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Supporting Information

All-organic liquid crystalline radicals with a spin unit in the outer position of a bent-core system

Kvetoslava Bajzíková, Michal Kohout, Ján Tarábek, Jiří Svoboda, Vladimíra Novotná, Jana Vejpravová, Damian Pociecha and Ewa Gorecka*

[a]*Department of Organic Chemistry, Institute of Chemical Technology, CZ-166 28 Prague 6, Czech Republic. E-mail: Michal.Kohout@vscht.cz*

[b]*Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nám. 2, CZ-16610 Prague 6, Czech Republic*

[c]*Institute of Physics, Academy of Science of the Czech Republic, Na Slovance 2, CZ-182 21 Prague 8, Czech Republic. E-mail: novotna@fzu.cz*

[d]*Laboratory of Dielectrics and Magnetics, Chemistry Department, Warsaw University, Al. Zwirki i Wigury 101, 02-089 Warsaw, Poland*

Contents

1. SYNTHESIS

1.1 SYNTHESIS OF INTERMEDIATES

The molecular structure of the central core **1,** its hydroxylic group protected derivatives **2**,**3**, and the lengthening arms **4-8** for the synthesis of target materials of series **I-IV** are shown in Fig. S1.

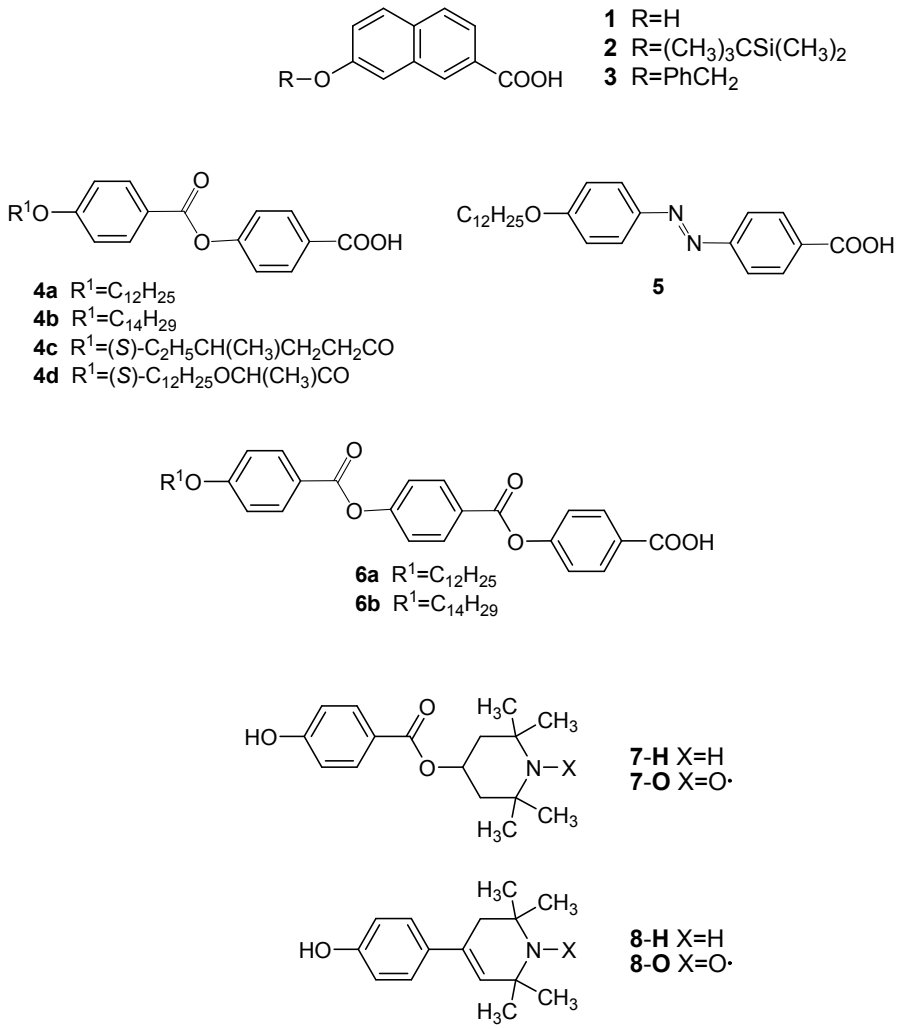
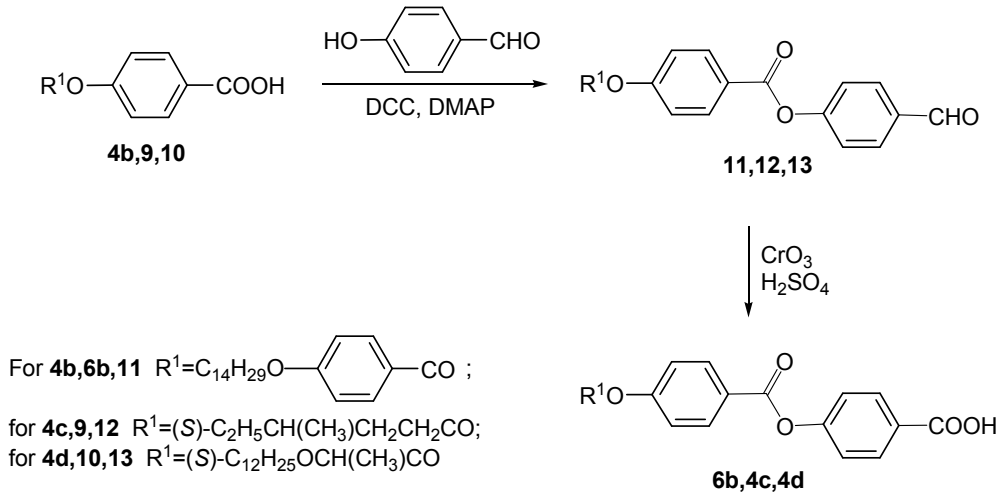


Fig. S1. The structures of the central cores and lengthening arms

7-Hydroxynaphthalene-2-carboxylic acid (**1**) served as the parent central core in the design of the bent-shaped materials. For synthetic reasons, in the preparations of compounds possessing a radical moiety in their structure, a silyl protecting group was utilized. For the other compounds the utilization of a benzyl protecting group was sufficient. Naphthalenecarboxylic acid **1**,**3** and acids **4a**,**4b** and **6a** (see Fig. S1) as well as 4-(4-dodecyloxyphenylazo)benzoic acid (**5**) have been prepared according to known procedures[S1-S4]. Acid **2** was obtained by a standard silylation of **1** with *tert*-butyl(dimethyl)silyl chloride (TBSCl).

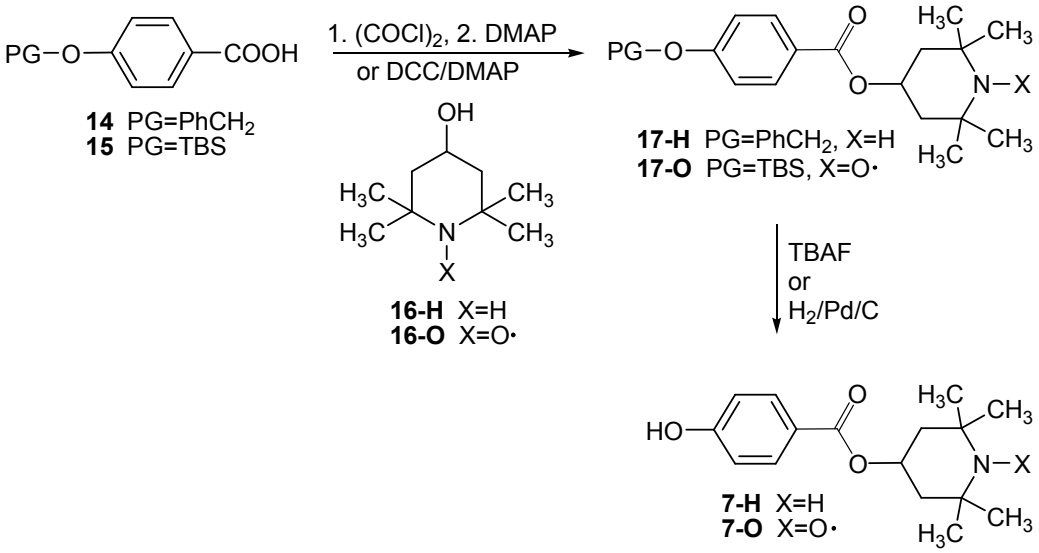
The synthesis of new compounds **4c**, **4d**, **6b** was performed analogously to reference[S1] and is depicted in scheme S1. It started from 4-substituted benzoic acid **4b**[S1], **9**[S5] and **10**[S6],

which were esterified with 4-hydroxybenzaldehyde in a *N*,*N*-dicyclohexylcarbodiimide (DCC)-mediated reaction catalysed with 4-dimethylaminopyridine (DMAP). The formyl group of the corresponding esters **11-13** was subsequently oxidized with the Jones reagent to acids **4c**, **4d**, **6b**, resp.



Scheme S1. The synthesis of the elongating arms 4c, 4d, and 6b.

The TEMPO-derived nitroxyl radicals **8-O** and their deoxy-analogues **8-H** have been obtained by the reported procedure[S7,S8]. Compounds **7-O**,**7-H** have been prepared by two-step procedures (Scheme S2) starting with benzyl **14**[S9] and *tert*-butyl(dimethyl)silyl (TBS)[S10] protected acid **15**, resp. Acid **14** was first transformed by the means of oxalyl chloride to the corresponding acid chloride which subsequently acylated the alcohol **16-H** in the presence of DMAP to yield the protected ester **17-H**. In the second step, the protecting benzyl group was removed by standard hydrogenation on Pd/C. The nitroxyl radical intermediate **7-O** was obtained by a DCC-mediated coupling of acid **15** with radical **16-O** and the formed intermediate **17-O** was deprotected with tetrabutylammonium fluoride (TBAF) in wet tetrahydrofuran (THF).



Scheme S2. The synthetic route to TEMPO-derived side chain and its deoxy-analogue.

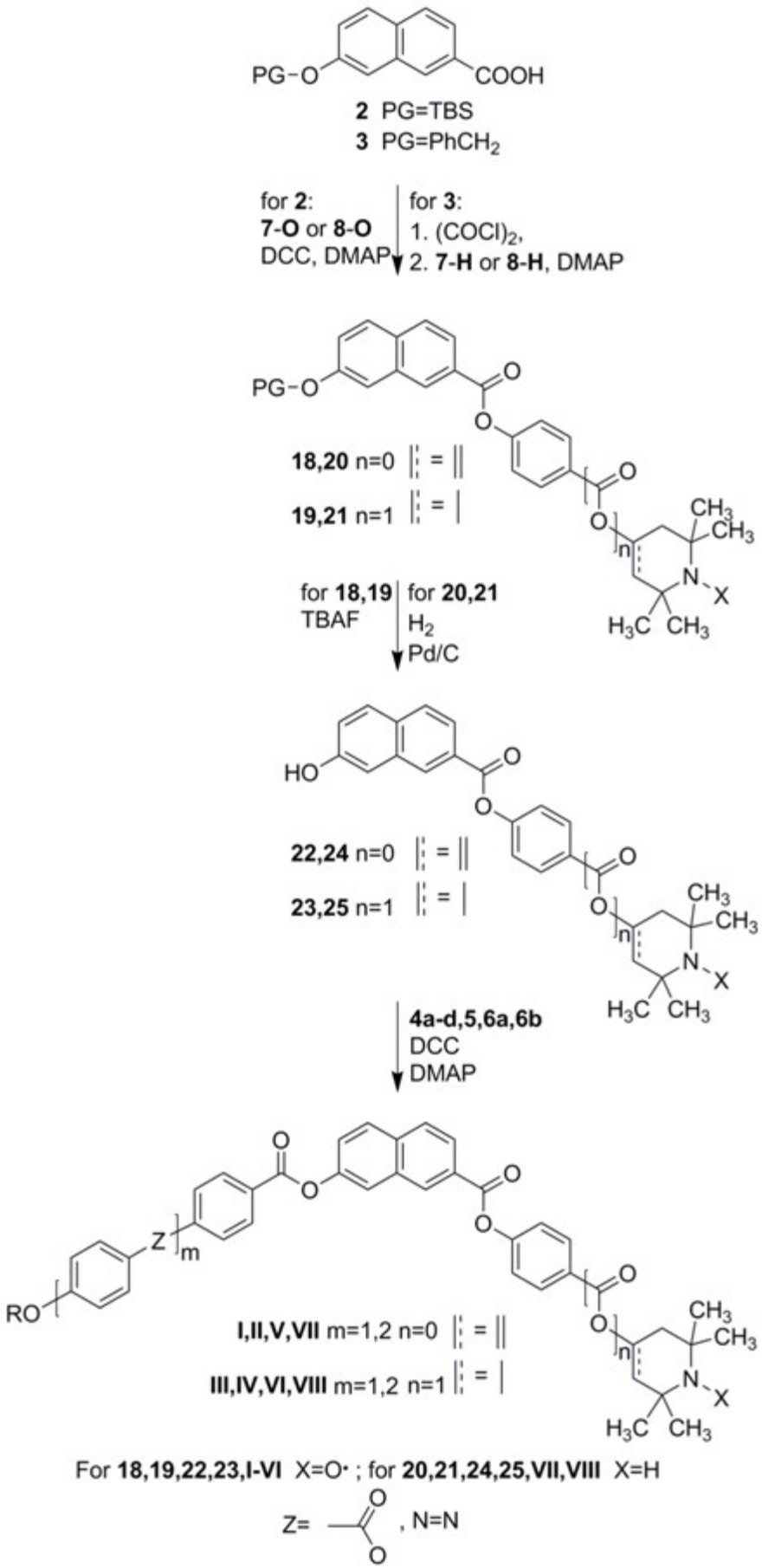
1.2. SYNTHESIS OF THE TARGET COMPOUNDS I-IV

The generalized scheme S3 summarizes the synthesis procedures for the preparation of all intermediates and target compounds of the series **I-VIII**. The detailed structures of materials **I-VIII** are shown in the main document in Figure 1 and 2. In the scheme S3, the symbol ⁞ stands for the representation of a double bond ‖ or a single bond | in the generalized molecular formulae of intermediates and materials **I-VIII**.

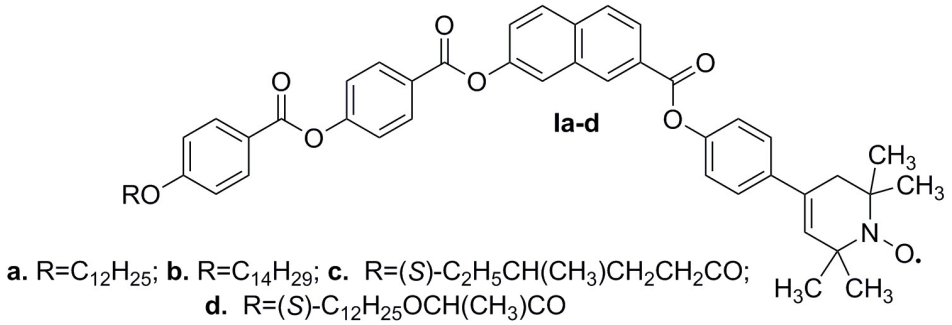
The synthesis of target materials is based on a step wise connecting of the lengthening arms to the central naphthalene based cores **2** and **3**. In the first step, the standard esterification of acid **2** with radicals **7-O**, **8-O** was achieved in the presence of DCC under catalysis with DMAP to yield the corresponding protected esters **18,19**, resp. For acylation of analogous **7-H**,8-**H** with acid **3**, the acid chloride method was used and the intermediate esters **20,21** were isolated.

In the next step, the protecting groups in compounds **18-21** were removed. While the desilylation of **18**, **19** was performed with TBAF in wet THF, the benzyl protecting group was removed by catalytic hydrogenation on palladium catalyst to yield hydroxy derivatives **22-25**.

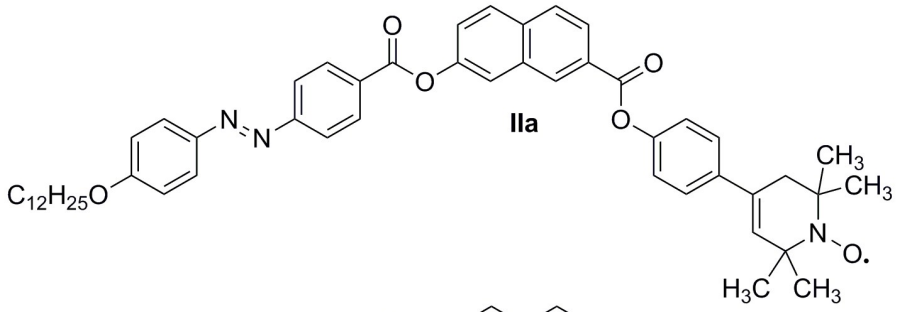
To introduce the second lengthening arms, the DCC/DMAP coupling of acids **4a-d**, **5**,**6a**, **6b** with compounds **22-25** was accomplished to yield materials of series **I-VIII**.

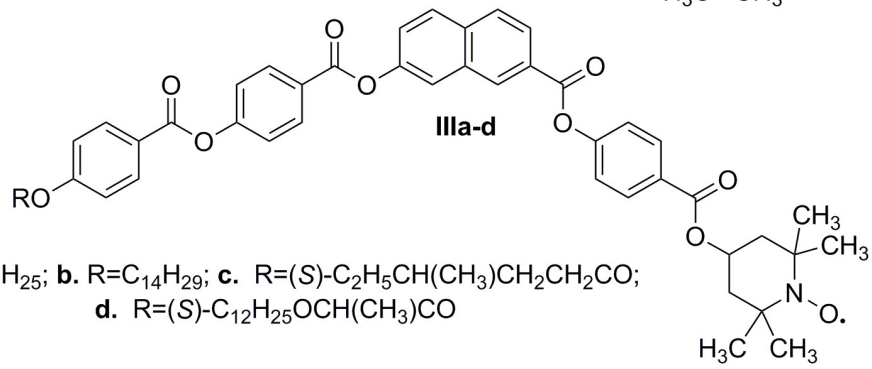


Scheme S3. General synthetic route to the target compounds **I-VIII**.



a. R=$C_{12}H_{25}$; **b.** R=$C_{14}H_{29}$; **c.** R=(*S*)-$C_2H_5CH(CH_3)CH_2CH_2CO$;
d. R=(*S*)-$C_{12}H_{25}OCH(CH_3)CO$





a. R=$C_{12}H_{25}$; **b.** R=$C_{14}H_{29}$; **c.** R=(*S*)-$C_2H_5CH(CH_3)CH_2CH_2CO$;
d. R=(*S*)-$C_{12}H_{25}OCH(CH_3)CO$

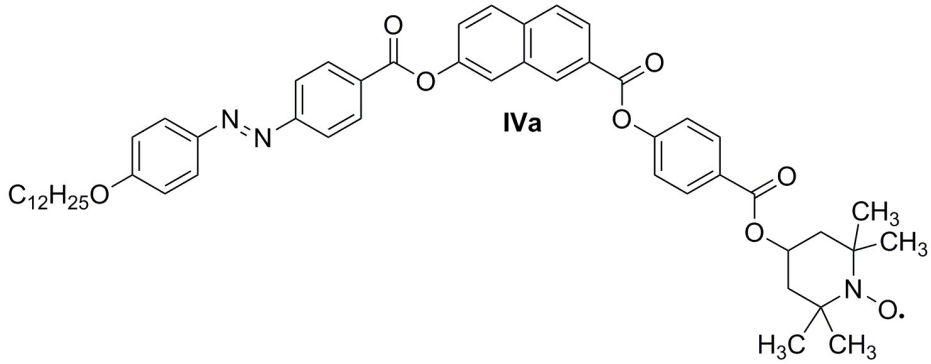


Fig. S2. The structures and designation of bent-core materials with five rings in the molecular structure.

