Electronic Supplementary Information (ESI)

Aza-capped cyclodextrins for intra-cavity metal complexation

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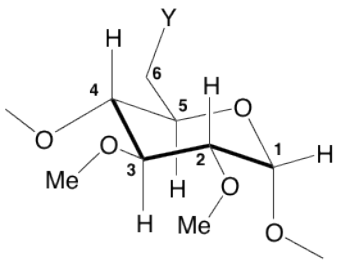
Content

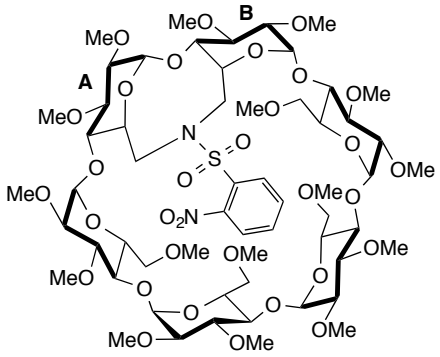
General methods

All commercial reagents were used as supplied. All manipulations were performed in Schlenk-type flasks under N_2 with degassed solvent. Solvents were dried by conventional methods and distilled immediately prior to use. Column chromatography was performed on silica gel 60 (particle size 40-63 μm, 230-240 mesh). $CDCl_3$ was passed down a 5-cm-thick alumina column and stored under N_2 over molecular sieves (3 Å). Routine ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded with Bruker FT instruments (AVANCE 300, 400, 500, 600 spectrometers). ^1H NMR spectral data were referenced to residual protiated solvents (δ = 7.26 ppm for $CDCl_3$), ^{13}C chemical shifts are reported relative to deuterated solvents (δ = 77.00 ppm for $CDCl_3$), and the ^{31}P NMR data are given relative to external H_3PO_4. Mass spectra were recorded with a Bruker MicroTOF spectrometer (ESI) using CH_2Cl_2, MeCN or MeOH as solvent. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie UMR 7177, Strasbourg. Melting points were determined with a Büchi 535 capillary melting point apparatus. High pressure liquid chromatography were performed on a Varian Prostar instrument (Prostar 230 solvent delivery module, Prostar 355 differential refractor and Prostar 335 UV detector with reverse-phase column Pursuit C18). Diols **1**[1] and **4**[2,] dimesylates **2**[3] and **5**[2], tetramesylate **9**[4] were synthesized according to literature procedures. In this publication, the cyclodextrins are depicted as seen from the secondary face, the glucose units being ranged counterclocwise in the following order: A, B, C, D, E, F, G. The numbering of the atoms within a glucose unit is as follows:



Synthesis and characterisation

6^A,6^B-dideoxy-6^A,6^B-*N*-[(2-nitrophenyl)sulfonyl]aza-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F, 6^C,6^D,6^E,6^F-hexadeca-*O*-methyl-α-cyclodextrin (3)



Method 1

To a solution of 2-nitrobenzenesulfonamide (83 mg, 0.41 mmol) and diol **1** (397 mg, 0.33 mmol) in dry toluene (5 mL), were added simultaneously and dropwise a solution of triphenylphosphine (PPh_3) (349 mg, 1.33 mmol) in dry toluene (4 mL) and a solution of diisopropyl azodicarboxylate (DIAD) (269 mg, 262 μL, 1.33 mmol) in dry toluene (4 mL) over a period of 45 min at room temperature. The yellow solution was stirred under nitrogen for 3 h. If necessary, extra PPh_3 (86 mg, 0.33 mmol) and DIAD (67 mg, 65 μL, 0.33 mmol) were added to complete the reaction. The suspension was then evaporated to dryness. Finally, the crude was subjected to column chromatography (SiO_2; CH_2Cl_2/MeOH, 97:3 then 95:5, *v/v*) to afford 6^A,6^B-dideoxy-6^A,6^B-*N*-((2-nitrophenyl)sulfonyl)aza-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^C, 6^D,6^E,6^F-hexadeca-*O*-methyl-alpha-cyclodextrin (**3**) as a colourless solid (277 mg, 61%).

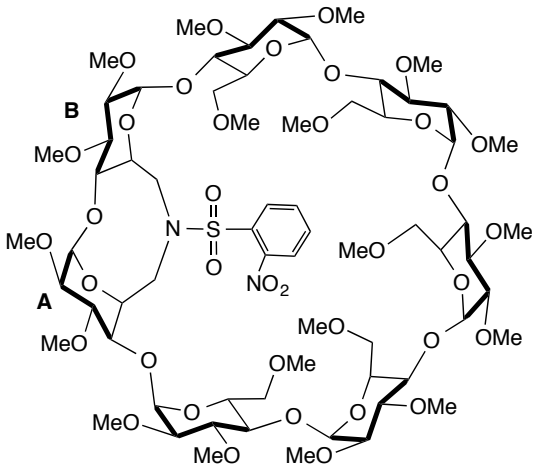
Method 2

Potassium carbonate (2.75 g, 19.89 mmol) was added to a solution of dimesylate **2** (4.5 g, 3.32 mmol) and 2-nitrobenzenesulfonamide (1.1 g, 5.44 mmol) in anhydrous *N*,*N*-dimethylformamide (DMF) (90 mL). The reaction mixture was stirred for 15 h at 80°C before being evaporated to dryness *in vacuo*. The residue was retaken in $CHCl_3$ (100 mL) and the organic solution washed twice with distilled water (2 x 100 mL) and once with saturated NaCl solution (50 mL) before being dried ($MgSO_4$) and evaporated to dryness *in vacuo* to afford a yellow residue, which was subjected to column chromatography (SiO_2, CH_2Cl_2/MeOH, 97 :3 then 95:5, *v/v*) to give **3** (4.26 g, 94 %) as a colourless solid.

R_f (SiO_2, CH_2Cl_2/MeOH, 90:10, *v/v*) = 0.45; ^{1}H NMR (400.1 MHz, $CDCl_3$, 25ºC): δ (partial assignment by COSY and HSQC) = 3.01 (dd, 1 H, $^2J_{H6a\text{-}H6b}$ = 13.0 Hz, $^3J_{H6a\text{-}H5}$ = 9.4 Hz, H-$6a^{A\ or\ B}$), 3.09–3.22 (6 H, H-2, H-4), 3.34 (s, 3 H, OMe), 3.38 (s, 3 H, OMe), 3.40 (s, 3 H, OMe), 3.44 (s, 3 H, OMe), 3.46 (s, 3 H, OMe), 3.47 (s, 3 H, OMe), 3.49 (s, 3 H, OMe), 3.51 (s, 3 H, OMe), 3.52 (s, 6 H, OMe), 3.59 (s, 3 H, OMe), 3.62 (s, 3 H, OMe), 3.63 (s, 3 H, OMe), 3.65 (s, 6 H, OMe), 3.70 (s, 3 H, OMe), 3.30–3.99 (25 H, H-2, H-3, H-4, H-5, H-6),

4.15 (d, 1 H, $^{2}J_{H6b\text{-}H6a}$ = 13.0 Hz, H-6b$^{A\text{ or }B}$), 4.22–4.31 (2 H, H-5$^{A\text{ or }B}$), 4.34 (d, 1 H, $^{2}J_{H6b\text{-}H6a}$ = 12.0 Hz, H-6), 4.99–5.03 (4 H, H-1), 5.08 (d, 1 H, $^{3}J_{H1\text{-}H2}$ = 3.2 Hz, H-1), 5.10 (d, 1 H, $^{3}J_{H1\text{-}H2}$ = 3.3 Hz, H-1), 7.63–7.75 (4 H, aromatic-H) ppm; $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$, 25ºC): δ (partial assignment by HSQC and HMBC) = 49.72, 54.63 (C-6^{A,B}), 57.44, 57.61, 57.74, 57.94 [×2], 58.66, 58.83 [×2], 59.02, 59.17, 60.86, 61.53, 61.65, 64.75 [×3] (OMe), 69.32 (C-5), 70.33, 70.44 (C-6), 70.84 [×2], 70.91 (C-5), 71.07, 71.26 (C-6), 71.70, 75.03 (C-5), 80.15, 81.07, 81.17, 81.24, 81.35 [×4], 81.76, 81.83, 81.90 [×2], 81.95, 82.16 [×2], 82.55, 83.71, 86.16 (C-2, C-3, C-4), 96.88, 97.38, 99.61, 100.27, 100.45, 100.81 (C-1), 124.49, 128.59, 131.38, 132.64, 133.35, 148.61 (C aromatic) ppm; elemental analysis (%) calcd for $C_{58}H_{94}N_2O_{32}S{\cdot}CH_2Cl_2$ (1363.43 + 84.93): C 48.93, H 6.68, N 1.93 found: C 49.29, H 6.66, N 1.99; MS (ESI-TOF): *m/z* (%): 1385.54 (100) $[M + Na]^+$.

6^{A},6^{B}-dideoxy-6^{A},6^{B}-[*N*-(2-nitrophenyl)sulfonyl]aza-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},2^{G},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},3^{G},6^{C},6^{D},6^{E},6^{F},6^{G}-hexadeca-*O*-methyl-β-cyclodextrin (6)



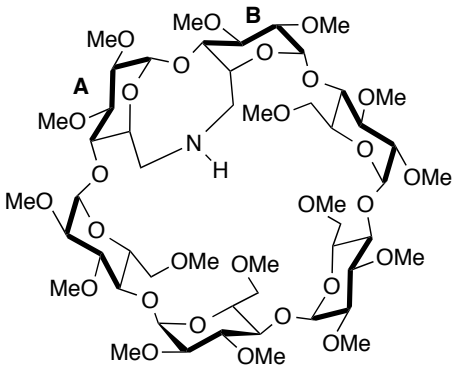
6 (colourless solid, 135 mg, 60 %) was synthesized from diol **4** (200 mg, 0.14 mmol), 2-nitrobenzenesulfonamide (36 mg, 0.18 mmol), PPh_3 (150 mg, 0.57 mmol) and DIAD (115 mg, 112 μL, 0.57 mmol) in toluene (2.5 mL) according to method 1.

6 (colourless solid, 659 mg, 65 %) was also synthesized from dimesylate **5** (1 g, 0.642 mmol), 2-nitrobenzenesulfonamide (286 mg, 1.414 mmol), potassium carbonate (534 mg, 3.86 mmol) in DMF (20 mL) according to method 2.

R_f (SiO_2, CH_2Cl_2/MeOH, 90:10, *v*/*v*) = 0.41; ^{1}H NMR (500.1 MHz, $CDCl_3$, 25ºC): δ (partial assignment by COSY and HSQC) = 3.01 (dd, 1 H, $^{2}J_{H6a\text{-}H6b}$ = 13.0 Hz, $^{3}J_{H6a\text{-}H5}$ = 9.2 Hz, H-6a$^{A\text{ or }B}$), 3.10 (dd, 1 H, $^{3}J_{H2\text{-}H3}$ = 10.0 Hz, $^{3}J_{H2\text{-}H1}$ = 3.0 Hz, H-2) , 3.13 (t, 1 H, $^{3}J_{H4\text{-}H5}$ = $^{3}J_{H3\text{-}H4}$ = 9.7 Hz, H-4), 3.15–3.22 (5 H, H-2), 3.20 (s, 3 H, OMe), 3.26 (s, 3 H, OMe), 3.37 (s, 3 H, OMe), 3.40 (s, 3 H, OMe), 3.45 (s, 3 H, OMe), 3.47 (s, 3 H, OMe), 3.48 (s, 3 H, OMe), 3.49 (s, 3 H, OMe), 3.51 (s, 6 H, OMe), 3.52 (s, 3 H, OMe), 3.53 (s, 3 H, OMe), 3.58 (s, 3 H, OMe), 3.60 (s, 3 H, OMe), 3.62 (s, 3 H, OMe), 3.63 (s, 3 H, OMe), 3.65 (s, 3 H, OMe), 3.69 (s, 3 H, OMe), 3.70 (s, 3 H, OMe), 3.30–3.89 (27 H, H-2, H-3, H-4, H-5, H-6), 3.89–3.99 (3 H, H-6), 4.17 (d, 1 H, $^{3}J_{H5\text{-}H6}$ = 9.3 Hz, H-5), 4.18 (dd, 1 H, $^{3}J_{H5\text{-}H6b}$ = 19.7 Hz, $^{3}J_{H5\text{-}H6a}$ = 9.8

Hz, H-5), 4.28 (d, 1 H, $^{2}J_{H6b\text{-}H6a}$, 13.0 Hz, H-6b$^{A\text{ or }B}$), 4.32 (d, 1 H, $^{3}J_{H6a\text{-}H6b}$ = 10.5 Hz, H-6), 4.99 (d, 1 H, $^{3}J_{H1\text{-}H2}$ = 4.8 Hz, H-1), 5.05–5.07 (2 H, H-1), 5.08 (d, 1 H, $^{3}J_{H1\text{-}H2}$ = 3.1 Hz, H-1), 5.12 (d, 1 H, $^{3}J_{H1\text{-}H2}$ = 3.6 Hz, H-1), 5.13 (d, 1 H, $^{3}J_{H1\text{-}H2}$ = 3.4 Hz, H-1), 5.34 (d, 1 H, $^{3}J_{H1\text{-}H2}$ = 3.6 Hz, H-1), 7.63–7.68 (2 H, aromatic-H), 7.68–7.75 (m, 1 H, aromatic-H), 7.86–7.91 (m, 1 H, aromatic-H) ppm; $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$, 25ºC): δ (partial assignment by HSQC) = 49.19, 54.34 (C-6^{A,B}), 57.73, 57.75, 58.18, 58.29, 58.46, 58.81 [×2], 58.96 [×2], 59.02 [×2], 59.24, 60.48, 61.13, 61.43, 61.61, 61.67 [×2], 61.75 (OMe), 69.42, 69.77, 70.49 (C-5), 70.65, 70.67, 70.74 (C-6), 70.80 (C-5), 71.02 [×2] (C-6), 71.31, 75.49, 75.72 (C-5), 79.78, 79.82, 80.16, 80,31, 80.50, 80.62, 81.26 [×2], 81.66 [×3], 81.71 [×3], 81.81, 81.88, 82.04, 82.44, 82.64, 84.93, 86.37 (C-2, C-3, C-4), 96.30, 97.71 [×2], 98.36, 98.45, 98.67, 100.32 (C-1), 124.31, 130.16, 131.05, 132.11, 133.50, 148.37 (C aromatic) ppm; elemental analysis (%) calcd for $C_{67}H_{110}N_2O_{37}S$ (1567,65) : C 51.33, H 7.07, N 1.79 found C 51.24, H 7.14, N 1.94; MS (ESI-TOF): *m/z* (%): 1584.69 (100) $[M + H_3O]^+$.

6^{A},6^{B}-dideoxy-6^{A},6^{B}-aza-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{C},6^{D},6^{E},6^{F}-hexadeca-*O*-methyl-α-cyclodextrin (7)

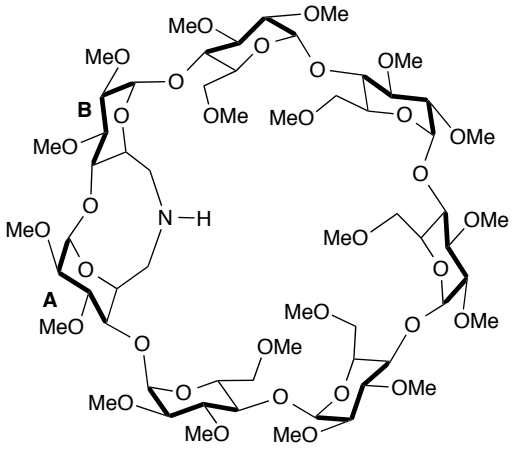


Cesium carbonate (Cs_2CO_3) (28 mg, 0.09 mmol) was added to a solution of **3** (79 mg, 0.06 mmol) in 2 mL of acetonitrile (MeCN). Thiophenol (8 mg, 7.5 μL, 0.07 mmol) was added and the yellow solution stirred for 2 h at room temperature before being evaporated to dryness. The residue was dissolved in ethyl acetate (AcOEt) (50 mL) and the organic solution washed successively with 2M sodium hydroxide (NaOH) solution (3 × 50 mL) and saturated aqueous sodium bicarbonate solution ($NaHCO_3$) (50 mL), and dried on magnesium sulfate ($MgSO_4$). Finally the solvent was removed *in vacuo* and the resulting residue subjected to column chromatography (SiO_2; CH_2Cl_2/MeOH, 95:5, *v/v*) to afford **7** (65 mg, 96 %) as a colourless solid.

R_f (SiO_2, CH_2Cl_2/MeOH, 90:10, *v/v*) = 0.38; ^{1}H NMR (500.1 MHz, $CDCl_3$, 25ºC): δ (partial assignment by COSY and HSQC) = 2.72 (dd,1 H, $^{2}J_{H6a\text{-}H6b}$ = 12.7 Hz, $^{3}J_{H6a\text{-}H5}$ = 9.1 Hz, H-6a$^{A\text{ or }B}$), 3.08–3.19 (6 H, H-2, H-6a$^{B\text{ or }A}$), 3.24 (t, 1 H, $^{3}J_{H4\text{-}H5} = {}^{3}J_{H4\text{-}H3}$ = 8.9 Hz, H-4$^{A\text{ or }B}$), 3.28 (dd, 1 H, $^{3}J_{H4\text{-}H5}$ = 10.4 Hz, $^{3}J_{H4\text{-}H3}$ = 7 Hz, H-4$^{B\text{ or }A}$), 3.36 (s, 6 H, OMe), 3.37 (s, 6 H, OMe), 3.45 (s, 3 H, OMe), 3.46 (s, 3 H, OMe), 3.47 (s, 3 H, OMe), 3.47 (s, 3 H, OMe), 3.48 (s, 3 H,

OMe), 3.51 (s, 3 H, OMe), 3.57 (s, 3 H, OMe), 3.61 (s, 3 H, OMe), 3.62 (s, 6 H, OMe), 3.65 (s, 3 H, OMe), 3.66 (s, 3 H, OMe), 3.33–3.72 (18 H, H-2, H-3, H-4, H-5, H-6), 3.75–3.81 (3 H, H-4, H-5), 3.82 (dd, 1 H, $^{2}J_{H6a-H6b}$ = 9.9 Hz, $^{3}J_{H6a-H5}$ = 4.0 Hz, H-6a), 3.85–3.92 (4 H, H-4, H-5, H-6), 4.02 (t, 1 H, $^{3}J_{H5-H6}$ =, $^{3}J_{H5-H4}$ = 9.9 Hz, H-5), 4.94 (d, 1 H, $^{3}J_{H1-H2}$ = 3.3 Hz, H-1), 4.96 (d, 1 H, $^{3}J_{H1-H2}$ = 3.3 Hz, H-1), 5.00–5.03 (3 H, H-1), 5.04 (d, 1 H, $^{3}J_{H1-H2}$ = 3.3 Hz, H-1) ppm; $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$, 25ºC): δ (partial assignment by combined HSQC) = 47.20, 54.60 (C-$6^{A,B}$), 57.61, 57.72 [×2], 57.77 [×2], 58.33, 58.83, 58.88 [×3], 61.35, 61.55 [×2], 61.68, 61.88, 61.98 (OMe), 70.71, 70.97, 71.08 (C-5), 71.11 (C-6), 71.16 [×2], 71.18 (C-5), 71.19, 71.27, 71.60 (C-6), 81.09, 81.14 [×2], 81.23 [×2], 81.28, 81.55, 81.59, 81.76 [×2], 81.86, 82.09, 82.15 [×2], 82.36, 83.94 [×2], 86.28 (C-2, C-3, C-4), 96.95, 99.05, 99.47, 99.57, 99.63, 99.86 (C-1) ppm; elemental analysis (%) calcd for $C_{52}H_{91}NO_{28}$ (1178.28) : C 53.01, H 7.78, N 1.19 found C 53.42, H 7.81, N 1.17; MS (ESI-TOF): *m/z* (%): 1178.58 (100) $[M + H]^{+}$.

6^{A},6^{B}-dideoxy-6^{A},6^{B}-aza-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},2^{G},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},3^{G},6^{C},6^{D},6^{E},6^{F},6^{G}-nonadeca-*O*-methyl-β-cyclodextrin (8)

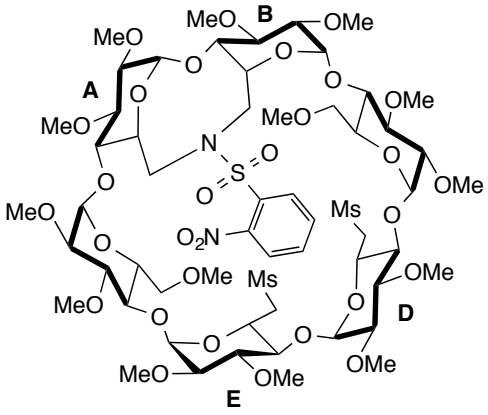


8 (colourless solid, 90 mg, 82%) was synthesized from **6** (125 mg, 0.09 mmol), Cs_2CO_3 (42 mg, 0.13 mmol) and thiophenol (12 mg, 11 μL, 0.11 mmol) in acetonitrile (3mL) according to the above procedure.

R_f (SiO_2, CH_2Cl_2/MeOH, 90:10, *v*/*v*) = 0.36; ^{1}H NMR (500.1 MHz, $CDCl_3$, 25ºC): δ (partial assignment by COSY) = 2.75 (1 H, H-$6a^{A\ or\ B}$), 3.12 (dd, 1 H, $^{3}J_{H2-H3}$ = 9.8 Hz, $^{3}J_{H2-H1}$ = 3.4 Hz, H-2), 3.15–3.21 (5 H, H-2), 3.30 (t, 1 H, $^{3}J_{H4-H5}$ = $^{3}J_{H4-H3}$ = 8.9 Hz, H-$4^{A\ or\ B}$), 3.37 (s, 9 H, OMe), 3.38 (s, 6 H, OMe), 3.47 (s, 3 H, OMe), 3.48 (s, 3 H, OMe), 3.49 (s, 3 H, OMe), 3.50 (s, 3 H, OMe), 3.51 (s, 3 H, OMe), 3.52 (s, 3 H, OMe), 3.53 (s, 3 H, OMe), 3.60 (s, 3 H, OMe), 3.62 (s, 6 H, OMe), 3.63 (s, 6 H, OMe), 3.64 (s, 3 H, OMe), 3.65 (s, 3 H, OMe), 3.33–3.68 (23 H, H-2, H-3, H-4, H-5, H-6), 3.75–3.90 (10 H, H-5, H-6), 3.99 (1 H, H-5), 4.96 (d, 1 H, $^{3}J_{H1-H2}$ = 3.0 Hz, H-1), 5.01 (d, 1 H, $^{3}J_{H1-H2}$ = 3.0 Hz, H-1), 5.03 (d, 1 H, $^{3}J_{H1-H2}$ = 4.3 Hz, H-1), 5.09 (d, 1 H, $^{3}J_{H1-H2}$ = 3.5 Hz, H-1), 5.13 (d, 1 H, $^{3}J_{H1-H2}$ = 3.5 Hz, H-1), 5.14–5.17 (2 H, H-1) ppm; $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$, 25ºC): δ (partial assignment by combined HSQC) =

47.48, 54.33 (C-$6^{A,B}$), 58.08, 58.18, 58.40 [×2], 58.43 [×2], 58.61, 58.92, 58.98 [×4], 61.16, 61.21 [×2], 61.29 [×2], 61.46, 61.55 (OMe), 70.74 [×4], 70.79 [×2], 70.99 (C-5), 71.02 [×2], 71.11, 71.22, 71.38 (C-6), 79.53, 80.05, 80.22, 80.30 [×3], 81.01, 81.40, 81.44, 81.58, 81.66, 81.77 [×3], 81.86 [×3], 82.00 [×3], 82.06 (C-2, C-3, C-4), 97.59, 98.20, 98.68, 98.87, 98.95, 99.08, 99.52 (C-1) ppm; elemental analysis (%) calcd for $C_{61}H_{107}NO_{33}$•1.5$CHCl_3$ (1382.50 + 179.07) : C 48.07, H 7.00, N 0.90 found C 48.22, H 7.05, N 0.93; MS (ESI-TOF): *m/z* (%): 1382.67 (100) $[M + H]^+$.

6^A,6^B-dideoxy-6^A,6^B-*N*-[(2-nitrophenyl)sulfonyl]aza-6^D,6^E-di-*O*-(methylsulfonyl)-2^A,2^B, 2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^C,6^D,6^E,6^F-tetradeca-*O*-methyl-α-cyclodextrin (10)



Potassium carbonate (151 mg, 1.09 mmol) was added to a solution of tetramesylate **9** (273 mg, 0.181 mmol) and 2-nitrobenzenesulfonamide (74 mg, 0.363 mmol) in anhydrous DMF (5 mL). The reaction mixture was stirred for 15 h at 80°C, whereupon it was evaporated to dryness *in vacuo*. The residue was then retaken in $CHCl_3$ (100 mL) and the organic solution washed twice with distilled water (2 x 100 mL) and once with saturated NaCl solution (50 mL) before being dried ($MgSO_4$) and evaporated to dryness *in vacuo* to afford a yellow residue which was subjected to column chromatography (SiO_2, CH_2Cl_2/MeOH, 97 :3, then 95:5) to give **10** (209 mg, 77 %) as a colourless solid.

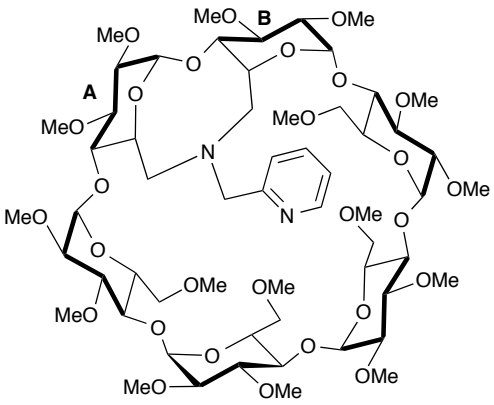
R_f (SiO_2, CH_2Cl_2/MeOH, 95:5, *v*/*v*) = 0.32; ^{1}H NMR (400.1 MHz, $CDCl_3$, 25ºC): δ (partial assignment by COSY, HSQC, HMBC, ROESY): 2.91 (s, 3 H, SO_2Me), 2.96 (s, 3 H, SO_2Me), 3.08 (1H, H-$6b^B$), 3.09 (1H, H-2^A), 3.17 (1H, H-4^A), 3.37 (1H, H-4^B), 3.39 (s, 3 H, OMe), 3.41 (s, 3 H, OMe), 3.47 (s, 6 H, OMe), 3.48 (s, 3 H, OMe), 3.50 (7 H, H-2^B, H-3^A, H-3^B, H-$6a^A$, OMe), 3.51 (s, 3 H, OMe), 3.52 (s, 3 H, OMe), 3.57 (s, 3 H, OMe), 3.60 (s, 3 H, OMe), 3.61 (s, 3 H, OMe), 3.63 (s, 3 H, OMe), 3.65 (s, 6 H, OMe), 3.71 (s, 3 H, OMe), 3.87 (d, 1 H, H-$6b^A$), 4.05 (d, 1 H, $^2J_{H6b\text{-}H6a}$ = 13.2 Hz, H-$6a^B$), 4.22 (t, 1 H, $^2J_{H5\text{-}H6a}$ = $^2J_{H5\text{-}H6b}$ = 9 Hz, H-5^B), 4.27 (1H, H-5^A), 3.04–4.48 (24 H, H-2, H-3, H-4, H-5, H-6), 5.00 (H-1^B), 5.02 (H-1^A), 5.00–5.03 (3 H, H-1), 5.06 (d, 1 H, $^3J_{H1\text{-}H2}$ = 3.4 Hz, H-1), 7.66–7.84 (4 H, aromatic-H) ppm; $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25ºC): δ (assignment by combined HSQC and HMBC): 36.9 (SO_2Me), 36.99 (SO_2Me), 50,12 (C-6^B), 54.70 (C-6^A), 57.78, 57.85, 58.00, 58.19, 58.34, 59.05, 59.09, 59.50, 60.87, 61.76, 61.78, 61.86, 61.92, 61.99 (OMe), 60.16 (C-5), 69.44 (C-

6), 69.53 (C-5), 69.67 (C-6), 69.79 (C-5), 70.85 (C-6), 71.14 (C-6), 70.85 (C-5), 71.14 (C-5), 74.98 (C-5), 79.94, 80.73, 81.20 [x2], 81.26, 81.39, 81.44, 81.53 [x2], 81.87 [x2], 82.02 [x3], 82.29, 82.35, 83.90, 86.22 (C-2, C-3, C-4), 96.65, 97.53, 99.35, 100.44, 100.63, 100.82 (C-1), 124.76, 130.61, 132.17, 132.36, 133.88, 148.14 (C arom.) ppm; elemental analysis (%) calcd for $C_{58}H_{94}N_2O_{36}S_3 \bullet H_2O$ (1491.55 + 18.01): C 46.15, H 6.41, N 1.86 found: C 46.25, H 6.36, N 1.78; MS (ESI-TOF): *m/z* (%): 1513.50 (100) $[M + Na]^+$, 1508.54 (20) $[M + NH_4]^+$.

Full ^{1}H NMR assignement of glucose units A and B of compound **10** was achieved by COSY, HSQC, TOCSY and ROESY.

	H-1	H-2	H-3	H-4	H-5	H-6a	H-6b
Unit A	5.02	3.09	3.50	3.17	4.27	3.50	3.87
Unit B	5.00	3.46	3.50	3.37	4.22	4.05	3.08

6^A,6^B-dideoxy-6^A,6^B-*N*-(pyridin-2-ylmethyl)-(*S*)-aza-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F, 6^C,6^D,6^E,6^F-hexadeca-*O*-methyl-α-cyclodextrin (11a)

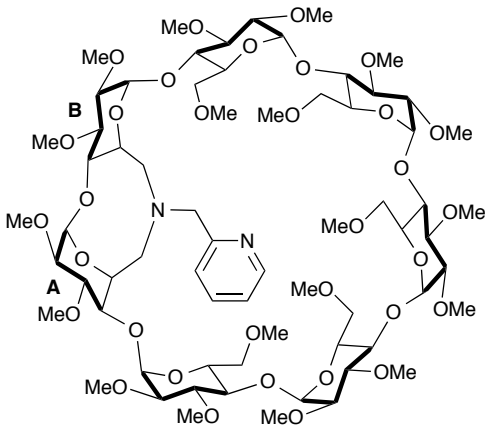


To a solution of 2-pyridinecarboxaldehyde (15 mg, 13 μL, 0.14 mmol) and **7** (150 mg, 0.13 mmol) in a mixture of methanol (5 mL) and acetic acid (30 μl, 0.52 mmol) were added sodium cyanoborohydride ($NaBH_3CN$) (10 mg, 0.16 mmol). The yellow solution was stirred for 3 h at room temperature. If necessary, extra $NaBH_3CN$ (10 mg, 0.16 mmol) and 2-pyridinecarboxaldehyde (7 mg, 6 μL, 0.7 mmol) were added to complete the reaction. The suspension was then evaporated to dryness *in vacuo*. The residue was dissolved in dichloromethane (CH_2Cl_2) (50 mL) and the organic solution washed with aqueous 2M NaOH (3 × 50 mL) and dried (Na_2SO_4). Finally the solvent was removed *in vacuo*. The residue was retaken in toluene (50 mL) and refluxed for 2 h before being evaporated to dryness *in vacuo*. The residue subjected to column chromatography (SiO_2; CH_2Cl_2/MeOH, 97:3, *v/v*) to afford **11a** (137 mg, 83%) as a colourless solid.

R_f (SiO_2, CH_2Cl_2/MeOH, 90:10, *v/v*) = 0.56; ^{1}H NMR (500.13 MHz, $CDCl_3$, 25ºC): δ (partial assignment by COSY, HSQC and ROESY) = 2.86 (dd, 1 H, $^2J_{H6a\text{-}H6b}$ = 12.8 Hz, $^3J_{H6\text{-}H5}$ = 8.8 Hz, H-6$_a^{A \text{ or } B}$), 3.04 (d, 1 H, $^2J_{H6a\text{-}H6b}$ = 15.7 Hz, H-6$_a^{B \text{ or } A}$), 3.08 (dd, 1 H, $^3J_{H2\text{-}H1}$ = 3.1 Hz,

$^{3}J_{H2\text{-}H3}$ = 10 Hz, H-2), 3.13 (s, 3 H, OMe), 3.18 (s, 3 H, OMe), 3.37 (s, 3 H, OMe), 3.40 (s, 3 H, OMe), 3.45 (s, 3 H, OMe), 3.47 (s, 6 H, OMe), 3.48 (s, 3 H, OMe), 3.50 (s, 3 H, OMe), 3.52 (s, 3 H, OMe), 3.60 (s, 3 H, OMe), 3.61 (s, 3 H, OMe), 3.62 (s, 3 H, OMe), 3.64 (s, 3 H, OMe), 3.66 (s, 3 H, OMe), 3.69 (s, 3 H, OMe), 3.10–3.88 (31 H, H-2, H-3, H-4, H-5, H-6), 3.90 (d, 1 H, ^{2}J = 15.9 Hz, -CH_2Py), 4.01 (d, 1 H, ^{2}J = 15.9 Hz, -CH_2Py), 4.11 (dd, 1 H, $^{3}J_{H5\text{-}H4}$ = 9.1 Hz, $^{3}J_{H5\text{-}H6}$ = 5.0 Hz, H-5), 4.16 (dd, 1 H, $^{3}J_{H5\text{-}H4}$ = 10.4 Hz, $^{3}J_{H5\text{-}H6}$ = 8.8 Hz, H-5), 4.90 (d, 1 H, $^{3}J_{H1\text{-}H2}$ = 3.2 Hz, H-1), 4.96 (d, 1 H, $^{3}J_{H1\text{-}H2}$ = 3.0 Hz, H-1), 5.01 (d, 1 H, $^{3}J_{H1\text{-}H2}$ = 3.3 Hz, H-1), 5.03 (d, 1 H, $^{3}J_{H1\text{-}H2}$ = 4.8 Hz, H-1), 5.04 (d, 1 H, $^{3}J_{H1\text{-}H2}$ = 3.3 Hz, H-1), 5.08 (d, 1 H, $^{3}J_{H1\text{-}H2}$ = 3.2 Hz, H-1), 7.14 (1 H, aromatic-H), 7.31 (1 H, aromatic-H), 7.60 (1 H, aromatic-H), 8.53 (1 H, aromatic-H) ppm; $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$, 25ºC): δ (partial assignment by HSQC) = 53.55 (C-$6^{A\text{ or }B}$), 57.86, 57.90, 57.93, 58.04 [×2], 58.13, 58.85, 58.98, 59.13, 59.21 (OMe), 60.89 (-CH$_2$Py), 61.62, 61.71, 61.75, 61.89, 62.11, 62.14 (OMe), 63.87 (C-$6^{B\text{ or }A}$), 69.80 (C-5), 71.03, 71.21 (C-6), 71.36, 71.43 (C-5), 71.45 (C-6), 71.51 (C-5), 71.61 (C-6), 71.64, 75.83 (C-5), 81.19 [×3], 81.35, 81.41, 81.50 [×2], 81.62, 82.16 [×3], 82.30, 82.45, 82.57, 82.67, 84.13, 84.22, 86.08 (C-2, C-3, C-4), 97.00, 98.74, 100.07, 100.21, 100.26, 100.44 (C-1), 121.78, 121.91, 136.20, 149.35, 160.52 (C aromatic) ppm; elemental analysis (%) calcd for $C_{58}H_{96}N_2O_{28}$•0.66 CH_2Cl_2 (1269.39 + 56.05): C 53.14, H 7.40, N 2.11 found: C 53.12, H 7.31, N 2.07; MS (ESI-TOF): *m/z* (%): 1269.63 (100) [M + H]$^{+}$.

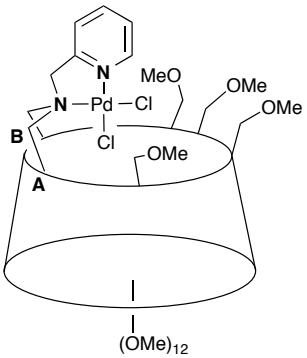
6^{A},6^{B}-dideoxy-6^{A},6^{B}-*N*-(pyridin-2-ylmethyl)aza-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},2^{G},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},3^{G}, 6^{C},6^{D},6^{E},6^{F},6^{G}-nonadeca-*O*-methyl-β-cyclodextrin (12a/b)



12a/b (colourless solid, 239 mg, 90%) was synthesized from 2-pyridinecarboxaldehyde (21 mg, 19 μL, 0.20 mmol), $NaBH_3CN$ (14 mg, 0.22 mmol) and **8** (249 mg, 0.18 mmol) in a mixture of methanol (8 mL) and acetic acid (41 μl, 0.72 mmol) according to the above procedure. R_f (SiO_2, CH_2Cl_2/MeOH, 90:10, *v*/*v*) = 0.45; ^{1}H NMR (500.13 MHz, $CDCl_3$, 25ºC): δ (partial assignment by COSY and HSQC) = 2.71 (dd, 1 H, $^{2}J_{H6a\text{-}H6b}$ = 11.8 Hz, $^{3}J_{H6\text{-}H5}$ = 10.0 Hz, H-$6a^{A\text{ or }B}$), 3.04 (dd, 1 H, $^{3}J_{H2\text{-}H1}$ = 3.0 Hz, $^{3}J_{H2\text{-}H3}$ = 9.7 Hz, H-2), 3.23 (s, 3 H, OMe), 3.24 (s, 3 H, OMe), 3.28 (s, 3 H, OMe), 3.34 (s, 3 H, OMe), 3.35 (s, 3 H, OMe), 3.41 (s, 3 H, OMe), 3.43 (s, 3 H, OMe), 3.44 (s, 3 H,

OMe), 3.45 (s, 3 H, OMe), 3.47 (s, 3 H, OMe), 3.48 (s, 3 H, OMe), 3.51 (s, 3 H, OMe), 3.58 (s, 6 H, OMe), 3.59 (s, 6 H, OMe), 3.60 (s, 3 H, OMe), 3.62 (s, 3 H, OMe), 3.63 (s, 3 H, OMe), 3.07–3.84 (39 H, H-2, H-3, H-4, H-5, H-6), 3.93 (d, 1 H, ^{2}J = 15.5 Hz, -CH_2Py), 4.05 (d, 1 H, ^{2}J = 15.5 Hz, -CH_2Py), 4.10 (dd, 1 H, $^{3}J_{H5\text{-}H4}$ = 9.9 Hz, $^{3}J_{H5\text{-}H6}$ = 10.0 Hz, H-5), 4.87 (d, 1 H, $^{3}J_{H1\text{-}H2}$ = 2.1 Hz, H-1), 4.90 (d, 1 H, $^{3}J_{H1\text{-}H2}$ = 2.4 Hz, H-1), 5.04 (1 H, H-1), 5.05 (1 H, H-1), 5.07 (d, 1 H, $^{3}J_{H1\text{-}H2}$ = 3.1 Hz, H-1), 5.10 (d, 1 H, $^{3}J_{H1\text{-}H2}$ = 2.9 Hz, H-1), 5.12 (d, 1 H, $^{3}J_{H1\text{-}H2}$ = 2.8 Hz, H-1), 7.12 (1 H, aromatic-H), 7.46 (1 H, aromatic-H), 7.61 (1 H, aromatic-H), 8.50 (1 H, aromatic-H) ppm; $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$, 25ºC): δ (partial assignment by HSQC) = 54.09 (C-6$^{A\text{ or }B}$), 58.06, 58.25, 58.41, 58.48 [×2], 58.66, 58.70, 58.95 [×2], 59.01, 59.10, 59.13, 61.30, 61.33, 61.39, 61.46, 61.49, 61.63, 61.72 (OMe), 65.29 (-*C*H_2Py), 70.82 (C-5), 70.91 (C-6), 71.04 [×3], 71.08[×2], 71.17 [×2], 71.22 [×2], (C-6, C-5), 71.38, 71.45 (C-6), 79.99 [×2], 80.04 [×2], 80.66, 80.81, 81.56, 81.68 [×2], 81.79, 81.91, 81.96 [×3], 82.24 [×3], 82.50, 82.65, 83.21, 85.40 (C-2, C-3, C-4), 97.45, 98.07, 99.04 [×3], 99.25, 99.55 (C-1), 121.81, 122.42, 136.30, 149.05, 160.36 (C aromatic) ppm; elemental analysis (%) calcd for $C_{67}H_{112}N_2O_{33}$•0.5CH_2Cl_2 (1473.61 + 42.46): C 53.48, H 7.51, N 1.85 found: C 53.49, H 7.44, N 1.61; MS (ESI-TOF): *m/z* (%): 1473.72 (100) $[M + H]^+$.

