

# Self-Assembled Lamellar Nanostructures of Wholly Aromatic Rod-Rod Type Block Molecules

Teruaki Hayakawa,\* † Raita Goseki, † Masa-aki Kakimoto, † Masatoshi Tokita, † Junji Watanabe, † Yonngui Liao, ‡ Shin Horiuchi ‡

*Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-2-S8-26 O-okayama, Meguro-ku, Tokyo 152-8552, Japan, and Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology, Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan*

*thayakaw@o.cc.titech.ac.jp*

## Supporting Information

### Materials.

4,4'-Difluorodiphenyl sulfone, 4-Methoxy phenol, 4,4'-Difluorobenzophenone and 4-*tert*-Butylphenol were purchased from Tokyo Chemical Industry Co. Ltd (Tokyo, Japan). Boron tribromide, 99.999% was purchased from Wako Pure Chemical Co. Ltd (Osaka, Japan). Potassium carbonate was purchased from Takahashi Pure Chemical, Co. Ltd (Tokyo, Japan). Dimethyl-*d*<sub>6</sub> sulfoxide was purchased from ISOTEC (Miamisburg). Chloroform-*d* was purchased from Aldrich. All solvents were used as received.

### Characterization

Thin layer chromatography was performed on Merck silicagel 60F<sub>254</sub>. Silica used for chromatography was Fuji silysia chemical BW-127ZH (150-75  $\mu$ m). Infrared spectrum was recorded on a JASCO FT / IR-460 Plus spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectrum were recorded on JEOL JNM-AL 300 spectrometer at 300 MHz and 75 MHz, respectively. Matrix Assisted Laser Desorption Ionization Time of Flight Mass Spectrometry (MALDI-ToF-MS) was taken on a Shimadzu AXIMA-CFR mass spectrometer. The spectrometer was equipped with nitrogen laser ( $\lambda$  = 337 nm) and with pulsed ion extraction. The operation was performed at an accelerating potential of 20 kV by a linear-positive ion mode. Samples for MALDI-ToF-MS were prepared by casting the matrix compound (dithranol) onto the slide. Thermal analyses of the compounds, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), were carried out using a Seiko SSC / 6000 (TG / DTA 6200 and DSC6200) thermal analyzer with *ca.* 5 mg of samples at a heating rate of 10 °C min<sup>-1</sup>. Nitrogen was used as purge gas at a flow rate of 50 mL

min<sup>-1</sup> in TGA and DSC measurements. A polarized optical microscope (OLYMPUS BX51) was used to observe phase transition to an isotropic phase of compounds. Wide-angle X-ray diffraction (WAXD) patterns were recorded on a flat imaging plate by using Ni-filtered Cu K $\alpha$  radiation generated by a Rigaku RU-200BH. Small-angle X-ray scattering (SAXS) profiles were obtained using a Bruker NanoSTAR (45 kV / 110 mA) with a 2D-PSPC detector (camera length 1055 nm). A leo922 Energy-filtering transmission electron microscope (EFTEM), with which an omega-type electron spectrometer is equipped, was operated at an acceleration voltage of 200 kV. For specimen preparation, the films after annealed at 160 °C for OES-*b*-OEK and 200 °C for OEK-*b*-OES-*b*-OEK, respectively, after cooling from 250 °C, was sectioned to give thin specimens with 50 nm thickness after embedding in epoxy resin.

### **Synthesis of 4-fluoro-4'-(4''-methoxyphenyloxy)diphenyl sulfone (3)**

A round bottom flask was charged with 10 g (39.3 mmol) of 4,4'-difluorodiphenyl sulfone, 4.88 g (39.3 mmol) of 4-methoxy phenol, 8.15 g (58.95 mmol) of potassium carbonate. To this mixture was added 30 mL of DMAc and the resulting solution was heated to 180 °C over the course of 4 hours under a nitrogen atmosphere. The reaction mixture was diluted with dichloromethane and washed with saturate NaCl water for three times to remove DMAc and potassium carbonate. The organic layer was dried over MgSO<sub>4</sub>, filtered, evaporated. The yellow residue was purified by column chromatography on silica using a 1:1 n-hexane/dichloromethane mixture as the eluent. The solvent was removed and the white solid was dried *in vacuo* at 40 °C for 3 hours (6.34 g, 17.7 mmol, 45%). IR (KBr): 3094, 1590, 1504, 1489, 1324, 1295, 1233, 1151, 1104, 1031, 845, 832 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, r.t.):  $\delta$  7.91 (dd, *J* = 8.8, 5.0 Hz, 2H), 7.81 (d, *J* = 8.8 Hz, 2H), 7.14 (t, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 9.2 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 9.2 Hz, 2H), 3.80 (s, 3H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, r.t.):  $\delta$  166.9, 163.5, 163.1, 156.9, 147.8, 138.18, 138.18, 134.1, 130.2, 130.1, 129.6, 121.7, 116.9, 116.6, 116.3, 115.1, 55.6 ppm.

### **Synthesis of 4-fluoro-4'-(4''-methoxyphenyloxy)diphenyl ketone (4)**

A round bottom flask was charged with 10 g (45.8 mmol) of 4,4'-difluorobenzophenone, 5.64 g (45.8 mmol) of 4-methoxy phenol, 9.50 g (68.7 mmol) of potassium carbonate. To this mixture was added 30 mL of DMAc and the resulting solution was heated to 180 °C over the course of 4 hours under a nitrogen atmosphere. The reaction mixture was diluted with dichloromethane and washed with saturate NaCl water for three times to remove the DMAc and potassium carbonate. The organic layer was dried over MgSO<sub>4</sub>, filtered, evaporated. The obtained powder was dissolved in ethylacetate, filtered, and then obtained filtrate. The solvent

was evaporated, recrystallized from methanol gave white solid and dried *in vacuo* at 80 °C for 3 hours. (5.45 g, 16.9 mmol, 37%). IR (KBr): 3063, 1643, 1599, 1507, 1244, 1230, 1295, 1150, 1105, 1032, 843, 766 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, r.t.): δ 7.79 (dd, *J* = 8.4, 5.5 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.13 (t, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, r.t.): δ 194.0, 166.8, 163.4, 162.6, 156.7, 148.4, 134.1, 132.4, 131.1, 121.7, 116.2, 115.5, 115.2, 115.0, 55.6 ppm.

### Synthesis of (5)

A round bottom flask was charged with a 2 g (5.58 mmol) sample of **3**, 1.01 g (6.67 mmol) of 4-*tert*-butylphenol, 1.39 g (10.0 mmol) of potassium carbonate. To this mixture was added 4 mL of DMAc and the resulting solution was heated to 180 °C over the course of 4 hours under a nitrogen atmosphere. The reaction mixture was diluted with dichloromethane and washed with saturate NaCl water for three times to remove DMAc and potassium carbonate. The organic layer was dried over MgSO<sub>4</sub>, filtered, evaporated. The yellow residue was purified by column chromatography on silica using a 1:2 n-hexane/dichloromethane mixture as the eluent. The solvent was removed and the white solid was dried *in vacuo* at 40 °C for 3 hours (2.53 g, 5.19 mmol, 93%). IR (KBr): 3092, 2951, 1586, 1504, 1487, 1318, 1297, 1229, 1195, 1154, 1105, 1033, 874, 845 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, r.t.): δ 7.82 (d, *J* = 9.0 Hz, 2H), 7.81 (d, *J* = 9.0 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.00-6.89 (m, 10H), 3.80 (s, 3H), 1.38 (s, 9H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, r.t.): δ 162.7, 162.2, 156.8, 152.4, 148.0, 147.9, 135.1, 134.9, 129.63, 129.60, 126.9, 121.7, 119.8, 117.4, 116.8, 115.1, 55.6, 34.4, 31.4 ppm.

### Synthesis of (6)

A 2.53 g (5.19 mmol) sample of **5** in 30 mL of dichloromethane was treated dropwise with 5 mL (55 mmol) of boron tribromide and stirred for 1 hour at 0 °C under a nitrogen atmosphere. After the homogeneous solution to stir for 5 hours at room temperature, the solution was poured into water (1 L). The precipitate was filtered, dissolved in dichloromethane, dried over MgSO<sub>4</sub>, filtered and evaporated. Recrystallized from n-hexane/chloroform (4:1) mixture and dried *in vacuo* at 40 °C for 3 hours (1.92 g, 4.0 mmol, 78%). IR (KBr): 3429, 3097, 2962, 1589, 1499, 1486, 1319, 1289, 1238, 1190, 1151, 1107, 872, 834 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, r.t.): δ 7.82 (d, *J* = 8.8 Hz, 2H), 7.81 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 9.1 Hz, 2H), 6.83 (d, *J* = 9.1 Hz, 2H), 1.31 (s, 9H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, r.t.): δ 162.7, 162.2, 152.9, 152.4, 148.08, 148.04, 135.1, 134.8, 129.64, 129.61, 126.9, 121.9, 119.8, 117.4, 116.8, 116.6, 34.4, 31.4 ppm.

### Synthesis of (7)

A round bottom flask was charged with a 2.37 g (5.0 mmol) sample of **6**, a 2.15 g (6.0 mmol) sample of **3**, 1.04 g (7.5 mmol) of potassium carbonate. To this mixture was added 2 mL of DMAc and the resulting solution was heated to 180 °C over the course of 4 hours under a nitrogen atmosphere. The reaction mixture was diluted with dichloromethane and washed with saturate NaCl water for three times to remove DMAc and potassium carbonate. The organic layer was dried over MgSO<sub>4</sub>, filtered, evaporated. The yellow residue was purified by column chromatography on silica using a 1:4 n-hexane/dichloromethane mixture as the eluent. The solvent was removed and the white solid was dried *in vacuo* at 40 °C for 3 hours (3.83 g, 4.7 mmol, 94%). IR (KBr): 3096, 2960, 1589, 1499, 1486, 1319, 1288, 1237, 1151, 1107, 872, 834 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, r.t.): δ 7.87-7.80 (m, 8H), 7.38 (d, *J* = 8.8 Hz, 2H), 7.04-6.91 (m, 18H), 3.80 (s, 3H), 1.31 (s, 9H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, r.t.): δ 162.8, 162.2, 161.65, 161.63, 156.8, 152.3, 151.7, 148.0, 147.8, 135.9, 135.7, 134.9, 134.6, 129.79, 129.73, 129.71, 129.65, 129.61, 126.9, 121.8, 121.7, 119.7, 117.5, 117.4, 116.8, 115.1, 55.5, 34.4, 31.3 ppm. MS (MALDI-ToF) *m/z* calcd for (C<sub>47</sub>H<sub>40</sub>O<sub>9</sub>S<sub>2</sub>) 812.9, found 835.5 [M + Na]<sup>+</sup>.

### Synthesis of (8)

A 3.12 g (3.84 mmol) sample of **7** in 30 mL of dichloromethane was treated dropwise with 4 mL (42.7 mmol) of boron tribromide and stirred for 1 hour at 0 °C under a nitrogen atmosphere. After the homogeneous solution to stir for 5 hours at room temperature, the solution was poured into water (800 mL). The precipitate was filtered and dried *in vacuo* at 80 °C for 3 hours (2.50 g, 3.11 mmol, 81%). IR (KBr): 3434, 3070, 2963, 1589, 1498, 1486, 1319, 1290, 1236, 1189, 1151, 1106, 871, 834 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, r.t.): δ 7.87-7.80 (m, 8H), 7.37 (d, *J* = 8.6 Hz, 2H), 7.04-6.85 (m, 18H), 5.27 (s, 1H), 1.31 (s, 9H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, r.t.): δ 162.8, 162.3, 161.68, 161.67, 153.2, 152.2, 151.6, 148.0, 147.5, 135.68, 135.66, 134.6, 134.4, 129.69, 129.66, 129.60, 126.9, 121.9, 121.8, 119.7, 117.5, 117.4, 116.8, 116.6, 34.3, 31.3 ppm. MS (MALDI-ToF) *m/z* calcd for (C<sub>46</sub>H<sub>38</sub>O<sub>9</sub>S<sub>2</sub>) 798.92, found 821.9 [M + Na]<sup>+</sup>.

### Synthesis of (9)

A round bottom flask was charged with a 0.48 g (0.59 mmol) sample of **8**, a 0.23 g (0.65 mmol) sample of **3**, 0.098 g (0.712 mmol) of potassium carbonate. To this mixture was added 2 mL of DMAc and the resulting solution was heated to 180 °C over the course of 4 hours under a

nitrogen atmosphere. The reaction mixture was diluted with dichloromethane and washed with saturate NaCl water for three times to remove DMAc and potassium carbonate. The organic layer was dried over MgSO<sub>4</sub>, filtered, evaporated. The brown residue was purified by column chromatography on silica using a dichloromethane. The solvent was removed and the white solid was dried *in vacuo* at 40 °C for 3 hours (0.66 g, 0.58 mmol, 98%). IR (KBr): 3097, 2962, 1589, 1499, 1486, 1320, 1289, 1235, 1189, 1151, 1107, 871, 834 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, r.t.): δ 7.88-7.80 (m, 12H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.05-6.87 (m, 26H), 3.79 (s, 3H), 1.31 (s, 9H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, r.t.): δ 162.8, 162.3, 161.7, 161.63, 161.62, 156.8, 152.2, 151.7, 151.6, 148.0, 147.8, 135.9, 135.8, 135.6, 134.8, 134.6, 129.8, 129.73, 129.71, 129.66, 129.64, 126.9, 121.9, 121.7, 119.8, 117.5, 117.4, 116.8, 115.1, 55.6, 34.4, 31.3 ppm. MS (MALDI-ToF) *m/z* calcd for (C<sub>65</sub>H<sub>52</sub>O<sub>13</sub>S<sub>3</sub>) 1137.3, found 1138.7 [M]<sup>+</sup>, 1160.8 [M + Na]<sup>+</sup>.

### Synthesis of (10)

A 0.65 g (0.57 mmol) sample of **9** in 14 mL of dichloromethane was treated dropwise with 1 mL (10 mmol) of boron tribromide and stirred for 1 hour at 0 °C under a nitrogen atmosphere. After the homogeneous solution to stir for 5 hours at room temperature, the solution was poured into water (400 mL). The precipitate was filtered and dried *in vacuo* at 80 °C for 3 hours (0.58 g, 0.51 mmol, 90%). IR (KBr) 3436, 3096, 3069, 1589, 1486, 1320, 1295, 1233, 1188, 1150, 1106, 869, 834 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, r.t.): δ 7.88-7.79 (m, 12H), 7.37 (d, *J* = 8.6 Hz, 2H), 7.04-6.86 (m, 26H), 1.31 (s, 9H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, r.t.): δ 162.9, 162.4, 161.8, 161.7, 161.6, 153.6, 152.4, 151.98, 151.97, 151.8, 148.1, 147.7, 136.2, 136.1, 135.8, 135.0, 134.7, 129.87, 129.81, 129.79, 129.71, 126.9, 121.9, 121.8, 119.8, 117.7, 117.5, 116.9, 116.7, 34.4, 31.4 ppm. MS (MALDI-ToF) *m/z* calcd for (C<sub>64</sub>H<sub>50</sub>O<sub>13</sub>S<sub>3</sub>) 1123.27, found 1146.1 [M + Na]<sup>+</sup>.

### Synthesis of (11)

A round bottom flask was charged with a 0.35 g (0.31 mmol) sample of **10**, a 0.12 g (0.37 mmol) sample of **4**, 0.051 g (0.37 mmol) of potassium carbonate. To this mixture was added 1.5 mL of DMAc and the resulting solution was heated to 180 °C over the course of 4 hours under a nitrogen atmosphere. The reaction mixture was diluted with dichloromethane and washed with saturate NaCl water for three times to remove DMAc and potassium carbonate. The organic layer was dried over MgSO<sub>4</sub>, filtered, evaporated. The brown residue was purified by column chromatography on silica using a dichloromethane. The solvent was removed and the white solid was dried *in vacuo* at 40 °C for 3 hours (0.37 g, 0.26 mmol, 84%). IR (KBr): 3068, 2961,

1652, 1590, 1486, 1322, 1297, 1230, 1150, 1106, 865, 836  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , r.t.):  $\delta$  7.89-7.73 (m, 16H), 7.36 (d,  $J$  = 8.8 Hz, 2H), 7.08-6.88 (m, 34H), 3.79 (s, 3H), 1.30 (s, 9H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , r.t.):  $\delta$  194.0, 162.3, 162.2, 161.9, 161.74, 161.72, 161.6, 161.5, 160.9, 156.5, 152.5, 152.2, 151.7, 151.68, 151.64, 151.60, 151.1, 148.4, 148.0, 135.8, 135.66, 135.60, 135.5, 135.4, 134.8, 132.5, 132.1, 131.4, 129.76, 129.70, 129.6, 126.9, 121.9, 121.59, 121.57, 119.7, 117.5, 117.4, 117.3, 117.0, 116.1, 114.9, 55.5, 34.3, 31.3 ppm. MS (MALDI-ToF)  $m/z$  calcd for ( $\text{C}_{84}\text{H}_{64}\text{O}_{16}\text{S}_3$ ) 1425.6, found 1426.7  $[\text{M}]^+$ , 1449.1  $[\text{M} + \text{Na}]^+$ .

