SUPPORTING INFORMATION

Substituted 2,1,3-benzothiadiazole- and thiophene-based polymers for solar cells – Introducing a new thermocleavable precursor

Martin H. Petersen[1,*], Suren A. Gevorgyan[1], Frederik C. Krebs[1] and René A. J. Janssen[2]

[1]*Risø National Laboratory for Sustainable Energy, Technical University of Denmark, Frederiksborgvej 399, DK-4000 Roskilde, Denmark.*

[2]*Molecular Materials and Nanosystems, Departments of Applied Physics and Chemical Engineering & Chemistry, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands.*

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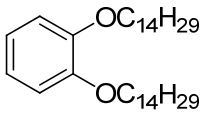
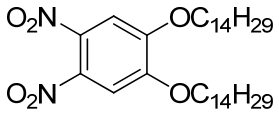
General methods. Molecular weights were determined using size exclusion chromatography in HPLC-grade *o*-dichlorobenzene (ODCB) at 80 °C against polystyrene standards on a Polymer Laboratories-GPC 120 high temperature chromatograph, a PD 2040 high-temperature light scattering detector, and a Midas autosampler. A mixed-C 300 × 7.5 mm column was used, together with a precolumn. The flow rate was 1 mL/min and the injection volume 100 μL. UV-vis absorption spectra were measured with a Perkin-Elmer Lambda 900 spectrometer. TGA experiments were performed with a dynamic heat rate (10 °C/min) under an argon atmosphere (50 ml/min) in the temperature range 50-500 °C. Unless stated otherwise all reagents and solvents were obtained from Aldrich and used without further purification. Dichloromethane, DMF and toluene were dried with molecular sieves (3 Å) and used directly without filtration or distillation. NBS was recrystallised from water and dried at 70 °C in vacuum. Evaporation was performed on a rotary evaporator at 40 °C. NMR spectra were obtained on Bruker 500 MHz or 250 MHz spectrometers. High resolution

mass spectra were recorded on a tandem mass spectrometer. Melting points were determined on an electrothermal instrument and are uncorrected. The samples were dried at 50 °C for 24 hours in a vacuum oven prior to analysis. 5-bromothiophene-3-carboxylic acid[1] was prepared according to literature procedures.



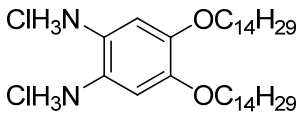
1,2-bis(tetradecyloxy)benzene[2] **(1).** To a solution of catechol (10 g, 0.091 mol) in dry DMF (50 ml) was added 1-bromotetradecane (0.209 mol, 58 g, 62 mL) and K_2CO_3 (38 g, 0.27 mol). The mixture was stirred at 100 °C under a nitrogen atmosphere for 40 hours. After cooling the mixture to room temperature (RT), 100 ml of water were added. The organic layer was separated and the aqueous layer was extracted with DCM. The combined organic phase was dried over $MgSO_4$. After filtration, the mixture was concentrated under vacuum. The product was recrystallized twice from acetone. Yield: 41 g (90%), white needlelike crystals. *Mp* = 53-54 °C. ^{1}H NMR ($CDCl_3$): δ = 6.89 (s, 4H), 4.00 (t, J = 6.6 Hz, 4H), 1.88 – 1.75 (m, 4H), 1.57 – 1.22 (m, 44H), 0.89 (t, J = 6.6 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ = 149.31, 121.02, 114.22, 69.33, 31.94, 29.71, 29.67, 29.65, 29.46, 29.37, 26.07, 22.69, 14.11.



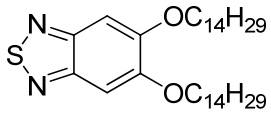
1,2-dinitro-4,5-bis(tetradecyloxy)benzene[3] **(2).** To a two neck round-bottom flask containing dichloromethane (140 mL), acetic acid (140 mL), and 1,2-bisdodecyloxybenzene (10 g, 19.9 mmol) cooled to 10 °C was added dropwise 65% nitric acid (20 mL). The reaction was allowed to warm to room temperature and stirred for 1 hour. The mixture was again cooled to 10 °C and 100% nitric acid (50 mL) was added dropwise. The mixture was allowed to warm to room temperature and the mixture was stirred for 40 hours. After completion of the reaction, the reaction mixture was poured into ice-water and the dichloromethane layer separated. The water phase was extracted with dichloromethane. The combined organic phase was washed with water, sat. $NaHCO_{3\,(aq)}$, brine and dried over $MgSO_4$. Concentration in vacuum gave the crude product that was recrystallized from

[1] E. Campaigne, and R. C. Bourgeois*, J. Am. Chem. Soc*. **1954**, 76 (9), 2445-2447
[2] D. Zhang, C.A. Tessler, W.J. Youngs, *Chem. Mater*. **1999**, 11,3050-3057
[3] J. L. Sessler, W. B. Callaway, S. P. Dudek, R. W. Date, D. W. Bruce, *Inorganic Chemistry* **2004**, 43, 6650-6653

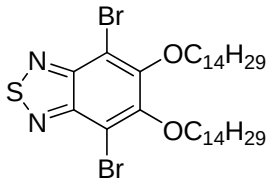
ethanol. Yield: 11.4 g (97%), yellow solid. *Mp* = 79-80 °C. ^{1}H NMR ($CDCl_3$): δ = 7.29 (s, 2H), 4.10 (t, J = 6.5 Hz, 4H), 1.94 – 1.81 (m, 4H), 1.56 – 1.18 (m, 44H), 0.88 (t, J = 6.6 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ = 151.82, 136.49, 107.94, 70.21, 31.92, 29.70, 29.69, 29.67, 29.66, 29.57, 29.54, 29.36, 29.23, 28.71, 25.81, 22.68, 14.09.



4,5-bis(tetradecyloxy)benzene-1,2-diaminium chloride. A mixture of 1,2-dinitro-4,5-bis-(tetradecyloxy)-benzene (2 g, 3.37 mmol) and Sn(II)Cl_2 (26.9 mmol, 5.1 g) in ethanol (50 ml) and conc. HCl (20 ml) was heated to 85 ^{o}C over the night. After cooling to room temperature the product was filtered and washed with water and methanol. Finally it was dried at RT under a stream of argon and used directly (unstable). Yield: 1.8 g (88 %), off-white solid.



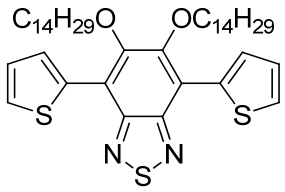
5,6-bis(tetradecyloxy)benzo[*c*][1,2,5]thiadiazole[4] **(3).** To a mixture of 4,5-bis(tetradecyloxy)-benzene-1,2-diaminium chloride (1.54 g, 2.54 mmol) and triethylamine (25.1 mmol, 3.5 ml) in 40 ml dichloromethane was slowly added a solution of thionyl chloride (4.83 mmol, 352 µL) in 5 ml dichloromethane. After addition the mixture was heated to reflux for 6 hours. The cooled solution was concentrated in vacuum followed by trituration in water. After stirring for 30 min the product was filtered and recrystallized from ethanol. Yield: 1.1 g (77 %), off-white solid. *Mp* = 90-91 °C. ^{1}H NMR ($CDCl_3$): δ = 7.13 (s, 2H), 4.09 (t, J = 6.5 Hz, 4H), 2.04 – 1.79 (m, 4H), 1.58 – 1.16 (m, 44H), 0.95 – 0.81 (m, 6H). ^{13}C NMR ($CDCl_3$): δ = 154.17, 151.40, 98.44, 69.13, 31.92, 29.71, 29.69, 29.66, 29.61, 29.36, 28.75, 26.02, 22.68, 14.09.



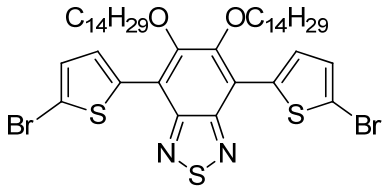
4,7-dibromo-5,6-bis(tetradecyloxy)benzo[*c*][1,2,5]thiadiazole[4] **(4).** To a solution of **3** (8.00 g, 14.3 mmol) in a mixture of dichloromethane (400 mL) and acetic acid (175 mL) was added bromine

[4] Jean Bouffard and Timothy M. Swager, *Macromolecules* **2008**, 41, 5559-5562

(5 mL, 97.5 mmol), and the resulting mixture wass stirred in the dark for ca. 48 h at room temperature. The mixture was then poured in water (500 mL), extracted with dichloromethane, sequentially washed with water, saturated $NaHCO_{3\ (aq)}$, 1M $Na_2SO_{3\ (aq)}$ and the solvents are evaporated under reduced pressure. The crude product was purified by recrystallization from ethanol twice to give fluffy needle-like microcrystals. Yield: 9.60 g (94 %). *Mp* = 65-66 °C. ^{1}H NMR ($CDCl_3$): δ = 4.16 (t, *J* = 6.6 Hz, 4H), 1.97 – 1.81 (m, 4H), 1.62 – 1.46 (m, 4H), 1.46 – 1.19 (m, 40H), 0.88 (t, *J* = 6.6 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ = 154.53, 150.39, 106.25, 75.16, 31.92, 30.27, 29.71, 29.70, 29.68, 29.66, 29.63, 29.61, 29.43, 29.36, 25.99, 22.68, 14.10.