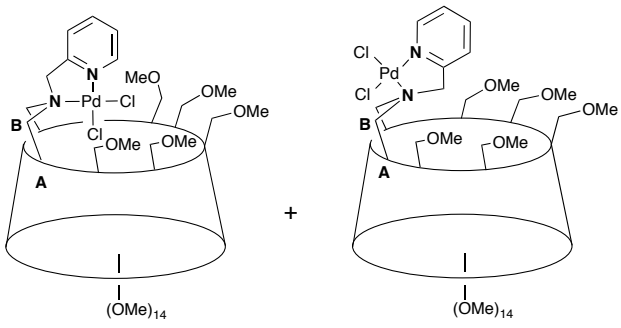
Cis-*N*,*N*'-dichlorido-[6^{A},6^{B}-dideoxy-6^{A},6^{B}-*N*-(pyridin-2-ylmethyl)-(*S*)-aza-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{C},6^{D},6^{E},6^{F}-hexadeca-*O*-methyl-α-cyclodextrin]palladium(II) (13)



[$PdCl_2$(COD)] (12 mg, 0.04 mmol) was added to a solution of **11a** (50 mg, 0.04 mmol) in CH_2Cl_2 (10 mL). The yellow solution was stirred for 3 h whereupon the solvent was removed *in vacuo* and the resulting residue subjected to column chromatography (SiO_2; CH_2Cl_2/MeOH, 95:5, *v/v*) to afford **13** (36 mg, 62%) as a yellow solid. Single crystals suitable for X-ray diffraction were obtained by diffusion of *n*-pentane into a $CHCl_3$ solution of **13**. R_f (SiO_2, CH_2Cl_2/MeOH, 90:10, *v/v*) = 0.38; ^{1}H NMR (500.13 MHz, $CDCl_3$, 25ºC): δ (partial assignment by COSY, TOCSY, HSQC and ROESY) = 2.44-2.50 (2 H, H-6a$^{A\text{ or }B}$), 2.99 (dd, 1 H, $^{3}J_{H2\text{-}H1}$ = 2.8 Hz, $^{2}J_{H2\text{-}H3}$ = 10.1 Hz, H-2), 3.04–3.16 (5 H, H-2, H-4), 3.19 (dd, 1 H, $^{3}J_{H2\text{-}H1}$ = 3.2 Hz, $^{3}J_{H2\text{-}H3}$ = 9.7 Hz, H-2), 3.25 (1 H, H-2), 3.23 (s, 3 H, OMe), 3.39 (s, 3 H, OMe), 3.43 (s, 3 H, OMe), 3.44 (s, 6 H, OMe), 3.45 (s, 3 H, OMe), 3.46 (s, 6 H, OMe), 3.47 (s, 3 H, OMe), 3.52 (s, 3 H, OMe), 3.59 (s, 3 H, OMe), 3.60 (s, 3 H, OMe), 3.62 (s, 3 H, OMe), 3.64 (s, 3 H, OMe), 3.66 (s, 6 H, OMe), 3.36–3.89 (18 H, H-3, H-4, H-6, -CH_2Py), 3.90 (d, 1 H,

$^{2}J_{H6a-H6b}$ = 15.7 Hz, H-6), 4.09 (d, 1 H, $^{3}J_{H5-H6}$ = 10.7 Hz, H-5), 4.10 (d, 1 H, $^{3}J_{H5-H6}$ = 10.1 Hz, H-5), 4.16 (d, 1 H, $^{3}J_{H6-H5}$ = 10.1 Hz, H-6), 4.29 (d, 1 H, $^{3}J_{H6-H5}$ = 10.7 Hz, H-6), 4.41 (d, 1 H, $^{3}J_{H5-H6}$ = 10.0 Hz, H-5), 4.67 (d, 1 H, ^{2}J = 14.4 Hz, -CH_2Py), 4.80 (d, 1 H, $^{3}J_{H6-H5}$ = 13.1 Hz, H-$6_b^{A\ or\ B}$), 4.86 (d, 1 H, $^{3}J_{H5-H6}$ = 10.6 Hz, H-5), 4.91 (2 H, H-1), 4.96 (d, 1 H, $^{3}J_{H6-H5}$ = 10.0 Hz, H-6), 5.02 (d, 1 H, $^{3}J_{H1-H2}$ = 3.1 Hz, H-1), 5.05 (1 H, H-5), 5.08 (2 H, H-1), 5.09 (d, 1 H, $^{3}J_{H1-H2}$ = 3.1 Hz, H-1), 5.59 (d, 1 H, $^{3}J_{H5-H6}$ = 8.9 Hz, H-5), 7.45 (2 H, aromatic-H), 7.95 (1 H, aromatic-H), 9.17 (1 H, aromatic-H) ppm; $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$, 25ºC): δ (assignment by HSQC and HMBC) = 57.42, 57.54, 57.62, 57.73, 57.97, 58.24, 59.08, 59.15, 59.21, 59.83, 61.73, 61.80 [×2], 61.82, 61.87, 62.51 (OMe), 65.28 (C-5), 66.06, 68.36 (C-6), 70.23, 70.70 [×3] (C-5), 71.63, 72.03 (C-6), 72.33 (-CH$_2$Py), 72.66 (C-6), 73.18 (C-5), 73.46 (C-6), 79.85, 80.48, 80.59, 80.89, 81.13, 81.36, 81.66, 82.09, 82.16, 82.27, 82.46, 82.73 [×2], 83.15, 83.24, 83.50, 86.05, 86.59 (C-2, C-3, C-4), 96.53, 97.84, 100.02, 100.29, 100.41, 101.77 (C-1), 122.16, 124.44, 139.99, 150.85, 158.45 (C aromatic) ppm; elemental analysis (%) calcd for $C_{58}H_{96}Cl_2N_2O_{28}Pd$ (1446.71): C 48.15, H 6.69, N 1.94 found: C 48.15, H 6.79, N 1.94; MS (ESI-TOF): *m/z* 1469.45 (100) $[M + Na]^+$.

Cis-_N_,_N_'-dichlorido-[6^{A},6^{B}-dideoxy-6^{A},6^{B}-_N_-(pyridin-2-ylmethyl)-(_S_)-aza-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F}, 2^{G},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},3^{G}, 6^{C},6^{D},6^{E},6^{F},6^{G}-nonadeca-_O_-methyl-β-cyclodextrin] palladium(II) (14a) and **_cis_-_N_,_N_'-dichlorido-[6^{A},6^{B}-dideoxy-6^{A},6^{B}-_N_-(pyridin-2-ylmethyl)-(_R_)-aza-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F}, 2^{G},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},3^{G}, 6^{C},6^{D},6^{E},6^{F},6^{G}-nonadeca-_O_-methyl-β-cyclodextrin] palladium(II) (14b)**



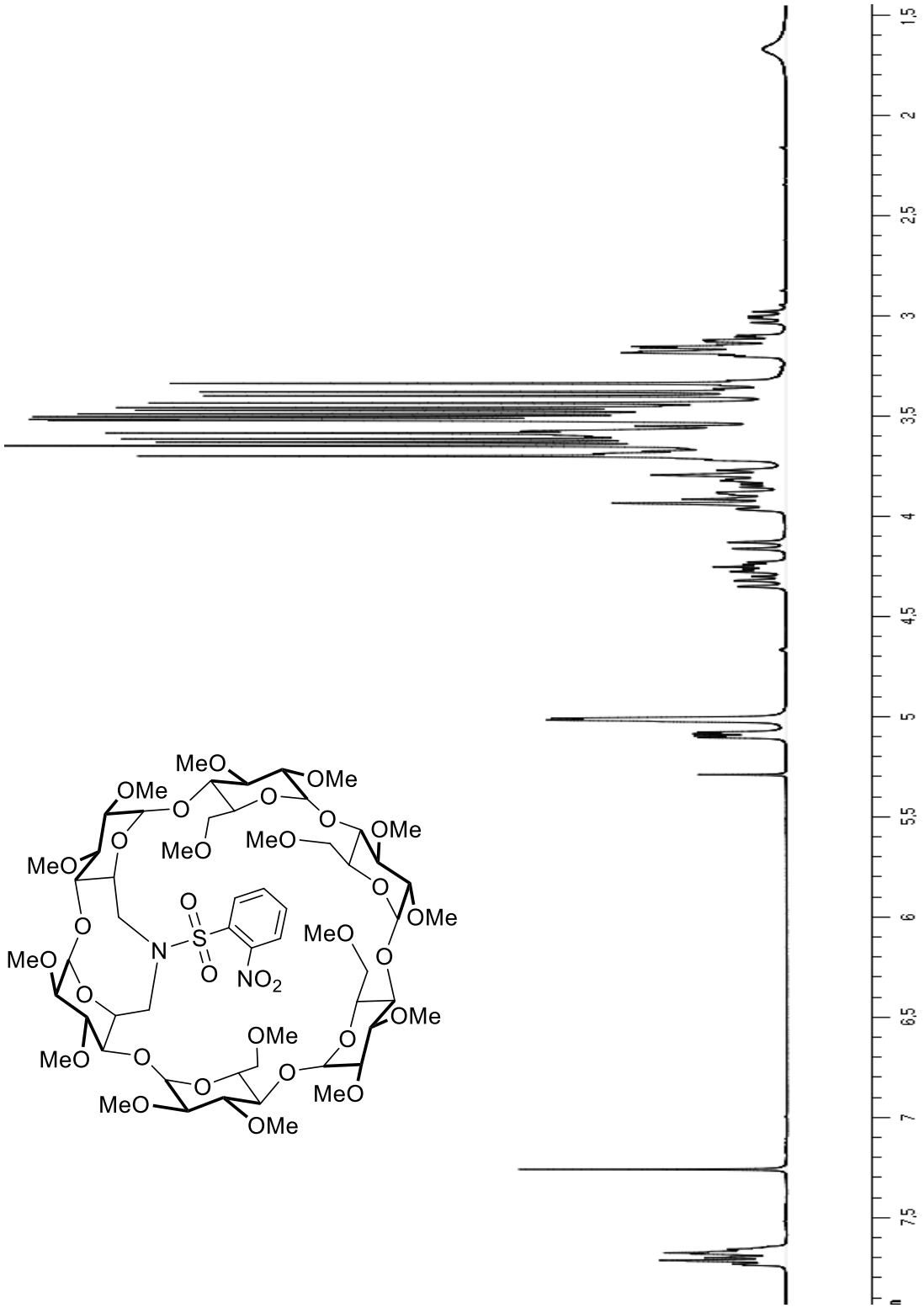
14a **14b**

[$PdCl_2$(COD)] (7 mg, 0.023 mmol) was added to a solution of **12a/b** (33 mg, 0.023 mmol) in CH_2Cl_2 (10 mL). The yellow solution was stirred for 3 h whereupon the solvent was removed *in vacuo* and the resulting residue subjected to column chromatography (SiO_2; CH_2Cl_2/MeOH, 95:5, *v/v*) to afford a 1/1 inseparable mixture (total amount 31 mg) of **14a** (40%) and **14b** (40%) as a yellow solid. Elemental analysis (%) calcd for $C_{67}H_{112}Cl_2N_2O_{33}Pd•C_7H_{16}$ (1648.56 + 100.12): C 50.76, H 7.37, N 1.60 found: C 50.86, H 7.25, N 1.38; (ESI-TOF): *m/z* 1673.55 (100) $[M + Na]^+$. Single crystals of **14a** were obtained by slow diffusion of heptane into a solution of the mixture **14a**/**14b** in CH_2Cl_2.

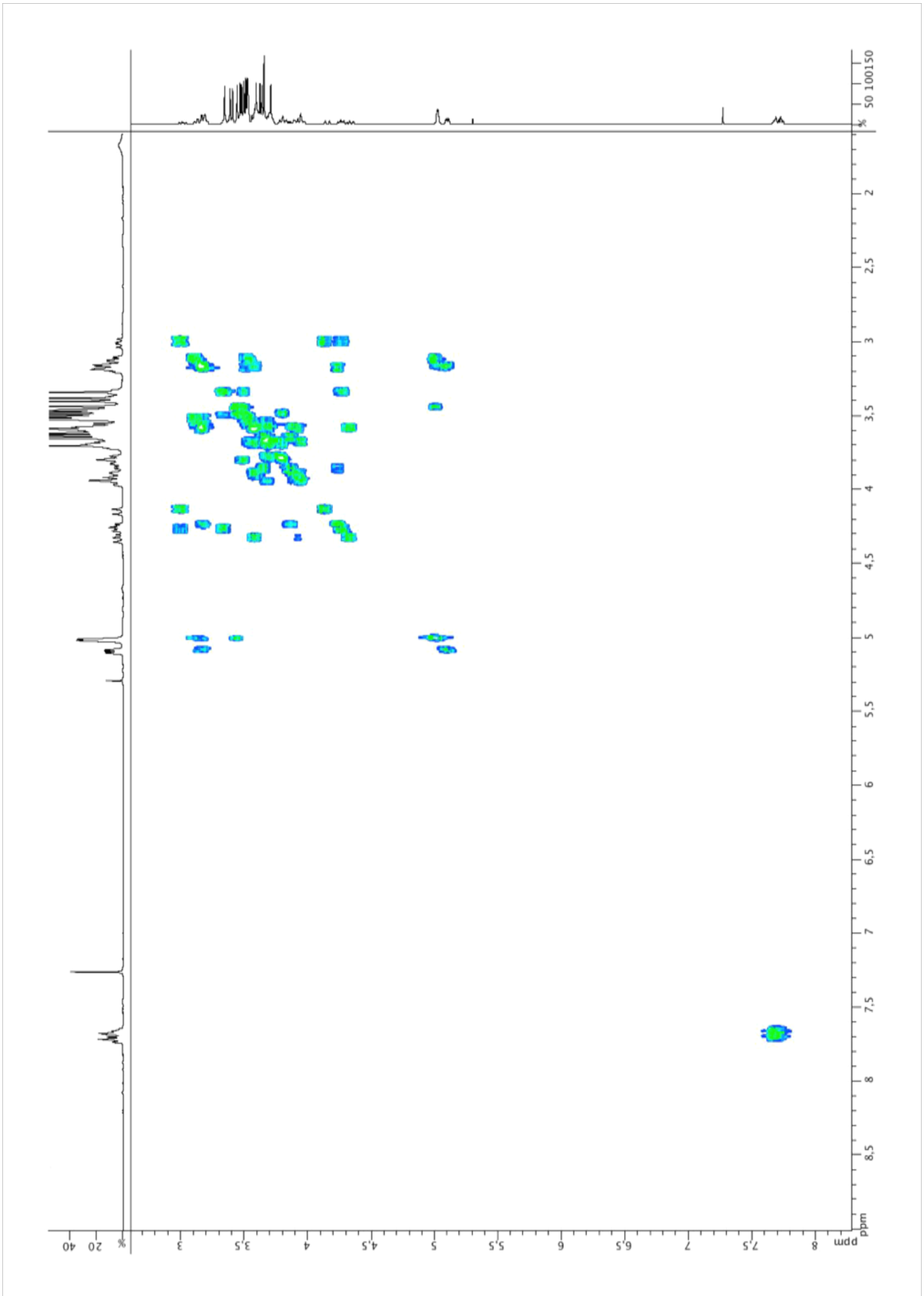
NMR and mass spectra

NMR spectra of all compounds were recorded in $CDCl_3$ at 25 °C except stated otherwise.

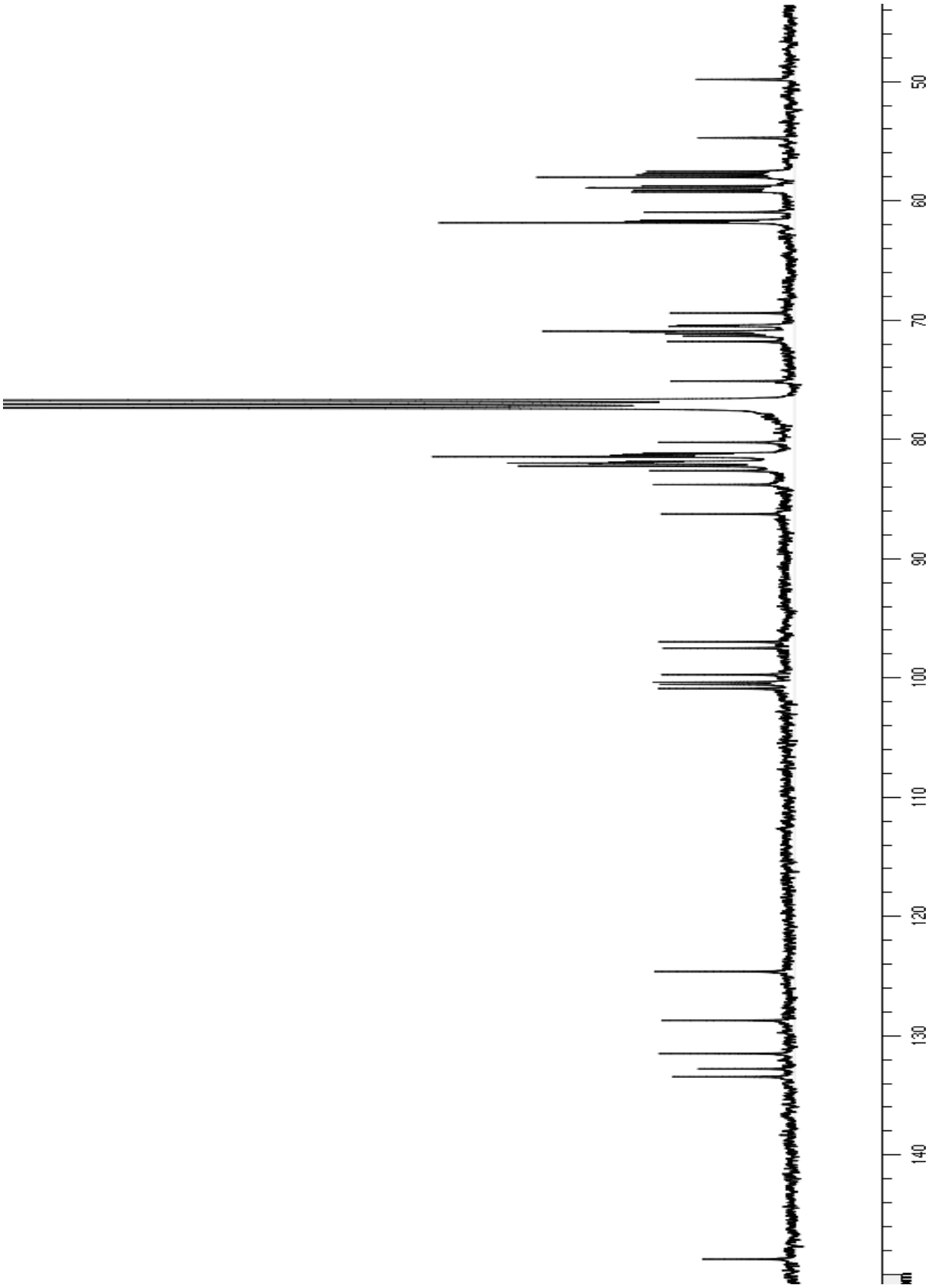
***Cis*-*N*,*N*'-dichlorido-[6^{A},6^{B}-dideoxy-6^{A},6^{B}-*N*-(pyridin-2-ylmethyl)-(*S*)-aza-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F}, 2^{G},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},3^{G}, 6^{C},6^{D},6^{E},6^{F},6^{G}-nonadeca-*O*-methyl-β-cyclodextrin] palladium(II) (14a)** and ***cis*-*N*,*N*'-dichlorido-[6^{A},6^{B}-dideoxy-6^{A},6^{B}-*N*-(pyridin-2-ylmethyl)-(*R*)-aza-2^{A},2^{B},2^{C},2^{D},2^{E},2^{F}, 2^{G},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},3^{G}, 6^{C},6^{D},6^{E},6^{F},6^{G}-nonadeca-*O*-methyl-β-cyclodextrin] palladium(II) (14b)**



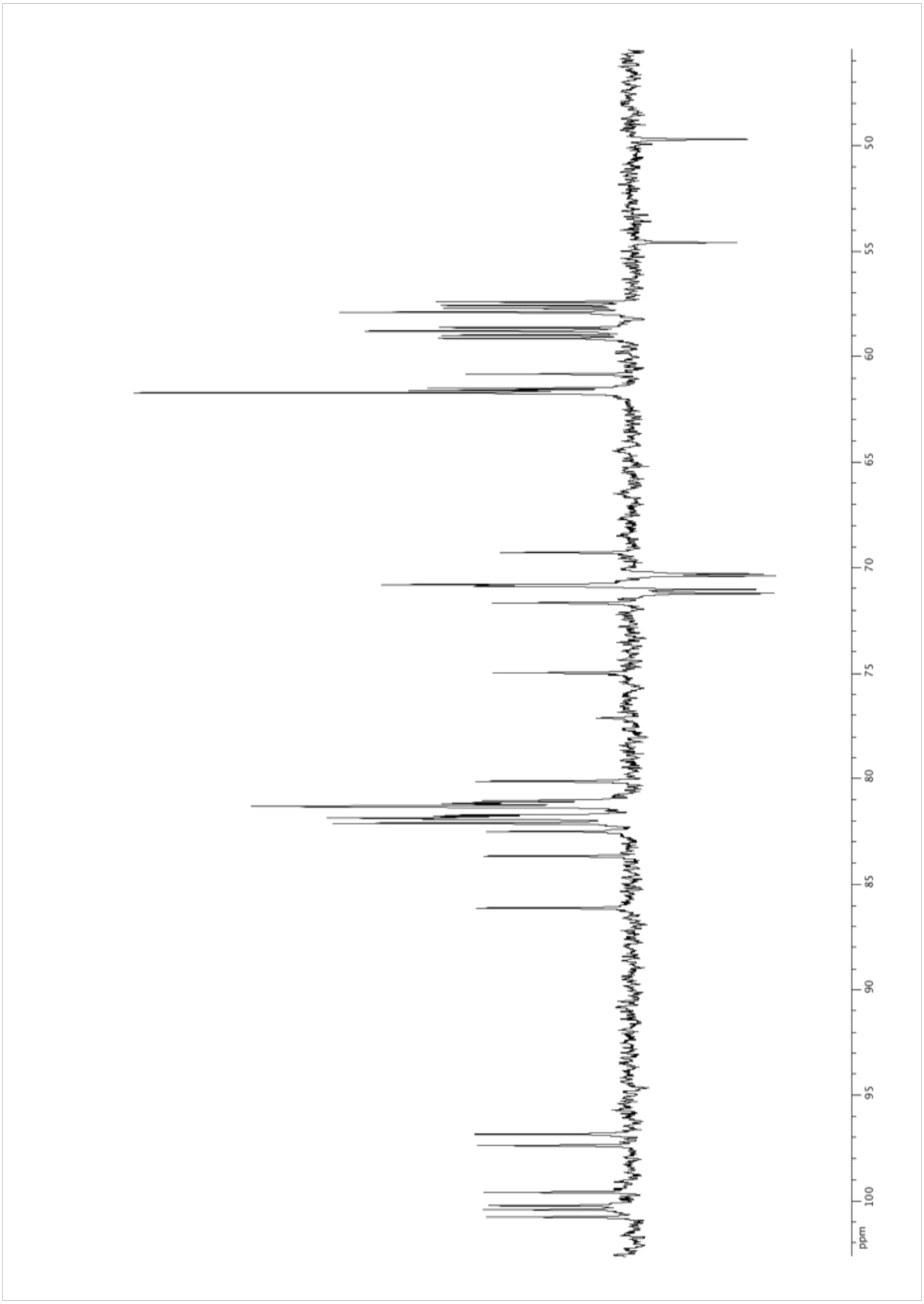
^{1}H NMR spectrum of **3**



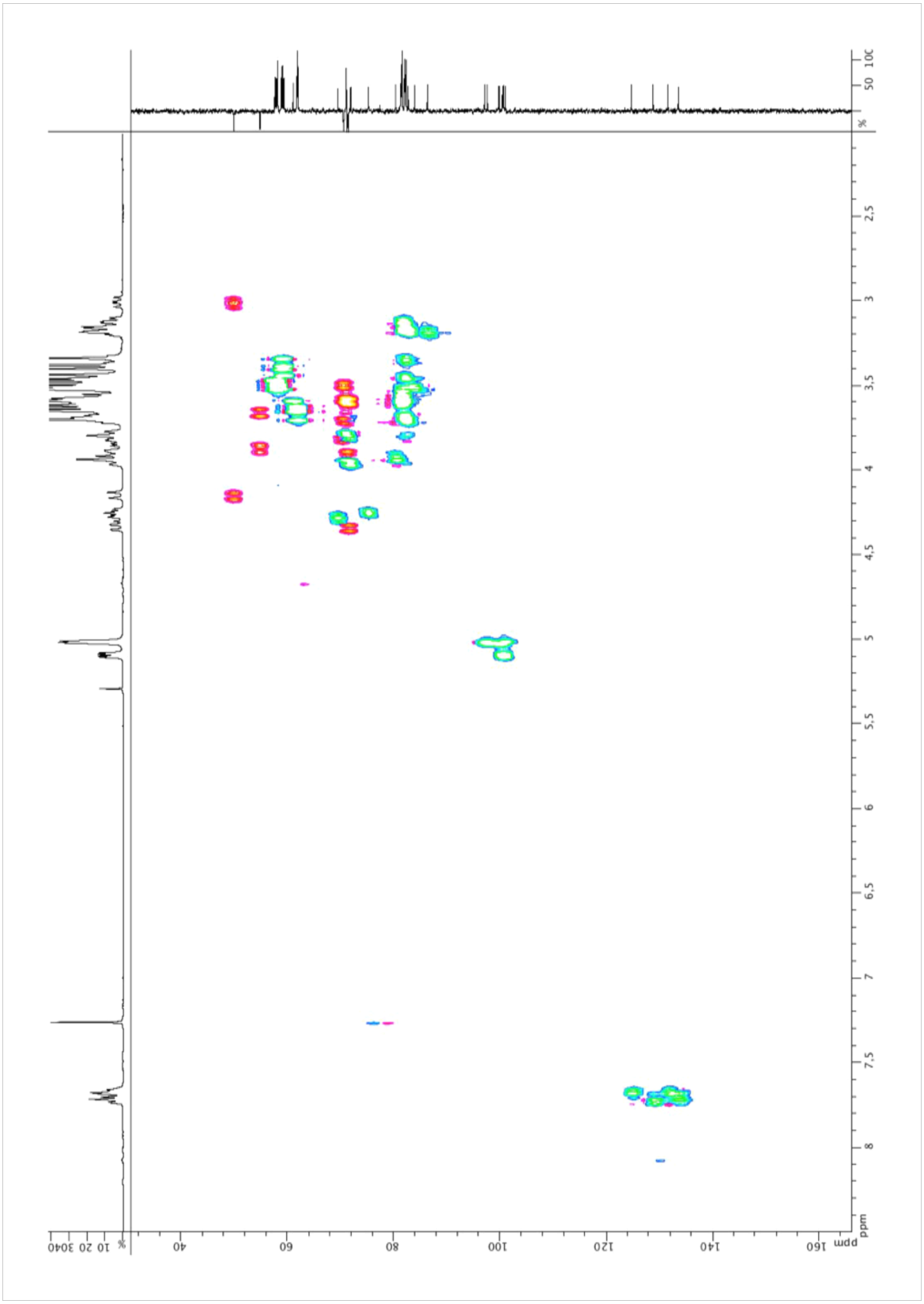
^{1}H-^{1}H COSY NMR spectrum of **3**



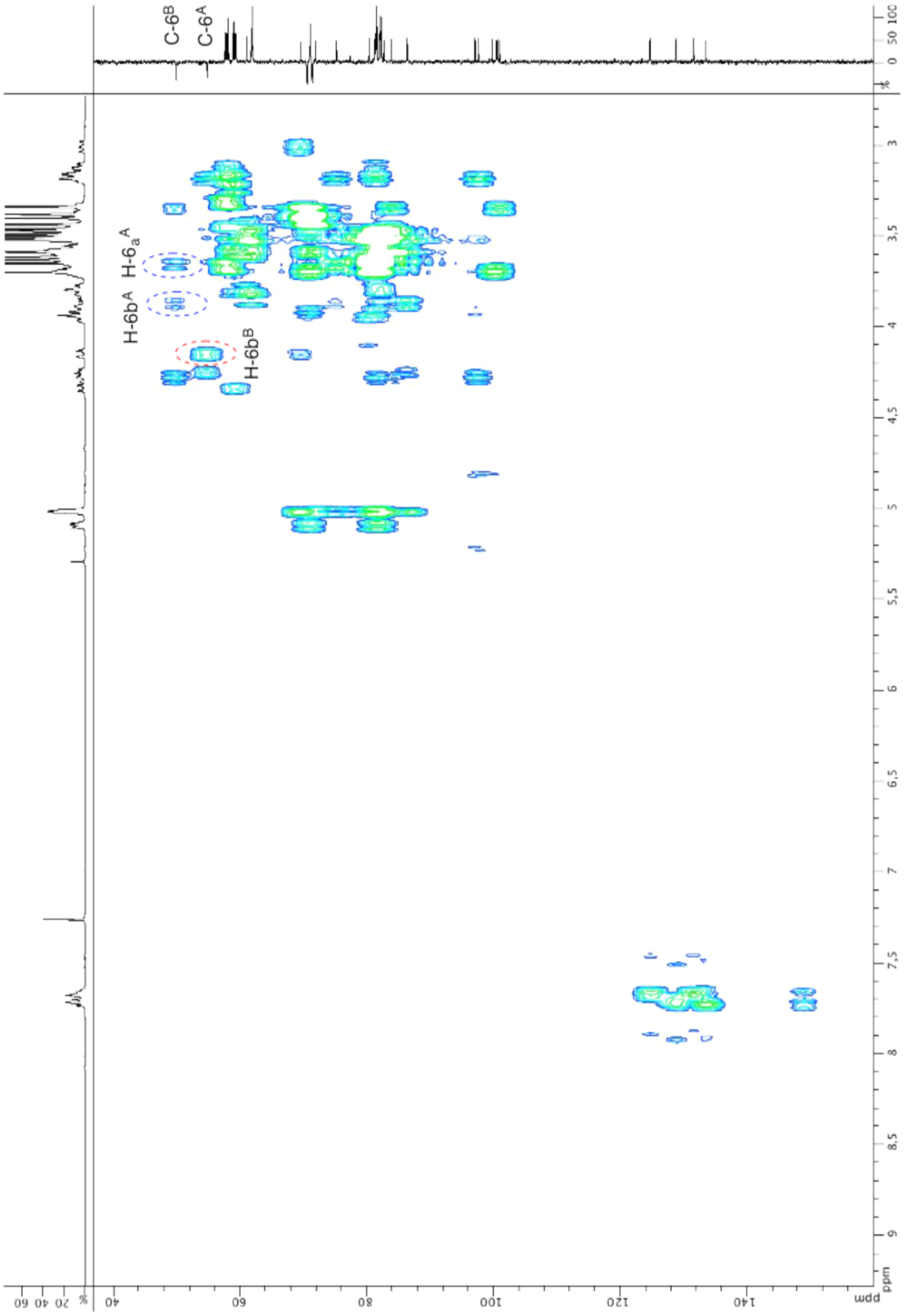
^{13}C NMR spectrum of **3**



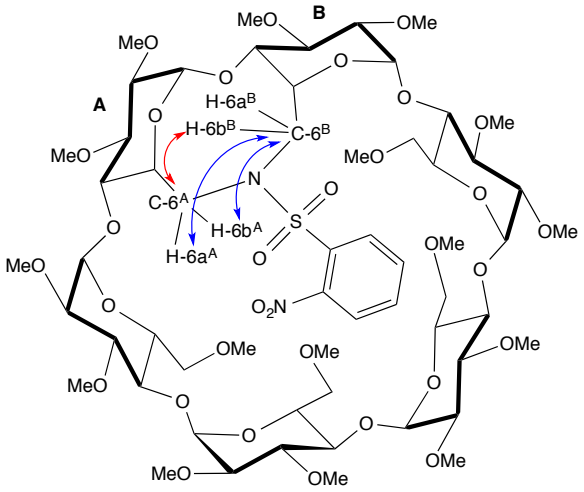
DEPT 135 NMR spectrum of **3**



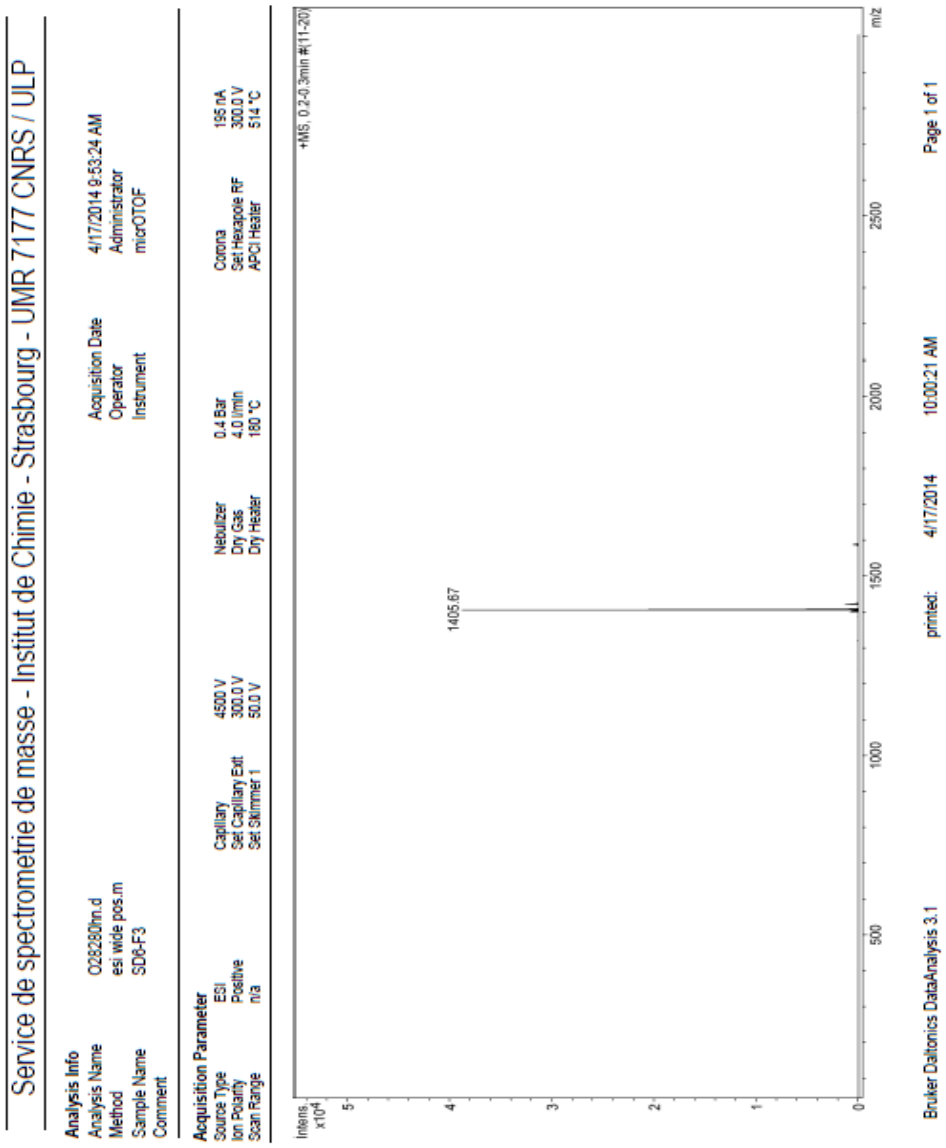
^{1}H-^{13}C Edited HSQC NMR spectrum of **3**



