Supplementary Material

Oblique heliconical cholesteric based on N_{tb} phase doped by chiral azo-compound

Vitalii Chornous[a], Alina Grozav[a], Mykhailo Vovk[b], Daria Bratova[c,d], Natalia Kasian[e], Longin Lisetski[e], Igor Gvozdovskyy[d]*

Author Address

[a]Department of Medical and Pharmaceutical Chemistry, Bukovinian State Medical University, Chernivtsi, Ukraine;

[b]Department of Mechanisms of Organic Reactions, Institute of Organic Chemistry of the National Academy of Sciences of Ukraine, Kyiv, Ukraine;

[c]Department of Information and Measuring Technologies, National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute";

[d]Department of Optical Quantum Electronics, Institute of Physics of the National Academy of Sciences of Ukraine, Kyiv, Ukraine;

[e]Department of Nanostructured Materials, Institute for Scintillation Materials of STC "Institute for Single Crystals" of the National Academy of Sciences of Ukraine, Kharkiv, Ukraine;

*E-mail: igvozd@gmail.com

S1. Synthesis and chemical characterization of ChD-3816

Recently, basing on the synthesized chiral azo-compound 2-(1R,2S,5R)-[(2-isopropyl-5-methylcyclohexyl)oxy]-2-oxoethyl 4-{(E)-[4-(decyloxy)phenyl]diazenyl}benzoate (or CD-3501 for short) that used for inducing helical twisting in nematic E7 [1], we have continued the synthesis of novel light-sensitive chiral dopant, having higher HTP and solubility, to form heliconical structure in a N_{tb}-forming mixture.

For the synthesis of the **(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl-4-{(*E*)-[4-(hexanoyloxy)phenyl]diazenyl}benzoate** (or ChD-3816 for short) the initial materials and reagents were used from Enamine Ltd (Kyiv, Ukraine); the "p.a." grade solvents were used.

The NMR spectra were recorded with Varian VXR-400(500) instrument (400 MHz for ^{1}H and 125.7, 150.8 MHz for ^{13}C) in DMSO-d_6 and $CDCl_3$ solutions, with TMS as an internal standard. Chemical shifts (δ) and J values of spectra are given in ppm and Hz, respectively. Structures of spectral lines are designed as: s (singlet), d (doublet), t (triplet), td (triplet of doublet) and m (multiplet).

LC-MS spectra were recorded by means of an Agilent 1100 Series high performance liquid chromatograph (Hewlett-Packard, California, USA) equipped with a diode matrix with an Agilent LC\MSD SL mass selective detector. The approximate values of melting points were determined by a Kofler bench.

The synthesis of (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-{(E)-[4-(hexanoyloxy)phenyl] diazenyl} benzoate (ChD-3816 for short) was performed according to the following scheme:

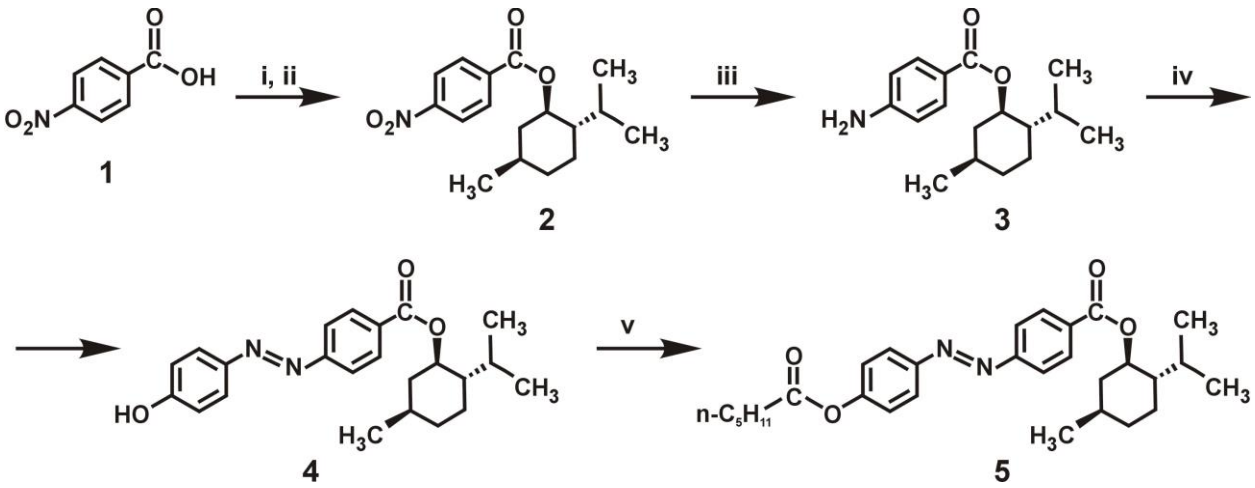

Figure 1S1. Synthesis of (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-{(E)-[4-(hexanoyloxy)phenyl] diazenyl} benzoate (**5**) by using the reagents and conditions for various stages: (i) - toluene, $SOCl_2$, reflux; (ii) - *l*-menthol, Et_3N, acetonitrile, reflux; (iii) - $SnCl_2 \cdot 2H_2O$, ethanol, reflux; (iv) - $NaNO_2$, HCl, C_6H_5OH, 0-5^oC; and (v) - n-$C_5H_{11}COCl$, Et_3N, acetonitrile, reflux.

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl-4-nitrobenzoate (compound 2). 16.7 g (0.1 mol) of 4-nitrobenzoic acid, 100 ml of dry toluene and 1 drop of DMF were added to a 500 ml reactor equipped with a magnetic stirrer. 17.9 g (0.15 mol) of $SOCl_2$ were added by dropwise to the reaction mixture with stirring and external cooling. After the reaction mixture was heating under reflux within 2 hours to complete gas evolution, and further the solvent was evaporated under reduced pressure. The residue was dissolved in 100 ml of acetonitrile and 15.6 (0.1 mol) of *l*-menthol was added, and to the resulting mixture 13.3 g (0.13 mol) of triethylamine was added by dropwise with stirring and external cooling. The mixture was heating under reflux within 2 hours, and the solvent was evaporated under reduced pressure and washed with water. The compound **2** was crystallized from ethanol.

M. p. 64 - 65 °C. **^{1}H-NMR** (400MHz, DMSO-d_6): δ 8.33 (d, J = 8.8 Hz, 2H, ArH), 8.16 (d, J = 8.8 Hz, 2H, ArH), 4.86 (td, J^1 = 4.0 Hz, J^2 6.8 Hz, 1H, OCH), 2.00-1.98 (m, 1H, CH), 1.87-1.81 (m, 1H, CH), 1.66-1.64 (m, 2H, CH_2), 1.55-1.49 (m, 2H, CH_2), 1.13-1.03 (m, 2H, CH_2), 0.89-0.85 (m, 7H, $2CH_3$+CH), 0.72 (d, J = 6.8 Hz, 3H, CH_3).

