Electronic Supplementary Material (ESI) for Soft Matter

Supporting Information

Effects of molecular chirality on superstructural chirality in liquid crystalline dark conglomerate phases

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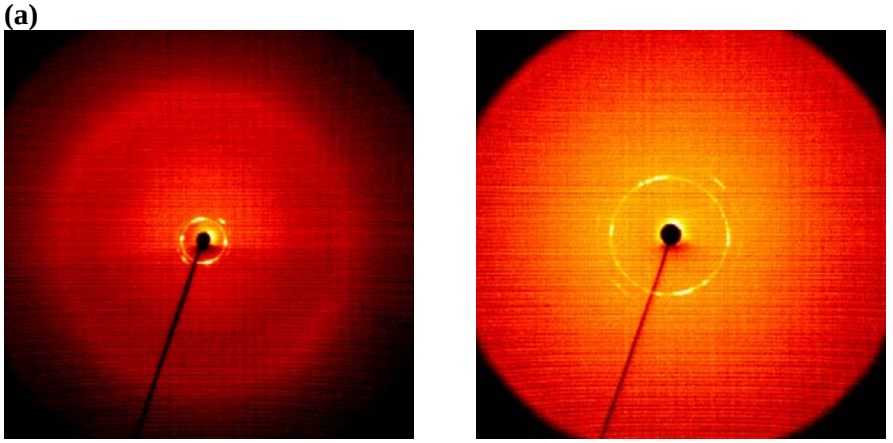
1. Additional data

1.1 Conditions for X-ray scattering

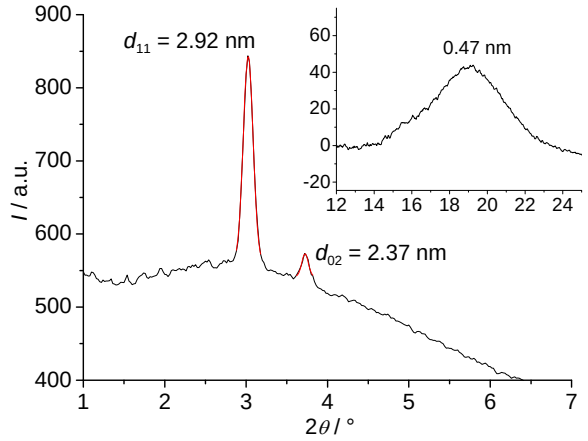
The X-ray diffraction patterns of aligned or partially aligned samples were recorded with a 2D detector (HI-STAR, Siemens). Ni filtered and pin hole collimated CuK_α radiation was used. The exposure time was normally 60 min. The sample to detector distance was 8.8 cm and 26.9 cm for the wide angle and small angle measurements, respectively. Alignment was achieved upon slow cooling (rate: 1 $K \cdot min^{-1}$ – 0.1 $K \cdot min^{-1}$) of a small droplet of the sample on a glass plate and takes place at the sample–glass or at the sample–air interface, with domains fiber-like disordered around an axis perpendicular to the interface. The aligned samples were held on a temperature-controlled heating stage.

1.2 XRD patterns

(a)



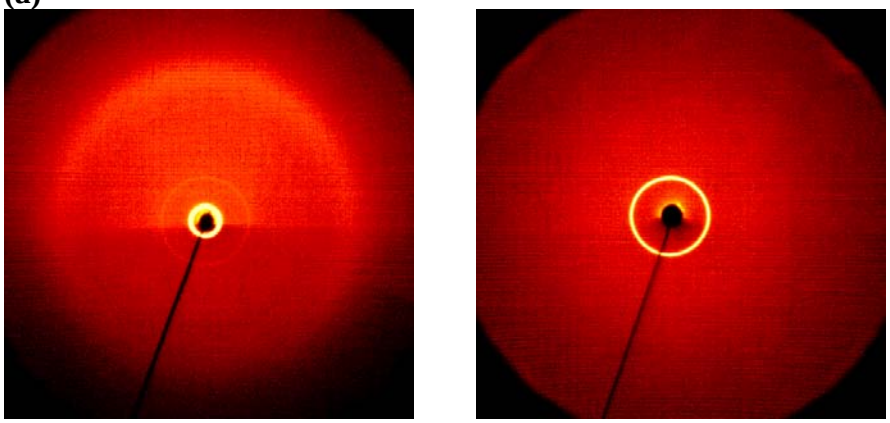
(b)



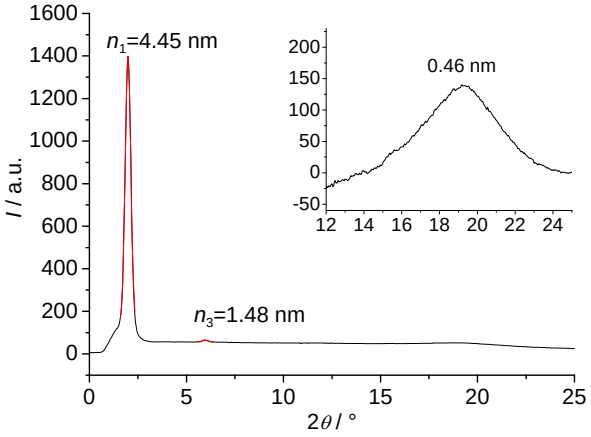
θ_{obs}/°	d_{obs}/nm	*hk*
1.51	2.92	11
1.86	2.37	02
9.48	0.47	diff

Fig. S1. (a) X-ray diffraction patterns of compound ***rac*-3b** in the B_1 mesophase (a = 3.7 nm; b = 4.8 nm) at T = 110 ºC; the left picture shows wide angle pattern, the right picture shows the the small angle pattern; (b) θ-scan over the small angle pattern the inset shows the diffuse scattering in the wide angle region.

(a)



(b)

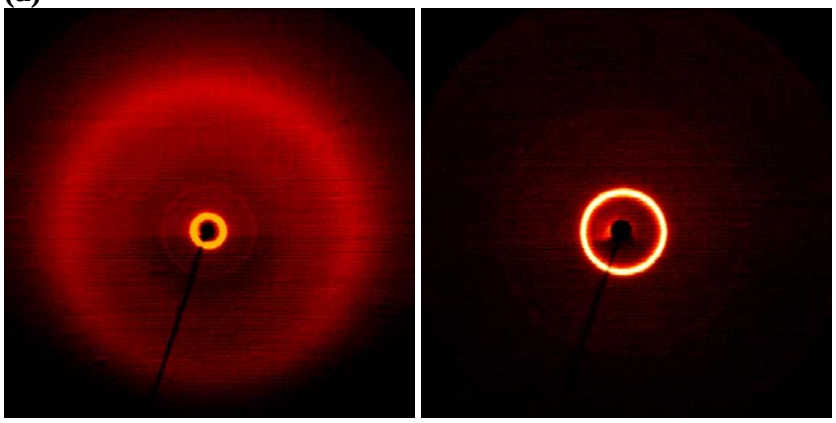


θ_{obs}/°	d_{obs}/nm	*n*
0.99	4.45	1
2.98	1.48	3
9.55	0.46	diff

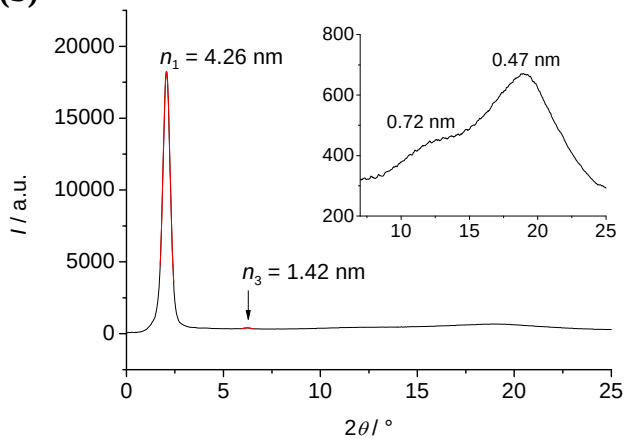
Fig. S2. X-ray diffraction patterns of compound ***rac*-Si$_3$-3b** in the Dark conglomerate phase at T = 100 ºC; the left picture shows wide angle pattern, the right picture shows the the small

angle pattern; (b) θ-scan over the wide angle pattern the inset shows the diffuse scattering in the wide angle region.

(a)



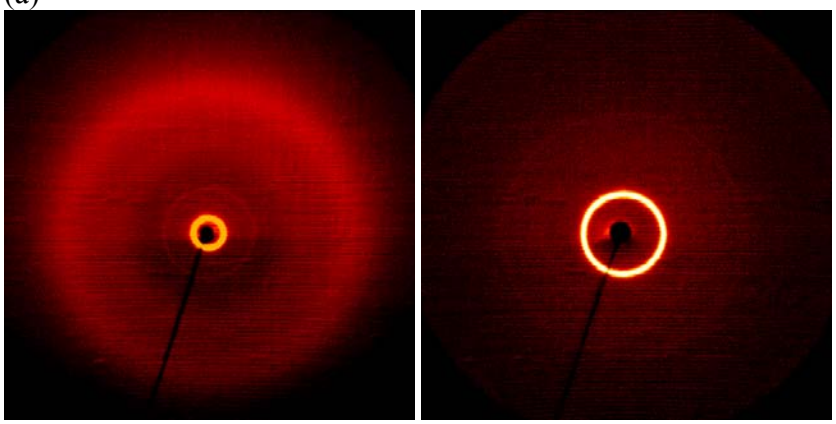
(b)



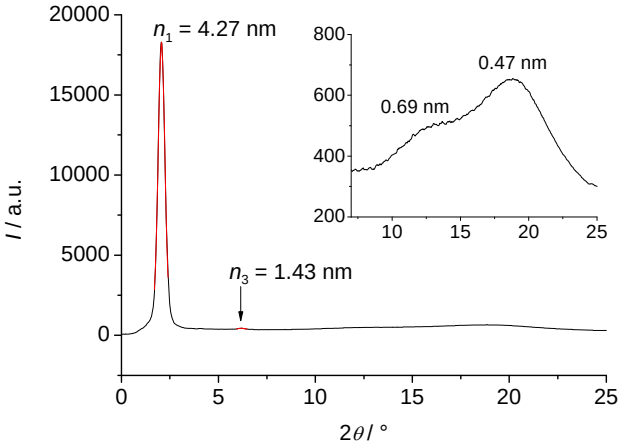
θ_{obs}/°	d_{obs}/nm	n
1.04	**4.26**	1
3.11	**1.42**	3
6.18	**0.72**	diff
9.54	**0.47**	diff

Fig. S3. X-ray diffraction patterns of compound ***rac*-Si$_{3i}$-2b** in the Dark conglomerate phase at T = 120 ºC; the left picture shows wide angle pattern, the right picture shows the the small angle pattern; (b) θ-scan over the wide angle pattern the inset shows the diffuse scattering in the wide angle region.

(a)



(b)

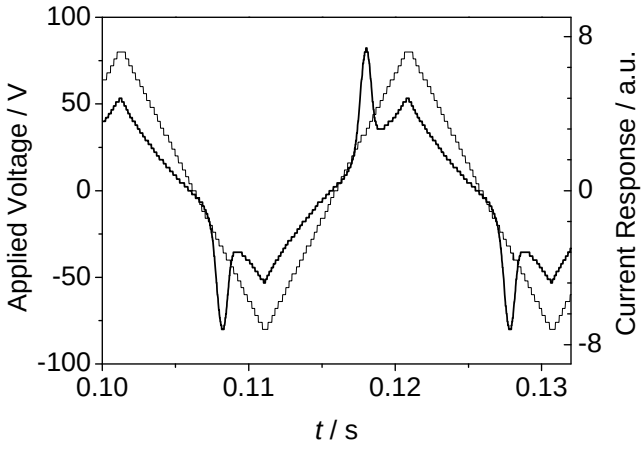


θ_{obs}/°	d_{obs}/nm	n
1.03	**4.27**	1
3.09	**1.43**	3
6.42	**0.69**	diff
9.53	**0.47**	diff

Fig. S4. X-ray diffraction patterns of compound ***rac*-Si$_3$-2b** in the Dark conglomerate phase at T = 120 ºC; the left picture shows wide angle pattern, the right picture shows the the small angle pattern; (b) θ-scan over the wide angle pattern the inset shows the diffuse scattering in the wide angle region.

1.3 Electrooptical investigations

a)



b)

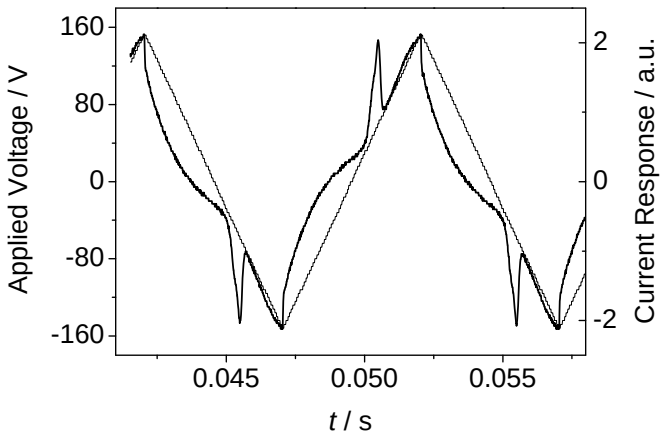


Fig. S5. Switching current response obtained under a triangular wave field (6 μm noncoated ITO cells); a) ***(S)*-Si$_3$-1a** (114 °C, 160 Vpp, 51 Hz, 5 kΩ); b) ***rac*-Si$_3$-2a** (108 °C, 300 Vpp, 100 Hz, 5 kΩ).

