Electronic Supplementary Material (ESI) for Chemical Science
This journal is © The Royal Society of Chemistry 2012

Boronic Esters: A Simple Route to Discotic Liquid Crystals that Are Electron Deficient

Luke A. Tatum, Carey J. Johnson, Ashantha A. P. Fernando,
Brianna C. Ruch, Krishna K. Barakoti, Mario A. Alpuche-Aviles,
Benjamin T. King*

Department of Chemistry, University of Nevada, Reno, Reno, Nevada 89557-0216

This journal is © The Royal Society of Chemistry 2012

Synthesis

All reactions were run under N_2. THF was distilled from Na and benzophenone.

General Synthesis of p-(3,7-dimethyloctyloxy)bromobenzene- p-bromophenol (1.5 g, 8.67 mmol), 1-bromo-3,7-dimethyloctane (2.1 g, 9.537 mmol), K_2CO_3 (2.39 g, 17.3 mmol), and 60 mL of dimethylformamide were added to a round bottom flask then put under N_2 atmosphere. The reaction was stirred at reflux for 12 hours. After aqueous extraction with ether (3 X 100 mL) the organic phases were combined, dried with $MgSO_4$, and concentrated under vacuum yielding yellow oil. The crude yellow oil was purified by flash column chromatography (silica gel, hexanes) to produce 2.126 g of colorless oil with 78.3% yield.

(**1a**) p-hexyloxybromobenzene- ^{1}H NMR: ($CDCl_3$, 400 MHz) δ = 0.91 (t, *J* = 7.2 Hz, 3 H), 1.30-1.37 (m, 4 H), 1.40-1.50 (m, 2 H), 1.77 (qnt, *J* = 7.6 Hz, 2 H), 3.90 (t, *J* = 6.8 Hz, 2 H), 6.75-6.79 (m, 2 H) 7.34-7.38 (m, 2 H) ppm. IR ν_{max} (film) [cm^{-1}]: 2928, 2857, 1591, 1488, 1285, 1240, 1169, 1071, 818. GCMS (EI, M^+) found 256.

(**1b**) p-octyloxybromobenzene- ^{1}H NMR: ($CDCl_3$, 400 MHz) δ = 0.89 (t, *J* = 7.2 Hz, 3 H), 1.25-1.40 (m, 8 H), 1.40-1.47 (m, 2 H), 1.76 (qnt, *J* = 8 Hz, 2 H), 3.91 (t, *J* = 6.4 Hz, 2 H), 6.75-6.79 (m, 2 H) 7.34-7.38 (m, 2 H) ppm. IR ν_{max} (film) [cm^{-1}]: 2922, 2853, 1590, 1488, 1285, 1242, 1169, 1071, 819. GCMS (EI, M^+) found 284.

(**1c**) p-decyloxybromobenzene- ^{1}H NMR: ($CDCl_3$, 400 MHz) δ = 0.87 (t, *J* = 6.8 Hz, 3 H), 1.25-1.40 (m, 12 H), 1.40-1.47 (m, 2 H), 1.76 (qnt, *J* = 8 Hz, 2 H), 3.91 (t, *J* = 6.8 Hz, 2 H), 6.77 (d, *J* = 8.8 Hz, 2 H) 7.36 (d, *J* = 8.8 Hz, 2 H) ppm; GCMS (EI, M^+) found 312.

(**1d**) p-dodecyloxybromobenzene- ^{1}H NMR: ($CDCl_3$, 400 MHz) δ = 0.88 (t, *J* = 6.8 Hz, 3 H), 1.25-1.37 (m, 16 H), 1.40-1.50 (m, 2 H), 1.77(qnt, *J* = 7.6 Hz, 2 H), 3.91 (t, *J* = 6.8 Hz, 2 H), 6.75-6.79 (m, 2 H) 7.34-7.38 (m, 2 H) ppm. IR ν_{max} (film) [cm^{-1}]: 2915, 2848, 1591, 1578, 1490, 1475, 1282, 1236, 1172, 819. GCMS (EI, M^+) found 340.

(**1e**) p-(3,7-dimethyloctyloxy)bromobenzene- ^{1}H NMR: ($CDCl_3$, 400 MHz) δ = 0.87 (d, *J* = 6.8 Hz, 6 H), 0.93 (d, *J* = 6.8 Hz, 3 H), 1.12-1.20 (m, 3 H), 1.25-1.34 (m, 3 H), 1.50-1.60 (m, 2 H), 1.62-1.69 (m, 1 H), 1.76-1.84 (m, 1 H), 3.88-3.97 (m, 2 H), 6.73-6.77 (m, 2 H), 7.31-7.35 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 158.6, 132.5, 116.6, 112.9, 66.8, 39.6, 37.6, 36.4, 30.2, 28.3, 25.0, 23.1, 23.0, 20.0 ppm. IR ν_{max} (film) [cm^{-1}]: 2930, 2854, 1595, 1573, 1436, 1161, 1045, 828. HRMS (APPI-TOF, M^+) $C_{16}H_{21}BrO$ calc 312.1089, found 312.1309.

(**1f**) p-(2-ethylhexyloxy)bromobenzene- ^{1}H NMR: ($CDCl_3$, 400 MHz) δ = 0.87-0.92 (m, 6 H), 1.27-1.33 (m, 4 H), 1.35-1.50 (m, 4 H), 1.69 (spt, *J* = 6 Hz, 1 H) 3.78 (dd, J_1 = 6 Hz, J_2 = 10.4 Hz 2 H), 3.80 (dd, J_1 = 6 Hz, J_2 = 10.4 Hz 2 H), 6.74-6.78 (m, 2 H), 7.32-7.36 (m, 2 H) ppm. IR ν_{max} (film) [cm^{-1}]: 2959, 2924, 2857, 1590, 1488, 1466, 1284, 1241, 1169, 1071, 818. GCMS (EI, M^+) found 284.

This journal is © The Royal Society of Chemistry 2012

General synthesis for 3,5-dihexyloxybromobenzene- 5-bromoresorcinol (1.199 g, 6.35 mmol), 1-bromohexane (2.199 g, 13.33 mmol), K_2CO_3 (2.633 g, 19.05 mmol), and 60 mL of dimethylformamide were added to a round bottom flask then put under N_2 atmosphere. The reaction was then stirred at reflux for 15 hours. After aqueous extraction with ether (3 X 100 mL) the organic phases were combined, dried with $MgSO_4$, and concentrated under vacuum yielding yellow oil. The crude yellow oil was purified by flash column chromatography (silica gel, hexanes) to produce 2.013 g of colorless oil with 88.8% yield.

(**1g**) 3,5-dihexyloxybromobenzene- ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.90 (t, *J* = 7.2 Hz, 6 H), 1.29-1.38 (m, 8 H), 1.40-1.47 (m, 4 H), 1.75 (qnt, *J* = 8 Hz 4 H), 3.89 (t, *J* = 6.8 Hz, 4 H), 6.36 (t, *J* = 2.4, 1 H), 6.64 (d, *J* = 2.4 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 161.1, 123.1, 110.6, 100.9, 68.6, 31.9, 29.4, 26.0, 22.9, 14.4 ppm. IR ν_{max} (film) [cm^{-1}]: 2930, 2854, 1595, 1573, 1436, 1161, 1045, 828. HRMS (APPI-TOF, M^+) $C_{18}H_{29}BrO_2$ calc 356.1351, found 355.9176.

(**1h**) 3,5-dioctyloxybromobenzene- ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.89 (t, *J* = 6.8 Hz, 6 H), 1.21-1.35 (m, 16 H), 1.40-1.48 (m, 4 H), 1.74 (qnt, J= 8 Hz, 4 H), 3.89 (t, *J* =6.4 Hz, 4), 6.36 (t, *J* = 2.2 Hz, 1 H), 6.63 (d, *J* = 2.2 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 160.7, 122.8, 110.2, 100.6, 68.3, 31.8, 29.3, 29.2, 29.1, 26.0, 22.6, 14.1 ppm. IR ν_{max} (film) [cm^{-1}]: 2920, 2851, 1595, 1571, 1433, 1163, 1045, 829. HRMS (APPI-TOF, M^+) calcd for $C_{22}H_{37}BrO_2$ calc 412.1977, found 412.1786.

(**1i**) 3,5-didecyloxybromobenzene- ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.88 (t, *J* = 7.2 Hz, 6 H), 1.20-1.34 (m, 24 H), 1.38-1.46 (m, 4 H), 1.74 (qnt, J= 8 Hz, 4 H), 3.88 (t, *J* = 6.4 Hz, 4), 6.35 (t, *J* = 2.2 Hz, 1 H), 6.62 (d, *J* = 2.2 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 160.7, 122.8, 110.2, 68.2, 31.9, 29.7, 29.7, 29.6, 29.6, 29.4, 29.1, 26.0, 22.7, 14.1 ppm. IR ν_{max} (film) [cm^{-1}]: 2920, 2851, 1595, 1571, 1433, 1163, 1045, 829. HRMS (APPI-TOF, M^+) $C_{26}H_{45}BrO_2$ calc 468.2604, found 468.2705.

(**1j**) 3,5-didodecyloxybromobenzene- ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.88 (t, *J* = 7.2 Hz, 6 H), 1.20-1.34 (m, 32 H), 1.38-1.46 (m, 4 H), 1.74 (qnt, *J* = 6.4, 4 H), 3.88 (t, *J* = 6.4 Hz, 4), 6.35 (t, *J* = 2.2 Hz, 1 H), 6.62 (d, *J* = 2.2 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 160.7, 122.8, 110.2, 68.2, 31.9, 29.7, 29.7, 29.6, 29.6, 29.4, 29.1, 26.0, 22.7, 14.1 ppm. IR ν_{max} (film): 2915, 2845, 1595, 1561, 1436, 1155, 1045, 837. HRMS (APPI-TOF, M^+) $C_{30}H_{53}BrO_2$ calc 524.3231 found 524.2992. M.P. 35-37 °C.

(**1k**) 3,5-di(3,7-dimethyloctyloxy)bromobenzene- ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.87 (d, *J* = 6.8 Hz, 12 H), 0.92 (d, *J* = 6.8 Hz, 6 H), 1.13-1.19 (m, 6 H), 1.24-1.37 (m, 6 H), 1.50-1.59 (m, 4 H), 1.63-1.70 (m, 2 H), 1.79 (sxt, *J* = 6.8 Hz, 2 H), 3.88-3.95 (m, 4 H), 6.36 (t, *J* = 2.2 Hz, 1 H), 6.63 (d, *J* = 2.2 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 161.1, 123.2, 110.5, 100.9, 66.9, 39.6, 37.6, 36.4, 30.2, 28.3, 25.0, 23.1, 23.0, 20.0 ppm. IR ν_{max} (film) [cm^{-1}]: 2952, 2942, 2868, 1595, 1574, 1436, 1163, 1051, 830. HRMS (APPI-TOF, M^+) $C_{26}H_{45}BrO_2$ calc 468.2604, found 468.2423.

This journal is © The Royal Society of Chemistry 2012

(**1l**) 3,5-di(2-ethylhexyl)bromobenzene- ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.90 (t, *J* = 7.2 Hz, 6 H), 0.92 (t, *J* = 7.2 Hz, 6 H), 1.27-1.35 (m, 10 H), 1.35-1.56 (m, 8 H), 1.69 (spt, *J* = 2 Hz, 2 H), 3.78 (dd, J_1 = 5.6 Hz, J_2 = 9.1 Hz, 2 H), 3.80 (dd, J_1 = 5.6 Hz, J_2 = 9.1 Hz, 2 H), 6.35 (t, *J* = 2.2 Hz, 1 H), 6.62 (d, *J* = 2.2 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 161.0, 122.7, 110.1, 100.5, 70.7, 39.3, 30.5, 29.0, 23.8, 26.0, 14.0, 11.1 ppm. IR v_{max} (film) [cm^{-1}]: 2958, 2920, 2858, 1591, 1574, 1433, 1164, 1050, 825. HRMS (APPI-TOF, M^+) $C_{22}H_{37}BrO_2$ calc 412.1977, found 412.1858.

General synthesis for p-hexyloxybenzene boronic acid- p-hexyloxybromobenzene (2.733 g, 10.63 mmol) in 40 mL of THF was put under N_2 atmosphere in a schlenck flask. 1.6 M BuLi in hexanes (9.97 mL, 15.95 mmol) was added drop-wise and let stir for 30 minutes at -78° C. Triisopropylborate (7.36 mL, 31.9 mmol) was added dropwise at -78° C then let stir and warm to room temperature for 12 hours. 10 mL of 3 M HCl was then added and the reaction was stirred for 30 minutes. The resulting crude boronic acid was then taken directly on to further synthesis. For characterization, the crude boronic acid (116 mg, 0.523 mmol) and N-methyliminodiactetic acid (85 mg, 0.575 mmol) were dissolved in 20 ml of toluene and 2 mL of DMSO. The reaction was then refluxed with a Dean Stark trap for 3 hours. The solvent was removed resulting in yellow oil, which was purified by flash column chromatography (silica gel, ethylacetate). The product 120 mg of colorless solid was obtained in 69.2% yield.

(**2a**) p-hexyloxybenzene MIDA boronate- ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.90 (t, *J* = 7.2 Hz, 3 H), 1.30-1.36 (s, 4 H), 1.40-1.47 (m, 2 H), 1.75 (qnt, *J* = 8 Hz, 2 H), 2.47 (s, 3 H), 3.90 (t, J= 6.4 Hz, 2 H), 4.00 (dd, J_1 = 16.8, J_1 = 166.8, 4 H), 6.85 (d, *J* = 8 Hz, 2 H), 7.38 (d, *J* = 8 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.1, 160.4, 133.7, 125.6, 114.4, 67.8, 61.8, 47.7, 31.6, 29.2, 25.7, 22.6, 14.0 ppm; IR v_{max} (film) [cm^{-1}]: 2924, 2860, 1777, 1746, 1598, 1339, 1241, 1170, 1027, 831, 818, 744, 686. HRMS (APPI-TOF, M^+) $C_{17}H_{24}BNO_5$ calc 333.1748 found 332.9671; M.P. 88-91 °C.

(**2b**) p-octyloxybenzene MIDA boronate- ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.88 (t, *J* = 7.2 Hz, 3 H), 1.25-1.35 (m, 16 H), 1.39-1.46 (m, 4 H), 1.75 (qnt, *J* = 8 Hz, 2 H), 2.51 (s, 3 H), 3.89 (t, *J* = XXX, 2 H), 4.00 (dd, J_1 = 17.2, J_2 = 170.4, 4 H), 6.84 (d, *J* = 8.4 Hz, 2 H), 7.37 (d, *J* = 8.4 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.5, 160.8, 134.0, 114.7, 68.1, 62.1, 48.0, 32.1, 29.7, 29.6, 29.5, 26.4, 23.0, 14.4 ppm; IR v_{max} (film) [cm^{-1}]: 3007, 2924, 2849, 1742, 1601, 1460, 1305, 1223, 1173, 1034, 993, 821 HRMS (APPI-TOF, M^+) $C_{19}H_{28}BNO_5$ calc 361.2061 found 360.9792; M.P. 86-88 °C.

(**2c**) p-decyloxybenzene MIDA boronate- ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.88 (t, *J* = 6.8 Hz, 3 H), 1.22-1.39 (m, 12 H), 1.40-1.48 (m, 2 H), 1.77 (qnt, *J* =6.8 Hz, 2 H), 2.51 (s, 3 H), 3.92 (dd, J_1 = 16.8 Hz, J_2 = 126.8 Hz, 4 H), 3.93 (t, *J* = 6.8 Hz, 2 H), 6.88 (d, *J* = 8.4 Hz, 2 H), 7.40 (d, *J* = XXX Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 168.2, 160.6, 133.7, 114.4, 67.8, 61.7, 47.5, 29.5, 29.4, 29.3, 29.2, 26.0, 22.7, 14.1 ppm; IR v_{max} (film) [cm^{-1}]: 3009, 2914, 2848, 1742, 1605, 1457, 11302, 1220, 1177, 1032, 992, 818. HRMS (APPI-TOF, M^+) $C_{21}H_{32}BNO_5$ calc 389.2374 found 389.2631; M.P. 112-119 °C.

This journal is © The Royal Society of Chemistry 2012

(**2d**) p-dodecyloxybenzene MIDA boronate- ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.88 (t, *J* = 7.2 Hz, 3 H), 1.23-1.39 (m, 16 H), 1.40-1.48 (m, 2 H), 1.77 (qnt, *J* = 8.4 Hz, 2 H), 2.51 (s, 3 H), 3.93 (t, *J* = 6.4 Hz, 2 H), 3.93 (dd, J_1 = 16.8 Hz, J_2 = 130.8 Hz, 4 H), 6.88 (d, *J* = 8.4 Hz, 2 H), 7.40 (d, *J* = 8.4 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 168.6, 160.9, 134.0, 114.8, 68.2, 62.1, 47.9, 30.0, 30.0, 30.0, 29.9, 29.8, 29.7, 29.6, 23.0, 14.5 ppm; IR v_{max} (film) [cm^{-1}]: 3007, 2914, 2847, 1742, 1603, 1460, 1228, 1032, 993, 821. HRMS (APPI-TOF, M^+) $C_{23}H_{36}BNO_5$ calc 417.2687 found 417.0125; M.P. 116-121 °C.

(**2e**) p- (3,7-dimethyloctyloxy)benzene MIDA boronate- ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.80 (d, *J* = 6.4 Hz, 6 H), 0.86 (d, *J* = 6.4 Hz, 3 H), 1.04-1.14 (m, 3 H), 1.19-1.30 (m, 3 H), 1.41-1.53 (m, 2H), 1.54-1.64 (m, 1 H), 1.69-1.80 (m, 1 H), 2.43 (s, 3 H), 3.84-3.94 (m, 2 H), 3.93 (dd, J_1 = 16.8 Hz, J_2 = 130.8 Hz, 4 H), 6.80 (d, *J* = 8.4 Hz, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 167.8, 159.5, 132.7, 113.4, 65.1, 60.8, 46.7, 38.2, 36.3, 35.2, 28.8, 27.0, 23.6, 21.7, 21.6, 18.6 ppm; IR v_{max} (film) [cm^{-1}]: 2955, 2962, 2869, 1743, 1603, 1459, 1217, 1178, 1034, 988, 822. HRMS (APPI-TOF, M^+) $C_{21}H_{32}BNO_5$ calc 389.2374 found 388.9968; M.P. 127-130 °C.

(**2f**) p- (2-ethylhexyloxy)benzene MIDA boronate- ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.89-0.92 (m, 6 H), 1.30-1.35 (m, 4 H), 1.35-1.42 (m, 4 H), 1.64-1.72 (s, 1 H), 2.48 (s, 3 H), 3.78 (m, 4 H), 4.24 (m, 2 H), 6.86 (d, *J* = 8 Hz, 2 H), 7.38 (d, *J* = 8 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.6, 161.0, 134.0, 125.8, 114.7, 70.5, 62.1, 48.0, 39.7, 30.8, 29.4, 24.1, 23.3, 14.4, 11.4 ppm; IR v_{max} (film) [cm^{-1}]: 2958, 2927, 2856, 1763, 1739, 1601, 1512, 1284, 1213, 1176, 1034, 987, 825, 632. HRMS (APPI-TOF, M^+) $C_{19}H_{28}BNO_5$ calc 361.2061 found 361.2107 M.P. 178-180 °C.

General synthesis for 3,5-dihexyloxybenzene MIDA boronates- 3,5-dihexyloxybromobenzene (3.874 g, 15.13 mmol) in 40 mL of THF was put under N_2 atmosphere in a schlenck flask. 1.6 M BuLi in hexanes (11.35 mL, 18.17 mmol) was added drop-wise and let stir for 30 minutes at -78° C. triisopropylborate (6.98 mL, 30.25 mmol) was added dropwise at -78° C then let warm to room temperature and stir for 12 hours. 20 mL of 3 M HCl was then added and the reaction was stirred for 30 minutes the resulting crude boronic acid was then take directly on to further synthesis. For characterization, the crude boronic acid (60 mg 0.187 mmol) and N-methyliminodiactetic acid (30 mg, 0.224 mmol) were dissolved in 15 ml of toluene and 1.2 mL of DMSO. The reaction was then refluxed with a Dean Stark trap for 3 hours. The solvent was removed resulting in yellow oil, which was purified with flash column chromatography (silica gel, ethylacetate). The product 87 mg a colorless solid, was obtained in 90% yield.

(**2g**) 3,5-dihexyloxybenzene MIDA boronate- ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.91 (t, *J* = 6.4 Hz, 6 H), 1.26-1.38 (m, 8 H), 1.41-1.48 (m, 4 H), 1.76 (qnt, *J* = 8 Hz, 4 H), 2.59 (s, 3 H), 3.84 (dd J_1 = 16.4, J_2 = 54, 4H), 3.93 (t, *J* = 6.6 Hz, 4 H), 6.49 (t, *J* = 2.4 Hz, 1 H), 6.61 (d, *J* = 2.4 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 167.0, 160.6, 110.2, 102.6, 68.1, 61.7, 47.3, 31.6, 29.3, 25.7, 22.6, 14.0 ppm; IR v_{max} (film) [cm^{-1}]: 2923, 2851, 1765, 1584, 1465, 1424, 1287, 1166, 1027. HRMS (APPI-TOF, M^+) $C_{23}H_{36}BNO_5$ calc 433.2636 found 433.2873.

This journal is © The Royal Society of Chemistry 2012

(**2h**) 3,5-dioctyloxybenzene MIDA boronate- ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.88 (t, *J* = 6.8 Hz, 6 H), 1.25-1.35 (m, 16 H), 1.37-1.47 (m, 4 H), 1.72 (qnt, *J* = 2.4 Hz, 4 H), 2.55 (s, 3 H), 3.90 (t, *J* = 6.4 Hz, 4 H), 4.03 (dd J_1 = 17.2, J_2 = 171.6, 4H), 6.45 (t, *J* = 2 Hz, 1 H), 6.60 (d, *J* = 2 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.0, 160.5, 137.0, 110.1, 102.4, 68.1, 61.9, 47.8, 31.8, 29.4, 29.3, 29.2, 26.1, 22.6, 14.1 ppm; IR v_{max} (film) [cm^{-1}]: 2923, 2854, 1764, 1582, 1424, 1286, 1159, 1025, 834. HRMS (APPI-TOF, M^+) $C_{27}H_{44}BNO_5$ calc 489.3262 found 489.0255; M.P. 71-74 °C.

(**2i**) 3,5-bisdecyloxy benzene MIDA boronate- ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.85 (t, *J* = 6.8 Hz, 6 H), 1.20-1.30 (m, 24 H), 1.35-1.45 (m, 4 H), 1.71 (qnt, *J* = 8 Hz, 4 H), 2.53 (s, 3 H), 3.88 (t, *J* = 6.8 Hz, 4 H), 3.94 (dd, J_1 = 16.8, J_1 = 137.2, 4 H), 6.44 (t, *J* = 2 Hz, 1 H), 6.57 (d, *J* = 2 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 168.7, 160.9, 137.1, 110.5, 102.8, 68.4, 62.2, 48.0, 32.2, 29.9, 29.9, 29.8, 29.7, 29.7, 26.4, 23.0, 14.4 ppm; IR v_{max} (film) [cm^{-1}]: 2923, 2852, 1766, 1582, 1423, 1336, 1286, 1159, 1024, 836. HRMS (APPI-TOF, M^+) $C_{31}H_{52}BNO_5$ calc 545.3889 found 545.4114.

(**2j**) 3,5-didodecyloxybenzene MIDA boronate- ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.81 (t, *J* = 6.8 Hz, 6 H), 1.20-1.30 (m, 32 H), 1.30-1.40 (m, 4 H), 1.67 (qnt, *J* = 8 Hz, 4 H), 2.55 (s, 3 H), 3.84 (t, *J* = 6.8 Hz, 4 H), 3.84 (dd, J_1 = 16.4, J_1 = 105.2, 4 H), 6.53 (t, *J* = 2.4 Hz, 1 H), 6.41 (d, *J* = 2.4 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 168.2, 160.9, 110.5, 102.9, 68.6, 62.2, 47.9, 32.3, 30.0, 30.0, 30.0, 29.9, 29.8, 29.7, 26.4, 23.0, 14.5 ppm; IR v_{max} (film) [cm^{-1}]: 2923, 2853, 1769, 1423, 1338, 1286, 1161, 1026. HRMS (APPI-TOF, M^+) $C_{35}H_{60}BNO_5$ calc 601.4515 found 601.4729; M.P. 116-117 °C.

(**2k**) 3,5-di(3,7-dimetyloctyloxy)benzene MIDA boronate- ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.80 (d, *J* = 6.8 Hz, 12 H), 0.86 (d, *J* = 6.4 Hz, 6 H), 1.05-1.12 (m, 6 H), 1.16-1.30 (m, 6 H), 1.41-1.51 (m, 4 H), 1.54-1.62 (m, 2 H), 1.69-1.78 (m, 2 H), 2.50 (s, 3 H), 3.84-3.93 (m, 4 H), 3.85 (dd, J_1 = 16.4 Hz, J_1 = 112.4 Hz, 4 H), 6.41 (t, *J* = 2 Hz, 2 H), 6.53 (d, *J* = 2 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 167.0, 159.5, 109.2, 101.5, 65.4, 60.8, 46.6, 38.2, 36.3, 35.3, 28.8, 27.0, 23.6, 21.7, 18.6 ppm; IR v_{max} (film) [cm^{-1}]: 2953, 2924, 2868, 1769, 1585, 1424, 1335, 1286, 1163, 1028, 840. HRMS (APPI-TOF, M^+) $C_{31}H_{52}BNO_5$ calc 545.3889 found 545.4109.

(**2l**) 3,5-di(2-ethylhexyloxy)benzene MIDA boronate- ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.88-0.92 (m, 12 H), 1.27-1.34 (m, 8 H), 1.35-1.55 (m, 8 H), 1.67 (spt, *J* = 4.8 Hz, 2 H), 2.43 (s, 3 H), 3.80-3.82 (m, 4 H), 3.98 (dd, J_1 = 13.6 Hz, J_1 = 141.2 Hz, 4 H), 6.48 (t, *J* = 1.6 Hz, 2 H), 6.60 (d, *J* = 1.6 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 168.4, 160.8, 136.6, 110.1, 102.4 70.5, 61.9, 47.7, 39.5, 30.5, 29.1, 23.8, 23.0, 14.1, 11.1 ppm; IR v_{max} (flim IR v_{max} (flim) [cm^{-1}]: 2957, 2927, 2858, 1766, 1584, 1423, 1338, 1281, 1167, 1024, 836, 768. HRMS (APPI-TOF, M^+) $C_{27}H_{44}BNO_5$ calc 489.3262 found 489.3308; M.P. 179-180 °C.

General synthesis for p-substituted triphenylene catechol boronate discotics- p-(3,7-dimethyloctyl)oxybenzene boronic acid (1.38 g, 5.54 mmol) and hexahydroxytriphenylene (0.449 g, 1.39 mmol) were dissolved in 60 mL of acetonitrile

This journal is © The Royal Society of Chemistry 2012

and refluxed for 12 hours or until the product precipitated out of solution. The product was then obtained by vacuum filtration, and purified by dissolving in chloroform and passing through a celite pad, then precipitated with acetonitrile resulting in 0.540 g of an off-white solid obtained with 40% yield.

(**4a**) p-hexyloxy discotic - ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.96 (t, *J* = 5.6 Hz, 9 H), 1.35-1.42 (m, 12 H), 1.45-1.55 (m, 6 H), 1.81 (qnt, *J* = 7.2 Hz, 6 H), 3.93 (t, *J* = 6.4 Hz, 6 H), 6.91 (d, *J* = 8 Hz, 6 H), 7.91 (d, *J* = 8 Hz, 6 H) 7.94 (s, 6 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 163.2, 148.8, 137.3, 125.9, 114.8, 105.8, 68.3, 32.1, 29.7, 26.1, 23.0, 14.4 ppm; IR ν_{max} (film) [cm^{-1}]: 2913, 2850, 1757, 1593, 1601, 1219, 1177, 998, 859, 816, 622. HRMS (APPI-TOF, M^+) $C_{54}H_{57}B_3O_9$ calc 882.4277 found 882.4117.

(**4b**) p-octyloxy discotic - ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.93 (t, *J* = 6.8 Hz, 9 H), 1.30-1.43 (m, 24 H), 1.47-1.54 (m, 6 H), 1.83 (qnt, *J* = 7.2, 6 H), 3.95 (t, *J* = 6.8 Hz, 6 H), 6.92 (d, *J* = 8.4 Hz, 6 H), 7.93 (d, *J* = 8.4 Hz, 6 H), 7.97 (s, 6 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 163.0, 148.6, 137.3, 125.7, 114.7, 68.2, 60.5, 32.3, 29.8, 29.7, 29.7, 26.5, 23.1, 14.5 ppm; IR ν_{max} (film) [cm^{-1}]: 2912, 2847, 1759, 1742, 1591, 1604, 1219, 1176, 996, 858, 815, 623. HRMS (APPI-TOF, M^+) $C_{60}H_{69}B_3O_9$ calc 966.5215 found 966.4987.

(**4c**) p-decyloxy discotic - ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.92 (t, *J* = 6.8 Hz, 9 H), 1.26-1.40 (m, 36 H), 1.45-1.54 (m, 6 H), 1.82 (qnt, *J* = 8 Hz, 6 H), 3.96 (t, *J* = 6.4 Hz, 6 H), 6.93 (d, *J* = 8.4 Hz, 6 H), 7.95 (d, *J* = 8.4 Hz, 6 H), 8.03 (s, 6 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 162.8, 148.3, 137.1, 125.5, 114.5, 105.4, 68.1, 32.3, 30.1, 30.0, 29.9, 29.8, 29.7, 26.5, 23.1, 14.5 ppm; IR ν_{max} (film) [cm^{-1}]: 2911, 2850, 1759, 1740, 1590, 1603, 1222, 1177, 993, 816, 624. HRMS (APPI-TOF, M^+) $C_{66}H_{81}B_3O_9$ calc 1050.6152 found 1050.5898.

(**4d**) p-dodecyloxy discotic - ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.90 (t, *J* = 7.2 Hz, 9 H), 1.26-1.40 (m, 48 H), 1.45-1.54 (m, 6 H), 1.82 (qnt, *J* = 7.6 Hz, 6 H), 3.96 (t, *J* = 8.8 Hz, 6 H), 6.92 (d, *J* = 8.4 Hz, 6 H), 7.94 (d, *J* = 8.4 Hz, 6 H), 8.01 (s, 6 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 162.6, 148.1, 136.8, 125.3, 116.8, 114.3, 105.4, 67.8, 31.9, 29.7, 29.6, 29.6, 29.5, 29.3, 29.3, 26.0, 22.6, 14.0 ppm; IR ν_{max} (film) [cm^{-1}]: 2913, 2848, 1755, 1738, 1594, 1602, 1219, 1176, 996, 858, 815, 623. HRMS (APPI-TOF, M^+) $C_{72}H_{93}B_3O_9$ calc 1134.7087 found 1134.6882.

(**4m**) p-octadecyloxy discotic - ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.89 (t, *J* = 7.2 Hz, 9 H), 1.25-1.44 (m, 84 H), 1.45-1.52 (m, 6 H), 1.80 (qnt, *J* = 7.6 Hz, 6 H), 3.91 (t, *J* = 6.8 Hz, 6 H), 6.89 (d, *J* = 8.8 Hz, 6 H), 7.87 (d, *J* = 8.8 Hz, 6 H), 7.9 (s, 6 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 163.3, 148.9, 137.4, 126.0, 126.0, 114.9, 105.9, 68.4, 32.3, 30.1, 30.0, 30.0, 30.0, 29.9, 29.7, 29.7, 26.5, 23.0, 14.4 ppm; IR ν_{max} (film) [cm^{-1}]: 2910, 2849, 1760, 1742, 1590, 1602, 1217, 1179, 996, 858, 815, 623. HRMS (APPI-TOF, M^+) $C_{90}H_{129}B_3O_9$ calc 1387.9900 found 1387.9525.

(**4e**) p- (3,7-dimethyloctyloxy) discotic - ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.93 (d, *J* = 6.4 Hz, 18 H), 0.97 (d, *J* = 6.4 Hz, 9 H), 1.17-1.26 (m, 9 H), 1.30-1.42 (m, 9 H), 1.49-

This journal is © The Royal Society of Chemistry 2012

1.62 (m, 6 H), 1.62-1.69 (m, 3 H), 1.74-1.83 (m, 3 H), 3.78 (t, J = 5.6, 6 H), 6.67 (d, J = 8.4 Hz, 6 H), 7.56 (d, J = 8.0 Hz, 6 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 162.6, 147.9, 137.0, 125.0, 116.9, 114.3, 105.0, 66.4, 39.7, 37.9, 36.6, 30.4, 28.4, 25.1, 23.1, 23.0, 20.1 ppm; IR v_{max} (film) [cm^{-1}]: 2954, 2927, 2856, 1601, 1491, 1351, 1237, 1174, 1066, 832, 744. HRMS (APPI-TOF, M^+) $C_{66}H_{81}B_3O_9$ calc 1050.6152 found 1050.5684.

(**4f**) p- (2-ethylhexyloxy) discotic - ^{1}H NMR ($CDCl_3$, 400MHz) δ =0.86 (m, J = 7.2 Hz, 9 H), 0.91 (t, J = 7.6 Hz, 9 H), 1.29-1.31 (m, 12 H), 1.35-1.52 (m, 12 H), 1.71(sep, J = 6Hz, 3 H), 3.83 (d, J_1 = 5.6, J_2= 1.2 Hz, 6 H), 6.93 (d, J = 8.4 Hz, 6 H), 7.95 (d, J = 8.4 Hz, 6 H), 8.08 (s, 6 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 163.0, 148.4, 137.0, 125.5, 114.4, 105.5, 70.4, 39.3, 30.5, 29.1, 23.8, 23.1, 14.1, 11.1 ppm; IR v_{max} (film) [cm^{-1}]: 2959, 2922, 2851, 1604, 1492, 1355, 1239, 1175, 1065, 831, 731. HRMS (APPI, M^+) $C_{60}H_{69}B_3O_9$ calc 966.5215 found 966.5004.

General synthesis for 3,5-substituted triphenylene catechol boronate discotics- 3,5-bisdodecyloxybenzene boronic acid (1.818 g, 4.20 mmol) and hexahydroxytriphenylene (0.380 g, 1.05 mmol) were dissolved in 60 mL of acetonitrile and refluxed for 12 hours or until the product precipitated out of solution. The product was then obtained by vacuum filtration, and purified by passing through a celite pad with chloroform then precipitated with acetonitrile resulting in 0.1.23 g of an off-white solid obtained with 77% yield.

(**4g**) 3,5- bishexyloxy discotic - ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.89 (t, J = 7.2 Hz, 18 H), 1.29-1.36 (m, 24 H), 1.40-1.47 (m, 12 H), 1.75 (qnt, J = 7.6 Hz, 12 H), 3.87 (t, J = 6.8 Hz, 2 H), 6.49 (t, J = 2 Hz, 3 H), 7.00 (d, J = 2 Hz, 6 H), 7.93 (s, 6 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 160.1, 148.1, 125.4, 112.4, 106.3, 105.5, 68.1, 31.7, 29.4, 25.8, 22.7, 14.1 ppm; IR v_{max} (film) [cm^{-1}]: 2927, 2856, 1589, 1491, 1353, 1240, 1158, 1054, 974, 834, 690. HRMS (APPI-TOF, M^+) $C_{72}H_{93}B_3O_{12}$ calc 1182.6938 found 389.2594.

(**4h**) 3,5- bisoctyloxy discotic - ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.89 (t, J = 7.2 Hz, 18 H), 1.30-1.45 (m, 48 H), 1.45-1.57 (m, 12 H), 1.82 (qnt, J = 7.6 Hz, 12 H), 3.95 (t, J = 6.8 Hz, 2 H), 6.55 (t, J = 2 Hz, 3 H), 7.06 (d, J = 2 Hz, 6 H), 7.99 (s, 6 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 159.7, 147.4, 126.0, 124.8, 111.9, 105.9, 104.8, 67.8, 32.0, 29.7, 29.5, 29.4, 26.1, 22.7, 14.1 ppm; IR v_{max} (film) [cm^{-1}]: 2919, 2848, 1587, 1493, 1356, 1239, 1156, 1049, 976, 833, 693. HRMS (APPI-TOF, M^+) $C_{84}H_{117}B_3O_{12}$ calc 1350.8811 found 389.2594.

(**4i**) 3,5- bisdecyloxy discotic - ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.86 (t, J = 7.2 Hz, 18 H), 1.20-1.35 (m, 72 H), 1.35-1.45 (m, 12 H), 1.71 (qnt, J = 7.6 Hz, 12 H), 3.77 (t, J = 6.8 Hz, 2 H), 6.37 (t, J = 1.6 Hz, 2 H), 6.85 (d, J = 1.6 Hz, 2 H), 7.67 (s, 6 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 160.3, 148.2, 126.6, 125.5, 112.6, 106.5, 105.5, 68.3, 32.3, 30.1, 30.1, 30.0, 29.9, 29.8, 26.5, 23.1, 14.5 ppm; IR v_{max} (flim) [cm^{-1}]: 2914, 2843, 1588, 1490, 1357, 1241, 1165, 1051, 976, 832, 691. HRMS (APPI-TOF, M^+) $C_{96}H_{141}B_3O_{12}$ calc 1519.0686 found.

(**4j**) 3,5- bisdodecyloxy discotic - ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.83 (t, J = 6.4 Hz, 18 H), 1.29-1.36 (m, 100 H), 1.40-1.47 (m, 12 H), 1.74 (qnt, J = 7.2 Hz, 12 H), 3.81 (t, J =

This journal is © The Royal Society of Chemistry 2012

6.4 Hz, 12 H), 6.45 (t, *J* = 2.4 Hz, 3 H), 6.96 (d, *J* = 2 Hz, 6 H), 7.85 (s, 6 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 159.0, 146.9, 124.2, 111.3, 110.4, 105.2, 104.3, 67.0, 28.8, 28.8, 28.7, 28.7, 28.7, 28.5, 28.4, 25.2, 21.7, 13.1 ppm; IR ν_{max} (film) [cm^{-1}]: 2914, 2851, 2591, 2430, 1578, 1353, 1234, 1121, 1004, 973, 825, 640. HRMS (APPI-TOF, M^+) $C_{108}H_{165}B_3O_{12}$ calc 1687.2561 found 389.2594.

(**4k**) 3,5- bis(3,7-dimetyloctyloxy) discotic - ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.71 (d, *J* = 6.8 Hz, 36 H), 0.75 (d, *J* = 6.4, 18 H), 0.9-1.01 (m, 18 H), 1.06-1.20 (m, 18 H), 1.27-1.43 (m, 12 H), 1.45-1.52 (6 H), 1.63-1.71 (m, 6 H), 3.65-3.69 (m, 12 H), 6.54 (d, *J* = 2 Hz, 2 H), 6.87 (s, 6 H), 7.11 (d, *J* = 2 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 160.4, 148.4, 126.8, 125.7, 112.7, 106.6, 105.7 66.8, 39.7, 37.8, 36.8, 30.4, 28.4, 25.1, 23.1, 23.0, 20.1 ppm; IR ν_{max} (film) [cm^{-1}]: 2953, 2927, 2868, 1588, 1360, 1239, 1157, 1054, 975, 894, 833, 695. HRMS (APPI-TOF, M^+) $C_{96}H_{141}B_3O_{12}$ calc 1519.0686 found 1519.0372.

(**4l**) 3,5- bis(2-ethylhexyloxy) discotic - ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.91-1.01 (m, 36 H), 1.35-1.43 (m, 24 H), 1.46-1.61 (m, 24 H), 1.73-1.78 (m, 6 H), 3.86-3.91 (m, 12 H), 6.63 (s, 3 H), 7.08 (s, 6 H), 8.02 (s, 6 H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 160.8, 148.6, 126.9, 125.9, 112.8, 106.7, 106.0 71.0, 38.8, 30.9, 29.5, 24.2, 23.5, 14.5, 11.5 ppm; IR ν_{max} (film) [cm^{-1}]: 2958, 2926, 2857, 1584, 1426, 1352, 1236, 1157, 1052, 891, 831, 692. HRMS (APPI-TOF, M^+) $C_{84}H_{117}B_3O_{12}$ calc 1350.8811 found 389.2594.

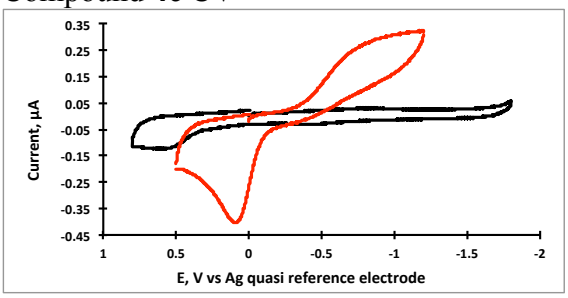
This journal is © The Royal Society of Chemistry 2012

Electrochemistry

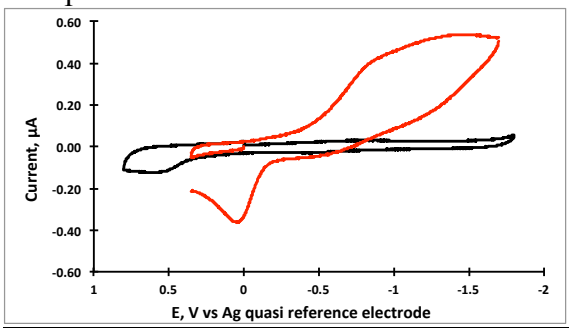
The following procedure was used to purify THF. First, THF was distilled over sodium with benzophenone under nitrogen environment. The distillate (60 ml) was collected with a cleaned, dried syringe and was transferred to the round-bottomed flask of the distillation apparatus. Next, 1.0 M Lithium aluminum hydride in THF (6 ml) was added to the same round-bottomed flask. This solution was distilled under argon atmosphere. The purified THF was used for the electrochemical studies. In this case, a three-electrode system was used where the working electrode was a Pt disc electrode (d = 0.134 cm). A Ag quasi reference electrode was used as the reference. The counter electrode was a platinum coil.

First, cyclic voltammograms (CVs) were run for the blank, which is tetrabutylammonium tetrafluoroborate (0.1 M) in THF. Next CVs were run for the DLC in the blank. Finally CVs were taken for Ferrocene in sample for the calibration.

