Supplementary Material (ESI) for Chemical Communications

Supporting Information

Antiaromatic twinned triphenylene discotics showing nematic phases

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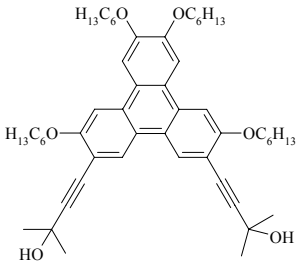
General procedures:

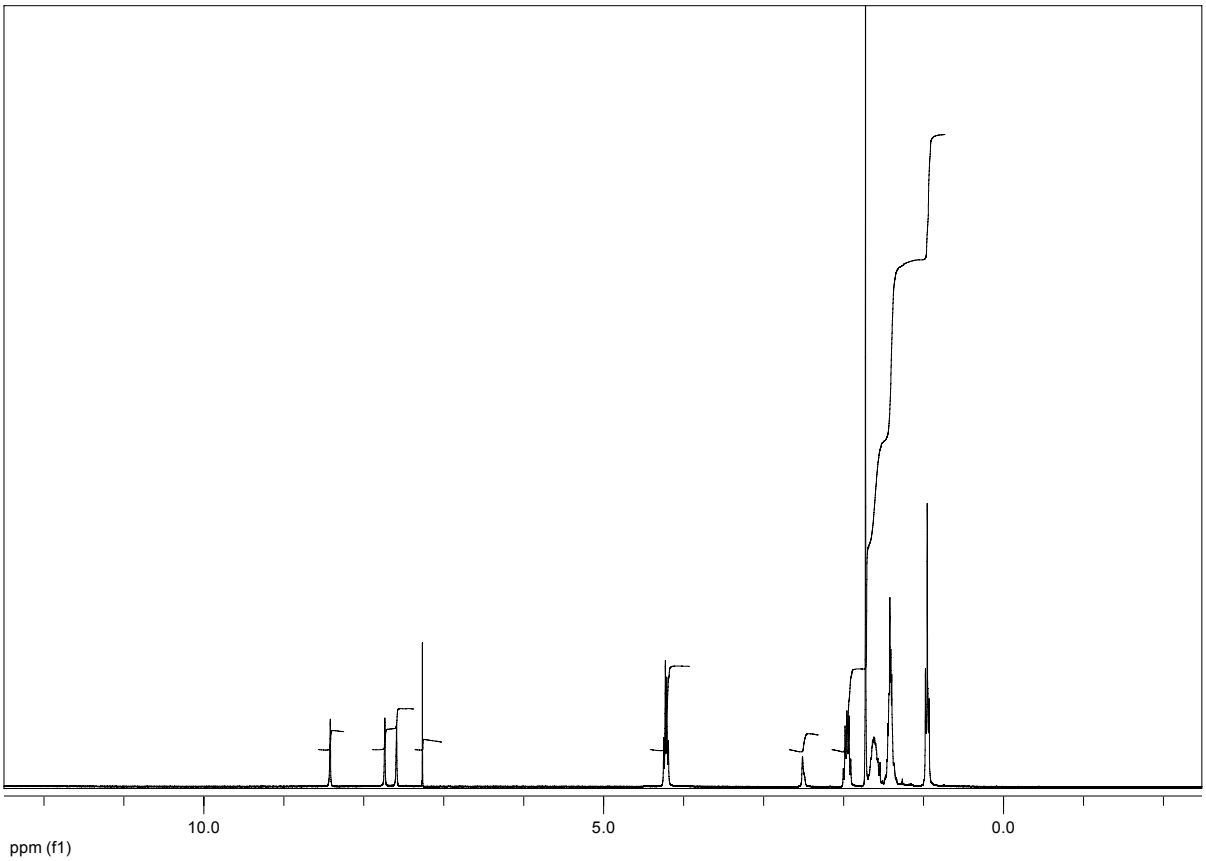
Pyridine was dried over calcium hydride before use and all the other solvents were used as purchased. NMR spectra were recorded on Varian Gemini 300 MHz and Varian Unity Plus 400MHz spectrometers. ^{1}H and ^{13}C NMR signals are reported in ppm. ^{1}H signals are referenced to the residual proton of a deuterated solvent 7.26 ppm for $CDCl_3$ and 5.32 ppm for CD_2Cl_2. ^{13}C NMR signals are referenced to the solvent signal $CDCl_3$ at 77.0 ppm and CD_2Cl_2 at 53.8 ppm. EI and HRMS analyses were performed at the EPSRC National Mass Spectrometry Service Centre at Swansea University. MALDI-MS analyses were recorded on AXIMA-CFRplus equipment. UV spectra were recorded on an HITACHI U300 instrument. Fluorescence spectra were recorded on a PerkinElmer LS45 instrument. Elemental analyses were performed in the Science Centre at London Metropolitan University.

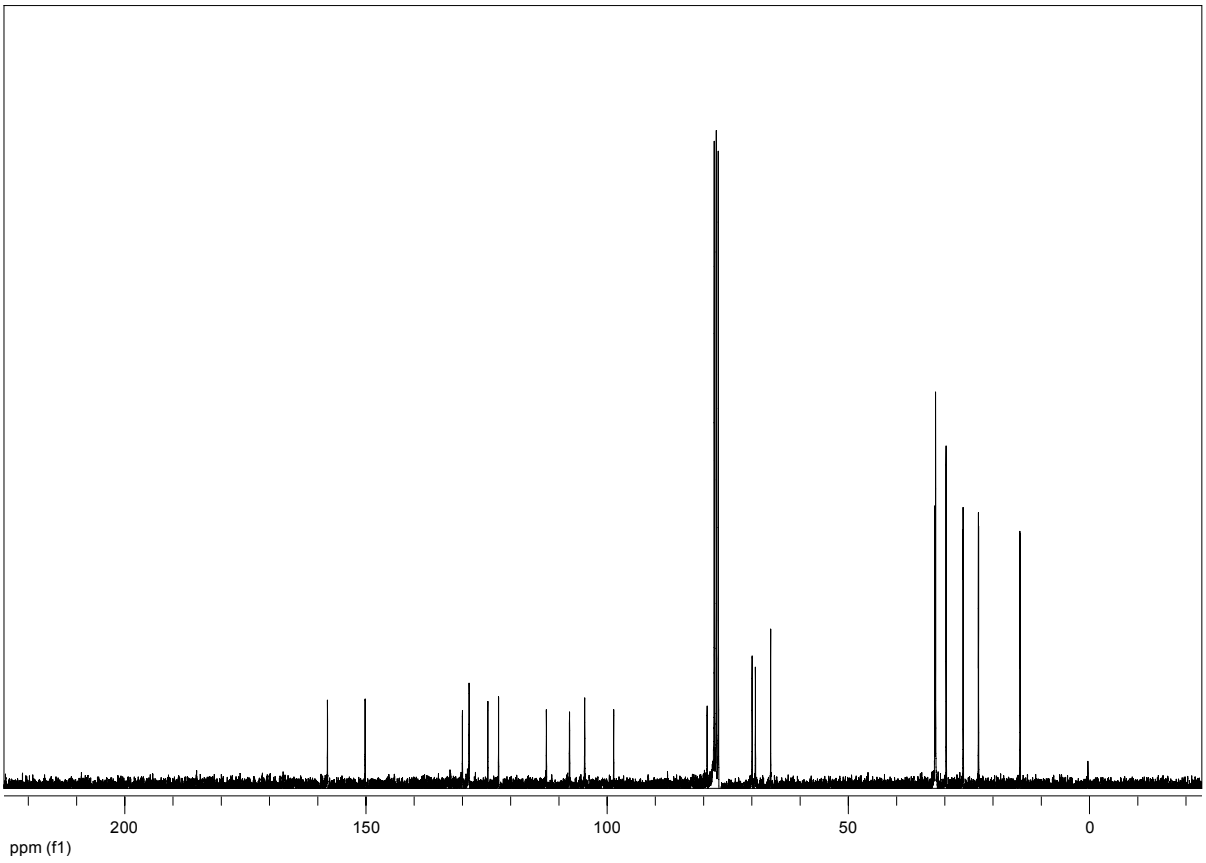
2,7,10,11-Tetrakis(hexyloxy)-3,6-bis(3-methyl-3-hydroxybutynyl)triphenylene 5a



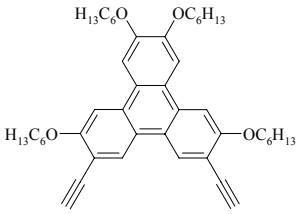
3,6-Dibromo-2,7,10,11-tetrakis(hexyloxy)triphenylene (3.00 g, 3.81 mmol), CuI (0.10 g, 0.52 mmol), $Pd(PPh_3)_2Cl_2$ (0.16 g, 0.22 mmol) and PPh_3 (0.24 g, 0.91 mmol) were stirred in refluxing triethylamine (50 mL) under an atmosphere of nitrogen for 15 min. The heating source was then removed and 2-methyl-but-3-yn-2-ol (1.60 g, 20 mmol) was added dropwise to the mixture. The solution was heated under reflux for a further 24 h. The mixture was cooled to room temperature and water was added. The mixture was extracted with DCM (3×100 mL) and the solvent removed in *vacuo* to leave a dark-brown solid which was purified by column chromatography (ethyl acetate/petroleum ether=1:4) to give the pure title compound (2.44 g, 81%) as a pale yellow solid.

Mp I 190 °C Col_h 90 °C Cr; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.45 (s, 2 H), 7.76 (s, 2 H), 7.61 (s, 2 H), 4.28-4.22 (m, 8 H), 2.45 (br, 2 H), 1.98-1.91 (m, 8 H), 1.71 (s, 12 H), 1.67-1.37 (m, 24 H), 0.95-0.92 (m, 12 H); ^{13}C NMR ($CDCl_3$, 75.45 MHz): δ 157.8, 150.0, 129.8, 128.4, 124.5, 122.3, 112.4, 107.6, 104.4, 98.4, 79.1, 69.7, 69.0, 65.8, 31.8, 31.7, 31.6, 29.4, 25.9, 25.8, 22.8, 22.7, 14.1, 14.0; MS (EI): *m/z* 792.6 (M^+, 100%); HRMS: Calcd. For $C_{52}H_{72}O_6$: 792.5323. Found: 792.5326.


10.0
5.0
0.0
ppm (f1)

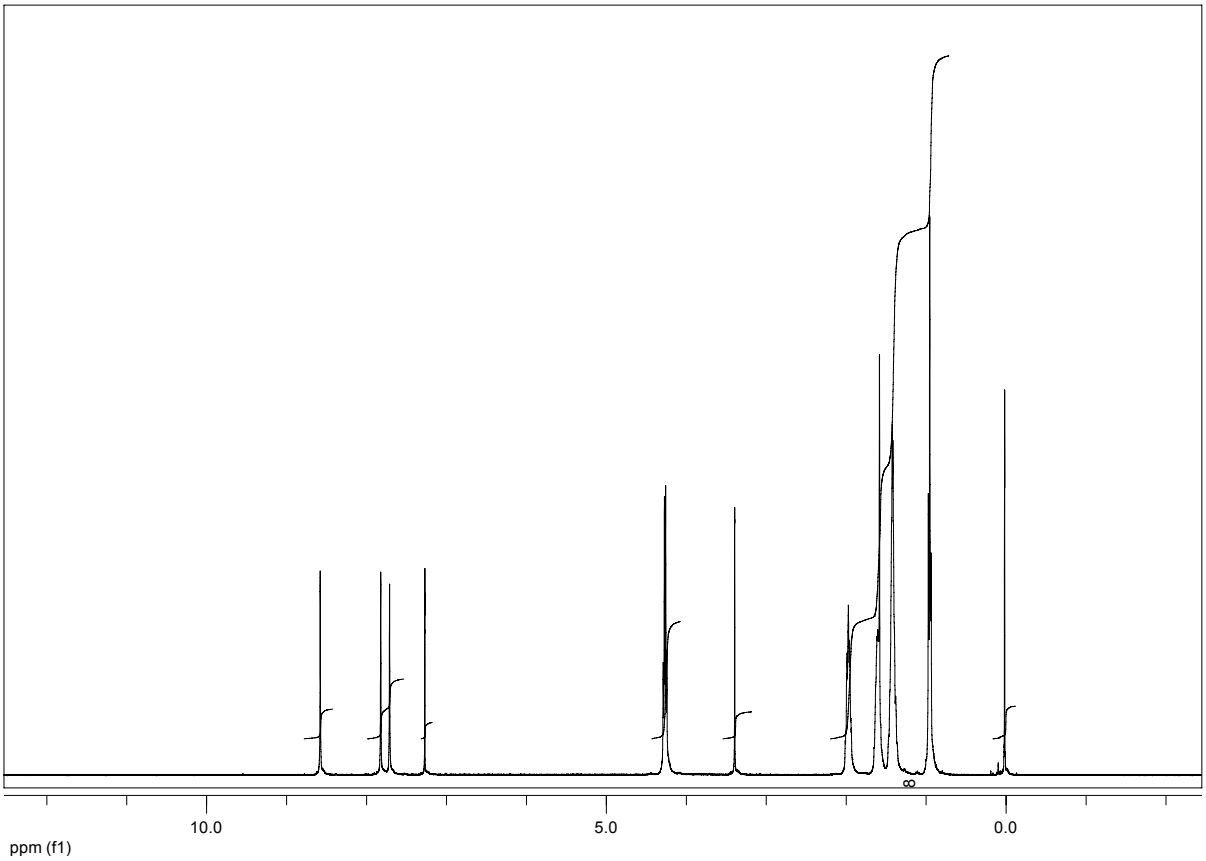

200
150
100
50
0
ppm (f1)

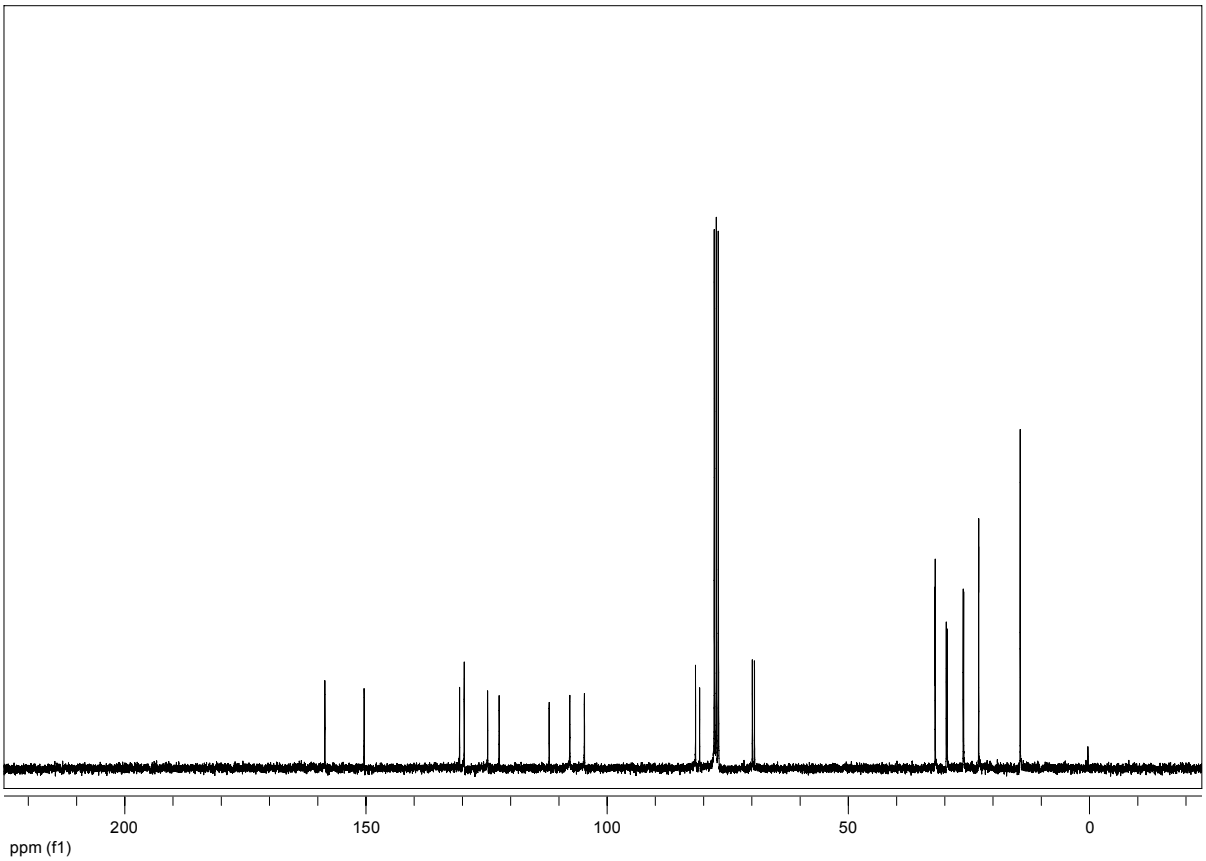
3,6-Diethynyl-2,7,10,11-tetrakis(hexyloxy)triphenylene 6a



2,7,10,11-Tetrakis(hexyloxy)-3,6-bis(3-methyl-3-hydroxybutynyl)triphenylene **5a** (3.0 g, 3.78 mmol) was dissolved in refluxing dry toluene (50 mL) under an atmosphere of nitrogen. NaH (60% dispersion in oil) (0.67 g, 17.0 mmol NaH) was added in small portions and the mixture heated under reflux for 2 h. The solution was then poured onto ice-cold water and the organic layer was extracted with DCM (3×100 mL). The solvent was removed in *vacuo* to leave a dark-brown oil which was purified by column chromatography (ethyl acetate/petroleum ether=1:9) to give the pure title compound (1.82 g, 71%) as a pale yellow solid.

Mp 140 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.57 (s, 2 H), 7.82 (s, 2 H), 7.70 (s, 2 H), 4.27-4.23 (m, 8 H), 3.38 (s, 2 H), 1.99-1.92 (m, 8 H), 1.60-1.36 (m, 24 H), 0.95-0.92 (m, 12 H); ^{13}C NMR ($CDCl_3$, 75.45 MHz): δ 158.4, 150.3, 130.4, 129.5, 124.6, 122.2, 111.8, 107.6, 104.5, 81.5, 80.6, 69.6, 69.2, 31.8, 31.7, 29.4, 29.3, 25.9, 25.8, 22.8, 22.7, 14.0; MS (EI): *m/z* 676.6 (M^+, 100%); HRMS: Calcd. For $C_{46}H_{60}O_4$: 676.4486. Found: 676.4478.

