

# Supplementary Information

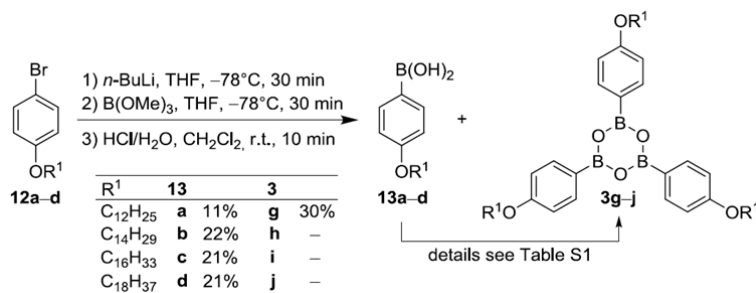
## 2. Results and Discussion

### 2.1. Synthesis of Boroxines

The *p*-alkoxybromobenzenes **12**, which were obtained by Williamson etherification according to the procedure by An [1–3] were submitted to halogen-lithium exchange with *n*-BuLi, followed by treatment with B(OMe)<sub>3</sub> and subsequent acidic hydrolysis providing the boronic acids **13** together with the arylboroxines **3** as byproducts (Scheme S1). In case of the dodecyloxy-substituted derivative, boronic acid **13a** was isolated in only 11% together with 30% of the boroxine **3g** after column chromatography. For longer alkyl chains (R = C<sub>14</sub>H<sub>29</sub>–C<sub>18</sub>H<sub>37</sub>) the boroxines **3h–j** were only detected in the crude product but could not be isolated, whereas the isolated yields of boronic acids **13b–d** were still quite low (21%–22%).

Several conditions were tried for the condensation (Table S1). Heating of **13c** in toluene in a Dean-Stark trap for 16 h under reflux (method A) or in the presence of 6 mol% of TsOH under Dean-Stark conditions (method B) resulted in a (1:1:1) mixture of boronic acid **13c**, boroxine **3i** and byproduct, which could not be separated by column chromatography. Condensation of the neat compound **13c** under reduced pressure according to the method by Wu [4] (method C). Again varying mixtures of boronic acid **13c**, boroxine **3i** and byproduct were obtained (entries 3–6). The most promising result is shown in entry 5, but the boroxine **3i** again could not be isolated in pure form.

**Scheme S1.** Synthesis of boroxines **3g–j**. Boroxines **3h–i** were only detected in the crude product by <sup>1</sup>H-NMR.



**Table S1.** Condensation of 4-dodecyloxyphenyl boronic acid **13c** to the corresponding boroxine **3i** under various conditions. <sup>a,b</sup>

| Entry | Method | Temperature [°C] | Pressure [mbar] | Time    | Product Ratio |            |         |
|-------|--------|------------------|-----------------|---------|---------------|------------|---------|
|       |        |                  |                 |         | <b>3i</b>     | <b>13c</b> | Byprod. |
| (1)   | A      | 115              | 760             | 16 h    | 1             | 1          | 1       |
| (2)   | B      | 115              | 760             | 24 h    | 1             | 1          | 1       |
| (3)   | C      | 110              | 600             | 120 min | 0.25          | 1          | 1       |
| (4)   | C      | 120              | 700             | 90 min  | 0.5           | 1          | 0.5     |
| (5)   | C      | 120              | 700             | 40 min  | 0             | 1          | 0.5     |
| (6)   | C      | 120              | 700             | 17 min  | 1             | 0.25       | 0       |

<sup>a</sup> Reaction conditions: method A: Dean-Stark trap, toluene, 1.00 mM, 115 °C; method B: 6 mol% TsOH, Dean-Stark trap, toluene, 1.00 mM, 125 °C; method C: neat, heating in a revolver oven. <sup>b</sup> Product ratio was determined by <sup>1</sup>H-NMR of the crude product.

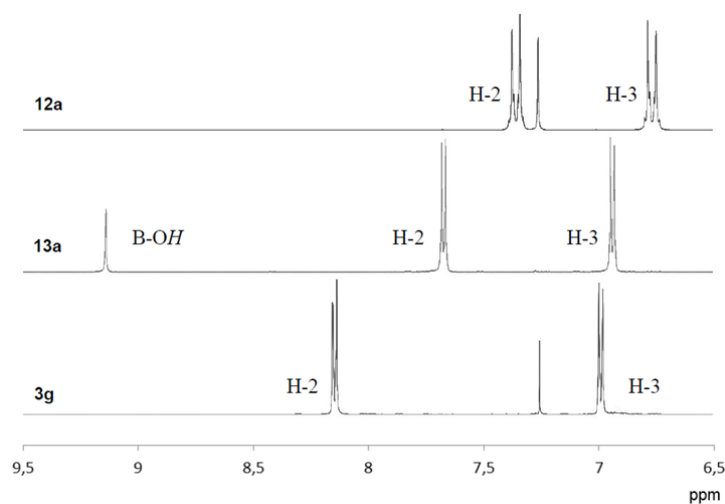
## 2.2. Identification of Boroxines

It should be noted, that boronic acids **13** and boroxines **3** could be easily distinguished by  $^1\text{H}$  NMR, because the aryl C-H signals are downfield shifted for boroxine **3** as compared to boronic acid **13**. Furthermore boronic acid **13** shows a B-OH signal at 9.15 ppm in DMSO- $d_6$ . If the spectrum was measured in  $\text{CDCl}_3$ , the B-OH signal was upfield shifted to 5.51 ppm. Typical spectra are shown in Figure S1 for **12a**, **13a**, **3g**.

Further evidence came from the IR spectra for **13a**, **3g** (Figure S2). Boronic acid **13a** displays the O-H stretching frequency at  $3607\text{ cm}^{-1}$ . The same procedure was used to identify boroxines **5** and **11** hence boronic acids **6c** and **10d** were synthesised, and characteristic IR bands which allow distinguishing between boronic acids and boroxines **3g**, **5b–d**, and **11a–d** are listed in Table S2.

From the compounds listed in Table S2 only the boronic acids **13a**, **6c** and **10d** show the BO-H vibration. The B-O band, which slightly varies from  $1320$  to  $1352\text{ cm}^{-1}$  and is visible for all compounds, is nearly constant in each series of derivatives with identical substitution pattern. A similar trend was observed for the anhydride band BX [5], which was found only in the case of boroxines. Increasing the number of alkyloxy substituents shifted the BX band to larger wave numbers from  $688$  to  $726\text{ cm}^{-1}$ , whereas the alkyl chain lengths in the same substitution pattern has no (or a minor) effect on the absorption. The presence, or absence, of this absorption band strongly indicates the presence, or absence, of a boroxine. Comparable data can be found in a work from Snyder, Konecky and Lennarz [5].

**Figure S1.** Comparison of chemical shifts of aryl C-H signals for **12a**, **13a** and **3g**. (Spectra of **12a** and **3g** in  $\text{CDCl}_3$ , of **13a** in DMSO- $d_6$ ).