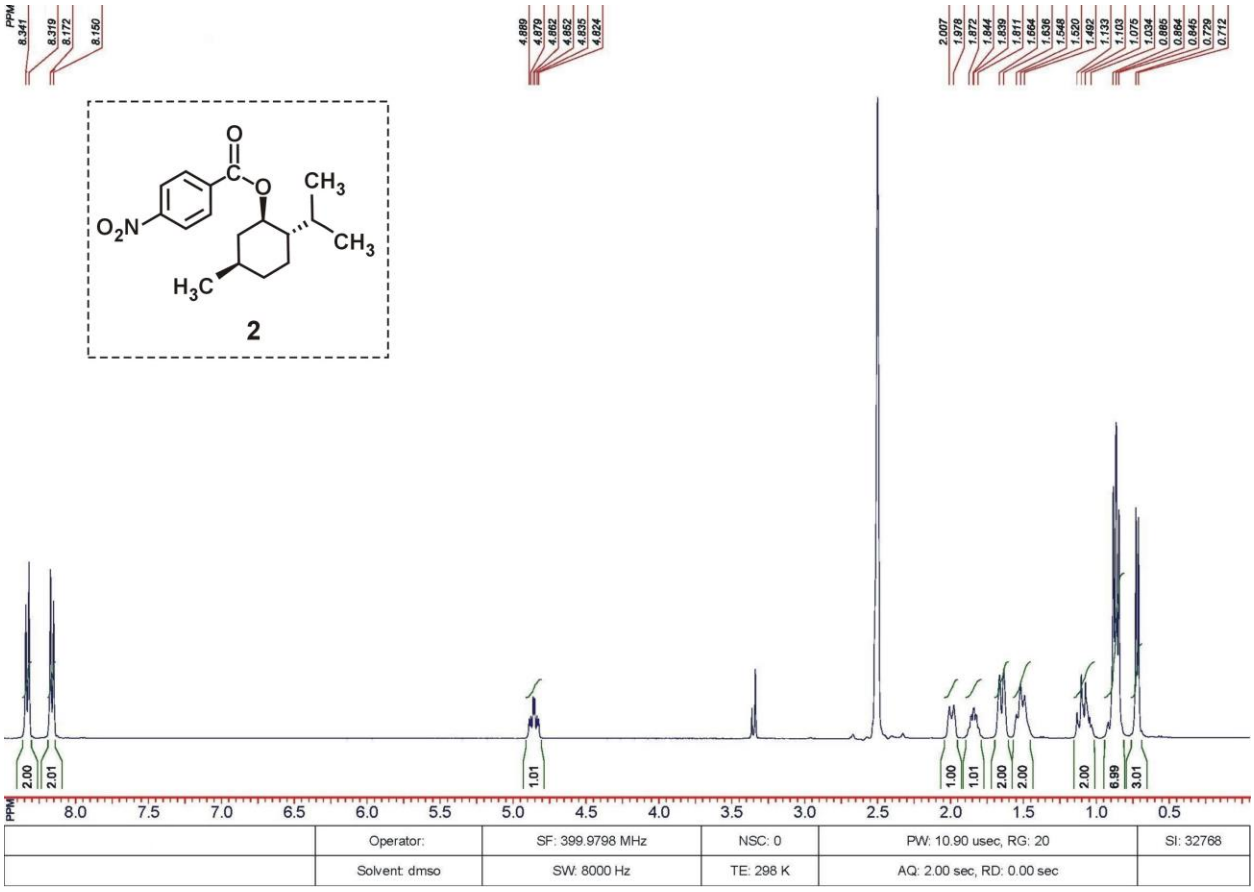

Figure 2S1. ^{1}H-NMR spectrum of the (1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl-4-nitrobenzoate (compound **2**).

^{13}C-NMR (151 MHz, DMSO-d_6): δ 164.2 (C = O), 150.7, 135.7, 130.9, 124.3, 75.7, 46.6, 40.8, 34.1, 31.3, 26.6, 23.6, 22.3, 20.9, 16.8. LC-MS, *m/z* (%): 306(100) [M+1].Anal. Calcd for $C_{17}H_{23}NO_4$, (305.38): C, 66.86 %; H, 7.59 %; N, 4.59 %; O, 20.96 %. Found: C, 66.76 %; H, 7.47 %; N, 4.65 %; O, 21.08 %.

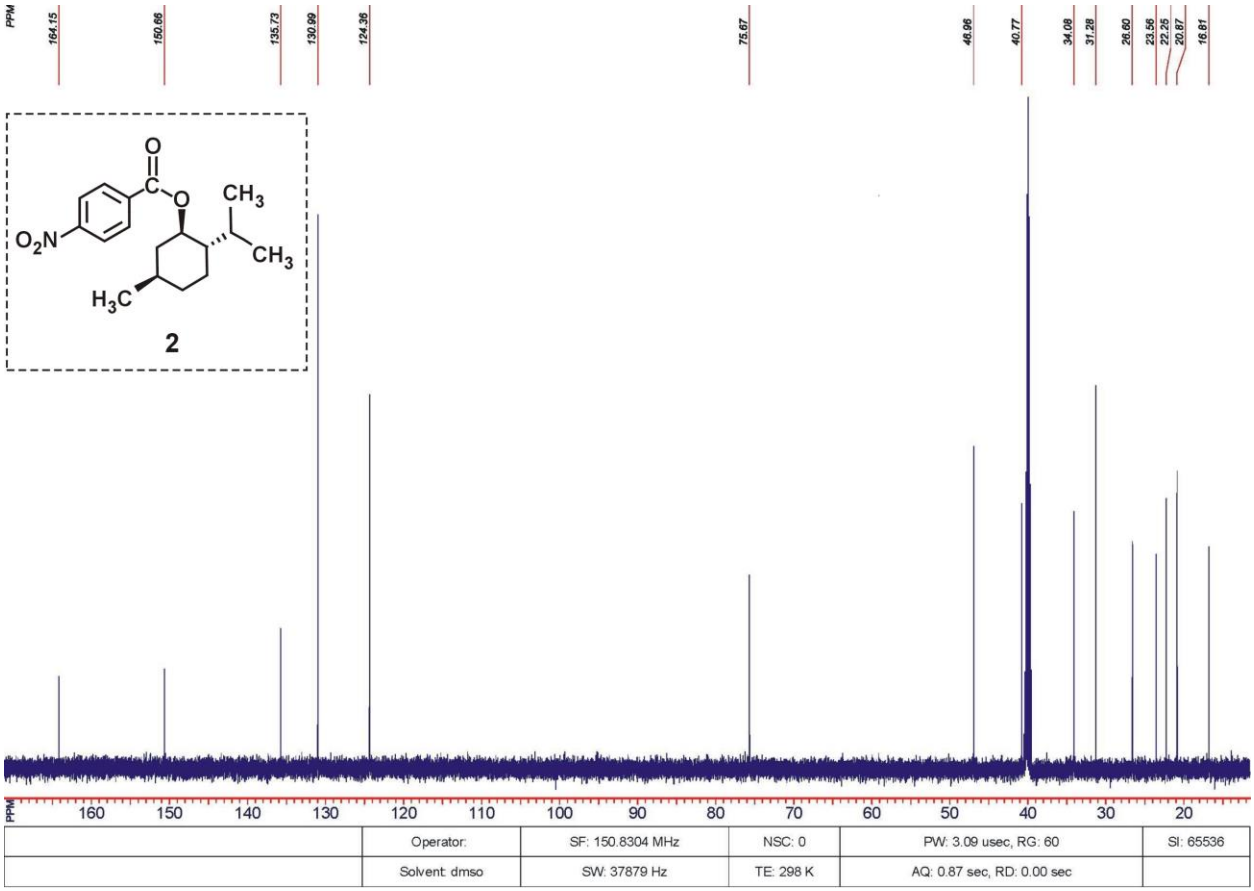

Figure 3S1. ^{13}C-NMR spectrum of the (1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl-4-nitrobenzoate (compound **2**).