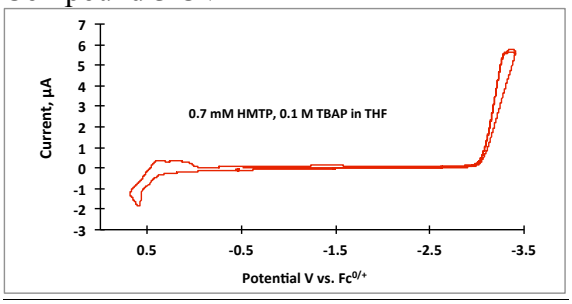
Compound **4c** CV



Compound **4k** CV



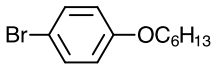
Compound **5** CV

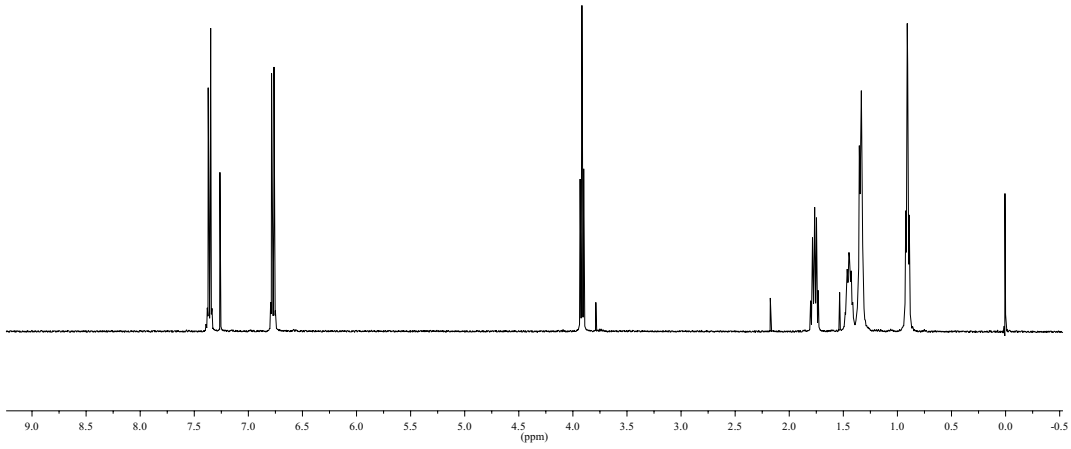


This journal is © The Royal Society of Chemistry 2012

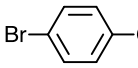
Spectra-NMR

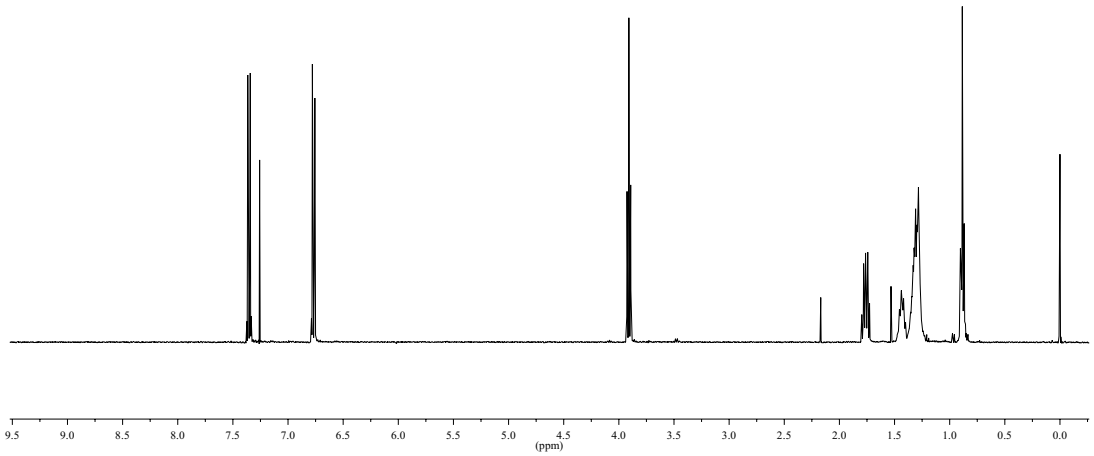
p-hexyloxybromobenzene





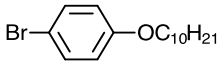
p-octyloxybromobenzene



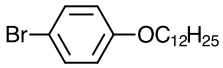


This journal is © The Royal Society of Chemistry 2012

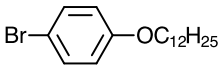
p-decyloxybromobenzene

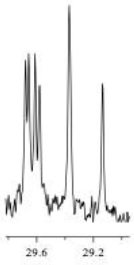


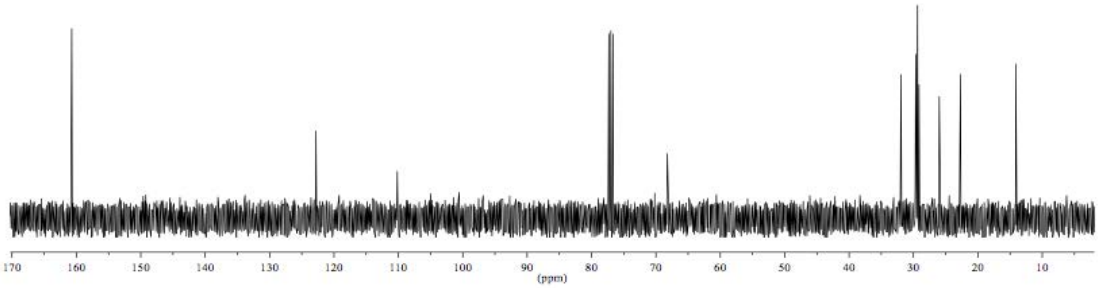
p-dodecyloxybromobenzene



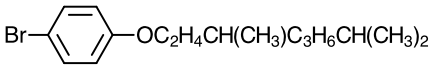
This journal is © The Royal Society of Chemistry 2012





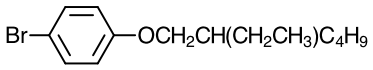


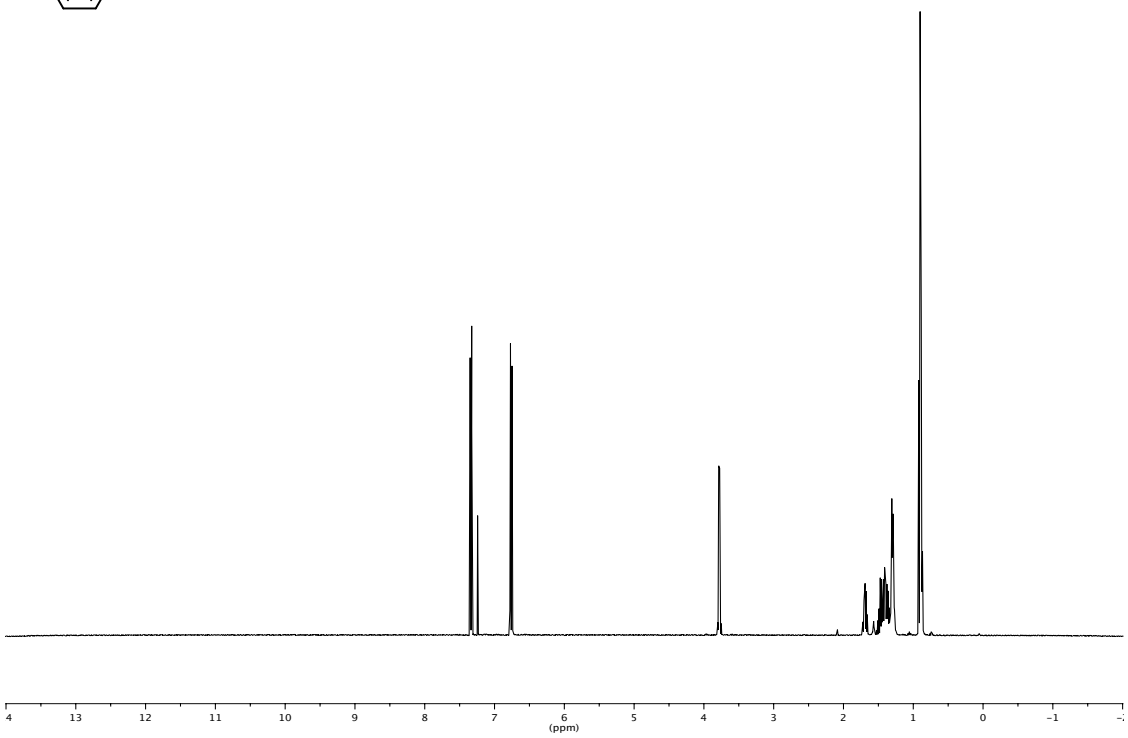
p-3,7-dimethyloctyloxybromobenzene



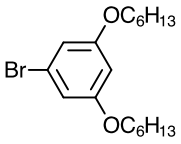
This journal is © The Royal Society of Chemistry 2012

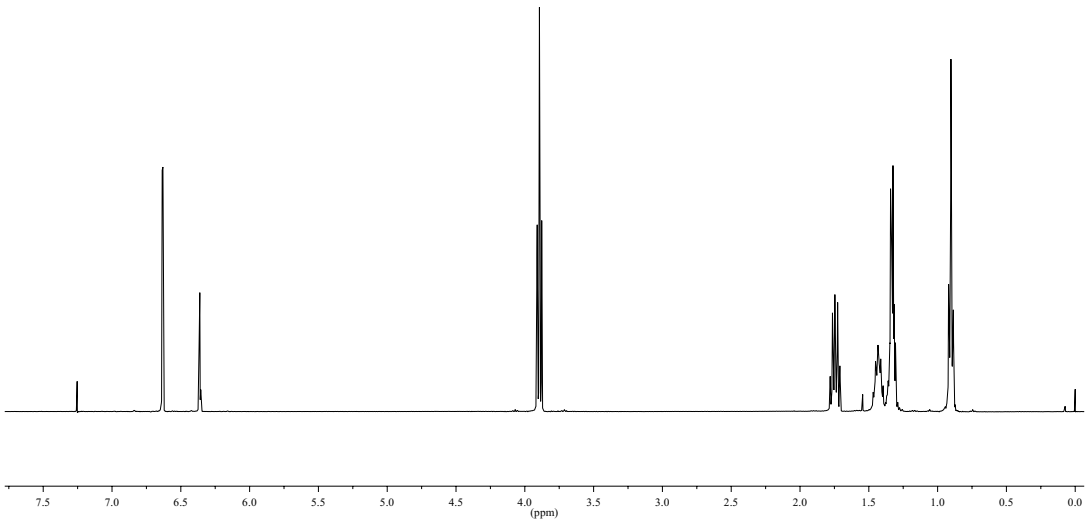
p-2-ethylhexyloxybromobenzene



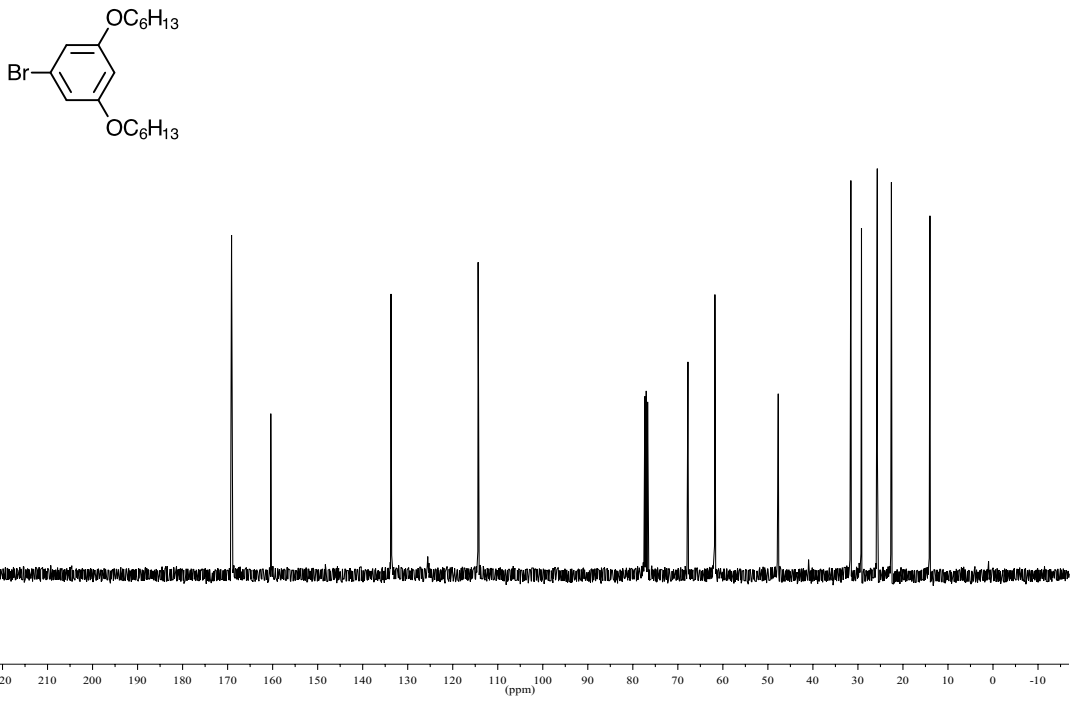


3,5-dihexyloxybromobenzene

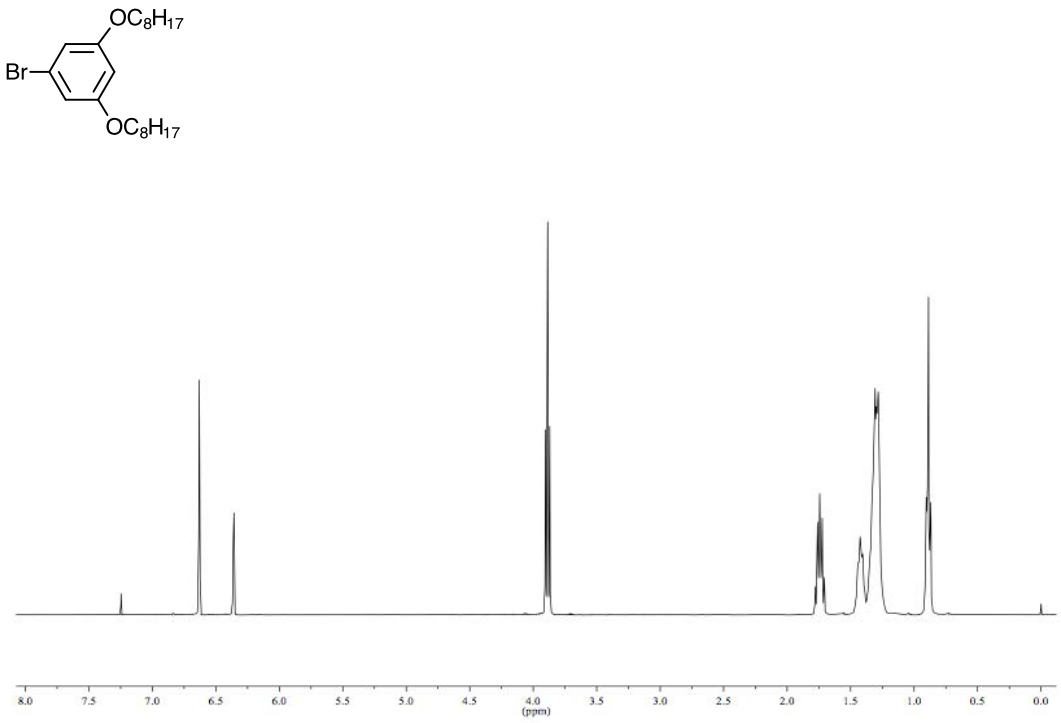


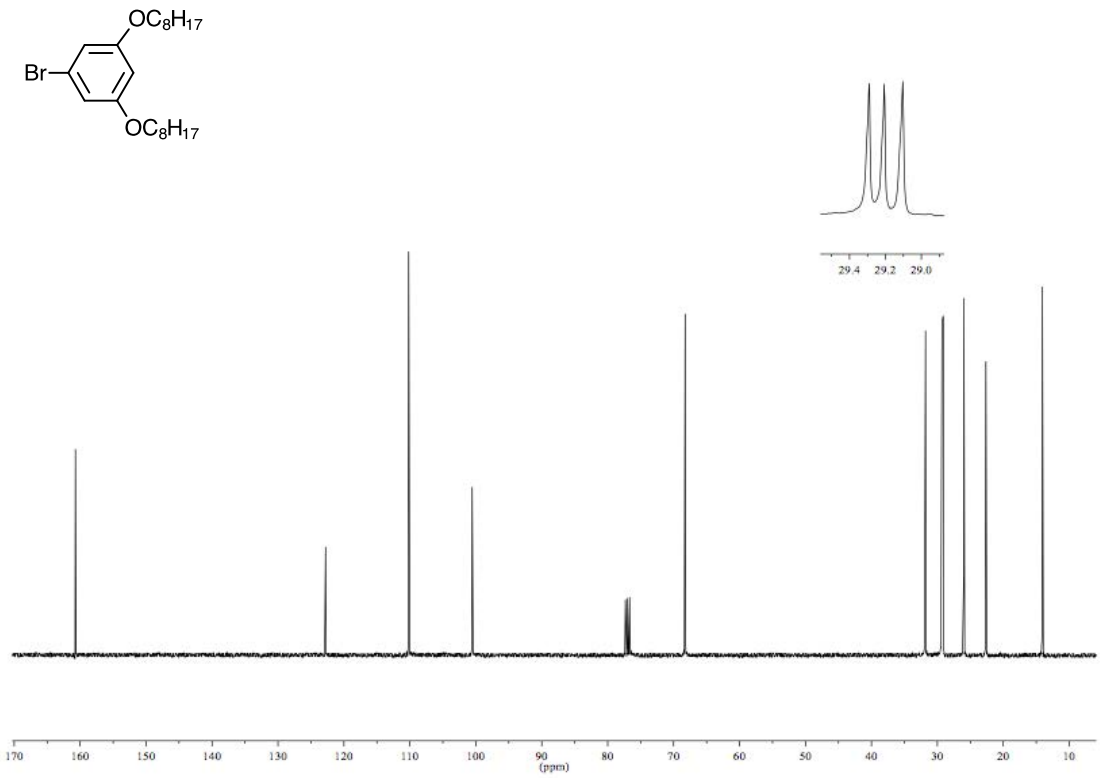


This journal is © The Royal Society of Chemistry 2012

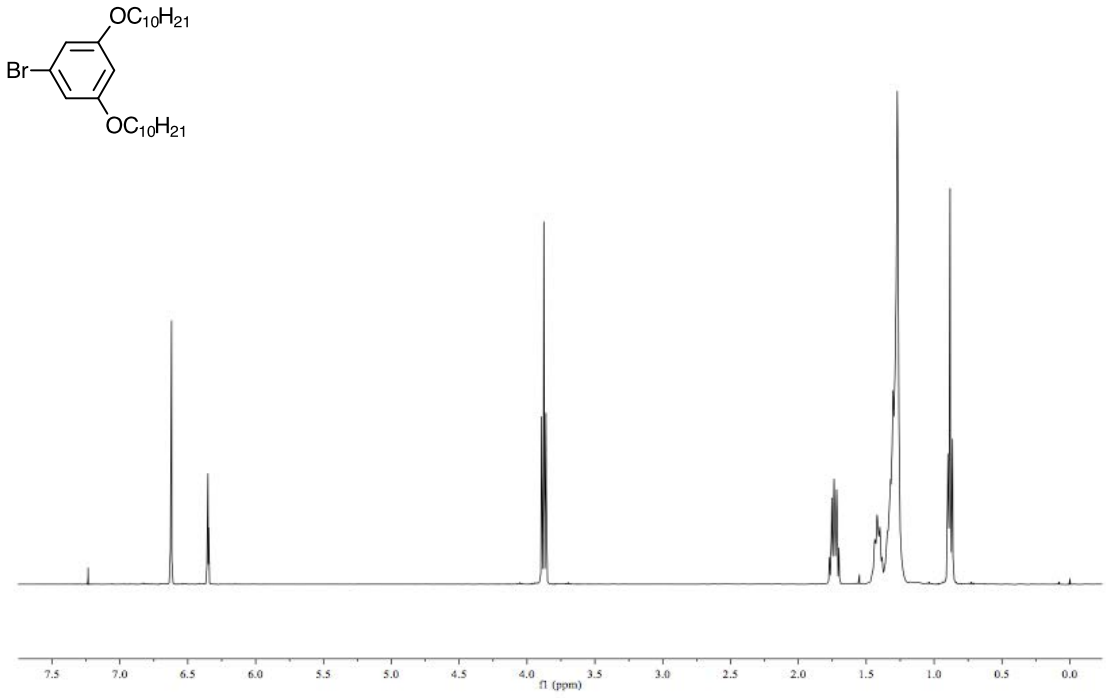


3,5-octyloxybromobenzene

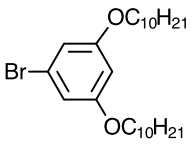


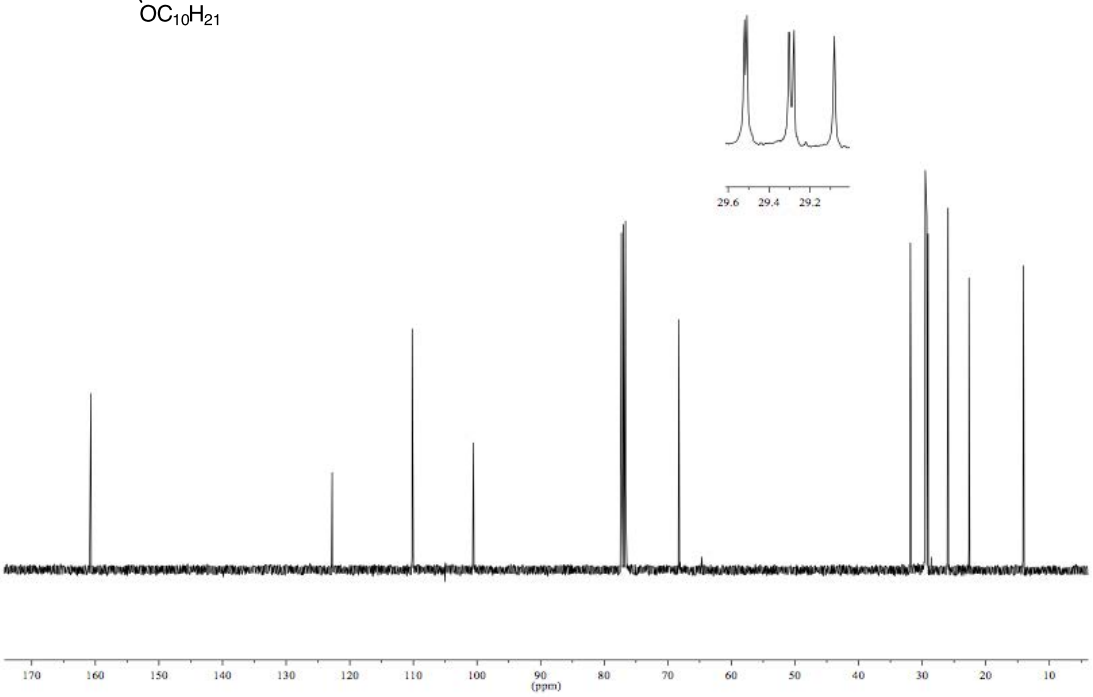


3,5-didecyloxybromobenzene

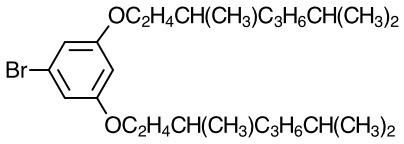


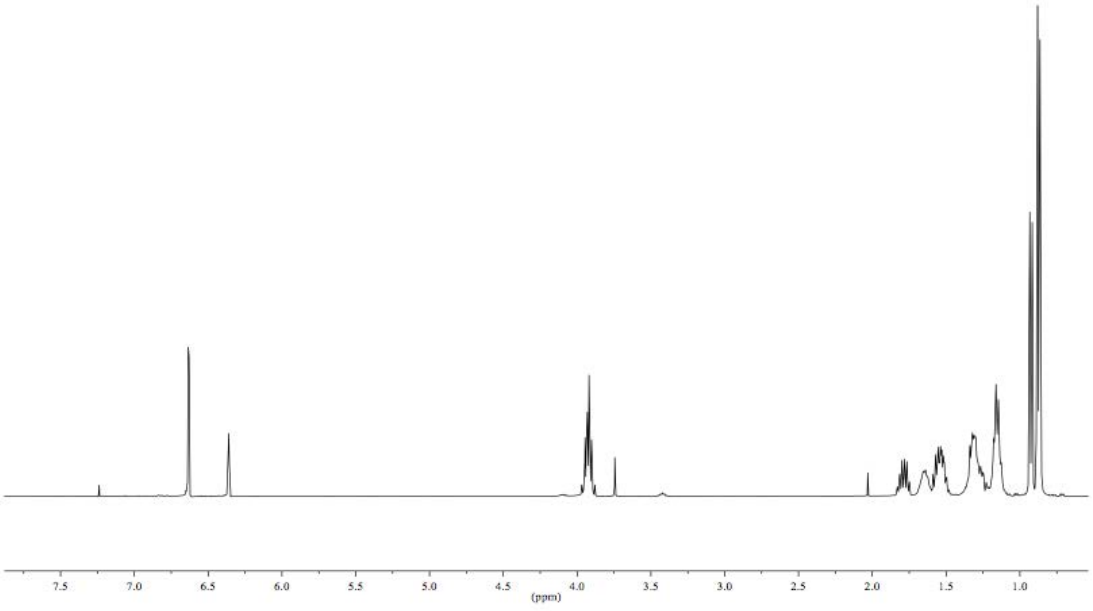
This journal is © The Royal Society of Chemistry 2012



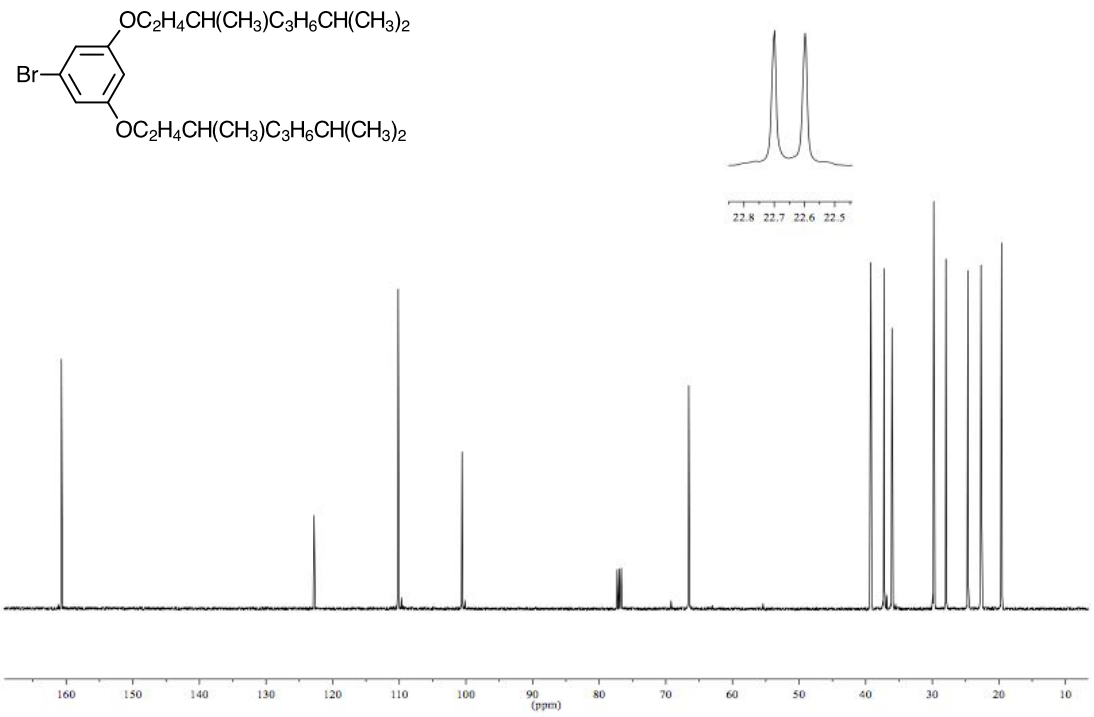


3,5-di(3,7-dimethyloctyloxy)bromobenzene

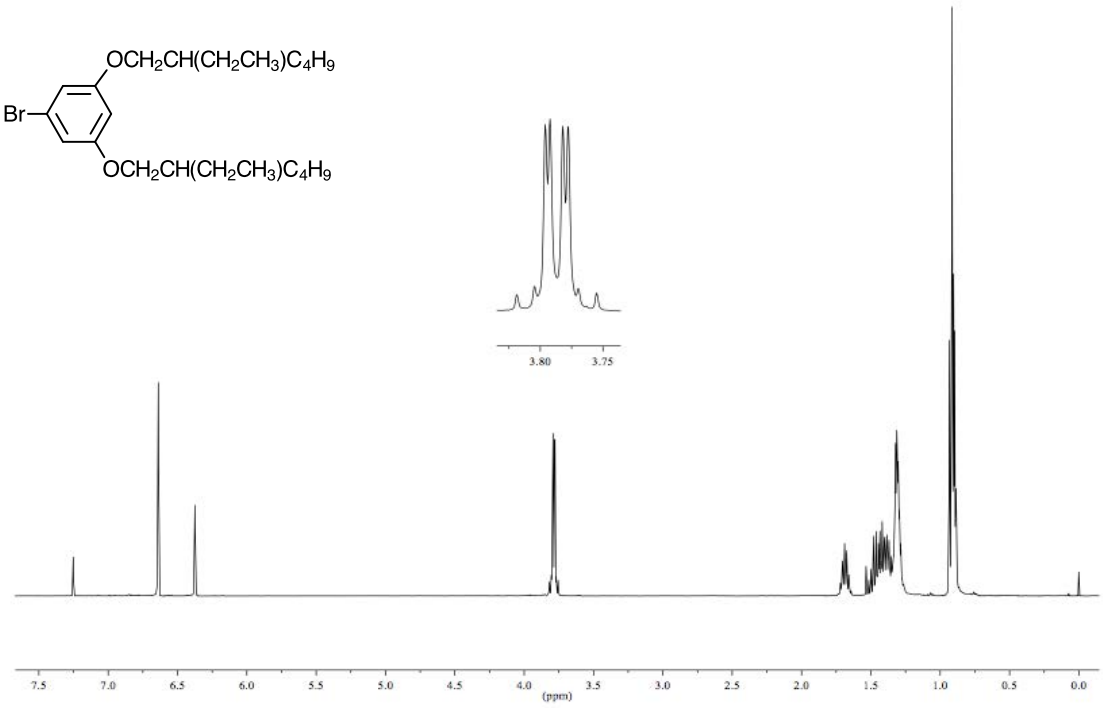


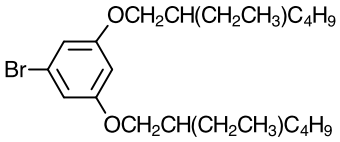


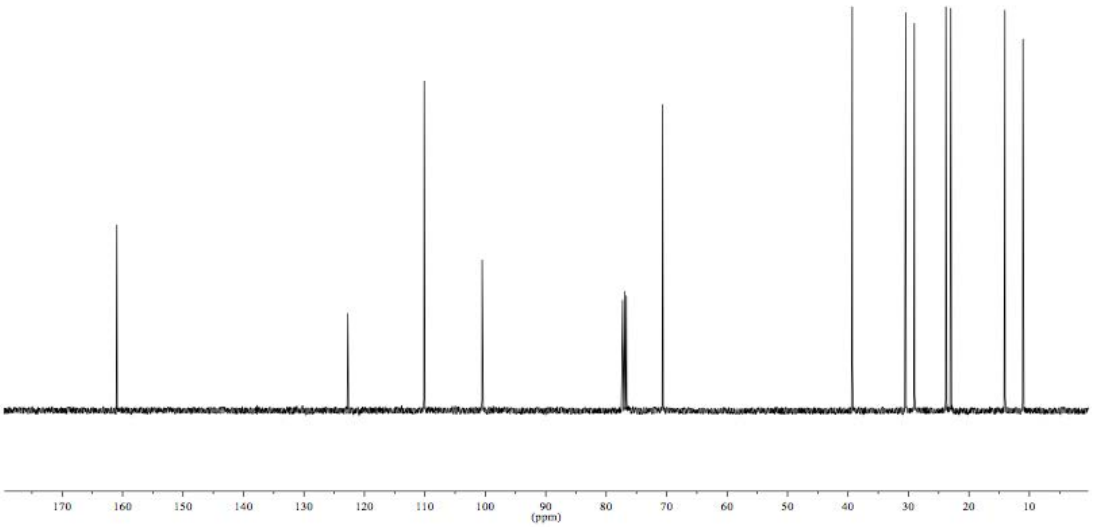
This journal is © The Royal Society of Chemistry 2012



3,5-di(2-ethylhexyloxy)bromobenzene

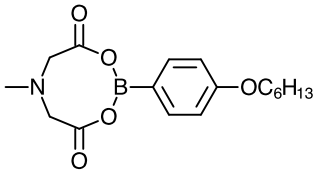


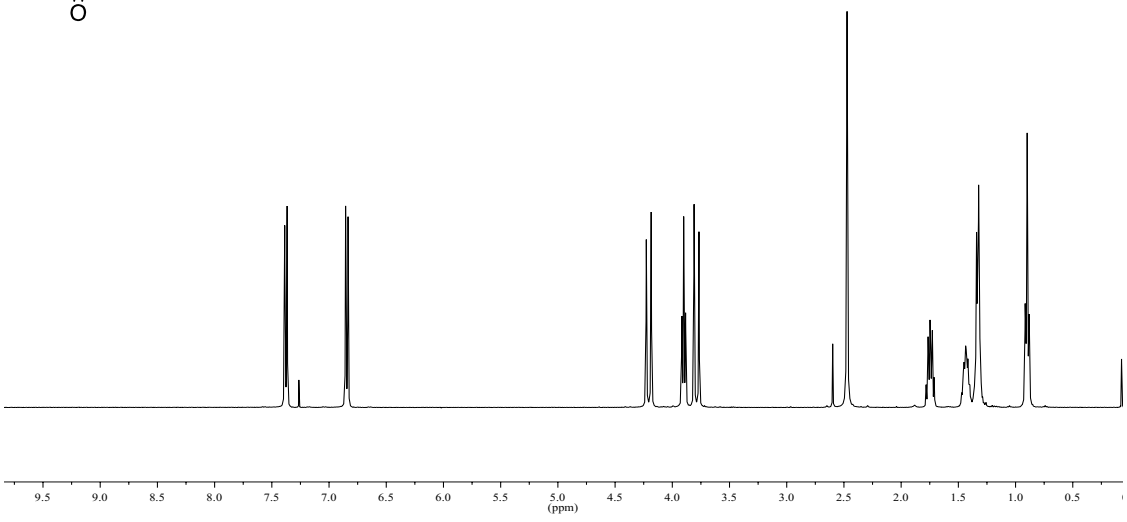


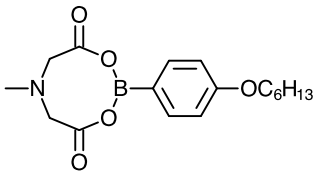


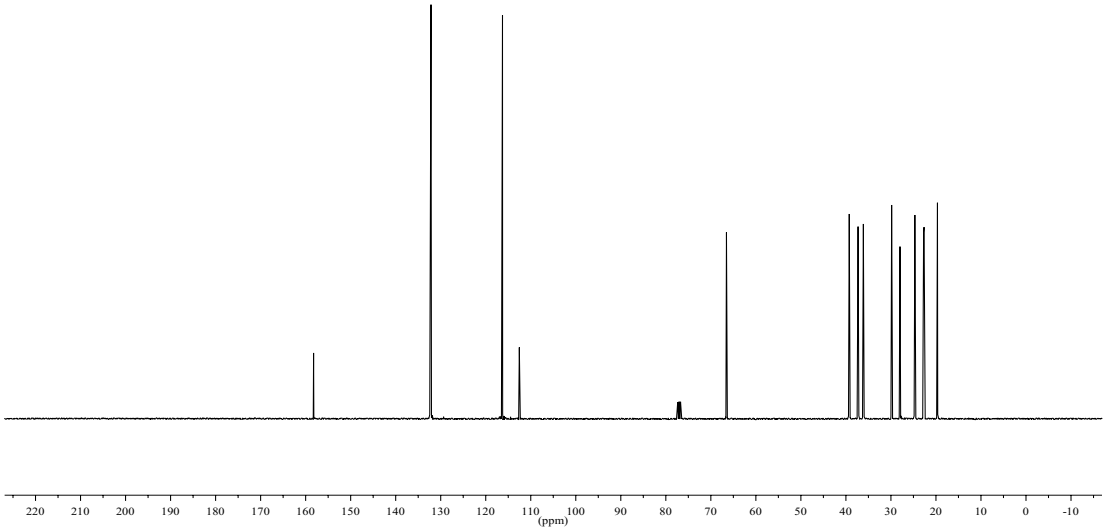
MIDA protected benzene boronic esters

p-hexyloxy MIDA

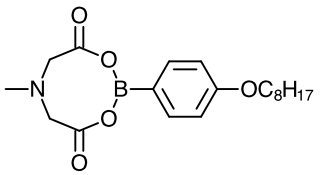


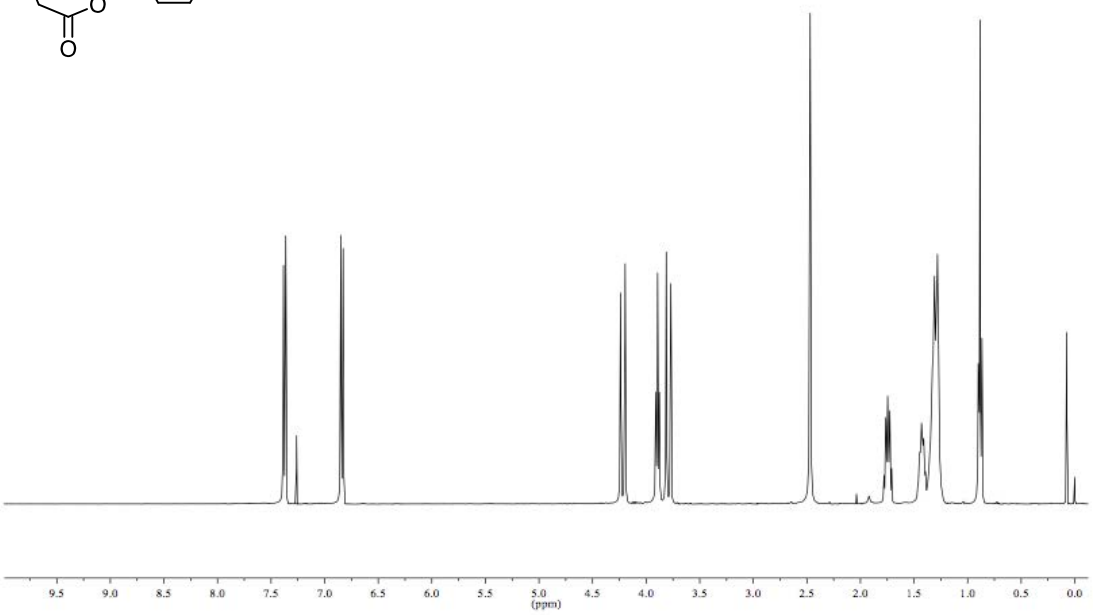




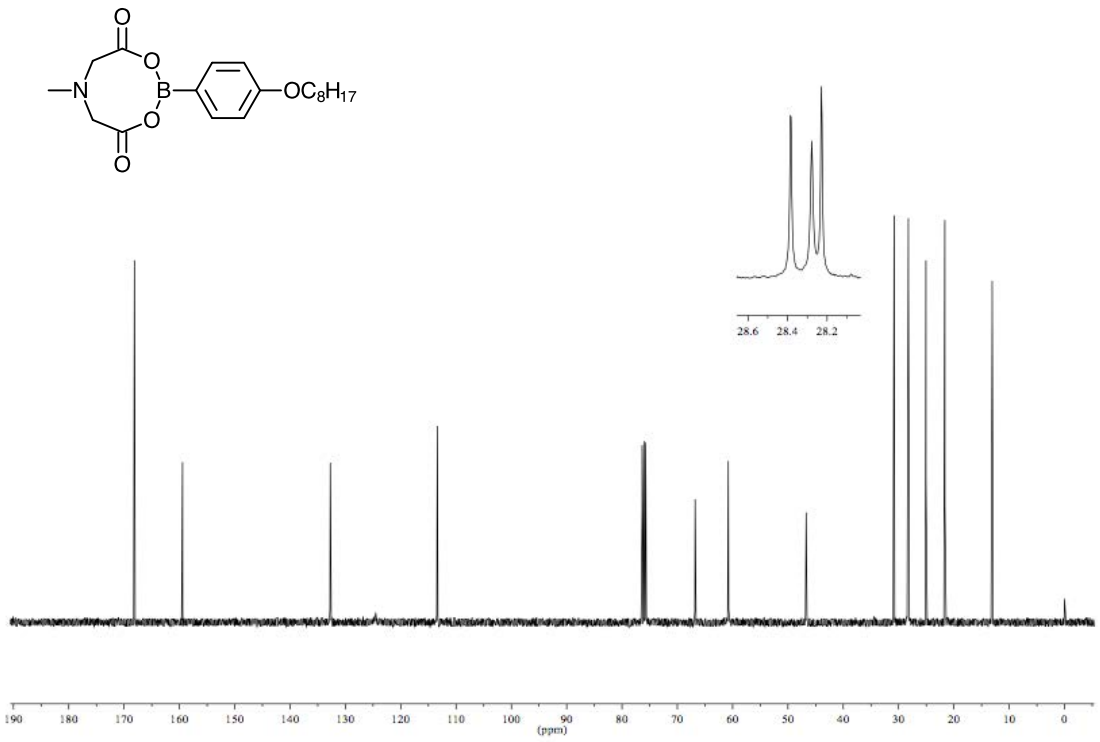


p-octyloxy MIDA

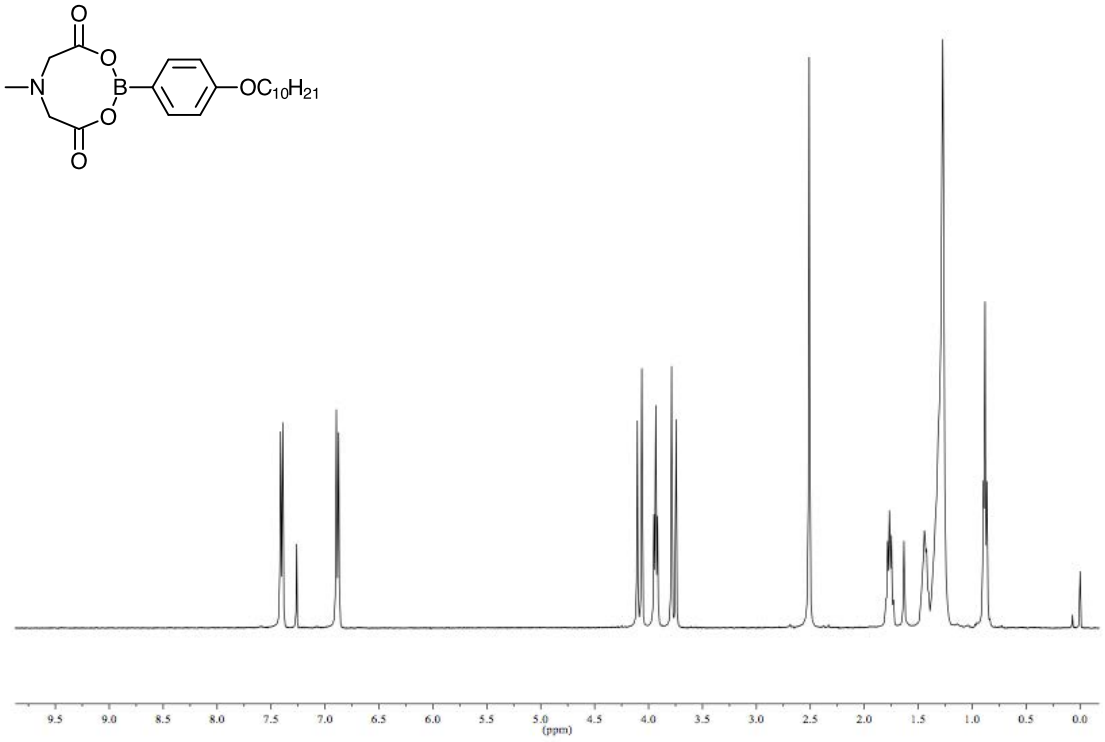


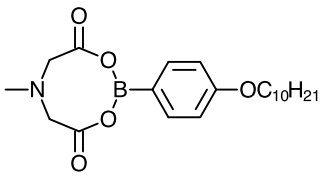


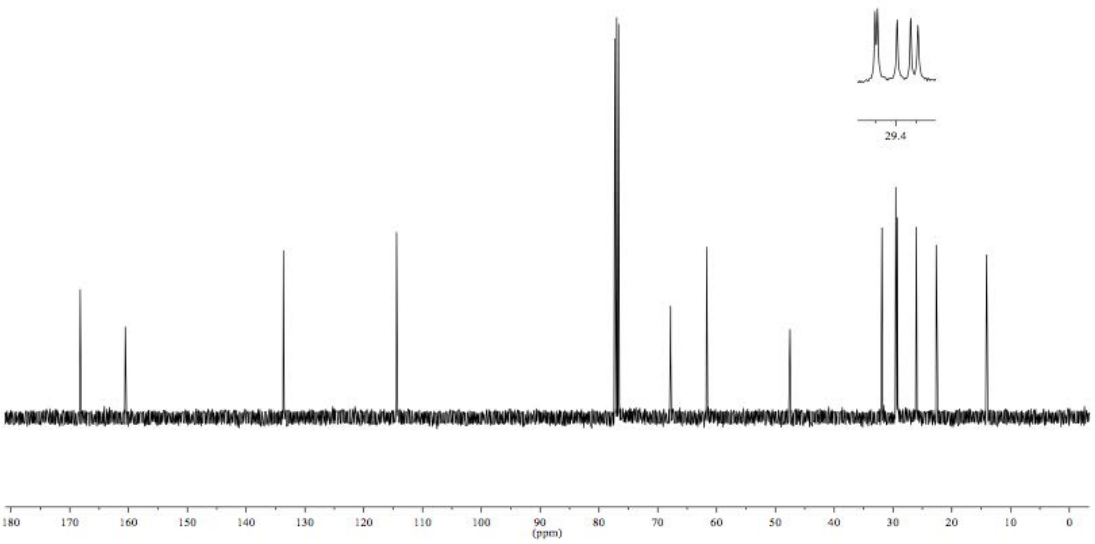
This journal is © The Royal Society of Chemistry 2012



