Supporting Informations

A Toolset of Functionalized Porphyrins with Different Linker Strategies for Application in Bioconjugation

Michael H. Staegemann, Susanna Gräfe, Rainer Haag,* and Arno Wiehe*

[*] M. H. Staegemann M.Sc., Dr. A. Wiehe, Prof. Dr. R. Haag,
Institut für Chemie und Biochemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin, Germany
E-mail: haag@chemie.fu-berlin.de

[*] Dr. S. Gräfe, Dr. A. Wiehe
Biolitec research GmbH, Otto-Schott-Str. 15, 07745 Jena, Germany
E-mail: arno.wiehe@biolitec.com

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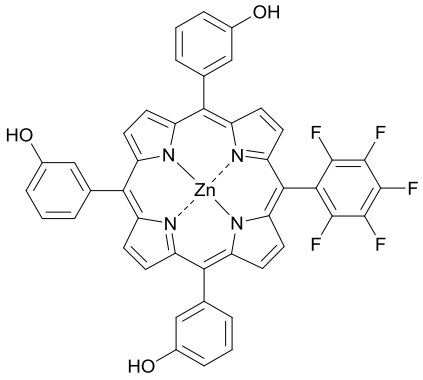
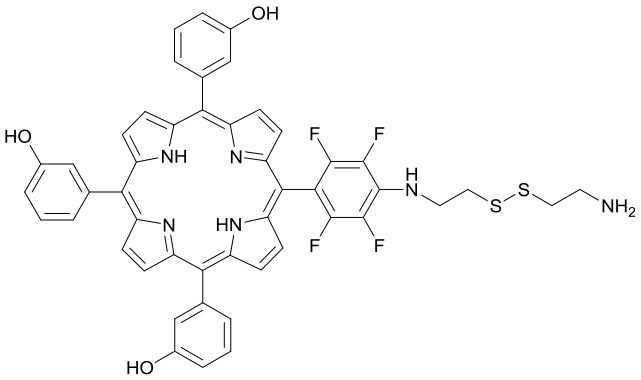
1. Synthesis of porphyrins **1d**, **2a-f**, **2h-i**, **4**, and **5c**



{5,10,15-Tris(3-hydroxyphenyl)-20-pentafluorophenylporphyrinato}-zinc (II) (1d) In a 25 mL flask with magnetic stirrer 5,10,15-tris(3-hydroxyphenyl)-20-pentafluorophenyl-porphyrin (**1c**) (42.0 mg, 55.8 µmol) was dissolved in 5 mL of methanol. A point of a spatula of sodium acetate and zinc acetate dihydrate (120 mg, 547 µmol) was added to the stirred solution. The solution was stirred for 2 h at RT. The crude product was diluted with 100 mL of ethyl acetate and washed three times with 50 mL of H_2O. Afterwards the organic layer was dried over Na_2SO_4 and the solution was evaporated to dryness. The crude product was purified by recrystallization from DCM/*n*-hexane to obtain {5,10,15-tris(3-hydroxyphenyl)-20-pentafluorophenylporphyrinato}-zinc (II) (**1d**) (46.0 mg, 56.4 µmol, quant. yield) as a pink solid.

