Supplementary Materials (SM) for

Amplification of Enantiomeric Excess without Any Chiral Source in Prebiotic Case

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List of the SM

Item 1. Reactions of tryptophan esters with biacetyl and computational methods

1. General synthetic procedure:

A/. Synthesis of tryptophan methyl ester. To methanol (100 mL) was added $SOCl_2$ (3.0 equiv. of L-tryptophan) at -10 °C. After 10 min, L-tryptophan (1.0 g) powder was added into the solution quickly. The powder quickly dissolved in methanol. After reacting over night at room temperature, the solution was heated to reflux for 2 h. Methanol was then removed under the reduced pressure. The residue was then dissolved in ethyl acetate/water (3/1) solution, the aqueous NaOH solution was added to adjust the pH to near 10. After the organic layer was separated from the water phase, the aqueous phase was extracted with ethyl acetate three times. The combined organic layer was then dried over Na_2SO_4. TLC analysis exhibited that only one major compound found. The organic layer was filtered and ethyl acetate was removed under the reduced pressure. The residue was L-tryptophan methyl ester (L-TME).

B/. Typical condensation reaction. To a solution of L-tryptophan methyl ester (for example, 0.55 mmol of **1** and 0.45 mmole of **2**) in CH_2Cl_2 (50 mL), biacetyl (0.405 mmol) was added at 0 °C. It was stirred for several hours (2 to 36 h) to reach equilibrium before molecular sieves (MS) and TFA were added. Then MS and TFA were added and stirring was continued for over 10 h. Na_2CO_3 powder was then added to neutralize the TFA. Two major products **3** and **4** were obtained by using column chromatography over silica gel using the mixture of CH_2Cl_2 and methanol. Their NMR spectra are listed in the next part. The enantiomers of **3** and **4** were separated by HPLC using chiral chromatography as mentioned below.

C/. Preparation of different %ee L-TME sample. The commercially available mixture of L-tryptophan and D-tryptophan has about 10%ee. Thus, adding different quantities of optical pure L-TME (99%ee) can afford various concentrations of L-TME (different %ee) for the reactions. These samples with different L-TME %ee were then used for enrichment reactions.

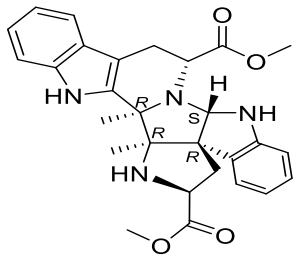
The measurement of NMR was performed under the Bruck AVANCE III

General computational methods

All possible conformations were searched by using MMFF94S force field for all compounds involved in this study. All of these conformations were then optimized at the B3LYP/6-31G(d) level in the gas phase first. Then, the lower energy conformers with relative energy of 0-6 kcal/mol were further optimized at the B3LYP/6-311+G(d) level in the gas phase and in solution using PCM model, respectively. These B3LYP/6-311+G(d)-optimized conformers may be re-optimized at the B3LYP/6-311++G(2d,p) level in the gas phase or in solution using PCM model if necessary. Optical rotation (OR) and electronic circular dichriosm (ECD) or ^{13}C NMR were computed at the corresponding levels as marked in each notice for the corresponding compounds. For more details, please see the following examples.

Item 2. ^{1}H, ^{13}C NMR, HMBC spectra for the two major products.

Compound named in the text: (*R,S*)-**3**(2)



(*R,S*)-**3**(2) ^{1}H-NMR

Fig. S1 ^{1}H NMR spectra for (*R,S*)-**3**(2)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (1 H, d, *J*=7.8Hz, H-5), 7.31 (1 H, d, *J*=7.86 Hz, H-1), 7.05 (1 H, t, *J*=7.2 Hz, H-6), 6.99 (1 H, H-4), 6.99 (1 H, H-25), 6.88 (1 H, d, *J*=7.2 Hz, H-27), 6.63 (1 H, t, *J*=7.2 Hz, H-26), 6.49 (1 H, d, *J*=8.4 Hz, H-28), 5.10 (1 H, s, H-18), 4.45 (1 H, dd, *J*=12, 7.2 Hz, H-20), 4.12 (1 H, dd, *J*=12.0, 5.1 Hz, H-10), 3.76 (3 H, s, H-12), 3.39 (3 H, s, H-22), 3.27 (1 H, dd, *J*=15.6, 12 Hz, H-19a), 2.88 (1 H, dd, *J*=15.6, 4.8 Hz, H-19b), 2.15 (1 H, dd, *J*=13.2, 7.2 Hz, H-19a), 1.38 (3 H, s, H-14), 1.30 (1 H, t, H-19b), 1.11 (3 H, s, H-16)

(*R,S*)-**3**(2) ^{13}C-NMR

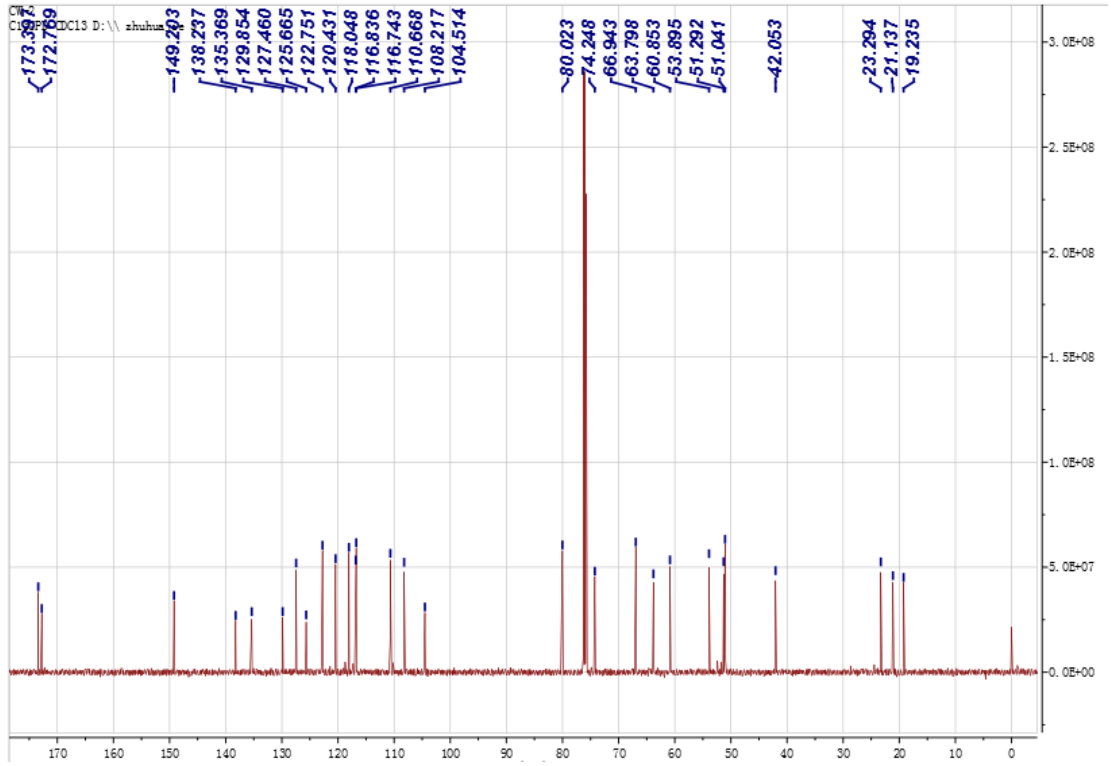


Fig. S2 ^{13}C NMR spectra for (*R,S*)-**3**(2)

^{13}C NMR:

(150MHz, $CDCl_3$) δ 173.4 (C, C-11), 172.8 (C, C-21), 149.2 (C, C-23), 138.2 (C, C-8), 135.4 (C, C-2), 129.9 (C, C-24), 127.5 (CH, C-25), 125.7 (C, C-3), 122.8 (CH, C-27), 120.4 (CH, C-6), 118.0 (C, C-4), 116.8 (CH, C-26), 116.6 (CH, C-5), 110.7 (CH, C-1), 108.2 (CH, C-28), 104.5 (C, C-7), 80.0 (CH, C-18), 74.2 (C, C-15), 66.9 (C, C-13), 63.7 (C, C-17), 60.8 (CH, C-20), 53.9 (CH, C-10), 51.3 (CH_3, C-12), 51.0 (CH_3, C-22), 42.0 (CH_2, C-19), 23.3 (CH_3, C-14), 21.1 (CH_3, C-16), 19.2 (CH_2, C-9).

(*R,S*)-**3**(2) HMBC spectrum

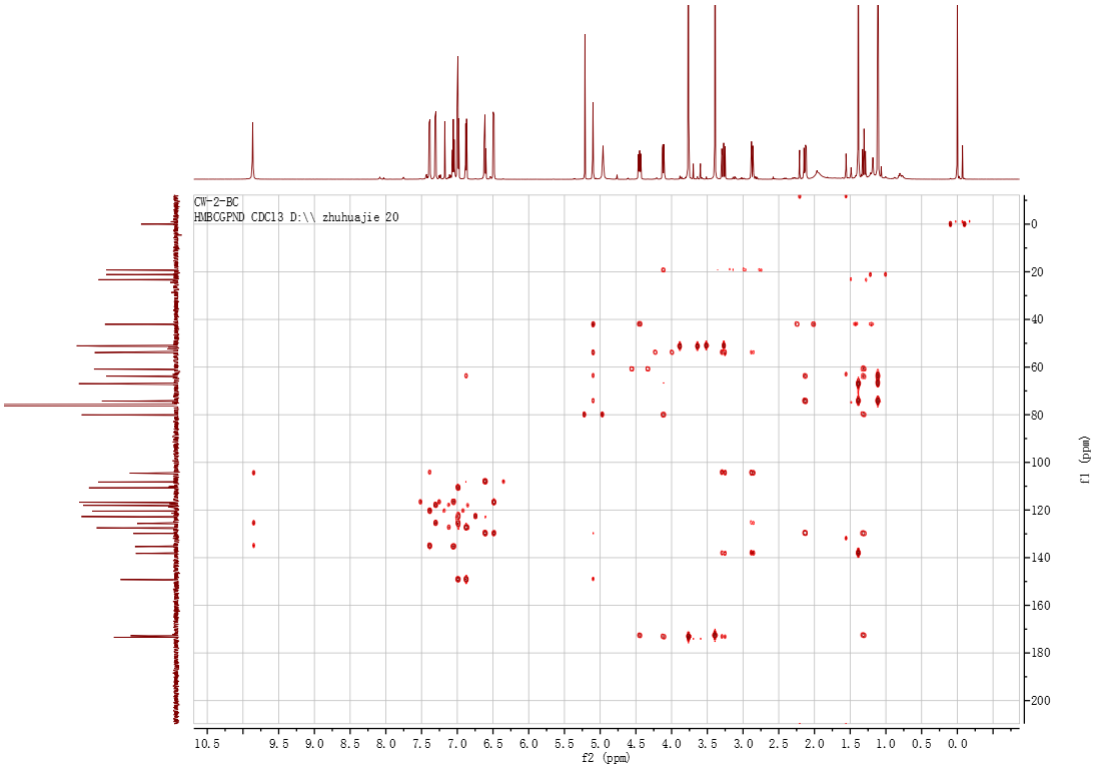
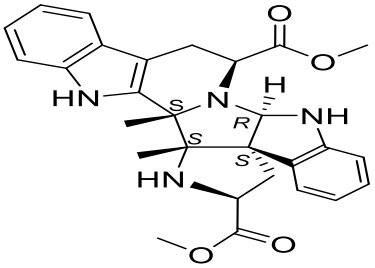


Fig. S3 The HMBC spectrum for (*R,S*)-**3**(2)

The relationship of ^{1}H and ^{13}C in the HMBC is summarized in Table S1 too.

Compound named in the text: (*S,S*)-**4**(*1*)



(*S,S*)-**4**(*1*) ^{1}H-NMR

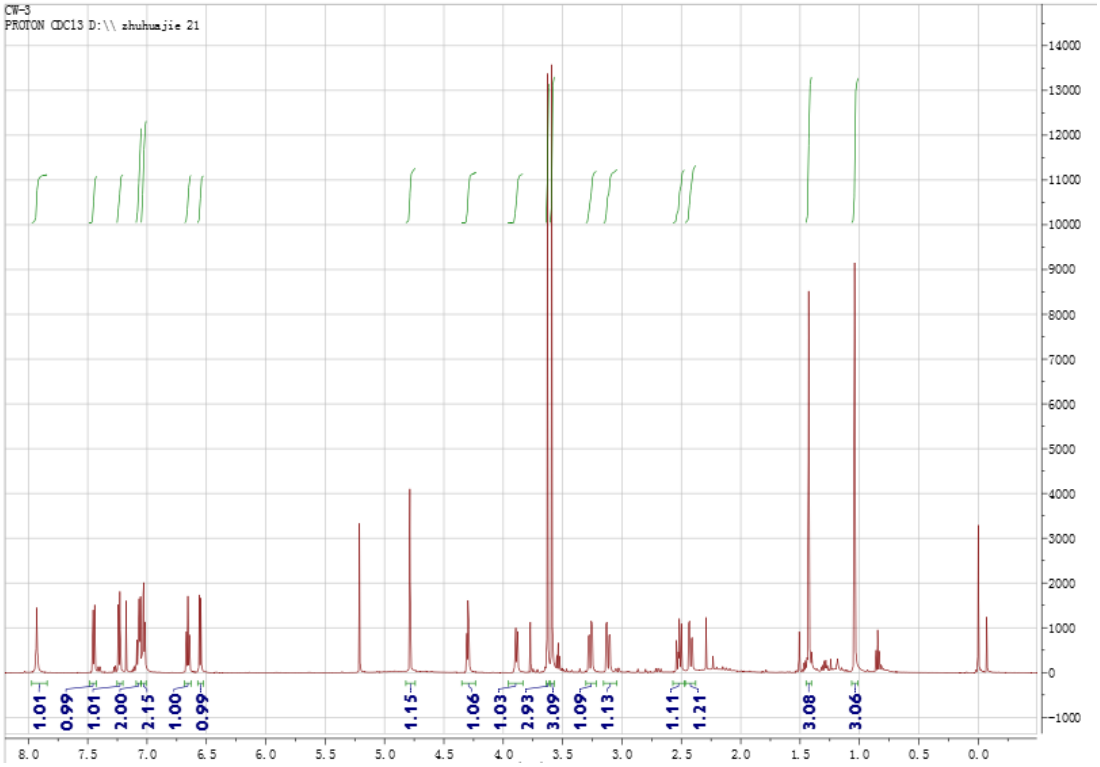


Fig. S4 The ^{1}H NMR for (*S,S*)-**4**(*1*) compound in $CDCl_3$.

^{1}H NMR:

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (1 H, d, *J*=7.8 Hz, H-26), 7.24 (1 H, d, *J*=7.8 Hz, H-1), 7.07 (1 H, H-6), 7.05 (1 H, H-27), 7.02 (1 H, H-4), 7.02 (1 H, H-25), 6.65 (1 H, t, *J*=7.2 Hz, H-5), 6.54 (1 H, d, *J*=7.8 Hz, H-28), 4.78 (1 H, s, H-18), 4.29 (1 H, t, *J*=5.4 Hz, H-10), 3.89 (1 H, dd, *J*=10.2, 4.8 Hz, H-20), 3.62 (3 H, s, H-22), 3.58 (3 H, s, H-12), 3.27 (1 H, dd, *J*=15, 6.0 Hz, H-9a), 3.12 (1 H, dd, *J*=15, 5.4 Hz, H-9b), 2.51 (1 H, dd, H-19a), 2.41 (1 H, dd, *J*=14.4, 4.8 Hz, H-19b), 1.43 (3 H, H-16), 1.04 (3 H, s, H-14)

(*S,S*)-**4**(*1*) ^{13}C-NMR

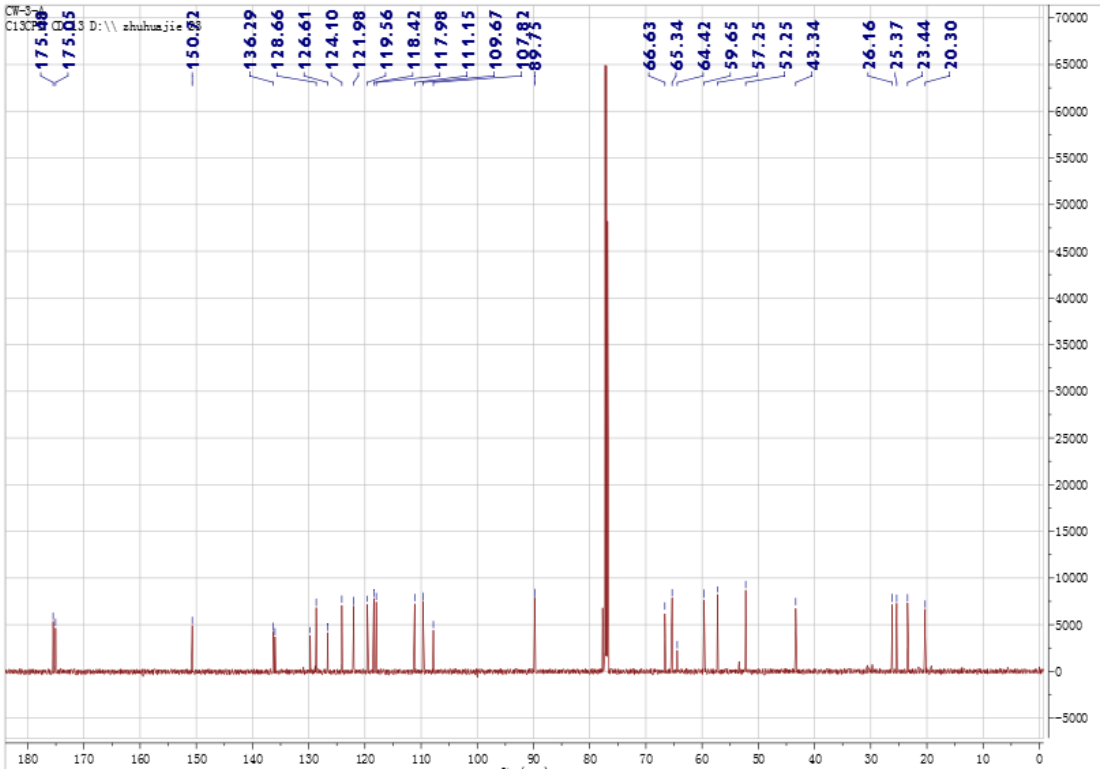


Fig. S5 The ^{13}C NMR for (*S,S*)-**4**(*1*) compound in $CDCl_3$.

^{13}C NMR (150 MHz, $CDCl_3$) δ 175.5 (C, C-11), 175.0 (C, C-21), 150.7 (C, C-23), 136.3 (C, C-2), 136.0 (C, C-8), 129.7 (C, C-24), 128.7 (CH, C-25), 126.6 (C, C-3), 124.1 (CH, C-27), 122.0 (CH, C-6), 119.6 (CH, C-4), 118.4 (CH, C-26), 118.0 (CH, C-5), 111.2 (CH, C-1) 109.7 (CH, C-28), 107.8 (C, C-7), 89.7 (CH, C-18), 77.7 (C, C-15), 66.6 (C, C-13), 65.3 (C, C-17), 59.6 (CH, C-10), 57.3 (CH, C-20), 52.3 (CH_3, C-12), 52.2 (CH_3, C-22), 43.3 (CH_2, C-19), 26.2 (CH_3, C-14), 26.2 (CH_3, C-16) 23.4 (CH_2, C-9)

(*S*,*S*)-**4**(*1*) HMBC spectrum

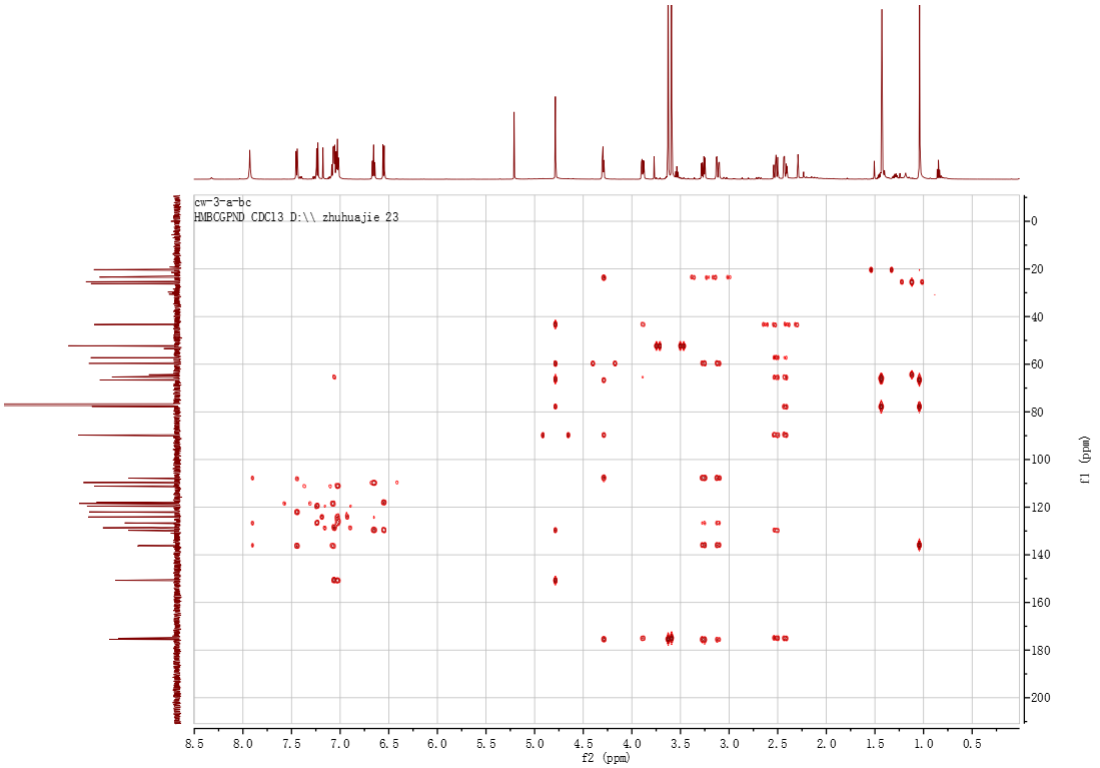
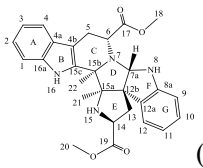


Fig. S6. The HMBC spectrum for (*S*,*S*)-**4**(*1*). The relationship of H and C in the HMBC is summarized below (also see the specific data in Table S2)

Table S1. Relationship of C and H in HMBC spectra for (*R,S*)-**3**(2)

No.	δC	Type	δ_H (*J* in Hz)	HMBC
1	110.7	CH	7.31 (d, *J*=7.86)	H-4
2	120.4	CH	7.05 (t, *J*=7.2)	H-4,H-3
3	116.6	CH	7.39 (d, *J*=7.8)	H-2
4	118.0	CH	6.99 (s)	H-1
4a	125.7	C		H-1,H-4,H-2,H-5
4b	104.5	C		H-3,H-5
5	19.2	CH_2	3.27 (dd, *J*=12, *J*=15.6) , 2.88 (dd, *J*=4.8, *J*=15.6)	H-6
6	53.9	CH	4.12 (dd, *J*= 5.1, *J*=12)	H-5
7		N		
7a	80.0	CH	5.10 (s)	H-6
8		NH	4.96	
8a	149.2	C		H-12,H-10
9	108.2	CH	6.49 (d, *J*= 8.4)	H-11,H-10
10	127.5	CH	6.99	H-12
11	116.8	CH	6.63 (t, *J*=7.2)	H-12,H-9
12	122.8	CH	6.88 (d, *J*= 7.2)	H-10
12a	129.9	C		H-13,H-9,H-11
12b	63.7	C		H-21, H-13
13	42.0	CH_2	2.15 (dd, *J*= 7.2, *J*=13.2)	H-7a, H-14
14	60.8	CH	4.45 (dd, *J*= 7.2, *J*=12)	H-13
15		NH	5.21(s)	
15a	74.2	C		H-22,H-21,H-7a,H-13
15b	66.9	C		H-22,H-21
15c	138.2	C		H-5,H-22
16		NH	9.86 (s)	
16a	135.4	C		H-3,H-2
17	173.4			H-5,H-6,H-18
18	51.3	CH_3	3.76 (s)	
19	172.8			H-13,H-14,H-20
20	51.0	CH_3	3.39 (s)	
21	21.1	CH_3	1.11 (s)	H-22
22	23.3	CH_3	1.38 (s)	H-21,H-13

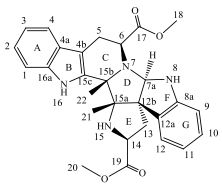
The key correlations of H-6 with C-7a, H13, H21 with C-12b, H7a with C-13, H7a, H13 with C-15a clearly exhibited the key ring structures as illustrated below. The ROSEY of H-6 and H-21 and H7a exhibited that the protons on the corresponding C located at the same side.



