Electronic Supplementary Material (ESI) for Soft Matter.

# Supporting Information

# Encapsulating propeller-like columnar liquid crystals with an aromatic outer shell: influence of phenoxy-terminated side chains on the phase behaviour of triphenylbenzenes

Korinna Bader, Tobias Wöhrle, Esra Öztürk, Angelika Baro and Sabine Laschat*

Institut für Organische Chemie, Universität Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany. E-mail: sabine.laschat@oc.uni-stuttgart.de

## General Informations

The following instruments were used for characterization of the compounds. NMR: The spectra were recorded on *Bruker Avance 250* ($^1$H, 250 MHz; $^{13}$C, 63 MHz), *Bruker Avance 300* ($^1$H, 300 MHz; $^{13}$C, 75 MHz) and *Bruker Avance 500* ($^1$H, 500 MHz; $^{13}$C, 126 MHz). The following abbreviations were used: s (singlet), d (doublet), t (triplet), $m_c$ (centered multiplet), m (multiplet). The measurements were carried out in $CDCl_3$ at 296 K. The chemical shift δ is in parts per million (ppm) with tetramethylsilane (TMS) as a reference. The assignment of the signals was conducted with COSY, HSQC and HMBC experiments. MS (EI): *Varian MAT 711* spectrometer. MS (ESI): *Bruker Daltonics microTOF-Q* spectrometer. IR: *Bruker Vektor22* FT-IR spectrometer with *MKII Golden Gate single reflection diamond ATR-system*. To describe the intensities following abbreviations were used: vs (very strong), s (strong), m (medium), w (weak). Elemental analyses: *Carlo Erba Strumentazione Elemental Analyzer Model 1106*. Polarising optical microscopy: *Olympus BX 50* polarising microscope combined with a *Linkam TP93* central controller. DSC: *Mettler-Toledo DSC 822e* differential scanning calorimeter (heating / cooling rates: 5 K $min^{-1}$). X-ray diffraction (WAXS, SAXS): *Bruker AXS Nanostar C* diffractometer employing Ni-filtered $Cu_{K\alpha}$ radiation ($\alpha$ = 1.5418 Å), calibrated using silver behenate. All commercial reagents were used without further purification. Abs. solvents were dried and distilled under nitrogen prior to use and all reactions were carried out under a nitrogen atmosphere with Schlenk-type glassware. Flash chromatography was performed on silica gel, grain size 40–63 µm (*Fluka*) and aluminium sheets precoated with silica gel 60 $F_{254}$ (*Merck*) were used for thin layer chromatography (TLC).

## General Procedures

### General procedure for the preparation of the bromoalkyloxybenzenes 2a-e (GP 1)[1]

The respective dibromoalkane (105.3 mmol) was dissolved in EtOH (80 mL). The solution was heated up to 60 °C, sodium phenolate or sodium 4-fluorophenolate (35.1 mmol in THF) was added dropwise and the reaction mixture refluxed for 60 h. The precipitated solid (NaBr) was filtered off and the filtrate was evaporated under reduced pressure. The residue was washed with $H_2O$ (3 x 20 mL) and dried ($MgSO_4$). The crude product was purified twice by column chromatography on silica gel (hexanes/$CH_2Cl_2$ 10:1).

### General procedure for the preparation of the 1,2,3-tris(phenoxyalkyloxy)-5-bromobenzenes 3a-e (GP 2)[2]

$K_2CO_3$ (47.70 mmol) was added to a solution of 5-bromobenzene-1,2,3-triol (6.36 mmol) in degassed DMF (30 mL). The reaction mixture was degassed for 30 min, the respective bromoalkyloxybenzene **2a–e** (21.00 mmol) was added and the reaction mixture stirred over night at 80 °C equipped with a drying tower. The solution was filtered, evaporated under reduced pressure and the crude product was purified by column chromatography on silica gel (hexanes/EtOAc 100:1).

### General procedure for the preparation of the pinacolborolanes 4a-e (GP 3)[3]

*n*-BuLi (6.00 mmol in *n*-hexane) was added at –78 °C to a solution of the respective 1,2,3-tris(phenoxyalkyloxy)-5-bromobenzene **3a–e** (3.00 mmol) in abs. THF (50 mL). The reaction mixture was stirred for 60 min, then isopropyl pinacol borate (6.30 mmol) was added at –78 °C and the reaction mixture was stirred for further 1 h at this temperature. After warming to room temperature over 24 h, the reaction was terminated by addition of $NH_4Cl$ (25 mL, saturated solution) and stirring for 20 min. The resulted aqueous suspension was extracted with $Et_2O$ (50 mL). The organic layer was washed with $H_2O$ (2 x 50 mL), dried ($MgSO_4$) and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (hexanes/$Et_2O$ 50:1).

### General procedure for the Suzuki coupling reactions (GP 4)[4]

Tribromobenzene (0.236 mmol) and degassed $H_2O$ (7 mL) were added to a solution of the respective tris(3,4,5-phenoxyalkoxyphenyl)pinacolborolane **4a–e** (0.900 mmol) in degassed DMF (25 mL). Then $K_2CO_3$ (1.062 mmol) and $Pd[PPh_3]_4$ (12 µmol) were added and the reaction mixture was stirred for 24 h at 90 °C. The dark-colored solution was poured onto $H_2O$ (50 mL) and extracted with $CH_2Cl_2$ (3 x 80 mL). The combined organic layers were washed with $H_2O$ (2 x 100 mL), dried ($MgSO_4$) and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (hexanes/EtOAc 20:1).

## Precursors

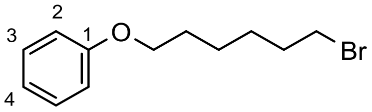
### Standard solution of sodium phenolate in THF[5]

Sodium (2.45 g, 106 mmol) was added at 0 °C to a solution of phenol **1a** (10 g, 106 mmol) in THF (400 mL) and the reaction mixture stirred for 18 h at room temperature to give a standard solution of sodium phenolate **16** with c = 0.27 mol/L.

### Standard solution of sodium 4-fluorophenolate in THF[5]

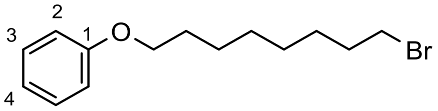
Sodium (2.36 g, 103 mmol) was added at 0 °C to a solution of 4-fluorophenol **1b** (11.50 g, 103 mmol) in THF (120 mL) and the reaction mixture stirred for 18 h at room temperature to give a standard solution of sodium 4-fluorophenolate with c = 0.85 mol/L.

**((6-Bromohexyl)oxy)benzene (2a)**



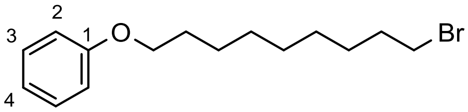
Synthesis according to GP 1. From sodium phenolate (130 mL. 35.1 mmol, 0.27 M in THF), 1,6-dibromohexane (16.20 mL, 25.70 g, 105 mmol), EtOH (70 mL); yield: 5.61 g, 21.82 mmol, 62 %; colorless oil; $^1$H-NMR (250 MHz, $CDCl_3$): $\delta$ = 1.42–1.59 (m, 4H, $\mathrm{C}H_2$), 1.73–1.97 (m, 4H, $\mathrm{OCH_2C}H_2$, $\mathrm{BrCH_2C}H_2$), 3.43 (t, *J* = 6.8 Hz, 2H, Br-$\mathrm{C}H_2$), 3.96 (t, *J* = 6.5 Hz, 2H, $\mathrm{OC}H_2$), 6.88–6.96 (m, 3H, 2-H, 4-H), 7.25-7.31 (m, 2H, 3-H) ppm; $^{13}$C-NMR (63 MHz, $CDCl_3$): $\delta$ = 25.3, 27.9, 29.1, 32.7, 33.8 ($CH_2$), 67.6 ($\mathrm{O}C\mathrm{H_2}$), 114.5 (C-2), 120.5 (C-4), 129.4 (C-3), 159.0 (C-1) ppm; the experimental data are in agreement with literature values.[1]

**((8-Bromooctyl)oxy)benzene (2b)**



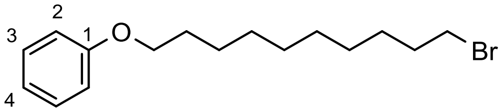
Synthesis according to GP 1. From sodium phenolate (130 mL, 35.1 mmol, 0.27 M in THF), 1,8-dibromooctane (19.51 mL, 28.64 g, 105.3 mmol), EtOH (70 mL); yield: 5.47 g, 19.20 mmol, 55 %; colorless oil; $^1$H-NMR (250 MHz, $CDCl_3$): $\delta$ = 1.29–1.53 (m, 8H, $\mathrm{C}H_2$), 1.73–1.92 (m, 4H, $\mathrm{OCH_2C}H_2$, $\mathrm{BrCH_2C}H_2$), 3.41 (t, *J* = 6.8 Hz, 2H, Br-$\mathrm{C}H_2$), 3.95 (t, *J* = 6.5 Hz, 2H, $\mathrm{OC}H_2$), 6.88–6.96 (m, 3H, 2-H, 4-H), 7.25-7.28 (m, 2H, 3-H) ppm; $^{13}$C-NMR (63 MHz, $CDCl_3$): $\delta$ = 26.0, 28.1, 28.7, 29.2, 29.3, 32.8, 34.0 ($CH_2$), 67.8 ($\mathrm{O}C\mathrm{H_2}$), 114.5 (C-2), 120.5 (C-4), 129.4 (C-3), 159.1 (C-1) ppm; the experimental data are in agreement with literature values.[1]

**((9-Bromononyl)oxy)benzene (2c)**



Synthesis according to GP 1. From sodium phenolate (130 mL, 35.1 mmol, 0.27 M in THF), 1,9-dibromononane (21.41 mL, 30.13 g, 105.3 mmol), EtOH (70 mL); yield: 4.95 g, 16.54 mmol, 47 %; colorless oil; $^1$H-NMR (250 MHz, $CDCl_3$): $\delta$ = 1.25–1.53 (m, 10H, $\mathrm{C}H_2$), 1.72–1.91 (m, 4H, $\mathrm{OCH_2C}H_2$, $\mathrm{BrCH_2C}H_2$), 3.41 (t, *J* = 6.8 Hz, 2H, $\mathrm{BrC}H_2$), 3.95 (t, *J* = 6.5 Hz, 2H, $\mathrm{OC}H_2$), 6.88–6.96 (m, 3H, 2-H, 4-H), 7.25-7.31 (m, 2H, 3-H) ppm; $^{13}$C-NMR (63 MHz, $CDCl_3$): $\delta$ = 26.0, 26.9, 28.1, 28.7, 29.2, 29.4, 32.8, 34.1 ($CH_2$), 67.8 ($\mathrm{O}C\mathrm{H_2}$), 114.5 (C-2), 120.5 (C-4), 129.4 (C-3), 159.1 (C-1) ppm; the experimental data are in agreement with literature values.[1]

**((10-Bromodecyl)oxy)benzene (2d)**

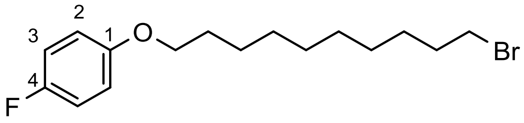


Synthesis according to GP 1. From sodium phenolate (50 mL, 42.5 mmol, 0.85 M in THF), 1,10-dibromodecane (28.7 mL, 38.3 g, 127.5 mmol), EtOH (70 mL); yield: 8.03 g, 25.64 mmol, 60 %;

colorless solid; $^1$H-NMR (300 MHz, CDCl$_3$): δ = 1.24–1.50 (m, 12H, C*H*$_2$), 1.72–1.92 (m, 4H, OCH$_2$C*H*$_2$, BrCH$_2$C*H*$_2$), 3.41 (t, *J* = 6.8 Hz, 2H, BrC*H*$_2$), 3.95 (t, *J* = 6.6 Hz, 2H, OC*H*$_2$), 6.86–6.98 (m, 3H, 2-H, 4-H), 7.23–7.32 (m, 2H, 3-H) ppm; $^{13}$C-NMR: (75 MHz, CDCl$_3$): δ = 26.0, 28.2, 28.7, 29.28, 29.33, 29.4, 32.8, 34.0 (*C*H$_2$), 67.8 (O*C*H$_2$), 114.5 (C-2), 120.4 (C-4), 129.4 (C-3), 159.1 (C-1) ppm; the experimental data are in agreement with literature values.[1]

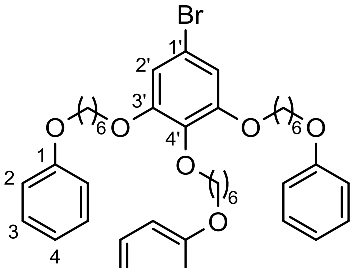
**1-((10-Bromodecyl)oxy)-4-fluorobenzene (2e)**

Synthesis according to GP 1. From sodium 4-fluorophenolate (97 mL, 82.03 mmol, 0.85 M in THF), 1,10-dibromodecane (55.31 mL, 73.84 g, 246.09 mmol), EtOH (70 mL); yield: 14.07 g, 42.48 mmol, 52 %; colorless solid; $^1$H-NMR (300 MHz, CDCl$_3$): δ = 1.23–1.51 (m, 12H, C*H*$_2$), 1.69–1.92 (m, 4H, OCH$_2$C*H*$_2$, BrCH$_2$C*H*$_2$), 3.40 (t, *J* = 6.8 Hz, 2H, BrC*H*$_2$), 3.90 (t, *J* = 6.6 Hz, 2H, OC*H*$_2$), 6.78–6.86 (m, 2H, 2-H), 6.91–7.00 (m, 2H, 3-H) ppm; $^{13}$C-NMR (75 MHz, CDCl$_3$): δ = 26.0, 28.2, 28.7, 29.27, 29.33, 29.35, 29.43 32.8, 34.0 (*C*H$_2$), 68.6 (O*C*H$_2$), 115.4 (d, *J* = 8.0 Hz, C-2), 115.7 (d, *J* = 23.1 Hz, C-3), 155.3 (d, *J* = 2.0 Hz, C-1), 157.1 (d, *J* = 237.6 Hz, C-4) ppm; ; MS (EI): *m/z* = 330 (10) [M]$^+$, 112 (100); HRMS (EI): calcd. for $C_{16}H_{24}BrFO$: 330.0995 [M($^{79}$Br)]$^+$, 332.0976 [M($^{81}$Br)]$^+$, found: 330.0993 [M($^{79}$Br)]$^+$, 332.0976 [M($^{81}$Br)]$^+$; FT-IR (ATR): $\tilde{\nu}$ = 424 (w), 513 (s), 562 (w), 645 (w), 721 (s), 756 (s), 793 (w), 825 (vs), 916 (w), 1027 (w), 1096 (w), 1152 (w), 1206 (vs), 1247 (s), 1293 (w), 1392 (w), 1470 (s), 1504 (vs), 1600 (w), 2854 (s), 2926 (s) cm$^{-1}$.



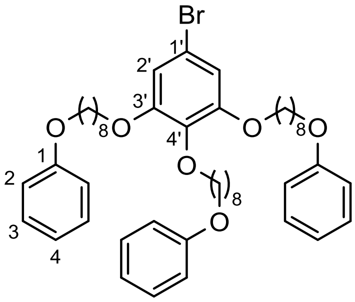
**1,2,3-Tris(phenoxyhexyloxy)-5-bromobenzene (3a)**

Synthesis according to GP 2. From 5-bromobenzene-1,2,3-triol (1.31 g, 6.36 mmol), bromohexyloxybenzene **2a** (5.40 g, 21.00 mmol), K$_2$CO$_3$ (6.60 g, 47.70 mmol), DMF (50 mL); yield: 4.61 g, 6.28 mmol, 98 %; colorless solid; $^1$H-NMR (250 MHz, CDCl$_3$): δ = 1.45–1.62 (m, 12H, C*H*$_2$), 1.68–1.91 (m, 12H, OCH$_2$C*H*$_2$), 3.89–3.97 (m, 12H, OC*H*$_2$), 6.68 (s, 2H, 2'-H), 6.87–6.95 (m, 9H, 2-H, 4-H), 7.22–7.27 (m, 6H, 3-H) ppm; $^{13}$C-NMR (63 MHz, CDCl$_3$): δ = 25.8, 25.9, 26.0, 26.9, 29.2, 29.26, 29.33, 30.1 (*C*H$_2$), 67.7, 69.1, 73.2 (O*C*H$_2$), 110.1 (C-2'), 114.4 (C-2), 115.7 (C-1'), 120.4 (C-4), 129.4 (C-3), 137.2 (C-4'), 153.7 (C-3'), 159.0 (C-1) ppm; MS (ESI): *m/z* = 757.29 [M + Na]$^+$; HRMS (ESI): calcd. for $C_{42}H_{53}BrO_6Na$: 756.2952 [M($^{79}$Br)+ Na]$^+$, 758.2935 [M($^{81}$Br) + Na]$^+$, found: 756.2935 [M($^{79}$Br) + Na]$^+$, 758.2918 [M($^{81}$Br)+ Na]$^+$; FT-IR (ATR): $\tilde{\nu}$ = 511 (m), 577 (w), 690 (s), 751 (vs), 811 (m), 991 (m), 1006 (m), 1033 (s),



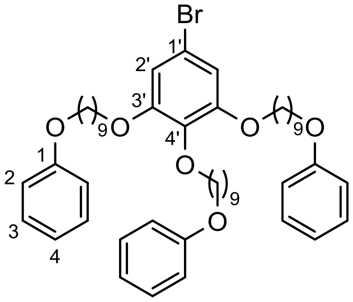
1079 (s), 1111 (s), 1153 (w), 1171 (s), 1225 (vs), 1241 (vs), 1301 (m), 1386 (m), 1421 (m), 1470 (s), 1494 (s), 1585 (s), 1599 (m), 1725 (w), 2863 (m), 2937 (m), 3039 (w) cm$^{-1}$.

**1,2,3-Tris(phenoxyoctyloxy)-5-bromobenzene (3b)**



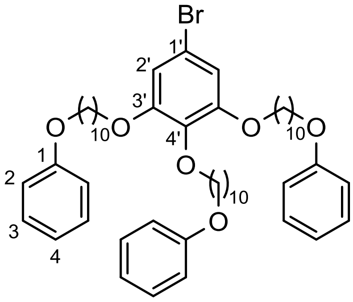
Synthesis according to GP 2. From 5-bromobenzene-1,2,3-triol (1.14 g, 5.53 mmol), bromooctyloxybenzene **2b** (5.20 g, 18.23 mmol), $K_2CO_3$ (5.73 g, 41.48 mmol), DMF (50 mL); yield: 3.78 g, 4.62 mmol, 84 %; colorless solid; $^1$H-NMR (250 MHz, $CDCl_3$): $\delta$ = 1.31–1.54 (m, 24H, $CH_2$), 1.66–1.86 (m, 12H, $OCH_2CH_2$), 3.88–3.97 (m, 12H, $OCH_2$), 6.67 (s, 2H, 2'-H), 6.87–6.95 (m, 9H, 2-H, 4-H), 7.23–7.29 (m, 6H, 3-H) ppm; $^{13}$C-NMR (63 MHz, $CDCl_3$): $\delta$ = 25.9, 26.0, 26.9, 29.2, 29.3, 29.4, 29.5, 30.2 ($CH_2$), 67.8, 69.1, 73.4 ($OCH_2$), 110.0 (C-2'), 114.4 (C-2), 115.6 (C-1'), 120.4 (C-4), 129.4 (C-3), 137.3 (C-4'), 153.8 (C-3'), 159.1 (C-1) ppm; MS (EI): *m/z* = 818 (25) $[M]^+$, 614 (20), 204 (12), 94 (22), 69 (100); HRMS (EI): calcd. for $C_{48}H_{65}BrO_6$: 816.3965 $[M(^{79}Br)]^+$, 818.3956 $[M(^{81}Br)]^+$, found: 816.3956 $[M(^{79}Br)]^+$, 819.3942 $[M(^{81}Br)]^+$; FT-IR (ATR): $\tilde{\nu}$ = 511 (m), 577 (w), 691 (s), 724 (w), 751 (vs), 811 (m), 881 (m), 1033 (m), 1079 (m), 1110 (s), 1171 (m), 1242 (vs), 1301 (m), 1386 (m), 1421 (m), 1469 (s), 1494 (s), 1585 (s), 1599 (m), 1725 (w), 2855 (m), 2929 (m), 3039 (w) cm$^{-1}$.

**1,2,3-Tris(phenoxynonyloxy)-5-bromobenzene (3c)**



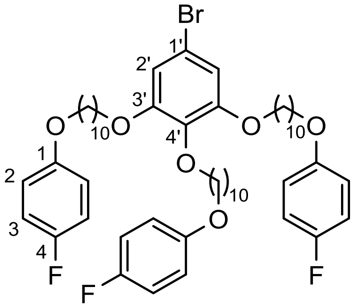
Synthesis according to GP 2. From 5-bromobenzene-1,2,3-triol (0.980 g, 4.76 mmol), bromononyloxybenzene **2c** (4.70 g, 15.70 mmol), $K_2CO_3$ (4.93 g, 35.70 mmol), DMF (50 mL); yield: 3.64 g, 4.23 mmol, 89 %; colorless solid; $^1$H-NMR (250 MHz, $CDCl_3$): $\delta$ = 1.27–1.54 (m, 30H, $CH_2$), 1.66–1.88 (m, 12H, $OCH_2CH_2$), 3.88–3.97 (m, 12H, $OCH_2$), 6.67 (s, 2H, 2'-H), 6.87–6.95 (m, 9H, 2-H, 4-H), 7.24–7.30 (m, 6H, 3-H) ppm; $^{13}$C-NMR (63 MHz, $CDCl_3$): $\delta$ = 26.0, 26.1, 26.9, 29.2, 29.3, 29.35, 29.44, 29.5, 29.6, 30.2 ($CH_2$), 67.8, 69.2, 73.4 ($OCH_2$), 110.0 (C-2'), 114.4 (C-2), 115.6 (C-1'), 120.4 (C-4), 129.4 (C-3), 137.3 (C-4'), 153.8 (C-3'), 159.1 (C-1) ppm; MS (EI): *m/z* = 860 (25) $[M]^+$, 642 (20), 204 (20), 69 (100); HRMS (EI): calcd. for $C_{51}H_{71}BrO_6$: 858.4434 $[M(^{79}Br)]^+$, 860.4426 $[M(^{81}Br)]^+$, found: 858.4443 $[M(^{79}Br)]^+$, 860.4430 $[M(^{81}Br)]^+$; FT-IR (ATR): $\tilde{\nu}$ = 511 (m), 577 (w), 691 (s), 724 (w), 752 (vs), 811 (m), 880 (m), 1035 (m), 1079 (m), 1111 (s), 1171 (m), 1242 (vs), 1301 (m), 1386 (m), 1421 (m), 1469 (s), 1495 (s), 1585 (s), 1599 (m), 2854 (m), 2926 (s), 3039 (w) cm$^{-1}$.

### 1,2,3-Tris(phenoxydecyloxy)-5-bromobenzene (3d)



Synthesis according to GP 2. From 5-bromobenzene-1,2,3-triol (1.10 g, 5.37 mmol), bromodecyloxybenzene **2d** (5.55 g, 17.71 mmol), $K_2CO_3$ (5.56 g, 40.25 mmol), DMF (50 mL); yield: 2.81 g, 3.11 mmol, 58 %; colorless solid; $^1$H-NMR (300 MHz, $CDCl_3$): δ = 1.28–1.49 (m, 36H, $C\mathit{H}_2$), 1.67–1.83 (m, 12H, $OCH_2C\mathit{H}_2$), 3.87–3.96 (m, 12H, $OC\mathit{H}_2$), 6.66 (s, 2H, 2'-H), 6.84–6.94 (m, 9H, 2-H, 4-H), 7.22–7.29 (m, 6H, 3-H) ppm; $^{13}$C-NMR: (75 MHz, $CDCl_3$): δ = 26.0, 26.07, 26.09, 29.2, 29.31, 29.32, 29.4, 29.47, 29.53, 29.61, 29.64, 30.3 ($\mathit{C}H_2$), 67.8, 69.2, 73.4 ($O\mathit{C}H_2$), 110.1 (C-2'), 114.5 (C-2), 115.6 (C-1'), 120.4 (C-4), 129.4 (C-3), 137.4 (C- 4'), 153.8 (C-3'), 159.1 (C-1) ppm; MS (ESI): *m/z* = 925.48 [M + Na]$^+$; HRMS (ESI): calcd. for $C_{54}H_{77}BrO_6Na$: 923.4796 [M($^{79}$Br) + Na]$^+$, 925.4789 [M($^{81}$Br) + Na]$^+$, found: 923.4794 [M($^{79}$Br) + Na]$^+$, 925.4791 [M($^{81}$Br) + Na]$^+$; FT-IR (ATR): $\tilde{\nu}$ = 510 (s), 577 (w), 690 (vs), 723 (w), 751 (vs), 811 (s), 880 (w), 1034 (s), 1079 (w), 1110 (vs), 1153 (w), 1171 (s), 1242 (vs), 1301 (s), 1386 (s), 1421 (s), 1468 (s), 1495 (s), 1585 (s), 1599 (w), 2853 (s), 2923 (vs), 3039 (w) cm$^{-1}$.