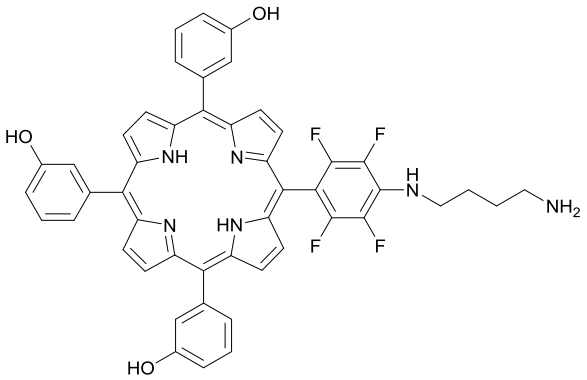
^{1}H NMR (Acetone-D_6, 700 MHz): δ = 9.04 (d, ^{3}J(H,H) = 4.5 Hz, 2H, 2,1β), 9.01 (d, ^{3}J(H,H) = 4.5 Hz, 2H, 3,17-β), 8.97 (d, ^{3}J(H,H) = 4.5 Hz, 2H, 7,13-β), 8.95 (d, ^{3}J(H,H) = 4.5 Hz, 2H, 8,12-β), 8.80 (s, 3H, O*H*), 7.74–7.72 (m, 3H, 5,10,15-*meso*-2-Ar), 7.70 (d, ^{3}J(H,H) = 7.2 Hz, 3H, 5,10,15-*meso*-6-Ar), 7.62–7.58 (m, 3H, 5,10,15-*meso*-5-Ar), 7.32–7.29 ppm (m, 3H, 5,10,15-*meso*-4-Ar). ^{13}C NMR (Acetone-D_6, 176 MHz): δ = 156.55, 156.52, 151.33, 150.90, 150.73, 150.39, 148.31, 146.92, 145.25, 145.16, 139.31, 137.92, 133.79, 132.86, 132.49, 130.63, 128.26, 128.23, 127.25, 123.20, 122.89, 122.01, 118.68, 115.47, 101.30 ppm. ^{19}F NMR (Acetone-D_6, 376 MHz): δ = −139.45–(−139.87) (m, 2F, *m*-Ar_F), −156.90 (q, ^{3}J(F,F) = 19.7 Hz, 1F, *p*-Ar_F), −165.22–(−165.49) ppm (m, 2F, *o*-Ar_F). m.p.: 143 °C. HRMS (ESI): calc. for $C_{44}H_{24}F_5N_4O_3Zn^+$ ([M + H]$^+$): 815.1060 found: 815.1127. UV/Vis (Ethanol): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 596 (5000), 555 (19 000), 422 nm (412 000).



5,10,15-Tris(3-hydroxyphenyl)-20-[4-((2-((2-aminoethyl)disulfanyl)ethyl)amino)tetrafluorophenyl]porphyrin (2a) In a 100 mL flask with magnetic stirrer sodium hydroxide (99%, 1.55 g, 38.4 mmol) was dissolved in 20 mL of H_2O. To the stirred solution cystamine dihydrochloride (97%, 2.71 g, 11.7 mmol) was added. After 10 min of stirring the aqueous solution was extracted four times with 100 mL of DCM. Afterwards the organic layer was dried over Na_2SO_4. The product was evaporated to dryness and the remaining residue was dissolved in 1.5 mL of DMSO (*Roth*). 5,10,15-Tris(3-hydroxyphenyl)-20-pentafluorophenylporphyrin (**1c**) (151 mg, 177 µmol) was added. The solution was stirred at 100 °C for 30 min in the microwave oven (300 W). The crude product was diluted with 100 mL of ethyl acetate and washed once with 50 mL of saturated NaCl-solution and twice with H_2O. Afterwards the organic layer was dried over Na_2SO_4. The crude product was evaporated to dryness and the remaining residue was purified by column chromatography (DCM/methanol = 85/15, v/v, *Fluka*) and recrystallization from DCM to obtain 5,10,15-tris(3-hydroxyphenyl)-20-[4-((2-((2-aminoethyl)disulfanyl)ethyl)amino)tetrafluorophenyl]porphyrin (**2a**) (136 mg, 154 µmol, 87% yield) as a purple solid.