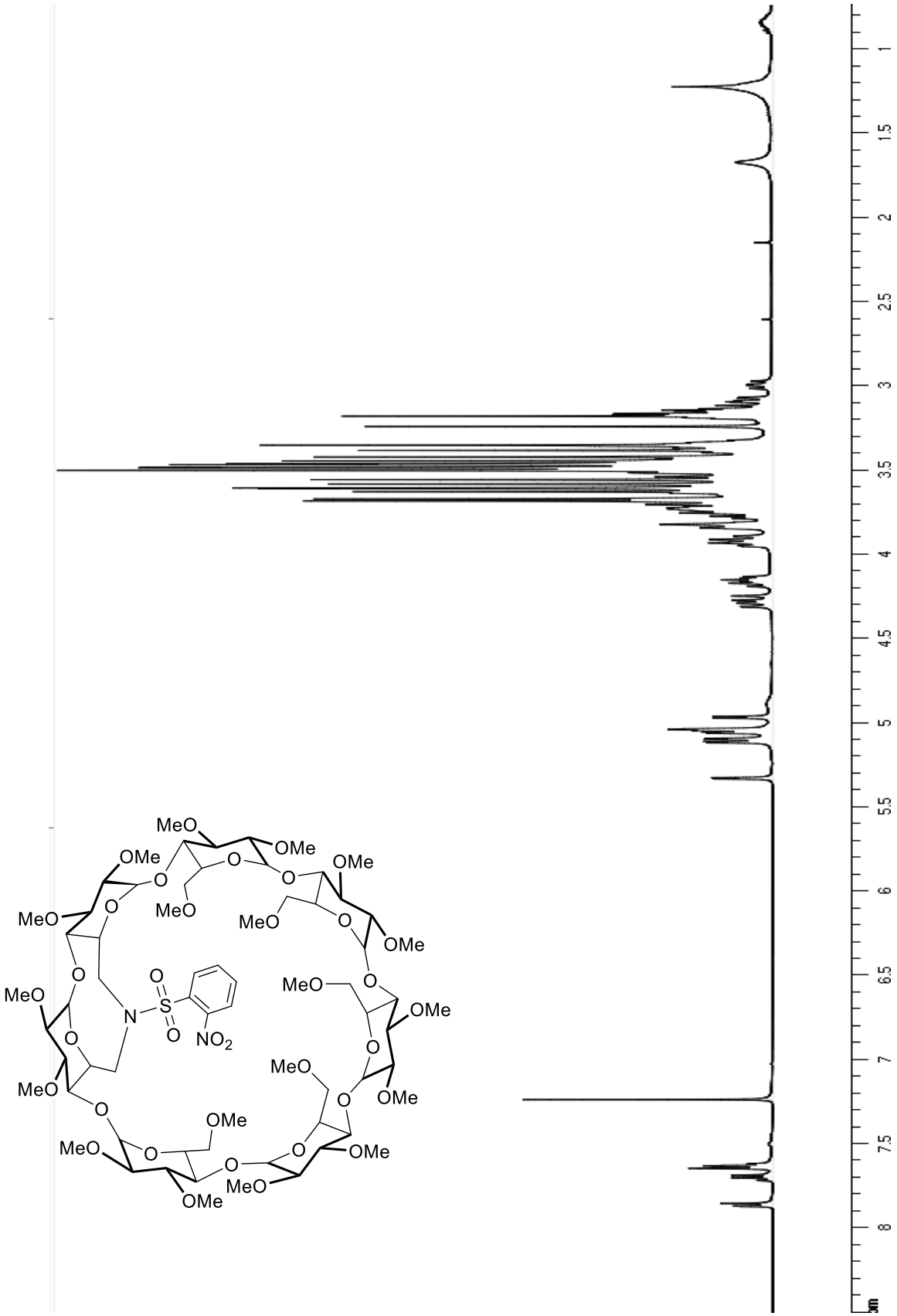
^{1}H-^{13}C HMBC NMR spectrum of **3**



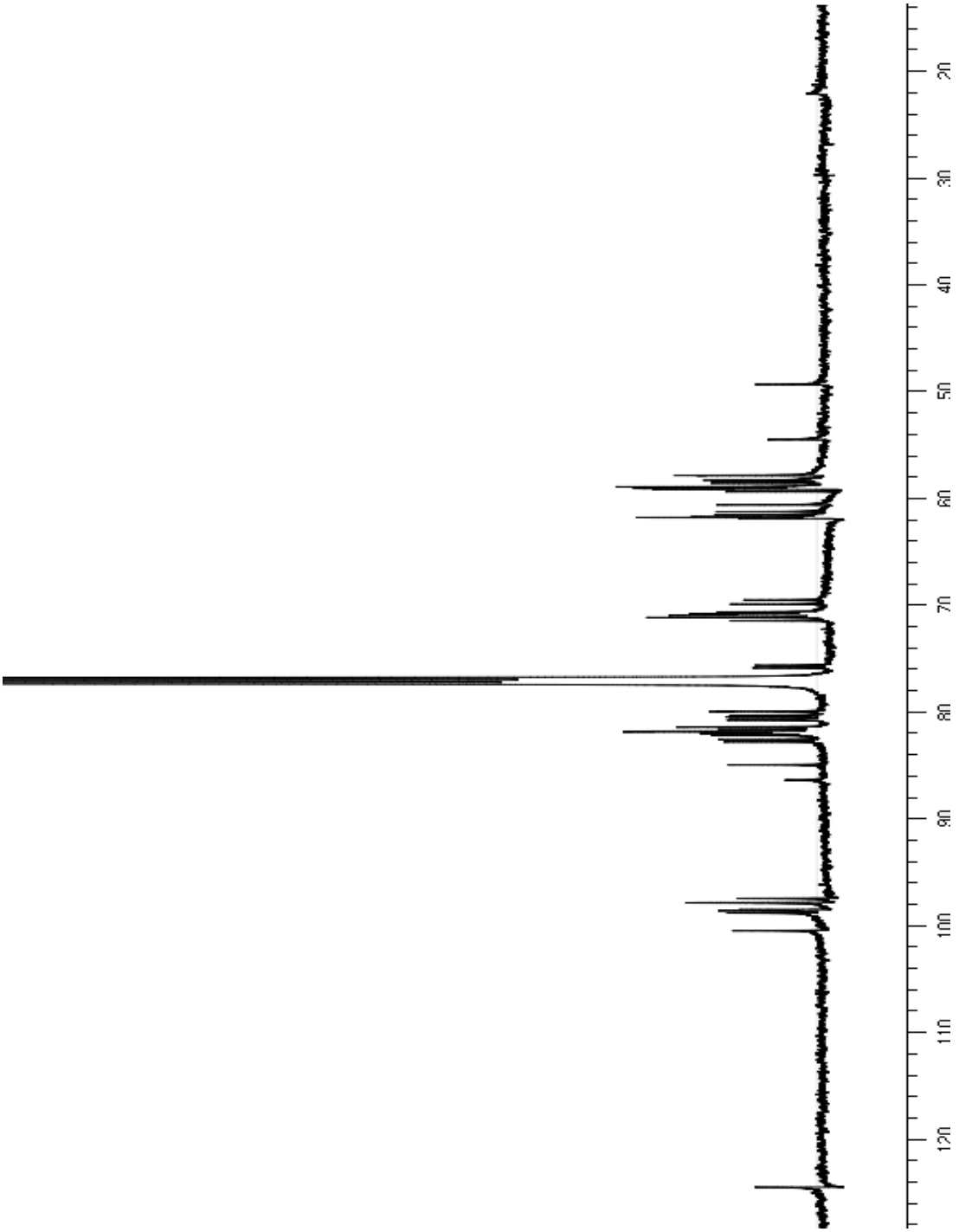
^{1}H-^{13}C HMBC cross-peaks (circled above) proving the presence of the N-bridge in **3**



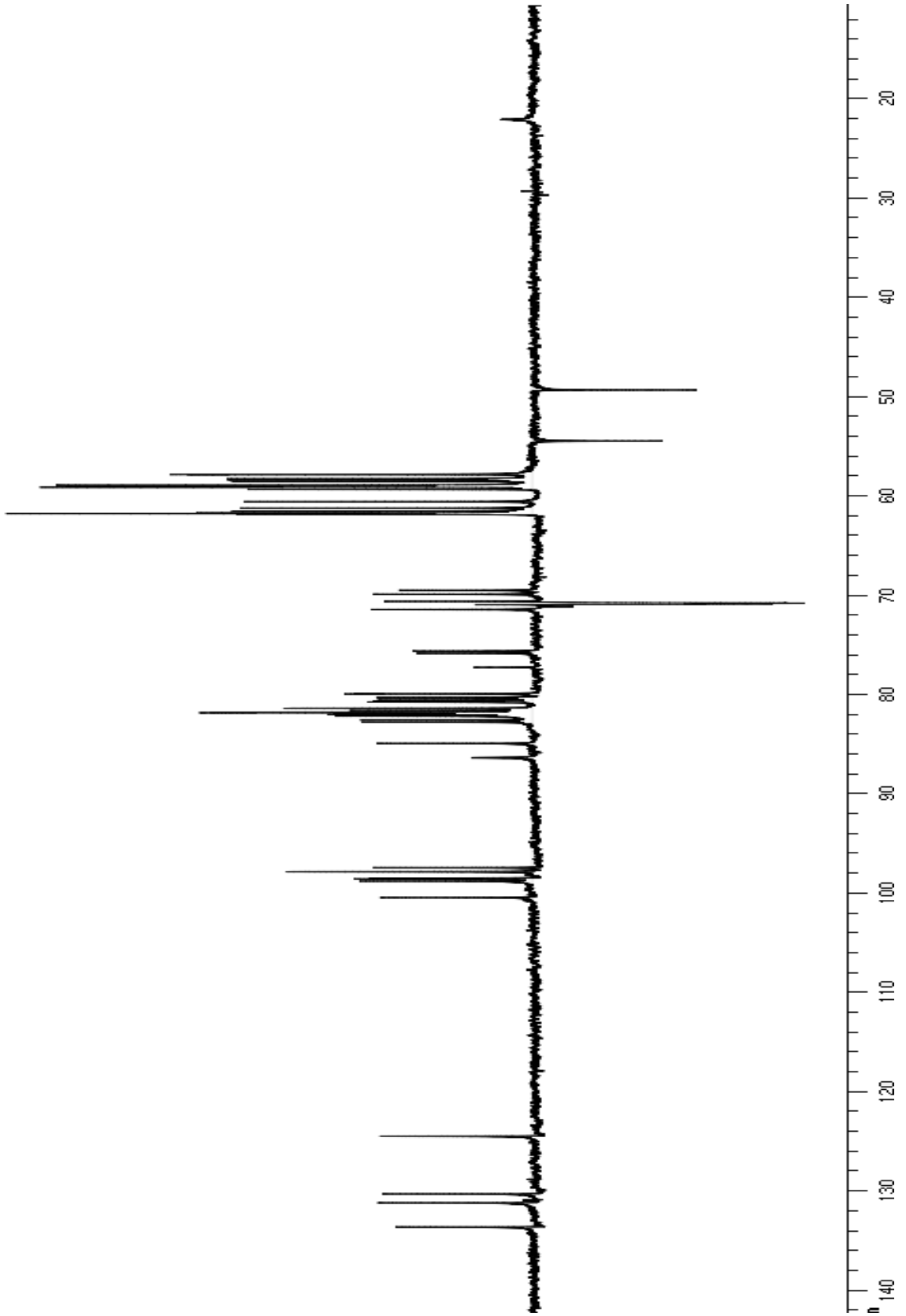
Mass spectrum of **3**



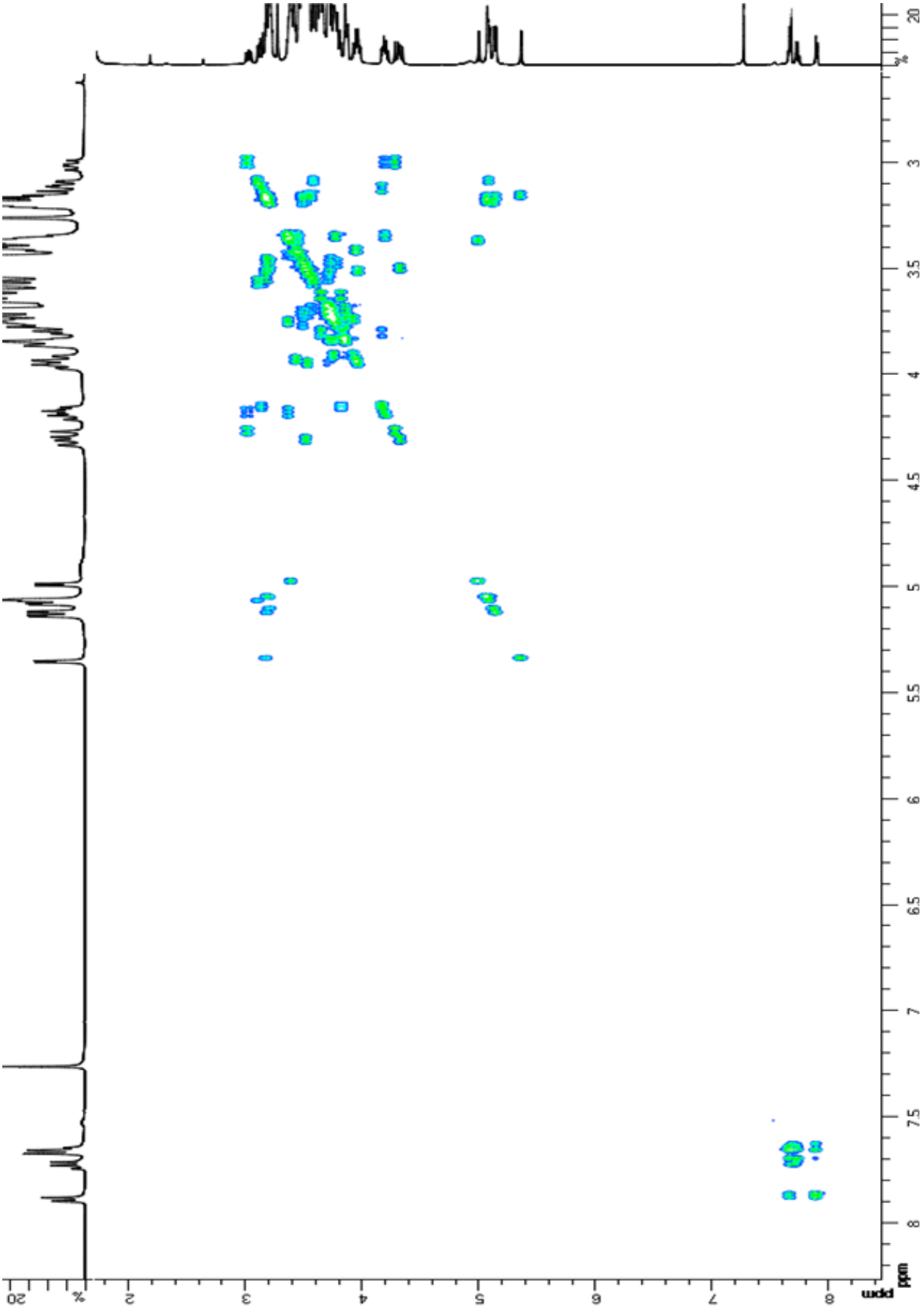
^{1}H NMR spectrum of **6**



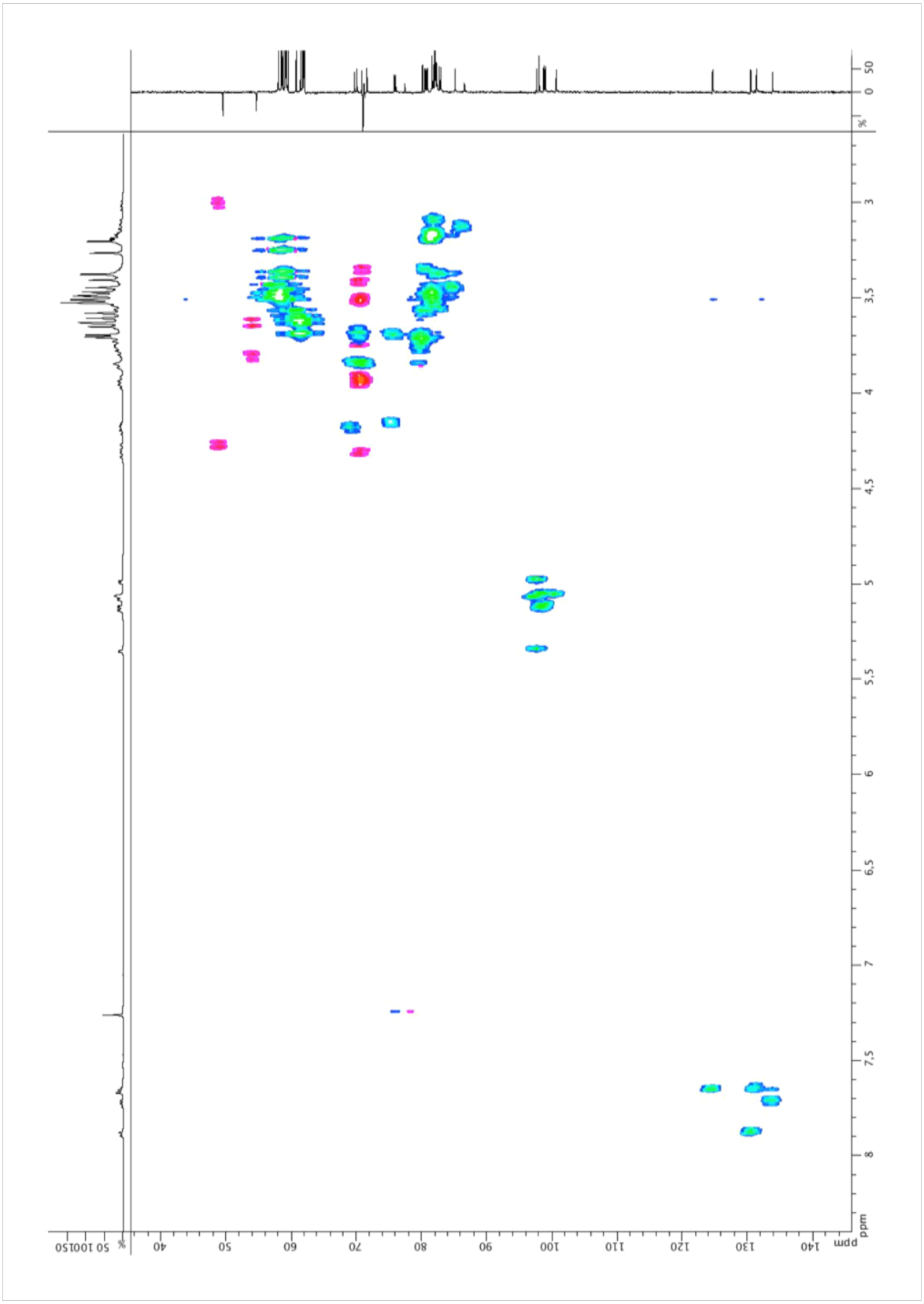
^{13}C NMR spectrum of **6**



DEPT 135 NMR spectrum of **6**



^{1}H-^{1}H COSY NMR spectrum of **6**



^{1}H-^{13}C Edited HSQC NMR spectrum of **6**

Mass spectrum of **6**

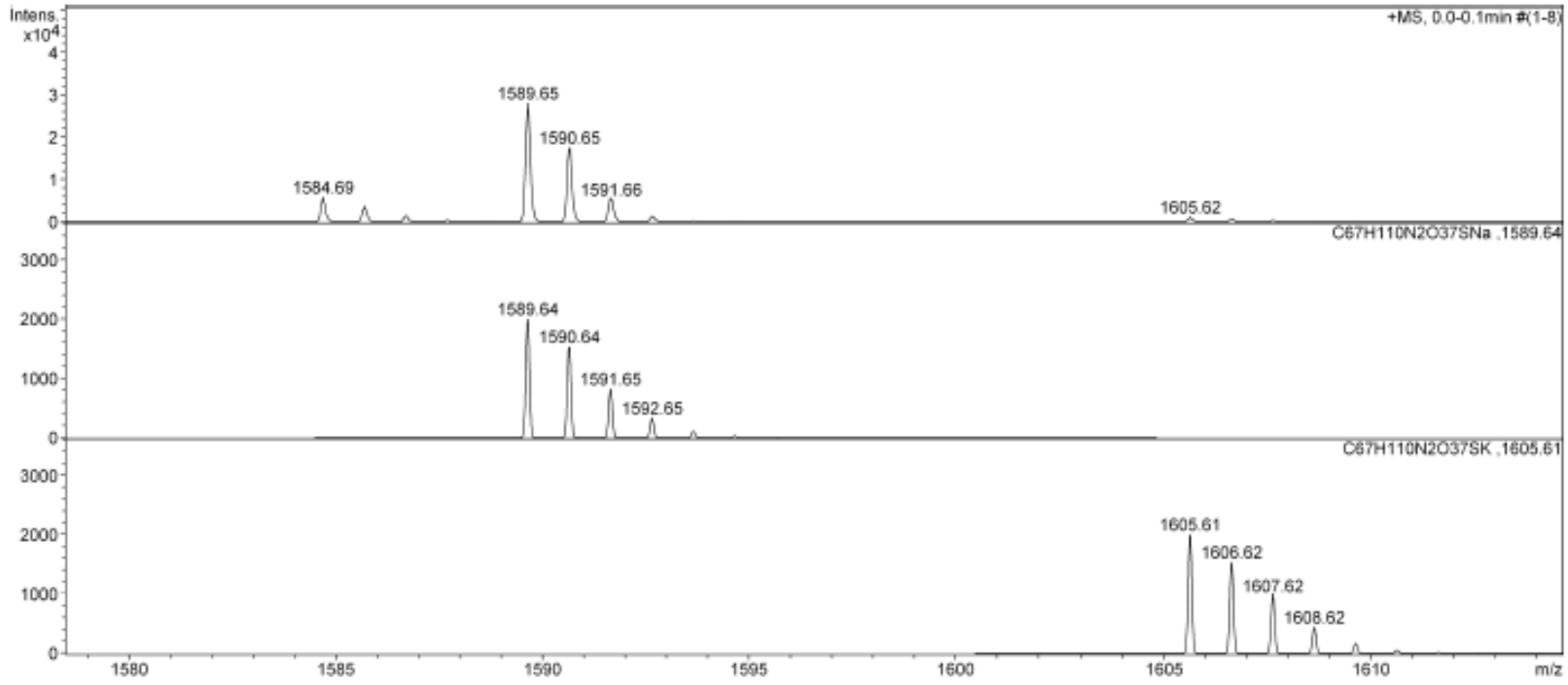
Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

Analysis Info

Analysis Name	O28909hn.d	Acquisition Date	5/23/2014 2:16:20 PM
Method	esi wide pos.m	Operator	Administrator
Sample Name	SD20	Instrument	micrOTOF
Comment			

Acquisition Parameter

Source Type	ESI	Capillary	4500 V	Nebulizer	0.4 Bar	Corona	195 nA
Ion Polarity	Positive	Set Capillary Exit	80.0 V	Dry Gas	4.0 l/min	Set Hexapole RF	220.0 V
Scan Range	n/a	Set Skimmer 1	50.0 V	Dry Heater	180 °C	APCI Heater	514 °C



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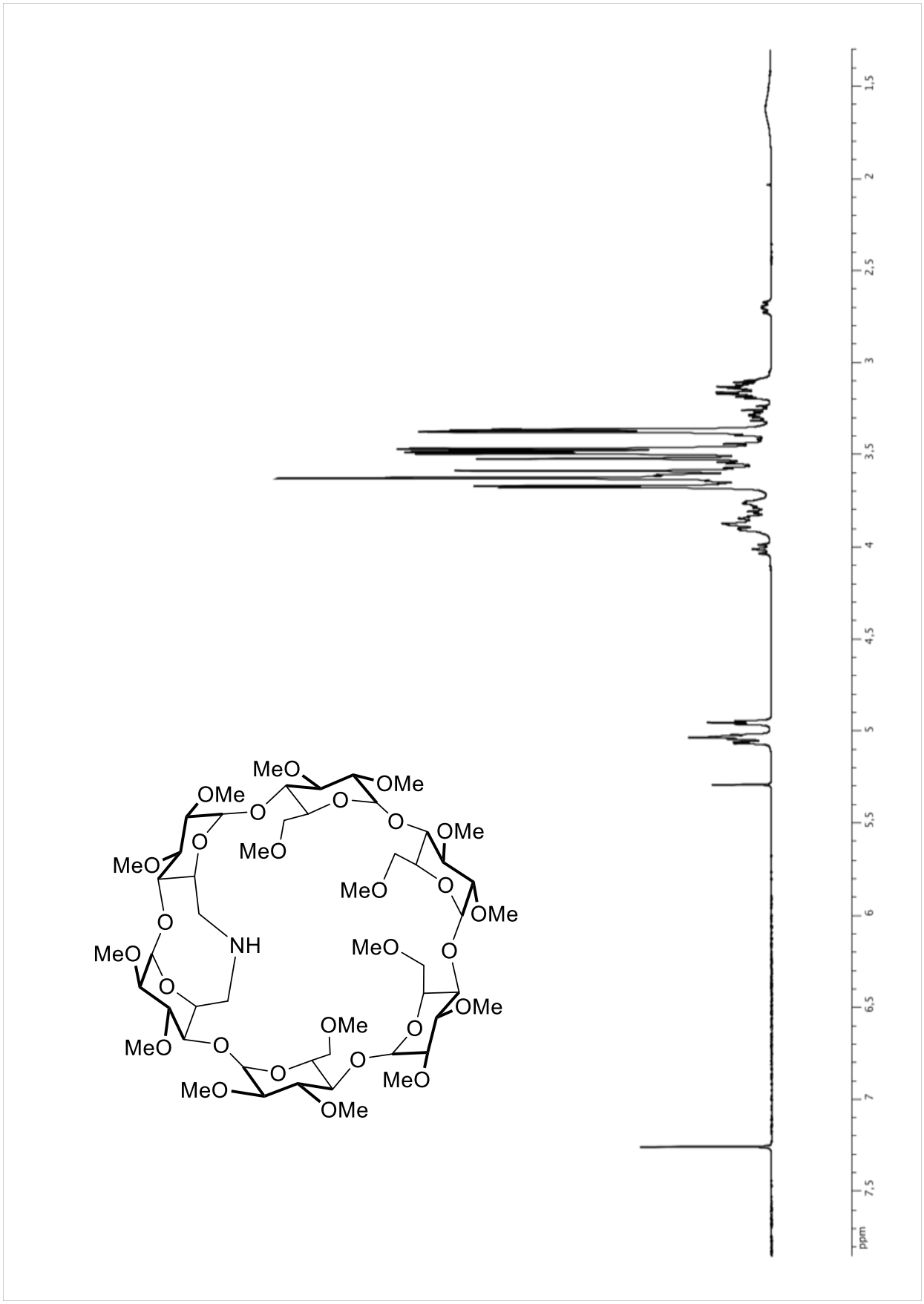
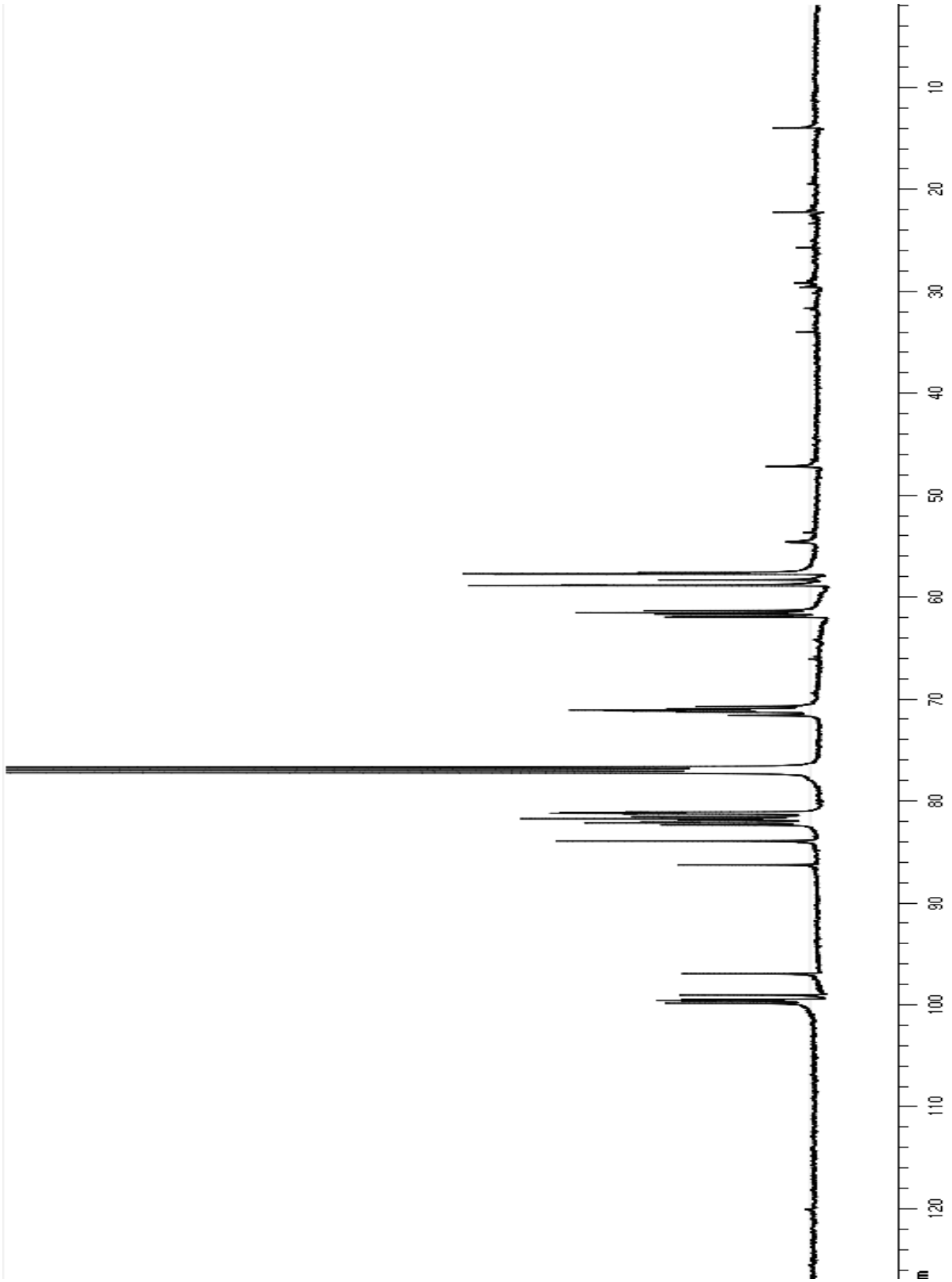
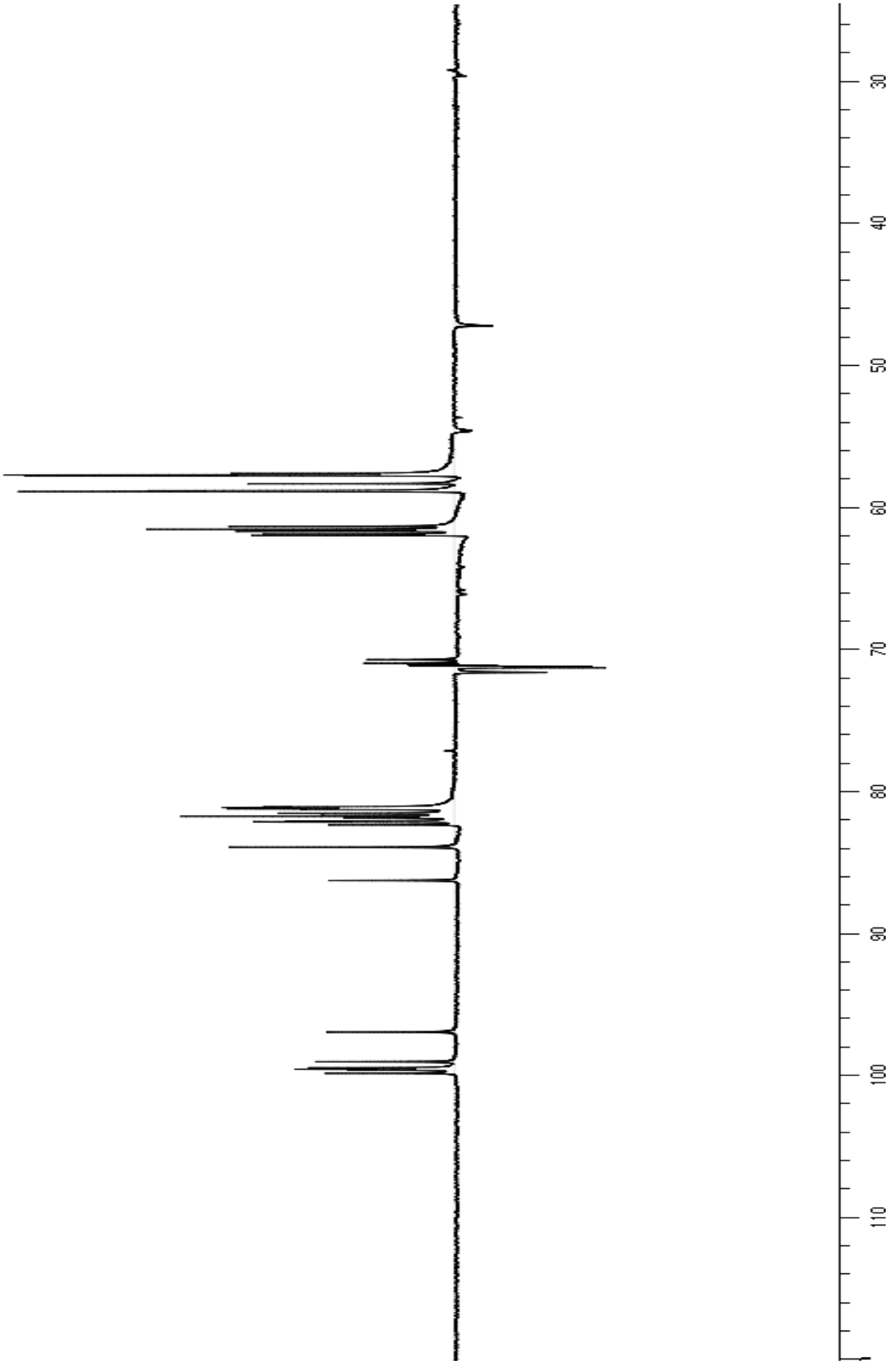


