Supporting Information for:

N-Alkylated and N,N-Dialkylated 1,6-Diaminoperylene Diimides via Copper Catalyzed Direct Aromatic Amination

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1 Synthesis

1.1 General methods

Commercially available chemicals were used as received, unless otherwise stated. Prior to characterization and further processing, all solids and oils were dried at room temperature under vacuum. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 300, DPX 400 and DRX 500 (300, 400, and 500 MHz for ^{1}H and 75.5, 100.6 and 125.8 MHz for ^{13}C). Chemical shifts are given in parts per million (ppm) referenced to residual ^{1}H or ^{13}C signals in deuterated solvents. Mass spectra were measured on a Finnigan ThermoQuest MAT 95 XL (EI-MS) and a Bruker Daltronics autoflex TOF/TOF (MALDI-MS; matrix material: *trans*-2-[3-(4-t-Butyl-phenyl)-2-methyl-2-propenylidene]malononitrile (DCTB), dithranol). Thin layer chromatography was conducted on silica gel coated aluminium plates (Macherey-Nagel, Alugramm SIL G/UV254, 0.25 mm coating with fluorescence indicator). Silica gel 60 M (Macherey-Nagel, 0.04-0.063 mm) was used as the stationary phase for column chromatography. Gel permeation chromatography (GPC) was performed in THF (HPLC grade, stabilized with 2.5 ppm BHT) at room temperature. GPC analyses were run on an Agilent Technologies system at a flow rate of 1 mL/min using an IsoPump G1310 A, a UV detector (G1314B) and PSS columns (Polymer Standards Service, Mainz, Germany; 10^2, 10^3, and 10^5 Å, 5µ, 8 x 300 mm). For purification, a Shimadzu Recycling GPC system, equipped with a LC-20 AD pump, a SPD-20 A UV detector and a set of three preparative columns from PSS (10^3 Å, 5µ, 20 x 300 mm) was employed. The system operated at a flow rate of 6 mL/min.

1.2 Synthesis

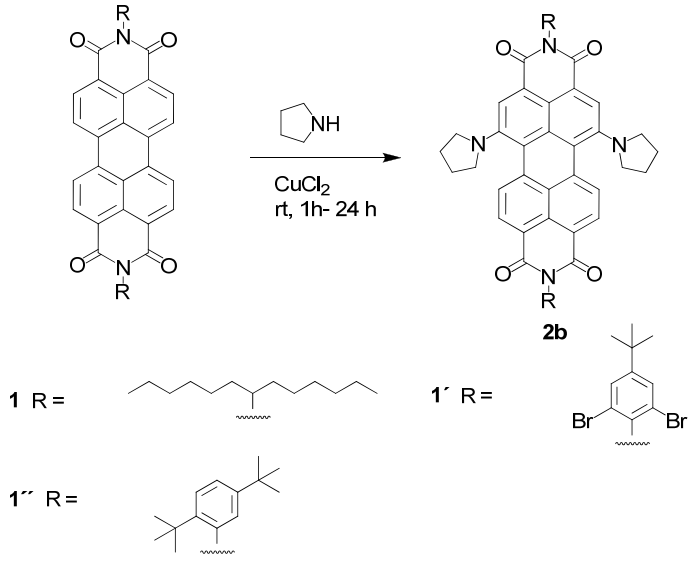
1

The compound was synthesized according to literature procedure,[1] starting from 1-hexylheptylamine and perylene-3,4,9,10-tetracarboxylicdianhydrid.

1´ [2]

Perylene-3,4,9,10-tetracarboxylicdianhydrid (0,78 g , 2,0 mmol), 2,6-dibromo-4-*tert*-butyl-aniline (1,84 g, 6 mmol), $Zn(OAc)_2$ (0,11 g, 0,6 mmol) and imidazole (2,72 g, 40 mmol) were heated at 180 °C for 72 h. After cooling to rt, the cold mixture was poured into dichloromethane (200 mL). The organic layer was washed with 1M HCl (50 mL) and water (50 mL) and concentrated under vacuum. Product purification was performed by column chromatography on silica gel (cyclohexane/CH_2Cl_2 1:9) to give **1´** (670 mg, 688 µmol, 35 %) as a red solid.

^{1}H NMR (400 MHz, CD_2Cl_2, rt): δ = 8.82 (d, *J* = 8.0 Hz, 4H), 8.75 (d, *J* = 8.1 Hz, 4H), 7.73 (s, 4H), 1.39 (s, 18H) ppm; MS (MALDI TOF, matrix: DCTB) $C_{44}H_{30}Br_4N_2O_4$ (965.9): *m/z*(%): 965.9 (100) $[M]^+$.



Scheme 1: Synthesis of 1,6-dipyrrolidine-PDIs.

2b

Pyrrolidine (0.6 mL) was added to **1** (28 mg, 37.2 µmol) and $CuCl_2$ (5 mg, 37.2 µmol) . After stirring overnight at rt, the mixture was poured into dichloromethane (20 mL) and H_2O (20 mL). The organic layer was separated, washed with aq H_2SO_4 (20 mL), water (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated under vacuum. Product purification was performed by column chromatography on silica gel (cyclohexane/CH_2Cl_2, 1:1) to give **2b** (16 mg, 18 µmol, 49 %) as a dark blue solid.

^{1}H NMR (400 MHz, CD_2Cl_2, rt): δ = 8.67-8.56 (m, 2H), 8.34-8.28 (m, 2H), 7.93 (d, *J* = 8.09 Hz, 2H), 5.27-5.11 (m, 2H), 3.72 (br, 4H), 2.79 (br, 4H), 2.34-2.18 (m, 4H), 2.01 (br, 8H), 1.89-1.77 (m, 4H), 1.39-1.16 (m, 32H), 0.87-0.80 (m, 12H) ppm; ^{1}H NMR (400 MHz, CD_2Cl_2, 333 K): δ = 8.65 (d, *J* = 7.66 Hz, 2H), 8.36 (s, 2H), 8.03 (d, *J* = 8.09 Hz, 2H), 5.26 (m, 1H), 5.19 (m, 1H), 3.73 (br, 8H), 2.36-2.22 (m, 4H), 2.03 (s, 8H), 1.95-1.82 (m, 4H), 1.44-1.20 (m, 32H), 0.89-0.81 (m, 12H).

^{13}C-NMR (100 MHz, $CDCl_3$): *δ* = 165.67*, 165.36*, 164.57*, 164.43*, 150.01, 135.58*, 135.49*, 131.05, 130.70, 129.87, 128.45*, 128.42*, 123.43 ,123.32, 122.70, 118.42*, 118.13*, 117.63*, 117.38*, 117.32*, 116.97*, 54.63, 54.27, 52.09, 32.50, 31.79, 31.76, 29.32, 29.23, 27.01, 26.89, 25.65, 22.62, 22.58, 14.05 ppm; [1] MS (MALDI TOF, matrix: DCTB) $C_{58}H_{76}N_4O_4$ (892.59): *m/z*(%): 892.6 (100) $[M]^+$.

2´b

Pyrrolidine (2 mL) was added to **1´** (30 mg, 31 µmol) and $CuCl_2$ (2 mg, 15 µmol). After 1 h stirring at rt, the mixture was poured into dichloromethane (20 mL) and H_2O (20 mL). The organic layer was separated, washed with aq H_2SO_4 (20 mL), water (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated under vacuum. Product purification was performed by column chromatography on silica gel (cyclohexane/CH_2Cl_2, 3:1) to give **2´b** (28 mg, 25 µmol, 82 %) as a dark blue solid.

^{1}H NMR (500 MHz, $C_2D_2Cl_4$): δ = 8.66 (d, *J* = 8.06 Hz, 2H), 8.30 (s, 2H), 7.72 (d, *J* = 8.03 Hz, 2H), 7.67 (s, 2H), 7.66 (s, 2H), 3.68 (br, 4H), 2.73 (br, 4H), 2.20 (br, 4H), 1.91 (br, 4H), 1.31 (s, 9H), 1.30 (s, 9H) ppm; ^{13}C-NMR (125 MHz, $C_2D_2Cl_2$): *δ* = 163.32, 162.95, 155.80, 155.51, 150.30, 136.68, 132.85, 132.11, 131.70, 131.21, 130.14, 129.57, 128.88, 124.13, 123.97, 123.49, 122.74, 118.09, 117.28, 116.96, 52.82, 35.41, 35.38,

[1] * : doubled signals

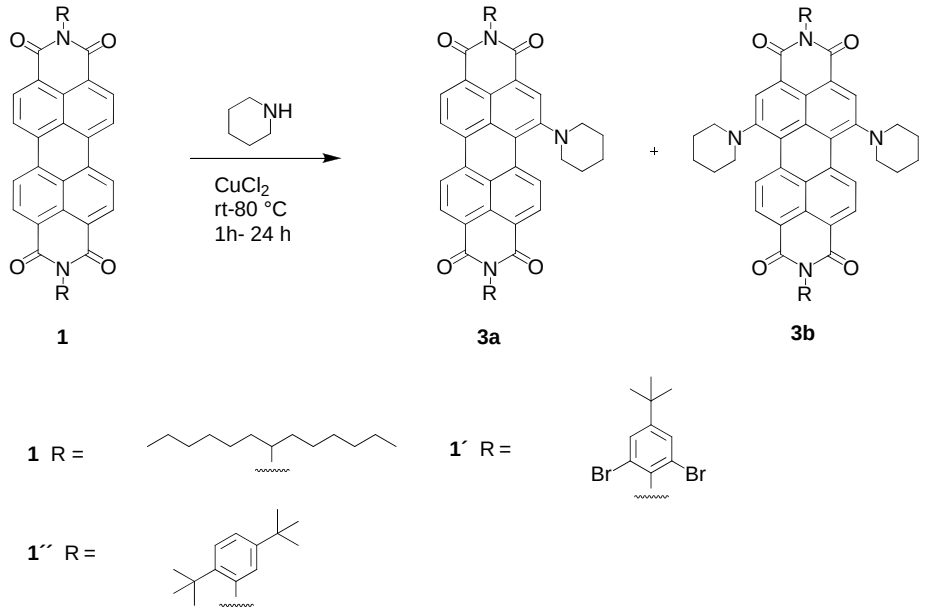
31.39, 31.37, 26.12.ppm; MS (MALDI TOF, matrix: DCTB) $C_{52}H_{44}Br_4N_4O_4$ (1108.01): *m/z*(%): 1107.8 (100) $[M]^+$.

2´´b

Pyrrolidine (1 mL) was added to **1´´** (10 mg, 13 µmol) and $CuCl_2$ (2 mg, 15 µmol). After 3 h stirring at rt, the mixture was poured into dichloromethane (20 mL) and H_2O (20 mL). The organic layer was separated, washed with aq H_2SO_4 (20 mL), water (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated under vacuum. Product purification was performed by column chromatography on silica gel (CH_2Cl_2) to give **2´´b** (8 mg, 9 µmol, 68 %) as a dark blue solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.74 (d, *J* = 8.05 Hz, 2H), 8.41 (d, *J* = 1.09 Hz, 2H), 7.92 (dd, *J* = 8.05, 2.00 Hz, 2H), 7.62-7.59 (m, 2H), 7.49-7.45 (m, 2H), 7.02 (t, *J* = 1.93 Hz, 1H), 7.00 (t, *J* = 1.92 Hz, 1H), 3.77 (br, 4H), 2.85 (br, 4H), 2.21-1.90 (m, 8H), 1.38-1.31 (m, 36H) ppm, ^{13}C-NMR (125 MHz, $CDCl_3$): *δ* = 165.36, 165.16, 150.06*, 150.05*, 150.02*, 149.99*, 149.94*, 149.92*, 143.87*, 143.84*, 136.03*, 136.02*, 133.59*, 133.56*, 132.95*, 132.93*, 131.45, 130.66, 128.87*, 128.86*, 128.73*, 128.72*, 128.66, 127.78, 127.67, 126.18, 126.01, 123.34, 123.24, 118.10, 117.93, 117.38, 117.37, 117.14, 52.20, 35.58, 35.58, 35.56, 34.23, 31.85, 31.83, 31.82, 31.26, 31.22, 25.72 ppm,[2] MS (MALDI TOF, matrix: DCTB) $C_{60}H_{64}N_4O_4$ (904.49): *m/z*(%): 904.6 (100) $[M]^+$.

[2] * : doubled signals



Scheme 2: Synthesis of 1-piperidin-PDIs and 1,6-dipiperidin-PDIs 3a, 3b, 3´b, 3´´ a and 3´´b.

3a/3b

Piperidine (2 mL) was added to **1** (100 mg, 132 µmol) and $CuCl_2$ (3 mg, 22 µmol). After stirring overnight at 60 °C, the mixture was poured into dichloromethane (20 mL) and H_2O (20 mL). The organic layer was separated, washed with aq H_2SO_4 (20 mL), water (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated under vacuum. Product purification was performed by column chromatography on silica gel (cyclohexane/CH_2Cl_2, 1:1) to give **3b** (35 mg, 38 µmol, 28 %) as a dark blue solid and **3a** (67 mg, 80 µmol, 60 %) as a green solid.

3b

^{1}H NMR (400 MHz, $CDCl_3$, 333 K): δ = 9.73 (d, *J* = 8.29 Hz, 2H), 8.59 (d, *J* = 8.13 Hz, 2H), 8.42 (s, 2H), 5.25-5.13 (m, 2H), 3.43-3.35 (m, 4H), 2.95-2.87 (m, 4H), 2.31-2.21 (m, 4H), 1.94-1.74 (m, 14H), 1.40-1.21 (m, 34H), 0.87-0.82 (m, 12H)

^{1}H NMR (400 MHz, $CDCl_3$, 273 K): δ = 9.74 (d, *J* = 8.17 Hz, 2H), 8.65-8.54 (m, 2H), 8.44-8.36 (m, 2H), 5.26-5.11 (m, 2H), 3.43-3.35 (m, 4H), 2.94-2.83 (m, 4H), 2.33-2.18 (m, 4H), 1.96-1.72 (m, 14H), 1.38-1.16 (m, 34H), 0.8-0.77 (m, 12H) ppm, ^{13}C-NMR (100 MHz, $CDCl_3$): δ =164.81 (br), 163.78 (br), 152.76, 135.85, 134.71, 133.91, 131.77, 131.37, 131.02, 130.61, 130.59, 130.57, 129.33, 128.98, 128.27, 127.01, 125.92, 125.25,

125.19, 125.18, 124.64, 124.05, 123.58, 123.35, 123.33, 123.31, 123.07, 122.62, 122.34, 122.31, 122.29, 121.84, 121.45, 121.07, 54.70, 54.68, 54.52, 52.96, 32.40, 31.75, 29.25, 29.21, 26.95, 26.93, 25.84, 23.73, 22.58, 14.03 ppm;[3] MS (MALDI TOF, matrix: DCTB) $C_{60}H_{80}N_4O_4$ (920.62): *m/z*(%): 920.7$[M]^+$.

3a

^{1}H NMR (400 MHz, $CDCl_3$, 333 K): δ = 9.84 (d, *J* = 8.33 Hz, 1H), 8.66-8.58 (m, 3H), 8.54-8.49 (m, 3H), 5.24-5.14 (m, 2H), 3.51-3.45 (m, 2H), 3.02-32.95 (m, 2H), 2.31-2.21 (m, 4H), 1.98-1.81 (m, 8H), 1.42-1.20 (m, 34H), 0.89-0.81 (m, 12H) ppm

^{1}H NMR (400 MHz, $CDCl_3$, 273 K): δ = 9.79 (d, *J* = 8.32 Hz, 1H), 8.66-8.51 (m, 3H), 8.51-8.34 (m, 3H), 5.24-5.12 (m, 2H), 3.49-3.41 (m, 2H), 2.98-2.89 (m, 2H), 2.31-2.18 (m, 4H), 1.97-1.77 (m, 8H), 1.40-1.15 (m, 34H), 0.87-0.76 (m, 12H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): *δ* =165.05 (br), 163.93 (br), 153.31, 135.83, 135.80, 131.69, 131.17, 130.38, 128.97, 127.99, 123.85, 123.19, 123.16, 122.89, 122.21, 121.04, 54.68, 54.38, 53.12, 32.46, 31.76, 29.27, 29.21, 26.98, 26.89, 25.86, 23.81, 22.60, 22.57, 14.03 ppm;[4] MS (MALDI TOF, matrix: DCTB) $C_{55}H_{71}N_3O_4$ (837.54): *m/z*(%): 837.6 (100) $[M]^+$.

3´b

Piperidine (2 mL) was added to **1´** (20 mg, 21 µmol) and $CuCl_2$ (2 mg, 15 µmol). After stirring over night at rt, the mixture was poured into dichloromethane (20 mL) and H_2O (20 mL). The organic layer was separated, washed with aq H_2SO_4 (20 mL), water (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated under vacuum. Product purification was performed by column chromatography on silica gel (cyclohexane/CH_2Cl_2, 3:1) to give **3´b** (21 mg, 18 µmol, 89 %) as a dark blue solid.

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 9.77 (d, *J* = 8.30 Hz, 2H), 8.68 (d, *J* = 8.31 Hz, 2H), 7.78 (d, *J* = 2.36 Hz, 4H), 3.49-3.41 (m, 4H), 3.01-2.92 (m, 4H), 1.93-1.73 (m, 12H), 1.44-1.38 (m, 12H) ppm, ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 162.37, 162.21, 155.25, 154.97, 153.48, 136.75, 132.15, 132.11, 131.67, 131.44, 129.87, 129.84, 129.68, 128.39, 123.76, 123.70, 123.57, 123.41, 123.04, 122.98, 121.24, 119.82, 53.12, 35.17, 35.12,

[3] Not all signals are visible, doubled signals
[4] Not all signals are visible, doubled signals

31.08, 31.07, 25.81, 23.75 ppm, MS (MALDI TOF, matrix: DCTB) $C_{54}H_{48}Br_4N_4O_4$ (1136.04): *m/z*(%): 1135.8 (100) $[M]^+$.

3´´a/3´´b

Pyrrolidine (1 mL) was added to **1´´** (40 mg, 52 µmol) and $CuCl_2$ (3 mg, 22 µmol). After 14 h stirring at 80 °C, the mixture was poured into dichloromethane (20 mL) and H_2O (20 mL). The organic layer was separated, washed with aq H_2SO_4 (20 mL), water (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated under vacuum. Product purification was performed by column chromatography on silica gel (cyclohexane/CH_2Cl_2, 2:3 to 1:3) to give **3´´b** (3 mg, 4 µmol, 7 %) as a dark blue solid and **3´´a** (25 mg, 29 µmol, 56 %) as a dark green solid.

