Electronic Supplementary Information (ESI)

Regioselective opening of proximally sulfato-capped cyclodextrins

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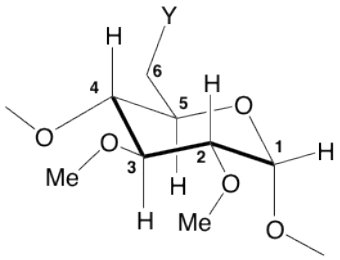
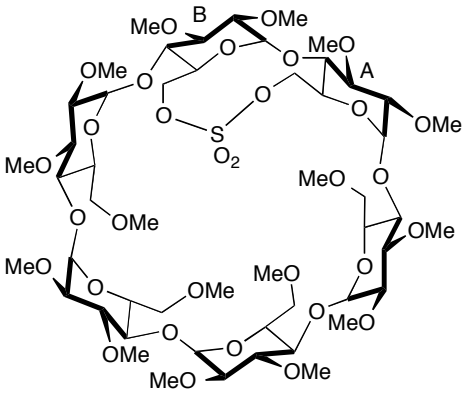
General methods

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 ^{1}H, $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectra were recorded with Bruker FT instruments (AVANCE 300, 400, 500, 600 spectrometers). ^{1}H 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). $2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{C},6^{D},6^{E},6^{F}$-Hexadeca-*O*-methyl-$\alpha$-cyclodextrin,[1] $2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},2^{G},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},3^{G},6^{C},6^{D},6^{E},6^{F},6^{G}$-Nonadeca-*O*-methyl-$\beta$-cyclodextrin,[2] and **3**[3] 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. When not indicated, the letter A refers to a glucose unit bearing a corresponds The numbering of the atoms within a glucose unit is as follows:



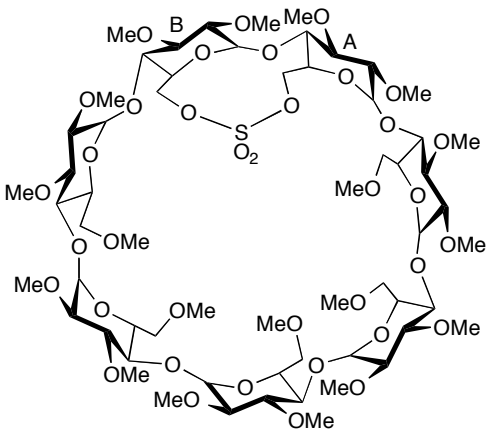
Synthesis and characterisation



$6^{A},6^{B}$-Dideoxy-$6^{A},6^{B}$-sulfato-$2^{A},2^{B},2^{C},2^{D},2^{E},$ $2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{C},6^{D},6^{E},6^{F}$-hexadeca-*O*-methyl-$\alpha$-cyclodextrin (1):

A solution of freshly distilled thionyl chloride (0.112 g, 69 μL, 0.94 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of $2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{C},6^{D},6^{E},6^{F}$-hexadeca-*O*-methyl-$\alpha$-cyclodextrin (0.500 g, 0.42 mmol) and NEt_3 (0.106 g, 145 μL, 1.05 mmol) in CH_2Cl_2 (100 mL) at –78°C. The reaction mixture was stirred for 1 h at –78°C whereupon it was allowed to reach room temperature for an additional 1 h, quenched with saturated aqueous $NaHCO_3$ (80 mL), and extracted with $CHCl_3$ (3 × 50 mL). The combined organic extracts were dried ($MgSO_4$) before being evaporated to dryness to afford a colourless residue, which was dissolved in a mixture of CH_2Cl_2 (6 mL), MeCN (6 mL) and water (12 mL). Ruthenium trichloride (0.005 g, 30×10^{-3} mmol) and sodium periodate (0.225 g, 1.05 mmol) were then added and the reaction mixture was stirred for 12 h at room temperature before adding saturated aqueous $NaHCO_3$ (200 mL). Subsequent extraction with $CHCl_3$ (3 × 50 mL) was followed by drying of the organic extracts ($MgSO_4$). Removal of the solvent in vacuo gave a colourless residue, which was subjected to column chromatography (SiO_2; CH_2Cl_2/MeOH, 97:3 to 95:5, *v*/*v*) to afford **1** (0.498 g, 96%) as a colourless solid. R_f (SiO_2, CH_2Cl_2/MeOH, 90:10, *v*/*v*) = 0.63; m.p. 147°C; ^{1}H NMR (400.1 MHz, $CDCl_3$, 25ºC): δ (assignment by COSY) = 3.08 (t, 1 H, $^3J_{H4\text{-}H3} = {}^3J_{H4\text{-}H2} = 9.3$ Hz, H-$4^{A \text{ or } B}$), 3.12–3.21 (6 H, H-2), 3.26 (t, 1 H, $^3J_{H4\text{-}H3} = {}^3J_{H4\text{-}H5} = 9.5$ Hz, H-$4^{B \text{ or } A}$), 3.37 (s, 6 H, OMe), 3.38 (s, 3 H, OMe), 3.39 (s, 3 H, OMe), 3.47 (s, 6 H, OMe), 3.49 (s, 6 H, OMe), 3.50 (s, 3 H, OMe), 3.53 (s, 3 H, OMe), 3.61 (s, 3 H, OMe), 3.62 (s, 3 H, OMe), 3.63 (s, 3 H, OMe), 3.64 (s, 3 H, OMe), 3.65 (s, 3 H, OMe), 3.66 (s, 3 H, OMe), 3.45–3.67 (12 H, H-3, H-6), 3.72–3.85 (8 H, H-4, H-5, H-6a or H-6b), 3.89–3.96 (2 H, H-5, H-6a or H-6b), 4.11 (t, 1 H, $^2J_{H6a\text{-}H6b} = {}^3J_{H6a\text{-}H5} = 11.3$ Hz, H-$6a^{A \text{ or } B}$), 4.15 (dd, 1 H, $^3J_{H5\text{-}H6b} = 3.5$ Hz, $^3J_{H5\text{-}H4} = 9.5$ Hz, H-$5^{B \text{ or } A}$), 4.30 (d, 1 H, $^2J_{H6a\text{-}H6b} = 10.0$ Hz, H-$6a^{B \text{ or } A}$), 4.43 (ddd, 1 H, $^3J_{H5\text{-}H6a} = 11.3$ Hz, $^3J_{H5\text{-}H4} = 8.2$ Hz, $^3J_{H5\text{-}H6b} = 1.8$ Hz , H-$5^{A \text{ or } B}$), 4.90 (d, 1 H, $^3J_{H1\text{-}H2} = 2.7$ Hz, H-1), 4.91 (dd, 1 H, $^2J_{H6b\text{-}H6a} = 10.0$ Hz, $^3J_{H6b\text{-}H5} = 3.5$ Hz, H-$6b^{B \text{ or } A}$), 5.03 (d, 1 H, $^3J_{H1\text{-}H2} = 3.3$ Hz, H-1), 5.06 (d, 1 H, $^3J_{H1\text{-}H2} = 3.4$ Hz, H-1), 5.07–5.10 (3 H, H-1), 5.11 (dd, 1 H, $^2J_{H6b\text{-}H6a} = 11.3$, $^3J_{H6b\text{-}H5} =$

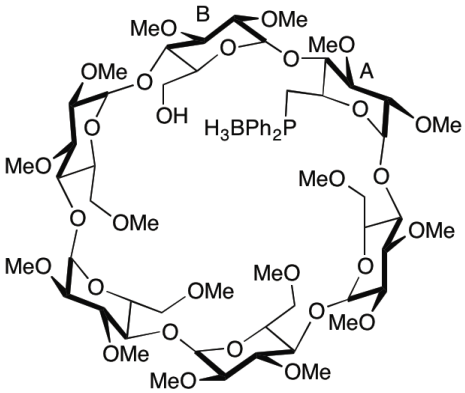
1.8, H-6b$^{A\ or\ B}$) ppm; $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25ºC): δ (assignment by HMQC) = 57.85, 58.05, 58.17, 58.28, 58.41, 58.60, 59.06, 59.15, 59.24, 59.32, 61.85, 61.92 [×2], 62.07, 62.14, 62.32 (OMe), 67.57, 70.07 (C-5), 70.44, 70.82 (C-6), 70.90, 71.25, 71.29 (C-5), 71.41 [×2] (C-6), 71.86 (C-5), 73.94 (C-6$^{A\ or\ B}$), 75.76 (C-6$^{B\ or\ A}$), 81.44, 81.54, 81.63, 81.72 [×3], 81.81 [×2], 81.91, 81.96, 82.07 [×2], 82.28, 82.31, 82.35, 82.47 (C-2, C-3, C-4), 83.98 (C-4$^{A\ or\ B}$), 86.63 (C-4$^{B\ or\ A}$), 98.81, 99.89, 100.04, 100.09, 100.26, 101.12 (C-1) ppm; elemental analysis (%) calcd for $C_{52}H_{90}O_{32}S{\cdot}C_7H_8$ (1281.50 + 92): C 52.43, H 7.31, found: C 52.25, H 7.53; MS (ESI-TOF): *m/z* (%): 1281.50 (100) $[M + Na]^+$.



6^A,6^B-Dideoxy-6^A,6^B-sulfato-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 (2):

This compound was prepared from 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 (0.530 g, 0.38 mmol) according to the above procedure (0.420 g, 76 %). R_f (SiO_2, CH_2Cl_2/MeOH, 90:10, *v*/*v*) = 0.56; m.p. 150°C; ^1H NMR (400.1 MHz, $CDCl_3$, 25ºC): δ (assignment by COSY) = 3.04–3.18 (8 H, H-2, H-4$^{B\ or\ A}$), 3.30 (s, 3 H, OMe), 3.31 (s, 9 H, OMe), 3.31 (1 H, H-4$^{A\ or\ B}$), 3.32 (s, 3 H, OMe), 3.41 (s, 3 H, OMe), 3.42 (s, 9 H, OMe), 3.43 (s, 3 H, OMe), 3.45 (s, 3 H, OMe), 3.49 (s, 3 H, OMe), 3.55 (s, 9 H, OMe), 3.56 (s, 3 H, OMe), 3.57 (s, 3 H, OMe), 3.58 (s, 3 H, OMe), 3.59 (s, 3 H, OMe), 3.28–3.68 (16 H, H-3, H-4, H-6), 3.69–3.80 (8 H, H-5, H-6), 3.81–3.87 (2 H, H-5, H-6), 3.90 (m, 1 H, H-5), 4.05 (ddd, 1 H, $^3J_{H5\text{-}H6a}$ = 1.2 Hz, $^3J_{H5\text{-}H6b}$ = 3.5 Hz, $^3J_{H5\text{-}H\text{-}4}$ = 9.8 Hz, H-5$^{A\ or\ B}$), 4.13 (dd, 1 H, $^2J_{H6a\text{-}H6b}$ = 10.5 Hz, $^3J_{H6a\text{-}H5}$ = 12.3 Hz, H-6a$^{B\ or\ A}$), 4.28 (ddd, 1 H, $^3J_{H5\text{-}H6a}$ =12.3 Hz, $^3J_{H5\text{-}H6b}$ =2.4 Hz, $^3J_{H5\text{-}H\text{-}4}$ = 7.6 Hz, H-5$^{B\ or\ A}$), 4.33 (dd, 1 H, $^2J_{H6a\text{-}H6b}$ = 10.0 Hz, $^3J_{H6a\text{-}H5}$ = 1.2 Hz, H-6a$^{A\ or\ B}$), 4.60 (dd, 1 H, $^2J_{H6b\text{-}H6a}$ = 10.0 Hz, $^3J_{H6b\text{-}H5}$ = 3.5 Hz, H-6b$^{A\ or\ B}$), 4.82 (d, 1 H, $^3J_{H1\text{-}H2}$ = 3.7 Hz, H-1), 4.96 (dd, 1 H, $^2J_{H6b\text{-}H6a}$ = 10.5 Hz, $^3J_{H6\text{-}H5}$ = 2.4 Hz, H-6b$^{B\ or\ A}$), 4.98 (d, 1 H, $^3J_{H1\text{-}H2}$ = 3.6 Hz, H-1), 5.02 (d, 1 H, $^3J_{H1\text{-}H2}$ =3.7 Hz, H-1), 5.04 (d, 1 H, $^3J_{H1\text{-}H2}$ = 3.6 Hz, H-1), 5.05 (d, 1 H, $^3J_{H1\text{-}H2}$ = 4.3 Hz, H-1), 5.09 (d, 1 H, $^3J_{H1\text{-}H2}$ = 3.9 Hz, H-1), 5.19 (d, 1 H, $^3J_{H1\text{-}H2}$ = 4.2 Hz, H-1) ppm; $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25ºC): δ (assignment by HMQC) = 57.97, 58.04, 58.17, 58.27, 58.56, 58.76, 58.81[×3], 58.87, 58.96, 59.02, 60.73, 61.13, 61.16, 61.34, 61.40, 61.52 [×2] (OMe), 68.06 (C-5$^{B\ or\ A}$), 68.68 (C-5$^{A\ or\ B}$), 70.23 (C-6), 70.31, 70.62, 70.70 (C-5), 70.85 (C-6), 70.88 (C-5), 71.00 [×2] (C-6),

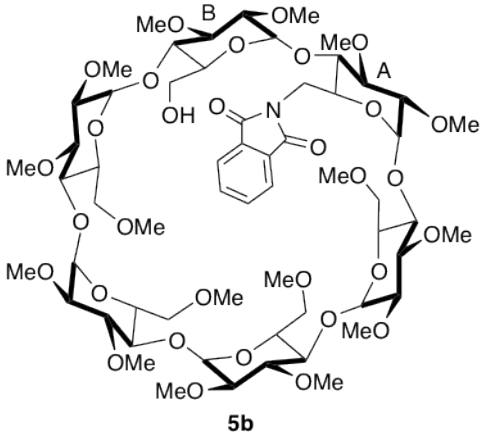
71.26 (C-5), 71.30 (C-6), 73.93 (C-$6^{B \text{ or } A}$), 74.26 (C-$6^{A \text{ or } B}$), 77.96, 79.49, 80.01, 80.28, 80.80, 81.25, 81.30, 81.35 [×2], 81.37 [×2], 81.45, 81.55, 81.60, 81.69, 81.77, 81.80, 81.87, 82.06, 82.28, 82.48 (C-2, C-3, C-4), 98.22, 98.41, 98.46, 98.55, 98.63, 99.82, 100.39 (C-1) ppm; elemental analysis (%) calcd for $C_{61}H_{106}O_{37}S{\cdot}CH_2Cl_2$ (1463.54 + 84.93): C 48.09, H 7.03, found: C 48.22, H 7.22; MS (ESI-TOF): *m/z* (%): 1485.60 (100) $[M + Na]^+$.



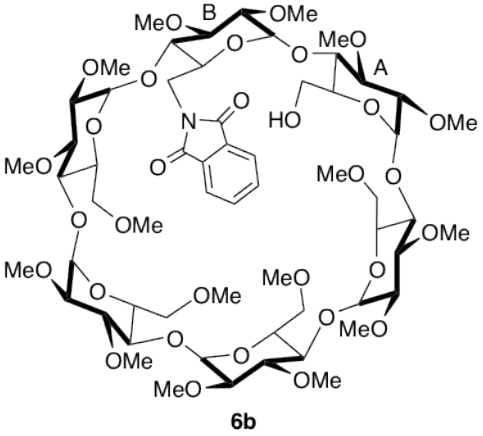
***P*-{6^A-Deoxy-6^A-diphenylphosphinyl-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^C,6^D,6^E,6^F-hexadeca-*O*-methyl-α-cyclodextrin} borane (5a):**

n-BuLi (1.60 M in hexane, 1.20 mL, 1.94 mmol) was added dropwise at –78°C to a stirred solution of diphenylphosphine (0.347 g, 485 μL of 20.3% *wt/wt* in hexane, 0.37 mmol) in THF (10 mL). After 30 min, the dark red diphenylphosphide solution was transferred via a cannula to a stirred solution of **1** (0.200 g, 0.16 mmol) in THF (10 mL) kept at –78°C. The solution was further stirred at –78°C for 1 h before being allowed to reach 0°C over 1 h. $BH_3{\cdot}THF$ (1.00 M in THF, 10 mL, 10 mmol) was then added dropwise at 0°C, and the reaction mixture allowed to reach room temperature before being stirred for an additional 12 h. Once the solvent was removed *in vacuo*, the solid was taken in THF (8 mL) and H_2SO_4 (0.20 mL, 50% *wt/wt* solution in water) was added. The reaction mixture was stirred for 1 h at room temperature before adding saturated aqueous $NaHCO_3$ (50 mL). Subsequent extraction with $CHCl_3$ (3 × 50 mL) was followed by drying of the organic extracts ($MgSO_4$). Removal of the solvent under vacuum gave a colourless residue, which was subjected to column chromatography (SiO_2; CH_2Cl_2/MeOH, 97:3, *v/v*) to afford **5a** (0.215 g, 97%) as a colourless solid. R_f (SiO_2, CH_2Cl_2/MeOH, 90:10, *v/v*) = 0.43; Retention time (reverse-phase column Pursuit C18, isocratic elution with MeCN:H_2O, 1:1, with a flow rate of 1mL.min^{-1}) = 10.79 min; m.p. 210–212°C; ^{1}H NMR (400.1 MHz, $CDCl_3$, 25ºC): δ (assignment by combined COSY, TOCSY, HMQC, and ROESY) = 0.86 (br s, 3 H, P-BH_3), 2.39 (d, 1 H, $^2J_{H\text{-}6a,H\text{-}6b}$ = 11.8 Hz, H-6a^B), 2.52 (dd, 1 H, $^2J_{H\text{-}6a,H\text{-}6b}$ = 11.5 Hz, $^3J_{H\text{-}6a,H\text{-}5}$ = 2.8 Hz, H-6a^A), 2.54 (d, 1 H, $^2J_{H\text{-}6a,H\text{-}6b}$ = 11.0 Hz, H-6a^F), 2.76 (s, 3 H, OMe-6^F), 2.82 (d, $^2J_{H\text{-}6b,H\text{-}6a}$ =11.4 Hz, H-6b^B), 2.89 (m, 1 H, H-6b^A), 2.99 (dd, 1 H, $^3J_{H\text{-}2,H\text{-}3}$ = 9.5 Hz, $^3J_{H\text{-}2,H\text{-}1}$ = 3.4 Hz, H-2^B), 3.03 (dd, 1 H, $^3J_{H\text{-}2,H\text{-}3}$ = 9.9 Hz, $^3J_{H\text{-}2,H\text{-}1}$ = 3.4 Hz, H-2^F), 3.11 (dd, 1 H, $^3J_{H\text{-}2,H\text{-}3}$ = 9.8 Hz, $^3J_{H\text{-}2,H\text{-}1}$ = 2.9 Hz, H-2^A), 3.13 (dd, 1 H, $^3J_{H\text{-}2,H\text{-}3}$ = 9.3 Hz, $^3J_{H\text{-}2,H\text{-}1}$ = 2.9 Hz, H-2^C), 3.17 (dd, 1 H, $^3J_{H\text{-}2,H\text{-}3}$ = 9.5 Hz, $^3J_{H\text{-}2,H\text{-}1}$ = 3.1 Hz, H-2^E), 3.18 (dd, 1 H, $^3J_{H\text{-}2,H\text{-}3}$ = 9.5 Hz, $^3J_{H\text{-}2,H\text{-}1}$ = 2.7 Hz, H-2^D), 3.20 (dd, 1 H, $^3J_{H\text{-}4,H\text{-}3}$ = $^3J_{H\text{-}$

$_{4,H\text{-}5}$ = 9.0 Hz, H-4^{A}), 3.39 (s, 3 H, OMe-2), 3.42 (s, 3 H, OMe-6^{D}), 3.43 (s, 6 H, OMe-2), 3.44 (s, 3 H, OMe-2), 3.45 (s, 6 H, OMe-6^{C,E}), 3.46 (1 H, H-6a^{C}), 3.47 (s, 6 H, OMe-2), 3.53 (1 H, H-3^{A}), 3.54 (1 H, H-3^{C}), 3.55 (1 H, H-6a^{D}), 3.56 (1 H, H-3^{D}), 3.58 (s, 3 H, OMe-3), 3.58 (1 H, H-3^{E}), 3.59 (1 H, H-5^{B}), 3.60 (s, 3 H, OMe-3), 3.61 (s, 3 H, OMe-3), 3.61 (1 H, H-3^{F}), 3.62 (1 H, H-3^{B}), 3.63 (s, 3 H, OMe-3), 3.63 (1 H, H-4^{B}), 3.67 (s, 3 H, OMe-3), 3.67 (1 H, H-4^{E}), 3.68 (s, 3 H, OMe-3), 3.68 (2 H, H-4^{C}, H-6b^{B}), 3.69 (1 H, H-4^{D}), 3.70 (2 H, H-4^{F}, H-6b^{D}), 3.75 (d, 1 H, $^{2}J_{H\text{-}6a,H\text{-}6b}$ = 10.3 Hz, H-6a^{E}), 3.85 (d, 2 H, $^{3}J_{H\text{-}5,H\text{-}4}$ = 9.7 Hz, H-5^{C,F}), 3.93 (d, 1 H, $^{3}J_{H\text{-}5,H\text{-}4}$ = 13.8 Hz, H-5^{D}), 3.94 (d, 1 H, $^{3}J_{H\text{-}5,H\text{-}4}$ = 12.4 Hz, H-5^{E}), 3.99 (dd, 1 H, $^{2}J_{H\text{-}6b,H\text{-}6a}$ = 10.6 Hz, $^{3}J_{H\text{-}6b,H\text{-}5}$ = 2.8 Hz, H-6b^{E}), 4.05 (dd, 1 H, $^{2}J_{H\text{-}6b,H\text{-}6a}$ = 10.3 Hz, $^{3}J_{H\text{-}6b,H\text{-}5}$ = 2.1 Hz, H-6b^{C}), 4.45 (td, 1 H, $^{3}J_{H\text{-}5,H\text{-}6a}$ = $^{3}J_{H\text{-}5,P}$ = 9.6 Hz, $^{3}J_{H\text{-}5,H\text{-}4}$ = 9.0 Hz, H-5^{A}), 4.63 (d, 1 H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 2.9 Hz, H-1^{A}), 4.96 (d, 1 H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 2.9 Hz, H-1^{C}), 4.99 (d, 1 H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.4 Hz, H-1^{B}), 5.01 (d, 1 H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.4 Hz, H-1^{F}), 5.09 (d, 1 H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 2.7 Hz, H-1^{D}), 5.10 (d, 1 H, $^{3}J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, H-1^{E}), 7.36–7.45 (6 H, *m*-H, *p*-H), 7.64 (td, 2 H, $^{3}J_{o\text{-}H,m\text{-}H}$ = $^{3}J_{o\text{-}H,P}$ = 8.8, $^{4}J_{o\text{-}H,p\text{-}H}$ = 2.1 Hz, *o*-H), 7.83–7.86 (2 H, *o*-H) ppm, OH^{B} not assigned; $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$, 25ºC): δ (assignment by HMQC) = 27.53 (d, $^{1}J_{C,P}$ = 41.3 Hz, C-6^{A}), 57.63 [×2], 57.70, 58.25, 58.26, 58.88, 58.90, 59.14, 59.25 [×2] (OMe), 60.43 (C-6), 61.34, 61.52, 61.86, 61.90, 61.93, 62.01 (OMe), 68.02 (C-6), 68.68 (C-5), 69.79 (C-6^{B}), 70.74 [×2] (C-5), 70.98 (C-6), 71.15 [×2] (C-5), 71.28, 71.34 (C-6), 72.00 (C-5), 79.85, 80.74, 80.82, 81.11, 81.23, 81.28, 81.35, 81.40, 81.56, 81.72, 81.82, 81.92, 82.08, 82.27, 82.37, 82.79, 82.82 (C-2, C-3, C-4), 87.75 (d, $^{3}J_{C,P}$ = 41.3 Hz, C-4^{A}), 97.16, 99.40, 100.14, 100.37, 100.46, 100.84 (C-1), 128.92 (d, $^{3}J_{C,P}$ = 10.0, C_{meta}), 128.99 (d, $^{3}J_{C,P}$ = 10.0, C_{meta}), 130.51 (d, $^{1}J_{C,P}$ = 53.4 , C_{ipso}), 131.27 (d, $^{2}J_{C,P}$ = 8.3 Hz, C_{ortho}), 131.29 (s, C_{para}), 131.41 (s, C_{para}), 131.69 (d, $^{2}J_{C,P}$ = 9.9 Hz, C_{ortho}), 132.24 (d, $^{1}J_{C,P}$ = 56.7 , C_{ipso}) ppm; $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$, 25ºC): δ = 12.1 (br s) ppm; elemental analysis (%) calcd for $C_{64}H_{104}BO_{29}P{\cdot}2MeOH$ (1401.63 + 64): C 54.62, H 8.11, found: C 54.92, H 7.83; MS (ESI-TOF): *m/z* (%): 1401.63 (100) $[M + Na]^{+}$.



5b

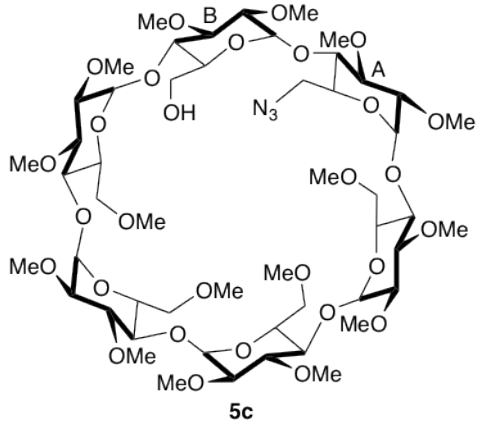


6b

6^{A}-Deoxy-6^{A}-(1,3-dioxoisoindolin-2-yl)-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 (5b) and 6^{B}-deoxy-6^{B}-(1,3-dioxoisoindolin-2-yl)-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 (6b):

Powdered potassium phthalimide (0.135 g, 0.64 mmol) was added to a stirred solution of **1** at 0°C (0.200 g, 0.16 mmol) in DMF (0.80 mL). After 1 h, the reaction mixture was allowed to reach room temperature and then kept at this temperature for 12 h under stirring. It was then evaporated to dryness and the residue was retaken in THF (8 mL). H_2SO_4 (0.20 mL, 50% *wt/wt* solution in water) was added and the reaction mixture was stirred for 1 h at room temperature before adding saturated aqueous $NaHCO_3$ (50 mL). Subsequent extraction with $CHCl_3$ (3 × 50 mL) was followed by drying of the organic extracts ($MgSO_4$). Removal of the solvent in vacuo gave a colourless residue, which was subjected to column chromatography (SiO_2; CH_2Cl_2/MeOH, 97:3, v/v) to afford 2 colourless solids, **5b** (0.180 g, 87%) and **6b** (0.006 g, 5 %). **5b** R_f (SiO_2, CH_2Cl_2/MeOH, 90:10, *v*/*v*) = 0.58; m.p. 228–230°C; ^{1}H NMR (400.1 MHz, $CDCl_3$, 25ºC): δ (assignment by combined COSY, TOCSY, HMQC, and ROESY) = 2.24 (br s, 1 H, OH), 2.70 (dd, 1 H, $^2J_{H\text{-}6a,H\text{-}6b}$ = 10.3 Hz, $^3J_{H\text{-}6a,H\text{-}5}$ = 1.5 Hz, H-6a), 2.99 (s, 3 H, OMe), 3.06 (dd, 1 H, $^3J_{H\text{-}2,H\text{-}3}$ = 9.8 Hz, $^3J_{H\text{-}2,H\text{-}1}$ = 3.5 Hz, H-2), 3.16 (m, 1 H, H-2^{A}), 3.17 (m, 1 H, H-2^{B}), 3.18 (s, 3 H, OMe), 3.12–3.21 (3 H, H-2), 3.31 (t, 1 H, $^3J_{H\text{-}4,H\text{-}3}$ = $^3J_{H\text{-}4,H\text{-}5}$ = 9.3 Hz, H-4^{A}), 3.37 (s, 3 H, OMe), 3.34–3.38 (m, 1 H, H-5), 3.43 (s, 3 H, OMe), 3.44 (s, 3 H, OMe), 3.46 (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, 3 H, OMe), 3.52 (m, 1 H, H-3^{A}), 3.59 (s, 3 H, OMe), 3.60 (s, 3 H, OMe), 3.61 (s, 3 H, OMe), 3.61 (m, 1 H, H-4^{B}), 3.62 (s, 3 H, OMe), 3.64 (m, 1 H, H-3^{B}), 3.65 (s, 3 H, OMe), 3.67 (s, 3 H, OMe), 3.41–3.70 (12 H, H-3, H-4, H-6), 3.73–3.76 (m, 1 H, H-5), 3.79–3.86 (2 H, H-6a), 3.86–3.91 (2 H, H-6a or H-6b, H-6a^{B}), 3.92–4.03 (4 H, H-5, H-6a^{A}, H-6b^{B}), 4.12 (ddd, 1 H, $^3J_{H\text{-}5,H\text{-}6a}$ = $^3J_{H\text{-}5,H\text{-}4}$ = 9.0 Hz, $^3J_{H\text{-}5,H\text{-}6b}$ = 2.6 Hz, H-5^{A}), 4.15–4.19 (m, 1 H, H-5^{B}), 4.34 (dd, 1 H, $^2J_{H\text{-}6b,H\text{-}6a}$ = 14.2, Hz, $^3J_{H\text{-}6b,H\text{-}5}$ = 2.5 Hz, H-6b^{A}), 4.91 (d, 1 H, $^3J_{H1\text{-}H2}$ = 2.8 Hz, H-1^{A}), 4.95 (d, 1 H, $^3J_{H1\text{-}H2}$ = 3.1 Hz, H-1), 5.03 (d, 1 H, $^3J_{H1\text{-}H2}$ = 3.1 Hz, H-1), 5.07 (d, 1 H, $^3J_{H1\text{-}H2}$ = 3.1 Hz, H-1), 5.09 (d, 1 H, $^3J_{H1\text{-}H2}$

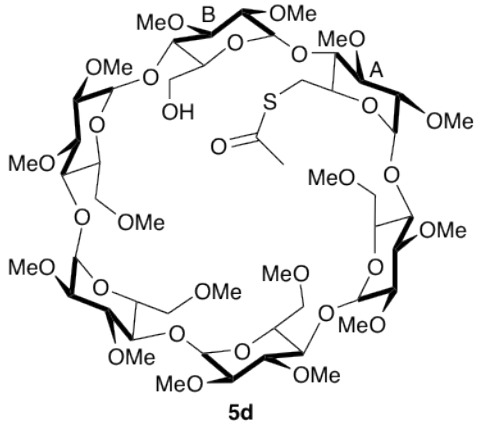
= 3.4 Hz, H-1), 5.18 (d, 1 H, $^{3}J_{H1\text{-}H2}$ = 3.3 Hz, H-1^{B}), 7.73–7.75 (2 H, *m*-H), 7.81–7.83 (2 H, *o*-H) ppm; $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$, 25ºC): δ (assignment by HMQC) = 39.78 (C-6^{A}), 57.83 [×3], 58.02 [×2], 58.13, 58.65, 58.96, 59.00, 59.14, 61.65, 61.80 [×3], 61.88, 61.98 (OMe), 62.14 (C-6^{B}), 69.44 (C-5), 69.68 (C-6), 70.92 (C-6), 70.94 (C-5), 70.98 (C-6), 71.23, 71.27, 71.34 (C-5), 71.66 (C-6), 72.25 (C-5), 80.92, 81.06, 81.17, 81.29, 81.30, 81.47, 81.60, 81.78, 81.87, 81.97, 82.19 [×2], 82.23 [×3], 82.37, 82.60, 85.43 (C-2, C-3, C-4), 99.15, 99.83, 99.88, 100.06, 100.11, 100.47 (C-1), 123.11 (C_{meta}), 132.17 (C_{ipso}), 134.06 (C_{ortho}), 168.08 (CO) ppm; elemental analysis (%) calcd for $C_{60}H_{95}NO_{31}\cdot CH_2Cl_2$ (1326.38 + 84.93): C 51.91, H 6.93, N 0.99, found: C 51.83, H 6.92, N 0.98; MS (ESI-TOF): *m/z* (%): 1348.58 (100) [*M* + Na]$^{+}$. **6b** R_f (SiO_2, CH_2Cl_2/MeOH, 90:10, *v*/*v*) = 0.54; m.p. 228–230°C; ^{1}H NMR (400.1 MHz, $CDCl_3$, 25ºC): δ = 3.24 (s, 3 H, OMe), 3.32 (s, 3 H, OMe), 3.41 (s, 3 H, OMe), 3.45 (s, 3 H, OMe), 3.46 (s, 3 H, OMe), 3.47 (s, 3 H, OMe), 3.49 (s, 3 H, OMe), 3.50 (s, 3 H, OMe), 3.51 (s, 3 H, OMe), 3.53 (s, 3 H, OMe), 3.62 (s, 3 H, OMe), 3.63 (s, 3 H, OMe), 3.64 (s, 3 H, OMe), 3.65 (s, 3 H, OMe), 3.66 (s, 3 H, OMe), 3.68 (s, 3 H, OMe), 3.05–4.22 (36 H, H-2, H-3, H-4, H-5, H-6), 4.98 (d, 1 H, $^{3}J_{H1\text{-}H2}$ = 3.2 Hz, H-1), 4.99 (d, 1 H, $^{3}J_{H1\text{-}H2}$ = 3.3 Hz, H-1), 5.06 (d, 1 H, $^{3}J_{H1\text{-}H2}$ = 2.9 Hz, H-1), 5.09 (d, 1 H, $^{3}J_{H1\text{-}H2}$ = 3.3 Hz, H-1), 5.11 (d, 1 H, $^{3}J_{H1\text{-}H2}$ = 3.5 Hz, H-1), 5.37 (d, 1 H, $^{3}J_{H1\text{-}H2}$ = 3.6 Hz, H-1), 7.73–7.75 (2 H, *m*-H), 7.83–7.87 (2 H, *o*-H) ppm; elemental analysis (%) calcd for $C_{60}H_{95}NO_{31}\cdot H_2O$ (1326.38 + 18.02): C 53.60, H 7.27, N 1.04, found: C 53.67, H 7.26, N 0.98; MS (ESI-TOF): *m/z* (%): 1348.58 (100) [*M* + Na]$^{+}$.



5c

6^A-Deoxy-6^A-azido-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 (5c) and 6^B-deoxy-6^B-azido-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 (6c):

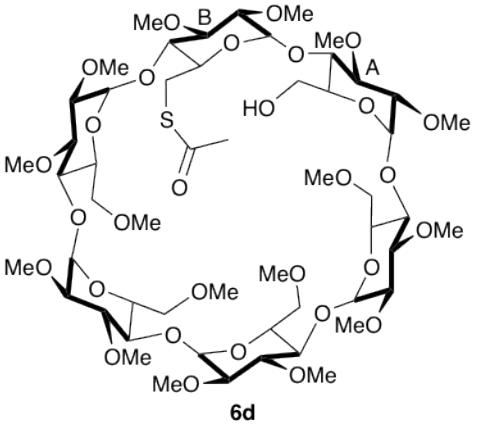
Powdered sodium azide (0.042 g, 0.64 mmol) was added to a stirred solution of **1** (0.200 g, 0.16 mmol) in DMF (0.80 mL) at 0°C. The same procedure as that used for **5b**/**6b** was then applied. The crude product consisted in an inseparable mixture of regioisomers **5c** and **6c** (0.180 g, 94 %). R_f(SiO_2, CH_2Cl_2/MeOH, 90:10, *v*/*v*) = 0.70; Retention time (reverse-phase column Pursuit C18, isocratic elution with MeCN:H_2O, 1:1, with a flow rate of 1mL.min^{-1}) = 17.49 and 18.16 min; elemental analysis (%) calcd for $C_{52}H_{91}N_3O_{29}\cdot H_2O$ (1221.55 + 18.02): C 50.36, H 7.56, N 3.39, found: C 50.33, H 7.50, N 3.18; MS (ESI-TOF): *m*/*z* (%): 1244.55 (100) $[M + Na]^+$.



5d

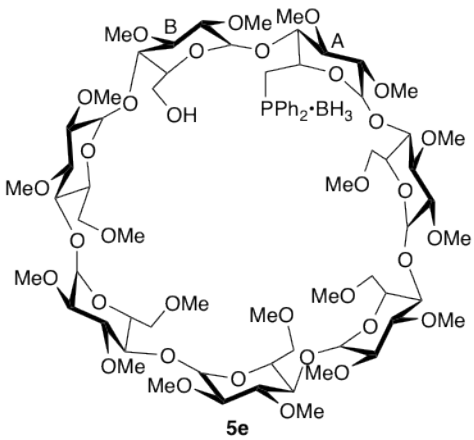
6^A-Deoxy-6^A-(S-thioacetylmethyl)-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^C,6^D,6^E,6^F-hexadeca-*O*-methyl-α-cyclodextrin (5d) and 6^B-deoxy-6^B-(S-thioacetylmethyl)-2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^C,6^D,6^E,6^F-hexadeca-*O*-methyl-α-cyclodextrin (6d):

Powdered potassium thioacetate (0.073 g, 0.64 mmol) was added to a stirred solution of **1** (0.200 g, 0.16 mmol) in DMF (0.80 mL) at 0°C. The same procedure as that for **5b**/**6b** was then applied. The crude product consisted in an inseparable mixture of regioisomers **5d** and **6d** (0.180 g, 91 %). R_f (SiO_2, CH_2Cl_2/MeOH, 90:10, *v*/*v*) = 0.55; Retention time

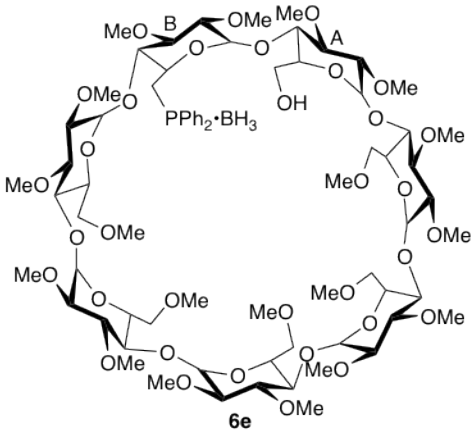


6d

(reverse-phase column Pursuit C18, elution with MeCN:H_2O 1:1 over 40 min with a flow rate of 1mL.min^{-1}) = 14.82 and 16.32 min; Selected ^{1}H NMR signals (400.1 MHz, $CDCl_3$, 25ºC): δ = 2.30 (s, 0.87 H, $CH_3C(O)S$) and 2.33 (s, 3 H, $CH_3C(O)S$) ppm; elemental analysis (%) calcd for $C_{54}H_{94}O_{30}S{\cdot}0.5H_2O$ (1255.37 + 9.01): C 51.30, H 7.57, found: C 51.37, H 7.69; MS (ESI-TOF): *m/z* (%): 1277.54 (100) $[M + Na]^+$.



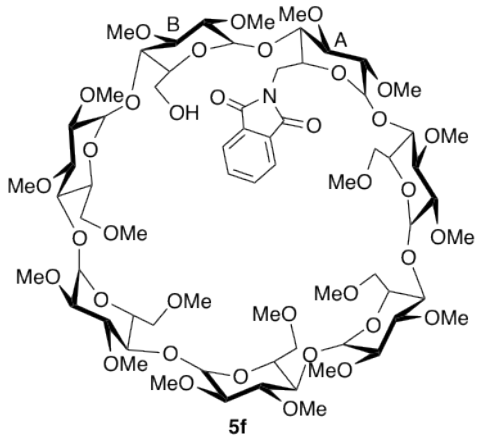
5e



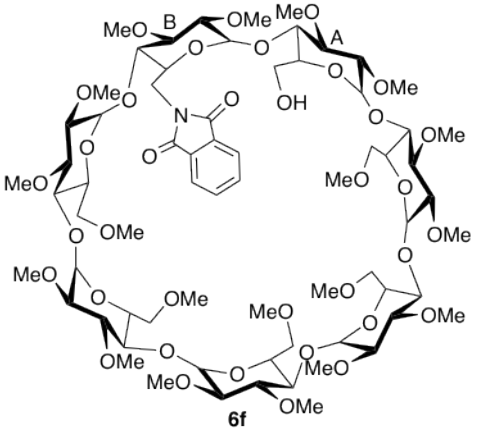
6e

***P*-{6^A-Deoxy-6^A-diphenylphosphinyl-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} borane (5e) and *P*-{6^B-deoxy-6^B-diphenylphosphinyl-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} borane (6e):**

5e and **6e** were prepared from **2** (0.200 g, 0.14 mmol) according to the procedure used for the synthesis of **5a**. The crude product consisted in an inseparable mixture of regioisomers **5e** and **6e** (0.204 g, 96 %). R_f (SiO_2, CH_2Cl_2/MeOH, 90:10, *v*/*v*) = 0.51; Selected $^{31}P\{^1H\}$ NMR signals (121.5 MHz, $CDCl_3$, 25ºC): δ = 13.43 and 14.25 ppm; elemental analysis (%) calcd for $C_{73}H_{120}BO_{34}P{\cdot}2CH_2Cl_2$ (1583.50 + 169.87): C 51.38, H 7.13, found: C 51.45, H 7.10; MS (ESI-TOF): *m/z* (%): 1605.74 (100) $[M + Na]^+$.



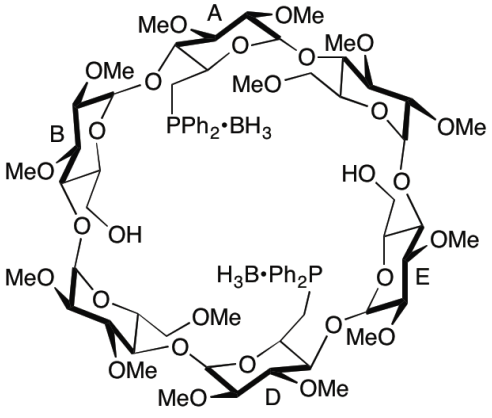
5f



6f

6^A-Deoxy-6^A-(1,3-dioxoisoindolin-2-yl)-$2^A,2^B,2^C,2^D,2^E,2^F,2^G,3^A,3^B,3^C,3^D,3^E,3^F,3^G,6^C,6^D,6^E,6^F,6^G$-nonadeca-*O*-methyl-$\beta$-cyclodextrin (5f) and 6^B-deoxy-6^B-(1,3-dioxoisoindolin-2-yl)-$2^A,2^B,2^C,2^D,2^E,2^F,2^G,3^A,3^B,3^C,3^D,3^E,3^F,3^G,6^C,6^D,6^E,6^F,6^G$-nonadeca-*O*-methyl-$\beta$-cyclodextrin (6f):

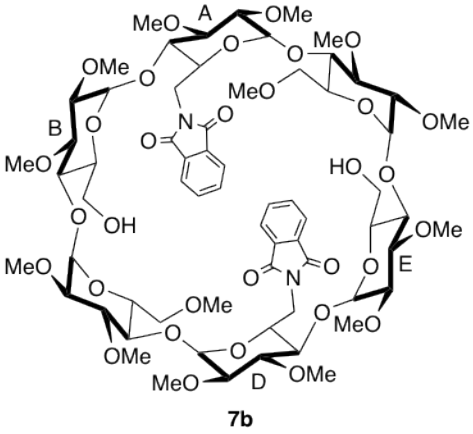
5f and **6f** were prepared from **2** (0.200 g, 0.14 mmol) according to the procedure used for the synthesis of **5b**. The crude product consisted in an inseparable mixture of regioisomers **5f** and **6f** (0.160 g, 76 %). R_f (SiO_2, CH_2Cl_2/MeOH, 90:10, *v*/*v*) = 0.46; elemental analysis (%) calcd for $C_{69}H_{111}NO_{36}\cdot CH_3C(O)OC_2H_5$ (1530.60 + 88.11): C 54.17, H 7.41, N 0.87 found: C 54.23, H 7.39, N 0.89; MS (ESI-TOF): *m*/*z* (%): 1552.68 (100) $[M + Na]^+$.



