

## SUPPORTING INFORMATION

### **Multiple glassy dynamics in dipole functionalized triphenylene-based discotic liquid crystals revealed by broadband dielectric spectroscopy and advanced calorimetry – Assessment of the molecular origin**

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**KEYWORDS:** Discotic liquid crystals, dipole functionalization, glass transition, molecular dynamics

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### **General Information and Experimental Procedures**

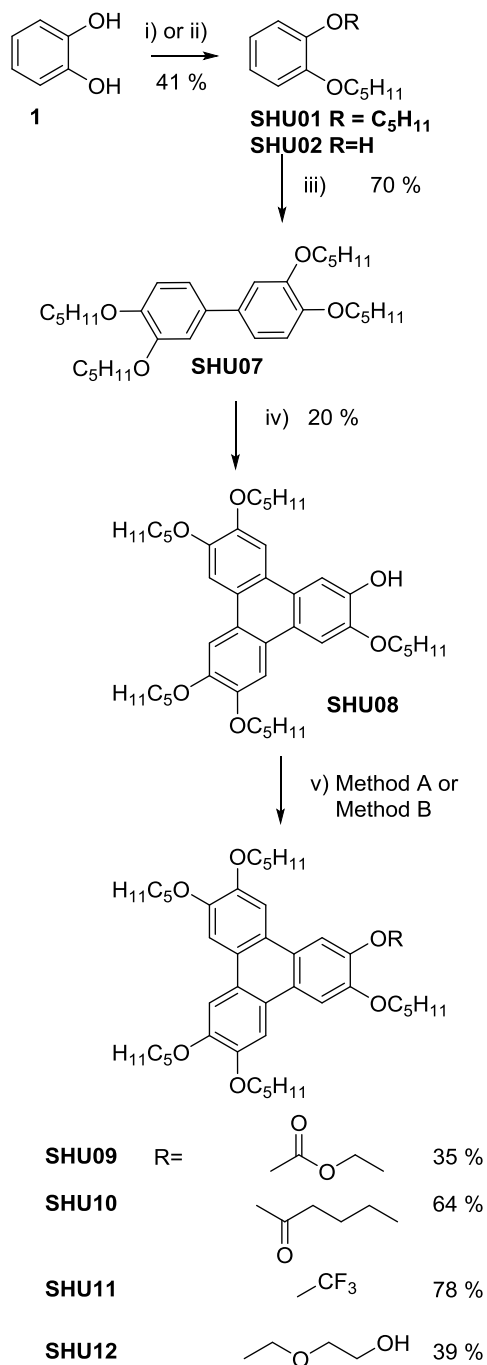
The following instruments were used for characterization of the compounds. NMR: *Bruker Avance 700* ( $^1\text{H}$ , 500 MHz;  $^{13}\text{C}$ , 176 MHz), *Bruker Avance 500* ( $^1\text{H}$ , 500 MHz;  $^{13}\text{C}$ , 126 MHz), *Bruker Avance 400* ( $^1\text{H}$ , 400 MHz;  $^{13}\text{C}$ , 100 MHz).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were referenced to TMS ( $\text{Me}_4\text{Si}$   $\delta_{\text{H}} = 0.0$  ppm,  $\delta_{\text{C}} = 0.0$  ppm) as an internal standard. All spectra were recorded

at room temperature. Assignment of the resonances was supported by 2D experiments (COSY and HMBC). Elemental analyses: Carlo Erba Strumentazione Elemental Analyzer, Modell 1106. MS (ESI): *Bruker Daltonics microTOF-Q* spectrometer. IR: *Bruker* Vector 22 FT-IR Spectrometer with MKII golden gate single reflection Diamant ATR system. Polarizing optical microscopy: *Olympus* BX50 polarizing microscope combined with a *Linkam* TP93 central controller. X-ray diffraction (WAXS, SAXS regions): *Bruker* AXS Nanostar C diffractometer employing Ni-filtered  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ).

Flash chromatography was performed on silica gel, grain size 40-63  $\mu\text{m}$  (*Fluka*) and aluminum sheets precoated with silica gel 60 F<sub>254</sub> (*Merck*) were used for thin layer chromatography (TLC). All commercial reagents were used without further purification. Solvents were dried and distilled under nitrogen prior to use and unless otherwise stated all reactions were carried out under a nitrogen atmosphere with Schlenk-type glassware.

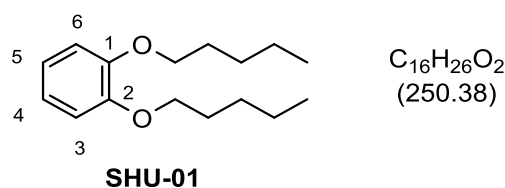
## Synthesis

### Scheme S1. Synthesis of the Monofunctionalized Triphenylene Derivatives SHU09-SHU12



- i) C<sub>5</sub>H<sub>11</sub>Br (2.2 eq), K<sub>2</sub>CO<sub>3</sub>, MeCN, 85 °C, 24 h;  
ii) C<sub>5</sub>H<sub>11</sub>Br (2.2 eq), K<sub>2</sub>CO<sub>3</sub>, MeCN, 85 °C, 24 h;  
iii) 1) **SHU01**, H<sub>2</sub>SO<sub>4</sub>, I<sub>2</sub>, HIO<sub>3</sub>, AcOH, H<sub>2</sub>O, CH<sub>2</sub>Cl<sub>2</sub>, 40 °C, 16 h; 2) Zn, Pd/C, Acetone, Water, 50 °C, 24 h;  
iv) **SHU02**, FeCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>NO<sub>2</sub>, 0 °C, 1 h;  
v) A) Valeric acid, DCC, DMAP, CH<sub>2</sub>Cl<sub>2</sub>, rt, 48 h  
B) Br-R, K<sub>2</sub>CO<sub>3</sub>, DMF/DMSO, 80 °C, 48 h

### 1,2-Bis(pentyloxy)benzene (SHU-01)



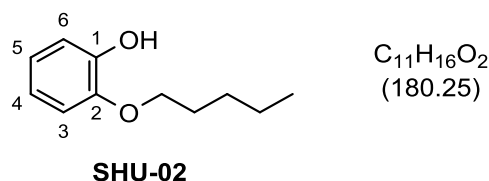
1,2-Dihydroxybenzene (35.0 g, 318 mmol) was heated under reflux with 1-Bromopentane (88 mL, 106 g, 699 mmol),  $K_2CO_3$  (176 g, 1.27 mol) in Acetonitrile (400 mL) for 24 h. After cooling to room temperature, the reaction mixture was filtered, and the solvent was removed. Subsequent column chromatography afforded the product.

Yield: 70 % (56.0 g, 224 mmol) yellow liquid.

$^1H$ -NMR (500 MHz,  $CDCl_3$ ):  $\delta$  = 0.93 (t,  $J$  = 7.2 Hz, 6H,  $CH_3$ ), 1.23–1.51 (m, 8H,  $CH_2$ ), 1.74–1.89 (m, 4H,  $OCH_2CH_2$ ), 3.99 (t,  $J$  = 6.6 Hz, 4H,  $OCH_2$ ), 6.88 (m, 4H, Ar-H) ppm;  
 $^{13}C$ -NMR (126 MHz,  $CDCl_3$ )  $\delta$  = 14.1 ( $CH_3$ ), 22.5, 28.2, 29.0 ( $CH_2$ ), 69.3 ( $OCH_2$ ), 114.1, 121.0 (C3, C4, C5, C6), 149.2 (C1, C2) ppm.

The spectral data are in good agreement with ref. 1.

### 2-(Pentyloxy)phenol (SHU-02)



1-Bromopentane (40 mL, 48.0 g, 318 mmol) was slowly added to a mixture of 1,2-Dihydroxybenzene (35.0 g, 318 mmol) and  $K_2CO_3$  (176 g, 1.27 mol) in Acetonitrile (400 mL). After stirring for 1 h at room temperature, the temperature was raised to 50 °C for 1 h, followed by 70 °C for 1 h. Then, the reaction mixture was heated under reflux for 24 h. The solvent was removed under reduced pressure and  $CH_2Cl_2$  (400 mL) and water (400 mL) were added. The phases were separated, and the organic phase was washed with 1 M NaOH solution (4 × 200 mL). The combined NaOH solutions were acidified with 1 M HCl, extracted with  $CH_2Cl_2$  (400 mL), dried over  $MgSO_4$  and the solvent was removed under reduced pressure.

Yield: 38 % (22.4 g, 123 mmol) colorless liquid.

$^1H$ -NMR (500 MHz,  $CDCl_3$ ):  $\delta$  = 0.94 (t,  $J$  = 7.1 Hz, 3H,  $CH_3$ ), 1.29–1.49 (m, 4H,  $CH_2$ ), 1.74–1.88 (m, 2H,  $OCH_2CH_2$ ), 4.03 (t,  $J$  = 6.6 Hz, 2H,  $OCH_2$ ), 5.66 (s, 1H, OH), 6.77–6.90 (m, 3H, 3 × Ar-H), 6.89–6.97 (m, 1H, Ar-H) ppm;  $^{13}C$ -NMR (126 MHz,  $CDCl_3$ )  $\delta$  = 14.0 ( $CH_3$ ), 22.4

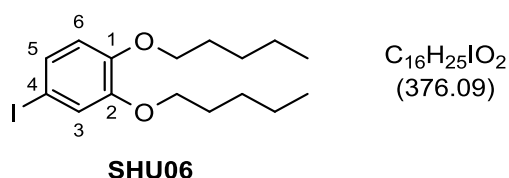
(CH<sub>2</sub>), 28.2 (CH<sub>2</sub>), 29.0 (OCH<sub>2</sub>CH<sub>2</sub>), 68.9 (OCH<sub>2</sub>), 111.6, 114.4, 120.1, 121.3 (C-3, C-4, C-5, C-6), 145.8, 146.0 (C-1, C-2) ppm.

FT-IR:  $\tilde{\nu}$  = 3540 (w), 3053 (w), 3955 (w), 2932 (w), 2871 (w), 1612 (w), 1596 (w), 1499 (s), 1467 (w), 1393 (w), 1361 (w), 1301 (w), 1256 (s), 1220 (s), 1196 (s), 1106 (s), 1072 (w), 1034 (w), 1017 (w), 988 (w), 913 (w), 839 (w), 788 (w), 738 (s), 597 (w), 517 (w), 436 (w) cm<sup>-1</sup>.

MS (EI):  $m/z$  (%) = 180.1 (22), 121.0 (2), 110.0 (100), 95.0 (2), 81.0 (4), 64.0 (2), 55.0 (2), 43.1(9), 29.0 (2).

HRMS (ESI):  $m/z$  for C<sub>11</sub>H<sub>16</sub>O<sub>2</sub>: 180.1150 [ $M^+$ ], found.: 180.1149.

#### 4-Iodo-1,2-bis(pentyloxy)benzene (SHU-06)



1,2-Bis(pentyloxy)benzene (45.7 g, 183 mmol), H<sub>2</sub>SO<sub>4</sub> (0.9 mL, 1.61 g, 16.4 mmol), I<sub>2</sub> (18.5 g, 73.1 mmol), HIO<sub>3</sub> (7.30 g, 41.5 mmol), Acetic acid (137 mL, 144 g; 2.34 mol), Water (23 mL) and CH<sub>2</sub>Cl<sub>2</sub> (28 mL) were heated to 40 °C for 16 h. An aqueous solution of NaSO<sub>3</sub> (200 mL) was added, the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 150 mL) and the organic phases were washed with K<sub>2</sub>CO<sub>3</sub> solution (200 mL). Drying over MgSO<sub>4</sub> and under reduced pressure afforded the product.

Yield: 87 % (60.0 g, 183 mmol) red liquid.

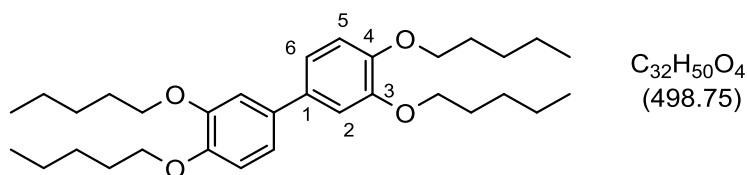
<sup>1</sup>H-NMR (700 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.95 (m, 6H, CH<sub>3</sub>), 1.31–1.53 (m, 8H, CH<sub>2</sub>), 1.76–1.88 (m, 4H, CH<sub>2</sub>), 3.97 (t,  $J$  = 6.6 Hz, 4H, CH<sub>2</sub>), 6.64 (d,  $J$  = 8.4 Hz, 1H, H<sub>6</sub>), 7.15 (d,  $J$  = 2.1 Hz, 1H, H<sub>3</sub>), 7.20 (dd,  $J$  = 8.4 Hz, 2.1 Hz, 1H, H<sub>5</sub>) ppm; <sup>13</sup>C-NMR (176 MHz, CDCl<sub>3</sub>)  $\delta$  = 14.1 (CH<sub>3</sub>), 22.5, 22.5, 28.2, 28.2, 28.9, 28.9 (CH<sub>2</sub>), 69.3, 69.4(OCH<sub>2</sub>), 82.5 (C<sub>4</sub>), 115.7 (C<sub>6</sub>), 122.7 (C<sub>3</sub>), 129.8 (C<sub>5</sub>), 149.2 (C<sub>2</sub>), 150.1 (C<sub>1</sub>) ppm.

FT-IR:  $\tilde{\nu}$  = 2953 (w), 2930 (w), 2869 (w), 1580 (w), 1497 (s), 1467 (s), 1391 (w), 1320 (w), 1291 (w), 1246 (s), 1135 (s), 1073 (w), 1048 (w), 988 (w), 917 (w), 837 (w), 795 (w), 730 (w), 630 (w), 574 (w), 456 (w) cm<sup>-1</sup>.

MS (ESI):  $m/z$  = 399 [ $M+Na^+$ ].

HRMS (ESI):  $m/z$  for C<sub>47</sub>H<sub>68</sub>NaO<sub>8</sub><sup>+</sup>: 399.0793 [ $M+Na^+$ ], found.: 399.0793.

### 3,3',4,4'-Tetrakis(pentyloxy)-1,1'-biphenyl (SHU-07)



#### SHU-07

A mixture of 4-Iodo-1,2-bis(pentyloxy)benzene (30.2 g, 80.3 mmol), Zinc (15.7 g, 281 mmol) and Pd/C (1.00 g) in Acetone (400 mL) and water (400 mL) were heated to 50 °C for 24 h. After cooling to room temperature, the reaction mixture was filtered. The liquid phase was concentrated under reduced pressure and the product was collected by filtration and recrystallized from Methanol.

Yield: 47 % (9.47 g, 19.0 mmol) colorless solid.