2. Synthesis and analytical data

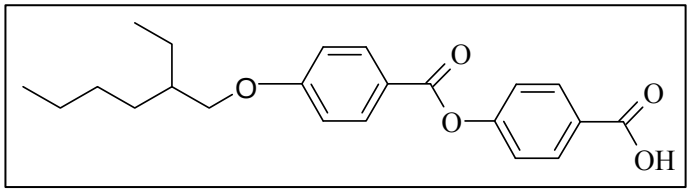
The characterization of the synthesized compounds are based on ^{1}H-, ^{13}C-NMR (Varian Unity 500 and Varian Unity 400 spectrometers, in $CDCl_3$ solutions, with tetramethylsilane as internal standard), MS [AMD 402 (electron impact, 70 eV)]. Microanalyses were performed using a Leco CHNS-932 elemental analyzer.
Transition temperatures were measured using a Mettler FP-82 HT hot stage and control unit in conjunction with a Nikon Optiphot-2 polarizing microscope. The associated enthalpies were obtained from DSC-thermograms which were recorded on a Perkin-Elmer DSC-7, heating and cooling rate: 10 °C min^{-1}. The electro-optical switching characteristics were examined using a triangular-wave method or under a DC field using non-polyimide coated ITO cells, EHC Japan.

Materials: (*S*)-(-)-2-Methyl-1-butanol (Fluka, 95.0%, $[\alpha]_D^{20}$ -6.3 ± 0.5°, *c* = 10 in EtOH), (*S*)-(-)-β-Citronellol (Aldrich, ≥99.0%, $[\alpha]_D^{20}$ -5.3°, neat), 3,7-Dimethyl-1-octanol (Aldrich, 99.0%) and 2-Ethyl-1-hexanol (Fluka, ≥99.0%) were purchased commercially. The optical rotation of 3,7-Dimethyl-1-octanol was also measured using a Perkin-Elmer polarimeter 341 Serial No. 7146 and found $[\alpha]_{589}^{20}$ -1.5° (neat). As the stereogenic center of chiral alcohols is not touched during the synthesis it can be assumed that the optical purity of the final products corresponds to the starting material.

The preparation procedures and spectroscopic data for *4'-Benzyloxybiphenyl-3-ol* (**A**) are given in ref.[S1,S2]. *4-[4-(Alkenyloxy)benzoyloxy]benzoic acids* **D/*n*** were first reported by Achten et al.[S3] and Schiewe et al.[S4]. The synthesis was carried out by using known procedures[S5]. The alkyl tosylates were prepared from the corresponding starting alcohols as described by Otterholm et al.[S6] and used in the first step of the synthesis of *4-(4-alkyloxybenzoyloxy)benzoic acids* **B/*n***. *4-(4-alkenyloxybenzoyloxy)benzoic acids* **D/*n*** which are attached to on the one sides of the biphenyl central unit were carried out according to similar procedures described in ref.[S5]. *4-[4-(S)-2-Methylbutoxybenzoyloxy]benzoic acid (S)*-**B/1**) and *4-[4-(3,7-dimethyloctyloxy)benzoyloxy]benzoic acid* (*rac*-**B/3**) were first reported by Xie et al.[S7] and Ocak et al.[S8], respectively. Spectroscopic data and mesomorphic data for these compounds were given in ref.[S8]

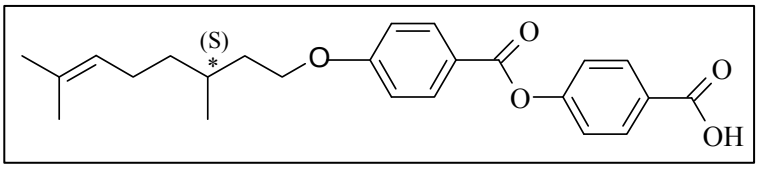
2.1 4-(4-Alkoxybenzoyloxy)benzoic acids B/1-B/4

***4-[4-(2-Ethylhexyloxy)benzoyloxy]benzoic acid* B/2** *($C_{22}H_{26}O_5$; 370.44 g/mol)*



Yield: 76%, white crystals; *T*/°C [Δ*H* kJ/mol]: Cr_1 65 [1.8] Cr_2 97 [7.2] Cr_3 134 [7.7] N 155 [1.4] Iso. **^{1}H-NMR:** δ (ppm) = 8.17 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 8.12 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 7.32 (d, *J* ≈ 8.7 Hz; 2 Ar-H), 6.97 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 3.92 (d, *J* ≈ 6.0 Hz; 2H, OCH_2), 1.78-1.72 (m; 1H, CH), 1.55-1.24 (m; 8H, 4 CH_2), 0.95-0.88 (m; 6H, 2 CH_3). **^{13}C-NMR:** δ (ppm) =170.02 (COOH), 164.33 (CO), 164.06, 155.52, 126.49, 120.90 (Ar-C), 132.39, 131.86, 122.01, 114.45 (Ar-CH), 70.87 (OCH_2), 39.29 (CH), 30.47, 29.06, 23.83, 23.01 (CH_2), 14.06, 11.09 (CH_3). **MS** (**EI**): m/z (%) = 370 (4) [M^+], 191 (76) [M^+-$C_7H_5O_3$], 121 (100) [C_5H_{11}]. .

***4-[4-((S)-Citronellyloxy)benzoyloxy]benzoic acid (S)*-B/4** *($C_{24}H_{28}O_5$; 396.48 g/mol)*



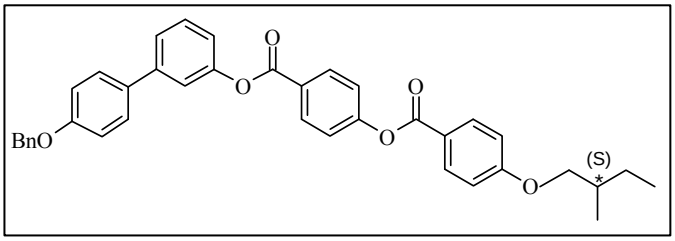
Yield: 86%, white crystals; *T*/°C [Δ*H* kJ/mol]: Cr 88 [5.6] SmC* 143 [1.1] N* 184 [1.7] Iso. **^{1}H-NMR:** δ (ppm) = 8.17 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 8.12 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 7.32 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 6.96 (d, *J* ≈ 8.9 Hz; 2 Ar-H), 5.09 (t, *J* ≈ 7.1 Hz; 1H, C<u>H</u>=$C(CH_3)_2$), 4.12-4.03 (m; 2H, OCH_2), 2.05-1.96 (m; 2H, C<u>H</u>$_2$-CH=$C(CH_3)_2$), 1.89-1.79 (m; 1H, CH), 1.72-1.55 (m; 8H, CH_2, 2 CH_3), 1.44-1.18 (m; 2H, C<u>H</u>$_2$$CH_2$CH=$C(CH_3)_2$), 0.96 (d, *J* ≈ 6.4 Hz; 3H, CH_3). **^{13}C-NMR:** δ (ppm) = 169.81 (COOH), 164.14 (CO), 163.65, 155.39, 126.43, 120.95 (Ar-C), 132.31, 131.76, 121.91, 114.38 (Ar-CH), 131.33 (CH=<u>C</u>$(CH_3)_2$), 124.46 (<u>C</u>H=$C(CH_3)_2$), 66.73 (OCH_2), 37.17 (CH), 36.01, 29.62, 25.79 (CH_2), 25.54, 19.65, 17.77 (CH_3).

2.2 4'-Benzyloxy-3-[4-(alkoxy)benzoyloxy]benzoyloxy]biphenyls Bz-C/1 - Bz-C/3 and 3'-[4-(alkoxy)benzoyloxy]benzoyloxy]biphenyl-4-ols C/1 – C/3

Following earlier descriptions[S9], the synthesis of the *4'-benzyloxy-3-[4-(alkoxy)benzoyloxy]benzoyloxy]biphenyls* **Bz-C/1 - Bz-C/4** was carried out by the esterification of *4'-benzyloxybiphenyl-3-ol* (**A**) with the corresponding *4-(4-alkyloxybenzoyloxy)benzoic acid*s **B/1-B/4**. The crude products were purified by column chromatography on silica gel, elution with dichloromethane and crystallized from ethanol.
The 3'-[4-(alkoxy)benzoyloxy]benzoyloxy]biphenyl-4-ols **C/1–C/3** were obtained by catalytic hydrogenation of the *4'-benzyloxy-3-[4-(alkoxy)benzoyloxy]benzoyloxy]biphenyls* **Bz-C/1 - Bz-C/4** according to procedures described in ref.[S2]. The double bond in the terminal chain of *(S)*-(-)- *4'-benzyloxy-3-[4-(ß-citronellyloxy)benzoyloxy]benzoyloxy]biphenyl (S)*-**Bz-C/4** was also reduced under catalytic hydrogenation conditions (H_2, Pd/C in THF) to give

(S)-3'-[4-(3,7-dimethyloctyloxy)benzoyloxy]benzoyloxy]biphenyl-4-ol *(S)*-**C/3**. The compounds were purified by column chromatography on silica gel using dichloromethane as eluent.

4'-Benzyloxy-3-[4-((S)-2-methylbutoxy)benzoyloxy]benzoyloxy]biphenyl *(S)*-**Bz-C/1** *($C_{38}H_{34}O_6$; 586.68 g/mol)*

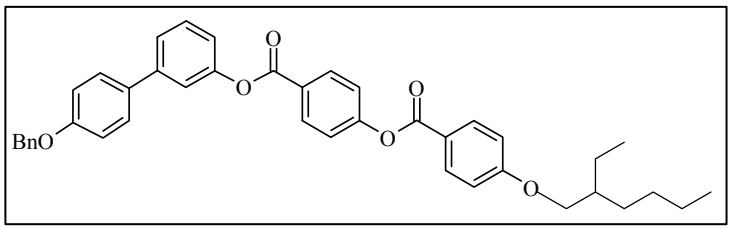


Yield: 72%, white crystals; m.p.: 136 °C **^{1}H-NMR:** δ (ppm) =8.28 (d, $J \approx 8.7$ Hz; 2 Ar-H), 8.14 (d, $J \approx 8.9$ Hz; 2 Ar-H), 7.53 (d, $J \approx 8.7$ Hz; 2 Ar-H), 7.45-7.43 (m, 4 Ar-H), 7.40-7.30 (m, 6 Ar-H), 7.16-7.14 (m, 1 Ar-H), 7.03 (d, $J \approx 8.7$ Hz; 2 Ar-H), 6.98 (d, $J \approx 8.9$ Hz; 2 Ar-H), 5.10 (s, 2H, OCH_2Ph), 3.91, 3.82 (2dd, $J \approx 9.1$ Hz and $J \approx 6.0$ Hz each; 2H, OCH_2, (chiral alkyl chain)), 1.94-1.85 (m, 1H, CH), 1.63-1.24 (m, 2H, CH_2), 1.04 (d, $J \approx 6.6$ Hz; 3H, CH_3), 0.96 (t, $J \approx 7.5$ Hz; 3H, CH_3). **^{13}C-NMR:** δ (ppm) =164.51, 164.35 (CO), 163.99, 158.66, 155.40, 151.31, 142.50, 136.90, 132.96, 126.94, 120.94 (Ar-C), 132.40, 131.80, 129.72, 128.61, 128.25, 128.00, 127.48, 124.24, 122.10, 119.97, 119.85, 115.20, 114.45 (Ar-CH), 73.16, 70.10 (OCH_2), 34.63 (CH), 26.08 (CH_2), 16.47, 11.28 (CH_3). **MS** (**EI**): m/z (%) = 586 (19) [M^+], 311 (10) [M^+-$C_{19}H_{15}O_2$], 191 (100) [$C_7H_4O_2$], 121 (50) [C_5H_{11}], 91 (40) [C_2H_6].

3'-[4-((S)-2-Methylbutoxy)benzoyloxy]benzoyloxy]biphenyl-4-ol *(S)*-**C/1** *($C_{31}H_{28}O_6$; 496.56 g/mol)*

Yield: 73%, yellowish crystals; m.p.: 138 °C. **^{1}H-NMR:** δ (ppm) =8.28 (d, $J \approx 8.7$ Hz; 2 Ar-H), 8.14 (d, $J \approx 8.9$ Hz; 2 Ar-H), 7.47 (d, $J \approx 8.7$ Hz; 2 Ar-H), 7.45-7.42 (m, 2 Ar-H), 7.37-7.35 (m, 3 Ar-H), 7.16-7.13 (m, 1 Ar-H), 6.98 (d, $J \approx 8.9$ Hz; 2 Ar-H), 6.88 (d, $J \approx 8.7$ Hz; 2 Ar-H), 4.81 (s, 1H, OH), 3.91, 3.82 (2dd, $J \approx 9.1$ Hz and $J \approx 6.0$ Hz each; 2H, OCH_2, (chiral alkyl chain)), 1.94-1.84 (m, 1H, CH), 1.61-1.24 (m, 2H, CH_2), 1.04 (d, $J \approx 6.6$ Hz; 3H, CH_3), 0.96 (t, $J \approx 7.5$ Hz; 3H, CH_3). **^{13}C-NMR:** δ (ppm) =164.47, 164.28 (CO), 163.97, 155.38, 151.29, 142.46, 132.97, 126.92, 120.95 (Ar-C), 132.37, 131.77, 129.69, 128.45, 124.20, 122.07, 119.95, 119.84, 115.69, 114.45 (Ar-CH), 73.21 (OCH_2), 34.69 (CH), 26.14 (CH_2), 16.52, 11.32 (CH_3).

