Electronic Supplementary Materials

Different-Molecular-Weight Chitosan Derivatives Employed for Enantiomeric Separation

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1. ^{1}H NMR spectrum of chitosan

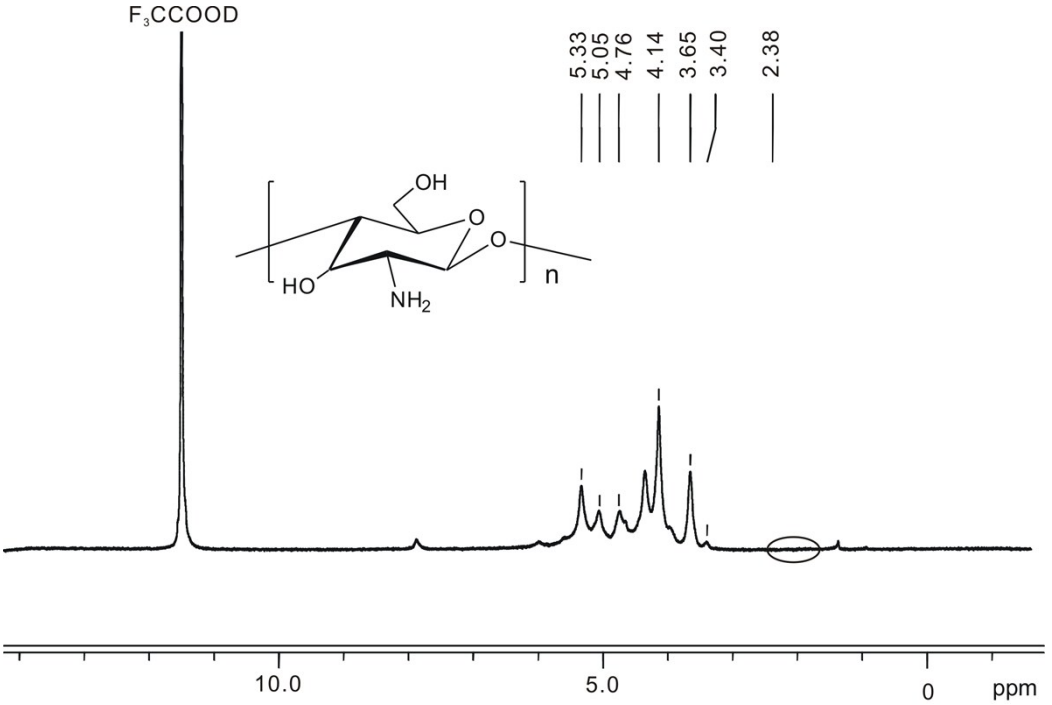

Fig. S1 ^{1}H NMR spectrum of chitosan 3 (Chi-3) (400 MHz, TFA-*d*, 25 °C).

2. ^{1}H NMR spectrum of chitosan (cyclopentylurea)s

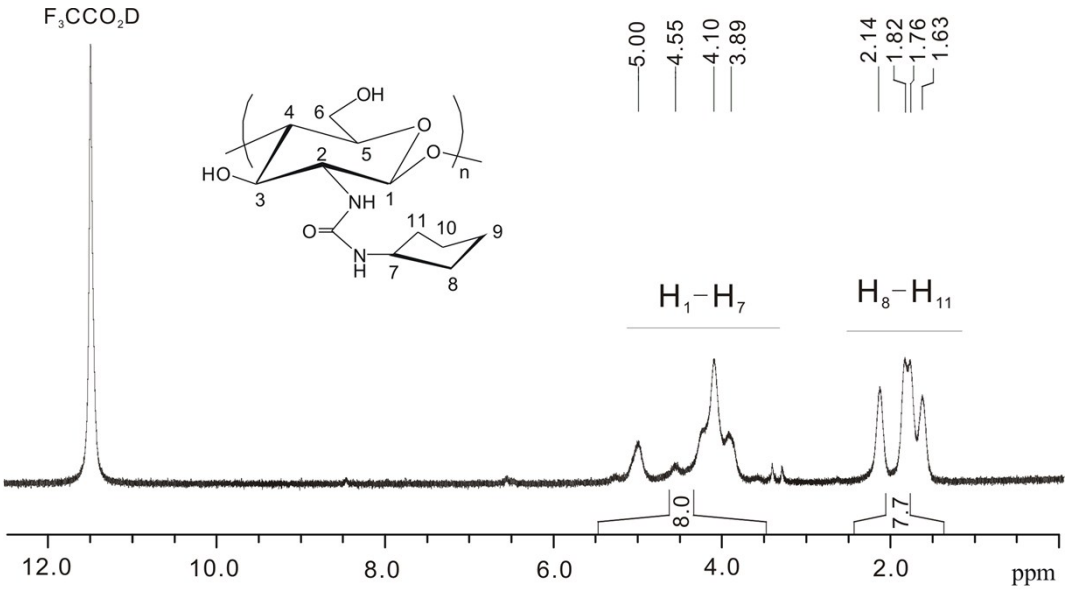

Fig. S2 ^{1}H NMR spectrum of chitosan (cyclopentylurea) (Chi-cPU 1) (400 MHz, TFA-*d*, 25 °C).