3´´b

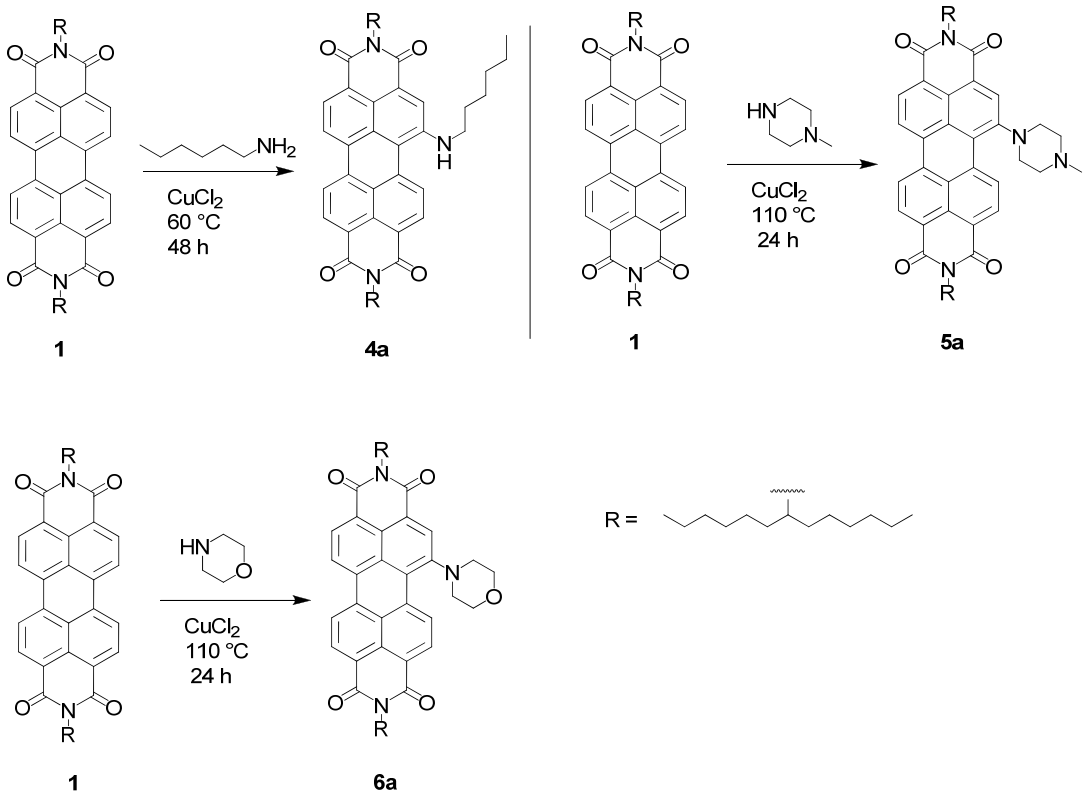
^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.79 (d, *J* = 8.28 Hz, 2H), 8.67 (d, *J* = 8.26 Hz, 2H), 8.46 (s, 2H), 7.62-7.59 (m, 2H), 7.49-7.45 (m, 2H), 7.02-7.01 (m, 1H), 6.99-6.98 (m, 1H); 3.49-3.37 (m, 4H), 2.99-2.87 (m, 4H), 1.94-1.74 (m, 12H), 1.35-1.31 (m, 36H) ppm, ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 164.78, 164.67*, 164.66*, 153.43, 150.07*, 150.05*, 149.98*, 149.95*, 143.89*, 143.88*, 143.81, 136.39*, 136.37*, 133.21*, 133.18*, 132.73*, 132.71*, 132.08, 131.14, 129.35*, 129.34*, 128.77*, 128.75*, 128.71*, 128.69*, 128.30, 127.74, 127.57, 126.24*, 126.13*, 123.87*, 123.86*, 123.58*, 123.57*, 123.46*, 123.43*, 122.86*, 122.85*, 121.16, 120.59*, 120.59*, 53.22, 53.19, 53.08, 53.05, 35.57, 35.56, 35.55, 34.24, 34.23, 31.83, 31.82, 31.80, 31.25, 31.22, 29.69, 26.90, 25.86, 25.84, 23.77, ppm,[5] MS (MALDI TOF, matrix: DCTB) $C_{62}H_{68}N_4O_4$ (932.52): *m/z*(%): 932.5 (100) $[M]^+$.

3´´a

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 9.94 (dd, *J* = 6.45 Hz, *J* =8.29 Hz, 1H), 8.77-8.71 (m, 2H), 8.68 (d, *J* = 1.98 Hz, 1H), 8.66-8.59 (m, 3H), 7.64-7.58 (m, 2H), 7.51-7.45 (m, 2H), 3.64-3.47 (m, 2H), 3.11-2.93 (m, 2H), 2.00-1.78 (m, 6H), 1.39-1.29 (m, 36H) ppm, ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 164.77, 164.69, 164.49, 164.42, 152.94*, 152.92*, 150.10*, 150.07*, 150.06*, 150.04*, 143.79*, 143.77*, 136.50,* 136.47*, 135.38*,

[5] * : doubled signals

135.34*, 134.49*, 134.47*, 132.86*, 132.85*, 132.63*, 132.62*, 131.85, 131.43, 129.73, 129.69, 129.44*, 129.42*, 129.00, 128.75, 127.71*, 127.70*, 127.63*, 127.62*, 127.45*, 127.43*, 126.28, 126.23, 125.95, 125.52, 125.48, 124.68, 123.97, 123.90*, 123.88*, 123.19*, 123.16*, 122.96*, 122.93*, 122.83*, 122.81*, 121.72, 121.58*, 121.56*, 53.22, 53.07, 52.92, 52.75, 35.53, 34.23, 31.76, 31.21, 29.67, 26.89, 25.86, 25.80, 23.68 ppm,[6] MS (MALDI TOF, matrix: DCTB) $C_{57}H_{59}N_3O_4$ (849,45): *m/z*(%): 849.5(100) $[M]^+$.



Scheme 3: Synthesis of 1-amino-PDIs 4a-6a.

4a

Hexylamine (4 mL) was added to **1** (200 mg, 265 µmol) and $CuCl_2$ (36 mg, 268 µmol). After stirring 24 h at 90 °C, the mixture was poured into dichloromethane (20 mL) and H_2O (20 mL). The organic layer was separated, washed with aq H_2SO_4 (20 mL), water (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated under vacuum. Product purification was performed by column chromatography on silica gel

[6] * : doubled signals

(cyclohexane/CH_2Cl_2, 3:2) and by recGPC to give **5a** (14 mg, 15 µmol, 4 %) as a turquoise solid.

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.88 (d, *J* = 8.24 Hz, 1H), 8.70-8.55 (m, 2H), 8.55-8.38 (m, 3H), 5.24-5.12 (m. 2H), 3.52 (t, *J* = 7.13 Hz, 1H), 2.31-2.18 (m, 4H), 1.91-1.79 (m, 6 H), 1.58-1.49 (m, 2H), 1.44-1.15 (m, 37H), 0.97-0.91 (m, 3H), 0.86-0.77 (m, 12H). MS (MALDI TOF, matrix: DCTB) $C_{55}H_{72}N_4O_4$ (853.58): *m/z*(%):853.6 (100) $[M]^+$.

5a

1-Methylpiperazine (2 mL) was added to **1** (28 mg, 37 µmol) and $CuCl_2$ (5 mg, 37 µmol). After stirring 24 h at 110 °C, the mixture was poured into dichloromethane (20 mL) and H_2O (20 mL). The organic layer was separated, washed with aq H_2SO_4 (20 mL), water (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated under vacuum. Product purification was performed by column chromatography on silica gel (EtOAc/CH_2Cl_2, 2:1) to give **6a** (8 mg, 9.4 µmol, 25 %) as a dark grey blue solid.

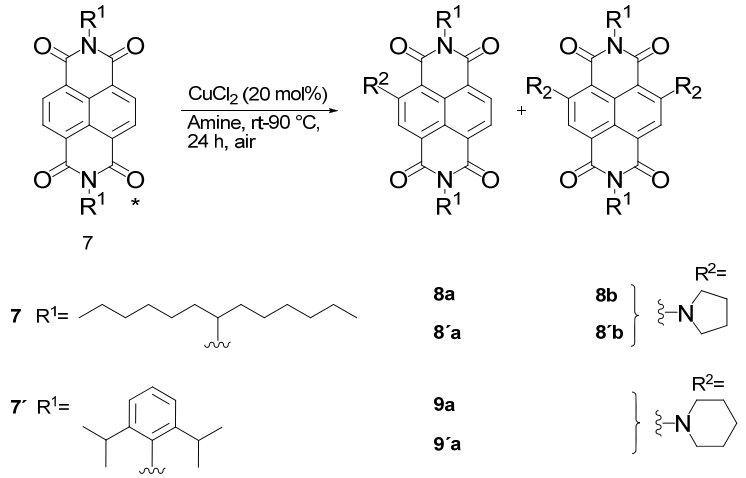
^{1}H NMR (400 MHz, CD_2Cl_2, rt): δ = 9.94 (d, *J* = 8.28 Hz, 1H), 8.67-8.45 (m, 6H), 5.23 - 5.11 (m, 2H), 3.49-3.42 (m, 2H), 3.17-3.08 (m, 2H), 2.89-2.81 (m, 2H), 2.60-2.51 (m, 2H), 2.40 (s, 3H), 2.30-2.17 (m, 4H), 1.89-1.79 (m, 4H), 1.38-1.16 (m, 32H), 0.86-0.80 (m, 12H) ppm. MS (MALDI TOF, matrix: DCTB) $C_{55}H_{72}N_4O_4$ (852.56): *m/z*(%):(100) $[M]^+$.

6a

Morpholine (2 mL) was added to **1** (30 mg, 40 µmol) and $CuCl_2$ (5 mg, 37 µmol). After stirring 24 h at 110 °C, the mixture was poured into dichloromethane (20 mL) and H_2O (20 mL). The organic layer was separated, washed with aq H_2SO_4 (20 mL), water (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated under vacuum. Product purification was performed by column chromatography on silica gel (CH_2Cl_2/cyclohexane, 3:1) and recGPC to give **7a** (6 mg, 7.1 µmol, 18 %) as a dark grey blue solid.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ = 10.12-10.02 (m, 1H), 8.74-8.51 (m, 6H), 5.25-5.12 (m, 2H), 4.09-3.93 (m, 4H), 3.46-3.36 (m, 2H), 3.23-3.12 (m, 2H), 2.33-2.16 (m, 4H),

1.95-1.77 (m, 4H), 1.44-1.11 (m, 32H), 0.92-0.75 (m, 12H).ppm; MS (MALDI TOF, matrix: DCTB) $C_{54}H_{69}N_3O_5$ (839.52): *m/z*(%): 839.5 (100) $[M]^+$.



Scheme 4: synthesis of 2-amino-NDIs and 2,7-amino-NDIs.

7

The compound was synthesized according to literature procedure [H. Langhals, S. Kinzel, *J. Org. Chem.*, **2010**, *75*, 7781-7784.] starting from 1,4,5,8-naphthalenetetracarboxylic dianhydride and 1-hexylheptylamine.

7´

2,6-Diisopropylaniline (1.72 g, 1.12 mL, 9.69 mmol) was added to a mixture of 1,4,5,8-Naphthalenetetracarboxylic dianhydride (1.00 g, 3.73 mmol) in DMF (30 mL). After stirring 4 h at 130 °C, the solution was poured into dichloromethane (20 mL) and H_2O (20 mL). The organic layer was separated, washed with water (50 mL), 1M HCl (50 mL), water (50 mL) and brine (50 mL), dried over $MgSO_4$ and concentrated under vacuum. Product purification was performed by column chromatography on silica gel (CH_2Cl_2/cyclohexane, 2:1) to give **7´** (188 mg, 320 µmol, 9 %) as a white solid.
^{1}H NMR (400 MHz, $CDCl_3$, rt): δ = 8.89 (s, 4H), 7.53 (t, *J* = 7.77 Hz, 2H), 7.37 (d, *J* = 7.78 Hz, 4H), 2.71 (sept., *J* = 6.81 Hz, 4H), 1.17 (d, *J* = 6.86 Hz, 24H) ppm, ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 162.90, 145.51, 131.56, 129.99, 129.96, 127.65, 126.89, 124.21, 29.30, 23.94, ppm

8a/ 8b

Pyrrolidine (2 mL) was added to **7** (100 mg, 159 µmol) and $CuCl_2$ (10 mg, 74 µmol). After stirring 24 h at rt, the mixture was poured into dichloromethane (20 mL) and H_2O (20 mL). The organic layer was separated, washed with aq H_2SO_4 (20 mL), water (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated under vacuum. Product purification was performed by column chromatography on silica gel (CH_2Cl_2/cyclohexane, 1:1) to give **8b** (15 mg, 20 µmol, 12 %) and **8a** (25 mg, 36 µmol, 22 %) as red solids.

8b:

^{1}H NMR (400 MHz, $CDCl_3$, 333 K): δ = 8.00 (s, 2H), 5.17-5.08 (m, 2H), 3.56-3.51 (m, 8H), 2.39-2.30 (m, 2H), 2.25- 2.15 (m, 2H), 2.08-2.03 (m, 8H), 1.86-1.73 (m, 4H), 1.38-1.17 (m, 32H), 0.87-0.80 (m, 12H) ppm, ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ = 7.99 (d, *J* = 11.91 Hz, 2H), 5.18-5.06 (m, 2H), 3.55-3.48 (m, 8H), 2.41-2.29 (m, 2H), 2.25-2.14 (m, 2H), 2.08-2.01 (m, 8H), 1.84-1.68 (m, 4H), 1.39-1.12 (m, 32H), 0.85-0.79 (m, 12H) ppm, ^{13}C NMR (100 MHz, $CDCl_3$): 165.50*, 164.38*, 164.08*, 163.13*, 150.45*, 150.12*, 132.95, 132.24, 125.42, 124.68, 116.06, 115.30, 112.01, 106.23, 105.45, 54.99, 54.73, 52.53, 33.18, 32.42, 31.86, 31.73, 29.27, 29.18, 27.12, 26.93, 26.82, 25.92, 22.57, 14.05, 14.03 ppm;[7] MS (MALDI TOF, matrix: DCTB) $C_{48}H_{72}N_4O_4$ (768.56): *m/z*(%): 768.5 (100) $[M]^+$.

8a:

^{1}H NMR (400 MHz, $CDCl_3$, 333 K): δ =8.62 (d, *J* = 7.77 Hz, 1H), 8.40 (s, 1H), 8.35 (d, *J* = 7.78 Hz, 1H), 5.22-5.09 (m, 2H), 3.61-3.52 (m, 4H), 2.33-2.17 (m, 4H), 2.14-2.07 (m, 4H), 1.89-1.78 (m, 4H), 1.39-1.16 (m, 32H), 0.88-0.80 (m, 12H) ppm, ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ = 8.62 (s, 1H), 8.44-8.29 (m, 2H), 5.23-5.07 (m, 2H), 3.55 (br, 4H), 2.39-2.14 (m, 4H), 2.13-2.05 (m, 4H), 1.88-1.71 (m, 4H), 1.38-1.11 (m, 32H), 0.86-0.76 (m, 12H) ppm, ^{13}C NMR (100 MHz, $CDCl_3$): 164.81*, 164.62*, 163.78*, 163.66*, 163.42*, 163.15*, 162.36*, 150.01, 149.65, 130.86, 130.05, 126.18, 125.99, 125.52,

[7] *: doubled signals

125.29, 124.93, 124.19, 123.78, 123.03, 120.06, 55.00*, 54.81*, 54.63*, 54.61*, 52.87, 32.85, 32.33*, 32.21*, 31.77, 31.70, 29.14, 26.88, 26.82, 25.81, 22.55, 22.53, 14.03, 14.01 ppm;[8]

MS (MALDI TOF, matrix: DCTB) $C_{44}H_{65}N_3O_4$ (699.50): *m/z*(%):699.5 (100) $[M]^+$.

8´a/ 8´b

Pyrrolidine (4 mL) was added to **7´** (50 mg, 85 µmol) and $CuCl_2$ (10 mg, 74 µmol). After stirring 24 h at rt, the mixture was poured into dichloromethane (20 mL) and H_2O (20 mL). The organic layer was separated, washed with aq H_2SO_4 (20 mL), water (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated under vacuum. Product purification was performed by column chromatography on silica gel (CH_2Cl_2/cyclohexane, 6:1) to give **8´b** (22 mg, 30 µmol, 36 %) and **8´a** (11 mg, 17 µmol, 20 %) as red solids.

8´b

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ = 8.10 (s, 2H), 7.49 (t, *J* = 7.76 Hz, 1H), 7.48 (t, *J* = 7.73 Hz, 1H), 7.34 (d, *J* = 7.81 Hz, 2H), 7.33 (d, *J* = 7.64 Hz, 2H), 3.55 (broad, 8H), 2.87 (sept, *J* = 6.80 Hz, 2H), 2.74 (sept, *J* = 6.83 Hz, 2H), 2.01 (broad, 8H), 1.18 (d, *J* = 6.81 Hz, 12H), 1.17 (d, *J* = 6.84 Hz, 12H) ppm, ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 164.13, 162.26, 151.01, 146.25, 145.59, 133.99, 131.85, 130.67, 129.55, 129.28, 125.31, 124.02, 123.97, 116.19, 112.42, 105.39, 52.88, 29.15, 29.12, 26.89, 25.75, 24.20, 23.96 ppm. MS (MALDI TOF, matrix: DCTB) $C_{46}H_{52}N_4O_4$ (724.40): *m/z*(%): 724.4 (100) $[M]^+$.

8´a:

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ = 8.76 (d, *J* = 7.76 Hz, 1H), 8.52 (s, 1H), 8.48 (d, *J* = 7.77 Hz, 1H), 7.51 (t, *J* = 7.76 Hz, 1H), 7.50 (t, *J* = 7.74 Hz, 1H), 7.35 (d, *J* = 7.77 Hz, 2H), 7.35 (d, *J* = 7.72 Hz, 2H), 3.59 (braod, 4H), 2.81-2.67 (m, 4H), 2.07 (broad, 4H), 1.20-1.15 (m, 24H) ppm, ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 163.68, 163.65, 163.30, 161.56, 150.31, 145.71, 145.56, 131.27, 131.18, 131.04, 130.32, 129.76, 129.53, 126.03, 125.98, 125.02, 124.88, 124.22, 124.11, 124.05, 120.86, 103.41, 53.17, 29.69, 29.23,

[8] *: doubled signals

29.18, 26.91, 25.73, 24.20, 23.98, 23.96, 23.73 ppm. MS (MALDI TOF, matrix: DCTB) $C_{42}H_{45}N_3O_4$ (655.34): *m/z*(%): 655.4 (100) $[M]^+$.

