Electronic Supplementary Information

for

Chitosan bis(halophenylcarbamate)-(isobutyrylamide)s based chiral stationary phases for enantiomeric separation

Sheng Tang,[a] Qin Bin, [a] Zi-Wei Feng,[a] Wei Chen,[a] Shao-Hua Huang[b] and Zheng-Wu Bai[a]*

[a]*School of Chemistry and Environmental Engineering, Wuhan Institute of Technology, Wuhan 430073, China.*

[b]*Key Laboratory of Biobased Materials, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China.*

*Corresponding author:

Zheng-Wu Bai (Z.W. Bai), E-mail Address: zwbai@wit.edu.cn

Tel. and fax: +86 27 87195680

Table of Contents

1. ^{1}H NMR spectrum of chitosan

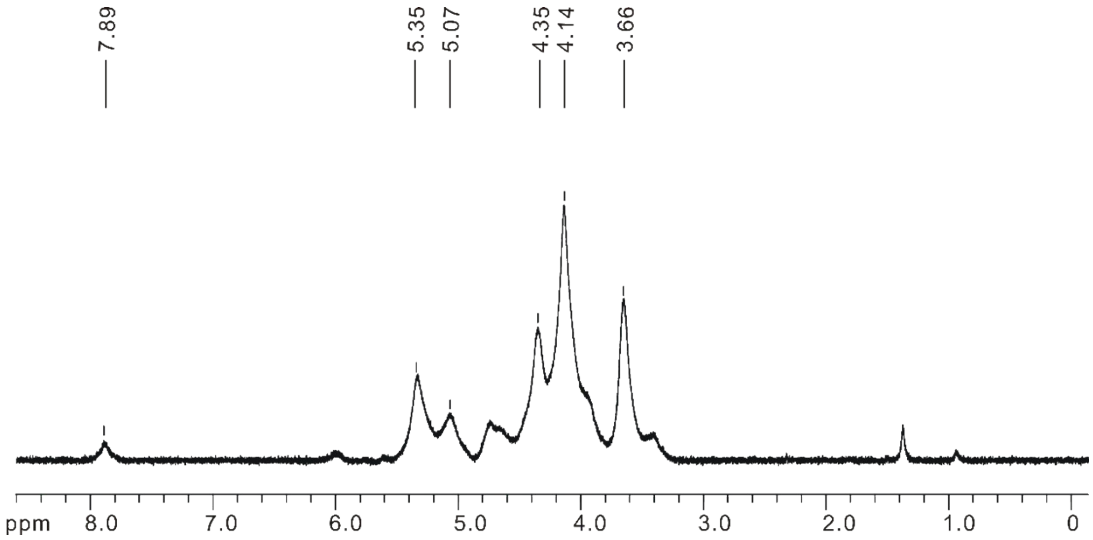

Fig. S1 ^{1}H NMR spectrum of chitosan (400 MHz, TFA-*d*, 25 °C)

2. ^{1}H NMR spectra of chitosan bis(halophenylcarbamate)-(isobutyrylamide)s

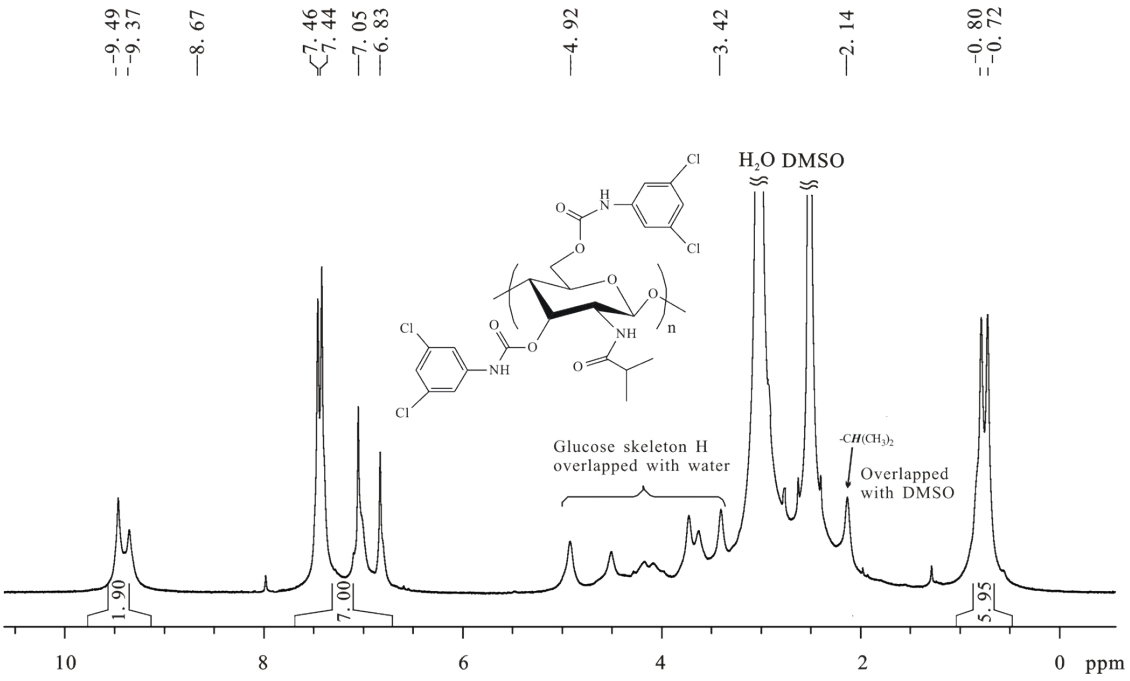

Fig. S2 ^{1}H NMR spectrum of chitosan bis(3,5-dichlorophenylcarbamate)-(isobutyrylamide) (P2) (600 MHz, DMSO-d_6, 90 °C)

