Supplementary Material (ESI) for Chemical Communications

Simplified Methods for the Functionalisation of 3-Hexoxythiophenes at 5-Position and Further Reactions to Alkynyl and Vinyl Derivatives.

Supporting Information

Mike Joachim Zöllner,[a] Ullrich Jahn,[b] Eike Becker, [a] Wolfgang Kowalsky,[a] Hans-Hermann Johannes*[a]

*author to whom correspondence should be addressed:

e-mail: h2.johannes@ihf.tu-bs.de

phone: +49-531-391-2006

fax: +49-531-391-8004

[a] *Labor für Elektrooptik am Institut für Hochfrequenztechnik, technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany. E-mail: h2.johannes@ihf.tu-bs.de, phone: +49-531-391-2006, fax: +49-531-391-8004*

[b] *Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo Namesti 2, 16610 Prague, Czech Republic.*

General: All chemicals were used as supplied. Dry solvents stored over molecular sieve were used for all reactions except the Suzuki coupling. Reactions were performed in flame dried flasks under nitrogen atmosphere. 3-Hexoxythiophene **1**, 4-hexoxythiophene-2-boronicacid **4** and diethyl-(2,5-dibromothiophen-3-yl)methylphosphonate **13** were synthesised by literature procedures.[1,2,3]

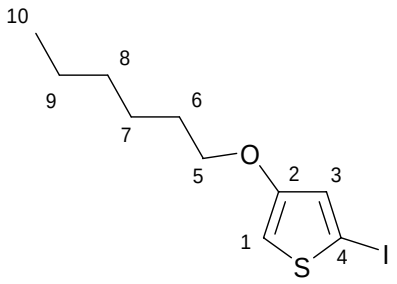
Chromatography: TLC plates and silica gel were purchased from Machery Nagel GmbH & Co KG.

Analytical methods: NMR experiments were recorded on a Varian MercuryPlus 200 (^{1}H NMR / 199.98 MHz; ^{13}C NMR / 50.29 MHz) and Bruker DRX-400 (^{1}H NMR / 400.14 MHz; ^{13}C NMR / 100.62 MHz). ^{1}H NMR resonances are referenced relative to tetramethylsilane (TMS) and ^{13}C NMR spectra to $CDCl_3$ at 77.3 ppm. Data are reported as follows: s = singlet, d = dublett, t = triplet, dd = doublet of doublets, dddd = doublet of doublets of doublet of doublets. If a signal can not be assigned to a special carbon or hydrogen clearly, the possible atom numbers are separated by a slash, e.g. 2/5/7. If one signal belongs to two ore more carbon or hydrogen atoms, the atom numbers are separated by a comma, e.g. 2,5,7. High and low resolution EI (electron ionisation at 70 eV) mass spectra measurements were performed by the Institut für Organische Chemie, Technische Universität Braunschweig using a Thermofinnigan MAT 95. Peak matching method was used at a resolution of 10000 with PFK as mass calibrant. Data are reported relative to the base ion, which is set to 100%. For recording GC-MS spectra, an Agilent 6890 gas chromatograph, equipped with a 30 m analytical column (Phenomenex ZB5-MS, 30m x 0.25 mm ID, t_f=0.25 µm), was used. A split injection port at 250°C was used for sample introduction and the split ratio was set to 10:1. Start temperature was set to 70 °C for 3 minutes. The rate of heating was 10 °C per minute to a final temperature of 310 °C. The helium carrier gas flow rate was set to 1.0 ml/minute (constant flow mode). The transfer line was kept at 250°C. A JMS-T100GC (GCAccuTOF, JEOL, Japan) time of flight mass spectrometer was used in electron ionization (EI) mode at 70eV. The source and transfer line temperature were set at 200°C and 270°C respectively. The detector voltage was set at 2000V. The acquisition range was from m/z 41 to 700 with spectrum recoding interval of 0.4 s. The system was tuned with PFK to achieve a resolution of 5000 (FWHM) at m/z 292.9824. UV-Vis and IR spectra were measured on Carry 100 Bio (Varian) and an ATR Diamond Tensor 27 (Bruker) instruments, respectively. IR bands are characterised by intensity: w - weak, m - medium, s - strong Elemental analyses was

performed by Institut für Pharmazeutische Chemie, Technische Universität Braunschweig. Melting points were determined using a Stuart Melting Point SMP3 instrument.

Cyclic Voltammetry: Cyclic Voltammetry was performed using a Metrohm μAutolab equipped with a 1 mm platin disc working electrode, a platin wire counter electrode and a saturated Ag/AgCl reference electrode. The ferrocene/ferrocenium redox couple was determined at 0.65 V. The electrolyte Bu_4NPF_6 was dissolved in acetonitrile to generate a 0.1 M stock solution. Monomer concentrations were set to 0.1 mM.

4-Hexoxy-3-iodothiophene (5):



Diisopropylamine (3.40 g, 33.60 mmol, 1.1 eq) and THF (30 ml) were cooled to –80 °C. *n*-Butyllithium (20.5 ml, 32.80 mmol, 1.1 eq, 1.6 M in hexane) was added slowly. The resulting solution was warmed to 0 °C for five minutes and recooled to –80 °C. 3-Hexoxythiophene (5.66 g, 30.76 mmol) was added dropwise and the mixture was stirred for 30 minutes. In a seprate flask iodine (7.76 g, 30.58 mmol, 1.0 eq) was dissolved in THF (20 ml), transferred into a syringe and added as quickly as possible in one shot to the vigorously stirred thienyllithium solution. The mixture decoloured within some seconds, indicating the end of the reaction. Aqueous $Na_2S_2O_3$ (40 ml) was immediately added to eliminate residual iodine and lithiated compounds. After warming to room temperature, the reaction mixture was extracted three times with CH_2Cl_2 (3x 120 ml). The combined organic layers were dried over $MgSO_4$, filtered and evaporated to drymess. Column chromatography (SiO_2, Hex:CH_2Cl_2 5:1, R_f = 0.46) gave a mixture of monoiodothiophene **5** and diiodothiophene **7** as a pale yellow oil (8.4 g, 88%). The ratio of **5** and **7** was determined by ^{1}H NMR and ranged from 6:1 to 9:1. The mixture can be used without further separation for subsequent syntheses of the acetylene derivatives **8, 9** and **10**, because the resulting products can be purified by chromatography more easily. When a vacuum distillation was performed after column chromatography (140 – 145 °C/1 mbar) **5** can be isolated in ratios of >50:1.

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 6.89 (d, $^4J_{3,1}$ = 1.8 Hz, 1 H, 3-H), 6.23 (d, $^4J_{1,3}$ = 1.8 Hz, 1H, 1-H), 3.88 (t, $^3J_{5,6}$ = 6.5 Hz, 2H, 5-H), 1.82 – 1.65 (m, 2 H, 6-H), 1.51 – 1.23 (m, 6 H, 7 – 9 H), 0.90 (t, $^3J_{10,9}$ = 6.6 Hz, 3 H, 10-H); **^{13}C NMR** ($CDCl_3$, 50 MHz): δ = 158.1 (s, C-2), 129.3 (d, C-3), 103.4 (d, C-1), 72.5 (s, C-4), 70.5 (t, C-5), 31.8 (t, C-8), 29.3 (t, C-6), 25.9 (t, C-7), 22.8 (t, C-9), 14.3 (q, C-10); **GC:** t_R [min] = 12.83 (**5**), 15.99 min (**7**); **GC-MS:** t_R [min] (M^+) = 16.90 (310), 20.11 (436);); **UV/Vis** (CH_2Cl_2): λ [nm] (ε) = 266 (4800), 234 (8500); **FT-IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3115 (w), 2952 (w), 2927 (w), 2857 (w), 1538 (s), 1467 (w), 1419 (w), 1354 (s), 1166 (s), 1046 (w), 1025 (m), 971 (w), 939 (w), 904 (w), 862 (w),

817 (m), 726 (w); **Elemental analysis** ($C_{10}H_{15}OIS$, 310.2): calc. C 38.72 H 4.87 S 10.34 found C 38.70 H 4.73 S 9.87.

The signal of the β-proton at δ = 6.80 ppm (s, 1 H) is characteristic for diiodothiophene **7** in ^{1}H NMR (figure 1).