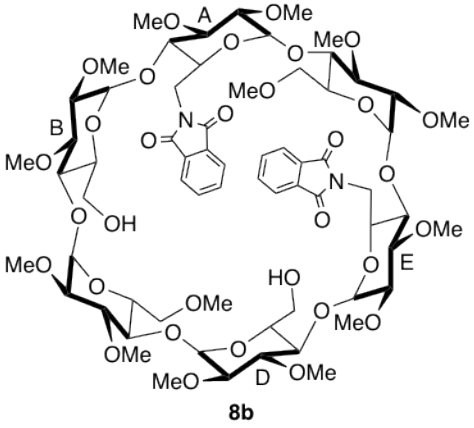
P,P'-{$6^A,6^D$-Dideoxy-$6^A,6^D$-di(diphenylphosphinyl)-$2^A,2^B,2^C,2^D,2^E,2^F$, $3^A,3^B,3^C,3^D,3^E,3^F,6^C,6^F$-tetradeca-*O*-methyl-$\alpha$-cyclodextrin} diborane (7a):

n-BuLi (1.60 M in hexane, 1.83 mL, 2.87 mmol) was added dropwise at –78°C to a stirred solution of diphenylphosphine (0.520 g, 725 µL of a 20.3% *wt/wt* solution in hexane, 0.57 mmol) in THF (10 mL). After 30 min, the dark red diphenylphosphide solution was transferred via a cannula to a stirred solution of **3** (0.200 g, 0.16 mmol) in THF (10 mL) kept at –78°C. The solution was further stirred at –78°C for 1 h before being allowed to reach 0°C over 1 h. $BH_3\cdot$THF (1.00 M in THF, 10 mL, 10 mmol) was then added dropwise at 0°C, and the reaction mixture allowed to reach room temperature before being stirred for an additional 12 h. Once the solvent was removed *in vacuo*, the solid was taken in THF (8 mL) and H_2SO_4 (0.20 mL, 50% *wt/wt* solution in water) was added. The reaction mixture was stirred for 1 h at room temperature

before adding saturated aqueous $NaHCO_3$ (50 mL). Subsequent extraction with $CHCl_3$ (3 × 50 mL) was followed by drying of the organic extracts ($MgSO_4$). Removal of the solvent in vacuo gave a colourless residue, which was subjected to column chromatography (SiO_2; CH_2Cl_2/MeOH, 97:3, v/v) to afford **7a** (0.140 g, 59%) as a colourless solid. R_f (SiO_2, CH_2Cl_2/MeOH, 92:8, *v*/*v*) = 0.38; Retention time (reverse-phase column Pursuit C18, isocratic elution with MeCN:H_2O, 1:1, with a flow rate of 1mL.min^{-1}) = 18.27 min; m.p. 142-145 °C.; ^{1}H NMR (300.1 MHz, $CDCl_3$, 25ºC): δ (assignment by COSY) = 1.10 (br s, 6 H, P-BH_3), 2.77 (s, 6 H, OMe-6), 2.85 (d, 2 H, $^2J_{H\text{-}6a,H\text{-}6b}$ = 11.2 Hz, H-6a^{C,F}), 3.02 (d, 4 H, $^2J_{H\text{-}6a,H\text{-}6b}$ = $^2J_{H\text{-}6b,H\text{-}6a}$ = 11.9 Hz, H-6^{B,E}), 3.07–3.13 (8 H, H-2^{B,C,E,F}, H-6^{A,D}), 3.18 (d, 2 H, $^1J_{H\text{-}6b,H\text{-}6a}$ = 11.2 Hz, H-6b^{C,F}), 3.23 (dd, 2 H, $^3J_{H\text{-}2,H\text{-}3}$ = 9.9 Hz, $^3J_{H\text{-}2,H\text{-}1}$ = 2.8 Hz, H-2^{A,D}), 3.46 (s, 6 H, OMe), 3.47 (s, 6 H, OMe), 3.49 (s, 6 H, OMe), 3.59 (s, 6 H, OMe), 3.64 (s, 6 H, OMe), 3.69 (s, 6 H, OMe), 3.43–3.85 (18 H, H-3, H-4, H-5^{B,C,E,F}, OH), 4.39 (m, 2 H, H-5^{A,D}), 4.67 (d, 2 H, $^3J_{H\text{-}1,H\text{-}2}$ = 2.8 Hz, H-1^{A,D}), 5.01 (d, 2 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, H-1^{C,F}), 5.17 (d, 2 H, $^3J_{H\text{-}1,H\text{-}2}$ = 2.9 Hz, H-1^{B,E}), 7.36–7.50 (12 H, *m*-H, *p*-H), 7.73–7.86 (8 H, *o*-H) ppm; ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 25ºC): δ (assignment by HMQC) = 26.91 (d, $^1J_{C,P}$ = 37 Hz, C-6^{A,D}), 58.09 [×2], 58.76, 61.29, 61.38, 61.47, 61.76 (OMe), 61.29 (C-6^{B,E}), 69.23, 71.22, 71.49 (C-5), 69.93 (C-6^{C,F}), 79.63, 80.76, 80.84, 81.15, 81.28, 81.41, 82.03, 82.55 (C-2, C-3, C-4), 86.26 (d, $^1J_{C,P}$ = 5.7 Hz, C-4^{A,D}), 97.60, 100.00, 100.23 (C-1), 128.66 (d, $^3J_{C,P}$ = 10.5, C_{meta}), 128.80 (d, $^3J_{C,P}$ = 10.5, C_{meta}), 130.94 (s, C_{para}), 131.03 (s, C_{para}), 130.83 (d, $^1J_{C,P}$ = 16.0 Hz, C_{ipso}), 131.32 (d, $^1J_{C,P}$ = 21.0 Hz, C_{ipso}), 131.78 (d, $^2J_{C,P}$ = 9.0 Hz, C_{ortho}), 131.87 (d, $^2J_{C,P}$ = 9.0 Hz, C_{ortho}) ppm; ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 25ºC): δ = 12.5 (br s) ppm; elemental analysis (%) calcd for $C_{74}H_{112}B_2O_{28}P_2$·0.5MeOH (1532.70 + 16): C 57.76, H 7.42, found: C 57.97, H 7.36; MS (ESI-TOF): *m/z* (%): 1555.70 (100) $[M + Na]^+$.



7b

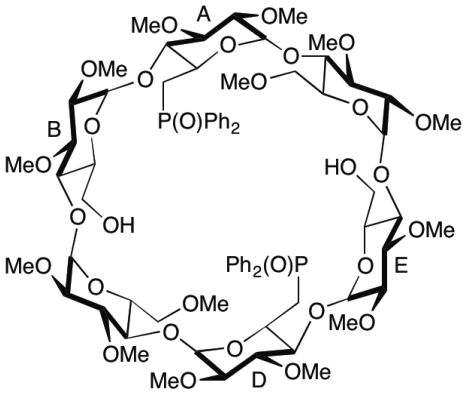


8b

$6^{A},6^{D}$-Dideoxy-$6^{A},6^{D}$-di(1,3-dioxoisoindolin-2-yl)-$2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{C},6^{F}$-tetradeca-*O*-methyl-$\alpha$-cyclodextrin (7b) and $6^{A},6^{E}$-dideoxy-$6^{A},6^{E}$-di(1,3-dioxoisoindolin-2-yl)-$2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{B},6^{E}$-tetradeca-*O*-methyl-$\alpha$-cyclodextrin (8b):

Powdered potassium phthalimide (0.230 g, 1.24 mmol) was added to a stirred solution of **3** at 0°C (0.200 g, 0.16 mmol) in DMF (1.60 mL). The reaction mixture was allowed to reach room temperature in an ice bath for 12 h under stirring. It was then evaporated to dryness and the residue was retaken in THF (8 mL). H_2SO_4 (0.20 mL, 50% *wt/wt* solution in water) was added and the reaction mixture was stirred for 1 h at room temperature before adding saturated aqueous $NaHCO_3$ (50 mL). Subsequent extraction with $CHCl_3$ (3 × 50 mL) was followed by drying of the organic extracts ($MgSO_4$). Removal of the solvent in vacuo gave a colourless residue, which was subjected to column chromatography (SiO_2; CH_2Cl_2/MeOH, 97:3, v/v) to afford 2 colourless solids, **7b** (0.110 g, 50%) and **8b** (0.071 g, 28 %). **7b** R_f (SiO_2, CH_2Cl_2/MeOH, 90:10, *v*/*v*) = 0.50; m.p. 164°C; ^{1}H NMR (400.1 MHz, $CDCl_3$, 25ºC): δ (assignment by combined COSY, TOCSY, HMQC, and ROESY) = 2.71 (d, 2 H, $^2J_{H\text{-}6a,H\text{-}6b}$ = 11.1 Hz, H-$6a^{C,F}$), 2.72 (s, 3 H, OMe-$6^{C,F}$), 3.08 (dd, 2 H, $^3J_{H\text{-}2,H\text{-}3}$ = 9.7 Hz, $^3J_{H\text{-}2,H\text{-}1}$ = 3.8 Hz, H-$2^{C,F}$), 3.20 (dd, 2 H, $^3J_{H\text{-}2,H\text{-}3}$ = 9.9 Hz, $^3J_{H\text{-}2,H\text{-}1}$ = 2.7 Hz, H-$2^{A,D}$), 3.23 (dd, 2 H, $^3J_{H\text{-}2,H\text{-}3}$ = 5.1, $^3J_{H\text{-}2,H\text{-}1}$ = 3.3 Hz, H-$2^{B,E}$), 3.25 (t, 2 H, $^3J_{H\text{-}4,H\text{-}3}$ = $^3J_{H\text{-}4,H\text{-}5}$ = 10.1 Hz, H-$4^{B,E}$), 3.35 (t, 2 H, $^3J_{H\text{-}4,H\text{-}3}$ = $^3J_{H\text{-}4,H\text{-}5}$ = 9.0 Hz, H-$4^{A,D}$), 3.46 (s, 6 H, OMe-2), 3.50 (s, 6 H, OMe-2), 3.51 (s, 6 H, OMe-2), 3.52 (m, 2 H, H-$6b^{C,F}$), 3.58 (m, 2 H, H-$3^{C,F}$), 3.59 (m, 2 H, H-$3^{A,D}$), 3.60 (m, 2 H, H-$6a^{B,E}$), 3.61 (m, 2 H, H-$3^{B,E}$), 3.62 (s, 6 H, OMe-3), 3.63 (s, 6 H, OMe-3), 3.66 (m, 4 H, H-$4^{C,F}$, H-$5^{C,F}$), 3.67 (m, 2 H, H-$3^{C,F}$), 3.70 (s, 6 H, OMe-3), 3.99 (t, 2 H, $^2J_{H\text{-}6b,H\text{-}6a}$ = $^3J_{H\text{-}6b,H\text{-}5}$ = 12.8 Hz, H-$6b^{B,E}$), 4.03 (d, 2 H, $^2J_{H\text{-}6a,H\text{-}6b}$ = 13.9 Hz, H-$6a^{A,D}$), 4.30 (dd, 2 H, $^3J_{H\text{-}5,H\text{-}6b}$ = 12.8 Hz, $^3J_{H\text{-}5,H\text{-}4}$ = 10.1 Hz, H-$5^{B,E}$), 4.45 (ddd, 2 H, $^3J_{H\text{-}5,H\text{-}6a}$ = 3.2 Hz, $^3J_{H\text{-}5,H\text{-}6b}$ = 17.4 Hz, $^3J_{H\text{-}5,H\text{-}4}$ = 9.0 Hz, H-$5^{A,D}$), 4.87 (dd, 2 H, $^2J_{H\text{-}6b,H\text{-}6a}$ = 13.9 Hz, $^3J_{H\text{-}6b,H\text{-}5}$ = 3.2 Hz, H-$6b^{A,D}$), 4.88 (d, 2 H, $^3J_{H\text{-}1,H\text{-}2}$ = 2.7 Hz, H-$1^{A,D}$), 5.03 (d, 2 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.8 Hz, H-$1^{C,F}$), 5.15 (d, 2 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.3 Hz, H-$1^{B,E}$), 7.62–

7.65 (4 H, *m*-H), 7.93–7.96 (4 H, *o*-H) ppm; $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25ºC): δ (assignment by HMQC) = 40.11 (C-$6^{A,D}$), 57.49, 57.83, 58.45, 59.19, 61.33, 62.03, 62.18 (OMe), 62.69 (C-$6^{B,E}$), 68.05 (C-5), 70.03 (C-$6^{C,F}$), 71.18, 72.54 (C-5), 81.34, 81.39, 81.45, 81.52, 81.71, 81.78, 81.84, 82.90, 86.99 (C-2, C-3, C-4), 98.61, 99.42, 100.72 (C-1), 123.70 ($C_{meta}^{A,D}$), 132.19 ($C_{ipso}^{A,D}$), 134.21 ($C_{ortho}^{A,D}$), 168.93 (CO) ppm; elemental analysis (%) calcd for $C_{66}H_{94}N_2O_{32}\cdot 0.5CHCl_3$ (1427.45 + 58.96): C 53.71, H 6.40, N 1.58, found: C 53.71, H 6.68, N 1.58; MS (ESI-TOF): *m/z* (%): 1449.57 (100) $[M + Na]^+$. **8b** R_f (SiO_2, CH_2Cl_2/MeOH, 90:10, *v/v*) = 0.53; m.p. 164°C; ^1H NMR (400.1 MHz, $CDCl_3$, 25ºC): δ (assignment by COSY) = 2.98 (s, 3 H, OMe), 3.28 (s, 3 H, OMe), 3.43 (s, 3 H, OMe), 3.45 (s, 3 H, OMe), 3.47 (s, 3 H, OMe), 3.51 (s, 3 H, OMe), 3.52 (s, 3 H, OMe), 3.55 (s, 3 H, OMe), 3.60 (s, 3 H, OMe), 3.63 (s, 3 H, OMe), 3.65 (s, 3 H, OMe), 3.68 (s, 9 H, OMe), 3.05–4.40 (36 H, H-2, H-3, H-4, H-5, H-6), 4.94 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 2.7 Hz, H-1), 4.98 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, H-1), 5.00 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.2 Hz, H-1), 5.13 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.1 Hz, H-1), 5.31 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 2.9 Hz, H-1), 5.42 (d, 1 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.3 Hz, H-1), 7.64–7.91 (8 H, aromatic-H); $^{13}C\{^1H\}$ NMR (100.6 MHz, CDCl3, 25ºC): δ (assignment by HMQC) = 37.72 (C-$6^{A\text{ or }D}$), 38.82 (C-$6^{D\text{ or }A}$), 57.78 [×2], 58.03 [×2], 58.31, 58.38, 58.61, 59.09, 61.61, 61.66, 61.76, 61.82, 61.86, 62.05 (OMe), 61.35, 62.31, 71.31, 71.54 (C-6), 69.31, 69.40, 71.17, 71.46, 72.19, 72.24 (C-5), 81.08, 81.25 [×2], 81.43, 81.50, 81.59 [×2], 81.68, 81.70 [×2], 81.80, 81.88 [×2], 82.09 [×2], 82.43, 84.73, 85.21 (C-2, C-3, C-4), 98.97, 99.15, 99.33, 99.55, 99.91 [×2] (C-1), 123.17, 123.47 (C_{meta}), 132.11 [×2] (C_{ipso}), 134.09 [×2] (C_{ortho}), 168.51, 168.70 (CO) ppm; elemental analysis (%) calcd for $C_{66}H_{94}N_2O_{32}\cdot CH_2Cl_2$ (1427.45 + 84.93): C 53.21, H 6.40, N 1.85, found: C 53.01, H 6.64, N 1.61; MS (ESI-TOF): *m/z* (%): 1449.57 (100) $[M + Na]^+$.



$6^A,6^D$-Dideoxy-$6^A,6^D$-di(diphenyloxophosphinyl)-$2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^C,6^F$-tetradeca-*O*-methyl-$\alpha$-cyclodextrin (10):

n-BuLi (1.60 M solution in hexane, 1.20 mL, 1.94 mmol) was added dropwise at –78°C to a stirred solution of diphenylphosphine (0.520 g, 725 µL of a 20.3% *wt/wt* solution in hexane, 0.57 mmol) in THF (10 mL). After 30 min, the dark red diphenylphosphide solution was transferred via a cannula to a stirred solution of **3** (0.200 g, 0.16 mmol) in THF

(10 mL) kept at –78°C. The solution was stirred at –78°C for a further 1h. The reaction mixture was quenched at –78°C with distilled water (0.50 mL) and the colourless precipitate was filtered over Celite and the filtrate was evaporated to dryness. The dried filtrate was taken in THF (8 mL) and H_2SO_4 (0.20 mL, 50% *wt/wt* solution in water) was added. The reaction mixture was stirred for 1 h at room temperature before adding saturated aqueous $NaHCO_3$ (50 mL). Subsequent extraction with $CHCl_3$ (3 × 50 mL) was followed by drying of the organic extracts ($MgSO_4$). Removal of the solvent in vacuo gave a colourless residue which was dissolved in CH_2Cl_2 (20 mL) and then aqueous H_2O_2 (58 μL, 35% *wt/wt* solution in water, 0.56 mmol) was added. The mixture was stirred for 2 h at room temperature whereupon it was quenched with saturated aqueous $NaHCO_3$ (50 mL) then extracted with $CHCl_3$ (3 × 30 mL) and dried ($MgSO_4$). Evaporation of the solvents gave a colourless powder, which was subjected to column chromatography (SiO_2; CH_2Cl_2/MeOH, 97:3, v/v) to afford **10** (0.120 g, 50%) as a colourless solid. R_f (SiO_2, CH_2Cl_2/MeOH, 92:8, *v*/*v*) = 0.42; m.p. 135-137 °C; ^{1}H NMR (400.1 MHz, $CDCl_3$, 25ºC): δ (assignment by combined COSY, TOCSY, HMQC, and ROESY) = 2.53 (ddd, 2 H, $^2J_{H\text{-}6a,P}$ = 15.3 Hz, $^2J_{H\text{-}6a,H\text{-}6b}$ = 11.1 Hz, $^2J_{H\text{-}6a,H\text{-}5}$ = 3.2 Hz, H-6a^{A,D}), 2.63 (s, 6 H, OMe-6^{C,F}), 3.13 (dd, 2 H, $^3J_{H\text{-}2,H\text{-}3}$ = 9.8 Hz, $^3J_{H\text{-}2,H\text{-}1}$ = 2.7 Hz, H-2^{A,D}), 3.16 (dd, 2 H, $^3J_{H\text{-}2,H\text{-}3}$ = 10.1 Hz, $^3J_{H\text{-}2,H\text{-}1}$ = 3.8 Hz, H-2^{C,F}), 3.17 (m, 2 H, H-6a^{C,F}), 3.29 (dd, 2 H, $^3J_{H\text{-}2,H\text{-}3}$ = 9.5 Hz, $^3J_{H\text{-}2,H\text{-}1}$ = 3.9 Hz, H-2^{B,E}), 3.39 (s, 6 H, OMe-3), 3.43–3.48 (4 H, H-6b^{C,F}, H-4^{A,D}), 3.51 (s, 6 H, OMe-2), 3.54 (s, 6 H, OMe-2), 3.57 (s, 6 H, OMe-2), 3.64 (m, 2 H, H-6b^{A,D}), 3.66 (m, 2 H, H-3^{A,D}), 3.68 (s, 6 H, OMe-3), 3.72 (dd, 2 H, $^3J_{H\text{-}3,H\text{-}2}$ = 10.1 Hz, $^3J_{H\text{-}3,H\text{-}4}$ = 18.1 Hz, H-3^{C,F}), 3.73 (dd, 2 H, $^3J_{H\text{-}3,H\text{-}2}$ = 9.5 Hz, $^3J_{H\text{-}3,H\text{-}4}$ = 18.1 Hz, H-3^{B,E}), 3.82 (dd, 2 H, $^3J_{H\text{-}4,H\text{-}3}$ = 18.0 Hz, $^3J_{H\text{-}4,H\text{-}5}$ = 8.8 Hz, H-4^{C,F}), 3.85 (s, 6 H, OMe-3), 3.89 (d, 2 H, $^3J_{H\text{-}5,H\text{-}4}$ = 8.8 Hz, H-5^{C,F}), 3.95–4.03 (4 H, H-5^{B,E}, H-6a^{B,E}), 4.02 (dd, 2 H, $^3J_{H\text{-}4,H\text{-}3}$ = 18.1 Hz, $^3J_{H\text{-}4,H\text{-}5}$ = 10.3 Hz, H-4^{B,E}), 4.42 (d, 2 H, $^2J_{H\text{-}6b,H\text{-}6a}$ = 11.1 Hz, H-6b^{B,E}), 4.48 (ddd, 2 H, $^3J_{H\text{-}5,H\text{-}6a}$ = 3.2 Hz, $^3J_{H\text{-}5,H\text{-}6b}$ = 17.4 Hz, $^3J_{H\text{-}5,H\text{-}4}$ = 8.8 Hz, H-5^{A,D}), 4.69 (d, 2 H, $^3J_{H\text{-}1,H\text{-}2}$ = 2.7 Hz, H-1^{A,D}), 4.94 (d, 2 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.9 Hz, H-1^{B,E}), 5.58 (d, 2 H, $^3J_{H\text{-}1,H\text{-}2}$ = 3.8 Hz, H-1^{C,F}), 6.03 (br s, 2 H, OH^{B,E}), 7.12 (td, 4 H, $^3J_{o\text{-}H,m\text{-}H}$ = $^3J_{o\text{-}H,P}$ = 7.6, $^4J_{o\text{-}H,p\text{-}H}$ = 3.0 Hz, *o*-H), 7.23 (td, 2 H, $^3J_{m\text{-}H,o\text{-}H}$ = $^3J_{m\text{-}H,p\text{-}H}$ = 7.6, $^4J_{m\text{-}H,P}$ = 1.3 Hz, *m*-H), 7.47–7.57 (10H, *o*-H, *m*-H, *p*-H), 7.78–7.84 (4H, *m*-H) ppm; ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 25ºC): δ (assignment by HMQC) = 32.26 (d, $^1J_{C,P}$ = 73.4 Hz, C-6^{A,D}), 56.98, 58.18, 58.32, 59.60, 59.65 (OMe), 60.08 (C-6^{B,E}), 61.82, 62.14 (OMe), 68.23 (d, $^2J_{C,P}$ = 7.3 Hz, C-5^{A,D}), 70.43 (C-5), 70.88 [×2] (C-4, C-5), 71.54 (C-6^{C,F}), 80.40, 80.98, 81.16, 81.78 [×2], 81.88, 84.15, 88.08 (C-2, C-3, C-4), 96.81, 96.95, 97.01(C-1), 128.46 (d, $^3J_{C,P}$ = 11.7, C$_{meta}$), 128.53 (d, $^3J_{C,P}$ = 11.7, C$_{meta}$), 130.34 (s, C$_{para}$), 130.44 (s, C$_{para}$), 131.28 (d, $^2J_{C,P}$ = 18.6 Hz, C$_{ortho}$), 131.41 (d, $^2J_{C,P}$ = 26.1 Hz, C$_{ortho}$),

133.57 (d, $^{1}J_{C,P}$ = 100.8 , C_{ipso}), 135.40 (d, $^{1}J_{C,P}$ = 102.8 , C_{ipso}) ppm; $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$, 25ºC): δ = 32.66 (s) ppm; elemental analysis (%) calcd for $C_{74}H_{106}O_{30}P_2 \cdot 0.5CH_2Cl_2$ (1537.56 + 42.5): C 56.63, H 6.83, found: C 56.81, H 7.10; MS (ESI-TOF): *m/z* (%): 1559.62 (100) $[M + Na]^+$.

Crystal structure analyses

X-ray crystallographic data of 5b: Single crystals of **5b** were obtained by slow diffusion of pentane into a dichloromethane solution of the compound. Crystal data for $C_{60}H_{95}NO_{31}\cdot 0.5CH_2Cl_2\cdot H_2O\cdot 1.5C_5H_{12}$ (**5b**$\cdot 0.5CH_2Cl_2\cdot H_2O\cdot 1.5C_5H_{12}$), M_r = 1495.07, monoclinic, space group $P2_1$, a = 15.2970(10), b = 15.7262(8), c = 16.6710(10) Å, β = 90.778(6)°, V = 4010.1(4) Å^3, Z = 2, ρ_{calcd} = 1.238 g cm^{-3}, $\lambda(Mo_{K\alpha})$ = 0.71073 Å, μ = 0.129 mm^{-1}, $F(000)$ = 1608, T = 120 K. The sample (0.26 × 0.16 × 0.08 mm) was studied with an Oxford Diffraction Xcalibur Saphir 3 CCD with graphite monochromatised Mo Kα radiation. The structure was solved with SIR-97,[4] 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 SHELX-97[5] and full-matrix least-square techniques. Use of F^2 magnitude; x, y, z, β_{ij} for C, O, S atoms, x, y, z, in riding mode for H atoms, 917 variables and 7789 observations with [$I > 2.0\sigma(I)$], calcd $w = 1/[\sigma^2(F_o^2) + (0.1186\ P)^2]$ where $P = (F_o^2 + 2\ F_o^2)/3$ with the resulting R = 0.0680, R_w = 0.1911, and S_w = 0.830, $\Delta\rho < 0.929$ e Å^{-3}. The compound was rather poorly diffracting. It crystallized with half a molecule of pentane inside the cavity and one molecule of pentane, half a molecule of CH_2Cl_2 and one water molecule lying outside the CD. It must be emphasised that the O46-C49 O-methyl and C62....C67 aromatic groups are disordered. The disordered aromatic group was refined in the isotropical mode because of correlations in the anisotropical mode. The A-level alerts are mainly due to the external pentane molecule, which was difficult to refine. CCDC 826891.

X-ray crystallographic data of 7a: Single crystals of **7a** were obtained by slow diffusion of pentane into a dichloromethane solution of the compound. Crystal data for $C_{74}H_{112}B_2O_{28}P_2\cdot 3CH_2Cl_2\cdot 1.5C_5H_{12}$ (**7a**$\cdot 3CH_2Cl_2\cdot 1.5C_5H_{12}$), M_r = 1896.19, orthorhombic, space group $P2_12_12_1$, a = 16.0969(4), b = 22.4367(5), c = 27.7517(7) Å, V = 10022.8(4) Å^3, Z = 4, ρ_{calcd} = 1.257 g cm^{-3}, λ(Mo Kα) = 0.71073 Å, μ = 0.274 mm^{-1}, $F(000)$ = 4036, T = 120 K. The sample (0.22 × 0.12 × 0.10 mm) was studied with an Oxford Diffraction Xcalibur Saphir 3 CCD with graphite monochromatised Mo $_{K\alpha}$ radiation. The structure was solved with SIR-97,[4] 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 SHELX-97[5] and full-matrix least-square techniques. Use of F^2

magnitude; *x*, *y*, *z*, β_{ij} for C, O, S atoms, *x*, *y*, *z*, in riding mode for H atoms, 1029 variables and 8413 observations with [$I > 2.0\sigma(I)$], calcd $w = 1/[\sigma^2(F_o^2) + (0.1186\ P)^2]$ where $P = (F_o^2 + 2\ F_o^2)/3$ with the resulting $R = 0.0935$, $R_w = 0.2645$, and $S_w = 0.932$, $\Delta\rho < 0.658$ e Å^{-3}. CCDC 822184.

CCDC-822184 (**7a**) and CCDC-826891 (**5b**) contain the supplementary crystallographic data for this report. These data can be obtained free of charge from The Cambridge Christallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif.

NMR and mass spectra

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

$6^A,6^B$-Dideoxy-$6^A,6^B$-sulfato-$2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^C,6^D,6^E,6^F$-hexadeca-*O*-methyl-$\alpha$-cyclodextrin (1):

^{1}H NMR spectrum 23
^{1}H/^{1}H COSY spectrum 24
^{13}C{^{1}H} NMR spectrum 25
DEPT 135 spectrum 26
^{1}H/^{13}C HMQC spectrum 27
Mass spectrum 28

$6^A,6^B$-Dideoxy-$6^A,6^B$-sulfato-$2^A,2^B,2^C,2^D,2^E,2^F,2^G,3^A,3^B,3^C,3^D,3^E,3^F,3^G,6^C,6^D,6^E,6^F,6^G$-nonadeca-*O*-methyl-$\beta$-cyclodextrin (2):

^{1}H NMR spectrum 29
^{1}H/^{1}H COSY spectrum 30
^{13}C{^{1}H} NMR spectrum 31
DEPT 135 spectrum 32
^{1}H/^{13}C HMQC spectrum 33
Mass spectrum 34

***P*-{6^A-Deoxy-6^A-diphenylphosphinyl-$2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^C,6^D,6^E,6^F$-hexadeca-*O*-methyl-$\alpha$-cyclodextrin} borane (5a):**

^{1}H NMR spectrum 35
^{1}H/^{1}H COSY spectrum 36
^{1}H/^{1}H TOCSY spectrum 37
^{1}H/^{1}H ROESY spectrum 38
^{13}C{^{1}H} NMR spectrum 39
DEPT 135 spectrum 40
^{1}H/^{13}C HMQC spectrum 41
^{31}P{^{1}H} NMR spectrum 42
Mass spectrum 43

6^A-Deoxy-6^A-(1,3-dioxoisoindolin-2-yl)-$2^A,2^B,2^C,2^D,2^E,2^F,3^A,3^B,3^C,3^D,3^E,3^F,6^C,6^D,6^E,6^F$-hexadeca-*O*-methyl-$\alpha$-cyclodextrin (5b):

^{1}H NMR spectrum 44
^{1}H/^{1}H COSY spectrum 45
^{1}H/^{1}H TOCSY spectrum 46
^{1}H/^{1}H ROESY spectrum 47
^{13}C{^{1}H} NMR spectrum 48
DEPT 135 spectrum 49
^{1}H/^{13}C HMQC spectrum 50
Mass spectrum 51

6^B-Deoxy-6^B-(1,3-dioxoisoindolin-2-yl)-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 (6b):

^{1}H NMR spectrum 52
Mass spectrum 53

6^A-Deoxy-6^A-azido-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 (5c) and 6^B-deoxy-6^B-azido-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 (6c):

^{1}H NMR spectrum 54
Mass spectrum 55

6^A-Deoxy-6^A-(S-thioacetylmethyl)-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 (5d) and 6^B-deoxy-6^B-(S-thioacetylmethyl)-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 (6d):

^{1}H NMR spectrum 56
Mass spectrum 57

***P*-{6^A-Deoxy-6^A-diphenylphosphinyl-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} borane (5e) and *P*-{6^B-deoxy-6^B-diphenylphosphinyl-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} borane (6e):**

^{1}H NMR spectrum 58
Part of the ^{1}H NMR spectrum showing the anomeric signals (mixture of **5e**/**6e**) 59
^{31}P{^{1}H} NMR spectrum 60
Mass spectrum 61

6^A-Deoxy-6^A-(1,3-dioxoisoindolin-2-yl)-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 (5f) and 6^B-deoxy-6^B-(1,3-dioxoisoindolin-2-yl)-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 (6f):

^{1}H NMR spectrum 62
Part of the ^{1}H NMR spectrum showing the anomeric signals (mixture of **5f**/**6f**) 63
Mass spectrum 64

***P*,*P*'-{6^A,6^D-Dideoxy-6^A,6^D-di(diphenylphosphinyl)-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^F-tetradeca-*O*-methyl-α-cyclodextrin} diborane (7a):**

^{1}H NMR spectrum 65
^{1}H/^{1}H COSY spectrum 66
^{13}C{^{1}H} NMR spectrum 67
DEPT 135 spectrum 68
^{1}H/^{13}C HMQC spectrum 69
^{31}P{^{1}H} NMR spectrum 70
Mass spectrum 71

$6^{A},6^{D}$-Dideoxy-$6^{A},6^{D}$-di(1,3-dioxoisoindolin-2-yl)-$2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{C},6^{F}$-tetradeca-*O*-methyl-$\alpha$-cyclodextrin (7b):

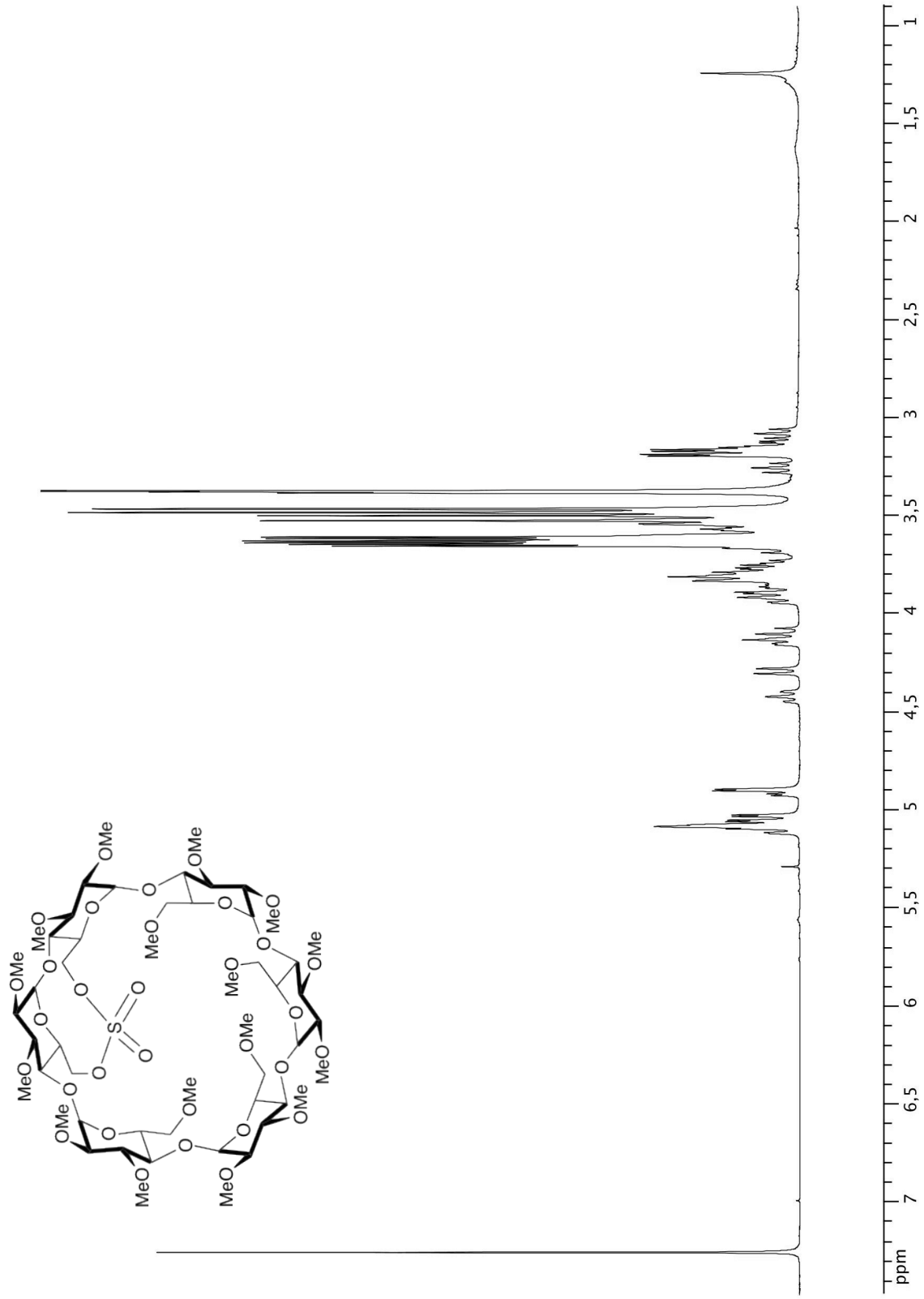
^{1}H NMR spectrum 72
^{1}H/^{1}H COSY spectrum 73
^{1}H/^{1}H TOCSY spectrum 74
^{1}H/^{1}H ROESY spectrum 75
^{13}C{^{1}H} NMR spectrum 76
DEPT 135 spectrum 77
^{1}H/^{13}C HMQC spectrum 78
Mass spectrum 79

$6^{A},6^{E}$-Dideoxy-$6^{A},6^{E}$-di(1,3-dioxoisoindolin-2-yl)-$2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{C},6^{F}$-tetradeca-*O*-methyl-$\alpha$-cyclodextrin (8b):

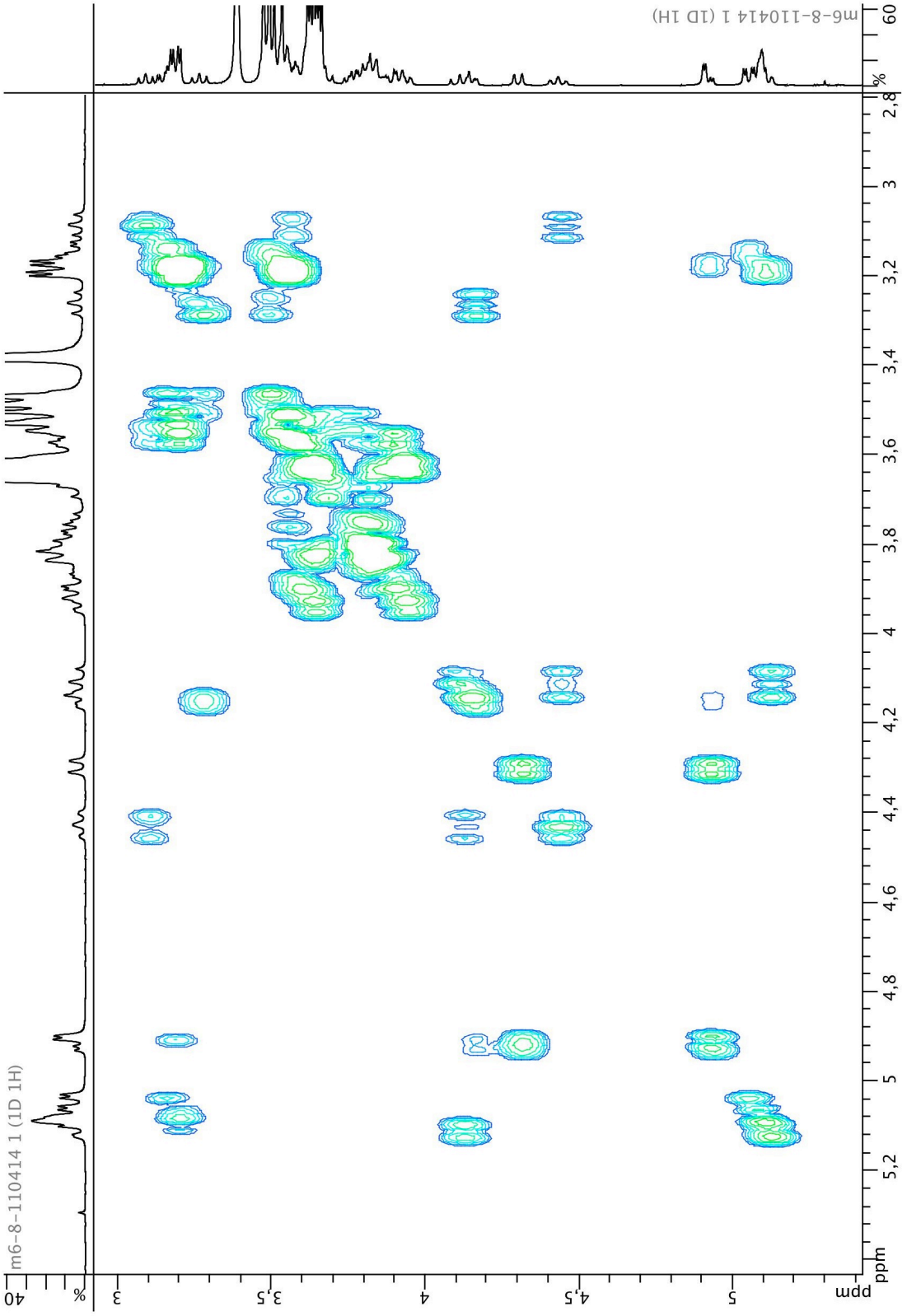
^{1}H NMR spectrum 80
^{1}H/^{1}H COSY spectrum 81
^{13}C{^{1}H} NMR spectrum 82
DEPT 135 spectrum 83
^{1}H/^{13}C HMQC spectrum 84
Mass spectrum 85

$6^{A},6^{D}$-Dideoxy-$6^{A},6^{D}$-di(diphenyloxophosphinyl)-$2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{C},6^{F}$-tetradeca-*O*-methyl-$\alpha$-cyclodextrin (10):

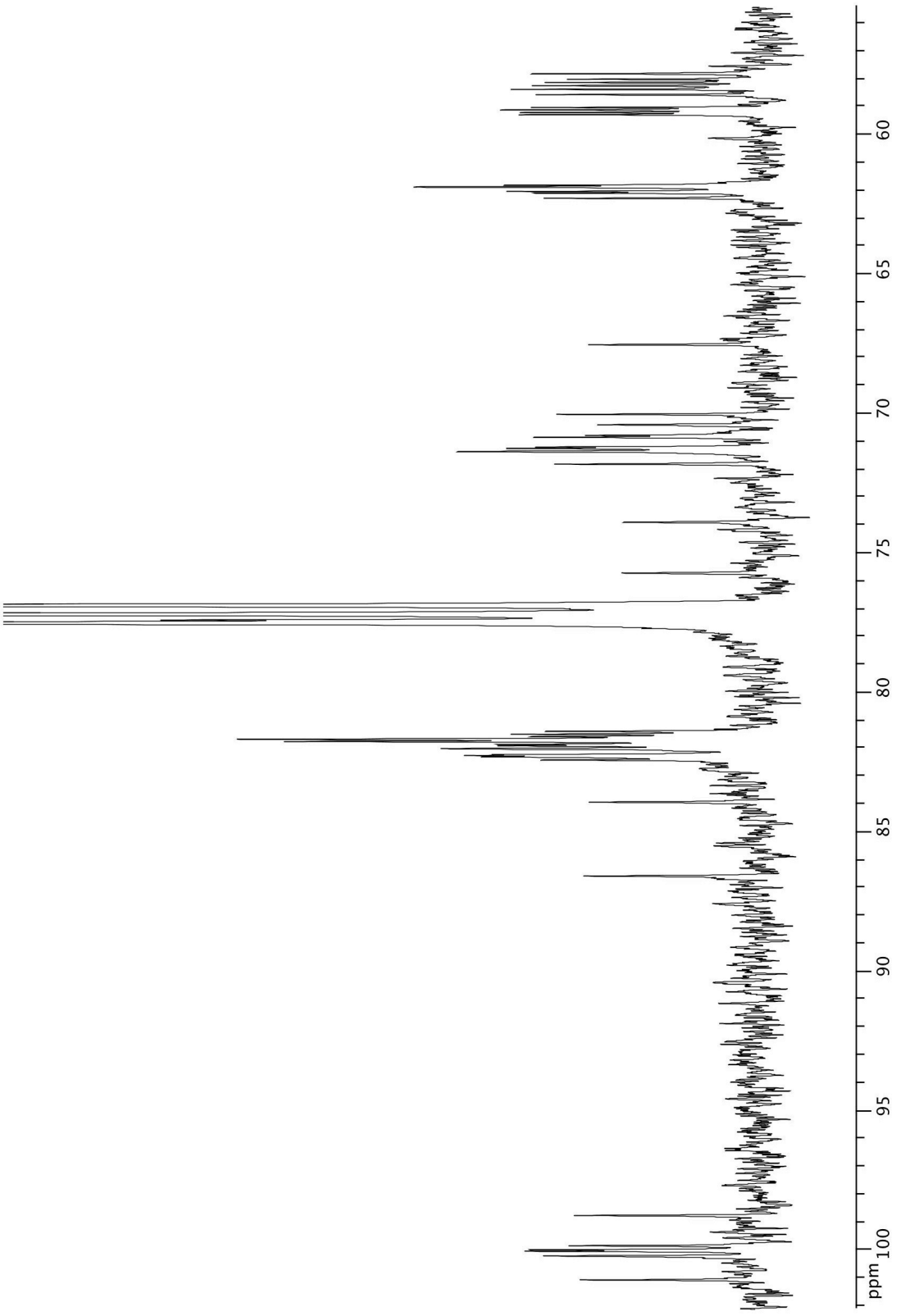
^{1}H NMR spectrum 86
^{1}H/^{1}H COSY spectrum 87
^{1}H/^{1}H TOCSY spectrum 88
^{1}H/^{1}H ROESY spectrum 89
^{13}C{^{1}H} NMR spectrum 90
DEPT 135 spectrum 91
^{1}H/^{13}C HMQC spectrum 92
^{31}P{^{1}H} NMR spectrum 93
Mass spectrum 94