(*R,S*)-**3**(2) (Its enantiomer is (*S,R*)-**3**(*2*))

Table S2 Relationship of C and H in HMBC spectra ((*S,S*)-**4**(*1*) in DMSO-d_6)

No.	δC (ppm)	Type	δH (ppm, *J* in Hz)	HMBC
1	111.2	CH	7.24 (d, *J*=7.8)	H4, H2
2	122.0	CH	7.07	H4,H3
3	118.0	CH	6.65 (t, *J*=7.2)	H4a,H4,H2
4	119.6	CH	7.02	H3,H2
4a	126.6	C		H4,H2,H5
4b	107.8	C		H5,H6
5	23.4	CH_2	3.12 (dd, *J*=5.4, *J*=15) , 3.27 (dd, *J*= 6,*J*=15)	H5,H6
6	59.6	CH	4.29 (t, *J*=5.4)	H5,H7a
7		N		
7a	89.7	CH	4.78 (s)	H6,H15a,H13,H8a
8		NH		
8a	150.7	C		H7a,H12,H10
9	109.7	CH	6.54 (d, *J*= 7.8)	H10
10	124.1	CH	7.05	H12,H11
11	118.4	CH	7.44 (d, *J*=7.8)	H12,H10
12	128.7	CH	7.02	H11,H10
12a	129.7	C		H7a,H9
12b	65.3	C		H7a,H13
13	43.3	CH_2	2.41 (dd, *J*= 4.8, *J*=14.4) , 2.51 (dd, *J*=10.2, *J*=14.4)	H14
14	57.3	CH	3.89 (dd, *J*= 4.8,*J*=10.2)	H13
15		NH	5.21	
15, 15a	77.7	C		H22,H7a
15b	66.6	C		H6,H22,H7a
15c	136.0	C		H5,H22
16		NH	9.86(s)	
16a	136.3	C		H2
17	175.5	O		
18	52.3	CH_3	3.58 (s)	
19	175.0			H13,H14
20	52.2	CH_3	3.62 (s)	H13,H14
21	26.2	CH_3	1.43 (s)	H17
22	26.2	CH_3	1.04 (s)	H17

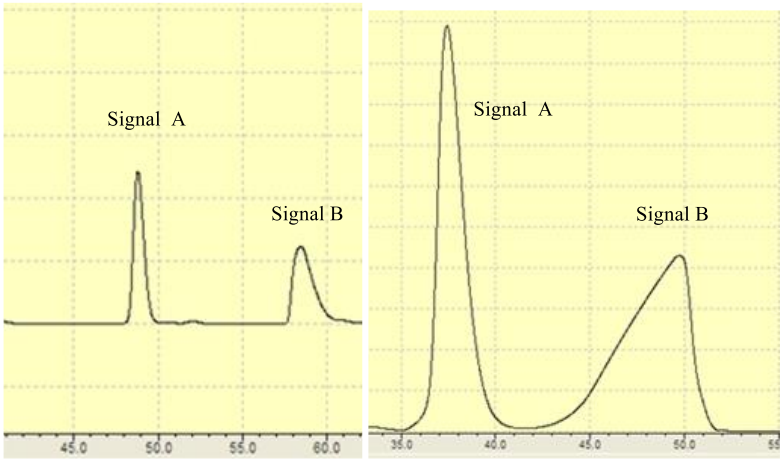


(*S,S*)-**4**(*1*)

Item 3. Experimental OR values and ECD experimental spectra for 3 and 4

3.1 Experimental OR values

(1) The isolated **3** and **4** gave two HPLC signals upon separation using a Chiralcel-IA stationary phase using 1%ee of the starting material L-tryptophan methyl ester. The mixture of petroleum ether and isopropanol (80:20) were used in the HPLC separation of enantiomer **3**. The mixtures of petroleum ether and isopropanol (v/v: 85:15) were used for **4** isolation. The HPLC plots for the two compounds are illustrated below:



3 **4**

Fig. S7 The HPLC plots for major products **3** and **4** using Chiracel-IA. The specific optical rotations are +32.0 for signal A (named as **3SA**) and almost -32.0 for signal B (**3SB**). The specific optical rotation values are +104.0 for signal A (**4SA**) and -104.0 for signal B (**4SB**). The solvent is chloroform.

Table S3 Experimental ECD spectra for **(+)-3SA** and **(-)-4SB**

Wavelength (nm)	ECD for (+)-**3SA**	ECD for **(-)-4SB**
190	1.78976	-0.0760804
190.25	2.42079	0.737725
190.5	2.97889	1.44478
190.75	3.54152	2.14615
191	4.06652	2.77566
191.25	4.56689	3.33791
191.5	4.99908	3.78333
191.75	5.33063	4.06254
192	5.50605	4.1175
192.25	5.48897	3.92019
192.5	5.26765	3.48237
192.75	4.86275	2.86395
193	4.31677	2.16448
193.25	3.68669	1.50073
193.5	3.02997	0.983113

193.75	2.3997	0.694884
194	1.84649	0.675148
194.25	1.40733	0.931213
194.5	1.1157	1.43163
194.75	0.995483	2.111
195	1.04361	2.88567
195.25	1.22198	3.66842
195.5	1.48435	4.37016
195.75	1.77645	4.92417
196	2.04577	5.31293
196.25	2.27063	5.54702
196.5	2.46751	5.65955
196.75	2.65777	5.69595
197	2.85378	5.69536
197.25	3.06462	5.64952
197.5	3.27694	5.53082
197.75	3.44749	5.31222
198	3.54053	4.97346
198.25	3.55744	4.51369
198.5	3.51588	3.98117
198.75	3.45409	3.45484
199	3.44899	3.00376
199.25	3.57998	2.68718
199.5	3.8802	2.53896
199.75	4.35389	2.55536
200	4.97556	2.70023
200.25	5.65925	2.93655
200.5	6.2905	3.21809
200.75	6.77545	3.49837
201	7.04268	3.74022
201.25	7.05161	3.91716
201.5	6.82828	4.00672
201.75	6.43901	4.00298
202	5.97017	3.92732
202.25	5.50821	3.80917
202.5	5.12161	3.67955
202.75	4.83412	3.56991
203	4.64148	3.50585
203.25	4.50646	3.48767
203.5	4.38523	3.51202
203.75	4.2511	3.5784
204	4.10068	3.67547
204.25	3.93764	3.78378

204.5	3.78272	3.88889
204.75	3.65505	3.96453
205	3.54891	3.97177
205.25	3.44389	3.89209
205.5	3.33396	3.72568
205.75	3.21918	3.48201
206	3.10956	3.20538
206.25	3.03453	2.9654
206.5	3.02885	2.82387
206.75	3.10277	2.81698
207	3.24152	2.96506
207.25	3.41007	3.2355
207.5	3.56984	3.5677
207.75	3.68836	3.88624
208	3.7477	4.14755
208.25	3.75251	4.33128
208.5	3.72471	4.46136
208.75	3.6664	4.57495
209	3.55914	4.72182
209.25	3.37788	4.91043
209.5	3.09982	5.11282
209.75	2.7114	5.27313
210	2.24265	5.33043
210.25	1.76458	5.23183
210.5	1.36536	4.97476
210.75	1.11151	4.61131
211	1.03469	4.23634
211.25	1.12518	3.96436
211.5	1.31896	3.89334
211.75	1.52738	4.07181
212	1.6851	4.48303
212.25	1.76718	5.03602
212.5	1.76318	5.60135
212.75	1.71347	6.05688
213	1.67226	6.3163
213.25	1.67378	6.34474
213.5	1.72169	6.18044
213.75	1.8219	5.90104
214	1.93967	5.58807
214.25	2.03495	5.30221
214.5	2.07697	5.07842
214.75	2.04357	4.91249
215	1.91161	4.76825

215.25	1.69619	4.59923
215.5	1.42979	4.36413
215.75	1.16322	4.03799
216	0.965299	3.61755
216.25	0.909212	3.13853
216.5	1.02727	2.65987
216.75	1.32025	2.26464
217	1.75314	2.02041
217.25	2.267	1.96729
217.5	2.789	2.10099
217.75	3.27153	2.38171
218	3.6819	2.7216
218.25	3.99578	3.04012
218.5	4.18411	3.27944
218.75	4.22319	3.40726
219	4.09562	3.41759
219.25	3.80348	3.34726
219.5	3.38011	3.23221
219.75	2.89409	3.1057
220	2.42802	2.99761
220.25	2.04293	2.93569
220.5	1.77215	2.9284
220.75	1.62041	2.98917
221	1.56219	3.12155
221.25	1.56158	3.33243
221.5	1.60217	3.62178
221.75	1.68268	3.98845
222	1.80761	4.41695
222.25	1.99396	4.88852
222.5	2.25481	5.3615
222.75	2.58696	5.77861
223	2.9746	6.07929
223.25	3.39519	6.21057
223.5	3.80438	6.14407
223.75	4.1498	5.8845
224	4.38637	5.47481
224.25	4.47875	4.98069
224.5	4.40759	4.48341
224.75	4.19313	4.0444
225	3.88393	3.71308
225.25	3.53131	3.51116
225.5	3.19253	3.44074
225.75	2.91611	3.47944

226	2.7213	3.60076
226.25	2.61198	3.75822
226.5	2.59492	3.91007
226.75	2.66026	4.01109
227	2.79889	4.03492
227.25	3.00888	3.97652
227.5	3.27196	3.86628
227.75	3.55845	3.73559
228	3.85815	3.62828
228.25	4.15561	3.56027
228.5	4.43195	3.51211
228.75	4.69388	3.42423
229	4.95048	3.23972
229.25	5.18278	2.89791
229.5	5.38545	2.38268
229.75	5.56427	1.72386
230	5.71496	0.991463
230.25	5.85002	0.254584
230.5	6.01657	-0.425369
230.75	6.24313	-1.03321
231	6.54373	-1.59667
231.25	6.9319	-2.18265
231.5	7.39559	-2.87479
231.75	7.8972	-3.75133
232	8.4137	-4.85919
232.25	8.93037	-6.21824
232.5	9.42384	-7.80908
232.75	9.88951	-9.56722
233	10.3354	-11.4133
233.25	10.7757	-13.2772
233.5	11.2359	-15.0887
233.75	11.7695	-16.7971
234	12.4273	-18.3957
234.25	13.2521	-19.8981
234.5	14.2585	-21.3121
234.75	15.4293	-22.6586
235	16.7066	-23.9619
235.25	18.0123	-25.2263
235.5	19.2648	-26.4426
235.75	20.4016	-27.6112
236	21.378	-28.7236
236.25	22.1719	-29.7627
236.5	22.7852	-30.7168

236.75	23.2328	-31.589
237	23.5333	-32.3831
237.25	23.7179	-33.1095
237.5	23.8316	-33.7863
237.75	23.9137	-34.433
238	24.0009	-35.0552
238.25	24.1257	-35.6511
238.5	24.3003	-36.2176
238.75	24.5134	-36.7492
239	24.7457	-37.2399
239.25	24.9701	-37.6924
239.5	25.1546	-38.1175
239.75	25.2795	-38.5206
240	25.3392	-38.9039
240.25	25.3387	-39.2682
240.5	25.2939	-39.6096
240.75	25.2285	-39.9197
241	25.1607	-40.1983
241.25	25.1024	-40.4514
241.5	25.0552	-40.6875
241.75	25.0111	-40.9184
242	24.9561	-41.1558
242.25	24.8787	-41.4041
242.5	24.7712	-41.66
242.75	24.6322	-41.917
243	24.4677	-42.1627
243.25	24.2875	-42.3854
243.5	24.1002	-42.5753
243.75	23.9112	-42.7276
244	23.7244	-42.8401
244.25	23.5393	-42.9198
244.5	23.3527	-42.9775
244.75	23.1626	-43.0282
245	22.9699	-43.0887
245.25	22.7742	-43.1733
245.5	22.5761	-43.2871
245.75	22.3763	-43.4244
246	22.1718	-43.572
246.25	21.9558	-43.7106
246.5	21.7222	-43.8218
246.75	21.4657	-43.8957
247	21.1841	-43.9349
247.25	20.8818	-43.9483

247.5	20.5681	-43.9505
247.75	20.254	-43.9552
248	19.9494	-43.9692
248.25	19.6619	-43.991
248.5	19.393	-44.0156
248.75	19.1407	-44.0343
249	18.901	-44.0396
249.25	18.67	-44.0273
249.5	18.4443	-43.9959
249.75	18.2223	-43.9437
250	18.0008	-43.8713
250.25	17.7772	-43.78
250.5	17.5467	-43.6706
250.75	17.3034	-43.544
251	17.0418	-43.4016
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251.75	16.1467	-42.8477
252	15.8246	-42.5994
252.25	15.503	-42.3103
252.5	15.1853	-41.9808
252.75	14.8742	-41.618
253	14.5693	-41.2319
253.25	14.2673	-40.8321
253.5	13.9647	-40.4236
253.75	13.6617	-40.0081
254	13.3577	-39.5819
254.25	13.0542	-39.1399
254.5	12.7532	-38.6786
254.75	12.4559	-38.2005
255	12.1605	-37.7097
255.25	11.8667	-37.2121
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255.75	11.2758	-36.2121
256	10.9753	-35.7069
256.25	10.6715	-35.1921
256.5	10.3633	-34.663
256.75	10.0507	-34.1182
257	9.73589	-33.5579
257.25	9.42158	-32.9854
257.5	9.1108	-32.4031
257.75	8.8088	-31.8123
258	8.52121	-31.2117

258.25	8.25147	-30.6012
258.5	8.00062	-29.9819
258.75	7.76702	-29.3583
259	7.54479	-28.7365
259.25	7.32474	-28.1248
259.5	7.09717	-27.5293
259.75	6.85435	-26.9534
260	6.59186	-26.3972
260.25	6.31067	-25.8597
260.5	6.01596	-25.3377
260.75	5.71574	-24.8281
261	5.41803	-24.3276
261.25	5.1301	-23.8325
261.5	4.85568	-23.3378
261.75	4.59622	-22.8408
262	4.35092	-22.3394
262.25	4.11731	-21.8342
262.5	3.89076	-21.3296
262.75	3.66755	-20.8315
263	3.44456	-20.3443
263.25	3.22031	-19.8714
263.5	2.99614	-19.4132
263.75	2.77653	-18.967
264	2.5661	-18.5285
264.25	2.36929	-18.0955
264.5	2.18797	-17.6659
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265	1.8599	-16.8189
265.25	1.70139	-16.4058
265.5	1.53738	-16.0013
265.75	1.36314	-15.6074
266	1.178	-15.2247
266.25	0.984338	-14.8545
266.5	0.785602	-14.4981
266.75	0.587299	-14.1576
267	0.394322	-13.8338
267.25	0.208822	-13.5282
267.5	0.0312864	-13.2402
267.75	-0.137818	-12.9675
268	-0.299794	-12.7075
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268.5	-0.607451	-12.2168
268.75	-0.753425	-11.982

269	-0.895489	-11.7544
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269.5	-1.17521	-11.3188
269.75	-1.31729	-11.1081
270	-1.46451	-10.8998
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271	-2.06966	-10.0715
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271.75	-2.3983	-9.53429
272	-2.4776	-9.39564
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272.5	-2.6432	-9.18973
272.75	-2.7514	-9.12097
273	-2.8856	-9.07033
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273.75	-3.39539	-8.96908
274	-3.56465	-8.92984
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278.5	-4.53363	-7.50326
278.75	-4.57925	-7.45912
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283	-5.40468	-4.95787
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284	-5.47311	-3.85498
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285.5	-5.58589	-2.13218
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286	-5.58576	-1.61322
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286.75	-5.59797	-0.855296
287	-5.61106	-0.58725
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355	-0.797549	-0.695473
355.25	-0.787923	-0.684368
355.5	-0.778655	-0.675013
355.75	-0.769886	-0.668014
356	-0.761692	-0.66311
356.25	-0.754004	-0.659727
356.5	-0.747082	-0.657666
356.75	-0.741838	-0.657106
357	-0.73894	-0.658397
357.25	-0.739058	-0.662406
357.5	-0.742927	-0.669578
357.75	-0.750882	-0.679428
358	-0.761911	-0.690668
358.25	-0.774378	-0.701245
358.5	-0.786449	-0.708712
358.75	-0.79602	-0.711179
359	-0.801032	-0.707723
359.25	-0.800511	-0.698154
359.5	-0.794368	-0.683449
359.75	-0.782765	-0.665088
360	-0.766364	-0.644553
360.25	-0.746568	-0.623215
360.5	-0.725175	-0.602823
360.75	-0.704092	-0.584792
361	-0.68547	-0.570675
361.25	-0.671405	-0.561996
361.5	-0.663065	-0.559686
361.75	-0.660351	-0.563403
362	-0.662165	-0.571843
362.25	-0.6669	-0.582566
362.5	-0.672391	-0.592552
362.75	-0.676923	-0.599151
363	-0.679434	-0.600487
363.25	-0.679644	-0.596009
363.5	-0.677308	-0.586361
363.75	-0.672556	-0.572814
364	-0.665251	-0.556674
364.25	-0.655424	-0.539623
364.5	-0.642971	-0.522581
364.75	-0.628374	-0.506245
365	-0.612584	-0.491509
365.25	-0.597179	-0.479299
365.5	-0.583592	-0.469504

365.75	-0.573181	-0.462153
366	-0.566758	-0.456721
366.25	-0.564076	-0.451843
366.5	-0.564066	-0.446136
366.75	-0.565434	-0.43944
367	-0.566785	-0.431812
367.25	-0.56664	-0.423857
367.5	-0.564518	-0.41707
367.75	-0.560554	-0.412818
368	-0.555184	-0.411452
368.25	-0.54909	-0.413126
368.5	-0.54352	-0.417796
368.75	-0.539087	-0.424471
369	-0.535885	-0.431916
369.25	-0.533739	-0.439181
369.5	-0.531982	-0.444766
369.75	-0.529234	-0.446951
370	-0.524279	-0.444948
370.25	-0.516476	-0.438615
370.5	-0.505404	-0.42799
370.75	-0.491372	-0.414433
371	-0.475261	-0.399574
371.25	-0.45803	-0.384338
371.5	-0.439992	-0.369089
371.75	-0.421341	-0.35423
372	-0.401744	-0.338926
372.25	-0.380745	-0.322549
372.5	-0.358238	-0.305134
372.75	-0.335148	-0.287218
373	-0.312827	-0.269284
373.25	-0.293195	-0.252781
373.5	-0.278261	-0.238877
373.75	-0.269359	-0.228238
374	-0.266559	-0.221037
374.25	-0.269051	-0.217348
374.5	-0.274983	-0.216435
374.75	-0.282036	-0.217553
375	-0.288318	-0.22021
375.25	-0.292832	-0.224372
375.5	-0.295258	-0.229788
375.75	-0.296198	-0.236439
376	-0.296437	-0.2441
376.25	-0.296263	-0.252038

376.5	-0.29531	-0.258776
376.75	-0.29307	-0.263421
377	-0.288768	-0.265524
377.25	-0.282198	-0.264958
377.5	-0.27408	-0.262425
377.75	-0.266116	-0.259589
378	-0.26003	-0.257324
378.25	-0.257477	-0.255624
378.5	-0.259223	-0.25446
378.75	-0.264989	-0.252966
379	-0.272911	-0.249299
379.25	-0.280684	-0.242473
379.5	-0.285813	-0.232504
379.75	-0.286571	-0.219496
380	-0.282047	-0.204378
380.25	-0.273294	-0.189292
380.5	-0.262263	-0.175922
380.75	-0.251526	-0.165431
381	-0.243059	-0.158472
381.25	-0.238204	-0.154993
381.5	-0.236578	-0.153482
381.75	-0.23683	-0.152267
382	-0.236759	-0.14948
382.25	-0.234566	-0.143927
382.5	-0.228978	-0.134909
382.75	-0.219588	-0.123056
383	-0.206788	-0.109595
383.25	-0.191879	-0.096445
383.5	-0.176224	-0.0851387
383.75	-0.161051	-0.0769441
384	-0.147821	-0.0723995
384.25	-0.137689	-0.0714281
384.5	-0.1311	-0.0731481
384.75	-0.128039	-0.0767773
385	-0.128241	-0.0816432
385.25	-0.130665	-0.0871315
385.5	-0.133951	-0.0928341
385.75	-0.137006	-0.0987546
386	-0.139159	-0.104634
386.25	-0.140011	-0.109857
386.5	-0.139534	-0.113675
386.75	-0.13816	-0.115287
387	-0.136191	-0.11379

387.25	-0.133579	-0.108568
387.5	-0.129957	-0.0995406
387.75	-0.125116	-0.0871652
388	-0.118569	-0.0720858
388.25	-0.11006	-0.0551418
388.5	-0.0998175	-0.03736
388.75	-0.0885398	-0.0195984
389	-0.0769277	-0.00246178
389.25	-0.0661897	0.0132705
389.5	-0.0575787	0.0269451
389.75	-0.0518888	0.0383097
390	-0.0495726	0.0470689
390.25	-0.0504419	0.0532138
390.5	-0.0532367	0.0573472
390.75	-0.0562483	0.0598706
391	-0.0580735	0.060728
391.25	-0.0573276	0.0602193
391.5	-0.0536657	0.0581839
391.75	-0.0478929	0.0540727
392	-0.0411339	0.0481179
392.25	-0.0341631	0.0414254
392.5	-0.0280099	0.0346716
392.75	-0.022858	0.0288905
393	-0.0183437	0.0249877
393.25	-0.0140436	0.0228684
393.5	-0.00975019	0.0214808
393.75	-0.00457557	0.020137
394	0.00204967	0.0182388
394.25	0.0106545	0.0158815
394.5	0.0215129	0.0140088
394.75	0.0345583	0.0142816
395	0.0484996	0.018225
395.25	0.0620349	0.0270019
395.5	0.0740003	0.0407958
395.75	0.0837929	0.0589532
396	0.0915142	0.080148
396.25	0.0984598	0.102717
396.5	0.105847	0.125137
396.75	0.114422	0.14645
397	0.124195	0.166181
397.25	0.134491	0.184168
397.5	0.144047	0.200482
397.75	0.151672	0.214716

398	0.156474	0.226076
398.25	0.158173	0.233567
398.5	0.156911	0.236359
398.75	0.152823	0.233659
399	0.14631	0.226219
399.25	0.137941	0.214757
399.5	0.127972	0.201628
399.75	0.11726	0.186913
400	0.105198	0.173797

Item 4. Energy computations for 32 enantiomers of 3 and 4 at the B3LYP/6-31G(d) level

The products formed in the reactions have six stereogenic centers. Thus, it has 64 enantiomers (2^6). Theoretically, half of 64 enantiomers need to be investigated for their relative energy study.

Optimizations for all 32 compounds were performed using well-known density functional theory (DFT), such as at the B3LYP/6-31G(d) level in the gas phase. The energy data are in au. and their relative energy values in kcal/mol are listed below the corresponding geometries. It could be found that compound DL-9 had the lowest energy among all the 32 compounds. LL-8 had the lowest energy in series of 16 compounds named as LL-1 to LL-16. The specific data are illustrated in the corresponding sections below.

Table S4 The specific isomer structures and their energetics.