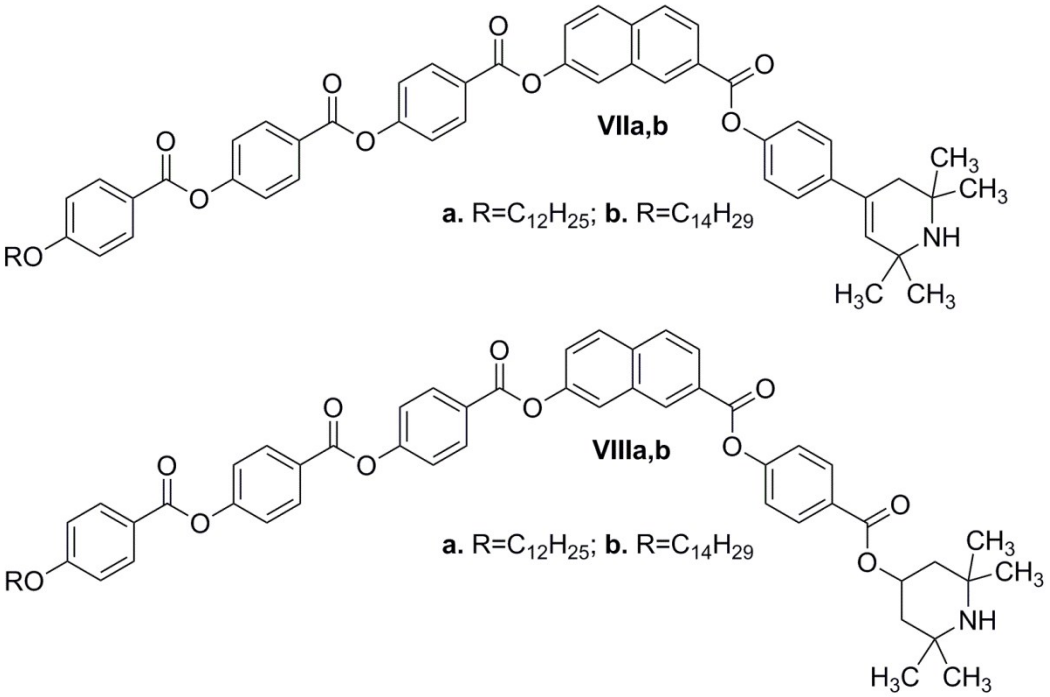


Fig. S3. The structures of the formal amine precursors of the six ring hockey-stick paramagnetic materials.

1.3. GENERAL PROCEDURES

The structures of intermediates and products were confirmed by ^{1}H NMR spectroscopy (Varian Gemini 300 HC instrument), deuteriochloroform, and dimethylsulfoxide-d_6 were used as solvents and the signals of the solvents served as internal standard, *J* values are given in Hz. Due to the presence of an unpaired nitroxyl radical moiety in the molecules of intermediates and target compounds, it was not possible to fully assign their molecular structure by NMR spectroscopy. Therefore the ^{1}H NMR measurements have been performed in the presence of a small amount of phenyl hydrazine, which reduces the present nitroxyl radical to the corresponding hydroxylamine, structure of which can be then fully assigned.

The structural integrity of the compounds was further verified by elemental analysis and mass spectrometry which were carried out using a Perkin-Elmer 2400 instrument and LTQ Orbitrap Velos (Thermo Scientific) under APCI positive or negative ionization mode conditions, resp. Purity of all final compounds was verified by HPLC analysis (Luna Silica 5μ, 150 × 4.6 mm) and were found >99.8%. Column chromatography was carried out using Merck Kieselgel 60 (60-100 μm). The experimental part summarizes syntheses and spectral data of the intermediates, and all target compounds of series **I-VIII**.

1.4. SYNTHESIS OF COMPOUNDS 1-8 (Scheme S1 and S2)

7-(*t*-Butyldimethylsilyloxy)naphtalene-2-carboxylic acid (2)

To a solution of 7-hydroxynaphthalene-2-carboxylic acid[S1] (1.02 g; 5.40 mmol) in dry DMF (20 mL), a solution of *t*-butyldimethylsilyl chloride (2.44 g; 16.2 mmol) in dry DMF (5 mL) was added drop wise. The mixture was stirred at room temperature for 4 h in an argon atmosphere and then poured on 2% aq. HCl (50 mL) and the product was extracted with toluene (3 × 50 mL). The combined organic solution was washed with water (50 mL), brine (50 mL), and dried with anhydrous magnesium sulphate. The solvent was evaporated and the crude bis-silyl derivative was dissolved in a mixture of 1% aq. K_2CO_3 (10 mL), THF (16 mL), and methanol (10 mL) to remove the carboxyl silyl protecting group. The mixture was stirred at room temperature for 30 min, diluted with water (30 mL), and extracted with toluene (3 × 20 mL). The toluene solution was washed with water (100 mL), brine (100 mL), and dried with anhydrous magnesium sulphate. After removing the solvent, 1.52 g (93%) of **1** was obtained, white crystals, mp 204-205°C (hexane). ^{1}H NMR (300 MHz, $CDCl_3$ δ): 1.26 (s, 6H, 2 × CH_3), 1.02 (s, 9H, $(CH_3)_3C$), 7.20 (d, J = 9.4 Hz, 1H, Ar H), 7.29 (s, 1H, Ar H), 7.79 (m, 2H, Ar H), 7.95 (d, J = 9.4 Hz, 1H, Ar H), 8.53 (s, 1H, Ar H); Anal. calcd for $C_{17}H_{22}O_3Si$ (302.45): C 67.51, H 7.33; found: C 67.38, H 7.26.

4-Formylphenyl 4-[(4-tetradecyloxy)benzoyloxy]benzoate (11)

Acid **4b**[S1] (2.0 g; 4.40 mmol), 4-hydroxybenzaldehyde (591 mg; 4.84 mmol), DCC (1.36 g; 6.60 mmol) and DMAP (5 mg) were dissolved in dichloromethane (100 mL) and stirred at room temperature for 24 h in an argon atmosphere. The reaction mixture was decomposed with water (5 mL), the deposited dicyclohexylurea was was filtered off and washed with dichloromethane (2 × 10 mL). The combined organic solution was washed with water (50 mL), brine (50 mL), and dried with anhydrous magnesium sulphate. After evaporation, the crude product was purified by column chromatography (toluene/*tert*-butyl methyl ether 12/1) to yield 1.78 g (73%) of **11**, mp 108-111°C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.88 (t, J = 7.0 Hz, 3H, CH_3), 1.10-1.58 (m, 22H, $(CH_2)_{11}$), 1.81 (m, 2H, CH_2), 4.05 (t, J = 6.7 Hz, 2H, OCH_2), 6.99 (d, J = 9.1 Hz, 2H, Ar H), 7.41 (m, 4H, Ar H), 7.99 (d, J = 8.5 Hz, 2H, Ar H), 8.15 (d, J = 9.1 Hz, 2H, Ar H), 8.28 (d, J = 8.8 Hz, 2H, Ar H), 10.04 (s, 1H, CHO); Anal calcd for $C_{35}H_{42}O_6$ (558.72): C 75.24, H 7.58; found: C 75.19, H 7.49.

4-[4-(4-Tetradecyloxybenzoyloxy)benzoyloxy]benzoic acid (6b)

To a suspension of **11** (520 mg; 0.93 mmol) in acetone (50 mL), a solution of CrO_3 in H_2SO_4 (0.5 mL) was added, and the mixture was stirred at room temperature for 16 h. The reaction was quenched with isopropyl alcohol (3 mL), and then poured on ice (100 mL). The deposited solid was filtered, washed with water (2 × 15 mL), and dried. Crystallization from toluene yielded 535 mg (77%) of **6b,** mp 187-300°C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.88 (t, J = 7.0 Hz,

3H, CH_3), 1.19-1.90 (m, 24H, $(CH_2)_{12}$), 4.05 (t, J = 6.7 Hz, 2H, OCH_2), 6.99 (d, J = 8.5 Hz, 2H, Ar H), 7.37 (m, 4H, Ar H), 8.17 (m, 4H, Ar H), 8.28 (d, J = 8.5 Hz, 2H, Ar H); EA for $C_{35}H_{42}O_7$ (574.72): calc.: C 73.15, H 7.37; found: C 73.11, H 7.39%. Anal. calcd for $C_{35}H_{42}O_7$ (574.72): C 73.15, H 7.37; found: C 73.11, H 7.39.

4-Formylphenyl *(S)*-4-(4-methylhexanoyloxy)benzoate (12)

To a solution of chiral acid **9**[S5] (0.50 g; 2.00 mmol) and DCC (0.50 g; 2.40 mmol) in dry dichloromethane (20 mL), 4-hydroxybenzaldehyde (366 mg; 3.00 mmol) and DMAP (8 mg) were added. The mixture was stirred at room temperature for 10 h, filtered and the solvent was evaporated. The crude product was purified by column chromatography (toluene/*tert*-butyl methyl ether 30/1) to yield 380 mg (54%) of **12**, mp 60-62°C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.94 (m, 6H, 2 × CH_3), 1.23 (m, 1H), 1.44 (m, 2H), 1.60 (m, 1H), 1.82 (m, 1H), 2.61 (m, 2H), 7.26 (d, J = 8.8 Hz, 2H, Ar H**),** 7.41 (d, J = 8.5 Hz, 2H, Ar H), 7.98 (d, J = 8.5 Hz, 2H, Ar H), 8.24 (d, J = 8.5 Hz, 2H, Ar H), 10.03 (s, 1H, CHO); Anal. calcd for $C_{21}H_{22}O_5$ (354.41): C 71.17, H 6.26; found: C 71.06, H 6.28.

***(S)*-4-{4-[4-Methylhexanoyloxy]benzoyloxy}benzoic acid (4c)**

The aldehyde **12** was oxidized by the procedure as for **6b**. Crystallization from toluene left acid **4c**, yield 56%, mp 178-237 °C. ^{1}H NMR (300 MHz, DMSO-d_6, δ): 0.87 (m, 6H, 2 × CH_3), 1.16 (m, 1H), 1.41 (m, 3H); 1.68 (m, 1H), 2.60 (m, 2H), 7.35 (d, J = 8.5 Hz, 2H, Ar H), 7.41 (d, J = 8.2 Hz, 2H, Ar H), 8.02 (d, J = 8.5 Hz, 2H, Ar H), 8.18 (d, J = 8.5 Hz, 2H, Ar H); Anal. calcd for $C_{21}H_{22}O_6$ (370.41): C 68.10, H 5.99; found: C 68.01, H 5.89.

4-Formylphenyl *(S)*-4-[2-(dodecyloxy)propanoyloxy]benzoate (13)

Compound **13** was obtained as for **12** by the reaction of acid 10[S6] (250 mg; 0.66 mmol) with 4-hydroxybenzaldehyde (121 mg; 0.99 mmol) in the presence of DCC (210 mg; 1 mmol) and DMAP (12 mg) in dichloromethane (20 mL). The product was purified by column chromatography (hexane/ethyl acetate 8/1), yield 126 mg (39%), mp 45-47 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.88 (t, J = 7.0 Hz, 3H, CH_3), 1.0-1.50 (m, 18H, $(CH_2)_9$), 1.59 (d, J = 7.0 Hz, 3H, CH_3), 1.66 (m, 2H), 3.50 (m, 1H, OCH_2), 3.69 (m, 1H, OCH_2), 4.22 (q, J = 6.7 Hz, 1H, CH), 7.29 (d, J = 9.1 Hz, 2H, Ar H), 7.41 (d, J = 8.5 Hz, 2H, Ar H), 7.98 (d, J = 8.8 Hz, 2H,), 8.25 (d, J = 9.1 Hz, 2H, Ar H), 10.03 (s, 1H, CHO); Anal. calcd for $C_{29}H_{38}O_6$ (482.62): C 72.17, H 7.94; found: C 72.15, H 7.88.

***(S)*-4-[4-(2-Dodecyloxypropanoyloxy)benzoyloxy]benzoic acid (4d)**

The aldehyde **13** was oxidized by the same method as for **6b**. After crystallization from toluene, 177 mg (75%) of acid **4d** was isolated, mp 117-179 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.88 (t, J = 6.7 Hz, 3H, CH_3), 1.19-1.50 (m, 18H, $(CH_2)_9$), 1.59 (d, J = 6.7 Hz, 3H, CH_3),

1.66 (m, 2H), 3.50 (m, 1H, OCH_2), 3.68 (m, 1H, OCH_2), 4.22 (q, J = 7.0 Hz, 1H, CH), 7.29 (d, J = 9.1 Hz, 2H, Ar H), 7.34 (d, J = 8.8 Hz, 2H, Ar H), 8.19 (d, J = 8.8 Hz, 2H, Ar H), 8.25 (d, J = 8.8 Hz, 2H, Ar H) Anal. calcd for $C_{29}H_{38}O_7$ (498.62): C 69.86, H 7.68; found: C 69.74, H 7.72.

2,2,6,6-Tetramethylpiperidin-4-yl 4-benzyloxybenzoate (17-H)

To a solution of 4-benzyloxybenzoic acid **14**[S9] (4.0 g; 17.5 mmol) in dry dichloromethane (140 mL), oxalyl chloride (4.5 mL; 52.5 mmol) was added and the mixture was stirred at room temperature for 16 h. The volatile components were evaporated and the crude acid chloride was dissolved in toluene (60 mL) and added to a mixture of 2,2,6,6-tetramethylpiperidin-4-ol (16-H) (1.84 g; 11.7 mmol) and DMAP (2.14 g; 17.5 mmol) in toluene (180 mL). The reaction mixture was then heated to 80°C for 5 h, and after cooling, it was decomposed with 2% aq. HCl (250 mL). The toluene layer was separated and the aqueous was extracted with chloroform (3 × 100 mL). The combined organic solution was washed with water (100 mL), brine (100 mL), and dried with anhydrous magnesium sulphate. The solvent was evaporated and the residue was purified by column chromatography (chloroform/methanol/trimethylamine 90/10/0.1). Yield 1.80 g (42%) of **17-H**, mp 116-117°C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.54 (m, 12H, 4 × CH_3), 1.78 (m, 2H, CH_2), 2.10 (dd, ^2J = 12.9 Hz, ^3J = 3.8 Hz, 2H, CH_2), 5.11 (s, 2H, OCH_2), 5.40 (m, 1H, CH), 6.99 (d, J = 9.1 Hz, 2H, Ar H), 7.39 (m, 5H, Ar H), 7.96 (d, J = 8.9 Hz, 2H, Ar H); Anal. calcd for $C_{23}H_{29}NO_3$ (367.49): C 75.17, H 7.95, N 3.81; found: C 75.06, H 7.88, N 3.76.

2,2,6,6-Tetramethylpiperidin-4-yl 4-hydroxybenzoate (7-H)

Benzyl derivative **17-H** (1.79 g; 4.87 mmol) was hydrogenated in a Parr apparatus on 10% Pd/C (179 mg) in ethyl acetate (50 mL) for 2 d. The catalyst was filtered off and washed subsequently with chloroform (20 mL) and ethanol (3 × 20 mL). After evaporation of the filtrate, the product was purified by column chromatography (chloroform/methanol/trimethylamine 90/10/0.1), and crystallization from an ethanol/ethyl acetate mixture to afford 1.19 g (88%) of **7-H**, mp 267-269°C, mp[S15] 252°C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.28 (m, 14H), 1.64 (bs, 1H, NH), 2.06 (dd, ^{2}J = 12.7 Hz, ^{3}J = 4.1 Hz, 2H, CH_2), 5.40 (m, 1H, CH), 6.85 (d, J = 8.8 Hz, 2H, Ar H), 7.94 (d, J = 8.8 Hz, 2H, Ar H); Anal. calcd for $C_{16}H_{23}NO_3$ (277.37): C 69.29, H 8.36, N 5.05; found: C 69.19, H 8.29, N 4.98.

4-[4-(*t*-Butyldimethylsilyloxy)benzoyloxy]-2,2,6,6-tetramethylpiperidine-1-oxyl (17-O)

4-Hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (**16-O**) (1.50 g; 8.71 mmol) was added to a solution of acid **15**[S10] (2.50 g; 10 mmol), DCC (2.36 g; 10 mmol), and DMAP (80 mg) in dichloromethane (60 mL) and the mixture was stirred at room temperature for 2 h. The deposited solid was filtered off and washed with dichloromethane (20 mL). The filtrate was evaporated and the product was purified by column chromatography (toluene/ethyl acetate 95/5) to yield 1.03 g (29%) of **17-O**, orange crystals, mp 81-82°C. ^{1}H NMR (300 MHz, $CDCl_3$, δ)with added phenyl hydrazine, its signals omitted (spectrum of hydroxylamine): 0.22 (s, 6H, 2 × CH_3), 0.98 (s, 9H, $(CH_3)_3C$), 1.27 (m, 12H, 4 × CH_3), 1.75 (m, 2H, CH_2), 2.05 (m, 2H, CH_2), 5.27 (m, 1H, CH), 6.85 (d, *J* = 8.8 Hz, 2H, Ar H), 7.90 (d, *J* = 8.8 Hz, 2H, Ar H); IR (KBr): **ν** = 2932, 2859, 1715 (C=O), 1603, 1509, 1267, 1162, 1113, 1096, 910 cm^{-1}; HRMS (APCIpos) m/z: $[M + H]^+$ calcd for $C_{22}H_{36}O_4NSi$, 407.24864; found, 407.24861. Anal. calcd for $C_{22}H_{36}NO_4Si$ (406.62): C 64.99, H 8.92, N 3.44; found: C 64.86, H 8.89, N 3.49.

4-[4-Hydroxybenzoyloxy]-2,2,6,6-tetramethylpiperidine-1-oxyl (7-O)

A solution of TBAF in THF (0.56 mL; 0.56 mmol) was added to a solution of silyl derivative **17-O** (1.00 g; 2.47 mmol) in a mixture of THF (60 mL) and water (18 mL). The mixture was stirred at room temperature 30 min and then diluted with water (60 mL). The product was extracted with ethyl acetate (3 × 50 mL), the combined organic solution was washed with brine (50 mL) and dried with anhydrous magnesium sulphate. The solvent was evaporated to dryness. 715 mg (99%) of **7-O** was isolated in the form of orange crystals, mp 169-172°C, mp[S11] 175°C. ^{1}H NMR (300 MHz, $CDCl_3$, δ) with added phenyl hydrazine, its signals omitted (spectrum of hydroxylamine): 1.37 (s, 6H, 2 × CH_3), 1.44 (s, 6H, 2 × CH_3), 2.03 (m, 2H), 2.14 (m, 2H), 5.29 (m, 1H, CH), 6.87 (d, *J* = 7.6 Hz, 2H, Ar H); 7.90 (d, *J* = 8.2 Hz, 2H, Ar H); IR (KBr): **ν** = 3397 (OH), 2932, 2859, 1701, 1609, 1277, 1163, 1113, 1097 cm^{-1};. HRMS (APCIneg) m/z: $[M^-]$ calcd for $C_{16}H_{22}O_4N$, 292.15543; found, 292.15552. Anal. calcd for $C_{16}H_{22}NO_4$ (292.36): C 65.73, H 7.58, N 4.79; found: C 65.85, H 7.64, N 4.81

1.5. SYNTHESIS OF THE INTERMEDIATES AND THE TARGET COMPOUNDS

3,6-Dihydro-4-{4-[7-(*t*-butyldimethylsilyloxy)naphthalene-2-carbonyloxy]phenyl}-2,2,6,6-tetramethylpyridine-1(2*H*)-oxyl (18)

A mixture of protected acid **2** (184 mg; 0.61 mmol), N-oxyl radical **8-O** (150 mg; 0.61 mmol), DCC (126 mg; 0.61 mmol) and DMAP (6 mg) in dry dichloromethane (13 mL) was stirred at room temperature for 2 h in an inert argon atmosphere. The deposited solid was filtered off

and the filtrate was evaporated. The product was purified by column chromatography (eluent toluene/ethyl acetate, 95/5) to yield 300 mg (93%) of **18**; mp 168-173°C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.29 (s, 6H, 2 × CH_3), 1.05 (s, 9H, $(CH_3)_3C$), 7.23 (m, 1H, Ar H), 7.36 (s, 1H, Ar H), 7.83 (d, *J* = 8.8 Hz, 1H, Ar H), 7.89 (d, *J* = 8.2 H, 1H, Ar H), 8.06 (m, 1H, Ar H), 8.66 (s, 1H, Ar H); (protons of dihydropyridine and adjacent phenyl unit were not detected); ^{1}H NMR (300 MHz, $CDCl_3$, δ) with added phenyl hydrazine, its signals omitted: 1.27 (s, 6H, 2 × CH_3), 1.02 (s, 9H, $(CH_3)_3C$), 1.49 (s, 6H, 2 × CH_3), 1.55 (s, 6H, 2 × CH_3), 2.80 (s, 2H, CH_2), 5.86 (s, 1H, CH), 7.25 (m, 2H, Ar H), 7.44 (d, *J* = 8.5 Hz, 2H, Ar H), 7.80 (d, *J* = 8.8 Hz, 2H, Ar H), 7.87 (d, *J* = 8.5 Hz, 2H, Ar H), 8.04 (dd, ^3J = 8.9 Hz, ^4J = 1.5 Hz, 1H, Ar H), 8.63 (s, 1H, Ar H) (one doublet covered by phenyl hydrazine signals); IR (KBr): **ν** = 2931, 2859, 1733 (C=O), 1629, 1602, 1508, 1461, 1331, 1200, 1169, 1061 cm^{-1}; HRMS (APCIneg) m/z: [M^-] calcd for $C_{32}H_{40}O_4NSi$, 530.27321; found, 530.27396**.** Anal. calcd for $C_{32}H_{40}NO_4Si$ (530.77): C 72.42, H 7.60, N 2.64; found: C 72.55, H 7.63, N 2.60.