### Synthesis of (12)

A 0.36 g (0.26 mmol) sample of **11** in 14 mL of dichloromethane was treated dropwise with 1 mL (10 mmol) of boron tribromide and stirred for 1 hour at 0 °C under a nitrogen atmosphere. After the homogeneous solution to stir for 5 hours at room temperature, the solution was poured into water (400 mL). The precipitate was filtered and dried *in vacuo* at 80 °C for 3 hours (0.30 g, 0.21 mmol, 81%). IR (KBr): 3435, 3069, 2963, 1651, 1590, 1486, 1319, 1296, 1230, 1188, 1150, 1106, 867, 835  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , r.t.):  $\delta$  7.88-7.73 (m, 16H), 7.37 (d,  $J$  = 8.6 Hz, 2H), 7.11-6.84 (m, 34H), 1.31 (s, 9H) ppm;  $^{13}\text{C}$  NMR( $\text{CDCl}_3$ , r.t.):  $\delta$  194.2, 162.5, 162.3, 162.0, 161.85, 161.82, 161.7, 161.6, 161.1, 153.1, 152.7, 152.4, 151.9, 151.88, 151.84, 151.7, 151.3, 148.4, 148.1, 136.0, 135.9, 135.8, 135.7, 135.6, 135.0, 132.7, 132.2, 131.5, 129.8, 129.79, 129.70, 126.9, 121.9, 121.8, 121.7, 121.6, 119.8, 117.7, 117.6, 117.5, 117.1, 116.6, 116.2, 34.4, 31.4 ppm. MS (MALDI-ToF)  $m/z$  calcd for ( $\text{C}_{83}\text{H}_{62}\text{O}_{16}\text{S}_3$ ) 1411.5, found 1412.5  $[\text{M}]^+$ , 1434.8  $[\text{M} + \text{Na}]^+$

### Synthesis of diblock OES-*b*-OEK (1)

A round bottom flask was charged with a 0.30 g (0.21 mmol) sample of **11**, a 0.081 g (0.25 mmol) sample of **4**, 0.035 g (0.25 mmol) of potassium carbonate. To this mixture was added 1 mL of DMAc and the resulting solution was heated to 180 °C over the course of 4 hours under a nitrogen atmosphere. The reaction mixture was diluted with dichloromethane and washed with saturate NaCl water for three times to remove DMAc and potassium carbonate. The organic layer was dried over  $\text{MgSO}_4$ , filtered, evaporated. The brown residue was purified by column chromatography on silica using a dichloromethane. The solvent was removed and the solid was dried *in vacuo* at 40 °C for 3 hours (0.26 g, 0.15 mmol, 72%).  $T_g$  (DSC) 119 °C. m.p. (DSC) 202 °C. IR (KBr): 3068, 2960, 1645, 1591, 1486, 1317, 1296, 1230, 1188, 1150, 1105, 868, 835  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ , r.t.):  $\delta$  7.93-7.87 (m, 12H), 7.77 (m, 8H), 7.41 (d,  $J$  = 8.3 Hz, 2H), 7.16-6.99 (m, 42H), 3.80 (s, 3H), 1.31 (s, 9H)ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , r.t.):  $\delta$  194.0, 162.2, 161.9,

161.7, 161.6, 161.4, 161.2, 156.6, 152.5, 152.4, 151.88, 151.81, 151.3, 148.6, 148.0, 136.0, 135.8, 135.6, 135.0, 132.5, 132.1, 131.6, 129.7, 129.6, 126.9, 121.8, 121.5, 119.7, 117.6, 117.4, 117.1, 117.0, 116.2, 115.0, 55.6, 34.3, 31.3 ppm. MS (MALDI-ToF)  $m/z$  calcd for (C<sub>103</sub>H<sub>76</sub>O<sub>19</sub>S<sub>3</sub>) 1712.4, found 1712.9 [M]<sup>+</sup>, 1734.8 [M + Na]<sup>+</sup>.

#### Synthesis of 4,4'-(4'', 4'''-dimethoxyphenyloxy)diphenyl sulfone (**18**)

A round bottom flask was charged with 5.085 g (20.0 mmol) of 4,4'-difluorodiphenyl sulfone, 4.967 g (40.0 mmol) of 4-methoxyphenol, 6.08 g (44.0 mmol) of potassium carbonate. To this mixture was added 30 mL of DMAc and the resulting solution was heated to 180 °C over the course of 4 hours under a nitrogen atmosphere. The reaction mixture was diluted with dichloromethane and washed with saturate NaCl water for three times to remove DMAc and potassium carbonate. The organic layer was dried over MgSO<sub>4</sub>, filtered, evaporated. The white solid was recrystallized from the mixture of n-hexane/chloroform (5:1), filtered and dried *in vacuo* at 60 °C for 3 hours (7.99 g, 18.6 mmol, 93%). IR (KBr): 3070, 1589, 1499, 1486, 1319, 1289, 1237, 1150, 1107, 872, 834 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, r.t.): δ 7.74 (d,  $J$  = 8.8 Hz, 2H), 7.05 (d,  $J$  = 8.8 Hz 2H), 6.94 (d,  $J$  = 8.8 Hz, 2H), 6.91 (d,  $J$  = 8.8 Hz, 2H), 3.75 (s, 3H) ppm; <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, r.t.): δ 162.2, 156.5, 147.3, 134.6, 129.6, 121.7, 116.8, 115.2, 55.3 ppm.

#### Synthesis of (**13**)

A 5.94 g (13.8 mmol) sample of **18** in 200 mL of dichloromethane was treated dropwise with 10 mL (110 mmol) of boron tribromide and stirred for 1 hour at 0 °C under a nitrogen atmosphere. After the homogeneous solution to stir for 5 hours at room temperature, the solution was poured into water (2 L). The precipitate was filtered and dried *in vacuo* at 80 °C for 3 hours (5.22 g, 12.3 mmol, 89%). IR (KBr): 3378, 3093, 1590, 1507, 1488, 1451, 1293, 1232, 1194, 1142, 1106, 1070, 875, 835 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, r.t.): δ 9.52 (s, 2H), 7.85 (d,  $J$  = 9.0 Hz, 4H), 6.98 (d,  $J$  = 9.0 Hz, 4H), 6.94 (d,  $J$  = 8.8 Hz, 4H), 6.80 (d,  $J$  = 8.8 Hz, 4H) ppm; <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, r.t.): δ 162.6, 154.9, 146.0, 134.5, 129.7, 121.9, 116.7, 116.5 ppm.

#### Synthesis of (**14**)

A round bottom flask was charged with a 1.2 g (2.75 mmol) sample of **13**, a 2.36 g (6.60 mmol) sample of **3**, 1.30 g (8.25 mmol) of potassium carbonate. To this mixture was added 3 mL of DMAc and the resulting solution was heated to 180 °C over the course of 4 hours under a nitrogen atmosphere. The reaction cooled down to room temperature and the product was

filtered and washed with water and methanol. The filtered white solid was made to conduct a Soxhlet extraction with methanol to remove excess compound **3** and dried *in vacuo* at 80 °C for 3 hours (2.95 g, 2.65 mmol, 96%).  $T_g$  (DSC) 128 °C. IR (KBr): 3070, 1590, 1500, 1485, 1318, 1288, 1236, 1190, 1150, 1107, 872, 834  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (DMSO- $d_6$ , r.t.):  $\delta$  7.93-7.87 (m, 6H), 7.21-6.97 (m, 14H), 3.75 (s, 3H) ppm;  $^{13}\text{C}$  NMR (DMSO- $d_6$ , at 120 °C):  $\delta$  161.6, 160.8, 160.7, 156.2, 151.14, 151.10, 147.5, 135.4, 135.2, 134.5, 129.2, 129.1, 129.0, 121.2, 120.8, 117.4, 116.7, 115.0, 55.1 ppm.

### Synthesis of (15)

A 2.22 g (2.0 mmol) sample of **14** in 35 mL of dichloromethane was treated dropwise with 4 mL (43 mmol) of boron tribromide and stirred for 1 hour at 0 °C under a nitrogen atmosphere. After the homogeneous solution to stir for 5 hours at room temperature, the solution was poured into water (1 L). The precipitate was filtered and dried *in vacuo* at 80 °C for 3 hours (2.13 g, 1.96 mmol, 98%). IR (KBr): 3379, 3091, 1591, 1506, 1488, 1450, 1294, 1231, 1195, 1141, 1106, 1073, 875, 836  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (DMSO- $d_6$ , r.t.):  $\delta$  9.57 (br, 1H), 7.93-7.85 (m, 6H), 7.19-7.11 (m, 8H), 6.99 (d,  $J$  = 8.8 Hz, 2H), 6.93 (d,  $J$  = 8.1 Hz, 2H), 6.80 (d,  $J$  = 8.1 Hz, 2H) ppm;  $^{13}\text{C}$  NMR (DMSO- $d_6$ , r.t.):  $\delta$  162.7, 161.6, 161.5, 154.9, 151.4, 151.3, 146.0, 135.5, 135.2, 134.3, 129.9, 129.8, 122.4, 121.9, 117.8, 116.8, 116.6 ppm. MS (MALDI-ToF)  $m/z$  calcd for ( $\text{C}_{60}\text{H}_{42}\text{O}_{14}\text{S}_3$ ) 1083.17, found 1082.6  $[\text{M}]^+$ , 1106.7  $[\text{M} + \text{Na}]^+$ .

### Synthesis of (16)

A round bottom flask was charged with a 0.65 g (0.60 mmol) sample of **15**, a 0.45 g (1.44 mmol) sample of **4**, 0.25 g (1.80 mmol) of potassium carbonate. To this mixture was added 1 mL of DMAc and the resulting solution was heated to 180 °C over the course of 4 hours under a nitrogen atmosphere. The reaction cooled down to room temperature and the product was filtered and washed with water and methanol. The filtered white solid was made to conduct a Soxhlet extraction with methanol to remove excess compound **4** and dried *in vacuo* at 80 °C for 3 hours (0.71 g, 0.42 mmol, 70%). IR (KBr): 3069, 1651, 1594, 1486, 1318, 1297, 1231, 1189, 1151, 1107, 870, 835  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (DMSO- $d_6$ , r.t.):  $\delta$  7.93-7.89 (m, 6H), 7.74 (d,  $dJ$  = 5.5 Hz, 4H), 7.21-7.19 (m, 8H), 7.14-7.08 (m, 10H), 7.01-6.97 (m, 4H), 3.75 (s, 6H) ppm;  $^{13}\text{C}$  NMR (DMSO- $d_6$ , at 120 °C):  $\delta$  192.4, 161.0, 160.9, 160.8, 160.0, 155.9, 151.7, 151.1, 150.7, 148.1, 135.2, 135.1, 132.0, 131.1, 129.1, 121.2, 120.9, 120.6, 117.48, 117.40, 116.7, 116.0, 115.0, 55.1 ppm.



### Synthesis of (17)

A 0.65 g (0.39 mmol) sample of **16** in 14 mL of dichloromethane was treated dropwise with 1 mL (11 mmol) of boron tribromide and stirred for 1 hour at 0 °C under a nitrogen atmosphere. After the homogeneous solution to stir for 5 hours at room temperature, the solution was poured into water (500 mL). The precipitate was filtered and dried *in vacuo* at 80 °C for 3 hours (0.56 g, 0.34 mmol, 87%). IR (KBr): 3444, 3069, 1645, 1593, 1497, 1487, 1316, 1288, 1233, 1189, 1150, 1107, 869, 835 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, r.t.): δ 9.45 (s, 1H), 7.86-7.83 (m, 6H), 7.69-7.64 (m, 4H), 7.14-7.01 (m, 8H), 7.07-7.01 (m, 8H), 6.92-6.89 (m, 4H), 6.77-6.73 (d, *J* = 8.8Hz 2H) ppm; <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, at 120 °C): δ 192.4, 161.4, 160.9, 160.8, 160.0, 153.9, 151.7, 151.1, 150.7, 146.6, 135.29, 135.25, 135.1, 132.0, 131.1, 130.9, 129.1, 121.25, 121.21, 120.9, 120.6, 117.47, 117.40, 116.7, 116.0, 115.7 ppm. MS (MALDI-ToF) *m/z* calcd for (C<sub>98</sub>H<sub>66</sub>O<sub>20</sub>S<sub>3</sub>) 1659.76, found 1659.3 [M]<sup>+</sup>, 1681.4 [M + Na]<sup>+</sup>.

### Synthesis of triblock OEK-*b*-OES-*b*-OEK (2)

A round bottom flask was charged with a 0.50 g (0.30 mmol) sample of **17**, a 0.23 g (0.72 mmol) sample of **4**, 0.12 g (0.90 mmol) of potassium carbonate. To this mixture was added 1 mL of DMAc and the resulting solution was heated to 180 °C over the course of 4 hours under a nitrogen atmosphere. The reaction cooled down to room temperature and the product was filtered and washed with water and methanol. The solid product was made to conduct a Soxhlet extraction with methanol to remove excess compound **4** and dried *in vacuo* at 80 °C for 3 hours (0.64 g, 0.29 mmol, 96%). *T*<sub>g</sub> (DSC) 126 °C. m.p. (DSC) 223 °C. IR (KBr): 3067, 1646, 1597, 1487, 1312, 1229, 1188, 1150, 1106, 930, 866, 836 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, r.t.): δ 7.91-7.89 (m, 6H), 7.79-7.72 (m, 8H), 7.20-6.98 (m, 30H), 3.78 (s, 3H) ppm; <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, at 130 °C): δ 192.4, 160.9, 160.8, 160.7, 160.1, 160.0, 155.9, 151.7, 151.46, 151.40, 151.3, 151.1, 150.7, 135.2, 131.9, 131.0, 129.0, 121.1, 120.7, 120.49, 120.44, 117.4, 116.7, 116.0, 114.9, 55.1 ppm.

### Synthesis of hydroxyl terminated triblock OEK-*b*-OES-*b*-OEK (19)

0.45 g (0.2 mmol) of **2** in 14 mL of dichloromethane was treated dropwise with 1 mL (11 mmol) of boron tribromide and stirred for 1 hour at 0 °C under a nitrogen atmosphere. After the heterogeneous solution to stir 5 hours at room temperature, the solution was poured into water (500 mL). The precipitate was filtered and dried *in vacuo* at 80 °C for 3 hours (0.38 g 0.17 mmol 85 %). IR (KBr): 3444, 3069, 1645, 1593, 1497, 1487, 1316, 1288, 1233, 1189, 1150,

1107, 869, 835  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , r.t.):  $\delta$  9.50 (s, 1H), 7.92-7.89 (m, 6H), 7.78-7.70 (m, 8H), 7.24-7.12 (m, 24H), 6.98-6.95 (m, 4H), 6.81 (d,  $J$  = 8.7 Hz, 2H) ppm;  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ , at 120  $^\circ\text{C}$ ):  $\delta$  192.5, 161.4, 160.9, 160.8, 160.2, 160.1, 153.9, 151.7, 151.4, 151.3, 151.1, 150.7, 146.7, 135.2, 135.1, 131.99, 131.90, 131.8, 131.2, 131.1, 130.9, 129.1, 121.2, 120.8, 120.6, 117.47, 117.40, 116.79, 116.72, 116.0, 115.7 ppm. MS (MALDI-ToF)  $m/z$  calcd for ( $\text{C}_{136}\text{H}_{90}\text{O}_{26}\text{S}_3$ ) 2236.4, found 2236.7  $[\text{M}]^+$ , 2259.1  $[\text{M} + \text{Na}]^+$ .

#### Synthesis of 4-(4''-tert-butylphenoxy)-4'-(4'''-methoxyphenoxy) benzophenone (20)

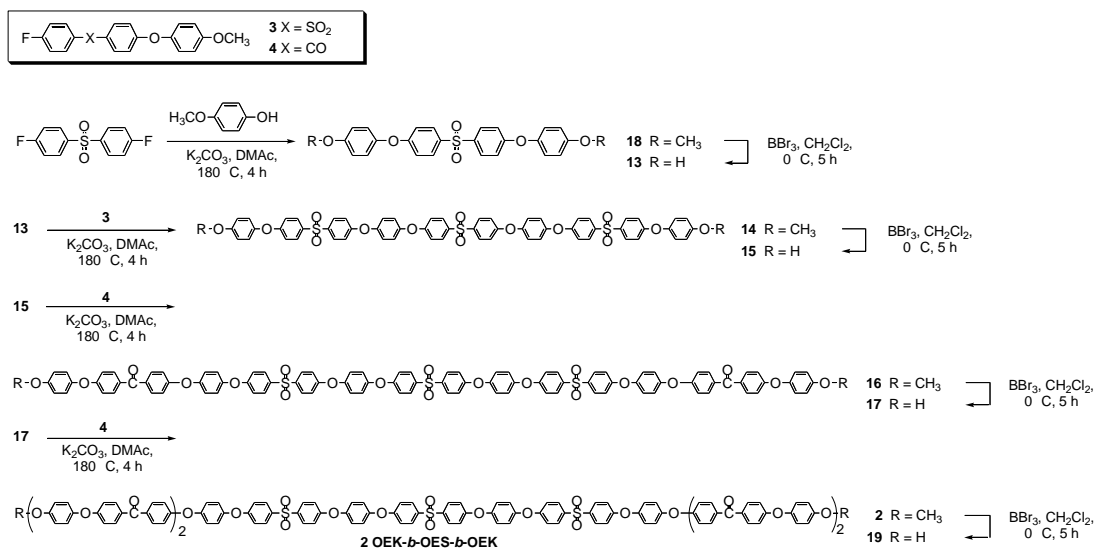
A round bottom flask was charged with a 2 g (6.20 mmol) sample of **4**, 1.13 g (7.50 mmol) of 4-*tert*-butylphenol, 1.55 g (11.2 mmol) of potassium carbonate. To this mixture was added 8.6 mL of DMAc and the resulting solution was heated to 180  $^\circ\text{C}$  over the course of 4 hours under a nitrogen atmosphere. The reaction mixture was diluted with dichloromethane and washed with saturate NaOH and NaCl water for three times to remove DMAc, potassium carbonate and excess 4-*tert*-butylphenol. The organic layer was dried over  $\text{MgSO}_4$ , filtered, evaporated. The white solid was recrystallized from the mixture of n-hexane/chloroform (4:1) gave white solid and dried *in vacuo* at 40  $^\circ\text{C}$  for 3 hours (2.31 g, 5.1 mmol, 83%). IR (KBr): 3059, 2996, 1644, 1596, 1500, 1312, 1235, 1161, 1150, 1113, 1105, 1036, 876, 836  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , r.t.):  $\delta$  7.76 (d,  $J$  = 8.8 Hz, 2H), 7.75 (d,  $J$  = 8.8 Hz, 2H), 7.33 (d,  $J$  = 8.4 Hz, 2H), 7.04-6.89 (m, 10H), 3.81 (s, 3H), 1.32 (s, 9H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , r.t.):  $\delta$  194.3, 162.3, 161.6, 156.6, 153.0, 148.6, 147.4, 132.2, 132.1, 132.0, 131.7, 126.8, 121.6, 119.6, 116.9, 116.2, 115.0, 55.6, 34.4, 31.4 ppm.