9a

Piperidine (4 mL) was added to **7** (202 mg, 0.32 mmol) and $CuCl_2$ (32 mg, 0.24 mmol). After stirring 24 h at 90 °C, the mixture was poured into dichloromethane (20 mL) and H_2O (20 mL). The organic layer was separated, washed with aq H_2SO_4 (20 mL), water (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated under vacuum. Product purification was performed by column chromatography on silica gel (CH_2Cl_2/cyclohexane, 1:1) to give **9a** (13 mg, 18 µmol, 6 %) as a red solid.
^{1}H NMR (400 MHz, $CDCl_3$, rt): δ = 8.79-8.29 (m, 3H), 5.25-5.07 (m, 2H), 3.57-3.45 (m, 4H), 2.34-2.11 (m, 4H), 1.89-1.73 (m, 10H), 1.39-1.09 (m, 32H), 0.95-0.75 (12H) ppm. MS (MALDI TOF, matrix: DCTB) $C_{45}H_{67}N_3O_4$ (713.51): *m/z*(%): 713.5 (100) $[M]^+$.

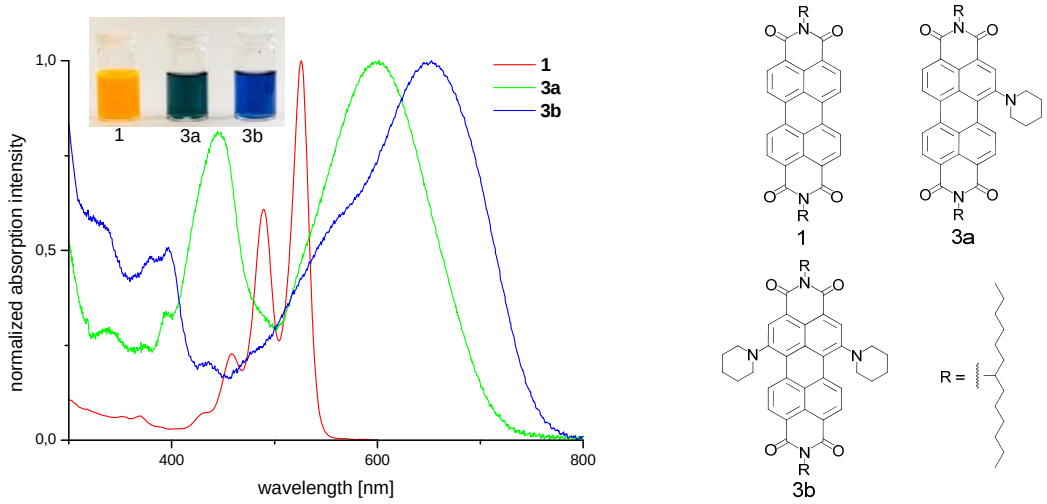
9´a

Piperidine (4 mL) was added to **7´** (50 mg, 85 µmol) and $CuCl_2$ (10 mg, 74 µmol). After stirring 24 h at 60 °C, the mixture was poured into dichloromethane (20 mL) and H_2O (20 mL). The organic layer was separated, washed with aq H_2SO_4 (20 mL), water (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated under vacuum. Product purification was performed by column chromatography on silica gel (CH_2Cl_2/cyclohexane, 6:1) to give **9´a** (11 mg, 16 µmol, 19 %) as a red solid.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ = 8.73 (d, *J* = 7.8 Hz, 1H), 8.57 (s, 1H), 8.50 (d, *J* = 7.7 Hz, 1H), 7.53-7.46 (m, 2H), 7.36 (d, *J* = 5.8 Hz, 2H), 7.34 (d, *J* = 5.8 Hz, 2H), 3.57-3.52 (m, 4H), 2.78-2.65 (m, 4H), 1.85-1.70 (m, 6H), 1.20-1.14 (m, 24H) ppm, ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 163.54, 163.37, 163.27, 161.75, 154.27, 145.54, 145.51, 131.70, 131.21, 131.11, 130.28, 129.77, 129.49, 127.33, 126.33, 126.01, 125.88, 125.29, 124.10, 124.05, 121.70, 106.37, 53.51, 29.69, 29.24, 26.91, 26.29, 24.15, 23.99, 23.95, 23.76, 23.63 ppm. MS (MALDI TOF, matrix: DCTB) $C_{43}H_{47}N_3O_4$ (669.36): *m/z*(%): 669.4 (100) $[M]^+$.

2 UV/Vis

Figure 1: Normalized absorption spectra of **1** (red line), **3a** (green line) and **3b** (blue line).



In Figure 1the absorption spectra of the unsubstituted (**1**), the mono (**3a**) and the diamino (**3b**) substituted PDIs are compared. While **1** has its longest wavelength absorption maximum at 526 nm, the maximum is shifted for the monosubstituted PDI **3a** to 602 nm and disubstituted PDI **3b** to 653 nm, respectively. The data are well in accordance with those of similar reference products.[3-6]

Figure 2: Normalized absorption spectra of **4a, 5a** and **6a.**

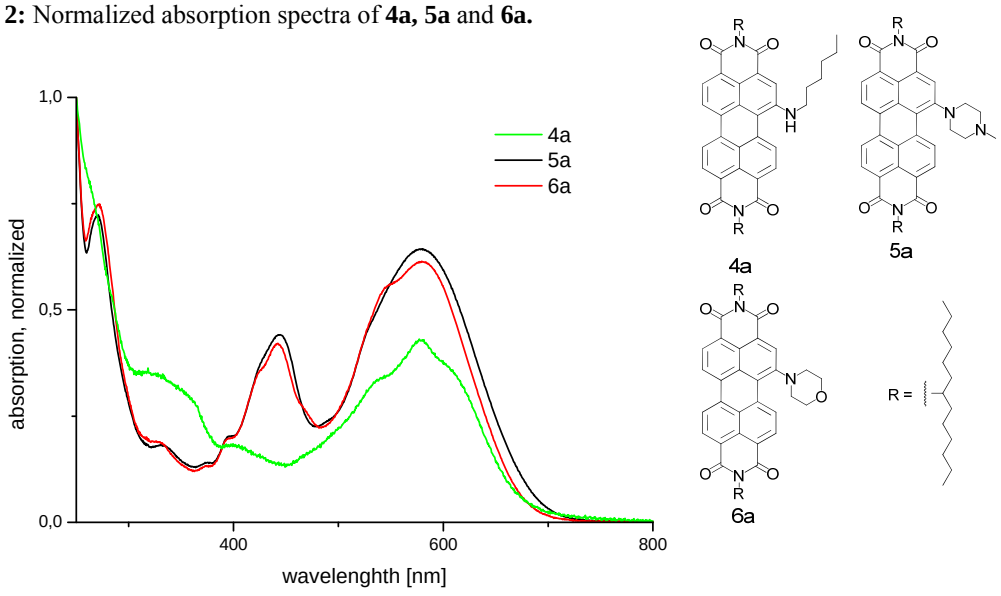


Figure 3: Normalized absorption spectra of 2b and 3b.

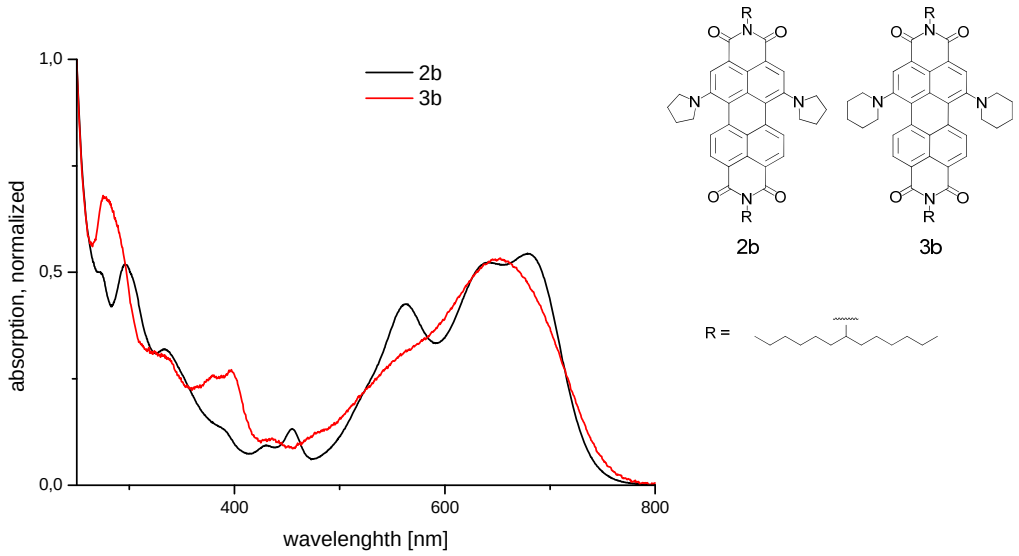
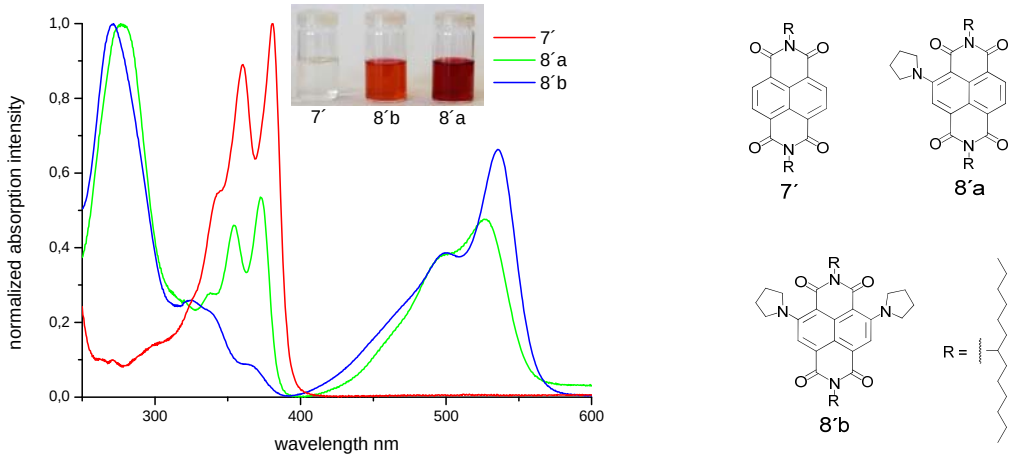


Figure 4: Normalized absorption spectra of **7´** (red line), **8´a** (green line) and **8´b** (blue line).



In Figure 4 the absorption spectra of the unsubstituted (**7´**), the mono (**8´a**) and the diamino (**8´b**) substituted NDIs are compared. While **7´** has its longest wavelength absorption maximum at 381 nm, the maximum of monosubstitued NDI **8´a** is shifted to 527 nm and similar to disubstituted NDI **8´b** (536 nm).

