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Ferroelectric and Antiferroelectric Odd-Even Behavior in a Tricarbosilane-Terminated Liquid Crystal Homologous Series

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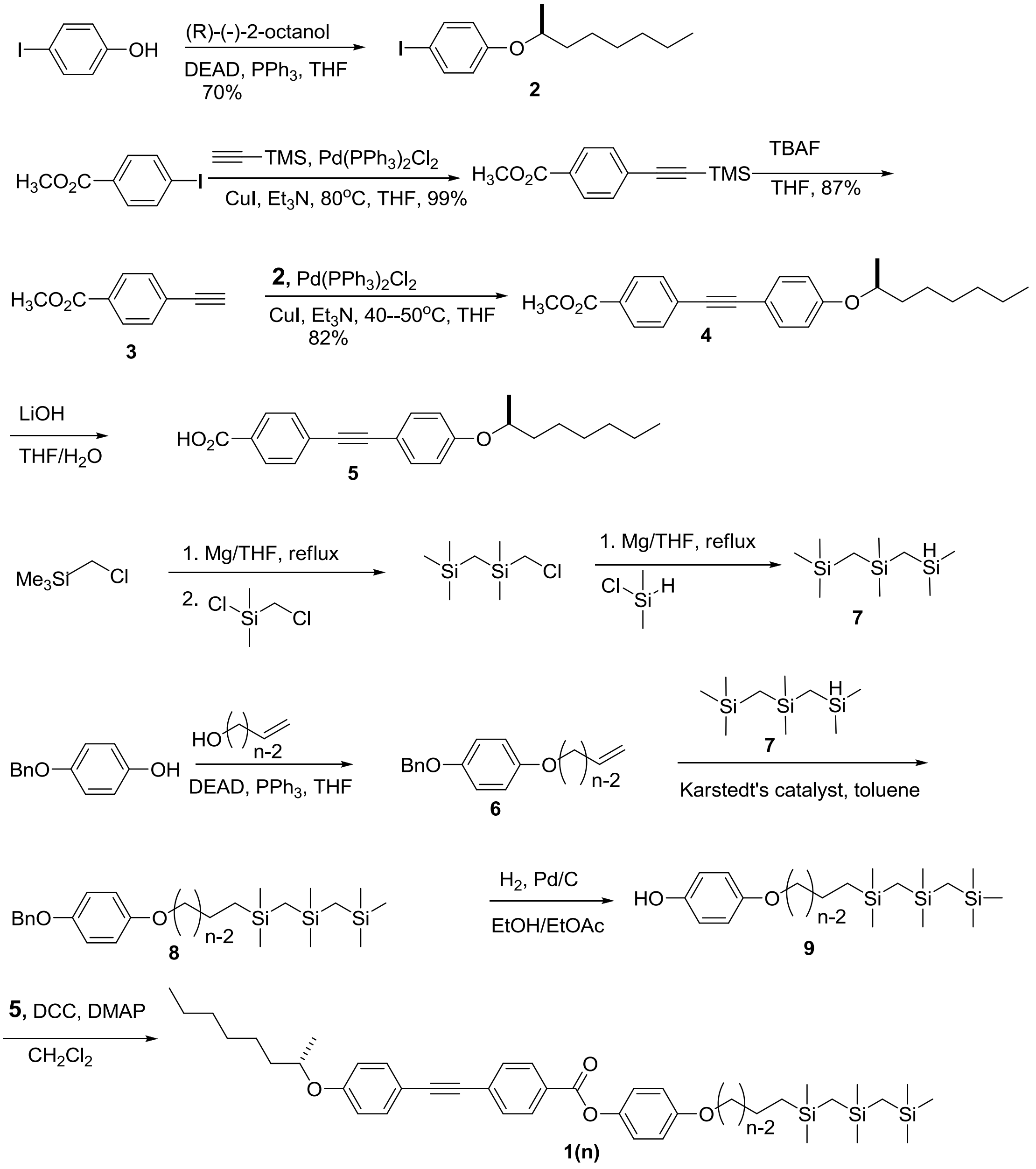
Supporting information:

General Information:

All glassware was oven-dried or flame-dried. CH_2Cl_2 and toluene were distilled from CaH_2 under nitrogen; THF were distilled from sodium benzophenone ketyl under nitrogen. Unless specifically mentioned, all chemicals are commercially available and were used as received. Flash chromatography was performed using 60 Å silica gel (37-75 μm). ^{1}H NMR spectra were recorded at either 400 MHz or 500 MHz, and ^{13}C NMR spectra were recorded at 100 MHz or 101 MHz in $CDCl_3$.Chemical shifts are reported in ppm referenced to residual solvent peaks as follows: $CDCl_3$ (7.26 ppm for^{1}H NMR; 77.23 ppm for ^{13}C NMR). Phase transition temperatures were determined by DSC using a Mettler Toledo DSC823. POM data was collected using a Nikon-HCS400 microscope with an Instec STC200 temperature-controlled stage. X-ray experiments were temperature controlled by an Instec STC200 hotstage, which was mounted on a Huber four-circle goniometer. The data were collected using a point detector with either of the following: synchrotron radiation at beamline X10A of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (High Resolution); or Cu K(α) radiation from a Rigaku UltraX-18 rotating anode generator, operated by the Liquid Crystal Materials Research Center, University of Colorado Boulder (Low Resolution).). Portion of Small-angle X-ray scattering (SAXS) was taken at the Advanced Light Source (ALS) beamline 7.3.3 at Lawrence Berkeley National Lab. A silver behenate sample was used as a standard calibrant. The 2D scattering patterns were collected on a 1M Pilatus detector from Dectris (www.dectris.com). The measured two-dimensional scattering data were calibrated and converted to q-space using the Nika macro for Igor Pro developed by Jan Ilavsky at Argonne National Laboratory, where the scattering wave vector $q = 4\pi \sin(\theta/2)/\lambda$, λ is the wavelength of the incident X-rays (0.124 nm) and θ is the scattering angle.

Experimental Section:

1. Synthesis



(S)-1-iodo-4-(octan-2-yloxy) benzene 2

To a solution of 4-iodophenol (3.0 g, 13.64 mmol), triphenylphosphine (4.65 g, 17.73 mmol) and (R)-2-octanol (3.25 mL, 20.45 mmol) in THF at room temperature was added DEAD (3.22 mL, 20.45 mmol). The mixture was stirred overnight, quenched by the addition of sodium hydroxide solution (0.5 N, 50 mL) and extracted with ether (50 mL×3). The combined organic layers were washed with brine and dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (EtOAc/Hexane 1:49) to give (S)-1-iodo-4-(octan-2-yloxy) benzene **2** (4.3 g, 94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.51 (m, 2H), 6.73 – 6.64 (m, 2H), 4.32 (h, *J* =

6.1 Hz, 1H), 1.86 – 1.66 (m, 1H), 1.65 – 1.51 (m, 1H), 1.50 – 1.21 (m, 11H), 0.92 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.21, 138.35, 138.28, 118.35, 118.28, 82.42, 74.14, 74.12, 36.50, 31.96, 29.43, 25.63, 22.78, 19.76, 14.30. (more peaks are observed due to H-C coupling).