#### Synthesis of (21)

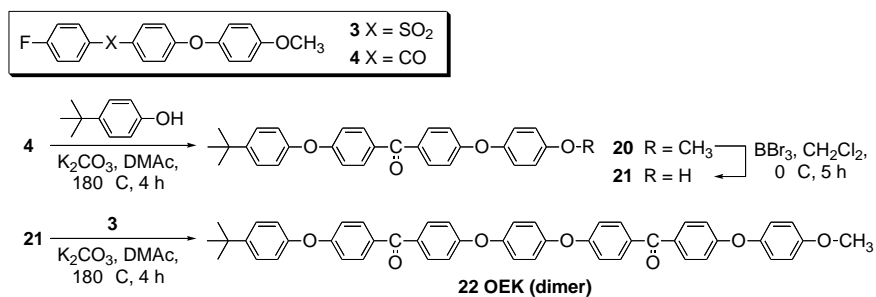
A 1.46 g (3.30 mmol) sample of **20** in 36 mL of dichloromethane was treated dropwise with 3 mL (33 mmol) of boron tribromide and stirred for 1 hour at 0  $^\circ\text{C}$  under a nitrogen atmosphere. After the homogeneous solution to stir for 5 hours at room temperature, the solution was poured into water (1 L). The precipitate was filtered and dried *in vacuo* at 80  $^\circ\text{C}$  for 3 hours. (1.30 g, 3.0 mmol, 91%). IR (KBr): 3349, 3065, 2962, 1644, 1597, 1500, 1458, 1416, 1364, 1311, 1284, 1240, 1194, 1160, 1112, 839, 819  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , r.t.):  $\delta$  7.77 (d,  $J$  = 8.8 Hz, 2H), 7.76 (d,  $J$  = 8.8 Hz, 2H), 7.39 (d,  $J$  = 8.4 Hz, 2H), 7.00 (d,  $J$  = 8.8 Hz 4H), 6.96-6.93 (m, 4H), 6.86 (d,  $J$  = 8.4 Hz, 2H), 5.81 (br, 1H), 1.32 (s, 9H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , r.t.):  $\delta$  194.9, 162.5, 161.8, 152.9, 148.3, 147.5, 132.33, 132.30, 131.7, 131.5, 126.8, 121.8, 119.6, 116.8, 116.5, 116.1, 34.4, 31.4 ppm.

### Synthesis of OEK dimer (22)

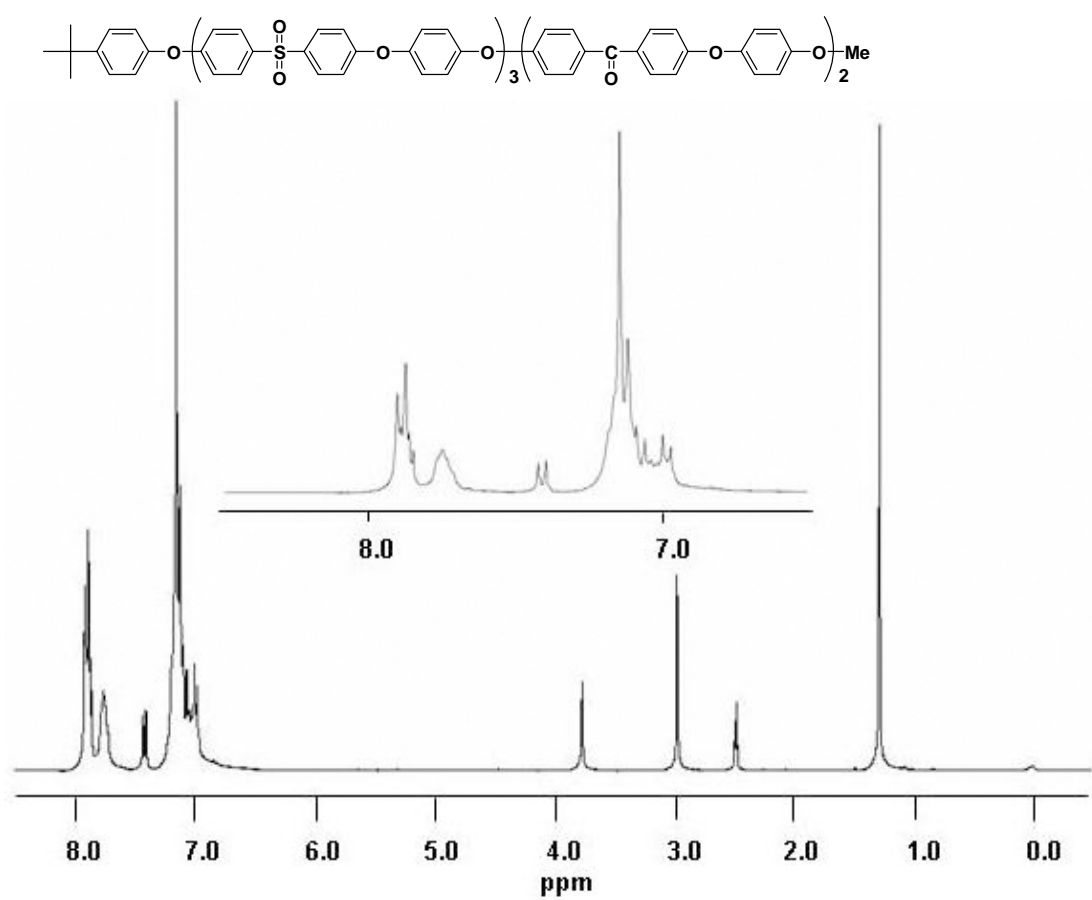
A round bottom flask was charged with a 1.30 g (3.0 mmol) sample of **21**, a 1.16 g (3.6 mmol) sample of **4**, 0.62 g (4.5 mmol) of potassium carbonate. To this mixture was added 2 mL of DMAc and the resulting solution was heated to 180 °C over the course of 4 hours under a nitrogen atmosphere. The reaction cooled down to room temperature and the product was filtered and washed with water and methanol. The filtered white solid was made to conduct a Soxhlet extraction with methanol to remove excess compound **4** and dried *in vacuo* at 80 °C for 3 hours (2.10 g, 2.8 mmol, 93%). m.p. (DSC) 213 °C. IR (KBr): 3059, 2960, 1644, 1597, 1507, 1463, 1312, 1247, 1162, 1149, 835, 765 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, r.t.): δ 7.82-7.72 (m, 8H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.04-6.91 (m, 18H), 3.81 (s, 3H), 1.32 (s, 9H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, r.t.): δ 162.8, 162.2, 161.65, 161.63, 156.8, 152.3, 151.8, 148.1, 147.9, 135.9, 135.7, 134.9, 134.7, 129.8, 129.73, 129.71, 129.65, 129.61, 126.9, 121.8, 121.7, 119.7, 117.5, 117.4, 116.8, 115.1, 55.5, 34.4, 31.3 ppm. MS (MALDI-ToF) *m/z* calcd for (C<sub>49</sub>H<sub>40</sub>O<sub>7</sub>) 740.8, found 741.5 [M]<sup>+</sup>, 763.8 [M + Na]<sup>+</sup>.



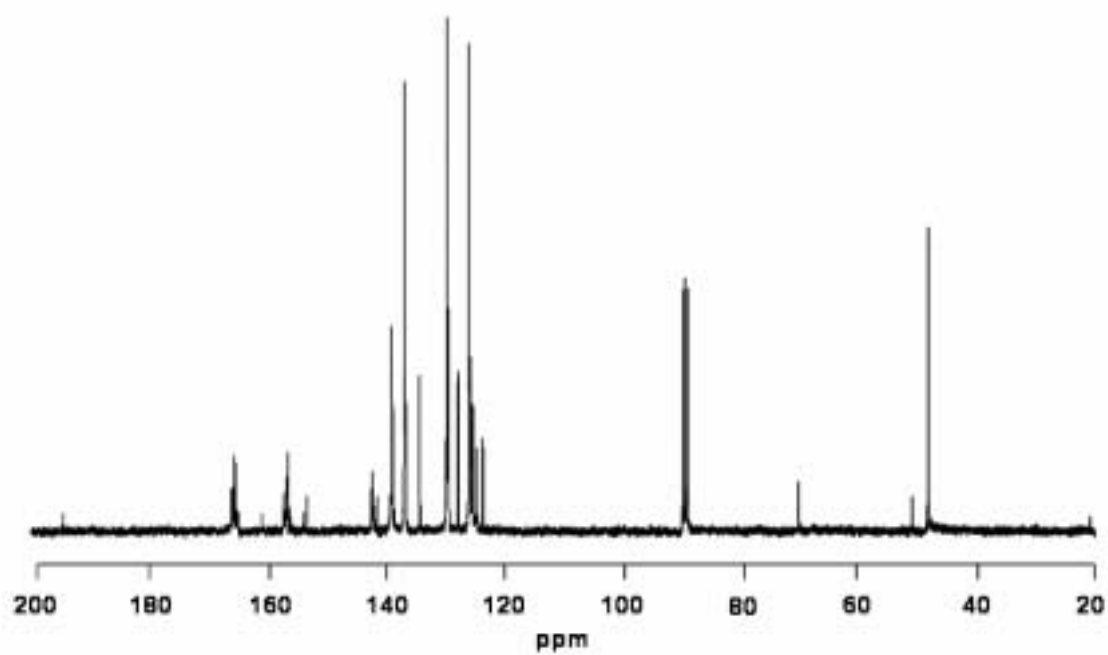
**S-Scheme 1.** Synthesis of Triblock OEK-*b*-OES-*b*-OEK **2**



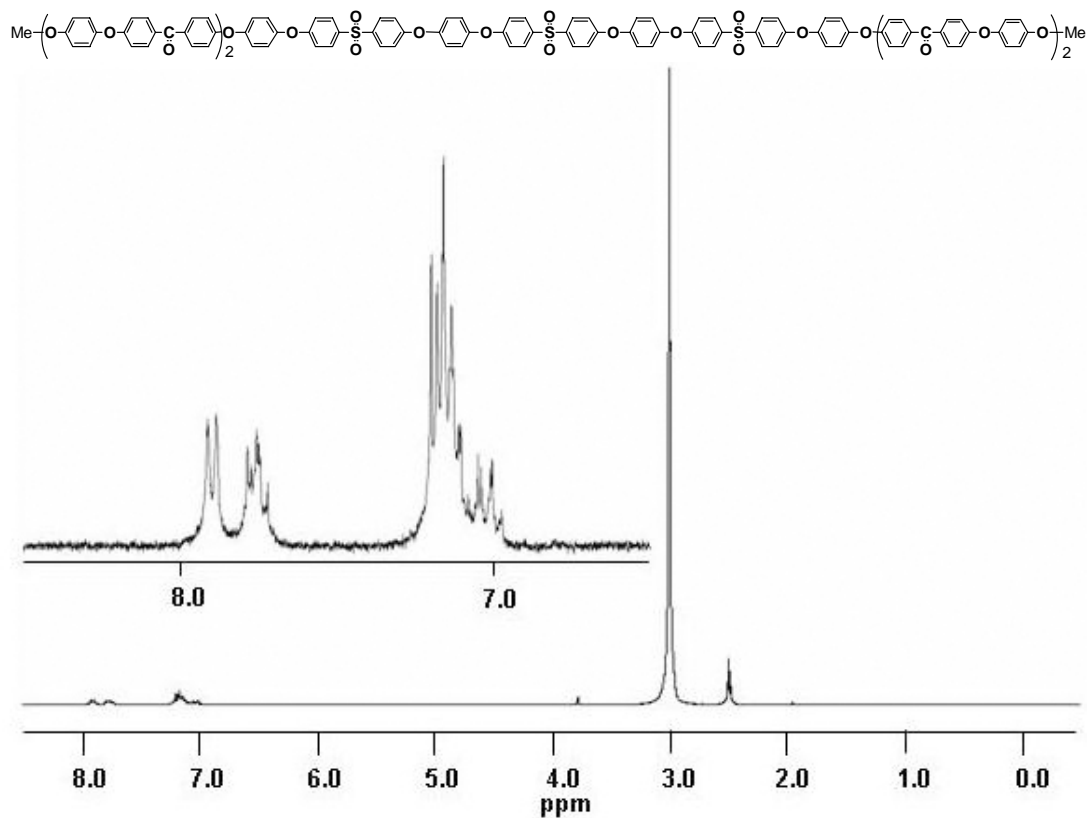
**S-Scheme 2.** Synthesis of OEK Dimer



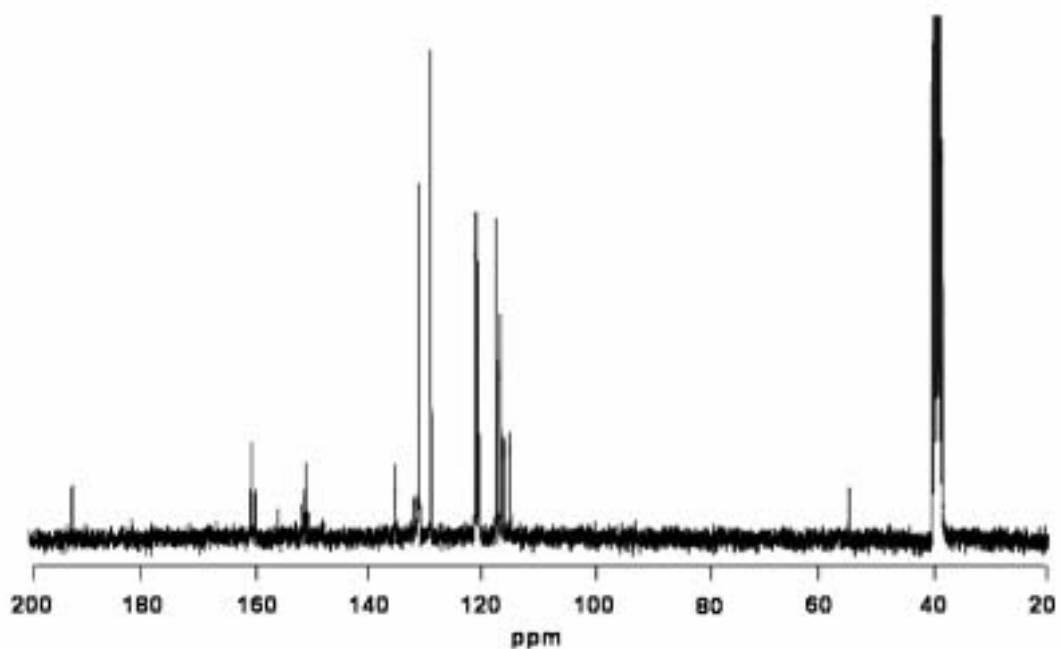
**S-Figure 1.**  $^1\text{H}$ -NMR spectrum of diblock OES-*b*-OEK **1** in  $\text{DMSO-}d_6$  r.t..



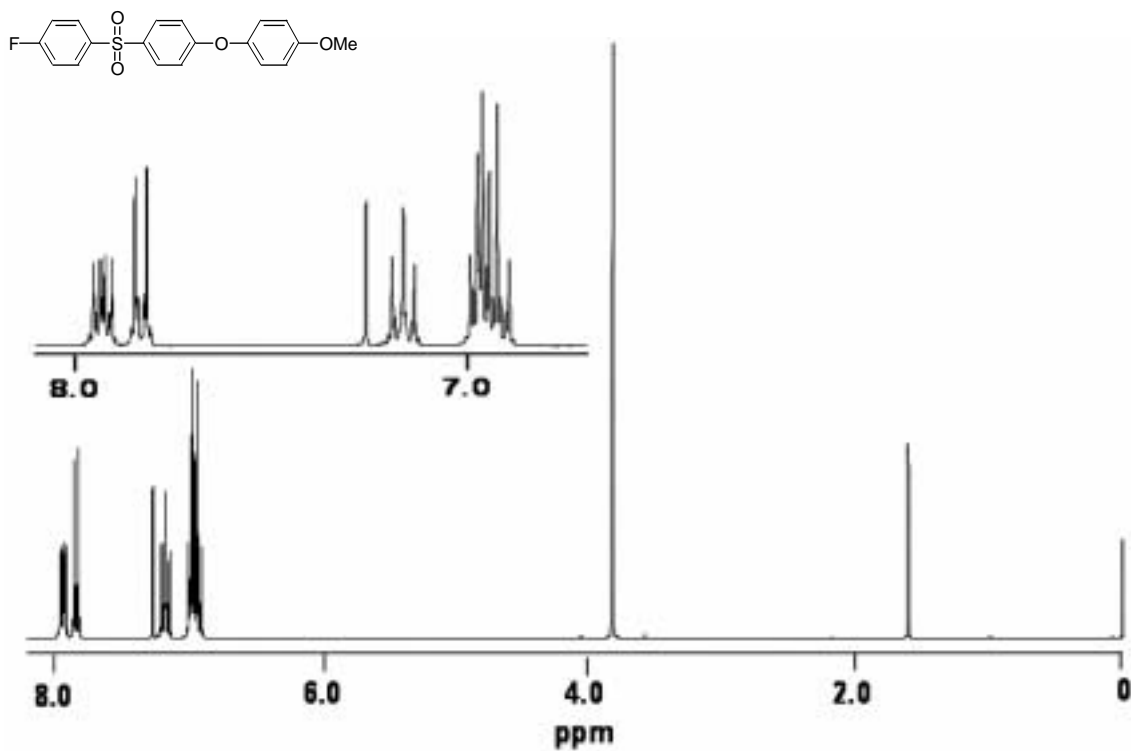
**S-Figure 2.**  $^{13}\text{C}$ -NMR spectrum of diblock OES-*b*-OEK **1** in  $\text{CDCl}_3$  r.t..



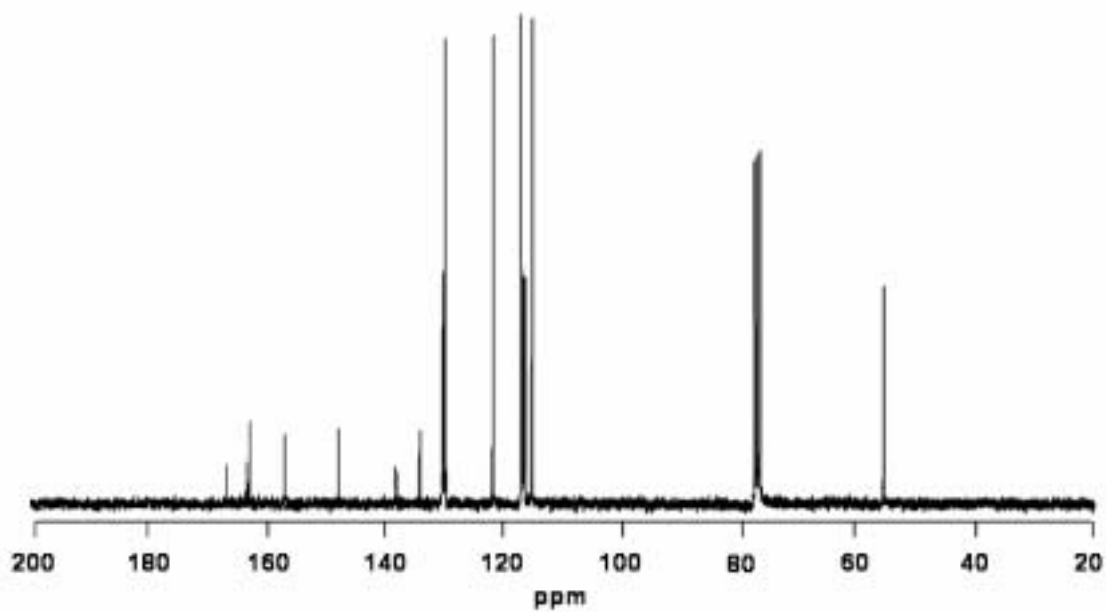
**S-Figure 3.** <sup>1</sup>H-NMR spectrum of triblock OEK-*b*-OES-*b*-OEK **2** in DMSO-*d*<sub>6</sub> at 100 °C.