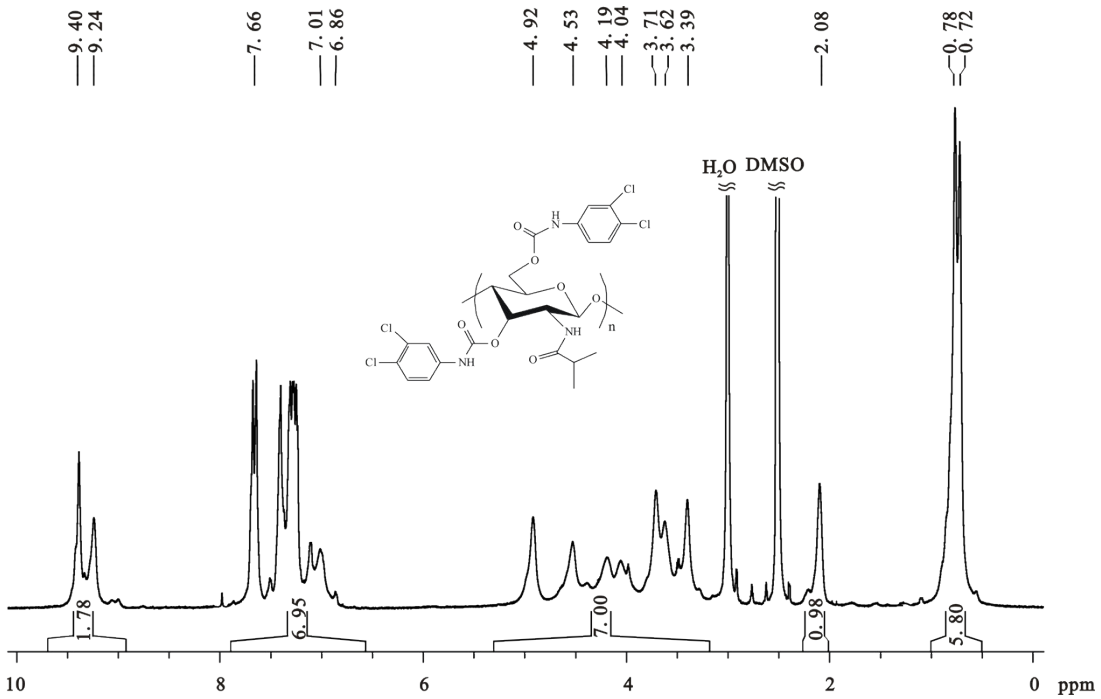

Fig. S3 ^{1}H NMR spectrum of chitosan bis(3,4-dichlorophenylcarbamate)-(isobutyrylamide) (P3) (600 MHz, DMSO-d_6, 90 ^{o}C)

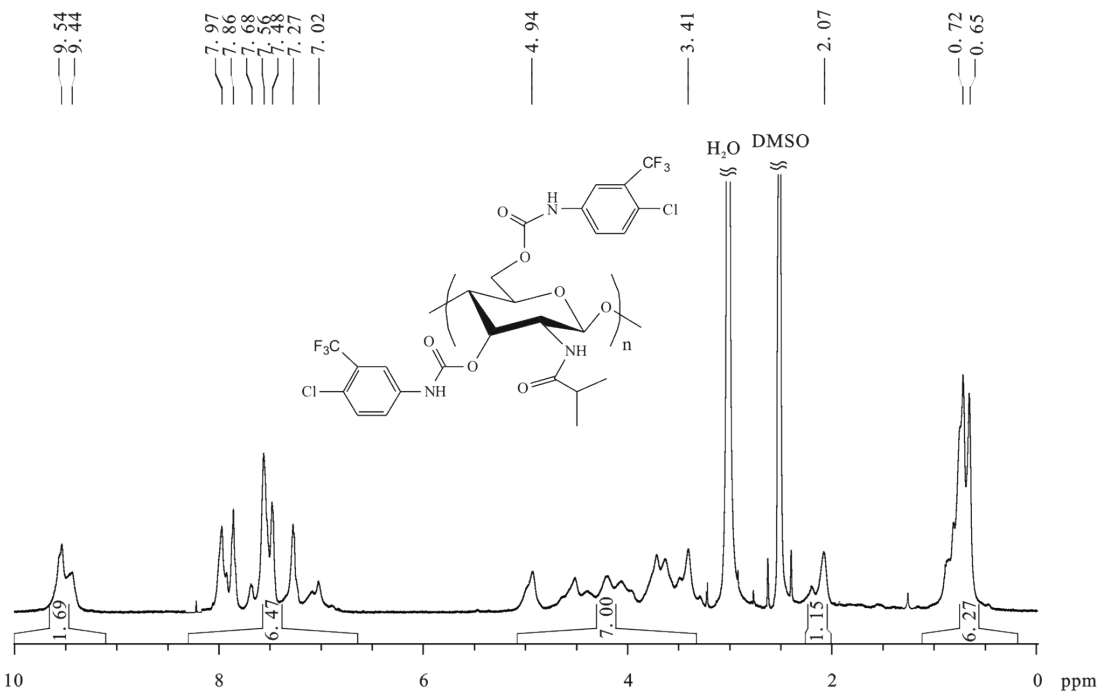

Fig. S4 ^{1}H NMR spectrum of chitosan bis(4-chloro-3-trifluoromethylphenyl-carbamate)-(isobutyrylamide) (P4) (600 MHz, DMSO-d_6, 90 ^{o}C)

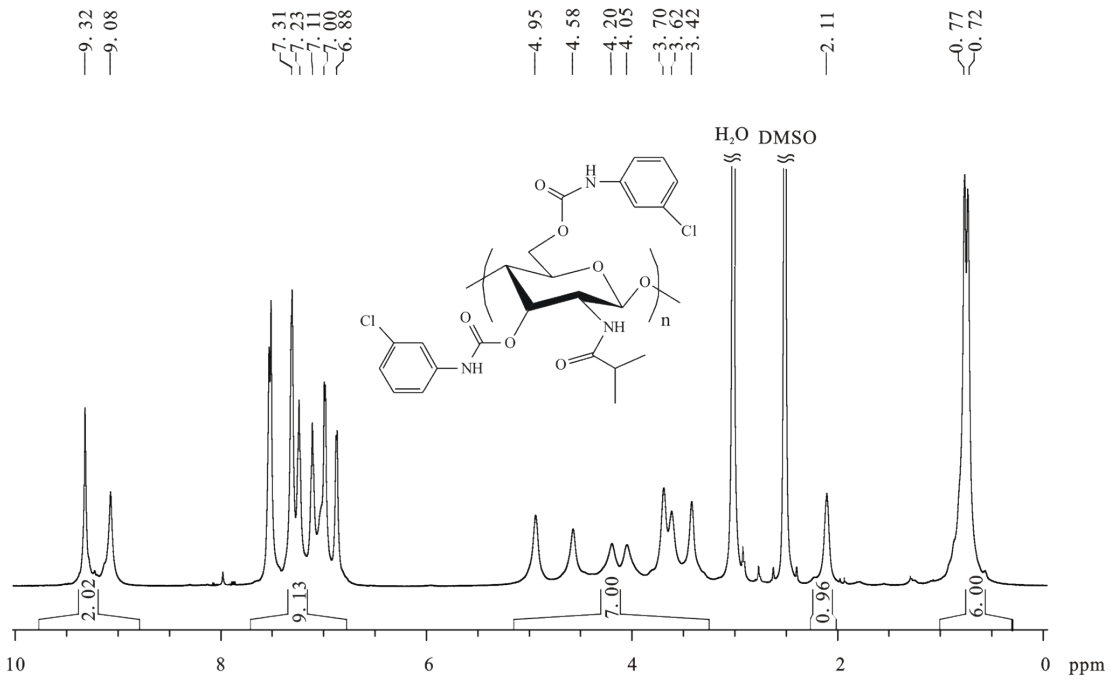

Fig. S5 ^{1}H NMR spectrum of chitosan bis(3-chlorophenylcarbamate)-(isobutyrylamide) (P5) (600 MHz, DMSO-d_6, 90 ^{o}C)

