structure of monomer **5** was confirmed by NMR and mass spectral analyses.

For the emulsion polymerization, a certain amount of organocatalyst monomer (1-20 mol%) was dissolved in ethyl acrylate (80-99 mol%) under continuous stirring. Then cetyltrimethylammonium bromide (CTAB, 1 mol%), crosslinker *N*, *N'*-methylenebisacrylamide (BIS, 3 mol%), and water were added. Dissolved oxygen was removed by purging nitrogen through the mixture within 60 min. In order to build an emulsion, the flask with the mixture was placed in an ultrasonic bath for 15 min. Then the flask was placed in oil bath and heated up to 70 °C under constant stirring. Finally, a water solution of the initiator 2, 2′-azobis(2-methylpropionamidine) dihydrochloride (AMPA, 1 mol%) was added to the reaction mixture. After 6 hours reaction time, the mixture was cooled down to room temperature and dialyzed for 5 days against water to purify the microgel.



Catalyst	X/%	Y/%	Z/%

6a	96	4	3
6b	99	1	3
6c	80	20	3

Scheme S2: Structures and composition of organocatalysts **6a-c**.

3.2 Elemental analysis

To verify the incorporation of the organocatalyst **5** into the microgel, elemental analysis was performed by the external provider shiyanjia lab. The content of conventional organic elements in the sample was analyzed by using the principle of high temperature combustion method under high temperature and aerobic conditions. Reported values in Table S1 represent the average value of the C, H, N, S, element in the catalyst **6a-c**. Among them, sulfur element as the characteristic element of monomer is used to accurately determine the true proportion of monomer contained in the polymer microgel **6a-c**. As control experiments also the monomeric organocatalysts **5** were measured. All measured sulfur contents are in very good agreement with the calculated values. The only exception is catalyst **6c** (poly-**EA-5** (80:20)), catalyst **6c** was thought to have a ratio of 0 : 100 (poly-**EA-5**).

Table S1 Elemental analysis

Entry	Sample	N(%)	C(%)	H(%)	S(%)
1	**6a**	1.94	61.07	6.974	0.907
2	**6a**	2.06	61.31	7.046	1.012
3	**6b**	1.22	59.73	7.253	0.285
4	**6b**	1.14	59.48	7.174	0.196
5	**6c**	6.24	69.48	5.497	4.347
6	**6c**	6.36	69.72	5.583	4.451
7	**5**	6.49	70.48	5.73	4.89
8	**5**	6.46	70.6	5.68	4.93
9[a]	**5**	6.48	70.4	5.7	4.94

[a] Theoretical calculation of organic elements (C, H, N, S) for monomeric compound **5**.

3.3 Sedimentation velocity of microgels at different temperatures

In order to further investigate the relationship between the swelling/collapse behavior of thermo-sensitive microgel colloidal particles and the external ambient temperature, we also conducted a sedimentation analysis experiment of the colloidal particles besides the DLS dynamic light scattering experiment.

Fig S1 (a) presents median particle migration velocity for microgels measured at different temperatures by sedimentation analysis experiment. For the microgel sample, we observed a rapid increase of the sedimentation velocity by heating the sample from 10 °C to 50 °C. This can be attributed to that when the temperature is lower, the microgels undergo volume expansion, and the expanded particles exhibit lower sedimentation velocity due to greater buoyancy. In contrast, with the gradual increase of the temperature, the solvent existing in the highly cross-linked microgel network structure is discharged, the volume of the microgel particles shrinks. This also causes a rapid increase in the settling velocity of the particles. Reported data in Table S2 represented actual particle sedimentation velocity and distribution data. The integral distribution of particle migration velocity (Fig S1 (b)) shows that the particles in the system settle with different migration velocities in the sedimentation.

Table S2 Actual particle sedimentation velocity and distribution data

Sample Name	Median in nm	Harmonic Mean in nm	Std.Dev. in nm	Span (x90 x10)/x50	Mean RCA in g	10% ≤ in nm	16% ≤ in nm	50% ≤ in nm	84% ≤ in nm	90% ≤ in nm
10°C-1	1,406	1,036	842.3	1.594	532.5	530.2	677.9	1,406	2,500	2,772
10°C-2	1,449	792.9	1,038	1.873	531.3	532.3	680.0	1,518	2,857	3,059
20°C-1	1,518	1,052	1,022	1.679	531.3	532.3	680.0	1,518	2,857	3,082
20°C-2	1,594	1,292	981.5	1.648	530.4	676.2	793.2	1,594	2,969	3,303
25°C-1	1,705	1,264	1,039	1.597	528.7	771.3	910.3	1,705	3,000	3,496
25°C-2	1,767	1,325	981.8	1.418	530.0	735.2	897.4	1,767	2,913	3,241
30°C-1	1,910	1,439	1,225	1.717	529.2	765.5	926.6	1,910	3,644	4,044
30°C-2	1,971	1,431	1,150	1.581	529.5	638.5	1,020	1,971	3,348	3,754
40°C-1	2,123	1,415	951.1	1.200	531.9	748.7	1,066	2,123	3,030	3,296
40°C-2	2,128	1,557	934.1	1.196	531.7	772.0	1,149	2,128	2,964	3,317
50°C-1	2,245	1,672	1,167	1.391	531.1	835.6	1,091	2,245	3,649	3,958
50°C-2	2,351	1,703	1,065	1.237	530.9	831.8	1,193	2,351	3,367	3,740

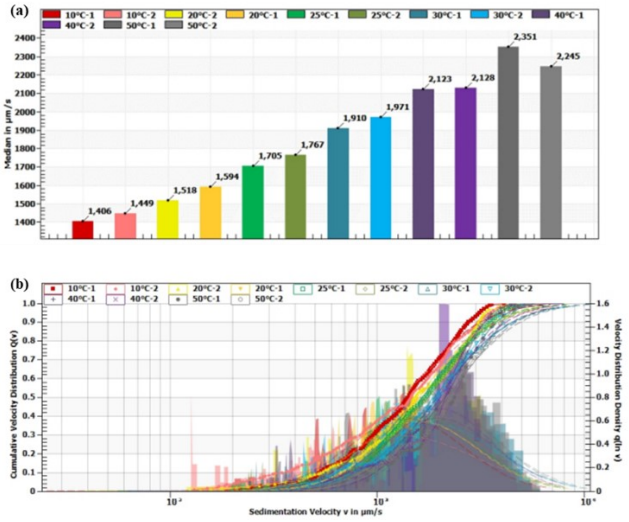


Fig S1. (a) Median particle migration velocity and (b) particle velocity distribution (2000 rpm) versus temperature plots for microgel-supported catalyst **6a** in isopropyl alcohol.

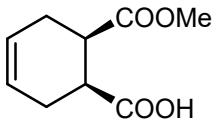
4. General Procedure for the asymmetric alcoholysis of cyclic anhydrides

4.1 Synthetic procedure and characterization

To perform the catalytic test reaction, the polymer catalyst (1-20 mol%) was dissolved/suspended in the appropriate mixture of solvents, 1 *equiv. meso*-anhydride and the nucleophile (5 *equiv.*) were added. The reaction mixture was stirred at 20 °C (TLC control, petroleum ether/ethyl acetate 2 : 1, $KMnO_4$ stained). Once the anhydride consumption was complete, heating the reaction mixture to 40-50 °C. The microgel catalyst, which precipitated from the solvent, was immediately separated by centrifuging the mixture for 5 min. The supernatant was concentrated under reduced pressure to afford the corresponding hemiester without further purification by flash chromatography. The recovered catalyst was repeatedly washed with fresh solvent to remove residual contaminants.