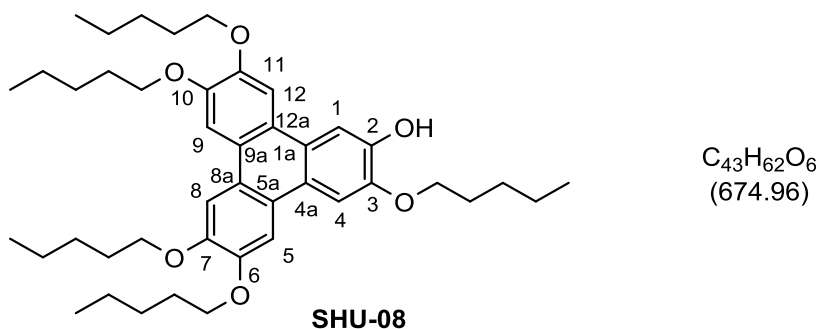
$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.94 (t,  $J$  = 7.1 Hz, 12H,  $\text{CH}_3$ ), 1.34–1.52 (m, 16H,  $\text{CH}_2$ ), 1.78–1.90 (m, 8H,  $\text{CH}_2$ ), 4.04 (dt,  $J$  = 12.3 Hz, 6.6 Hz, 8H,  $\text{OCH}_2$ ), 6.92 (d,  $J$  = 7.9 Hz, 2H, H2), 7.02–7.10 (m, 4H, H5, H6) ppm.  $^{13}\text{C-NMR}$  (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 14.1 ( $\text{CH}_3$ ), 22.5, 28.3, 29.1, 29.1 ( $\text{CH}_2$ ), 69.4, 69.5 ( $\text{OCH}_2$ ), 113.2 (C5), 114.2 (C2), 119.3 (C6), 134.4 (C1), 148.5 (C3), 149.3 (C4) ppm.

FT-IR:  $\tilde{\nu}$  = 2955 (w), 2931 (w), 2250 (w), 2152 (w), 2039 (w), 1604 (w), 1574 (w), 1499 (w), 1468 (w), 1389 (w), 1293 (w), 1252 (w), 1221 (w), 1146 (w), 1053 (w), 990 (w), 906 (s), 833 (w), 803 (w), 789 (w), 729 (s), 648 (w), 618 (w), 460 (w)  $\text{cm}^{-1}$ .

MS (ESI):  $m/z$  = 521 [ $\text{M}+\text{Na}^+$ ].

HRMS (ESI):  $m/z$  for  $\text{C}_{47}\text{H}_{68}\text{NaO}_8^+$ : 521.3601 [ $\text{M}+\text{Na}^+$ ], found.: 521.3592.

### 3,6,7,10,11-Pentakis(pentyloxy)triphenylen-2-ol (SHU-08)



3,3',4,4'-Tetrakis(pentyloxy)-1,1'-biphenyl (5.10 g, 16.6 mmol) and 2-(Pentyloxy)phenol (3.00 g, 16.6 mmol) were dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (80 mL) and cooled to 0 °C. FeCl<sub>3</sub> (20.8 g, 128 mmol) dissolved in Nitromethane (45 mL) was added slowly and the reaction mixture was stirred for 1 h. The reaction mixture was poured onto MeOH (200 mL) and the precipitated product was collected by filtration.

Yield: 20 % (2.20 g, 3.26 mmol) yellow solid.

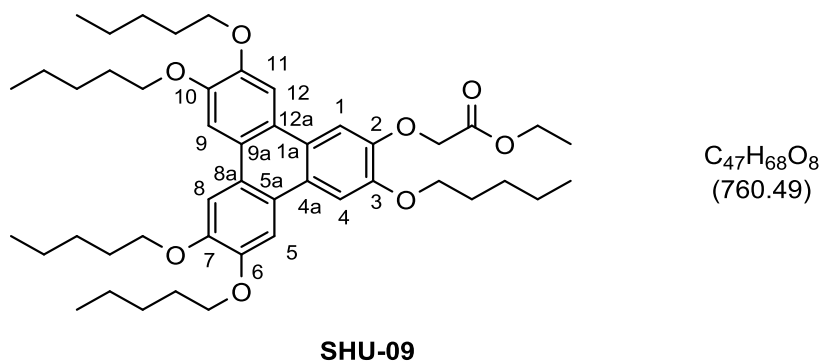
<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): δ = 0.97 (t, *J* = 7.2 Hz, 15H, CH<sub>2</sub>CH<sub>3</sub>), 1.51 (dq, *J* = 50.3 Hz, 7.6 Hz, 20H, CH<sub>2</sub>), 1.81–2.05 (m, 10H, CH<sub>2</sub>), 4.03–4.34 (m, 10H, CH<sub>2</sub>), 5.90 (s, 1H, OH), 7.76 (s, 1H, H1), 7.79-7.85 (m, 4H, H5, H8, H9, H12), 7.95 (s, 1H, H4) ppm; <sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>) δ = 14.1, 14.1, 14.1 (CH<sub>2</sub>CH<sub>3</sub>), 22.6, 22.6 (CH<sub>2</sub>CH<sub>3</sub>), 28.3, 28.3, 28.4, 28.4, 29.0, 29.1, 29.2, 29.2 (CH<sub>2</sub>), 69.1, 69.1, 69.6, 69.9, 69.9 (OCH<sub>2</sub>), 104.4 (C1), 106.5, 107.3, 107.3, 107.4, 107.6 (C4, C5, C8, C9, C12), 123.0, 123.2, 123.6, 123.6, 123.7, 124.0 (C1a, C4a, C5a, C8a, C9a, C12a), 145.3, 145.8 (C2, C3), 148.8, 148.8, 149.0, 149.2 (C6, C7, C10, C11) ppm.

The spectral data are in good agreement with ref. 2.

### General Procedure for the synthesis of the Pentaalkoxytriphenylenes (SHU-09 – SHU-13)

3,6,7,10,11-pentakis(pentyloxy)triphenylen-2-ol (500 mg, 741 μmol), K<sub>2</sub>CO<sub>3</sub> (154 mg, 1.11 mmol) and the corresponding primary Bromide (1.48 mmol) were suspended in dry DMF (0.7 mL) or dry DMSO and heated for 48 h. After cooling to room temperature, water (20 mL) was added and the mixture was extracted with pentane (3 × 20 mL). The combined organic phases were washed with brine, dried over MgSO<sub>4</sub> and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel using petrol ether and ethyl acetate as eluent.

### Ethyl 2-((3,6,7,10,11-pentakis(pentyloxy)triphenylen-2-yl)oxy)acetate (SHU-09)





Setup according to general procedure: 3,6,7,10,11-Pentakis(pentyloxy)triphenylen-2-ol (500 mg, 741  $\mu\text{mol}$ ),  $\text{K}_2\text{CO}_3$  (154 mg, 1.11 mmol), Ethyl bromoacetate (247 mg, 1.48 mmol), dry DMF (0.7 mL). Eluent for flash chromatography

Yield: 35 % (200 mg, 0.263 mmol) white solid.

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.98 (t,  $J$  = 7.2 Hz, 1.6 Hz, 15H,  $\text{CH}_3$ ), 1.32 (t,  $J$  = 7.1 Hz, 3H,  $\text{CH}_3$ ), 1.46 (m,  $J$  = 7.1 Hz, 10H), 1.52–1.63 (m, 10H), 1.88–2.03 (m, 10H), 4.18–4.28 (m, 10H,  $\text{CH}_2$ ), 4.31 (q,  $J$  = 7.2 Hz, 2H,  $\text{OCH}_2\text{CO}$ ), 7.79 (s, 1H, Ar-H), 7.81–7.86 (m, 4H, Ar-H), 7.94 (s, 1H, Ar-H) ppm.;  $^{13}\text{C-NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 14.1, 14.1, 14.3 ( $\text{CH}_3$ ), 22.6, 22.6, 28.3, 28.4, 28.4, 29.1, 29.1, 29.2 ( $\text{CH}_2$ ), 61.3, 67.9, 69.4, 69.6, 69.8 ( $\text{OCH}_2$ ), 77.2 ( $\text{OCH}_2\text{CO}$ ), 106.8, 107.0, 107.2, 107.4, 107.6, 110.4 (C1, C4, C5, C8, C9, C12), 123.2, 123.3, 123.4, 123.5, 124.1, 125.1 (C1a, C4a, C5a, C8a, C9a, C12a), 147.3, 148.9, 149.0, 149.1, 149.2, 149.3 (C2, C3, C6, C7, C10, C11), 169.3 (COO) ppm.

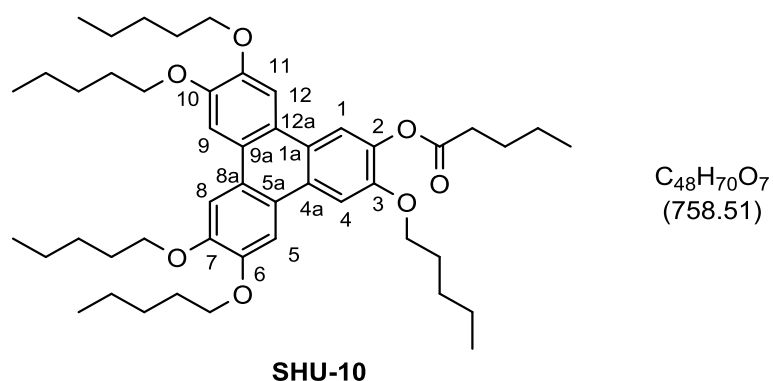
FT-IR:  $\tilde{\nu}$  = 2955 (w), 2931 (w), 2859 (w), 1760 (w), 1736 (w), 1618 (w), 1516 (s), 1467 (w), 1435 (s), 1389 (w), 1259 (s), 1161 (s), 1078 (w), 1038 (w), 826 (w), 774 (w), 731 (w), 658 (w), 599 (w)  $\text{cm}^{-1}$ .

MS (EI):  $m/z$  (%) = 760.5 (100), 690.4 (5), 674.5 (7).

HRMS (EI):  $m/z$  for  $\text{C}_{47}\text{H}_{68}\text{O}_8^+$ : 760.4914 [ $M^+$ ], found.: 760.4910.

CHN für $\text{C}_{47}\text{H}_{68}\text{O}_8$ :	calcd.	C 74.18	H 9.01
	found.	C 74.08	H 8.81

### 3,6,7,10,11-Pentakis(pentyloxy)triphenylen-2-yl pentanoate (SHU-10)



Setup according to general procedure: 3,6,7,10,11-Pentakis(pentyloxy)triphenylen-2-ol (250 mg, 370  $\mu\text{mol}$ ); DCC (88.0 mg, 426  $\mu\text{mol}$ ); DMAP (9.1 mg, 74.0  $\mu\text{mol}$ ); Valeric acid (38.0 mg, 370  $\mu\text{mol}$ ); dry  $\text{CH}_2\text{Cl}_2$  (0.7 mL) were stirred for 48 h at room temperature. The solvent was removed under reduced pressure. Eluent for flash chromatography

Yield: 64 % (180 mg, 0.237 mmol) white solid.

$^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.90–1.07 (m, 18H,  $\text{CH}_3$ ), 1.38–1.62 (m, 22H,  $\text{CH}_2$ ), 1.77–2.01 (m, 12H,  $\text{CH}_2$ ), 2.68 (t,  $J$  = 7.6 Hz, 2H,  $\text{OOCCH}_2$ ), 4.15–4.28 (m, 10H,  $\text{OCH}_2$ ), 7.75 (s, 1H), 7.79 (d,  $J$  = 2.2 Hz, 2H, H), 7.83 (d,  $J$  = 2.2 Hz, 2H, H), 8.03 (s, 1H, H) ppm.;  $^{13}\text{C-NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 13.8, 14.1( $\text{CH}_3$ ), 22.4, 22.6, 22.6, 27.2, 28.3, 28.4, 28.4, 29.1 ( $\text{OCH}_2$ ), 33.9 ( $\text{OOCCH}_2$ ), 68.8, 69.3, 69.5, 69.8, 69.9 ( $\text{OCCH}_2$ ), 105.9, 106.6, 106.9, 107.3, 108.0, 116.7 (C1, C4, C5, C8, C9, C12), 123.0, 123.1, 123.2, 123.5, 124.6, 127.9 (C1a, C4a, C5a, C8a, C9a, C12a), 139.8, 148.8, 148.9, 149.2, 149.5, 149.7 (C2, C3, C6, C7, C10, C11), 172.1 ( $\text{OOCCH}_2$ ) ppm.

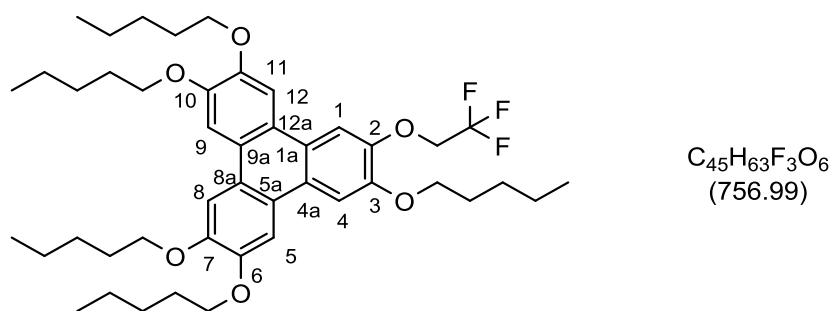
FT-IR:  $\tilde{\nu}$  = 2956 (w), 2930 (w), 2859 (w), 1749 (w), 1618 (w), 1516 (w), 1467 (w), 1435 (s), 1393 (w), 1260 (s), 1187 (w), 1165 (s), 1143 (w), 1104 (w), 1079 (w), 1053 (w), 1037 (w), (w), 893 (w), 865 (w), 827 (w), 774 (w), 731 (w), 600 (w), 446 (w)  $\text{cm}^{-1}$ .

MS (EI):  $m/z$  (%) = 758.5 (100), 674.5 (43), 604.4 (8), 463.2 (5), 393.1 (5), 323.1 (5), 295.1 (5), 43.1 (5).

HRMS (EI):  $m/z$  for  $\text{C}_{48}\text{H}_{70}\text{O}_7$  calcd.: 758.5122, found.: 758.5132.

CH für $\text{C}_{48}\text{H}_{70}\text{O}_7$ :	calcd.	C 75.95	H 9.30
	found.	C 75.71	H 9.08

### 2,3,6,7,10-Pentakis(pentyloxy)-11-(2,2,2-trifluoroethoxy)triphenylene (SHU-11)



SHU-11

Setup according to general procedure: 3,6,7,10,11-Pentakis(pentyloxy)triphenylene-2-ol (250 mg, 370  $\mu\text{mol}$ ),  $\text{K}_2\text{CO}_3$  (77 mg, 556  $\mu\text{mol}$ ), 2-bromo-1,1,1-trifluoroethane (156 mg, 741 mmol), dry DMSO (0.4 mL). Eluent for flash chromatography

Yield: 78 % (220 mg, 0.291 mmol) purple solid.

