Supporting information

Development of Strategies for the Regiocontrolled Synthesis of *meso*-5,10,20-Triaryl-2,3-chlorins

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All solvents used were reagent grade. Methylene chloride was distilled from calcium hydride and kept over activated 4 Å sieves. Dimethylformamide was distilled under slow argon flow and kept over activated 4 Å sieves. Pyridine was distilled under KOH. Column chromatography was performed with the indicated solvents using E. Merck silica gel 60 (particle size 0.035-0.070 mm). Macherey-Nagel precoated plates (SIL G-200, 2 mm) were used for preparative thin-layer chromatography. Yields refer to chromatographically and spectroscopically pure compounds. All compounds were characterized by ^{1}H and ^{13}C NMR spectra (HMQC, HMBC and 1D Nuclear Overhauser Difference Spectroscopy) recorded on a Bruker AC-300 spectrometer at ambient temperature using an internal deuterium lock. Chemical shift values are given in ppm relative to tetramethyl silane (TMS). Acidic impurities in $CDCl_3$ were removed by treatment with anhydrous K_2CO_3. Quantitative UV-visible spectra were obtained using a Varian DMS 200 spectrometer. ESI mass spectra were obtained by infusion using a ZQ 2000 waters mass spectrometer. Microanalyses were performed by the ICSN-CNRS Elemental Analysis Center at Gif-sur-Yvette, France.

5,15-di(4-isopropyloxyphenyl)porphyrin : **5b** Dry methylene chloride (3.7 L) was placed in a three-necked flask equipped with magnetic stirrer, gas inlet (argon) and a reflux condenser. Dipyrromethane **4** (2.23 g, 15.2 mmol) and 4-isopropyloxybenzaldehyde (2.5 g, 15.2 mmol) were added. The flask was shielded from ambient light and then 0.256 mL (3.32 mmol) of trifluoroacetic acid in dry methylene chloride (100 mL) were added and the reaction mixture stirred for 18 h at 20°C. Subsequently, 5 g (22 mmol) of DDQ suspended in dry methylene chloride (100 mL) were added and the mixture was stirred for 1 h. Then, triethylamine (11 mL) were added and the reaction mixture was filtered through a silica gel column (740 mL). Silica gel was washed with chloroform until the washing solution becomes nearly colorless. The red solution was concentrated under vacuum. The crude product was crystallized from a mixture of methylene chloride and methanol. The filtrate was washed with methanol and dried in vacuum at 100°C for 5 hours to yield 2.38 g (54 %) of the title compound as a purple amorphous solid. (Rf = 0.51, SiO_2, toluene). Anal. ($C_{38}H_{36}N_4O_2$) calc. C 78.59, H 6.25 N

9.65, found C 78.34, H 5.81, N 8.91. UV-vis spectrum in CH_2Cl_2 : λ_{max}, nm (ε L.mmol^{-1}.cm^{-1}) : 410.5 (326.3), 505.5 (15.3), 541.5 (7.2), 578.5 (5.1), 634 (2.2). ^{1}H NMR ($CDCl_3$) δ (ppm) : 10.30 (s, 2H, H-10, 20), 9.39 (d, 4H, *J* = 4.6 Hz, H-pyr), 9.13 (d, 4H, *J* = 4.6 Hz, H-pyr), 8.17 (d, 4H, *J* = 8.5 Hz, H-*o*-phenoxy), 7.33 (d, 4H, *J* = 8.6 Hz, H-*m*-phenoxy), 4.90 [sept, 2H, *J* = 6.0 Hz, C<u>H</u>$(CH_3)_2$], 1.60 [d, 12H, *J* = 6.0 Hz, CH(C<u>H</u>$_3)_2$], -3,07 (s, 2H, NH). ^{13}C NMR ($CDCl_3$) δ (ppm) : 157.9 (C-*p*-phenoxy), 148 (C-4, 6, 14, 16), 145 (C-1, 9, 11, 19), 136.10 (C-*o*-phenoxy), 133.6 (C-1, C-phenoxy), 131.5 (C-2, 3, 7, 8, 12, 13, 17, 18), 119.2 (C-5, C-15), 114.50 (C-*m*-phenoxy), 105.31 (C-10, C-20), 70.50 [-O-<u>C</u>H$(CH_3)_2$], 22.40 [-O-CH(<u>C</u>H$_3)_2$].

5,15-di(4-isopropyloxyphenyl)-10-(4-hydroxyphenyl)porphyrin: *n*-Butyl lithium (12 mL of a 1.6 M solution in *n*-hexane, 19.2 mmol) was added under an argon atmosphere to a dry Schlenk flask charged with a solution of *p*-bromophenol (1.73 g, 10 mmol) in 15 ml of dry diethyl ether at 0 °C. After addition of *n*-butyl lithium, the cold bath was removed and stirring was continued for 18 h at room temperature. The solution slowly became beige opaque. To this vigorously stirred mixture was added rapidly a solution of 5,15-di(*p*-isopropyloxyphenyl)porphyrin **5b** (289 mg, 0.5 mmol) in 100 ml of dry tetrahydrofurane (THF) under an argon atmosphere. The color of the mixture changed from deep purple to brown green. The solution was stirred during two hours. The end of the reaction was checked by thin layer chromatography (silica gel, toluene). A mixture of water and THF (2 mL, 100 mL) was added for the hydrolysis and the solution was stirred for 15 min. (green solution). The oxidation of the mixture was performed by air bubbling for one hour (deep purple solution) and the solution was concentrated under vacuum. The crude product was dissolved in methylene chloride, chromatographied on silica gel column eluted with methylene chloride, yielded 294 mg (87 %) of porphyrin as purple crystals used without purification. Anal. ($C_{44}H_{38}N_4O_3$), 0.5 H_2O calc. C 77.74, H 5.78, N 8.24, found C 77.71, H 5.51, N 8.32. UV-vis spectrum in CH_2Cl_2 : λ_{max}, nm (ε L.mmol^{-1}.cm^{-1}) : 416 (415.4), 512 (16.7), 548 (8.1), 586 (5.1), 642 (3.5). ^{1}H NMR ($CDCl_3$) δ (ppm) : 10.18 (s, 1H, H-20), 9.32 (d, 2H, *J* = 4.6 Hz, H-2, 18-pyr), 9.06 (d, 2H, *J* = 4.6 Hz, H-3, 17), 8.94 (d, 2H, *J* = 4.8 Hz, H-7, 13/8, 12), 8.88 (d, 2H, *J* = 4.8 Hz, H-7, 13/8, 12), 8.12 (d, 4H, *J* = 8.6 Hz, H-*o*-phenoxy), 8.06 (d, 2H, *J* = 8.5 Hz, H, *o*-hydroxyphenyl), 7.29 (d, 4H, *J* = 8.6 Hz, H-*m*-phenoxy), 7.18 (d, 2H, *J* = 8.5 Hz, H, *m*-hydroxyphenyl), 5.04 (s, 1H, OH), 4.87 [sept, 2H, *J* = 6.0 Hz, C<u>H</u>$(CH_3)_2$], 1.58 [d, *J* = 6.0 Hz, 6H, CH(C<u>H</u>$_3)_2$], -2.98 (s, 2H, NH). ^{13}C NMR ($CDCl_3$) δ (ppm) : 157.79 (C-*p*-phenoxy),

155.38 (C-*p*-hydroxyphenyl), 147.2 (C-4, 6, 9, 11, 14, 16), 145.6 (C-1, 19), 135.82 (C-*o*-phenoxy), 135.67 (C-*o*-hydroxyphenyl), 135.27 (C-1, C-hydroxyphenyl), 133.92 (C-1, C-phenoxy), 131 (very broad, C-2, 3, 7, 8, 12, 13, 17, 18), 119.47 (C-5, C-10, C-15), 114.15 (C-*m*-phenoxy), 113.54 (C-*m*-hydroxyphenyl), 104.69 (C-20), 70.21 [-O-$\underline{C}H(CH_3)_2$], 22.35 [-O-CH($\underline{C}H_3)_2$].

5,10,15-tri(4-isopropyloxyphenyl)porphyrin : **13** A mixture of 5,15-di(4-isopropyloxy-phenyl)-10-(4-hydroxyphenyl)porphyrin (290 mg, 0.43 mmol), potassium carbonate (1.38 g, 10 mmol) and isopropyl bromide (2.5 mL, 26.6 mmol) in dimethylformamide (50 mL) was stirred at 50-55°C overnight under argon. The solution was concentrated under vacuum. The crude product was diluted in toluene, filtered, evaporated then crystallized from a mixture of methyl chloride-methanol. The title compound was obtained as purple crystals (yield 259 mg, 84 %). Anal. ($C_{47}H_{44}N_4O_3$), 0.5 H_2O calc. C 78.20, H 6.28, N 7.76, found C 78.34, H 6.02, N 7.71. UV-vis spectrum in CH_2Cl_2 : λ_{max}, nm (ε L.mmol^{-1}.cm^{-1}) : 416 (414.7), 512 (16.8), 548.5 (8.4), 586 (5.1), 641.5 (3.6). ^{1}H NMR ($CDCl_3$) δ (ppm) : 10.11 (s, 1H, H-20), 9.26 (d, 2H, *J* = 4.6 Hz, H-2, 18), 9.03 (d, 2H, *J* = 4.6 Hz, H-3, 17), 8.93 (d, 2H, *J* = 4.8 Hz, H-7, 13/8 12), 8.90 (d, 2H, *J* = 4.8 Hz, H-7, 13/8,12), 8.09 (d, 4H, *J* = 8.3 Hz, H-5, H-15, H-*o*-phenoxy), 8.07 (d, 2H, *J* = 8.0 Hz, H-10, H-*o*-phenoxy), 7.24 (d, 4H, *J* = 8.7 Hz, H-5, H-15, H-*m*-phenoxy), 7.21 (d, 2H, *J* = 9.0 Hz, H-10, H-*m*-phenoxy), 4.80 [sept, 2H, *J* = 6 Hz, H-5, 15, -$\underline{C}H(CH_3)_2$], 4.79 (sept, 1H, *J* = 6 Hz, H-10, -$\underline{C}H(CH_3)_2$), 1.53 [d, 12H, *J* = 6.0 Hz, H-5, 15, -CH($\underline{C}H_3)_2$], 1.52 [d, 6H, *J* = 6.0 Hz, H-10, -CH($\underline{C}H_3)_2$], -2.96 (s. 2H, NH). ^{13}C NMR ($CDCl_3$) δ (ppm) : 157.72 (C-*p*-phenoxy), 157.68 (C-*p*-phenoxy), 147.18-145.76 (C-1, 4, 6, 9, 11, 14, 16, 19), 135.79 (C-*o*-phenoxy), 135.62 (C-*o*-phenoxy), 134.77 (C-1-phenoxy), 133.90 (C-1-phenoxy), 131.41-130.59 (C-2, 3, 7, 8, 12, 13, 17, 18), 120.47 (C-10), 119.40 (C-5, C-15), 114.09 (C-*m*-phenoxy), 113.77 (C-*m*-phenoxy), 104.43 (C-20), 70.12 [-O-$\underline{C}H(CH_3)_2$], 22.30 [-O-CH($\underline{C}H_3)_2$].

General procedure for the synthesis of chlorins

The porphyrin (1 eq.) and anhydrous potassium carbonate (9 eq.) were dissolved in dry pyridine. *p*-Toluenesulfonhydrazide (2 eq.) in dry pyridine was added. The mixture was heated at 100-105°C under argon for 24 hours. Further quantities of *p*-toluenesulfonhydrazide (2 eq. in dry pyridine) were added after 2, 4, 6 and 8 hours. After cooling, the mixture was treated with ethyl acetate/water (2v/1v) and heated at 100°C. After cooling, the organic phase

was separated and washed twice with aqueous HCl (2 M), twice with water then saturated aqueous sodium hydrogen carbonate solution. The presence of chlorin and bacteriochlorin in the solution was controlled by UV-visible spectroscopy (bands at 651 and 738 nm, respectively). *o*-Chloranil (2.5 eq.) was slowly added to the stirred organic solution at room temperature until the absorption peak of bacteriochlorin species disappeared. The solution was washed with aqueous solution of $NaHSO_3$ (5 %), water and dried over sodium sulfate. The filtered solution was concentrated under vacuum. The crude product was purified by crystallization. The chlorin was obtained as mauve/green powder.

5,15-diphenyl-2,3-chlorin : **6a** The compound **6a** was prepared from 5,15-diphenylporphyrin **5a** (583 mg, 1.26 mmol). The chlorin **6a** after chromatography on silica gel eluted with a mixture of methylene chloride/n-heptane (1/1, v/v), crystallized from a mixture of methylene chloride/n-heptane (543 mg, yield 93 %). (Rf = 0.54, SiO_2, CH_2Cl_2/n-heptane, v/v, 1/1). Anal. ($C_{32}H_{24}N_4$), 2 CH_2Cl_2 calc. C 64.37, H 4.45, N 8.83, found C 65.61, H 3.76, N 8.77. UV-vis spectrum in CH_2Cl_2 : λ_{max}, nm (ε L.mmol^{-1}.cm^{-1}) : 409 (99.9), 504,5 (7.2), 531 (3.4), 590 (2.8), 642 (17.9). ^{1}H NMR ($CDCl_3$) δ (ppm) : 9.82 (s, 1H, H-10), 9.08 (d, 1H, *J* = 4.7 Hz, H-8), 8.97 (s, 1H, H-20), 8.94 (d, 1H, *J* = 4.3 Hz, H-12), 8.80 (d, 1H, *J* = 4.7 Hz, H-18), 8.77 (d, 1H, *J* = 4.7 Hz, H-17), 8.63 (d, 1H, *J* = 4.3 Hz, H-13), 8.36 (d, 1H, *J* = 4.7 Hz, H-7), 8.15-8.18 (m, 2H, H-*o*-phenyl), 7.89-7.92 (m, 2H, H-*o*-phenyl), 7.69-7.76 (m, 6H, H-*m, p*-phenyl), 4.64 (m, 2H, H-2), 4.32 (m, 2H, H-3), -1.44 (s, 1H, NH), -1.93 (s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ (ppm) : 167.7 (C-4), 167.1 (C-1), 152.4 (C-14), 151.5 (C-11), 142.06 (C-9), 141.2 (C-6), 139.9 (C-19), 135.7 (C-16), 134.2 (C-*o*-phenyl), 132.39 (C-*o*-phenyl), 132.19 (C-12), 131.5 (C-13), 128.3 (C-18), 128.2 (C-8), 127.6 (C-*m, p*-phenyl), 123.9 (C-17), 123.08 (C-7), 121.2 (C-15), 111.9 (C-5), 107.9 (C-10), 97.1 (C-20), 35.7 (C-2), 35.4 (C-3).

5,15-di(4-isopropyloxyphenyl)-2,3-chlorin : **6b** The title compound was prepared from 5,15-di(*4*-isopropyloxyphenyl-2,3-porphyrin **5b** (100 mg, 0.73 mmol). The chlorin **6b** crystallized from a mixture of methylene chloride/methanol (77 mg, yield 77 %). (Rf = 0.41, SiO_2, $CHCl_3$/n-heptane, v/v, 1/1). Anal. ($C_{38}H_{36}N_4O_2$), 5 H_2O calc. C 68.04, H 6.91, N 8.35, found C 67.87, H 6.58, N 5.89. UV-vis spectrum in CH_2Cl_2 : λ_{max}, nm (ε L.mmol^{-1}.cm^{-1}) : 411 (118.5), 506.5 (7.7), 538 (4.3), 588 (2.9), 643 (14.6). ^{1}H NMR ($CDCl_3$) δ (ppm) : 9.81 (s, 1H, H-10), 9.08 (d, 1H, *J* = 4.6 Hz, H-8), 8.98 (s, 1H, H-20), 8.94 (d, 1H, *J* = 4.4 Hz, H-12), 8.84 (d, 1H, *J* = 4.6 Hz, H-17), 8.77 (d, 1H, *J* = 4.6 Hz, H-18), 8.67 (d, 1H, *J* = 4.4 Hz, H-13), 8.41

(d, 1H, *J* = 4.5 Hz, H-7), 8.06 (d, 2H, *J* = 8.4 Hz, H-*o*-phenyl), 7.76 (d, 2H, *J* = 8.3 Hz, H-*o*-phenyl), 7.34-7.20 (m, 4H, H-*m*-phenyl), 4.83 [sept., 4H, *J* = 6 Hz, O-C$\underline{H}_2(CH_3)_2$], 4.66 (m, 2H, H-2), 4.35 (m, 2H, H-3), 1.55 [t, 12H, *J* = 6 Hz, O-$CH_2(C\underline{H}_3)_2$], -1.93 (s, 2H, NH). ^{13}C NMR ($CDCl_3$) δ (ppm) : 167.9 (C-4), 166.8 (C-1), 158 (C-*p*-phenyl), 153.5 (C-14), 150 (C-11), 141 (C-6), 140 (C-19), 136 (C-16), 135.2 (C-*o*-phenyl*)*, 134 (C-phenyl, C-9), 133 (C-*o*-phenyl), 132.5 (C-12), 131.7 (C-13), 128.2 (C-17), 127.9 (C-8), 123.5 (C-18), 123 (C-7), 121.5 (C-15), 115 (C-*m*-phenyl), 114 (C-*m*-phenyl), 111.3 (C-5), 108 (C-10), 96.9 (C-20), 70.2 (O-CH), 35.5 (C-2, C-3), 22.4 (CH_3).

