

Columnar propeller-like 1,3,5-triphenylbenzenes: the missing link of shape-persistent hekates

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General information, experimental procedures and analytical data

The following instruments were used for characterization of the compounds. NMR: *Bruker* Avance 500 (^1H , 500 MHz; ^{13}C , 126 MHz), *Bruker* Avance 300 (^1H , 300 MHz; ^{13}C , 75 MHz) and *Bruker* Avance 250 (^1H , 250 MHz; ^{13}C , 63 MHz). ^1H and ^{13}C NMR spectra were referenced to TMS (Me_4Si $\delta_{\text{H}} = 0.0$ ppm, $\delta_{\text{C}} = 0.0$ ppm) as an internal standard. Unless otherwise stated, spectra were recorded at room temperature. Assignment of the resonances was supported by chemical shift calculations and 2D experiments (COSY and HMBC). Elemental analyses: Carlo Erba Strumentazione Elemental Analyzer, Modell 1106. MS (EI): *Varian* MAT 711 spectrometer. 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. Differential scanning calorimetry ($\alpha = 1.5418$ Å). (DSC): *Mettler-Toledo* DSC 822e (heating/cooling rates: 5 $\text{K}\cdot\text{min}^{-1}$). Melting points: *Büchi* SMP-20.

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). 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.

General Procedures

General procedure for the preparation of 4-Bromo-1,2-bisalkoxy benzenes (18) and 5-Bromo-1,2-bis-alkoxy-3-methoxybenzenes (10) (GP1)

4-Bromo-1,2-dihydroxybenzene **17** or 5-bromo-1,2-dihydroxy-3-methoxybenzene **19** (4.88 mmol) was dissolved in dimethylformamide (30 mL) and degassed by flushing nitrogen through the solution for 30 min. Potassium carbonate (4.00 g, 29.27 mmol) was added and the suspension was stirred for another 30 min at room temperature. After addition of the respective bromoalkane (10.74 mmol) the reaction mixture was stirred overnight at 80 °C. After completion the inorganic salts were removed via filtration and extracted with Et₂O (100 mL). The solvent was evaporated and the crude product was purified by flash chromatography or by recrystallization.

General procedure for the preparation of pinacolborolanes (8, 11, 12) (GP2)

To a solution of the appropriate bis- or trisalkoxybromo benzene **9**, **10**, **18** (4.225 mmol) in abs. THF (150 mL) at –78°C *n*-BuLi (4.50 mL, 7.2 mmol, 1.6 M in *n*-hexane) was added and the reaction mixture was stirred for 1 h. Then isopropyl pinacol borate (1.32 mL, 1.20 g, 6.34 mmol) was added and the reaction mixture was stirred for 1 h at –78°C. After warming to ambient temperature over 24 h, the reaction was terminated by addition of NH₄Cl (50 mL, saturated solution) and stirred for 1 h. The resulting aqueous suspension was extracted with Et₂O (3 × 50 mL). The combined organic layers were washed with H₂O (2 × 100 mL), brine (80 mL) and dried (MgSO₄). After removing the solvent *in vacuo* the crude product was purified by flash chromatography on silica gel using mixtures of hexanes and Et₂O as eluents.

General procedure for Suzuki coupling reactions (GP3)

The respective pinacol borolanes (0.35 mmol) and 1,3,5-tribromo benzene (0.03 g, 0.09 mmol) were dissolved in degassed dimethoxy ethane (15 mL). A mixture of degassed water (15 mL), potassium carbonate (0.99 g, 7.2 mmol) and Pd[P(Ph₃)₄] (10 mg, 0.87 μmol) was added and the reaction mixture was stirred at 80 °C over night. After addition of water (15 mL) the reaction solution was extracted with dichloromethane (2 × 25 mL). The combined organic phases were washed with water (2 × 25 mL) and brine (25 mL) and dried (MgSO₄). After removing the solvent *in vacuo* the crude product was purified by flash chromatography on silica gel using mixtures of hexanes and Et₂O as eluents.

General procedure for the formation of triphenylbenzenes **7** (GP4)

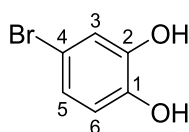
To a solution of **14** (0.3 g, 0.67 mmol) and K₂CO₃ (2.00 g, 15 mmol) in DMF (30 mL, degassed by flushing nitrogen through the solvent) the respective 1-bromoalkane (6.7 mmol)

was added and the suspension was stirred for 48 h at 80 °C. The reaction mixture was poured in water (200 mL), stirred for 30 min at room temperature and filtered. The precipitate was extracted with Et₂O (50 mL) and CH₂Cl₂ (50 mL) and the solvents were removed *in vacuo*. The crude product was purified by twofold flash chromatography on silica using petrol ether / ethyl acetate 60 : 1 and petrol ether / Et₂O 60 : 1 as eluent, respectively. The pure products were obtained as pale yellow solids.

Precursors

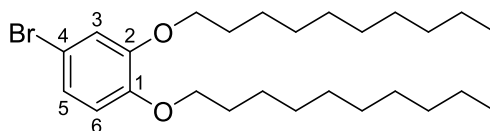
1,2-Hydroxy-4-bromo benzene (17)

5-Bromo-2-hydroxybenzaldehyde **16** (10.0 g, 50 mmol) was suspended in 3 M NaOH (20 mL, 52 mmol) and H₂O₂ (5.4 mL, 53 mmol, 30 % in H₂O) was added slowly under vigorous stirring. After cooling to ambient temperature the solution was neutralised with H₂SO₄ and extracted with Et₂O (6 × 75 mL). The combined organic phases were washed with water (2 × 100 mL) and dried (MgSO₄). After removing the solvent *in vacuo* the crude product was purified by flash chromatography on silica gel using a mixture of hexanes / ethyl acetate (3 : 1) as eluent giving the pure product as a grey solid (75 %, purity >95 %).



¹H-NMR (250 MHz, CDCl₃): δ = 5.91–6.34 (m, 2H, OH), 6.67–6.79 (m, 1H, 6-H), 6.85–6.96 (m, 1H, 5-H), 6.97–7.06 (m, 1H, 3-H) ppm; ¹³C-NMR (63 MHz, CDCl₃): δ = 112.5 (C-4), 116.7 (C-6), 118.6 (C-3), 123.9 (C-5), 142.8, 144.5 (C-1, C-2) ppm; spectroscopic data are in good agreement with those reported in ref.^[1]

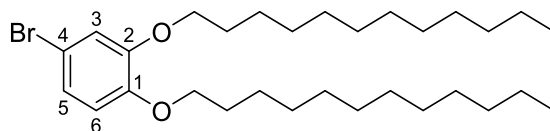
1,2-Bis(decyloxy)-4-bromo benzene (18a)



Synthesis according to GP1, purification by flash chromatography on silica gel using hexanes as eluent, colourless solid (60 %, purity >95 %), R_f = 0.3 (hexanes); ¹H-NMR (250 MHz, CDCl₃) δ = 0.79–0.96 (m, 6H, CH₂CH₃), 1.20–1.52 (m, 28H, CH₂), 1.72–1.88 (m, 4H, OCH₂CH₂), 3.90–4.01 (m, 4H, OCH₂), 6.70–6.76 (m, 1H, 6-H), 6.95–7.01 (m, 2H, 3-H, 5-H) ppm; ¹³C NMR (63 MHz, CDCl₃) δ = 14.1 (CH₃), 22.7 (CH₂CH₃), 26.0, 29.1, 29.2, 29.36, 29.4, 29.58, 29.62, 31.9 (CH₂), 69.4, 69.5 (OCH₂), 112.8 (C-4), 115.1, 116.9 (C-3, C-6),

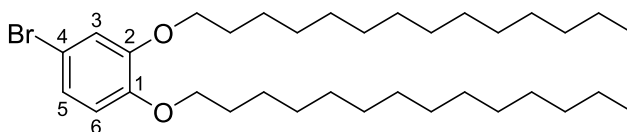
123.4 (C-5), 148.4, 150.0 (C-2,C-1) ppm; spectroscopic data are in good agreement with those reported in ref.^[2]

1,2-Bis(dodecyloxy)-4-bromo benzene (18b)



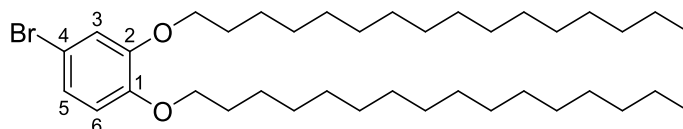
Synthesis according to GP1, purification by flash chromatography on silica gel using hexanes as eluent, colourless solid (74 %, purity >95 %), $R_f = 0.35$ (hexanes); $^1\text{H-NMR}$ (250 MHz, CDCl_3) $\delta = 0.83\text{--}0.93$ (m, 6H, CH_2CH_3), 1.18–1.53 (m, 36H, CH_2), 1.72–1.88 (m, 4H, OCH_2CH_2), 3.90–4.00 (m, 4H, OCH_2CH_2), 6.70–6.77 (m, 1H, 6-H), 6.94–7.01 (m, 2H, 3-H, 5-H) ppm; $^{13}\text{C-NMR}$ (63 MHz, CDCl_3): $\delta = 14.1$ (CH_3), 22.7 (CH_2CH_3), 26.0, 29.1, 29.2, 29.4, 29.6, 29.66, 29.70, 31.9 (CH_2), 69.4, 69.5 (OCH_2), 112.8 (C-4), 115.1, 116.9 (C-3, C-6), 123.4 (C-5), 148.3, 150.0 (C-2, C-1) ppm; spectroscopic data are in good agreement with those reported in ref.^[2]

1,2-Bis(tetradecyloxy)-4-bromo benzene (18c)



Synthesis according to GP1, purification by recrystallisation from ethanol at 5 °C, colourless solid (74 %, purity >95 %); $^1\text{H-NMR}$ (250 MHz, CDCl_3): $\delta = 0.83\text{--}0.93$ (m, 6H, CH_2CH_3), 1.15–1.54 (m, 44H, CH_2), 1.71–1.89 (m, 4H, OCH_2CH_2), 3.90–4.00 (m, 4H, OCH_2), 6.70–6.78 (m, 1H, 6-H), 6.94–7.00 (m, 2H, 3-H, 5-H) ppm; $^{13}\text{C-NMR}$ (63 MHz, CDCl_3): $\delta = 14.2$ (CH_3), 22.7(CH_2CH_3), 26.0, 29.2, 29.3, 29.4, 29.67, 29.72, 29.76, 32.0 (CH_2), 69.4, 69.6 (OCH_2), 112.9 (C-4), 115.2, 117.0 (C-3, C-6), 123.5 (C-5), 148.4, 150.0 (C-2, C-1) ppm; spectroscopic data are in good agreement with those reported in ref.^[2]

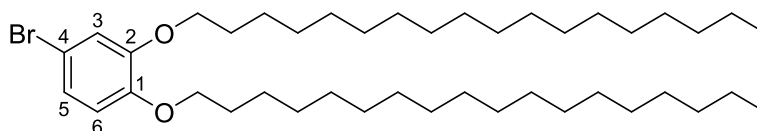
1,2-Bis(hexadecyloxy)-4-bromo benzene (18d)



Synthesis according to GP1, purification by recrystallisation from an 2-propanol / water mixture (7 : 1), slightly grey solid (50 %, purity >95 %); $^1\text{H-NMR}$ (250 MHz, CDCl_3): $\delta = 0.82\text{--}0.93$ (m, 6H, CH_2CH_3), 1.18–1.53 (m, 52H, CH_2), 1.72–1.88 (m, 4H, OCH_2CH_2),