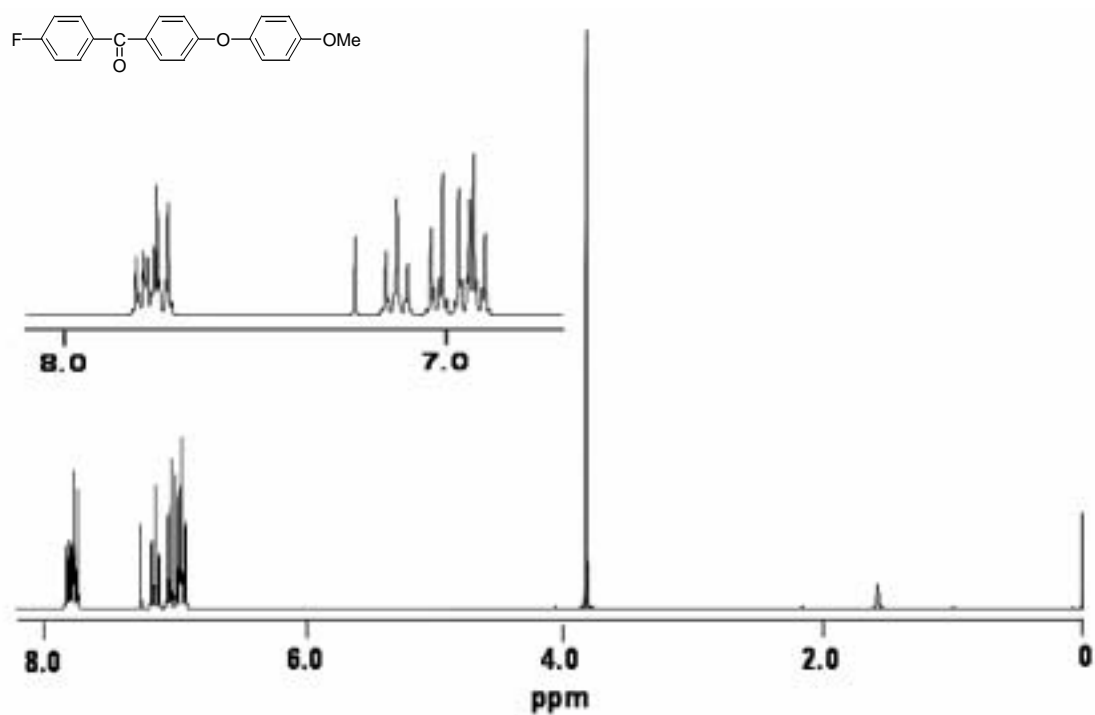
**S-Figure 4.** <sup>13</sup>C-NMR spectrum of triblock OEK-*b*-OES-*b*-OEK **2** in DMSO-*d*<sub>6</sub> at 130 °C.



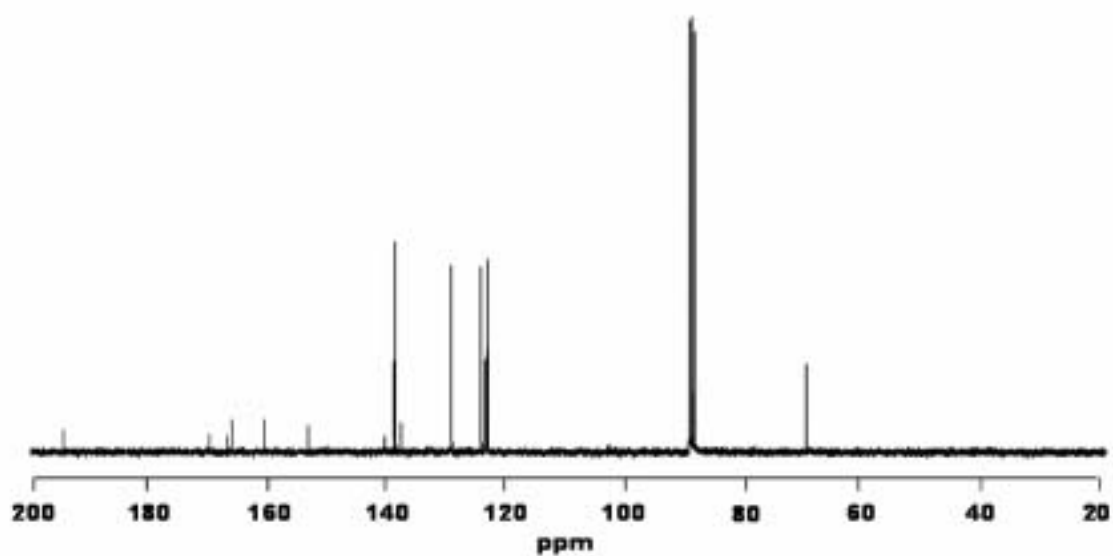
**S-Figure 5.** <sup>1</sup>H-NMR spectrum of **3** in CDCl<sub>3</sub> r.t..



**S-Figure 6.** <sup>13</sup>C-NMR spectrum of **3** in CDCl<sub>3</sub> r.t..

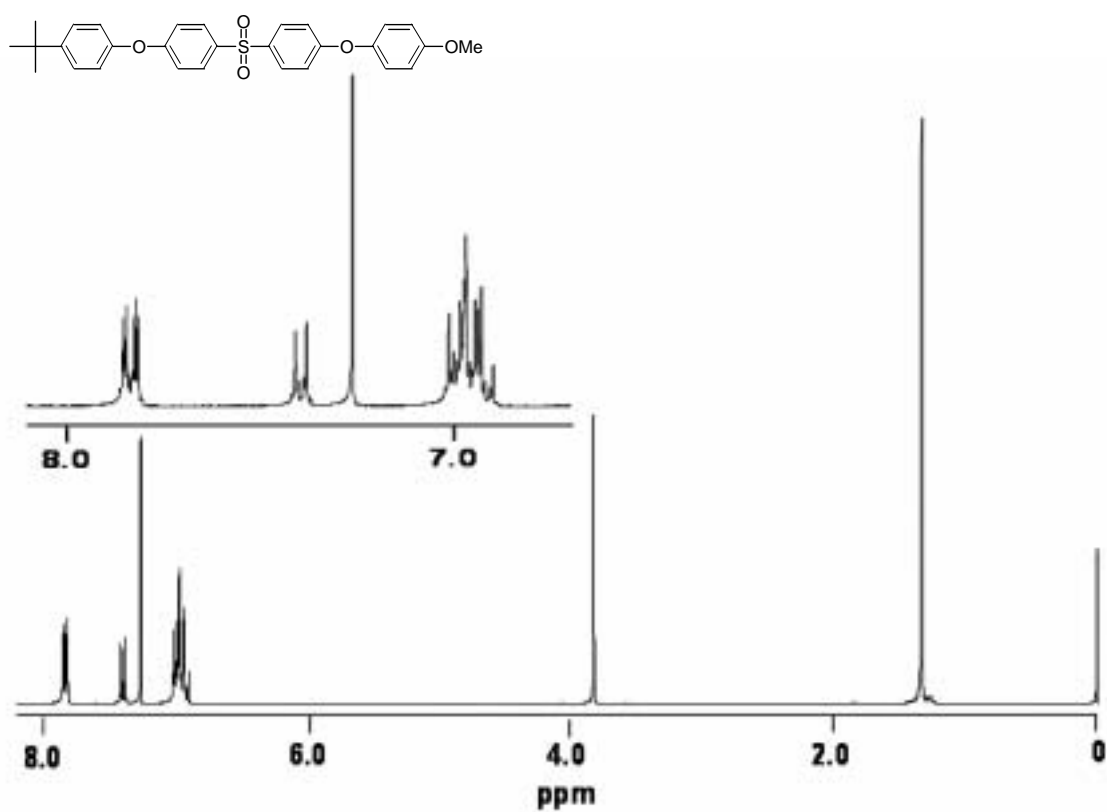


**S-Figure 7.** <sup>1</sup>H-NMR spectrum of **4** in CDCl<sub>3</sub> r.t..

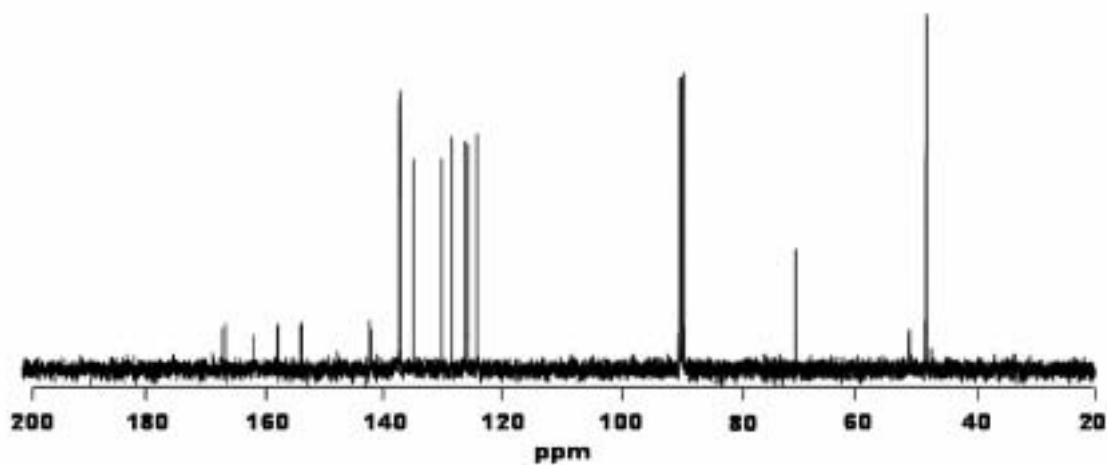


**S-Figure 8.** <sup>13</sup>C-NMR spectrum of **4** in CDCl<sub>3</sub> r.t..

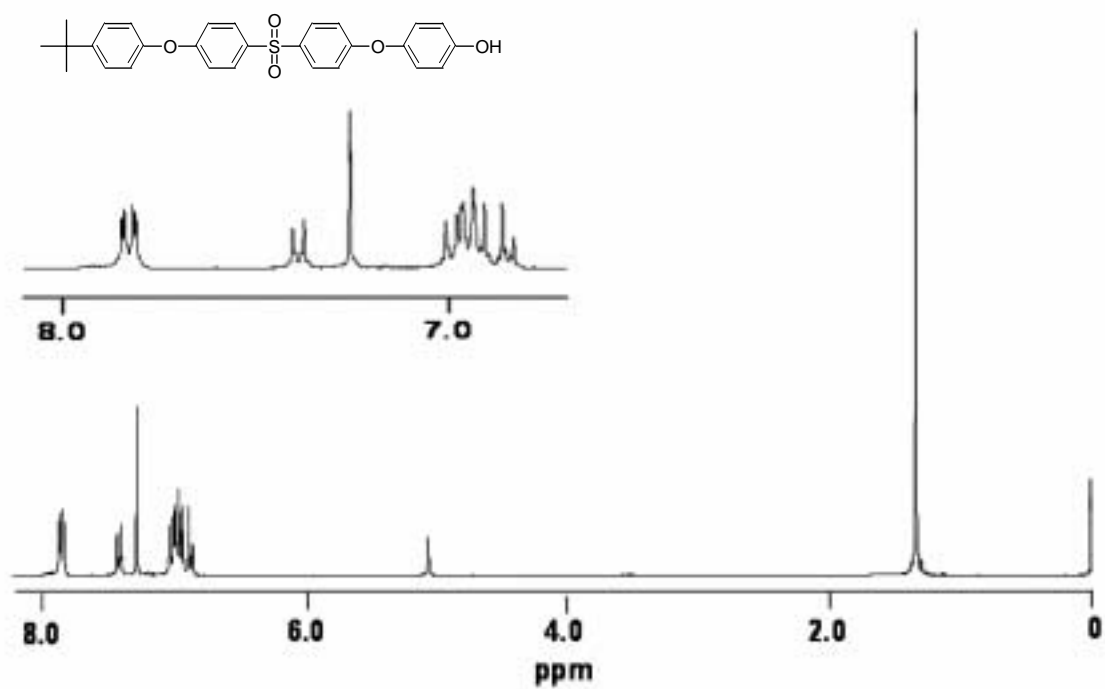




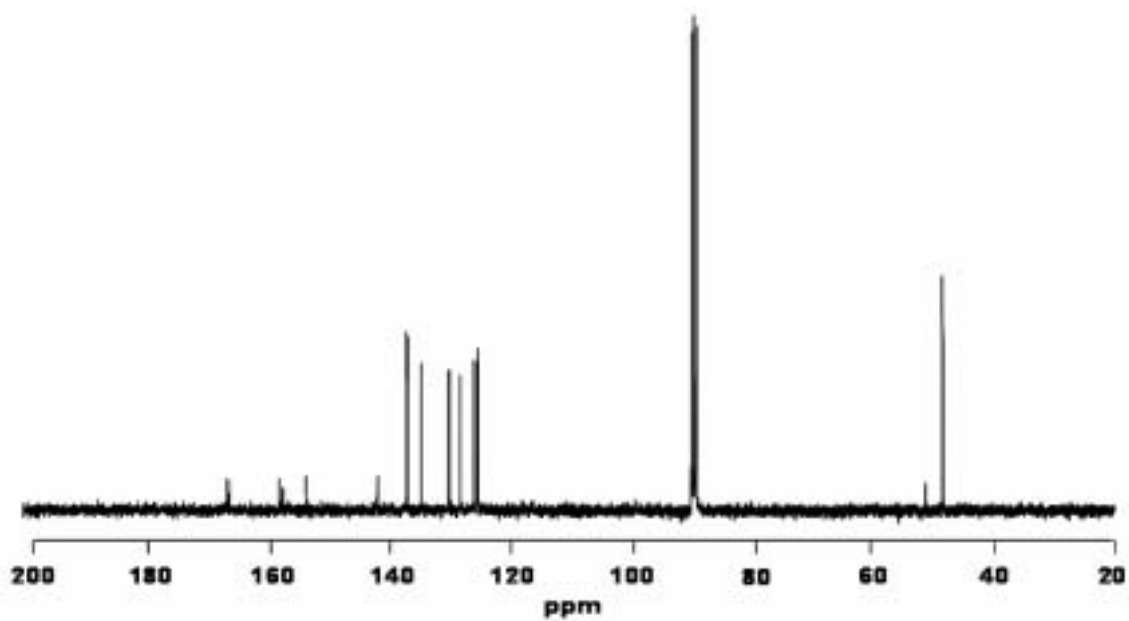
**S-Figure 9.** <sup>1</sup>H-NMR spectrum of **5** in CDCl<sub>3</sub> r.t..



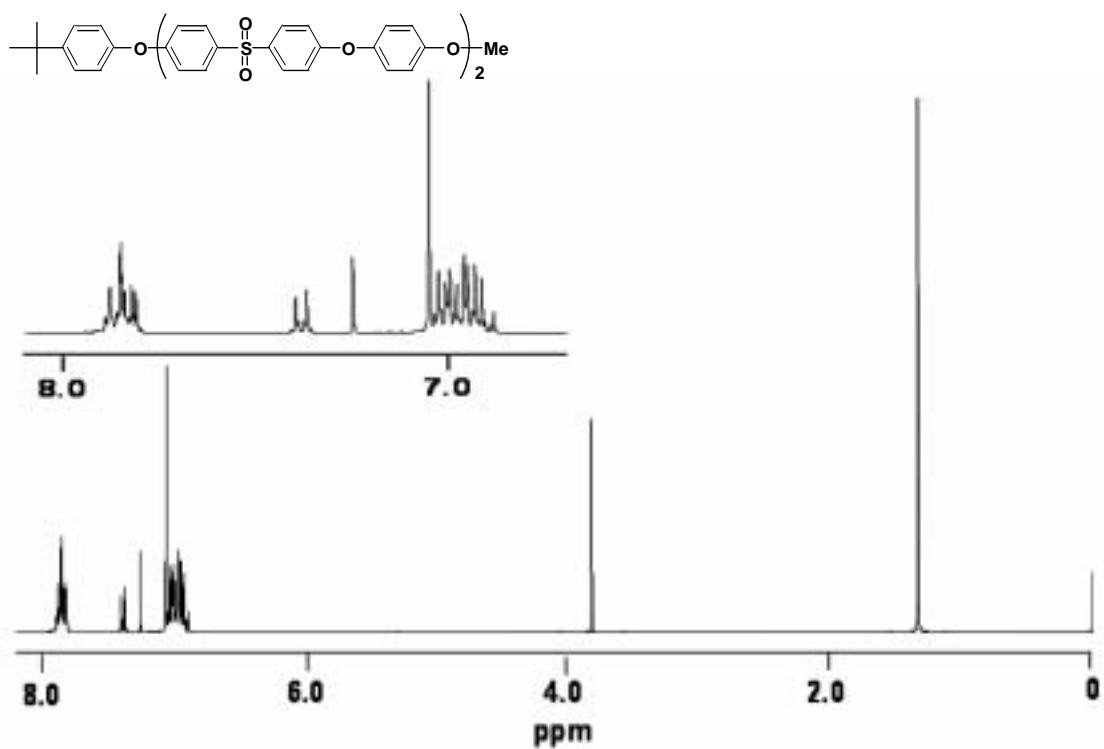
**S-Figure 10.** <sup>13</sup>C-NMR spectrum of **5** in CDCl<sub>3</sub> r.t..