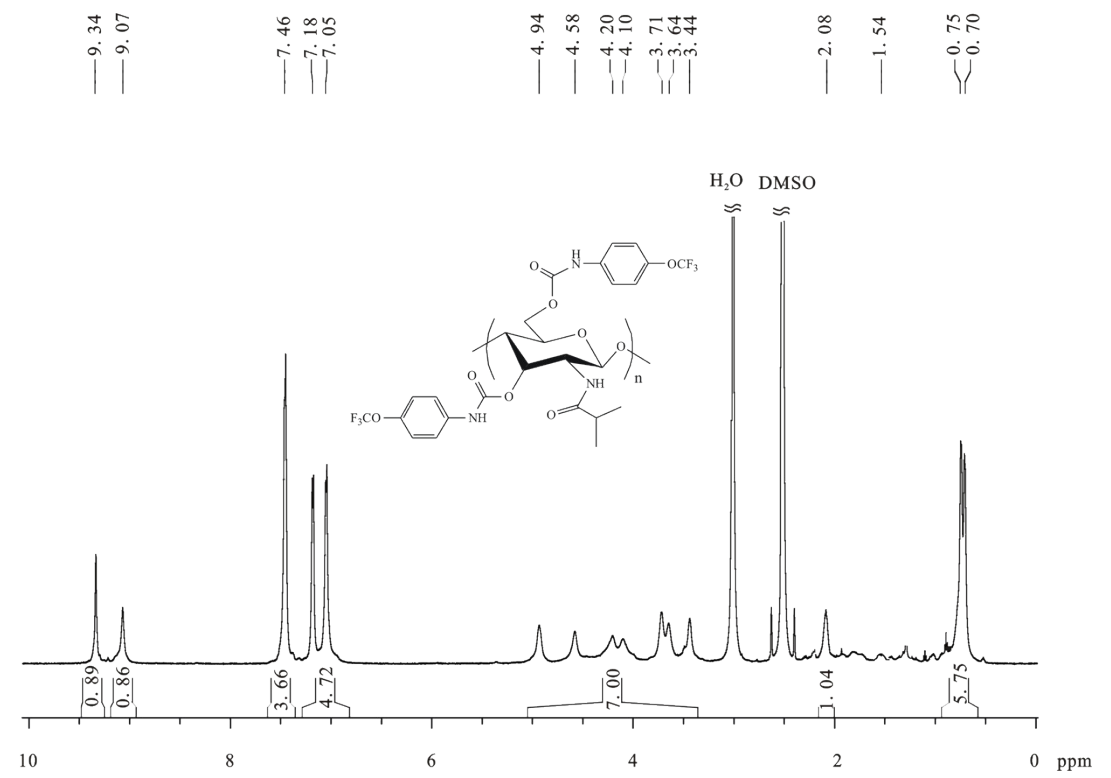

Fig. S6 ^{1}H NMR spectrum of chitosan bis(4-trifluoromethoxyphenylcarbamate)-(isobutyrylamide) (P6) (600 MHz, DMSO-d_6, 90 ^{o}C)

3. IR spectra of chitosan bis(halophenylcarbamate)-(isobutyrylamide)s

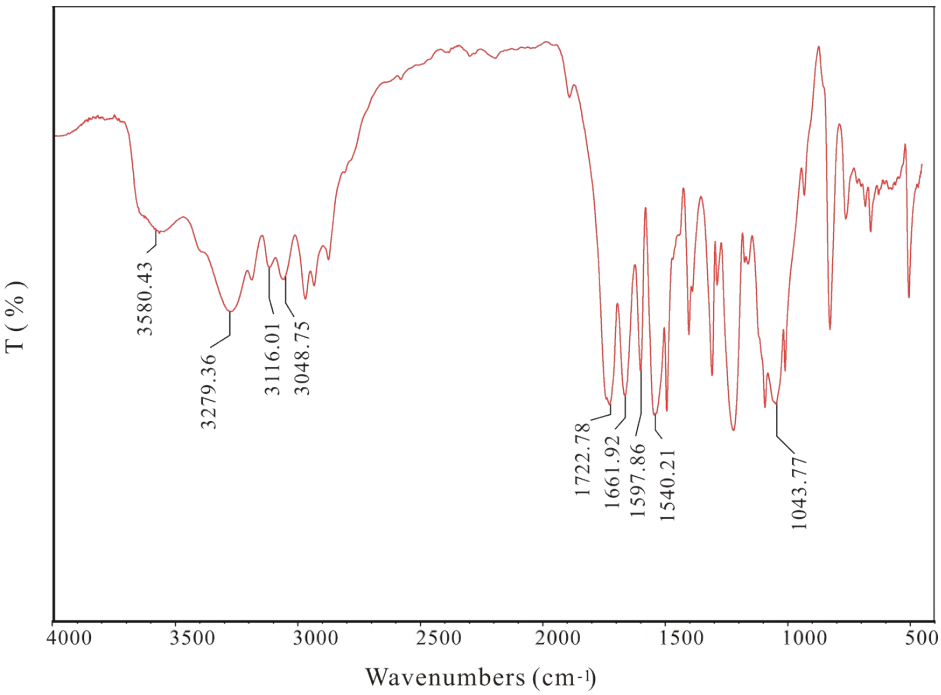

Fig. S7 IR spectrum of chitosan bis(4-chlorophenylcarbamate)-(isobutyrylamide) (P1)

