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Supporting Information

Directing the Self-Assembly of Aromatic Foldamer Helices using Acridine Appendages and Metal Coordination

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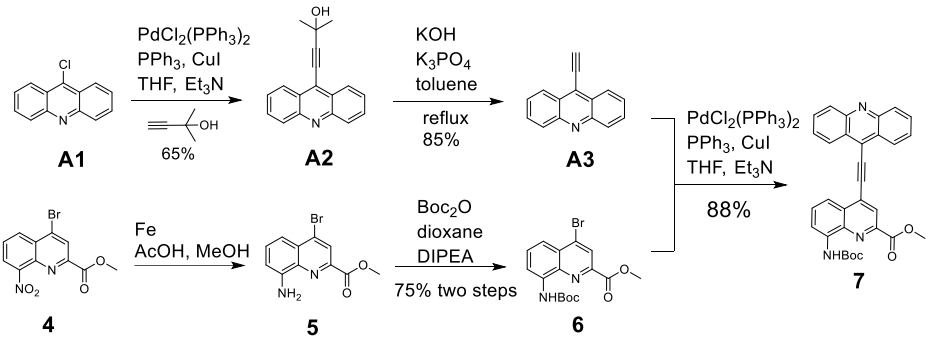
Contents

General Remarks: All the solvents and reagents were used as received from commercial sources unless otherwise specified. Dry dichloromethane (DCM, CH_2Cl_2) and dry THF were obtained from a solvent drying system passing through alumina columns; chloroform ($CHCl_3$), trimethylamine (Et_3N) and diisopropylethylamine (DIEA) were distilled over calcium hydride (CaH_2) prior to use. Reactions were monitored by thin layer chromatography (TLC) on Merck silica gel 60-F254 plates and observed under UV light. Silica gel column chromatography purifications were carried out on Merck GEDURAN Si60 (40-63 μm). Preparative recycling Gel Permeation Chromatography (GPC) was performed on a JAI LC-9130G NEXT using two JAIGEL 20×600 mm columns (Japan Analytical Industry) with 0.5 % Et_3N and 1% ethanol in chloroform (HPLC grade, ethanol stabilized), as mobile phase, with a flow rate of 7 mL/min. ^{1}H NMR, ^{13}C NMR and 2D NMR spectra were recorded on BRUKER AVANCE 300 MHz or 400 MHz spectrometers. Chemical shifts were presented in parts per million (δ, ppm) using solvent residue peaks as references (chloroform δ = 7.26 ppm). Coupling constants are reported as Hertz. ESI mass spectra were measured in the Mass Spectrometry Laboratory at the European Institute of Chemistry and Biology (UMS 3033 - IECB), Pessac, France.

1. Compounds Synthesis

1.1 monomer synthesis



Scheme S1: synthetic route for the acridine functionalized monomer **7**.

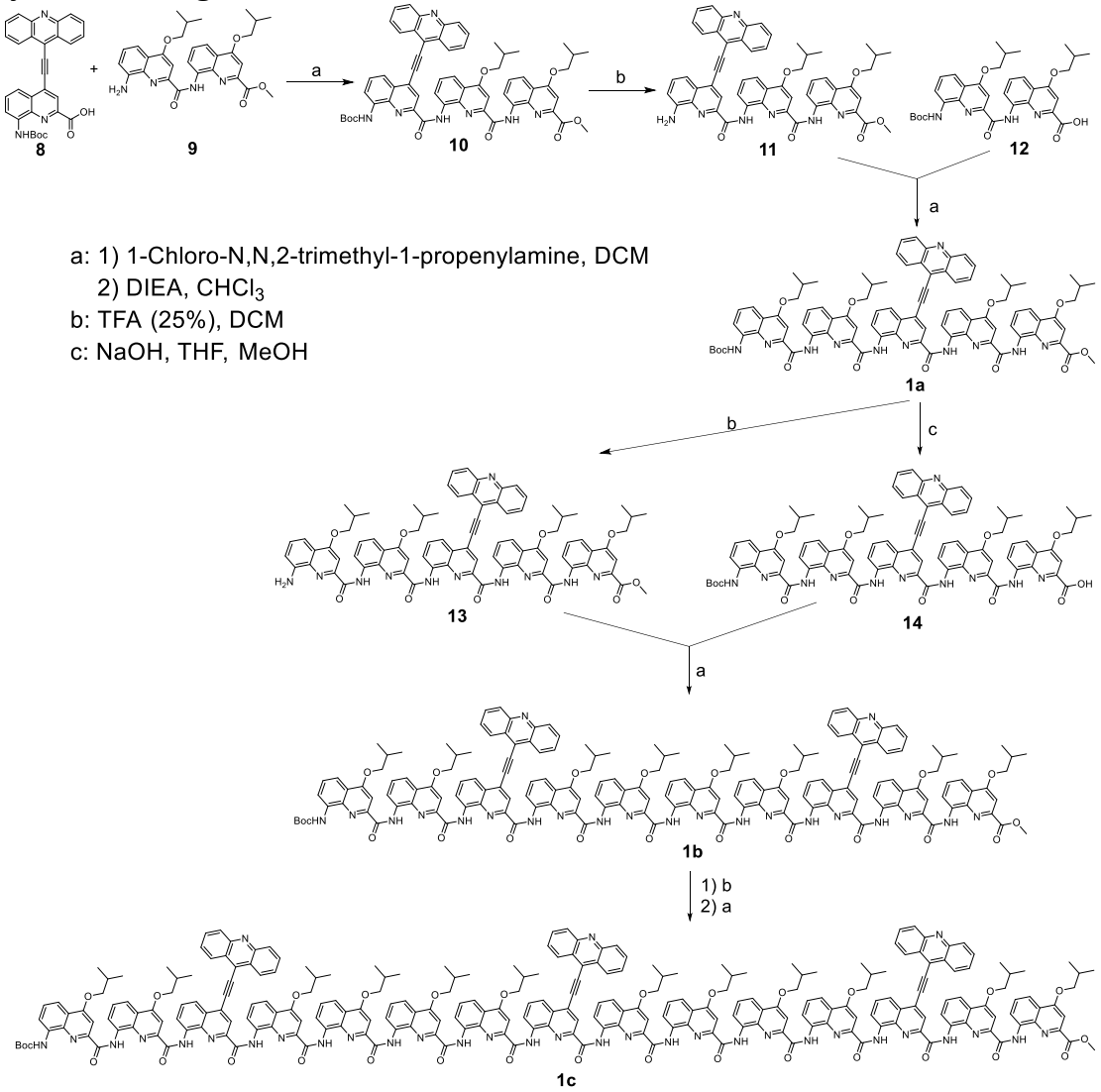
9-ethynylacridine **A3** was prepared according to a known procedure [1] with minor changes. Methyl 8-nitro-4-bromoquinoline-2-carboxylate **4**[2] and methyl 8-Boc-amino-4-bromoquinoline-2-carboxylate **6**[3] have been reported previously. Spectroscopic data of those compounds matched with reports.

Acridine monomer 7. Methyl 8-amine-4-bromoquinoline-2-carboxylate **5**: Compound **4** (1.56 g, 5 mmol), acetic acid (10 mL) and MeOH (20 mL) were added into a 100 mL flask. Iron powder (1.4 g, 25 mmol) was added slowly in portions into the mixture while maintaining proper stirring to avoid vigorous generation of gases. After completion of addition of iron powder, the reaction mixture was allowed to slowly heat at 65 ℃ for about 40 minutes. The heating was stopped to allow the reaction mixture to cool down to room temperature after the complete conversion of the starting material as indicated by TLC. The resulting sluggish solution was filtrated through a pad of celite which was washed thoroughly with dichloromethane. The organic solution was then dried over sodium sulfate, filtrated and the solvent was removed with rotatory evaporation. The residual orange solid (1.2 g) was used directly for the next step without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.40 (s, 1 H), 7.54-7.45 (m, 2 H), 6.98 (dd, *J* = 7.0, 1.7 Hz, 1 H), 5.24 (bs, 2 H), 4.04 (s, 3 H) ppm.

Methyl 8-Boc-amine-4-bromoquinoline-2-carboxylate **6**: The crude starting material of compound **5** (1.2 g, 4.27 mmol) and Boc_2O (5.45 g, 25 mmol) were added into a 100 mL flask together with dioxane (15 mL) and DIEA (5.6 mL). The reaction mixture was then heated at 80 ℃ for 5 days under N_2 with magnetic stirring. After cooling down to room temperature, solvent was evaporated and the resulting sluggish mixture was directly applied on a column. The product was eluted with dichloromethane/ethyl acetate (vol/vol 20/1). Some of the unreacted **5** was recovered from the column and recycled for the reaction. Yield 1.4 g (75% over two steps). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.00 (s, 1 H), 8.56 (d, *J* = 8.0 Hz, 1 H), 8.46 (s, 1 H), 7.80 (dd, *J* = 8.4, 1.3 Hz, 1 H), 7.71 (t, *J* =8.0 Hz, 1 H), 4.07 (s, 3 H), 1.59 (s, 9 H) ppm.

Monomer **7**: Compound **6** (1.22 g, 3.21 mmol), 9-ethynylacridine **A3** (0.85 g, 4.18 mmol), $PdCl_2(PPh_3)_2$ (120 mg, 0.16 mmol), CuI (61 mg, 0.32 mmol) and PPh_3 (84 mg, 0.32 mmol) were added into a dry 50 mL flask. The flask was then equipped with a condenser and sealed with rubber septum. Cycles of vacuum and back-fill with N_2 was done for three times. A mixture of degas dry THF and dry Et_3N (12 mL, vol/vol 2/1) was added into the flask through a syringe. The resulting mixture was heated at 75 ℃ for overnight under N_2. After cooling down to room temperature, the precipitate was filtrated and washed with methanol. The solid was dried under vacuum to give an orange powder (1.1 g, yield: 68%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.08 (s, 1 H), 8.63 (d, *J* = 8.4 Hz, 2 H), 8.60 (s, 1 H), 8.32 (d, *J* = 8.6 Hz, 2 H), 8.16 (d, *J* = 8.4 Hz, 1 H), 7.89 (d, *J* = 8.6, 1 H), 7.86 (d, *J* = 8.6 Hz, 1 H), 7.81 (t, *J* =8.2 Hz, 1 H), 7.75 (d, *J* = 8.4 Hz, 1 H), 7.72 (d, *J* = 8.4 Hz, 1 H), 4.14 (s, 3 H), 1.62 (s, 9 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.2, 152.8, 148.6, 148.6, 145.0, 137.7, 137.0, 131.2, 130.6, 130.6, 130.4, 130.4, 130.2, 128.5, 127.6, 127.5, 126.6, 126.4, 126.3, 125.8, 124.7, 117.8, 115.9, 99.4, 93.7, 81.2, 53.3, 28.5 ppm; ESI+ HRMS m/z: calcd for $C_{31}H_{26}N_3O_4$ $[M+H]^+$ 504.1923, found 504.1949.

1.2 synthesis of oligomers 1a-1d



Scheme S2: synthetic route for oligomers **1a-1c**.

Compounds **9**[4] and **12**[5] have been reported previously and were prepared again here according to the same procedure.

Monomer acid **8**: The monomer **7** (200 mg, 0.4 mmol), NaOH (40 mg, 1 mmol) were dissolved in 4 mL THF and 1 mL MeOH at room temperature. The resulting mixture was stirred at room temperature until complete consumption of the starting ester (followed by TLC, usually takes about 2 hours). Then the pH was adjusted to around 3 with 5% citric acid aqueous solution. The precipitate was filtrated and washed with water and MeOH. The yellow solid was collected and dried under high vacuum (180 mg, yield 91%). No further purification was done because of poor solubility in common solvents and was used directly for next steps.

General procedure for the acid chloride coupling: The carboxylic acid (1.05 to 1.1 equiv. with respect to the amine reactants) was activated to corresponding acid chloride by using 1-chloro-N,N,2-trimethyl-1-propenylamine. The activation was done by mixing the solution of the acid in dry dichloromethane and the activating reagent (for 1-chloro-N,N,2-trimethyl-1-propenylamine, 1.5 equiv. with respect to the acid) at room temperature for 2 hours. After activation, the solvent and excess activating reagents were removed under high vacuum

for at least 3 hours. The amine starting material (1 equiv.) was added into a separate flask and then back filled with N_2. The acid chloride was dissolved in minimum amount of dry $CHCl_3$ and transferred into the flask containing the amine. Dry DIEA (3 equiv. with respect to the amine) was added. The reaction mixture was then stirred at room temperature under N_2 for overnight. Then the solvent was evaporated and the residue was purified either by precipitation with appropriate solvent combinations or with flash silica gel chromatogram or preparative recycling GPC.

General procedure for Boc-deprotection: The Boc-protected compound was dissolved into 3 mL of dry dichloromethane and then 1 mL of TFA was added into the solution. The resulting mixture was stirred at room temperature for about 2 hours before diluting with dichloromethane. The solution was washed three times with water and saturated $NaHCO_3$ aqueous solution. The organic layer was separated and dried over Na_2SO_4. The solvent was removed after filtration and dried under high vacuum to yield the desired amine. The yield was quantitative as indicated by crude ^{1}H NMR spectra and the product was used for the subsequent reaction without any further purifications.

Oligomer **10**: This compound was prepared according to the general coupling procedure starting from monomer acid **8** (130 mg, 0.347 mmol) and dimer amine **9** (179 mg, 0.347 mmol). The pure product was obtained by precipitation from dichloromethane/methanol (5/1 vol/vol). (Yield: 230mg, 67%) ^{1}H NMR (300 MHz, $CDCl_3$) δ: 12.44 (s, 1 H), 12.41 (s, 1 H), 9.07 (d, *J* = 7.6 Hz, 1 H), 9.06 (d, *J* = 7.6 Hz, 1 H), 8.81 (s, 1 H), 8.73 (d, *J* = 8.3 Hz, 2 H), 8.40 (s, 1 H), 8.35 (d, *J* = 8.8 Hz, 2 H), 8.08 (d, *J* = 8.8 Hz, 1 H), 8.06 (d, *J* = 8.4 Hz, 1 H), 7.96-7.89 (m, 3 H), 7.82 (s, 1 H), 7.81 (d, *J* = 8.6 Hz, 1 H), 7.78 (d, *J* = 8.6 Hz, 1 H), 7.74 (t, *J* = 8.3 Hz, 1 H), 7.68 (t, *J* = 8.3 Hz, 1 H), 7.58 (d, *J* = 8.3 Hz, 1 H), 7.42 (t, *J* = 8.3 Hz, 1 H), 6.72 (s, 1 H), 4.19 (d, *J* = 6.6 Hz, 2 H), 3.82 (d, *J* = 6.3 Hz, 2 H), 3.61 (s, 3 H), 2.41-2.21 (m, 3 H), 1.38 (s, 9 H), 1.20 (d, *J* = 6.6 Hz, 6 H), 1.17 (d, *J* = 6.9 Hz, 6 H) ppm; ESI+ HRMS m/z: calcd for $C_{59}H_{54}N_7O_8$ $[M+H]^+$ 988.4034, found 988.4107.

Compound **11**: This compound was synthesized from oligomer **10** (40 mg, 0.04 mmol) according to the general Boc-deprotection procedure. The obtained solid product was used for the next step without any further purification after work-up. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 12.39 (s, 1 H), 12.35 (s, 1 H), 9.11 (d, *J* = 8.0 Hz, 1 H), 8.95 (d, *J* = 7.6 Hz, 1 H), 8.77 (s, 1 H), 8.73 (d, *J* = 8.6 Hz, 2 H), 8.33 (d, *J* = 8.9 Hz, 2 H), 8.05 (d, *J* = 8.5 Hz, 1 H), 7.98 (d, *J* = 8.4 Hz, 1 H), 7.91 (d, *J* = 8.6 Hz, 1 H), 7.88 (d, *J* = 8.8 Hz, 1 H), 7.80-7.69 (m, 6 H), 7.23 (t, *J* = 7.8 Hz, 1 H), 6.85 (s, 1 H), 6.06 (d, *J* = 7.7 Hz, 1 H), 4.18 (d, *J* = 6.4 Hz, 2 H), 3.86 (d, *J* = 6.4 Hz, 2 H), 3.57 (s, 1 H), 2.38-2.24 (m, 3 H), 1.19 (d, *J* = 6.3 Hz, 6 H), 1.17 (d, *J* = 6.3 Hz, 6 H).

Oligomer **1a**: This compound was prepared according to the general coupling steps from dimer acid **12** (129 mg, 0.214 mmol) and amine oligomer **11** (190 mg, 0.214 mmol). Yield: 240 mg, 76%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 11.98 (s, 1 H), 11.92 (s, 1 H), 11.83 (s, 1 H), 11.81 (s, 1 H), 8.76 (d, *J* = 8.4 Hz, 2 H), 8.72 (d, *J* = 7.8 Hz, 1 H), 8.62 (d, *J* = 7.8 Hz, 1 H), 8.39 (d, *J* = 8.4 Hz, 2 H), 8.34 (d, *J* = 6.9 Hz, 1 H), 8.18 (d, *J* = 7.5 Hz, 1 H) , 8.12 (d, *J* = 8.6 Hz, 1 H), 8.07 (s, 1 H), 8.05-7.85 (m, 9 H), 7.74 (t, *J* = 8.5 Hz, 1 H), 7.71 (t, *J* = 8.5 Hz, 1 H), 7.53 (t, *J* = 8.0 Hz, 1 H), 7.45 (s, 1 H), 7.40 (s, 1 H), 7.40 (d, *J* = 7.6 Hz, 1 H), 7.36 (t, *J* = 8.0 Hz, 1 H), 7.24 (t, *J* = 8.0 Hz, 1 H), 6.87 (s, 1 H), 6.63 (s, 1 H), 4.47-4.40 (m, 2 H), 4.26-4.17 (m, 2 H), 3.96 (d, *J* = 6.2 Hz, 2 H), 3.86-3.81 (m, 2 H), 3.29 (s, 3 H), 2.61-2.27 (m, 4 H), 1.36-1.17 (m, 24 H), 1.13 (s, 9 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.0, 163.9, 163.6, 163.3, 162.5, 161.7, 161.2, 161.1, 160.6, 151.6, 150.2, 149.8, 149.1, 148.82, 147.4, 145.5, 139.3, 138.4, 137.9, 137.0, 136.6, 134.4, 134.3, 133.8, 133.7, 133.5, 130.7, 130.4, 130.3, 129.4, 127.8, 127.8,

127.7, 127.3, 127.2, 127.1, 126.9, 126.5, 126.2, 122.6, 122.4, 122.1, 122.0, 121.2, 119.5, 117.4, 117.3, 117.2, 116.6, 116.3, 116.2, 115.6, 114.7, 114.6, 100.5, 99.7, 99.5, 99.3, 98.1, 93.6, 80.6, 75.7, 75.6, 75.3, 75.2, 52.3, 28.4, 28.4, 28.3, 28.3, 27.9, 19.6, 19.5, 19.5, 19.5, 19.4 ppm; ESI+ HRMS m/z: calcd for $C_{87}H_{82}N_{11}O_{12}$ $[M+H]^+$ 1472.6144, found 1472.6266.

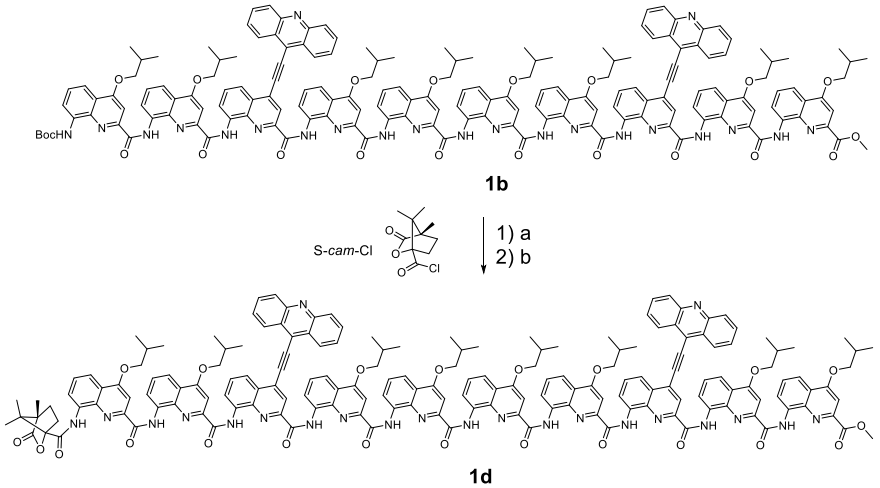
Compound **13**: This compound was prepared from oligomer **1a** (120 mg, 0.081 mmol) according to the general Boc-deprotection procedure. The obtained solid product was used for the next step without any further purifications after work-up. The yield was assumed to be quantitative. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 12.00 (s, 1 H), 11.97 (s, 1 H), 11.83 (s, 1 H), 11.71 (s, 1 H), 8.76 (d, *J* = 8.6 Hz, 2 H), 8.64 (d, *J* = 8.6 Hz, 1 H), 8.61 (d, *J* = 8.8 Hz, 1 H), 8.39 (d, *J* = 8.4 Hz, 2 H), 8.23 (s, 1 H), 8.20 (s, 1 H), 8.12 (d, *J* = 8.1 Hz, 2 H), 8.06-7,84 (m, 8 H), 7.71 (t, *J* = 8.1 Hz, 1 H), 7.70 (t, *J* = 8.4 Hz, 1 H), 7.62-7.56 (m, 2 H), 7.42 (s, 1 H), 7.35 (s, 1 H), 7.35 (t, *J* = 7.5 Hz, 1 H), 7.07 (t , *J* = 8.1 Hz, 1 H), 6.87 (s, 1 H), 6.67 (s, 1 H), 5.93 (d, *J* = 7.8 Hz, 1 H), 4.46-4.32 (m, 2 H), 4.25-4.11 (m, 2 H), 3.96 (d, *J* = 6.3 Hz, 2 H), 3.85 (q, *J* = 2.7 Hz, 2 H), 3.32 (s, 2 H), 2.58-2.27 (m, 4 H), 1.35-1.18 (m, 24 H) ppm.

Compound **14**: Oligomer **1a** (120 mg, 0.08 mmol) and NaOH (33 mg, 0.8 mmol) was dissolved into 1.8 mL of THF and 0.2 mL of MeOH in a 5 mL flask. The resulting mixture was stirred at room temperature for 2 hours. After completely consumption of the starting material, the pH of the reaction mixture was adjusted to 3. The orange precipitate was filtrated and washed three times with methanol and three times with water. The solid was collected and died under high vacuum. Yield: 100 mg, 84%. Crude ^{1}H NMR spectrum in $CDCl_3$ was very complicated, a clear one set of NMR spectrum was observed in the presence of excess of Et_3N in $CDCl_3$. ^{1}H NMR (300 MHz, $CDCl_3$ in the presence of excess of Et_3N) δ: 12.08 (s, 1 H), 12.01 (s, 1 H), 11.86 (s, 1 H), 11.80 (s, 1 H), 8.75 (d, *J* = 8.6 Hz, 2 H), 8.62 (dd, *J* = 7.8, 1.1 Hz, 1 H), 8.45 (dd, *J* = 7.8, 1.5 Hz, 1 H), 8.37 (d, *J* = 8.5 Hz, 2 H), 8.30 (d, *J* = 7.6 Hz, 1 H), 8.20 (d, *J* = 8.3 Hz, 1 H), 8.09 (dd, *J* = 8.5, 1.3 Hz, 1 H), 8.05 (s, 1 H), 8.02 (s, 2 H), 8.02 (dd, *J* = 8.5, 1.3 Hz, 1 H), 7.95 (dd, *J* = 8.5, 1.3 Hz, 1 H), 7.93 (dd, *J* = 8.5, 1.3 Hz, 1 H), 7.87 (dd, *J* = 8.5, 1.3 Hz, 1 H), 7.84 (dd, *J* = 8.5, 1.3 Hz, 1 H), 7.82 (dd, *J* = 8.5, 1.3 Hz, 1 H), 7.76 (s, 1 H), 7.71-7.53 (m, 4 H), 7.50 (s, 1 H), 7.43-7.24 (m, 5 H), 6.87 (s, 1 H), 6.72 (s, 1 H), 4.48-4.38 (m, 2 H), 4.26-4.13 (m, 2 H), 3.96 (dd, *J* = 6.3, 2.6 Hz, 2 H), 3.80 (d, *J* = 6.1 Hz, 2 H), 2.45-2.26 (m, 4 H), 1.35-1.14 (m, 24 H), 1.11 (s, 9 H) ppm;

Oligomer **1b**: This compound was prepared from **14** (50 mg, 0.0336 mmol) and **13** (35 mg, 0.0258 mmol) according to the general coupling procedures with minor changes. The acid **14** was activated with 1-chloro-N,N,2-trimethyl-1-propenylamine for overnight. The rest of the procedure was the same. The product was purified with silica gel column chromatography (eluent: DCM/EA 100/3). Yield: 40 mg, 55%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 11.34 (s, 1 H), 11.25 (s, 1 H), 11.18 (s, 1 H), 11.17 (s, 1 H), 10.98 (s, 1 H), 10.85 (s, 1 H), 10.73 (s, 1 H), 10.56 (s, 1 H), 10.53 (s, 1 H), 8.54 (m, 4 H), 8.29 (d, *J* = 8.8 Hz, 2 H), 8.26 (d, *J* = 8.5 Hz, 1 H), 8.19-8.05 (m, 8 H), 7.95 (d, *J* = 8.4 Hz, 2 H), 7.85 (d, *J* = 8.3 Hz, 1 H), 7.77 (d, *J* = 8.3 Hz, 1 H), 7.74-7.65 (m, 8 H), 7.65 (s, 1 H), 7.57-7.28 (m, 18 H), 7.23-7.07 (m, 7 H), 7.00 (s, 1 H), 6.95 (t, *J* = 7.9 Hz, 2 H), 6.90 (s, 1 H), 6.84 (s, 1 H), 6.55 (s, 1 H), 6.44 (s, 1 H), 6.35 (s, 1 H), 6.34 (s, 1 H), 6.27 (s, 1 H), 6.22 (s, 1 H), 4.15-3.77 (m, 14 H), 3.63 (d, *J* = 6.2 Hz, 2 H), 3.04 (s, 3 H), 2.55-2.13 (m, 8 H), 1.39-1.03 (m, 48 H), 0.93 (s, 9 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ: 163.3, 163.2, 162.9, 162.8, 162.7, 162.4, 162.0, 161.1, 160.6, 160.5, 160.1, 159.4, 159.2, 159.2, 159.1, 158.0, 151.4, 149.4, 149.1, 148.7, 148.6, 148.5, 148.5, 147.1, 146.2, 145.0, 138.7, 137.9, 137.4, 137.4, 137.3, 137.2, 136.4, 136.1, 134.1, 133.7, 133.5, 133.3, 133.2, 133.1, 132.9, 132.6, 132.4, 132.1, 130.6, 130.3, 130.2, 129.9, 129.8, 128.8, 128.7, 128.0, 127.6, 127.4, 127.2, 126.9, 126.8, 126.6, 126.6, 126.3, 126.0, 125.8, 122.5, 122.3, 122.2, 122.0, 121.9, 121.6, 121.5, 121.3,

120.2, 119.5, 117.4, 116.9, 116.7, 116.2, 116.1, 115.7, 115.2, 114.5, 114.4, 100.2, 99.8, 99.2, 99.0, 98.8, 98.6, 98.4, 97.7, 93.1, 92.9, 80.2, 75.4, 75.3, 75.0, 74.8, 52.0, 45.9, 28.3, 28.2, 28.1, 28.0, 27.7, 19.7, 19.7, 19.5, 19.5, 19.4, 19.4, 19.3, 19.3, 19.3, 19.2, 8.7 ppm; ESI+ HRMS m/z: calcd for $C_{168}H_{152}N_{22}O_{21}$ $[M+2H]^{2+}$ 1407.0768, found 1407.0869.