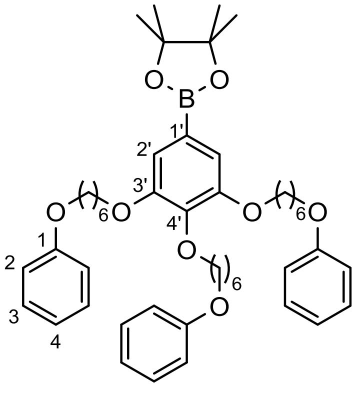
### 1,2,3-Tris(4'-fluorophenoxydecyloxy)-5-bromobenzene (3e)



Synthesis according to GP 2. From 5-bromobenzene-1,2,3-triol (1.00 g, 4.88 mmol), 1-((10-bromodecyl)oxy)-4-fluorobenzene **2e** (5.33 g, 16.10 mmol), $K_2CO_3$ (5.06 g, 36.60 mmol), DMF (50 mL); yield: 4.00 g, 4.18 mmol, 86 %; colorless solid; $^1$H-NMR (500 MHz, $CDCl_3$): δ = 1.28–1.49 (m, 36H, $C\mathit{H}_2$), 1.70–1.82 (m, 12H, $OCH_2C\mathit{H}_2$), 3.86–3.94 (m, 12H, $OC\mathit{H}_2$), 6.67 (s, 2H, 2'-H), 6.79–6.84 (m, 6H, 2-H), 6.92–6.97 (m, 6H, 3-H) ppm; $^{13}$C-NMR: (126 MHz, $CDCl_3$): δ = 25.8, 26.00, 26.03, 26.07, 26.08, 28.5, 29.1, 29.2, 29.29, 29.31, 29.39, 29.44, 29.5, 29.60, 29.63, 30.3 ($\mathit{C}H_2$), 64.1, 68.6, 69.2, 73.4 ($O\mathit{C}H_2$), 110.1 (C-2'), 115.37 (d, *J* = 8.0 Hz, C-2), 115.40 (C-1'), 115.7 (d, *J* = 23.1 Hz, C-3), 137.4 (C- 4'), 153.8 (C-3'), 155.3 (d, *J* = 2.0 Hz, C-1), 157.1 (d, *J* = 237.6 Hz, C-4) ppm; MS (ESI): *m/z* = 979.45 [M + Na]$^+$; HRMS (ESI): calcd. for $C_{54}H_{74}BrF_3O_6Na$: 977.4513 [M($^{79}$Br) + Na]$^+$, 979.4507 [M($^{81}$Br) + Na]$^+$, found: 977.4493 [M($^{79}$Br) + Na]$^+$, 979.4489 [M($^{81}$Br) + Na]$^+$; FT-IR (ATR): $\tilde{\nu}$ = 20 (w), 513 (s), 577 (w), 635 (w), 721 (s), 757 (s), 825 (vs), 942 (w), 1007 (w), 1032 (s), 1096 (s), 1111 (s), 1206 (vs), 1247 (s), 1294 (w), 1387 (w), 1421 (s), 1469 (s), 1504 (vs), 1586 (w), 1726 (w), 2854 (s), 2925 (s) cm$^{-1}$.

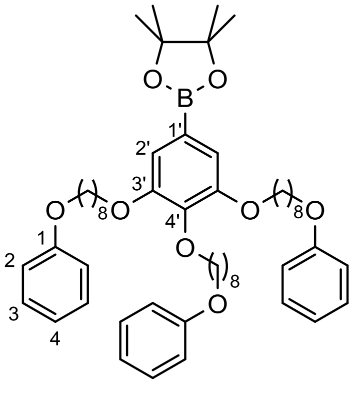
## Pinacolborolanes

### 2-(3',4',5'-Tris(phenoxyhexyloxy)phenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan (4a)



Synthesis according to GP 3. From 1,2,3-tris(phenoxyhexyloxy)-5-bromobenzene) **3a** (2.20 g, 3.00 mmol), *n*-BuLi (3.75 mL, 6.00 mmol, 1.6 M in *n*-hexane), isopropyl pinacol borate (1.29 mL, 1.17 g, 6.30 mmol), THF (50 mL); yield: 1.53 g, 1.96 mmol, 65 %; colorless solid; $^1$H-NMR (250 MHz, $CDCl_3$): $\delta = 1.34$ (br s, 12H, $\mathrm{C}H_3$), 1.43–1.60 (m, 12H, $\mathrm{C}H_2$), 1.69–1.92 (m, 12H, $\mathrm{OCH_2C}H_2$), 3.93–4.06 (m, 12H, $\mathrm{OC}H_2$), 6.87–6.95 (m, 9H, 2-H, 4-H), 7.00 (s, 2H, 2'-H), 7.24–7.30 (m, 6H, 3-H) ppm; $^{13}$C-NMR (63 MHz, $CDCl_3$): $\delta = 24.9$ ($C\mathrm{H_3}$), 25.9, 26.0, 26.9, 29.29, 29.34, 29.4, 30.3 ($C\mathrm{H_2}$), 67.7, 67.8, 68.9, 73.1 ($\mathrm{O}C\mathrm{H_2}$), 83.8 ($\mathrm{BO}C\mathrm{(CH_3)_2}$), 112.7 (C-2'), 114.5 (C-2), 120.4 (C-4), 129.4 (C-3), 140.9 (C-4'), 152.8 (C-3'), 159.1 (C-1) ppm; MS (ESI): *m/z* = 803.48 $[M + Na]^+$; HRMS (ESI): calcd. for $C_{48}H_{65}BO_8Na$: 803.4673 $[M + Na]^+$, found: 803.4755 $[M + Na]^+$; FT-IR (ATR): $\tilde{\nu}$ = 508 (m), 573 (w), 595 (w), 612 (w), 689 (vs), 729 (m), 750 (vs), 813 (m), 831 (m), 854 (w), 881 (m), 915 (m), 929 (m), 968 (m), 989 (m), 1002 (s), 1012 (m), 1034 (m), 1060 (m), 1079 (m), 1111 (vs), 1143 (s), 1171 (m), 1222 (s), 1242 (vs), 1289 (w), 1302 (m), 1322 (m), 1338 (s), 1367 (m), 1393 (s), 1415 (m), 1472 (m), 1497 (m), 1583 (m), 1600 (m), 2863 (m), 2978 (m), 3057 (w) $cm^{-1}$.

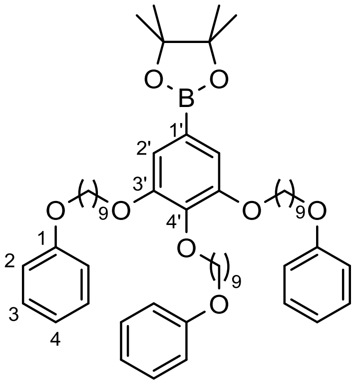
### 2-(3',4',5'-Tris(phenoxyoctyloxy)phenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan (4b)



Synthesis according to GP 3. From 1,2,3-tris(phenoxyoctyloxy)-5-bromobenzene) **3b** (1.70 g, 2.08 mmol), *n*-BuLi (2.60 mL, 4.16 mmol, 1.6 M in *n*-hexane), isopropyl pinacol borate (0.91 mL, 0.81 g, 4.37 mmol), THF (50 mL); yield: 1.70 g, 1.97 mmol, 95 %; colorless solid; $^1$H-NMR (250 MHz, $CDCl_3$): $\delta = 1.28$–1.56 (m, 36H, $\mathrm{C}H_2$, $\mathrm{C}H_3$), 1.67–1.89 (m, 12H, $\mathrm{OCH_2C}H_2$), 3.87–4.09 (m, 12H, $\mathrm{OC}H_2$), 6.87–6.95 (m, 9H, 2-H, 4-H), 6.99 (s, 2H, 2'-H), 7.24-7.30 (m, 6H, 3-H) ppm; $^{13}$C-NMR (63 MHz, $CDCl_3$): $\delta = 24.9$ ($C\mathrm{H_3}$), 26.0, 26.9, 29.3, 29.4, 29.5, 30.3 ($C\mathrm{H_2}$), 67.8, 68.9, 73.3 ($\mathrm{O}C\mathrm{H_2}$), 83.8 ($\mathrm{BO}C\mathrm{(CH_3)_2}$), 112.7 (C-2'), 114.5 (C-2), 120.4 (C-4), 129.4 (C-3), 141.0 (C-4'), 152.8 (C-3'), 159.1 (C-1) ppm; MS (EI): *m/z* = 864.6 (100) $[M]^+$, 660 (30), 252 (33), 152 (15), 94 (30), 69 (85); HRMS (EI): calcd. for $C_{54}H_{77}BO_8$: 864.5721, found: 864.5714 $[M]^+$; FT-IR (ATR): $\tilde{\nu}$ = 511 (m), 576 (w), 594 (w), 691 (vs), 713 (m), 753 (vs), 813 (w), 831 (m), 854 (m), 881 (w), 915 (w), 968 (m), 1034 (m), 1079 (m), 1106 (vs), 1143 (s), 1170 (s), 1222 (s), 1242 (vs), 1300 (m), 1319 (m), 1361 (vs), 1413 (s), 1470 (s), 1496 (m), 1586 (m), 1599 (m), 2855 (m), 2929 (m) cm$^{-1}$.

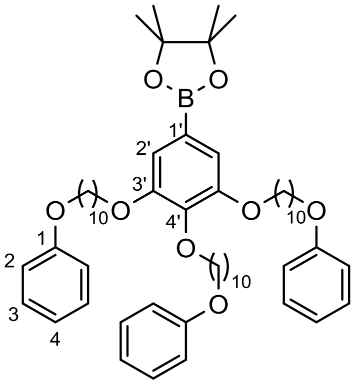
**2-(3',4',5'-Tris(phenoxynonyloxy)phenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan (4c)**

Synthesis according to GP 3. From 1,2,3-Tris(phenoxynonyloxy)-5-bromobenzene) **3c** (1.80 g, 2.09 mmol), *n*-BuLi (2.63 mL, 4.19 mmol, 1.6 M in *n*-hexane), isopropyl pinacol borate (0.90 mL, 0.82 g, 4.39 mmol), THF (50 mL); yield: 1.03 g, 1.14 mmol, 55 %; colorless solid; $^1$H-NMR (300 MHz, CDCl$_3$): δ = 1.29–1.53 (m, 42H, C$\mathit{H}_2$, C$\mathit{H}_3$), 1.70–1.84 (m, 12H, OCH$_2$C$\mathit{H}_2$), 3.89–4.04 (m, 12H, OC$\mathit{H}_2$), 6.87–6.94 (m, 9H, 2-H, 4-H), 6.99 (s, 2H, 2'-H), 7.24-7.30 (m, 6H, 3-H) ppm; $^{13}$C-NMR (75 MHz, CDCl$_3$): δ = 24.9 ($\mathit{C}$H$_3$), 26.1, 26.9, 29.4, 29.5, 29.6, 30.3 ($\mathit{C}$H$_2$), 67.8, 69.0, 73.3 (O$\mathit{C}$H$_2$), 83.8 (BO$\mathit{C}$(CH$_3$)$_2$), 112.7 (C-2'), 114.5 (C-2), 120.4 (C-4), 129.4 (C-3), 152.9 (C-3'), 159.1 (C-1) ppm; MS (ESI): *m/z* = 929.61 [M + Na]$^+$; HRMS (ESI): calcd. for $C_{57}H_{83}BO_8Na$: 929.6083, found: 929.6076 [M + Na]$^+$; FT-IR (ATR): $\tilde{\nu}$ = 511 (m), 576 (w), 594 (w), 654 (m), 691 (vs), 713 (m), 751 (vs), 813 (w), 831 (m), 854 (m), 877 (w), 922 (w), 969 (m), 1034 (m), 1042 (m), 1079 (m), 1109 (vs), 1141 (s), 1172 (s), 1223 (s), 1241 (vs), 1289 (m), 1301 (m), 1349 (m), 1367 (vs), 1392 (s) 1414 (s), 1471 (s), 1497 (m), 1584 (m), 1599 (m), 2852 (m), 2923 (m) cm$^{-1}$.



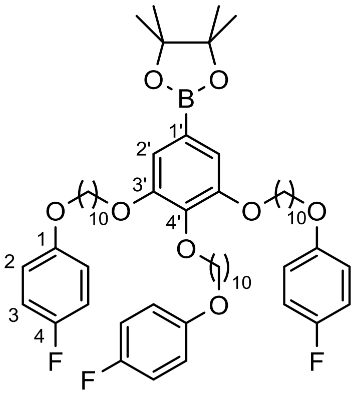
**2-(3',4',5'-Tris(phenoxydecyloxy)phenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan (4d)**

Synthesis according to GP 3. From 1,2,3-tris(phenoxydecyloxy)-5-bromobenzene) **3d** (2.81 g, 3.11 mmol), *n*-BuLi (2.50 mL, 6.23 mmol, 2.5 M in *n*-hexane), isopropyl pinacol borate (1.34 mL, 1.22 g, 6.53 mmol), THF (50 mL); yield: 1.32 g, 1.39 mmol, 45 %; colorless solid; $^1$H-NMR (300 MHz, CDCl$_3$): δ = 1.26–1.57 (m, 48H, C$\mathit{H}_2$), 1.68–1.88 (m, 12H, OCH$_2$C$\mathit{H}_2$), 3.85–4.05 (m, 12H, OC$\mathit{H}_2$), 6.85–6.95 (m, 9H, 2-H, 4-H), 6.99 (s, 2H, 2'-H), 7.22–7.30 (m, 6H, 3-H) ppm; $^{13}$C-NMR: (75 MHz, CDCl$_3$): δ = 24.9 ($\mathit{C}$H$_3$), 26.1, 26.9, 29.2, 29.3, 29.41, 29.43, 29.5, 29.56, 29.58, 29.63, 29.7, 30.4 ($\mathit{C}$H$_2$), 67.9, 69.1, 73.3 (O$\mathit{C}$H$_2$), 83.7 (BO$\mathit{C}$(CH$_3$)$_2$), 112.8 (C-2'), 114.5 (C-2), 120.4 (C-4), 129.4 (C-3), 141.1 (C-4'), 152.9 (C-3'), 159.1 (C-1) ppm; MS (ESI): *m/z* = 971.66 [M + Na]$^+$; HRMS (ESI): calcd. for $C_{60}H_{89}BO_8Na$: 971.6553, found: 971.6578 [M + Na]$^+$; FT-IR (ATR): $\tilde{\nu}$ = 511 (w), 593 (w), 691 (vs), 722 (w), 752 (vs), 813 (w), 854 (s), 881 (w), 969 (w), 1035 (s), 1080



(w), 1107 (vs), 1143 (s), 1171 (s), 1242 (vs), 1300 (w), 1362 (vs), 1413 (s), 1469 (s), 1496 (s), 1586 (w), 1599 (s), 2853 (s), 2924 (vs) cm$^{-1}$.

### 2-(3',4',5'-Tris((10-(4-fluorophenoxy)decyl)oxy)phenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan (4e)

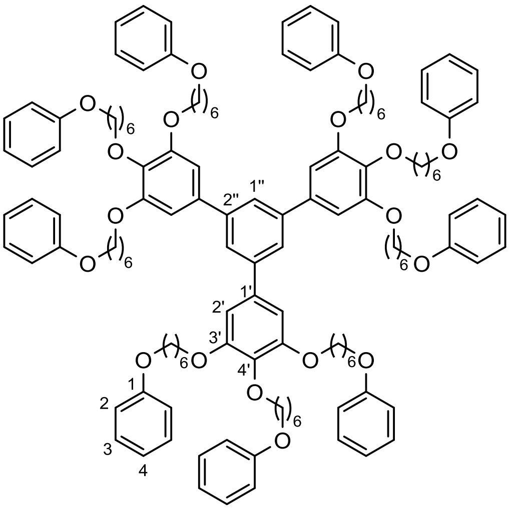


Synthesis according to GP 3. From 1,2,3-Tris(4'-fluorophenoxydecyloxy)-5-bromobenzene **3e** (2.90 g, 3.03 mmol), *n*-BuLi (2.43 mL, 6.07 mmol, 2.5 M in *n*-hexane), isopropyl pinacol borate (1.30 mL, 1.19 g, 6.37 mmol), THF (50 mL); yield: 2.65 g, 2.64 mmol, 87 %; colorless solid; $^1$H-NMR (500 MHz, $CDCl_3$): δ = 1.29–1.52 (m, 48H, $CH_2$), 1.69–1.83 (m, 12H, $OCH_2CH_2$), 3.86–3.92 (m, 6H, $OCH_2$), 3.95–4.04 (m, 6H, $OCH_2$), 6.78–6.85 (m, 6H, 2-H), 6.91–6.98 (m, 6H, 3-H) 6.99 (s, 2H, 2'-H) ppm; $^{13}$C-NMR: (126 MHz, $CDCl_3$): δ = 24.9 ($CH_3$), 26.0, 26.06, 26.10, 29.3, 29.38, 29.40, 29.45, 29.48, 29.53, 29.56, 29.60, 29.64, 30.3 ($CH_2$), 68.6, 69.0, 73.3 ($OCH_2$), 83.8 ($BOC(CH_3)_2$), 112.8 (C-2'), 115.4 (d, *J* = 8.0 Hz, C-2), 115.7 (d, *J* = 22.8 Hz, C-3), 141.1 (C-4'), 152.9 (C-3'), 155.3 (d, *J* = 2.0 Hz, C-1), 157.1 (d, *J* = 237.7 Hz, C-4) ppm; MS (ESI): *m/z* = 1025.63 [M + Na]$^+$, 765.53; HRMS (ESI): calcd. for $C_{60}H_{86}BF_3O_8Na$: 1025.6270, found: 1025.6286 [M + Na]$^+$; FT-IR (ATR): $\tilde{\nu}$ = 420 (w), 513 (m), 670 (w), 695 (w),731 (m), 757 (m), 826 (s), 853 (w), 912 (w), 968 (w), 1007 (w), 1036 (m), 1097 (m), 1143 (m), 1206 (s), 1246 (m), 1292 (m), 1320 (w), 1363 (m), 1415 (m), 1469 (m), 1505 (vs), 1590 (w), 2854 (m), 2925 (m) cm$^{-1}$.

## Triphenylbenzenes

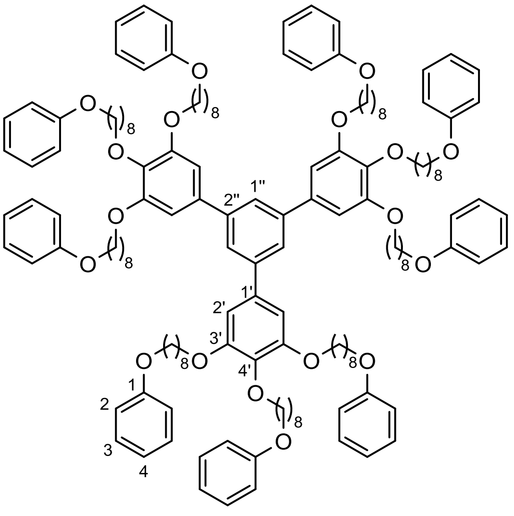
### 1,3,5-Tri-(5'-1',2',3'-tris(phenoxyhexyloxy)phenyl)benzene (5a)

Synthesis according to GP 4. From 1,3,5-tribromobenzene (74 mg, 0.236 mmol), 2-(3',4',5'-tris(phenoxyhexyloxy)phenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan **4a** (700 mg, 0.900 mmol), $K_2CO_3$ (147 mg, 1.062 mmol), Pd[$PPh_3$]$_4$ (13.87 mg, 0.012 mmol), DMF (25 mL), $H_2O$ (7 mL); yield: 360 mg, 0.177 mmol, 75 %; amber-colored solid; $^1$H-NMR (500 MHz, $CDCl_3$): δ = 1.49–1.63 (m, 36H, $CH_2$), 1.76–1.89 (m, 36H, $OCH_2CH_2$), 3.91–3.96 (m, 18H, $OCH_2$), 4.00–4.06 (m, 18H, $OCH_2$), 6.82 (s, 6H, 2'-H), 6.85–6.92 (m, 27H, 2-H,



4-H), 7.23–7.27 (m, 18H, 3-H), 7.61 (s, 3H, 1''-H) ppm; $^{13}$C-NMR (126 MHz, CDCl$_3$): $\delta$ = 25.5, 25.9, 25.95, 25.98, 26.01, 29.3, 29.36, 29.41, 30.3 (*C*H$_2$), 67.6, 67.8, 69.2, 73.4 (O*C*H$_2$), 106.3 (C-2'), 114.5 (C-2), 120.5 (C-4), 125.1 (C-1''), 129.4 (C-3), 136.8 (C-1'), 138.1 (C-4'), 142.7 (C-2''), 153.4 (C-3'), 159.1 (C-1) ppm; MS (MALDI-TOF): (*m/z*) calcd. for $C_{132}H_{162}O_{18}$: 2035.2 [M]$^+$, found: 2037.0 [M]$^+$; FT-IR (ATR): $\tilde{\nu}$ = 512 (m), 591 (w), 691 (s), 713 (m), 752 (vs), 811 (w), 833 (m), 881 (w), 907 (w), 1006 (m), 1036 (m), 1080 (m), 1118 (vs), 1141 (s), 1153 (m), 1172 (m), 1243 (vs), 1300 (m), 1382 (m), 1404 (m), 1417 (w), 1469 (s), 1499 (vs), 1585 (s), 1600 (s), 2862 (m), 2938 (m) cm$^{-1}$; Anal. calcd. for $C_{132}H_{162}O_{18}$ (2036.73 gmol$^{-1}$): C 77.84, H 8.02; found: C 77.54, H 7.79.

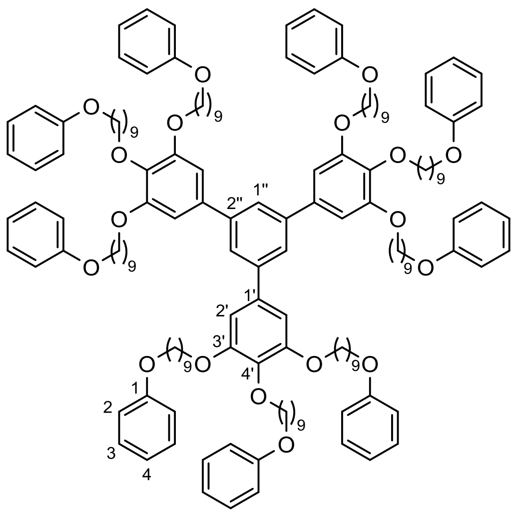
**1,3,5-Tri-(5'-1',2',3'-tris(phenoxyoctyloxy)phenyl)benzene (5b)**



Synthesis according to GP 4. From 1,3,5-tribromobenzene (77 mg, 0.243 mmol), 2-(3',4',5'-tris(phenoxyoctyloxy)phenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan **4b** (800 mg, 0.925 mmol), K$_2$CO$_3$ (151 mg, 1.094 mmol), Pd[PPh$_3$]$_4$ (14 mg, 12 µmol), DMF (30 mL), H$_2$O (10 mL); yield: 90 mg, 0.04 mmol, 16 %; amber-colored solid; $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ = 1.33–1.54 (m, 72H, C*H*$_2$), 1.73–1.85 (m, 36H, OCH$_2$C*H*$_2$), 3.90–3.95 (m, 18H, OC*H*$_2$), 4.00–4.04 (m, 18H, OC*H*$_2$), 6.82 (s, 6H, 2'-H), 6.85–6.92 (m, 27H, 2-H, 4-H), 7.23–7.27 (m, 18H, 3-H), 7.61 (s, 3H, 1''-H) ppm; $^{13}$C-NMR (126 MHz, CDCl$_3$): $\delta$ = 25.5, 25.9, 25.95, 25.98, 26.01, 29.3, 29.36, 29.41, 30.3 (*C*H$_2$), 67.6, 67.8, 69.2, 73.4 (O*C*H$_2$), 106.3 (C-2'), 114.5 (C-2), 120.5 (C-4), 125.1 (C-1''), 129.4 (C-3), 136.8 (C-1'), 138.1 (C-4'), 142.7 (C-2''), 153.4 (C-3'), 159.1 (C-1) ppm; MS (MALDI-TOF): (*m/z*) calcd. for $C_{150}H_{198}O_{18}$: 2287.4 [M]$^+$, found: 2291.6 [M]$^+$; FT-IR (ATR): $\tilde{\nu}$ = 511 (m), 593 (w), 648 (m), 691 (vs), 728 (vs), 752 (s), 811 (w), 831 (w), 907 (s), 1032 (m), 1079 (m), 1110 (s), 1171 (m), 1241 (vs), 1300 (w), 1385 (w), 1420 (w), 1469 (m), 1496 (s), 1585 (m), 1600 (m), 2855 (m), 2928 (m) cm$^{-1}$; Anal. calcd. for $C_{150}H_{198}O_{18}$ (2289.22 gmol$^{-1}$): C 78.70, H 8.72; found: C 78.46, H 8.87.