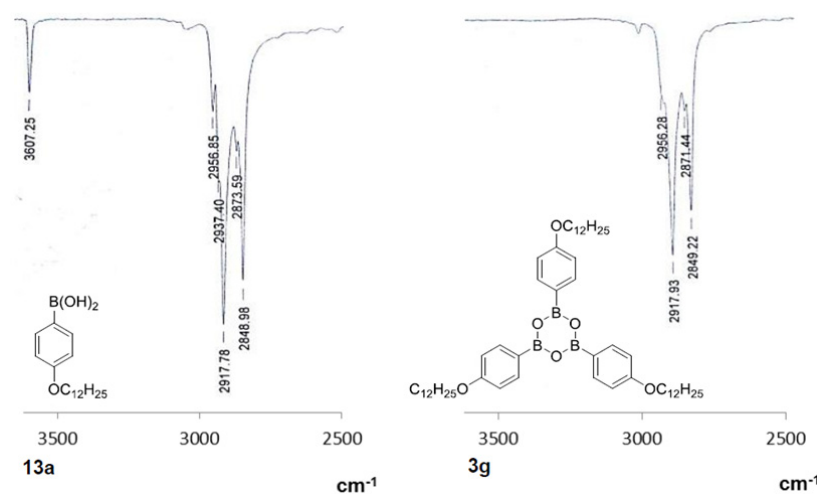


**Table S2.** Characteristic IR bands of boronic acids **3g**, **6c**, **10d** and the boroxines.

| Compound | BO-H Band/ $\text{cm}^{-1}$ | B-O Band/ $\text{cm}^{-1}$ | BX Band/ $\text{cm}^{-1}$ |
|----------|-----------------------------|----------------------------|---------------------------|
| 13a      | 3607                        | 1320                       | —                         |
| 3g       | —                           | 1351                       | 688                       |
| 6c       | 3453                        | 1334                       | —                         |
| 5b       | —                           | 1351                       | 710                       |
| 5c       | —                           | 1352                       | 710                       |

Table S2. Cont.

| Compound | BO-H Band/cm <sup>-1</sup> | B-O Band/cm <sup>-1</sup> | BX Band/cm <sup>-1</sup> |
|----------|----------------------------|---------------------------|--------------------------|
| 5d       | —                          | 1352                      | 710                      |
| 10d      | 3437                       | 1337                      | —                        |
| 11a      | —                          | 1333                      | 726                      |
| 11b      | —                          | 1334                      | 725                      |
| 11c      | —                          | 1333                      | 723                      |
| 11d      | —                          | 1336                      | 721                      |
| 11e      | —                          | 1336                      | 720                      |

Figure S2. Comparison of IR spectra of boronic acid **13a** and boroxine **3g**.

### 3. Experimental Section

#### 3.1. General Procedure for the Synthesis of Alkoxyphenylboronic Acids (**13**, **6c**, **10d**) and Boroxine (**3g**) [6–8]

A solution of the appropriate **12**, **4**, **7** (5.00 mmol) in abs. THF (20 mL) was added dropwise at  $-78\text{ }^{\circ}\text{C}$  to a solution of *n*-BuLi (3.38 mL, 5.25 mmol, 1.6 M in *n*-hexane, Merck KGaA, Darmstadt, Germany) and THF (80 mL). After stirring for 30 min, trimethylborate (0.85 mL, 0.78 g, 7.50 mmol, Sigma-Aldrich, Germany) was added, the reaction mixture stirred for a further 30 min at  $-78\text{ }^{\circ}\text{C}$  and then warmed to room temperature. The solvent was removed under vacuum, the residue taken up in  $\text{CH}_2\text{Cl}_2$  (50 mL) followed by addition of HCl (25 mL, 2 M Lösung.). After stirring for 10 min at room temperature, the layers were separated. The organic layer was washed with  $\text{H}_2\text{O}$  ( $2 \times 30\text{ mL}$ ) and brine (30 mL), dried ( $\text{MgSO}_4$ ) and the solvent removed under vacuum. The crude product was purified by column chromatography on  $\text{SiO}_2$ .

#### 3.2. 4-Dodecyloxyphenylboronic Acid (**13a**)

Purification by chromatography on  $\text{SiO}_2$  with hexanes/EtOAc (20:1), colorless solid (11%, purity > 95%), m.p.  $96\text{ }^{\circ}\text{C}$ ,  $R_f = 0.25$ .  $^1\text{H-NMR}$  (500 MHz,  $\text{DMSO-d}_6$ ,  $110\text{ }^{\circ}\text{C}$ )  $\delta = 0.88$  (t,  $J = 6.9\text{ Hz}$ , 3H,  $\text{CH}_3$ ), 1.22–1.50 (m, 18H,  $\text{CH}_2$ ), 1.70–1.79 (m, 2H,  $\text{OCH}_2\text{CH}_2$ ), 4.04 (t,  $J = 6.5\text{ Hz}$ , 2H,  $\text{OCH}_2$ ),

6.94 (d,  $J = 8.6$  Hz, 2H, H-3), 7.67 (d,  $J = 8.6$  Hz, 2H, H-2), 9.13 (s, 0.5H, OH) ppm.  $^{13}\text{C}$ -NMR (500 MHz, DMSO- $d_6$ , 110 °C)  $\delta = 14.1$  ( $\text{CH}_3$ ), 22.4 ( $\text{CH}_2\text{CH}_3$ ), 25.9, 29.00, 29.11, 29.22, 29.31, 29.34, 29.36, 31.7 ( $\text{CH}_2$ ), 68.2 ( $\text{OCH}_2$ ), 114.4 (C-3), 136.8 (C-2), 161.2 (C-4). FT-IR (ATR):  $\tilde{\nu} = 3607.3$  (w, BO-H), 2957 (w), 2937 (w), 2918 (s), 2874 (w), 2849 (s), 1599 (s), 1563 (w), 1511 (w), 1475 (w), 1462 (w), 1405 (w), 1393 (w), 1320 (s, B-O), 1302 (w), 1281 (s), 1247 (vs), 1178 (s), 1159 (w), 1112 (w), 1052 (s), 1021 (s), 1004 (s), 967 (w), 950 (w), 892 (w), 865 (s), 842 (w), 825 (w), 790 (w), 766 (w), 744 (w), 730 (w), 718 (w), 667 (w), 650 (w), 624 (w), 591 (s)  $\text{cm}^{-1}$ .

### 3.3. Tris[4-(dodecyloxy)phenyl]boroxine (3g)

Purification by chromatography on  $\text{SiO}_2$  with hexanes/EtOAc (20:1), colorless solid (30%, purity > 95%), m.p. 98 °C,  $R_f = 0.25$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.88$  (t,  $J = 6.9$  Hz, 9H,  $\text{CH}_3$ ), 1.19–1.43 (m, 48H,  $\text{CH}_2$ ), 1.42–1.52 (m, 6H,  $\text{OCH}_2\text{CH}_2\text{CH}_2$ ), 1.76–1.87 (m, 6H,  $\text{OCH}_2\text{CH}_2$ ), 4.03 (t,  $J = 6.6$  Hz, 6H,  $\text{OCH}_2$ ), 6.99 (d,  $J = 8.6$  Hz, 6H, 3-H), 8.14 (d,  $J = 8.5$  Hz, 6H, 2-H) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 14.1$  ( $\text{CH}_3$ ), 22.7 ( $\text{CH}_2\text{CH}_3$ ), 26.1, 29.30, 29.37, 29.43, 29.60, 29.62, 29.65, 29.68, 31.9 ( $\text{CH}_2$ ), 67.9 ( $\text{OCH}_2$ ), 114.0 (C-3), 137.5 (C-2), 162.8 (C-4) ppm. FT-IR (ATR):  $\tilde{\nu} = 2918$  (s), 2849 (s), 1601 (s), 1567 (w), 1512 (w), 1472 (w), 1413 (s), 1351 (s, B-O), 1305 (s), 1288 (s), 1270 (w), 1240 (vs), 1174 (s), 1115 (w), 1030 (w), 1005 (w), 999 (w), 973 (w), 916 (w), 891 (w), 834 (w), 819 (w), 747 (s), 720 (w), 688 (s, BX), 631 (w), 576 (s)  $\text{cm}^{-1}$ . MS (MALDI-TOF):  $m/z$  calcd. for  $[\text{C}_{54}\text{H}_{87}\text{BO}_6\text{H}^+]$  864.67; found 863.57. Elemental analysis calculated for  $\text{C}_{54}\text{H}_{87}\text{B}_3\text{O}_6$  (864.71  $\text{g}\cdot\text{mol}^{-1}$ ): C 75.01, H 10.14; found: C 75.11, H 10.08.

