

Supporting Information

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

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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. δ 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.

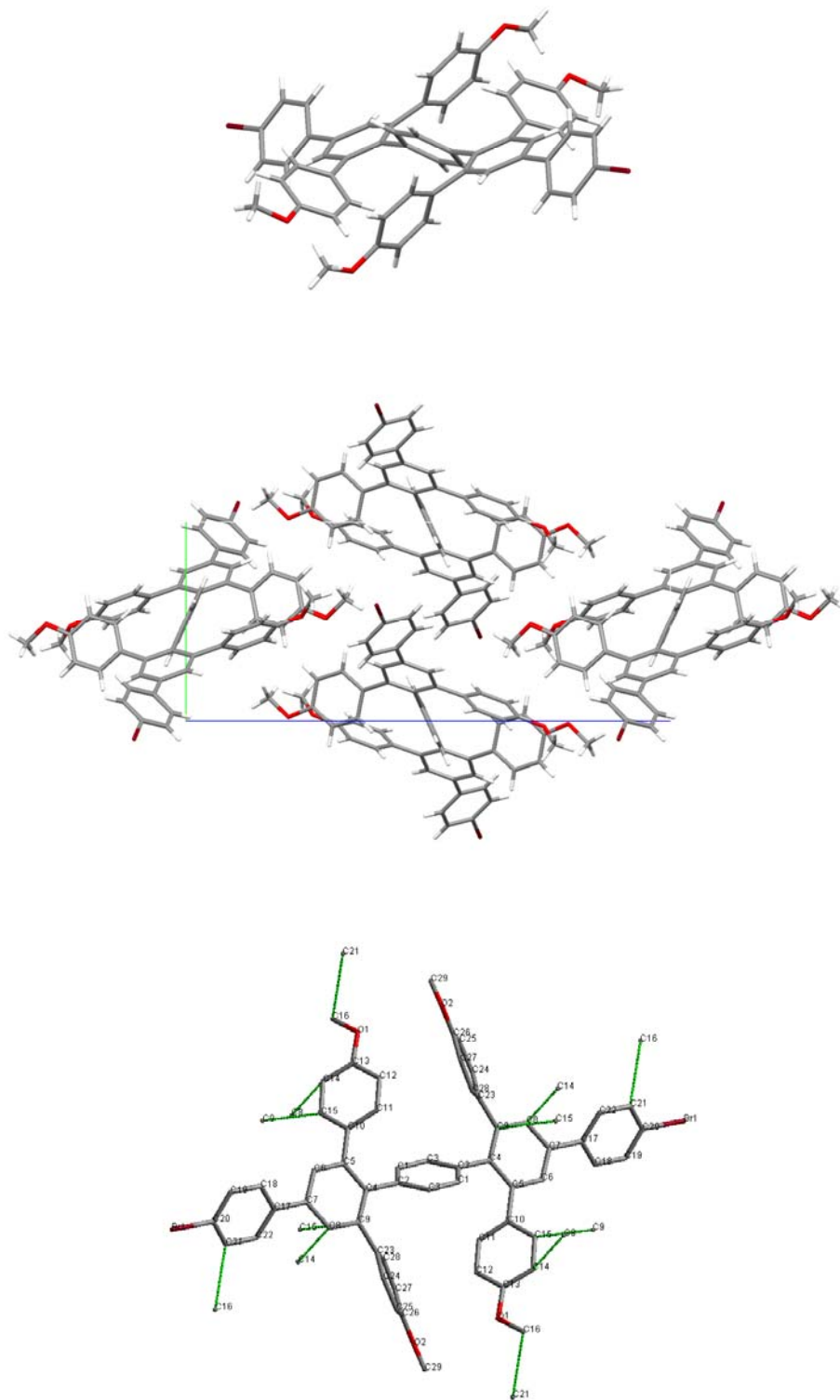
50 Mass spectrometric data were recorded on a Finnigan MAT 90 and MS-50 from A.E.I. (EI-MS), Concept 1H from KRATOS, matrix: m-NBA (FAB) and autoflex TOF/TOF from Bruker Daltonik GmbH (MALDI-TOF).

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).

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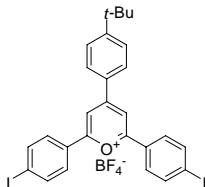
Crystal structure of **3b**¹:



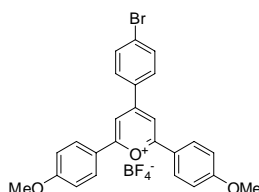
⁶⁵ **Figure 1:** Asymmetric unit of **3b** (top), packing of **3b** (center, view along *a*) and some short intermolecular contacts within the crystal structure of **3b** (below, view along *b*, C(16)-C(21) 3.371, C(9)-C(15) 3.399, C(8)-C(14) 3.275).

Synthesis:

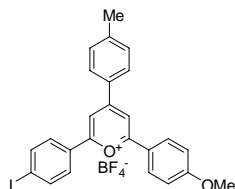
- 70 **1a.** Under an argon atmosphere, $\text{BF}_3 \cdot \text{OEt}_2$ (25 mL, 202.6 mmol) was added to a mixture of 4-iodoacetophenone (25.1 g, 101.65 mmol) and 4-*tert*-butylbenzaldehyde (8.5 mL, 50.82 mmol) without the use of further solvent. During the addition of $\text{BF}_3 \cdot \text{OEt}_2$ 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
75 room temperature. After drying in vacuum, **1a** (12.51 g, 35 %) was received as an orange powder. δ_{H} (400 MHz, CD_2Cl_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); δ_{C} (400 MHz, 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.