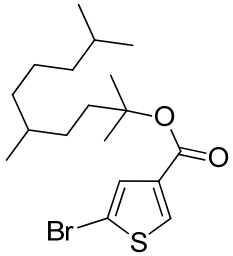


5,6-bis(tetradecyloxy)-4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (5). To a solution of **4** (900 mg, 1.25 mmol), Pd_2dba_3 (0.05 mmol, 46 mg) and tri-o-tolylphosphine (0.40 mmol, 122 mg) in dry toluene (10 ml) was added 2-tributylstannylthiophene (3.13 mmol, 994 µL) and the reaction mixture was heated to reflux for 16 hours under argon. The reaction mixture was concentrated directly on celit in vacuum. Dry column chromatography (silica gel 15 40 µm, eluted with Heptane/$CHCl_3$, gradient 1 10 % $CHCl_3$) afforded **5**. Yield: 848 mg (93 %), yellow solid. *Mp* = 59-60 °C. ^{1}H NMR ($CDCl_3$): δ = 8.47 (d, *J* = 2.8 Hz, 2H), 7.51 (d, *J* = 4.1 Hz, 2H), 7.26 – 7.20 (m, 2H), 4.11 (t, *J* = 7.1 Hz, 4H), 2.00 – 1.85 (m, 4H), 1.51 – 1.20 (m, 44H), 0.93 – 0.85 (m, 6H). ^{13}C NMR ($CDCl_3$): δ = 152.00, 151.02, 134.14, 130.55, 127.29, 126.74, 117.64, 74.37, 31.93, 30.33, 29.72, 29.68, 29.64, 29.55, 29.37, 25.97, 22.69, 14.10.

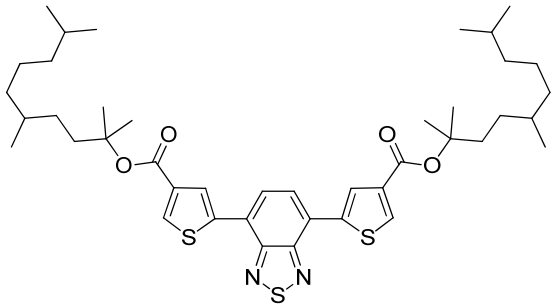


4,7-bis(5-bromothiophen-2-yl)-5,6-bis(tetradecyloxy)benzo[*c*][1,2,5]thiadiazole (6). To a solution of **5** (817 mg, 1.13 mmol) in $CHCl_3$ (40 ml) and glacial acetic acid (40 ml) was added NBS (2.26 mmol, 401 mg) in one portion. The mixture was stirred at room temperature for 20 hours in the dark. The reaction mixture was concentrated directly on celit in vacuum. Dry column chromatography (silica gel 15 40 µm, eluted with Heptane/$CHCl_3$, gradient 1 10 % $CHCl_3$)

afforded **6**. Yield: 912 mg (92 %), orange solid. *Mp* = 80-81 °C. ^{1}H NMR ($CDCl_3$): δ = 8.37 (d, J = 4.1 Hz, 2H), 7.17 (d, J = 4.1 Hz, 2H), 4.12 (t, J = 7.2 Hz, 4H), 2.01 – 1.86 (m, 4H), 1.52 – 1.20 (m, 44H), 0.88 (t, J = 6.6 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ = 151.52, 150.42, 135.72, 131.01, 129.67, 117.01, 115.46, 74.59, 31.93, 30.27, 29.72, 29.68, 29.63, 29.50, 29.37, 25.93, 22.69, 14.11.

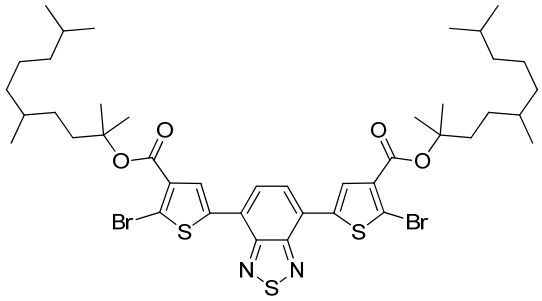


2,5,9-trimethyldecan-2-yl 5-bromothiophene-3-carboxylate (7). A mixture of 5-bromothiophene-3-carboxylic acid (6 g, 29 mmol), DMAP (3.9 g, 32 mmol), $HfCl_4$·2THF (675 mg, 1.45 mmol) and 2,5,9-trimethyl-2-decanol (6.4 g, 32 mmol) in dry methylene chloride (100 ml) was stirred at room temperature under argon for 30 min. *N,N′*-diisopropylcarbodiimide (5 ml, 32 mmol) was added and the reaction mixture was heated to reflux and stirred for 24 hours. After cooling to RT the reaction mixture was concentrated on celite in vacuum. Dry column chromatography (silica gel 15-40 μm, eluted with EtOAc/Heptane, gradient 0-3%) afforded **7**. Yield: 7.2 g (64 %), colourless oil. ^{1}H NMR ($CDCl_3$): δ = 7.88 (d, J = 1.5 Hz, 1H), 7.40 (d, J = 1.5 Hz, 1H), 1.93 – 1.72 (m, 2H), 1.53 (s, 6H), 1.45 – 1.06 (m, 10H), 0.91 – 0.82 (m, 9H). ^{13}C NMR ($CDCl_3$): δ = 160.61, 135.81, 132.74, 130.13, 112.21, 83.75, 39.22, 38.33, 37.01, 32.91, 30.77, 27.89, 26.13, 26.05, 24.73, 22.65, 22.56, 19.68.

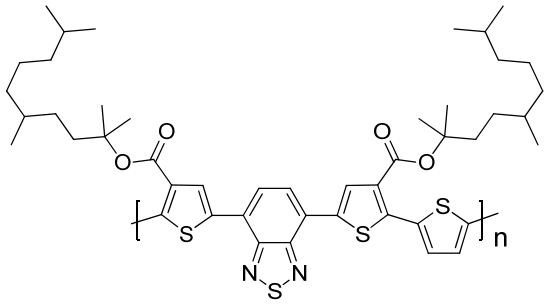


bis(2,5,9-trimethyldecan-2-yl)-5,5'-(benzo[*c*][1,2,5]thiadiazole-4,7-diyl)dithiophene-3-carboxylate (8). 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*c*][1,2,5]thiadiazole (1 g, 2.58 mmol), **7** (2.3 g, 5.93 mmol), Pd_2dba_3 (94 mg, 0.1 mmol) and tri-(o-tolyl)phosphine (251 mg, 0.83 mmol) was dissolved in dry toluene (20 ml) and stirred for 15 min at RT under argon.

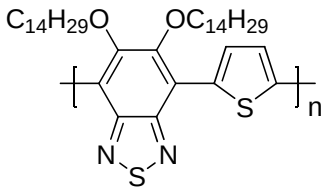
Then Cs_2CO_3 (6.7 g, 21 mmol), degassed water (7 ml) and 1 drop Aliquat® 336 was added. The reaction mixture was stirred at 90 °C for 48 hours. The reaction mixture was allowed to cool to room temperature followed by addition of water (25 ml). The mixture was extracted with ether (3 × 25 ml) and the combined organic phase was dried ($MgSO_4$), filtered and concentrated on celit in vacuum. Dry column chromatography (silica gel 15-40 µm, eluted with EtOAc/Heptane, gradient 0-5%) afforded **8**. Yield: 1 g (52 %), yellow oil. ^{1}H NMR ($CDCl_3$): δ = 8.39 (d, J = 1.2 Hz, 2H), 8.11 (d, J = 1.2 Hz, 2H), 7.89 (s, 2H), 1.96 – 1.83 (m, 4H), 1.59 (s, 12H), 1.56 – 1.10 (m, 20H), 0.91 (d, J = 5.2 Hz, 6H), 0.86 (d, J = 6.6 Hz, 12H). ^{13}C NMR ($CDCl_3$): δ = 161.83, 152.39, 139.30, 136.26, 132.93, 127.70, 125.81, 125.65, 83.60, 39.29, 38.61, 37.13, 33.05, 30.95, 27.94, 26.17, 26.13, 24.77, 22.66, 22.57, 19.74.



bis(2,5,9-trimethyldecan-2-yl)-5,5'-(benzo[*c*][1,2,5]thiadiazole-4,7-diyl)bis(2-bromothiophene-3-carboxylate) (9). To a solution of **8** (1 g, 1.33 mmol) in DMF (20 mL) was added NBS (0.52 g, 2.92 mmol). The resulting mixture was then stirred at room temperature for 24 hours. The resulting mixture was poured into water (30 ml) and extracted several times with dichloromethane. The combined organic phase was dried ($MgSO_4$), filtered and concentrated in vacuum. The crude product was purified by column chromatography (silica gel 70-230 µm, eluted with dichloromethane/cyclohexane 1:1) to afford **9**. Yield: 750 mg (62 %), orange oil. ^{1}H NMR ($CDCl_3$): δ = 8.15 (s, 2H), 7.80 (s, 2H), 1.99 – 1.83 (m, 4H), 1.62 (s, 12H), 1.56 – 1.08 (m, 20H), 0.92 (d, J = 6.1 Hz, 6H), 0.85 (d, J = 6.6 Hz, 12H). ^{13}C NMR ($CDCl_3$): δ = 160.94, 152.00, 138.22, 133.44, 128.50, 125.05, 124.99, 120.56, 84.77, 39.30, 38.48, 37.18, 33.09, 31.00, 27.93, 26.22, 26.19, 24.78, 22.65, 22.56, 19.75.