### 3.4. 3,4-Bis(dodecyloxy)phenylboronic Acid (6c)

Purification by chromatography (hexanes/EtOAc, 20:1), colorless solid (11%, purity > 95%), m.p. 67 °C,  $R_f = 0.3$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta = 0.88$  (mc, 6H,  $\text{CH}_2\text{CH}_3$ ), 1.18–1.54 (m, 28H,  $\text{CH}_2$ ), 1.72–1.91 (m, 4H,  $\text{OCH}_2\text{CH}_2$ ), 3.99–4.07 (m, 4H,  $\text{OCH}_2\text{CH}_2$ ), 5.67 (s, 2H, OH) 6.90–6.96 (m, 1H, 5-H), 7.32–7.39 (m, 2H, 2-H, 6-H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta = 14.1$  ( $\text{CH}_3$ ), 22.7 ( $\text{CH}_2\text{CH}_3$ ), 26.06, 26.09, 29.2, 29.38, 29.41, 29.45, 29.49, 29.61, 29.62, 29.66, 29.67, 31.9 ( $\text{CH}_2$ ), 68.9, 69.3 ( $\text{OCH}_2$ ), 112.8 (C-2), 119.8 (C-5), 128.8 (C-6), 148.4, 151.8 (C-3, C-4) ppm. FT-IR (ATR):  $\tilde{\nu} = 3453$  (w, BO-H), 2955 (w), 2915 (vs), 2849 (s), 1595 (w), 1515 (w), 1468 (s), 1410 (s), 1334 (s, B-O), 1292 (s), 1254 (s), 1203 (s), 1140 (s), 1095 (w), 1072 (w), 1030 (w), 999 (w), 975 (w), 956 (w), 866 (w), 811 (w), 791 (w), 765 (w), 740 (w), 703 (w), 683 (w), 599 (w), 535 (w)  $\text{cm}^{-1}$ .

### 3.5. 3,4,5-Tris(undecyloxy)phenylboronic Acid (10d)

Purification by chromatography (hexanes/EtOAc, 20:1), colorless solid (11%, purity > 95%), m.p. 53 °C,  $R_f = 0.3$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.84$ – $0.93$  (m, 9H,  $\text{CH}_3$ ), 1.19–1.40 (m, 42H,  $\text{CH}_2$ ), 1.40–1.54 (m, 6H,  $\text{OCH}_2\text{CH}_2\text{CH}_2$ ), 1.73–1.85 (m, 6H,  $\text{OCH}_2\text{CH}_2$ ), 3.95–4.06 (m, 6H,  $\text{OCH}_2$ ), 5.69 (s, 1H, BOH), 6.99 (s, 2H, H-2) ppm.  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta = 14.1$  ( $\text{CH}_3$ ), 22.7 ( $\text{CH}_2\text{CH}_3$ ), 26.15, 26.17, 29.39, 29.42, 29.47, 29.50, 29.64, 29.68, 29.69, 29.73, 29.76, 29.78, 30.4, 31.9, 32.0 ( $\text{CH}_2$ ), 69.2, 73.5 ( $\text{OCH}_2$ ), 113.00 (C-2), 131.65 (C-1), 141.06 (C-4), 152.90 (C-3) ppm. FT-IR (ATR):  $\tilde{\nu} = 3437$  (w), 2956 (w), 2917 (s), 2872 (w), 2849 (s), 1572 (w), 1502 (w),

1467 (w), 1407 (s), 1377 (w), 1337 (s, B-O), 1284 (w), 1240 (w), 1199 (w), 1115 (s), 1067 (w), 1002 (w), 972 (w), 943 (w), 888 (w), 845 (w), 831 (w), 703 (w), 640 (w), 607 (w), 586 (w)  $\text{cm}^{-1}$ . MS (ESI):  $m/z$  = 632  $[\text{M}-\text{H}^+]$ , 604, 472. HRMS (ESI):  $m/z$  calcd. for  $[\text{C}_{39}\text{H}_{73}\text{BO}_5]$  631.55; found 631.5453.

### 3.6. General Procedure for the Synthesis of Alkoxyphenylboroxines (5) [6–9]

To a solution of the appropriate **4** (2.50 mmol) in abs. THF (50 mL) at  $-78^\circ\text{C}$  was added *n*-BuLi (3.13 mL, 5.00 mmol, 1.6 M in *n*-hexane) and the reaction mixture stirred for 2 h. Then trimethylborate (0.68 mL, 0.63 mg, 6.00 mmol) was added and the reaction mixture stirred for a further 1 h at  $-78^\circ\text{C}$ . After warming to room temperature, the reaction was terminated by addition of HCl (25 mL, 2 M Lösung) and stirring for 1 h. The resulting aqueous suspension was extracted with  $\text{Et}_2\text{O}$  ( $3 \times 30$  mL). The combined organic layers were washed with  $\text{H}_2\text{O}$  ( $2 \times 20$  mL) and brine (30 mL) and dried ( $\text{MgSO}_4$ ). The solvent was removed under vacuum and the crude product purified by column chromatography on  $\text{SiO}_2$  and/or recrystallization.

### 3.7. Tris[3,4-bis(decyloxy)phenyl]boroxine (5b)

Purification by chromatography (hexanes/ $\text{EtOAc}$ , 20:1) and recrystallization from hexane at room temperature, colorless solid (31%, purity > 95%), m.p.  $118^\circ\text{C}$ ,  $R_f$  = 0.3 ( $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ , 10:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.88 (m, 18H,  $\text{CH}_3$ ), 1.19–1.60 (m, 84H,  $\text{CH}_2$ ), 1.77–1.94 (m, 12H,  $\text{OCH}_2\text{CH}_2$ ), 4.08 (t,  $J$  = 6.6 Hz, 6H,  $\text{OCH}_2\text{CH}_2$ ), 4.13 (t,  $J$  = 6.6 Hz, 6H,  $\text{OCH}_2\text{CH}_2$ ), 6.99 (d,  $J$  = 8.1 Hz, 3H, 5-H), 7.69 (d,  $J$  = 1.4 Hz, 3H, 2-H), 7.81 (dd,  $J$  = 8.1, 1.4 Hz, 3H, 6-H) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 14.1 ( $\text{CH}_3$ ), 22.7 ( $\text{CH}_2\text{CH}_3$ ), 26.05, 26.14, 29.2, 29.37, 29.40, 29.45, 29.5, 29.60, 29.64, 29.70, 31.93, 31.94 ( $\text{CH}_2$ ), 68.8, 69.5 ( $\text{OCH}_2$ ), 112.5 (C-2), 120.5 (C-5), 130.0 (C-6), 148.4, 153.3 (C-3, C-4) ppm. FT-IR (ATR):  $\tilde{\nu}$  = 2918 (s), 2849 (s), 1599 (w), 1520 (w), 1467 (w), 1413 (s), 1377 (s), 1351 (s, B-O), 1324 (s), 1272 (s), 1254 (vs), 1212 (s), 1199 (s), 1138 (s), 1096 (w), 1071 (w), 1020 (w), 986 (w), 935 (w), 874 (w), 814 (w), 791 (w), 741 (w), 710 (s, BX), 672 (w), 594 (w), 546 (w)  $\text{cm}^{-1}$ . MS (MALDI-TOF):  $m/z$  calcd. for  $[\text{C}_{78}\text{H}_{135}\text{B}_3\text{O}_9-2\text{H}]^+$  1249.04; found 1247.89. Elemental analysis calculated for  $\text{C}_{78}\text{H}_{135}\text{B}_3\text{O}_6$  (1249.36  $\text{g}\cdot\text{mol}^{-1}$ ): C 74.99, H 10.89; found: C 75.11, H 10.89.