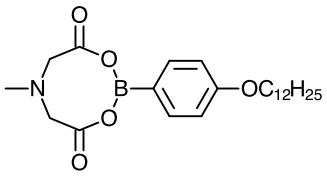
p-decyloxy MIDA

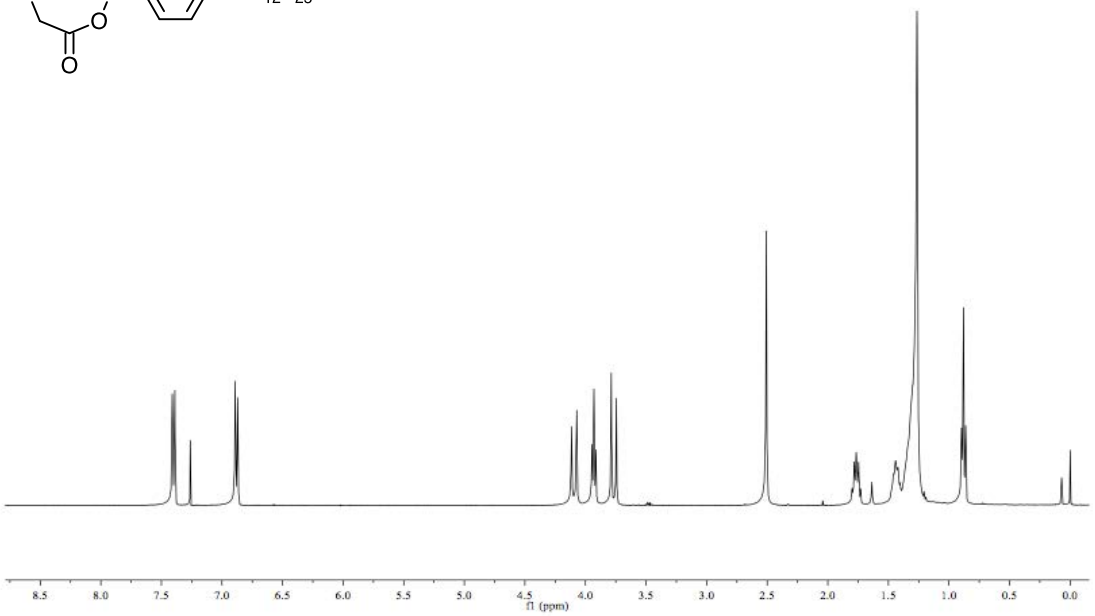


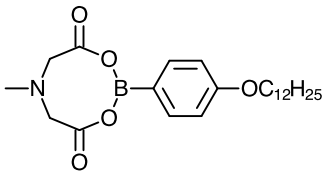


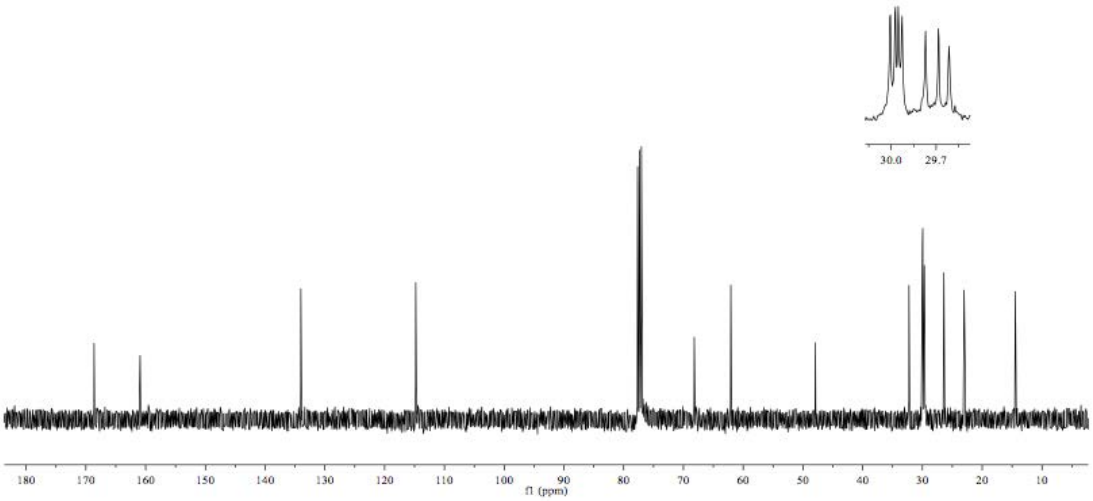


p-dodecyloxy MIDA

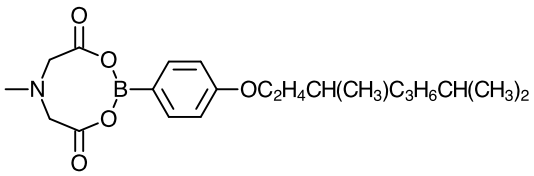


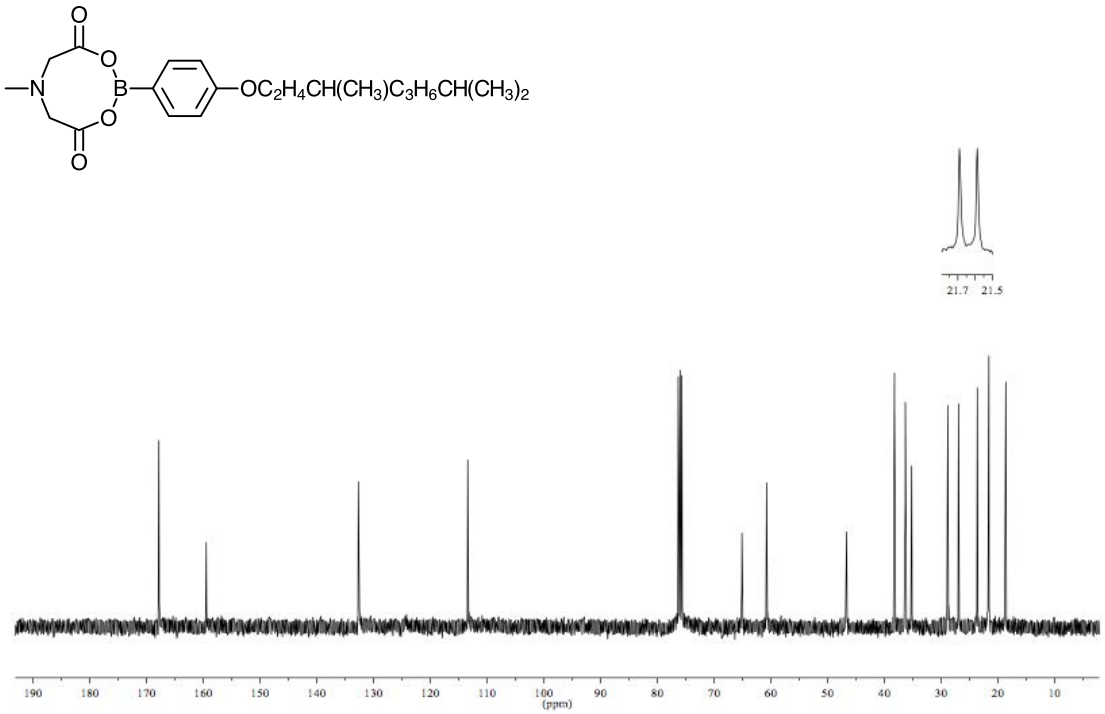




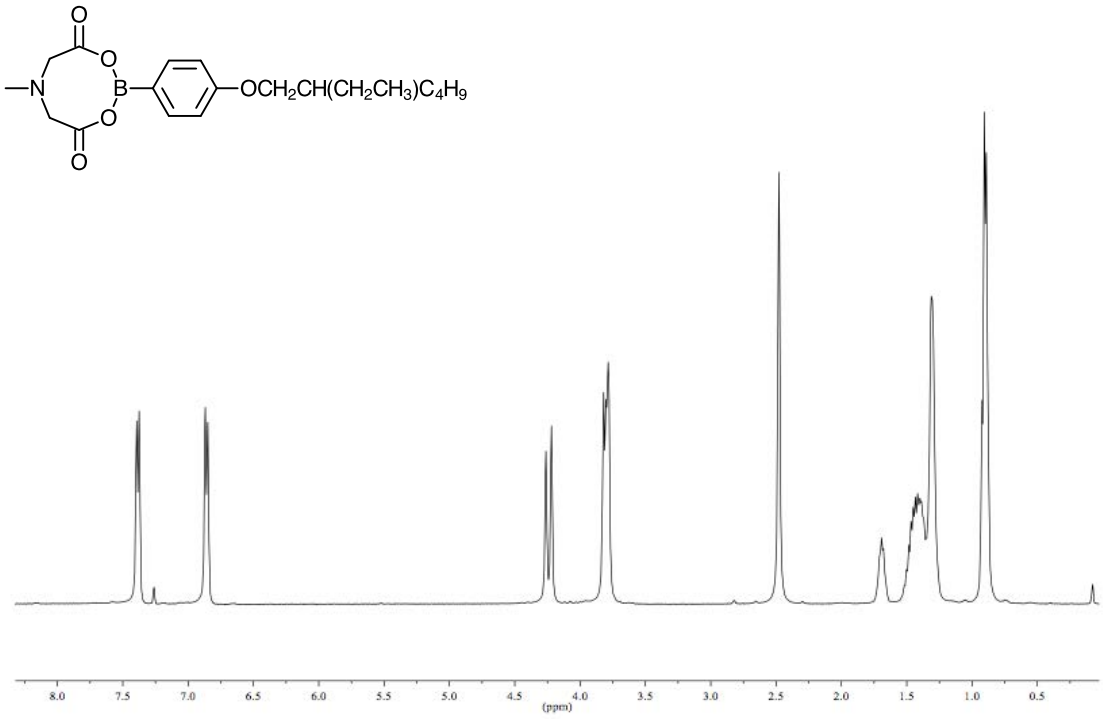


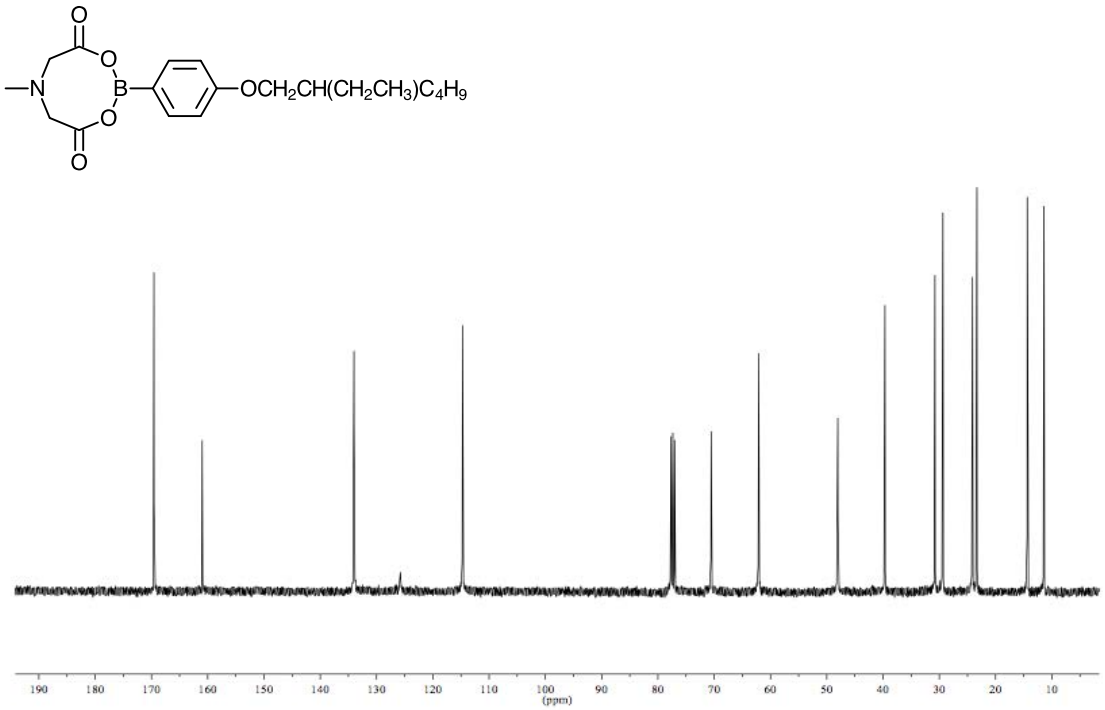
p-3,7-dimethyl octyloxy MIDA



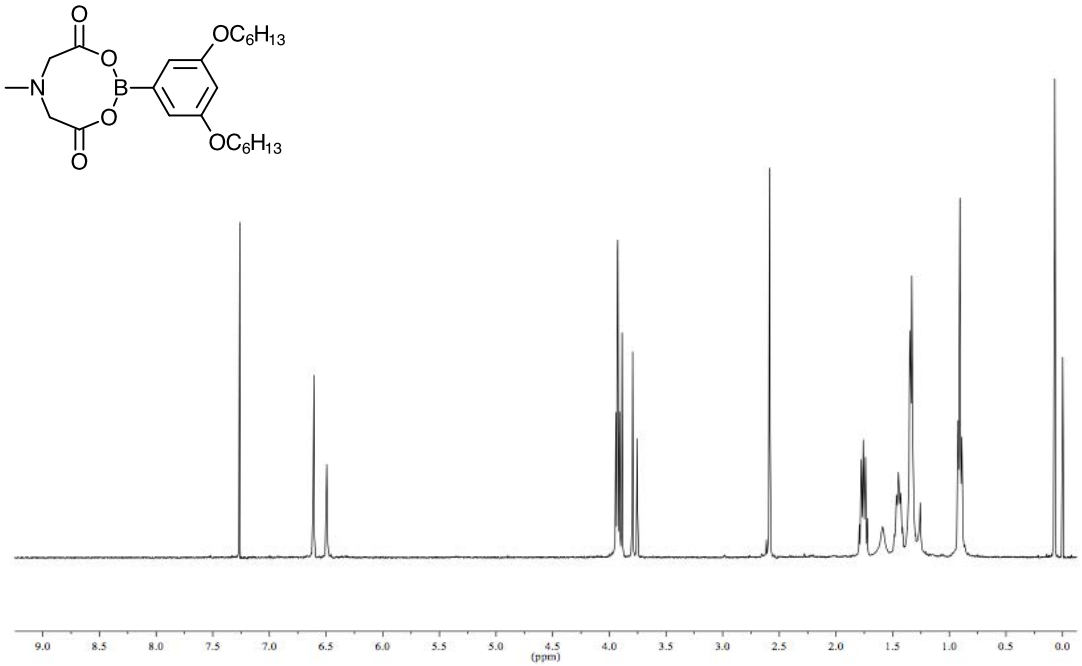


p-2-ethylhexyloxy MIDA

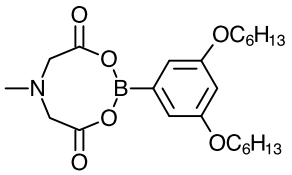


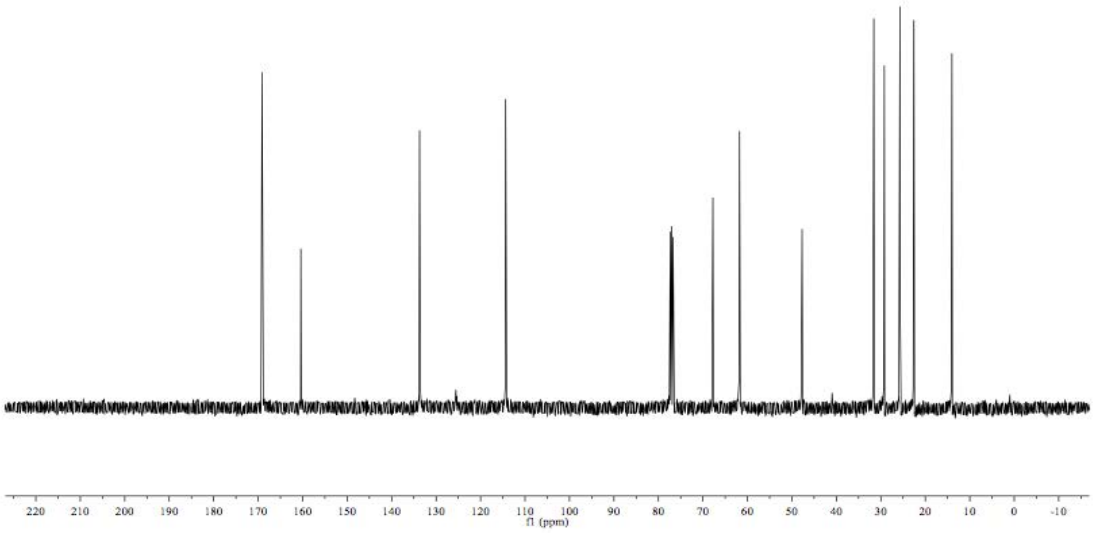


3,5-dihexyloxy MIDA

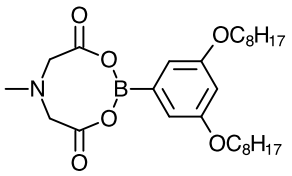


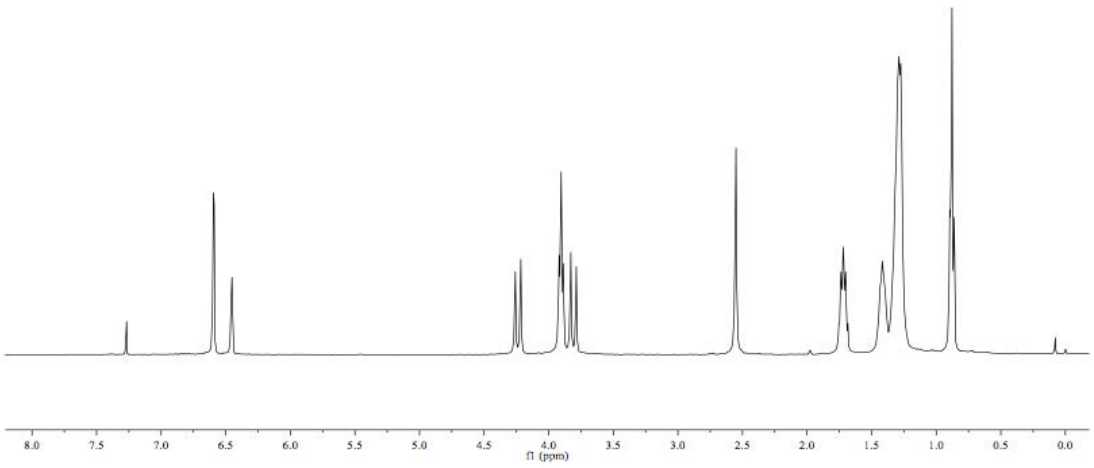
This journal is © The Royal Society of Chemistry 2012