3.90–4.00 (m, 4H, OCH₂), 6.70–6.76 (m, 1H, 6-H), 6.94–7.01 (m, 2H, 3-H, 5-H) ppm; ¹³C-NMR (63 MHz, CDCl₃): δ = 14.1 (CH₃), 22.7 (CH₂CH₃), 26.0, 29.1, 29.2, 29.4, 29.6, 29.68, 29.72, 31.9 (CH₂), 69.4, 69.5 (OCH₂), 112.8 (C-4), 115.1, 116.9 (C-3, C-6), 123.4 (C-5), 148.4, 150.0 (C-2, C-1) ppm; spectroscopic data are in good agreement with those reported in ref.^[3]

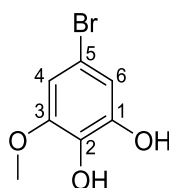
1,2-Bis(octadecyloxy)-4-bromo benzene (18e)



Synthesis according to GP1, purification by recrystallisation from an 2-propanol / water mixture (7 : 1), slightly grey solid (29 %, purity >95 %); ¹H-NMR (500 MHz, CDCl₃): δ = 0.85–0.91 (m, 6H, CH₂CH₃), 1.18–1.49 (m, 60H, CH₂), 1.74–1.84 (m, 4H, OCH₂CH₂), 3.93–3.98 (m, 4H, OCH₂), 6.72–6.75 (m, 1H, 6-H), 6.96–7.00 (m, 2H, 3-H, 5-H) ppm; ¹³C-NMR (125 MHz, CDCl₃): δ = 14.1 (CH₃), 22.7 (CH₂CH₃), 26.0, 29.1, 29.2, 29.38, 29.41, 29.6, 29.68, 29.72, 31.9 (CH₂) , 69.4, 69.6 (OCH₂), 112.8 (C-4), 115.2, 116.9 (C-3, C-6), 123.4 (C-5), 148.4, 150.0 (C-2, C-1) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2955 (w), 2914 (vs), 2847 (s), 1587 (w), 1505 (s), 1466 (s), 1391 (w), 1323 (w), 1254 (w), 1217 (s), 1131 (w), 1068 (w), 995 (w), 967 (w), 940 (w), 915 (w), 881 (w), 858 (w), 841 (w), 827 (w), 800 (w), 721 (w), 643 (w), 576 (w) cm⁻¹; MS (EI): *m/z*: 695 (100), 693 (93), 615 (5), 440 (3), 188 (21); HRMS (EI): *m/z*: calcd. for C₄₂H₇₇BrO₂: 694.5095 [M(⁸¹Br)]⁺, 692.5107 [M(⁷⁹Br)]⁺, found 694.5096 [M(⁸¹Br)]⁺, 692.5105 [M(⁷⁹Br)]⁺.

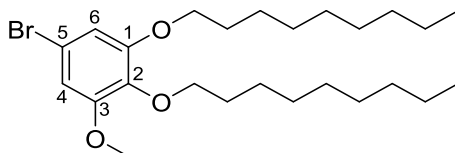
5-Bromo-1,2-dihydroxy-3-methoxy benzene (19)

5-Bromo-1,2,3-trimethoxybenzene **9** (5.00 g, 20.00 mmol), dissolved in CH₂Cl₂, was cooled to -78 °C and treated with BBr₃ (42 mL, 42 mmol, 1 M solution in heptane). The reaction mixture was stirred for 17 h at room temperature and subsequently ice was added to terminate the reaction. The solution was extracted with ethyl acetate and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography on silica gel using dichloromethane as eluent giving the pure product as a colourless solid (70 %, purity >95 %).



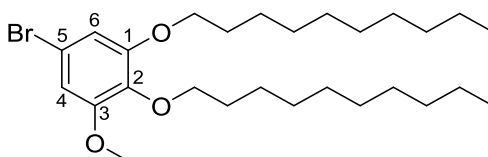
$^1\text{H-NMR}$ (300 MHz, DMSO): δ = 3.75 (s, 3H, OCH_3), 6.59 (m, 2H, 4-H, 6-H), 8.49 (s, 1H, $p\text{-OH}$), 9.34 (s, 1H, $m\text{-OH}$) ppm; $^{13}\text{C-NMR}$ (75 MHz, DMSO): δ = 56.1 (OCH_3), 106.6 (C-4), 109.2 (C-6), 111.8 (C-5), 133.7 (C-2), 146.9 (C-1), 149.3 (C-3) ppm; spectroscopic data are in good agreement with those reported in ref.^[4]

5-Bromo-1,2-bis(nonyloxy)-3-methoxy benzene (10a)



Synthesis according to GP1, purification by flash chromatography on silica gel using hexanes / dichloromethane 5 : 1 as eluent, colourless solid (74 %, purity >95 %), R_f = 0.6 (hexanes / ethyl acetate 20 : 1); $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = 0.84–0.93 (m, 6H, CH_3), 1.19–1.39 (m, 20H, CH_2), 1.40–1.51 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.66–1.84 (m, 4H, OCH_2CH_2), 3.81 (s, 3H, OCH_3), 3.86–3.99 (m, 4H, OCH_2), 6.60–6.76 (m, 2H, 4-H, 6-H) ppm; $^{13}\text{C-NMR}$ (126 MHz, CDCl_3): δ = 14.11, 14.12 (CH_3), 22.69, 22.70, 25.9, 26.1, 29.2, 29.30, 29.35, 29.38, 29.53, 29.59, 29.65, 30.2, 31.90, 31.93 (CH_2), 56.3 (OCH_3), 69.2, 73.5 (OCH_2), 108.9 (C-4), 110.1 (C-6), 115.7 (C-5), 137.0 (C-2), 153.7 (C-1), 154.2 (C-3) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2922 (s), 2853 (s), 1585 (s), 1493 (s), 1464 (w), 1447 (w), 1415 (w), 1381 (w), 1306 (w), 1224 (s), 1184 (w), 1119 (vs), 1000 (w), 910 (w), 848 (w), 809 (s), 723 (w), 650 (w), 578 (w), 540 (w) cm^{-1} ; MS (ESI): m/z : 493 $[\text{M} + \text{Na}]^+$; HRMS (ESI): m/z : calcd. for $\text{C}_{25}\text{H}_{43}\text{BrO}_3$: 495.2271 $[\text{M}(^{81}\text{Br}) + \text{Na}]^+$, 493.2288 $[\text{M}(^{79}\text{Br}) + \text{Na}]^+$, found: 495.2270 $[\text{M}(^{81}\text{Br}) + \text{Na}]^+$, 493.2283 $[\text{M}(^{79}\text{Br}) + \text{Na}]^+$.

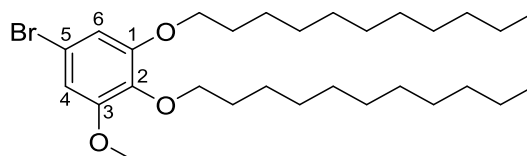
5-Bromo-1,2-bis(decoxy)-3-methoxy benzene (10b)



Synthesis according to GP1, purification by flash chromatography on silica gel using hexanes / dichloromethane 3 : 1 as eluent, colourless solid (87 %, purity >95 %), R_f = 0.7 (hexanes / ethyl acetate 20 : 1); $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = 0.83–0.93 (m, 6H, CH_3), 1.15–1.38 (m, 24H, CH_2), 1.39–1.51 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.65–1.87 (m, 4H, OCH_2CH_2), 3.81 (s, 3H, OCH_3), 3.87–3.98 (m, 4H, OCH_2), 6.64–6.74 (m, 2H, 4-H, 6-H) ppm; $^{13}\text{C-NMR}$ (126 MHz, CDCl_3): δ = 14.1 (CH_3), 22.69, 22.70, 25.9, 26.1, 29.2, 29.36, 29.38, 29.53, 29.59, 29.63, 29.64, 29.7, 30.2, 31.92, 31.93 (CH_2), 56.3 (OCH_3), 69.2, 73.5 (OCH_2), 108.9 (C-4),

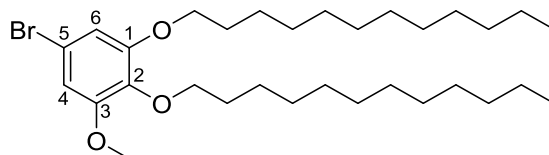
110.1 (C-6), 115.7 (C-5), 137.0 (C-2), 153.7 (C-1), 154.2 (C-3) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2921 (s), 2852 (s), 1585 (s), 1493 (s), 1465 (w), 1448 (w), 1415 (s), 1381 (w), 1305 (w), 1224 (s), 1183 (w), 1119 (vs), 1000 (w), 848 (w), 809 (s), 721 (w), 650 (w), 577 (w), 540 (w) cm^{-1} ; MS (ESI): m/z : 521 $[\text{M} + \text{Na}]^+$; HRMS (ESI): m/z : calcd. for $\text{C}_{27}\text{H}_{47}\text{BrO}_3$: 523.2584 $[\text{M}(^{81}\text{Br}) + \text{Na}]^+$, 521.2601 $[\text{M}(^{79}\text{Br}) + \text{Na}]^+$, found: 523.2593 $[\text{M}(^{81}\text{Br}) + \text{Na}]^+$, 521.2604 $[\text{M}(^{79}\text{Br}) + \text{Na}]^+$.

5-Bromo-1,2-bis(undecoxy)-3-methoxy benzene (10c)



Synthesis according to GP1, purification by flash chromatography on silica gel using hexanes / dichloromethane 3 : 1 as eluent, colourless solid (90 %, purity >95 %), R_f = 0.7 (hexanes / ethyl acetate 20 : 1); ^1H -NMR (500 MHz, CDCl_3): δ = 0.82–0.93 (m, 6H, CH_3), 1.19–1.39 (m, 28H, CH_2), 1.39–1.54 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.67–1.86 (m, 4H, OCH_2CH_2), 3.81 (s, 3H, OCH_3), 3.84–3.97 (m, 4H, OCH_2), 6.57–6.77 (m, 2H, 4-H, 6-H) ppm; ^{13}C -NMR (126 MHz, CDCl_3): δ = 14.1 (CH_3), 22.7, 26.0, 26.1, 29.2, 29.3, 29.4, 29.5, 29.64, 29.65, 29.69, 29.79, 31.93, 31.95 (CH_2), 56.3 (OCH_3), 69.2, 73.5 (OCH_2), 108.9 (C-4), 110.1 (C-6), 115.7 (C-5), 137.0 (C-2), 153.7 (C-1), 154.2 (C-3) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2921 (s), 2852 (s), 1730 (w), 1585 (s), 1493 (s), 1464 (s), 1448 (s), 1415 (s), 1381 (w), 1305 (w), 1224 (s), 1183 (w), 1120 (vs), 1001 (w), 848 (w), 809 (s), 721 (w), 650 (w), 577 (w), 540 (w) cm^{-1} ; MS (ESI): m/z : 549 $[\text{M} + \text{Na}]^+$; HRMS (ESI): m/z : calcd. for $\text{C}_{29}\text{H}_{51}\text{BrO}_3$: 551.2898 $[\text{M}(^{81}\text{Br}) + \text{Na}]^+$, 549.2914 $[\text{M}(^{79}\text{Br}) + \text{Na}]^+$, found: 551.2904 $[\text{M}(^{81}\text{Br}) + \text{Na}]^+$, 549.2920 $[\text{M}(^{79}\text{Br}) + \text{Na}]^+$.