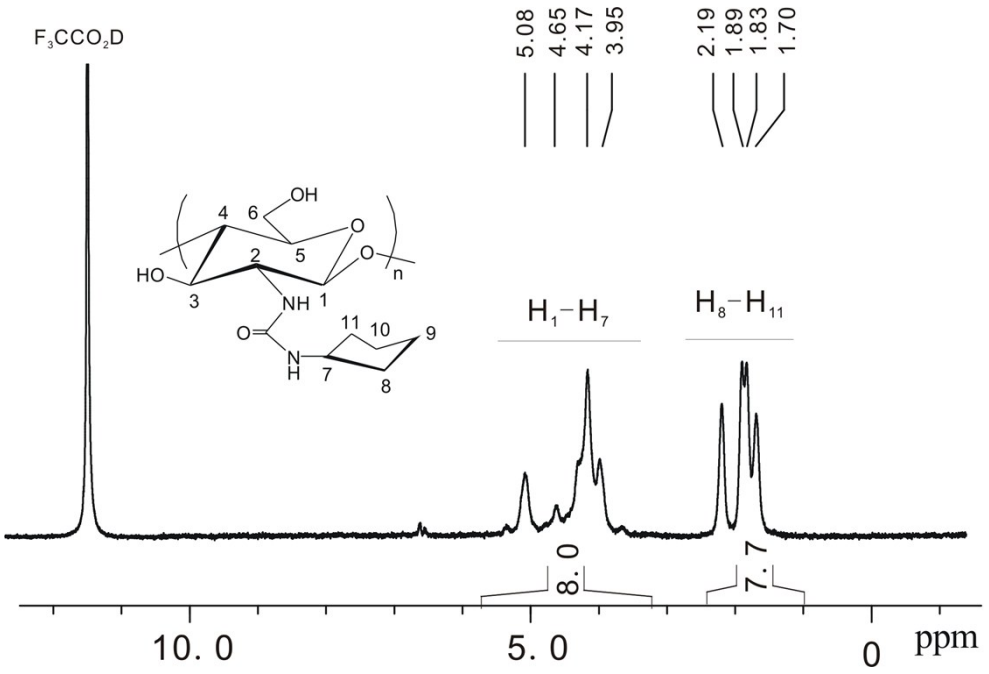

Fig. S3 ^{1}H NMR spectrum of chitosan (cyclopentylurea) (Chi-cPU 2) (400 MHz, TFA-*d*, 25 °C).

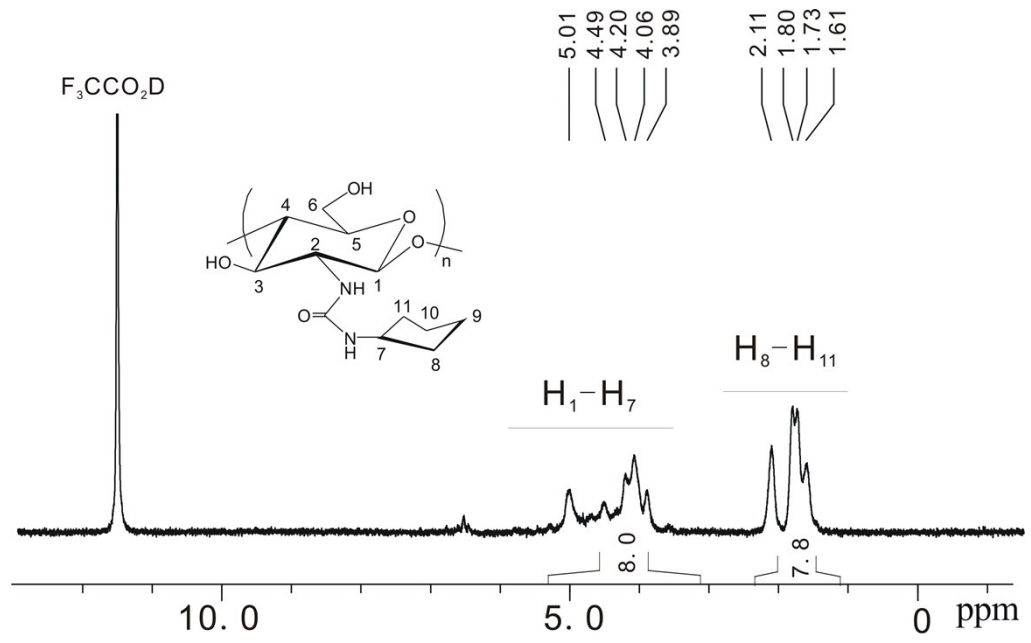

Fig. S4 ^{1}H NMR spectrum of chitosan (cyclopentylurea) (Chi-cPU 3) (400 MHz, TFA-*d*, 25 °C).

