

## SUPPLEMENTARY MATERIALS

# Novel brush-type chiral stationary phases for enantioseparation of pharmaceutical drugs

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**Table S1.** Enantioseparation results of racemates **1 – 7** and **9** on **CSP-1 – CSP-10**; mobile phase: hexane-2-PrOH = 90 : 10; flow: 1 mL/min; UV detection at 254 nm. Column dimensions were 150 x 4.6 mm I.D., except for **CSP-1** which had the dimensions of 250 x 4.6 mm I.D.

Compound		1	2	3	4	5	6	7	9
<b>CSP-1</b>	$k_2$	1.28	4.67	2.84	2.90	1.72	2.83	3.25	9.03
	$\alpha$	1.32	1.17	1.00	1.00	1.30	1.25	1.48	1.11
	$R_s$	2.16	1.76	0.00	0.00	2.45	2.18	3.20	1.61
<b>CSP-2</b>	$k_2$	0.29	0.97	0.69	0.75	0.52	0.58	0.90	1.37
	$\alpha$	1.26	1.19	1.00	1.00	1.23	1.19	1.48	1.08
	$R_s$	0.89	0.96	0.00	0.00	0.87	0.97	3.32	0.94
<b>CSP-3</b>	$k_2$	0.15	1.23	0.70	0.88	0.36	2.64	1.30	1.42
	$\alpha$	1.00	1.00	1.00	1.00	1.00	1.00	1.17	1.00
	$R_s$	0.00	0.00	0.00	0.00	0.00	0.00	1.39	0.00
<b>CSP-4</b>	$k_2$	0.12	0.83	0.36	0.40	0.36	0.21	0.37	0.72
	$\alpha$	1.33	1.00	1.00	1.00	1.13	1.00	1.46	1.08
	$R_s$	0.47	0.00	0.00	0.00	0.47	0.00	1.36	0.62
<b>CSP-5</b>	$k_2$	0.09	0.27	0.20	0.25	0.30	0.17	0.30	0.37
	$\alpha$	1.00	1.00	1.00	1.00	1.00	1.00	1.61	1.00
	$R_s$	0.00	0.00	0.00	0.00	0.00	0.00	1.30	0.00
<b>CSP-6</b>	$k_2$	0.70	2.72	1.68	1.82	1.26	1.36	1.51	3.11
	$\alpha$	1.43	1.27	1.00	1.00	1.34	1.05	1.20	1.13
	$R_s$	2.82	2.55	0.00	0.00	2.95	0.49	2.23	2.18
<b>CSP-7</b>	$k_2$	0.72	2.57	1.35	1.71	1.44	0.94	1.38	2.76
	$\alpha$	1.60	1.57	1.00	1.00	1.49	1.14	1.10	1.14
	$R_s$	4.13	4.43	0.00	0.00	4.28	1.05	0.90	2.36
<b>CSP-8</b>	$k_2$	0.37	1.01	0.68	0.91	0.51	0.74	1.45	1.50
	$\alpha$	1.29	1.10	1.00	1.03	1.16	1.14	1.84	1.00
	$R_s$	1.43	0.46	0.00	0.39	0.69	0.82	4.98	0.00
<b>CSP-9</b>	$k_2$	0.35	1.13	0.89	0.98	0.71	0.73	0.89	1.87
	$\alpha$	1.24	1.14	1.04	1.00	1.27	1.13	1.23	1.05
	$R_s$	1.18	1.06	0.49	0.00	1.86	0.90	1.62	0.69
<b>CSP-10</b>	$k_2$	0.69	2.24	1.51	1.84	1.74	1.17	1.10	2.74
	$\alpha$	1.45	1.25	1.05	1.06	1.46	1.00	1.21	1.03
	$R_s$	2.88	1.09	0.59	0.64	3.15	0.00	1.44	0.47

**Table S2.** Enantioseparation results of racemates **8** and **10 – 14** on **CSP-1 – CSP-10**; mobile phase: hexane-2-PrOH = 80 : 20; flow: 1 mL/min; UV detection at 254 nm. Column dimensions were 150 x 4.6 mm I.D., except for **CSP-1** which had the dimensions of 250 x 4.6 mm I.D.