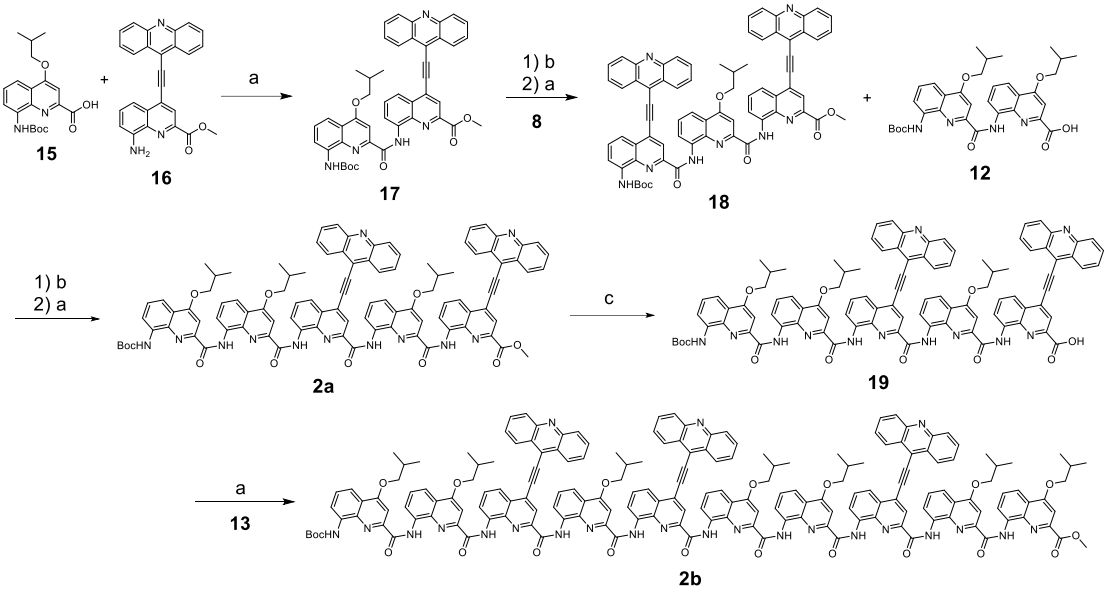
Oligomer **1c**: The corresponding free amine of **1b** (35 mg, 0.0124 mmol) was obtained first according to general Boc-deprotection procedure. The yield was considered to be quantitative by crude ^{1}H NMR and the compound was used for coupling with no further purifications. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 11.34 (s, 1 H), 11.25 (s, 1 H), 11.20 (s, 1 H), 11.03 (s, 1 H), 11.00 (s, 1 H), 10.88 (s, 1 H), 10.82 (s, 1 H), 10.60 (s, 1 H), 8.58-8.52 (m, 4 H), 8.29-8.20 (m, 5 H), 8.15-8.03 (m, 7 H), 7.97 (q, *J* = 3.3 Hz, 2 H), 7.84 (d, *J* = 8.2 Hz, 2 H), 7.76-7.26 (m, 22 H), 7.19 (t, *J* = 8.2 Hz, 1 H), 7.16 (s, 1 H), 7.13 (t, *J* = 7.6 Hz, 1 H), 7.10 (t, *J* = 7.6 Hz, 1 H), 6.84 (s, 1 H), 6.82 (s, 1 H), 6.79 (t, *J* = 7.6 Hz, 1 H), 6.56 (s, 1 H), 6.43 (s, 1 H), 6.36 (s, 1 H), 6.34 (s, 1 H), 6.30 (s, 1 H), 6.24 (s, 1 H), 5.65 (d, *J* = 7.6 Hz, 1 H), 4.16-3.78 (m, 14 H), 3.64 (d, *J* = 6.1 Hz, 2 H), 3.04 (s, 3 H), 2.54-2.13 (m, 8 H), 1.42-1.04 (m, 48 H) ppm. The oligomer **1c** was prepared by coupling of the corresponding free amine of **1b** and acid **14** (50 mg, 0.0336 mmol) according to the general coupling procedure with minor changes. The acid **14** was activated with 1-chloro-N,N,2-trimethyl-1-propenylamine for overnight. The rest of the procedure was the same. The pure product was obtained by GPC and silica gel column chromatography (eluent: DCM/EA 100/5). Yield: 25 mg, 44%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 11.15 (s, 1 H), 11.08 (s, 1 H), 10.99 (s, 1 H), 10.95 (s, 1 H), 10.70 (s, 1 H), 10.50 (s, 1 H), 10.32 (s, 1 H), 10.28 (s, 2 H), 10.22 (s, 1 H), 10.20 (s, 1 H), 10.18 (s, 1 H), 10.06 (s, 1 H), 10.02 (s, 1 H), 8.45-8.42 (m, 2 H), 8.38 (d, *J* = 8.3 Hz, 2 H), 8.25 (t, *J* = 8.7 Hz, 3 H), 8.15-7.95 (m, 8 H), 7.89 (dd, *J* = 8.2, 1.3 Hz, 3 H), 7.82-7.59 (m, 12 H), 7.52 (s, 1 H), 7.48 (d, *J* = 7.8 Hz, 1 H), 7.46-7.28 (m, 13 H), 7.23-7.04 (m, 14 H), 7.01-6.89 (m, 6 H), 6.84 (t, *J* = 8.1 Hz, 1 H), 6.83 (s, 1 H), 6.80 (s, 1 H), 6.77 (s, 1 H), 6.70 (s, 1 H), 6.44 (s, 1 H), 6.24 (s, 1 H), 6.23 (s, 1 H), 6.13 (s, 1 H), 6.08 (s, 1 H), 6.04 (s, 1 H), 5.93 (s, 1 H), 5.91 (s, 1 H), 5.88 (s, 1 H), 5.76 (s, 1 H), 4.02-3.53 (m, 24 H), 2.94 (s, 3 H), 2.44-2.04 (m, 12 H), 1.31-0.96 (m, 72 H), 0.85 (s, 9 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ: 163.2, 163.1, 162.7, 162.6, 162.5, 162.4, 162.2, 162.0, 162.0, 160.9, 160.5, 160.4, 160.0, 159.1, 158.9, 158.8, 158.8, 158.5, 157.7, 151.2, 149.3, 148.9, 148.7, 148.6, 148.4, 148.3, 148.3, 148.2, 148.1, 148.0, 147.7, 151.3, 149.3, 148.9, 148.7, 148.6, 148.4, 148.3, 148.3, 148.2, 148.1, 148.0, 147.7, 146.9, 146.0, 145.9, 144.9, 138.6, 137.8, 137.2, 137.1, 136.9, 136.9, 136.8, 136.7, 136.2, 136.0, 135.8, 133.9, 133.6, 133.3, 133.2, 133.2, 133.1, 133.0, 132.6, 132.4, 132.3, 132.1, 131.9, 131.6, 130.5, 130.4, 130.2, 130.0, 129.8, 129.7, 129.5, 128.7, 128.5, 127.9, 127.5, 127.2, 127.1, 127.0, 126.8, 126.7, 126.5, 126.4, 126.1, 125.7, 125.6, 122.3, 122.2, 122.1, 122.0, 121.9, 121.8, 121.6, 121.5, 121.4, 121.1, 120.2, 117.2, 117.1, 116.8, 116.6, 116.0, 115.6, 115.1, 114.3, 100.2, 100.1, 99.7, 99.1, 98.7, 98.2, 98.6, 93.0, 92.8, 92.5, 80.1, 75.4, 75.3, 75.2, 75.0, 52.0, 28.4, 28.2, 28.2, 28.1, 28.0, 28.0, 27.9, 27.7, 19.9, 19.8, 19.7, 19.7, 19.6, 19.6, 19.5, 19.5, 19.4, 19.4, 19.3, 19.3, 19.3, 19.2 ppm; ESI+ HRMS m/z: calcd for $C_{249}H_{221}N_{33}O_{30}$ $[M+2H]^{2+}$ 2077.3425, found 2077.4460.



Scheme S3: synthesis of **1d** with S-camphanyl group at the N-terminus of the oligomer. a) TFA (25vol%), DCM; b) DIEA, $CHCl_3$.

Oligomer **1d**: The oligomer **1b** was deprotected with TFA following the general procedure for Boc-deprotection to obtain it's corresponding free amine. The coupling of the free amine of **1b** and S-camphanyl acid chloride (1.6 equiv. with respect to the free amine) was done by mixing the two reactants in dry $CHCl_3$. Freshly distilled DIEA was added (2.2 equiv.). The reaction mixture was stirred at room temperature for overnight. The complete consumption of the free amine of **1b** was confirmed by checking the crude 1H NMR spectra. Then, the reaction mixture was diluted with dichloromethane and washed 3 times with water. The organic layer was collected, dried and solvent was removed. The crude product was purified by two times of precipitation with DCM/MeOH solvent mixture. A yellow solid was obtained as the pure product (yield: 73% calculating from starting **1b**). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 11.34 (s, 1H), 11.24 (s, 2H), 11.10 (s, 1H), 10.97 (s, 1H), 10.84 (s, 1H), 10.73 (s, 1H), 10.52 (s, 1H), 9.36 (s, 1H), 8.63 – 8.50 (m, 4H), 8.35 – 8.24 (m, 3H), 8.18 (dd, *J* = 8.1, 1.6 Hz, 2H), 8.15 – 7.99 (m, 7H), 7.94 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.85 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.80 – 7.61 (m, 10H), 7.61 – 7.46 (m, 9H), 7.46 – 7.26 (m, 8H), 7.24 – 7.01 (m, 6H), 6.99 (s, 1H), 6.88 (s, 1H), 6.77 (s, 1H), 6.55 (s, 1H), 6.45 (s, 1H), 6.35 (s, 1H), 6.33 (s, 1H), 6.25 (s, 1H), 6.22 (s, 1H), 4.24 – 3.74 (m, 15H), 3.63 (d, *J* = 6.3 Hz, 2H), 3.04 (s, 3H), 2.61 – 1.79 (m, 10H), 1.43 – 0.99 (m, 52H), 0.52 (d, *J* = 6.8 Hz, 6H), 0.02 (s, 3H) ppm; ESI+ HRMS m/z: calcd for $C_{173}H_{155}N_{22}O_{22}$ $[M+H]^+$ 2893.1720, found 2893.1872.

1.3 synthesis of oligomers 2a-2b



a: 1) 1-Chloro-N,N,2-trimethyl-1-propenylamine, DCM, 2) DIEA, $CHCl_3$
b: TFA (25%), DCM; c: NaOH, THF, MeOH

Scheme S4: Synthetic route for oligomers **2a** and **2b**.

Monomer acid **15**[5] has been reported before and was prepared again accordingly.

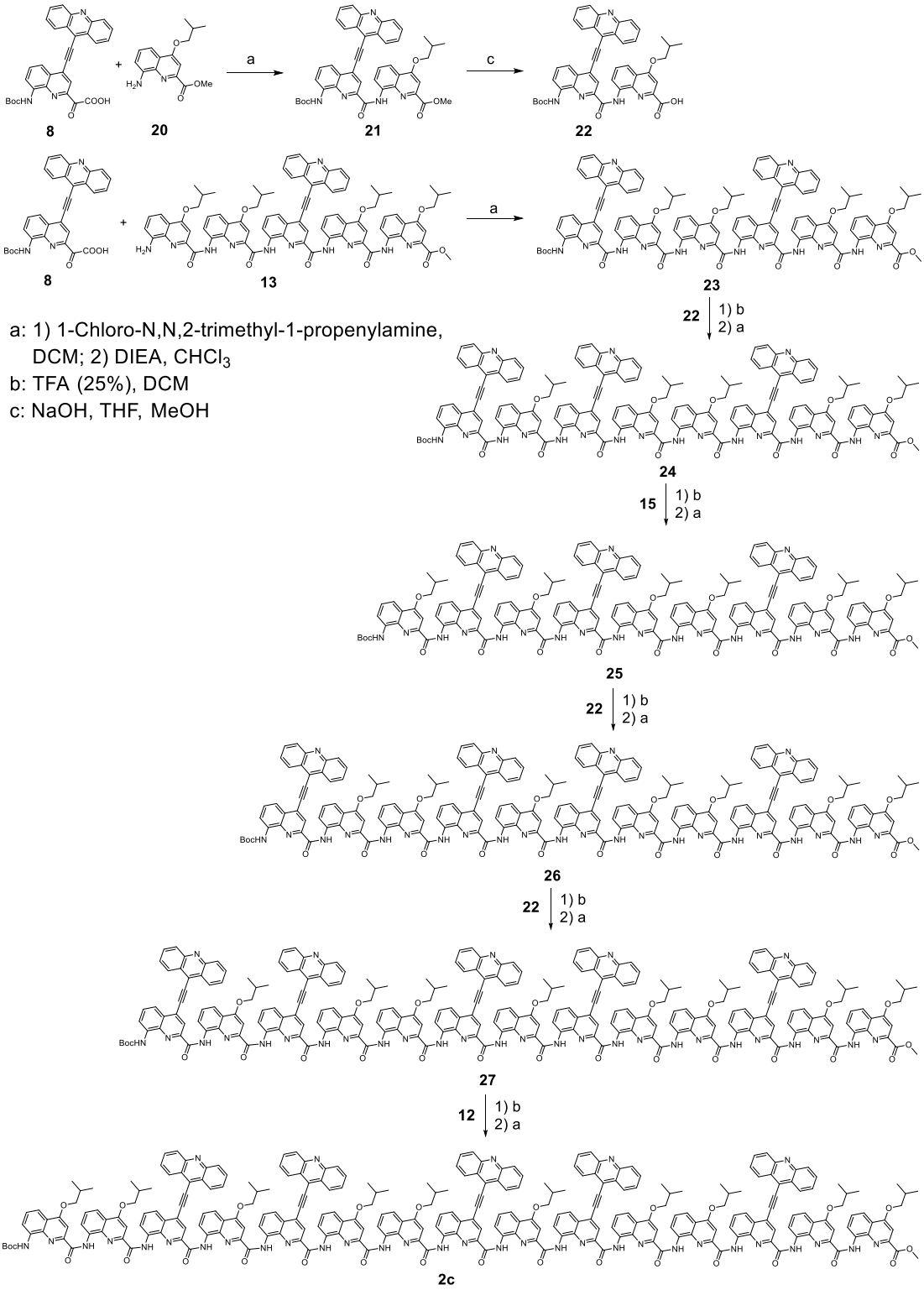
Compound **17**: The monomer **7** (200 mg, 0.4 mmol) was first deprotected with TFA according to the general Boc-deprotection procedure. The solid was used without further purification after work-up and the yield was assumed to be quantitative. The coupling between the monomer acid **15** (214 mg, 0.594 mmol) and the free amine **16** was followed with the general coupling procedure. The product was purified by precipitation with DCM/MeOH (1/5 vol/vol). A yellow solid was obtained after drying under vacuum. Yield: 120 mg, 40% over two steps. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 12.46 (s, 1 H), 9.07 – 8.98 (m, 1 H), 8.72 (s, 1 H), 8.66 (dd, *J* = 8.8, 1.4 Hz, 2 H), 8.50 (dd, *J* = 7.8, 1.3 Hz, 1 H), 8.32 (dd, *J* = 8.4, 1.2 Hz, 2 H), 8.00 – 7.82 (m, 3 H), 7.81 – 7.70 (m, 2 H), 7.60 (t, *J* = 8.1 Hz, 1 H), 4.12 (d, *J* = 7.0 Hz, 2 H), 4.11 (s, 3 H), 2.33 (m, 1 H), 1.51 (s, 9 H), 1.16 (d, *J* = 7.1 Hz, 6 H) ppm; ESI+ HRMS m/z: calcd for $C_{45}H_{40}N_5O_6$ $[M+H]^+$ 746.2979, found 746.3019.

Compound **18**: This compound was prepared from monomer acid **8** (118 mg, 0.24 mmol) and the corresponding free amine of oligomer **17** according to general coupling procedure. The oligomer **17** (120 mg, 0.16 mmol) was converted to its corresponding free amine according to the general Boc-deprotection procedure. The product was purified by precipitation from DCM/MeOH (1/5, vol/vol). A yellow solid was obtained after drying under vacuum. Yield: 120 mg (67% over two steps). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 12.47 (s, 1 H), 12.45 (s, 1 H), 9.23 (d, *J* = 7.9 Hz, 1 H), 9.08 (d, *J* = 7.5 Hz, 1 H), 8.83 (s, 1 H), 8.73 (d, *J* = 8.4 Hz, 2 H), 8.65 (d, *J* = 8.6 Hz, 2 H), 8.50 (s, 1 H), 8.34 (d, *J* = 8.7 Hz, 2 H), 8.27 (dd, *J* = 8.4, 1.3 Hz, 1 H), 8.11 (ddd, *J* = 8.5, 4.6, 1.3 Hz, 2 H), 8.00 – 7.82 (m, 6 H), 7.81 – 7.72 (m, 5 H), 7.65 (d, *J* = 7.8 Hz, 1 H), 7.54 (t, *J* = 8.0 Hz, 1 H), 4.21 (d, *J* = 6.5 Hz, 2H), 3.70 (s, 3 H), 2.39 (m, 1 H), 1.41 (s, 9 H), 1.22 (d, *J* = 6.7 Hz, 6 H) ppm; ESI+ HRMS m/z: calcd for $C_{70}H_{53}N_8O_7$ $[M+H]^+$ 1117.4037, found 1117.4121.

Oligomer **2a**: This compound was prepared from dimer acid **12** (92 mg, 0.15 mmol) and the corresponding free amine of oligomer **18** according to general coupling procedure. The oligomer **18** (120 mg, 0.10 mmol) was converted to its corresponding free amine according to the general Boc-deprotection procedure. The product **2a** was purified by precipitation from DCM/MeOH (1/5, vol/vol). A yellow solid was obtained after drying under vacuum. Yield: 150 mg (87% over two steps). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 12.08 (s, 1 H), 11.96 (s, 1 H), 11.89 (s, 1 H), 11.85 (s, 1 H), 8.84 – 8.66 (m, 6 H), 8.44 – 8.33 (m, 5 H), 8.29 (d, *J* = 7.6 Hz, 1 H), 8.25 (dd, *J* = 8.4, 1.1 Hz, 1 H), 8.13 (dd, *J* = 8.4, 1.3 Hz, 1 H), 8.09 (s, 1 H), 8.04 (d, *J* = 8.0 Hz, 2 H), 8.00 (d, *J* = 8.0 Hz, 1 H), 7.98 – 7.85 (m, 7 H), 7.84 – 7.74 (m, 3 H), 7.69 (s, 1 H), 7.66 (t, *J* = 8.0 Hz, 1 H), 7.52 (s, 1 H), 7.44 (s, 1 H), 7.42 – 7.34 (m, 2 H), 7.26 (t, J= 8.2 Hz, 1 H), 6.87 (s, 1 H), 4.51 – 4.40 (m, 2 H), 4.24 (dt, *J* = 12.2, 8.2 Hz, 2 H), 3.97 (d, *J* = 6.4 Hz, 2 H), 3.39 (s, 3 H), 2.66 – 2.48 (m, 2 H), 2.39 (dt, *J* = 13.1, 6.5 Hz, 1 H), 1.39 – 1.23 (m, 18 H), 1.12 (s, 9 H) ppm; ESI+ HRMS m/z: calcd for $C_{98}H_{81}N_{12}O_{11}$ $[M+H]^+$ 1602.6181, found 1602.6290.

Oligomer **2b**: The oligomer **2a** (150 mg, 0.09 mmol) was hydrolyzed with NaOH (38 mg, 0.94 mmol) in THF/MeOH (2.7 mL/0.3 mL) at room temperature for 1.5 hours. After adjust the pH to ~4 with citric acid (5% in H_2O), a yellow precipitate was formed. The precipitate was filtrated and washed with water. The solid was collected and dried under high vacuum. Then the solid was coupled with amine **13** (100 mg, 0.07 mmol) according to the general coupling procedure. After reaction, the residue after removing solvent was precipitate with DCM/MeOH (1/5 vol/vol). The precipitation was then further purified with GPC and followed by silica gel column chromatography to obtain a small amount of pure product as yellow solid. Yield: 25 mg, (7% over two steps). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 11.37 (s, 1 H), 11.32 (s, 1 H), 11.28 (s, 1 H), 11.20 (s, 1 H), 11.01 (s, 1 H), 10.78 (s, 1 H), 10.65 (s, 2 H), 10.61 (s, 1 H), 8.86 (d, *J* = 8.5 Hz, 2 H), 8.55 (m, 4 H), 8.47 – 8.40 (m, 3 H), 8.27 (d, *J* = 8.8 Hz, 2 H), 8.24 (d, *J* = 7.6 Hz, 1 H), 8.20 – 8.13 (m, 5 H), 8.09 (t, *J* = 6.4 Hz, 2 H), 8.04 – 7.96 (m, 4 H), 7.94 – 7.82 (m, 4 H), 7.80 – 7.65 (m, 7 H), 7.64 – 7.40 (m, 9 H), 7.39 – 7.30 (m, 4 H), 7.14 (dt, *J* = 14.1, 7.3 Hz, 3 H), 6.98 (d, *J* = 1.7 Hz, 2 H), 6.94 (d, *J* = 7.9 Hz, 1 H), 6.89 (s, 1 H), 6.56 (s, 1 H), 6.51 (s, 1 H), 6.43 (s, 1 H), 6.34 (s, 1 H), 6.16 (s, 1 H), 4.23 – 3.73 (m, 15 H), 3.55 (d, *J* = 6.6 Hz, 2 H), 3.06 (s, 3 H), 2.61 – 2.20 (m, 8 H), 2.06 – 1.94 (m, 1 H), 1.43 – 1.06 (m, 30 H), 0.94 – 0.79 (m, 21H) ppm; ESI+ HRMS m/z: calcd for $C_{179}H_{151}N_{23}O_{20}$ $[M+2H]^{2+}$ 1471.5770, found 1471.5913.

1.4 Synthesis of Oligomer 2c



Scheme S5: Synthetic route for oligomer **2c**.

Monomer amine **20**[4] has been reported and was prepared accordingly.

Dimer **21**: This compound was prepared from monomer acid **8** and amine **20** according to the general coupling procedure. Yield: 300 mg, 75%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 12.42 (s, 1 H), 9.08 (s, 1 H), 8.98 (dd, *J* = 7.8, 1.3 Hz, 1 H), 8.85 (s, 1 H), 8.69 (d, *J* = 8.6 Hz, 2 H), 8.32

(d, *J* = 8.8 Hz, 2 H), 8.28 (dd, *J* = 8.8, 1.3 Hz, 2 H), 8.03 (dd, *J* = 8.6, 1.3 Hz, 1 H), 7.90 (dd, *J* = 8.8, 1.4 Hz, 1 H), 7.87 (d, *J* = 8.8 Hz, 1 H), 7.86 (t, *J* = 8.5 Hz, 1 H), 7.78 (dd, *J* = 8.6, 1.1 Hz, 1 H), 7.75 (dd, *J* = 8.3, 1.2 Hz, 1 H), 7.72 (t, *J* = 8.2 Hz, 1 H), 7.68 (s, 1 H), 4.11 (d, *J* = 6.4 Hz, 2 H), 4.06 (s, 3 H), 2.38-2.29 (m, 1 H), 1.50 (s, 9 H), 1.18 (d, *J* = 6.8 Hz, 6 H) ppm; ESI+ HRMS m/z: calcd for $C_{45}H_{40}N_5O_6$ $[M+H]^+$ 746.2979, found 746.3028.

Dimer acid **22**: The dimer **21** (300 mg, 0.4 mmol) and NaOH (160 mg, 4 mmol) was dissolved in 3.6 mL of THF and 0.4 mL of MeOH. The resulting mixture was stirred at room temperature for 2 hours. After completion of the reaction as followed by TLC, the pH was adjusted to 3 with citric acid (5% in H_2O). The precipitate was filtrated and then precipitated again in $CHCl_3$ and methanol to obtain an orange solid after filtration, yield: 180 mg, 62 %. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 11.09 (s, 1 H), 8.82 (d, *J* = 7.3 Hz, 1 H), 8.46 (br, 1 H), 8.39 (s, 1 H), 8.34 (d, *J* = 7.8 Hz, 1 H), 8.29 (d, *J* = 7.8 Hz, 2 H), 8.12 (d, *J* = 8.2 Hz, 2 H), 8.05 (d, *J* = 8.2 Hz, 2 H), 7.79 (s, 1 H), 7.68 (t, *J* = 7.8 Hz, 1 H), 7.67 (t, *J* = 8.2 Hz, 1 H), 7.60-7.49 (m, 4 H), 4.18 (d, *J* = 6.8 Hz, 2 H), 2.42-2.31 (m, 1 H), 1.64 (s, 9 H), 1.21 (d, *J* = 6.4 Hz, 6 H) ppm.

Oligomer **23**: The compound was prepared from acid **8** (45 mg, 0.0874 mmol) and amine **13** (100 mg, 0.0728 mmol) according to the general coupling procedure. The product was purified by silica gel column chromatography (eluent: DCM/EA 20/1 vol/vol). Yield: 55 mg, 46%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 11.85 (s, 1 H), 11.76 (s, 1 H), 11.63 (s, 1 H), 11.60 (s, 1 H), 11.45 (s, 1 H), 8.84 (d, *J* = 8.1 Hz, 2 H), 8.76 (d, *J* = 8.5 Hz, 2 H), 8.70 (d, *J* = 7.8 Hz, 1 H), 8.42-8.34 (m, 5 H), 8.27 (d, *J* = 8.1 Hz, 1 H), 8.25 (d, *J* = 8.1 Hz, 1 H), 8.16 (dd, *J* = 8.4, 1.3 Hz, 1 H), 8.14 (s, 1 H), 8.12 (d, *J* = 8.2 Hz, 1 H), 8.08 (dd, *J* = 7.6, 1.1 Hz, 1 H), 8.04 (dd, *J* = 8.3, 1.0 Hz, 1 H), 8.02 (dd, *J* = 8.3, 1.3 Hz, 1 H), 7.98-7.78 (m, 15 H), 7.73 (t, *J* = 8.2 Hz, 2 H), 7.66 (t, *J* = 8.1 Hz, 2 H), 7.48 (s, 2 H), 7.46 (t, *J* = 7.8 Hz, 1 H), 7.46 (t, *J* = 8.2 Hz, 1 H), 7.43 (t, *J* = 8.2 Hz, 1 H), 7.39 (t, *J* = 8.2 Hz, 1 H), 7.36 (t, *J* = 7.9 Hz, 1 H), 6.79 (s, 1 H), 6.55 (s, 1 H), 6.51 (s, 1 H), 4.50-3.67 (m, 8 H), 3.27 (s, 3 H), 2.64-2.30 (m, 4 H), 1.38-1.01 (m, 24 H) ppm; ESI+ HRMS m/z: calcd for $C_{112}H_{95}N_{14}O_{13}$ $[M+H]^+$ 1844.7237, found 1844.7367.