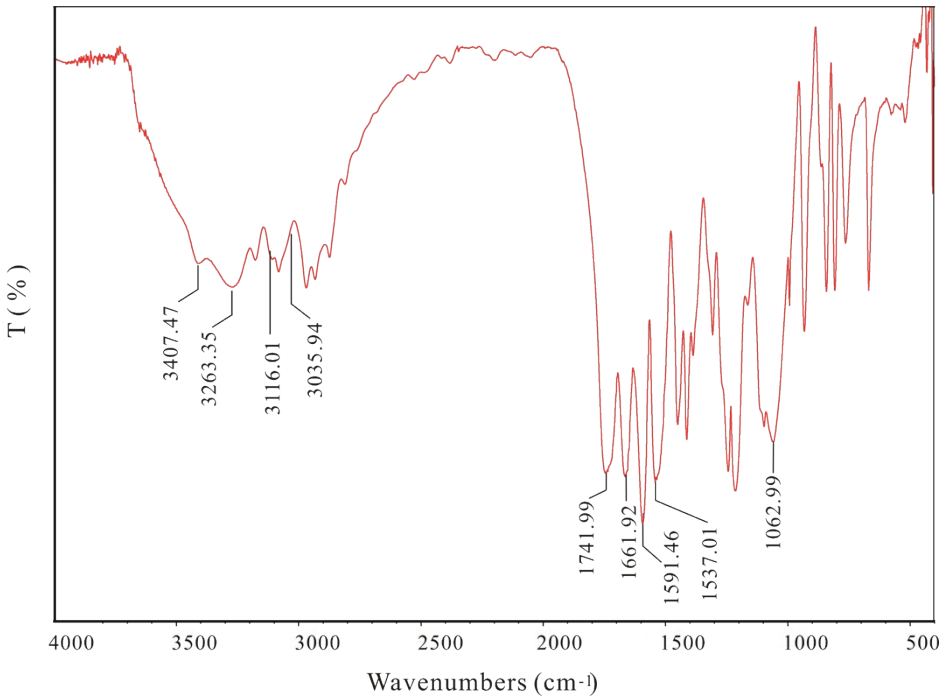

Fig. S8 IR spectrum of chitosan bis(3,5-dichlorophenylcarbamate)-(isobutyrylamide) (P2)

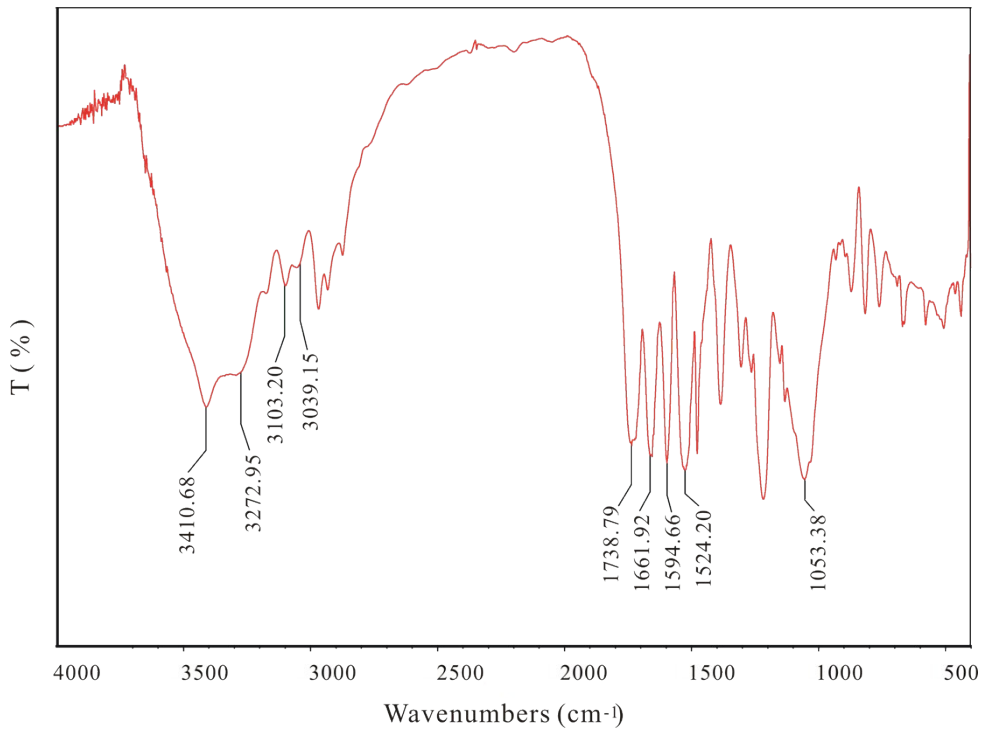

Fig. S9 IR spectrum of chitosan bis(3,4-dichlorophenylcarbamate)-(isobutyrylamide) (P3)

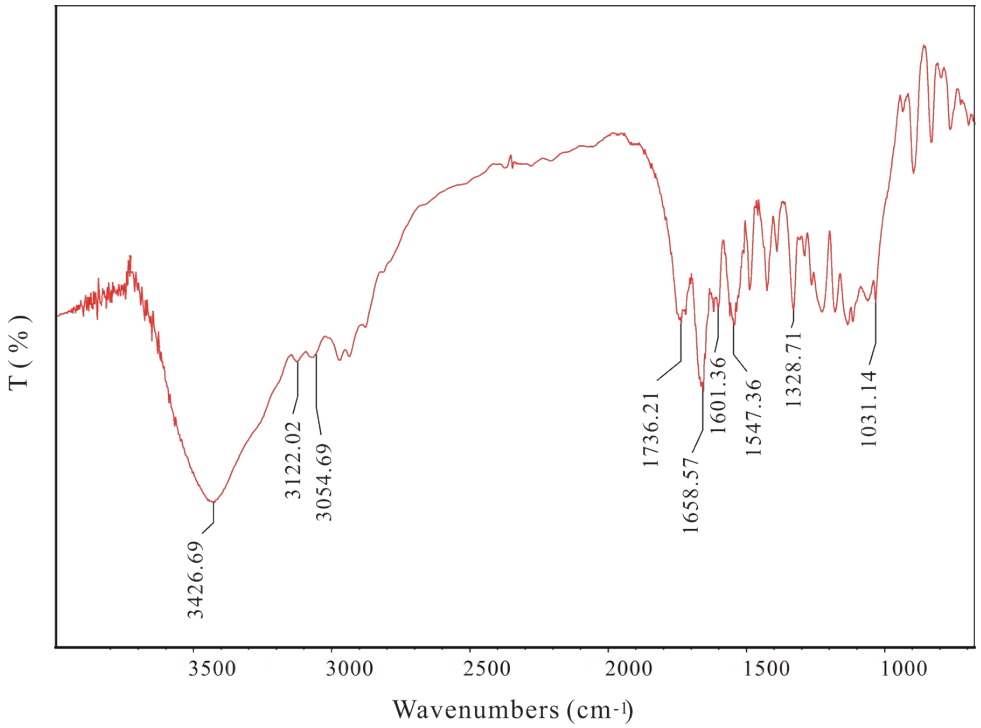

Fig. S10 IR spectrum of chitosan bis(4-chloro-3-trifluoromethylphenylcarbamate)-(isobutyrylamide) (P4)