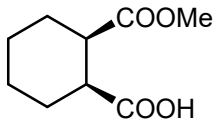
All monoesters are known compounds and their NMR spectra data were identical to those reported in the literature: S. X. Wang, F. E. Chen, *Adv. Synth. Catal.* **2009**, *351*, 547-552; S. E. Park, E. H. Nam, H. B. Jang, J. S. Oh, S. Some, Y. S. Lee, C. E. Song, *Adv. Synth. Catal.* **2010**, *352*, 2211-2217; L. Xu, S. Han, L. Yan, H. Wang, H. Peng, F. Chen, *Beilstein. J. Org. Chem.* **2018**, *14*, 309-317. The enantiomeric excess of the monoester was determined by chiral HPLC, analysis of the diastereoisomeric mixture of the corresponding amide ester derived from (*S*)-1-phenylethylamine according to the reported procedure.

(1*S*, 6*R*)-6-(methoxycarbonyl)cyclohex-3-enecarboxylic acid (8)



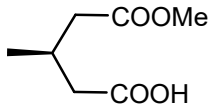
yield 93%, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.93 (dd, J = 24.1, 3.6 Hz, 2H), 3.67 (s, 3H), 3.05-2.99 (m, 2H), 1.84-1.82 (m, 2H), 1.56-1.51 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 179.7, 173.7, 125.1, 125.0, 51.9, 39.6, 39.4, 25.7, 25.5 ppm.

(1*S*, 2*R*)-2-(Methoxycarbonyl)cyclohexanecarboxylic acid (10)



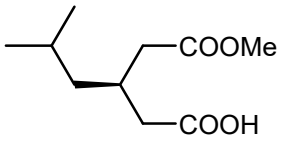
yield 94%, ^{1}H NMR (400MHz, DMSO): δ = 3.67 (s, 3H), 2.84 (s, 2H), 122.00 (br, 2H), 1.78 (br, 2H), 1.54-1.47 (m, 2H), 1.42-1.39 (m, 2H) ppm; ^{13}C NMR (100 MHz, DMSO) δ = 180.2, 174.2, 51.8, 42.6, 42.4, 26.3, 26.0, 23.8, 23.7 ppm.

(*R*)-5-Methoxy-3-methyl-5-oxopentanoic acid (12)



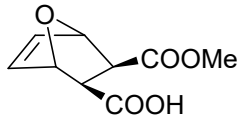
yield 85%, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.67 (s, 3H), 2.50-2.39 (m, 3H), 2.31-2.24 (m, 2H), 1.05 (d, J = 6.3 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO) δ = 173.8, 172.8, 51.6, 40.6, 40.3, 27.3, 19.8 ppm.

(*R*)-5-Methoxy-3-isobutyl -5-oxopentanoic acid (14)



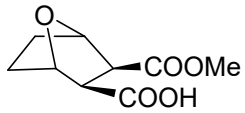
yield 88%, ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.86-0.88 (d, J = 6.6 Hz, 6H), 1.18-1.21 (m, 2H), 1.53-1.67 (m, 1H), 2.36-2.37 (m, 5H), 3.65 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 22.49, 25.15, 29.70, 38.39, 43.37, 51.50, 173.02, 178.91 ppm.

(1*S*, 2*R*, 3*S*, 4*R*)-3-(Methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylic acid (16)



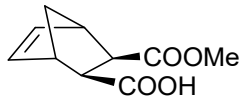
yield 90%, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69 (br, 1H), 6.49-6.45 (m, 2H), 5.29 (d, J = 16.7 Hz, 2H), 3.71 (s, 3H), 2.88-2.83 (m, 2H) ppm; ^{13}C NMR (100 MHz, DMSO) δ = 173.0, 172.5, 137.1, 137.0, 80.4, 80.1, 51.9, 47.0, 46.3 ppm.

Monomethyl 7-oxabicyclo[2.2.1]heptane-2,3-dicarboxylate (18)



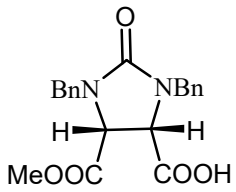
yield 87%, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.52-1.54 (m, 2H), 2.99-3.05 (m, 2H), 3.67 (s, 3H), 4.89-4.96 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 28.95, 29.02, 52.16, 52.27, 52.30, 78.34, 78.65, 171.31, 175.83 ppm.

(1*R*, 2*S*, 3*R*, 4*S*)-3-(Methoxycarbonyl)bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (20)



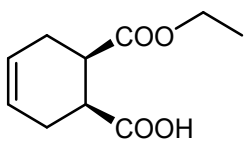
yield 97%, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.31 (dd, J = 5.1, 2.9 Hz, 1H), 6.22 (dd, J = 5.3, 2.8 Hz, 1H), 3.59 (s, 3H), 3.35-3.26 (m, 2H), 3.18 (d, J = 12.9 Hz, 2H), 1.49 (d, J = 8.6 Hz, 1H), 1.34 (d, J = 8.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 178.3, 172.9, 135.5, 134.3, 51.5, 48.7, 48.2, 48.0, 46.5, 46.1 ppm.

(4*R*, 5*R*)-1,3-diphenyl-5-(methoxycarbonyl)-2-oxo-4-carboxylic acid imidazolidine (22)



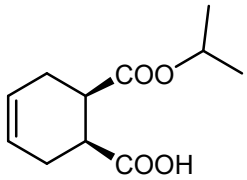
yield 78%, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.62 (s, 3H), 4.03-4.11 (m, 4H), 4.98 (d, J = 15.2Hz, 1H), 5.08 (d, J = 14.8 Hz, 1H), 7.20-7.32, (m, 10H), 7.85 (br, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 47.0, 47.2, 53.0, 57.1, 128.2, 128.8, 128.9, 129.2, 135.7,160.1, 168.9, 171.6 ppm.

(1*S*, 6*R*)-6-(Ethoxycarbonyl)cyclohex-3-enecarboxylic acid (23)



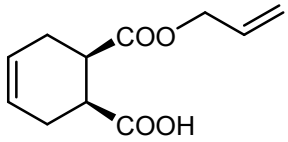
yield 88%, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 11.14 (br, 1H), 5.68-5.62 (m, 2H), 4.13 (q, J = 7.0 Hz, 2H), 3.03-3.02 (m, 2H), 2.58-2.51 (m, 2H), 2.34 (d, J = 18.4 Hz, 2H), 1.21 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 179.9, 173.2, 125.2, 125.0, 60.8, 39.7, 39.6, 25.9, 25.5, 14.0 ppm.

(1*S*, 6*R*)-6-(Isopropoxycarbonyl)cyclohex-3-enecarboxylic acid (24)



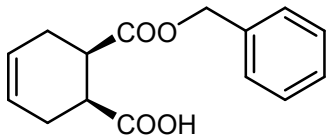
yield 76%, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 11.18 (br, 1H), 5.69-5.62 (m, 2H), 5.00 (dt, J = 12.4, 6.2 Hz, 1H), 3.02 (s, 2H), 2.58-2.50 (m, 2H), 2.33 (d, J = 16.5 Hz, 2H), 1.19-1.18 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 180.2, 172.6, 125.3, 125.0, 68.3, 39.7, 25.9, 25.4, 21.7, 21.6 ppm.

(1*S*, 6*R*)-6-((Allyloxy)carbonyl)cyclohex-3-enecarboxylic acid (25)



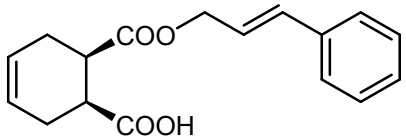
yield 92%, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 11.11 (br, 1H), 5.92-5.82 (m, 1H), 5.69-5.64 (m, 2H), 5.28 (d, J = 17.2Hz, 1H), 5.19 (d, J = 10.5Hz, 1H), 4.62-4.54 (m, 2H), 3.06 (d, J = 5.9 Hz, 2H), 2.62-2.53 (m, 2H), 2.39-2.34 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 179.7, 172.9, 132.1, 125.2, 118.1, 65.4, 39.7, 39.6, 25.9, 25.6 ppm.