Compound		8	10	11	12	13	14
<b>CSP-1</b>	$k_2$	7.03	2.77		22.37	2.27	11.85
	$\alpha$	1.57	1.52	1.27	1.46	1.56	1.32
	$R_s$	4.20	3.76		3.94	3.76	3.28
<b>CSP-2</b>	$k_2$	1.90	1.18	2.30	8.00	1.12	2.45
	$\alpha$	1.54	1.49	1.36	1.54	1.41	1.09
	$R_s$	4.83	2.88	3.85	4.38	3.54	1.00
<b>CSP-3</b>	$k_2$	3.00	0.54	1.68	2.04	0.85	9.12
	$\alpha$	1.22	1.08	1.11	1.07	1.22	1.21
	$R_s$	1.47	0.47	0.87	0.59	1.51	1.52
<b>CSP-4</b>	$k_2$	0.84	0.61	1.02	2.61	0.50	0.72
	$\alpha$	1.46	1.66	1.42	1.40	1.48	1.30
	$R_s$	2.84	2.46	3.08	3.47	2.36	1.85
<b>CSP-5</b>	$k_2$	0.33	0.21	0.41	0.82	0.17	0.37
	$\alpha$	1.14	1.00	1.16	1.23	1.18	1.00
	$R_s$	0.59	0.00	0.76	1.61	0.49	0.00
<b>CSP-6</b>	$k_2$	4.21	2.61	4.51	11.79	2.16	14.10
	$\alpha$	1.32	2.12	1.61	1.49	1.55	1.74
	$R_s$	3.56	6.68	7.38	4.91	6.57	3.44
<b>CSP-7</b>	$k_2$	4.08	3.60	5.56	16.94	2.40	11.68
	$\alpha$	1.57	2.82	1.90	1.68	1.64	1.48
	$R_s$	6.16	9.05	9.80	5.56	7.93	4.93
<b>CSP-8</b>	$k_2$	2.33	0.88	2.26	6.80	1.70	3.78
	$\alpha$	1.50	1.23	1.27	1.35	1.50	1.34
	$R_s$	4.91	1.50	3.21	3.30	5.22	4.13
<b>CSP-9</b>	$k_2$	2.78	1.64	2.98	8.02	1.41	6.94
	$\alpha$	1.43	1.57	1.35	1.43	1.35	1.09
	$R_s$	5.38	6.00	5.34	5.36	4.25	1.25
<b>CSP-10</b>	$k_2$	4.72	2.96	4.36	9.92	1.69	19.14
	$\alpha$	1.67	3.02	1.83	1.46	1.50	1.44
	$R_s$	4.96	7.12	7.01	3.77	5.22	2.93

**Table S3.** Enantioseparation results of racemates **15 – 21** on **CSP-1 – CSP-10**; mobile phase: hexane-2-PrOH = 80 : 20; flow: 1 mL/min; UV detection at 254 nm. Column dimensions were 150 x 4.6 mm I.D., except for **CSP-1** which had the dimensions of 250 x 4.6 mm I.D.