$^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.92–1.02 (m, 15H,  $\text{CH}_3$ ), 1.39–1.62 (m, 20H,  $\text{CH}_2$ ), 1.95 (m, 10H,  $\text{CH}_2$ ), 4.18–4.27 (m, 10H,  $\text{OCH}_2$ ), 4.57 (q,  $J$  = 8.4 Hz, 2H,  $\text{OCH}_2\text{CF}_3$ ), 7.77–7.85 (m,

5H, Ar-H), 8.02 (s, 1H, Ar-H) ppm;  $^{13}\text{C}$ -NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 14.0, 14.1, 14.1( $\text{CH}_3$ ), 22.5, 22.6, 28.4, 28.4, 29.1, 29.1, 29.1, 29.1, 29.2, 68.7( $\text{OCH}_2\text{CF}_3$ ), 69.0, 69.3, 69.5, 69.6, 69.8, 69.9, 106.8, 107.1, 107.1, 107.4, 107.7, 112.9 (C1, C4, C5, C8, C9, C12), 122.5, 123.0, 123.3, 123.4, 124.3 (C4a, C5a, C8a, C9a, C12a), 124.8 ( $\text{CF}_3$ ), 126.1 (C1a), 146.8, 148.9, 149.1, 149.3, 149.4, 149.6 (C2, C3, C6, C7, C10, C11) ppm.

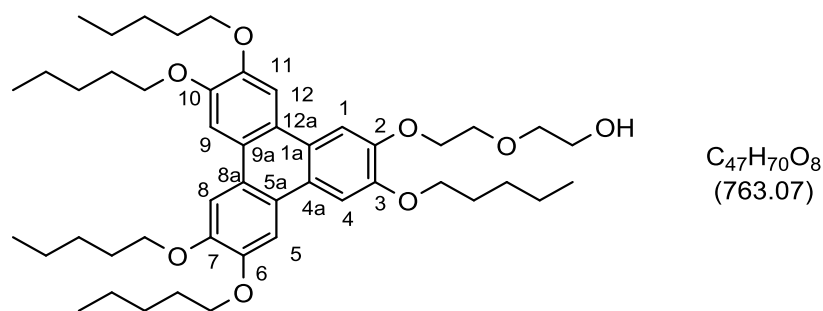
FT-IR:  $\tilde{\nu}$  = 2957 (w), 2931 (w), 2859 (w), 1618 (w), 1516 (s), 1467 (w), 1435 (s), 1390 (w), 1259 (s), 1159 (s), 1053 (w), 1038 (w), 978 (w), 964 (w), 825 (w), 774 (w), 731 (w), 649 (w), 600 (w), 450 (w)  $\text{cm}^{-1}$ .

MS (EI):  $m/z$  (%) = 756.5 (100), 686.4 (5), 615.3 (2), 545.2 (2), 475.1 (3), 405.1 (3), 377.1 (2), 294.0 (2), 43.1 (4).

HRMS (EI):  $m/z$  for  $\text{C}_{48}\text{H}_{63}\text{F}_3\text{O}_6$  calcd.: 756.4577, found.: 756.476.

CH für $\text{C}_{45}\text{H}_{63}\text{F}_3\text{O}_6$ :	calcd.	C 71.40	H 8.39
	found.	C 71.17	H 8.11

## 2-(2-((3,6,7,10,11-Pentakis(pentyloxy)triphenylen-2-yl)oxy)ethoxy)ethan-1-ol (SHU-12)



**SHU-12**

Setup according to general procedure: 3,6,7,10,11-Pentakis(pentyloxy)triphenylen-2-ol (250 mg, 370  $\mu\text{mol}$ ),  $\text{K}_2\text{CO}_3$  (77 mg, 556  $\mu\text{mol}$ ), 2-(2-bromoethoxy)ethan-1-ol (46 mg, 370 mmol), dry DMF (0.4 mL). Eluent for flash chromatography

Yield: 39 % (110 mg, 0.144 mmol) parpole solid.

$^1\text{H}$ -NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.98 (t,  $J$  = 7.3 Hz, 15H,  $\text{CH}_3$ ), 1.38–1.50 (m, 10H,  $\text{CH}_2$ ), 1.50–1.61 (m, 10H,  $\text{CH}_2$ ,  $\text{OCH}_2$ ), 1.86–2.01 (m, 10H,  $\text{CH}_2$ ), 3.74–3.78 (m, 2H), 3.78–3.83 (m, 2H,  $\text{OCH}_2$ ), 3.99–4.03 (m, 2H,  $\text{OCH}_2$ ), 4.20–4.26 (m, 10H,  $\text{OCH}_2$ ), 4.38–4.42 (m, 2H,  $\text{OCH}_2$ ), 7.83 (m, 5H, Ar-H), 7.90 (s, 1H, Ar-H) ppm;  $^{13}\text{C}$ -NMR (126 MHz,  $\text{CDCl}_3$ )  $^{13}\text{C}$ -NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 14.1( $\text{CH}_3$ ), 22.6, 22.6, 28.3, 28.4, 29.0, 29.1 ( $\text{CH}_2$ ), 61.9, 69.4, 69.5, 69.7, 69.7, 69.7, 69.8, 69.8, 72.7( $\text{OCH}_2$ ), 106.7, 107.2, 107.3, 107.4, 107.5, 108.4 (C1, C4,

C5, C8, C9, C12), 123.4, 123.4, 123.6, 123.6, 123.8, 124.2 (C1a, C4a, C5a, C8a, C9a C12a), 148.2, 149.0, 149.0, 149.0, 149.1, 149.1 (C2, C3, C6, C7, C10, C11) ppm.

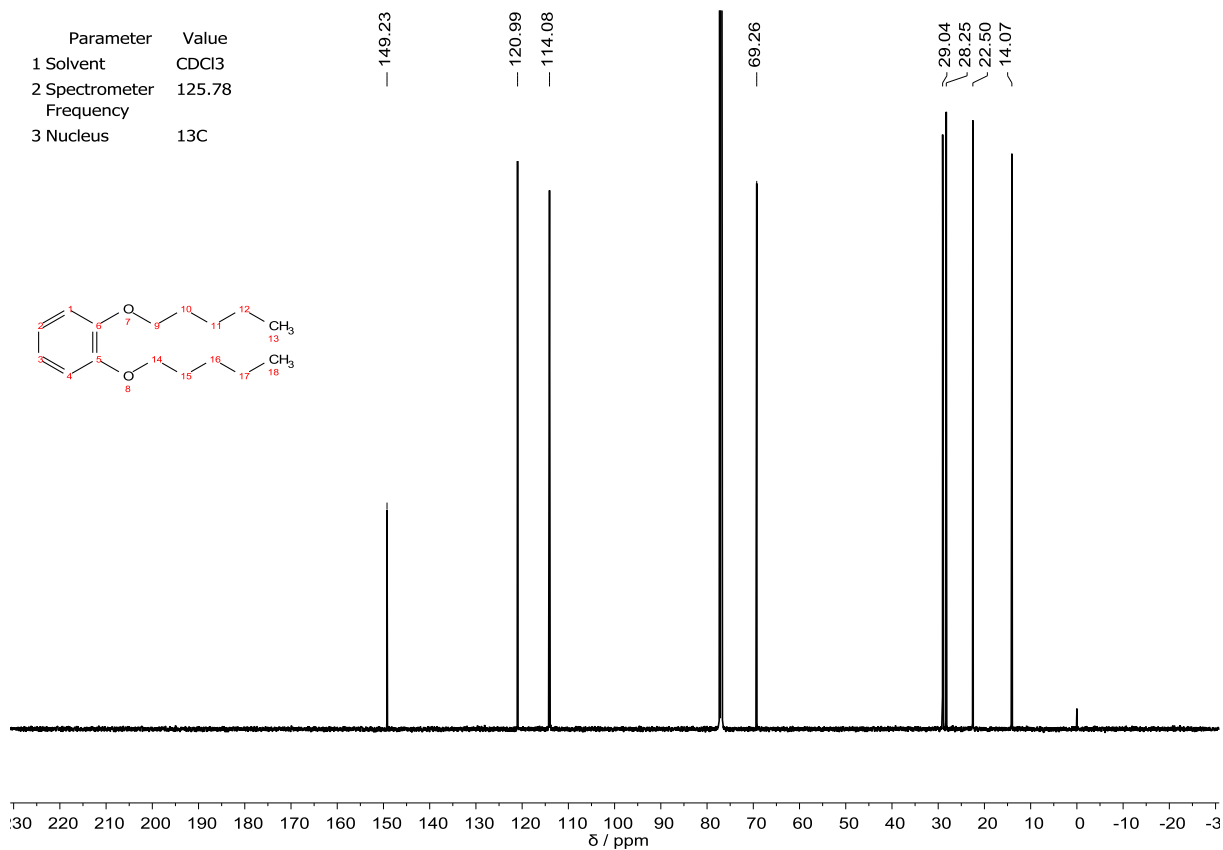
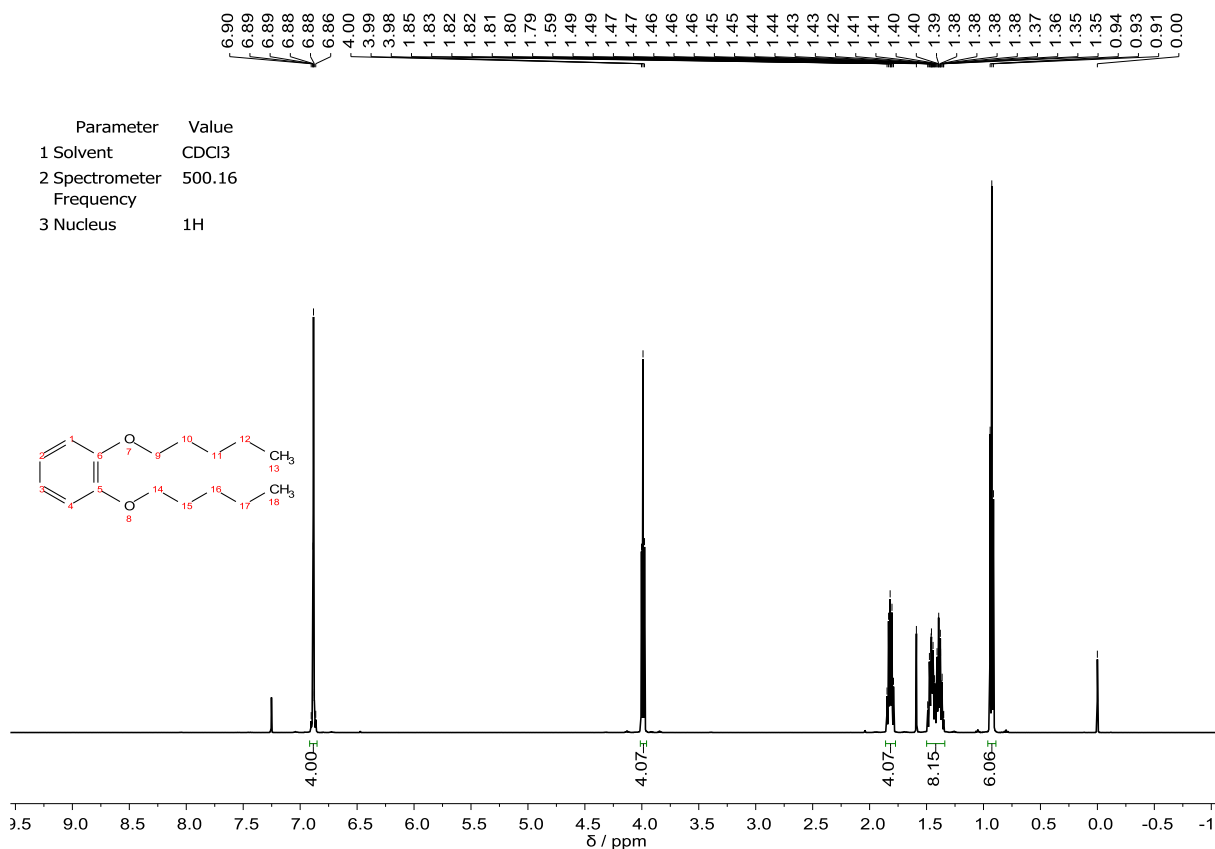
FT-IR:  $\tilde{\nu}$  = 2927 (w), 2857 (w), 1617 (w), 1516 (s), 1467 (w), 1435 (s), 1387 (w), 1259 (s), 1171 (s), 1132 (w), 1052 (w), 1031 (w), 986 (w), 836 (w), 769 (w), 730 (w), 616 (w), 600 (w)  $\text{cm}^{-1}$ .