Oligomer **24**: This compound was prepared from dimer acid **22** (36 mg, 0.0488 mmol) and the corresponding amine of **23** (60 mg, 0.0325 mmol) according to the general coupling procedure. The starting material **23** was converted to its corresponding amine according to the general Boc-deprotection procedure. The yield of the boc-deprotection was considered to be quantitative and was used for the coupling reaction without any further purification. ^{1}H NMR of the free amine of **23** (300 MHz, $CDCl_3$) δ: 11.87 (s, 1 H), 11.79 (s, 1 H), 11.69 (s, 1 H), 11.55 (s, 1 H), 11.47 (s, 1 H), 8.85 (d, *J* = 7.7 Hz, 2 H), 8.75 (d, *J* = 8.3 Hz, 2 H), 8.71 (d, *J* = 7.7 Hz, 1 H), 8.41 (d, *J* = 7.8 Hz, 2 H), 8.36 (d, *J* = 8.8 Hz, 2 H), 8.35 (d, *J* = 7.9 Hz, 1 H), 8.29 (d, *J* = 7.7 Hz, 1 H), 8.23 (d, *J* = 7.4 Hz, 1 H), 8.15 (d, *J* = 7.2 Hz, 2 H), 8.13 (s, 1 H), 8.09 (d, *J* = 8.5 Hz, 1 H), 8.08 (d, *J* = 8.5 Hz, 1 H), 8.00-7.70 (m, 14 H), 7.64 (t, *J* = 8.0 Hz, 1 H), 7.45 (t, *J* = 8.0 Hz, 3 H), 7.44 (s, 1 H), 7.20 (t, *J* = 8.0 Hz, 1 H), 6.82 (s, 1 H), 6.64 (s, 1 H), 6.55 (s, 1 H), 5.97 (d, *J* = 7.4 Hz, 1 H), 4.47 (m, 1 H), 4.27-4.15 (m, 2 H), 3.95-3.88 (m, 3 H), 3.77-3.67 (m, 2 H), 3.64 (br, 2 H), 3.29 (s, 3 H), 2.62-2.10 (m, 4 H), 1.38-1.24 (m, 18 H), 1.04 (dd, *J* = 6.6, 1.6 Hz, 6 H) ppm. After the coupling reaction, the product was purified by GPC. Yield 58 mg, 69%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 11.56 (s, 1 H), 11.43 (s, 1 H), 11.36 (s, 1 H), 11.31 (s, 1 H), 11.19 (s, 1 H), 11.01 (s, 1 H), 10.87 (s, 1 H), 8.77 (d, *J* = 8.2 Hz, 2 H), 8.59 (d, *J* = 8.6 Hz, 2 H), 8.55 (d, *J* = 7.8 Hz, 2 H), 8.41 (d, *J* = 8.6 Hz, 2 H), 8.39 (d, *J* = 7.2 Hz, 1 H), 8.35 (d, *J* = 8.6 Hz, 1 H), 8.34 (d, *J* = 7.8 Hz, 1 H), 8.27 (d, *J* = 8.9 Hz, 2 H), 8.20 (d, *J* = 8.5 Hz, 1 H), 8.17 (d, *J* = 7.8 Hz, 1 H), 8.15 (d, *J* = 8.6 Hz, 1 H), 8.12 (d, *J* = 7.8 Hz, 2 H), 8.08 (d, *J* = 7.8 Hz, 1 H), 7.97-7.93 (m, 6 H), 7.86-7.68 (m, 9 H), 7.64-7.30 (m, 17 H), 7.28 (s, 1 H), 7.05 (s, 1 H), 6.68 (s, 1 H), 6.66 (s, 1 H), 6.59 (s, 1 H), 6.40 (s, 1 H), 4.27-4.16 (m, 3 H), 4.11-3.97

(m, 3 H), 3.88 (d, *J* = 6.4 Hz, 2 H), 3.59 (d, *J* = 5.7 Hz, 2 H), 3.12 (s, 3 H), 2.61-2.31 (m, 5 H), 1.43-1.37 (m, 12 H), 1.28-1.21 (m, 12 H), 1.02 (s, 9 H), 0.90 (dd, *J* = 6.4, 2.5 Hz, 6 H) ppm; ESI+ HRMS m/z: calcd for $C_{151}H_{123}N_{19}O_{16}$ $[M+2H]^{2+}$ 1229.4714, found 1229.4825.

Oligomer **25**: This compound was prepared from monomer acid **15** (36 mg, 0.10 mmol) and the corresponding amine of **24** (55 mg, 0.0225 mmol) according to the general coupling procedure. The starting material **24** was converted to its corresponding amine according to the general Boc-deprotection procedure. The yield of the boc-deprotection was considered to be quantitative and was used for the coupling reaction without any further purification. ^{1}H NMR of the free amine of **24** (300 MHz, $CDCl_3$) δ: 11.58 (s, 1 H), 11.46 (s, 1 H), 11.37 (s, 1 H), 11.27 (s, 1 H), 11.16 (s, 1 H), 11.09 (s, 1 H), 10.96 (s, 1 H), 8.77 (d, *J* = 7.9 Hz, 2 H), 8.61 (d, *J* = 7.9 Hz, 2 H), 8.56 (dd, *J* = 7.9, 2.0 Hz, 2 H), 8.42 (d, *J* = 8.8 Hz, 2 H), 8.36-8.31 (m, 4 H), 8.27 (d, *J* = 7.8 Hz, 2 H), 8.20-8.14 (m, 4 H), 8.10 (d, *J* = 7.9 Hz, 1 H), 8.06 (d, *J* = 7.6 Hz, 1 H), 8.01-7.92 (m, 5 H), 7.90 (s, 1 H), 7.86 (d, *J* = 8.6 Hz, 1 H), 7.84 (d, *J* = 8.4 Hz, 1 H), 7.80 (s, 1 H), 7.75-7.46 (m, 16 H), 7.42 (s, 1 H), 7.41-7.29 (m, 5 H), 7.16 (t, *J* = 7.9 Hz, 1 H), 7.01 (s, 1 H), 6.69 (s, 1 H), 6.67 (s, 1 H), 6.61 (s, 1 H), 6.41 (s, 1 H), 5.89 (d, *J* = 7.5 Hz, 1 H), 4.26-4.17 (m, 3 H), 4.11-3.96 (m, 3 H), 3.89 (d, *J* = 6.1 Hz, 2 H), 3.60 (d, *J* = 6.3 Hz, 2 H), 3.51 (br, 2 H), 3.13 (s, 3 H), 2.63-2.29 (m, 5 H), 1.42-1.37 (m, 12 H), 1.28-1.21 (m, 12 H), 0.91 (d, *J* = 6.8 Hz, 6 H) ppm. The coupling reaction followed the general coupling procedure and the product was purified by GPC. Yield 50 mg, 68%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 11.47 (s, 1 H), 11.42 (s, 1 H), 11.33 (s, 1 H), 11.28 (s, 1 H), 11.10 (s, 1 H), 10.85 (s, 1 H), 10.78 (s, 1 H), 10.76 (s, 1 H), 8.84 (d, *J* = 7.8 Hz, 2 H), 8.58 (d, *J* = 7.5 Hz, 2 H), 8.57 (d, *J* = 8.2 Hz, 2 H), 8.43 (d, *J* = 8.5 Hz, 2 H), 8.40 (dd, *J* = 7.1, 2.1 Hz, 2 H), 8.30 (d, *J* = 7.4 Hz, 1 H), 8.28 (d, *J* = 8.5 Hz, 2 H), 8.17-8.07 (m, 7 H), 8.01-7.85 (m, 10 H), 7.79 (s, 1 H), 7.76-7.31 (m, 23 H), 7.17 (d, *J* = 7.8 Hz, 1 H), 7.11 (t, *J* = 8.2 Hz, 1 H), 6.99 (t, *J* = 7.8 Hz, 1 H), 6.93 (s, 1 H), 6.64 (s, 1 H), 6.58 (s, 1 H), 6.47 (m, 1 H), 6.38 (s, 1 H), 6.04 (s, 1 H), 4.24-3.84 (m, 7 H), 3.79 (d, *J* =6.4 Hz, 2 H), 3.64 (t, *J* = 8.2 Hz, 1 H), 3.58 (d, *J* = 5.7 Hz, 2 H), 3.10 (s, 3 H), 2.62-2.22 (m, 6 H), 1.41 (d, *J* = 6.7 Hz, 6 H), 1.38 (d, *J* = 6.4 Hz, 3 H), 1.34 (d, *J* = 6.7 Hz, 3 H), 1.28-1.14 (m, 18 H), 0.96 (s, 9 H), 0.90 (dd, *J* = 6.7, 1.4 Hz, 6 H) ppm; ESI+ HRMS m/z: calcd for $C_{165}H_{137}N_{21}O_{18}$ $[M+2H]^{2+}$ 1350.5242, found 1350.5368.

Oligomer **26**: This compound was prepared from dimer acid **22** (36 mg, 0.048 mmol) and the corresponding amine of **25** (58 mg, 0.0223 mmol) according to the general coupling procedure. The starting material **25** was converted to its corresponding amine according to the general Boc-deprotection procedure. The yield of the boc-deprotection was considered to be quantitative and was used for the coupling reaction without any further purification. ^{1}H NMR of the free amine of **25** (300 MHz, $CDCl_3$) δ: 11.49 (s, 1 H), 11.34 (s, 1 H), 11.30 (s, 2 H), 11.12 (s, 1 H), 10.92 (s, 1 H), 10.82 (s, 2 H), 8.85 (d, *J* = 8.7 Hz, 2 H), 8.58 (d, *J* = 8.7 Hz, 4 H), 8.42 (d, *J* = 8.7 Hz, 2 H), 8.39 (d, *J* = 8.2 Hz, 1 H), 8.37 (d, *J* = 8.2 Hz, 1 H), 8.29 (d, *J* = 9.4 Hz, 2 H), 8.29 (d, *J* = 7.7 Hz, 1 H), 8.14-8.08 (m, 7 H), 8.02-7.95 (m, 6 H), 7.92 (s, 1 H), 7.91-7.84 (m, 4 H), 7.80 (s, 1 H), 7.76-7.69 (m, 4 H), 7.67 (d, *J* = 8.3 Hz, 1 H), 7.61-7.28 (m, 21 H), 7.12 (t, *J* = 8.2 Hz, 1 H), 6.91 (s, 1 H), 6.84 (t, *J* = 7.7 Hz, 1 H), 6.65 (s, 1 H), 6.59 (s, 1 H), 6.47 (s, 1 H), 6.38 (s, 1 H), 6.17 (s, 1 H), 5.70 (d, *J* = 7.2 Hz, 1 H), 4.25-3.58 (m, 12 H), 3.17 (br, 2 H), 3.10 (s, 3 H), 2.61-2.22 (m, 6 H), 1.42-1.12 (m, 30 H), 0.90 (dd, *J* = 6.8, 1.4 Hz, 6 H) ppm. The coupling reaction followed the general coupling procedure and the product was purified by GPC. Yield 35 mg, 66%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 11.32 (s, 1 H), 11.22 (s, 1 H), 11.14 (s, 1 H), 11.12 (s, 1 H), 10.90 (s, 1 H), 10.75 (s, 1 H), 10.66 (s, 1 H), 10.58 (s, 1 H), 10.53 (s, 1 H), 10.51 (s, 1 H), 8.65 (d, *J* =7.5 Hz, 2 H), 8.61 (d, *J* = 8.7 Hz, 2 H), 8.53 (d, *J* = 8.7 Hz, 2 H), 8.51-8.47 (m, 2 H), 8.38 (d, *J* = 7.1 Hz, 1 H), 8.32 (d, *J* = 8.5 Hz, 2 H), 8.27 (d, *J* = 8.5 Hz, 2 H), 8.22 (d, *J* = 7.5 Hz, 1 H), 8.19 (d, *J* = 7.9 Hz, 2 H), 8.18 (dd, *J* = 8.3, 1.3 Hz, 1 H), 8.14-

8.10 (m, 4 H), 8.03 (d, *J* = 7.3 Hz, 2 H), 7.98 (d, *J* = 7.7 Hz, 1 H), 7.96 (d, *J* = 7.7 Hz, 1 H), 7.91 (d, *J* = 8.2 Hz, 1 H), 7.89 (s, 1 H), 7.86-7.29 (m, 39 H), 7.24 (s, 1 H), 7.22-7.16 (m, 3 H), 7.15 (s, 1 H), 7.06 (t, *J* = 8.1 Hz, 1 H), 6.98 (s, 1 H), 6.51 (s, 1 H), 6.49 (s, 1 H), 6.30 (s, 2 H), 6.12 (s, 1 H), 6.04 (s, 1 H), 4.20-3.75 (m, 14 H), 3.52 (d, *J* = 6.7 Hz, 2 H), 3.03 (s, 3 H), 2.59-2.17 (m, 10 H), 1.41-1.13 (m, 36 H), 0.93 (s, 9 H), 0.84 (d, *J* = 6.6 Hz, 3 H), 0.83 (d, *J* = 6.6 Hz, 3 H) ppm; ESI+ HRMS m/z: calcd for $C_{204}H_{164}N_{26}O_{21}$ $[M+2H]^{2+}$ 1657.6316, found 1657.6472.

Oligomer **27**: This compound was prepared from dimer acid **22** (35 mg, 0.048 mmol) and the corresponding amine of **26** (50 mg, 0.0134 mmol) according to the general coupling procedure. The starting material **26** was converted to its corresponding amine according to the general Boc-deprotection procedure. The yield of the boc-deprotection was considered to be quantitative and was used for the coupling reaction without any further purification. ^{1}H NMR of the free amine of **26** (300 MHz, $CDCl_3$) δ: 11.32 (s, 1 H), 11.23 (s, 1 H), 11.16 (s, 1 H), 11.01 (s, 1 H), 10.91 (s, 1 H), 10.85 (s, 1 H), 10.69 (s, 1 H), 10.63 (s, 1 H), 10.59 (s, 1 H), 10.56 (s, 1 H), 8.65 (d, *J* = 7.4 Hz, 2 H), 8.63 (d, *J* =7.4 Hz, 2 H), 8.52 (d, *J* = 8.5 Hz, 2 H), 8.49 (d, *J* = 8.9 Hz, 2 H), 8.36 (d, *J* = 7.8 Hz, 1 H), 8.31 (d, *J* = 8.9 Hz, 2 H), 8.27 (d, *J* = 8.7 Hz, 2 H), 8.24-8.12 (m, 8 H), 8.01 (d, *J* = 8.1 Hz, 1 H), 8.04 (d, *J* = 7.4 Hz, 1 H), 7.98 (d, *J* = 8.1 Hz, 2 H), 7.92 (d, *J* = 8.1 Hz, 1 H), 7.89 (s, 1 H), 7.83 (d, *J* = 8.5 Hz, 4 H), 7.78-7.28 (m, 36 H), 7.22 (s, 2 H), 7.15 (s, 2 H), 7.15 (t, *J* = 8.3 Hz, 1 H), 7.07 (t, *J* = 7.8 Hz, 1 H), 7.03 (t, *J* = 7.8 Hz, 1 H), 6.93 (s, 1 H), 6.51 (s, 1 H), 6.49 (s, 1 H), 6.32 (s, 1 H), 6.30 (s, 1 H), 6.17 (s, 1 H), 6.14 (s, 1 H), 5.75 (d, *J* = 8.1 Hz, 1 H), 4.21-3.75 (m, 15 H), 3.63 (t, *J* = 7.4 Hz, 1 H), 3.52 (d, *J* = 6.1 Hz, 2 H), 3.27 (br, 2 H), 3.04 (s, 3 H), 2.57-2.32 (m, 7 H), 1.39-1.13 (m, 42 H), 0.84 (d, *J* = 6.5 Hz, 3 H), 0.83 (d, *J* = 6.8 Hz, 3 H) ppm. The coupling reaction followed the general coupling procedure and the product was purified by GPC. Yield 30 mg, 66%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 11.23 (s, 1 H), 11.15 (s, 1 H), 11.00 (s, 2 H), 10.77 (s, 1 H), 10.50 (s, 2 H), 10.46 (s, 2 H), 10.35 (s, 2 H), 10.33 (s, 1 H), 8.56 – 8.47 (m, 4 H), 8.45 – 8.32 (m, 4 H), 8.32 – 7.95 (m, 12 H), 7.89 (q, *J* = 8.8, 8.1 Hz, 2 H), 7.82 – 7.68 (m, 7 H), 7.68 – 7.54 (m, 2 H), 7.54 – 7.39 (m, 9 H), 7.37 (d, *J* = 4.0 Hz, 1 H), 7.32 (dd, *J* = 9.0, 4.3 Hz, 4 H), 7.22 (d, *J* = 7.0 Hz, 4 H), 7.18 (s, 1 H), 7.15 (s, 1 H), 7.13 (s, 1H), 7.10 (s, 1 H), 7.08 (s, 1 H), 7.05 (s, 1 H), 7.04 (s, 1 H), 7.02 (s, 1 H), 6.99 (s, 1 H), 6.92 (s, 1 H), 6.47 (s, 1 H), 6.37 (s, 1 H), 6.26 (s, 1 H), 6.24 (s, 1 H), 6.13 (s, 1 H), 6.10 (s, 1 H), 5.98 (s, 1 H), 4.14 – 3.19 (m, 10 H), 2.98 (s, 3 H), 2.59 – 2.09 (m, 8 H), 1.39 – 1.08 (m, 72 H), 0.91 (s, 9 H), 0.79 (d, *J* = 6.7 Hz, 6 H); ESI+ HRMS m/z: calcd for $C_{243}H_{191}N_{31}O_{24}$ $[M+2H]^{2+}$ 1964.2373, found 1964.2473.

Oligomer **2c**: The starting material **27** (35 mg, 0.0089 mmol) was converted to its corresponding amine according to the general Boc-deprotection procedure. The yield of the boc-deprotection was considered to be quantitative and was used for the coupling reaction without any further purification. The oligomer 2c was prepared from dimer acid **12** (22 mg, 0.036 mmol) and the corresponding amine of **27** according to the general coupling procedure. The compound was purified with GPC. Yield 25 mg, 44%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 11.23 (s, 1 H), 11.52 (s, 1 H), 11.00 (s, 2 H), 10.77 (s, 1 H), 10.50 (s, 2 H), 10.46 (s, 2 H), 10.35 (s, 2 H), 10.33 (s, 1 H), 8.54-8.49 (m, 4 H), 8.42-7.97 (m, 28 H), 7.90 (q, *J* = 6.8 Hz, 4 H), 7.80-7.30 (m, 42 H), 7.24-6.99 (m, 15 H), 6.92 (s, 1 H), 6.47 (s, 1 H), 6.36 (s, 1 H), 6.26 (s, 1 H), 6.24 (s, 1 H), 6.13 (s, 1 H), 6.10 (s, 1 H), 5.98 (s, 1 H), 4.09-3.71 (m, 17 H), 3.48 (d, *J* = 6.0 Hz, 2 H), 2.98 (s, 3 H), 2.54-2.17 (m, 12 H), 1.34-1.10 (m, 104 H), 0.91 (s, 9 H), 0.80 (d, *J* = 6.6 Hz, 3 H), 0.78 (d, *J* = 6.6 Hz, 3 H) ppm; ESI+ HRMS m/z: calcd for $C_{271}H_{219}N_{35}O_{28}$ $[M+2H]^{2+}$ 2206.3428, found 2206.3615.

2. Complexation with Pd(II)

General procedure for the formation of complexes with *trans*-$Pd(CH_3CN)_2Cl_2$: The formation of complexes between the oligomers and *trans*-$Pd(CH_3CN)_2Cl_2$ was done by mixing the oligomers and the palladium salt at the exact ratio of the stoichiometry of the complexation take place. After mixing the two components in a small vial or NMR tube, $CHCl_3$ or $CDCl_3$ was added to dissolve organic reactant, concentration of the reaction varied from ~2 mM to ~20 mM. The palladium salt that initially not dissolving in chloroform slowly dissolved either by keeping the solution at room temperature or heating the solution at 60 °C. The reaction process was followed with NMR spectroscopy until complete of reaction (no further changes observed in ^{1}H NMR spectra).

Complex Pd(**1a**)$_2Cl_2$: The yield of this complex was considered to be quantitative as judged by crude ^{1}H NMR spectrum. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 12.01 (s, 1H), 11.94 (s, 1H), 11.85 (s, 1H), 11.82 (s, 1H), 11.13 (s, 1H), 11.10 (s, 1H), 8.88 (dd, *J* = 8.6, 1.4 Hz, 2H), 8.74 (dd, *J* = 7.6, 1.3 Hz, 1H), 8.67 – 8.61 (m, 1H), 8.54 – 8.45 (m, 2H), 8.28 (dd, *J* = 7.7, 1.2 Hz, 1H), 8.17 – 7.99 (m, 9H), 7.92 (s, 1H), 7.91 – 7.86 (m, 1H), 7.80 – 7.68 (m, 2H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.49 (s, 1H), 7.47 – 7.43 (m, 1H), 7.42 (s, 1H), 7.41 – 7.28 (m, 1H), 7.25 (d, *J* = 7.8 Hz, 1H), 6.88 (s, 1H), 6.65 (s, 1H), 4.45 (dt, *J* = 8.7, 6.2 Hz, 2H), 4.23 (ddd, *J* = 10.9, 8.9, 7.0 Hz, 2H), 3.97 (d, *J* = 6.4 Hz, 2H), 3.86 (t, *J* = 6.3 Hz, 2H), 3.32 (s, 3H), 2.62 – 2.28 (m, 4H), 1.42 – 1.11 (m, 34H) ppm; ESI+ HRMS m/z: calcd for $C_{174}H_{163}N_{22}O_{24}PdCl_2$ $[M+H]^+$ 3123.0655, found 3123.0629.

Complex Pd_2(**1b**)$_2Cl_4$: The yield of this complex was considered to be quantitative as judged by crude ^{1}H NMR spectrum. Four sets of signals were observed in ^{1}H NMR spectrum. One of the set of signal is: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 11.42 (s, 1H), 11.30 (s, 1H), 11.22 (m, 3H), 11.20 (s, 1H), 11.12 (s, 1H), 11.05 (s, 2H), 11.02 (s, 1H), 10.81 (s, 1H), 10.54 (s, 1H), 10.51 (s, 1H), 8.67 (d, *J* = 8.6 Hz, 2H), 8.56 (d, *J* = 8.5 Hz, 2H), 8.47 (t, *J* = 7.6 Hz, 2H), 8.40 (d, *J* = 7.5 Hz, 1H), 8.24 (m, 2H), 8.19 – 7.99 (m, 6H), 7.94 (d, *J* = 7.9 Hz, 2H), 7.89 (d, *J* = 8.3 Hz, 1H), 7.82 – 7.30 (m, 22H), 7.22 – 7.10 (m, 4H), 7.09 (s, 1H), 6.99 – 6.89 (m, 2H), 6.83 (s, 1H), 6.58 (s, 1H), 6.47 (s, 1H), 6.38 (s, 1H), 6.34 (s, 1H), 6.29 (s, 1H), 6.25 (s, 1H), 4.28 – 3.74 (m, 12H), 3.63 (d, *J* = 6.2 Hz, 2H), 3.15 (s, 3H), 2.63 – 2.07 (m, 10H), 1.46 – 0.73 (m, 82H) ppm; ESI+ HRMS m/z: calcd for $C_{336}H_{302}N_{44}O_{42}Pd_2Cl_4$ $[M+2H]^{2+}$ 2990.9932, found 2990.9873.

Complex Pd_3(**1c**)$_2Cl_6$: The yield of this complex was considered to be quantitative as judged by crude ^{1}H NMR spectrum. Four sets of signals were observed in ^{1}H NMR spectrum. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 11.26 – 9.99 (m, 14H), 8.62 – 5.34 (m, 58H), 4.14 – 3.38 (m, 36H), 3.13 – 2.92 (m, 3H), 2.54 – 1.86 (m, 12H), 1.42 – 0.58 (m, 72H) ppm; ESI+ HRMS m/z: calcd for $C_{498}H_{438}N_{66}O_{60}Pd_3Cl_6$ $[M+3H]^{3+}$ 2947.3018, found 2947.3038.

Complex Pd_2(**1d**)$_2Cl_4$: The yield of this complex was considered to be quantitative as judged by crude ^{1}H NMR spectrum. Two sets of signals were observed. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 11.39 (s, 1H), 11.34 (s, 1H), 11.28 (s, 1H), 11.18 (d, *J* = 3.4 Hz, 1H), 11.15 (s, 2H), 11.11 (s, 1H), 11.08 (s, 2H), 10.93 (d, *J* = 6.7 Hz, 1H), 10.77 (d, *J* = 5.1 Hz, 1H), 10.46 (s, 2H), 10.42 (s, 1H), 9.41 (s, 1H), 8.68 (d, *J* = 8.6 Hz, 2H), 8.64 – 8.57 (m, 2H), 8.39 – 8.26 (m, 3H), 8.25 – 8.02 (m, 8H), 8.02 – 7.91 (m, 2H), 7.89 – 7.71 (m, 6H), 7.71 – 7.56 (m, 6H), 7.56 – 7.34 (m, 8H), 7.24 – 7.03 (m, 5H), 6.93 (s, 1H), 6.73 (d, *J* = 3.2 Hz, 1H), 6.58 (s, 1H), 6.49 (s, 1H), 6.45 (d, *J* = 2.3 Hz, 1H), 6.38 (d, *J* = 4.6 Hz, 1H), 6.31 (d, *J* = 3.0 Hz, 2H), 4.28 – 3.54 (m, 16H), 3.10 (d, *J* = 1.4 Hz, 3H), 2.64 – 1.83 (m, 8H), 1.45 – 1.05 (m, 56H), 0.92 – 0.76 (m, 6H), 0.55 (d, *J* = 10.0 Hz, 6H) ppm.

Complex **2a**-$PdCl_2$: complicated ^{1}H NMR spectrum observed indicating multiple assemblies were obtained. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 12.08 – 11.86 (m, 2H), 11.23 – 11.02 (m, 2H), 8.92 – 8.73 (m, 3H), 8.54 – 7.38 (m, 14H), 6.87 (s, 1H), 4.49 (d, *J* = 12.9 Hz, 2H),

4.36 – 4.18 (m, 2H), 3.99 (d, *J* = 6.4 Hz, 2H), 3.60 – 3.35 (m, 2H), 2.72 – 2.48 (m, 1H), 2.48 – 2.30 (m, 1H), 1.46 – 0.95 (m, 18H), 0.95 – 0.73 (m, 2H) ppm.

3. X-ray crystallography

The single crystals were obtained by layered diffusion method. The single crystals of **1b** were obtained by diffusion of hexane into the stock solutions in chloroform/chlorobenzene. The single crystals **1c** were obtained by diffusion of acetonitrile into the stock solutions of the respective compounds in chloroform. The single crystals of **2b** were obtained by diffusion of hexane into the stock solutions in chloroform. The single crystal of Pd(**1a**)$_2$Cl$_2$ was obtained by diffusion of methanol into the stock solution in chloroform. The single crystal of Pd$_2$(**1b**)$_2$Cl$_4$ was obtained by diffusion of acetonitrile into the stock solution in chloroform. In all cases, a layer of chlorobenzene was added as a buffer layer between the solvent and precipitant. Typically, the crystals were obtained in around 1 to 2 weeks and suitable single crystals were picked for x-ray diffraction analysis.

The diffraction data for selected single crystals were collected at the IECB x-ray facility (CNCR AUR 3033 – INSERM US001) with a Rigaku FRX rotating anode (2.9 kW) diffractometer. CuKα radiation monochromated with high flux Osmic Varimax HF mirrors were used for data collection. The x-ray source was equipped with a Dectris Pilatus 200K detector and partial chi goniometer. All crystals were kept at 100(2) K during data collection. The data were processed with CrystAlis PRO software[6] with a multiscan absorption correction. Structures were solved with the ShelXT[7] structure solution program using a dual-space algorithm. Crystal model refinement was performed with ShelXL[8] package using Least Squares minimization implemented in Olex2[9].

During refinement, anisotropic displacement parameters were used for backbones, some solvent molecules, isobutyl side chains and acridine moiety, except one in **1c**. Hydrogen atoms were placed at an idealized position and were refined in the riding-model approximation, with U_{iso}(H)=1.2U_{eq}(CH, CH$_2$, NH). EADP, SIMU, and RIGU instructions were employed to model temperature parameters. The geometry of the molecules was improved with DFIX, FLAT, FRAG or AFIX commands.

The solvent masks procedure implemented in Olex2[9] was employed to remove disordered solvents molecules that could not be reliably modelled. The solvent radius was set to 1.2 Å, calculated total potential solvent-accessible void volume and electron counts per unit-cell were: 1024 Å^3 and 274 for **1b** 4283 Å^3 and 841 for **1c**, 11128 Å^3 and 3384 for **2b**, 31210 Å^3 and 6744 for **Pd(1a)$_2$Cl$_2$**, 5468 Å^3, 957 for **Pd(1b)$_2$Cl$_4$**.

