Electronic Supplementary Material (ESI) for Analyst.

Supplementary Information

for

Synthesis of substituted phenylcarbamates of *N*-cyclobutylformylated chitosan and their application as chiral selectors in enantioseparation

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1. Characterization of chitosan and its derivatives

^{1}H NMR spectra of chitosan and *N*-cyclobutylformylated chitosan were measured with deuterated trifluoroacetic acid (TFA-D) as the solvent at 25 ^{o}C. TFA-D was also employed as internal standard (δ 11.50 ppm). ^{1}H NMR spectra of substituted phenylcarbamates of *N*-cyclobutylformylated chitosan were measured at 90 ^{o}C with DMSO-d_6 as the solvent, scanning 256 times. Elemental analysis was conducted in a usual C, H and N model. IR spectra were measured with KBr pellets.

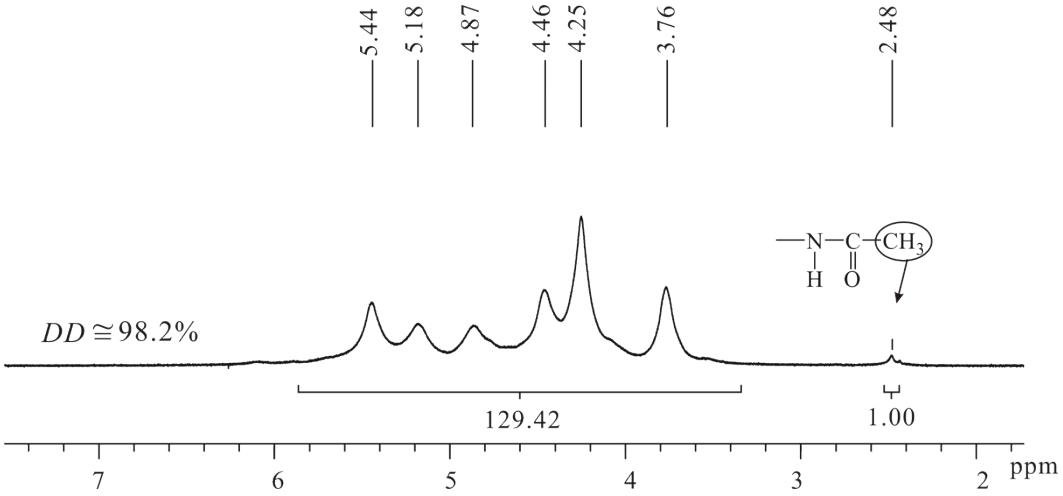

Fig. S1 ^{1}H NMR spectrum of chitosan.