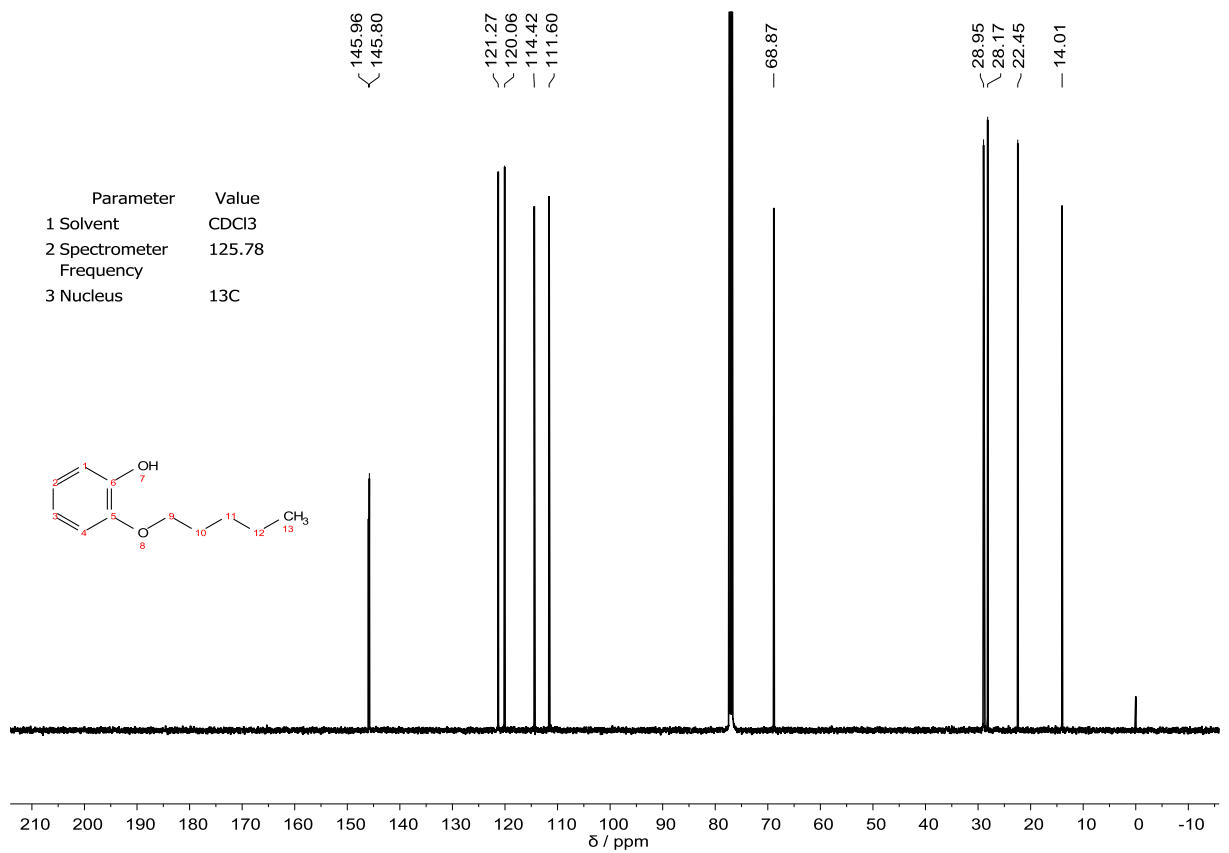
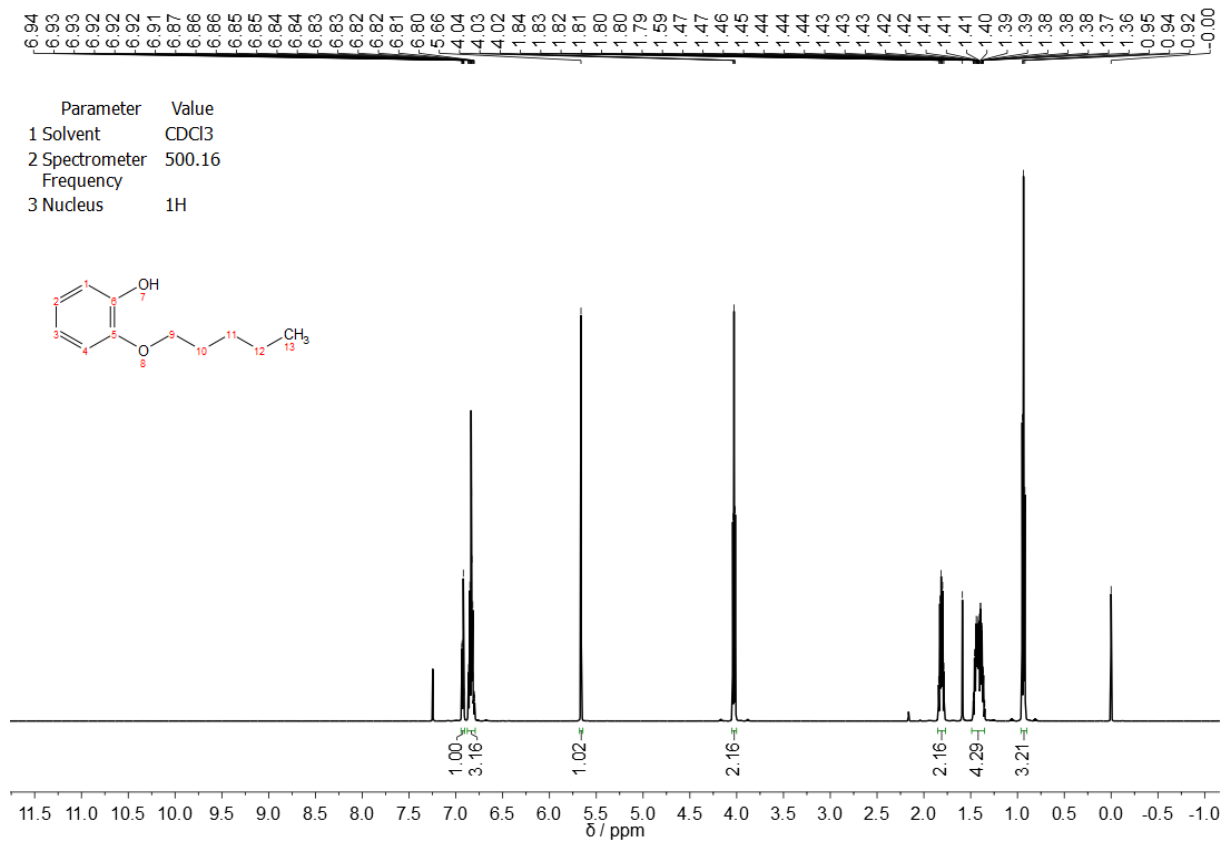
MS (EI):  $m/z$  (%) = 762.5 (100), 692.4 (4), 43.1 (4).

HRMS (EI):  $m/z$  for  $\text{C}_{48}\text{H}_{70}\text{O}_8$  calcd.: 762.5071, found.: 762,5081.

CHN für $\text{C}_{47}\text{H}_{70}\text{O}_8$ :	calcd.	C 73.98	H 9.25
	found.	C 73.98	H 9.06

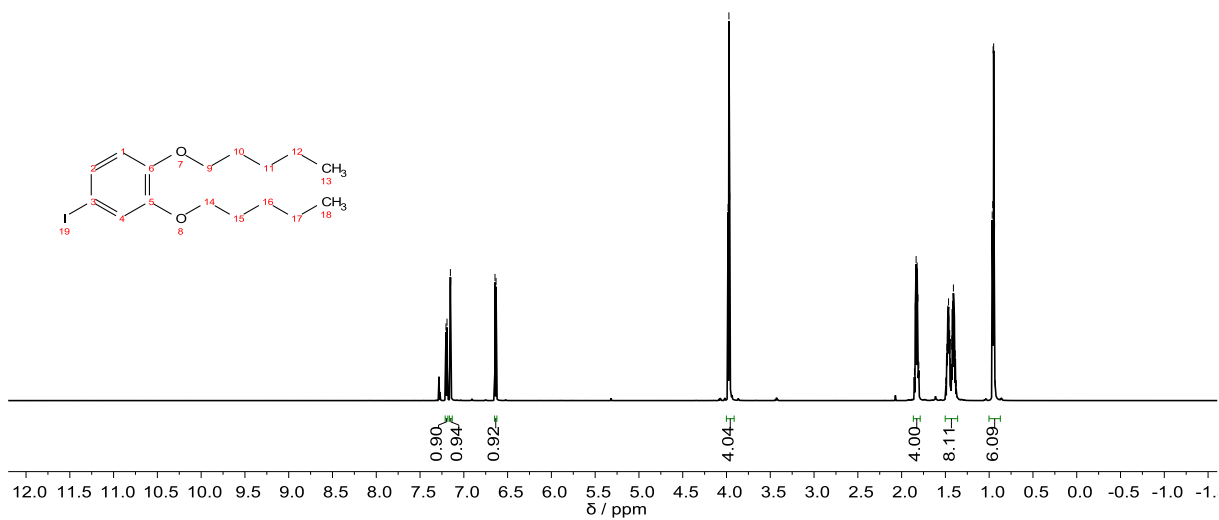
# NMR Spectra





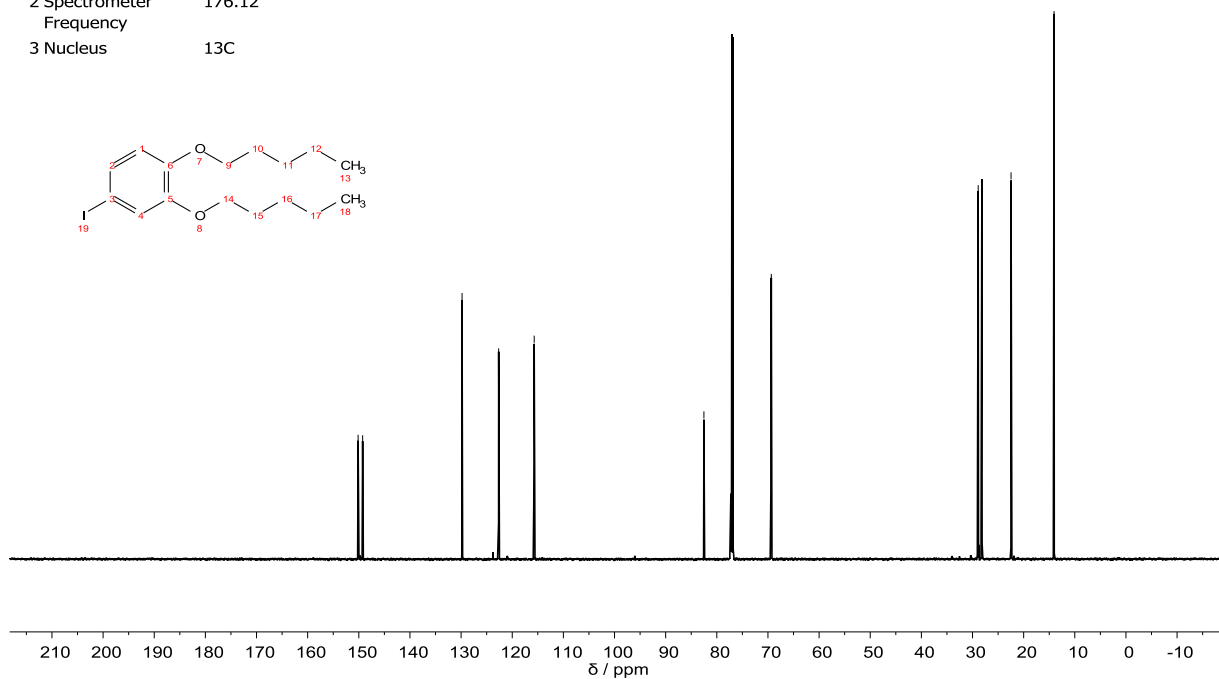
7.21  
7.20  
7.19  
7.19  
7.15  
7.15  
6.64  
6.63  
3.98  
3.97  
3.96  
1.85  
1.84  
1.83  
1.83  
1.82  
1.82  
1.81  
1.80  
1.49  
1.49  
1.49  
1.48  
1.48  
1.48  
1.47  
1.47  
1.46  
1.46  
1.46  
1.45  
1.45  
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1.38  
0.97  
0.96  
0.95  
0.95  
0.94

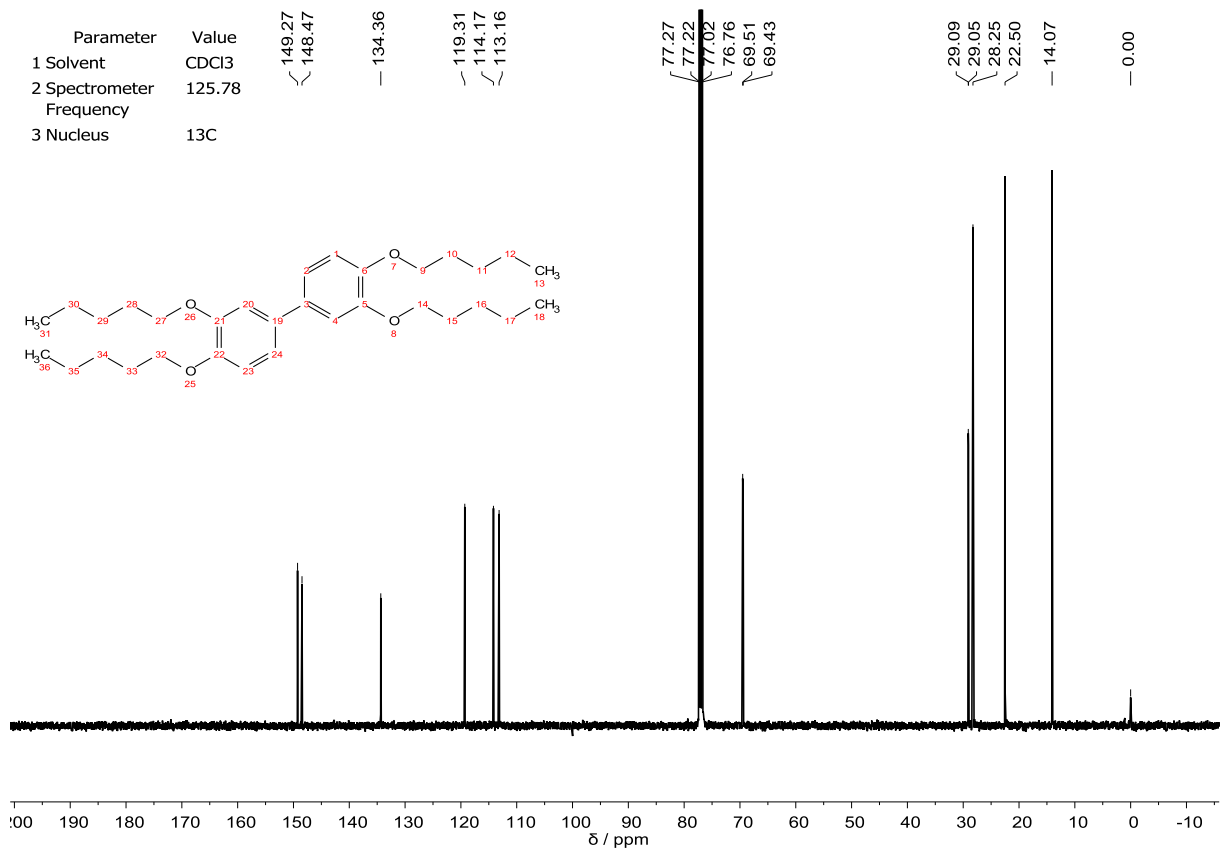
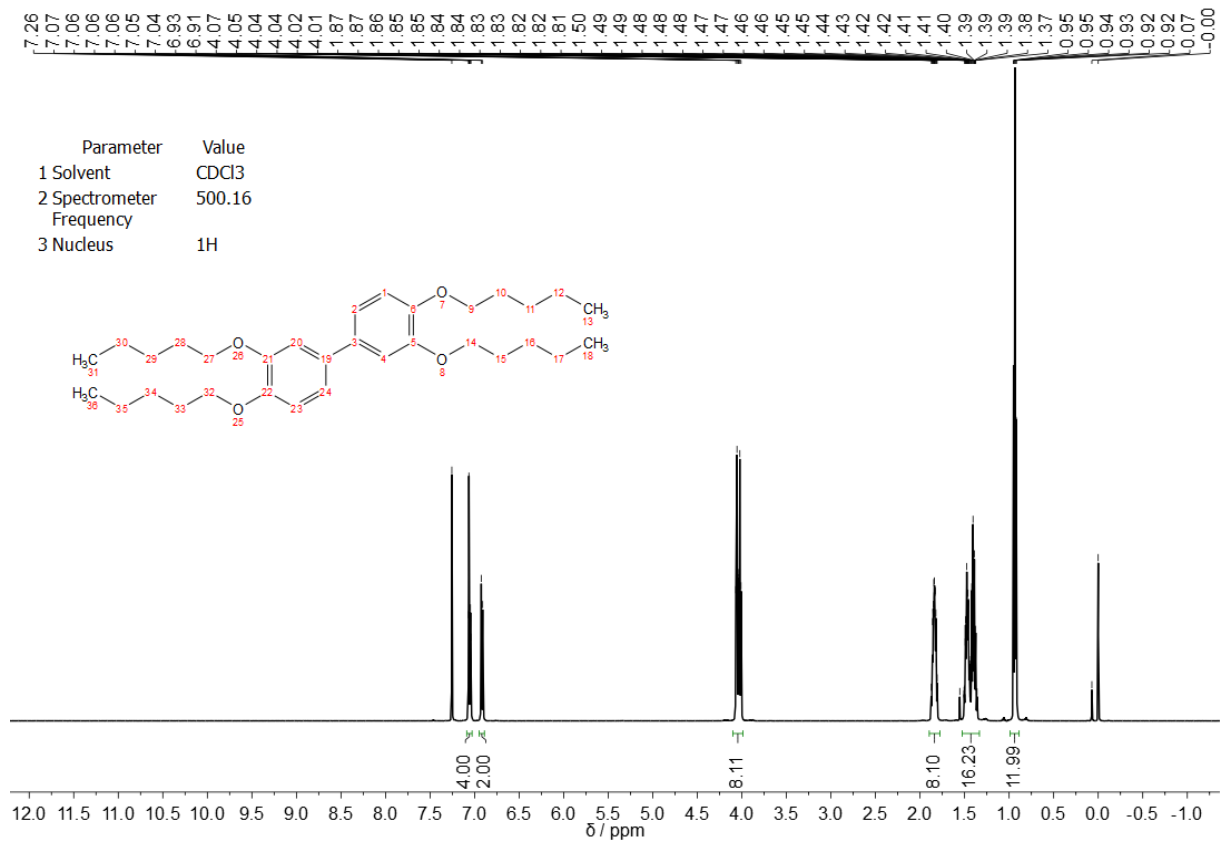
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2 Spectrometer 700.36  
Frequency  
3 Nucleus 1H