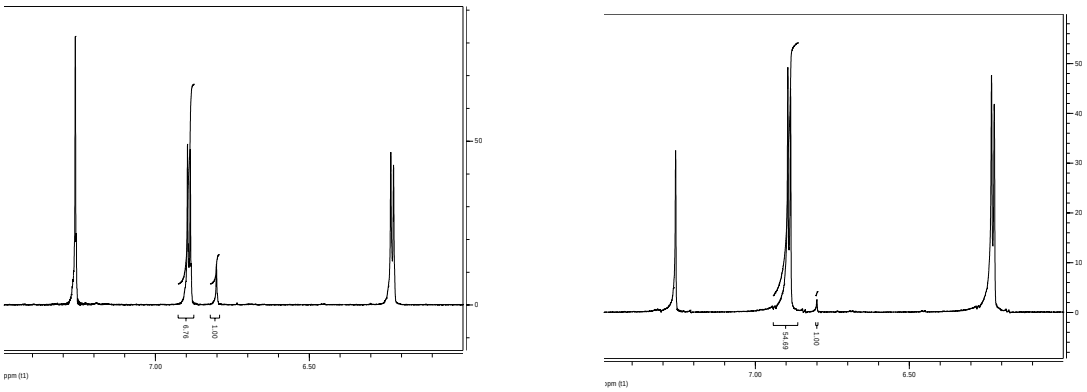
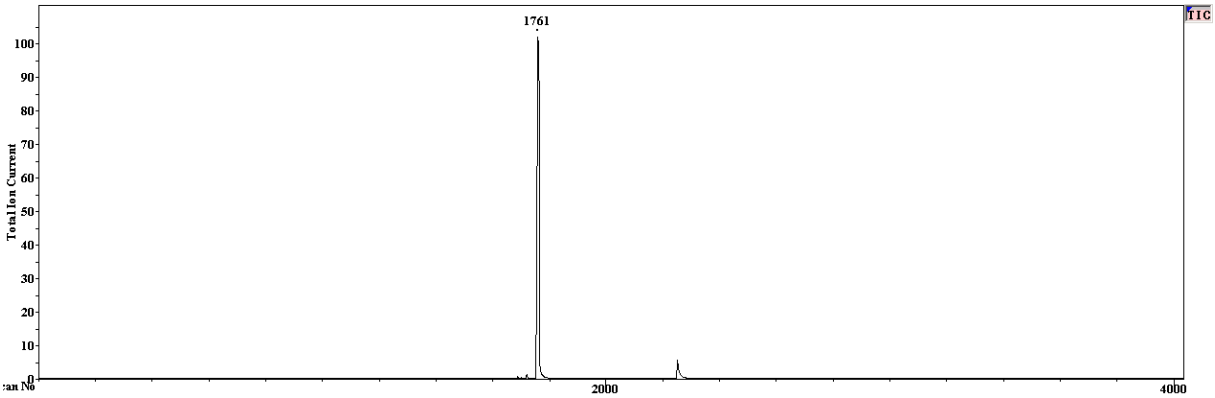
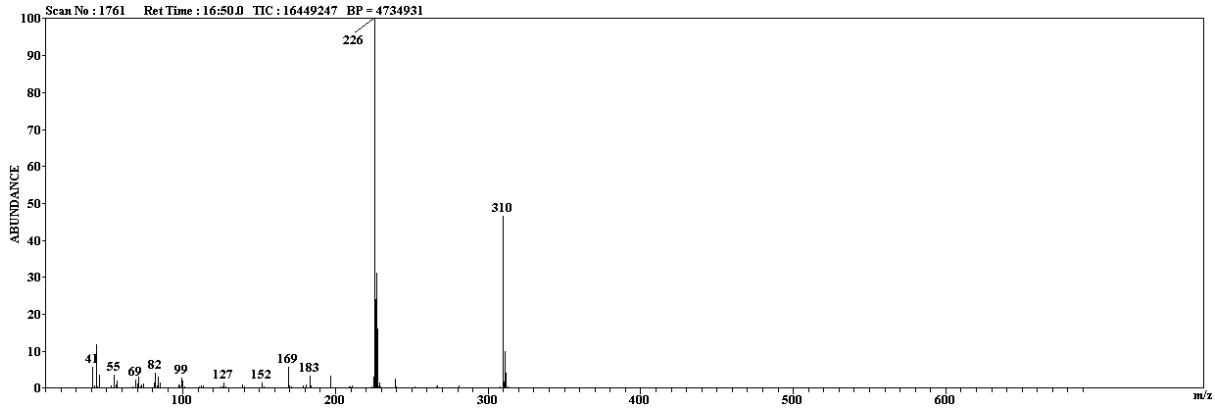


Figure 1: ^{1}H NMR data of the aromatic region of **5** after column chromatography (left) and distillation (right).



Peak #	RT	Start	End	Abs Area	Area(%)	Height
1	16.84	16.77	17.36	144638061	94.118	16449247
2	20.11	20.07	20.55	9039594	5.882	879549



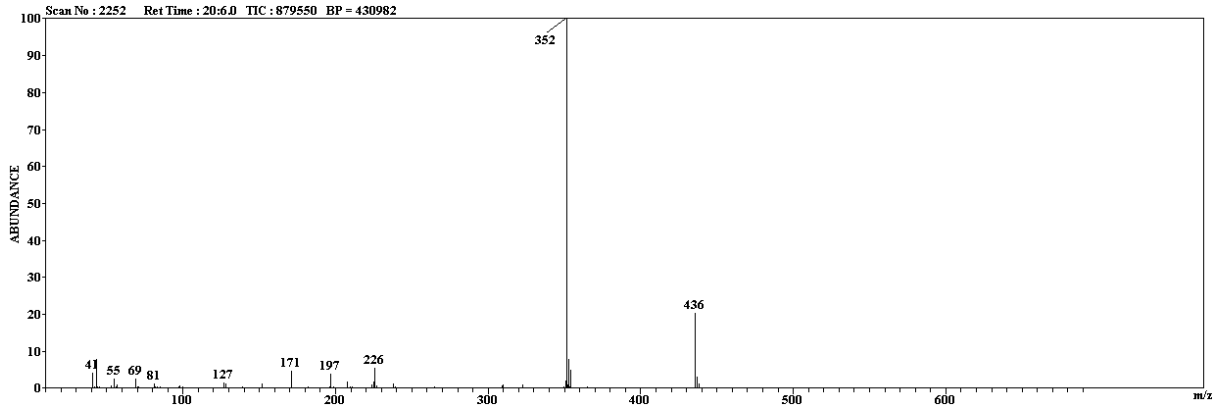
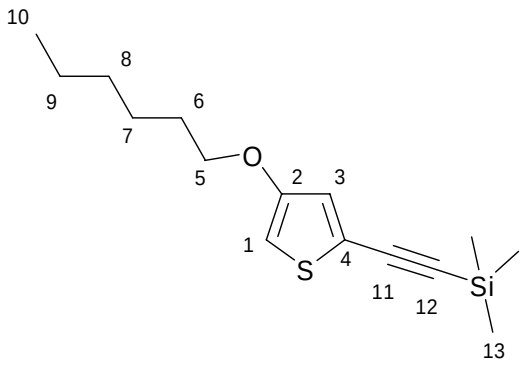


Figure 4: GC-MS data of **5** after column chromatography and distillation.

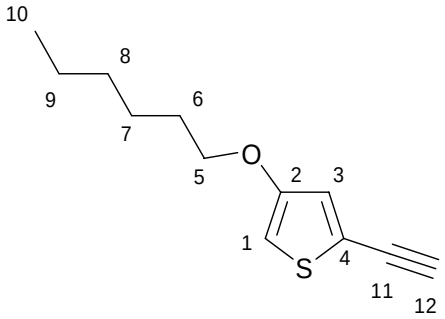
4-Hexoxy-2-(trimethylsilylethynyl)thiophene (8):



Trimethylsilylacetylene (2.26 g, 23.00 mmol), diisopropylamine (3.04 g, 30.00 mmol), $PdCl_2(PPh_3)_2$ (670 mg) and CuI (95 mg) were consecutively added to a stirred solution of pure iodothiophene **5** (5.00 g, 16.12 mmol) in THF (30 ml). After stirring at room temperature for two hours DC indicated consumption of **5** and water (100 ml) was added. The mixture was extracted three times with CH_2Cl_2 (3 x 80 ml). The combined organic layers were dried ($MgSO_4$), filtered and concentrated in vacuum. Column chromatography (SiO_2, Hex:CH_2Cl_2 10:1, R_f = 0.39) provided 4.45 g (15.86 mmol, 98%) of **8** as pale yellow oil .