### 3.8. Tris[3,4-bis(dodecyloxy)phenyl]boroxine (5c)

Recrystallization from pentane at room temperature and acetone at  $-28^\circ\text{C}$ , colorless solid (20%, purity > 95%), m.p.  $108^\circ\text{C}$ ,  $R_f$  = 0.3 ( $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ , 10:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.81 (t,  $J$  = 6.9 Hz, 18H,  $\text{CH}_3$ ), 1.10–1.52 (m, 108H,  $\text{CH}_2$ ), 1.70–1.87 (m, 12H,  $\text{OCH}_2\text{CH}_2$ ), 3.98–4.10 (m, 12H,  $\text{OCH}_2$ ), 6.99 (d,  $J$  = 8.1 Hz, 3H, 5-H), 7.62 (d,  $J$  = 1.3 Hz, 3H, 2-H), 7.74 (dd,  $J$  = 8.1, 1.3 Hz, 3H, 6-H) ppm.  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 14.1 ( $\text{CH}_3$ ), 22.7 ( $\text{CH}_2\text{CH}_3$ ), 26.1, 26.15, 29.2, 29.39, 29.40, 29.46, 29.5, 29.65, 29.68, 29.71, 29.72, 29.76, 31.9 ( $\text{CH}_2$ ), 68.8 ( $\text{OCH}_2$ ), 69.5 ( $\text{OCH}_2$ ), 112.5 (C-2), 120.5 (C-5), 129.9 (C-6), 148.4, 153.3 (C-3, C-4) ppm. FT-IR (ATR):  $\tilde{\nu}$  = 2954 (w), 2917 (s), 2848 (s), 1599 (w), 1520 (w), 1467 (w), 1415 (s), 1352 (s, B-O), 1274 (s), 1257 (vs), 1213 (s), 1138 (s), 1096 (w), 1073 (w), 996 (w), 960 (w), 874 (w), 814 (w), 791 (w), 741 (w),

710 (s, BX), 672 (w), 595 (w), 553 (w)  $\text{cm}^{-1}$ . MS (MALDI-TOF):  $m/z$  calcd. for  $[\text{C}_{90}\text{H}_{159}\text{B}_3\text{O}_9 - 4 \text{ H}]^+$  1417.23; found 1413.34.

### 3.9. Tris[3,4-bis(tetradecyloxy)phenyl]boroxine (5d)

Recrystallization from  $\text{Et}_2\text{O}$  at  $-28\text{ }^\circ\text{C}$ , colorless solid (7%, purity > 95%), m.p.  $112\text{ }^\circ\text{C}$ ,  $R_f = 0.3$  ( $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ , 10:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.88$  (t,  $J = 6.9$  Hz, 18H,  $\text{CH}_3$ ), 1.21–1.59 (m, 132H,  $\text{CH}_2$ ), 1.77–1.93 (m, 12H,  $\text{OCH}_2\text{CH}_2$ ), 4.04–4.17 (m, 12H,  $\text{OCH}_2$ ), 6.99 (d,  $J = 8.1$  Hz, 3H, 5-H), 7.69 (d,  $J = 1.3$  Hz, 3H, 2-H), 7.81 (dd,  $J = 8.1, 1.3$  Hz, 3H, 6-H) ppm.  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta = 14.1$  ( $\text{CH}_3$ ), 22.7 ( $\text{CH}_2\text{CH}_3$ ), 26.1, 26.2, 29.2, 29.4, 29.5, 29.6, 29.66, 29.69, 29.70, 29.72, 29.8, 31.9 ( $\text{CH}_2$ ), 68.8 ( $\text{OCH}_2$ ), 69.5 ( $\text{OCH}_2$ ), 112.5 (C-2), 120.5 (C-5), 129.9 (C-6), 148.4, 153.3 (C-3, C-4) ppm. FT-IR (ATR):  $\tilde{\nu} = 2954$  (w), 2917 (vs), 2848 (s), 1599 (w), 1520 (w), 1467 (w), 1415 (s), 1378 (s), 1352 (s, B-O), 1256 (s), 1212 (s), 1138 (s), 1097 (w), 1074 (w), 1019 (w), 1006 (w), 974 (w), 873 (w), 815 (w), 792 (w), 741 (w), 710 (s, BX), 672 (w), 595 (w)  $\text{cm}^{-1}$ . MS (MALDI-TOF):  $m/z$  calcd. for  $[\text{C}_{102}\text{H}_{183}\text{B}_3\text{O}_9 + \text{Na}]^+$  1608.39; found 1604.32. Elemental analysis calculated for  $\text{C}_{102}\text{H}_{183}\text{B}_3\text{O}_9$  (1586.00  $\text{g}\cdot\text{mol}^{-1}$ ): C 77.25, H 11.63; found: C 77.27, H 11.33.

### 3.10. 3,4,5-Tris(dodecyloxy)phenyl-boro-diethanolamino Complex (9e)

$^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.76$ – $0.98$  (m, 9H,  $\text{CH}_3$ ), 1.11–1.54 (m, 54H,  $\text{CH}_2$ ), 1.58–1.95 (m, 6H,  $\text{OCH}_2\text{CH}_2$ ), 2.78 (s, 2H, a-H oder b-H), 3.26 (s, 2H, a-H oder b-H), 3.77–4.12 (m, 10H,  $\text{OCH}_2$ , a-H oder b-H), 4.86 (s, 1H, N-H), 6.72 (s, 2H, 2-H) ppm.  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta = 14.1$  ( $\text{CH}_3$ ), 22.7, 26.2, 29.4, 29.5, 29.7, 30.4, 31.9 ( $\text{CH}_2$ ), 51.5, 63.6 (C-a, C-b), 69.05, 73.39 ( $\text{OCH}_2$ ), 110.51 (C-2), 137.64 (C-4), 152.55 (C-3) ppm.

## 4. DSC Traces

**Figure S3.** DSC traces of the boroxines **11** (2nd heating/cooling cycle; heating/cooling rate  $5\text{ K}\cdot\text{min}^{-1}$ ).

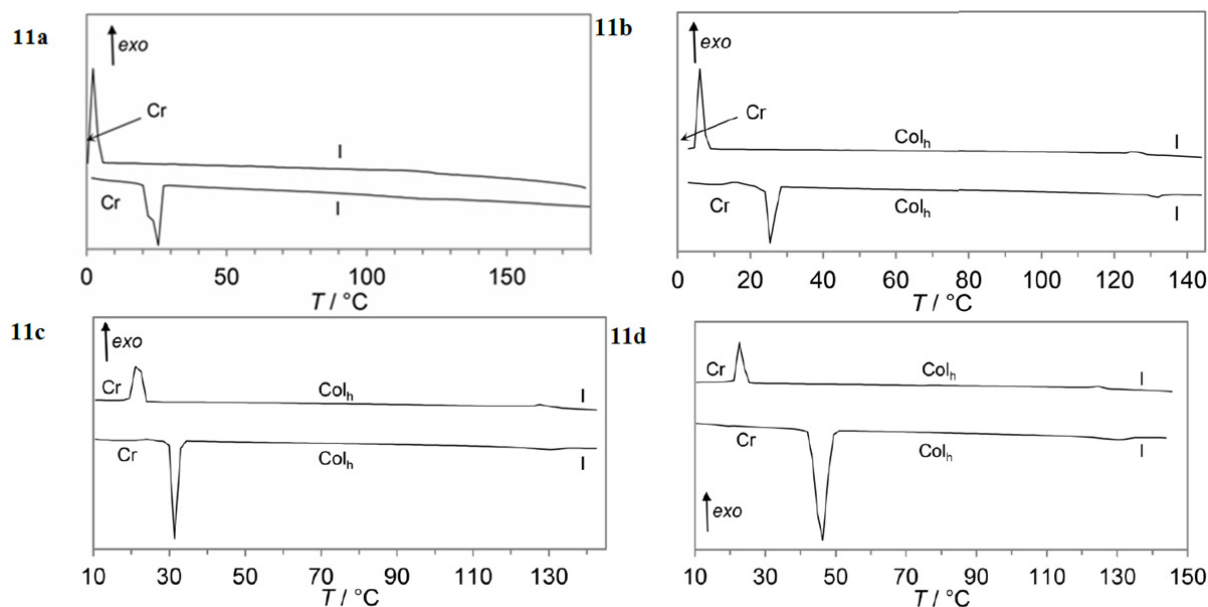
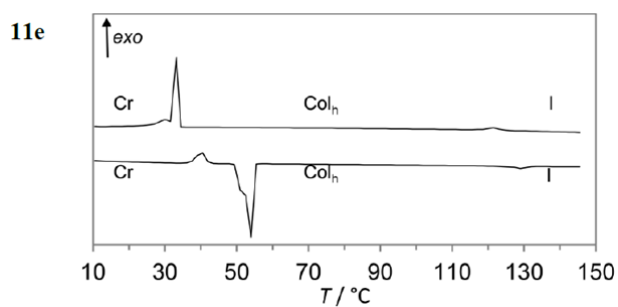
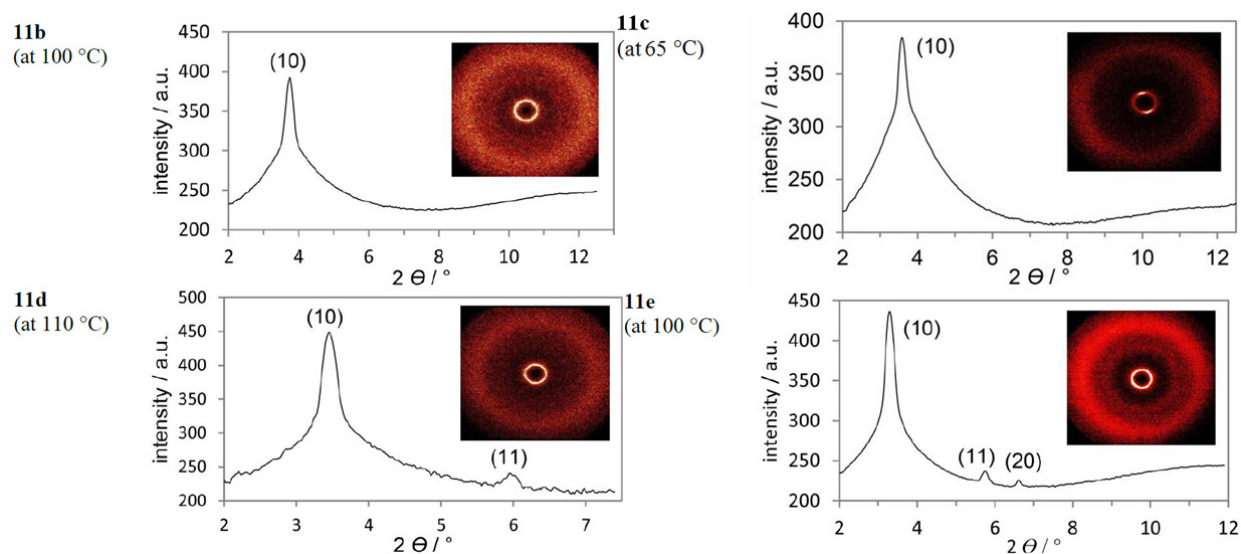