4-{4-[7-(*t*-Butyldimethylsilyloxy)naphthalene-2-carbonyloxy]benzoyloxy}-2,2,6,6-tetramethylpiperidine-1-oxyl (19)

The compound **19** was prepared by the reaction of **2** (750 mg; 2.48 mmol) with radical **7-O** (604 mg; 2.07 mmol) as for **18**. Yield 1.12 g (94%) of dark orange crystals, mp 114-115 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.28 (s, 6H, 2 × CH_3), 1.04 (s, 9H, $(CH_3)_3C$), 7.24 (m, 1H, Ar H), 7.35 (m, 1H, Ar H), 7.82 (d, *J* = 8.8 Hz, 1H, Ar H), 7.89 (d, *J* = 8.5 Hz, 1H, Ar H), 8.05 (d, *J* = 8.8 Hz, 1H, Ar H), 8.65 (s, 1H, Ar H). ^{1}H NMR (300 MHz, $CDCl_3$, δ) with added phenyl hydrazine, its signals omitted: 0.27 (s, 6H, 2 × CH_3), 1.02 (s, 9H, $(CH_3)_3C$), 1.32 (s, 6H, 2 × CH_3), 1.35 (s, 6H, 2 × CH_3), 1.88 (m, 2H), 2.09 (m, 2H), 5.40 (m, 1H), 7.17 (m, 1H, Ar H); 7.35 (m, 3H, Ar H), 7.81 (d, *J* = 8.9 Hz, 1H, Ar H), 7.87 (d, *J* = 8.9 Hz, 1H, Ar H), 8.03 (dd, ^3J = 8.9 Hz, ^4J = 1.7 Hz, 1H, Ar H), 8.12 (m, 2H, Ar H); 8.64 (s, 1H, Ar H); IR (KBr): **ν** = 2931, 2858, 1739, 1719 (C=O), 1602, 1460, 1272, 1202, 1056, 1016 cm^{-1}; HRMS (APCIneg) m/z: [M^-] calcd for $C_{33}H_{42}O_6NSi$: 576.27869, found: 576.27820**.** Anal. calcd for $C_{33}H_{42}NO_6Si$ (576.79): C 68.72, H 7.34, N 2.43; found: C 68.86, H 7.39, N 2.39.

4-(1,2,3,6-Tetrahydro-2,2,6,6-tetramethylpyridin-4-yl)phenyl 7-benzyloxynaphthalene-2-carboxylate (20)

Oxalyl chloride (1.9 mL; 21.6 mmol) was added to a solution of acid **3** (2.0 g; 7.19 mmol) in dry dichloromethane (100 mL) and the mixture was stirred at room temperature for 2 days and then evaporated. The crude acid chloride was dissolved in toluene (150 mL) and added to a

solution of hydroxy derivative **8-H**[S6] (1.39 g; 5.99 mmol) and DMAP (878 mg; 7.19 mmol) in toluene (150 mL) and the reaction mixture was stirred to boiling for 8 h. The mixture was then poured into 2% aq. HCl (150 mL) and separated. The aqueous layer was extracted with chloroform (3 × 100 mL). The combined organic solution was washed with water (100 mL), brine (100 mL), and dried with anhydrous magnesium sulphate. The solvent was evaporated and the product was purified by column chromatography (chloroform/methanol/triethylamine 90/10/0.1) and crystallization from a chloroform/hexane mixture. Yield 2.61 g (89%), mp 249-261°C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.56 (m, 12H, 4 × CH_3), 2.55 (s, 2H, CH_2), 5.22 (s, 2H, OCH_2), 5.93 (s, 1H, CH), 7.24 (m, 2H, Ar H), 7.32-7.52 (m, 9H, Ar H); 7.84 (d, *J* = 8.8 Hz, 1H, Ar H), 7.88 (d, *J* = 8.8 Hz, 1H, Ar H), 8.04 (m, 1H, Ar H), 8.66 (s, 1H, Ar H); Anal. calcd for $C_{33}H_{33}NO_3$ (491.64): C 80.62, H 6.77, N 2.85; found: C 80.48, H 6.66, N 2.67.

(2,2,6,6-Tetramethylpiperidin-4-yl) 4-(7-benzyloxynaphthalene-2-carbonyloxy)benzoate (21)

Oxalyl chloride (1.3 mL; 14.3 mmol) was added to a solution of acid **3** (1.32 g; 4.76 mmol) in dry dichloromethane (30 mL). The mixture was stirred at room temperature for 17 h and then evaporated. The formed acid chloride was dissolved in dichloromethane (50 mL) and added drop wise to a solution of phenol **7-H** (1.10 g; 3.97 mmol) and DMAP (581 mg; 4.76 mmol) in dichloromethane (100 mL). The mixture was heated to boiling under stirring for 5 h. After cooling, it was poured on 5% aq. solution of HCl (150 mL) and extracted with dichloromethane (3 × 50 mL). The combined organic layers were washed with water (50 mL), brine (50 mL), and dried with anhydrous magnesium sulphate. The solvent was evaporated and the product was purified by two subsequent column chromatographies (toluene/methanol/trimethylamine 90/10/0.1). Yield 1.82 g (85%) of **21**, mp 195-196°C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.21 (s, 6H, 2 × CH_3), 1.31 (m, 8H), 1.52 (bs, 1H, NH), 2.08 (m, 2H); 5.22 (s, 2H, OCH_2), 5.43 (m, 1H, CH), 7.30-7.52 (m, 9H, Ar H), 7.84 (d, *J* = 8.5 Hz, 1H, Ar H), 7.89 (d, *J* = 8.5 Hz, 1H, Ar H), 8.05 (m, 1H, Ar H), 8.14 (d, *J* = 8.8 Hz, 2H,), 8.66 (s, 1H, Ar H); Anal. calcd for $C_{34}H_{35}NO_5$ (537.66): C 75.95, H 6.56, N 2.61; found: C 75.88, H 6.52, N 2.50.

3,6-Dihydro-4-[4-(7-hydroxynaphthalene-2-carbonyloxy)phenyl]-2,2,6,6-tetramethyl-pyridine-1(2*H*)-oxyl (22)

A 1 M solution of TBAF in THF (0.22 mL; 0.22 mmol) was added to a solution of **18** (517 mg; 0.97 mmol) in a THF/H_2O mixture (30 mL/9 mL). After stirring for 40 min at room

temperature, the mixture was diluted with water (60 mL) and extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed with brine (50 mL) and dried with anhydrous $MgSO_4$. The solvent was evaporated to yield 400 mg (98%) of yellow crystals of **22**, mp 230-233 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.53 (bs, 12H, 4 × CH_3), 7.12 (m, 2H, Ar H), 7.87 (m, 2H, Ar H), 8.05 (d, *J* = 8.5 Hz, 1H, Ar H), 8.63 (s, 1H, Ar H); ^{1}H NMR (300 MHz, $CDCl_3$, δ) with added phenyl hydrazine, its signals omitted: 1.32 (s, 6H, 2 × CH_3), 1.38 (s, 6H, 2 × CH_3), 2.56 (s, 2H, CH_2), 5.89 (s, 1H, CH), 7.84 (m, 2H, Ar H), 8.04 (m, 1H, Ar H); 8.60 (s, 1H, Ar H). IR (KBr): ν = 3261 (OH), 2976, 1732 (C=O), 1605, 1508, 1229, 1203, 1170, 1062 cm^{-1}. HRMS (APCIneg) m/z: [M$^-$] calcd for $C_{26}H_{26}O_4N$, 416.18673; found, 416.18576. Anal.calcd for $C_{26}H_{26}NO_4$ (416.50): C 74.98, H 6.29, N 3.36; found: C 75.11, H 6.33, N 3.31.

4-[4-(7-Hydroxynaphthalene-2-carbonyloxy)benzoyloxy]-2,2,6,6-tetramethylpiperidine-1-oxyl (23)

The silyl protecting group in **19** (1.09 g; 1.90 mmol) was removed in the same was as for **22**. Yield 573 mg (65%) of yellow crystals, mp 165-168°C. ^{1}H NMR (300 MHz, $CDCl_3$, δ) with added phenylhydrazine, its signals omitted: 1.44 (s, 6H, 2 × CH_3), 1.54 (s, 6H, 2 × CH_3), 2.21 (m, 4H), 5.39 (m, 1H), 7.17 (m, 1H, Ar H), 7.33 (m, 3H, Ar H), 7.81 (d, *J* = 8.8 Hz, 1H, Ar H), 7.86 (d, *J* = 8.8 Hz, 1H, Ar H), 8.01 (m, 1H, Ar H), 8.07 (d, *J* = 8.8 Hz, 2H, Ar H), 8.60 (s, 1H, Ar H); IR (KBr): **ν** = 3408 (OH), 2975, 2863, 1736, 1716 (C=O), 1604, 1275, 1203, 1163 cm^{-1}. HRMS (APCIneg) m/z: [M$^-$] calcd for $C_{27}H_{28}O_6N$, 462.19221; found, 462.19187. Anal. calcd for $C_{27}H_{28}NO_6$ (462.53): C 70.12, H 6.10, N 3.03; found: C 70.13, H 6.09, N 2.99.

4-(1,2,3,6-Tetrahydro-2,2,6,6-tetramethylpyridin-4-yl)phenyl 7-hydroxynaphthalene-2-carboxylate (24)

A suspension of benzyl derivative **20** (200 mg; 0.41 mmol) and 10% palladium on carbon (20 mg) in ethyl acetate (50 mL) was stirred in a hydrogen atmosphere for 20 h. The catalyst was filtered off and the filtrate evaporated. The crude product was purified by column chromatography (chloroform/methanol/triethylamine 90/10/0.1). It was isolated 81 mg (50%) of **24**, mp 236-238°C. ^{1}H NMR (300 MHz, DMSO-d_6, δ): 1.19 (s, 6H, 2 × CH_3), 1.25 (s, 6H, 2 × CH_3), 2.27 (s, 2H, CH_2), 6.09 (s, 1H, CH), 7.26 (m, 3H, Ar H), 7.36 (s, 1H, Ar H), 7.50 (d, *J* = 8.5 Hz, 2H, Ar H), 7.91 (m, 3H, Ar H), 8.58 (s, 1H, Ar H), 10.08 (bs, 1H, OH); Anal. calcd for $C_{26}H_{27}NO_3$ (401.51): C 77.78, H 6.78 N 3.49; found: C 77.59, H 6.76, N 3.32.

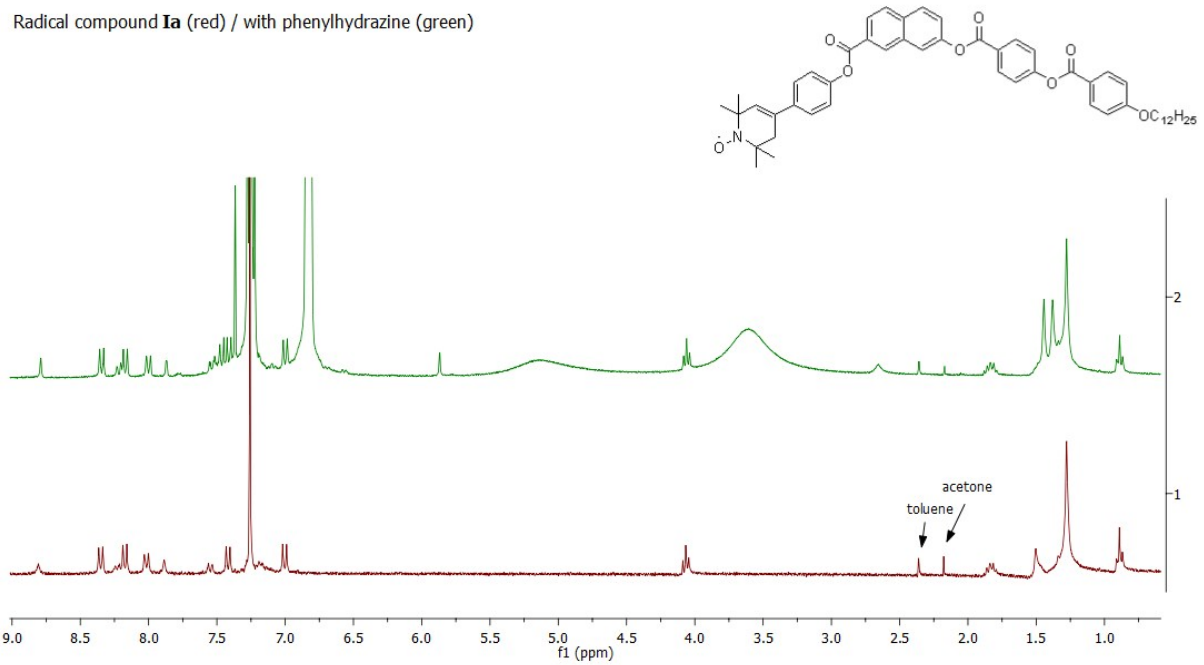
4-[(2,2,6,6-Tetramethylpiperidin-4-yloxy)carbonyl]phenyl 7-hydroxynaphthalene-2-carboxylate (25)

Benzyl derivative **21** (300 mg; 0.56 mmol) was hydrogenated as for **8-H** on Pd/C (30 mg) in acetone (50 mL) for 12 h, the catalyst was filtered off and washed with 0.1% Et_3N in $CHCl_3$ (2 × 20 mL). The filtrate was washed with water (50 mL) and dried with anhydrous magnesium sulphate. The solvent was evaporated and the crude product purified by crystallization from ethanol. It was obtained 210 mg (84%) of **25**, mp 220-223°C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.22 (s, 6H, 2 × CH_3), 1.31 (m, 8H), 1.53 (bs, 1H, NH), 2.08 (m, 2H), 5.47 (m, 1H, CH), 7.29 (m, 2H, Ar H), 7.35 (d, *J* = 9.1 Hz, 2H, Ar H), 7.84 (d, *J* = 8.8 Hz, 1H, Ar H), 7.88 (d, *J* = 8.8 Hz, 1H, Ar H), 8.04 (m, 1H, Ar H), 8.14 (d, *J* = 8.8 Hz, 2H, Ar H), 8.62 (s, 1H, Ar H); Anal.calcd for $C_{27}H_{29}NO_5$ (447.54): C 72.46, H 6.53 N 3.13; found: C 72.37, H 6.50, N 3.03.

3,6-Dihydro-4-[4-(7-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]naphthalene-2-carbonyl-oxy)phenyl]-2,2,6,6-tetramethylpyridine-1(2*H*)-oxyl (Ia)

To a solution of acid **4a** (184 mg; 0.43 mmol), DCC (80 mg; 0.43 mmol), and DMAP (4 mg) in dichloromethane (10 mL), the intermediate **22** (150 mg; 0.36 mmol) was added. The mixture was stirred at room temperature for 3 h in an argon atmosphere and then filtered. The filtrate was evaporated and the product was purified by column chromatography (toluene/ethyl acetate, 95/5) and crystallization from a hexane/ethyl acetate mixture. Yield 262 mg (88%) of orange crystals. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.89 (t, *J* = 6.7 Hz, 3H, CH_3), 1.00-1.55 (m, 18H $(CH_2)_9$), 1.83 (m, 2H, CH_2), 4.07 (t, *J* = 6.7 Hz, 2H, OCH_2), 7.00 (d, *J* = 9.3 Hz, 2H, Ar H), 7.42 (d, *J* = 8.5 Hz, 2H, Ar H), 7.55 (d, *J* = 8.8 Hz, 1H, Ar H), 7.89 (s, 1H, Ar H), 8.02 (d, *J* = 8.8 Ar H, 2H, Ar H), 8.17 (d, *J* = 8.8 Hz, 2H, Ar H), 8.23 (d, *J* = 9.7 Hz, 1H, Ar H), 8.35 (d, *J* = 8.5 Hz, 2H, Ar H), 8.81 (s, 1H, Ar H) (protons of the dihydropyridine and adjacent phenyl unit not detected); ^{1}H NMR (300 MHz, $CDCl_3$, δ) with added phenylhydrazine, its signals omitted (spectrum of hydroxylamine): 0.89 (t, *J* = 6.7 Hz, 3H, CH_3), 1.00-1.58 (m, 30H, 9 × CH_2, 4 × CH_3), 1.84 (m, 2H, CH_2), 2.65 (s, 2H, CH_2), 4.06 (t, *J* = 6.7 Hz, 2H, OCH_2), 5.87 (s, 1H, CH), 7.00 (d, *J* = 8.8 Hz, 2H, Ar H), 7.26 (m, 2H, Ar H), 7.41 (d, *J* = 8.5 Hz, 2H, Ar H), 7.46 (d, *J* = 8.5 Hz, 2H, Ar H), 7.53 (dd, ^3J = 8.8 Hz, ^4J = 2.4 Hz, 1H, Ar H), 7.87 (s, 1H, Ar H), 8.00 (d, *J* = 8.2 Hz, 2H, Ar H), 8.17 (d, *J* = 8.8 Hz, 2H, Ar H), 8.22 (d, *J* = 6.0 Hz, 1H, Ar H), 8.34 (d, *J* = 8.5 Hz, 2H, Ar H), 8.79 (s, 1H, Ar H); IR (KBr): **ν** = 2922, 2852, 1736 (C=O), 1604, 1263, 1196, 1162, 1059 cm^{-1}; HRMS (APCIneg)

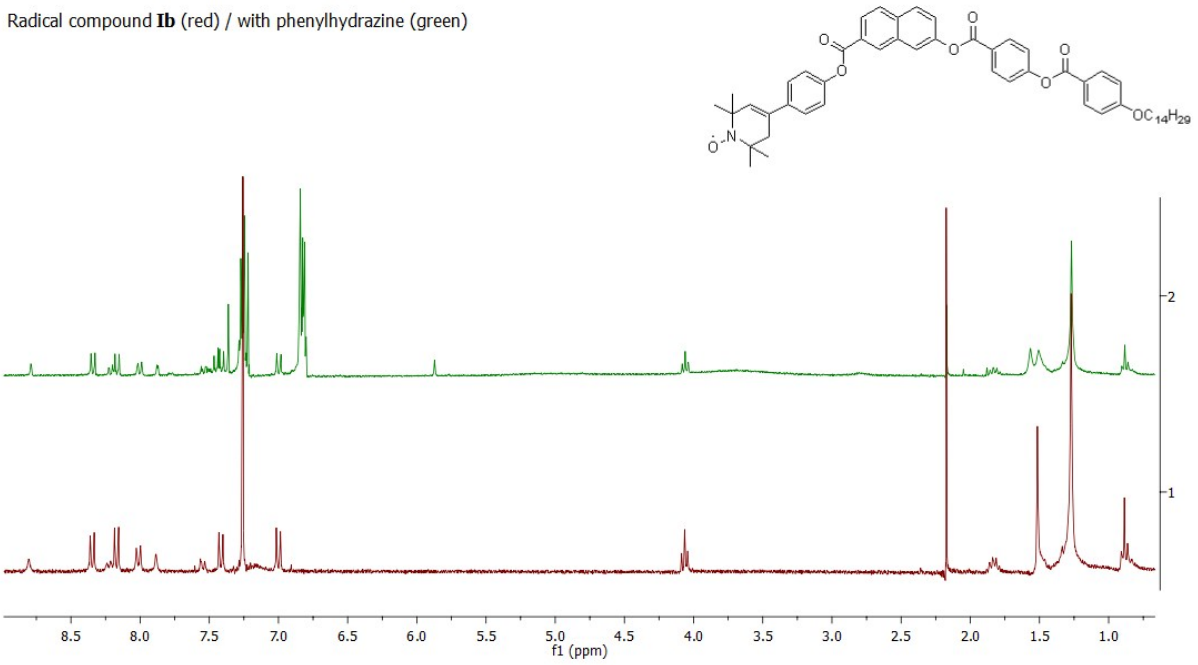
m/z: [M^-] calcd for $C_{52}H_{58}O_8N$, 824.41679; found 824.41734. Anal. calcd for $C_{52}H_{58}NO_8$ (825.04): C 75.70, H 7.09, N 1.70; found: C 75.83, H 7.11, N 1.68.