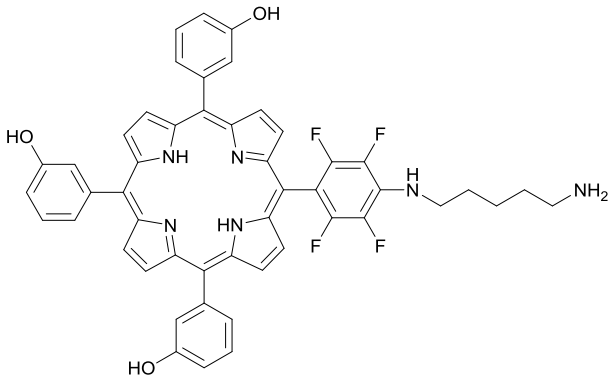
^{1}H NMR (THF-D_8, 700 MHz): δ = 9.04–8.81 (m, 11H, β + 5,10,15-*meso*-3-Ar-O*H*), 7.69–7.60 (m, 6H, 5,10,15-*meso*-2,6-Ar), 7.58–7.44 (m, 3H, 5,10,15-*meso*-5-Ar), 7.20 (d, ^3J(H,H) = 8.2 Hz, 1H, 10-*meso*-4-Ar), 7.18 (dd, ^3J(H,H) = 8.9, ^4J(H,H) = 2.1 Hz, 1H, 10-*meso*-4-Ar), 6.21–6.17 (bs, 1H, N*H*), 3.99 (q, ^3J(H,H) = 6.6 Hz, 2H, NHCH_2), 3.50 (t, ^3J(H,H) = 7.2 Hz, 2H, CH_2NH$_2$), 3.35 (t, ^3J(H,H) = 7.2 Hz, 2H, SCH_2), 3.24 (t, ^3J(H,H) = 6.8 Hz, 2H, SCH_2), −2.73 ppm (s, 2H, pyrrole-N*H*). ^{13}C NMR (THF-D_8, 176 MHz): δ = 157.41, 148.83, 147.46, 144.37, 144.20, 138.86, 137.57, 130.01, 128.44, 128.39, 127.13, 123.16, 122.40, 121.50, 115.93, 108.36, 103.65, 45.62, 40.00, 39.80, 35.57 ppm. ^{19}F NMR (THF-D_8, 376 MHz): δ = −142.15–(−143.15) (m, 2F, *m*-Ar$_F$), −161.73–(−162.85) ppm (m, 2F, *o*-Ar$_F$). m.p.: > 230 °C. HRMS (ESI): calc. for $C_{48}H_{37}F_4N_6O_3S_2^+$ ([M + H]$^+$): 885.2305 found: 885.2342. UV/Vis

(Ethanol): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 645 (2000), 589 (4000), 547 (5000), 512 (14 000), 416 nm (257 000).



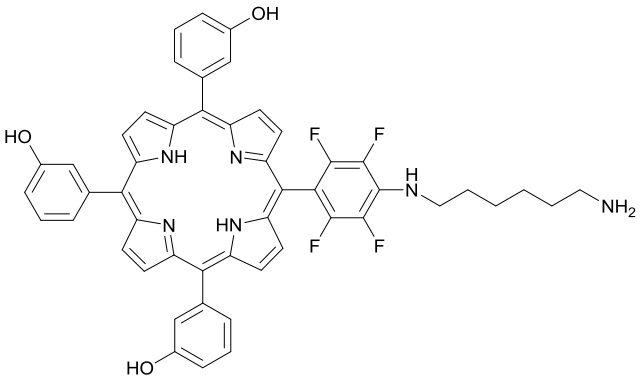
5,10,15-Tris(3-hydroxyphenyl)-20-[4-(4-aminobutylamino)tetrafluorophenyl]porphyrin (2b) In a 25 mL flask with magnetic stirrer 5,10,15-tris(3-hydroxyphenyl)-20-pentafluorophenylporphyrin (**1c**) (197 mg, 262 µmol) was dissolved in 7 mL of anhydrous DMSO (*Acros*) under argon. To the stirred solution 1,4-diaminobutane (99%, 4.00 g, 44.9 mmol) was added. The solution was stirred at 100 °C for 1 h. The crude product was diluted with 200 mL of ethyl acetate and washed twice with 300 mL of saturated NaCl-solution and twice with 300 mL of H_2O. Afterwards the organic layer was dried over Na_2SO_4. The crude product was evaporated to dryness and the remaining residue was purified by column chromatography (DCM/methanol = 8/2, v/v, *Fluka*) to obtain 5,10,15-tris(3-hydroxyphenyl)-20-[4-(4-aminobutylamino)tetrafluorophenyl]porphyrin (**2b**) (145 mg, 177 µmol, 69% yield) as a purple solid.