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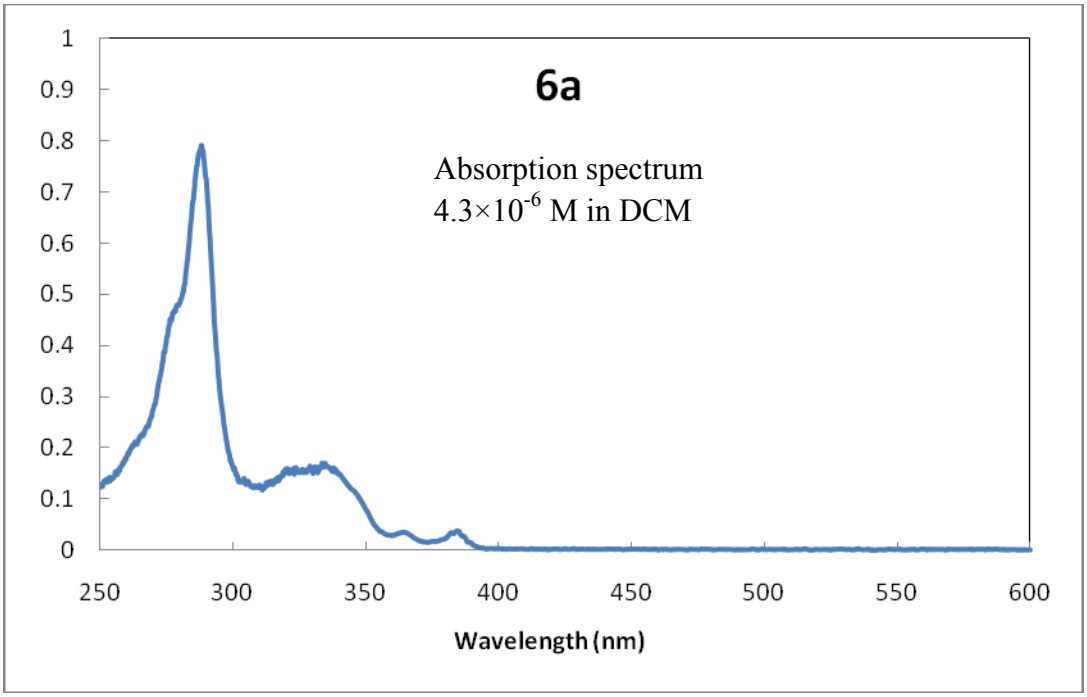
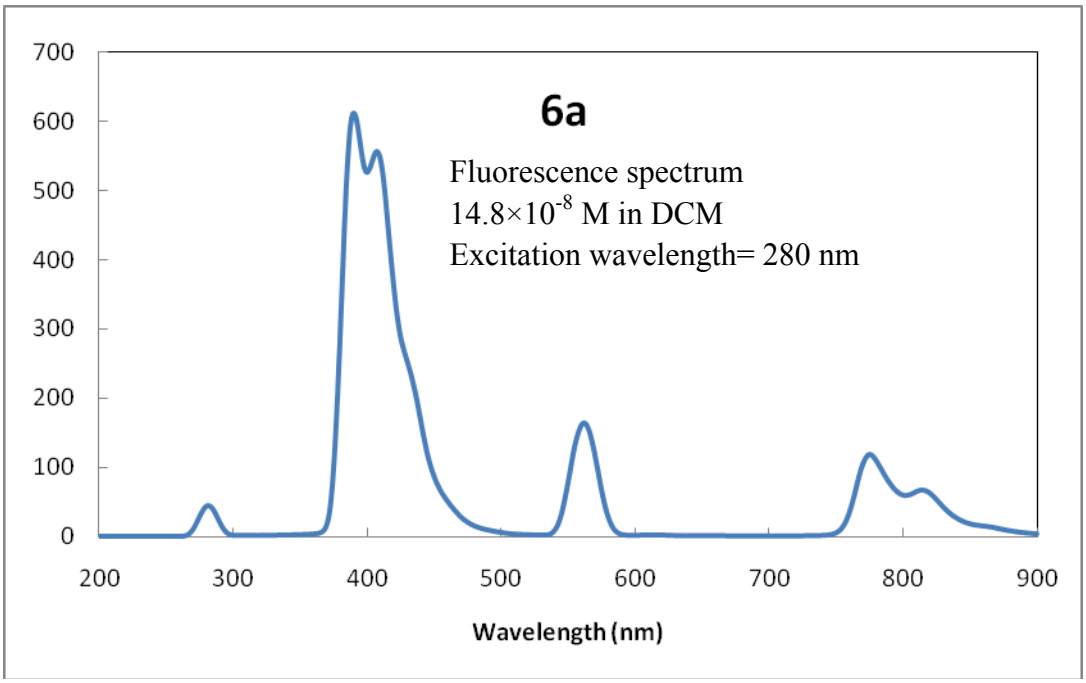
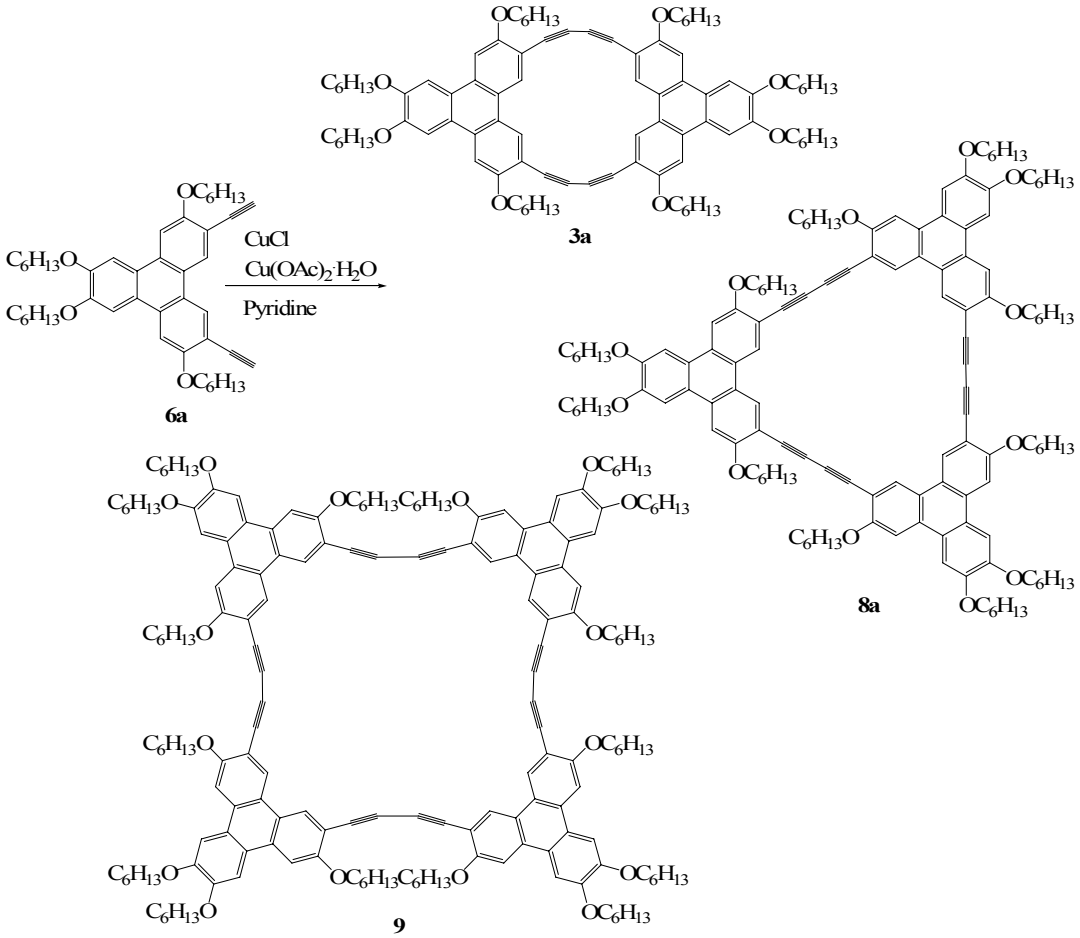
150
100
50
0
ppm (f1)


6a
Absorption spectrum
4.3×10-6 M in DCM
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
250
300
350
400
450
500
550
600
Wavelength (nm)

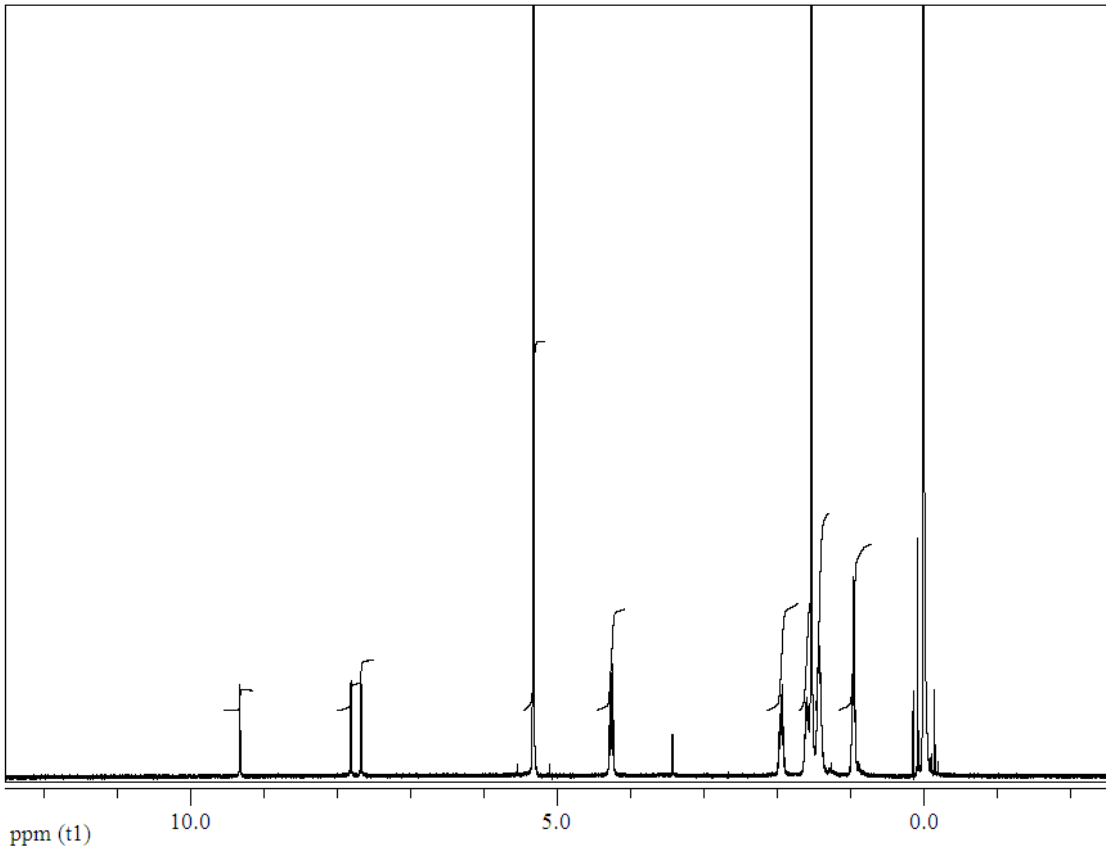


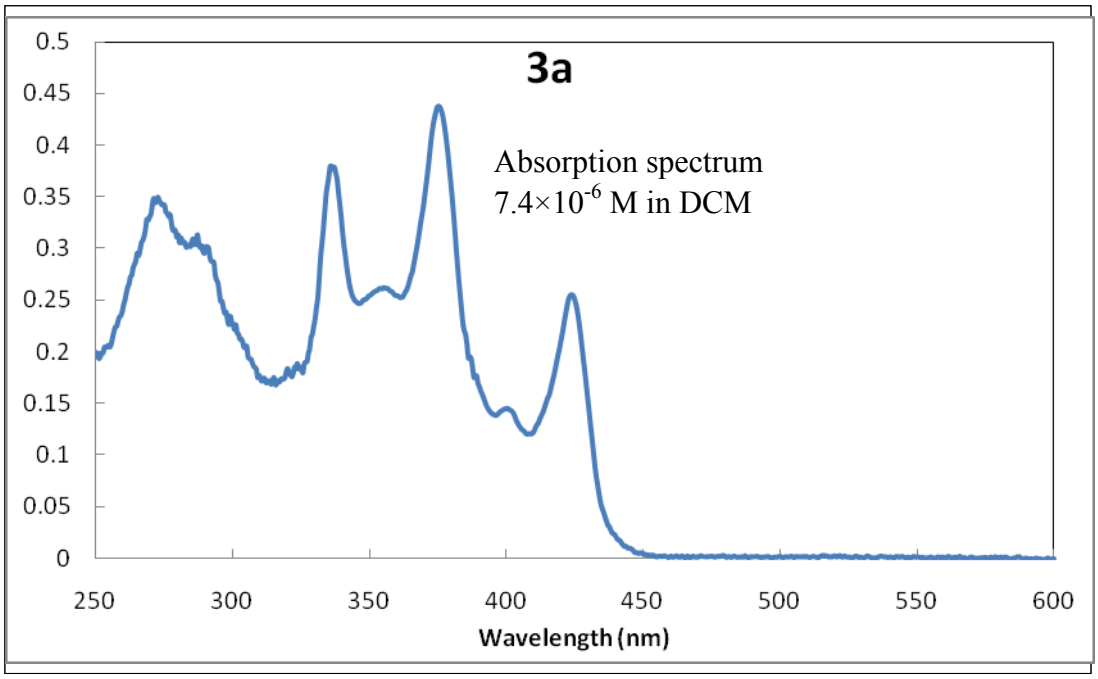
Synthesis of Twin 3a and higher oligomers

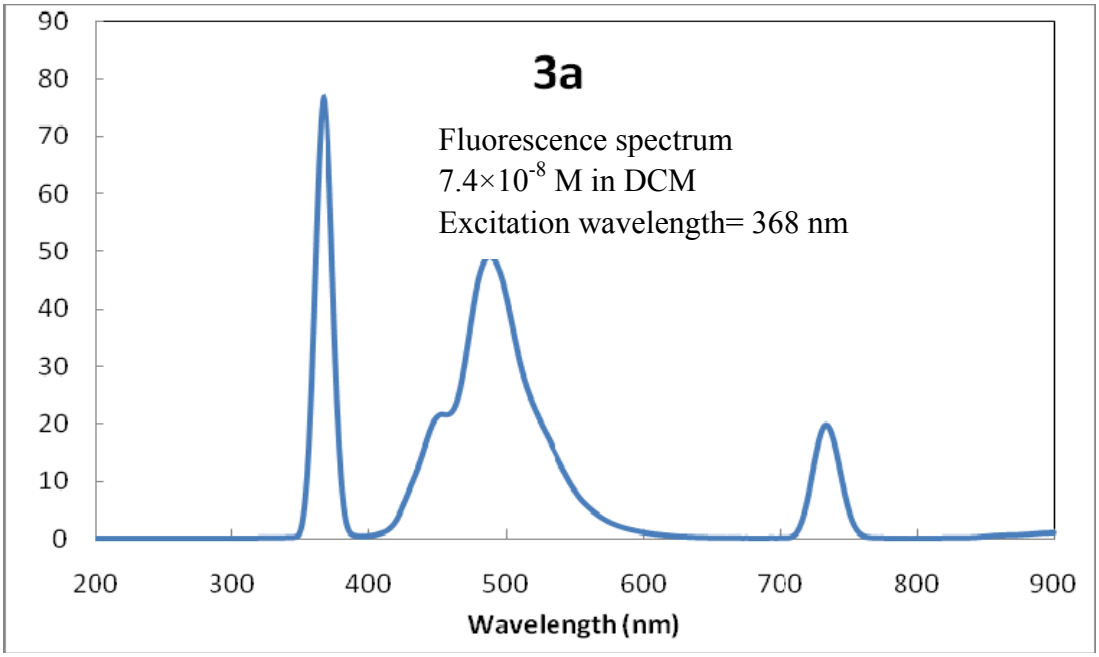


A mixture of CuCl (300 mg, 30.0 mmol) and $Cu(OAc)_2 \cdot H_2O$ (600 mg, 30.0 mmol) in freshly distilled pyridine (100 mL) was stirred and heated at 60 °C. Compound **6a** (677 mg, 1.0 mmol) in pyridine (13 mL) was added over 18 h, and the mixture was stirred at 60 °C for another 24 h. The solvent was evaporated and the residue was dissolved in DCM, washed with water (3×300 mL), dried over $MgSO_4$, evaporated under *vacuo* to dryness and subjected to purification by silica gel chromatography (DCM/cyclohexane=3:7-2:3) to yield compound **3a** (185 mg, 27%)**, 8a** (175 mg, 26%) and **9** (40 mg, 6%) as solids.

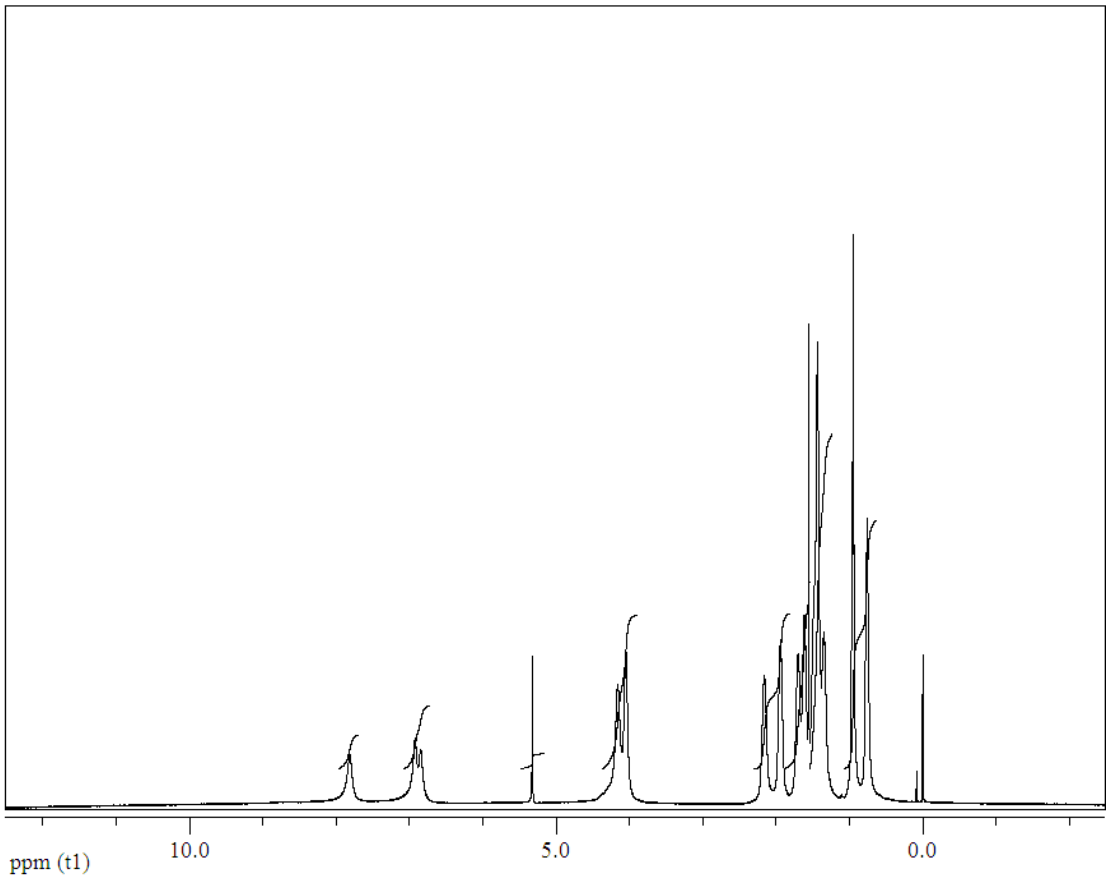
Compound **3a**: Mp Cr1 153 °C Cr2 209 °C N_D > 280 °C (Decomp); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.32 (s, 4 H), 7.81 (s, 4 H), 7.67 (s, 4 H), 4.28 (t, *J*=6.4 Hz, 8 H), 4.24 (t, *J*=6.4 Hz, 8 H), 1.99-1.89 (m, 16 H), 1.60-1.56 (m, 16 H), 1.45-1.40 (m, 32 H), 0.99-0.93 (m, 24 H); UV-Vis (CH_2Cl_2) λ_{max} (log ε) 336 (4.71), 355 (4.55), 375 (4.77), 400 (4.29), 424(4.54) nm; Anal. Calcd. For $C_{92}H_{118}O_8$: C, 81.86; H, 8.66; Found: C, 81.79; H, 8.68; MS (MALDI): *m/z* 1349.86 (M^+, 100%).