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 6.63 (d, $^4J_{3,1}$ = 1.7 Hz, 1 H, 3-H), 5.91 (d, $^4J_{1,3}$ = 1.7 Hz, 1H, 1-H), 3.67 (t, $^3J_{5,6}$ = 6.5 Hz, 2H, 5-H), 1.59 – 1.42 (m, 2 H, 6-H), 1.27 – 1.00 (m, 6 H, 7 – 9 H), 0.67 (t, $^3J_{10,9}$ = 6.6 Hz, 3 H, 10-H), 0.00 (s, 9 H, 13-H); **^{13}C NMR** ($CDCl_3$, 50 MHz): δ = 156.7 (s, C-2), 124.4 (d, C-3), 121.9 (s, C-4), 100.0 (d, C-1), 98.8 (s, C-12), 98.0 (s, C-11), 70.5 (t, C-5), 31.7 (t, C-8), 29.3 (t, C-6), 25.8 (t, C-7), 22.8 (t, C-9), 14.2 (q, C-10), 0 (q, C13); **MS** (EI): *e/z* % 280 (23) [M^+], 196 (52), 181 (100); **HRMS** (EI): $C_{15}H_{24}OSSi$ calc. 280.1317 found 280.1321; **UV/Vis** (CH_2Cl_2): λ [nm] (ε) = 335 (900, sh), 297 (9100), 265 (10400), 256 (11400); **FT-IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3116 (w), 2957 (w), 2931 (w), 2860 (w), 2147 (w), 1545 (m), 1445 (w), 1366 (w), 1249 (w), 1178 (w), 1143 (m), 1025 (w), 839 (s), 758 (m); **Elemental analysis** ($C_{15}H_{24}OSSi$, 280.5): calc. C 64.23 H 8.62 S 11.43 found C 64.13 H 8.32 S 11.07.

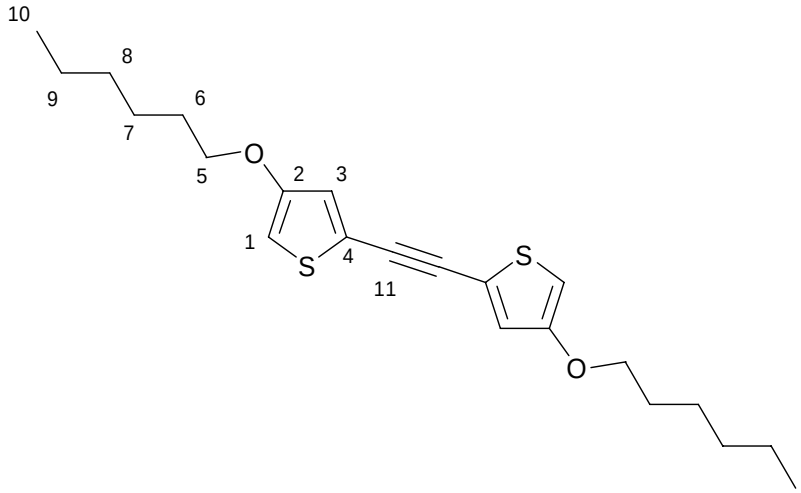
2-Ethynyl-4-hexoxythiophene (9):



Trimethylsilyl compound **8** (4.40 g, 15.69 mmol) was dissolved in methanol (20 ml). K_2CO_3 (5.2 g, 37.63 mmol) was added and the mixture was stirred at room temperature for two hours. DC indicated total consumption of the starting material. After addition of a saturated NH_4Cl solution (20 ml), the mixture was extracted with CH_2Cl_2 (3x 60 ml). The combined organic layers were dried ($MgSO_4$), filtered and evaporated. Column chromatography (SiO_2, Hex:CH_2Cl_2 5:1, R_f = 0.30) afforded 3.24 g (15.55 mmol, 99%) of **9** as pale yellow oil.

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 6.91 (d, $^4J_{3,1}$ = 1.7 Hz, 1 H, 3-H), 6.17 (d, $^4J_{1,3}$ = 1.7 Hz, 1H, 1-H), 3.91 (t, $^3J_{5,6}$ = 6.5 Hz, 2 H, 5-H), 3.30 (s, 1 H 12-H), 1.83 – 1.57 (m, 2 H, 6-H), 1.52 – 1.24 (m, 6 H, 7 – 9 H), 0.90 (t, $^3J_{10,9}$ = 6.7 Hz, 3 H, 10-H); **^{13}C NMR** ($CDCl_3$, 50 MHz): δ = 156.8 (s, C-2), 125.1 (d, C-3), 120.8 (s, C-4), 100.1 (d, C-1), 81.4 (d, C-12), 77.5 (s, C-11), 70.6 (t, C-5), 31.8 (t, C-8), 29.4 (t, C-6), 25.9 (t, C-7), 22.8 (t, C-9), 14.3 (q, C-10); **MS** (EI): *e/z* % 208 (20) [M^+], 124 (100); **HRMS** (EI): $C_{12}H_{16}OS$ calc. 208.0922 found 208.0929; **UV/Vis** (CH_2Cl_2): λ [nm] (ε) = 291 (6300), 248 (9900); **FT-IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3306 (w), 3118 (w), 2954 (w), 2929 (w), 2859 (w), 2105 (m), 1545 (s), 1443 (m), 1364 (m), 1174 (s), 1120 (m), 1023 (m), 874 (w), 829 (m), 711 (m); **Elemental analysis** ($C_{12}H_{16}OS$, 208.3): calc. C 69.19 H 7.74 S 15.39 found C 69.25 H 7.49 S 15.15.

1,2-Bis[4-(hexoxy)thiophen-2-yl]ethyne (10):

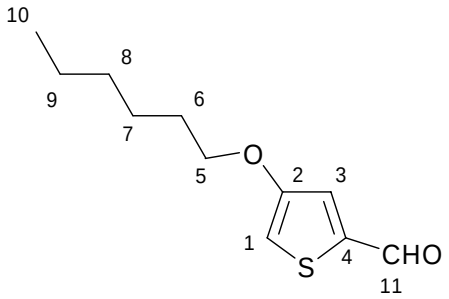


2-Iodothiophene **5** (500 mg, 1.61 mmol), 2-ethynylthiophene **9** (416 mg, 2.00 mmol), diisopropylamine (305 mg, 3.01 mmol) and $PdCl_2(PPh_3)_2$ (70 mg) were dissolved in THF (5 ml) and CuI (20 mg) was added. The solution was stirred at room temperature for three days. DC showed a new spot, which could be assigned to the product later. CH_2Cl_2 (50 ml) was added and the organic layer was washed first with water (50 ml) and then with brine (50 ml). The organic layer was dried ($MgSO_4$), filtered and evaporated. Column chromatography (SiO_2, Hex:CH_2Cl_2 2:1, R_f = 0.78) gave **10** as a dark red solid (580 mg, 1.48 mmol, 92%). In ^{1}H NMR a small amount of a contaminant was observed which can be removed by refluxing the solid in methanol (5 ml). The yellow coloured methanol phase was transferred via a pipette to another flask while still hot. Cooling of the solution in a refrigerator gave yellow crystals (m.p. 71 °C). Alternatively, the red solid can be sublimed (275 °C / 1 mbar) to yield the same yellow solid.

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 6.90 (d, $^4J_{3,1}$ = 1.7 Hz, 2 H, 3-H), 6.22 (d, $^4J_{1,3}$ = 1.7 Hz, 2 H, 1-H), 3.93 (t, $^3J_{5,6}$ = 6.5 Hz, 4 H, 5-H), 1.84 – 1.67 (m, 4 H, 6-H), 1.51 – 1.25 (m, 12 H, 7 – 9 H), 0.90 (t, $^3J_{10,9}$ = 6.5 Hz, 6 H, 10-H); **^{13}C NMR** ($CDCl_3$, 50 MHz): δ = 157.1 (s, C-2), 124.0 (d, C-3), 121.5 (s, C-4), 100.5 (d, C-1), 86.7 (s, C-11), 70.6 (t, C-5), 31.8 (t, C-8), 29.4 (t, C-6), 25.9 (t, C-7), 22.8 (t, C-9), 14.3 (q, C-10); **MS** (EI): *e/z* % 390 (53) [M^+], 306 (19), 222 (100); **HRMS** (EI): $C_{22}H_{30}O_2S_2$ calc. 390.1687 found 390.1675; **UV/Vis** (CH_2Cl_2): λ [nm] (ε) = 342 (14200), 330 (17400), 278 (12000), 261 (12500); **FT-IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3125 (w), 2937 (m), 2922 (m), 2865 (m), 2852 (m), 1560 (m), 1484 (w), 1466 (m), 1371 (m), 1345 (w), 1243 (m), 1172 (s), 1125 (m), 1057 (w), 1024 (s), 1003 (w), 958 (w), 869 (m),

827 (m), 732 (m), 700 (s); **Elemental analysis** ($C_{22}H_{30}O_2S_2$, 390.6): calc. C 67.65 H 7.74 S 16.42 found C 67.77 H 7.60 S 16.00.