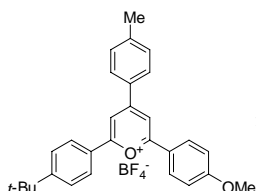
- 80 **1b:** Under an argon atmosphere, $\text{BF}_3 \cdot \text{OEt}_2$ (15 mL, 15 mmol) was added to a mixture of **7** (5.0 g, 10.7 mmol) and chalcone (2.23 g, 10.7 mmol) without use of further solvent. The mixture was stirred at 100 °C for 2 h. After cooling to room temperature, 30 mL diethyl ether 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
85 (4.4 g, 77 %). δ_{H} (400 MHz, 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); δ_{C} (400 MHz, 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.



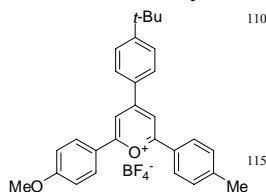
- 90 **1c.** Under an argon atmosphere, to a mixture of **4** (6.95 g, 27.5 mmol) and *p*-iodoacetophenone (3.38 g, 13.8 mmol) in 1,2-dichloroethane (20 mL), $\text{HBF}_4 \cdot \text{OEt}_2$ (51-57 % in diethyl ether, 4.6 mL) was added via a syringe over a period of 5 minutes. The mixture was stirred 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. δ_{H} (400 MHz, 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),
95 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); δ_{C} (400 MHz, 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.



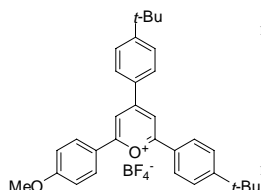
- 100 **1d** was obtained by the same procedure applied for **1c**, starting from **4** (15.15 g, 60 mmol), *p*-*tert*-butylacetophenone (5.24 g, 30 mmol), 50 mL 1,2-dichloroethane, $\text{HBF}_4 \cdot \text{OEt}_2$ (51-57 % in diethyl ether, 10 mL) and 500 mL diethyl ether. **1d** (4.2 g, 28.3 %) was obtained as an orange powder. δ_{H} (400 MHz, 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); δ_{C} (400 MHz, DMSO-d_6) 170.4, 169.5,
105 165.9, 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.



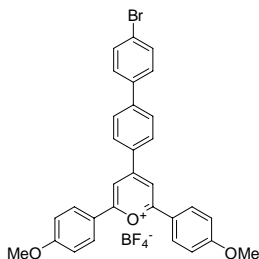
- 1e.** was obtained by the same procedure applied for **1c**, starting from **5** (11.48 g, 36 mmol), *p*-methylacetophenone (2.40 g, 18 mmol),
110 36 mL 1,2-dichloroethane, $\text{HBF}_4 \cdot \text{OEt}_2$ (51-57 % in diethyl ether, 6.4 mL) and 150 mL diethyl ether. **1e** (2.10 g, 23.5 %) was obtained as an orange powder. δ_{H} (400 MHz, 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); δ_{C} (400 MHz, 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.



- 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),
120 28 mL 1,2-dichloroethane, $\text{HBF}_4 \cdot \text{OEt}_2$ (51-57 % in diethyl ether, 9.7 mL) and 200 mL diethyl ether. For 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. δ_{H} (300 MHz, 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); δ_{C} (300 MHz, CDCl_3) 169.6, 168.6, 165.8, 163.8, 159.8, 159.5, 131.2, 129.7, 129.2, 128.1, 127.4,
125 127.3, 125.9, 120.7, 116.0, 112.3, 111.9, 56.0, 35.6, 35.4, 30.9, 30.6.

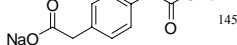


1g. Under an argon atmosphere, $\text{BF}_3 \cdot \text{OEt}_2$ (18.5 mL, 149.92 mmol) was added via a syringe to a mixture of **6** (9.41 g, 36.04 mmol) and 4-methoxyacetophenone (11.23 g, 74.96 mmol). The mixture was stirred at 100 °C for 3 h. After cooling to room temperature, 50 mL MTBE (*tert*-butyl 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. δ_{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); δ_{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.

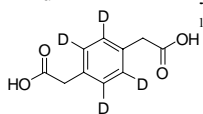


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2. A mixture of *p*-phenylenediacetic acid (21.6 g, 111 mmol) and NaOMe (11.4 g, 211 mmol) in 450 mL MeOH was stirred at room temperature. After 30 minutes the solvent was removed in vacuum to receive the product as a white solid. The product was used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

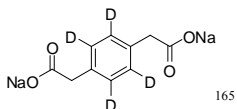


2-d⁴-COOH was synthesized by a modified method described by Werstuijk and Timmins²: 1,4-phenylenediacetic acid (Aldrich, CAS: 7325-46-4) was converted to the disodium salt with NaOD in D_2O . The isolated salt was dissolved in D_2O and first perdeuterated by exchange with Adam's catalyst (PtO_2 -pre-reduced with deuterium gas) in a stainless steel high pressure vessel at 170-175 °C under stirring for 24 hours. The water was removed by distillation and the exchange was repeated twice using new D_2O and fresh prepared catalyst. After the 3rd exchange the catalyst was carefully removed by diaphragm (0.45 μ) filtration and acidified with HCl in D_2O . The isolated perdeuterated diacid was back exchanged on the $-\text{CD}_2-$ and $-\text{COOD}$ groups by dissolving the product in NaOH/ H_2O , pH = 14 at 160 °C for 24 hours in a stainless steel vessel. The cooled solution was acidified with HCl/ H_2O and the 1,4-phenylenediacetic acid-d₄ isolated after filtration showed a precise deuteration of the aromatic hydrogens (NMR, DMSO-d_6) better than 97%. δ_{H} (400 MHz, DMSO-d_6) 12.29 (s, 2 H), 3.53 (s, 4 H); δ_{C} (400 MHz, DMSO-d_6) 172.8, 133.1, 128.9 (t, J 24.05), 40.3; MS (EI): m/z = 198.1.