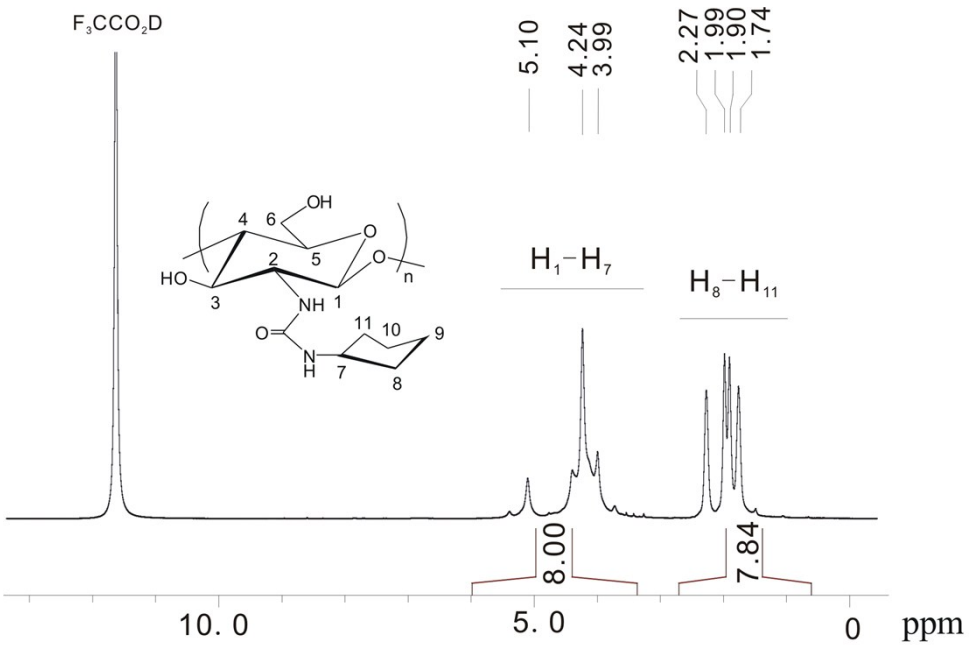

Fig. S5 ^{1}H NMR spectrum of chitosan (cyclopentylurea) (Chi-cPU 4) (400 MHz, TFA-*d*, 25 °C).

3. IR spectrum of chitosan (cyclopentylurea)s

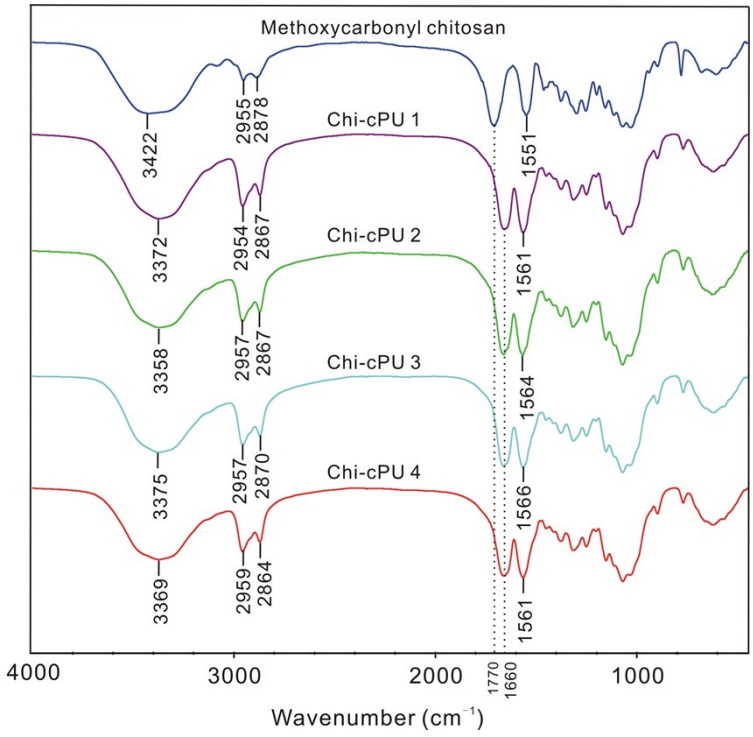

Fig. S6 IR spectrum of chitosan (cyclopentylurea)s.

4. ^{1}H-^{13}C HSQC NMR, ^{1}H-^{1}H COSY NMR and ^{1}H NMR spectra of chitosan bis(3,5-dimethylphenylcarbamate)-(cyclopentylurea)s

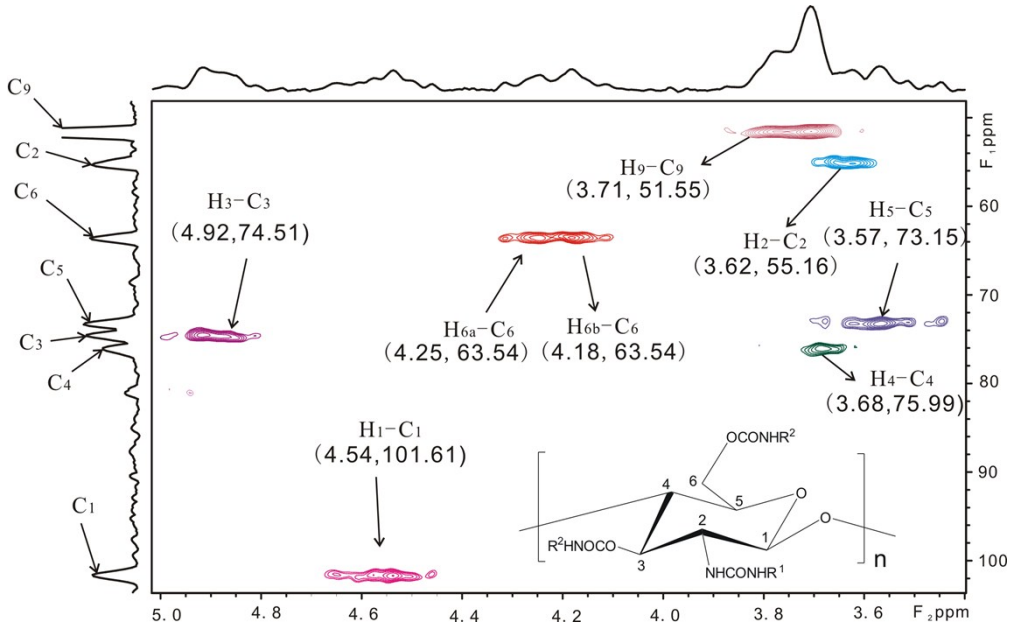

Fig. S7 ^{1}H-^{13}C HSQC NMR spectrum of CDMP-cPU 3 (600 MHz, DMSO-d_6, 90 °C).