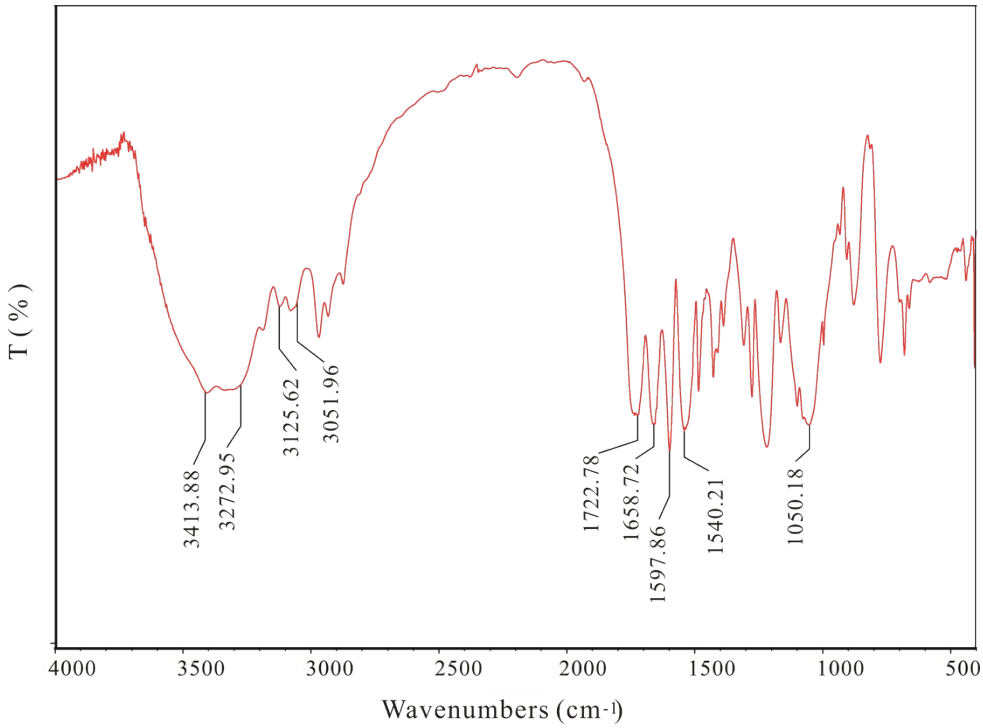

Fig. S11 IR spectrum of chitosan bis(3-chlorophenylcarbamate)-(isobutyrylamide) (P5)

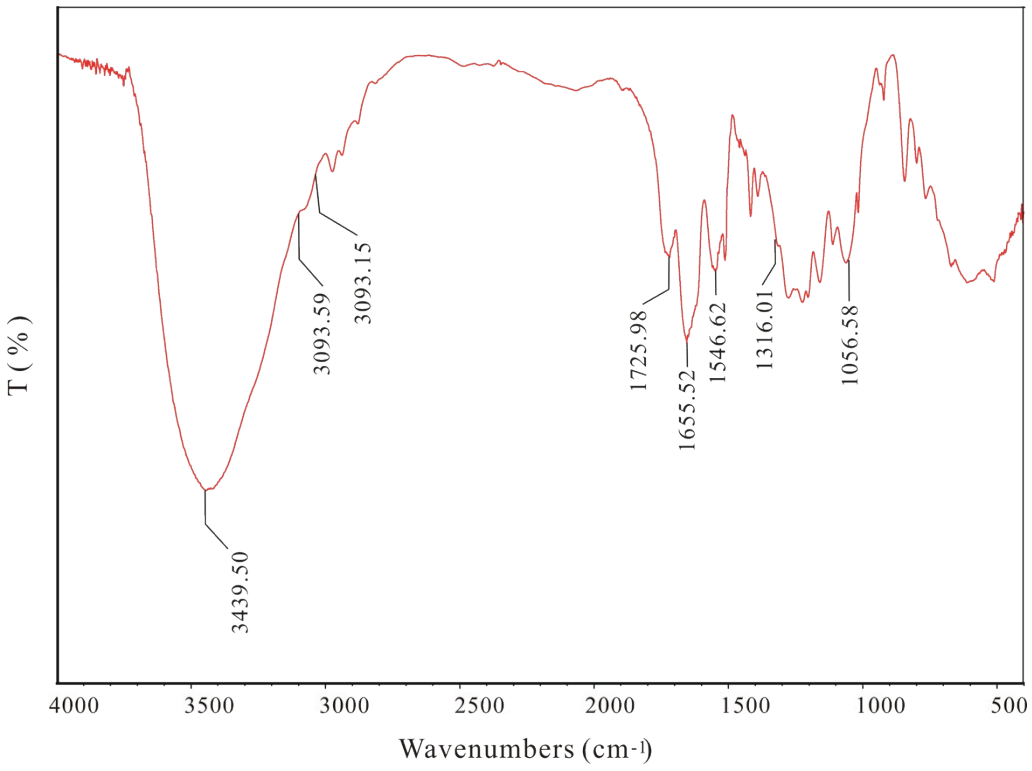

Fig. S12 IR spectrum of chitosan bis(4-trifluoromethoxyphenylcarbamate)-(isobutyrylamide) (P6)