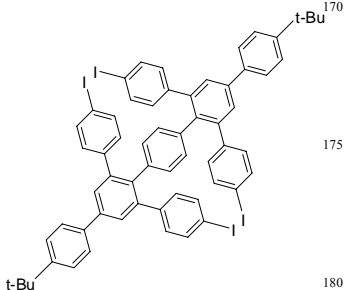
155

2-d⁴-COONa. A mixture of **2-d⁴-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.



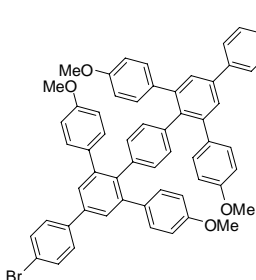
160

3a. A mixture of **1a** (18.40 g, 26.13 mmol), **2** (2.83 g, 11.88 mmol) and 56 mL Ac_2O was stirred at 150 °C for 3 h. Further Ac_2O (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. δ_{H} (500 MHz, CDCl_3) 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); δ_{C} (500 MHz, CDCl_3) 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_2Cl_2): λ_{max} = 260.5 nm; fluorescence (CH_2Cl_2): λ = 384 nm, 365 nm; MS (FAB): m/z = 1302.0; m.p.: > 350 °C.



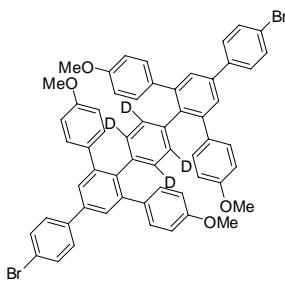
180

3b. A mixture of **1b** (15.1 g, 28.2 mmol), **2** (3.02 g, 12.8 mmol) and 125 mL Ac_2O was stirred at 150 °C for 3 h. After cooling to room temperature, Ac_2O 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 addition of petrolether. **3b** (660 mg, 9.8 %) was obtained as a white solid. δ_{H} (500 MHz, CD_2Cl_2) 7.57 (s, 8 H), 7.53 (s, 4 H), 6.98 (d, J 8.81, 8H), 6.74 (d, J 8.81, 8H), 6.57 (s, 4 H), 3.78 (s, 12 H); δ_{C} (500 MHz, CD_2Cl_2) 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; UV (CH_2Cl_2): λ_{max} = 260.5 nm; fluorescence (CH_2Cl_2): λ = 388 nm; MS (FAB): m/z = 964.3; m.p.: 299 - 302 °C.



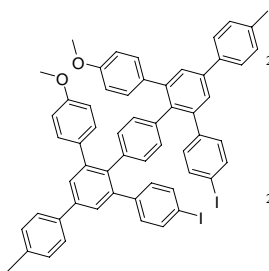
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195 **3b-d⁴**. A mixture of **1b** (9.2 g, 17.2 mmol), **2-d⁴-COONa** (1.86 g, 7.81 mmol) and 80 mL Ac₂O was stirred at 150 °C for 6 h. After cooling to room temperature, Ac₂O was removed in vacuum and the residue was digested in dichloromethane and 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-d⁴** (945 mg, 12.4 %) was obtained as a white solid. δ_H (500 MHz, CD₂Cl₂) 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); δ_C (500 MHz, CD₂Cl₂) 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.



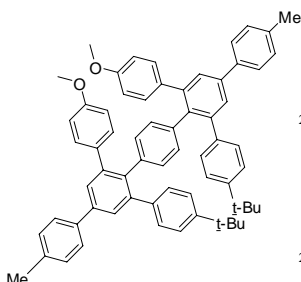
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3c. A mixture of **1c** (1.63 g, 2.88 mmol), **2** (0.32 g, 1.37 mmol) and Ac₂O (12 mL) was stirred at 150 °C for 2.5 h. After cooling to room temperature, Ac₂O was removed in vacuum and the residue was dissolved in dichloromethane and washed with H₂O, NaOH (10 % in H₂O) and saturated NaCl-solution. After drying over MgSO₄, solvent was
210 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. δ_H (400 MHz, CD₂Cl₂) 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, Et₂O), 2.38 (s, 6 H), 1.15 (t, *J* 7.01, 3.6 H, Et₂O); δ_C (400 MHz,
215 CD₂Cl₂) 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 (Et₂O), 55.3, 20.9, 15.2 (Et₂O); UV (CH₂Cl₂): λ_{max} = 261.5 nm; fluorescence (CH₂Cl₂): λ = 386 nm, 367 nm; MS (FAB): *m/z* = 1026.2; m.p.: 271 – 272 °C.



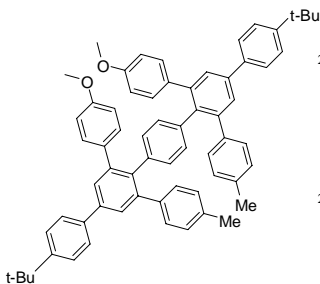
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220 **3d**. A mixture of **1d** (4.18 g, 8.42 mmol), **2** (0.95 g, 4.01 mmol) and Ac₂O (25 mL) was stirred at 150 °C for 2 h. After cooling to room temperature, Ac₂O was removed in vacuum, the residue was digested in dichloromethane and filtered over 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.
225 δ_H (400 MHz, CD₂Cl₂) 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); δ_C (400 MHz, CD₂Cl₂) 158.5, 149.5, 142.4, 141.9, 139.8, 139.3, 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 (CH₂Cl₂): λ_{max} = 305 nm; fluorescence (CH₂Cl₂): λ = 383 nm, 367 nm; MS (FAB): *m/z* = 886.6; m.p.: 287 – 288 °C.



