Chiroptical binaphthopyran switch: amplified CD response in polystyrene film

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Supporting Information

Preparations

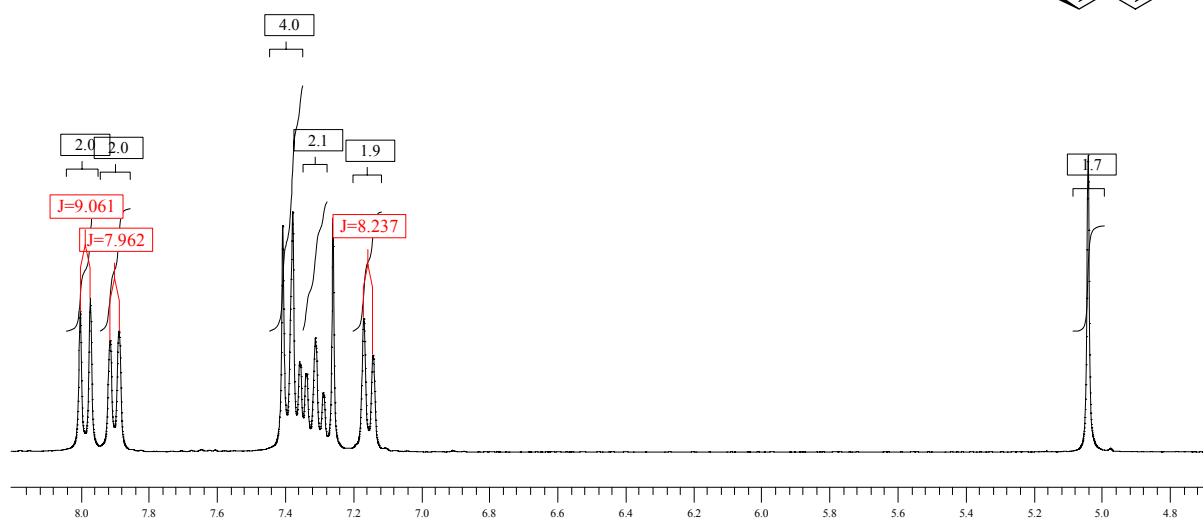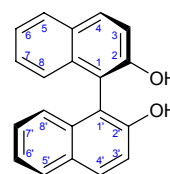**(R)-1,1'-Binaphthalene-2,2'-diol (6)** [S1,S2]

Fig. S1 ^{1}H NMR (300 MHz; CDCl$_3$; Me$_4$Si) of compound (R)-**6**.

^{1}H NMR: δ_H(300 MHz; CDCl$_3$; Me$_4$Si) 5.04 (2H, br s, 2 × O*H*), 7.16 (2H, d, *J* 8.2, C(8)*H*, C(8')*H*), 7.31 (2H, ddd, *J* 1.4 6.9 and 8.2, C(7)*H*, C(7')*H*), 7.35-7.41 (4H, m, C(3)*H*, C(3')*H* and C(6)*H*, C(6')*H*), 7.90 (2H, d, *J* 8.0, C(5)*H*, C(5')*H*), 7.99 (2H, d, *J* 9.1, C(4)*H*, C(4')*H*).
mp 206-208 ºC (from benzene) (lit.[S1] 206-207 ºC).
$[\alpha]_D^{22}$ + 35.4 (*c* 1 in THF) (lit.[S2] +35.4 (*c* 1 in THF)).
>99.9% *ee* (Chiralcel Daicel OD-H column, hexane-isopropyl alcohol (90:10), temperature 21 ºC, flow rate 0.75 mL/min, pressure 27.5 bar, λ = 275 nm: t$_1$ = 22.34 min (*S*)-**6**; t$_2$ = 25.69 min (*R*)-**6**).
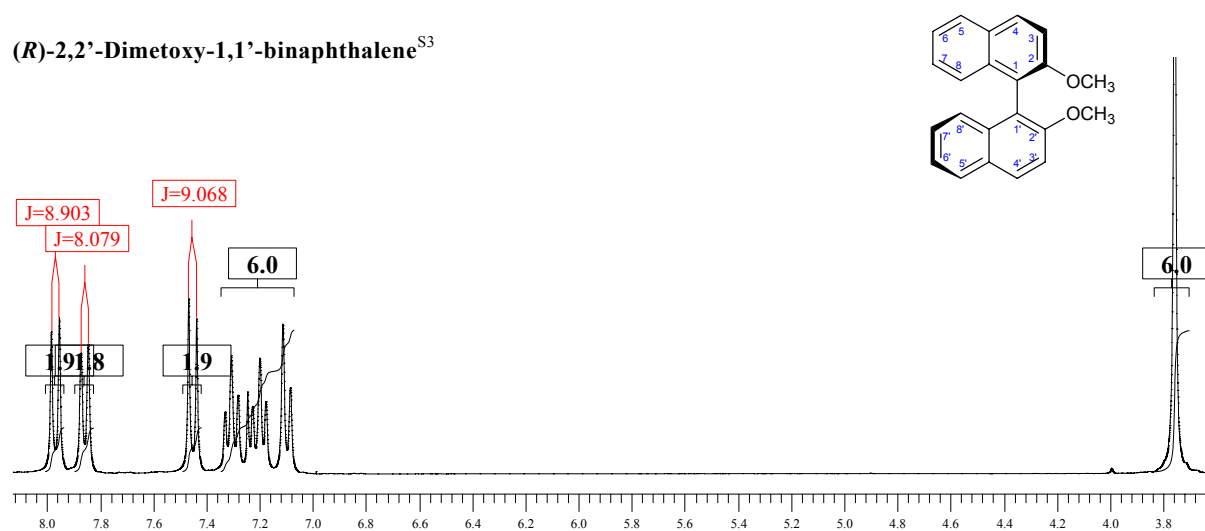
(*R*)-2,2'-Dimetoxy-1,1'-binaphthalene[S3]

Fig. S2 ^{1}H NMR(300 MHz; CDCl$_3$; Me$_4$Si) of (*R*)-2,2'-dimetoxy-1,1'-binaphthalene.

^{1}H NMR: δ_H(300 MHz; CDCl$_3$; Me$_4$Si) 3.76 (6H, s, 2 × OC*H*$_3$), 7.10 (2H, d, *J* 8.4, C(8)*H*, C(8')*H*), 7.20 (2H, ddd, *J* 1.3 6.8 and 8.1, C(6)*H*, C(6')*H*), 7.31 (2H, ddd, *J* 1.3 6.8 and 8.1, C(7)*H*, C(7')*H*), 7.45 (2H, d, *J* 9.1 Hz, C(4)*H*, C(4')*H*), 7.86 (2H, d, *J* 8.1 Hz, C(5)*H*, C(5')*H*), 7.97 (2H, d, *J* 8.9, C(3)*H*, C(3')*H*).
mp 224-226 ºC (lit.[S3] 224-225 ºC).