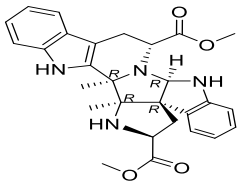
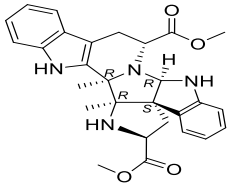
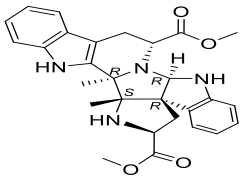
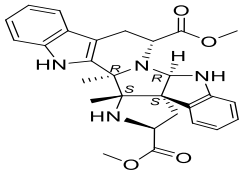
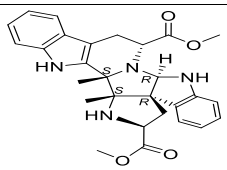
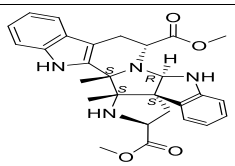
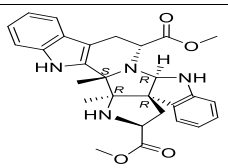
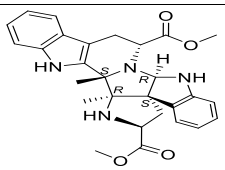
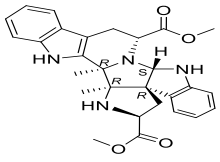
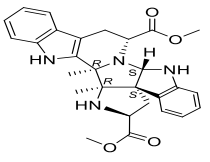
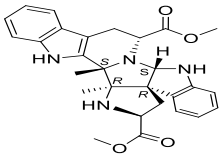
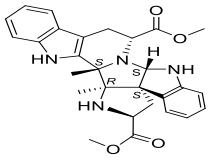
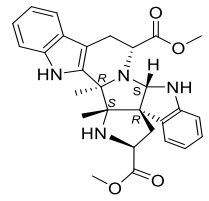
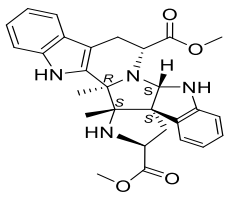
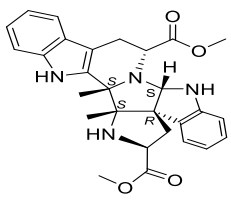
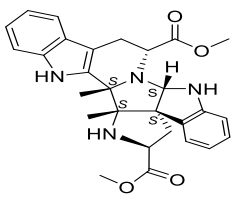
			
DL-1 E=-1604.923486 (au) ΔE=24.529 kcal/mol	DL-2 E=-1604.919527 (au) ΔE=27.013 kcal/mol	DL-3 E=-1604.820336 (au) ΔE=89.256 kcal/mol	DL-4 E=-1604.947719 (au) ΔE=9.323 kcal/mol
			
DL-5 E=-1604.824436 (au) ΔE=86.683 kcal/mol	DL-6 (**(*R*,*S*)-3(*1*) in text**) E=-1604.960288 (au) ΔE=1.436 kcal/mol	DL-7 E=-1604.929503 (au) ΔE=20.753 kcal/mol	DL-8 E=-1604.922946 (au) ΔE=24.868 kcal/mol
			
DL-9 E=-1604.962576 (au) ΔE=0.000 kcal/mol	DL-10 E=-1604.810426 (au) ΔE=95.474 kcal/mol	DL-11 E=-1604.955313 (au) ΔE=4.558 kcal/mol	DL-12 E=-1604.820019 (au) ΔE=89.455 kcal/mol

Table S4 Continued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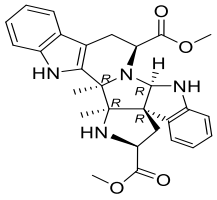
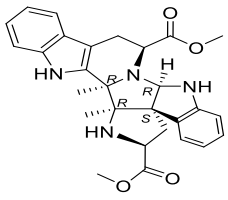
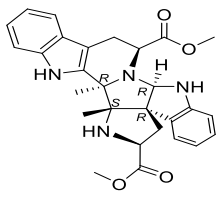
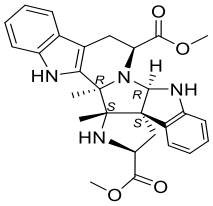
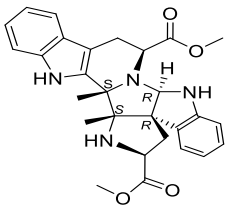
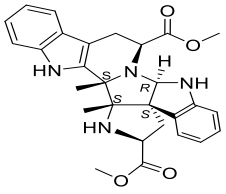
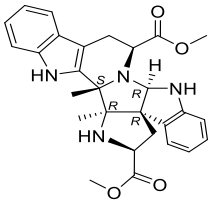
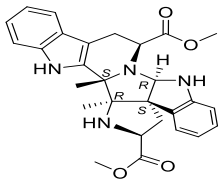
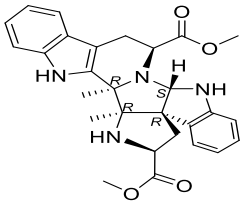
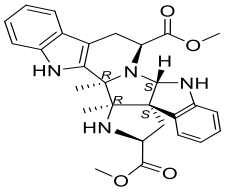
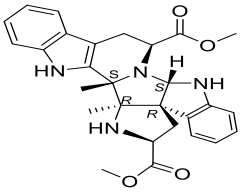
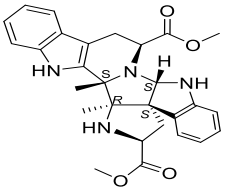
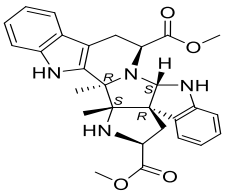
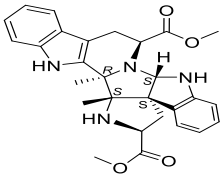
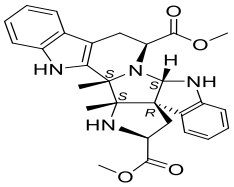
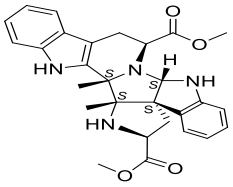
			
LL-1 E=-1604.919621 (au) ΔE=26.954 kcal/mol	LL-2 E=-1604.922976 (au) ΔE=24.849 kcal/mol	LL-3 E=-1604.822613 (au) ΔE=87.827 kcal/mol	LL-4 E=-1604.958986 (au) ΔE=2.253 kcal/mol
			
LL-5 E=-1604.816599 (au) ΔE=91.601 kcal/mol	LL-6(**(*S*,*S*)-4(*1*)in text)** E=-1604.961737 (au) ΔE=0.526 kcal/mol	LL-7 E=-1604.922153 (au) ΔE=25.365 kcal/mol	LL-8 E=-1604.925961 (au) ΔE=22.976 kcal/mol
			
LL-9(**(*S*,*S*)-4(*2*) in text)** E=-1604.959764 (au) ΔE=1.765 kcal/mol	LL-10 E=-1604.817760 (au) ΔE=90.872 kcal/mol	LL-11 E=-1604.952776 (au) ΔE=6.149 kcal/mol	LL-12 E=-1604.817929 (au) ΔE=90.766 kcal/mol

Table S4 Continued

			
LL-13 E=-1604.925895 (au) ΔE=23.017 kcal/mol	LL-14 E=-1604.933716 (au) ΔE=18.110 kcal/mol	LL-15 E=-1604.925049 (au) ΔE=23.548 kcal/mol	LL-16 E=-1604.928409 (au) ΔE=21.440 kcal/mol

Note: DL-6, DL-9, LL-8 and **LL-9** are the numbers for series of energy investigations for **3** and **4**. They are corresponding to the compound numbers of (*R,S*)-**3**(*1*)**,** (*R,S*)-**3**(2)**,** (*S,S*)-**4**(*1*) and (*S,S*)-**4**(*2*) in the paper text.

Item 5. Computations of five enantiomers of 3 and 4: Energies, coordinates at three different quantum levels

The following five geometries were optimized at the B3LYP/6-311+G(d) level in the gas phase first. Then, these compounds named as LL-8, LL-9, DL-6 and DL-9 were used in further calculations at the levels of B3LYP/6-311++G(2d,p) in the gas phase and in solution (CH_2Cl_2) using PCM model. The lowest energy conformation is LL-8. DL-9 had the second lowest energy. The specific data are listed below the corresponding geometries.

Energy unit of E is au. ΔE unit is in kcal/mol.

Table S5 The predicted relative energy for the four isomers of **3** and **4**.

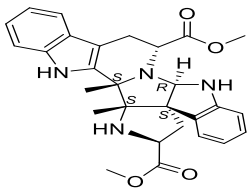
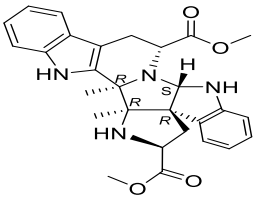
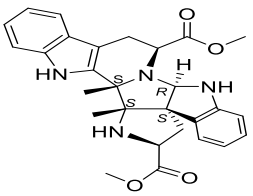
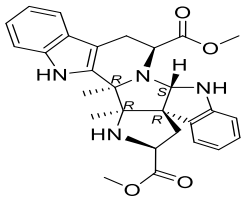
	
DL-6 ((*R*,*S*)-**3**(*1*) in paper) E_1=-1605.342488， ΔE_1=1.730 E_2=-1605.425883，ΔE_2=1.751 E_3=-1605.4415281，ΔE_3=1.452	DL-9 ((*R*,*S*)-**3**(*2*) in paper) E_1=-1605.344416，ΔE_1=0.520 E_2=-1605.427947，ΔE_2=0.456 E_3=-1605.442763，ΔE_3=0.677
	
LL-6((*S*,*S*)-**4**(*1*) in paper) E_1=-1605.345244，ΔE_1=0.000 E_2=-1605.428674，ΔE_2=0.000 E_3=-1605.443842，ΔE_3=0.000	LL-9((*S*,*S*)-**4**(*2*) in paper) E_1=-1605.341896， ΔE_1=2.101 E_2=-1605.425447，ΔE_2=2.025 E_3=-1605.4412202， ΔE_3=1.645

Table S6 The summarized energetics and yields for the four compounds.

Computational method	(*R*,*S*)-**3**(*1*)	(*R*,*S*)-**3**(*2*)	(*S*,*S*)-**4**(*1*)	(*S*,*S*)-**4**(*2*)
	ΔE^d / yield (%)[e]	ΔE^d / yield (%)[e]	ΔE^d / yield (%)[e]	ΔE^d / yield (%)[e]
Method 1 [a]	1.730 / 3.5	0.520 / 27.7	0.000 / 66.8	2.101 / 2.0
Method 2 [b]	1.751 / 3.3	0.456 / 29.9	0.000 / 64.6	2.025 / 2.1
Method 3 [c]	1.452 / 5.8	0.677 / 21.7	0.000 / 68.3	1.645 / 4.2

[a]Optimizations at the B3LYP/6-311+G(d) level in the gas phase. [b]At the B3LYP/6-311++G(2d,p) level in the gas phase. [c]At the B3LYP/6-311++G(2d,p) level in CH_2Cl_2 using PCM model. [d]Relative energy (ΔE) unit: kcal/mol. [e]These are the predicted yields based on the calculated ΔE values.

Item 6. Coordinates for the four low energy compounds at the B3LYP/6-311++G(2d,p) level in CH_2Cl_2 using PCM.

Table S7 Coordinates for (*R,S*)-**3**(2) (=DL-9 in SM)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.907581	-2.473706	0.215170
2	6	0	-3.787241	-1.729434	-0.156576
3	6	0	-3.895612	-0.411955	-0.676259
4	6	0	-5.169648	0.151360	-0.845309
5	6	0	-6.286758	-0.589642	-0.483235
6	6	0	-6.156493	-1.887482	0.045582
7	6	0	-2.550769	0.046005	-0.903467
8	6	0	-1.702976	-0.959573	-0.536430
9	7	0	-2.442327	-2.058483	-0.119664
10	1	0	-2.067974	-2.802884	0.445180
11	6	0	-2.023320	1.330124	-1.445020
12	6	0	-0.645946	1.610455	-0.800936
13	6	0	-0.064271	2.846311	-1.494739
14	8	0	-0.706942	3.952402	-1.072364
15	6	0	-0.305442	5.193163	-1.679847
16	7	0	0.268436	0.473028	-0.895707
17	6	0	-0.208439	-0.937997	-0.737653
18	6	0	0.606461	-1.481533	0.489193
19	1	0	-1.922460	1.294586	-2.538011
20	1	0	-2.686000	2.166699	-1.212230
21	1	0	-0.828418	1.898620	0.245482
22	1	0	-0.918186	5.958169	-1.208604
23	1	0	0.752609	5.382178	-1.496027
24	1	0	-0.484006	5.167858	-2.755456
25	6	0	1.557054	0.669020	-0.228580
26	6	0	1.957375	-0.682570	0.456801
27	6	0	2.330750	-0.543671	1.945117
28	6	0	0.974023	-0.601058	2.713295
29	6	0	0.594455	0.744136	3.313527
30	7	0	-0.037993	-1.052966	1.755327
31	1	0	-0.702660	-0.302398	1.592629
32	8	0	-0.236593	1.499337	2.863663
33	8	0	1.315942	1.002491	4.417220
34	6	0	1.069908	2.268709	5.058142
35	1	0	1.735508	2.292136	5.917663

36	1	0	1.293776	3.090582	4.377289
37	1	0	0.029245	2.337116	5.375750
38	1	0	2.901740	0.365830	2.142664
39	1	0	2.964120	-1.378811	2.251175
40	1	0	1.063893	-1.300470	3.550643
41	7	0	2.674455	0.973051	-1.133039
42	6	0	3.114562	-1.166189	-0.401417
43	6	0	3.866763	-2.333615	-0.349583
44	6	0	3.443413	-0.164477	-1.329526
45	6	0	4.908897	-2.528899	-1.263180
46	1	0	3.654156	-3.102850	0.385960
47	6	0	4.472867	-0.353082	-2.254590
48	6	0	5.194326	-1.546343	-2.213112
49	1	0	5.492158	-3.443064	-1.232143
50	1	0	4.717198	0.418711	-2.977812
51	1	0	5.999144	-1.704920	-2.924587
52	1	0	2.423322	1.548347	-1.926972
53	1	0	1.460481	1.487501	0.493757
54	1	0	-4.812329	-3.477914	0.617223
55	1	0	-7.047002	-2.442496	0.322695
56	1	0	-7.277467	-0.164119	-0.607338
57	1	0	-5.283561	1.152714	-1.249611
58	8	0	0.814161	2.873042	-2.324525
59	6	0	0.107366	-1.718255	-2.037644
60	1	0	-0.371771	-1.210187	-2.876009
61	1	0	1.181100	-1.752241	-2.230072
62	1	0	-0.274390	-2.741569	-1.998227
63	6	0	0.797375	-3.001372	0.523475
64	1	0	-0.160955	-3.522311	0.579827
65	1	0	1.337119	-3.377423	-0.344130
66	1	0	1.354470	-3.288560	1.419726

Table S8 Coordinates for (*R,S*)-**3**(*1*) (=DL-6 in SM)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.800775	1.063260	-2.270454
2	6	0	-3.697921	0.473110	-1.657492
3	6	0	-3.832466	-0.466034	-0.603052
4	6	0	-5.117364	-0.823460	-0.173628
5	6	0	-6.216467	-0.242363	-0.784905

6	6	0	-6.059533	0.693145	-1.821413
7	6	0	-2.501286	-0.842802	-0.213383
8	6	0	-1.632685	-0.143195	-1.004029
9	7	0	-2.348136	0.634983	-1.898790
10	1	0	-1.952108	1.315283	-2.524113
11	6	0	-2.050843	-1.831479	0.815207
12	6	0	-0.561183	-2.203564	0.570033
13	6	0	-0.075542	-2.963164	1.793707
14	8	0	-0.482173	-4.246376	1.721736
15	6	0	-0.189826	-5.062241	2.871299
16	7	0	0.188886	-0.990749	0.284556
17	6	0	-0.137018	-0.309213	-0.985356
18	6	0	0.691631	1.013655	-0.813188
19	1	0	-2.151654	-1.414125	1.823761
20	1	0	-2.657011	-2.740505	0.778027
21	1	0	-0.521601	-2.915255	-0.264295
22	1	0	-0.604489	-6.040742	2.644295
23	1	0	0.886577	-5.128202	3.026570
24	1	0	-0.655451	-4.643488	3.762987
25	6	0	1.594490	-0.835790	0.587055
26	6	0	1.997382	0.535828	-0.058995
27	6	0	2.224999	1.645718	0.978455
28	6	0	0.817579	2.048624	1.391590
29	6	0	0.719419	3.479051	1.908138
30	7	0	0.036772	1.938618	0.146474
31	1	0	-0.914703	1.654142	0.344342
32	8	0	1.545716	4.344641	1.764097
33	8	0	-0.453741	3.667558	2.545160
34	6	0	-0.704803	5.005076	3.011687
35	1	0	-0.707701	5.703217	2.174982
36	1	0	-1.682519	4.969842	3.485345
37	1	0	0.059127	5.307048	3.727689
38	1	0	2.729939	2.498422	0.522090
39	1	0	2.835360	1.311526	1.817984
40	1	0	0.433910	1.380816	2.171780
41	7	0	2.509619	-1.846101	-0.006165
42	6	0	3.232643	0.182717	-0.857937
43	6	0	4.107750	0.996637	-1.562906
44	6	0	3.500403	-1.185958	-0.741436
45	6	0	5.237480	0.440528	-2.164624
46	1	0	3.931746	2.063122	-1.637714
47	6	0	4.623713	-1.753243	-1.337206
48	6	0	5.488542	-0.924487	-2.047444
49	1	0	5.923453	1.072826	-2.714398

50	1	0	4.821668	-2.815259	-1.248443
51	1	0	6.370193	-1.350234	-2.512333
52	1	0	2.844632	-2.543808	0.644486
53	1	0	-4.683406	1.782921	-3.072569
54	1	0	-6.937547	1.132322	-2.279434
55	1	0	-7.214889	-0.509524	-0.460103
56	1	0	-5.252335	-1.540522	0.628101
57	8	0	0.536747	-2.516674	2.732590
58	6	0	0.278953	-1.093783	-2.258427
59	1	0	-0.170050	-2.087485	-2.249660
60	1	0	-0.081880	-0.588273	-3.155479
61	1	0	1.358043	-1.206892	-2.338146
62	6	0	0.954285	1.776388	-2.113207
63	1	0	1.547227	2.665727	-1.897952
64	1	0	1.476735	1.183827	-2.862802
65	1	0	0.015551	2.136509	-2.541464
66	1	0	1.721445	-0.841444	1.666752

Table S9 Coordinates for (*S,S*)-**4**(*1*) (=LL-8 in SM)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.759885	1.975253	-1.862045
2	6	0	-3.752693	1.138659	-1.380132
3	6	0	-4.023965	0.057224	-0.499006
4	6	0	-5.349341	-0.177736	-0.101966
5	6	0	-6.355001	0.650533	-0.582446
6	6	0	-6.063405	1.715697	-1.454668
7	6	0	-2.761035	-0.571448	-0.221538
8	6	0	-1.797420	0.113461	-0.903421
9	7	0	-2.387557	1.155411	-1.605132
10	1	0	-1.924353	1.753277	-2.267314
11	6	0	-2.416840	-1.757742	0.612851
12	6	0	-0.956509	-1.619334	1.092741
13	6	0	-0.569681	-2.925486	1.788040
14	8	0	-1.162162	-2.997929	2.997720
15	6	0	-0.935468	-4.205534	3.745849
16	7	0	-0.024883	-1.335033	0.001633
17	6	0	-0.348615	-0.273903	-1.003046
18	6	0	0.656374	0.887907	-0.653008
19	1	0	-3.060894	-1.833524	1.492574

20	1	0	-2.535018	-2.691710	0.047613
21	1	0	-0.940922	-0.825742	1.854837
22	1	0	-1.480966	-4.075905	4.677598
23	1	0	-1.311845	-5.070573	3.198983
24	1	0	0.128975	-4.339457	3.940390
25	6	0	1.362592	-1.174917	0.456160
26	6	0	1.940567	0.138675	-0.172343
27	6	0	2.549223	1.097956	0.866320
28	6	0	1.321296	1.778984	1.517308
29	6	0	1.554913	3.260000	1.781103
30	7	0	0.210335	1.532853	0.601298
31	1	0	-0.336358	2.369895	0.437543
32	8	0	1.014921	4.167264	1.193384
33	8	0	2.449348	3.437032	2.770917
34	6	0	2.762339	4.800373	3.112343
35	1	0	3.186426	5.320954	2.253294
36	1	0	1.865740	5.324479	3.444003
37	1	0	3.489405	4.737731	3.918307
38	1	0	3.179831	1.831303	0.356082
39	1	0	3.181718	0.584697	1.591827
40	1	0	1.119945	1.321843	2.494709
41	7	0	2.277416	-2.230041	0.015490
42	6	0	2.953717	-0.379961	-1.176002
43	6	0	3.754760	0.287218	-2.093066
44	6	0	3.069752	-1.773663	-1.025373
45	6	0	4.638382	-0.439678	-2.899579
46	1	0	3.700541	1.365785	-2.199414
47	6	0	3.941067	-2.509761	-1.831184
48	6	0	4.715735	-1.827212	-2.769692
49	1	0	5.260278	0.075330	-3.623797
50	1	0	4.024393	-3.586277	-1.720362
51	1	0	5.398367	-2.387832	-3.401042
52	1	0	1.883970	-3.161117	0.000505
53	1	0	1.372815	-1.136354	1.550795
54	1	0	-4.539322	2.800378	-2.532759
55	1	0	-6.869341	2.346481	-1.815435
56	1	0	-7.383497	0.476386	-0.282959
57	1	0	-5.588461	-0.996724	0.569785
58	8	0	0.135615	-3.800793	1.346039
59	6	0	-0.120262	-0.854336	-2.422135
60	1	0	0.920531	-1.132905	-2.586448
61	1	0	-0.736008	-1.747193	-2.537731
62	1	0	-0.407769	-0.144973	-3.203039
63	6	0	0.902269	1.910938	-1.768946

64	1	0	1.205905	1.448546	-2.708163
65	1	0	0.009426	2.515370	-1.954493
66	1	0	1.680322	2.617920	-1.472118

Table S10 Coordinates for (*S,S*)-**4**(*2*) (=LL-9 in SM)

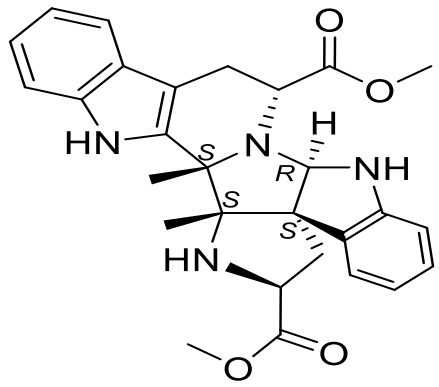
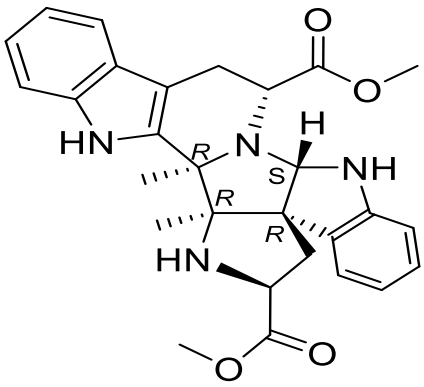
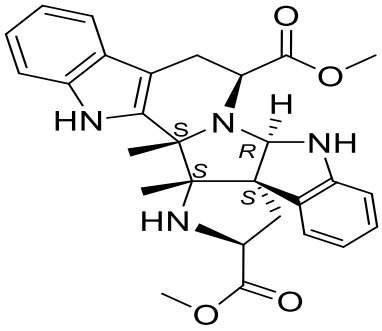
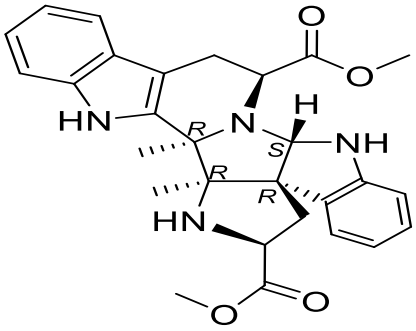
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.794757	1.399981	-2.160199
2	6	0	3.725921	0.711207	-1.593614
3	6	0	3.901962	-0.212760	-0.533490
4	6	0	5.194706	-0.460836	-0.056047
5	6	0	6.262021	0.218510	-0.622462
6	6	0	6.063471	1.142853	-1.660782
7	6	0	2.591746	-0.695432	-0.187823
8	6	0	1.700015	-0.070191	-1.010497
9	7	0	2.377057	0.747641	-1.901635
10	1	0	1.943238	1.515546	-2.386676
11	6	0	2.187834	-1.692521	0.851006
12	6	0	0.727204	-2.158043	0.597244
13	6	0	0.267685	-2.920391	1.829500
14	8	0	0.809655	-4.155565	1.820700
15	6	0	0.552443	-4.961136	2.985432
16	7	0	-0.092548	-1.001657	0.260774
17	6	0	0.220596	-0.353059	-1.033658
18	6	0	-0.704386	0.906513	-0.961138
19	1	0	2.845374	-2.565636	0.841570
20	1	0	2.251821	-1.247554	1.850898
21	1	0	0.743373	-2.891654	-0.218605
22	1	0	1.086929	-5.892212	2.816756
23	1	0	0.920148	-4.462180	3.881518
24	1	0	-0.516160	-5.146064	3.091354
25	6	0	-1.510689	-0.936643	0.520671
26	6	0	-1.975750	0.413789	-0.121209
27	6	0	-2.202887	1.546784	0.917448
28	6	0	-1.140589	2.631487	0.582272
29	6	0	-0.612464	3.299952	1.833072
30	7	0	-0.070080	1.951875	-0.136063
31	1	0	0.543458	1.522845	0.554665
32	8	0	0.362873	2.944437	2.445448
33	8	0	-1.402461	4.324165	2.208020