3,6-Dihydro-4-[4-(7-[4-(4-tetradecyloxybenzoyloxy)benzoyloxy]naphthalene-2-carbonyl-oxy)phenyl]-2,2,6,6-tetramethylpyridine-1(2*H*)-oxyl (Ib)

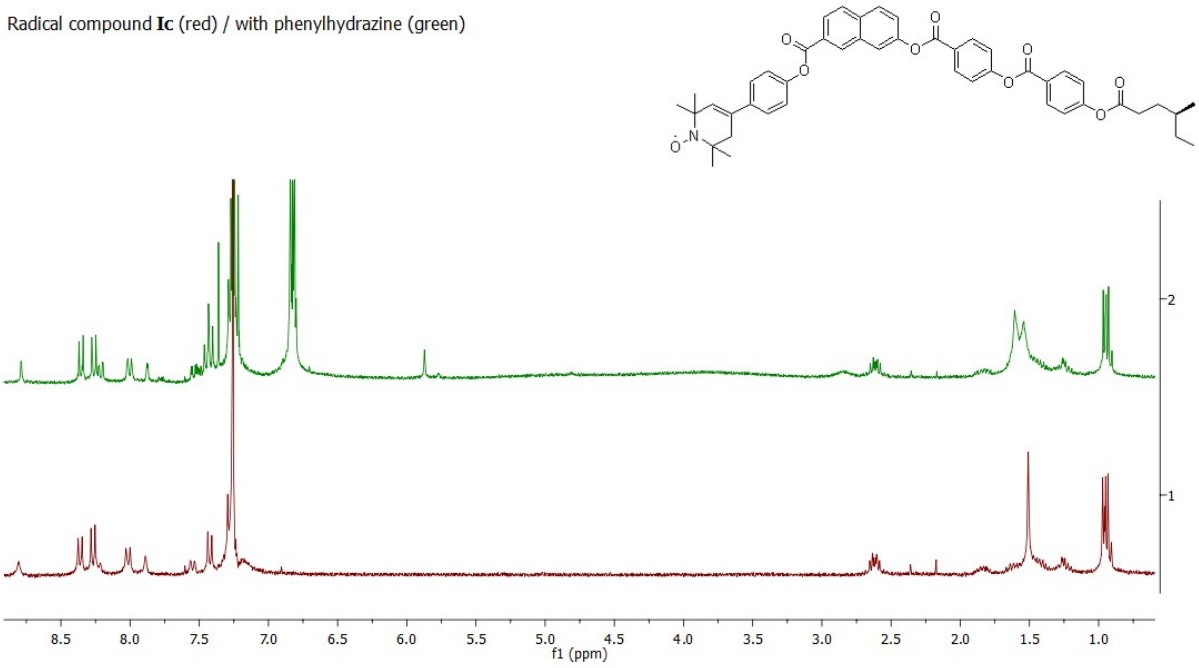
Radical compound **Ib** was prepared analogously to **Ia** by the reaction of acid **4b** with intermediate **22**. Column chromatography (toluene/ethyl acetate 95/5) yielded 74% of **Ib**. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.89 (t, J = 6.7 Hz, 3H, CH_3), 1.18-1.58 (m, 22H, $(CH_2)_{11}$), 1.84 (m, 2H, CH_2), 4.06 (t, J = 6.4 Hz, 2H, OCH_2), 7.00 (d, J = 9.1 Hz, 2H, Ar H), 7.42 (d, J = 8.5 Hz, 2H, Ar H), 7.55 (d, J = 8.8 Hz, 1H, Ar H), 7.88 (s, 1H, Ar H), 8.01 (d, J = 8.8 Hz, 2H, Ar H), 8.17 (d, J = 8.8 Hz, 2H, Ar H), 8.23 (d, J = 6.0 Hz, 1H, Ar H), 8.35 (d, J = 8.8 Hz, 2H, Ar H), 8.81 (s, 1H, Ar H) (the dihydropyridine unit and 4 protons from phenyl connected to it not detected); ^{1}H NMR (300 MHz, $CDCl_3$, δ) with added phenyl hydrazine, its signals omitted (spectrum of hydroxylamine): 0.87 (t, J = 7.0 Hz, 3H, CH_3), 1.20-1.60 (m, 36 H), 1.82 (m, 2H, CH_2), 4.06 (t, J = 6.7 Hz, 2H, OCH_2), 5.87 (s, 1H, CH), 7.00 (d, J = 9.1 Hz, 2H, Ar H), 7.26 (m, 2H, Ar H), 7.41 (d, J = 8.8 Hz, 2H, Ar H), 7.45 (d, J = 8.8 Hz, 2H, Ar H), 7.54 (dd, ^3J = 8.8 Hz, ^4J = 2.5 Hz, 1H, Ar H), 7.87 (d, J = 2.6 Hz, 1H, Ar H), 8.00 (d, J = 8.2 Hz, 2H, Ar H), 8.17 (d, J = 8.8 Hz, 2H, Ar H), 8.22 (dd, ^3J = 8.5 Hz, ^4J = 1.2 Hz, 1H, Ar H), 8.34 (d, J = 8.5 Hz, 2H, Ar H), 8.79 (s, 1H, Ar H). IR (KBr): **ν** = 2919, 2851; 1735 (C=O), 1605, 1510, 1468, 1265, 1196, 1165, 1062 cm^{-1}; HRMS (APCIneg) m/z: [M^-] calcd for $C_{54}H_{62}O_8N$, 852.44809;

found, 852.44782. Anal.calcd for $C_{54}H_{62}NO_8$ (853.10): C 76.03, H 7.33, N 1.64; found: C 75.88, H 7.27, N 1.62.



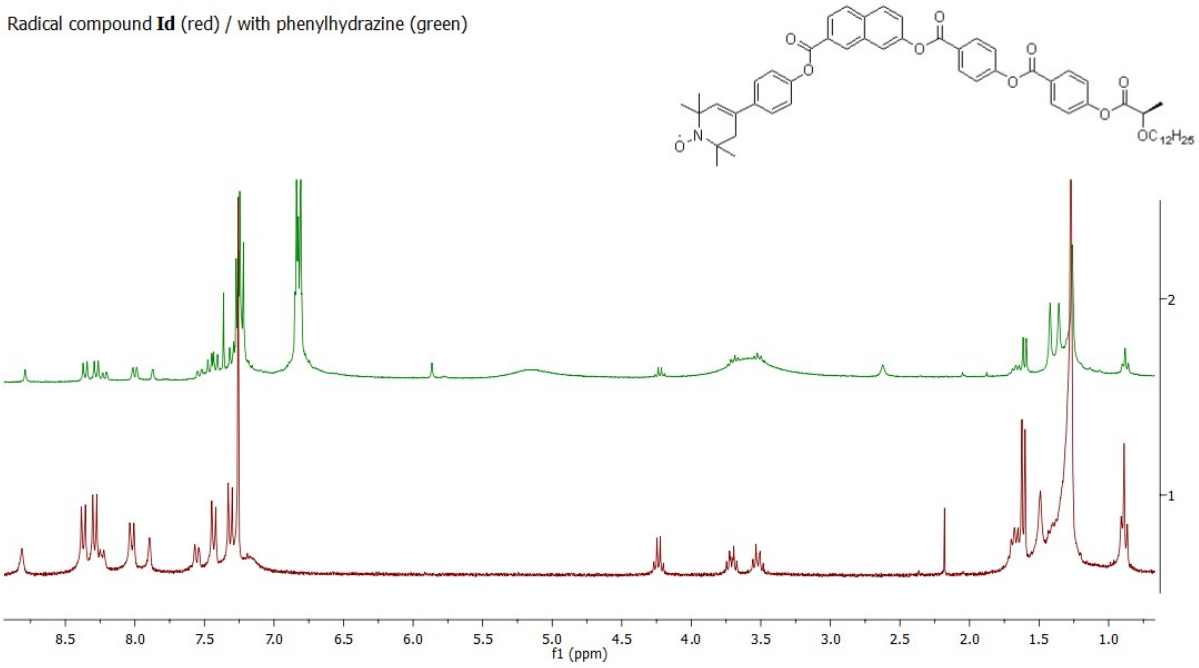
3,6-Dihydro-4-{4-[7-(4-{4-[*(4S)*-4-methylhexanoyloxy]benzoyloxy}benzoyloxy)-naphthalene-2-carbonyloxy]phenyl}-2,2,6,6-tetramethylpyridine-1(2*H*)-oxyl (Ic)

Radical compound **Ic** was prepared analogously as for **Ib** by the reaction of acid **4c** with the radical **22**. Yield 74%, crystallization from a toluene/hexane mixture. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.95 (m, 6H, 2 × CH_3), 1.12-1.70 (m, 4H, 2 × CH_2), 1.83 (m, 1H, CH), 2.62 (m, 2H, CH_2), 7.05-7.38 (m, 2H, Ar H), 7.42 (d, *J* = 8.8 Hz, 2H, Ar H), 7.55 (d, *J* = 9.4 Hz, 1H, Ar H), 7.89 (s, 1H, Ar H), 8.01 (d, *J* = 8.8 Hz, 2H,**),** 8.25 (m, 3H, Ar H), 8.34 (d, *J* = 8.8 Hz, 2H, Ar H), 8.80 (s, 1H, Ar H); (the dihydropyridine unit and 4 protons from phenyl connected to it not detected); ^{1}H NMR (300 MHz, $CDCl_3$, δ) with added phenyl hydrazine, its signals omitted (spectrum of hydroxylamine): 0.93 (m, 6H, 2 × CH_3), 1.10-1.90 (m, 17H), 2.60 (m, 2H, CH_2), 2.85 (s, 2H, CH_2), 5.87 (s, 1H, CH), 7.28 (m, 4H, Ar H), 7.42 (m, 4H, Ar H); 7.54 (dd, ^3J = 9.0 Hz, ^3J = 2.3 Hz, 1H, Ar H), 7.87 (s, 1H, Ar H), 8.00 (d, *J* = 7.9 Hz, 2H, Ar H), 8.21 (dd, ^3J = 8.8 Hz, ^3J=1.8 Hz, 1H, Ar H), 8.26 (d, *J* = 9.1 Hz, 2H, Ar H), 8.35 (d, *J* = 8.8 Hz, 2H, Ar H), 8.80 (s, 1H, Ar H); IR (KBr): **ν** = 2960, 2921, 2852, 1738, 1713 (C=O), 1602, 1505, 1270, 1197, 1161, 1059, 1015 cm^{-1};HRMS (APCIneg) m/z: [M$^-$] calcd for $C_{47}H_{46}O_9N$, 768.31781; found, 768.31747. Anal.calcd for $C_{47}H_{46}NO_9$ (768.89): C 73.42, H 6.03, N 1.82; found: C 73.31, H 5.99, N 1.79.



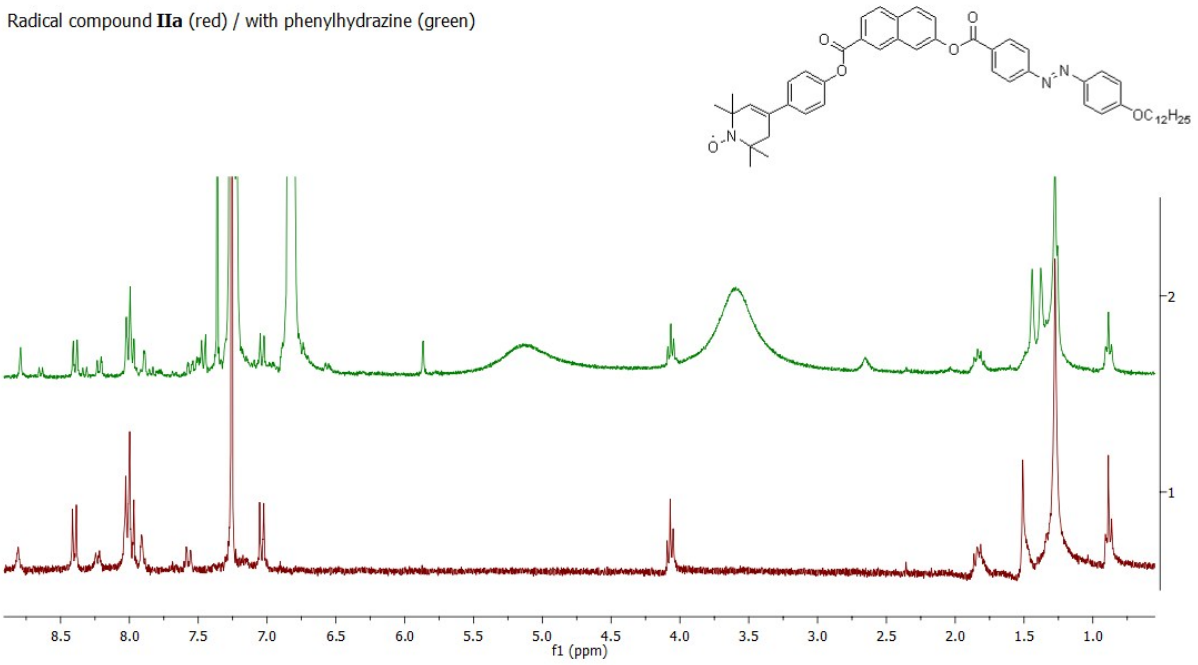
3,6-Dihydro-4-{4-[7-(4-{4-[*(2S)*-2-dodecyloxypropanoyloxy]benzoyloxy}benzoyloxy)-naphthalene-2-carbonyloxy]phenyl}2,2,6,6-tetramethylpyridine-1(2*H*)-oxyl (Id)

Radical compound **Id** was prepared analogously to **Ib** by the reaction of acid **4d** and compound **22**. Yield 57%, crystallization from a toluene/hexane mixture. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.89 (t, *J* = 6.9 Hz, 3H, CH_3), 1.20-1.79 (m, 23H), 3.54 (m, 1H), 3.71 (m, 1H), 4.23 (q, *J* = 6.7 Hz, 1H, CH), 7.31 (d, *J* = 8.8 Hz, 2H, Ar H), 7.43 (d, *J* = 8.8 Hz, 2H, Ar H), 7.55 (d, *J* = 8.5 Hz, 1H, Ar H**),** 7.90 (s, 1H), 8.02 (d, *J* = 8.5 Hz, 2H, Ar H), 8.24 (d, *J* = 8.2 Hz, 1H, Ar H), 8.29 (d, *J* = 8.8 Hz, 2H, Ar H), 8.37 (d, *J* = 8.5 Hz, 2H, Ar H), 8.81 (s, 1H, Ar H), (the dihydropyridine unit and 4 protons from phenyl connected to it not detected); ^{1}H NMR (300 MHz, $CDCl_3$, δ) with added phenyl hydrazine, its signals omitted (spectrum of hydroxylamine): 0.88 (t, *J* = 7.0 Hz, 3H, CH_3), 1.20-1.55 (m, 30H), 1.60-1.79 (m, 5H), 2.63 (m, 2H), 3.51 (m, 1H), 3.67 (m, 1H), 4.22 (q, *J* = 6.7 Hz, 1H, CH), 5.87 (s, 1H, CH), 7.30 (d, *J* = 8.8 Hz, 2H, Ar H), 7.26 (m, 2H, Ar H), 7.42 (d, *J* = 8.2 Hz, 2H, Ar H), 7.46 (d, *J* = 8.7 Hz, 2H, Ar H), 7.54 (dd, ^3J = 9.0 Hz, ^4J = 2.1 Hz, 1H, Ar H), 7.87 (s, 1H, Ar H), 8.00 (d, *J* = 8.1 Hz, 2H, Ar H), 8.22 (d, *J* = 8.1 Hz, 1H, Ar H), 8.28 (d, *J* = 8.6 Hz, 2H, Ar H), 8.36 (d, *J* = 8.6 Hz, 2H, Ar H), 8.79 (s, 1H, Ar H); IR (KBr): **ν =** 2920, 2854, 1736 (C=O), 1601; 1506, 1270, 1197, 1161, 1128, 1061, 1014 cm^{-1};. HRMS (APCIneg) m/z: [M^-] calcd for $C_{55}H_{62}O_{10}N$, 896.43792; found, 896.43884. Anal.calcd for $C_{55}H_{62}NO_{10}$ (897.11): C 73.64, H 6.97, N 1.56; found: C 73.53, H 6.93, N 1.54.



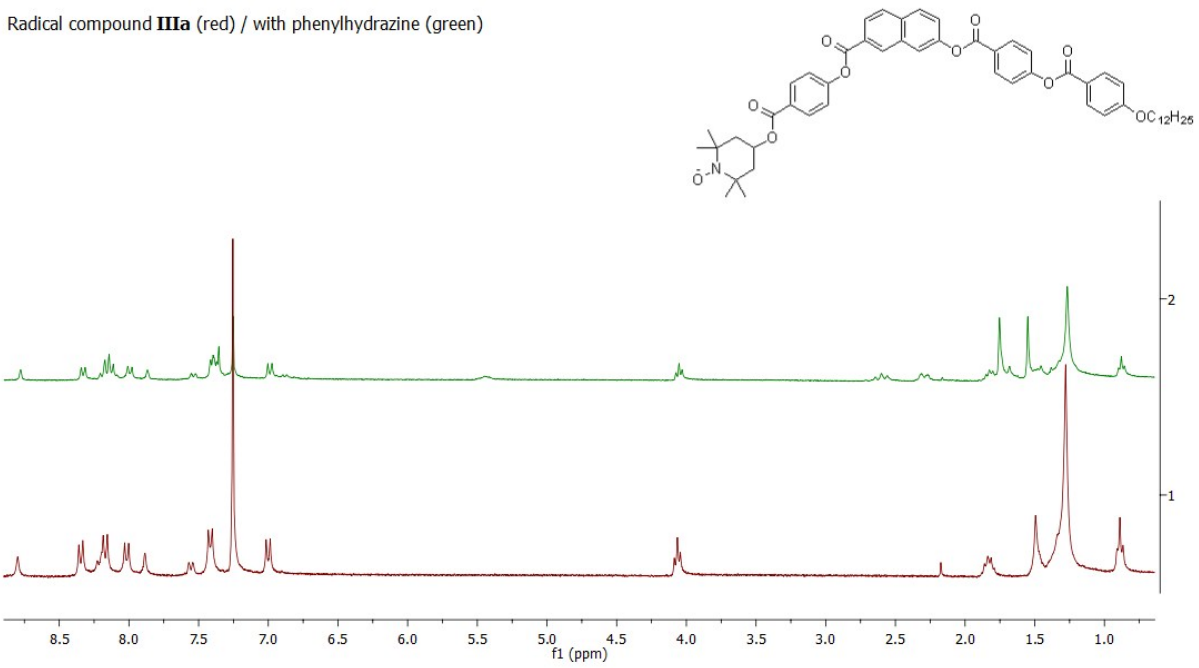
3,6-Dihydro-4-[4-(7-[4-(4-dodecyloxyphenylazo)benzoyloxy]naphthalene-2-carbonyl-oxy)phenyl]-2,2,6,6-tetramethylpyridine-1(2*H*)-oxyl (IIa)

Radical compound **IIa** was obtained analogously to **Ib** by the reaction of acid **5** and intermediate **22**. Yield 91% of yellow crystals, crystallization from a toluene/hexane mixture. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.89 (t, *J* = 6.9 Hz, 3H, CH_3), 1.00-1.55 (m, 18H), 1.82 (m, 2H, CH_2), 4.07 (t, *J* = 6.4 Hz, 2H, OCH_2), 7.04 (d, *J* = 8.8 Hz, 2H, Ar H), 7.57 (m, 1H, Ar H), 7.88-8.08 (m, 7H, Ar H), 8.24 (m, 1H, Ar H), 8.40 (d, *J* = 8.5 Hz, 2H, Ar H), 8.81 (s, 1H, Ar H) (the dihydropyridine unit and 4 protons from phenyl connected to it not detected); ^{1}H NMR (300 MHz, $CDCl_3$, δ) with added phenyl hydrazine, its signals omitted (spectrum of hydroxylamine): 0.89 (t, *J* = 6.4 Hz, 3H, CH_3), 1.00-1.56 (m, 30H), 1.75 (m, 2H, CH_2), 2.65 (m, 2H, CH_2), 4.07 (t, *J* = 6.6 Hz, 2H, OCH_2), 5.89 (s, 1H, CH), 7.04 (d, *J* = 7.9 Hz, 2H, Ar H), 7.26 (m, 2H, Ar H), 7.42-7.60 (m, 3H, Ar H), 7.89 (s, 1H, Ar H), 7.99 (m, 6H, Ar H), 8.22 (d, *J* = 8.5 Hz, 1H, Ar H), 8.39 (d, *J* = 7.6 Hz, 2H, Ar H), 8.79 (s, 1H, Ar H); IR (KBr): **ν** = 2955, 2918, 2850, 1731 (C=O), 1602, 1503, 1467, 1257, 1200, 1066 cm^{-1}. HRMS (APCIneg) m/z: [M$^-$] calcd for $C_{51}H_{58}O_6N_3$, 808.43311; found, 808.43306. Anal. calcd for $C_{51}H_{58}N_3O_6$ (809.05): C 75.71, H 7.23, N 5.19; found: C 75.73, H 7.23, N 5.13.