4. Structures of the tested chiral analytes

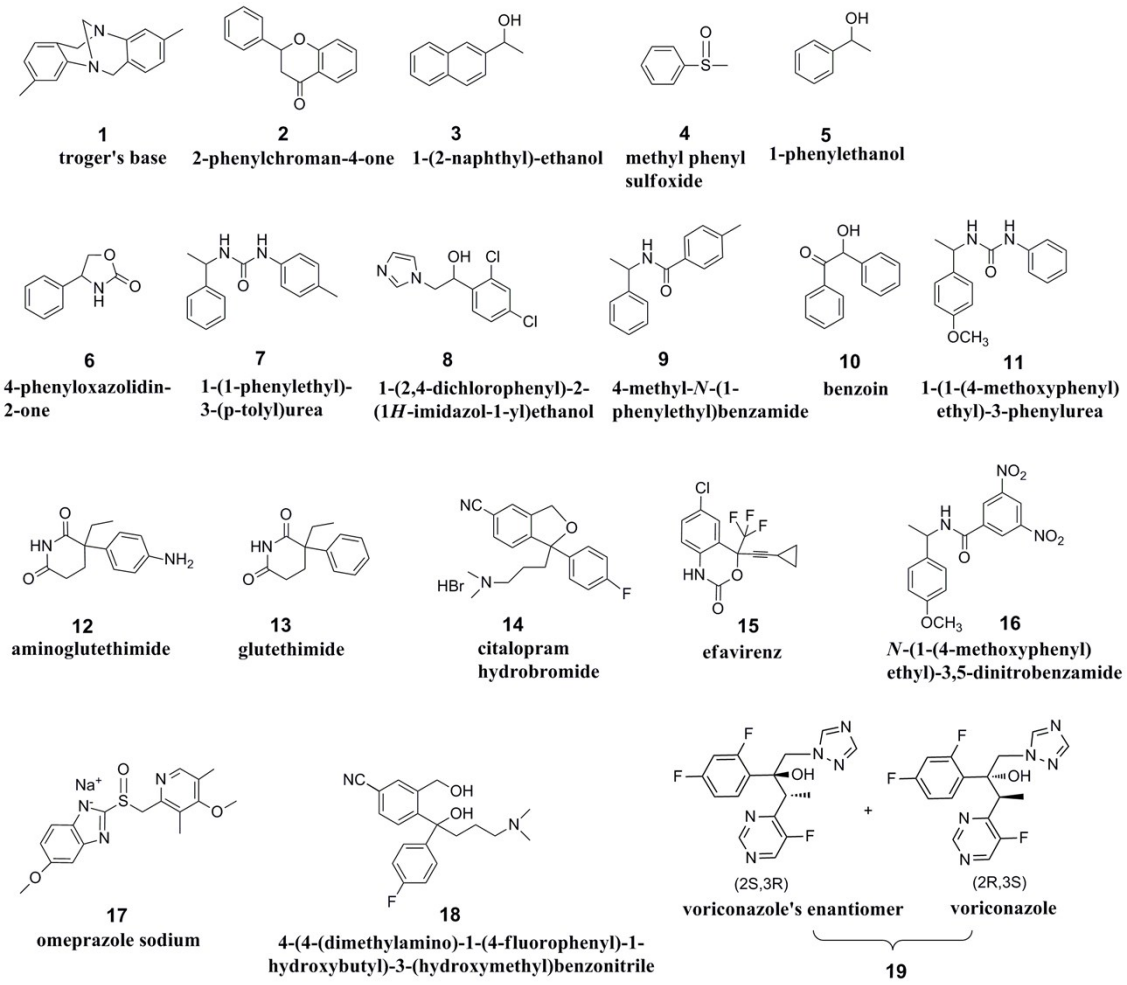

Fig. S13 Structures of the tested chiral analytes.[1]

5. Numbers of the racemates recognized and baseline separated by CSPs1-6, CSPa and CSPb in each mobile phase

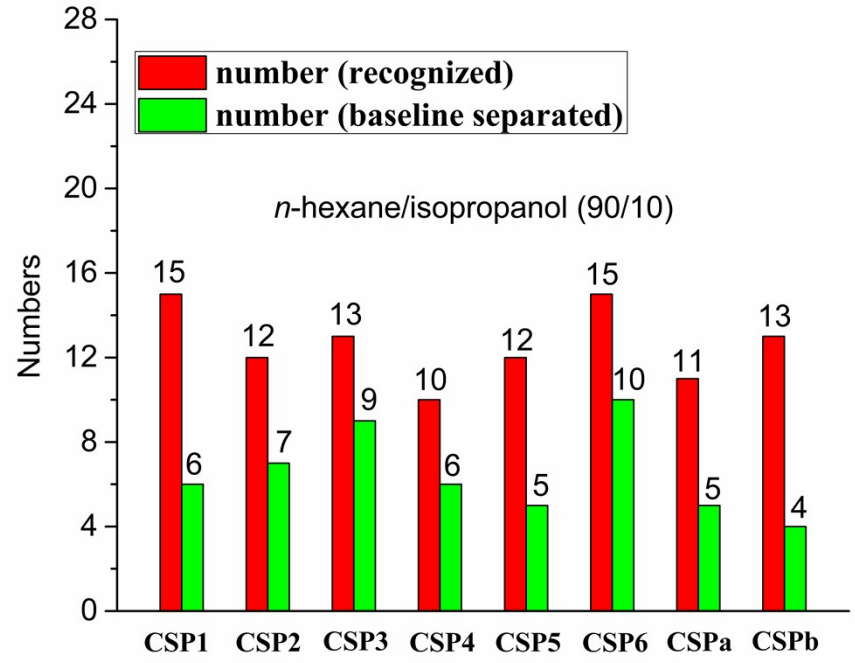

Fig. S14 Numbers of the racemates recognized and baseline separated in the mobile phase of *n*-hexane/isopropanol (90/10).

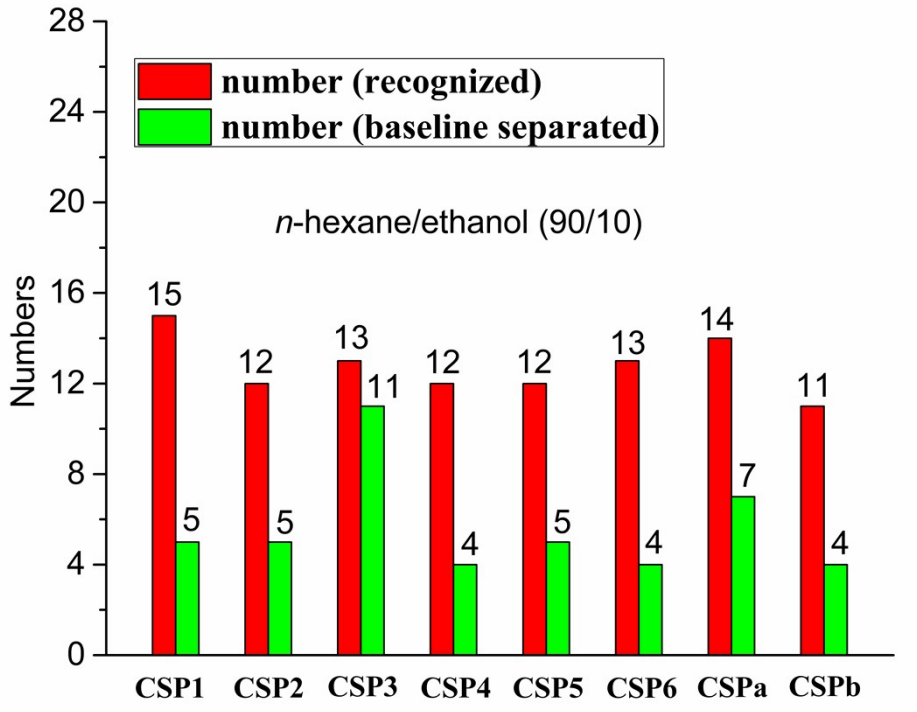

Fig. S15 Numbers of the racemates recognized and baseline separated in the mobile phase of *n*-hexane/ethanol (90/10).