34	6	0	-1.028859	4.982920	3.433253
35	1	0	-0.033450	5.415899	3.340845
36	1	0	-1.773643	5.759979	3.583590
37	1	0	-1.036839	4.275705	4.262147
38	1	0	-2.040998	1.164003	1.926699
39	1	0	-3.217377	1.942445	0.877401
40	1	0	-1.587018	3.403475	-0.048321
41	7	0	-2.350530	-1.992309	-0.111943
42	6	0	-3.221710	0.008812	-0.878327
43	6	0	-4.164337	0.785840	-1.536536
44	6	0	-3.400895	-1.377117	-0.798311
45	6	0	-5.275288	0.180080	-2.124370
46	1	0	-4.053727	1.863245	-1.587477
47	6	0	-4.505995	-1.994495	-1.380003
48	6	0	-5.439422	-1.201000	-2.041463
49	1	0	-6.013170	0.784182	-2.637467
50	1	0	-4.637856	-3.068563	-1.316728
51	1	0	-6.306816	-1.666804	-2.494560
52	1	0	-2.619462	-2.743176	0.509959
53	1	0	-1.670301	-0.963354	1.594683
54	1	0	4.645222	2.109450	-2.966078
55	1	0	6.916044	1.662518	-2.081269
56	1	0	7.266580	0.038784	-0.258522
57	1	0	5.360941	-1.166442	0.749995
58	8	0	-0.433139	-2.515785	2.724029
59	6	0	-0.090394	-1.226141	-2.278273
60	1	0	0.443139	-2.174594	-2.214039
61	1	0	-1.152836	-1.439139	-2.376668
62	1	0	0.253398	-0.728194	-3.185738
63	6	0	-1.060044	1.516070	-2.319102
64	1	0	-1.632826	0.838591	-2.948396
65	1	0	-1.652924	2.422057	-2.183742
66	1	0	-0.156906	1.809782	-2.856862

Item 7. Computations of both the OR and ECD spectra for four enantiomers at the B3LYP/6-311++G(2d,p) level in the gas phase and their comparison with experimental results

Table S11 The experimental and predicted OR values for the four compounds

	
(*R,S*)-**3**(*1*) (OR) (numbered as DL-6 in item 4 part) Calcd OR($[\alpha]_D$): 142.7 Exp. $[\alpha]_D$: +32 (*c* 3.25, CH_2Cl_2)	(*R,S*)-**3**(2) (OR) (numbered as DL-9 in item 4 part) Calcd OR ($[\alpha]_D$): -156.3 Exp. $[\alpha]_D$: +32 (c 3.25, CH_2Cl_2)
	
(*S,S*)-**4**(*1*) (LL-8 in text section 4) Calcd OR ($[\alpha]_D$) for current structure: 100.5 Exp. OR ($[\alpha]_D$): -104.76 (*c*, 5.25, $CHCl_3$)	(*S,S*)-**4**(*2*) (LL-9 in section 4) Calcd OR ($[\alpha]_D$): -225.2 Exp. OR ($[\alpha]_D$): -104.76 (*c*, 5.25, $CHCl_3$)

The ECD spectra are listed below:

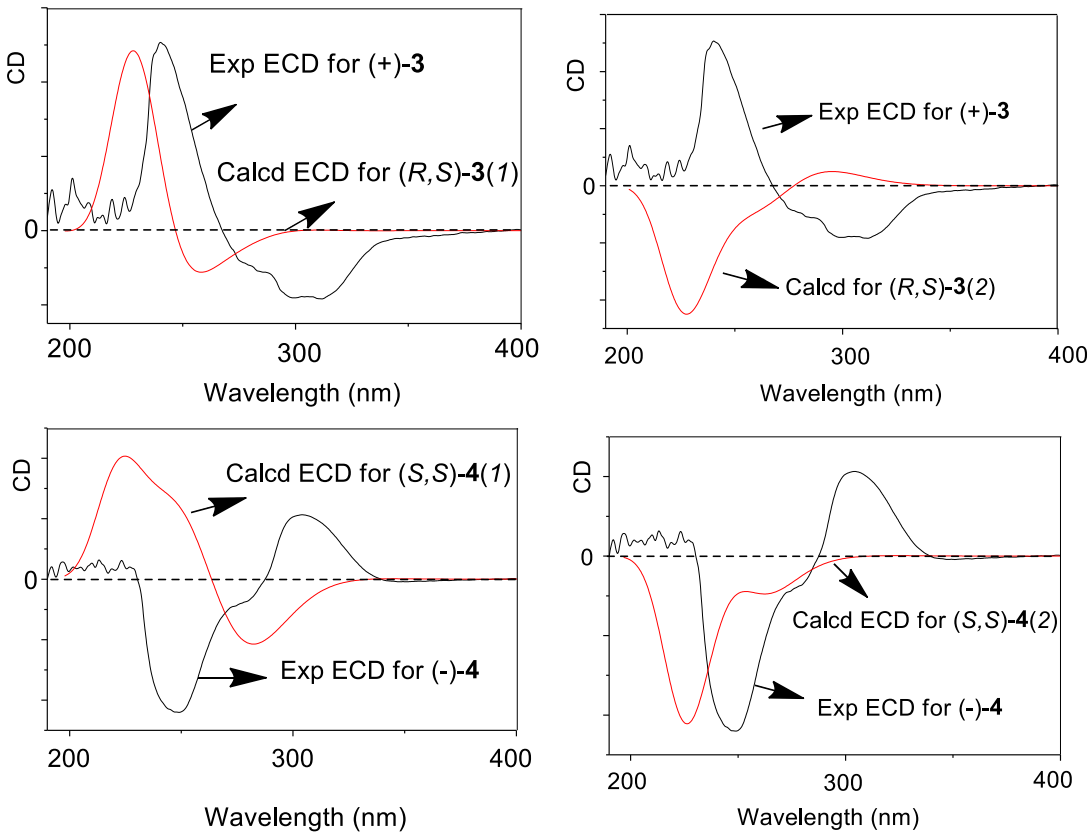


Fig. S8 The experimental and computed ECD for the two compounds **3** and **4**.

Conclusion:

(1) The ECD curve of (+)-**3** matched either (*R,S*)-**3**(2)'s enantiomer (namely (*S,R*)-**3(2))** or (*R,S*)-**3**(1). However, the energy of **3**(2) is lower than **3**(1) by near 0.8 – 1.2 kcal/mol (Table S6). By the way, the isolated yield of **3** was about 18%. This yield is close the theoretical yield (21-30%). In this case, (*S,R*)-**3**(2) is preferred.

(2) The ECD curve of (-)-**4** looked like its enantiomers ECD of (*S,S*)-**4**(1).

Based on the OR and ECD and the geometries with lowest energy among the diasteroisomers (Table S6), the (+)-**3** was assigned as (*S,R*)-**3**(*2*), and (-)-**4** was assigned as (*R,R*)-**4**(*1*).

Item 8. Analysis of %ee values of L-TME via HPLC

A: Computation of the yields to recovered 1 and 2.

The recovered yield may be named as below using the following reaction formula:

$$\underset{\mathbf{1}}{(R)\text{-M}} + \underset{\mathbf{2}}{(S)\text{-M}} \xrightarrow{\text{bisFG}} \sum_{i=1}^{n}(R,S)\text{-}\mathbf{3}(i) + \sum_{i=1}^{n}(S,R)\text{-}\mathbf{3}(i) + \sum_{j=1}^{m}(R,R)\text{-}\mathbf{4}(j) + \sum_{j=1}^{m}(S,S)\text{-}\mathbf{4}(j) + \begin{matrix}(R)\text{-M and}\\(S)\text{-M}\\\text{remaining}\\\text{in solution}\\\text{with \%ee}_2\end{matrix}$$

In this reaction, the quantity of **1** has been assumed larger quantity than **2**. For easy understanding the calculation procedure, an ideal example is listed here. Materials **1** (120 mg, 0.55 mmole) and 2 (98 mg, 0.45 mmol) in CH_2Cl_2 solution, the bisFG, biacetyl (35 mg, 0.405 mmole, 90% of mole of **2**) (since 1 mole of bisFG can react with 2 moles of **1** and **2** theoretically) was added into the solution at near 0 ºC. The 0.405 mole of bisFG theoretically consumed 0.81 mole of sum of **1** and **2**. Then, only total of 0.19 mmole of **1** and **2** (41.4 mg) will be left theoretically. Finally, silica column chromatography was used to isolate the unreacted **1** and **2**. The weight the recovered material was 23.3 mg, it's recovered yield was 56%.

In the series of the reactions, biacetyl was 90% of the mole of **2** used.

The smaller the $\%ee_1$ used in the reaction, the more the recovered material will be. In real cases, when the $\%ee_1$ was about 5%, then, the material used in the reactions were 700-800 mg. When the $\%ee_1$ was about 90%, the material used in the reactions were 200 to 300 mg. The specific yields are summarized in the Table S12 in the next section.

B. $\%ee_2$ analysis using HPLC.

All the data from the Tables S10 to S12 are finally summarized at the end of this section for clear reading.

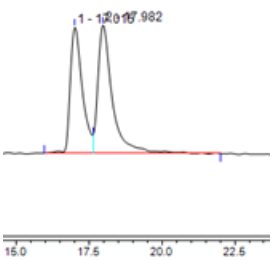
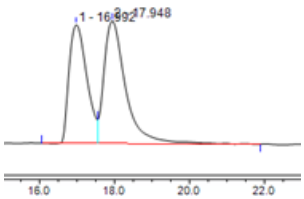
The content of L-tryptophan methyl ester and D- tryptophan methyl ester (%ee) was analyzed by HPLC using Chiralcel-IB column, employing a mixture of petroleum ether, dichloromethane and isopropanol (v/v/v: 60:10:30).

There are three series of Pictet-Spengler reactions.

The %ee values of L-TME recovered from the first condensation series are listed below.

"Before the reaction" refers to the HPLC and $\%ee_1$ of L-TME prepared as the starting material. "After the reaction" means the HPLC and the corresponding $\%ee_2$ of the L-TME that was recovered from the Pictet-Spengler reaction in HPLC analysis.

Table S12 HPLC analysis for the *first series of condensations*. Accurate determination of %ee values is very critical in HPLC analysis. The integration intervals (from starting retention time to its ending time) are fixed in all integration squares.

Before the reaction [a]	After the reaction [a]
	
10.3% of L-TME initially used	11.8% of L-TME recovered

HPLC area percentage for the left plot.

Signal Retention time sample area% area height type half peak wide - - -

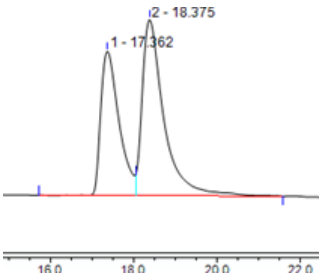
峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		17.015	n.a.	44.85	122.8869	255.42	BM *	0.433	n.a.	1.27	8566
2		17.982	n.a.	55.15	151.0868	260.41	MB*	0.465	n.a.	n.a.	8296
最大值			0.0000	55.15	151.0868	260.41		0.465	0.00	1.27	8566
最小值			0.0000	44.85	122.8869	255.42		0.433	0.00	1.27	8296
总和			0.0000	100.00	273.9737	515.83					

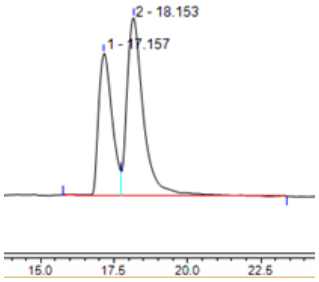
HPLC area percentage for the left plot.

Signal Retention time sample area% area height type half peak wide - - -

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		16.992	n.a.	44.09	251.4693	457.51	BM *	0.535	n.a.	1.02	558
2		17.948	n.a.	55.91	318.8901	472.82	MB*	0.576	n.a.	n.a.	538
最大值			0.0000	55.91	318.8901	472.82		0.576	0.00	1.02	558
最小值			0.0000	44.09	251.4693	457.51		0.535	0.00	1.02	538
总和			0.0000	100.00	570.3594	930.33					

The others have the same arrangement below:





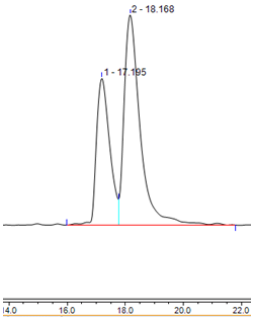
18.7% of L-TME initially used

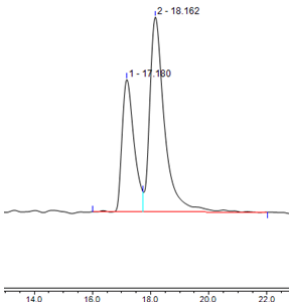
20.9% of L-TME recovered

Signal Retention time sample area% area height type half peak wide - - -

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		17.362	n.a.	40.66	102.1802	202.47	BM *	0.465	n.a.	1.24	772
2		18.375	n.a.	59.34	149.1388	247.08	MB*	0.498	n.a.	n.a.	754
最大值			0.0000	59.34	149.1388	247.08		0.498	0.00	1.24	772
最小值			0.0000	40.66	102.1802	202.47		0.465	0.00	1.24	754
总和			0.0000	100.00	251.3191	449.55					

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP
1		17.157	n.a.	39.54	271.7299	510.57	BM *	0.513	n.a.	1.10
2		18.153	n.a.	60.46	415.5243	639.67	MB*	0.556	n.a.	n.a.
最大值			0.0000	60.46	415.5243	639.67		0.556	0.00	1.10
最小值			0.0000	39.54	271.7299	510.57		0.513	0.00	1.10
总和			0.0000	100.00	687.2542	1150.24				





27.1% of L-TME initially used

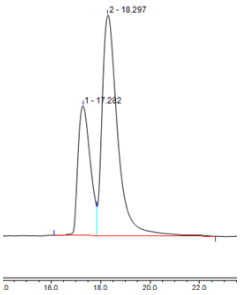
29.4% of L-TME recovered

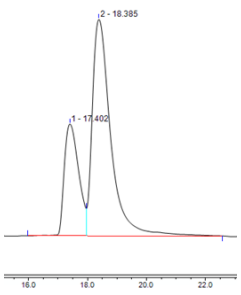
Signal Retention time sample area% area height type half peak wide - - -

Table S12 continued

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		17.195	n.a.	36.47	206.4828	391.03	BM *	0.501	n.a.	1.10	653
2		18.168	n.a.	63.53	359.7481	559.86	MB*	0.547	n.a.	n.a.	610
最大值			0.0000	63.53	359.7481	559.86		0.547	0.00	1.10	653
最小值			0.0000	36.47	206.4828	391.03		0.501	0.00	1.10	610
总和			0.0000	100.00	566.2309	950.89					

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		17.180	n.a.	35.32	127.2259	266.32	BM *	0.445	n.a.	1.23	8259
2		18.162	n.a.	64.68	233.0023	392.03	MB*	0.493	n.a.	n.a.	7507
最大值			0.0000	64.68	233.0023	392.03		0.493	0.00	1.23	8259
最小值			0.0000	35.32	127.2259	266.32		0.445	0.00	1.23	7507
总和			0.0000	100.00	360.2282	658.35					





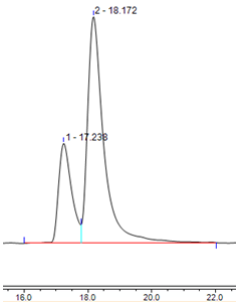
36.6% of L-TME initially used

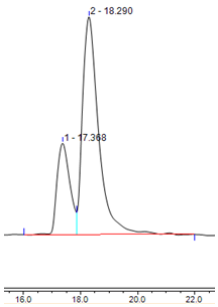
42.2% of L-TME recovered

Signal Retention time sample area% area height type half peak wide - - -

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		17.282	n.a.	31.69	359.4257	623.98	BM *	0.566	n.a.	1.00	516
2		18.297	n.a.	68.31	774.8411	1062.51	MB*	0.628	n.a.	n.a.	470
最大值			0.0000	68.31	774.8411	1062.51		0.628	0.00	1.00	516
最小值			0.0000	31.69	359.4257	623.98		0.566	0.00	1.00	470
总和			0.0000	100.00	1134.2668	1686.48					

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		17.402	n.a.	28.88	174.0920	306.44	BM *	0.557	n.a.	0.99	5403
2		18.385	n.a.	71.12	428.7598	593.03	MB*	0.617	n.a.	n.a.	4925
最大值			0.0000	71.12	428.7598	593.03		0.617	0.00	0.99	5403
最小值			0.0000	28.88	174.0920	306.44		0.557	0.00	0.99	4925
总和			0.0000	100.00	602.8519	899.47					





47.7% of L-TME initially used

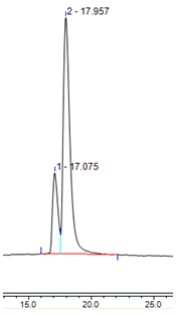
50.2% of L-TME recovered

Signal Retention time sample area% area height type half peak wide - - -

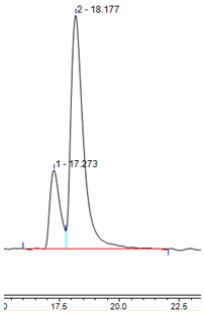
峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		17.238	n.a.	26.16	111.1861	234.07	BM *	0.440	n.a.	1.19	849
2		18.172	n.a.	73.84	313.9112	531.06	MB*	0.485	n.a.	n.a.	777
最大值			0.0000	73.84	313.9112	531.06		0.485	0.00	1.19	849
最小值			0.0000	26.16	111.1861	234.07		0.440	0.00	1.19	777
总和			0.0000	100.00	425.0973	765.13					

峰序号	峰名称	保留时间	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
			n.a.	24.91	95.2677	183.72	BM *	0.509	n.a.	1.00	645
			n.a.	75.09	287.1179	437.84	MB*	0.574	n.a.	n.a.	562
			0.0000	75.09	287.1179	437.84		0.574	0.00	1.00	645
			0.0000	24.91	95.2677	183.72		0.509	0.00	1.00	562
总和			0.0000	100.00	382.3856	621.56					

Table S12 continued



57.8% of L-TME initially used

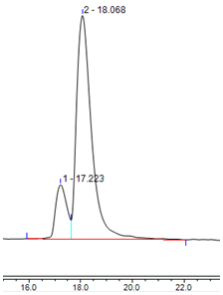


58.4% of L-TME recovered

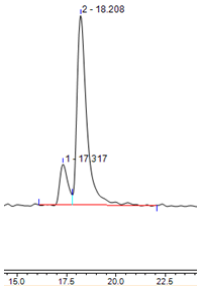
Signal Retention time sample area% area height type half peak wide - - -

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		17.075	n.a.	21.08	212.9558	433.72	BM *	0.483	n.a.	1.00	691
2		17.957	n.a.	78.92	797.3170	1268.20	MB*	0.553	n.a.	n.a.	584
最大值			0.0000	78.92	797.3170	1268.20		0.553	0.00	1.00	691
最小值			0.0000	21.08	212.9558	433.72		0.483	0.00	1.00	584
总和			0.0000	100.00	1010.2728	1701.92					

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板 EP
1		17.273	n.a.	20.81	75.7716	158.20	BM *	0.467	n.a.	1.07	75
2		18.177	n.a.	79.19	288.3187	470.02	MB*	0.527	n.a.	n.a.	66
最大值			0.0000	79.19	288.3187	470.02		0.527	0.00	1.07	75
最小值			0.0000	20.81	75.7716	158.20		0.467	0.00	1.07	66
总和			0.0000	100.00	364.0903	628.22					



69.4% of L-TME initially used

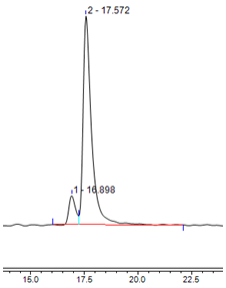


70.3% of L-TME recovered

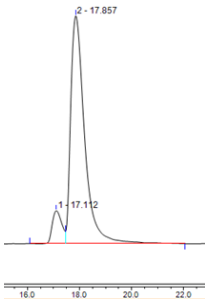
Signal Retention time sample area% area height type half peak wide - - -

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		17.223	n.a.	15.32	146.8727	291.31	BM *	0.511	n.a.	0.90	6285
2		18.068	n.a.	84.68	811.7688	1203.07	MB*	0.593	n.a.	n.a.	5137
最大值			0.0000	84.68	811.7688	1203.07		0.593	0.00	0.90	6285
最小值			0.0000	15.32	146.8727	291.31		0.511	0.00	0.90	5137
总和			0.0000	100.00	958.6415	1494.38					

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		17.317	n.a.	14.85	29.0059	61.69	BM *	0.455	n.a.	1.12	802
2		18.208	n.a.	85.15	166.3511	286.81	MB*	0.487	n.a.	n.a.	775
最大值			0.0000	85.15	166.3511	286.81		0.487	0.00	1.12	802
最小值			0.0000	14.85	29.0059	61.69		0.455	0.00	1.12	775
总和			0.0000	100.00	195.3570	348.49					



80.5% of L-TME initially used

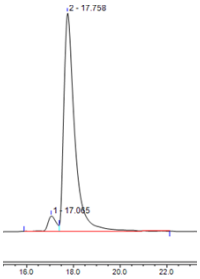


82.1% of L-TME recovered

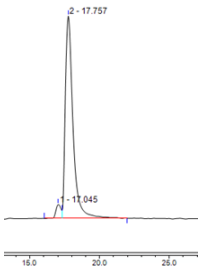
Signal Retention time sample area% area height type half peak wide - - -

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		16.898	n.a.	9.73	24.1430	68.12	BM *	0.347	n.a.	1.10	13168
2		17.572	n.a.	90.27	223.8867	490.69	MB*	0.376	1.75	n.a.	12113
最大值			0.0000	90.27	223.8867	490.69		0.376	1.75	1.10	13168
最小值			0.0000	9.73	24.1430	68.12		0.347	1.75	1.10	12113
总和			0.0000	100.00	248.0297	558.81					

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		17.112	n.a.	8.93	69.2341	164.00	BM *	0.437	n.a.	0.90	8485
2		17.857	n.a.	91.07	705.6747	1134.46	MB*	0.540	n.a.	n.a.	6046
最大值			0.0000	91.07	705.6747	1134.46		0.540	0.00	0.90	8485
最小值			0.0000	8.93	69.2341	164.00		0.437	0.00	0.90	6046
总和			0.0000	100.00	774.9088	1298.47					



90.4% of L-TME initially used



91.2% of L-TME recovered

Signal Retention time sample area% area height type half peak wide - - -

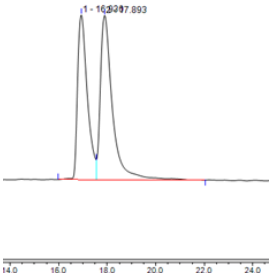
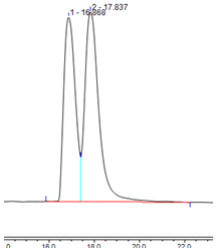
峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		17.065	n.a.	4.82	40.7488	104.28	BM *	0.394	n.a.	0.96	10387
2		17.758	n.a.	95.18	804.4848	1496.20	MB*	0.457	1.88	n.a.	8361
最大值			0.0000	95.18	804.4848	1496.20		0.457	1.88	0.96	10387
最小值			0.0000	4.82	40.7488	104.28		0.394	1.88	0.96	8361
总和			0.0000	100.00	845.2336	1600.48					

Table S12 continued

峰序号	峰名称	保留时间	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
			n.a.	4.39	35.5056	83.27	BM *	n.a.	n.a.	n.a.	n.a.
			n.a.	95.61	772.4494	1210.14	MB*	0.556	1.70	n.a.	5641
			0.0000	95.61	772.4494	1210.14		0.556	1.70	0.00	5641
			0.0000	4.39	35.5056	83.27		0.556	1.70	0.00	5641
总和			0.0000	100.00	807.9550	1293.41					

[a] "Before the reaction" means the HPLC and $\%ee_1$ of L-TME prepared as the starting material. "After the reaction" means HPLC and the corresponding $\%ee_2$ of the L-TME that was recovered from the Pictet-Spengler reaction in HPLC analysis.

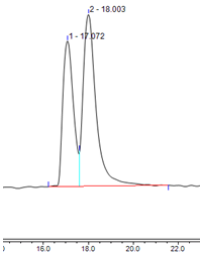
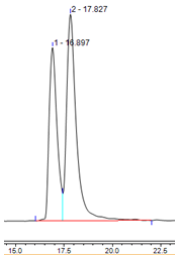
Table S13 The HPLC analysis for the L-TME recovered from the second series of condensation.