The final cif files were checked using IUCR's checkcif algorithm. For **1b**, the diffraction data were very high quality; thus, only the C and G alerts were detected. Due to the characteristics of the other crystals, i.e. large volume fractions of disordered solvent molecules, weak diffraction intensity, incompleteness of the data and moderate resolution, a number of A-level and B-level alerts remain in the check cif file. These alerts are inherent to the data and refinement procedures and do not reflect errors. They are explicitly listed below and have been divided into two groups. The first group illustrates the poor quality of the data and refinement statistics compared to that expected for small molecule structures from highly diffracting crystals. The second group is connected to decisions made during refinement and explained below.

Group 1:

THETM01_ALERT_3_A, B The value of sine(theta_max)/wavelength is less than 0.550 or 0.575

PLAT023_ALERT_3_A, B Resolution (too) Low [sin(theta)/Lambda < 0.6].

PLAT082_ALERT_2_A, B High R1 Value

PLAT084_ALERT_3_A High wR2 Value (i.e. > 0.25)

PLAT934_ALERT_3_A, B Number of (Iobs-Icalc)/Sigma(W) > 10 Outliers
PLAT973_ALERT_2_A Check Calcd Positive Resid. Density
RINTA01_ALERT_3_B The value of Rint is greater than 0.18
PLAT020_ALERT_3_B The Value of Rint is Greater Than 0.12
PLAT230_ALERT_2_B Hirshfeld Test Diff for
PLAT213_ALERT_2_B Atom N8E has ADP max/min Ratio
PLAT241_ALERT_2_B High 'MainMol' Ueq as Compared to Neighbors
PLAT242_ALERT_2_B Low 'MainMol' Ueq as Compared to Neighbors
PLAT250_ALERT_2_B Large U3/U1 Ratio for Average U(i,j) Tensor ....
PLAT340_ALERT_3_B Low Bond Precision on C-C Bonds

Group 2:
PLAT201_ALERT_2_A Isotropic non-H Atoms in Main Residue(s)
PLAT202_ALERT_3_A Isotropic non-H Atoms in Anion/Solvent
As mentioned above, not all atoms were refined with ADPs

PLAT315_ALERT_2_B Singly Bonded Carbon Detected (H-atoms Missing)

Table S1 Crystal data and refinement details for **1b**, **1c** and **2b**.

Identification code	**1b**	**1c**	**2b**
Chemical formula	$2(CHCl_3)\cdot C_{168}H_{150}N_{22}O_{21}\cdot 0.5(C_6H_5Cl)\cdot H_2O$ (solvent)*	$C_{250}H_{219}N_{33}O_{30}\cdot CHCl_3\cdot$ (solvent)*	$C_{179}H_{149}N_{23}O_{20}\cdot\cdot 3(CHCl_3)\cdot$(solvent)*
Formula weight	3126.12	4284.94	3300.31
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	*P*-1	*P*-1	*I*2/a
Unit cell dimensions (Å, °)	a=15.2660 (2), α=80.922 (1)	a=19.5840 (7), α=108.551 (3)	a=48.1108 (15), α=90
	b=20.6362 (3), β=86.389 (1)	b=24.7102 (7), β=90.984 (3)	b=20.4141 (6), β=105.205 (4)
	c=28.8331 (4), γ=69.304 (1)	c=31.7272 (10), γ=111.381 (3)	c=41.9540 (16), γ=90
Volume (Å^3)	8390.5 (2)	13398.9 (8)	39762 (2)
Z	2	2	8
Density (calculated) (Mg m^{-3})	1.237	1.062	1.103
Absorption coefficient (mm^{-1})	1.59	0.84	1.66
Crystal size (mm)	0.20 × 0.15 × 0.10	0.1 × 0.04 × 0.02	0.1 × 0.08 × 0.02
Completeness	99.1 (up to 67.68°)	99.4 (up to 50.43°)	99.9 (up to 58.93°)
Reflections collected	97763	110191	115730
Reflections observed [$I > 2\sigma(I)$]	26665	15773	14200
R_{int}	0.028	0.055	0.056
Data/parameters/restrains	33495/2087/6	27902/1903/428	28545/1716/195
Goodness-of-fit on F^2	1.07	2.36	1.58
Final R indices [$I > 2\sigma(I)$]	0.0659, 0.1895	0.2416, 0.5802	0.1538, 0.4346
R indices (all data)	0.0815, 0.2175	0.2834, 0.5615	0.2074, 0.4776
Largest diff. peak and hole	0.61, -1.28	1.56, -0.78	1.05, -0.62
CCDC #	2166701	2166702	2166705

Experiments were carried out at100 K with Cu *K*a radiation. Absorption was corrected by multi-scan

* Solvent mask was used to removed severely disordered solvent molecules

Table S2. Crystal data and refinement details for **$Pd(1a)_2Cl_2$** and **$Pd_2(1b)_2Cl_4$**.

Identification code	**$Pd(1a)_2Cl_2$**	**$Pd_2(1b)_2Cl_4$**
Chemical formula	$2(C_{174}H_{162}Cl_2N_{22}O_{24}Pd)\cdot C_{174}H_{162}Cl_2N_{22}O_{24}Pd\cdot 2(CHCl_3)$ (solvent)*	$C_{168}H_{150}Cl_2N_{22}O_{21}Pd\cdot 2(CHCl_3)$ (solvent)*·
Formula weight	9606.38	3229.13
Crystal system	Monoclinic	Triclinic
Space group	*C*2/c	*P*-1
Unit cell dimensions (Å, °)	a=40.6450 (11), α=90	a=19.7590 (7), α=81.546 (2)
	b=26.6345 (6), β=105.797 (4)	b=21.9203 (6), β=86.925 (3)
	c=68.4120 (19), γ=90	c=27.7592 (9), γ=86.641 (3)
Volume ($Å^3$)	71263 (3)	11859.7 (7)
Z	4	2
Density (calculated) (Mg m^{-3})	0.895	0.904
Absorption coefficient (mm^{-1})	1.47	1.87
Crystal size (mm)	0.10 × 0.05 × 0.03	0.20 × 0.10 × 0.02
Completeness	100 (up to 44.49°)	97.3 (up to 55.77°)
Reflections collected	238367	112367
Reflections observed [$I > 2\sigma(I)$]	18343	16522
R_{int}	0.181	0.055
Data/parameters/restrains	28014/1831/1861	29841/1466/127
Goodness-of-fit on F^2	1.71	1.74
Final R indices [$I > 2\sigma(I)$]	0.1606, 0.4383	0.1712, 0.4550
R indices (all data)	0.1886, 0.4668	0.2063, 0.4871
Largest diff. peak and hole	1.63, -0.67	1.93, -0.62
CCDC #	2166704	2166703

Experiments were carried out at100 K with Cu *K*a radiation. Absorption was corrected by multi-scan

* Solvent mask was used to removed severely disordered solvent molecules

Table S3 Geometry of hydrogen bonds. Atom numbers are those of cif file.

	***D*—H (Å)**	**H···*A* (Å)**	***D*···*A* (Å)**	***D*—H···*A***
1b				
C22-H22B···O5A[i]	0.95	2.53	3.387 (3)	149
1c				
C27-H27B···O10C[ii]	0.95	2.54	3.230 (10)	130
C37B-H37B···O5C[ii]	0.95	2.43	3.353 (12)	164

i) 1-x, -y, 1-z;(ii) 1-x, 1-y, 1-z

4. Additional Figures

4.1 oligomers 1a-1c

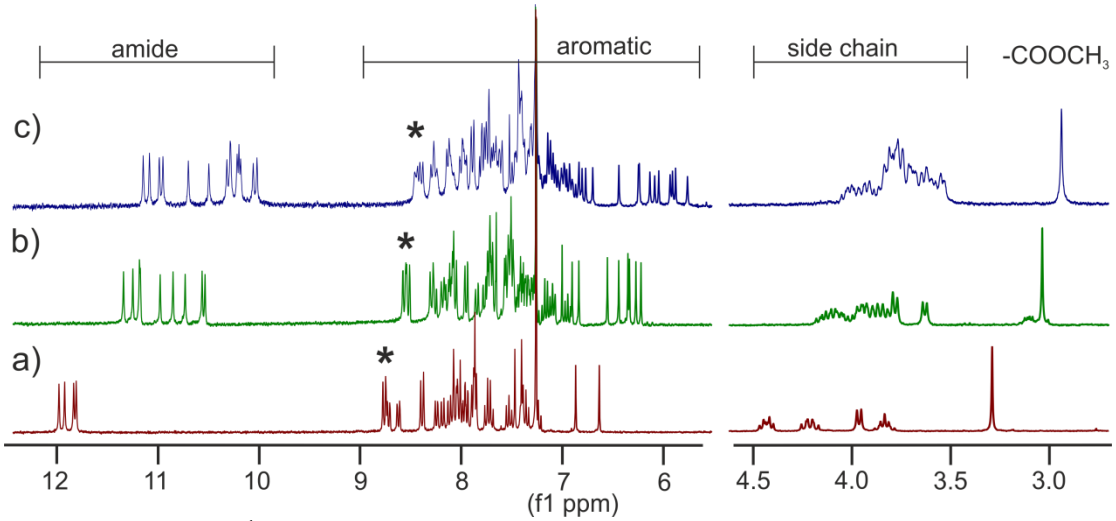


Figure S1: Part of ^{1}H NMR (300 MHz, $CDCl_3$) of acridine functionalized oligomers a) **1a**, b) **1b** and c) **1c**.

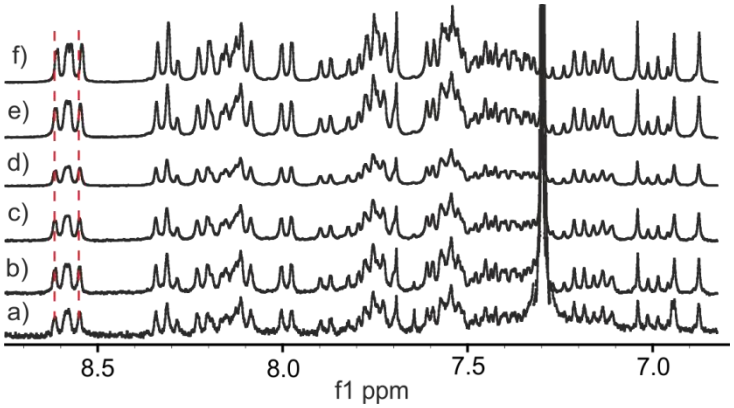


Figure S2: Part of the concentration dependent ^{1}H NMR spectra (300 MHz) of **1b** showing the aromatic region, a) 0.1 mM, b) 0.5 mM, c) 1 mM, d) 2.5 mM, e) 5 mM and f) 10 mM in $CDCl_3$.

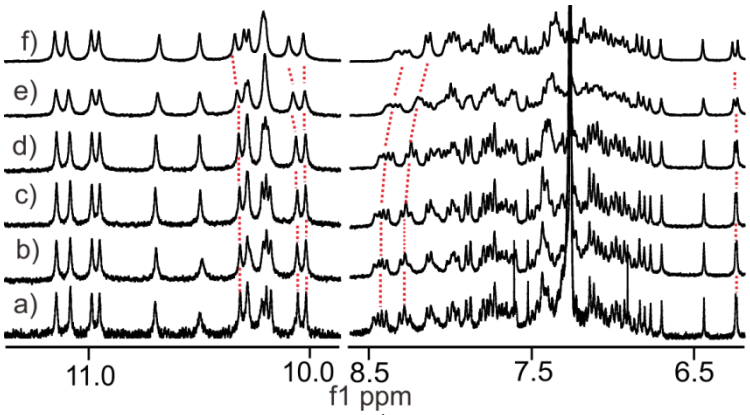


Figure S3: Part of the concentration dependent ^{1}H NMR spectra (300 MHz) of **1c** showing the amide and aromatic region, a) 0.1 mM, b) 0.5 mM, c) 1 mM, d) 2.5 mM, e) 5 mM and f) 15 mM in $CDCl_3$.

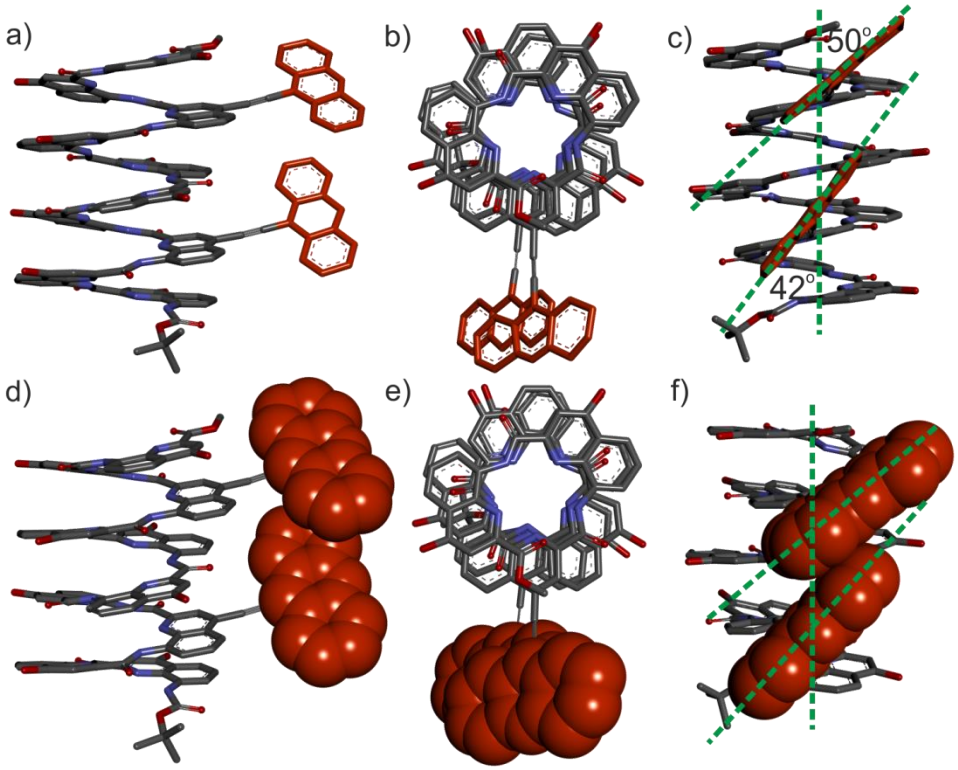


Figure S4: Single crystal x-ray structure of **1b**, a) side view form the helix axis; b) top view form the helix axis; c) side view to show relative orientation of the acridine rings with respect to the axis of helix; CPK view of acridine rings of d) side view; e) top view and f) side view to show the relative orientations.

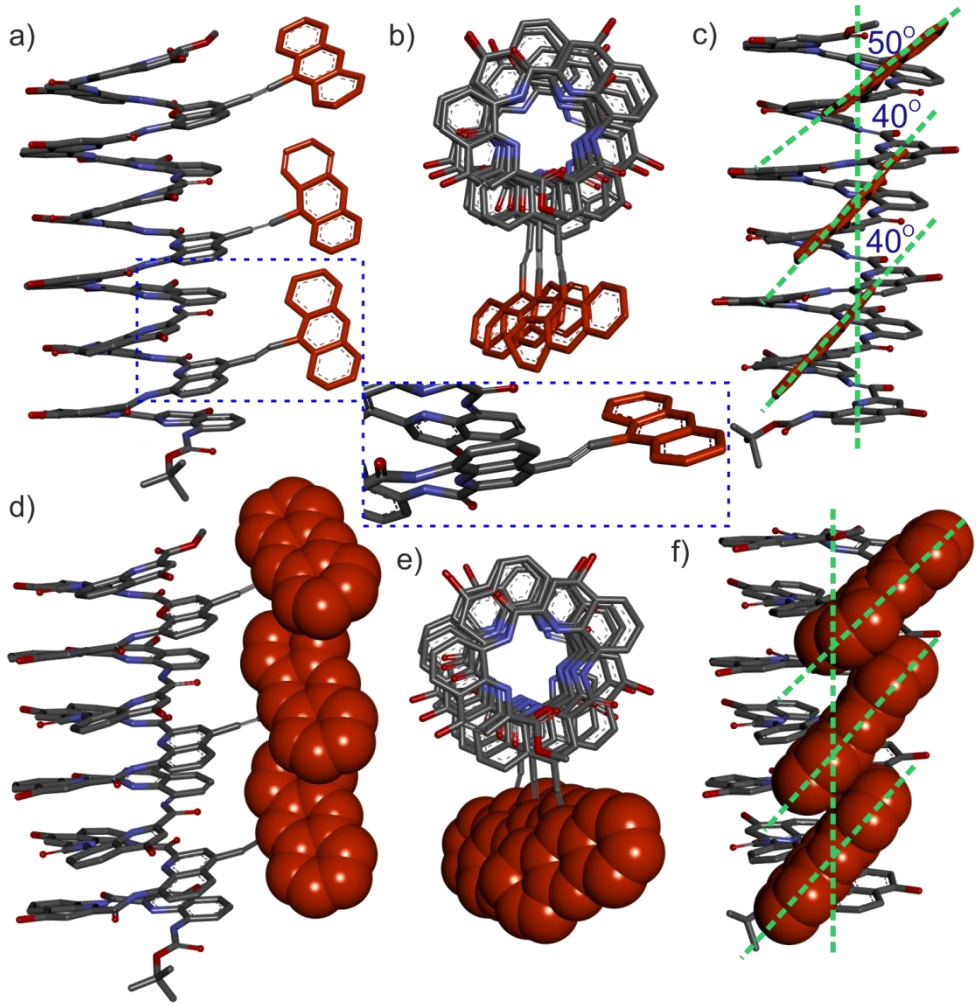


Figure S5: Single crystal x-ray structure of **1c**, a) side view form the helix axis, in the blue box is the zoom of the acetylene that have significant distortion; b) top view form the helix axis; c) side view to show relative orientation of the acridine rings with respect to the axis of helix; CPK view of acridine rings of d) side view; e) top view and f) side view to show the relative orientations.

3.2 oligomers 2a-2c

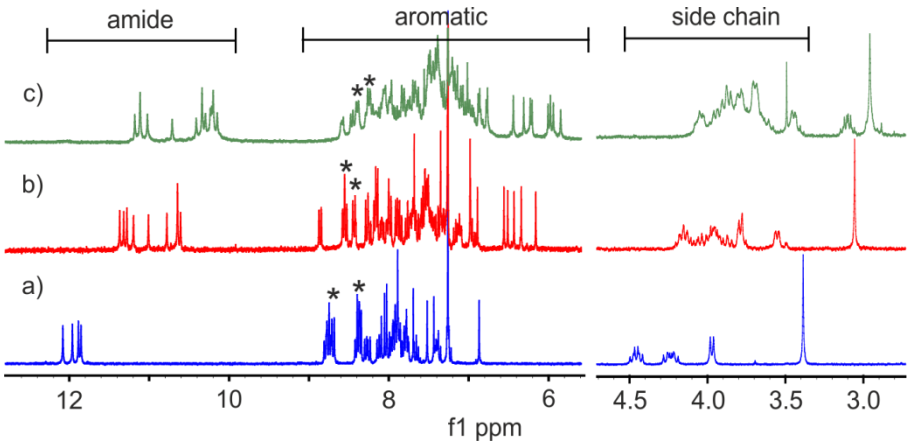


Figure S6: Part of the ^{1}H NMR spectra (300 MHz) of **2a**-**2c** in CDCl3, a) **2a**, b) **2b** and c) **2c**, stars indicate those signals are from acridine units.

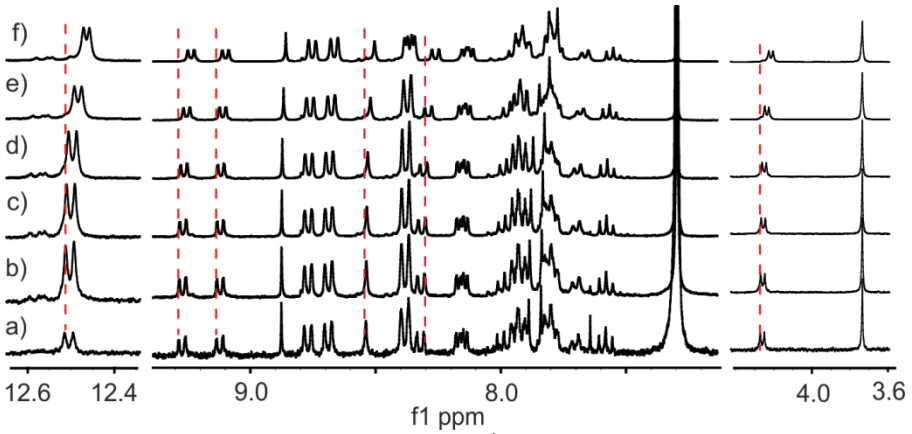


Figure S7: Part of the concentration dependent ^{1}H NMR spectra (300 MHz, $CDCl_3$) of **18** (Q^aQQ^a), a) 0.1 mM; b) 0.5 mM, c) 1 mM, d) 2.5 mM, e) 5 mM and f) 10 mM.

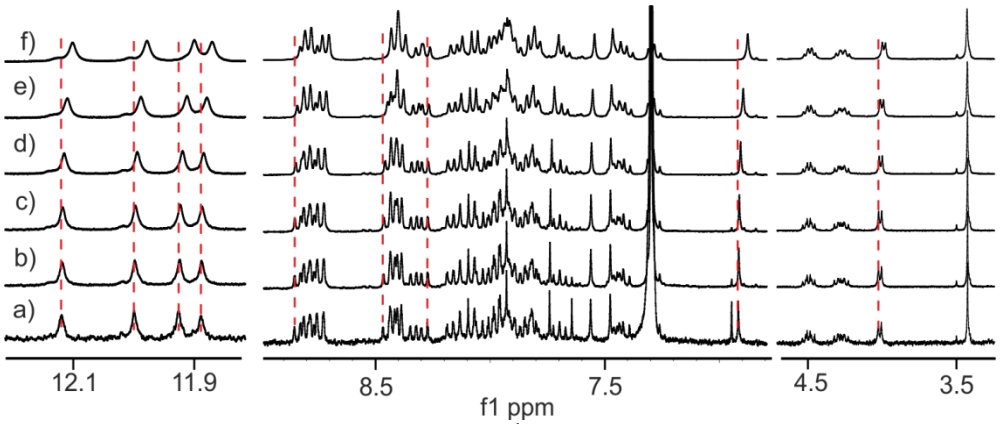


Figure S8: Part of the concentration dependent ^{1}H NMR spectra (300 MHz, $CDCl_3$) of **2a**, a) 0.1 mM; b) b) 0.5 mM, c) 1 mM, d) 2.5 mM, e) 5 mM and f) 10 mM.

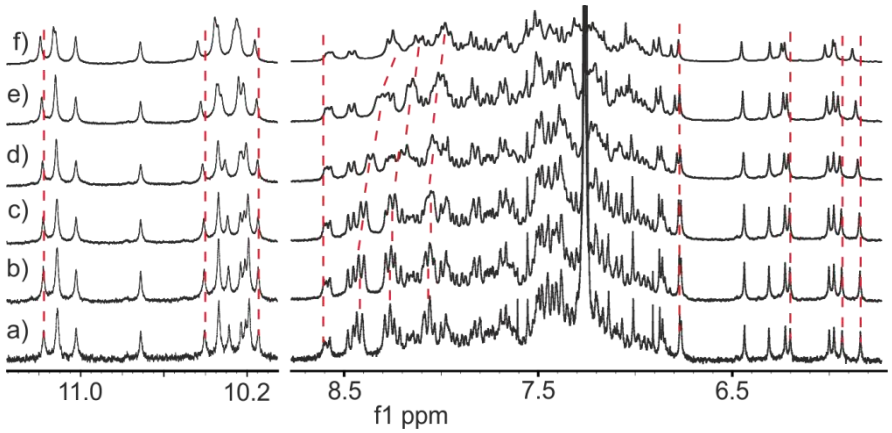


Figure S9: Part of concentration dependent ^{1}H NMR spectra (300 MHz, $CDCl_3$) of **2c** showing the amide and aromatic region, a) 0.1 mM; b) 0.5 mM, c) 1 mM, d) 2.5 mM, e) 5 mM and f) 10 mM.

3.3 complexation with Pd(II)

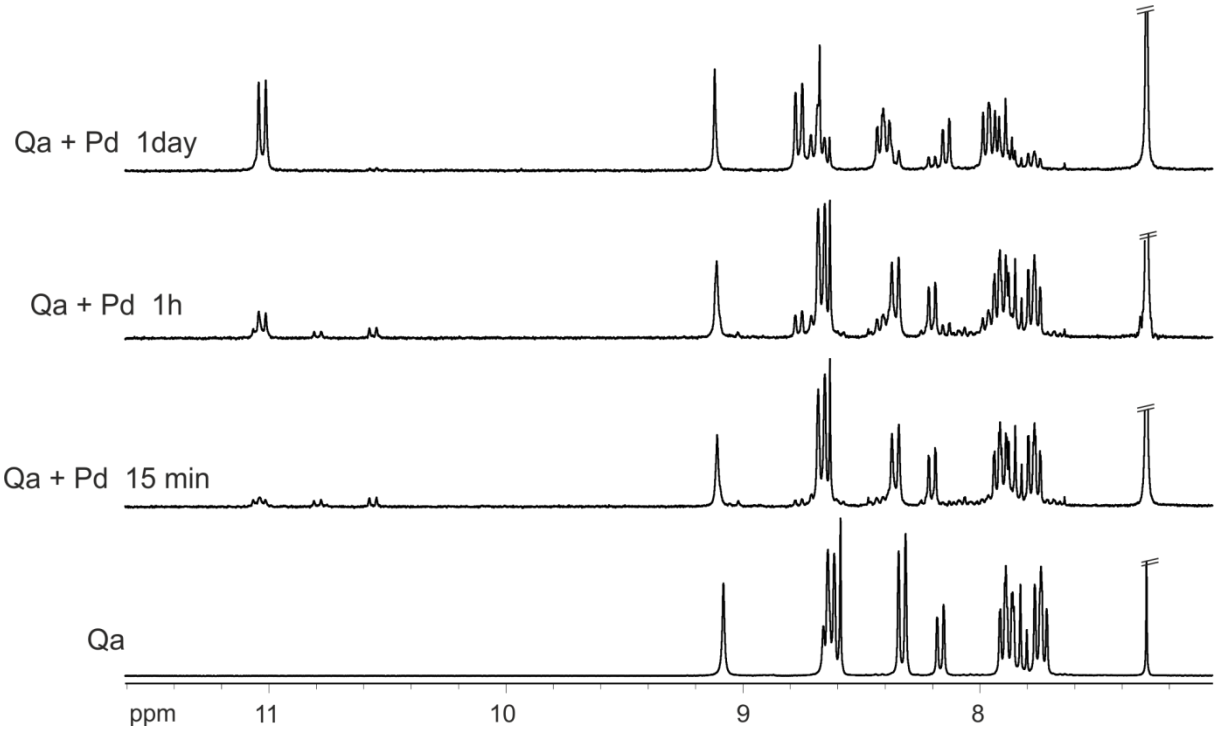


Figure S10: Part of ^{1}H NMR spectra (300 MHz, $CDCl_3$) of monomer **7** (**Q^{a}**) and its mixture with 0.5 equivalent of $PdCl_2(ACN)_2$ after different period of mixing.