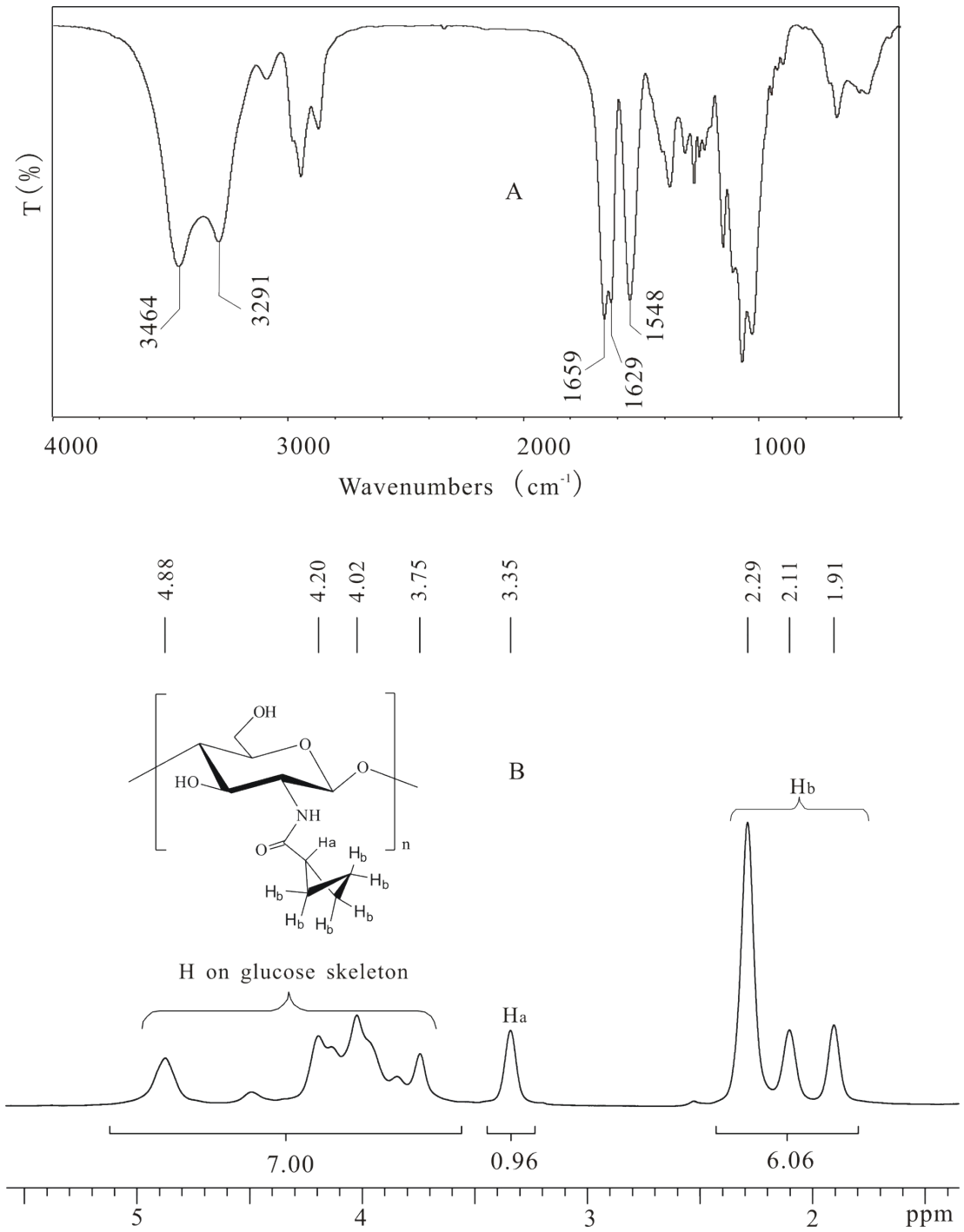

Fig. S2 IR (A) and ^{1}H NMR spectra (B) of N-cyclobutylformylated chitosan.