Before the reaction [a]	After the reaction [a]
	
10.6% of L-TME initially used	11.8% of L-TME recovered

Signal Retention time sample area% area height type half peak wide - - -

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		16.930	n.a.	44.72	266.6971	571.90	BM *	0.427	n.a.	1.26	870
2		17.893	n.a.	55.28	329.7375	569.92	MB*	0.474	n.a.	n.a.	790
最大值			0.0000	55.28	329.7375	571.90		0.474	0.00	1.26	870
最小值			0.0000	44.72	266.6971	569.92		0.427	0.00	1.26	790
总和			0.0000	100.00	596.4346	1141.82					

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		16.868	n.a.	44.09	619.0041	1053.26	BM *	0.584	n.a.	0.94	4629
2		17.837	n.a.	55.91	784.9343	1084.73	MB*	0.632	n.a.	n.a.	4407
最大值			0.0000	55.91	784.9343	1084.73		0.632	0.00	0.94	4629
最小值			0.0000	44.09	619.0041	1053.26		0.584	0.00	0.94	4407
总和			0.0000	100.00	1403.9384	2137.99					

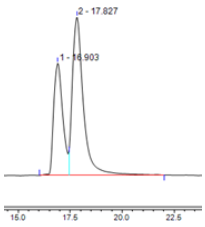
	
17.9% of L-TME initially used	19.0% of L-TME recovered

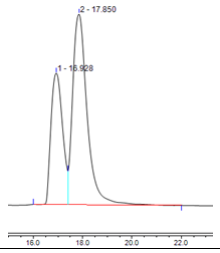
Signal Retention time sample area% area height type half peak wide - - -

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		17.072	n.a.	41.04	163.0883	297.17	BM *	0.529	n.a.	0.99	576
2		18.003	n.a.	58.96	234.3166	350.96	MB*	0.577	n.a.	n.a.	539
最大值			0.0000	58.96	234.3166	350.96		0.577	0.00	0.99	576
最小值			0.0000	41.04	163.0883	297.17		0.529	0.00	0.99	539
总和			0.0000	100.00	397.4048	648.13					

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		16.897	n.a.	40.48	316.3315	663.73	BM *	0.449	n.a.	1.17	7862
2		17.827	n.a.	59.52	465.2138	791.71	MB*	0.492	n.a.	n.a.	7271
最大值			0.0000	59.52	465.2138	791.71		0.492	0.00	1.17	7862
最小值			0.0000	40.48	316.3315	663.73		0.449	0.00	1.17	7271
总和			0.0000	100.00	781.5453	1455.43					

[a] "Before the reaction" means the HPLC plot analyzed for $\%ee_1$ of L-TME prepared as the starting material. [b] "After the reaction" means HPLC plot analyzed for the corresponding $\%ee_2$ of the L-TME that was recovered after the Pictet-Spengler reaction.





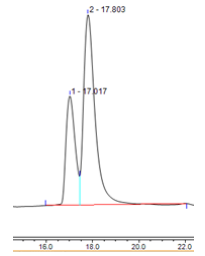
26.5% of L-TME initially used

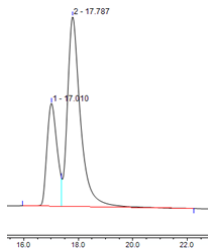
28.8% of L-TME recovered

Signal Retention time sample area% area height type half peak wide - - -

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		16.903	n.a.	36.73	342.0223	675.79	BM *	0.480	n.a.	1.08	6875
2		17.827	n.a.	63.27	589.1061	953.39	MB*	0.529	n.a.	n.a.	6297
最大值			0.0000	63.27	589.1061	953.39		0.529	0.00	1.08	6875
最小值			0.0000	36.73	342.0223	675.79		0.480	0.00	1.08	6297
总和			0.0000	100.00	931.1284	1629.19					

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		16.928	n.a.	35.59	529.4750	970.47	BM *	0.544	n.a.	0.95	537
2		17.850	n.a.	64.41	958.2383	1407.48	MB*	0.603	n.a.	n.a.	485
最大值			0.0000	64.41	958.2383	1407.48		0.603	0.00	0.95	537
最小值			0.0000	35.59	529.4750	970.47		0.544	0.00	0.95	485
总和			0.0000	100.00	1487.7133	2377.95					





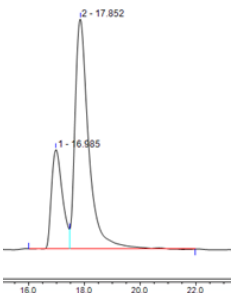
36.7% of L-TME initially used

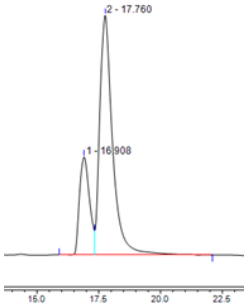
41.5% of L-TME recovered

Signal Retention time sample area% area height type half peak wide - - -

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		17.017	n.a.	31.67	225.0382	492.55	BM *	0.446	n.a.	0.98	808
2		17.803	n.a.	68.33	485.5694	859.15	MB*	0.499	n.a.	n.a.	705
最大值			0.0000	68.33	485.5694	859.15		0.499	0.00	0.98	808
最小值			0.0000	31.67	225.0382	492.55		0.446	0.00	0.98	705
总和			0.0000	100.00	710.6075	1351.70					

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		17.010	n.a.	29.26	322.8895	759.58	BM *	0.423	n.a.	1.02	893
2		17.787	n.a.	70.74	780.6347	1401.53	MB*	0.473	n.a.	n.a.	783
最大值			0.0000	70.74	780.6347	1401.53		0.473	0.00	1.02	893
最小值			0.0000	29.26	322.8895	759.58		0.423	0.00	1.02	783
总和			0.0000	100.00	1103.5242	2161.11					





48.4% of L-TME initially used

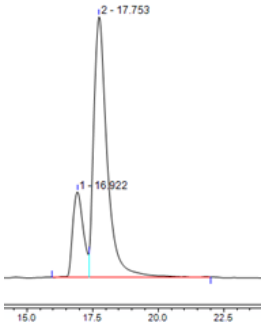
54.2% of L-TME recovered

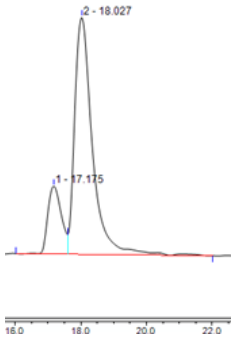
Signal Retention time sample area% area height type half peak wide - - -

Table S13 continued

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		16.985	n.a.	25.82	156.3227	343.02	BM *	0.432	n.a.	1.12	854
2		17.852	n.a.	74.18	449.0213	794.45	MB*	0.481	n.a.	n.a.	763
最大值			0.0000	74.18	449.0213	794.45		0.481	0.00	1.12	854
最小值			0.0000	25.82	156.3227	343.02		0.432	0.00	1.12	763
总和			0.0000	100.00	605.3439	1137.46					

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		16.908	n.a.	22.90	287.2445	639.31	BM *	0.465	n.a.	1.01	732
2		17.760	n.a.	77.10	967.1523	1559.48	MB*	0.526	n.a.	n.a.	631
最大值			0.0000	77.10	967.1523	1559.48		0.526	0.00	1.01	732
最小值			0.0000	22.90	287.2445	639.31		0.465	0.00	1.01	631
总和			0.0000	100.00	1254.3968	2198.78					



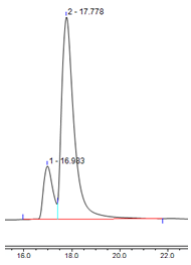


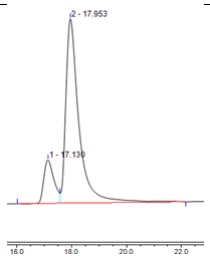
59.0% of L-TME initially used	64.4% of L-TME recovered

Signal Retention time sample area% area height type half peak wide - - -

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		16.922	n.a.	20.50	217.2808	466.32	BM *	0.455	n.a.	1.01	765
2		17.753	n.a.	79.50	842.3683	1423.57	MB*	0.517	n.a.	n.a.	652
最大值			0.0000	79.50	842.3683	1423.57		0.517	0.00	1.01	765
最小值			0.0000	20.50	217.2808	466.32		0.455	0.00	1.01	652
总和			0.0000	100.00	1059.6491	1889.89					

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		17.175	n.a.	17.78	44.2575	93.24	BM *	0.470	n.a.	1.00	739
2		18.027	n.a.	82.22	204.7276	325.25	MB*	0.536	n.a.	n.a.	627
最大值			0.0000	82.22	204.7276	325.25		0.536	0.00	1.00	739
最小值			0.0000	17.78	44.2575	93.24		0.470	0.00	1.00	627
总和			0.0000	100.00	248.9851	418.49					





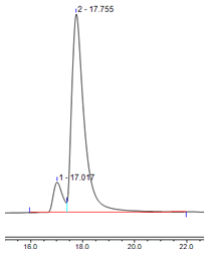
67.2% of L-TME initially used	69.5% of L-TME recovered

Signal Retention time sample area% area height type half peak wide - - -

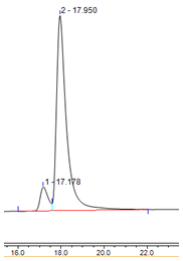
峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		16.983	n.a.	16.39	195.3745	435.62	BM *	0.440	n.a.	0.98	8250
2		17.778	n.a.	83.61	996.7091	1653.93	MB*	0.521	n.a.	n.a.	6456
最大值			0.0000	83.61	996.7091	1653.93		0.521	0.00	0.98	8250
最小值			0.0000	16.39	195.3745	435.62		0.440	0.00	0.98	6456
总和			0.0000	100.00	1192.0836	2089.55					

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		17.130	n.a.	15.26	53.0016	124.61	BM *	0.408	n.a.	1.13	978
2		17.953	n.a.	84.74	294.4109	529.11	MB*	0.452	n.a.	n.a.	873
最大值			0.0000	84.74	294.4109	529.11		0.452	0.00	1.13	978
最小值			0.0000	15.26	53.0016	124.61		0.408	0.00	1.13	873
总和			0.0000	100.00	347.4125	653.72					

Table S13 continued



79.9% of L-TME initially used

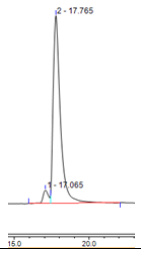


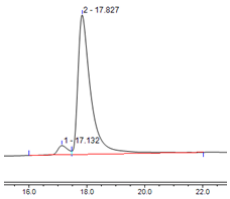
82.5% of L-TME recovered

Signal Retention time sample area% area height type half peak wide - - -

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		17.017	n.a.	10.03	111.3924	271.61	BM *	0.402	n.a.	0.99	993
2		17.755	n.a.	89.97	999.1459	1784.01	MB*	0.480	n.a.	n.a.	759
最大值			0.0000	89.97	999.1459	1784.01		0.480	0.00	0.99	993
最小值			0.0000	10.03	111.3924	271.61		0.402	0.00	0.99	759
总和			0.0000	100.00	1110.5383	2055.62					

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		17.178	n.a.	8.77	33.1522	78.81	BM *	0.407	n.a.	1.07	988
2		17.950	n.a.	91.23	344.8191	641.24	MB*	0.442	1.90	n.a.	914
最大值			0.0000	91.23	344.8191	641.24		0.442	1.90	1.07	988
最小值			0.0000	8.77	33.1522	78.81		0.407	1.90	1.07	914
总和			0.0000	100.00	377.9713	720.04					





90.2% of L-TME initially used

90.2% of L-TME recovered

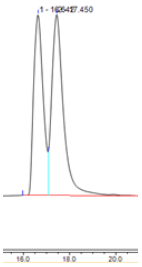
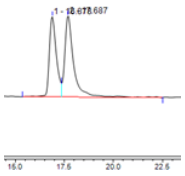
Signal Retention time sample area% area height type half peak wide - - -

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		17.065	n.a.	4.91	44.2486	106.87	BM *	0.403	n.a.	0.93	992
2		17.765	n.a.	95.09	856.7635	1533.37	MB*	0.484	1.76	n.a.	745
最大值			0.0000	95.09	856.7635	1533.37		0.484	1.76	0.93	992
最小值			0.0000	4.91	44.2486	106.87		0.403	1.76	0.93	745
总和			0.0000	100.00	901.0121	1640.24					

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		17.132	n.a.	4.89	30.3378	76.09	BM *	0.395	n.a.	1.00	1042
2		17.827	n.a.	95.11	590.0644	1144.13	MB*	0.422	2.04	n.a.	986
最大值			0.0000	95.11	590.0644	1144.13		0.422	2.04	1.00	1042
最小值			0.0000	4.89	30.3378	76.09		0.395	2.04	1.00	986
总和			0.0000	100.00	620.4023	1220.22					

Table S13 continued

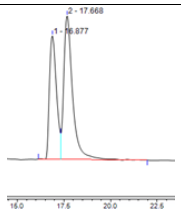
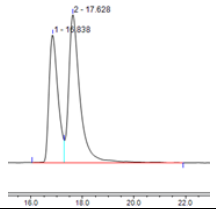
Table S14 The HPLC analysis for recovered L-TME from the third series of reactions.

Before the reaction [a]	After the reaction [a]
	
11.3% of L-TME initially used	12.2% of L-TME recovered

Signal Retention time sample area% area height type half peak wide - - -

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		16.642	n.a.	44.36	597.4715	1268.69	BM *	0.464	n.a.	0.98	7119
2		17.450	n.a.	55.64	749.2548	1270.69	MB*	0.511	n.a.	n.a.	6463
最大值			0.0000	55.64	749.2548	1270.69		0.511	0.00	0.98	7119
最小值			0.0000	44.36	597.4715	1268.69		0.464	0.00	0.98	6463
总和			0.0000	100.00	1346.7263	2539.37					

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		16.878	n.a.	43.90	106.5404	254.81	BM *	0.379	n.a.	1.21	10973
2		17.687	n.a.	56.10	136.1750	257.43	MB*	0.412	n.a.	n.a.	10217
最大值			0.0000	56.10	136.1750	257.43		0.412	0.00	1.21	10973
最小值			0.0000	43.90	106.5404	254.81		0.379	0.00	1.21	10217
总和			0.0000	100.00	242.7154	512.24					

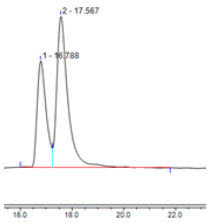
	
17.9% of L-TME initially used	18.8% of L-TME recovered

Signal Retention time sample area% area height type half peak wide - - -

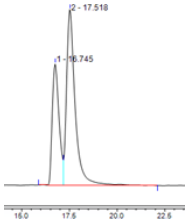
峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		16.877	n.a.	41.06	235.0304	530.43	BM *	0.425	n.a.	1.05	8728
2		17.668	n.a.	58.94	337.3636	616.96	MB*	0.466	n.a.	n.a.	7965
最大值			0.0000	58.94	337.3636	616.96		0.466	0.00	1.05	8728
最小值			0.0000	41.06	235.0304	530.43		0.425	0.00	1.05	7965
总和			0.0000	100.00	572.3940	1147.39					

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		16.838	n.a.	40.58	277.2027	689.13	BM *	0.379	n.a.	1.17	10949
2		17.628	n.a.	59.42	405.8928	798.17	MB*	0.418	n.a.	n.a.	9863
最大值			0.0000	59.42	405.8928	798.17		0.418	0.00	1.17	10949
最小值			0.0000	40.58	277.2027	689.13		0.379	0.00	1.17	9863
总和			0.0000	100.00	683.0955	1487.30					

[a]"Before the reaction" means the HPLC and %ee$_1$ of L-TME prepared as the starting material. "After the reaction" means HPLC and the corresponding %ee$_2$ of the L-TME that was recovered from the Pictet-Spengler reaction in HPLC analysis.



27.4% of L-TME initially used

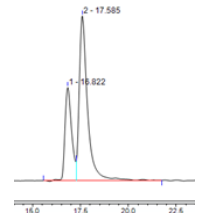


29.7% of L-TME recovered

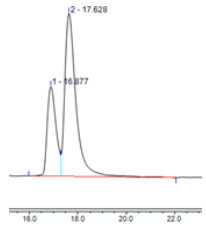
Signal Retention time sample area% area height type half peak wide - - -

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		16.788	n.a.	36.32	231.7504	574.85	BM *	0.377	n.a.	1.16	11004
2		17.567	n.a.	63.68	406.3239	815.43	MB*	0.415	n.a.	n.a.	9909
最大值			0.0000	63.68	406.3239	815.43		0.415	0.00	1.16	11004
最小值			0.0000	36.32	231.7504	574.85		0.377	0.00	1.16	9909
总和			0.0000	100.00	638.0742	1390.28					

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		16.745	n.a.	35.14	322.1469	778.04	BM *	0.399	n.a.	1.08	9754
2		17.518	n.a.	64.86	594.5839	1129.64	MB*	0.442	n.a.	n.a.	8689
最大值			0.0000	64.86	594.5839	1129.64		0.442	0.00	1.08	9754
最小值			0.0000	35.14	322.1469	778.04		0.399	0.00	1.08	8689
总和			0.0000	100.00	916.7308	1907.67					



37.6% of L-TME initially used

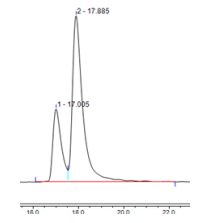


40.7% of L-TME recovered

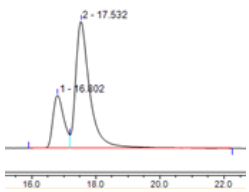
Signal Retention time sample area% area height type half peak wide - - -

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		16.822	n.a.	31.22	159.2300	395.16	BM *	0.375	n.a.	1.13	11129
2		17.585	n.a.	68.78	350.7180	698.14	MB*	0.418	n.a.	n.a.	9786
最大值			0.0000	68.78	350.7180	698.14		0.418	0.00	1.13	11129
最小值			0.0000	31.22	159.2300	395.16		0.375	0.00	1.13	9786
总和			0.0000	100.00	509.9479	1093.30					

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		16.877	n.a.	29.66	201.4859	481.71	BM *	0.408	n.a.	1.03	9476
2		17.628	n.a.	70.34	477.7727	877.88	MB*	0.456	n.a.	n.a.	8289
最大值			0.0000	70.34	477.7727	877.88		0.456	0.00	1.03	9476
最小值			0.0000	29.66	201.4859	481.71		0.408	0.00	1.03	8289
总和			0.0000	100.00	679.2585	1359.59					



47.9% of L-TME initially used



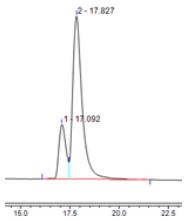
51.4% of L-TME recovered

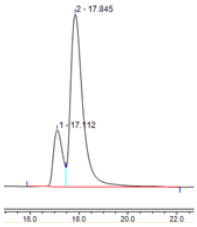
Signal Retention time sample area% area height type half peak wide - - -

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		17.005	n.a.	26.06	131.8176	304.98	BM *	0.397	n.a.	1.25	10183
2		17.885	n.a.	73.94	373.9723	695.38	MB*	0.436	n.a.	n.a.	9306
最大值			0.0000	73.94	373.9723	695.38		0.436	0.00	1.25	10183
最小值			0.0000	26.06	131.8176	304.98		0.397	0.00	1.25	9306
总和			0.0000	100.00	505.7899	1000.36					

Table S14 continued

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		16.802	n.a.	24.28	174.9958	445.25	BM *	0.380	n.a.	1.07	10845
2		17.532	n.a.	75.72	545.8648	1064.34	MB*	0.428	n.a.	n.a.	9287
最大值			0.0000	75.72	545.8648	1064.34		0.428	0.00	1.07	10845
最小值			0.0000	24.28	174.9958	445.25		0.380	0.00	1.07	9287
总和			0.0000	100.00	720.8606	1509.58					





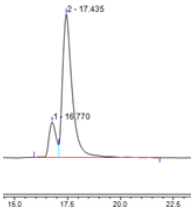
60.2% of L-TME initially used

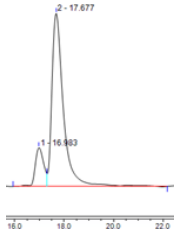
61.7% of L-TME recovered

Signal Retention time sample area% area height type half peak wide - - -

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		17.092	n.a.	19.91	144.3525	351.13	BM *	0.408	n.a.	0.98	9734
2		17.827	n.a.	80.09	580.7376	1049.80	MB*	0.475	n.a.	n.a.	7787
最大值			0.0000	80.09	580.7376	1049.80		0.475	0.00	0.98	9734
最小值			0.0000	19.91	144.3525	351.13		0.408	0.00	0.98	7787
总和			0.0000	100.00	725.0901	1400.92					

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		17.112	n.a.	19.15	99.4853	233.82	BM *	0.431	n.a.	0.93	8715
2		17.845	n.a.	80.85	419.8940	714.23	MB*	0.502	n.a.	n.a.	7002
最大值			0.0000	80.85	419.8940	714.23		0.502	0.00	0.93	8715
最小值			0.0000	19.15	99.4853	233.82		0.431	0.00	0.93	7002
总和			0.0000	100.00	519.3793	948.04					





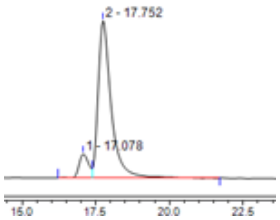
69.8% of L-TME initially used

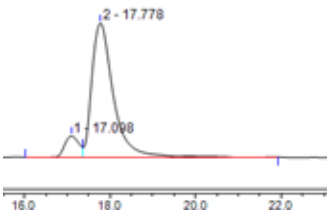
71.8% of L-TME recovered

Signal Retention time sample area% area height type half peak wide - - -

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		16.770	n.a.	15.10	187.0141	489.44	BM *	0.383	n.a.	0.93	10613
2		17.435	n.a.	84.90	1051.3968	1986.90	MB*	0.458	n.a.	n.a.	8040
最大值			0.0000	84.90	1051.3968	1986.90		0.458	0.00	0.93	10613
最小值			0.0000	15.10	187.0141	489.44		0.383	0.00	0.93	8040
总和			0.0000	100.00	1238.4109	2476.34					

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		16.983	n.a.	14.08	49.6434	125.16	BM *	0.388	n.a.	0.97	10604
2		17.677	n.a.	85.92	302.8691	560.61	MB*	0.452	n.a.	n.a.	8462
最大值			0.0000	85.92	302.8691	560.61		0.452	0.00	0.97	10604
最小值			0.0000	14.08	49.6434	125.16		0.388	0.00	0.97	8462
总和			0.0000	100.00	352.5126	685.77					





80.1% of L-TME initially used

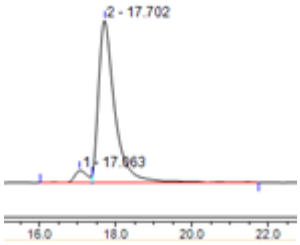
81.2% of L-TME recovered

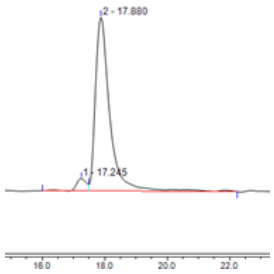
Signal Retention time sample area% area height type half peak wide - - -

Table S14 continued

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		17.078	n.a.	9.93	58.3722	156.05	BM *	0.375	n.a.	0.98	11470
2		17.752	n.a.	90.07	529.7426	1032.46	MB*	0.436	n.a.	n.a.	9194
最大值			0.0000	90.07	529.7426	1032.46		0.436	0.00	0.98	11470
最小值			0.0000	9.93	58.3722	156.05		0.375	0.00	0.98	9194
总和			0.0000	100.00	588.1148	1188.51					

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		17.098	n.a.	9.38	50.0182	131.21	BM *	0.413	n.a.	0.87	9495
2		17.778	n.a.	90.62	483.3435	831.36	MB*	0.507	n.a.	n.a.	6818
最大值			0.0000	90.62	483.3435	831.36		0.507	0.00	0.87	9495
最小值			0.0000	9.38	50.0182	131.21		0.413	0.00	0.87	6818
总和			0.0000	100.00	533.3617	962.57					





89.1% of L-TME initially used

90.6% of L-TME recovered

Signal Retention time sample area% area height type half peak wide - - -

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		17.063	n.a.	5.44	27.5114	71.68	BM *	0.377	n.a.	0.94	11323
2		17.702	n.a.	94.56	477.8001	959.20	MB*	0.421	1.75	n.a.	9790
最大值			0.0000	94.56	477.8001	959.20		0.421	1.75	0.94	11323
最小值			0.0000	5.44	27.5114	71.68		0.377	1.75	0.94	9790
总和			0.0000	100.00	505.3115	1030.88					

峰序号	峰名称	保留时间 min	样品量 n.a.	相对峰面积 %	峰面积 mAU*min	峰高 mAU	类型	峰宽 (50%) min	不对称度 EP	分离度 EP	塔板数 EP
1		17.245	n.a.	4.69	15.8514	42.65	BM *	n.a.	n.a.	n.a.	n.a.
2		17.880	n.a.	95.31	321.8258	599.47	MB*	0.446	1.69	n.a.	8897
最大值			0.0000	95.31	321.8258	599.47		0.446	1.69	0.00	8897
最小值			0.0000	4.69	15.8514	42.65		0.446	1.69	0.00	8897
总和			0.0000	100.00	337.6772	642.12					

Table S14 continued

These data from Tables S13 to S15 (three series of experiments) are summarized in Table S15

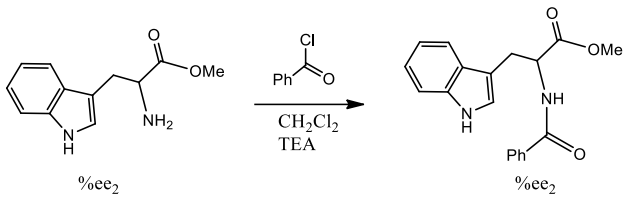
Table S15 The summaries from the Tables S13 to S14 [a,b]

Entry	%ee$_1$ of L-TME initially used			%ee$_2$ of L- TME recovered			Δ%ee (%ee$_2$-%ee$_1$)		
	1st series	2nd series	3rd series	1st series (yield) [b]	2nd series	3rd series	1st series	2nd series	3rd series
1	10.3	10.6	11.3	11.8 (62%)	11.8 (61%)	12.2 (55%)	1.5	1.2	0.9
2	18.7	17.9	17.9	20.9 (60%)	19.0 (56%)	18.8 (53%)	2.2	1.1	0.9
3	27.1	26.5	27.4	29.4 (58%)	28.8 (55%)	29.7 (55%)	2.3	2.3	2.3
4	36.6	36.7	37.6	42.2 (59%)	41.5 (55%)	40.7 (51%)	5.6	4.8	3.1
5	47.7	48.4	47.9	50.2 (56%)	54.2 (56%)	51.4 (52%)	2.5	5.8	3.5
6	57.8	59.0	60.2	58.4 (60%)	64.4 (62%)	61.7 (53%)	0.6	5.4	1.5
7	69.4	67.2	69.8	70.3 (64%)	69.5 (61%)	71.8 (53%)	0.9	2.3	2.0
8	80.5	79.9	80.1	82.1 (62%)	82.5 (63%)	81.2 (56%)	1.6	2.6	1.1
9	90.4	90.2	89.1	91.2 (60%)	90.22 (56%)	90.6 (52%)	0.8	0.0 (0.04)	1.5

[a]The equilibrium time was 2 h in the first series of reactions, 10 h in the second series, and 36 h. in the third series. [b]Table S13 data are listed in the "%ee$_1$ 1st series" column; Table S14 data are listed in the 2nd series of column; the Table S15 data are listed in 3rd series of column. The data in parentheses are the yields to the recovered material of **1** and **2**.