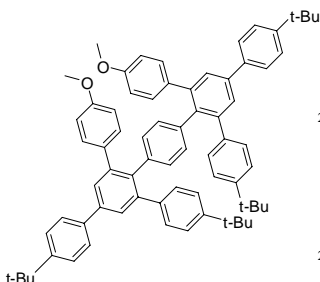
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3e. A mixture of **1e** (2.1 g, 4.2 mmol), **2** (0.48 g, 2 mmol) and Ac₂O (5.5 mL) was stirred at 150 °C for 4 h. After cooling to room temperature, Ac₂O was removed in vacuum. Then the residue was digested in dichloromethane and filtered over a short 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. δ_H (400 MHz, CDCl₃) 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), δ_C (400 MHz, CDCl₃) 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 (CH₂Cl₂): λ_{max} = 262 nm; fluorescence (CH₂Cl₂): λ = 382 nm; MS (MALDI-TOF): *m/z* = 886.4; m.p.: >300 °C.



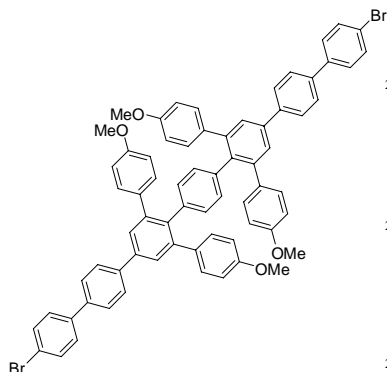
240

245 **3f**. A mixture of **1f** (2.47 g, 4.7 mmol), **2** (0.53 g, 2.3 mmol) and Ac₂O (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. δ_H (400 MHz, CDCl₃) 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*
250 3.09, 6H), 1.41 (s, 18H), 1.35 (d, *J* 2.77, 18H); δ_C (400 MHz, CDCl₃) 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 (CH₂Cl₂): λ_{max} = 308 nm; fluorescence (CH₂Cl₂): λ = 380 nm; MS (FAB): *m/z* = 970.5; m.p.: >300 °C.



255

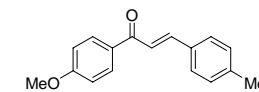
3g. To a suspension of **2** (0.99 g, 4.15 mmol) in Ac₂O (13 mL), **1g** (5.1 g, 8.3 mmol) was added over a period of 4.5 h at 150 °C. After addition of **1g**, 1680 mg of **2** and 3 mL Ac₂O were added and the mixture was stirred for 2.5 h at 150 °C. After cooling to room temperature, the solution was 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. δ_H (400 MHz, CDCl₃) 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); δ_C (400 MHz, CDCl₃) 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 (CHCl₃): λ_{max} = 249 nm; fluorescence (CHCl₃): λ = 389 nm; MS (MALDI-TOF): *m/z* = 1116.2; m.p.: > 300 °C.

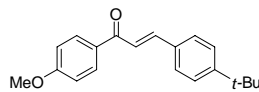
270

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 H₂O) and stirred for 10 minutes. 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. δ_H (400 MHz, CD₂Cl₂) 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); δ_C (400 MHz, CD₂Cl₂) 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.



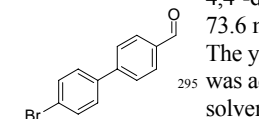
280

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 H₂O, 75 mL) and stirred for 10 minutes. 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. δ_H (400 MHz, CDCl₃) 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); δ_C (300 MHz, CD₂Cl₂) 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.



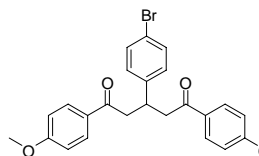
290

6. Compound **6** was synthesized by a modified method from Ferreira et al.³. Under an argon atmosphere, a solution of 4,4'-dibromobiphenyl (20g, 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 Na₂SO₄. 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). δ_H (300 MHz, THF-*d*₈) 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); δ_C (300 MHz, THF-*d*₈) 193.0, 147.5, 141.1, 138.4, 134.3, 132.2, 131.2, 129.5, 124.8; MS (EI): *m/z* = 260.0.