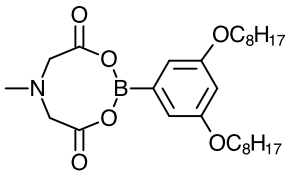




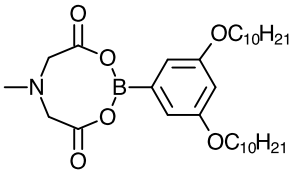
3,5-dioctyloxy MIDA

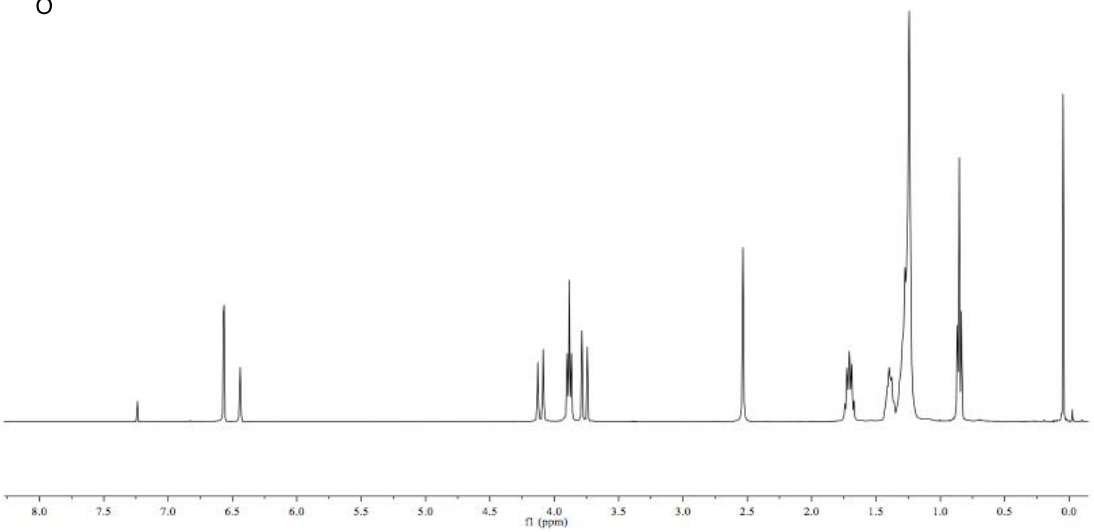


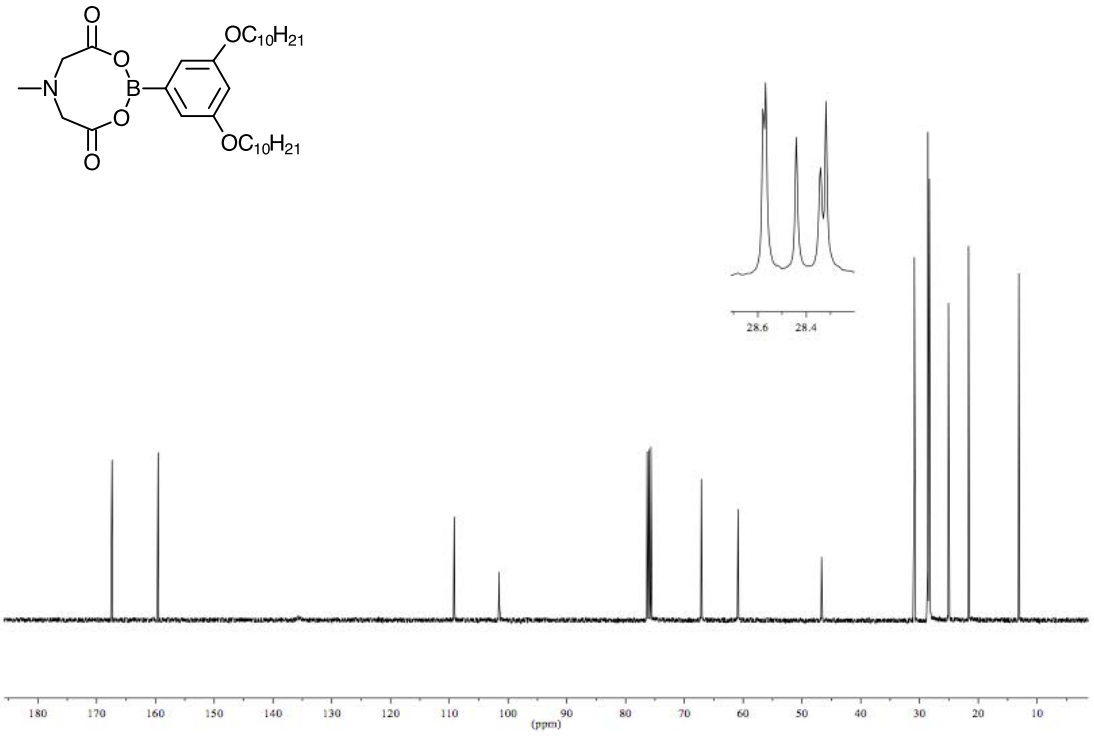




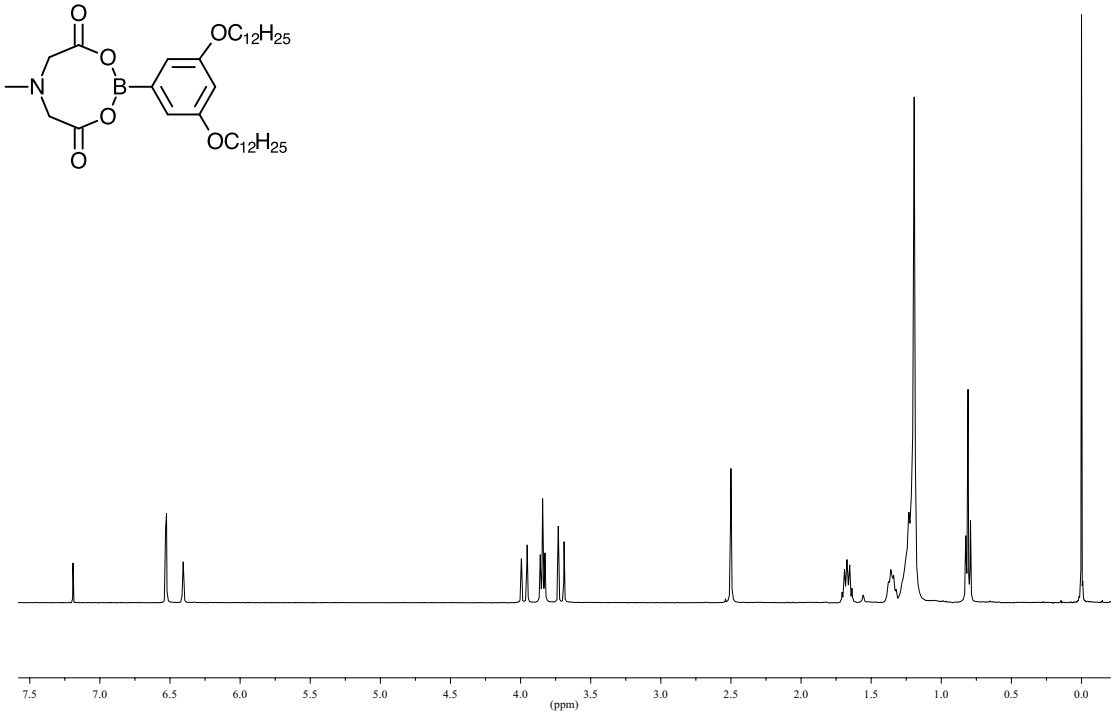
3,5-didecyloxy MIDA

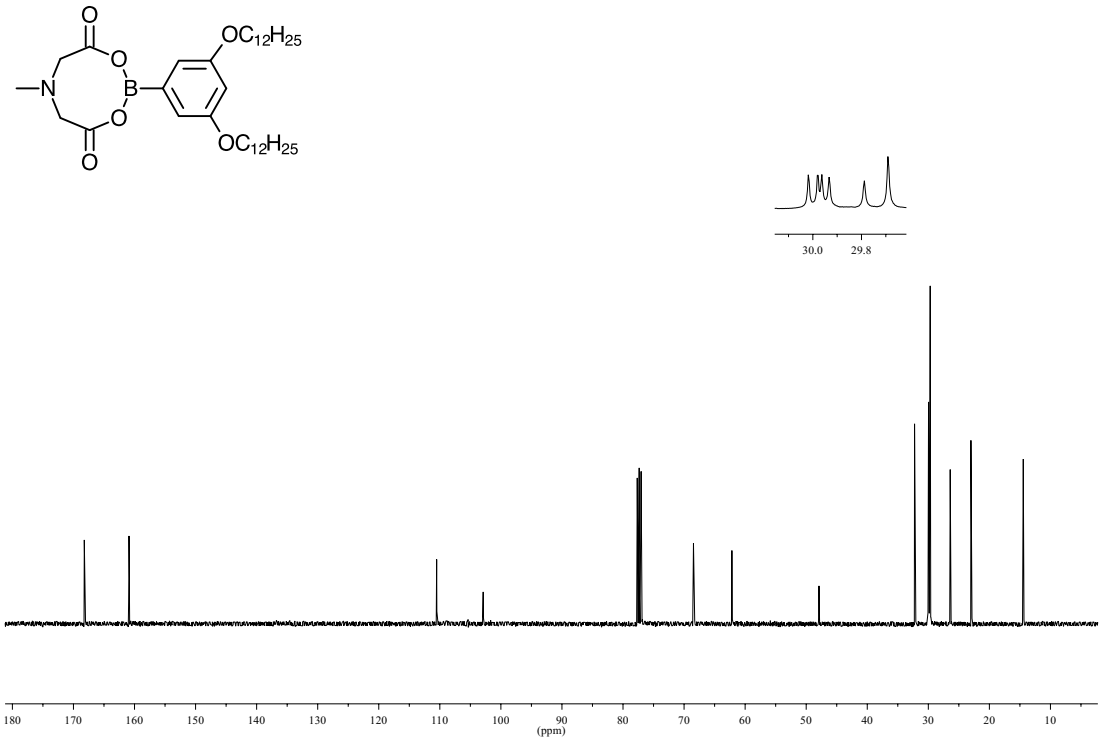




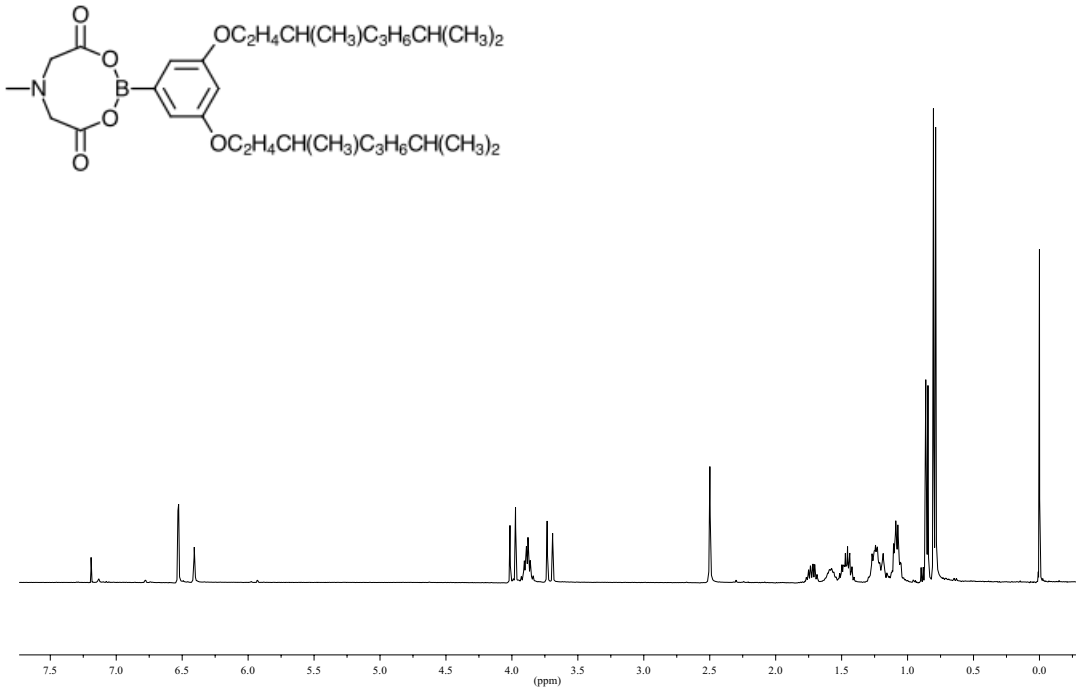


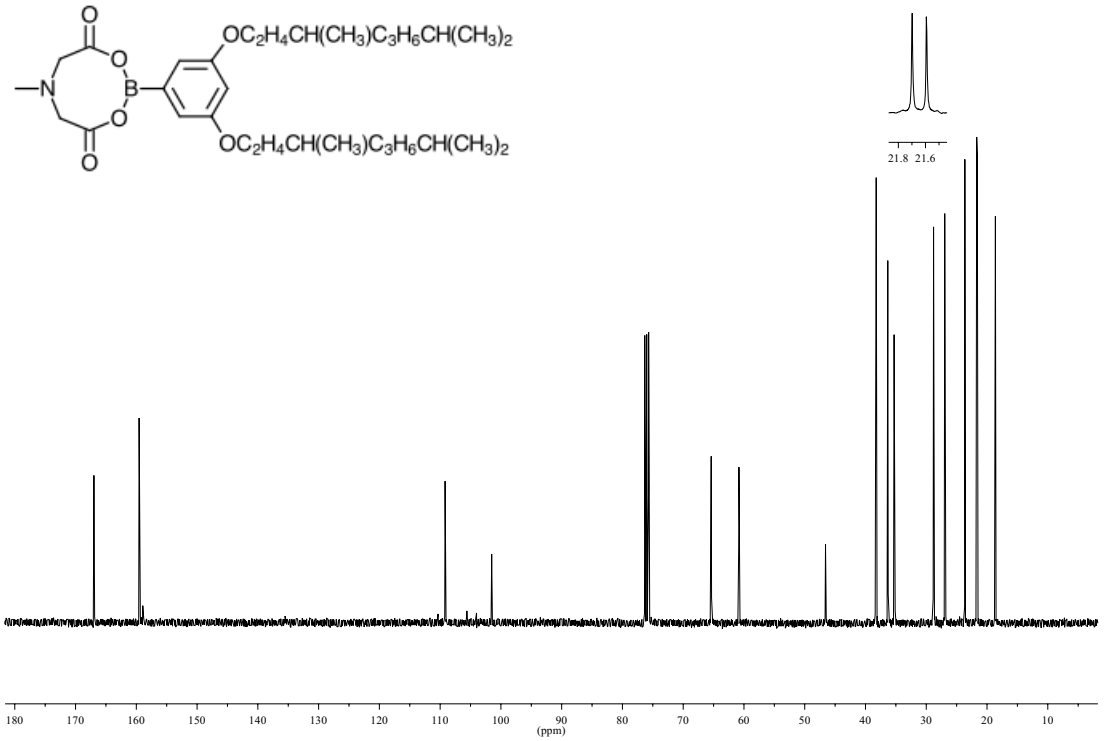
3,5-didodecyloxy MIDA



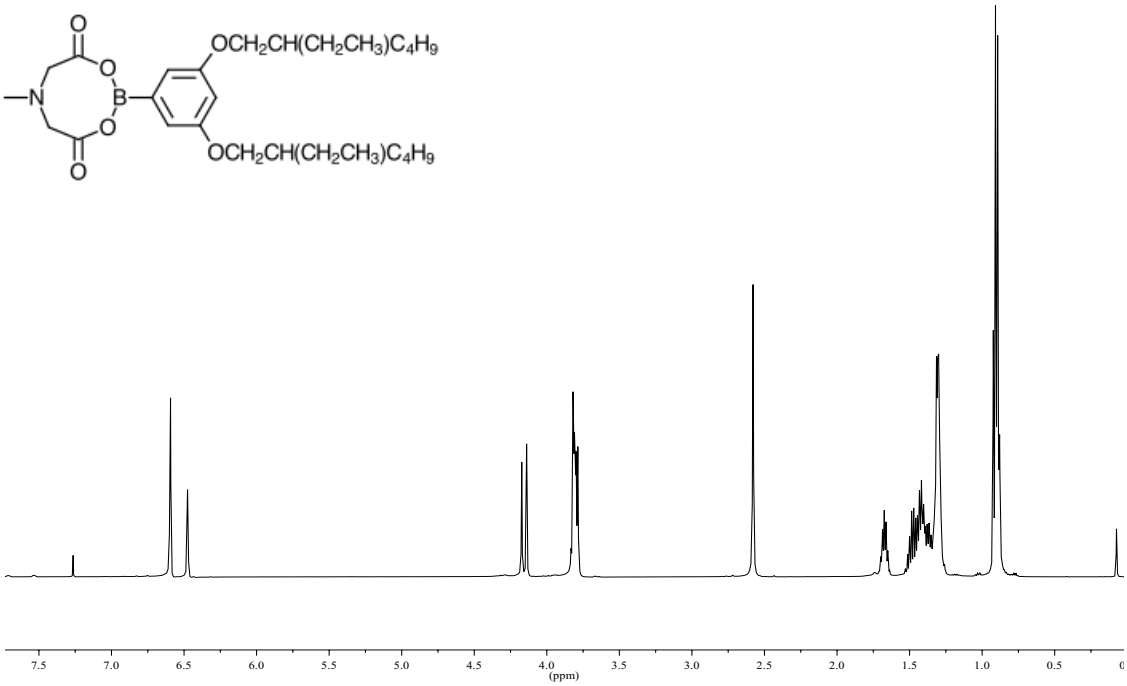


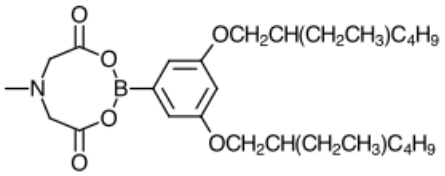
3,5-di(3,7-dimethyloctyloxy) MIDA

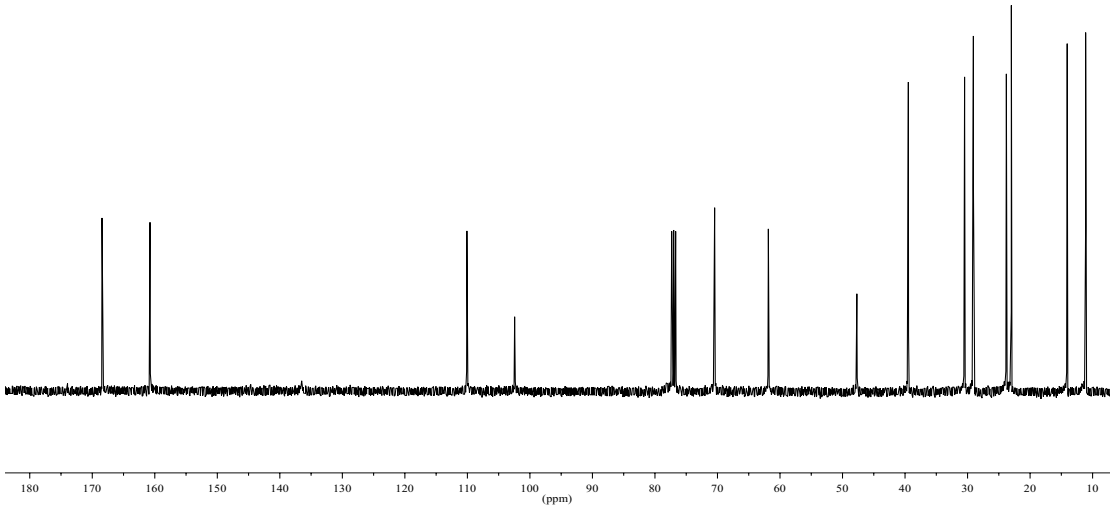




3,5-di(2-ethylhexyloxy) MIDA

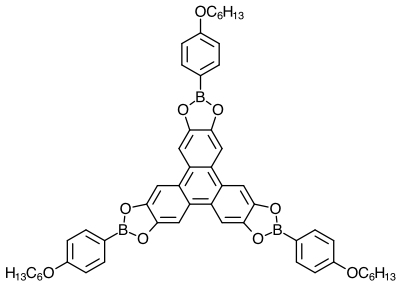


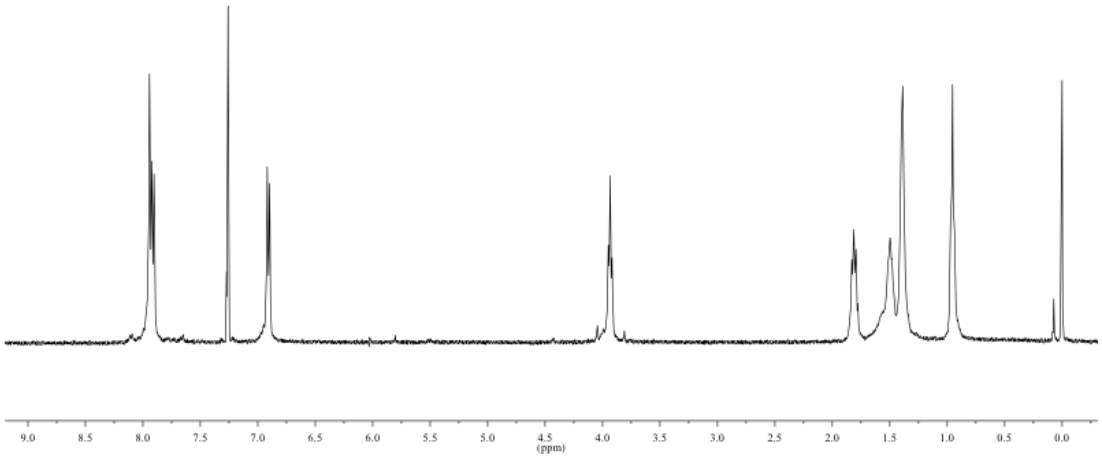


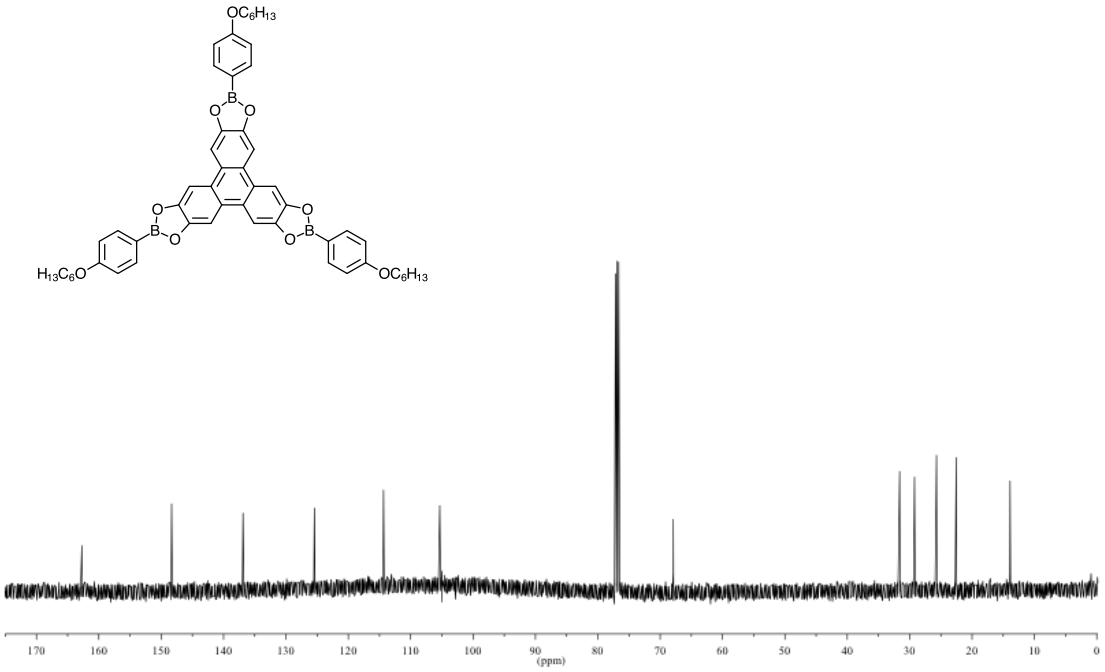


Discotics

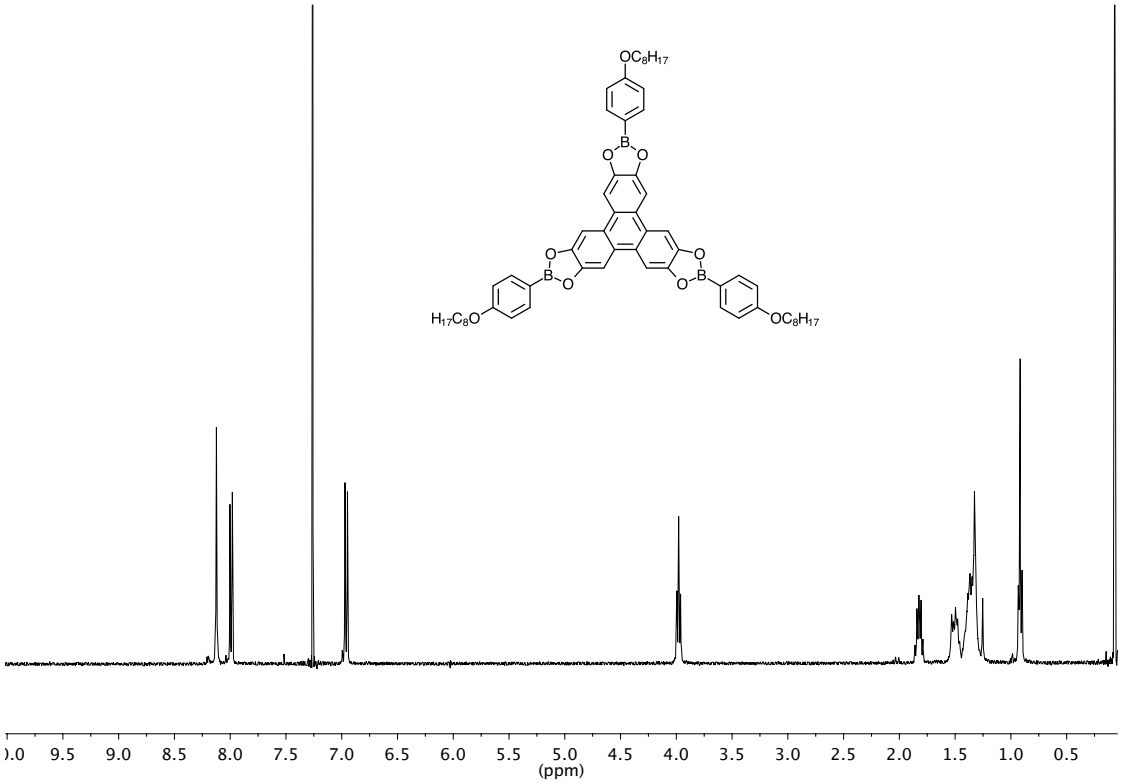
p-hexyloxy discotic



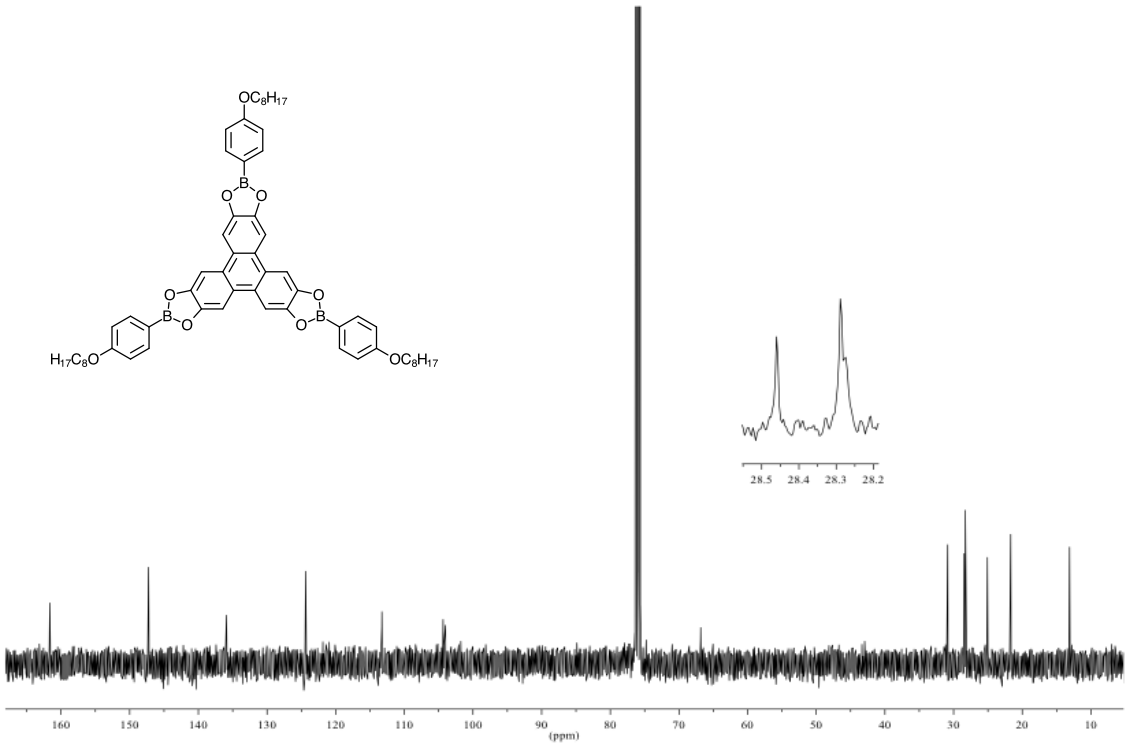




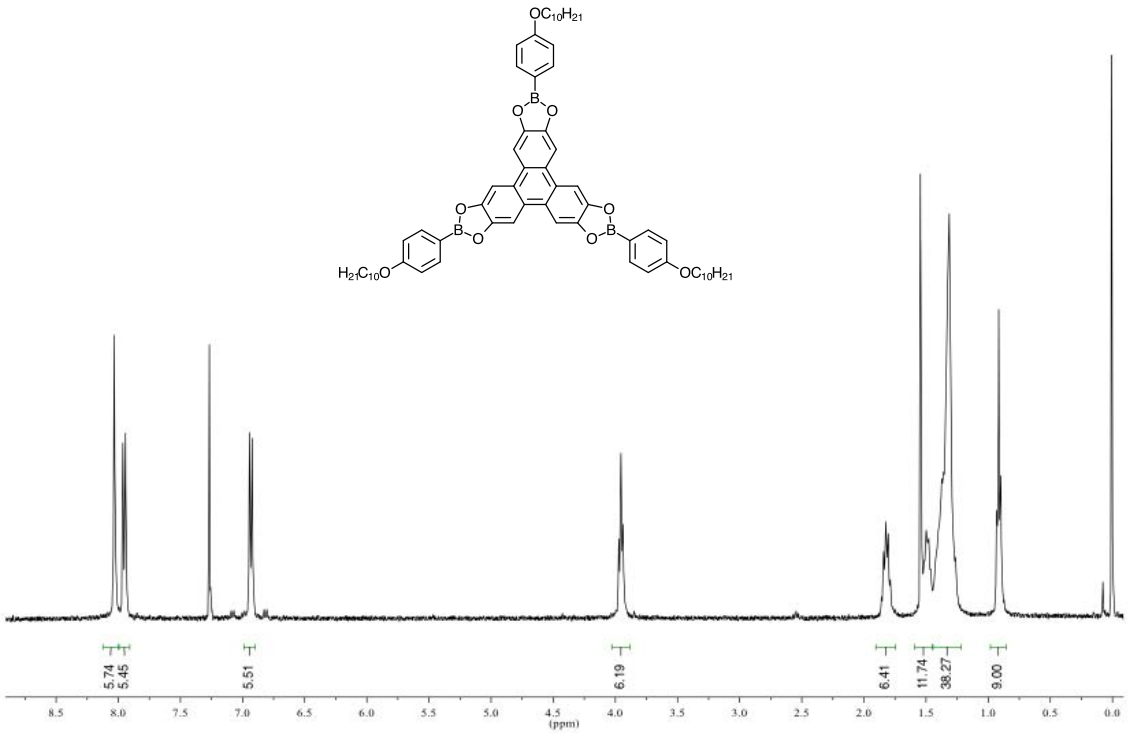
p-octyloxy discotic

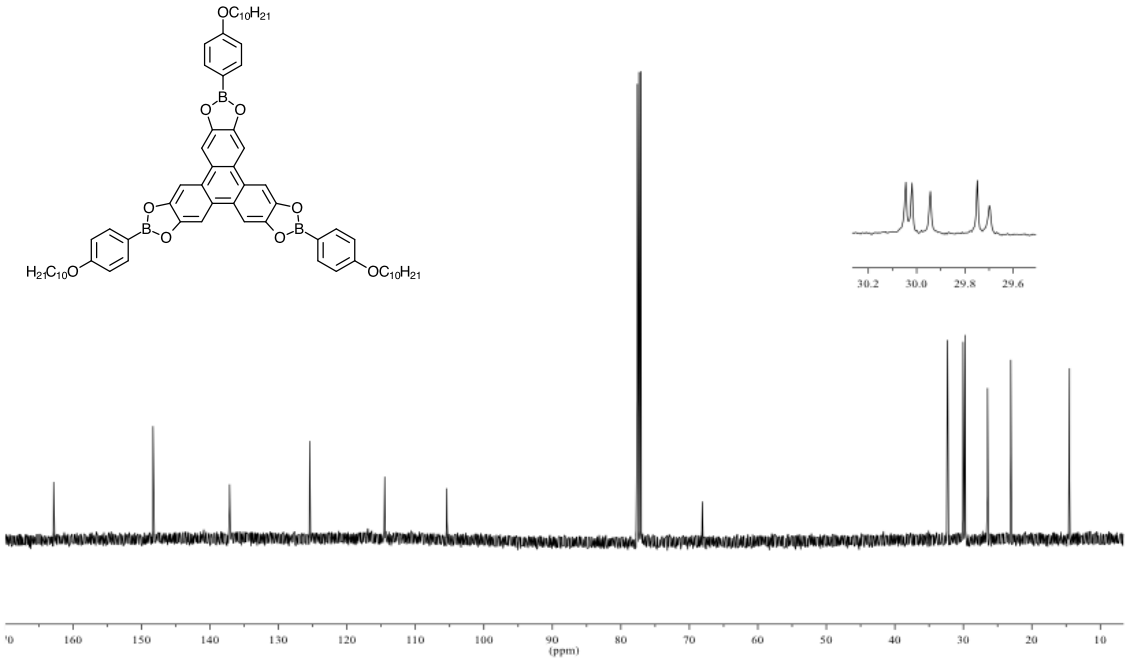


This journal is © The Royal Society of Chemistry 2012

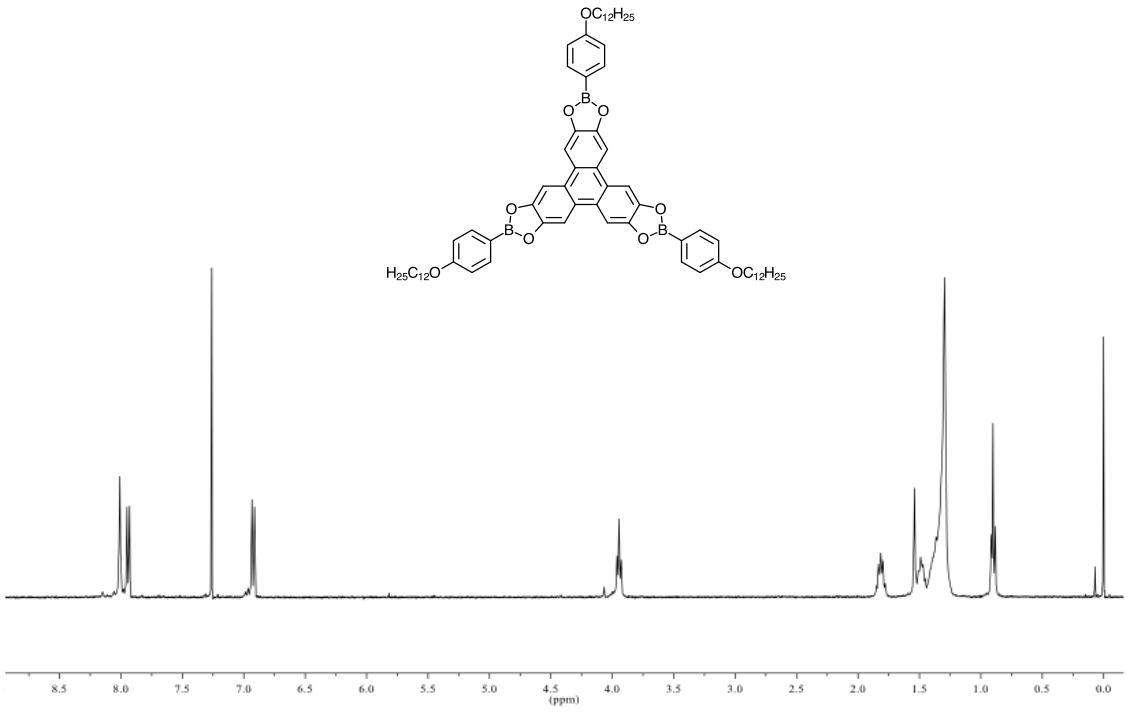


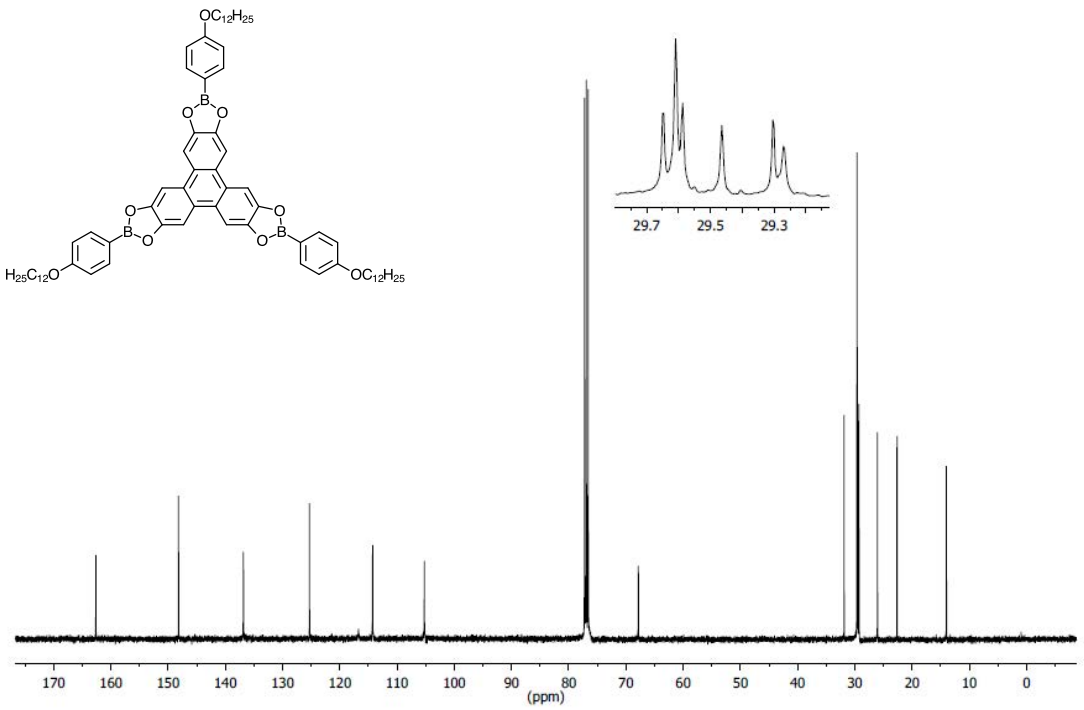
p-decyloxy discotic



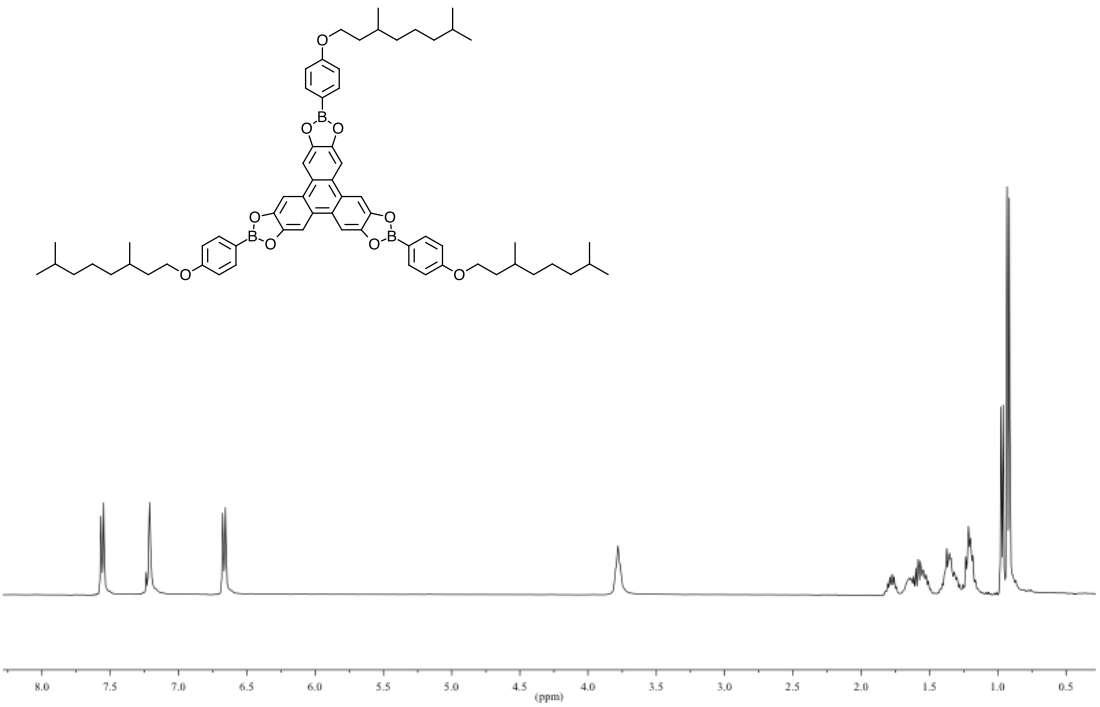


p-dodecyloxy discotic

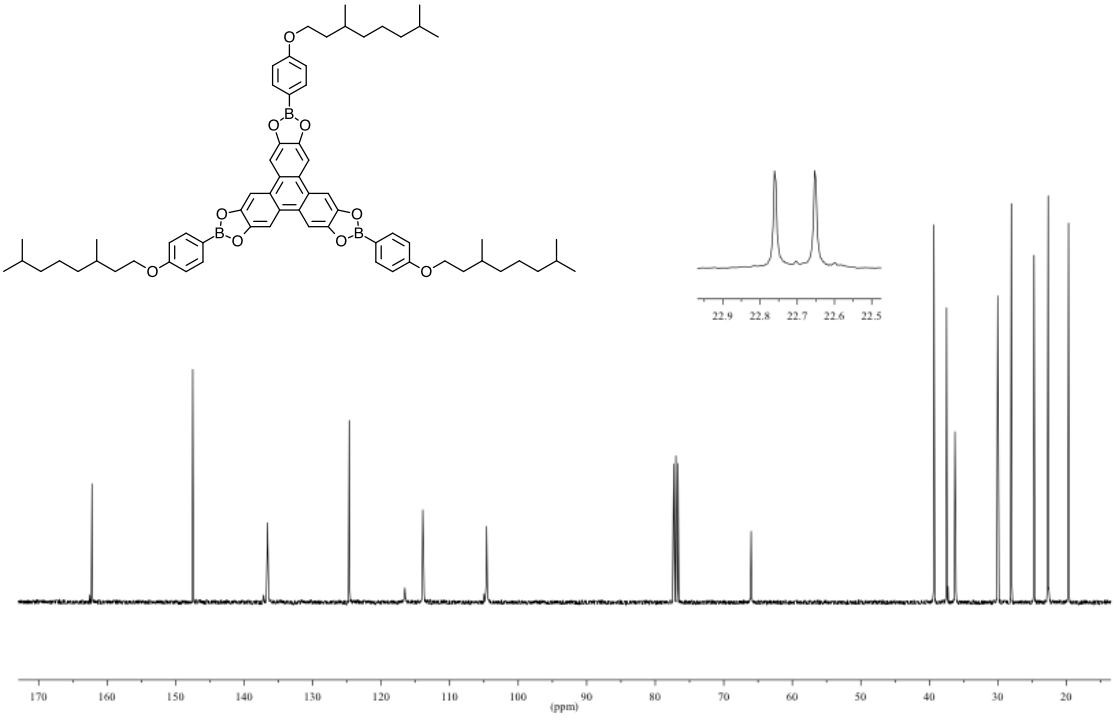




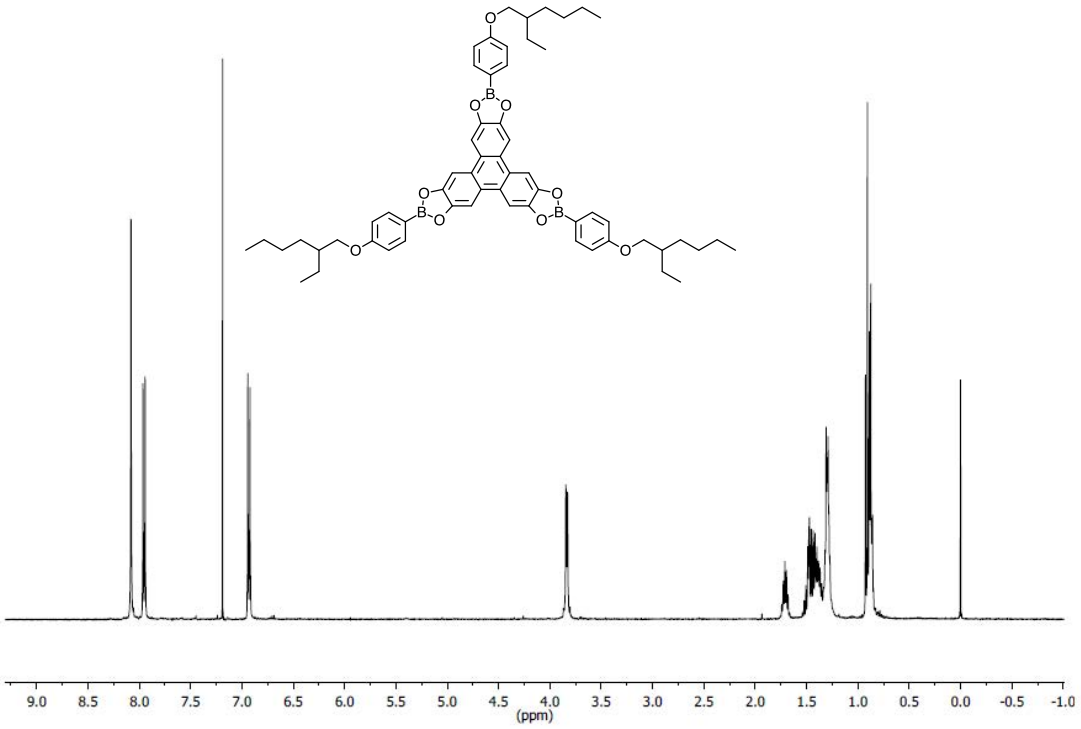
p-3,7-dimethyloctyloxy discotic

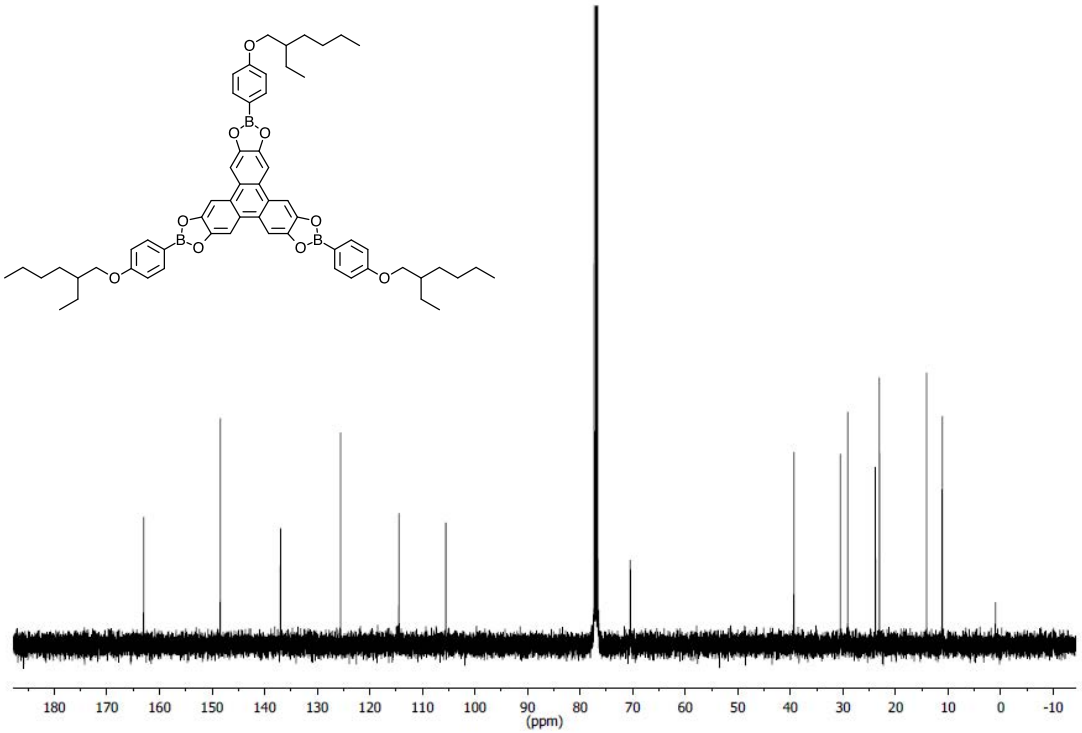


This journal is © The Royal Society of Chemistry 2012

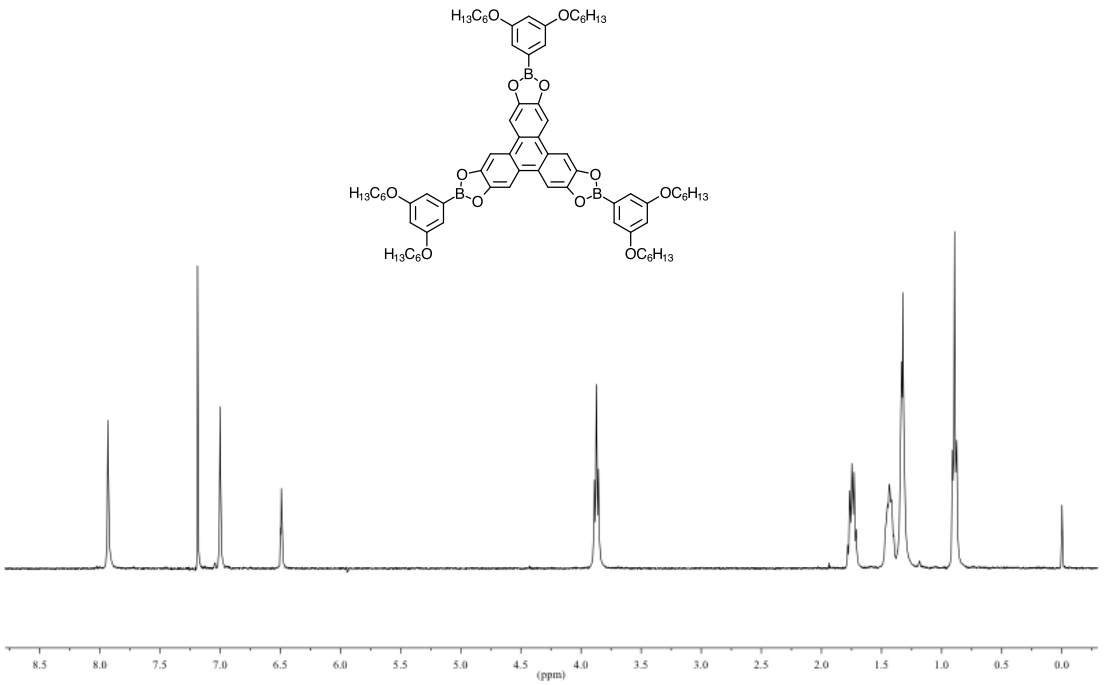


p-2-ethylhexyloxy discotic

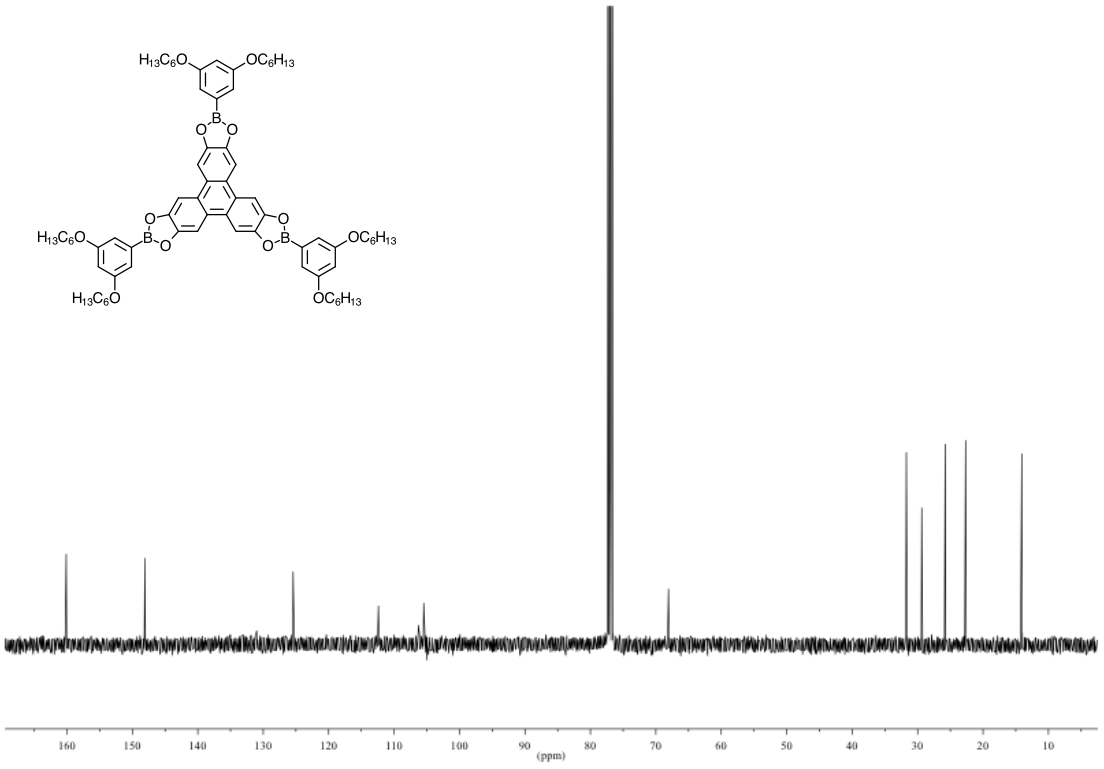




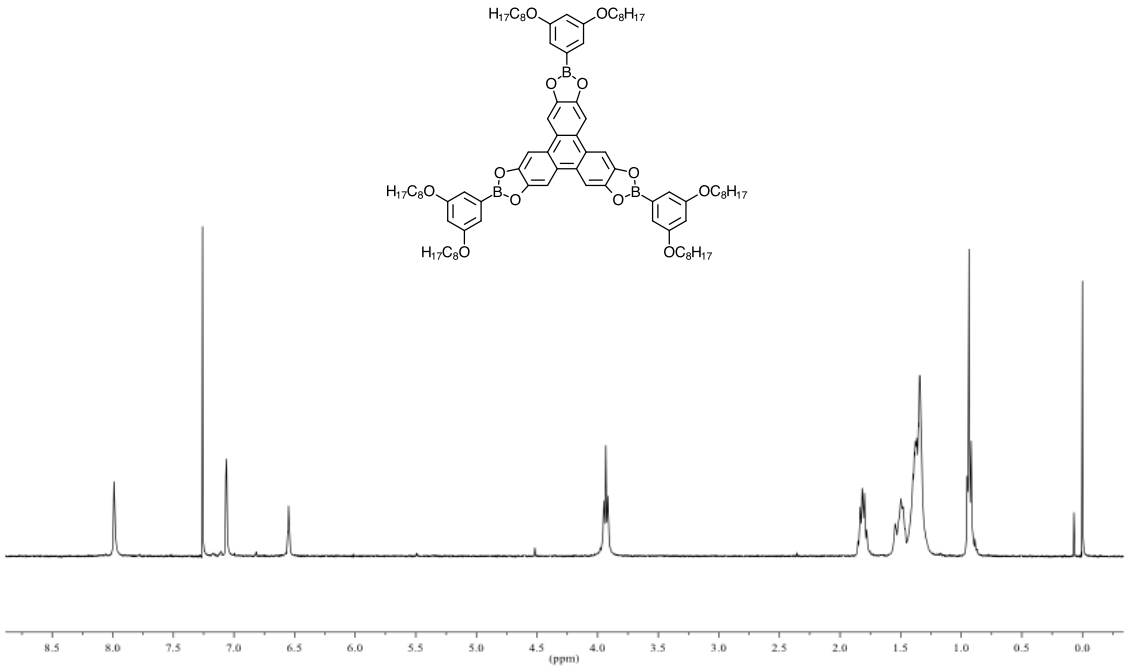
3,5-dihexyloxy discotic

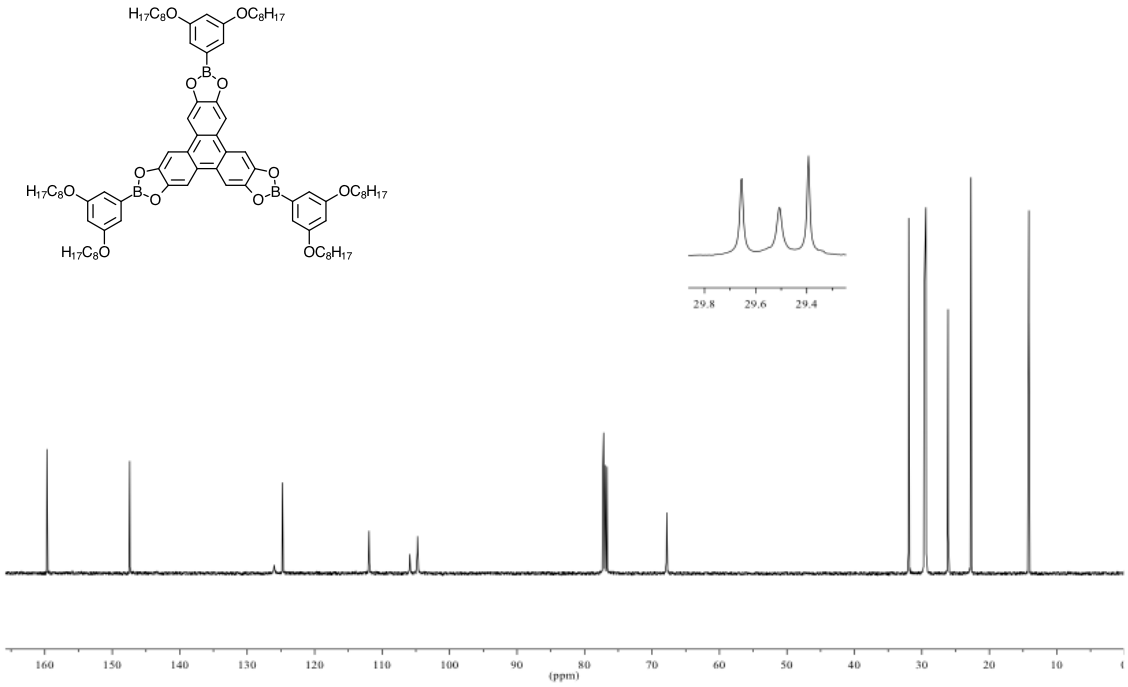


This journal is © The Royal Society of Chemistry 2012

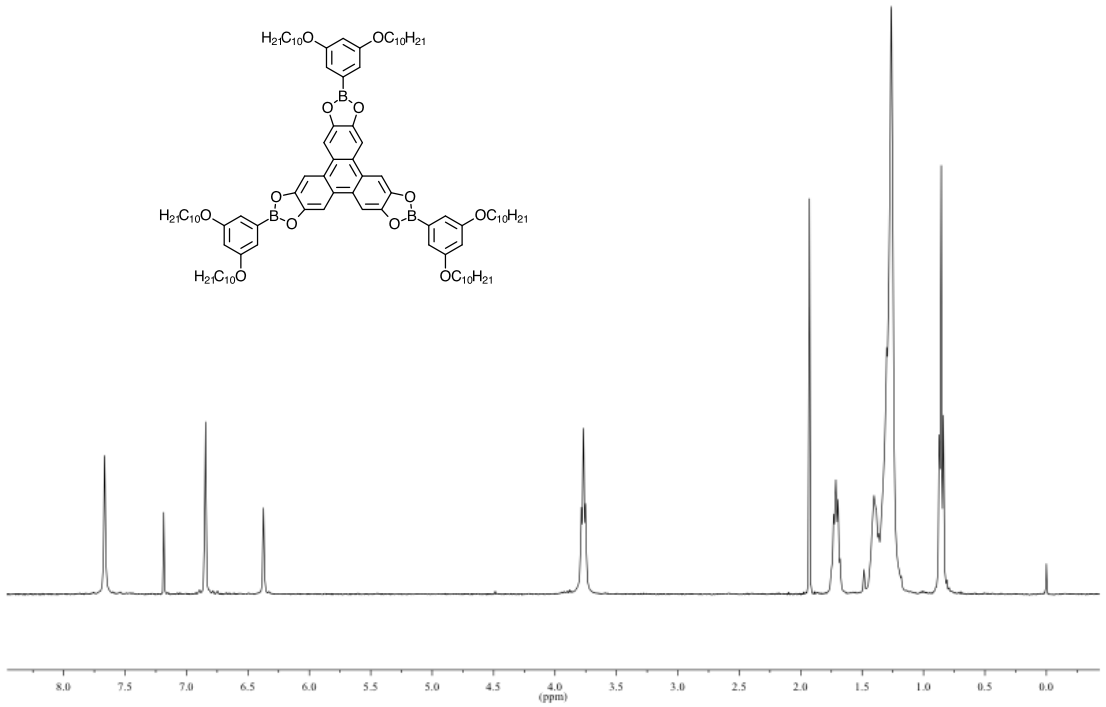


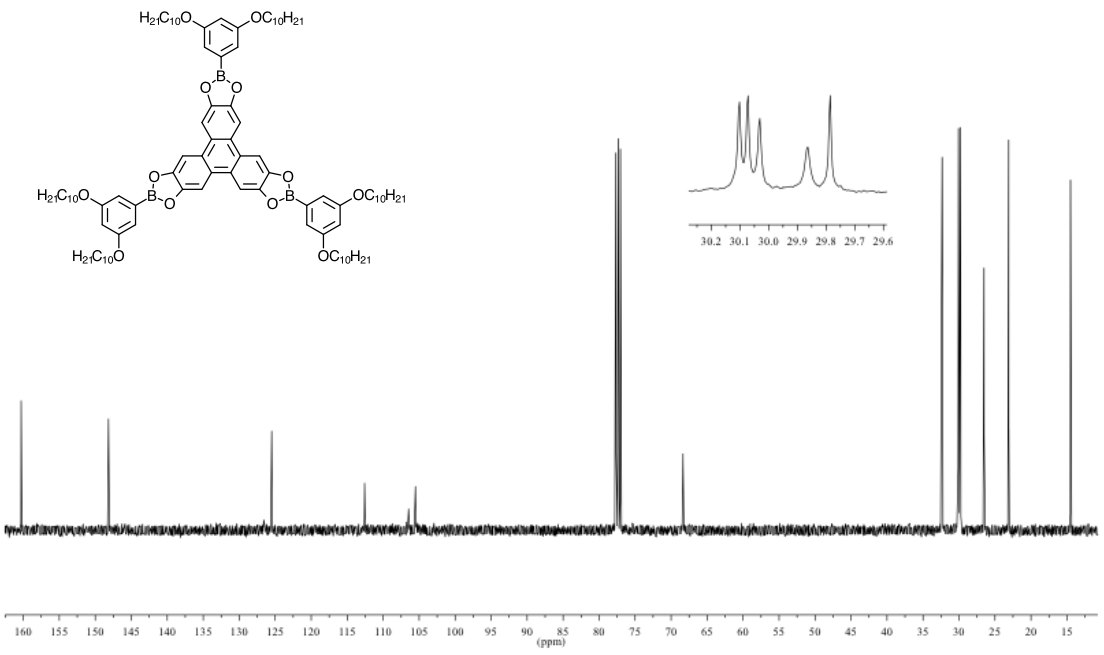
3,5-dioctyloxy discotic



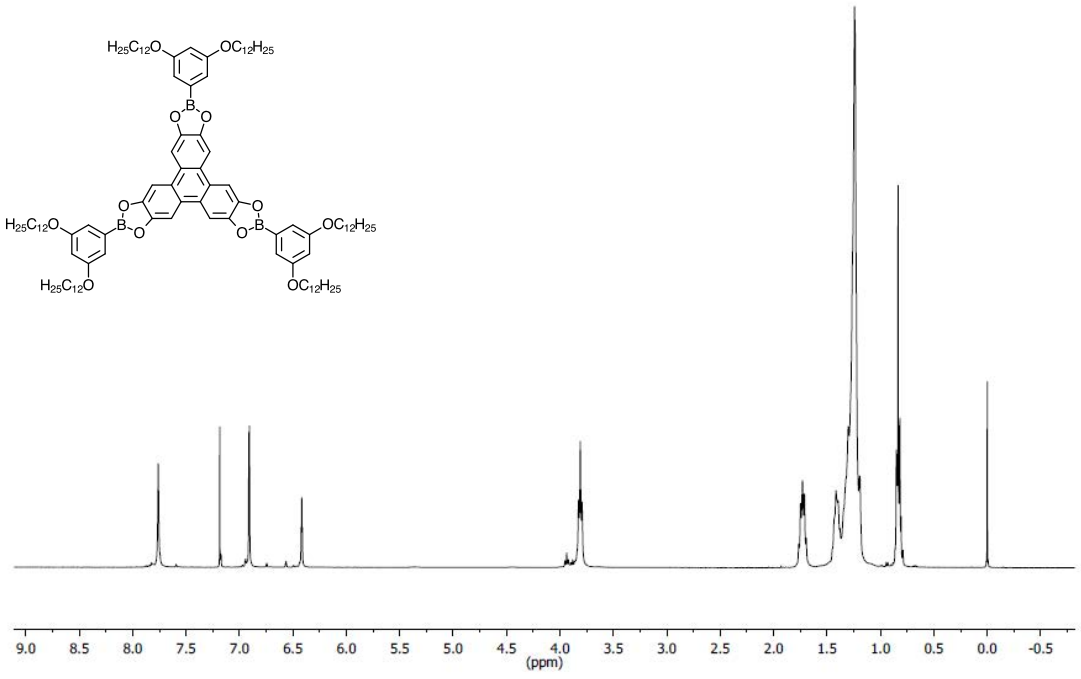