***20-bromo-5,15-diphenyl-2,3-chlorin :* 7a** *and* ***12,20-dibromo-5,15-diphenyl-2,3-chlorin :* 8a**
The 5,10-diphenyl chlorin **6a** (100 mg, 0.215 mmol) was dissolved in methylene chloride (30 mL) then N-bromo-succinimide (NBS), (38 mg, 0.215 mmol) was added. The disappearance of initial product was controlled by analytical thin layer chromatography (SiO_2, eluted by a mixture of n-heptane/methylene chloride, 7/3, v/v). After one hour, the solution was concentrated under vacuum. The crude material was washed with hot methanol (185 mL). The crystallized crude product was dried under vacuum (over night, 0.5 mm Hg). The two compounds were purified by preparative silica gel thin layer chromatography eluted by a mixture of methylene chloride/n-heptane, 7/3, v/v. The 20-bromo-5,15-diphenyl-2,3-chlorin (Rf = 0.35, SiO_2, CH_2Cl_2/n-heptane, v/v, 7/3, 30 mg, yield 26 %) and the 12,20-dibromo-5,15-diphenyl-2,3-chlorin (Rf = 0.47, SiO_2, CH_2Cl_2/n-heptane, v/v, 7/3, 27 mg, 20%) were obtained as purple powders.

***20-bromo-5,15-diphenyl-2,3-chlorin :* 7a** Anal. ($C_{32}H_{23}BrN_4$), CH_2Cl_2, 2 C_7H_{16}, Calc. C 66.84, H 6.39, N 7.25, found. C 66.11, H 5.92, N 6.85. UV-vis spectrum in CH_2Cl_2 : λ_{max}, nm (ε L.mmol^{-1}.cm^{-1}) : 412 (188.5), 514 (13.2), 542 (9.2), 595 (5.8), 648 (33.4). ^{1}H NMR ($CDCl_3$) δ (ppm) : 9.67 (s, 1H, H-10), 9.17 (d, 1H, *J* =4.9 Hz, H-8), 8.99 (d, 1H, *J* = 4.8 Hz, H-18), 8.83 (d, 1H, *J* = 4.4 Hz, H-12), 8.70 (d, 1H, *J* = 4.9 Hz, H-7), 8.56 (d, 1H, *J* = 4.4 Hz, H-13), 8.28 (d, 1H, *J* = 4.7 Hz, H-17), 8.12 (m, 2H, H- *o*-phenyl), 7.82 (m, 2H, H- *o'*-phenyl), 7.71 (m, 9H, H-*m, p'*-phenyl*)*, 4.62 (m, 2H, H-12), 4.21 (m, 2H, H-3), -1.60 (s, 1H, NH)-1.90 (s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ (ppm) : 169.20 (C-4), 166.33 (C-1), 152.43 (C-14, C-11), 141.82 (C-1 phenyl), 141.43 (C-1 phenyl), 141.01 (C-16), 138.10 (C-9), 135.55 (C-6 or C-19), 135.37 (C-19 or C-6), 133.95 (C-*o*-phenyl), 133.03 (C-13), 132.33 (C-12), 132.26 (C-*o'*-

phenyl), 128.42 (C-18), 128.30 (C-7), 128.14 (C-*p*-phenyl), 126.83 (C-*m*-phenyl), 124.41 (C-17, C-8), 123.54 (C-15), 112.20 (C-5), 107.39 (C-10), 96.94 (C-20), 39.06 (C-2), 35.98 (C-3).

12,20-dibromo-5,15-diphenyl-2,3-chlorin : **8a** Anal. ($C_{32}H_{22}N_4O_4$), CH_2Cl_2, 2 C_7H_{16}, Calc. C 60.65, H 5.68, N 6.58, found C 62.45, H 5.44, N 6.56. UV-vis spectrum in CH_2Cl_2 : λ_{max}, nm (ε L.mmol^{-1}.cm^{-1}) : 412 (188.5), 518 (10.7), 545 (6.8), 595 (4.8), 648 (25.9). ^{1}H NMR ($CDCl_3$) δ (ppm) : 9.84 (s, 1H, H-10), 9.13 (d, 1H, *J* = 4.8 Hz, H-18), 9.04 (d, 1H, *J* = 4.8 Hz, H-8), 8.67 (d, 1H, *J* = 4.5 Hz, H-17), 8.53 (s, 1H, H-13), 8.28 (d, 1H, *J* = 4.8 Hz, H-7), 8.06 (m, 2H, H-*o*-phenyl), 7.83 (m, 2H, H-*o'*-phenyl), 7.71 (m, 6H, H-*m, p*-phenyl), 4.60 (m, 2H, H-2), 4.20 (m, 2H, H-3), -1.64 (s 1H, NH), -1.90 (s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ (ppm) : 169.91 (C-4), 167.01 (C-1), 150.20 (C-14 or C-11), 148.28 (C-11 or C-14), 141.82 (C-1, phenyl), 141.43 (C-1, phenyl), 140.86 (C-6 or C-9), 138.54 (C-19), 135.72 (C-9 or C-6), 135.22 (C-16), 133.85 (*o*-phenyl), 132.92 (C-13), 132.20 (*o*-phenyl), 129.16 (C-8), 128.86 (C-17), 128.22 (*p*-phenyl), 126.97 (*m*-phenyl), 124.87 (C-7 or C-18), 124.74 (C-18 or C-7), 123.39 (C-15), 120.72 (C-12), 112.65 (C-5), 104.73 (C-10), 97.20 (C-20), 39.06 (C-2), 36.02 (C-3).

20-bromo-5,15-di(4-isopropyloxyphenyl)-2,3-chlorin **: 7a** and ***12,20-dibromo-5,15-di(4-isopropyloxyphenyl)-2,3-chlorin*** **: 8b** The 5,10-di(4-isopropyloxyphenyl)chlorin **6b** (100 mg, 0.17 mmol) was dissolved in THF (100 mL) then NBS (31 mg, 0.17 mmol) was added. The disappearance of initial product was controlled by analytical thin layer chromatography (SiO_2, eluted by toluene). After one hour, the solution was concentrated under vacuum. The crude material was washed with hot methanol (185 mL). The crystallized crude product was dried under vacuum (overnight, 0.5 mm Hg). The two compounds were purified by preparative silica gel thin layer chromatography eluted by toluene. The 20-bromo-5,15-di(4-isopropyloxyphenyl)-2,3-chlorin **7b** (Rf = 0.67, SiO_2, toluene, 62 mg, yield 44 %) and the 12,20-dibromo-5,15-di(4-isopropyloxyphenyl)-2,3-chlorin **8b** (Rf = 0.84, SiO_2, toluene, 18 mg, 12 %) were obtained as purple powders.

20-bromo-5,15-di(4-isopropyloxyphenyl)-2,3-chlorin : **7b** UV-vis spectrum in CH_2Cl_2 : λ_{max}, nm (ε L.mmol^{-1}.cm^{-1}) : 409.5 (155.7), 515 (11.7), 543.5 (12.1), 596 (5.4), 649 (34.8). ESI$^+$ MS calc. for $C_{38}H_{35}BrN_4O_2$, $(M+H)^+$ 659.19, found 659.2. ^{1}H NMR ($CDCl_3$) δ (ppm) : 9.68 (s, 1H, H-10), 9.18 (d, 1H, *J* = 4.6 Hz, H-8), 9.01 (d, 1H, *J* = 4.5 Hz, H-18), 8.85 (d, 1H,

J = 4.4 Hz, H-12), 8.76 (d, 1H, *J* = 4.9 Hz, H-7), 8.62 (d, 1H, *J* = 4.3 Hz, H-13), 8.35 (d, 1H, *J* = 4.5 Hz, H-17), 8.02 (d, 2H, *J* = 8.5 Hz, H-*o*-phenyl), 7.75 (d, 2H, *J* = 8.5 Hz, H-*o'*-phenyl), 7.23 (m, 4H, H-*m*-phenyl), 4.83 [sept, 2H, *J* = 6.2 Hz, C<u>H</u>$(CH_3)_2$], 4.67 (m, 2H, H-2), 4.29 (m, 2H, H-3), 1,57 [m, 12H, CH(C<u>H</u>$_3)_2$], -1.51 (s, 1H, NH), -1.84 (s, 1H, NH).

12, 20-dibromo-5,15-di(4-isopropyloxyphenyl)-2,3-chlorin : **8b** UV-vis spectrum in CH_2Cl_2 : λ_{max}, nm (ε L.mmol^{-1}.cm^{-1}) : 416 (181.9), 520 (13.9), 549.5 (11.2), 596 (6.7), 648.5 (35.8). ^{1}H NMR ($CDCl_3$) δ (ppm) : 9.83 (s, 1H, H-10), 9.15 (d, 1H, *J* = 4.3 Hz, H-18), 9.05 (d, 1H, *J* = 4.5 Hz, H-8), 8.74 (d, 1H, *J* = 3.7 Hz, H-17), 8.60 (s, 1H, H-13), 8.35 (d, 1H, *J* = 3.5 Hz, H-7), 7.97 (d, 2H, *J* = 8.5 Hz, H-*o*-phenyl), 7.72 (d, 2H, *J* = 8.5 Hz, H-*o'*-phenyl), 7.22 (m, 4H, H-*m*-phenyls), 4.82 [sept, 2H, *J* = 6.2 Hz, C<u>H</u>$(CH_3)_2$], 4.63 (m, 2H, H-2), 4.26 (m, 2H, H-3), 1,56 [m, 12H, CH(C<u>H</u>$_3)_2$], -1.55 (s, 1H, NH), -1.81 (s 1H, NH).

5,10,20-triphenyl-2,3-chlorin : **9a**

1) **By Suzuki's reaction** : 20-Bromo-5,15-diphenyl-2,3-chlorin **7a** (32 mg, 0.06 mmol) were dissolved in freshly distilled dimethylformamide (15 mL) and kept under argon during 1 hour. $Pd(PPh_3)_4$ (20.5 mg, 0.02 mmol), phenylboronic acid (36 mg, 0.3 mmol) and aqueous sodium carbonate (236 µL, 0.5 mMol) were added. The crude solution was refluxed for 3 hours. The solution was concentrated under vacuum. The crude product was purified by silica gel column chromatography (Rf = 0.35, CH_2Cl_2/cyclohexane, 1/1, v/v) and crystallized from a mixture of CH_2Cl_2-heptane. Titled compound was obtained as mauve/green powder (14 mg, yield 44 %).

2) **By modified Bonnett's method** : The 5,10,15-triphenyl porphyrin **10** (50 mg, 9.2 10^{-5} mol) and anhydrous potassium carbonate (384 mg, 2.78 mmol, 30 eq.) were dissolved in dry pyridine (4.5 mL). *p*-Toluenesulfonhydrazide (345 mg, 1.85 mmol, 20 eq.) in dry pyridine (1 mL) was added. The mixture was heated at 100-105°C under argon for 24 hours. Further quantities of *p*-toluenesulfonhydrazide (35 mg, 2 eq. in 1 mL of dry pyridine) were added after 2, 4, 6 and 8 hours. After cooling, the mixture was treated with a mixture of ethyl acetate/water (45 mL, 2/1, v/v) and heated at 100°C. After cooling, the organic phase was separated and washed twice with aqueous HCl (2 M), twice with water then saturated aqueous sodium hydrogen carbonate solution. The presence of bacteriochlorin was controlled by UV-visible spectroscopy (band at 738 nm). *o*-Chloranil (57 mg, 2.5 eq.) was slowly added to the stirred organic solution at room temperature until the absorption peak of bacteriochlorin species disappeared. The solution was washed with aqueous solution of $NaHSO_3$ (5 %), water

and dried over sodium sulfate. The filtered solution was concentrated under vacuum. The crude product was purified by crystallization from a mixture of methylene chloride/heptane. The chlorin was obtained as mauve/green powder (30 mg, yield 60 %). Anal. ($C_{38}H_{28}N_4$), H_2O Calc. C 81.70, H 5.41, N 10.03, found C 82.86, H 5.45, N 8.51. UV-vis spectrum in CH_2Cl_2 : λ_{max}, nm (ε $L.mmol^{-1}.cm^{-1}$) : 412 (99.4), 510 (7.6), 537 (4.1), 595 (2.8), 647 (18.7). ^1H NMR ($CDCl_3$) δ (ppm) : 9.77 (s. 1H, H-15), 9.05 (d, 1H, *J* = 6.0 Hz, H-17), 8.92 (d, 1H, *J* = 4.3 Hz, H-13), 8.62 (d, 1H, *J* = 4.9 Hz. H-8), 8.59 (d, 1H, *J* = 4.3 Hz, H-12), 8.33 (d, 1H, *J* = 6.0 Hz, H-18), 8.18 (d, 1H, *J* = 4.9 Hz, H-7), 8.13 (m, 2H, H-10, H-*o*-phenyl), 7.91-7.84 (m, 4H, H-5, 20, H-*o'*-phenyl), 7.72-7.64 (m, 9H, H-5, 10, 20, H-*m, p*-phenyl), 4.18 (s, 4H, H-2, 3), -1.55 (broad s, 1H, NH), -1.86 (broad s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ (ppm) : 167.61-166.53 (C-1, 4), 152.71 (C-11), 151.42 (C-14), 143.49-142.48 (C-1-phenyl), 141.66 (C-1-phenyl), 140.69 (C-19), 140.11 (C-6), 135.33 (C-9), 134.68 (C-16), 133.99 (C-*o*-phenyl), 132.32-131.90 (C-*p*-phenyl, C-*m*-phenyl, C-12, 13), 128.57-126.76 (C-*m*-phenyl, C-8, 17), 123.61-123.50 (C-7, 18), 122.19 (C-10), 112.42-111.90 (C-5, 20), 107.44 (C-15), 36.2-35.7 (C-2, 3).