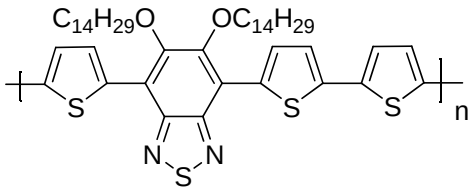


Poly{2,5,9-trimethyldecan-2-yl-5-(7-(4-((2,5,9-trimethyldecan-2-yloxy)carbonyl)thiophen-2-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)-2,2'-bithiophene-3-carboxylate} (10). 9 (323 mg, 0.355 mmol), 2,5-bis(trimethylstannyl)thiophene (0.355 mmol, 145 mg), Pd_2dba_3 (16 mg, 17.5 µmol) and tri-(o-tolyl)phosphine (43 mg, 0.141 mmol) was mixed in dry degassed toluene (25 ml). The reaction mixture was heated to reflux for 48 hours under argon. After cooling to room temperature the mixture was poured into 250 ml methanol and the polymer was allowed to precipitate. The polymer was filtered and purified by Soxhlet extraction using methanol, hexane and chloroform. The chloroform fraction was then stirred at room temperature for 16 hours with an aqueous EDTA solution (400 mg in 10 ml H_2O). Water was added followed by separation of the phases. The chloroform phase was concentrated in vacuum and the residue was redissolved in toluene and precipitated in methanol (1:10). Filtration and drying in vacuum afforded **10**. Yield: 177 mg (59 %), dark purple-brown solid. ^{1}H-NMR ($CDCl_3$): δ = 8.52 – 8.38 (m, 2H), 8.02 – 7.86 (m, 2H), 7.65 – 7.53 (m, 2H), 2.01 – 1.81 (m, 4H), 1.63 (s, 12H), 1.60 – 1.10 (m, 20H), 0.99 – 0.81 (m, 18H). GPC (ODCB): M_w = 173000, PDI = 2.6.

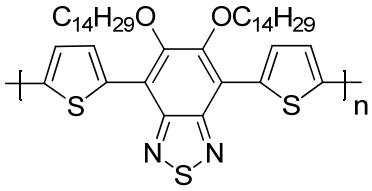


Poly{5,6-bis(tetradecyloxy)-4-(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole} (11). 4 (100 mg, 0.139 mmol), 2,5-bis(trimethylstannyl)thiophene (0.139 mmol, 57 mg), Pd_2dba_3 (6.4 mg, 6.95 µmol) and tri-(o-tolyl)phosphine (17 mg, 55.6 µmol) was mixed in dry degassed toluene (10 ml). The reaction mixture was heated to reflux for 48 hours under argon. After cooling to room temperature the mixture was poured into 100 ml methanol and the polymer was allowed to precipitate. The polymer was filtered and purified by Soxhlet extraction using methanol, hexane and chloroform. The chloroform fraction was then stirred at room temperature for 16 hours with an aqueous EDTA

solution (155 mg in 5 ml H_2O). Water was added followed by separation of the phases. The chloroform phase was concentrated in vacuum and the residue was redissolved in toluene and precipitated in methanol (1:10). Filtration and drying in vacuum afforded **11**. Yield: 70 mg (78 %), dark purple solid. ^{1}H-NMR ($CDCl_3$) δ = 8.77 – 8.61 (m, 2H), 7.24 – 7.17 (m, endgroup), 4.39 – 4.18 (m, 4H), 2.60 – 2.50 (m, 4H), 2.19 – 2.04 (m, 4H), 1.67 – 1.51 (m, 4H), 1.49 – 1.20 (m, 32H), 1.14 – 1.00 (m, 4H), 0.97 – 0.85 (m, 6H). GPC (ODCB): M_w = 16600, PDI = 1.7.



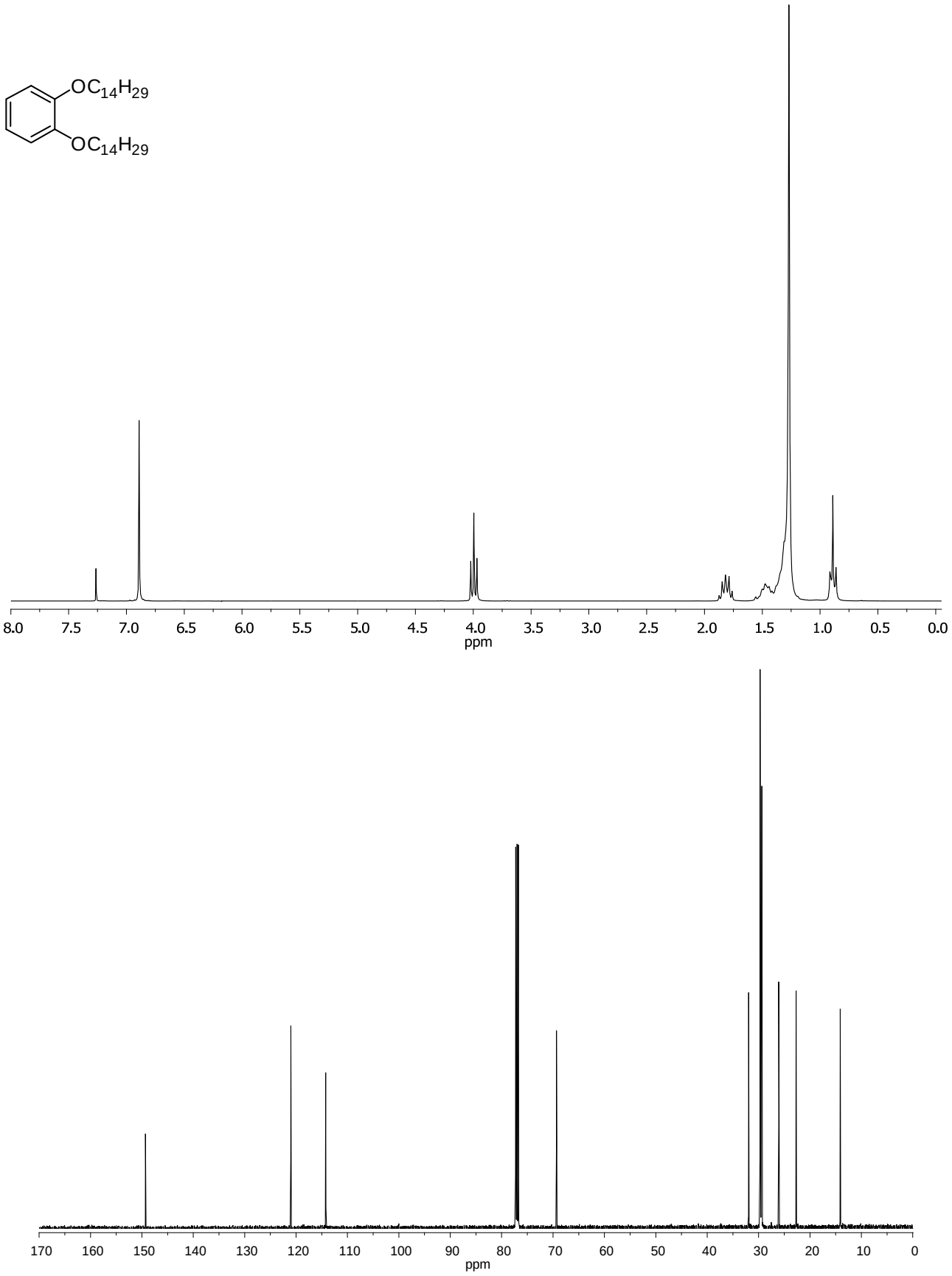
Poly{4-(2,2'-bithiophen-5-yl)-5,6-bis(tetradecyloxy)-7-(thiophen-2-yl)-benzo[*c*][1,2,5]thiadiazole} (12). 6 (195 mg, 0.221 mmol), 2,5-bis(trimethylstannyl)thiophene (0.221 mmol, 90 mg), Pd_2dba_3 (10 mg, 11.0 μmol) and tri-(o-tolyl)phosphine (27 mg, 88.3 μmol) was mixed in dry degassed toluene (20 ml). The reaction mixture was heated to reflux for 48 hours under argon. After cooling to room temperature the mixture was poured into 200 ml methanol and the polymer was allowed to precipitate. The polymer was filtered and purified by Soxhlet extraction using methanol, hexane and chloroform. The chloroform fraction was then stirred at room temperature for 16 hours with an aqueous EDTA solution (247 mg in 10 ml H_2O). Water was added followed by separation of the phases. The chloroform phase was concentrated in vacuum and the residue was redissolved in toluene and precipitated in methanol (1:10). Filtration and drying in vacuum afforded **12**. Yield: 50 mg (28 %), dark purple solid. ^{1}H-NMR ($CDCl_3$) δ = 8.66 – 8.02 (m, 4H), 7.14 – 6.66 (m, 2H), 4.36 – 4.04 (m, 4H), 2.29 – 1.93 (m, 8H), 1.80 – 1.12 (m, 40H), 1.09 – 0.79 (m, 6H). GPC (ODCB): M_w = 26000, PDI = 2.9.



