

## Supporting Information

### Synthesis of highly phenylene substituted *p*-phenylene oligomers from 5 pyrylium salts

Christian Mahler<sup>a</sup>, Ute Müller<sup>a</sup>, Walter M. Müller<sup>a</sup>, Volker Enkelmann<sup>b</sup>, Chulsoon Moon<sup>b</sup>, Gunther Brunklaus<sup>\*b</sup>, Herbert Zimmermann<sup>c</sup> and Sigurd Höger<sup>\*a</sup>

10 <sup>a</sup> Kekulé-Institut für Organische Chemie und Biochemie  
Rheinische Friedrich-Wilhelms-Universität Bonn  
Gerhard-Domagk-Strasse 1  
D-53121 Bonn, Germany  
Fax: (+49)228-73-5662  
15 Tel: (+49)228-73-3495  
e-mail: hoeger@uni-bonn.de

20 <sup>b</sup> MPI for Polymer Research  
Ackermannweg 10  
D-55128 Mainz, Germany  
Fax: (+49)6131-379-100  
Tel: (+49) 6131-379-240  
25 e-mail: brunklaus@mpi-mainz.mpg.de

30 <sup>c</sup> MPI für medizinische Forschung  
Jahnstrasse 29  
D-69120 Heidelberg, Germany

#### Contents:

<u>General methods</u>	<b>p2</b>
<u>35 Crystalstructure of 3b</u>	<b>p3</b>
<u>Synthesis</u>	<b>p4</b>
<u><sup>1</sup>H NMR spectra</u>	<b>p8</b>
<u>Footnotes and References</u>	<b>p11</b>

**General methods:**

40 Commercially available chemicals were used as received. THF was distilled over sodium prior to use. Dimethyl formamide was purchased in “water-free” quality and used as received. All other solvents (p.a. quality) and reagents were used as received.

45 Column chromatography was carried out using silica gel from Macherey-Nagel (MN-Kieselgel 60 M). Thin-layer chromatography (TLC) was performed on aluminum plates pre-coated with silica gel and fluorescence indicator from Macherey-Nagel (Alugram SIL G/UV 0.25 mm).

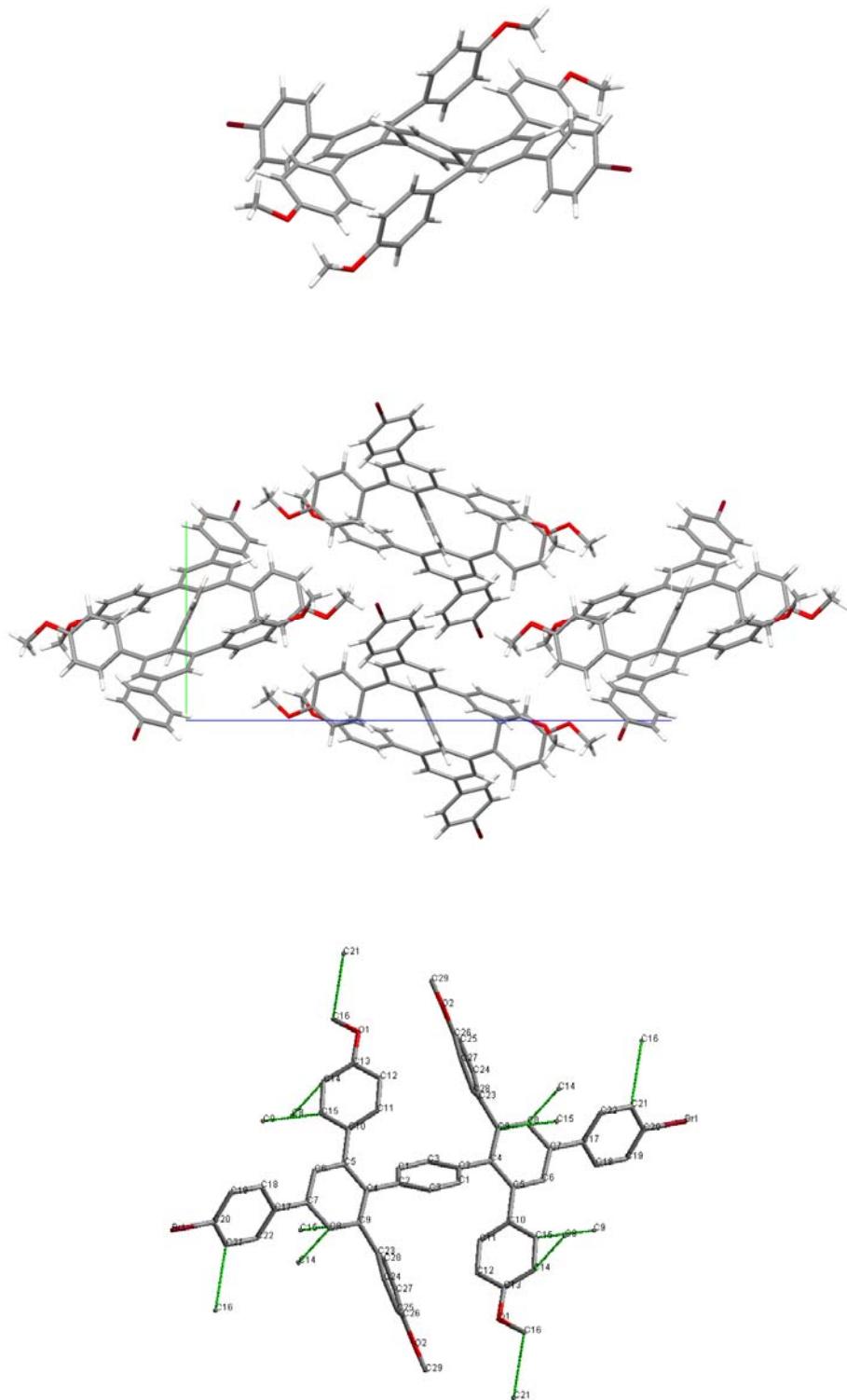
1H and 13C NMR spectra were recorded on: Bruker AC 250, Bruker Avance 400, Bruker AM 250, 300, 400 and 500.  $\delta$  values are given in ppm, coupling constants ( $J$ ) are given in Hz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; bs, broad signal.

50 Massspectrometric data were recorded on a Finnigan MAT 90 and MS-50 from A.E.I. (EI-MS), Concept 1H from KRATOS, matrix: m-NBA (FAB) and autoflex TOF/TOF from Bruker Daltonik GmbH (MALDI-TOF).

55 UV/VIS measurements were recorded on a UV.2100 from Shimadzu, fluorescence was measured with SLM-Amico, Bowman Series 2, Model FA257 and Fluoromax-4 from Horiba Jobin Yvon.

Melting points were measured on a microscope with heating table and polarisation lense (Leica DMLB, Leica LMW, Testo 925).

Crystal structure of **3b**<sup>1</sup>:



**Figure 1:** Asymmetric unit of **3b** (top), packing of **3b** (center, view along *a*) and some short intermolecular contacts within the crystal structure of **3b** (below, view along *b*, C(16)-C(21) 3.371, C(9)-C(15) 3.399, C(8)-C(14) 3.275).

**Synthesis:**

70 **1a.** Under an argon atmosphere,  $\text{BF}_3^*\text{OEt}_2$  (25 mL, 202.6 mmol) was added to a mixture of 4-iodoacetophenone (25.1 g, 101.65 mmol) and 4-*tert*-butylbenzaldehyde (8.5 mL, 50.82 mmol) without the use of further solvent. During the addition of  $\text{BF}_3^*\text{OEt}_2$  an orange solid precipitated. After stirring at 100 °C for 3 h, 100 mL MTBE (*tert*-butyl methyl ether) were added and the suspension was stirred for 12 h at room temperature. After filtration and washing with MTBE, the precipitate was stirred four times in 50 mL 1,2-dichloroethane at 50 °C and filtered after cooling to room temperature. After drying in vacuum, **1a** (12.51 g, 35 %) was received as an orange powder.  $\delta_{\text{H}}$  (400 MHz,  $\text{CD}_2\text{Cl}_2$ ) 9.16 (s, 2 H), 8.57 (d,  $J$  8.65, 2 H), 8.33 (d,  $J$  8.67, 4 H), 8.21 (d,  $J$  8.66, 4 H), 7.82 (d,  $J$  8.66, 2 H), 1.43 (s, 9 H);  $\delta_{\text{C}}$  (400 MHz,  $\text{DMSO-d}_6$ ) 170.1, 165.7, 160.3, 139.7, 131.2, 130.9, 130.7, 129.5, 127.7, 115.9, 105.4, 36.3, 31.6.