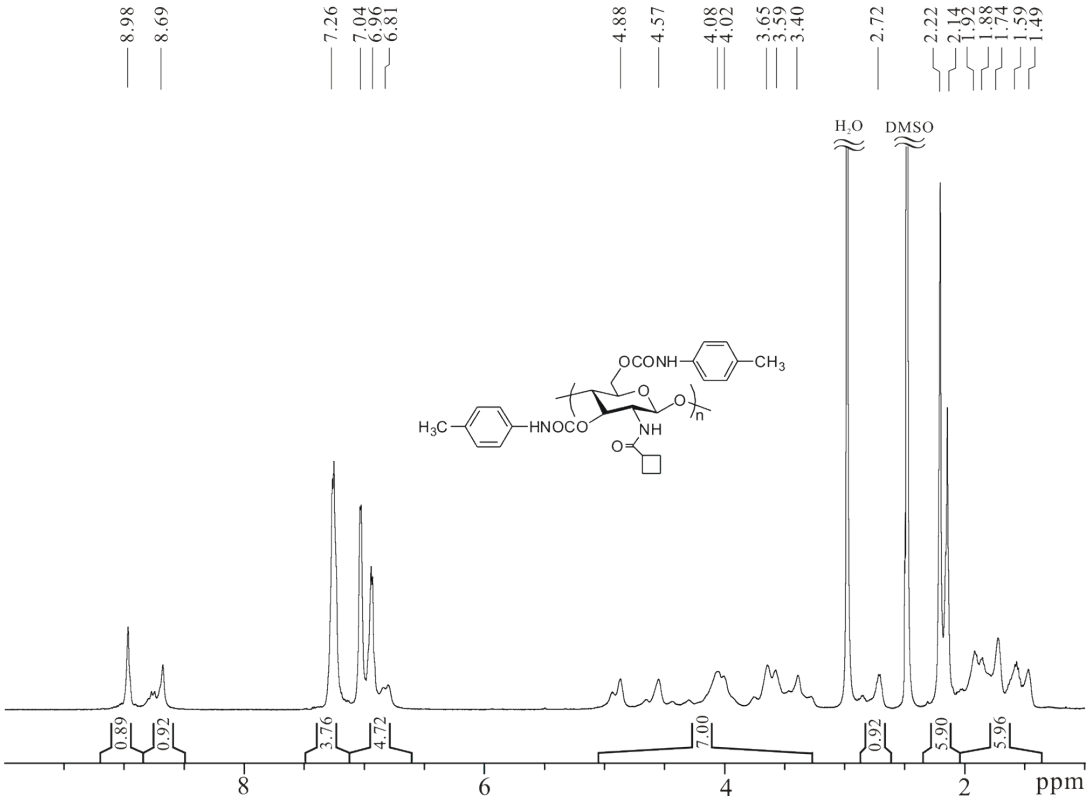

Fig. S3 [1]H NMR spectrum of chitosan bis(4-methylphenylcarbamate)-(cyclobutylformamide) (CS 1).

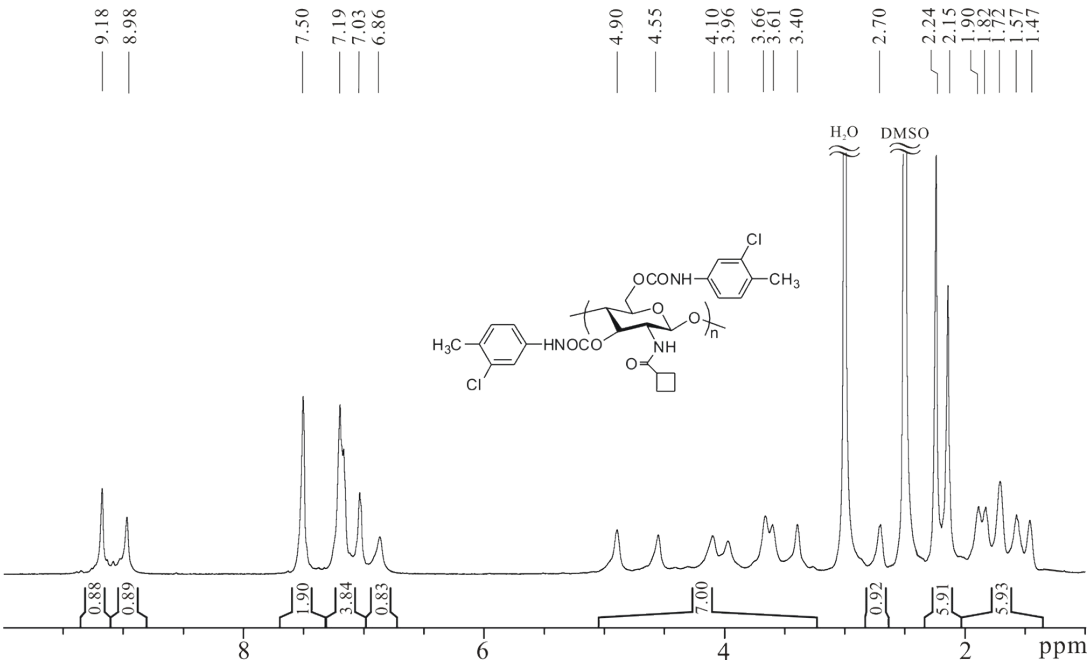

Fig. S4 [1]H NMR spectrum of chitosan bis(3-chloro-4-methylphenylcarbamate)-(cyclobutylformamide) (CS 2).