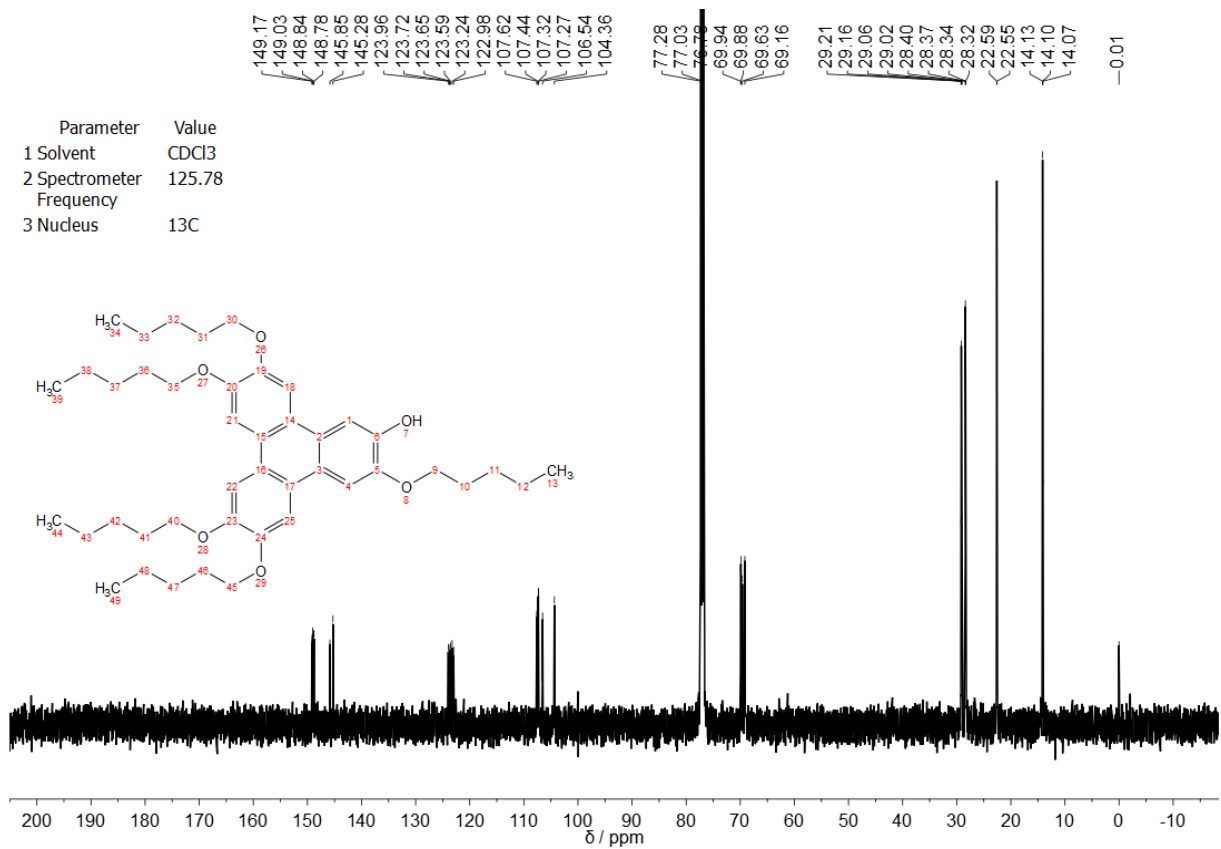
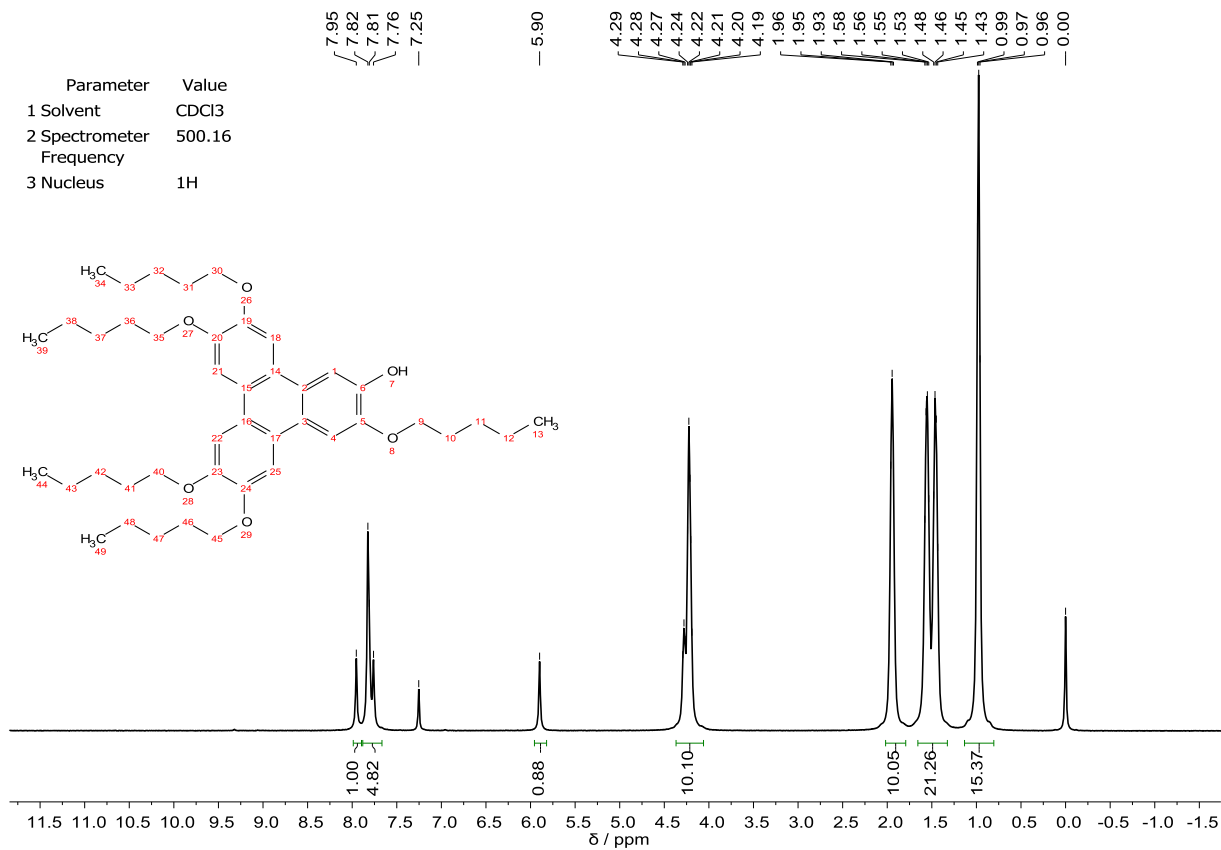
150.14  
149.25  
129.81  
122.65  
115.71  
82.52  
69.42  
69.34  
28.89  
28.88  
28.19  
28.17  
22.47  
22.45  
14.06

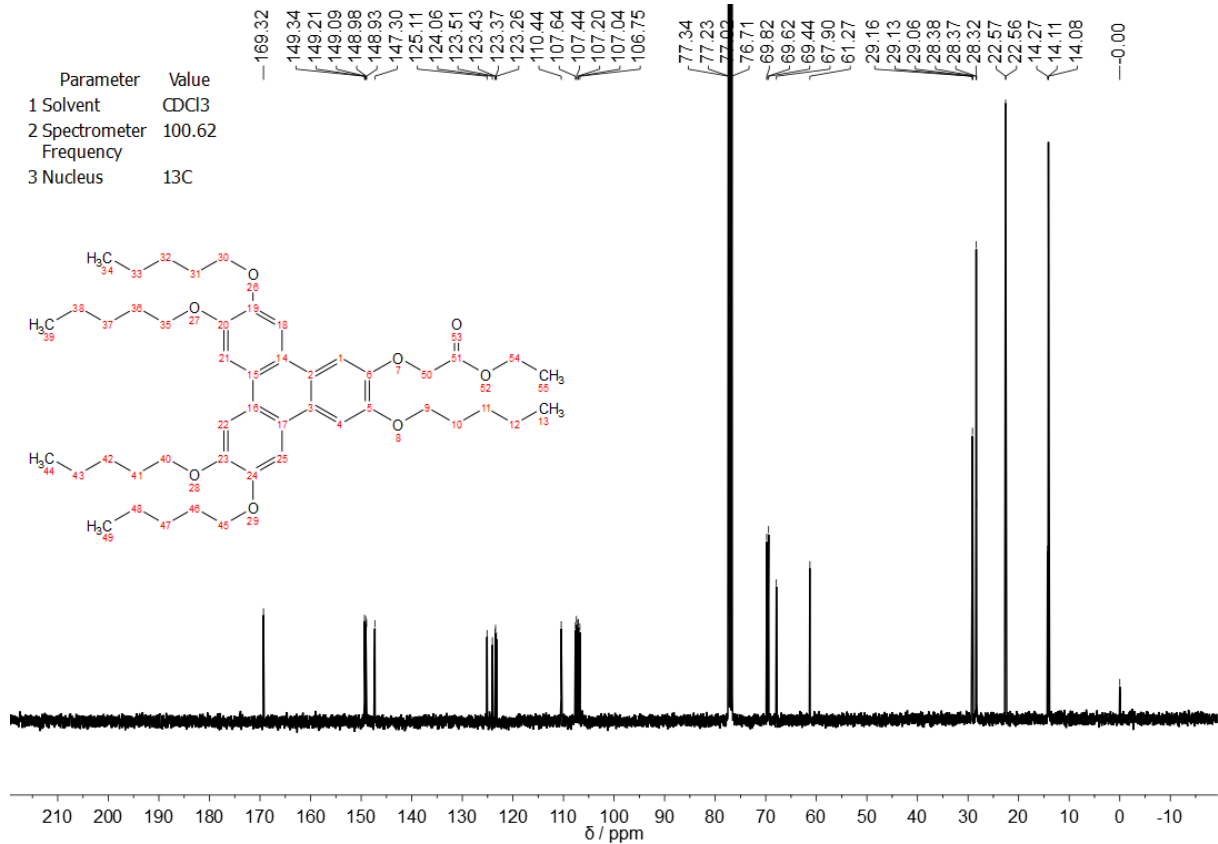
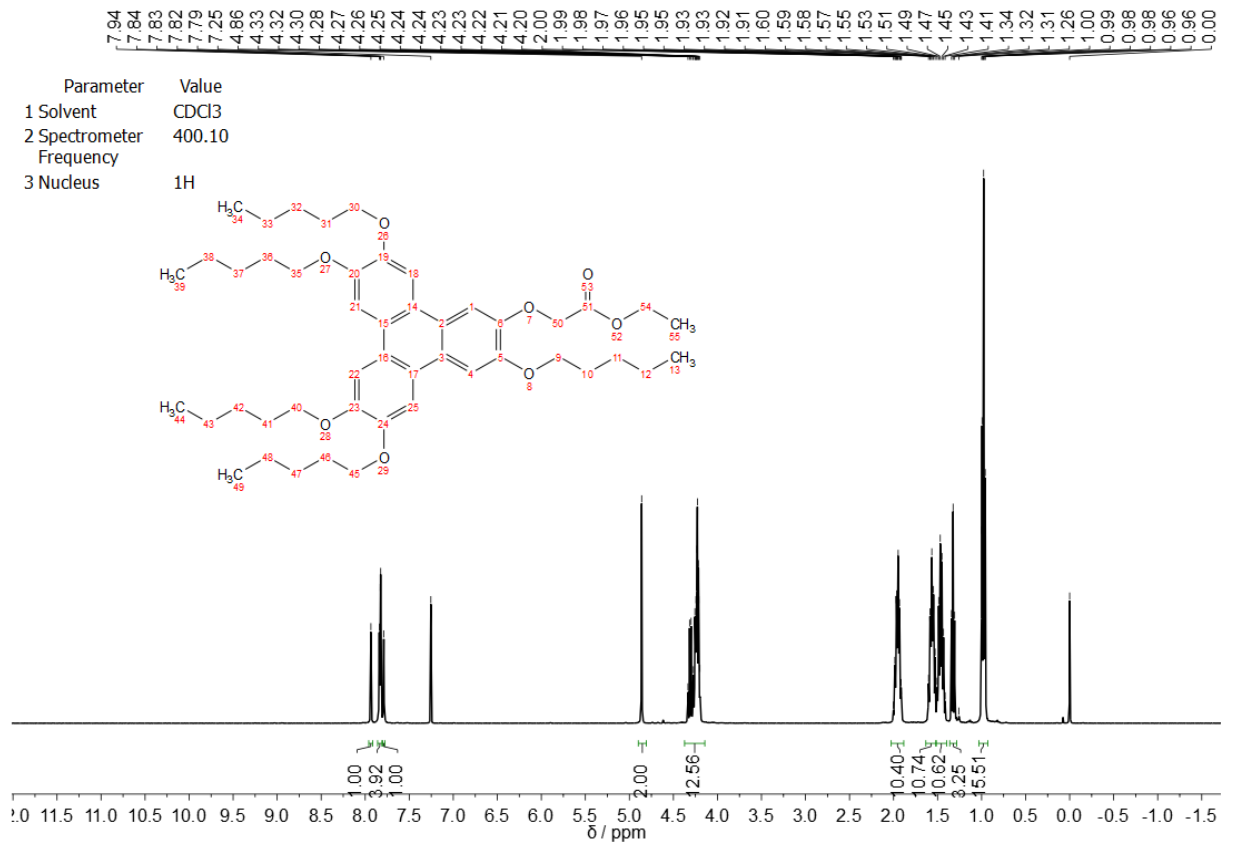
Parameter Value  
1 Solvent CDCl3  
2 Spectrometer 176.12  
Frequency  
3 Nucleus 13C