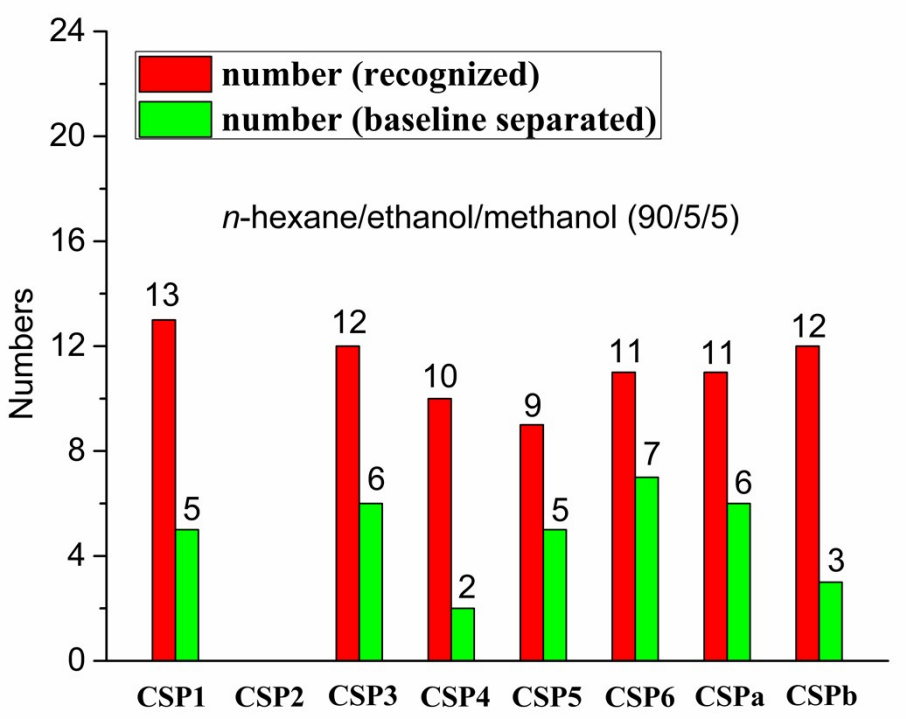

Fig. S16 Numbers of the racemates recognized and baseline separated in the mobile phase of *n*-hexane/ethanol/methanol (90/5/5). Since CSP2 was destroyed when it was tested in the eluent of *n*-hexane/ethanol/methaol methanol (90/5/5), the enantioseparation results of CSP2 were not available.

6. Elemental analysis results of P1-P6

Table S1 Elemental analysis results of P1-P6

Chiral selectors	Calculated values			Observed values		
	C	H	N	C	H	N
P1 $(C_{24}H_{25}Cl_2N_3O_7)_n$	53.54%	4.68%	7.80%	53.39%	5.16%	7.96%
P2 $(C_{24}H_{23}Cl_4N_3O_7)_n$	47.47%	3.82%	6.92%	47.45%	4.36%	7.22%
P3 $(C_{24}H_{23}Cl_4N_3O_7)_n$	47.47%	3.82%	6.92%	48.12%	4.63%	7.15%
P4 $(C_{26}H_{23}Cl_2F_6N_3O_7)_n$	46.31%	3.44%	6.23%	46.56%	4.26%	6.44%
P5 $(C_{24}H_{25}Cl_2N_3O_7)_n$	53.54%	4.68%	7.80%	53.77%	5.19%	7.88%
P6 $(C_{26}H_{25}F_6N_3O_9 \cdot 6H_2O)_n$	41.88%	5.00%	5.64%	41.86%	5.40%	6.13%

7. Enantioseparation results of CSPa and CSPb

Table S2 Enantioseparation results of CSPa and CSPb

S.N.	CSPa			CSPb			S.N.	CSPa			CSPb			M.P.
	k_1	α	R_s	k_1	α	R_s		k_1	α	R_s	k_1	α	R_s	
1	0.65(+)	1.51	1.68	1.03(+)	1.49	2.12	**8**	2.42(+)	1.57	2.45	5.71	1.00	0.00	A
	0.54(+)	1.87	3.07	0.70(+)	1.64	2.62		1.37(+)	2.98	6.28	1.75	1.00	0.00	B
	0.66(+)	1.79	3.79	0.72(+)	1.64	2.63		1.72(+)	2.87	6.98	1.36	1.00	0.00	C
2	1.24(+)	1.20	1.37	1.53(-)	1.30	1.80	**9**	5.16(R)	1.70	3.15	4.52(R)	1.18	1.01	A
	1.19(+)	1.46	2.94	1.15(-)	1.21	1.14		1.22(R)	1.46	2.04	1.15(R)	1.12	0.53	B
	1.43(+)	1.79	5.00	1.09(-)	1.21	1.19		1.58(R)	1.27	1.45	1.10（R）	1.16	0.54	C
3	1.19	1.00	0.00	2.09	1.00	0.00	**10**	3.99	1.00	0.00	2.90(+)	1.40	2.17	A
	0.68(+)	1.06	0.28	1.34	1.00	0.00		2.60(+)	1.08	0.48	2.06(+)	1.33	1.93	B
	0.98	1.00	0.00	1.24	1.00	0.00		2.76(+)	1.10	0.85	1.85(+)	1.34	1.96	C
4	2.95(-)	1.06	0.48	3.74(+)	1.10	0.57	**11**	10.01(R)	1.45	1.75	11.74(S)	1.20	0.96	A
	1.71	1.00	0.00	1.90	1.00	0.00		1.97(R)	1.28	1.33	2.25(S)	1.12	0.38	B
	2.29	1.00	0.00	1.60	1.00	0.00		2.36(R)	1.21	1.47	2.50（S）	1.10	0.35	C
5	0.63	1.00	0.00	0.95(+)	1.12	0.42	**12**	Retention time >120 min			39.05	1.00	0.00	A
	0.43	1.00	0.00	0.65(+)	1.13	0.22		Retention time >120 min			24.36	1.00	0.00	B
	0.69	1.00	0.00	0.57(+)	1.13	0.38		Retention time >120 min			12.20	1.00	0.00	C
6	5.71(R)	1.27	1.46	9.85(S)	1.09	0.96	**13**	Retention time >120 min			38.78	1.00	0.00	A
	3.23(R)	1.11	0.77	4.89	1.00	0.00		Retention time >120 min			23.56	1.00	0.00	B
	4.10	1.00	0.00	3.82(R)	1.10	0.45		Retention time >120 min			12.14	1.00	0.00	C
7	6.11(R)	2.09	3.00	7.61(R)	1.25	0.39	**14**	1.65	1.00	0.00	2.49	1.00	0.00	A