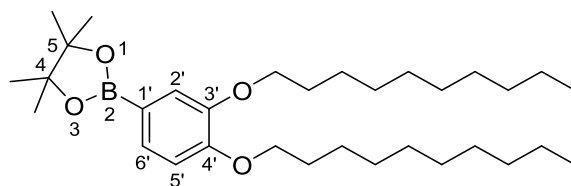
5-Bromo-1,2-bis(dodecoxy)-3-methoxy benzene (10d)



Synthesis according to GP1, purification by flash chromatography on silica gel using hexanes / dichloromethane 5 : 1 as eluent, colourless solid (82 %, purity >95 %), R_f = 0.8 (hexanes / ethyl acetate 20 : 1); $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = 0.88 (m, 6H, CH_3), 1.18–1.51 (m, 36H, CH_2), 1.65–1.87 (m, 4H, OCH_2CH_2), 3.81 (s, 3H, OCH_3), 3.86–3.98 (m, 4H, OCH_2CH_2), 6.58–6.76 (m, 2H, 4-H, 6-H) ppm; $^{13}\text{C-NMR}$ (126 MHz, CDCl_3): δ = 14.1 (CH_3), 22.7, 26.0, 26.1, 29.3, 29.4, 29.5, 29.63, 29.66, 29.70, 29.73, 30.2, 31.9 (CH_2), 56.32 (OCH_3), 69.23, 73.51 (OCH_2), 108.9 (C-4), 110.1 (C-6), 115.7 (C-5), 137.0 (C-2), 153.7 (C-1), 154.2 (C-3) ppm; FT-IR (ATR): $\tilde{\nu}$ = 2954 (w), 2913 (s), 2847 (s), 1585 (w), 1500 (s), 1489 (s), 1443 (w), 1416 (w), 1384 (w), 1305 (w), 1225 (s), 1201 (w), 1181 (w), 1120 (vs), 1060 (w), 1012 (w), 990 (w), 969 (w), 893 (w), 860 (w), 844 (w), 812 (s), 780 (w), 717 (w), 653 (w) cm^{-1} ; MS (EI): m/z : 556 (100) $[\text{M}]^+$, 476 (5) $[\text{M} + \text{H} - \text{Br}]^+$, 386 (28) $[\text{M} + \text{H} - \text{C}_{12}\text{H}_{25}]^+$, 17 (45); HRMS (EI): m/z : calcd. for $\text{C}_{31}\text{H}_{55}\text{BrO}_3$: 556.3319 $[\text{M}(^{81}\text{Br})]^+$, 554.3335 $[\text{M}(^{79}\text{Br})]^+$, found: 556.3321 $[\text{M}(^{81}\text{Br})]^+$, 554.3333 $[\text{M}(^{79}\text{Br})]^+$.

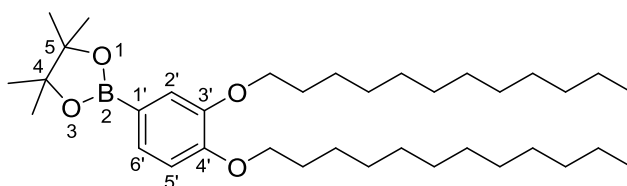
Pinacol borolanes

2-(3',4'-Bis(decyloxy)phenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (8a)



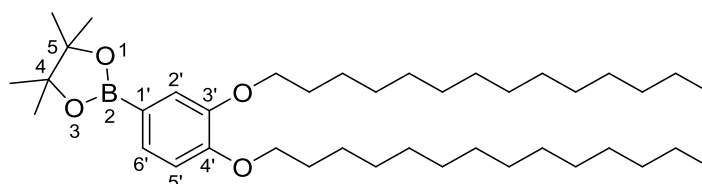
Synthesis according to GP2, purification by flash chromatography on silica gel using hexanes / Et_2O 30 : 1 as eluent, colourless oil (72 %, purity >95 %), R_f = 0.25 (hexanes / Et_2O 30 : 1); $^1\text{H-NMR}$ (250 MHz, CDCl_3): δ = 0.82–0.94 (m, 6H, CH_3), 1.18–1.55 (m, 40H, CH_2 , $\text{OC}(\text{CH}_3)_2$), 1.73–1.89 (m, 4H, OCH_2CH_2), 3.96–4.07 (m, 4H, OCH_2), 6.84–6.90 (m, 1H, 5'-H), 7.25–7.31 (m, 1H, 2'-H), 7.35–7.41 (m, 1H, 6'-H) ppm; $^{13}\text{C-NMR}$ (63 MHz, CDCl_3): δ = 14.1 (CH_3), 22.7 (CH_2CH_3), 24.9, 26.0, 26.1, 29.2, 29.37, 29.42, 29.5, 29.60, 29.63f, 29.7, 31.9 (CH_2 , $\text{OC}(\text{CH}_3)_2$), 68.9, 69.2 (OCH_2), 83.6 ($\text{OC}(\text{CH}_3)_2$), 112.6 (C-5'), 119.3 (C-2'), 128.6 (C-6'), 148.5 (C-3'), 151.9 (C-4') ppm; spectroscopic data are in good agreement with those reported in ref.^[2]

2-(3',4'-Bis(dodecyloxy)phenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (8b)



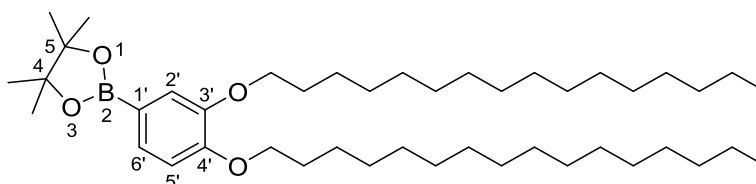
Synthesis according to GP2, purification by flash chromatography on silica gel using hexanes / Et₂O 30 : 1 as eluent, colourless oil (37 %, purity >95 %), R_f = 0.25 (hexanes / Et₂O 30 : 1); ¹H-NMR (250 MHz, CDCl₃): δ = 0.81–0.93 (m, 6H, CH₃), 1.14–1.53 (m, 48H, CH₂, OC(CH₃)₂), 1.73–1.88 (m, 4H, OCH₂CH₂), 3.96–4.06 (m, 4H, OCH₂), 6.83–6.90 (m, 1H, 5'-H), 7.24–7.31 (m, 1H, 2'-H), 7.34–7.41 (m, 1H, 6'-H) ppm; ¹³C-NMR (63 MHz, CDCl₃): δ = 14.1 (CH₃), 22.7 (CH₂CH₃), 24.9, 26.0, 26.1, 26.9, 29.2, 29.4, 29.5, 29.66, 29.71, 31.9 (CH₂, OC(CH₃)₂), 68.9, 69.2 (OCH₂), 83.6 (OC(CH₃)₂), 112.6 (C-5'), 119.3 (C-2'), 128.6 (C-6'), 148.5 (C-3'), 151.9 (C-4') ppm; spectroscopic data are in good agreement with those reported in ref.^[2]

2-(3',4'-Bis(tetradecyloxy)phenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (8c)



Synthesis according to GP2, purification by flash chromatography on silica gel using hexanes / Et₂O 30 : 1 as eluent, colourless oil (53 %, purity >95 %), R_f = 0.26 (hexanes / Et₂O 30 : 1); ¹H-NMR (250 MHz, CDCl₃): δ = 0.82–0.93 (m, 6H, CH₃), 1.17–1.53 (m, 56H, CH₂, OC(CH₃)₂), 1.74–1.89 (m, 4H, OCH₂CH₂), 3.97–4.06 (m, 4H, OCH₂), 6.84–6.89 (m, 1H, 5'-H), 7.24–7.30 (m, 1H, 2'-H), 7.35–7.41 (m, 1H, 6'-H) ppm; ¹³C-NMR (63 MHz, CDCl₃): δ = 14.1 (CH₃), 22.7 (CH₂CH₃), 24.9, 26.0, 26.1, 29.2, 29.4, 29.5, 29.68, 29.72, 31.9 (CH₂, OC(CH₃)₂), 68.9, 69.2 (OCH₂), 83.6 (OC(CH₃)₂), 112.6 (C-5'), 119.3 (C-2'), 128.6 (C-6'), 148.5 (C-3'), 151.9 (C-4') ppm; spectroscopic data are in good agreement with those reported in ref.^[2]

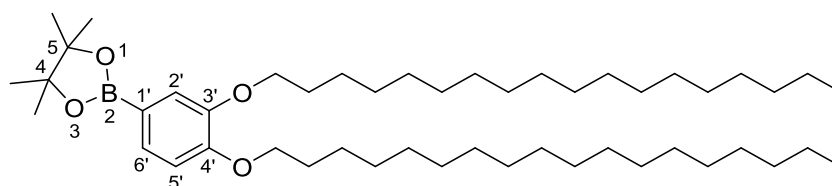
2-(3',4'-Bis(hexadecyloxy)phenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (8d)



Synthesis according to GP2, purification by flash chromatography on silica gel using hexanes / Et₂O 30 : 1 as eluent, colourless oil (37 %, purity >95 %), R_f = 0.28 (hexanes / Et₂O 30 : 1); ¹H-NMR (500 MHz, CDCl₃): δ = 0.84–0.90 (m, 6H, CH₃), 1.19–1.39 (m, 60H, CH₂, OC(CH₃)₂), 1.41–1.50 (m, 4H, OCH₂CH₂CH₂), 1.77–1.85 (m, 4H, OCH₂CH₂), 3.99–4.04 (m, 4H, OCH₂), 6.85–6.88 (m, 1H, 5'-H), 7.25–7.30 (m, 1H, 2'-H), 7.36–7.39 (m, 1H, 6'-H) ppm;

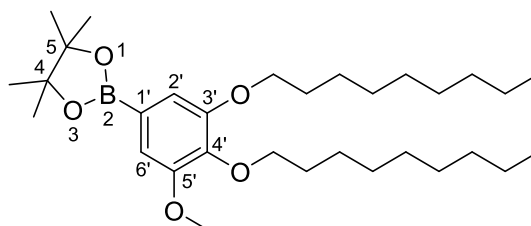
^{13}C -NMR (125 MHz, CDCl_3): δ = 14.1 (CH_3), 22.7 (CH_2CH_3), 24.9, 26.0, 26.1, 29.2, 29.38, 29.41, 29.43, 29.5, 29.6, 29.68, 29.73, 31.9 (CH_2 , $\text{OC}(\text{CH}_3)_2$), 68.9, 69.2 (OCH_2), 83.6 ($\text{OC}(\text{CH}_3)_2$), 112.7 (C-5'), 119.4 (C-2'), 128.6 (C-6'), 148.5 (C-3'), 151.9 (C-4') ppm; FT-IR (ATR): $\tilde{\nu}$ = 2920 (vs), 2851 (s), 1600 (w), 1518 (w), 1467 (w), 1418 (w), 1379 (w), 1353 (w), 1293 (w), 1258 (w), 1217 (w), 1138 (s), 1027 (w), 967 (w), 908 (w), 856 (w), 811 (w), 734 (w), 685 (w) cm^{-1} ; MS (ESI): m/z : 708 $[\text{M}+\text{Na}]^+$, 413, 335; HRMS (ESI): m/z : calcd. for $\text{C}_{44}\text{H}_{81}\text{BO}_4$: 707.6126 $[\text{M}+\text{Na}]^+$, found: 707.6115 $[\text{M}+\text{Na}]^+$.