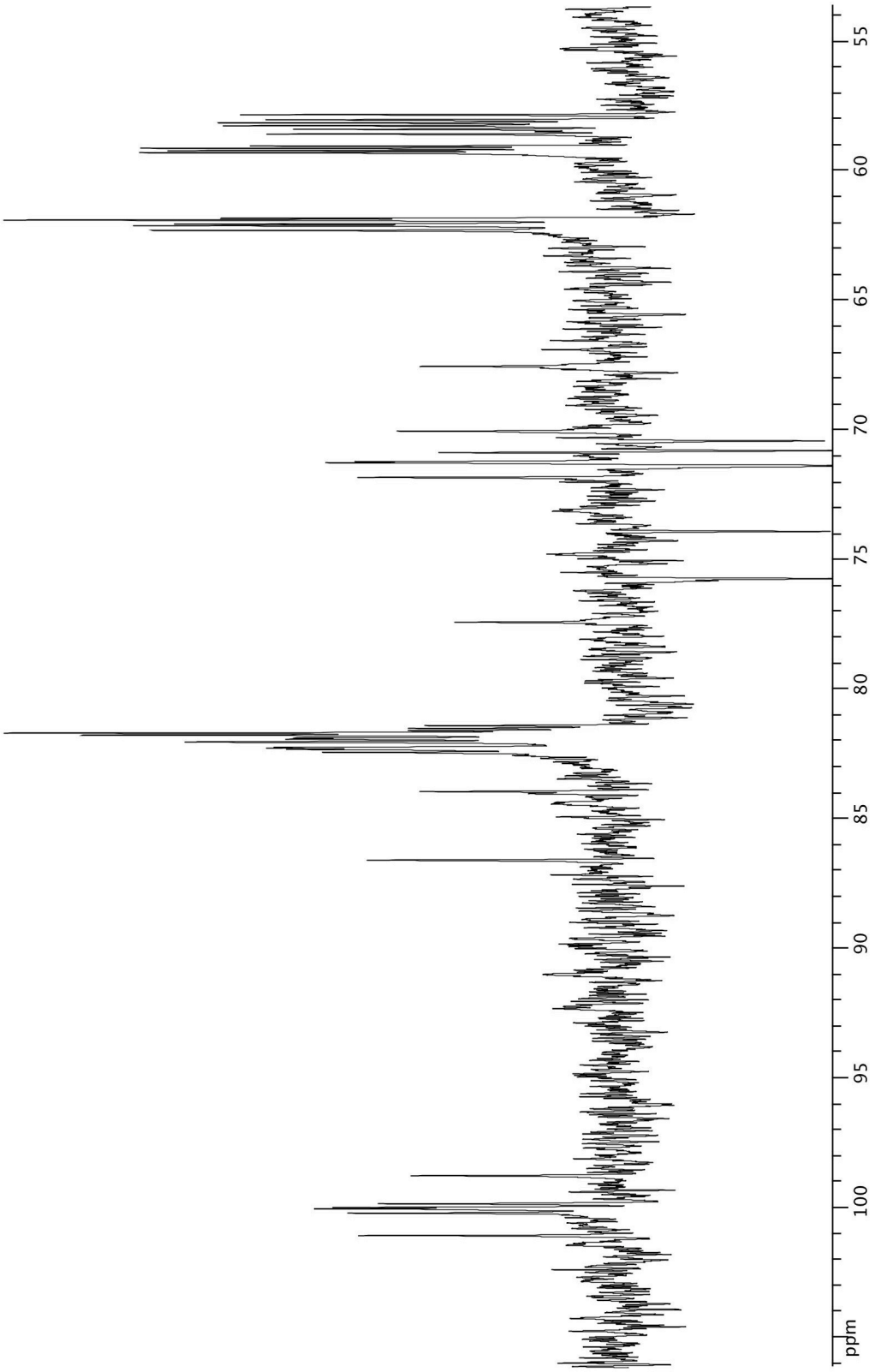
^{1}H NMR spectrum of 1



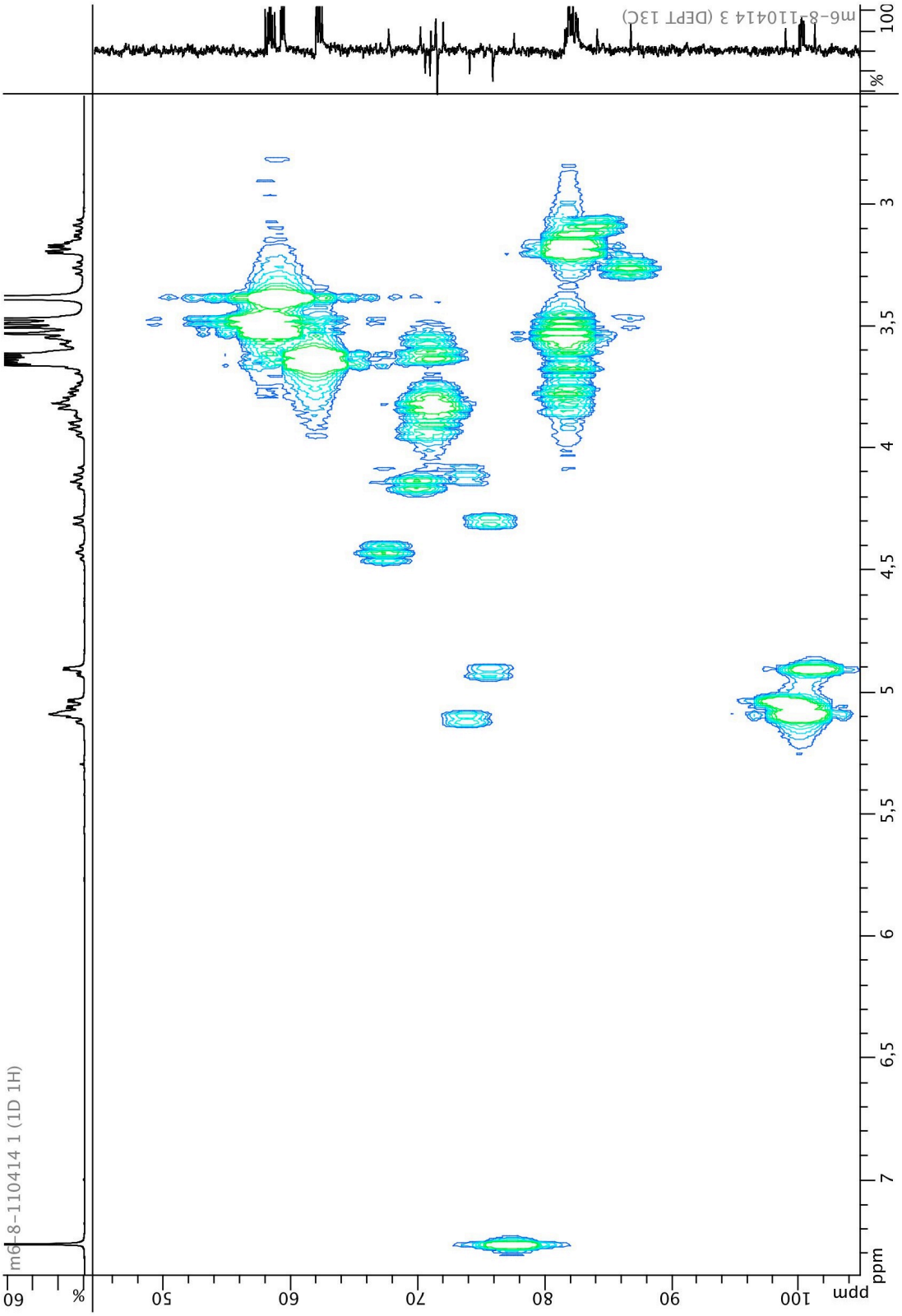
^{1}H-^{1}H COSY NMR spectrum of 1



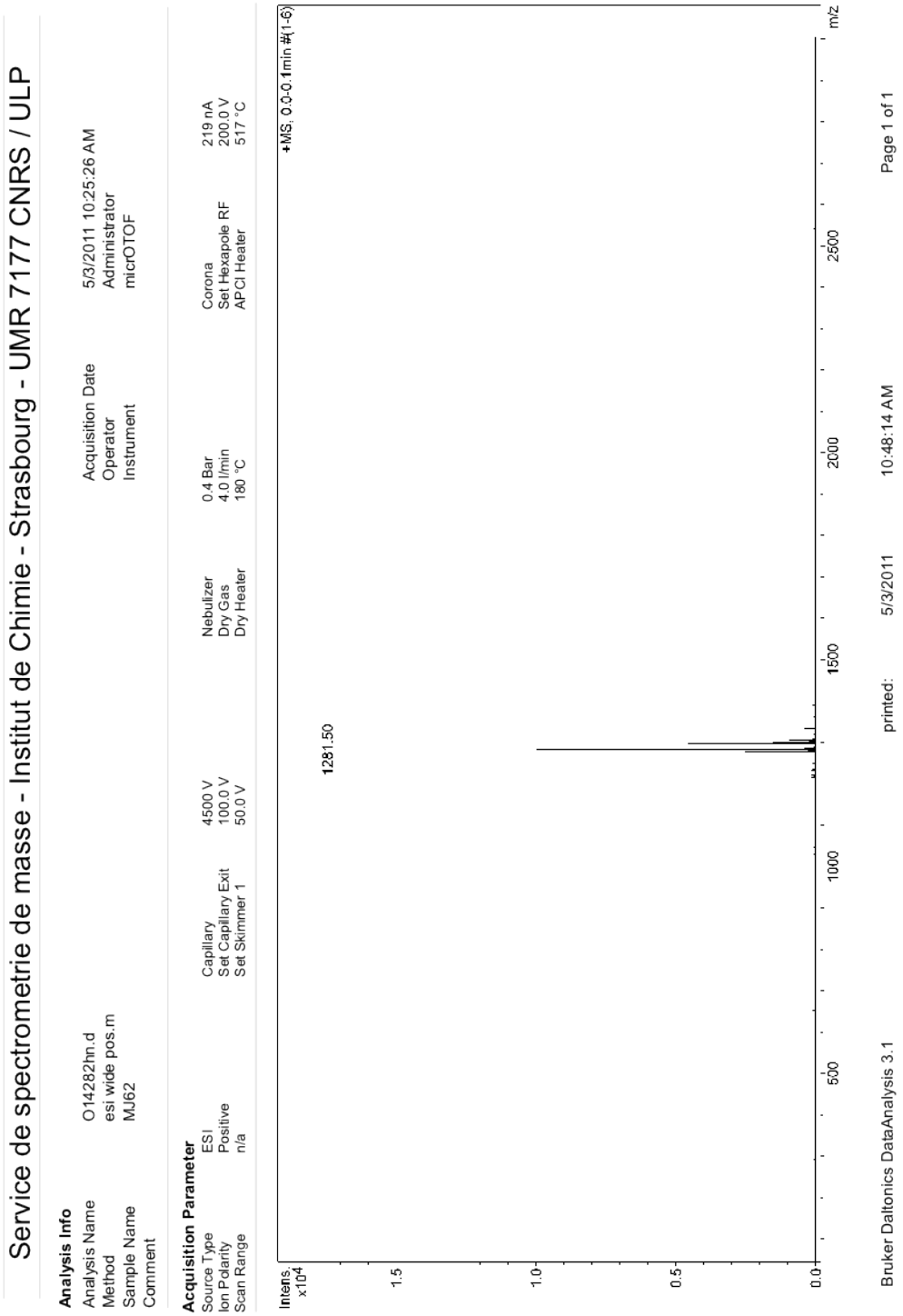
^{13}C NMR spectrum of 1



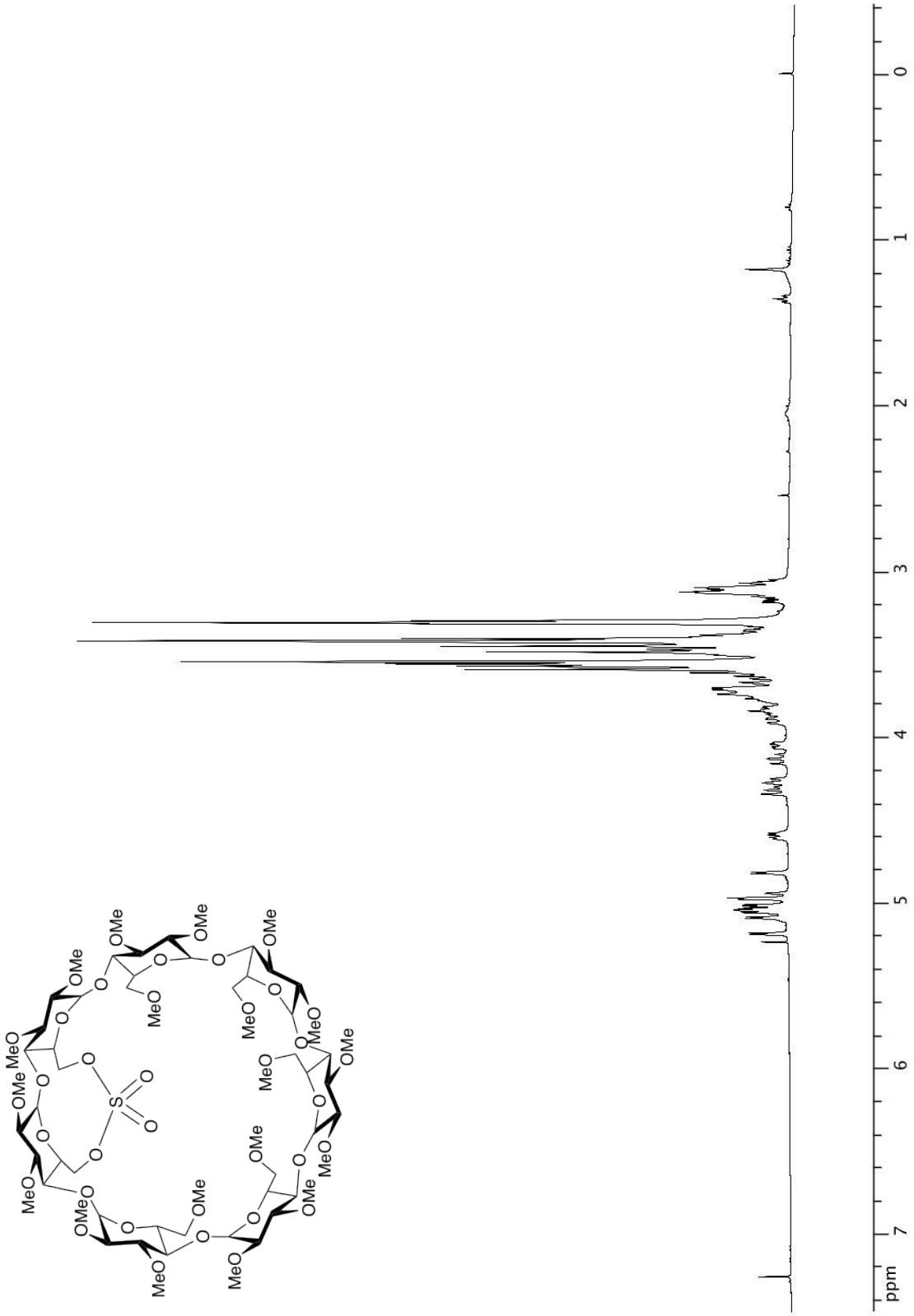
DEPT 135 NMR spectrum of 1



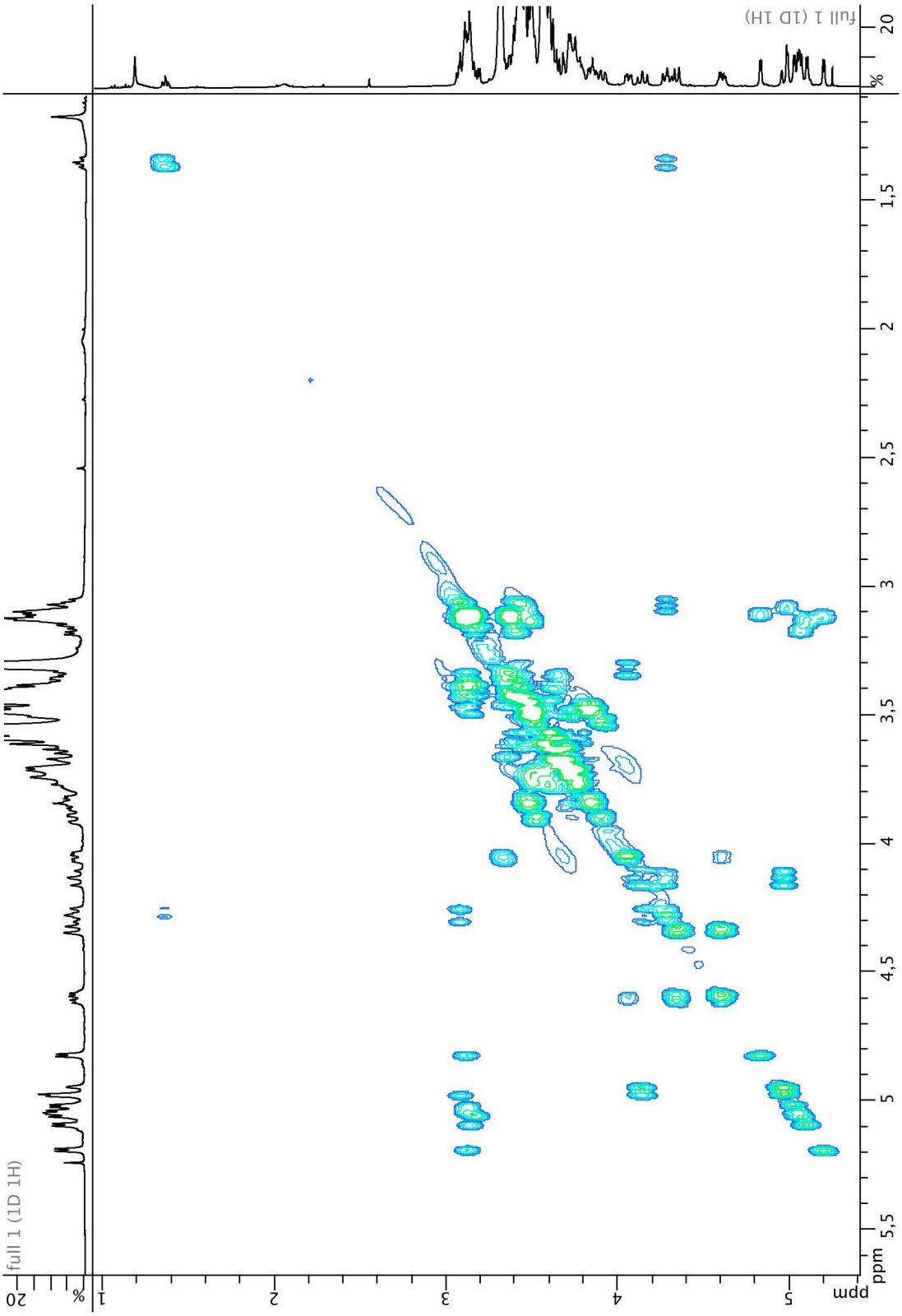
^{1}H-^{13}C HMQC NMR spectrum of 1



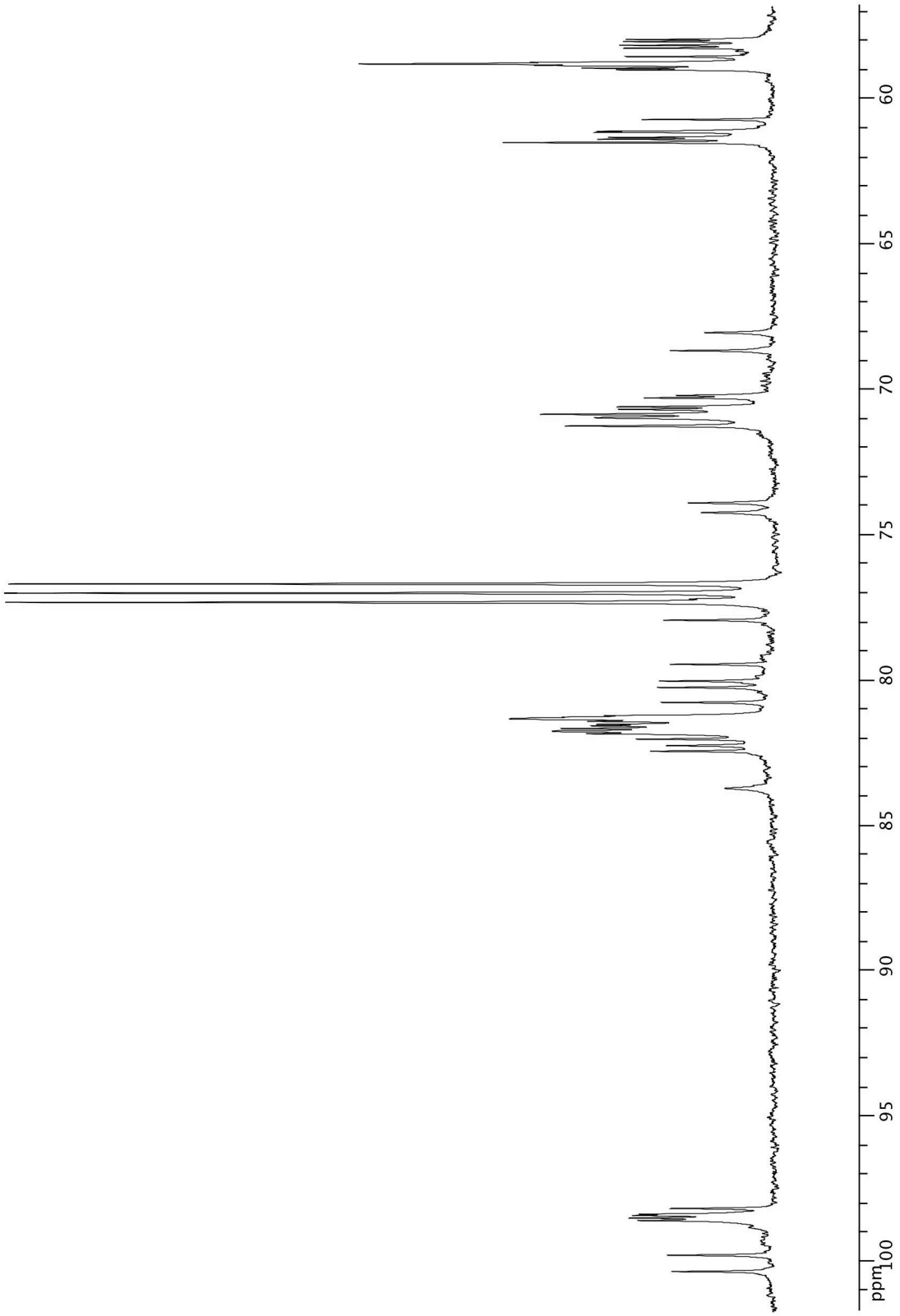
Mass spectrum of 1



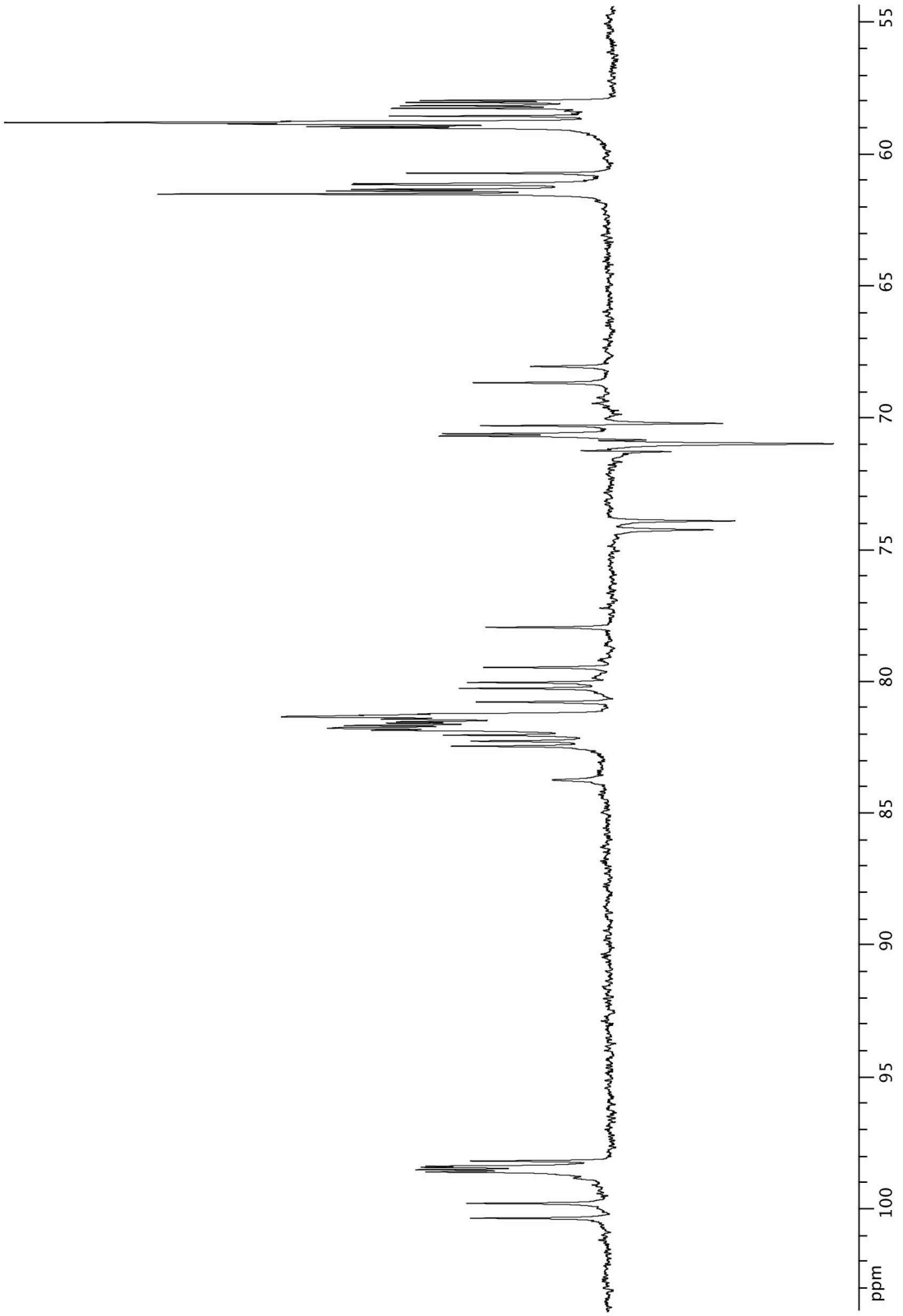
^{1}H NMR spectrum of 2



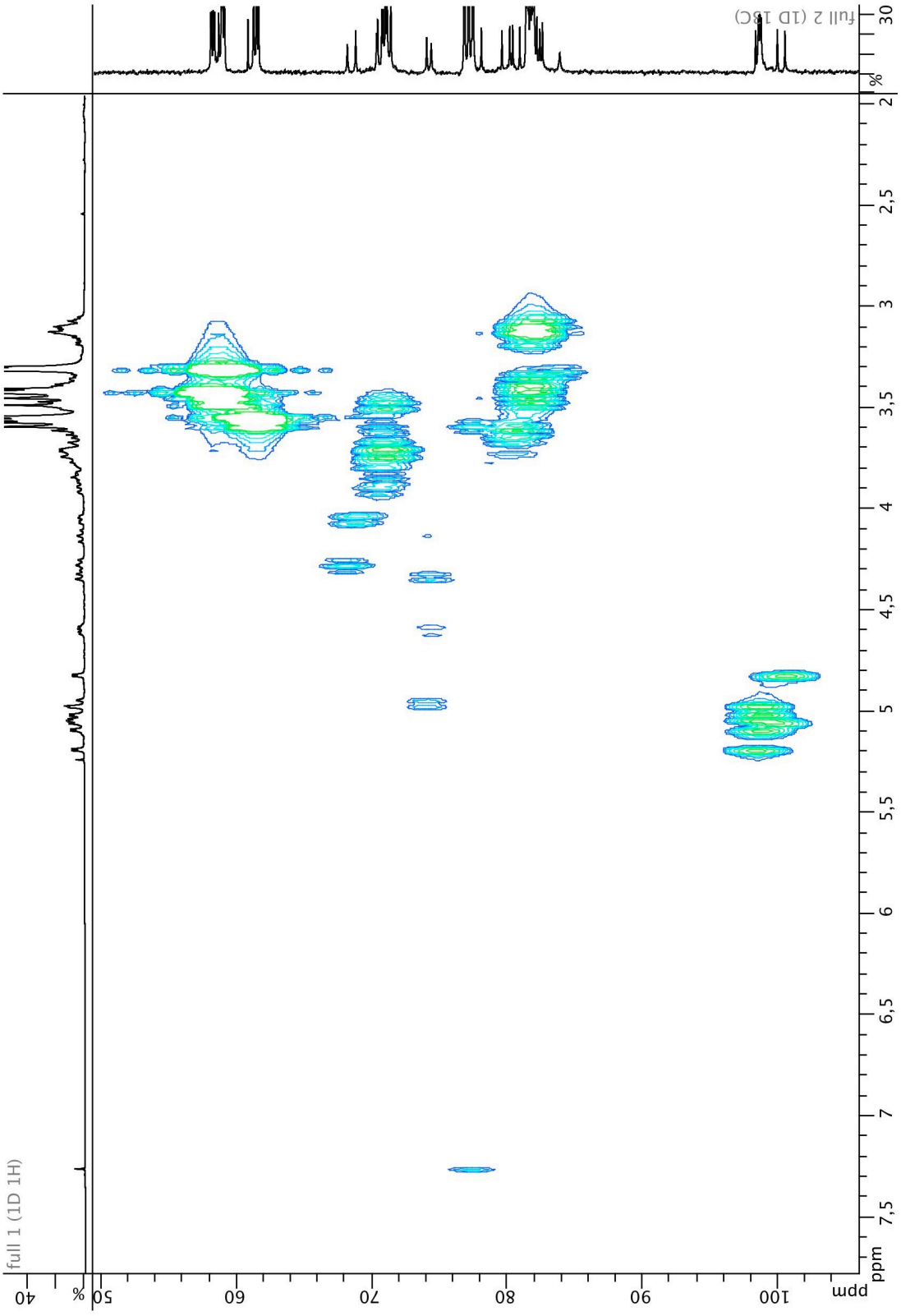
^{1}H-^{1}H COSY NMR spectrum of 2



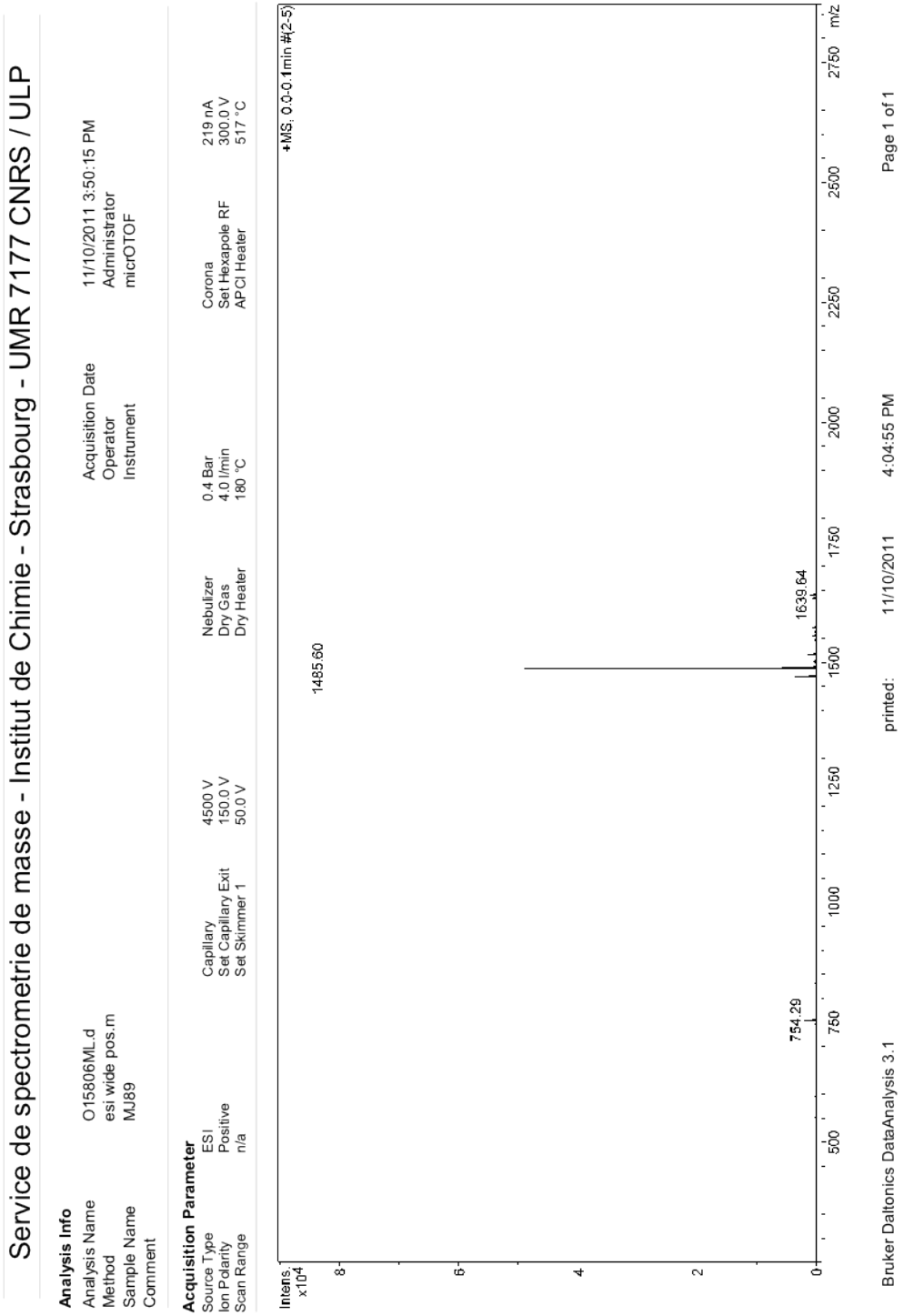
^{13}C NMR spectrum of 2



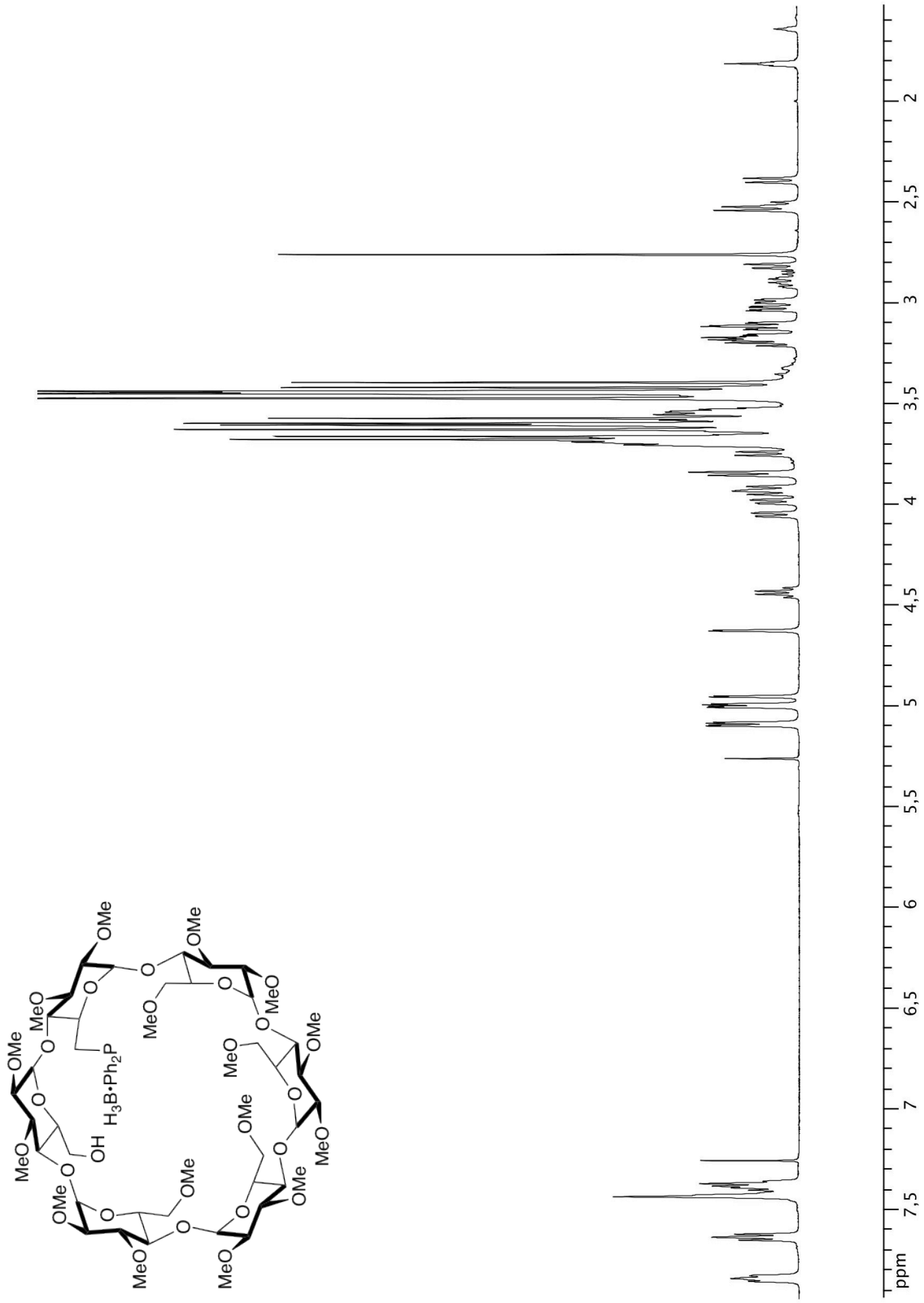
DEPT 135 NMR spectrum of 2



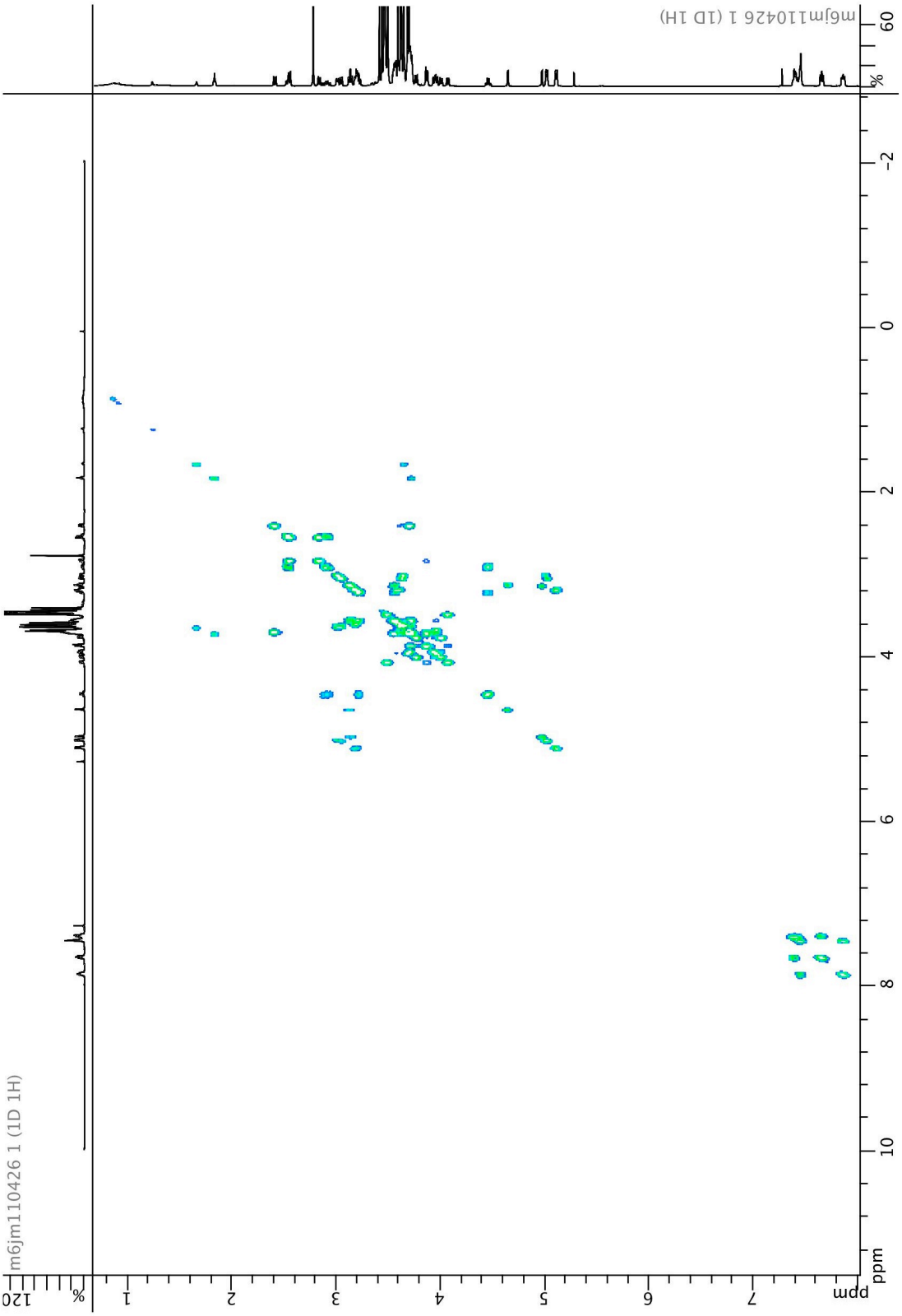
^{1}H-^{13}C HMQC NMR spectrum of 2



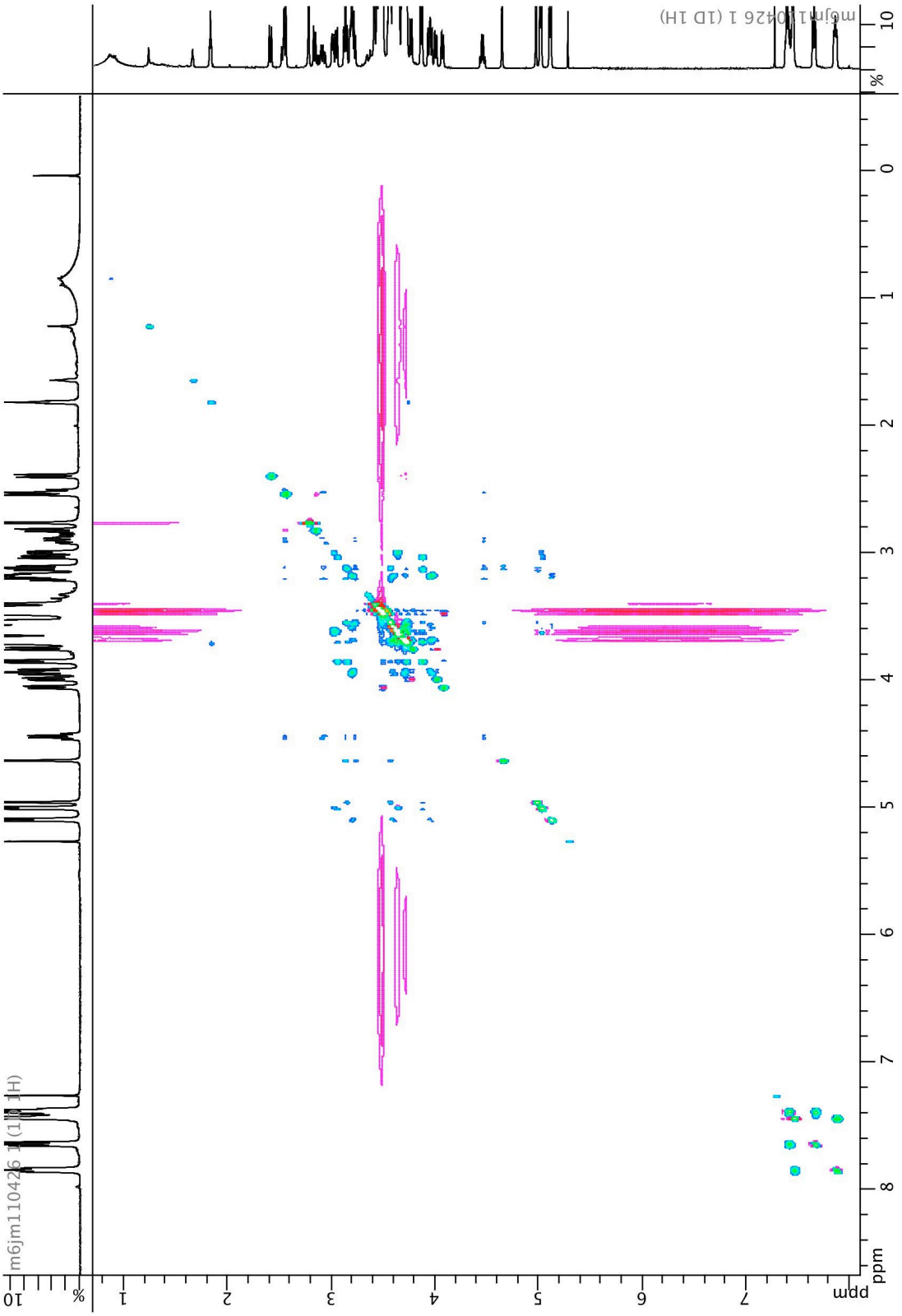