Figure S3. Cont.



## 5. XRD Investigations

**Figure S4.** SAXS profile of the liquid-crystalline Phase of **11** at respective temperatures (Inset: wide-angle scattering, WAXS).



**Table S3.** XRD results for boroxines **11b–d**.

| Compound | Mesophase                                | Lattice Spacing/Å | <i>d</i> spacing/Å<br>Observed (Calcd) | Miller Indices           | <i>Z</i> |
|----------|------------------------------------------|-------------------|----------------------------------------|--------------------------|----------|
| 11b      | Col <sub>h</sub> at 100 °C <i>p</i> 6 mm | <i>a</i> = 27.3   | 23.6 4.5                               | (10) (halo)              | 1.1      |
| 11c      | Col <sub>h</sub> at 65 °C <i>p</i> 6 mm  | <i>a</i> = 28.4   | 24.6 4.7                               | (10) (halo)              | 1.2      |
| 11d      | Col <sub>h</sub> at 110 °C <i>p</i> 6 mm | <i>a</i> = 29.5   | 25.6 14.8 4.6                          | (10) (11) (halo)         | 1.1      |
| 11e      | Col <sub>h</sub> at 100 °C <i>p</i> 6 mm | <i>a</i> = 31.0   | 26.8 15.4 (15.5) 13.3<br>(13.4) 4.7    | (10) (11) (20)<br>(halo) | 1.2      |

## 6. NMR Data

**Figure S5.**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of complex **9e**, boronic acid **6c** and boroxines **11a–e**.

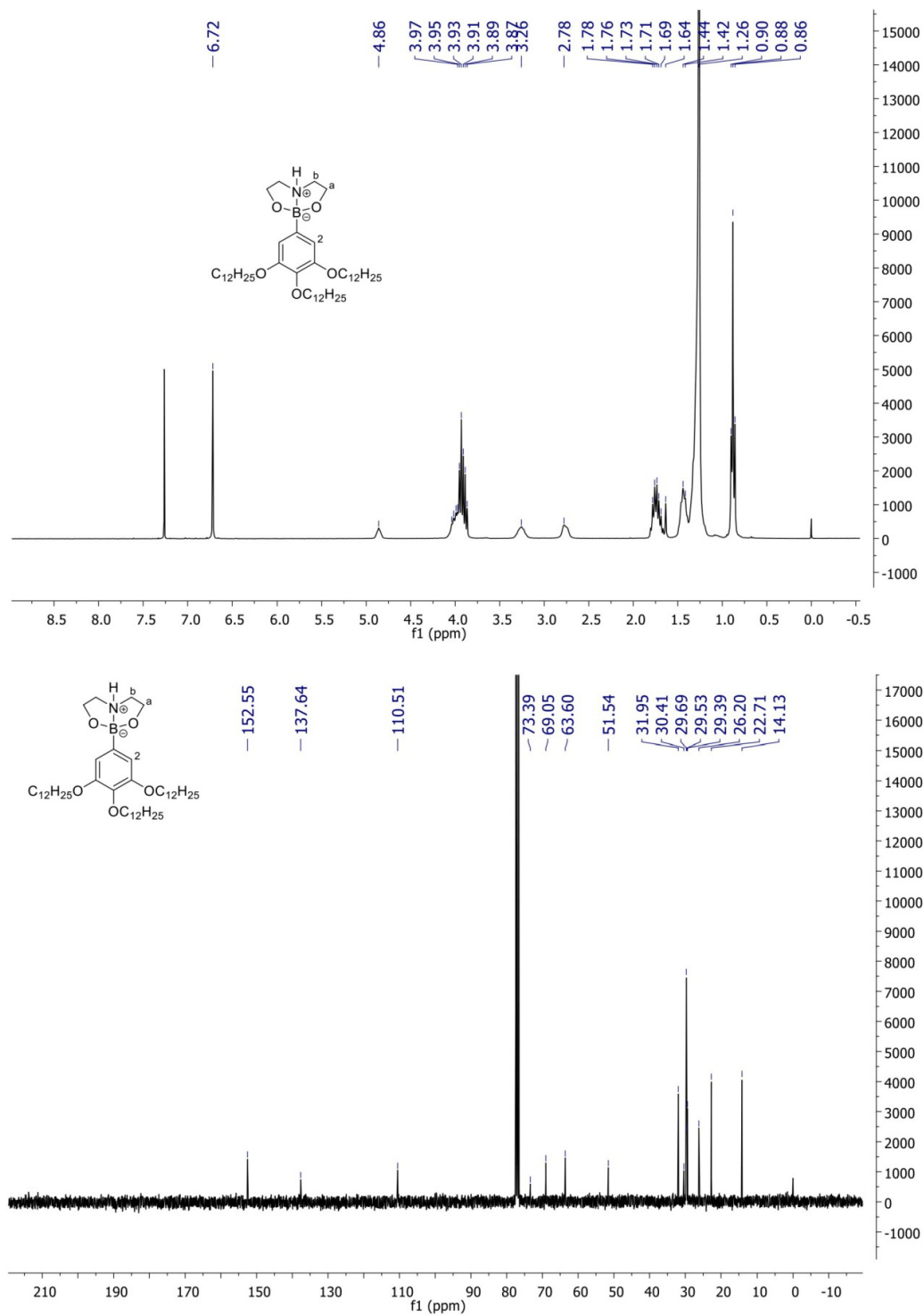


Figure S5. Cont.