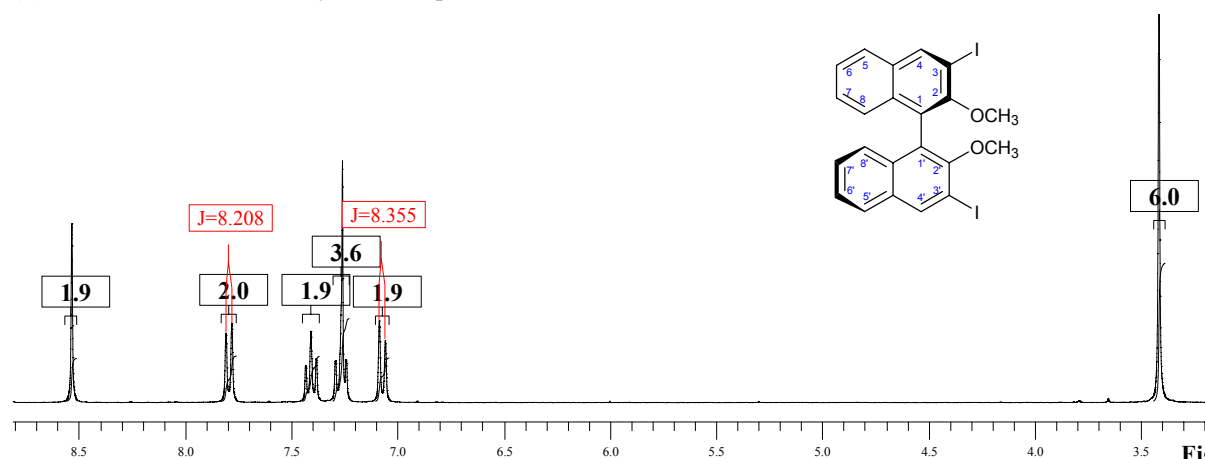**(*R*)-3,3'-Diiodo-2,2'-dimetoxy-1,1'-binaphthalene**[S4,S5]

S3 ^{1}H NMR(300 MHz; CDCl$_3$; Me$_4$Si) of (*R*)-3,3'-diiodo-2,2'-dimetoxy-1,1'-binaphthalene.

^{1}H NMR: δ_H(300 MHz; CDCl$_3$; Me$_4$Si) 3.42 (6H, s, 2 × OC*H*$_3$), 7.07 (2H, d, *J* 8.4, C(8)*H*, C(8')*H*), 7.27 (2H, ddd, *J* 1.2 6.9 and 8.2, C(6)*H*, C(6')*H*), 7.41 (2H, ddd, *J* 1.2 6.9 and 8.1, C(7)*H*, C(7')*H*), 7.79 (2H, d, *J* 8.2, C(5)*H*, C(5')*H*), 8.53 (2H, s, C(4)*H*, C(4')*H*).
mp 194-195 ºC (lit.[S5] 189-193 ºC).
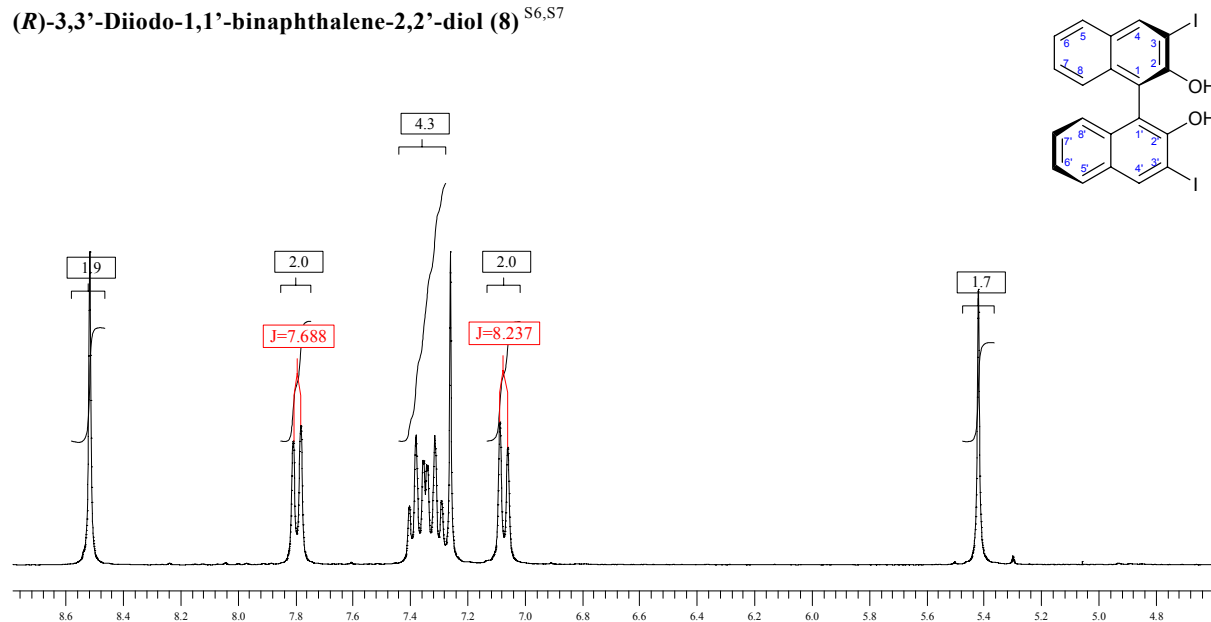
(*R*)-3,3'-Diiodo-1,1'-binaphthalene-2,2'-diol (8) [S6,S7]

Fig. S4 ^{1}H NMR(300 MHz; CDCl$_3$; Me$_4$Si) of compound (*R*)-**8**.

^{1}H NMR: δ_H(300 MHz; CDCl$_3$; Me$_4$Si) 5.42 (2H, bs, 2 × O*H*), 7.07 (2H, d, *J* 8.2, C(8)*H*, C(8')*H*), 7.31 (2H, ddd, *J* 1.3 6.9 and 8.2, C(6)*H*, C(6')*H*), 7.38 (2H, ddd, *J* 1.3 6.9 and 8.2, C(7)*H*, C(7')*H*), 7.79 (2H, d, *J* 7.7, C(5)*H*, C(5')*H*), 8.52 (2H, s, C(4)*H*, C(4')*H*).
mp 312-315 ºC (lit.[S7] 312-314 ºC).