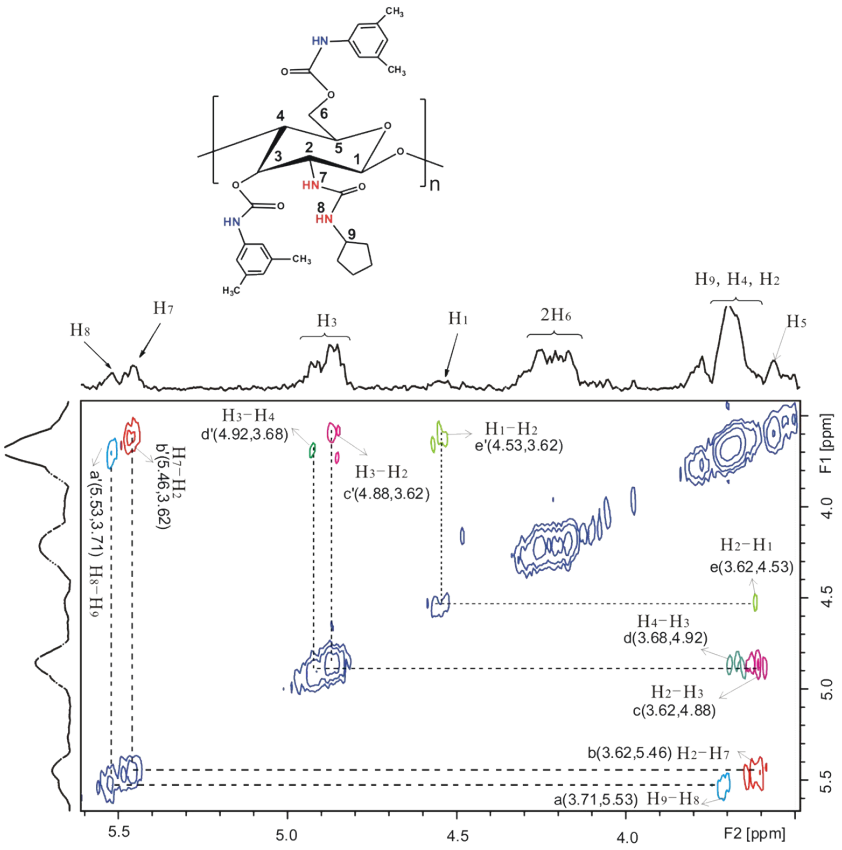

Fig. S8 ^{1}H-^{1}H COSY NMR spectrum of CDMP-cPU 3 (600 MHz, DMSO-d_6, 90 °C).

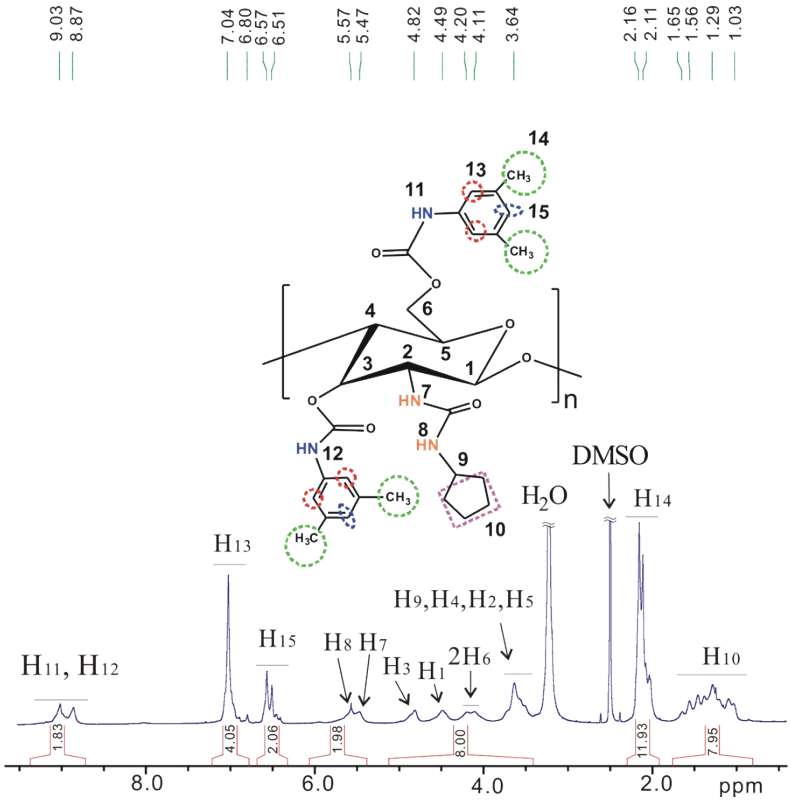

Fig. S9 ^{1}H NMR spectrum of CDMP-cPU 1 (600 MHz, DMSO-d_6, 90 °C).