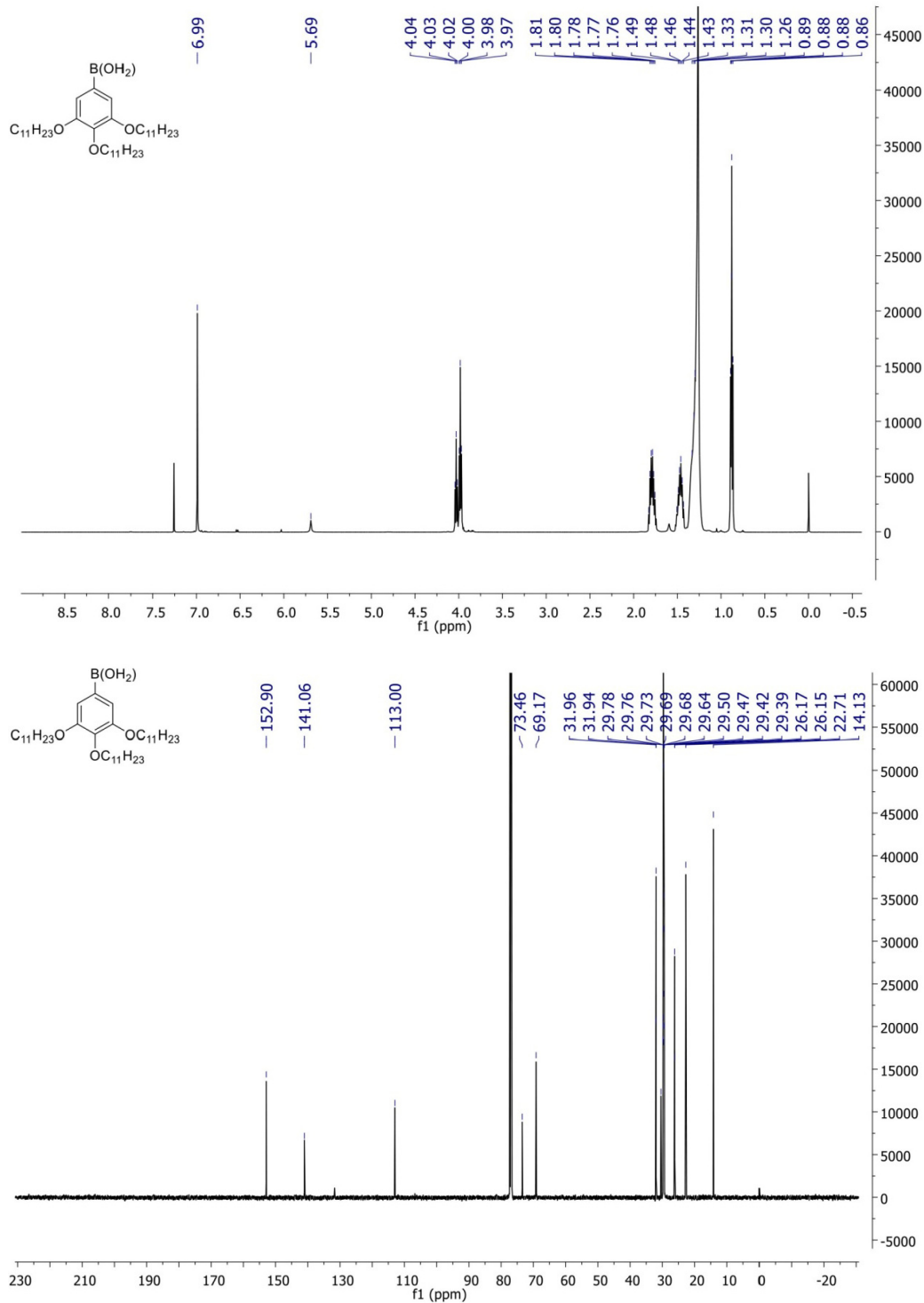


Figure S5. Cont.

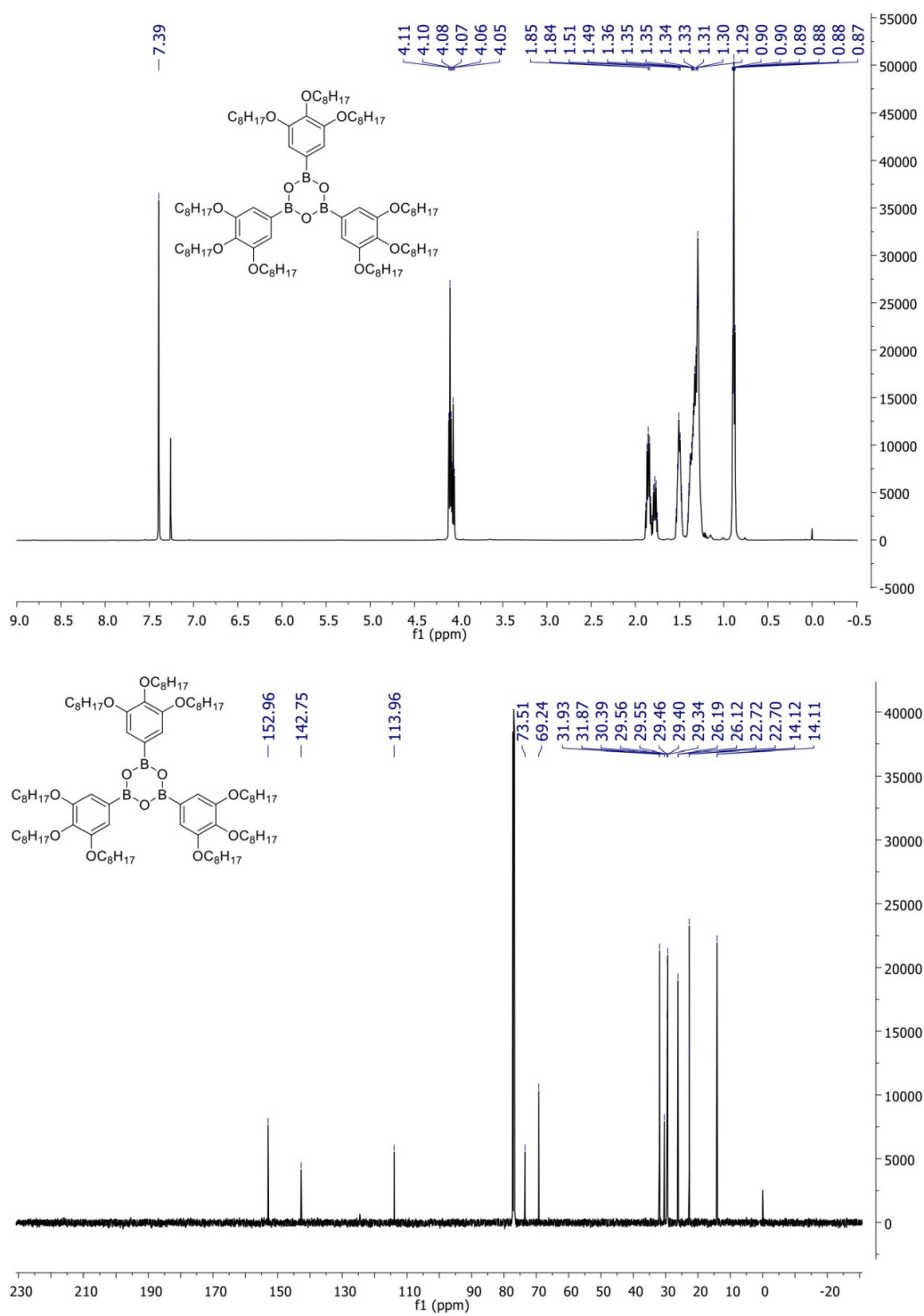


Figure S5. Cont.