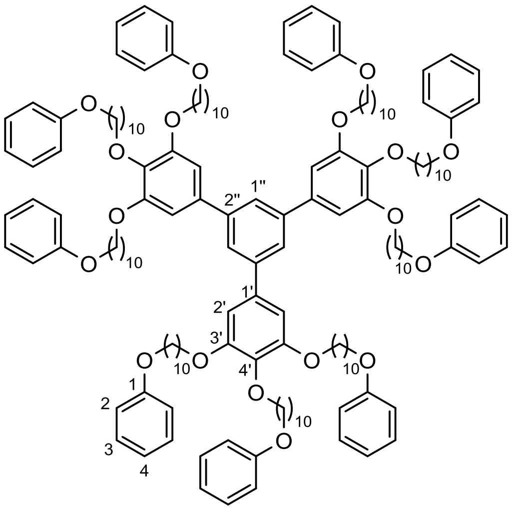
**1,3,5-Tri-(5'-1',2',3'-tris(phenoxynonyloxy)phenyl)benzene (5c)**

Synthesis according to GP 4. From 1,3,5-Tribromobenzene (32 mg, 0.102 mmol), 2-(3',4',5'-Tris(phenoxynonyloxy)phenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan **4c** (350 mg, 0.386 mmol), K$_2$CO$_3$ (63 mg, 0.459 mmol), Pd[PPh$_3$]$_4$ (6 mg, 5 µmol), DMF (25 mL), H$_2$O (5 mL); yield: 186 mg, 80 µmol, 76 %; amber-colored solid; $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ = 1.31–



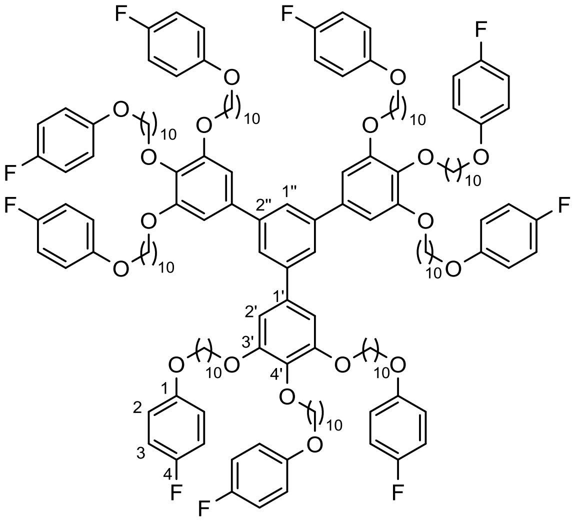
1.54 (m, 90H, $\mathrm{C}H_2$), 1.71–1.85 (m, 36H, $\mathrm{OCH_2C}H_2$), 3.89–3.95 (m, 18H, $\mathrm{OC}H_2$), 3.98–4.05 (m, 18H, $\mathrm{OC}H_2$), 6.82 (s, 6H, 2'-H), 6.87–6.92 (m, 27H, 2-H, 4-H), 7.23–7.27 (m, 18H, 3-H), 7.61 (s, 3H, 1''-H) ppm; $^{13}$C-NMR (126 MHz, $\mathrm{CDCl_3}$): δ = 26.08, 26.10, 26.12, 26.2, 29.30, 29.34, 29.4, 29.5, 29.6, 29.7, 30.4 ($C\mathrm{H_2}$), 67.80, 67.83, 69.4, 73.6 ($\mathrm{O}C\mathrm{H_2}$), 106.2 (C-2'), 114.5 (C-2), 120.4 (C-4), 125.1 (C-1''), 129.4 (C-3), 136.7 (C-1'), 138.2 (C-4'), 142.7 (C-2''), 153.5 (C-3'), 159.1 (C-1) ppm; MS (MALDI-TOF): (*m/z*) calcd. for $\mathrm{C_{159}H_{216}O_{18}}$: 2413.6 $[\mathrm{M}]^+$, found: 2416.1 $[\mathrm{M}]^+$; FT-IR (ATR): $\tilde{\nu}$ = 511 (m), 593 (w), 691 (vs), 713 (w), 723 (w), 751 (vs), 813 (w), 833 (m), 881 (w), 1034 (m), 1079 (m), 1116 (vs), 1152 (w), 1171 (m), 1242 (vs), 1301 (w), 1332 (m), 1382 (m), 1404 (m) 1417 (m), 1469 (s), 1496 (vs), 1585 (m), 1600 (m), 2854 (m), 2923 (m) cm$^{-1}$; Anal. calcd. $\mathrm{C_{159}H_{216}O_{18}}$ (2415.46 gmol$^{-1}$): C 79.06, H 9.01; found: C 79.25, H 8.97.

**1,3,5-Tri-(5'-1',2',3'-tris(phenoxydecyloxy)phenyl)benzene (5d)**



Synthesis according to GP 4. From 1,3,5-tribromobenzene (69 mg, 0.219 mmol), 2-(3',4',5'-tris(phenoxydecyloxy)phenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan **4d** (800 mg, 0.843 mmol), $\mathrm{K_2CO_3}$ (138 mg, 0.998 mmol), $\mathrm{Pd[PPh_3]_4}$ (13 mg, 11 µmol), DMF (30 mL), $\mathrm{H_2O}$ (10 mL); yield: 126 mg, 50 µmol, 23 %; amber-colored solid; $^1$H-NMR (500 MHz, $\mathrm{CDCl_3}$): δ = 1.27–1.53 (m, 108H, $\mathrm{C}H_2$), 1.67–1.84 (m, 36H, $\mathrm{OCH_2C}H_2$), 3.86–3.97 (m, 18H, $\mathrm{OC}H_2$), 3.97–4.06 (m, 18, $\mathrm{OC}H_2$), 6.81 (s, 6H, 2'-H), 6.84–6.95 (m, 27H, 2-H, 4-H), 7.21–7.29 (m, 18H, 3-H), 7.61 (s, 3H, 1''-H) ppm; $^{13}$C-NMR: (126 MHz, $\mathrm{CDCl_3}$): δ = 26.07, 26.12, 26.2, 29.31, 29.34, 29.4, 29.48, 29.54, 29.57, 29.62, 29.64, 29.7, 30.4 ($C\mathrm{H_2}$), 67.82, 67.84, 69.4, 73.6 ($\mathrm{O}C\mathrm{H_2}$), 106.2 (C-2'), 114.5 (C-2), 120.4 (C-4), 125.1 (C-1''), 129.4 (C-3), 136.6 (C-1'), 138.2 (C-4'), 142.6 (C-2''), 153.5 (C-3'), 159.1 (C-1) ppm; MS (MALDI-TOF): (*m/z*) calcd. for $\mathrm{C_{168}H_{234}O_{18}}$: 2539.7 $[\mathrm{M}]^+$, found: 2540.1 $[\mathrm{M}]^+$; FT-IR (ATR): $\tilde{\nu}$ = 510 (w), 593 (w), 691 (s), 714 (w), 723 (w), 752 (s), 814 (w), 833 (w), 881 (w), 1037 (w), 1080 (w), 1112 (s), 1152 (w), 1172 (w), 1245 (vs), 1301 (w), 1333 (w), 1383 (w), 1403 (w), 1417 (s), 1470 (s), 1498 (vs), 1585 (s), 1601 (s), 2079 (w), 2853 (s), 2922 (vs), 3039 (w) cm$^{-1}$; Anal. calcd. $C_{168}H_{234}O_{18}$ (2541.70 gmol$^{-1}$): C 79.39, H 9.28; found: C 79.10, H 9.09.

### 1,3,5-Tri-(5'-1',2',3'-tris((10-(4-fluorophenoxy)decyl)oxy)phenyl)benzene (5e)



Synthesis according to GP 4. From 1,3,5-tribromobenzene (90 mg, 0.285 mmol), 2-(3',4',5'-tris((10-(4-fluorophenoxy)decyl)oxy)phenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan **4e** (1.00 g, 0.997 mmol), $K_2CO_3$ (177 mg, 1.283 mmol), $Pd[PPh_3]_4$ (17 mg, 14 µmol), DMF (30 mL), $H_2O$ (10 mL); yield: 311 mg, 0.115 mmol, 40 %; amber-colored solid; $^1$H-NMR (500 MHz, $CDCl_3$): δ = 1.27–1.54 (m, 108H, C*H*$_2$), 1.69–1.86 (m, 36H, $OCH_2$C*H*$_2$), 3.85–3.91 (m, 18H, OC*H*$_2$), 3.99–4.06 (m, 18, OC*H*$_2$), 6.77–6.84 (m, 24H, 2-H, 2'-H), 6.90–6.97 (m, 18H, 3-H), 7.61 (s, 3H, 1''-H) ppm; $^{13}$C-NMR: (126 MHz, $CDCl_3$): δ = 26.0, 26.07, 26.11, 26.2, 29.29, 29.32, 29.4, 29.46, 29.48, 29.52, 29.55, 29.61, 29.62, 29.7, 30.4 (*C*H$_2$), 68.57, 68.59, 69.4, 73.6 (O*C*H$_2$), 106.2 (C-2'), 115.4 (d, *J* = 8.0 Hz, C-2), 115.7 (d, *J* = 23.1 Hz, C-3), 125.1 (C-1''), 136.6 (C-1'), 138.2 (C-4'), 142.6 (C-2''), 153.5 (C-3'), 155.2 (d, *J* = 2.0 Hz, C-1), 157.1 (d, *J* = 238.0 Hz, C-4) ppm; MS (MALDI-TOF): (*m/z*) calcd. for $C_{168}H_{225}F_9O_{18}$: 2701.7 $[M]^+$, found: 2703.5 $[M]^+$; FT-IR (ATR): $\tilde{\nu}$ = 513 (m), 636 (w), 721 (w), 757 (m), 826 (s), 944 (w), 1033 (w), 1097 (m), 1114 (m), 1208 (s), 1246 (m), 1293 (w), 1329 (w), 1387(w), 1415 (vs), 1471 (w), 1505 (vs), 1557 (w), 1582 (w), 1855 (w), 2854 (m), 2924 (s), 3053 (w) cm$^{-1}$; Anal. calcd. $C_{168}H_{225}F_9O_{18}$ (2703.62 gmol$^{-1}$): C 74.64, H 8.39; found: C 74.74, H 8.47.

## Literature

1 M. Staszewski, K. Walczyński, *Med. Chem. Res.* **2013**, *22*, 1287–1304.

2 T. Yasuda, T. Shimizu, F. Liu, G. Ungar, T. Kato, *J. Am. Chem. Soc.* **2011**, *133*, 13437–13444.

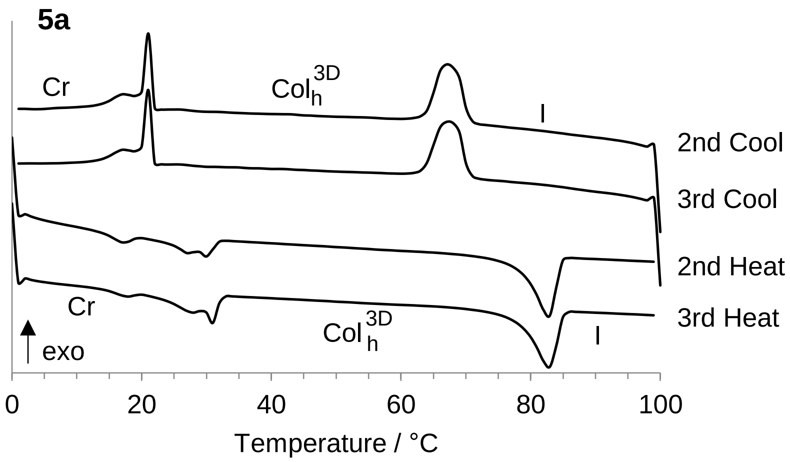
3 M.-C. Yeh, Y.-L. Su, M.-C. Tzeng, C. W. Ong, T. Kajitani, H. Enozawa, M. Takata, Y. Koizumi, A. Saeki, S. Seki, T. Fukushima, *Angew. Chem. Int. Ed.* **2013**, *52*, 1031–1034.

4 T. Wöhrle, S. J. Beardsworth, C. Schilling, A. Baro, F. Giesselmann, S. Laschat, *Soft Matter* **2016**, *12*, 3730–3736.

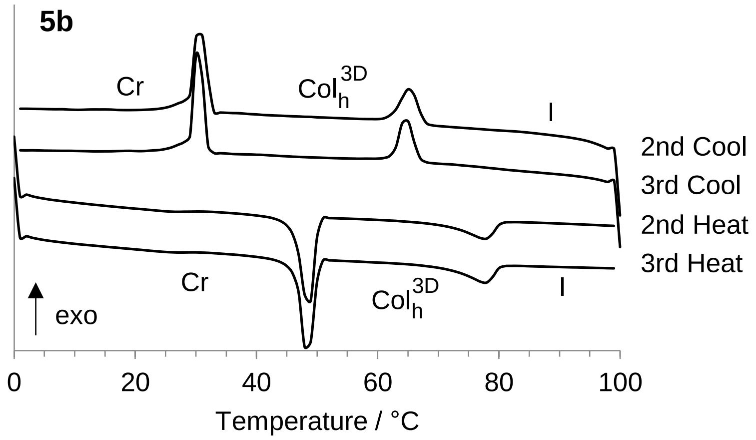
5 J. Min, P. N. Shah, J.-H. Ahn, J.-S. Lee, *Macromolecules* **2011**, *44*, 3211–3216.

## Differential Scanning Calorimetry (DSC) Traces

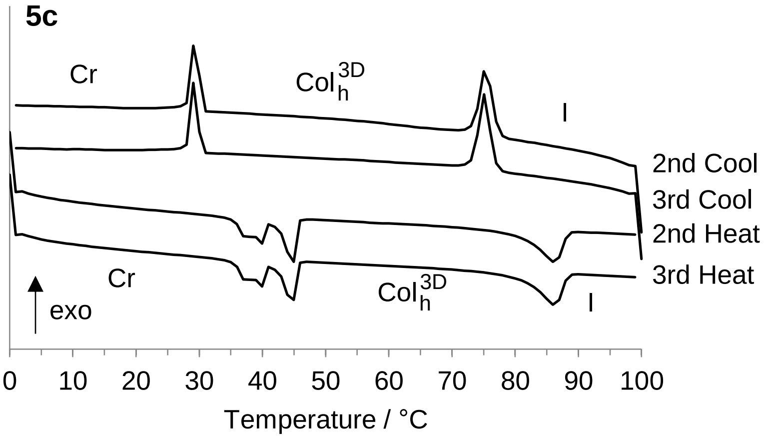
**5a**



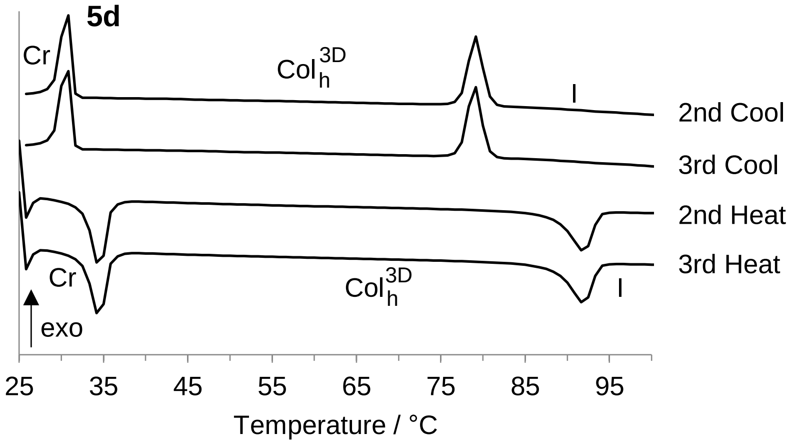
**5b**



**5c**



**5d**



**5e**

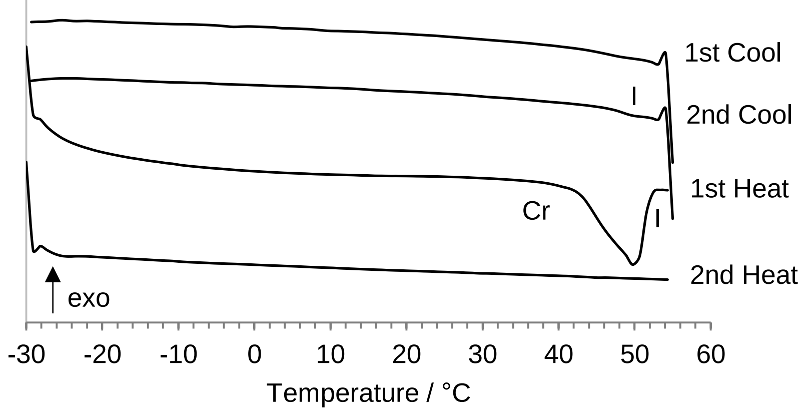


**Figure S1.** DSC traces of triphenylbenzenes **5a**–**e** (heating/cooling rate 5 K min$^{-1}$).

## X-ray Diffraction (XRD) Data

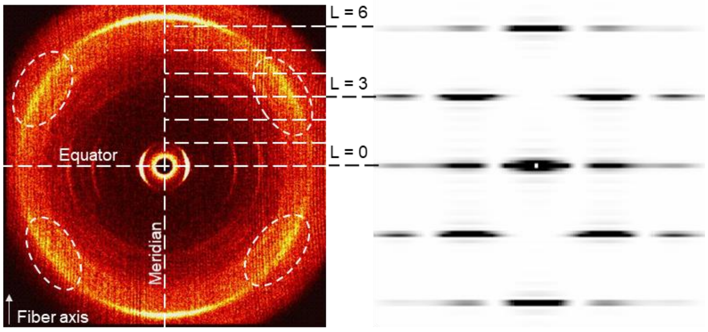


**Figure S2.** WAXS pattern of **5a** at 50°C (left) and simulated WAXS pattern via HELIX program (right).

**5a**

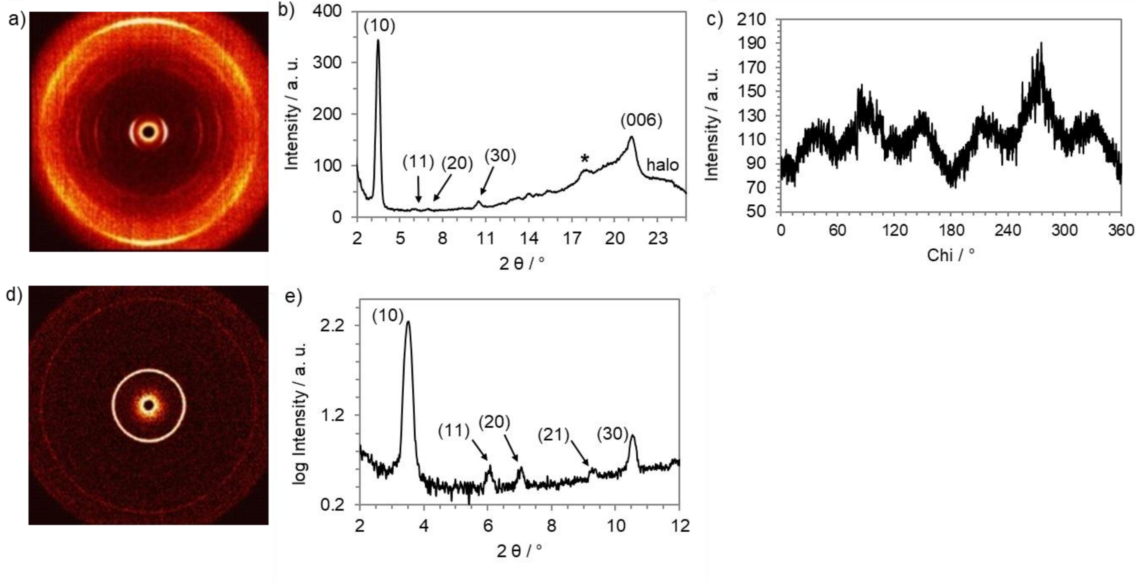


**Figure S3.** WAXS (a) and SAXS (d) diffraction patterns and the corresponding profiles (b, e) of **5a** at 50°C and integration of the halo signal of **5a** over 2 θ (c). The asterisk indicates an off-meridional signal of layer line $L = 3$ (b).

**5b**

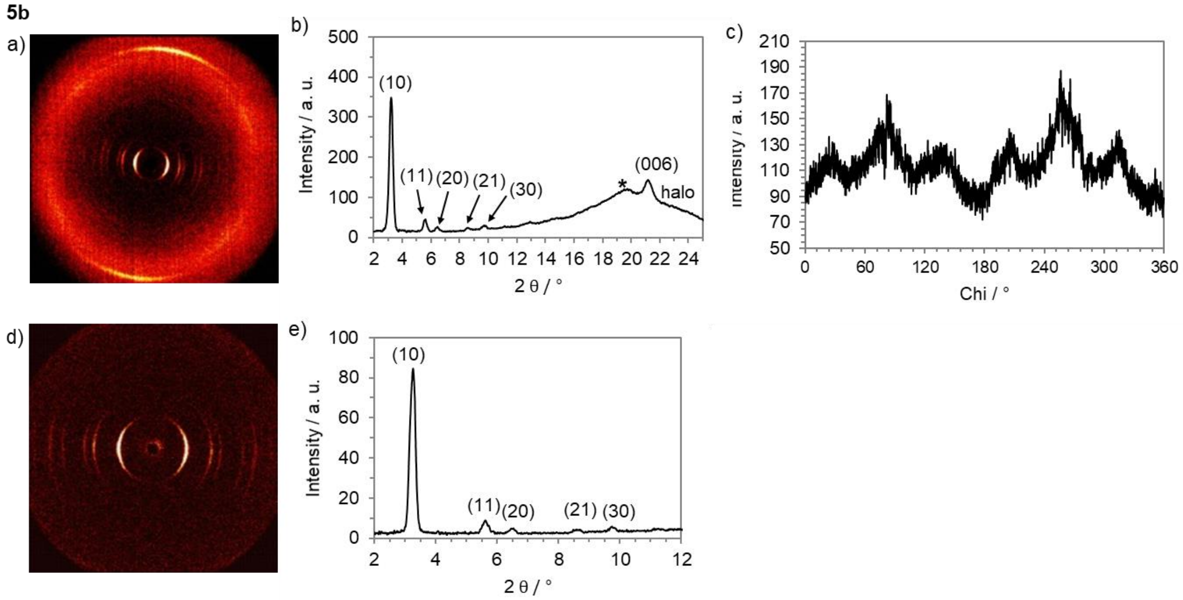


**Figure S4.** WAXS (a) and SAXS (d) diffraction patterns at 55°C and 60°C, resp., and the corresponding profiles (b, e) of **5b** and integration of the halo signal of **5b** over 2 θ (c). The asterisk indicates an off-meridional signal of layer line $L = 3$ (b).