80 **1b:** Under an argon atmosphere,  $\text{BF}_3^*\text{OEt}_2$  (15 mL, 15 mmol) was added to a mixture of **7** (5.0 g, 10.7 mmol) and chalcone (2.23 g, 10.7 mmol) without use of further solvent. The mixture was stirred at 100 °C for 2 h. After cooling to room temperature, 30 mL diethyl ether were added and the red suspension was stirred for 12 h. The red precipitate was filtered, washed with cold diethyl ether and dried in vacuum to obtain **1b** as a red powder (4.4 g, 77 %).  $\delta_{\text{H}}$  (400 MHz,  $\text{DMSO-d}_6$ ) 8.80 (s, 2 H), 8.46 (d,  $J$  9.01, 4 H), 8.41 (d,  $J$  8.75, 2 H), 7.93 (d,  $J$  8.69, 2 H), 7.25 (d,  $J$  9.05, 4 H), 3.95 (s, 6 H);  $\delta_{\text{C}}$  (400 MHz,  $\text{DMSO-d}_6$ ) 170.0, 165.8, 162.8, 133.6, 132.8, 132.3, 132.0, 130.0, 122.3, 116.4, 113.5, 57.0.

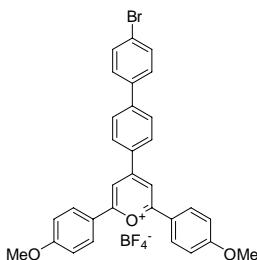
90 **1c.** Under an argon atmosphere, to a mixture of **4** (6.95 g, 27.5 mmol) and *p*-iodoacetophenone (3.38 g, 13.8 mmol) in 1,2-dichloroethane (20 mL),  $\text{HBF}_4^*\text{OEt}_2$  (51-57 % in diethyl ether, 4.6 mL) was added via a syringe over a period of 5 minutes. The mixture was stirred at 75 °C for 2 h, cooled to room temperature and 250 mL diethyl ether were added. After filtration, washing with diethyl ether and drying in vacuum, **1c** (1.68 g, 21.6 %) was obtained as an orange powder.  $\delta_{\text{H}}$  (400 MHz,  $\text{DMSO-d}_6$ ) 8.97 (d,  $J$  1.26, 1 H), 8.95 (d,  $J$  1.25, 1 H), 8.55 (d,  $J$  9.04, 2 H), 8.50 (d,  $J$  8.35, 2 H), 8.26 (d,  $J$  8.72, 2 H), 8.16 (d,  $J$  8.70, 2 H), 7.59 (d,  $J$  8.15, 2 H), 7.32 (d,  $J$  9.07, 2 H), 4.02 (s, 3 H), 3.44 (s, 3 H);  $\delta_{\text{C}}$  (400 MHz,  $\text{DMSO-d}_6$ ) 170.7, 168.4, 166.1, 164.3, 147.6, 139.6, 132.3, 131.4, 130.8, 130.5, 130.4, 129.5, 122.1, 116.4, 114.2, 113.8, 104.7, 57.1, 22.4.

100 **1d** was obtained by the same procedure applied for **1c**, starting from **4** (15.15 g, 60 mmol), *p*-*tert*-butylacetophenone (5.24 g, 30 mmol), 50 mL 1,2-dichloroethane,  $\text{HBF}_4^*\text{OEt}_2$  (51-57 % in diethyl ether, 10 mL) and 500 mL diethyl ether. **1d** (4.2 g, 28.3 %) was obtained as an orange powder.  $\delta_{\text{H}}$  (400 MHz,  $\text{DMSO-d}_6$ ) 8.97 (d,  $J$  1.44, 1 H), 8.94 (d,  $J$  1.43, 1 H), 8.58 (d,  $J$  9.07, 2 H), 8.52 (d,  $J$  8.39, 2 H), 8.47 (d,  $J$  8.70, 2 H), 7.82 (d,  $J$  8.72, 2 H), 7.61 (d,  $J$  8.06, 2 H), 7.34 (d,  $J$  9.08, 2 H), 4.02 (s, 3 H), 3.42 (s, 3 H), 1.43 (s, 9 H);  $\delta_{\text{C}}$  (400 MHz,  $\text{DMSO-d}_6$ ) 170.4, 169.5, 165.9, 164.3, 159.1, 147.3, 132.1, 131.4, 130.8, 130.7, 129.3, 127.6, 122.3, 116.4, 113.8, 113.7, 57.1, 55.8, 36.2, 31.6, 22.3.

110 **1e.** was obtained by the same procedure applied for **1c**, starting from **5** (11.48 g, 36 mmol), *p*-methylacetophenone (2.40 g, 18 mmol), 36 mL 1,2-dichloroethane,  $\text{HBF}_4^*\text{OEt}_2$  (51-57 % in diethyl ether, 6.4 mL) and 150 mL diethyl ether. **1e** (2.10 g, 23.5 %) was obtained as an orange powder.  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 8.42 (s, 1 H), 8.29 (m, 3 H), 8.21 (d,  $J$  8.59, 2 H), 8.13 (d,  $J$  8.29, 2 H), 7.56 (d,  $J$  8.52, 2 H), 7.46 (d,  $J$  8.05, 2 H), 7.16 (d,  $J$  8.94, 2 H), 3.90 (s, 3 H), 2.43 (s, 3 H), 1.24 (s, 9 H);  $\delta_{\text{C}}$  (400 MHz,  $\text{CDCl}_3$ ) 169.2, 168.3, 165.8, 163.6, 159.9, 146.6, 131.0, 129.6, 129.1, 128.1, 127.3, 125.6, 120.4, 116.0, 112.0, 111.6, 55.9, 35.4, 30.7, 21.9.

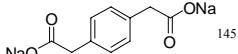
115 **1f.** was obtained by the same procedure applied for **1c**, starting from **5** (16 g, 54 mmol), 4-*tert*-butylacetophenone (4.78 g, 27 mmol), 28 mL 1,2-dichloroethane,  $\text{HBF}_4^*\text{OEt}_2$  (51-57 % in diethyl ether, 9.7 mL) and 200 mL diethyl ether. For 120 further purification, the orange precipitate was suspended in 60 mL diethyl ether and 3 mL dichloromethane and refluxed for 30 minutes. After cooling to room temperature, filtration and drying in vacuum, **1f** (2.53 g, 17.7 %) was obtained as an orange powder.  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ) 8.46 (s, 1 H), 8.34 (m, 3 H), 8.23 (m, 4 H), 7.73 (d,  $J$  8.65, 2 H), 7.50 (d,  $J$  8.60, 2 H), 7.16 (d,  $J$  9.03, 2 H), 3.90 (s, 3 H), 1.38 (s, 9 H), 1.15 (s, 9 H);  $\delta_{\text{C}}$  (300 MHz,  $\text{CDCl}_3$ ) 169.6, 168.6, 165.8, 163.8, 159.8, 159.5, 131.2, 129.7, 129.2, 128.1, 127.4, 127.3, 125.9, 120.7, 116.0, 112.3, 111.9, 56.0, 35.6, 35.4, 30.9, 30.6.