Mass spectrum of 2



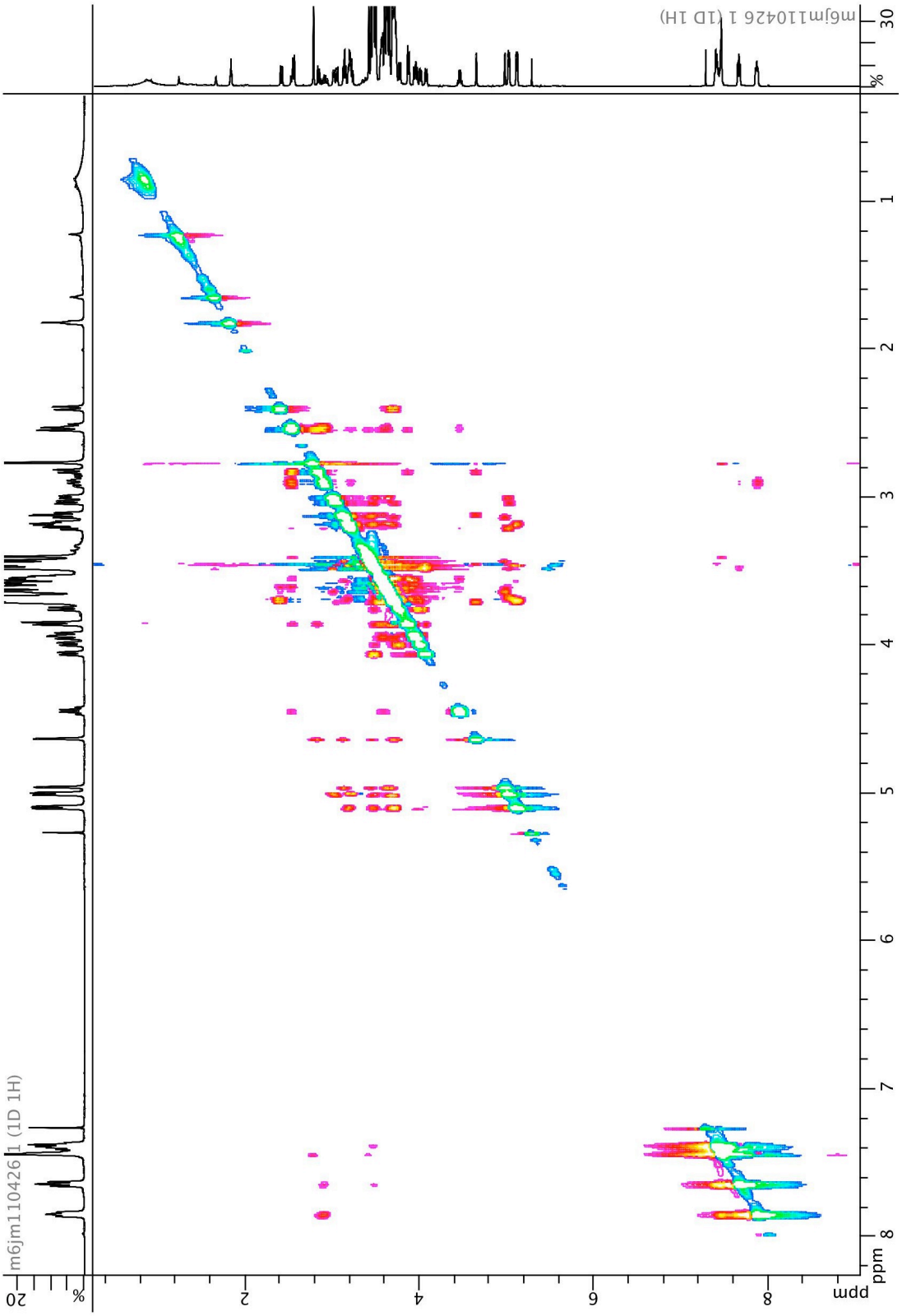
^{1}H NMR spectrum of 5a



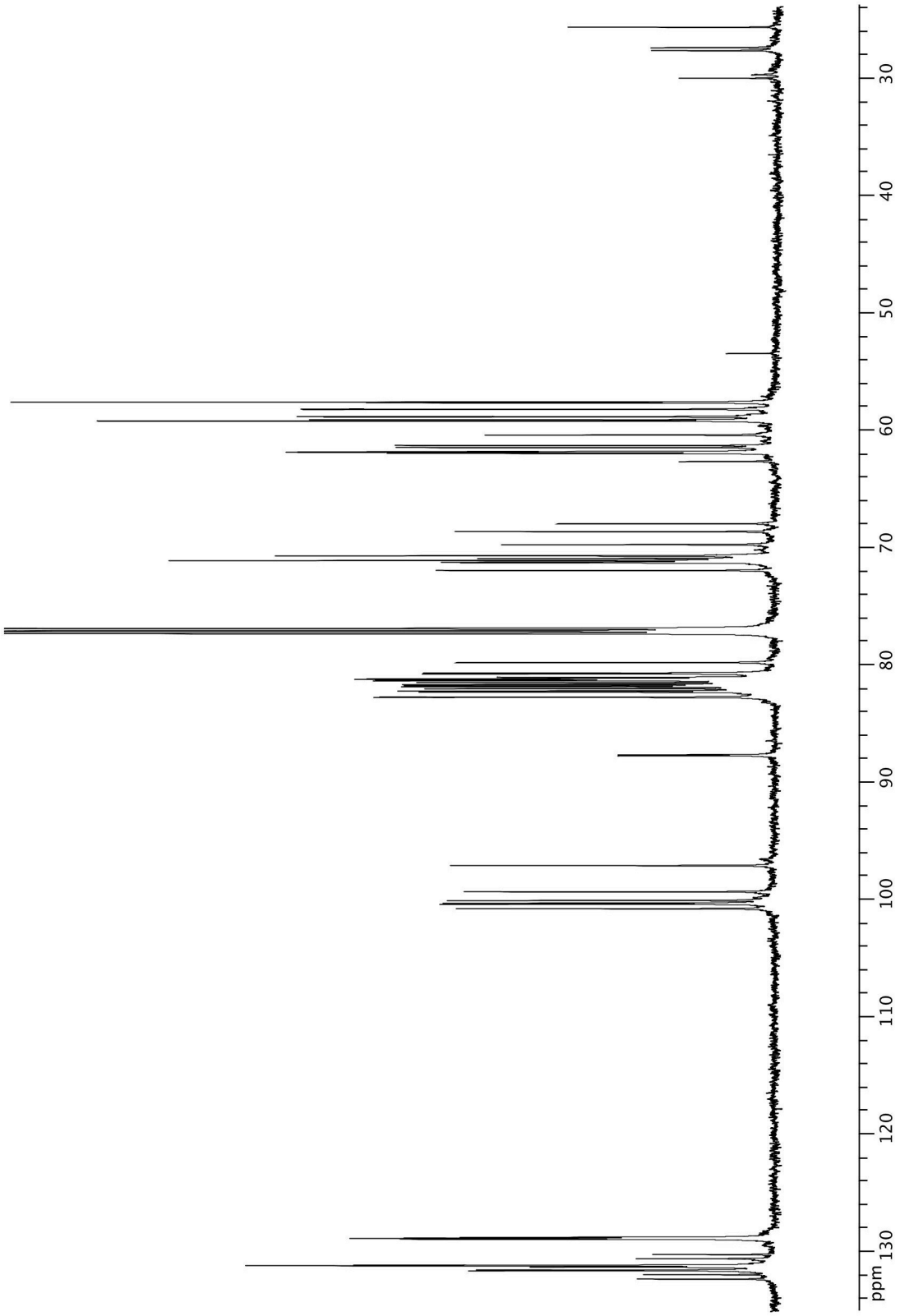
^{1}H-^{1}H COSY NMR spectrum of 5a



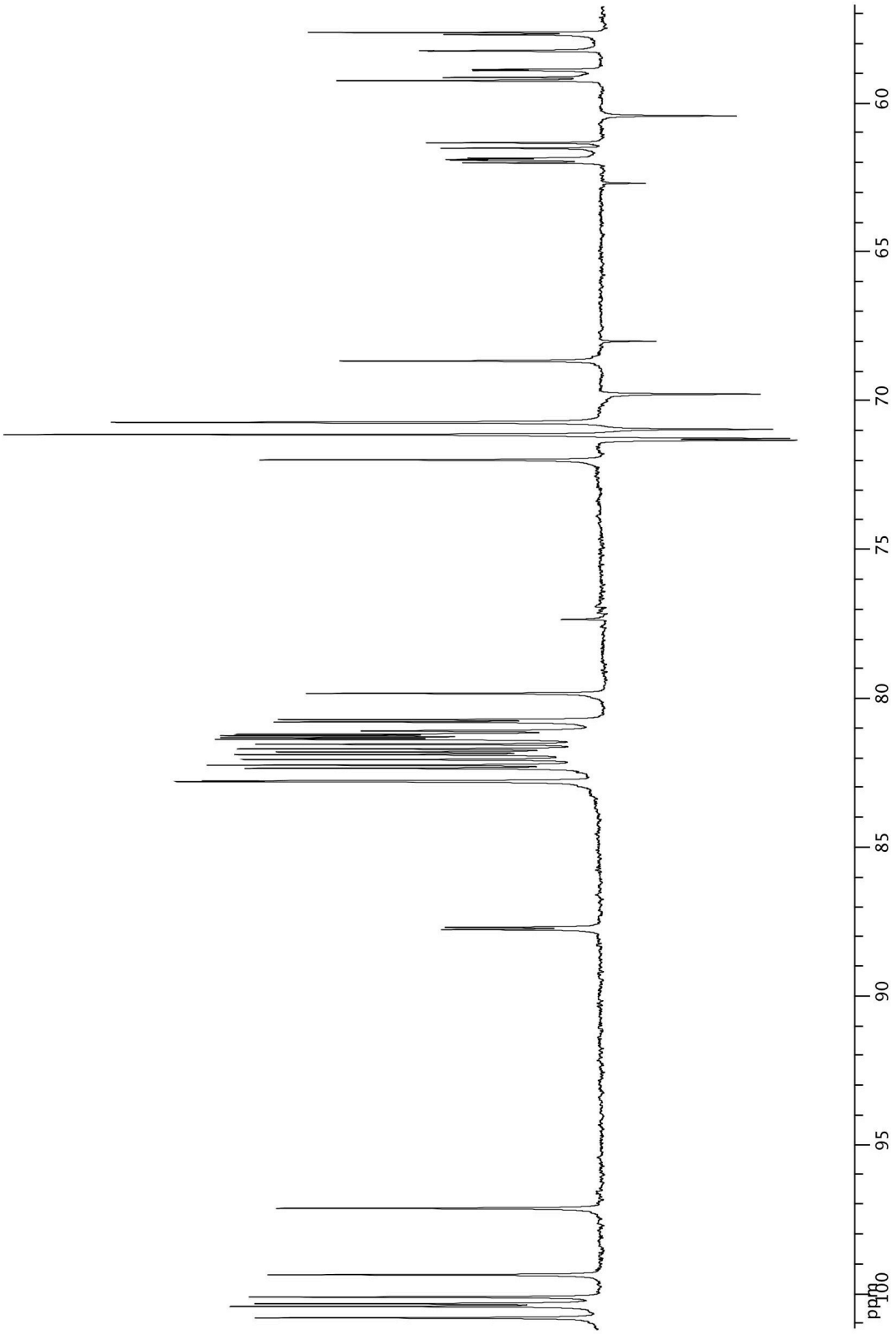
^{1}H-^{1}H TOCSY NMR spectrum of 5a



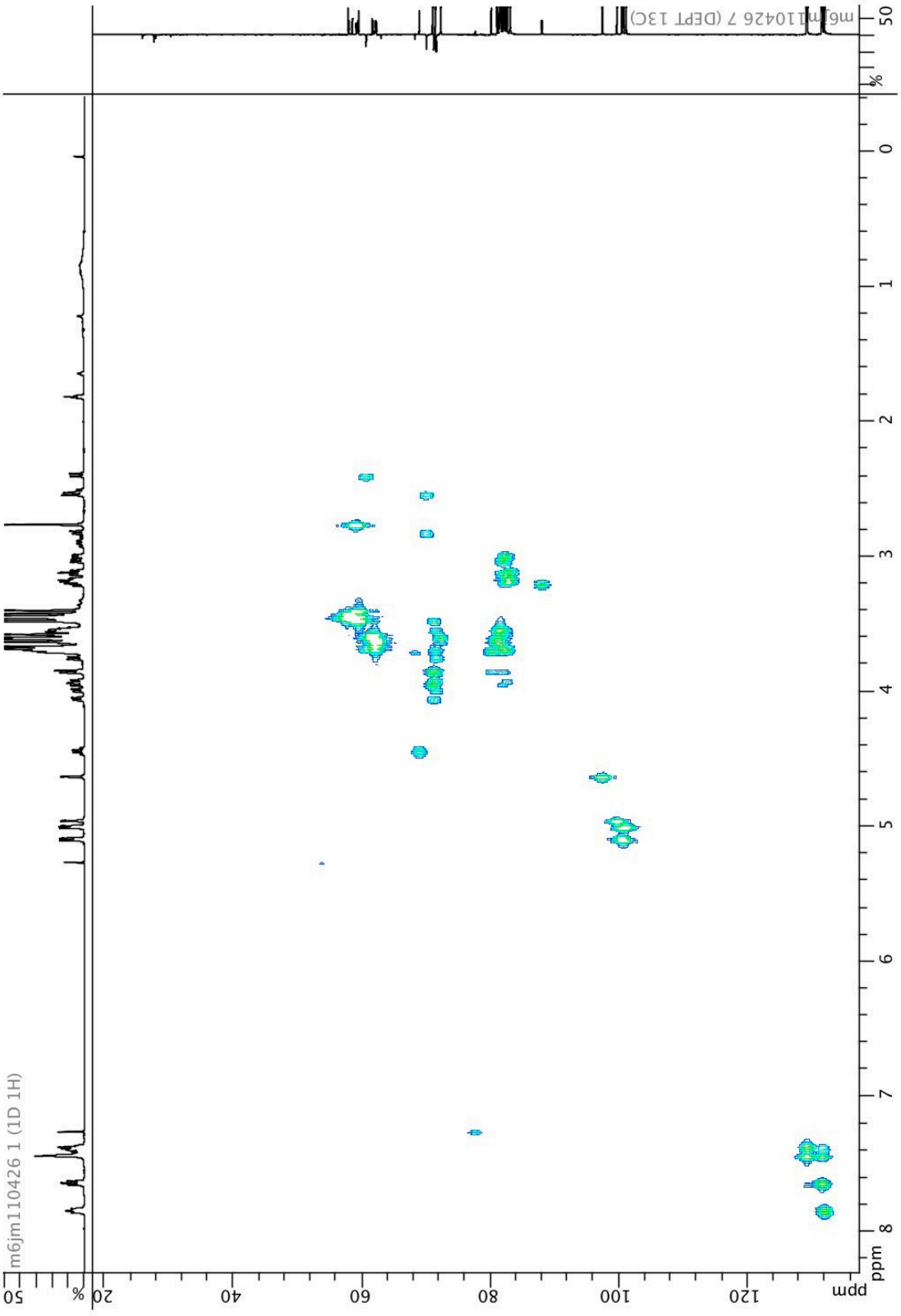
^{1}H-^{1}H ROESY NMR spectrum of 5a



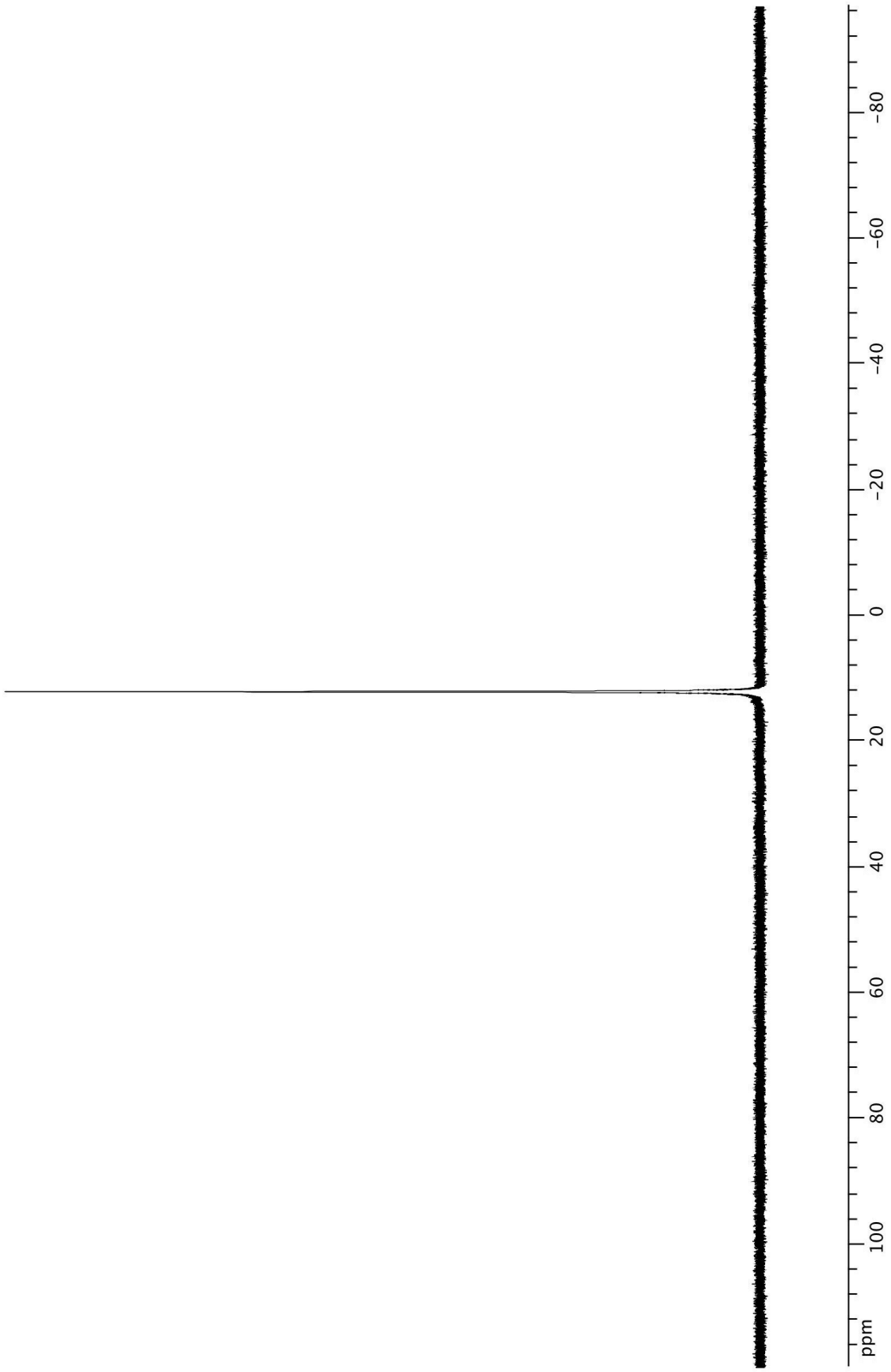
^{13}C NMR spectrum of 5a



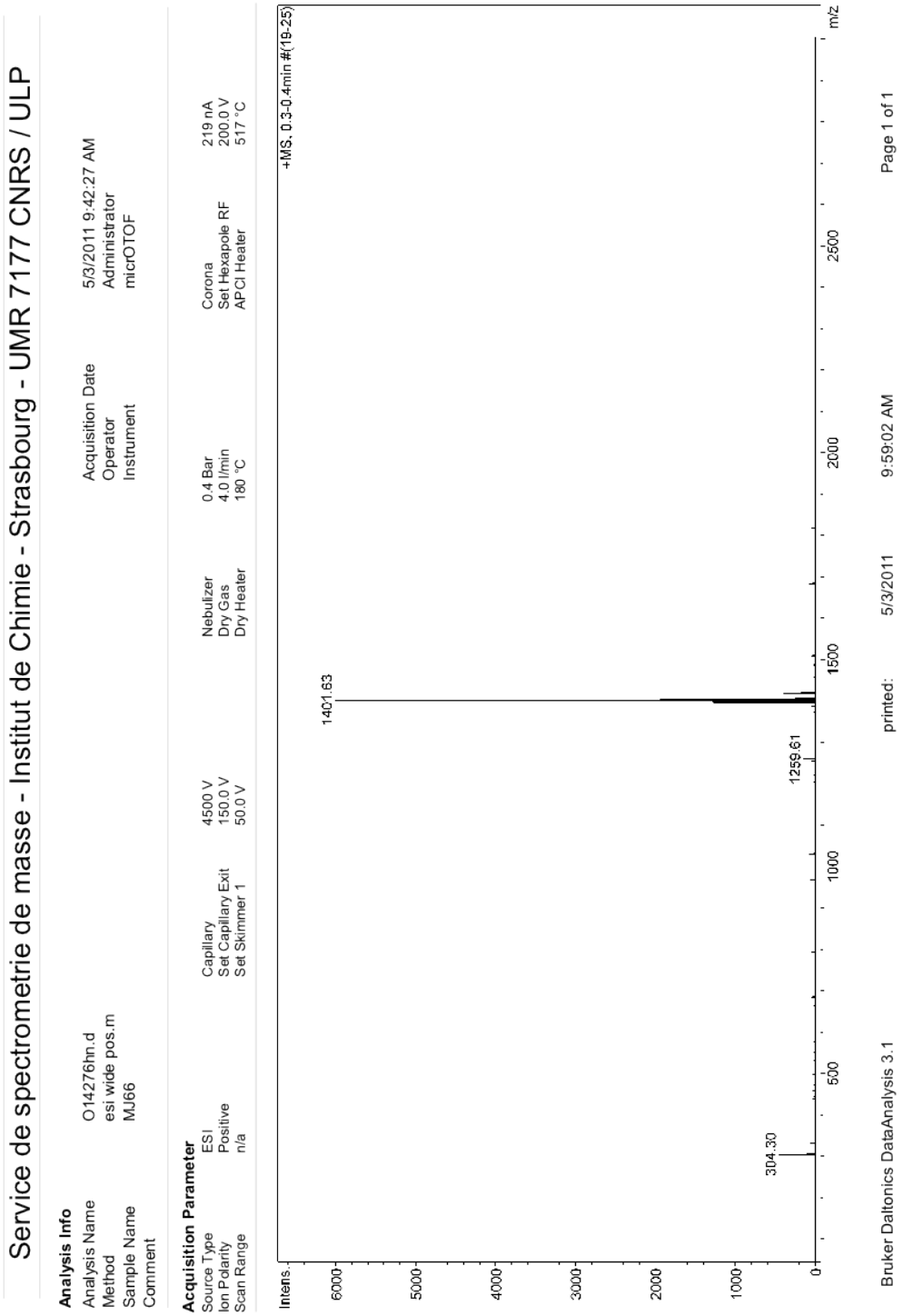
DEPT 135 NMR spectrum of 5a



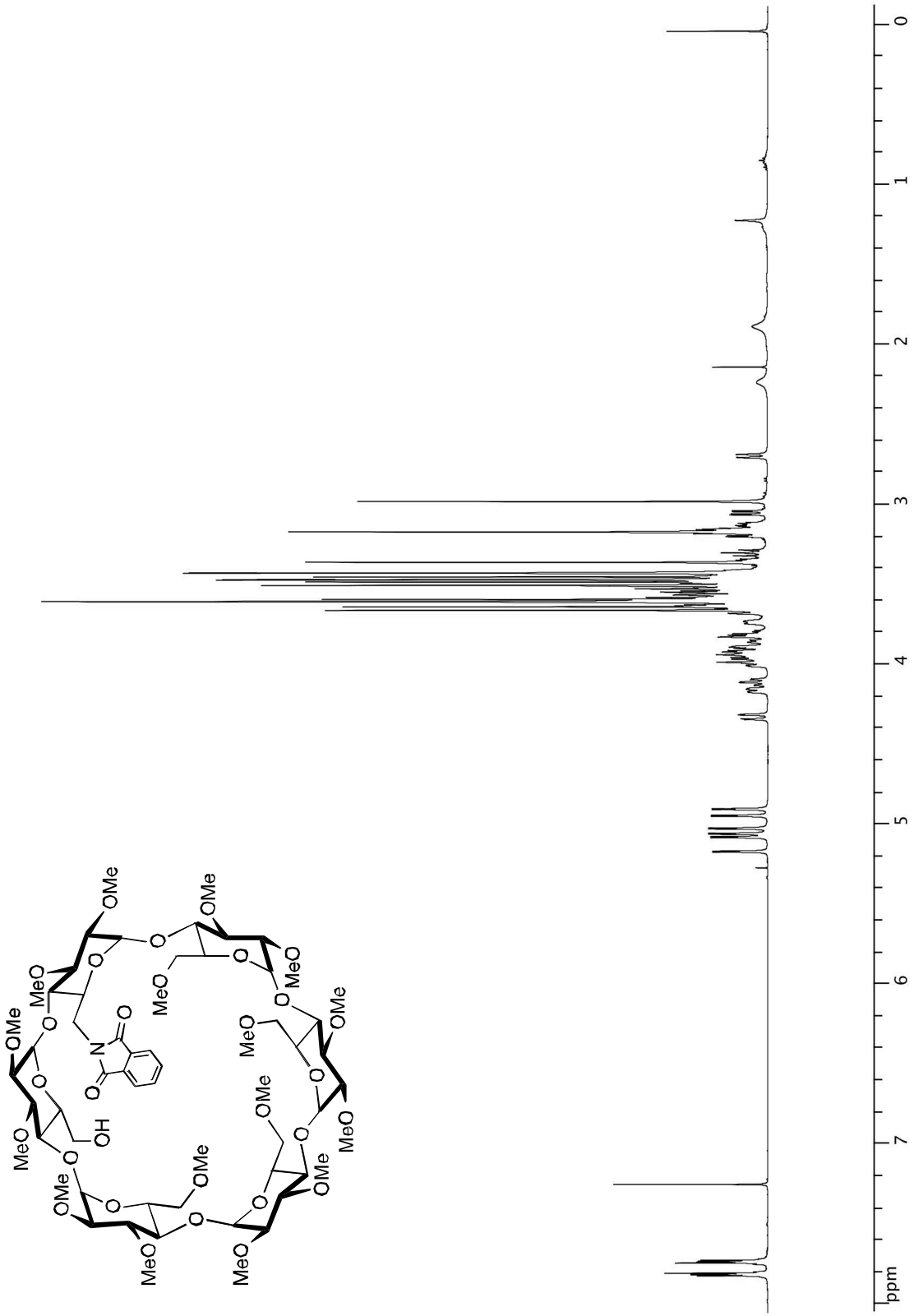
^{1}H-^{13}C NMR spectrum of 5a



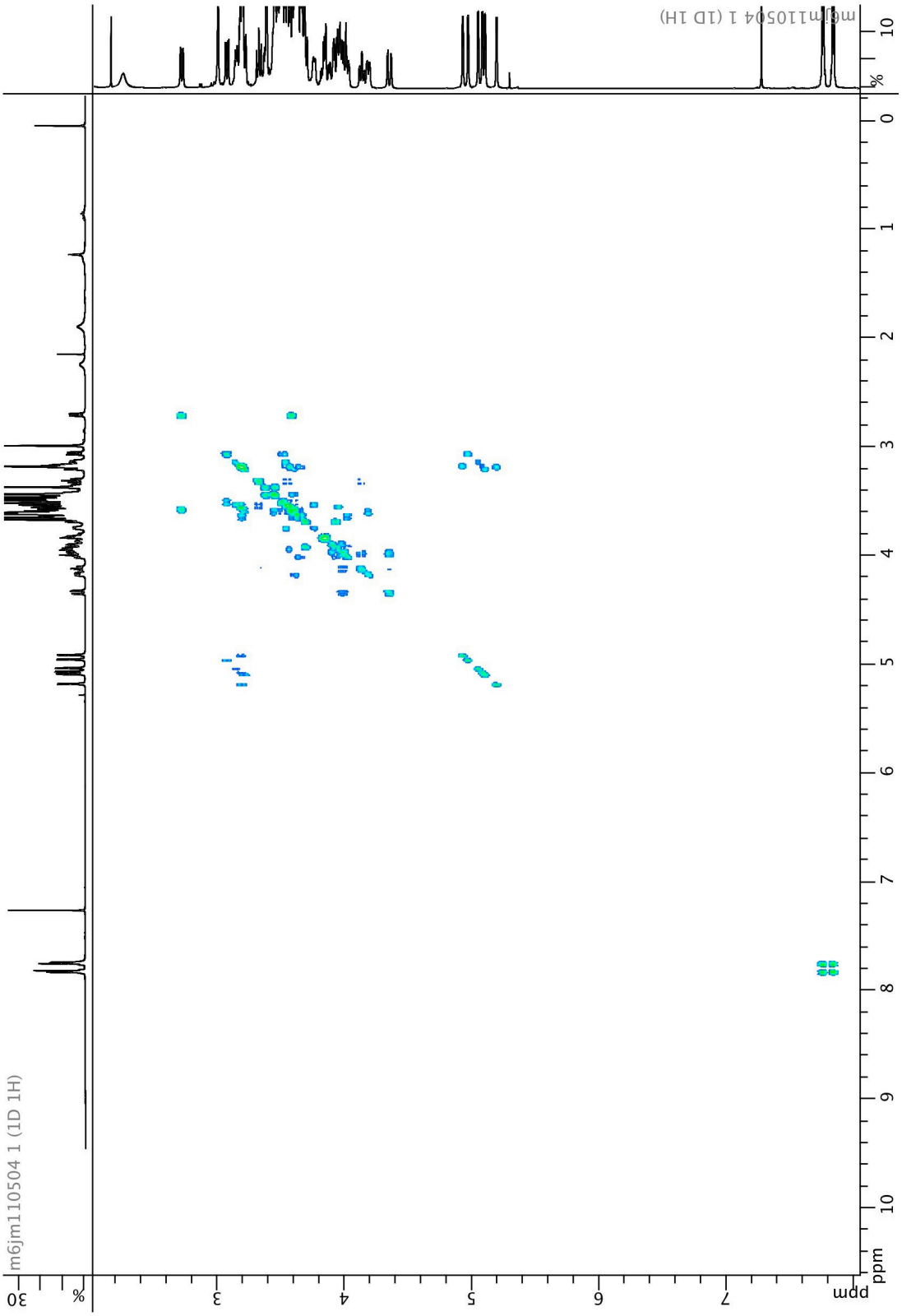
^{31}P {^{1}H} NMR spectrum of 5a



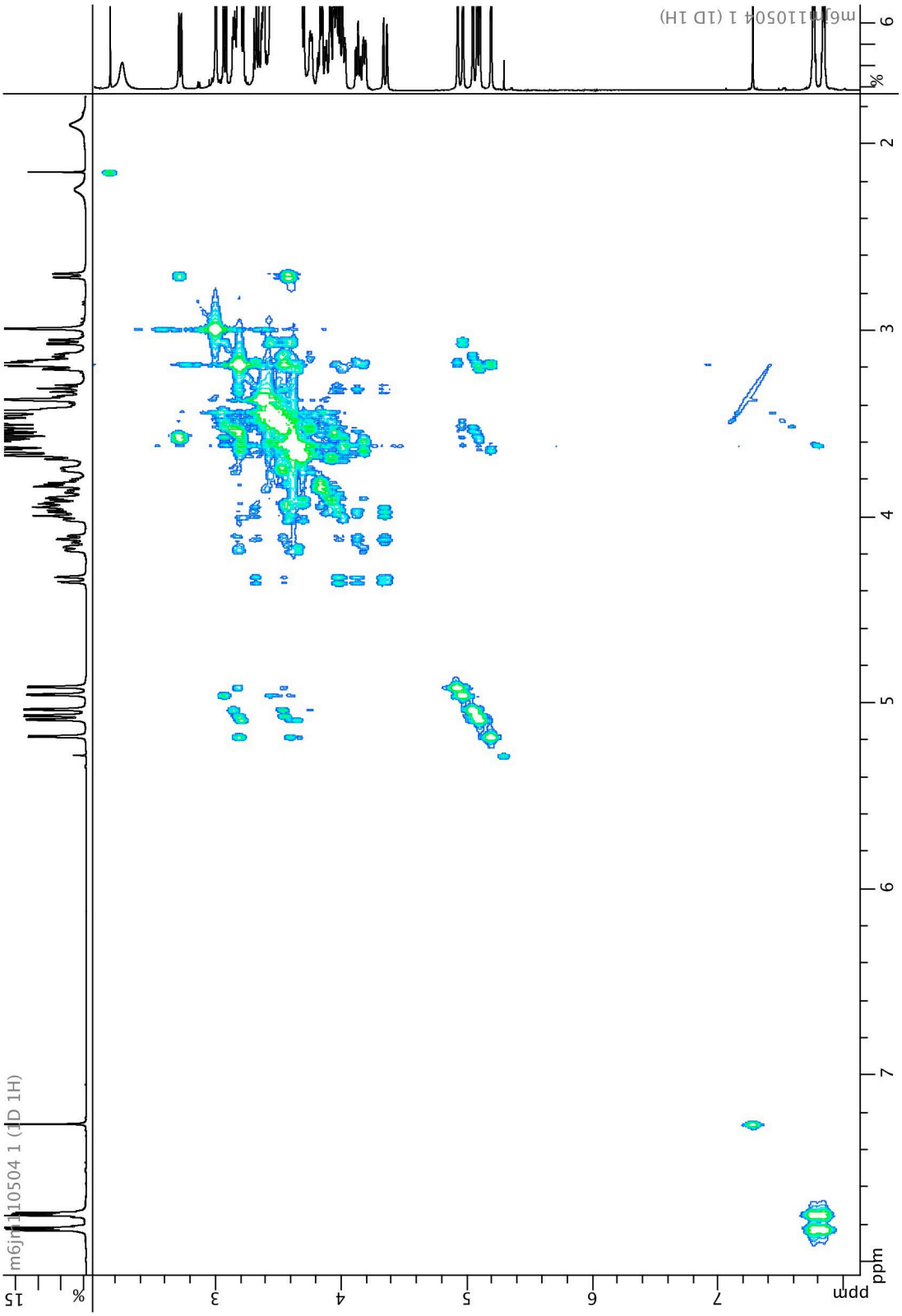
Mass spectrum of 5a



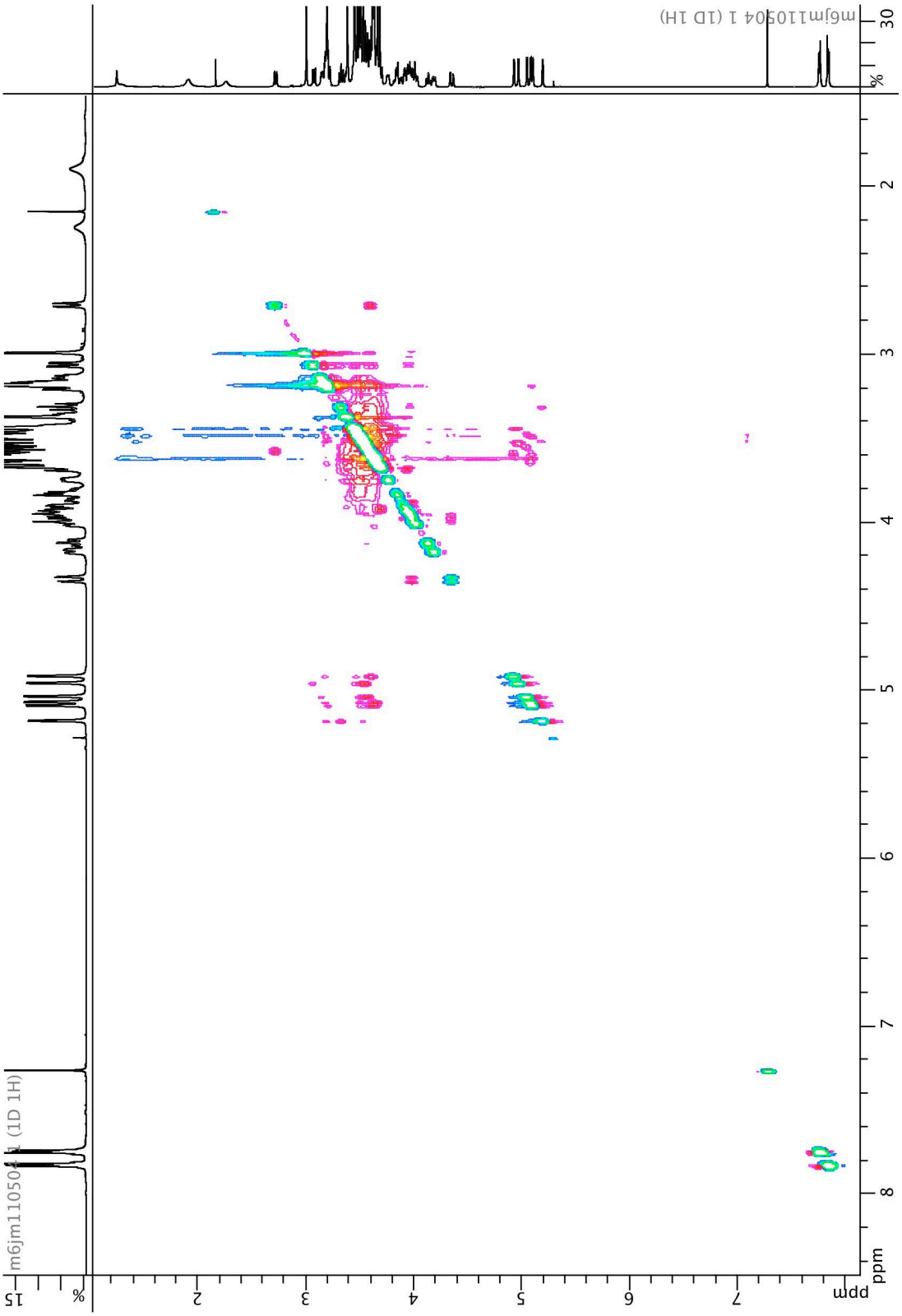
^{1}H NMR spectrum of 5b



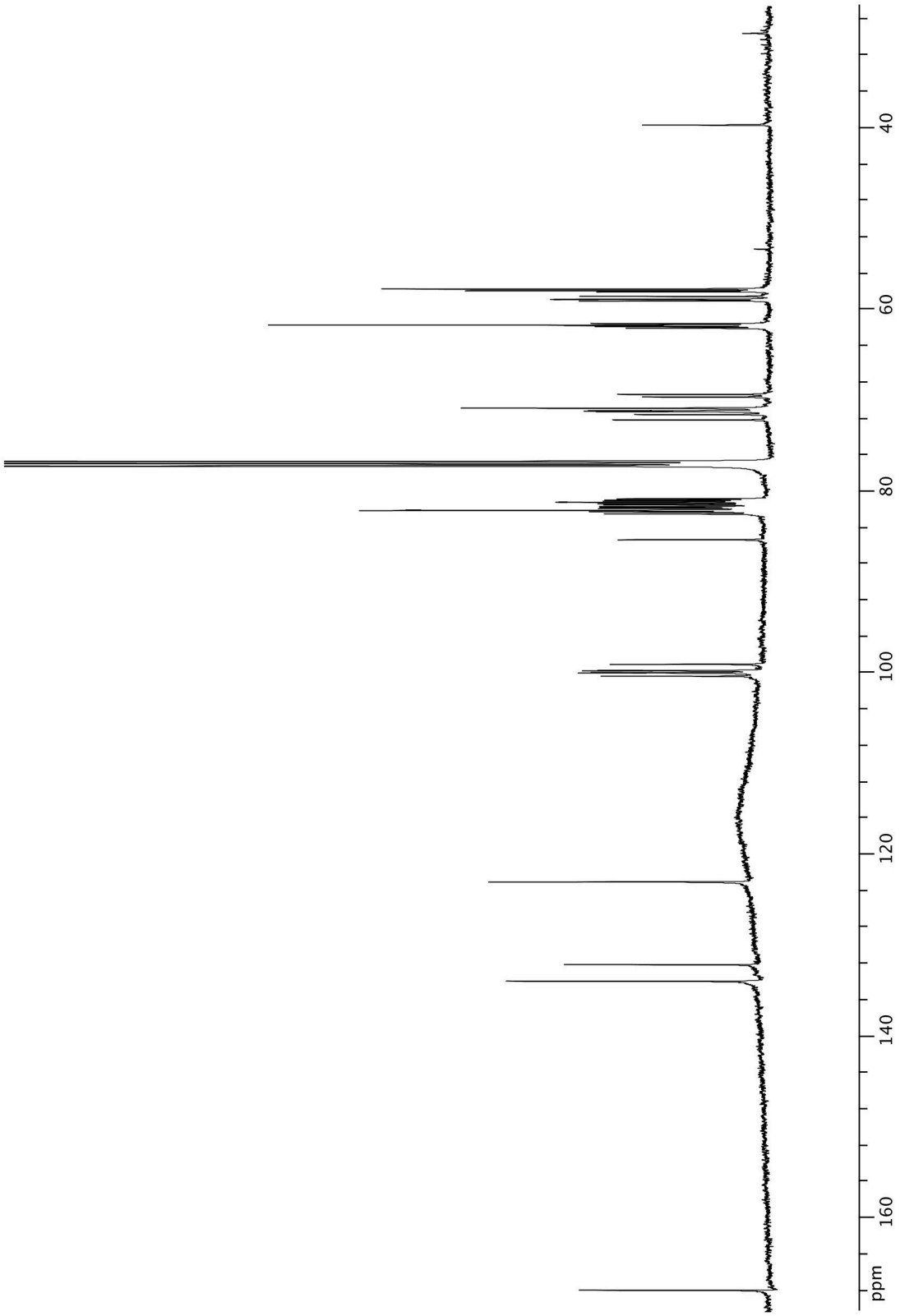
^{1}H-^{1}H COSY NMR spectrum of 5b