Methyl 4-((trimethylsilyl)ethynyl)benzoate

Methyl 4-iodobenzoate (3.0 g, 11.45 mmol), CuI (221.8 mg, 1.16 mmol), and $Pd(PPh_3)_2Cl_2$ (401.8 mg, 0.57 mmol) were charged in a 100 mL sealed tube, which was purged with Ar. Triethylamine (6.0 mL) in THF (30 mL) solution was degassed by sparging with Ar for 15 min and cannulated into the tube. Ethynyltrimethylsilane (1.94 mL, 13.74 mmol) was then added via syringe. The mixture was heated at 80^{o}C for 2h and then cooled to room temperature, and filtered. The filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography (CH_2Cl_2/Hexane 1:2) to give methyl 4-((trimethylsilyl)ethynyl)benzoate (2.6 g, 98%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.91 (m, 2H), 7.53 – 7.46 (m, 2H), 3.88 (s, 3H), 0.25 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.18, 131.80, 129.66, 129.35, 127.72, 104.15, 97.50, 52.06, -0.17.

Methyl 4-ethynylbenzoate 3

A 1.0 M solution of tetrabutylammonium fluoride (12 mL) was added to a stirred solution of methyl 4-((trimethylsilyl)ethynyl)benzoate (2.7 g, 11.6 mmol) in THF at -78^{o}C. After stirring for 20 min, the reaction mixture was stirred at 0^{o}C for 1h. The reaction mixture was diluted with EtOAc, and then quenched by addition of sat. NH_4Cl (50 mL). The biphasic mixture was extracted with EtOAc (50 mL×3), and the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash chromatography (1:9 EtOAc:hexane) to provide **3** (1.6 g, 87%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.86 (m, 2H), 7.55 – 7.42 (m, 3H), 3.85 (s, 4H), 3.23 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.33, 132.08, 130.11, 129.47, 126.77, 82.83, 80.29, 52.27.

(S)-methyl 4-((4-(octan-2-yloxy)phenyl)ethynyl)benzoate 4

Methyl 4-ethynylbenzoate **3** (1.56 g, 9.73 mmol), $Pd(PPh_3)_2Cl_2$ (341.6 mg, 0.49 mmol), and CuI (185.3 mg) were charged in 100 mL sealed tube and purged with Ar. The solution of (S)-1-iodo-4-(octan-2-yloxy) benzene **2** (3.64 g, 10.95 mmol) and Triethylamine (18.4 mL) in 40 mL THF was degassed by sparging with Ar for 15 min and then cannulated into the sealed tube. The mixture was heated for 20 h at 45 ^{o}C, and then cooled to room temperature. The heterogeneous mixture was filtered through a short pad of celite and concentrated under reduced pressure. Purification by flash chromatography (5:95 EtOAc:Hexane) provided **4** (3.1 g, 87%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.96 (m, 2H), 7.57 – 7.51 (m, 2H), 7.49 – 7.42

(m, 2H), 6.89 – 6.80 (m, 2H), 4.35 (h, *J* = 6.1 Hz, 1H), 3.89 (s, 3H), 1.72 (dddd, *J* = 11.5, 9.8, 6.3, 3.1 Hz, 1H), 1.65 – 1.48 (m, 1H), 1.48 – 1.16 (m, 11H), 1.03 – 0.74 (t, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.55, 158.83, 133.35, 131.31, 129.54, 129.06, 128.56, 115.76, 114.33, 92.92, 87.47, 73.94, 52.18, 36.46, 31.88, 29.36, 25.55, 22.70, 19.69, 14.18. **HRMS** m/z calcd for $C_{48}H_{56}O_6Li^+$: 735.4283; found: 735.4229.

(S)-4-((4-(octan-2-yloxy)phenyl)ethynyl)benzoic acid 5

(S)-methyl 4-((4-(octan-2-yloxy)phenyl)ethynyl)benzoate **4** (3.04 g, 8.51 mmol) was dissolved in THF (30 mL). The LiOH solution (30 mL of aqueous solution, 7.14 g, 170.2 mmol) was added into the THF solution. The resulted mixture was heated to reflux overnight, cooled to room temperature, and then quenched by addition of 1M HCl. The mixture was extracted with EtOAc (50 mL×3). The combined organic layers were dried over Na_2SO_4, decanted, and concentrated under reduced pressure to provide the crude acid (2.85 g, 98%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.06 (m, 2H), 7.63 – 7.56 (m, 2H), 7.50 – 7.45 (m, 2H), 6.89 – 6.84 (m, 2H), 4.39 (h, *J* = 6.1 Hz, 1H), 1.75 (dddd, *J* = 13.5, 9.9, 6.4, 5.0 Hz, 1H), 1.58 (ddt, *J* = 13.6, 11.1, 5.3 Hz, 1H), 1.49 – 1.19 (m, 11H), 0.93 – 0.84 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.83, 159.04, 133.54, 131.57, 130.33, 129.67, 128.27, 115.95, 114.35, 93.57, 87.55, 74.20, 36.59, 32.00, 29.47, 25.69, 22.82, 19.88, 14.31. **HRMS** m/z calcd for $C_{23}H_{25}O_3^-$: 349.1809; found: 349.1807.

Trisilane tail 7

Mg (1.35 g, 55.37 mmol) was charged in 250 mL three necked round bottom flask, 20 mL THF was added to the flask to barely cover the Mg(1.35 g, 55.37 mmol), and then the solution of chloromethyltrimethyl silane (5.66 g, 46.14 mmol) in 15 mL dry THF was cannulated into the flask slowly. The mixture was treated with a small amount of iodine, and heated with heat gun to initiate the reaction. The additional 20 mL THF was cannulated into the reaction mixture slowly. The mixture was heated to reflux for 2 h, cooled to room temperature, and transferred to a sealed flask via a cannular, and treated chloro(chloromethyl)dimethyl silane (5.5 mL, 41.55 mmol) through syringe. The mixture was heated to reflux overnight. The reaction was quenched by addition 200 mL sat. NH_4Cl solution and extracted with hexane (50 mL×3). The combined organic layers were dried over Na_2SO_4, and concentrated under reduced pressure. The crude was purified by distillation under vacuum to provide (chloromethyl)dimethyl((trimethylsilyl)methyl)silane.

To a solution of Mg (900.65 mg, 37.06 mmol) in THF (20 mL) was added (chloromethyl)dimethyl((trimethylsilyl)methyl)silane (6.017 g, 30.88 mmol in 20 mL THF) dropwise. The mixture was heated to reflux for 2 h and transferred to another flask via cannular. Chlorodimethylsilane (5.26 g, 55.58 mmol) was added dropwise to the flask in an ice bath. The mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched by addition of sat. NH_4Cl and extracted with hexane (50 mL×3). The combined organic layers was dried over Na_2SO_4, and concentrated under reduced pressure to obtain clear oil. The crude was purified by vacuum distillation to afford **7**.