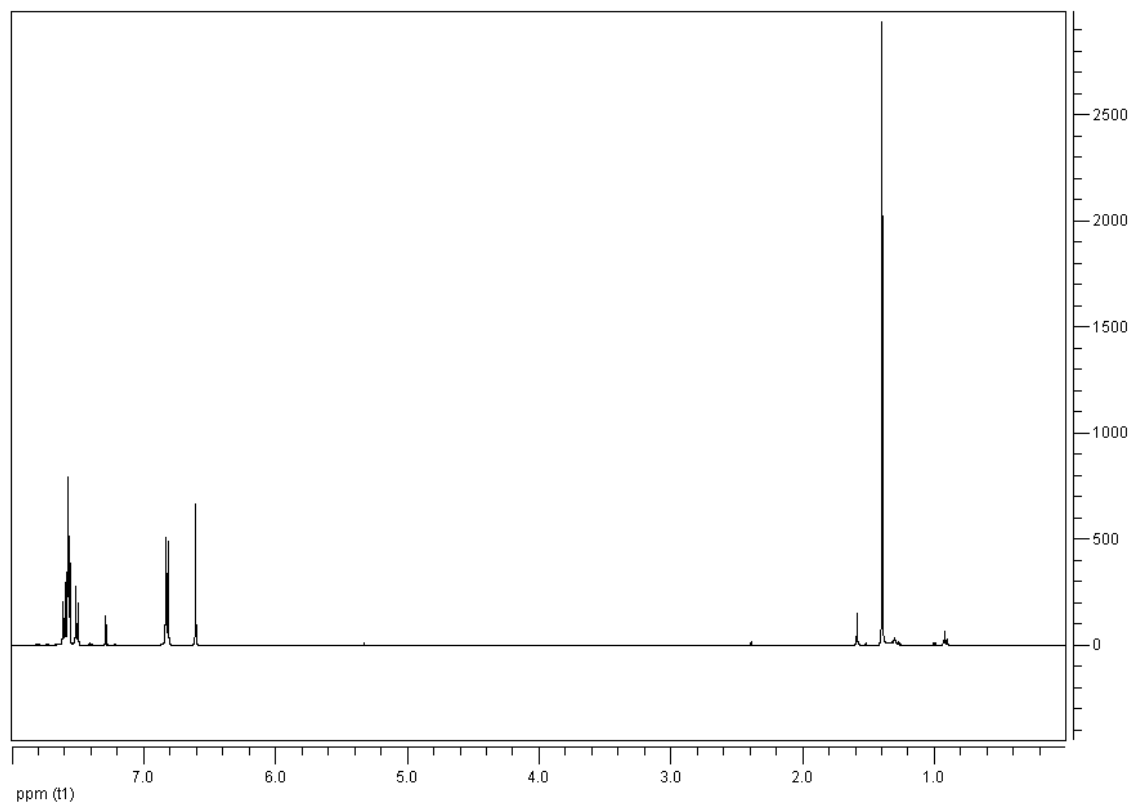
300

7: To a solution of 4-bromobenzaldehyde (50 g, 270 mmol) and 4-methoxyacetophenone (101.5 g, 677 mmol) in 500 mL ethanol, NaOH (40% in H₂O, 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 %). δ_H (250 MHz, CD₂Cl₂) 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); δ_C (400 MHz, CDCl₃) 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