4'-Benzyloxy-3-[4-(2-Ethylhexyloxy)benzoyloxy]benzoyloxy]biphenyl ***rac*-Bz-C/2** *($C_{41}H_{40}O_6$; 628.76 g/mol)*



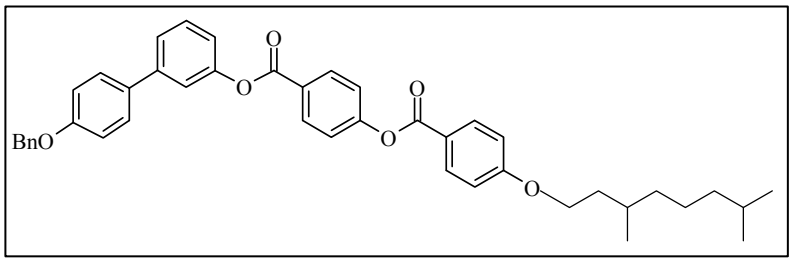
Yield: 62%, white crystals; m.p.: 93 °C. **^{1}H-NMR:** δ (ppm) =8.28 (d, $J \approx 8.7$ Hz; 2 Ar-H), 8.14 (d, $J \approx 8.9$ Hz; 2 Ar-H), 7.52 (d, $J \approx 8.7$ Hz; 2 Ar-H), 7.45-7.43 (m, 4 Ar-H), 7.40-7.29 (m, 6 Ar-H), 7.18-7.13 (m, 1 Ar-H), 7.03 (d, $J \approx 8.7$ Hz; 2 Ar-H), 6.97 (d, $J \approx 8.9$ Hz; 2 Ar-

H), 5.09 (s, 2H, OCH_2Ph), 3.93 (d, $J \approx 6.0$ Hz; 2H, OCH_2), 1.77-1.73 (m, 1H, CH), 1.52-1.24 (m, 8H, 4 CH_2), 0.95-0.90 (m, 6H, 2 CH_3). **^{13}C-NMR:** δ (ppm) =164.49, 164.33 (CO), 164.05, 158.62, 155.38, 151.27, 142.47, 136.88, 132.94, 126.91, 120.88 (Ar-C), 132.38, 131.79, 129.70, 128.59, 128.24, 127.98, 127.46, 124.23, 122.08, 119.95, 119.84, 115.18, 114.43 (Ar-CH), 70.86, 70.08 (OCH_2), 39.27 (CH), 30.45, 29.04, 23.80, 22.98 (CH_2), 14.03, 11.07 (CH_3). **MS** (**EI**): m/z (%) =628 (10) [M^+], 353 (5) [M^+-$C_{19}H_{15}O_2$], 233 (100) [$C_7H_4O_2$], 121 (89) [C_8H_{17}], 91 (54) [C_2H_6].

3'-[4-(2-Ethylhexyloxy)benzoyloxy]benzoyloxy]biphenyl-4-ol rac-C-2 *($C_{34}H_{34}O_6$; 538.64 g/mol)*

Yield: 83%, yellowish crystals; m.p.: 96 °C. **^{1}H-NMR:** δ (ppm) =8.28 (d, $J \approx 8.7$ Hz; 2 Ar-H), 8.14 (d, $J \approx 8.9$ Hz; 2 Ar-H), 7.47-7.43 (m, 4 Ar-H), 7.37-7.35 (m, 3 Ar-H), 7.16-7.13 (m, 1 Ar-H), 6.98 (d, $J \approx 8.9$ Hz; 2 Ar-H), 6.86 (d, $J \approx 8.7$ Hz; 2 Ar-H), 3.93 (d, $J \approx 5.8$ Hz; 2H, OCH_2), 1.79-1.72 (m, 1H, CH), 1.53-1.24 (m, 8H, 4 CH_2), 0.95-0.89 (m, 6H, 2 CH_3). **^{13}C-NMR:** δ (ppm) =164.62, 164.40 (CO), 164.07, 155.52, 155.40, 151.26, 142.51, 132.79, 126.89, 120.85 (Ar-C), 132.39, 131.81, 129.71, 128.42, 124.23, 122.11, 119.93, 119.80, 115.68, 114.45 (Ar-CH), 70.87 (OCH_2), 39.27 (CH), 30.45, 29.04, 23.80, 22.99 (CH_2), 14.04, 11.07 (CH_3).

4'-Benzyloxy-3-[4-(3,7-Dimethyloctyloxy)benzoyloxy]benzoyloxy]biphenyl rac-Bz-C-3 *($C_{43}H_{44}O_6$; 656.82 g/mol)*



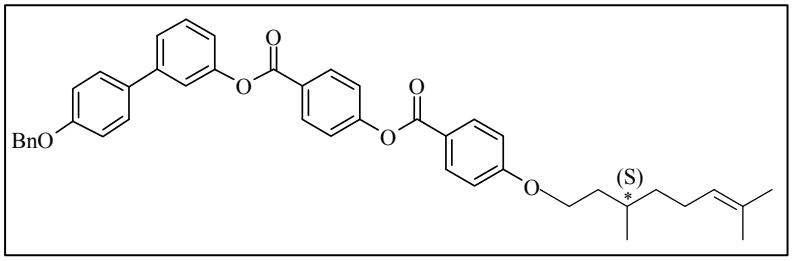
Yield: 77%, white crystals; m.p.: 117 °C. **^{1}H-NMR:** δ (ppm) =8.28 (d, $J \approx 8.7$ Hz; 2 Ar-H), 8.14 (d, $J \approx 8.7$ Hz; 2 Ar-H), 7.52 (d, $J \approx 8.7$ Hz; 2 Ar-H), 7.45-7.43 (m, 4 Ar-H), 7.40-7.29 (m, 6 Ar-H), 7.16-7.13 (m, 1 Ar-H), 7.03 (d, $J \approx 8.7$ Hz; 2 Ar-H), 6.97 (d, $J \approx 8.7$ Hz; 2 Ar-H), 5.09 (s, 2H, OCH_2Ph), 4.10-4.04 (m, 2H, OCH_2), 1.90-1.81 (m; 1H, CH), 1.68-1.47, 1.38-1.15 (2m; 9H, CH, 4 CH_2), 0.94 (d, $J \approx 6.4$ Hz; 3H, CH_3), 0.87 (d, $J \approx 6.6$ Hz; 6H, 2 CH_3). **^{13}C-NMR:** δ (ppm) =164.49, 164.31 (CO), 163.79, 158.64, 155.37, 151.29, 142.49, 136.88, 132.94, 126.92, 120.95 (Ar-C), 132.40, 131.79, 129.70, 128.59, 128.24, 127.98, 127.46, 124.23, 122.08, 119.95, 119.84, 115.18, 114.42 (Ar-CH), 70.09, 66.72 (OCH_2), 39.20, 29.81, 27.95, 24.62 (CH_2), 37.23, 35.97 (CH), 22.67, 22.57, 19.62 (CH_3). **MS** (**EI**): m/z (%) = 656 (7) [M^+], 381 (3) [M^+-$C_{19}H_{15}O_2$], 261 (100) [$C_7H_4O_2$], 121 (52) [$C_{10}H_{21}$], 91 (45) [C_2H_6].

3'-[4-(3,7-Dimethyloctyloxy)benzoyloxy]benzoyloxy]biphenyl-4-ol rac-C-3 *($C_{36}H_{38}O_6$; 566.69 g/mol)*

Yield: 92%, yellowish crystals; m.p.: 129 °C. **^{1}H-NMR:** δ (ppm) =8.28 (d, $J \approx 8.7$ Hz; 2 Ar-H), 8.14 (d, $J \approx 8.9$ Hz; 2 Ar-H), 7.47-7.43 (m, 4 Ar-H), 7.37-7.35 (m, 3 Ar-H), 7.16-7.13 (m, 1 Ar-H), 6.97 (d, $J \approx 8.9$ Hz; 2 Ar-H), 6.87 (d, $J \approx 8.7$ Hz; 2 Ar-H), 4.95 (s, 1H, OH), 4.10-4.05 (m, 2H, OCH_2), 1.88-1.81 (m; 1H, CH), 1.67-1.47, 1.38-1.15 (2m; 9H, CH, 4 CH_2), 0.95 (d, $J \approx 6.4$ Hz; 3H, CH_3), 0.86 (d, $J \approx 6.6$ Hz; 6H, 2 CH_3). **^{13}C-NMR:** δ (ppm) =164.59, 164.37 (CO), 163.80, 155.47, 155.39, 151.26, 142.49, 132.85, 126.89, 120.92 (Ar-C), 132.41,

131.81, 129.71, 128.43, 124.23, 122.10, 119.93, 119.82, 115.68, 114.43 (Ar-CH), 66.73 (OCH_2), 39.20, 29.81, 27.95, 24.62 (CH_2), 37.23, 35.96 (CH), 22.67, 22.57, 19.61 (CH_3).

4'-Benzyloxy-3-[4-((S)-Citronellyloxy)benzoyloxy]benzoyloxy]biphenyl ***(S)*-Bz-C-4**
($C_{43}H_{42}O_6$; 654.80 g/mol)



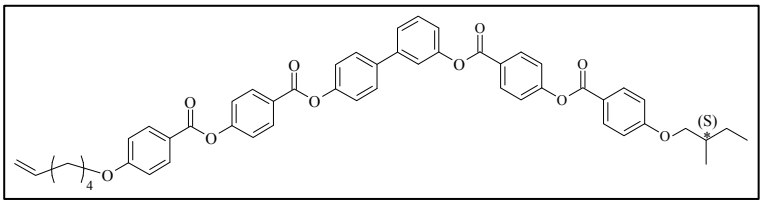
Yield: 42%, white crystals; m.p.: 109 °C. **^{1}H-NMR:** δ (ppm) =8.28 (d, $J \approx 8.7$ Hz; 2 Ar-H), 8.14 (d, $J \approx 8.7$ Hz; 2 Ar-H), 7.52 (d, $J \approx 8.9$ Hz; 2 Ar-H), 7.45-7.43 (m, 4 Ar-H), 7.40-7.29 (m, 6 Ar-H), 7.16-7.13 (m, 1 Ar-H), 7.03 (d, $J \approx 8.7$ Hz; 2 Ar-H), 6.97 (d, $J \approx 8.9$ Hz; 2 Ar-H), 5.09 (s, 3H, OCH_2Ph, CH=$C(CH_3)_2$), 4.10-4.05 (m, 2H, OCH_2), 2.05-1.96 (m, 2H, CH_2-CH=$C(CH_3)_2$), 1.91-1.79 (m, 1H, CH), 1.73-1.53 (m, 8H, CH_2, 2 CH_3), 1.44-1.17 (m, 2H, CH_2CH_2CH=$C(CH_3)_2$), 0.96 (d, $J \approx 6.4$ Hz; 3H, CH_3). **^{13}C-NMR:** δ (ppm) =164.51, 164.33 (CO), 163.79, 158.66, 155.39, 151.31, 142.51, 136.90, 132.97, 126.94, 120.99 (Ar-C), 132.42, 131.81, 129.72, 128.60, 128.25, 128.00, 127.48, 124.25, 122.09, 119.97, 119.85, 115.20, 114.44 (Ar-CH), 131.43 (CH=$C(CH_3)_2$), 124.53 (CH=$C(CH_3)_2$), 70.11, 66.69 (OCH_2), 37.08 (CH), 35.92, 29.49, 25.71 (CH_2), 25.43, 19.54, 17.67 (CH_3). **MS** (**EI**): m/z (%) =654 (12) [M^+], 379 (3) [M^+-$C_{19}H_{15}O_2$], 259 (100) [$C_7H_4O_2$], 121 (94) [$C_{10}H_{19}$], 91 (85) [C_2H_6].

3'-[4-(S)-(3,7-Dimethyloctyloxy)benzoyloxy]benzoyloxy]biphenyl-4-ol ***(S)*-C-3** *($C_{36}H_{38}O_6$; 566.69 g/mol)*
Yield: 95%, white crystals. **^{1}H-NMR:** δ (ppm) =8.28 (d, $J \approx 8.7$ Hz; 2 Ar-H), 8.14 (d, $J \approx 8.9$ Hz; 2 Ar-H), 7.47-7.43 (m, 4 Ar-H), 7.37-7.35 (m, 3 Ar-H), 7.16-7.13 (m, 1 Ar-H), 6.97 (d, $J \approx 8.9$ Hz; 2 Ar-H), 6.87 (d, $J \approx 8.7$ Hz; 2 Ar-H), 4.95 (s, 1H, OH), 4.10-4.05 (m, 2H, OCH_2), 1.88-1.81 (m; 1H, CH), 1.67-1.47, 1.38-1.15 (2m; 9H, CH, 4 CH_2), 0.95 (d, $J \approx 6.4$ Hz; 3H, CH_3), 0.86 (d, $J \approx 6.6$ Hz; 6H, 2 CH_3). **^{13}C-NMR:** δ (ppm) =164.57, 164.36 (CO), 163.80, 155.60 155.38, 151.26, 142.54, 132.70, 126.90, 120.93 (Ar-C), 132.41, 131.81, 129.70, 128.40, 124.22, 122.09, 119.92, 119.78, 115.68, 114.43 (Ar-CH), 66.73 (OCH_2), 39.20, 29.81, 27.95, 24.62 (CH_2), 37.23, 35.97 (CH), 22.67, 22.57, 19.62 (CH_3).