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.10 (s, 3H), 0.09 (s, 3H), 0.05 (s, 6H), 0.02 (s, 9H), -0.22 (s, 1H), -0.23 (s, 1H), -0.24 (s, 2H) (Si-H can not be observed due to multiplet coupling).

1-(benzyloxy)-4-(undec-10-enyloxy)benzene 6a

To a solution of 4-(benzyloxy)phenol (1.0 g, 5.0 mmol), triphenylphosphine (1.7 g, 6.5 mmol) and 10-Undecen-1-ol (1.46 mL, 7.49 mmol) in THF at room temperature was added diethylazodicarboxylate (DEAD 1.2 mL, 7.49 mmol). The mixture was stirred overnight, quenched by the addition of sodium hydroxide solution (0.5N, 50 mL) and extracted with ether (50 mL×3). The combined organic layers were washed with brine and dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (EtOAc/Hexane 1:20) to give **6a** (**n** = 11) (1.23 g, 70%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54-7.28 (m, 5H), 6.88 (m, 2H), 6.91 – 6.82 (m, 2H) (m, 2H), 5.86 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.07 (dt, *J* = 2.2, 1.6 Hz, 1H), 5.04 (s, 2H), 4.99 (ddt, *J* = 10.2, 2.2, 1.2 Hz, 1H), 3.93 (t, J = 6.5 Hz, 2H), 2.02 (m, 2H), 1.73 (p, J = 7.0 Hz, 2H), 1.44-1.13 (m, 12 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 152.8, 139.2, 137.3, 128.5, 127.9, 127.5, 115.7, 115.3, 114.1, 70.7, 68.6, 33.8, 29.5, 29.4, 29.4, 29.1, 28.9, 26.0.

In essentially the same manner, 1-(benzyloxy)-4-(dec-9-enyloxy)benzene **6b** (**n** = 10) was prepared in 69% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.29 (m, 5H), 6.99 – 6.90 (m, 2H), 6.91 – 6.82 (m, 2H), 5.86 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.09 – 5.01 (m, 3H), 4.99 (ddt, *J* = 10.2, 2.2, 1.2 Hz, 1H), 3.93 (t, *J* = 6.6 Hz, 2H), 2.17 – 2.02 (m, 2H), 1.79 (dq, *J* = 8.4, 6.6 Hz, 2H), 1.56 – 1.25 (m, 10H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.65, 152.97, 139.33, 137.48, 128.70, 128.02, 127.64, 115.91, 115.50, 114.35, 70.79, 68.70, 33.99, 29.61, 29.55, 29.25, 29.09, 26.23.

HRMS m/z calcd for $C_{23}H_{30}O_2Li^+$: 345.2401; found: 345.2402.

Componds **6c** (**n** = 9), **6d** (**n** = 8), **6e** (**n** = 7), **6f** (**n** = 6), **6g** (**n** = 5) were similarly prepared in 75%, 70%, 73%, 75% and 78% yield, respectively.

6c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.30 (m, 5H), 7.02 – 6.93 (m, 2H), 6.95 – 6.86 (m, 2H), 5.91 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.14 – 5.00 (m, 4H), 3.96 (t, *J* = 6.5 Hz, 2H), 2.24 – 2.04 (m, 2H), 1.83 (dq, *J* = 8.3, 6.6 Hz, 2H), 1.62 – 1.25 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.64, 152.97, 139.24, 137.49, 128.67, 127.99, 127.62, 115.89, 115.47, 114.42, 70.74, 68.63, 33.97, 29.54, 29.44, 29.24, 29.03, 26.20.

HRMS m/z calcd for $C_{44}H_{56}O_4Li^+$: 655.4335; found: 655.4335.

6d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.35 (m, 5H), 7.05 – 6.96 (m, 2H), 6.92 (dd, *J* = 9.1, 1.7 Hz, 2H), 5.92 (ddtd, *J* = 16.9, 10.1, 6.7, 1.8 Hz, 1H), 5.19 – 4.97 (m, 4H),

3.97 (t, *J* = 6.5 Hz, 2H), 2.17 (q, *J* = 6.9 Hz, 2H), 1.85 (p, *J* = 6.8 Hz, 2H), 1.65 – 1.28 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.59, 152.93, 139.09, 137.45, 128.62, 127.94, 127.56, 115.84, 115.42, 114.45, 70.68, 68.54, 33.87, 29.47, 29.02, 28.97, 26.06. **HRMS** m/z calcd for $C_{42}H_{52}O_4Li^+$: 627.4021; found: 627.4022.

6e: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.29 (m, 5H), 6.99 – 6.91 (m, 2H), 6.92 – 6.82 (m, 2H), 5.87 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.12 – 4.96 (m, 4H), 3.94 (t, *J* = 6.5 Hz, 2H), 2.20 – 2.06 (m, 2H), 1.88 – 1.75 (m, 2H), 1.58 – 1.42 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.61, 152.99, 139.01, 137.48, 128.70, 128.02, 127.64, 115.92, 115.49, 114.63, 70.79, 68.59, 33.89, 29.40, 28.84, 25.74. **HRMS** m/z calcd for $C_{40}H_{48}O_4Li^+$: 599.3708; found: 599.3735.

6f: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.39 (m, 5H), 7.07 – 7.00 (m, 2H), 7.00 – 6.92 (m, 2H), 5.98 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.25 – 5.05 (m, 4H), 4.01 (t, *J* = 6.4 Hz, 2H), 2.26 (m, 2H), 1.97 – 1.83 (m, 2H), 1.76 – 1.63 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.51, 152.91, 138.64, 137.40, 128.57, 127.89, 127.51, 115.79, 115.36, 114.82, 70.58, 68.26, 33.56, 28.91, 25.42. **HRMS** m/z calcd for $C_{38}H_{44}O_4Li^+$: 571.3395; found: 571.3405.

6g: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.33 (m, 5H), 7.02 – 6.92 (m, 2H), 6.94 – 6.85 (m, 2H), 5.92 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.19 – 5.03 (m, 4H), 3.97 (t, *J* = 6.5 Hz, 2H), 2.37 – 2.23 (m, 2H), 1.98 – 1.86 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.54, 153.02, 138.02, 137.45, 128.68, 128.00, 127.62, 115.89, 115.52, 115.29, 70.75, 67.86, 30.30, 28.67. **HRMS** m/z calcd for $C_{36}H_{40}O_4Li^+$: 543.3082; found: 543.3093.