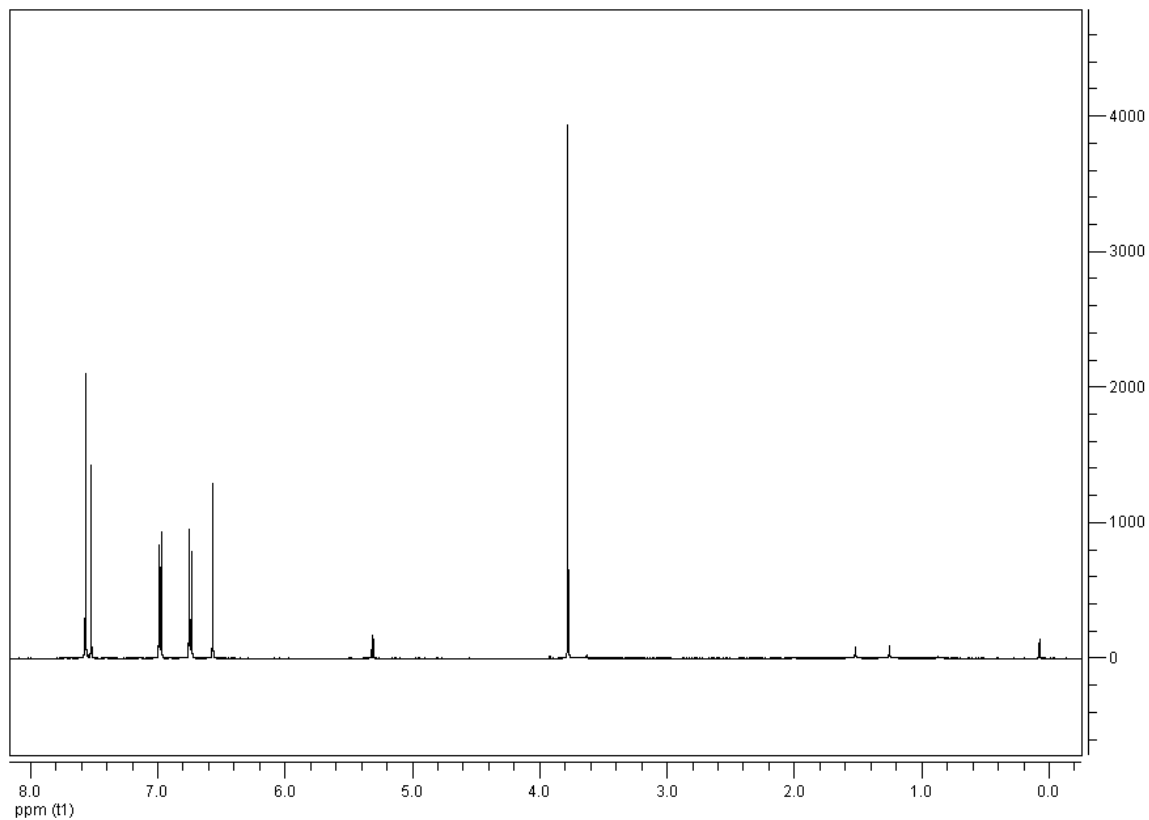


¹H NMR spectra of compounds 3a – 3g

315 **3a**

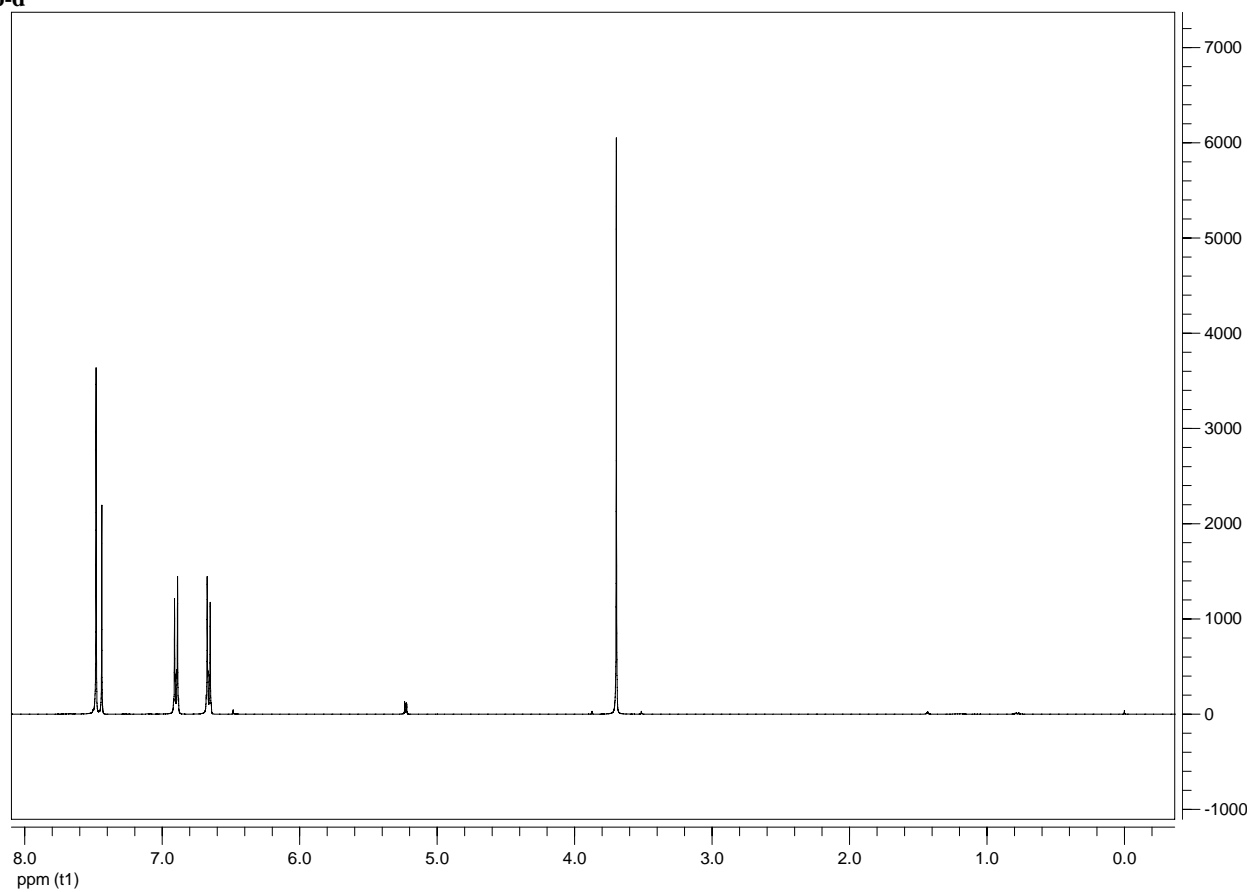


3b

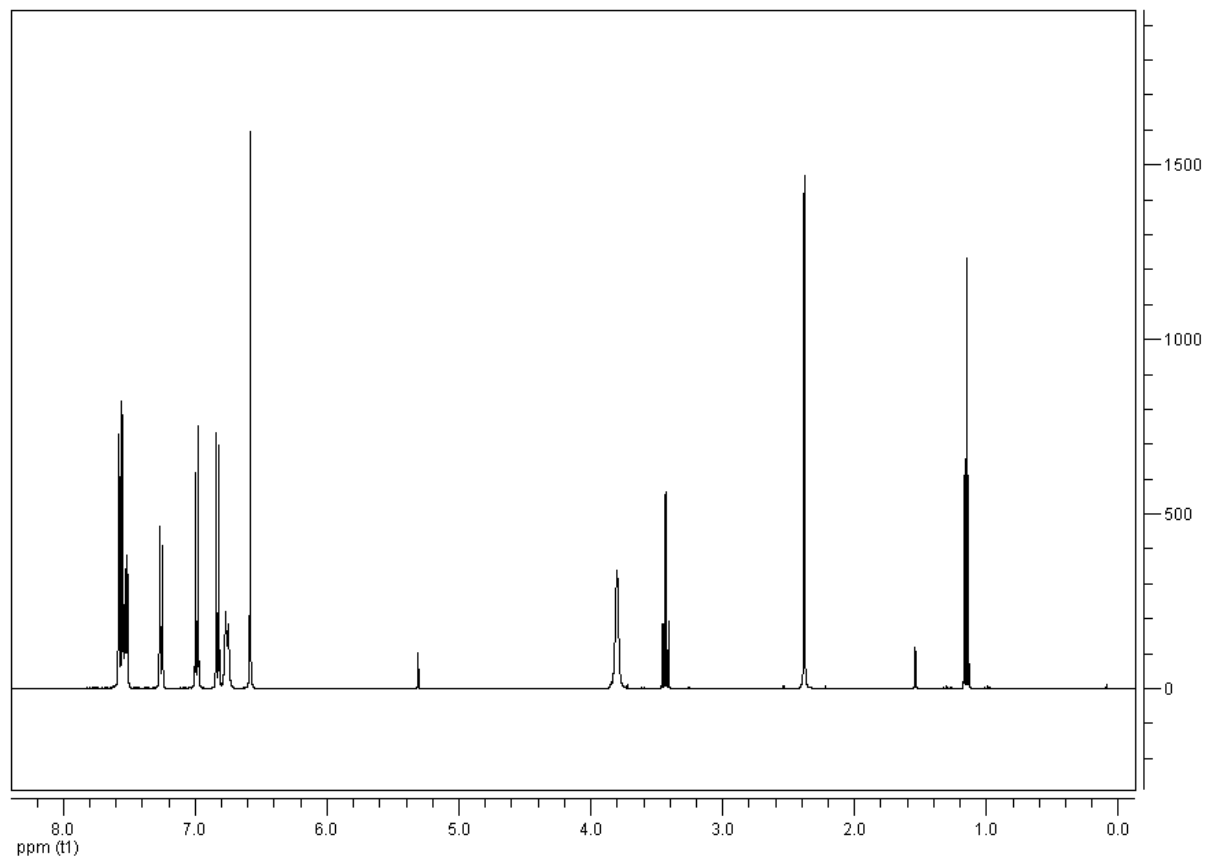