2.3 Olefins 1-3

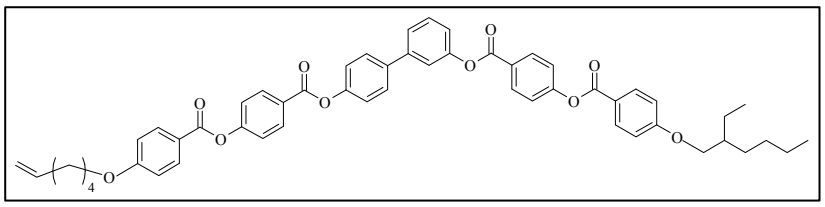
Compounds **1-3** with a terminal double bond were obtained by esterification of *3'-[4-(alkoxy)benzoyloxy]benzoyloxy]biphenyl-4-ols* **C1-C/3** (2 mmol) with the appropriate *4-[4-(alkenyloxy)benzoyloxy]benzoic acid* **D/*n*** (2 mmol), using 2.3 mmol of dicyclohexylcarbodiimide (DCC) as condensation agent and DMAP (0.4 mmol) as catalyst in 20 ml of dry dichloromethane. [S2,S9] The reaction mixture was stirred at room temperature under an argon atmosphere for 24 h. The precipitate was filtered, the solvent was evaporated. The crude products were purified by column chromatography on silica gel using dichloromethane as eluent and recrystallized from ethanol.

3'-{4-[4-((S)-2-Methylbutoxy)benzoyloxy]benzoyloxy}-4-{4-[4-(5-hexenyloxy) benzoyloxy]benzoyloxy}biphenyl *($C_{51}H_{46}O_{10}$; 818.92 g/mol)*



***(S)*-1a:** Yield: 0.91 g (56%) of white crystals. **^{1}H-NMR**: δ (ppm) =8.29 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 8.28 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 8.14 (d; *J* ≈ 8.9 Hz; 4 Ar-H), 7.65 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 7.51-7.50 (m; 2 Ar-H), 7.44 (broad s; 1 Ar-H), 7.37 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 7.36 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 7.30 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 7.22-7.20 (m, 1 Ar-H), 6.97 (d; *J* ≈ 8.9 Hz; 2 Ar-H), 6.96 (d; *J* ≈ 8.9 Hz; 2 Ar-H), 5.85-5.78 (m; 1H, CH_2=C<u>H</u>), 5.06-4.96 (m; 2H, C<u>H_2</u>=CH), 4.05 (t; *J* ≈ 6.4 Hz; 2H, OCH_2), 3.90, 3.82 (2dd, *J* ≈ 9.1 Hz and *J* ≈ 6.0 Hz each; 2H, OCH_2, (chiral alkyl chain)), 2.16-2.11 (m; 2H, CH_2=CH-C<u>H_2</u>), 1.92-1.87 (m; 1H, CH), 1.86-1.80 (m, 2H, CH_2), 1.64-1.24 (m; 2 CH_2), 1.03 (d; *J* ≈ 6.8 Hz; 3H, CH_3), 0.96 (t; *J* ≈ 7.5 Hz; 3H, CH_3). **^{13}C-NMR**: δ (ppm) = 164.42, 164.38, 164.26, 164.22 (CO), 163.92, 163.68, 155.39, 151.30, 150.61, 142.04, 138.00, 126.83, 121.06, 120.96 (Ar-C), 132.41, 132.37, 131.79, 129.82, 128.29, 124.66, 122.17, 122.09, 122.05, 120.43, 114.90, 114.46, 114.43 (Ar-CH), 138.27 (CH_2=<u>C</u>H), 114.14 (<u>C</u>H_2=CH), 73.26, 68.24 (OCH_2), 34.79 (CH), 33.49, 28.67, 26.26, 25.41 (CH_2), 16.65, 11.45 (CH_3). **MS (EI) :** m/z (%) =818 (4) [M^+], 323 (6) [M^+-$C_{31}H_{27}O_6$], 203 (67) [$C_7H_4O_2$], 191 (63) [M^+-$C_{39}H_{31}O_8$], 121 (100) [C_5H_{11}].

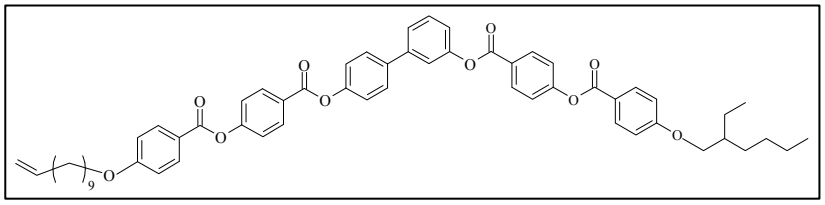
3'-{4-[4-(2-Ethylhexyloxy)benzoyloxy]benzoyloxy}-4-{4-[4-(5-hexenyloxy) benzoyloxy]benzoyloxy}biphenyl *($C_{54}H_{52}O_{10}$; 860.99 g/mol)*



***rac*-2a:** Yield: 0.98 g (57%) of white crystals. **^{1}H-NMR**: δ (ppm) = 8.29 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 8.28 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 8.14 (d; *J* ≈ 8.9 Hz; 4 Ar-H), 7.65 (d; *J* ≈ 8.5 Hz; 2 Ar-H), 7.51-7.50 (m; 2 Ar-H), 7.44 (broad s; 1 Ar-H), 7.37 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 7.36 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 7.30 (d; *J* ≈ 8.5 Hz; 2 Ar-H), 7.22-7.20 (m, 1 Ar-H), 6.98 (d; *J* ≈ 8.9 Hz; 2 Ar-H), 6.97 (d; *J* ≈ 8.9 Hz; 2 Ar-H), 5.87-5.77 (m; 1H, CH_2=C<u>H</u>), 5.06-4.97 (m; 2H, C<u>H_2</u>=CH), 4.05 (t; *J* ≈ 6.4 Hz; 2H, OCH_2), 3.93 (d; *J* ≈ 5.8 Hz; 2H, OCH_2), 2.17-2.11 (m; 2H, CH_2=CH-

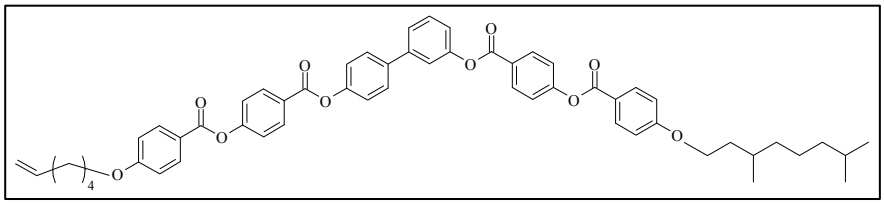
CH_2), 1.87-1.79 (m; 2H, CH_2), 1.77-1.73 (m; 1H, CH), 1.63-1.25 (m; 5 CH_2), 0.96-0.89 (m; 6H, 2 CH_3). **^{13}C-NMR**: δ (ppm) = 164.49, 164.46, 164.34, 164.31 (CO), 164.07, 163.76, 155.45, 151.34, 150.65, 142.08, 138.04, 126.86, 121.03, 120.90 (Ar-C), 132.43, 132.40, 131.84, 129.86, 128.33, 124.70, 122.11, 122.08, 122.04, 120.62, 120.45, 114.91, 114.46 (Ar-CH), 138.33 (CH_2=CH), 114.42 (CH_2=CH), 70.87, 68.14 (OCH_2), 39.29 (CH), 33.36, 30.47, 29.06, 28.50, 25.23, 23.82, 23.01 (CH_2), 14.05, 11.09 (CH_3). **MS (EI) :** m/z (%) = 323 (9) [M^+-$C_{34}H_{33}O_6$], 233 (66) [$C_{39}H_{31}O_8$], 203 (79) [M^+-$C_{41}H_{37}O_8$], 121 (100) [C_6H_{11}].

3'-{4-[4-(2-Ethylhexyloxy)benzoyloxy]benzoyloxy}-4-{4-[4-(10-undecenyloxy) benzoyloxy]benzoyloxy}biphenyl *($C_{59}H_{62}O_{10}$; 931.13 g/mol)*



***rac*-2b:** Yield: 1.34 g (72%) of white crystals. **^{1}H-NMR**: δ (ppm) = 8.29 (d; $J \approx 8.7$ Hz; 2 Ar-H), 8.28 (d; $J \approx 8.7$ Hz; 2 Ar-H), 8.14 (d; $J \approx 8.9$ Hz; 4 Ar-H), 7.65 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.51-7.50 (m; 2 Ar-H), 7.44 (broad s; 1 Ar-H), 7.37 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.36 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.30 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.23-7.20 (m, 1 Ar-H), 6.98 (d; $J \approx 8.9$ Hz; 2 Ar-H), 6.97 (d; $J \approx 8.9$ Hz; 2 Ar-H), 5.85-5.75 (m; 1H, CH_2=CH), 5.00-4.90 (m; 2H, CH_2=CH), 4.04 (t; $J \approx 6.6$ Hz; 2H, OCH_2), 3.93 (d; $J \approx 6.0$ Hz; 2H, OCH_2), 2.15-2.00 (m; 2H, CH_2=CH-CH_2), 1.85-1.79 (m; 2H, CH_2), 1.77-1.73 (m; 1H, CH), 1.55-1.24 (m; 10 CH_2), 0.95-0.89 (m; 6H, 2 CH_3). **^{13}C-NMR**: δ (ppm) = 164.44, 164.41, 164.30, 164.28 (CO), 164.05, 163.81, 155.44, 151.35, 150.66, 142.08, 138.03, 126.87, 121.01, 120.95 (Ar-C), 132.41, 132.39, 131.82, 129.85, 128.32, 124.68, 122.11, 122.07, 120.62, 120.45, 114.47, 114.45 (Ar-CH), 139.16 (CH_2=CH), 114.14 (CH_2=CH), 70.95, 68.43 (OCH_2), 39.37 (CH), 33.84, 30.56, 29.75, 29.53, 29.46, 29.38, 29.15, 29.14, 28.98, 26.03, 23.92, 23.07 (CH_2), 14.12, 11.17 (CH_3). **MS (EI) :** m/z (%) = 393 (4) [M^+-$C_{34}H_{33}O_6$], 273 (96) [$C_7H_4O_2$], 233 (55) [M^+-$C_{44}H_{41}O_8$], 121 (100) [C_8H_{17}].

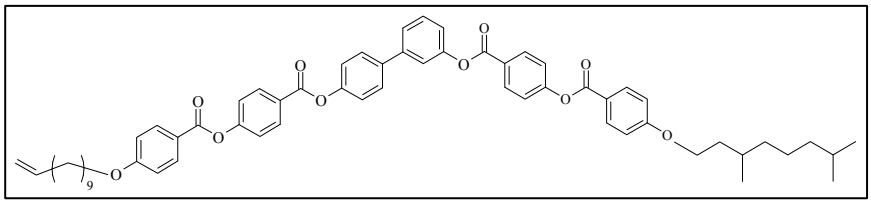
3'-{4-[4-(3,7-Dimethyloctyloxy)benzoyloxy]benzoyloxy}-4-{4-[4-(5-hexenyloxy) benzoyloxy]benzoyloxy}biphenyl ($C_{56}H_{56}O_{10}$; 889.05 g/mol)



***rac*-3a:** Yield: 0.99 g (56%) of white crystals. **^{1}H-NMR**: δ (ppm) = 8.29 (d; $J \approx 8.7$ Hz; 2 Ar-H), 8.28 (d; $J \approx 8.7$ Hz; 2 Ar-H), 8.14 (d; $J \approx 8.9$ Hz; 4 Ar-H), 7.65 (d; $J \approx 8.5$ Hz; 2 Ar-H), 7.51-7.50 (m; 2 Ar-H), 7.44 (broad s; 1 Ar-H), 7.37 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.36 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.30 (d; $J \approx 8.5$ Hz; 2 Ar-H), 7.23-7.19 (m, 1 Ar-H), 6.98 (d; $J \approx 8.9$ Hz; 2 Ar-H), 6.97 (d; $J \approx 8.9$ Hz; 2 Ar-H), 5.87-5.77 (m; 1H, CH_2=CH), 5.06-4.97 (m; 2H, CH_2=CH), 4.10-4.04 (m; 4H, 2 OCH_2), 2.17-2.11 (m; 2H, CH_2=CH-CH_2), 1.86-1.81 (m; 3H, CH_2, CH), 1.66-1.47, 1.35-1.15 (2m; 11H, CH, 5 CH_2), 0.95 (d; $J \approx 6.4$ Hz; 3H, CH_3), 0.87 (d; $J \approx 6.4$ Hz; 6H, 2 CH_3). **^{13}C-NMR**: δ (ppm) = 164.39, 164.37, 164.26, 164.21 (CO), 163.74, 155.38, 151.32, 150.55, 141.20, 138.00, 126.62, 126.40, 121.29, 120.93 (Ar-C), 132.39, 131.80,

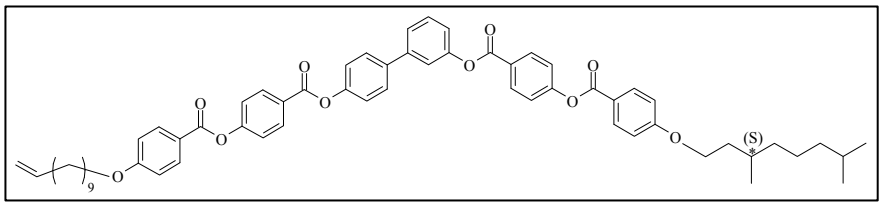
129.44, 128.28, 124.36, 122.09, 122.05, 120.61, 120.48, 114.90, 114.46 (Ar-CH), 138.27 (CH_2=$\underline{C}$H), 114.12 ($\underline{C}H_2$=CH), 68.25, 66.86 (OCH_2), 39.37 (CH_2), 37.40, 36.15 (CH), 33.50, 30.01, 28.67, 28.13, 25.42, 24.81 (CH_2), 22.85, 22.75, 19.82 (CH_3). **MS (EI) :** m/z (%) =323 (13) [M^+-$C_{36}H_{37}O_6$], 261 (89) [$C_{39}H_{31}O_8$], 203 (100) [$C_{43}H_{41}O_8$], 121 (97) [C_6H_{11}].