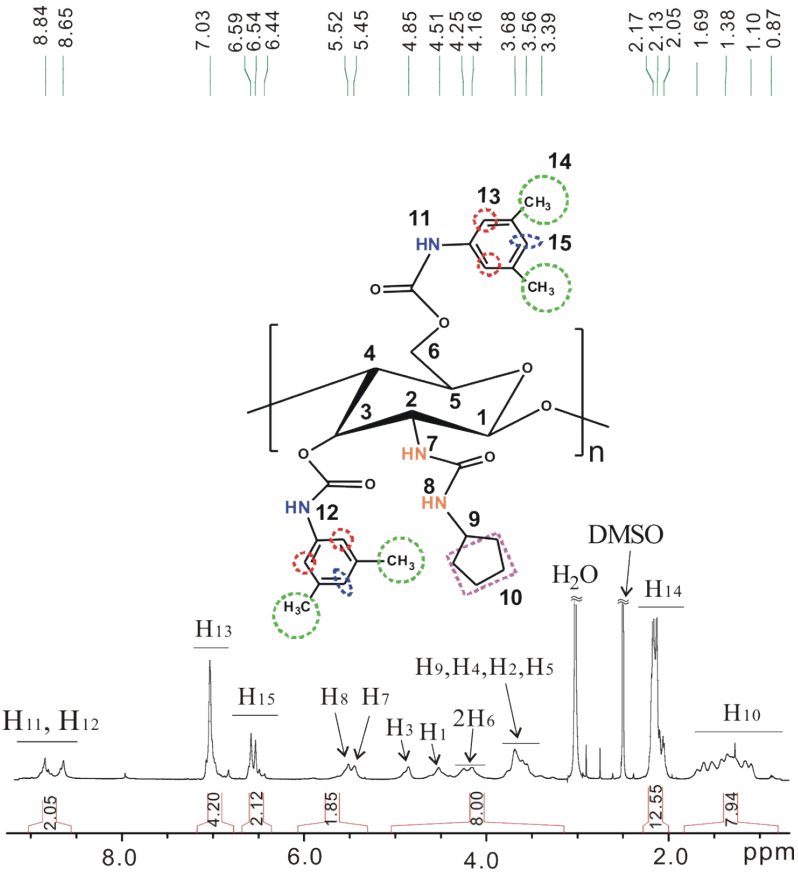

Fig. S10 ^{1}H NMR spectrum of CDMP-cPU 2 (600 MHz, DMSO-d_6, 90 °C).

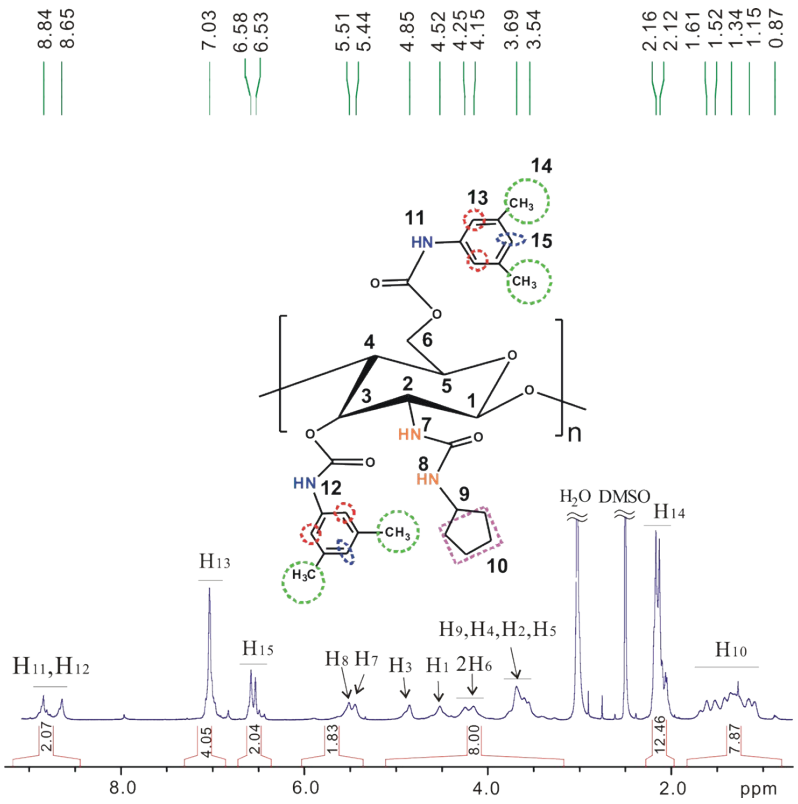

Fig. S11 ^{1}H NMR spectrum of CDMP-cPU 4 (600 MHz, DMSO-d_6, 90 °C).