**1g.** Under an argon atmosphere,  $\text{BF}_3^*\text{OEt}_2$  (18.5 mL, 149.92 mmol) was added via a syringe to a mixture of **6** (9.41 g, 36.04 mmol) and 4-methoxyacetophenone (11.23 g, 74.96 mmol). The mixture was stirred at 100 °C for 3 h. After cooling to room temperature, 50 mL MTBE (*tert*-butyl methyl ether) were added and the black precipitate was filtered. For further purification, the precipitate was washed three times with 50 mL MTBE and three times with 1,2-dichloroethane. After drying in vacuum, the product (5.07 g, 23 %) was obtained as an orange powder.  $\delta_{\text{H}}$  (400 MHz, DMSO- $d_6$ ) 8.89 (s, 2H), 8.61 (d,  $J$  8.49, 2H), 8.52 (d,  $J$  8.93, 4H), 8.04 (d,  $J$  8.48, 2H), 7.85 (d,  $J$  8.54, 2H), 7.74 (d,  $J$  8.50, 2H), 7.28 (d,  $J$  8.96, 4H), 3.96 (s, 6H);  $\delta_{\text{C}}$  (400 MHz, DMSO- $d_6$ ) 169.2, 165.2, 162.6, 145.0, 137.7, 132.5, 132.2, 131.5, 130.9, 129.7, 128.0, 123.1, 121.9, 115.9, 112.7, 56.5.



140

**2.** A mixture of *p*-phenylenediacetic acid (21.6 g, 111 mmol) and NaOMe (11.4 g, 211 mmol) in 450 mL MeOH was stirred at room temperature. After 30 minutes the solvent was removed in vacuum to receive the product as a white solid. The product was used without further purification.

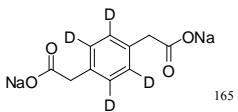


145

**2-d<sup>4</sup>-COOH** was synthesized by a modified method described by Werstiuk and Timmins<sup>2</sup>: 1,4-phenylenediacetic acid (Aldrich, CAS: 150 7325-46-4) was converted to the disodiumsalt with NaOD in D<sub>2</sub>O. The isolated salt was dissolved in D<sub>2</sub>O and first perdeuterated by exchange with Adam's catalyst (PtO<sub>2</sub>-prereduced with deuterium gas) in a stainless steel high pressure vessel at 170-175 °C under stirring for 24 hours. The water was removed by destillation and the exchange was repeated twice using new D<sub>2</sub>O and fresh prepared catalyst. After the 3rd exchange the catalyst was carefully removed by diaphragm (0.45 $\mu$ ) filtration and acidified with HCl in D<sub>2</sub>O. The isolated perdeuterated diacid was back exchanged on the -CD<sub>2</sub>- and -COOD groups by dissolving the product in NaOH/H<sub>2</sub>O, pH = 14 at 160°C for 24 hours in a stainless steel vessel. The cooled solution was acidified with HCl/H<sub>2</sub>O and the 1,4-phenylenediacetic acid-d<sub>4</sub> isolated after filtration showed a precise deuteration of the aromatic hydrogens (NMR, DMSO- $d_6$ ) better than 97%.  $\delta_{\text{H}}$  (400 MHz, DMSO- $d_6$ ) 12.29 (s, 2 H), 3.53 (s, 4 H);  $\delta_{\text{C}}$  (400 MHz, DMSO- $d_6$ ) 172.8, 133.1, 128.9 (t,  $J$  24.05), 40.3; MS (EI): *m/z* = 198.1.

155

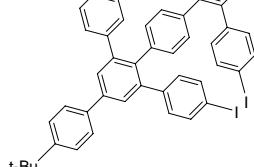
**2-d<sup>4</sup>-COONa.** A mixture of **2-d<sup>4</sup>-COOH** (2.03 g, 10.24 mmol) and NaOMe (1.05 g, 19.46 mmol) in 100 mL MeOH was stirred at room temperature. After 30 minutes the solvent was removed in vacuum to receive the product as a white solid. The product was used without further purification.



165

**3a.** A mixture of **1a** (18.40 g, 26.13 mmol), **2** (2.83 g, 11.88 mmol) and 56 mL Ac<sub>2</sub>O was stirred at 150 °C for 3 h. Further Ac<sub>2</sub>O

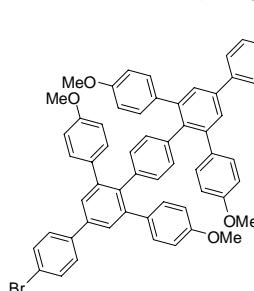
(120 mL) was added and stirred for 5 h. After cooling to room temperature, the precipitate was filtered and washed with acetonitrile three times. The final purification was carried out by column chromatography using dichloromethane/hexane (1:2) ( $R_f$  = 0.63 in dichloromethane/petrolether 1:3) to obtain **3a** as a white solid (2.07 g, 13.4 %). An impurity observed by TLC ( $R_f$  = 0.57 in dichloromethane/petrolether 1:3) could not be detected by NMR.  $\delta_{\text{H}}$  (500 MHz, CDCl<sub>3</sub>) 7.60- 7.52 (m, 16 H), 7.48 (d,  $J$  8.56, 4 H), 6.79 (d,  $J$  8.45, 8 H), 6.58 (s, 4 H), 1.37 (s, 18 H);  $\delta_{\text{C}}$  (500 MHz, CDCl<sub>3</sub>) 151.2, 141.7, 141.6, 140.5, 137.4, 137.2, 137.0, 136.8, 132.2, 131.3, 128.6, 127.1, 126.2, 92.7, 34.9, 31.7; UV (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  = 260.5 nm; fluorescence (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda$  = 384 nm, 365 nm; MS (FAB): *m/z* = 1302.0; m.p.: > 350 °C.



170

**3b.** A mixture of **1b** (15.1 g, 28.2 mmol), **2** (3.02 g, 12.8 mmol) and 125 mL Ac<sub>2</sub>O was stirred at 150 °C for 3 h. After cooling to room temperature, Ac<sub>2</sub>O was removed in vacuum and the residue was digested in dichloromethane and filtered over a short column of silica gel with dichloromethane as eluent. The final purification was

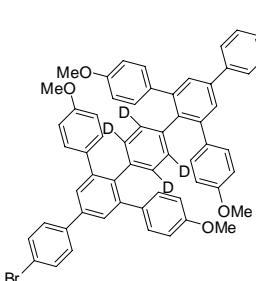
185 carried out by column chromatography using dichloromethane/petrolether (1:1) ( $R_f$  = 0.45 in dichloromethane/petrolether 1:1) and subsequent precipitation from dichloromethane by the addition of petrolether. **3b** (660 mg, 9.8 %) was obtained as a white solid.  $\delta_{\text{H}}$  (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 7.57 (s, 8 H), 7.53 (s, 4 H), 6.98 (d,  $J$  8.81, 8 H), 6.74 (d,  $J$  8.81, 8 H), 6.57 (s, 4 H), 3.78 (s, 12 H);  $\delta_{\text{C}}$  (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 158.4, 142.2, 139.5, 138.5, 137.9, 136.9, 134.3, 131.9, 131.1, 131.0, 128.7, 128.0, 121.6, 113.0, 55.2; 190 UV (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  = 260.5 nm; fluorescence (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda$  = 388 nm; MS (FAB): *m/z* = 964.3; m.p.: 299 - 302 °C.



180

195 **3b-d<sup>4</sup>**. A mixture of **1b** (9.2 g, 17.2 mmol), **2-d<sup>4</sup>**-COONa (1.86 g, 7.81 mmol) and 80 mL Ac<sub>2</sub>O was stirred at 150 °C for 6 h. After

cooling to room temperature, Ac<sub>2</sub>O was removed in vacuum and the residue was digested in dichloromethane and filtered over a short column of silica gel with dichloromethane as eluent. The final purification was carried out by column chromatography using dichloromethane/petrolether (1:1) ( $R_f$  = 0.45 in dichloromethane/petrolether 1:1) and subsequent precipitation from dichloromethane by the 200 addition of petrolether. **3b-d<sup>4</sup>** (945 mg, 12.4 %) was obtained as a white solid.  $\delta_H$  (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 7.55 (s, 8 H), 7.51 (s, 4 H), 6.98 (d,  $J$  8.79, 8 H), 6.74 (d,  $J$  8.80, 8 H), 3.77 (s, 12 H);  $\delta_C$  (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 158.8, 142.6, 139.9, 138.9, 138.3, 137.1, 134.7, 132.3, 131.5, 129.1, 128.4, 122.0, 113.4, 55.6; MS (FAB):  $m/z$  = 968.