Trisilanyl benzene 8a

Freshly dry toluene (12 mL) was cannulated to a flask charged with **6a** (1.23 g, 3.49 mmol) and **7** (1.14 g, 5.23 mmol). The flask was purged with Ar, treated with Karstedt’s catalyst (0.7 mL) dropwise and wrapped with aluminum foil. The mixture was stirred at room temperature for 3 days and concentrated under reduced pressure. The crude product was purified by column chromatography (Hexane/$CHCl_3$ 2:1) to give **8a** (1.3 g, 65%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.30 (m, 5H), 6.88 (m, 2H), 6.80 (m, 2H), 4.99 (s, 2H), 3.87 (t, 2H, J = 6.5 Hz), 1.73 (p, 2H, J = 7.0 Hz), 1.43-1.25 (m, 16 H), 0.44 (m, 2H), 0.00 (m, 21H), -0.30 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 152.8, 137.3, 128.5, 127.9, 127.5, 115.8, 115.4, 70.7, 68.6, 33.7, 29.7, 29.6, 29.6, 29.4, 29.4, 26.1, 23.4, 18.1, 5.8, 4.0, 2.5, 1.5, -0.4. **HRMS** m/z calcd for $C_{33}H_{58}O_2Si_3H^+$: 571.3818; found: 571.3821.

Componds **8b**, **8c**, **8d**, **8e**, **8f**, **8g** were similarly prepared in 65%, 66%, 65%, 68%, 66%, and 65% yield, respectively.

8b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.28 (m, 5H), 6.99 – 6.87 (m, 2H), 6.88 – 6.77 (m, 2H), 5.02 (s, 2H), 3.91 (t, *J* = 6.6 Hz, 2H), 1.76 (m, 2H), 1.45 (m, 2H), 1.40 – 1.15 (m, 12H), 0.49 (m, 2H), 0.06 (s, 6H), 0.04 (s, 9H), 0.01 (s, 6H), -0.24 (s, 2H), -0.27 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.70, 153.00, 137.53, 128.74, 128.07, 127.69, 115.97, 115.55, 70.87, 68.80, 33.95, 29.86, 29.79, 29.66, 29.61, 26.29, 24.20, 18.28, 5.98, 4.21, 2.70, 1.71, -0.20. **HRMS** m/z calcd for $C_{32}H_{56}O_2Si_3H^+$: 557.3661; found: 557.3664.

8c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.28 (m, 5H), 6.98 – 6.88 (m, 2H), 6.88 – 6.77 (m, 2H), 5.03 (s, 2H), 3.91 (t, *J* = 6.6 Hz, 2H), 1.87 – 1.69 (m, 2H), 1.55 – 1.14 (m, 12H), 0.62 – 0.44 (m, 2H), 0.07 (s, 6H), 0.05 (s, 9H), 0.02 (s, 6H), -0.23 (s, 2H), -0.26 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.69, 153.00, 137.52, 128.74, 128.06, 127.68, 115.96, 115.54, 70.86, 68.78, 33.93, 29.77, 29.69, 29.61, 29.56, 26.29, 24.20, 18.27, 5.98, 4.20, 2.70, 1.71, -0.20. **HRMS** m/z calcd for $C_{31}H_{54}O_2Si_3H^+$: 543.3505; found: 543.3509.

8d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.28 (m, 5H), 6.97 – 6.88 (m, 2H), 6.89 – 6.80 (m, 2H), 5.03 (s, 2H), 3.92 (t, *J* = 6.6 Hz, 2H), 1.85 – 1.70 (m, 2H), 1.54 – 1.19 (m, 10H), 0.60 – 0.45 (m, 2H), 0.08 (s, 6H), 0.05 (s, 9H), 0.03 (s, 6H), -0.23 (s, 2H), -0.25 (d, *J* = 1.2 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.70, 153.00, 137.53, 128.73, 128.06, 127.68, 115.96, 115.55, 70.86, 68.78, 33.87, 29.61, 29.54, 26.32, 24.19, 18.28, 5.99, 4.21, 2.71, 1.72, -0.20. **HRMS** m/z calcd for $C_{30}H_{52}O_2Si_3H^+$: 529.3348; found: 529.3345.

8e: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.29 (m, 5H), 6.96 – 6.88 (m, 2H), 6.88 – 6.79 (m, 2H), 5.03 (s, 2H), 3.91 (t, *J* = 6.6 Hz, 2H), 1.82 – 1.72 (m, 2H), 1.55 – 1.23 (m, 8H), 0.60 – 0.45 (m, 2H), 0.07 (s, 6H), 0.04 (s, 9H), 0.02 (s, 6H), -0.24 (s, 2H), -0.26 (s, 2H). **HRMS** m/z calcd for $C_{29}H_{50}O_2Si_3H^+$: 515.3192; found: 515.3192.

8f: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.29 (m, 5H), 6.94 (dd, *J* = 9.1, 2.2 Hz, 2H), 6.91 – 6.83 (dd, *J* = 9.1, 2.2 Hz, 2H), 5.04 (s, 2H), 3.93 (t, *J* = 6.6 Hz, 2H), 1.91 – 1.70 (m, 2H), 1.57 – 1.20 (m, 6H), 0.66 – 0.49 (m, 2H), 0.10 (s, 6H), 0.08 (s, 9H), 0.05 (s, 6H), -0.21 (s, 2H), -0.23 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.68, 152.99, 137.51, 128.72, 128.04, 127.66, 115.93, 115.52, 70.82, 68.75, 33.65, 29.55, 25.99, 24.14, 18.23, 5.97, 4.19, 2.71, 1.72, -0.22. **HRMS** m/z calcd for $C_{28}H_{48}O_2Si_3H^+$: 501.3035; found: 501.3041.

8g: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.30 (m, 5H), 6.98 – 6.91 (m, 2H), 6.87 (m, 2H), 5.04 (s, 2H), 3.93 (t, *J* = 6.6 Hz, 2H), 1.87 – 1.71 (m, 2H), 1.51 (m, 2H), 1.45 – 1.22 (m, 2H), 0.62 – 0.51 (m, 2H), 0.10 (s, 6H), 0.07 (s, 9H), 0.06 (s, 6H), -0.21 (s, 2H), -0.23 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.69, 153.00, 137.53, 128.72, 128.04, 127.66,

115.95, 115.54, 70.84, 68.75, 30.24, 29.35, 24.06, 18.24, 5.98, 4.20, 2.71, 1.72, -0.22.
HRMS m/z calcd for $C_{27}H_{46}O_2Si_3H^+$: 487.2879; found: 487.2878.