2-(3',4'-Bis(octadecyl)phenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (8e)



Synthesis according to GP2, purification by flash chromatography on silica gel using hexanes / Et_2O 30 : 1 as eluent, colourless solid (66 %, purity >95 %), R_f = 0.28 (hexanes / Et_2O 30 : 1); ^1H -NMR (500 MHz, CDCl_3): δ = 0.84–0.91 (m, 6H, CH_3), 1.20–1.38 (m, 68H, CH_2 , $\text{OC}(\text{CH}_3)_2$), 1.41–1.50 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.76–1.85 (m, 4H, OCH_2CH_2), 3.99–4.04 (m, 4H, OCH_2), 6.85–6.88 (m, 1H, 5'-H), 7.25–7.29 (m, 1H, 2'-H), 7.36–7.39 (m, 1H, 6'-H) ppm; ^{13}C -NMR (125 MHz, CDCl_3): δ = 14.1 (CH_3), 22.7 (CH_2CH_3), 24.9, 26.0, 26.1, 29.2, 29.38, 29.41, 29.43, 29.5, 29.6, 29.67, 29.72, 31.9 (CH_2 , $\text{OC}(\text{CH}_3)_2$), 68.9, 69.2 (OCH_2), 83.6 ($\text{OC}(\text{CH}_3)_2$), 112.7 (C-5'), 119.4 (C-2'), 128.6 (C-6'), 148.5 (C-3'), 151.9 (C-4') ppm; FT-IR (ATR): $\tilde{\nu}$ = 2918 (vs), 2850 (s), 1600 (w), 1518 (w), 1467 (w), 1419 (w), 1379 (w), 1353 (s), 1294 (w), 1258 (w), 1217 (w), 1137 (s), 1094 (w), 1020 (w), 966 (w), 907 (s), 856 (w), 812 (w), 733 (s), 685 (w), 649 (w) cm^{-1} ; MS (ESI): m/z : 764 $[\text{M} + \text{Na}]^+$, 384; HRMS (ESI): m/z : calcd. for $\text{C}_{48}\text{H}_{89}\text{BO}_4$: 763.6754 $[\text{M} + \text{Na}]^+$, found: 763.6744 $[\text{M} + \text{Na}]^+$.

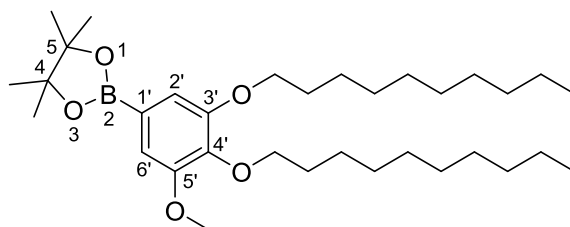
2-(3',4'-Bis(nonyloxy)-5'-methoxyphenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (11a)



Synthesis according to GP2, purification by flash chromatography on silica gel using hexanes / Et_2O 30 : 1 as eluent, colourless solid (45 %, purity >95 %), R_f = 0.3 (hexanes / ethyl acetate 20 : 1); ^1H -NMR (300 MHz, CDCl_3): δ = 0.84–92 (m, 6H, CH_3),

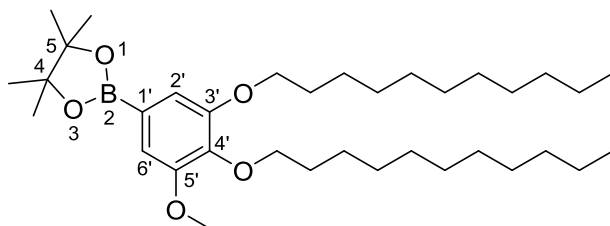
1.21–1.52 (m, 36H, CH_2 , $\text{OC}(\text{CH}_3)_2$), 1.69–1.87 (m, 4H, OCH_2CH_2), 3.87 (s, 3H, OCH_3), 3.95–4.05 (m, 4H, OCH_2), 6.91–7.9 (m, 2H, 2'-H, 6'-H) ppm; ^{13}C -NMR (75 MHz, CDCl_3): δ = 14.1 (CH_3), 22.7, 24.9, 26.0, 26.2, 29.32, 29.34, 29.45, 29.48, 29.56, 29.62, 29.66, 30.3, 31.9 (CH_2), 56.2 (OCH_3), 69.0 (*m*- OCH_2), 73.4 (*p*- OCH_2), 83.8 ($\text{OC}(\text{CH}_3)_2$), 111.3 (C-6'), 112.7 (C-2'), 140.6 (C-4'), 152.8 (C-3'), 153.3 (C-5') ppm; FT-IR (ATR): $\tilde{\nu}$ = 2923 (s), 2854 (w), 1574 (w), 1505 (w), 1465 (w), 1410 (s), 1364 (vs), 1319 (w), 1285 (w), 1221 (s), 1184 (w), 1144 (s), 1121 (s), 1004 (w), 968 (w), 912 (w), 854 (s), 713 (w), 695 (s) cm^{-1} ; MS (ESI): m/z : 541 [$\text{M} + \text{Na}$] $^+$, 519 [$\text{M} + \text{H}$] $^+$; HRMS-ESI: m/z : calcd for $\text{C}_{31}\text{H}_{55}\text{BO}_5$: 541.4040 [$\text{M} + \text{Na}$] $^+$, found: 541.4037 [$\text{M} + \text{Na}$] $^+$.

2-(3',4'-Bis(decoxy)-5'-methoxyphenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (11b)



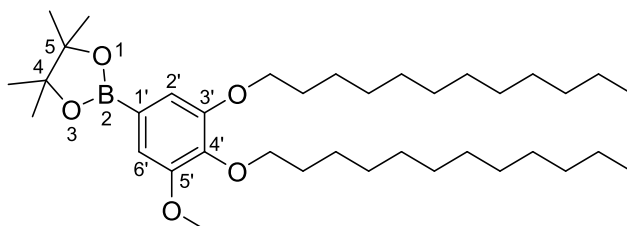
Synthesis according to GP2, purification by flash chromatography on silica gel using hexanes / Et_2O 30 : 1 as eluent, colourless solid (65 %, purity >95 %), R_f = 0.4 (hexanes / ethyl acetate 20 : 1); ^1H -NMR (300 MHz, CDCl_3): δ = 0.78–1.02 (m, 6H, CH_3), 1.15–1.59 (m, 40H, CH_2 , $\text{OC}(\text{CH}_3)_2$), 1.62–1.93 (m, 4H, OCH_2CH_2), 3.87 (s, 3H, OCH_3), 3.92–4.20 (m, 4H, OCH_2), 6.90–7.10 (m, 2H, 2'-H, 6'-H) ppm; ^{13}C -NMR (75 MHz, CDCl_3): δ = 14.1 (CH_3), 22.7, 24.9, 26.0, 26.2, 29.38, 29.45, 29.48, 29.56, 29.62, 29.65, 29.67, 29.71, 30.3, 31.9 (CH_2), 56.2 (OCH_3), 68.9 (*m*- OCH_2), 73.4 (*p*- OCH_2), 83.8 ($\text{OC}(\text{CH}_3)_2$), 111.2 (C-6'), 112.7 (C-2'), 140.6 (C-4'), 152.8 (C-3'), 153.3 (C-5') ppm; FT-IR (ATR): $\tilde{\nu}$ = 2922 (s), 2853 (s), 1574 (w), 1504 (w), 1465 (w), 1410 (s), 1363 (vs), 1318 (w), 1285 (w), 1223 (s), 1184 (w), 1144 (s), 1120 (s), 1004 (w), 967 (w), 854 (s), 713 (w), 695 (s) cm^{-1} ; MS (ESI): m/z : 1116 [$2 \times \text{M} + \text{Na}$] $^+$, 565, 548 [$\text{M} + \text{H}$] $^+$; HRMS-ESI: m/z : calcd for $\text{C}_{33}\text{H}_{59}\text{BO}_5$: 547.4534 [$\text{M} + \text{H}$] $^+$, found: 547.4571 [$\text{M} + \text{H}$] $^+$.

2-(3',4'-Bis(undecoxy)-5'-methoxyphenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (11c)



Synthesis according to GP2, purification by flash chromatography on silica gel using hexanes / Et₂O 30 : 1 as eluent, colourless solid (60 %, purity >95 %), R_f = 0.5 (hexanes / Et₂O 10 : 1); ¹H-NMR (500 MHz, CDCl₃): δ = 0.81–0.95 (m, 6H, CH₃), 1.20–1.39 (m, 40H, CH₂, OC(CH₃)₂), 1.39–1.52 (m, 4H, OCH₂CH₂CH₂), 1.67–1.88 (m, 4H, OCH₂CH₂), 3.87 (s, 3H, OCH₃), 3.95–4.06 (m, 4H, OCH₂), 6.97–7.05 (m, 2H, 2'-H, 6'-H) ppm; ¹³C-NMR (126 MHz, CDCl₃): δ = 14.12 (CH₃), 22.7, 24.9, 26.0, 26.2, 29.38, 29.45, 29.48, 29.58, 29.67, 29.68, 29.7, 30.2, 31.93, 31.94 (CH₂), 56.21 (OCH₃), 69.0, 73.4 (OCH₂), 83.8 (OC(CH₃)₂), 111.3 (C-6'), 112.7 (C-2'), 140.6 (C-4'), 152.8 (C-3'), 153.3 (C-5') ppm; FT-IR (ATR): $\tilde{\nu}$ = 2922 (s), 2853 (s), 1574 (w), 1504 (w), 1465 (w), 1410 (s), 1363 (vs), 1318 (w), 1285 (w), 1223 (s), 1184 (w), 1144 (s), 1120 (s), 1004 (w), 967 (w), 854 (s), 713 (w), 695 (s) cm⁻¹; MS (ESI): *m/z*: 598 [M + Na]⁺, 575 [M]⁺; HRMS-ESI: *m/z*: calcd. for C₃₅H₆₃BO₅: 575.4848 [M + H]⁺, found: 575.4836 [M + H]⁺.

2-(3',4'-Bis(dodecoxy)-5'-methoxyphenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (11d)

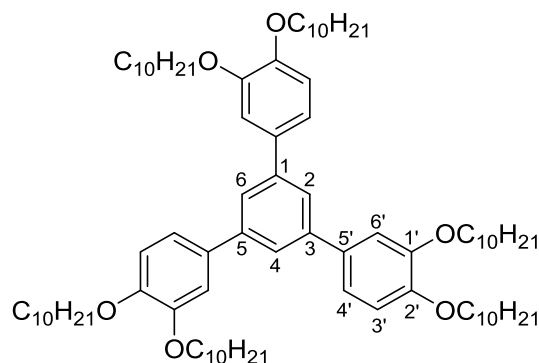


Synthesis according to GP2, purification by flash chromatography on silica gel using hexanes / Et₂O 30 : 1 as eluent, colourless solid (64 %, purity >95 %), R_f = 0.5 (hexanes / Et₂O 10 : 1); ¹H-NMR (500 MHz, CDCl₃): δ = 0.88 (t, 6H, CH₃), 1.16–1.54 (m, 48H, CH₂, OC(CH₃)₂), 1.67–1.86 (m, 4H, OCH₂CH₂), 3.87 (s, 3H, OCH₃), 3.92–4.07 (m, 4H, OCH₂), 6.98–7.02 (m, 2H, 2'-H, 6'-H) ppm; ¹³C-NMR (126 MHz, CDCl₃): δ = 14.1 (CH₃), 22.7, 24.9, 26.0, 26.2, 29.40, 29.45, 29.48, 29.6, 29.68, 29.70, 29.71, 29.73, 30.3, 31.9 (CH₂), 56.2 (OCH₃), 69.0, 73.4 (OCH₂), 83.8 (OC(CH₃)₂), 111.2 (C-6'), 112.7 (C-2'), 140.6 (C-4'), 152.8 (C-3'), 153.3 (C-5') ppm; FT-IR (ATR): $\tilde{\nu}$ = 2922 (s), 2853 (s), 1574 (w), 1465 (w),

1410 (w), 1363 (vs), 1318 (w), 1286 (w), 1224 (s), 1184 (w), 1144 (s), 1121 (s), 1005 (w), 967 (s), 914 (w), 854 (w), 713 (s), 695 (w), 579 (w) cm^{-1} ; MS (ESI): m/z : 626 $[\text{M} + \text{Na}]^+$, 604 $[\text{M} + \text{H}]^+$; HRMS-ESI: m/z : calcd. for $\text{C}_{37}\text{H}_{67}\text{BO}_5$, 625.4980 $[\text{M} + \text{Na}]^+$; found, 625.4984 $[\text{M} + \text{Na}]^+$.