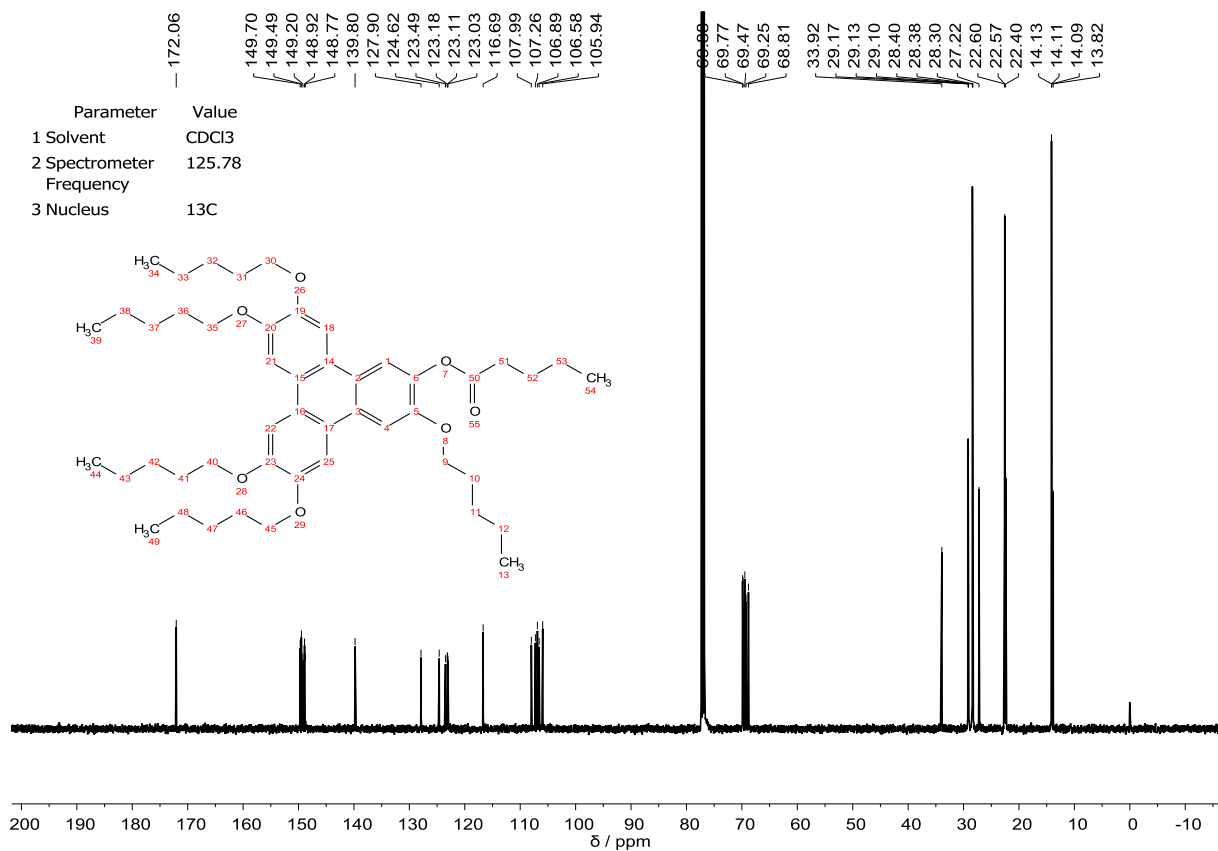
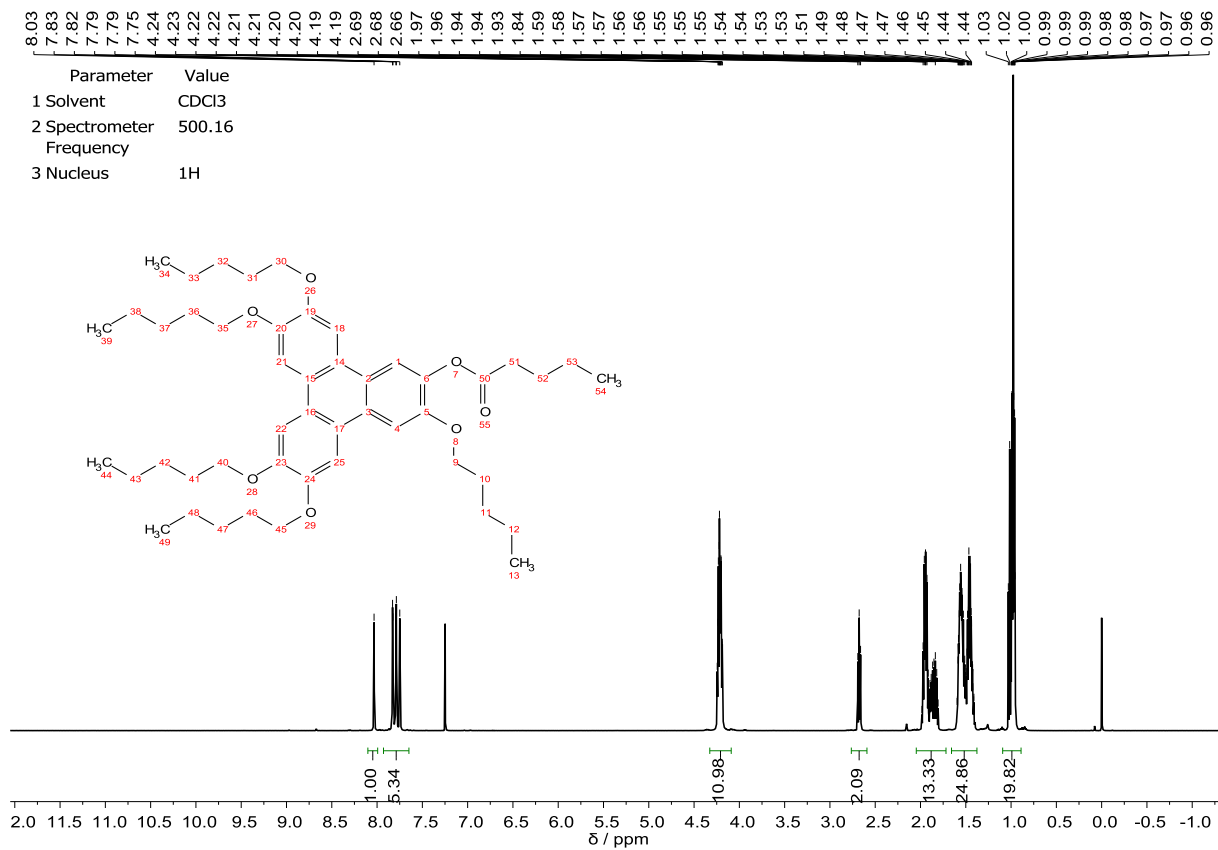


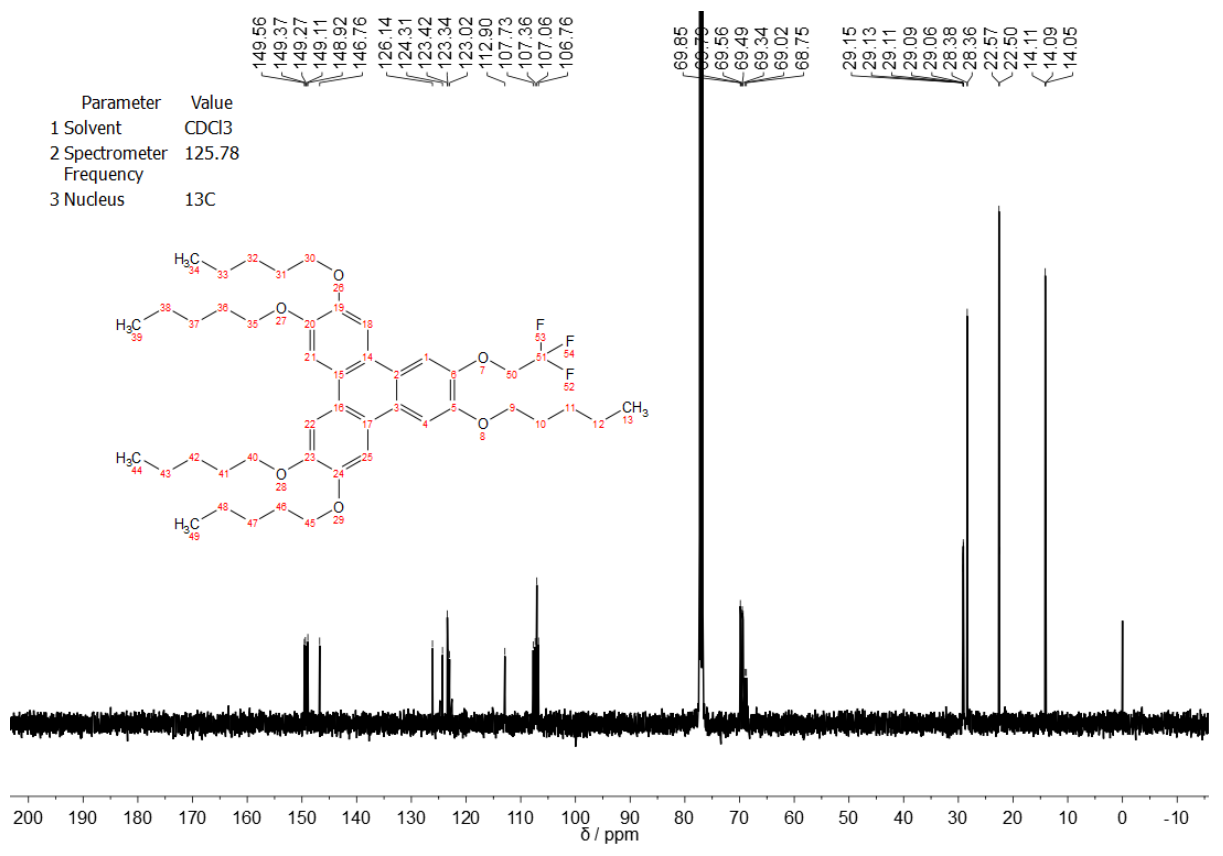
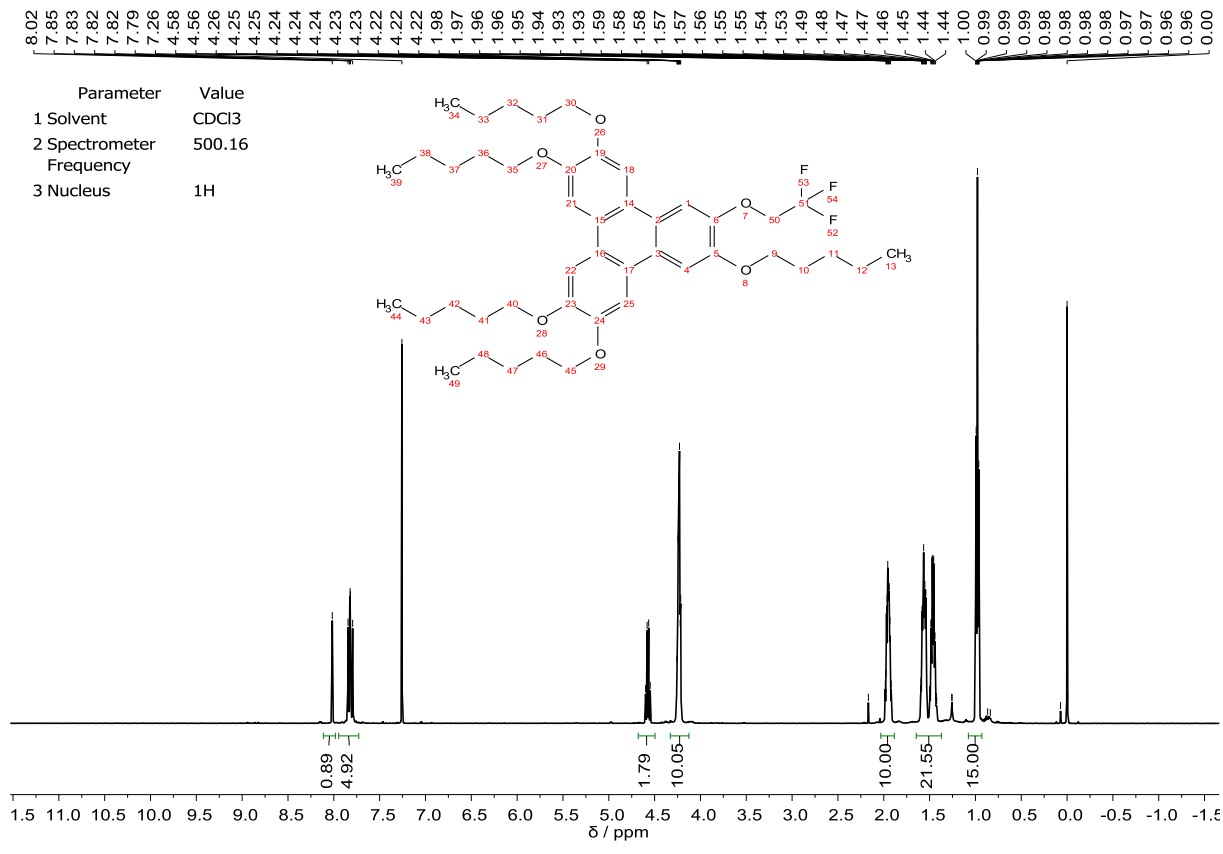