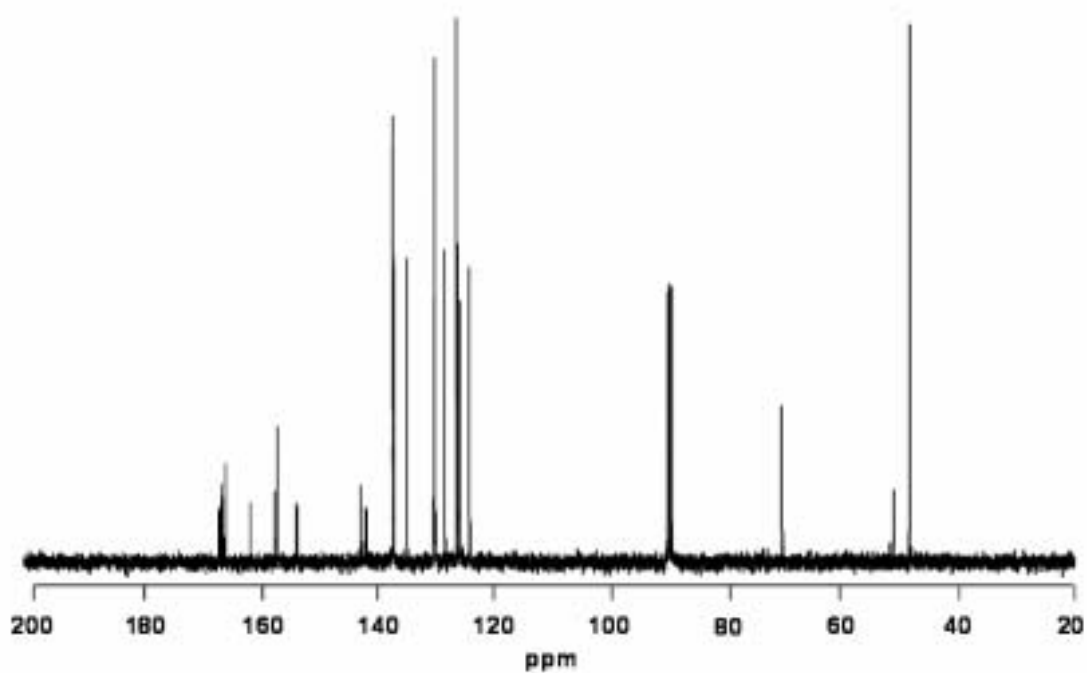
**S-Figure 11.**  $^1\text{H}$ -NMR spectrum of **6** in  $\text{CDCl}_3$  r.t..



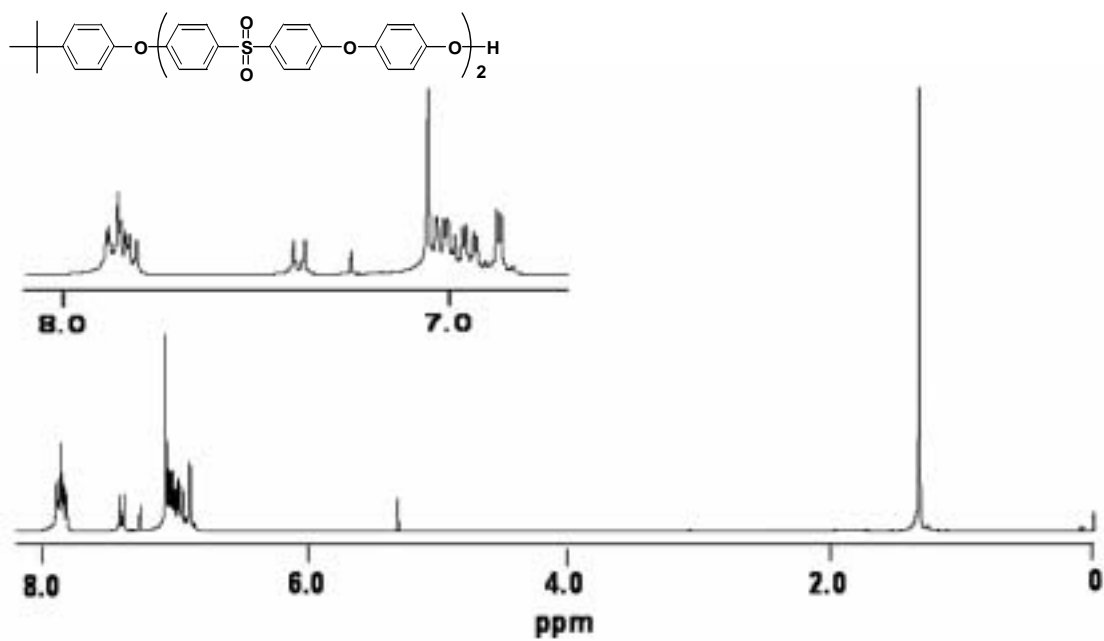
**S-Figure 12.**  $^{13}\text{C}$ -NMR spectrum of **6** in  $\text{CDCl}_3$  r.t..



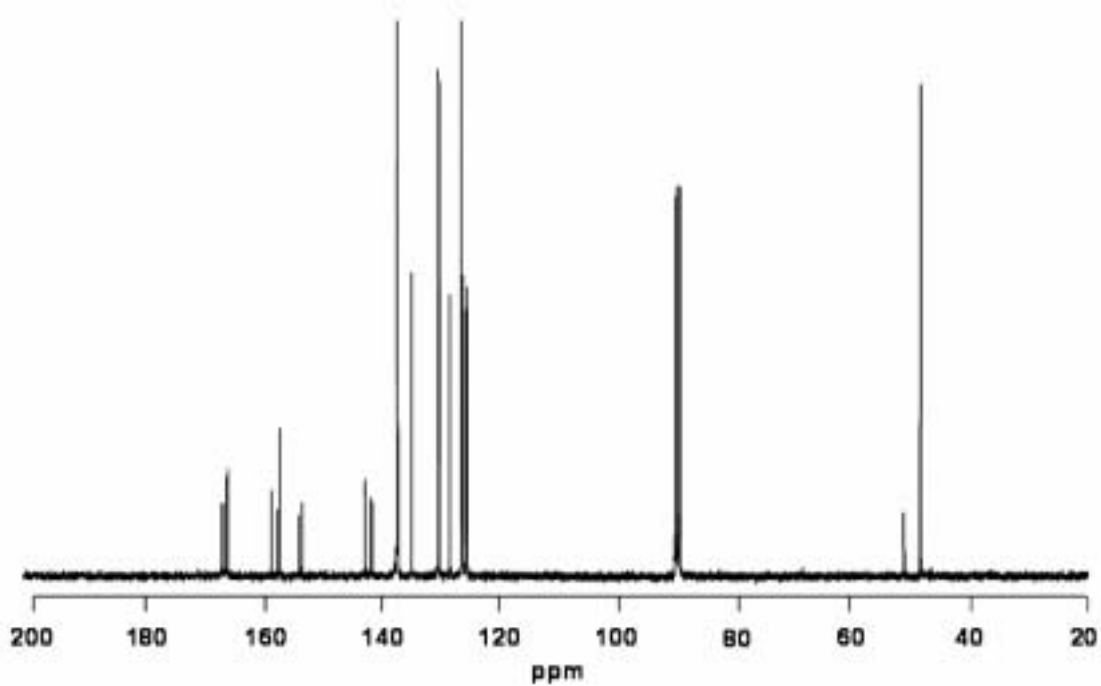
**S-Figure 13.** <sup>1</sup>H-NMR spectrum of **7** in CDCl<sub>3</sub> r.t..



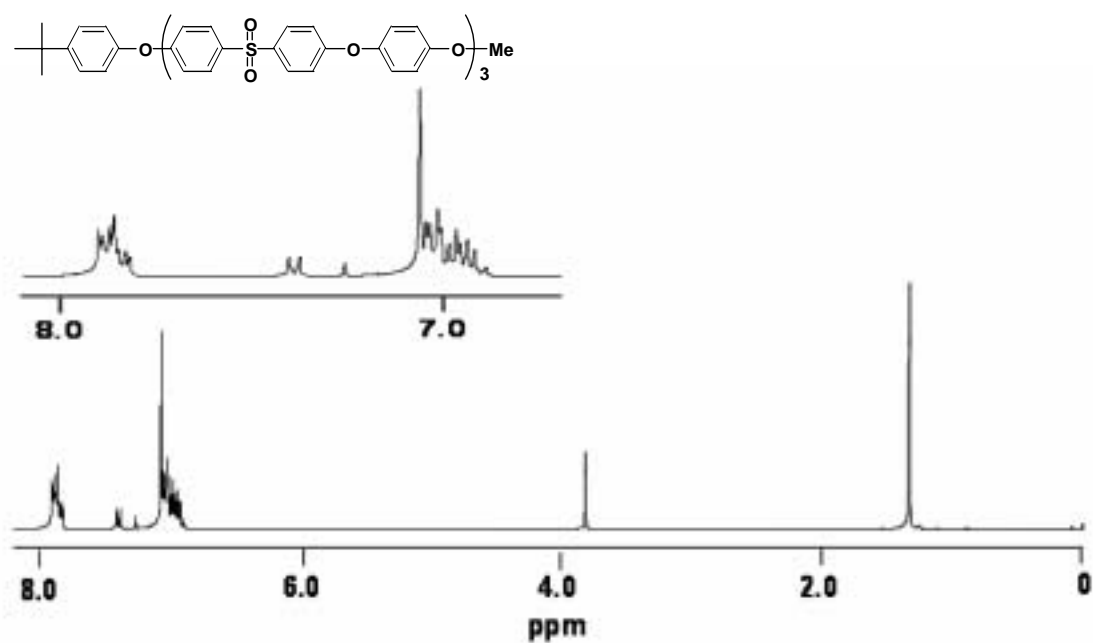
**S-Figure 14.** <sup>13</sup>C-NMR spectrum of **7** in CDCl<sub>3</sub> r.t..



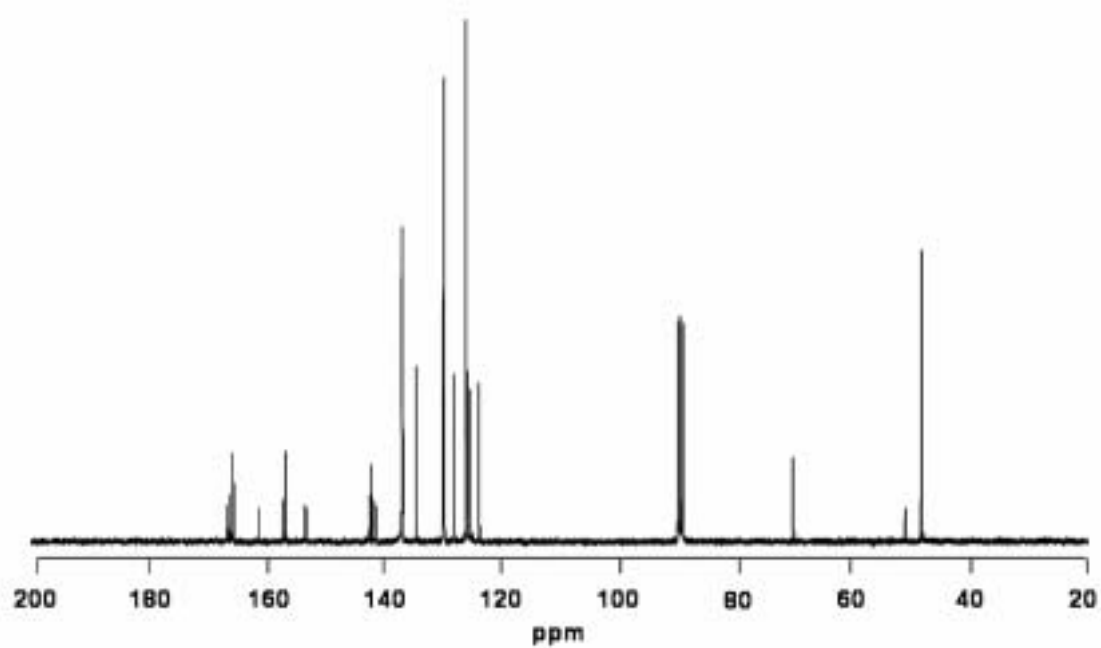
**S-Figure 15.** <sup>1</sup>H-NMR spectrum of **8** in CDCl<sub>3</sub> r.t..



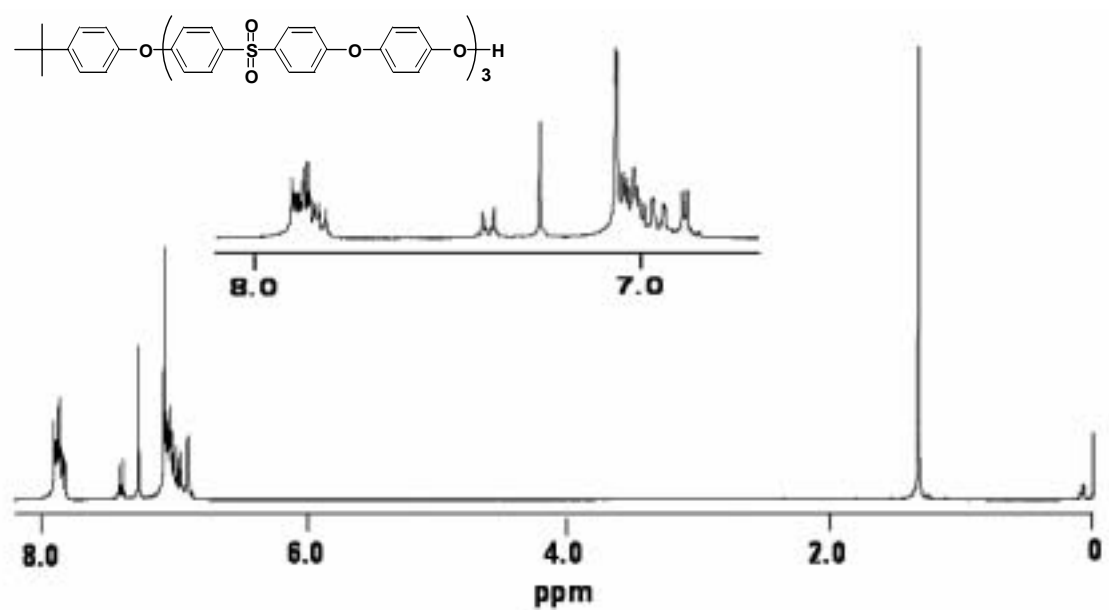
**S-Figure 16.** <sup>13</sup>C-NMR spectrum of **8** in CDCl<sub>3</sub> r.t..



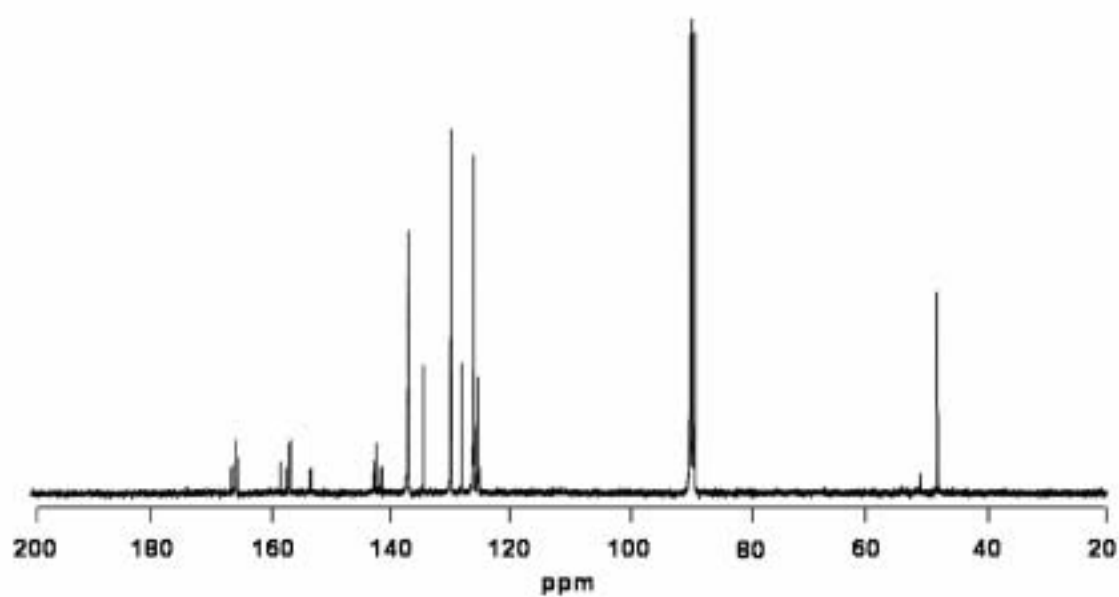
**S-Figure 17.** <sup>1</sup>H-NMR spectrum of **9** in CDCl<sub>3</sub> r.t..