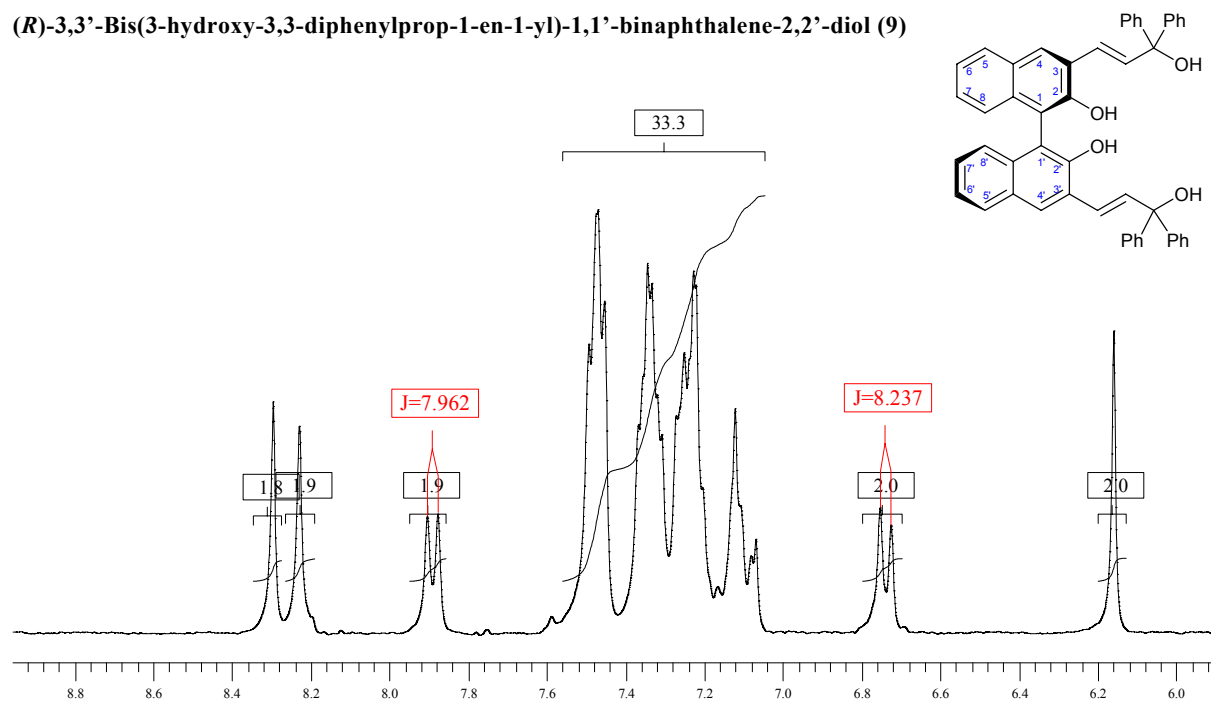**(*R*)-3,3'-Bis(3-hydroxy-3,3-diphenylprop-1-en-1-yl)-1,1'-binaphthalene-2,2'-diol (9)**

Fig. S5 ^{1}H NMR(300 MHz; DMSO-d$_6$; Me$_4$Si) of compound (*R*)-**9**.
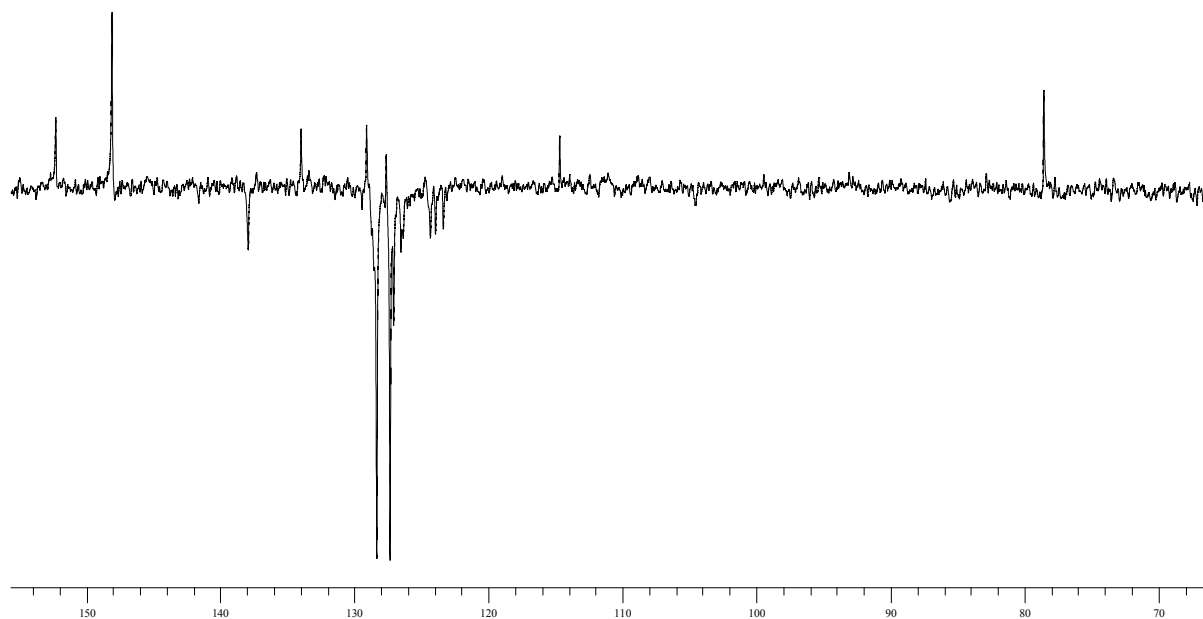
Fig. S6 ^{13}C NMR(75 MHz; DMSO-d[6]; Me[4]Si) of compound (*R*)-**9**.

(*R*)-2,2,2',2'-Tetraphenyl-10,10'-bi(2*H*-naphtho[2,3-*b*]pyran) (5a)
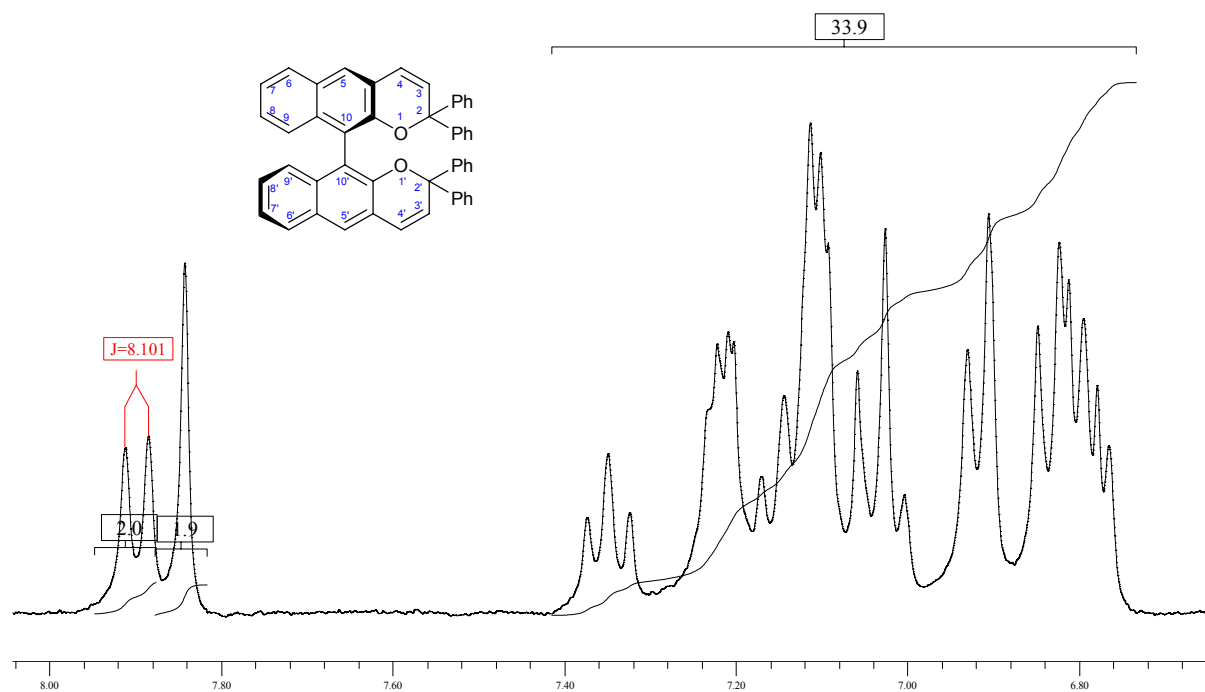
Fig. S7 ^{1}H NMR (300 MHz; DMSO-d[6]; Me[4]Si) of compound (*R*)-**5a**.
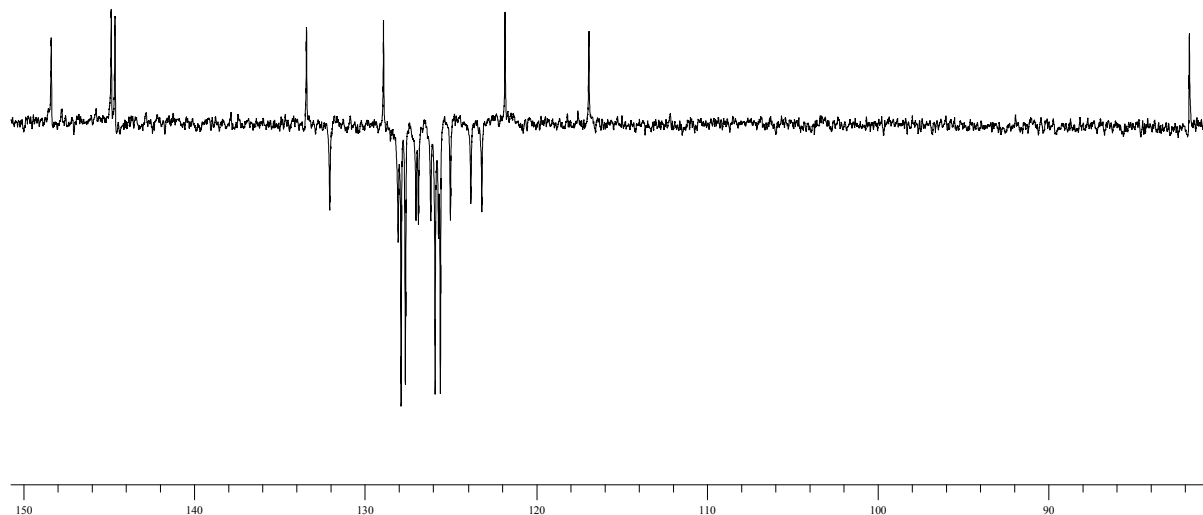
Fig. S8 ^{13}C NMR(75 MHz; DMSO-d$_6$; Me$_4$Si) of compound (*R*)-**5a**.