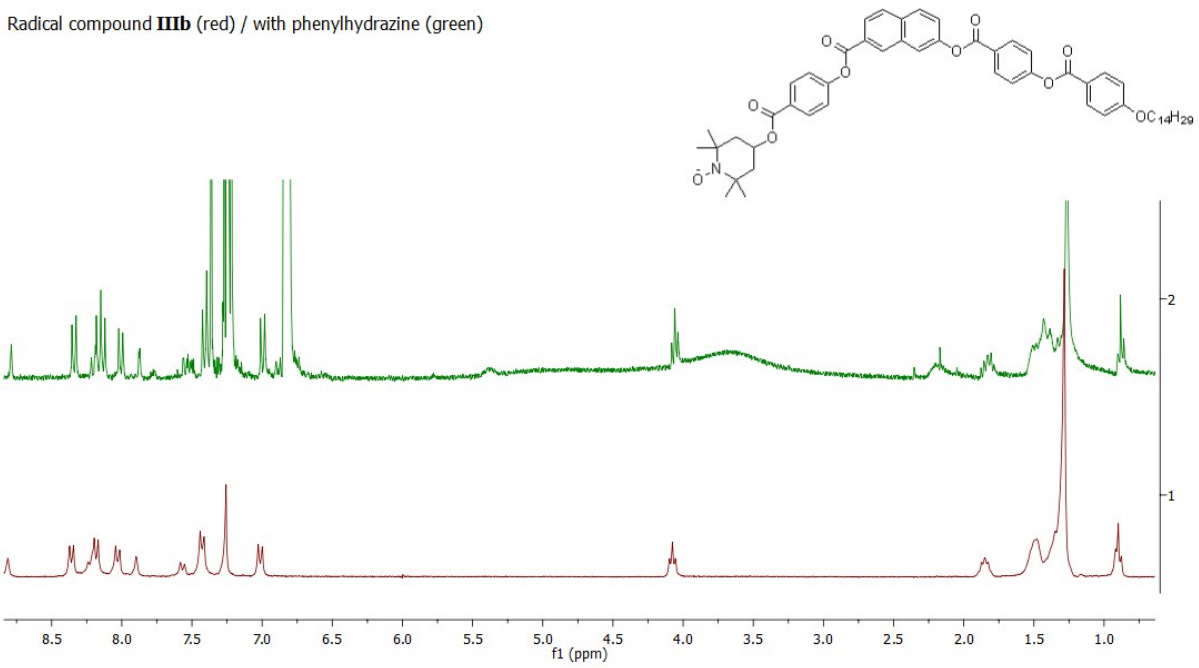
4-{7-[4-(4-Dodecyloxybenzoyloxy)benzoyloxy]naphthalene-2-carbonyloxy}benzoyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (IIIa)

Radical compound **IIIa** was prepared analogously to **Ia** by the reaction of acid **4a** (166 mg; 0.39 mmol) with intermediate **23** (150 mg; 0.32 mmol). Yield 209 mg (74%) of **IIIa**, orange crystals. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.89 (t, *J* = 6.7 Hz, 3H, CH_3), 1.18-1.59 (m, 18H, $(CH_2)_9$), 1.84 (m, 2H, CH_2), 4.06 (t, *J* = 6.4 Hz, 2H, OCH_2), 7.00 (d, *J* = 8.8 Hz, 2H, Ar H), 7.42 (d, *J* = 8.5 Hz, 2H, Ar H), 7.56 (m, 1H, Ar H), 7.89 (s, 1H, Ar H), 8.02 (d, *J* = 8.5 Hz, 2H, Ar H), 8.18 (m, 3H, Ar H), 8.34 (d, *J* = 8.8 Hz, 2H, Ar H), 8.80 (s, 1H, Ar H) (the piperidine unit and 4 protons from phenyl connected to it not detected); ^{1}H NMR (300 MHz, $CDCl_3$, δ) with added phenyl hydrazine, its signals omitted (spectrum of hydroxylamine): 0.88 (t, *J* = 6.4 Hz, 3H, CH_3), 1.20-1.96 (m, 32H), 2.29 (m, 2H, CH_2), 2.60 (m, 2H, CH_2) 4.05 (t, *J* = 6.9 Hz, 2H, OCH_2), 5.45 (m, 1H, CH), 6.99 (d, *J* = 8.6 Hz, 2H, Ar H), 7.39 (m, 4H, Ar H), 7.54 (m, 1H, Ar H), 7.87 (s, 1H, Ar H), 8.00 (d, *J* = 9.5 Hz, 2H, Ar H), 8.15 (m, 5H, Ar H), 8.33 (d, *J* = 8.0 Hz, 2H, Ar H), 8.78 (s, 1H, Ar H); IR (KBr): **ν** = 2960, 2922, 2852, 1738, 1713 (C=O), 1602, 1505, 1270, 1197, 1161, 1054, 1015 cm^{-1}; HRMS (APCIneg) m/z: [M$^-$] calcd for $C_{53}H_{60}O_{10}N$: 870.42227, found 870.42161. Anal. calcd for $C_{53}H_{60}NO_{10}$ (871.07): C 73.08, H 6.94, N 1.61; found: C 73.00, H 6.91, N 1.65.



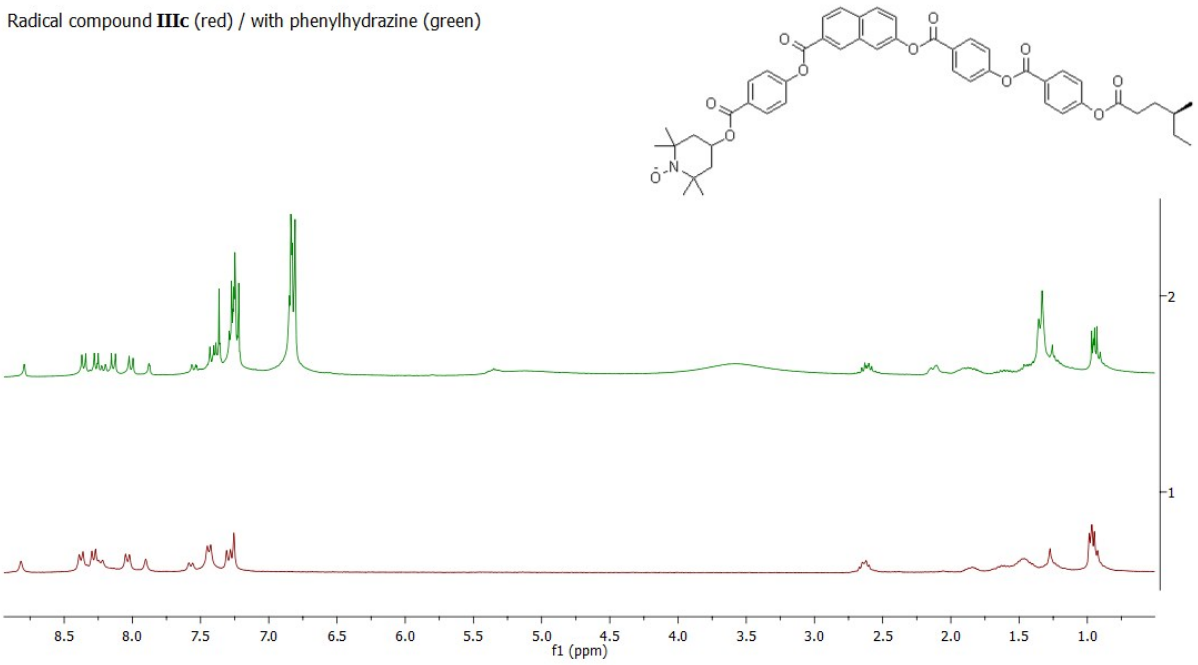
4-{7-[4-(4-Tetradecyloxybenzoyloxy)benzoyloxy]naphthalene-2-carbonyloxy}-benzoyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (IIIb)

Radical compound **IIIb** was prepared analogously to **Ia** from acid 4b (118 mg; 0.26 mmol) and compound **23** (100 mg; 0.22 mmol), yield 275 mg (83%) of **IIIb**, orange crystals. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.88 (t, J = 6.7 Hz, 3H, CH_3), 1.00-1.58 (m, 22H, $(CH_2)_{11}$), 1.84 (m, 2H, CH_2), 4.06 (t, J = 6.7 Hz, 2H, OCH_2), 7.00 (d, J = 8.8 Hz, 2H, Ar H), 7.41 (d, J = 8.8 Hz, 2H, Ar H), 7.55 (m, 1H, Ar H), 7.88 (s, 1H, Ar H), 8.02 (d, J = 8.5 Hz, 2H, Ar H), 8.18 (m, 3H, Ar H), 8.34 (d, J = 8.8 Hz, 2H, Ar H), 8.80 (s, 1H, Ar H) (the piperidine unit and 4 protons from phenyl connected to it not detected); ^{1}H NMR (300 MHz, $CDCl_3$, δ) with added phenyl hydrazine, its signals omitted (spectrum of hydroxylamine): 0.88 (t, J = 6.7 Hz, 3H, CH_3), 1.18-1.67 (m, 36H), 1.83 (m, 2H, CH_2), 2.21 (m, 2H, CH_2), 4.06 (t, J = 6.3 Hz, 2H, OCH_2), 5.38 (m, 1H), 7.00 (d, J = 9.5 Hz, 2H, Ar H), 7.40 (m, 4H, Ar H), 7.55 (m, 1H, Ar H), 7.87 (s, 1H, Ar H), 8.01 (d, J = 8.5 Hz, 2H, Ar H), 8.16 (m, 5H, Ar H), 8.34 (d, J = 8.5 Hz, 2H, Ar H), 8.79 (s, 1H, Ar H); IR (KBr): ν = 2920, 2851, 1736 (C=O), 1604, 1511, 1465, 1264, 1197, 1162, 1060 cm^{-1}. HRMS (APCIneg) m/z: [M$^-$] calcd for $C_{55}H_{64}O_{10}N$, 898.45357; found, 898.45286. Anal. calcd for $C_{55}H_{64}NO_{10}$ (899.12): C 73.47, H 7.17, N 1.56; found: C 73.49, H 7.17, N 1.48.



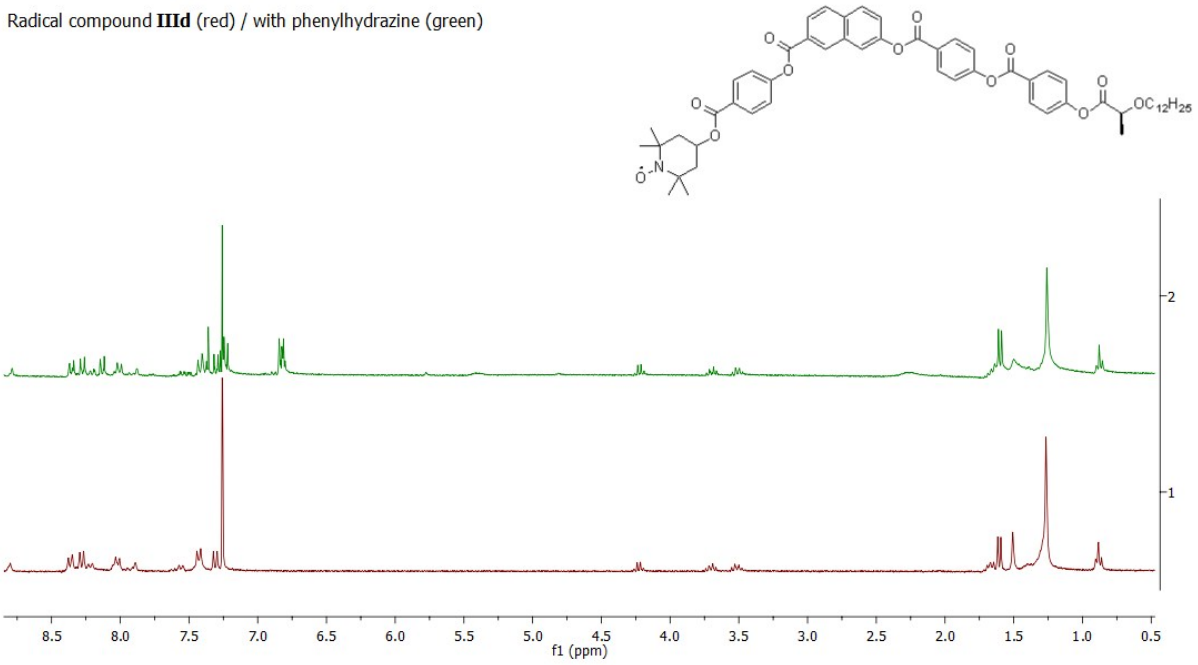
4-{4-[7-(4-{4-[*(4S)*-4-Methylhexanoyloxy]benzoyloxy}benzoyloxy)naphthalene-2-carbonyloxy]benzoyloxy}-2,2,6,6-tetramethylpiperidine-1-oxyl (IIIc)

Radical compound **IIIc** was prepared analogously to **Ia** from radical 23 (90 mg; 0.20 mmol) and acid **4c** (86 mg; 0.23 mmol). Yield 92 mg (58%), orange crystals. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.95 (m, 6H, 2 × CH_3), 1.10-1.94 (m, 5H), 2.62 (m, 2H, CH_2CO), 7.26 (m, 2H, Ar H), 7.42 (d, J = 8.2 Hz, 2H, Ar H), 7.56 (m, 1H, Ar H), 7.89 (s, 1H, Ar H), 8.02 (d, J = 9.1 Hz, 2H, Ar H), 8.22 (m, 1H, Ar H), 8.26 (d, J = 8.8 Hz, 2H, Ar H), 8.36 (d, J = 8.8 Hz, 2H, Ar H), 8.80 (s, 1H, Ar H) (the piperidine unit and 4 protons from phenyl connected to it not detected); ^{1}H NMR (300 MHz, $CDCl_3$, δ) with added phenyl hydrazine, its signals omitted (spectrum of hydroxylamine): 0.93 (m, 6H, 2 × CH_3), 1.00-2.20 (m, 19H), 2.21 (m, 2H), 2.60 (m, 2H, CH_2), 5.35 (m, 1H), 7.25 (m, 2H, Ar H), 7.37 (m, 2H, Ar H), 7.42 (d, J = 8.5 Hz, 2H, Ar H), 7.55 (m, 1H, Ar H), 7.87 (s, 1H, Ar H), 8.00 (d, J = 8.8 Hz, 2H, Ar H), 8.14 (d, J = 8.8, 2H, Ar H), 8.21 (m, 1H, Ar H), 8.26 (d, J = 8.8 Hz, 2H, Ar H), 8.35 (d, J = 8.8 Hz, 2H, Ar H), 8.79 (s, 1H, Ar H); IR (KBr): **ν** = 2960, 2921, 2852, 1738, 1713 (C=O), 1602, 1505, 1270, 1197, 1161, 1059, 1015 cm^{-1};. HRMS (APCIneg) m/z: [M$^-$] calcd for $C_{48}H_{48}O_{11}N$, 814.32328; found, 814.32330. Anal. calcd for $C_{48}H_{48}NO_{11}$ (814.92): C 70.75, H 5.94, N 1.72; found: C 70.68, H 5.91, N 1.71.



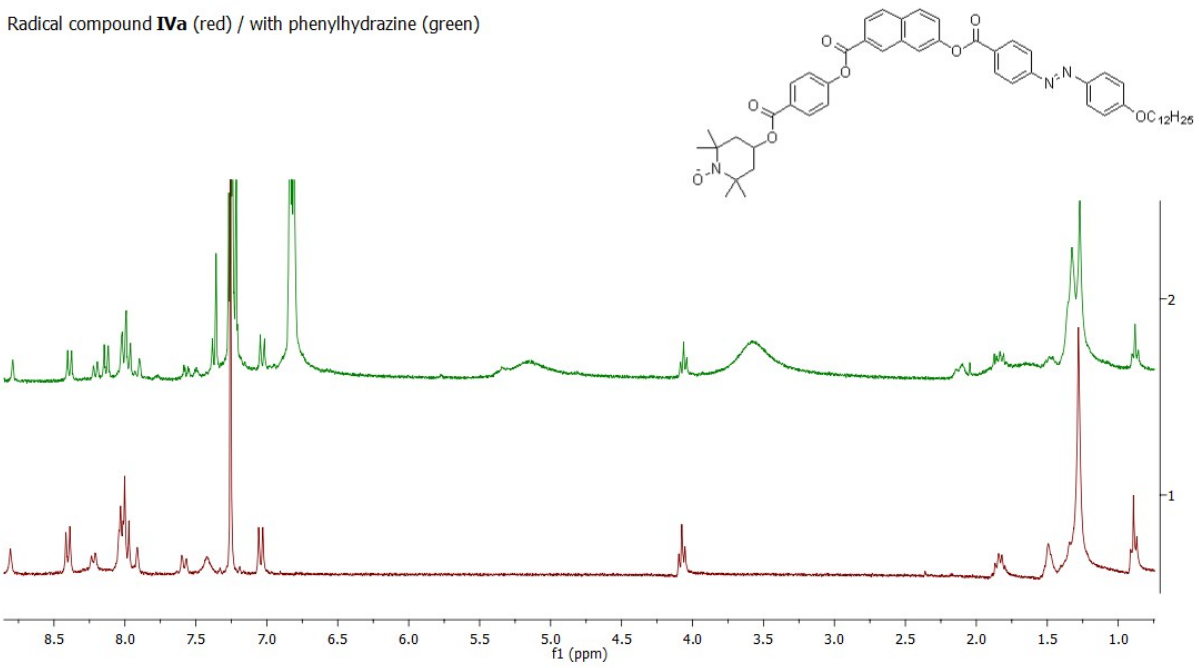
4-{4-[7-(4-{4-[*(2S)*-2-Dodecyloxypropanoyloxy]benzoyloxy}benzoyloxy)naphthalene-2-carbonyloxy]benzoyloxy}2,2,6,6-tetramethylpiperidine-1-oxyl (IIId)

Radical compound **IIId** was prepared analogously to **Ia** from radical 23 (80 mg; 0.17 mmol) and acid **4d** (86 mg; 0.17 mmol). Yield 78 mg (48%), orange crystals. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.88 (t, *J* = 6.7 Hz, 3H, CH_3), 1.10-1.45 (m, 18H, $(CH_2)_9$), 1.61 (d, *J* = 6.7 Hz, 3H, CH_3), 1.67 (m, 2H), 3.51 (m, 1H), 3.70 (m, 1H), 4.23 (m, 1H), 7.31 (d, *J* = 8.2 Hz, 2H, Ar H), 7.43 (d, *J* = 8.2 Hz, 2H, Ar H), 7.56 (d, *J* = 8.8 Hz, 1H, Ar H), 7.89 (s, 1H, Ar H), 8.02 (d, *J* = 9.1 Hz, 2H, Ar H), 8.22 (d, *J* = 8.8 Hz, 1H, Ar H), 8.28 (d, *J* = 8.8 Hz, 2H, Ar H), 8.36 (d, *J* = 8.5 Hz, 2H, Ar H), 8.80 (s, 1H, Ar H) (the piperidine unit and 4 protons from phenyl connected to it not detected); ^{1}H NMR (300 MHz, $CDCl_3$, δ) with added phenyl hydrazine, its signals omitted (spectrum of hydroxylamine): 0.88 (t, *J* = 7.0 Hz, 3H, CH_3), 0.91-1.73 (m, 37H), 2.21 (m, 2H), 3.51 (m, 1H, CH_2O), 3.68 (m, 1H, CH_2O), 4.22 (m, 1H), 5.40 (m, 1H, CH), 7.30 (d, *J* = 8.8 Hz, 2H, Ar H), 7.40 (m, 4H, Ar H), 7.55 (m, 1H, Ar H), 7.88 (m, 1H, Ar H), 8.01 (d, *J* = 8.8 Hz, 2H, Ar H), 8.13 (d, *J* = 8.8 Hz, 2H, Ar H), 8.21 (m, 1H, Ar H), 8.28 (d, *J* = 8.8 Hz, 2H, Ar H), 8.35 (d, *J* = 8.8 Hz, 2H, Ar H), 8.79 (s, 1H, Ar H); IR (KBr): **ν** = 2926, 2854, 1738 (C=O), 1602, 1270, 1198, 1161, 1118, 1061, 1015; HRMS (APCIneg) m/z: [M^-] calcd for $C_{56}H_{64}O_{12}N$, 942.44340; found, 942.44302. Anal. calcd for $C_{56}H_{64}NO_{12}$ (943.13): C 71.32, H 6.84, N 1.49; found: C 71.19, H 6.79, N 1.51.