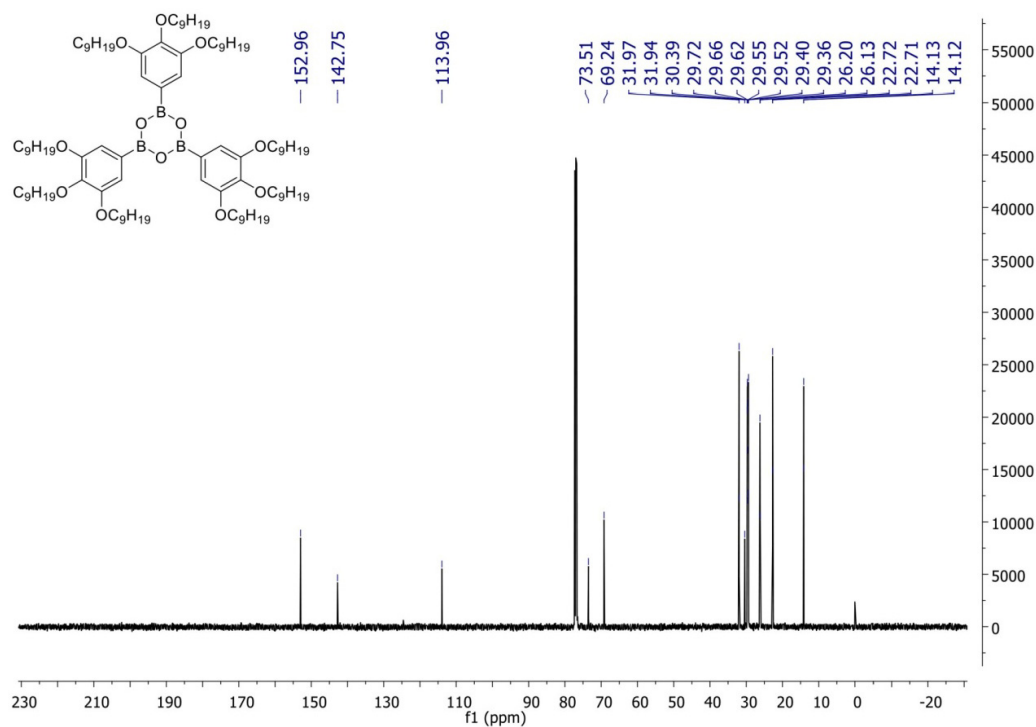
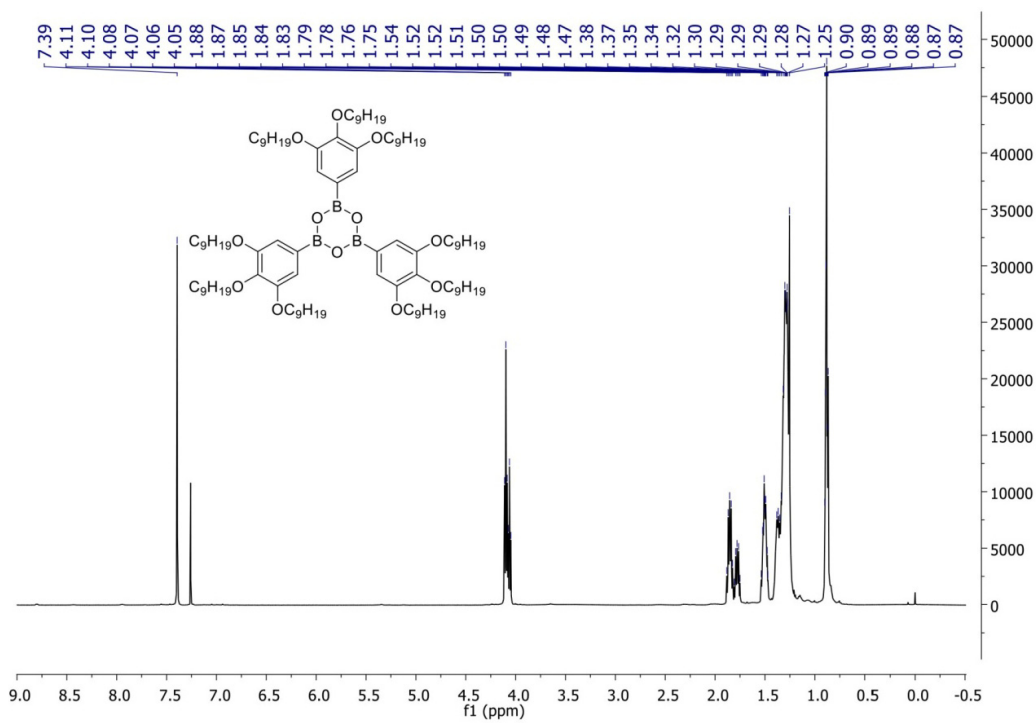


Figure S5. Cont.

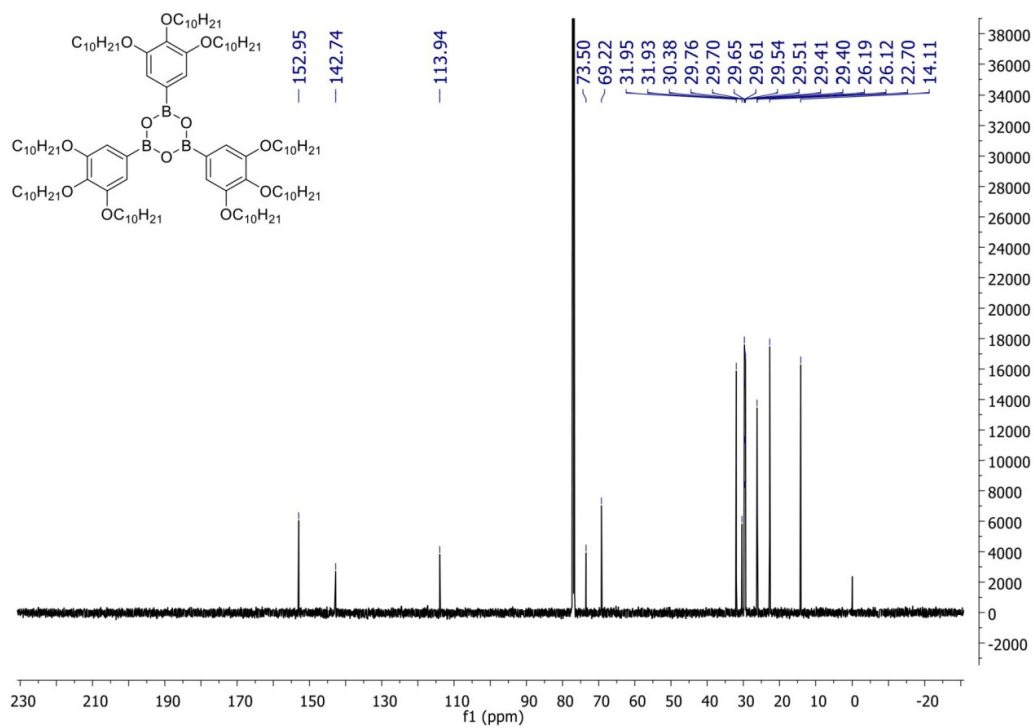
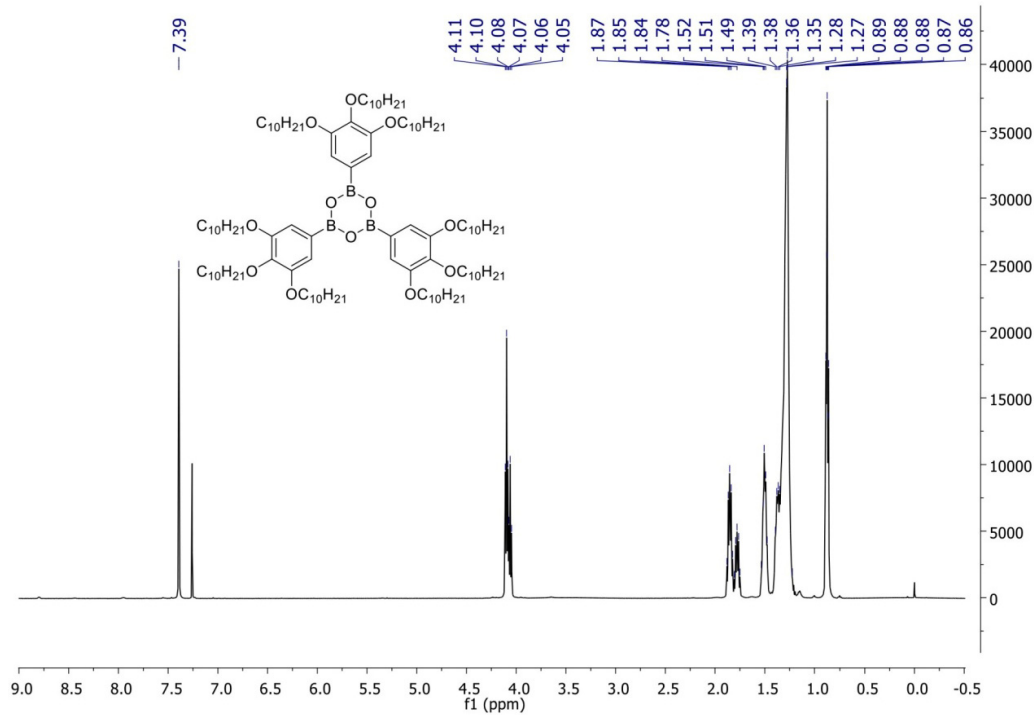


Figure S5. Cont.