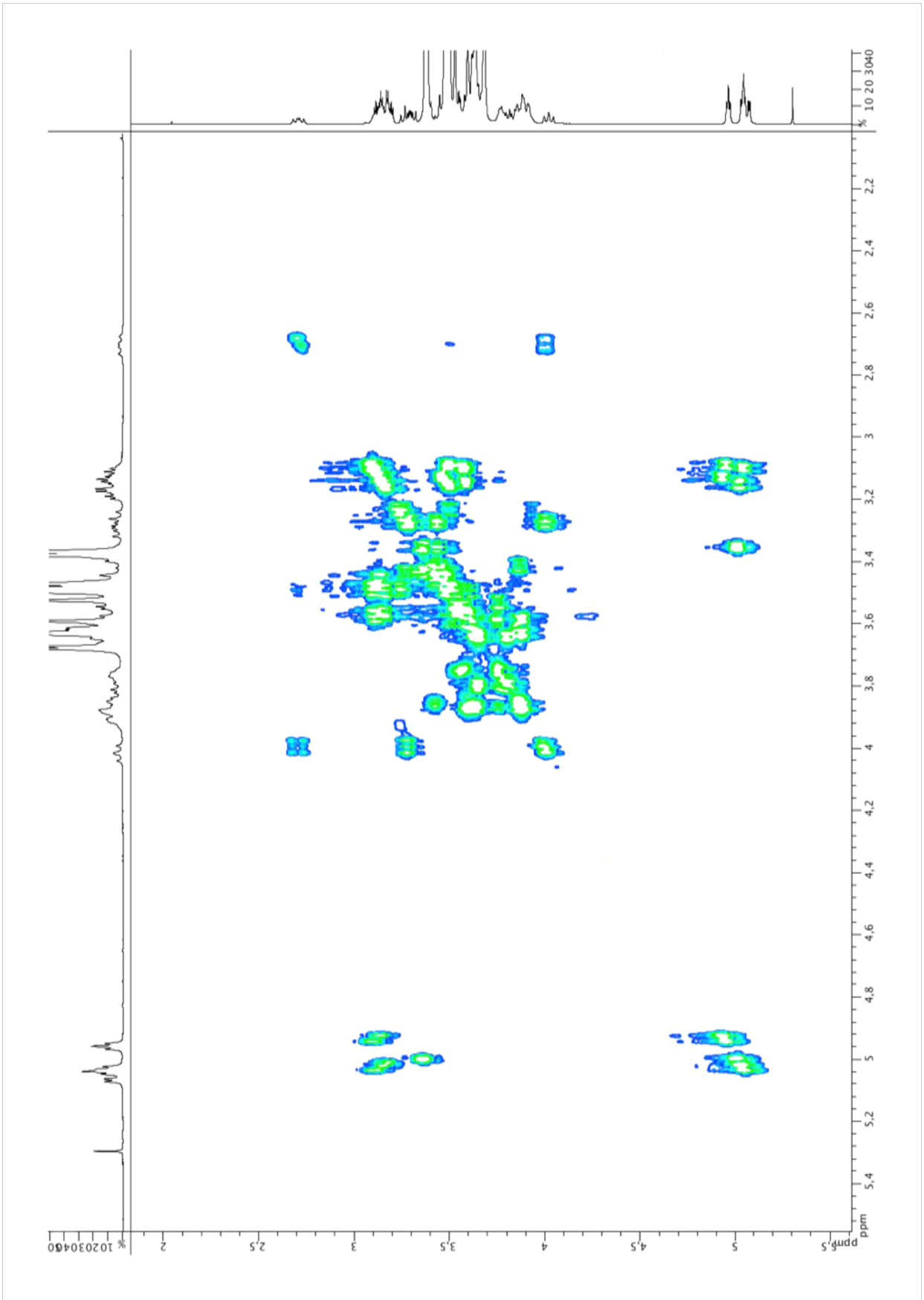
^{1}H NMR spectrum of **7**



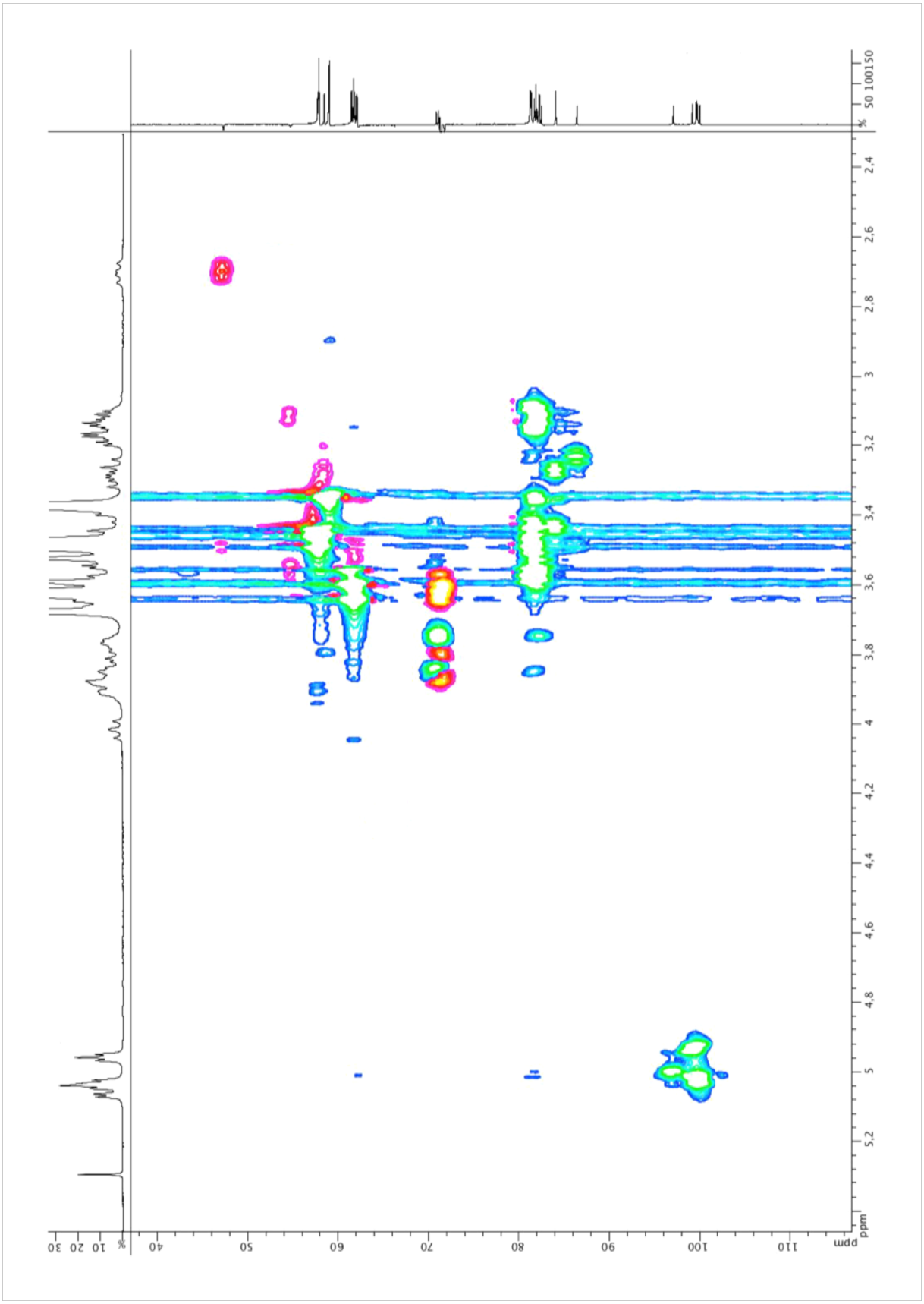
^{13}C NMR spectrum of **7**



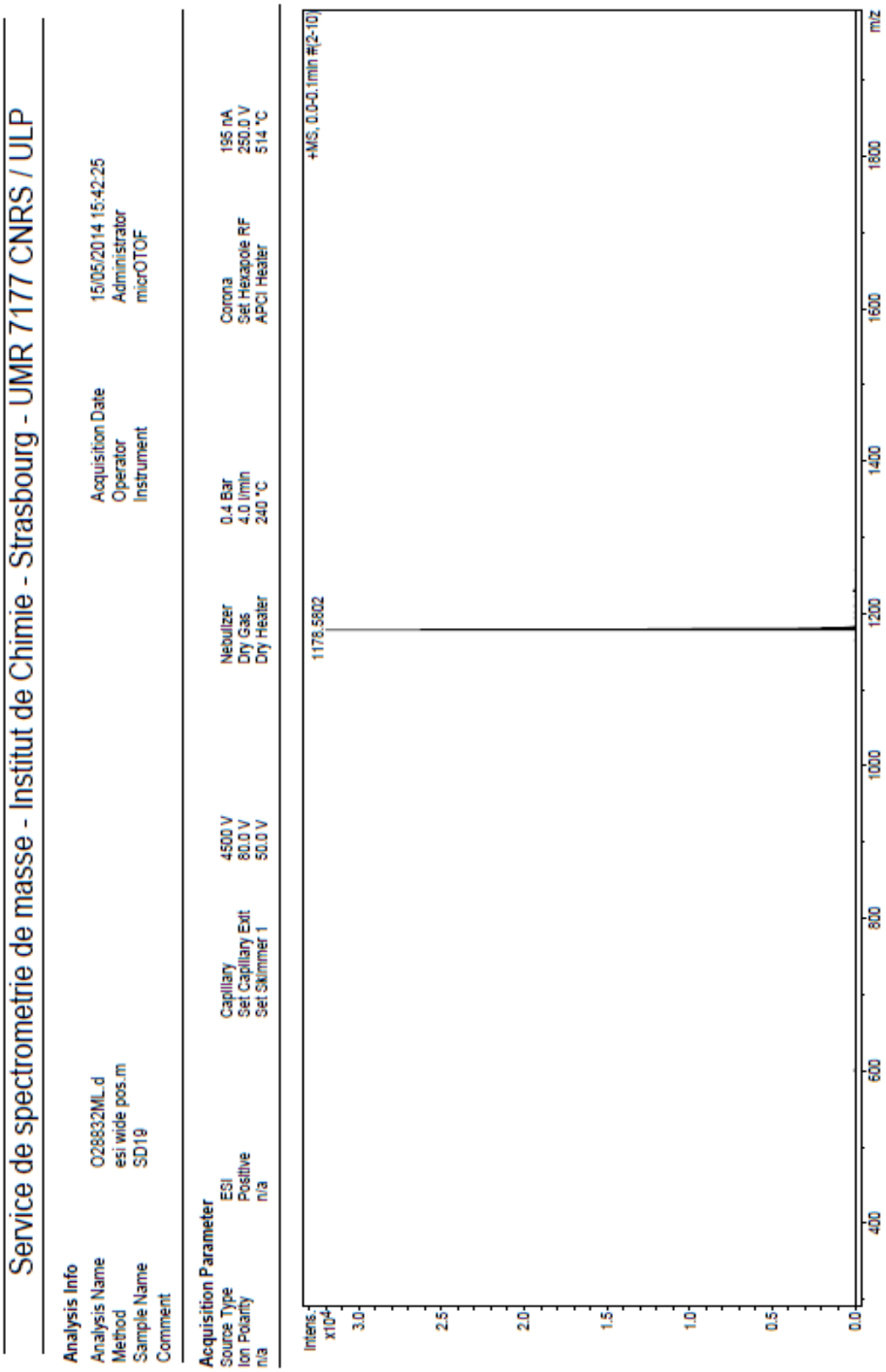
DEPT 135 NMR spectrum of **7**



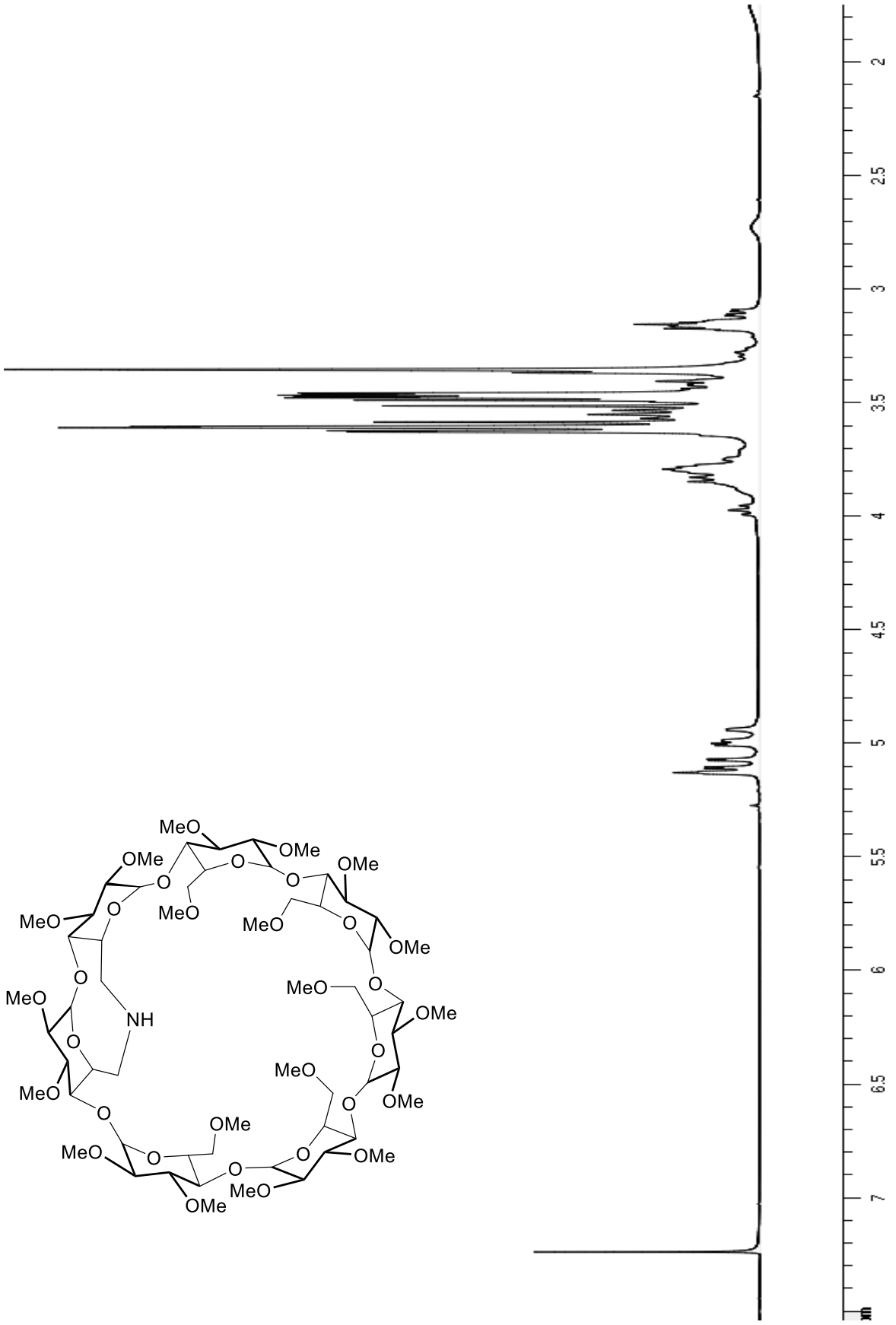
^{1}H-^{1}H COSY NMR spectrum of **7**



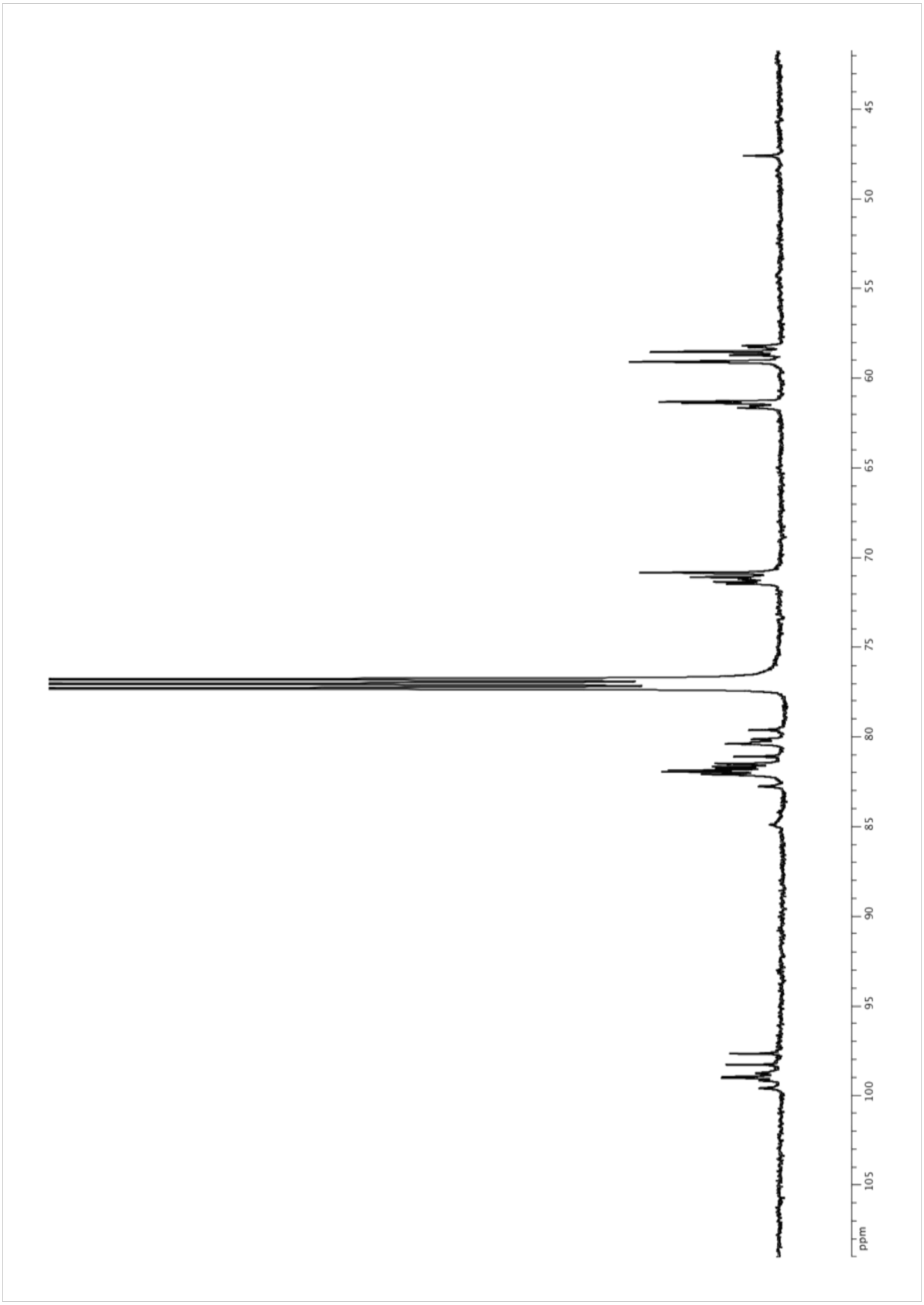
^{1}H-^{13}C Edited HSQC NMR spectrum of **7**