3 NMR Data

2b

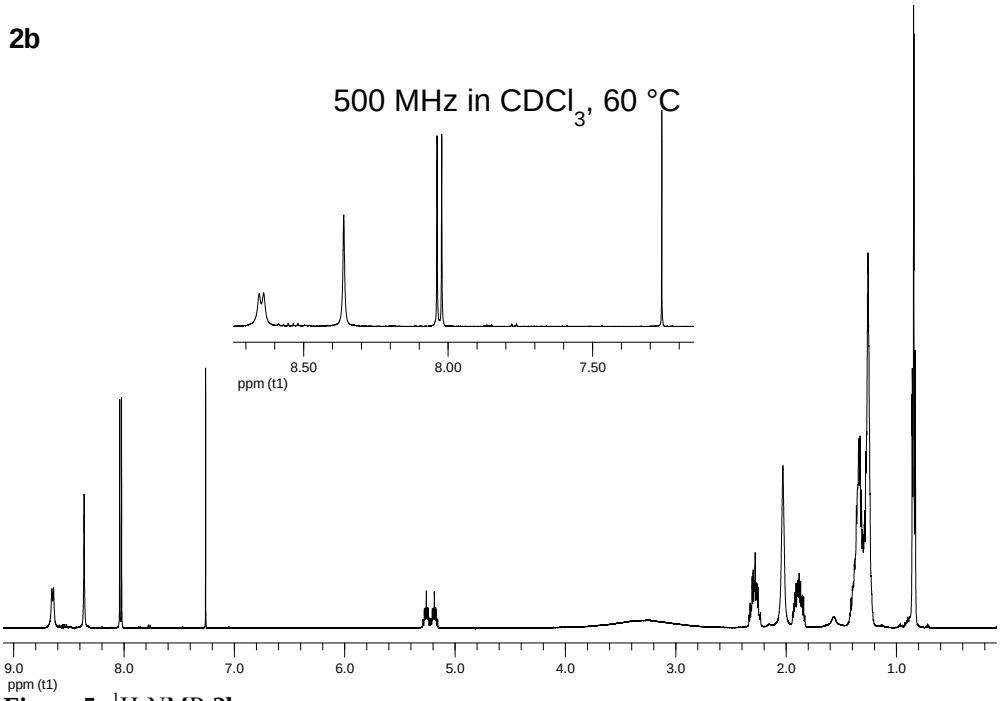


Figure 5: ^{1}H-NMR **2b.**

2´b

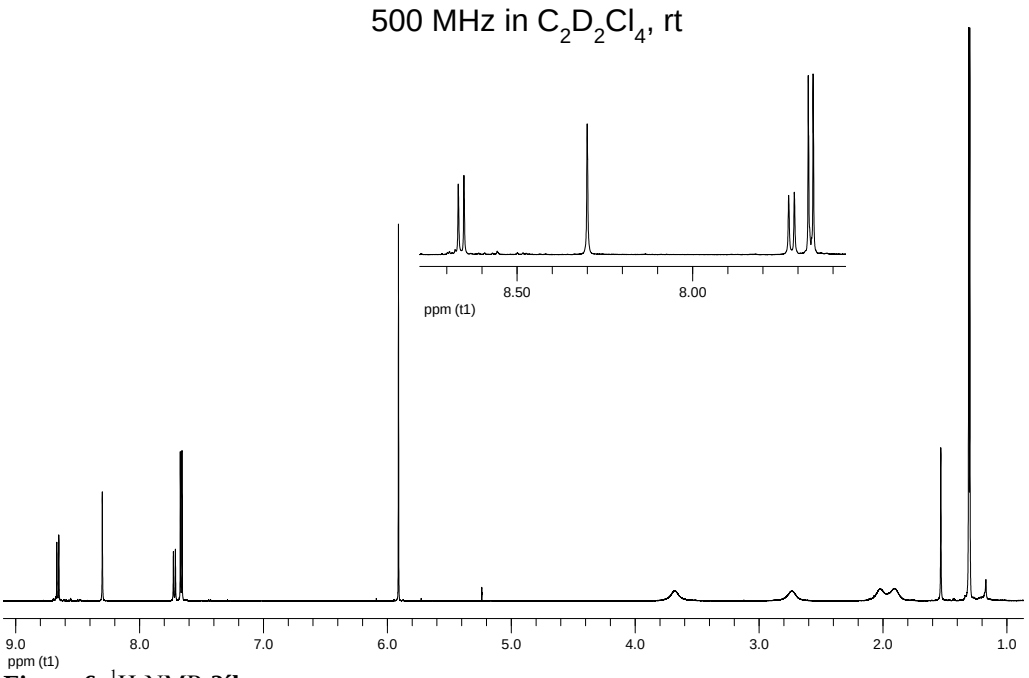


Figure 6: ^{1}H-NMR **2´b.**

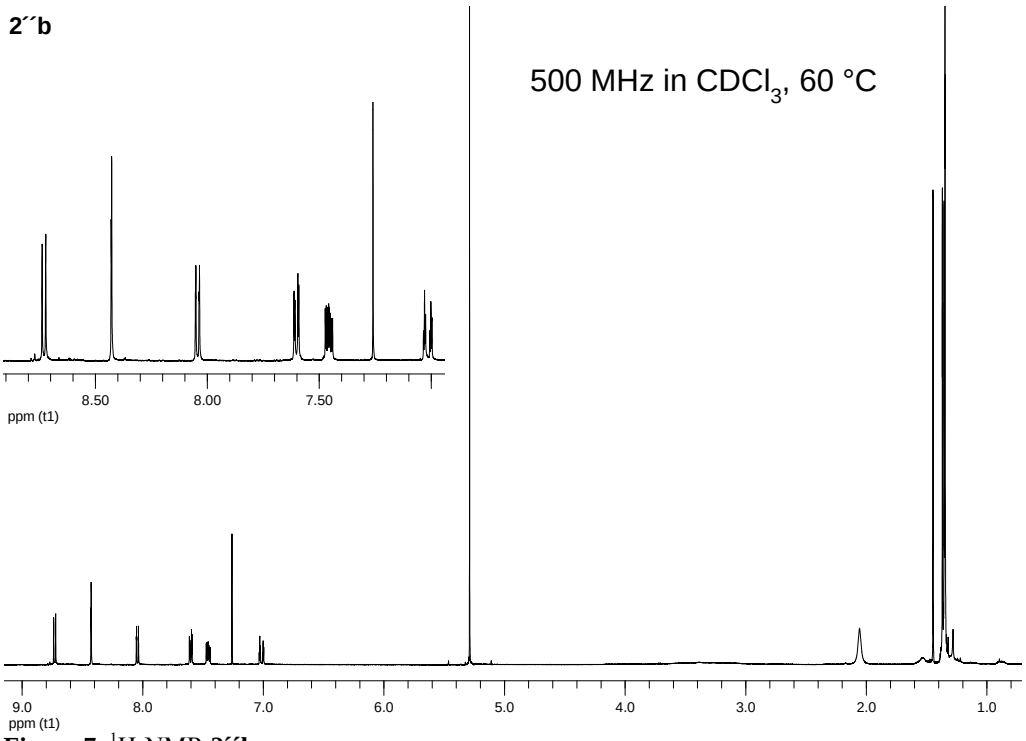


Figure 7: ^{1}H-NMR **2´´b.**

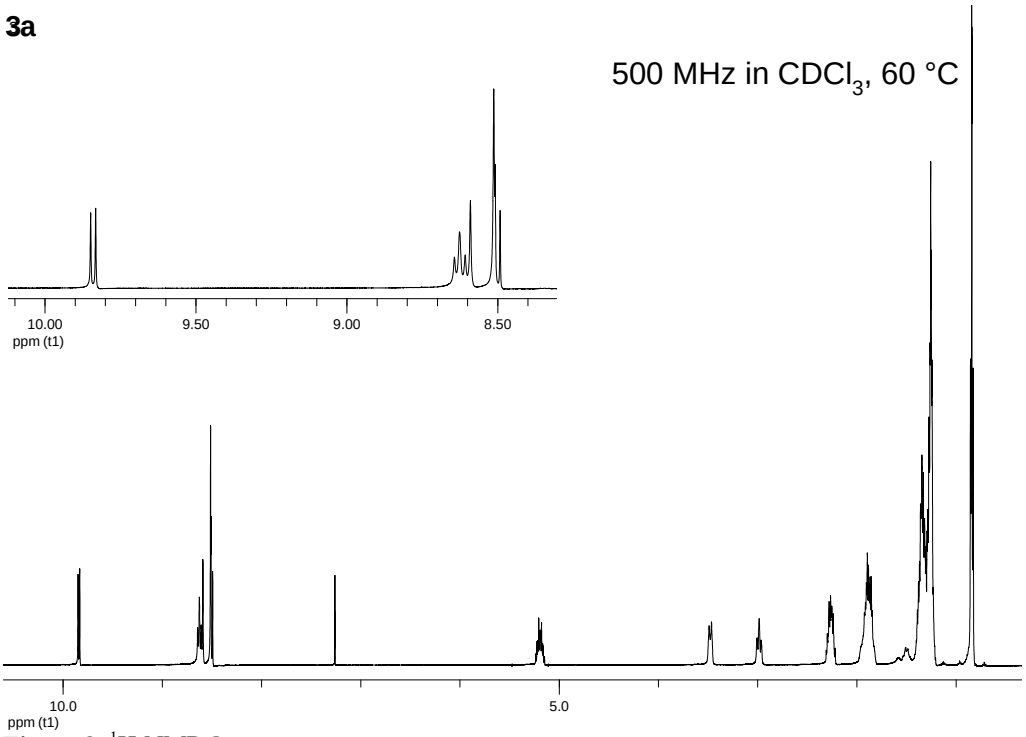


Figure 8: ^{1}H-NMR **3a.**

3b

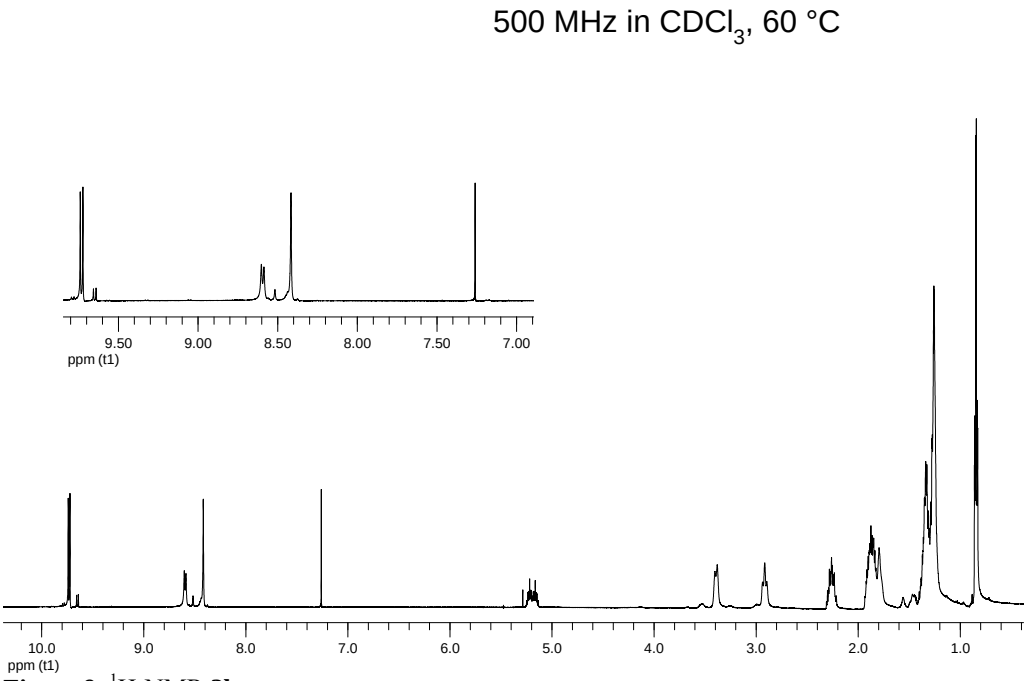


Figure 9: ^{1}H-NMR **3b.**

3´b

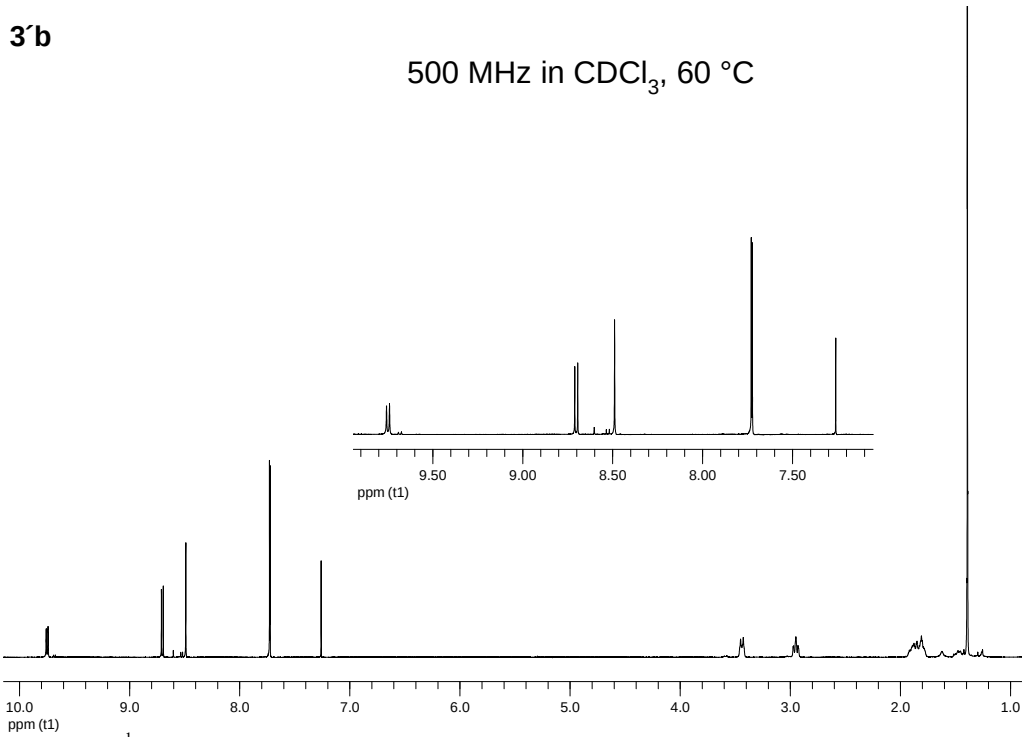


Figure 10: ^{1}H-NMR **3´b.**

3´´a

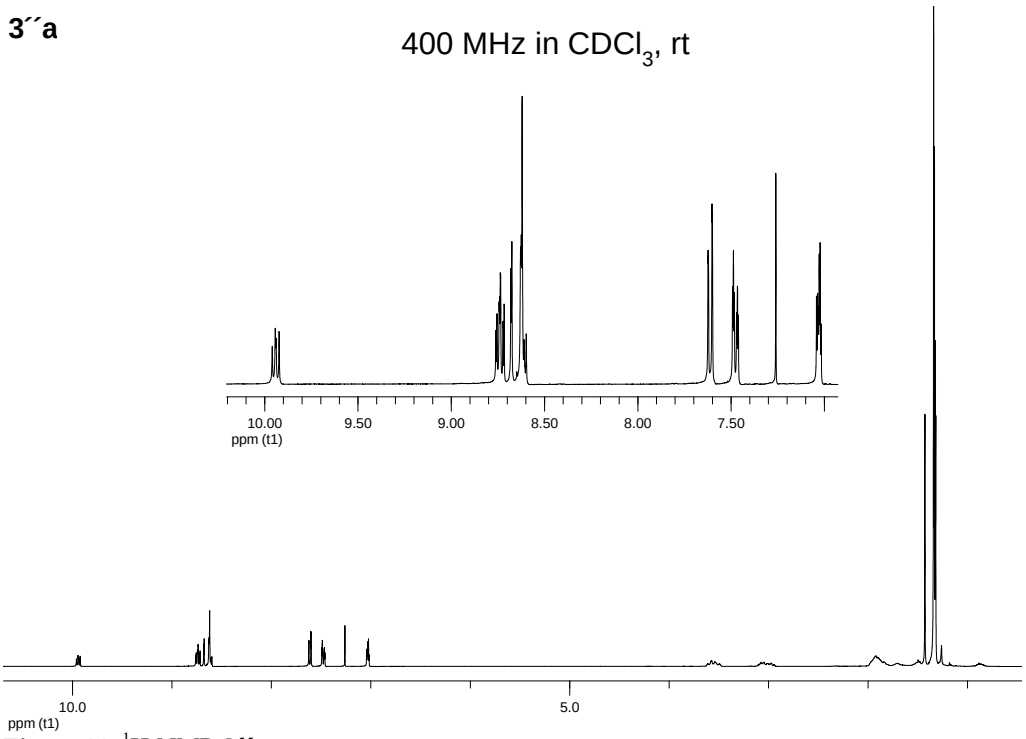


Figure 11: ^{1}H-NMR **3´´a.**

3´´b

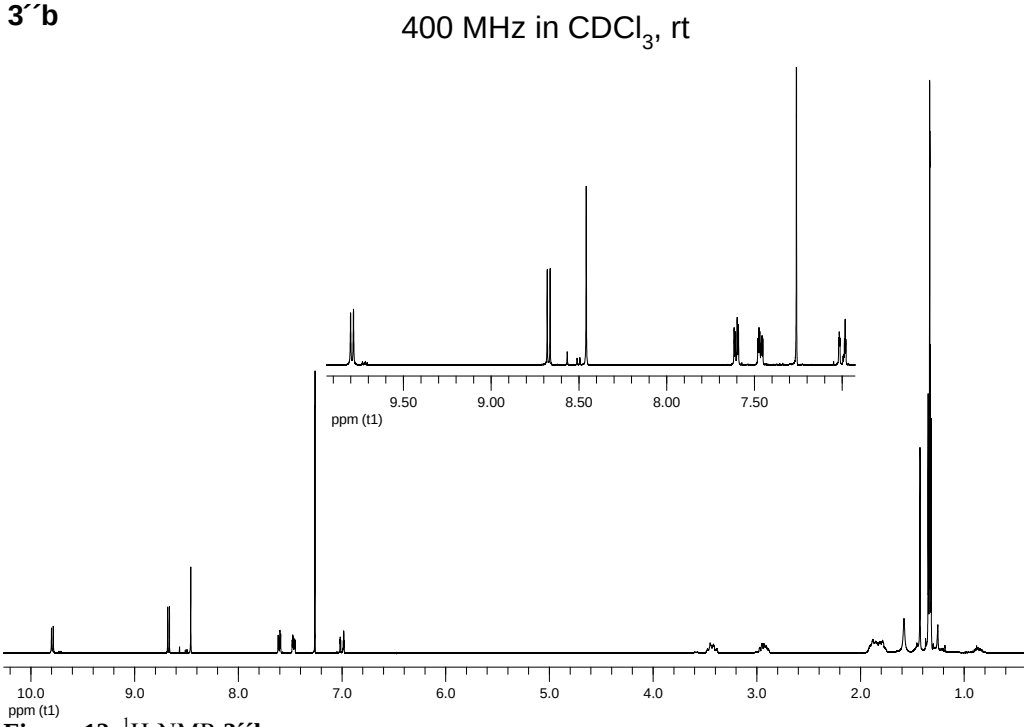


Figure 12: ^{1}H-NMR **3´´b.**

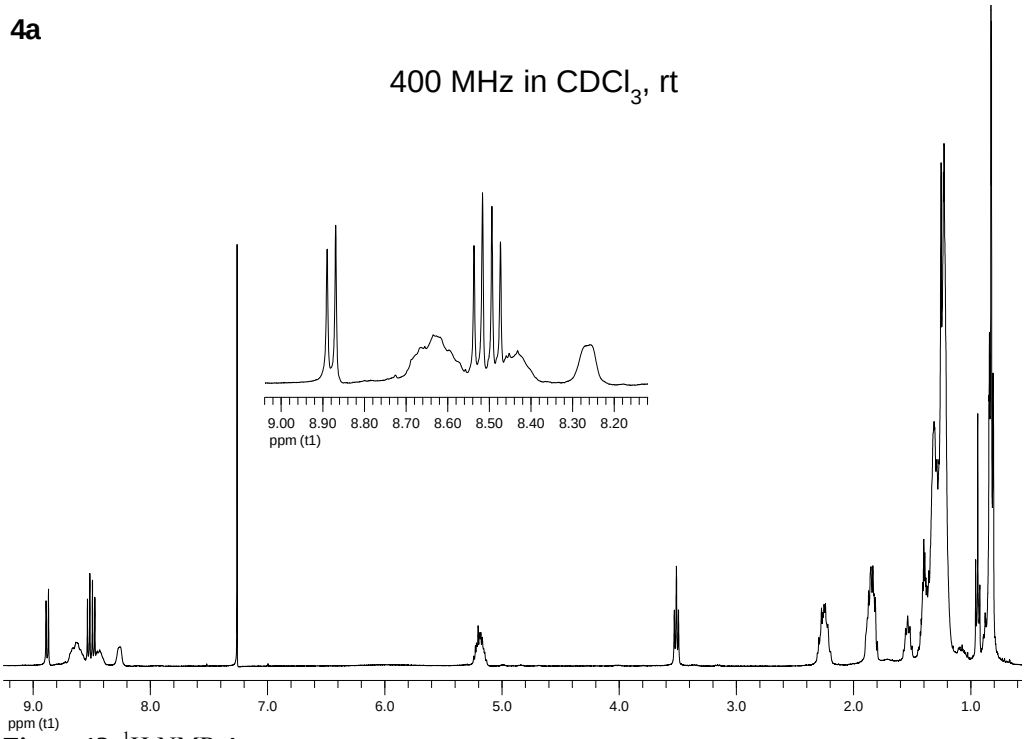


Figure 13: ^{1}H-NMR **4a.**

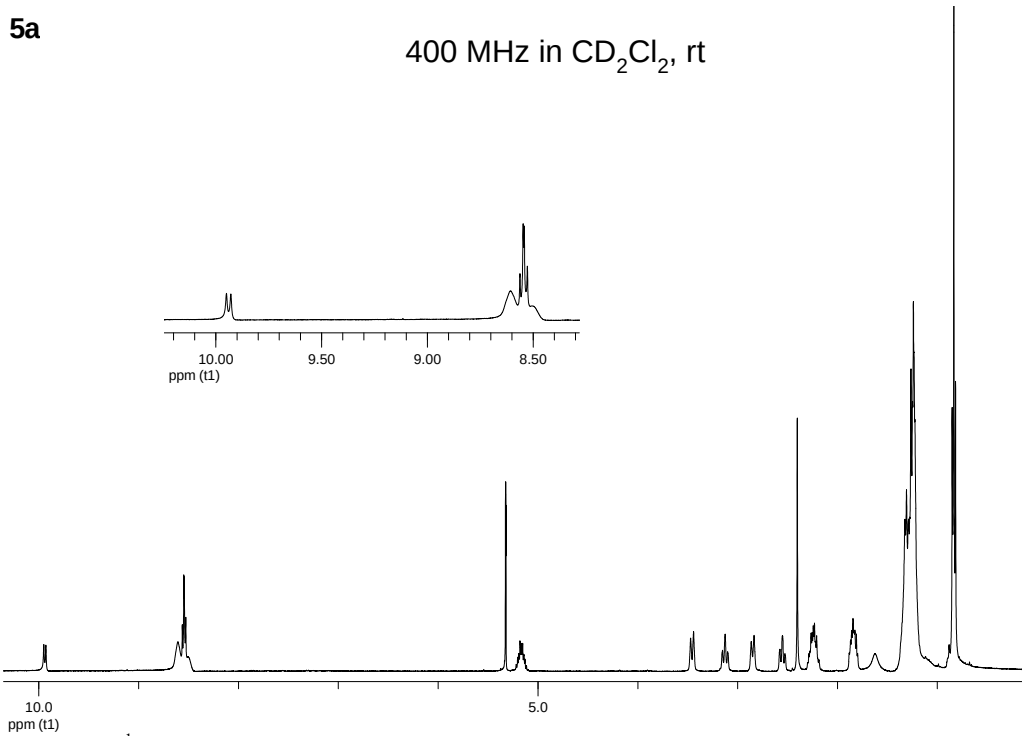


Figure 14: ^{1}H-NMR **5a.**

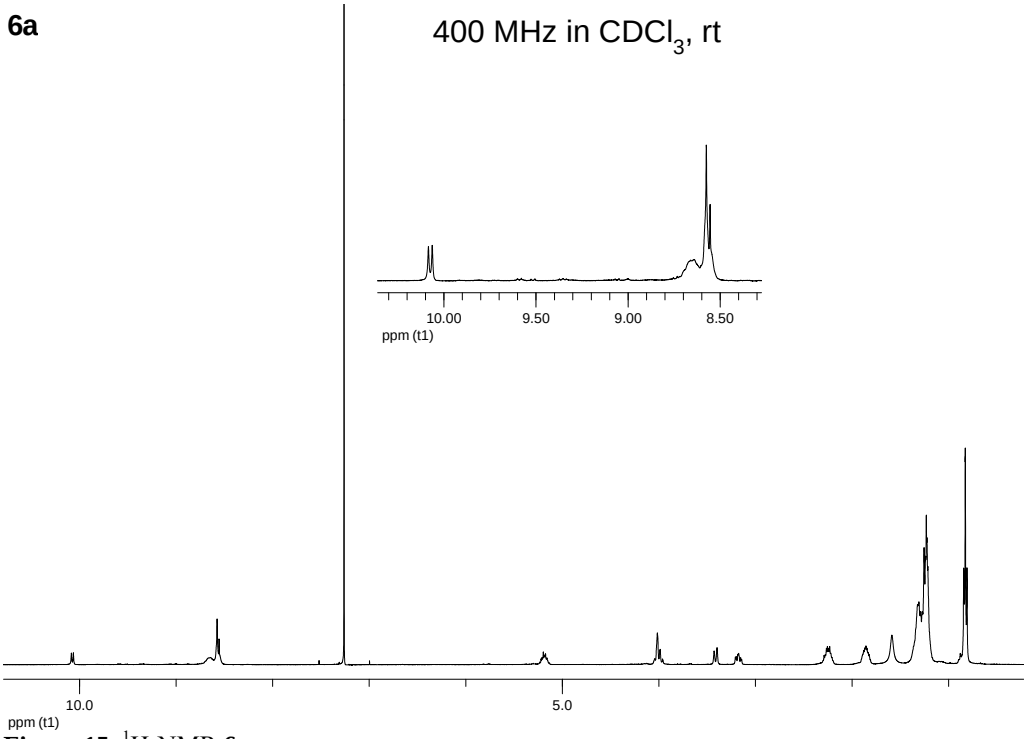


Figure 15: ^{1}H-NMR **6a.**

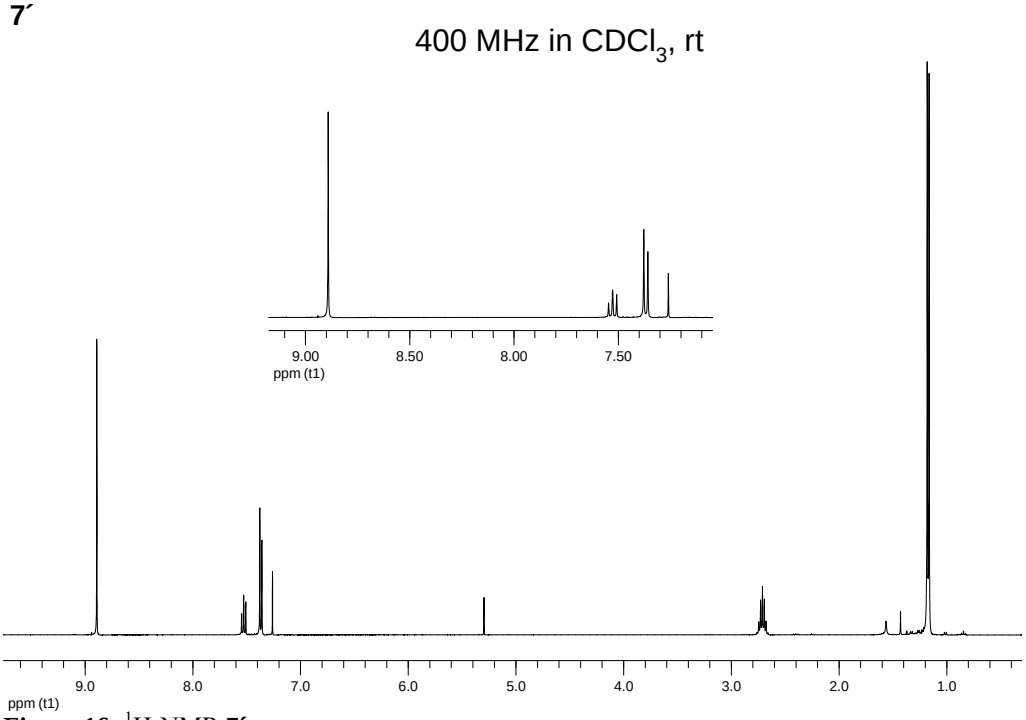


Figure 16: ^{1}H-NMR **7´.**

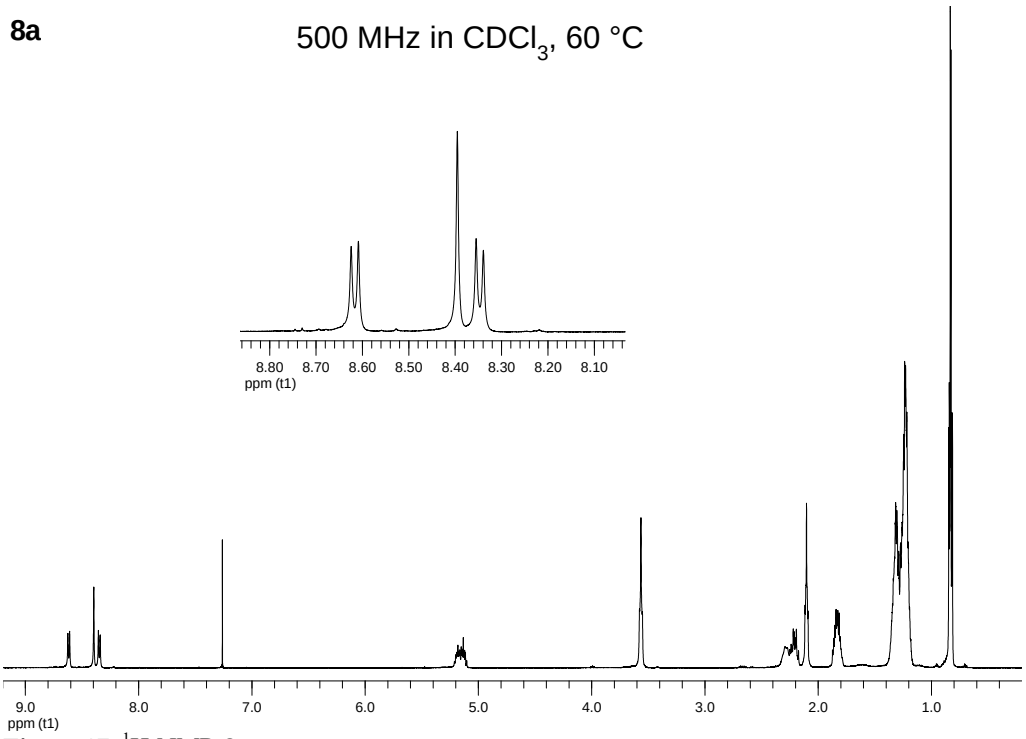


Figure 17: ^{1}H-NMR **8a.**

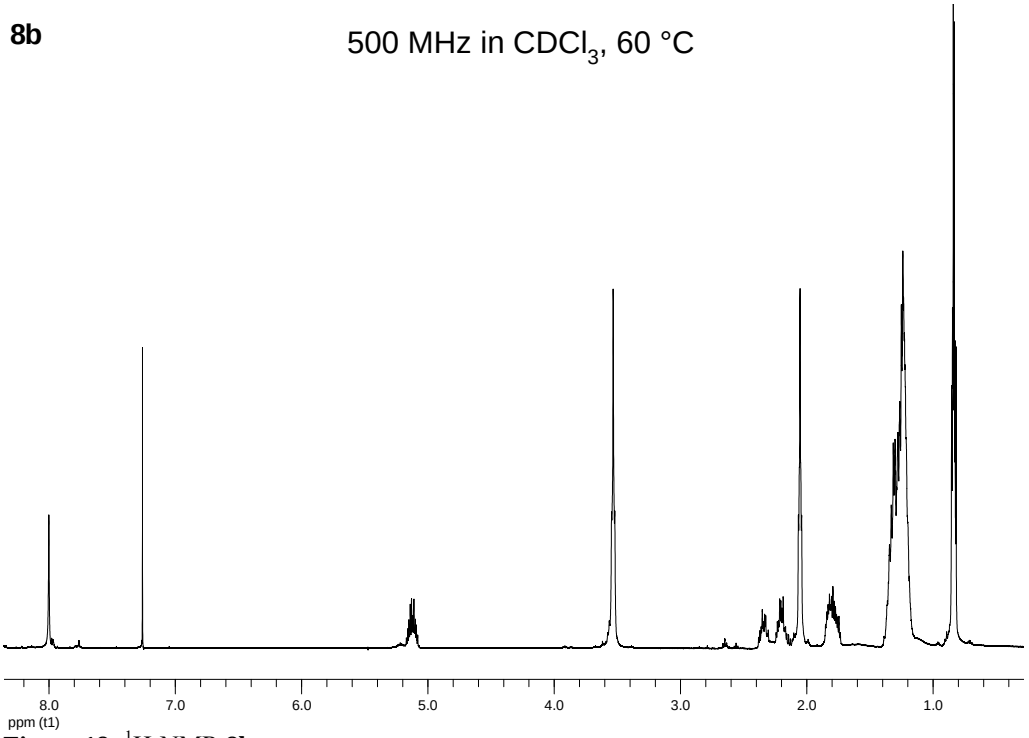


Figure 18: ^{1}H-NMR **8b.**

8´a

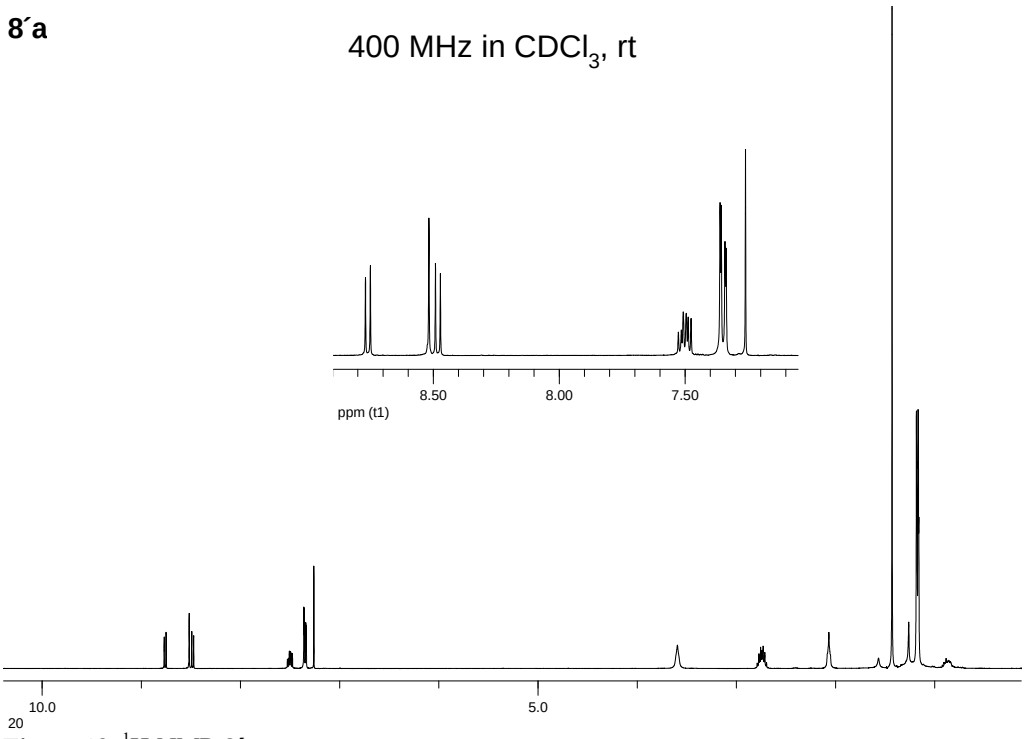


Figure 19: ^{1}H-NMR **8´a.**

8´b

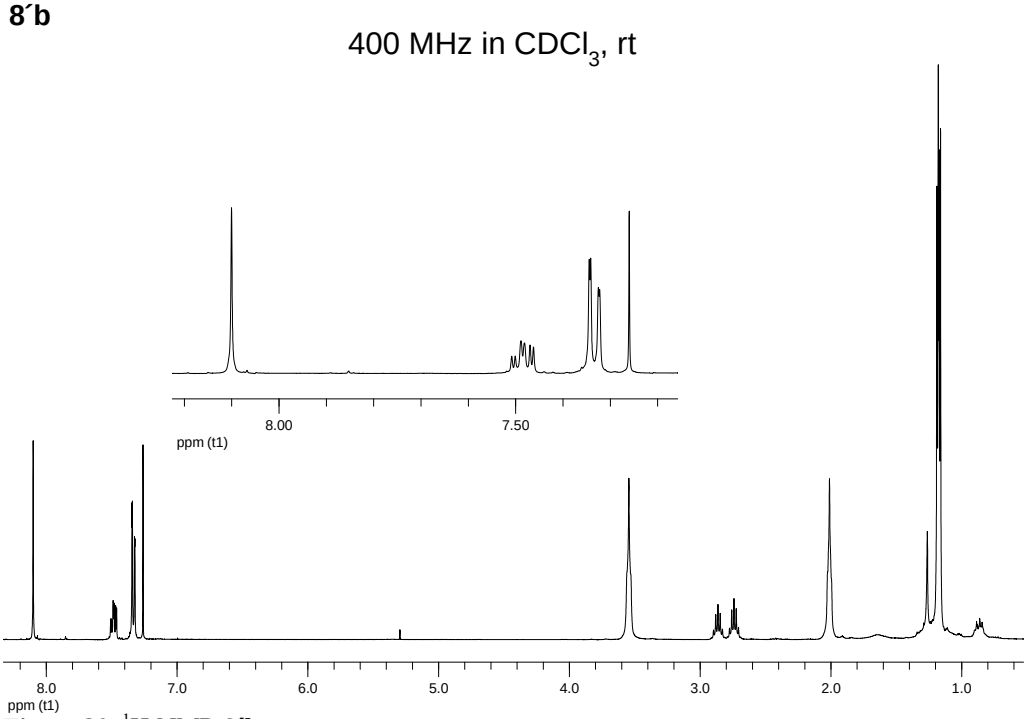


Figure 20: ^{1}H-NMR **8´b.**

9a

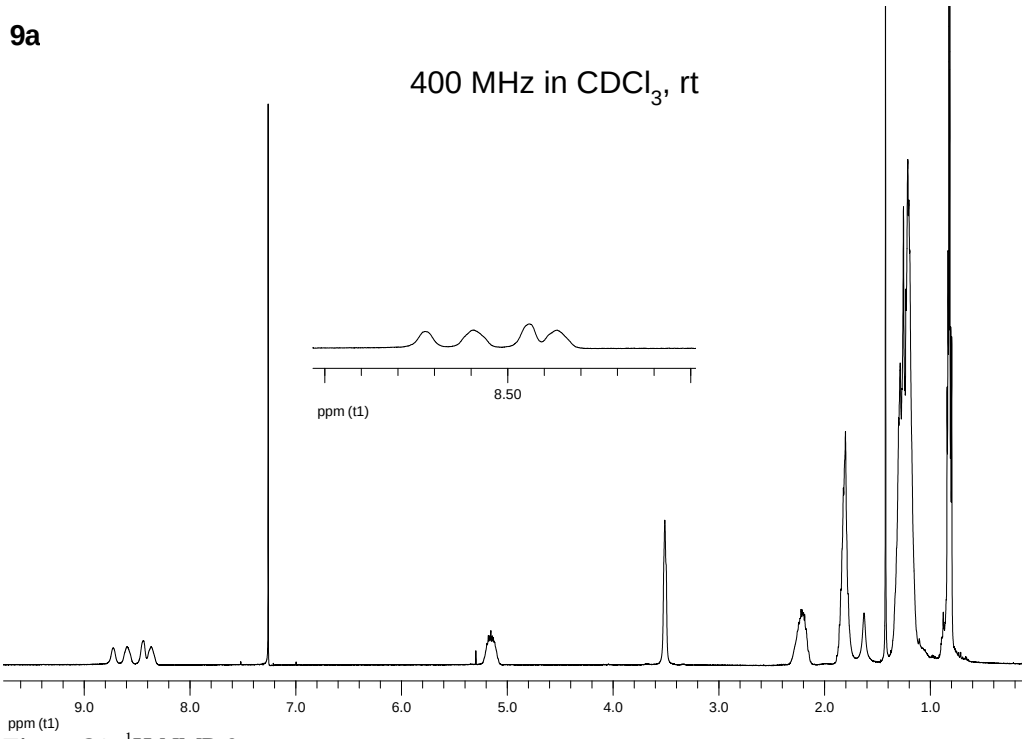


Figure 21: ^{1}H-NMR **9a.**

9´a

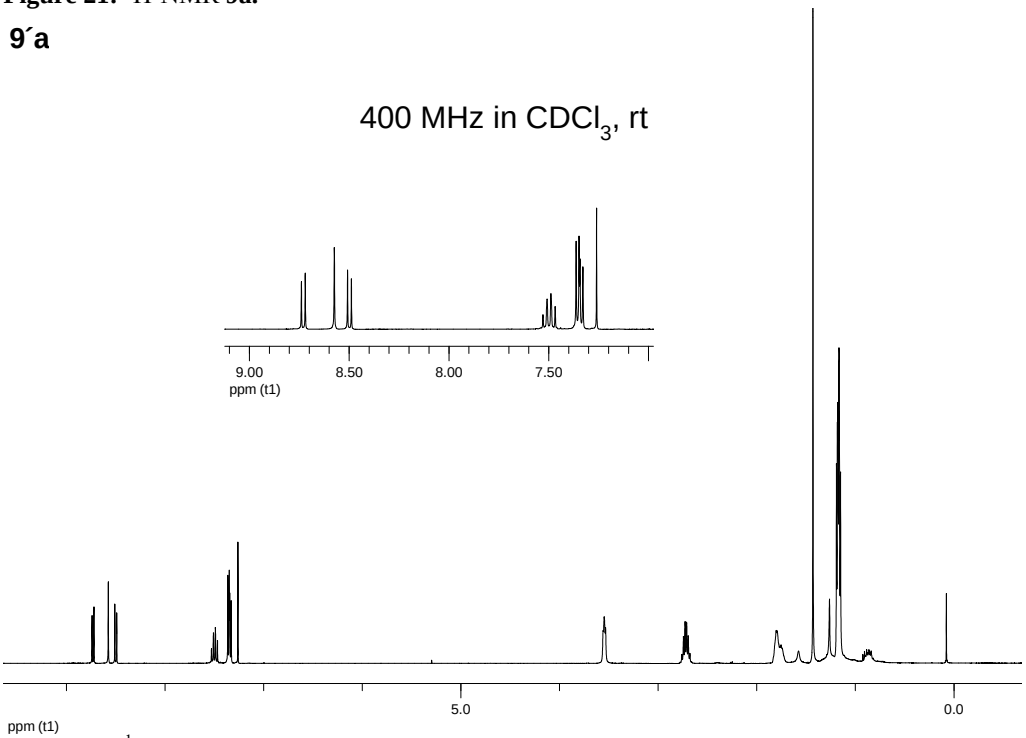


Figure 22: ^{1}H-NMR **9´a.**

3.1 Additional NMR spectra

3.1.1 NMR NOE-spectra of 2´b