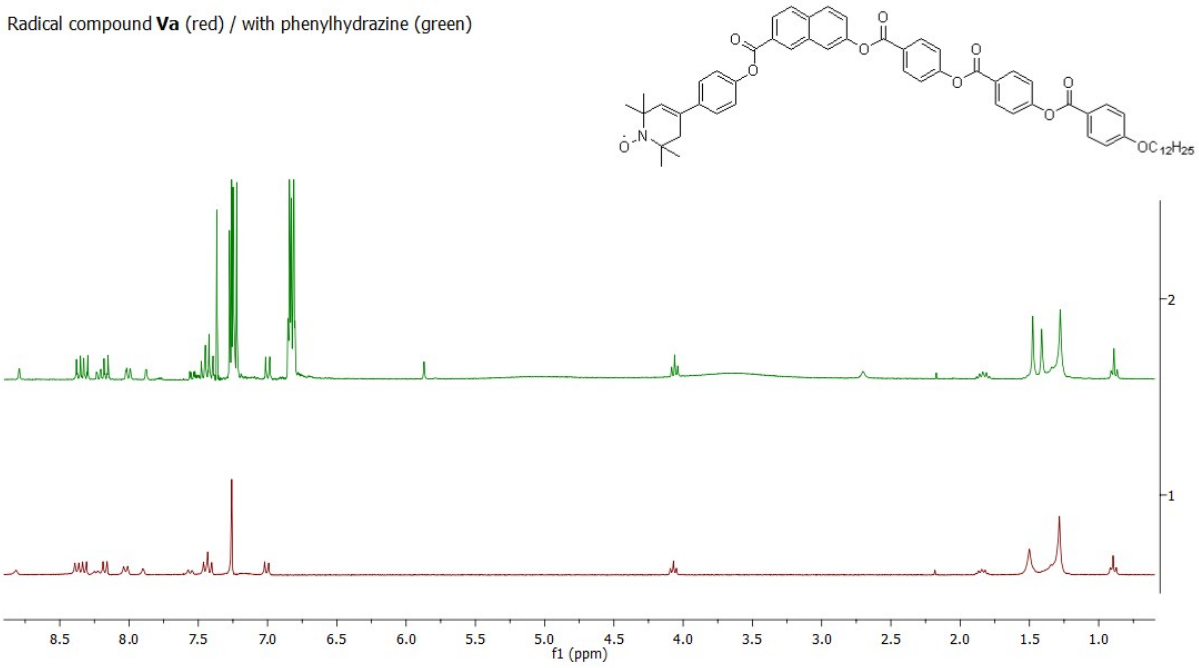
4-[4-(7-[4-(4-Dodecyloxyphenylazo)benzoyloxy]naphthalene-2-carbonyloxy)benzoyloxy]-2,2,6,6-tetramethylpiperidine-1-oxyl (IVa)

Radical compound **IVa** was prepared analogously to **Ia** by the reaction of **23** (150 mg; 0.32 mmol), with acid **5** (160 mg; 0.39 mmol), yield 203 mg (73%), dark orange crystals. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.89 (t, *J* = 6.9 Hz, 3H, CH_3), 0.99-1.59 (m, 18H, $(CH_2)_9$), 1.84 (m, 2H, CH_2), 4.08 (t, *J* = 6.4 Hz, 2H, OCH_2), 7.04 (d, *J* = 9.1 Hz, 2H, Ar H), 7.42 (m, 2H, Ar H), 7.58 (m, 1H, Ar H), 7.91 (s, 1H, Ar H), 8.00 (m, 4H, Ar H), 8.22 (m, 1H, Ar H), 8.40 (d, *J* = 8.2 Hz, 2H, Ar H), 8.81 (s, 1H, Ar H) (the piperidine unit and 4 protons from phenyl connected to it not detected); ^{1}H NMR (300 MHz, $CDCl_3$, δ) with added phenyl hydrazine, its signals omitted (spectrum of hydroxylamine): 0.88 (t, *J* = 7.0 Hz, 3H, CH_3), 0.98-1.59 (m, 32H), 1.83 (m, 2H, CH_2), 2.10 (m, 2H, CH_2), 4.06 (t, *J* = 6.7 Hz, 2H, OCH_2), 5.34 (m, 1H, CH), 7.03 (d, *J* = 9.1 Hz, 2H, Ar H), 7.36 (m, 4H, Ar H), 7.57 (m, 1H), 7.90 (s, 1H, Ar H), 7.99 (m, 4H, Ar H), 8.13 (d, *J* = 8.8 Hz, 2H, Ar H), 8.21 (m, 1H), 8.39 (d, *J* = 8.5 Hz, 2H, Ar H), 8.79 (s, 1H, Ar H); IR (KBr): **ν** = 2920, 2851, 1732 (C=O), 1602, 1503, 1272, 1197, 1064 cm^{-1}. HRMS (APCIneg) m/z: [M^-] calcd for $C_{52}H_{60}O_8N_3$, 854.43859; found, 854.43845. Anal. calcd for $C_{52}H_{60}N_3O_8$ (855.07): C 73.04, H 7.07, N 4.91; found: C 73.00, H 7.03, N 4.86.



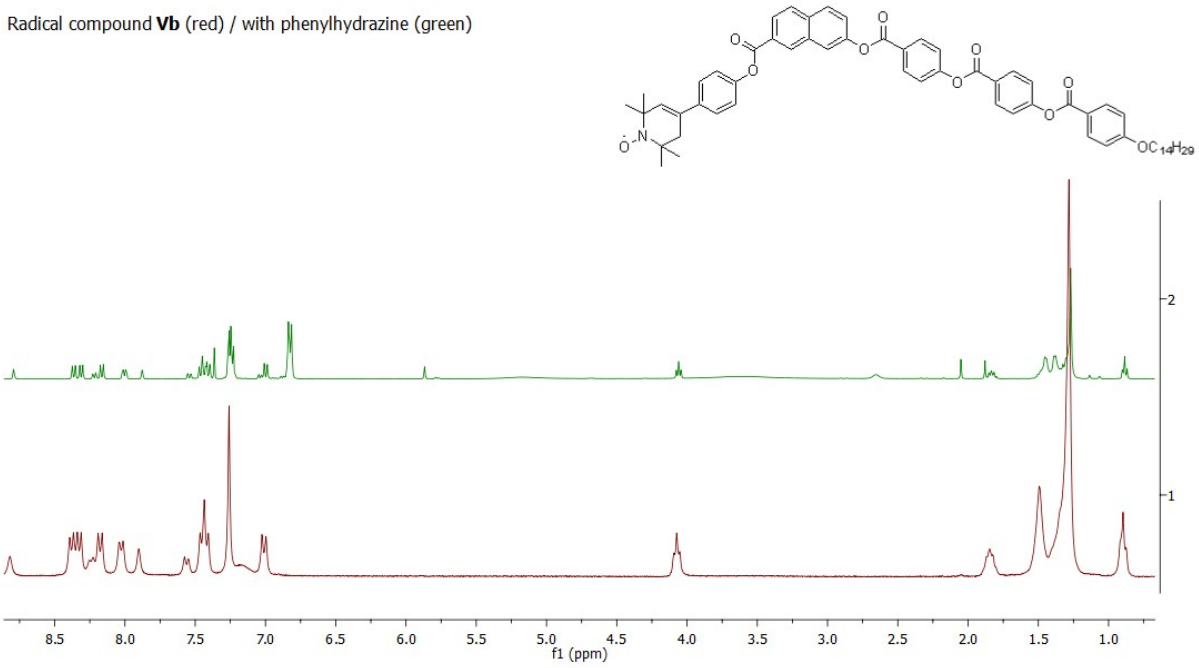
3,6-Dihydro-4-[4-(7-{4-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]benzoyloxy}-naphthalene-2-carbonyloxy)phenyl]-2,2,6,6-tetramethylpyridine-1(2*H*)-oxyl (Va)

Reaction of acid **6a** with radical **22** by the method as for **Ib** yielded the title compounds **Va**. Yield 68%, crystallization from an ethyl acetate/hexane mixture. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.89 (t, *J* = 6.8 Hz, 3H, CH_3), 1.19-1.60 (m, 18H, $(CH_2)_9$), 1.81 (m, 2H), 4.06 (t, *J* = 6.7 Hz, 2H, OCH_2), 7.00 (d, *J* = 8.8 Hz, 2H, Ar H), 7.42 (m, 4H, Ar H), 7.55 (d, *J* = 7.0 Hz, 1H, Ar H), 7.89 (s, 1H, Ar H), 8.02 (d, *J* = 9.1 Hz, 2H, Ar H), 8.17 (d, *J* = 8.8 Hz, 2H, Ar H), 8.23 (d, *J* = 8.5 Hz, 1H, Ar H), 8.32 (d, *J* = 8.8 Hz, 2H, Ar H), 8.37 (d, *J* = 8.8 Hz, 2H, Ar H), 8.81 (s, 1H, Ar H) (the dihydropyridine unit and 4 protons from phenyl connected to it not detected); ^{1}H NMR (300 MHz, $CDCl_3$, δ) with added phenyl hydrazine, its signals omitted (spectrum of hydroxylamine): 0.89 (t, *J* = 7.0 Hz, 3H, CH_3), 1.13-1.81 (m, 32H), 2.59 (m, 2H, CH_2), 4.06 (t, *J* = 6.7 Hz, 2H, OCH_2), 5.87 (s, 1H, CH), 7.00 (d, *J* = 8.8 Hz, 2H, Ar H), 7.26 (m, 2H, Ar H), 7.41 (d, *J* = 8.8, Hz, 2H, Ar H), 7.44 (d, *J* = 9.0 Hz, 2H, Ar H), 7.47 (d, *J* = 8.8 Hz, 2H, Ar H), 7.53 (dd, ^3J = 9.0 Hz, ^4J = 2.2 Hz, 1H, Ar H), 7.87 (s, 1H, Ar H), 8.00 (d, *J* = 8.8 Hz, 2H, Ar H), 8.17 (d, *J* = 9.1 Hz, 2H, Ar H), 8.23 (dd, ^3J = 8.5 Hz, ^4J = 1.8 Hz, 1 H, Ar H), 8.31 (d, *J* = 8.8 Hz, 2H, Ar H), 8.37 (d, *J* = 9.1 Hz, 2H, Ar H), 8.80 (s, 1H, Ar H); IR (KBr): **ν** = 2919, 2854, 1735 (C=O), 1602, 1261, 1191, 1155, 1134, 1076, 1055 cm^{-1}. HRMS (APCIneg) m/z: [M$^-$] calcd for $C_{59}H_{62}O_{10}N$, 944.43792; found, 944.43779. Anal. calcd for $C_{59}H_{62}NO_{10}$ (945.15): C 74.98, H 6.61, N 1.48; found: C 75.03, H 6.63, N 1.45.



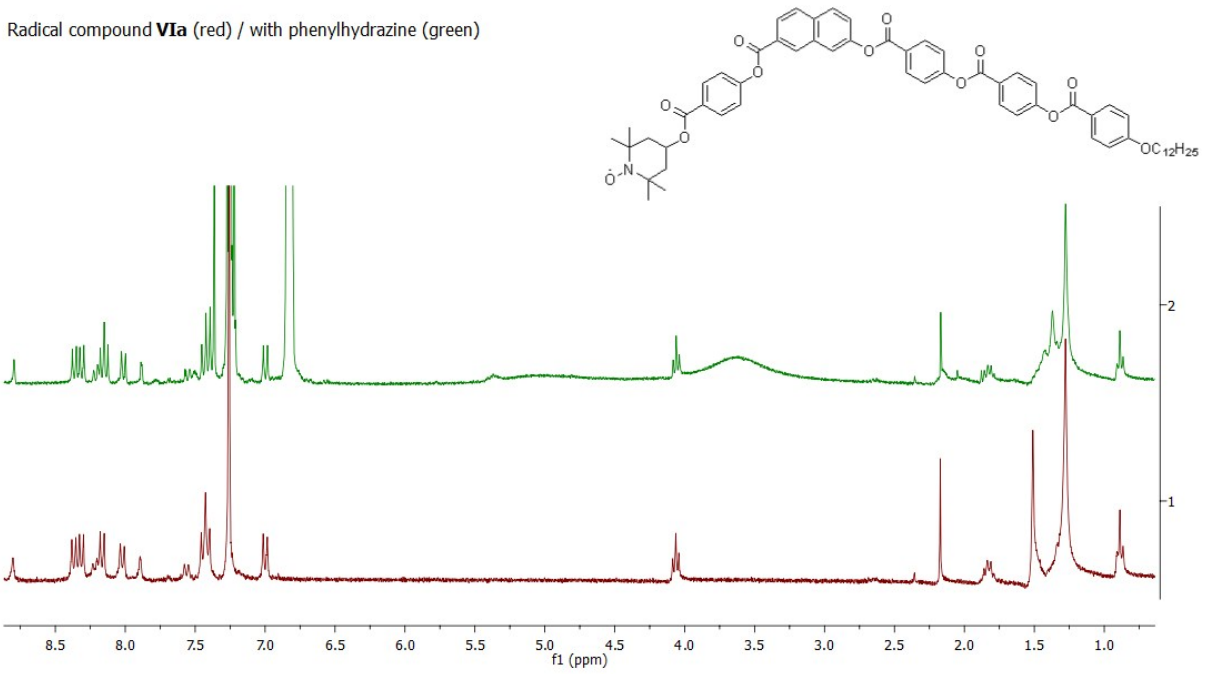
3,6-Dihydro-4-[4-(7-{4-[4-(4-tetradecyloxybenzoyloxy)benzoyloxy]benzoyloxy}-naphthalene-2-carbonyloxy)phenyl]-2,2,6,6-tetramethylpyridine-1(2*H*)-oxyl (Vb)

Radical compound **Vb** was obtained as for **Ib** by coupling of acid **6b** with radical **22**. Yield 66%. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.89 (t, *J* = 7.0 Hz, 3H, CH_3), 1.20-1.58 (m, 22H, $(CH_2)_{11}$), 1.84 (m, 2H, CH_2), 4.06 (t, *J* = 6.2 Hz, 2H, OCH_2), 7.00 (d, *J* = 8.8 Hz, 2H, Ar H), 7.43 (m, 4H, Ar H), 7.55 (d, *J* = 9.0 Hz, 1H, Ar H), 7.89 (s, 1H, Ar H), 8.02 (d, *J* = 8.2 Hz, 2H, Ar H), 8.17 (d, *J* = 8.8 Hz, 2H, Ar H), 8.23 (d, *J* = 8.5, 1H, Ar H), 8.31 (d, *J* = 8.5 Hz, 2H, Ar H), 8.37 (d, *J* = 8.8 Hz, 2H, Ar H), 8.81 (s, 1H, Ar H) (the dihydropyridine unit and 4 protons from phenyl connected to it not detected); ^{1}H NMR (300 MHz, $CDCl_3$, δ) with added phenyl hydrazine, its signals omitted (spectrum of hydroxylamine): 0.88 (t, *J* = 6.4 Hz, 3H, CH_3), 1.20-1.80 (m, 36H), 2.60 (m, 2H, CH_2), 4.06 (t, *J* = 6.5 Hz, 2H, OCH_2), 5.86 (s, 1H, CH), 7.00 (d, *J* = 8.8 Hz, 2H, Ar H), 7.25 (m, 2H, Ar H), 7.34-7.58 (m, 7H, Ar H), 7.87 (s, 1H, Ar H), 8.00 (d, *J* = 9.0 Hz, 2H, Ar H), 8.19 (m, 3H, Ar H), 8.31 (d, *J* = 8.5 Hz, 2H, Ar H), 8.36 (d, *J* = 9.1 Hz, 2H, Ar H), 8.79 (s, 1H, Ar H); IR (KBr): **ν** = 2918, 2850), 1736 (C=O), 1603, 1265, 1197, 1163, 1061 cm^{-1}. HRMS (APCIneg) m/z: [M$^-$] calcd for $C_{61}H_{66}O_{10}N$: 972.46922, found 972.46921. Anal.calcd for $C_{61}H_{66}NO_{10}$ (973.21): C 75.29, H 6.84, N 1.44; found: C 75.17, H 6.78, N 1.42.



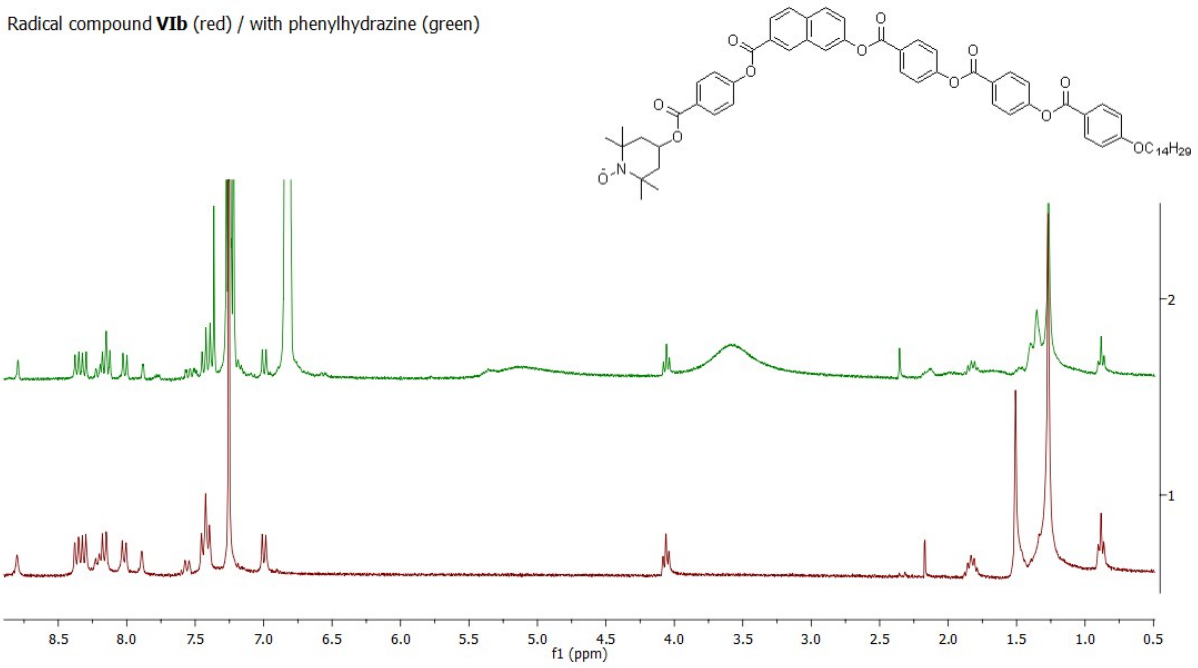
4-[4-(7-{4-[4-(4-Dodecyloxybenzoyloxy)benzoyloxy]benzoyloxy}naphthalene-2-carbonyl-oxy)benzoyloxy]-2,2,6,6-tetramethylpiperidine-1-oxyl (VIa)

Radical compound **VIa** was prepared analogously to **Ia** by the DCC-mediated coupling of **23** with acid **6a** (100 mg; 0.22 mmol). Purification by column chromatography (toluene/ethyl acetate 95/5) and crystallization from a toluene/hexane mixture afforded 142 mg (66%) of **VIa**, orange crystals. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.88 (t, *J* = 6.9 Hz, 3H, CH_3), 1.18-1.58 (m, 18H, $(CH_2)_9$), 1.84 (m, 2H, CH_2), 4.06 (t, *J* = 6.4 Hz, 2H, OCH_2), 7.00 (d, *J* = 9.1 Hz, 2H, Ar H), 7.42 (m, 4H, Ar H), 7.56 (m, 1H, Ar H), 7.89 (s, 1H, Ar H), 8.02 (d, *J* = 8.8 Hz, 2H, Ar H), 8.20 (m, 3H, Ar H), 8.31 (d, *J* = 9.0 Hz, 2 H, Ar H), 8.37 (d, *J* = 8.5 Hz, 2H, Ar H), 8.80 (s, 1H, Ar H) (the piperidine unit and 4 protons from phenyl connected to it not detected); ^{1}H NMR (300 MHz, $CDCl_3$, δ) with added phenyl hydrazine, its signals omitted (spectrum of hydroxylamine): 0.89 (t, *J* = 6.7 Hz, 3H, CH_3), 1.00-1.57 (m, 32H), 1.83 (m, 2H, CH_2), 2.15 (m, 2H), 4.06 (t, *J* = 6.7 Hz, 2H, OCH_2), 5.38 (m, 1H, CH), 7.00 (d, *J* = 8.8 Hz, 2H, Ar H), 7.41 (m, 6H, Ar H), 7.56 (m, 1H, Ar H), 7.89 (s, 1H, Ar H), 8.01 (d, *J* = 8.8 Hz, 2H, Ar H), 8.15 (m, 4H, Ar H), 8.21 (m, 1H, Ar H), 8.31 (d, *J* = 8.5 Hz, 2H, Ar H), 8.36 (d, *J* = 8.5 Hz, 2H, Ar H), 8.79 (s, 1H, Ar H); IR (KBr): **ν** = 2920, 2852, 1736 (C=O), 1604, 1510, 1268, 1198, 1162, 1061 cm^{-1}. HRMS (APCIneg) m/z: [M$^-$] calcd for $C_{60}H_{64}O_{12}N$, 990.44340; found, 990.44429. Anal. calcd for $C_{60}H_{64}NO_{12}$ (991.18): C 72.71, H 6.51, N 1.41; found: C 72.86, H 6.55, N 1.38.