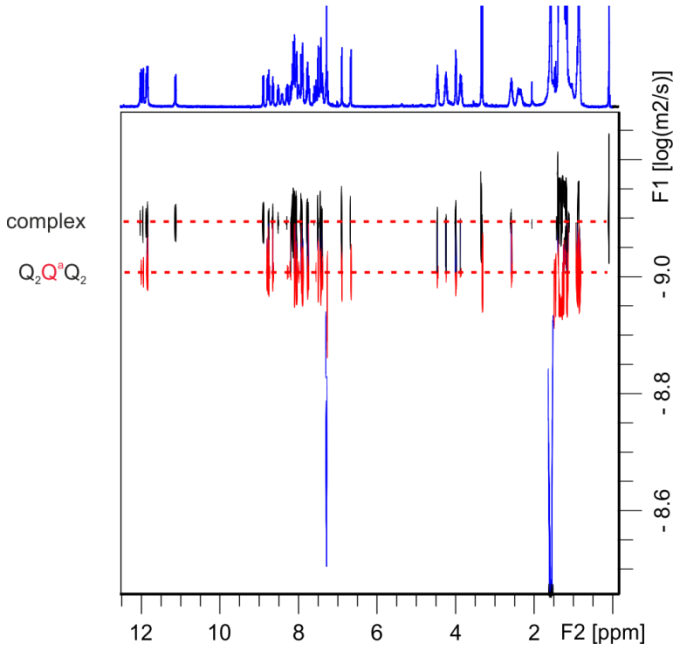


Figure S11: DOSY NMR spectra (400 MHz, $CDCl_3$, 298 K) spectra of the mixture of **1a** and the complex Pd(**1a**)$_2Cl_2$, the red peaks corresponding to **1a** and the black corresponding to the complex Pd(**1a**)$_2Cl_2$.

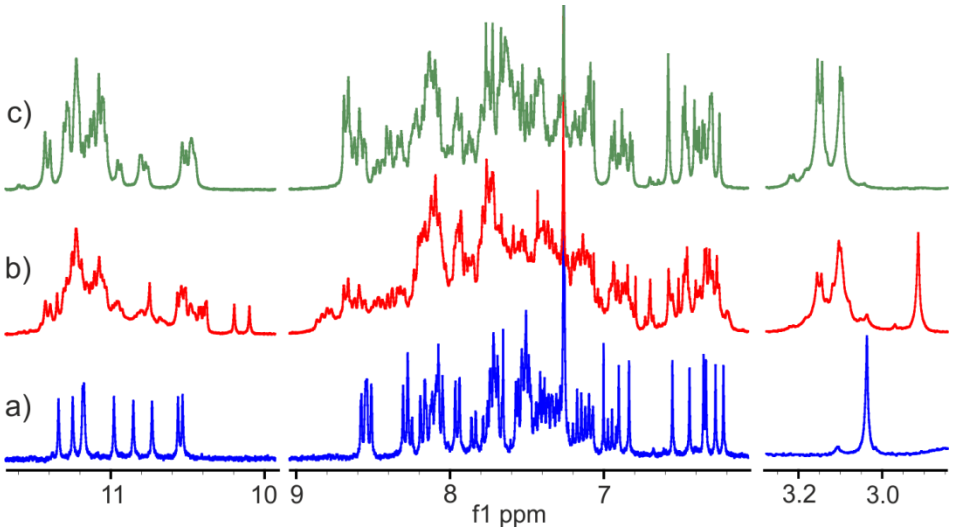


Figure S12: Parts of ^{1}H NMR spectra (300 MHz, $CDCl_3$) showing the amide, aromatic and methyl ester regions of a) **1b**; b) 18 hours after mixing **1b** with $PdCl_2(CH_3CN)_3$ and c) the complex Pd_2(**1b**)$_2Cl_4$.

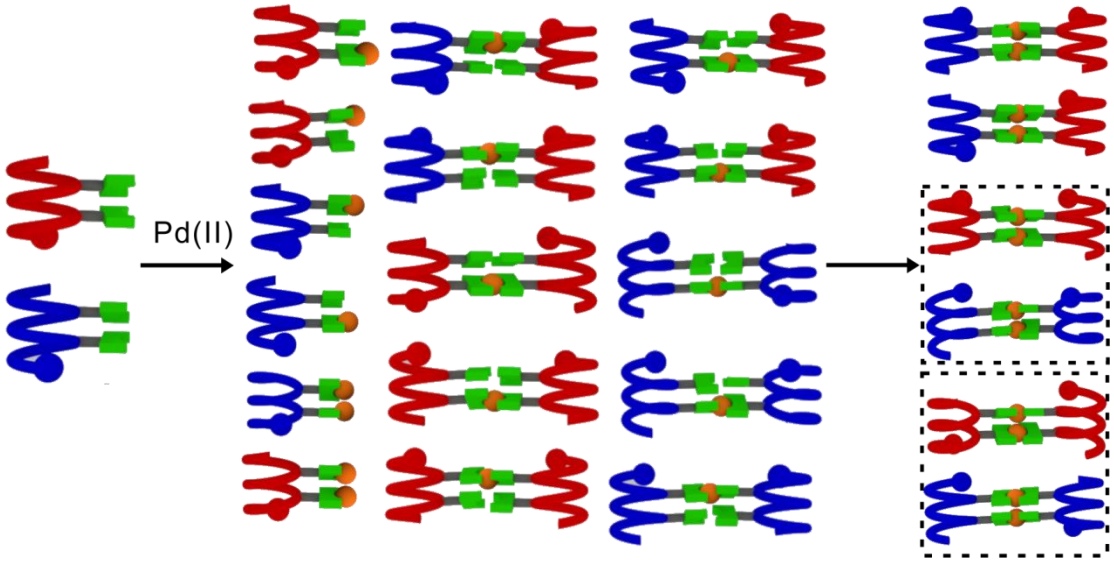


Figure S13: The possible complexes of incomplete complexation and the possible isomers of complete complexation of **2a** and $PdCl_2(CH_3CN)_2$, red color represent P-helix and blue color represent M-helix.

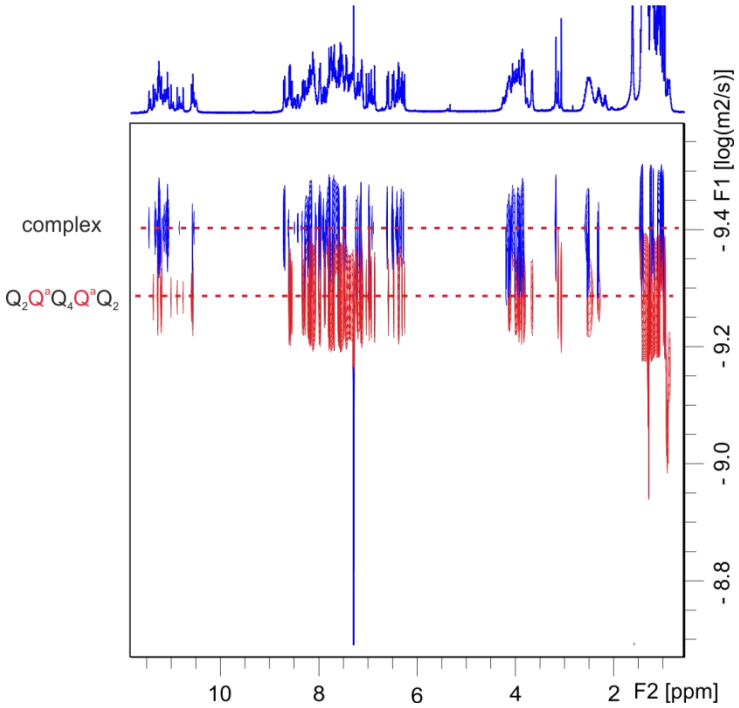


Figure S14: DOSY NMR (400 MHz, $CDCl_3$, 298 K) spectra of the mixture of **1b** and the complex Pd_2(**1b**)$_2Cl_4$, the red peaks corresponding to **1b** and the blue corresponding to the complex.

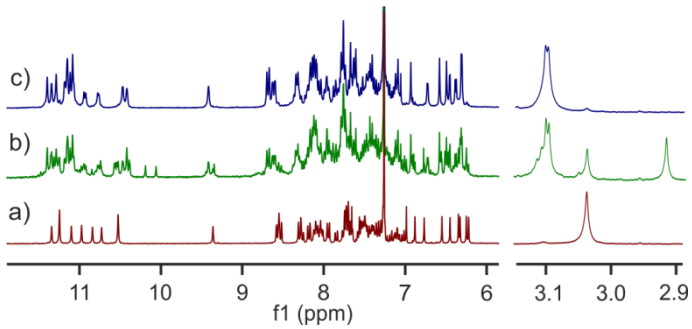


Figure S15: Parts of ^{1}H NMR spectra (300 MHz, $CDCl_3$) of **1d** and the complex Pd_2(**1d**)$_2Cl_4$ showing the amide, aromatic and methyl ester regions, a) **1d**; b) intermediate state of the complex formation between **1d** and $PdCl_2(AcN)_2$; c) the complex Pd_2(**1d**)$_2Cl_4$. In the methyl ester region (around 3.1 ppm), only two peaks are observed for Pd_2(**1d**)$_2Cl_4$.

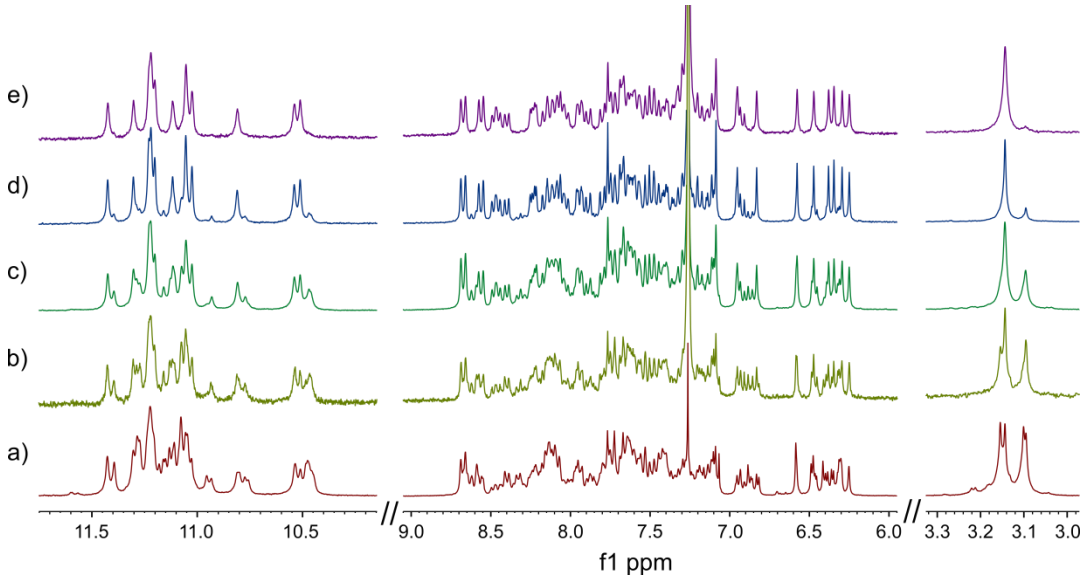


Figure S16 : Parts of ^{1}H NMR spectra (300 MHz, $CDCl_3$) of Pd_2(**1b**)$_2Cl_4$ before and after several repeated recrystallizations. a) before any crystallization (product after reaction); b) one time crystallization; c) two times of crystallization; d) four times of crystallization and e) five times of crystallization.

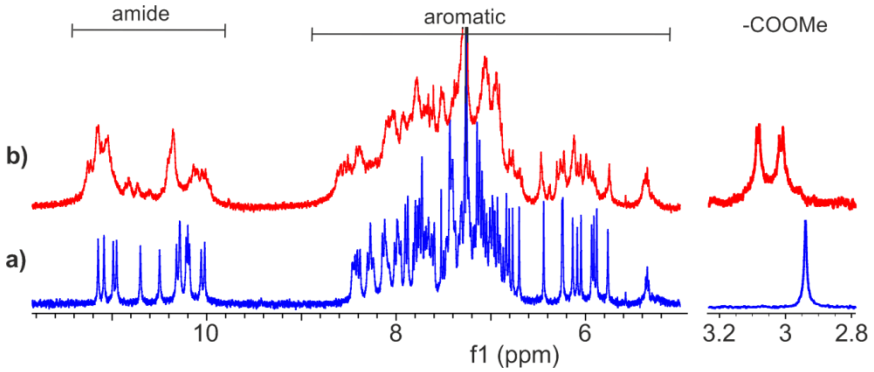


Figure S17: Parts of ^{1}H NMR spectra (300 MHz, $CDCl_3$) of **1c** and the complex Pd_3(**1c**)$_2Cl_6$ showing the amide, aromatic and methyl ester regions, a) **1c**; b) the complex Pd_3(**1c**)$_2Cl_6$.

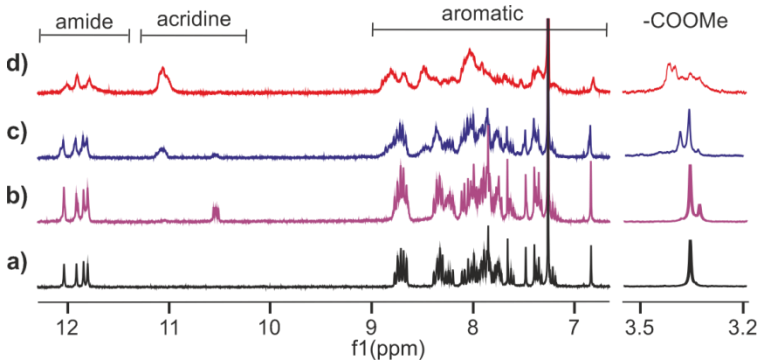


Figure S18: The changes of ^{1}H NMR spectra (300 MHz, $CDCl_3$) of **2a** after mixing with 1.5 equivalent of $PdCl_2(CH_3CN)_2$, a) **2a**; b) 50 minutes after mixing; c) 36 hours after mixing and d) 132 hours after mixing.

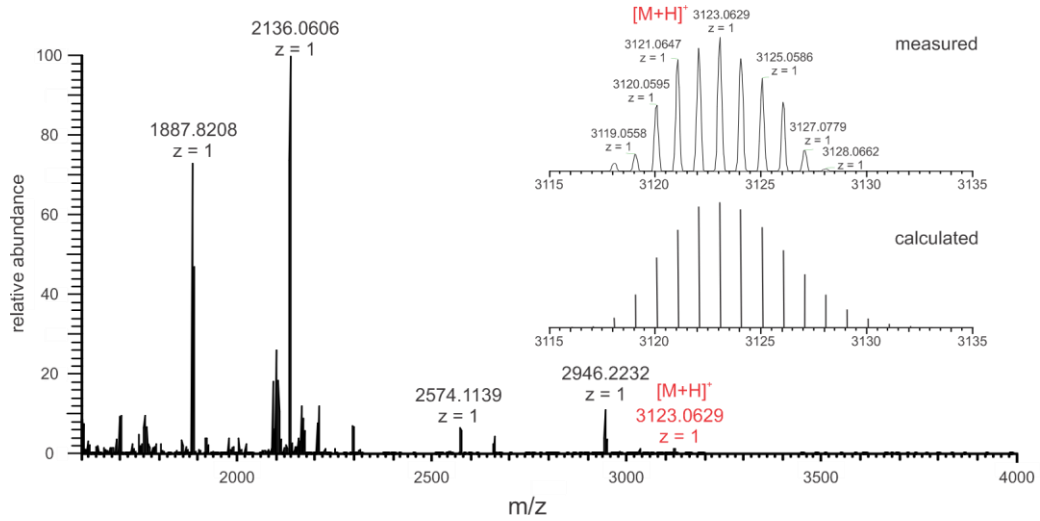


Figure S19: ESI+ HRMS of Pd(**1a**)$_2$Cl$_2$, the molecular mass marked in red, the inset shows observed and calculated isotope distributions of $[M+H]^+$, the observed isotope distribution matched with calculated one. Very low intensity found for the molecular mass probably due to poor ionization or poor stability in the gas phase.

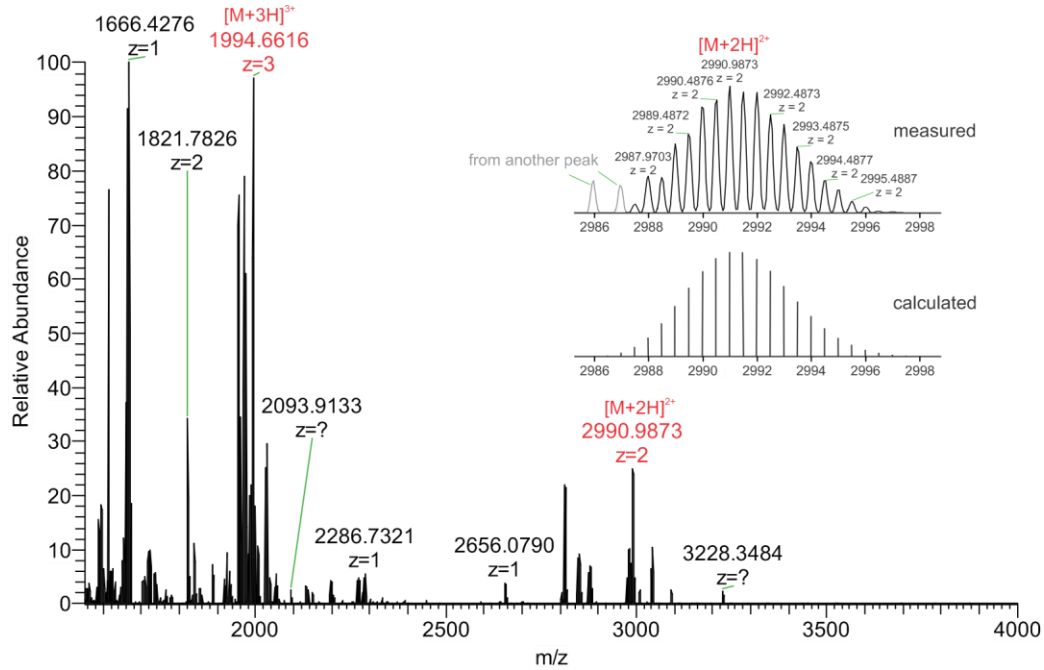


Figure S20: ESI+ HRMS of Pd$_2$(**1b**)$_2$Cl$_4$, different charge states observed (marked in red), the inset shows the observed and calculated isotope distributions of $[M+2H]^{2+}$, the observed isotope distribution matched with calculated one.

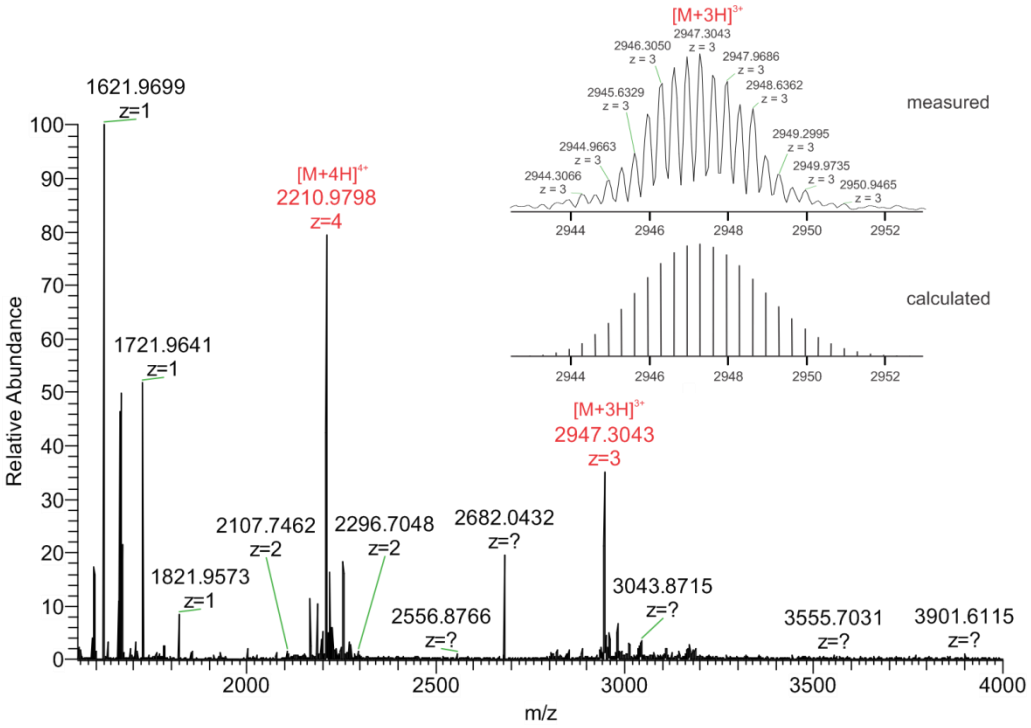


Figure S21: ESI+ HRMS of Pd_3(**1c**)$_2Cl_6$, different charge states observed (marked in red), the inset shows the observed and calculated isotope distributions of $[M+3H]^{3+}$, the observed isotope distribution matched with calculated one.

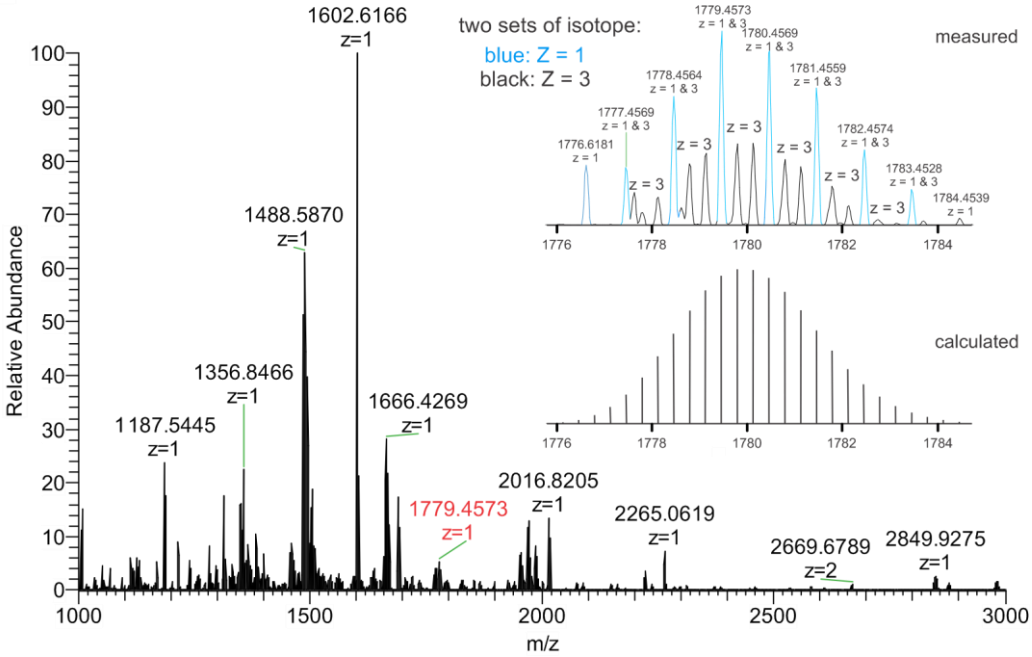


Figure S22: ESI+ HRMS of **2a**-$PdCl_2$, the peak with red label represents the molecular mass. The inset shows the observed and calculated isotope distributions, two sets of isotope distributions observed indicating possible formation of different assemblies. The calculated isotope distributions is Pd_3(**2a**)$_3Cl_6$ $[M+3H]^{3+}$, the small set of observed isotope distribution matched with calculated one. Very low intensity found for the molecular mass probably due to poor ionization or poor stability in the gas phase.

4. NMR spectra of new compounds

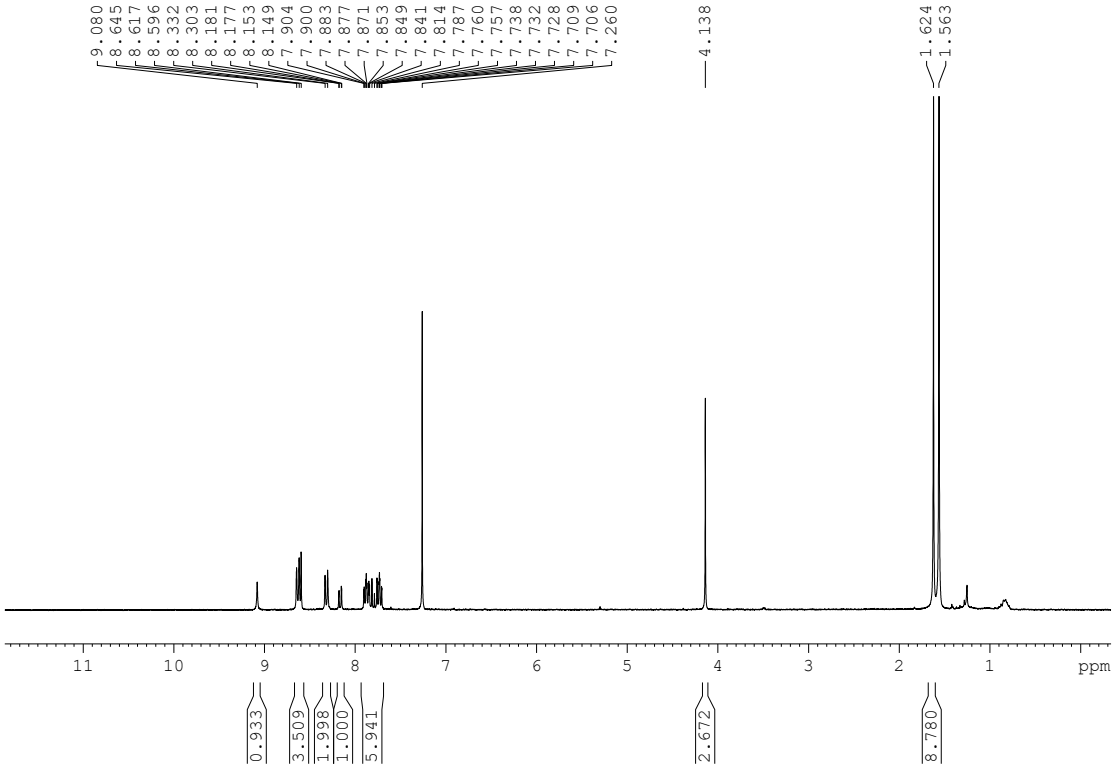


Figure S23: ^{1}H NMR (300 MHz, $CDCl_3$) of monomer **7**.

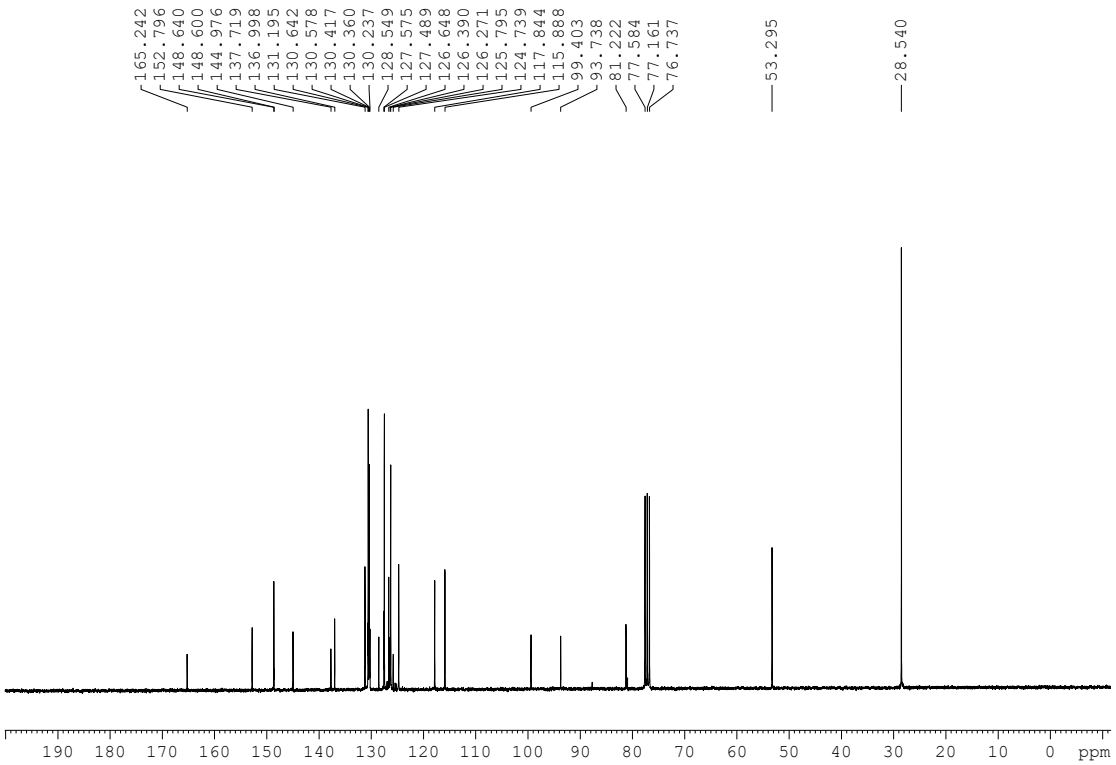


Figure S24: ^{13}C NMR (75 MHz, $CDCl_3$) of monomer **7**.