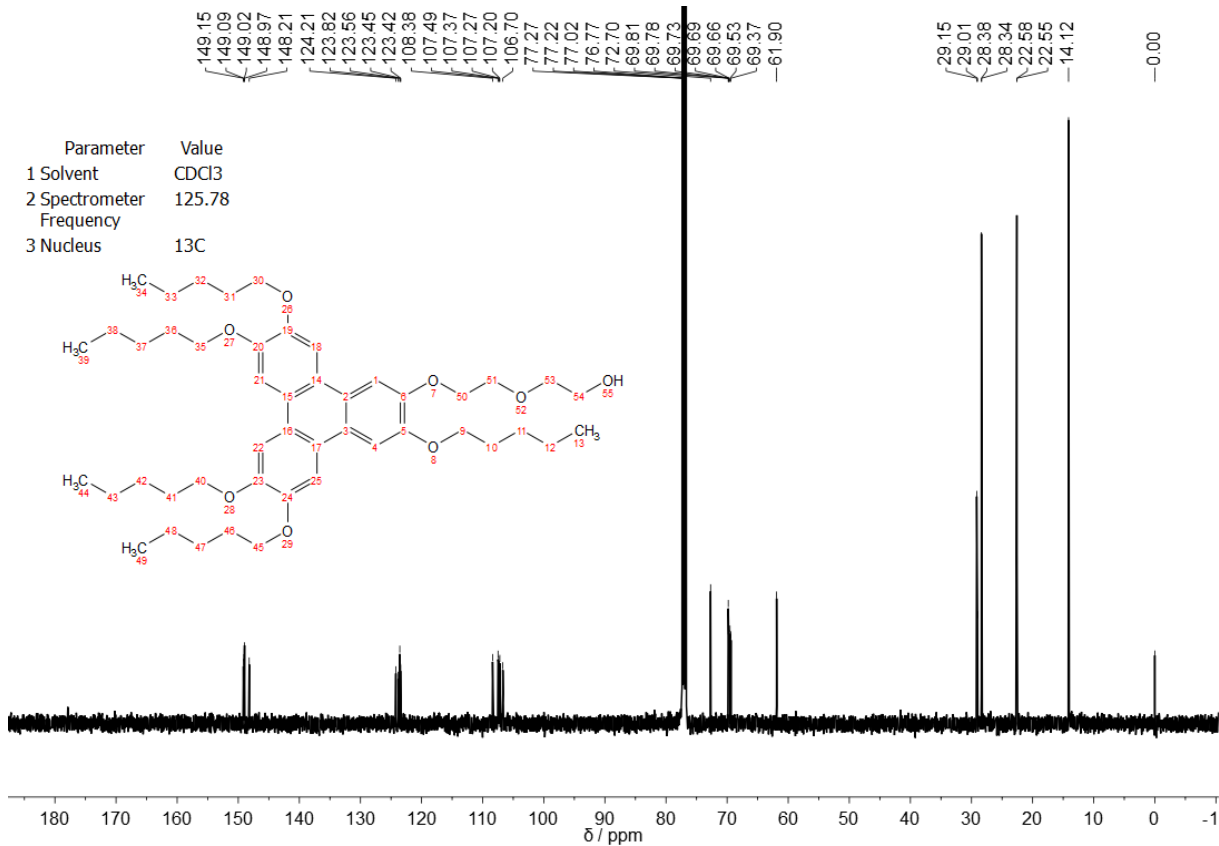
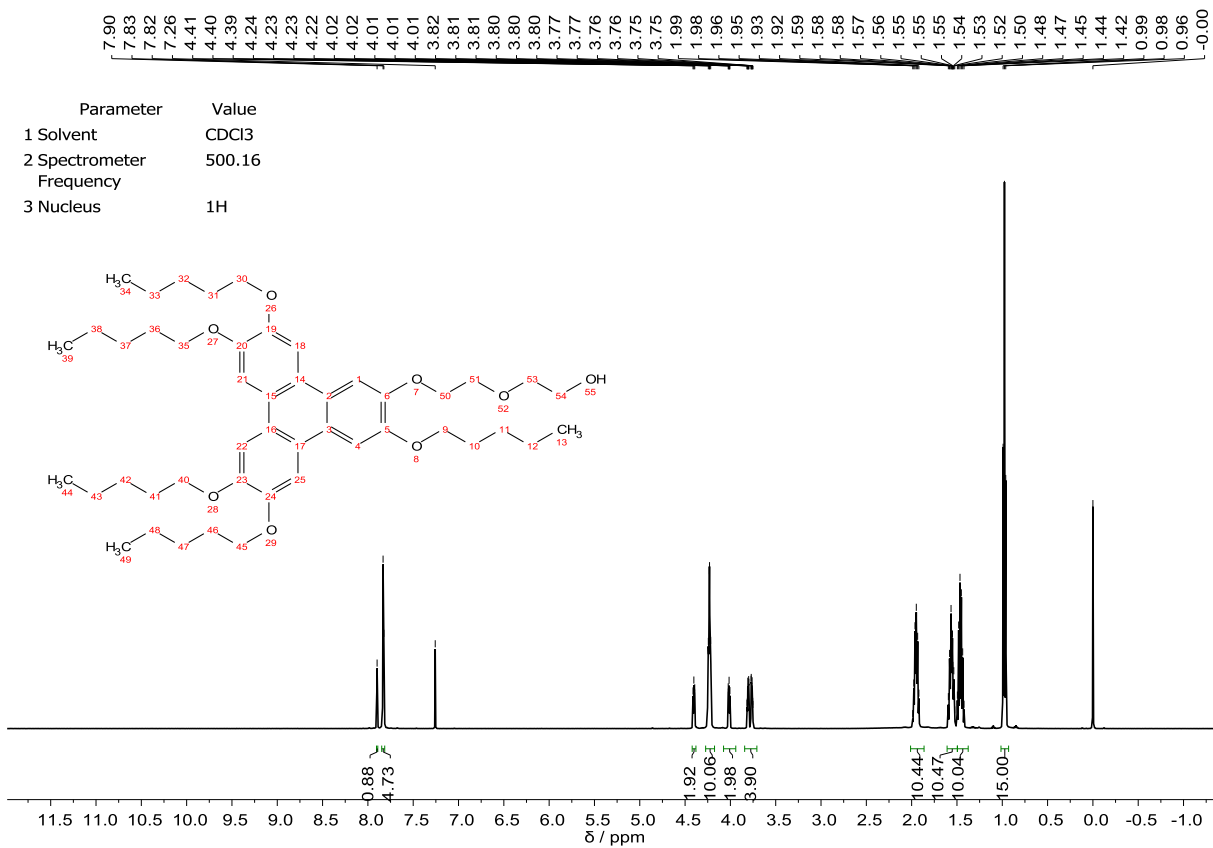








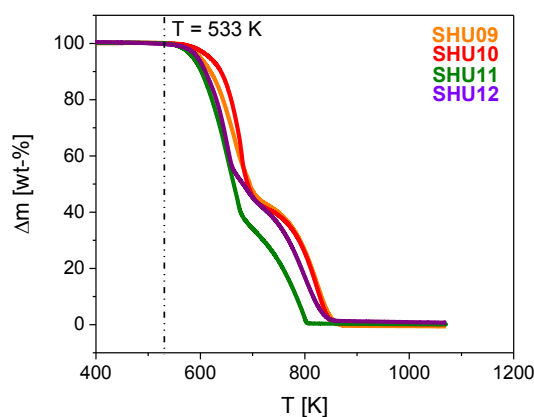




## Thermogravimetric Analysis (TGA)

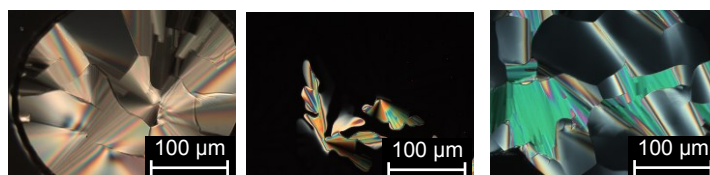
Measurements and sample preparation for the measurements may cause thermal decompositions of a sample. Thermal stability of the materials presented in this study was investigated using thermogravimetric analysis (TGA) in order to ensure that no thermal decomposition is taking place. TGA measurements were carried out by a Seiko TG/DTA 220 with a heating rate of 10 K/min, from room 303 K to 1073 K, under synthetic air.

Figure S1 shows mass loss profiles of the monofunctionalized triphenylene derivatives **SHU09-12** under synthetic air upon heating. All the samples shown in Figure S1 are thermally stable at least up to 533 K, which ensures that there was no thermal degradation during the sample preparation and the measurements.

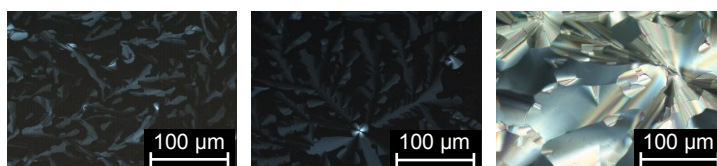


**Figure S1.** TGA curves for the monofunctionalized triphenylene derivatives **SHU09-SHU12**. Orange line shows data for **SHU09**, red line for **SHU10**, green line for **SHU11** and purple line for **SHU12**. Dashed-dotted line represent the temperature, 533K, below which thermal decomposition of the materials do not occur.

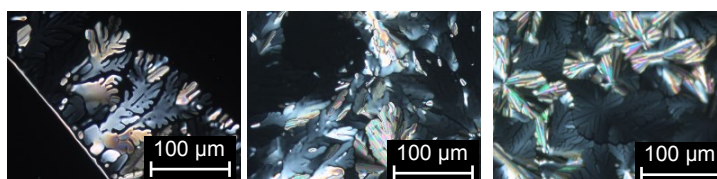
## POM Textures



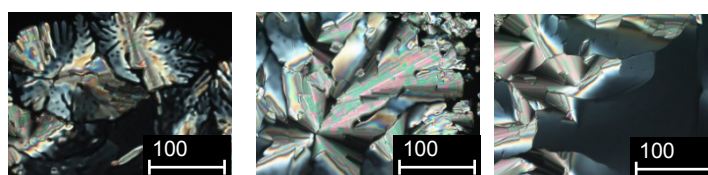
**Figure S2.** POM textures of SHU09 at 408 K (left), at 398 K (middle) and at 365 K (right) upon cooling from the isotropic liquid (cooling rate 5K/min, magnification 200x) showing pseudo focal conic fan-shaped textures and dendrimeric growth textures.



**Figure S3.** POM textures of SHU10 at 499 K (left), at 436 K (middle) and at 383 K (right) upon cooling from the isotropic liquid (cooling rate 5K/min, magnification 200x) showing dendrimeric growth and pseudo focal conic fan-shaped textures.

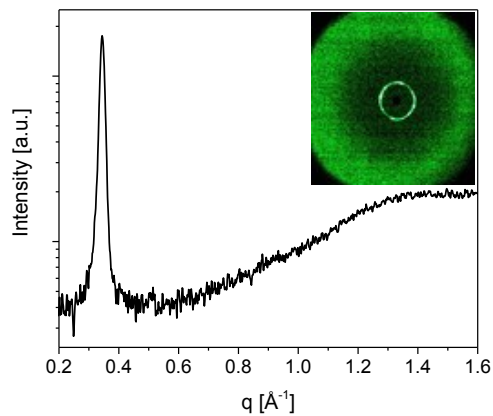


**Figure S4.** POM textures of SHU11 at 447 K (left) at 436 K (middle) and at 368 K (right) upon cooling from the isotropic liquid (cooling rate 5K/min, magnification 200x) showing dendrimeric growth textures.

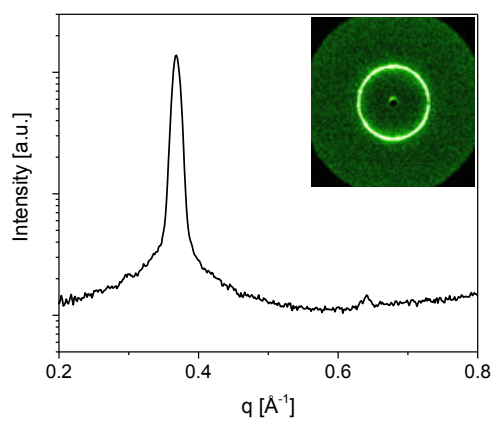


**Figure S5.** POM textures of SHU12 at 373 K (left), at 365 K (middle) and at 346 K (right) upon cooling from the isotropic liquid (cooling rate 5K/min, magnification 200x) showing dendrimeric growth and pseudo focal conic fan-shaped textures.

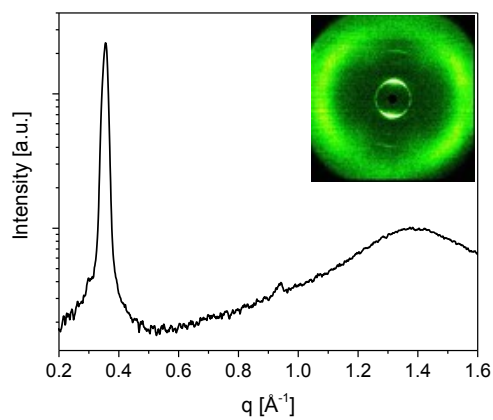
## XRD Data and Diffraction Patterns



**Figure S6.** WAXS diffractogram of **SHU09** at 363 K with the corresponding diffraction pattern (inset).

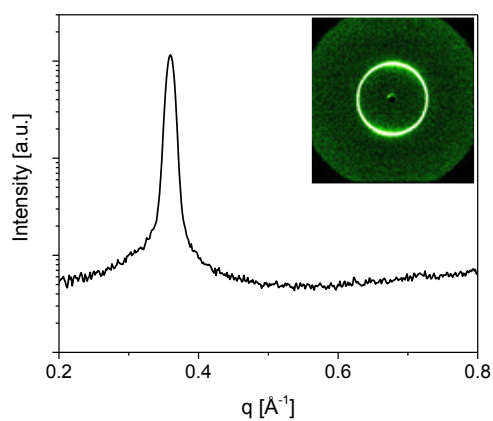


**Figure S7.** SAXS diffractogram of **SHU09** at 363 K with the corresponding diffraction pattern (inset).

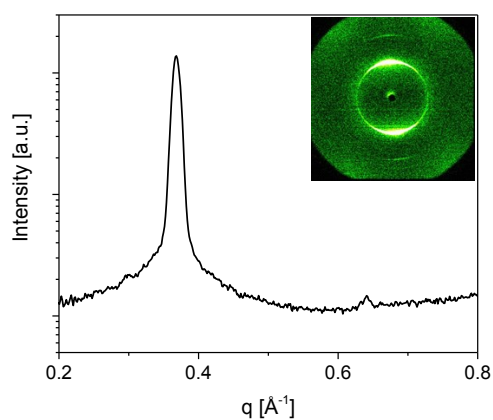


**Figure S8.** WAXS diffractogram of **SHU10** at 353 K with the corresponding diffraction pattern (inset).

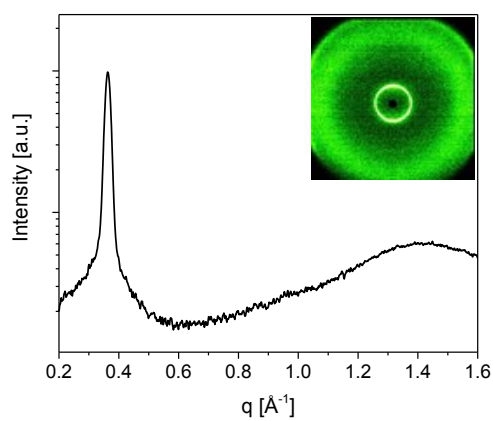




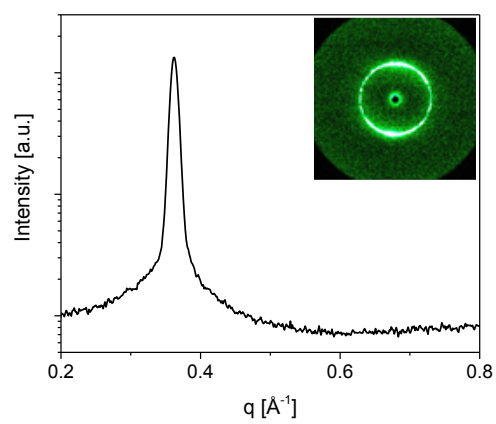
**Figure S9.** SAXS diffractogram of **SHU10** at 353 K with the corresponding diffraction pattern (inset).



**Figure S10.** SAXS diffractogram of **SHU11** at 353 K with the corresponding diffraction pattern (inset).



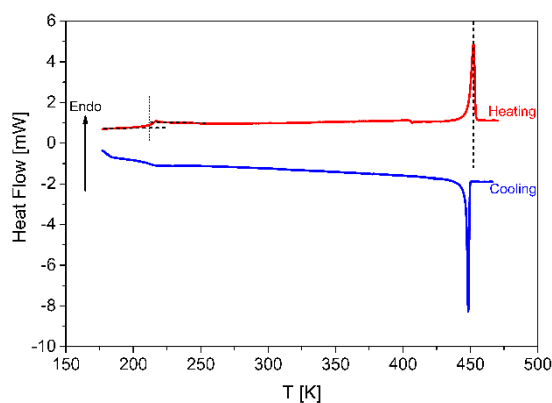
**Figure S11.** WAXS diffractogram of **SHU12** at 353 K with the corresponding diffraction pattern (inset).