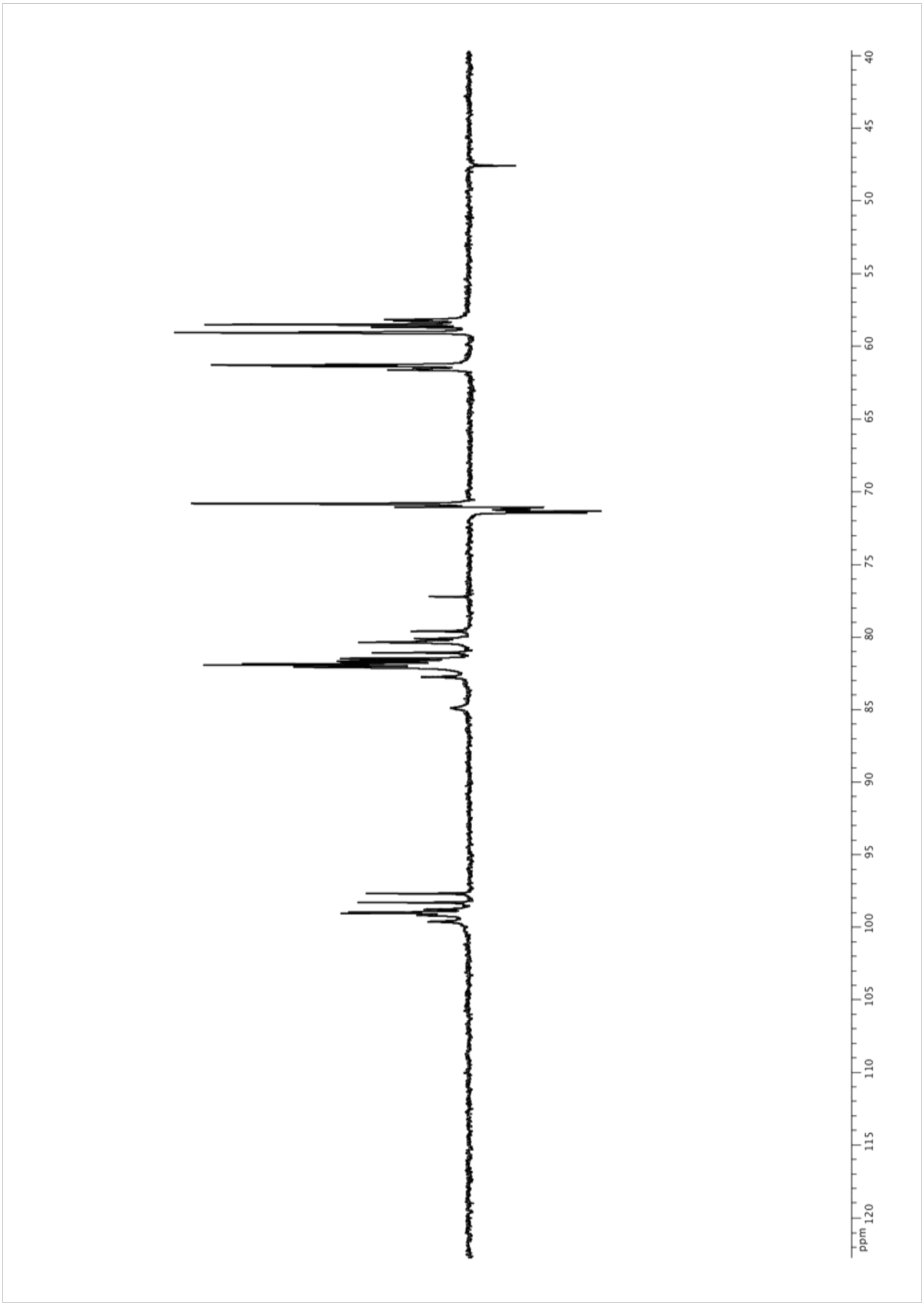
Mass spectrum of **7**



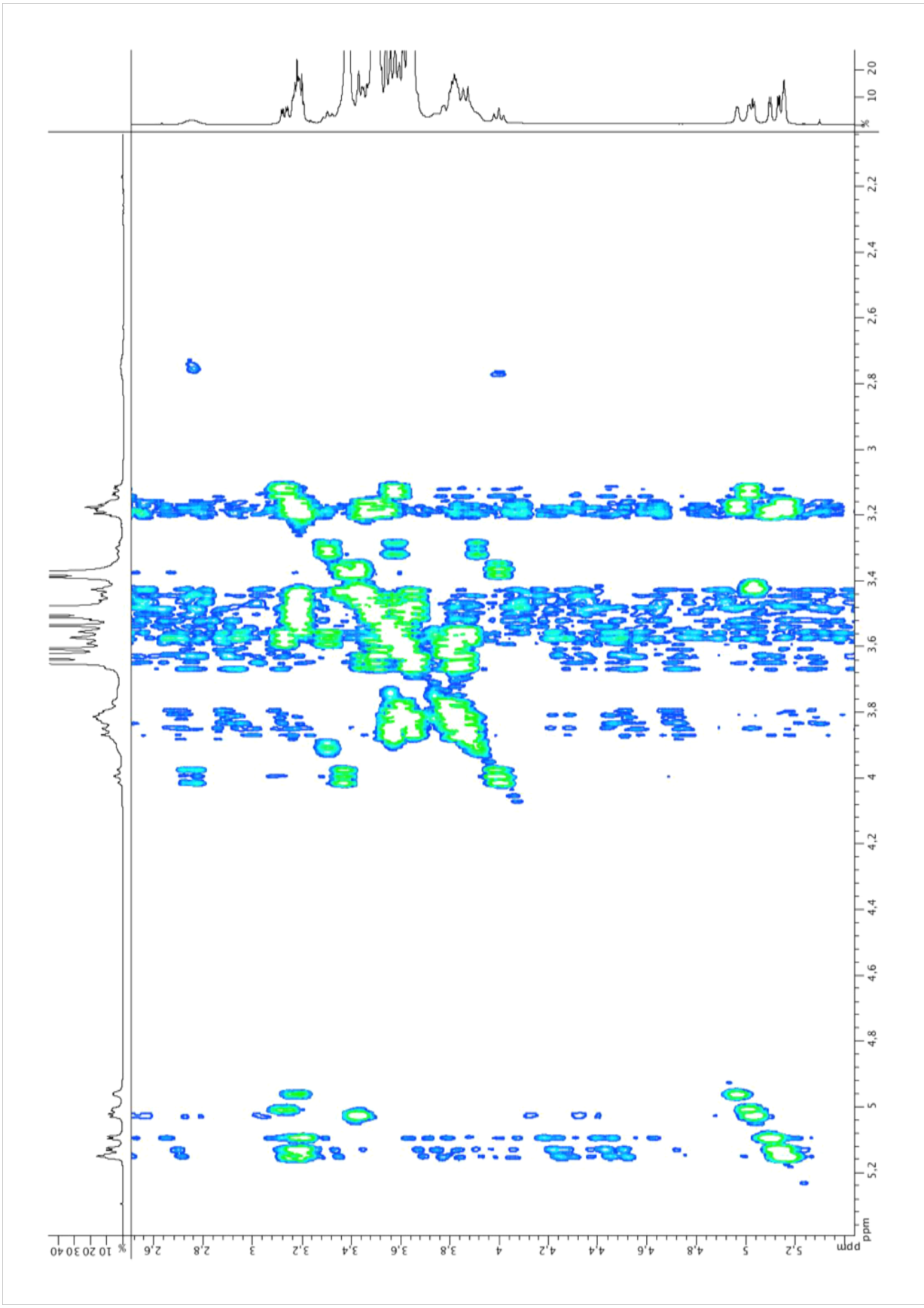
^{1}H NMR spectrum of **8**



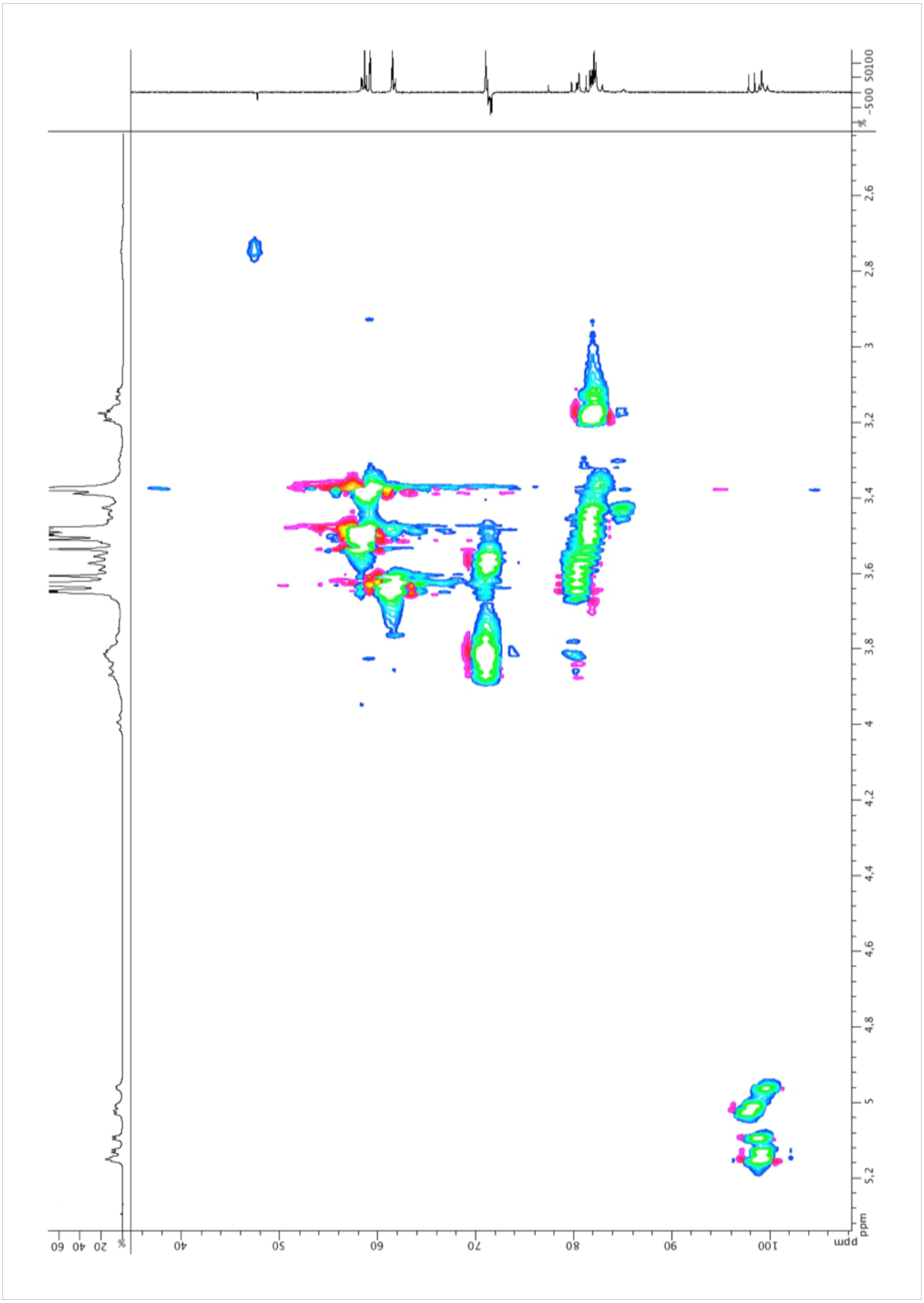
^{13}C NMR spectrum of **8**



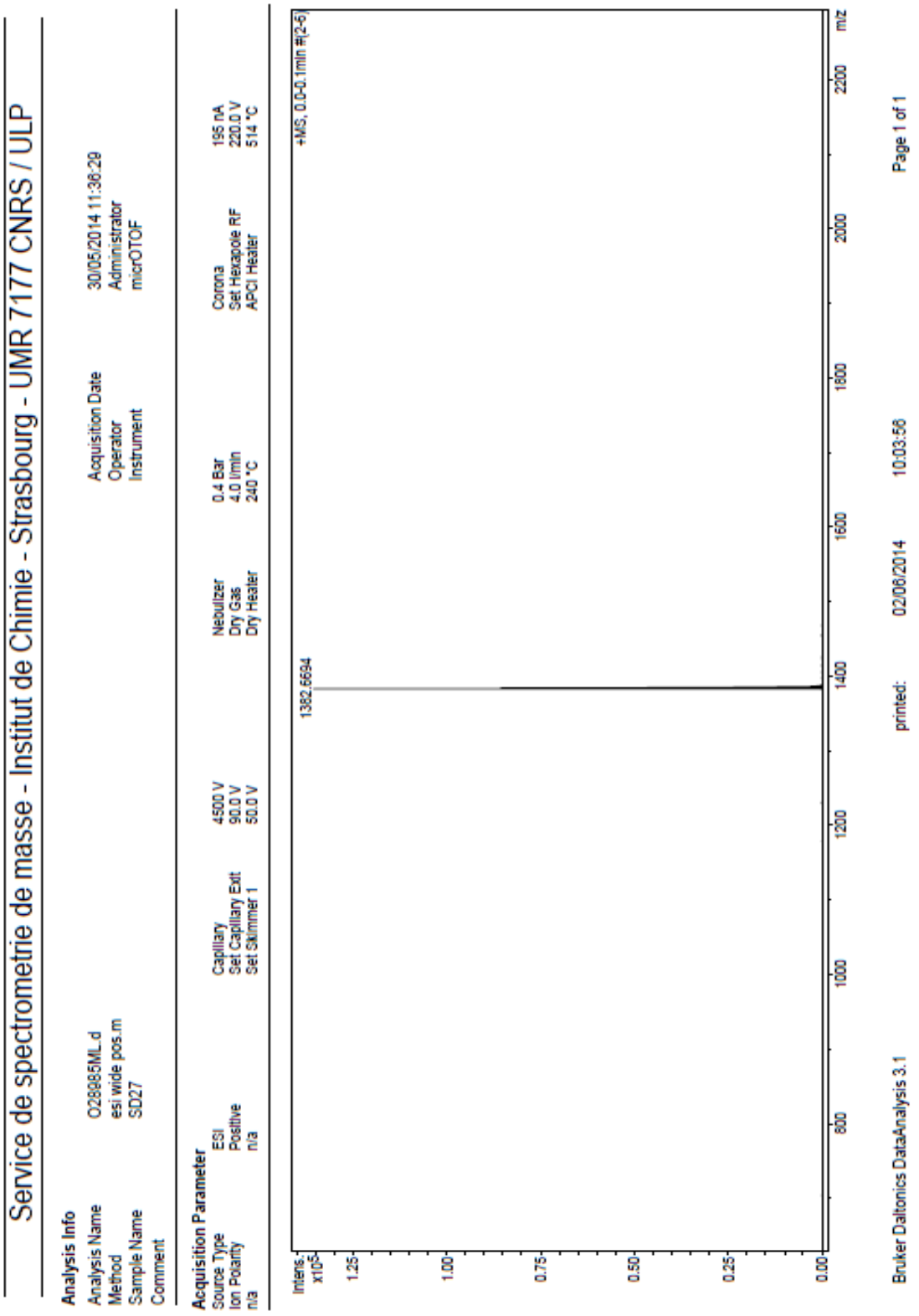
DEPT 135 NMR spectrum of **8**



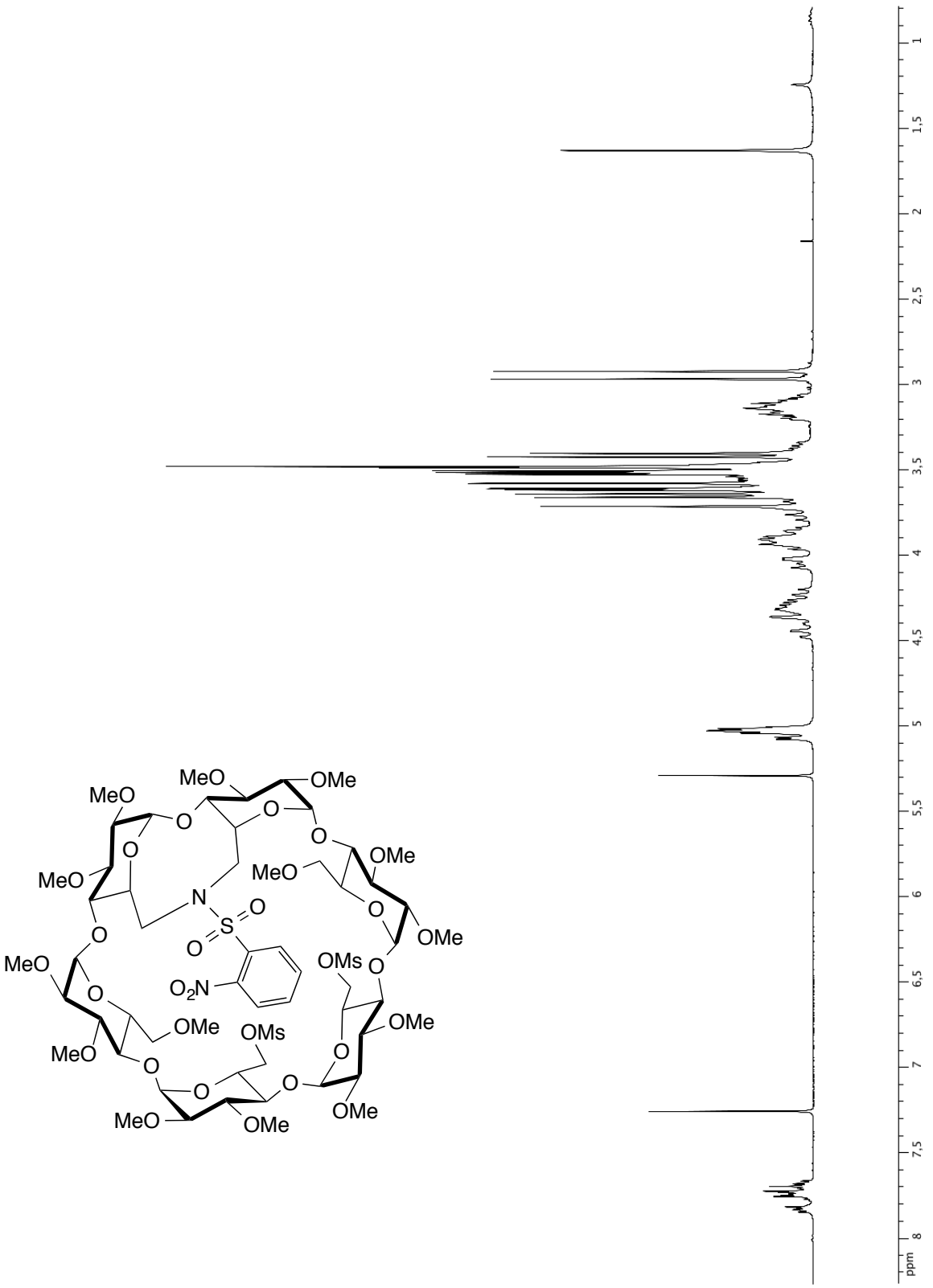
^{1}H-^{1}H COSY NMR spectrum of **8**



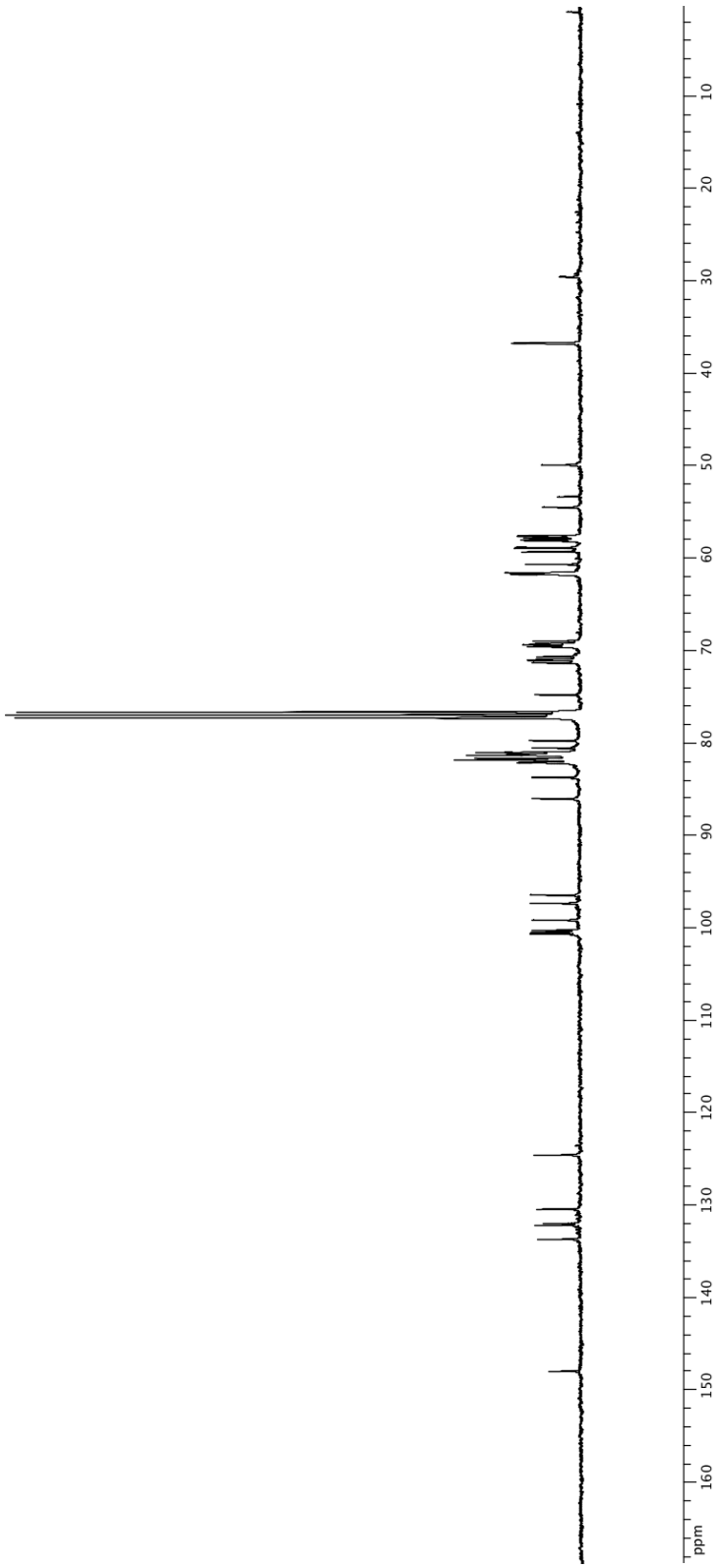
^{1}H-^{13}C HSQC NMR spectrum of **8**



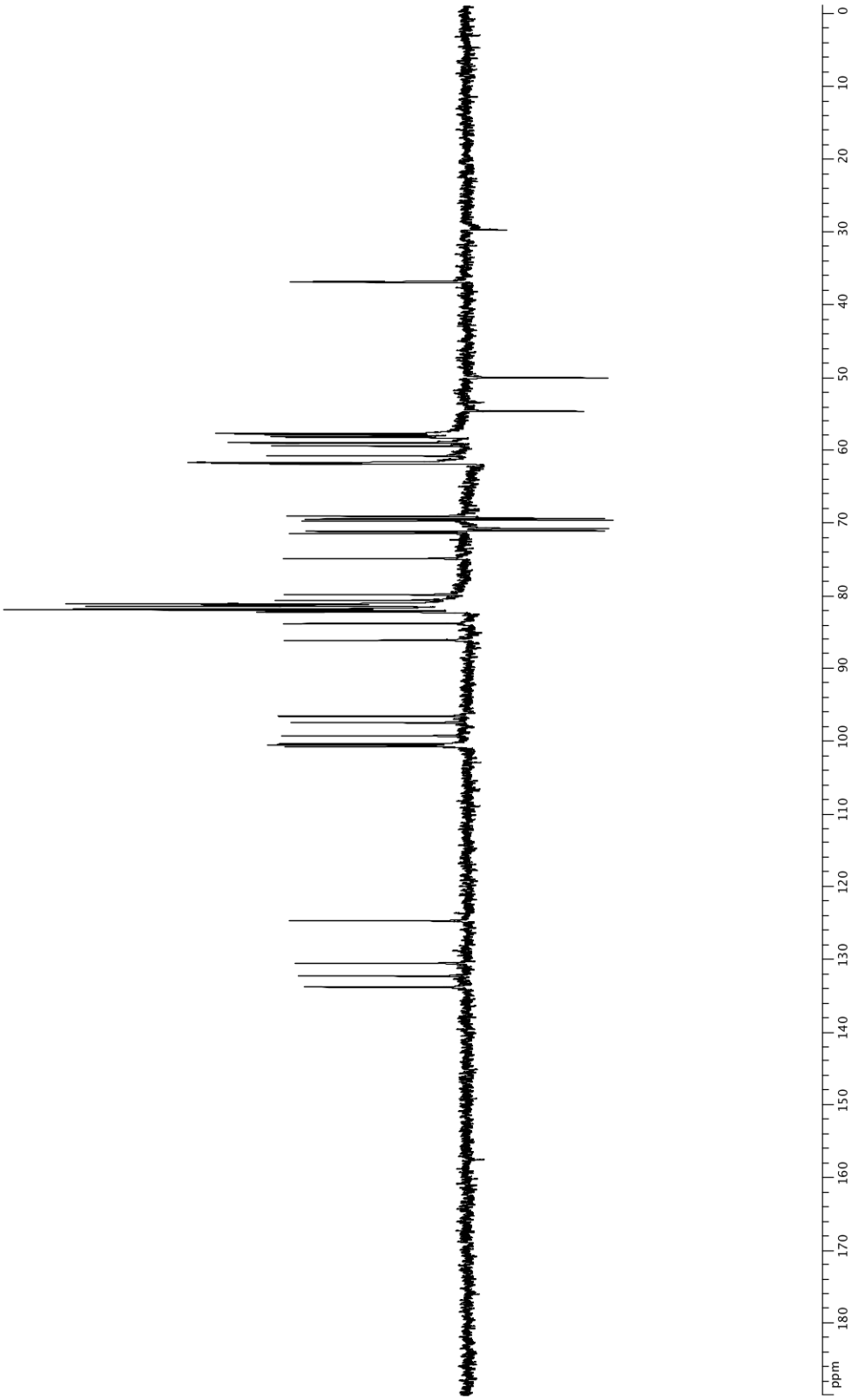
Mass spectrum of **8**



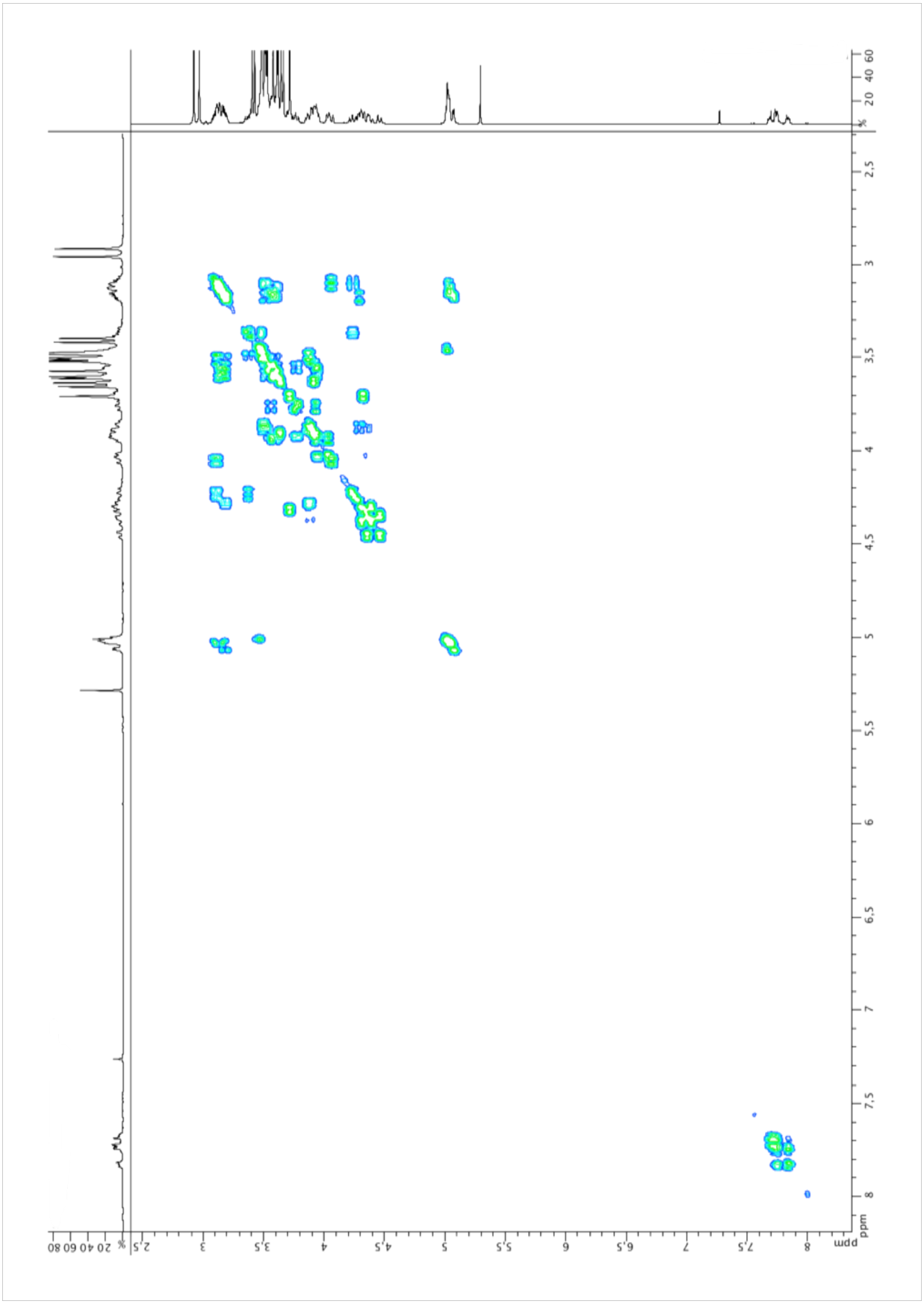
^{1}H NMR spectrum of **10**



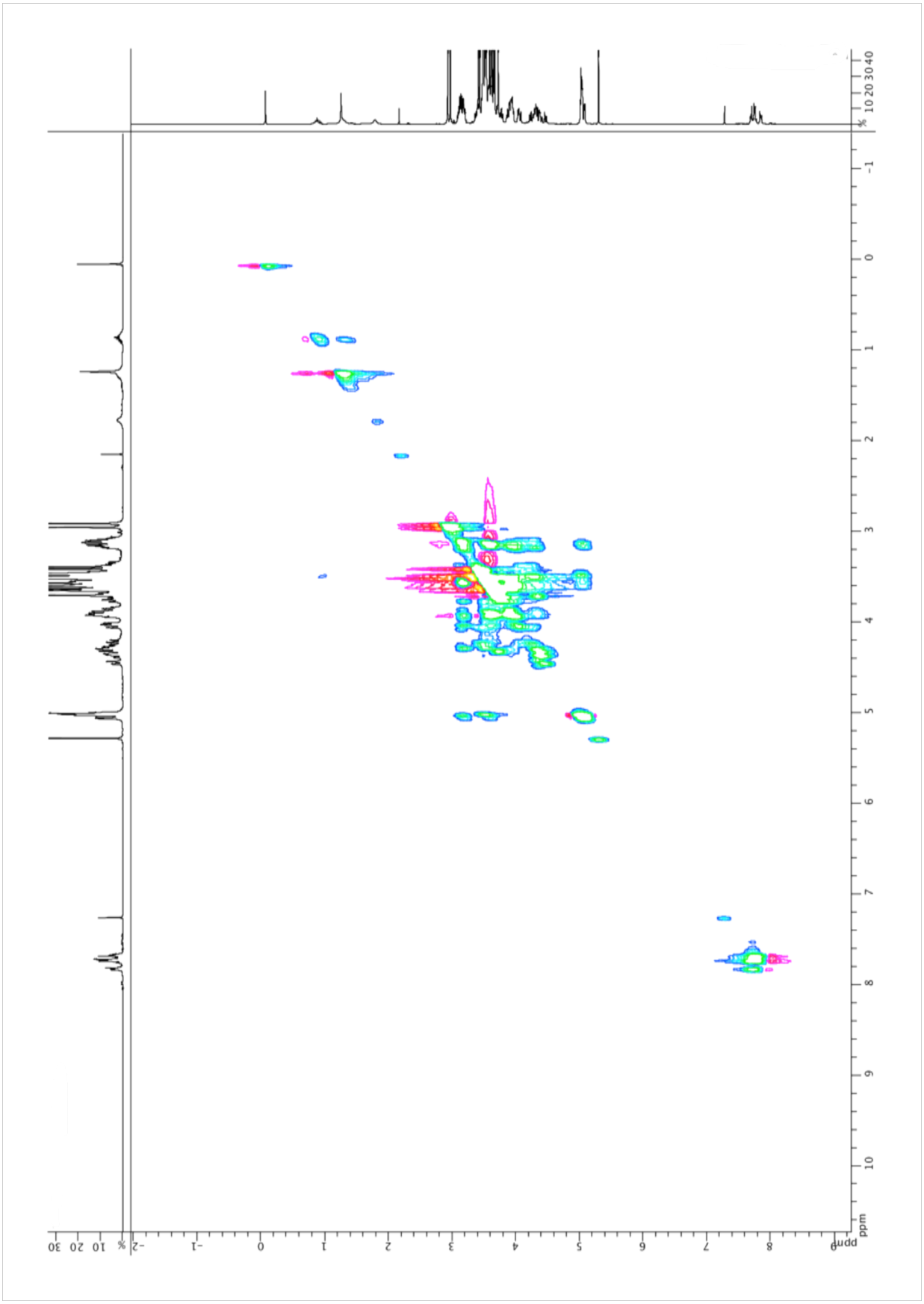
^{13}C NMR spectrum of **10**



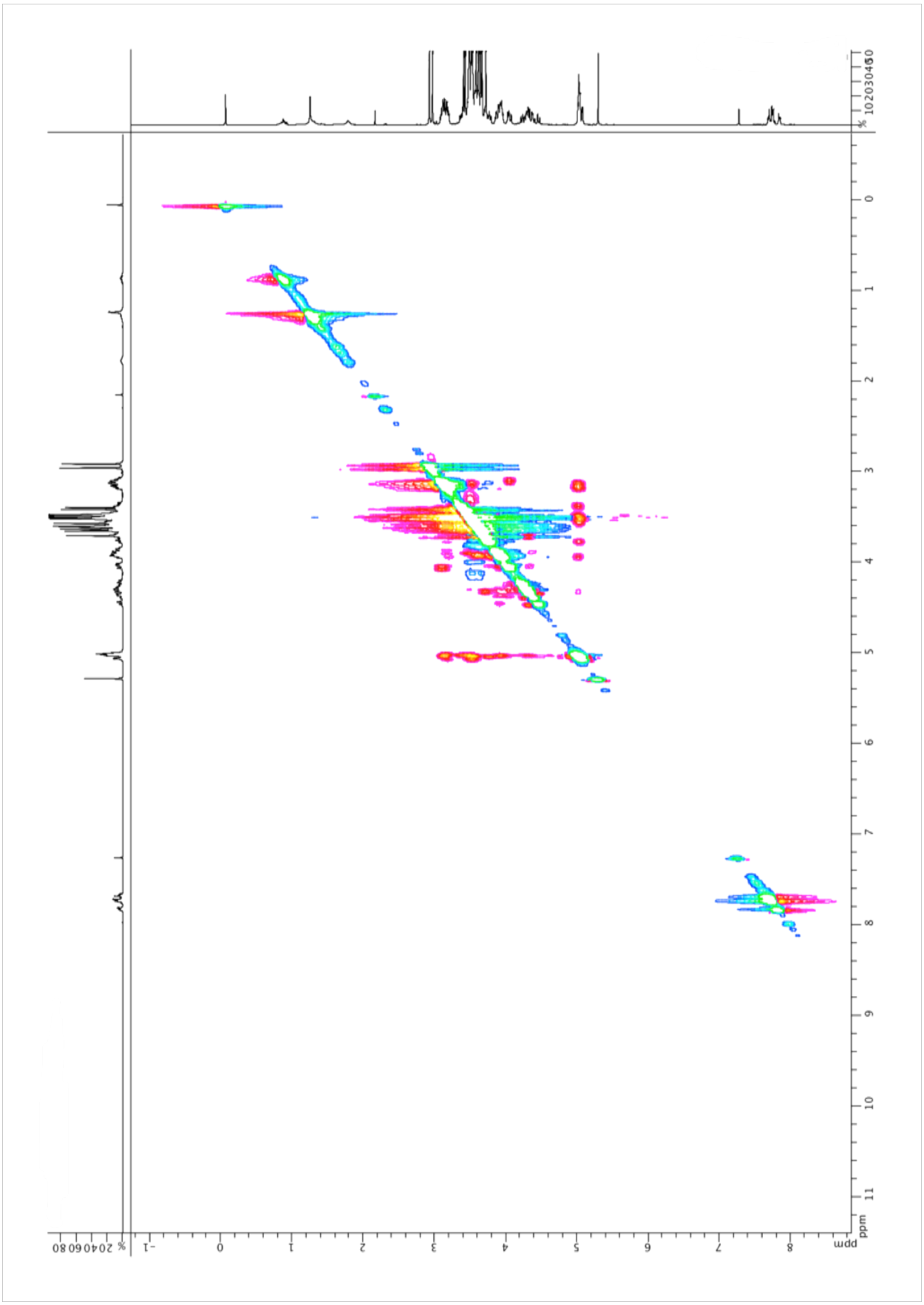
DEPT 135 NMR spectrum of **10**



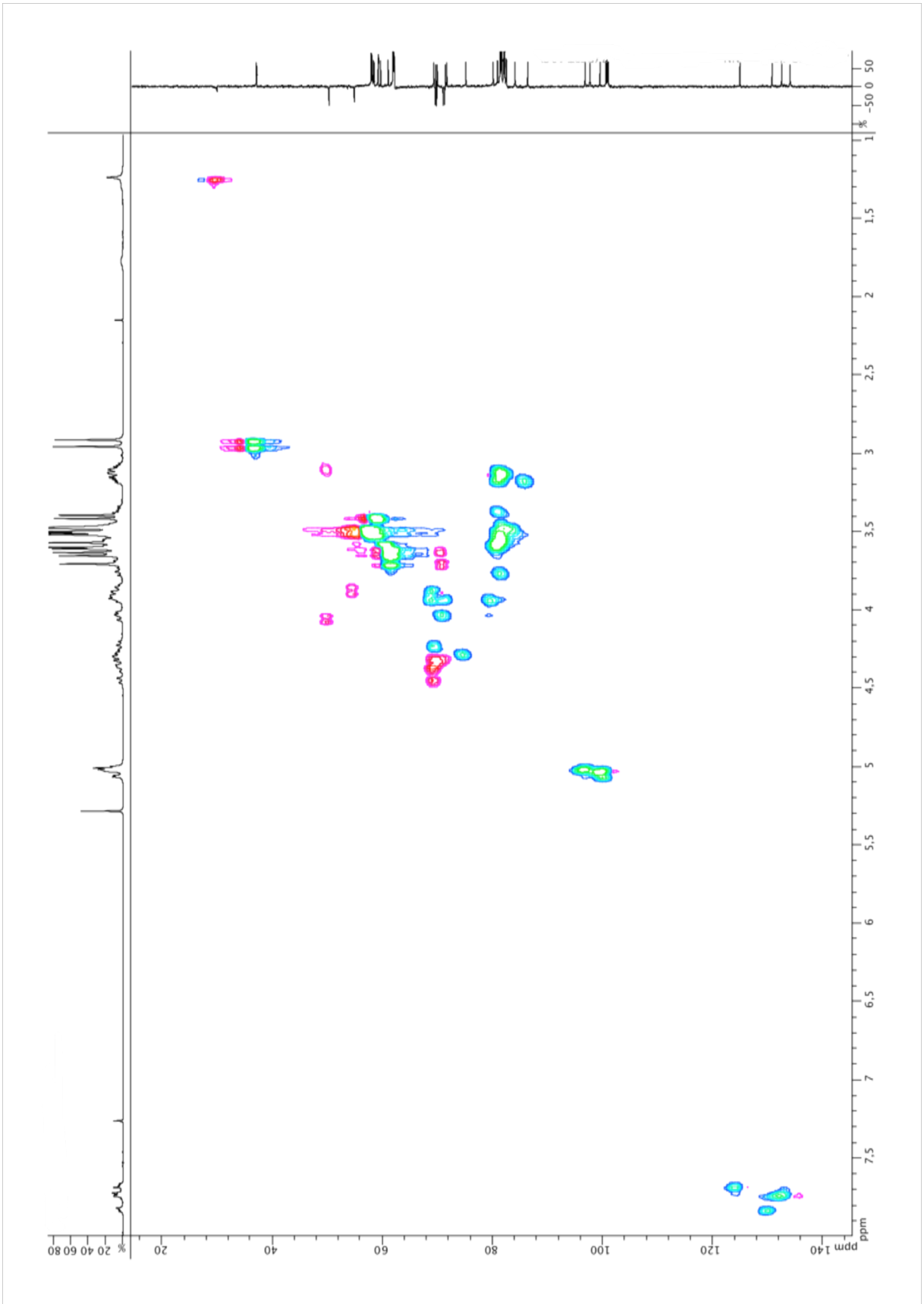
^{1}H-^{1}H COSY NMR spectrum of **10**



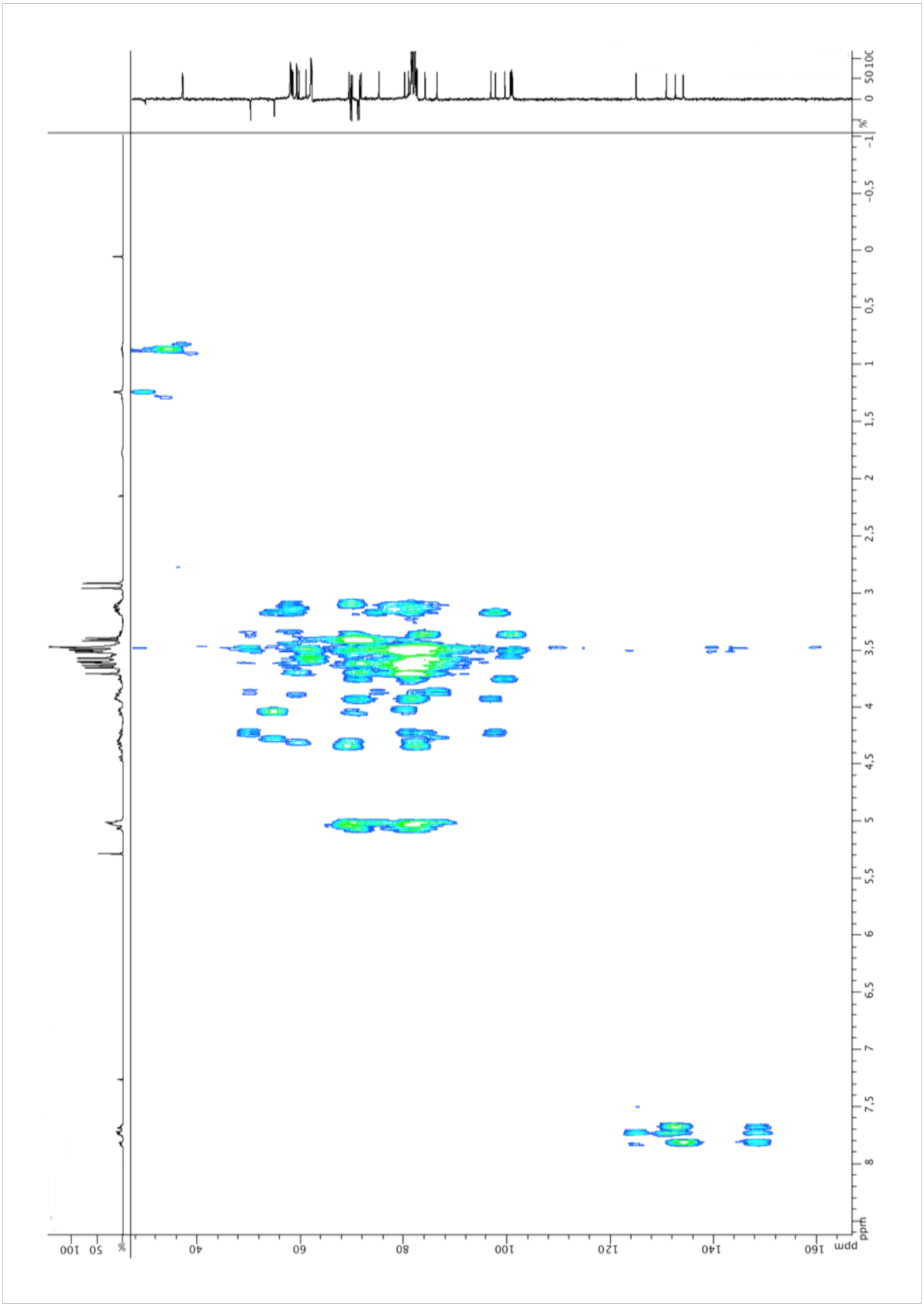
^{1}H-^{1}H TOCSY NMR spectrum of **10**



^{1}H-^{1}H ROESY NMR spectrum of **10**



^{1}H-^{13}C Edited HSQC NMR spectrum of **10**



^{1}H-^{1}H HMBC NMR spectrum of **10**

Mass spectrum of **10**

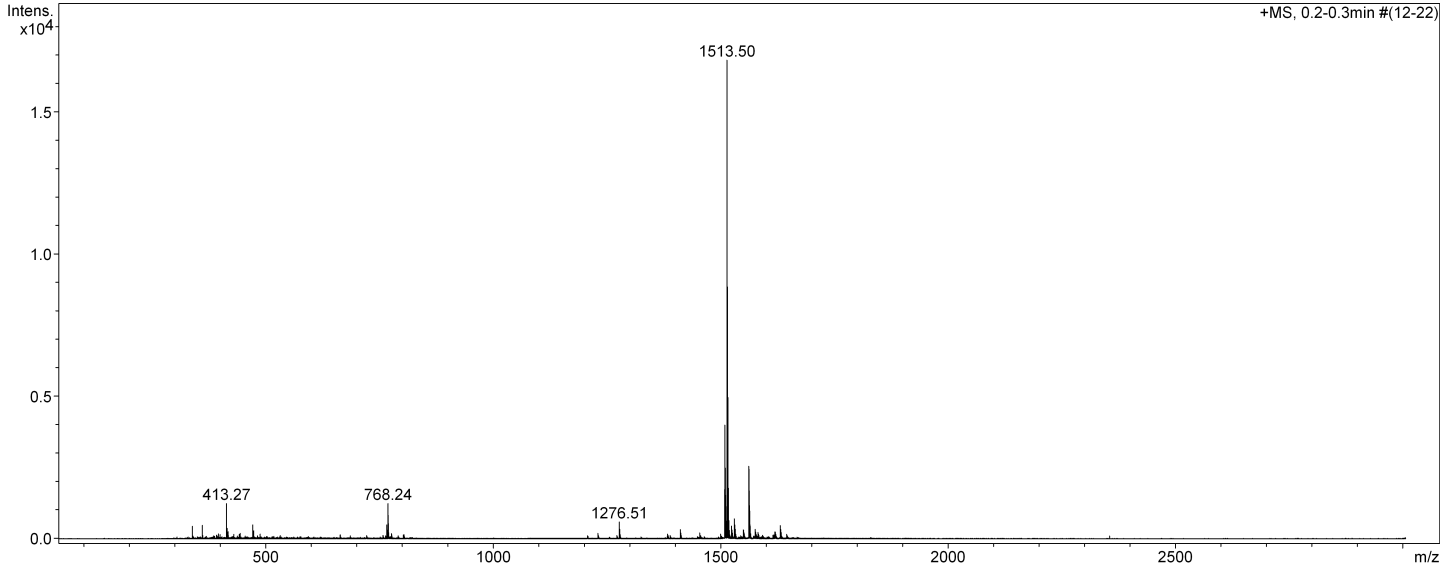
Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / UDS

Analysis Info

Analysis Name	O37126SK.d	Acquisition Date	9/2/2015 10:29:39 AM
Method	esi wide pos.m	Operator	Administrator
Sample Name	AD513	Instrument	micrOTOF
Comment			

Acquisition Parameter

Source Type	ESI	Capillary	4500 V	Nebulizer	0.4 Bar	Corona	122 nA
Ion Polarity	Positive	Set Capillary Exit	150.0 V	Dry Gas	4.0 l/min	Set Hexapole RF	220.0 V
Scan Range	n/a	Set Skimmer 1	50.0 V	Dry Heater	200 °C	APCI Heater	515 °C



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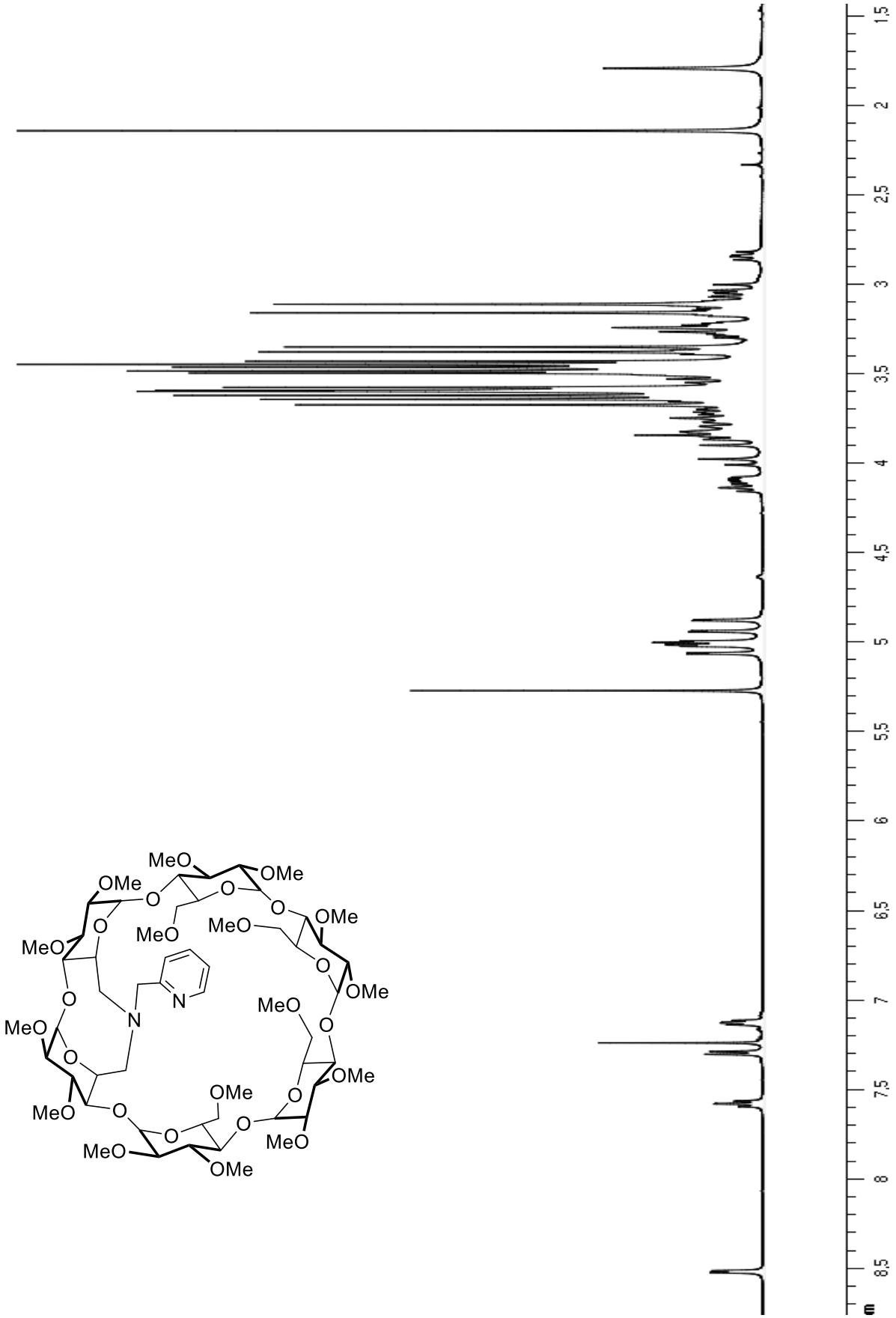
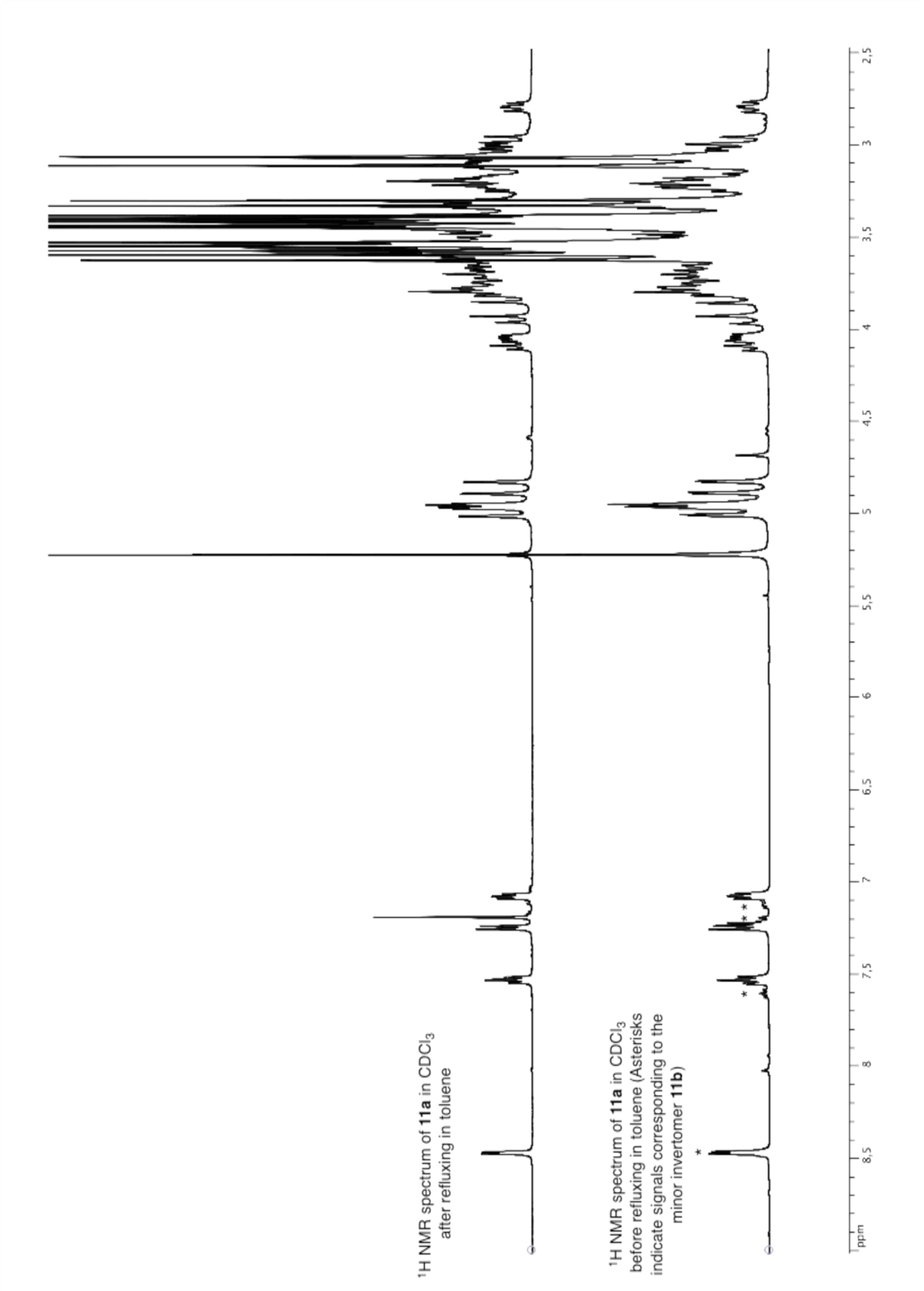
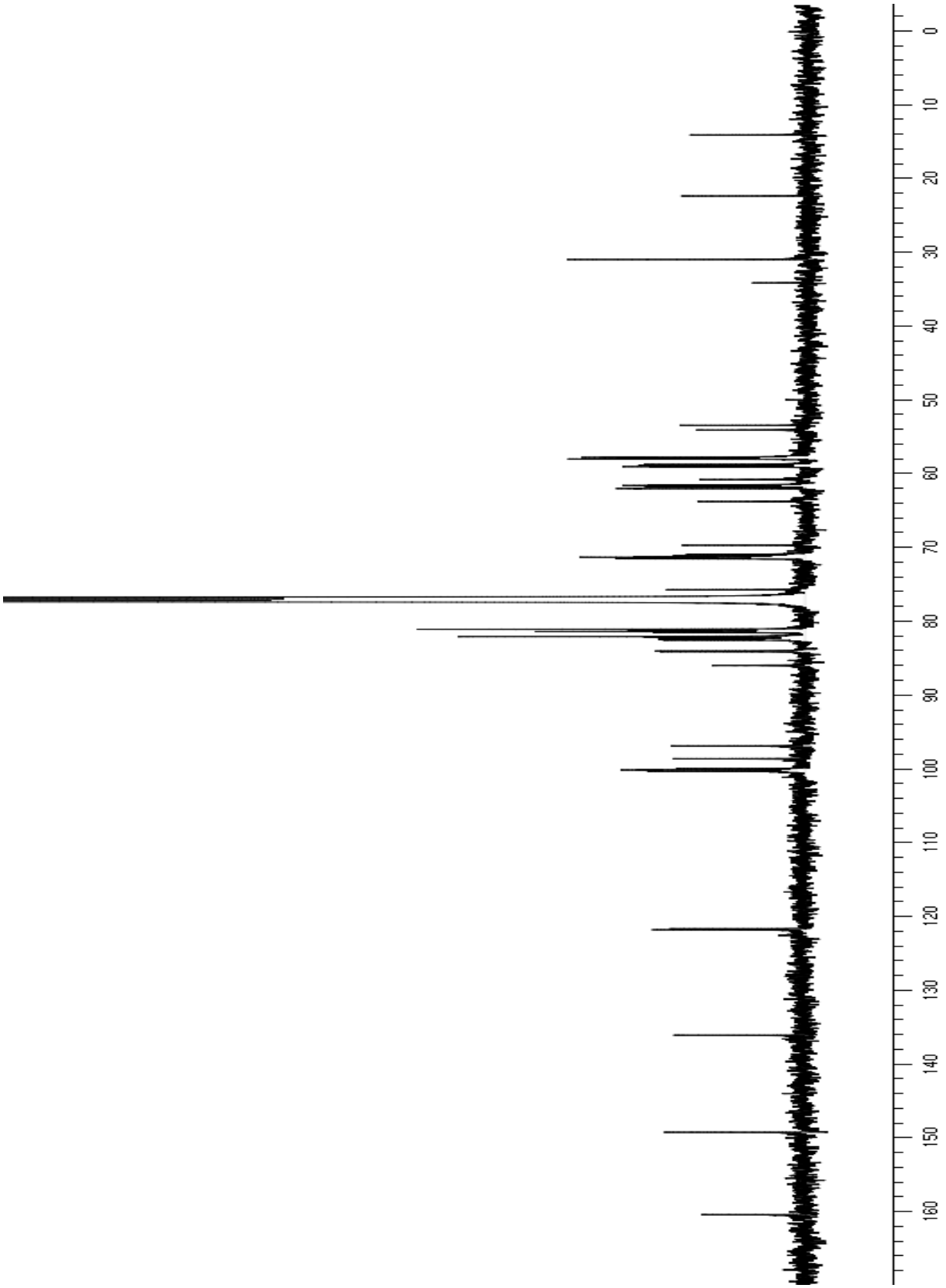


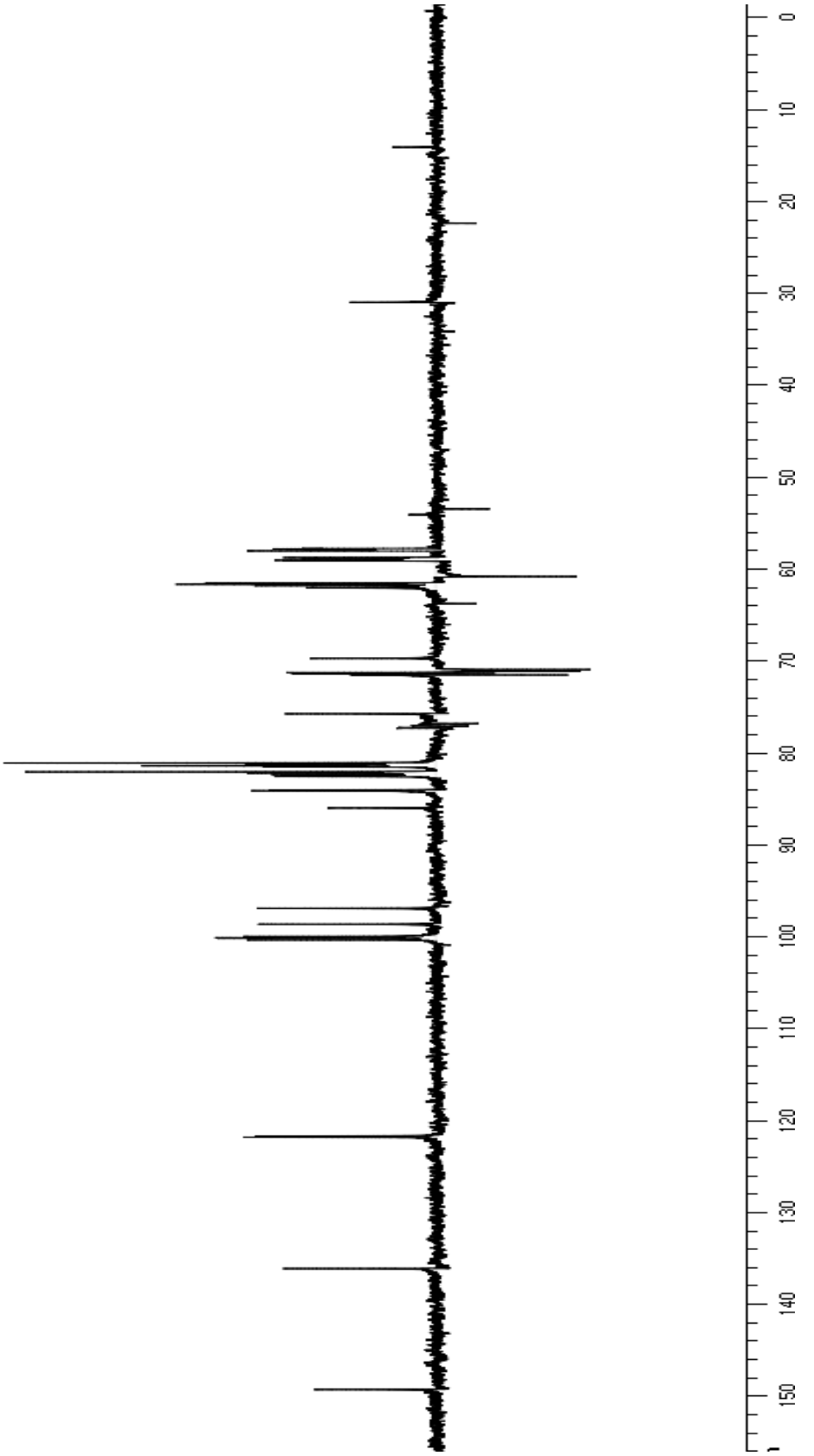
^{1}H NMR spectrum of **11a**



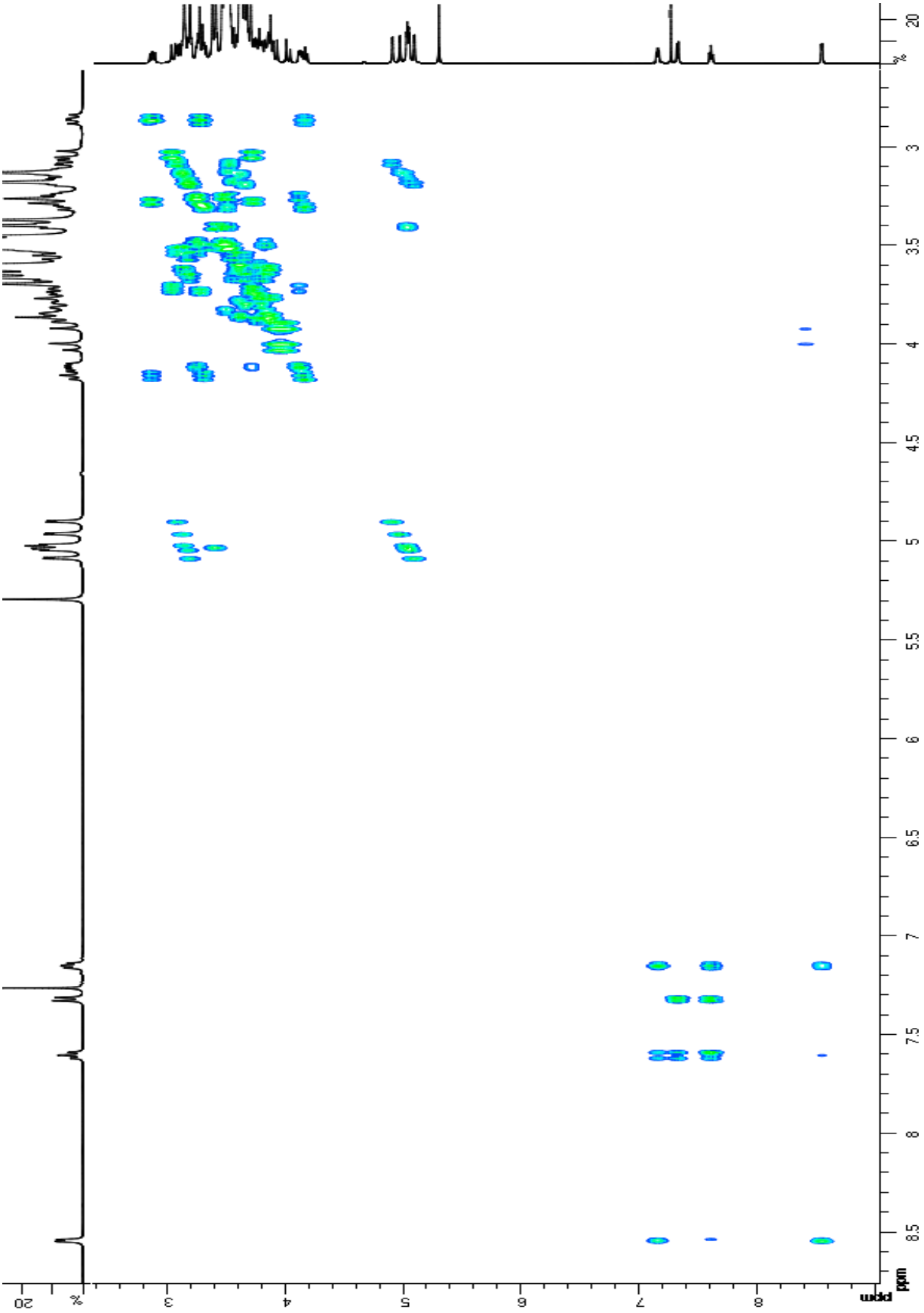
^{1}H NMR spectra of the **11a**/**11b** mixture before and after refluxing in toluene