Compound **8a**: Mp > 300 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.81 (s, 6 H), 6.92 (s, 6 H), 6.85 (s, 6 H), 4.30-3.90 (m,24 H), 2.18-2.10 (m, 12 H), 2.02-1.94 (m, 12 H), 1.76-1.61 (m, 24 H), 1.56-1.40 (m, 48 H), 0.99 (t, *J*=6.8 Hz, 18 H), 0.90 (t, *J*=7.2 Hz, 18 H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 158.7, 149.6, 129.7, 129.1, 123.9, 121.5, 111.3, 106.5, 103.0, 79.8, 79.5, 69.5, 69.3, 32.3, 30.1, 29.8, 26.4, 26.3, 23.2, 23.1, 14.2, 14.1; UV-Vis (CH_2Cl_2) λ_{max} (log ε) 319 (5.07), 376 (5.35), 395 (5.11), 418(5.31) nm; Anal. Calcd. For $C_{138}H_{174}O_{12}$: C, 81.86; H, 8.66; Found: C, 81.78; H, 8.71; MS (MALDI): *m/z* 2024.79 (M^+, 100%).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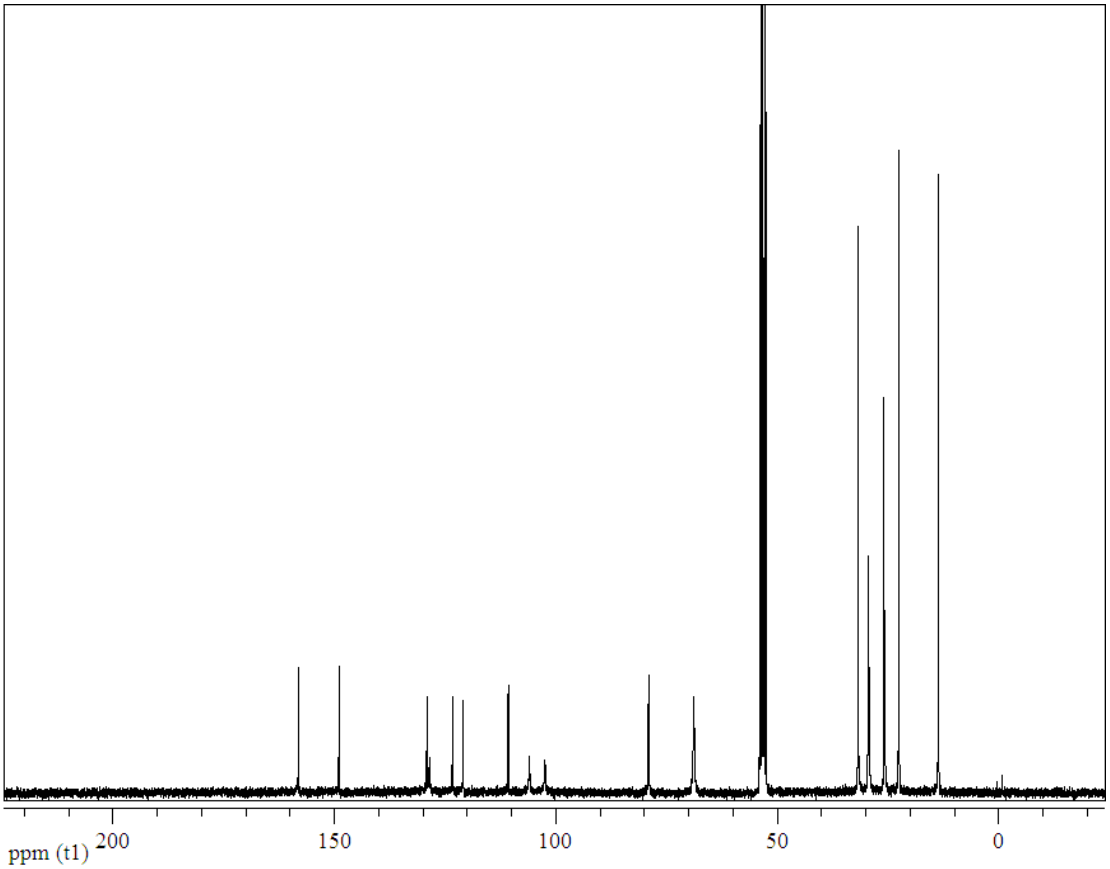
5.0
0.0


ppm (t1)
200
150
100
50
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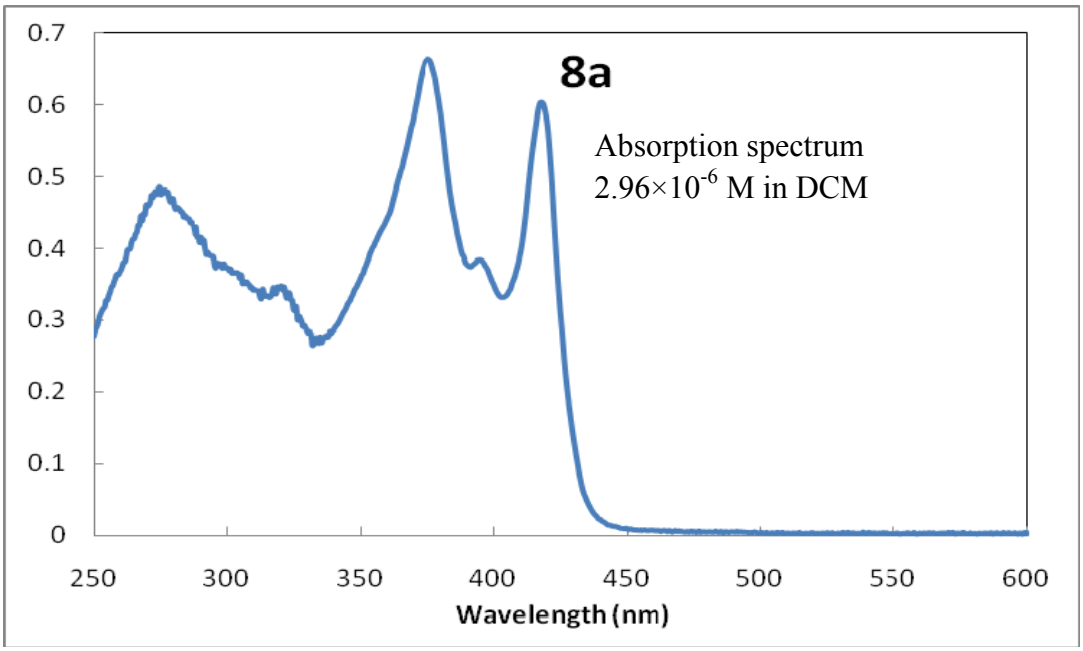
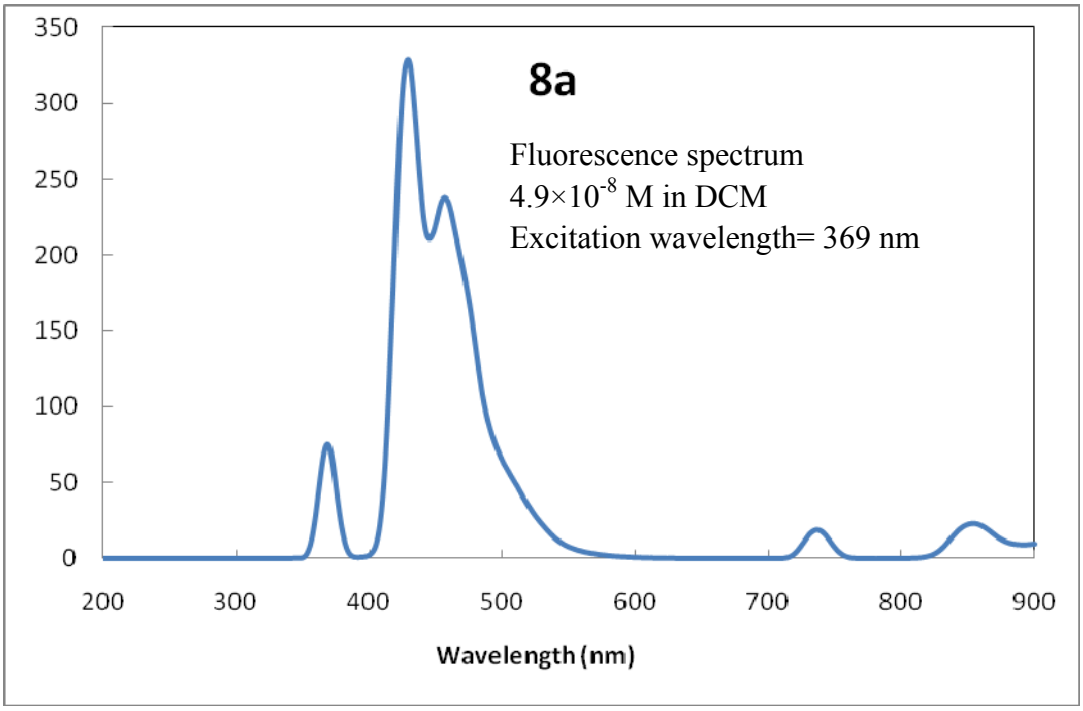
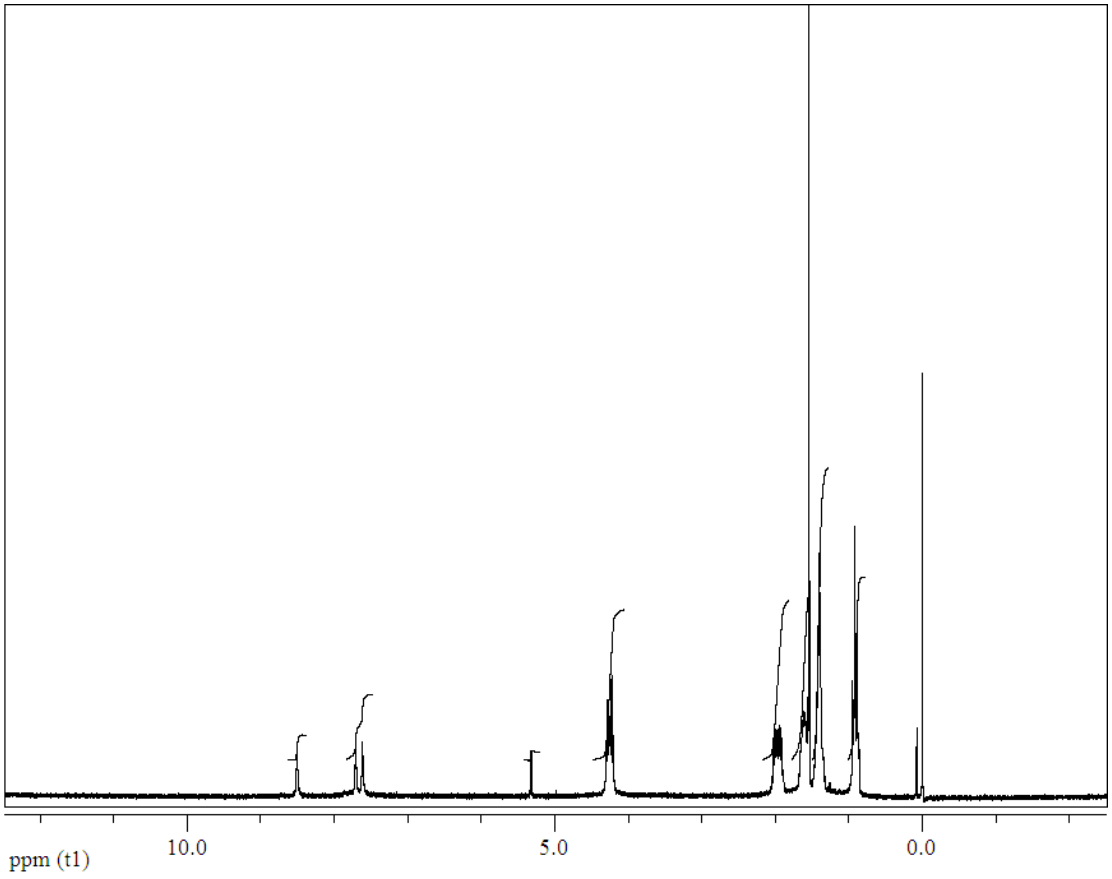




Compound **9**: Mp > 300 °C; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.50 (s, 8 H), 7.71 (s, 8 H), 7.61 (s, 8 H), 4.28 (t, *J*=8.4 Hz, 16 H), 4.22 (t, *J*=8.4 Hz, 16 H), 2.05-1.88 (m, 32 H), 1.64-1.55 (m, 32 H), 1.54-1.33 (m, 64 H), 0.95-0.86 (m, 48 H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 159.3, 150.4, 130.8, 129.7, 124.5, 122.1, 111.7, 107.2, 104.2, 79.5, 78.8, 69.7, 69.4, 32.09, 32.07, 29.8, 29.6, 26.2, 26.1, 23.0, 14.2, 14.1; UV-Vis (CH_2Cl_2) λ_{max} (log ε) 304 (5.73), 352 (5.50), 378 (5.36), 402 (5.26) nm; MS (MALDI): *m/z* 2699.65 (M^+,100%).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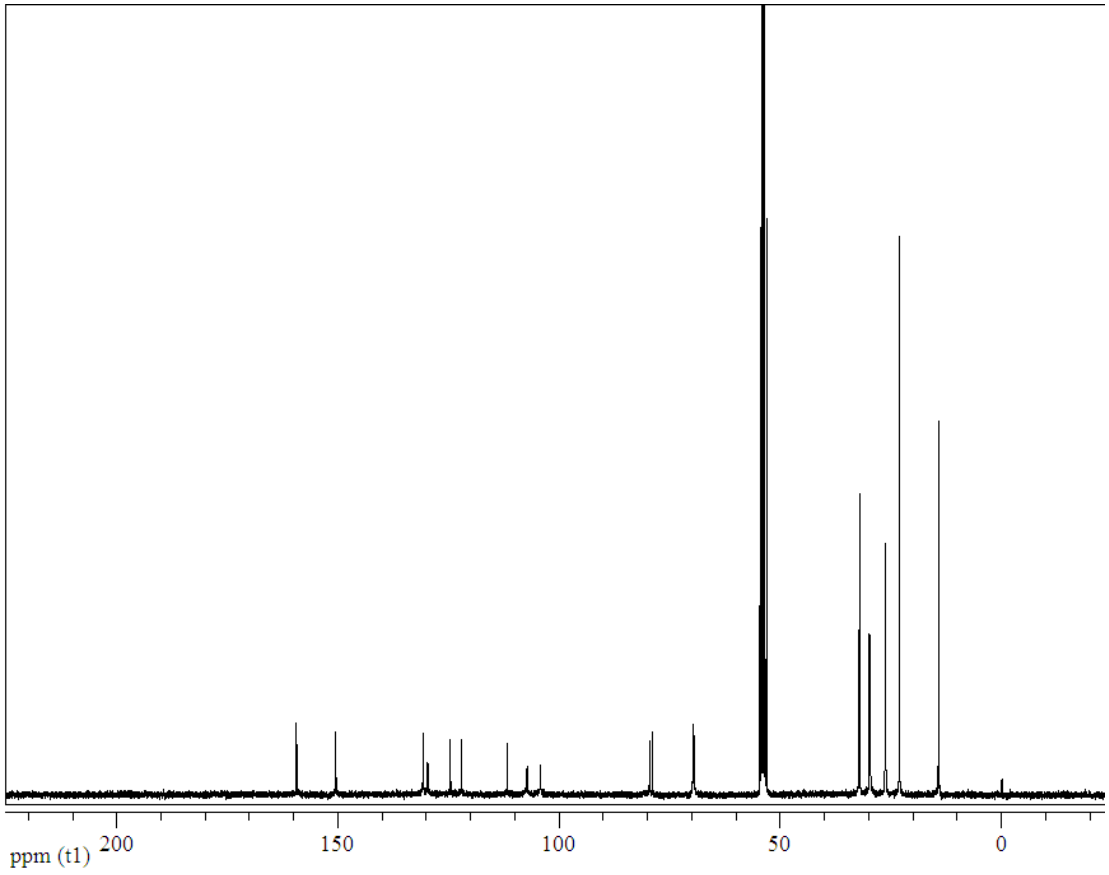
5.0
0.0
ppm (t1)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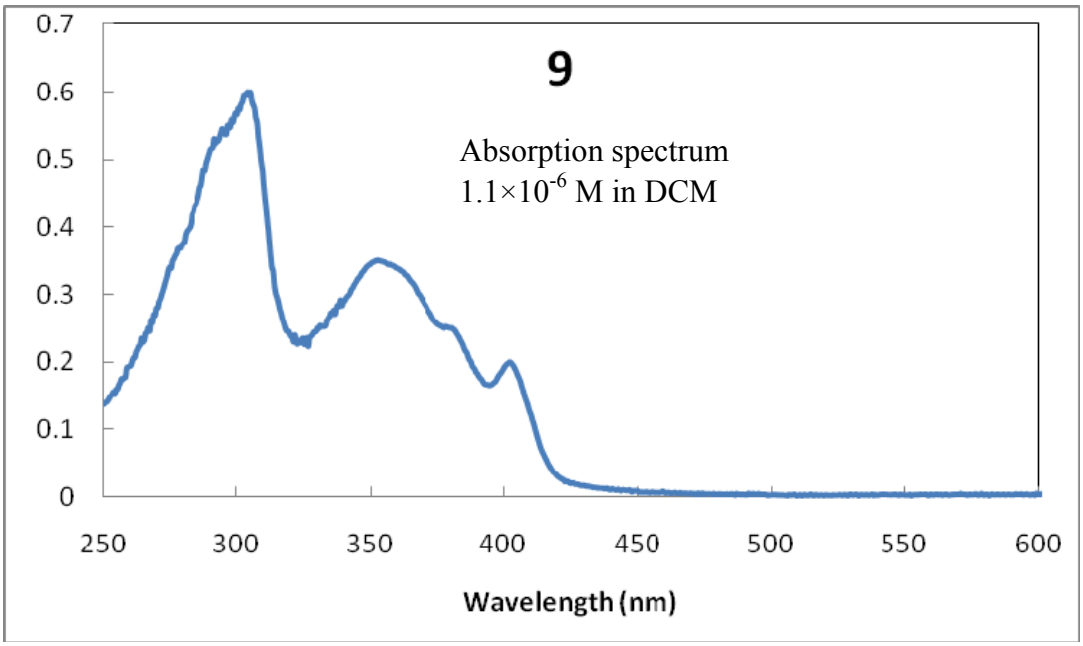
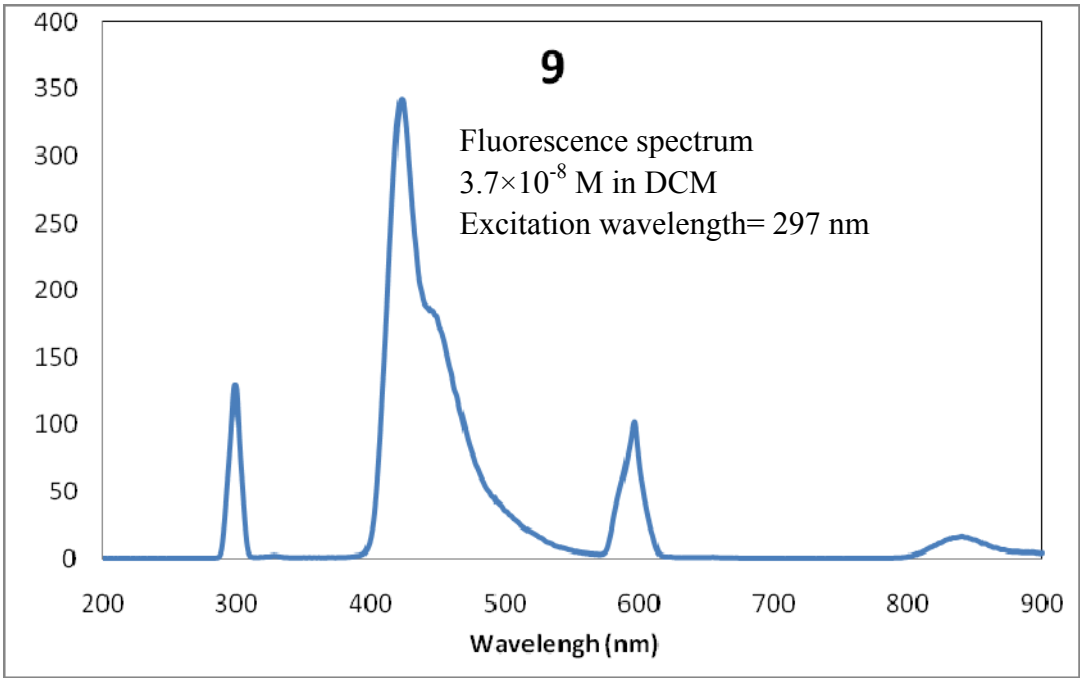
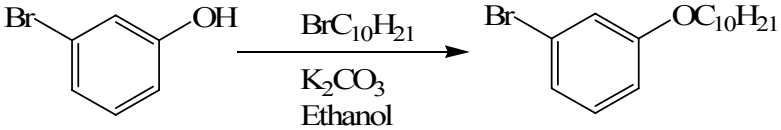
150
100
50
0
ppm (t1)