**5c**

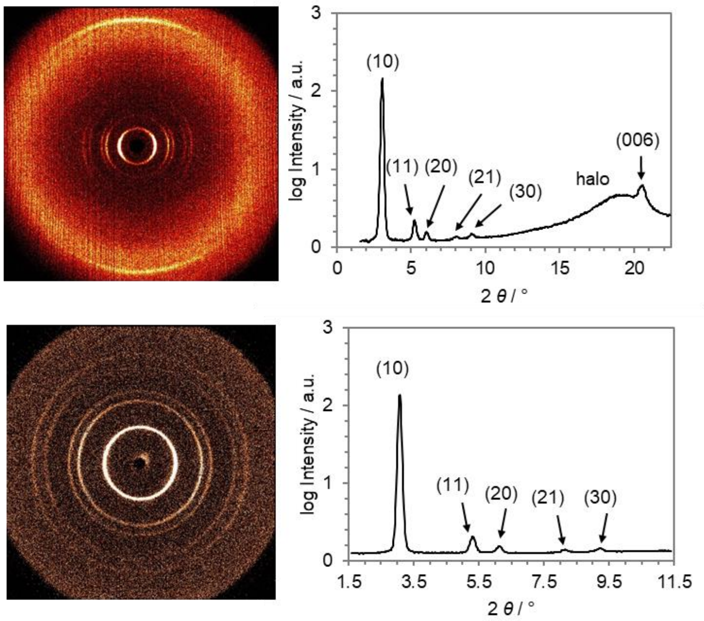


**Figure S5.** Left: WAXS (above) and SAXS (below) diffraction pattern of **5c** at 60°C, right: the corresponding profiles.

**5d**

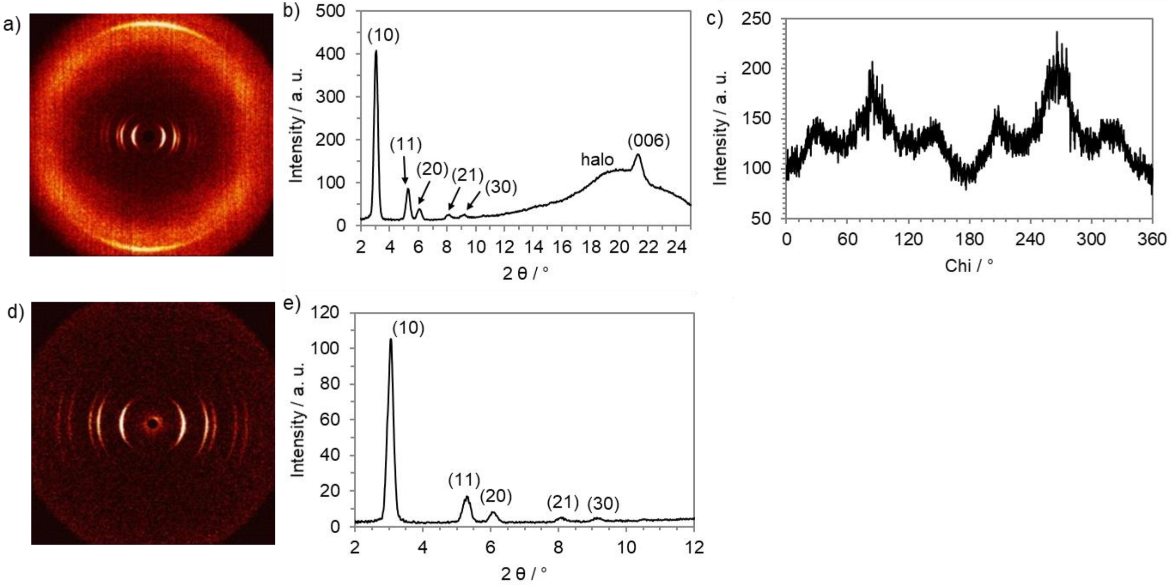
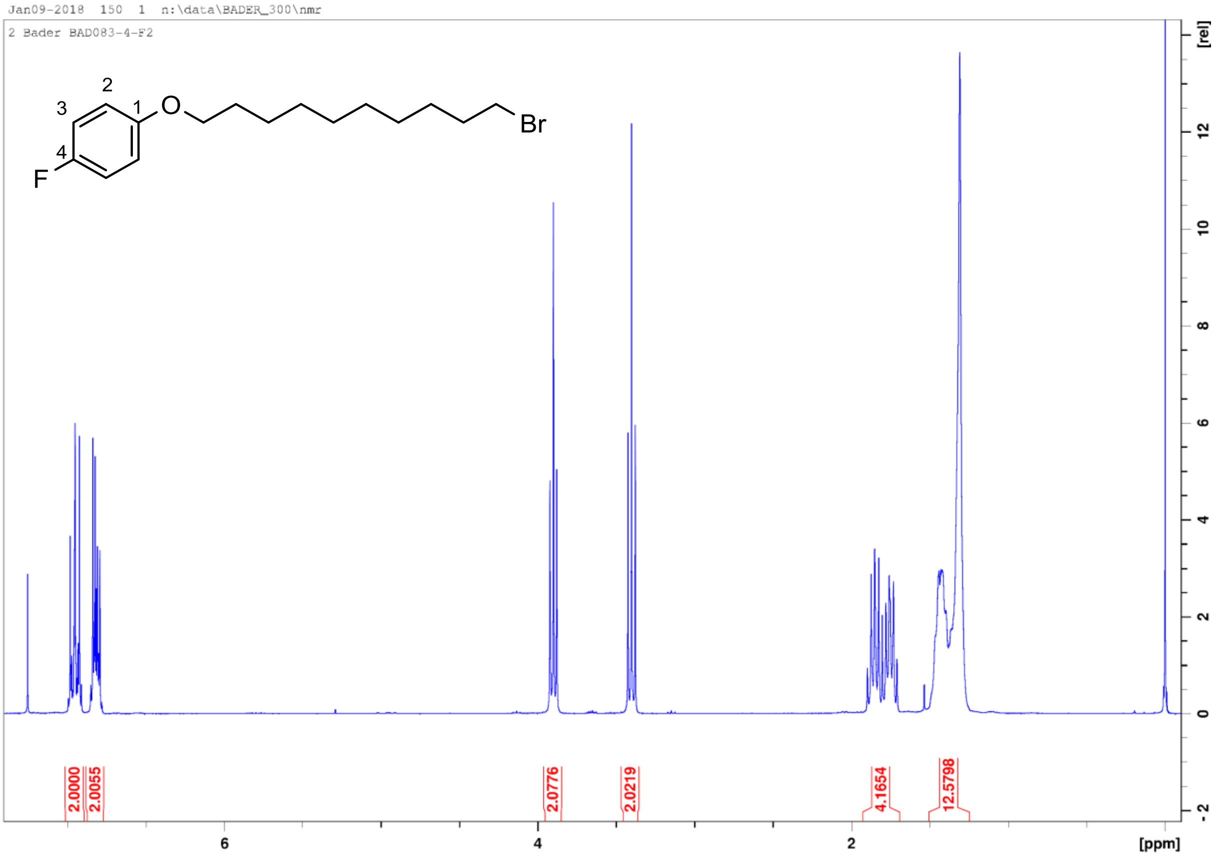
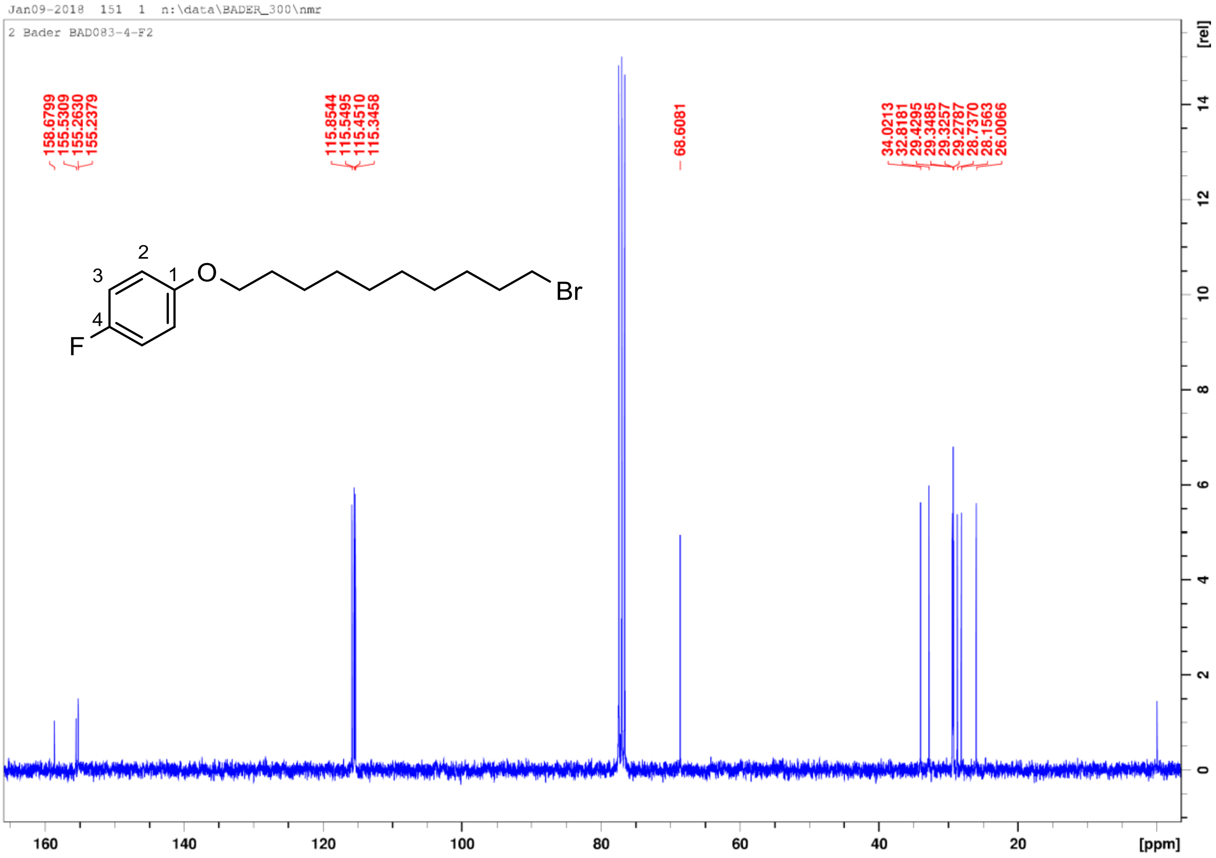
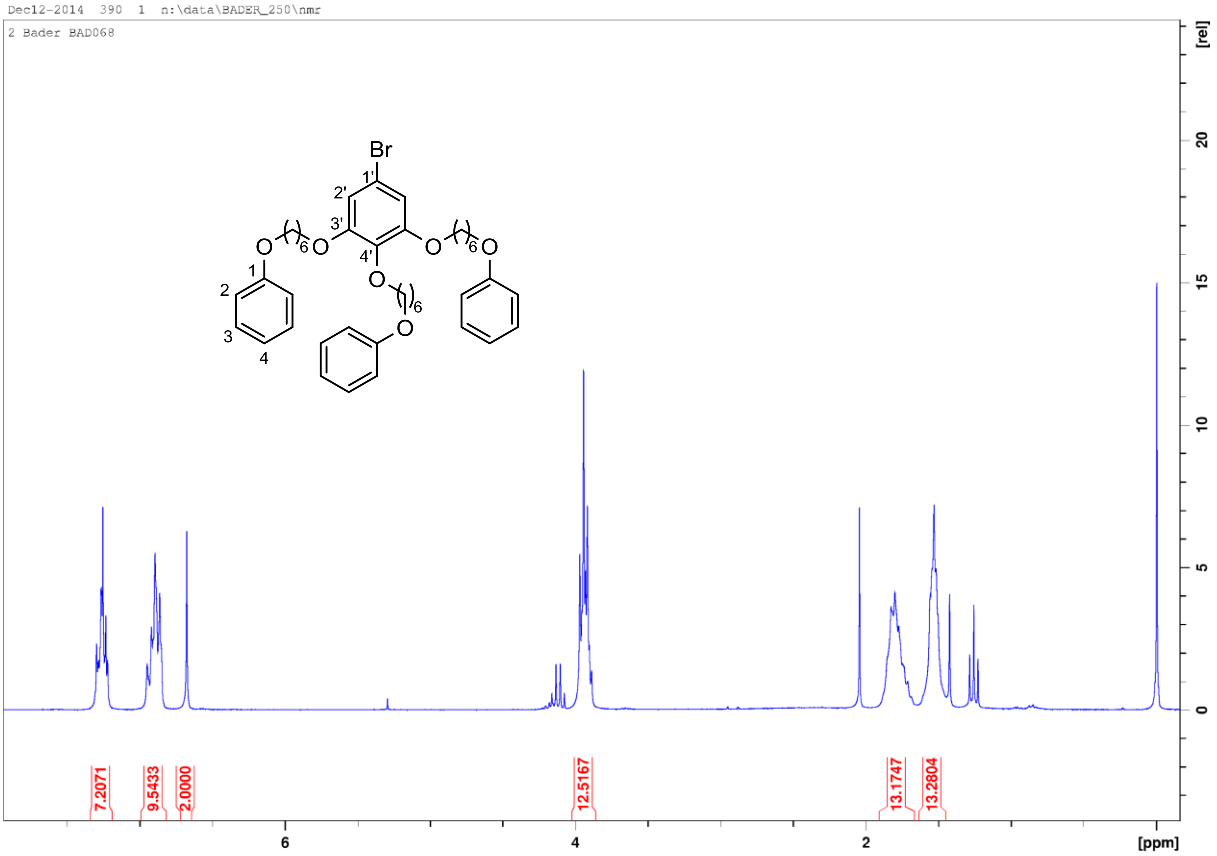


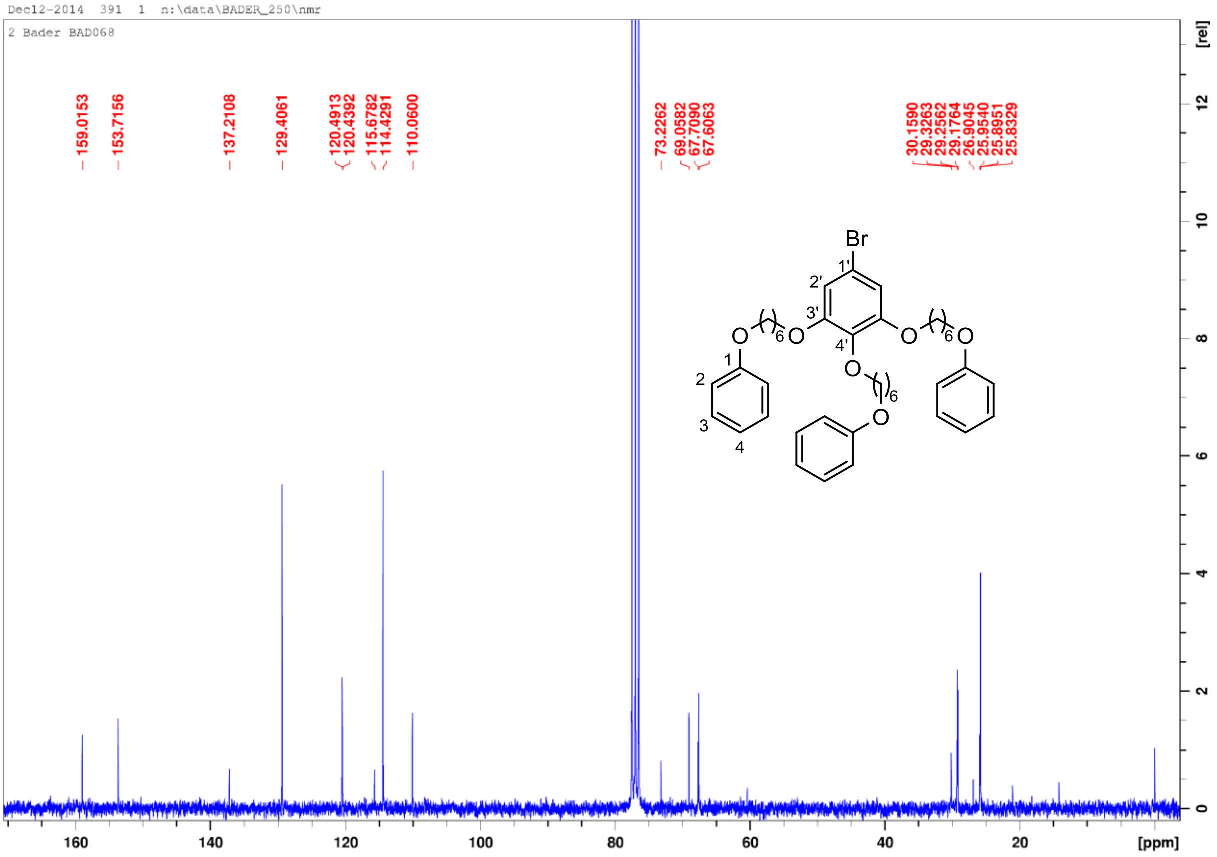
**Figure S6.** WAXS (a) and SAXS (d) diffraction patterns and the corresponding profiles (b, e) of **5d** at 50°C and integration of the halo signal of **5d** over 2 θ (c).