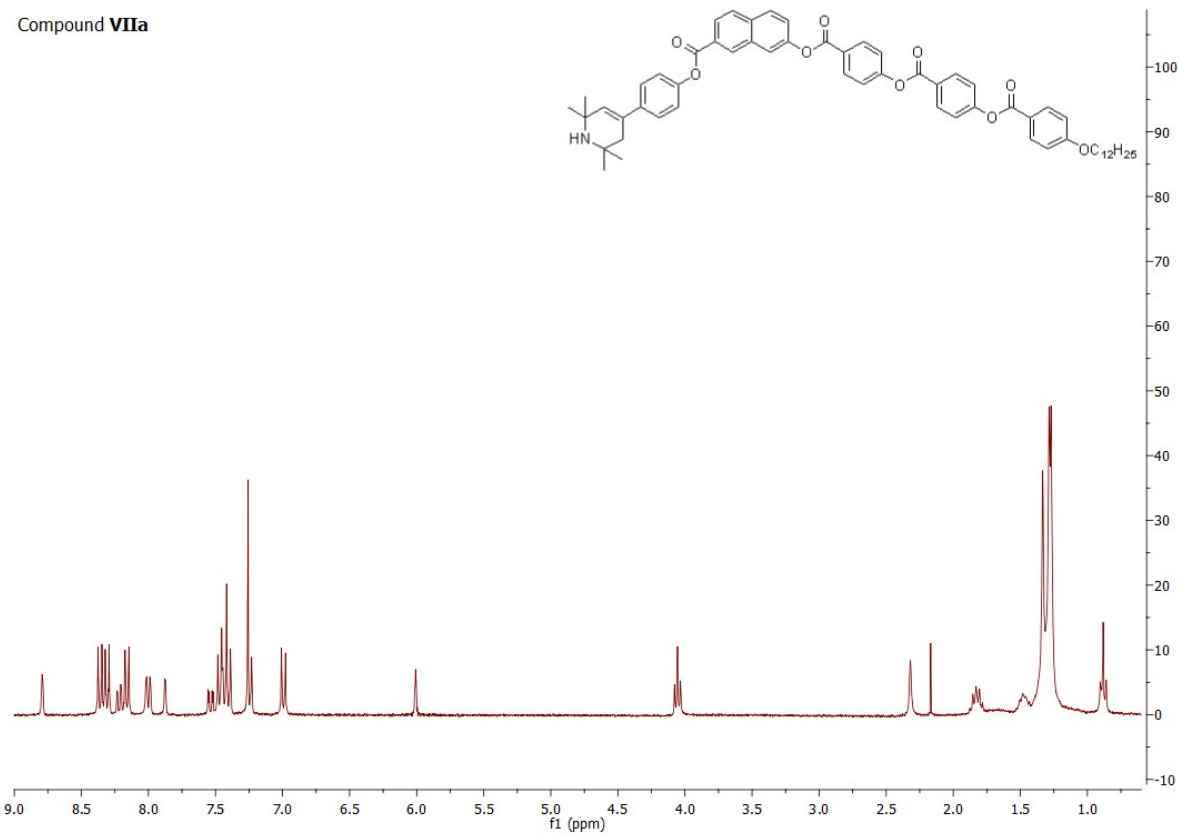
4-[4-(7-{4-[4-(4-Tetradecyloxybenzoyloxy)benzoyloxy]benzoyloxy}naphthalene-2-carbonyloxy)benzoyloxy]-2,2,6,6-tetramethylpiperidine-1-oxyl (VIb)

Radical compound **VIb** was prepared in the same way as for **Ia** from compound **23** (150 mg; 0.32 mmol) and acid **6b** (223 mg; 0.39 mmol). Yield 275 mg (83%) of **VIb**, orange crystals. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.88 (t, *J* = 7.0 Hz, 3H, CH_3), 1.0-1.59 (m, 22H, $(CH_2)_{11}$), 1.83 (m, 2H, CH_2), 4.06 (t, *J* = 6.4 Hz, 2H, OCH_2), 7.00 (d, *J* = 7.9 Hz, 2H, Ar H), 7.42 (m, 4H, Ar H), 7.56 (m, 1H, Ar H), 7.89 (s, 1H, Ar H), 8.02 (d, *J* = 8.8 Hz, 2H, Ar H), 8.19 (m, 3H, Ar H), 8.34 (m, 4H, Ar H), 8.80 (s, 1H, Ar H) (the piperidine unit and 4 protons from phenyl connected to it not detected); ^{1}H NMR (300 MHz, $CDCl_3$, δ) with added phenyl hydrazine, its signals omitted (spectrum of hydroxylamine): 0.88 (t, *J* = 6.4 Hz, 3H, CH_3), 1.00-1.58 (m, 36H), 1.82 (m, 2H, CH_2), 2.12 (m, 2H, CH_2), 4.05 (t, *J* = 6.7 Hz, 2H, OCH_2), 5.36 (m, 1H, CH), 7.00 (d, *J* = 8.5 Hz, 2H, Ar H), 7.41 (m, 6H, Ar H), 7.55 (m, 1H, Ar H), 7.88 (s, 1H, Ar H), 8.01 (d, *J* = 8.8 Hz, 2H, Ar H), 8.17 (m, 5H, Ar H), 8.31 (d, *J* = 8.5 Hz, 2H, Ar H), 8.36 (d, *J* = 8.8 Hz, 2H, Ar H), 8.80 (s, 1H, Ar H); IR (KBr): **ν** = 2919, 2852, 1737 (C=O), 1603, 1511, 1268, 1198, 1163, 1061 cm^{-1}. HRMS (APCIneg) m/z: [M$^-$] calcd for $C_{62}H_{68}O_{12}N_1$, 1018.47470; found, 1018.47408. Anal. calcd for $C_{62}H_{68}NO_{12}$ (1019.23): C 73.06, H 6.72, N 1.37; found: C 72.91, H 6.65, N 1.36.



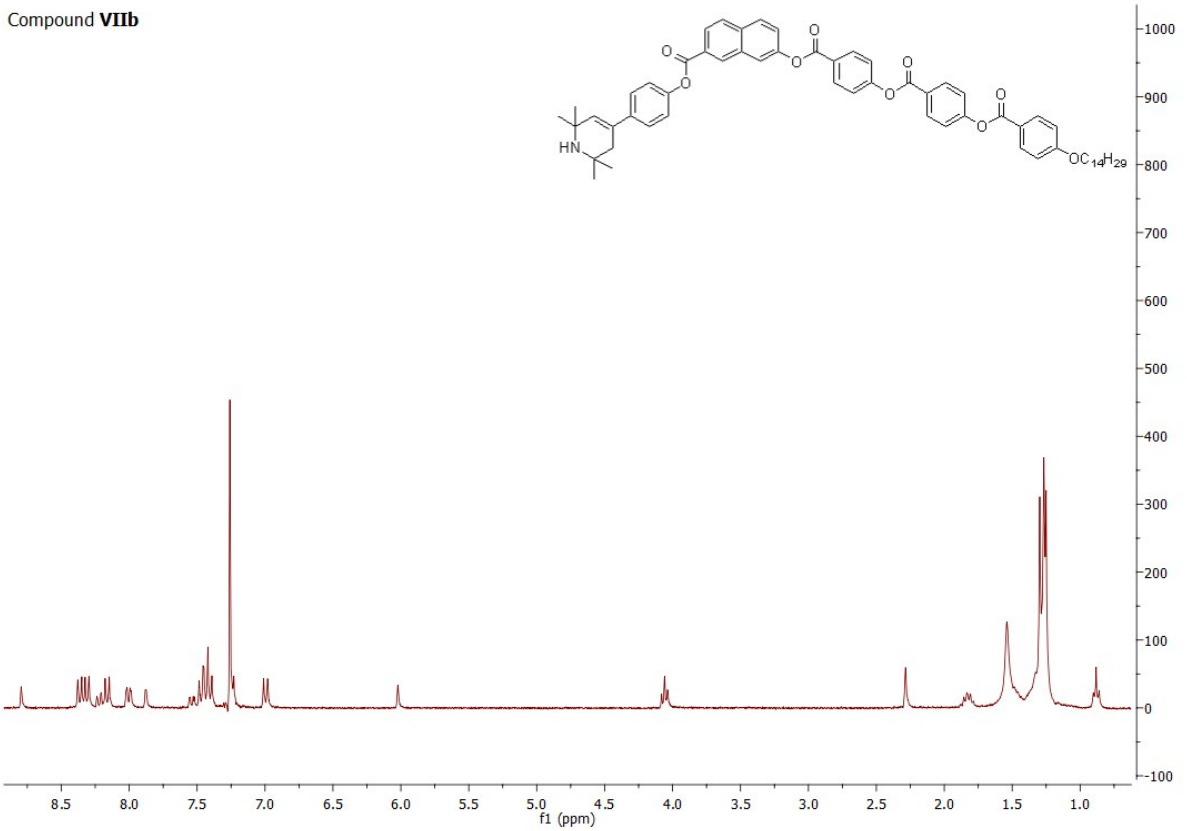
4-(1,2,3,6-Tetrahydro-2,2,6,6-tetramethylpyridin-4-yl)phenyl 7-{4-[4-(4-dodecyloxy-benzoyloxy)benzoyloxy]benzoyloxy}naphthalene-2-carboxylate (VIIa)

Hydroxy derivative **24** (250 mg, 0.62 mmol), acid **6a** (374 mg; 0.69 mmol), DCC (193 mg; 0.94 mmol) and DMAP (8 mg) were dissolved in dichloromethane (50 mL) and the mixture was stirred at room temperature in an inert argon atmosphere for 12 h. The deposited dicyclohexylurea was filtered off and the filtrate evaporated. Column chromatography (chloroform/methanol/triethylamine 90/10/0.1) and multiple crystallization from toluene and ethyl acetate yielded 448 mg (77%) of **VIIa**. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.88 (t, *J* = 6.7 Hz, 3H, CH_3), 1.00-1.90 (m, 32H), 2.32 (s, 2H, CH_2), 4.06 (t, *J* = 6.7 Hz, 2H, OCH_2), 6.01 (s, 1H, CH), 6.99 (d, *J* = 8.8 Hz, 2H, Ar H), 7.24 (m, 2H, Ar H), 7.44 (m, 6H, Ar H), 7.54 (m, 1H, Ar H), 7.88 (s, 1H, Ar H), 8.00 (m, 2H, Ar H), 8.16 (d, *J* = 9.1 Hz, 2H, Ar H), 8.22 (m, 1H, Ar H); 8.31 (d, *J* = 8.8 Hz, 2H, Ar H), 8.36 (d, *J* = 8.8 Hz, 2H, Ar H), 8.79 (s, 1H, Ar H); Anal. calcd for $C_{59}H_{63}NO_9$ (930.16): C 76.19, H 6.83 N 1.51; found: C 76.11, H 6.80, N 1.41.

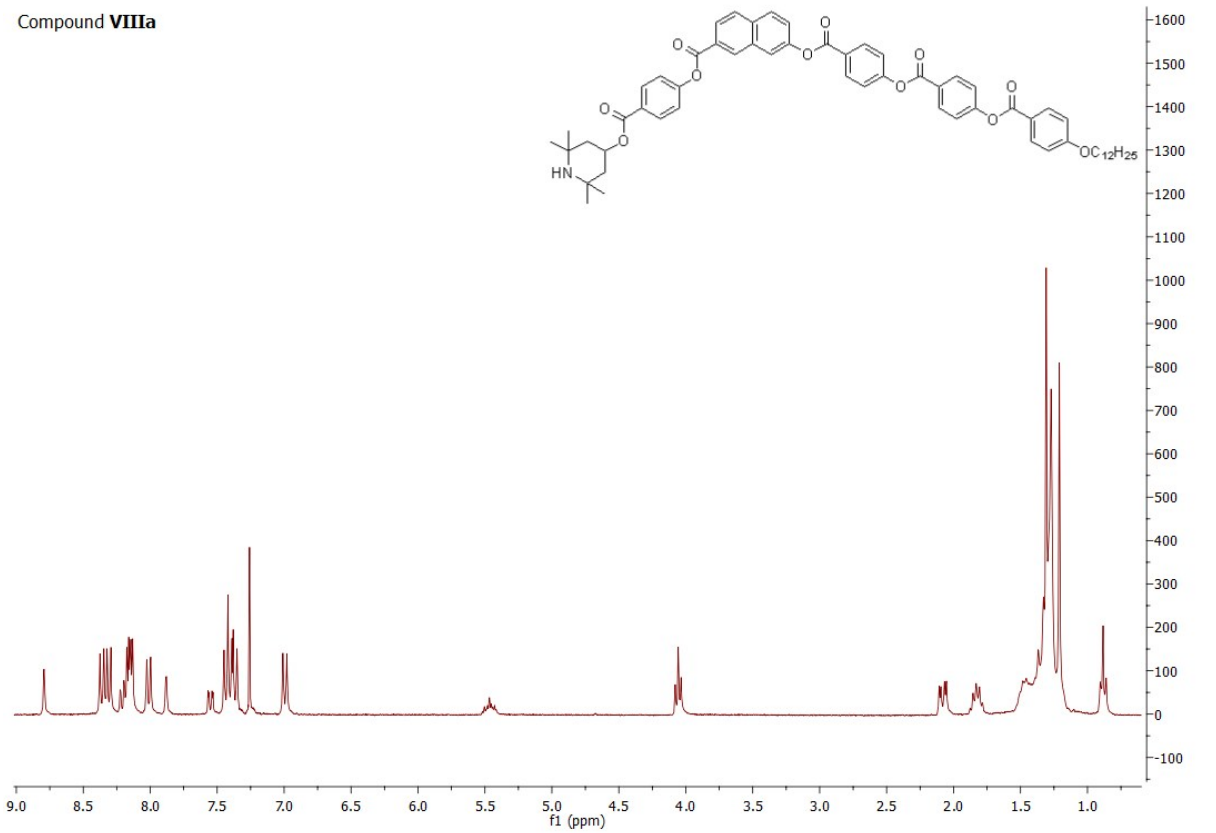


Analogously, compounds **VIIb**, **VIIIa** and **VIIIb** have been synthesised.

4-(1,2,3,6-Tetrahydro-2,2,6,6-tetramethylpyridin-4-yl)phenyl 7-{4-[4-(4-tetradecyloxy-benzoyloxy)benzoyloxy]benzoyloxy}naphthalene-2-carboxylate (VIIb). Yield 67% after crystallization from a THF/acetonitrile mixture. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.88 (t, *J* = 7.0 Hz, 3H, CH_3), 1.00-1.90 (m, 36H), 2.29 (s, 2H, CH_2), 4.06 (t, *J* = 6.7 Hz, 2H, OCH_2), 6.02 (s, 1H, CH), 7.00 (d, *J* = 8.8 Hz, 2H, Ar H), 7.24 (m, 2H, Ar H), 7.44 (m, 6H, Ar H), 7.54 (m, 1H, Ar H), 7.88 (d, *J* = 2.4 Hz, 1H, Ar H), 8.00 (m, 2H, Ar H), 8.16 (d, *J* = 8.8 Hz, 2H, Ar H), 8.22 (m, 1H, Ar H), 8.31 (d, *J* = 8.5 Hz, 2H, Ar H), 8.36 (d, *J* = 8.8 Hz, 2H, Ar H), 8.80 (s, 1H, Ar H); Anal.calcd for $C_{61}H_{67}NO_9$ (958.22): C 76.46, H 6.80 N 1.41; found: C 76.39, H 6.98, N 1.38.

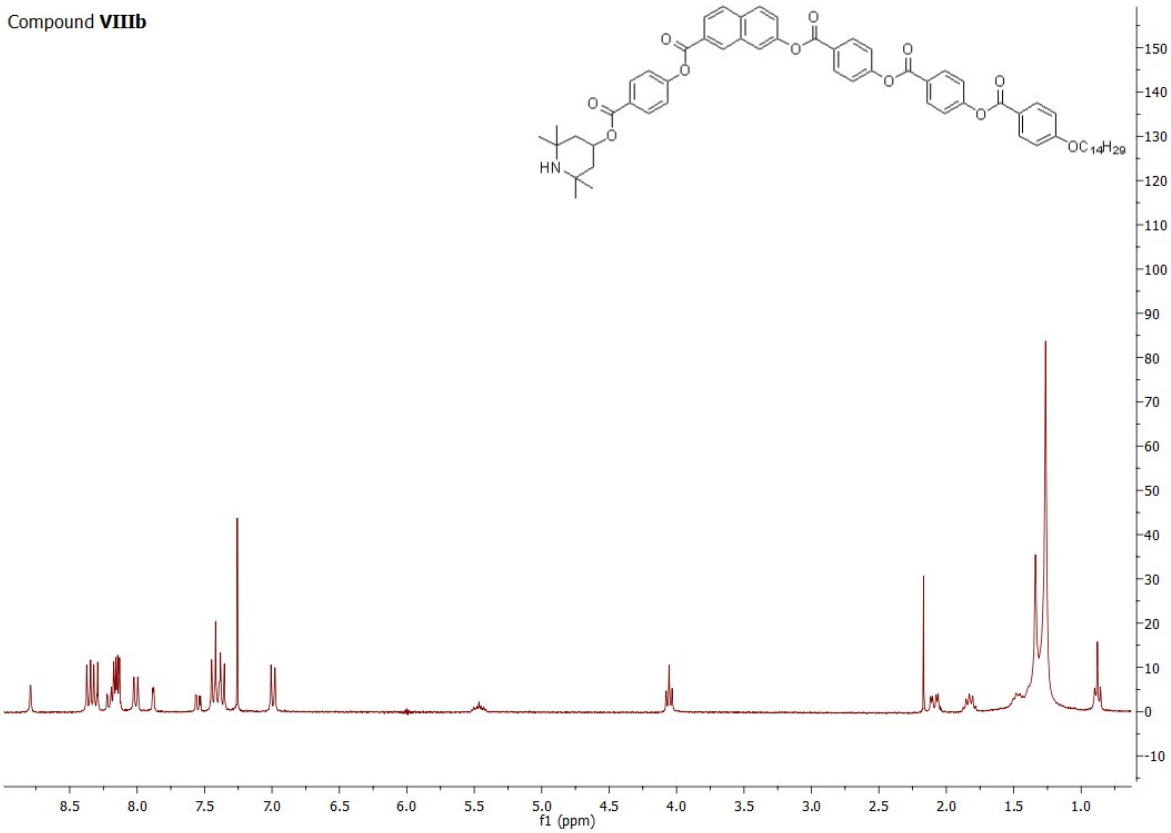


4-[2,2,6,6-Tetramethylpiperidin-4-yloxy)carbonyl]phenyl 7-{4-[4-(4-dodecyloxy-benzoyloxy)benzoyloxy]benzoyloxy}naphthalene-2-carboxylate (VIIIa). Final column chromatography (toluene/ethyl acetate/triethylamine 80/20/0.1) and crystallization from an ethanol/toluene mixture yielded **VIIIa** (41%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.88 (t, *J* = 7.0 Hz, 3H, CH_3), 1.10-1.90 (m, 34H), 2.10 (m, 2H, CH_2), 4.06 (t, *J* = 6.4 Hz, 2H, OCH_2), 5.47 (m, 1H, CH), 6.99 (d, *J* = 8.8 Hz, 2H, Ar H), 7.37 (d, *J* = 8.8 Hz, 2H, Ar H), 7.42 (m, 4H, Ar H), 7.55 (m, 1H, Ar H), 7.88 (s, 1H, Ar H), 8.01 (d, *J* = 7.9 Hz, 2H, Ar H), 8.15 (m, 4H, Ar H), 8.21 (m, 1H, Ar H), 8.31 (d, *J* = 8.5 Hz, 2H, Ar H), 8.36 (d, *J* = 8.8 Hz, 2H, Ar H), 8.79 (s, 1H, Ar H); Anal. calcd for $C_{60}H_{65}NO_{11}$ (976.19): C 73.82, H 6.71 N 1.43; found: C 73.70, H 6.73, N 1.35.