(1*S*, 6*R*)-6-((Benzyloxy)carbonyl)cyclohex-3-enecarboxylic acid (26)



yield 95%, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.51 (br, 1H), 7.37-7.29 (m, 5H), 5.69 (s, 2H), 5.19-5.11 (m, 2H), 3.11 (t, J = 5.2 Hz, 2H), 2.66-2.57 (m, 2H), 2.42-2.35 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 179.8, 173.0, 135.9, 128.5, 128.2, 128.1, 125.2, 125.1, 66.6, 39.7, 39.6, 25.8, 25.6 ppm.

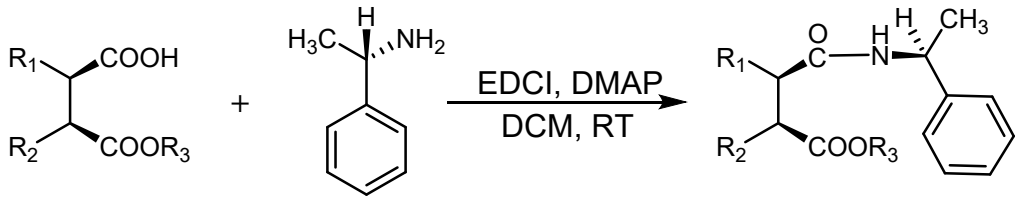
(1*S*, 6*R*)-6-((Cinnamyloxy)carbonyl)cyclohex-3-enecarboxylic acid (27)



yield 96%, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42-7.29 (m, 5H), 6.64 (d, J = 3.2 Hz, 2H), 6.41-6.36 (m, 1H), 5.73 (s, 2H), 4.34-4.33 (m, 2H), 3.14-3.09 (m, 2H), 2.66-2.62 (m, 2H), 2.43-2.39 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.7, 173.2, 136.7, 131.0, 128.5, 127.6, 126.4, 125.1, 123.1, 65.3, 63.4, 39.7, 39.6, 25.8, 25.6 ppm.

4.2 Derivatization of the hemiesters

To a solution of 1.0 *equiv.* hemiester in dry DCM was added 1.2 *equiv.* EDCI, 0.3 *equiv.* DMAP and 1.1 *equiv.* (*S*)-1-phenyl-ethylamine. The reaction mixture was stirred for 3 h at RT (TLC control, ethyl acetate : petroleum ether = 1 : 2), the solvent was concentrated under reduced pressure and the residue was washed 3 times with 10% aqueous hydrochloric acid. The enantiomeric excess of the hemiester was determined by HPLC analysis of the diastereoisomeric mixture of the corresponding amide-ester derived from (*S*)-1-phenyl-ethylamine according to the reported procedure (Scheme S3).



Scheme S3 General procedure for derivatization of hemiesters for HPLC analysis

4.3 Reaction optimization for the desymmetrization of *meso*-anhydrides

Table S3 Screening table for the desymmetrization of *meso*-anhydrides[a]

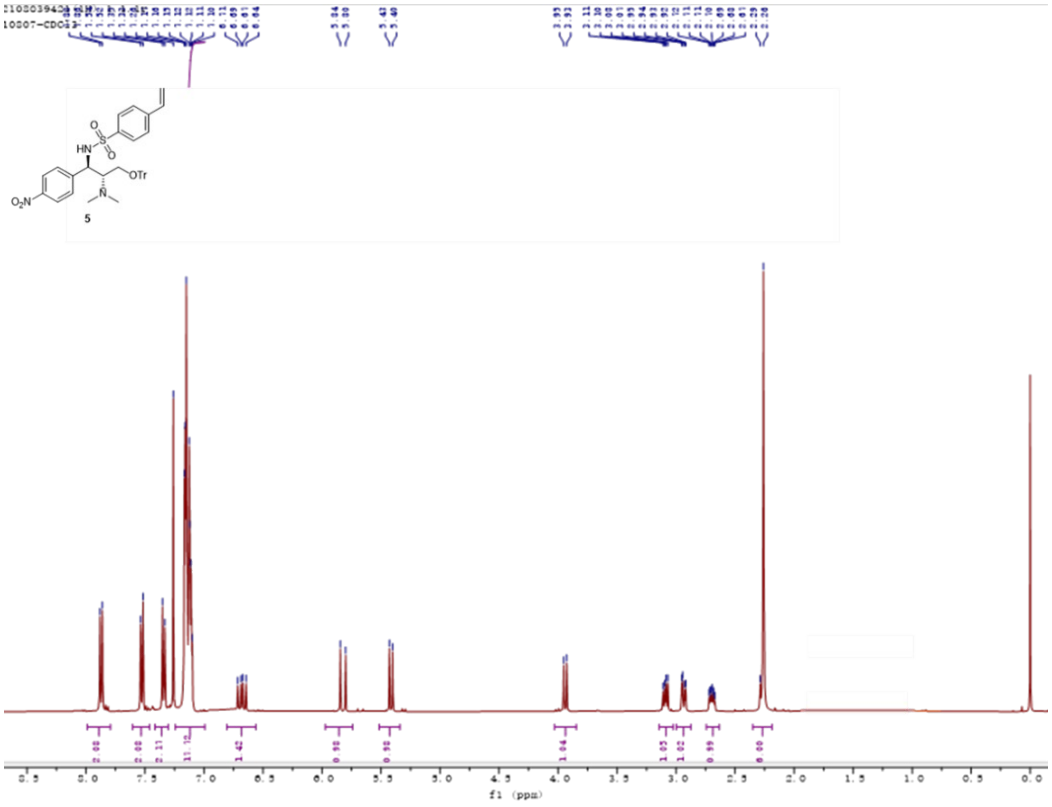
Entry	Catalyst	Mol [%]	Anhydride	Solvent	Nu	Conc. [M]	Time [h]	Yield [%]	Ee[f] [%]
1	**6a**	5	**7**	Et_2O	MeOH	0.02	120	94	31
2	**6b**	5	**7**	Et_2O	MeOH	0.02	120	87	25
3[b]	**6c (5)**	5	**7**	Et_2O	MeOH	0.02	120	95	33
4	**6a**	5	**7**	THF	MeOH	0.02	60	89	15
5	**6a**	5	**7**	Toluene	MeOH	0.02	36	96	60
6	**6a**	5	**7**	$CHCl_3$	MeOH	0.02	36	92	41
7	**6a**	5	**7**	MTBE	MeOH	0.02	70	91	61
8	**6a**	5	**7**	Acetone	MeOH	0.02	48	78	0
9	**6a**	5	**7**	Dioxane	MeOH	0.02	72	93	40
10	**6a**	5	**7**	CCl_4	MeOH	0.02	40	93	60
11	**6a**	5	**7**	MTBE	MeOH	0.02	70	91	61
12	**6a**	5	**7**	MTBE	MeOH	0.05	36	90	76
13	**6a**	5	**7**	MTBE	MeOH	0.1	20	93	71