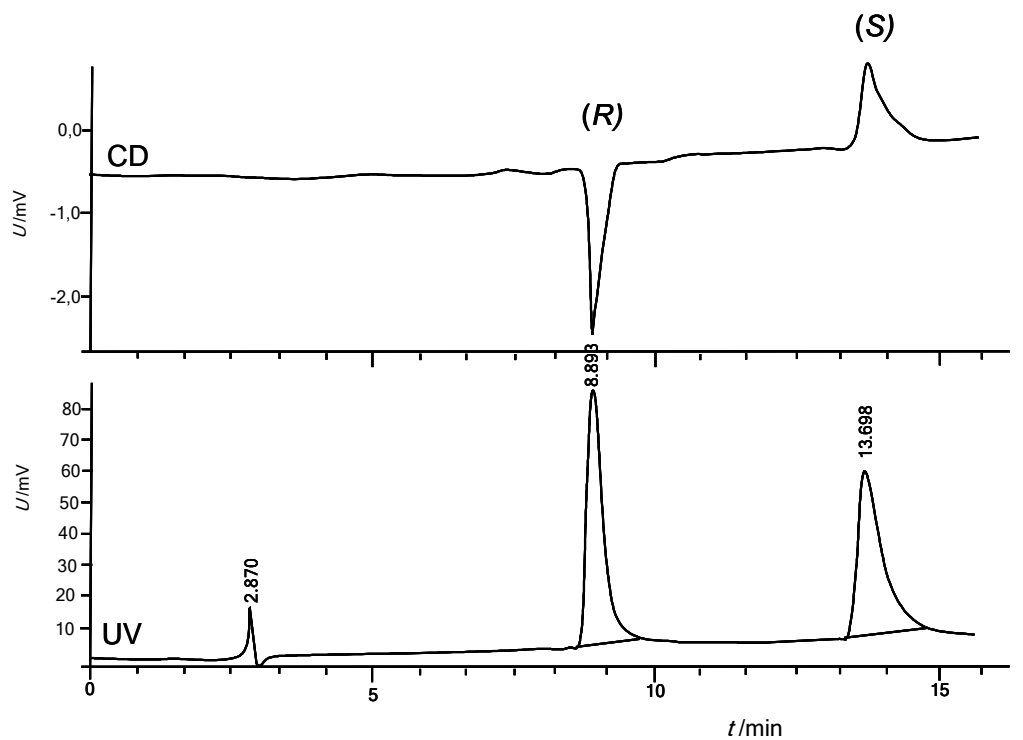
Compounds		15	16	17	18	19	20	21
<b>CSP-1</b>	$k_2$	5.07	5.17	3.93	4.73	8.54	7.00	7.70
	$\alpha$	1.07	1.06	1.10	1.06	1.15	1.04	1.07
	$R_s$	0.65	0.45	0.92	0.54	1.95	0.35	0.66
<b>CSP-2</b>	$k_2$	0.96	0.93	0.87	0.93	1.29	1.19	1.17
	$\alpha$	1.08	1.10	1.29	1.15	1.00	1.14	1.19
	$R_s$	0.68	0.87	2.25	1.35	0.00	1.37	1.82
<b>CSP-3</b>	$k_2$	5.27	3.64	3.58	3.09	4.78	5.87	4.78
	$\alpha$	1.14	1.19	1.17	1.19	1.06	1.06	1.17
	$R_s$	1.09	1.47	1.38	1.25	0.54	0.51	1.34
<b>CSP-4</b>	$k_2$	0.29	0.28	0.22	0.24	0.41	0.31	0.32
	$\alpha$	1.00	1.00	1.00	1.00	1.16	1.00	1.00
	$R_s$	0.00	0.00	0.00	0.00	0.65	0.00	0.00
<b>CSP-5</b>	$k_2$	0.21	0.21	0.15	0.17	0.28	0.23	0.20
	$\alpha$	1.00	1.00	1.00	1.00	1.17	1.00	1.00
	$R_s$	0.00	0.00	0.00	0.00	0.59	0.00	0.00
<b>CSP-6</b>	$k_2$	4.59	4.72	4.83	5.89	6.44	5.63	5.45
	$\alpha$	1.31	1.43	1.65	1.52	1.03	1.27	1.41
	$R_s$	2.66	3.54	4.21	3.02	0.31	2.04	3.10
<b>CSP-7</b>	$k_2$	3.88	4.45	4.21	4.34	6.39	5.69	5.19
	$\alpha$	1.31	1.48	1.81	1.51	1.10	1.37	1.45
	$R_s$	3.89	5.55	8.71	5.02	1.16	4.28	5.47
<b>CSP-8</b>	$k_2$	1.47	1.50	1.21	1.42	2.44	1.99	1.78
	$\alpha$	1.00	1.09	1.12	1.07	1.23	1.13	1.09
	$R_s$	0.00	1.01	1.33	0.69	2.77	1.77	1.07
<b>CSP-9</b>	$k_2$	3.57	3.53	4.18	3.61	4.57	4.83	4.60
	$\alpha$	1.45	1.51	2.08	1.64	1.18	1.45	1.67
	$R_s$	5.90	6.57	11.72	7.29	2.63	5.71	7.81
<b>CSP-10</b>	$k_2$	6.69	6.39	6.11	6.21	10.06	9.14	8.92
	$\alpha$	1.19	1.28	1.50	1.33	1.06	1.32	1.36
	$R_s$	1.57	2.27	4.14	2.31	0.53	2.40	2.86

**Table S4.** Enantioseparation results of NSAIDs on **CSP-6 – CSP-10**; flow: 1 mL/min; UV detection at 254 nm; column dimensions: 150 x 4.6 mm I.D.; mobile phase: top - hexane-2-PrOH-CH<sub>3</sub>COOH = 90:10:0.1; bottom - hexane-2-PrOH = 80:20 + 1 g dm<sup>-3</sup> NH<sub>4</sub>OAc.