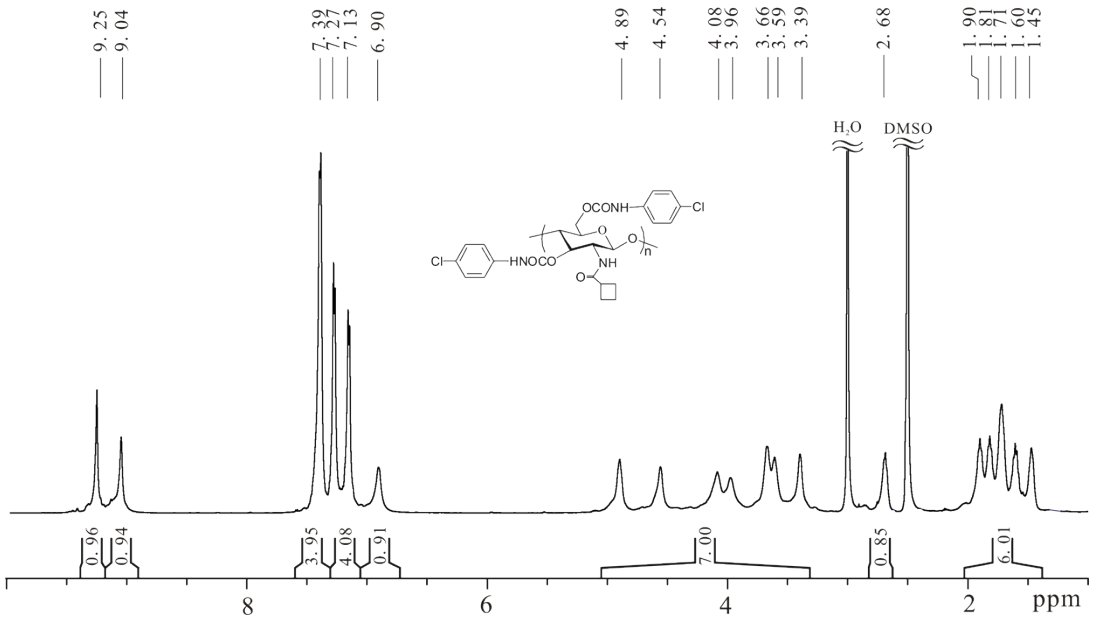

Fig. S5 ^{1}H NMR spectrum of chitosan bis(4-chlorophenylcarbamate)-(cyclobutylformamide) (CS 3).