4-[(2,2,6,6-Tetramethylpiperidin-4-yloxy)carbonyl]phenyl 7-{4-[4-(4-tetradecyloxy-benzoyloxy)benzoyloxy]benzoyloxy}naphthalene-2-carboxylate (VIIIb). After column chromatography (chloroform/methanol/triethylamine 90/10/0.1**)** and crystallization from an ethyl acetate/toluene mixture, **VIIIb** (41%) was isolated. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.88 (t, *J* = 7.0 Hz, 3H, CH_3), 1.11-1.91 (m, 38H), 2.10 (m, 2H, CH_2), 4.06 (t, *J* = 6.7 Hz, 2H, OCH_2), 5.47 (m, 1H, CH), 6.99 (d, *J* = 8.8 Hz, 2H, Ar H), 7.40 (m, 6H, Ar H), 7.55 (m, 1H, Ar H), 7.88 (s, 1H, Ar H), 8.01 (d, *J* = 8.8 Hz, 2H, Ar H), 8.16 (m, 5H, Ar H), 8.31 (d, *J* = 8.5 Hz, 2H, Ar H), 8.36 (d, *J* = 8.8 Hz, 2 H, Ar H), 8.79 (s, 1H, Ar H); Anal. calcd for $C_{62}H_{69}NO_{11}$ (1004.24): C 74.15, H 6.93 N 1.39; found: C 74.08, H 6.85, N 1.34.

Compound **VIIIb**



2. MESOMORPHIC PROPERTIES

Table S1.

Series **I** and **II:** melting point, Mp, phase transition temperatures, T_{tr}, and temperature of crystallization, T_{cr}, in °C and corresponding enthalpy changes, ΔH in kJ/mol, detected on the second temperature run at a rate of 5 K/min (in brackets).

Comp.	**Mp** **ΔH**	**T_{Cr}** **ΔH**	**Iso**
Ia	112 +16.2	86 –18.9	●
Ib	122 +64.8	98 –27.3	●
Ic	157 +42.0	85 –13.4	●
Id	119 +38.9	82 –21.2	●
Ie	139 +35.5	120 –35.5	●
IIa	123 +31.5	91 –21.5	●
IIb	134 +33.0	99 –17.7	●
IIc	98 +7.4	94 –5.0	●
IId	93 +13.6	82 –9.9	●
IIe	123 +39.0	120 –40.3	●

Table S2.

Series **I** and **II:** melting point, Mp, phase transition temperatures, T_{tr}, and temperature of crystallization, T_{cr}, in °C and corresponding enthalpy changes, ΔH in kJ/mol, detected on the second temperature run at a rate of 5 K/min (in brackets).

VIIa	150 +59.6	120 –45.1	-		-				SmC	204 –16.9	•
VIIb	150 +43.1	115 –39.7	-		-				SmC	189 –5.9	•
VIIIa	157 +79.2	125 –48.7	-		-				SmC	205 –17.8	•
VIIIb	137 +32.2	87 –17.0	-		-				SmC	184 –2.2	•

Textures and crystallographic parameters of B_{1Rev} and B_{1Rev}' mesophase.

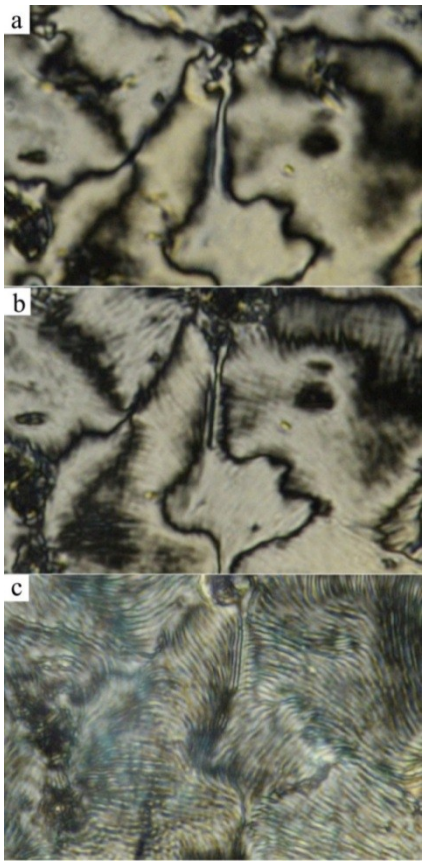


Fig. S4.

Texture for compound **VIa** in a) the SmC phase at temperature T= 170ºC, b) the columnar B_{1Rev} phase at T= 160ºC and c) the columnar B_{1Rev}' phase at T= 125ºC. The width of figures corresponds to 250 μm.

Table S3.

Parameters of the crystallographic unit cell measured by GADDS for compounds **VIa** and **VIb** at selected temperatures in the B_{1Rev} and $B_{1Rev'}$ phases

	T / °C	a / Å	c / Å	β / deg
VIa	140	160.5	44.6	95.5
	122	94.2	47.6	106.6
VIb	150	143.5	45.4	93.4
	130	89.6	49.2	103.8

3. MAGNETIC MEASUREMENTS

Supporting results on magnetic properties of the **VIa** (and **VIb**) sample(s) and data analysis are given in this section.

3.1 EPR DATA

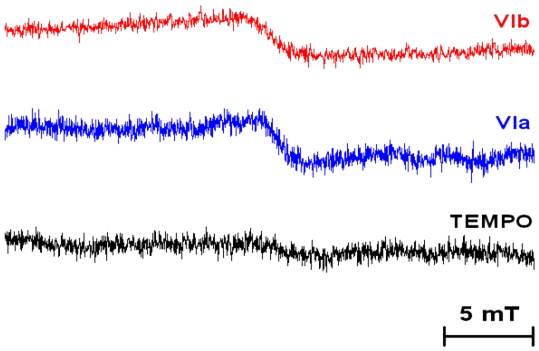


Fig. S5.

Double-quantum EPR transitions (ΔM_S=±2 at $g \approx 4.01$) of **VIa**, **VIb** and TEMPO powder, recorded at room temperature. These signals disappear at temperature > 360 K.

The double-integrated intensity (*DI*) of ΔM_S=±2 relative to ΔM_S=±1 EPR signal is indirectly proportional to r^6, where the r is the inter(intra)-molecular average distance (in Å) between the two unpaired electrons within the range of ≈ 4-12 Å.[S12-S15] The relation for organic radicals can be derived from the transition probabilities considering the same microwave frequency (ν in GHz),[S12-S15] applied to observe both transitions:

$DI(\Delta M_S=\pm 2)/DI(\Delta M_S=\pm 1)=[(A+B\cdot\Delta g)\cdot(9.1/\nu)^2] / r^6$

where A=19.5 and B=10.9 are empirical constants. These are obtained from the fitting of the *relative intensity* vs *v* relationship. For nitroxyl powder samples with small anisotropy: $\Delta g=g_{max}-g_{min} \rightarrow 0$. Prior to distance evaluation, the corresponding double integrals were corrected to microwave power, number of scans and modulation amplitude (additional instrumental parameters were kept constant). If the distance is known, one can evaluate the zero-field splitting parameter *D* by point-dipole approximation[S12,S15]:

$D = 3\cdot g^2\cdot\mu_B^2 / 2r^3$ (*D* in Gauss, r in Å)
$D = 0.433\cdot g^2/ r^3$ (*D* in cm^{-1}, r in Å)

3.2 SQUID DATA

The formula used for analysis of the modified Curie-Weiss law is given as:

$$\chi_m(T) = \frac{C}{T-\theta_P} + \chi_0; C = \frac{\mu_0 N_A}{3k_B} g^2 \mu_B^2 S(S+1) = \frac{\mu_0 N_A}{3k_B}\mu_{eff}^2,$$

where C – Curie constant, θ_p - paramagnetic Curie temperature, N_A - Avogadro number, *g* - Landau *g*-factor (*g* = 2 for free electron), *S* - spin quantum number, μ_B – Bohr magneton, k_B – Boltzman constant, μ_0 - permeability constant of vacuum, χ_0 - diamagnetic component of the molar susceptibility and μ_{eff} is the effective magnetic moment.

The Brillouin function was fitted in the spin-only form as:

.

$$B_j(x) = \frac{2S+1}{2S}\coth\left(\frac{2S+1}{2S}x\right) - \frac{1}{2S}\coth\left(\frac{1}{2S}x\right); x = \frac{gH\mu_B}{k_B T}$$

The upper bound of the dipole-dipole energy is give as:

$$E_{d-d} = \frac{\mu_0 \mu^2}{4\pi\cdot r^3},$$

where μ_0 represents the permeability constant of vacuum, μ is magnetic moment of the particle and *r* is interparticle separation.

Considering two single spins (magnetic moment of 1 μ_B), the dipole-dipole energy is in order of 10^{-3}, 1 and 100 K for *r* of 1, 0.1 and 0.01 nm, respectively. To reach dipole-dipole order at room temperature, the mutual spin-spin distance should be about 0.012 nm, which is

in order of a typical atomic diameter. Therefore the spontaneous magnetic ordering mediated by dipolar interaction is excluded in paramagnetic liquid crystal systems at ambient temperature. Dipolar interactions, however, are significant for electron spin-nuclear spin pairs in anisotropic molecules in liquids, where the intra-molecular dipole-dipole interactions are not fully averaged (the so-called residual anisotropic magnetic interactions or residual dipolar coupling), and they are evidenced by NMR. In such systems, the electron and nuclear spins are considered to be in intimate proximity and thus the resulting dipolar energy exceeds 300 K.

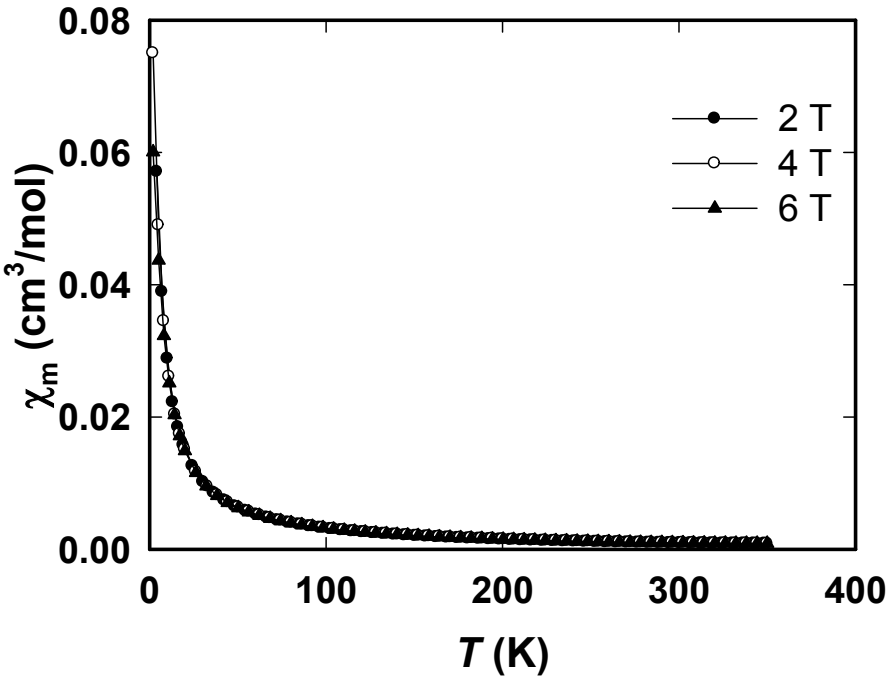


Fig. S6.

Temperature dependence of molar susceptibility, χ_m(T) of the **VIa** sample recorded in magnetic field of 2 T, 4 T and 6 T demonstrating invariance of the χ_m(T) in the applied magnetic field.

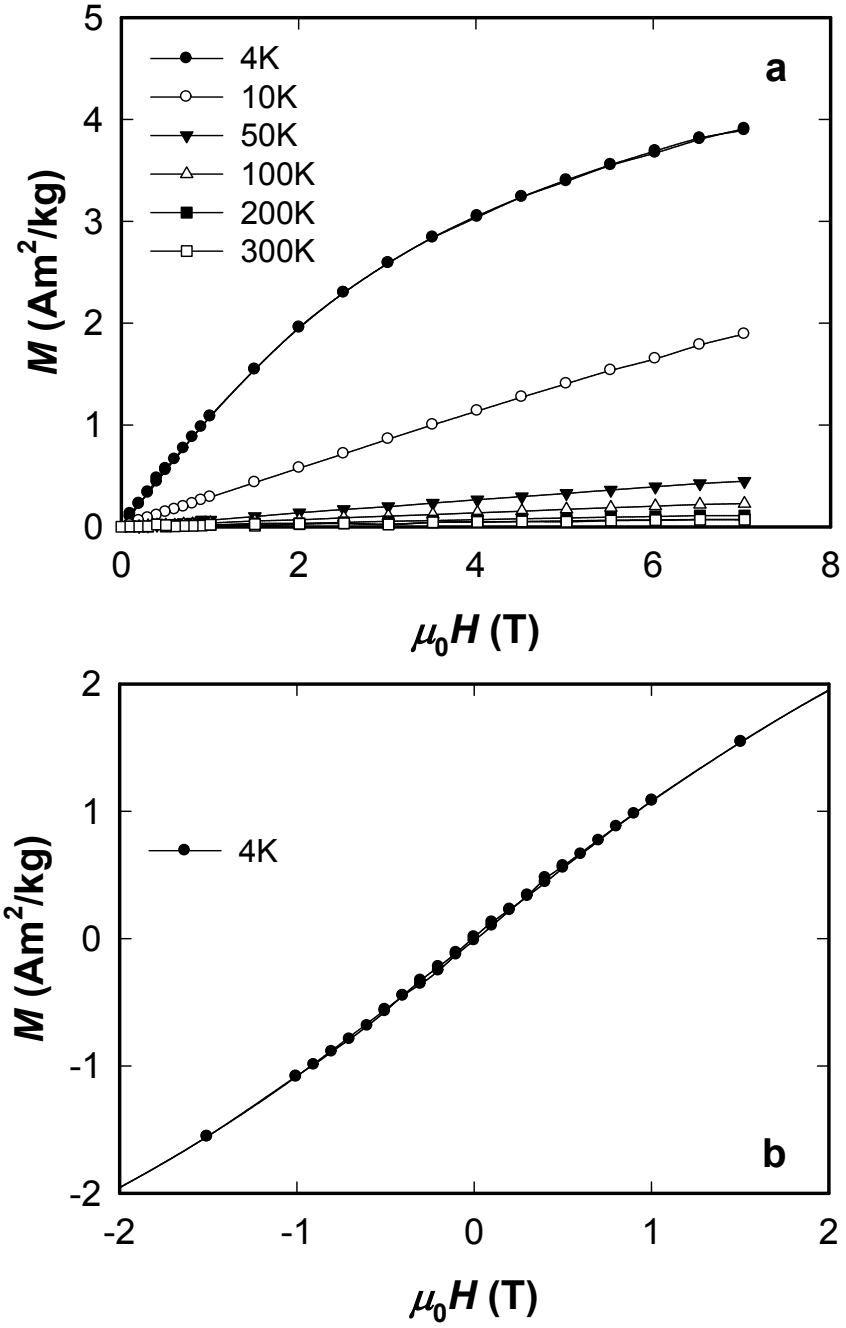


Fig. S7.

(a) Magnetization isotherms of the **VIa** sample at selected temperatures. (b) Detail of magnetization curve at 4 K, which reveals lack of hysteresis.

Other characteristic temperatures (cross points, minima on the ZFC and FC curves and their differences termed as T^1_{cr}, T^2_{cr}, T^1_{dip}, T^2_{dip}, ΔT_{cr} and ΔT_{dip}, respectively) were also evaluated (Table S4).

Table S4.

Summary of parameters obtained from the high-temperature magnetic measurements of sample **VIa** (for meaning of abbreviations, please see text). The typical error for all T values is ±2 K, considering the temperature sweep and numerical error of the analysis.

6 T			4 T			2 T		
$\Delta\chi_m^{\text{ZFC-FC}}$ (10^3cm^3/mol)		$\Delta\chi_m^{\text{max}}$ (10^3cm^3/mol)	$\Delta\chi_m^{\text{ZFC-FC}}$ (10^3cm^3/mol)		$\Delta\chi_m^{\text{max}}$ (10^3cm^3/mol)	$\Delta\chi_m^{\text{ZFC-FC}}$ (10^3cm^3/mol)		$\Delta\chi_m^{\text{max}}$ (10^3cm^3/mol)
0.7±0.1		1.8±0.1	0.7±0.1		1.7±0.1	0.6±0.1		2.0±0.2
T^1_{hys} (K)	T^2_{hys} (K)	ΔT_{hys} (K)	T^1_{hys} (K)	T^2_{hys} (K)	ΔT_{hys} (K)	T^1_{hys} (K)	T^2_{hys} (K)	ΔT_{hys} (K)
358	386	24	361	390	29	366	392	26
T^1_{cr} (K)	T^2_{cr} (K)	ΔT_{cr} (K)	T^1_{cr} (K)	T^2_{cr} (K)	ΔT_{cr} (K)	T^1_{cr} (K)	T^2_{cr} (K)	ΔT_{cr} (K)
361	376	15	364	387	23	366	389	23
T^1_{dip} (K)	T^2_{dip} (K)	ΔT_{dip}(K)	T^1_{dip} (K)	T^2_{dip} (K)	ΔT_{dip}(K)	T^1_{dip} (K)	T^2_{dip} (K)	ΔT_{dip}(K)
366	378	12	370	388	18	370	390	20

4. THERMOGRAVIMETRIC ANALYSIS

In order to verify the stability of the paramagnetic materials during measurements, we have performed the thermogravimetric analysis. The analysis was performed on Stanton-Redcroft TG 750 using about 5 mg of sample placed in a platinum container in the inert nitrogen atmosphere (40 mL min^{-1}). The analysis was performed in a temperature range from 20 to 860 °C with heating rate of 5 °C min^{-1}.

The studied materials were stable up to aproximately 250 °C. This is documented for **VIb** with the six ring structure and the longest terminal aliphatic chain (Fig. S8). The material **VIb** showed 99.66% mass integrity at 200 °C (the maximum temperature used in measurements).

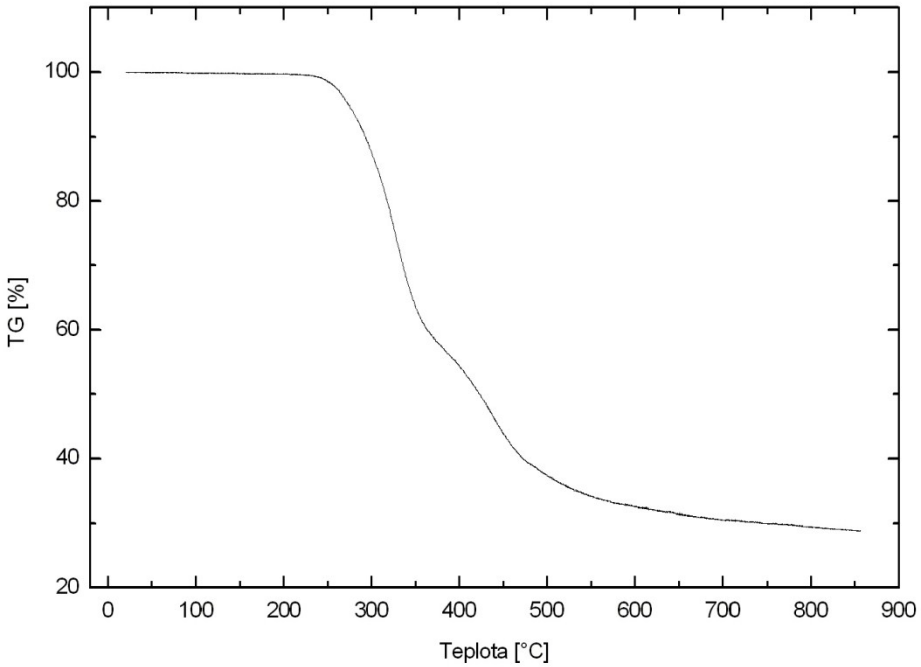


Fig. S8. Thermogravimetric analysis report on sample **VIb** in the temperature range 21-857 °C. The decomposition of the sample started at about 243 °C (99% of starting mass).

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