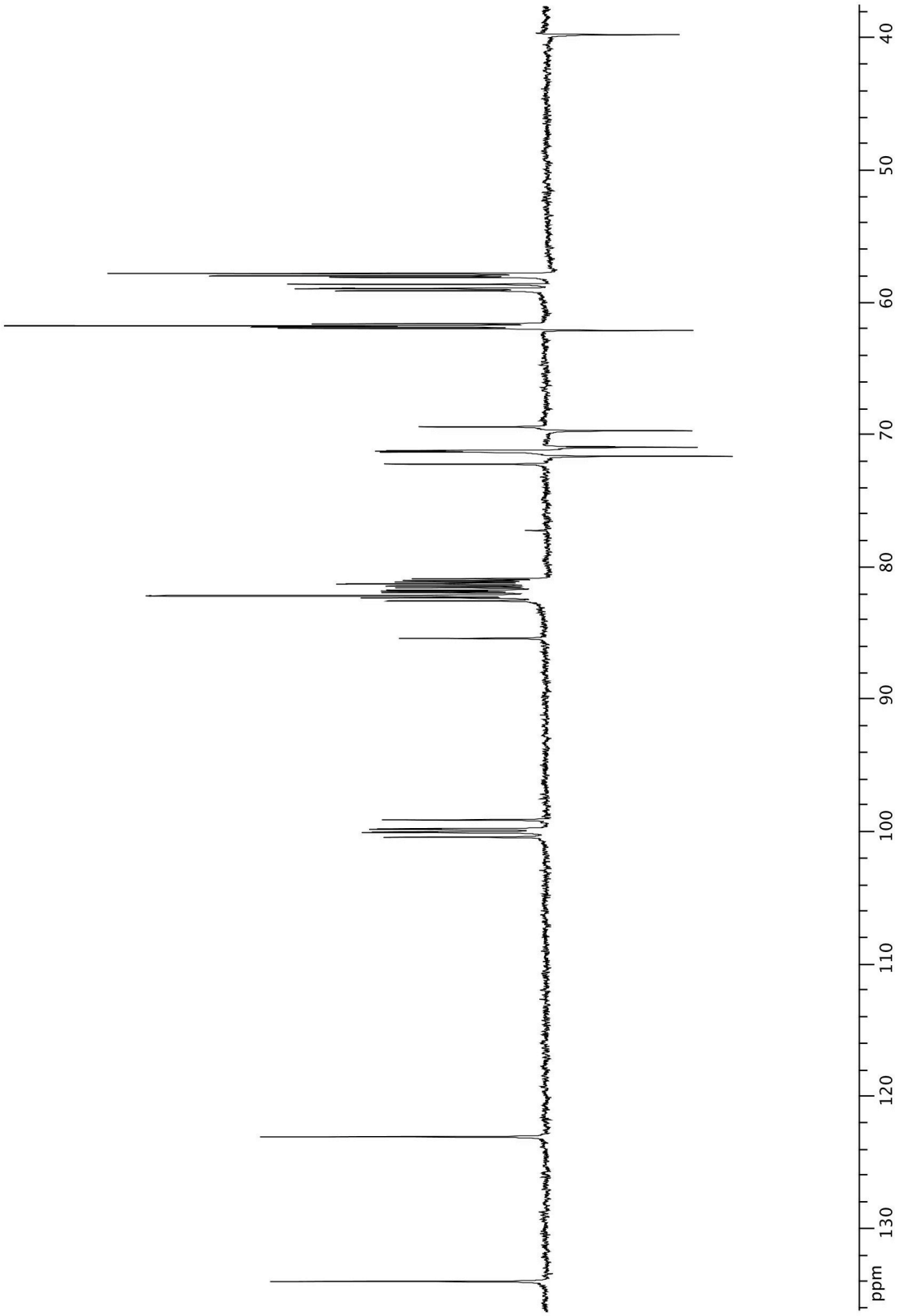
^{1}H-^{1}H TOCSY NMR spectrum of 5b



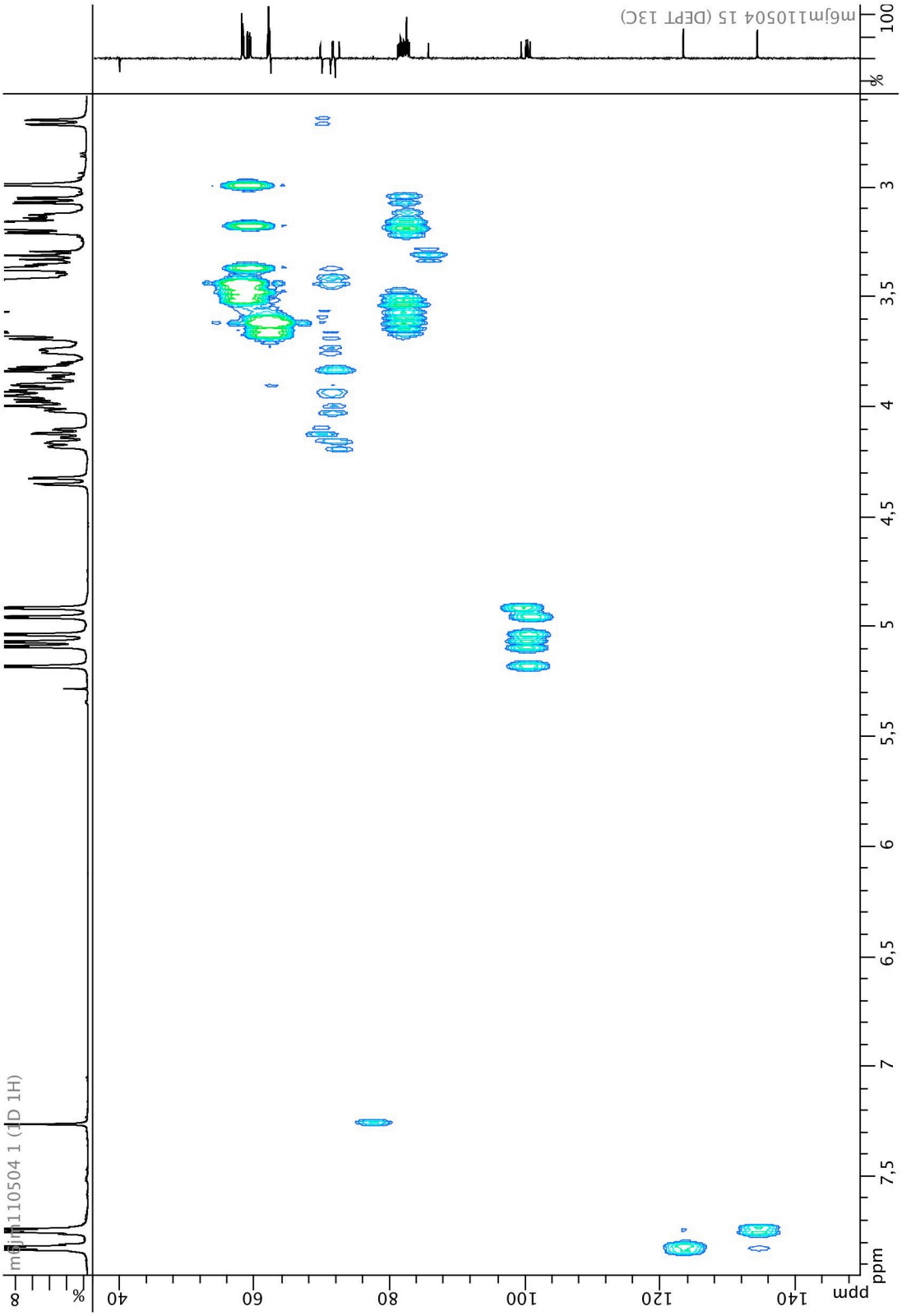
^{1}H-^{1}H ROESY NMR spectrum of 5b



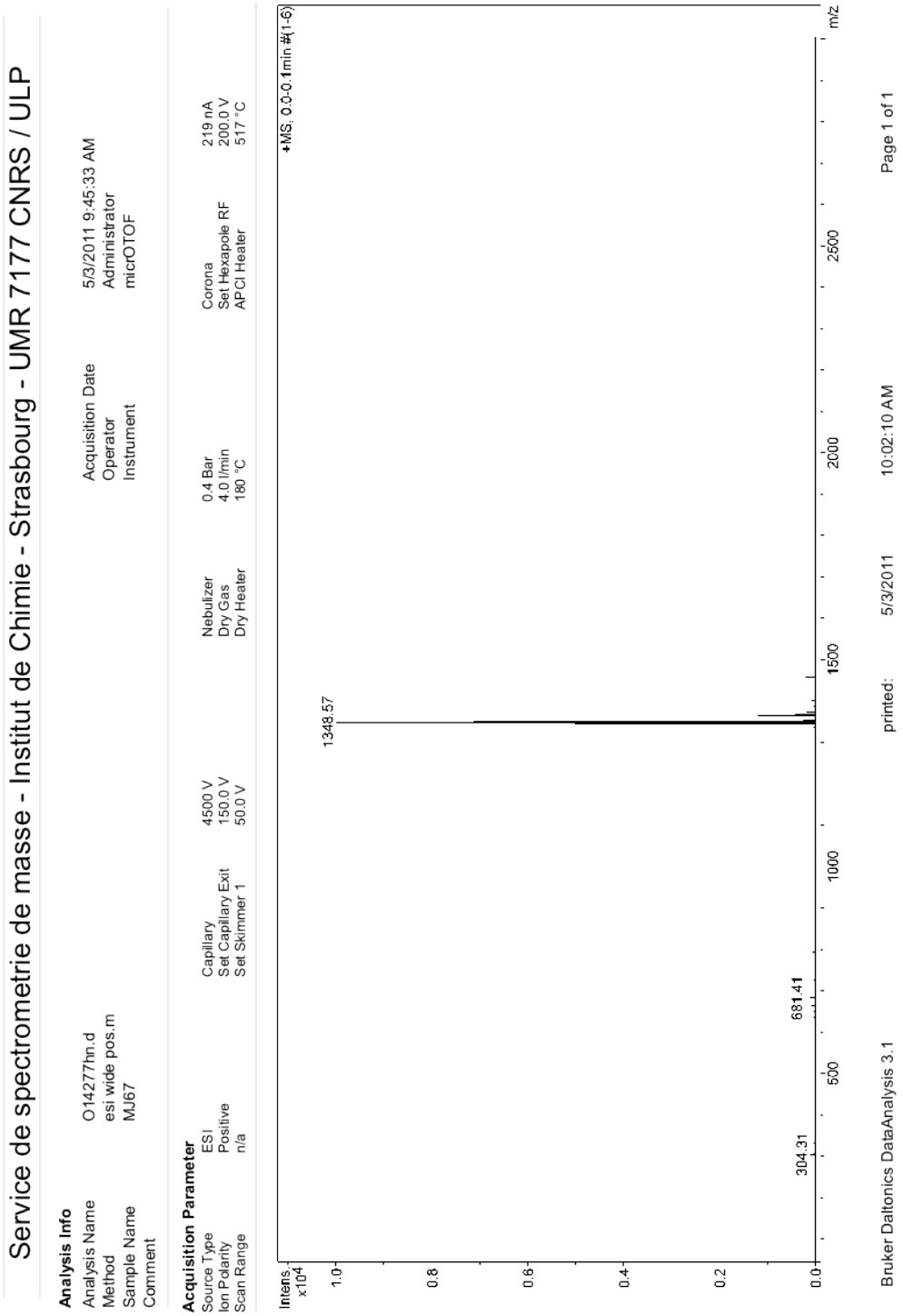
^{13}C NMR spectrum of 5b



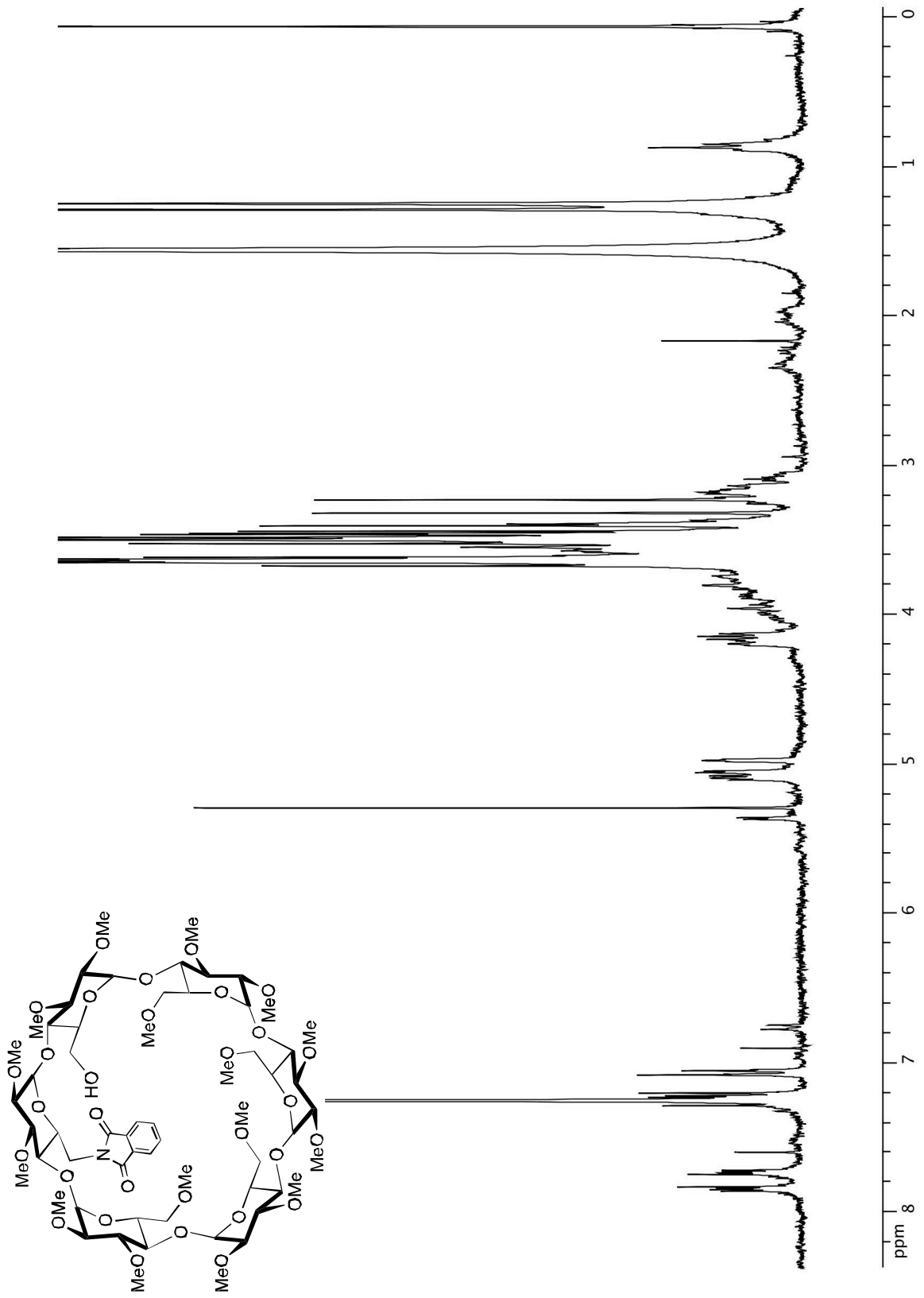
DEPT 135 NMR spectrum of 5b



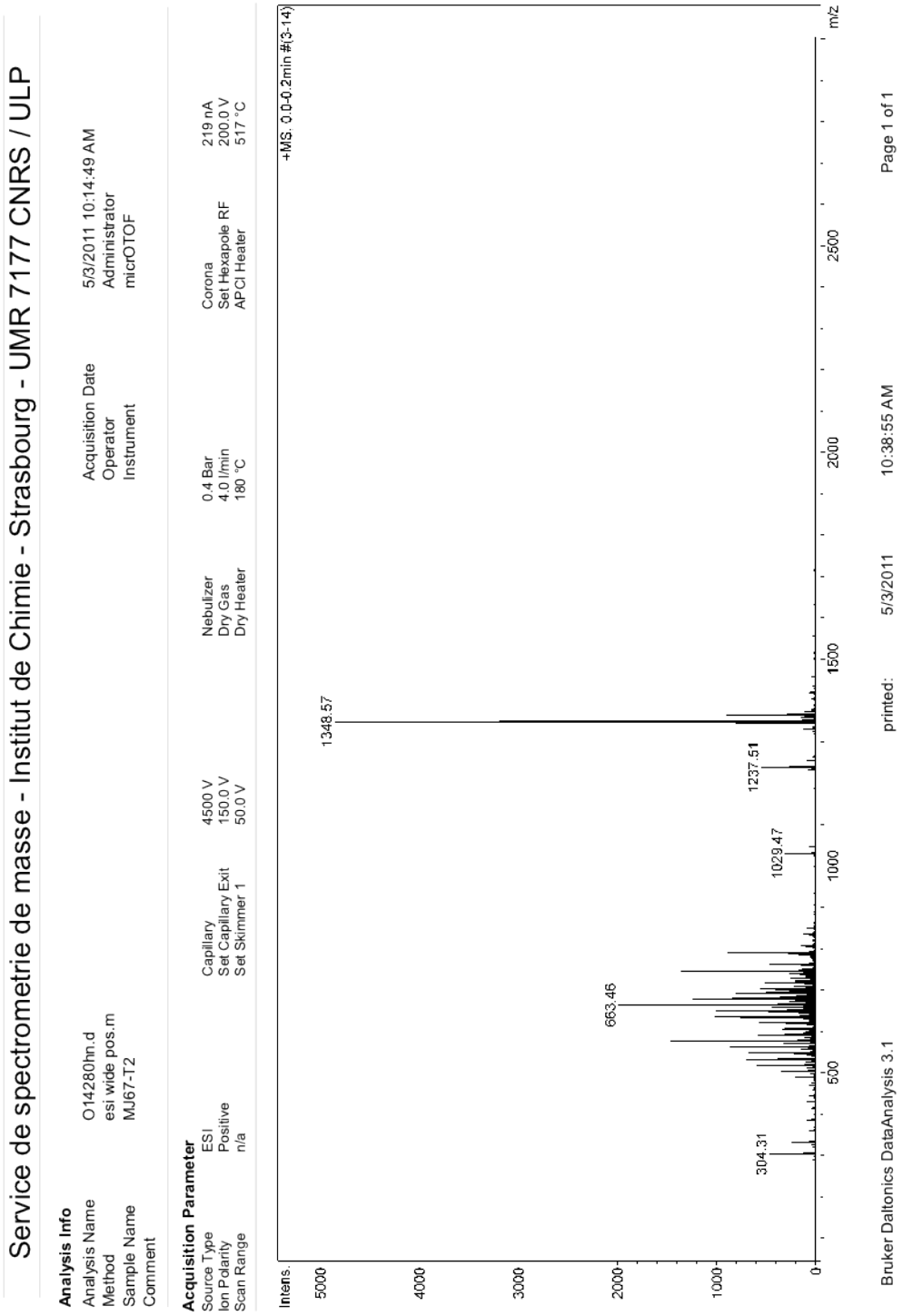
^{1}H-^{13}C HMQC NMR spectrum of 5b



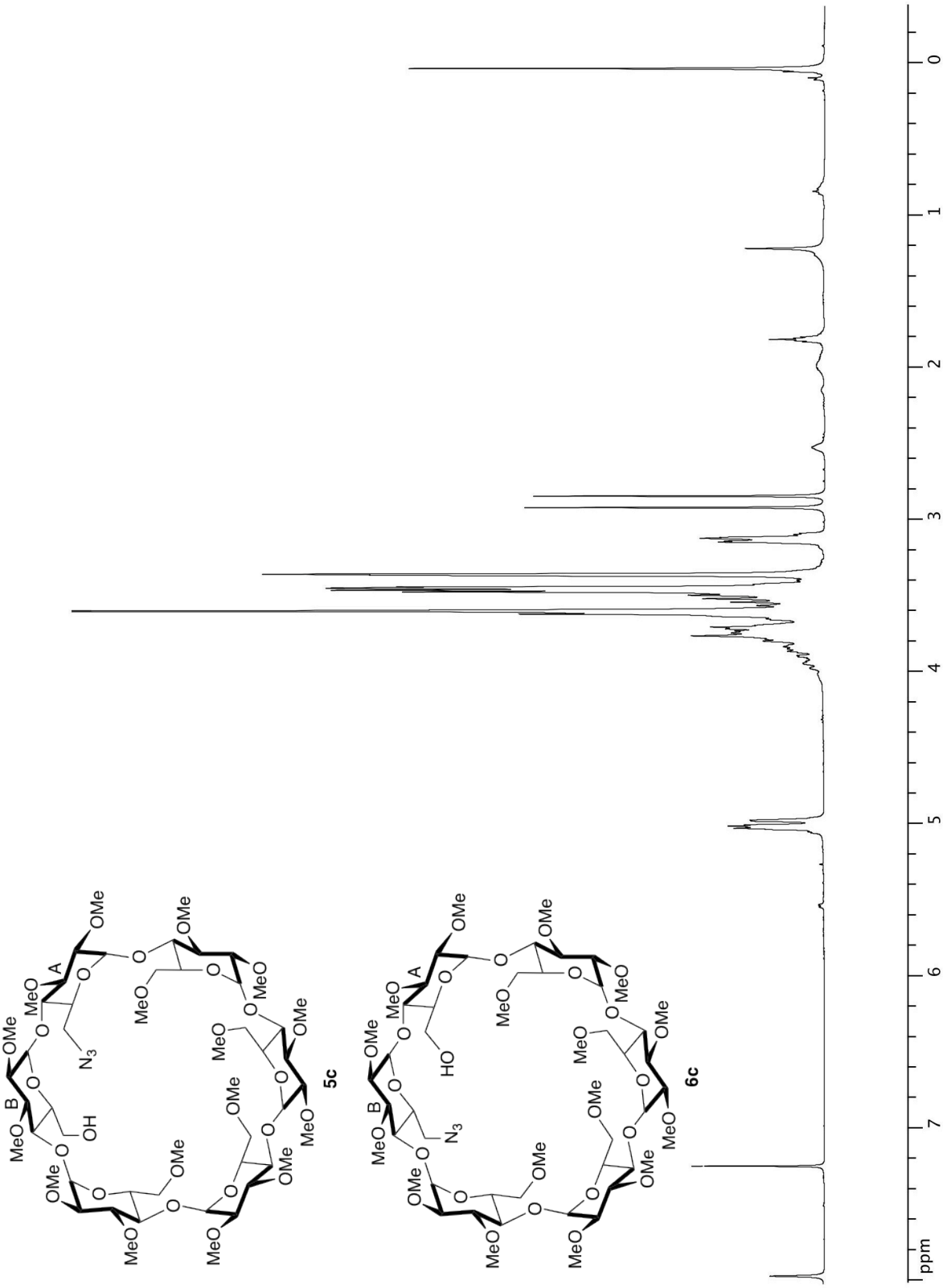
Mass spectrum of 5b



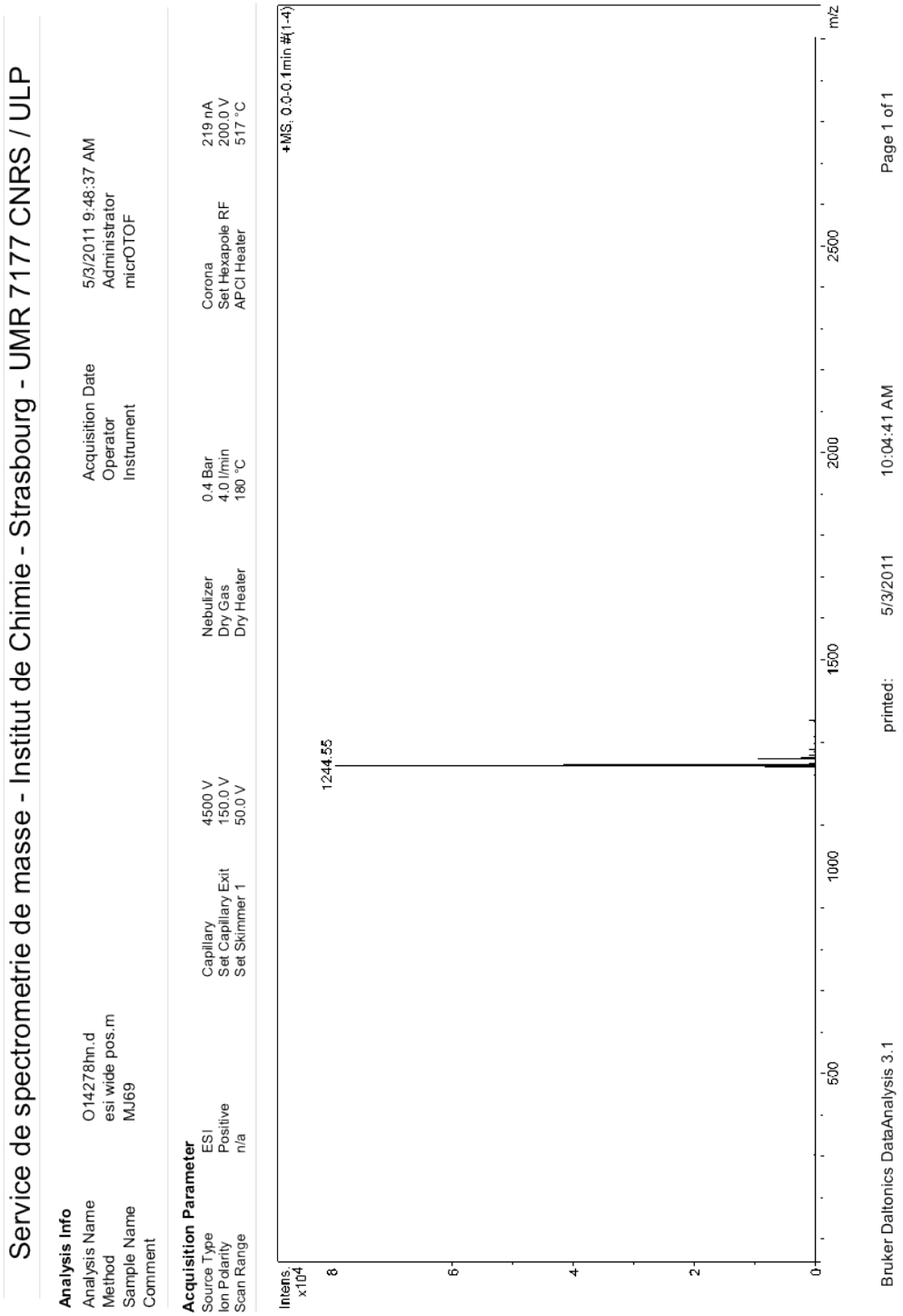
^{1}H NMR spectrum of 6b



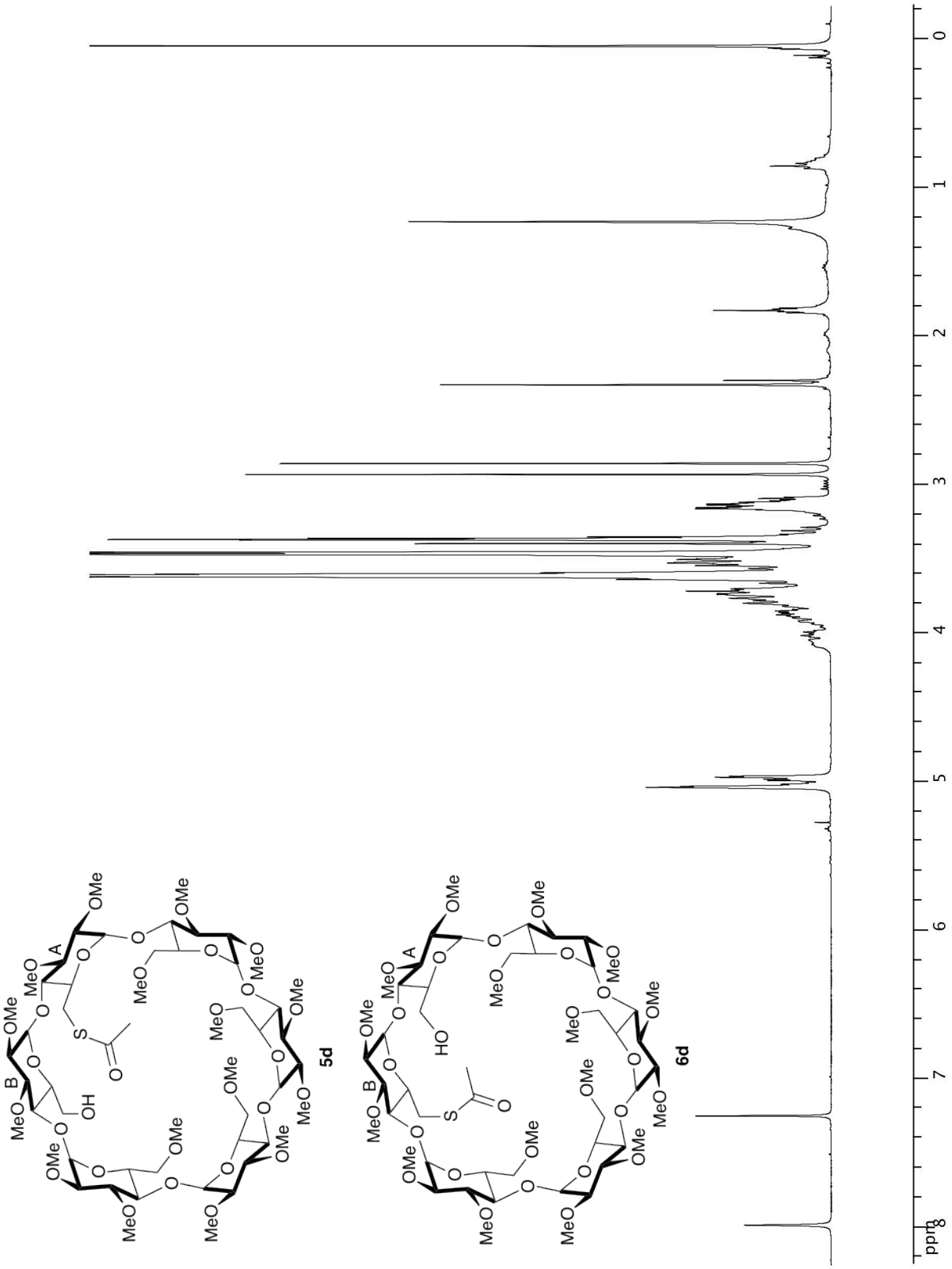
Mass spectrum of 6b



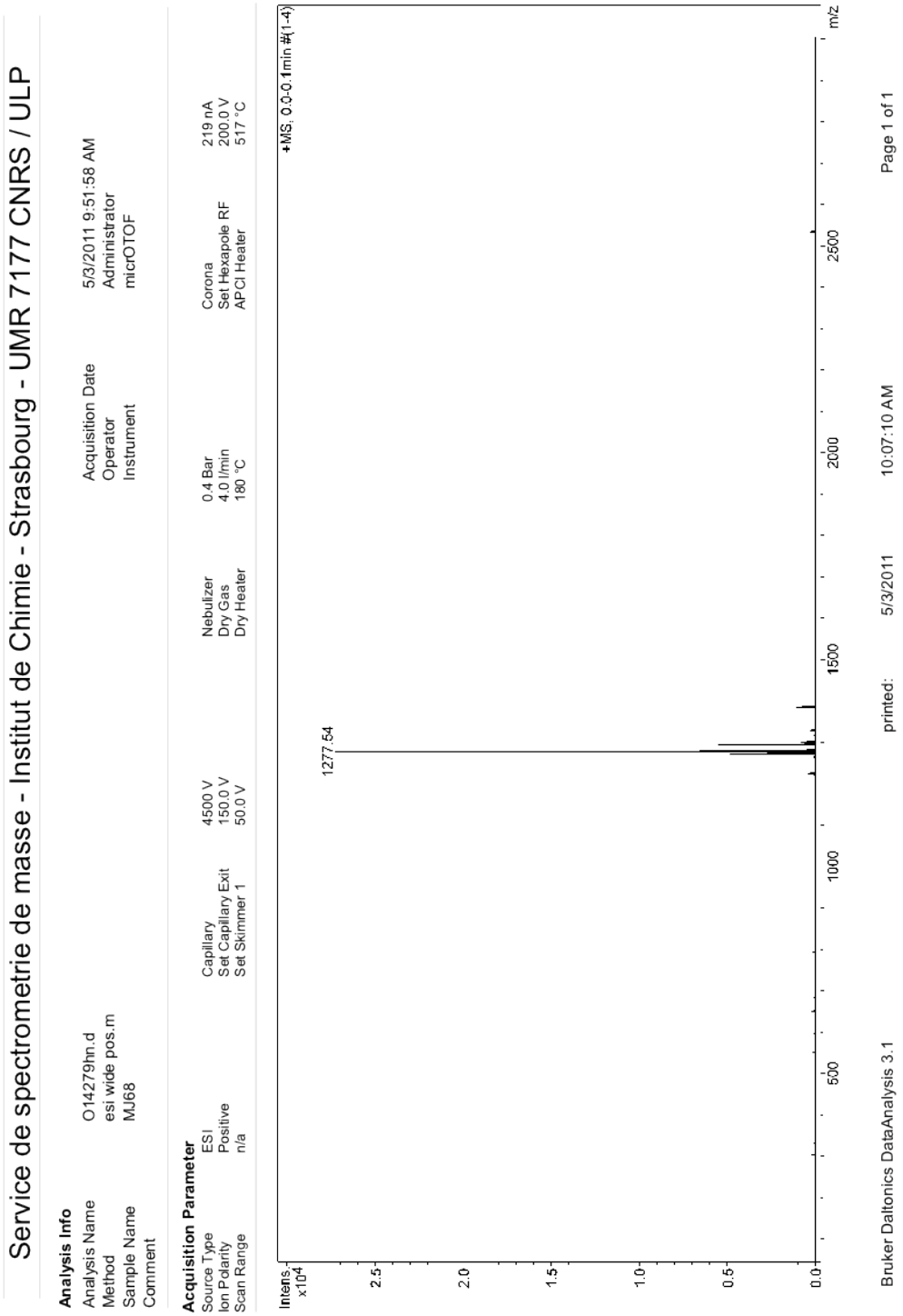
^{1}H NMR spectrum of 5c and 6c (mixture)



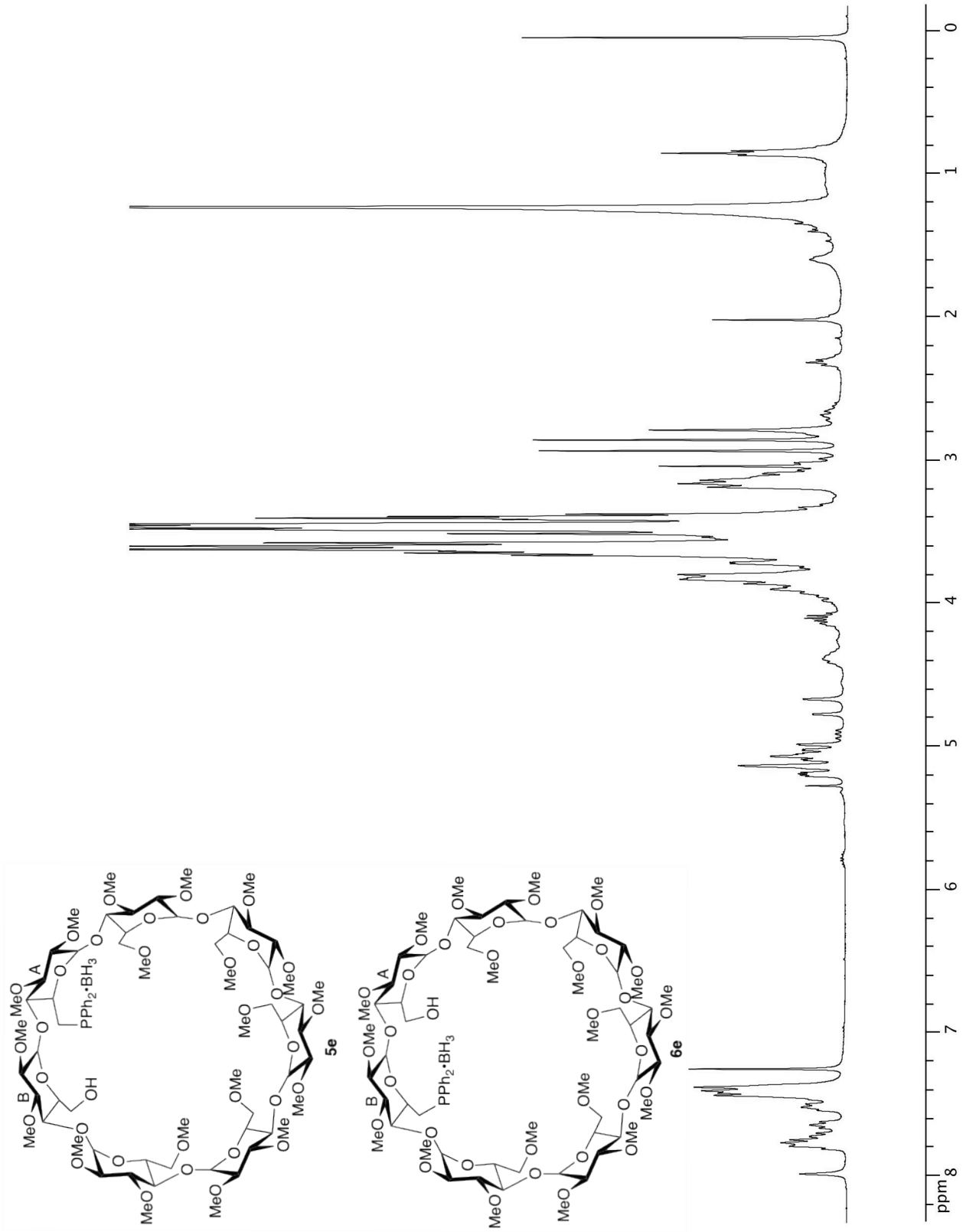
Mass spectrum of 5c and 6c (mixture)



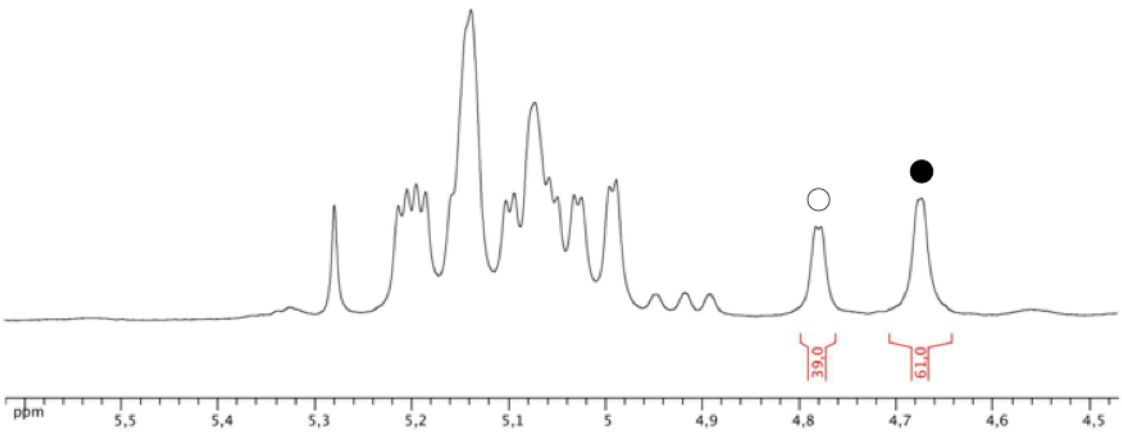
^{1}H NMR spectrum of 5d and 6d (mixture)