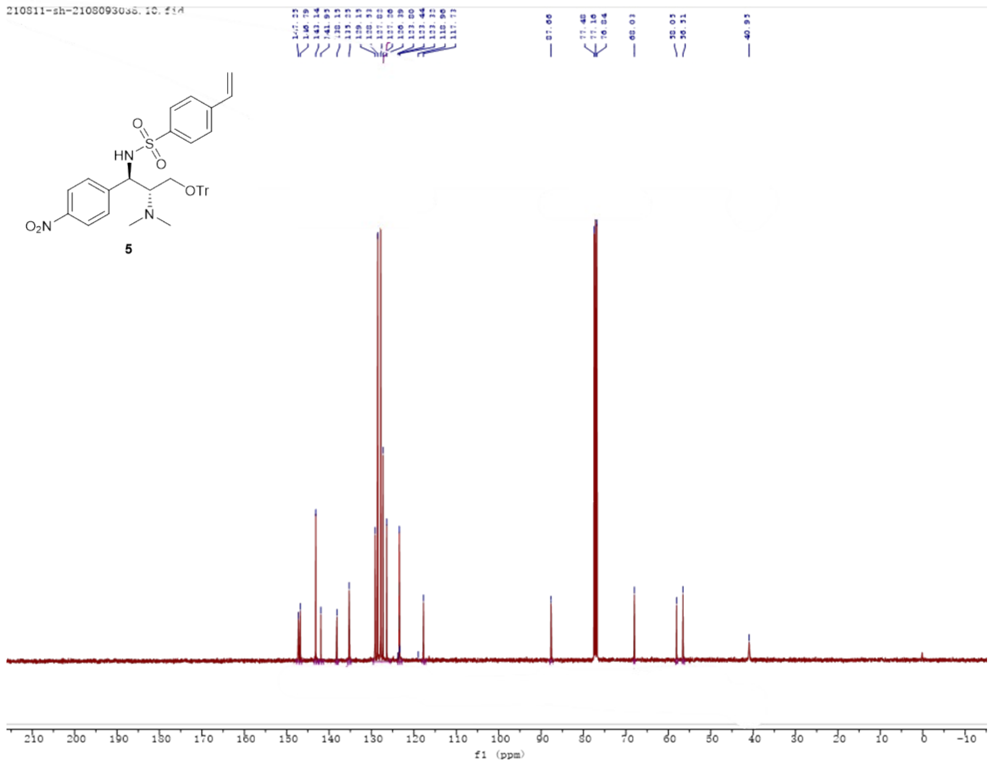
14	**6a**	5	**7**	MTBE	MeOH	0.15	20	90	65
15	**6a**	5	**7**	MTBE	MeOH	0.2	10	87	59
16	**6a**	1	**7**	MTBE	MeOH	0.05	120	91	54
17	**6a**	5	**7**	MTBE	MeOH	0.05	36	90	76
18	**6a**	10	**7**	MTBE	MeOH	0.05	20	93	83
19	**6a**	20	**7**	MTBE	MeOH	0.05	10	92	74
20	**6a**	10	**7**	MTBE	MeOH	0.05	20	93	83
21	**6a**	10	**9**	MTBE	MeOH	0.05	20	94	77
22	**6a**	10	**11**	MTBE	MeOH	0.05	36	85	67
23	**6a**	10	**13**	MTBE	MeOH	0.05	36	88	37
24	**6a**	10	**15**	MTBE	MeOH	0.05	12	90	60
25	**6a**	10	**17**	MTBE	MeOH	0.05	20	87	35
26	**6a**	10	**19**	MTBE	MeOH	0.05	24	97	53
27	**6a**	10	**21**	MTBE	MeOH	0.05	72	78	15
28[c]	**6a**	10	**7**	MTBE	MeOH	0.05	20	95	60
29	**6a**	10	**7**	MTBE	MeOH	0.05	20	93	83
30	**6a**	10	**7**	MTBE	EtOH	0.05	96	88	53
31[d]	**6a**	10	**7**	MTBE	*i*-PrOH	0.05	120	76	14
32	**6a**	10	**7**	MTBE	allyl-alcohol	0.05	48	92	77
33	**6a**	10	**7**	MTBE	BnOH	0.05	12	95	86
34	**6a**	10	**7**	MTBE	cinnamyl alcohol	0.05	12	96	90
35[e]	**6a**	10	**7**	MTBE	cinnamyl alcohol	0.05	12	95	88
36[e]	**6a**	10	**7**	MTBE	cinnamyl alcohol	0.05	15	95	89
37[e]	**6a**	10	**7**	MTBE	cinnamyl alcohol	0.05	12	97	85
38[e]	**6a**	10	**7**	MTBE	cinnamyl alcohol	0.05	16	93	89
39[e]	**6a**	10	**7**	MTBE	cinnamyl alcohol	0.05	20	95	87

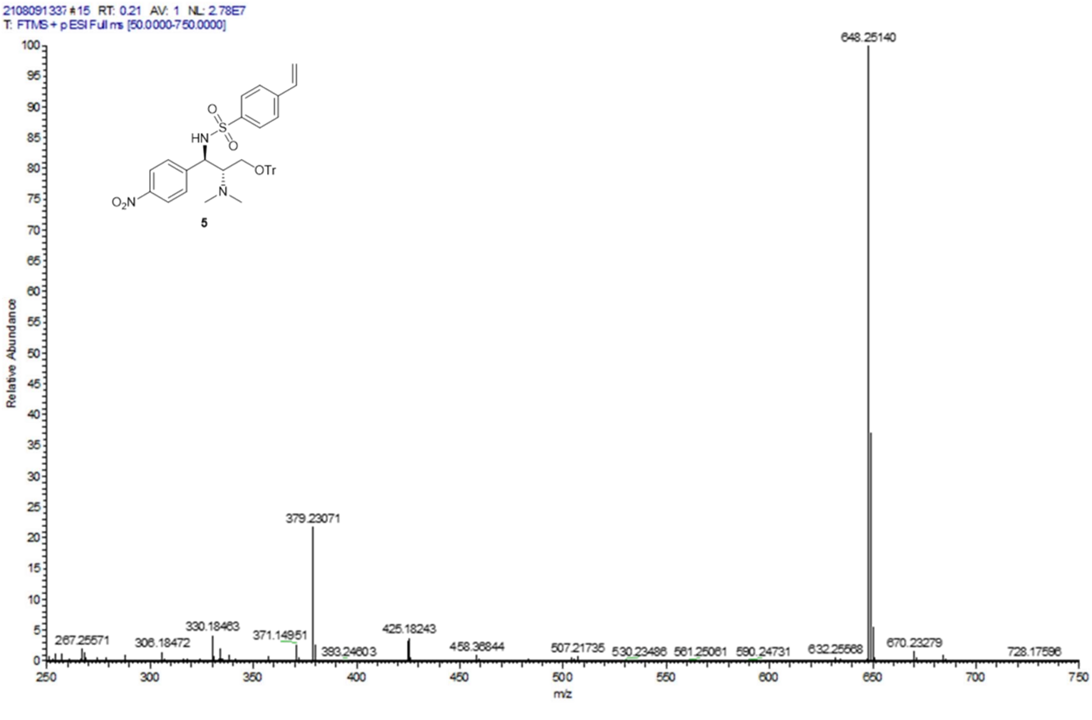
[a] unless otherwise noted, all reactions were carried out with anhydride and ROH in solvents at 20 °C. [b] elemental analysis shows that catalyst **6b** did not undergo polymerization reaction, thus, catalyst **6b** is equivalent to monomer compound **5.** [c] reaction performed at 50 °C. [d] incomplete conversion after 120 h. [e] catalyst **6a** recycling experiments. [f] determined by chiral HPLC analysis.

5. ^{1}H spectra, ^{13}C spectra, HRMS spectra and the HPLC spectra

All compounds except **5** are known compounds and their NMR spectra data were identical to those reported in the literature: H. J. Yang, F. J. Xiong, J. Li, F. E. Chen, *Chinese Chem. Lett.* **2013**, *24*, 553-558.