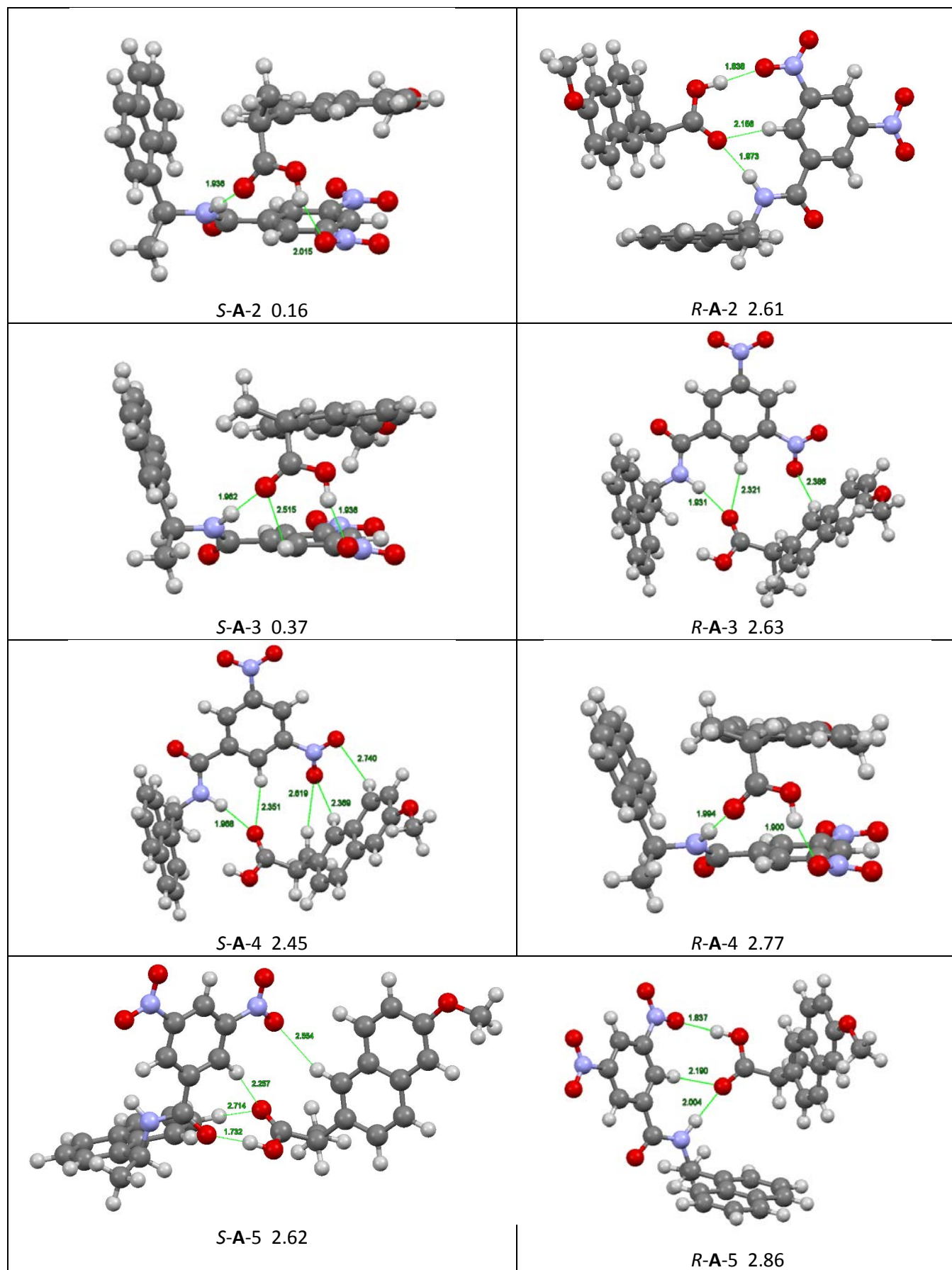
		Ibuprofen	Ketoprofen	Naproxen	Flurbiprofen	Suprofen	Fenoprofen
<b>CSP-6</b>	<i>k</i> <sub>2</sub>	0.28	2.51	2.79	0.63	4.16	0.62
	<i>α</i>	1.00	1.00	1.34	1.06	1.00	1.08
	<i>R</i> <sub>s</sub>	0.00	0.00	3.78	0.41	0.00	0.53
<b>CSP-7</b>	<i>k</i> <sub>2</sub>	0.24	2.33	4.35	0.52	3.79	0.52
	<i>α</i>	1.14	1.05	1.58	1.14	1.00	1.21
	<i>R</i> <sub>s</sub>	0.47	0.60	5.80	0.73	0.00	1.18
<b>CSP-8</b>	<i>k</i> <sub>2</sub>	0.12	1.34	0.99	0.31	2.25	0.31
	<i>α</i>	1.00	1.00	1.00	1.00	1.00	1.00
	<i>R</i> <sub>s</sub>	0.00	0.00	0.00	0.00	0.00	0.00
<b>CSP-9</b>	<i>k</i> <sub>2</sub>	0.16	1.45	1.24	0.32	2.22	0.36
	<i>α</i>	1.00	1.00	1.09	1.00	1.00	1.00
	<i>R</i> <sub>s</sub>	0.00	0.00	0.95	0.00	0.00	0.00
<b>CSP-10</b>	<i>k</i> <sub>2</sub>	0.22	2.28	2.89	0.53	4.09	0.50
	<i>α</i>	1.00	1.00	1.45	1.00	1.00	1.10
	<i>R</i> <sub>s</sub>	0.00	0.00	3.52	0.00	0.00	0.56
<b>CSP-6</b>	<i>k</i> <sub>2</sub>	0.45	6.25	8.95	2.00	11.01	1.14
	<i>α</i>	1.00	1.10	1.82	1.14	1.11	1.26
	<i>R</i> <sub>s</sub>	0.00	0.75	4.37	1.09	0.63	2.10
<b>CSP-7</b>	<i>k</i> <sub>2</sub>	0.16	1.31	3.51	0.43	2.03	0.45
	<i>α</i>	1.50	1.20	2.39	1.53	1.16	1.55
	<i>R</i> <sub>s</sub>	0.62	1.43	7.70	1.83	1.18	1.95
<b>CSP-8</b>	<i>k</i> <sub>2</sub>	0.06	0.67	0.64	0.17	1.05	0.18
	<i>α</i>	1.00	1.00	1.08	1.00	1.00	1.00
	<i>R</i> <sub>s</sub>	0.00	0.00	0.51	0.00	0.00	0.00
<b>CSP-9</b>	<i>k</i> <sub>2</sub>	0.11	0.81	1.03	0.23	1.22	0.25
	<i>α</i>	1.00	1.00	1.21	1.00	1.00	1.00
	<i>R</i> <sub>s</sub>	0.00	0.00	1.59	0.00	0.00	0.00
<b>CSP-10</b>	<i>k</i> <sub>2</sub>	0.31	1.83	3.35	0.67	2.94	0.63
	<i>α</i>	1.19	1.12	2.14	1.27	1.11	1.24
	<i>R</i> <sub>s</sub>	0.51	0.87	4.68	1.37	0.78	1.13