5,10,20-tri(4-isopropyloxyphenyl)-2,3-chlorin : **9b**

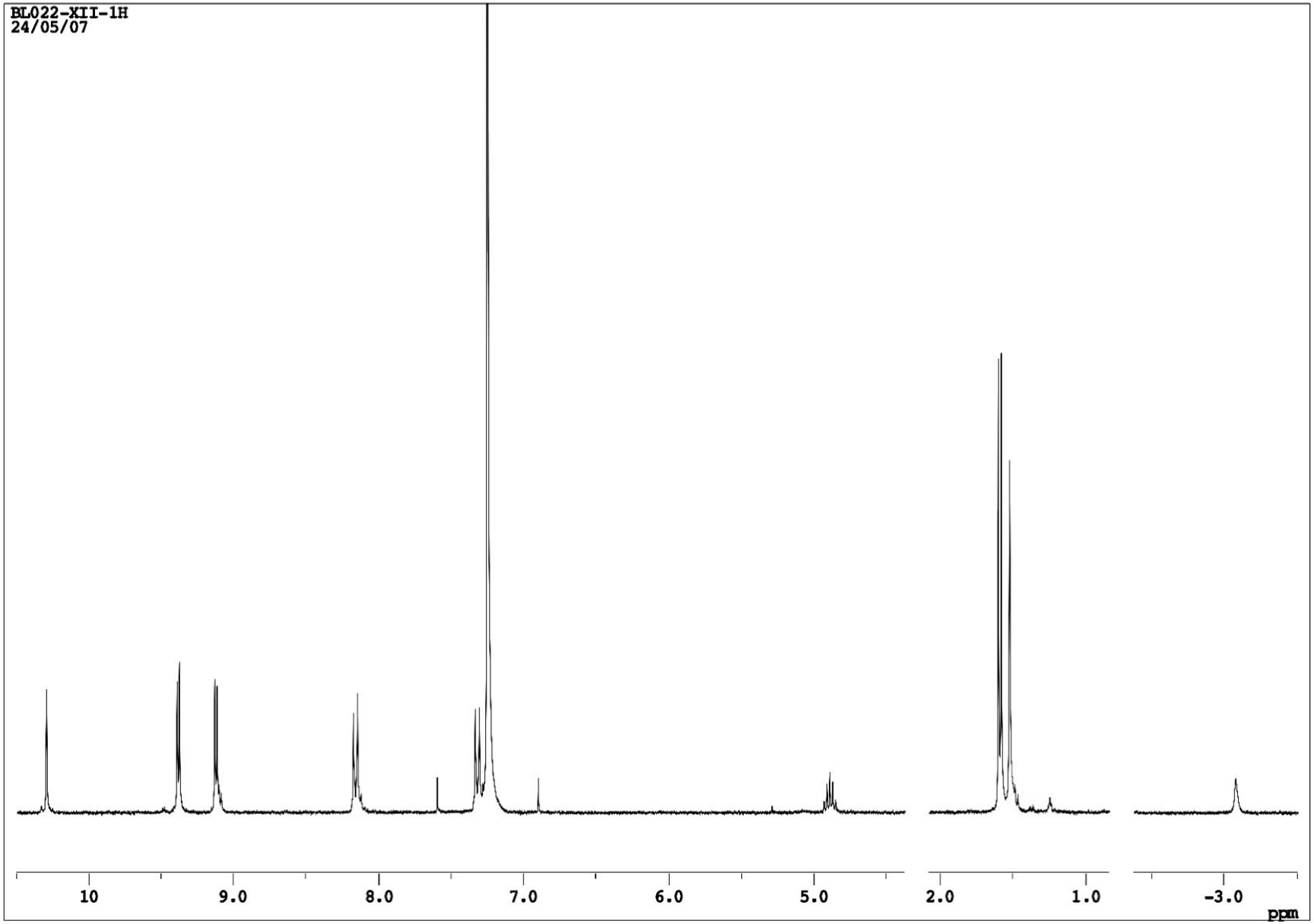
1) **By Suzuki's reaction** : 20-Bromo-5,15-di(4-isopropyloxyphenyl)-2,3-chlorin **7b** (61 mg, 0.082 mmol) were dissolved in a mixture of dioxane/water (6 mL/1 mL) and kept under argon during 1 hour. $Pd(PPh_3)_4$ (10 mg, 0.008 mmol), 4-isopropoxyphenylboronic acid (144 mg, 0.8 mmol) and aqueous sodium carbonate (140 mg, 1 mmol) were added. The crude solution was heated at 100°C for 1 hours. The solution was concentrated under vacuum. The crude product was purified by silica gel column chromatography (Rf = 0.25, toluene) and crystallized from a mixture of CH_2Cl_2-methanol. Titled compound was obtained as mauve/green powder (43 mg, yield 62 %).

2) **By modified Bonnett's method** : The 5,10,15-tri-(5-isopropyloxyphenyl)porphyrin **13** (50 mg, 7 10^{-5} mol) and anhydrous potassium carbonate (485 mg, 2.78 mmol, 40 eq.) were dissolved in dry pyridine (4.5 mL). *p*-Toluenesulfonhydrazide (263 mg, 1.4 mmol, 20 eq.) in dry pyridine (1 mL) was added. The mixture was heated at 100-105°C under argon for 24 hours. Further quantities of *p*-toluenesulfonhydrazide (40 mg, 5 eq. in 1 mL of dry pyridine) were added after 2, 4, 6 and 8 hours. After cooling, the mixture was treated with a mixture of chloroform/water (45 mL, 2v/1v) and heated at 100°C. After cooling, the organic phase was separated and washed twice with aqueous HCl (2 M), twice with water then saturated aqueous

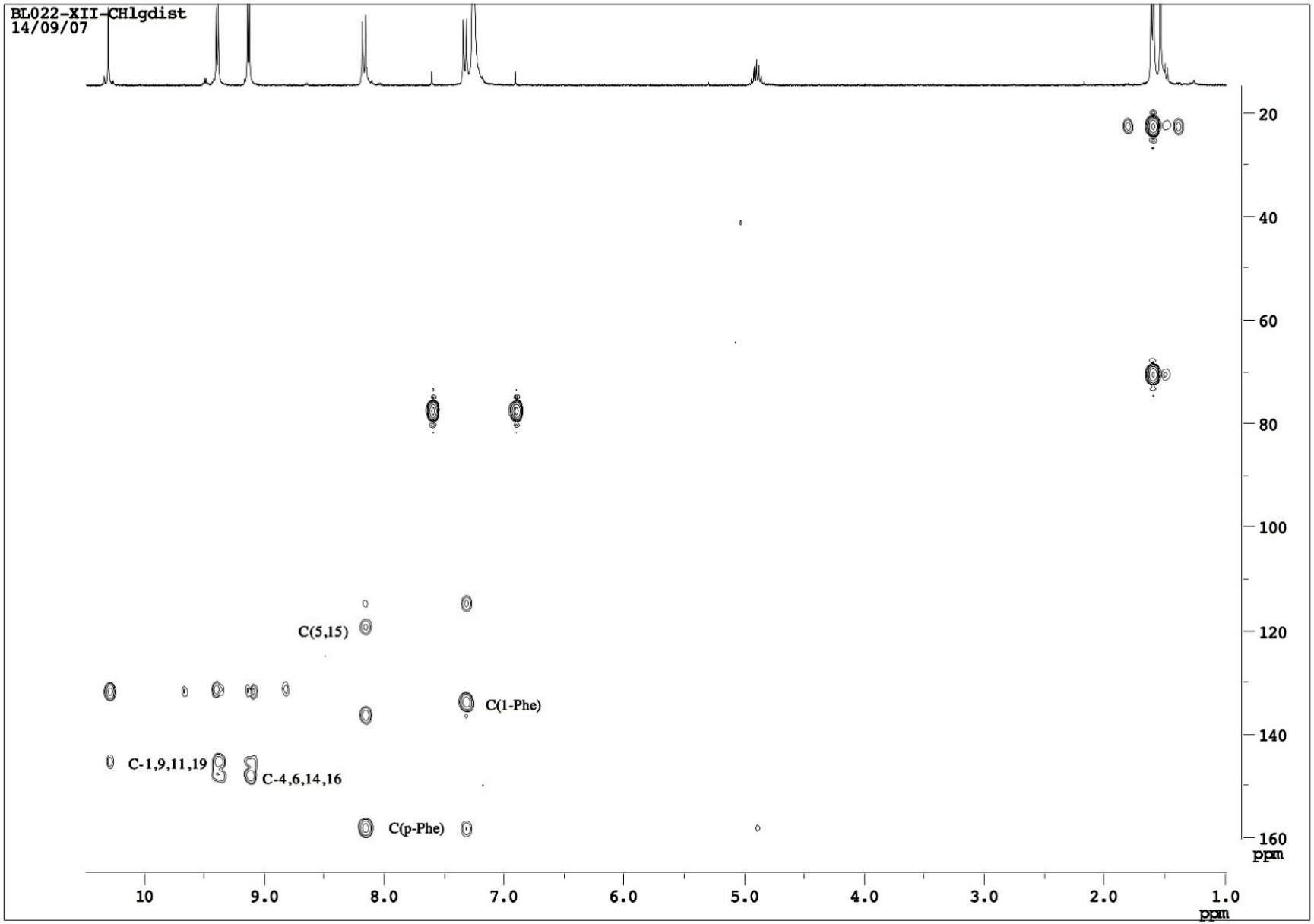
sodium hydrogen carbonate solution. The presence of bacteriochlorin was controlled by UV-visible spectroscopy (band at 738 nm). *O*-chloranil (25 mg, 1.2 eq.) was slowly added to the stirred organic solution at room temperature until the absorption peak of bacteriochlorin species disappeared. The solution was washed with aqueous solution of $NaHSO_3$ (5 %), water and dried over sodium sulfate. The filtered solution was concentrated under vacuum. The crude product was purified by crystallization (methylene chloride/heptane). The chlorin was obtained as mauve/green powder (30 mg, yield 60 %). Anal. ($C_{47}H_{46}N_4O_3$), H_2O calc. C 77.02, H 6.60, N 7.64, found C 76.11, H 6.38, N 7.39. UV-vis spectrum in CH_2Cl_2 : λ_{max}, nm (ε L.mmol^{-1}.cm^{-1}) : 416 (183.1), 513.5 (13.2), 542 (9.4), 595 (5.3), 648 (33.2). ^{1}H NMR ($CDCl_3$) δ (ppm) : 9.73 (s, 1H, H-15), 9.04 (d, 1H, *J* = 4.7 Hz, H-17), 8.89 (d, 1H, *J* = 4.3 Hz, H-13), 8.66 (d, 1H, *J* = 4.8 Hz, H-8), 8.62 (d, 1H, *J* = 4.3 Hz, H-12), 8.37 (d, 1H, *J* = 4.7 Hz, H-18), 8.22 (d, 1H, *J* = 4.8 Hz, H-7), 8.01 (d, 2H, *J* = 8.5 Hz, H-10, H-*o*-phenoxy), 7.72 (m, 4H, H-5, 20, H-*o'*-phenoxy), 7.18 (d, 2H, *J* = 8.5 Hz, H-10, H-*m*-phenoxy), 7.12 (m, 4H, H-5, 20, H-*m*-phenoxy), 4.80 [m, 3H, -O-C<u>H</u>-$(CH_3)_2$], 4.18 (s, 4H, H- 2, 3), 1.53 [m, 18H, -O-CH-$(C\underline{H}_3)_2$], -1.56 (broad s, 1H, NH), -1.87 (broad s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ (ppm) : 168.03-166.93 (C-1, 4), 157.6 (*p*-phenoxy), 153.06 (C-11), 151.28 (C-14), 141.25 (C-19), 140.42 (C-6), 135.60-133.90 (C-*m*-phenoxy, C-*o*-phenoxy, C-9, C-16), 132.40 (C-12, C-13), 128.18-127.50 (C-17, C-8), 122.97 (C-7, C-18), 122.05 (C-10), 115.93-114.12 (C-*m*-phenoxy), 111.9 (C-5, C-20), 106.33 (C-15), 70.91-69.11 [O-<u>C</u>H-$(CH_3)_2$], 35.9 (C-2, C-3), 23.04-21.54 [CH-$(CH_3)_2$].

12-iodo-5,15-diphenyl-2,3-chlorin : 5,15-diphenylchlorin **6a** (46 mg, 0.1 mmol) and iodine (38.7 mg, 0.15 mmol) were dissolved in chloroform (50 mL). A solution of [bis(fluoroacetoxy)iodo]benzene (15.4 mg, 0.036 mmol) in chloroform (0.5 mL) was added slowly. The end of the reaction was checked by thin layer chromatography (chloroform/cyclohexane, 1/1, v/v). After 15 min, the solution was washed with water (3x), dried over sodium sulfate, filtered and concentrated under vacuum. The crude product was purified by silica gel chromatography (Rf = 0.72, SiO_2, chloroform/cyclohexane, 1/1, v/v). The iodochlorin was obtained as mauve/green powder (19 mg, yield 35 %). UV-vis spectrum in CH_2Cl_2, trace of triethylamine : λ_{max}, nm : 416 (1), 512 (0.08), 542 (shoulder), 589.5 (0.037), 648 (0.178). ESI$^+$ MS calc. for $C_{32}H_{23}IN_4$, $(M+H)^+$ 591.10, found 591.16. ^{1}H NMR ($CDCl_3$) δ (ppm) : 9.89 (s, 1H, H-10), 9.12 (dd, 1H, *J* = 4.73, 1.89 Hz, H-8), 8.94 (s, 1H, H-20), 8.78 (s, H-13), 8.74 (d, 1H, *J* = 4.8 Hz, H-18), 8.71 (d, 1H, *J* = 4.8 Hz, H-17), 8.34 (dd, 1H, *J* = 4.73, 3.02, H-7), 8.10 (m, 2H, H-*o*-phenyl), 7.86 (m, 2H, H-*o'*-phenyl), 7.70 (m, 6H,

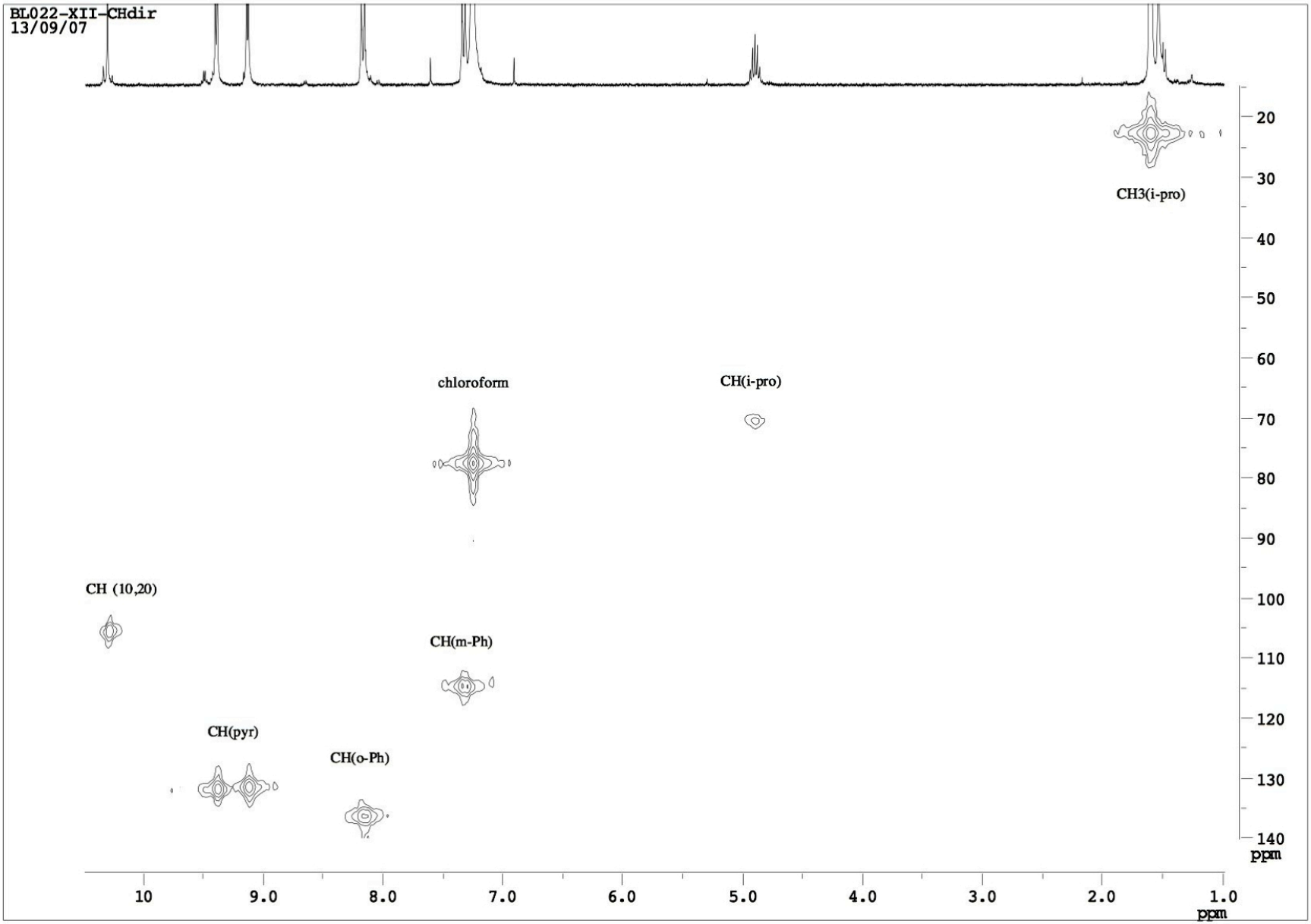
H-*m, p*-phenyl), 4.58 (dd, 2H, *J* = 4.58, 8.08 Hz, H-2), 4.27 (dd, 2H, *J* = 4.77, 8.03 Hz, H-3), -1.53 (broad s, 1H, NH), -1.89 (s, 1H, NH).