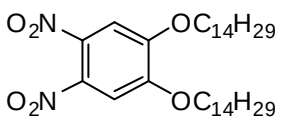
Poly{5,6-bis(tetradecyloxy)-4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole} (13). $Ni(COD)_2$ (187 mg, 0.681 mmol) and 2,2'-dipyridyl (0.681 mmol, 106 mg) was mixed in dry degassed toluene (30 ml). The mixture was heated to 80 ^{o}C followed by addition of **6** (200 mg, 0.227 mmol). After stirring for 9 hours under argon the mixture was poured into 300 ml methanol and the polymer was

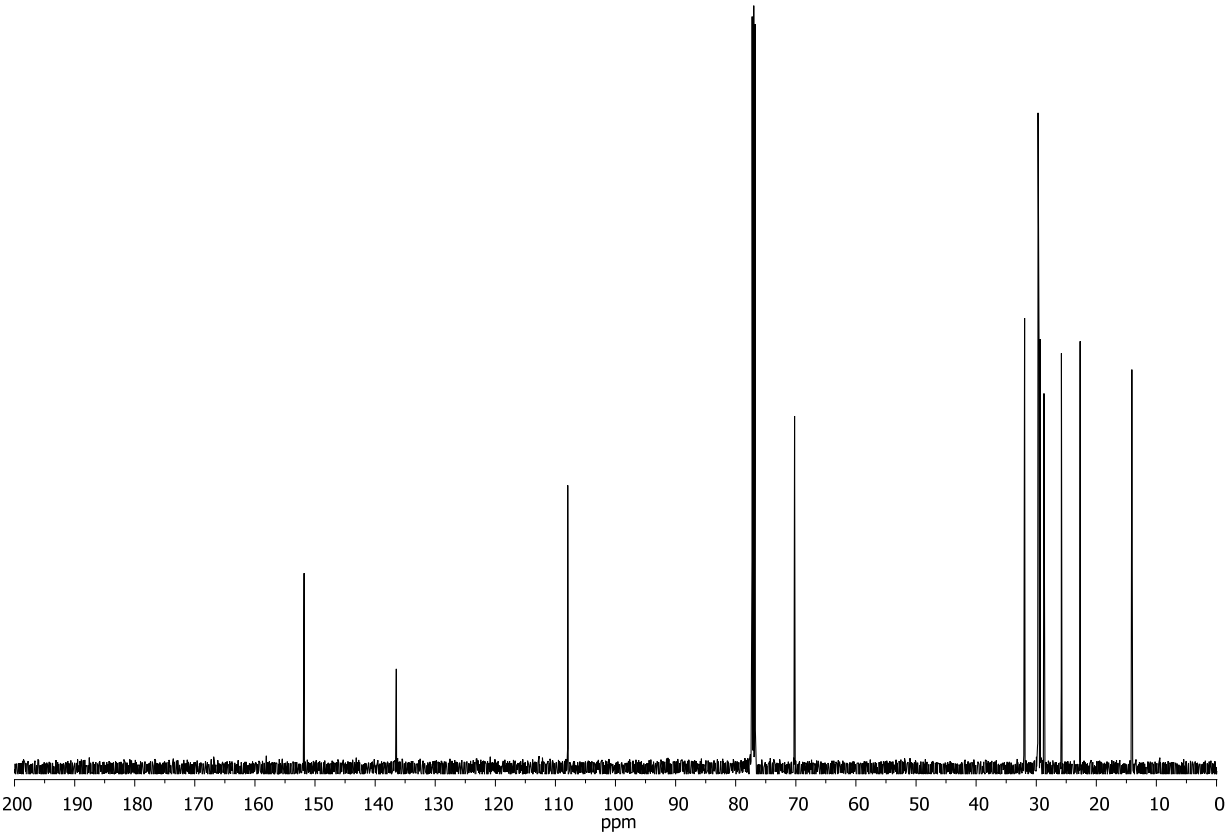
allowed to precipitate. Then the polymer was filtered and purified by Soxhlet extraction using methanol, hexane and chloroform. The chloroform fraction was then stirred at room temperature for 16 hours with an aqueous EDTA solution (760 mg in 20 ml H_2O). Water was added followed by separation of the phases. The chloroform phase was concentrated in vacuum and the residue was redissolved in toluene and precipitated in methanol (1:10). Filtration and drying in vacuum afforded **13**. Yield: 33 mg (20 %), dark purple solid. ^{1}H-NMR ($CDCl_3$) δ = 8.65 – 8.56 (m, 2H), 8.44 – 8.40 (m, endgroup), 7.49 – 7.42 (m, 2H), 7.23 – 7.19 (m, endgroup), 4.34 – 4.14 (m, 4H), 2.16 – 1.95 (m, 8H), 1.66 – 1.49 (m, 8H), 1.49 – 1.13 (m, 32H), 0.99 – 0.83 (m, 6H). GPC (ODCB): M_w = 7100, PDI = 1.7.