(*R*)-1-(2,2-Diphenyl-2*H*-naphtho[2,3-*b*]pyran-10-yl)-3-(3,3-diphenylprop-2-enylidene)naphthalen-2(3*H*)-one (5b):
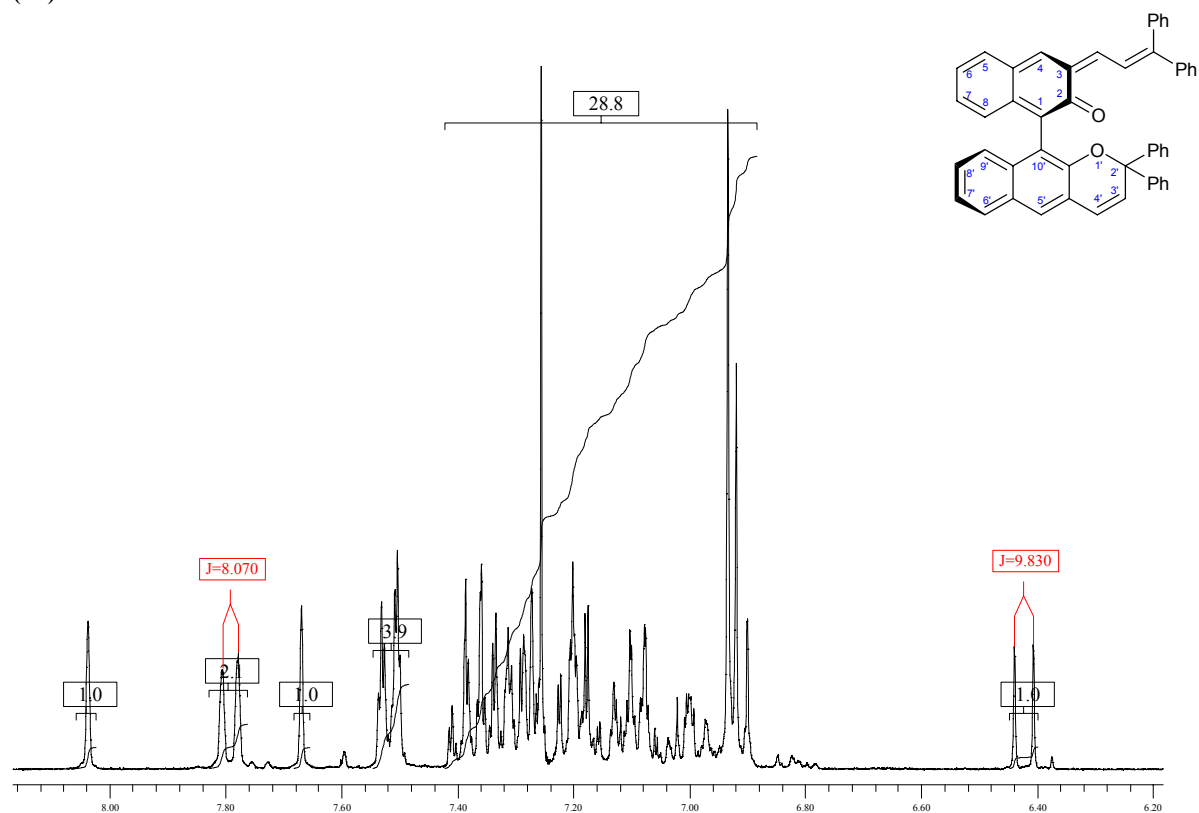
Fig. S9 ^{1}H NMR (300 MHz; CDCl$_3$; Me$_4$Si) of compound (*R*)-**5b**.
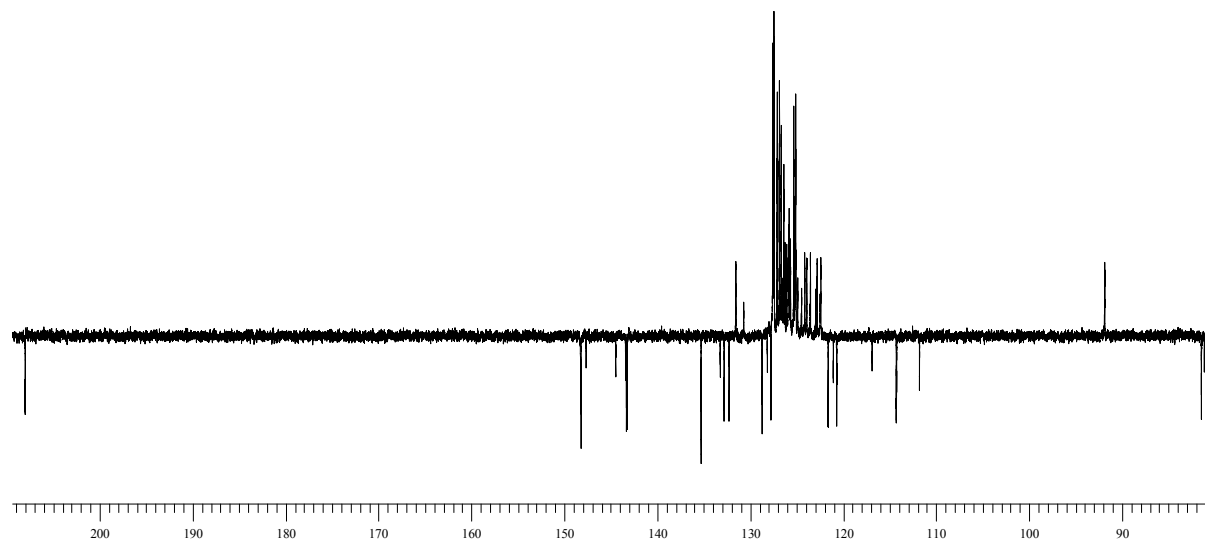
Fig. S10 ^{13}C NMR (75 MHz; CDCl$_3$; Me$_4$Si) of mixture (*R*)-**5a** and (*R*)-**5b**.