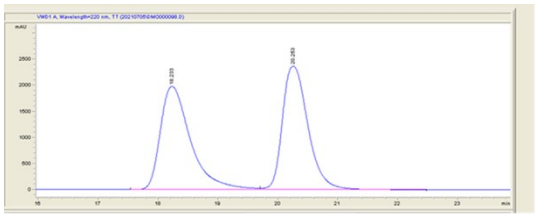


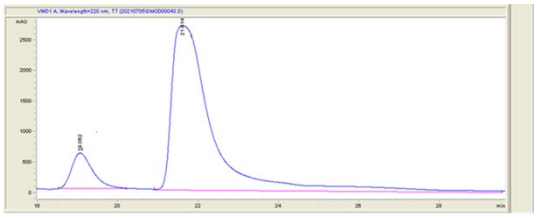

HN
O
S
O
OTr
N
O_2N
5
f1 (ppm)


2108091337 #15 RT: 0.21 AV: 1 NL: 2.78E7
T: FTMS + p ESI Full ms [50.0000-750.0000]
648.25140
379.23071
267.25571
306.18472
330.18463
371.14951
393.24603
425.18243
458.36844
507.21735
530.23486
561.25061
590.24731
632.25568
670.23279
728.17596
Relative Abundance
m/z
HN
O
S
O
OTr
N
O_2N
5

(1*S*,6*R*)-6-(methoxycarbonyl)cyclohex-3-enecarboxylic acid (8)

Chiralcel OD-H, hexane/IPA: 90/10, Flow rate: 0.50 mL/min, UV detection at 220 nm, T = 25 °C, retention time: *t* (major) = 19.062 min, *t* (minor) = 21.614 min;



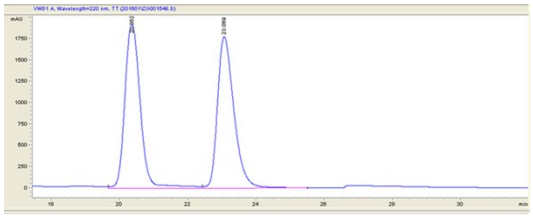


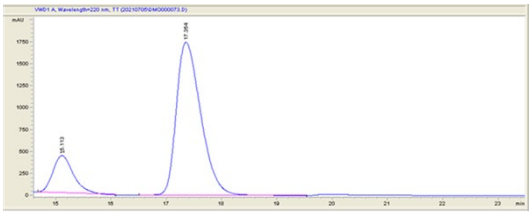
Entry	Time	Height	Width	Area%
1	18.233	1965.1	0.5326	49.867
2	20.253	2375.4	0.4583	50.133

Entry	Time	Height	Width	Area%
1	19.062	578.5	0.6005	8.169
2	21.614	2694.7	1.1871	91.831

(1*S*, 2*R*)-2-(Methoxycarbonyl)cyclohexanecarboxylic acid (10)

Chiralcel OD-H, hexane/IPA: 90/10, Flow rate: 0.50 mL/min, UV detection at 220 nm, T = 25 °C, retention time: *t* (major) = 23.326 min, *t* (minor) = 25.834 min;



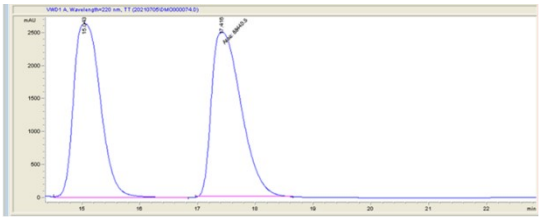


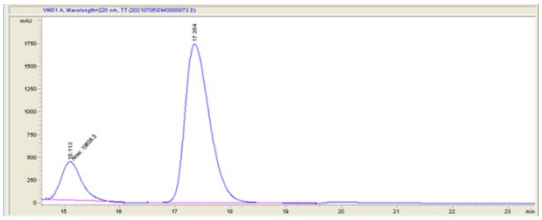
Entry	Time	Height	Width	Area%
1	20.362	1930.2	0.4943	50.450
2	23.069	1779.9	0.5183	49.550

Entry	Time	Height	Width	Area%
1	23.326	543.9	0.5612	11.557
2	25.837	2634.1	0.8614	88.443

(*R*)-5-Methoxy-3-methyl-5-oxopentanoic acid (12)

Chiralcel OD-H, hexane/IPA: 85/15, Flow rate: 0.50 mL/min, UV detection at 220 nm, T = 25 °C, retention time: *t* (major) = 15.113 min, *t* (minor) = 17.354 min;



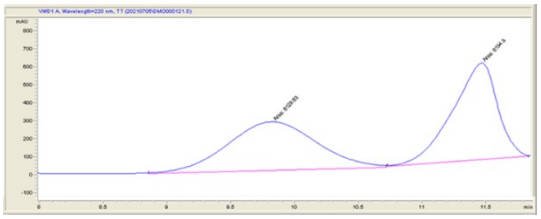


Entry	Time	Height	Width	Area%
1	15.043	2638.9	0.5098	49.110
2	17.416	2498	0.5901	50.890

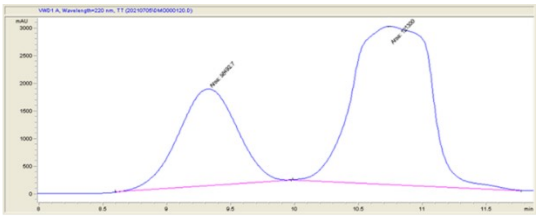
Entry	Time	Height	Width	Area%
1	15.113	423	0.427	16.725
2	17.354	1744.6	0.4774	83.275

(*R*)-5-Methoxy-3-isobutyl -5-oxopentanoic acid (14)

Chiralcel OD-H, hexane/IPA: 80/20, Flow rate: 0.50 mL/min, UV detection at 220 nm, T = 25 °C, retention time: *t* (major) = 9.326 min, *t* (minor) = 10.7455 min;



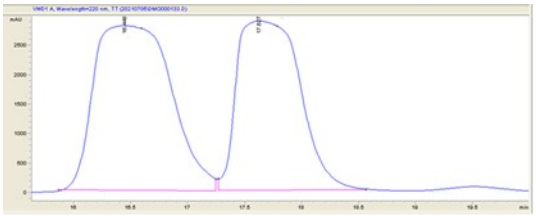
Entry	Time	Height	Width	Area%
1	9.8566	271.1	0.3769	49.899
2	11.445	538.6	0.1905	50.101



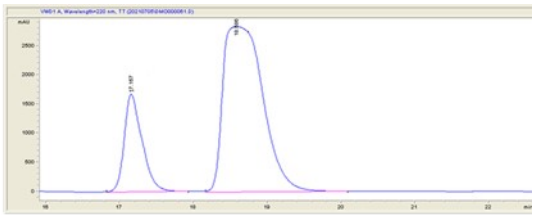
Entry	Time	Height	Width	Area%
1	9.326	1754.6	0.5366	31.774
2	10.745	2600.2	0.7068	68.226

(1*S*, 2*R*, 3*S*, 4*R*)-3-(Methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylic acid (16)

Chiralcel AD-H, hexane/IPA: 90/10, Flow rate: 0.50 mL/min, UV detection at 220 nm, T = 25 °C, retention time: *t* (major) = 17.157min, *t* (minor) = 18.586 min;



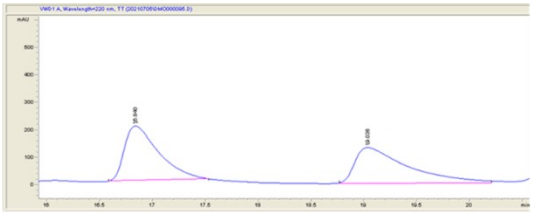
Entry	Time	Height	Width	Area%
1	16.448	2796.2	0.7905	51.436
2	17.627	2876.2	0.6432	48.564



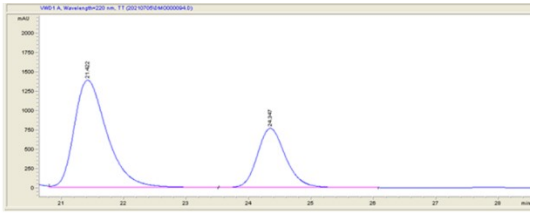
Entry	Time	Height	Width	Area%
1	17.157	1676.7	0.2793	19.794
2	18.586	2841.8	0.6276	80.206

7-Oxa-bicyclo[2.2.1]heptane-2,3-dicarboxylic acid monomethyl ester (18)