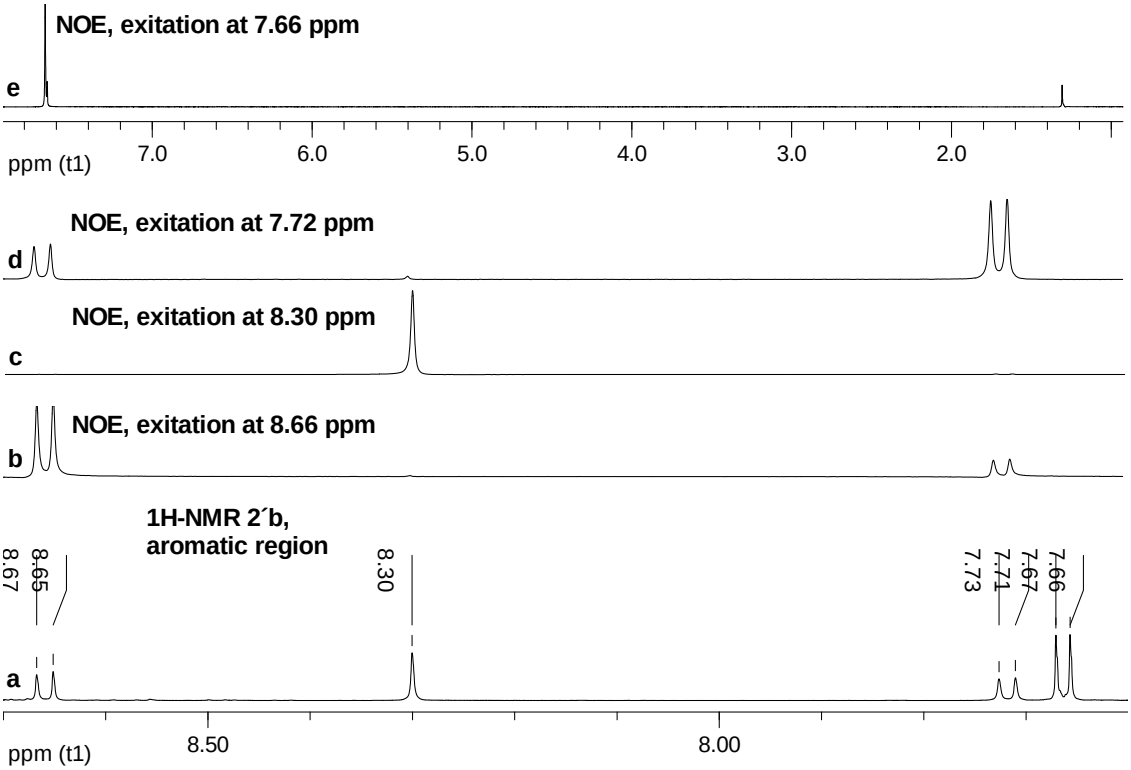


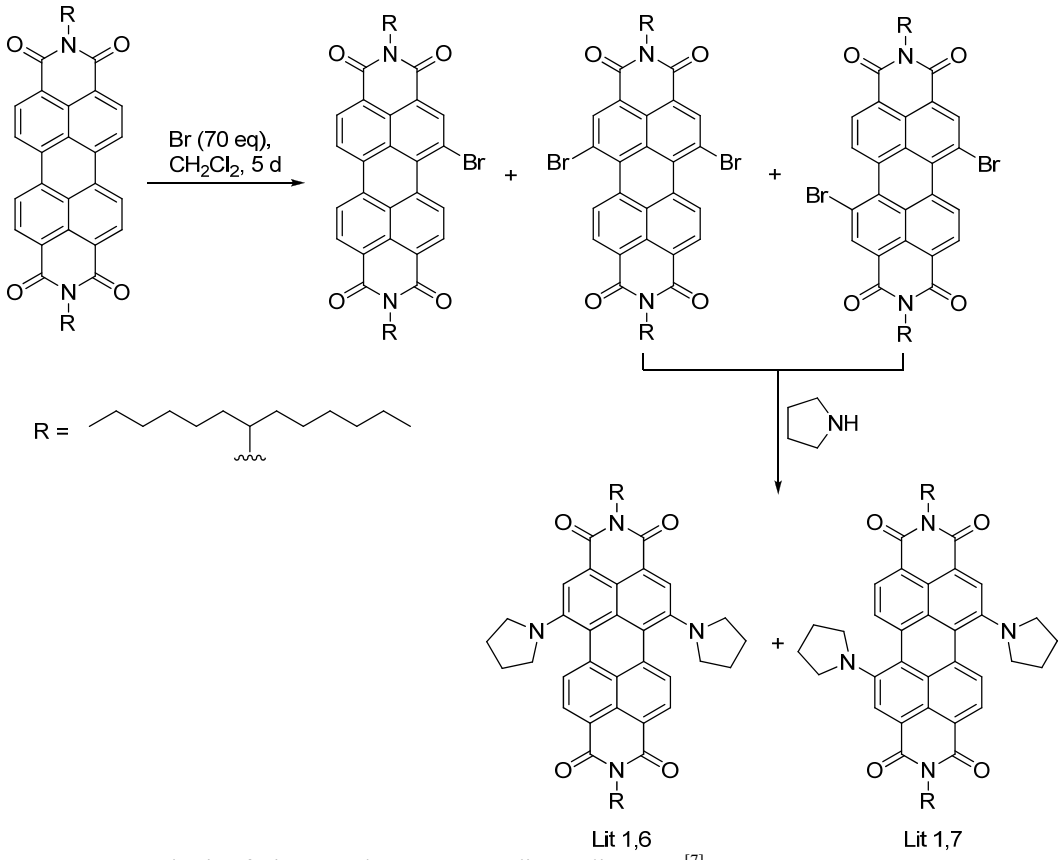
Figure 23: a) 1H-NMR spectra of 2´b (aromatic part); b-e) respective NOE spectra.

The ^{1}H-NMR spectra (**Figure 23**, a) of **2´b** is in accordance with a molecule of high symmetry. By using NOE spectroscopy we were able to relate the two doublets at 8.66 ppm and 7.72 ppm to the hydrogen atoms 7, 8, 11 and 12 because they interact with each other exclusively (**Figure 23**, b and d). The singlet at 8.30 ppm shows no interaction at all since the hydrogen atoms 2 and 5 are rather isolated from the other protons (**Figure 23**, c). The two singlet signals at 7.67 and 7.66 ppm are assigned to the hydrogens located at the dibromo-*tert*-butyl phenyl substituents; they interact with the *t*-butyl groups. The data are well in accordance with those of similar reference products.[3, 6]

3.1.2 Comparison of 2b and PDIs synthesized according to literature

We synthesized 1,7-diamino PDI and 1,6-diamino PDI according to literature[7] in a two-step syntheses (Scheme 5). Mono and di substituted PDI were separated after

bromination. After amination it was possible to separate 1,6-diamino PDI and 1,7-diamino PDI.



Scheme 5: Synthesis of Lit **1,6** and **Lit 1,7** according to literature[7].

In Figure 24 ^{1}-H-NMR spectra (aromatic parts) at room temperature of **2b**, **Lit 1,6** and **Lit 1,7** are shown. The shifts of **Lit 1,6** and **2b** are the same and they show an obvious difference to the spectra of **Lit 1,7**.