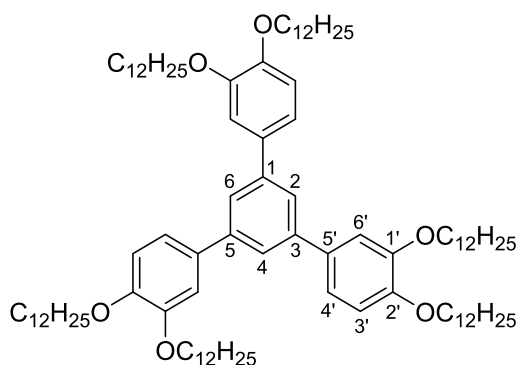
Triphenylbenzenes

1,3,5-Tri(1',2'-bis(decyloxy)phenyl) benzene (5b)



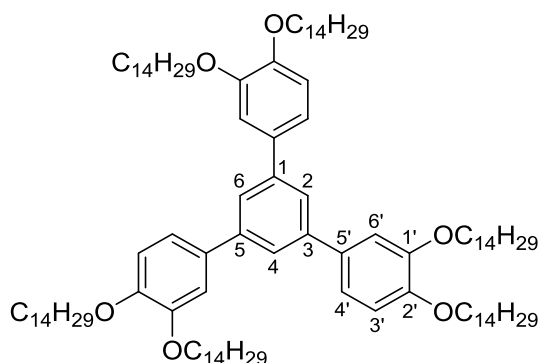
Synthesis according to GP3, purification by flash chromatography on silica gel using hexanes / Et_2O 30 : 1 as eluent, following recrystallisation from pentane at $-18\text{ }^\circ\text{C}$, colourless solid (75 %, purity >95 %), $R_f = 0.24$ (hexanes / Et_2O 30 : 1); ^1H -NMR (500 MHz, CDCl_3): $\delta = 0.84\text{--}0.91$ (m, 18H, CH_3), $1.19\text{--}1.42$ (m, 72H, CH_2), $1.44\text{--}1.53$ (m, 12H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), $1.80\text{--}1.88$ (m, 12H, OCH_2CH_2), $4.02\text{--}4.09$ (m, 12H, OCH_2), $6.96\text{--}7.00$ (m, 3H, 3'-H), $7.18\text{--}7.22$ (m, 6H, 6'-H, 4'-H), 7.62 (s, 3H, 2-H, 4-H, 6-H) ppm; ^{13}C -NMR (125 MHz, CDCl_3): $\delta = 14.1$ (CH_3), 22.69, 22.70 (CH_2CH_3), 26.1, 29.35, 29.37, 29.40, 29.46, 29.60, 29.66, 31.92, 31.92 (CH_2), 69.4, 69.6 (OCH_2), 113.4, 119.9 (C-6', C-4'), 114.1 (C-3'), 124.2 (C-2, C-4, C-6), 134.4 (C-5'), 142.2 (C-1, C-3, C-5), 149.0, 149.4 (C-1', C-2') ppm; FT-IR (ATR): $\tilde{\nu} = 2918$ (s), 2849 (s), 1607 (w), 1585 (w), 1522 (s), 1467 (s), 1455 (w), 1408 (w), 1391 (w), 1312 (w), 1252 (vs), 1216 (s), 1197 (w), 1146 (s), 1091 (w), 1072 (w), 1047 (w), 1022 (w), 987 (w), 937 (w), 875 (w), 835 (s), 791 (s), 755 (w), 722 (w), 670 (w), 623 (w), 605 (w) cm^{-1} ; MS (ESI): m/z : 1267 $[\text{M} + \text{Na}]^+$; Anal. calcd. for $\text{C}_{84}\text{H}_{138}\text{O}_6$ ($1244.02\text{ g mol}^{-1}$): C 81.10, H 11.18; found: C 80.97, H 11.26.

1,3,5-Ttri(1',2'-bis(dodecyloxy)phenyl) benzene (5c)



Synthesis according to GP3, purification by flash chromatography on silica gel using hexanes / Et₂O 30 : 1 as eluent, following recrystallisation from pentane at -18 °C, colourless solid (54 %, purity >95 %), *R_f* = 0.25 (hexanes / Et₂O 30 : 1); ¹H-NMR (500 MHz, CDCl₃): δ = 0.83–0.92 (m, 18H, CH₃), 1.18–1.42 (m, 96H, CH₂) 1.42–1.53 (m, 12H, OCH₂CH₂CH₂), 1.79–1.89 (m, 12H, OCH₂CH₂), 4.02–4.09 (m, 12H, OCH₂), 6.95–7.00 (m, 3H, 3'-H), 7.18–7.22 (m, 6H, 6'-H, 4'-H), 7.62 (s, 3H, 2-H, 4-H, 6-H) ppm; ¹³C-NMR (125 MHz, CDCl₃): δ = 14.1 (CH₃), 22.7 (CH₂CH₃), 26.1, 29.35, 29.38, 29.41, 29.46, 29.48, 29.67, 29.72, 31.9 (CH₂), 69.4, 69.6 (OCH₂), 113.5, 119.9 (C-6', C-4'), 114.1 (C-3'), 124.2 (C-2, C-4, C-6), 134.4 (C-5'), 142.2 (C-1, C-3, C-5), 149.0, 149.4 (C-1',C-2') ppm; FT-IR (ATR): $\tilde{\nu}$ = 2955 (s), 2919 (vs), 2850 (s), 1602 (w), 1579 (w), 1513 (s), 1468 (s) 1410 (w), 1381 (w)1310 (w), 1262 (s), 1245 (s), 1211 (w), 1189 (s), 1137 (w), 1095 (w), 1065 (w), 1030 (w),996 (w), 915 (w), 850 (w), 812 (w), 721 (w), 641 (w), 618 (w) cm⁻¹; MS (ESI): *m/z*: 1435.2 [M + Na]⁺; Anal. calcd. for C₉₆H₁₆₂O₆ (1412.35 g mol⁻¹): C 81.64, H 11.41; found: C 81.65, H 11.56.

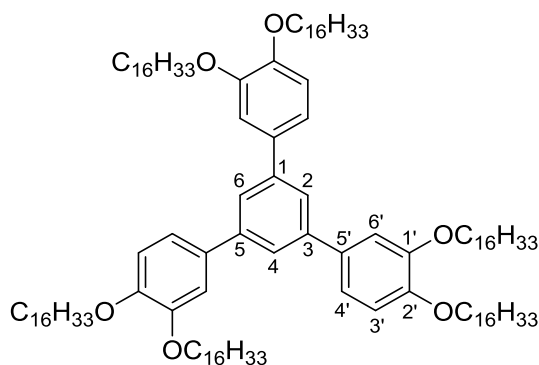
1,3,5-Tri(1',2'-bis(tetradecyloxy)phenyl) benzene (5d)



Synthesis according to GP3, purification by flash chromatography on silica gel using hexanes / Et₂O 30 : 1 as eluent, following recrystallisation from pentane at -18 °C, colourless solid (65 %, purity >95 %), *R_f* = 0.25 (hexanes / Et₂O 30 : 1); ¹H-NMR (500 MHz, CDCl₃): δ = 0.82–0.91 (m, 18H, CH₃), 1.19–1.40 (m, 120H, CH₂), 1.44–1.53 (m, 12H,

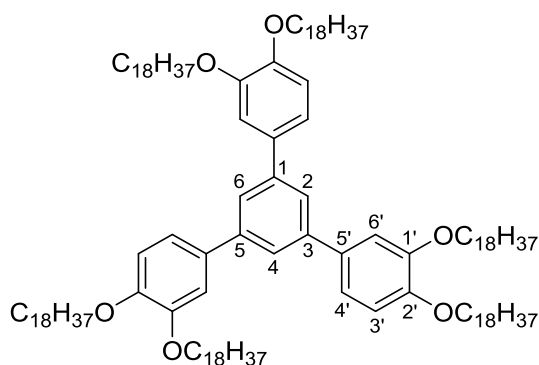
OCH₂CH₂CH₂), 1.80–1.89 (m, 12H, OCH₂CH₂), 4.02–4.09 (m, 12H, OCH₂), 6.96–7.00 (m, 3H, 3'-H), 7.17–7.22 (m, 6H, 6'-H, 4'-H), 7.62 (s, 3H, 2-H, 3-H, 4-H) ppm; ¹³C-NMR (125 MHz, CDCl₃): δ = 14.1 (CH₃), 22.7 (CH₂CH₃), 26.1, 29.35, 29.38, 29.41, 29.47, 29.48, 29.67, 29.68, 29.73, 31.9 (CH₂), 69.4, 69.6 (OCH₂), 113.4, 119.8 (C-6', C-4'), 114.1 (C-3'), 124.2 (C-2, C-4, C-6), 134.4 (C-5'), 142.2 (C-1, C-3, C-5), 149.0, 149.4 (C-1', C-2') ppm; FT-IR (ATR): $\tilde{\nu}$ = 2956 (w), 2917 (vs), 2849 (s), 1602 (w), 1578 (w), 1511 (s), 1467 (s), 1409 (w), 1389 (w), 1310 (w), 1262 (s), 1243 (s), 1210 (w), 1188 (w), 1136 (s), 1095 (w), 1052 (w), 1036 (w), 1006 (w), 979 (w), 936 (w), 891 (w), 850 (w), 811 (w), 760 (w), 721 (w), 640 (w), 618 (w), 606 (w); MS (ESI): *m/z*: 1603.4 [M + Na]⁺; Anal. calcd. for C₁₀₈H₁₈₆O₆ (1580.67 g·mol⁻¹): C 82.07, H 11.59; found: C 81.93, H 11.59.

1,3,5-Tri(1',2'-bis(hexadecyloxy)phenyl) benzene (5e)



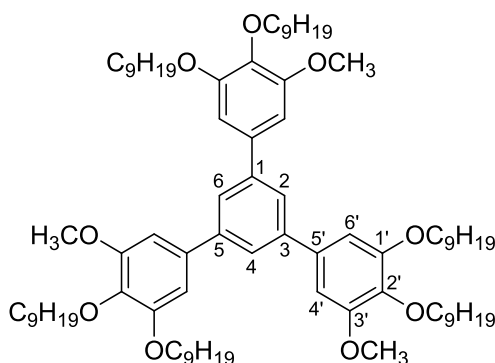
Synthesis according to GP3, purification by flash chromatography on silica gel using hexanes / Et₂O 30 : 1 as eluent, following recrystallisation from pentane at -18 °C, colourless solid (33 %, purity >95 %), R_f = 0.26 (hexanes / Et₂O 30 : 1); ¹H-NMR (500 MHz, CDCl₃): δ = 0.84–0.91 (m, 18H, CH₃), 1.18–1.41 (m, 144H, CH₂), 1.43–1.53 (m, 12H, OCH₂CH₂CH₂), 1.80–1.89 (m, 12H, OCH₂CH₂), 4.02–4.09 (m, 12H, OCH₂), 6.96–7.00 (m, 3H, 3'-H), 7.18–7.22 (m, 6H, 2'-H, 4'-H), 7.62 (s, 3H, 2-H, 4-H, 6-H) ppm; ¹³C-NMR (125 MHz, CDCl₃): δ = 14.1 (CH₃), 22.7 (CH₂CH₃), 26.1, 29.38, 29.41, 29.48, 29.49, 29.68, 29.73, 31.9 (CH₂), 69.4, 69.6 (OCH₂), 113.4, 119.9 (C-6', C-4'), 114.1 (C-3'), 124.2 (C-2, C-4, C-6), 134.4 (C-5'), 142.2 (C-1, C-3, C-5), 149.0, 149.4 (C-1', C-2') ppm; FT-IR (ATR): $\tilde{\nu}$ = 2955 (s), 2919 (vs), 2850 (s), 1602 (w), 1579 (w), 1513 (s), 1568 (s), 1410 (w), 1381 (w), 1310 (w), 1262 (s), 1245 (s), 1211 (w), 1189 (s), 1137 (w), 1063 (w), 1015 (w), 995 (w), 850 (w), 813 (w), 721 (w) cm⁻¹; MS (MALDI-TOF): *m/z*: calcd. for C₁₂₀H₂₁₀O₆: 1747.61, found 1748.50; Anal. calcd. for C₁₂₀H₂₁₀O₆ (1789.99 g·mol⁻¹): C 82.41, H 12.10; found: C 82.34, H 11.96.