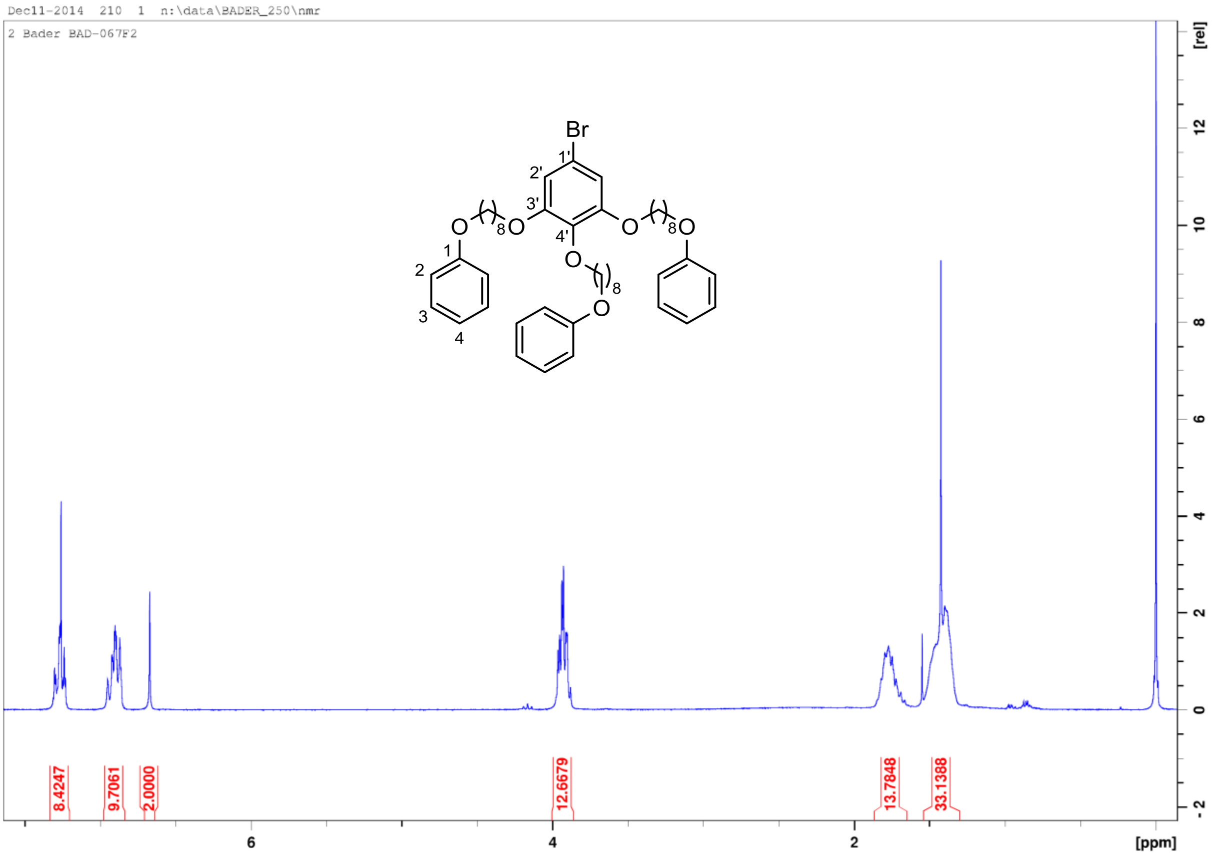
# NMR Data of All New Compounds

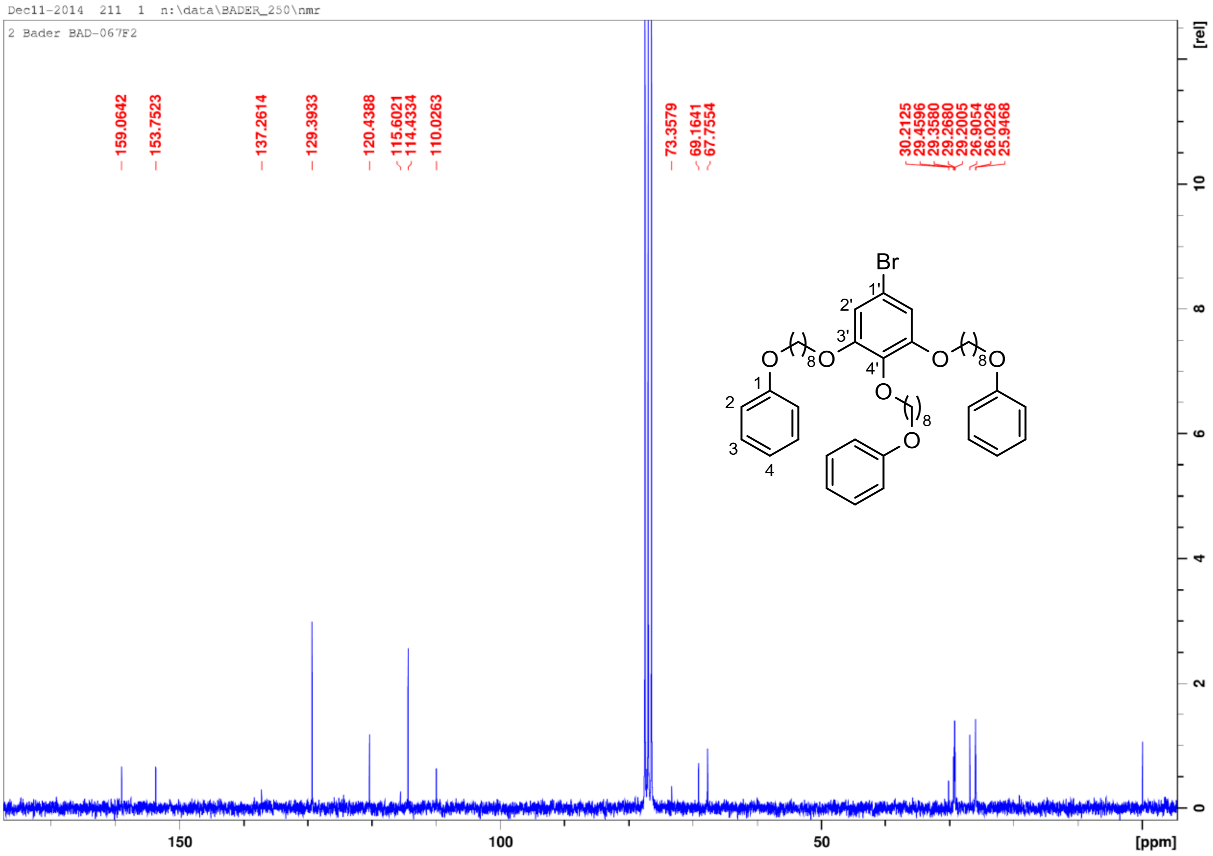


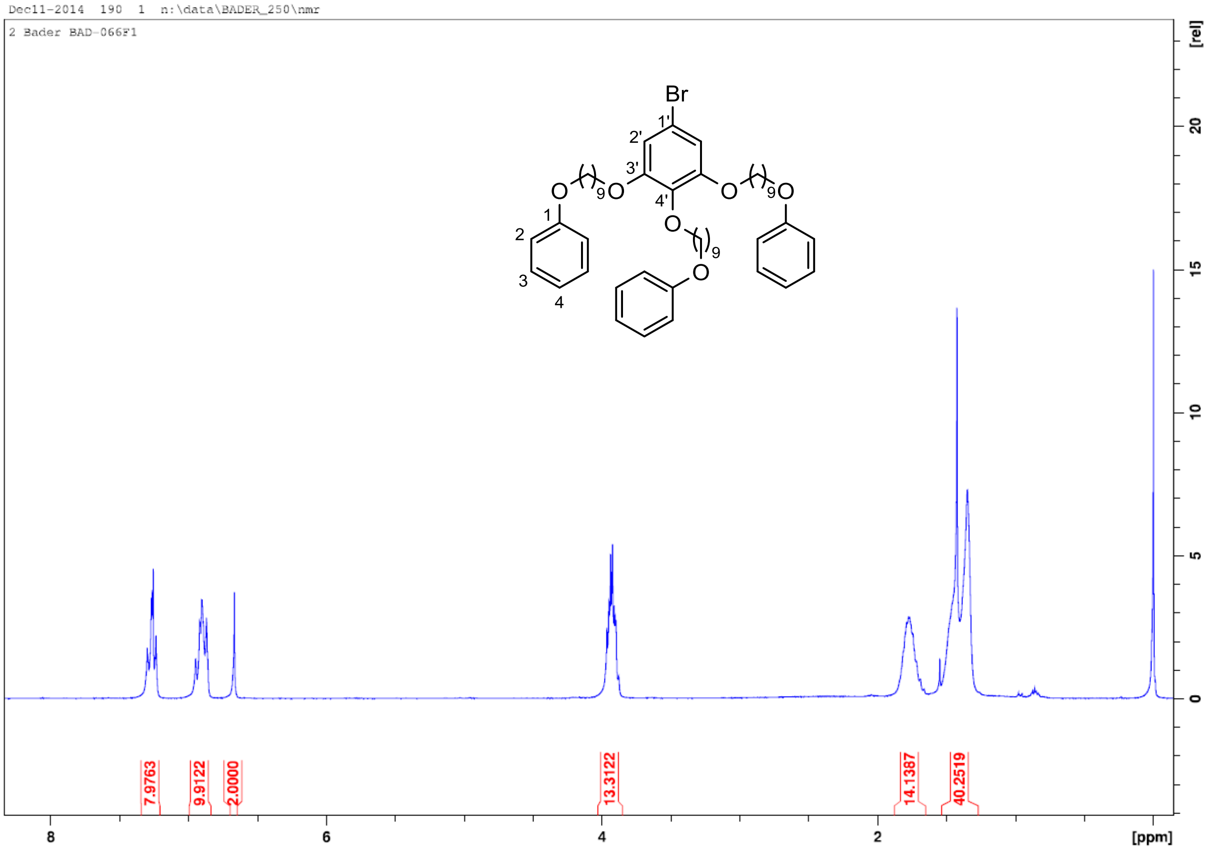


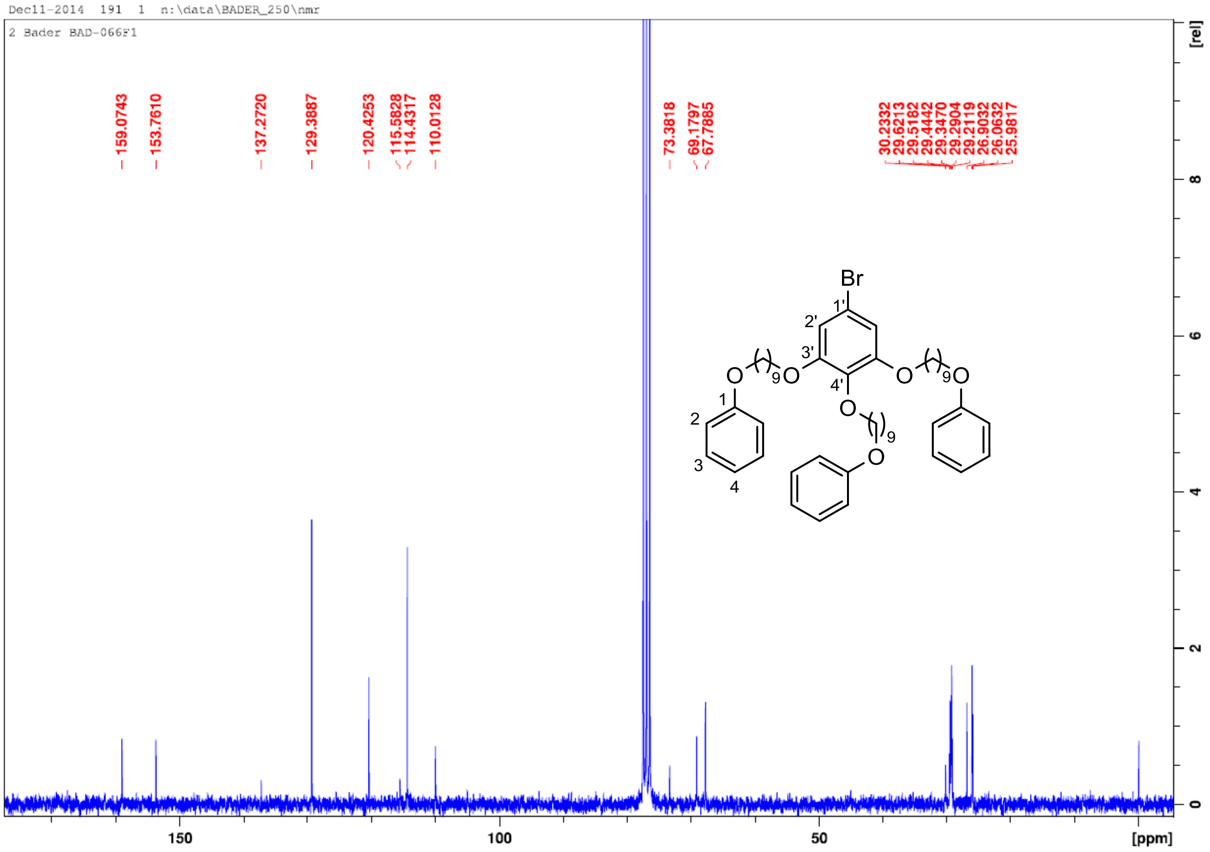

Dec12-2014 390 1 n:\data\BADER_250\nmr
2 Bader BAD068
Br
1'
2'
3'
4'
O
6
1
2
3
4
7.2071
9.5433
2.0000
12.5167
13.1747
13.2804
6
4
2
[ppm]
[rel]
20
15
10
5
0


Dec12-2014 391 1 n:\data\BADER_250\nmr
2 Bader BAD068
159.0153
153.7156
137.2108
129.4061
120.4913
120.4392
115.6782
114.4291
110.0600
73.2262
69.0582
67.7090
67.6063
30.1590
29.3263
29.2562
29.1764
26.9045
25.9540
25.8951
25.8329
Br
1'
2'
3'
4'
O
6
1
2
3
4
160
140
120
100
80
60
40
20
[ppm]
[rel]
12
10
8
6
4
2
0

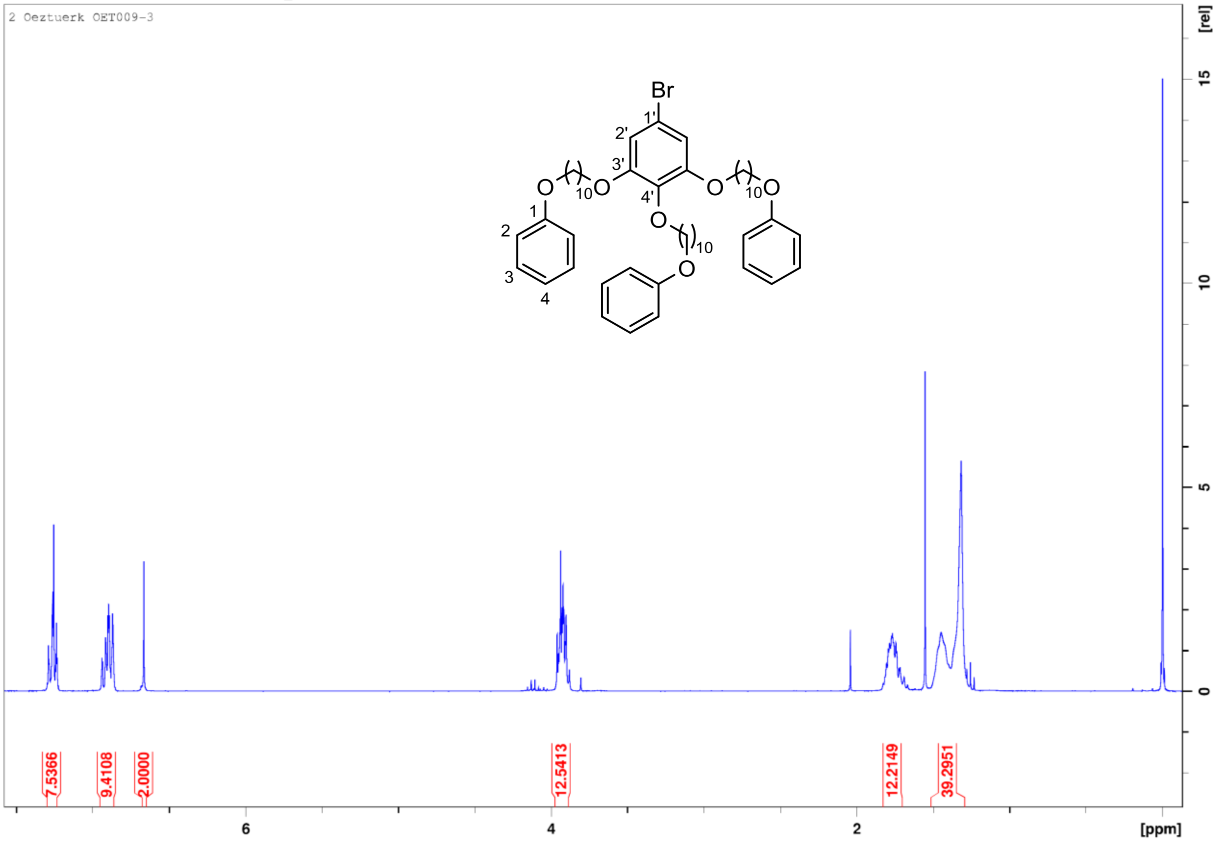

Dec11-2014 210 1 n:\data\BADER_250\nmr
2 Bader BAD-067F2
Br
1'
2'
3'
4'
O
8
1
2
3
4
8.4247
9.7061
2.0000
12.6679
13.7848
33.1388
6
4
2
[ppm]
[rel]
12
10
8
6
4
2
0
- 2


Dec11-2014 211 1 n:\data\BADER_250\nmr
2 Bader BAD-067F2
159.0642
153.7523
137.2614
129.3933
120.4388
115.6021
114.4334
110.0263
73.3579
69.1641
67.7554
30.2125
29.4596
29.3580
29.2680
29.2005
26.9054
26.0226
25.9468
Br
1'
2'
3'
4'
O
8
1
2
3
4
150
100
50
[ppm]
[rel]
10
8
6
4
2
0

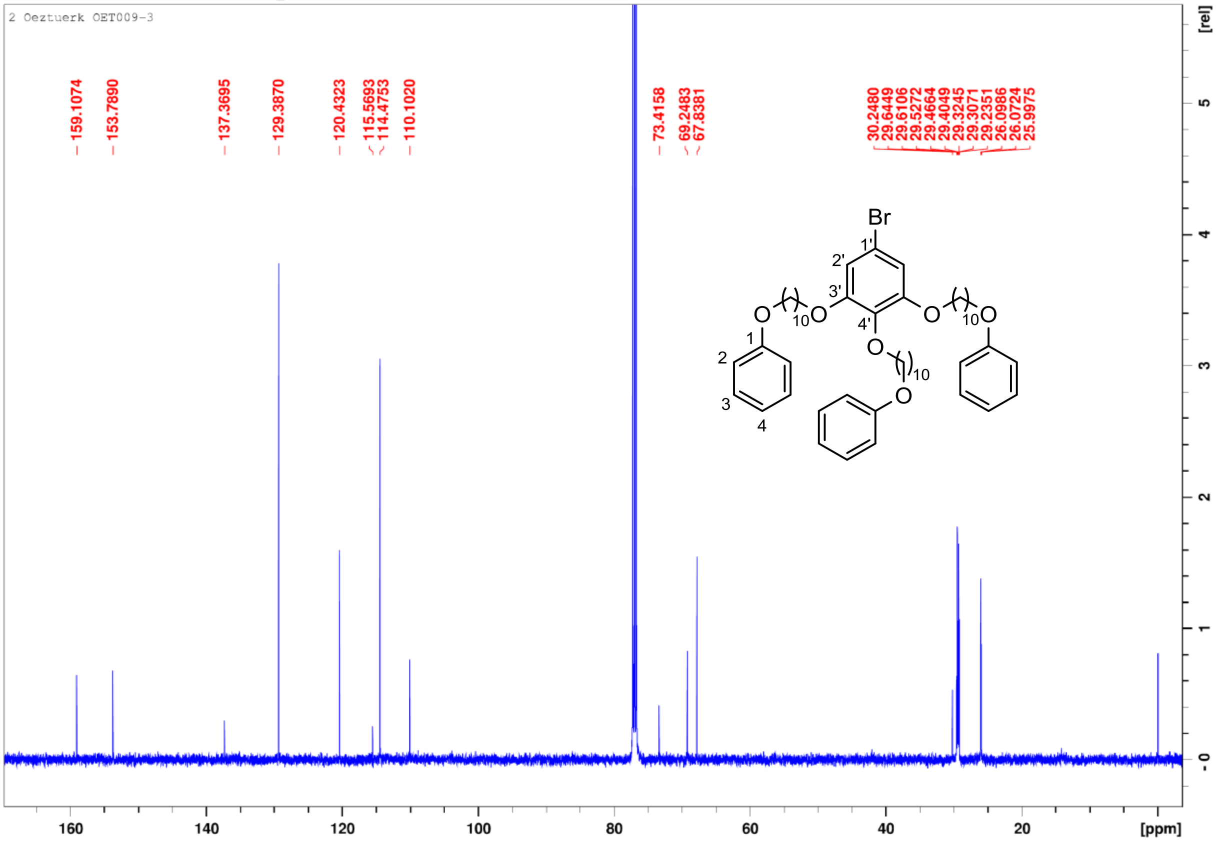

Dec11-2014 190 1 n:\data\BADER_250\nmr
2 Bader BAD-066F1
Br
1'
2'
3'
4'
O
9
1
2
3
4
7.9763
9.9122
2.0000
13.3122
14.1387
40.2519
8
6
4
2
[ppm]
[rel]
0
5
10
15
20

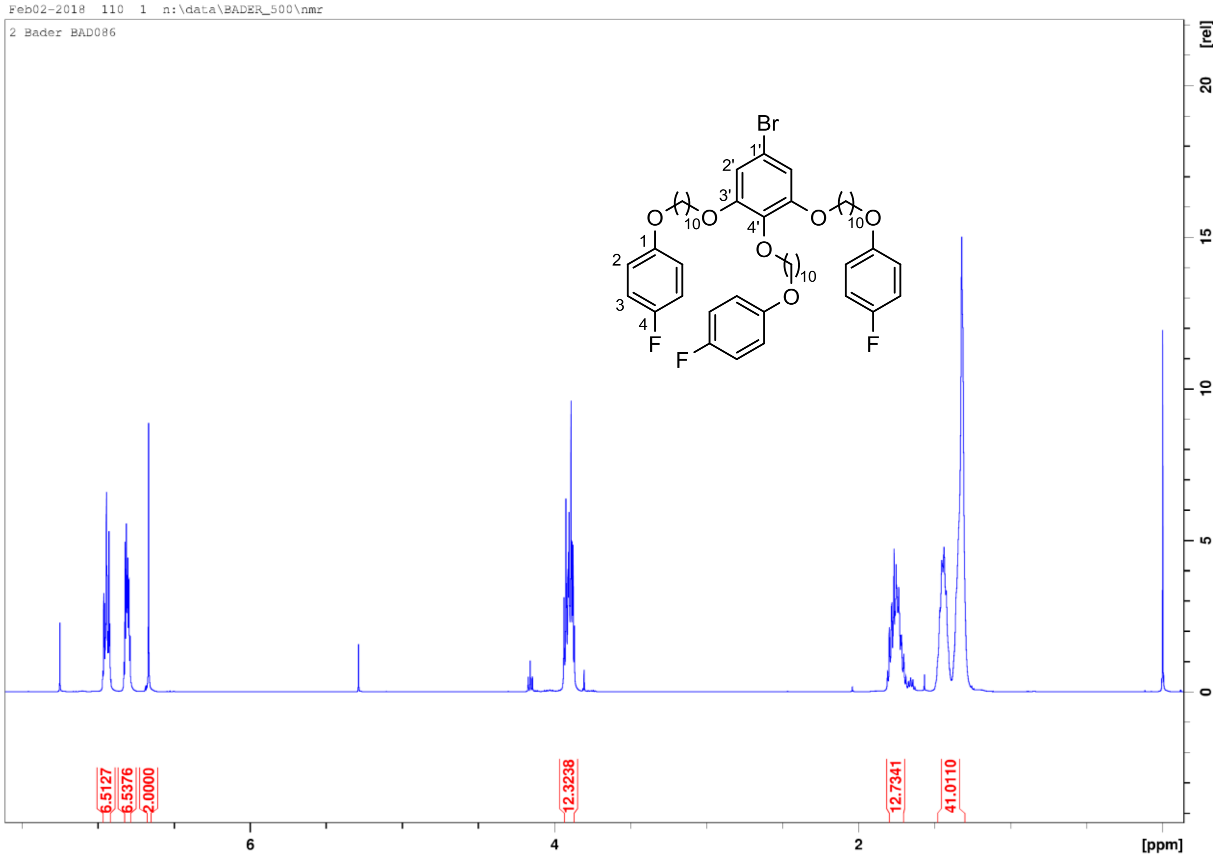

Dec11-2014 191 1 n:\data\BADER_250\nmr
2 Bader BAD-066F1
159.0743
153.7610
137.2720
129.3887
120.4253
115.5828
114.4317
110.0128
73.3818
69.1797
67.7885
30.2332
29.6213
29.5182
29.4442
29.3470
29.2904
29.2119
26.9032
26.0632
25.9817
Br
1'
2'
3'
4'
O
9
1
2
3
4
150
100
50
[ppm]
[rel]
0
2
4
6
8

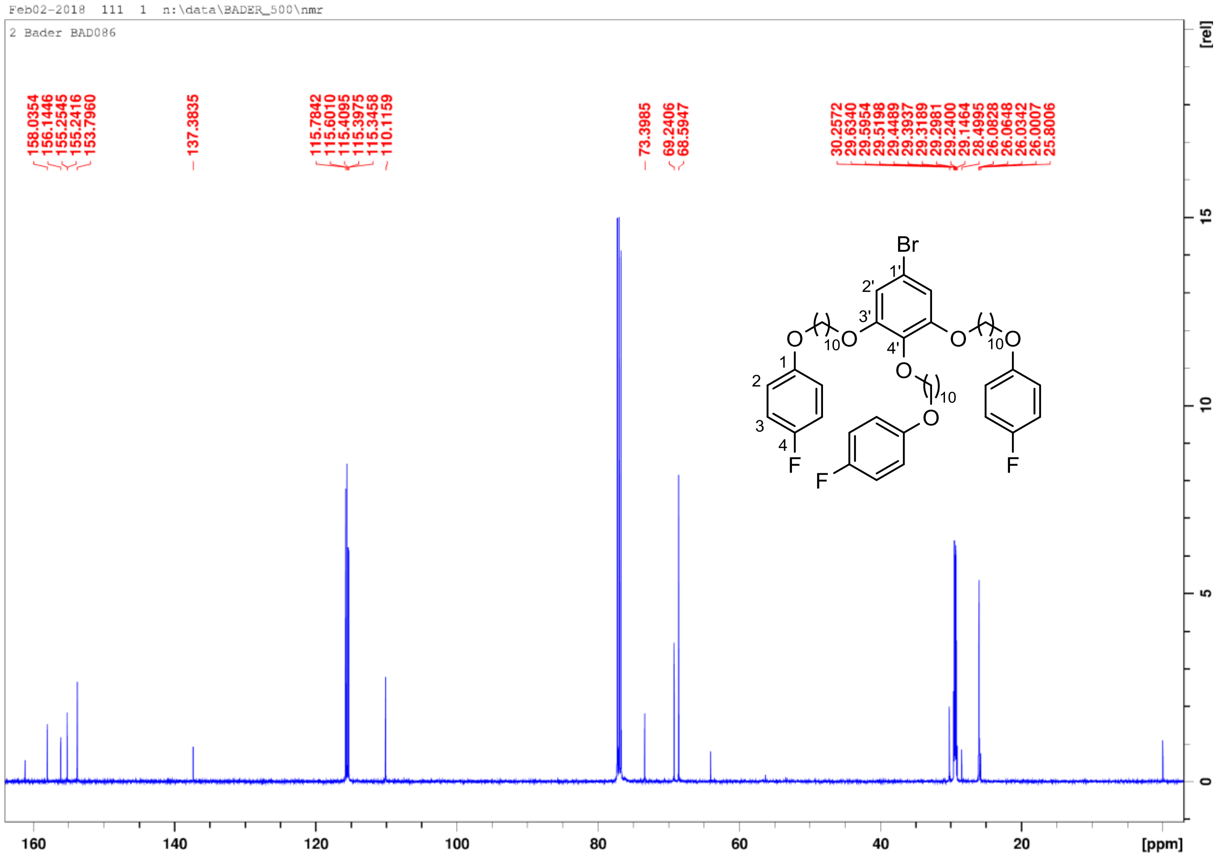
Jun06-2016 320 1 n:\data\OEZTUERK_300\nmr