Phenol 9a

An ethanol solution (20 mL) of **8a** (1.3 g, 2.28 mmol) was treated with palladium on charcoal (10%, 242.6 mg) at room temperature overnight under a hydrogen atmosphere. The reaction mixture was filtered through a short pad of celite and rinsed with EtOAc. Evaporation of the solvent gave **9a** (1.04 g, 95%) without further purification.
9a: ^{1}H NMR (400 MHz, $CDCl_3$) δ6.79 (d, *J* = 9.2 Hz, 2H), 6.75 (d, *J* = 9.2 Hz, 2H), 5.67 (s, 1H), 3.89 (t, *J* = 6.6 Hz, 2H), 1.96 – 1.60 (m, 2H), 1.65 – 1.00 (m, 16H), 0.50 (m, 2H), 0.07 (s, 6H), 0.04 (s, 9H), 0.02 (s, 6H), -0.24 (s, 2H), -0.26 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.23, 149.67, 116.24, 115.87, 69.05, 33.93, 29.91, 29.86, 29.75, 29.65, 29.57, 29.54, 26.24, 24.18, 18.25, 5.96, 4.19, 2.70, 1.70, -0.21

Componds **9b**, **9c**, **9d**, **9e**, **9f**, **9g** were similarly prepared in 95%, 97%, 96%, 98%, 98%, and 99% yield, respectively.
9b: ^{1}H NMR (400 MHz, $CDCl_3$) δ6.79 (d, *J* = 9.2 Hz, 2H), 6.75 (d, *J* = 9.2 Hz, 2H), 5.87 (s, 1H), 3.90 (t, *J* = 6.3 Hz, 2H), 1.90 – 1.62 (m, 2H), 1.62 – 1.00 (m, 14H), 0.50 (m, 2H), 0.07 (s, 6H), 0.05 (s, 9H), 0.02 (s, 6H), -0.23 (s, 2H), -0.26 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.20, 149.69, 116.25, 115.86, 69.05, 33.93, 29.84, 29.77, 29.63, 29.59, 29.55, 26.24, 24.18, 18.25, 5.95, 4.18, 2.69, 1.70, -0.21.

9c: ^{1}H NMR (400 MHz, $CDCl_3$) δ6.79 (d, *J* = 9.2 Hz, 2H), 6.75 (d, *J* = 9.2 Hz, 2H), 5.64 (s, 1H), 3.90 (t, *J* = 6.6 Hz, 2H), 1.96 – 1.60 (m, 2H), 1.38 (m, 12H), 0.50 (m, 2H), 0.07 (s, 6H), 0.04 (s, 9H), 0.02 (s, 6H), -0.24 (s, 2H), -0.26 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.25, 149.67, 116.24, 115.87, 69.05, 33.91, 29.75, 29.67, 29.57, 29.54, 26.24, 24.18, 18.25, 5.96, 4.19, 2.70, 1.70, -0.21.

9d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (d, *J* = 9.2 Hz, 2H), 6.75 (d, *J* = 9.2 Hz, 2H), 4.74 (s, 1H), 3.89 (t, *J* = 6.6 Hz, 2H), 1.82 – 1.68 (m, 2H), 1.54 – 1.10 (m, 10H), 0.58 – 0.42 (m, 2H), 0.04 (s, 6H), 0.02 (s, 9H), -0.01 (s, 6H), -0.26 (s, 2H), -0.28 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.47, 149.55, 116.18, 115.80, 68.95, 33.86, 29.59, 29.53, 26.31, 24.18, 18.27, 5.98, 4.21, 2.70, 1.70, -0.22.

9e: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (d, *J* = 9.4 Hz, 2H), 6.75 (d, *J* = 9.4 Hz, 2H), 4.83 (s, 1H), 3.90 (t, *J* = 6.6 Hz, 2H), 1.83 – 1.66 (m, 2H), 1.53 – 1.19 (m, 8H), 0.59 – 0.42 (m, 2H), 0.05 (s, 6H), 0.03 (s, 9H), 0.00 (s, 6H), -0.25 (s, 2H), -0.28 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.44, 149.52, 116.20, 115.83, 68.97, 33.84, 29.61, 29.36, 26.21, 24.14, 18.26, 5.98, 4.20, 2.70, 1.71, -0.22.

9f: ^{1}H NMR (500 MHz, $CDCl_3$) δ6.79 (d, *J* = 9.4 Hz, 2H), 6.75 (d, *J* = 9.4 Hz, 2H), 3.88 (t, *J* = 6.6 Hz, 2H), 1.81 – 1.67 (m, 2H), 1.50 – 1.28 (m, 6H), 0.63 – 0.41 (m, 2H), 0.05 (s, 6H), 0.03 (s, 9H), 0.00 (s, 6H), -0.25 (s, 2H), -0.28 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.31, 149.59, 116.23, 115.86, 69.06, 33.64, 29.50, 25.96, 24.12, 18.22, 5.96, 4.18, 2.70, 1.71, -0.23.

9g: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (d, *J* = 9.4 Hz, 1H), 6.75 (d, *J* = 9.3 Hz, 1H), 4.92 (s, 1H), 3.90 (t, *J* = 6.6 Hz, 2H), 1.83 – 1.70 (m, 2H), 1.53 – 1.41 (m, 2H), 1.41 – 1.29 (m, 2H), 0.59 – 0.45 (m, 2H), 0.06 (s, 6H), 0.03 (s, 9H), 0.01 (s,6H), -0.25 (s, 2H), -0.27 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.41, 149.53, 116.21, 115.85, 69.00, 30.21, 29.31, 24.04, 18.24, 5.97, 4.19, 2.70, 1.71, -0.24.

Benzoate 1(11)
9a (504.1 mg, 1.07 mmol), **5** (374.5 mg, 1.07 mmol) and DMAP (13.1 mg) were charged with a 50 mL round bottom flask. Dry DCM (10 mL) was added, followed by DCC (264.9 mg, 1.28 mmol). The reaction was stirred at room temperature for 1 day, diluted with DCM, quenched by addition of 5% HCl (50 mL) and extracted with DCM (50 mL×3). The combined organic layers were washed with brine and dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (EtOAc/Hexane 3:97) to give **1(11)** (767.3 mg, 90%). The final product was purified further via recrystallization with CH_3CN.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.13 (m, 2H), 7.65 – 7.60 (m, 2H), 7.52 – 7.47 (m, 2H), 7.18 – 7.08 (m, 2H), 6.98 – 6.91 (m, 2H), 6.91 – 6.85 (m, 2H), 4.40 (h, *J* = 6.1 Hz, 1H), 3.96 (t, *J* = 6.5 Hz, 2H), 1.89 – 1.53 (m, 4H), 1.52 – 1.20 (m, 28H), 0.95 – 0.85 (m, 2H), 0.59 – 0.44 (m, 2H), 0.07 (s, 6H), 0.05 (s, 9H), 0.02 (s, 6H), -0.23 (s, 2H), -0.26 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.23, 159.01, 157.10, 144.33, 133.49, 131.54, 130.21, 129.27, 128.66, 122.53, 115.87, 115.20, 114.36, 93.44, 87.57, 74.11, 68.56, 36.58, 33.94, 31.99, 29.87, 29.83, 29.81, 29.64, 29.62, 29.49, 29.46, 26.26, 25.67, 24.19, 22.81, 19.86, 18.25, 14.31, 5.96, 4.19, 2.69, 1.70, -0.21. **HRMS** m/z calcd for $C_{49}H_{76}O_4Si_3Li^+$: 819.5207; found: 819.5202. EA found: C, 72.64; H, 9.37. (calcd for $C_{49}H_{76}O_4Si_3$: C, 72.36; H, 9.42).