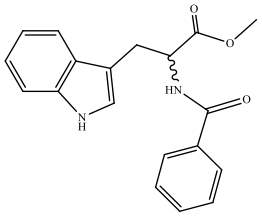
Item 9. Analysis of %ee values of (*S*)-benzamide via HPLC

To make sure the original $\%ee_1$ values, the L-TME prepared with about 1%ee was converted into the corresponding benzamide as illustrated below. Theoretically, the %ee of the L-TME will equal to the (*S*)- bezamide's %ee.



$\%ee_2$ $\%ee_2$

The amide structure was identified by NMR spectra below (Figures S11 and S12)



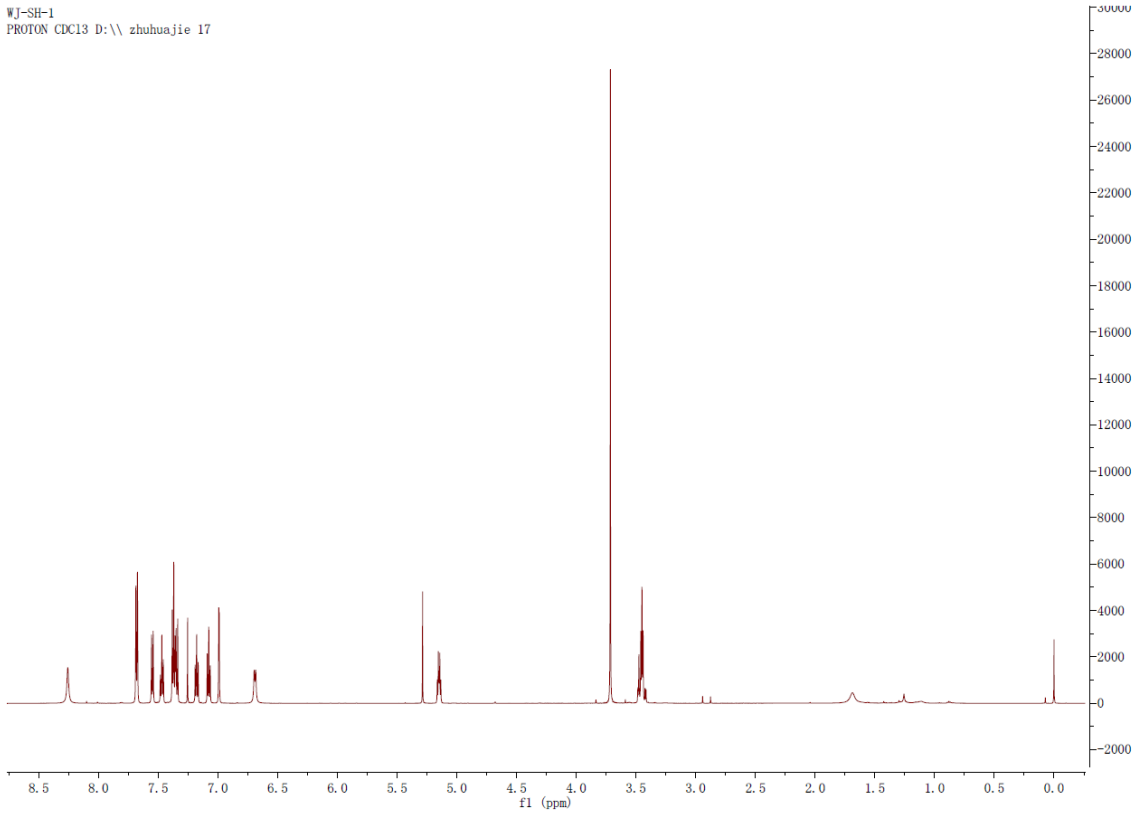


Fig. S9 The ^{1}H NMR spectra for the structure of methyl 2-benzamido-3-(1H-indol-3-yl)propanoate

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.26 (s, 1 H), 7.68 (d, *J* = 7.9 Hz, 2 H), 7.55 (d, *J* = 7.9 Hz, 1 H), 7.47 (t, *J* = 7.4 Hz, 1 H), 7.40 – 7.32 (m, 3 H), 7.18 (t, *J* = 7.6 Hz, 1 H), 7.08 (t, *J* = 7.5 Hz, 1 H), 6.99 (d, *J* = 2.1 Hz, 1 H), 6.69 (d, *J* = 7.4 Hz, 1 H), 5.15 (dt, *J* = 7.5, 5.3 Hz, 1 H), 3.71 (s, 3 H), 3.45 (t, *J* = 5.8 Hz, 2 H).

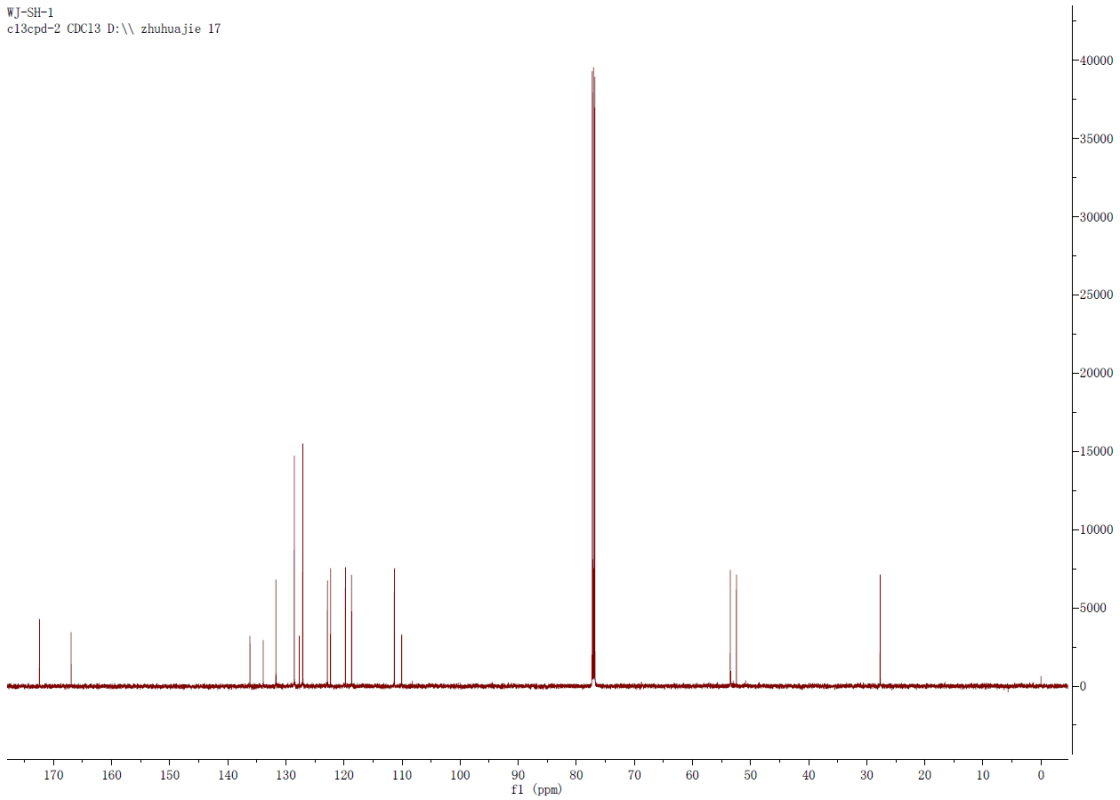
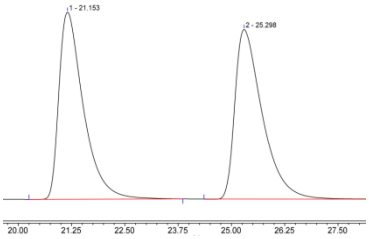


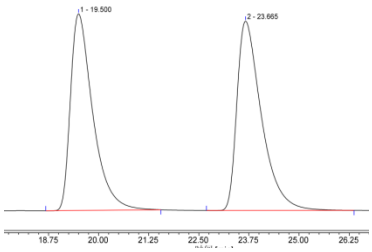
Fig. S10 The ^{13}C NMR spectra for the structure of methyl 2-benzamido-3-(1H-indol-3-yl)propanoate

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.42 (s), 166.96 (s), 136.17 (s), 133.89 (s), 131.71 (s), 128.55 (s), 127.69 (s), 127.09 (s), 122.84 (s), 122.30 (s), 119.74 (s), 118.68 (s), 111.32 (s), 110.06 (s), 53.50 (s), 52.43 (s), 27.69 (s). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.42 (s), 166.96 (s), 136.17 (s), 133.89 (s), 131.71 (s), 128.55 (s), 127.69 (s), 127.09 (s), 122.84 (s), 122.30 (s), 119.74 (s), 118.68 (s), 111.32 (s), 110.06 (s), 53.50 (s), 52.43 (s), 27.69 (s).

Table S16 The %ee values of (*S*)-benzamide analyzed by HPLC using a Chiralcel-IA column and mixtures of petroleum and isopropanol (v/v, 60:40) (Specific HPLC plots are listed below. The compound is pure enough for HPLC analysis. The integration time ranges that were used for %ee value calculations are strictly held the same in different measurements.)

The %ee values of (*S*)-amide derived from the stating material prepared with a 0.7%ee of L-TME before the Pictet-Spengler reaction using 5.0 g in the first biomimic chiral enrichment experiments	The %ee for (*S*)-amide derived from the recovered L-TME from the second Pictet-Spengler reaction by **using 5.00 g of L-TME** as the starting material (after the reactions)





Entry Retention Time Area Height Relative area (%)

积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		21.153	576.803	865.172	49.64	52.43	n.a.
2		25.298	585.270	784.849	50.36	47.57	n.a.
总和:			**1162.074**	**1650.021**	**100.00**	**100.00**	

$\%ee_1$ = 0.7%

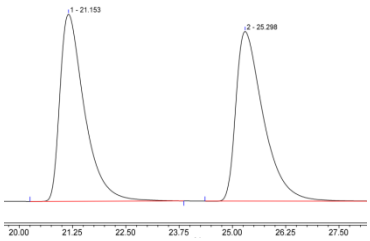
Entry Retention Time Area Height Relative area (%)

积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		19.500	319.148	493.189	48.65	50.94	n.a.
2		23.665	336.903	474.953	51.35	49.06	n.a.
总和:			**656.050**	**968.141**	**100.00**	**100.00**	

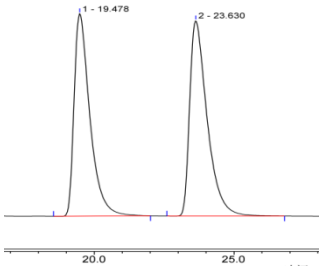
$\%ee_2$ = 2.7%

The second time to do the amplification experiment



$\%ee_1$ = 0.7%

The %ee for (*S*)-amide derived from the recovered L-TME from the second condensation reaction **using 11.50 g of L-TME**



$\%ee_2$ = 3.3%

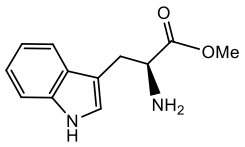
Entry	Retention Time	Area	Height	Relative area (%)

积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		19.478	407.053	621.259	48.36	50.90	n.a.
2		23.630	434.647	599.211	51.64	49.10	n.a.
总和:			**841.700**	**1220.470**	**100.00**	**100.00**	

$\%ee_2$ = 3.3%

Item 10. The specific optical rotations for different L-TME samples

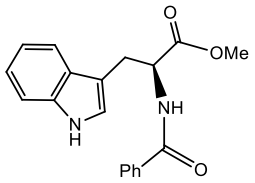


A. Optically pure L-TME with 99%ee had a specific optical rotation of +18.0 in chloroform.

B. L-TME prepared as 0.8%ee was measured in chloroform. Its OR was +0.157 with a concentration of 126.7 mg/ml. This is the smallest concentration that can be used to record α values for specific optical rotation calculation. The corresponding $\%ee_1$ is 0.87% (near 0.9%). The α value cannot be recorded for concentrations lower than this.

C. After two Pictet-Spengler reactions, the recovered L-TME had an optical rotation $[\alpha]_D$ of 0.58 using a concentration of 34 mg/ml. This is also the smallest concentration to record α values for the specific optical rotation calculation. The corresponding $\%ee_1$ is 3.2%. A higher concentration (76.5 mg/ml) gave a specific optical rotation of 0.65. This corresponds to a $\%ee_1$ of 3.5%.

The specific optical rotation values ($[\alpha]_D$) of (*S*)-benzamide derived from L-TME



A. Optically pure (*S*)-benzamide from L-TME with a >99%ee has an OR value of 80.2 in chloroform.

B. The OR value of (*S*)-benzamide derived from L-TME that was prepared as the starting material with an 0.8%ee: the first time, $[\alpha]_D = 0.88$, concentration is 50.2 mg/ml. Its corresponding %ee is 1.1%; the second measured $[\alpha]_D = 0.84$, the concentration was 19 mg/ml. Its corresponding %ee is 1.05%.

C. The OR value of (*S*)-benzamide derived from L-TME (5.0 g) that was recovered from the second Pictet-Spengler reaction. The $[\alpha]_D$ value was +2.65 with a concentration of 8 mg/ml. Its corresponding %ee is 3.3%.

D. The OR value of (*S*)-benzamide derived from L-TME (11.50 g) that was recovered from the second Pictet-Spenglar reaction. The $\alpha]_D$ value was +2.38 with a concentration of 6 mg/ml. Its corresponding %ee is 2.96%ee, which is near 3.0%ee and this value is used in the paper.

Item 11. The energy for the compounds 5 and 6 at the B3LYP/6-31G(d) level

The products formed in the reactions have six stereogenic centers. Thus, it has 64 enantiomers (2^6). Theoretically, half of 64 enantiomers need to be investigated for their relative energy study.

Optimizations for all 32 compounds were performed at the B3LYP/6-31G(d) level in the gas phase first. The energy data in au and their relative energy values in kcal/mol are listed below the corresponding geometries. It could be found that compound DL-4 had the lowest energy among all the 32 compounds. LL-9 had the lowest energy in series of 16 compounds named as LL-1 to LL-16. All the compounds with relative energy from 0 to 4.0 kcal/mol were further used in optimizations again at the higher level, such as using 6-311+G(d) and 6-311++G(2d,p) level in the gas phase and in liquid, respectively. These compounds have the names of DL-4, DL-6, DL-9, DL-11, DL-13, LL-4, LL-6, LL-9. The specific data are illustrated in the corresponding sections below.

Table S17 The total 32 enantiomers optimized at the B3LYP/6-31G(d) level in the gas phase and their energy values

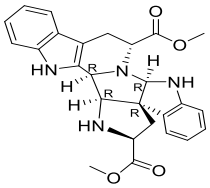
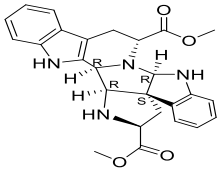
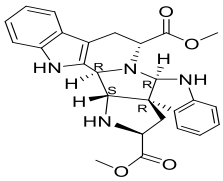
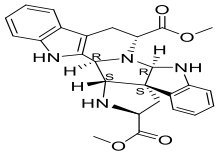
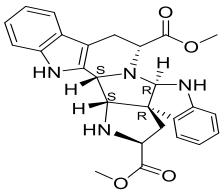
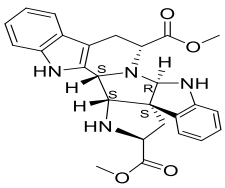
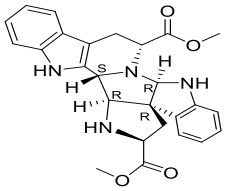
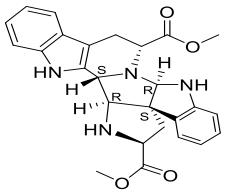
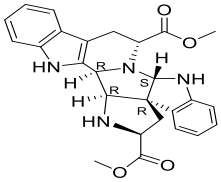
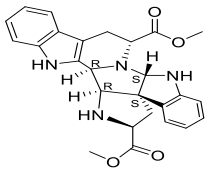
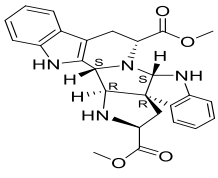
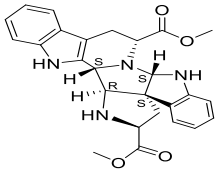
			
DL-1 E=-1526.300328 (au) ΔE=25.367 kcal/mol	DL-2 E=-1526.305275 (au) ΔE=22.264 kcal/mol	DL-3 E=-1526.225389 (au) ΔE=72.392 kcal/mol	DL-4((R,S)-**5**(1) in text) E=-1526.340755 (au) ΔE=0.000 kcal/mol
			
DL-5 E=-1526.226604 (au) ΔE=71.629 kcal/mol	DL-6 E=-1526.339501 (au) ΔE=0.786 kcal/mol	DL-7 E=-1526.304280 (au) ΔE=22.888 kcal/mol	DL-8 E=-1526.316202 (au) ΔE=15.407 kcal/mol
			
DL-9 E=-1526.340172 (au) ΔE=0.365 kcal/mol	DL-10 E=-1526.221978 (au) ΔE=74.532 kcal/mol	DL-11 E=-1526.337495 (au) ΔE=2.045 kcal/mol	DL-12 E=-1526.228845 (au) ΔE=70.223 kcal/mol

Table S17 continued

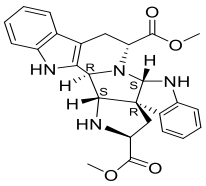
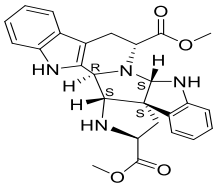
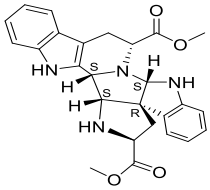
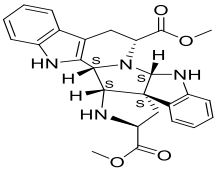
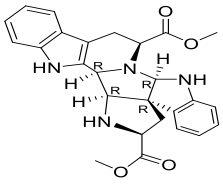
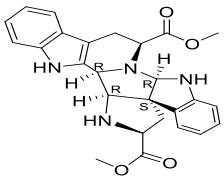
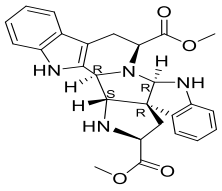
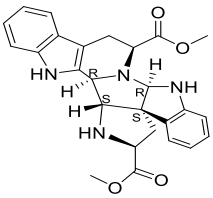
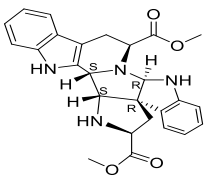
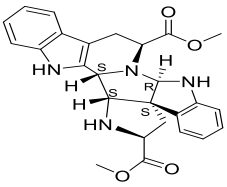
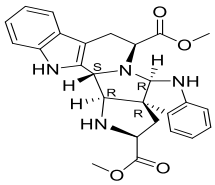
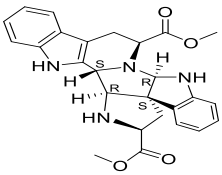
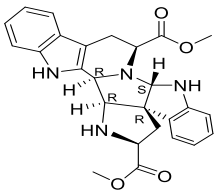
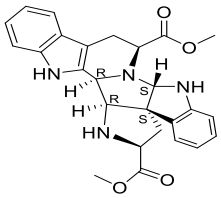
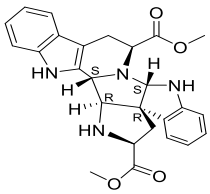
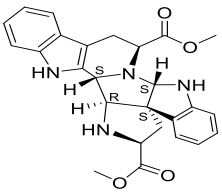
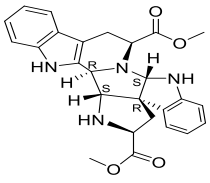
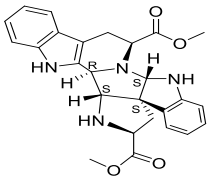
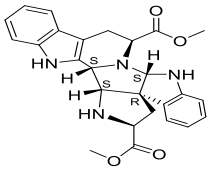
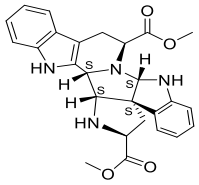
			
DL-13 E=-1526.337496 (au) ΔE=1.803	DL-14 E=-1526.228846 (au) ΔE=69.981	DL-15 E=-1526.312960 (au) ΔE=17.120	DL-16 E=-1526.307145 (au) ΔE=20.849
			
LL-1 E=-1526.301140 (au) ΔE=24.859 kcal/mol	LL-2 E=-1526.307755 (au) ΔE=20.707 kcal/mol	LL-3 E=-1526.226303 (au) ΔE=71.818 kcal/mol	LL-4 E=-1526.338153 (au) ΔE=1.632 kcal/mol
			
LL-5 E=-1526.222192 (au) ΔE=74.398 kcal/mol	LL-6 E=-1526.338075 (au) ΔE=1.681 kcal/mol	LL-7 E=-1526.305053 (au) ΔE=22.403 kcal/mol	LL-8 E=-1526.317506 (au) ΔE=14.588 kcal/mol
			
LL-9 E=-1526.340370 (au) ΔE=0.241 kcal/mol	LL-10 E=-1526.225784 (au) ΔE=72.144 kcal/mol	LL-11 E=-1526.333614 (au) ΔE=4.480 kcal/mol	LL-12 E=-1526.228257 (au) ΔE=70.592 kcal/mol

Table S17 continued

			
LL-13 E=-1526.315686 (au) ΔE=15.730 kcal/mol	LL-14 E=-1526.310696 (au) ΔE=18.862 kcal/mol	LL-15 E=-1526.309895 (au) ΔE=19.365 kcal/mol	LL-16 E=-1526.306535 (au) ΔE=21.473 kcal/mol

Note: The numbers of these compounds are not the numbers which appeared in Text. The compound numbers used in the published text are listed behind the specific numbers of the compounds used in the SM, and labeled in red for clarity. For example, DL-4, DL-9 and LL-6 are the compound numbers for the series of compounds used here for energy investigations. They correspond to the compound numbers (*R*,*S*)-**5**(*1*)*,* (*R*,*S*)-**5**(*2*)*, and* (*S*,*S*)-**6**(*1*) *used in the text.*

Item 12 Computations of six isomers of 5 and 6: Energies, coordinates at three different quantum levels

All B3LYP/6-31G(d)-optimized geometries with relative energy from 0-4 kcal/mol were optimized at the B3LYP/6-311+G(d) level in the gas phase first. DL-11 and DL-13 were not computed furthermore in higher levels since its relative energy is over 4.0 kcal/mol that means its Boltzmann fraction is small. Then, these compounds named as DL-4, DL-6, DL-9 LL-4, L,L-6 and LL-9 were used in further calculations at the levels of B3LYP/6-311++G(2d,p) in the gas phase and in solution (CH_2Cl_2) using PCM model. The lowest energy compound is DL-4. LL-6 had the second lowest energy. The specific data are listed below the corresponding geometries.