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl-4-aminobenzoate (compound 3). In a 500 ml single-necked flask was added 100 ml of ethanol, 15 g (0.05 mol) of compound **2** and 56.5 g (0.25 mol) of $SnCl_2 \cdot 2H_2O$ under argon. The reaction mixture was heating under reflux for one hour and the solvent was evaporated under reduced pressure. The residue was dissolved in ethyl acetate and washed with 30 % NaOH solution (3 × 20 ml). The organic layer was separated and dried over anhydrous Na_2SO_4. After evaporation of the solvent in a vacuum, the residue was purified by silica gel column chromatography by using hexane as eluent.

M.p. 90 – 91 ºC. **^{1}H-NMR** (400 MHz, DMSO-d_6): δ 7.62 (d, J = 8.4 Hz, 2H, ArH), 6.56 (d, J = 8.4 Hz, 2H, ArH), 5.93 (s, 1H, NH), 4.83 (td, J^1 = 4.4 Hz, J^2 = 6.4 Hz, 1H, OCH), 1.95-1.92 (m, 1H, CH), 1.87-1.83 (m, 1H, CH), 1.66-1.63 (m, 2H, CH_2), 1.48-1.43 (m, 2H, CH_2), 1.09-0.99 (m, 2H, CH_2), 0.92-0.85 (m, 7H, 2CH_3+CH), 0.72 (d, J = 7.2 Hz, 3H, CH_3).

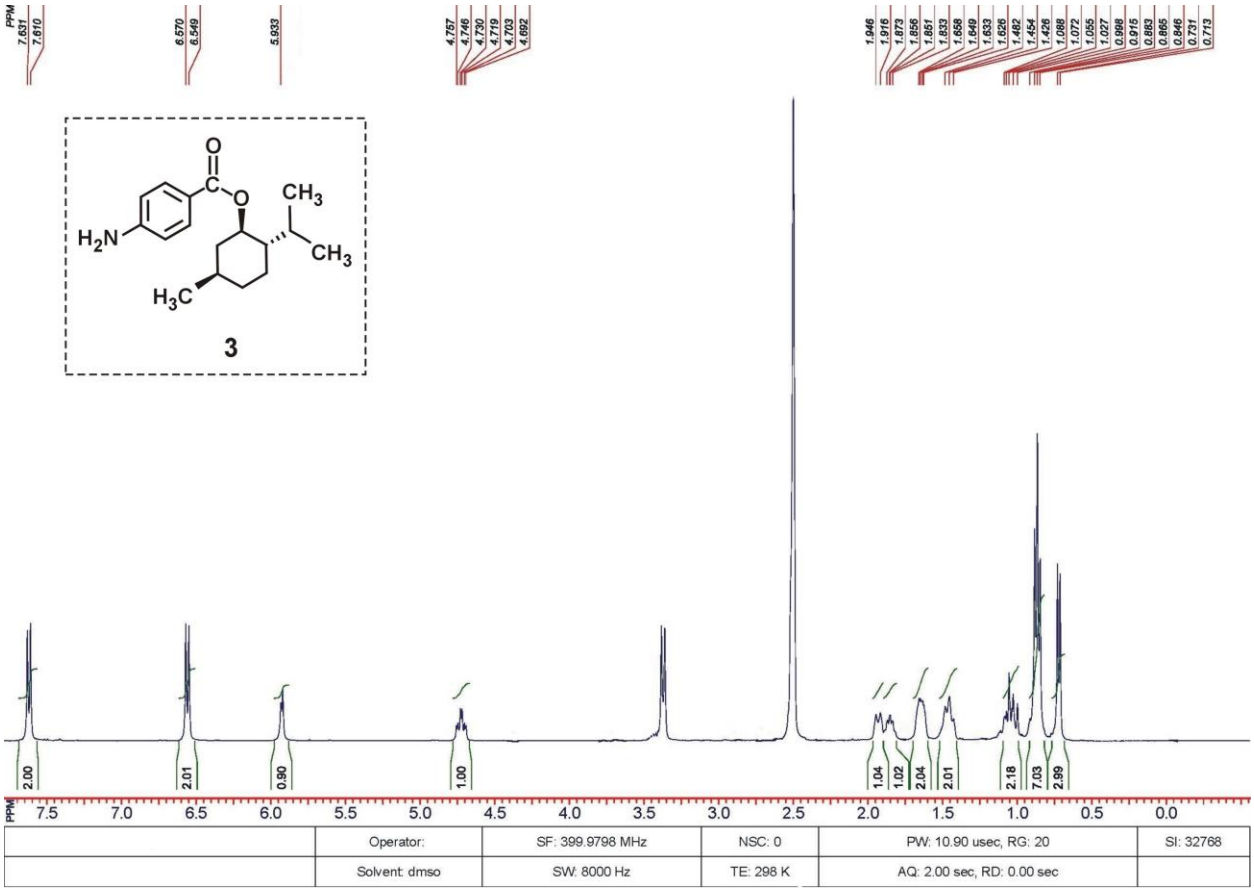

Figure 4S1. ^{1}H-NMR spectrum of the (1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl-4-aminobenzoate (compound **3**).

^{13}C-NMR (125.7 MHz, DMSO- d_6): δ 165.4 (C = O), 153.4, 131.0, 116.3, 112.6, 72.7, 46.8, 40.9, 33.9, 30.9, 26.2, 23.4, 21.9, 20.5, 16.6. LC-MS, *m/z* (%): 276(100) [M+1].Anal. Calcd for $C_{17}H_{25}NO_2$ (275.39): C, 74.14%; H, 9.15%; N, 5.09%; O, 11.62%. Found: C, 74.23%; H, 9.03 %; N, 5.18 %; O, 11.53 %.