Switching in solution

Fig. S11 HPLC chromatogram of (*R*)-**5** in ground state: t$_{(R)\text{-}\textbf{5a}}$ = 22.73 min, 100%.

Fig. S12 HPLC chromatogram of (*R*)-**5** in the first cycle: after irradiation at 313 nm for 5 minutes: t$_{(R)\text{-}\textbf{5a}}$ = 22.75 min, 93.36%; t$_{(R)\text{-}\textbf{5b}}$ = 24.33 min, 6.64%.

Fig. S13 HPLC chromatogram of (*R*)-**5** in the first cycle: after heating at 84 ºC for 5 minutes: $t_{(R)\text{-}\mathbf{5a}}$ = 22.70 min, 99.64%; $t_{(R)\text{-}\mathbf{5b}}$ = 24.21 min, 0.36%.
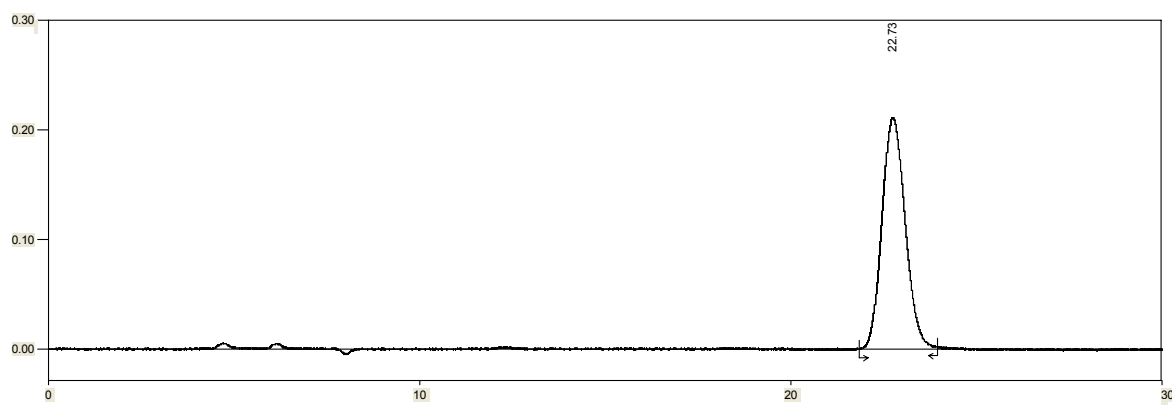

Fig. S14 HPLC chromatogram of (*R*)-**5** in the second cycle: after irradiation at 313 nm for 5 minutes: $t_{(R)\text{-}\mathbf{5a}}$ = 22.72 min, 93.55%; $t_{(R)\text{-}\mathbf{5b}}$ = 24.36 min, 6.45%.