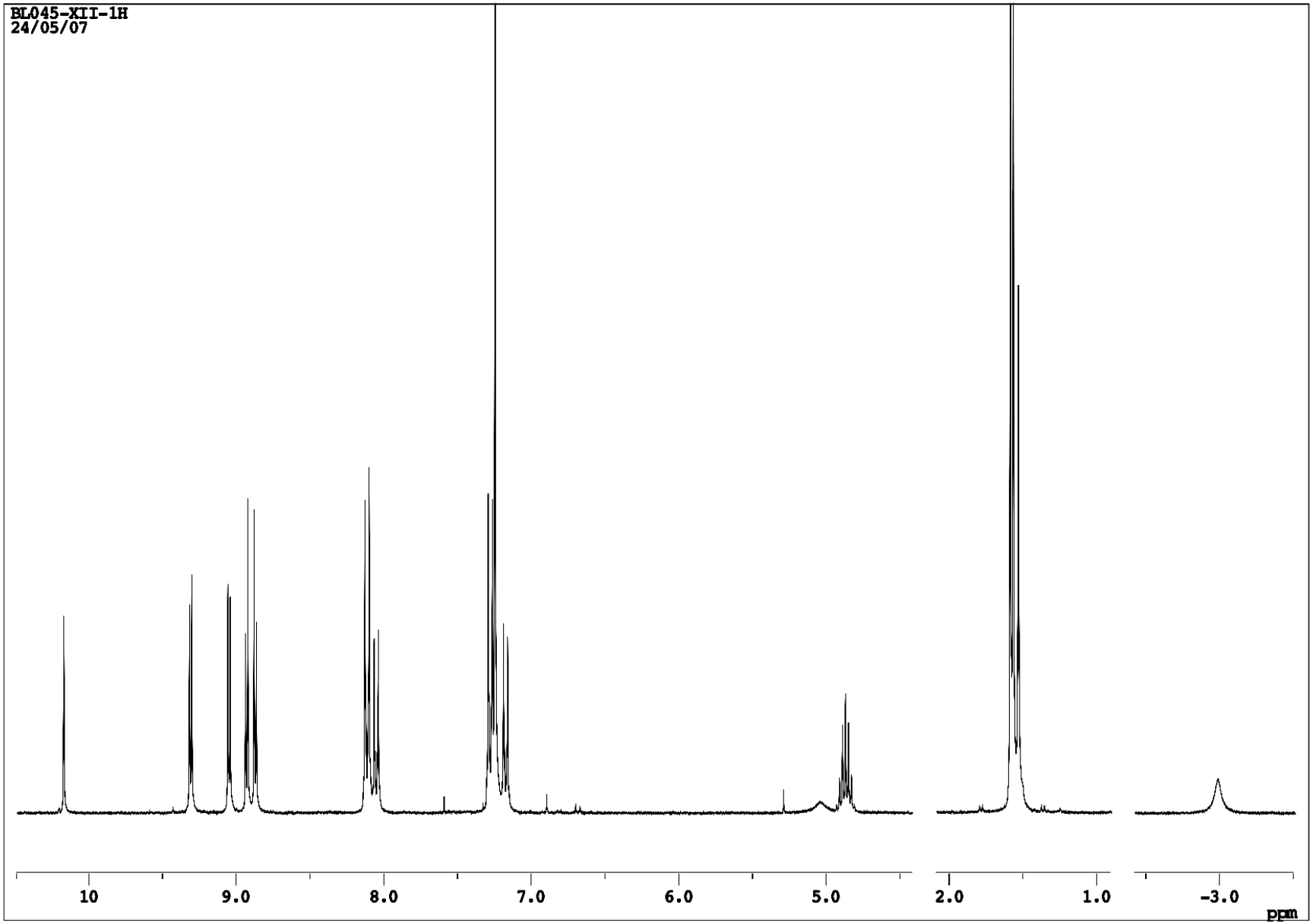
^{1}H NMR spectrum of chlorin **5b** in $CDCl_3$



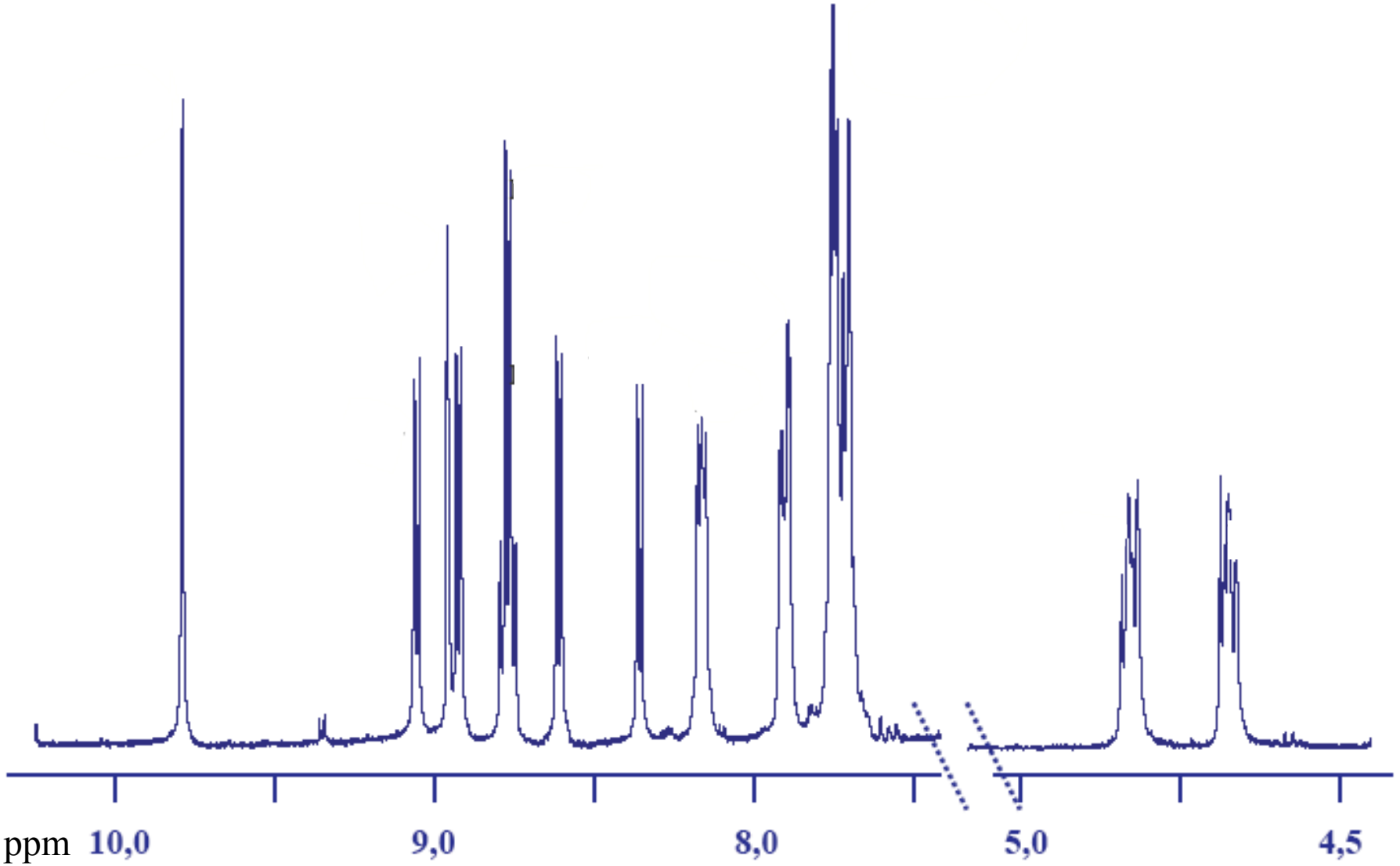
2D NMR spectrum (HMBC) of chlorin **5b** in $CDCl_3$



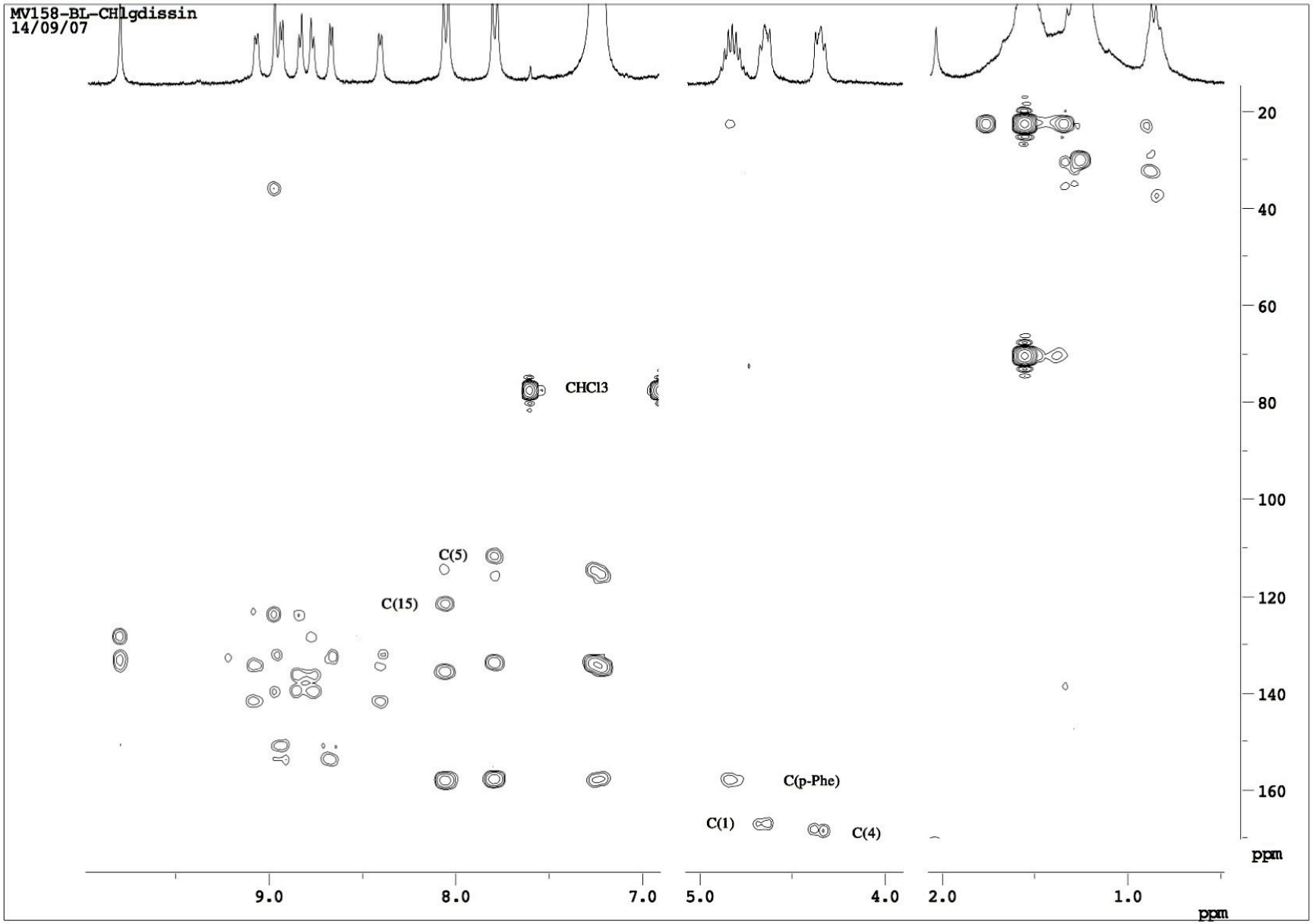
2D NMR spectrum (HMQC) of chlorin **5b** in $CDCl_3$



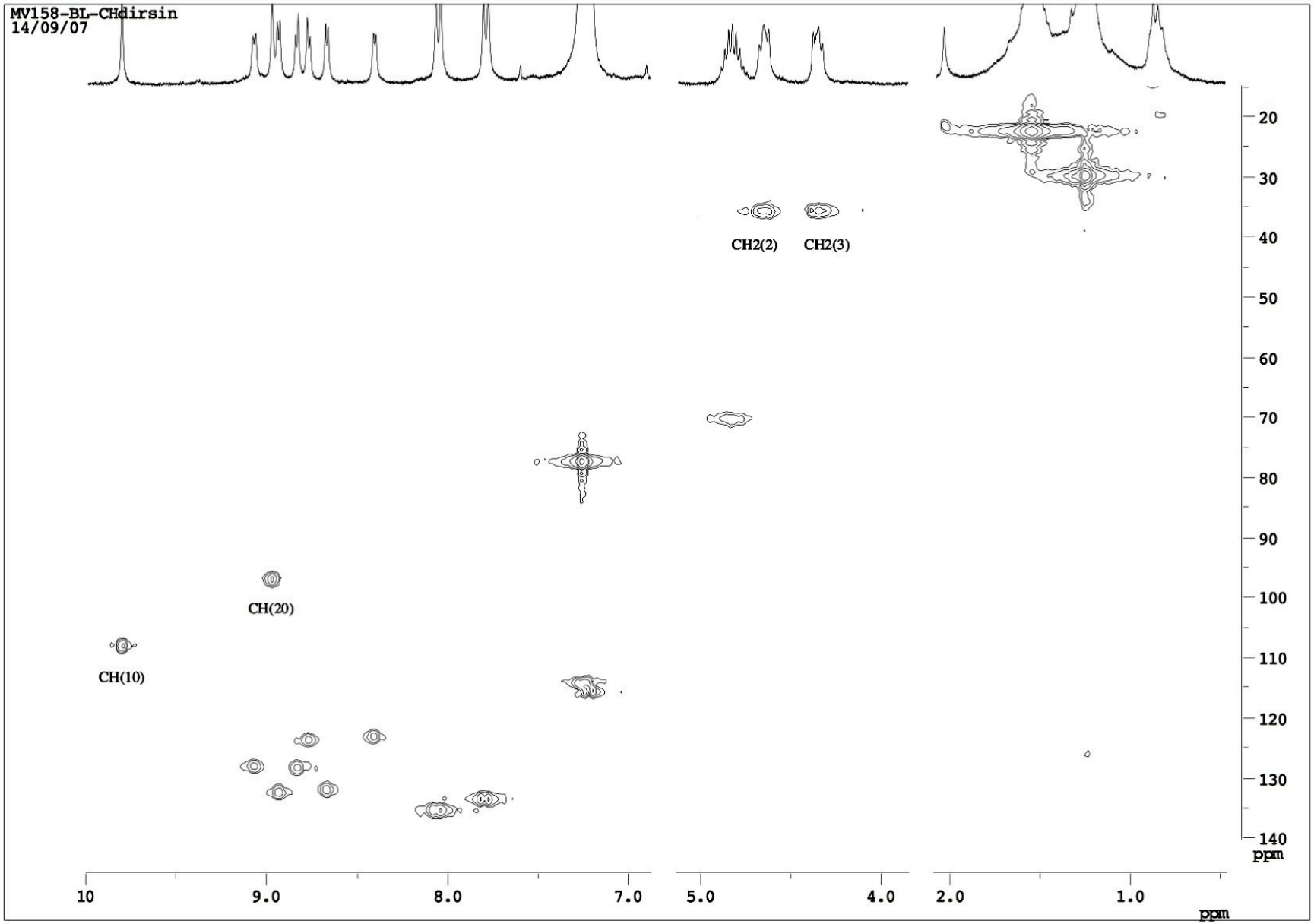
^{1}H NMR spectrum of 5,15-di(*p*-*iso*-propyloxyphenyl)-10-(*p*-hydroxyphenyl)porphyrin in $CDCl_3$