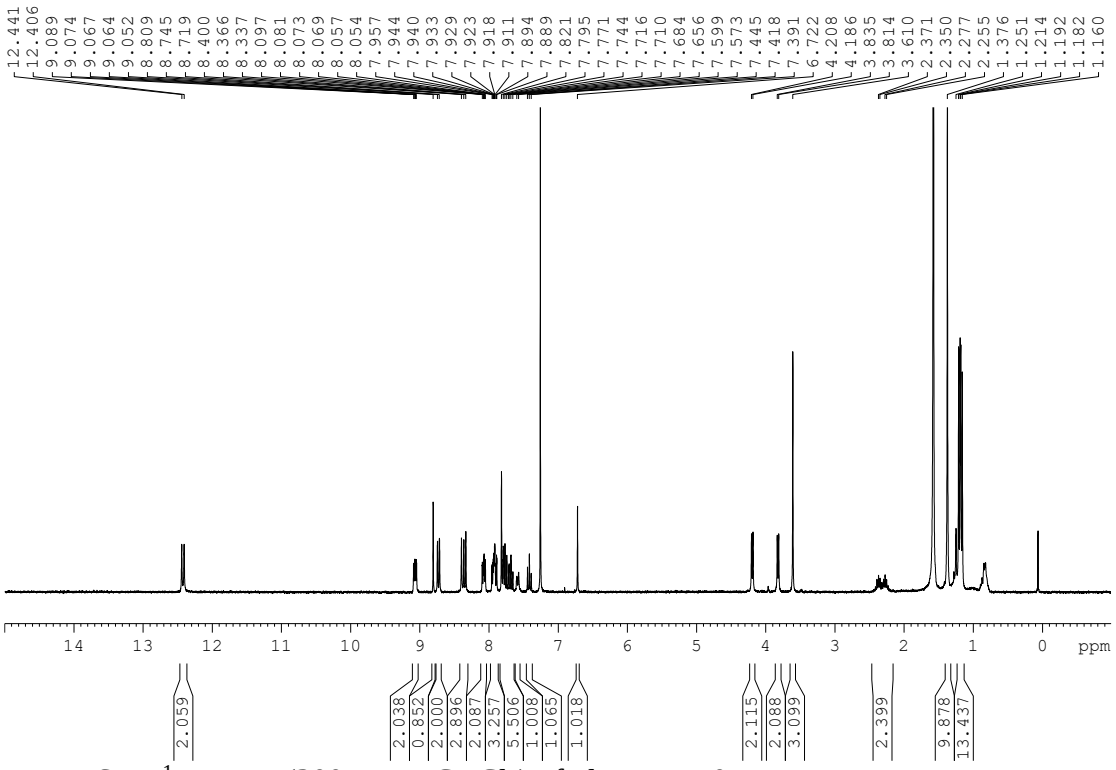


Figure S25: ^{1}H NMR (300 MHz, $CDCl_3$) of oligomer **10**.

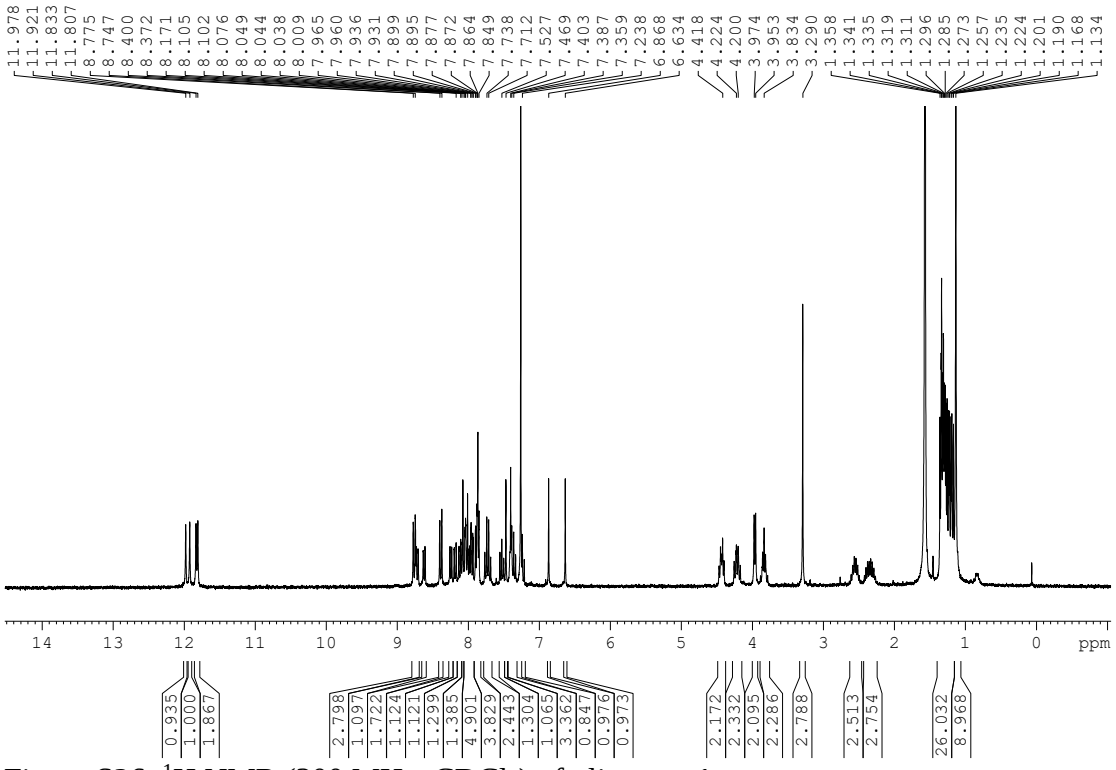


Figure S26: ^{1}H NMR (300 MHz, $CDCl_3$) of oligomer **1a**.

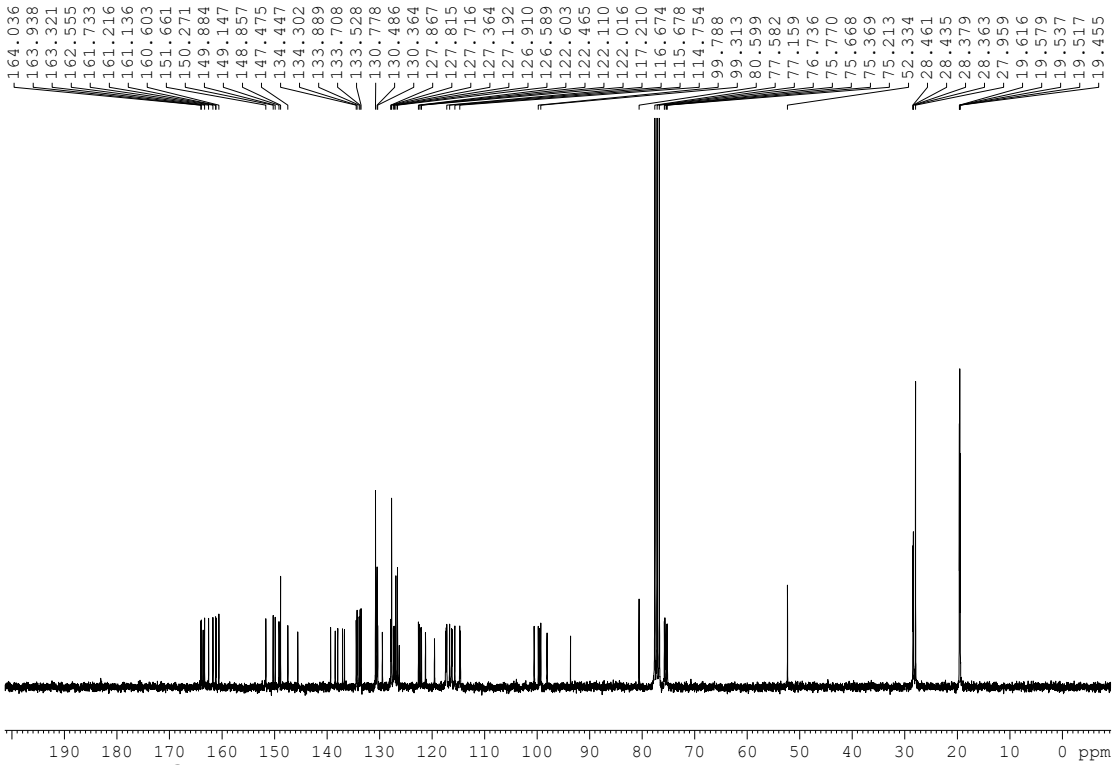


Figure S27: ^{13}C NMR (75 MHz, $CDCl_3$) of oligomer **1a**.

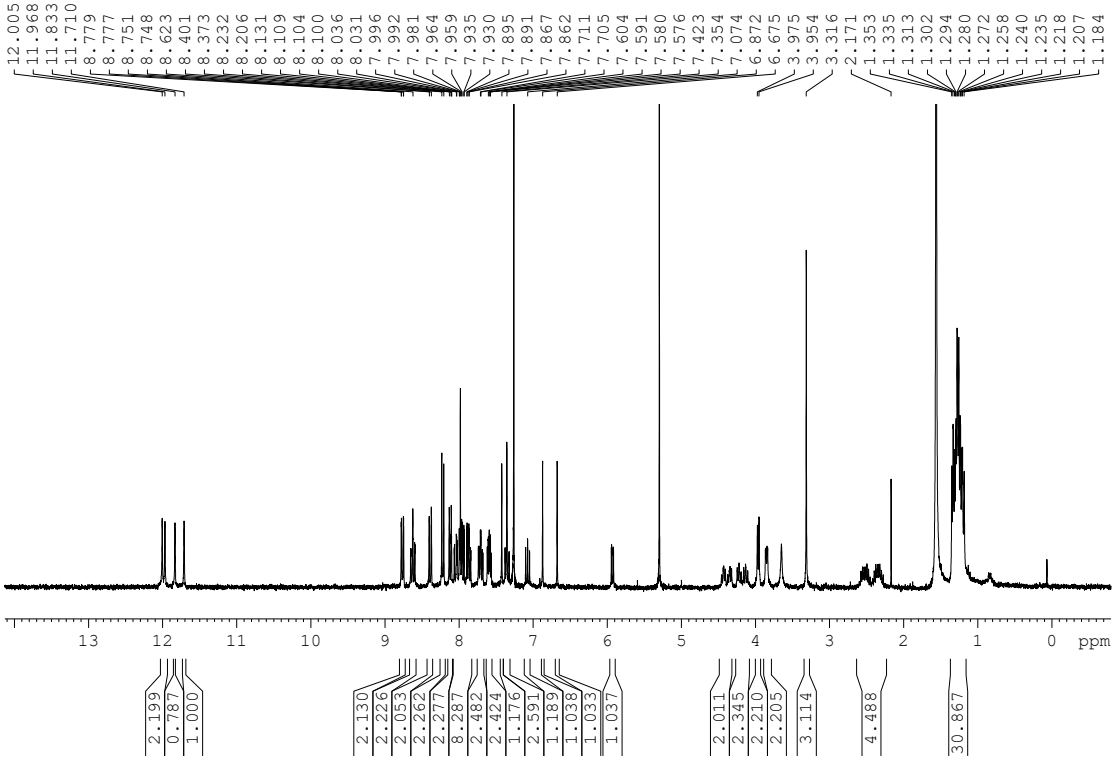


Figure S28: ^{1}H NMR (300 MHz, $CDCl_3$) of oligomer **13**, peak at 5.32 ppm is the residue CH_2Cl_2.

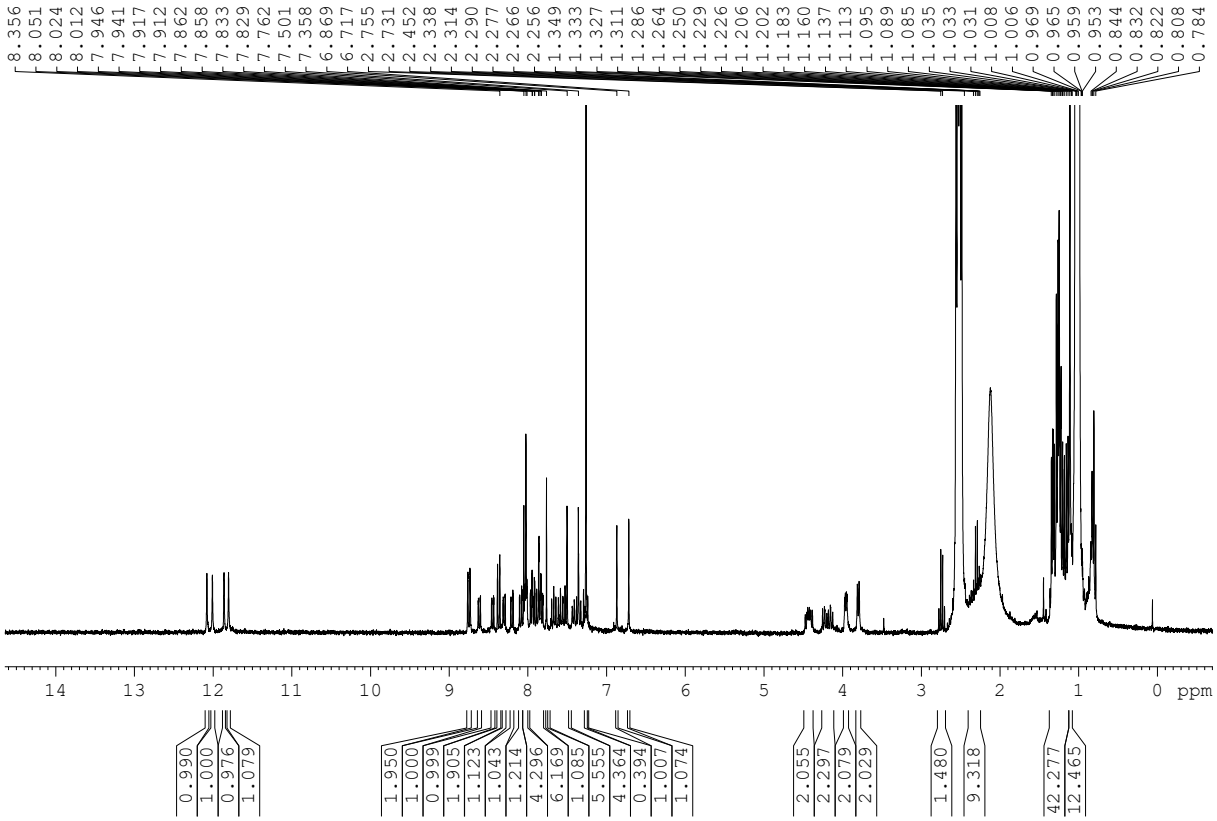


Figure S29: ^{1}H NMR (300 MHz, $CDCl_3$) of oligomer **14**.

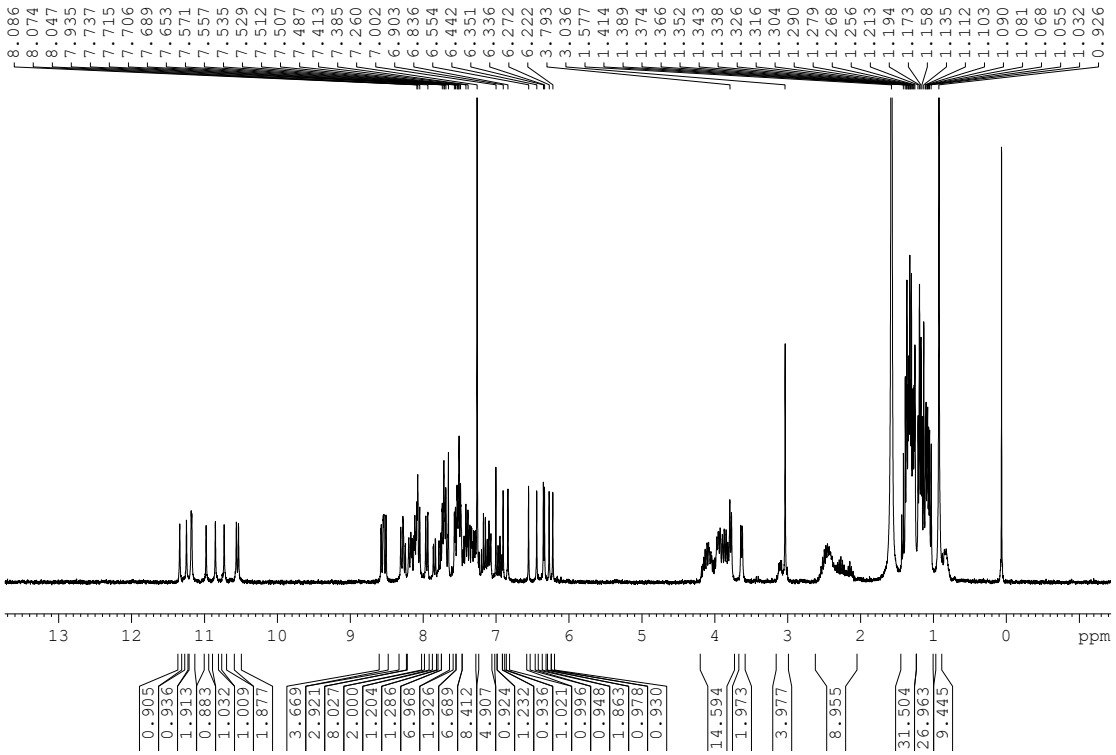


Figure S30: ^{1}H NMR (300 MHz, $CDCl_3$) of oligomer **1b**.

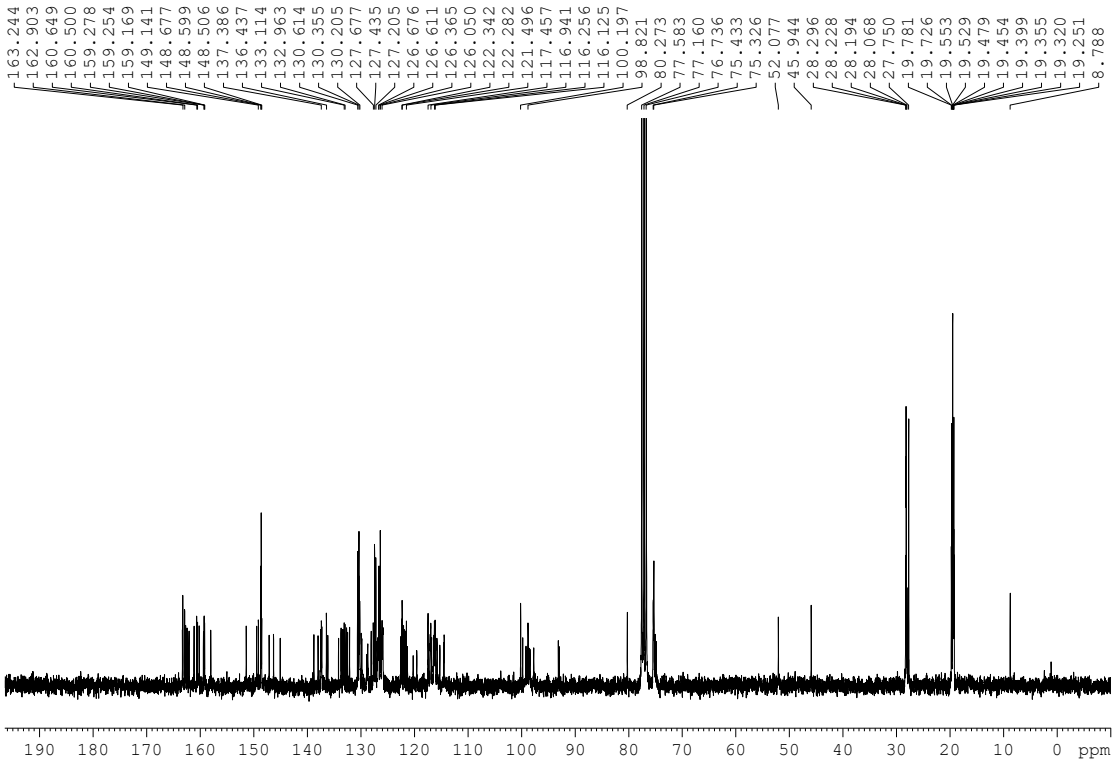


Figure S31: ^{13}C NMR (75 MHz, $CDCl_3$) of oligomer **1b**.

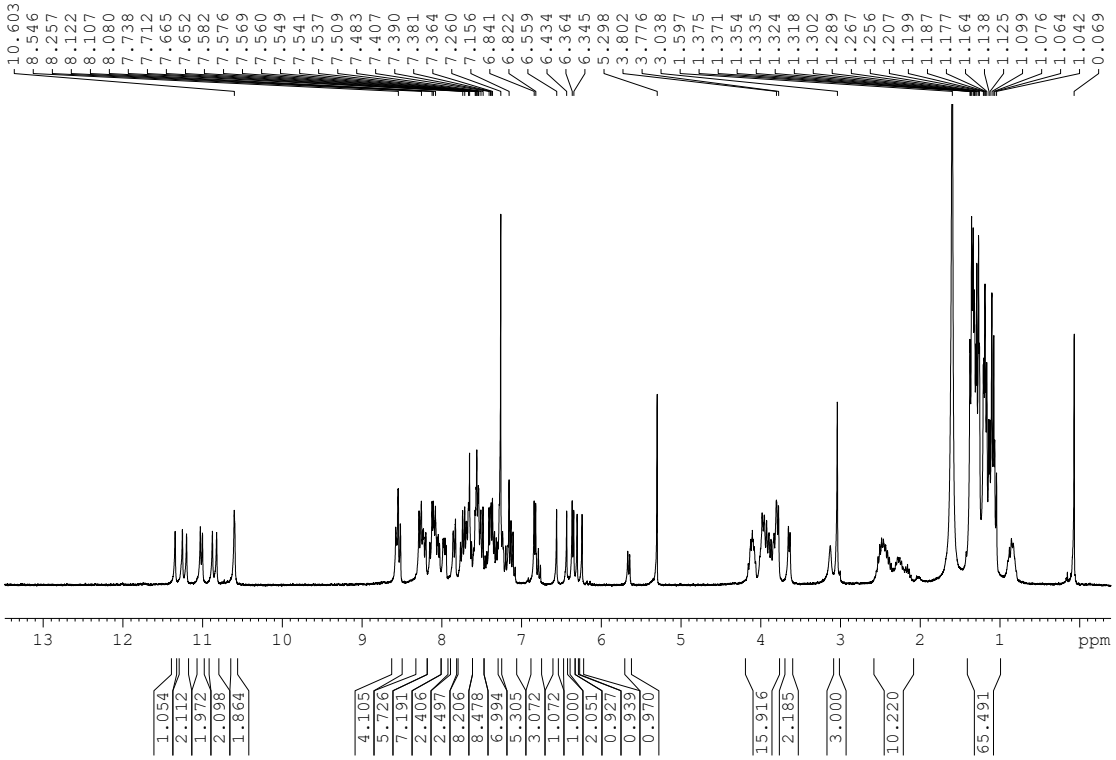


Figure S32: ^{1}H NMR (300 MHz, $CDCl_3$) of oligomer NH_2-**1b**.

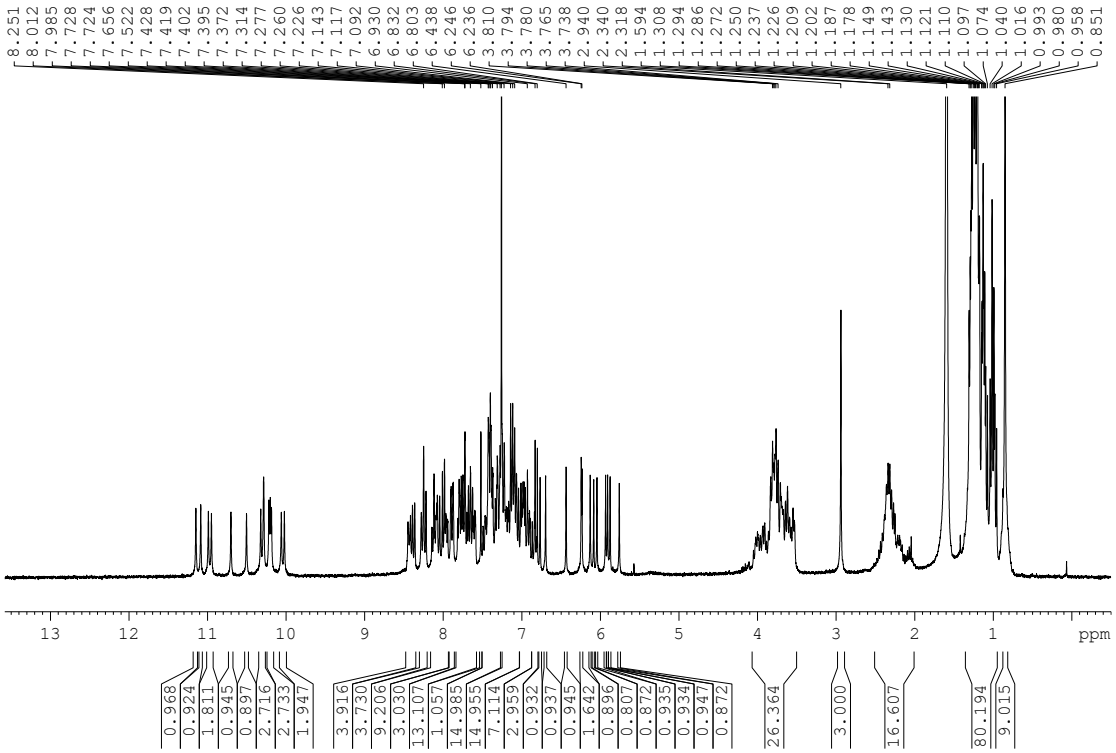


Figure S33: ^{1}H NMR (300 MHz, $CDCl_3$) of oligomer **1c**.