**S-Figure 18.** <sup>13</sup>C-NMR spectrum of **9** in CDCl<sub>3</sub> r.t..

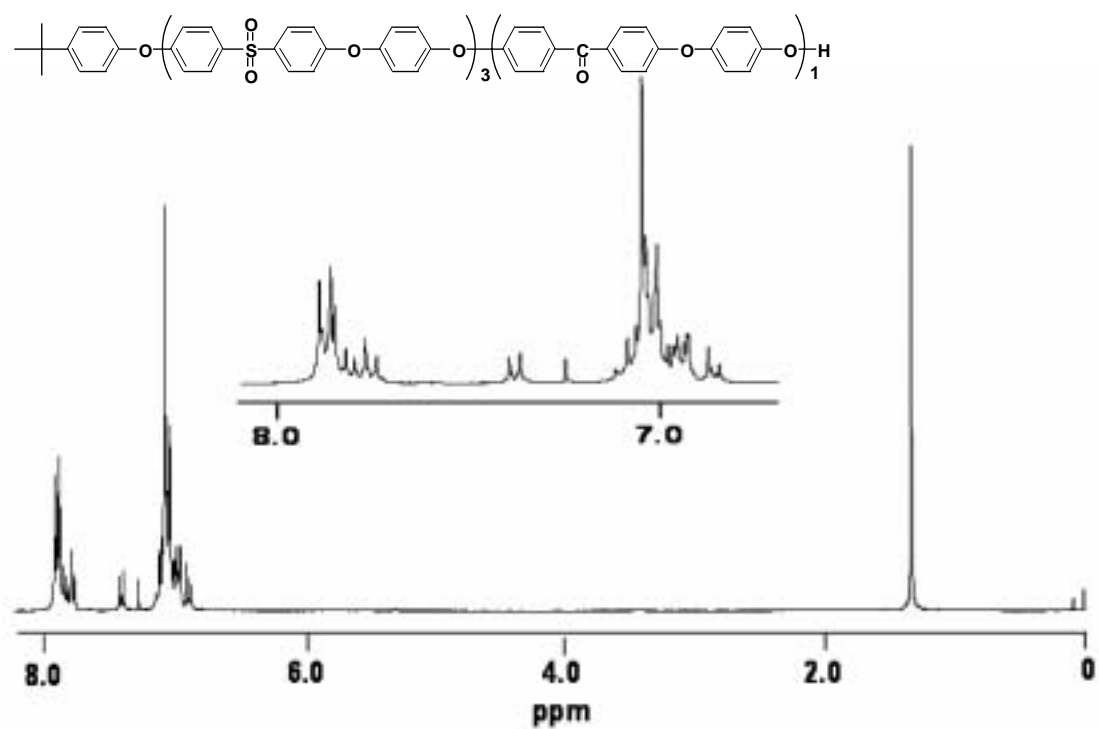


**S-Figure 19.** <sup>1</sup>H-NMR spectrum of **10** in CDCl<sub>3</sub> r.t..

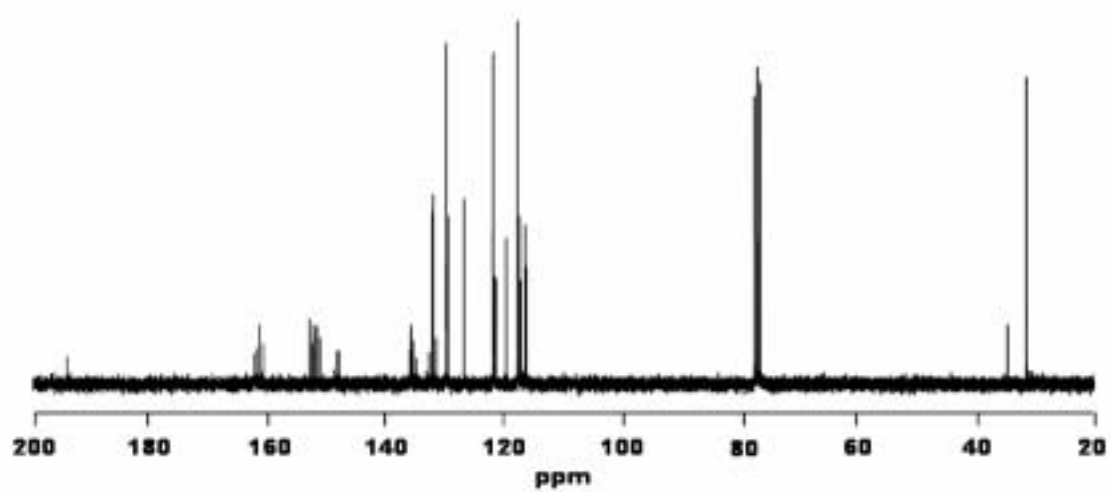


**S-Figure 20.** <sup>13</sup>C-NMR spectrum of **10** in CDCl<sub>3</sub> r.t..



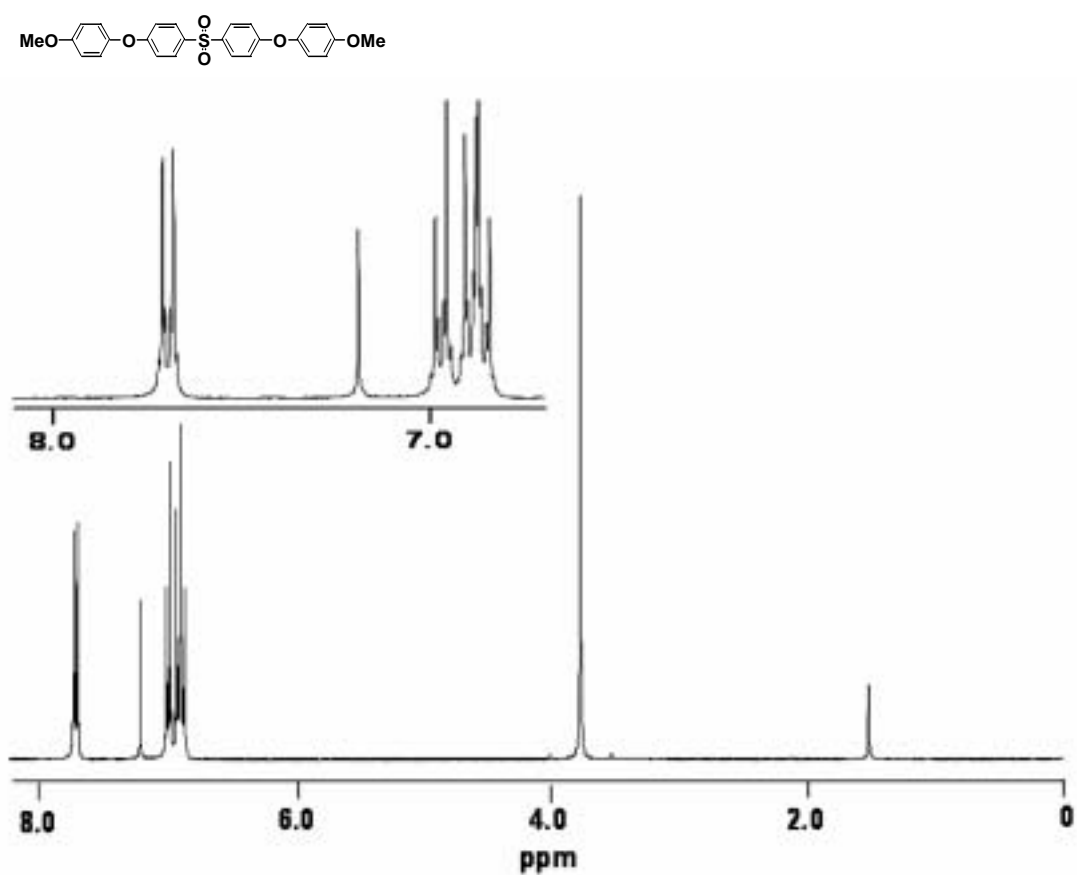


**S-Figure 23.**  $^1\text{H-NMR}$  spectrum of **12** in  $\text{CDCl}_3$  r.t..

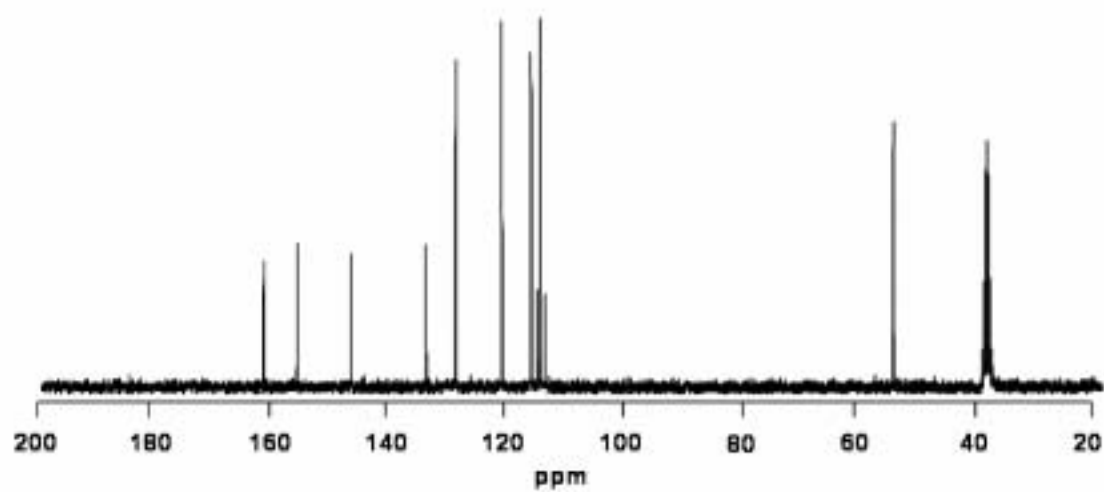


**S-Figure 24.**  $^{13}\text{C-NMR}$  spectrum of **12** in  $\text{CDCl}_3$  r.t..

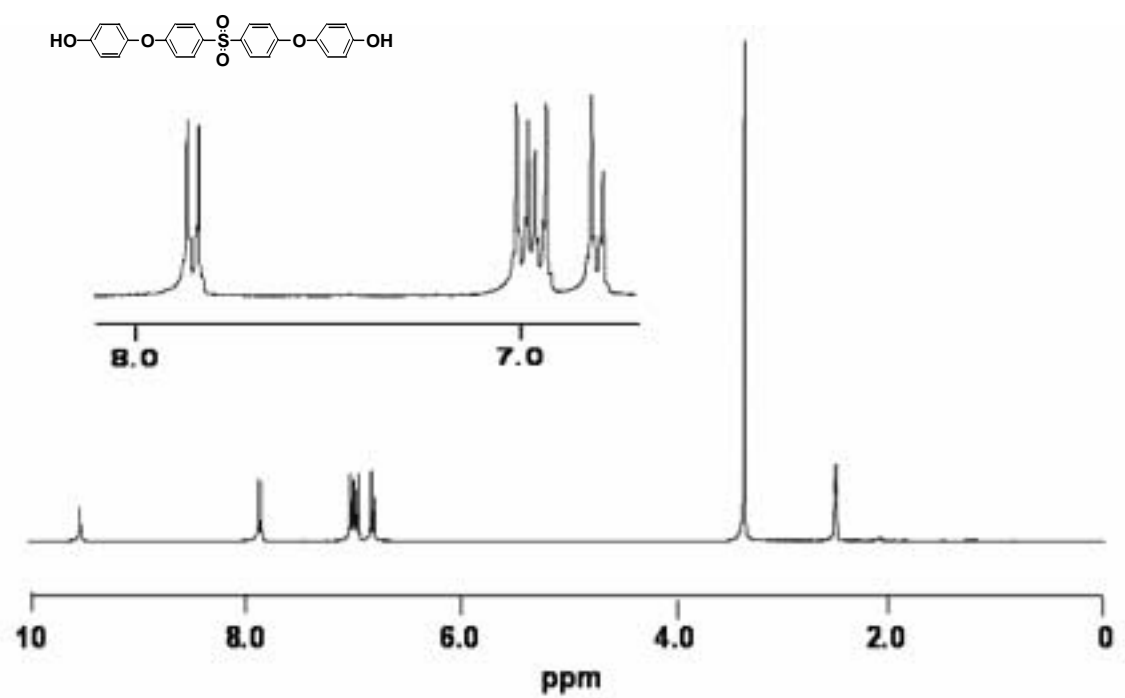




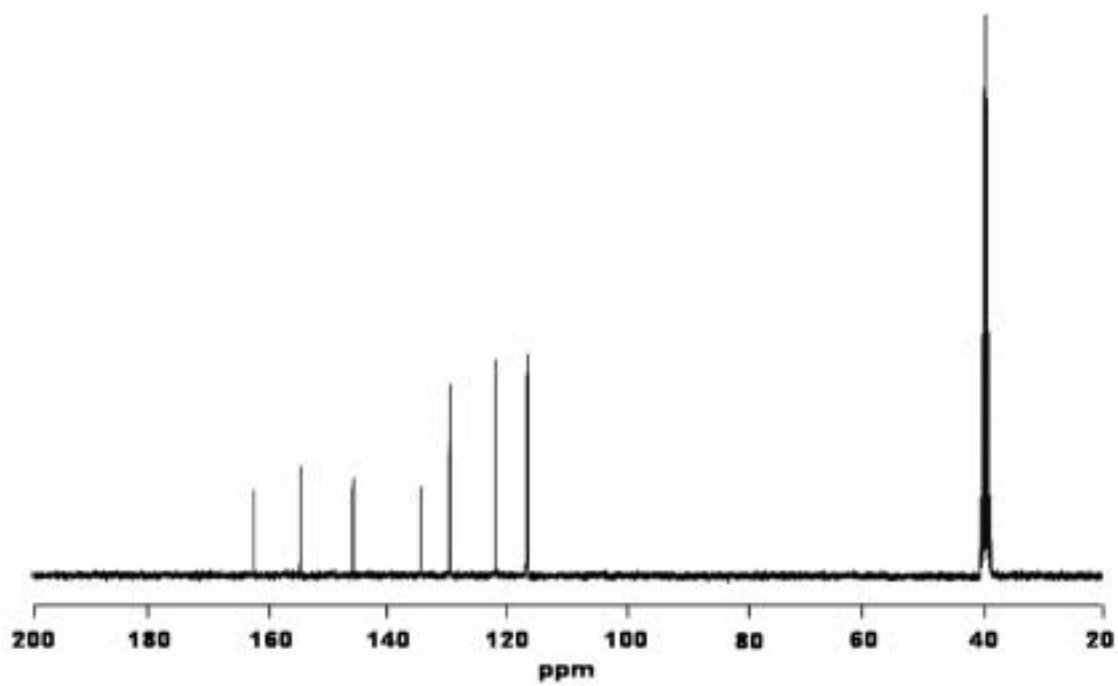
**S-Figure 25.** <sup>1</sup>H-NMR spectrum of **18** in CDCl<sub>3</sub> r.t..



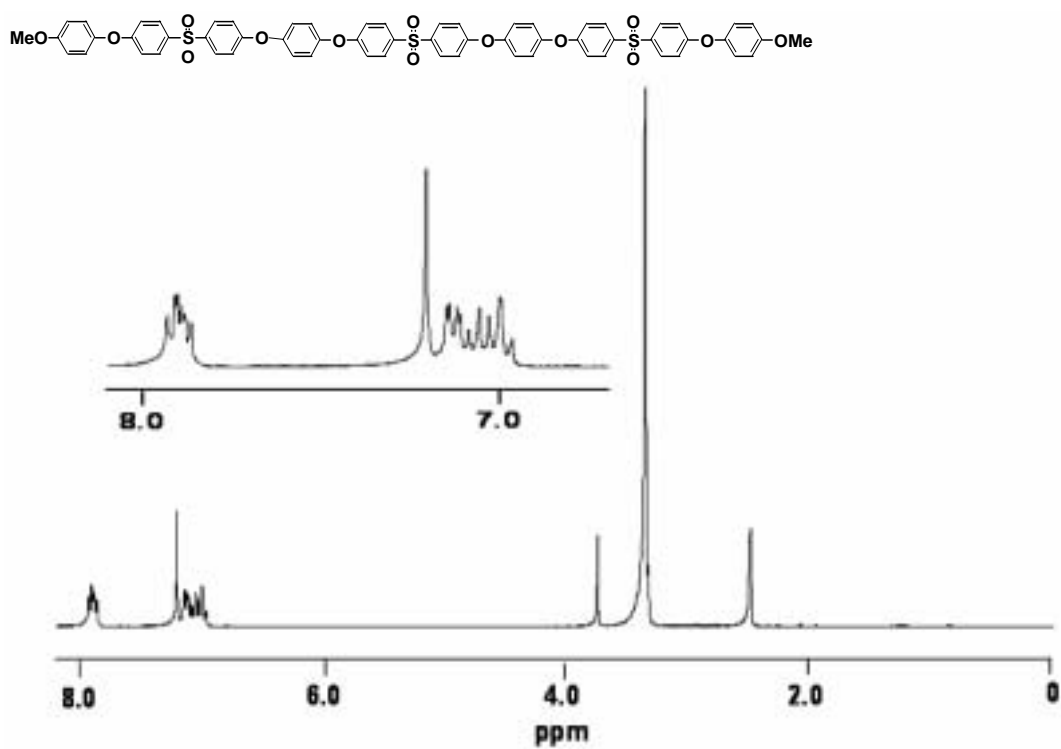
**S-Figure 26.** <sup>13</sup>C-NMR spectrum of **18** in DMSO-*d*<sub>6</sub> r.t..



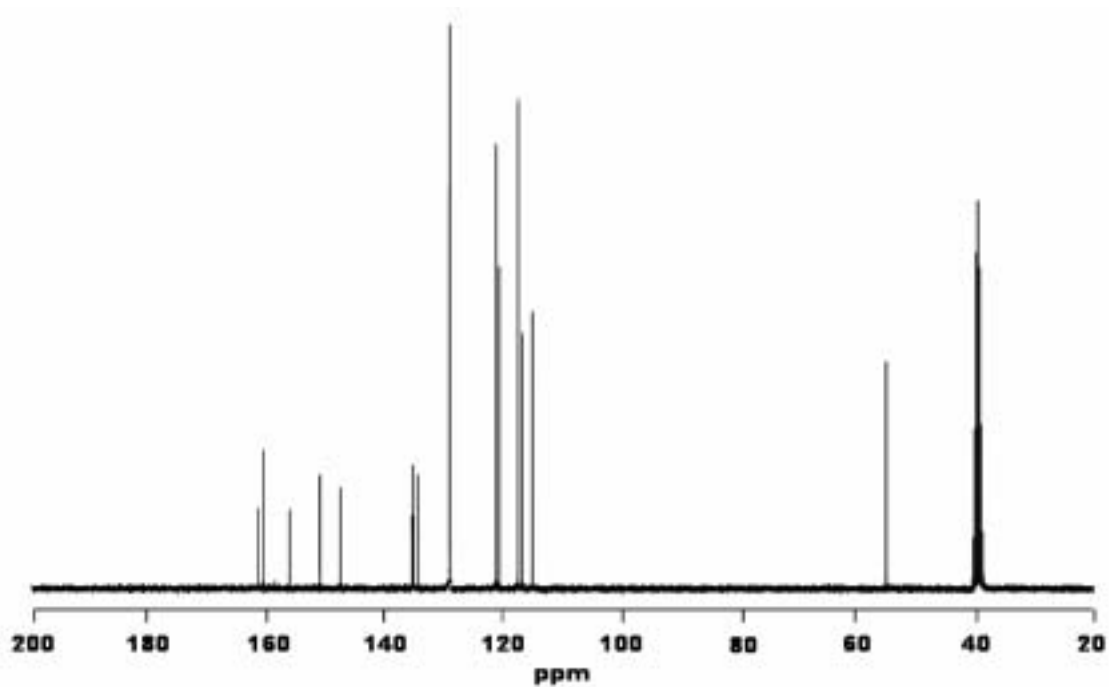
**S-Figure 27.**  $^1\text{H}$ -NMR spectrum of **13** in  $\text{DMSO-}d_6$  r.t..