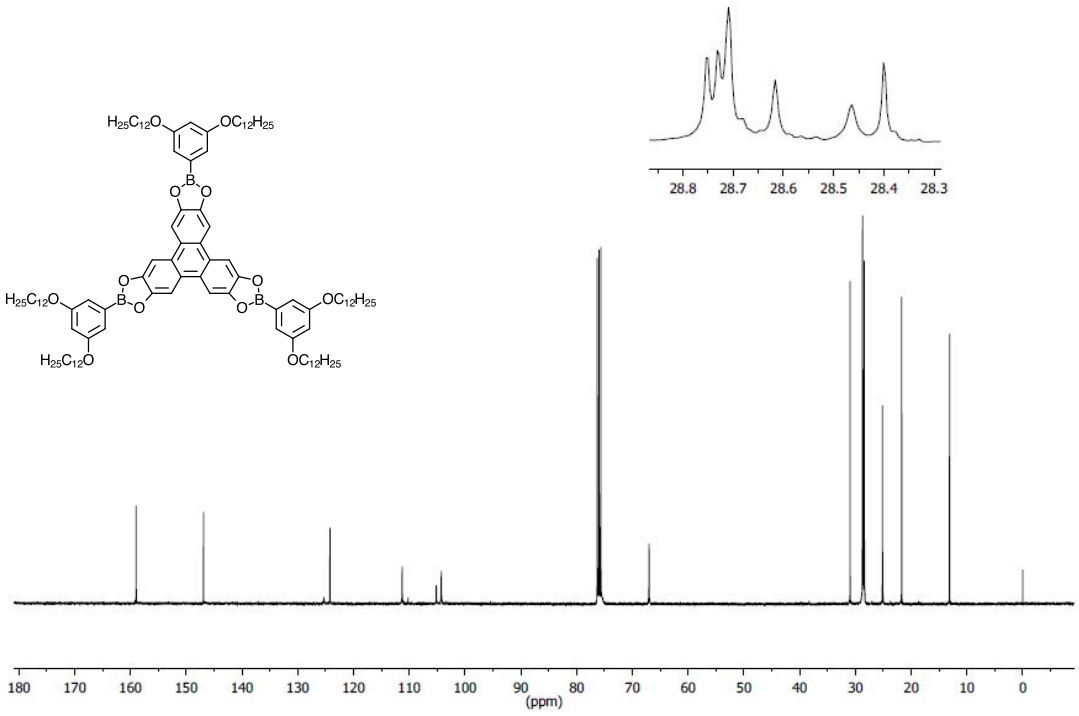
3,5-didecyloxy discotic



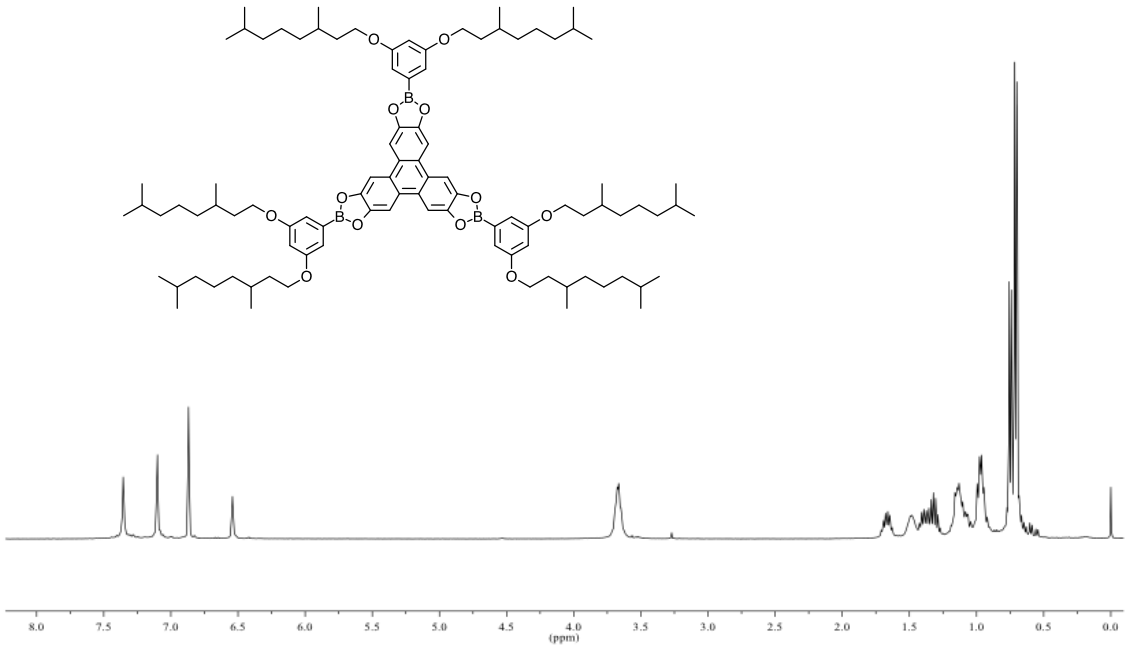


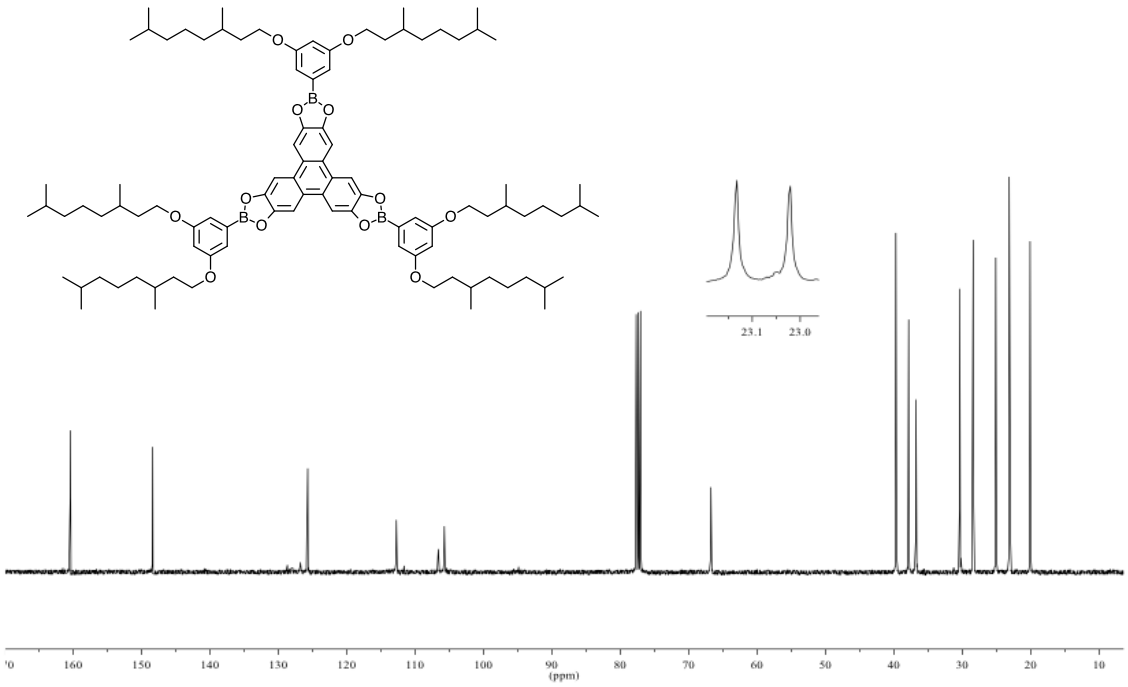
3,5-didodecyloxy discotic



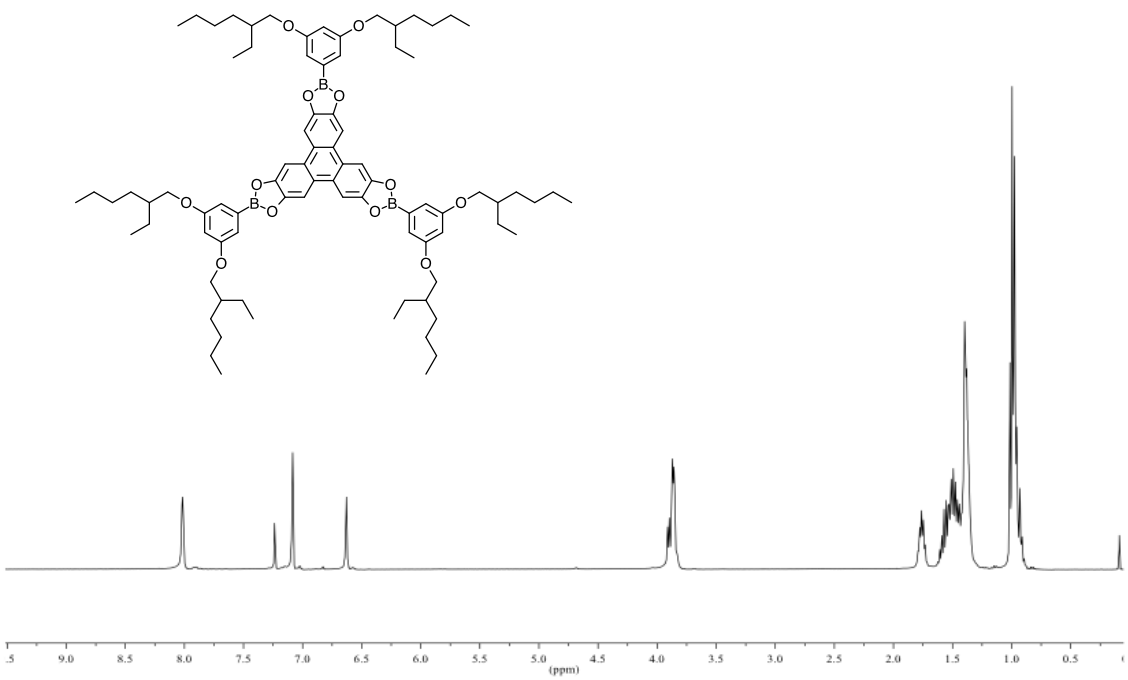


3,5-di(3,7-dimethyloctyloxy) discotic

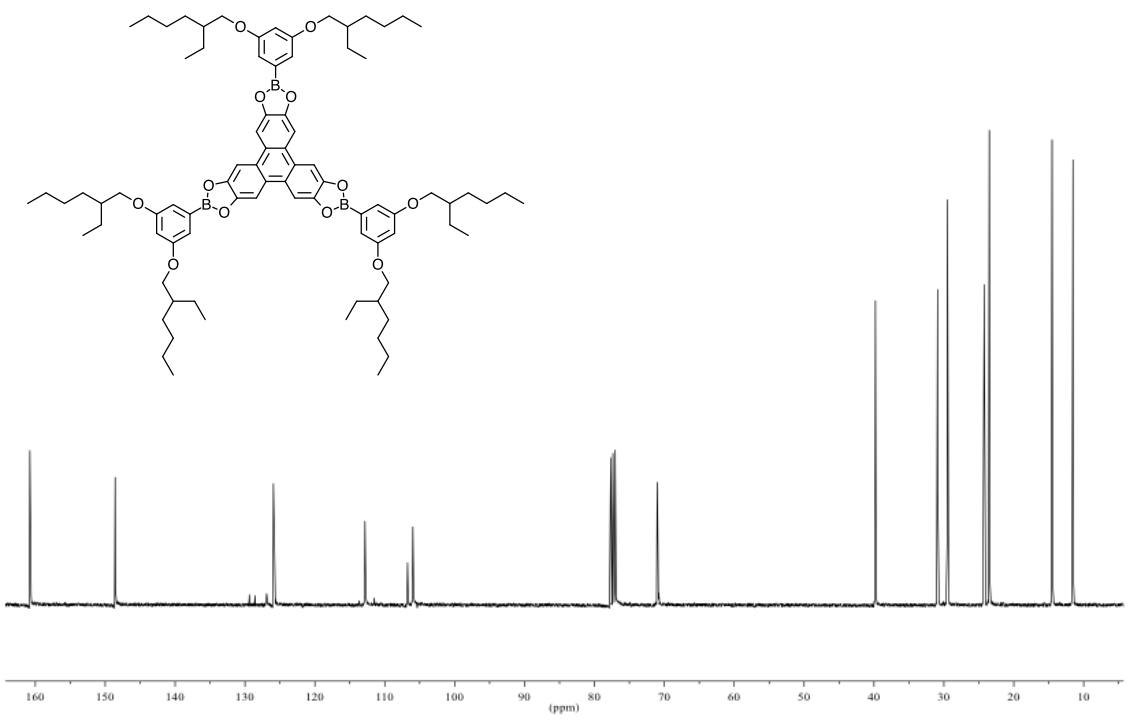




3,5-di(2-ethylhexyloxy) discotic



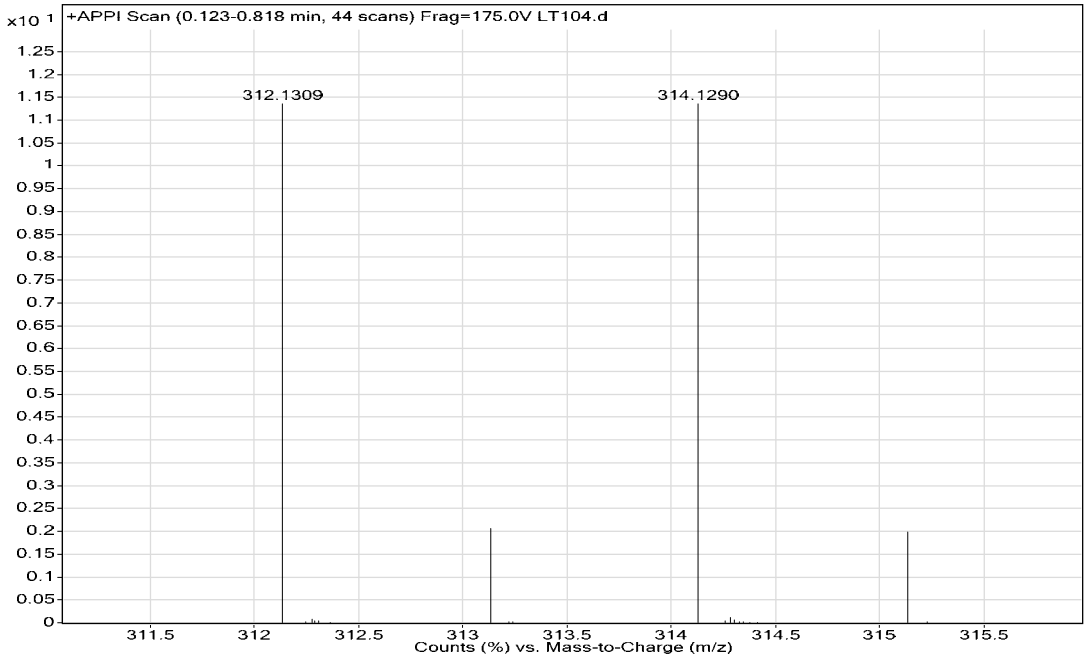
This journal is © The Royal Society of Chemistry 2012



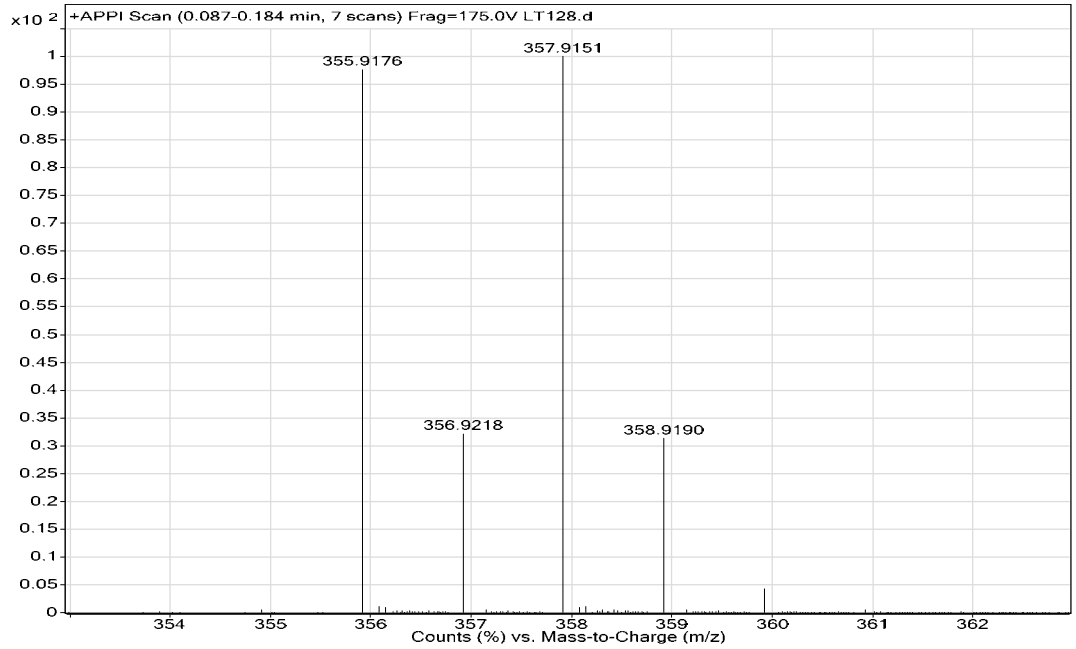
This journal is © The Royal Society of Chemistry 2012

Mass Spectra

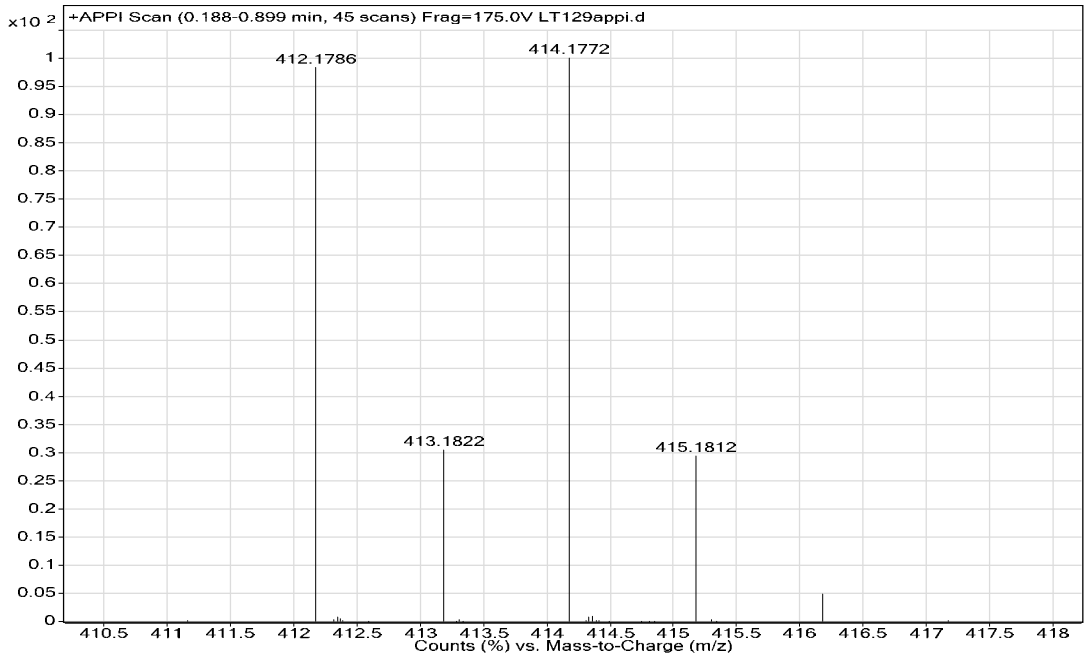
p-3,7-dimethyloctyloxy bromobenzene



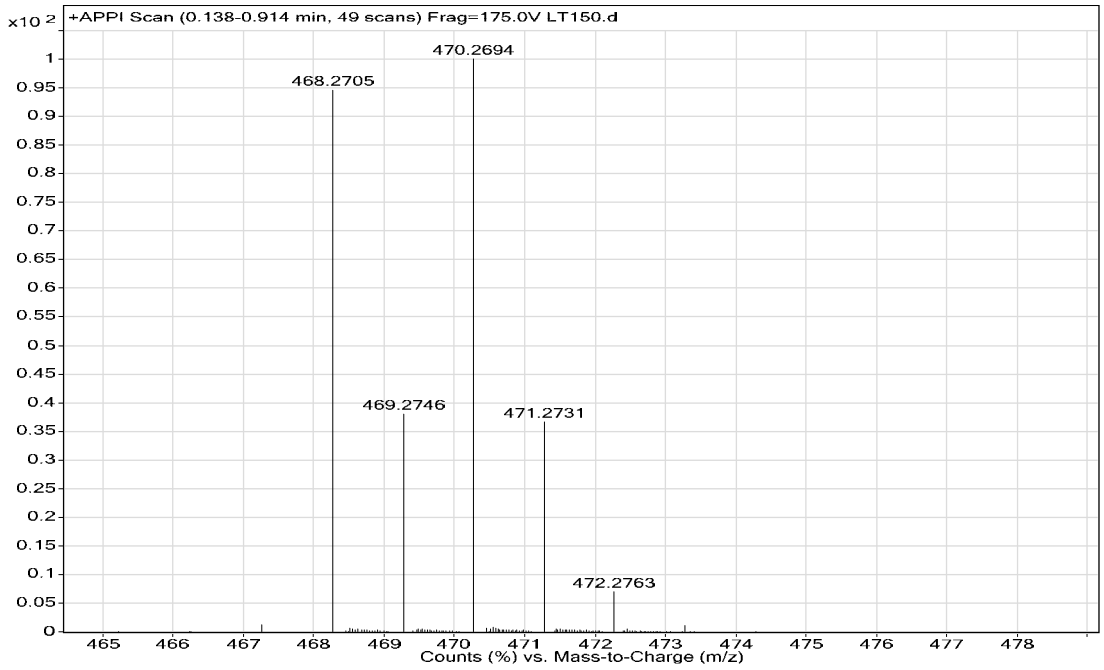
3,5-dihexyloxy bromobenzene



3,5-dioctyloxy bromobenzene

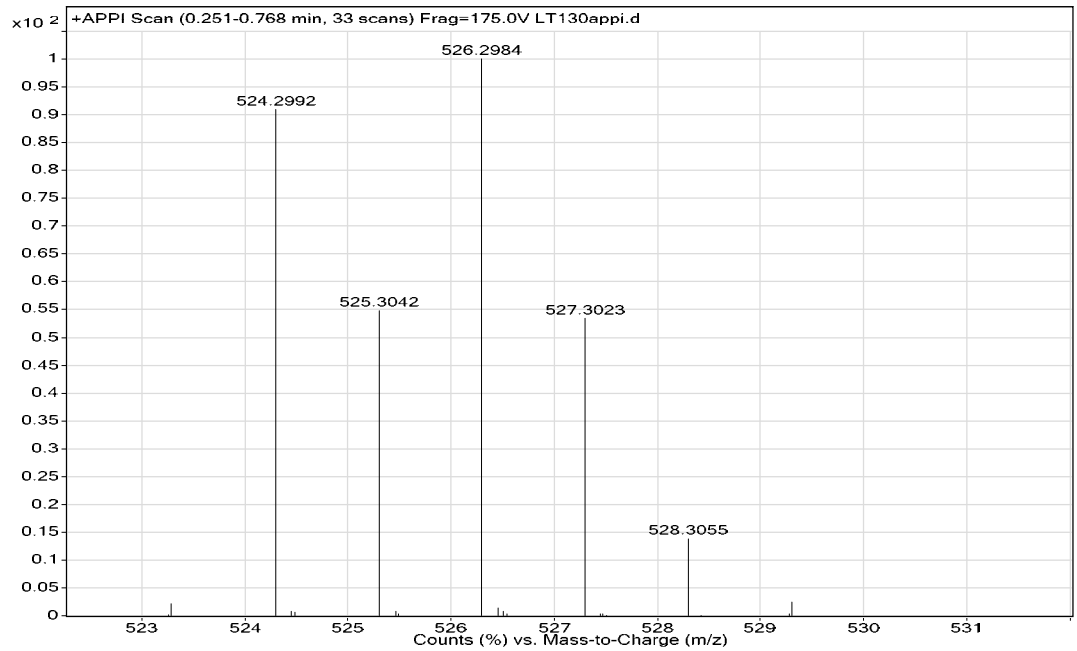


3,5-didecyloxy bromobenzene

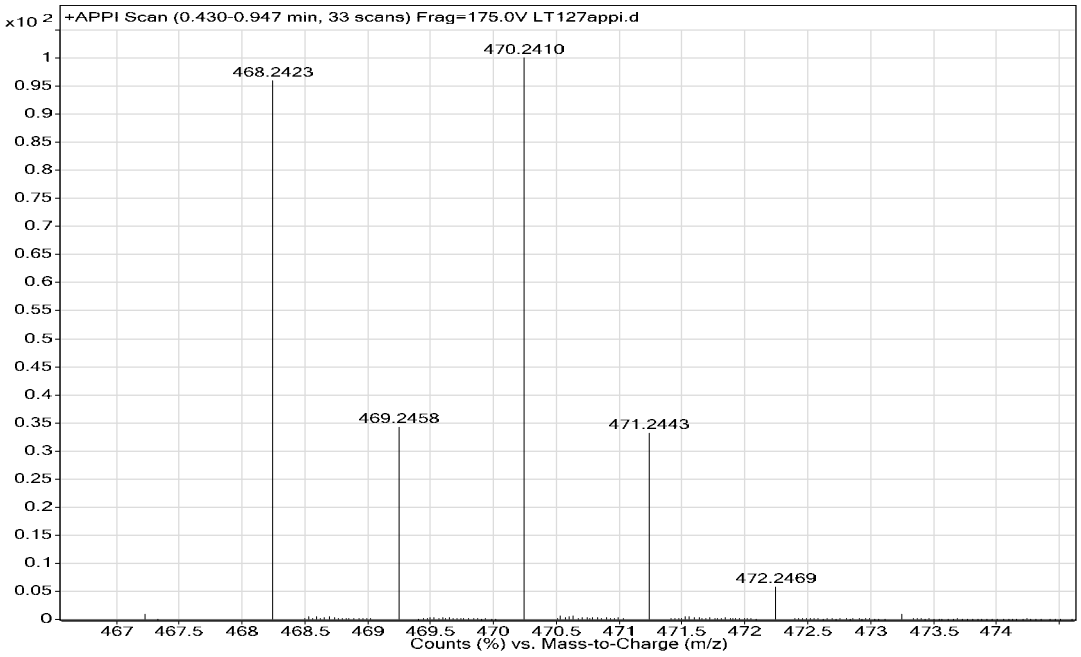


This journal is © The Royal Society of Chemistry 2012

3,5-didodecyloxy bromobenzene

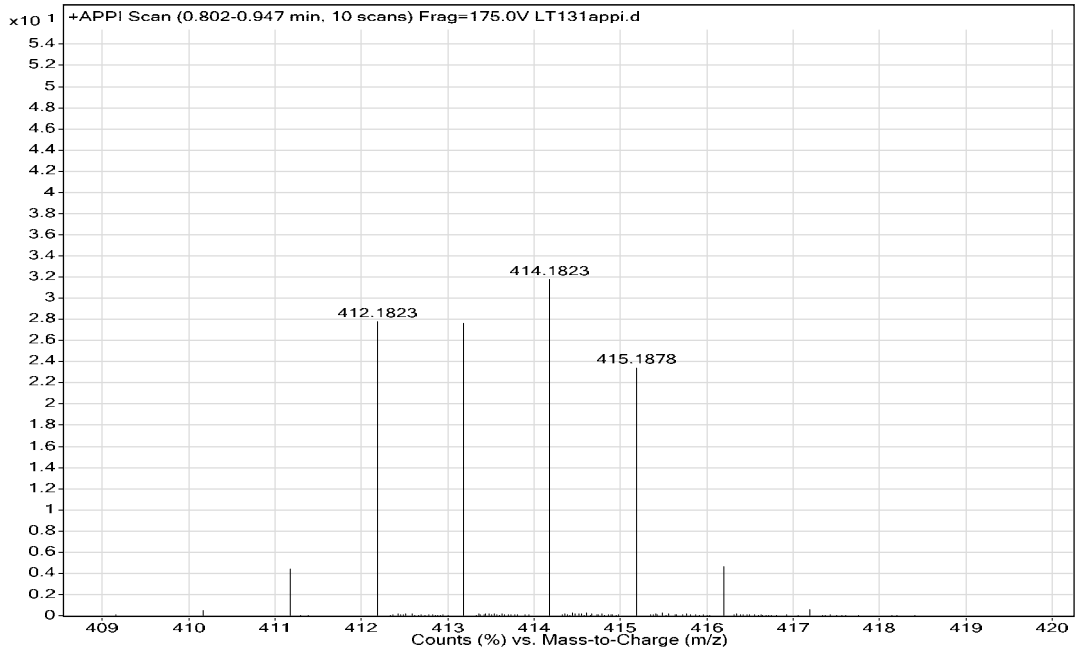


3,5-di(3,7-dimethyloctyloxy) bromobenzene

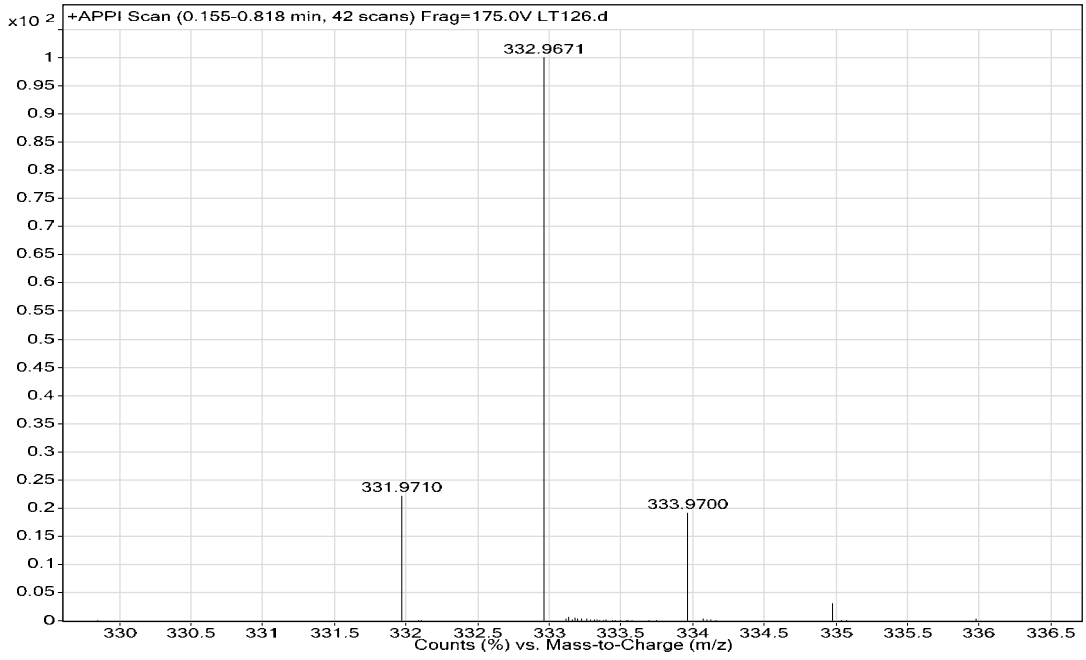


This journal is © The Royal Society of Chemistry 2012

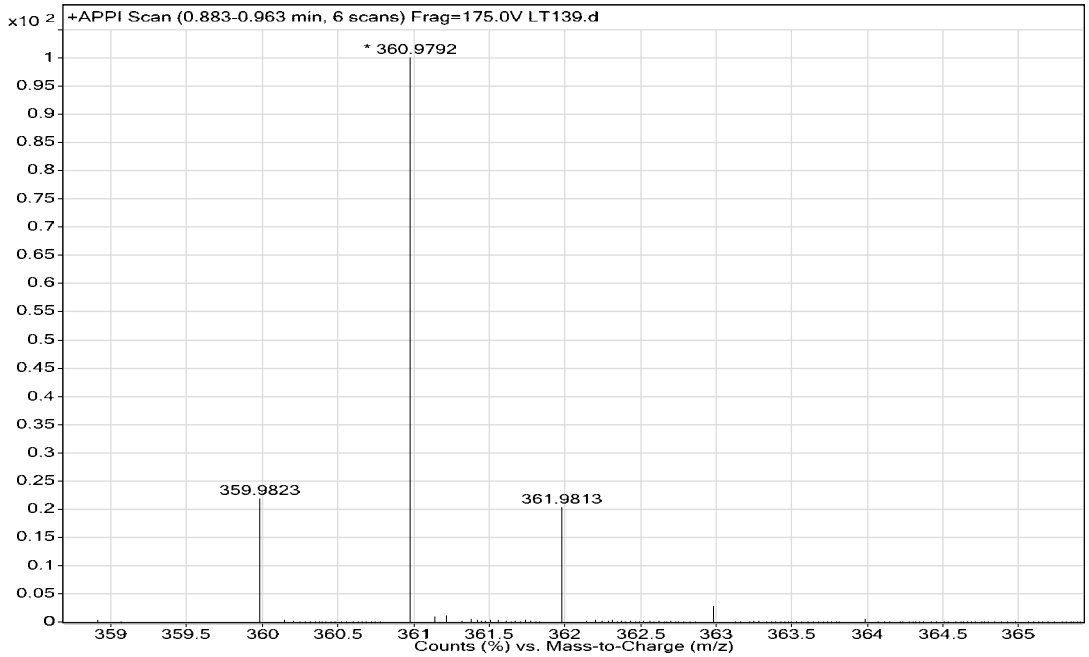
3,5-di(2-ethylhexyloxy) bromobenzene



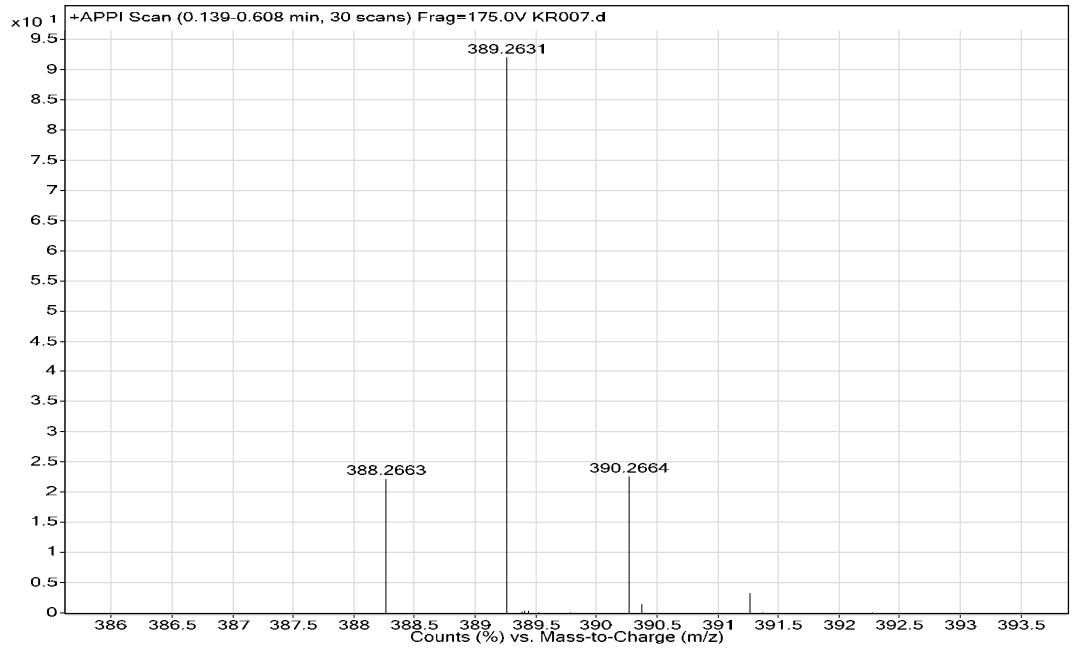
p-hexyloxy MIDA



p-octyloxy MIDA



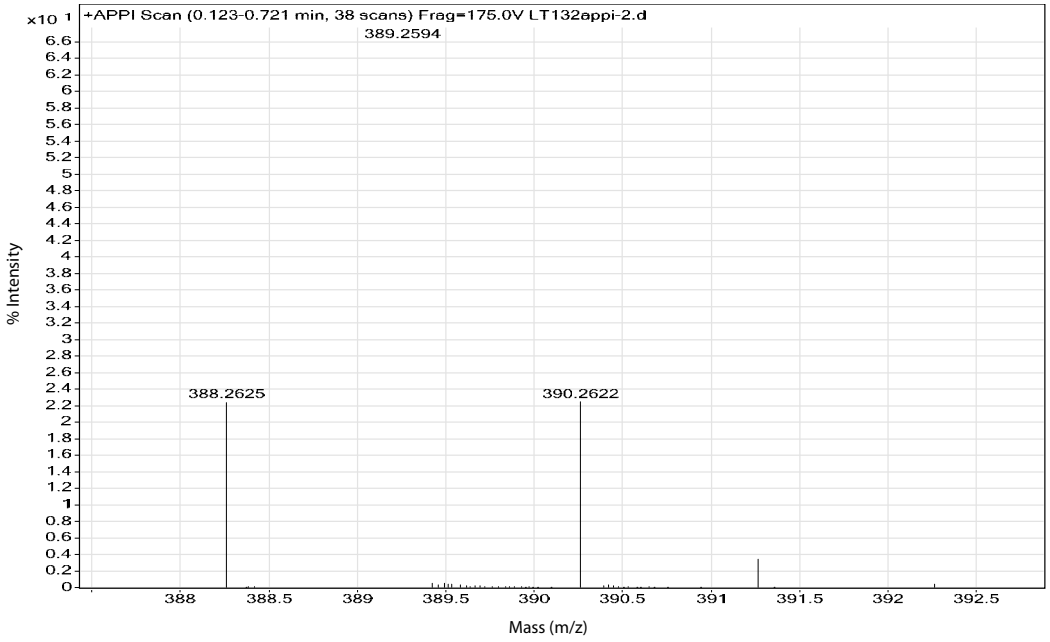
p-decyloxy MIDA



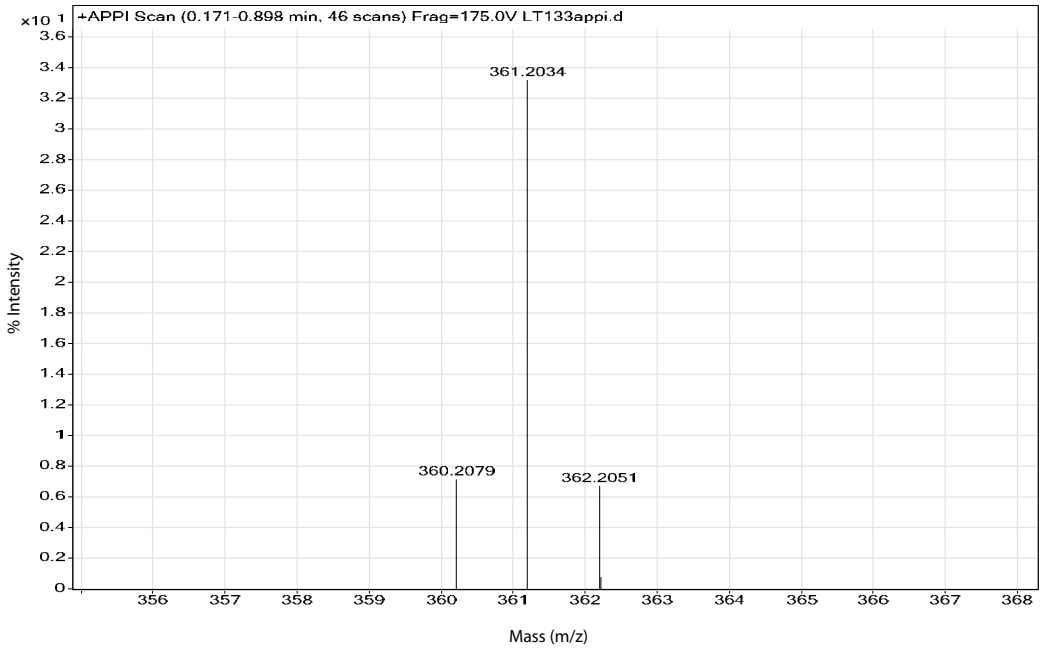
This journal is © The Royal Society of Chemistry 2012

p-dodecyloxy MIDA

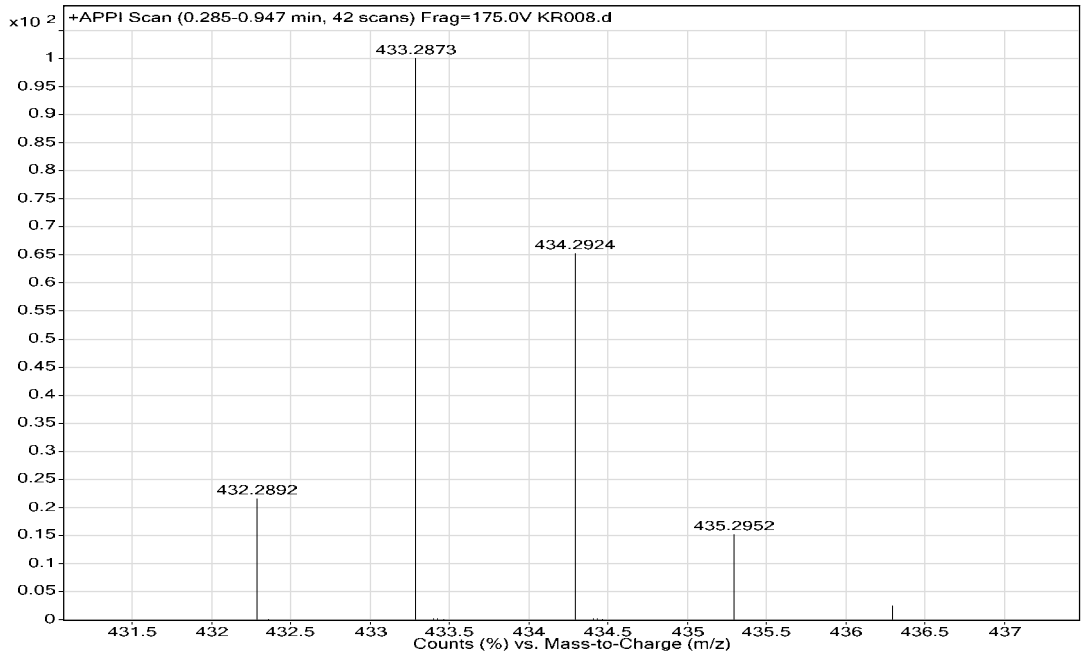
p-3,7-dimethyloctyloxy MIDA



p-2-ethylhexyloxy MIDA

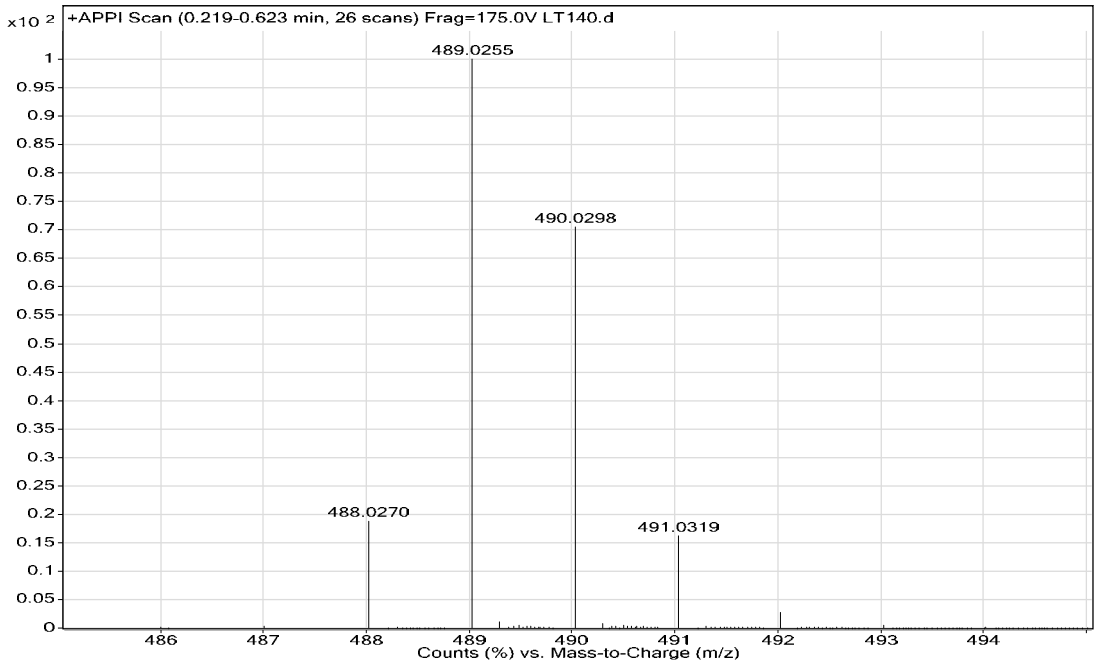


3,5-dihexyloxy MIDA



This journal is © The Royal Society of Chemistry 2012

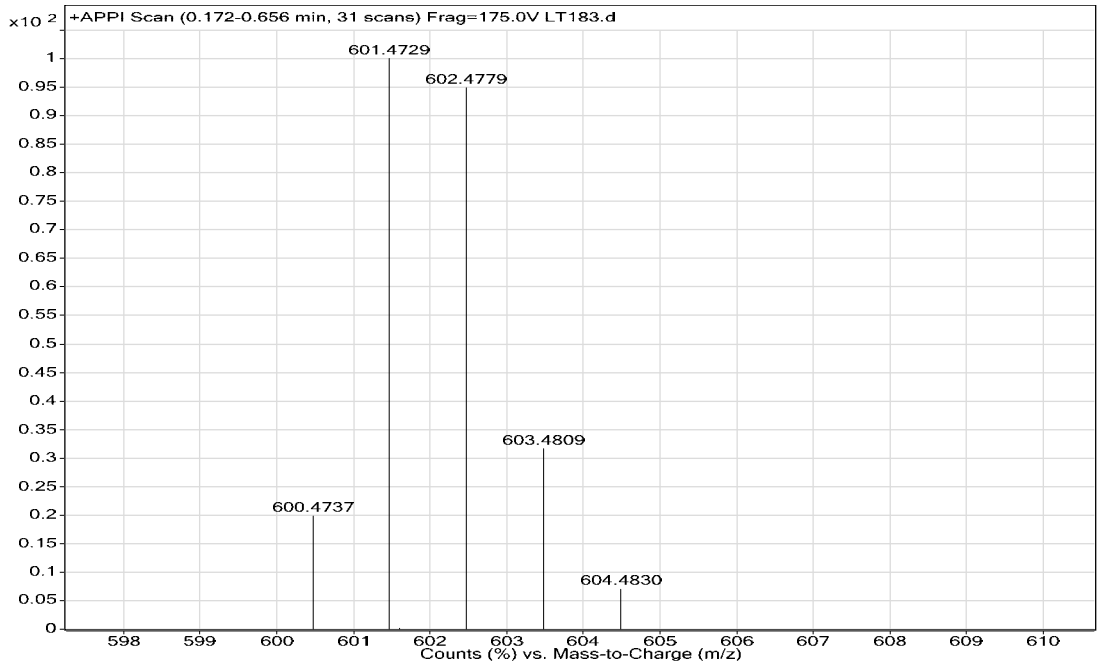
3,5-dioctyloxy MIDA



3,5-didecyloxy MIDA

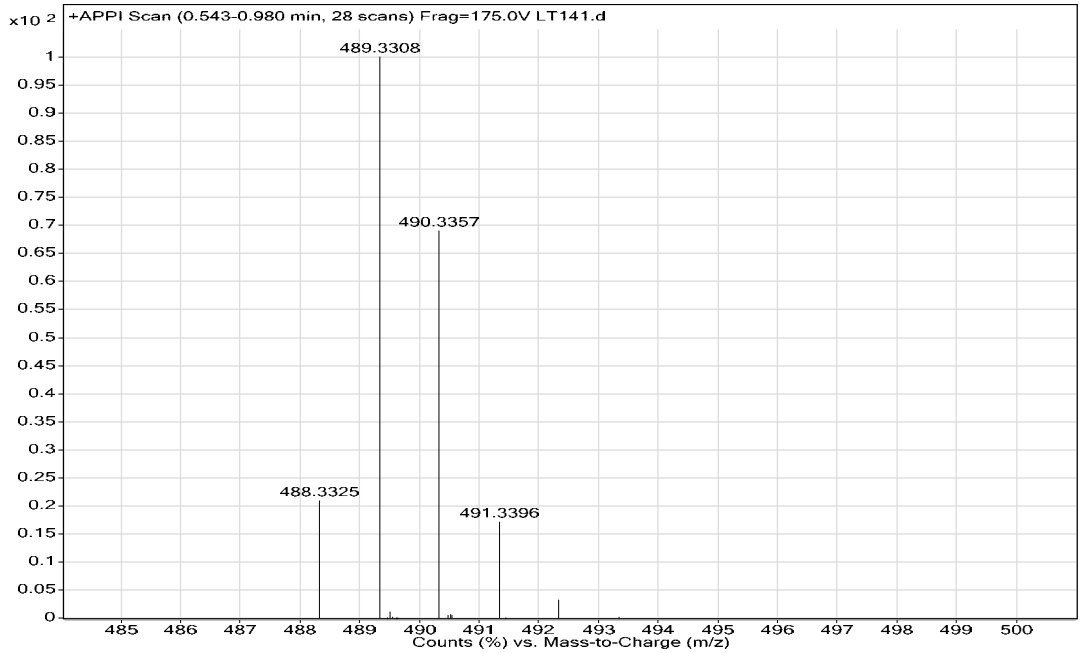
This journal is © The Royal Society of Chemistry 2012