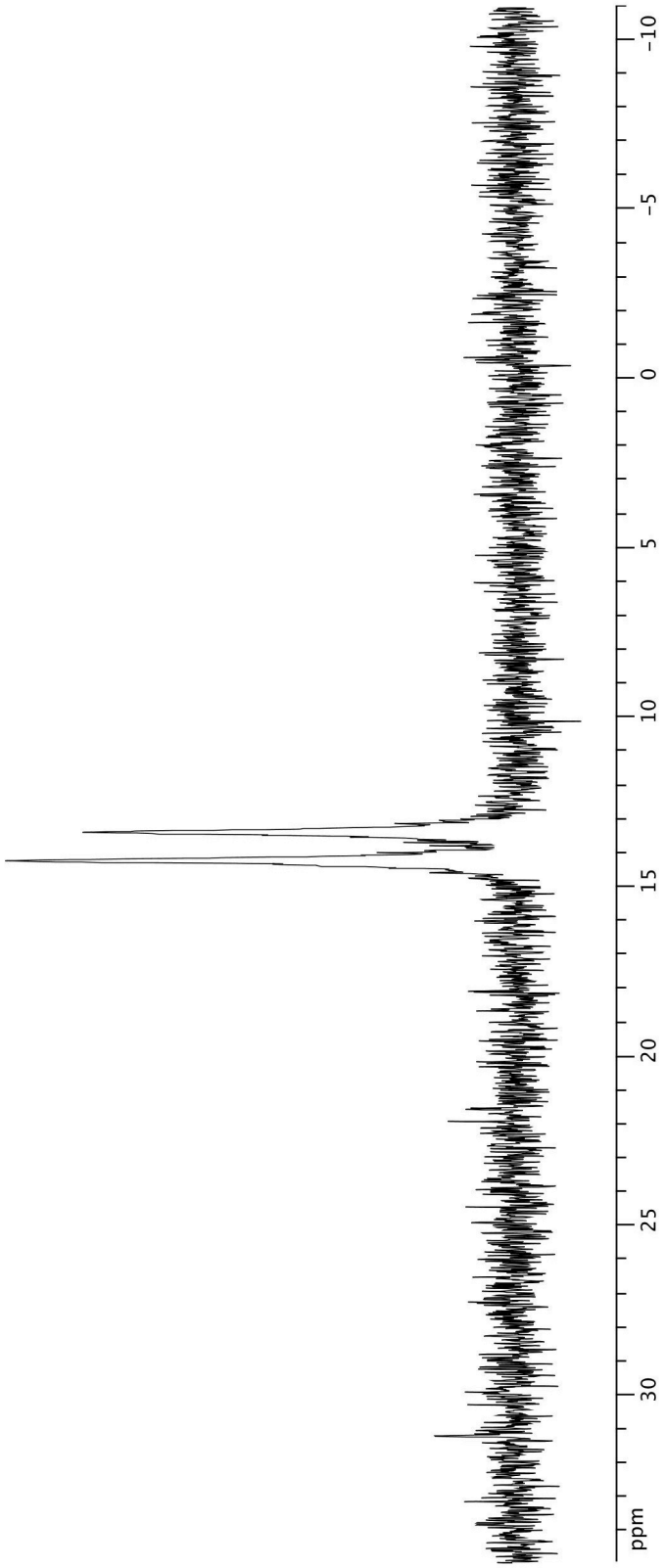
Mass spectrum of 5d and 6d (mixture)



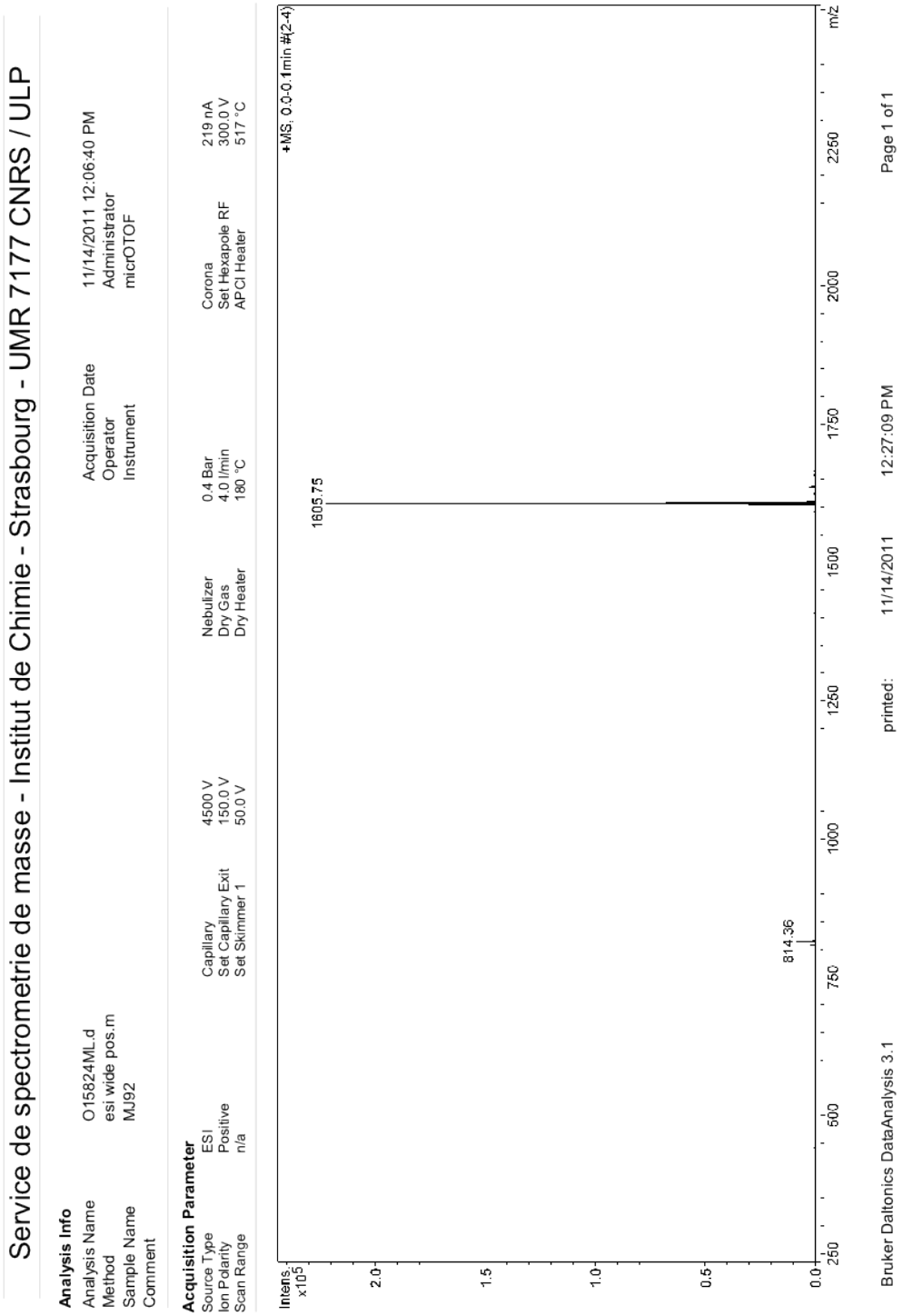
^{1}H NMR spectrum of 5e and 6e (mixture)



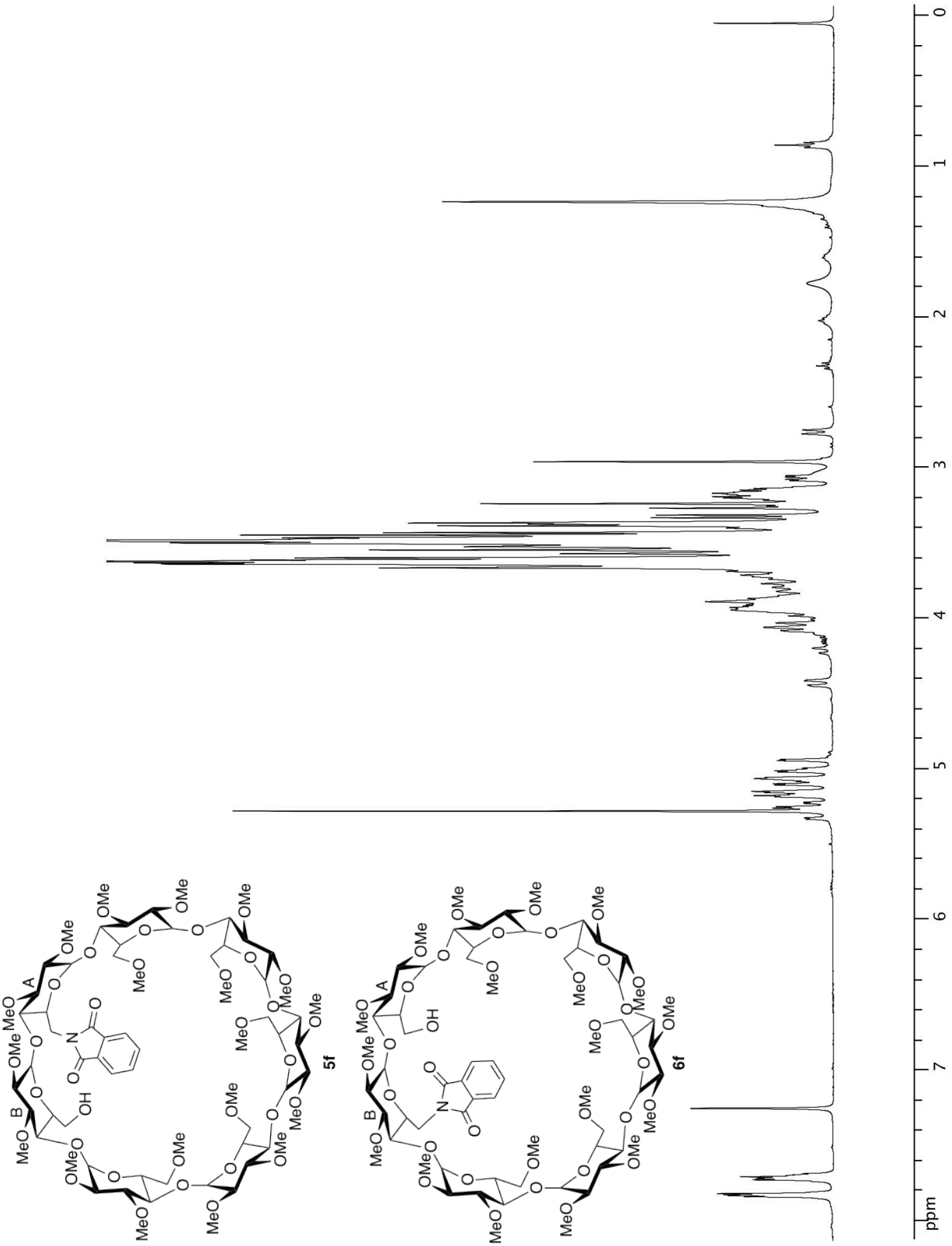
Part of the ^{1}H NMR spectrum showing the anomeric signals of both major (black dot) and minor (circle) isomers of the 5e/6e mixture.



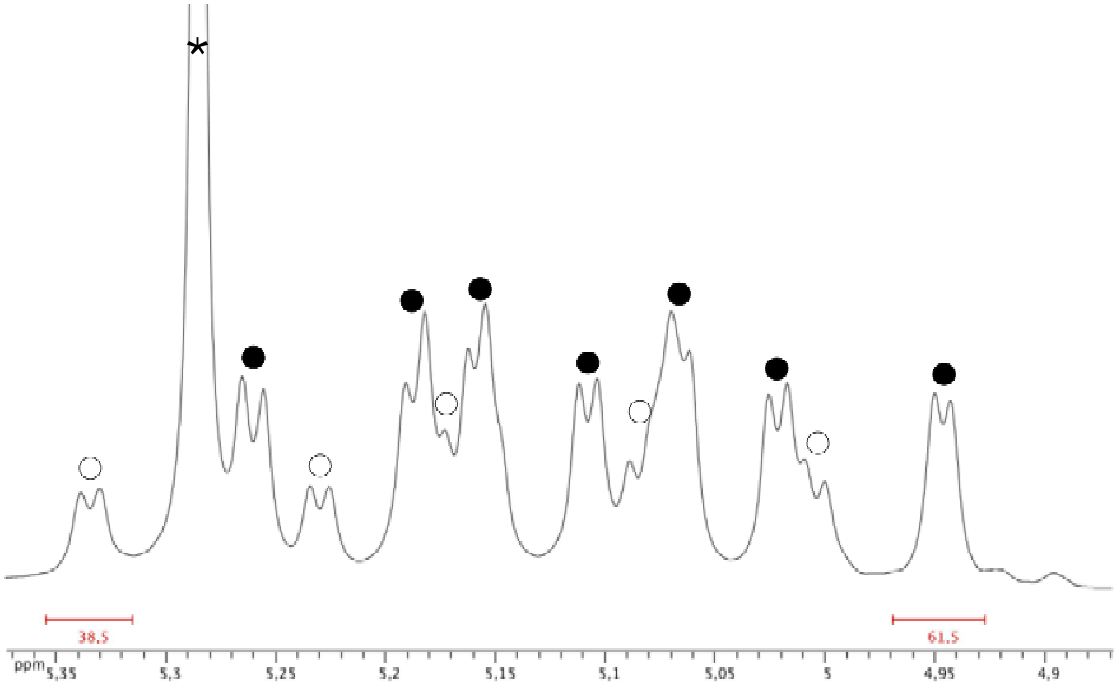
$^{31}P\{^{1}H\}$ NMR spectrum of 5e and 6e (mixture)



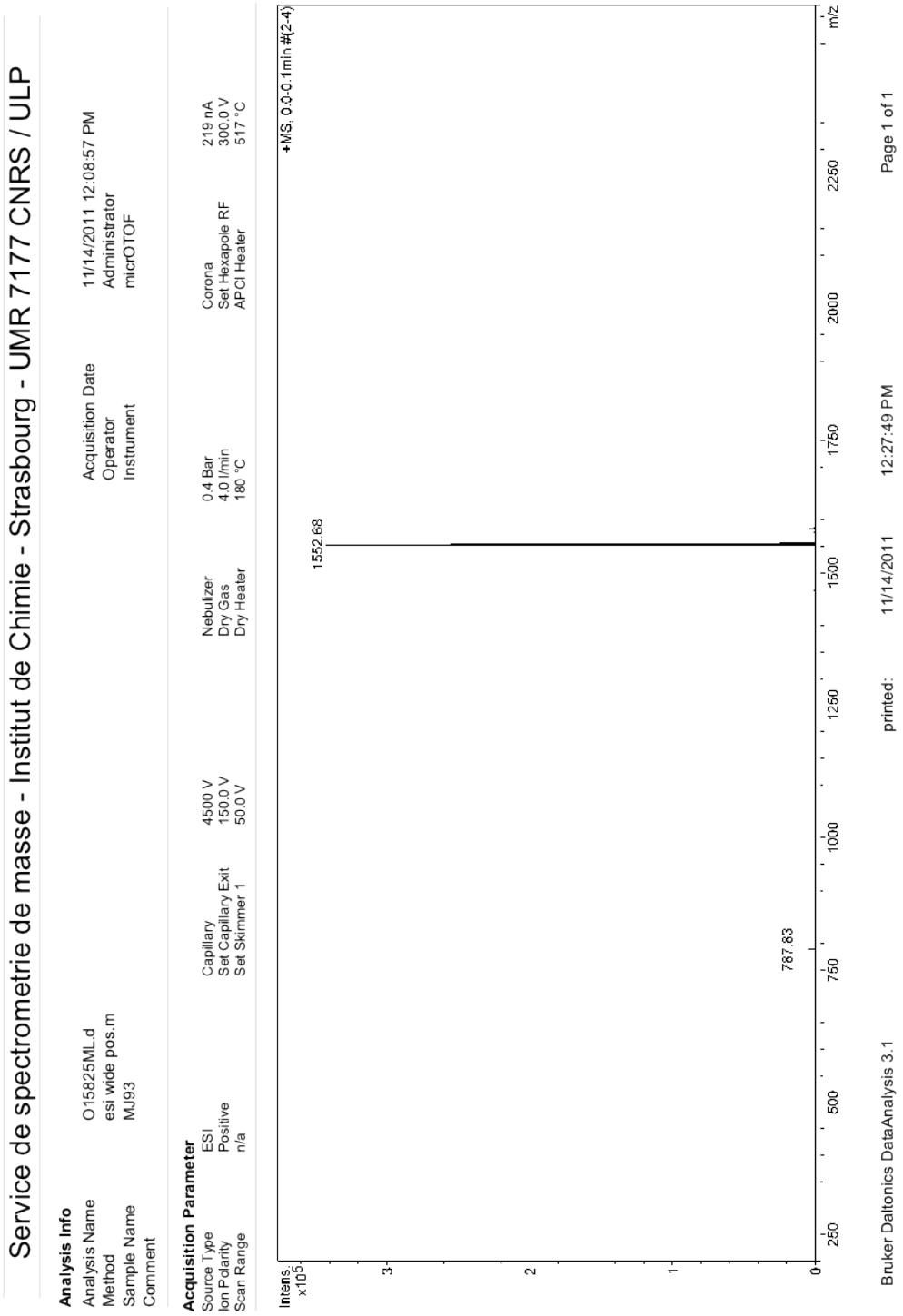
Mass spectrum of 5e and 6e (mixture)



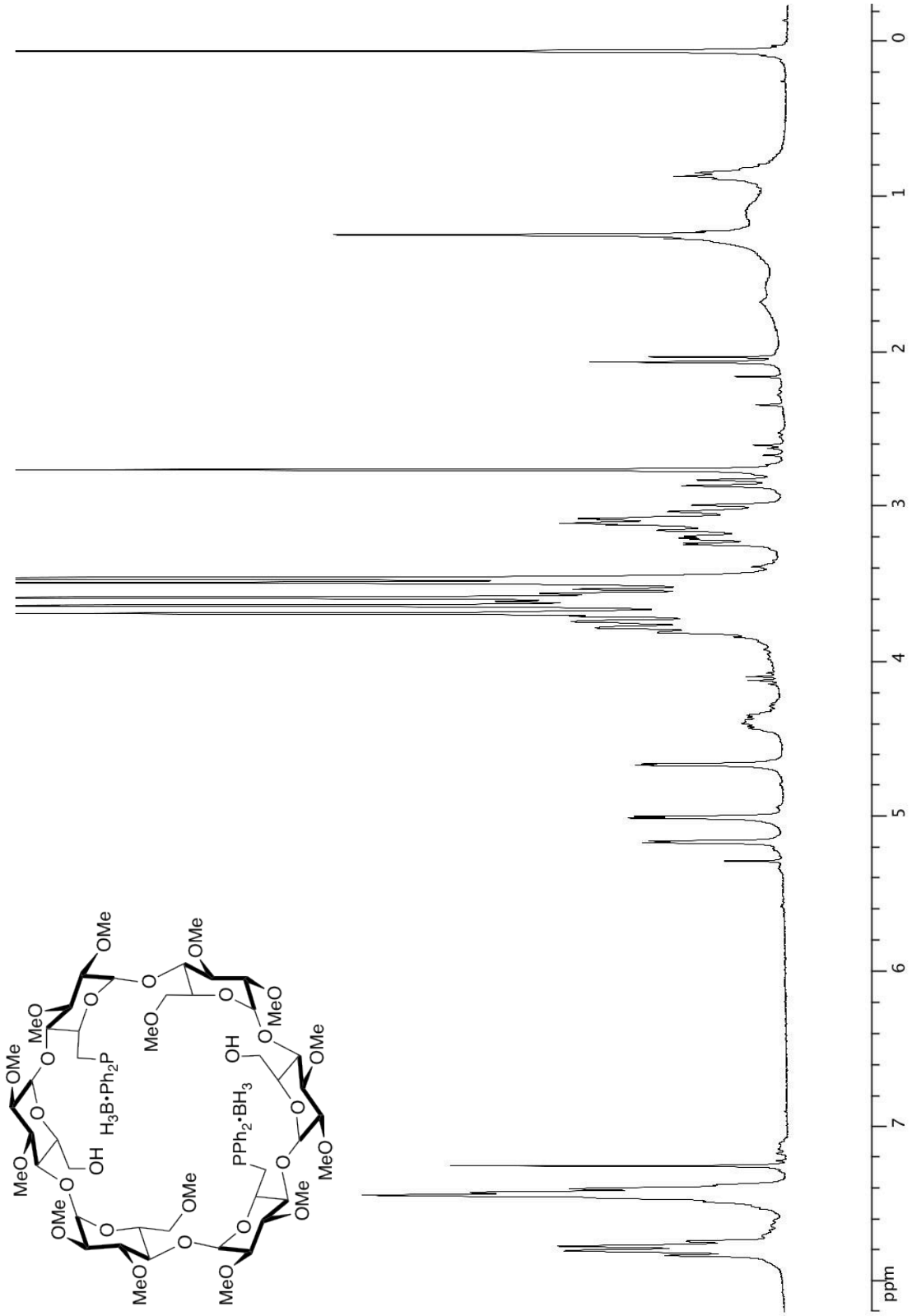
^{1}H NMR spectrum of 5f and 6f (mixture)



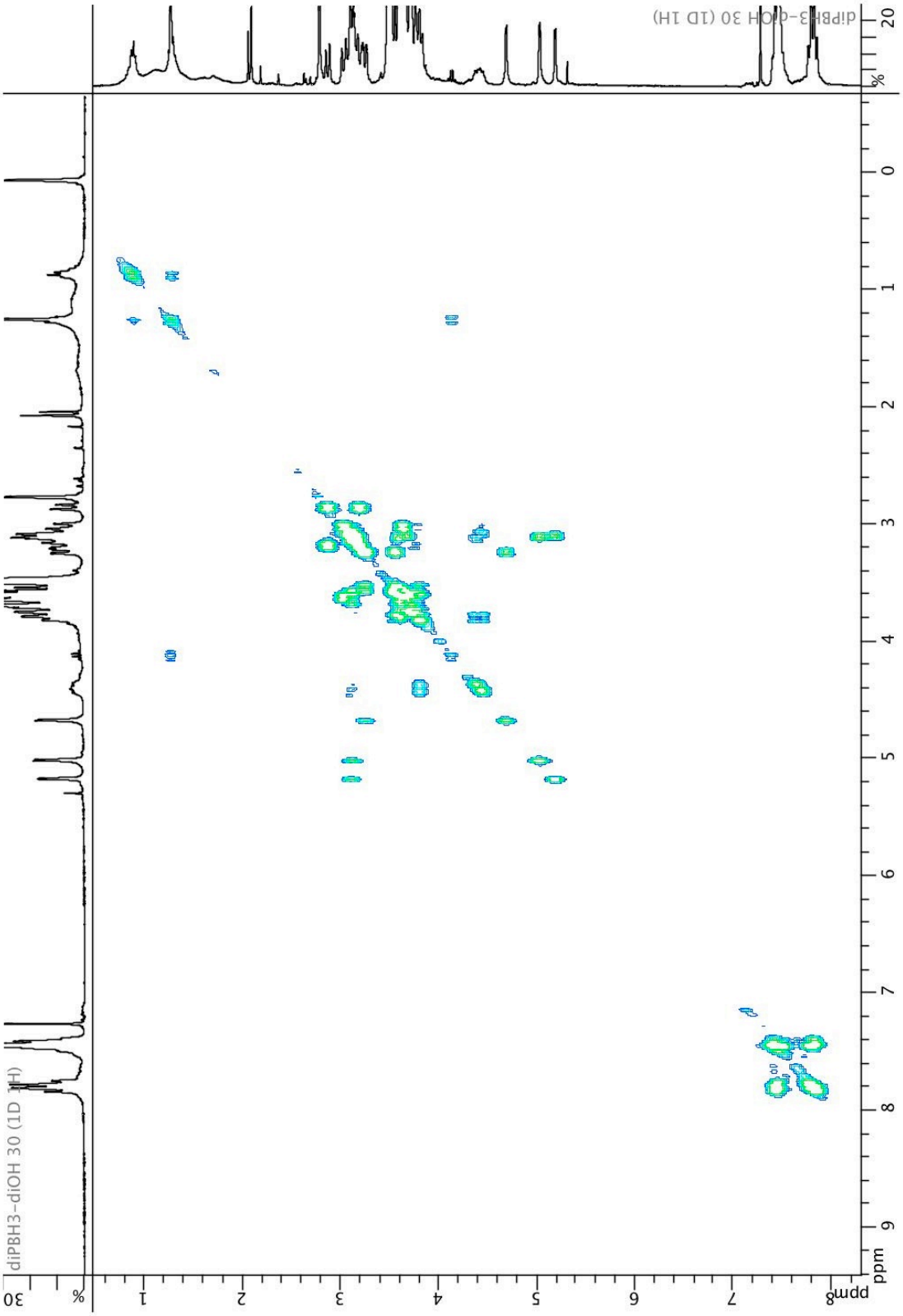
Part of the ^{1}H NMR spectrum showing the anomeric signals of both major (black dot) and minor (circle) isomers of the 5f/6f mixture. The peak marked with an asterisk corresponds to CH_2Cl_2.



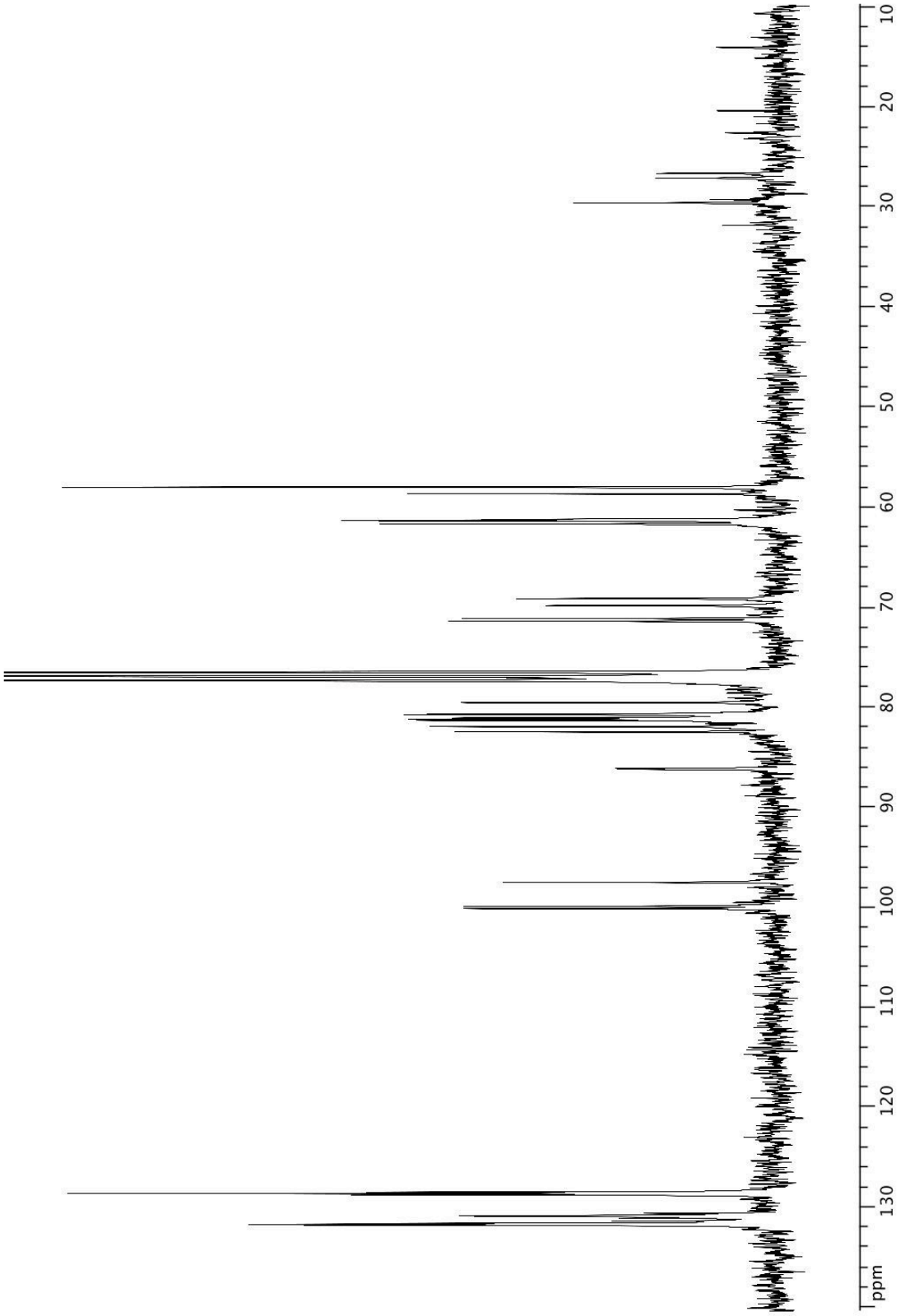
Mass spectrum of 5f and 6f (mixture)