2-Formyl-4-hexoxythiophene (6):

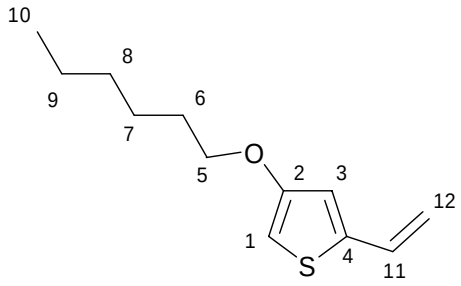


Diisopropylamine (20 ml) and THF (50 ml) were cooled to –80 °C. *n*-Butyllithium (22.5 ml, 36.00 mmol, 1.6 M in hexane) was added slowly. The solution was warmed to 0 °C for five minutes and recooled to –80 °C. 3-Hexoxythiophene (5.48 g, 29.73 mmol) was added dropwise and the mixture was stirred for further 30 minutes. DMF (7.40 g, 84.24 mmol) was added at once to the solution. After one hour at –80 °C the reaction was warmed to 0 °C and stirring was continued for another hour. DC showed almost total conversion of the starting material. The mixture was hydrolyzed with aqueous KOH (5%, 100 ml) and stirred for ten minutes. The aqueous layer was extracted with CH_2Cl_2 (3x 150 ml), the combined organic layers were washed with brine (100 ml), dried ($MgSO_4$) and evaporated. The crude product was purified by column chromatography (SiO_2, Hex:CH_2Cl_2 3:2, R_f = 0.20) to give **6** as a colourless oil (5.96 g, 28.07 mmol, 94%).

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 9.82 (d, $^4J_{11,1}$ = 1.2 Hz 1 H, 11-H), 7.40 (d, $^4J_{3,1}$ = 1.8 Hz, 1 H, 3-H), 6.22 (dd, $^4J_{1,3}$ = 1.8 Hz, $^5J_{1,11}$ = 1.2 Hz, 1 H, 1-H), 3.97 (t, $^3J_{5,6}$ = 6.5 Hz, 2 H, 5-H), 1.86 – 1.70 (m, 2 H, 6-H), 1.54 – 1.24 (m, 6 H, 7 – 9 H), 0.91 (t, $^3J_{10,9}$ = 6.5 Hz, 3 H, 10-H); **^{13}C NMR** ($CDCl_3$, 50 MHz): δ = 183.0 (d, C-11), 158.4 (s, C-2), 141.4 (s, C-4), 126.9 (d, C-3), 108.5 (d, C-1), 71.0 (t, C-5), 31.8 (t, C-8), 29.3 (t, C-6), 25.9 (t, C-7), 22.8 (t, C-9), 14.3 (q, C-10); **MS** (EI): *e/z* % 212 (24) [M^+], 128 (100); **HRMS** (EI): $C_{11}H_{16}O_2S$ calc. 212.0871 found 212.0870; **UV/Vis** (CH_2Cl_2): λ [nm] (ε) = 327 (5000), 261 (12800); **FT-IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3104 (w), 2929 (w), 2858 (w), 1670 (s), 1551 (m), 1441 (s), 1409 (w), 1355 (m), 1231 (m), 1184 (m), 1150 (w), 1020 (m), 917 (w), 877 (w), 836 (w), 725 (m);

Elemental analysis ($C_{11}H_{16}O_2S$, 212.3): calc. C 62.23 H 7.60 S 15.10 found C 62.02 H 7.47 S 14.70.

4-Hexoxy-2-vinylthiophene (11):



1. method (Stille coupling):

2-Iodothiophene **5** (1.00 g, 3.22 mmol) was dissolved in DMF (50 ml). $PdCl_2(PPh_3)_2$ (50 mg) and tributylvinylstannane (1.51 g, 4.76 mmol) were added and the mixture was heated to 60 °C for two days. Although DC did not show any changes workup was started .The reaction mixture was cooled to room temperature and water (30 ml) was added. The mixture was extracted with CH_2Cl_2 (3x 50 ml), dried ($MgSO_4$) and evaporated. Column chromatography (SiO_2, Hex:CH_2Cl_2 5:1, R_f = 0.60) provided **11** as a slightly yellow oil (550 mg, 2.60 mmol, 81%). NMR analysis revealed that **11** is still contaminated with tributyltin units (figure 5, ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 28.1, 27.1, 17.8, 13.9).

2. method (Wittig reaction), which is preferred for synthesis 11:

A solution of methyl(triphenyl)phosphonium bromide (3.37 g, 9.42 mmol) and KO^{t}Bu (1.37 g, 12.20 mmol) in THF (100 ml) was stirred at 0 °C for 15 minutes. Aldehyde **6** (1.00 g, 4.70 mmmol) was added dropwise. After 2.5 h, saturated NH_4Cl (50 ml) was added to the mixture. The layers were separated and the aqueous one was extracted three times with CH_2Cl_2 (3x 50 ml). The combined organic layers were dried ($MgSO_4$), filtered and evaporated. Column chromatography (SiO_2, Hex:CH_2Cl_2 5:1, R_f = 0.60) gave **11** as a colourless oil (970 mg, 4.60 mmol, 98%).

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 6.76 (dddd, $^3J_{11,12trans}$ = 17.2 Hz, $^3J_{11,12cis}$ = 11.0 Hz, $^4J_{11,3}$ = 0.5 Hz, $^5J_{11,1}$ = 0.5 Hz, 1 H, 11-H), 6.66 (d, $^4J_{3,1}$ = 1.6 Hz, 1 H, 3-H), 6.07 (d, $^4J_{1,3}$ = 1.6 Hz, 1 H, 1-H), 5.54 (d, $^3J_{12,11}$ = 17.2 Hz, 1 H, 12-H_{trans}), 5.12 (d, $^3J_{12,11}$ = 11.0 Hz, 1 H, 12-H_{cis}),

3.91 (t, $^3J_{5,6}$ = 6.5 Hz, 2 H, 5-H), 1.83 – 1.67 (m, 2 H, 6-H), 1.49 – 1.24 (m, 6 H, 7 – 9 H), 0.90 (t, $^3J_{10,9}$ = 6.6 Hz, 3 H, 10-H); **^{13}C NMR** ($CDCl_3$, 50 MHz): δ = 157.6 (s, C-2), 141.3 (s, C-4**)**, 130.2 (d, C-11), 118.1 (d, C-3), 113.4 (t C-12), 96.3 (d, C-1), 70.3 (t, C-5), 31.8 (t, C-8), 29.4 (t, C-6), 25.9 (t, C-7), 22.8 (t, C-9), 14.3 (q, C-10); **MS** (EI): *e/*z% 210 (18) [M^+], 126 (100); **HRMS** (EI): $C_{12}H_{18}OS$ calc. 210.1079 found 210.1082; **UV/Vis** (CH_2Cl_2): λ [nm] (ε) = 298 (5500), 258 (11500); **FT-IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3120 (w), 3090 (w), 2954 (w), 2929 (w), 2859 (w), 1623 (w), 1549 (s), 1458 (n), 1361 (m), 1227 (w), 1177 (m), 1149 (m), 1028 (m), 976 (m), 896 (m), 871 (w), 824 (m), 701 (m).