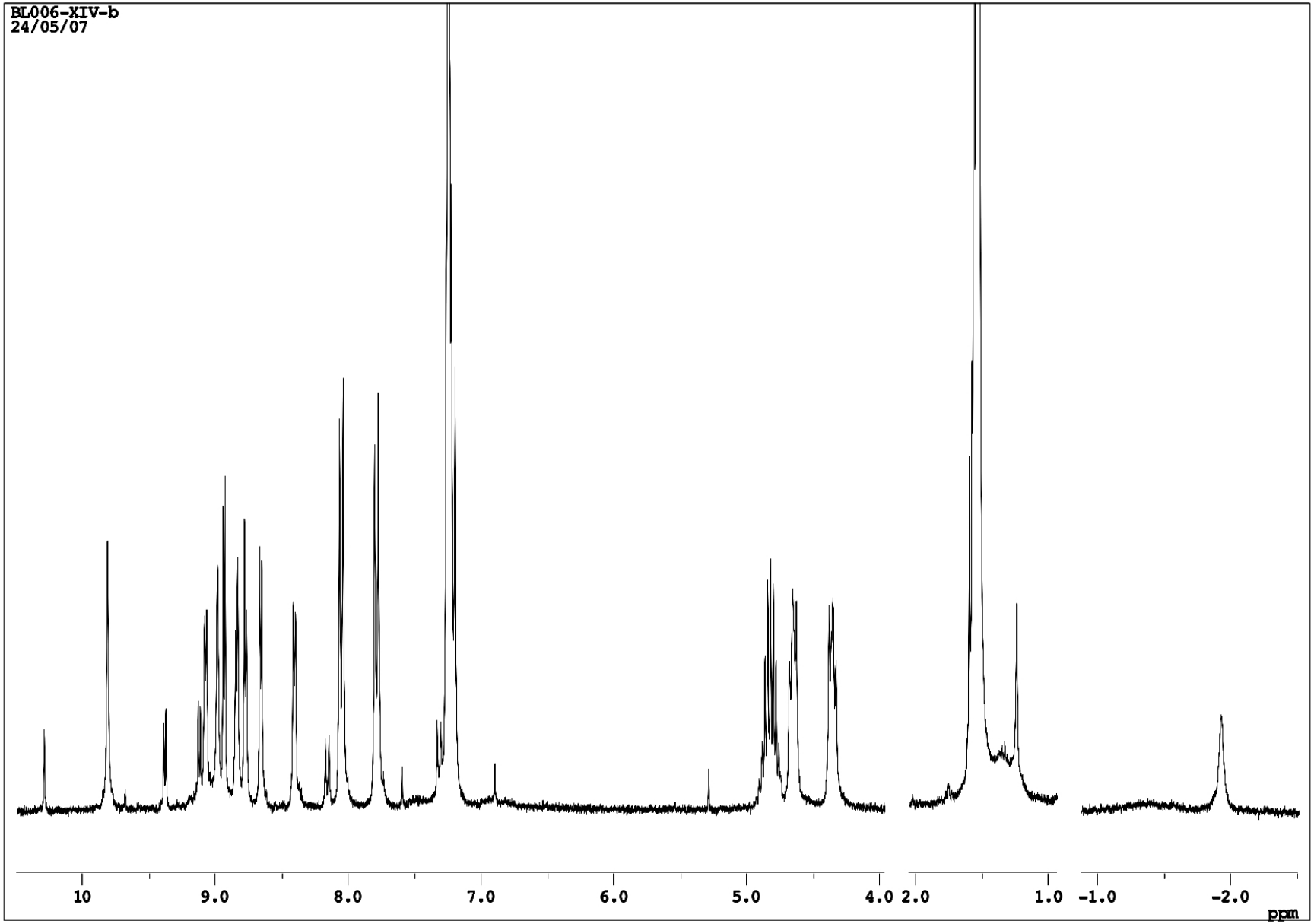
^{1}H NMR spectrum of chlorine **6a** in $CDCl_3$



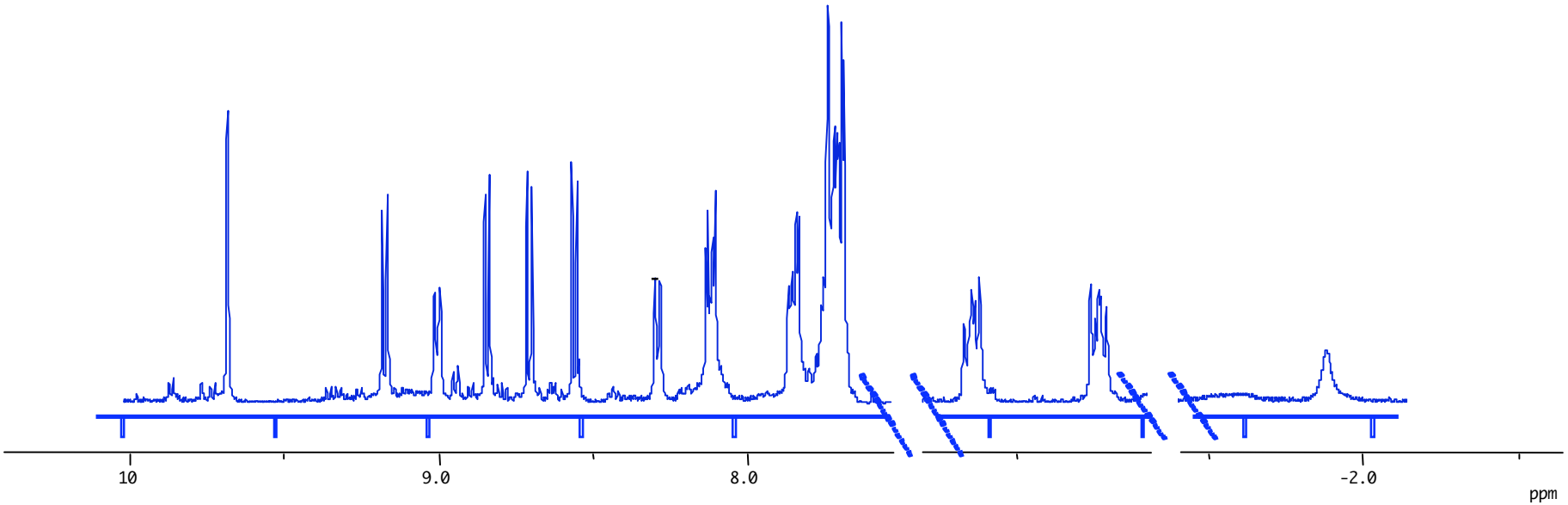
2D NMR spectrum (HMBC) of chlorin **6a** in $CDCl_3$



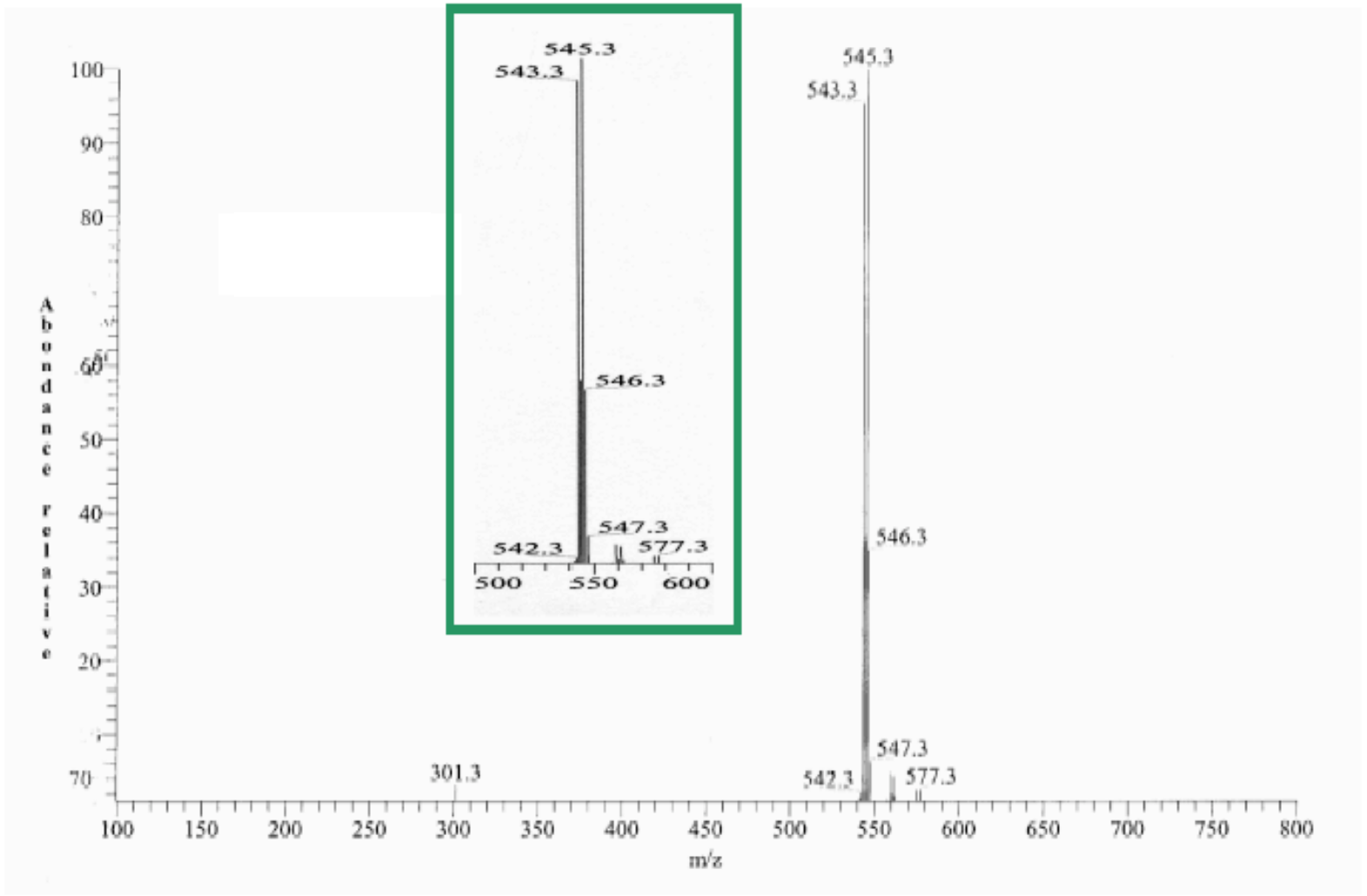
2D NMR spectrum (HMQC) of chlorin **6a** in $CDCl_3$



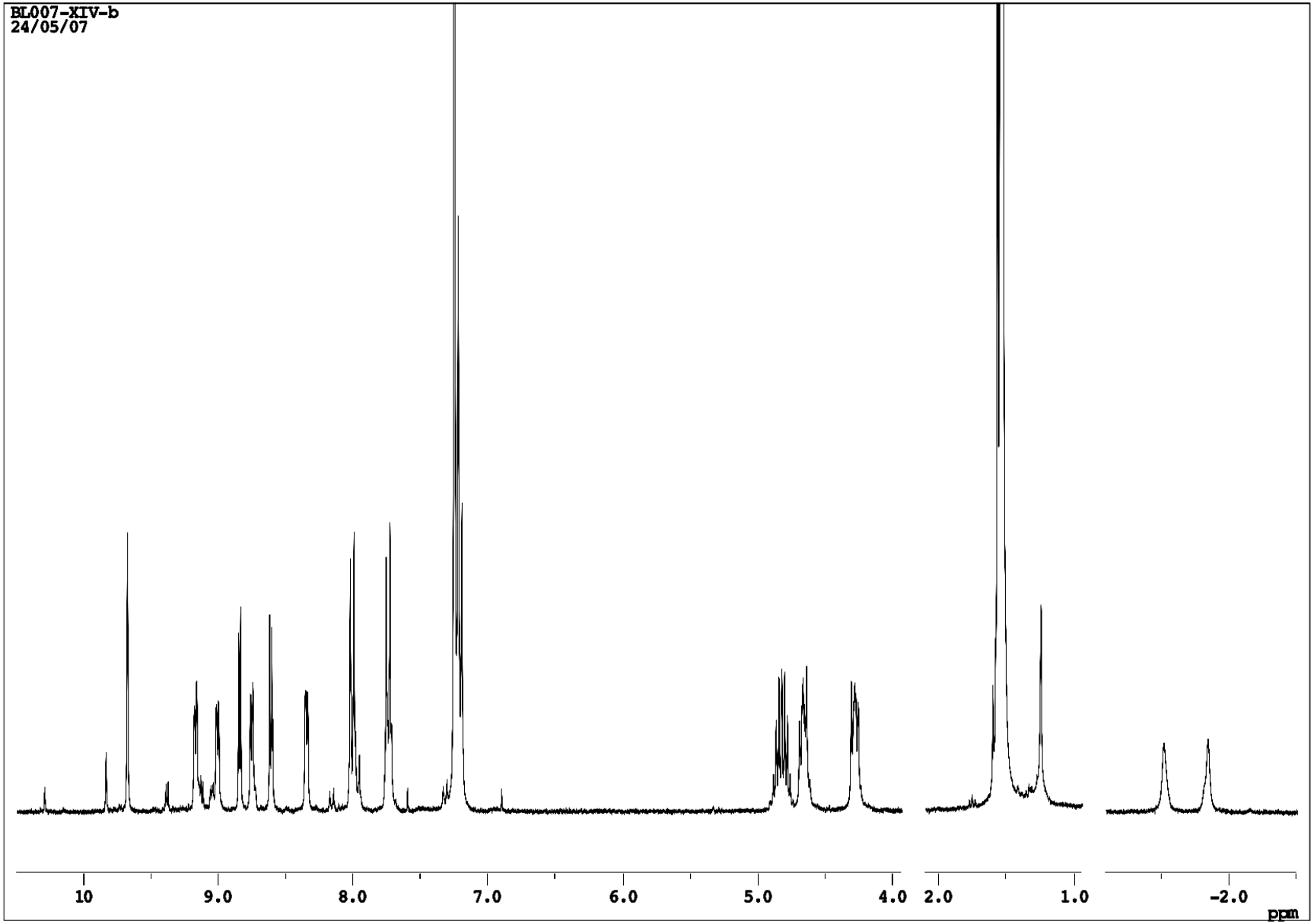
^{1}H NMR spectrum of chlorin **6b** in $CDCl_3$