1,3,5-Tri(1',2'-bis(octadecyloxy)phenyl) benzene (5f)



Synthesis according to GP3, purification by flash chromatography on silica gel using hexanes / Et₂O 30 : 1 as eluent, following recrystallisation from pentane at -18 °C, colourless solid (7 %, purity >95 %), R_f = 0.28 (hexanes / Et₂O 30 : 1); ¹H-NMR (500 MHz, CDCl₃): δ = 0.84–0.91 (m, 18H, CH₃), 1.09–1.41 (m, 168H, CH₂), 1.43–1.53 (m, 12H, OCH₂CH₂CH₂), 1.79–1.89 (m, 12H, OCH₂CH₂), 4.02–4.09 (m, 12H, OCH₂), 6.96–7.00 (m, 3H, 3'-H), 7.18–7.22 (m, 6H, 6'-H, 4'-H), 7.62 (s, 3H, 2-H, 4-H, 6-H) ppm; ¹³C-NMR (125 MHz, CDCl₃): δ = 14.1 (CH₃), 22.7 (CH₂CH₃), 26.1, 29.38, 29.41, 29.48, 29.49, 29.68, 29.73, 31.9 (CH₂), 69.4, 69.6 (OCH₂), 113.4, 119.9 (C-6', C-4'), 114.1 (C-3'), 124.2 (C-2, C-4, C-6), 134.4 (C-5'), 142.2 (C-1, C-3, C-5), 149.0, 149.4 (C-1', C-2') ppm; FT-IR (ATR): $\tilde{\nu}$ = 2954 (w), 2917 (vs), 2850 (s), 1602 (w), 1578 (w), 1510 (w), 1468 (w), 1380 (w), 1264 (w), 1243 (w), 1186 (w), 1139 (w), 1020 (w), 849 (w), 809 (w) cm⁻¹; MS (MALDI-TOF): m/z : calcd. for C₁₃₂H₂₃₄O₆: 1915.80, found 1916.17; Anal. calcd. for C₁₃₂H₂₃₄O₆ (1917.32 g mol⁻¹): C 82.69, H 12.30; found: C 82.73, H 12.15.

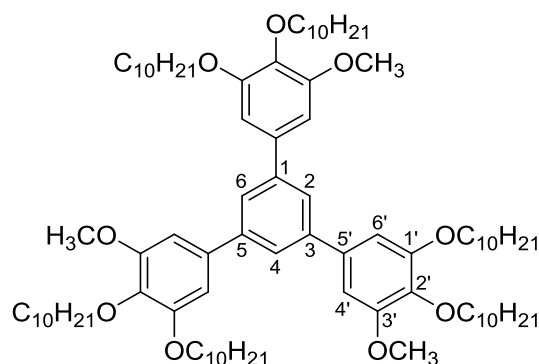
1,3,5-Tri(1',2'-bis(nonyloxy)-3'-methoxyphenyl) benzene (6a)



Synthesis according to GP3, purification by flash chromatography on silica gel using hexanes / ethyl acetate 30 : 1 as eluent, colourless solid (44 %, purity >95 %), R_f = 0.25 (hexanes / ethyl acetate 30 : 1); ¹H-NMR (500 MHz, CDCl₃): δ = 0.84–0.92 (m, 18H, CH₃), 1.17–1.40 (m, 60H, CH₂), 1.44–1.53 (m, 12H, OCH₂CH₂CH₂), 1.75–1.87 (m, 12H,

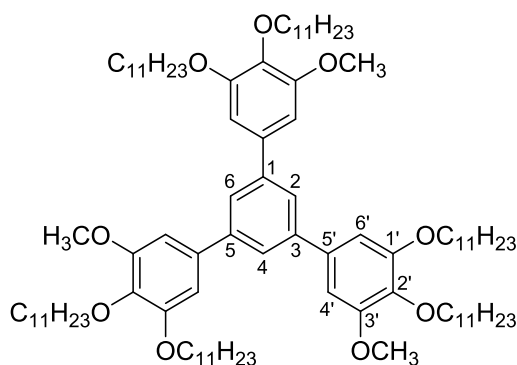
OCH₂CH₂), 3.90 (s, 9H, OCH₃), 3.99–4.07 (m, 12H, OCH₂), 6.80–6.85 (m, 6H, 6'-H, 4'-H), 7.63 (s, 3H, 2-H, 4-H, 6-H) ppm; ¹³C-NMR (125 MHz, CDCl₃): δ = 14.10, 14.13 (CH₃), 22.68, 22.70 (CH₂CH₃), 26.05, 26.14, 29.3, 29.36, 29.44, 29.46, 29.58, 29.60, 29.7, 30.29, 31.90, 31.94 (CH₂), 56.4 (OCH₃), 69.3, 73.7 (OCH₂), 104.8, 106.2 (C-6', C-4'), 125.1 (C-2, C-4, C-6), 136.7 (C-5'), 137.7 (C-2'), 142.7 (C-1, C-3, C-5), 153.4 (C-1'), 153.9 (C-3') ppm; FT-IR (ATR): $\tilde{\nu}$ = 2921(s), 2853 (s), 1576 (s), 1501 (w), 1464 (w), 1415 (w), 1399 (w), 1380 (w), 1331 (s), 1233 (s), 1175 (vs), 1120 (vs), 1030 (w), 909 (w), 832 (s), 803 (w), 714 (w), 692 (w) cm⁻¹; MS (MALDI-TOF): *m/z*: calcd. for C₈₁H₁₃₂O₉: 1248.99, found 1248.87; Anal. calcd. for C₈₁H₁₃₂O₉ (1249.94 g mol⁻¹): C 77.84, H 10.65; found: C 77.73, H 10.60.

1,3,5-Tri (1',2'-bis(decyloxy)-3'-methoxyphenyl) benzene (6b)



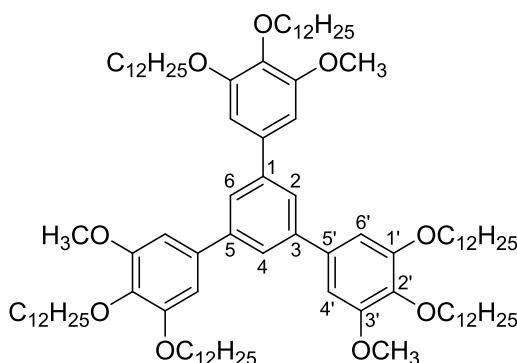
Synthesis according to GP3, purification by flash chromatography on silica gel using hexanes / Et₂O 30 : 1 as eluent, colourless solid (51 %, purity >95 %), R_f = 0.25 (hexanes / Et₂O 30 : 1); ¹H-NMR (500 MHz, CDCl₃): δ = 0.79–0.92 (m, 18H, CH₃), 1.18–1.41 (m, 72H, CH₂), 1.44–1.52 (m, 12H, OCH₂CH₂CH₂), 1.75–1.87 (m, 12H, OCH₂CH₂), 3.90 (s, 9H, OCH₃), 3.99–4.07 (m, 12H, OCH₂), 6.81–6.85 (m, 6H, 6'-H, 4'-H), 7.63 (s, 3H, 2-H, 4-H, 6-H) ppm; ¹³C-NMR (125 MHz, CDCl₃): δ = 14.11, 14.13 (CH₃), 22.68, 22.71 (CH₂CH₃), 26.05, 26.2, 29.35, 29.39, 29.44, 29.46, 29.58, 29.60, 29.66, 22.73, 30.29, 31.91, 31.94 (CH₂), 56.4 (OCH₃), 69.3, 73.7 (OCH₂), 104.8, 106.2 (C-6', C-4'), 125.1 (C-2, C-4, C-6), 136.7 (C-5'), 137.7 (C-2'), 142.7 (C-1, C-3, C-5), 153.4 (C-1'), 153.9 (C-3') ppm; FT-IR (ATR): $\tilde{\nu}$ = 2954 (s), 2921(s), 2853 (s), 1576 (s), 1502 (s), 1465 (w), 1415 (w), 1400 (w), 1380 (w), 1332 (s), 1234 (w), 1175 (vs), 1100 (w), 1044 (w), 1008 (w), 889 (w), 833 (w), 714 (w), 693 (w) cm⁻¹; MS (MALDI-TOF): *m/z*: calcd. for C₈₇H₁₄₄O₉: 1333.08, found: 1332.45; Anal. calcd. for C₈₇H₁₄₄O₉ (1334.10 g mol⁻¹): C 78.33, H 10.88; found: C 78.57, H 10.86.

1,3,5-Tri (1',2'-bis(undecyloxy)-3'-methoxyphenyl) benzene(6c)



Synthesis according to GP3, purification by flash chromatography on silica gel using hexanes / Et₂O 30 : 1 as eluent, colourless solid (67 %, purity >95 %), R_f = 0.27 (hexanes / Et₂O 30 : 1); ¹H-NMR (500 MHz, CDCl₃): δ = 0.83–0.92 (m, 18H, CH₃), 1.19–1.40 (m, 84H, CH₂), 1.43–1.52 (m, 12H, OCH₂CH₂CH₂), 1.75–1.87 (m, 12H, OCH₂CH₂), 3.90 (s, 9H, OCH₃), 3.97–4.07 (m, 12H, OCH₂), 6.81–6.86 (m, 6H, 6'-H, 4'-H), 7.63 (s, 3H, 2-H, 4-H, 6-H) ppm; ¹³C-NMR (125 MHz, CDCl₃): δ = 14.12, 14.13 (CH₃), 22.69, 22.71 (CH₂CH₃), 26.1, 26.2, 29.36, 29.39, 29.5, 29.6, 29.66, 29.69, 29.71, 29.73, 30.3, 31.9, 32.0 (CH₂), 56.4 (OCH₃), 69.3, 73.7 (OCH₂), 104.8, 106.2 (C-6', C-4'), 125.1 (C-2, C-4, C-6), 136.7 (C-5'), 137.7 (C-2'), 142.7 (C-1, C-3, C-5), 153.4 (C-1'), 153.9 (C-3') ppm; FT-IR (ATR): $\tilde{\nu}$ = 2922(vs), 2853 (s), 1577 (s), 1502 (s), 1466 (w), 1415 (w), 1400 (w), 1381 (w), 1332 (s), 1235 (s), 1175 (w), 1124 (s), 1007 (w), 956 (w), 891 (w), 833 (w), 714 (w), 693 (w) cm⁻¹; MS (MALDI-TOF): m/z : calcd. for C₉₃H₁₅₆O₉: 1417.17, found: 1417.86; Anal. calcd. for C₉₃H₁₅₆O₉ (1418.26 g mol⁻¹): C 78.76, H 11.09; found: C 78.69, H 10.98.