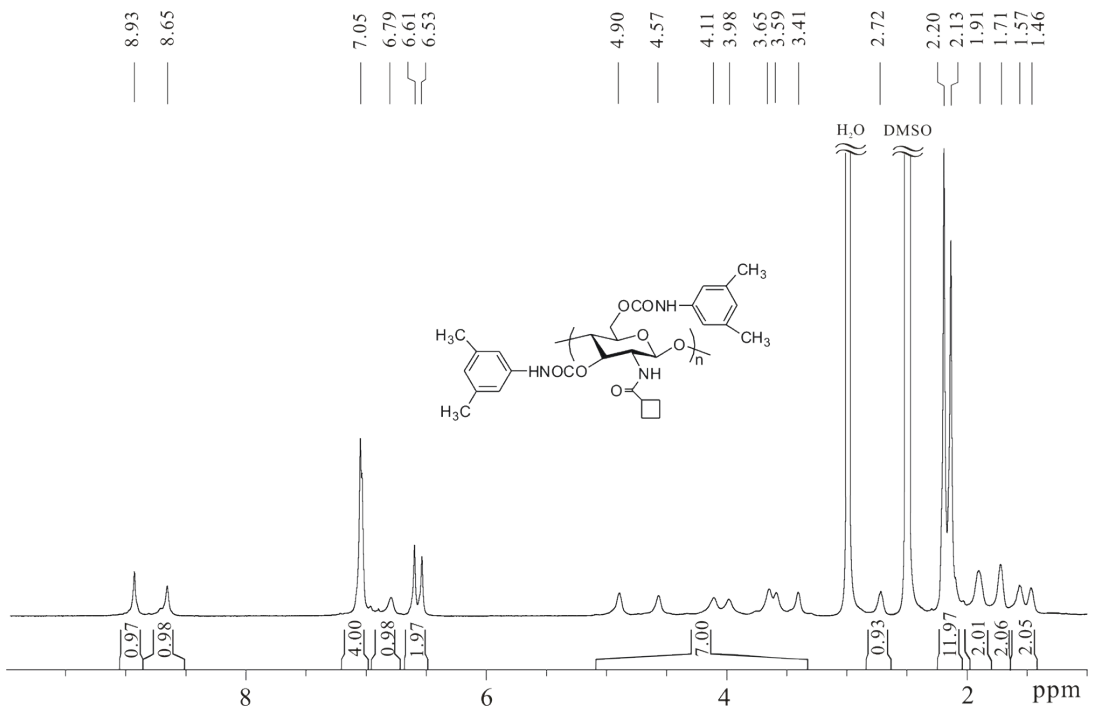

Fig. S6 ^{1}H NMR spectrum of chitosan bis(3,5-dimethylhenylcarbamate)-(cyclobutylformamide) (CS 4).

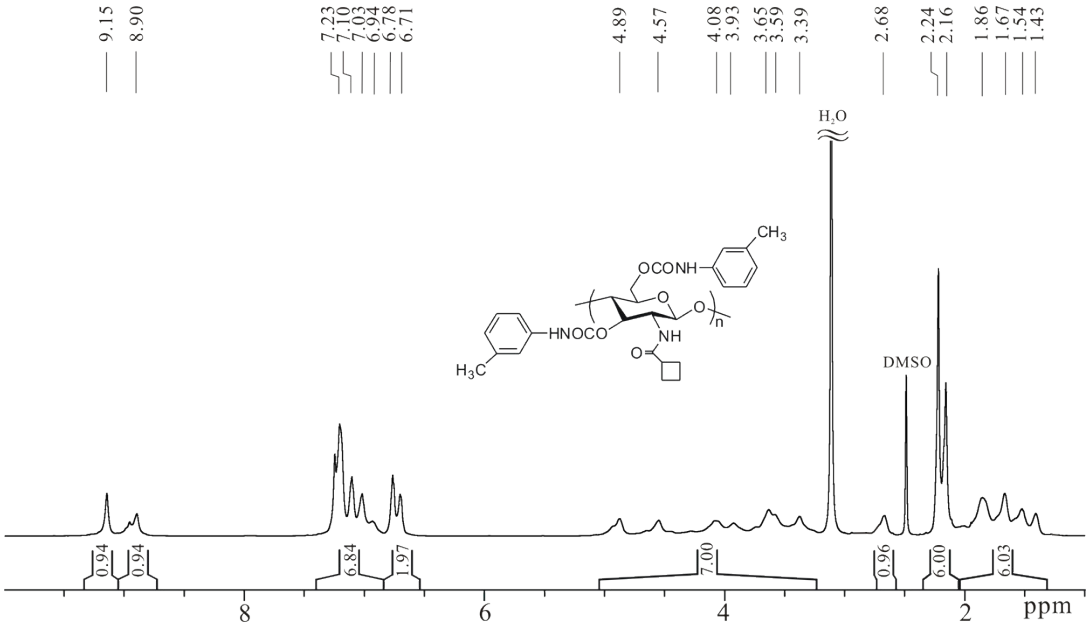

Fig. S7 ^{1}H NMR spectrum of chitosan bis(3-methylphenylcarbamate)-(cyclobutylformamide) (CS 5).