The data of E_1, ΔE_1 were obtained at the B3LYP/ 6-311+G(d) level in the gas phase

The data of E_2, ΔE_2 were obtained at the B3LYP/ 6-311++G(2d,p) level in the gas phase

The data of E_3, ΔE_3 were obtained at the B3LYP/ 6-311++G(2d,p) level in CH_2Cl_2 using PCM model.

Energy unit of E is in a.u.

Delat E unit is in kcal/mol.

Table S18 The predicted energy for the eight compounds

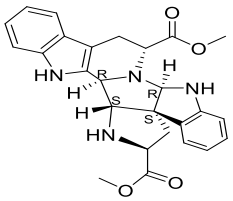
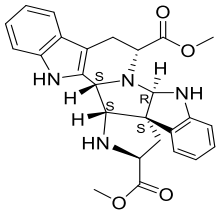
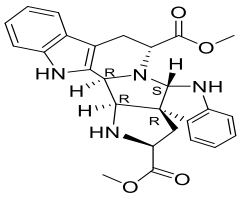
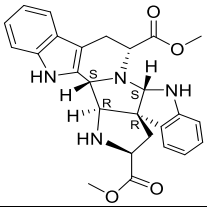
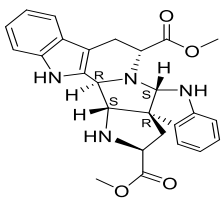
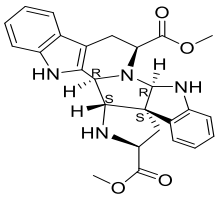
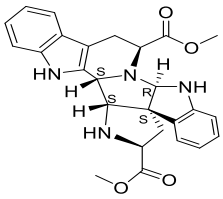
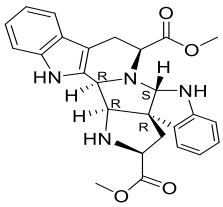
		
DL-4((*R*,*S*)-**3**(*1*) in paper) E_1=-1526.710662 ΔE_1=0.000 E_2=-1526.788189 ΔE_2=0.000 E_3=-1526.804445 ΔE_3=0.000	DL-6 E_1=-1526.708812 ΔE_1=1.160 E_2=-1526.786158 ΔE_2=1.274 E_3=-1526.801796 ΔE_3=1.662	DL-9((*R*,*S*)-**3**(*2*) in paper) E_1=-1526.708990 ΔE_1=1.049 E_2=-1526.785996 ΔE_2=1.376 E_3=-1526.802090 ΔE_3=1.478
		
DL-11 E_1=-1526.704542 ΔE_1=3.839 The relative energy is too big, further computation was not performed	DL-13 E_1=-1526.687444 ΔE_1=14.568 The relative energy is too big, further computation was not performed	

Table S18 continued

		
LL-4 E_1=-1526.707144 ΔE_1=2.206 E_2=-1526.784365 ΔE_2=2.399 E_3=-1526.800037 ΔE_3=2.766	LL-6 ((S,S)-**4**(I) in paper) E_1=-1526.706464 ΔE_1=2.633 E_2=-1526.785940 ΔE_2=1.411 E_3=-1526.802362 ΔE_3=1.307	LL-9 E_1=-1526.708010 ΔE_1=1.664 E_2=-1526.784668 ΔE_2=2.209 E_3=-1526.800011 ΔE_3=2.782

Coordinates for the four low energy compounds (**5**(*1*), **5**(*2*) and **6**(*1*)) at the B3LYP/6-311++G(2d,p) level in CH_2Cl_2 using PCM.

Table S19 coordinate for (*R,S*)-**5**(*1*) in text (=DL-4 in the Table S18)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.130830	2.772989	-1.928590
2	6	0	-3.333208	1.802383	-1.327947
3	6	0	-3.835123	0.516465	-0.987206
4	6	0	-5.175571	0.219063	-1.265459
5	6	0	-5.971244	1.184670	-1.861449
6	6	0	-5.454190	2.448677	-2.189743
7	6	0	-2.745626	-0.209296	-0.393310
8	6	0	-1.663378	0.624160	-0.405329
9	7	0	-2.003047	1.839979	-0.957687
10	1	0	-1.374955	2.621855	-1.048824
11	6	0	-2.675177	-1.600540	0.161466
12	6	0	-1.430826	-1.752176	1.077147
13	6	0	-1.681704	-1.233944	2.505389
14	8	0	-2.755950	-1.826754	3.060022
15	6	0	-3.064834	-1.432484	4.411250
16	7	0	-0.285403	-1.152410	0.425776
17	6	0	-0.338500	0.286453	0.171672
18	6	0	0.915972	0.512047	-0.691442
19	1	0	-3.574509	-1.853284	0.725568
20	1	0	-2.585234	-2.335632	-0.645159
21	1	0	-1.239725	-2.824693	1.189455
22	1	0	-3.944524	-2.007725	4.687361
23	1	0	-2.230234	-1.661847	5.073046
24	1	0	-3.274795	-0.364405	4.453598
25	6	0	1.084971	-1.433491	0.862180
26	6	0	1.929648	-0.550178	-0.122433
27	6	0	3.043185	0.311495	0.517016
28	6	0	2.439353	1.744248	0.598965
29	6	0	3.508386	2.807625	0.476074
30	7	0	1.481209	1.848007	-0.506273
31	1	0	1.987343	2.149990	-1.334049
32	8	0	3.844745	3.319274	-0.564464
33	8	0	4.070407	3.081848	1.664129
34	6	0	5.152381	4.033552	1.641459
35	1	0	4.801802	4.993783	1.265113

36	1	0	5.481493	4.121672	2.673237
37	1	0	5.961459	3.671781	1.007806
38	1	0	3.915781	0.320000	-0.139324
39	1	0	3.361786	-0.064014	1.489823
40	1	0	1.926706	1.876450	1.554029
41	7	0	1.531568	-2.798589	0.617567
42	6	0	2.425625	-1.581888	-1.111859
43	6	0	3.089536	-1.418644	-2.315545
44	6	0	2.120174	-2.864752	-0.648397
45	6	0	3.435161	-2.544252	-3.067878
46	1	0	3.337661	-0.427801	-2.682185
47	6	0	2.453809	-3.994269	-1.387291
48	6	0	3.113490	-3.816661	-2.602840
49	1	0	3.949882	-2.426478	-4.013237
50	1	0	2.214306	-4.988762	-1.028427
51	1	0	3.380375	-4.686039	-3.192324
52	1	0	0.921739	-3.551679	0.900495
53	1	0	1.239141	-1.171977	1.915046
54	1	0	-3.734691	3.749145	-2.184130
55	1	0	-6.099677	3.183527	-2.655619
56	1	0	-7.009106	0.964129	-2.080958
57	1	0	-5.586829	-0.753711	-1.020608
58	8	0	-0.989935	-0.435075	3.087887
59	1	0	-0.204474	0.866239	1.100205
60	1	0	0.685958	0.338711	-1.741600

Table S20 coordinate for (*R,S*)-**5**(*2*) in text (=DL-9 in Table S18)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.601272	1.366254	2.159915
2	6	0	-3.607662	0.784033	1.377954
3	6	0	-3.864673	0.301830	0.068401
4	6	0	-5.164765	0.391535	-0.444443
5	6	0	-6.157681	0.963967	0.335052
6	6	0	-5.877592	1.450624	1.622141
7	6	0	-2.615302	-0.194724	-0.442036
8	6	0	-1.683460	-0.002573	0.534503
9	7	0	-2.272733	0.548923	1.658490
10	1	0	-1.755900	1.022854	2.381730

11	6	0	-2.298343	-0.815501	-1.767481
12	6	0	-0.894250	-1.468660	-1.790855
13	6	0	-0.911905	-2.965723	-1.439234
14	8	0	-1.578237	-3.229862	-0.305532
15	6	0	-1.602779	-4.610240	0.106793
16	7	0	0.037246	-0.691990	-0.981990
17	6	0	-0.269785	-0.459005	0.434826
18	6	0	0.858212	0.501485	0.850207
19	1	0	-3.049777	-1.563171	-2.039835
20	1	0	-2.325005	-0.052763	-2.553099
21	1	0	-0.513929	-1.447850	-2.813707
22	1	0	-2.192626	-4.628996	1.019239
23	1	0	-2.063849	-5.226909	-0.663868
24	1	0	-0.589821	-4.964818	0.294468
25	6	0	1.456976	-0.922102	-1.088161
26	6	0	2.081403	0.099448	-0.081191
27	6	0	2.517141	1.444180	-0.703080
28	6	0	1.816952	2.517969	0.174895
29	6	0	1.566283	3.798314	-0.591784
30	7	0	0.561044	1.914715	0.613277
31	1	0	-0.116781	2.013556	-0.140698
32	8	0	0.580361	4.018774	-1.249978
33	8	0	2.604658	4.646612	-0.485012
34	6	0	2.490916	5.870677	-1.236661
35	1	0	3.407060	6.419728	-1.036403
36	1	0	2.395225	5.654927	-2.300359
37	1	0	1.621431	6.437081	-0.905275
38	1	0	2.137906	1.521710	-1.725057
39	1	0	3.600573	1.559575	-0.732457
40	1	0	2.438863	2.748691	1.043680
41	7	0	1.939606	-2.238047	-0.611145
42	6	0	3.156133	-0.707228	0.603190
43	6	0	4.149621	-0.317383	1.485625
44	6	0	3.033284	-2.052255	0.233014
45	6	0	5.035421	-1.272473	1.990789
46	1	0	4.253947	0.722116	1.778497
47	6	0	3.911606	-3.013185	0.725978
48	6	0	4.912638	-2.605206	1.606029
49	1	0	5.820079	-0.975616	2.675370
50	1	0	3.820985	-4.053121	0.434307
51	1	0	5.606753	-3.341013	1.995198
52	1	0	1.978684	-2.983890	-1.292096
53	1	0	1.768509	-0.758218	-2.124778
54	1	0	-4.390066	1.736659	3.156551

55	1	0	-6.672579	1.896957	2.207364
56	1	0	-7.166458	1.041586	-0.052517
57	1	0	-5.393046	0.025332	-1.438967
58	8	0	-0.366576	-3.813546	-2.108320
59	1	0	-0.150166	-1.379404	1.027986
60	1	0	1.129490	0.359612	1.898716

Table S21 coordinate for (*S,S*)-**6**(*1*) in text (=LL-6 in Table S18)

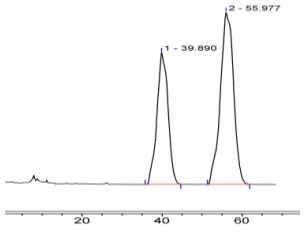
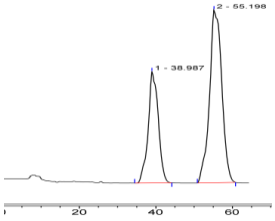
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.395942	1.893793	-0.897558
2	6	0	-3.358033	1.005575	-0.624994
3	6	0	-3.437964	0.054619	0.426680
4	6	0	-4.605074	-0.007588	1.198816
5	6	0	-5.640965	0.871641	0.924816
6	6	0	-5.535530	1.815526	-0.110274
7	6	0	-2.190291	-0.659972	0.429643
8	6	0	-1.422970	-0.132171	-0.574023
9	7	0	-2.134421	0.843961	-1.244718
10	1	0	-1.667808	1.522188	-1.829679
11	6	0	-1.726949	-1.790007	1.292672
12	6	0	-0.505634	-2.494090	0.631409
13	6	0	-0.949328	-3.549025	-0.384010
14	8	0	-1.650086	-4.521905	0.236973
15	6	0	-2.142773	-5.574108	-0.613270
16	7	0	0.458859	-1.575137	0.032128
17	6	0	-0.078248	-0.656631	-0.990779
18	6	0	1.063501	0.385135	-1.179914
19	1	0	-1.431244	-1.430016	2.285476
20	1	0	-2.519000	-2.521722	1.464160
21	1	0	0.015930	-3.060622	1.408701
22	1	0	-1.314524	-6.084160	-1.104221
23	1	0	-2.676237	-6.253990	0.045889
24	1	0	-2.812717	-5.167019	-1.369940
25	6	0	1.223419	-0.778240	1.002589
26	6	0	1.915397	0.308625	0.133066
27	6	0	1.868764	1.746192	0.698475
28	6	0	0.671337	2.407425	-0.032549
29	6	0	0.854662	3.902519	-0.173973

30	7	0	0.605716	1.769005	-1.351769
31	1	0	1.220412	2.278028	-1.980157
32	8	0	1.328478	4.442205	-1.144750
33	8	0	0.465194	4.552538	0.933179
34	6	0	0.663754	5.980221	0.926399
35	1	0	1.720233	6.214502	0.800356
36	1	0	0.094168	6.435725	0.117327
37	1	0	0.304684	6.326231	1.891703
38	1	0	2.791068	2.268193	0.434430
39	1	0	1.770593	1.770633	1.784053
40	1	0	-0.253082	2.217931	0.518364
41	7	0	2.319630	-1.511170	1.636252
42	6	0	3.314275	-0.252944	-0.009237
43	6	0	4.364050	0.148941	-0.817299
44	6	0	3.471618	-1.334251	0.860910
45	6	0	5.574154	-0.546935	-0.765041
46	1	0	4.254572	0.991187	-1.492913
47	6	0	4.668679	-2.038713	0.921891
48	6	0	5.715875	-1.631888	0.096695
49	1	0	6.399942	-0.245437	-1.397231
50	1	0	4.789123	-2.880736	1.593795
51	1	0	6.655559	-2.170825	0.129055
52	1	0	2.114942	-2.450221	1.948509
53	1	0	0.582762	-0.347019	1.781678
54	1	0	-4.321188	2.616858	-1.701683
55	1	0	-6.360685	2.491475	-0.300203
56	1	0	-6.547540	0.834273	1.517049
57	1	0	-4.697946	-0.728376	2.003524
58	8	0	-0.716724	-3.551827	-1.564146
59	1	0	-0.205241	-1.215906	-1.920352
60	1	0	1.651145	0.092239	-2.047833

Item 13. Analysis of %ee values of TME via HPLC

Table S22 The HPLC plots for the $\%ee_2$ of L-TME analysis (L-TME was converted into the corresponding benzamide for this measurement, see details at the end of this Table [a]).

Before the reaction [b]	After the reaction [b]
	
A %ee of 21.88% initial used ($\%ee_1$)	A %ee of 30.8% was recovered ($\%ee_2$)

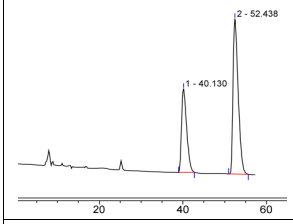
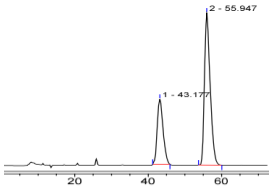
Signal Retention Area Height Area% Height%

积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		39.890	728.836	227.187	39.06	43.38	n.a.
2		55.977	1137.041	296.563	60.94	56.62	n.a.
总和:			**1865.877**	**523.750**	**100.00**	**100.00**	

积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		38.987	671.215	218.788	34.60	39.15	n.a.
2		55.198	1268.790	340.069	65.40	60.85	n.a.
总和:			**1940.005**	**558.857**	**100.00**	**100.00**	

Before the reaction	After the reaction
	
30.68% ($\%ee_1$)	38.86% ($\%ee_2$)

Signal Retention Area Height Area% Height%

积分结果

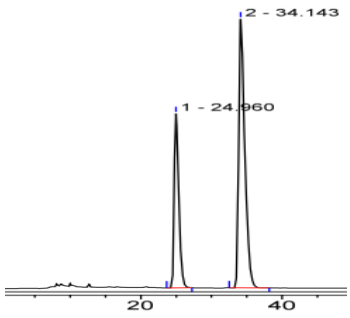
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		40.130	137.043	97.114	34.66	34.96	n.a.
2		52.438	258.347	180.644	65.34	65.04	n.a.
总和:			**395.390**	**277.758**	**100.00**	**100.00**	

积分结果

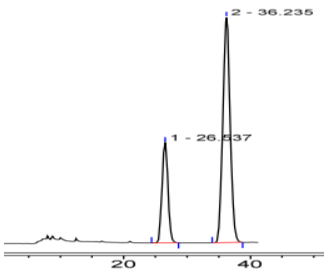
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		43.177	199.557	107.919	30.57	29.93	n.a.
2		55.947	453.250	252.701	69.43	70.07	n.a.
总和:			**652.807**	**360.619**	**100.00**	**100.00**	

[a] The reaction equation is illustrated at the end of this Table. [b] "Before the reaction" means the HPLC plot analyzed for $\%ee_1$ of L-TME prepared as the starting material. "After the reaction" means HPLC plot analyzed for the corresponding $\%ee_2$ of the L-TME that was recovered after the Pictet-Spengler reaction.

Table 22 continued



35.72% (%ee$_1$)

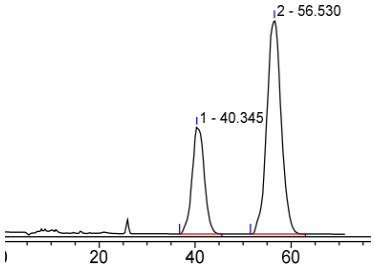


47.14% (%ee$_2$)

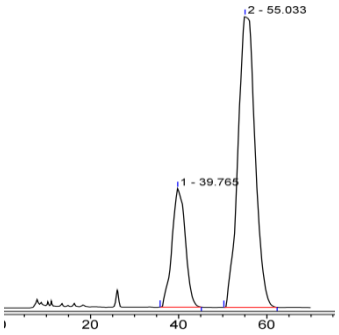
Signal Retention Area Height Area% Height%

积分结果							
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		24.960	372.346	510.605	32.14	39.32	n.a.
2		34.143	786.107	788.118	67.86	60.68	n.a.
总和:			**1158.454**	**1298.724**	**100.00**	**100.00**	

积分结果							
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		26.537	116.577	107.772	26.43	30.77	n.a.
2		36.235	324.431	242.514	73.57	69.23	n.a.
总和:			**441.008**	**350.285**	**100.00**	**100.00**	



40.3% (%ee$_1$)



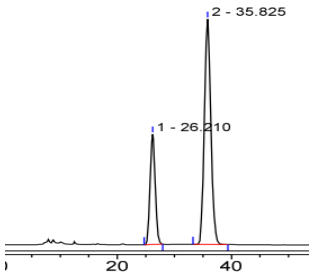
51.8% (%ee$_2$)

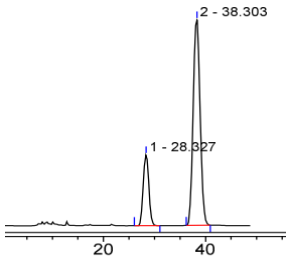
Signal Retention Area Height Area% Height%

积分结果							
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		40.345	624.678	211.733	29.81	33.37	n.a.
2		56.530	1470.814	422.791	70.19	66.63	n.a.
总和:			**2095.493**	**634.524**	**100.00**	**100.00**	

积分结果							
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		39.765	1242.053	355.084	24.10	28.95	n.a.
2		55.033	3911.881	871.264	75.90	71.05	n.a.
总和:			**5153.933**	**1226.348**	**100.00**	**100.00**	

Table S22 continued





44.22% (%ee$_1$)

56.48% (%ee$_2$)

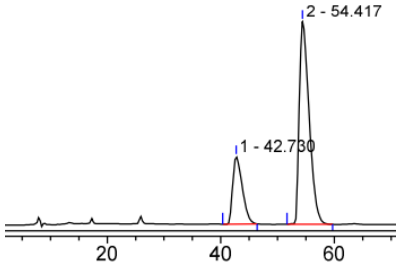
Signal Retention Area Height Area% Height%

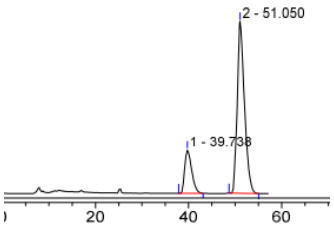
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		26.210	191.229	183.777	27.89	32.90	n.a.
2		35.825	494.458	374.839	72.11	67.10	n.a.
总和:			**685.686**	**558.616**	**100.00**	**100.00**	

积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		28.327	135.793	105.676	21.76	25.59	n.a.
2		38.303	488.379	307.220	78.24	74.41	n.a.
总和:			**624.173**	**412.896**	**100.00**	**100.00**	





51.2% (%ee$_1$)

60.8% (%ee$_2$)

Signal Retention Area Height Area% Height%

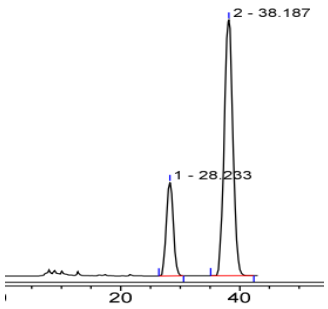
积分结果

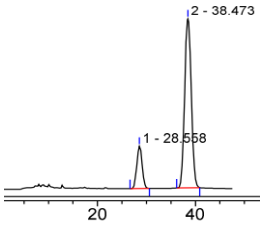
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		42.730	231.639	117.969	24.32	24.91	n.a.
2		54.417	720.708	355.587	75.68	75.09	n.a.
总和:			**952.347**	**473.556**	**100.00**	**100.00**	

积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		39.738	160.155	91.636	19.60	20.01	n.a.
2		51.050	657.028	366.306	80.40	79.99	n.a.
总和:			**817.183**	**457.942**	**100.00**	**100.00**	

Table S22 continued





54.92% (%ee$_1$) | 66.54% (%ee$_2$)

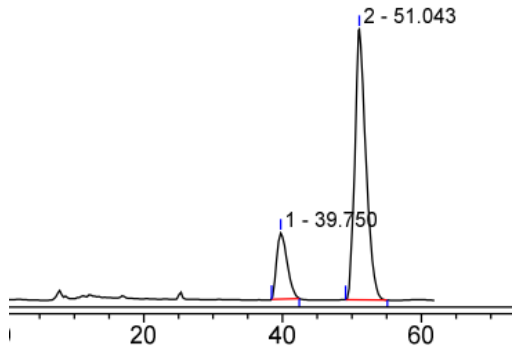
Signal Retention Area Height Area% Height%

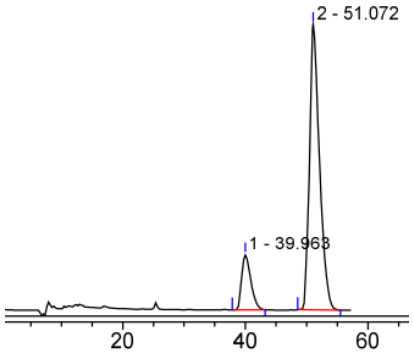
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		28.233	207.775	152.001	22.54	26.72	n.a.
2		38.187	714.191	416.881	77.46	73.28	n.a.
总和:			**921.965**	**568.882**	**100.00**	**100.00**	

积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		28.558	76.400	60.124	16.73	20.01	n.a.
2		38.473	380.236	240.316	83.27	79.99	n.a.
总和:			**456.636**	**300.440**	**100.00**	**100.00**	





62.3% (%ee$_1$) | 70.2% (%ee$_2$)

Signal Retention Area Height Area% Height%

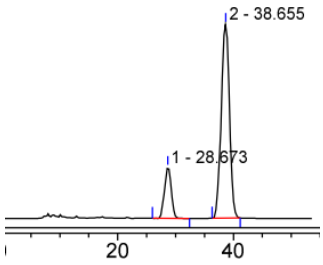
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		39.750	165.897	94.491	18.85	19.65	n.a.
2		51.043	713.963	386.455	81.15	80.35	n.a.
总和:			**879.860**	**480.946**	**100.00**	**100.00**	

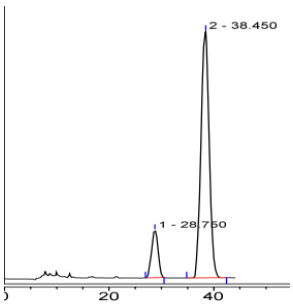
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		39.963	155.072	88.953	15.07	16.12	n.a.
2		51.072	874.067	462.817	84.93	83.88	n.a.
总和:			**1029.139**	**551.769**	**100.00**	**100.00**	

Table S22 continued



64.42% (%ee$_1$)

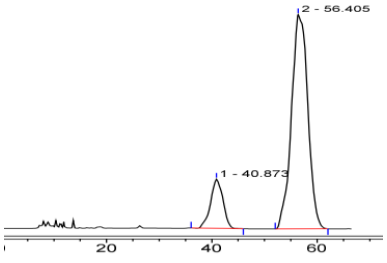


73.3% (%ee$_2$)