3,5-didodecyloxy MIDA



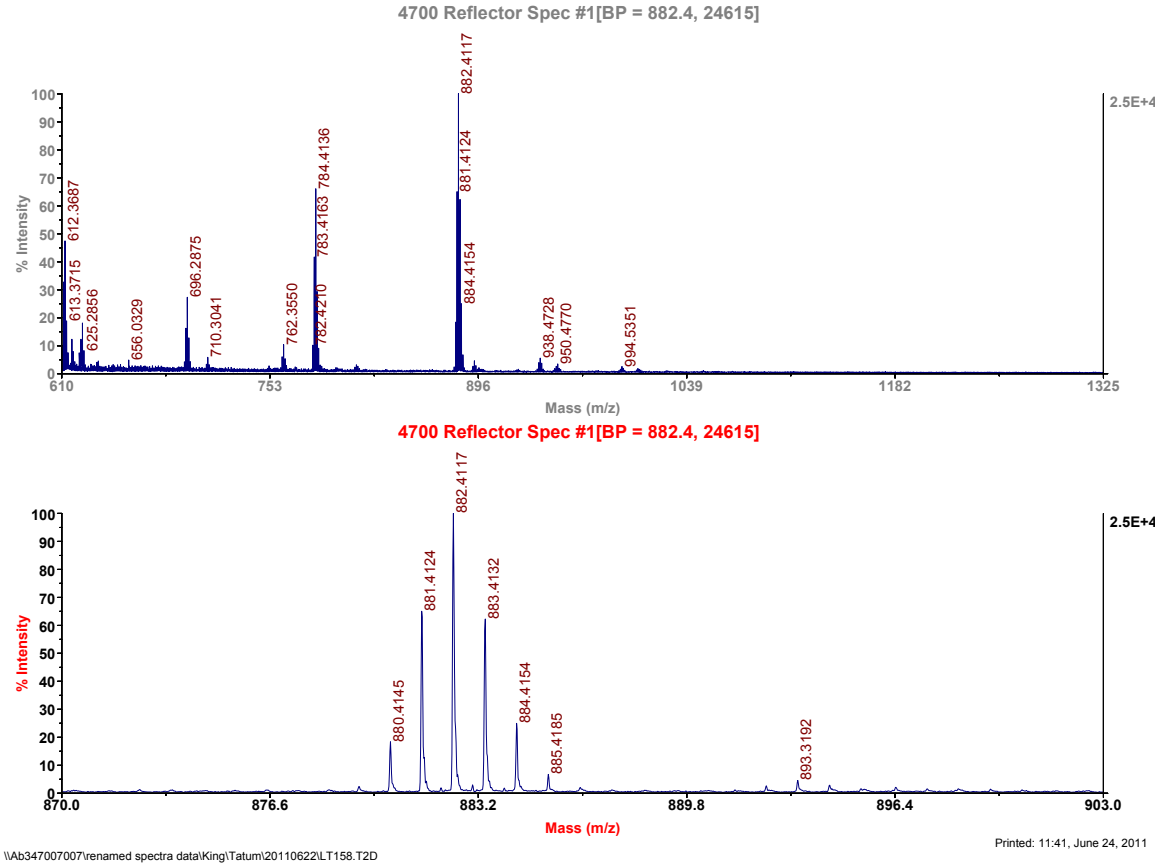
3,5-di3,7-dimethyloctyloxy) MIDA

3,5-di(2-ethylhexyloxy) MIDA

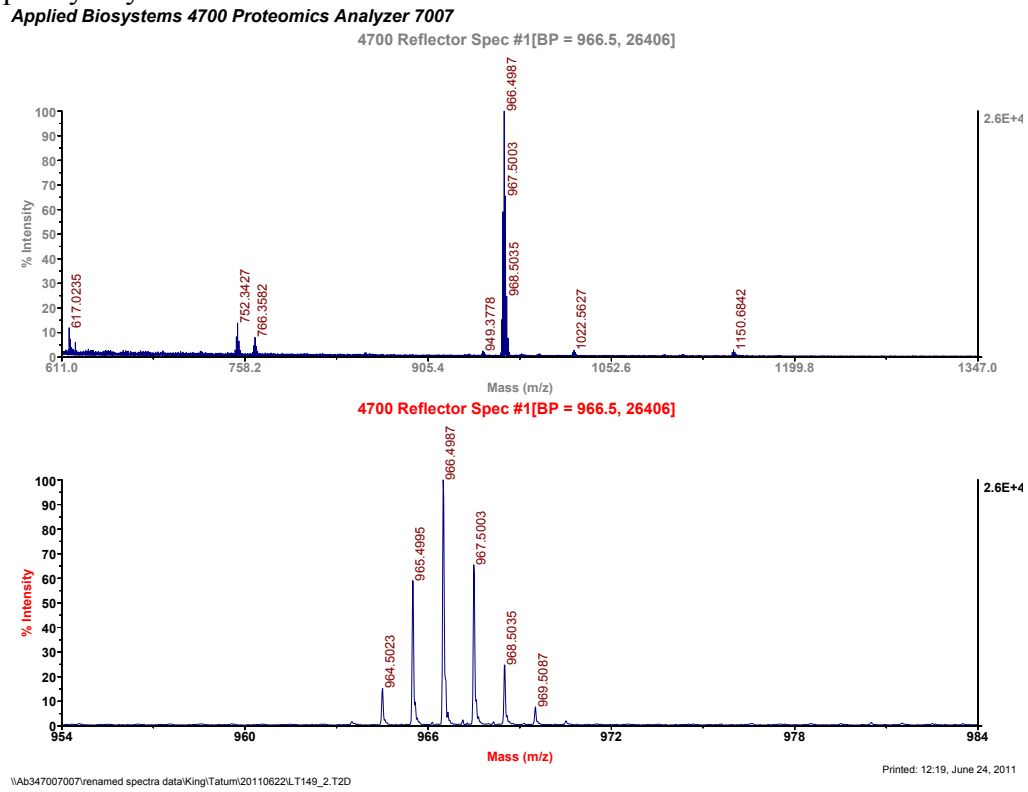


p-hexyloxy discotic

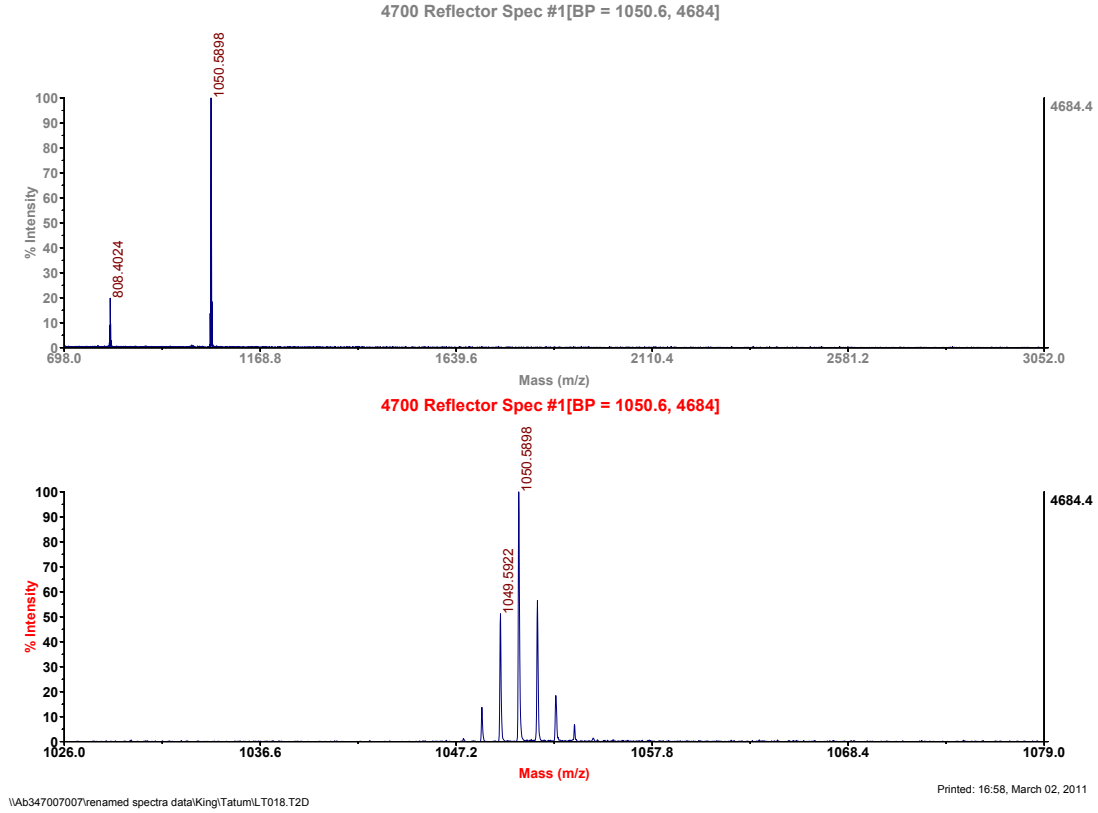
Applied Biosystems 4700 Proteomics Analyzer 7007



p-octyloxy discotic

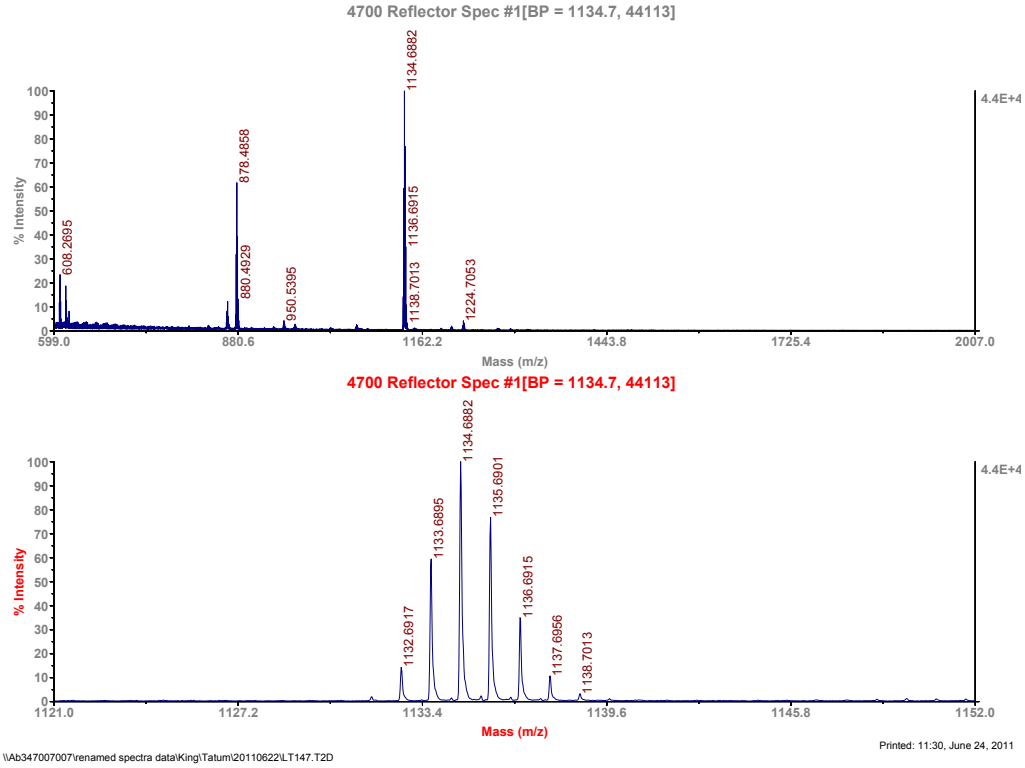


p-decyloxy discotic



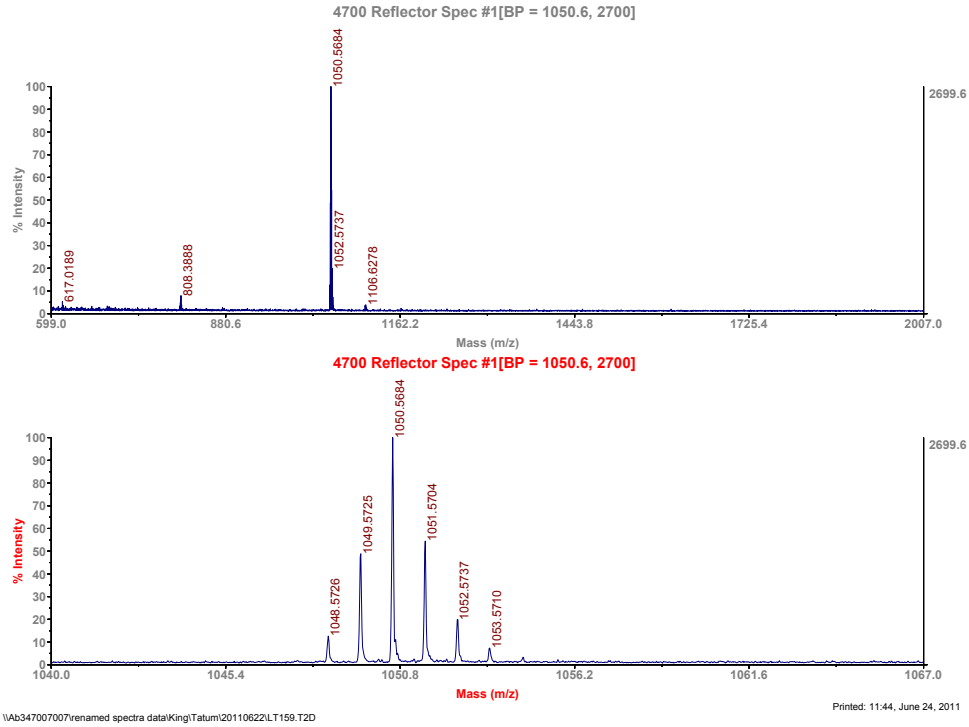
p-dodecyloxy discotic

Applied Biosystems 4700 Proteomics Analyzer 7007

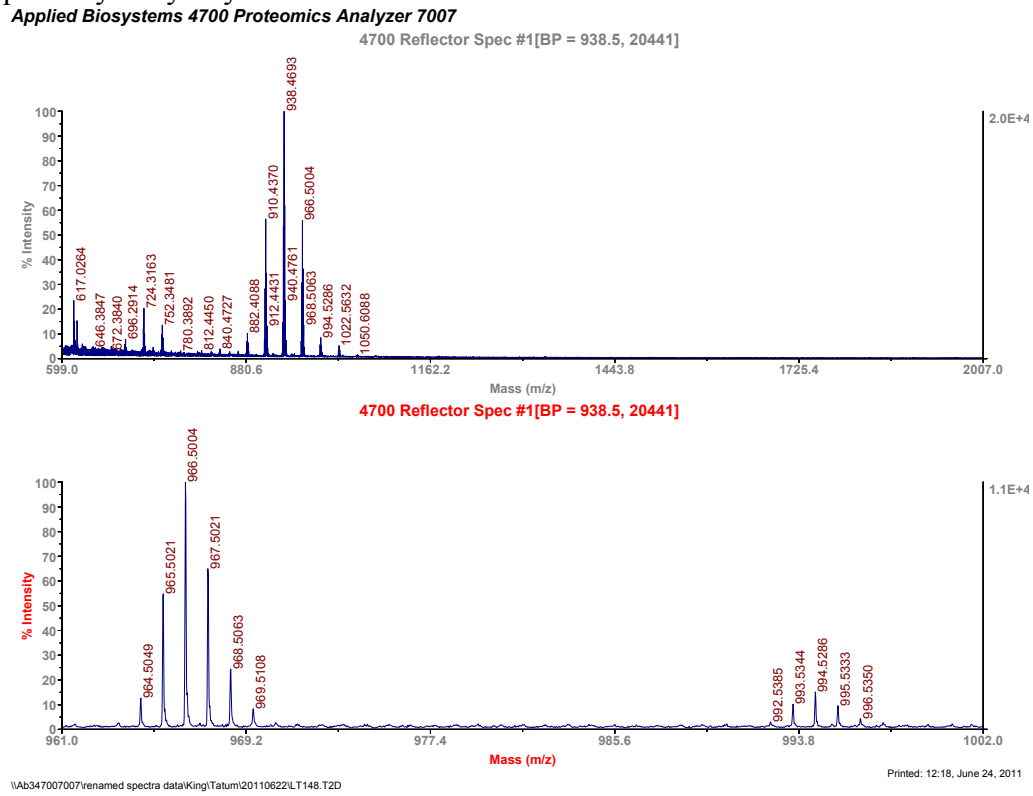


p-3,7-dimethyloctyloxy discotic

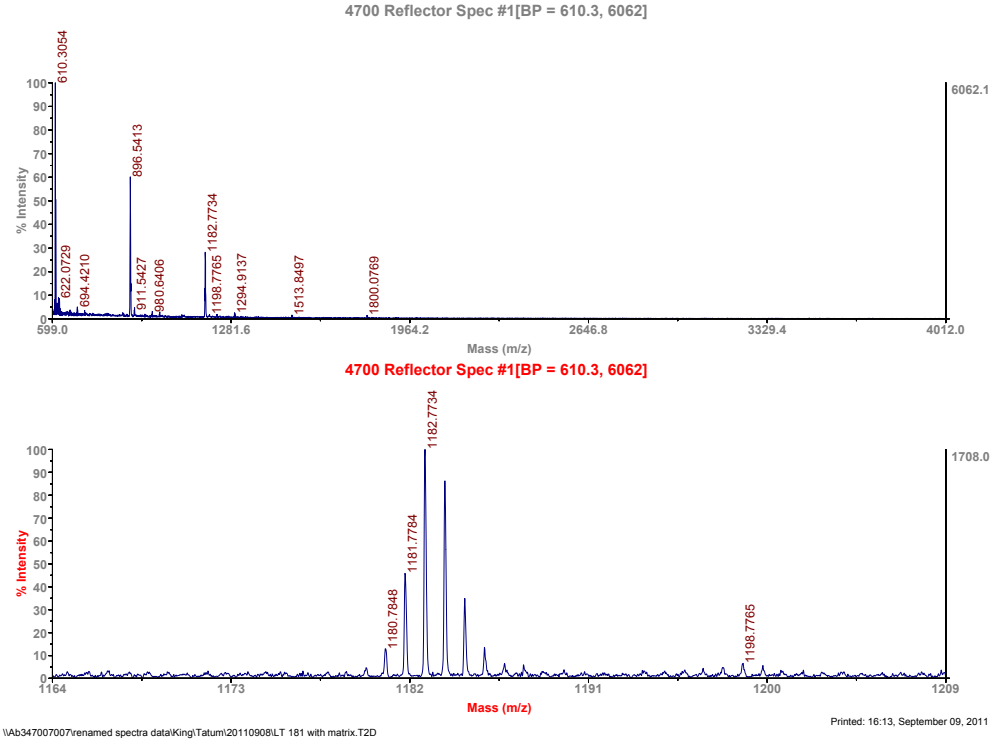
Applied Biosystems 4700 Proteomics Analyzer 7007



p-2-ethylhexyloxy discotic

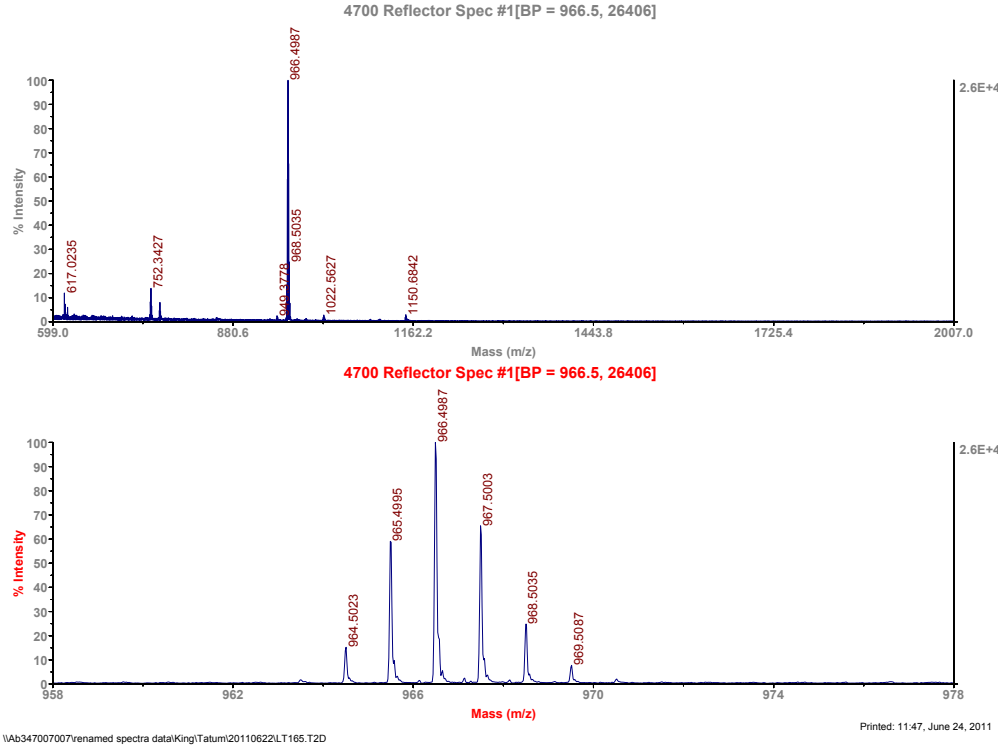


3,5-dihexyloxy discotic



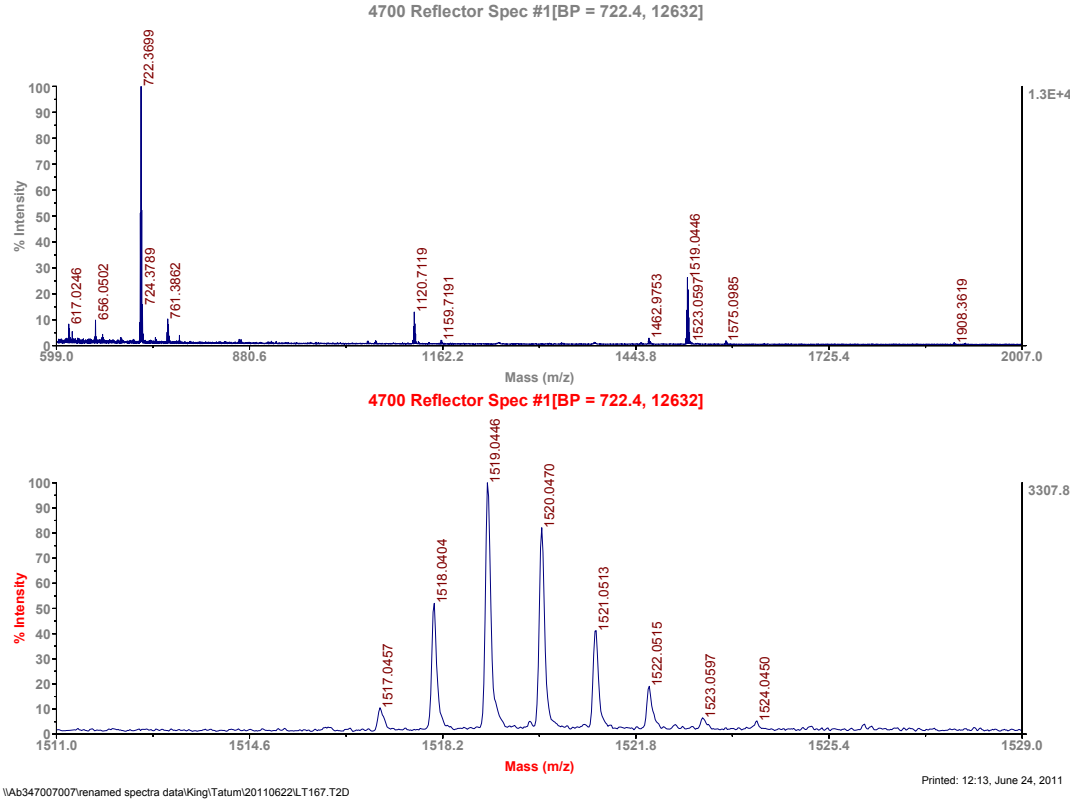
3,5-dioctyloxy discotic

Applied Biosystems 4700 Proteomics Analyzer 7007



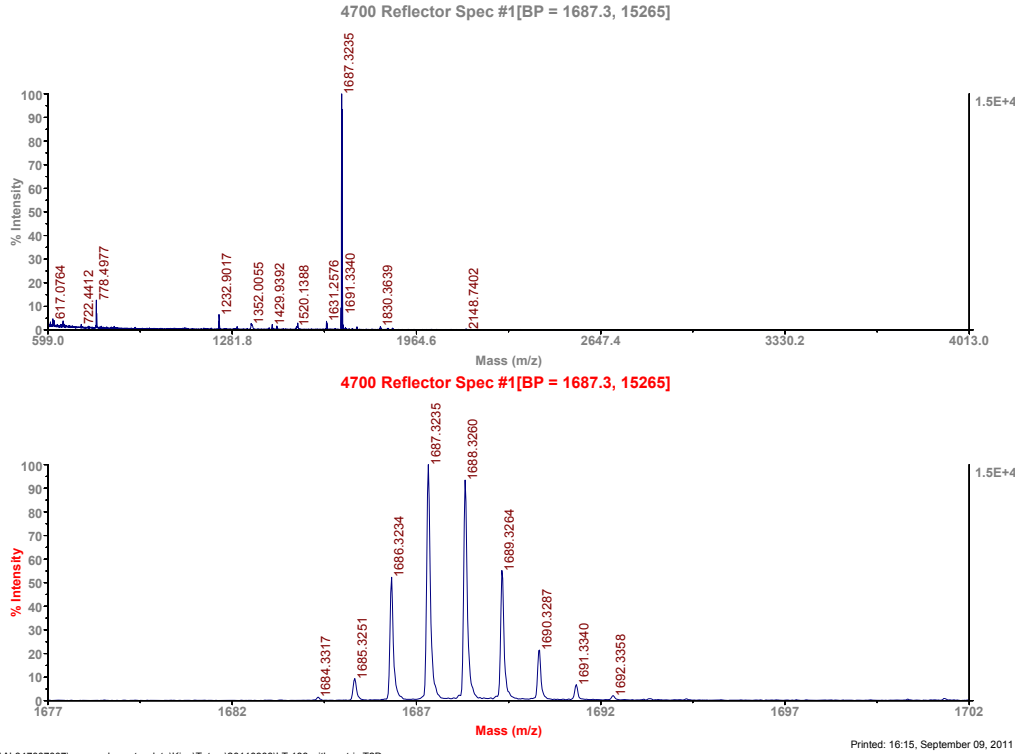
3,5-didecyloxy discotic

Applied Biosystems 4700 Proteomics Analyzer 7007



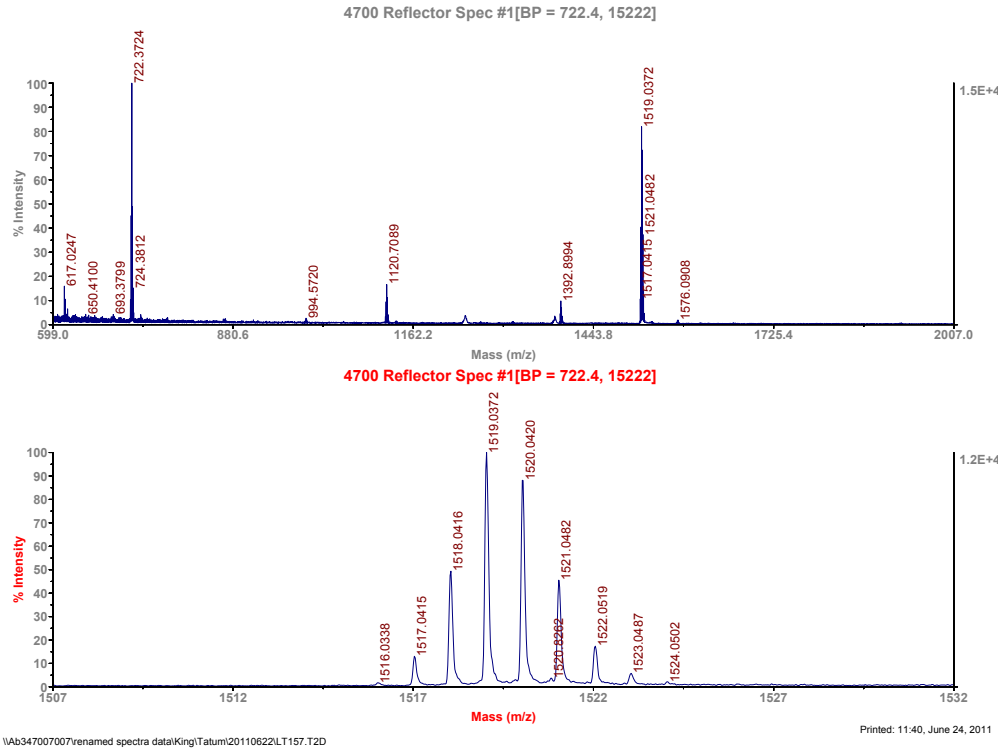
3,5-didodecyloxy discotic

Applied Biosystems 4700 Proteomics Analyzer 7007

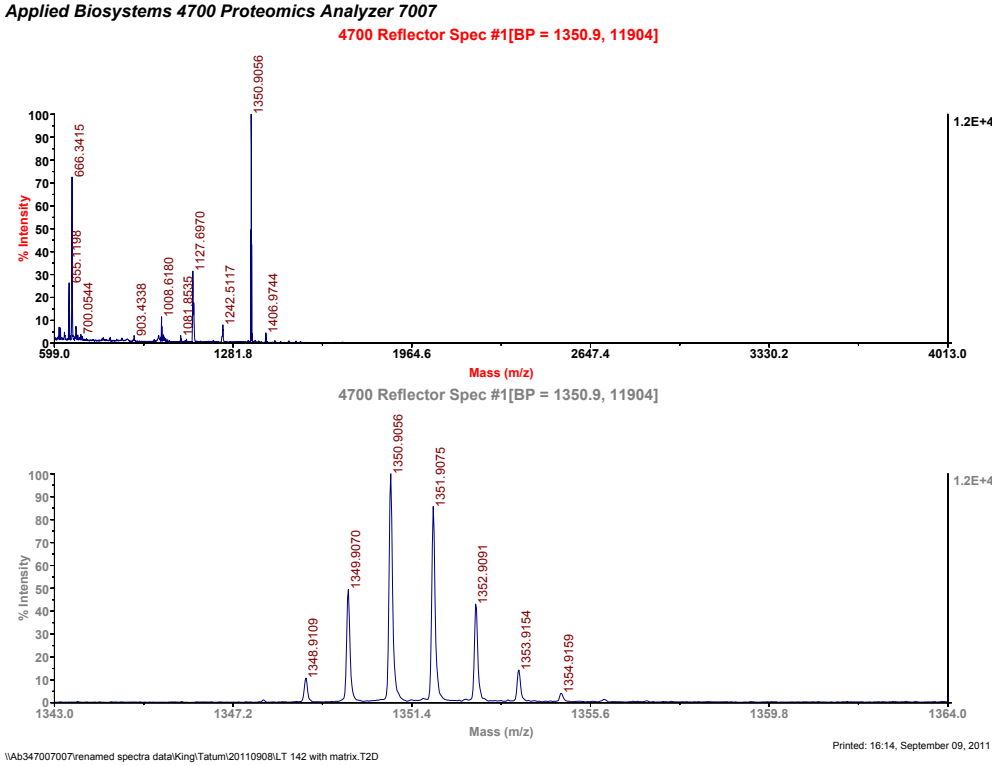


3,5-di(3,7-dimethyloctyloxy) discotic

Applied Biosystems 4700 Proteomics Analyzer 7007



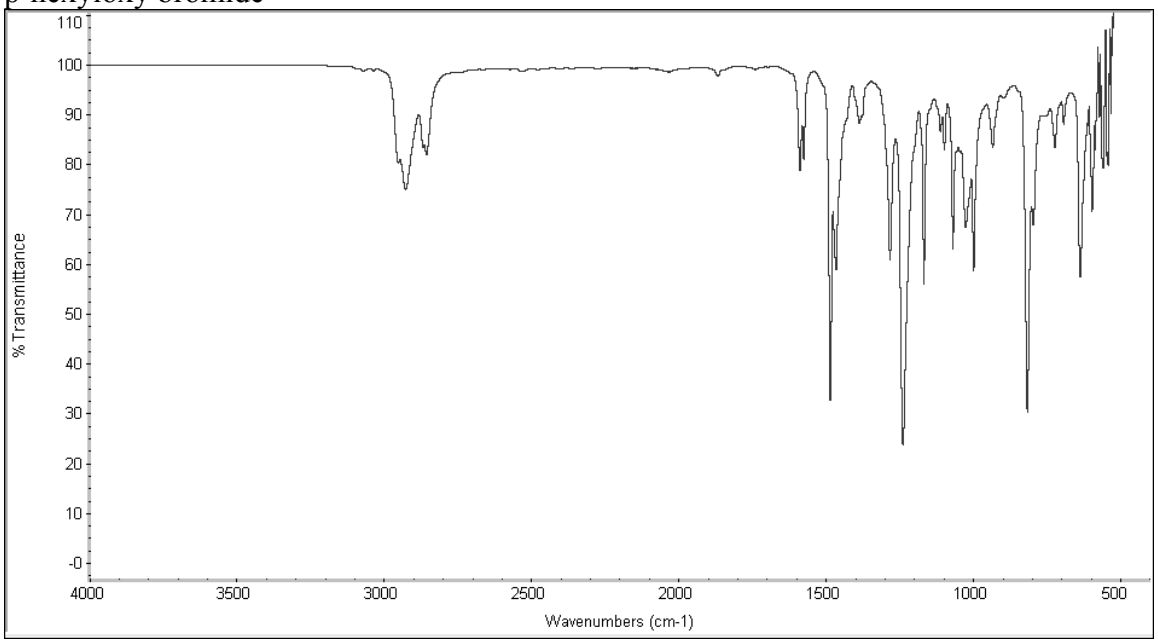
3,5-di(2-ethylhexyloxy) discotic



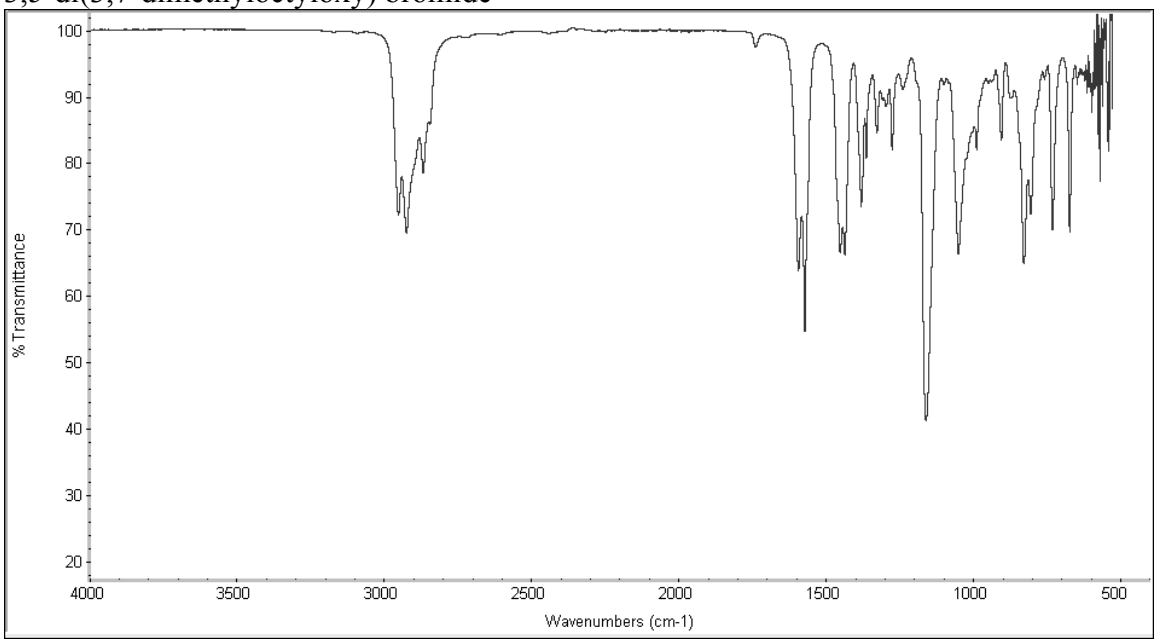
This journal is © The Royal Society of Chemistry 2012