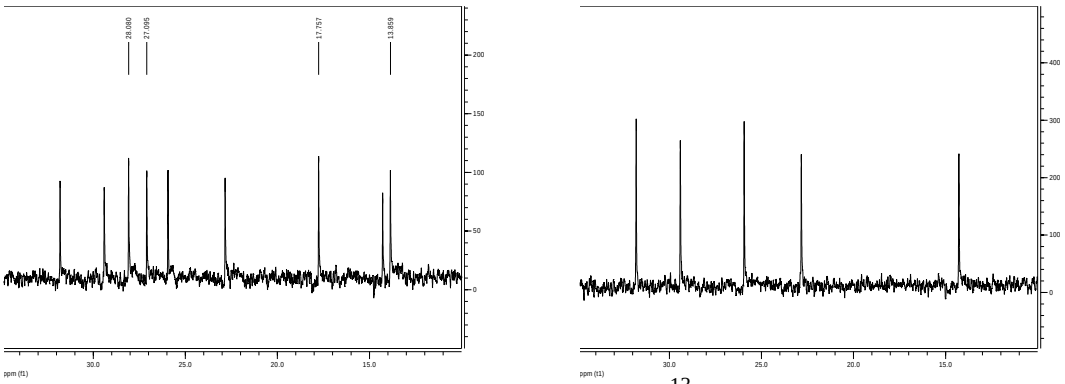
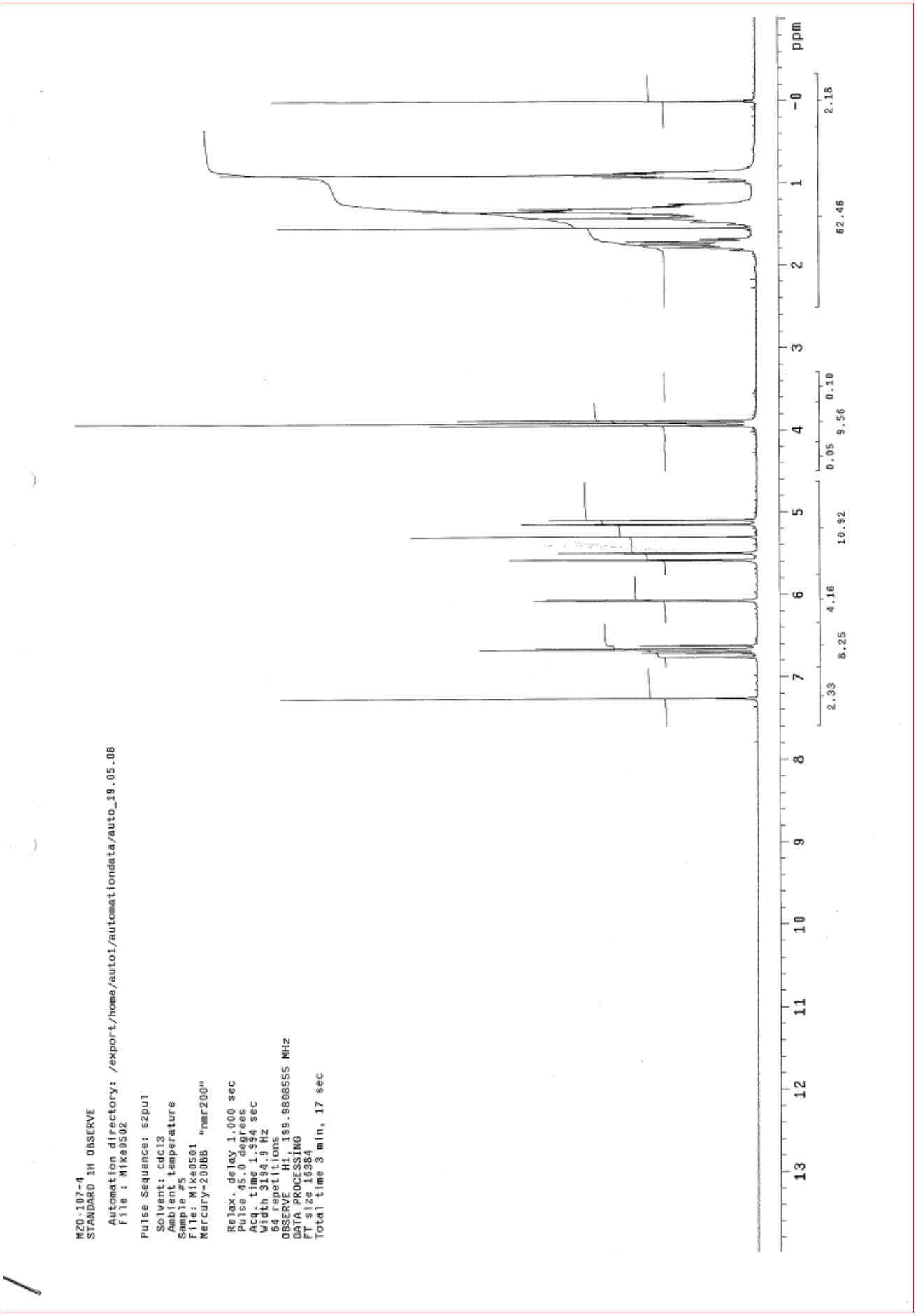
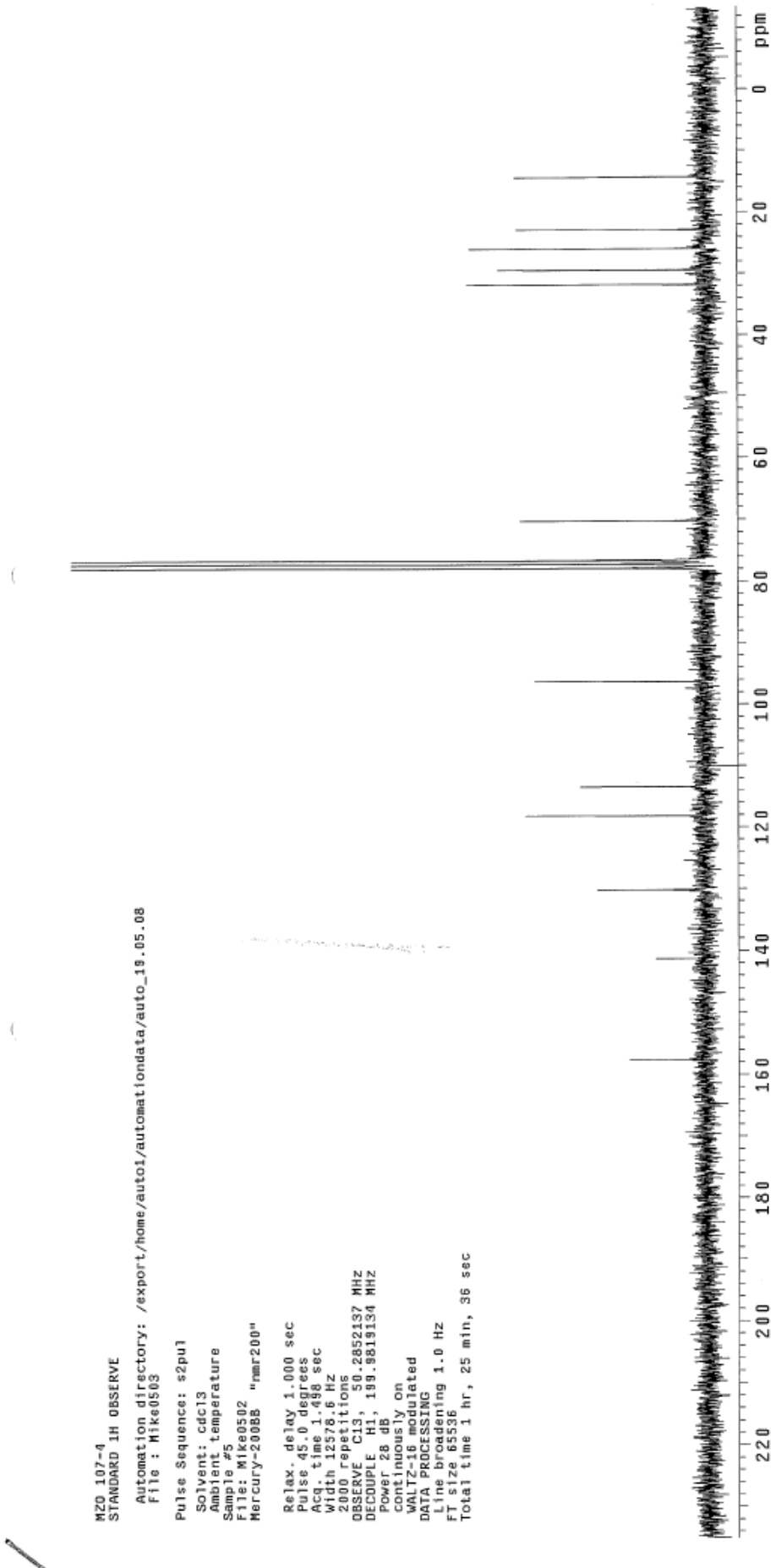
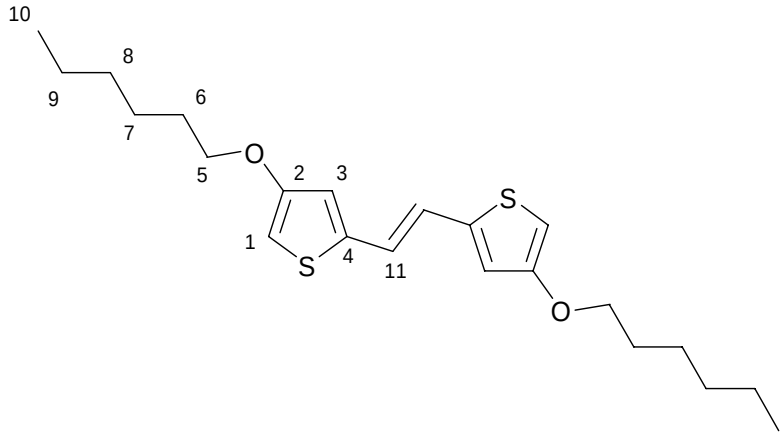


Figure 5: Stannane contamination can be identified by ^{13}C NMR: left Stille coupling, right Wittig reaction.