3'-{4-[4-(3,7-Dimethyloctyloxy)benzoyloxy]benzoyloxy}-4-{4-[4-(10-undecenyloxy) benzoyloxy]benzoyloxy}biphenyl *($C_{61}H_{66}O_{10}$; 959.19 g/mol)*



***rac*-3b:** Yield: 1.02 g (53%) of white crystals. **^{1}H-NMR**: δ (ppm) =8.29 (d; $J \approx 8.7$ Hz; 2 Ar-H), 8.28 (d; $J \approx 8.7$ Hz; 2 Ar-H), 8.14 (d; $J \approx 8.9$ Hz; 2 Ar-H), 8.13 (d; $J \approx 8.9$ Hz; 2 Ar-H), 7.65 (d; $J \approx 8.5$ Hz; 2 Ar-H), 7.51-7.50 (m; 2 Ar-H), 7.44 (broad s; 1 Ar-H), 7.37 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.36 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.30 (d; $J \approx 8.5$ Hz; 2 Ar-H), 7.23-7.19 (m, 1 Ar-H), 6.98 (d; $J \approx 8.9$ Hz; 2 Ar-H), 6.97 (d; $J \approx 8.9$ Hz; 2 Ar-H), 5.85-5.75 (m; 1H, CH_2=C$\underline{H}$), 5.00-4.90 (m; 2H, C$\underline{H_2}$=CH), 4.10-4.07 (m; 2H, OCH_2), 4.04 (t; $J \approx 6.6$ Hz; 2H, OCH_2), 2.06-2.00 (m; 2H, CH_2=CH-C$\underline{H_2}$), 1.89-1.78 (m; 3H, CH_2, CH), 1.68-1.43, 1.37-1.15 (2m; 21H, CH, 10 CH_2), 0.95 (d; $J \approx 6.4$ Hz; 3H, CH_3), 0.87 (d; $J \approx 6.6$ Hz; 6H, 2 CH_3). **^{13}C-NMR**: δ (ppm) = 164.48, 164.45, 164.34, 164.31 (CO), 163.82, 155.43, 151.34, 150.65, 142.07, 138.03, 126.86, 126.82, 121.06, 120.96 (Ar-C), 132.41, 131.83, 129.86, 128.32, 124.69, 122.11, 122.07, 120.61, 120.44, 114.42, 114.41 (Ar-CH), 139.18 (CH_2=$\underline{C}$H), 114.14 ($\underline{C}H_2$=CH), 68.38, 66.74 (OCH_2), 39.22 (CH_2), 37.25, 35.99 (CH), 33.78, 29.83, 29.47, 29.39, 29.32, 29.09, 29.07, 28.91, 27.96, 25.96, 24.64 (CH_2), 22.69, 22.59, 19.63 (CH_3). **MS (EI) :** m/z (%) = 393 (6) [M^+-$C_{36}H_{37}O_6$], 273 (67) [$C_7H_4O_2$], 121 (100) [$C_{11}H_{21}$].

3'-{4-[4-((S)-3,7-Dimethyloctyloxy)benzoyloxy]benzoyloxy}-4-{4-[4-(10-undecenyloxy) benzoyloxy]benzoyloxy}biphenyl *($C_{61}H_{66}O_{10}$; 959.19 g/mol)*



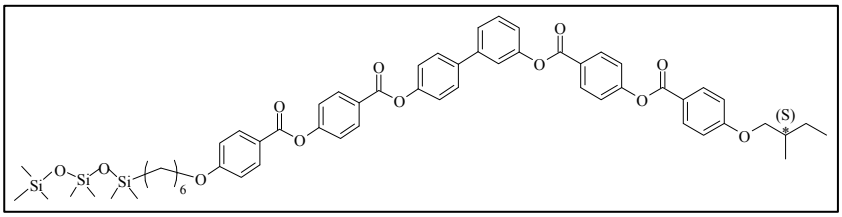
***(S)*-3b:** Yield: 0.48 g (25%) of white crystals. **^{1}H-NMR**: δ (ppm) = 8.29 (d; $J \approx 8.7$ Hz; 2 Ar-H), 8.28 (d; $J \approx 8.7$ Hz; 2 Ar-H), 8.15 (d; $J \approx 8.7$ Hz; 2 Ar-H), 8.14 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.65 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.51-7.50 (m; 2 Ar-H), 7.45 (broad s; 1 Ar-H), 7.37 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.36 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.30 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.23-7.19 (m, 1 Ar-H), 6.98 (d; $J \approx 8.7$ Hz; 2 Ar-H), 6.97 (d; $J \approx 8.7$ Hz; 2 Ar-H), 5.84-5.77 (m; 1H, CH_2=C$\underline{H}$), 5.00-4.91 (m; 2H, C$\underline{H_2}$=CH), 4.11-4.08 (m; 2H OCH_2), 4.04 (t; $J \approx 6.5$ Hz; 2H, OCH_2), 2.06-2.00 (m; 2H, CH_2=CH-C$\underline{H_2}$), 1.88-1.78 (m; 3H, CH_2, CH), 1.68-1.46, 1.37-1.15 (2m; 21H, CH, 10 CH_2), 0.96 (d; $J \approx 6.2$ Hz; 3H, CH_3), 0.87 (d; $J \approx 6.6$ Hz; 6H, 2 CH_3). **^{13}C-NMR**: δ (ppm) = 164.49, 164.46, 164.34, 164.30 (CO), 163.81, 155.42, 151.32, 150.63, 142.06, 138.01, 126.85, 126.81, 121.80, 120.95 (Ar-C), 132.39, 131.81, 129.84, 128.30, 124.67, 122.09, 122.05, 120.60, 120.42, 114.41, 114.39 (Ar-CH), 139.16 (CH_2=$\underline{C}$H), 114.11

($\underline{C}H_2$=CH), 68.36, 66.73 (OCH_2), 39.20 (CH_2), 37.23, 35.97 (CH), 33.75, 29.81, 29.44, 29.36, 29.29, 29.09, 29.07, 28.89, 27.94, 25.93, 24.62 (CH_2), 22.66, 22.56, 19.61 (CH_3). **MS (EI) :** m/z (%) =393 (7) [M^+-$C_{36}H_{37}O_6$], 273 (96) [$C_7H_4O_2$], 121 (100) [$C_{11}H_{21}$].

2.4 Final compounds Si_x-1 - Si_x-3

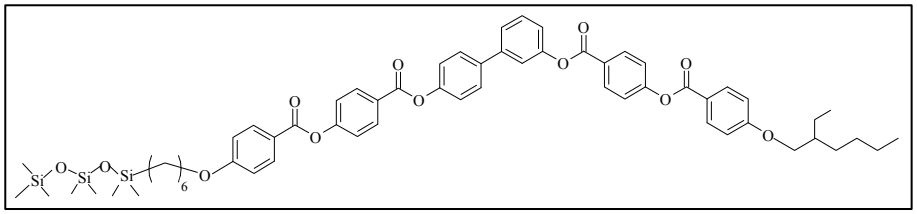
The appropriate olefin **1-3** (0.5 mmol) was dissolved in anhydrous toluene (6 ml) under an argon atmosphere. To this solution, 1H-heptamethyldisiloxane or 2H-heptamethyldisiloxane (0.6 mmol) and two drops of Karstedt's catalyst (platinum-divinyltetramethyl-siloxane complex in xylene) were added.[S2,S10] The reaction mixture was stirred at room temperature under an argon atmosphere for 48 h. The solvent was evaporated. All target compounds were purified by column chromatography (silica gel, eluent dichloromethane) followed by crystallization from ethanol.

3'-{4-[4-((S)-2-Methylbutoxy)benzoyloxy]benzoyloxy}-4-{4-[4-[6-(1,1,3,3,5,5,5-heptamethyltrisiloxan-1-yl)hex-1-yloxy]benzoyloxy]benzoyloxy}biphenyl



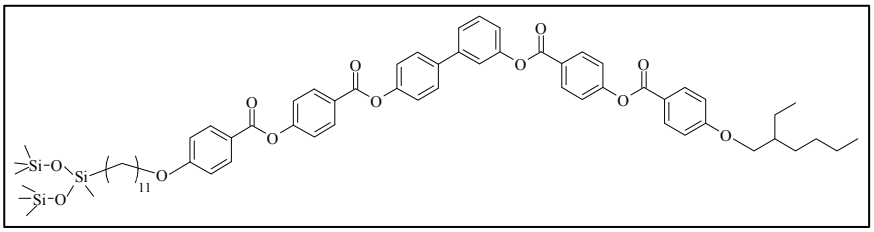
***(S)*-Si_3-1a:** Yield: 0.24 g (47%) of white crystals. **^{1}H-NMR**: δ (ppm) = 8.29 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 8.28 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 8.14 (d; *J* ≈ 8.9 Hz; 4 Ar-H), 7.65 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 7.51-7.50 (m; 2 Ar-H), 7.44 (broad s; 1 Ar-H), 7.37 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 7.36 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 7.30 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 7.23-7.19 (m, 1 Ar-H), 6.98 (d; *J* ≈ 8.9 Hz; 2 Ar-H), 6.97 (d; *J* ≈ 8.9 Hz; 2 Ar-H), 4.04 (t; *J* ≈ 6.6 Hz; 2H, OCH_2), 3.91, 3.82 (2dd, *J* ≈ 9.1 Hz and *J* ≈ 6.0 Hz each; 2H, OCH_2, (chiral alkyl chain)), 1.93-1.88 (m; 1H, CH), 1.83-1.78 (m, 2H, CH_2), 1.62-1.24 (m; 4 CH_2), 1.04 (d; *J* ≈ 6.6 Hz; 3H, CH_3), 0.96 (t; *J* ≈ 7.5 Hz; 3H, CH_3), 0.57-0.52 (m; 2H, $SiCH_2$), 0.08 [s; 9H, Si-$(CH_3)_3$], 0.06 [s; 6H, Si-$(CH_3)_2$], 0.02 [s; 6H, Si-$(CH_3)_2$]. **^{13}C-NMR**: δ (ppm) =164.47, 164.44, 164.31, 164.30 (CO), 163.97, 163.81, 155.42, 151.32, 150.63, 142.06, 138.01, 126.83, 126.80, 120.92 (Ar-C), 132.39, 131.82, 129.84, 128.31, 124.68, 122.09, 122.05, 120.60, 120.43, 114.42, 114.40 (Ar-CH), 73.14, 68.38 (OCH_2), 34.61 (CH), 33.05, 29.00, 26.06, 25.67, 23.13 (CH_2), 18.19 ($SiCH_2$), 16.45, 11.26 (CH_3), 1.79, 1.25, 0.17 (CH_3). **^{29}Si-NMR**: δ (ppm) = 7.38, 7.09, -20.97. **$C_{58}H_{68}O_{12}Si_3$** (1041.42); Anal. Calc.: C, 66.89; H, 6.58. Found: C, 66.85; H, 6.47%.

3'-{4-[4-(2-Ethylhexyloxy)benzoyloxy]benzoyloxy}-4-{4-[4-[6-(1,1,3,3,5,5,5-heptamethyltrisiloxan-1-yl)hex-1-yloxy]benzoyloxy]benzoyloxy}biphenyl



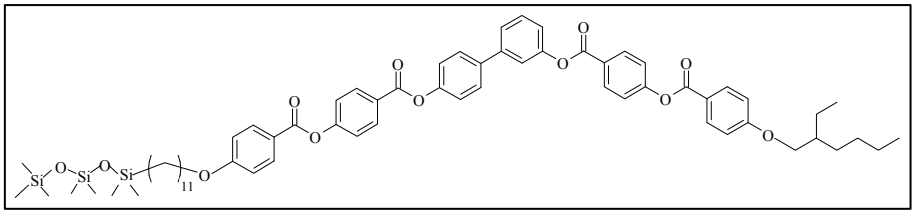
***rac*-Si$_3$-2a:** Yield: 0.30 g (56%) of white crystals. **^{1}H-NMR**: δ (ppm) = 8.29 (d; *J* ≈ 8.5 Hz; 2 Ar-H), 8.28 (d; *J* ≈ 8.5 Hz; 2 Ar-H), 8.14 (d; *J* ≈ 8.9 Hz; 4 Ar-H), 7.66 (d; *J* ≈ 8.5 Hz; 2 Ar-H), 7.51-7.50 (m; 2 Ar-H), 7.45 (broad s; 1 Ar-H), 7.37 (d; *J* ≈ 8.5 Hz; 2 Ar-H), 7.36 (d; *J* ≈ 8.5 Hz; 2 Ar-H), 7.30 (d; *J* ≈ 8.5 Hz; 2 Ar-H), 7.23-7.19 (m, 1 Ar-H), 6.98 (d; *J* ≈ 8.9 Hz; 2 Ar-H), 6.97 (d; *J* ≈ 8.9 Hz; 2 Ar-H), 4.04 (t; *J* ≈ 6.6 Hz; 2H, OCH_2), 3.93 (d; *J* ≈ 5.8 Hz; 2H, OCH_2), 1.85-1.78 (m; 2H, CH_2), 1.76-1.73 (m; 1H, CH), 1.56-1.24 (m; 7 CH_2), 0.96-0.89 (m; 6H, 2 CH_3), 0.57-0.52 (m; 2H, $SiCH_2$), 0.08 [s; 9H, Si-$(CH_3)_3$], 0.06 [s; 6H, Si-$(CH_3)_2$], 0.02 [s; 6H, Si-$(CH_3)_2$]. **^{13}C-NMR**: δ (ppm) = 164.46, 164.44, 164.32, 164.30 (CO), 164.05, 163.82, 155.42, 151.32, 150.63, 142.06, 138.01, 126.83, 126.80, 120.94, 120.88 (Ar-C), 132.39, 132.38, 131.81, 129.84, 128.31, 124.68, 122.09, 122.05, 120.60, 120.43, 114.43, 114.40 (Ar-CH), 70.85, 68.38 (OCH_2), 39.27 (CH), 33.05, 30.45, 29.04, 29.00, 25.67, 23.80, 23.14, 22.99 (CH_2), 18.19 ($SiCH_2$), 14.03, 11.07 (CH_3), 1.79, 1.25, 0.17 (CH_3). **^{29}Si-NMR**: δ (ppm) = 7.38, 7.09, -20.97. **$C_{61}H_{74}O_{12}Si_3$** (1083.50); Anal. Calc.: C, 67.62; H, 6.88. Found: C, 67.52; H, 6.74%.