Fig. S15 HPLC chromatogram of (*R*)-**5** in the second cycle: after heating at 84 ºC for 5 minutes: $t_{(R)\text{-}5a}$ = 22.70 min, 99.57%; $t_{(R)\text{-}5b}$= 24.23 min, 0.43%.
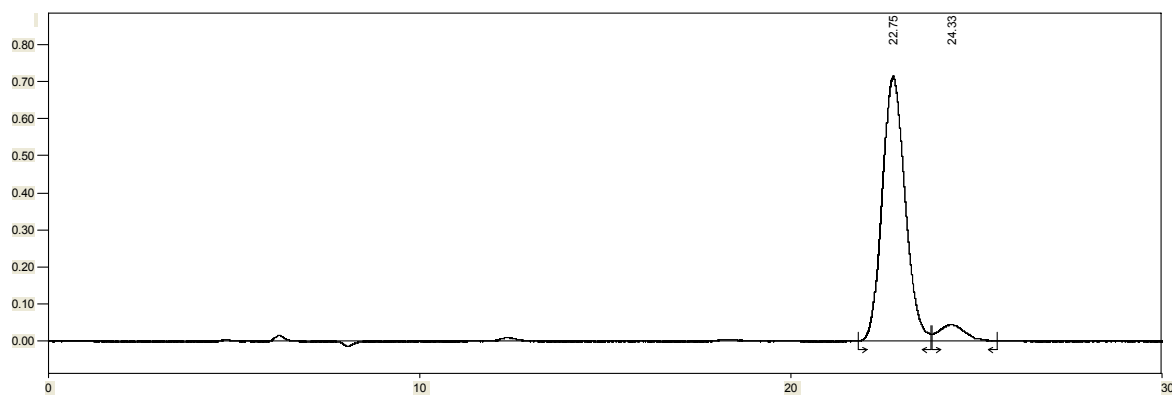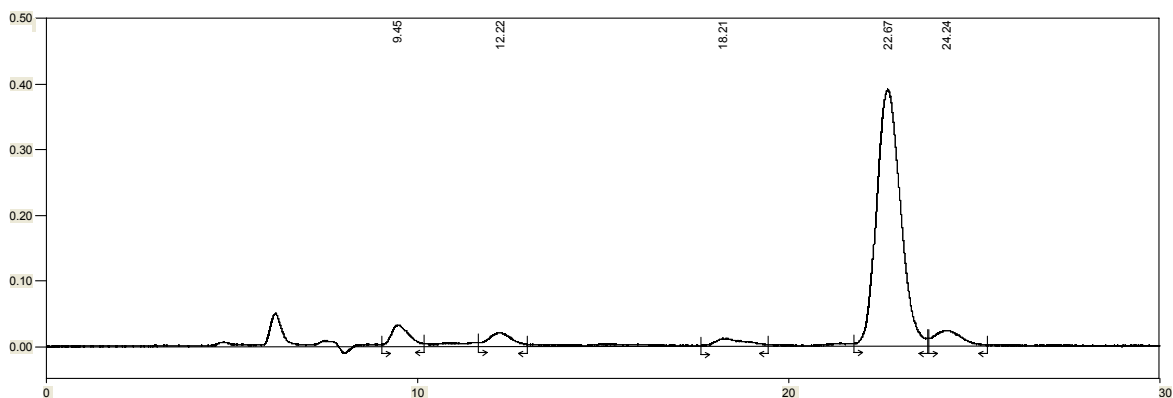
Fig. S16 HPLC chromatogram of (*R*)-**5** in the tenth cycle: after irradiation at 313 nm for 5 minutes: $t_{(R)\text{-}5a}$ = 22.67 min, 84.46%; $t_{(R)\text{-}5b}$ = 24.24 min, 5.12% (9.45 min, 4.32%; 12.22 min., 3.34%; 18.21 min, 2.76%).
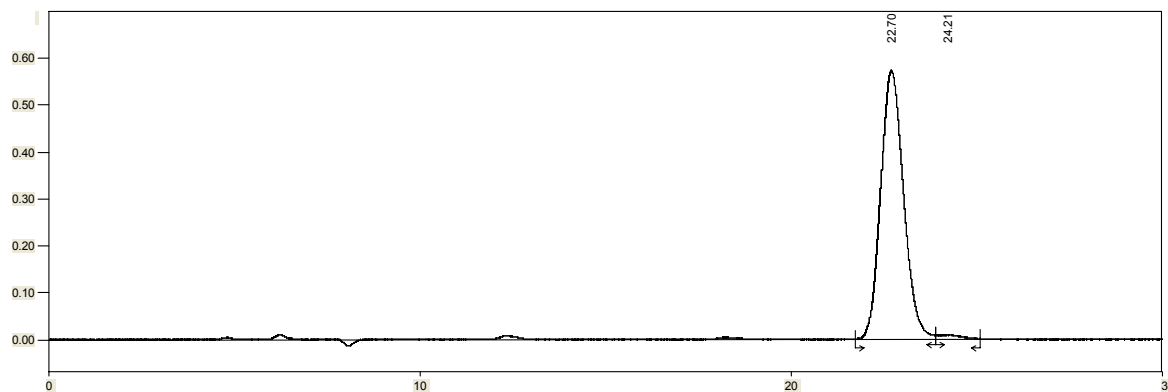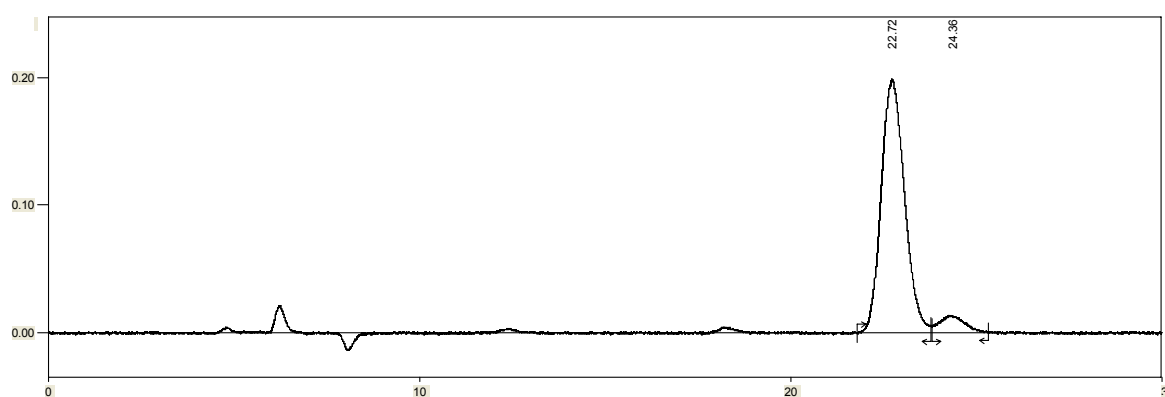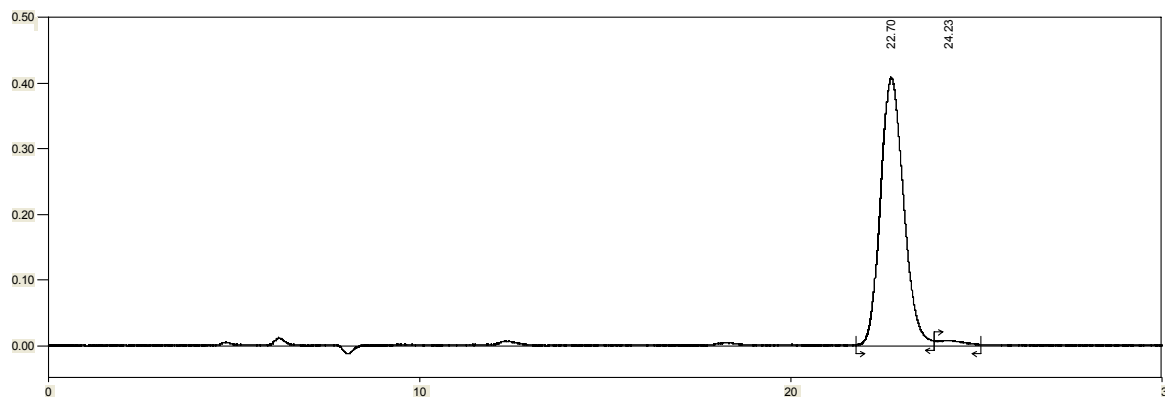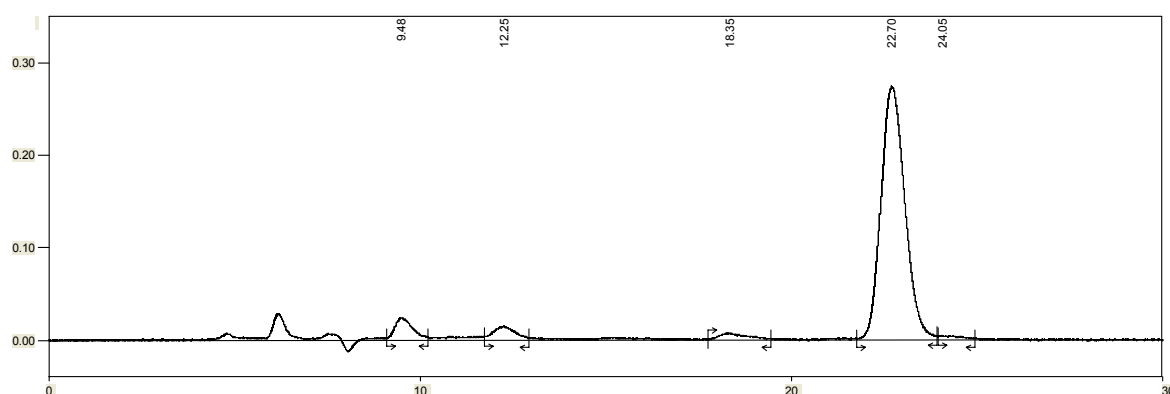

Fig. S17 HPLC chromatogram of (*R*)-**5** in tenth cycle: after heating at 84 °C for 5 minutes: $t_{(R)\text{-}5a}$ = 22.70 min, 89.66%; $t_{(R)\text{-}5b}$ = 24.05 min, 0.31% (9.48 min, 4.87%; 12.25 min., 3.22%; 18.35 min, 1.95%).

Table S1 Switching of the absorption intensity of (*R*)-**5** (sample irradiated/heated in d-benzene at c = 1.52×10^{-2} M, diluted for measurement of absorbance by benzene to c = 3.5×10^{-5} M) at 298 nm. Increase of the intesity after irradiation with UV light (313 nm) for 5 min., decrease after heating (84 °C) for 5 min..

Cycle No.	Absorbance (AU) at 298 nm
0	1.08
0.5	1.10
1	0.97
1.5	1.09
2	0.99
2.5	1.10
3	1.00
3.5	1.10
4	1.04
4.5	1.11
5	1.03
5.5	1.10
6	1.04
6.5	1.12
7	1.08
7.5	1.12
8	1.08
8.5	1.12
9	1.07
9.5	1.10
10	1.07

Kinetic measurements

Switching procces (*R*)-5a → (*R*)-5b at 26.5 ˚C:

Table S2 Calculated values of molar ratio of compound (*R*)-**5a** during irradiation sample in d-benzene at c = 1.52×10^{-2} M in time at 26.5 ˚C.