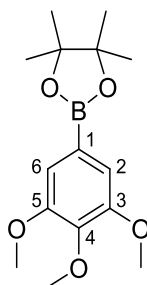
1,3,5-Tri (1',2'-bis(dodecyloxy)-3'-methoxyphenyl) benzene (6d)



Synthesis according to GP3, purification by flash chromatography on silica gel using hexanes / Et₂O 30 : 1 as eluent, colourless solid (70 %, purity >95 %), R_f = 0.29 (hexanes / Et₂O 30 : 1); ¹H-NMR (500 MHz, CDCl₃): δ = 0.82–0.92 (m, 18H, CH₃), 1.18–1.40 (m, 96H, CH₂), 1.43–1.52 (m, 12H, OCH₂CH₂CH₂), 1.75–1.87 (m, 12H, OCH₂CH₂), 3.90

(s, 9H, OCH_3), 3.98–4.07 (m, 12H, OCH_2), 6.80–6.85 (m, 6H, 6'-H, 4'-H), 7.63 (s, 3H, 2-H, 4-H, 6-H) ppm; ^{13}C -NMR (125 MHz, CDCl_3): δ = 14.1 (CH_3), 22.7 (CH_2CH_3), 26.1, 26.2, 29.37, 29.39, 29.5, 29.6, 29.66, 29.69, 29.71, 29.74, 30.3, 31.93, 31.94 (CH_2), 56.4 (OCH_3), 69.3, 73.7 (OCH_2), 104.8, 106.1 (C-6', C-4'), 125.1 (C-2, C-4, C-6), 136.7 (C-5'), 137.7 (C-2'), 142.7 (C-1, C-3, C-5), 153.4 (C-1'), 153.9 (C-3') ppm; FT-IR (ATR): $\tilde{\nu}$ = 2920 (s), 2852 (s), 1575 (s), 1501 (s), 1466 (s), 1415 (w), 1399 (w), 1380 (w), 1331 (s), 1176 (w), 1122 (vs), 1099 (s), 1007 (w), 960 (w), 905 (w), 833 (w), 714 (w), 693 (w) cm^{-1} ; MS (MALDI-TOF): m/z : calcd. for $\text{C}_{99}\text{H}_{168}\text{O}_9$: 1501.27, found: 1500.74; Anal. calcd. for $\text{C}_{99}\text{H}_{168}\text{O}_9$ (1502.42 g mol^{-1}): C 79.14, H 11.27; found: C 79.42, H 11.16.

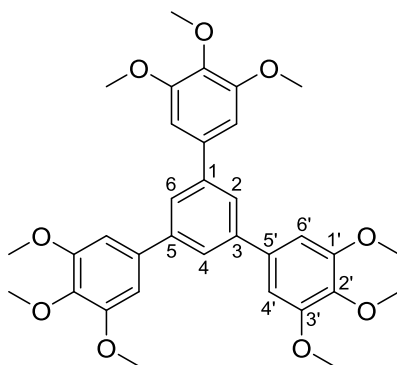
2-(3',4',5'-Bis(methoxy)phenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (12)



Synthesis according to GP2, purification by flash chromatography on silica gel using hexanes / Et_2O 3 : 1 as eluent, colourless solid (85 %, purity >95 %), R_f = 0.3 (hexanes / ethyl acetate 10 : 1); ^1H -NMR (300 MHz, CDCl_3): δ = 1.35 (s, 12H, $\text{OC}(\text{CH}_3)_2$), 3.87 (s, 3H, $p\text{-OCH}_3$), 3.91 (s, 6H, $m\text{-OCH}_3$), 7.04 (s, 2H, 2-H, 6-H) ppm; ^{13}C -NMR (75 MHz, CDCl_3) δ = 24.9 $\text{OC}(\text{CH}_3)_2$, 56.2 ($m\text{-OCH}_3$), 60.8 ($p\text{-OCH}_3$), 83.9 ($\text{OC}(\text{CH}_3)_2$), 111.2 (C-2, C-6), 140.8 (C-4), 152.9 (C-3, C-5) ppm. Spectroscopic data are in good agreement with those reported in ref.^[5]

1,3,5-Tri-(5'-1',2',3'-tris(methoxy)phenyl) benzene (13)

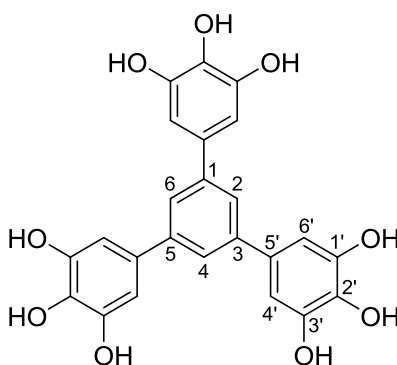
A solution of 1,3,5-tribromobenzene (120 mg, 0.38 mmol), **12** (400 mg, 1.44 mmol), K_2CO_3 (250 mg, 1.70 mmol) and $\text{Pd}[\text{P}(\text{Ph})_3]_4$ in a DMF (5 mL) and water (1.5 mL) was stirred for one hour at 90 °C under microwave irradiation. The reaction mixture was poured into water (100 mL) and stirred for another 15 min at room temperature. The resulting precipitate was filtered and purified by flash chromatography on silica gel using hexanes / ethyl acetate 3 : 1 as eluent. The pure product was obtained as a colourless solid (85 %, purity >95 %).



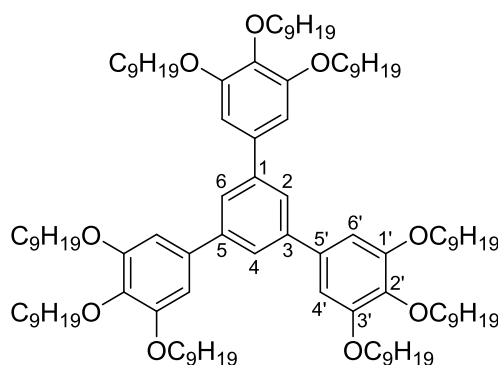
$^1\text{H-NMR}$ (300 MHz, CDCl_3): δ = 3.86–4.00 (m, 27H, CH_3), 6.85 (s, 6H, 4'-H, 6'-H), 7.66 (s, 3H, 2-H, 4-H, 6-H) ppm; $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ = 56.3 (*m*- OCH_3), 61.0 (*p*- OCH_3), 104.7 (C-4', C-6'), 125.3 (C-2, C-4, C-6), 137.1 (C-5'), 137.9 (C-1, C-3, C-5), 142.7 (C-2'), 153.6 (C-1', C-3') ppm; FT-IR (ATR): $\tilde{\nu}$ = 3000 (w), 2934 (w), 2829 (w), 1577 (s), 1502 (s), 1459 (w), 1427 (w), 1409 (s), 1394 (s), 1330 (s), 1233 (s), 1167 (w), 1125 (vs), 1028 (w), 1001 (s), 961 (w), 925 (w), 909 (w), 834 (s) 785 (w), 726 (w), 714 (w), 689 (w), 674 (w), 647 (w), 528 (w); MS (ESI): m/z : 577 $[\text{M} + \text{H}]^+$; HRMS-ESI: m/z : calcd. for $\text{C}_{33}\text{H}_{36}\text{O}_9$: 577.2432 $[\text{M} + \text{H}]^+$, found: 577.2415 $[\text{M} + \text{H}]^+$. Spectroscopic data are in good agreement with those reported in ref.^[6]

1,3,5-Tri-(5'-1',2',3'-trishydroxyphenyl) benzene (13)

12 (120 mg, 0.21 mmol) was dissolved in abs. CH_2Cl_2 (1 mL), cooled to $-78\text{ }^\circ\text{C}$ and treated with BBr_3 (2.1 mL, 2.06 mmol, 1M in CH_2Cl_2). The reaction mixture was stirred for 96 h at room temperature and subsequently quenched with ice. The resulting precipitate was filtered and, due to the sensibility towards oxidation, used directly for the next step.

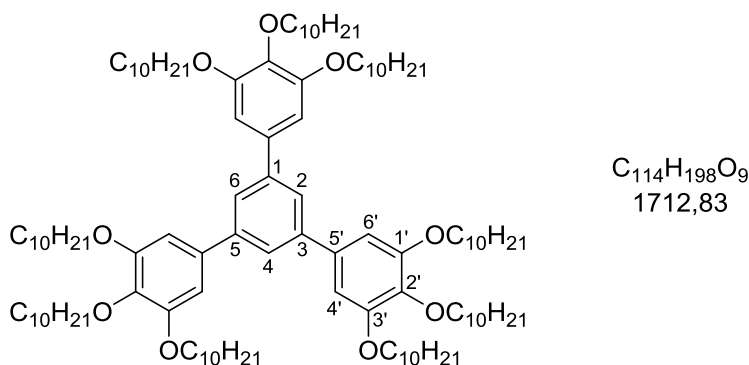


1,3,5-Tri-(5'-1',2',3'-tris(nonyloxy)phenyl) benzene (7a)



Synthesis according to GP4, pale yellow solid (20 %, purity >95 %); $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = 0.83–0.92 (m, 27H, CH_3), 1.19–1.39 (m, 90H, CH_2), 1.43–1.54 (m, 18H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.69–1.91 (m, 18H, OCH_2CH_2), 3.87–4.17 (m, 18H, OCH_2), 6.82 (s, 6H, 4'-H, 6'-H), 7.61 (s, 3H, 2-H, 4-H, 6-H) ppm; $^{13}\text{C-NMR}$ (126 MHz, CDCl_3) δ = 14.11, 14.13 (CH_3), 22.68, 22.72, 26.12, 26.17, 29.3, 29.40, 29.44, 29.48, 29.61, 29.65, 29.72, 30.4, 31.9, 32.0 (CH_2), 69.4 (*m*- OCH_2), 73.6 (*p*- OCH_2), 106.2 (C-4', C-6'), 125.0 (C-2, C-4, C-6), 136.6 (C-5'), 138.1 (C-1, C-3, C-5), 142.6 (C-2'), 153.5 (C-1', C-3') ppm; FT-IR (ATR): $\tilde{\nu}$ = 2921 (s), 2853 (s), 1738 (w), 1575 (w), 1501 (w), 1466 (w), 1417 (w), 1404 (w), 1380 (w), 1332 (s), 1233 (s), 1178 (w), 1112 (vs), 905 (w), 833 (w), 713 (w), 698 (w), 579 (w) cm^{-1} ; MS (MALDI-TOF): *m/z*: calcd. for $\text{C}_{105}\text{H}_{180}\text{O}_9$: 1585.36; found, 1585.24; Anal. calcd. for $\text{C}_{105}\text{H}_{180}\text{O}_9$ (1586.59 g mol^{-1}): C 79.49, H 11.44; found: C 79.41, H 11.41.