MZ0-107-4
STANDARD 1H OBSERVE
Automation directory: /export/home/auto1/automationdata/auto_19.05.08
File : Mike0502
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Sample #5
File: Mike0501
Mercury-200BB "mar200"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.994 sec
Width 3194.9 Hz
64 repetitions
OBSERVE H1, 199.9808555 MHz
DATA PROCESSING
FT size 16384
Total time 3 min, 17 sec
ppm
2.18
62.46
0.05
9.56
0.10
2.33
8.25
4.16
10.92


MZO 107-4
STANDARD 1H OBSERVE
Automation directory: /export/home/auto1/automationdata/auto_19.05.08
File : Mike0503
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Sample #5
File: Mike0502
Mercury-200BB "nmr200"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.488 sec
Width 12578.6 Hz
2000 repetitions
OBSERVE C13, 50.2852137 MHz
DECOUPLE H1, 199.9819134 MHz
Power 28 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 1 hr, 25 min, 36 sec
220
200
180
160
140
120
100
80
60
40
20
0
ppm

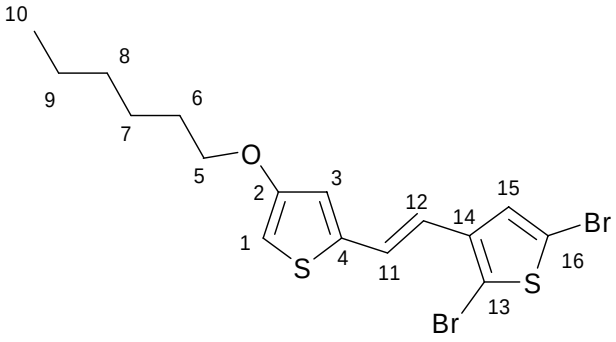
(*E*)-1,2-Bis[4-(hexoxy)thiophen-2-yl]ethene (12):



Vinylthiophene **11** (900 mg, 4.28 mmol) and Grubbs' 2nd generation catalyst (100 mg, 118 µmol, 3 mol%) were dissolved in toluene (15 ml). The mixture was refluxed for 18 hours. DC indicated almost complete consumption of the starting material. After cooling to room temperature the solvent was evaporated. Column chromatography (SiO2, Hex:CH_2Cl_2, 5:1, R_f = 0.17) gave a pale yellow solid (810 mg). This solid was recrystallised from ethanol (15 ml) to yield **12** as a pale yellow solid (680 mg, 1.73 mmol, 81%, m.p. 96 – 98 °C).

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 6.88 (s, 2 H, 11-H), 6.71 (d, $^4J_{3,1}$ = 1.6 Hz, 2 H, 3-H), 6.17 (d, $^4J_{1,3}$ = 1.6 Hz, 2 H, 1-H), 3.92 (t, $^3J_{5,6}$ = 6.5 Hz, 4 H, 5-H), 1.84 – 1.67 (m, 4 H, 6-H), 1.53 – 1.22 (m, 12 H, 7 – 9 H), 0.90 (t, $^3J_{10,9}$ = 6.7 Hz, 6 H, 10-H); **^{13}C NMR** ($CDCl_3$, 50 MHz): δ = 157.8 (s, C-2), 140.4 (s, C-4), 121.5 (d, C-11), 118.3 (d, C-3), 96.6 (d, C-1), 70.3 (t, C-5), 31.8 (t, C-8), 29.4 (t, C-6), 25.9 (t, C-7), 22.8 (t, C-9), 14.3 (q, C-10); **MS** (EI): *e/z* % 392 (100) [M^+], 224 (39), 226 (74); **HRMS** (EI): $C_{22}H_{32}O_2S_2$ calc. 392.1844 found 392.1840; **UV/Vis** (CH_2Cl_2): λ [nm] (ε) = 357 (21300), 285 (11800), 226 (6000); **FT-IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3108 (w), 2957 (w), 2918 (m), 2873 (m), 2853 (m), 1552 (m), 1476 (m), 1458 (m), 1369 (m), 1271 (m), 1202 (m), 1179 (m), 1153 (m), 1074 (w), 1044 (w), 999 (m), 981 (w), 936 (m), 915 (w), 869 (w), 819 (m), 707 (s); **Elemental analysis** ($C_{22}H_{32}O_2S_2$, 392.6): calc. C 67.30 H 8.22 S 16.33 found C 67.54 H 8.00 S 15.97.

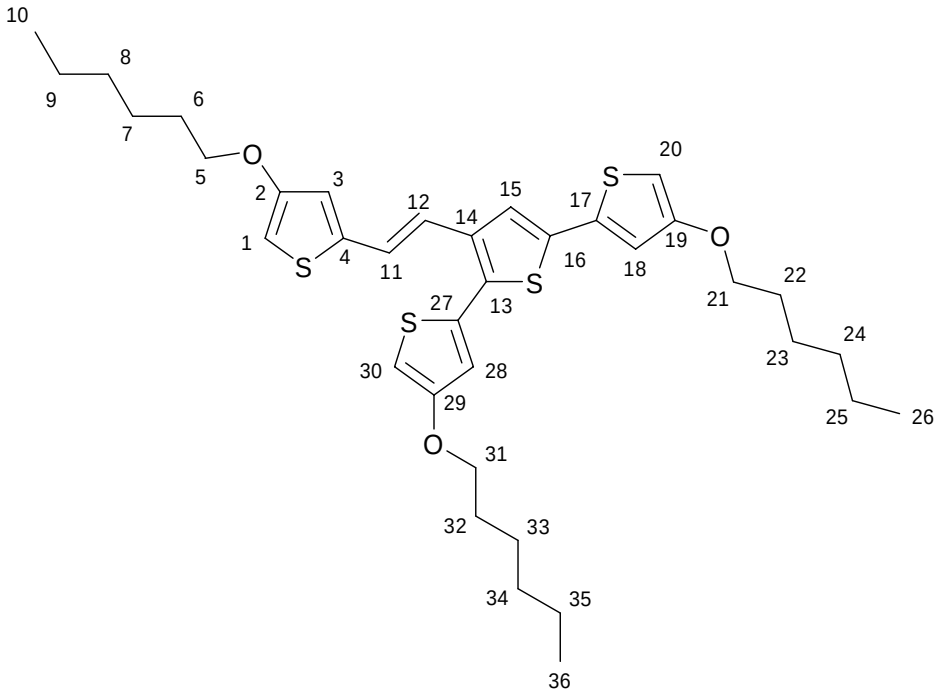
(E)-2,5-Dibromo-3-[2-(4-(hexoxy)thiophen-2-yl)vinyl]thiophene (14):



2-Formyl-4-hexoxythiophene **6** (1.80 g, 8.48 mmol) and phosphonate **13** were dissolved in DME (20 ml). NaH (420 mg, 10.50 mmol, 1.1 eq, 60% in mineral oil) was added and the reaction mixture was stirred at reflux for 90 minutes. After cooling to room temperature, water (50 ml) was added. The layers were separated and the aqueous was extracted three times with CH_2Cl_2 (3x 50 ml). The combined organic layers were dried ($MgSO_4$), filtered and evaporated. Column chromatography (SiO_2, Hex:CH_2Cl_2 2:1, R_f = 0.60) gave **14** as a yellow solid (3.20 g, 7.11 mmol, 83%, m.p. 78 – 80 °C).