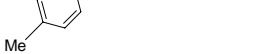
205

206 **3c**. A mixture of **1c** (1.63 g, 2.88 mmol), **2** (0.32 g, 1.37 mmol) and Ac<sub>2</sub>O (12 mL) was stirred at 150 °C for 2.5 h. After cooling to room

temperature, Ac<sub>2</sub>O was removed in vacuum and the residue was dissolved in dichloromethane and washed with H<sub>2</sub>O, NaOH (10 % in H<sub>2</sub>O) and saturated NaCl-solution. After drying over MgSO<sub>4</sub>, solvent was removed in vacuum and the final purification was carried out by column chromatography, using dichloromethane/petrolether (1:2) ( $R_f$  = 0.6 in dichloromethane/petrolether 1:1) and recrystallization from diethyl ether. **3c** (141 mg, 10 %) was obtained as a white solid.  $\delta_H$  (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 7.59- 7.51 (m, 12 H), 7.26 (d,  $J$  7.90, 4 H), 6.99 (d,  $J$  8.80, 4 H), 6.83 (d,  $J$  8.45, 4 H), 6.76 (d,  $J$  8.17, 4 H), 6.58 (s, 4 H), 3.80 (s, 6 H), 3.43 (q,  $J$  7.01, 2.3 H, Et<sub>2</sub>O), 2.38 (s, 6 H), 1.15 (t,  $J$  7.01, 3.6 H, Et<sub>2</sub>O);  $\delta_C$  (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 158.5, 142.2, 142.0, 141.3, 139.9, 137.7, 137.3, 137.2, 136.8, 136.7, 134.2, 132.1, 131.1, 131.0, 129.6, 128.6, 127.6, 126.9, 113.1, 92.0, 65.8 (Et<sub>2</sub>O), 55.3, 20.9, 15.2 (Et<sub>2</sub>O); UV (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  = 261.5 nm; fluorescence (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda$  = 386 nm, 367 nm; MS (FAB):  $m/z$  = 1026.2; m.p.: 271 – 272 °C.

220 **3d**. A mixture of **1d** (4.18 g, 8.42 mmol), **2** (0.95 g, 4.01 mmol) and Ac<sub>2</sub>O (25 mL) was stirred at 150 °C for 2 h. After cooling to room

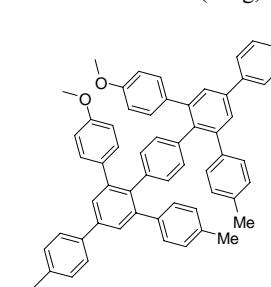
temperature, Ac<sub>2</sub>O was removed in vacuum, the residue was digested in dichloromethane and filtered over a short column of silica gel with dichloromethane as eluent. The final purification was carried out by column chromatography in dichloromethane/petrolether (1:3) ( $R_f$  = 0.28 in dichloromethane/petrolether 1:2) and recrystallization from diethyl ether. **3d** (84 mg, 2.4 %) was obtained as a white solid.  $\delta_H$  (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 7.64- 7.59 (m, 8 H), 7.35- 7.26 (m, 8 H), 7.06- 7.01 (m, 8 H), 6.83 (d,  $J$  7.18, 4 H), 6.51 (s, 4 H), 3.80 (s, 6 H), 2.40 (s, 6 H), 1.33 (s, 18 H);  $\delta_C$  (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 158.5, 149.5, 142.4, 141.9, 139.8, 139.3, 137.6, 137.6, 137.5, 136.8, 134.6, 131.3, 131.1, 129.9, 129.6, 128.1, 127.9, 126.9, 124.4, 113.0, 55.2, 34.4, 31.3, 20.9; UV (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  = 305 nm; fluorescence (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda$  = 383 nm, 367 nm; MS (FAB):  $m/z$  = 886.6; m.p.: 287 - 288 °C.



230

231 **3e**. A mixture of **1e** (2.1 g, 4.2 mmol), **2** (0.48 g, 2 mmol) and Ac<sub>2</sub>O (5.5 mL) was stirred at 150 °C for 4 h. Afte cooling to room

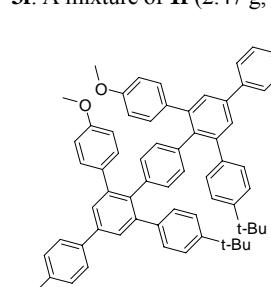
temperature, Ac<sub>2</sub>O was removed in vacuum. Then the residue was digested in dichloromethane and filtered over a short column of silica gel with dichloromethane as eluent. The final purification was 235 carried out by column chromatography with dichloromethane/petrolether (2:3) ( $R_f$  = 0.41 in dichloromethane/petrolether 2:3). **3e** (91 mg, 5.1 %) was obtained as a white solid.  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 7.62-7.57 (m, 8H), 7.46 (d,  $J$  8.49, 4H), 7.05-6.95 (m, 12H), 6.75 (d,  $J$  8.76, 4H), 6.52 (s, 4H), 3.79 (s, 6H), 2.32 (s, 6H), 1.36 (s, 18H),  $\delta_C$  (400 MHz, CDCl<sub>3</sub>) 158.2, 150.4, 142.1, 141.7, 139.8, 139.2, 137.7, 137.3, 136.5, 135.8, 134.6, 131.2, 131.1, 130.0, 128.2, 128.1, 126.7, 125.7, 112.9, 55.1, 240 34.6, 31.4, 21.1; UV (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  = 262 nm; fluorescence (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda$  = 382 nm; MS (MALDI-TOF):  $m/z$  = 886.4; m.p.: >300 °C.



230

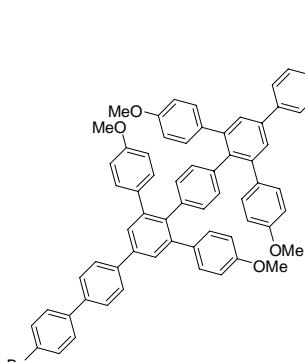
245 **3f**. A mixture of **1f** (2.47 g, 4.7 mmol), **2** (0.53 g, 2.3 mmol) and Ac<sub>2</sub>O (3.2 mL) was stirred at 150 °C for 4 h. After cooling to room

temperature the precipitate was filtered and washed with methanol. The final purification was carried out by column chromatography with dichloromethane/petrolether (1:2) ( $R_f$  = 0.4 in dichloromethane/petrolether 1:2). **3f** (137 mg, 6.1 %) was obtained as a white solid.  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 7.69-7.63 (m, 8H), 7.51 (d,  $J$  8.46, 4H), 7.32 (m, 4H), 7.05 (d,  $J$  8.52, 8H), 6.83 (m, 4H), 6.52 (s, 4H), 3.83 (d,  $J$  3.09, 6H), 1.41 (s, 18H), 1.35 (d,  $J$  2.77, 18H);  $\delta_C$  (400 MHz, CDCl<sub>3</sub>) 158.2, 150.4, 149.2, 142.1, 141.6, 139.8, 139.1, 137.7, 137.5, 136.5, 134.5, 131.2, 131.0, 129.8, 128.1, 128.0, 126.8, 125.7, 124.2, 112.8, 55.1, 4.6, 34.4, 31.4, 31.4; UV (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  = 308 nm; fluorescence (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda$  = 380 nm; MS (FAB):  $m/z$  = 970.5; m.p.: >300 °C.