3'-{4-[4-(2-Ethylhexyloxy)benzoyloxy]benzoyloxy}-4-{4-[4-[11-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)undec-1-yloxy]benzoyloxy]benzoyloxy}biphenyl



***rac*-Si$_{3i}$-2b:** Yield: 0.37 g (65%) of white crystals. **^{1}H-NMR**: δ (ppm) = 8.30 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 8.29 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 8.15 (d; *J* ≈ 8.9 Hz; 4 Ar-H), 7.67 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 7.51-7.50 (m; 2 Ar-H), 7.46 (broad s; 1 Ar-H), 7.38 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 7.37 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 7.31 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 7.24-7.22 (m, 1 Ar-H), 6.99 (d; *J* ≈ 8.9 Hz; 2 Ar-H), 6.98 (d; *J* ≈ 8.9 Hz; 2 Ar-H), 4.05 (t; *J* ≈ 6.6 Hz; 2H, OCH_2), 3.94 (d; *J* ≈ 6.0 Hz; 2H, OCH_2), 1.84-1.78 (m; 2H, CH_2), 1.77-1.73 (m; 1H, CH), 1.52-1.24 (m; 12 CH_2), 0.96-0.90 (m; 6H, 2 CH_3), 0.47-0.42 (m; 2H, $SiCH_2$), 0.08 [s; 18H, 2 Si-$(CH_3)_3$], -0.01 (s; 3H, Si-CH_3). **^{13}C-NMR**: δ (ppm) = 164.48, 164.45, 164.32, 164.31 (CO), 164.07, 163.84, 155.45, 151.35, 150.66, 142.08, 138.04, 126.86, 126.82, 120.96, 120.91 (Ar-C), 132.40, 131.84, 129.87, 128.33, 124.70, 122.12, 122.08, 120.60, 120.45, 114.46, 114.43 (Ar-CH), 70.88, 68.41 (OCH_2), 39.29 (CH), 33.22, 30.47, 29.61, 29.56, 29.36, 29.09, 29.06, 25.98, 23.83, 23.06, 23.01 (CH_2), 17.62 ($SiCH_2$), 14.06, 11.09 (CH_3), 1.85, -0.26 (CH_3). **^{29}Si-NMR**: δ (ppm) = 6.82, -21.18. **$C_{66}H_{84}O_{12}Si_3$** (1153.64); Anal. Calc.: C, 68.72; H, 7.34. Found: C, 68.80; H, 7.29%.

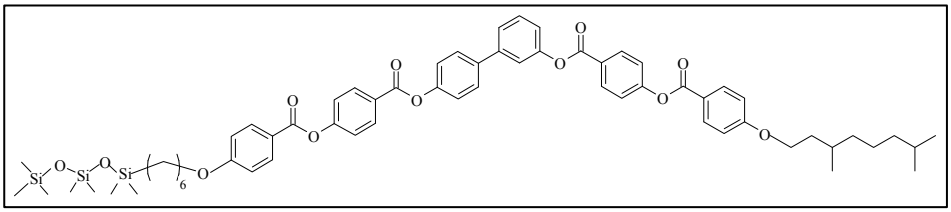
3'-{4-[4-(2-Ethylhexyloxy)benzoyloxy]benzoyloxy}-4-{4-[4-[11-(1,1,3,3,5,5,5-heptamethyltrisiloxan-1-yl)undec-1-yloxy]benzoyloxy]benzoyloxy}biphenyl



***rac*-Si$_3$-2b:** Yield: 0.34 g (59%) of white crystals. **^{1}H-NMR**: δ (ppm) =8.29 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 8.28 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 8.14 (d; *J* ≈ 8.9 Hz; 4 Ar-H), 7.65 (d; *J* ≈ 8.6 Hz; 2 Ar-

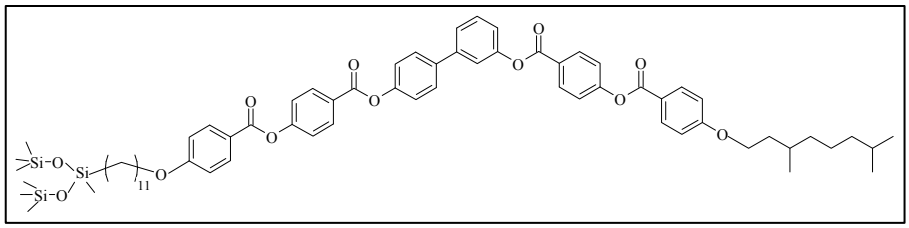
H), 7.51-7.50 (m; 2 Ar-H), 7.44 (broad s; 1 Ar-H), 7.37 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.36 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.30 (d; $J \approx 8.6$ Hz; 2 Ar-H), 7.22-7.20 (m, 1 Ar-H), 6.98 (d; $J \approx 8.9$ Hz; 2 Ar-H), 6.97 (d; $J \approx 8.9$ Hz; 2 Ar-H), 4.04 (t; $J \approx 6.6$ Hz; 2H, OCH_2), 3.93 (d; $J \approx 5.9$ Hz; 2H, OCH_2), 1.82-1.78 (m; 2H, CH_2), 1.77-1.74 (m; 1H, CH), 1.54-1.23 (m; 12 CH_2), 0.95-0.89 (m; 6H, 2 CH_3), 0.52-0.49 (m; 2H, $SiCH_2$), 0.07 [s; 9H, Si-$(CH_3)_3$], 0.04 [s; 6H, Si-$(CH_3)_2$], 0.00 [s; 6H, Si-$(CH_3)_2$]. **^{13}C-NMR**: δ (ppm) =164.47, 164.44, 164.32, 164.30 (CO), 164.05, 163.82, 155.42, 151.32, 150.63, 142.06, 138.01, 126.83, 126.80, 120.88 (Ar-C), 132.39, 132.38, 131.81, 129.85, 128.30, 124.68, 122.10, 122.05, 120.43, 114.43, 114.40 (Ar-CH), 70.85, 68.38 (OCH_2), 39.27 (CH), 33.41, 30.45, 29.60, 29.55, 29.53, 29.36, 29.35, 29.07, 29.04, 25.96, 23.80, 23.20, 22.99 (CH_2), 18.27 ($SiCH_2$), 14.03, 11.07 (CH_3), 1.78, 1.24, 0.18 (CH_3). **^{29}Si-NMR**: δ (ppm) = 7.49, 7.05, -21.05. **$C_{66}H_{84}O_{12}Si_3$** (1153.64); Anal. Calc.: C, 68.71; H, 7.33. Found: C, 68.65; H, 7.26%.

3'-{4-[4-(3,7-Dimethyloctyloxy)benzoyloxy]benzoyloxy}-4-{4-[4-[6-(1,1,3,3,5,5,5-heptamethyltrisiloxan-1-yl)hex-1-yloxy]benzoyloxy]benzoyloxy}biphenyl



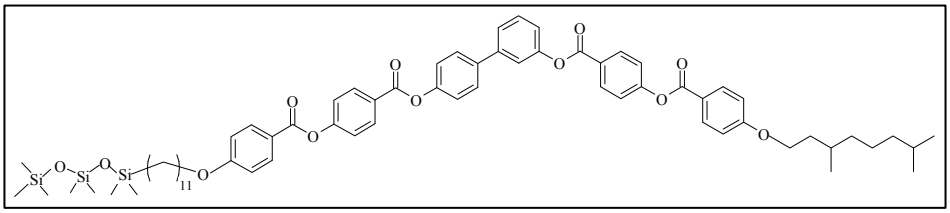
***rac*-Si$_3$-3a:** Yield: 0.16 g (30%) of white crystals. **^{1}H-NMR**: δ (ppm) = 8.29 (d; $J \approx 8.7$ Hz; 2 Ar-H), 8.28 (d; $J \approx 8.7$ Hz; 2 Ar-H), 8.15 (d; $J \approx 8.9$ Hz; 2 Ar-H), 8.14 (d; $J \approx 8.9$ Hz; 2 Ar-H), 7.66 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.51-7.50 (m; 2 Ar-H), 7.45 (broad s; 1 Ar-H), 7.37 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.36 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.30 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.23-7.19 (m, 1 Ar-H), 6.98 (d; $J \approx 8.9$ Hz; 2 Ar-H), 6.97 (d; $J \approx 8.9$ Hz; 2 Ar-H), 4.11-4.08 (m; 2H OCH_2), 4.04 (t; $J \approx 6.5$ Hz; 2H, OCH_2), 1.85-1.79 (m; 3H, CH_2, CH), 1.66-1.47, 1.39-1.15 (2m; 15H, CH, 7 CH_2), 0.95 (d; $J \approx 6.4$ Hz; 3H, CH_3), 0.87 (d; $J \approx 6.6$ Hz; 6H, 2 CH_3), 0.57-0.53 (m; 2H, $SiCH_2$), 0.08 [s; 9H, Si-$(CH_3)_3$], 0.06 [s; 6H, Si-$(CH_3)_2$], 0.02 [s; 6H, Si-$(CH_3)_2$]. **^{13}C-NMR**: δ (ppm) = 164.45, 164.43, 164.31, 164.30 (CO), 164.16, 163.69, 155.34, 151.26, 150.58, 141.99, 137.95, 126.86, 126.82, 121.99, 120.97 (Ar-C), 132.32, 131.74, 129.77, 128.24, 124.60, 122.08, 122.03, 120.62, 120.38, 114.42, 114.41 (Ar-CH), 68.45, 66.81 (OCH_2), 39.31 (CH_2), 37.35, 36.10 (CH), 33.15, 29.96, 29.13, 28.07, 25.80, 24.75, 23.26 (CH_2), 22.78, 22.69, 19.76 (CH_3), 18.35 ($SiCH_2$), 1.95, 1.41, 0.34 (CH_3). **^{29}Si-NMR**: δ (ppm) = 7.37, 7.09, -20.97. **$C_{63}H_{78}O_{12}Si_3$** (1111.56); Anal. Calc.: C, 68.07; H, 7.07. Found: C, 68.36; H, 6.76%.

3'-{4-[4-(3,7-Dimethyloctyloxy)benzoyloxy]benzoyloxy}-4-{4-[4-[11-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)undec-1-yloxy]benzoyloxy]benzoyloxy}biphenyl



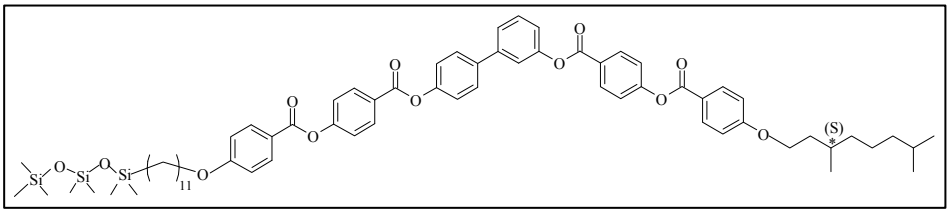
***rac*-Si$_{3i}$-3b:** Yield: 0.33 g (56%) of white crystals. **^{1}H-NMR**: δ (ppm) = 8.29 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 8.28 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 8.15 (d; *J* ≈ 8.9 Hz; 2 Ar-H), 8.14 (d; *J* ≈ 8.9 Hz; 2 Ar-H), 7.65 (d; *J* ≈ 8.5 Hz; 2 Ar-H), 7.51-7.50 (d; 2 Ar-H), 7.45 (broad s; 1 Ar-H), 7.37 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 7.36 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 7.30 (d; *J* ≈ 8.5 Hz; 2 Ar-H), 7.23-7.20 (m, 1 Ar-H), 6.98 (d; *J* ≈ 8.9 Hz; 2 Ar-H), 6.97 (d; *J* ≈ 8.9 Hz; 2 Ar-H), 4.11-4.08 (m; 2H OCH_2), 4.04 (t; *J* ≈ 6.6 Hz; 2H, OCH_2), 1.85-1.79 (m; 3H, CH_2, CH), 1.69-1.45, 1.35-1.15 (2m; 25H, CH, 12 CH_2), 0.95 (d; *J* ≈ 6.4 Hz; 3H, CH_3), 0.87 (d; *J* ≈ 6.4 Hz; 6H, 2 CH_3), 0.44-0.42 (m; 2H, $SiCH_2$), 0.07 [s; 18H, 2 Si-$(CH_3)_3$], -0.02 (s; 3H, Si-CH_3). **^{13}C-NMR**: δ (ppm) = 164.46, 164.44, 164.32, 164.30 (CO), 163.82, 163.79, 155.42, 151.32, 150.63, 142.06, 138.01, 126.84, 126.80, 120.96 (Ar-C), 132.40, 131.82, 129.84, 128.31, 124.67, 122.10, 122.05, 120.60, 120.43, 114.42, 114.41 (Ar-CH), 68.38, 66.72 (OCH_2), 39.20 (CH_2), 37.23, 35.97 (CH), 33.20, 29.81, 29.58, 29.54, 29.34, 29.07, 27.94, 25.96, 24.62, 23.04 (CH_2), 22.67, 22.57, 19.62 (CH_3), 17.60 ($SiCH_2$), 1.83, -0.28 (CH_3). **^{29}Si-NMR**: δ (ppm) = 6.83, -21.17. **$C_{68}H_{88}O_{12}Si_3$** (1181.69); Anal. Calc.: C, 69.11; H, 7.50. Found: C, 69.18; H, 7.43%.