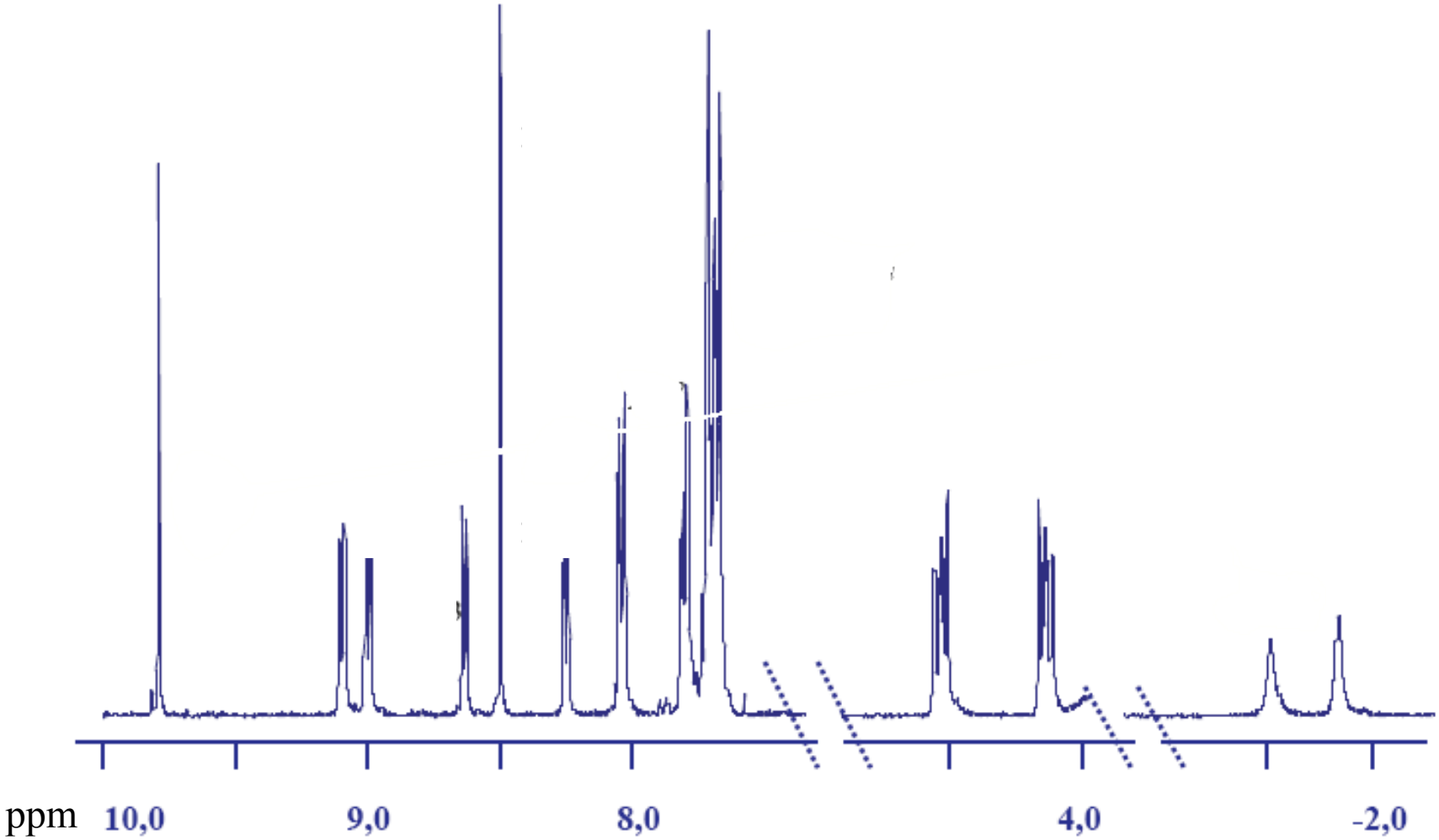
^{1}H NMR spectrum of chlorin **7a** in $CDCl_3$



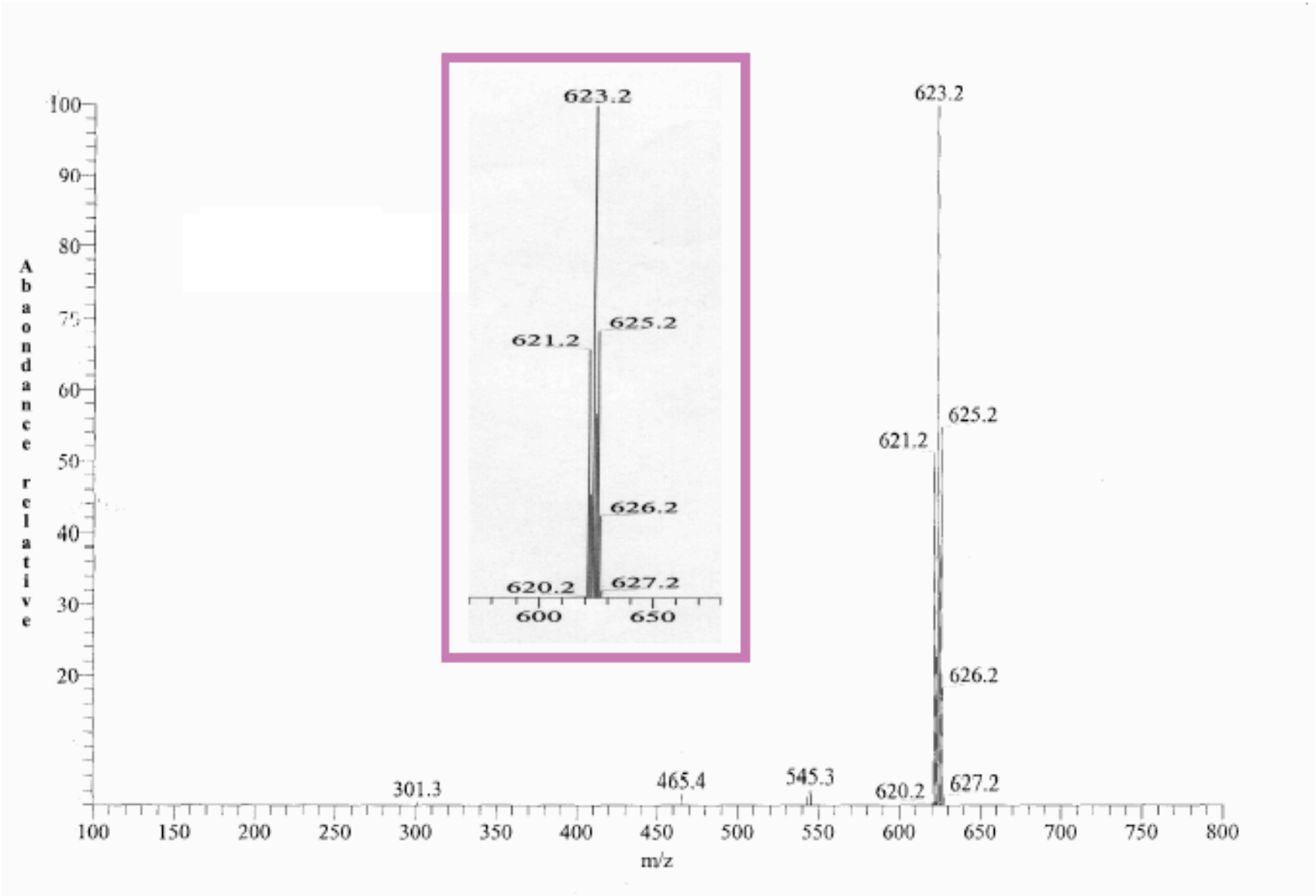
MALDI-TOF mass spectrum of chlorin **7a**



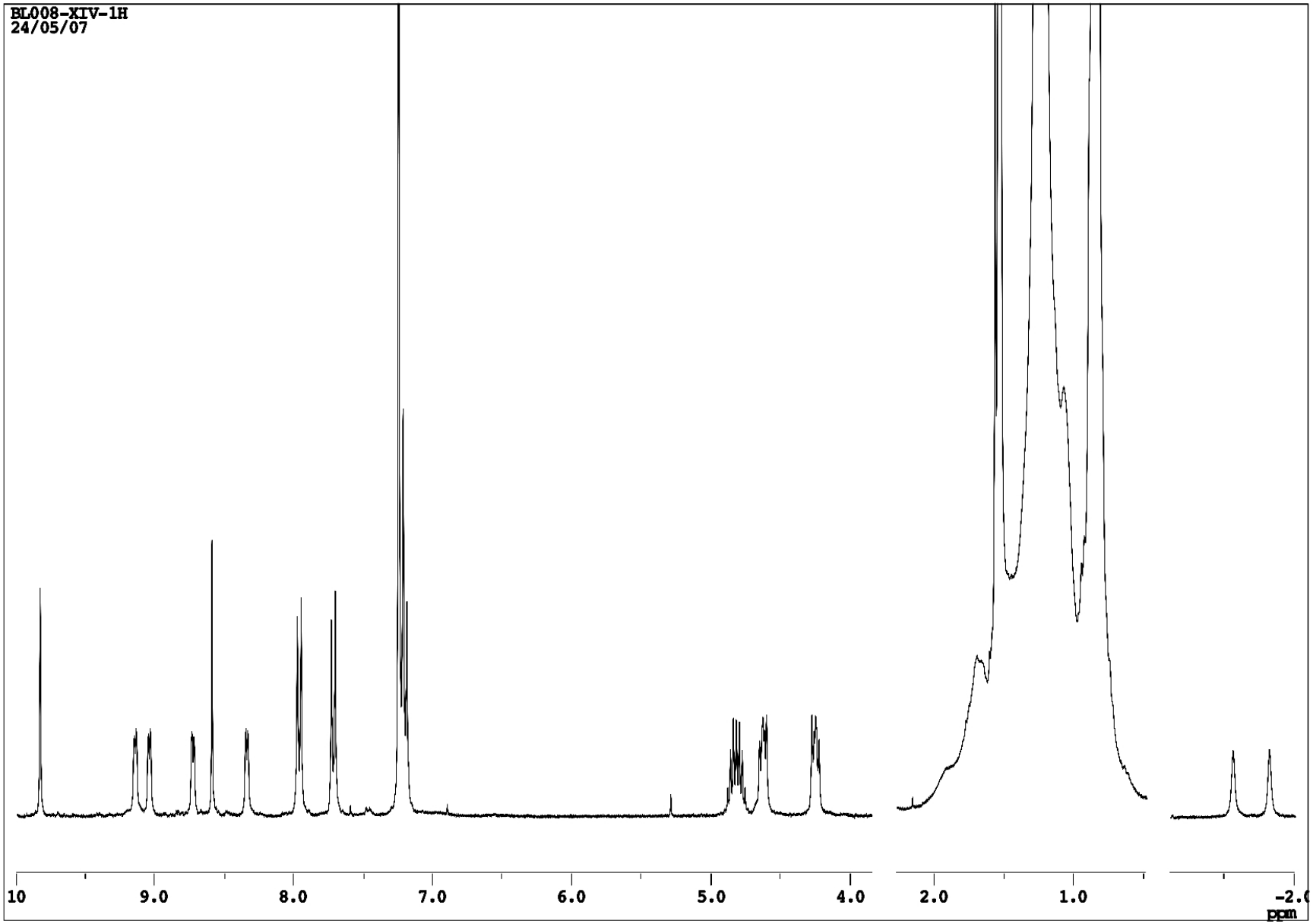
^{1}H NMR spectrum of chlorin **7b** in $CDCl_3$



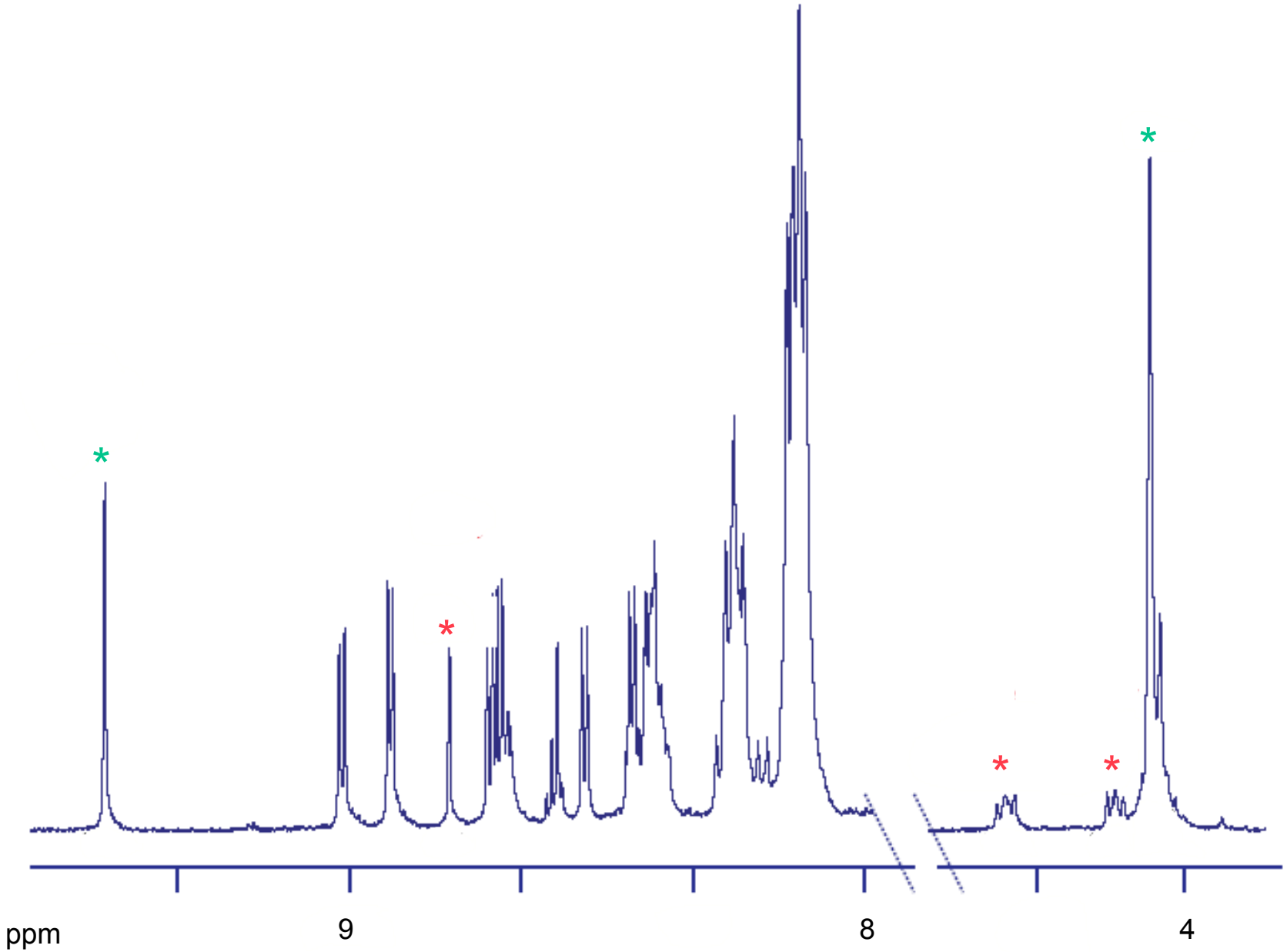
^{1}H NMR spectrum of chlorin **8a** in $CDCl_3$



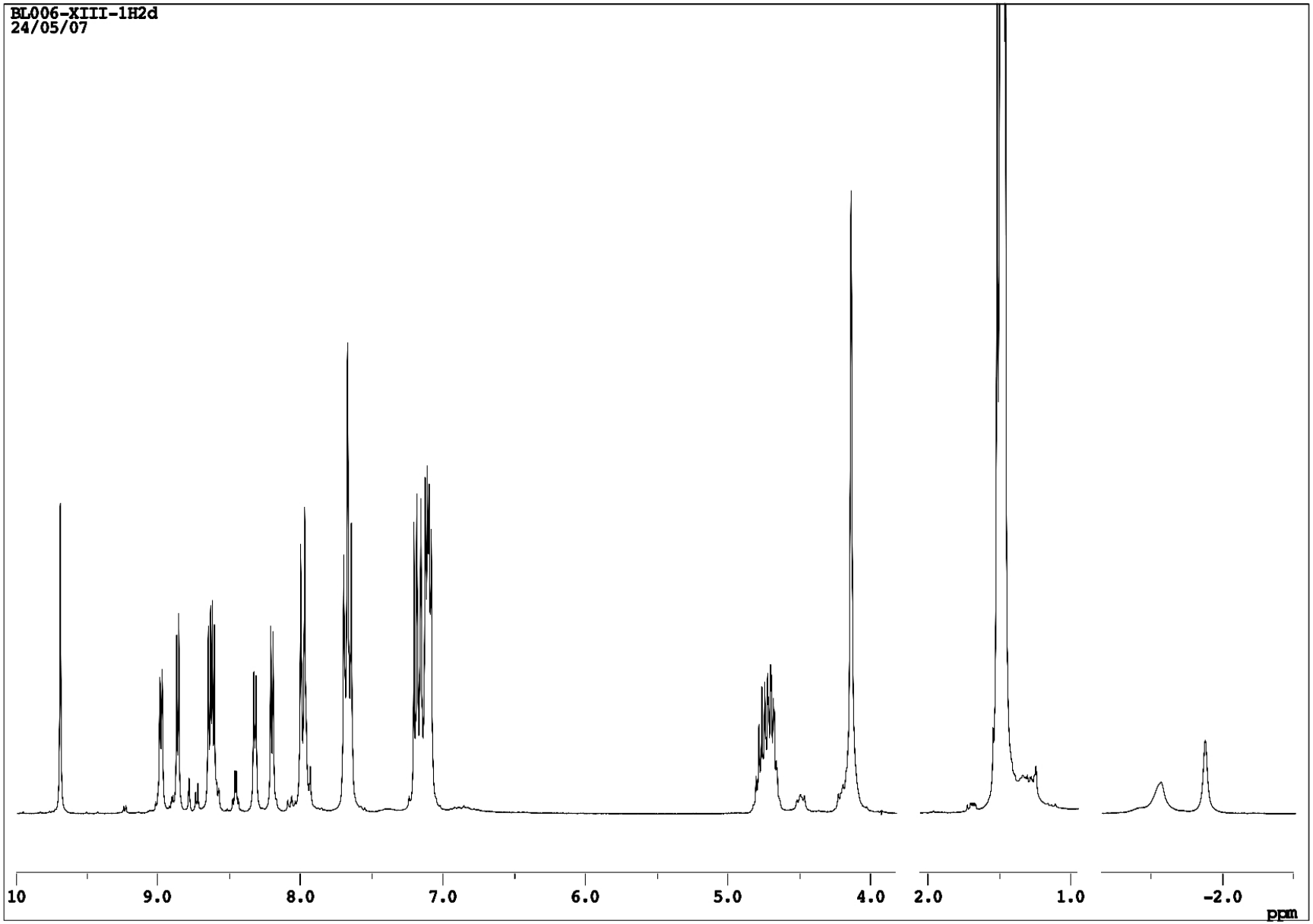
MALDI-TOF mass spectrum of chlorin **8a**