^{1}H- and ^{13}C-NMR Spectrum of **1** in $CDCl_3$

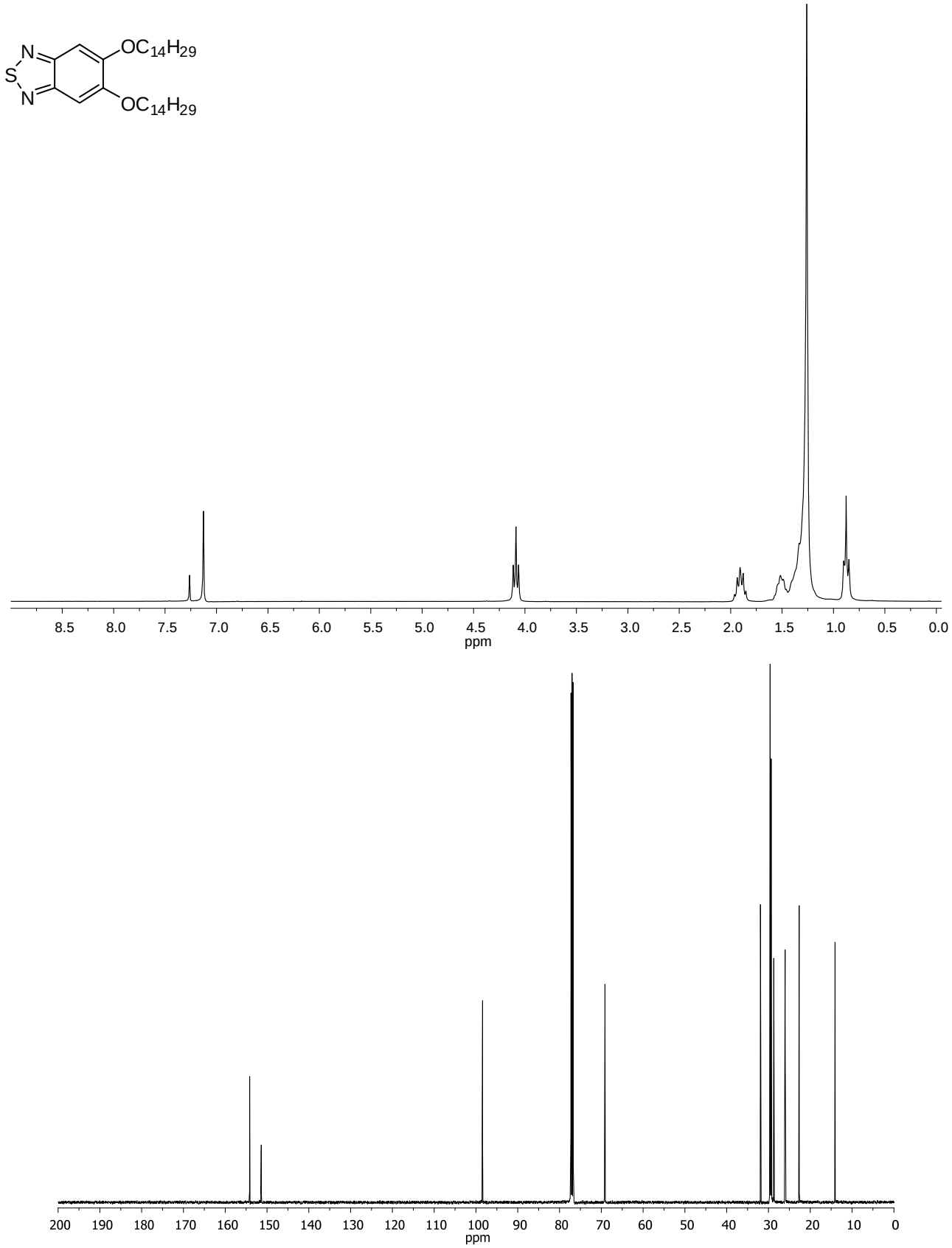


^{1}H- and ^{13}C-NMR Spectrum of **2** in $CDCl_3$

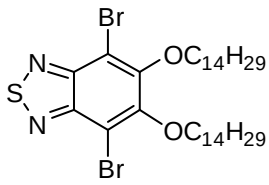


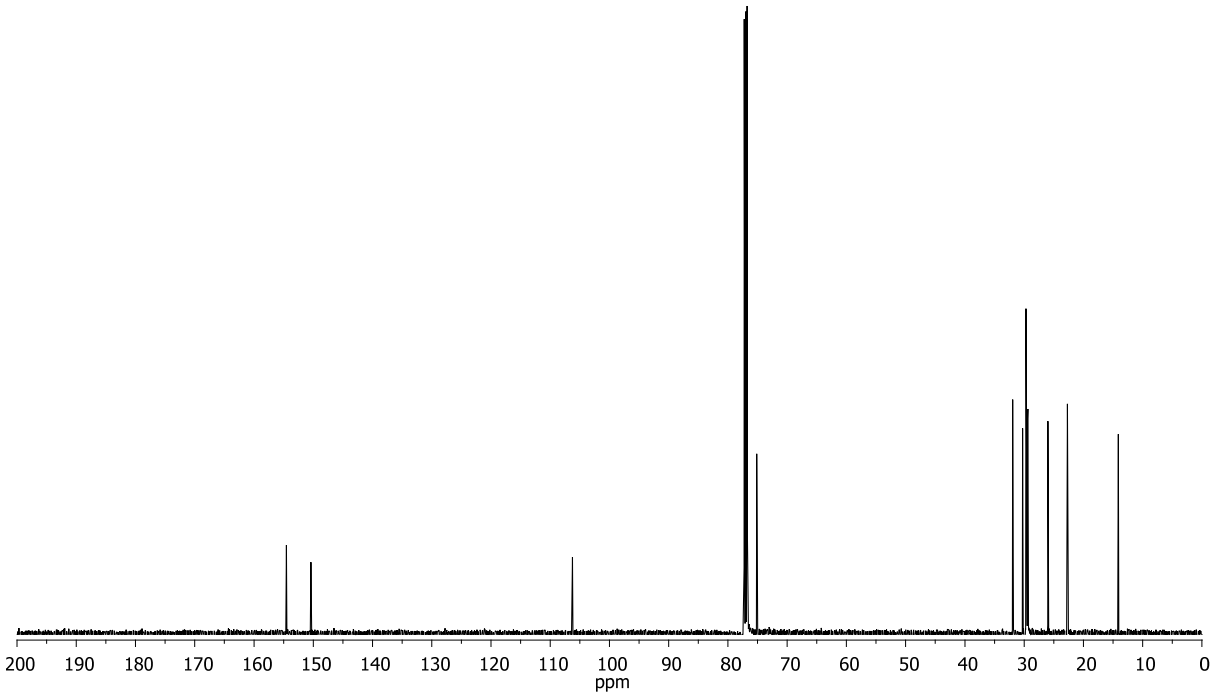


^{1}H- and ^{13}C-NMR Spectrum of **3** in $CDCl_3$

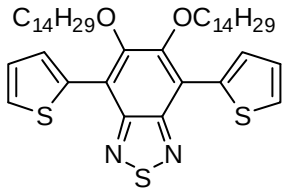


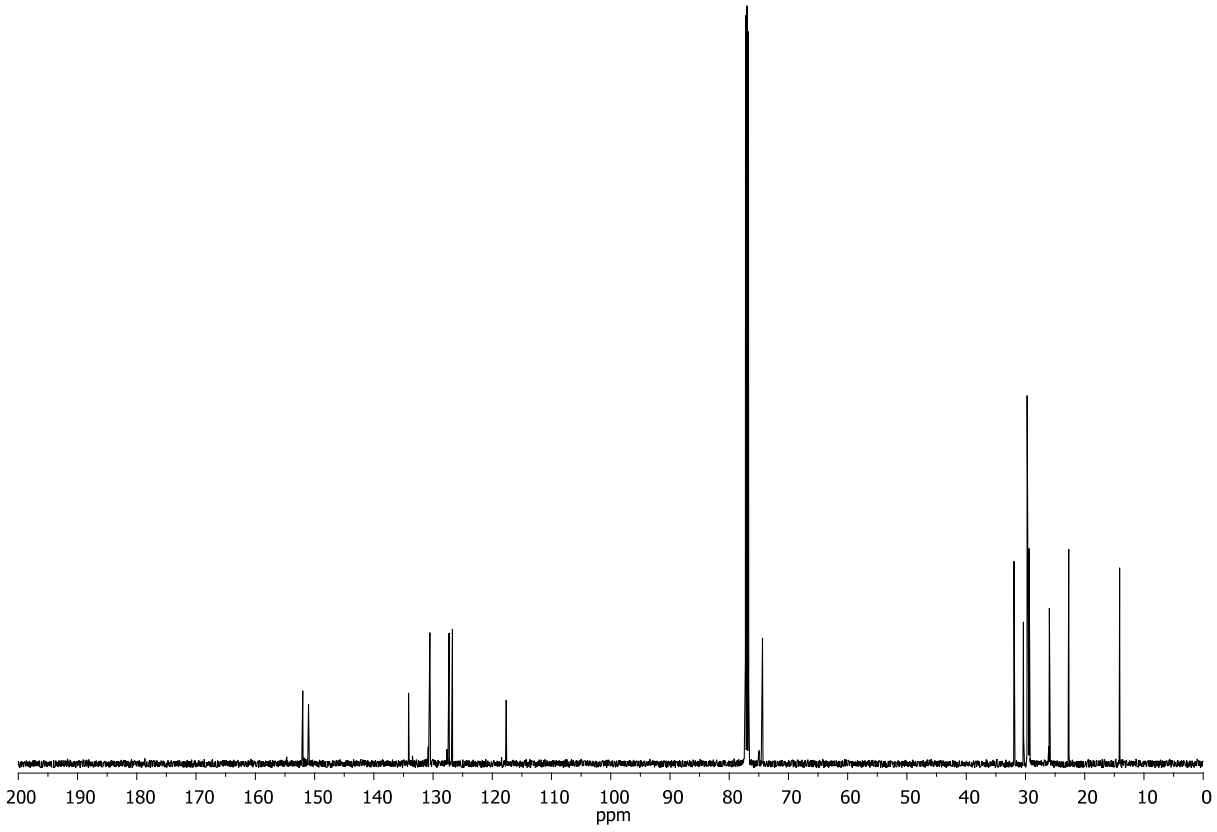
^{1}H- and ^{13}C-NMR Spectrum of **4** in $CDCl_3$