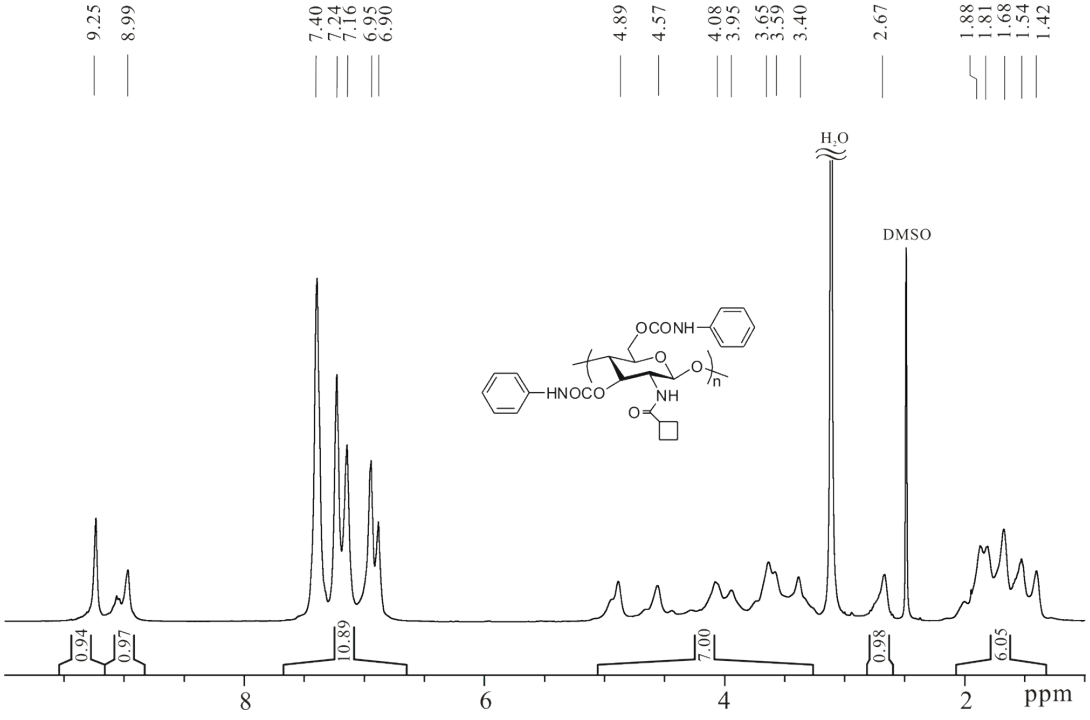

Fig. S8 ^{1}H NMR spectrum of chitosan bis(phenylcarbamate)-(cyclobutylformamide) (CS 6).