Chiralcel AD-H, hexane/IPA: 80/20, Flow rate: 0.50 mL/min, UV detection at 220 nm, T = 25 °C, retention time: *t* (major) = 21.422 min, *t* (minor) = 24.347 min;



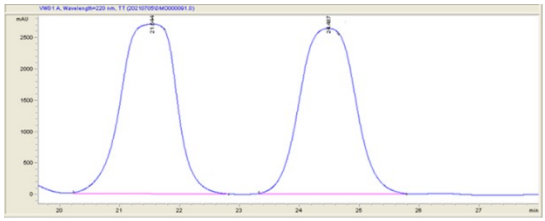
Entry	Time	Height	Width	Area%
1	16.84	197.3	0.3767	49.933
2	19.036	129.6	0.5752	50.067

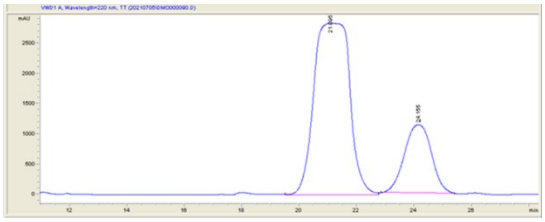


Entry	Time	Height	Width	Area%
1	21.422	1387.1	0.5602	67.878
2	24.347	765.7	0.4832	32.122

(1*R*, 2*S*, 3*R*, 4*S*)-3-(Methoxycarbonyl)bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (20)

Chiralcel AD-H, hexane/IPA: 91/9, Flow rate: 0.50 mL/min, UV detection at 220 nm, T = 25 °C, retention time: *t* (major) = 21.095 min, *t* (minor) = 24.155 min;



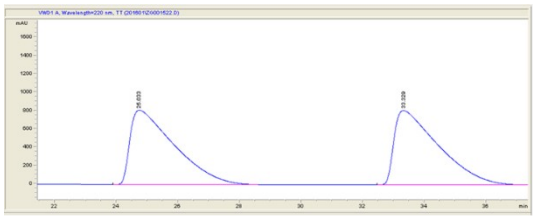


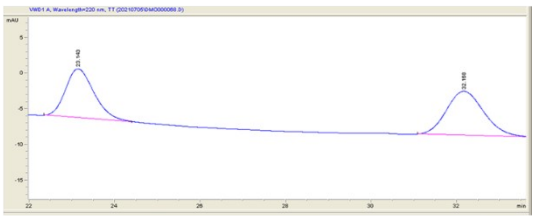
Entry	Time	Height	Width	Area%
1	21.544	2701	1.0607	50.626
2	24.487	2645.5	1.0562	49.374

Entry	Time	Height	Width	Area%
1	21.095	2838.7	1.0358	76.816
2	24.155	1132.9	1.0938	23.814

(4*R*, 5*R*)-1,3-diphenyl-5-(methoxycarbonyl)-2-oxo-4-carboxylic acid imidazolidine (22)

Chiralcel OD-H, hexane/IPA: 80/20, Flow rate: 0.50 mL/min, UV detection at 220 nm, T = 25 °C, retention time: *t* (major) = 23.143 min, *t* (minor) = 32.168 min;



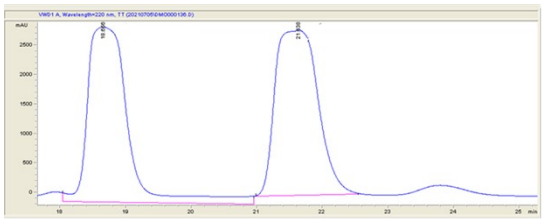


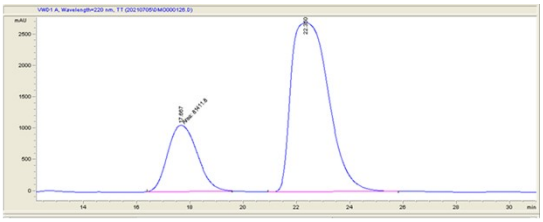
Entry	Time	Height	Width	Area%
1	25.033	81400.5	1.4608	48.933
2	33.329	80570.99	1.4750	51.067

Entry	Time	Height	Width	Area%
1	23.143	6.9	0.7045	42.065
2	32.168	6.2	0.9072	57.935

(1*S*, 6*R*)-6-(Ethoxycarbonyl)cyclohex-3-enecarboxylic acid (23)

Chiralcel OD-H, hexane/IPA: 90/10, Flow rate: 0.50 mL/min, UV detection at 220 nm, T = 25 °C, retention time: *t* (major) = 17.667 min, *t* (minor) = 22.35 min;



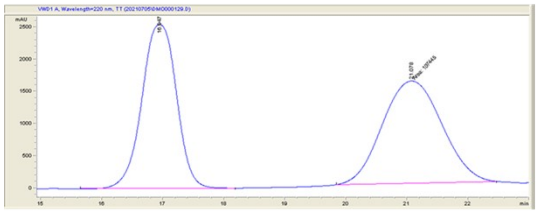


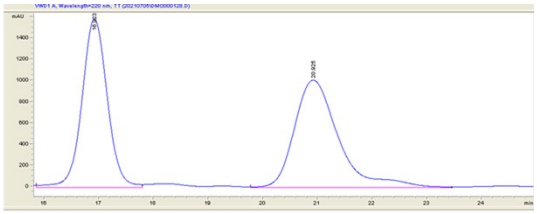
Entry	Time	Height	Width	Area%
1	18.656	2973.3	0.7193	50.281
2	21.638	2812.5	0.752	49.719

Entry	Time	Height	Width	Area%
1	17.667	1057.6	1.283	23.637
2	22.35	2696.8	1.3796	76.363

(1*S*, 6*R*)-6-(Isopropoxycarbonyl)cyclohex-3-enecarboxylic acid (24)

Chiralcel OD-H, hexane/IPA: 80/20, Flow rate: 0.50 mL/min, UV detection at 220 nm, T = 25 °C, retention time: *t* (major) = 16.923 min, *t* (minor) = 20.925 min;



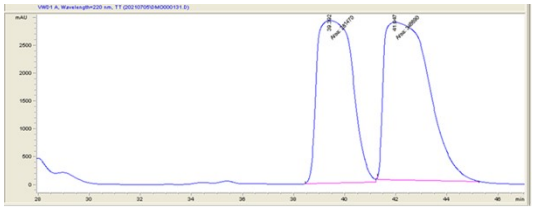


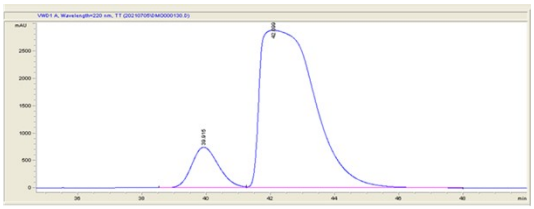
Entry	Time	Height	Width	Area%
1	16.947	2552.7	0.6223	48.484
2	21.078	1587.5	1.128	51.516

Entry	Time	Height	Width	Area%
1	16.923	1589	0.4996	43.194
2	20.925	1013.3	0.8547	56.806

(1*S*, 6*R*)-6-((Allyloxy)carbonyl)cyclohex-3-enecarboxylic acid (25)

Chiralcel AD-H, hexane/IPA: 80/20, Flow rate: 0.50 mL/min, UV detection at 220 nm, T = 25 °C, retention time: *t* (major) = 39.915 min, *t* (minor) = 41.099 min;