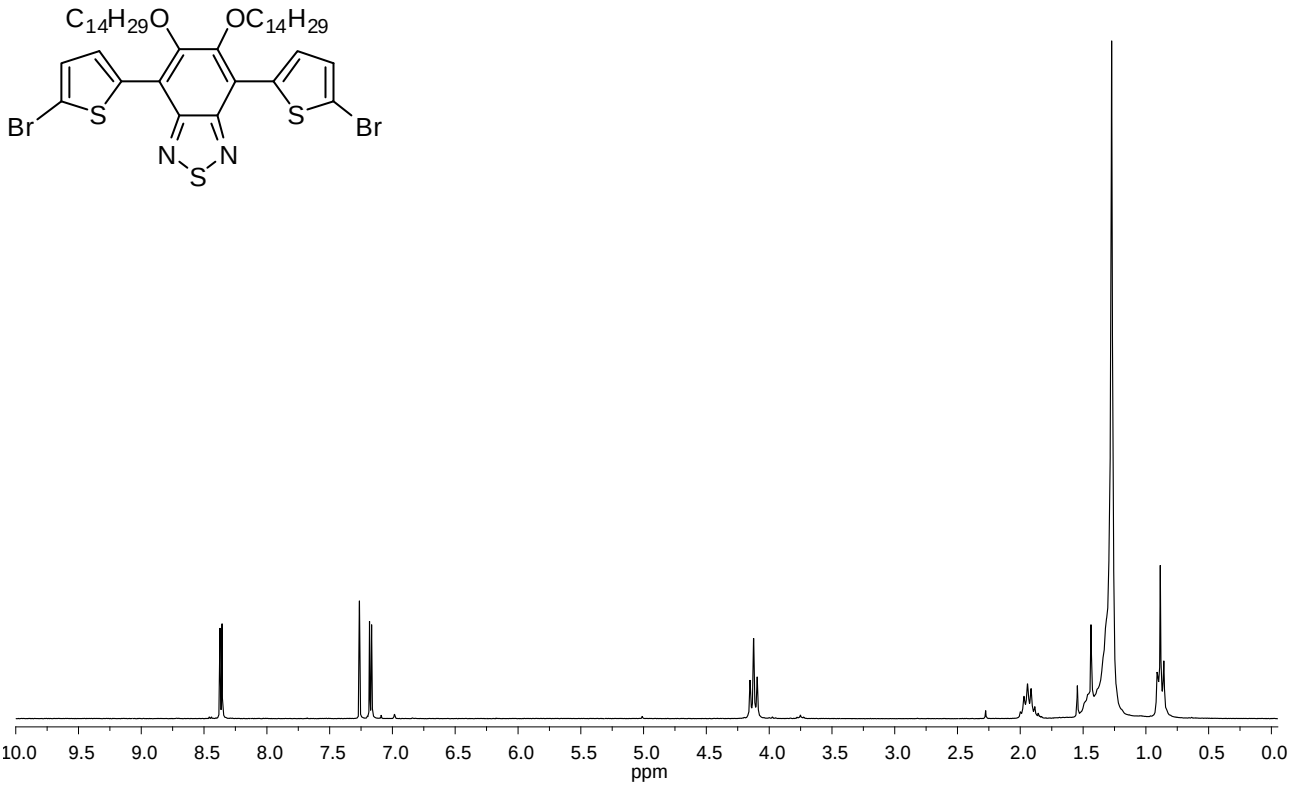


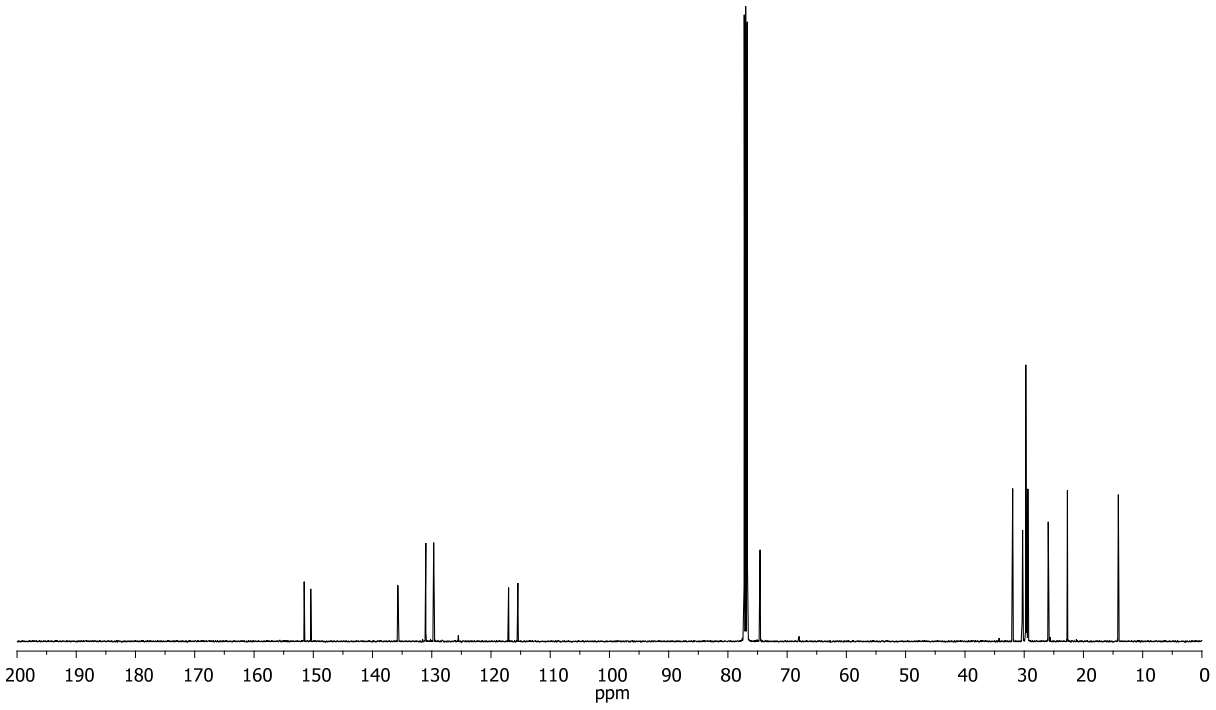
^{1}H- and ^{13}C-NMR Spectrum of **5** in $CDCl_3$



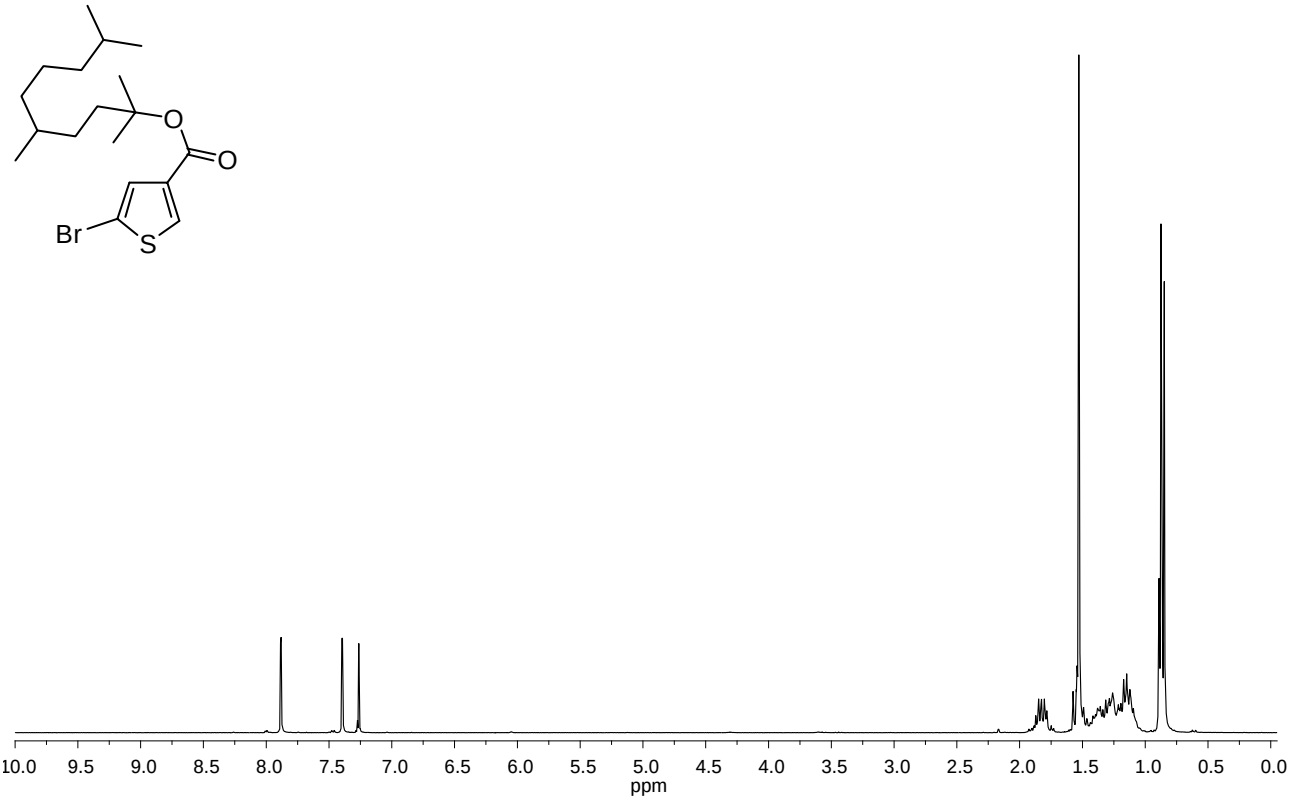


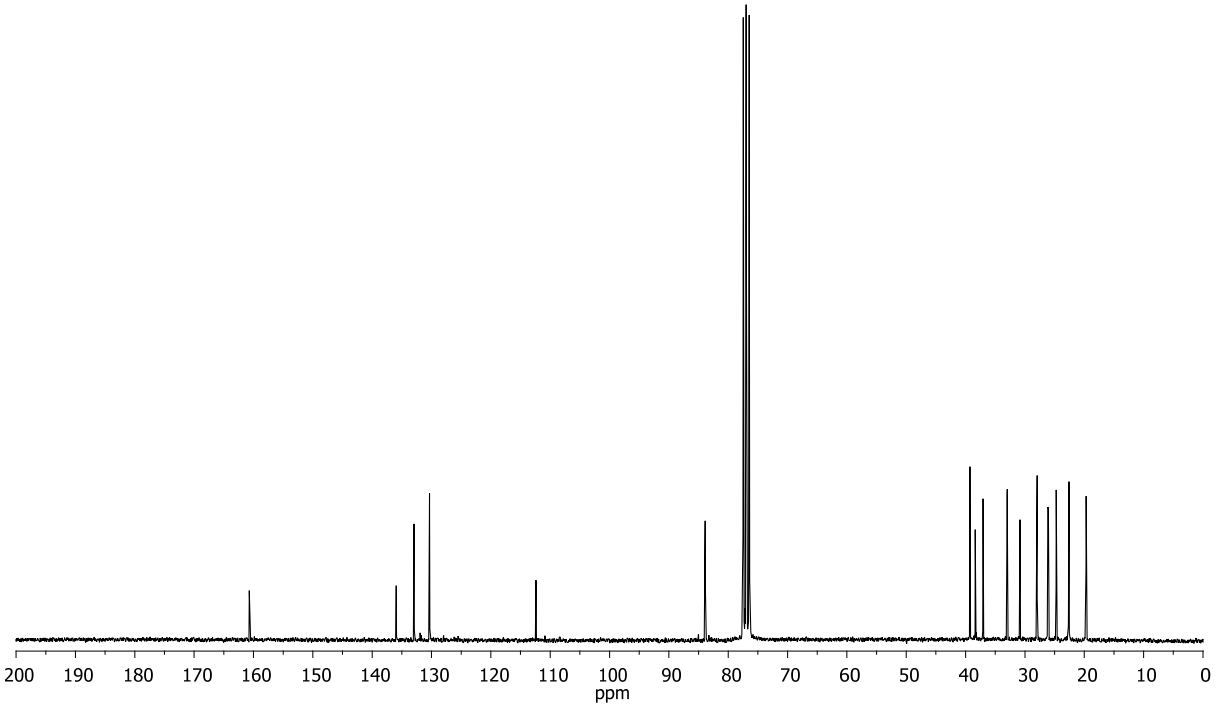
^{1}H- and ^{13}C-NMR Spectrum of **6** in $CDCl_3$