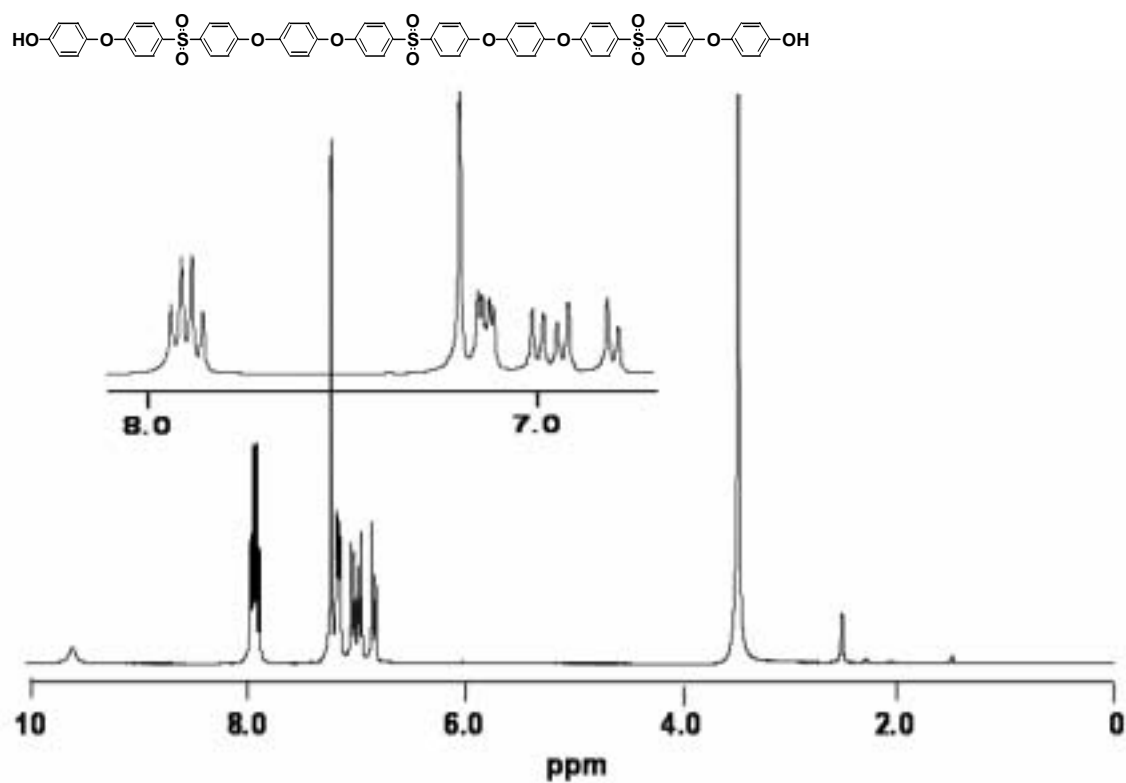
**S-Figure 28.**  $^{13}\text{C}$ -NMR spectrum of **13** in  $\text{DMSO-}d_6$  r.t..



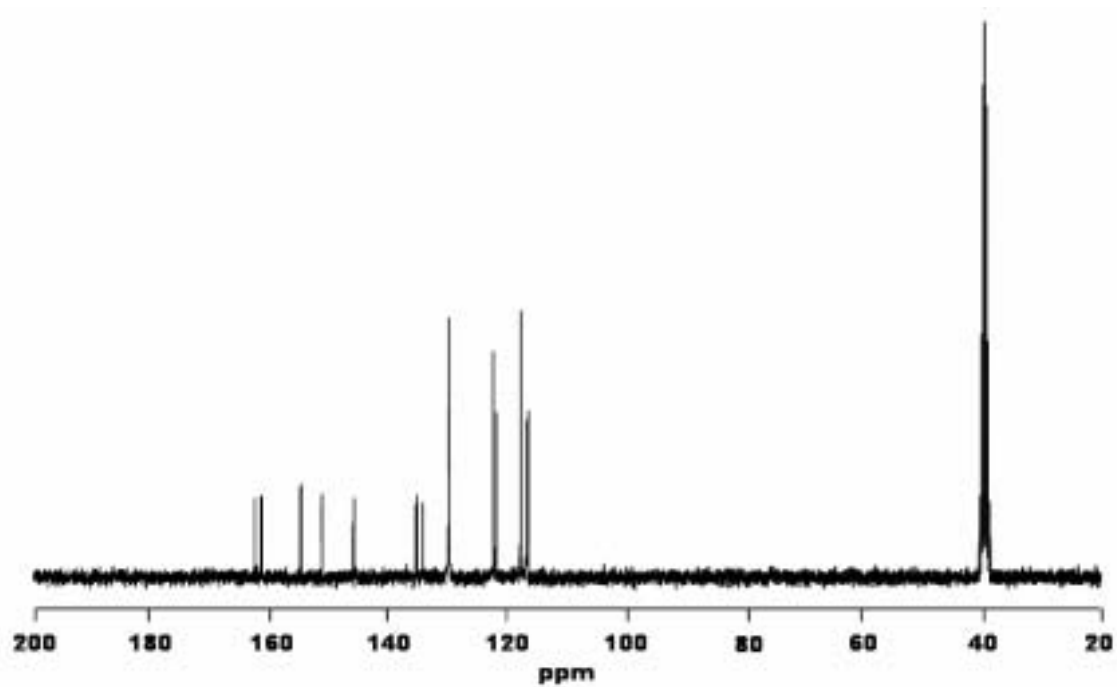
**S-Figure 29.**  $^1\text{H}$ -NMR spectrum of **14** in  $\text{DMSO}-d_6$  r.t..



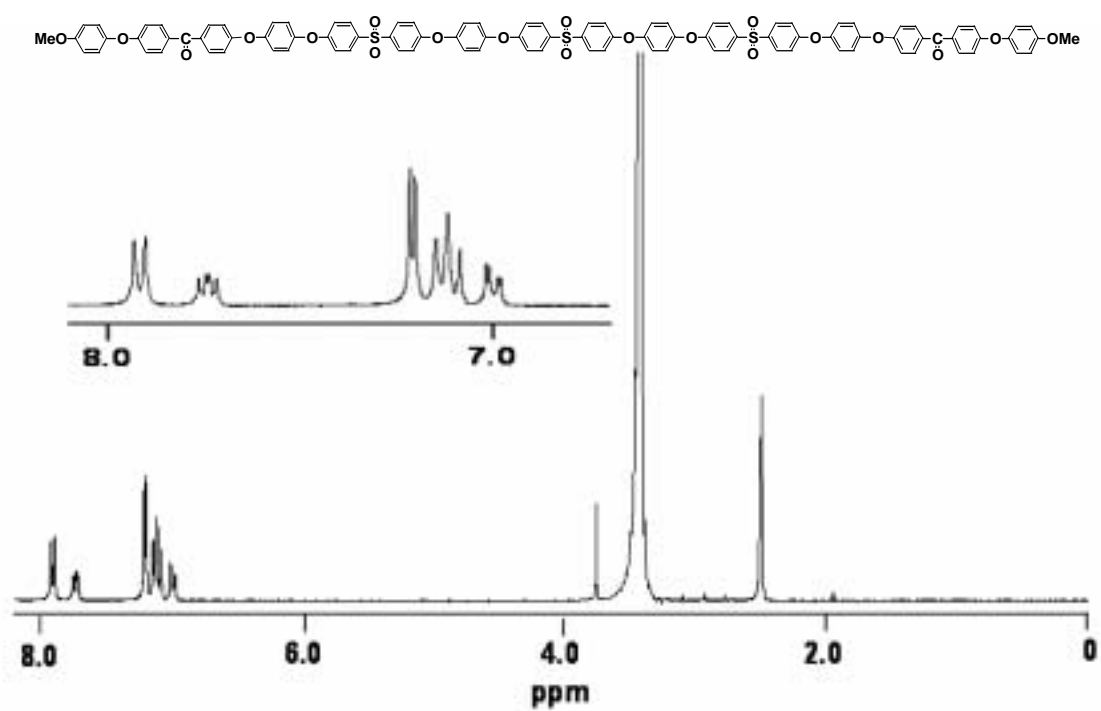
**S-Figure 30.**  $^{13}\text{C}$ -NMR spectrum of **14** in  $\text{DMSO}-d_6$  at  $120\text{ }^\circ\text{C}$ .



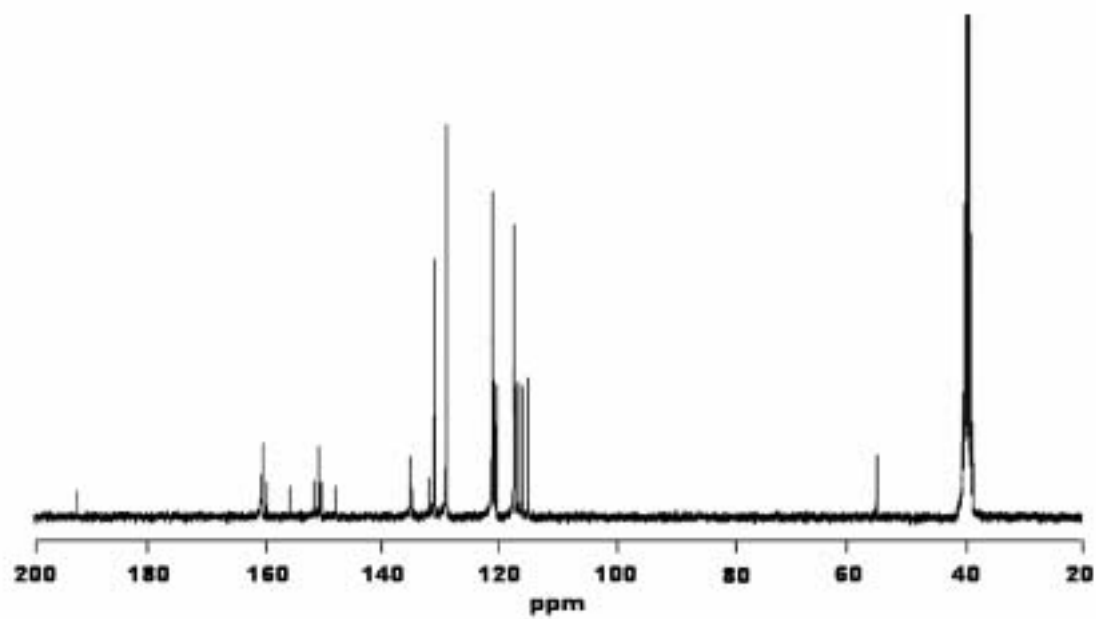
**S-Figure 31.**  $^1\text{H}$ -NMR spectrum of **15** in  $\text{DMSO-}d_6$  r.t..



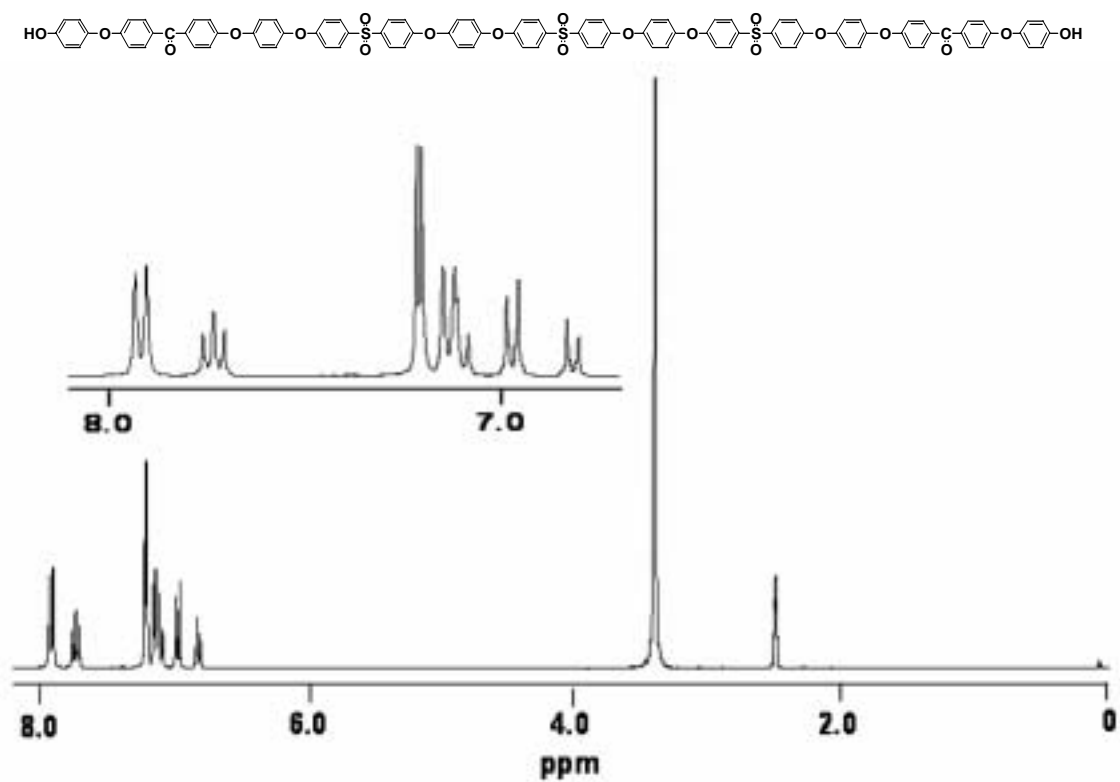
**S-Figure 32.**  $^{13}\text{C}$ -NMR spectrum of **15** in  $\text{DMSO-}d_6$  r.t..



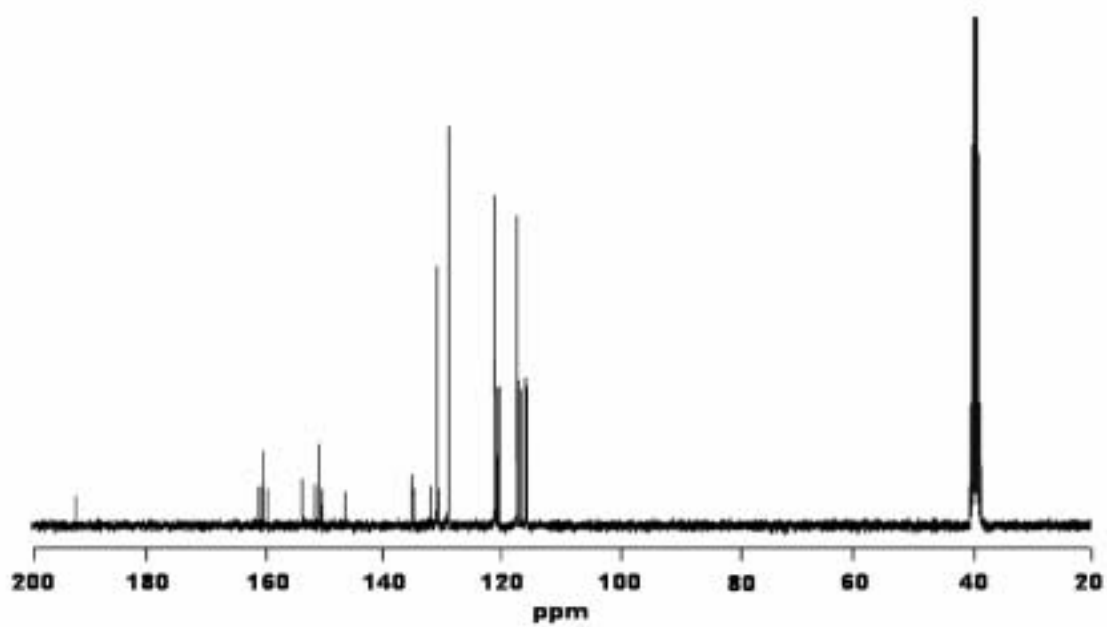
**S-Figure 33.**  $^1\text{H}$ -NMR spectrum of **16** in  $\text{DMSO-}d_6$  r.t..



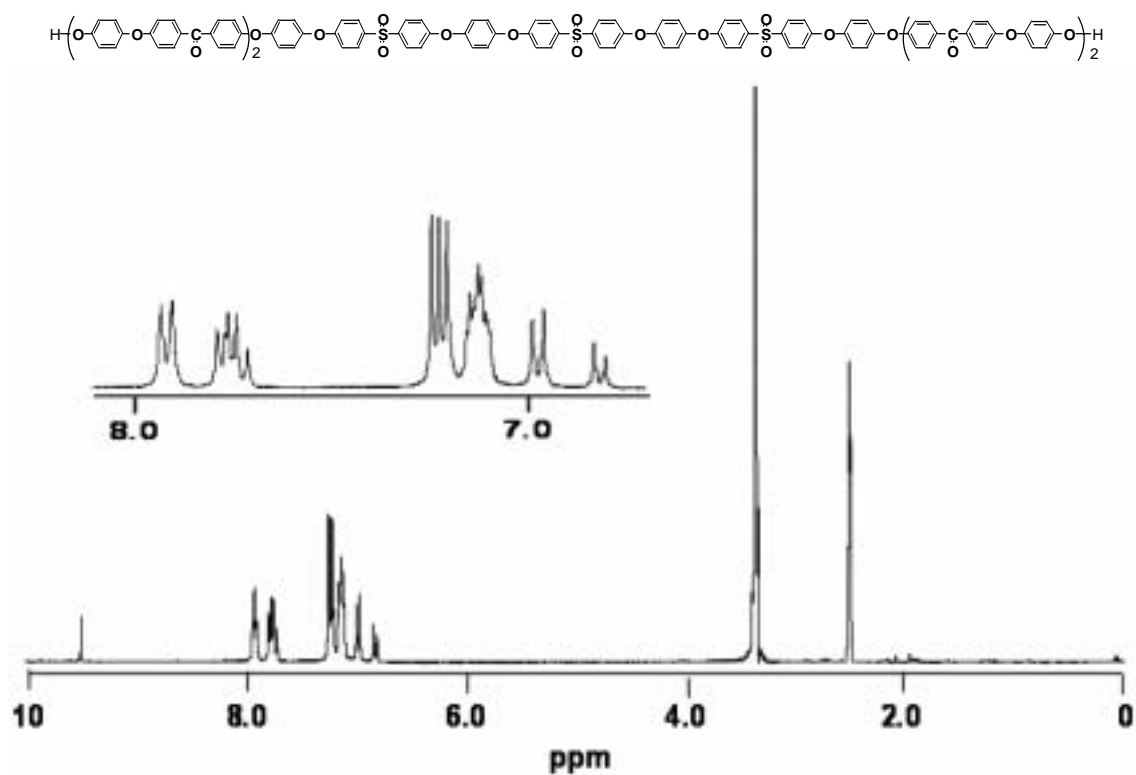
**S-Figure 34.**  $^{13}\text{C}$ -NMR spectrum of **16** in  $\text{DMSO-}d_6$  at  $120\text{ }^\circ\text{C}$ .