320

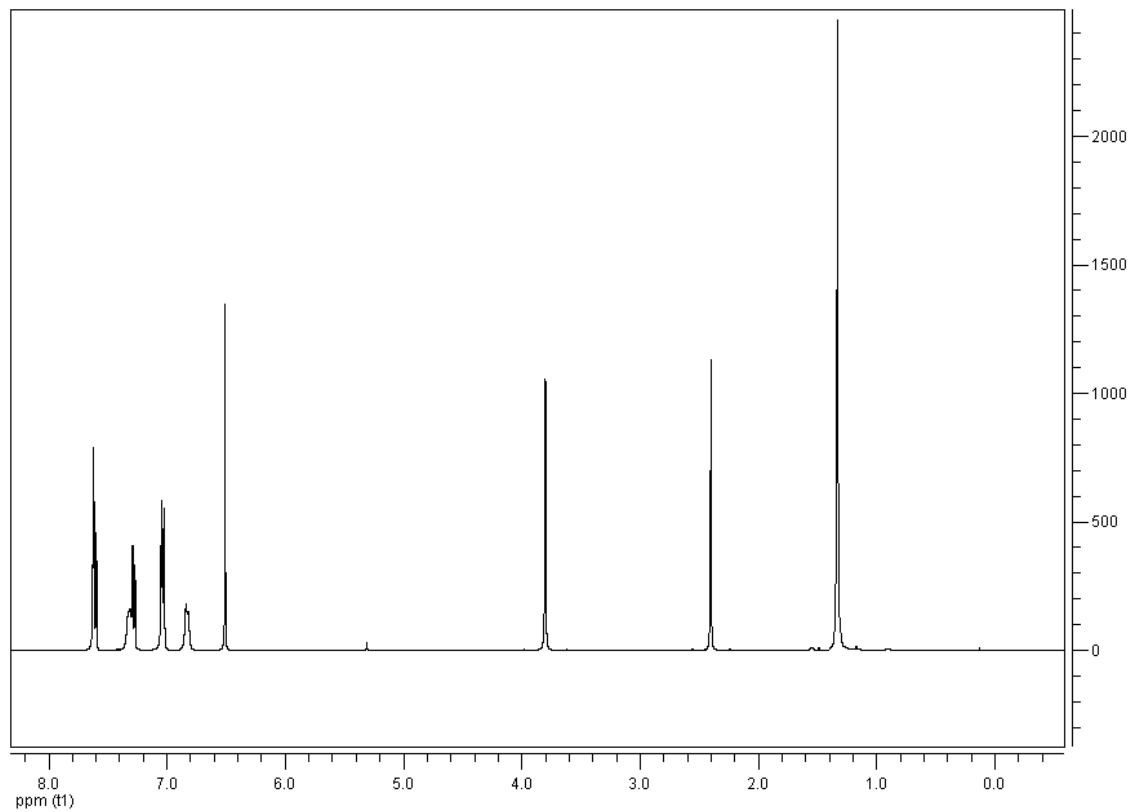
3b-d⁴



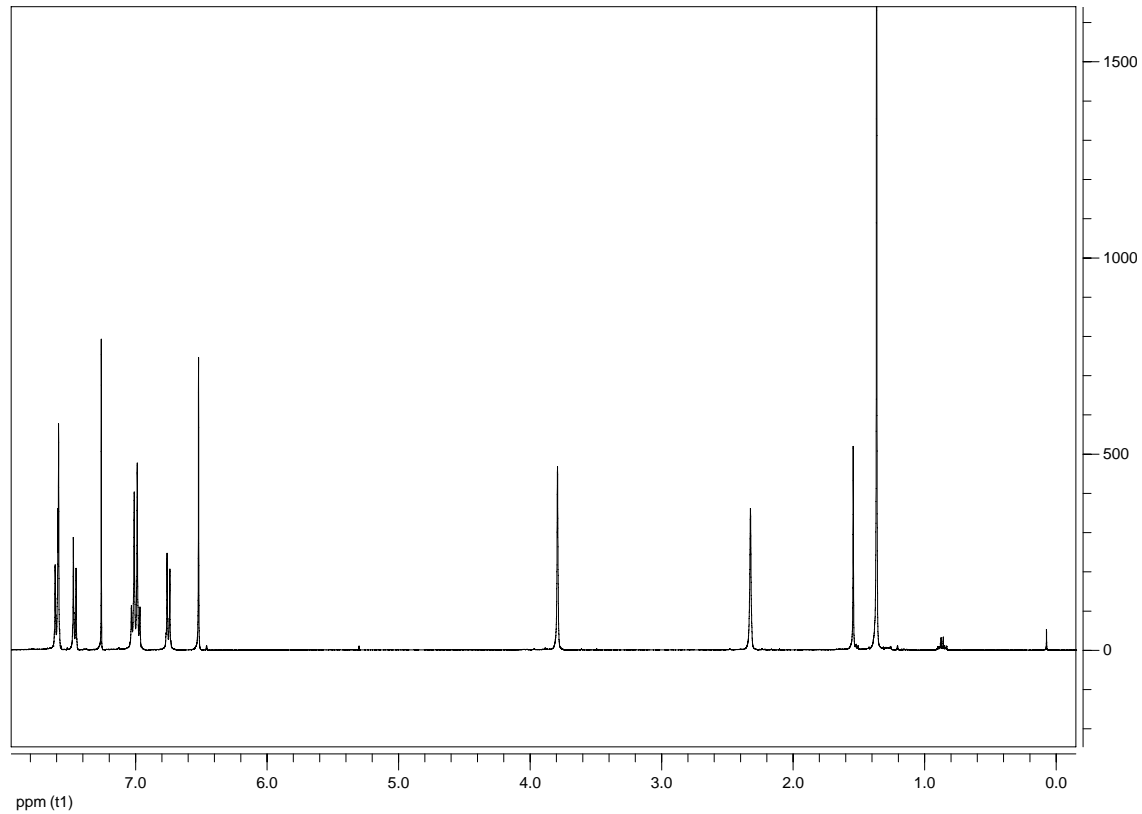
3c



325 **3d**

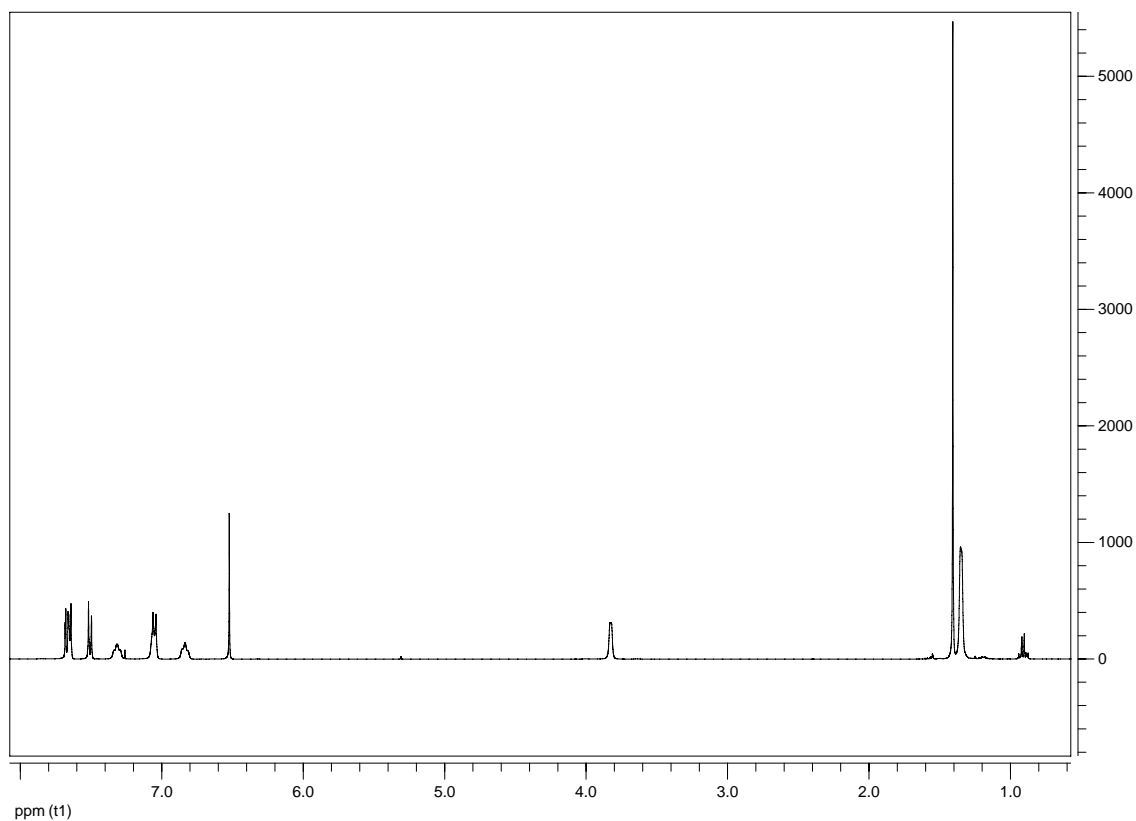


3e