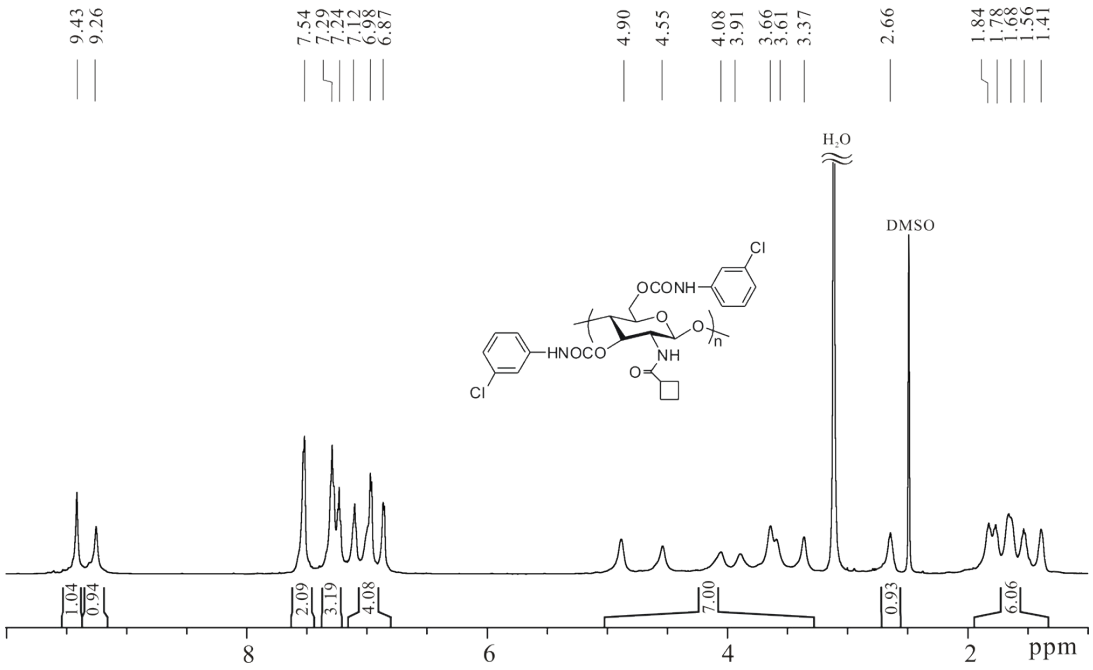

Fig. S9 ^{1}H NMR spectrum of chitosan bis(3-chlorophenylcarbamate)-(cyclobutylformamide) (CS 7).

Table S1. Elemental analysis of chitosan derivatives

Derivatives	Calculated (%)			Found (%)		
	C	H	N	C	H	N
CS 1 ($C_{27}H_{31}N_3O_7 \cdot 0.5H_2O$)	62.54	6.22	8.10	62.20	6.32	7.71
CS 2 ($C_{27}H_{29}Cl_2N_3O_7$)	56.06	5.05	7.26	55.59	5.18	6.69
CS 3 ($C_{25}H_{25}Cl_2N_3O_7$)	54.56	4.58	7.63	54.29	4.99	7.61
CS 4 ($C_{29}H_{35}N_3O_7 \cdot 0.5H_2O$)	63.72	6.64	7.69	63.32	6.65	7.28
CS 5 ($C_{27}H_{31}N_3O_7 \cdot 0.75H_2O$)	62.00	6.26	8.03	61.70	6.28	7.60
CS 6 ($C_{25}H_{27}N_3O_7 \cdot 0.75H_2O$)	60.66	5.80	8.49	60.16	5.91	7.95
CS 7 ($C_{25}H_{25}Cl_2N_3O_7 \cdot 0.5H_2O$)	53.68	4.68	7.51	53.84	4.84	7.10

Table S2. IR spectra data of chitosan derivatives

Derivatives	IR (KBr, cm^{-1}) υ
CS 1	3333 (-NH-), 3099-3012 (Ph-H), 2986-2864 (-C-H), 1719 (-CO_2-), 1665, 1612, 1543 (-CONH-, -Ph)
CS 2	3405-3325 (-NH-), 3099-3042 (Ph-H), 2982-2863 (-C-H), 1718 (-CO_2-), 1661, 1584, 1525 (-CONH-, -Ph)
CS 3	3408-3325 (-NH-), 3119-3063 (Ph-H), 2982-2869 (-C-H), 1718 (-CO_2-), 1659, 1596, 1525 (-CONH-, -Ph)
CS 4	3331 (-NH-), 3128-3036 (Ph-H), 2982-2869 (-C-H), 1721 (-CO_2-), 1661, 1602, 1525 (-CONH-, -Ph)
CS 5	3328 (-NH-), 3149-3045 (Ph-H), 2982-2861 (-C-H), 1718 (-CO_2-), 1664, 1617, 1542 (-CONH-, -Ph)
CS 6	3393-3322 (-NH-), 3134-3063 (Ph-H), 2988-2866 (-C-H), 1721 (-CO_2-), 1661, 1602, 1528 (-CONH-, -Ph)
CS 7	3405-3316 (-NH-), 3119-3072 (Ph-H), 2988-2869 (-C-H), 1721 (-CO_2-), 1659, 1593, 1531 (-CONH-, -Ph)

2. Enantioseparation comparison of CSPs

The enantioseparation capability of newly prepared CSPs was evaluated in *n*-hexane/2-propanol (90/10, v/v), *n*-hexane/ethanol (90/10, v/v) and *n*-hexane/ethanol/methanol/ (90/10, v/v) with the same chiral analytes. These capabilities were compared to those of CSPs I and II prepared from cellulose tris(3,5-dimethylphencarbamate) (CDMPC) and amylose tris(3,5-dimethylphencarbamate) (ADMPC), respectively.