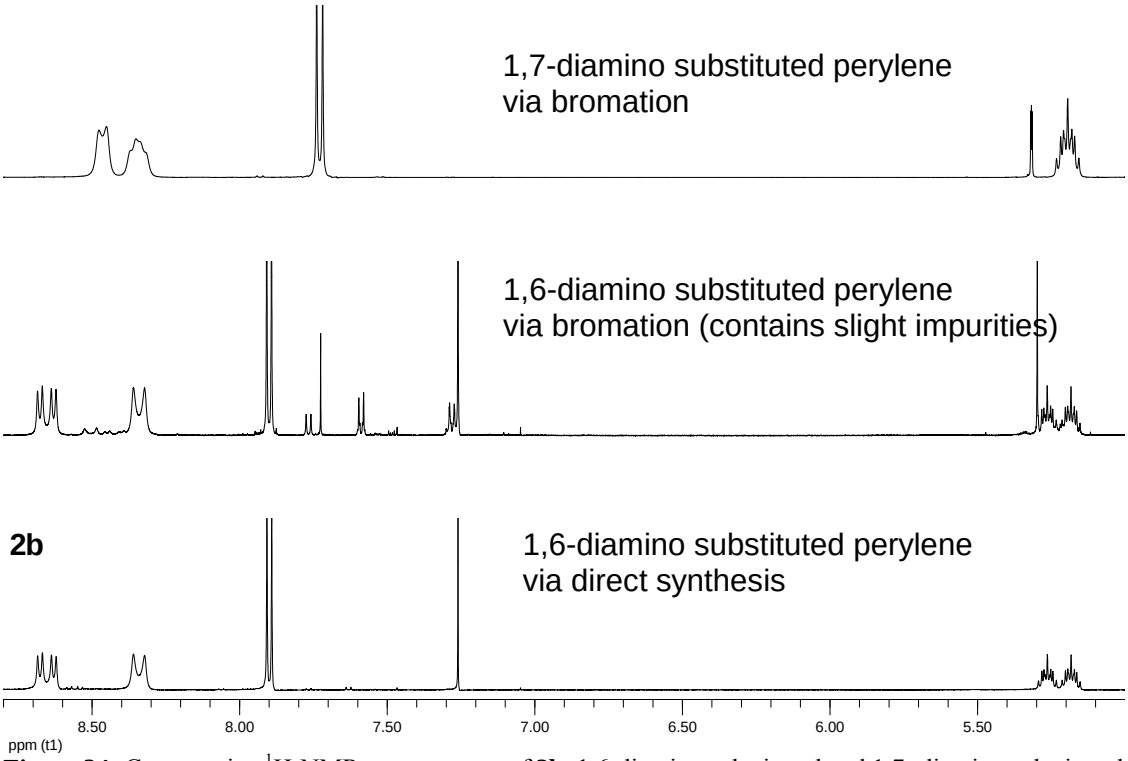


Figure 24: Comparative ^{1}H-NMR spectroscopy of **2b**, 1,6-diamino substituted and 1,7- diamino substituted perylene.

3.1.3 Temperature dependence in 1H-NMR spectra

The NMR spectra of molecules with a swallow tail at the imid (R^1= ´) show at room temperature (298 K) a doubled signal set in the aromatic region. In Figure 25 the ^{1}H-NMR spectra for **2b** at rt (top) and 60 °C (bottom) are displayed. At rt the signals at 8.67 ppm and 8.34 ppm are doubled. At 60 °C they were converted to a doublet at 8.64 ppm and a singlet at 8.36 ppm, as expected.

We investigated the concentration dependence (Figure 26) and solvent dependence (Figure 27) of the splitting. There is no concentration effect. Because of this we suppose that the molecules form two rotamers and no π-π stacking. The rotation of the swallow tail is hindered at room temperature. These results are in accordance with literature.[4]

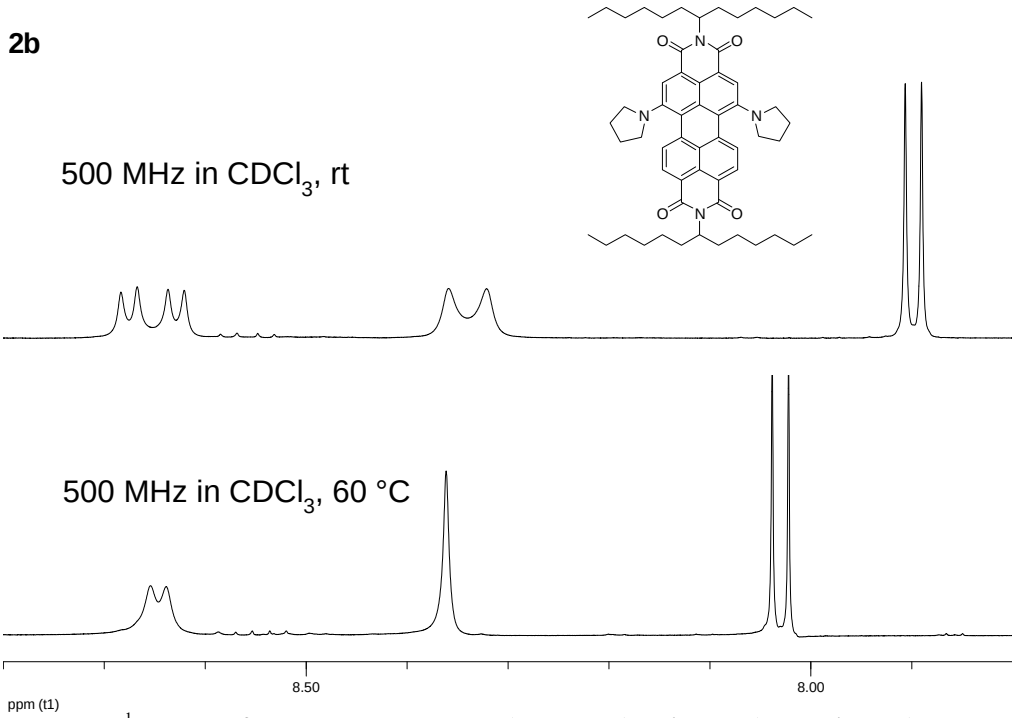


Figure 25: ^{1}H-NMR of **2b** at room temperature (298 K, top) and 60 °C (333 K, bottom).

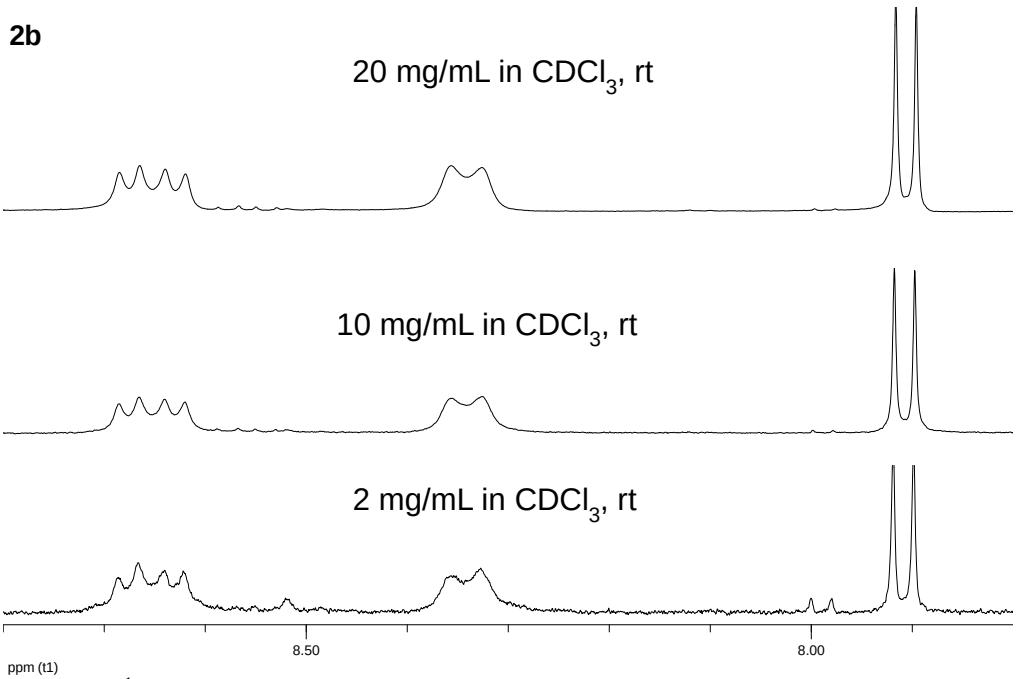


Figure 26: ^{1}H-NMR of **2b**, different concentrations.

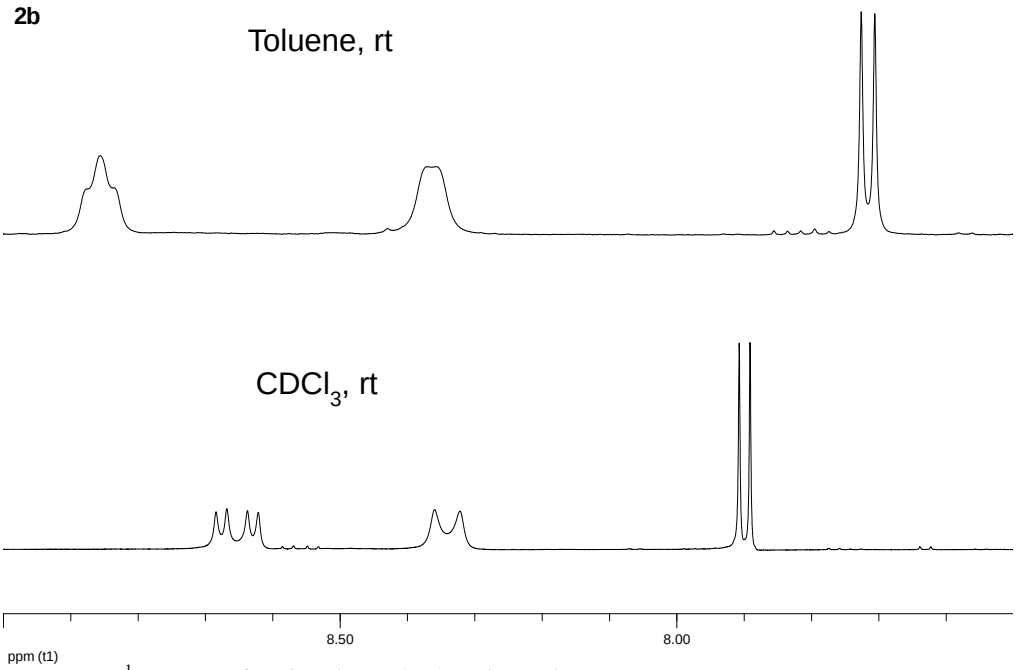


Figure 27: ^{1}H-NMR of **2b** in toluene (top) and $CDCl_3$ at room temperature.