5. Typical chromatograms of enantioseparations on CSPs 1–4

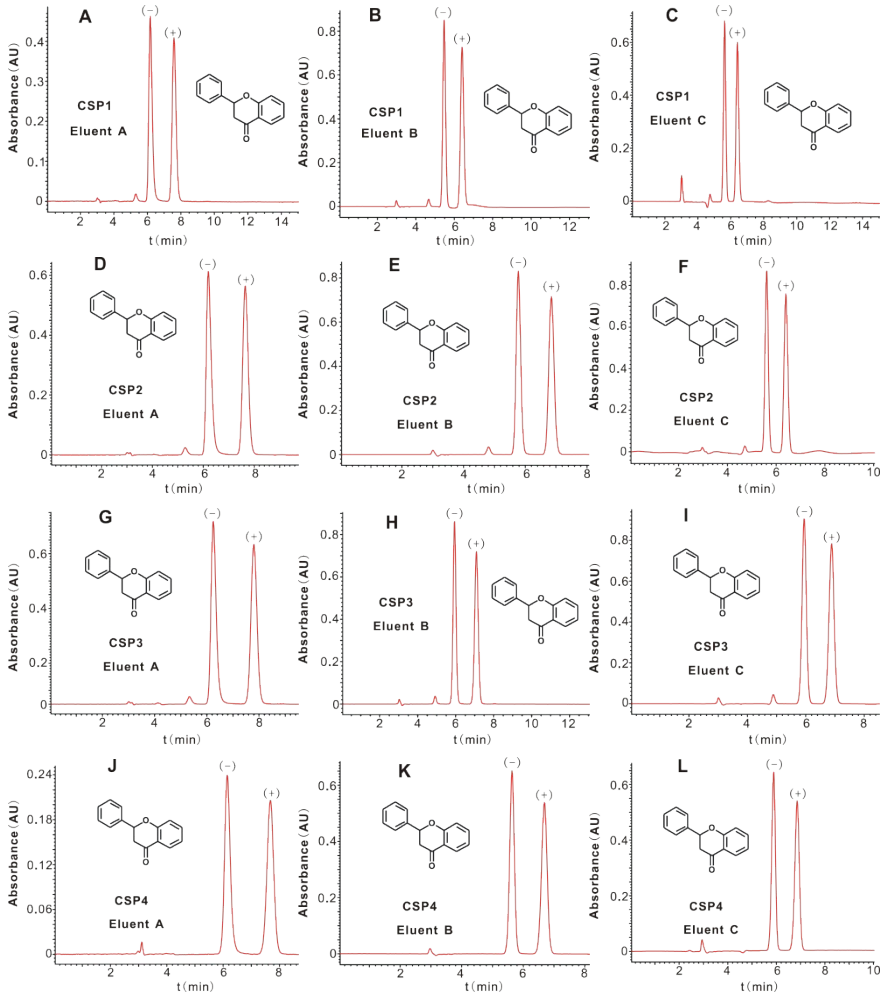

Fig. S12 Chromatograms of analyte 2 separated by CSP 1 (A-C), CSP 2 (D-F), CSP 3 (G-I), CSP 4 (J-L).

Eluents, A: *n*-hexane/isopropanol (90/10, v/v); B: *n*-hexane/ethanol (90/10, v/v); C: *n*-hexane/ethanol/methanol (90/5/5, v/v/v). Flow rate: 1.0 ml/min; detection temperature: 25 °C; column size: Φ 250 mm × 4.6 mm; particle size of silica gel: 7 μm.

6. Enantioseparation evaluation of CSPs1–4

Table S1. Enantioseparation evaluation of CSPs1–4

S.N.	CSP1			CSP2			CSP3			CSP4			Eluents
	k_1	α	R_s	k_1	α	R_s	k_1	α	R_s	k_1	α	R_s	
1	0.31	1.00	0.00	0.35	1.00	0.00	0.38	1.00	0.00	0.34	1.00	0.00	A
	0.31	1.00	0.00	0.34	1.00	0.00	−0.34	1.13	0.16	0.32	1.00	0.00	B
	0.30	1.00	0.00	− 0.28	1.11	~0.1	−0.33	1.17	0.28	0.33	1.00	0.00	C
2	−0.97	1.47	3.51	− 1.05	1.46	3.81	−1.07	1.48	3.93	− 1.06	1.49	3.75	A
	−0.82	1.38	3.11	− 0.94	1.38	3.53	−0.99	1.39	3.54	− 0.90	1.39	3.35	B
	−0.88	1.30	2.68	− 0.86	1.31	2.88	−1.00	1.32	3.04	− 1.01	1.33	3.04	C
3	−1.35	1.09	0.74	− 1.42	1.10	0.96	−1.46	1.12	1.04	− 1.37	1.07	0.23	A
	−1.01	1.06	~0.1	− 1.19	1.08	0.35	−1.24	1.09	0.81	− 1.05	1.06	0.08	B
	0.96	1.00	0.00	0.93	1.00	0.00	−2.26	1.10	~0.1	0.98	1.00	0.00	C
4	+2.16	1.05	0.32	2.03	1.00	0.00	2.04	1.00	0.00	1.76	1.00	0.00	A
	+1.44	1.06	0.47	+1.70	1.08	0.94	+1.73	1.08	0.87	+1.47	1.09	0.78	B
	+1.32	1.03	~0.1	+1.19	1.04	~0.1	+1.30	1.03	~0.1	+1.35	1.04	~0.1	C
5	0.71	1.00	0.00	0.73	1.00	0.00	−0.75	1.04	~0.1	0.71	1.00	0.00	A
	0.66	1.00	0.00	0.70	1.00	0.00	0.62	1.00	0.00	0.64	1.00	0.00	B
	0.60	1.00	0.00	0.55	1.00	0.00	0.60	1.00	0.00	0.63	1.00	0.00	C
6	R10.07	1.16	1.29	R9.43	1.20	1.80	R9.56	1.27	2.14	R9.00	1.19	1.60	A
	R7.90	1.50	5.05	R8.07	1.57	5.91	R6.59	1.53	5.24	R7.40	1.65	5.68	B
	R5.54	1.50	5.48	R5.39	1.53	6.14	R5.01	1.49	5.19	R6.74	1.68	6.59	C
7	S11.02	1.18	0.83	S8.32	1.36	1.92	S9.04	1.37	2.03	S7.71	1.34	1.87	A