**Table S5.** Enantioseparation results of 3-hydroxy-benzodiazepine drugs on **CSP-6 – CSP-10**; flow: 1 mL/min; UV detection at 254 nm; column dimensions: 150 x 4.6 mm I.D.; mobile phase: hexane-2-PrOH = 80:20 + 1 g dm<sup>-3</sup> NH<sub>4</sub>OAc.

		Lorazepam	Oxazepam	Temazepam
<b>CSP-6</b>	<i>k</i> <sub>2</sub>	14.20	9.78	14.34
	<i>α</i>	1.93	1.39	1.31
	<i>R</i> <sub>s</sub>	6.38	3.08	3.13
<b>CSP-7</b>	<i>k</i> <sub>2</sub>	5.44	3.13	6.31
	<i>α</i>	2.54	1.59	1.39
	<i>R</i> <sub>s</sub>	8.11	4.28	3.87
<b>CSP-8</b>	<i>k</i> <sub>2</sub>	1.94	1.45	2.67
	<i>α</i>	1.47	1.20	1.12
	<i>R</i> <sub>s</sub>	3.63	1.34	1.24
<b>CSP-9</b>	<i>k</i> <sub>2</sub>	2.46	1.82	3.83
	<i>α</i>	1.53	1.17	1.14
	<i>R</i> <sub>s</sub>	4.84	1.66	1.53
<b>CSP-10</b>	<i>k</i> <sub>2</sub>	6.59	4.27	8.61
	<i>α</i>	2.48	1.59	1.45
	<i>R</i> <sub>s</sub>	6.00	1.89	3.02