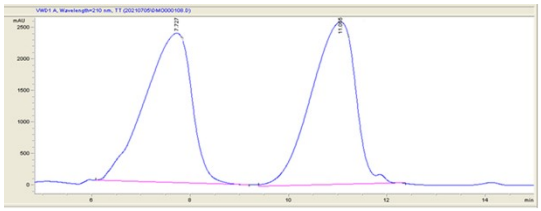


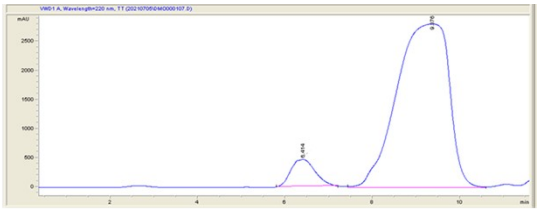
Entry	Time	Height	Width	Area%
1	39.392	2927.3	1.6025	48.809
2	41.947	2834.7	2.0384	51.191

Entry	Time	Height	Width	Area%
1	39.915	743.6	0.9235	11.458
2	41.099	2875.8	1.3842	88.542

(1*S*, 6*R*)-6-((Benzyloxy)carbonyl)cyclohex-3-enecarboxylic acid (26)

Chiralcel AD-H, hexane/IPA: 80/20, Flow rate: 0.80 mL/min, UV detection at 210 nm, T = 25 °C, retention time: *t* (major) = 6.414 min, *t* (minor) = 9.376 min;



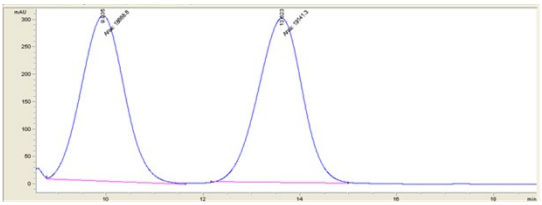


Entry	Time	Height	Width	Area%
1	7.727	2374.3	1.1061	49.211
2	11.055	2578.1	1.1512	50.789

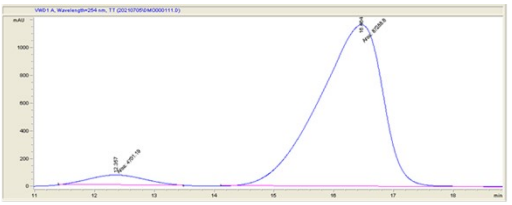
Entry	Time	Height	Width	Area%
1	6.414	459.3	0.6398	6.996
2	9.376	2813.1	1.0972	93.004

(1*S*, 6*R*)-6-((Cinnamyloxy)carbonyl)cyclohex-3-enecarboxylic acid (27)

Chiralcel AD-H, hexane/IPA: 80/20, Flow rate: 0.80 mL/min, UV detection at 254 nm, T = 25 °C, retention time: *t* (major) = 12.357 min, *t* (minor) = 16.463 min;

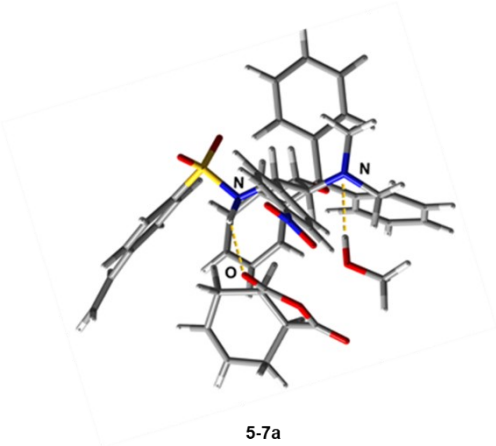
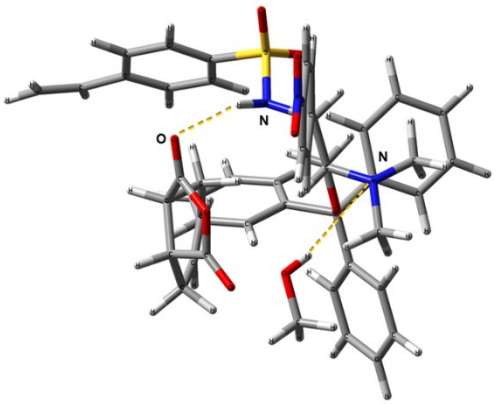


Entry	Time	Height	Width	Area%
1	9.935	301.8	1.0309	49.375
2	13.623	300	1.0639	50.625



Entry	Time	Height	Width	Area%
1	12.357	72.6	1.0796	4.951
2	16.463	1166.6	1.247	95.049

6. Cartesian coordinates of the molecular complexes

 5-7a	 5-*ent*-7a
C 5.41474400 -1.80846500 -1.62158400	C 5.57110300 -1.40399800 -1.57508400
C 4.09265400 -1.47643000 -1.89206400	C 4.25150300 -1.06460900 -1.84857900
C 3.09268900 -1.64525800 -0.92176500	C 3.22269300 -1.38242300 -0.94832500
C 3.44414100 -2.14323900 0.33789600	C 3.54205200 -2.03874100 0.24562100
C 4.76311000 -2.47749900 0.62734500	C 4.85792500 -2.38295400 0.53748300
C 5.73071200 -2.31078400 -0.36013100	C 5.85505500 -2.06555300 -0.38129100
H 6.19613600 -1.68476700 -2.36031100	H 6.37455700 -1.16643100 -2.26036900
H 3.83380300 -1.05391200 -2.85866200	H 4.01627500 -0.52075600 -2.75892400
H 2.69845000 -2.26653800 1.11149200	H 2.77303800 -2.27991300 0.96684300
H 5.05005600 -2.85618600 1.59972700	H 5.11994200 -2.88361200 1.46049800
N 7.12588300 -2.66734800 -0.06174600	N 7.24729700 -2.43156800 -0.08067900
O 7.37773800 -3.11774300 1.05672400	O 7.47091400 -3.02366000 0.97605400
O 7.96456300 -2.49637000 -0.94793900	O 8.11197700 -2.12614300 -0.90347900
C 1.68429300 -1.19203600 -1.27622200	C 1.81681800 -0.91335100 -1.29200600
H 1.47046400 -1.54165900 -2.29124800	H 1.64726900 -1.12701300 -2.35211800
C 0.54960600 -1.72809600 -0.36640000	C 0.66456200 -1.58946400 -0.50598600
H 0.73815800 -1.39617600 0.65812700	H 0.80896100 -1.39511900 0.56020200
C -0.77145000 -1.10598000 -0.84196800	C -0.65397700 -0.93501900 -0.94363900
H -0.94883100 -1.39976000 -1.87700200	H -0.78778600 -1.08994300 -2.01469400
H -0.70587300 -0.01598400 -0.81331000	H -0.61629100 0.14222900 -0.76663700
C -3.18349600 -1.05544600 -0.30831600	C -3.08371400 -1.00442400 -0.49994700
C -3.23443800 0.47399900 -0.11450500	C -3.17903000 0.48360100 -0.10490900
C -4.03610900 1.30799800 -0.90352600	C -3.97291800 1.40045600 -0.80484000
C -2.55748700 1.03978100 0.97694200	C -2.55477400 0.91021500 1.07743400
C -4.14586500 2.67289500 -0.61888000	C -4.12611800 2.71205900 -0.34414500
H -4.59332300 0.89326900 -1.73519400	H -4.49034400 1.09080300 -1.70514200
C -2.65713800 2.40112500 1.25624100	C -2.69760500 2.21921900 1.53274100
H -1.97293300 0.40138000 1.62800600	H -1.97779700 0.20146600 1.65873900
C -3.45426800 3.22511900 0.45818000	C -3.48639300 3.12747100 0.82268800
H -4.78060100 3.29792500 -1.24055200	H -4.75392900 3.40261000 -0.90004200
H -2.11486100 2.81971800 2.09906400	H -2.19558600 2.53090100 2.44404000
H -3.53847400 4.28505000 0.68028000	H -3.60437500 4.14589400 1.18153000
C -3.56999900 -1.50984700 -1.73124600	C -3.40894300 -1.27026800 -1.98458400
C -4.38408700 -2.63016700 -1.94536300	C -4.18722700 -2.36727900 -2.37770500
C -3.04403500 -0.85415400 -2.85965500	C -2.86015800 -0.45813900 -2.99411900
C -4.65471400 -3.08636500 -3.23681700	C -4.40123700 -2.65035500 -3.72799300
H -4.81727400 -3.15280500 -1.10174600	H -4.63664100 -3.00735500 -1.62882500
C -3.30540100 -1.31387100 -4.14895700	C -3.06490400 -0.74481000 -4.34239600
H -2.41243700 0.01804500 -2.74156900	H -2.25473300 0.40242600 -2.73628300
C -4.11386200 -2.43428400 -4.34385200	C -3.83823500 -1.84439400 -4.71628100
H -5.29179200 -3.95542600 -3.37258400	H -5.01159600 -3.50553500 -4.00312500
H -2.86867300 -0.79446100 -4.99633100	H -2.61174200 -0.10735500 -5.09529500