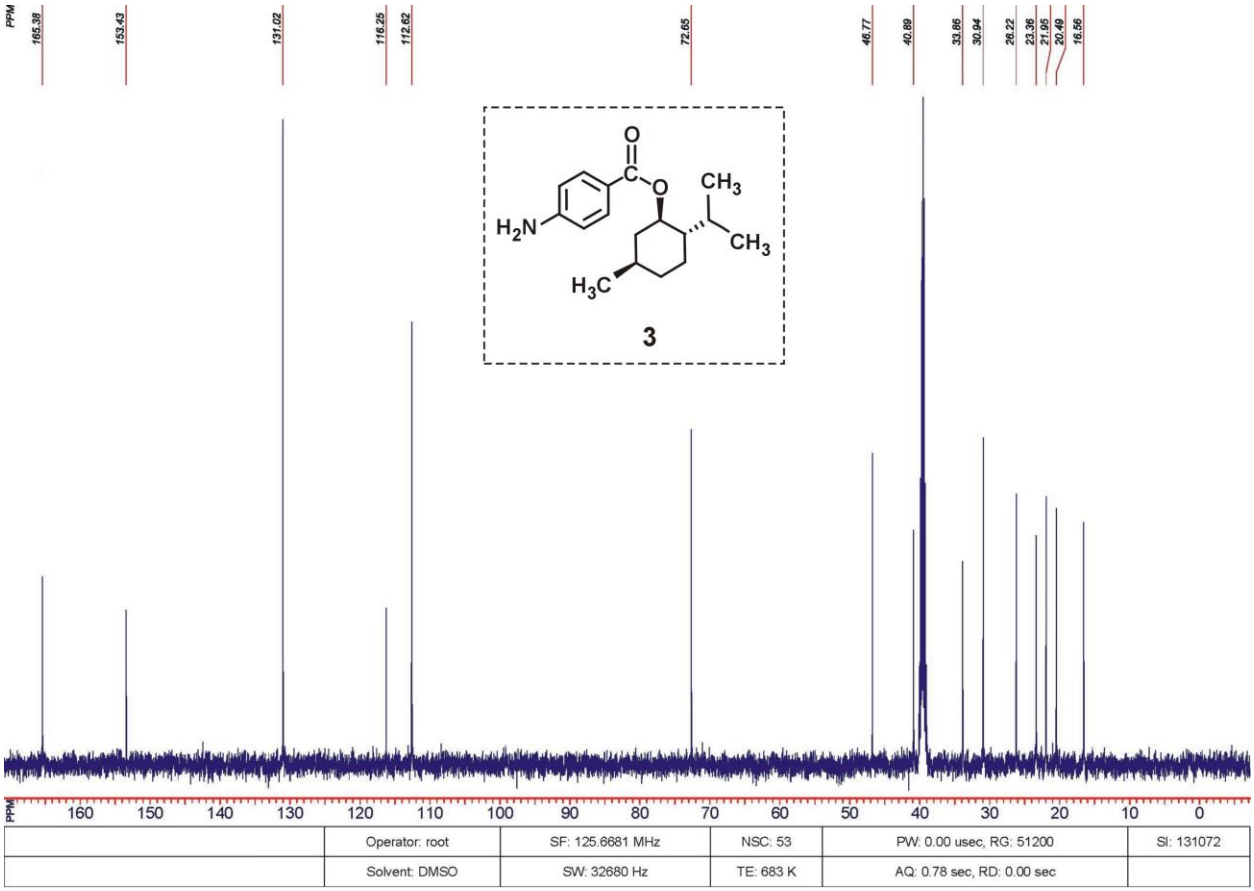

Figure 5S1. ^{13}C-NMR spectrum of the (1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl-4-aminobenzoate (compound **3**).

(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl-4-[(*E*)-(4-hydroxyphenyl)diazenyl]benzoate (compound 4). To a solution of 2.75 g (0.01 mol) of compound **3** in 20 ml of CH_3COOH was added 6 g (0.05 mol) of 30 % HCl and 10 g of crushed ice. A solution of 0.78 g (0.011 mol) of sodium nitrite in 3 ml of water was added dropwise to the resulting mixture with stirring. After 15 min, the resulting diazonium salt solution was added to a solution obtained by dissolving 1 g (0.011 mol) of phenol and 2.8 g (0.07 mol) of sodium hydroxide in 50 ml of water. The red precipitate was filtered off, dried and purified by chromatography on silica gel by using mixture of the eluent hexane:ethyl acetate, 1:1. The compound **4** was as yellow-red crystals.

M.p. 97-98 °C. **^{1}H-NMR** (400 MHz, DMSO-d_6): δ 10.5 (s, 1H, OH), 8.10 (d, J = 8.4 Hz, 2H, ArH), 7.90-7.85 (m, 4H, ArH), 6.97 (d, J = 8.4 Hz, 2H, ArH), 4.87-4.82 (m, 1H, OCH), 2.00-1.97 (m, 1H, CH), 1.88-1.85 (m, 1H, CH), 1.66-1.63 (m, 2H, CH_2), 1.54-1.49 (m, 2H, CH_2), 1.13-1.04 (m, 2H, CH_2), 0.88-0.85 (m, 7H, $2CH_3$ +CH), 0.73 (d, J = 6.8 Hz, 3H, CH_3).

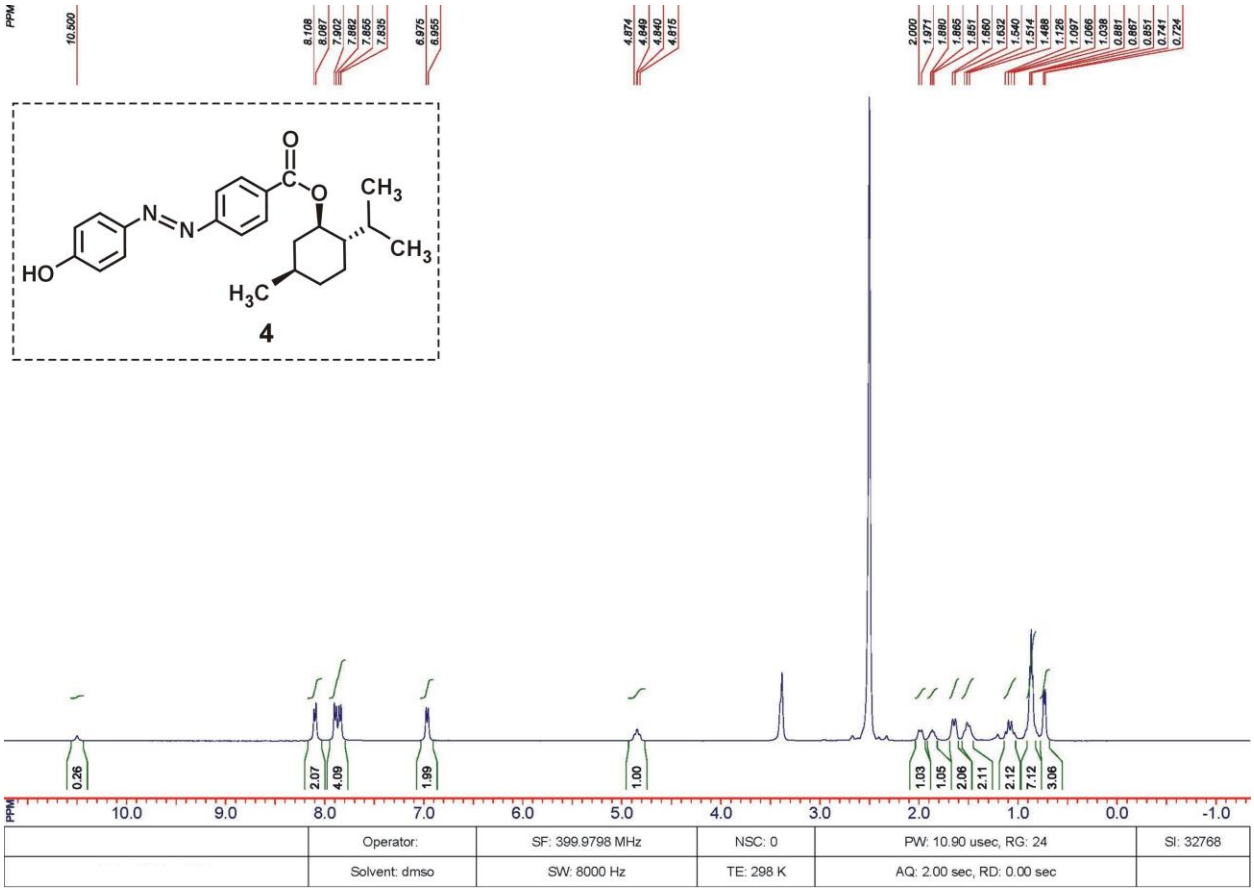

Figure 6S1. ^{1}H-NMR spectrum of the (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl-4-[(*E*)-(4-hydroxyphenyl)diazenyl]benzoate (compound **4**).

^{13}C-NMR (150.8 MHz, DMSO-d_6): δ 165.1(C = O), 155.2, 145.8, 131.4, 130.8, 125.8 (2C), 122.7, 116.4, 74.8, 46.9, 40.9, 34.1, 31.3, 26.6, 23.6, 22.2, 20.8, 16.9. LC-MS, *m/z* (%): 381(100) [M+1]. Anal. Calcd for $C_{23}H_{28}N_2O_3$ (380.49): C, 72.61%; H, 7.42%; N, 7.36%; O, 12.61%. Found: C, 72.48%; H, 7.34%; N, 7.47%; O, 12.54%.