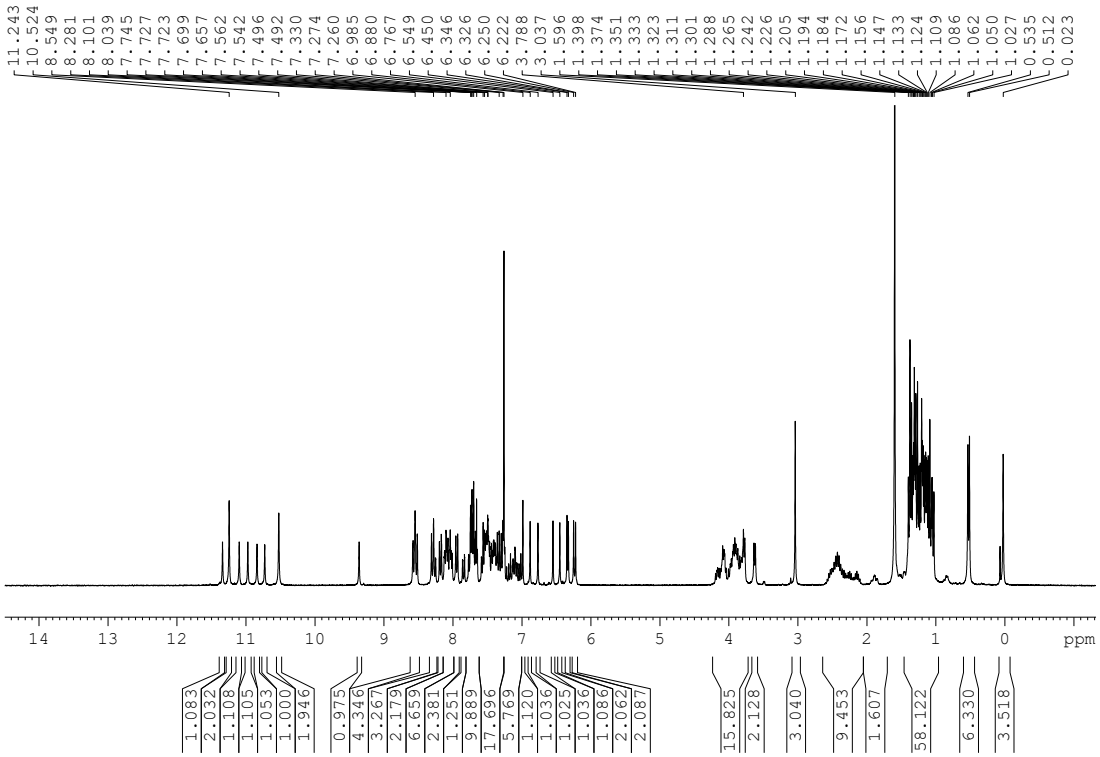


Figure S34: ^{1}H NMR (300 MHz, $CDCl_3$) of oligomer **1d**.

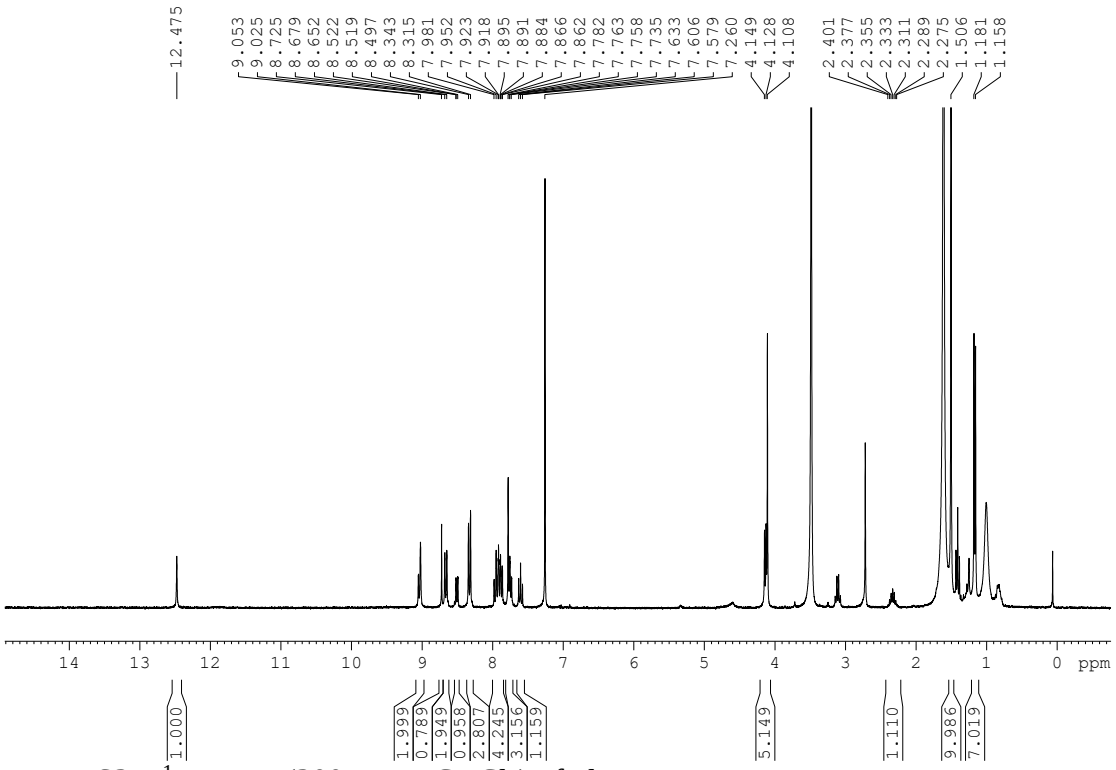


Figure S35: ^{1}H NMR (300 MHz, $CDCl_3$) of oligomer **17**.

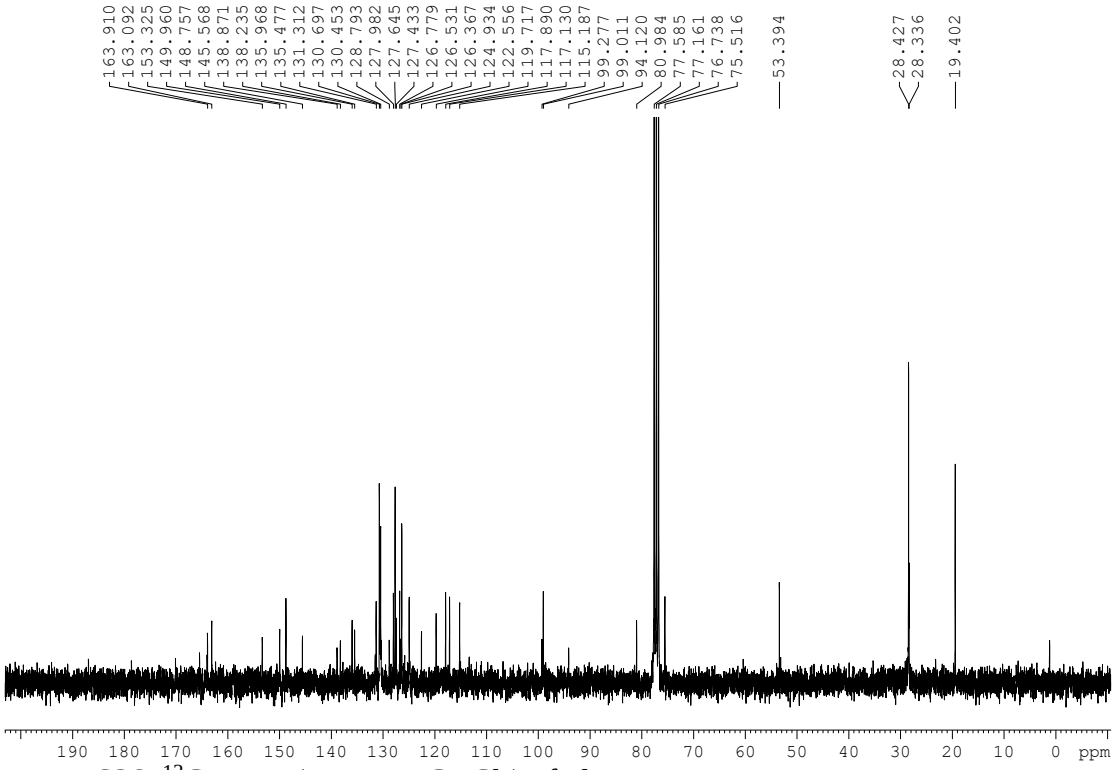


Figure S36: ^{13}C NMR (75 MHz, $CDCl_3$) of oligomer **17**.

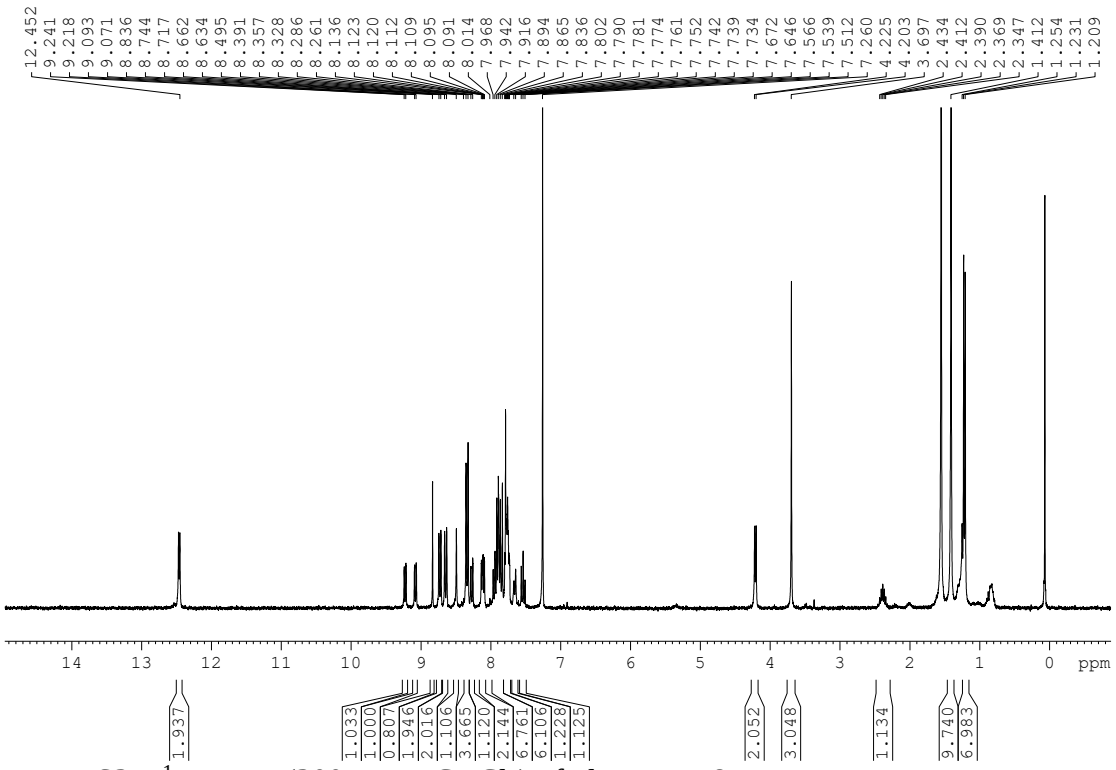


Figure S37: ^{1}H NMR (300 MHz, $CDCl_3$) of oligomer **18**.

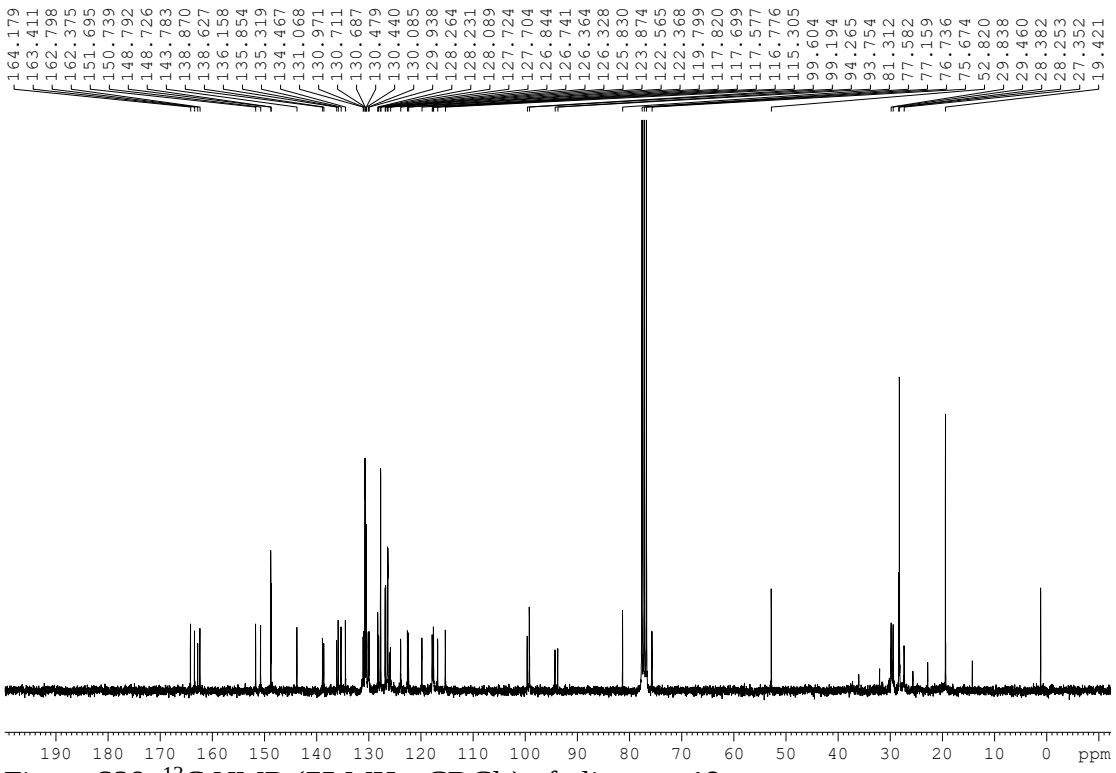


Figure S38: ^{13}C NMR (75 MHz, $CDCl_3$) of oligomer **18**.

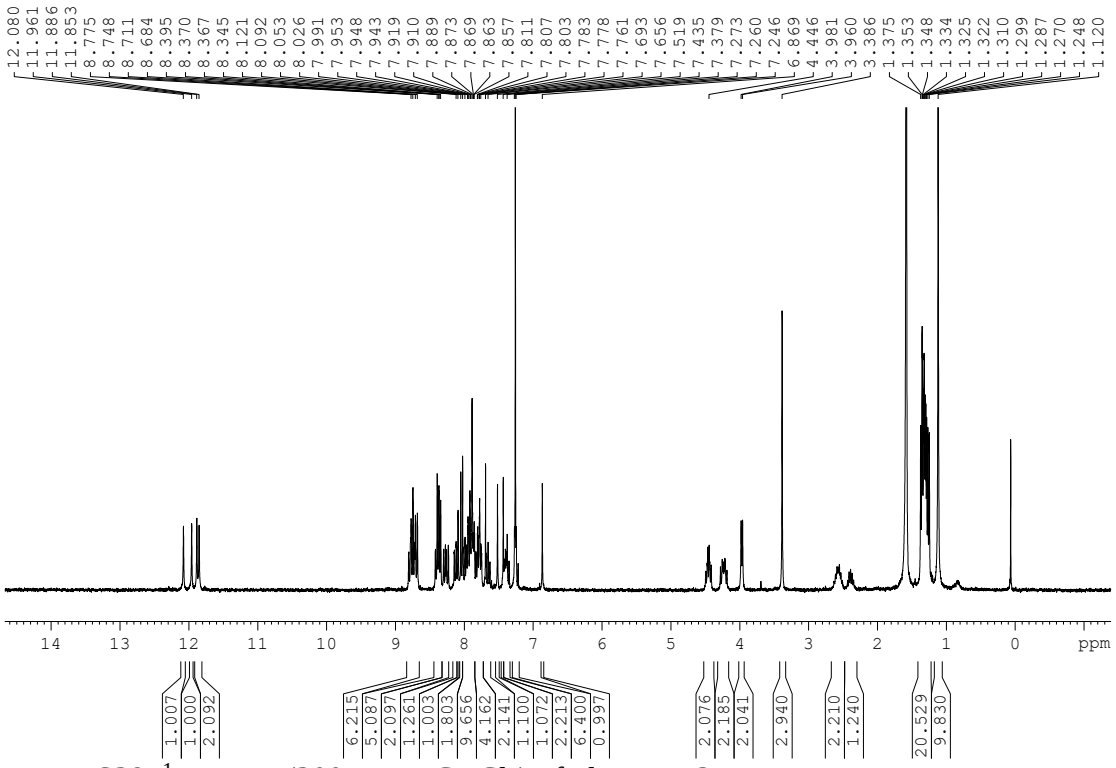


Figure S39: ^{1}H NMR (300 MHz, $CDCl_3$) of oligomer **2a**.

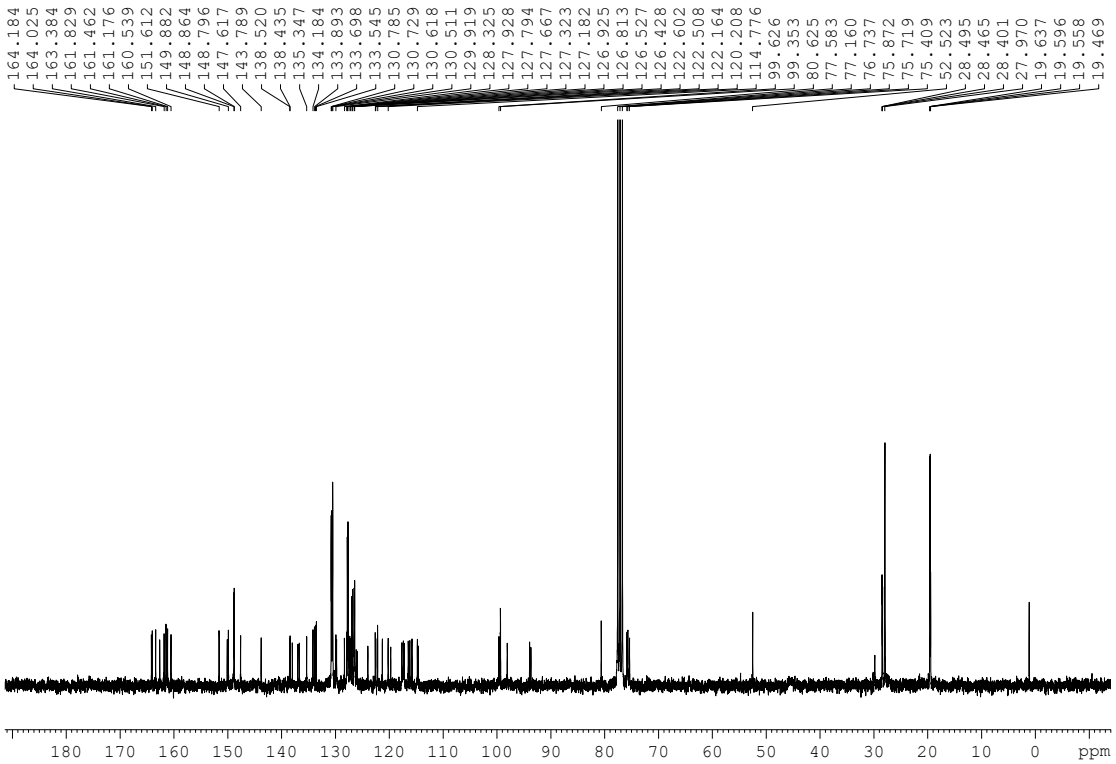


Figure S40: ^{13}C NMR (75 MHz, $CDCl_3$) of oligomer **2a**.

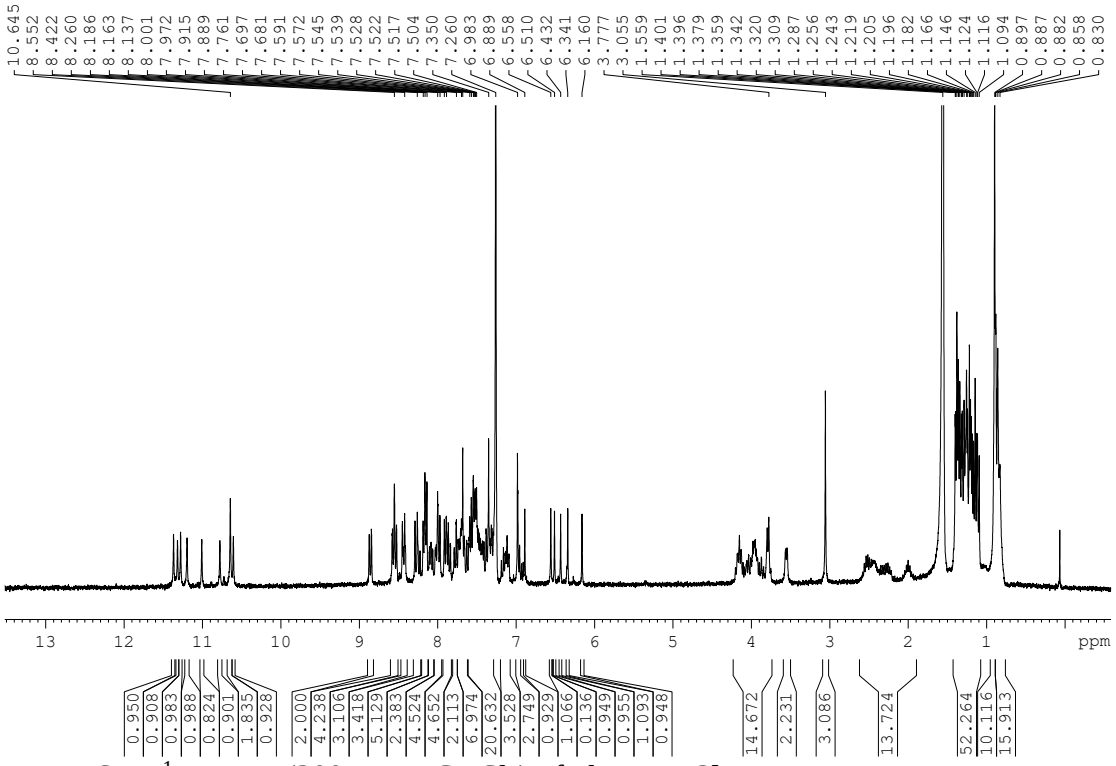


Figure S41: ^{1}H NMR (300 MHz, $CDCl_3$) of oligomer **2b**.

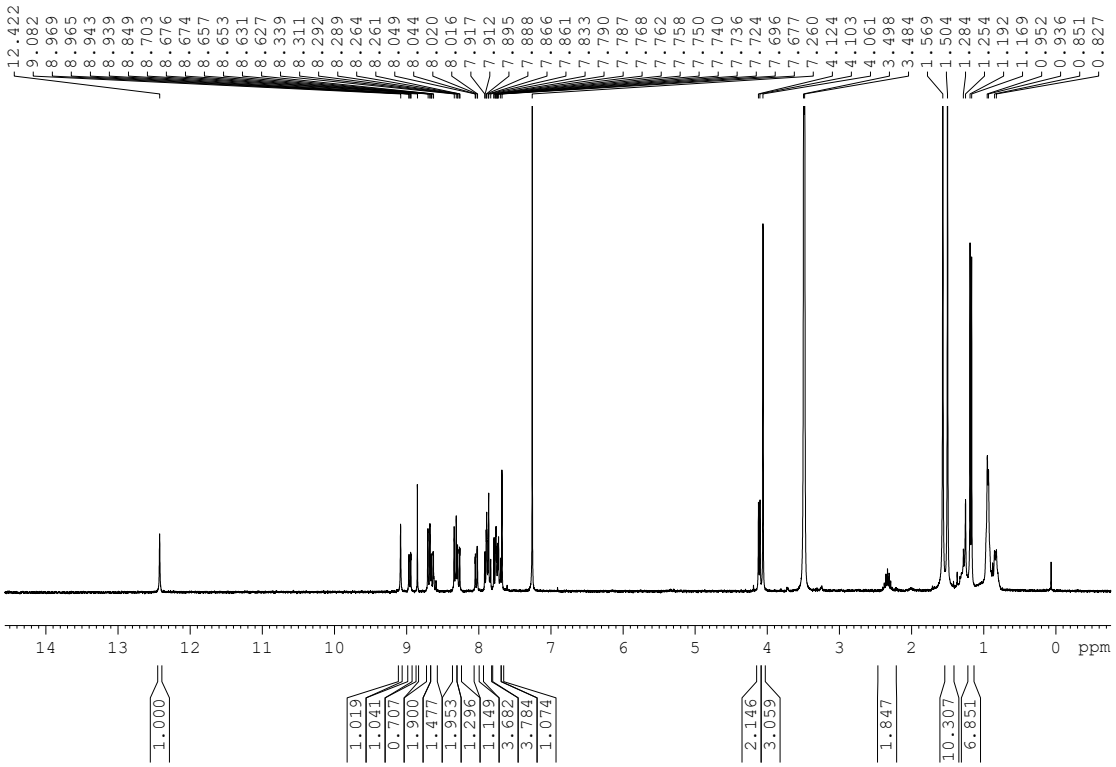


Figure S42: ^{1}H NMR (300 MHz, $CDCl_3$) of oligomer **21**, the peak at 3.49 ppm is the residue MeOH.

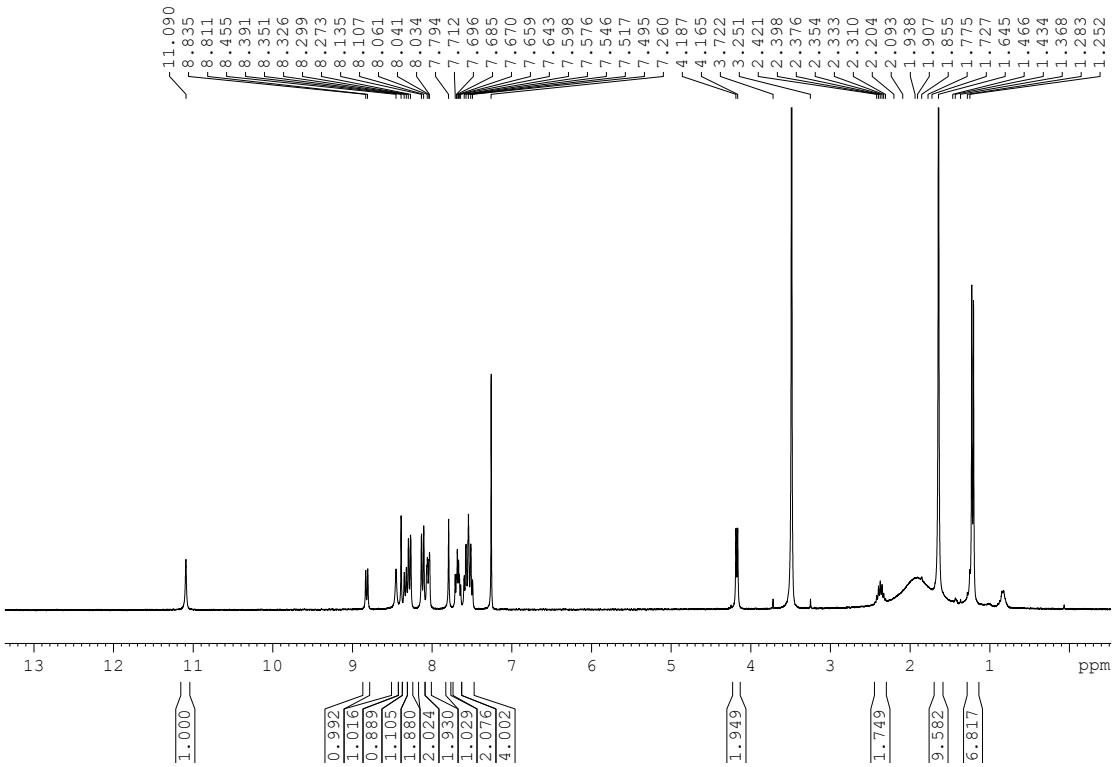


Figure S43: ^{1}H NMR (300 MHz, $CDCl_3$) of oligomer **22**, the peak at 3.49 ppm is the residue MeOH.