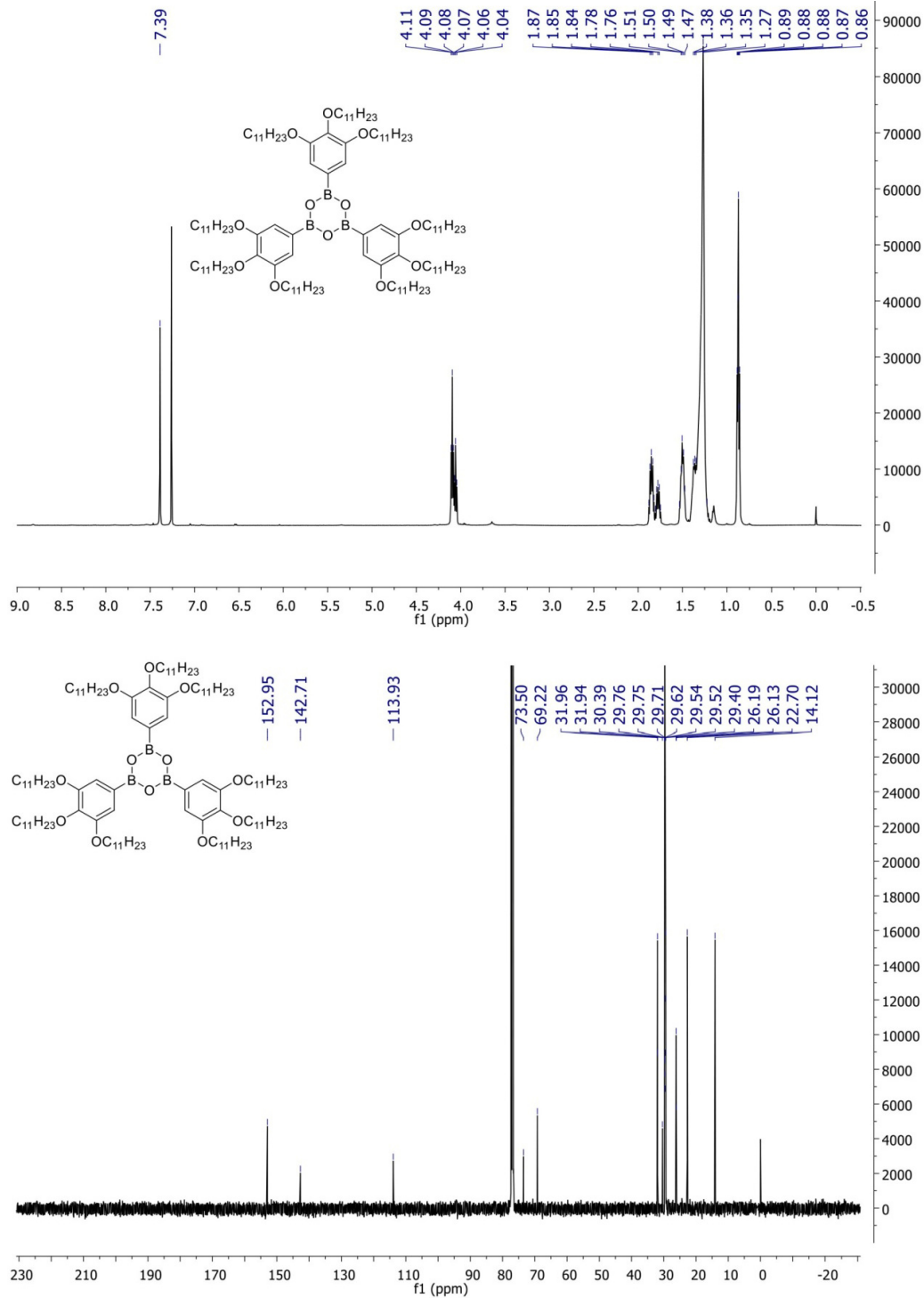
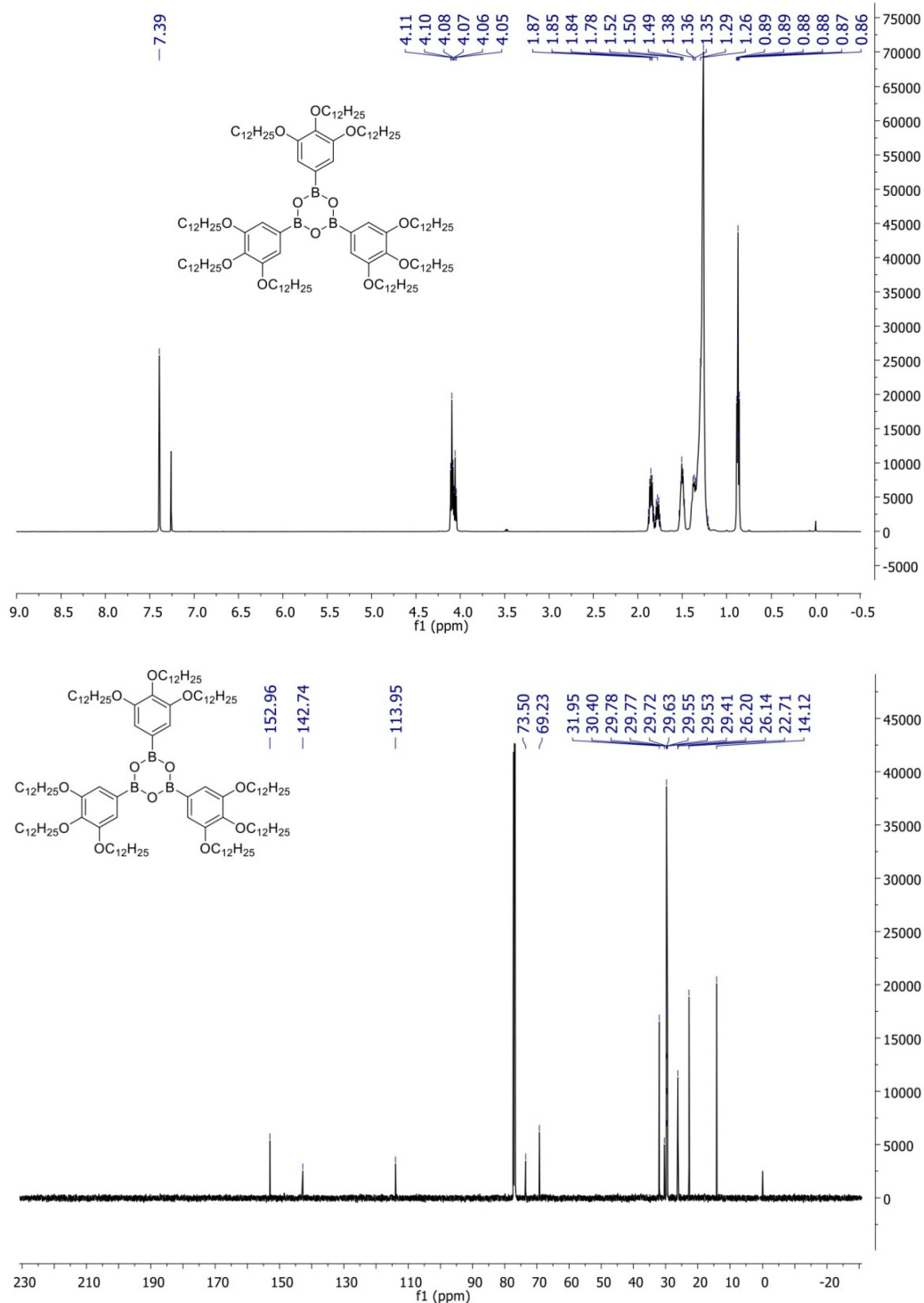


Figure S5. Cont.



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