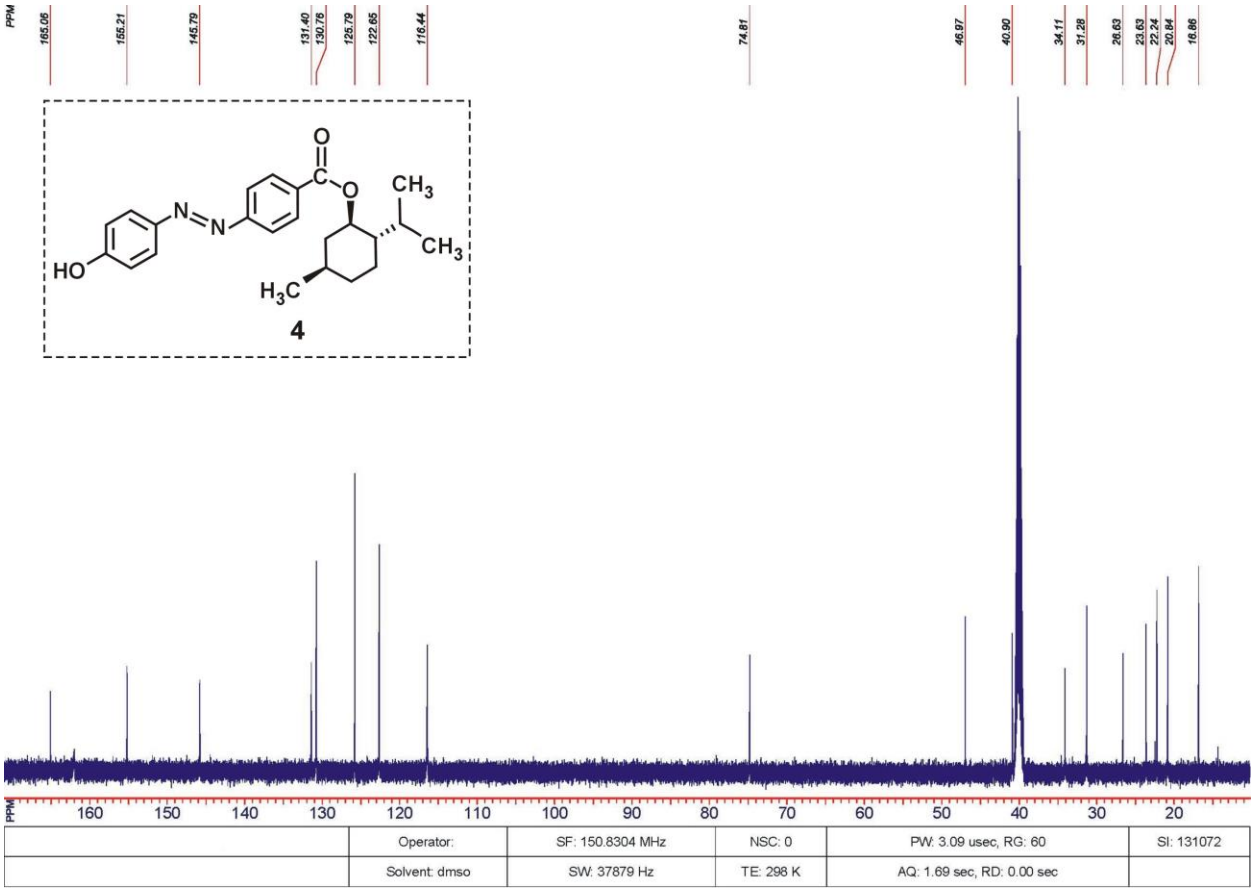

Figure 7S1. ^{13}C-NMR spectrum of the (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl-4-[(*E*)-(4-hydroxyphenyl)diazenyl] benzoate (compound **4**).

(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl-4-{(*E*)-[4-(hexanoyloxy)phenyl]diazenyl}benzoate 5 (ChD-3816). To solution of 11.4 g (0.03 mol) of compound **4** and 3 g (0.03 mol) of triethylamine in 50 ml of acetonitrile was added 4 g (0.03 mol) of hexanoyl chloride. The reaction mixture was heating under reflux within 2 hours; the solvent was evaporated under reduced pressure. The red precipitate was filtered off, dried and purified by chromatography on silica gel. It was used hexane as eluent. The compound **5** (ChD-3816) was as yellow plates.

M.p.65.7 ^{o}C. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.4 Hz, 2H, ArH), 8.02-7.94 (m, 4H, ArH), 7.28 (d, *J* = 8.0 Hz, 2H, ArH), 4.99 (td, J^1 = 4.2 Hz, J^2 = 6.4 Hz, 1H, OCH), 2.61(t, *J* = 8.0 Hz, 2H, CH_2COO), 2.19-2.16 (m, 1H, CH), 2.02-1.98 (m, 1H, CH), 1.82-1.75 (m, 4H, CH_3+CH), 1.63-1.58 (m, 2H, CH_2), 1.45-1.42 (m, 4H, $2CH_2$), 1.21-1.11 (m, 2H, CH_2), 0.97-0.95 (m, 10H, $2CH_3$+$2CH_2$), 0.83 (d, *J* = 6.8 Hz, 3H, CH_3).