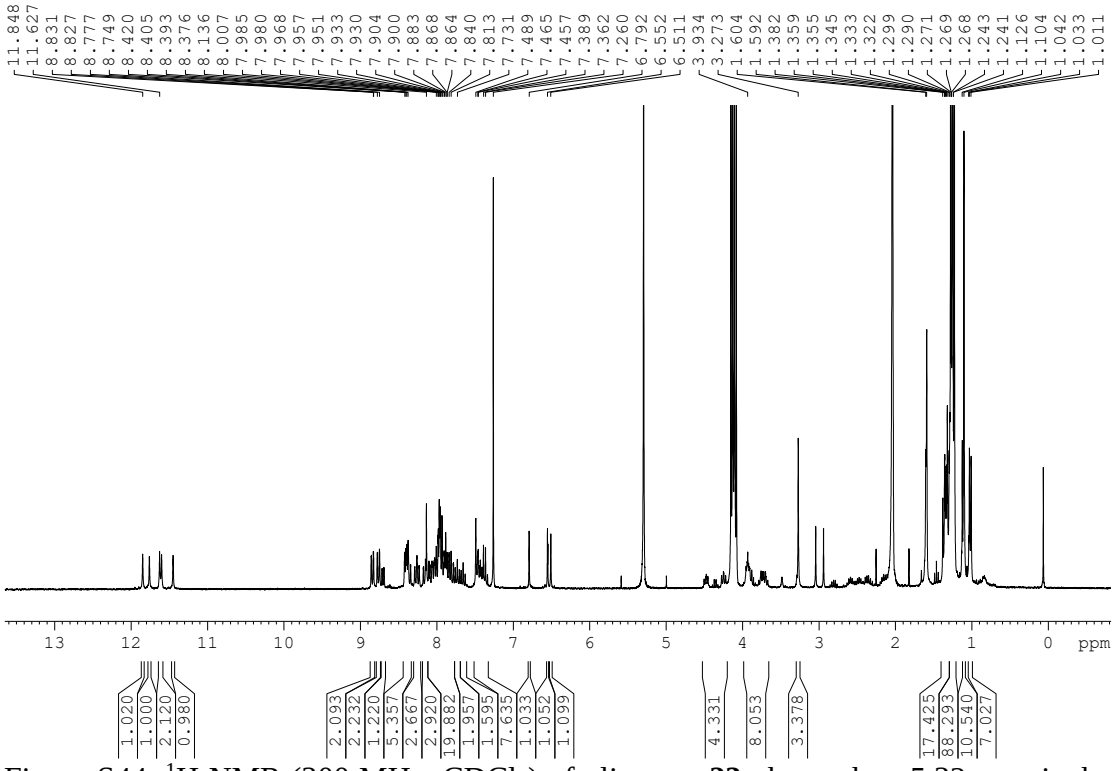


Figure S44: ^{1}H NMR (300 MHz, $CDCl_3$) of oligomer **23**, the peak at 5.32 ppm is the residue CH_2Cl_2, and peaks at 4.12, 2.04, 1.26 ppm are the residue of ethyl acetate.

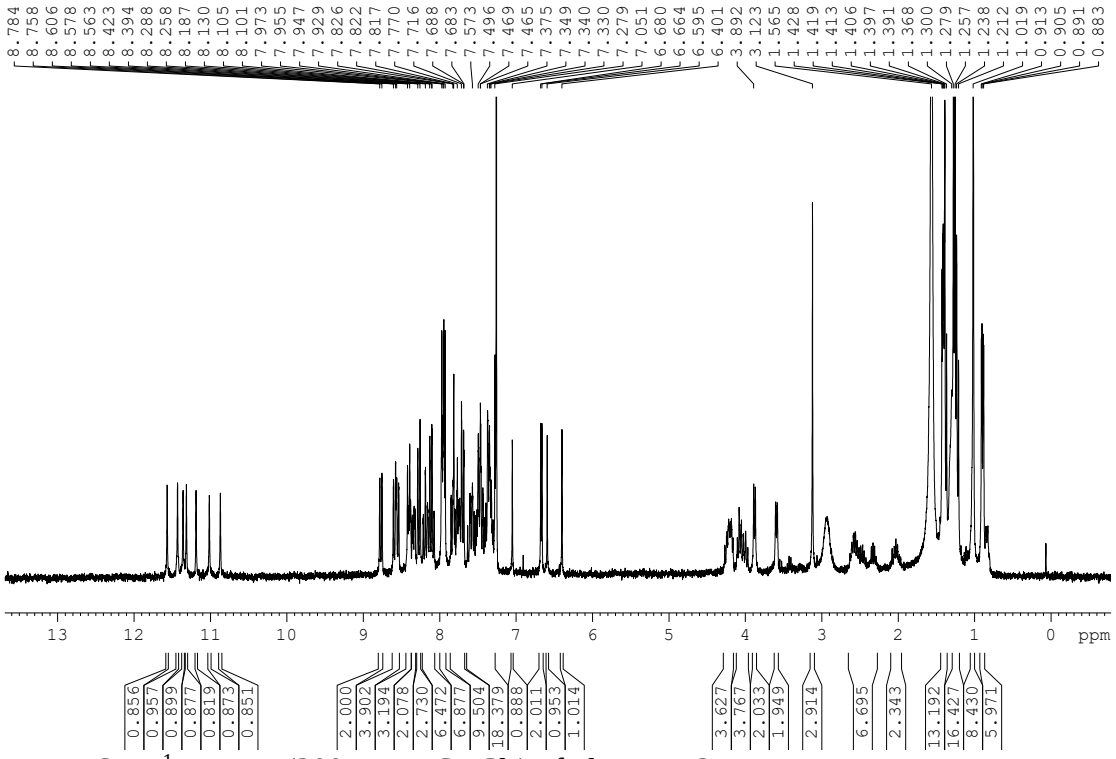


Figure S45: ^{1}H NMR (300 MHz, $CDCl_3$) of oligomer **24**.

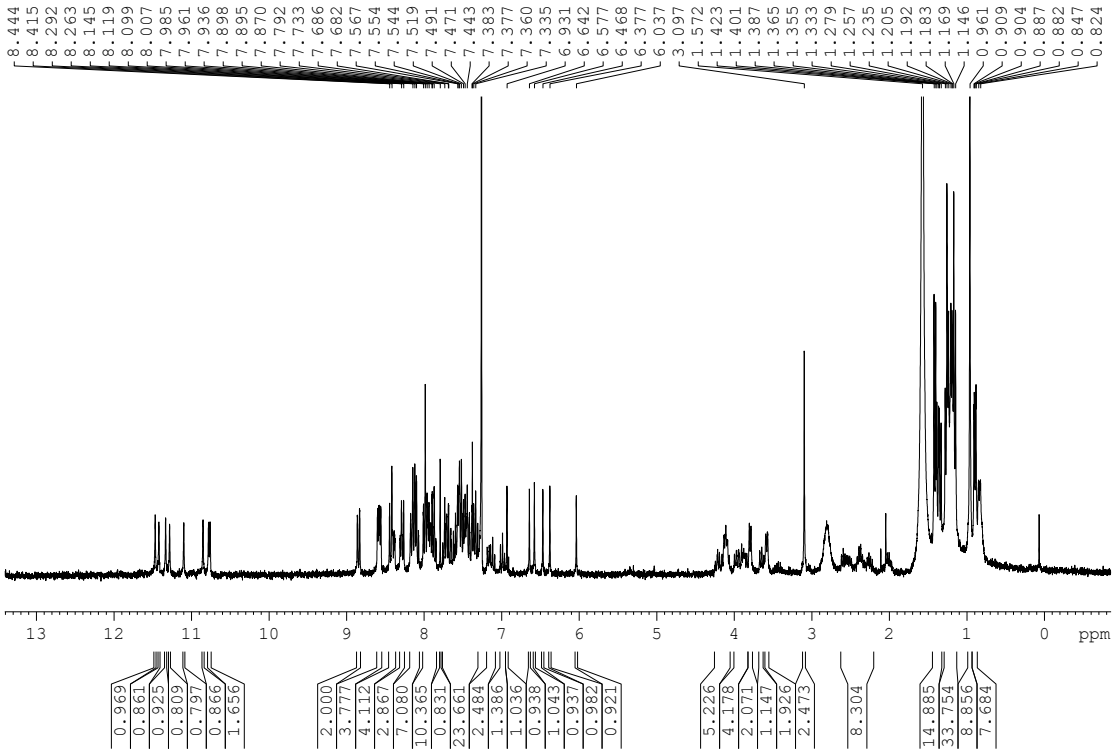


Figure S46: ^{1}H NMR (300 MHz, $CDCl_3$) of oligomer **25**.

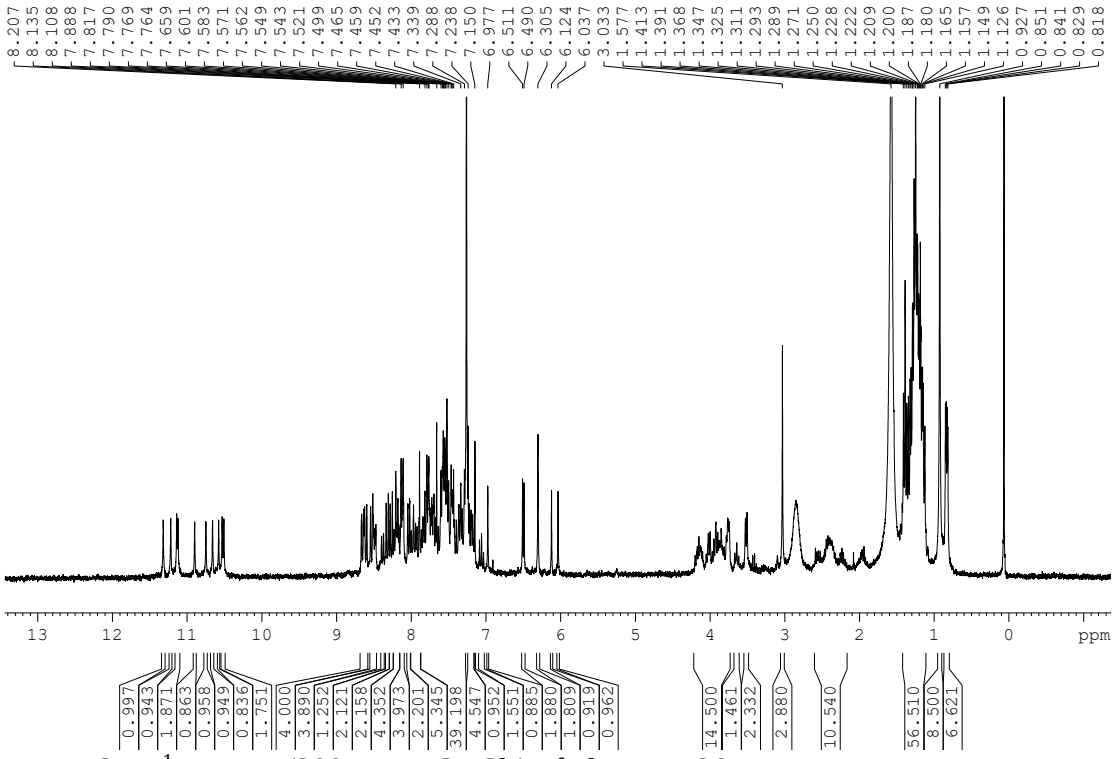


Figure S47: ^{1}H NMR (300 MHz, $CDCl_3$) of oligomer **26**.

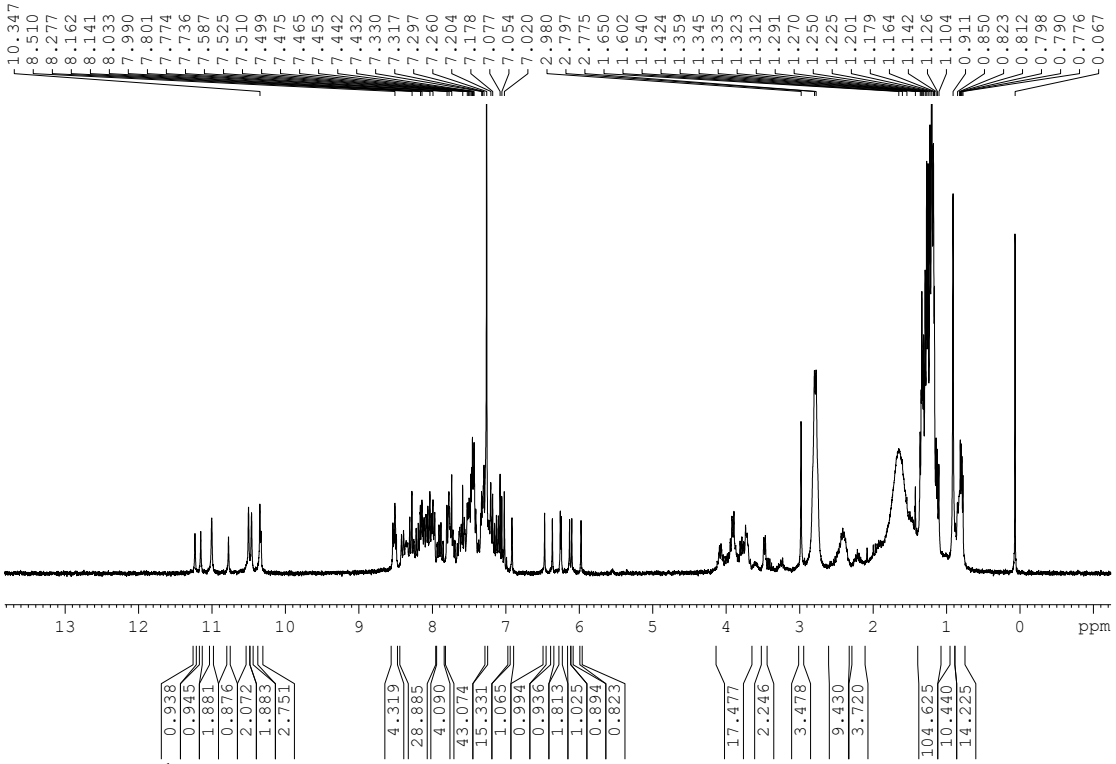


Figure S48: ^{1}H NMR (300 MHz, $CDCl_3$) of oligomer **27**.

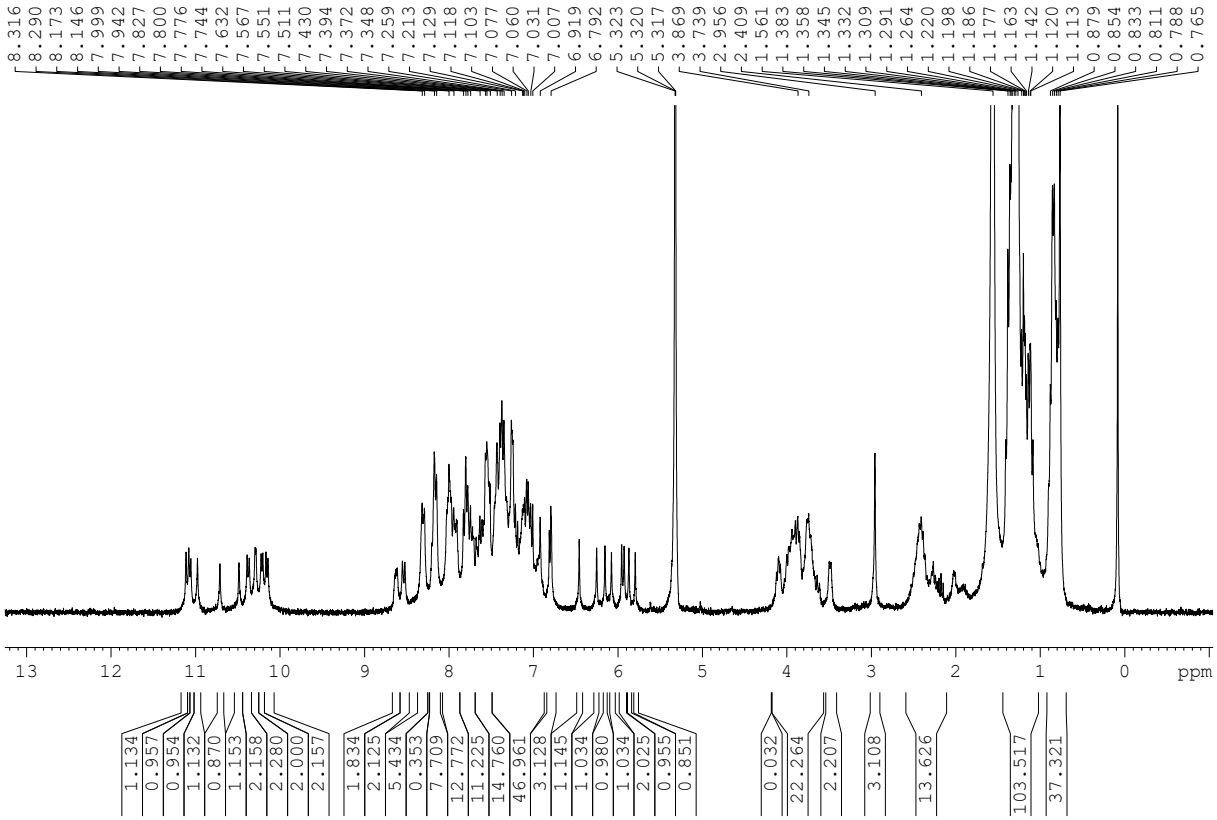


Figure S49: ^{1}H NMR (300 MHz, CD_2Cl_2) of oligomer **2c**.

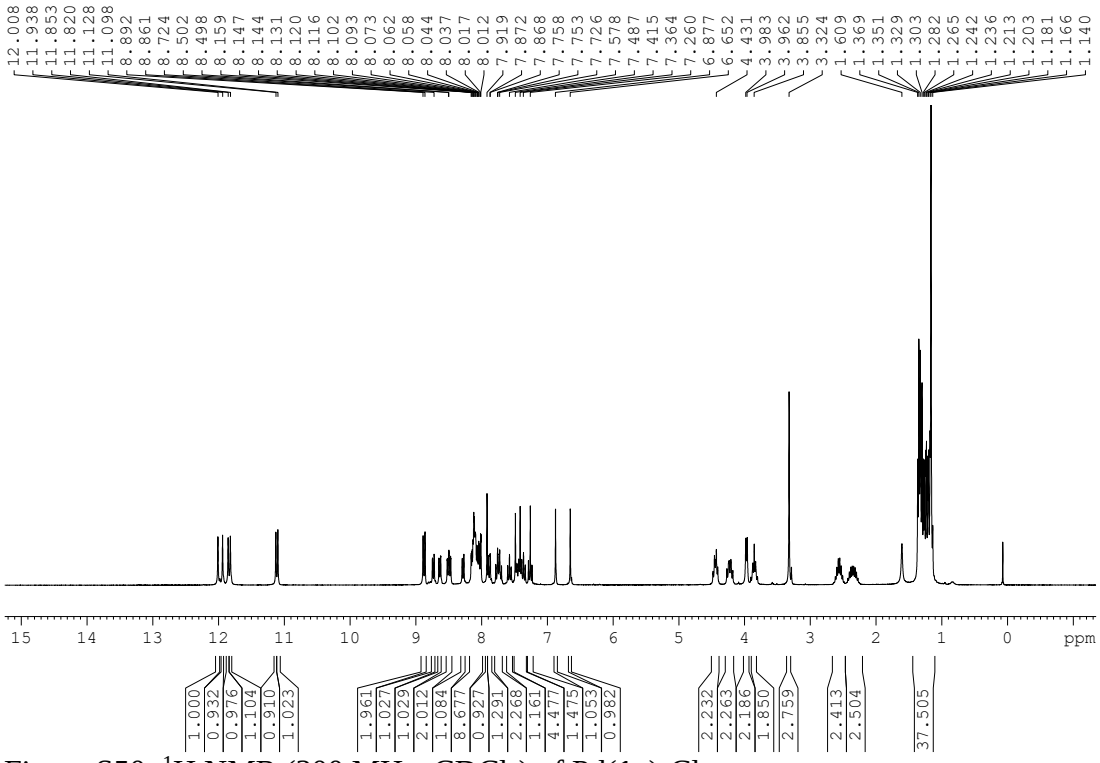


Figure S50: ^{1}H NMR (300 MHz, $CDCl_3$) of Pd(**1a**)$_2Cl_2$.

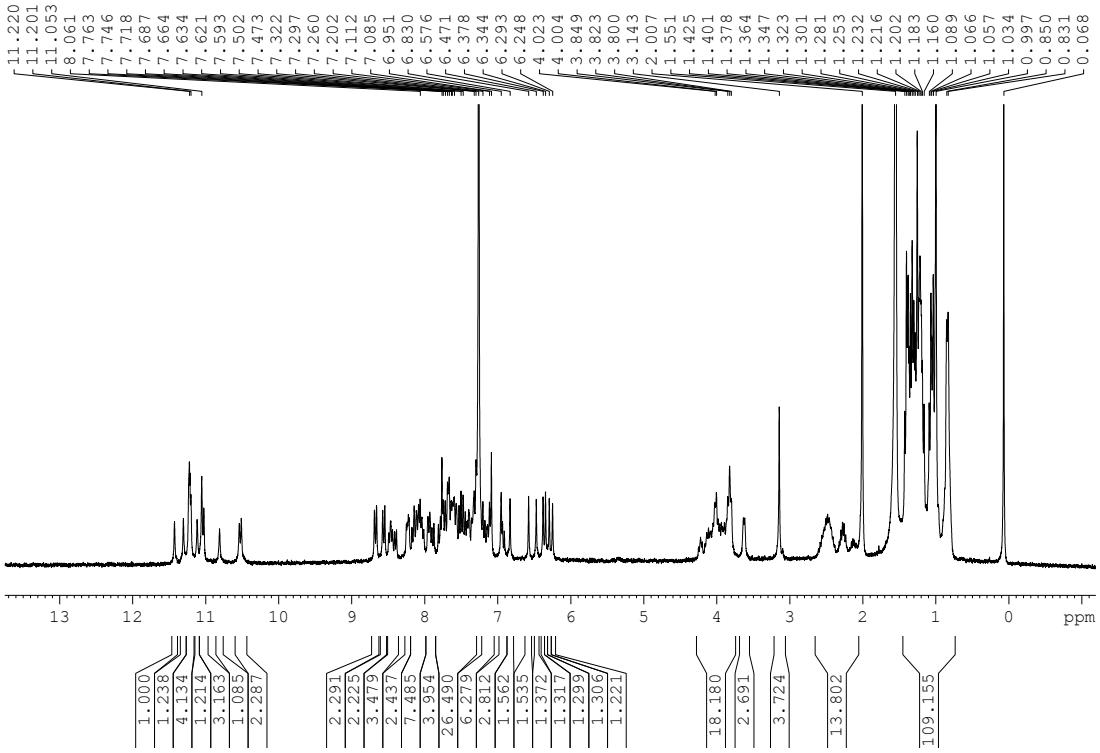


Figure S51：^{1}H NMR (300 MHz, $CDCl_3$) of one of the four isomers of Pd_2(**1b**)$_2Cl_4$.

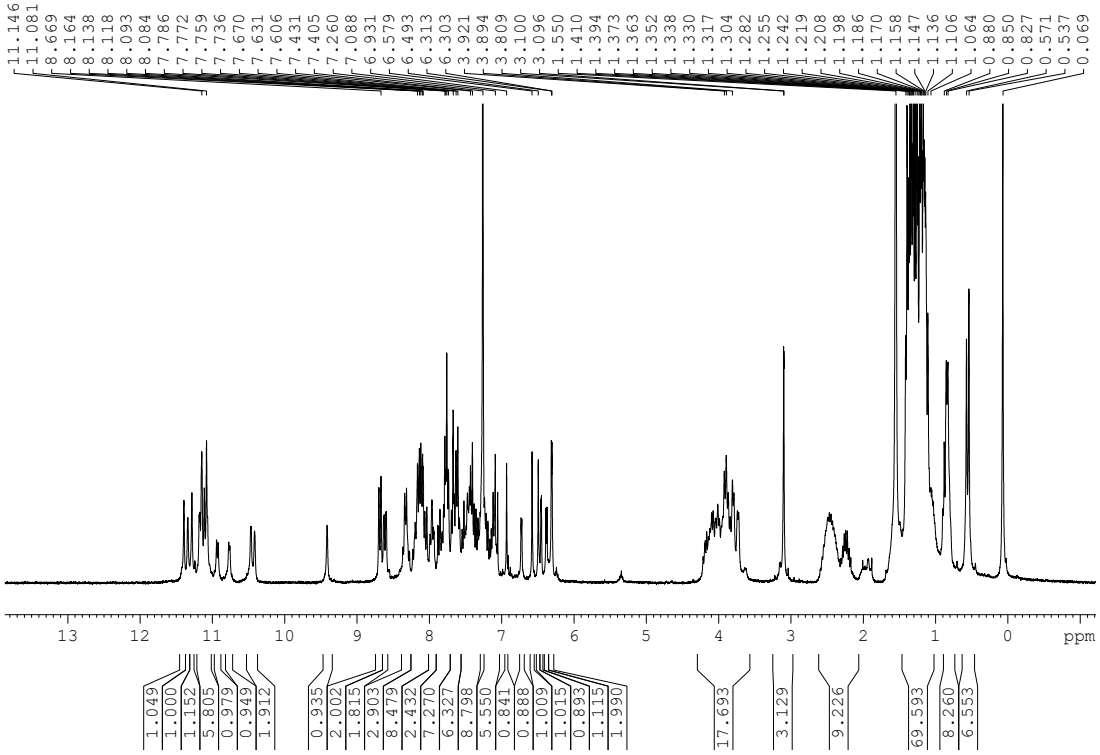


Figure S52: ^{1}H NMR (300 MHz, $CDCl_3$) of Pd_2(**1d**)$_2Cl_4$.

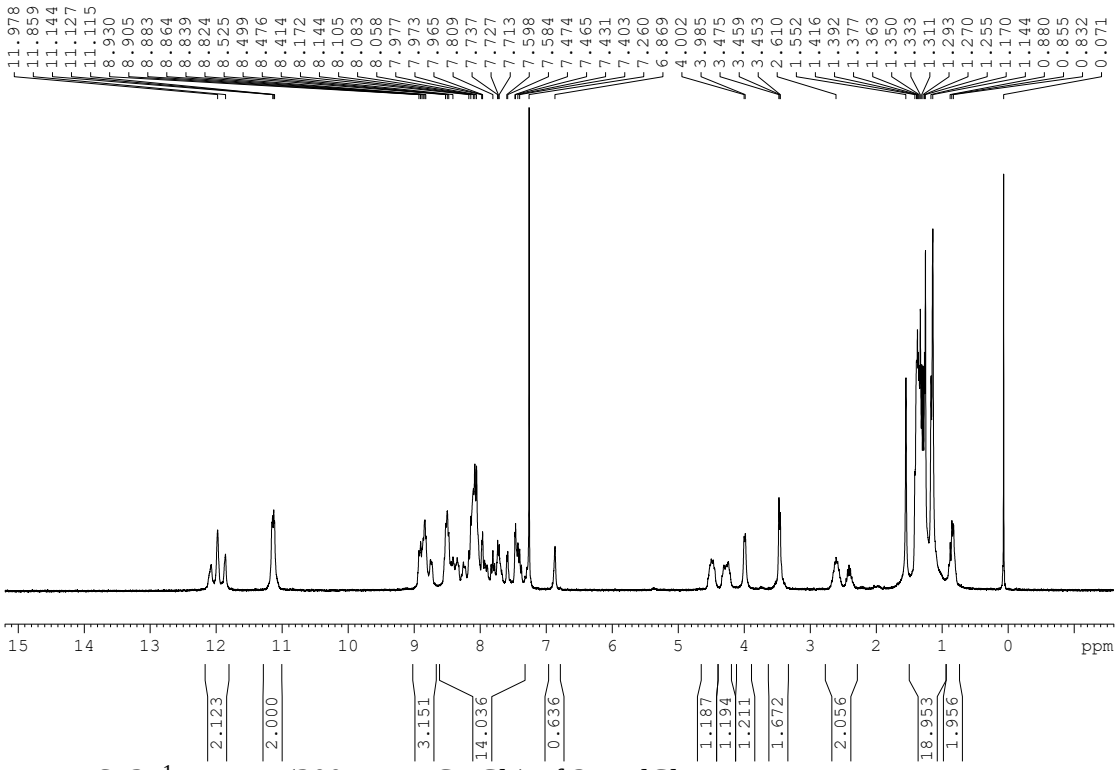


Figure S53: ^{1}H NMR (300 MHz, $CDCl_3$) of **2a**-$PdCl_2$.

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