Table S3. Enantioseparation of CSP I and CSP II

No.	CSP I			CSP II			No.	CSP I			CSP II			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**	6.11(R)	2.09	3.00	7.61(R)	1.25	0.39	A
	0.54(+)	1.87	3.07	0.70(+)	1.64	2.62		1.32(R)	1.41	1.60	1.42(R)	1.28	1.19	B
	0.66(+)	1.79	3.79	0.72(+)	1.64	2.63		1.57(R)	1.21	1.37	1.05(R)	1.20	0.89	C
2	1.24(+)	1.20	1.37	1.53(–)	1.30	1.80	**9**	2.42(+)	1.57	2.45	5.71	1.00	0.00	A
	1.19(+)	1.46	2.94	1.15(–)	1.21	1.14		1.37(+)	2.98	6.28	1.75	1.00	0.00	B
	1.43(+)	1.79	5.00	1.09(–)	1.21	1.19		1.72(+)	2.87	6.98	1.36	1.00	0.00	C
3	1.19	1.00	0.00	2.09	1.00	0.00	**10**	5.16(R)	1.70	3.15	4.52(R)	1.18	1.01	A
	0.68(+)	1.06	0.28	1.34	1.00	0.00		1.22(R)	1.46	2.04	1.15(R)	1.12	0.53	B
	0.98	1.00	0.00	1.24	1.00	0.00		1.58(R)	1.27	1.45	1.10(R)	1.16	0.54	C
4	2.95(–)	1.06	0.48	3.74(+)	1.10	0.57	**11**	3.99	1.00	0.00	2.90(+)	1.40	2.17	A
	1.71	1.00	0.00	1.90	1.00	0.00		2.60(+)	1.08	0.48	2.06(+)	1.33	1.93	B
	2.29	1.00	0.00	1.60	1.00	0.00		2.76(+)	1.10	0.85	1.85(+)	1.34	1.96	C
5	0.63	1.00	0.00	0.95(+)	1.12	0.42	**12**	10.01(R)	1.45	1.75	11.74(S)	1.20	0.96	A
	0.43	1.00	0.00	0.65(+)	1.13	0.22		1.97(R)	1.28	1.33	2.25(S)	1.12	0.38	B
	0.69	1.00	0.00	0.57(+)	1.13	0.38		2.36(R)	1.21	1.47	2.50(S)	1.10	0.35	C
6	4.25	1.82	2.73	6.38	1.23	0.85	**13**	Retention time>120min			39.05	1.00	0.00	A
	2.57	3.82	7.18	3.27	1.25	1.25		Retention time>120min			24.36	1.00	0.00	B
	2.55	4.51	9.59	2.42	1.31	1.64		Retention time>120min			12.20	1.00	0.00	C
7	5.71(R)	1.27	1.46	9.85(S)	1.09	0.96	**14**	1.65	1.00	0.00	2.49	1.00	0.00	A
	3.23(R)	1.11	0.77	4.89	1.00	0.00		1.46	1.00	0.00	1.37	1.00	0.00	B
	4.10	1.00	0.00	3.82(R)	1.10	0.45		1.95	1.00	0.00	1.23	1.00	0.00	C

Table S3 to be continued

Continued Table S3

No.	CSP I			CSP II			No.	CSP I			CSP II			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>120min			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

No.: series number of chiral analytes; M.P.: A: *n*-hexane/2-propanol (90/10, v/v); B: *n*-hexane/ethanol (90/10, v/v); C: *n*-hexane/ethanol/methanol (90/5/5, v/v/v). “R”, “S”, “+”, “–” and “2R, 3S” refer to the first-eluted enantiomer. The elution order of analyte 6 was not available because of its low optical rotation.