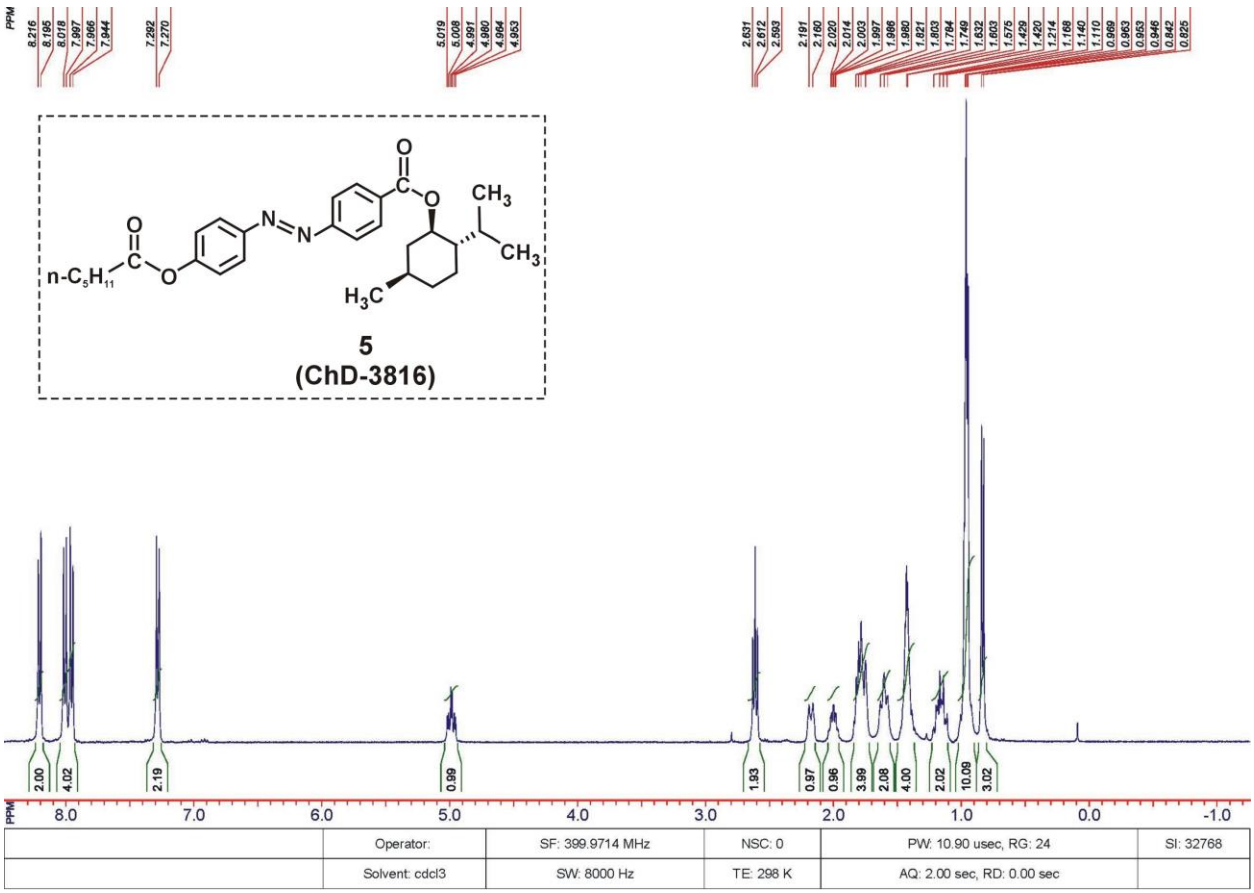

Figure 8S1. ^{1}H-NMR spectrum of the (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl-4-{(*E*)-[4-(hexanoyloxy)phenyl]diazenyl}benzoate (compound **5** or, for short, ChD-3816).

^{13}C-NMR (150.8 MHz, DMSO-d_6): δ 171.90 (C = O), 165.0 (C = O), 154.8, 153.8, 149.9, 132.4, 130.9, 124.6, 123.4, 123.2, 75.0, 47.0, 40.9, 34.1, 33.9, 31.3, 31.0, 26.7, 24.4, 23.7, 22.3, 22.2, 20.9, 16.9, 14.2. LC-MS, *m/z* (%): 479 (100) [M+1]. Anal. Calcd for $C_{29}H_{38}N_2O_4$ (478.64): C, 72.77%; H, 8.00%; N, 5.85%; O, 13.37%. Found: C, 72.85 %; H, 8.11 %; N, 5.93 %; O, 13.21 %.

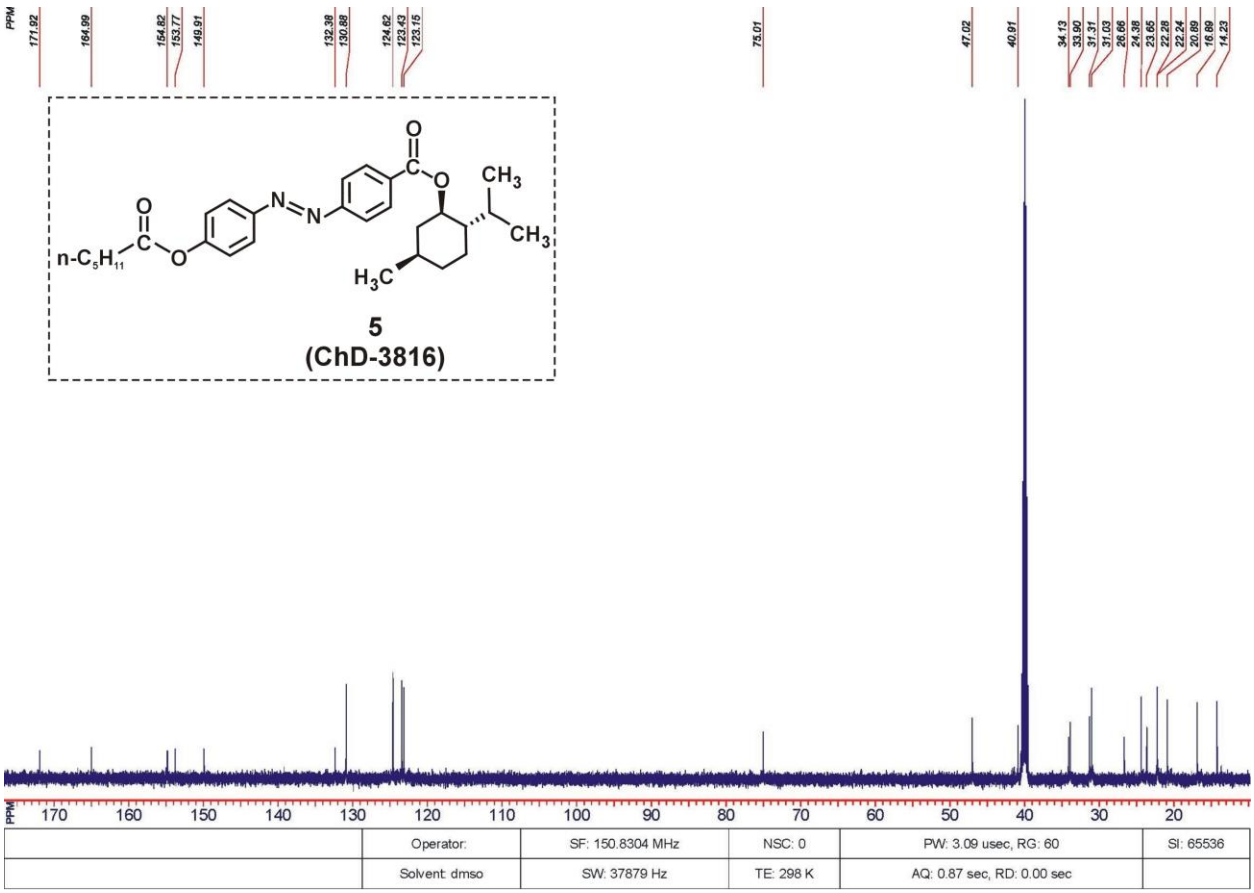

Figure 9S1. ^{13}C-NMR spectrum of the (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl-4-{(*E*)-[4-(hexanoyloxy)phenyl]diazenyl}benzoate (compound **5** or , for short, ChD-3816).

S2. *Trans-cis* isomerisation of the ChD-3816 in ethanol solution

The compound ChD-3816 is a photosensitive chiral molecule possessing reversible *trans-cis* isomerisation under UV, vis and temperature. Figure 2S1 shows the scheme of the of the *trans-cis* and *cis-trans* isomerisations of the ChD-3501 molecule under UV, vis irradiation and temperature *ΔT*.

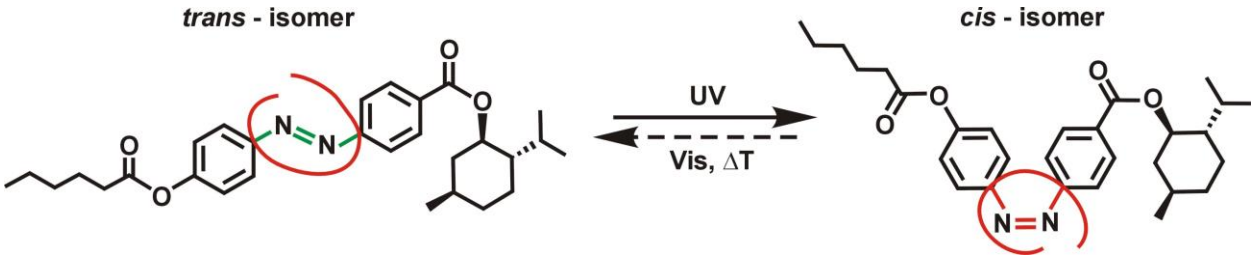

Figure 2S1. Scheme of the *trans-cis* and *cis-trans* isomerisations of the ChD-3501 molecule under UV, vis irradiation and temperature Δ*T*.