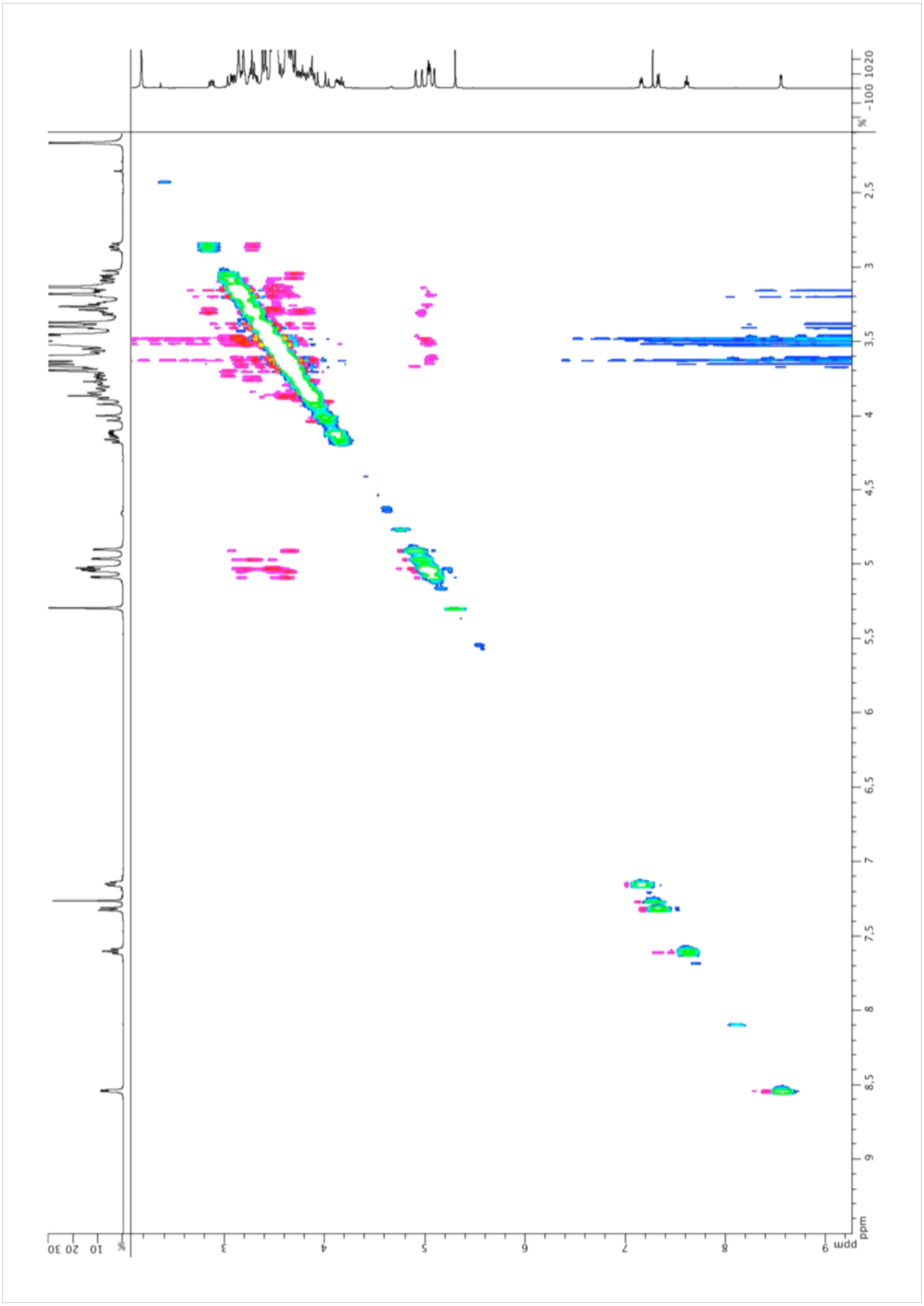
^{13}C NMR spectrum of **11a**



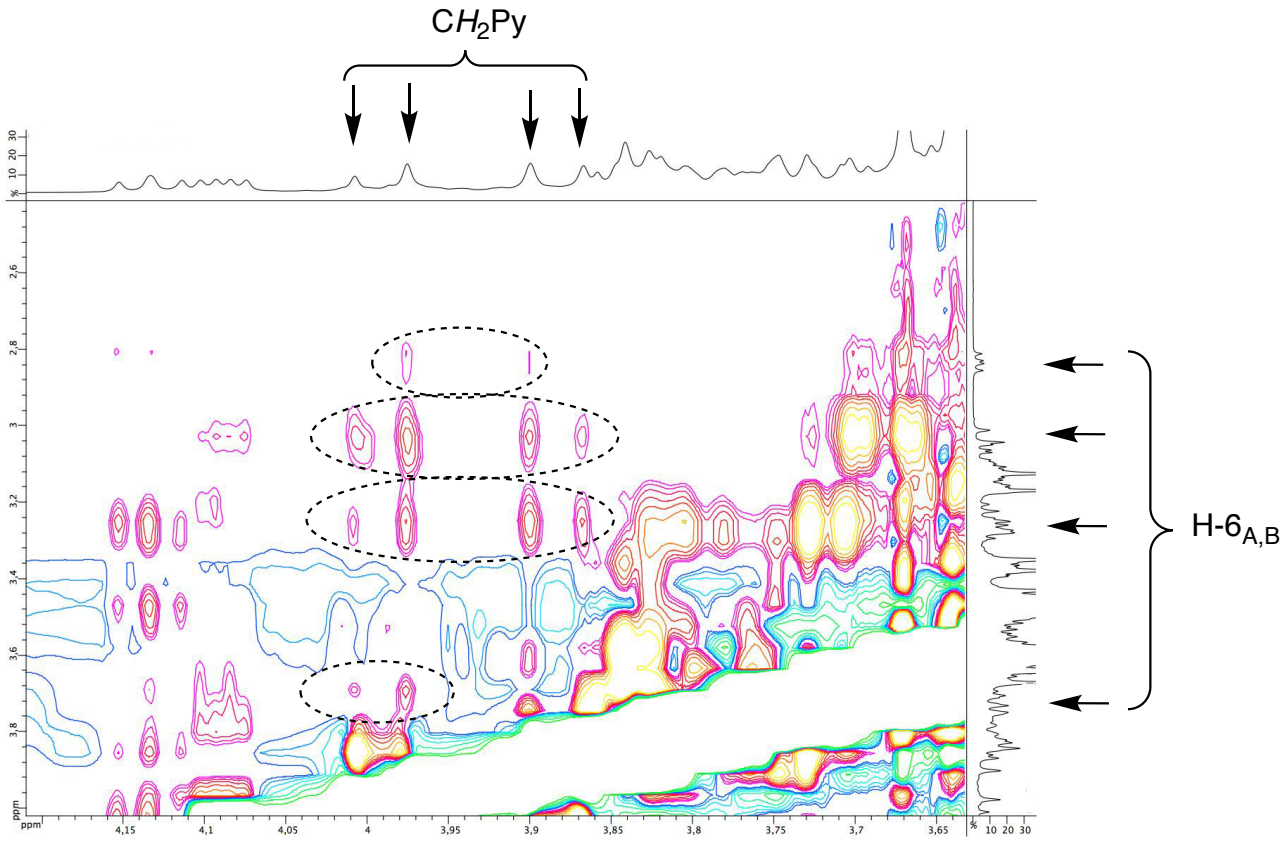
DEPT 135 NMR spectrum of **11a**



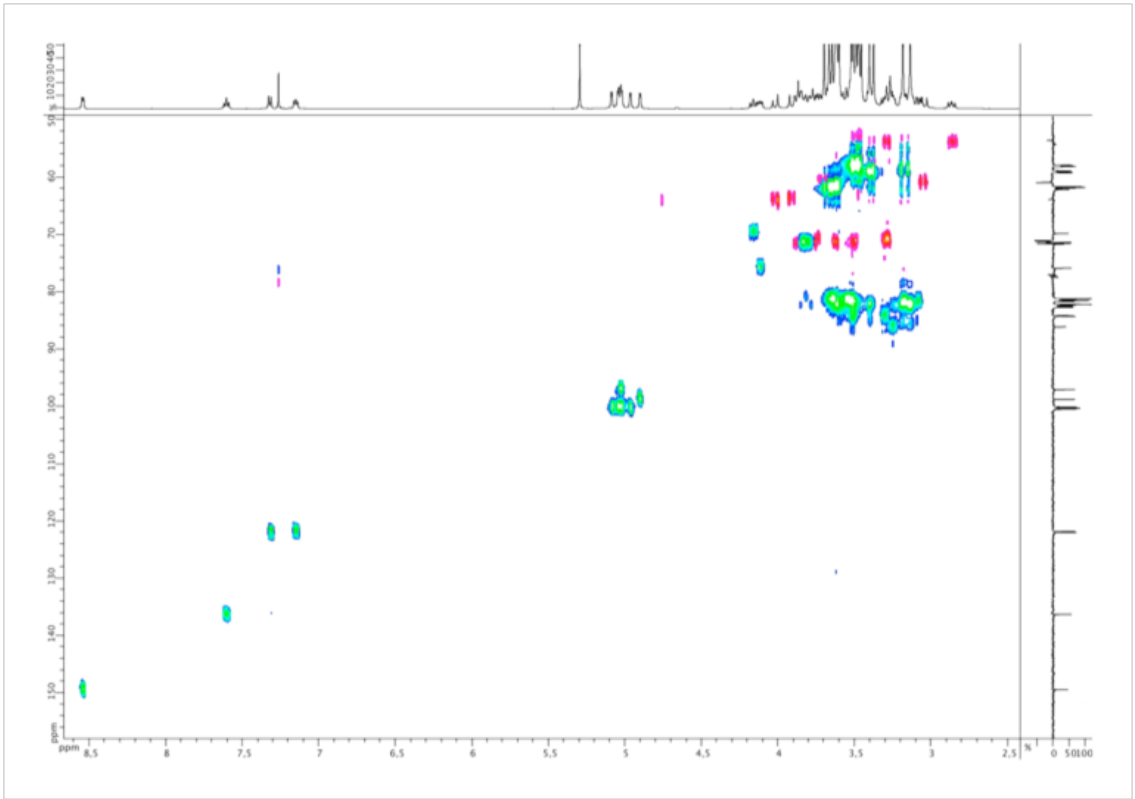
^{1}H-^{1}H COSY NMR spectrum of **11a**



^{1}H-^{1}H ROESY NMR spectrum of **11a**



Part of the ROESY spectrum of **11a** showing cross-peaks (circled) for H-$6_{A,B}$–CH_2Py interactions



^{1}H-^{13}C Edited HSQC NMR spectrum of **11a**

Mass spectrum of **11a**

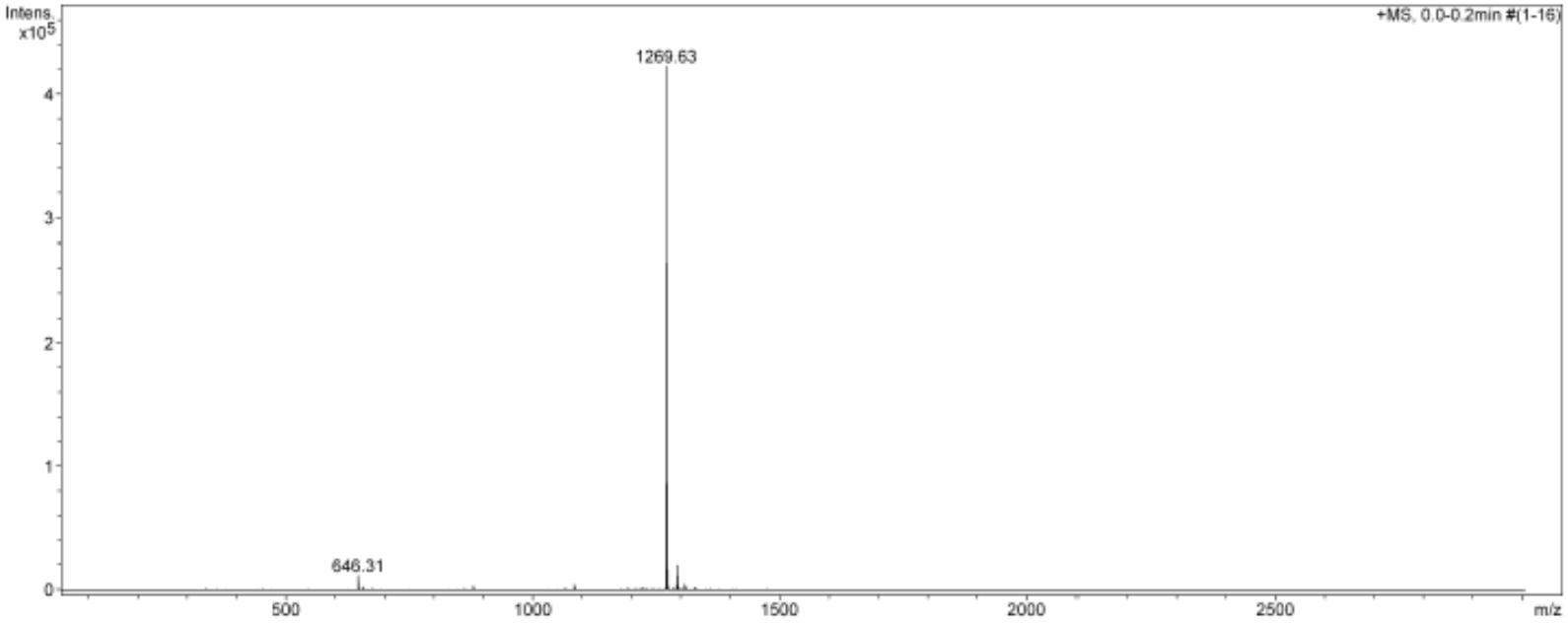
Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / UDS

Analysis Info

Analysis Name	O35504SK.d	Acquisition Date	4/2/2015 9:05:23 AM
Method	esi wide pos.m	Operator	Administrator
Sample Name	AD	Instrument	micrOTOF
Comment			

Acquisition Parameter

Source Type	ESI	Capillary	4500 V	Nebulizer	0.4 Bar	Corona	195 nA
Ion Polarity	Positive	Set Capillary Exit	150.0 V	Dry Gas	4.0 l/min	Set Hexapole RF	220.0 V
Scan Range	n/a	Set Skimmer 1	50.0 V	Dry Heater	179 °C	APCI Heater	514 °C



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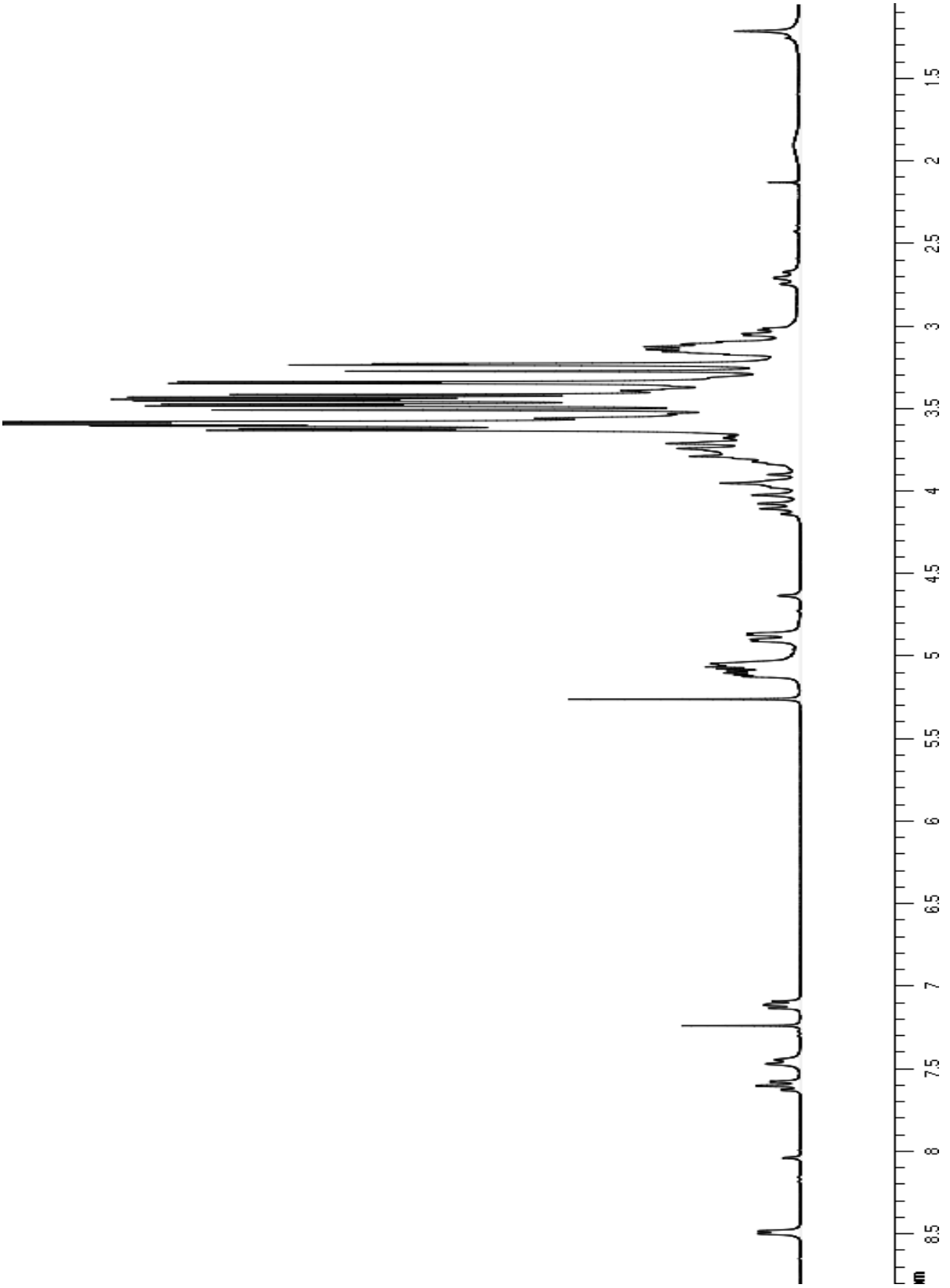
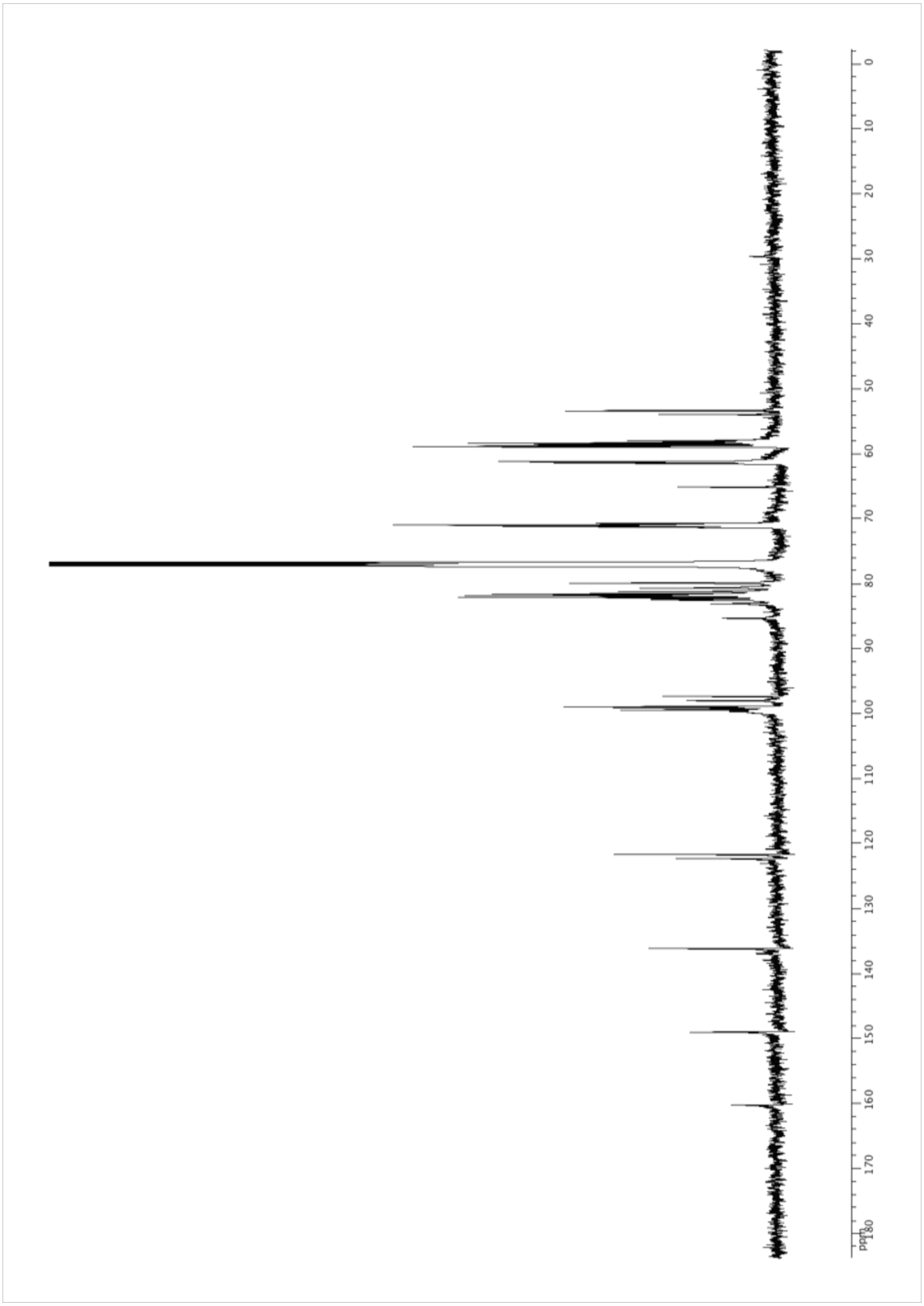
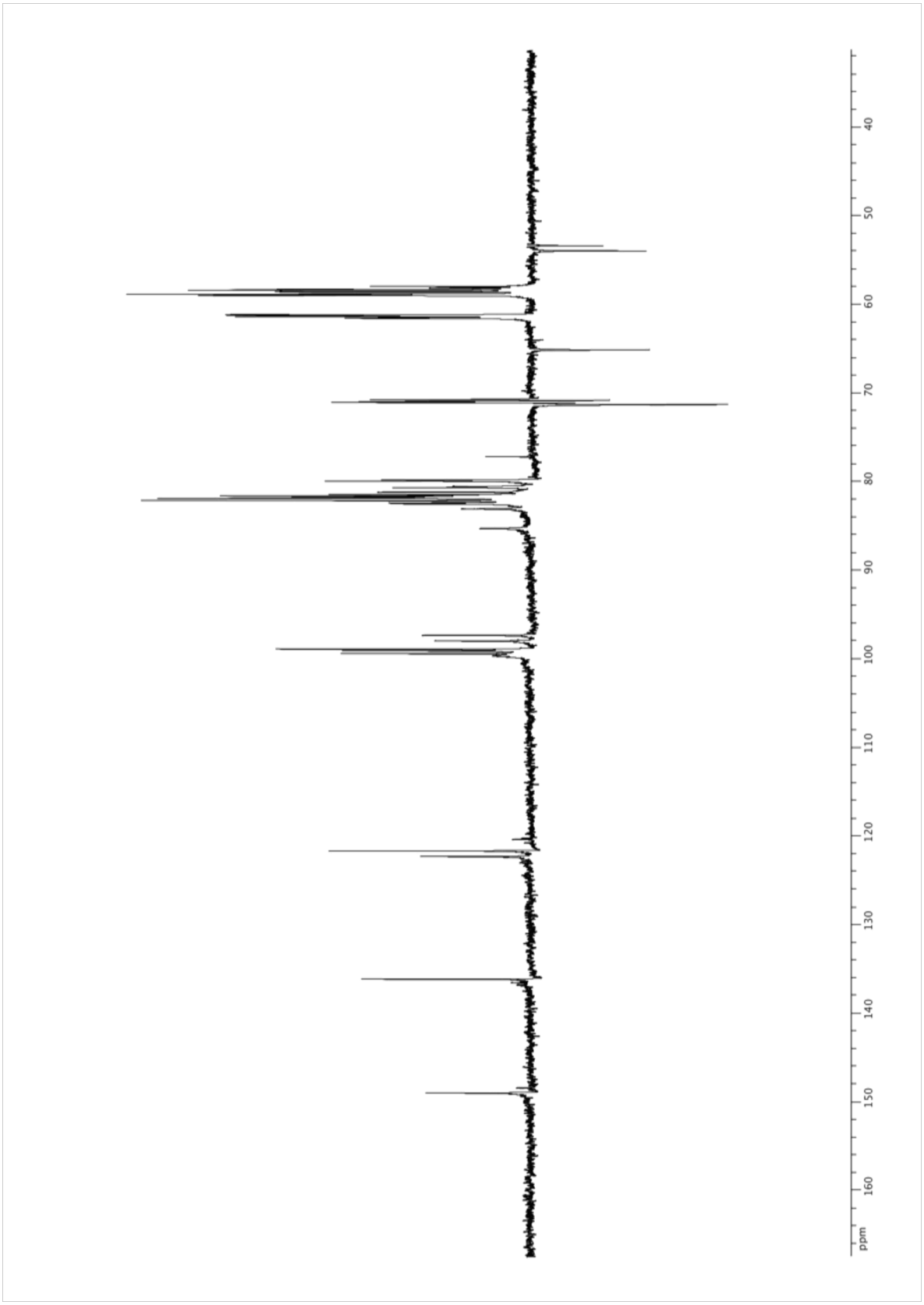


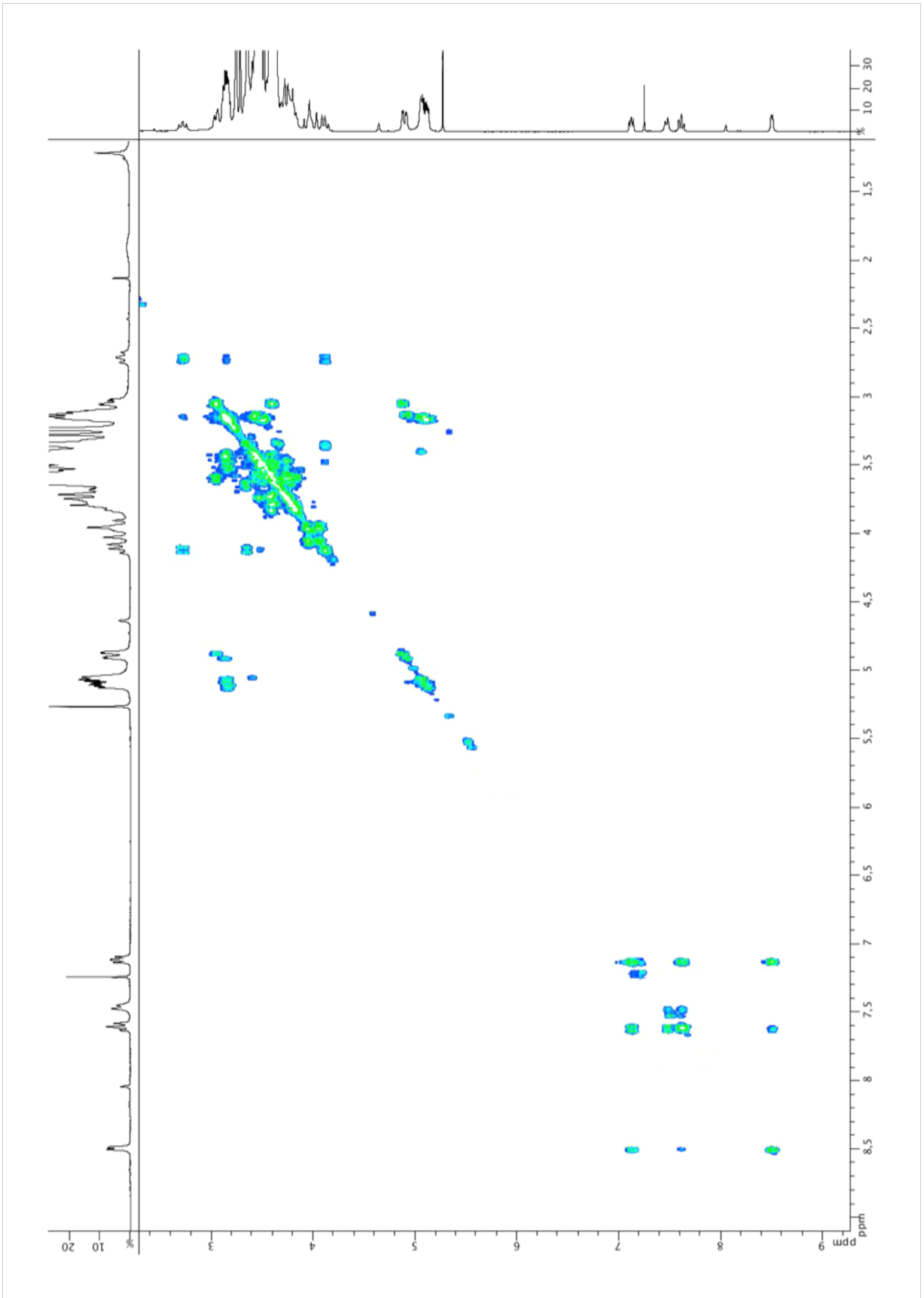
^{1}H NMR spectrum of **12a/b**



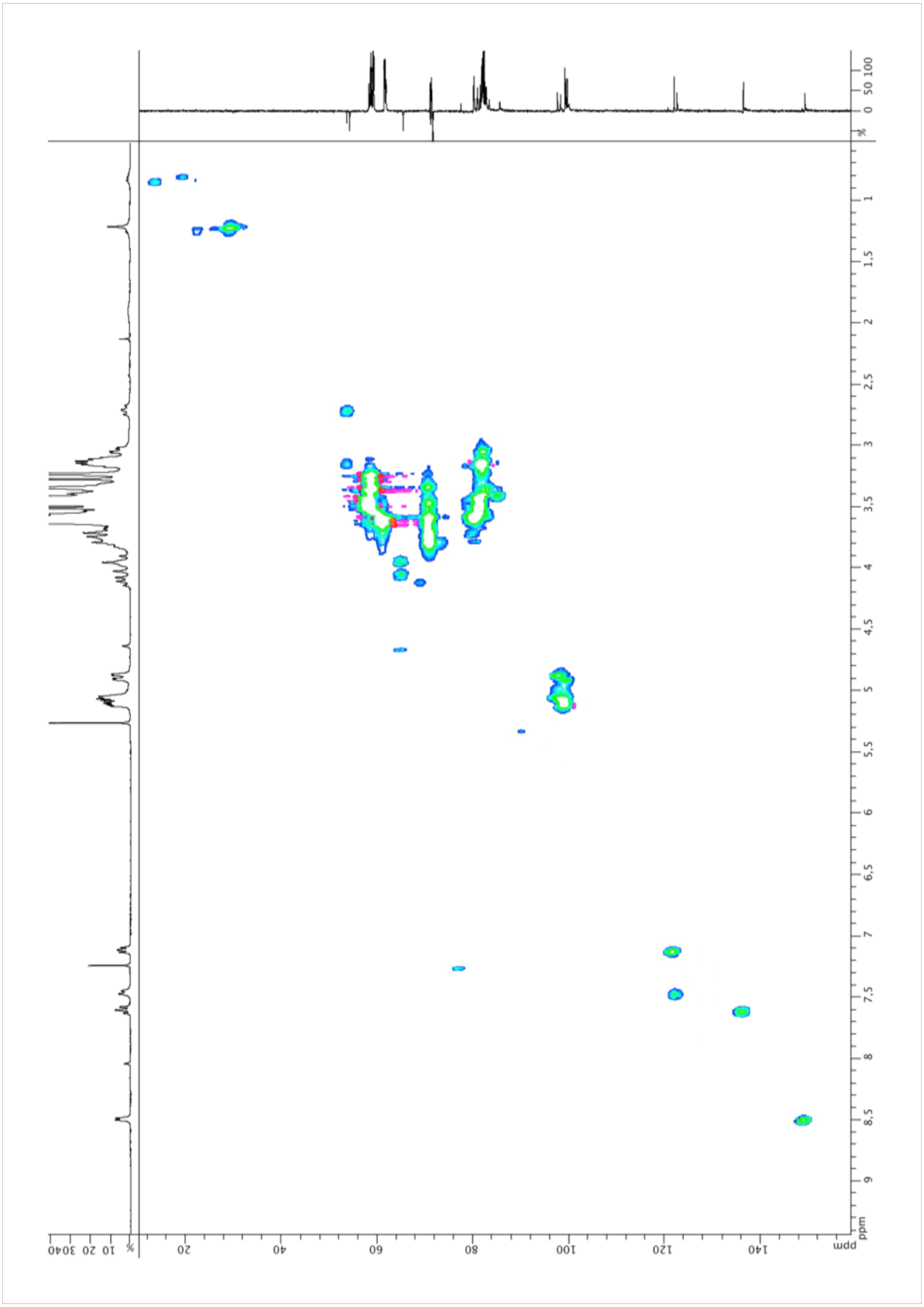
^{13}C NMR spectrum of **12a/b**



DEPT 135 NMR spectrum of **12a/b**



^{1}H-^{1}H COSY NMR spectrum of **12a/b**



^{1}H-^{13}C HSQC NMR spectrum of **12a/b**

Mass spectrum of **12a/b**

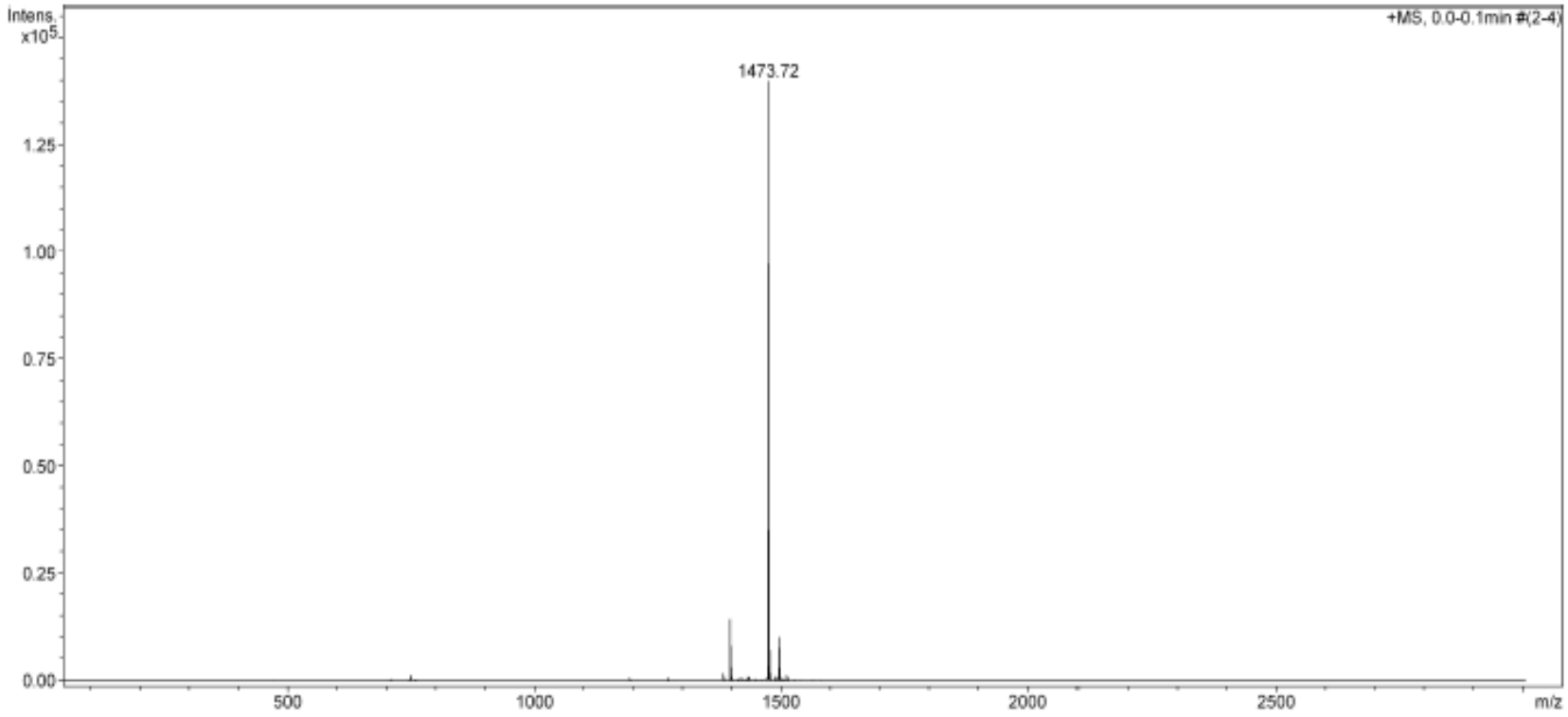
Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / UDS

Analysis Info

Analysis Name	O35853SK.d	Acquisition Date	4/30/2015 10:55:37 AM
Method	esi wide pos.m	Operator	Administrator
Sample Name	SD60	Instrument	micrOTOF
Comment			

Acquisition Parameter

Source Type	ESI	Capillary	4500 V	Nebulizer	0.4 Bar	Corona	195 nA
Ion Polarity	Positive	Set Capillary Exit	150.0 V	Dry Gas	4.0 l/min	Set Hexapole RF	220.0 V
Scan Range	n/a	Set Skimmer 1	50.0 V	Dry Heater	200 °C	APCI Heater	514 °C