H -4.32089800 -2.79300700 -5.34773100	H -4.00116400 -2.06844100 -5.76631800
C -4.06377000 -1.72109200 0.76532500	C -3.98432600 -1.82600100 0.44057400
C -3.73513000 -2.99410400 1.25204400	C -3.64166500 -3.14631000 0.76434500
C -5.22154900 -1.09965300 1.24783700	C -5.17320800 -1.29823800 0.95776100
C -4.52977500 -3.61893100 2.21310700	C -4.45379600 -3.91057900 1.60210900
H -2.85599800 -3.49507500 0.86785900	H -2.73757700 -3.57347800 0.35010300
C -6.01984700 -1.72661100 2.20535300	C -5.98881300 -2.06421200 1.79158800
H -5.49891800 -0.11661200 0.88502700	H -5.46183900 -0.28089800 0.71976000
C -5.67497000 -2.98583200 2.69738900	C -5.63045500 -3.37125600 2.12308900
H -4.25041900 -4.60163400 2.58177000	H -4.16339300 -4.92833500 1.84602600
H -6.91048400 -1.22385300 2.57066000	H -6.90377900 -1.63295400 2.18693900
H -6.29295900 -3.46909000 3.44819900	H -6.26222700 -3.96344000 2.77833400
O 2.66821700 1.16120900 -3.55076300	O 2.82142200 1.74409300 -3.19152500
O 0.26439400 0.33710500 -3.42313600	O 0.43562000 0.86314000 -3.26684800
C 0.89836800 2.65780000 -2.27677700	C 0.97182400 3.02003400 -1.79648000
C -0.45872300 2.93087100 -2.10878800	C -0.39662000 3.24117900 -1.64501700
C 1.87360300 3.62158200 -2.00833600	C 1.91306100 3.95781300 -1.36443700
C -0.83619500 4.18385100 -1.63655100	C -0.82109400 4.41133700 -1.02372500
H -1.20210300 2.17466400 -2.33248600	H -1.11288800 2.50756800 -1.99612600
C 1.48167000 4.86107300 -1.51616100	C 1.47377400 5.11163400 -0.72575900
H 2.91887700 3.39795400 -2.19280800	H 2.96933200 3.78173400 -1.53742700
C 0.12237800 5.15517800 -1.29818300	C 0.10086700 5.34683100 -0.52205800
H -1.88966900 4.39581800 -1.49163300	H -1.88388800 4.58103800 -0.89177800
H 2.23686700 5.61286900 -1.31305000	H 2.20267700 5.84388600 -0.39517900
C -0.33133000 6.42905900 -0.71672600	C -0.40410600 6.52146200 0.20729800
H -1.38935800 6.64827000 -0.85416900	H -1.46175800 6.73633500 0.06043700
C 0.41617400 7.29391000 -0.01983400	C 0.29706900 7.29896100 1.04170800
H -0.01106100 8.20781900 0.37883100	H -0.16620600 8.14215600 1.54279800
H 1.46874200 7.12183200 0.18498800	H 1.34575100 7.12158500 1.26140300
N 1.63488200 0.29863300 -1.30400200	N 1.73173200 0.56617900 -1.12153700
H 2.39936600 0.73685700 -0.78770800	H 2.46668400 0.94572600 -0.52251800
N 0.58944400 -3.19087100 -0.36015500	N 0.74015000 -3.03864400 -0.69440300
C 0.23911200 -3.83717800 0.89523200	C 0.36216700 -3.85514300 0.44879400
H -0.84710900 -3.89973900 1.07477700	H -0.72779700 -3.96272300 0.57698100
H 0.63609100 -4.85886400 0.89727600	H 0.78386000 -4.85975300 0.32890600
H 0.67622300 -3.29602000 1.73715100	H 0.75613100 -3.42398900 1.37164000
C -0.02664800 -3.84751900 -1.50465400	C 0.18078800 -3.54692200 -1.93915300
H 0.26404800 -4.90297100 -1.50833400	H 0.49732700 -4.58630300 -2.07326900
H -1.12934800 -3.79455600 -1.49797300	H -0.92244100 -3.51706400 -1.96728000
H 0.32592300 -3.41001400 -2.44293900	H 0.55506400 -2.98000300 -2.79625000
O -1.84053900 -1.55574600 -0.00436100	O -1.74029500 -1.51461200 -0.21507100
S 1.40710100 1.02843500 -2.80612900	S 1.53870000 1.48729200 -2.51981100
C -1.40881200 -2.03257400 3.65858100	C -1.42525700 -2.47254900 3.36459500
H -0.90007600 -1.72067500 4.57235200	H -0.95660300 -2.27679500 4.33057300
H -2.48320900 -1.82891400 3.74792800	H -2.50680800 -2.30399400 3.43960500
H -1.27222500 -3.11590400 3.53658600	H -1.25786600 -3.52662400 3.10373200
O -0.81992500 -1.30632700 2.58253600	O -0.81717300 -1.59634900 2.41876000
H -1.27970500 -1.54040500 1.75299900	H -1.24177600 -1.72540600 1.54848500
C 0.47379000 3.91001400 2.33112600	C -1.62250000 1.30442200 3.06815300
C 0.50622000 3.77221400 3.65915300	C -1.23547700 1.68047800 1.84647700
H 0.19893100 4.86558400 1.88913700	H -2.67417500 1.34813000 3.34398600
H 0.26511800 4.61644400 4.30055700	H -1.97136700 2.02393100 1.12345600
C 0.91621900 2.48688900 4.33185900	C 0.19981200 1.60661200 1.39130400
H 0.45779000 2.38621100 5.32008800	H 0.41329900 2.34499900 0.61278100
H 2.00293800 2.49891600 4.50504200	H 0.38424700 0.62393500 0.93149500
C 0.81325400 2.81388100 1.35992500	C -0.68893900 0.79226200 4.12934600
H 1.75810000 3.04794500 0.85479100	H -0.86827700 -0.27707100 4.29379800
H 0.06176000 2.79820400 0.56787800	H -0.93506700 1.27279700 5.07846900
C 0.91401300 1.41567900 1.99256300	C 0.80184100 1.01065100 3.82074600
H 0.28926200 0.72031600 1.42119100	H 1.27587300 1.49762800 4.68008100

C 0.53478400 1.25697100 3.47380600	C 1.17579600 1.82542200 2.57199100
H -0.51944100 1.01641000 3.60608700	H 1.27523100 2.88857500 2.78780500
O 2.43378400 -0.08617400 2.99596900	O 2.67636300 -0.00038200 2.80287100
C 1.36825300 0.06710100 3.90290900	C 2.53666300 1.26803500 2.20873900
C 2.29167300 0.78832800 1.94061700	C 1.60867100 -0.25771800 3.63505300
O 3.16742200 0.93480900 1.12601400	O 1.44606500 -1.34537400 4.12753100
O 1.28080500 -0.63248200 4.86768500	O 3.38303200 1.70089000 1.48475500