To study the effects of UV-vis radiation and temperature on the reversible *trans-cis* isomerisation (Figure 2S1), ChD- 3816 was dissolved in absolute ethanol (Enamine Ltd). The

ethanol solution of the ChD-3816 (C = 0.03 mg/ml) possesses initial optical density OD ~ 1.7 in quartz cuvette with thickness 1 cm. The ethanol solution was of light orange colour.

Transformations of absorption spectrum of the ethanol solution of the ChD-3816 upon irradiation by UV lamp with λ_{max} = 365 nm (*trans-cis* isomerisation) and incandescent lamp (*cis-trans* isomerisation) are shown in Figure 2S2.

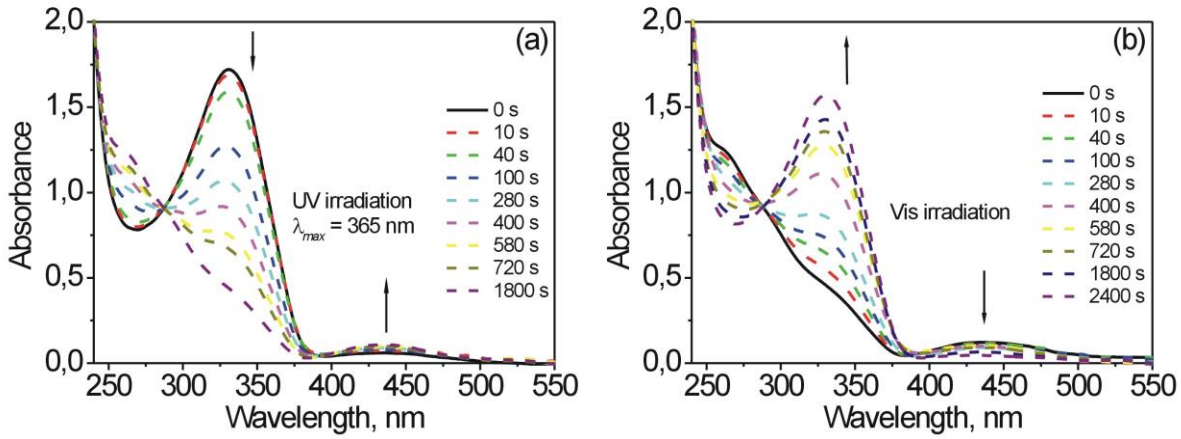

Figure 2S2. Transformations of absorption spectrum of the ethanol solution of the ChD-3816 upon irradiation by: (a) UV lamp with λ_{max} = 365 nm (0 - 0 s, 1 - 10 s, 2 - 40 s, 3 - 100 s, 4 - 280 s, 5 - 400 s, 6 – 580s, 7 - 720 s, 8 – 1800s), (b) incandescent lamp (0 - 0 s, 1 - 10 s, 2 - 40 s, 3 – 100 s, 4 – 280 s, 5 – 400 s, 6 – 580 s, 7 – 720 s, 8 – 1800 s, 9 - 2400 s). Thickness of quartz cuvette is 1 cm.

Figure 2S3 shows transformations of absorption spectrum of the ethanol solution of the ChD-3816 previously irradiated by UV lamp with λ_{max} = 365 nm within 1800 s (*trans-cis* isomerisation), during storage process of it at 80 °C (*cis-trans* isomerisation).

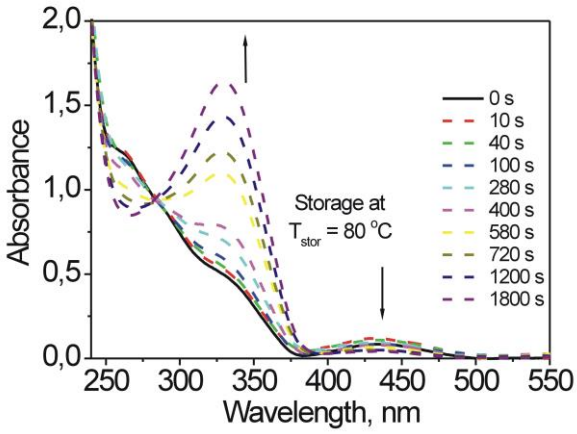

Figure 2S3. Transformations of absorption spectrum of the ethanol solution of ChD-3816 during storage at 80 °C (0 - 0 s, 1 - 10 s, 2 - 40 s, 3 - 100 s, 4 - 280 s, 5 - 400 s, 6 – 580s, 7 - 720 s, 8 – 1200 s, 9 – 1800s),

S3. Cholesteric phase induced by ChD-3816

Dissolution of ChD-3816 in nematic E7 (Merck, Darmstadt, Germany) leads to induction of the helicoidal structure possessing the helix with pitch that can be change in wide range of values (*i.e.* from nm to μm). Figure 3S1 shows the length of cholesteric pitch P_0 (a) and reciprocal cholesteric pitch $1/P_0$ (b) as function of concentration C of ChD-3816.

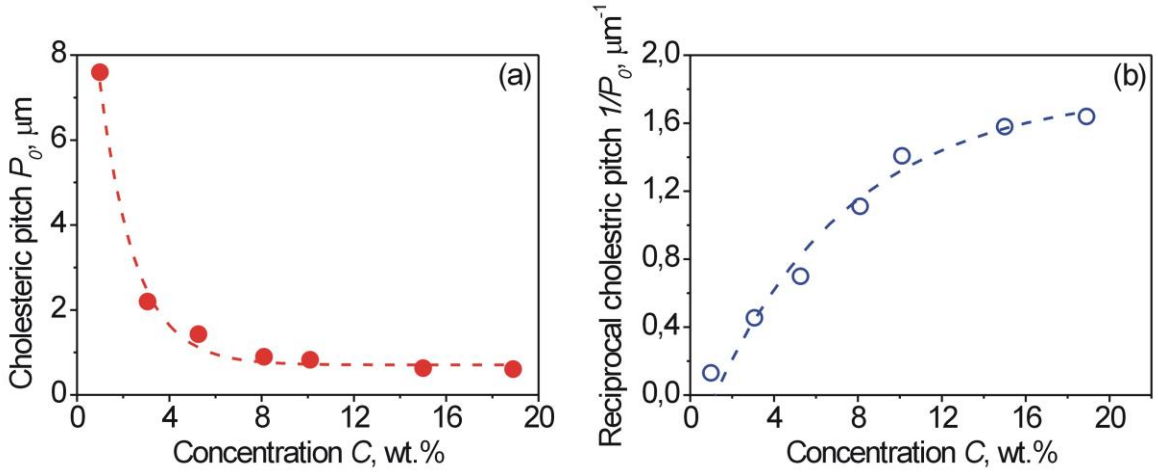

Figure 3S1. Dependence of the cholesteric pitch P_0 (a) and reciprocal cholesteric pitch $1/P_0$ (b) on concentration C of the ChD-3816 in nematic E7.

To calculate the helical twisting power (HTP, β) of the ChD-3816 in nematic E7, we used the linear part of $1/P_0(C)$ plot, which should pass though the origin of coordinates (Figure 3S2).

It is known that the tangent of tilt angle of linear plot is the value of HTP of ChD dissolved in the nematic host [2]. The average value of HTP of the Ch-3816 is about 0.138 (μm × wt. %)$^{-1}$. The handedness of the cholesteric helix was measured by means of the effect of rotation of solid crystals of the ChD-3816 during the process of dissolution at the top of the nematic E7 droplet. The clockwise rotation of the solid crystal of chiral dopant ChD-3816 in POM was observed. As described elsewhere in detail [3-6], the clockwise rotation of small crystals of the various ChDs is typical for left-handed cholesteric helix induced by these chiral dopants. This is confirmed by the Grandjean-Cano method used to determine the helix handedness [7].