1-Bromo-3-decyloxybenzene 10

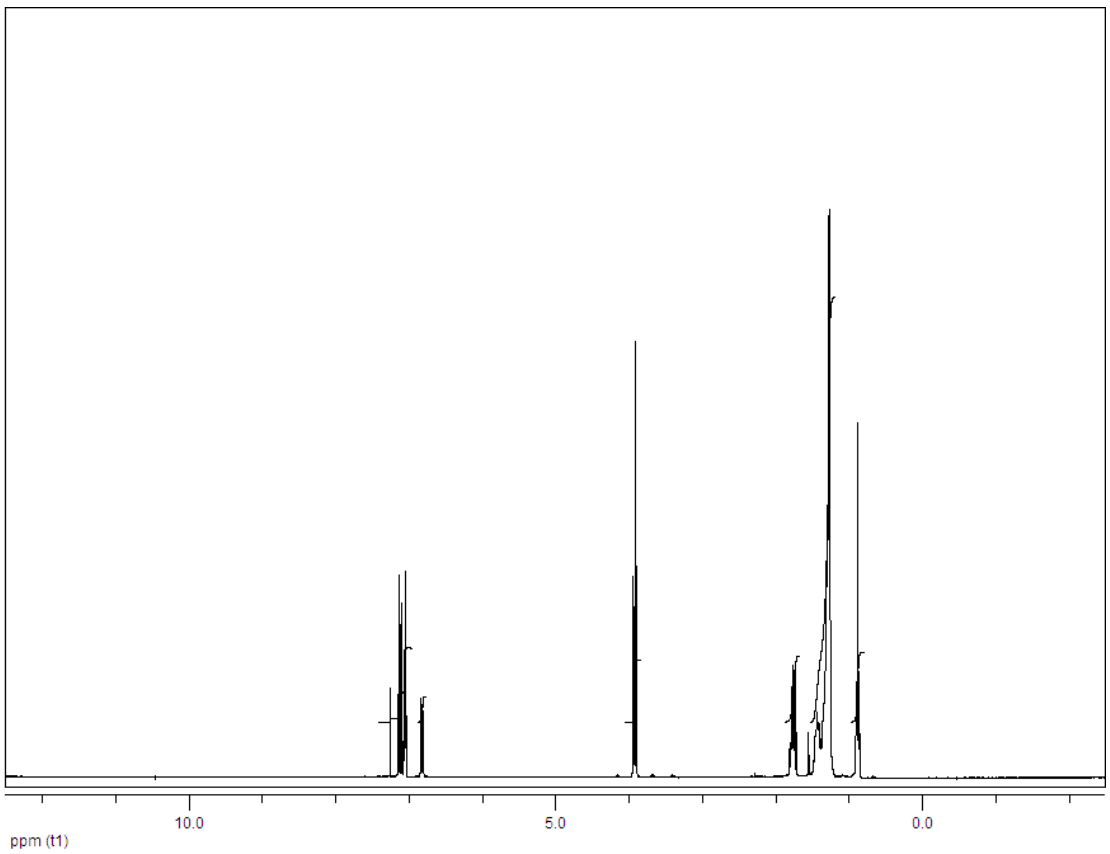


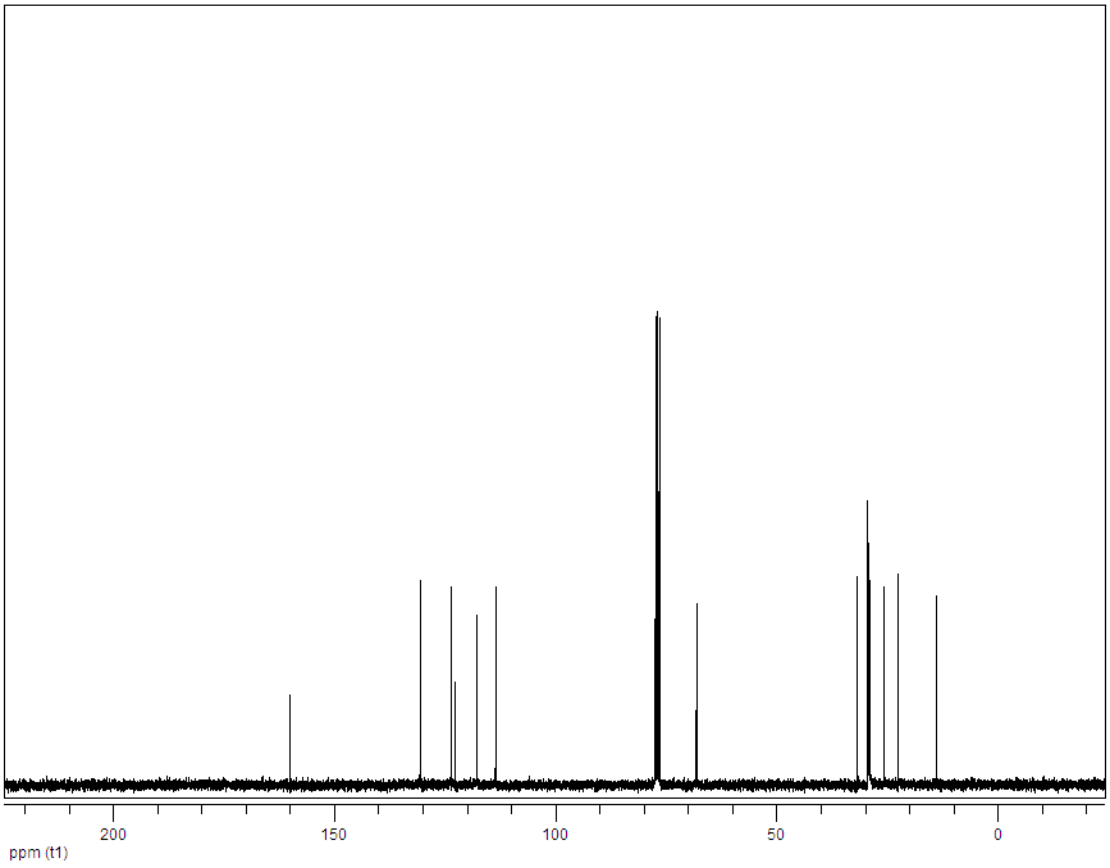
10

3-Bromophenol (17.30 g, 0.10 mol) was heated at reflux with 1-bromodecane (44.24 g, 0.20 mol) and potassium carbonate (27.64, 0.20 mol) in ethanol (200 mL) for 24 h. The solution was filtered and the filter cake was washed thoroughly with ethanol. The solvent was evaporated under vacuum to yield the title compound **10** as a colourless oil (30.39g, 97%).

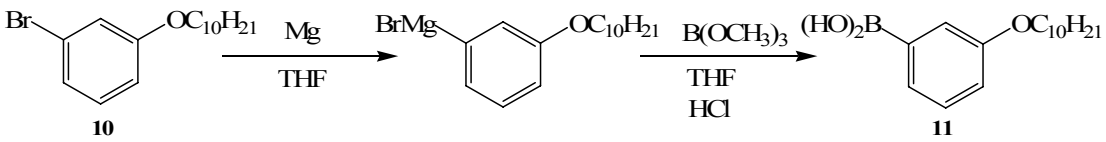
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16-7.10 (m, 1 H), 7.08-7.04 (m, 2 H), 6.84-6.80(m, 1 H), 3.92 (t, *J*=6.6 Hz, 2 H),

1.81-1.72 (m, 2 H), 1.46-1.25 (m, 14 H), 0.89 (t, *J*=6.6 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.1, 130.5, 123.6, 122.8, 117.7, 113.6, 68.2, 31.8, 29.5, 29.3, 29.2, 29.0, 25.9, 22.6, 14.0; HRMS: Calcd. For $C_{16}H_{25}OBr$: 312.1083. Found: 312.1082.





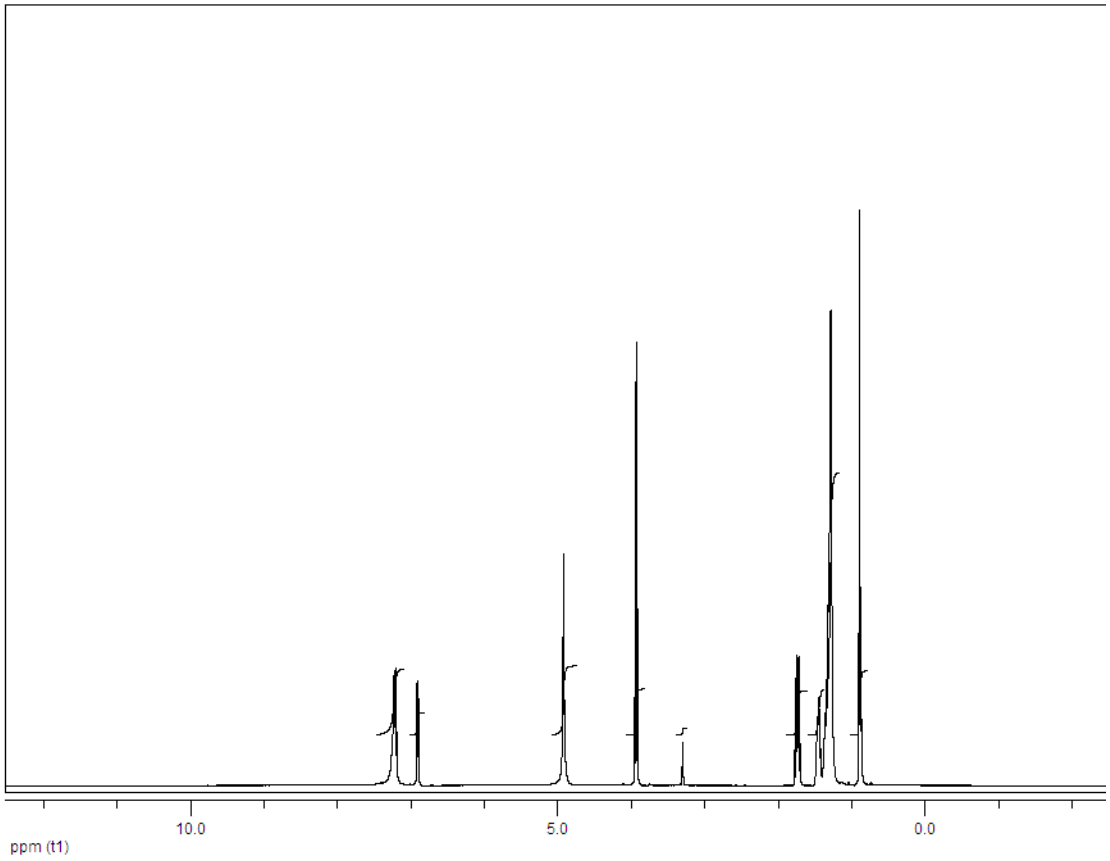
3-Decyloxyphenylboronic acid 11

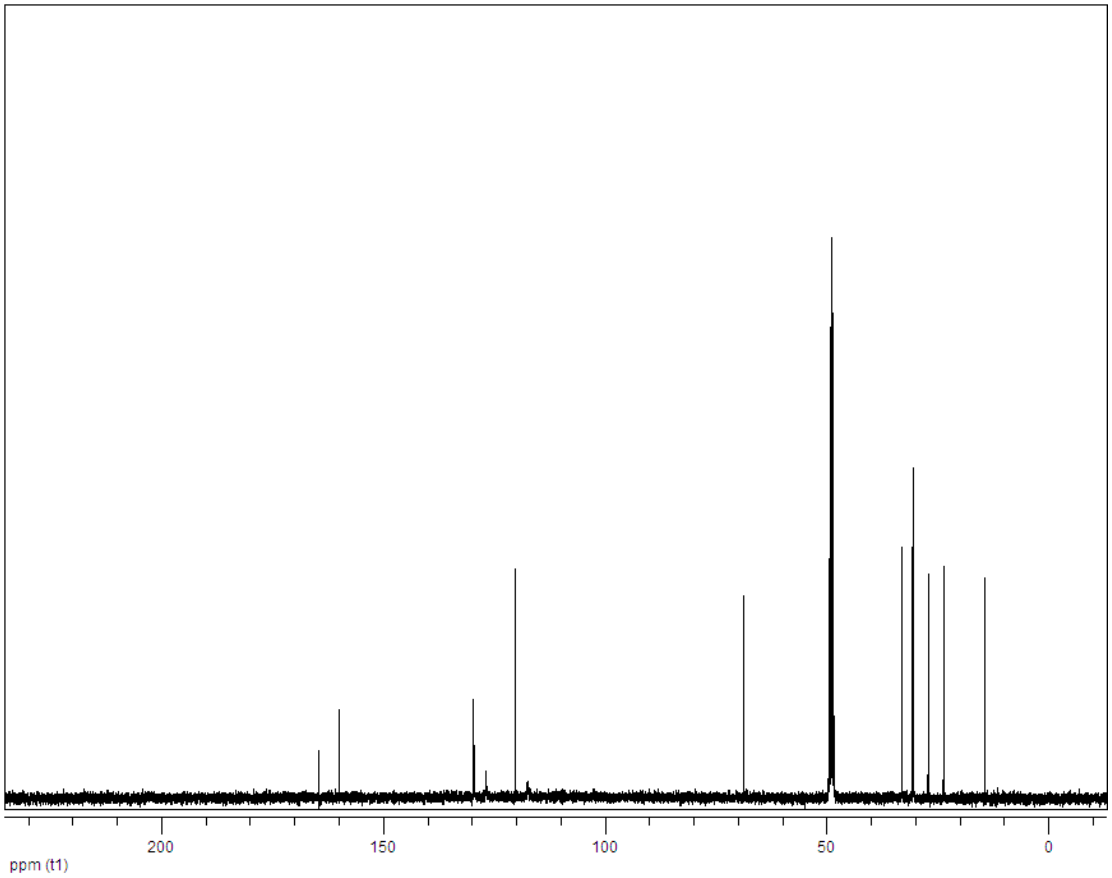


10 **11**

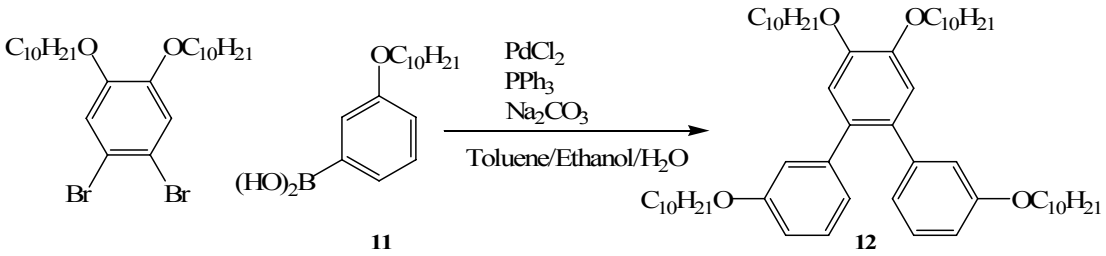
1-Bromo-3-decyloxybenzene **10** (25.06 g, 0.08 mol) was added slowly to the mixture of magnesium turnings (2.30 g, 0.096 mol) and freshly distilled THF (100 mL). The mixture was then heated at reflux for 3 h before it was transferred to a solution of trimethyl borate (16.63g, 0.16 mol) in freshly distilled THF (200 mL) at -78 °C. After addition the mixture was stirred and allowed to warm gradually to room temperature overnight. 10% Hydrochloride was added slowly and the solution was extracted with diethyl ether. The organic layer was dried over $MgSO_4$ and evaporated to give a solid that can recrystallized from hexane to give **11** as a white solid (17.8 g, 80%).

^{1}H NMR (300 MHz, CD_3OD) δ 7.23-7.19 (m, 3 H), 6.92-6.89(m, 1 H), 3.94 (t, *J*=4.8 Hz, 2 H), 1.77-1.70 (m, 2 H), 1.49-1.26 (m, 14 H), 0.89 (t, *J*=5.1 Hz, 3 H); ^{13}C NMR (75 MHz, CD_3OD) δ 164.5, 159.9, 129.7, 126.9, 120.3, 117.4, 68.8, 33.1, 30.8, 30.7, 30.6, 30.5, 27.2, 23.8, 14.5; HRMS: Calcd. For $[C_{16}H_{27}O_3B+F]^-$: 297.2046. Found: 297.2045.


10.0
5.0
0.0
ppm (t1)


200
150
100
50
0
ppm (t1)

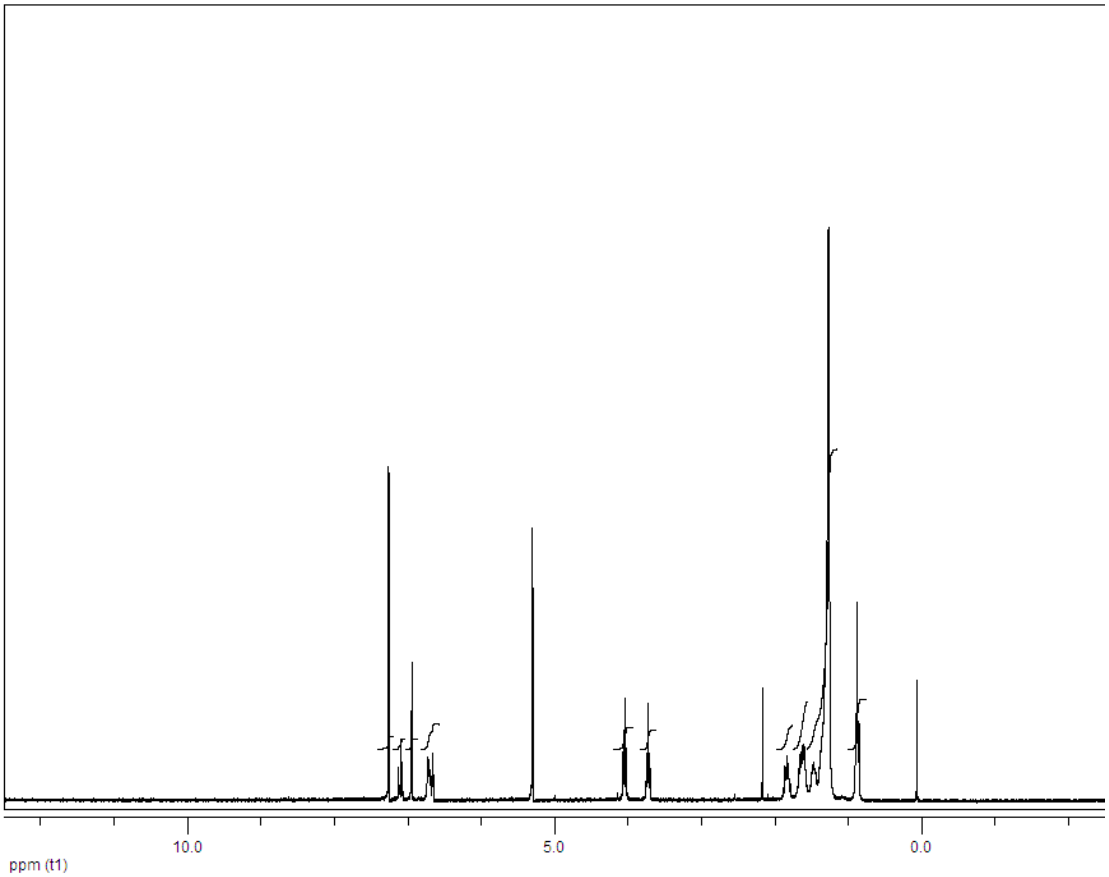
1,2-Didecoxy-4,5-bis(3-decoxyphenyl)benzene 12