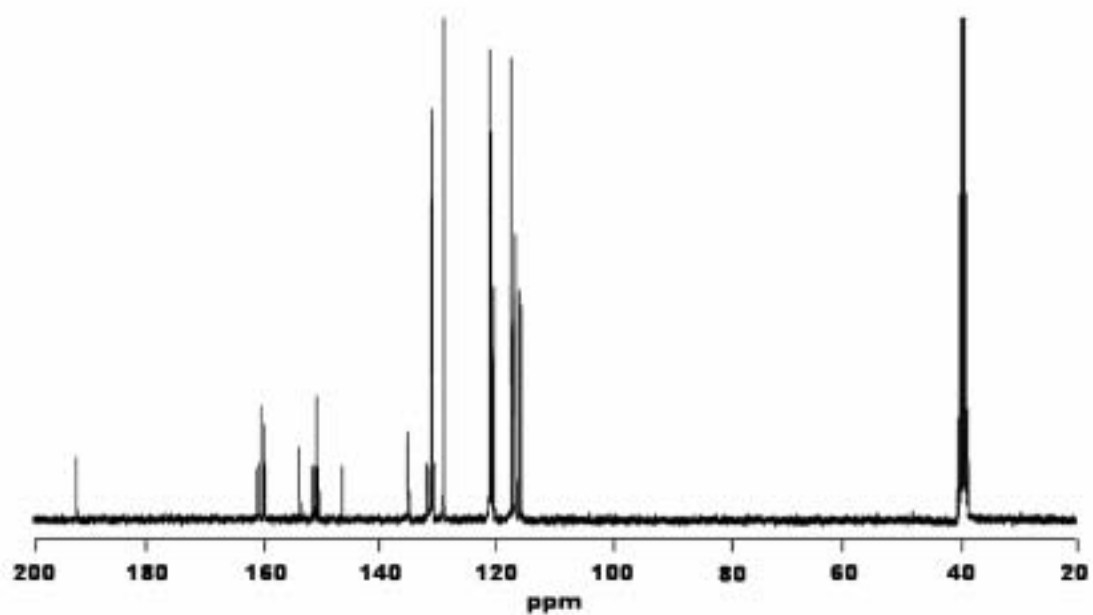
**S-Figure 35.**  $^1\text{H}$ -NMR spectrum of **17** in  $\text{DMSO-}d_6$  r.t..



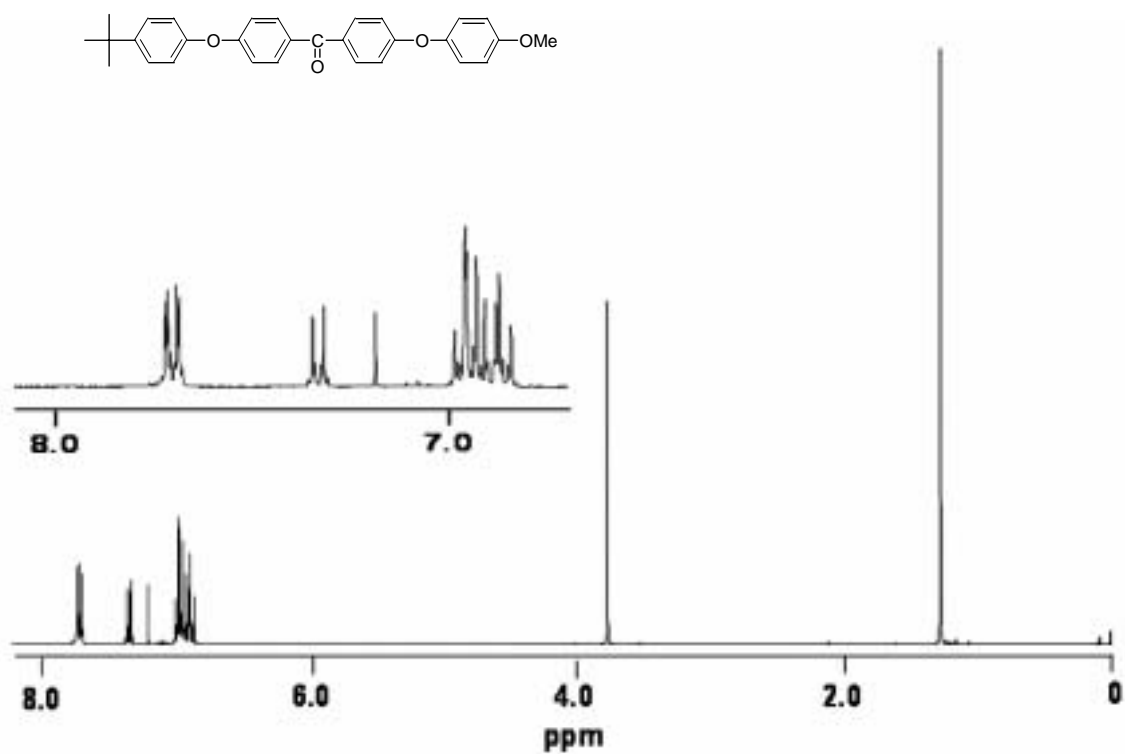
**S-Figure 36.**  $^{13}\text{C}$ -NMR spectrum of **17** in  $\text{DMSO-}d_6$  at  $120\text{ }^\circ\text{C}$ .



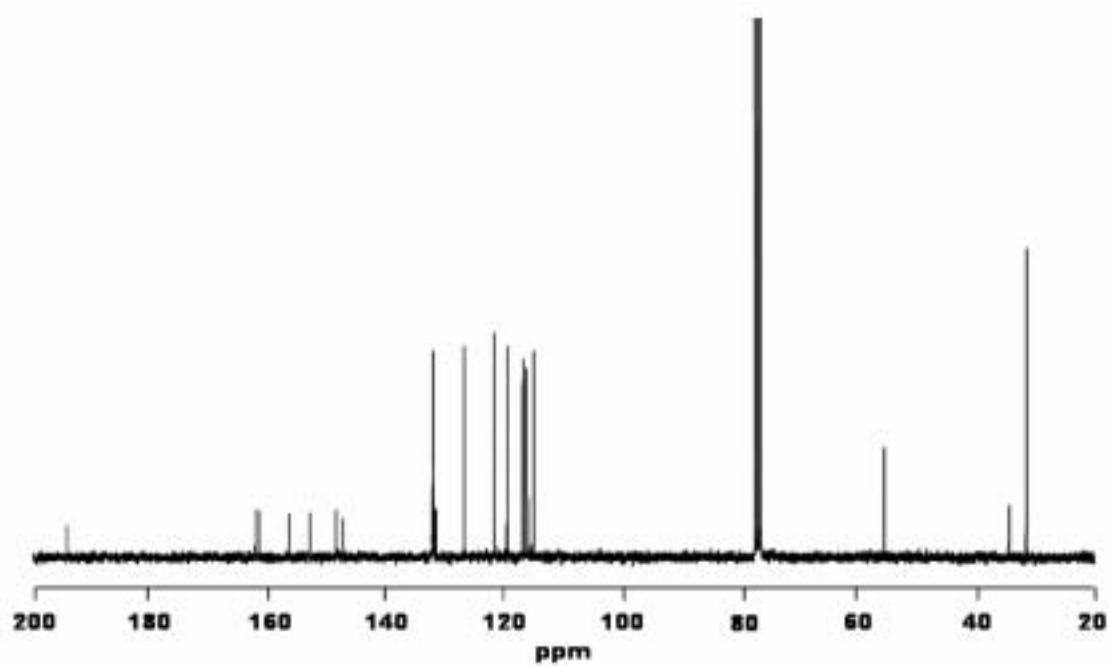
**S-Figure 37.**  $^1\text{H}$ -NMR spectrum of **19** in  $\text{DMSO}-d_6$  r.t..



**S-Figure 38.**  $^{13}\text{C}$ -NMR spectrum of **19** in  $\text{DMSO}-d_6$  at  $120\text{ }^\circ\text{C}$ .

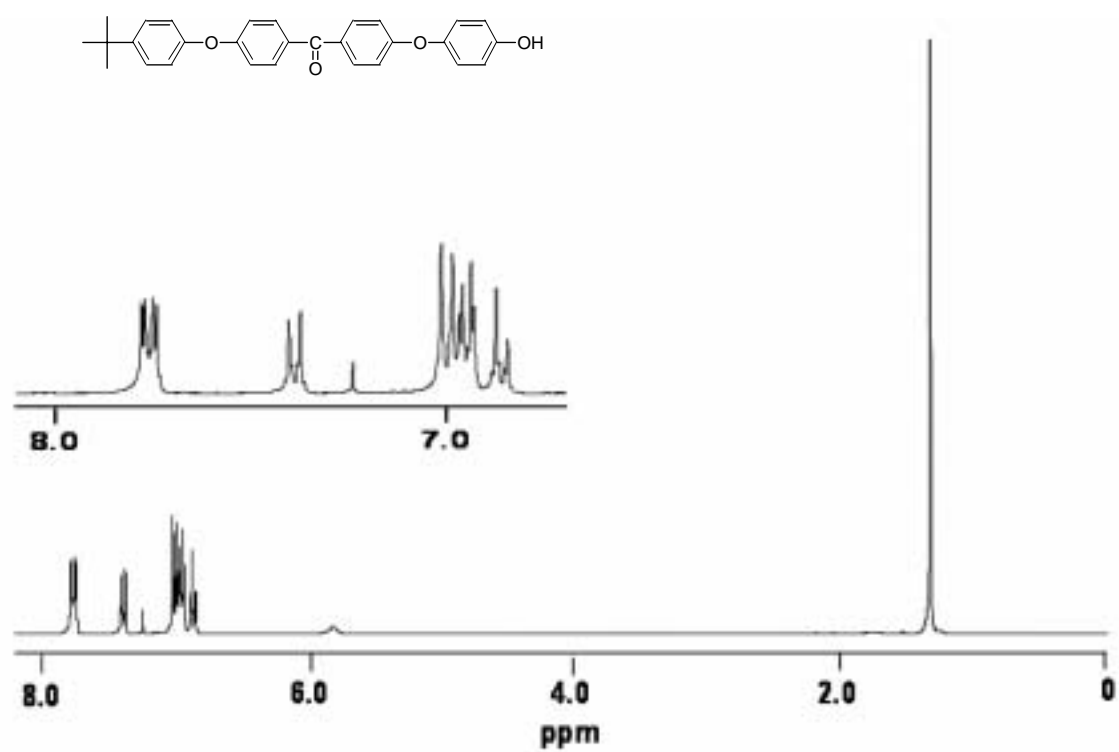


**S-Figure 39.**  $^1\text{H}$ -NMR spectrum of **20** in  $\text{CDCl}_3$  r.t..

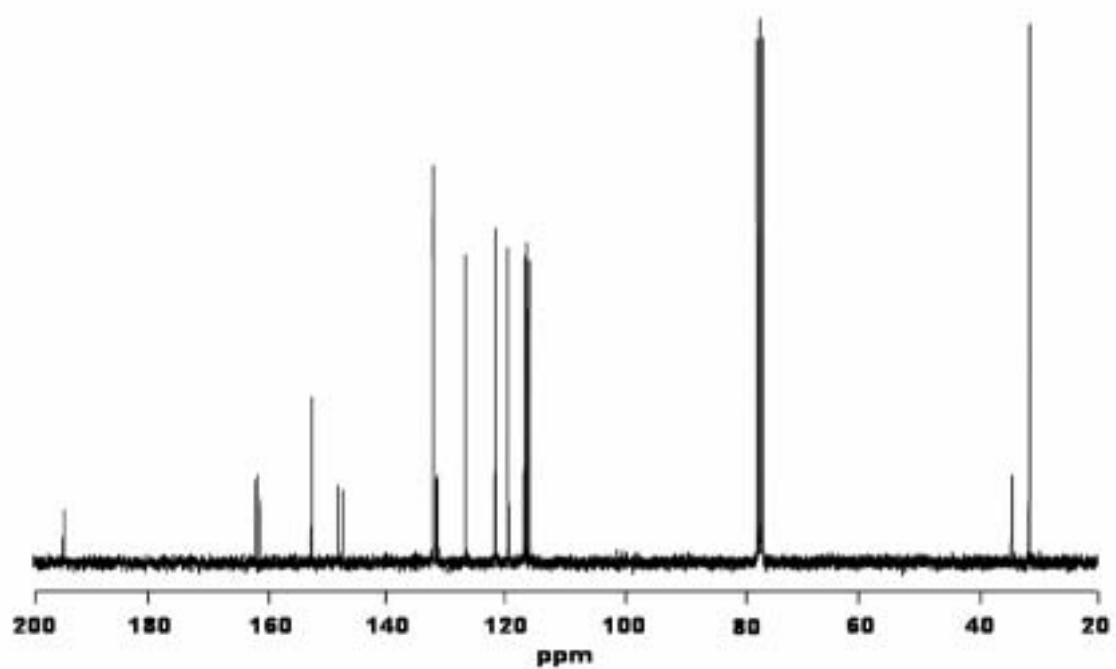


**S-Figure 40.**  $^{13}\text{C}$ -NMR spectrum of **20** in  $\text{CDCl}_3$  r.t..

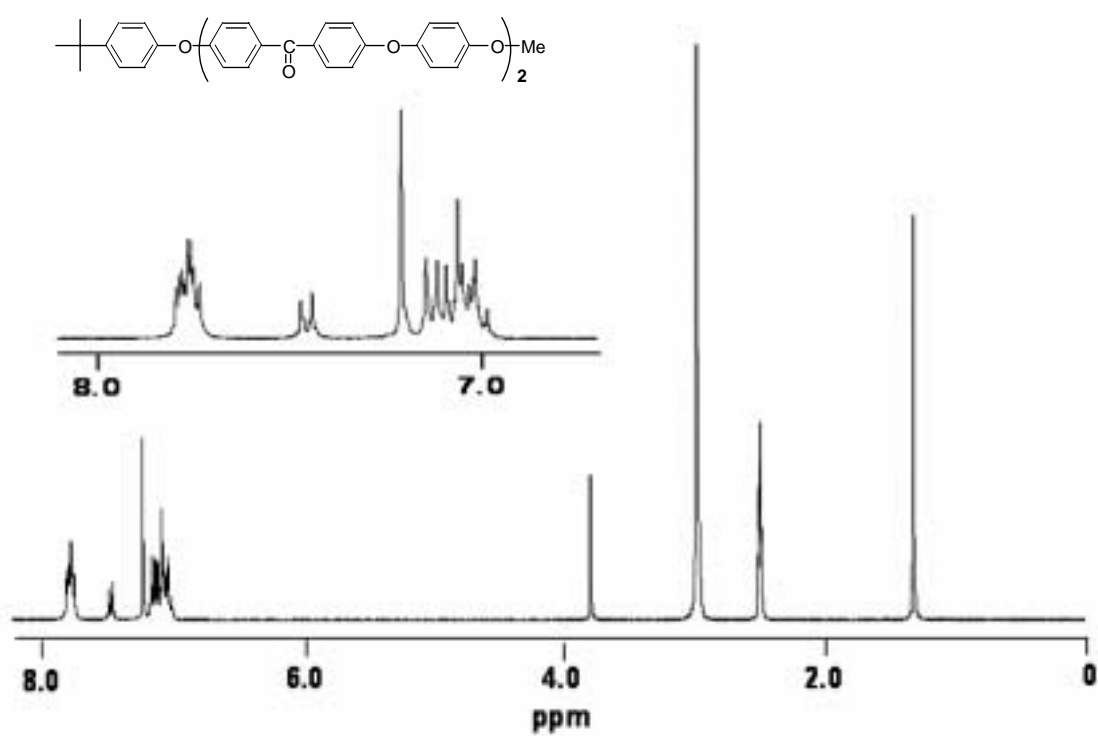




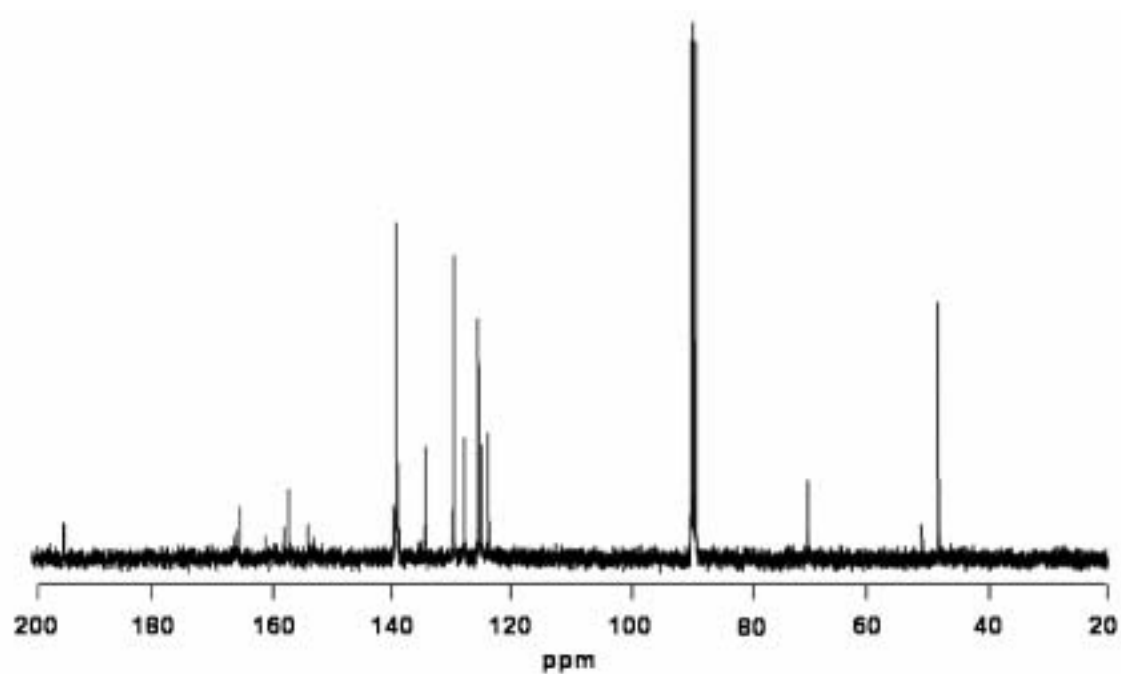
**S-Figure 41.**  $^1\text{H}$ -NMR spectrum of **21** in  $\text{CDCl}_3$  r.t..



**S-Figure 42.**  $^{13}\text{C}$ -NMR spectrum of **21** in  $\text{CDCl}_3$  r.t..



**S-Figure 43.** <sup>1</sup>H-NMR spectrum of **22** in DMSO-*d*<sub>6</sub> r.t..



**S-Figure 44.** <sup>13</sup>C-NMR spectrum of **22** in CDCl<sub>3</sub> r.t..