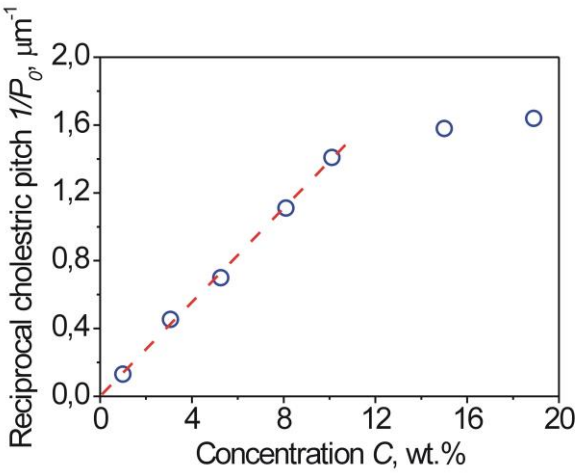

Figure 3S2. Linear part of the dependence $1/P_0(C)$ for ChD-3816 in E7.

S4. UV irradiation of the induced cholesteric phase, based on ChD-3816 and nematic E7

The irradiation of the cholesteric mixture, formed by 10 wt.% ChD-3816 added to the nematic E7 and filled into wedge-like LC cell, was carried out by UV lamp (λ_{max} = 365 nm and power P = 6 W). The wedge-like LC cell was assembled from two glass plates covered by PI2555 (HD MicroSystems, USA) as aligning layer. PI2555 film was rubbed 15 times to obtain strong anchoring. The thickness of the thick end d of the wedge-like LC cell was set as 5 μm by using Mylar spacers.

Figure 4S1 shows the change in the number of Grandjean-Cano lines (N_{GC}) in wedge-like LC cell during UV irradiation.

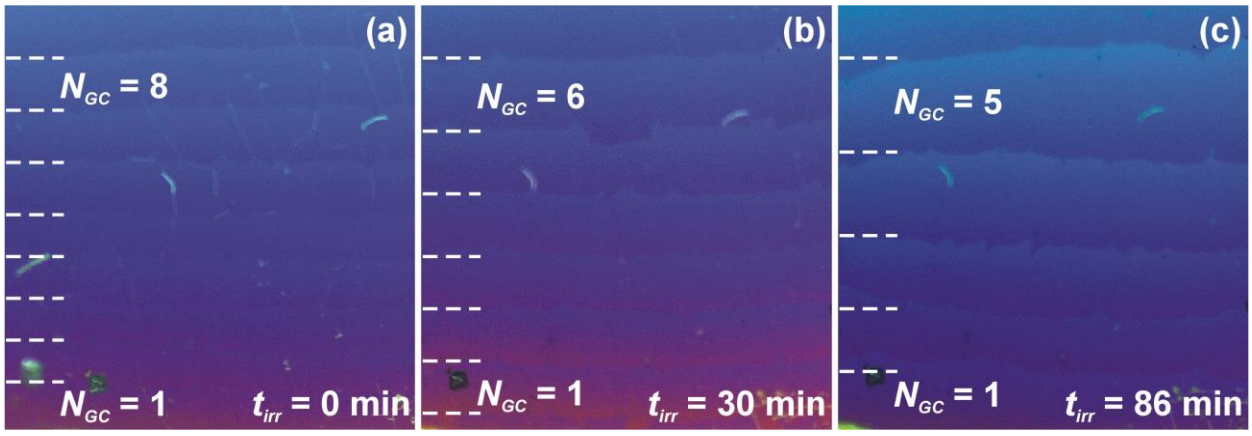

Figure 4S1. The change in N_{GC} during irradiation by UV-lamp with λ_{max} = 365 nm: (a) N_{GC} = 8 at t_{irr} = 0 min; (b) N_{GC} = 6 at t_{irr} = 30 min; and (c) N_{GC} = 5 at t_{irr} = 86 min.

Figure 4S2 shows the dependence of cholesteric helix pitch P on irradiation time t_{irr} during UV (a) and vis (b) illumination.

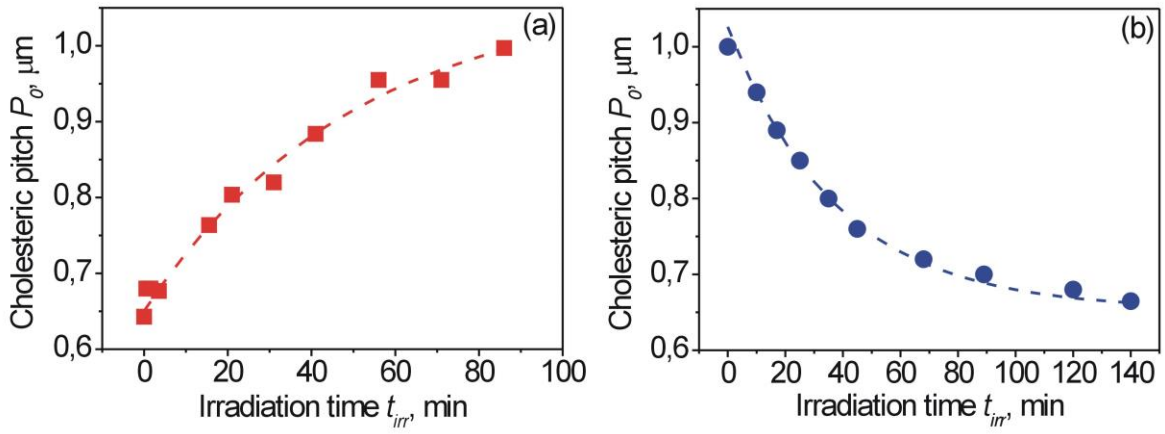

Figure 4S2. Dependence of cholesteric helix pitch P_0 on irradiation time t_{irr} during illumination by: (a) UV-lamp with λ_{max} = 365 nm and (b) incandescent lamp.

Reference:

1. Chornous V, Vovk M, Bratenko M, Yu. et al. Light-controllable chiral dopant based on azo-fragment: synthesis and characterisation. Liq Cryst. 2022: 49:1322-1337. DOI:10.1080/02678292.2022.2031326.
2. Chilaya GS, Lisetski LN. Cholesteric liquid crystals: physical properties and molecular-statistical theories. Mol Cryst Liq Cryst. 1986; 140: 243-286.
3. Gvozdovskyy I, Terenetskaya I. Steroid motor: dynamics of cholesteric helix induction in the nematic droplets. Liq Cryst Today. 2002; 11: 8-12.
4. Gvozdovskyy I, Lisetski L. Rotation of single crystals of chiral dopants at the top of a nematic droplet: analogy with Lehmann effect. Eur Phys J E. 2007; 24:211-215.
5. Gvozdovskyy IA, Lisetski LN. Rotation of single crystals of chiral dopants at the top of a nematic droplet: factors affecting the angular velocity. Mol Crys Liq Cryst. 2007; 475: 113-122. Doi: 10.1080/15421400701681331.
6. Gvozdovskyy IA, Lisetski LN. Rotation of single crystals of chiral dopants at the top of a nematic droplet: a hydrodynamical analogy. J Func Mater. 2007; 14: 332-337.
7. Gerber PR. On the determination of cholesteric screw sense by the Grandjean-Cano-method. Z Naturforsch. 1980; 35: 619-622.