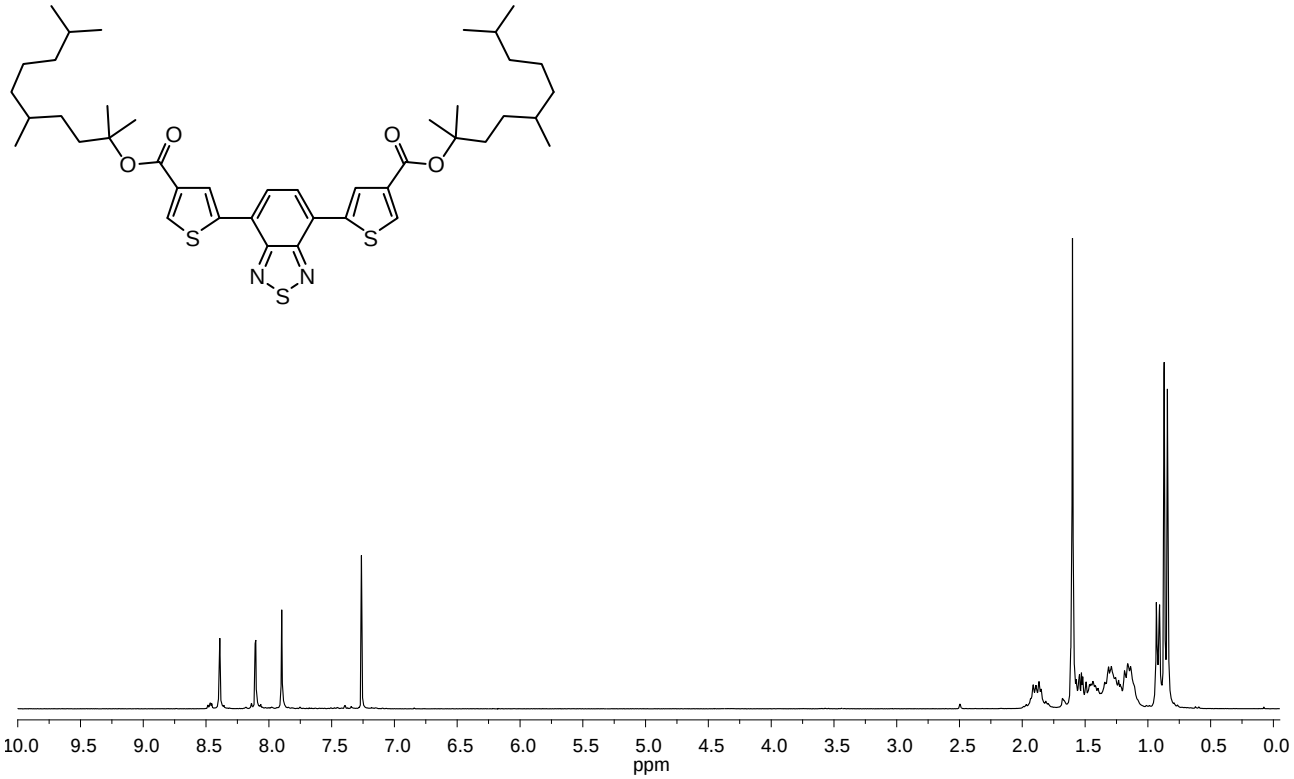


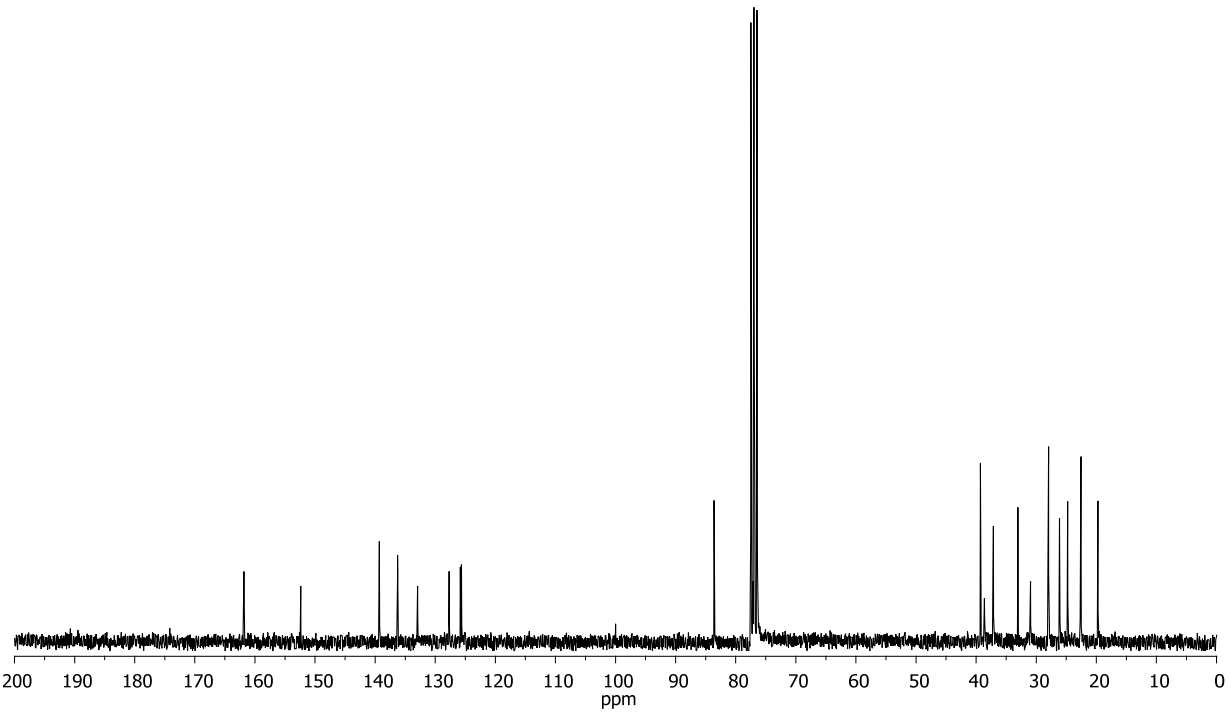
^{1}H- and ^{13}C-NMR Spectrum of **7** in $CDCl_3$



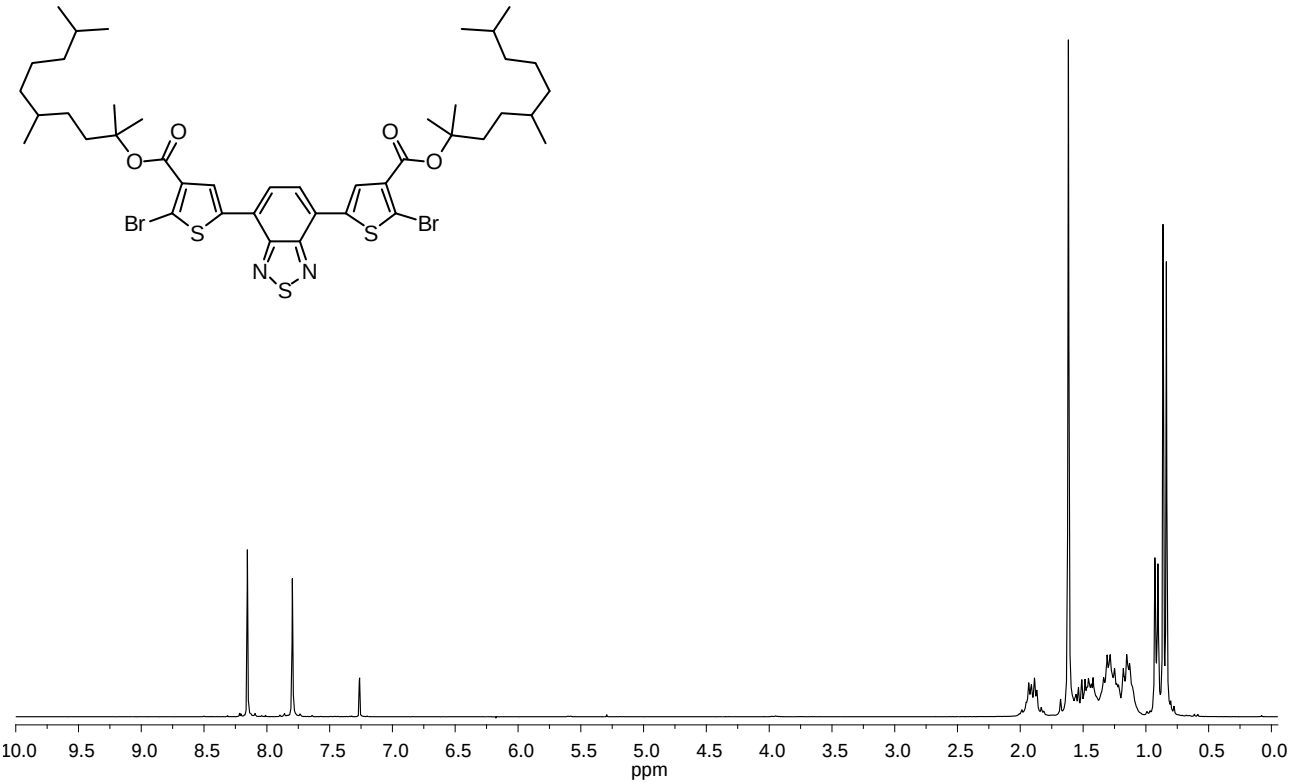


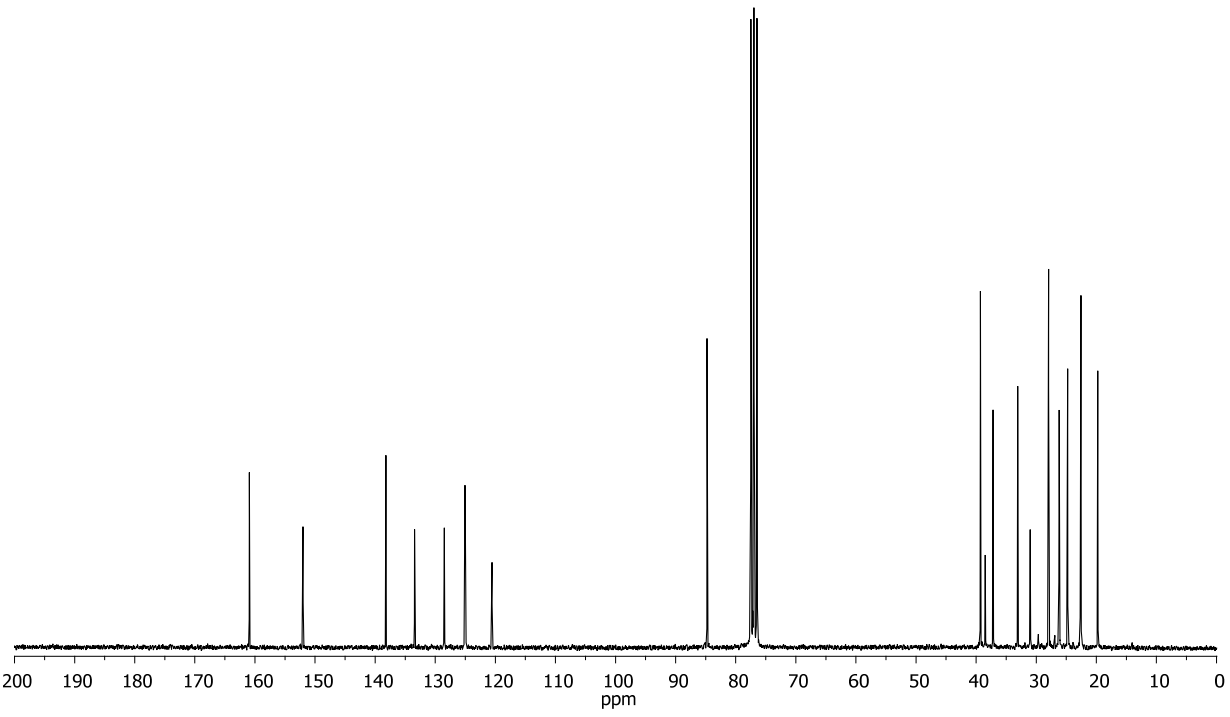
^{1}H- and ^{13}C-NMR Spectrum of **8** in $CDCl_3$