Componds **1(10)**, **1(9)**, **1(8)**, **1(7)**, **1(6)**, **1(5)** were similarly prepared in 92%, 90%, 89%, 93%, 90%, and 91% yield, respectively.

1(10): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.7 Hz, 2H), 7.62 (d, *J* = 8.7 Hz, 2H), 7.48 (d, *J* = 8.9 Hz, 2H), 7.12 (d, *J* = 9.0 Hz, 2H), 6.93 (d, *J* = 9.1 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 4.40 (h, *J* = 6.1 Hz, 1H), 3.96 (t, *J* = 6.5 Hz, 2H), 1.85 – 1.68 (m, 2H), 1.66 – 1.53 (m, 2H), 1.53 – 1.19 (m, 26H), 0.94 – 0.85 (m, 2H), 0.59 – 0.42 (m, 2H), 0.06 (s, 6H), 0.03 (s, 9H), 0.01 (s, 6H), -0.25 (s, 2H), -0.27 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.30, 159.03, 157.12, 144.35, 133.53, 131.59, 130.23, 129.29, 128.67, 122.54, 115.94, 115.28, 114.37, 93.44, 87.57, 74.17, 68.61, 36.59, 33.95, 32.00, 29.85, 29.79, 29.63, 29.61, 29.49, 29.47, 26.27, 25.69, 24.20, 22.82, 19.87, 18.27, 14.32, 5.97, 4.20, 2.69, 1.70, -0.21. **HRMS** m/z calcd for

$C_{48}H_{74}O_4Si_3Li^+$: 805.5050; found: 805.5051. EA found: C, 71.90; H, 9.44. (calcd for $C_{48}H_{74}O_4Si_3$: C, 72.12; H, 9.33).

1(9): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.7 Hz, 2H), 7.62 (d, *J* = 8.7 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 9.0 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 4.40 (h, *J* = 6.1 Hz, 1H), 3.96 (t, *J* = 6.5 Hz, 2H), 1.91 – 1.67 (m, 2H), 1.66 – 1.53 (m, 2H), 1.53 – 1.19 (m, 24H), 0.96 – 0.80 (m, 2H), 0.56 – 0.41 (m, 2H), 0.05 (s, 6H), 0.03 (s, 9H), 0.00 (s, 6H), -0.25 (s, 2H), -0.28 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.31, 159.03, 157.13, 144.35, 133.53, 131.60, 130.24, 129.29, 128.68, 122.55, 115.94, 115.29, 114.37, 93.44, 87.57, 74.18, 68.62, 36.59, 33.93, 32.00, 29.77, 29.67, 29.56, 29.50, 29.47, 26.26, 25.69, 24.20, 22.82, 19.88, 18.27, 14.32, 5.97, 4.20, 2.69, 1.70, -0.21. **HRMS** m/z calcd for $C_{47}H_{72}O_4Si_3NH_4^+$: 802.5077; found: 819.5061. EA found: C, 72.05; H, 9.22. (calcd for $C_{47}H_{72}O_4Si_3$: C, 71.88; H, 9.24).

1(8): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.12 (m, 2H), 7.66 – 7.58 (m, 2H), 7.53 – 7.44 (m, 2H), 7.15 – 7.09 (m, 2H), 6.97 – 6.91 (m, 2H), 6.91 – 6.83 (m, 2H), 4.40 (h, *J* = 6.1 Hz, 1H), 3.96 (t, *J* = 6.5 Hz, 2H), 1.88 – 1.73 (m, 2H), 1.63 – 1.52 (m, 2H), 1.52 – 1.17 (m, 22H), 0.98 – 0.79 (m, 2H), 0.60 – 0.41 (m, 2H), 0.05 (s, 6H), 0.03 (s, 9H), 0.01 (s, 6H), -0.25 (s, 2H), -0.27 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.30, 159.03, 157.13, 144.35, 133.53, 131.59, 130.23, 129.29, 128.68, 122.54, 115.94, 115.29, 114.37, 93.43, 87.57, 74.17, 68.62, 36.59, 33.87, 32.00, 29.58, 29.54, 29.49, 29.47, 26.30, 25.69, 24.19, 22.82, 19.88, 18.27, 14.32, 5.98, 4.20, 2.70, 1.70, -0.21. **HRMS** m/z calcd for $C_{46}H_{70}O_4Si_3H^+$: 771.4655; found: 771.4629. EA found: C, 71.63; H, 9.07. (calcd for $C_{46}H_{70}O_4Si_3$: C, 71.63; H, 9.15).