3'-{4-[4-(3,7-Dimethyloctyloxy)benzoyloxy]benzoyloxy}-4-{4-[4-[11-(1,1,3,3,5,5,5-heptamethyltrisiloxan-1-yl)undec-1-yloxy]benzoyloxy]benzoyloxy}biphenyl



***rac*-Si$_3$-3b:** Yield: 0.40 g (68%) of white crystals. **^{1}H-NMR**: δ (ppm) = 8.29 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 8.28 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 8.15 (d; *J* ≈ 8.9 Hz; 2 Ar-H), 8.14 (d; *J* ≈ 8.9 Hz; 2 Ar-H), 7.65 (d; *J* ≈ 8.5 Hz; 2 Ar-H), 7.51-7.50 (m; 2 Ar-H), 7.45 (broad s; 1 Ar-H), 7.37 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 7.36 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 7.30 (d; *J* ≈ 8.5 Hz; 2 Ar-H), 7.23-7.20 (m, 1 Ar-H), 6.98 (d; *J* ≈ 8.9 Hz; 2 Ar-H), 6.97 (d; *J* ≈ 8.9 Hz; 2 Ar-H), 4.10-4.06 (m; 2H OCH_2), 4.04 (t; *J* ≈ 6.5 Hz; 2H, OCH_2), 1.87-1.79 (m; 3H, CH_2, CH), 1.68-1.45, 1.37-1.14 (2m; 25H, CH, 12 CH_2), 0.95 (d; *J* ≈ 6.5 Hz; 3H, CH_3), 0.87 (d; *J* ≈ 6.5 Hz; 6H, 2 CH_3), 0.53-0.50 (m; 2H, $SiCH_2$), 0.07 [s; 9H, Si-$(CH_3)_3$], 0.05 [s; 6H, Si-$(CH_3)_2$], 0.00 [s; 6H, Si-$(CH_3)_2$]. **^{13}C-NMR**: δ (ppm) = 164.48, 164.46, 164.32, 164.30 (CO), 163.84, 163.81, 155.44, 151.34, 150.65, 142.08, 138.03, 126.86, 126.82, 120.97, 120.96 (Ar-C), 132.42, 131.83, 129.86, 128.32, 124.69, 122.11, 122.07, 120.62, 120.44, 114.44, 114.42 (Ar-CH), 68.40, 66.74 (OCH_2), 39.22 (CH_2), 37.25, 35.99 (CH), 33.43, 29.83, 29.61, 29.57, 29.55, 29.38, 29.37, 29.09, 27.96, 25.98, 24.64, 23.22 (CH_2), 22.69, 22.59, 19.64 (CH_3), 18.28 ($SiCH_2$), 1.80, 1.26, 0.20 (CH_3). **^{29}Si-NMR**: δ (ppm) = 7.48, 7.04, -21.05. **$C_{68}H_{88}O_{12}Si_3$** (1181.69); Anal. Calc.: C, 69.11; H, 7.50. Found: C, 68.81; H, 7.70%.

3'-{4-[4-((S)-3,7-Dimethyloctyloxy)benzoyloxy]benzoyloxy}-4-{4-[4-[11-(1,1,3,3,5,5,5-heptamethyltrisiloxan-1-yl)undec-1-yloxy]benzoyloxy]benzoyloxy}biphenyl



***(S)*-Si$_3$-3b:** Yield: 0.24 g (41%) of white crystals. **^{1}H-NMR**: δ (ppm) = 8.29 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 8.28 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 8.14 (d; *J* ≈ 8.9 Hz; 2 Ar-H), 8.13 (d; *J* ≈ 8.9 Hz; 2 Ar-H), 7.65 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 7.51-7.50 (m; 2 Ar-H), 7.44 (broad s; 1 Ar-H), 7.37 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 7.36 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 7.29 (d; *J* ≈ 8.7 Hz; 2 Ar-H), 7.22-7.18 (m, 1 Ar-H), 6.97 (d; *J* ≈ 8.9 Hz; 2 Ar-H), 6.96 (d; *J* ≈ 8.9 Hz; 2 Ar-H), 4.10-4.08 (m; 2H OCH_2), 4.04 (t; *J* ≈ 6.6 Hz; 2H, OCH_2), 1.85-1.78 (m; 3H, CH_2, CH), 1.68-1.46, 1.35-1.14 (2m; 25H, CH, 12 CH_2), 0.95 (d; *J* ≈ 6.4 Hz; 3H, CH_3), 0.86 (d; *J* ≈ 6.6 Hz; 6H, 2 CH_3), 0.51-0.49 (m; 2H, $SiCH_2$), 0.07 [s; 9H, Si-$(CH_3)_3$], 0.04 [s; 6H, Si-$(CH_3)_2$], 0.00 [s; 6H, Si-$(CH_3)_2$]. **^{13}C-NMR**: δ (ppm) = 164.46, 164.44, 164.31, 164.30 (CO), 163.82, 163.79, 155.42, 151.32, 150.63, 142.06, 138.01, 126.85, 126.80, 120.96 (Ar-C), 132.40, 131.82, 129.84, 128.31, 124.68, 122.10, 122.05, 120.43, 114.42, 114.40 (Ar-CH), 68.38, 66.72 (OCH_2), 39.20 (CH_2), 37.23, 35.97 (CH), 33.41, 29.81, 29.59, 29.55, 29.53, 29.36, 29.34, 29.06, 27.94, 25.96, 24.62, 23.20 (CH_2), 22.67, 22.57, 19.61 (CH_3), 18.27 ($SiCH_2$), 1.78, 1.24, 0.18 (CH_3). **^{29}Si-NMR**: δ (ppm) = 7.48, 7.04, -21.05. **$C_{68}H_{88}O_{12}Si_3$** (1181.69).

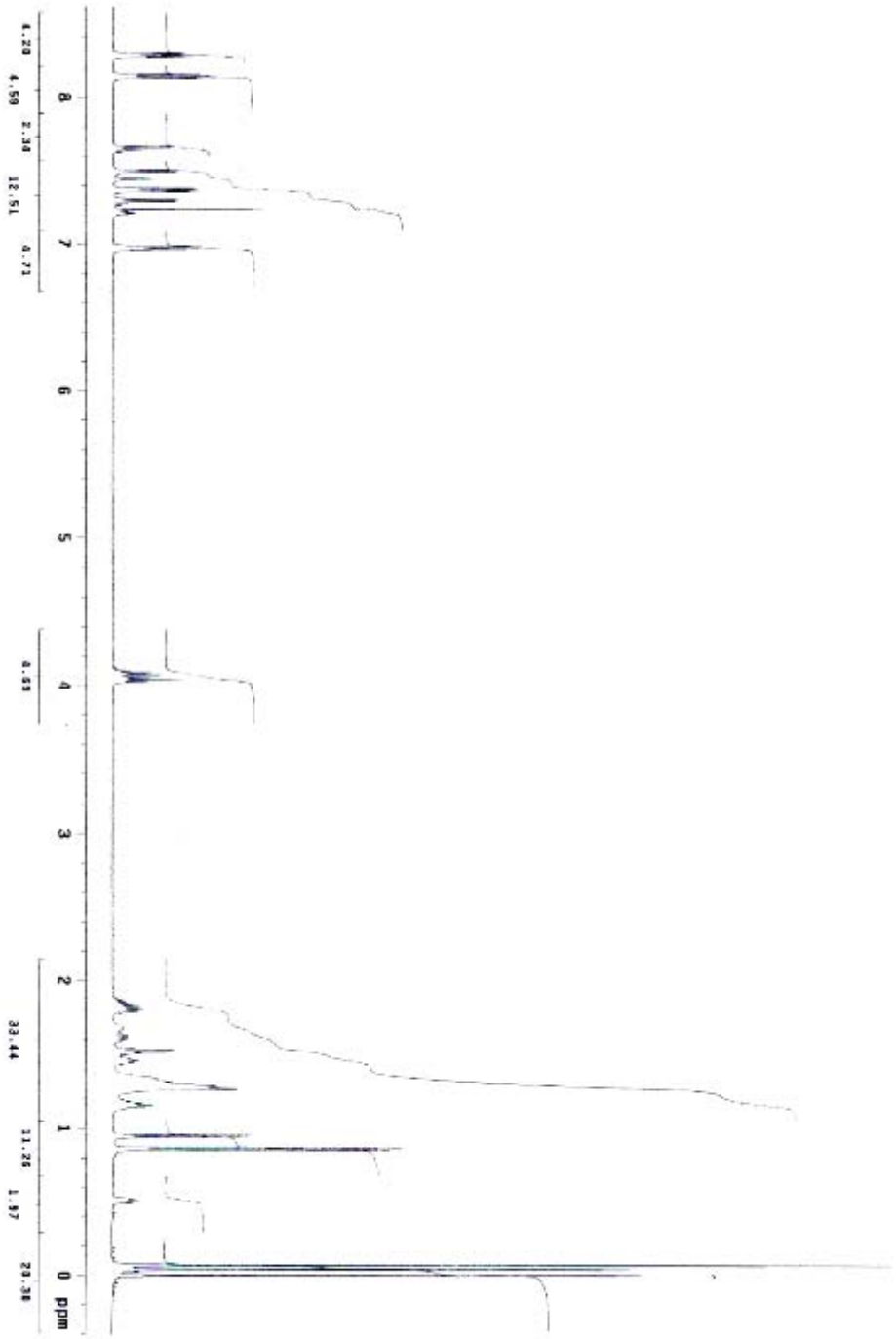


Fig. S6. ^{1}H-NMR spectrum ($CDCl_3$, 500 MHz) of compound ***rac*-Si$_3$-3b**.

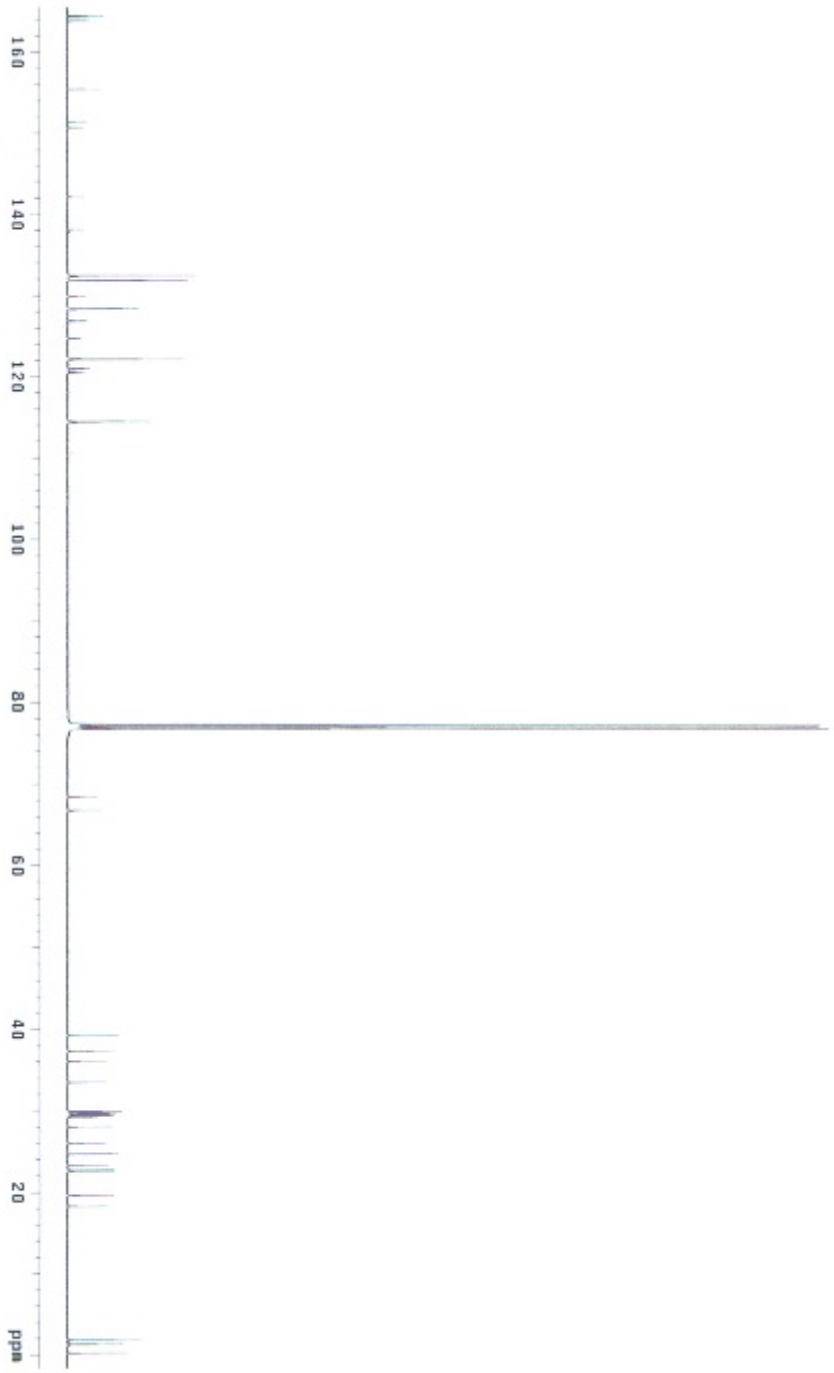


Fig. S7. ^{13}C-NMR spectrum ($CDCl_3$, 125 MHz) of compound ***rac*-Si$_3$-3b**.