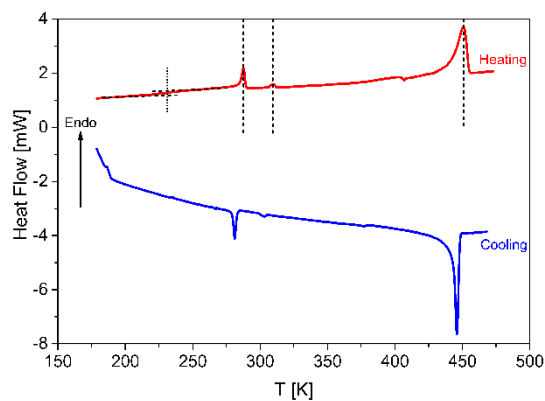
**Figure S12.** SAXS diffractogram of SHU12 at 353 K with the corresponding diffraction pattern (inset).

## Differential Scanning Calorimetry (DSC)

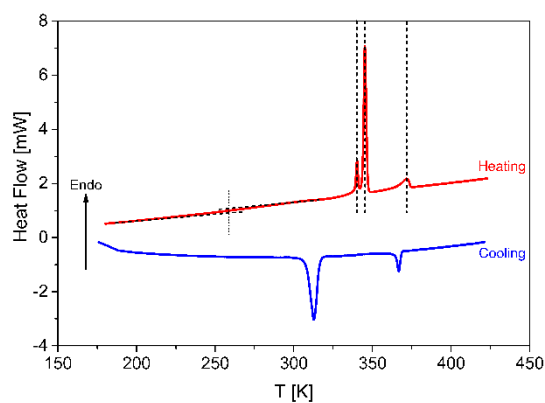
Conventional DSC measurements of SHU10, SHU11, SHU12 and HAT5 were carried out at temperatures down to 173 K under nitrogen purge. DSC traces of SHU10, SHU11, SHU12 and HAT5 measured under nitrogen purge are given in Figure S13-S16. In addition, conventional DSC measurements of the compounds were also conducted at temperatures down to 103 K under helium purge (see Figure S17). The measurements were performed in the temperature range from 103 K to 303 K with a heating/cooling rate of 10 K/min. Helium was used as a purge gas at a flow rate of 20 ml/min. Similar to the measurements performed under nitrogen purge, baseline measurements were conducted by measuring an empty 50  $\mu$ l aluminum pan under the same conditions. The baselines were subtracted from the data measured for the samples. The calibration of the DSC was checked before the measurement by measuring an indium standard.



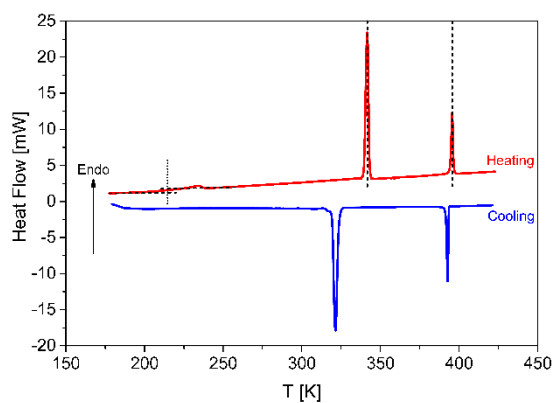
**Figure S13.** DSC thermograms of SHU10 for the first cooling and the second heating run at a heating/cooling rate of 10 K/min. Dashed lines point out the phase transition temperatures observed during the second heating run. Dotted line indicates the glass transition temperature observed during the second heating run.



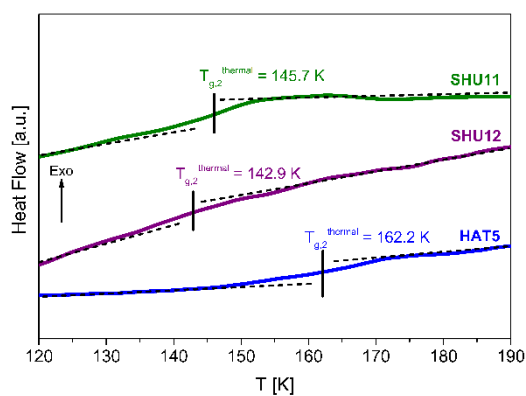
**Figure S14.** DSC thermograms of SHU11 for the first cooling and the second heating run at a heating/cooling rate of 10 K/min. Dashed lines point out the phase transition temperatures observed during the second heating run. Dotted line indicates the glass transition temperature observed during the second heating run.



**Figure S15.** DSC thermograms of SHU12 for the first cooling and the second heating run at a heating/cooling rate of 10 K/min. Dashed lines point out the phase transition temperatures observed during the second heating run. Dotted line indicates the glass transition temperature observed during the second heating run.



**Figure S16.** DSC thermograms of **HAT5** for the first cooling and the second heating run at a heating/cooling rate of 10 K/min. Dashed lines point out the phase transition temperatures observed during the second heating run. Dotted line indicates the glass transition temperature observed during the second heating run.

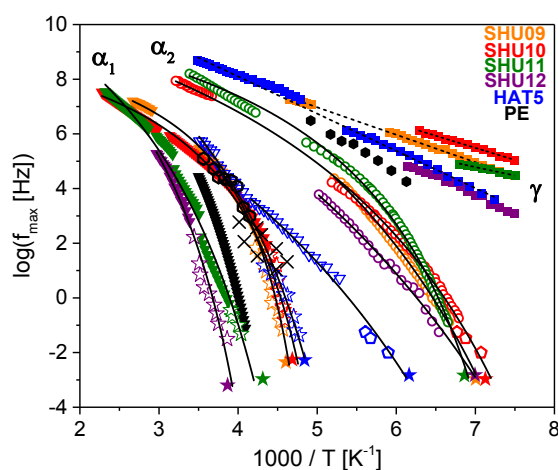


**Figure S17.** DSC thermograms of **SHU11**-**SHU12** and **HAT5** for the second heating run at a heating rate of 10 K/min at low temperatures. Solid lines point out the glass transition temperatures observed during the second heating run.

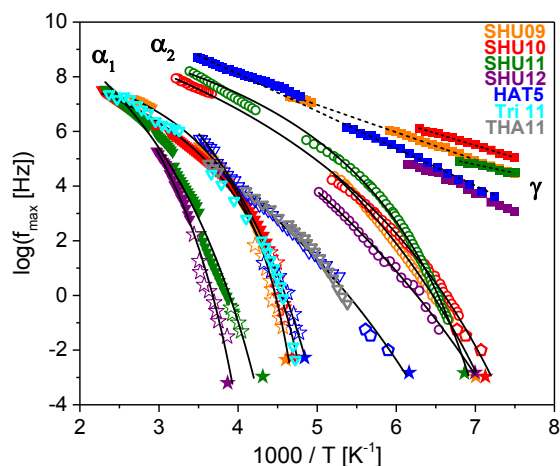
## **Broadband Dielectric Spectroscopy (BDS)**

The relaxation maps, containing the data for **SHU09-12** and **HAT5** as well as the data taken from the literature for the related relaxation processes, are given in Figure S18 and Figure S19. VFT parameters obtained from VFT equation fits and activation energies estimated from Arrhenius equation fits are presented in

Table *S1*. Furthermore, the plot of the lattice spacing versus the relaxation rates of  $\gamma$ -processes at chosen temperature is shown in Figure S20.



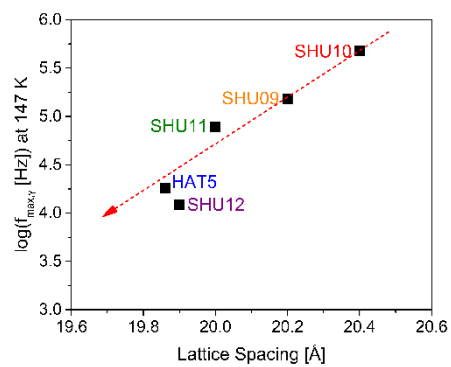
**Figure S18.** Combined relaxation map of **SHU09-SHU12** constructed from data obtained by BDS, Flash DSC and DSC. Orange symbols – data for **SHU09**; red symbols – data for **SHU10**; green symbols – data for **SHU11**; purple symbols – data for **SHU12**; and blue symbols – data for **HAT5**. Triangles –  $\alpha_1$ -relaxations (BDS); open circles –  $\alpha_2$ -relaxation (BDS); filled squares –  $\gamma$ -relaxations (BDS); open stars –  $\alpha_1$ -relaxations (FSC); open pentagons –  $\alpha_2$ -relaxation (SHS); and filled stars – thermal glass transition temperatures (DSC). Solid lines are the fits of VFT-equation to the data. Dashed line is the fit of the Arrhenius equation to the data. Black filled triangles denote the dielectric  $\alpha$ -relaxation of polyethylene taken from ref. 3. Black hexagons symbolize the dielectric  $\gamma$ -relaxation of polyethylene taken from ref. 4. Black crosses represent the calorimetric  $\alpha$ -relaxation of polyethylene taken from ref. 5. Black open hexagons symbolize the dielectric  $\beta$ -relaxation of poly(n-decyl methacrylate) taken from ref. 6.



**Figure S19.** Combined relaxation map of SHU09-SHU12 constructed from data obtained by BDS, Flash DSC and DSC. Orange symbols – data for SHU09; red symbols – data for SHU10; green symbols – data for SHU11; purple symbols – data for SHU12; blue symbols – data for HAT5; cyan blue symbols – data for Tri11 taken from ref. 7; and gray symbols – data for THA11 taken from ref. 7. Triangles –  $\alpha_1$ -relaxations (BDS); open pentagons –  $\alpha_2$ -relaxation (SHS); open circles –  $\alpha_2$ -relaxation (BDS); filled squares –  $\gamma$ -relaxations (BDS); open stars –  $\alpha_1$ -relaxations (FSC); and filled stars – thermal glass transition temperatures (DSC). Solid lines are the fits of VFT-equation to the data. Dashed line is the fit of the Arrhenius equation to the data.

**Table S1.** VFT parameters and activation energies obtained from VFT and Arrhenius equations fits

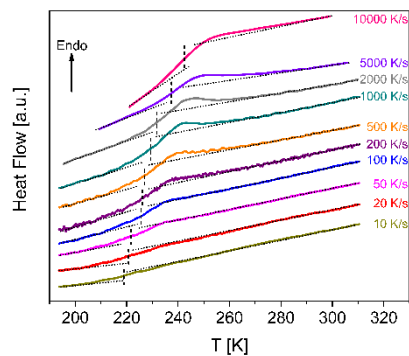
Compound	Process	Dependence	$\log(f_\infty)$ [Hz]	$T_0$ [K]	$E_A$ [kJ/mol]
SHU09	$\alpha_1$	VFT	$9.1 \pm 0.1$	$184.5 \pm 1.2$	-
	$\alpha_2$	VFT	$12.0 \pm 0.3$	$91.2 \pm 2.2$	-
	$\gamma$	Arrhenius	$12.0 \pm 0.1$	-	$19.2 \pm 0.1$
SHU10	$\alpha_1$	VFT	$9.0 \pm 0.2$	$172.5 \pm 1.3$	-
	$\alpha_2$	VFT	$10.8 \pm 0.1$	$93.5 \pm 1.4$	-
	$\gamma$	Arrhenius	$11.7 \pm 0.1$	-	$17.0 \pm 0.3$
SHU11	$\alpha_1$	VFT	$12.0 \pm 0.3$	$163.3 \pm 4.7$	-
	$\alpha_2$	VFT	$10.3 \pm 0.1$	$114.8 \pm 0.4$	-
	$\gamma$	Arrhenius	$9.1 \pm 0.2$	-	$11.9 \pm 0.6$
SHU12	$\alpha_1$	VFT	$12.0 \pm 1.3$	$190.5 \pm 11.6$	-
	$\alpha_2$	VFT	$12.0 \pm 0.9$	$73.1 \pm 7.5$	-
	$\gamma$	Arrhenius	$13.1 \pm 0.4$	-	$25.6 \pm 1.0$
HAT5	$\alpha_1$	VFT	$12.0 \pm 1.0$	$147.5 \pm 9.3$	-
	$\alpha_2$	VFT	$10.2 \pm 1.1$	$85.8 \pm 12.2$	-
	$\gamma$	Arrhenius	$13.6 \pm 0.1$	-	$26.1 \pm 0.2$



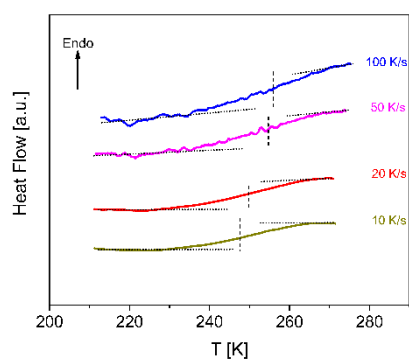
**Figure S20.** Relaxation rates of  $\gamma$ -processes at 147 K versus lattice spacing for SHU09-SHU12 and HAT5 as indicated. The arrow is a guide for the eye.



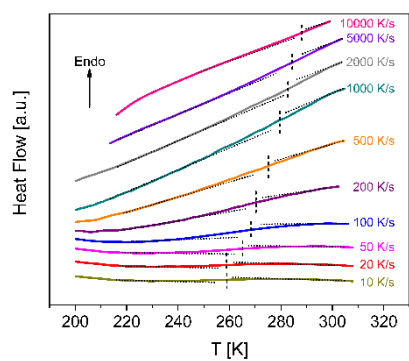
## Fast Scanning Calorimetry (FSC)



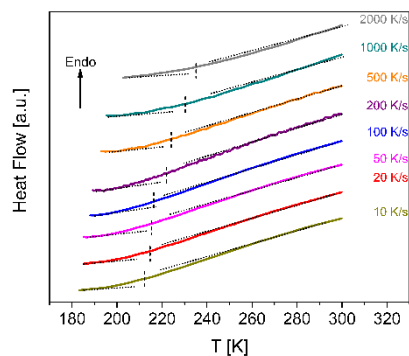
**Figure S21.** FSC thermograms of SHU09 for heating runs at different heating rates as indicated. Dashed lines indicate the thermal glass transition temperatures estimated.



**Figure S22.** FSC thermograms of SHU11 for heating runs at different heating rates as indicated. Dashed lines indicate the thermal glass transition temperatures estimated.



**Figure S23.** FSC thermograms of SHU12 for heating runs at different heating rates as indicated. Dashed lines indicate the thermal glass transition temperatures estimated.



**Figure S24.** FSC thermograms of **HAT5** for heating runs at different heating rates as indicated. Dashed lines indicate the thermal glass transition temperatures estimated.

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