IR

p-hexyloxy bromide

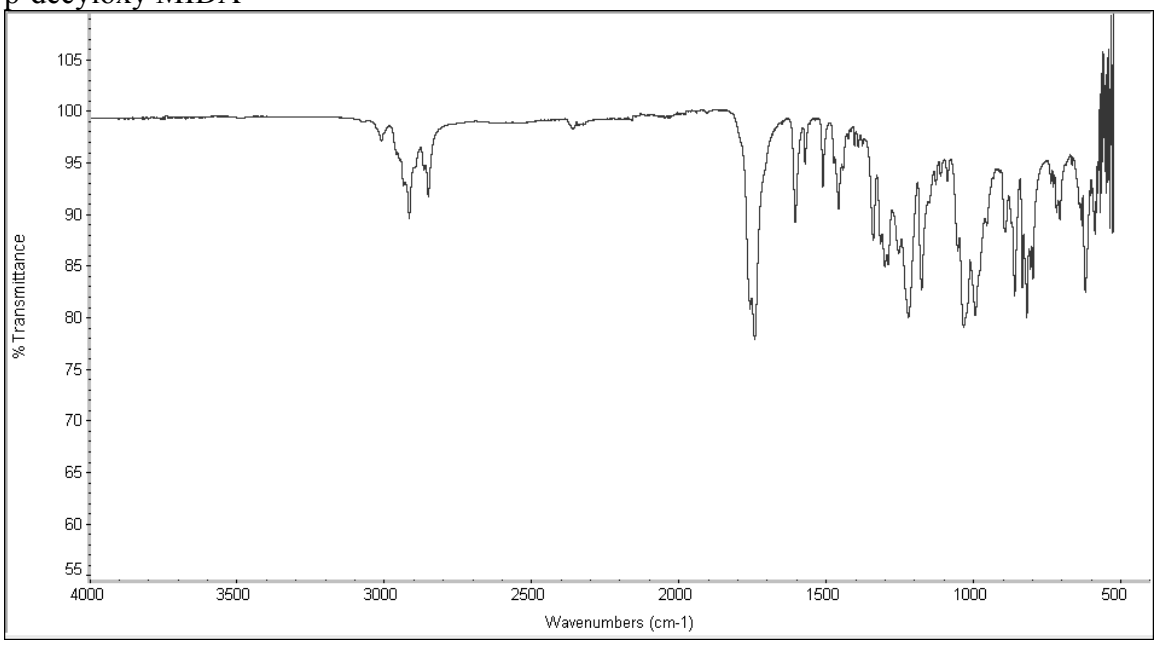


3,5-di(3,7-dimethyloctyloxy) bromide

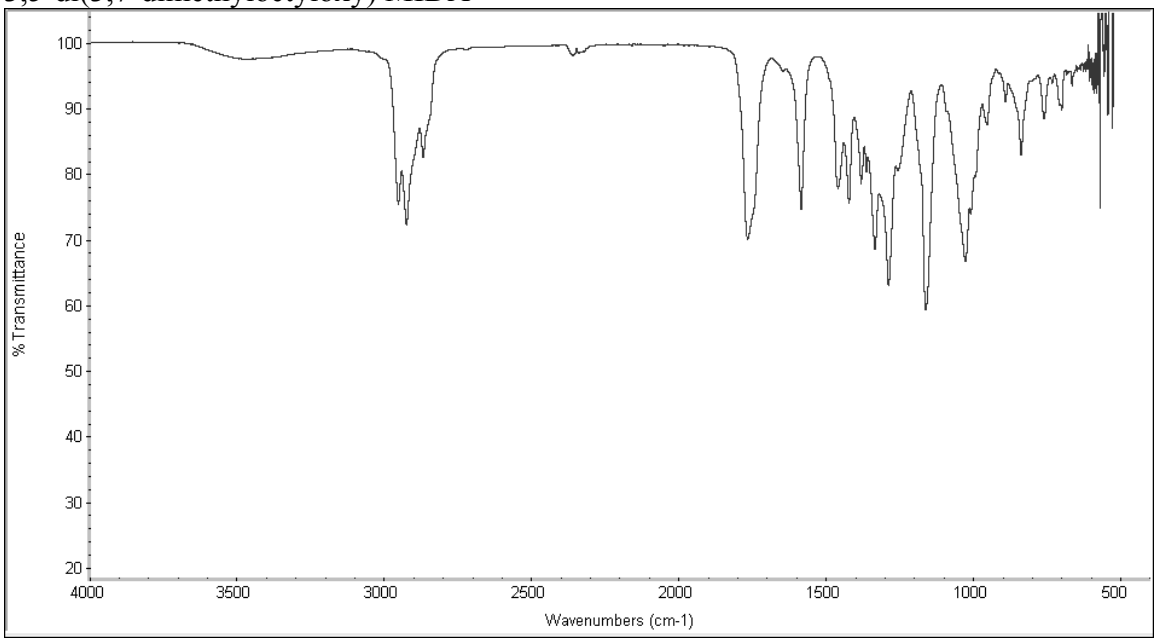


This journal is © The Royal Society of Chemistry 2012

p-decyloxy MIDA

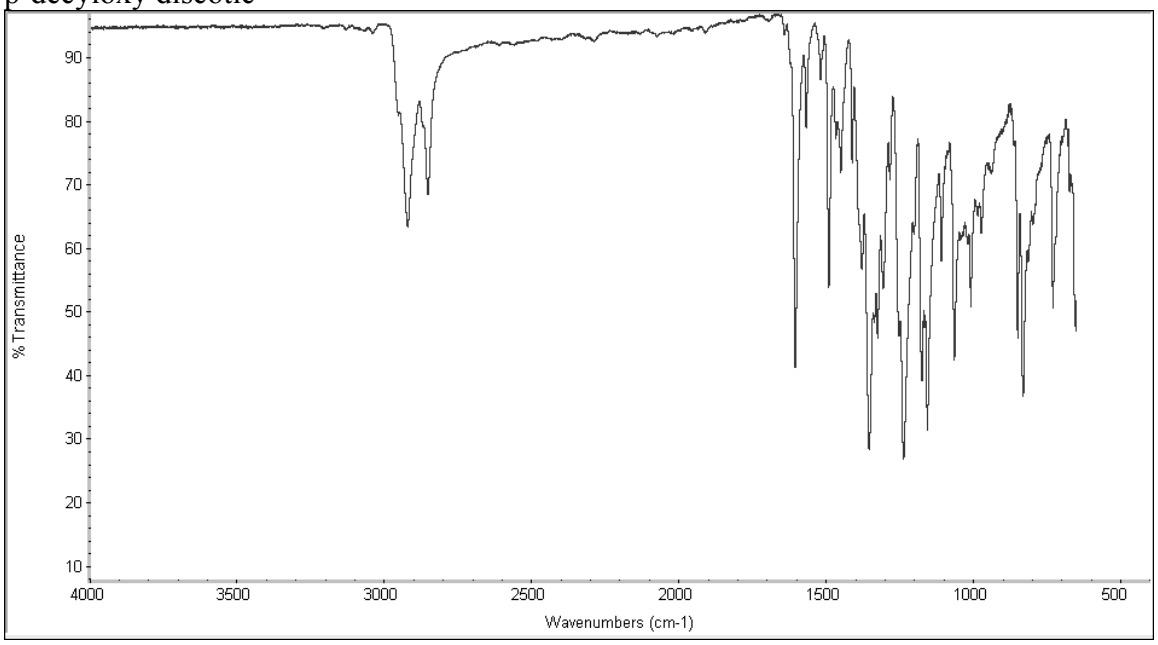


3,5-di(3,7-dimethyloctyloxy) MIDA

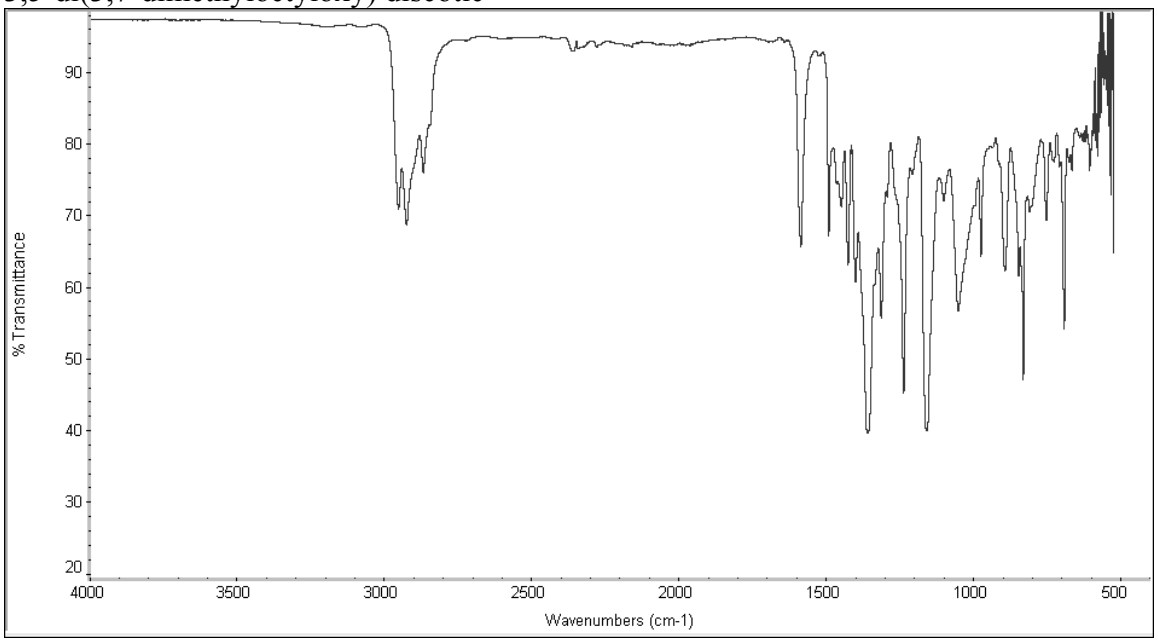


This journal is © The Royal Society of Chemistry 2012

p-decyloxy discotic



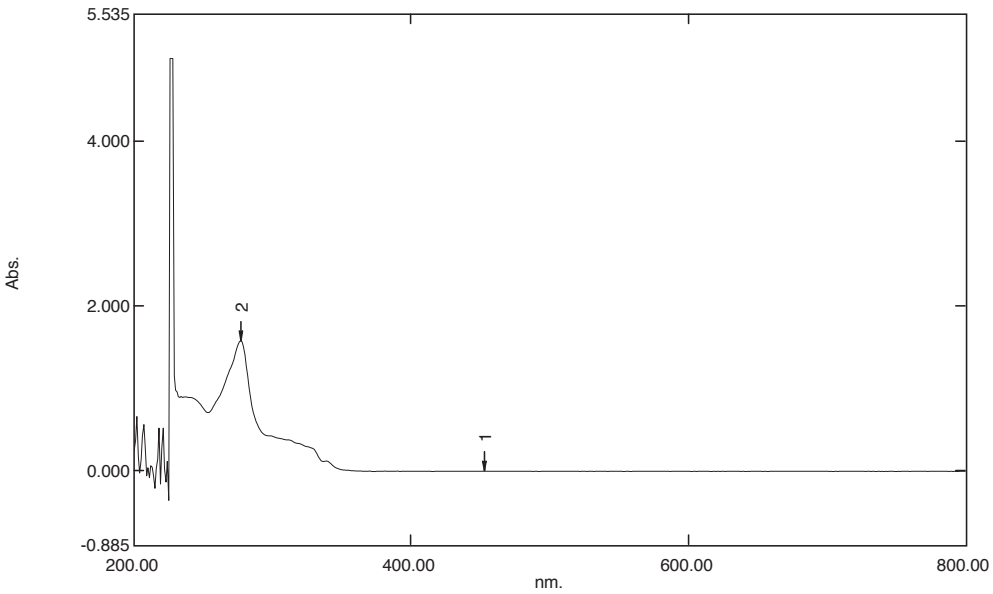
3,5-di(3,7-dimethyloctyloxy) discotic



This journal is © The Royal Society of Chemistry 2012

UV

p-decyloxy discotic

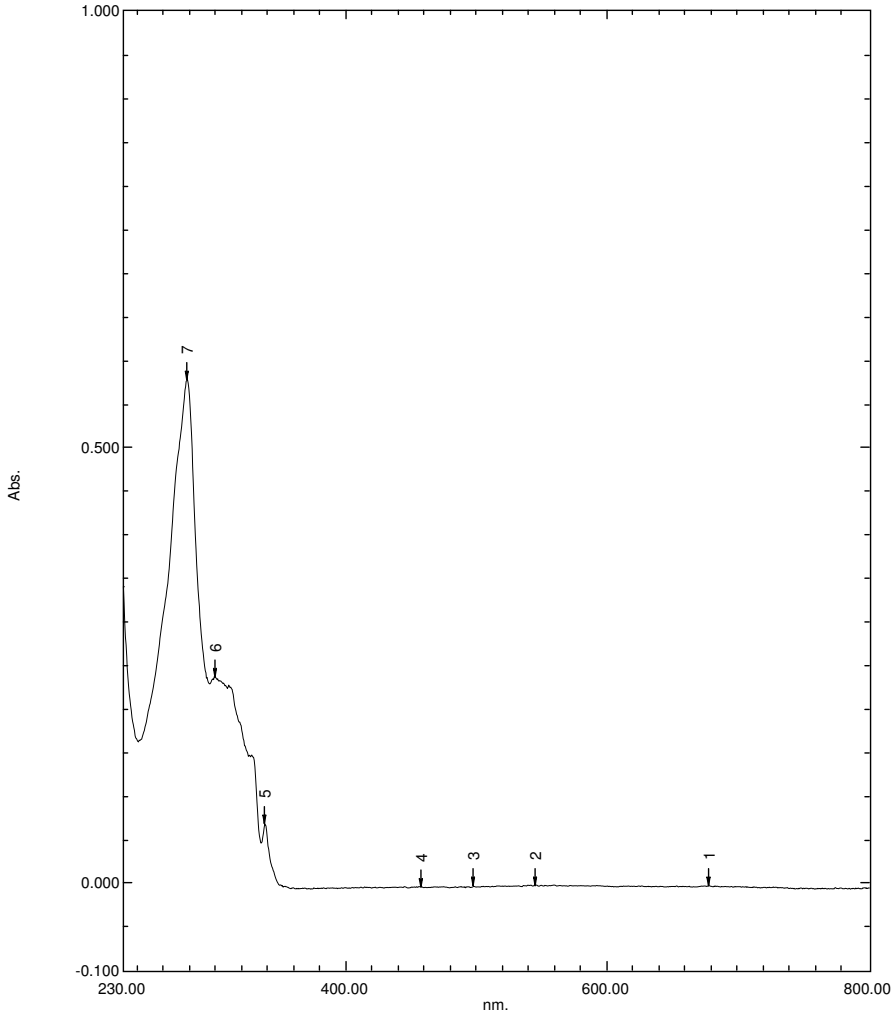


3,5-di(3,7-dimethyloctyloxy) discotic

Overlay Spectrum Graph Report

07/19/2011 12:54:09 PM

LT185 - RawData - Z:\uvvis\data\King\ltatum\LT185.spc



Page 1 / 1

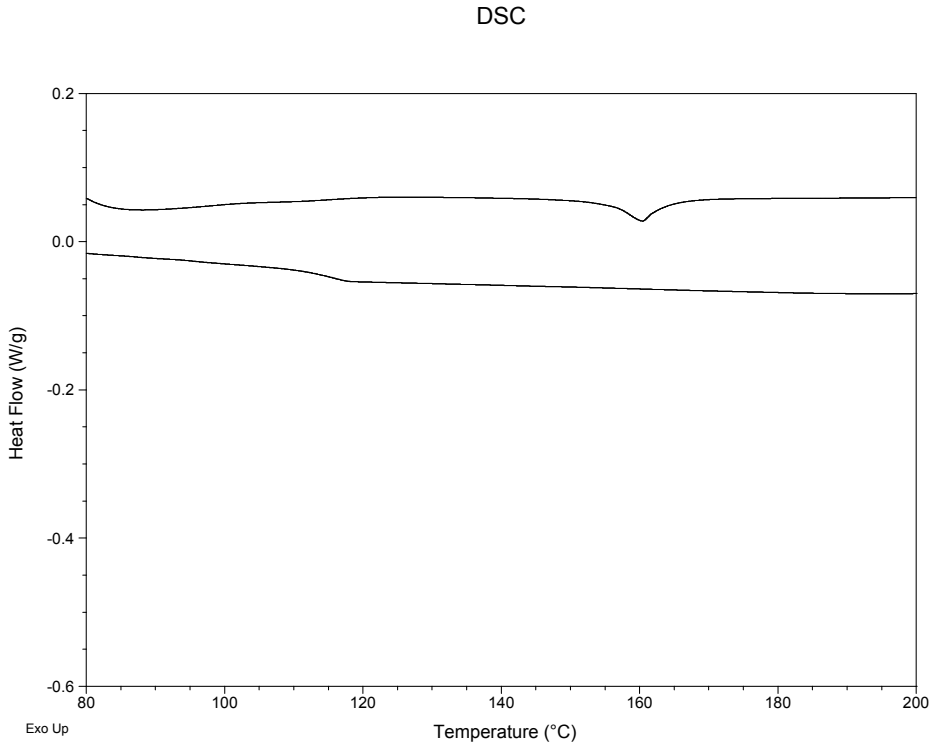
This journal is © The Royal Society of Chemistry 2012

DSC

Melting points of non-liquid crystalline discotics along with DSC traces of those found to be liquid crystalline are reported.

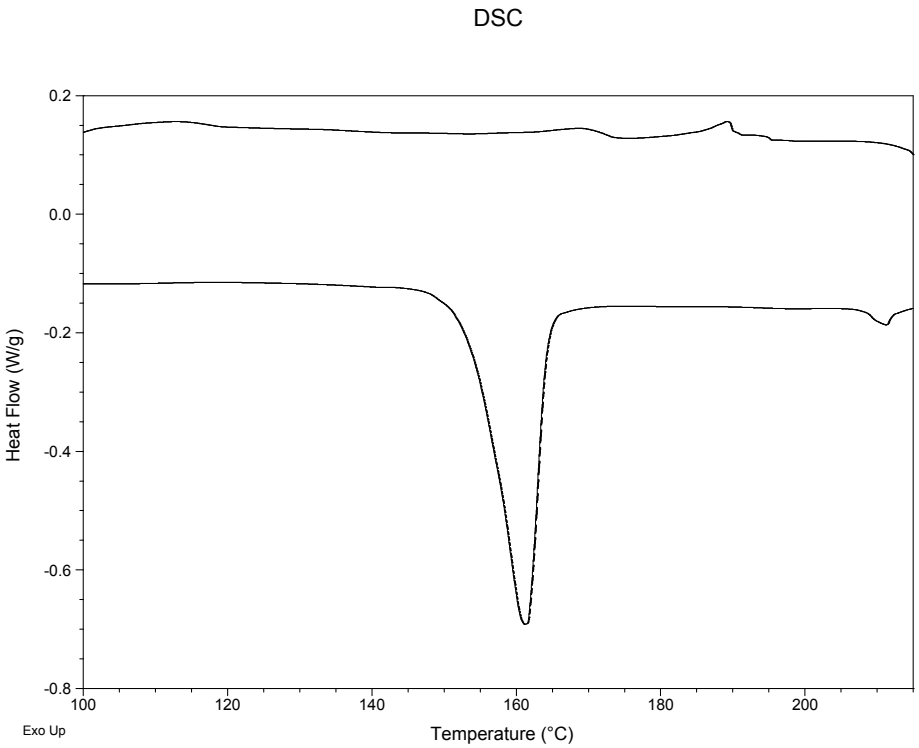
Compound	Thermal Behavior
4a	Cr 174 °C Iso
4b	Cr 158 °C Iso
4c	Cr 140 Col_h °C 200 Iso
4d	Cr 80 Col_h °C 197 Iso
4e	Cr 82 °C Iso
4f	Cr 156 °C Iso
4g	Cr 138 °C Iso
4h	Cr 127 °C Iso
4i	Cr 120 °C Iso
4j	Cr 45 Col_h °C 80 Iso
4k	Col_h 200 °C Iso
4l	Glassy solid 160 °C Iso

4a p-hexyloxy discotic

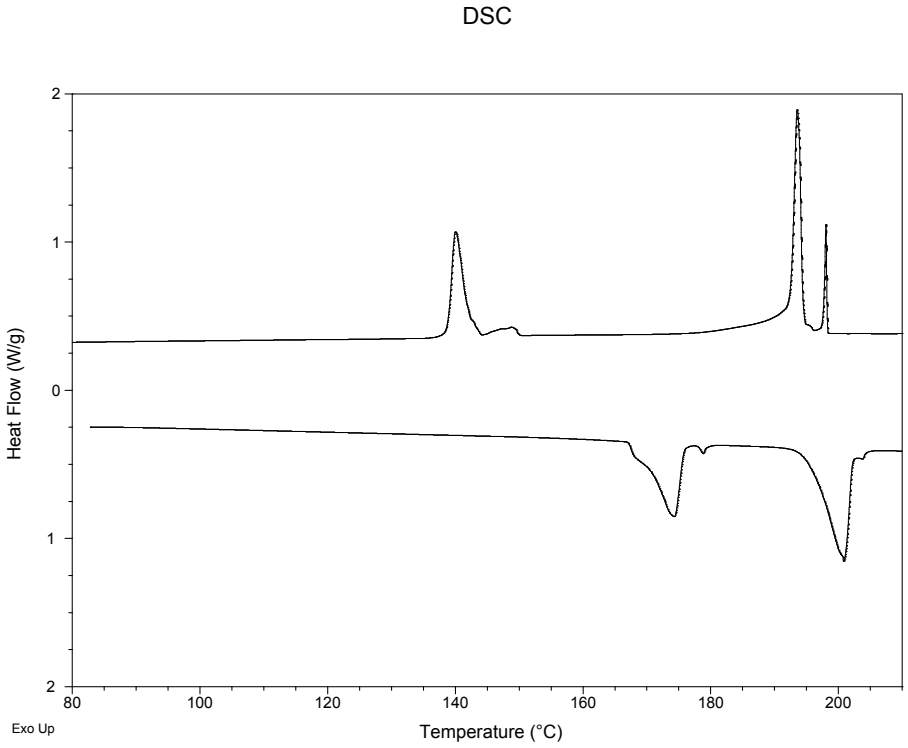


4b p-octyloxy discotic

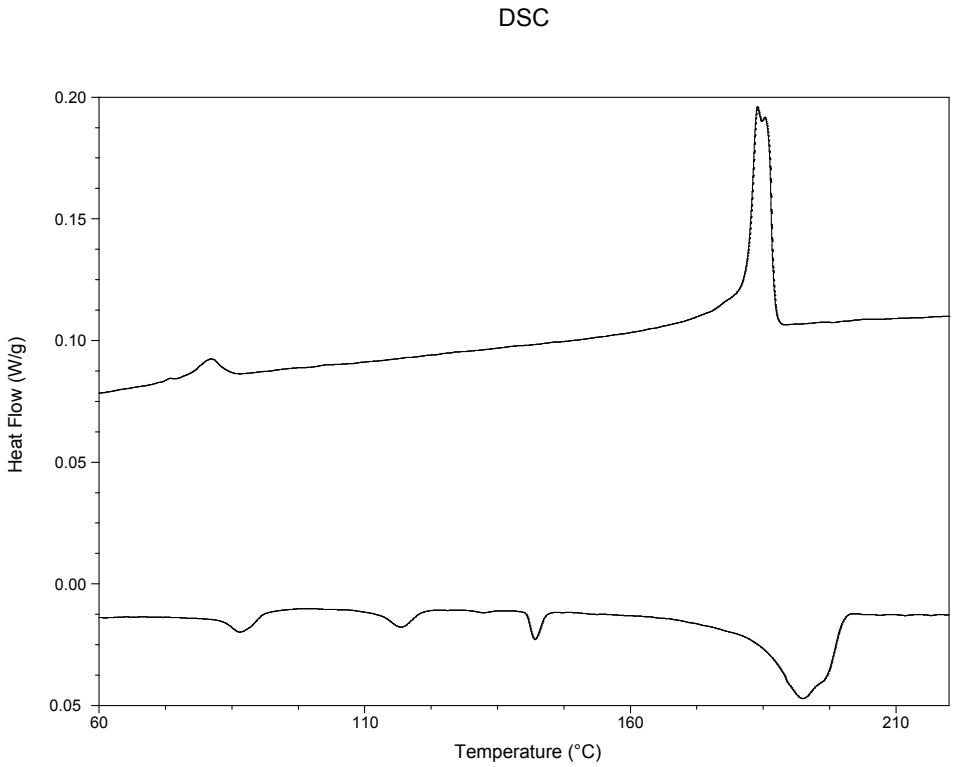
This journal is © The Royal Society of Chemistry 2012



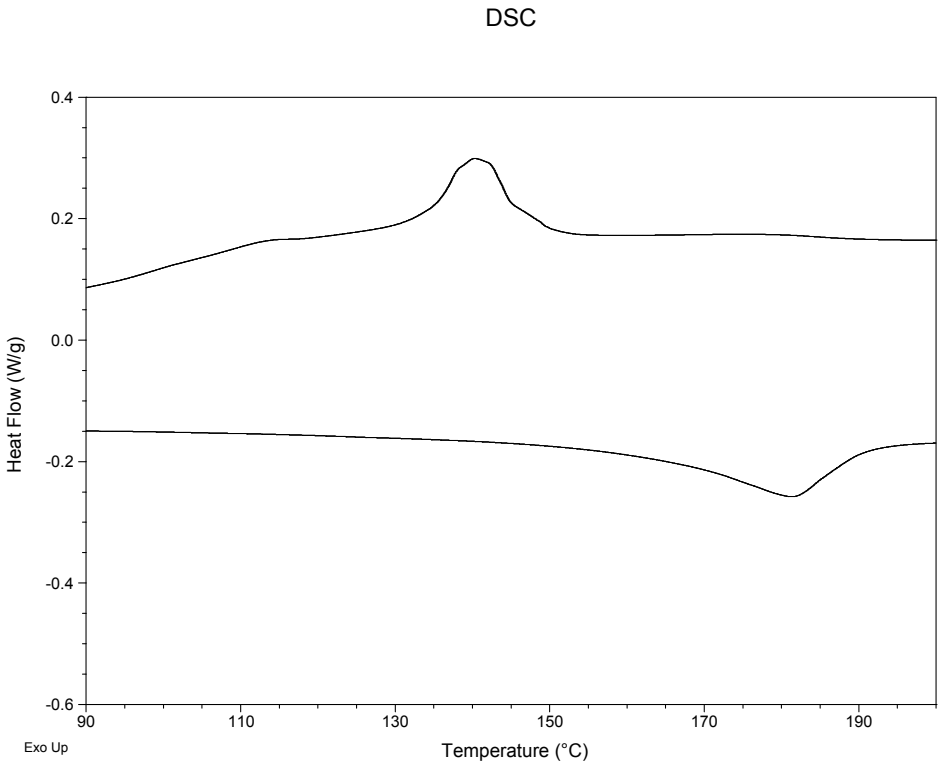
4c p-decyloxy discotic



4d p-dodecyloxy discotic

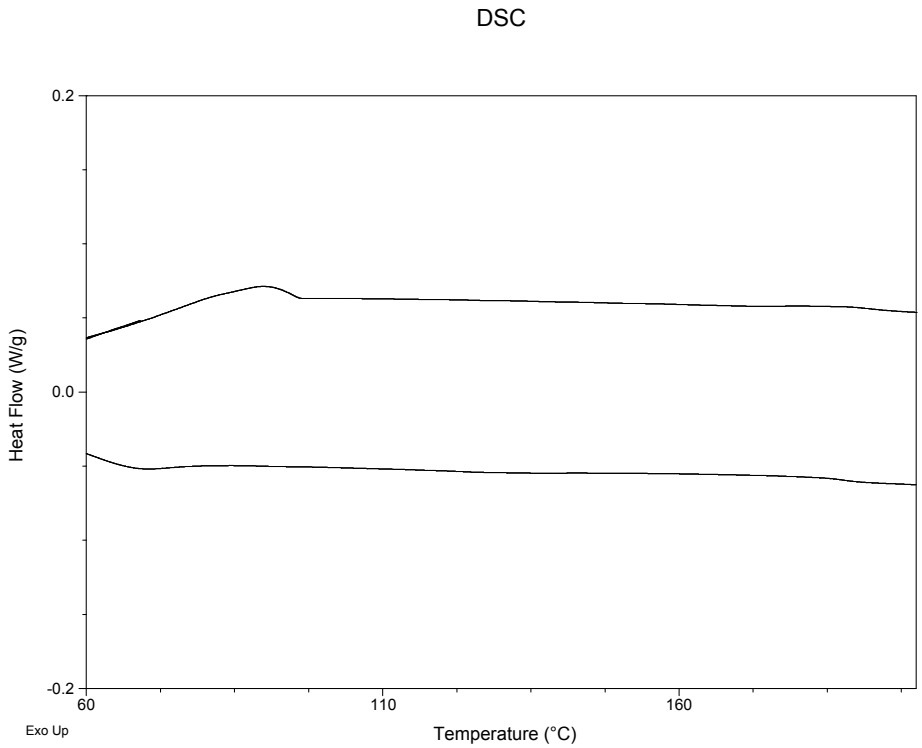


4e p-(3,7-dimethyloctyloxy) discotic

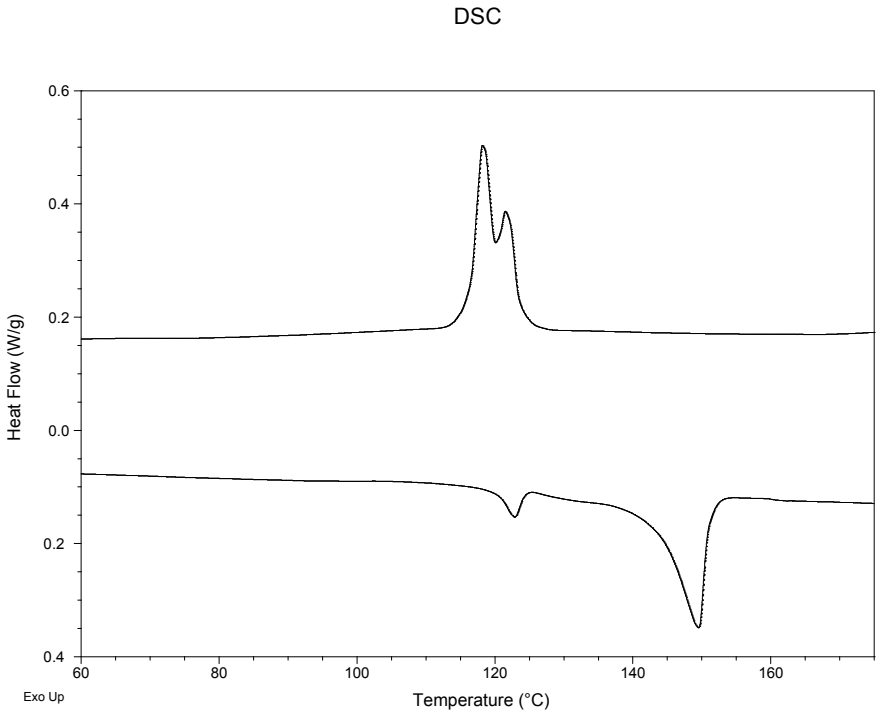


4f p-(2-ethylhexyloxy) discotic

This journal is © The Royal Society of Chemistry 2012



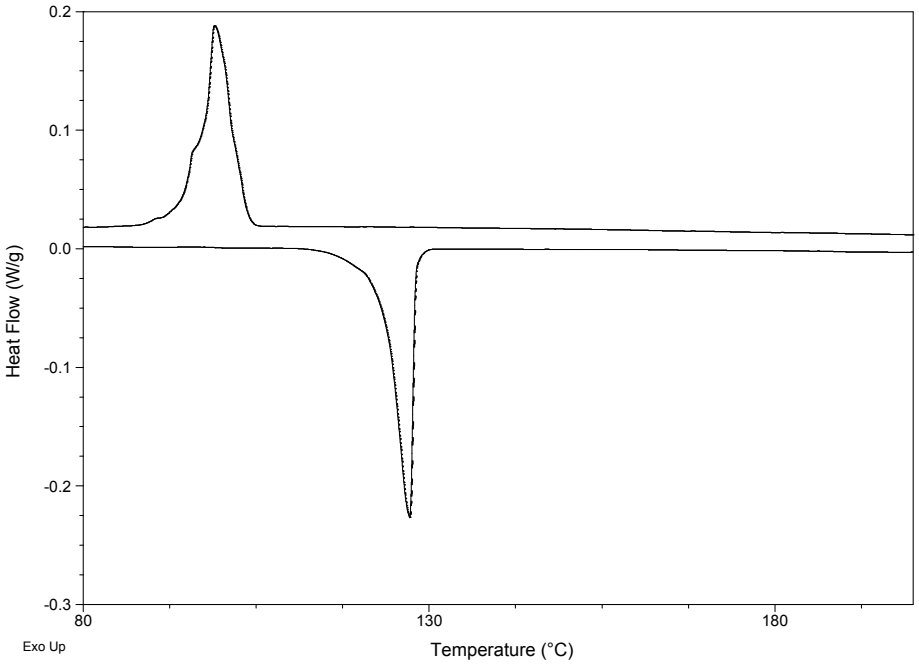
4g 3,5-dihexyloxy discotic



4h 3,5-dioctyloxy discotic

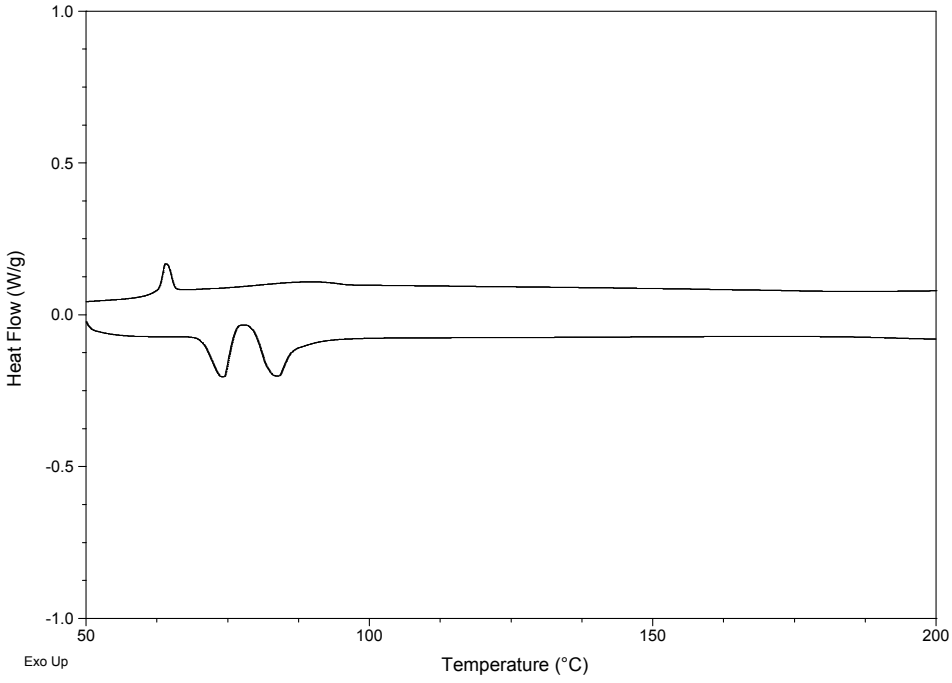
This journal is © The Royal Society of Chemistry 2012

DSC

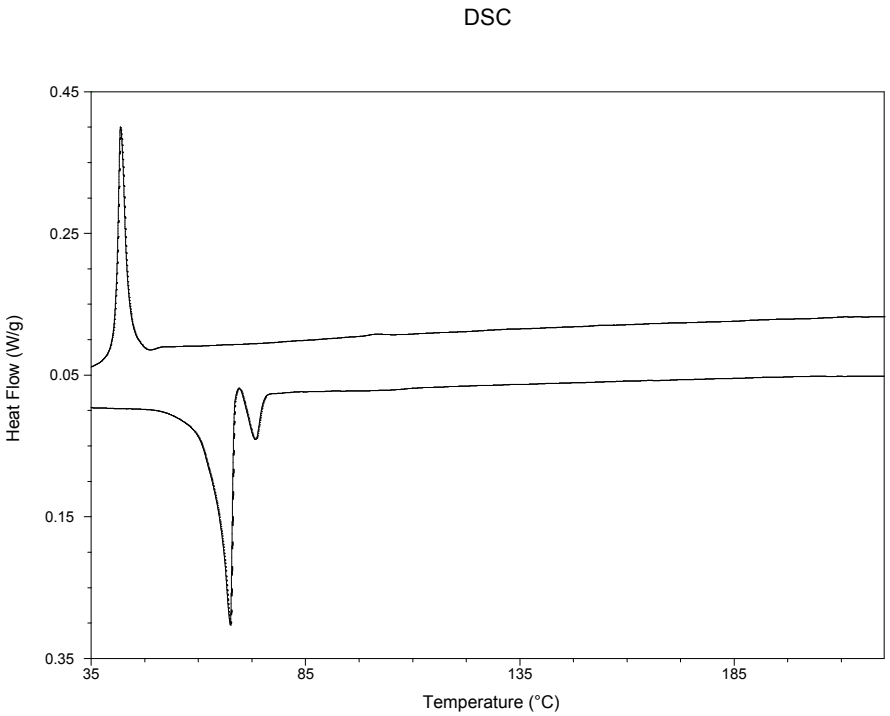


4i 3,5-didecyloxy discotic

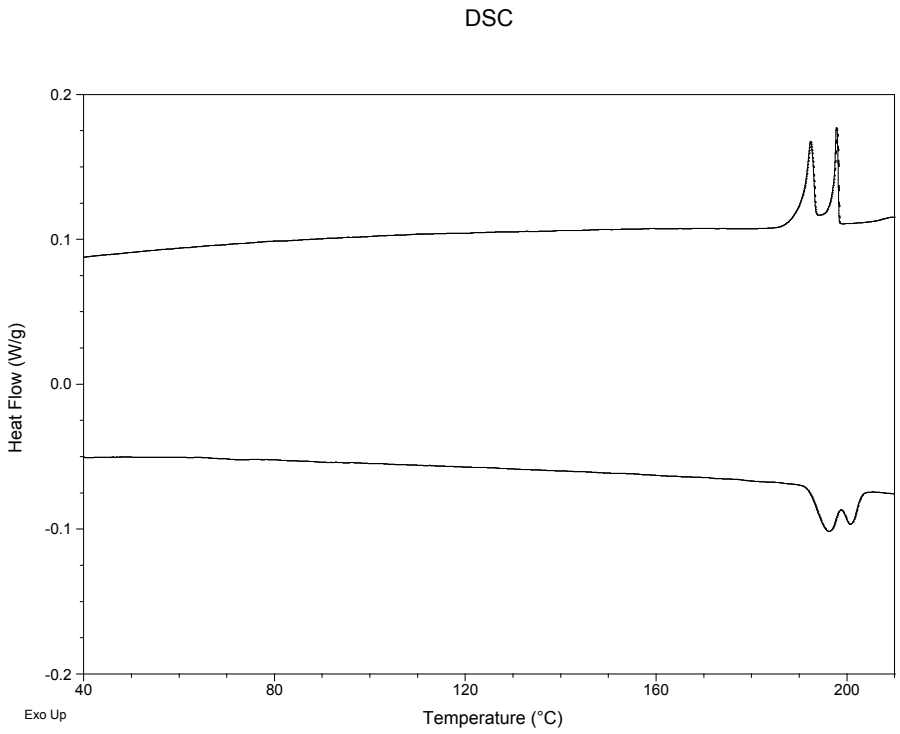
DSC



4j 3,5-didodecyloxy discotic



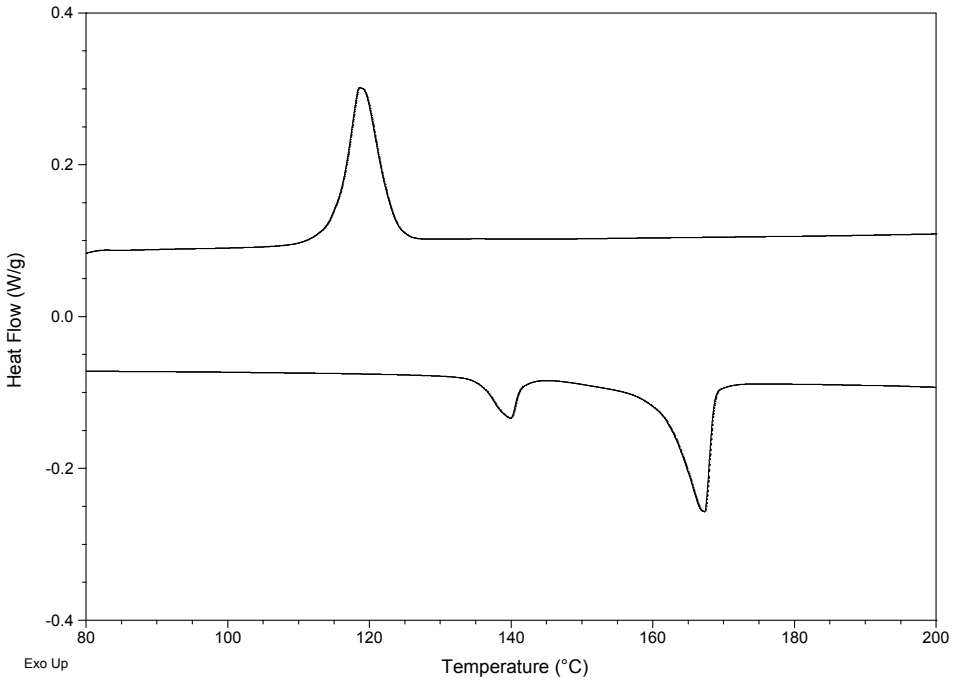
4k 3,5-di(3,7-dimethyloctyloxy) discotic



4l 3,5-di(2-ethylhexyloxy) discotic

This journal is © The Royal Society of Chemistry 2012

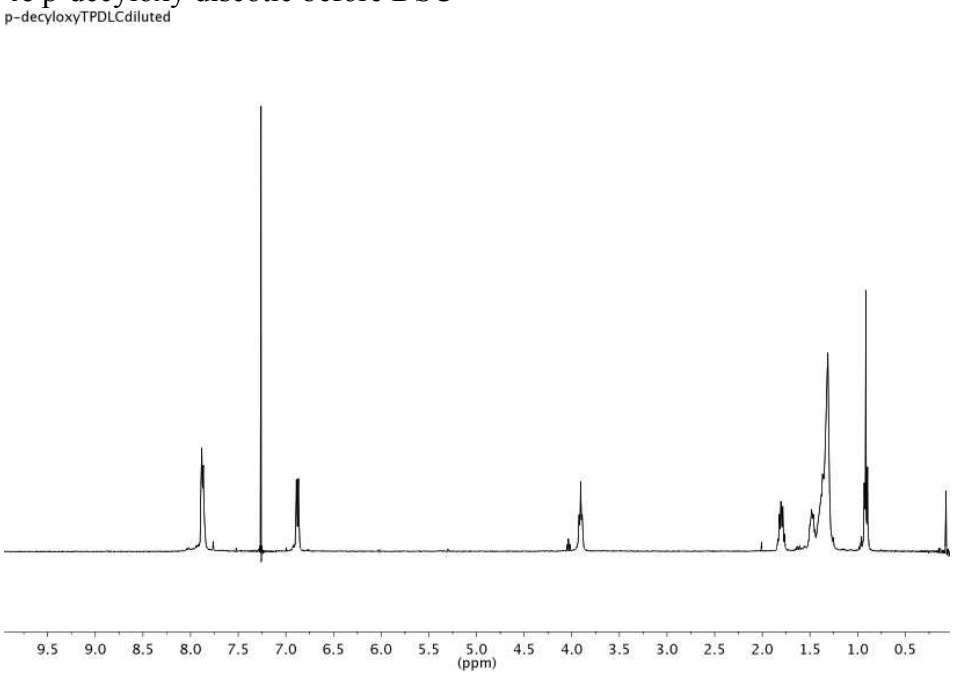
DSC



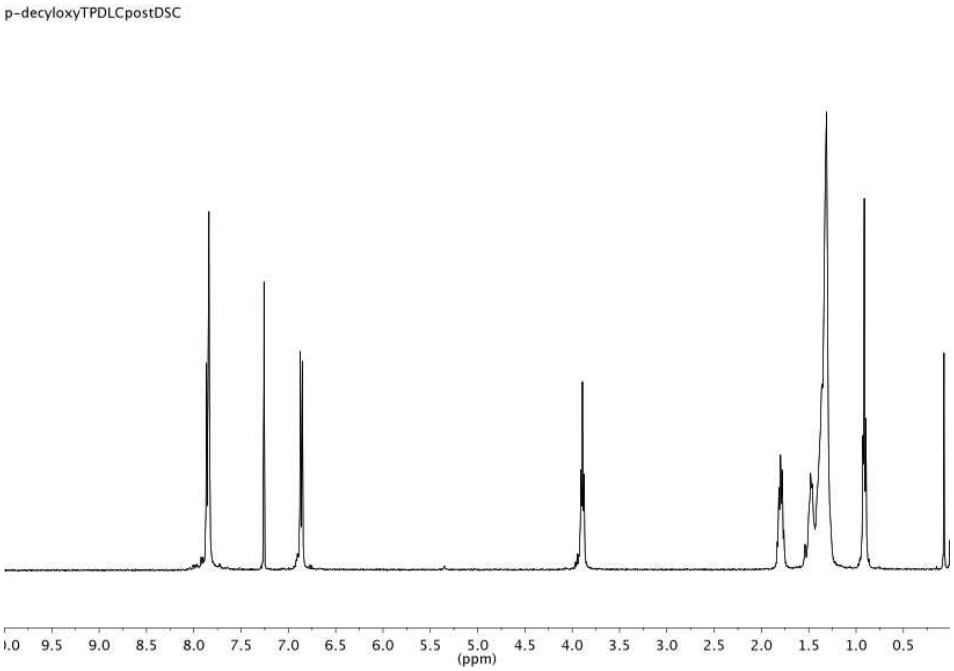
DLC Stability

DLCs **4c**, and **4k** were submitted to 3 thermal cycles in a DSC under N_2 from room temperature to 250° C, neither showed evidence of decomposition by NMR. Addition of protic solvents to DLCs **4c**, and **4k** cleaved the boronic ester linkages. Compound **4k** was also left out in a vial on the bench top under ambient conditions and showed no major decomposition.

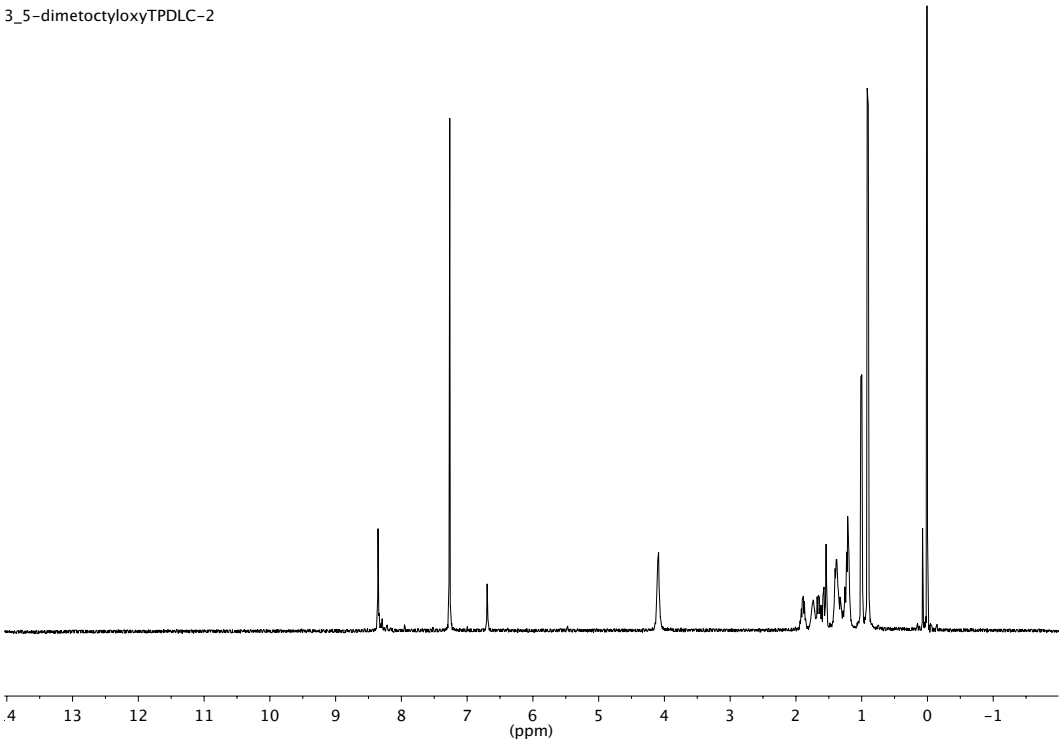
4c p-decyloxy discotic before DSC



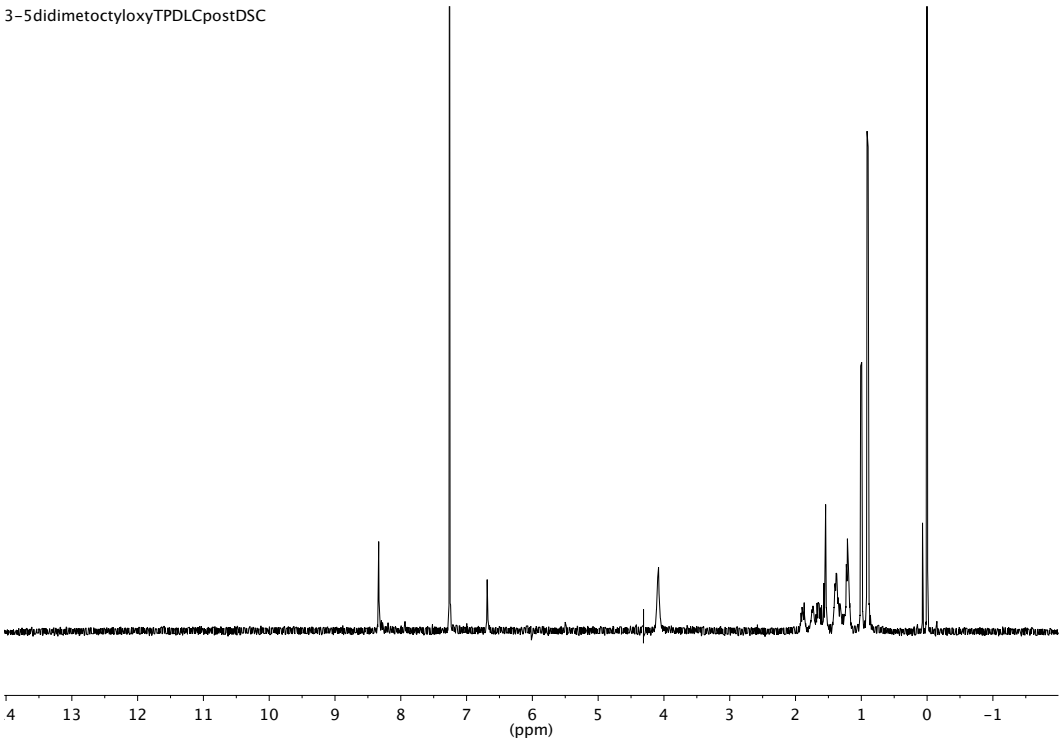
4c p-decyloxy discotic after DSC



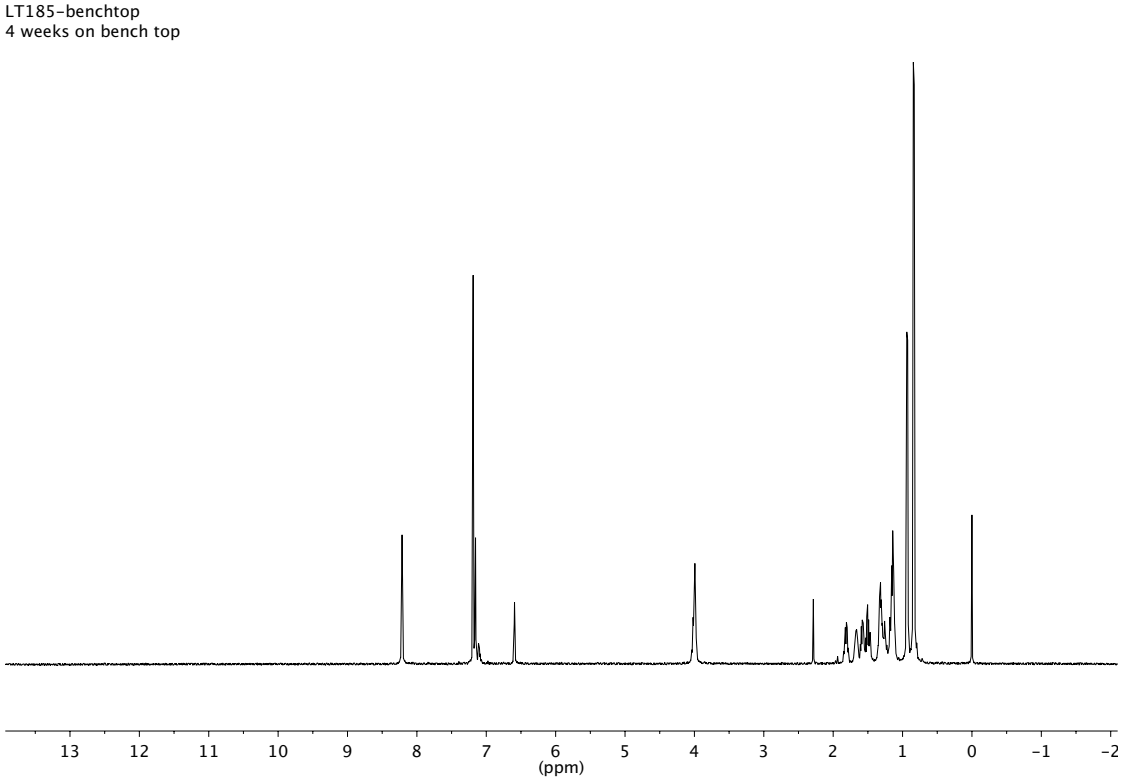
4k 3,5-di(3,7-dimethyloctyloxy) discotic before DSC



4k 3,5-di(3,7-dimethyloctyloxy) discotic after DSC

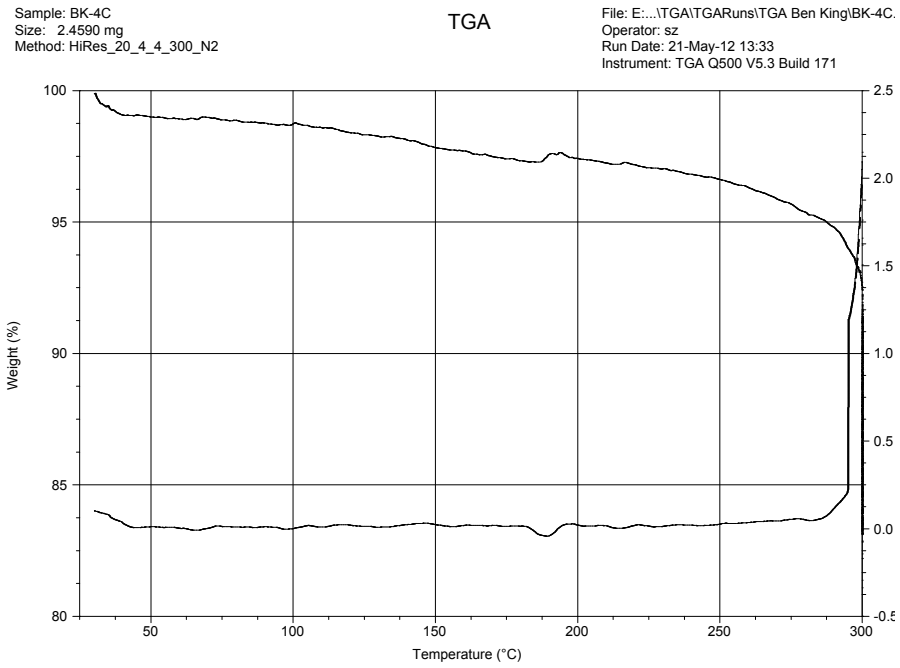


NMR of DLC **4k** acquired after sitting in a vial on a bench top under ambient conditions.