Time (min)	% (*R*)-**5a**	% (*R*)-**5b**	$x_{(R)\text{-}5a}$	$\ln x_{(R)\text{-}5a}$
1.5	96.63	3.37	0.97	-0.03
5	93.36	6.64	0.94	-0.06
8	89.42	10.58	0.90	-0.10
10	87.94	12.06	0.89	-0.12
12	86.7	13.3	0.87	-0.13
14	85.68	14.32	0.87	-0.14
16	82.69	17.31	0.84	-0.18
18	81.96	18.04	0.83	-0.19
20	81.68	18.32	0.83	-0.19
40	67.11	32.89	0.69	-0.38

$$\ln x_{(R)\text{-}5a} = -8.77 \times 10^{-3}t - 2.6 \times 10^{-2}$$
$$R = 0.9968$$
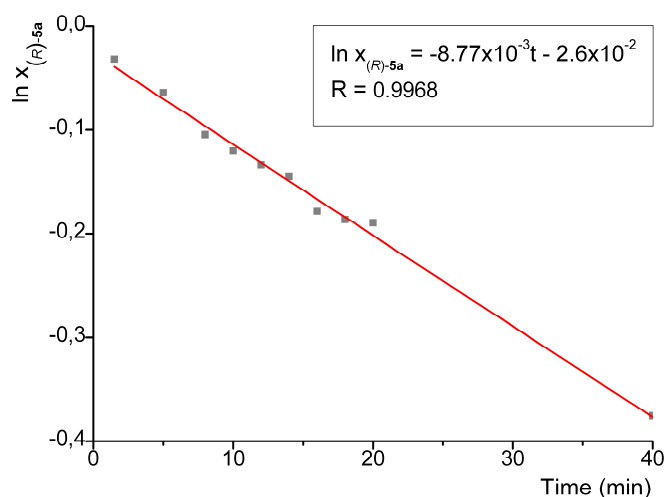
Fig. S18 Dependence of natural logarithm of molar ratio of compound (*R*)-**5a** against time at 26.5 ˚C (apparent rate constant: $k_1 = (8.77 \pm 0.25) \times 10^{-3}$ min^{-1}, reaction half time: $t_{1/2} = 79.0 \pm 2.3$ min).

Rate constant of reversed procces (*R*)-5b → (*R*)-5a at 14 ˚C:

Table S3 Calculated values of molar ratio of compound (*R*)-**5b** in time at 14 ˚C (from the sample irradiated in d-benzene at c = 1.52×10^{-2} M).

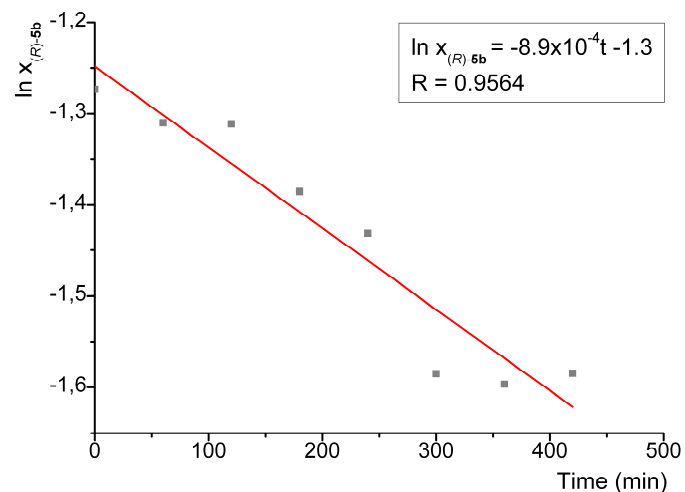| Time (min)	% (*R*)-**5a**	% (*R*)-**5b**	$x_{(R)\text{-}5b}$	$\ln x_{(R)\text{-}5b}$
0	70.56	29.44	0.28	-1.27
60	71.6	28.4	0.27	-1.31
120	71.63	28.37	0.27	-1.31
180	73.62	26.38	0.25	-1.39
240	74.79	25.21	0.24	-1.43
300	78.32	21.68	0.20	-1.58
360	78.57	21.43	0.20	-1.60
420	78.31	21.69	0.21	-1.58

Fig. S19 Dependence of natural logarithm of molar ratio of compound (*R*)-**5b** against time at 14 ˚C (rate constant: k_{-1} = $(0.89\pm0.11) \times 10^{-3}$ min^{-1}, half time of the reaction: $t_{1/2}$ = (778.8 ± 97.8) min).

Rate constant of reversed procces (*R*)-5b → (*R*)-5a at 26.5 ˚C:

Table S4 Calculated values of molar ratio of compound (*R*)-**5b** in time at 26.5 ˚C (from the sample irradiated in d-benzene at c = 1.52×10^{-2} M).

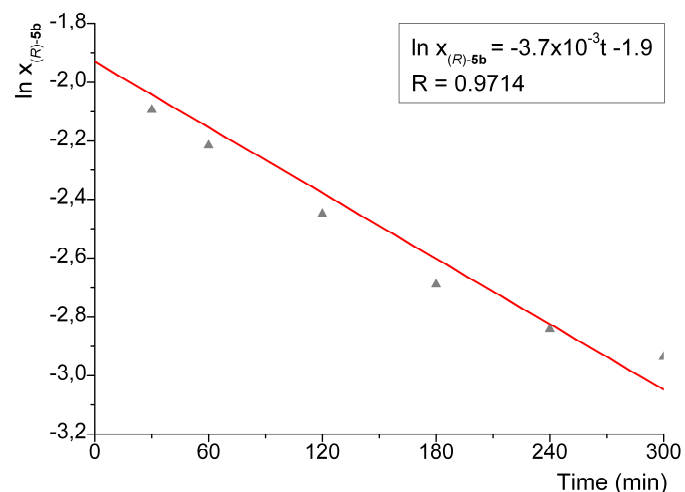| Time (min)	% (*R*)-**5a**	% (*R*)-**5b**	$x_{(R)\text{-}5b}$	$\ln x_{(R)\text{-}5b}$
0	81.68	18.32	0.17	-1.76
30	86.89	13.11	0.12	-2.09
60	88.38	11.62	0.11	-2.22
120	90.78	9.22	0.09	-2.45
180	92.74	7.26	0.07	-2.69
240	93.77	6.23	0.06	-2.84
300	94.33	5.67	0.05	-2.94

Fig. S20 Dependence of natural logarithm of molar ratio of compound (*R*)-**5b** against time at 26.5 ˚C (rate constant: k_{-1} = $(3.73\pm0.41) \times 10^{-3}$ min^{-1}, half time of the reaction: $t_{1/2}$ = (185.8 ± 20.7) min).

Rate constant of reversed procces (R)-5b → (R)-5a at 35 ˚C:

Table S5 Calculated values of molar ratio of compound (R)-**5b** in time at 35 ˚C
(from the sample irradiated in d-benzene at c = 1.52×10^{-2} M).