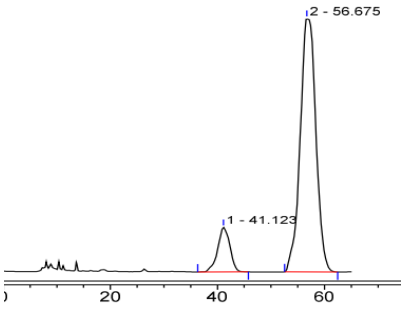
Signal Retention Area Height Area% Height%

积分结果							
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		28.673	76.697	56.020	17.79	20.79	n.a.
2		38.655	354.468	213.375	82.21	79.21	n.a.
总和:			**431.166**	**269.395**	**100.00**	**100.00**	

积分结果							
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		28.750	140.511	95.574	13.33	16.06	n.a.
2		38.450	913.419	499.400	86.67	83.94	n.a.
总和:			**1053.929**	**594.974**	**100.00**	**100.00**	



70.56% (%ee$_1$)



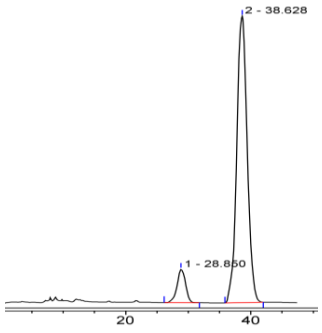
76.1% (%ee$_2$)

Signal Retention Area Height Area% Height%

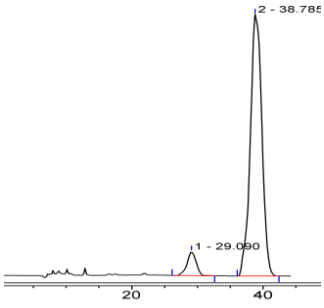
积分结果							
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		40.873	177.858	65.374	14.72	18.67	n.a.
2		56.405	1030.735	284.835	85.28	81.33	n.a.
总和:			**1208.593**	**350.209**	**100.00**	**100.00**	

积分结果							
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		41.123	121.370	46.048	11.95	14.93	n.a.
2		56.675	894.134	262.403	88.05	85.07	n.a.
总和:			**1015.504**	**308.452**	**100.00**	**100.00**	

Table S22 continued



82.8% (%ee$_1$)

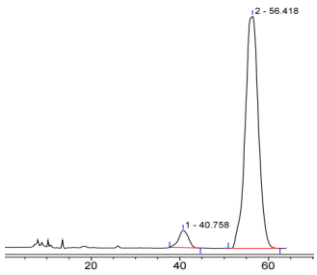


86.62% (%ee$_2$)

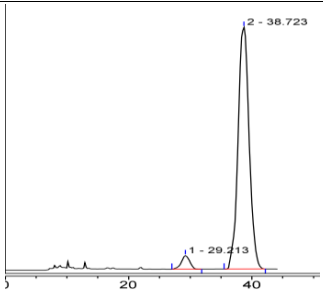
Signal Retention Area Height Area% Height%

积分结果							
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		28.850	102.349	65.139	8.60	10.43	n.a.
2		38.628	1087.488	559.502	91.40	89.57	n.a.
总和:			**1189.837**	**624.641**	**100.00**	**100.00**	

积分结果							
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		29.090	50.897	31.465	6.69	8.33	n.a.
2		38.785	710.409	346.327	93.31	91.67	n.a.
总和:			**761.306**	**377.792**	**100.00**	**100.00**	



89.6% (%ee$_1$)



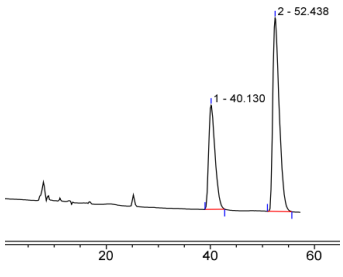
91.92% (%ee$_2$)

Signal Retention Area Height Area% Height%

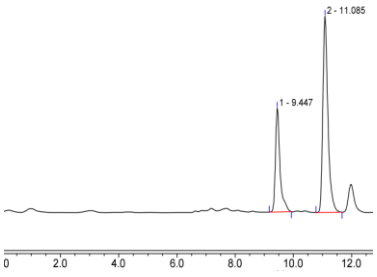
积分结果							
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		40.758	63.483	25.114	5.20	6.97	n.a.
2		56.418	1157.243	335.298	94.80	93.03	n.a.
总和:			**1220.726**	**360.412**	**100.00**	**100.00**	

积分结果							
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		29.213	67.104	42.394	4.04	5.26	n.a.
2		38.723	1594.298	763.380	95.96	94.74	n.a.
总和:			**1661.402**	**805.774**	**100.00**	**100.00**	

Table S22 continued



30.68% (%ee$_1$)



35.62% (%ee$_2$)

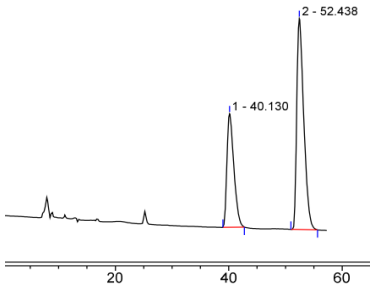
Signal Retention Area Height Area% Height%

积分结果

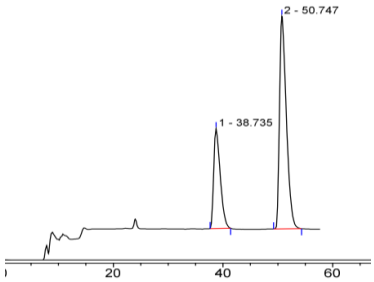
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		40.130	137.043	97.114	34.66	34.96	n.a.
2		52.438	258.347	180.644	65.34	65.04	n.a.
总和:			**395.390**	**277.758**	**100.00**	**100.00**	

积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		9.447	98.745	543.999	32.19	34.60	n.a.
2		11.085	208.017	1028.264	67.81	65.40	n.a.
总和:			**306.762**	**1572.263**	**100.00**	**100.00**	



30.68% (%ee$_1$)



38.12% (%ee$_2$)

Signal Retention Area Height Area% Height%

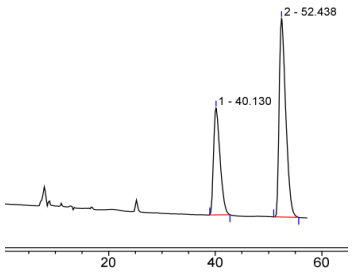
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		40.130	137.043	97.114	34.66	34.96	n.a.
2		52.438	258.347	180.644	65.34	65.04	n.a.
总和:			**395.390**	**277.758**	**100.00**	**100.00**	

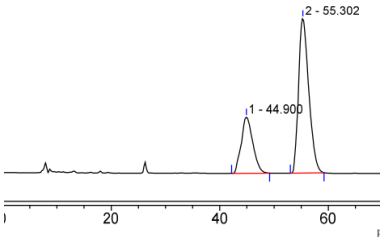
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		38.735	124.057	89.835	30.94	31.94	n.a.
2		50.747	276.850	191.433	69.06	68.06	n.a.
总和:			**400.907**	**281.268**	**100.00**	**100.00**	

Table S22 continued



30.68% (%ee$_1$)



41.86% (%ee$_2$)

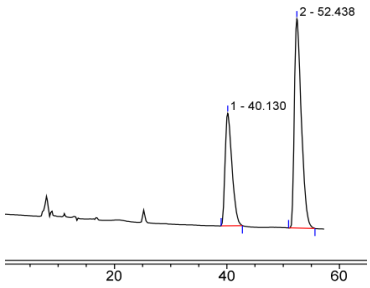
Signal Retention Area Height Area% Height%

积分结果

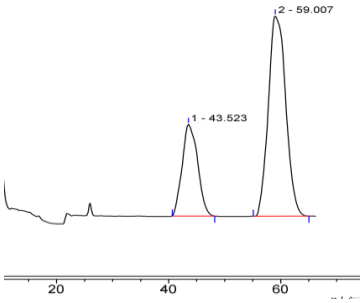
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		40.130	137.043	97.114	34.66	34.96	n.a.
2		52.438	258.347	180.644	65.34	65.04	n.a.
总和:			**395.390**	**277.758**	**100.00**	**100.00**	

积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		42.095	463.147	210.820	29.37	27.50	n.a.
2		54.595	1113.572	555.678	70.63	72.50	n.a.
总和:			**1576.719**	**766.498**	**100.00**	**100.00**	



30.68% (%ee$_1$)



42.22% (%ee$_2$)

Signal Retention Area Height Area% Height%

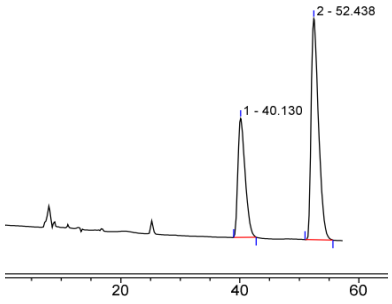
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		40.130	137.043	97.114	34.66	34.96	n.a.
2		52.438	258.347	180.644	65.34	65.04	n.a.
总和:			**395.390**	**277.758**	**100.00**	**100.00**	

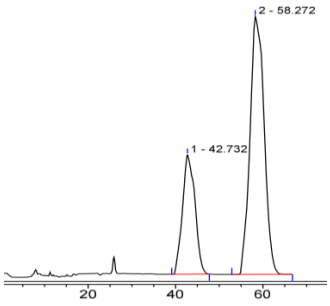
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		43.523	444.496	138.693	28.89	31.42	n.a.
2		59.007	1094.313	302.786	71.11	68.58	n.a.
总和:			**1538.808**	**441.479**	**100.00**	**100.00**	

Table S22 continued



30.68% (%ee$_1$)



42.06% (%ee$_2$)

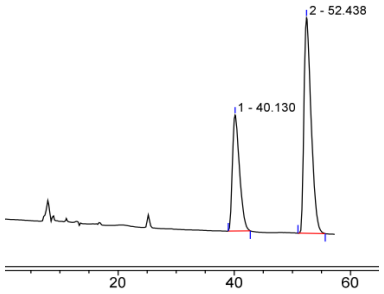
Signal Retention Sample Height Area% Height%

积分结果

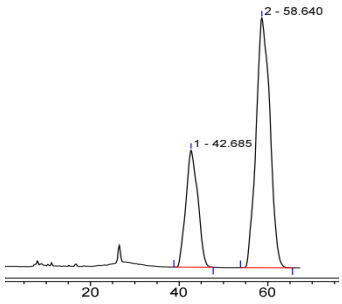
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		40.130	137.043	97.114	34.66	34.96	n.a.
2		52.438	258.347	180.644	65.34	65.04	n.a.
总和:			**395.390**	**277.758**	**100.00**	**100.00**	

积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		42.732	493.065	148.493	28.97	31.60	n.a.
2		58.272	1208.632	321.363	71.03	68.40	n.a.
总和:			**1701.698**	**469.857**	**100.00**	**100.00**	



30.68% (%ee$_1$)



42.5% (%ee$_2$)

Signal Retention Area Height Area% Height%

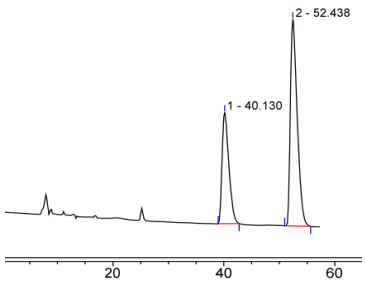
积分结果

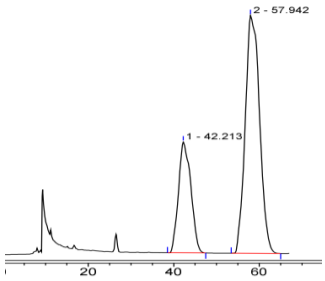
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		40.130	137.043	97.114	34.66	34.96	n.a.
2		52.438	258.347	180.644	65.34	65.04	n.a.
总和:			**395.390**	**277.758**	**100.00**	**100.00**	

积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		42.685	316.308	101.181	28.75	31.88	n.a.
2		58.640	783.878	216.213	71.25	68.12	n.a.
总和:			**1100.186**	**317.394**	**100.00**	**100.00**	

Table S22 continued





30.68% (%ee$_1$)

42.64% (%ee$_2$)

Signal Retention Area Height Area% Height%

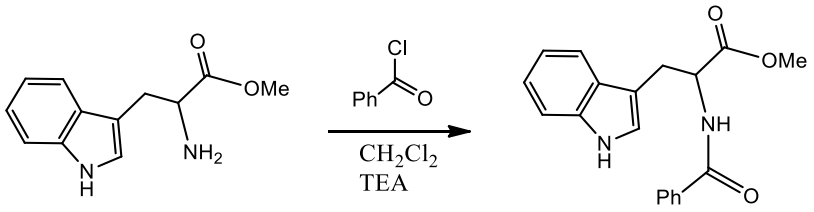
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		40.130	137.043	97.114	34.66	34.96	n.a.
2		52.438	258.347	180.644	65.34	65.04	n.a.
总和:			**395.390**	**277.758**	**100.00**	**100.00**	

积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		42.213	655.890	195.229	28.68	31.81	n.a.
2		57.942	1630.929	418.424	71.32	68.19	n.a.
总和:			**2286.819**	**613.653**	**100.00**	**100.00**	

[a] It was found that the benzamide could be well isolated by chiral column. The L-TME with %ee$_2$ was converted into the corresponding amide as illustrated below. Theoretically, the %ee value of the benzamide will be the same as that of the L-TME (%ee$_2$).



%ee$_2$ %ee$_2$

The amide structure was identified by NMR spectra.

Item 14. The %ee$_2$ values of TME via HPLC (Table S23)

Table 23A The %ee$_2$ changes when starting material %ee$_1$ changes from 6.1% to 89.6% summarized from Table S22.

%ee$_1$	%ee$_2$	Δ%ee
6.1	11.7	5.6
9.3	15.8	6.5
21.9	30.8	8.9
30.6	38.9	8.3
35.7	47.1	11.4
40.3	51.8	10.5
44.2	56.5	12.3
51.2	60.8	9.6
54.92	66.54	11.6
62.3	70.2	7.9
64.4	73.3	8.9
70.5	76.1	5.6
82.8	86.6	3.8
89.6	91.9	2.3

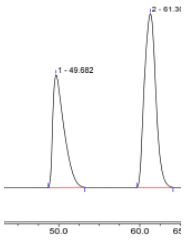
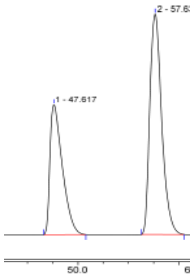
Table 23B The %ee$_2$ change tendency when the starting material's %ee$_1$ was fixed and the mole ratio of oxalaldehyde to D-TME increased from 0.7 to 1.3 summarized from Table S22.

	%ee$_1$	%ee$_2$	Δ%ee
0.7	30.6	35.7	5.1
0.8	30.6	38.2	7.6
0.9	30.6	41.9	11.3
1.0	30.6	42.3	11.7
1.1	30.6	42.1	11.5
1.2	30.6	42.5	11.9
1.3	30.6	42.7	12.1

Item 15. HPLC analysis of %ee values of recovered L-phenylalanine (Tables S24-S25)

This was performed by converting it into the corresponding benzamide after the reaction of oxalyl dichloride with L-phenylalanine.

Table S24 Analysis of %ee values of L-phenylalanine benzamide via HPLC [a].

HPLC peaks before the reaction [b]	HPLC peaks after the reaction [c]
	
$\%ee_1 = 22.04\%$	$\%ee_2 = 23.80\%$

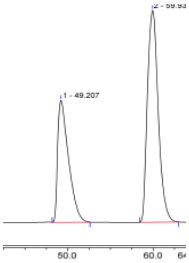
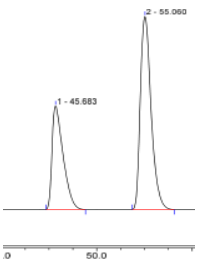
Signal Retention Sample Height Area% Height%

积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		49.682	537.814	335.758	38.98	39.35	n.a.
2		61.302	842.072	517.481	61.02	60.65	n.a.
总和:			**1379.885**	**853.238**	**100.00**	**100.00**	

积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		47.617	379.514	267.309	38.10	37.11	n.a.
2		57.638	616.651	452.941	61.90	62.89	n.a.
总和:			**996.165**	**720.250**	**100.00**	**100.00**	

	
$\%ee_1 = 26.76\%$	$\%ee_2 = 29.06\%$

Signal Retention Sample Height Area% Height%

积分结果

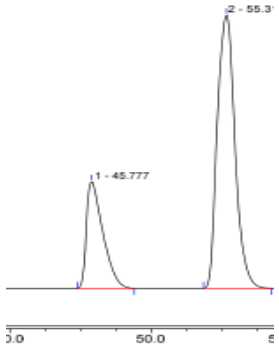
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		49.207	393.105	266.941	36.62	36.56	n.a.
2		59.933	680.336	463.252	63.38	63.44	n.a.
总和:			**1073.441**	**730.193**	**100.00**	**100.00**	

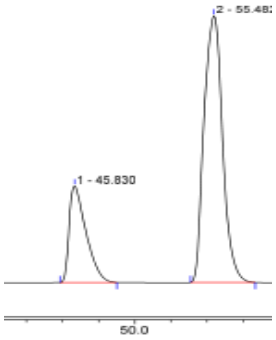
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		45.683	390.070	290.705	35.47	34.92	n.a.
2		55.060	709.674	541.677	64.53	65.08	n.a.
总和:			**1099.744**	**832.382**	**100.00**	**100.00**	

[a] More details could be found in the end of the Table. [b] "Before the reaction" means the HPLC plot analyzed for $\%ee_1$ of L-TME prepared as the starting material. [c] "After the reaction" means HPLC plot analyzed for the corresponding $\%ee_2$ of the L-TME that was recovered after the Pictet-Spengler reaction.

Table 24 continued





%ee$_1$=46.56% | %ee$_2$=50.50%

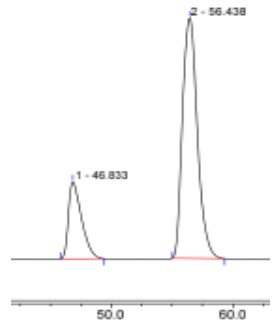
Signal Retention Sample Height Area% Height%

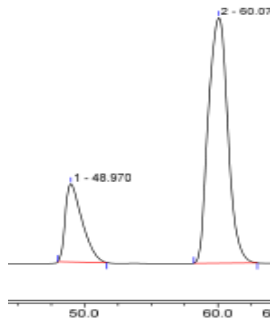
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		45.777	390.013	289.182	26.72	28.07	n.a.
2		55.315	1069.559	741.019	73.28	71.93	n.a.
总和:			**1459.571**	**1030.201**	**100.00**	**100.00**	

积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		45.830	385.215	285.785	24.75	26.62	n.a.
2		55.482	1171.499	787.894	75.25	73.38	n.a.
总和:			**1556.714**	**1073.680**	**100.00**	**100.00**	





%ee$_1$=56.02% | %ee$_2$=56.82%

Signal Retention Sample Height Area% Height%

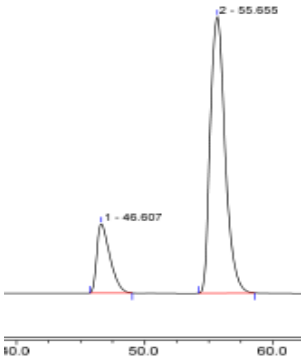
积分结果

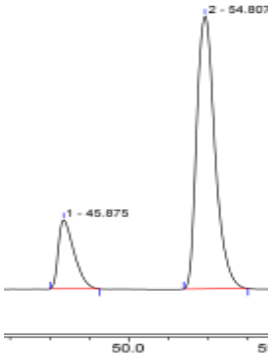
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		46.833	229.971	185.459	21.99	24.34	n.a.
2		56.438	815.981	576.366	78.01	75.66	n.a.
总和:			**1045.953**	**761.824**	**100.00**	**100.00**	

积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		48.970	314.046	214.856	21.59	24.13	n.a.
2		60.075	1140.361	675.428	78.41	75.87	n.a.
总和:			**1454.407**	**890.284**	**100.00**	**100.00**	

Table 24 continued





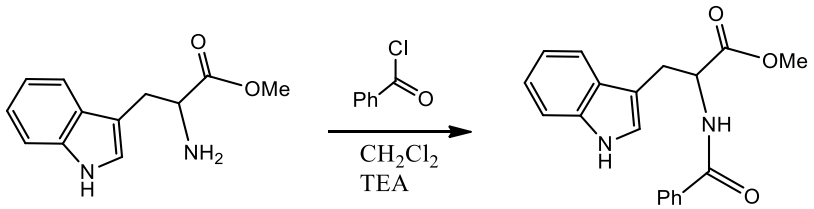
%ee$_1$=63.86%	%ee$_2$=64.16%

Signal Retention Sample Height Area% Height%

积分结果							
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		46.607	187.748	158.714	18.07	20.02	n.a.
2		55.655	851.469	633.870	81.93	79.98	n.a.
总和:			**1039.218**	**792.584**	**100.00**	**100.00**	

积分结果							
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		45.875	178.606	154.786	17.92	20.14	n.a.
2		54.807	817.819	613.651	82.08	79.86	n.a.
总和:			**996.425**	**768.437**	**100.00**	**100.00**	

[a] During the conversion of L-TME to the corresponding (S)-methyl 2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole-3-carboxylate, the students found the reaction required much long time. The other master students tried other methods for the isolation of the recovered L-TME. Finally, it was found that the benzamide could be well isolated by chiral column. The L-TME with %ee$_2$ was converted into the corresponding amide as illustrated below. Theoretically, the %ee value of the benzamide will be the same as that of the L-TME (%ee$_2$).



%ee$_2$ %ee$_2$

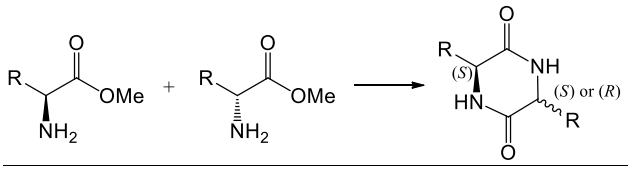
The amide structure was identified by NMR spectra.

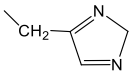
Table 25 The $\%ee_2$ changes when starting material $\%ee_1$ varies (summary of Table S24).

$\%ee_1$	$\%ee_2$	$\Delta\%ee$
22.0%	23.8%	1.8%
26.7%	29.0%	2.3%
46.6%	50.5%	3.9%
56.0%	56.8%	0.8%
63.9%	64.2%	0.3%

Item 16 The computed relative energies for the cyclodimers of six selected amino acids.

Table S26 The predicted energy for six selected amino acids using DFT methods in the gas phase and in liquid using PCM model.



Entry	R (Amino acid)	$E_{L,L\text{-product}}$ (a.u.) [a]	$E_{D,L\text{-product}}$ (a.u.)	ΔE [b]
1	-Me (Alanine)	-494.805868 (g)	-494.805516 (g)	+0.221 (g)
		-494.822208 (l)	-494.822517 (l)	-0.194 (l)
2	-CHMeCH$_2$Me	-730.751373 (g)	-730.751961 (l)	-0.369 (g)
	(isoleucine)	-730.766768 (l)	-730.767541 (l)	-0.485 (l)
3	-CHMe$_2$	-652.104422 (g)	-652.104962 (g)	-0.339 (g)
	(Valine)	-652.119857 (l)	-652.120556 (l)	-0.438 (l)
4	-CH$_2$SH	-1291.236420 (g)	-1291.236050 (g)	+0.232 (g)
	(Cysteine)	-1291.254319 (l)	-1291.254291(l)	+0.018 (l)
5	-CH$_2$CO$_2$H	H-bond formed:		
	(Aspartic acid)	-872.081036 (g)	-872.080993 (g)	+0.027 (g)
		-872.103256 (l)	-872.103551 (l)	-0.185 (l)
		Non-H-bond:		
		-872.072699 (g)	-872.073684 (g)	-0.618 (g)
		-872.100224 (l)	-872.101097 (l)	-0.547 (l)
6		H-bond formed:		
		-944.987923 (g)	-944.986684 (g)	0.777 (g)
	(Histidine)	-945.017233 (l)	-945.016235(l)	0.626 (l)
		Non-H-bond:		
		-944.976114 (g)	-944.979602 (g)	-2.189 (g)
		-945.009154 (l)	-945.010790 (l)	-1.026 (l)

[a]The computed total electronic energy was obtained at the B3LYP/6-311++G(2d,p) level in the gas phase (g) and in liquid water (l) using the PCM model, respectively, atom unit (a.u.) was used. [b]The energy difference were computed using the formula: $\Delta E = 627.5 \times (E_{D,L\text{-product}} - E_{L,L\text{-product}})$, unit in kcal/mol.