	3.53	1.00	0.00	S3.41	1.19	1.57	S3.10	1.21	1.64	S2.85	1.18	1.11	B
	1.53	1.00	0.00	1.52	1.00	0.00	1.79	1.00	0.00	1.67	1.00	0.00	C
8	+3.13	1.24	1.44	+2.64	1.25	1.56	+2.83	1.25	1.51	+2.46	1.32	1.73	A
	+2.07	1.20	1.40	+2.14	1.21	1.56	+1.88	1.20	1.48	+1.88	1.26	1.78	B
	+1.44	1.12	1.07	+1.59	1.13	1.32	+1.63	1.12	1.23	+1.79	1.15	1.22	C
9	R2.54	1.65	2.15	1.83	1.00	0.00	1.83	1.00	0.00	1.66	1.00	0.00	A
	R1.15	1.20	1.10	R1.20	1.13	0.25	R1.11	1.12	0.47	R1.04	1.14	0.23	B
	R0.79	1.12	0.55	R0.75	1.10	0.23	R0.88	1.08	0.15	R0.86	1.08	0.14	C
10	−2.95	1.12	1.21	−3.05	1.12	1.29	−3.14	1.43	1.21	− 2.87	1.14	1.25	A
	−2.24	1.17	1.65	−2.70	1.16	1.73	−2.85	1.15	1.66	− 2.35	1.17	1.53	B
	−2.15	1.11	1.22	−2.10	1.11	1.21	−2.62	1.11	1.19	− 2.24	1.12	0.34	C
11	S13.41	1.24	1.51	S9.21	1.53	2.51	S10.38	1.61	2.77	S8.27	1.54	2.41	A
	S4.10	1.24	1.54	S3.30	1.20	1.37	S4.13	1.41	2.76	S3.41	1.36	2.03	B
	2.24	1.00	0.00	S1.96	1.14	1.08	S2.04	1.15	1.21	S2.50	1.12	0.69	C
12	0.81	1.00	0.00	R0.77	1.10	~0.1	0.80	1.00	0.00	R0.71	1.17	0.15	A
	R0.73	1.11	0.10	R1.36	1.21	0.33	R0.69	1.12	0.13	S0.72	1.17	0.23	B
	R0.75	1.15	0.24	R0.81	1.18	0.57	R0.77	1.15	0.25	S0.78	1.19	0.92	C

To be continued

Continued Table S1

S.N.	CSP1			CSP2			CSP3			CSP4			Eluents
	k_1	α	R_s	k_1	α	R_s	k_1	α	R_s	k_1	α	R_s	
13	S2.58	1.38	2.10	S1.99	1.36	2.27	S2.10	1.36	2.27	S1.88	1.36	2.25	A
	S1.72	1.11	0.65	S1.86	1.12	1.10	S1.69	1.12	1.08	S1.69	1.10	0.45	B

	^{R}1.43	1.09	0.36	^{R}1.47	1.08	0.35	^{R}1.56	1.05	0.11	^{R}1.69	1.12	1.17	C
14	^{2R,3S}5.99	4.00	8.21	^{2R,3S}5.12	3.43	7.69	^{2R,3S}5.25	2.94	6.50	^{2R,3S}4.64	4.15	8.19	A
	^{2R,3S}3.37	3.30	9.08	^{2R,3S}3.56	3.13	8.82	^{2R,3S}3.73	2.77	7.93	^{2R,3S}3.19	4.02	9.25	B
	^{2R,3S}2.20	2.51	8.50	^{2R,3S}1.98	2.42	7.66	^{2R,3S}2.07	2.19	6.62	^{2R,3S}2.29	2.91	8.64	C
15	1.23	1.00	0.00	1.09	1.00	0.00	1.22	1.00	0.00	0.96	1.00	0.00	A
	0.87	1.00	0.00	0.86	1.00	0.00	0.85	1.00	0.00	0.76	1.00	0.00	B
	0.70	1.00	0.00	0.72	1.00	0.00	0.77	1.00	0.00	0.73	1.00	0.00	C
16	0.75	1.00	0.00	0.67	1.00	0.00	0.69	1.00	0.00	0.58	1.00	0.00	A
	0.55	1.00	0.00	1.06	1.00	0.00	0.52	1.00	0.00	0.53	1.00	0.00	B
	0.49	1.00	0.00	0.61	1.00	0.00	0.52	1.00	0.00	0.55	1.00	0.00	C
17	^{S}14.26	1.08	0.81	^{S}10.73	1.10	0.63	^{S}13.88	1.10	0.78	^{S}11.49	1.09	0.61	A
	^{S}7.52	1.18	1.26	^{S}7.84	1.22	1.69	^{S}7.90	1.19	1.44	^{S}7.55	1.19	1.36	B
	^{S}4.65	1.14	1.15	^{S}4.64	1.16	1.49	^{S}4.79	1.15	1.30	^{S}5.55	1.15	1.32	C
18	$^{-}$3.54	1.15	1.36	$^{-}$3.32	1.14	1.35	$^{-}$3.39	1.12	1.17	$^{-}$3.24	1.16	1.49	A
	$^{-}$3.08	1.08	0.93	$^{-}$3.36	1.08	1.01	$^{-}$3.45	1.07	0.73	$^{-}$2.90	1.09	1.01	B
	$^{-}$2.37	1.04	0.21	$^{-}$2.20	1.04	0.37	$^{-}$2.28	1.03	~0.1	$^{-}$2.38	1.04	0.16	C
19	^{R}3.03	1.91	3.99	^{R}2.35	1.47	1.84	^{R}2.50	1.45	1.83	^{R}2.09	1.47	1.88	A
	^{R}1.34	1.30	1.60	^{R}1.40	1.21	1.24	^{R}1.26	1.20	0.95	^{R}1.19	1.22	1.21	B
	^{R}0.89	1.16	1.11	^{R}0.97	1.14	0.97	^{R}1.00	1.12	0.93	^{R}1.10	1.14	0.99	C