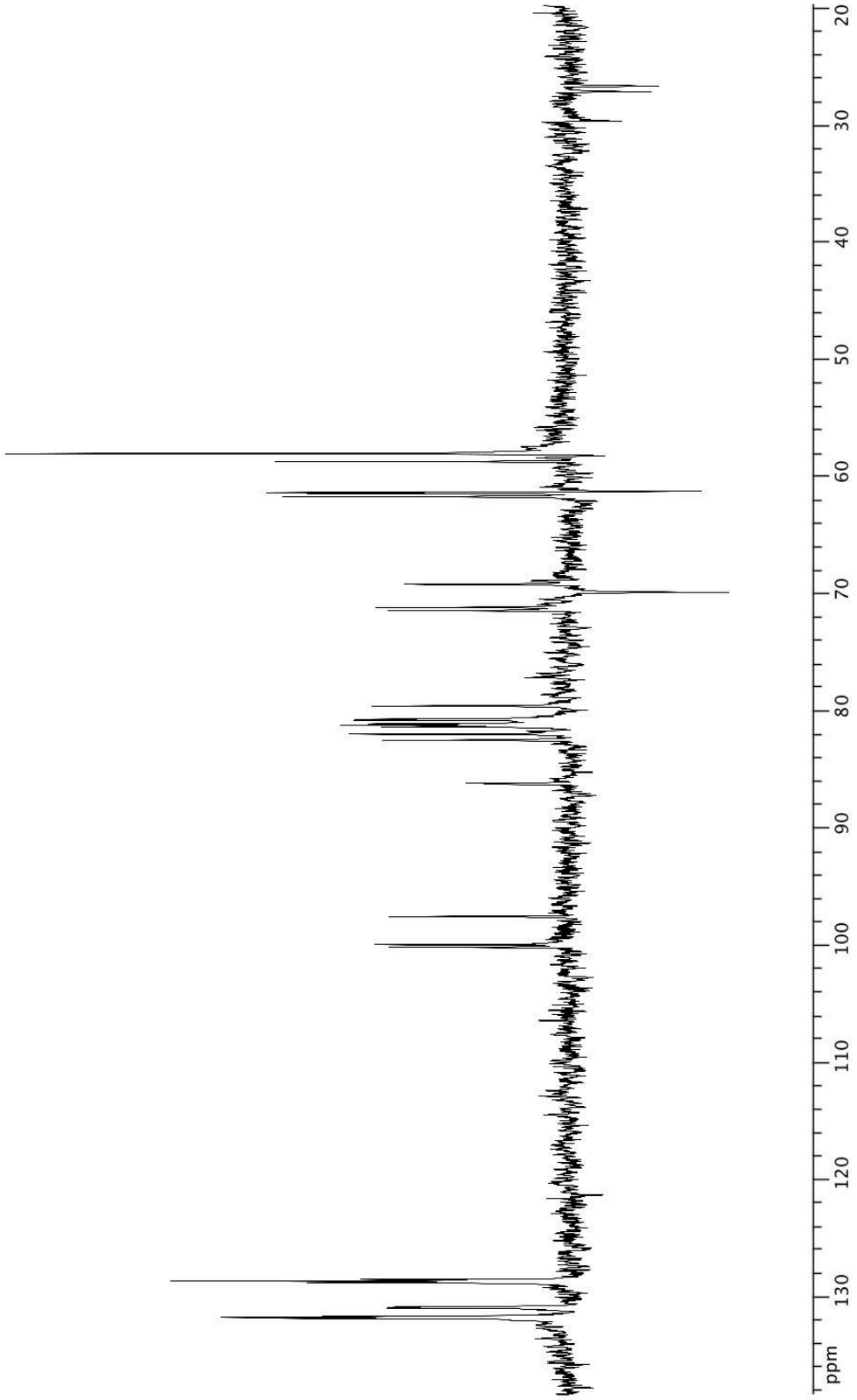
^{1}H NMR spectrum of 7a



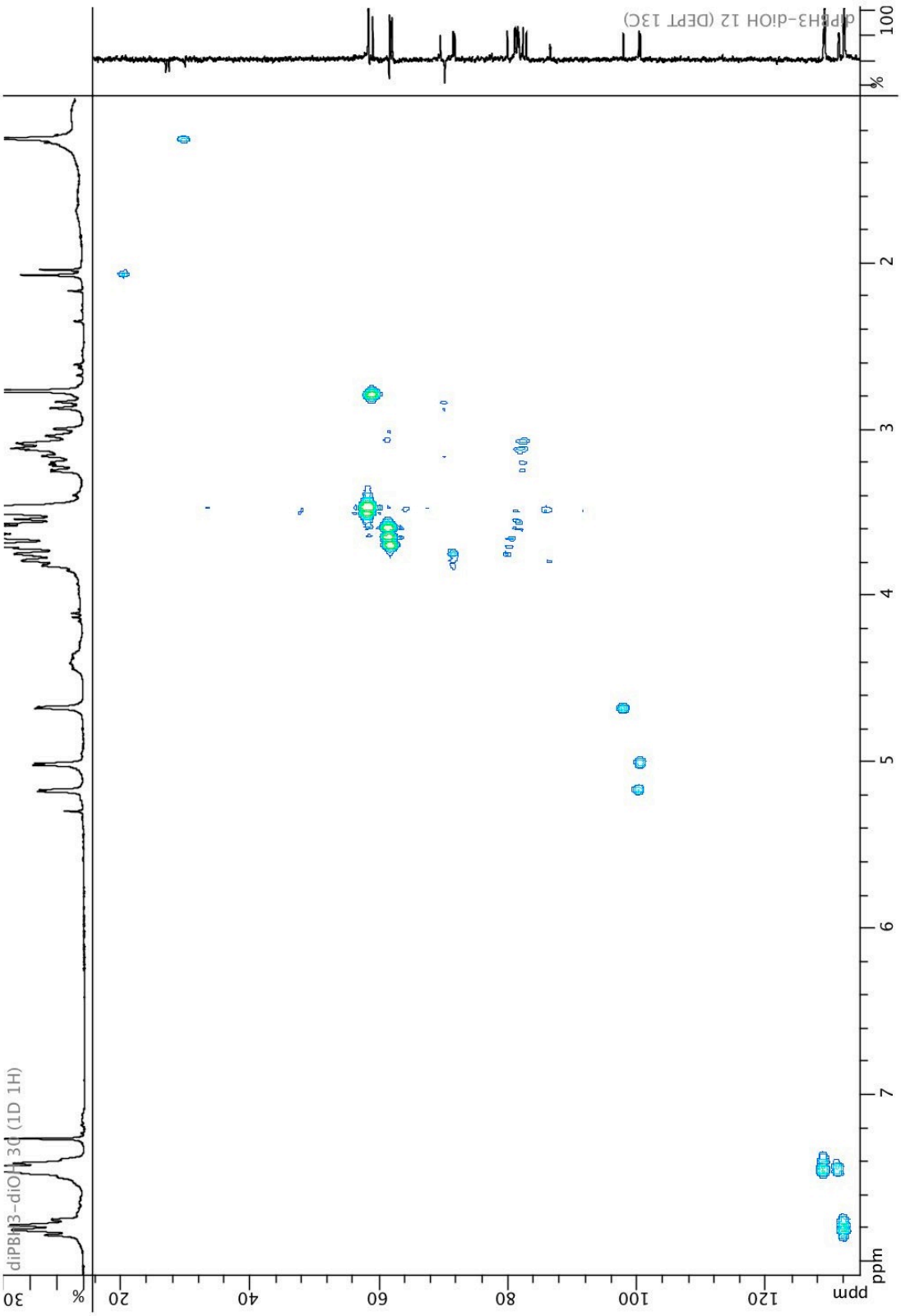
^{1}H-^{1}H COSY NMR spectrum of 7a



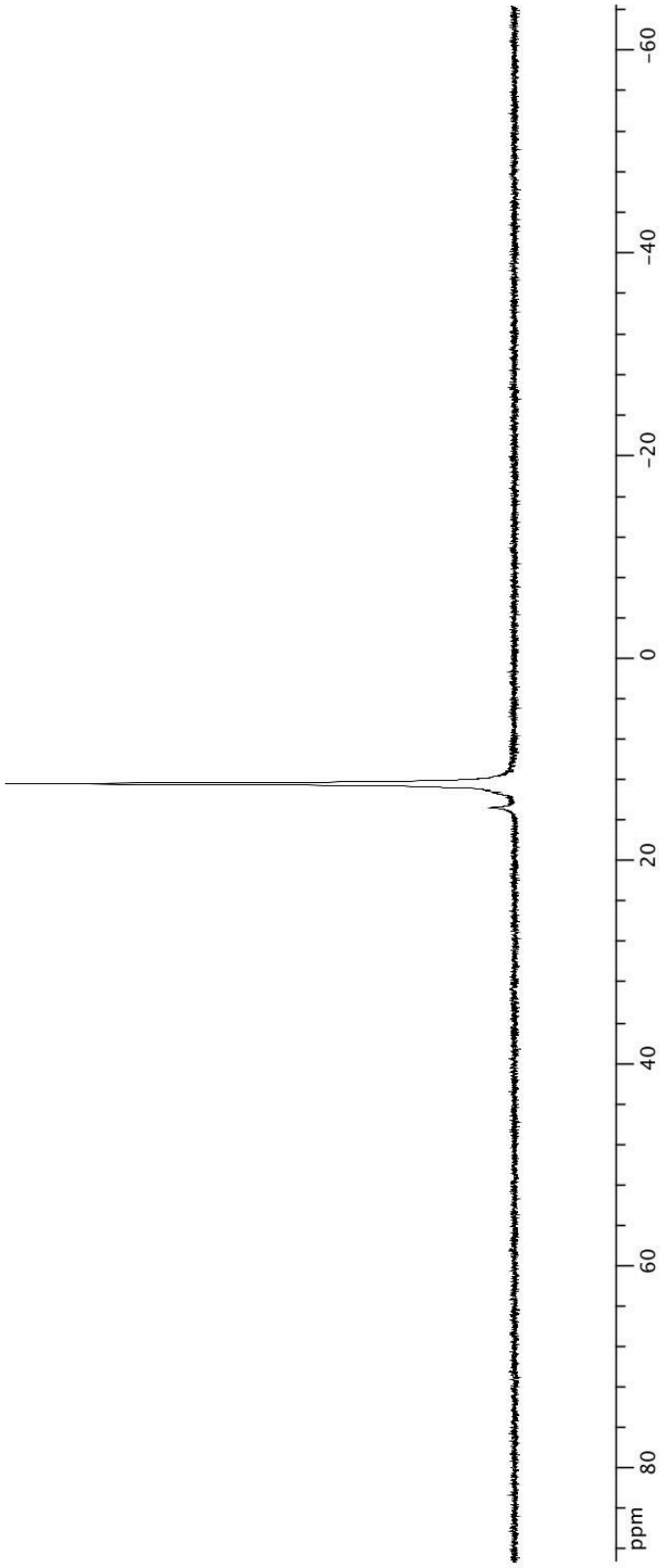
^{13}C NMR spectrum of 7a



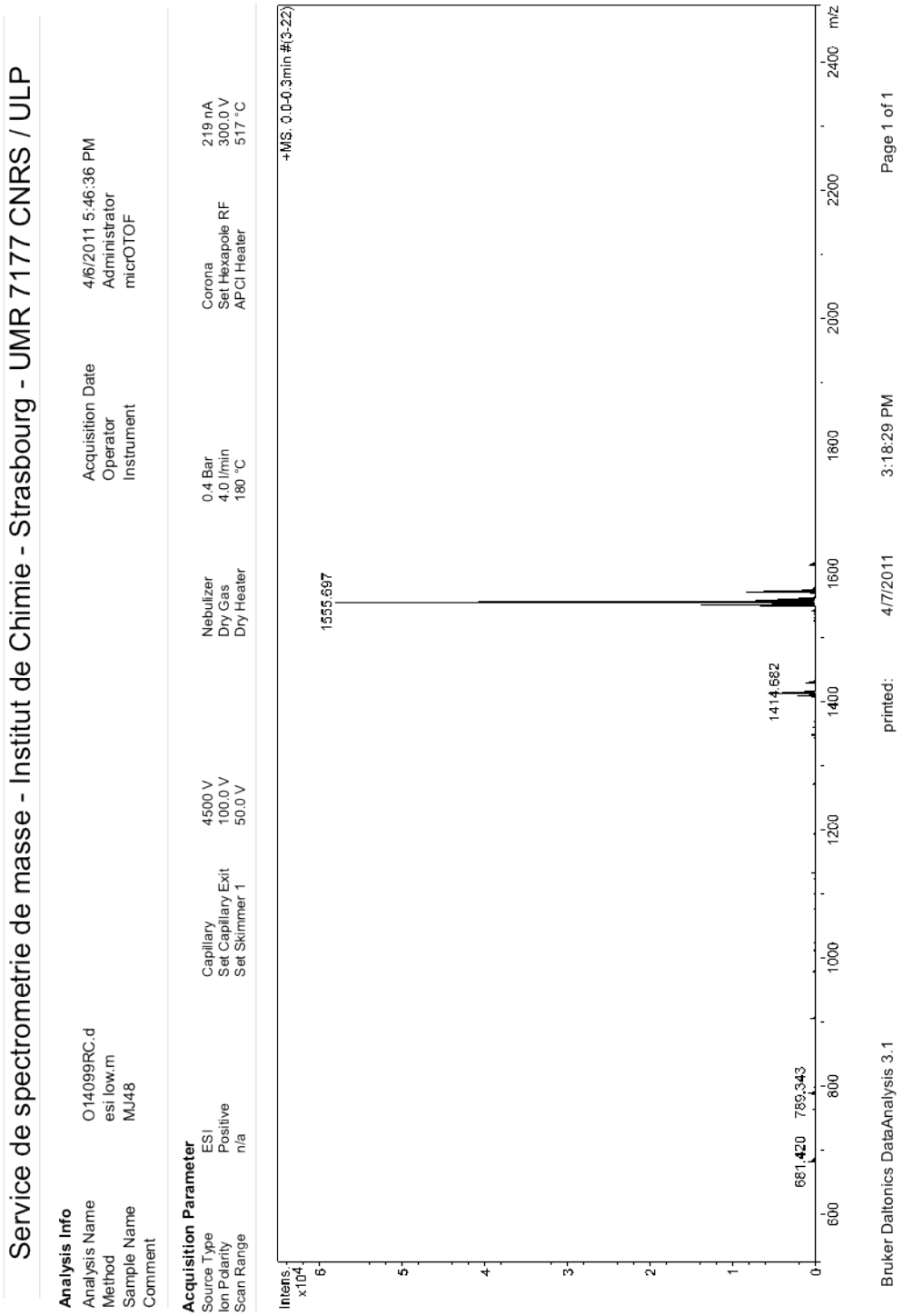
DEPT 135 NMR spectrum of 7a



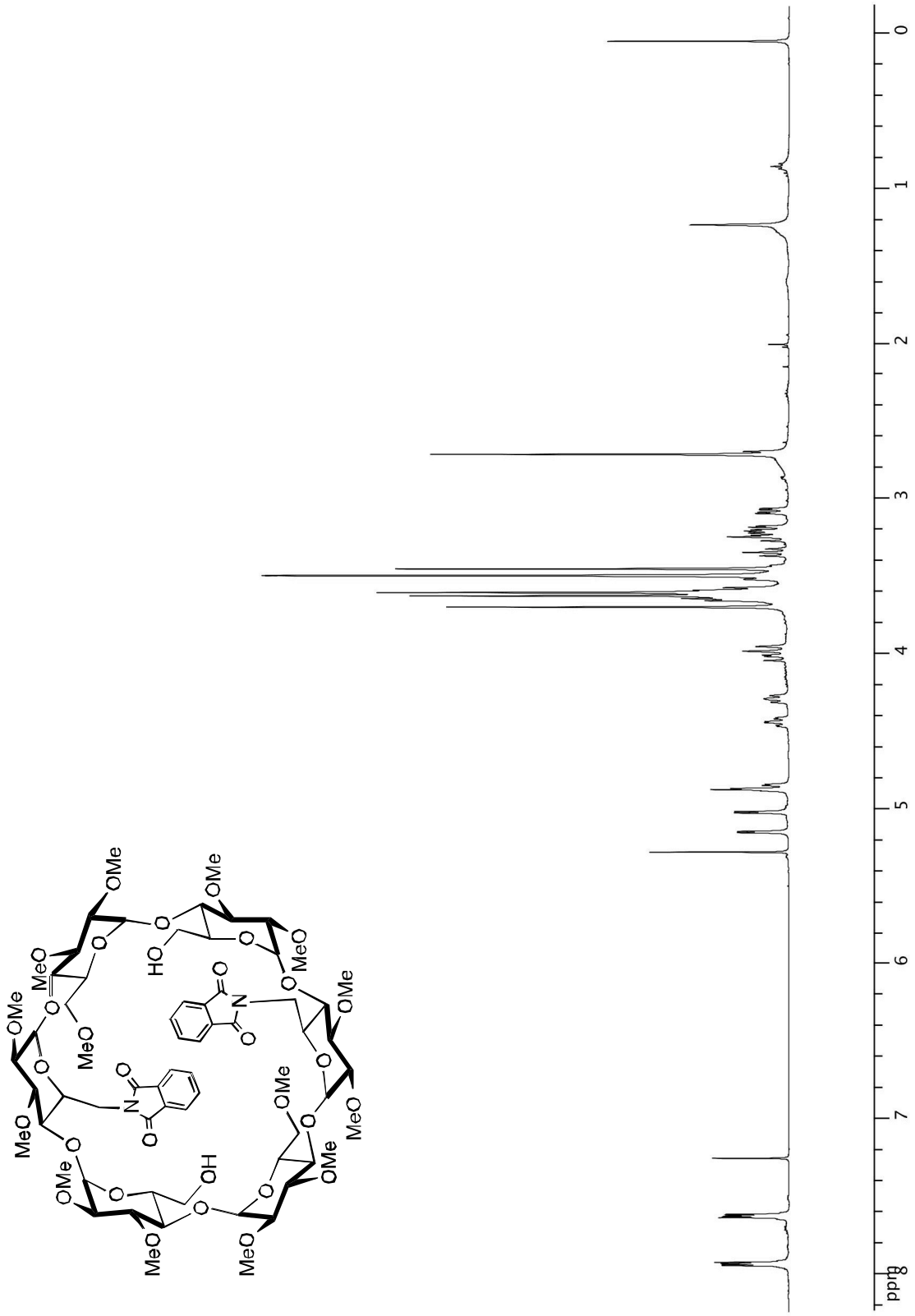
^{1}H-^{13}C HMQC NMR spectrum of 7a



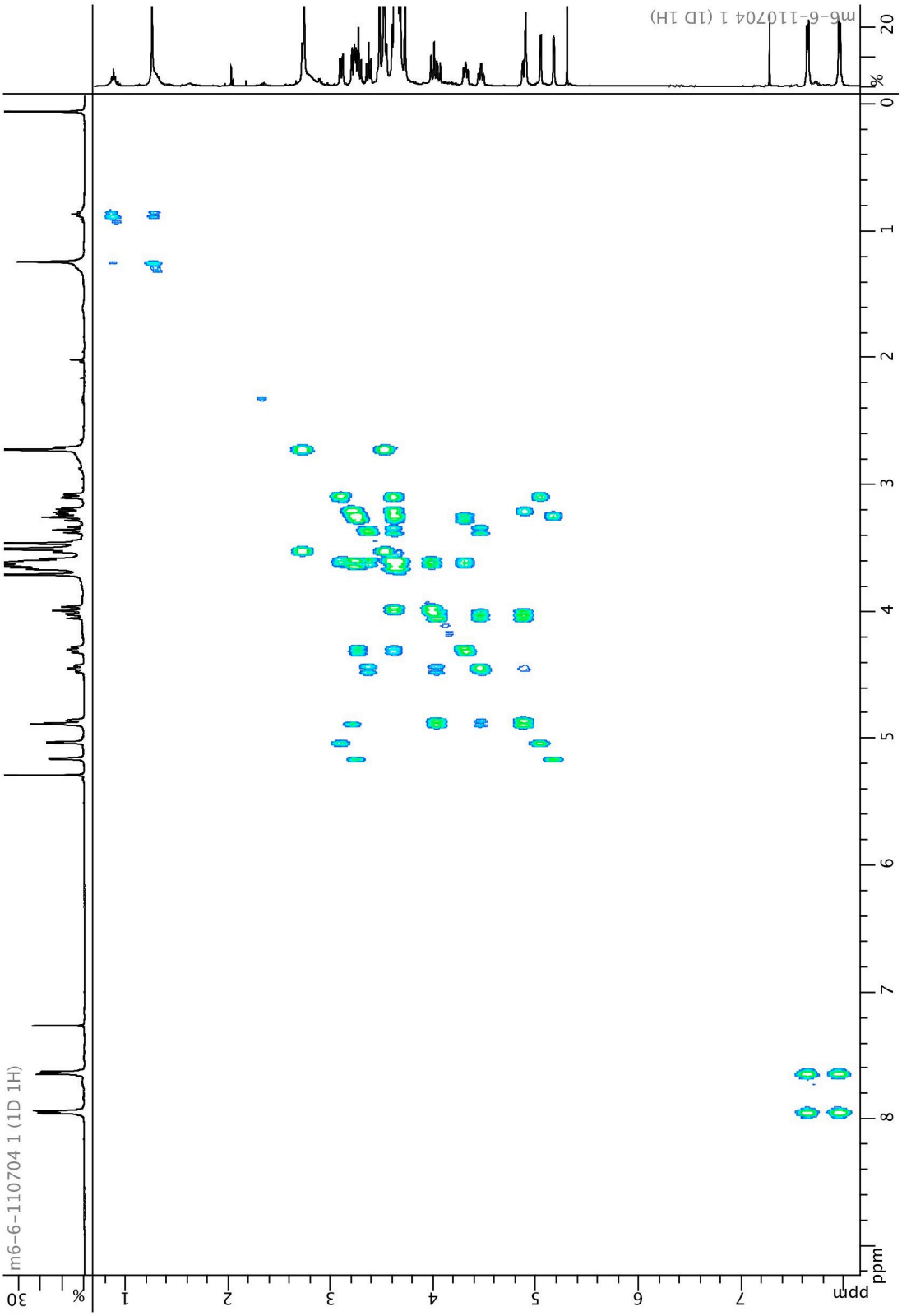
$^{31}P\{^{1}H\}$ NMR spectrum of 7a



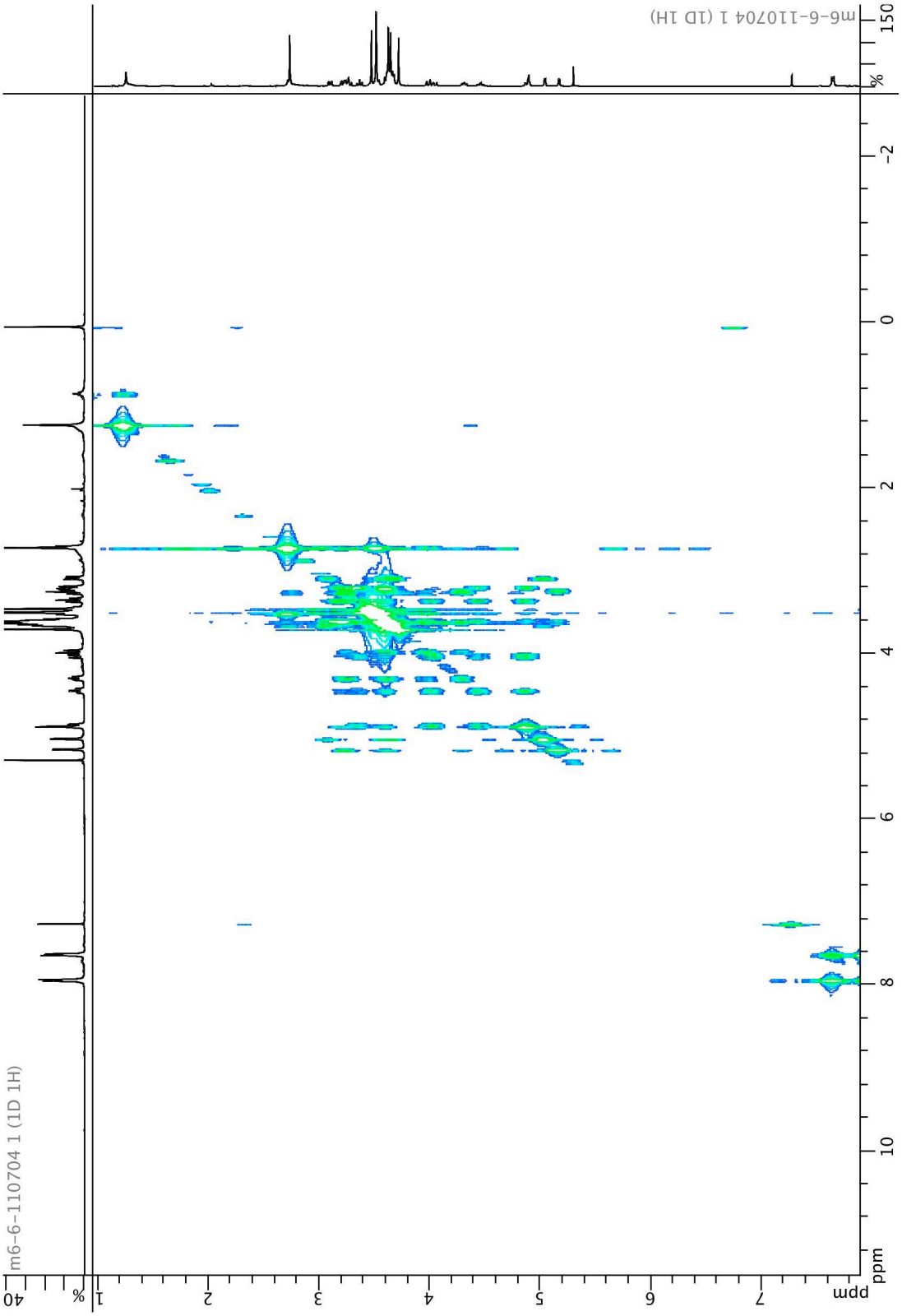
Mass spectrum of 7a



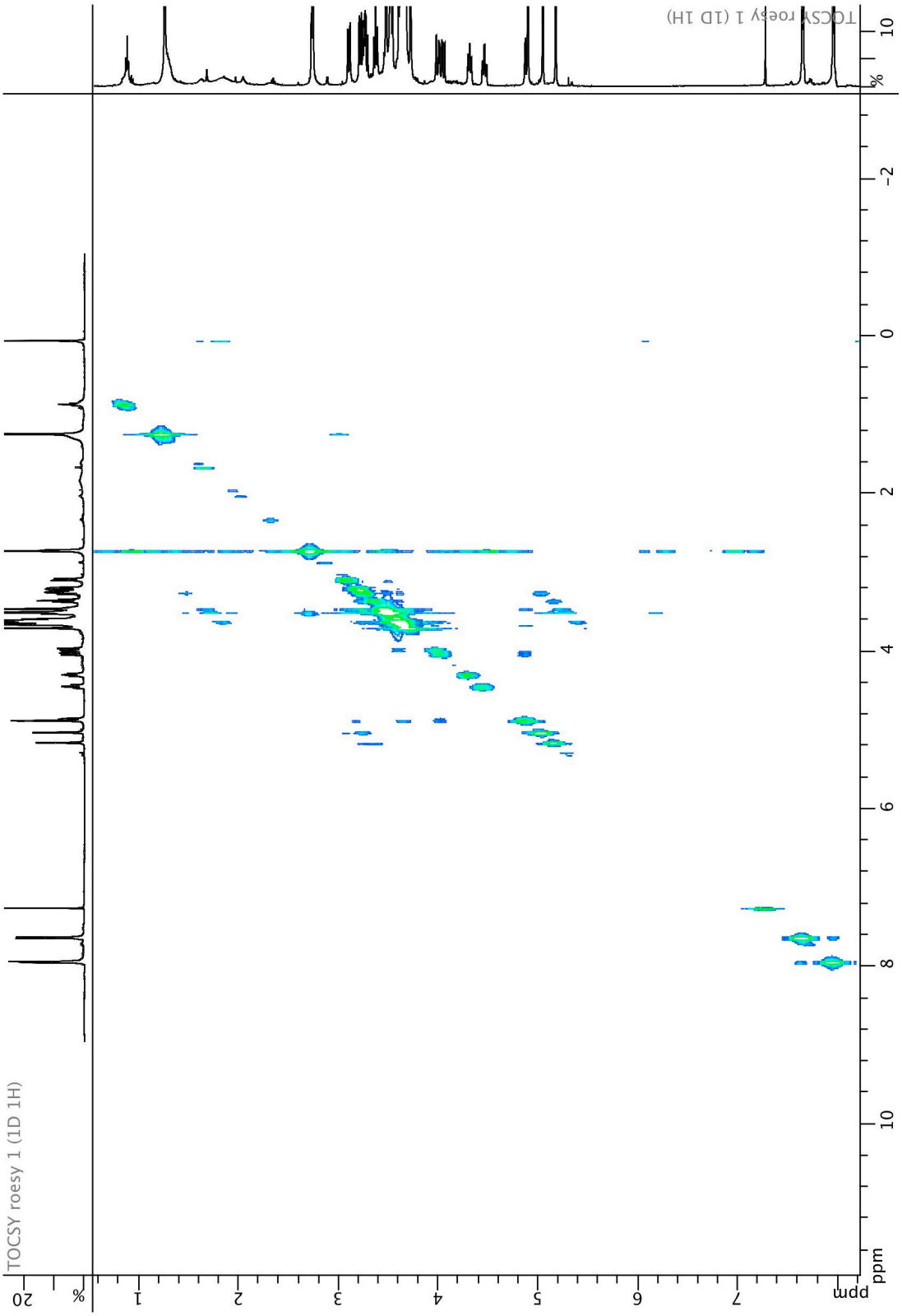
^{1}H NMR spectrum of 7b



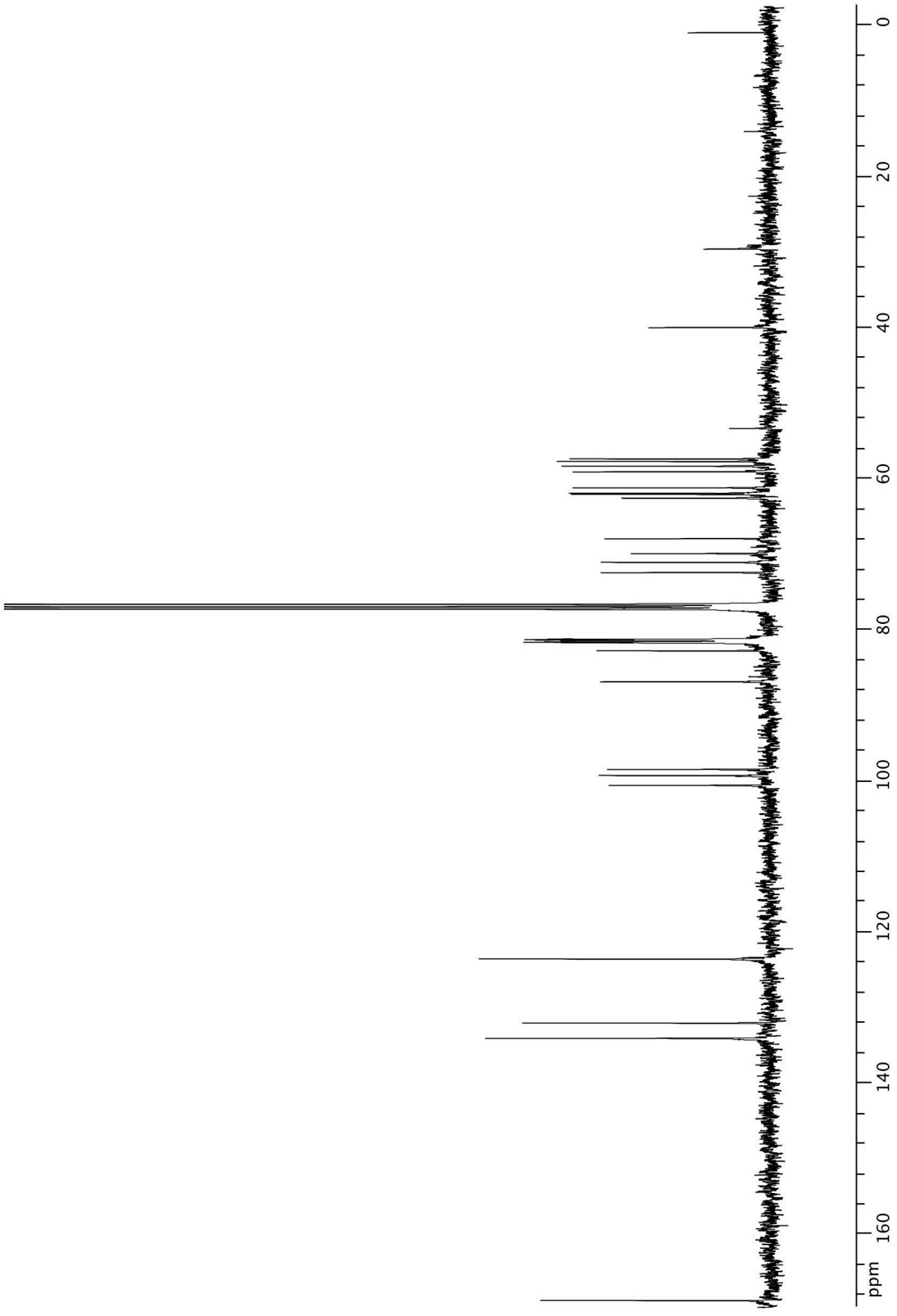
^{1}H-^{1}H COSY NMR spectrum of 7b



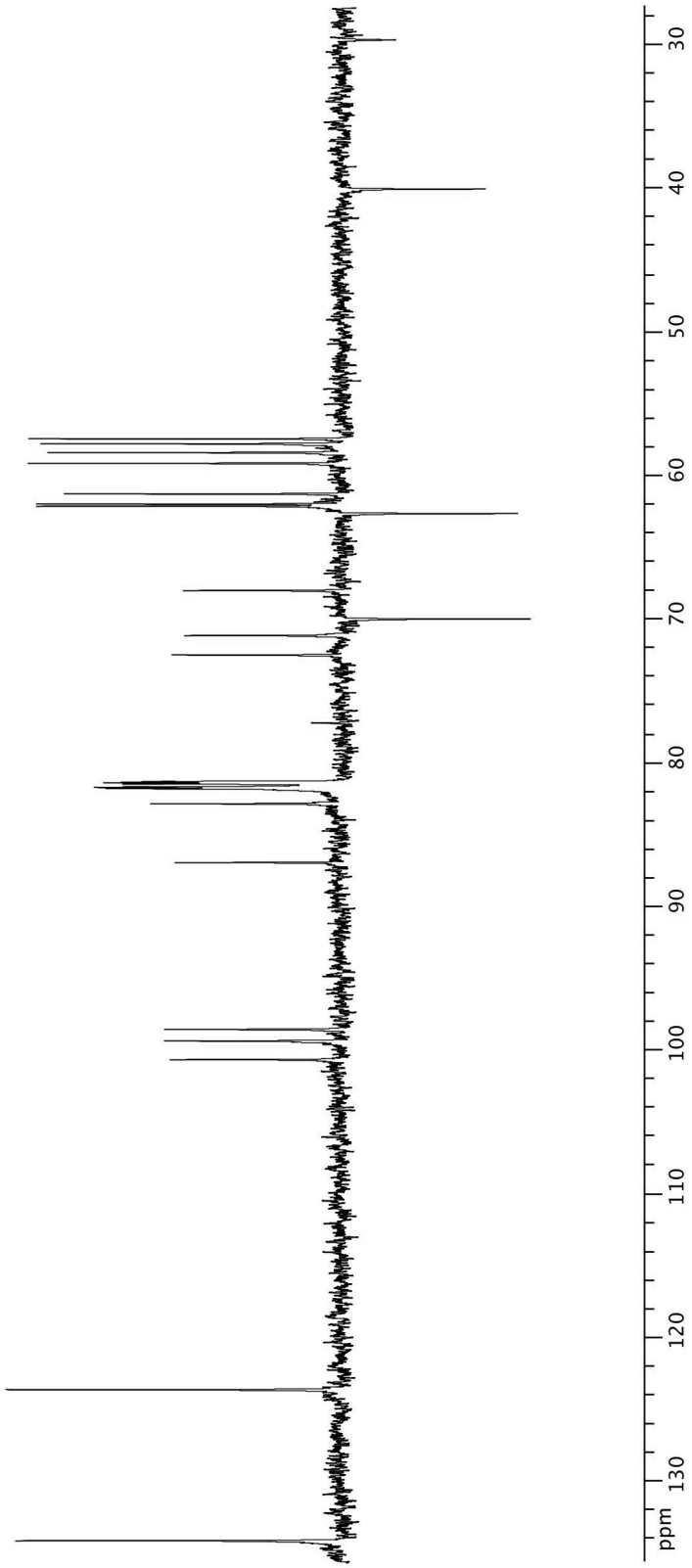
^{1}H-^{1}H TOCSY NMR spectrum of 7b



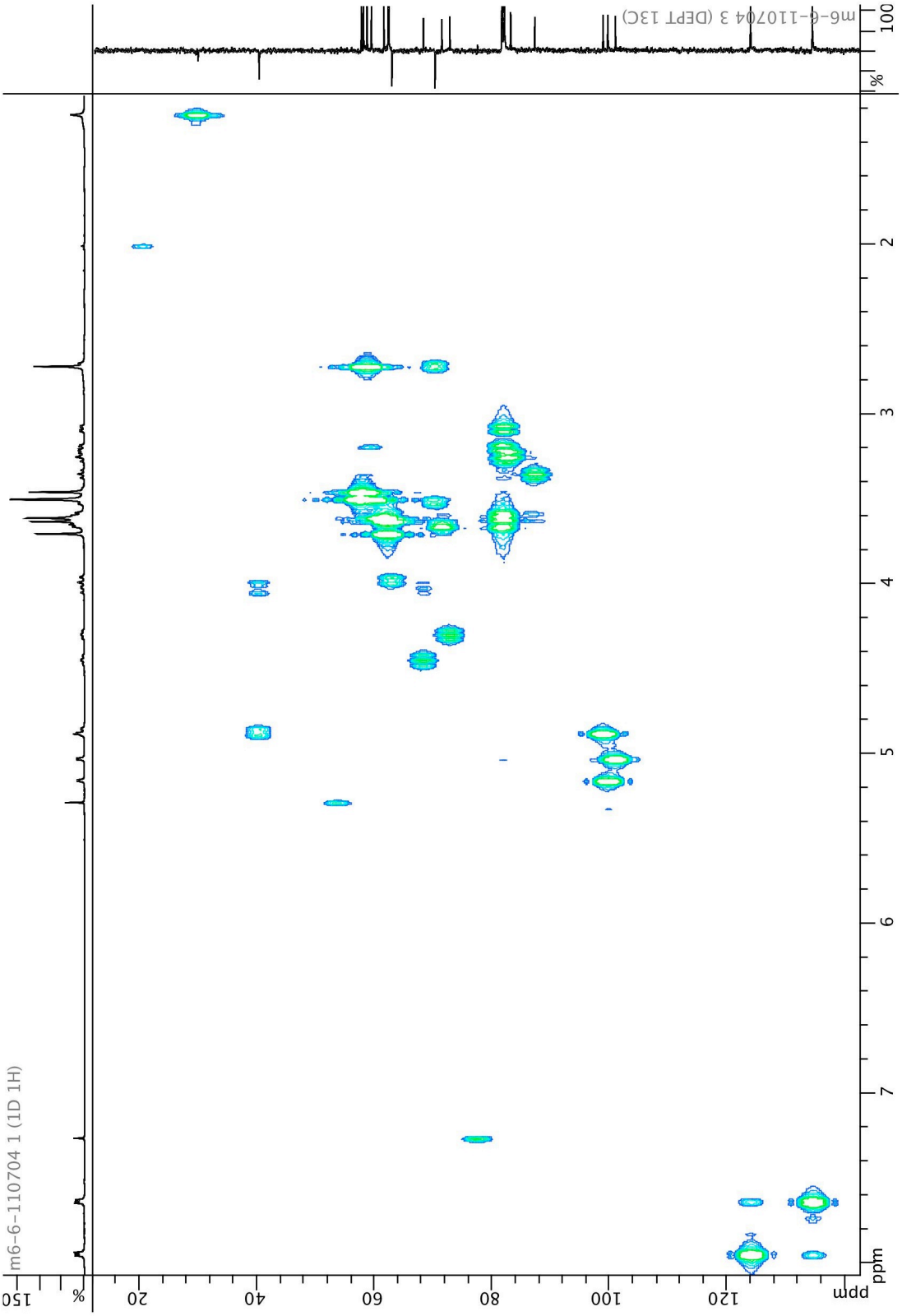
^{1}H-^{1}H ROESY NMR spectrum of 7b



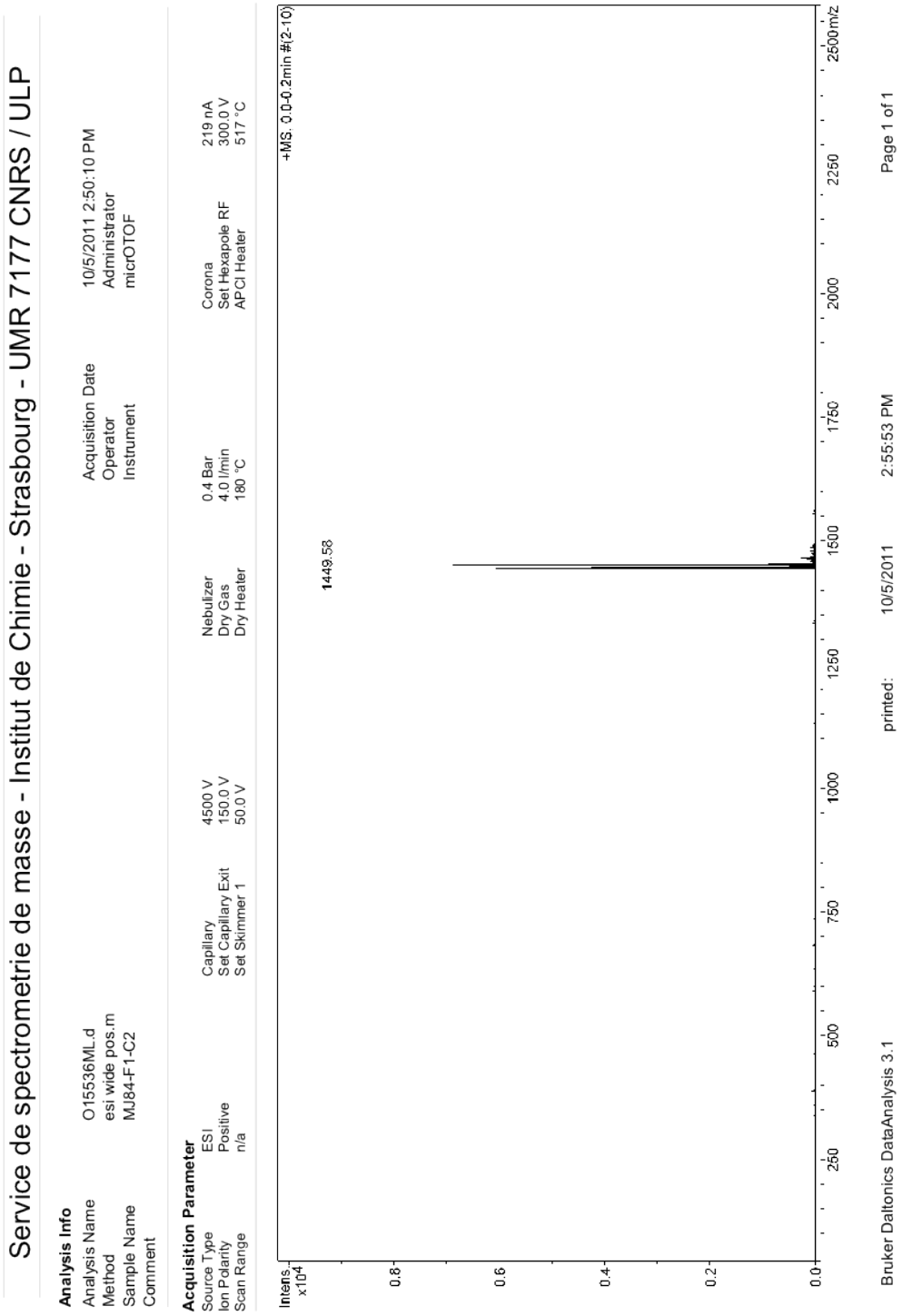
^{13}C NMR spectrum of 7b



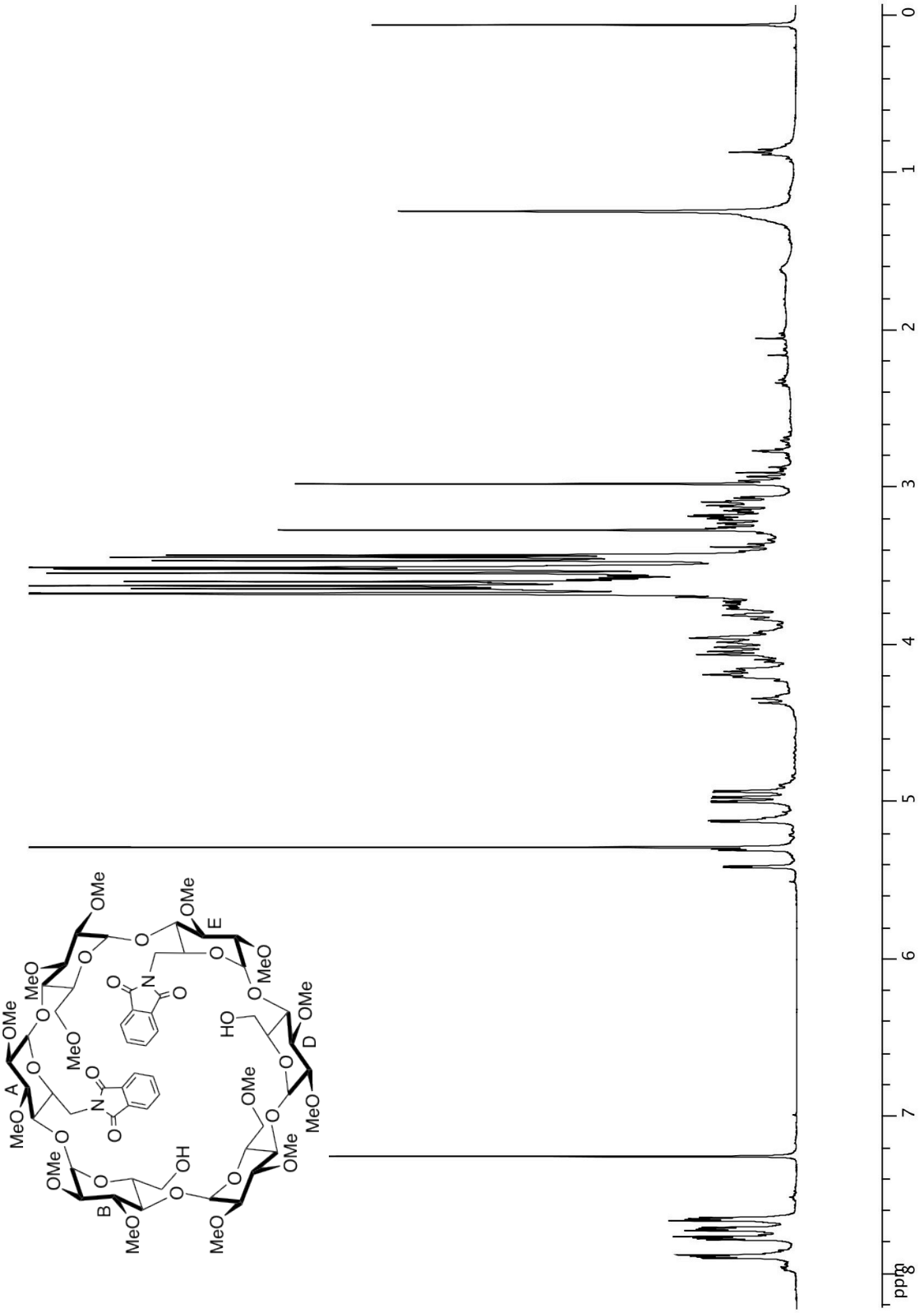
DEPT 135 NMR spectrum of 7b



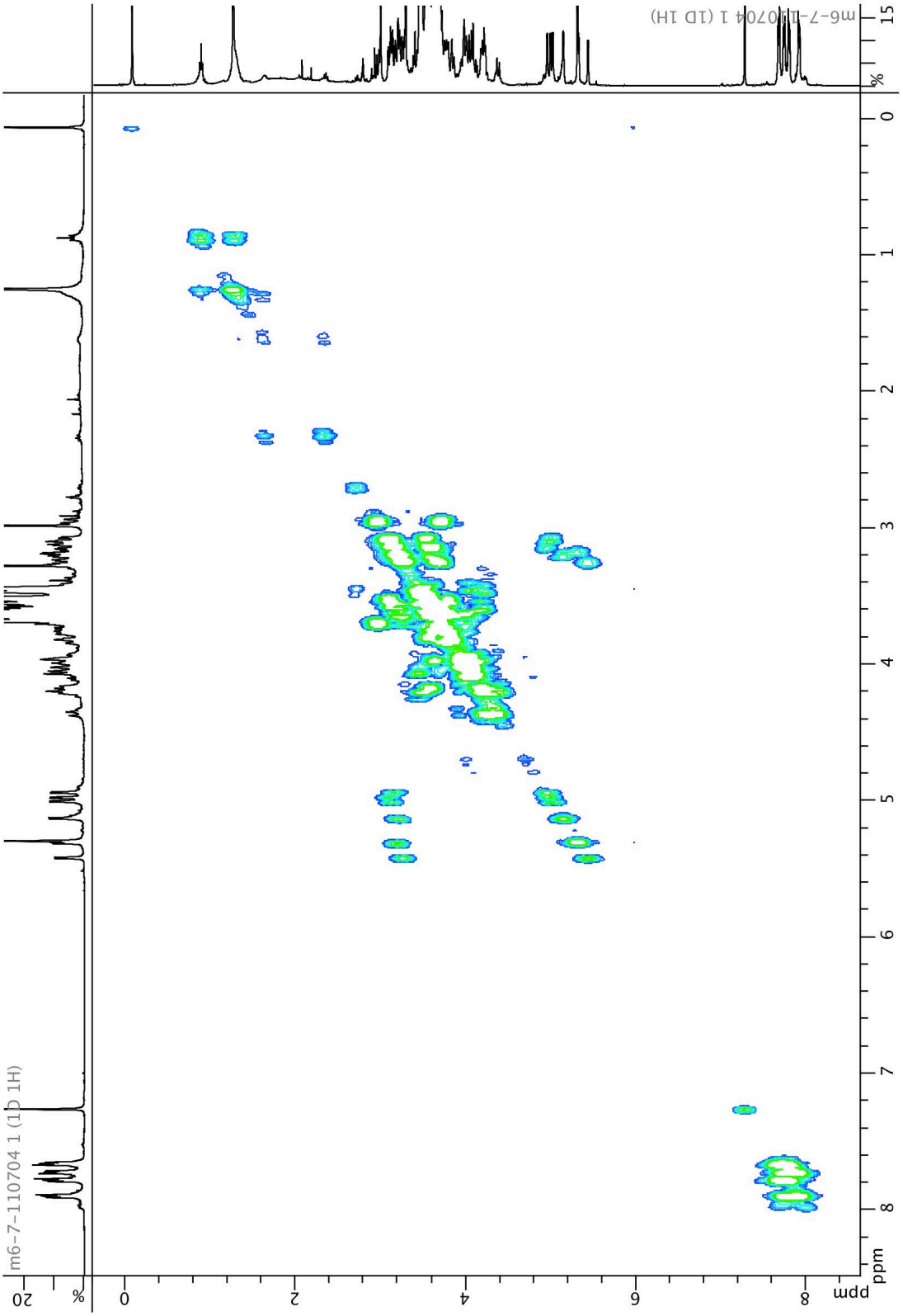
^{1}H-^{13}C HMQC NMR spectrum of 7b



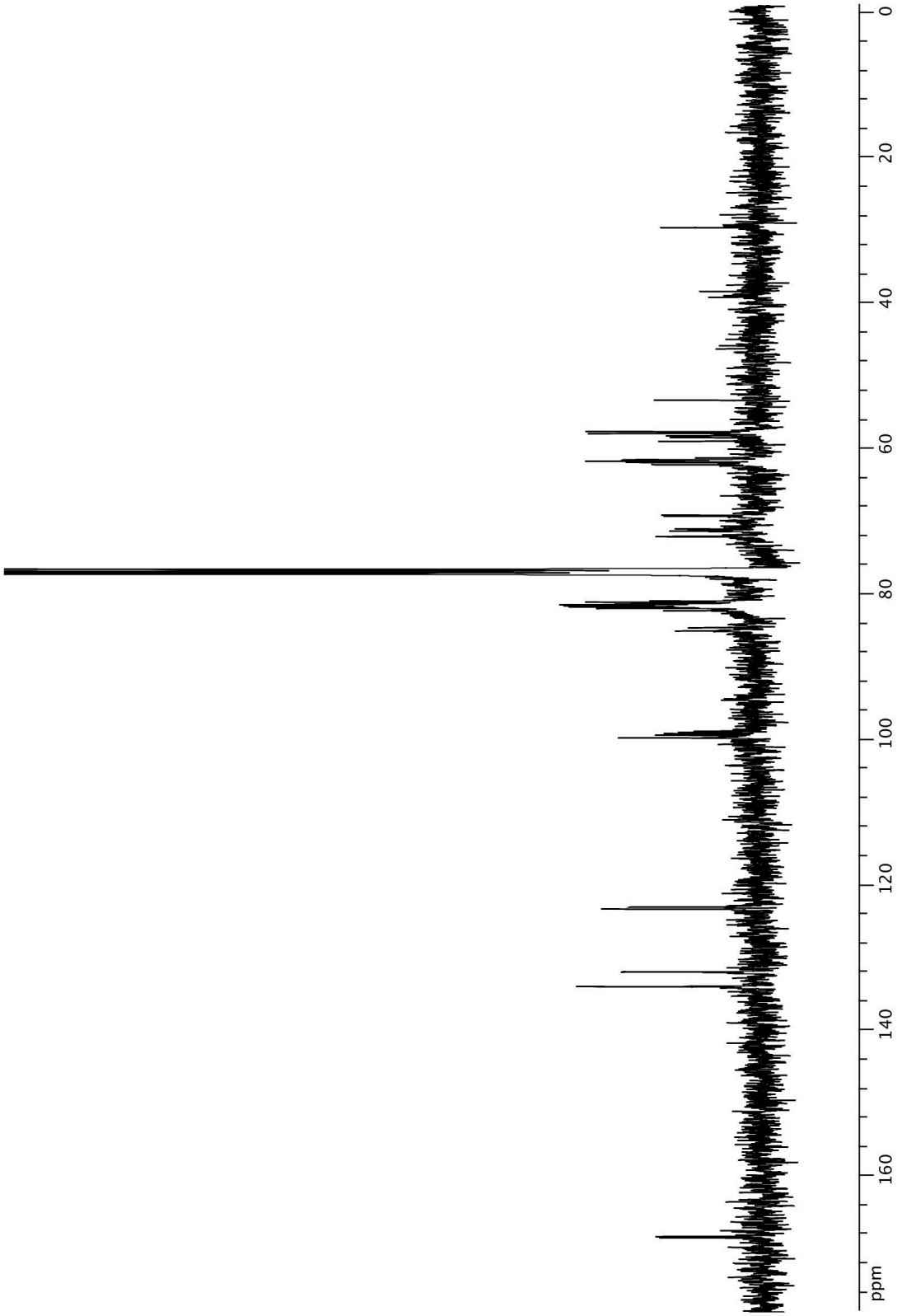
Mass spectrum of 7b



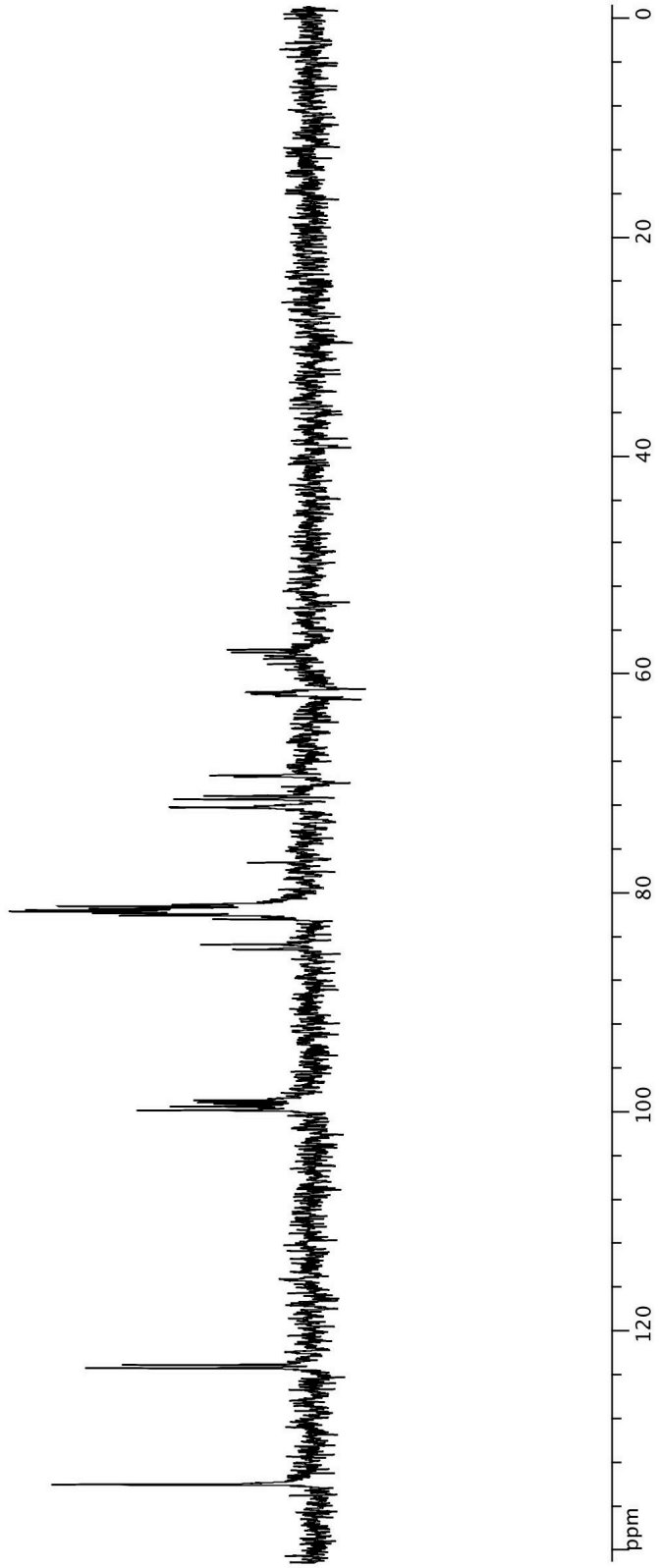
^{1}H NMR spectrum of 8b



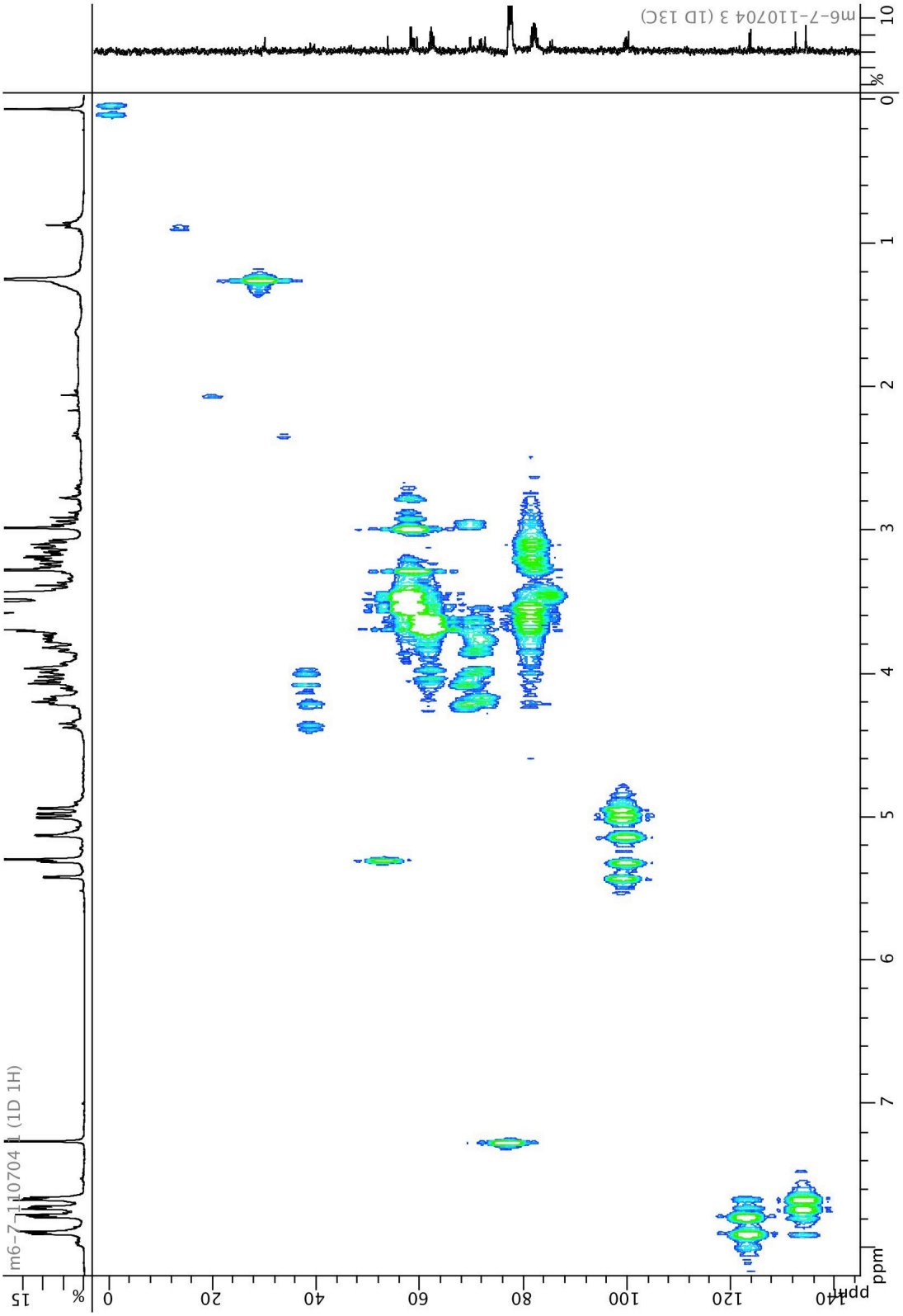
^{1}H-^{1}H COSY NMR spectrum of 8b



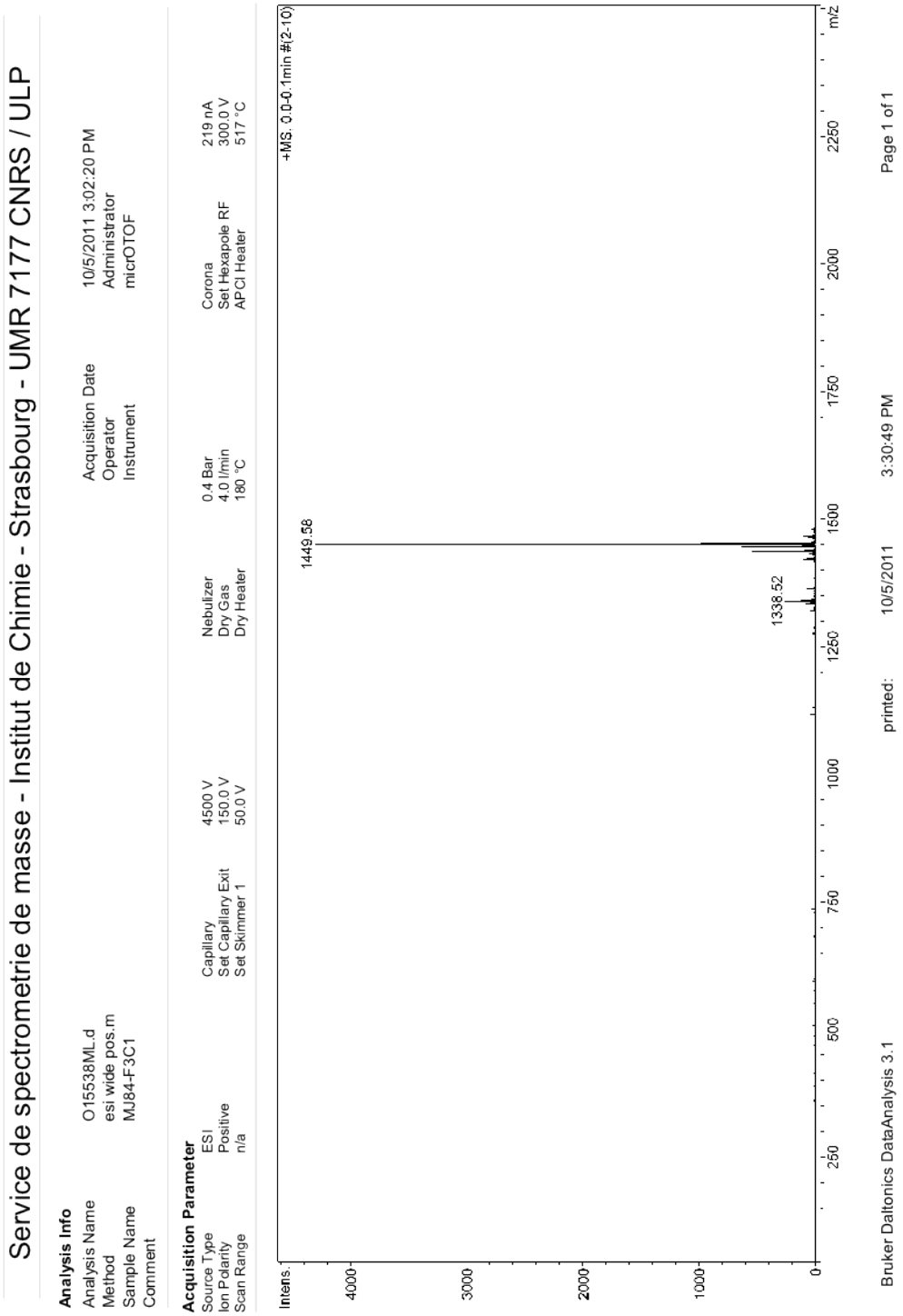
^{13}C NMR spectrum of 8b



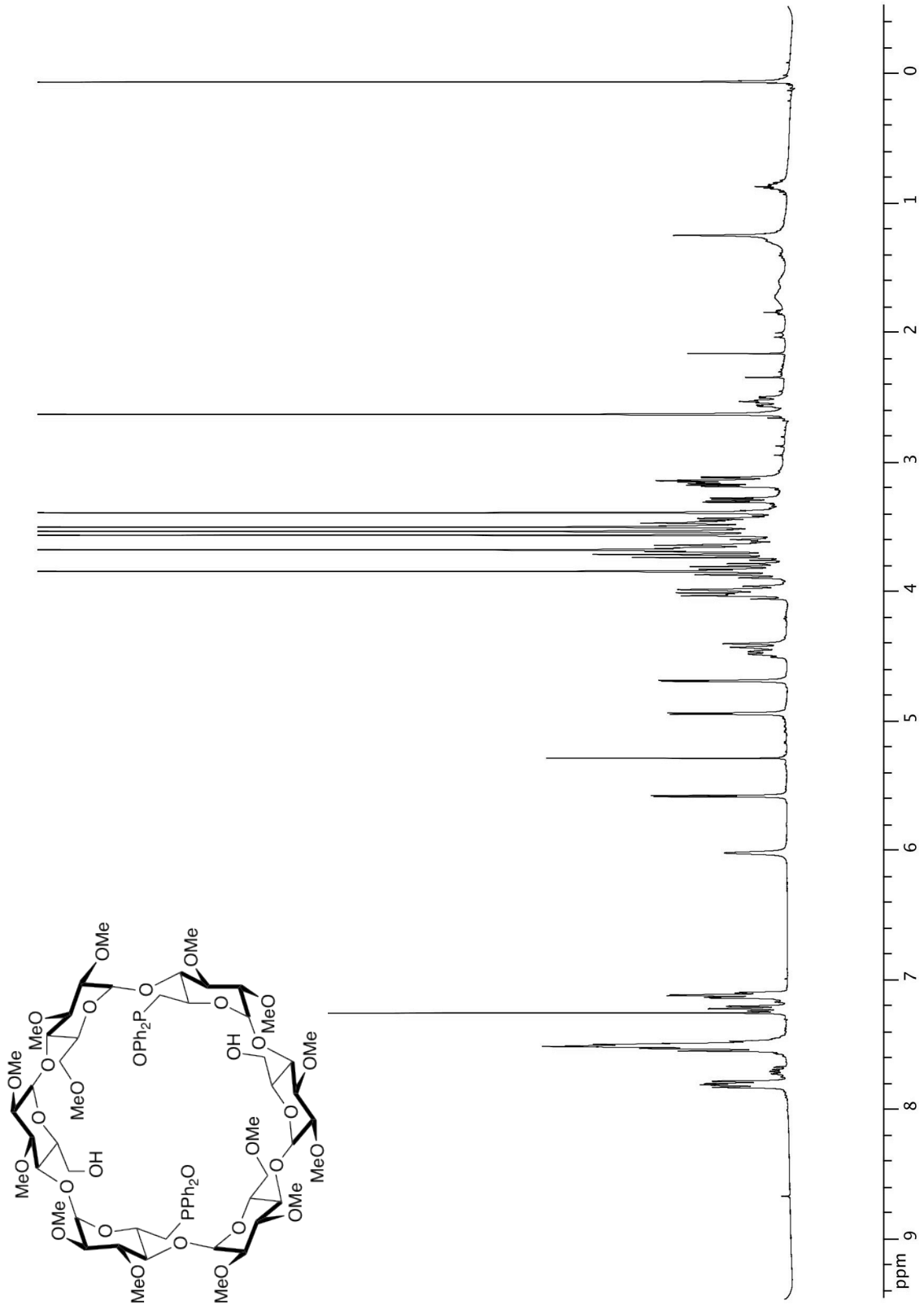
DEPT 135 NMR spectrum of 8b



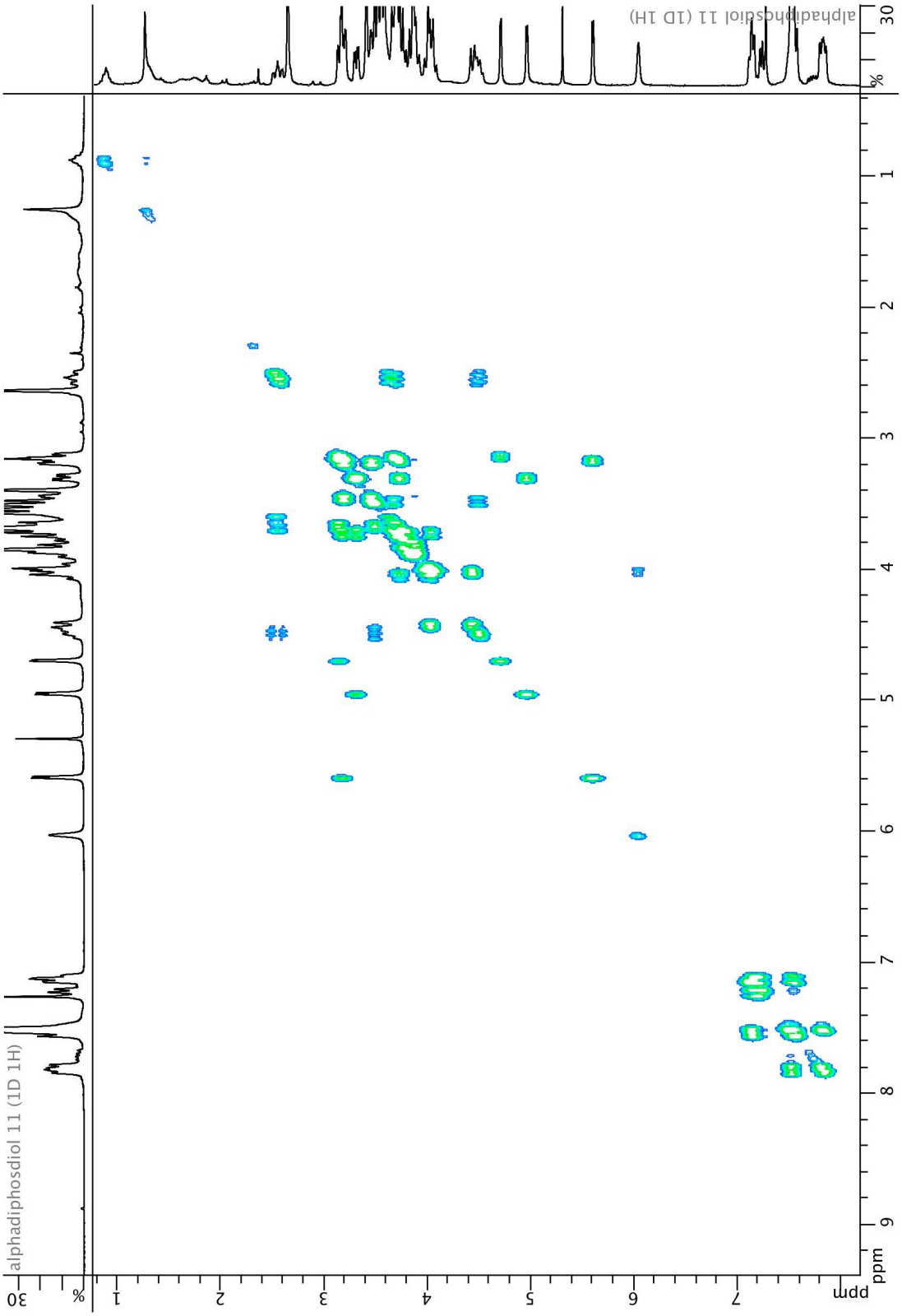
^{1}H-^{13}C HMQC NMR spectrum of 8b



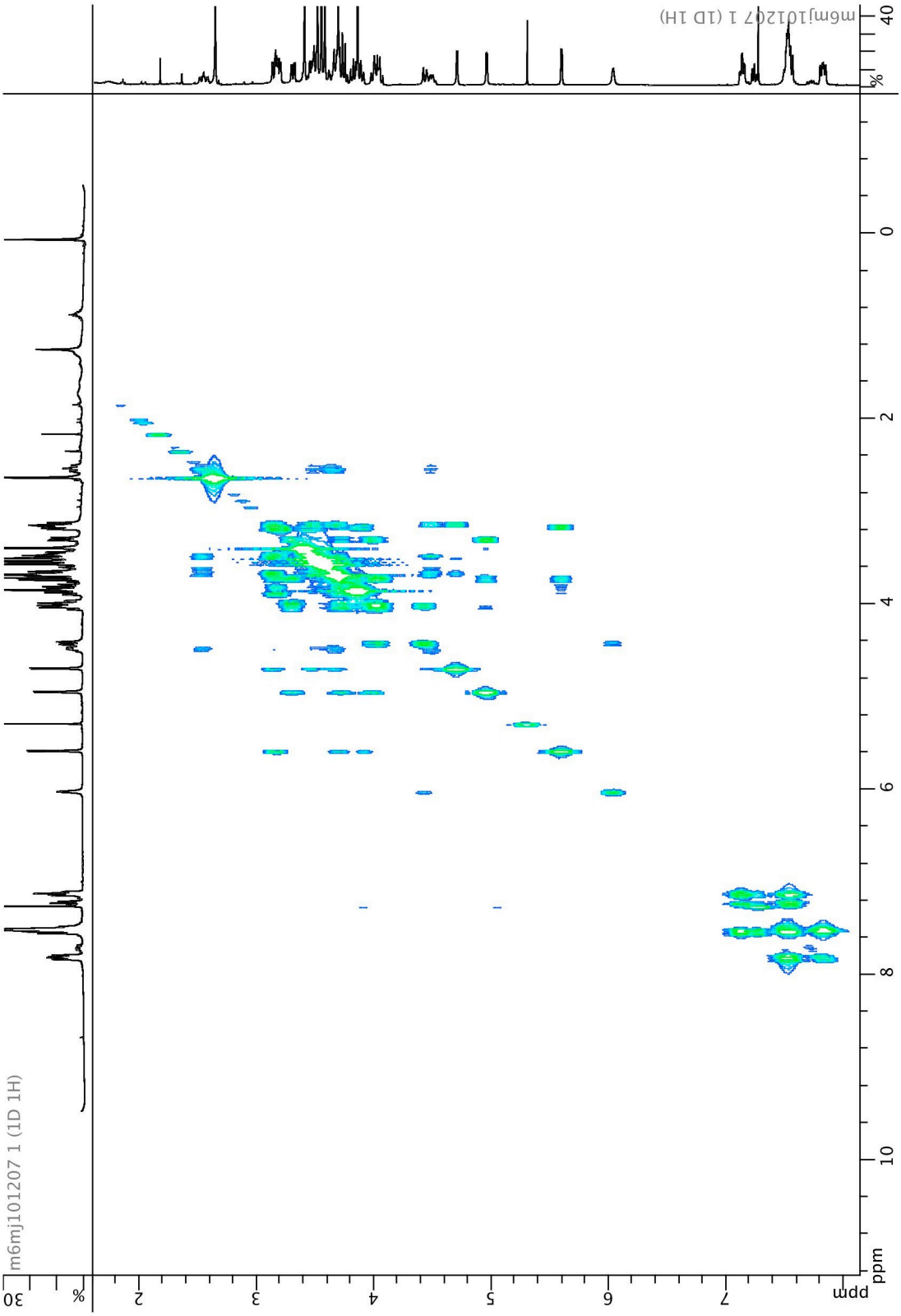