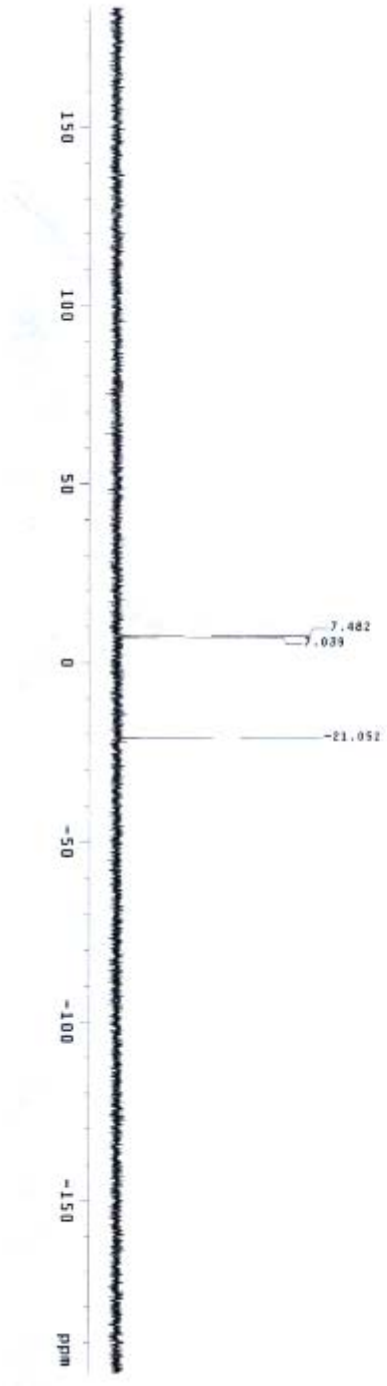


Fig. S8. ^{29}Si-NMR spectrum ($CDCl_3$, 100 MHz) of compound ***rac*-Si$_3$-3b**.

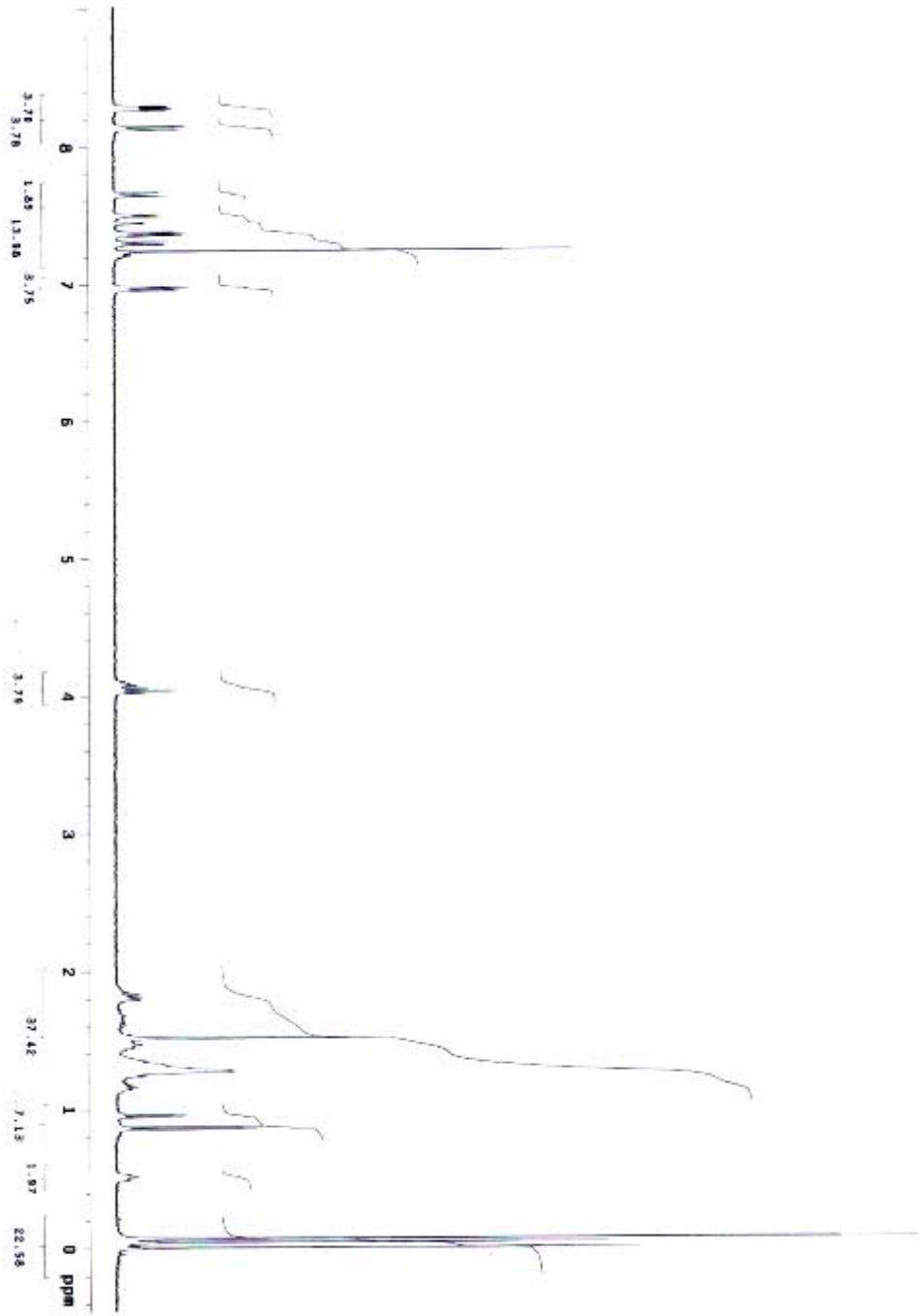


Fig. S9. ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of compound ***(S)*-Si$_3$-3b**.

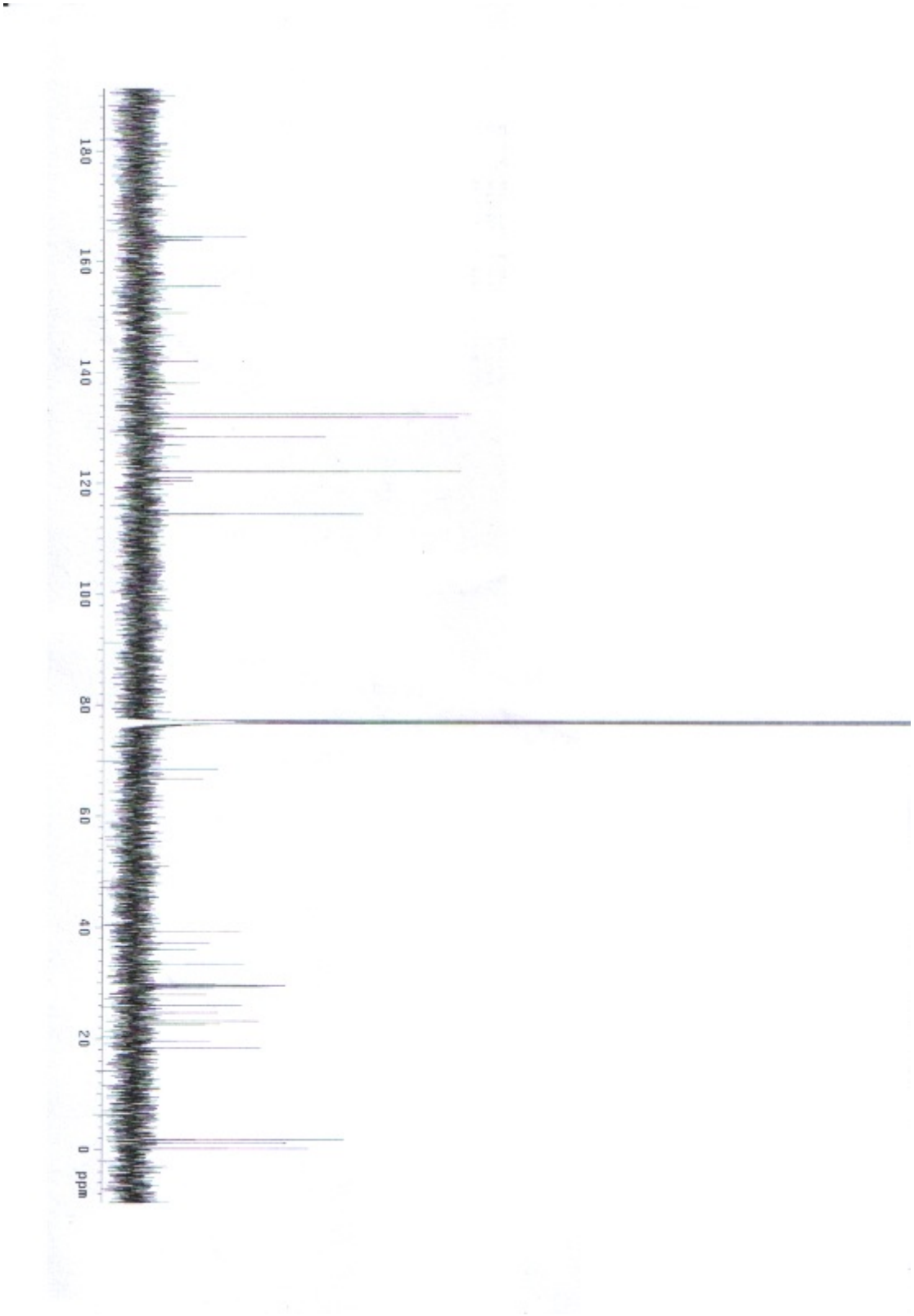


Fig. S10. ^{13}C-NMR spectrum ($CDCl_3$, 125 MHz) of compound ***(S)*-Si$_3$-3b**.

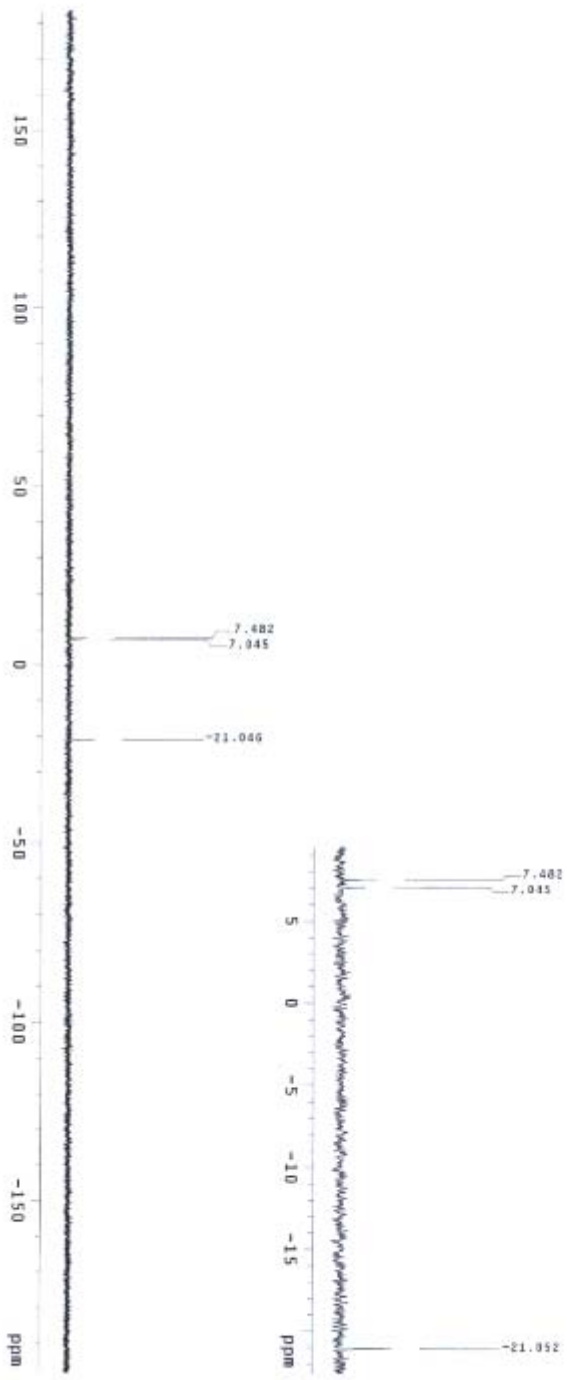


Fig. S11. ^{29}Si-NMR spectrum ($CDCl_3$, 100 MHz) of compound ***(S)*-Si$_3$-3b**.

3. References

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