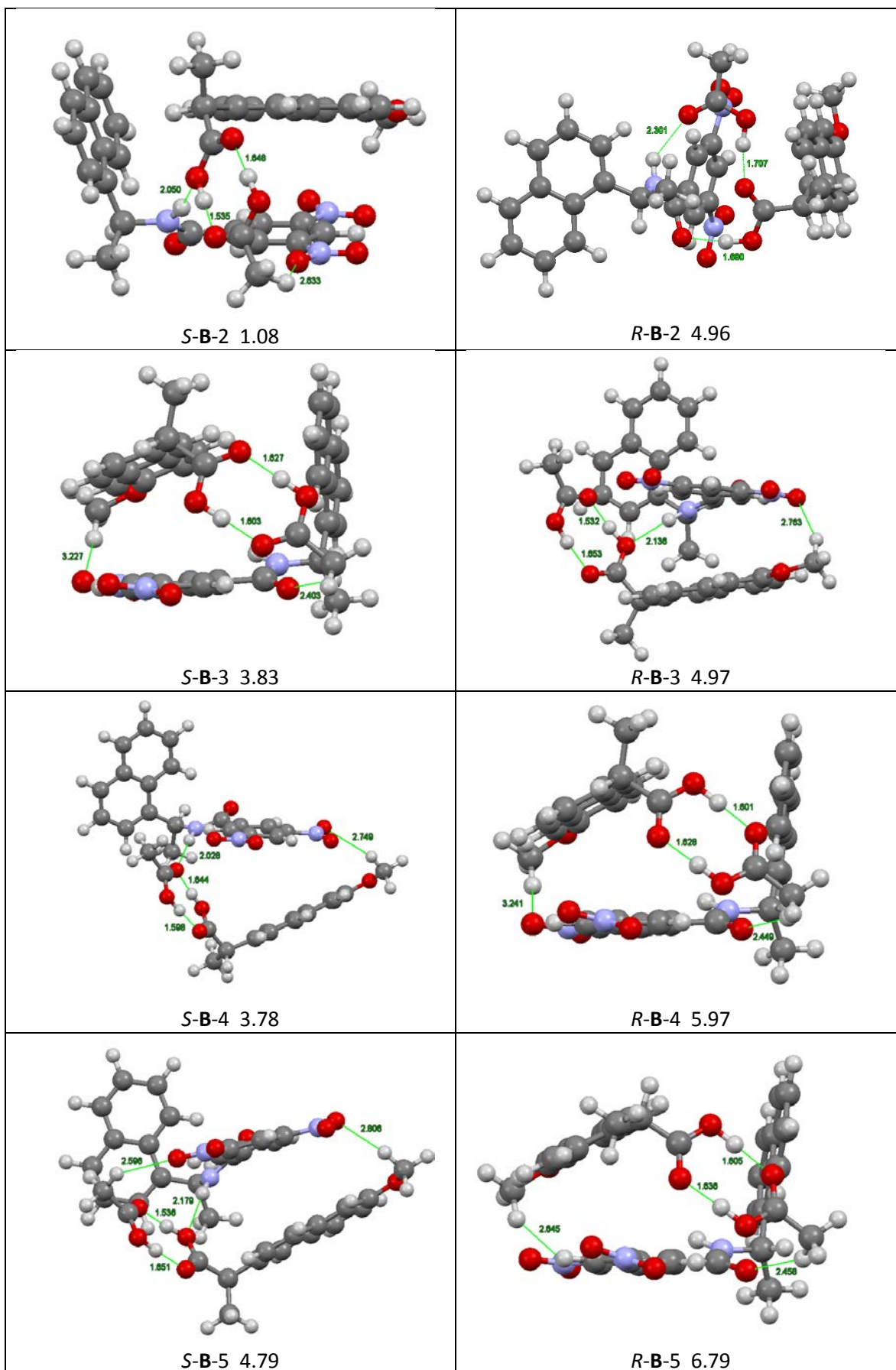


**Figure S1.** Enantioseparation of naproxen on **CSP-6**, column dimensions 250 x 4.6 mm I.D., mobile phase hexane-2-propanol = 80:20 + 1 g dm<sup>-3</sup> NH<sub>4</sub>OAc, flow 1mL/min, UV detection at 271 nm.



**Figure S2.** Higher energy structures of *S-A* (left) and *R-A* (right). Relative energies (in kcal mol<sup>-1</sup>) to *S-A* are shown. B3LYP/def2-TZVPP// M06-2X/def2-TZVPP (COSMO,  $\epsilon=2.78$ ).





**Figure S3.** Higher energy structures of S-B (left) and R-B (right). Relative energies (in kcal mol<sup>-1</sup>) to S-B are shown. B3LYP/def2-TZVPP// M06-2X/def2-TZVPP (COSMO,  $\epsilon=2.78$ ).