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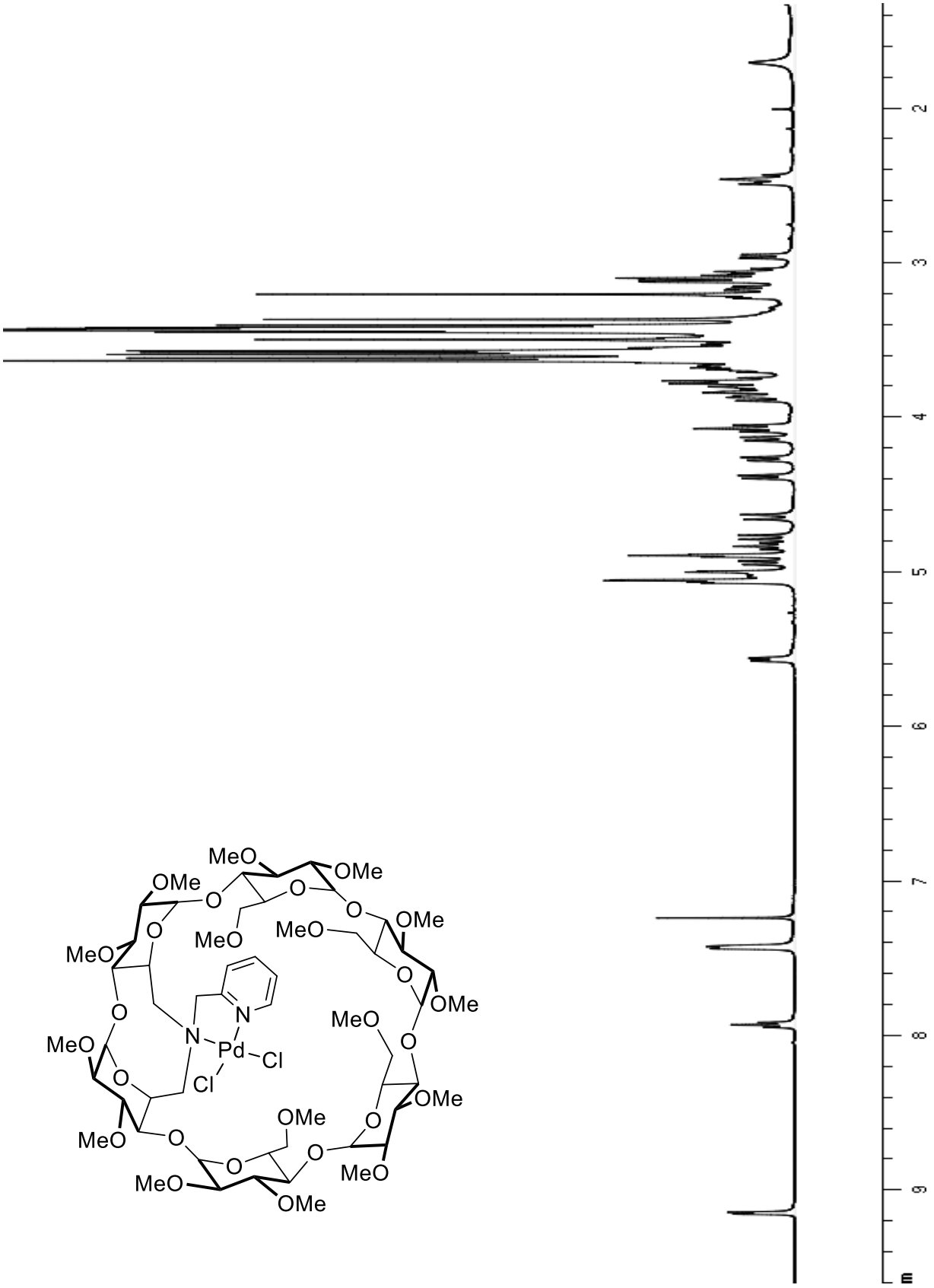
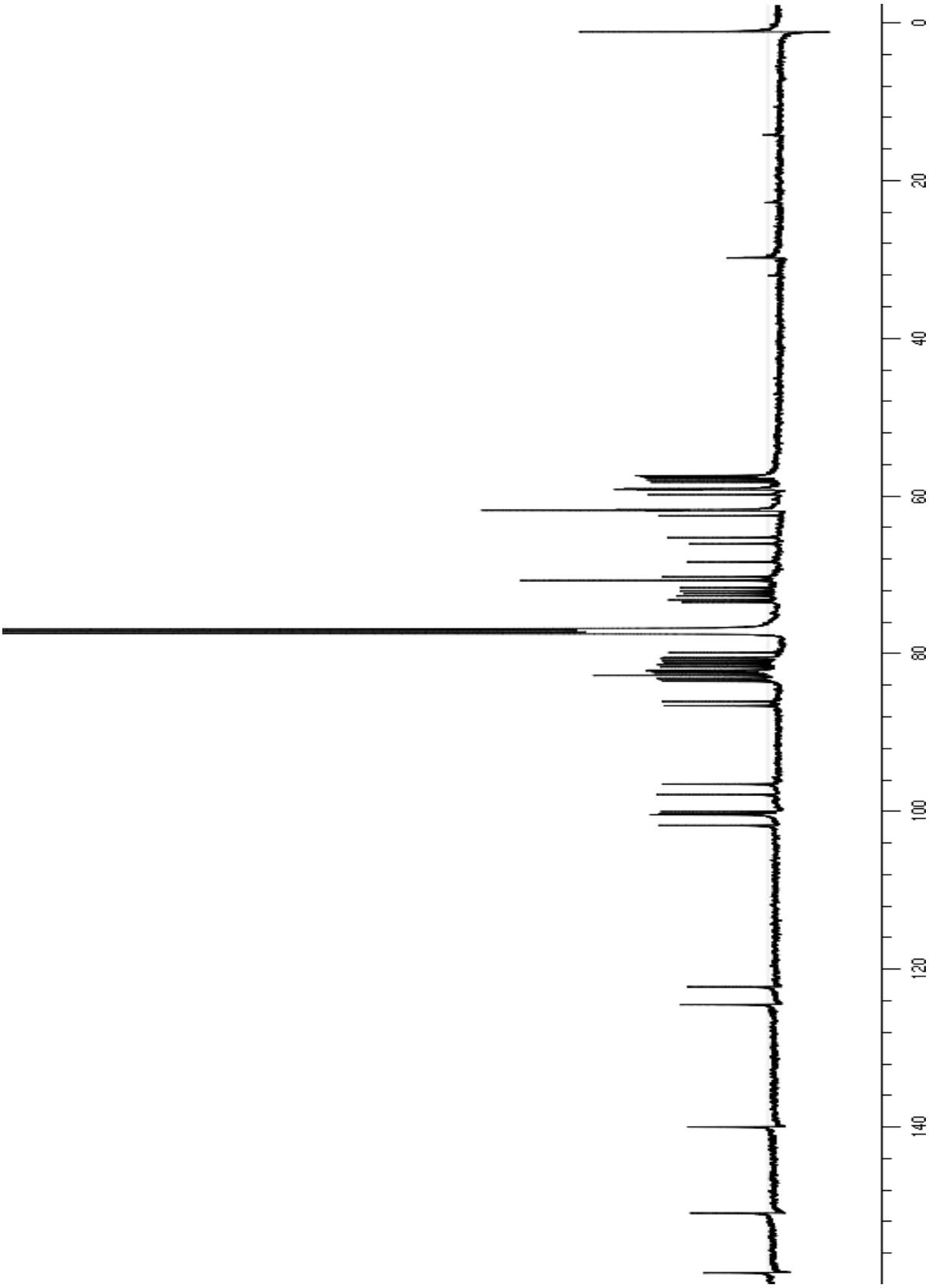
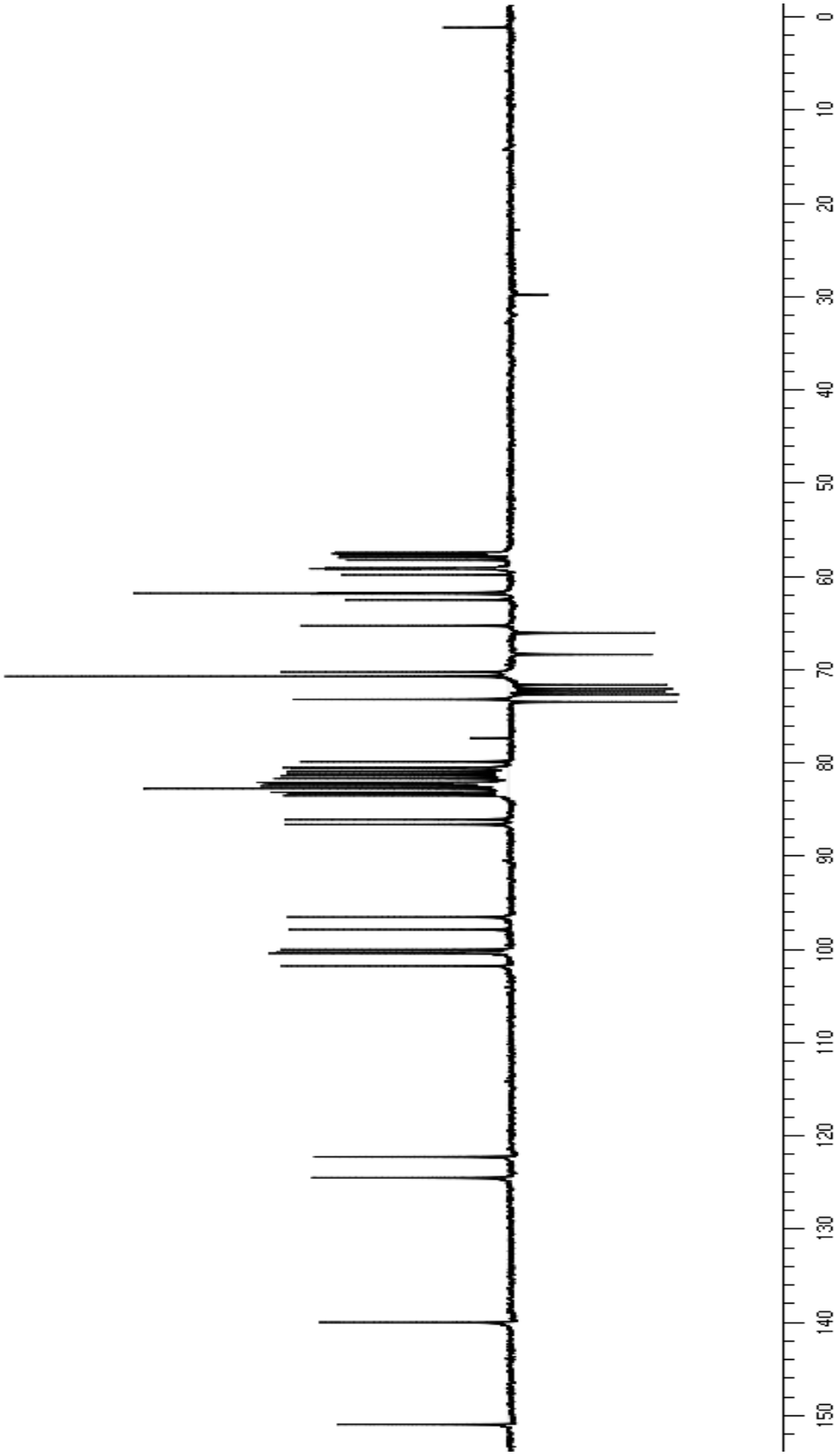


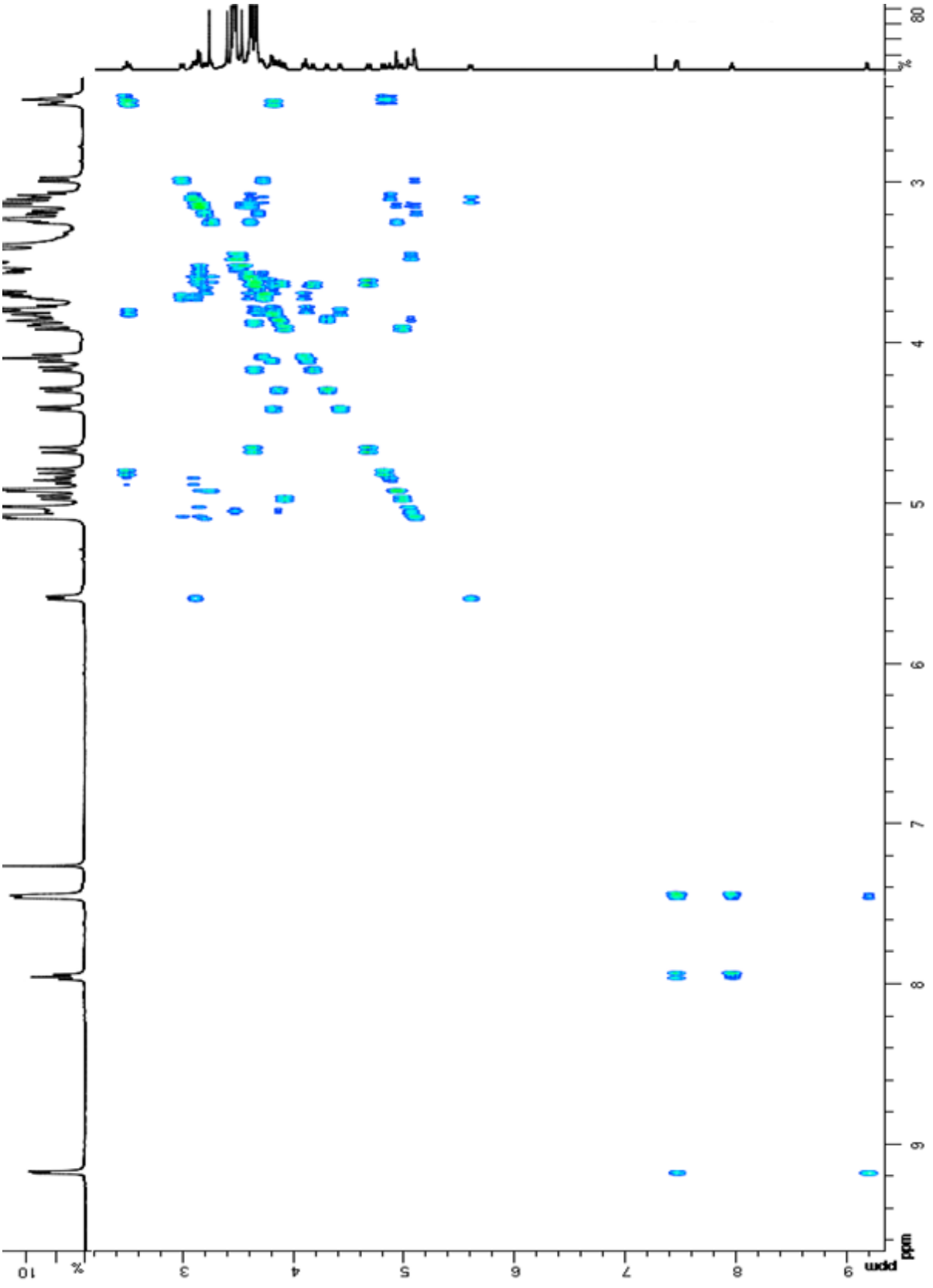
^{1}H NMR spectrum of **13**



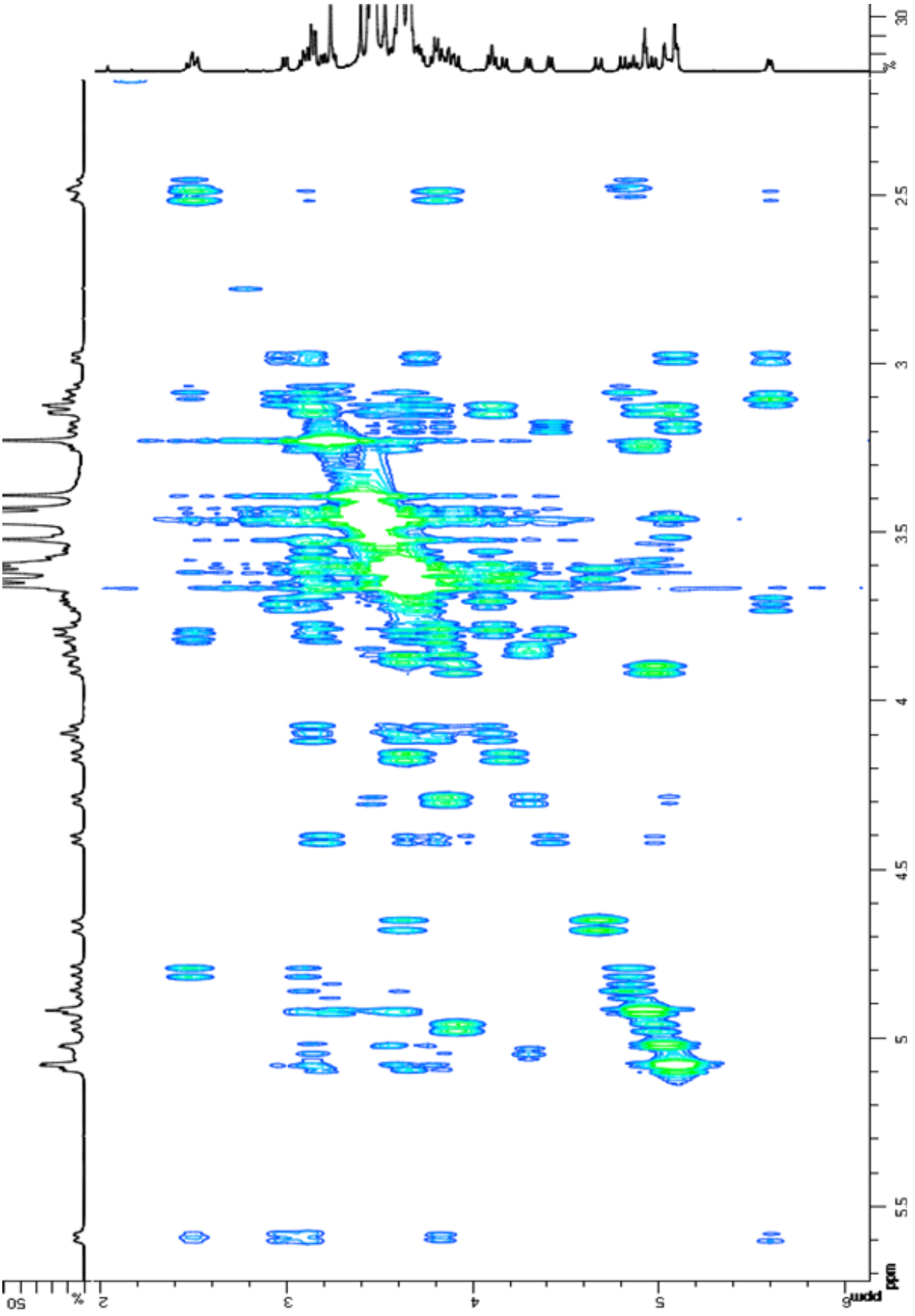
^{13}C NMR spectrum of **13**



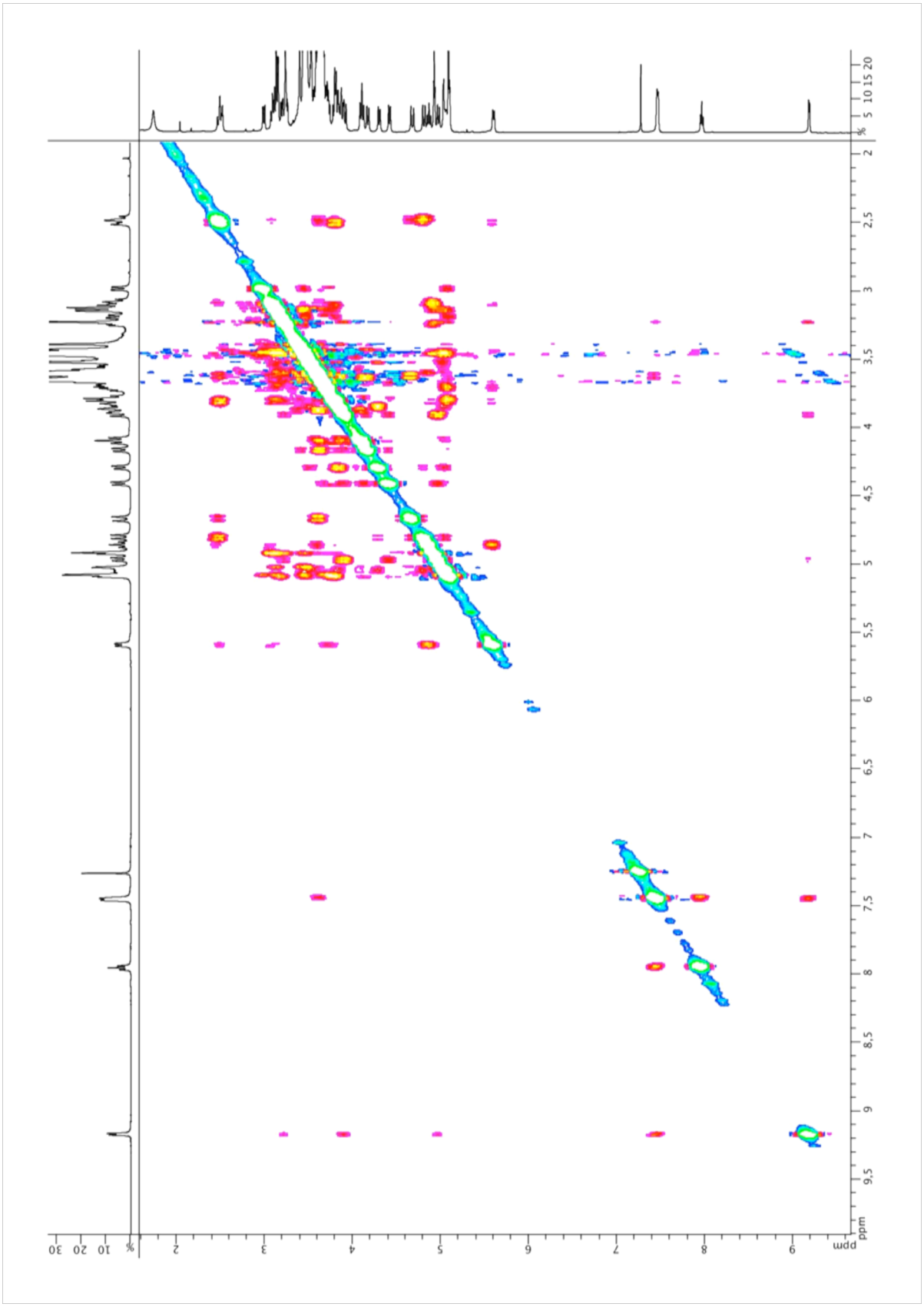
DEPT 135 NMR spectrum of **13**



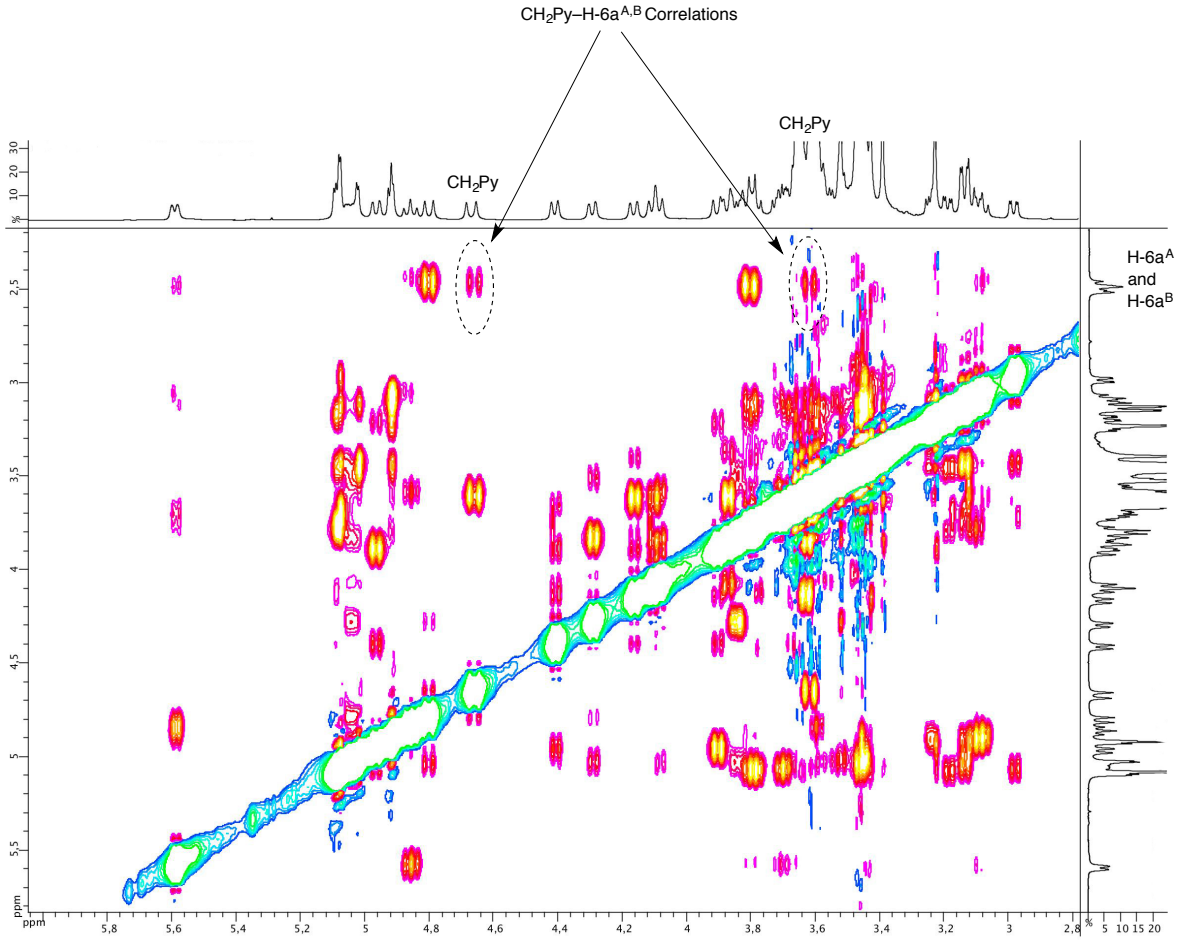
^{1}H-^{1}H COSY NMR spectrum of **13**



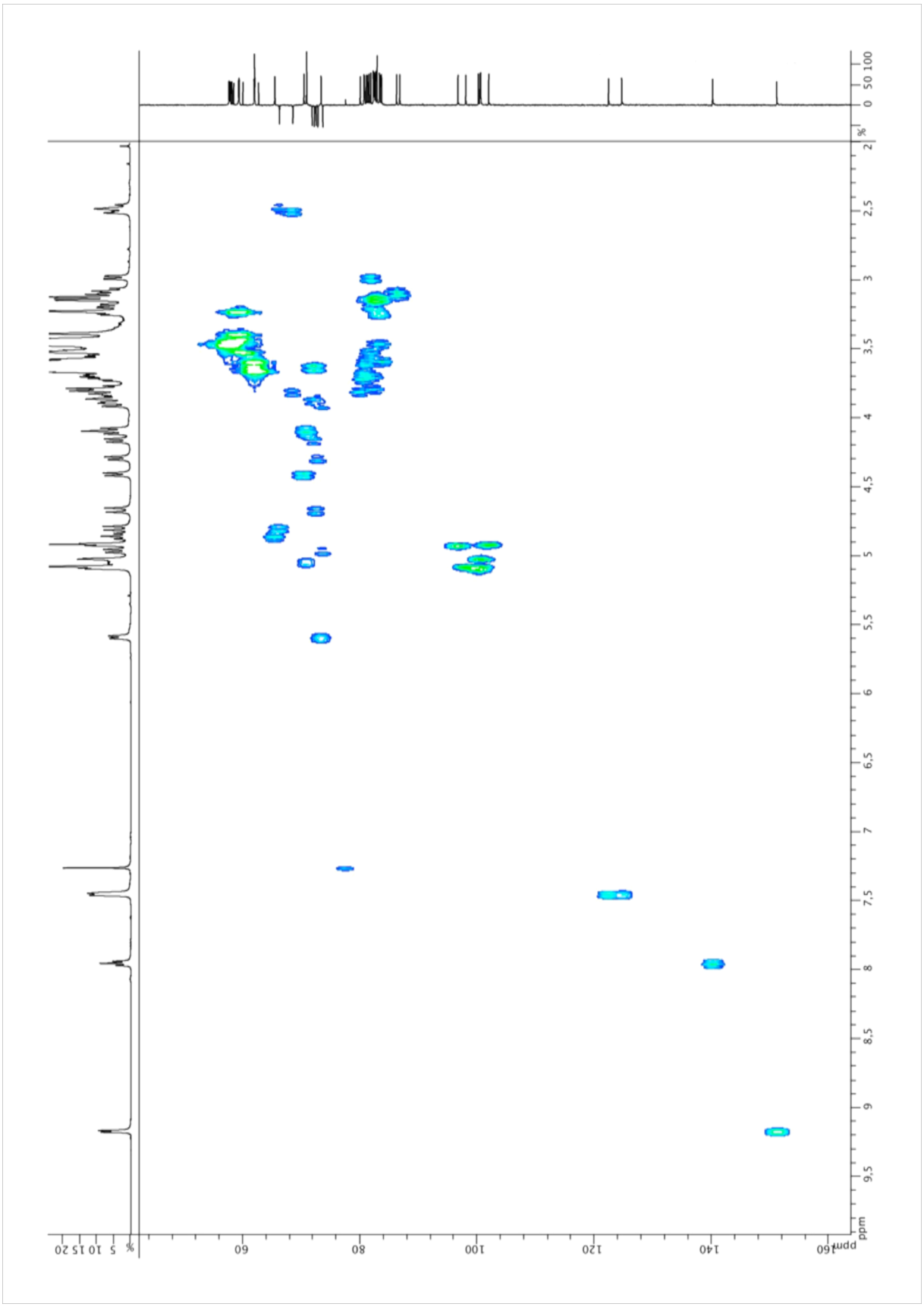
^{1}H-^{1}H TOCSY NMR spectrum of **13**



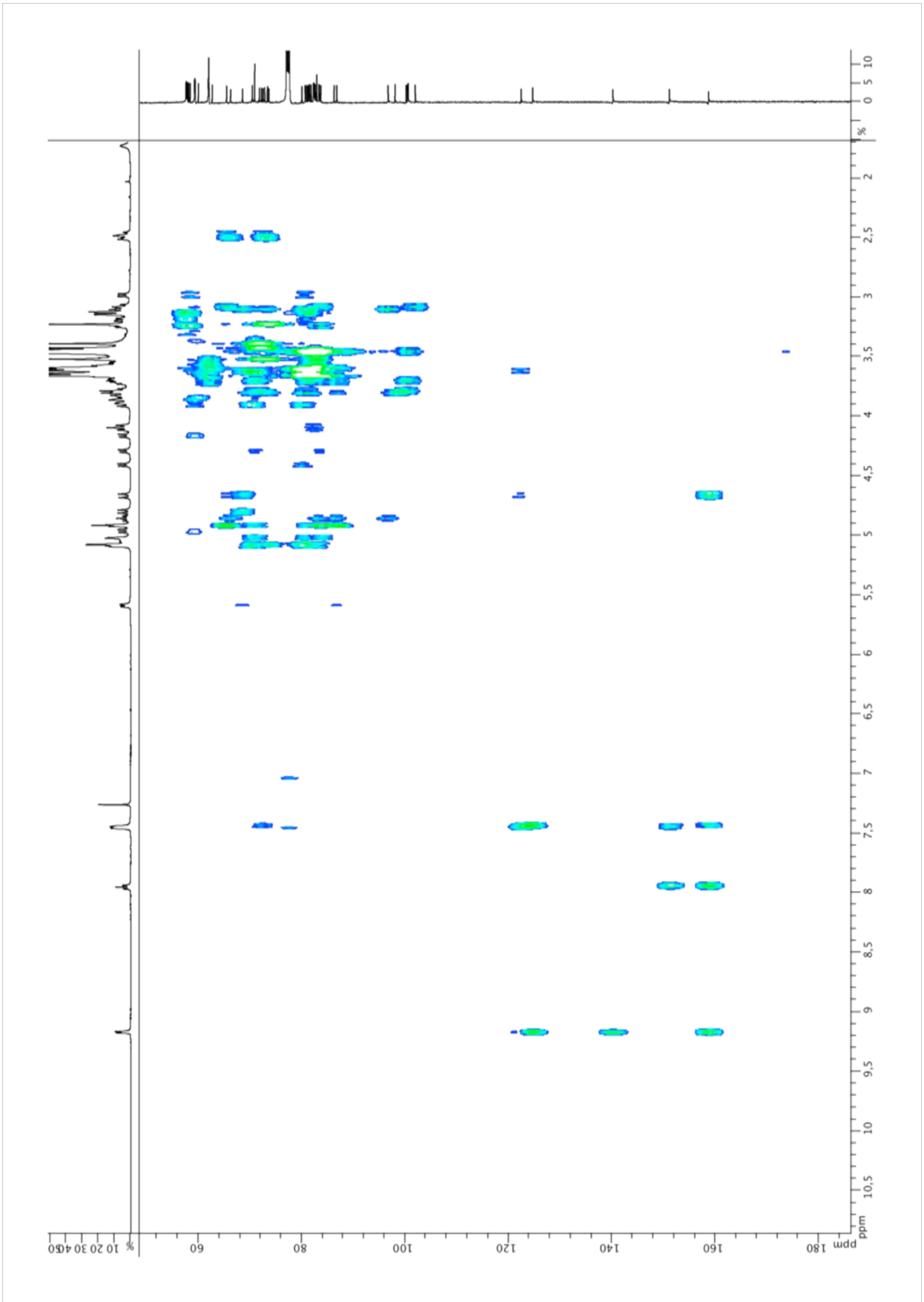
^{1}H-^{1}H ROESY NMR spectrum of **13**



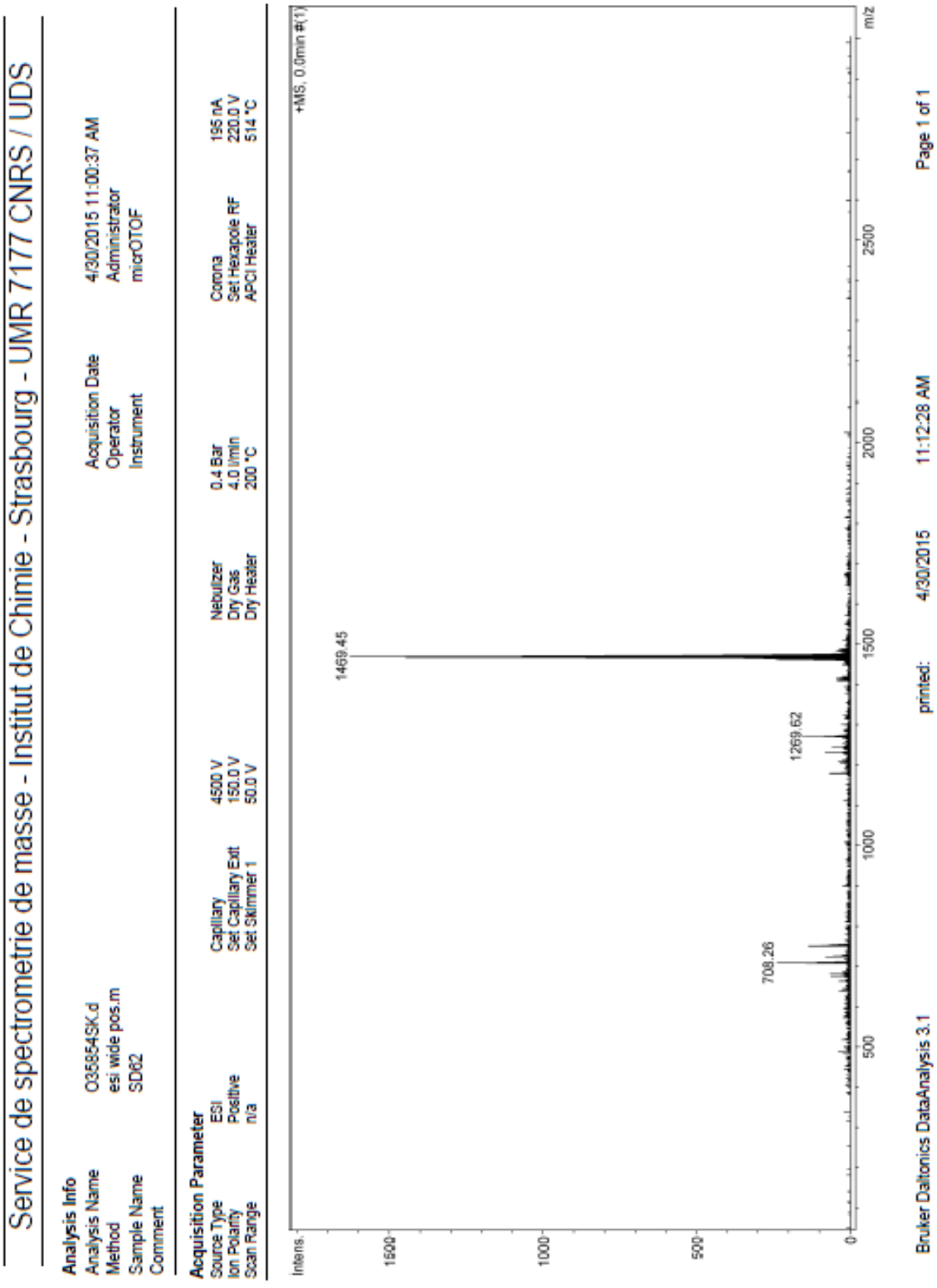
Part of the ^{1}H-^{1}H ROESY NMR spectrum of **13** showing cross-peaks (circled) arising from through-space correlations between CH_2Py protons and H-6 protons of the AB bridged glucose units