255

3g. To a suspension of **2** (0.99 g, 4.15 mmol) in Ac<sub>2</sub>O (13 mL), **1g** (5.1 g, 8.3 mmol) was added over a period of 4.5 h at 150 °C. After addition of **1g**, 1680 mg of **2** and 3 mL Ac<sub>2</sub>O were added and the mixture was stirred for 2.5 h at 150 °C. After cooling to room temperature, the solution was decanted and the precipitate was washed with acetonitrile and water. The final purification was carried out by MPLC (235 g Lichroprep 15-25 µm; dichloromethane/heptane = 2:1) ( $R_f$  = 0.26 in dichloromethane/hexane 2:1). **3g** (321 mg, 6.9%) was obtained as a white solid.  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 7.75 (d, *J* 8.40, 4H), 7.58-7.54 (m, 8H), 7.58 (d, *J* 8.57, 4H), 7.51 (d, *J* 8.60, 4H), 7.02 (d, *J* 8.73, 8H), 6.77 (d, *J* 8.77, 8H), 6.56 (s, 4H), 3.80 (s, 12H);  $\delta_C$  (400 MHz, CDCl<sub>3</sub>) 158.2, 142.0, 139.8, 139.6, 139.1, 139.0, 137.8, 136.5, 134.4, 131.9, 131.2, 131.1, 128.6, 128.1, 127.6, 127.3, 121.6, 112.9, 55.2; UV (CHCl<sub>3</sub>):  $\lambda_{max}$  = 249 nm; fluorescence (CHCl<sub>3</sub>):  $\lambda$  = 389 nm; MS (MALDI-TOF): *m/z* = 1116.2; m.p.: > 300 °C.



270

4. 4-Methoxyacetophenone (15 g, 99.9 mmol) was dissolved in 50 mL ethanol and cooled to 0 °C. Then the solution was added to a cooled aqueous solution of NaOH (5.12 g NaOH in 40 mL H<sub>2</sub>O) and stirred for 10 minutes. 275 4-methylbenzaldehyde (12 g, 99.9 mmol) was added dropwise and the mixture was stirred for 12 h at room temperature. After filtration, the precipitate was washed with cold methanol to obtain **4** (22.34 g, 89 %) as a yellowish solid.  $\delta_H$  (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 8.02 (d, *J* 8.96, 2 H), 7.74 (d, *J* 15.62, 1 H), 7.58-7.51 (m, 3 H), 7.24 (d, *J* 7.95, 2 H), 6.99 (d, *J* 8.95, 2 H), 3.88 (s, 3 H), 2.38 (s, 3 H);  $\delta_C$  (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 188.3, 163.5, 143.6, 141.0, 132.4, 131.3, 130.7, 129.7, 128.4, 120.9, 113.9, 55.6, 21.3; MS (EI): *m/z* = 252.1; m.p.: 130 °C.

280

5. 4-Methoxyacetophenone (22.58 g, 150 mmol) was dissolved in 85 mL ethanol and cooled to 0 °C. Then the solution was added to a cooled aqueous solution of NaOH (10 % in H<sub>2</sub>O, 75 mL) and stirred for 10 minutes. 285 4-*tert*-butylbenzaldehyde (24.39 g, 150 mmol) was added dropwise and the mixture was stirred for 12 h at room temperature. After filtration the precipitate was washed with cold methanol to obtain **5** (40.91 g, 92.6 %) as a yellowish solid.  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 8.02 (d, *J* 8.93, 2 H), 7.75 (d, *J* 15.63, 1 H), 7.61 (d, *J* 8.33, 2 H), 7.55 (d, *J* 15.62, 1 H), 7.45 (d, *J* 8.40, 2 H), 6.99 (d, *J* 8.91, 2 H), 3.88 (s, 3 H), 1.33 (s, 9 H);  $\delta_C$  (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 188.7, 163.3, 153.9, 143.9, 132.3, 131.2, 130.7, 128.2, 125.8, 121.0, 113.8, 55.4, 34.9, 31.1; MS (EI): *m/z* = 294.1; m.p.: 100 °C.

290

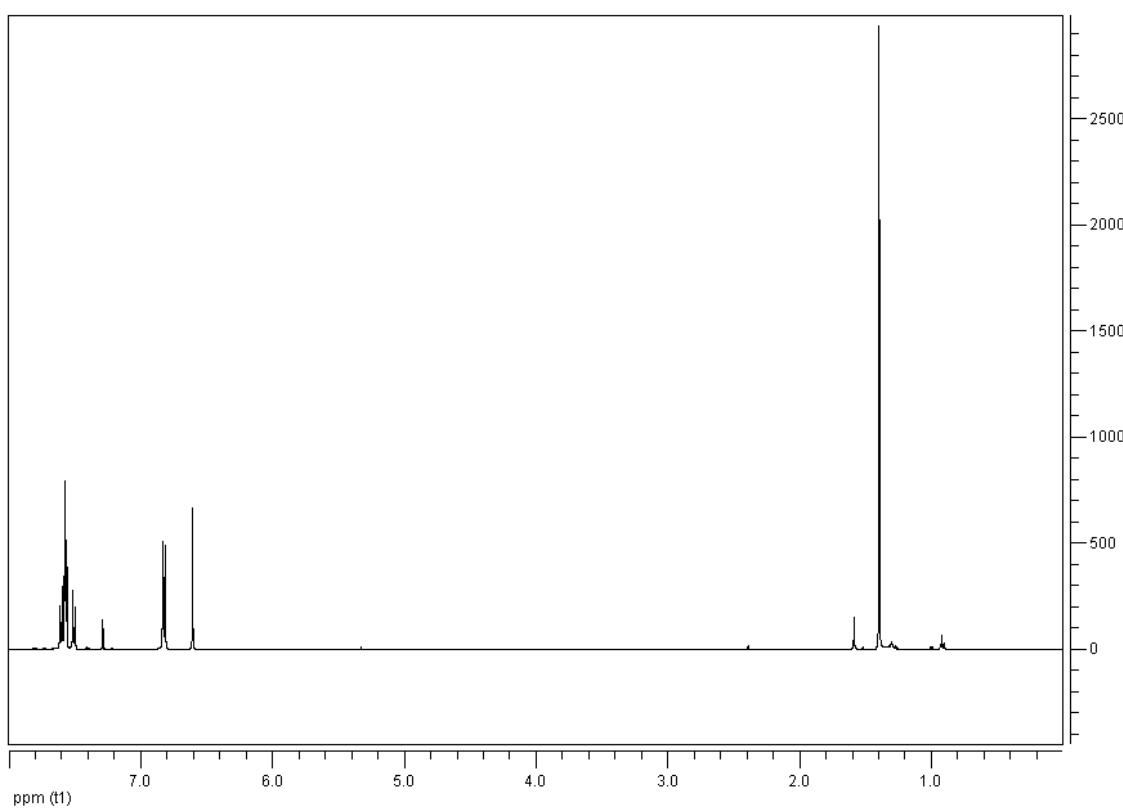
6. Compound **6** was synthesized by a modified method from Ferreira et al.<sup>3</sup>. Under an argon atmosphere, a solution of 4,4'-dibromobiphenyl (20 g, 64.1 mmol) in 200 mL dry THF was cooled to -76 °C and *n*-butyllithium (46 mL, 73.6 mmol, 1.6 M in hexane) was added under vigorous stirring, keeping the inner temperature lower than -72 °C. The yellowish, viscous suspension was stirred for 3 h at -76 °C, then dimethyl formamide (abs.) (15 mL, 195 mmol) was added. The mixture was stirred and allowed to rise to room temperature slowly over a period of 12 h. Then the solvent was removed in vacuum and 900 mL dichloromethane were added to the residue. The organic phase was washed with 300 mL water and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed in vacuum and the yellow solid was recrystallised from 65 mL ethylacetate to gain the product (9.63 g, 58 %) as a white solid. The product was used as received. An analytical sample was obtained by column chromatography with dichloromethane/petrolether (1:1) ( $R_f$  = 0.32 in dichloromethane/petrolether 1:1). 295  $\delta_H$  (300 MHz, THF-d<sub>8</sub>) 10.09 (s, 1 H), 8.02 (d, *J* 8.53, 2 H), 7.89 (d, *J* 8.25, 2 H), 7.71 (s, 4 H);  $\delta_C$  (300 MHz, THF-d<sub>8</sub>) 193.0, 147.5, 141.1, 138.4, 134.3, 132.2, 131.2, 129.5, 124.8; MS (EI): *m/z* = 260.0.