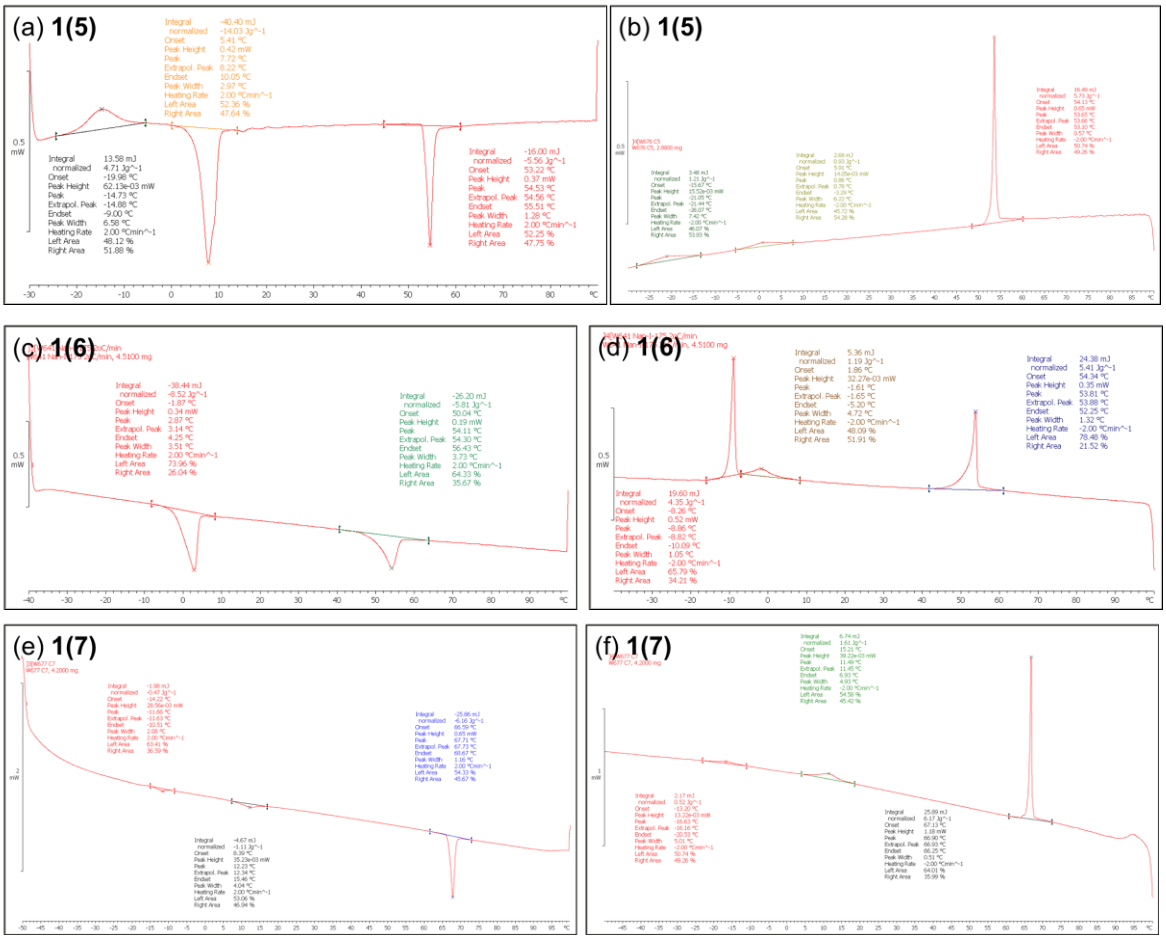
1(7): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 – 8.12 (m, 2H), 7.64 – 7.59 (m, 2H), 7.51 – 7.44 (m, 2H), 7.15 – 7.09 (m, 2H), 6.97 – 6.91 (m, 2H), 6.90 – 6.84 (m, 2H), 4.40 (h, *J* = 6.1 Hz, 1H), 3.96 (t, *J* = 6.6 Hz, 2H), 1.86 – 1.67 (m, 2H), 1.65 – 1.52 (m, 2H), 1.52 – 1.21 (m, 20H), 0.98 – 0.80 (m, 2H), 0.58 – 0.44 (m, 2H), 0.05 (s, 6H), 0.03 (s, 9H), 0.00 (s, 6H), -0.25 (s, 2H), -0.27 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.30, 159.04, 157.13, 144.36, 133.53, 131.59, 130.23, 129.29, 128.69, 122.55, 115.95, 115.29, 114.37, 93.44, 87.57, 74.18, 68.61, 36.59, 33.84, 32.00, 29.52, 29.47, 29.35, 26.21, 25.69, 24.15, 22.82, 19.89, 18.27, 14.32, 5.99, 4.21, 2.70, 1.70, -0.22. **HRMS** m/z calcd for $C_{45}H_{68}O_4Si_3H^+$: 757.4499; found: 757.4488. EA found: C, 71.46; H, 9.07. (calcd for $C_{45}H_{68}O_4Si_3$: C, 71.37; H, 9.05).

1(6): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.14 (m, 2H), 7.66 – 7.59 (m, 2H), 7.52 – 7.45 (m, 2H), 7.17 – 7.08 (m, 2H), 6.98 – 6.91 (m, 2H), 6.91 – 6.83 (m, 2H), 4.40 (h, *J* = 6.1 Hz, 1H), 3.96 (t, *J* = 6.5 Hz, 2H), 1.98 – 1.68 (m, 2H), 1.68 – 1.53 (m, 2H), 1.53 – 1.11 (m, 18H), 0.97 – 0.82 (m, 2H), 0.59 – 0.45 (m, 2H), 0.06 (s, 6H), 0.04 (s, 9H), 0.02 (s, 6H), -0.24 (s, 2H), -0.26 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.28, 159.02, 157.12, 144.34, 133.52, 131.58, 130.22, 129.28, 128.67, 122.54, 115.93, 115.27, 114.36, 93.44, 87.57, 74.15, 68.61, 36.58, 33.63, 32.00, 29.47, 29.43, 25.97, 25.68, 24.14, 22.82, 19.87, 18.23, 14.32, 5.97, 4.19, 2.70, 1.70, -0.23. **HRMS** m/z calcd for $C_{44}H_{66}O_4Si_3Li^+$: 749.4424; found: 749.4436. EA found: C, 70.83; H, 9.15. (calcd for $C_{44}H_{66}O_4Si_3$: C, 71.10; H, 8.95).

1(5): ^1H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.12 (m, 2H), 7.65 – 7.58 (m, 2H), 7.52 – 7.42 (m, 2H), 7.16 – 7.07 (m, 2H), 6.97 – 6.90 (m, 2H), 6.90 – 6.82 (m, 2H), 4.40 (h, *J* = 6.1 Hz, 1H), 3.96 (t, *J* = 6.6 Hz, 2H), 1.96 – 1.66 (m, 2H), 1.65 – 1.52 (m, 2H), 1.52 – 1.12 (m, 16H), 0.95 – 0.81 (m, 2H), 0.60 – 0.48 (m, 2H), 0.06 (s, 6H), 0.03 (s, 9H), 0.02 (s, 6H), -0.25 (s, 2H), -0.26 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.30, 159.03, 157.12, 144.35, 133.53, 131.59, 130.23, 129.29, 128.68, 122.54, 115.94, 115.29, 114.37, 93.43, 87.57, 74.18, 68.62, 36.59, 32.00, 30.22, 29.47, 29.23, 25.69, 24.05, 22.82, 19.88, 18.25, 14.32, 5.98, 4.20, 2.70, 1.70, -0.24. **HRMS** m/z calcd for $C_{43}H_{64}O_4Si_3H^+$: 729.4186; found: 729.4179. EA found: C, 70.72; H, 9.02. (calcd for $C_{43}H_{64}O_4Si_3$: C, 70.82; H, 8.85).