^{1}H NMR (TMS, $CDCl_3$, 200 MHz): δ = 7.13 (s, 1 H, 15-H), 6.89 (d, $^3J_{12,11}$ = 16.1 Hz, 1 H, 12-H), 6.76 (d, $^4J_{3,1}$ = 1.5 Hz, 1 H, 3-H), 6.74 (d, $^3J_{11,12}$ = 16.1 Hz, 1 H, 11-H), 6.14 (d, $^4J_{1,3}$ = 1.5 Hz, 1 H, 1-H), 3.92 (t, $^3J_{5,6}$ = 6.5 Hz, 2 H, 5-H), 1.84 – 1.67 (m, 2 H, 6-H), 1.53 – 1.21 (m, 6 H, 7 – 9 H), 0.91 (t, $^3J_{10,9}$ = 6.4 Hz, 3 H, 10-H); **^{13}C NMR** ($CDCl_3$, 50 MHz): δ = 157.9 (s, C-2), 140.2 (s, C-4), 138.8 (s, C-14), 127.4 (d, C-15), 124.6 (d, C-12), 119.5 (d, C-11), 118.9 (d, C-3), 112.2 (s, C-13), 110.3 (s, C-16), 97.3 (d, C-1), 70.3 (t, C-5), 31.8 (t, C-8), 29.4 (t, C-6), 26.0 (t, C-7), 22.9 (t, C-9), 14.3 (q, C-10); **MS** (EI): *e/z* % 448/450/452 (9/20/11) [M^+], 206 (100); **UV/Vis** (CH_2Cl_2): λ [nm] (ε) = 341 (20900), 287 (15100), 274 (15800), 229 (11100); **FT-IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3115 (w), 3024 (w), 2951 (w), 2932 (m), 2853 (m), 1620 (w), 1552 (s), 1522 (m), 1452 (s), 1368 (m), 1346 (w), 1270 (m), 1181 (m), 1153 (m), 1127 (m), 1059 (w), 1024 (m), 1005 (m), 945 (s), 929 (m), 895 (w), 870 (m), 827 (w), 812 (m), 729 (w); **Elemental analysis** ($C_{16}H_{18}Br_2OS_2$, 450.3): calc. C 42.68 H 4.03 S 14.24 found C 42.55 H 4.03 S 14.14.

(*E*)-2,5-Bis[(4-(hexoxy)thiophen-2-yl)-3-[2-(4-(hexoxy)thiophen-2-yl]vinyl]thiophene (15):



A mixture of dibromide **14** (1.50 g, 3.33 mmol), boronic acid **4** (1.83 g, 8.00 mmol), $Pd(PPh_3)_4$ (390 mg), 2 M Na_2CO_3 solution (20 ml) and DME (25 ml) was stirred at reflux for two hours. The mixture was cooled to room temperature and water (50 ml) was added. The layers were separated and the aqueous was extracted three times with CH_2Cl_2 (3x 50 ml). The combined organic layers were dried ($MgSO_4$), filtered and evaporated. Column chromatography (SiO_2, Hex:CH_2Cl_2 2:1, R_f = 0.47) furnished **15** as a yellow oil (1.90 g, 2.89 mmol, 86%). Dissolving the oil in ethanol and cooling it for three days at –18 °C resulted a yellow solid precipitating.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.25 (s, 1 H, 15-H), 7.13 (d, $^3J_{12,11}$ = 15.9 Hz, 1 H, 12-H), 6.98 (d, $^3J_{11,12}$ = 15.9 Hz, 1 H, 11-H), 6.84 (d, $^4J_{18,20}$ = 1.7 Hz, 1 H, 18-H), 6.83 (d, $^4J_{28,30}$ = 1.7 Hz, 1 H, 28-H), 6.74 (d, $^4J_{3,1}$ = 1.6 Hz, 1 H, 3-H), 6.24 (d, $^4J_{30,28}$ = 1.7 Hz, 1 H, 30-H), 6.11 (d, $^4J_{20,18}$ = 1.7 Hz, 1 H, 20-H), 6.08 (d, $^4J_{1,3}$ = 1.6 Hz, 1 H, 1-H), 3.97 (t, ^3J = 6.6 Hz, 2 H, 5/21/31-H), 3.95 (t, ^3J= 6.4 Hz, 2 H, 5/21/31-H), 3.93 (t, ^3J= 6.4 Hz, 2 H, 5, 21 or 31-H), 1.82 – 1.73 (m, 6 H, 6,22,32-H), 1.54 – 1.29 (m, 18 H, 7 – 9,23 – 25,33 –35-H), 0.97 – 0.88 (m, 9 H, 10, 26, 36-H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 157.75 (s, C-29), 157.70 (s, C-2), 157.67 (s, C-19), 140.8 (s, C-4), 136.3 (s, C-16), 135.7 (s, C-13), 134.9 (s, C-17), 133.6 (s, C-

27), 132.0 (s, C-14), 123.6 (d, C-11), 121.7 (d, C-15), 121.0 (d, C-12), 119.1 (d, C-28), 117.8 (d, C-3), 116.5 (d, C-18), 98.6 (d, C-30), 96.8 (d, C-20), 96.6 (d, C-1), 70.24 (t, C-5/21/31), 70.20 (t, C-5/21/31), 70.1 (t, C-5/21/31), 31.6 (t, 3 C, C-8,24,34), 29.2 (t, 3 C, C-6,22,32), 25.7 (t, 3 C, C-7,23,33), 22.6 (t, 3 C, C-9,25,35), 14.0 (q, 3 C, C-10,26,36); **MS** (EI): *e/z* % 656/657/658 (100/42/25) [M^+]; **HRMS** (EI): $C_{36}H_{48}O_3S_3$ calc. 656.2487 found 656.2474; **UV/Vis** (CH_2Cl_2): λ [nm] (ε) = 345 (34900), 288 (20300), 227 (13600), 224 (13700); **FT-IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3120 (w), 2928 (m), 2856 (m), 1569 (w), 1551 (s), 1526 (m), 1488 (m), 1465 (m), 1350 (s), 1277 (w), 1168 (s), 1151 (s), 1070 (w), 1047 (w), 1031 (m), 1016 (w), 1000 (m), 918 (w), 863 (w), 828 (w), 809 (s), 725 (w).

CV-data:

Cyclic voltammetry measurements showed **15**s first oxidation peak at 1.12 V (figure **6**). This oxidation was irreversible due to the beginning of the polymerisation process. Polymerisation proceeded until the point, where overoxidation takes place. This point is indicated by decreasing currents, whereby the cycles collapse during further measurement. In case of choosing +1.75 V as 1st reverse potential degeneration begins after ten cycles. For lower reverse potentials, e. g. 1.50 V, degeneration was observed after 30 cycles. It can be concluded, that **15** forms a polymer, which seems not be stable under chosen conditions, especially higher anodic voltages.