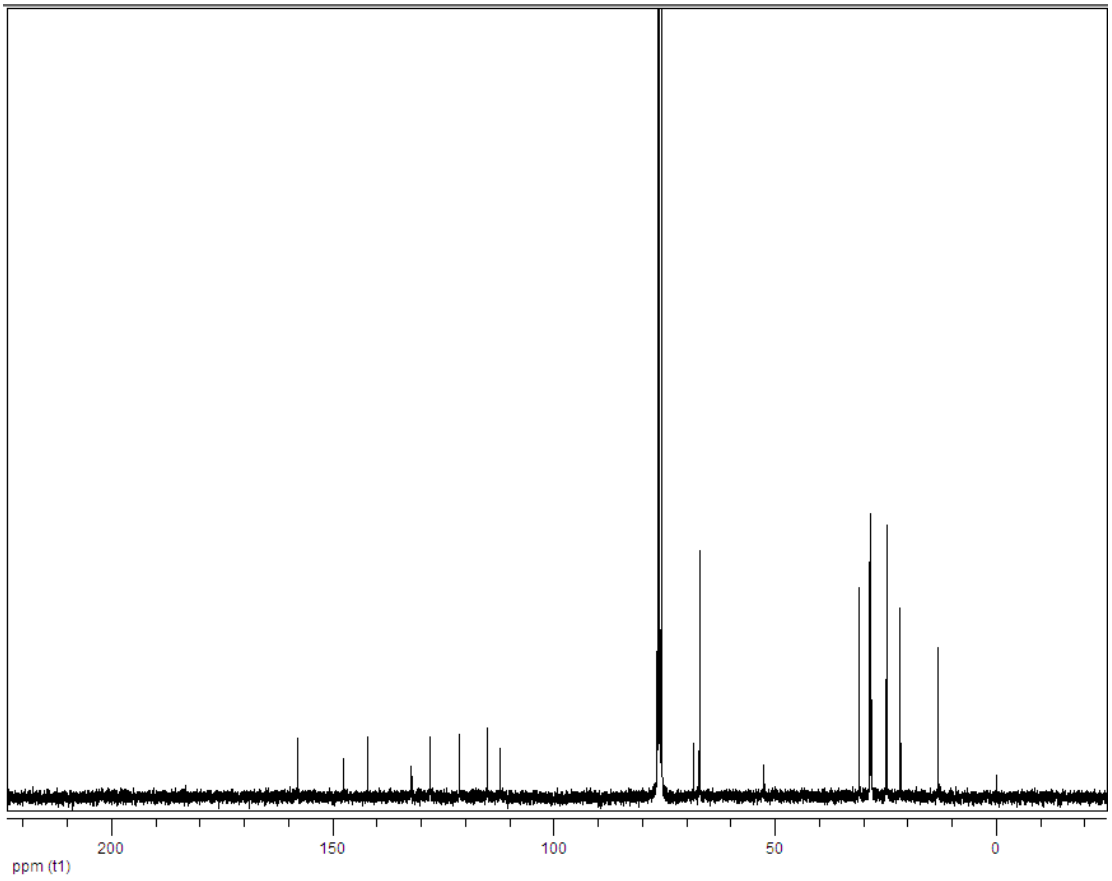


11 **12**

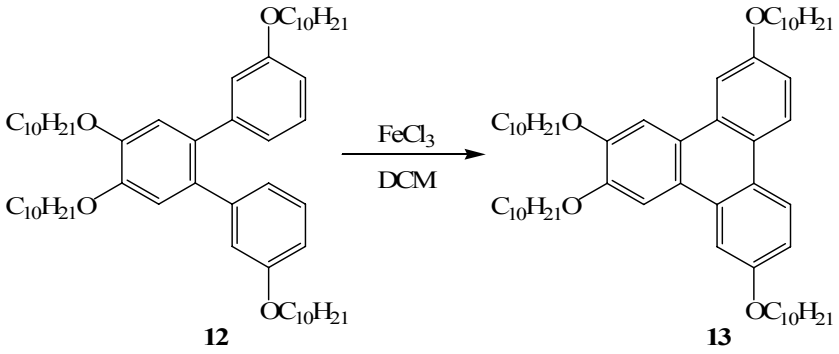
1,2-Dibromo-4,5-bis(decyloxy)benzene (10.97 g, 0.02 mol), 3-decyloxy-phenylboronic acid **11** (16.69 g, 0.06 mol), $PdCl_2$ (283.7 mg, 1.6 mmol), PPh_3 (1.68 g ,6.4 mmol) and Na_2CO_3 (10.6 g, 0.1 mol) were heated at reflux in toluene-ethanol-water (3:3:1) (140 mL) for 72 h. The mixture was evaporated to dryness, DCM was added and it was washed with water. After drying over $MgSO_4$ and evaporation, the residue was subjected to chromatography (DCM/petroleum ether =1:4) on silica gel to yield the title compound **12** as colourless oil (14.54g, 85%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10 (t, *J*=7.8 Hz, 2 H), 6.95 (s, 2 H), 6.73-6.65(m, 6 H), 4.05 (t, *J*=6.6 Hz, 4 H), 3.73 (t, *J*=6.6 Hz, 4 H), 1.89-1.79 (m, 4 H), 1.70-1.57 (m, 4 H), 1.52-1.23 (m, 56 H), 0.90-0.86 (m, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.7, 148.4, 143.0, 133.1, 128.8, 122.2, 116.0, 113.0, 69.4, 68.0, 31.8, 29.5, 29.33, 29.25, 29.0, 26.0, 25.9, 25.5, 22.6, 14.0, 13.98; HRMS: Calcd. For $C_{58}H_{94}O_4$: 854.7147. Found: 854.7155.





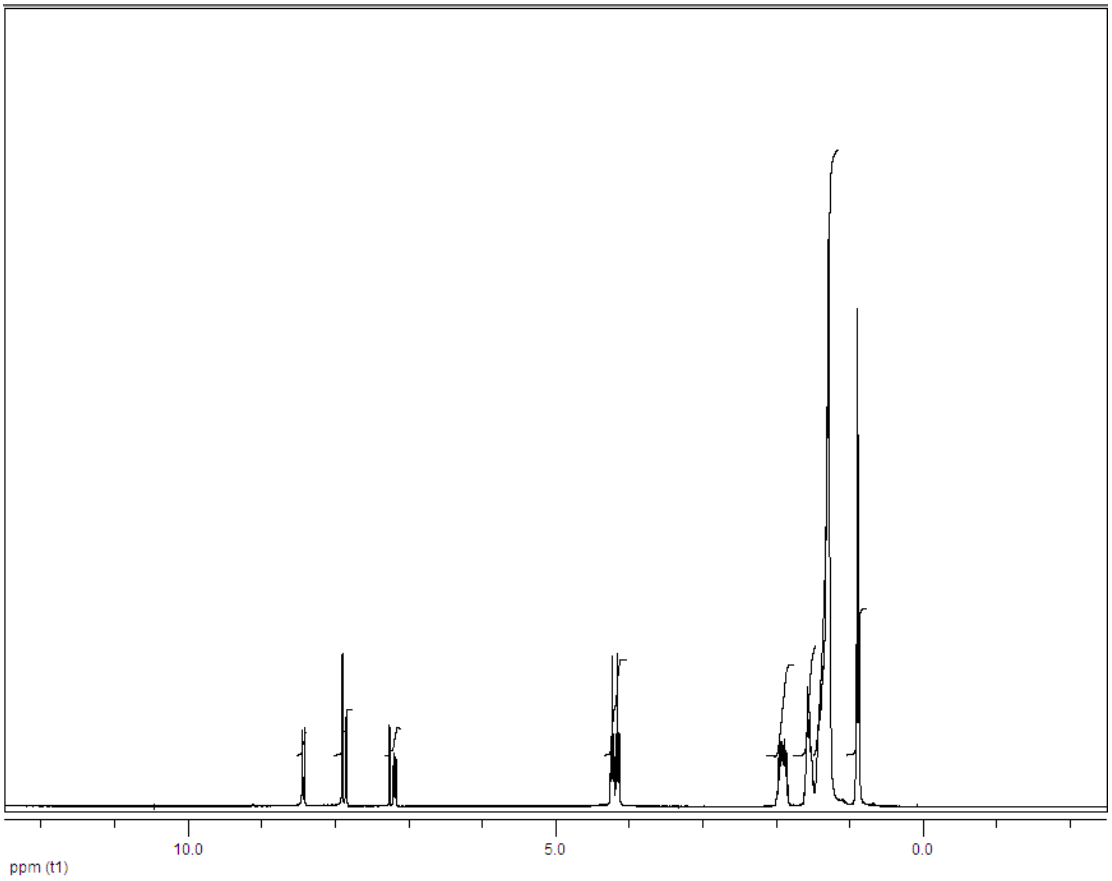
2,3,6,11-Tetrakis(decyloxy)triphenylene 13



12 **13**

Iron (III) chloride (4.87 g, 30 mmol) was added to compound **12** (5.13 g, 6.0 mmol) in DCM (200 mL). The blue suspension was stirred at room temperature for 20 min and then methanol was added. The mixture was extracted with DCM (3×200 mL) and the organic layer was dried over $MgSO_4$ and evaporated. The title compound **13** was recrystallized from DCM and methanol to yield a pale yellow solid (4.56 g, 89%).

Mp 86 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.44 (d, *J*=9.0 Hz, 2 H), 7.90 (s, 2 H), 7.85 (d, *J*=2.4 Hz, 2 H), 7.19 (dd, *J*=2.4 Hz, *J*=9.0 Hz, 2 H), 4.23 (t, *J*=6.6 Hz, 4 H), 4.16 (t, *J*=6.6 Hz, 4 H), 2.00-1.84 (m, 8 H), 1.62-1.50 (m, 8 H), 1.42-1.22 (m, 48 H), 0.89 (t, *J*=6.3 Hz, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 149.4, 129.9, 124.3, 124.2, 123.2, 114.4, 107.0, 106.9, 69.4, 68.2, 31.92, 31.90, 29.7, 29.62, 29.59, 29.51, 29.49, 29.47, 29.4, 29.3, 26.1, 22.7, 14.1; HRMS: Calcd. For $C_{58}H_{92}O_4$: 852.6990. Found: 852.6985.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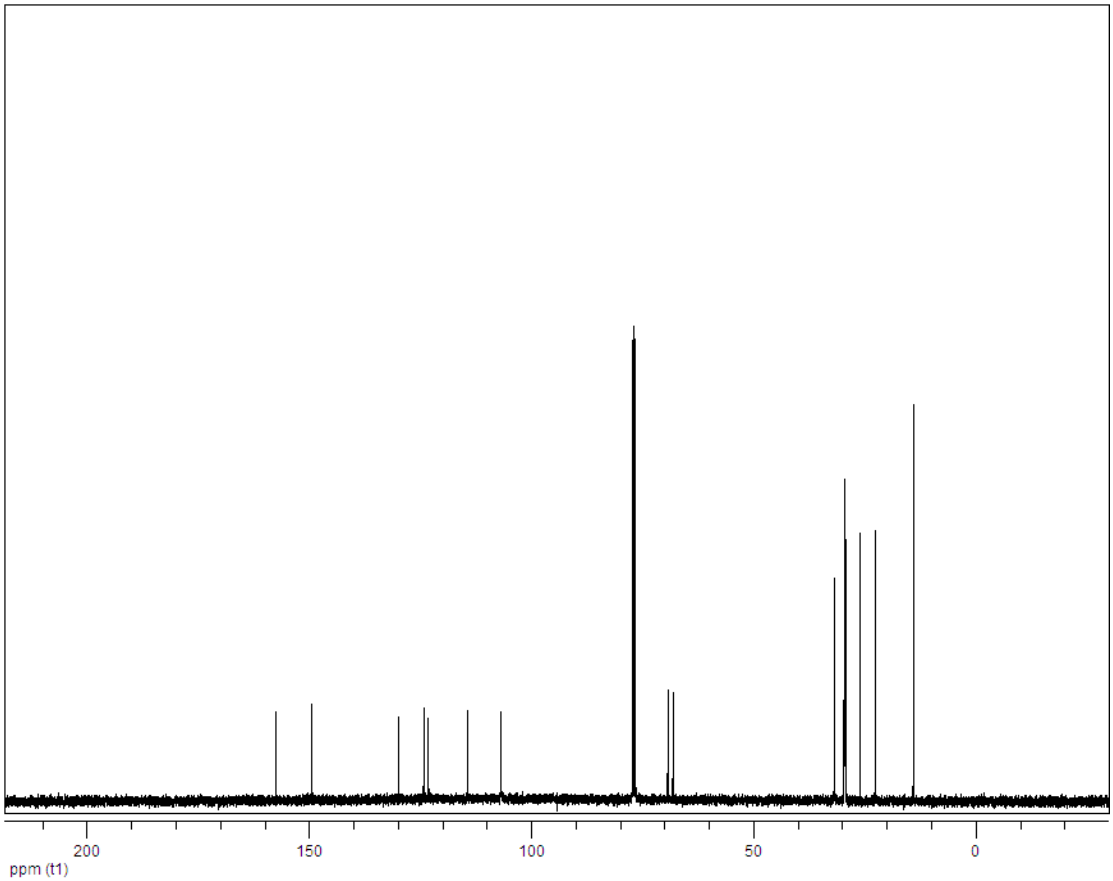
ppm (t1)


200
150
100
50
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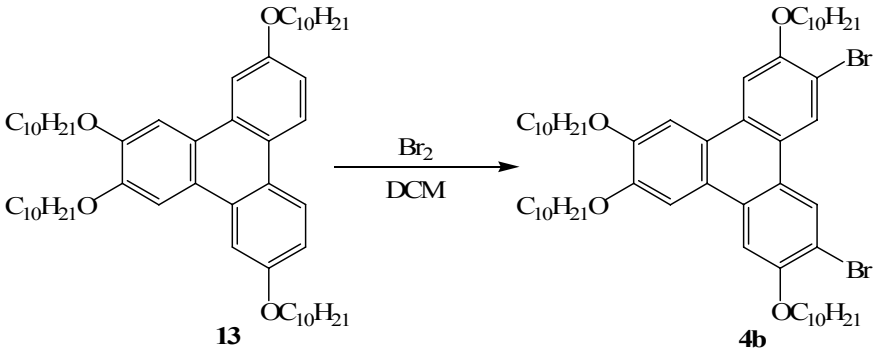
ppm (t1)

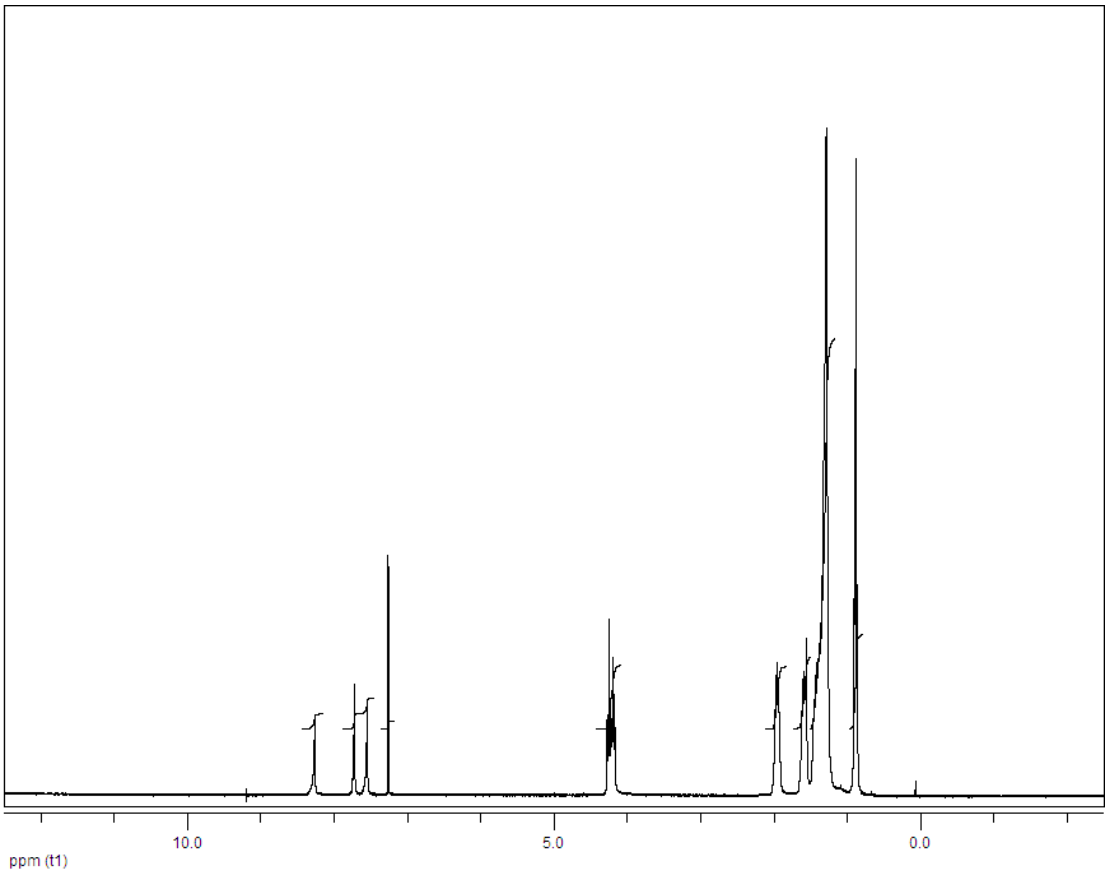
3,6-Dibromo-2,7,10,11-tetrakis(decyloxy)triphenylene 4b

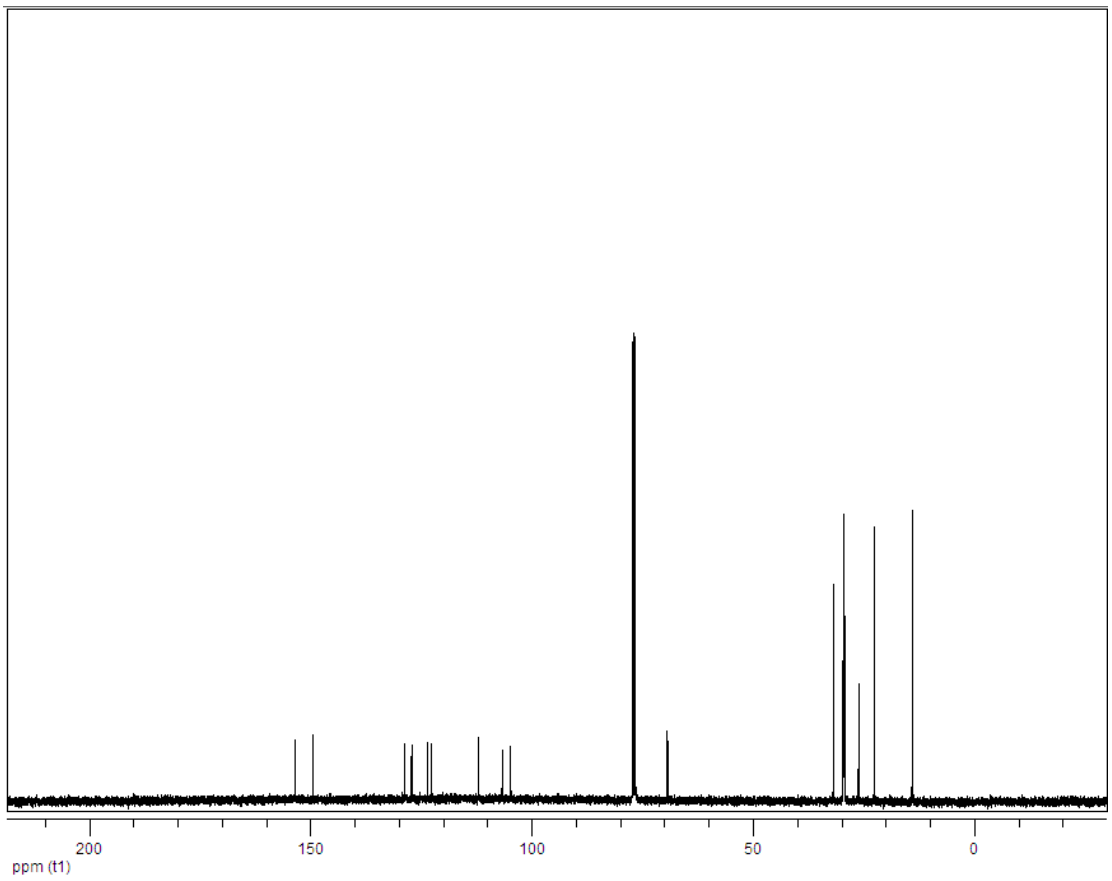


13 **4b**

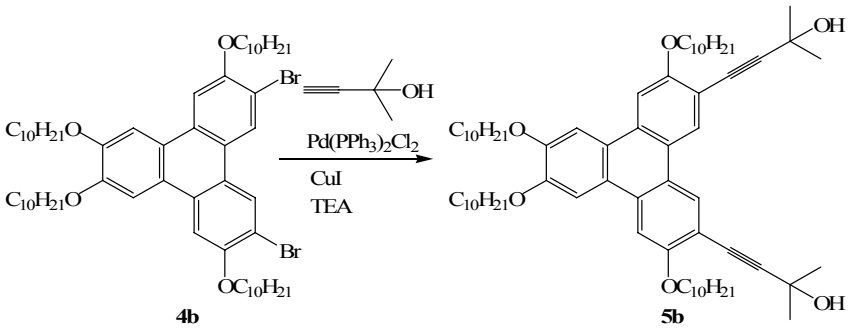
Bromine (1.66 g, 10.4 mmol) was added dropwise to the solution of compound **13** (4.22 g, 4.95 mmol) stirred in DCM (200 mL) at 0 °C. After addition, the reaction was stirred at 0 °C for 2 h. Saturated aqueous sodium metabisulfite was added. The mixture was extracted with DCM (3×200 mL) and the organic layer was dried over $MgSO_4$ and evaporated. The titile compound **4b** was recrystallized from DCM and methanol to give a pale yellow sticky solid (4.55 g, 91%).