300

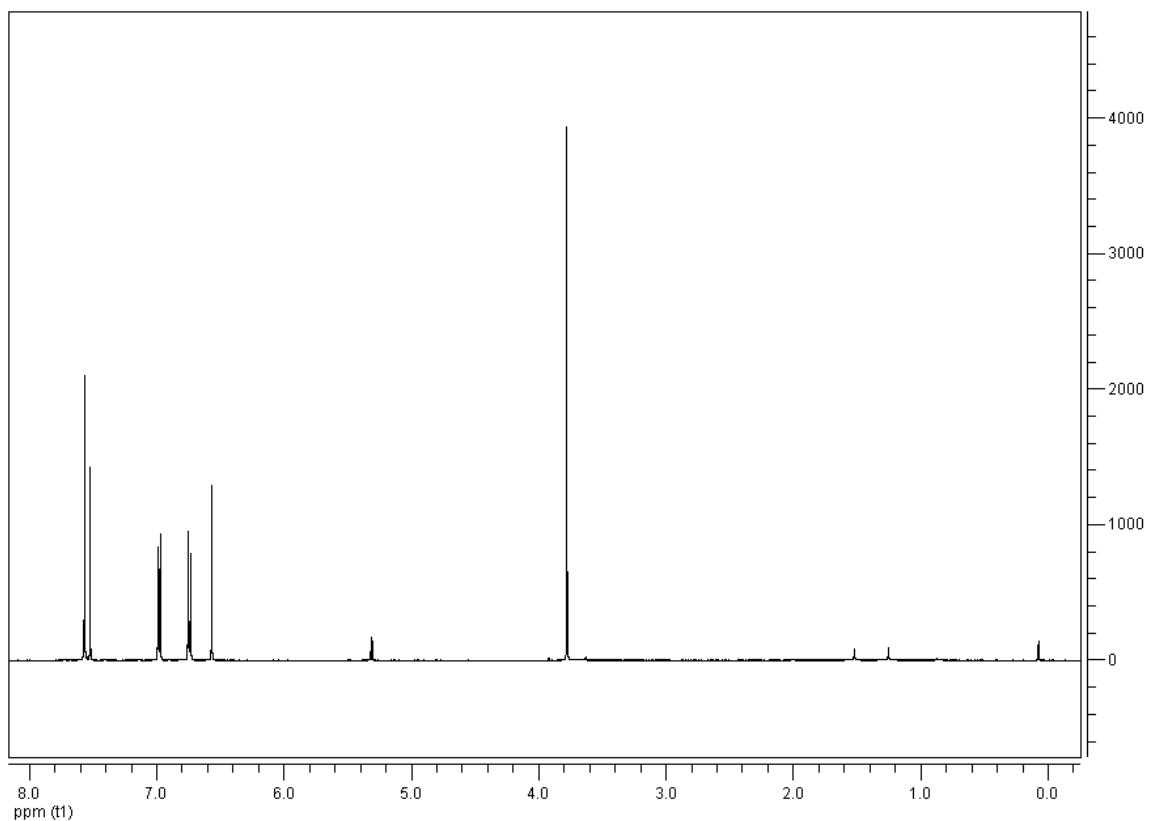
7: To a solution of 4-bromobenzaldehyde (50 g, 270 mmol) and 4-methoxyacetophenone (101.5 g, 677 mmol) in 500 mL ethanol, NaOH 305 (40% in H<sub>2</sub>O, 68 mL) was added and the mixture was refluxed for 1 h. After cooling to room temperature, 500 mL water were added and the liquid phase was decanted. The precipitate was refluxed in 150 mL methanol and cooled to room temperature. After filtration and drying in vacuum, **7** was obtained as a yellow solid (75.5 g, 60 %).  $\delta_H$  (250 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 7.87 (d, *J* 8.55, 4 H), 7.34 (d, *J* 8.55, 4 H), 7.15 (d, *J* 8.55, 2 H), 6.87 (d, *J* 8.55, 4 H), 3.95 (quintet, *J* 7.02, 1 H), 3.83 (s, 6 H), 3.50-3.28 (m, 4 H);  $\delta_C$  (400 MHz, CDCl<sub>3</sub>) 196.8, 163.5, 143.0, 131.6, 130.4, 129.8, 129.3, 120.3, 113.7, 55.4, 44.4, 37.0; MS (EI): *m/z* = 466.1

<sup>1</sup>H NMR spectra of compounds 3a – 3g

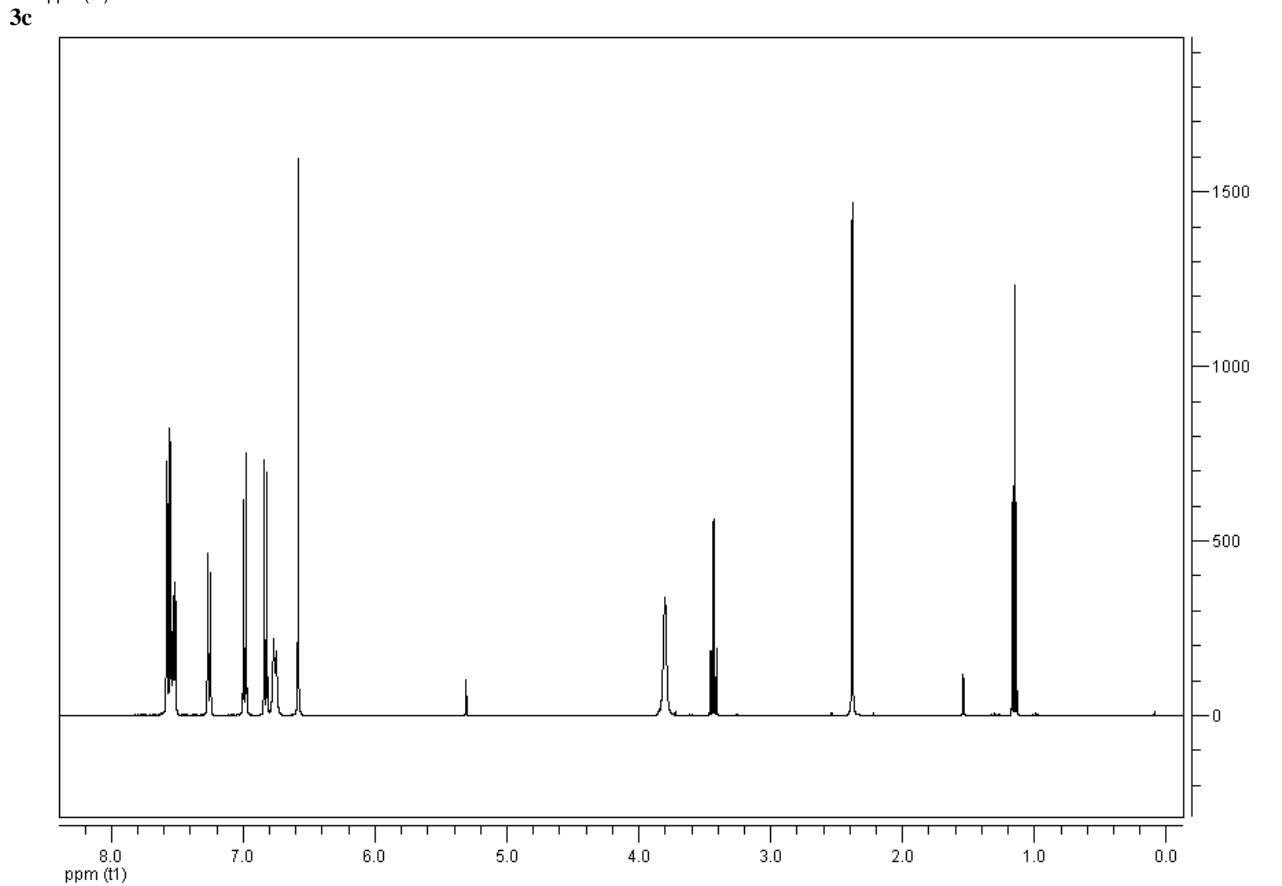
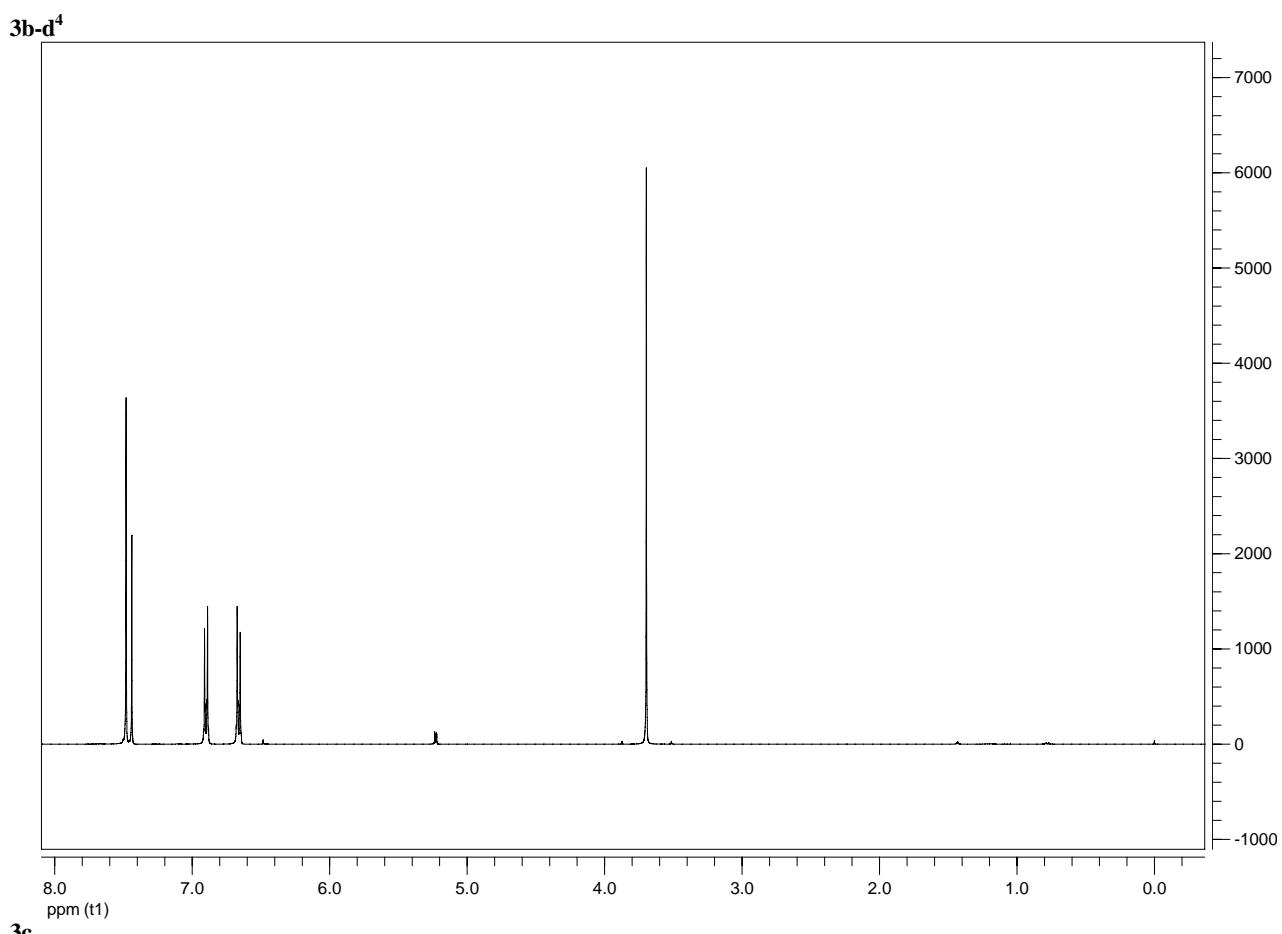
315 3a