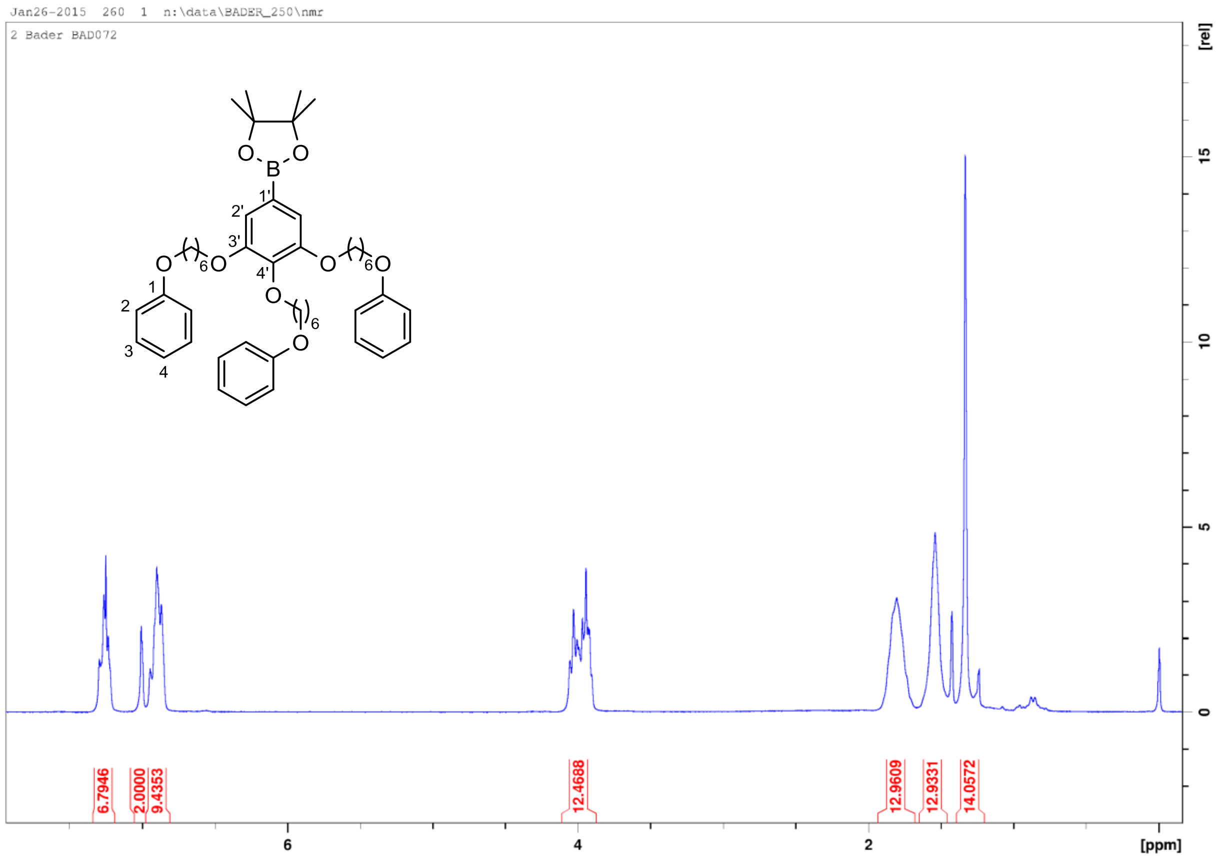


Jun07-2016 80 1 n:\data\OEZTUERK_500\nmr

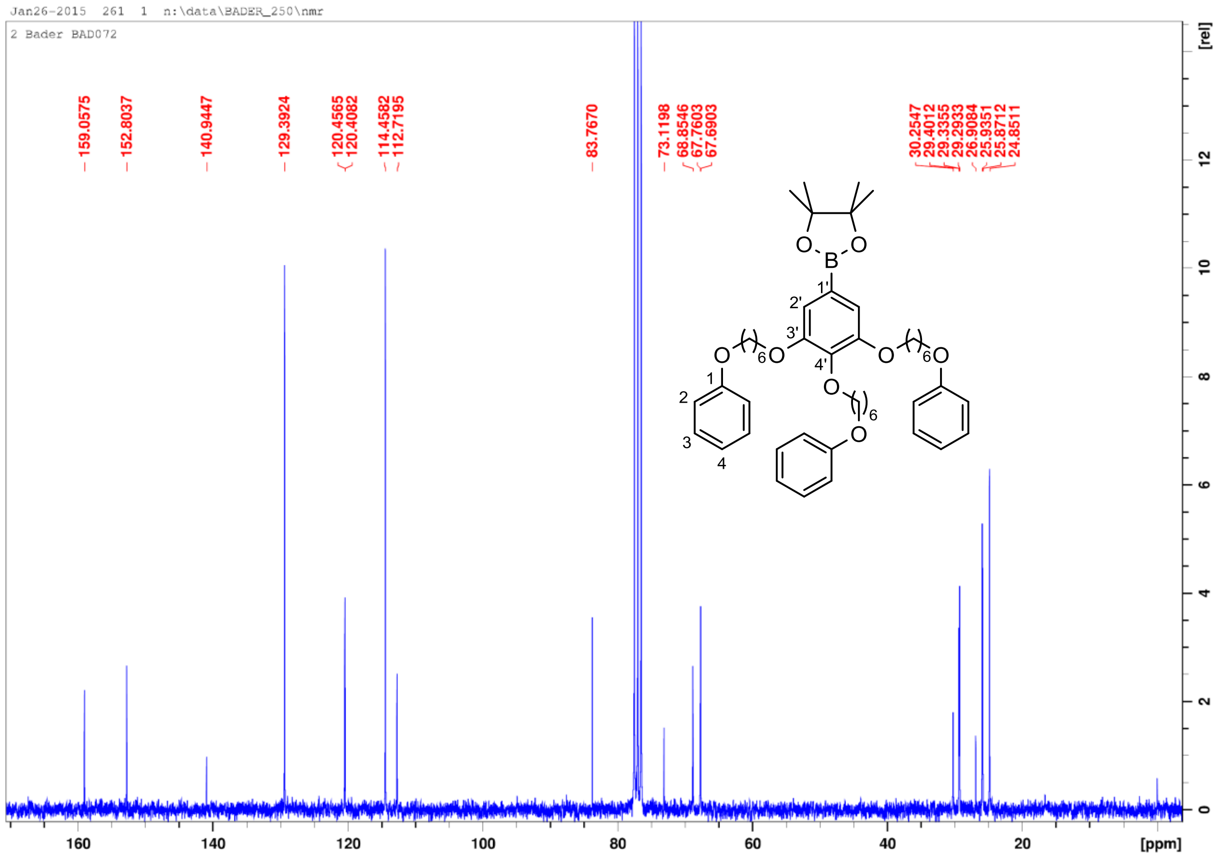



Feb02-2018 110 1 n:\data\BADER_500\nmr
2 Bader BAD086
Br
1'
2'
3'
4'
1
2
3
4
O
10
F
6.5127
6.5376
2.0000
12.3238
12.7341
41.0110
6
4
2
[ppm]
[rel]
0
5
10
15
20

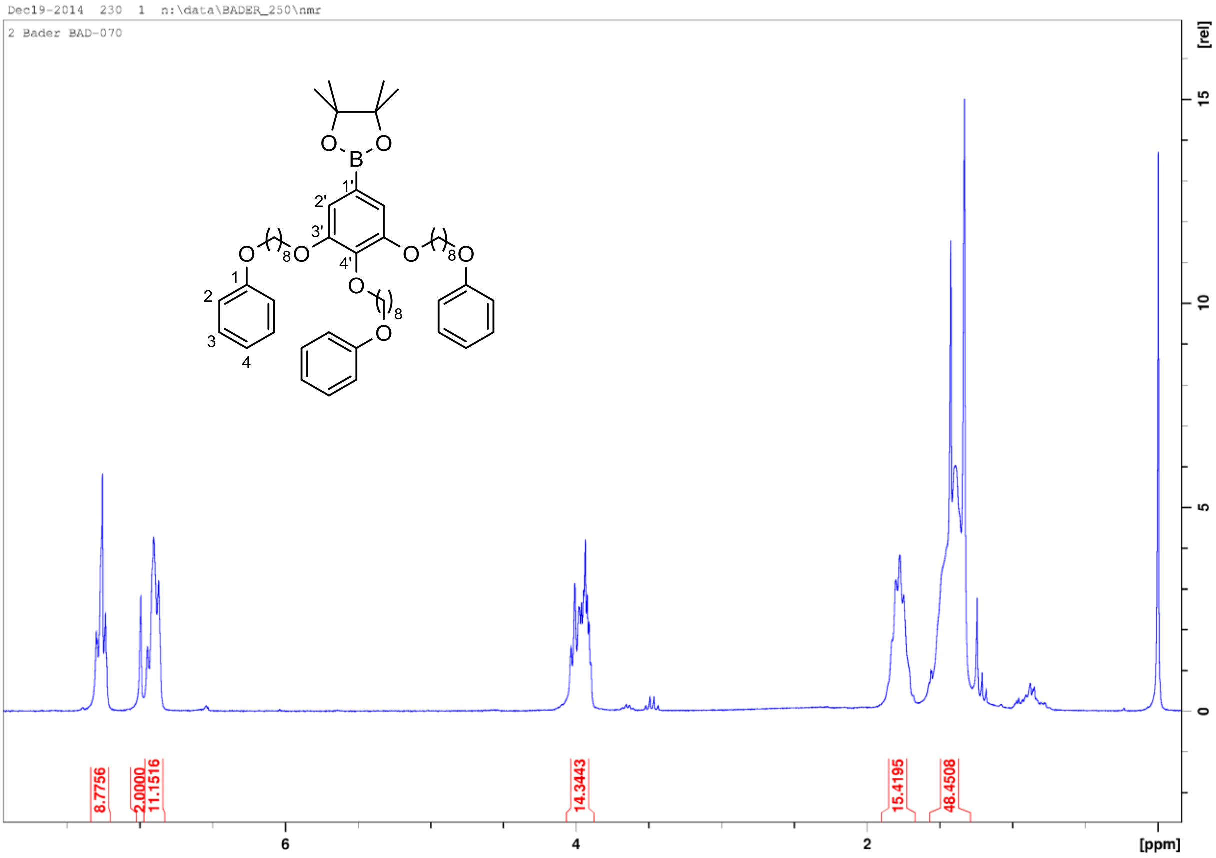

Feb02-2018 111 1 n:\data\BADER_500\nmr
2 Bader BAD086
158.0354
156.1446
155.2545
155.2416
153.7960
137.3835
115.7842
115.6010
115.4095
115.3975
115.3458
110.1159
73.3985
69.2406
68.5947
30.2572
29.6340
29.5954
29.5198
29.4489
29.3937
29.3189
29.2981
29.2400
29.1464
28.4995
26.0828
26.0648
26.0342
26.0007
25.8006
Br
1'
2'
3'
4'
1
2
3
4
O
10
F
160
140
120
100
80
60
40
20
[ppm]
[rel]
0
5
10
15

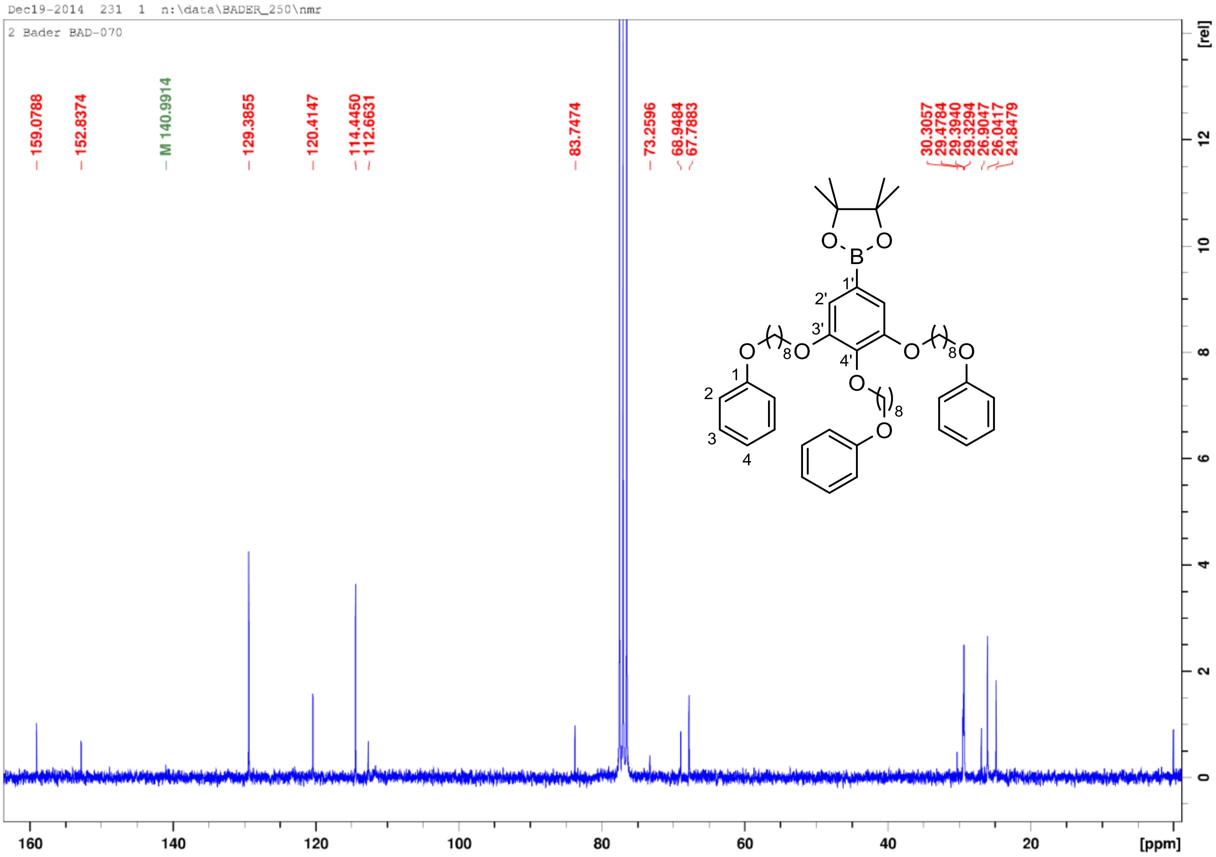


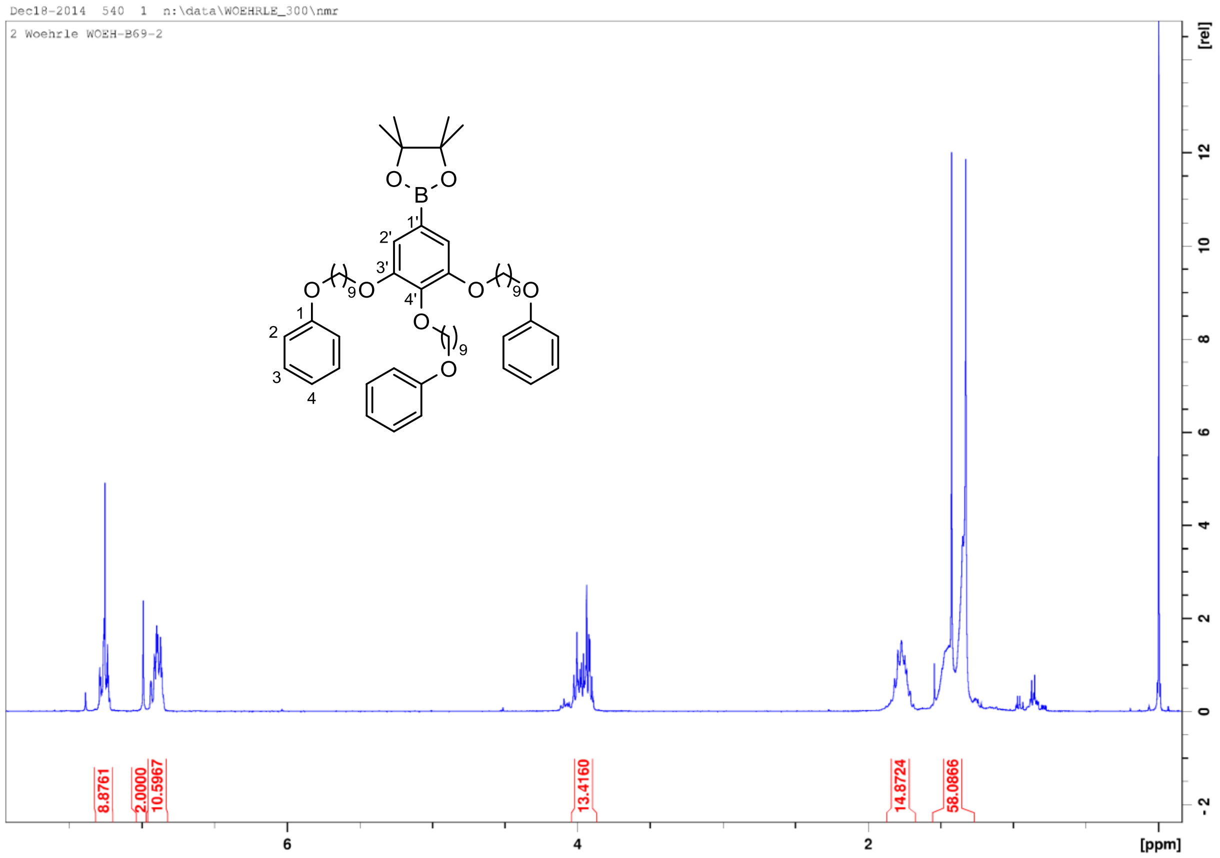
Jan26-2015 260 1 n:\data\BADER_250\nmr
2 Bader BAD072
1'
2'
3'
4'
1
2
3
4
6
O
B
6.7946
2.0000
9.4353
12.4688
12.9609
12.9331
14.0572
6
4
2
[ppm]
[rel]
0
5
10
15

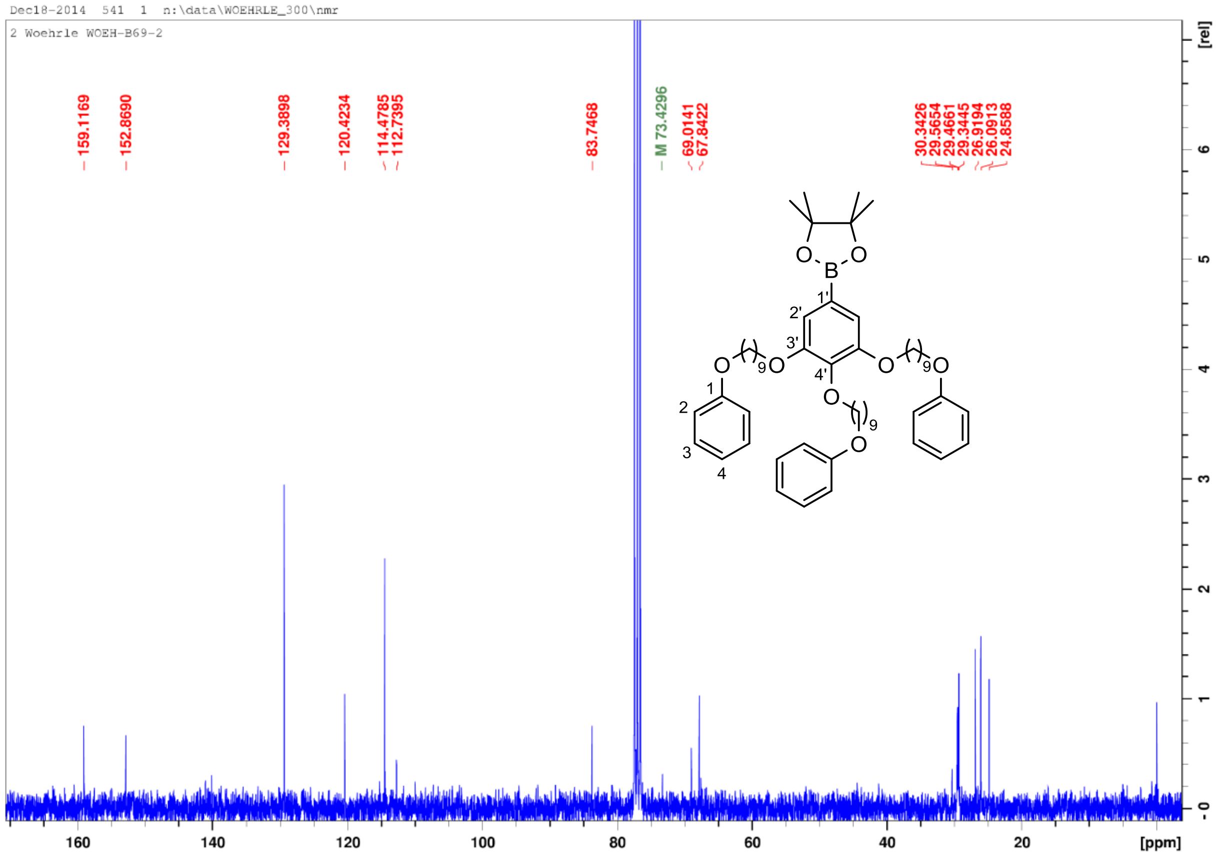


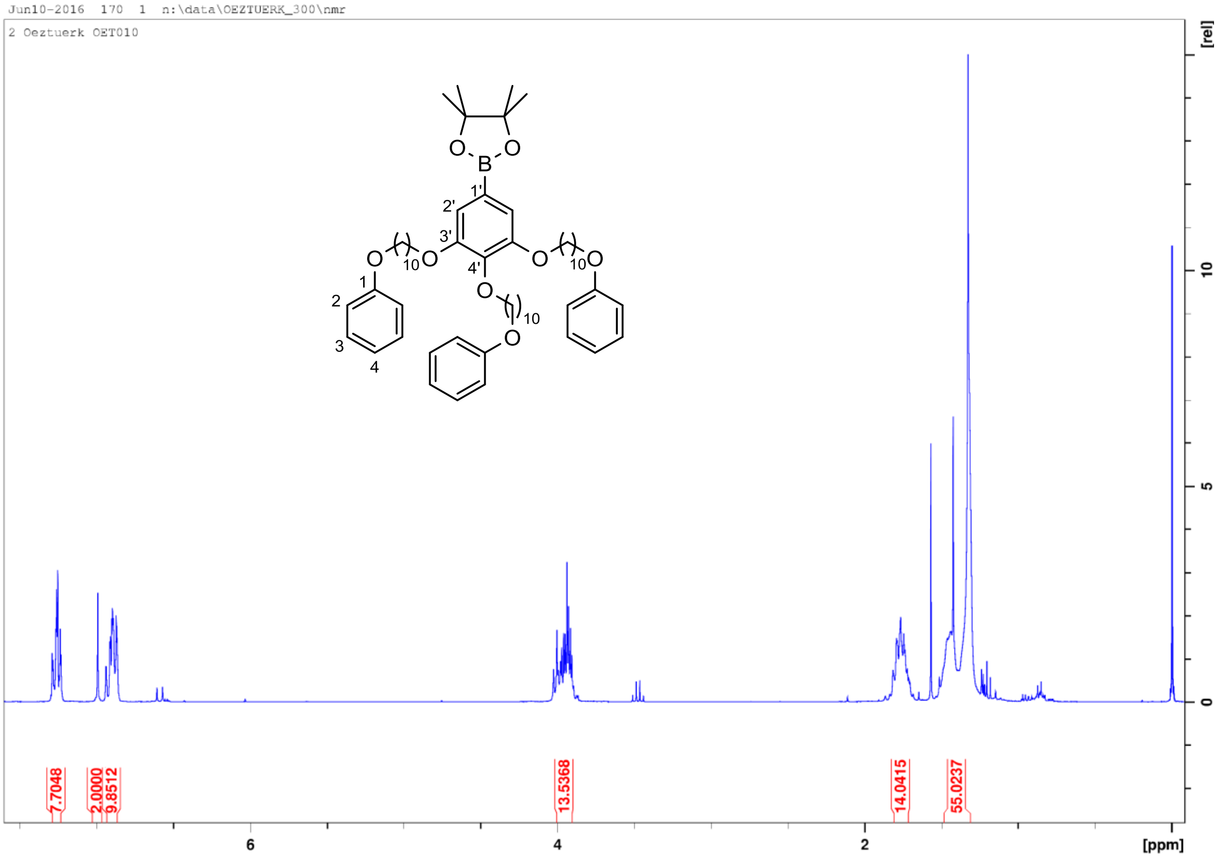
Jan26-2015 261 1 n:\data\BADER_250\nmr
2 Bader BAD072
159.0575
152.8037
140.9447
129.3924
120.4565
120.4082
114.4582
112.7195
83.7670
73.1198
68.8546
67.7603
67.6903
30.2547
29.4012
29.3355
29.2933
26.9084
25.9351
25.8712
24.8511
1'
2'
3'
4'
1
2
3
4
6
O
B
160
140
120
100
80
60
40
20
[ppm]
[rel]
0
2
4
6
8
10
12

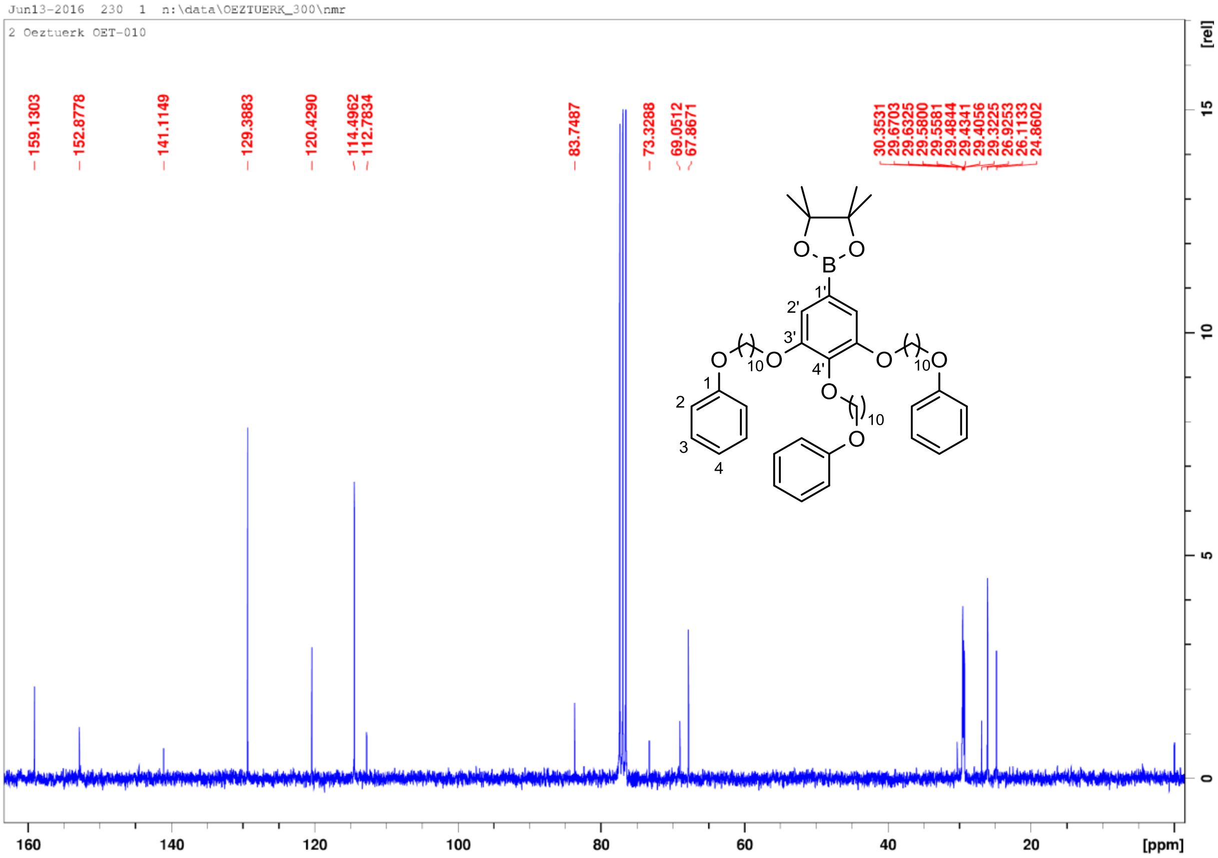

Dec19-2014 230 1 n:\data\BADER_250\nmr
2 Bader BAD-070
O
B
O
1'
2'
3'
4'
O
8
O
O
8
O
O
8
O
1
2
3
4
8.7756
2.0000
11.1516
14.3443
15.4195
48.4508
6
4
2
[ppm]
[rel]
15
10
5
0