Mp Cr 65 °C Col_h 132 °C I; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26(s, 2 H), 7.72 (s, 2 H), 7.55 (s, 2 H), 4.25 (t, *J*=6.6 Hz, 4 H), 4.19 (t, *J*=6.6 Hz, 4 H), 2.00-1.84 (m, 8 H), 1.62-1.52 (m, 8 H), 1.45-1.22 (m, 48 H), 0.89 (t, *J*=6.6 Hz, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 149.6, 128.8, 127.2, 123.6, 122.7, 112.2, 106.2, 104.8, 69.4, 69.2, 31.9, 29.73, 29.65, 29.62, 29.6, 29.5, 29.41, 29.37, 29.3, 26.4, 26.2, 22.7, 14.1; MS (MALDI): *m/z* 1010.11 (M^+, 100%).



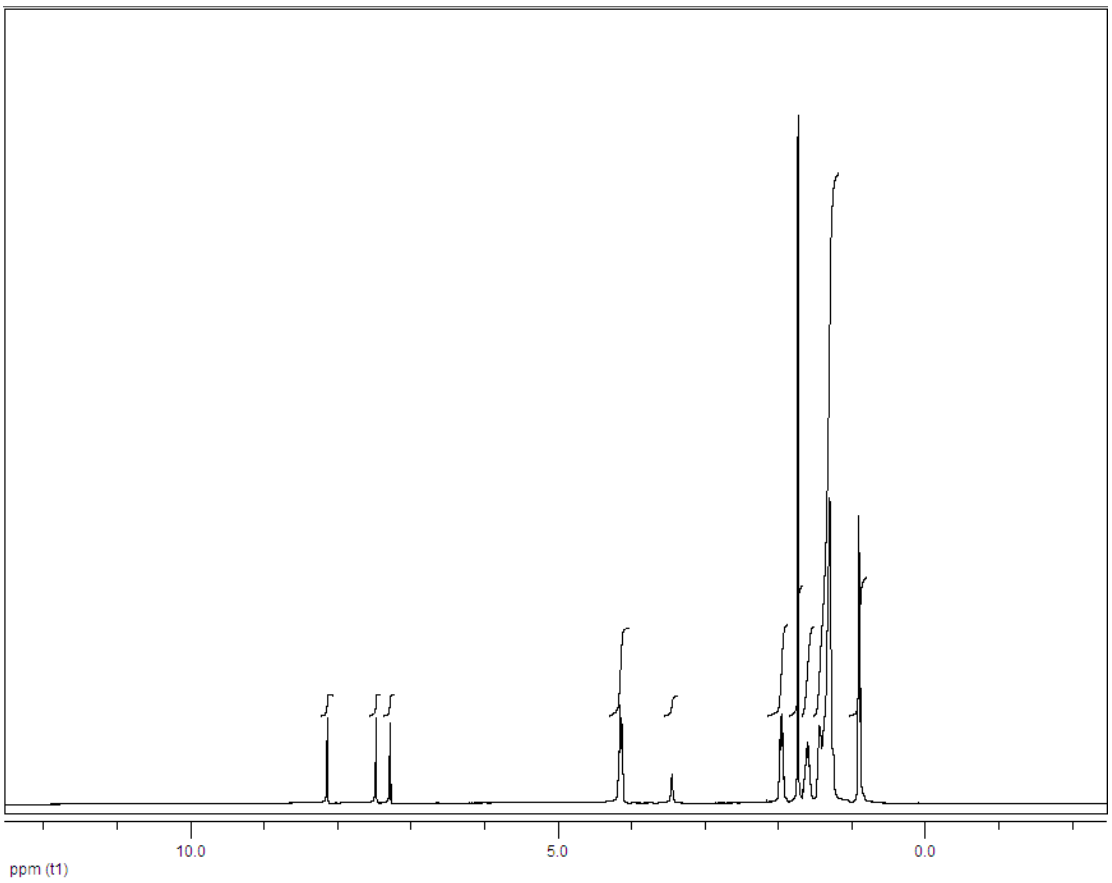


2,7,10,11-Tetrakis(decyloxy)-3,6-bis(3-methyl-3-hydroxybutynyl)triphenylene 5b



Compound **4b** (2.50 g, 2.47 mmol), $Pd(PPh_3)_3Cl_2$ (173.5 mg, 0.247 mmol) and CuI (94.1 mg, 0.494 mmol) in triethylamine (40 mL) was heated at reflux for 15 min. 2-Methyl-3-butyn-2-ol (841 mg, 10 mmol) was added dropwise to the mixture. The solution was heated under reflux for a further 24 h. The mixture was cooled to room temperature and water was added. The mixture was extracted with DCM (3×100 mL) and the solvent removed in *vacuo* to leave a dark-brown solid which was purified by column chromatography (ethyl acetate/petroleum ether=1:4) to yield the title compound **5b** as a yellow sticky solid (2.26 g, 90%).

Mp Cr 44 °C Col_h 109 °C I; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (s, 2 H), 7.48 (s, 2 H), 7.29 (s, 2 H), 4.18-4.12 (m, 8 H), 3.45 (s, 2 H), 2.00-1.92 (m, 8 H), 1.73 (s, 12 H), 1.67-1.61 (m, 8 H), 1.45-1.25 (m, 48 H), 0.92-0.88 (m, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 149.4, 129.1, 127.8, 124.1, 121.8, 111.8, 107.0, 103.9, 98.2, 78.8, 69.4, 68.7, 65.5, 31.92, 31.89, 31.5, 29.74, 29.66, 29.65, 29.6, 29.48, 29.45, 29.40, 29.36, 26.2, 22.7, 14.1; MS (MALDI): *m/z* 1016.42 (M^+, 100%).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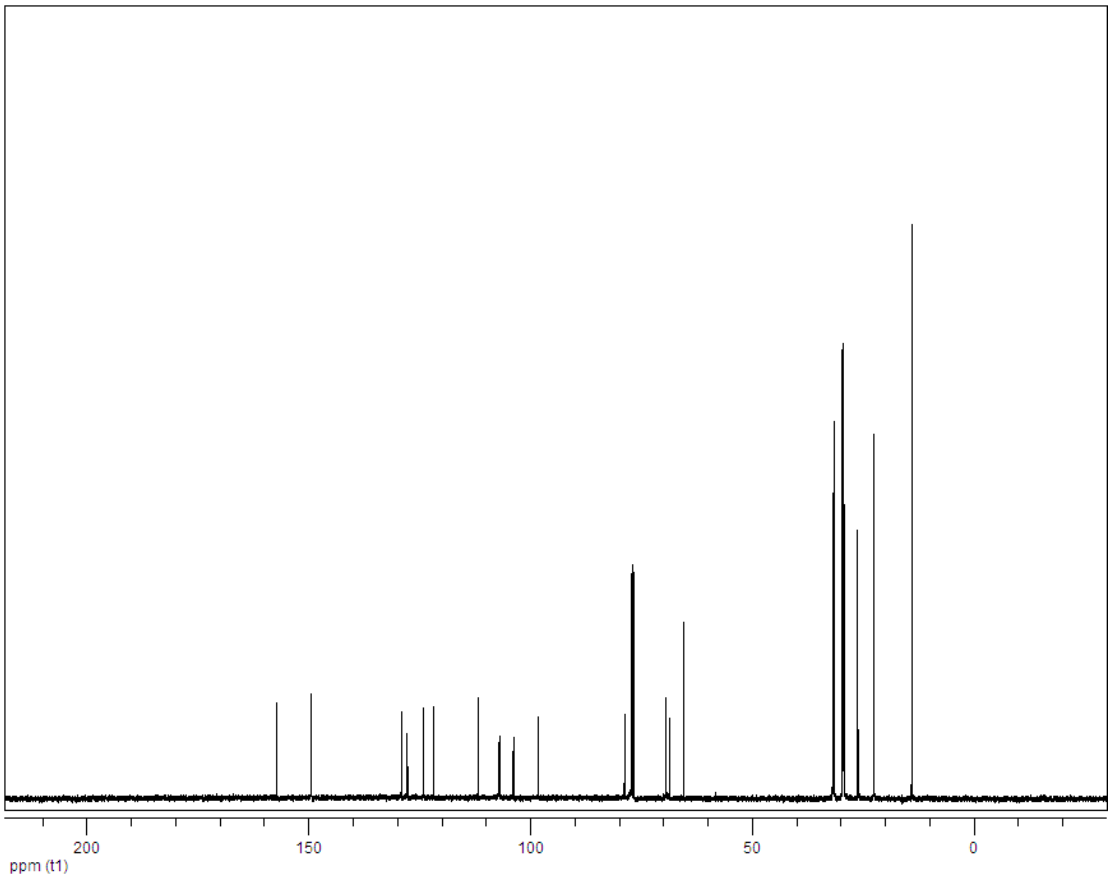
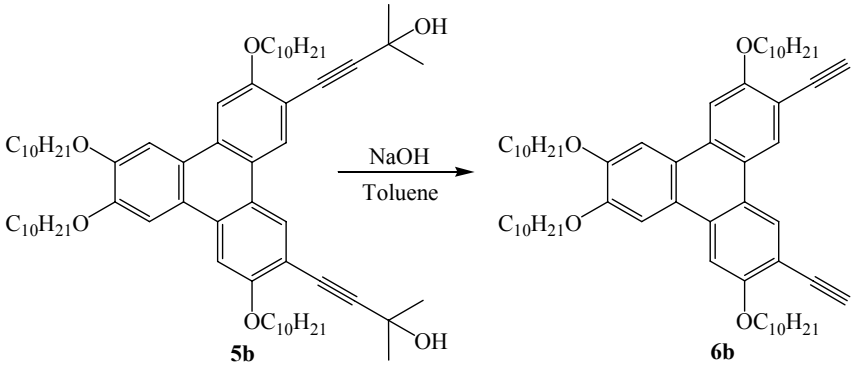
ppm (t1)

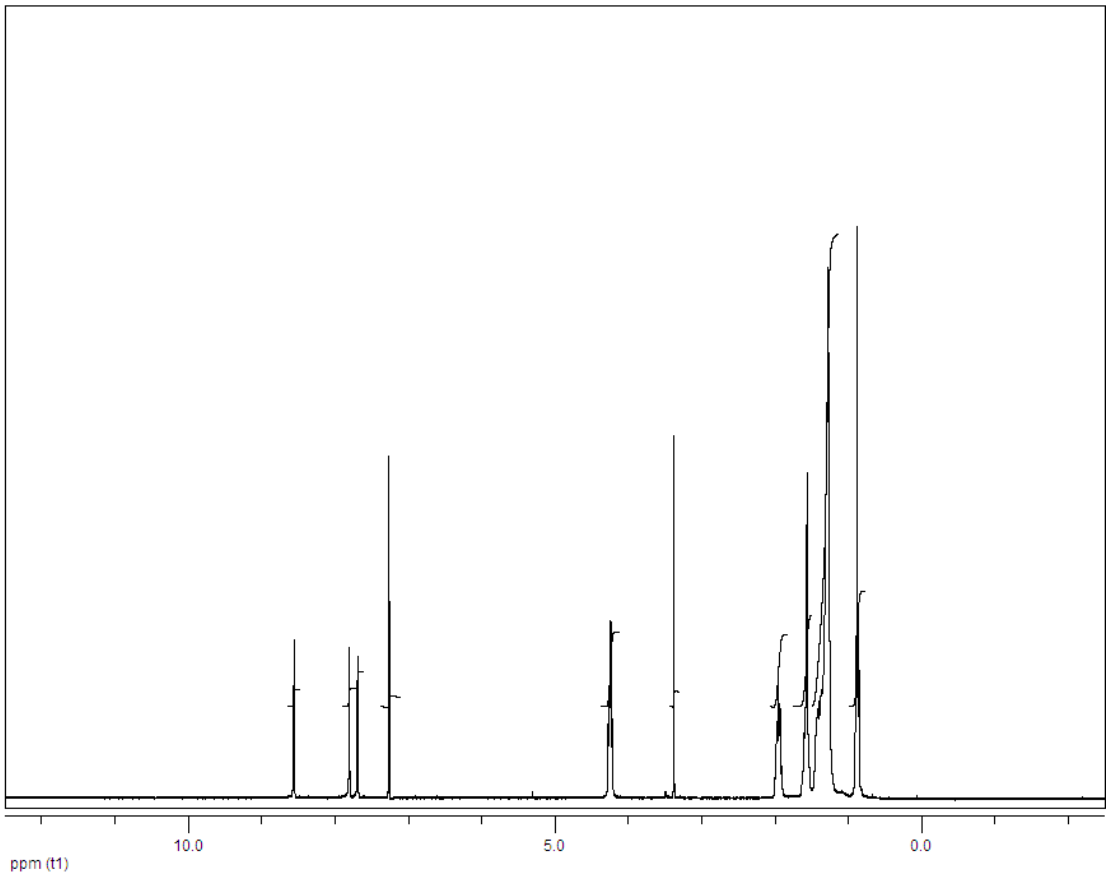

200
150
100
50
0
ppm (t1)

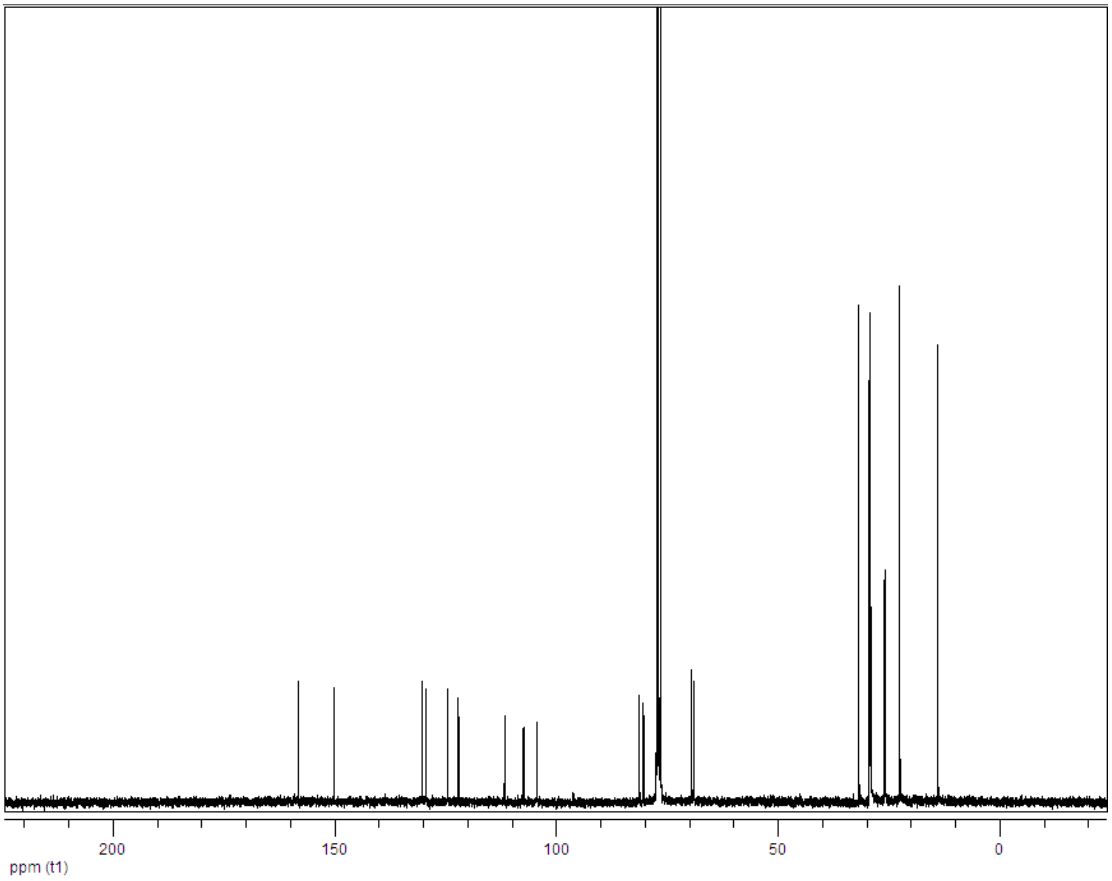
3,6-Diethynyl-2,7,10,11-tetrakis(decyloxy)triphenylene 6b



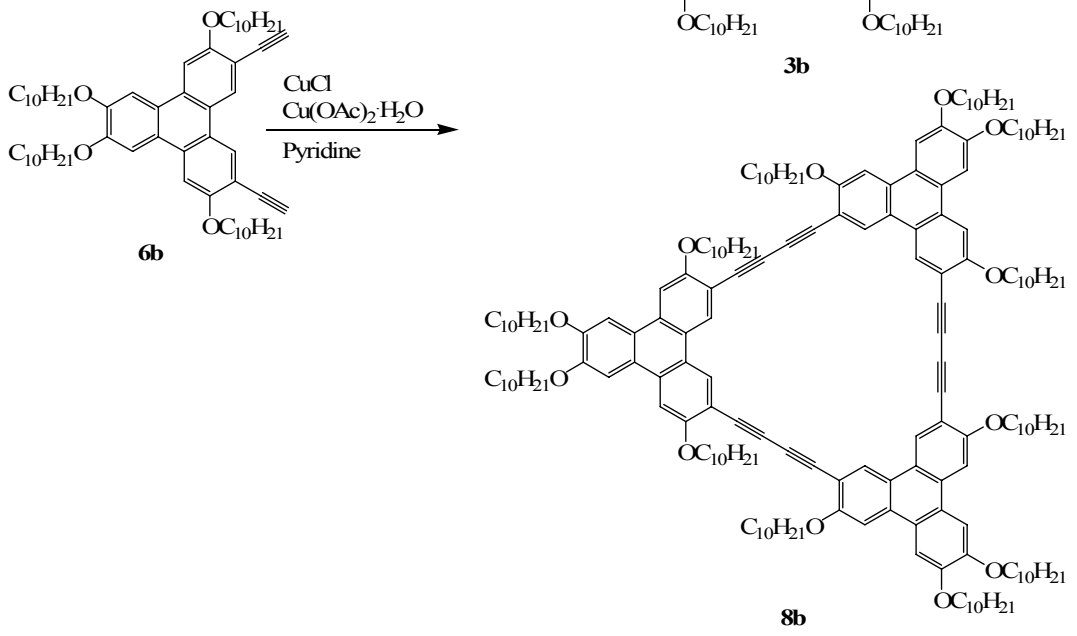
Compound **5b** (1.85 g, 1.82 mmol) was heated at reflux with excess of sodium hydroxide in toluene for 2 h. The mixture was filtered and the solvent was evaporated. The title compound **6b** was recrystallized from DCM and methanol (1.56 g, 95%).

Mp Cr 59 °C Col_h 91 °C I; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56 (s, 2 H), 7.80 (s, 2 H), 7.69 (s, 2 H), 4.27-4.22 (m, 8 H), 3.38 (s, 2 H), 2.00-1.90 (m, 8 H), 1.61-1.52 (m, 8 H), 1.48-1.26 (m, 48 H), 0.88 (t, *J*=6.6 Hz, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.3, 150.1, 130.3, 129.4, 124.5, 122.1, 111.7, 107.4, 104.4, 81.3, 80.4, 69.5, 69.1, 31.8, 29.6, 29.54, 29.49, 29.44, 29.38, 29.29, 29.27, 29.1, 26.1, 26.0, 22.6, 14.0; Anal. Calcd. For $C_{62}H_{92}O_4$: C, 82.61; H, 10.29; Found: C, 82.67; H, 10.26; HRMS: Calcd. For $C_{62}H_{92}O_4$: 900.6990. Found: 900.6991.