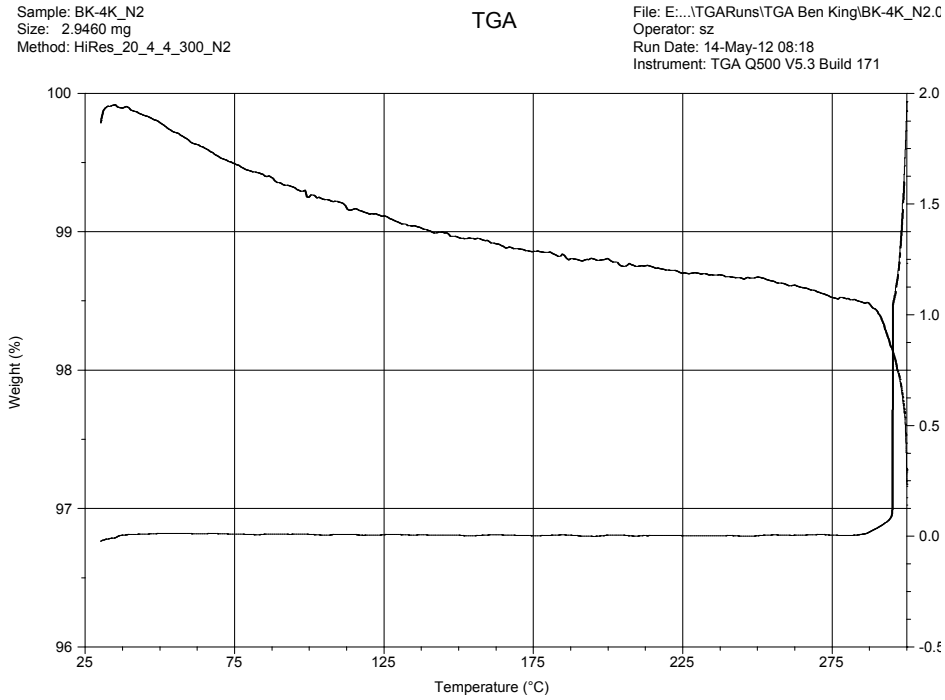
DLC TGA

TGA data acquired for **4c**



This journal is © The Royal Society of Chemistry 2012

TGA data acquired for **4k**



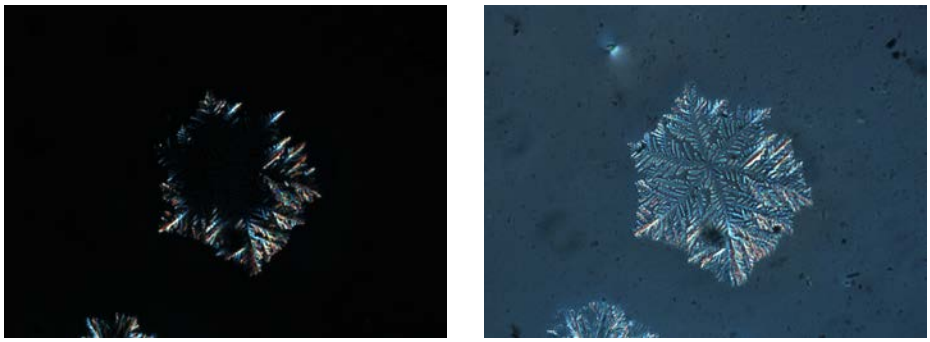
This journal is © The Royal Society of Chemistry 2012

POM

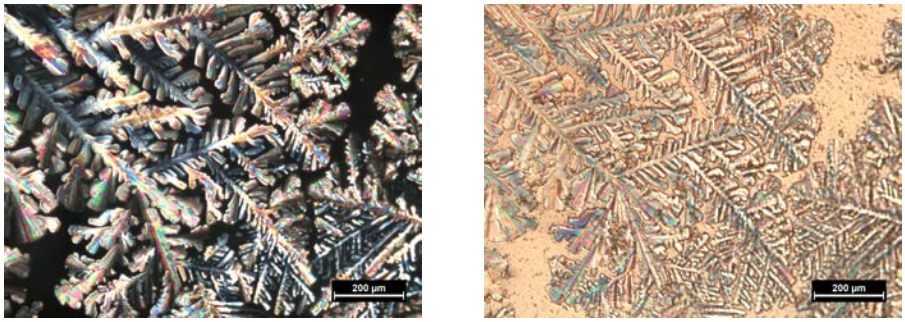
4k 3,5-di(3,7-dimethyloctyloxy) discotic

Left: POM image of **4k** between glass at 180° C right: DIC image of **4k** between glass, same location and temperature as POM picture.

4c p-decyloxy discotic

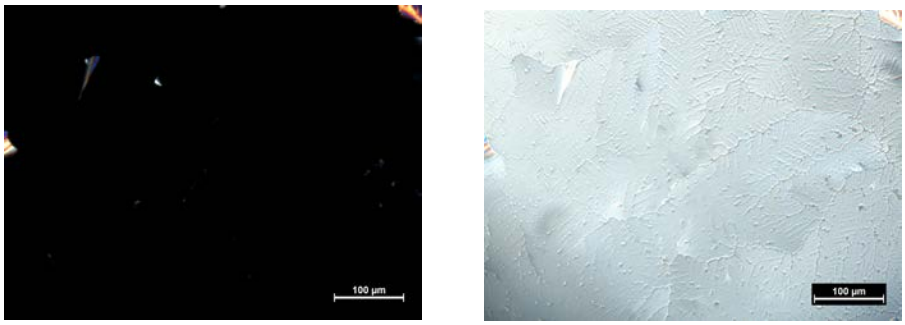


Left: POM image of **4c** at 198° C between glass right: DIC image of **4c** between glass, same location and temperature as POM picture.



Left: POM image of **4d** between glass at 190° C; right: DIC image of **4d** between glass, same location and temperature as POM picture.

This journal is © The Royal Society of Chemistry 2012



Left: POM image of **4j** between glass at 70° C; right: DIC image of **4j** between glass, same location and temperature as POM picture.

This journal is © The Royal Society of Chemistry 2012

Computational Methods

All compounds were modeled using the freeware Avogadro program[1] followed by geometry optimization at the semi-empirical UF F level of theory. These geometries were saved as *.xyz files then edited to include appropriate input parameters for geometry optimization at the density functional level of theory. Density functional geometry optimizations were then conducted at the B3LYP/6-31G* level of theory using the Gaussian '03 program suite.[2] Each computation produced a binary checkpoint file upon completion. The frontier orbital diagrams were modeled by using the "formchk" script and the graphics were rendered in Avogadro.

This journal is © The Royal Society of Chemistry 2012

Sample Gaussian Input

File: ~john1887/01/133/hexamethoxytriphenylene.in

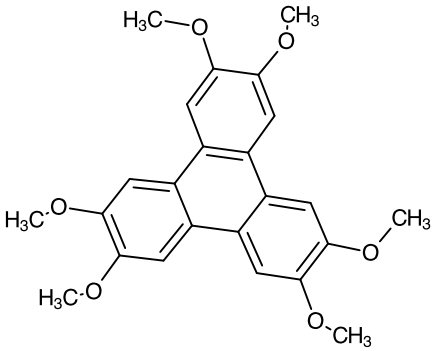
```
%nproc=4
%chk=hexamethoxytriphenylene.chk
%mem=3GB
#N opt B3LYP/6-31G*

hexamethoxytriphenylene, dft gas, b3lyp, 6-31g*

0 1
 C    -1.103750    -2.942300    -1.596690
 C    -0.496330    -1.787540    -1.066060
 C    -1.276350    -0.603880    -0.969630
 C    -2.617220    -0.648670    -1.421890
 C    -3.155498    -1.710927    -2.132746
 C    -2.321690    -2.848898    -2.387777
 C    -0.649195     0.666541    -0.855219
 C     0.763262     0.774015    -0.937165
 C     1.549682    -0.421362    -0.973073
 C     0.935840    -1.699012    -1.012802
 C    -1.397628     1.860454    -0.666458
 C    -0.809095     3.112145    -0.637065
 C     0.578202     3.234077    -0.821727
 C     1.347486     2.070800    -0.959760
 C     1.776242    -2.863228    -0.995432
 C     3.184443    -2.748915    -0.914643
 C     3.760064    -1.467577    -0.880250
 C     2.956015    -0.347084    -0.919674
 O    -1.638797     4.179993    -0.471925
 C    -1.352522     5.494278    -0.755380
 O     1.161795     4.456863    -0.820582
 C     2.239930     4.847600    -1.591279
 O     3.992938    -3.846472    -0.849143
 C     3.612913    -5.173072    -0.804213
 O     5.095562    -1.221736    -0.787713
 C     6.135609    -2.111687    -0.840061
 O    -4.429613    -1.486840    -2.559129
 C    -5.233099    -2.136623    -3.444715
 O    -2.632560    -3.979790    -3.068435
 C    -3.750690    -4.718509    -3.369109
 H    -3.154607     0.243644    -1.679502
 H    -0.515854    -3.763698    -1.965477
 H     1.369753    -3.854172    -1.010140
 H     3.481699     0.579372    -0.868593
 H    -2.461483     1.857278    -0.532100
 H     2.401507     2.228044    -1.074110
 H    -2.266751     6.096721    -0.593895
```

This journal is © The Royal Society of Chemistry 2012

H	-1.061030	5.572685	-1.824982
H	-0.559792	5.896447	-0.091544
H	2.015984	5.854429	-2.003408
H	2.406993	4.165944	-2.452688
H	3.151501	4.924020	-0.964760
H	7.074048	-1.531817	-0.722808
H	6.145555	-2.609412	-1.830855
H	6.073932	-2.840874	-0.007261
H	4.529491	-5.797952	-0.734850
H	3.069581	-5.458762	-1.728437
H	2.993279	-5.378224	0.095125
H	-4.645451	-4.405727	-3.874375
H	-3.667410	-4.811403	-4.467343
H	-4.270527	-5.000656	-2.424913
H	-6.116489	-1.506933	-3.650309
H	-5.672872	-3.015725	-2.945884
H	-4.697202	-2.282849	-4.412509

This journal is © The Royal Society of Chemistry 2012

B3LYP/6-31G* Optimized Geometries



File:
~john1887/01/133/hexamethoxytriphenylene.out

B3LYP/6-31G* Energy:
-1380.2949023 Hartree

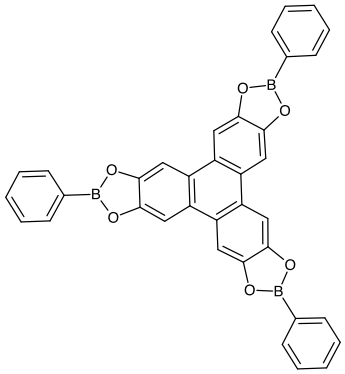
HOMO Energy: -5.23 eV
LUMO Energy: -0.64 eV

NImag: 0

Coordinates (in Å):

C	-2.793198	0.281429	-0.039983
C	-1.388218	0.137773	-0.044509
C	-0.845255	-1.175925	-0.045916
C	-1.736010	-2.270692	0.004430
C	-3.108347	-2.107944	0.030154
C	-3.649500	-0.803225	-0.013722
C	0.602822	-1.368807	-0.095356
C	1.468232	-0.247428	-0.131928
C	0.910386	1.104094	-0.093395
C	-0.493796	1.296031	-0.057081
C	1.181372	-2.658266	-0.112658
C	2.543528	-2.862256	-0.180909
C	3.408870	-1.739454	-0.246038
C	2.864099	-0.466499	-0.212782
C	-1.001708	2.616757	-0.030264
C	-0.173211	3.726389	-0.036241
C	1.232398	3.534808	-0.048083
C	1.736194	2.251305	-0.076970
O	3.020384	-4.147376	-0.265401
C	3.795977	-4.600422	0.846484
O	4.741390	-2.016787	-0.353632
C	5.644401	-0.930245	-0.486663
O	-0.601682	5.022916	-0.038015
C	-1.999121	5.267587	-0.066070
O	2.106547	4.592911	-0.100752
C	2.160650	5.417763	1.065694
O	-3.916374	-3.224138	0.048801
C	-4.644150	-3.416585	1.267235
O	-5.010324	-0.583460	0.013023
C	-5.702706	-0.983604	-1.175597
H	-1.371816	-3.290587	0.025703
H	-3.261571	1.258003	-0.063434
H	-2.071144	2.770489	-0.008435
H	2.816272	2.169828	-0.089307
H	0.567995	-3.550787	-0.089013
H	3.529982	0.382843	-0.269305
H	4.045318	-5.642723	0.634153
H	3.212139	-4.549660	1.775564
H	4.715906	-4.018823	0.959034
H	6.635371	-1.376700	-0.586641
H	5.626832	-0.278656	0.397158
H	5.422416	-0.332362	-1.379990
H	2.930523	6.167369	0.868095
H	2.446727	4.827935	1.947090
H	1.203974	5.914689	1.251824
H	-2.111368	6.353073	-0.086536
H	-2.497791	4.867094	0.826518
H	-2.463246	4.836829	-0.962742
H	-5.582431	-2.054858	-1.365823
H	-6.756968	-0.753305	-1.004767
H	-5.341550	-0.415256	-2.042659
H	-5.230941	-4.327747	1.129269
H	-5.310959	-2.572724	1.471708
H	-3.955452	-3.551999	2.111362

This journal is © The Royal Society of Chemistry 2012



File:
~john1887/01/126/triphenylene-ph.out

B3LYP/6-31G* Energy:
-1910.7558186 Hartree

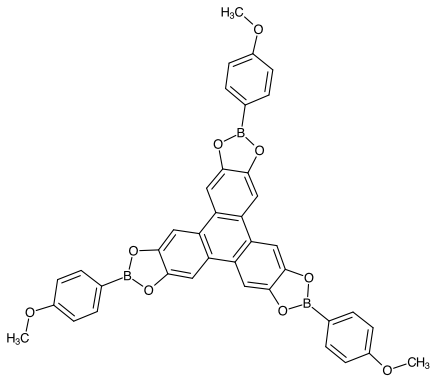
HOMO Energy: -5.65 eV
LUMO Energy: -1.23 eV

NImag: 0

Coordinates (in Å):

C	5.490473	7.732417	-0.032187
C	4.750867	8.917227	0.008884
C	3.354806	8.870478	0.044803
C	2.701000	7.639845	0.039669
C	3.427984	6.435366	-0.000938
C	4.833378	6.503530	-0.036856
B	2.703713	5.075832	-0.005218
O	1.316715	4.918050	0.021435
C	1.103006	3.557591	0.010619
C	2.336824	2.900434	-0.020241
C	2.422538	1.533311	-0.033777
C	1.220915	0.774827	-0.015892
C	-0.038686	1.445661	0.009248
C	-0.079463	2.866080	0.024775
C	1.271172	-0.689633	-0.017654
C	0.060210	-1.445150	-0.003809
C	-1.233318	-0.756295	0.000269
C	-1.282030	0.670172	0.013618
C	0.116460	-2.865095	0.007837
C	1.343438	-3.474116	-0.000615
C	2.529713	-2.734059	-0.018905
C	2.521974	-1.364257	-0.026152
C	-2.539932	1.331479	0.024175
C	-3.680851	0.573554	0.018230
C	-3.633149	-0.823745	-0.000556
C	-2.443119	-1.502044	-0.010165
O	-4.996720	0.980086	0.021813
B	-5.748281	-0.196431	0.004196
C	-7.287744	-0.249020	-0.002291
C	-8.049896	0.934042	0.018294
C	-9.442665	0.888152	0.011852
C	-10.098377	-0.345446	-0.015529
C	-9.359464	-1.531211	-0.036274
C	-7.966810	-1.481604	-0.029615
O	-4.918223	-1.318934	-0.010399
O	3.346789	3.836772	-0.030871
O	1.649277	-4.816866	0.010260
B	3.043900	-4.879481	-0.002623
C	3.859300	-6.186287	0.005034
C	3.216556	-7.438110	0.033397
C	3.953482	-8.620833	0.041266
C	5.349764	-8.571322	0.020703
C	6.006421	-7.338244	-0.007663
C	5.266302	-6.157513	-0.015303
O	3.601179	-3.599411	-0.020772
H	-2.624452	2.409459	0.032729
H	-2.453389	-2.583115	-0.030803
H	-0.774965	-3.476782	0.028232
H	3.463416	-0.832417	-0.034234
H	-7.393569	-2.404887	-0.045921
H	-9.870078	-2.490334	-0.057586
H	-11.184810	-0.382722	-0.020710
H	-7.541342	1.894376	0.039388
H	-10.017912	1.810069	0.027904
H	2.130527	-7.478769	0.049604
H	5.925825	-9.493193	0.026799
H	3.443140	-9.580087	0.063373
H	7.092426	-7.300148	-0.023542
H	5.778593	-5.199198	-0.037038
H	1.615010	7.605377	0.067554
H	2.779992	9.792254	0.076626
H	5.262231	9.876510	0.012792
H	6.576280	7.769346	-0.060097
H	5.410225	5.582895	-0.068563
H	-1.010369	3.415878	0.047757
H	3.397974	1.067222	-0.057266

This journal is © The Royal Society of Chemistry 2012



File: ~john1887/01/109/triphenylene-ch3_geom-opt.out

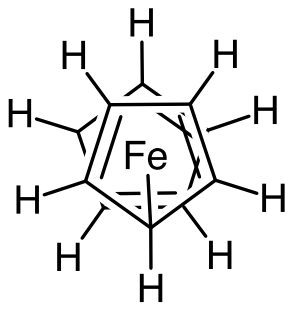
B3LYP/6-31G* Energy: -3399.1498113 Hartree

HOMO Energy: --5.45 eV
LUMO Energy: -0.97 eV

NImag:0

Coordinates (in Å):

C	-1.431692	0.206134	-0.000500
C	-0.911896	-1.123178	-0.000561
C	0.536767	-1.343283	-0.000433
C	1.427882	-0.228468	0.000427
C	0.894286	1.136185	0.000410
C	-0.516698	1.350581	-0.000295
C	-1.805800	-2.228322	-0.000582
C	-3.153765	-1.984414	-0.000655
C	-3.663074	-0.681836	-0.000625
C	-2.838175	0.411757	-0.000474
C	1.062154	-2.664105	-0.001065
C	2.421777	-2.831584	-0.000513
C	3.294865	-1.738975	0.000629
C	2.831917	-0.449766	0.001054
C	1.775655	2.251348	0.000868
C	-1.026789	2.677334	-0.000712
C	-0.141588	3.722754	-0.000275
C	1.241130	3.512607	0.000540
H	-1.456427	-3.251710	-0.000401
H	-3.275879	1.400631	-0.000233
H	-2.087724	2.886514	-0.001471
H	2.850807	2.135749	0.001356
H	0.424719	-3.537635	-0.002021
H	3.543368	0.364583	0.001851
O	-4.200463	-2.878802	-0.000650
O	-5.038833	-0.734644	-0.000514
O	3.155799	-3.996380	-0.000902
O	4.592887	-2.197746	0.001011
O	1.883204	4.730485	0.000812
O	-0.392870	5.076369	-0.000561
B	-5.358802	-2.095570	-0.000561
B	4.494305	-3.592575	0.000073
B	0.864594	5.688051	0.000047
C	1.095103	7.205047	0.000131
C	-7.026936	-4.038459	0.000259
C	-8.318464	-4.563039	0.000684
C	2.397368	7.749684	0.000848
C	2.608569	9.119058	0.000878
C	1.511929	9.997665	0.000203
C	0.015801	8.104062	-0.000519
C	0.207082	9.484864	-0.000486
H	-0.999523	7.715994	-0.001074
H	-0.652448	10.145427	-0.000974
H	3.608764	9.541051	0.001404
H	3.254072	7.080937	0.001349
O	1.820945	11.322817	0.000326
C	0.759614	12.266924	-0.000765
H	1.235081	13.249221	-0.000955
H	0.131537	12.167435	0.893859
H	0.132594	12.166581	-0.896030
C	-11.003696	-5.475298	0.001379
H	-12.092109	-5.554824	0.002023
H	-10.602802	-5.968655	0.896166
H	-10.603966	-5.968893	-0.893786
C	10.244640	-6.790895	0.000913
H	10.857482	-7.693900	0.000648
H	10.471421	-6.198320	0.896583
H	10.472927	-6.196783	-0.893357
C	-9.414841	-3.689209	0.000570
C	-9.202136	-2.300185	-0.000071
C	-7.910532	-1.798626	-0.000487
O	-10.716992	-4.084132	0.001059
H	-10.067588	-1.644859	-0.000185
C	5.513730	-5.950482	-0.001376
C	6.594028	-6.818056	-0.001538
C	7.903263	-6.307591	-0.000290
C	7.011286	-4.065102	0.001207
C	8.111482	-4.921117	0.001100
H	9.113194	-4.506823	0.002081
O	8.896365	-7.237790	-0.000594
C	5.693100	-4.550386	-0.000012
H	7.182871	-2.991760	0.002254
H	4.506179	-6.357886	-0.002295
H	6.459380	-7.895246	-0.002597
C	-6.787887	-2.654300	-0.000281
H	-8.460873	-5.637666	0.001145
H	-6.183202	-4.723724	0.000344
H	-7.759438	-0.722368	-0.000899



File:
~john1887/01/151/ferrocene.out

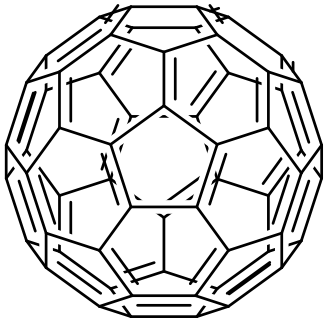
B3LYP/6-31G* Energy:
-1650.7030409 Hartree

HOMO Energy: -5.15 eV
LUMO Energy: 0.26 eV

NImag: 1

Coordinates (in Å):

C	1.652095	-0.480334	1.116658
C	1.657139	-1.208892	-0.110847
C	1.659836	-0.266628	-1.183063
C	1.656408	1.044547	-0.618641
C	1.652772	0.912418	0.802576
Fe	0.000299	-0.001021	-0.003238
C	-1.655398	-1.046529	0.615823
C	-1.652767	0.261307	1.187097
C	-1.654136	1.208904	0.119708
C	-1.658690	0.486375	-1.111320
C	-1.658483	-0.907586	-0.805021
H	-1.628164	0.493696	2.243957
H	-1.635953	2.286019	0.225001
H	-1.647843	0.920038	-2.102966
H	-1.651353	-1.715859	-1.524866
H	-1.639911	-1.981125	1.161578
H	1.632967	1.726415	1.515796
H	1.632684	-0.908514	2.110547
H	1.644563	-2.286458	-0.212054
H	1.649697	-0.504049	-2.239059
H	1.642885	1.974912	-1.171575



File:
~john1887/01/110/g03/c60.out

B3LYP/6-31G* Energy:
-2286.1734331 Hartree

HOMO Energy: -5.98 eV
LUMO Energy: -3.23 eV

NImag: 0

Coordinates (in Å):

C	0.000000	1.236140	3.327546
C	-1.175639	0.381988	3.327546
C	-0.726585	-1.000058	3.327546
C	0.726585	-1.000058	3.327546
C	1.175639	0.381988	3.327546
C	-2.600095	-2.342583	0.593644
C	-1.424456	-3.196735	0.593644
C	-0.697871	-2.960653	1.829784
C	-1.424456	-1.960595	2.593761
C	-2.600095	-1.578607	1.829784
C	1.424456	-3.196735	0.593644
C	2.600095	-2.342583	0.593644
C	2.600095	-1.578607	1.829784
C	1.424456	-1.960595	2.593761
C	0.697871	-2.960653	1.829784
C	-3.031402	0.251178	-1.829784
C	-2.304818	-0.748881	-2.593761
C	-2.304818	-1.985021	-1.829784
C	-3.031402	-1.748939	-0.593644
C	-3.480457	-0.366892	-0.593644
C	-1.175639	-2.805417	-1.829784
C	0.000000	-2.423429	-2.593761
C	1.175639	-2.805417	-1.829784
C	0.726585	-3.423487	-0.593644
C	-0.726585	-3.423487	-0.593644
C	2.304818	-1.985021	-1.829784
C	2.304818	-0.748881	-2.593761
C	3.031402	0.251178	-1.829784
C	3.480457	-0.366892	-0.593644
C	3.031402	-1.748939	-0.593644

This journal is © The Royal Society of Chemistry 2012

C	3.480457	0.366892	0.593644
C	3.031402	1.748939	0.593644
C	2.304818	1.985021	1.829784
C	2.304818	0.748881	2.593761
C	3.031402	-0.251178	1.829784
C	0.726585	3.423487	0.593644
C	-0.726585	3.423487	0.593644
C	-1.175639	2.805417	1.829784
C	0.000000	2.423429	2.593761
C	1.175639	2.805417	1.829784
C	-3.031402	1.748939	0.593644
C	-3.480457	0.366892	0.593644
C	-3.031402	-0.251178	1.829784
C	-2.304818	0.748881	2.593761
C	-2.304818	1.985021	1.829784

C	2.600095	1.578607	-1.829784
C	1.424456	1.960595	-2.593761
C	0.697871	2.960653	-1.829784
C	1.424456	3.196735	-0.593644
C	2.600095	2.342583	-0.593644
C	-0.697871	2.960653	-1.829784
C	-1.424456	1.960595	-2.593761
C	-2.600095	1.578607	-1.829784
C	-2.600095	2.342583	-0.593644
C	-1.424456	3.196735	-0.593644
C	-0.726585	1.000058	-3.327546
C	0.726585	1.000058	-3.327546
C	1.175639	-0.381988	-3.327546
C	0.000000	-1.236140	-3.327546
C	-1.175639	-0.381988	-3.327546

This journal is © The Royal Society of Chemistry 2012

Table of Frontier Molecular Orbital Energies for Figure Xx

File:
~john1887/01/160/hexamethoxytriphenylene_c3v/g03/hexamethoxytriphenylene_c3v.out

Molecular Orbital*	Orbital Symmetry	Energy/Hartree
1	E''	-0.24288
2	E''	-0.24288
3	A2''	-0.22443
4	A1''	-0.21549
5 (HOMO)	E''	-0.17969
6 (HOMO)	E''	-0.17969
7 (LUMO)	E''	-0.01390
8 (LUMO)	E''	-0.01390
9	A2''	-0.00537
10	E''	0.04955
11	E''	0.04955

*Arbitrary numbering

Table of Frontier Molecular Orbital Energies for Figure 4 in Paper

File:
~john1887/01/160/triphenylene-ph_c3h/g03/triphenylene-ph_c3h.out

Molecular Orbital**	Orbital Symmetry	Energy/Hartree
1	A2''	-0.28015
2	E''	-0.27754
3	E''	-0.27754
4	E''	-0.25615
5	E''	-0.25615
6	A1''	-0.25402
7	E''	-0.25390
8	E''	-0.25390
9	A2''	-0.24848
10	A1''	-0.23630
11 (HOMO)	E''	-0.20762
12 (HOMO)	E''	-0.20762
13 (LUMO)	A2''	-0.04504
14	E''	-0.04347
15	E''	-0.04347
16	E''	-0.02600
17	E''	-0.02600
18	A2''	-0.02058
19	A1''	-0.00284
20	E''	-0.00278
21	E''	-0.00278
22	E''	0.02931
23	E''	0.02931

**Arbitrary numbering

This journal is © The Royal Society of Chemistry 2012

Time of Flight

Our time of flight (TOF) apparatus consisted of a SRS NL100 nitrogen laser that irradiated the sample with a 337 nm, 3 ns, 200 mJ max pulse. The laser and power supply were isolated into separate Faraday cages in order to isolate the rf noise produced from the laser. Our samples were sandwiched between FTO plates with a thickness of 3-12 μm, controlled by mylar film. The sample thickness was confirmed by interferometry. The signal was amplified with a Stanford Research Systems DC to 350 MHz amplifier. The transients were measured across a 50-Ω resistor using a LeCroy 1 GHz digital oscilloscope. The samples were monitored via polarized optical microscopy to ensure homeotropic alignment. Our instrument was first tested using hexabutyloxytriphenylene and hexahexyloxytriphenylene, figure 1 and figure 2 respectively. The charge carrier mobilities found matched previously reported values.[3]

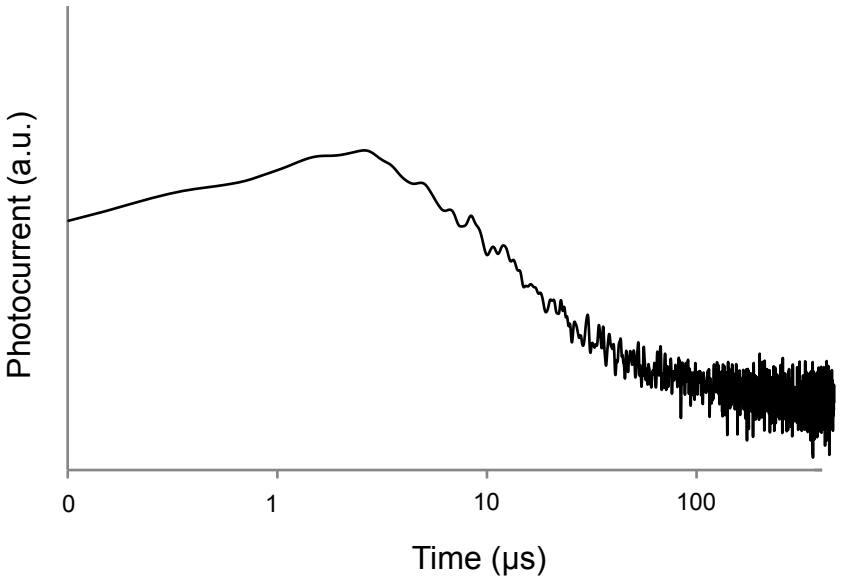


Figure 1: A standard TOF signal from hexabutyloxytriphenylene.

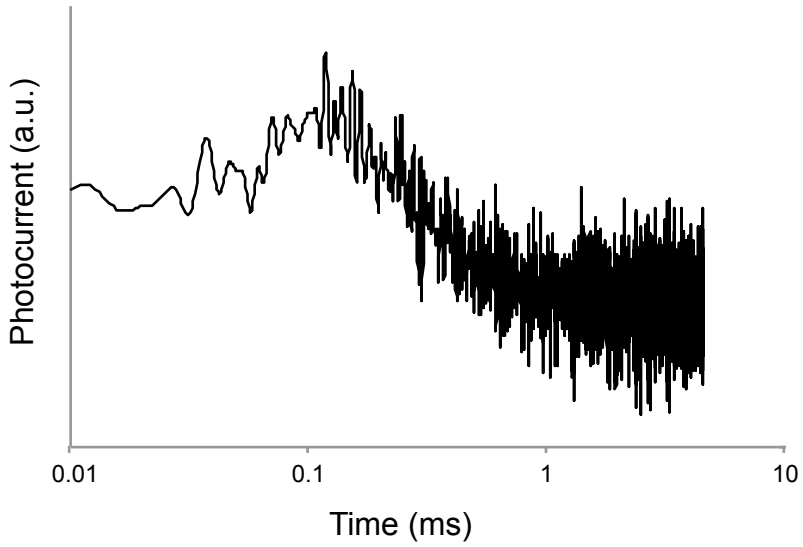


Figure 2: A TOF signal from hexahexyloxytriphenylene.

DLC **4c** displayed hole mobilities of 8×10^{-2} cm^2 V^{-1} s^{-1}as seen in figure 3. Figure 3 shows a 3.8 μm thick sample with an electric field of 0.157 V cm^{-1}.

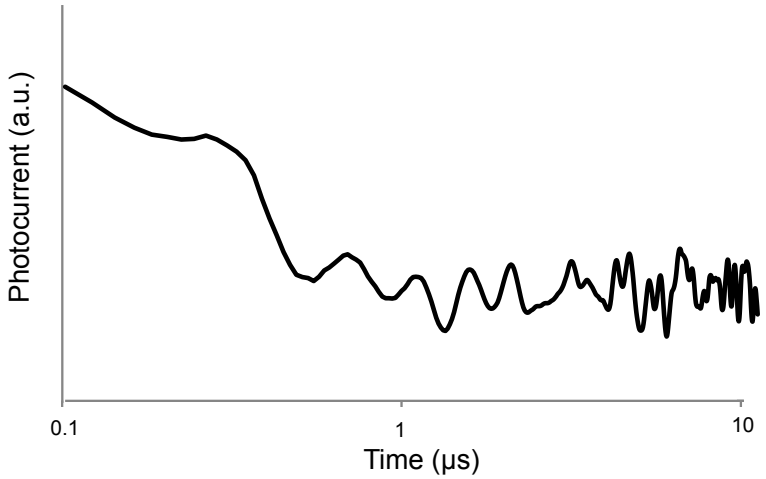


Figure 3: A typical TOF signal from compound **4c** at 180 °C.

DLC **4d** displayed hole mobilities of 1.1×10^{-3} cm^2 V^{-1} s^{-1}as seen in figure 4. Also, the thermal dependence of the hole mobility for compounds **4d** is shown in figure 5. The voltage dependence of the hole drift velocity of compound **4d** was studied at 130 °C (figure 6).

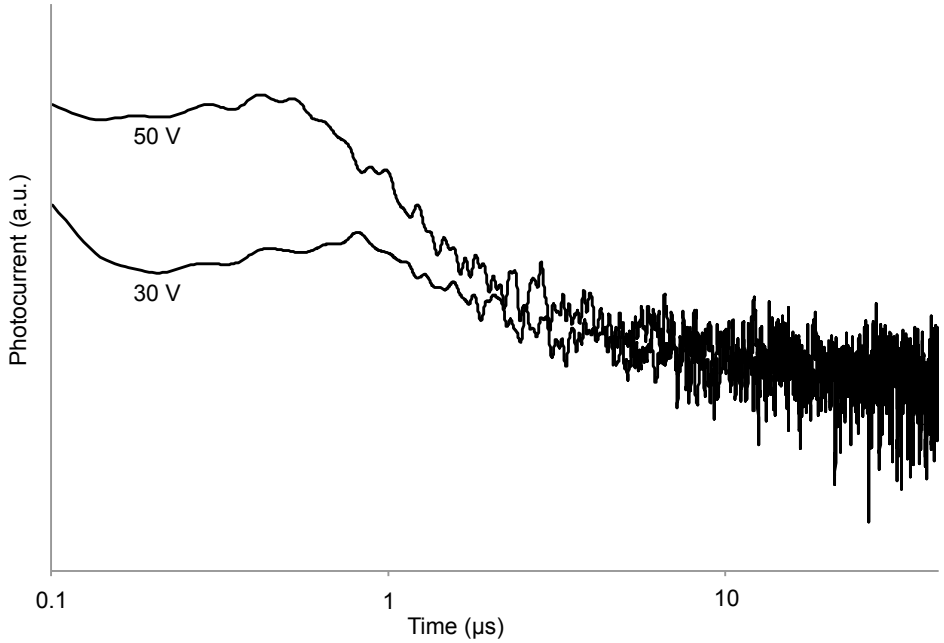


Figure 4: An overlay of typical TOF signals from compound **4d** at 30 (bottom) and 50 V (top), held at 130 °C (sample thickness 3.3 μm) .

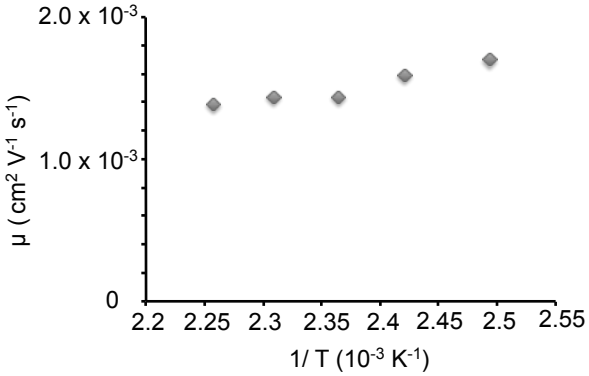


Figure 5: Thermal dependence of the hole mobility of compound **4d**.

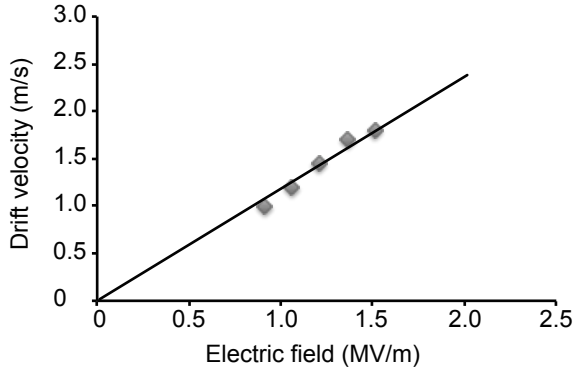


Figure 6: Voltage dependence of the hole drift velocity of compound **4d**.

DLC **4j** displayed hole mobilities of 1.5×10^{-2} cm^2 V^{-1} s^{-1}as seen in figure 7.

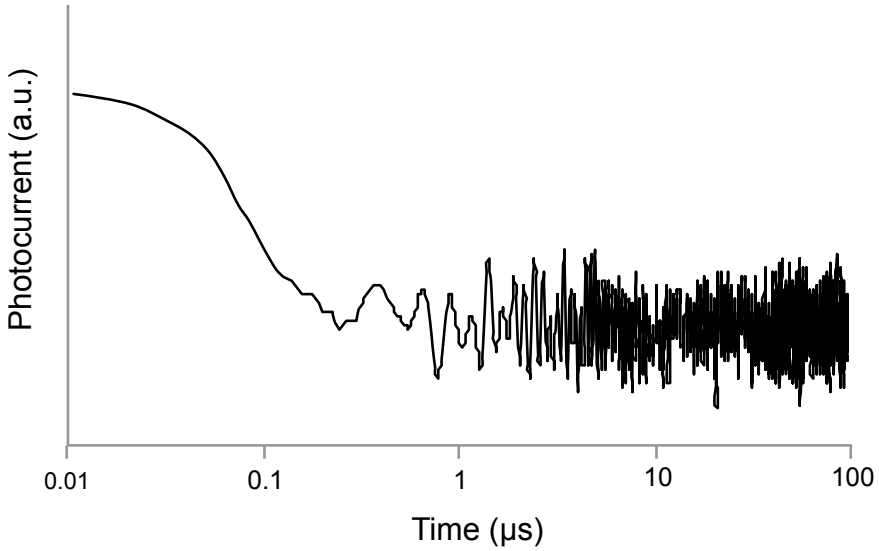


Figure 7: A typical TOF signal from compound **4j** (sample thickness 3 μm, 60 V)

The thermal dependence of the hole mobility for compound **4k** is shown in figure 8.

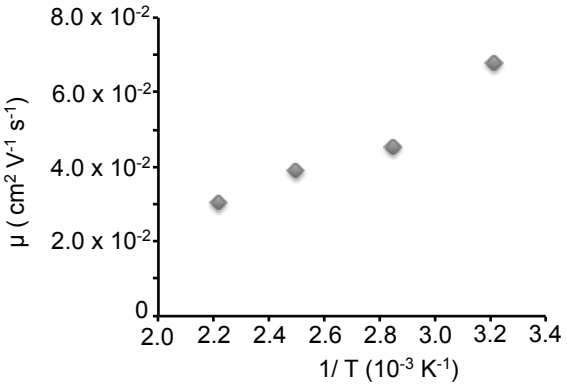


Figure 8: Thermal dependence of hole drift mobility for **4k** at 180 °C.

---

[1] Avogadro: an open-source molecular builder and visualization tool. Version 1.0.1.

[2] Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

[3] (a) K. J. Donovan, T. Kreauzis, J. C. Bunning, R. J. Bushby, N. Boden, O. R. Lozman. B. Movaghar, *Mol. Liq. Cryst.,* **2003**, 396, 91-112. (b) R. J. Bushby, O. R. Lozman, *Curr. Opin. in Solid State and Mater. Sci.,* **2002**, 6, 569–578.