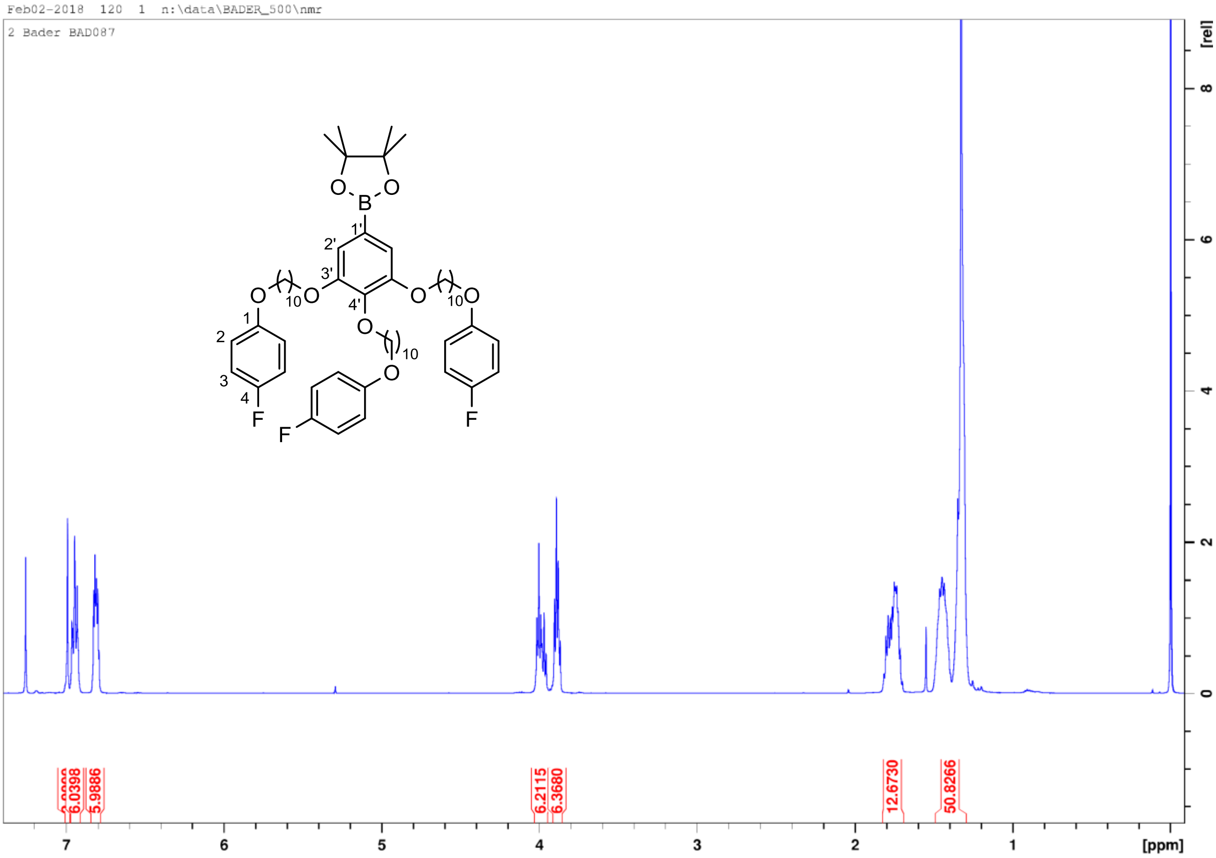

Dec19-2014 231 1 n:\data\BADER_250\nmr
2 Bader BAD-070
159.0788
152.8374
M 140.9914
129.3855
120.4147
114.4450
112.6631
83.7474
73.2596
68.9484
67.7883
30.3057
29.4784
29.3940
29.3294
26.9047
26.0417
24.8479
O
B
O
1'
2'
3'
4'
O
8
O
O
8
O
O
8
O
1
2
3
4
160
140
120
100
80
60
40
20
[ppm]
[rel]
12
10
8
6
4
2
0

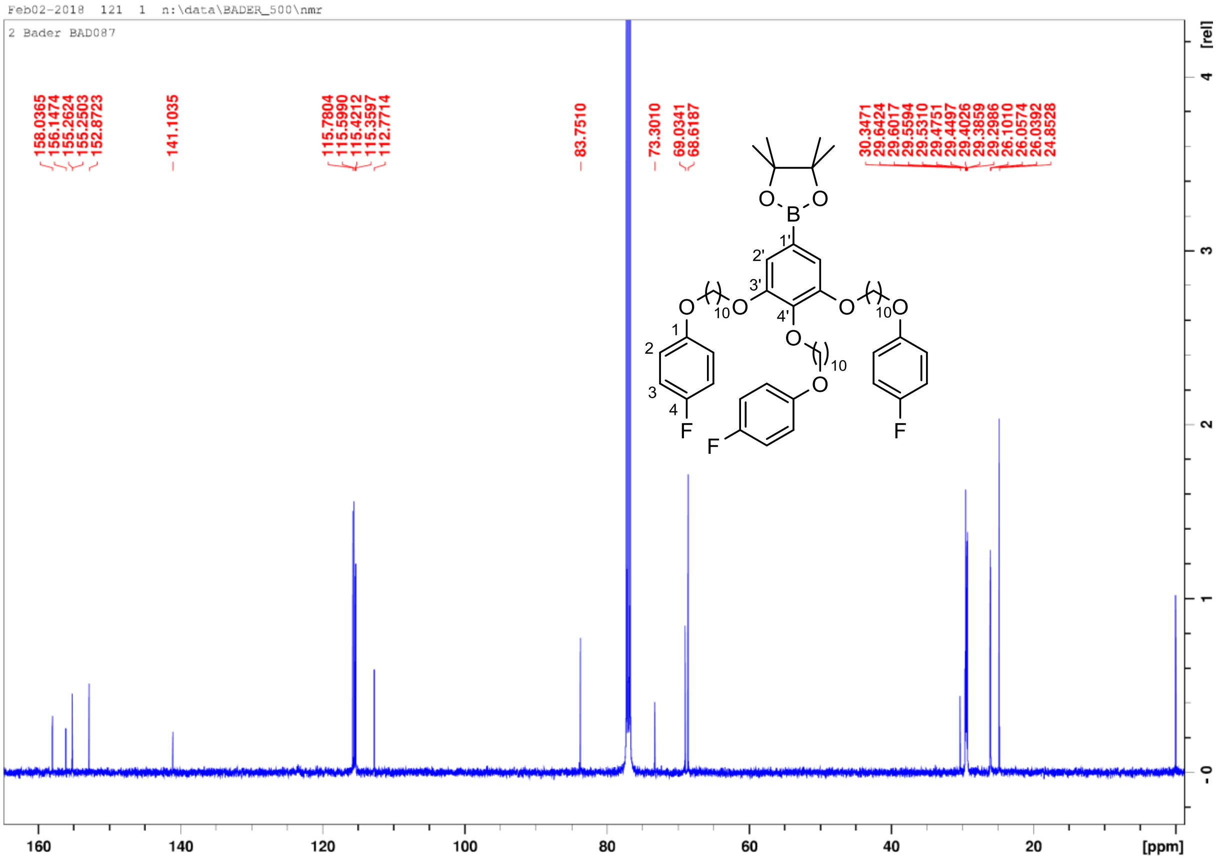

Dec18-2014 540 1 n:\data\WOEHRLE_300\nmr
2 Woehrle WOEH-B69-2
O B O
1'
2'
3'
4'
O
O
O
O
O
O
9
9
9
1
2
3
4
8.8761
2.0000
10.5967
13.4160
14.8724
58.0866
6
4
2
[ppm]
[rel]
12
10
8
6
4
2
0
- 2

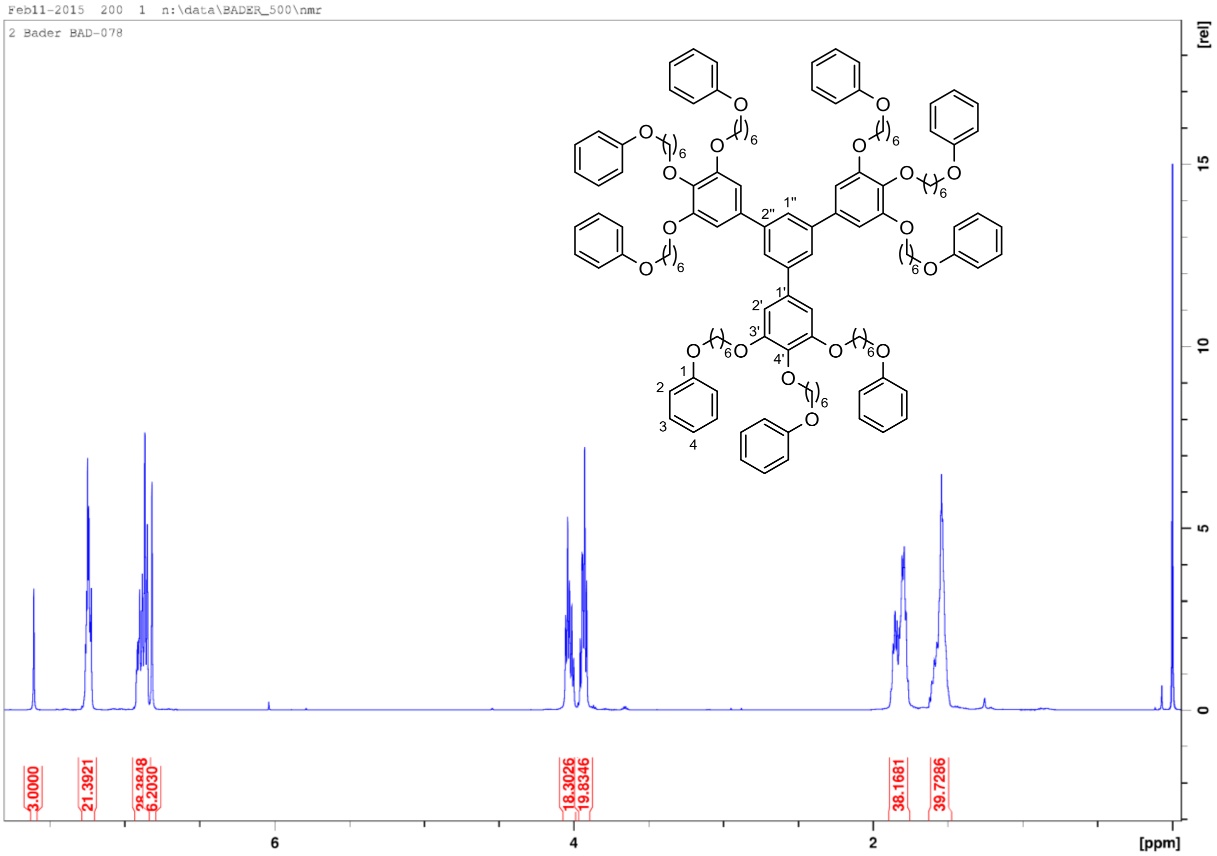

Dec18-2014 541 1 n:\data\WOEHRLE_300\nmr
2 Woehrle WOEH-B69-2
159.1169
152.8690
129.3898
120.4234
114.4785
112.7395
83.7468
M 73.4296
69.0141
67.8422
30.3426
29.5654
29.4661
29.3445
26.9194
26.0913
24.8588
O B O
1'
2'
3'
4'
O
O
O
O
O
O
9
9
9
1
2
3
4
160
140
120
100
80
60
40
20
[ppm]
[rel]
6
5
4
3
2
1
0

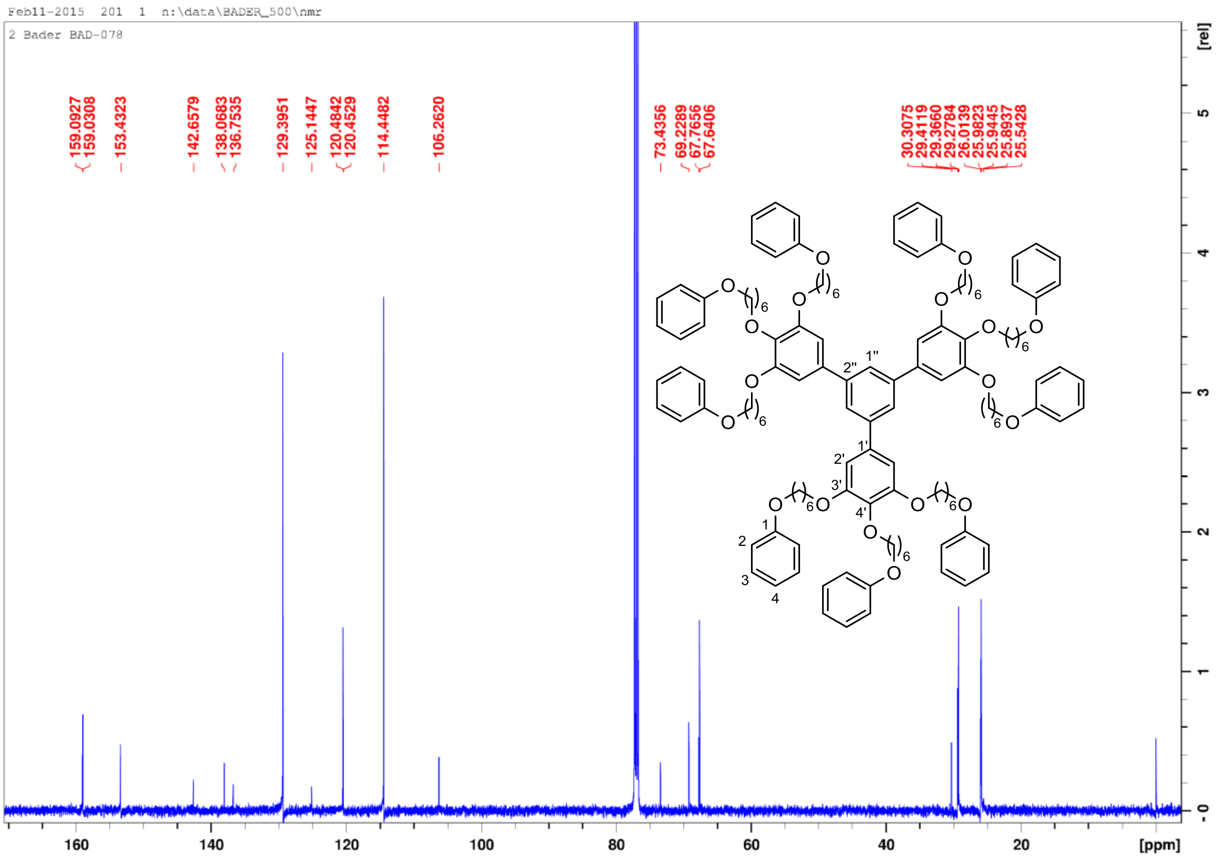

Jun10-2016 170 1 n:\data\OEZTUERK_300\nmr
2 Oezteurk OET010
B
O
O
1'
2'
3'
4'
10
1
2
3
4
7.7048
2.0000
9.8512
13.5368
14.0415
55.0237
6
4
2
0
[ppm]
[rel]
0
5
10

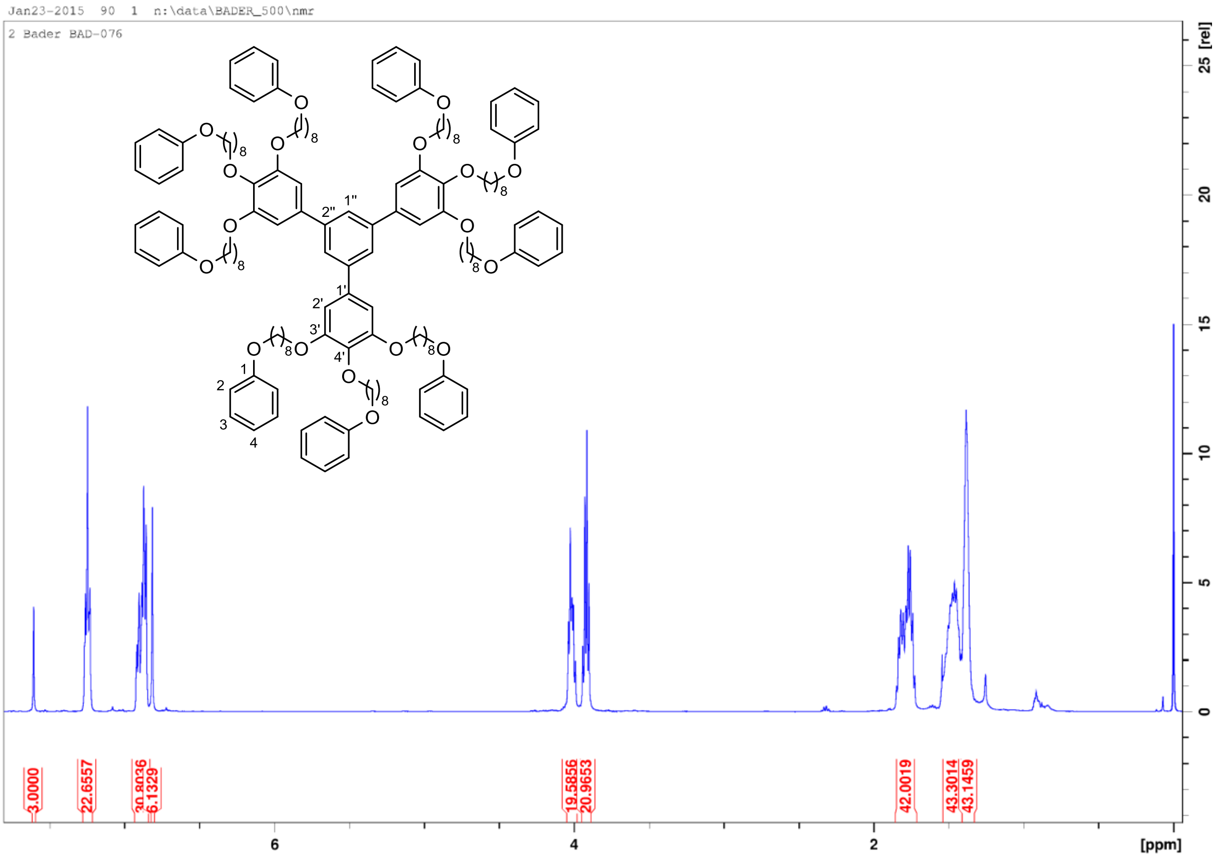

Jun13-2016 230 1 n:\data\OEZTUERK_300\nmr
2 Oezteurk OET-010
159.1303
152.8778
141.1149
129.3883
120.4290
114.4962
112.7834
83.7487
73.3288
69.0512
67.8671
30.3531
29.6703
29.6325
29.5800
29.5581
29.4844
29.4341
29.4056
29.3225
26.9253
26.1133
24.8602
B
O
O
1'
2'
3'
4'
10
1
2
3
4
160
140
120
100
80
60
40
20
[ppm]
[rel]
0
5
10
15

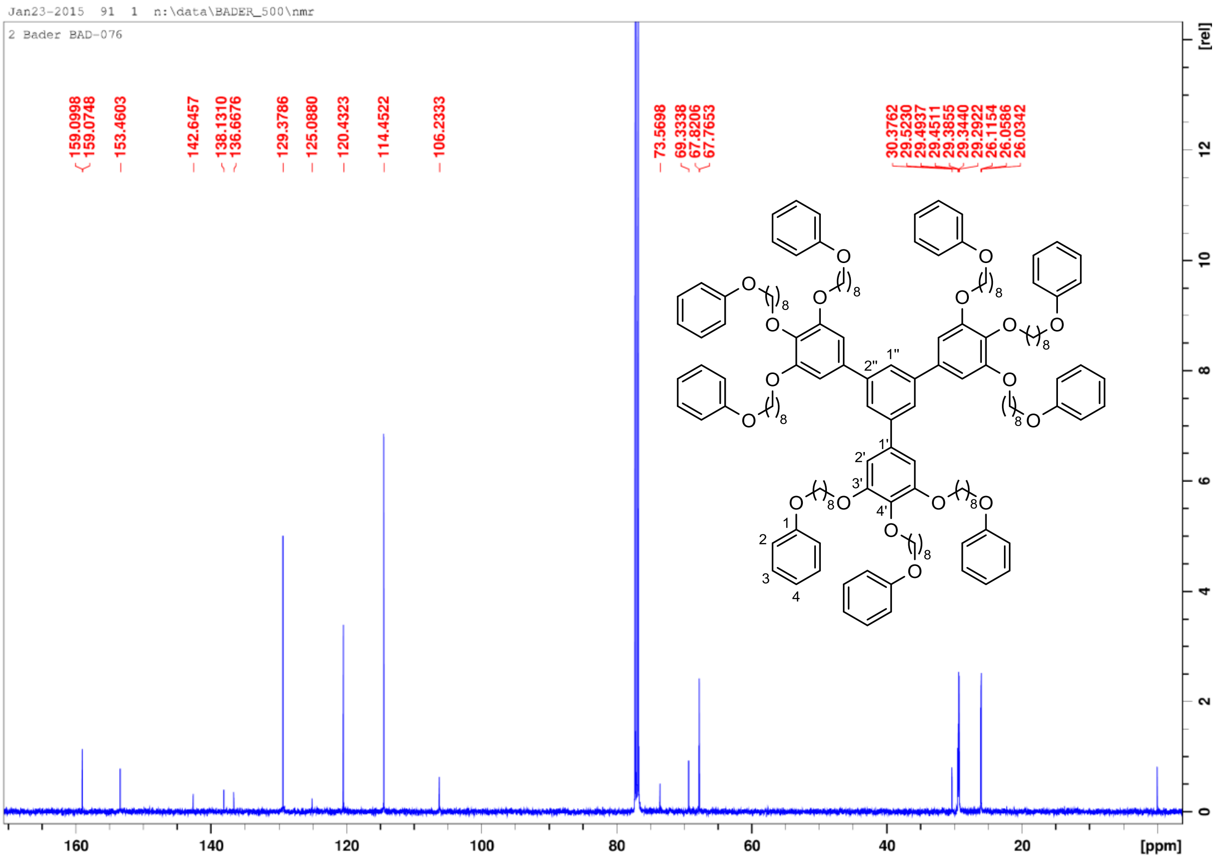

Feb02-2018 120 1 n:\data\BADER_500\nmr
2 Bader BAD087
O
B
O
1'
2'
3'
4'
O
O
O
O
O
O
10
10
10
1
2
3
4
F
F
F
6.0398
5.9886
6.2115
6.3680
12.6730
50.8266
7
6
5
4
3
2
1
[ppm]
[rel]
8
6
4
2
0