	1.32(R)	1.41	1.60	1.42(R)	1.28	1.19		1.46	1.00	0.00	1.37	1.00	0.00	B
	1.57(R)	1.21	1.37	1.05(R)	1.20	0.89		1.95	1.00	0.00	1.23	1.00	0.00	C

Table S1 to be continued

Continued Table S2

S.N.	CSPa			CSPb			S.N.	CSPa			CSPb			M.P.
	k_1	α	R_S	k_1	α	R_S		k_1	α	R_S	k_1	α	R_S	
15	1.14(S)	1.22	0.84	1.62(R)	1.34	1.60	**18**	4.49(S)	1.06	0.25	2.97(S)	1.06	0.29	A
	0.58(S)	1.12	0.32	0.83(R)	1.34	1.55		2.72(R)	1.35	0.80	1.73	1.00	0.00	B
	0.97	1.00	0.00	0.73(R)	1.21	0.47		1.96(R)	1.39	1.78	1.80	1.00	0.00	C
16	25.10	1.00	0.00	32.69(R)	1.30	1.27	**19**	5.62(2R,3S)	1.16	0.78	19.21	1.00	0.00	A
	7.73(R)	1.63	2.20	11.45(R)	1.18	0.99		4.65(2R,3S)	1.18	1.11	9.47(2R,3S)	1.29	1.81	B
	9.07(R)	1.50	2.98	7.77(R)	1.13	0.68		3.81(2R,3S)	1.17	1.16	6.53(2R,3S)	1.27	1.82	C
17	Retention time >120 min			17.56(R)	1.28	0.43								A
	10.37(R)	1.61	2.57	6.37(R)	1.25	0.99								B
	9.62（R）	1.79	3.63	3.94(R)	1.15	0.54								C

S.N.: serials number of the analytes; M.P.: mobile phase: A: *n*-hexane/isopropanol (90/10); B: *n*-hexane/ethanol (90/10); C: *n*-hexane/ethanol/methanol (90/5/5).

"+", "-", "R", "S" and "(2R,3S)" refer to the optical rotation or configuration of the first-eluted enantiomer. Flow rate: 1.0 ml min^{-1}. Dectetion temperature: 25 °C.

Enantioseparation results of CSPa and CSPb were cited from our most recently reported work.[1]

8. Eluent tolerance of CSP3 towards organic solvents

Table S3 Comparison in enantioseparation ability of CSP3 before and after being flushed by various organic solvents

S.N.	a			b			c			d			e		
	k_1	α	R_S	k_1	α	R_S	k_1	α	R_S	k_1	α	R_S	k_1	α	R_S
1	0.39	1.43	2.51	0.43	1.54	3.24	0.41	1.57	3.37	0.42	1.56	3.49	0.38	1.52	2.75
2	1.44	1.29	3.14	1.87	1.32	4.36	1.79	1.29	3.13	1.88	1.31	4.66	1.58	1.29	2.99
3	0.59	1.00	0.00	0.78	1.00	0.00	0.78	1.00	0.00	0.76	1.00	0.00	0.62	1.00	0.00
4	4.72	1.36	5.46	7.01	1.42	5.88	5.91	1.44	6.26	6.82	1.43	6.28	4.69	1.41	5.57
5	0.47	1.00	0.00	0.60	1.00	0.00	0.53	1.00	0.00	0.58	1.00	0.00	0.46	1.00	0.00
6	8.90	1.22	3.20	15.25	1.21	3.21	15.17	1.17	3.08	15.42	1.20	3.16	9.44	1.22	2.90
7	1.24	1.16	1.56	1.87	1.19	1.76	1.61	1.19	2.04	1.88	1.20	2.11	1.30	1.18	1.56
8	1.64	1.00	0.00	2.74	1.00	0.00	2.61	1.00	0.00	2.54	1.00	0.00	1.68	1.00	0.00
9	1.28	1.16	1.61	2.00	1.18	1.96	1.79	1.18	2.28	2.00	1.18	2.31	1.34	1.17	1.71
10	2.23	1.05	0.39	3.11	1.08	0.22	2.85	1.00	0.00	3.06	1.06	0.31	2.37	1.03	0.10
11	1.84	1.18	1.66	3.04	1.19	1.66	2.61	1.19	1.62	2.91	1.19	1.71	1.84	1.25	1.14
12	31.65	1.11	1.56	Retention time > 120 min			37.84	1.05	0.44	43.29	1.04	0.43	28.80	1.17	1.91
13	25.47	1.12	1.52	Retention time > 120 min			45.20	1.00	0.00	33.64	1.03	0.20	23.57	1.16	1.37
14	2.90	1.00	0.00	4.44	1.00	0.00	4.54	1.00	0.00	4.46	1.00	0.00	3.35	1.00	0.00
15	1.36	1.00	0.00	2.11	1.00	0.00	2.13	1.05	0.33	1.98	1.07	0.68	1.43	1.00	0.00
16	7.56	1.00	0.00	12.89	1.00	0.00	10.31	1.00	0.00	12.73	1.00	0.00	8.18	1.00	0.00

17	13.25	1.07	0.51	Retention time > 120 min			18.53	1.04	0.31	23.26	1.04	0.18	14.30	1.05	0.18
18	3.62	1.16	1.69	6.44	1.19	1.98	5.41	1.18	2.05	6.67	1.18	2.11	4.28	1.17	1.48
19	4.03	1.81	7.79	6.10	1.91	6.95	5.31	1.98	8.26	6.10	1.97	8.14	3.95	1.86	6.74

S.N.: serials number of the analytes; (a) initial enantioseparation results of CSP3; (b) after CSP3 worked for 100 h during the initial enantioseparation and then was placed aside for two months; (c) after CSP3 was flushed by pure ethyl acetate; (d) after CSP3 was flushed by pure chloroform; (e) after CSP3 was flushed by *n*-hexane/THF (70/30); mobile phase for enantioseparations: *n*-hexane/ethanol (90/10); flow rate: 1.0 ml min^{-1}; dectetion temperature: 25 ^{o}C.

References

1. S. Tang, Q. Bin, W. Chen, Z.W. Bai and S.H. Huang, *J. Chromatogr. A*, 2016, **1440**, 112-122.