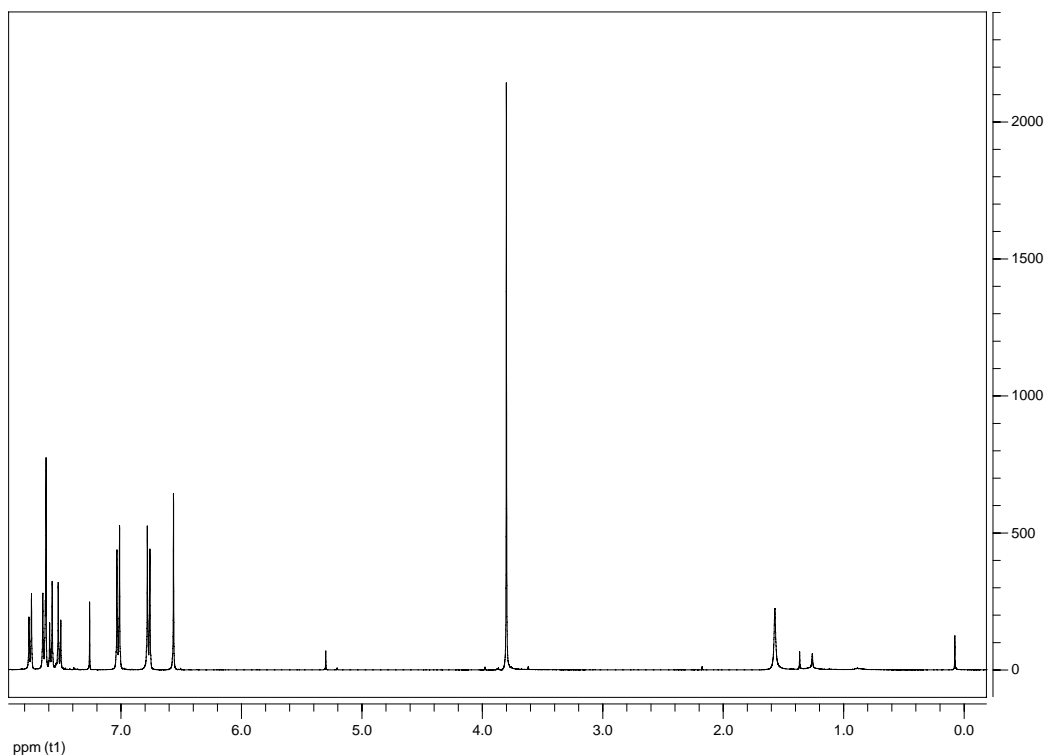


330

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. Bezuidenhout, D. J. Ferreira, *J. Chem. Soc., Perkin Trans. 1*, 1997, 1141-1146.