Synthesis of 3b and 8b



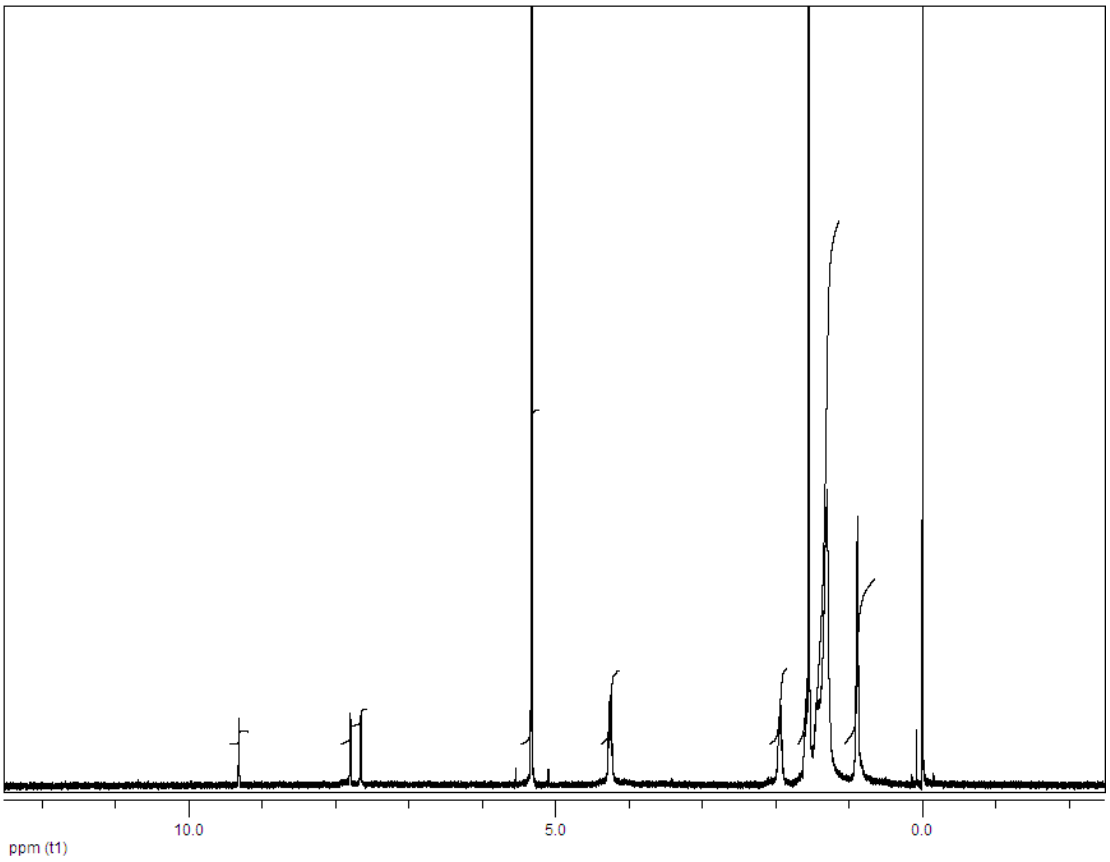
6b

3b

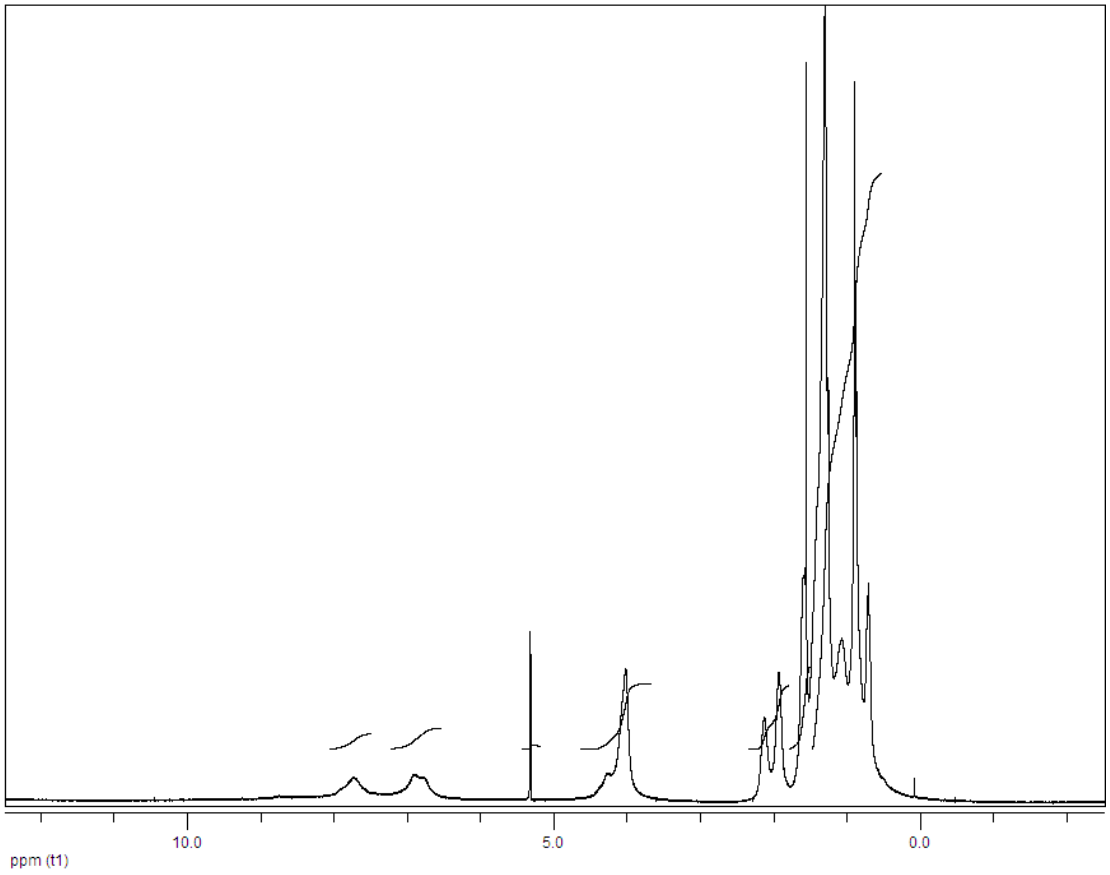
8b

A mixture of CuCl (300 mg, 30.0 mmol) and $Cu(OAc)_2 \cdot H_2O$ (600 mg, 30.0 mmol) in freshly distilled pyridine (100 mL) was stirred and heated at 60 °C. Compound **6b** (901 mg, 1.0 mmol) in pyridine (13 mL) was added over 18h and the mixture was stirred at 60 °C for another 24 h. The solvent was evaporated and the residue was dissolved in DCM, washed with water (3×300 mL), dried over $MgSO_4$, evaporated under *vacuo* to dryness and subjected to purification by silica gel chromatography (DCM/cyclohexane=3:7-4:6) to yield the title compound **3b** (224 mg, 25%) and **8b** (207 mg, 23%) as solids.

Compound **3b**: Mp Cr 110 °C N_D 131 °C I; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.32 (s, 4 H), 7.81 (s, 4 H), 7.67 (s, 4 H), 4.28 (t, *J*=6.4 Hz, 8 H), 4.24 (t, *J*=6.4 Hz, 8 H), 1.99-1.89 (m, 16 H), 1.60-1.56 (m, 16 H), 1.45-1.40 (m, 32 H), 0.99-0.93 (m, 24 H); UV-Vis (CH_2Cl_2) λ_{max} (log ε) 336 (4,71), 355 (4.55), 375 (4.77), 400 (4.29), 424(4.54) nm; Anal. Calcd. For $C_{124}H_{180}O_8$: C, 82.80; H, 10.09; Found: C, 82.78; H, 10.03; MS (MALDI): *m/z* 1797.78 (M^+, 100%).



Compound **8b**: Mp > 300 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.70 (brs, 6 H), 6.89 (brs, 6 H), 6.78 (brs, 6 H), 4.40-3.90 (brm, 24 H), 2.20-2.05 (brm, 12 H), 2.02-1.85 (brm, 12 H), 1.78-0.6 (brm, 108 H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 158.7, 149.6, 129.7, 129.1, 123.9, 121.5, 111.3, 106.5, 103.0, 79.8, 79.5, 69.5, 69.3, 32.3, 30.1, 29.8, 26.4, 26.3, 23.2, 23.1, 14.2, 14.1; Anal. Calcd. For $C_{186}H_{270}O_{12}$: C, 82.80; H, 10.09; Found: C, 82.71; H, 9.97; MS (MALDI): *m/z* 2697.64 (M^+, 100%).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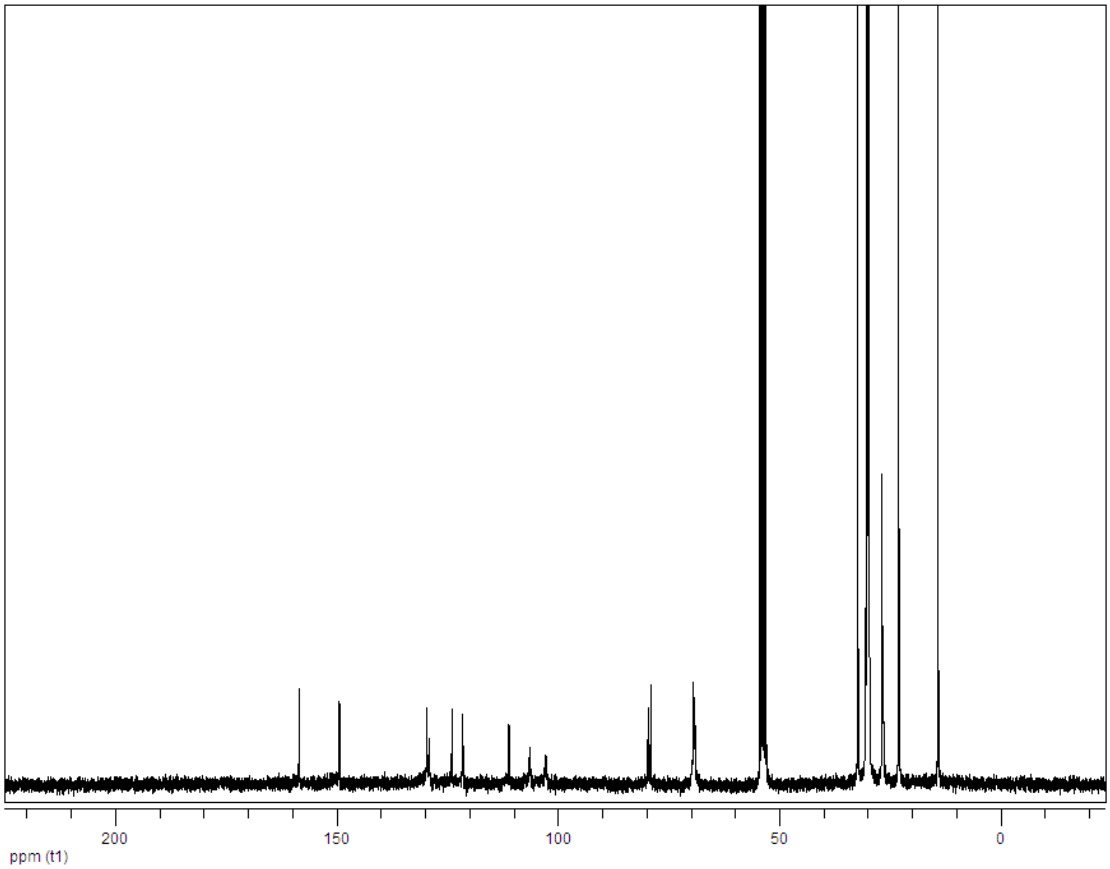
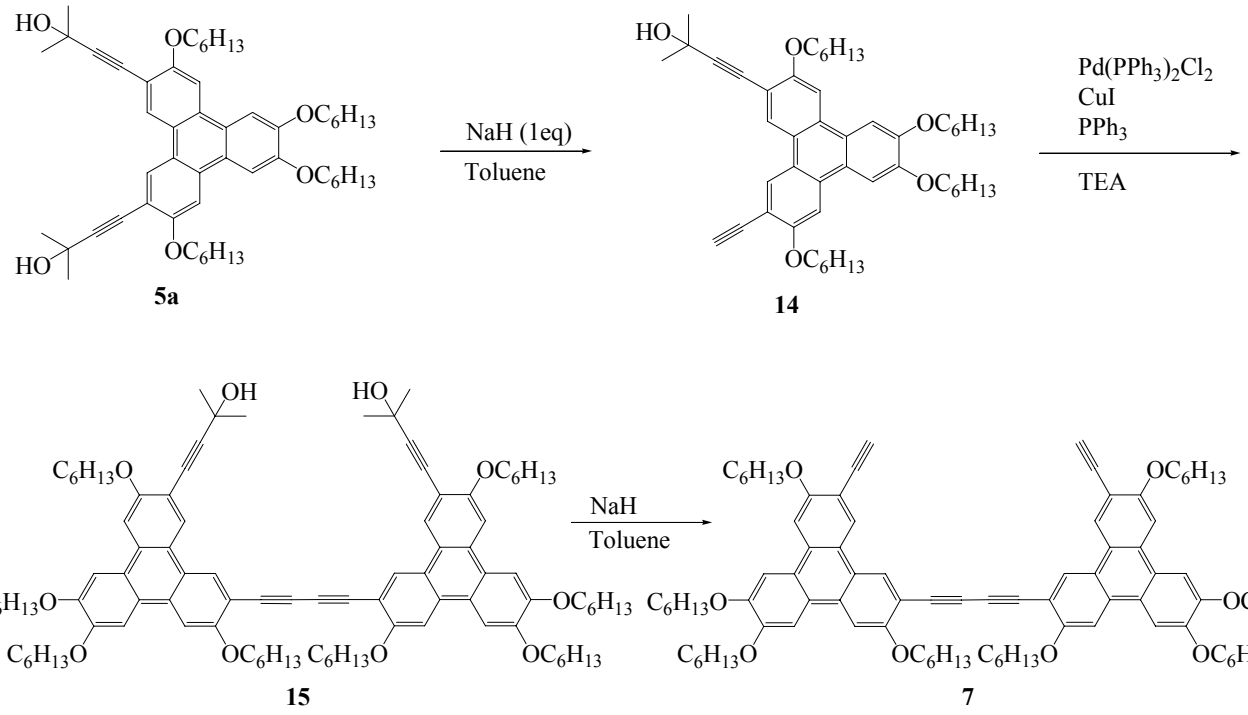
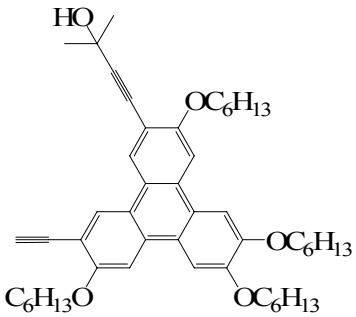
ppm (t1)


200
150
100
50
0
ppm (t1)

Stepwise synthesis of 7

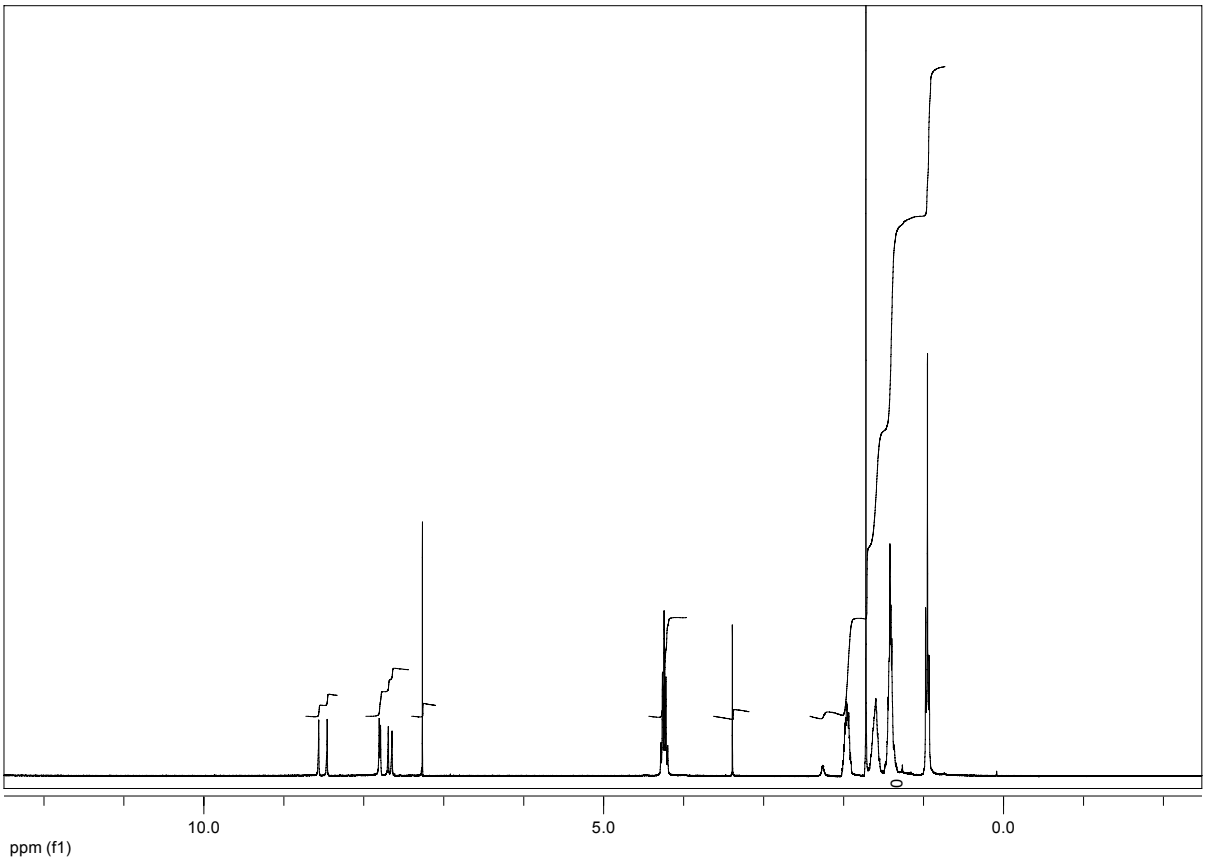


11-Ethynyl-3,6,7,10-tetrakis(hexyloxy)-2-(3-methyl-3-hydroxybutynyl)triphenylene 14



2,7,10,11-Tetrakis(hexyloxy)-3,6-bis(3-methyl-3-hydroxybutynyl)triphenylene **5a** (1.50 g, 1.89 mmol) was dissolved in refluxing dry toluene (30 mL) under an atmosphere of nitrogen. NaH (60% dispersion in oil) (0.075 g, 1.89 mmol NaH) was added in one portion and the mixture heated under reflux for 30 min. The solution was the poured onto ice-cold water and the organic layer was extracted with DCM (3×100 mL). The solvent was removed in *vacuo* to leave a dark-brown oil which was purified by column chromatography (ethyl acetate/petroleum ether=1:9) to give the pure title compound (0.50 g, 35%) as a yellow solid.