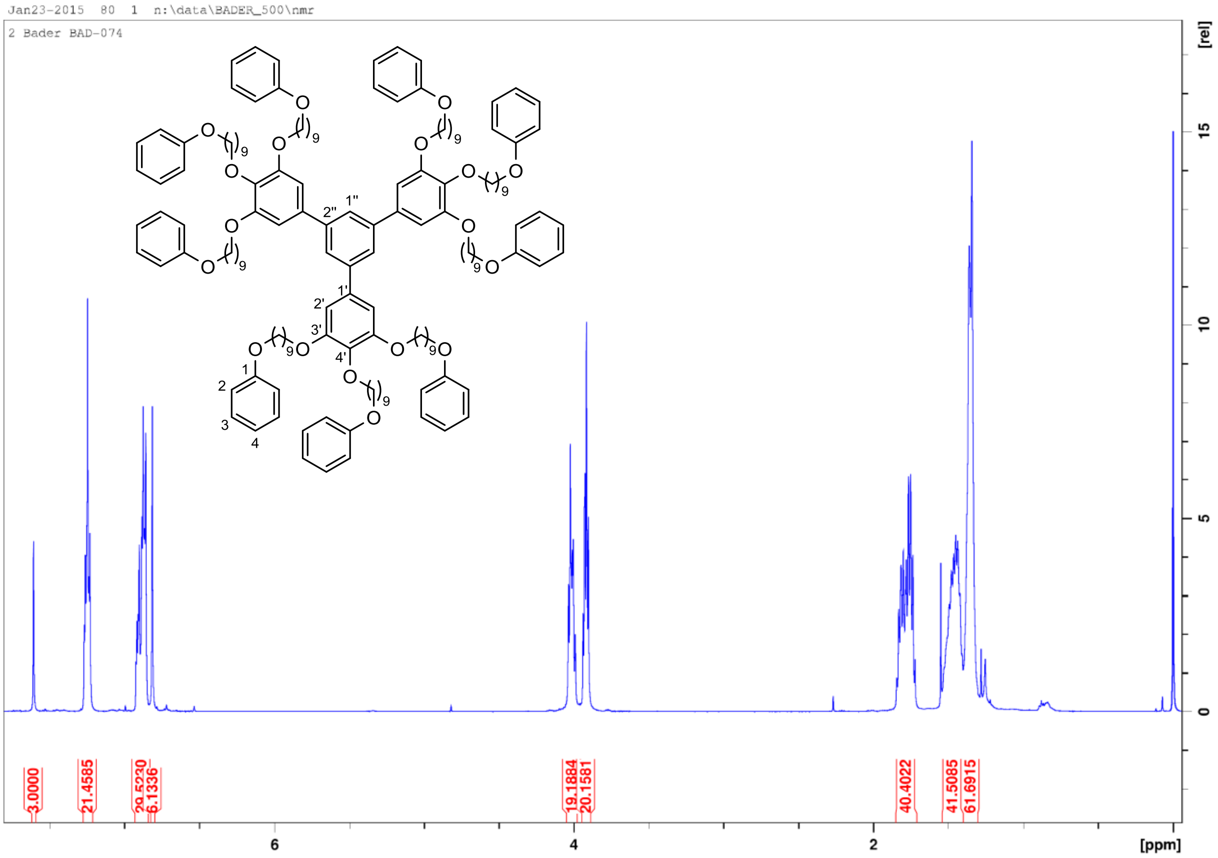

Feb02-2018 121 1 n:\data\BADER_500\nmr
2 Bader BAD087
158.0365
156.1474
155.2624
155.2503
152.8723
141.1035
115.7804
115.5990
115.4212
115.3597
112.7714
83.7510
73.3010
69.0341
68.6187
30.3471
29.6424
29.6017
29.5594
29.5310
29.4751
29.4497
29.4026
29.3859
29.2986
26.1010
26.0574
26.0392
24.8528
O
B
O
1'
2'
3'
4'
O
O
O
O
O
O
10
10
10
1
2
3
4
F
F
F
160
140
120
100
80
60
40
20
[ppm]
[rel]
4
3
2
1
0

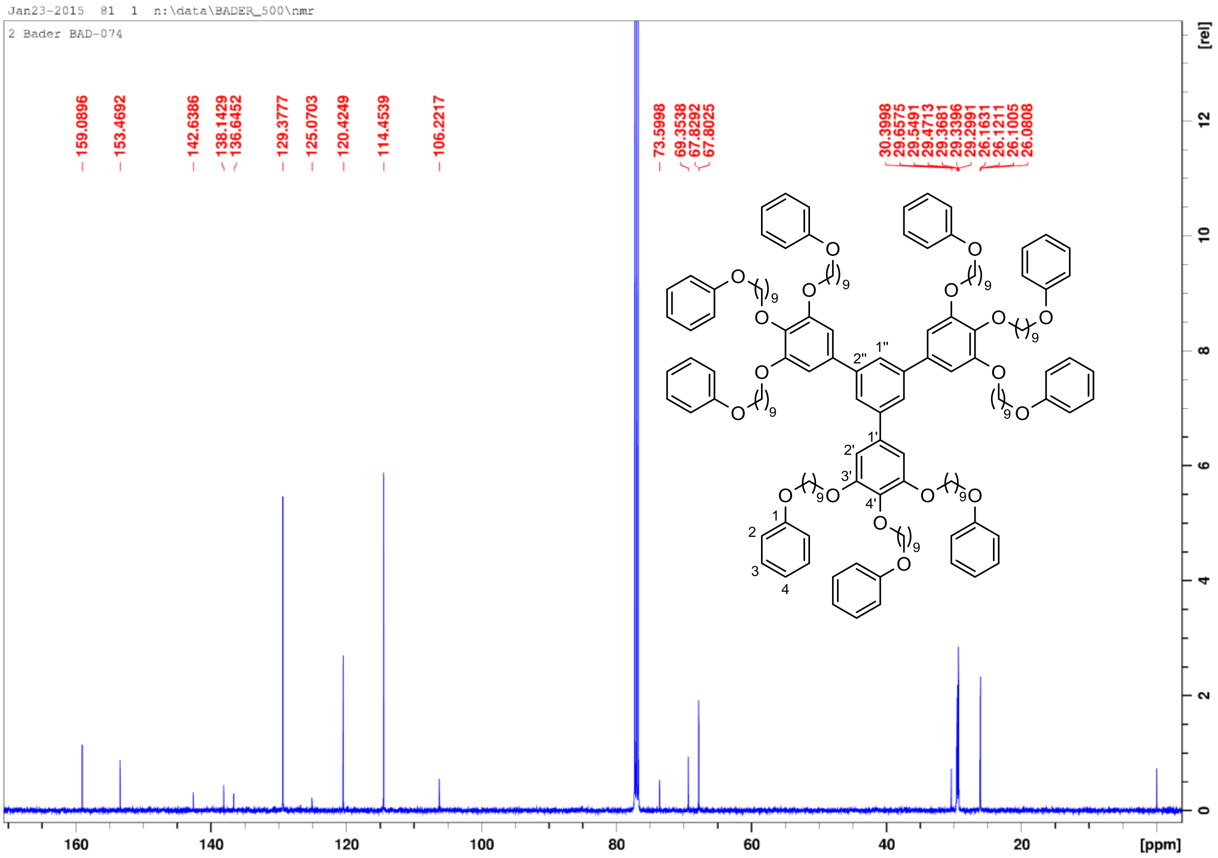

Feb11-2015 200 1 n:\data\BADER_500\nmr
2 Bader BAD-078
[rel]
15
10
5
0
3.0000
21.3921
28.3848
6.2030
18.3026
19.8346
38.1681
39.7286
6
4
2
[ppm]
1''
2''
1'
2'
3'
4'
1
2
3
4
O
6

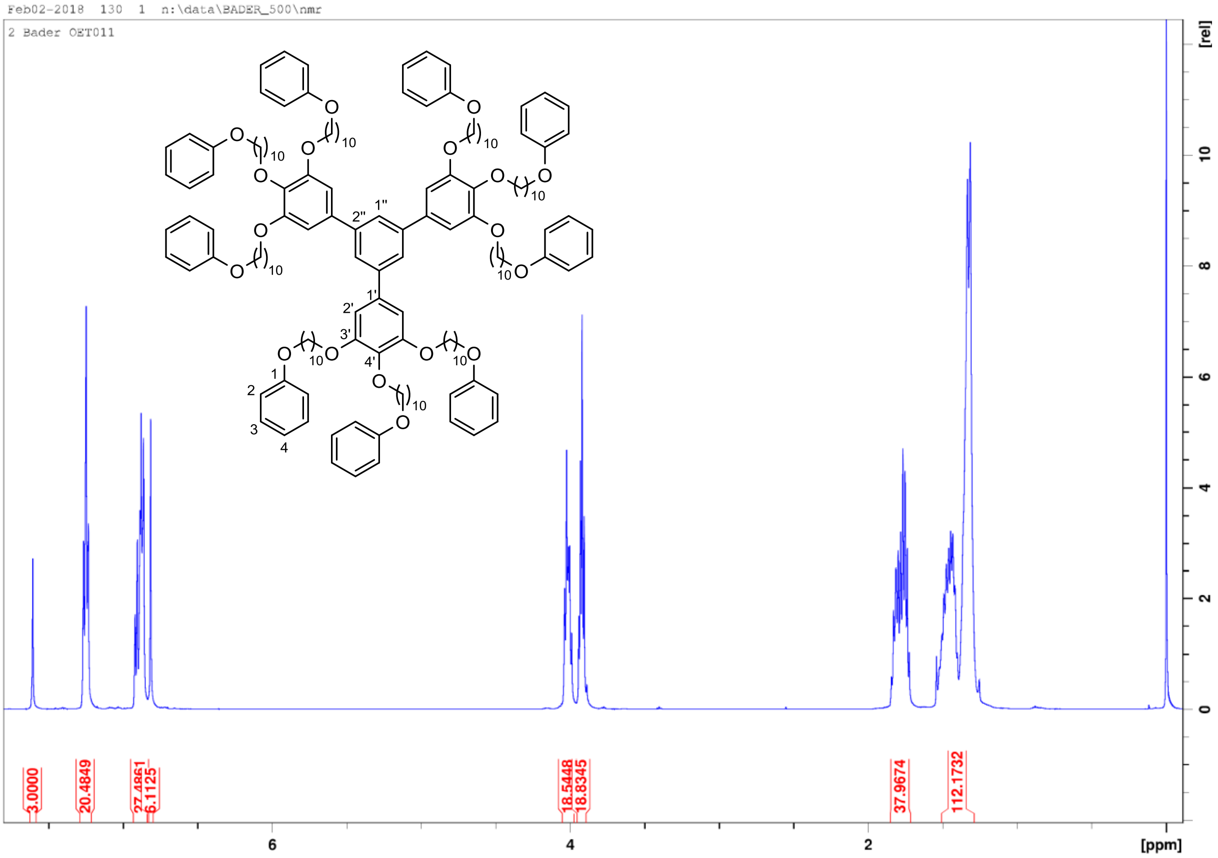

Feb11-2015 201 1 n:\data\BADER_500\nmr
2 Bader BAD-078
[rel]
159.0927
159.0308
153.4323
142.6579
138.0683
136.7535
129.3951
125.1447
120.4842
120.4529
114.4482
106.2620
73.4356
69.2289
67.7656
67.6406
30.3075
29.4119
29.3660
29.2784
26.0139
25.9823
25.9445
25.8937
25.5428
5
4
3
2
1
0
160
140
120
100
80
60
40
20
[ppm]
1''
2''
1'
2'
3'
4'
1
2
3
4
O
6

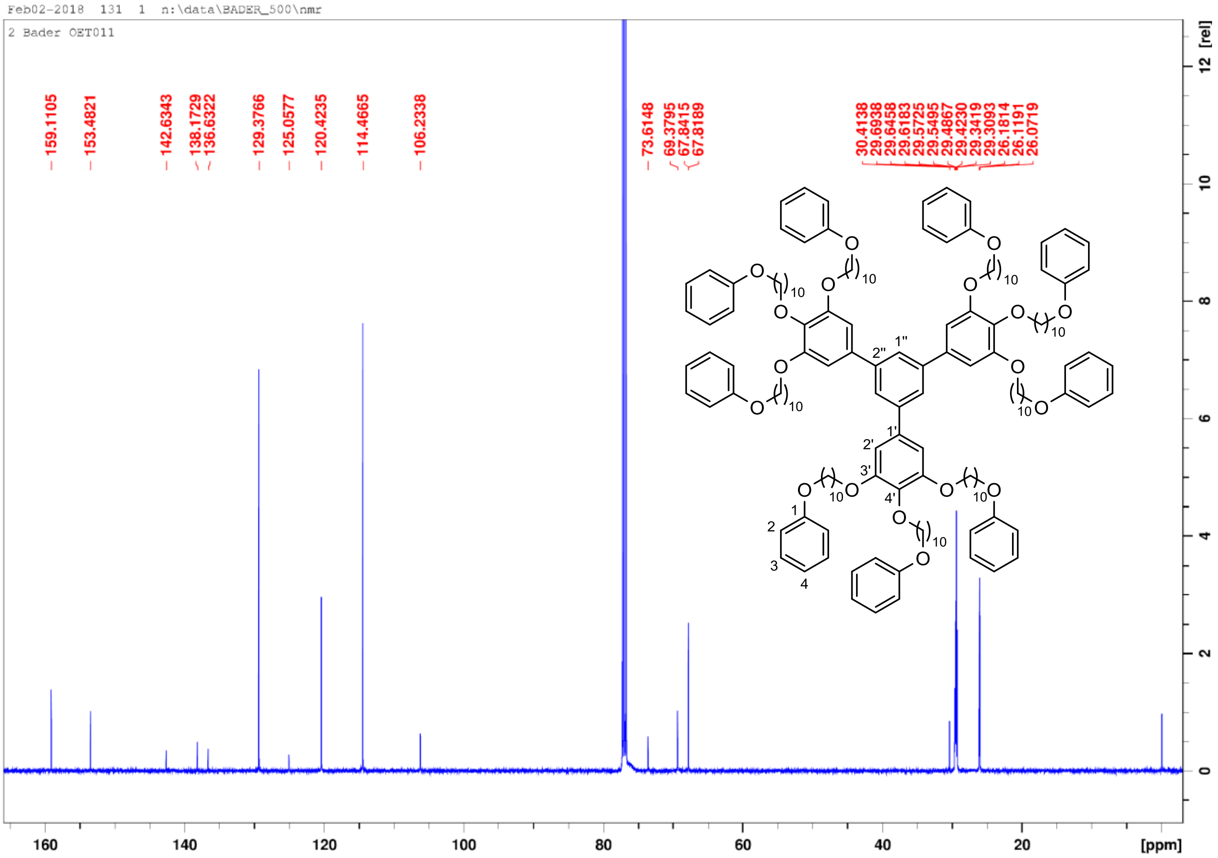

Jan23-2015 90 1 n:\data\BADER_500\nmr
2 Bader BAD-076
1"
2"
1'
2'
3'
4'
1
2
3
4
O
8
3.0000
22.6557
30.8036
6.1329
19.5856
20.9653
42.0019
43.3014
43.1459
6
4
2
[ppm]
25 [rel]
20
15
10
5
0

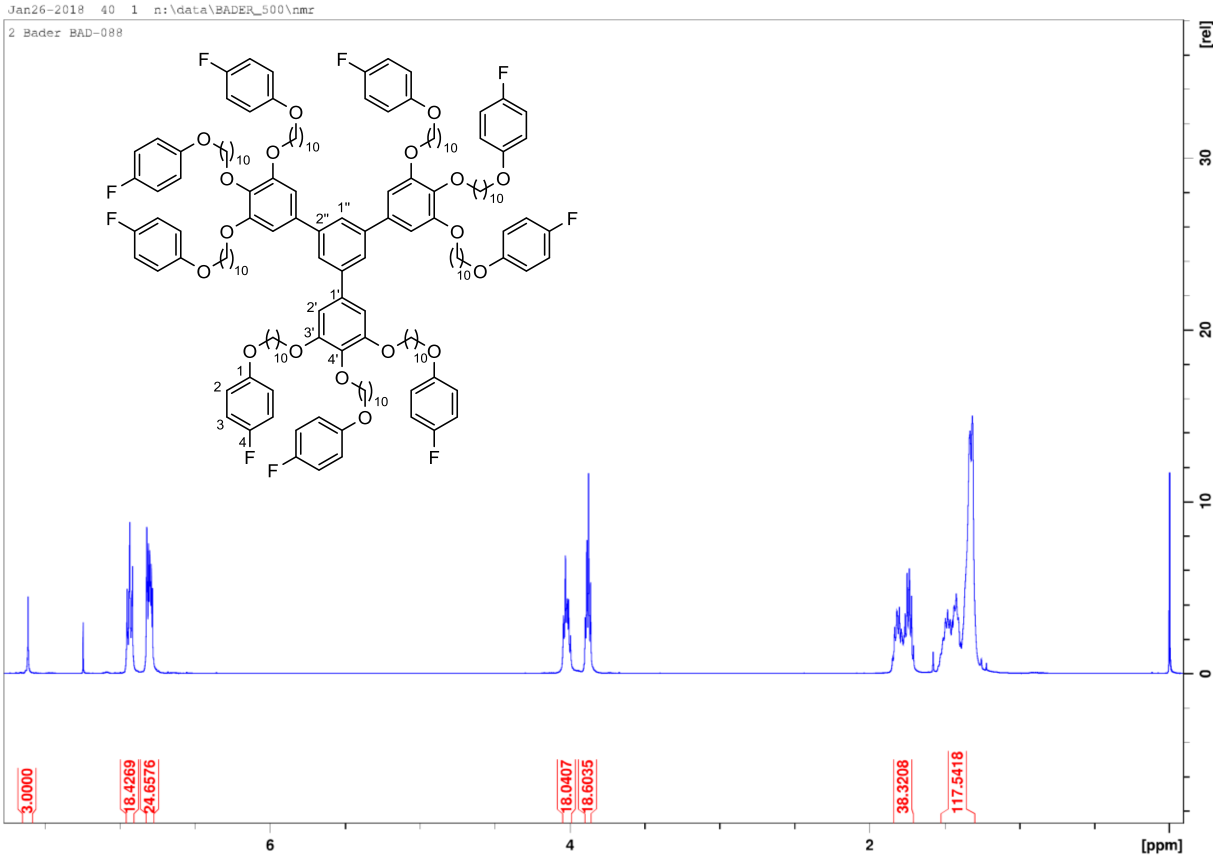

Jan23-2015 91 1 n:\data\BADER_500\nmr
2 Bader BAD-076
159.0998
159.0748
153.4603
142.6457
138.1310
136.6676
129.3786
125.0880
120.4323
114.4522
106.2333
73.5698
69.3338
67.8206
67.7653
30.3762
29.5230
29.4937
29.4511
29.3855
29.3440
29.2922
26.1154
26.0586
26.0342
1"
2"
1'
2'
3'
4'
1
2
3
4
O
8
160
140
120
100
80
60
40
20
[ppm]
[rel]
12
10
8
6
4
2
0


Jan23-2015 80 1 n:\data\BADER_500\nmr
2 Bader BAD-074
O
9
1"
2"
1'
2'
3'
4'
1
2
3
4
3.0000
21.4585
29.5230
6.1336
19.1884
20.1581
40.4022
41.5085
61.6915
6
4
2
[ppm]
[rel]
15
10
5
0

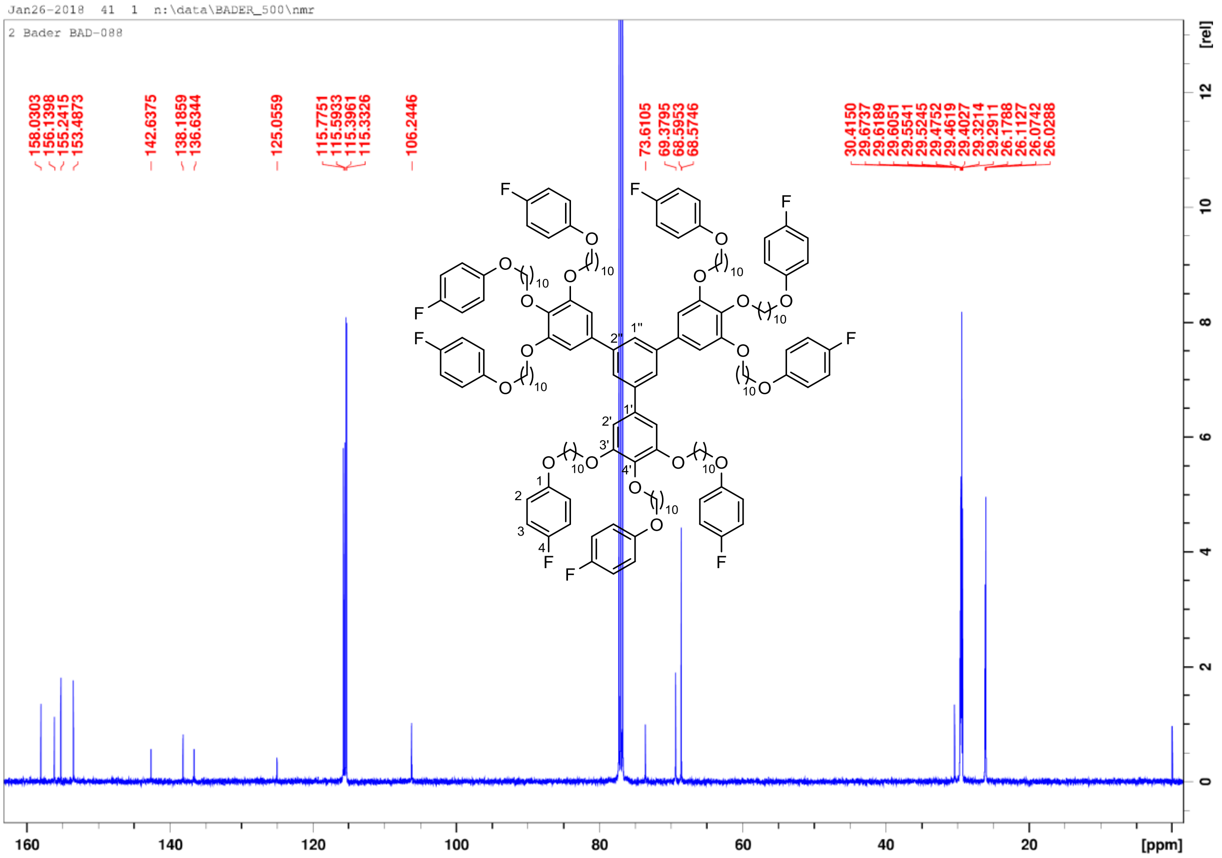

Jan23-2015 81 1 n:\data\BADER_500\nmr
2 Bader BAD-074
159.0896
153.4692
142.6386
138.1429
136.6452
129.3777
125.0703
120.4249
114.4539
106.2217
73.5998
69.3538
67.8292
67.8025
30.3998
29.6575
29.5491
29.4713
29.3681
29.3396
29.2991
26.1631
26.1211
26.1005
26.0808
O
9
1"
2"
1'
2'
3'
4'
1
2
3
4
160
140
120
100
80
60
40
20
[ppm]
[rel]
12
10
8
6
4
2
0


Feb02-2018 130 1 n:\data\BADER_500\nmr
2 Bader OET011
1''
2''
1'
2'
3'
4'
1
2
3
4
O
10
3.0000
20.4849
27.4861
6.1125
18.5448
18.8345
37.9674
112.1732
6
4
2
[ppm]
0
2
4
6
8
10
[rel]


Feb02-2018 131 1 n:\data\BADER_500\nmr
2 Bader OET011
159.1105
153.4821
142.6343
138.1729
136.6322
129.3766
125.0577
120.4235
114.4665
106.2338
73.6148
69.3795
67.8415
67.8189
30.4138
29.6938
29.6458
29.6183
29.5725
29.5495
29.4867
29.4230
29.3419
29.3093
26.1814
26.1191
26.0719
1''
2''
1'
2'
3'
4'
1
2
3
4
O
10
160
140
120
100
80
60
40
20
[ppm]
0
2
4
6
8
10
12
[rel]



Jan26-2018 40 1 n:\data\BADER_500\nmr
2 Bader BAD-088
F
O
O
( )10
1"
2"
1'
2'
3'
4'
1
2
3
4
3.0000
18.4269
24.6576
18.0407
18.6035
38.3208
117.5418
6
4
2
[ppm]
[rel]
30
20
10
0



Jan26-2018 41 1 n:\data\BADER_500\nmr
2 Bader BAD-088
158.0303
156.1398
155.2415
153.4873
142.6375
138.1859
136.6344
125.0559
115.7751
115.5933
115.3961
115.3326
106.2446
73.6105
69.3795
68.5953
68.5746
30.4150
29.6737
29.6189
29.6051
29.5541
29.5245
29.4752
29.4619
29.4027
29.3214
29.2911
26.1788
26.1127
26.0742
26.0288
F
O
( )10
1"
2"
1'
2'
3'
4'
1
2
3
4
160
140
120
100
80
60
40
20
[ppm]
[rel]
12
10
8
6
4
2
0