Mass spectrum of 8b



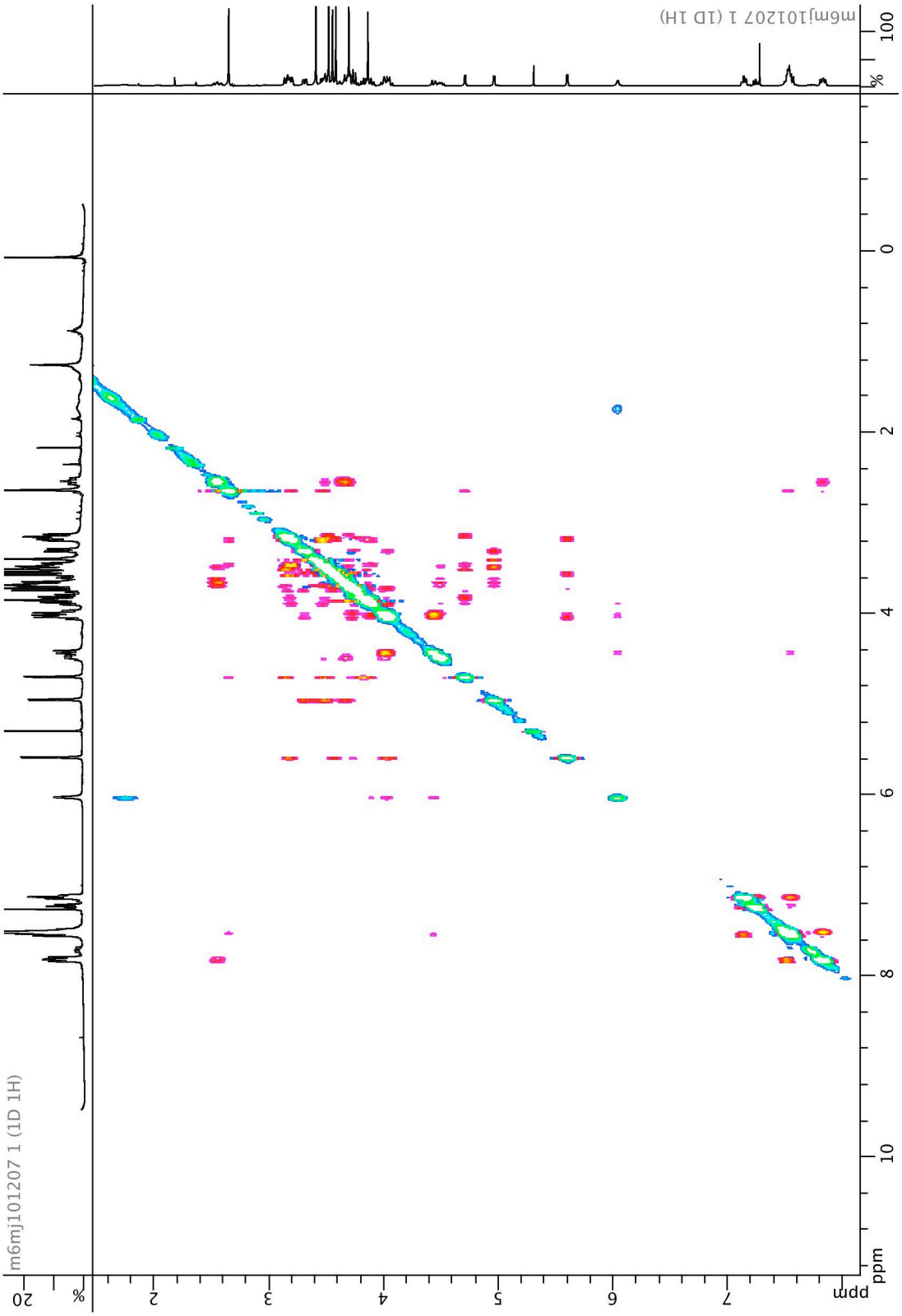
^{1}H NMR spectrum of 10



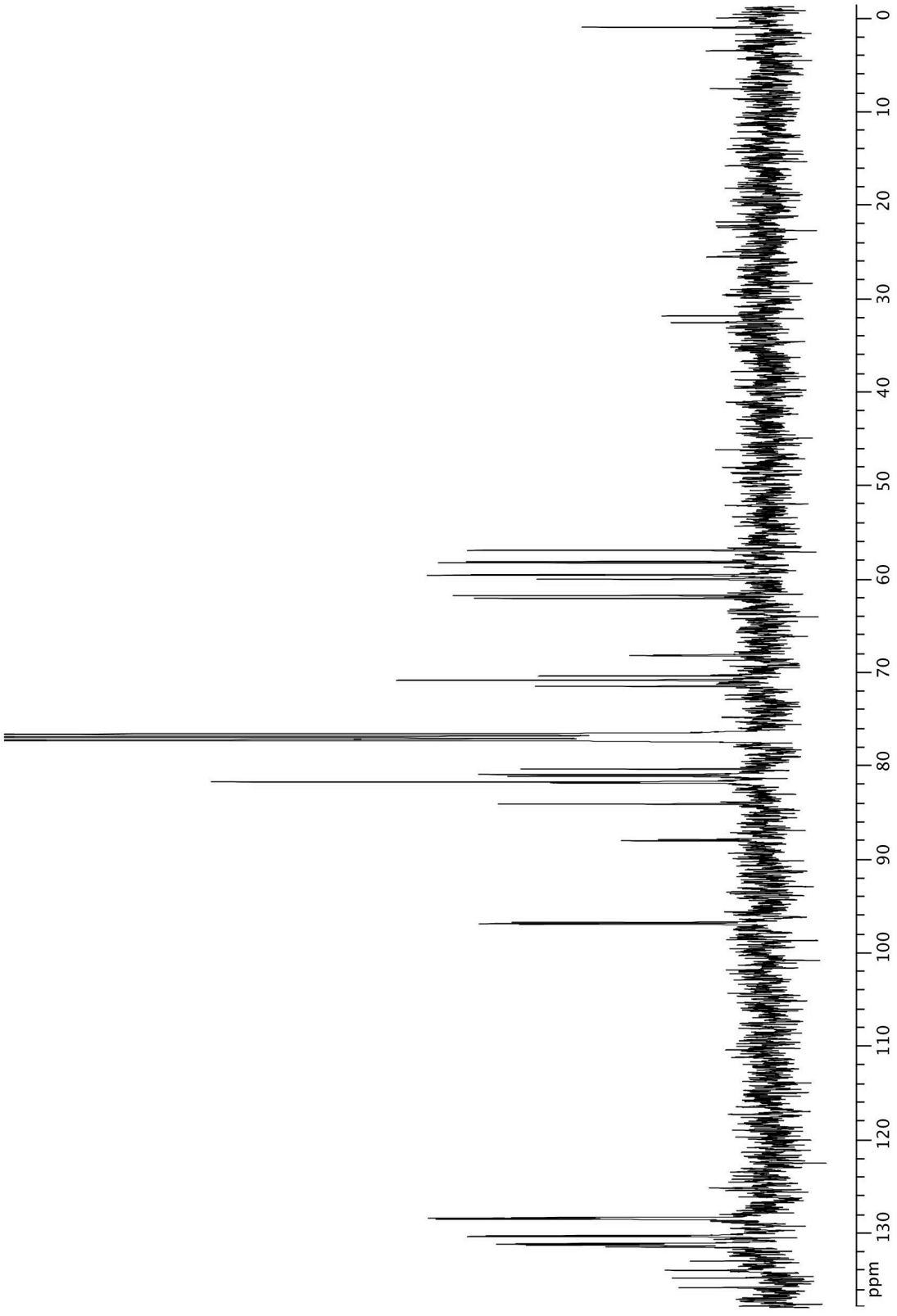
^{1}H-^{1}H COSY NMR spectrum of 10



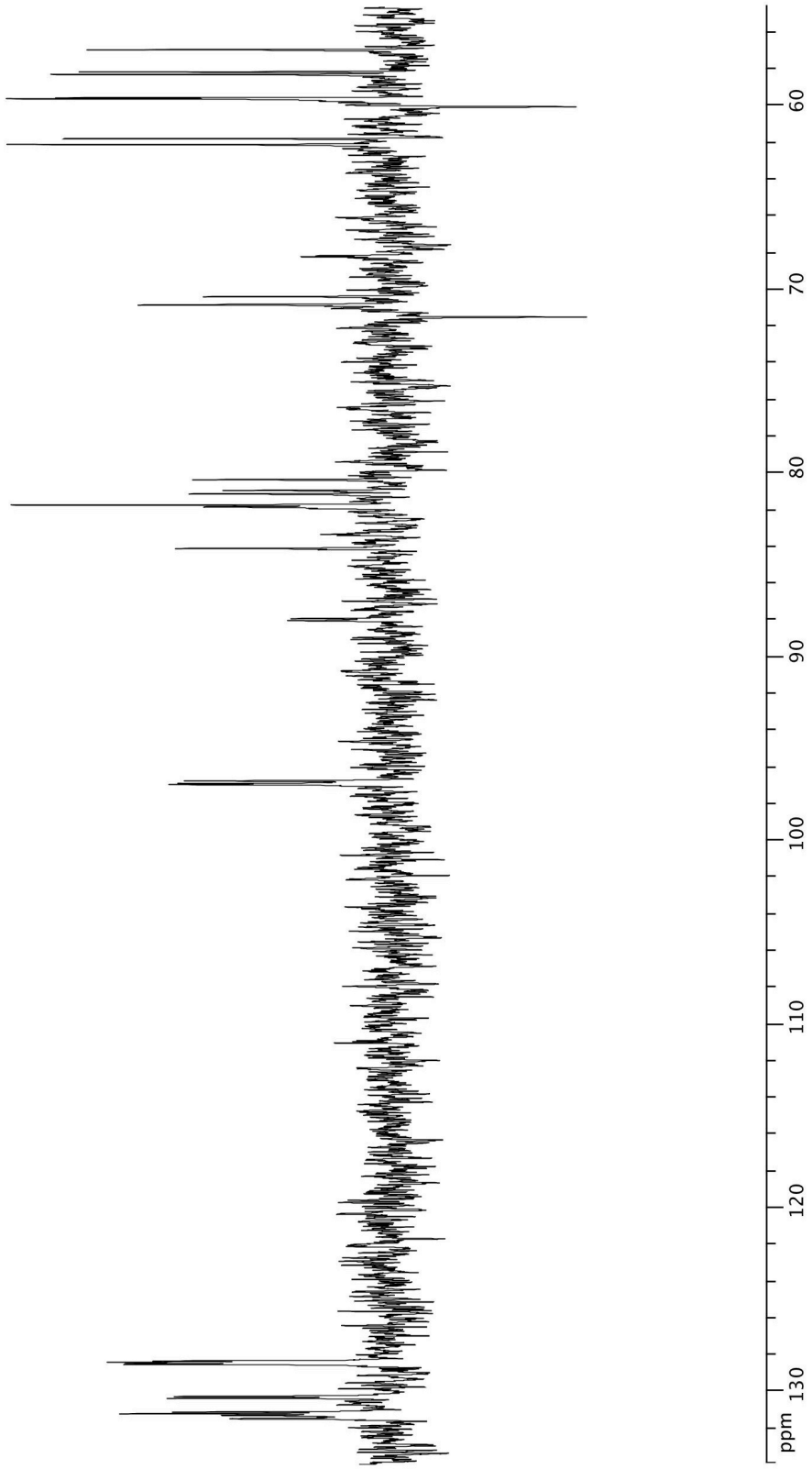
^{1}H-^{1}H TOCSY NMR spectrum of 10



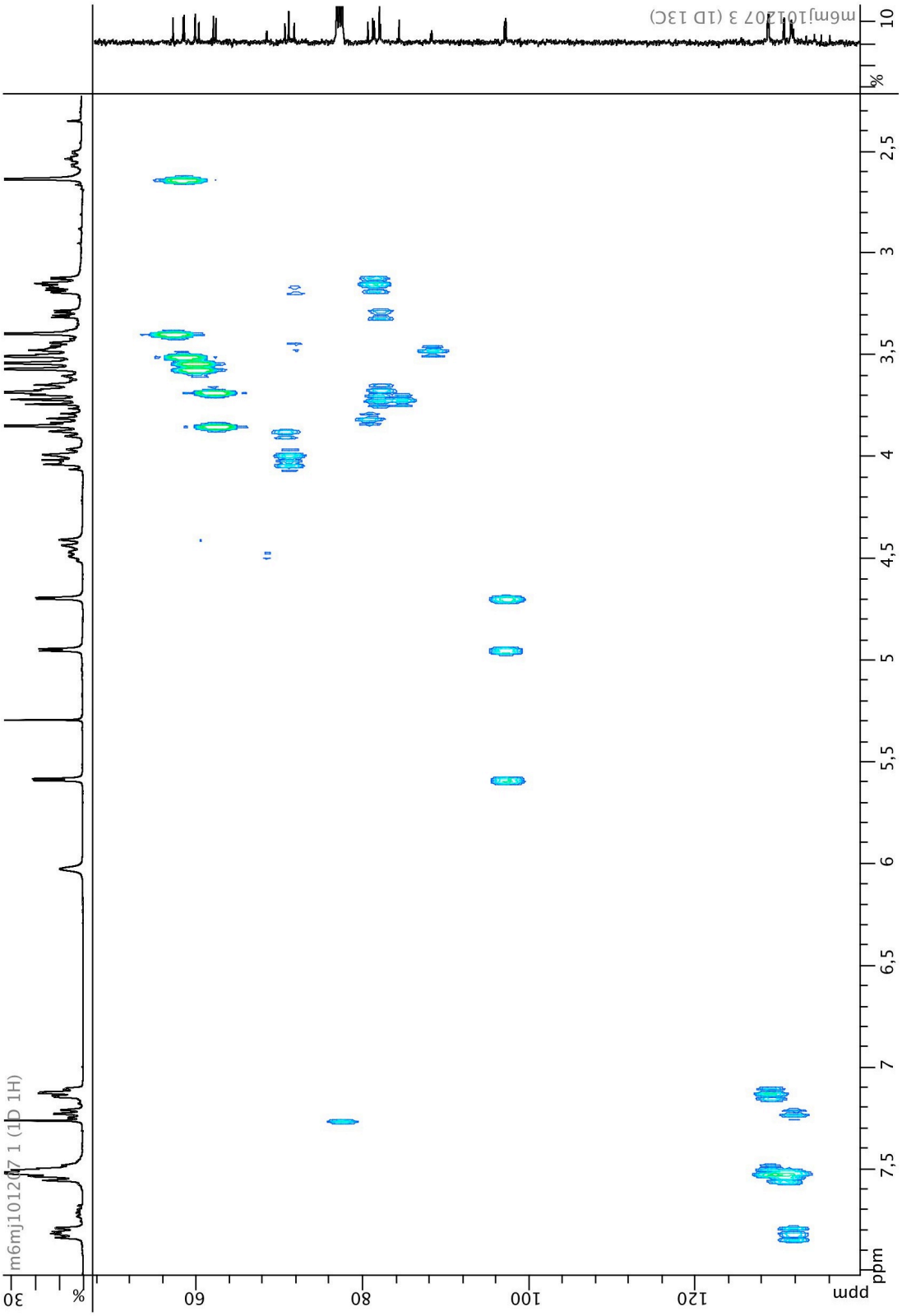
^{1}H-^{1}H ROESY NMR spectrum of 10



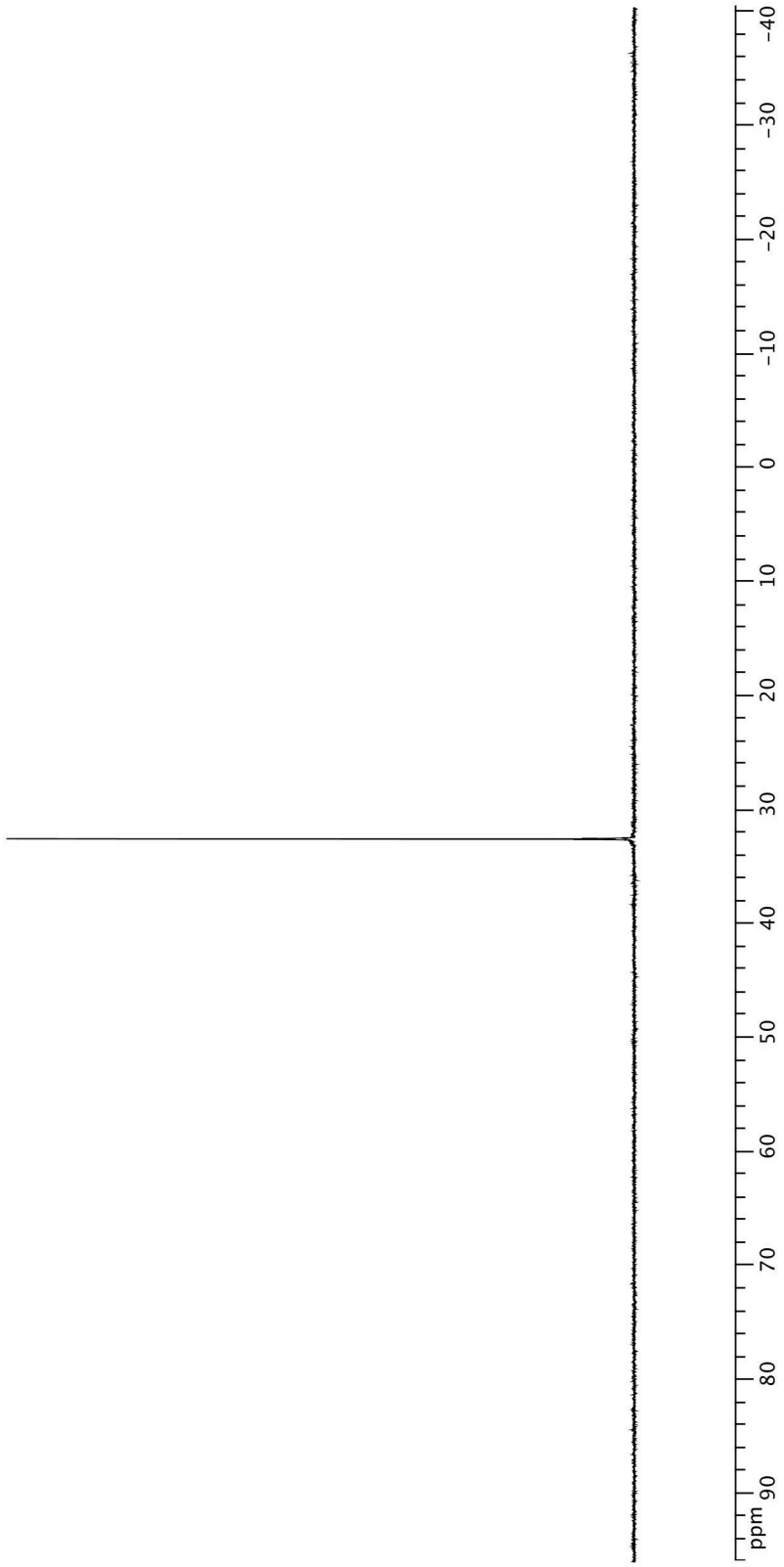
^{13}C NMR spectrum of 10



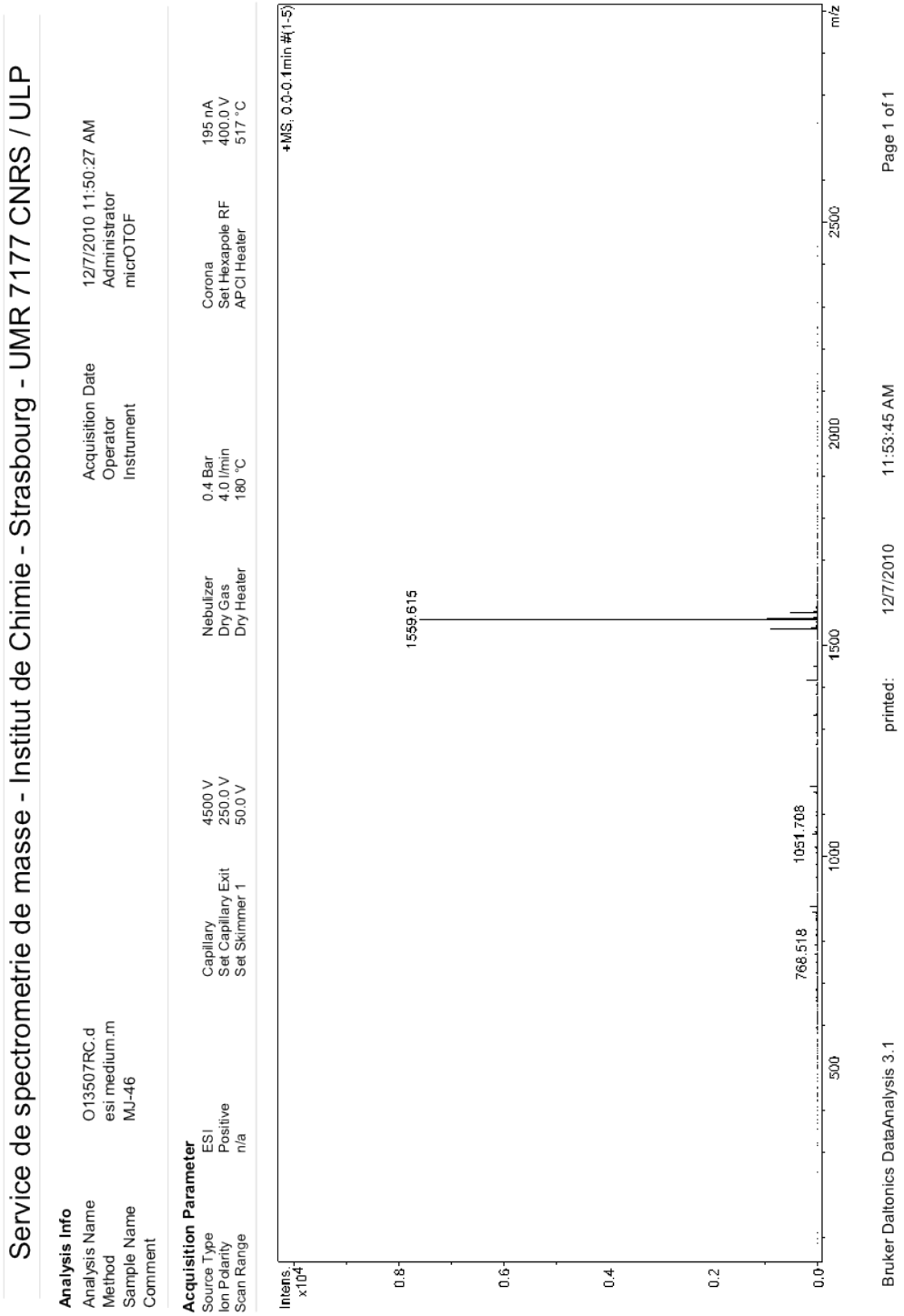
DEPT 135 NMR spectrum of 10



^{1}H-^{13}C HMQC NMR spectrum of 10



^{31}P NMR spectrum of 10



Mass spectrum of 10

General procedure for determining the glucose units linked by a given capping unit.[6]

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 Overhause 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 labeled in the alphabetical order).

References

1. Z. Chen, J. S. Bradshaw, Y.-F. Shen, Y. Habata and M. L. Lee, *J. Org. Chem.*, 1997, **62**, 8529-8534.
2. D. Armspach, L. Poorters, D. Matt, B. Benmerad, F. Balegroune and L. Toupet, *Org. Biomol. Chem.*, 2005, **3**, 2588-2592.
3. R. Gramage-Doria, D. Rodriguez-Lucena, D. Armspach, C. Egloff, M. Jouffroy, D. Matt and L. Toupet, *Chem. Eur. J.*, 2011, **17**, 3911-3921.
4. A. Altomare, J. Foadi, C. Giacovazzo, A. G. G. Moliterni, M. C. Burla and G. Polidori, *J. Appl. Crystallogr.*, 1998, **31**, 74-77.
5. G. M. Sheldrick, SHELXL-97, *Program for Crystal Structure Refinement*, 1997, University of Göttingen, Göttingen (Germany).
6. H.-J. Schneider, F. Hacket and V. Rüdiger, *Chem. Rev.*, 1998, **98**, 1755-1785.