S.N.: serial number of the analytes; eluents: A: *n*-hexane/isopropanol (90/10, v/v), B: *n*-hexane/ethanol (90/10, v/v), C: *n*-hexane/ethanol/methanol (90/5/5, v/v/v); flow rate: 1.0 ml/min; detection temperature: 25 ^{o}C; column size: Φ 250 mm × 4.6 mm; particle size of silica gel: 7 μm. "+", "–", "R", "S" and "(2R,3S)" at the superscript of k_1 refer to the optical rotation direction or configuration of the first-eluted enantiomer.

7. Enantioseparation evaluation of CDMPC

Table S2. Enantioseparation evaluation of CDMPC

S.N.	Separation results			S.N.	Separation results			S.N.	Separation results			S.N.	Separation results			Eluents
	k_1	α	R_s		k_1	α	R_s		k_1	α	R_s		k_1	α	R_s	
1	$^{+}$1.08	1.42	3.17	6	^{S}7.44	1.12	0.81	11	^{S}8.88	1.13	1.01	16	1.19	1.00	0.00	A
	$^{+}$0.97	1.49	3.90		6.06	1.00	0.00		^{S}3.08	1.10	0.90		0.89	1.00	0.00	B
	$^{+}$1.01	1.31	2.71		^{R}6.09	1.08	0.70		^{S}2.78	1.10	0.89		0.97	1.00	0.00	C
2	$^{-}$1.68	1.30	3.49	7	^{R}6.02	1.23	1.56	12	^{R}2.12	1.15	0.75	17	2.30	1.00	0.00	A
	$^{-}$1.48	1.23	2.68		^{R}2.03	1.31	2.10		1.67	1.00	0.00		1.89	1.00	0.00	B
	$^{-}$1.53	1.28	2.84		^{R}1.84	1.22	1.72		1.74	1.00	0.00		1.89	1.00	0.00	C
3	$^{-}$2.15	1.12	1.23	8	4.46	1.00	0.00	13	^{R}1.38	1.38	2.37	18	2.31	1.00	0.00	A
	$^{-}$1.78	1.07	0.87		2.43	1.00	0.00		^{R}1.11	1.34	2.62		1.91	1.00	0.00	B
	$^{-}$1.83	1.06	0.74		2.25	1.00	0.00		^{R}1.16	1.22	1.93		1.89	1.00	0.00	C
4	$^{+}$3.33	1.14	1.78	9	^{R}3.49	1.25	2.36	14	r. t. > 120 min			19	^{R}3.50	1.47	3.47	A
	$^{+}$2.21	1.08	1.02		^{R}1.54	1.21	2.02		^{2R,3S}10.48	1.28	2.48		^{R}1.60	1.25	2.17	B
	$^{+}$2.06	1.06	2.77		^{R}1.45	1.18	1.83		^{2R,3S}7.87	1.26	2.64		^{R}1.56	1.18	1.77	C
5	$^{+}$0.94	1.16	0.48	10	$^{+}$2.82	1.45	4.55	15	3.75	1.00	0.00					A
	$^{+}$0.87	1.17	0.73		$^{+}$2.37	1.40	4.12		^{4R,1S}2.13	2.32	7.29					B
	$^{+}$0.90	1.23	1.50		$^{+}$2.46	1.39	4.47		^{4R,1S}2.15	2.11	7.45					C

S.N.: serial number of the analytes; r. t.: retention time; eluents: A: *n*-hexane/isopropanol (90/10, v/v), B: *n*-hexane/ethanol (90/10, v/v), C: *n*-hexane/ethanol/methanol (90/5/5, v/v/v); flow rate: 1.0 ml/min; detection temperature: 25 °C; column size: Φ 250 mm × 4.6 mm; particle size of silica gel: 7 μm. "+", "–", "R", "S", "(2R,3S)" and "(4R,1S)" at the superscript of k_1 refer to the optical rotation direction or configuration of the first-eluted enantiomer.