Mp I 164 °C Col_h 72 °C K; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.61 (s, 1 H), 8.52 (s, 1 H), 7.84 (s, 1 H), 7.83 (s, 1 H), 7.73 (s, 1 H), 7.70 (s, 1 H), 4.28-4.22 (m, 8 H), 3.39 (s, 1 H), 2.17 (br, 1 H), 1.98-1.92 (m, 8 H), 1.72 (s, 6 H), 1.61-1.34 (m, 24 H), 0.96-0.88 (m, 12 H); ^{13}C NMR ($CDCl_3$, 75.45 MHz): δ 157.9, 157.5, 149.7, 149.6, 129.9, 129.5, 129.0, 128.1, 124.3, 123.9, 121.8, 121.7, 112.0, 111.3, 107.3, 107.1, 104.1, 103.9, 97.9, 80.9, 80.1, 79.2, 69.2, 68.7, 68.5, 65.4, 31.2, 31.1, 31.0, 29.2, 28.8, 28.7, 25.3, 25.2, 22.2, 22.1, 13.6, 13.5; MS (ES): *m/z* 735.5 (M^+, 100%); HRMS: Calcd. For $[C_{49}H_{66}O_5+NH_4]^+$: 752.5249. Found: 752.5257.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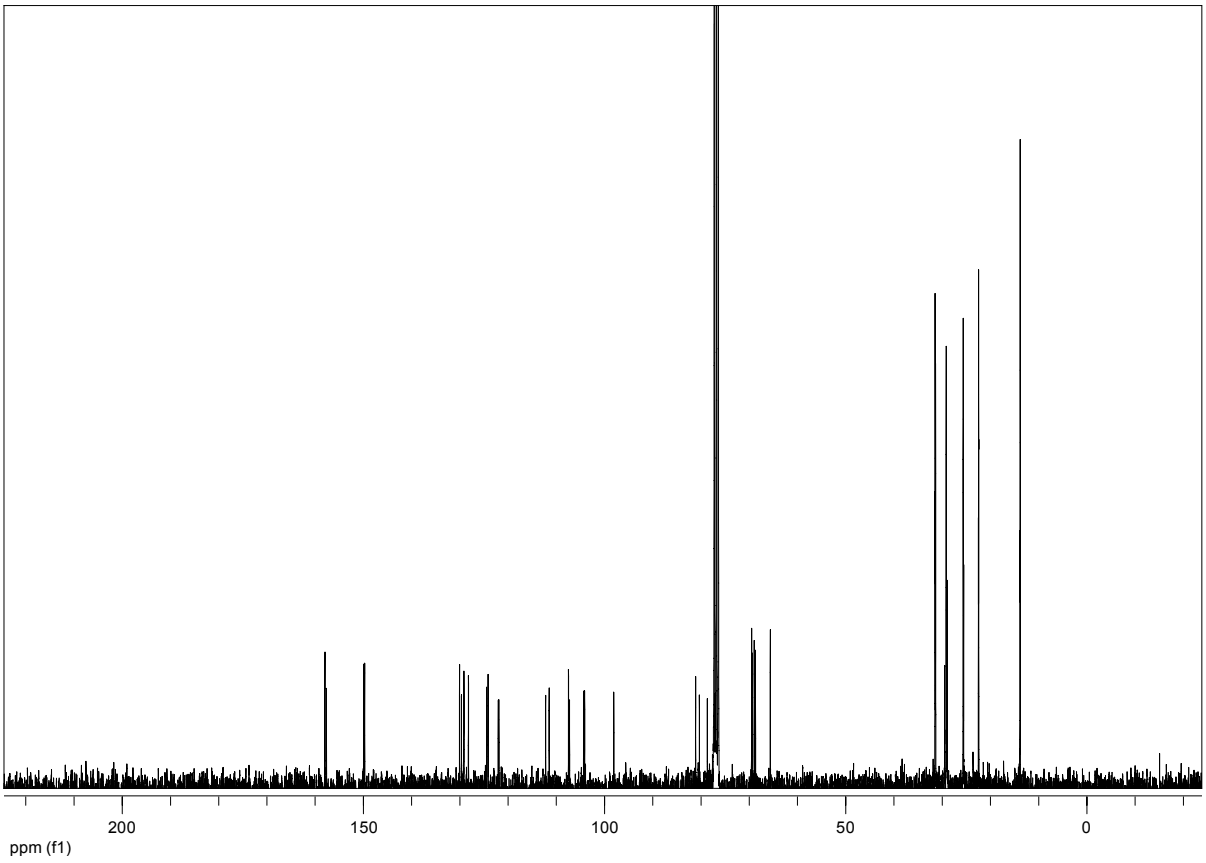
ppm (f1)


200
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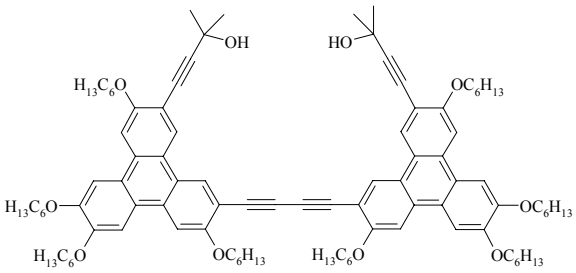
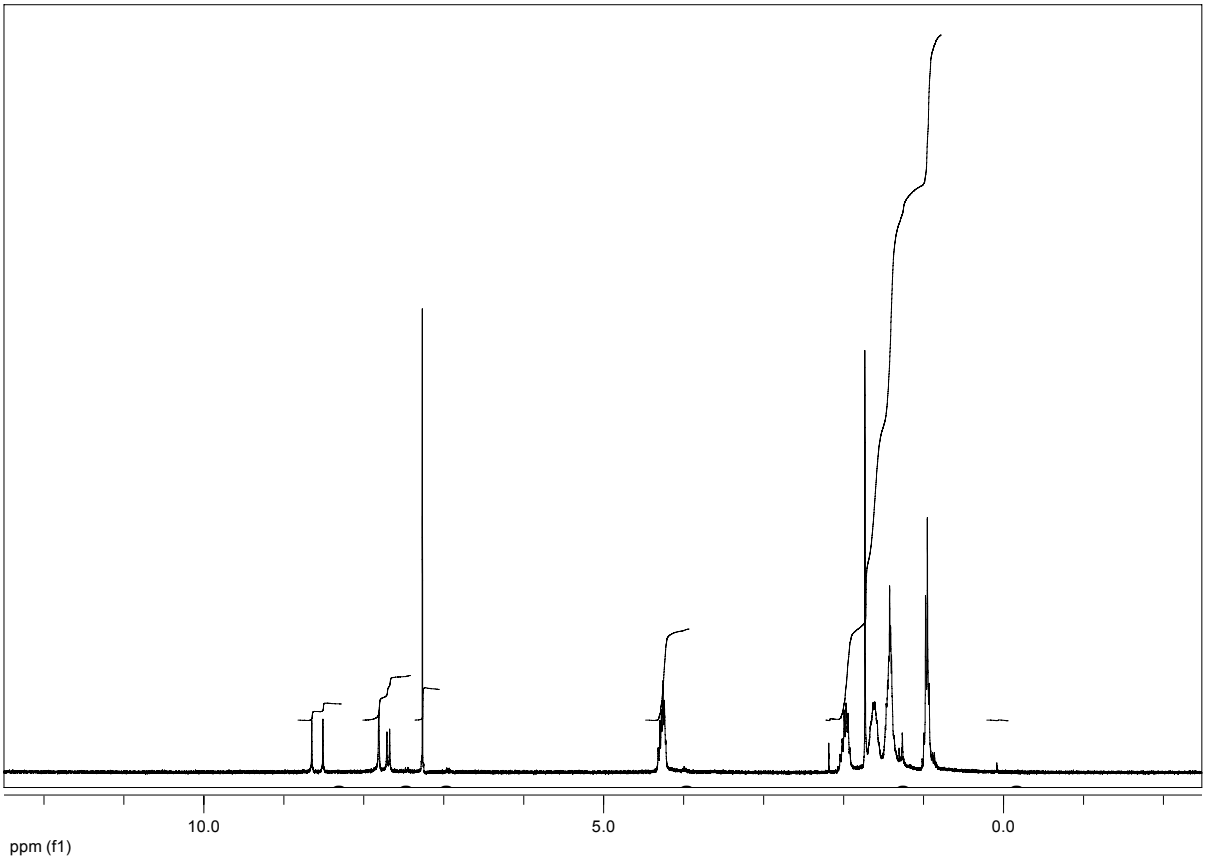
ppm (f1)

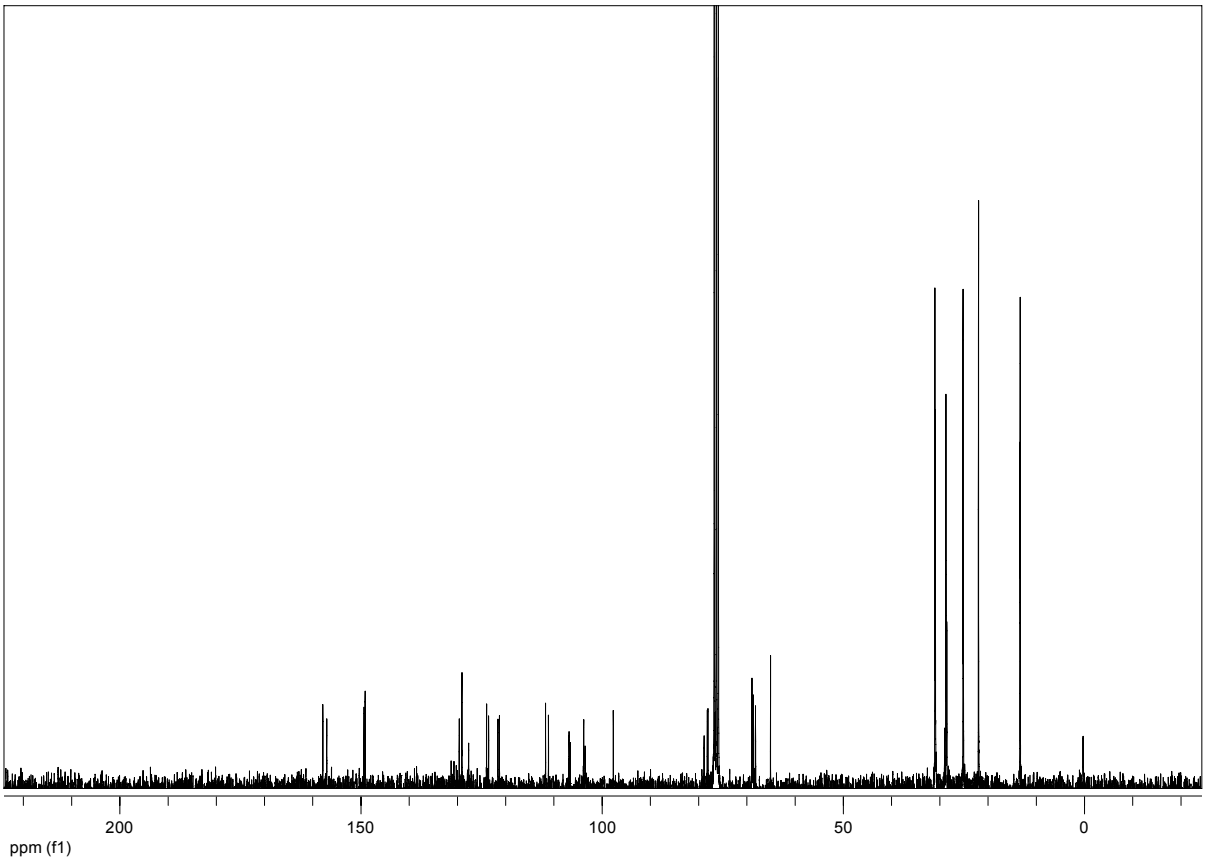
Dimer 15



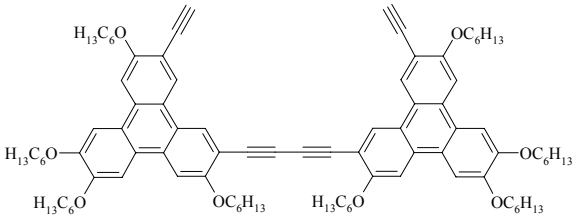
Compound **14** (0.40 g, 0.54 mmol), CuI (0.05 g, 0.26 mmol), $Pd(PPh_3)_2Cl_2$ (0.10 g, 0.14 mmol), PPh_3 (0.12 g, 0.45 mmol) were stirred in refluxing triethylamine (50 mL) under an atmosphere of nitrogen for 24 h. The mixture was cooled to room temperature and water added. The mixture was extracted with DCM (3×100 mL) and solvent was removed in *vacuo* to leave a dark-brown solid which was purified by column chromatography (ethyl acetate/petroleum ether=1:4) to give the pure title compound (0.23 g, 58%) as an off-white solid.

Mp 185 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.59 (s, 2 H), 8.45 (s, 2 H), 7.76 (s, 4 H), 7.65 (s, 2 H), 7.61 (s, 2 H), 4.29-4.22 (m, 16 H), 2.48 (br, 2 H), 2.03-1.93 (m, 16 H), 1.73 (s, 12 H), 1.60-1.25 (m, 48 H), 0.98-0.85 (m, 24 H); ^{13}C NMR ($CDCl_3$, 75.45 MHz): δ 157.8, 156.9, 149.3, 149.0, 129.4, 128.9, 127.5, 123.8, 123.4, 121.5, 121.1, 111.6, 110.9, 106.7, 106.5, 103.6, 103.4, 97.5, 78.0, 77.5, 68.7, 68.6, 68.4, 67.9, 64.8, 30.7, 30.6, 28.7, 28.4, 28.3, 24.9, 24.8, 21.7, 13.1, 13.0; MS (MALDI): *m/z* 1468 (M^+, 100%).



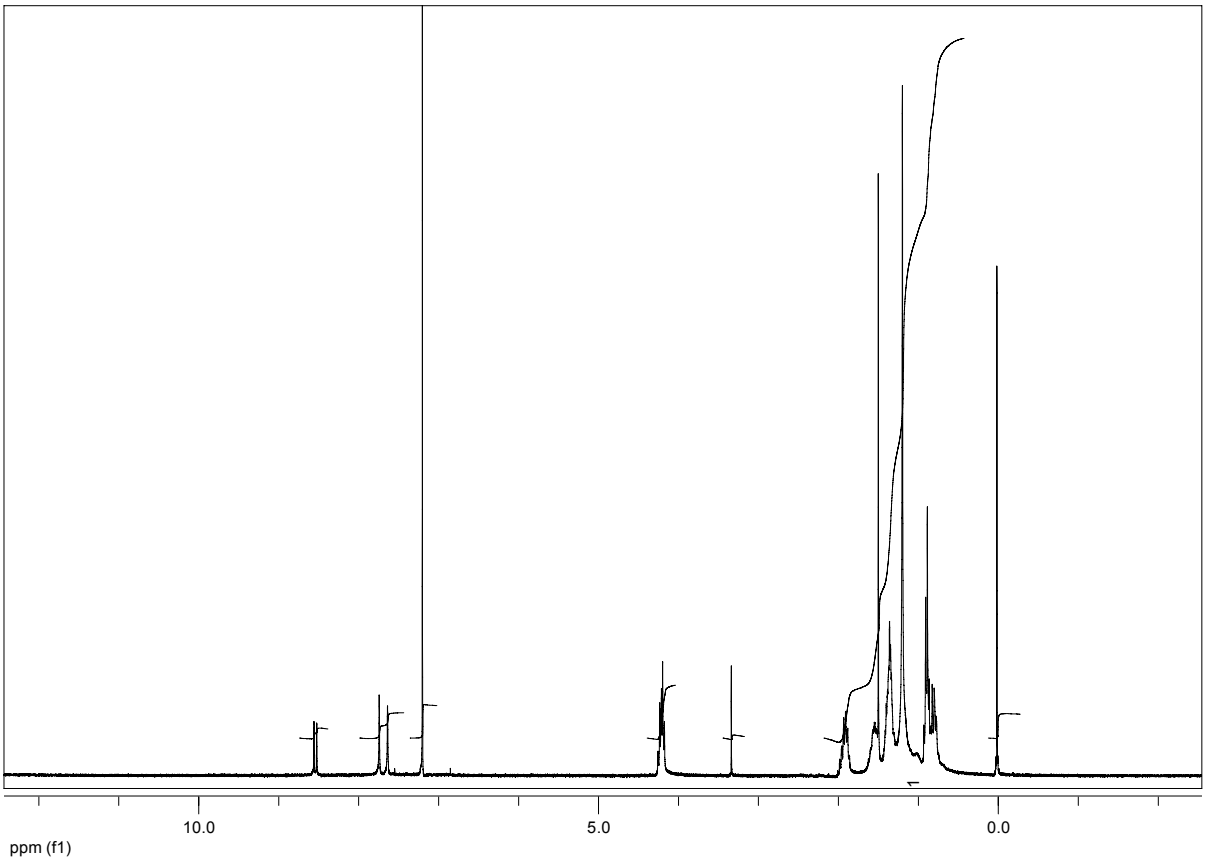


Open twin 7



Dimer **15 (**0.23 g, 0.16 mmol) was dissolved in refluxing dry toluene (50 mL) under an atmosphere of nitrogen. NaH (60% dispersion in oil) (0.067 g, 1.7 mmol NaH) was added in small portions and the mixture heated under reflux for 2 h. The solution was the poured onto ice-cold water and the organic layer was extracted with DCM (3×100 mL). The solvent was removed in *vacuo* to leave a dark-brown oil which was purified by column chromatography (ethyl acetate/petroleum ether=1:9) to give the pure title compound (0.16 g, 75%) as a pale yellow solid.

Mp 153 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.64 (s, 2 H), 8.60 (s, 2 H), 7.82 (s, 4 H), 7.72 (s, 4 H), 4.31-4.24 (m, 16 H), 3.39 (s, 2 H), 1.99-1.92 (m, 16 H), 1.65-1.40 (m, 48 H), 0.99-0.83 (m, 24 H); ^{13}C NMR ($CDCl_3$, 75.45 MHz): δ 158.4, 157.8, 149.6, 129.8, 129.2, 124.1, 121.7, 111.5, 111.2, 106.9, 103.9, 80.9, 79.0, 78.4, 77.0, 69.1, 68.8, 31.2, 29.2, 28.9, 28.7, 25.4, 25.3, 22.2, 13.6, 13.5; MS (MALDI): *m/z* 1351.9 (M^+, 100%).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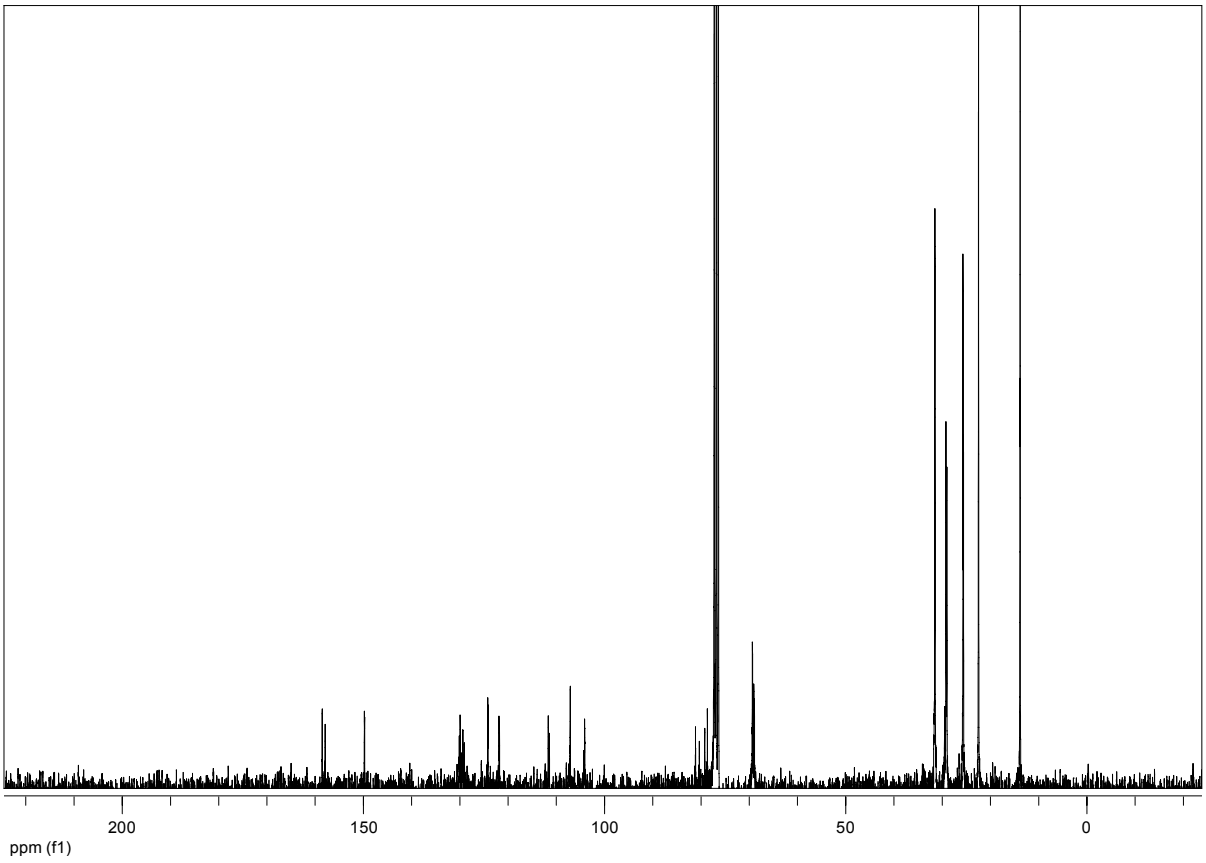
ppm (f1)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50
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ppm (f1)