3.1.4 Additional ^{1}H-NMR spectra at different temperatures

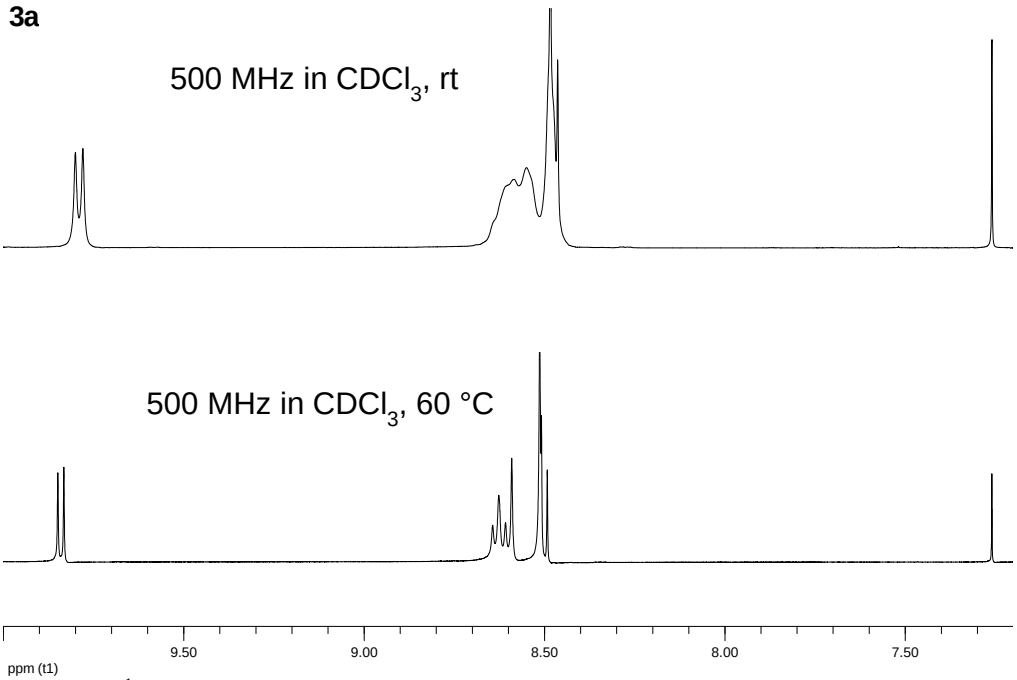


Figure 28: ^{1}H-NMR of **3a** at room temperature (298 K, top) and 60 °C (333 K, bottom).

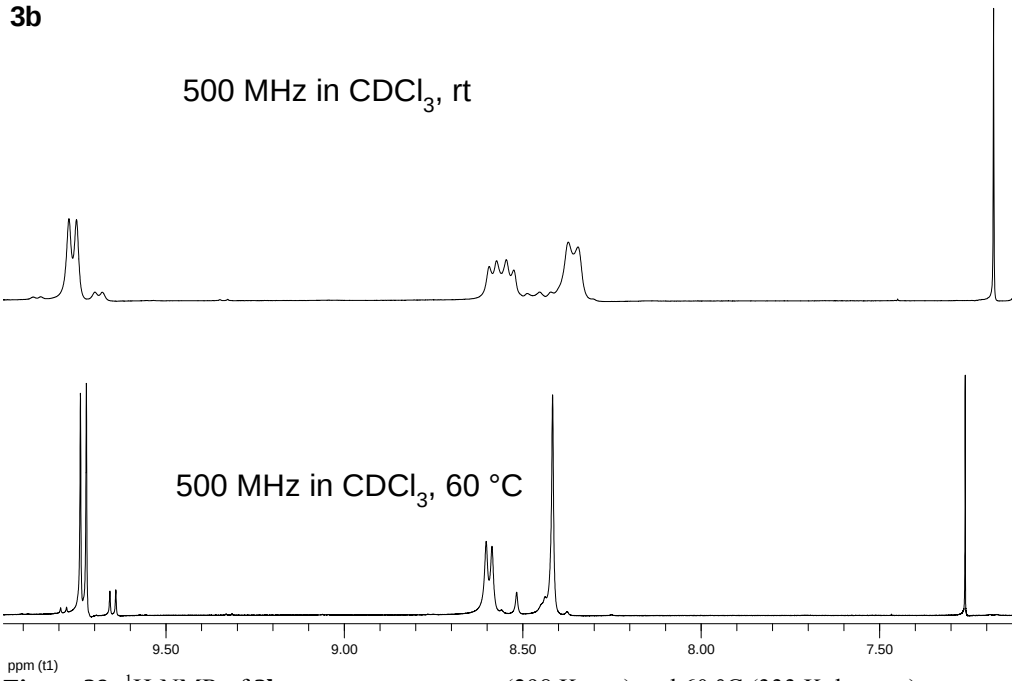


Figure 29: ^{1}H-NMR of **3b** at room temperature (298 K, top) and 60 °C (333 K, bottom).

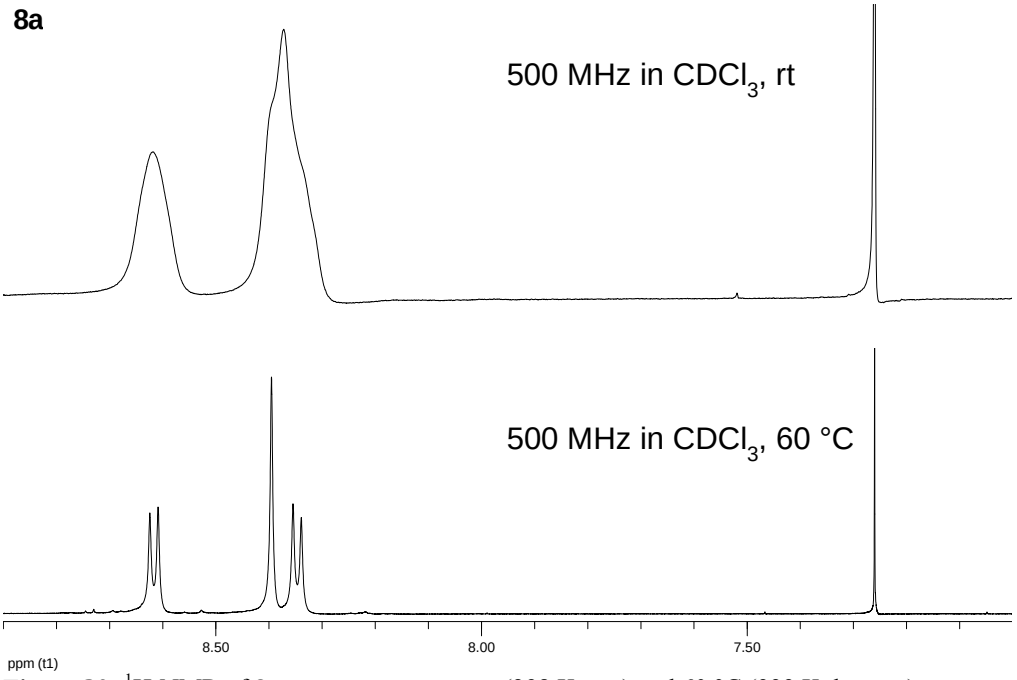


Figure 30: ^{1}H-NMR of **8a** at room temperature (298 K, top) and 60 °C (333 K, bottom).

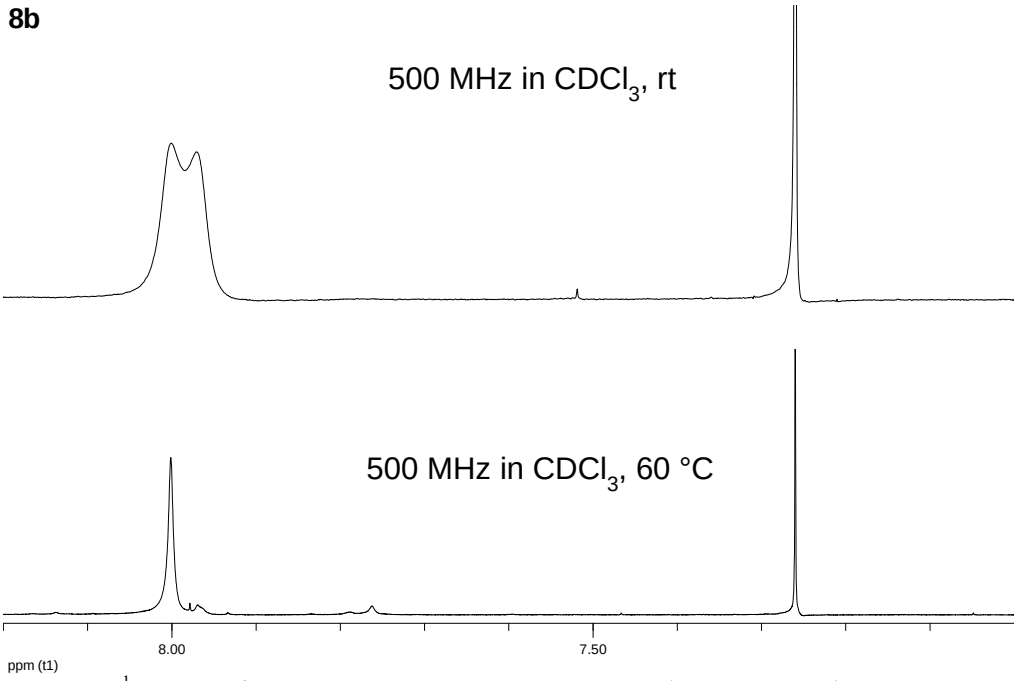


Figure 31: ^{1}H-NMR of **8b** at room temperature (298 K, top) and 60 °C (333 K, bottom).