2. DSC Data for 1(n)



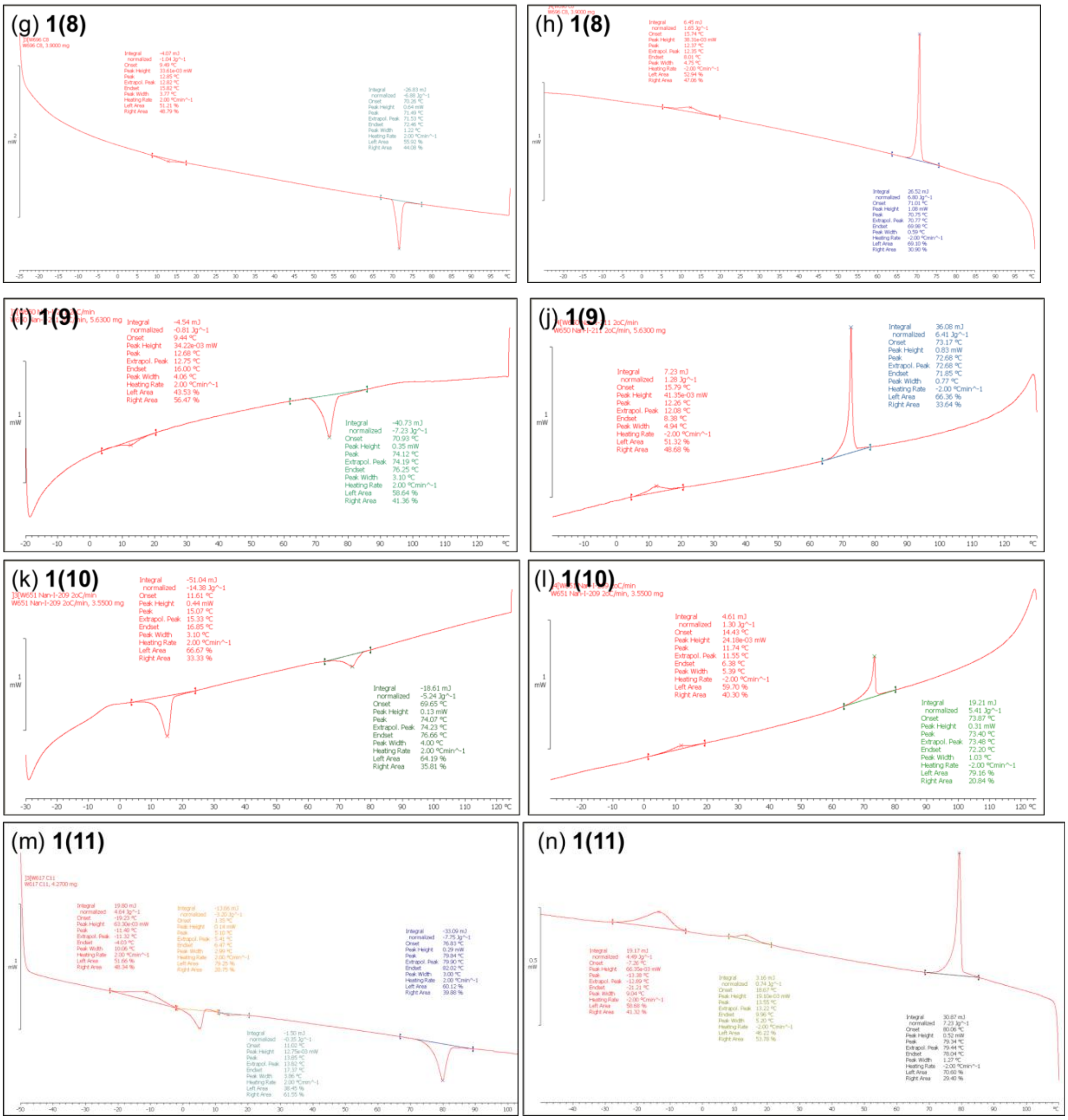


Fig. S1 DSC traces of **1(n)** on second heating/cooling at a scan rate of 2 ℃ min^{-1}.

3. Spontaneous Polarization

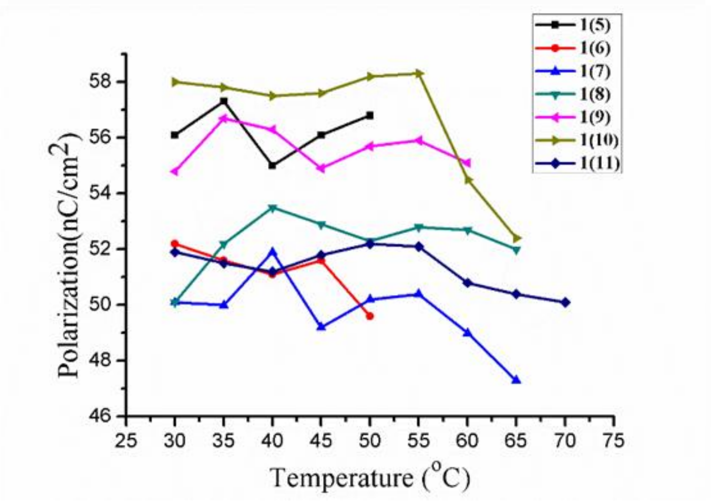


Fig. S2 Spontaneous polarization of the mesogens **1(n)** in these series, as a function of T.

4. POM Textures

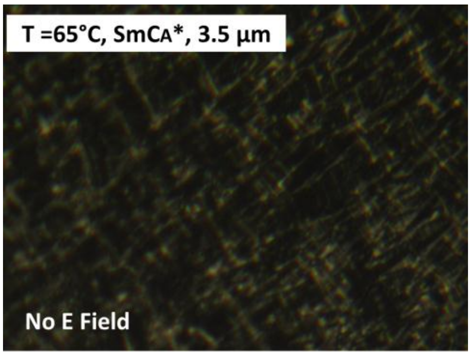


Fig. S3 Photomicrograph of **1(5)** was obtained using 3.5 μm ITO/glass cell with nylon alignment layers and one surface rubbed.

5. Homeotropic cell

The ~4 μm-think commercial homeotropic test cells were from LC Vision. The videos show the behavior of the homologues when cooling from the isotropic phase to the corresponding LC phase in the homeotropic cells. They were uploaded as separate files that named “the odd number homologous” and “the even number homologous”.

6. The ratio of peak intensities of X-ray diffraction patterns

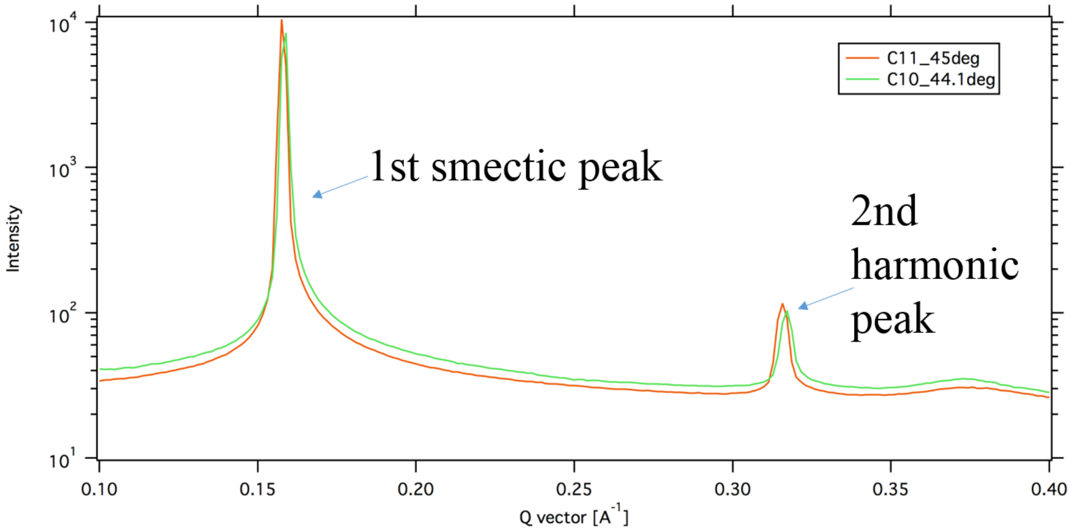


Fig. S4 The peak intensities obtained from 2D X-ray diffraction patterns.