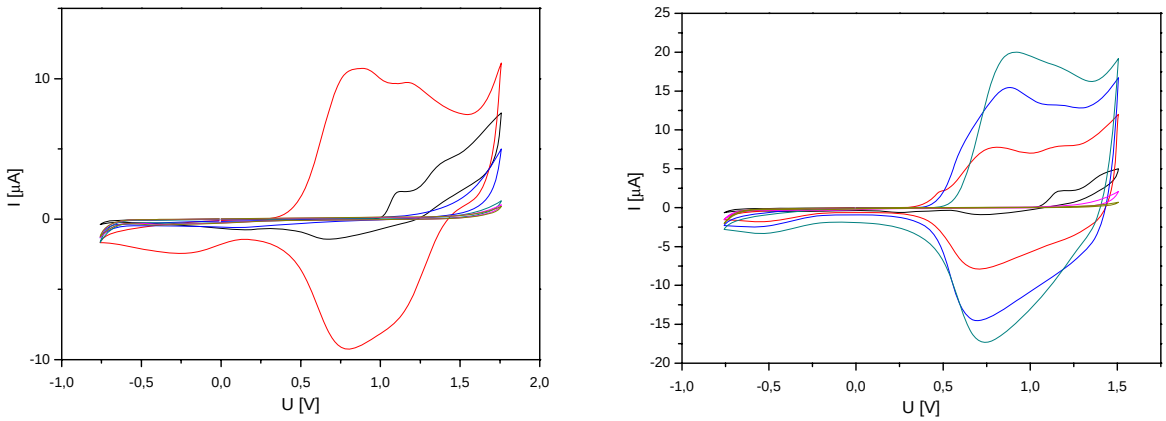
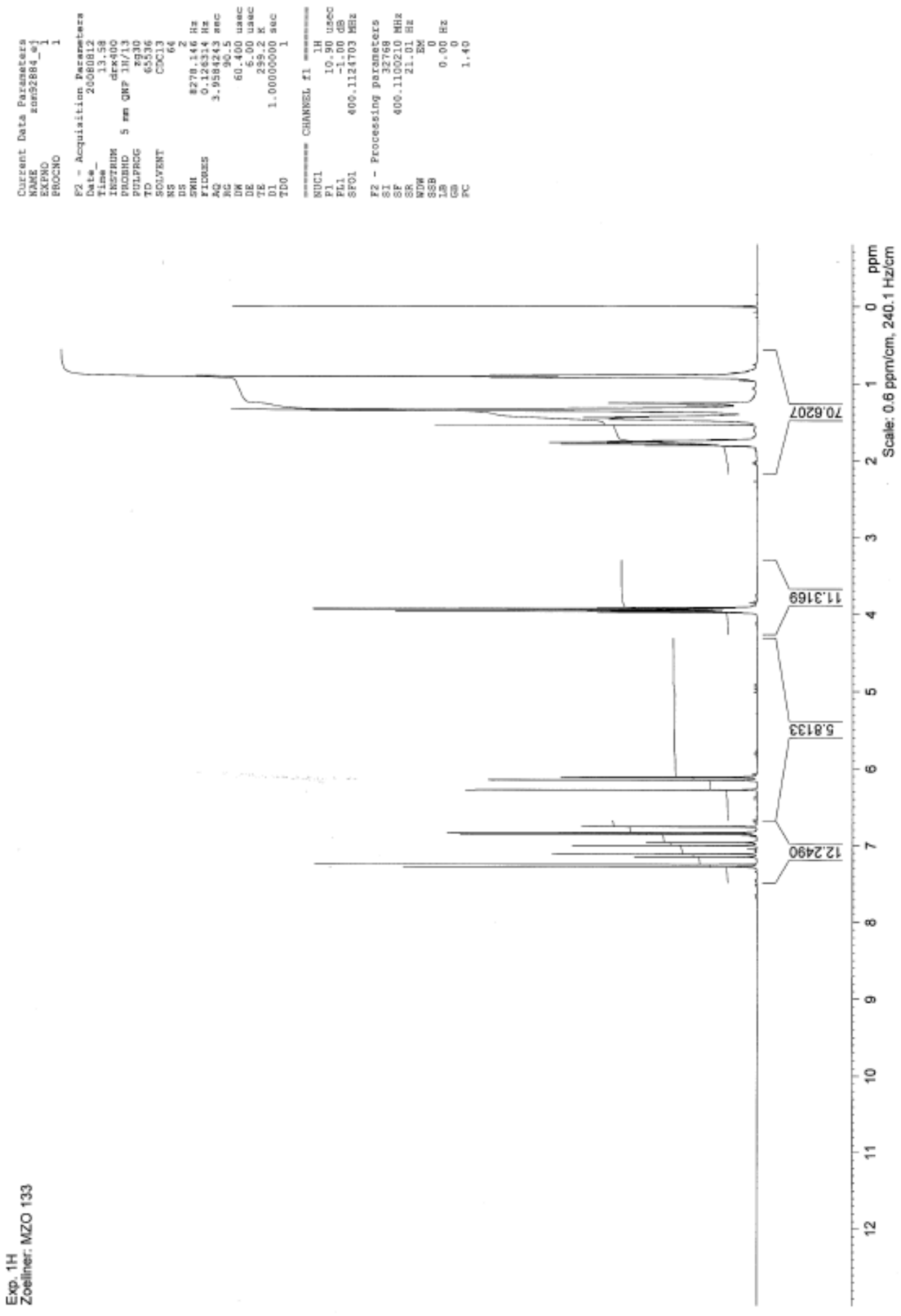
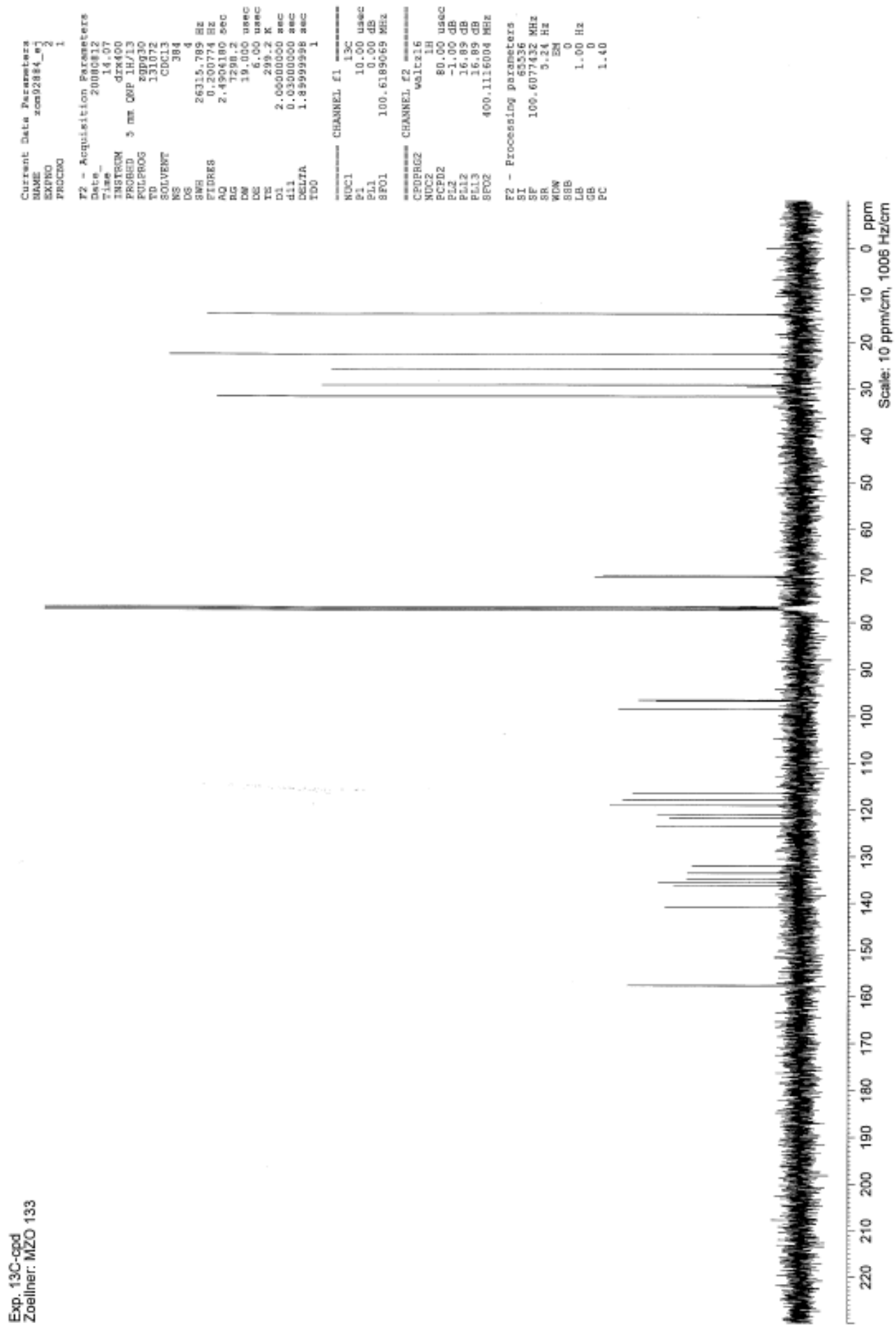


Figure 6: Cyclic voltammogram of **15**. 45 cycles, 1st reverse potential +1.75 V (left) and +1.50 V (right) respectively. 1st cycle (black), 10th cycle (red), 20th cycle(blue), 30th cycle(turquoise), 40th cycle(pink), 45th cycle(green).


Current Data Parameters
NAME zm92884_mj
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080812
Time 13.58
INSTRUM drx400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 90.5
DW 60.400 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.90 usec
PL1 -1.00 dB
SF01 400.1124703 MHz
F2 - Processing parameters
SI 32768
SF 400.1100210 MHz
SR 21.01 Hz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
70.6207
11.3169
5.8133
12.2490
ppm
Scale: 0.6 ppm/cm, 240.1 Hz/cm
Exp. 1H
Zoeliner: MZO 133


Exp. 13C-cpd
Zoellner: MZO 133
Current Data Parameters
NAME zcm92884_e1
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080812
Time 14.07
INSTRUM drx400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 384
DS 4
SWH 26315.789 Hz
FIDRES 0.200774 Hz
AQ 2.4904180 sec
RG 7298.2
DW 19.000 usec
DE 6.00 usec
TE 299.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13c
P1 10.00 usec
PL1 0.00 dB
SFO1 100.6189069 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 16.89 dB
PL13 16.89 dB
SFO2 400.1116004 MHz
F2 - Processing parameters
SI 65536
SF 100.6077432 MHz
SR 5.24 Hz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
Scale: 10 ppm/cm, 1006 Hz/cm

References:

[1] E. E. Sheina, S. M. Khersonsky, E. G. Jones, R. D. McCullough, Chem. Mater., 2005, **17**, 3317-3319

[2] G. Zotti, M. C. Gallazzi, G. Zerbi, S. V. Meille, Synth. Met., 1995, **73**, 217-225

[3] J. Hou, C. Yang, C. He, Y. Li, Chem. Comm., 2006, 871-873