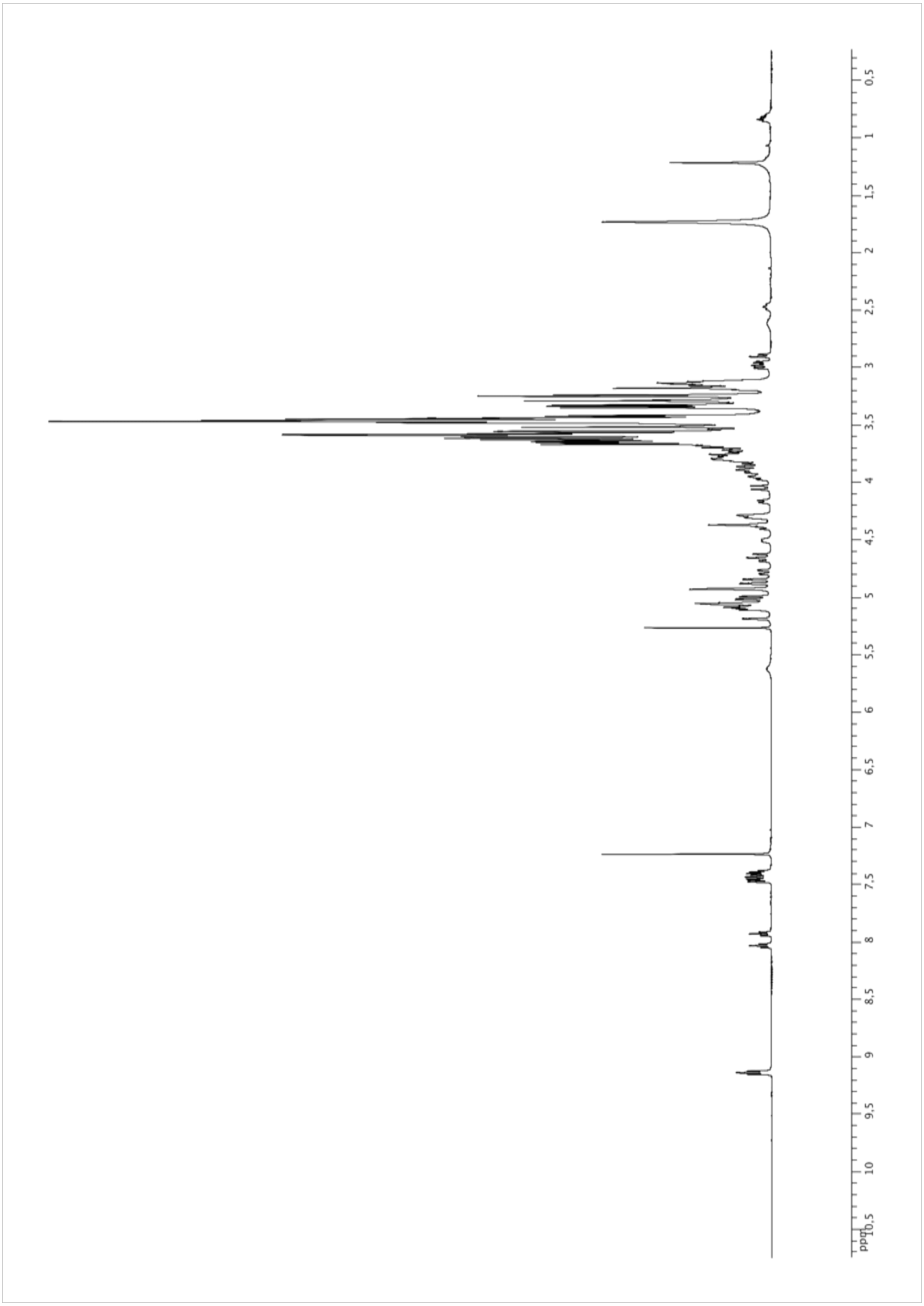
^{1}H-^{13}C HSQC NMR spectrum of **13**



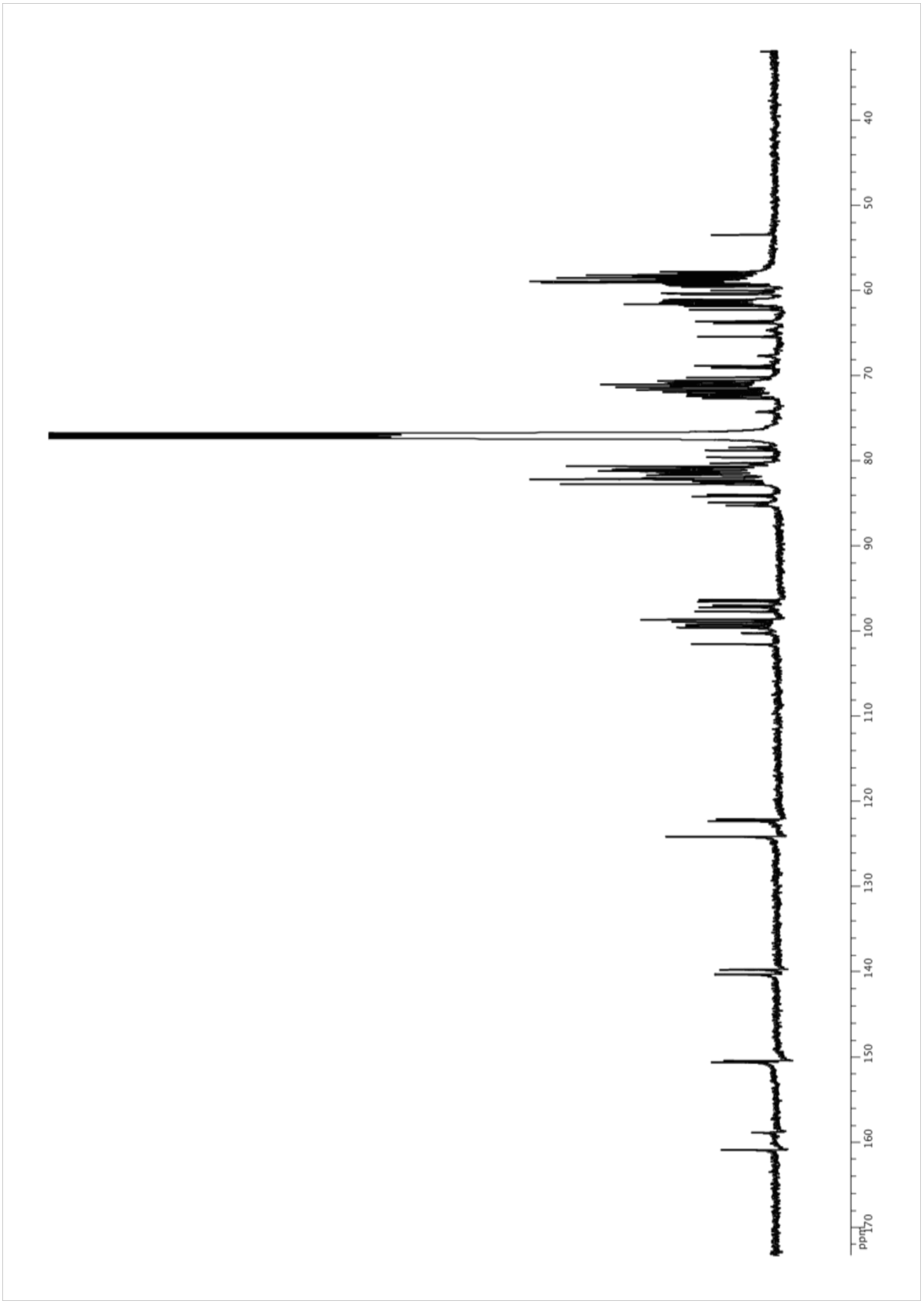
^{1}H-^{13}C HMBC NMR spectrum of **13**



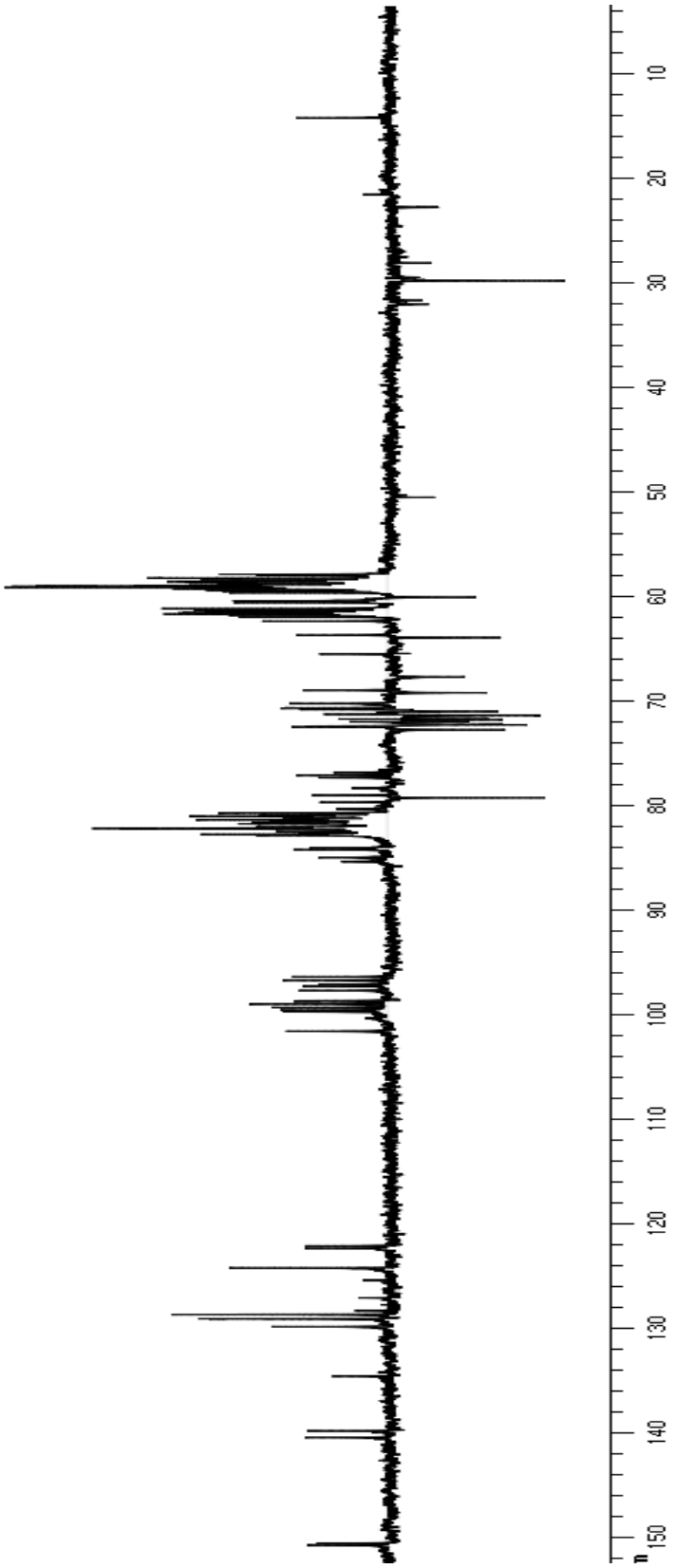
Mass spectrum of **13**



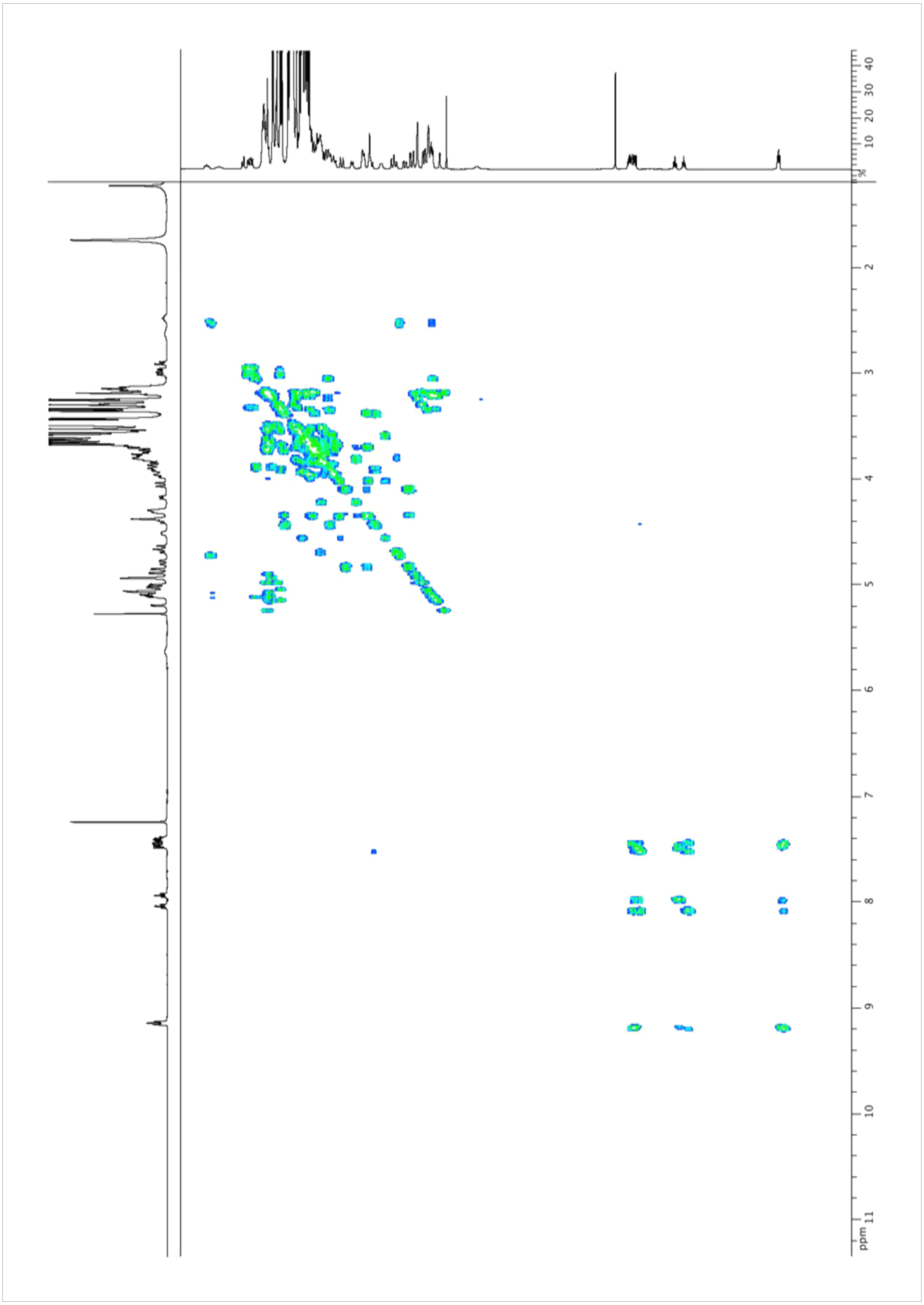
^{1}H NMR spectrum of **14a/b**



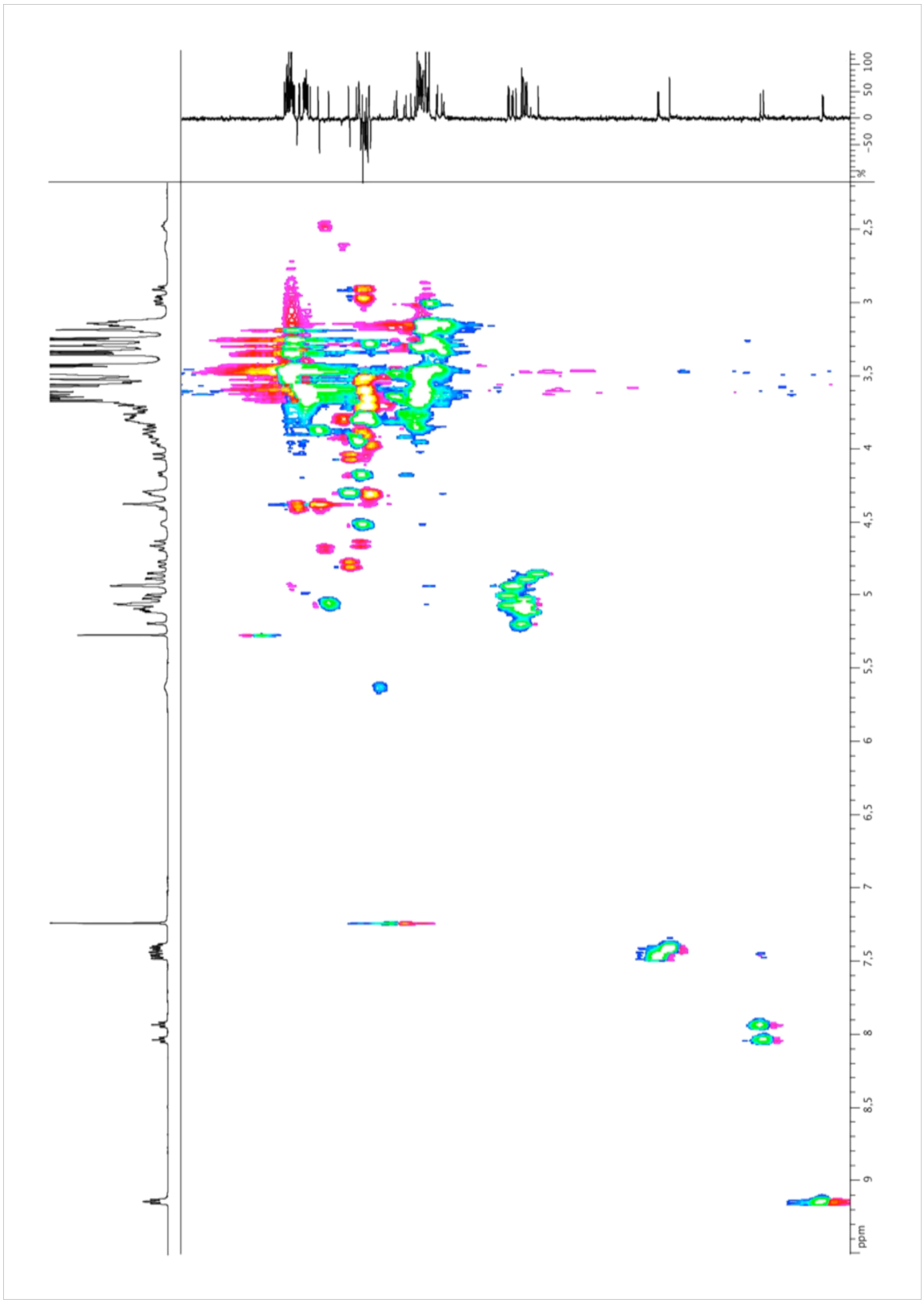
^{13}C NMR spectrum of **14a/b**



DEPT 135 NMR spectrum of **14a/b**



^{1}H-^{1}H COSY NMR spectrum of **14a/b**



^{1}H-^{13}C Edited HSQC NMR spectrum of **14a/b**

Mass spectrum of **14a/b**

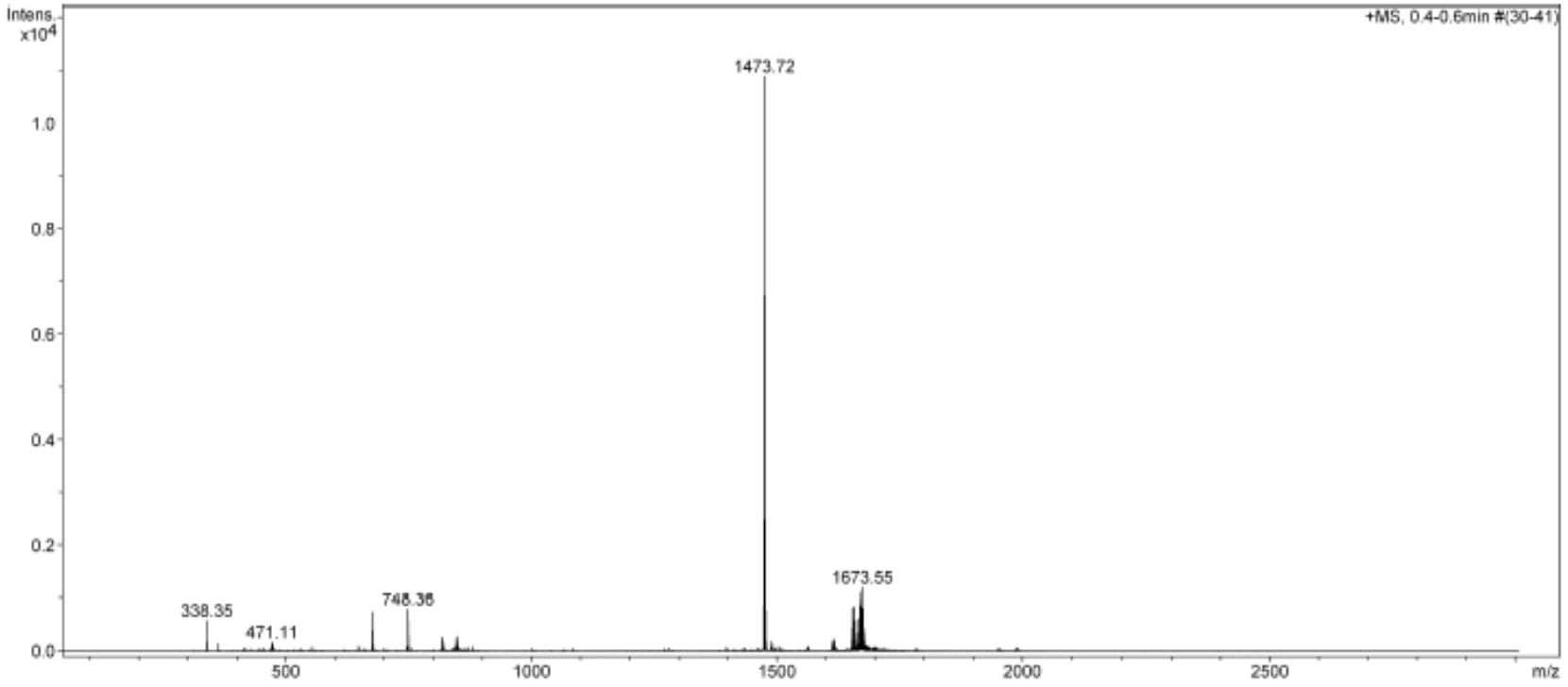
Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / UDS

Analysis Info

Analysis Name	O36525SK.d	Acquisition Date	6/11/2015 2:36:15 PM
Method	esi wide pos.m	Operator	Administrator
Sample Name	SD65A	Instrument	micrOTOF
Comment			

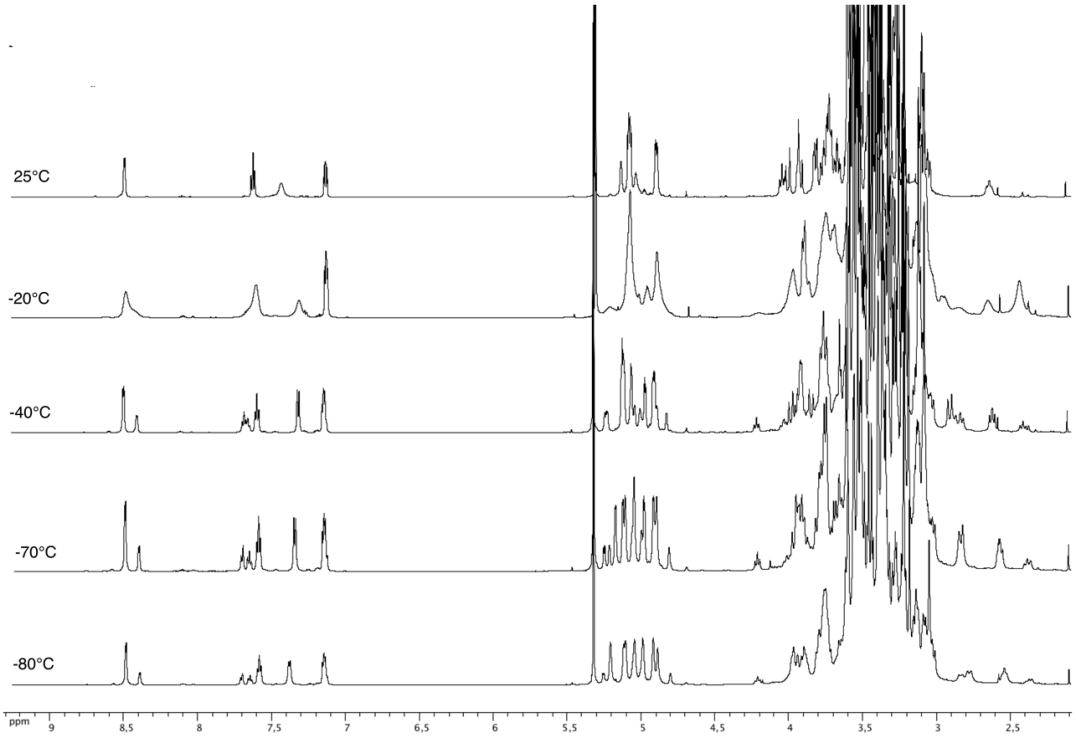
Acquisition Parameter

Source Type	ESI	Capillary	4500 V	Nebulizer	0.4 Bar	Corona	219 nA
Ion Polarity	Positive	Set Capillary Exit	150.0 V	Dry Gas	4.0 l/min	Set Hexapole RF	220.0 V
Scan Range	n/a	Set Skimmer 1	50.0 V	Dry Heater	200 °C	APCI Heater	514 °C

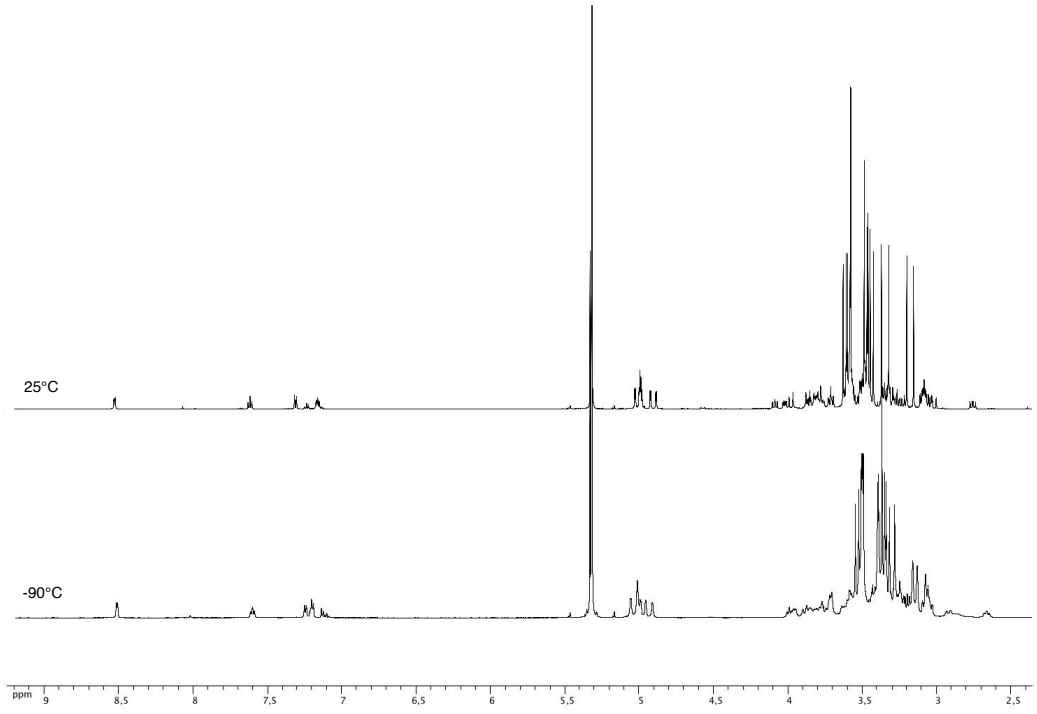


Bruker Daltonics DataAnalysis 3.1 printed: 6/11/2015 3:24:31 PM Page 1 of 1

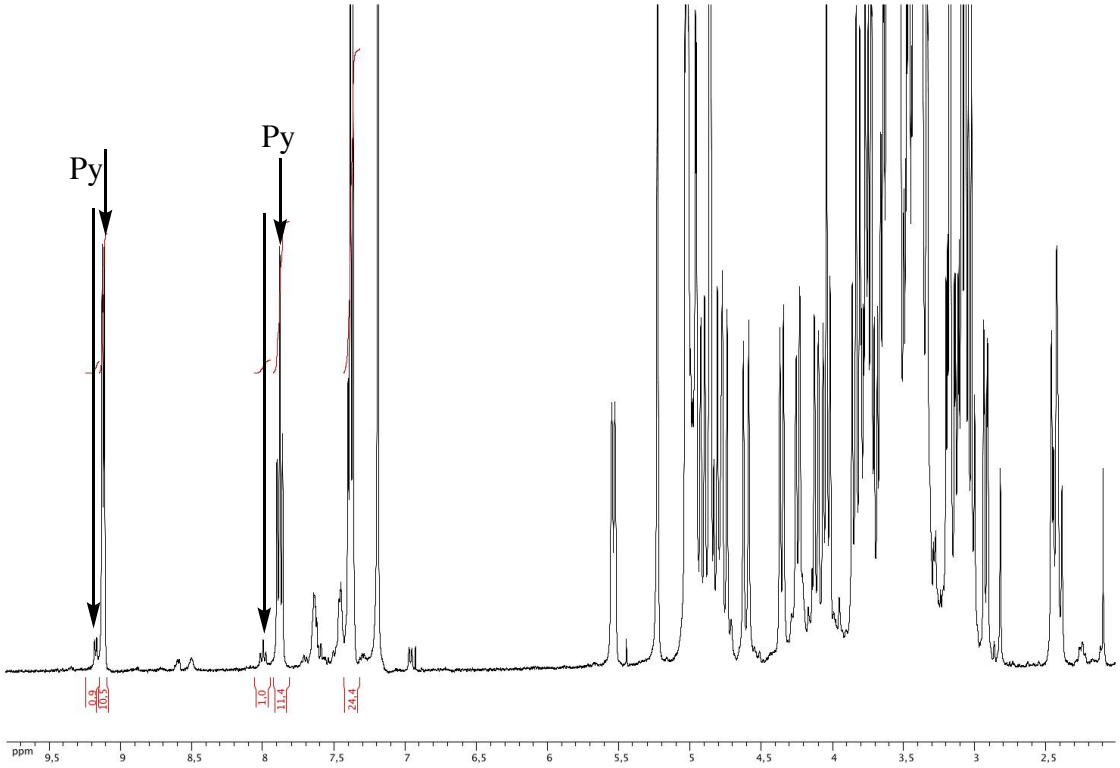
Variable-temperature (VT) NMR spectroscopic studies of ligands **11a** and **12a/b**



^{1}H NMR spectra (600.1 MHz) of ligand **12a/b** recorded in CD_2Cl_2 in the range -80ºC–25ºC



^{1}H NMR spectra (600.1 MHz) of ligand **11a** recorded in CD_2Cl_2 at 25°C and – 90°C

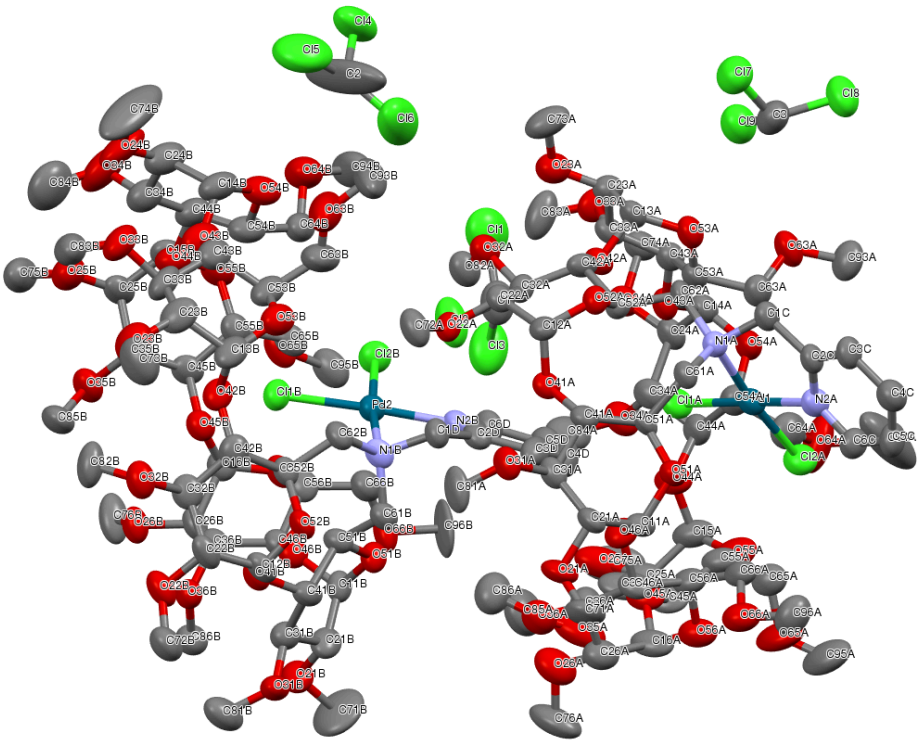


^{1}H NMR spectrum obtained upon reaction of a mixture of ligands **11a**/**11b** (9:1) with [$PdCl_2$(COD)]. The spectrum shows that the ratio of the complexes formed is similar to that of the ligand mixture.

Crystal structure analyses

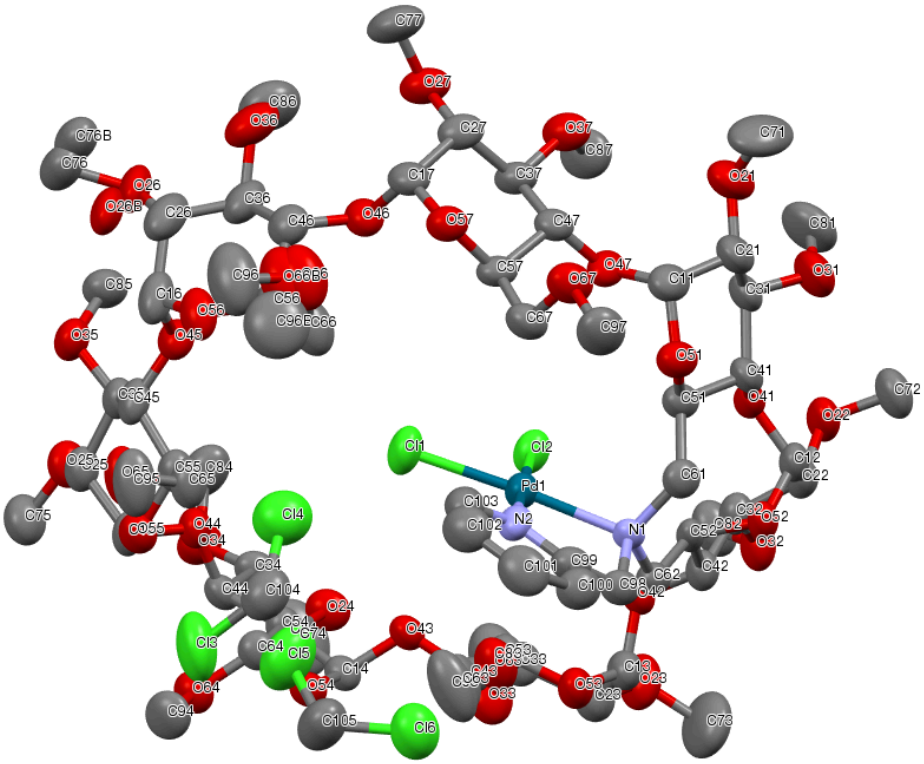
X-ray crystallographic data of 13: Single crystals of **13** were obtained by slow diffusion of *n*-pentane into a $CHCl_3$ solution of the compound. Crystal data for $C_{118.5}H_{194.5}Cl_{11.5}N_4O_{56}Pd_2$ (2•**5**•2.5$CHCl_3$) , M_r = 3191.74; orthorhombic; space group $P2_12_12_1$; a = 15.7481(2), b = 31.2188(5), c = 33.7366(4) Å; V = 16586.2(4) Å^3; Z = 4; ρ_{calcd} = 1.278 Mg.m^{-3}; λ(Cu-K_α) = 1.54184 Å; μ = 4.116 mm^{-1}; F(000) = 6676; T = 150 K. The sample (0.301 × 0.130 × 0.088 mm) was studied with a SuperNova EosS2 diffractometer using a mirror-monochromatised $Cu_{K\alpha}$ radiation. The structure was solved with SIR-97,[5] which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, many hydrogen atoms were found with a Fourier difference analysis. The whole structure was refined with SHELXL-2014/6[6] and full-matrix least-square techniques. Use of F^2 magnitude; x, y, z, β_{ij} for C, Cl, N, O, Pd atoms, x, y, z, in riding mode for H atoms, 1748 variables and 29211 observations with $I > 2.0\ \sigma(I)$; calcd $w = 1/[\sigma^2(F_o^2) + (0.2000\ P)^2]$ where $P = (F_o^2 + 2\ F_c^2)/3$ with the resulting R = 0.1236, R_W =

0.3546, and S_w = 1.531 ; $\Delta\rho$ < 2.960 e.Å^{-3}. The asymmetric unit contains two CD complexes linked together by a CH_{arom}…Cl hydrogen bond. The dimer co-crystallized with 2.5 molecules of chloroform. Some disorder was observed in the O(24B)-, O(63B)- and O(64A)-bound methyl groups. The A-level alert in the checkcif corresponds to a disordered molecule of chloroform. CCDC 1400713.



X-ray crystallographic data of 14a: Single crystals of **14a** were obtained by slow diffusion of *n*-heptane into a CH_2Cl_2 solution of a **14a**/**14b** mixture. Crystal data for $C_{69}H_{116}Cl_6N_2O_{33}Pd$ (**14a**•2CH_2Cl_2, M_r = 1820.73; orthorhombic; space group $P2_12_12$; a = 28.2881(8), b =29.3527(8), c = 10.8184(3) Å; V = 8982.9(4) Å^3; Z = 4; ρ_{calcd} = 1.346 Mg.m^{-3}; λ(Cu-K_α) = 1.54178 Å; μ = 3.976 mm^{-1}; F(000) = 3824; T = 173 K. The sample (0.220 × 0.100 × 0.080 mm) was studied with an Bruker APEX-II CCD with a mirror-monochromatised $Cu_{K\alpha}$ radiation. The structure was solved with SHELXS-2013,[7] which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, many hydrogen atoms were found with a Fourier difference analysis. The whole structure was refined with SHELXS-2013,[7] and full-matrix least-square techniques. Use of F^2 magnitude; x, y, z, β_{ij} for C, Cl, N, O, Pd atoms, x, y, z, in riding mode for H atoms, 1045 variables and 11401 observations with I > 2.0 σ(I); calcd w = 1/[σ^2(F_o^2) + (0.0475 P)^2] where P = (F_o^2 + 2

F_c^2)/3 with the resulting $R = 0.0575$, $R_W = 0.1365$, and $S_w = 1.048$; $\Delta\rho < 0.555$ e.Å^{-3}.
The level B alert is mainly due to a disordered external heptane molecule and O26- and O66-methoxy groups each disordered over two positions. Residual electronic density is likely due to the presence of the heptane molecule, the contribution of which has been taken out by the SQUEEZE procedure[8] in the final refinement. CCDC 1546409.



General procedure for determining the glucose units linked by a given capping unit.[9]

Our strategy for full structural assignment began with the differentiation between capped and non-capped C-6 carbon atoms by DEPT 135. These appear as two distinct sets of signals. The H-6 protons could then be identified using ^{1}H-^{13}C HMQC (Heteronuclear Multiple Qantum Coherence spectroscopy). By using TOCSY (TOtal Correlation SpectroscopY) and COSY (COrrelated SpectroscopY), each H-6 proton was correlated to the set of protons belonging to the same glucose residue. The connectivity between individual glucose units was then established via a ROESY (Rotating frame Overhauser Effect SpectroscopY) experiment showing the proximity between H-4$_N$ and H-1$_{N+1}$ protons (N and N+1 standing for neighbouring glucose moieties labelled in the alphabetical order).

References

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7. G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112-122.
8. A. L. Spek*, Acta Crystallogr.*, 2009*,* **D65***,* 148–155.
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