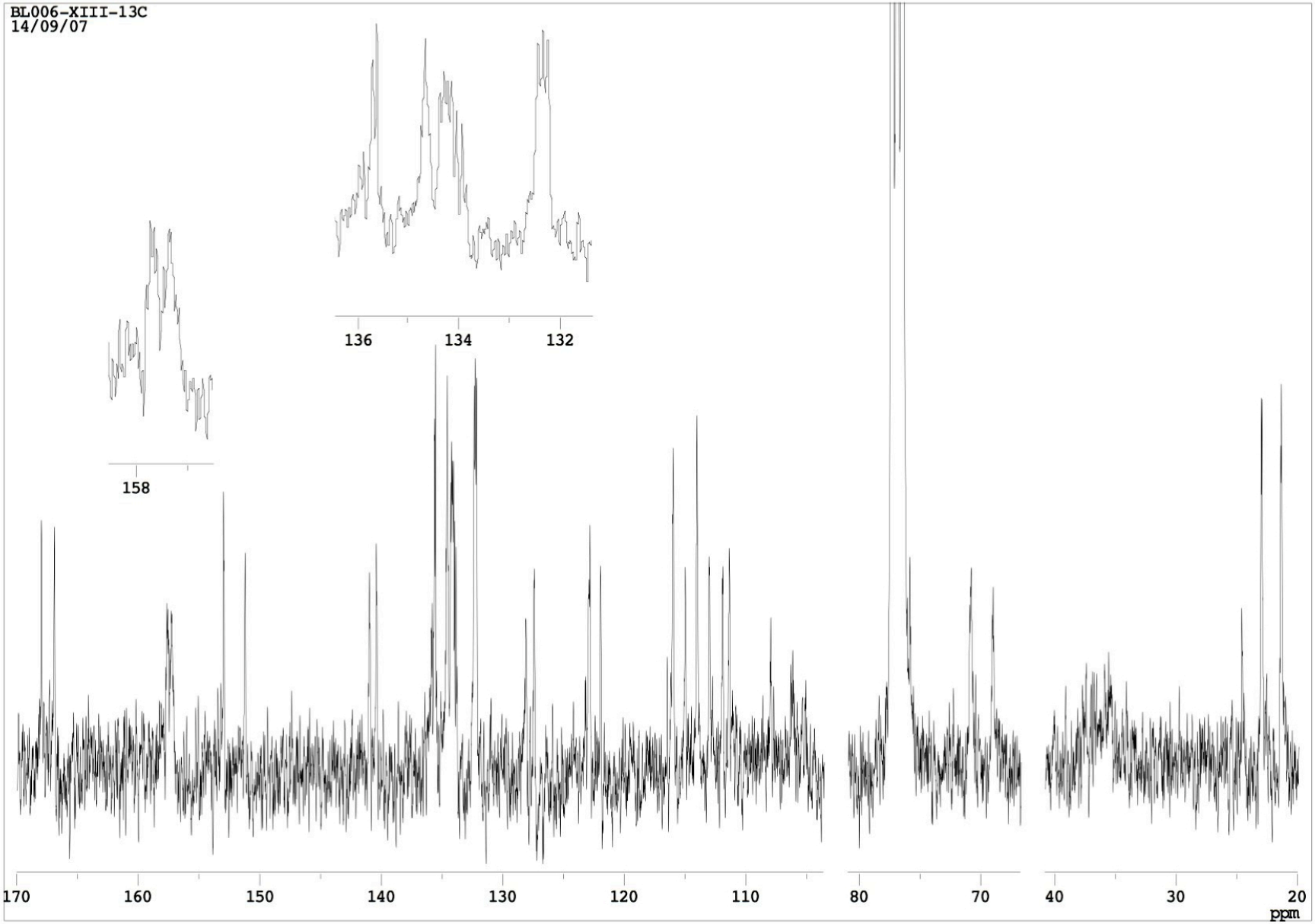
^{1}H NMR spectrum of chlorin **8b** in $CDCl_3$



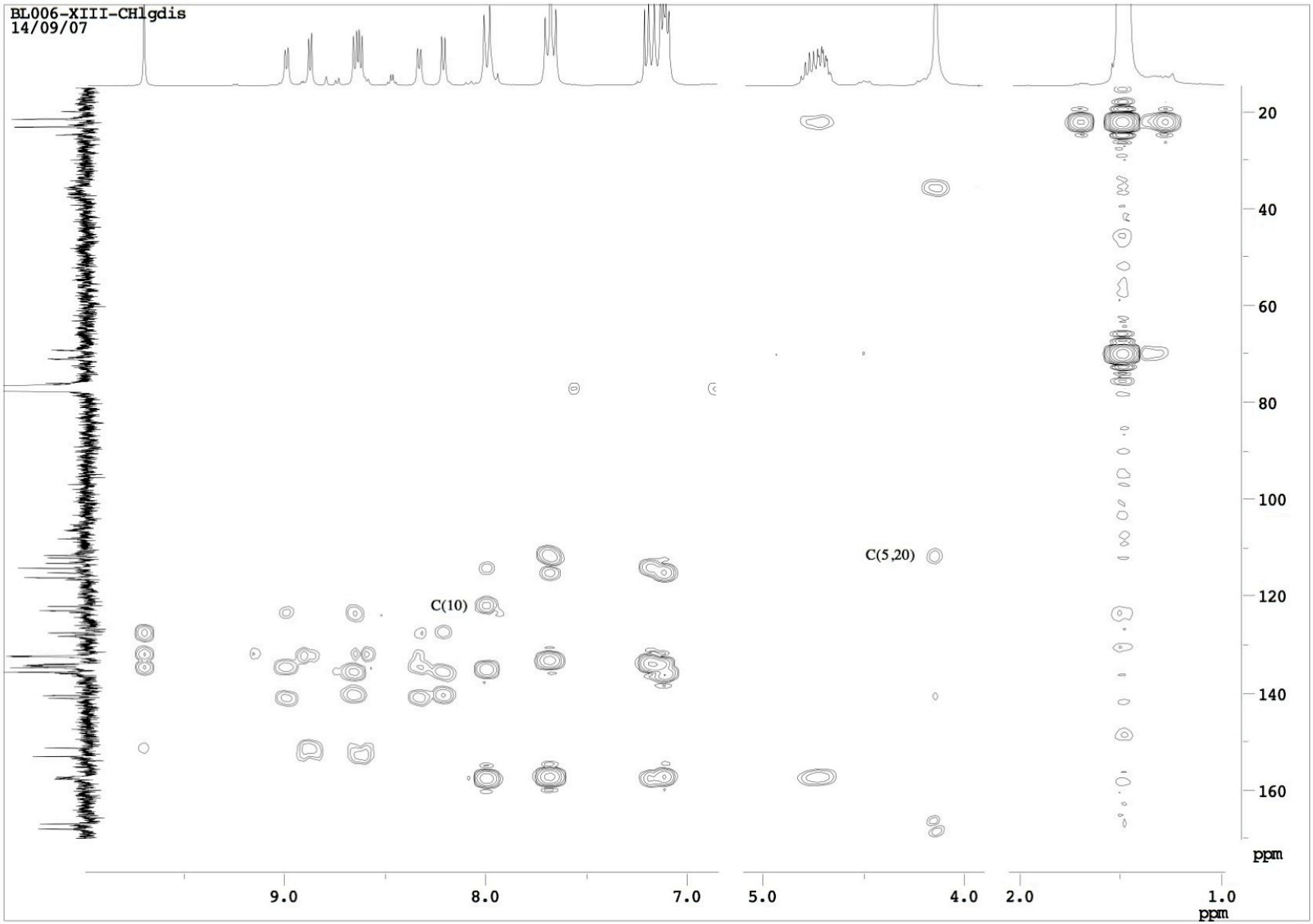
^{1}H NMR spectrum of mixture of chlorins **9a**/**11** in $CDCl_3$ (green **9a**, red **11**)



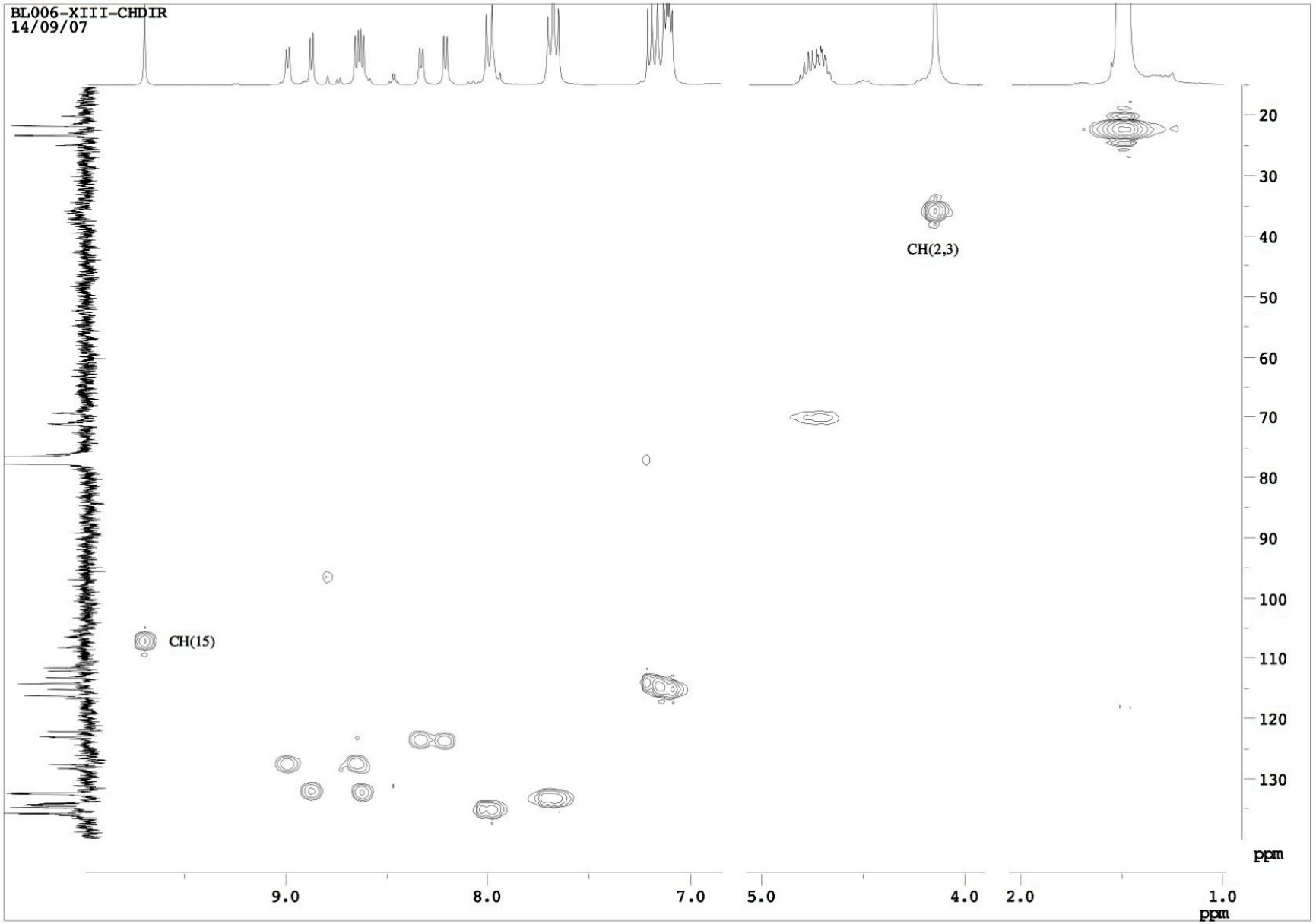
^{1}H NMR spectrum of chlorine **9b** in $CDCl_3$



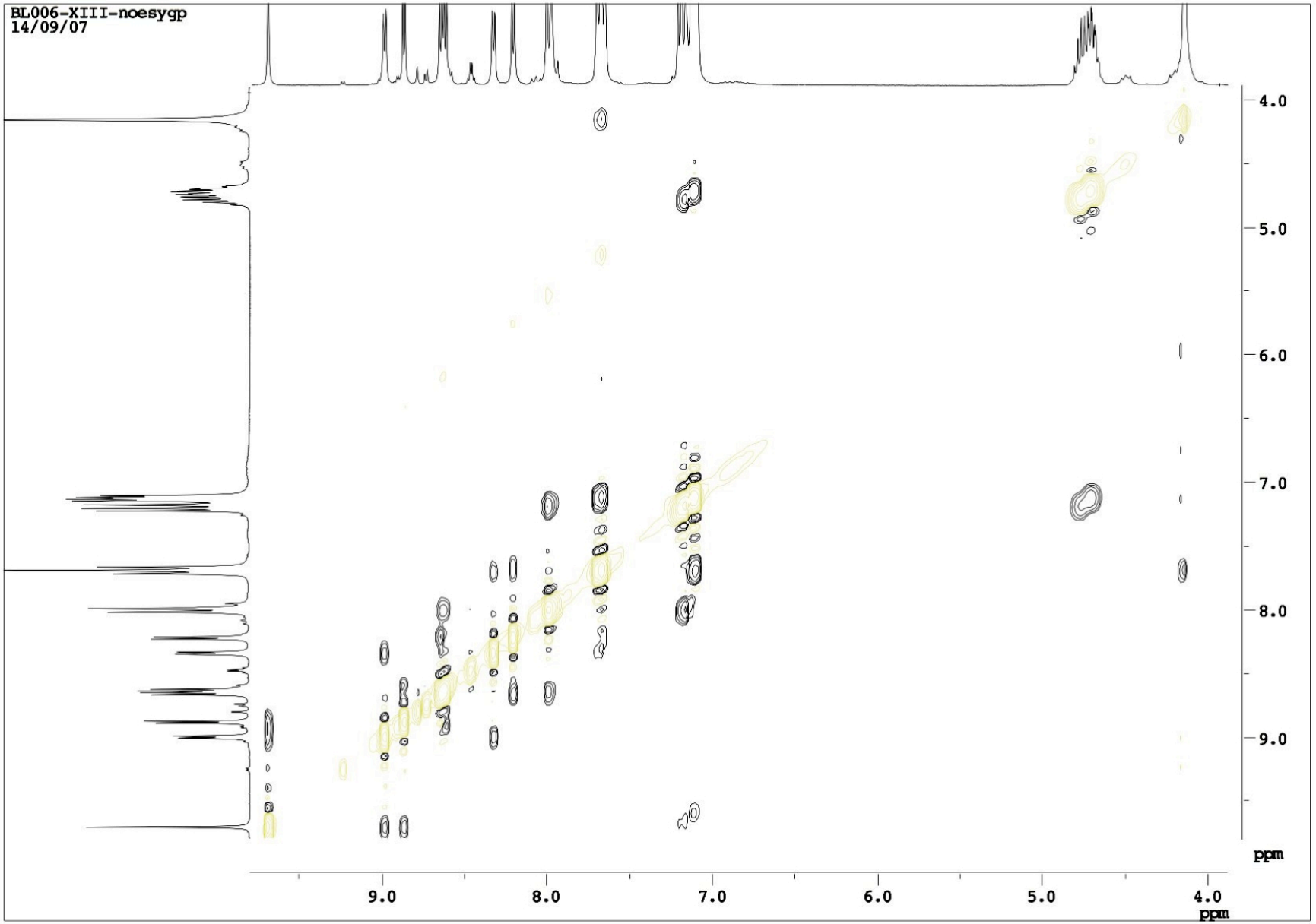
^{13}C NMR spectrum of chlorin **9b** in $CDCl_3$