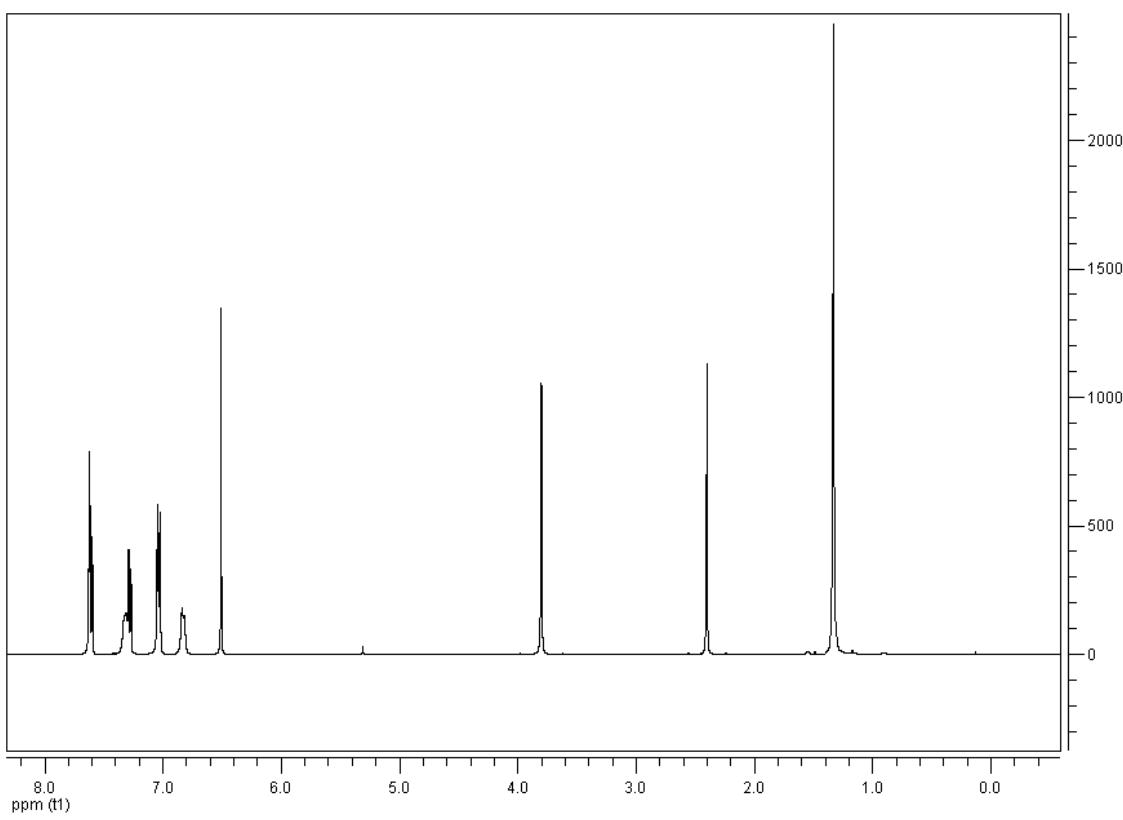
3b



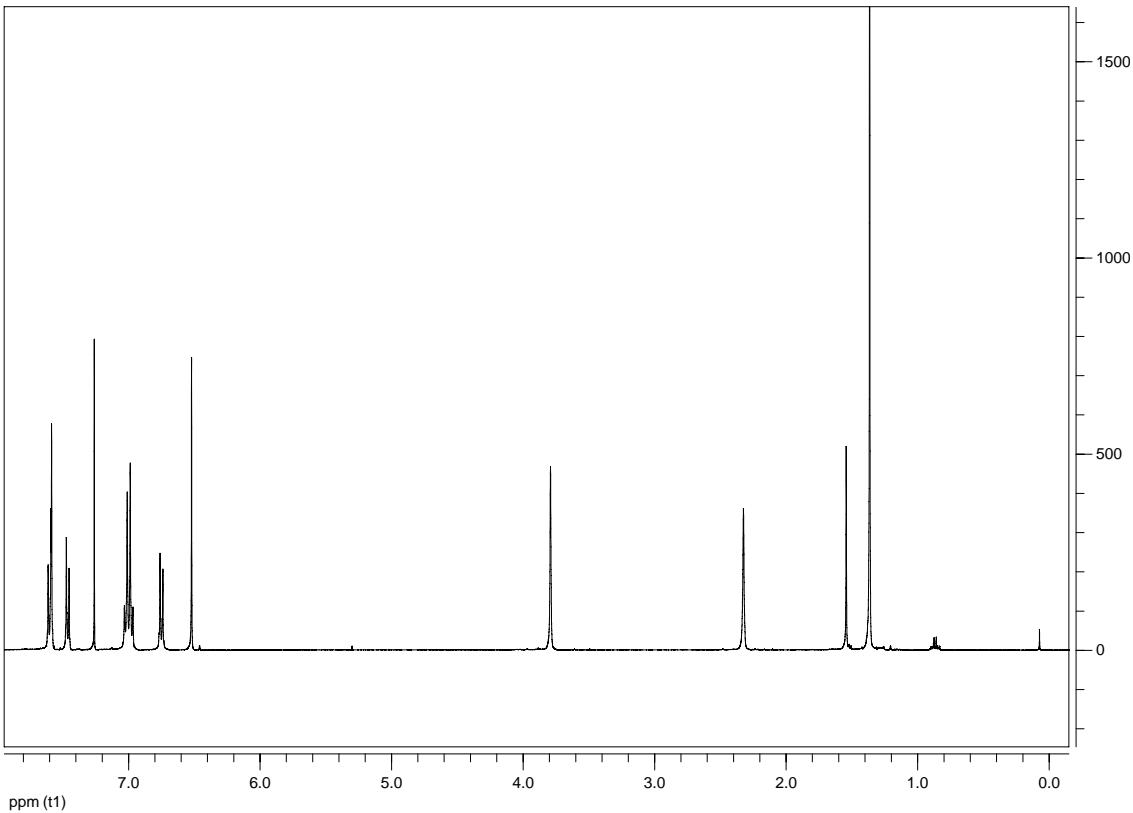
320



325 **3d**

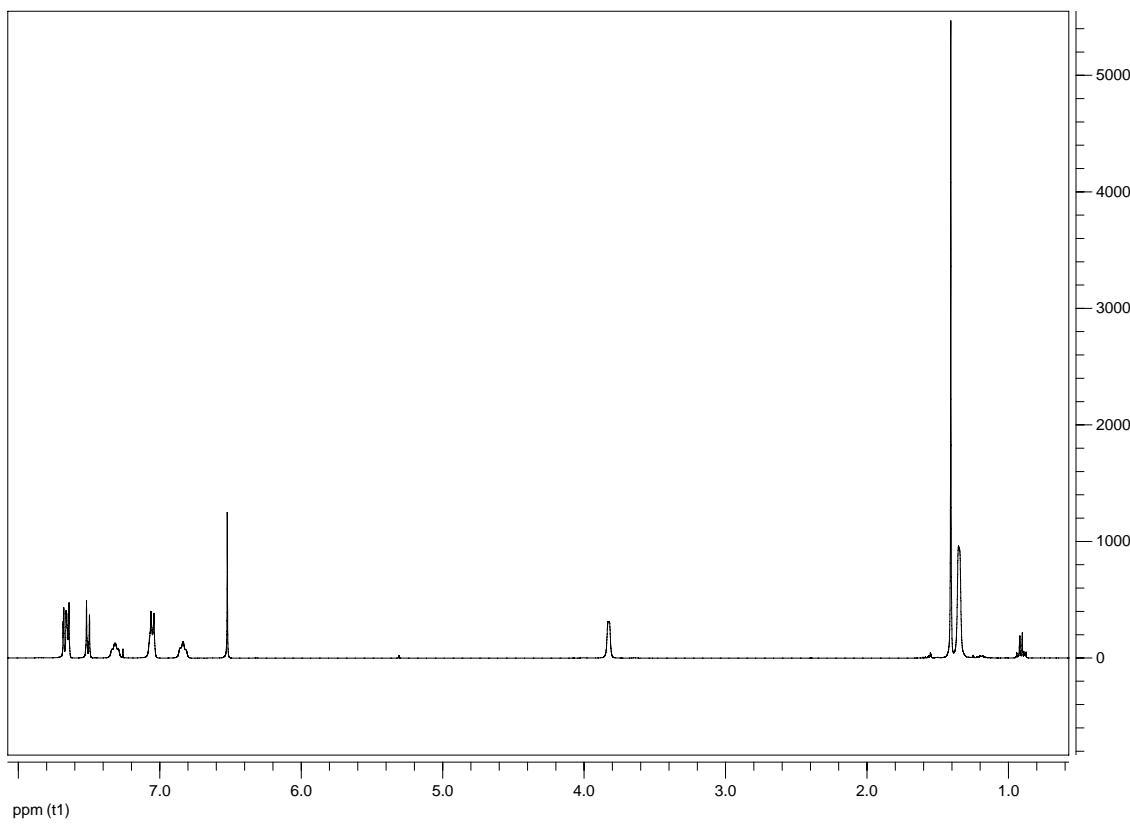


**3e**

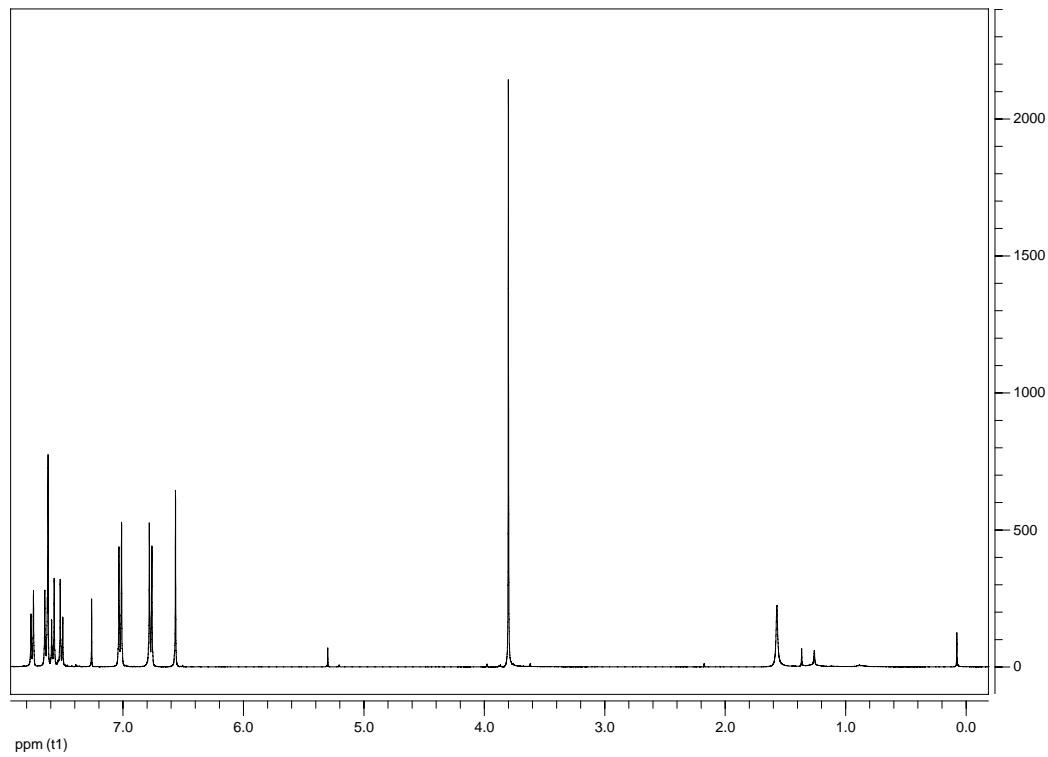


330

3f



3g



---

- 1 Nonius KappaCCD diffractometer, Mo Kalpha radiation, 120K; Structure solved by heavy atom method (Patterson) and refined on F with anisotropic temp. factors for all non H atoms. H atoms were refined with fixed TF in the riding mode. Lattice parameters were refined from the angular settings of all measured reflections by the program Denzo.
- 2 Nick Henry Werstiuk, George Timmins, *Can. J. Chem.*, 1986, **64**, 1072-6.
- 3 P. S. van Heerden, B. C. B. Bezuidenhoudt, D. J. Ferreira, *J. Chem. Soc., Perkin Trans. 1*, 1997, 1141-1146.