4 Mass spectra

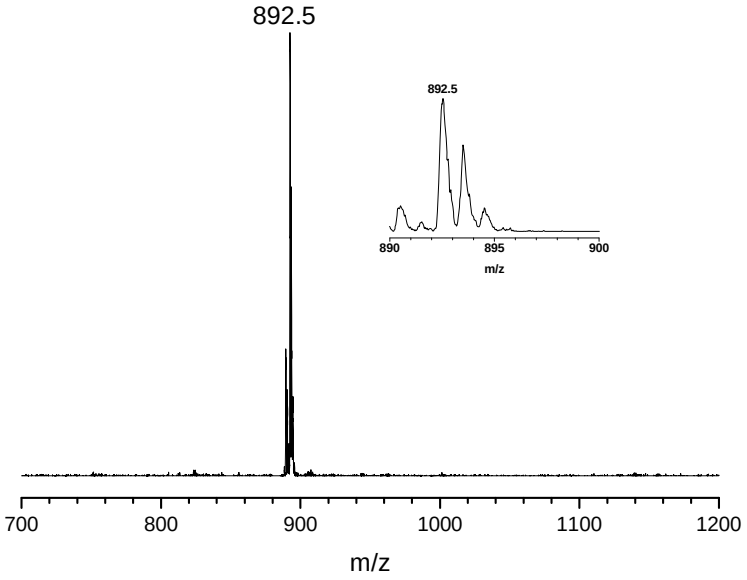


Figure 32: MS (Maldi-pos, DCTB) of **2b.**

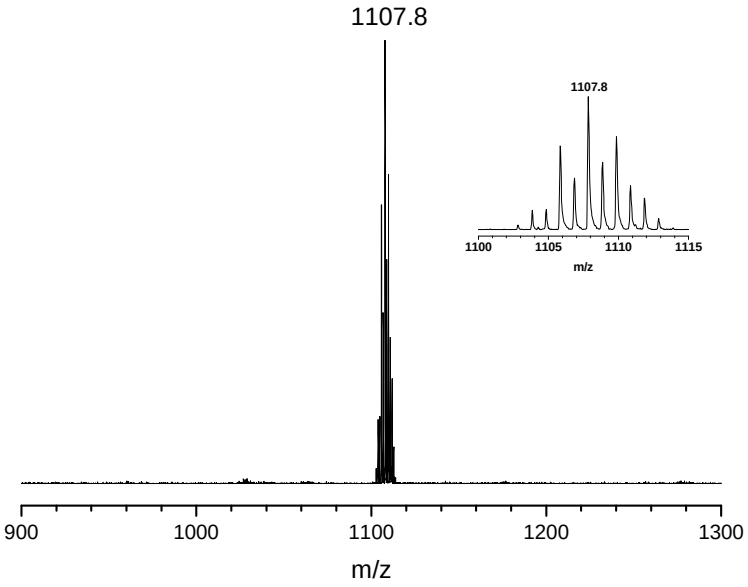


Figure 33: MS (Maldi-pos, DCTB) of **2´b.**

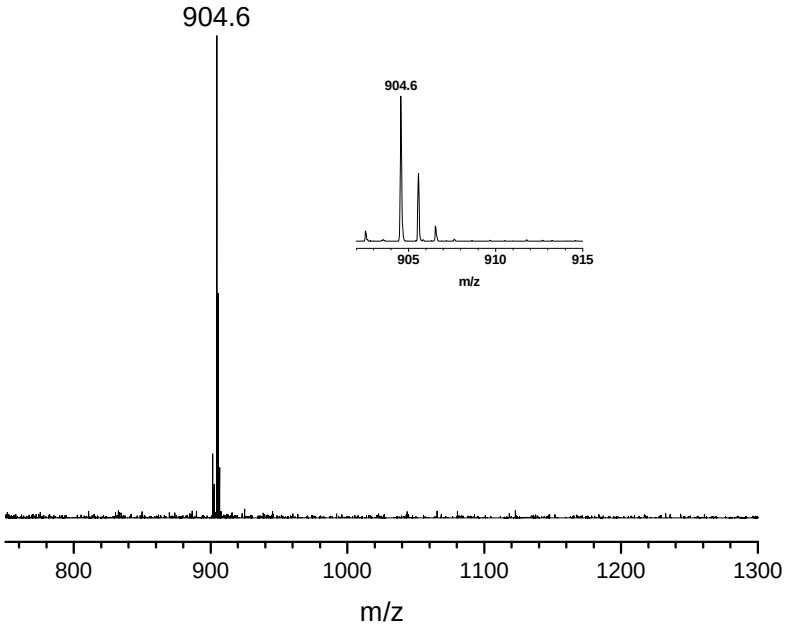


Figure 34: MS (Maldi-pos, DCTB) of **2´´b.**

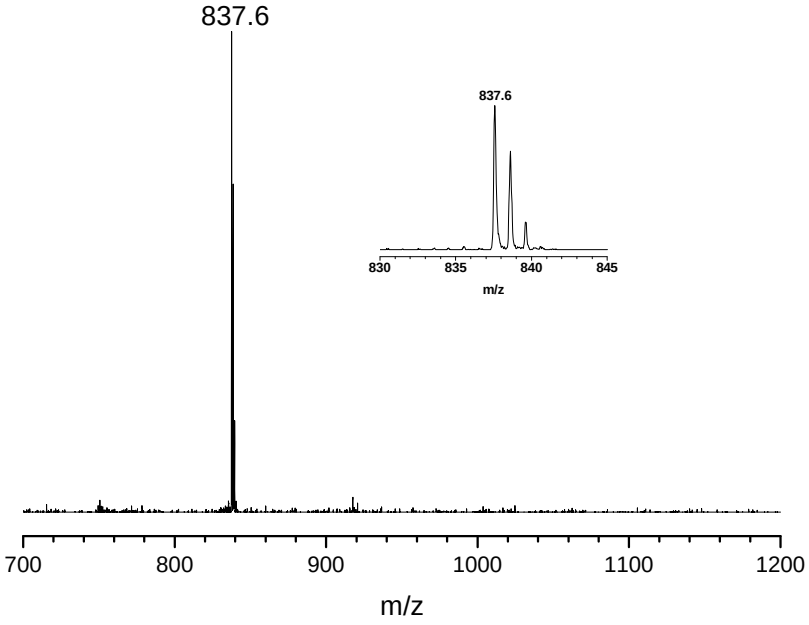


Figure 35: MS (Maldi-pos, DCTB) of **3a.**

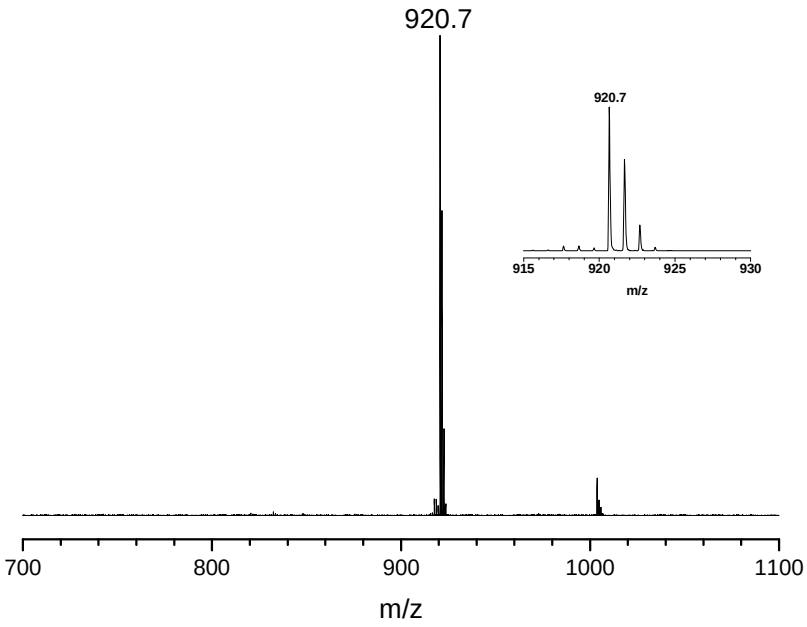


Figure 36: MS (Maldi-pos, DCTB) of **3b.**

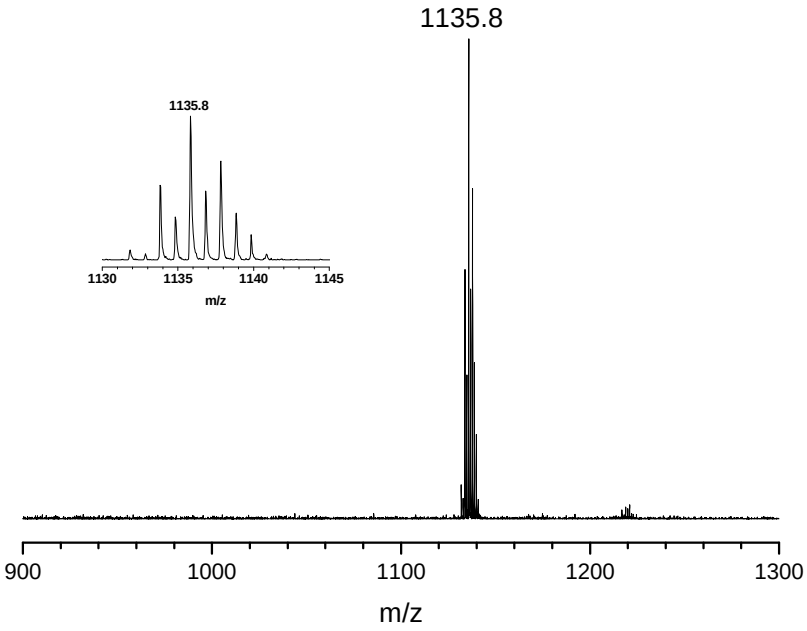


Figure 37: MS (Maldi-pos, DCTB) of **3´b.**

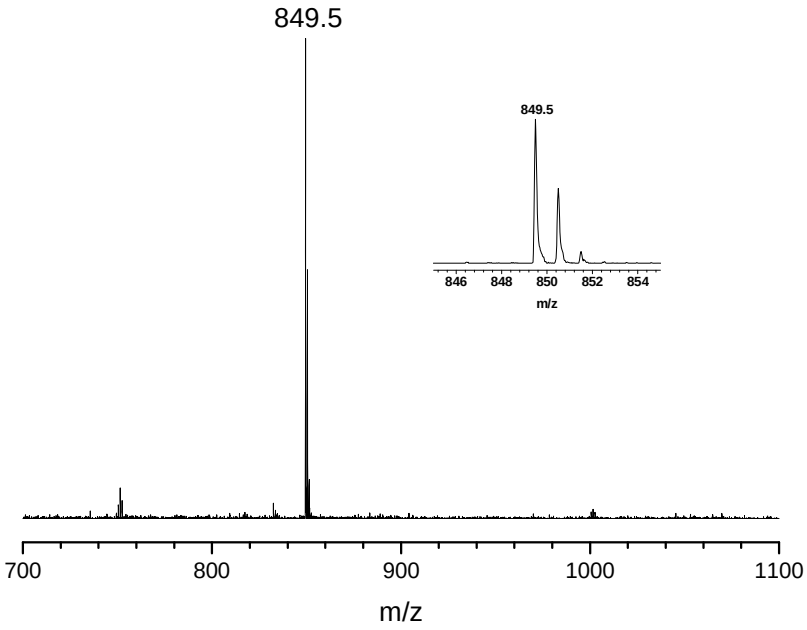


Figure 38: MS (Maldi-pos, DCTB) of **3´´a.**

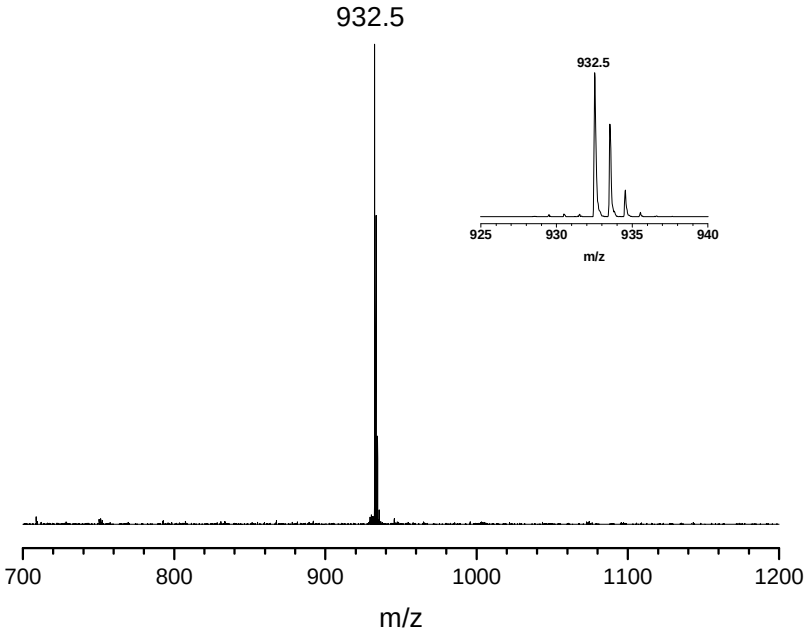


Figure 39: MS (Maldi-pos, DCTB) of **3´´b.**

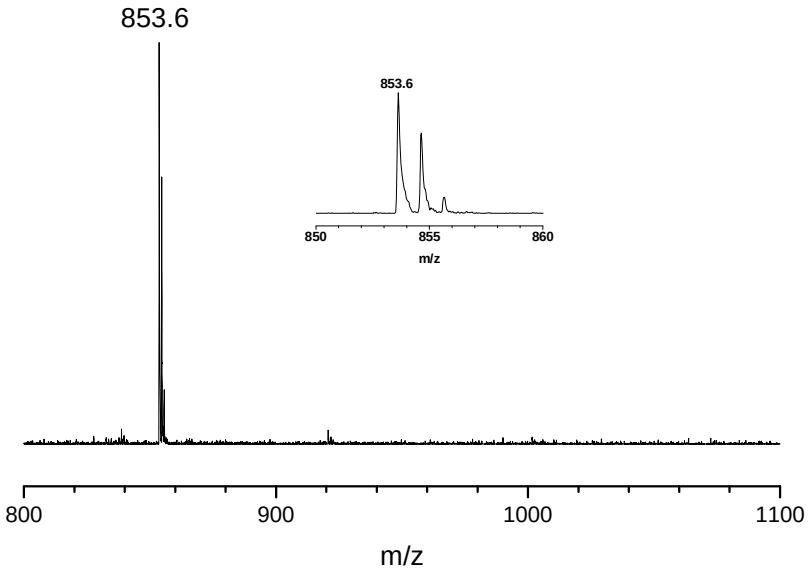


Figure 40: MS (Maldi-pos, DCTB) of **4a.**

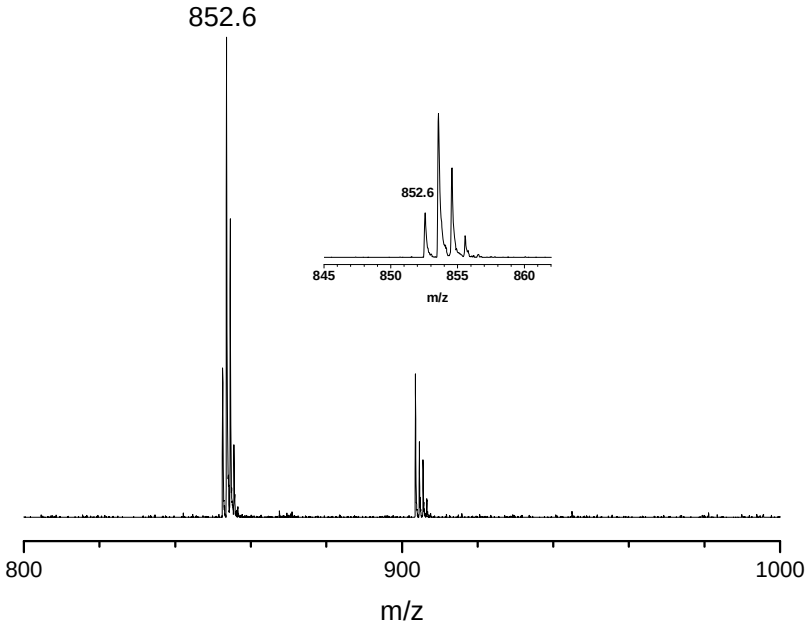


Figure 41: MS (Maldi-pos, DCTB) of **5a.**

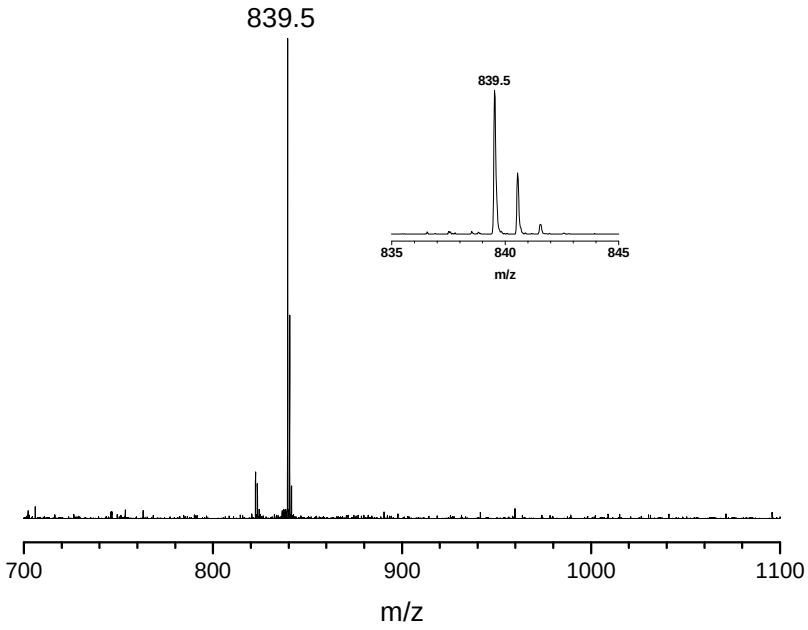


Figure 42: MS (Maldi-pos, DCTB) of **6a.**

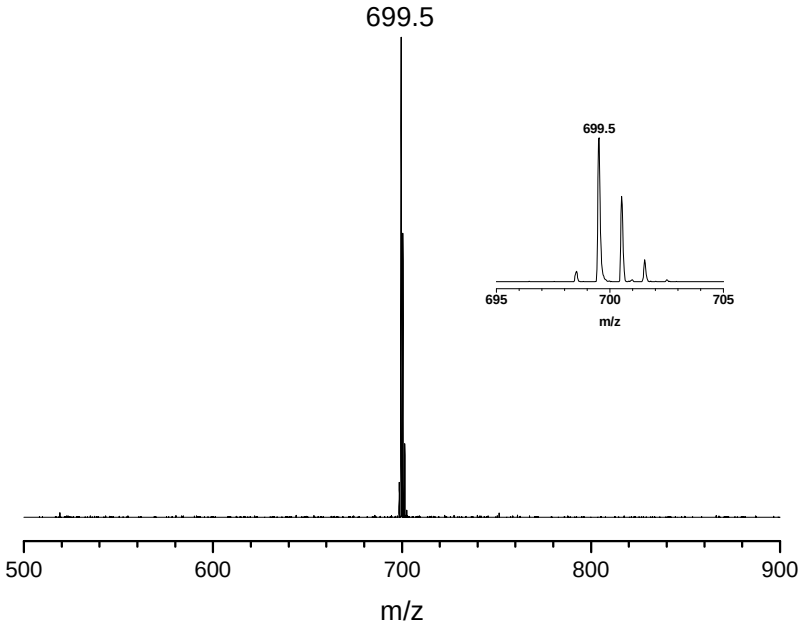


Figure 43: MS (Maldi-pos, DCTB) of **8a.**

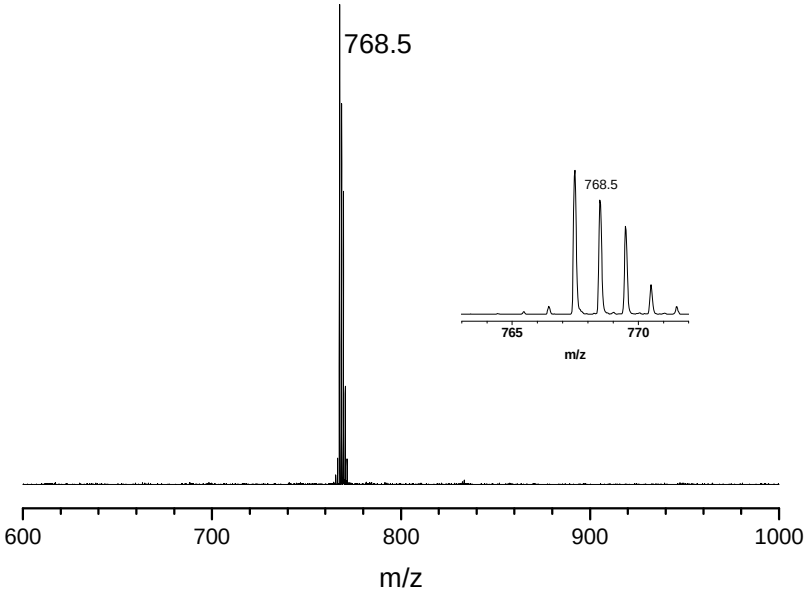


Figure 44: MS (Maldi-pos, DCTB) of **8b.**

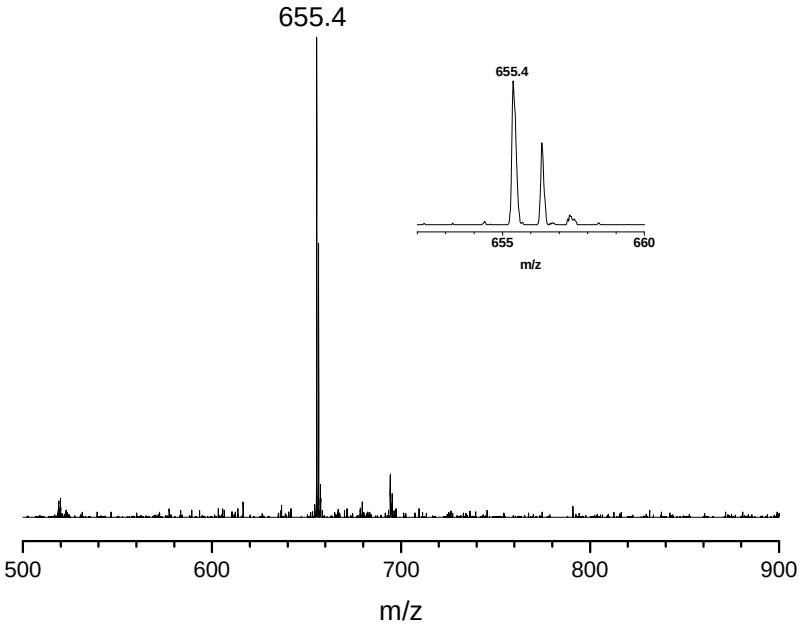


Figure 45: MS (Maldi-pos, DCTB) of **8´a.**

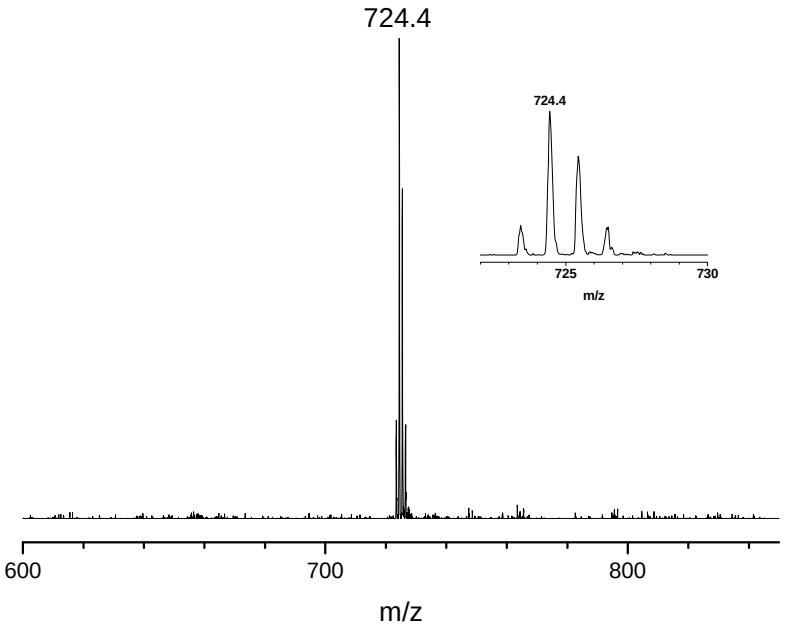


Figure 46: MS (Maldi-pos, DCTB) of **8´b.**

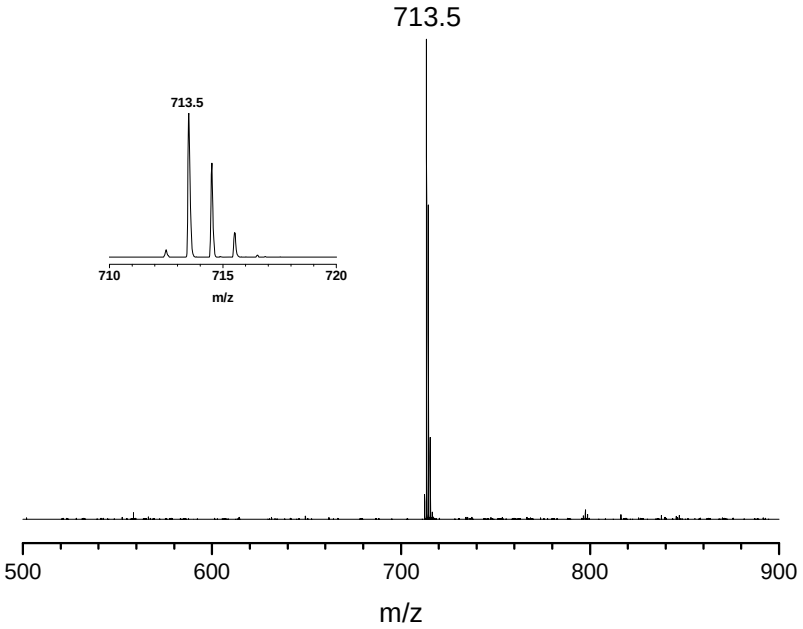


Figure 47: MS (Maldi-pos, DCTB) of **9a.**

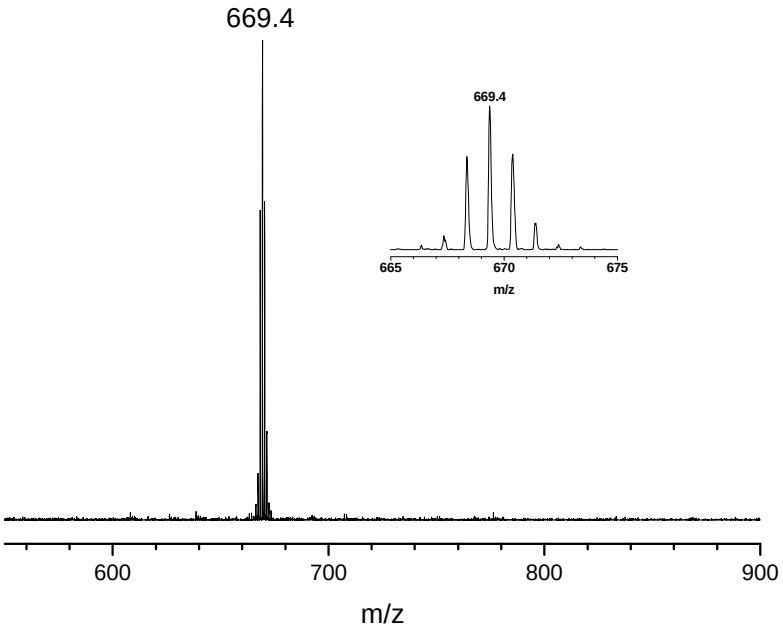


Figure 48: MS (Maldi-pos, DCTB) of **9´a.**

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