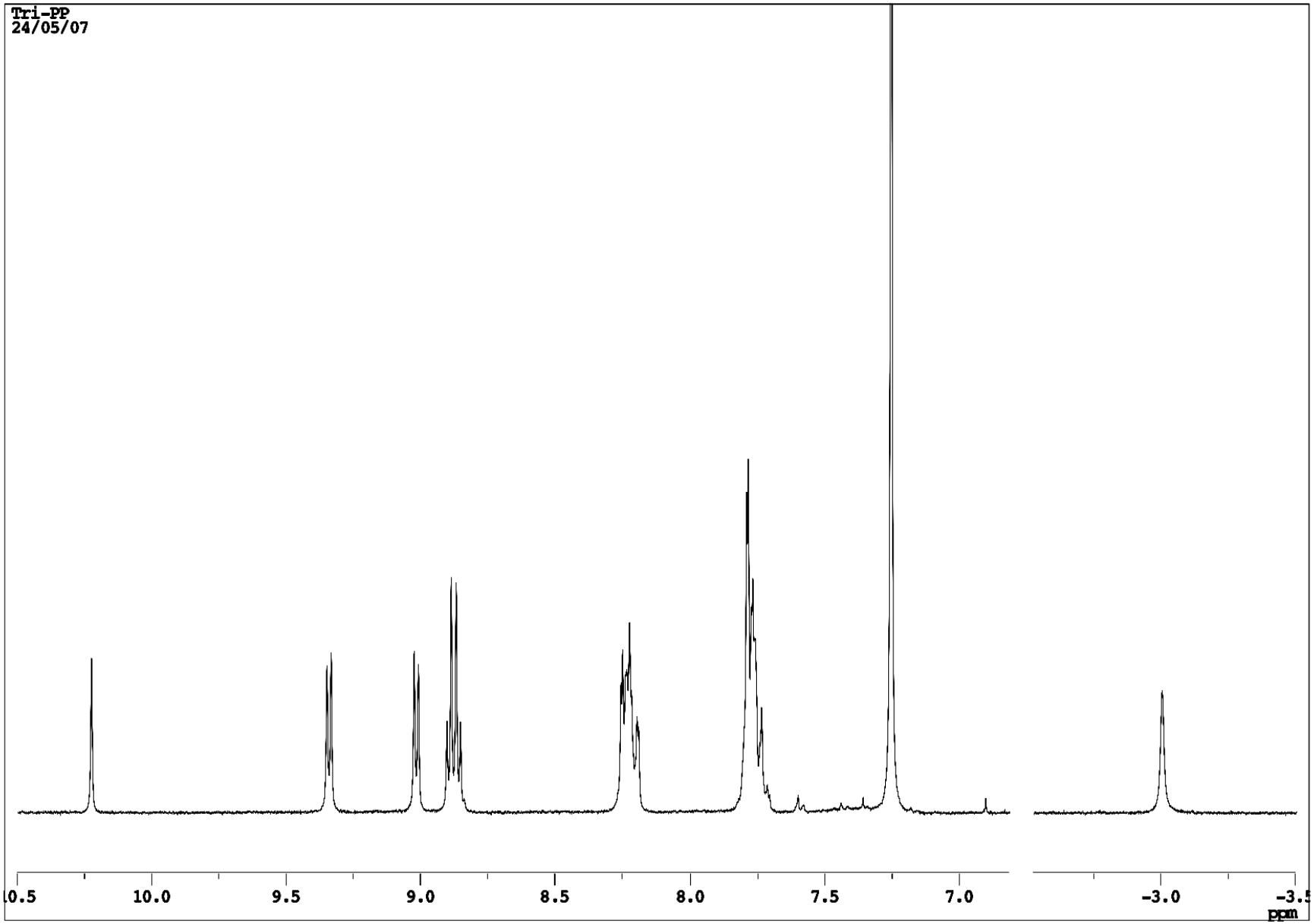
2D NMR spectrum (HMBC) of chlorin **9b** in $CDCl_3$



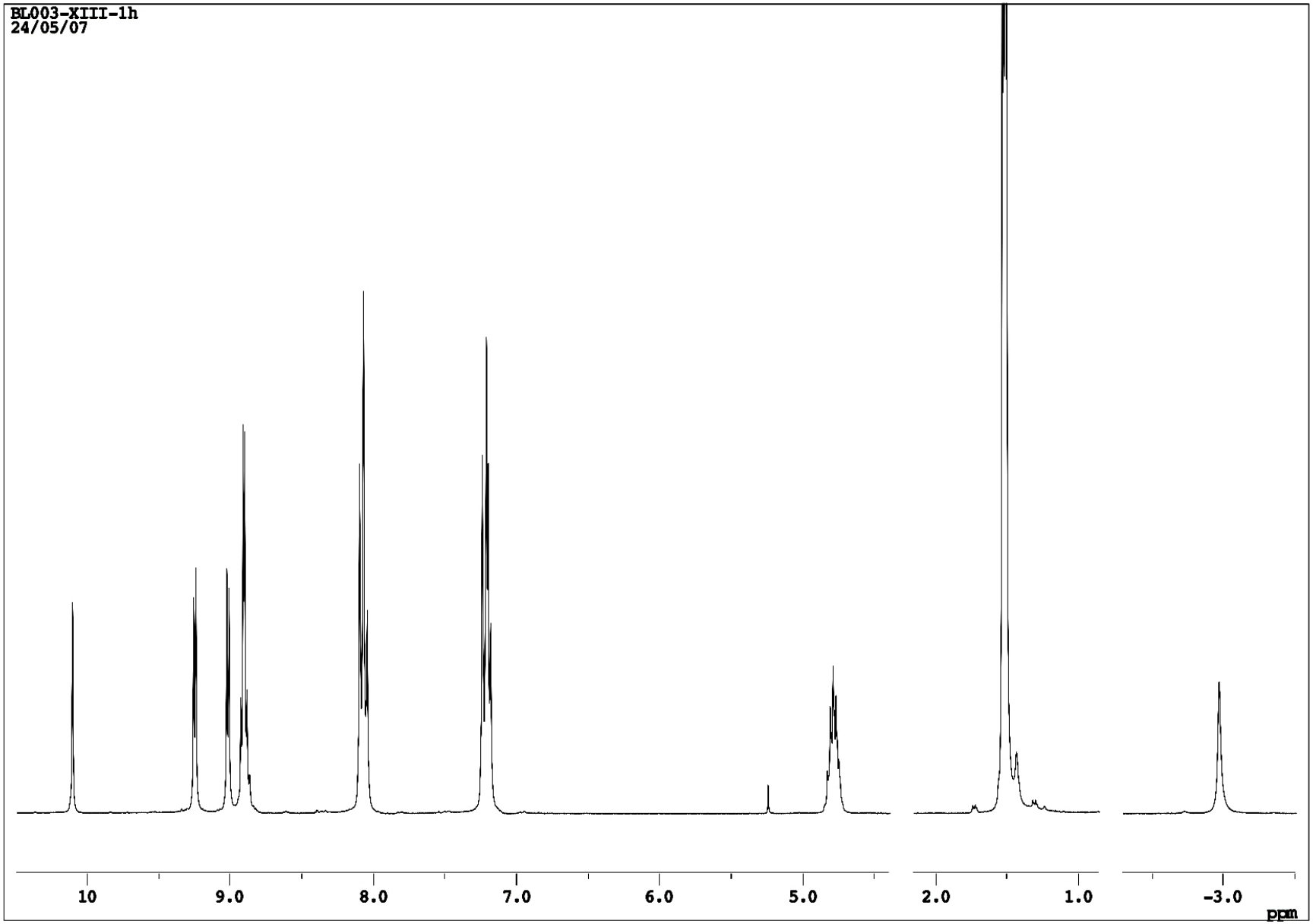
2D NMR spectrum (HMQC) of chlorin **9b** in $CDCl_3$



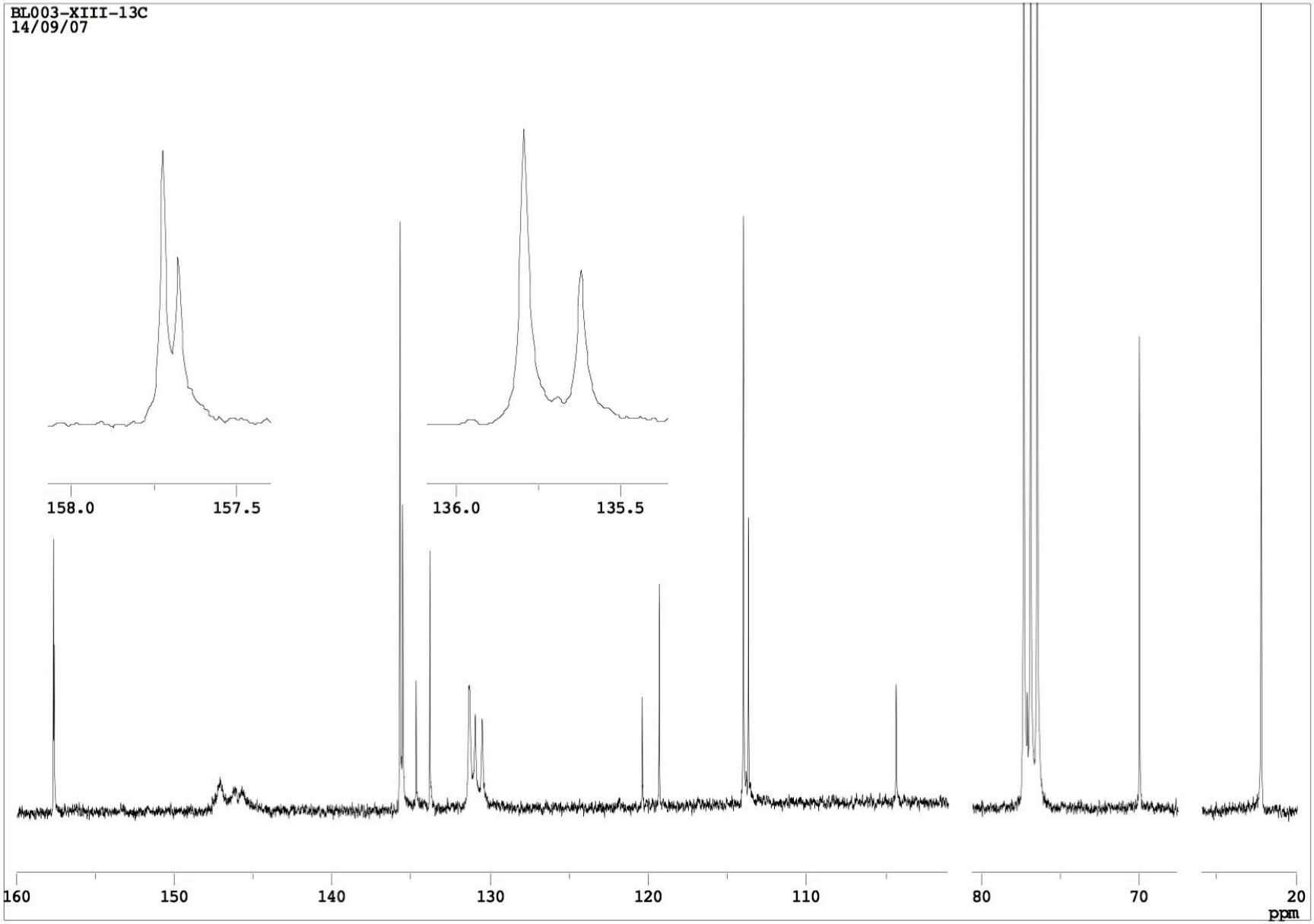
2D NMR spectrum (NOESY) of chlorin **9b** in $CDCl_3$



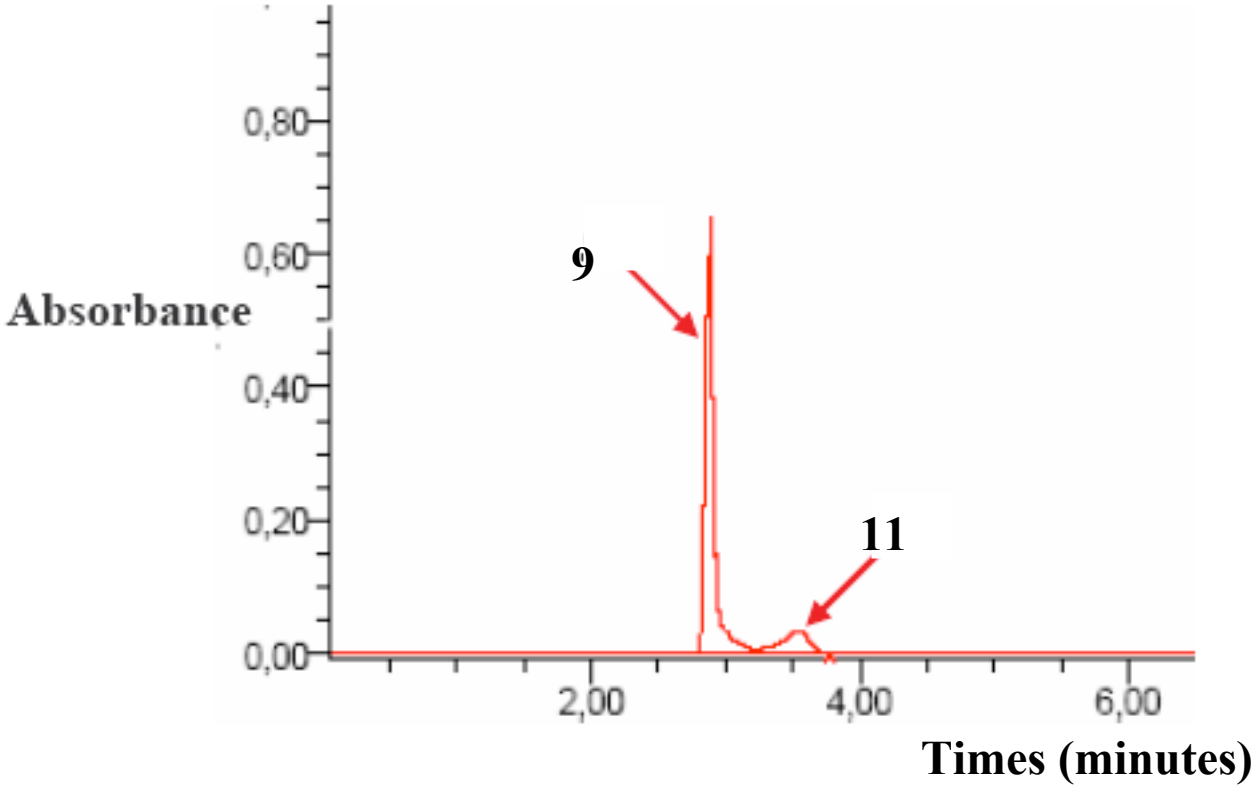
^{1}H NMR spectrum of chlorin **10** in $CDCl_3$



^{1}H NMR spectrum of chlorin **13** in $CDCl_3$



^{13}C NMR spectrum of chlorin **13** in $CDCl_3$



HPLC chromatogram of mixture of chlorins **9a** and **11**,
Apparatus : Waters P600 PDA-996, column : Lichrospher 100 SiO_2 5 μm, 250x4, Solvents : methylene chloride/heptane, 1/1, v/v, 1 mL/min.