Time (min)	% (R)-**5a**	% (R)-**5b**	$x_{(R)\text{-}5b}$	ln $x_{(R)\text{-}5b}$
0	72.78	27.22	0.26	-1.35
15	74.54	25.46	0.24	-1.42
30	75.89	24.11	0.23	-1.48
45	78.7	21.3	0.20	-1.60
60	79.79	20.21	0.19	-1.66
75	81.13	18.87	0.18	-1.73
90	83.95	16.05	0.15	-1.89
105	87.94	12.06	0.11	-2.18
120	88.09	11.91	0.11	-2.19

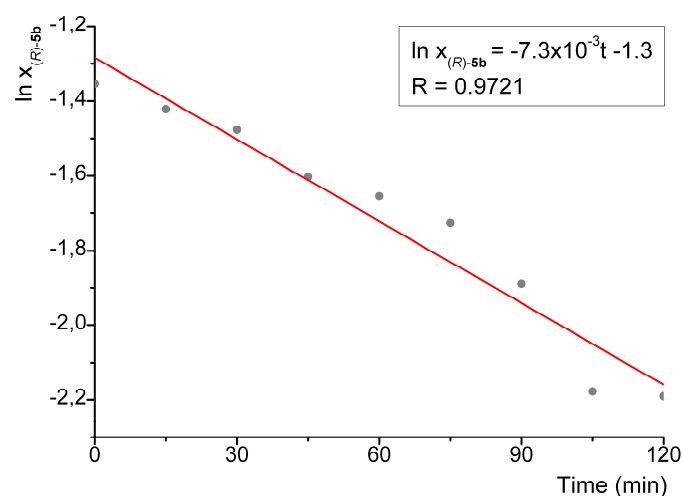$$\ln x_{(R)\text{-}5b} = -7.3 \times 10^{-3} t - 1.3$$
$$R = 0.9721$$

Fig. S21 Dependence of natural logarithm of molar ratio of compound (R)-**5b** against time at 35 ˚C (rate constant: k_{-1} = $(7.30 \pm 0.66) \times 10^{-3}$ min^{-1}, half time of the reaction: $t_{1/2}$ = (95.0 ± 8.7) min).

Activation free energy:

Table S6 Calculated values of natural logarithm of rate constants reversed reactions (R)-**5b** → (R)-**5a** at different temperatures.

t (ºC)	T (K)	1/T (1/K)	k (min^{-1})	ln k (min^{-1})
14	287.15	3.48E-03	0.89E-03	-7.02
26.5	299.65	3.34E-03	3.73E-03	-5.59
35	308.15	3.25E-03	7.30E-03	-4.92

From dependence of natural logarithm of rate constants reversed reaction against reciprocal values of temperature (**Fig. 3**; Arrhenius equation: ln k = -8.96×10^3/T + 24.2) was estimated activation energy: E_A = 8.96×10^3 K $\times$ R = 74.5 ± 5.8 kJ mol^{-1} and pre-exponential factor: A = $e^{24,2}$ = 3.23×10^{10} min^{-1} = 5.39×10^8 s^{-1}.

Switching in polymer film

Table S7 Switching of the absorption intensity of (*R*)-**5** in PMMA film (concentration of irradiated/heated film *c* = 0.02 mol/kg) at 296 nm. Increase of the intesity after irradiation with UV light (313 nm) for 1 h, decrease after heating (70 °C) for 8 min..

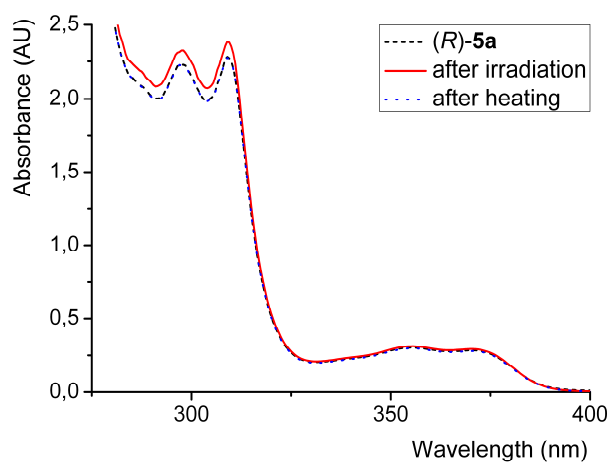| Cycle No.	Absorbance (AU) at 296 nm
0	1.31
0.5	1.41
1	1.29
1.5	1.41
2	1.29
2.5	1.40
3	1.30
3.5	1.41
4	1.29
4.5	1.41
5	1.29
5.5	1.41
6	1.29
6.5	1.41
7	1.30
7.5	1.41
8	1.30
8.5	1.41
9	1.30
9.5	1.41
10	1.30

Fig. S22 The absorption spectra of (*R*)-**5** in 50 µm PS film (concentration of irradiated/heated film c = 0.02 mol/kg), before and after irradiation with UV light (313 nm) for 1 h and after heating (70 °C) for 8 min.

Table S8 Switching of the CD signal intensity of (*R*)-**5** in PS film (concentration of irradiated/heated film c = 0.02 mol/kg) at 282 nm. Decrease of the intesity after irradiation with UV light (313 nm) for 1 h, increase after heating (70 °C) for 8 min..

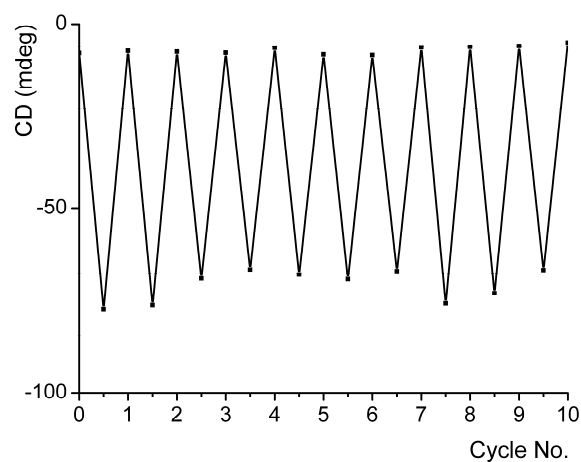| Cycle No.	CD (mdeg) at 282 nm
0	-7.98
0.5	-77.18
1	-7.38
1.5	-76.15
2	-7.60
2.5	-69.09
3	-7.90
3.5	-66.60
4	-6.55
4.5	-68.05
5	-8.37
5.5	-69.23
6	-8.54
6.5	-67.11
7	-6.42
7.5	-75.67
8	-6.31
8.5	-73.02
9	-6.07
9.5	-66.80
10	-5.17

Fig. S23 Switching of the CD signal intensity of (*R*)-**5** in 50 μm PS film (0.02 mol/kg) at 282 nm. Decrease of the intesity after irradiation with UV light (313 nm) for 1 h, increase after heating (70 °C) for 8 min.

Table S9 Switching of the CD signal intensity of (*R*)-**5** in PS film (concentration of irradiated/heated film *c* = 0.02 mol/kg) at 308 nm. Increase of the intesity after irradiation with UV light (313 nm) for 1 h, decrease after heating (70 °C) for 8 min..

Cycle No.	CD (mdeg) at 308 nm
0	17.25
0.5	132.28
1	16.14
1.5	128.82
2	15.20
2.5	118.80
3	15.62
3.5	116.63
4	13.02
4.5	119.45
5	16.77
5.5	124.16
6	18.56
6.5	119.32
7	11.31
7.5	126.06
8	14.31
8.5	125.74
9	12.36
9.5	116.71
10	8.85

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