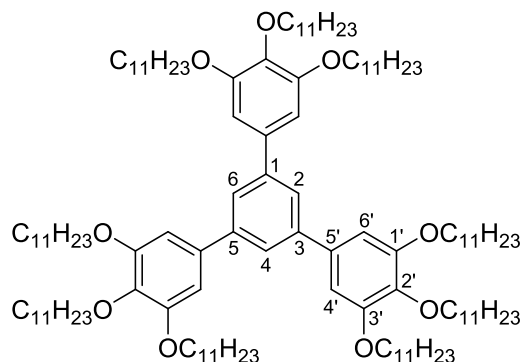
1,3,5-Tri-(5'-1',2',3'-tris(decoxy)phenyl) benzene (7b)



Synthesis according to GP4, pale yellow solid (18 %, purity >95 %); $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = 0.83–0.92 (m, 27H, CH_3), 1.19–1.41 (m, 108H, CH_2), 1.43–1.55 (m, 18H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.73–1.88 (m, 18H, OCH_2CH_2), 3.92–4.12 (m, 18H, OCH_2), 6.82 (s, 6H, 4'-H, 6'-H), 7.61 (s, 3H, 2-H, 4-H, 6-H) ppm; $^{13}\text{C-NMR}$ (126 MHz, CDCl_3) δ = 14.11, 14.13 (CH_3), 22.69, 22.72, 26.13, 26.18, 29.36, 29.42, 29.44, 29.48, 29.60, 29.66, 29.71, 29.78, 30.4, 31.92, 31.96, 32.0 (CH_2), 69.4 (*m*- OCH_2), 73.7 (*p*- OCH_2), 106.2 (C-4', C-

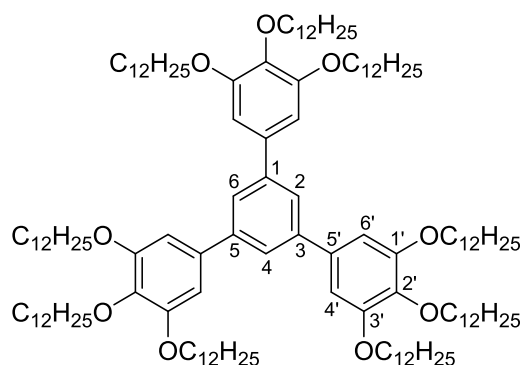
6'), 125.0 (C-2, C-4, C-6), 136.6 (C-5'), 138.1 (C-1, C-3, C-5), 142.6 (C-2'), 153.5 (C-1', C-3') ppm; FT-IR (ATR): $\tilde{\nu}$ = 2920 (s), 2852 (s), 1738 (w), 1575 (w), 1501 (w), 1466 (s), 1418 (w), 1405 (w), 1379 (w), 1332 (s), 1232 (s), 1180 (w), 1113 (vs), 1010 (w), 888 (w) 833 (s), 720 (w), 714 (w), 698 (w), 652 (w), 578 (w) cm^{-1} ; MS (MALDI-TOF): m/z : calcd. for $\text{C}_{105}\text{H}_{180}\text{O}_9$: 1711.50; found, 1711.72; Anal. calcd. for $\text{C}_{114}\text{H}_{198}\text{O}_9$ (1712.83 gmol^{-1}): C 79.94, H 11.65; found: C 79.78, H 11.64.

1,3,5-Tri-(5'-1',2',3'-tris(undecoxy)phenyl) benzene (7c)



Synthesis according to GP4, pale yellow solid (14 %, purity >95 %); ^1H -NMR (500 MHz, CDCl_3): δ = 0.84–0.92 (m, 27H, CH_3), 1.19–1.40 (m, 126H, CH_2), 1.43–1.54 (m, 18H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.68–1.91 (m, 18H, OCH_2CH_2), 3.93–4.12 (m, 18H, OCH_2), 6.82 (s, 6H, 4'-H, 6'-H), 7.61 (s, 3H, 2-H, 4-H, 6-H) ppm; ^{13}C -NMR (126 MHz, CDCl_3) δ = 14.12 (CH_3), 22.70, 22.72, 26.13, 26.18, 29.37, 29.41, 29.45, 29.48, 29.66, 29.73, 29.76, 29.78, 30.4, 31.93, 31.96, (CH_2), 69.4 ($m\text{-OCH}_2$), 73.6 ($p\text{-OCH}_2$), 106.2 (C-4', C-6'), 125.0 (C-2, C-4, C-6), 136.6 (C-5'), 138.1 (C-1, C-3, C-5), 142.6 (C-2'), 153.5 (C-1', C-3') ppm; FT-IR (ATR): $\tilde{\nu}$ = 2919 (s), 2851 (s), 1737 (w), 1575 (w), 1501 (w), 1467 (s), 1418 (w), 1405 (w), 1379 (w), 1332 (s), 1233 (s), 1114 (vs), 1007 (w), 891 (w) 833 (s), 721 (w), 714 (w), 698 (w) 578 (w) cm^{-1} ; MS (MALDI-TOF): m/z : calcd. for $\text{C}_{105}\text{H}_{180}\text{O}_9$: 1837.64; found, 1838.12; Anal. calcd. for $\text{C}_{123}\text{H}_{216}\text{O}_9$ (1839.07 gmol^{-1}): C 80.33, H 11.84; found: C 80.17, H 11.86.

1,3,5-Tri-(5'-1',2',3'-tris(dodecoxy)phenyl) benzene (7e)

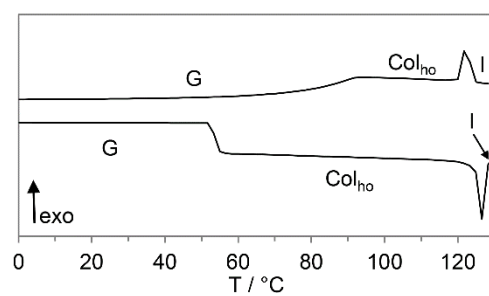
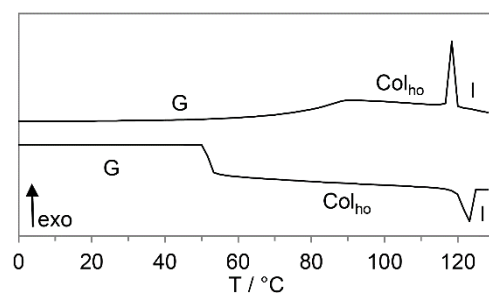
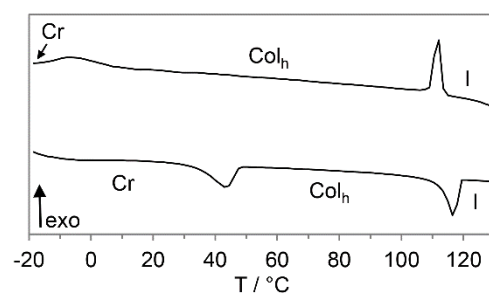
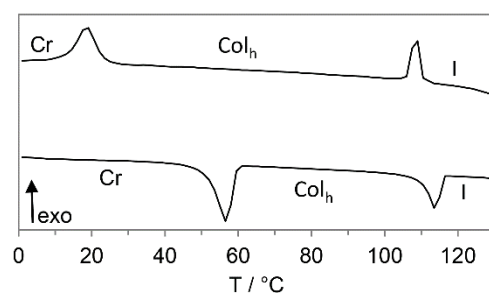


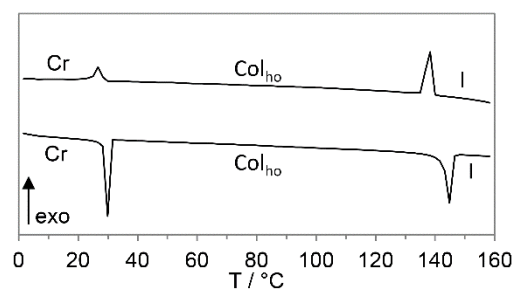
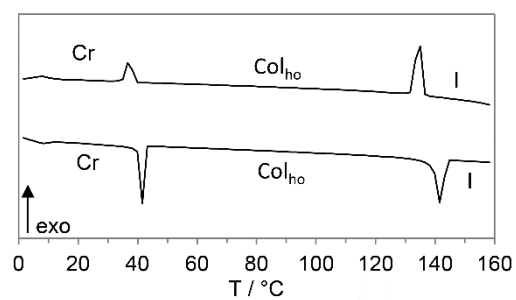
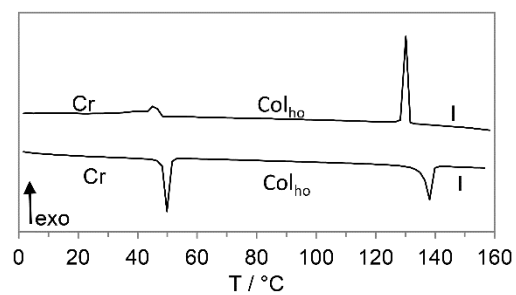
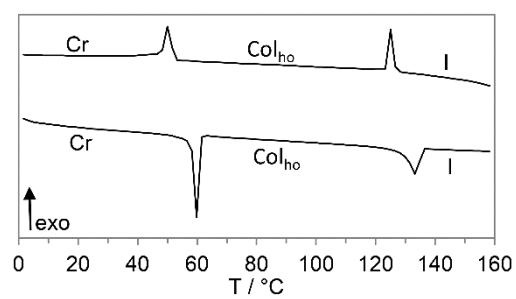
Synthesis according to GP4, pale yellow solid (11 %., purity >95 %); $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = 0.84–0.91 (m, 27H, CH_3), 1.20–1.40 (m, 144H, CH_2), 1.42–1.55 (m, 18H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.74–1.87 (m, 18H, OCH_2CH_2), 3.88–4.11 (m, 18H, OCH_2), 6.82 (s, 6H, 4'-H, 6'-H), 7.61 (s, 3H, 2-H, 4-H, 6-H) ppm; $^{13}\text{C-NMR}$ (126 MHz, CDCl_3) δ = 14.12 (CH_3), 22.70, 22.72, 26.14, 26.19, 29.38, 29.41, 29.45, 29.49, 29.67, 29.72, 29.76, 29.78, 30.4, 31.94, 31.96, (CH_2), 69.4 (*m*- OCH_2), 73.6 (*p*- OCH_2), 106.2 (C-4', C-6'), 125.0 (C-2, C-4, C-6), 136.6 (C-5'), 138.1 (C-1, C-3, C-5), 142.6 (C-2'), 153.5 (C-1', C-3') ppm; FT-IR (ATR): $\tilde{\nu}$ = 2918 (s), 2850 (s), 1732 (w), 1574 (w), 1500 (w), 1467 (s), 1418 (w), 1405 (w), 1379 (w), 1332 (s), 1232 (s), 1114 (vs), 1010 (w), 898 (w) 833 (s), 721 (w), 699 (w) 575 (w) cm^{-1} ; MS (MALDI-TOF): *m/z*: calcd. for $\text{C}_{105}\text{H}_{180}\text{O}_9$: 1963.79; found, 1962.95; Anal. calcd. for $\text{C}_{132}\text{H}_{234}\text{O}_9$ (1965.32 gmol^{-1}): C 80.67, H 12.00; found: C 80.73, H 12.00.

Original DSC traces

Table S1 Melting points of **5b-f**

compound	Melting Point / °C
5b	62
5c	64
5d	65
5e	68
5f	78

6a**6b****6c****6d**

7a**7b****7c****7d**

XRD Data

Table S2: Detailed assignment of the XRD Data

Compound	Mesophase	Lattice spacing / Å	<i>d</i> -spacing / Å observed (calcd.)	Miller Indices
6a	Col _{ho} at 105 °C <i>p6mm</i>	<i>a</i> = 25.3	21.9	(10)
			11.0 (10.97)	(20)
			4.5	halo
			4.0	π - π
6d	Col _h at 85 °C <i>p6mm</i>	<i>a</i> = 28.4	24.6	(10)
			14.2 (14.19)	(11)
			9.3 (9.29)	(21)
			8.2 (8.20)	(30)
			4.5	halo
7b	Col _{ho} at 88 °C <i>p6mm</i>	<i>a</i> = 28.3	24.5	(10)
			14.1 (14.15)	(11)
			12.2 (12.25)	(20)
			9.2 (9.24)	(21)
			8.1 (8.17)	(30)
			4.6	halo
			4.3	π - π
7d	Col _{ho} at 90 °C <i>p6mm</i>	<i>a</i> = 31.8	27.5	(10)
			15.9 (15.88)	(11)
			10.3 (10.4)	(21)
			9.1 (9.17)	(30)
			7.9 (7.94)	(22)
			4.6	halo
			4.3	π - π

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