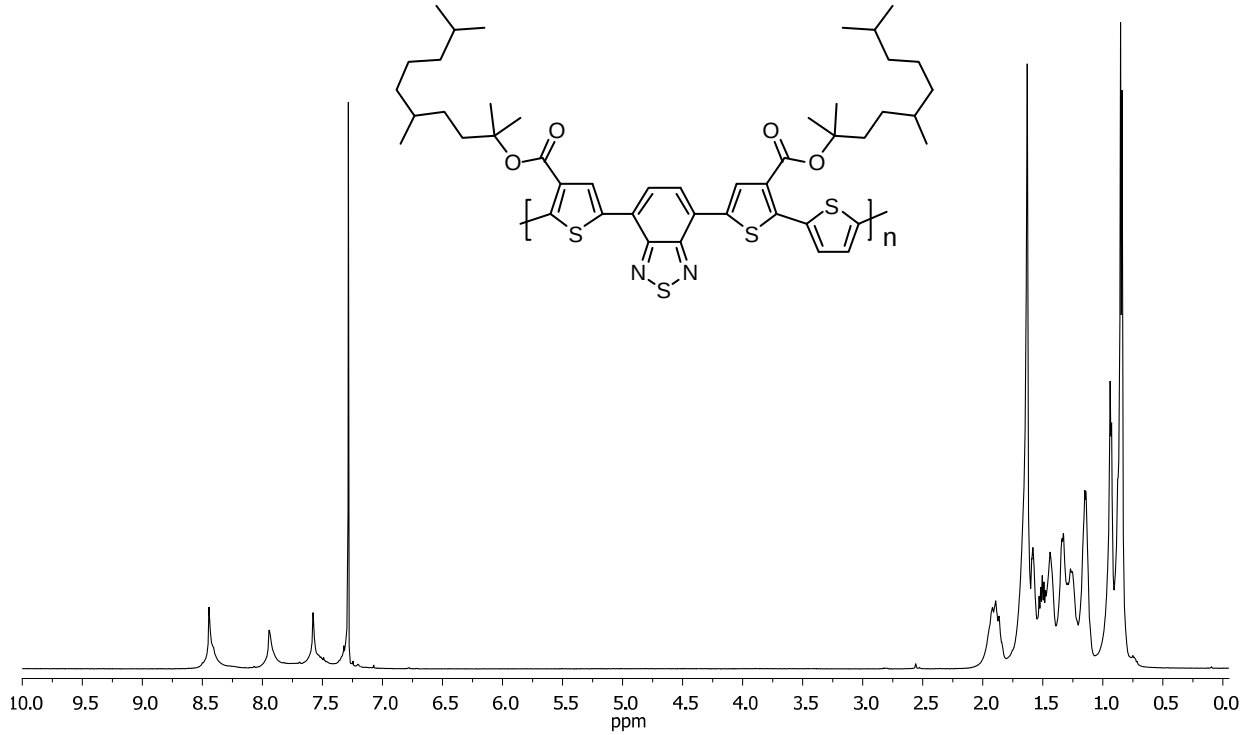


^{1}H- and ^{13}C-NMR Spectrum of **9** in $CDCl_3$

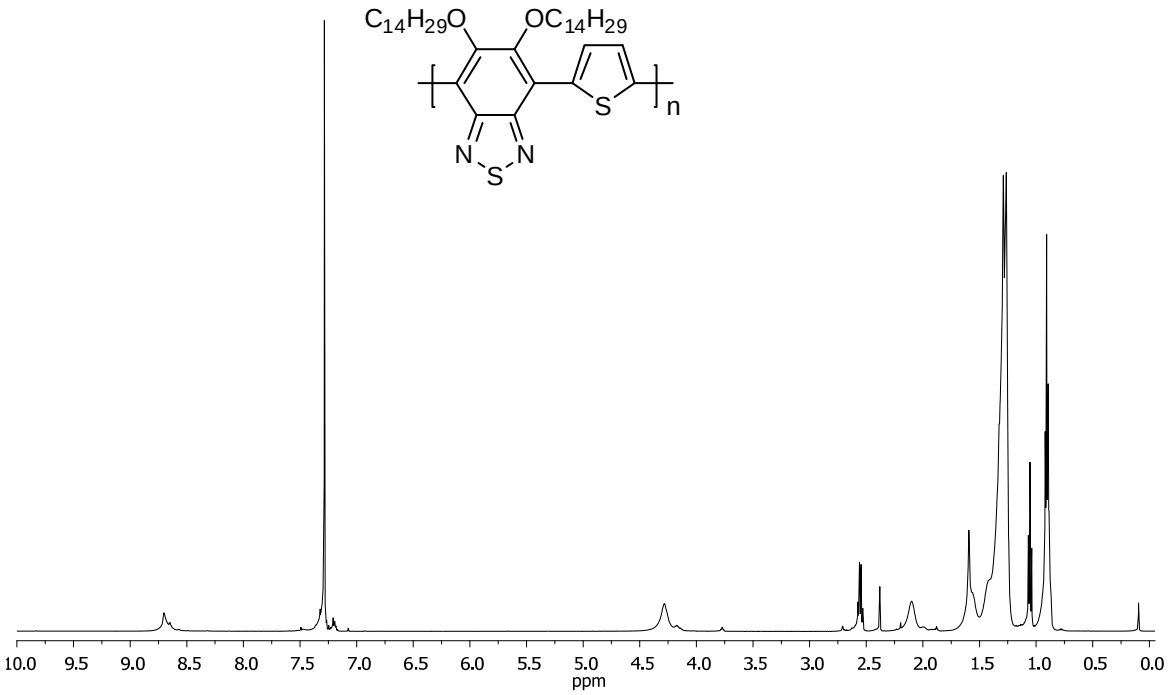




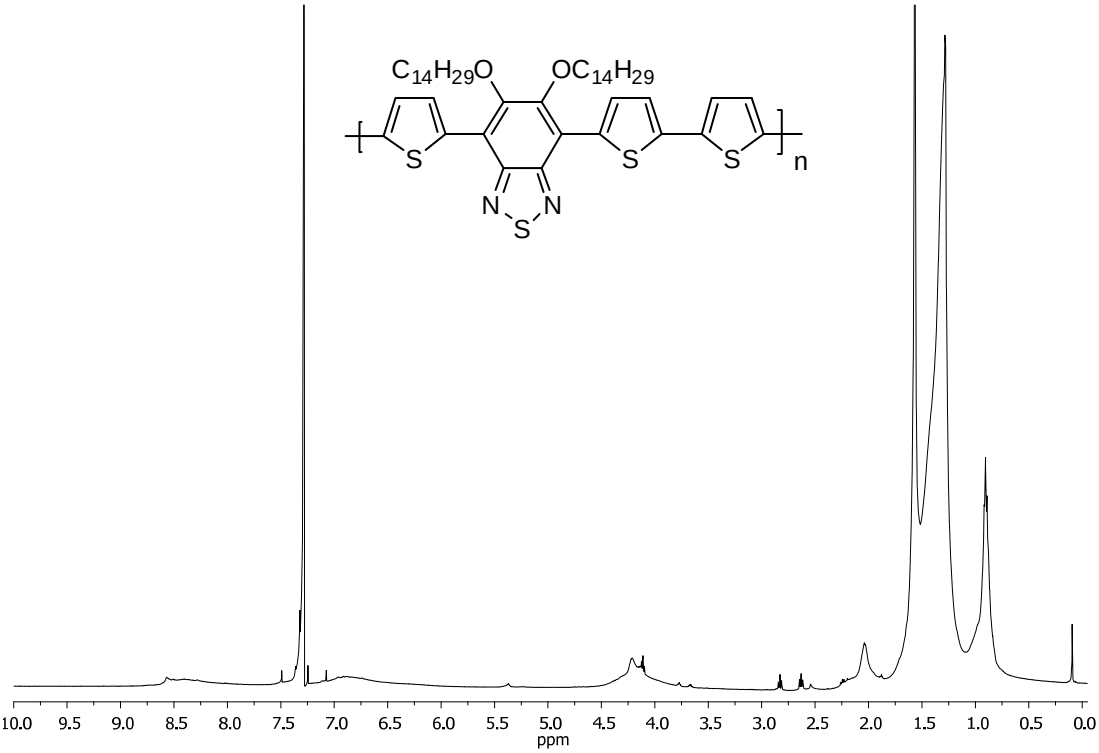
^{1}H-NMR Spectrum of **10** in $CDCl_3$



^{1}H-NMR Spectrum of **11** in $CDCl_3$



^{1}H-NMR Spectrum of **12** in $CDCl_3$



^{1}H-NMR Spectrum of **13** in $CDCl_3$