^{1}H NMR (CD_3OD, 700 MHz): δ = 9.21–8.66 (bs, 8H, β), 7.70–7.61 (m, 6H, 5,10,15-*meso*-2,6-Ar), 7.55 (q, ^3J(H,H) = 7.2 Hz, 3H, 5,15-*meso*-5-Ar), 7.24 (d, ^3J(H,H) = 8.4 Hz, 3H, 5,15-*meso*-4-Ar), 3.62 (t, ^3J(H,H) = 6.8 Hz, 2H, NHCH_2), 2.84 (t, ^3J(H,H) = 7.3 Hz, 2H, NHCH_2), 1.83 (quin, ^3J(H,H) = 7.2 Hz, 2H, NHCH$_2$CH_2), 1.72 ppm (quin, ^3J(H,H) = 7.5 Hz, 2H, NHCH$_2$CH_2). ^{13}C NMR (CD_3OD, 176 MHz): δ = 157.24, 157.19, 149.01, 147.67, 144.35, 144.23, 139.03, 137.67, 130.82, 128.78, 128.72, 127.52, 127.48, 123.23, 123.19, 122.78, 121.84, 116.12, 108.04, 104.03, 46.23, 41.74, 29.27 ppm. ^{19}F NMR (CD_3OD, 376 MHz): δ = −143.75–(−143.99) (m, 2F, *m*-Ar$_F$), −163.31 ppm (d, ^3J(F,F) = 16.3 Hz, 2F, *o*-Ar$_F$). m.p.: > 300 °C. HRMS (ESI): calc. for $C_{48}H_{37}F_4N_6O_3^+$ ([M + H]$^+$): 821.2858; found: 821.2884. UV/Vis (Acetone): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 644 (3000), 589 (5000), 545 (6000), 512 (16 000), 416 nm (251 000).



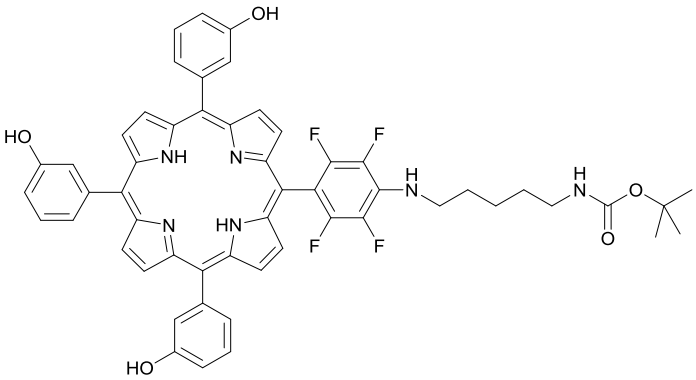
5,10,15-Tris(3-hydroxyphenyl)-20-[4-(5-aminopentylamino)tetrafluorophenyl]porphyrin (2c) In a 10 mL flask with magnetic stirrer 5,10,15-tris(3-hydroxyphenyl)-20-pentafluorophenylporphyrin (**1c**) (120 mg, 160 µmol) was dissolved in 4 mL of anhydrous DMSO (*Acros*) under argon. To the stirred solution 1,5-diaminopentane (98%, 2.80 mL, 2.44 g, 23.4 mmol) was added. The solution was stirred at 100 °C for 1 h. The crude product was diluted with 100 mL of ethyl acetate and washed twice with 150 mL of saturated NaCl-solution and twice with 150 mL of H_2O. Afterwards the organic layer was dried over Na_2SO_4. The crude product was evaporated to dryness and the remaining residue was purified by column chromatography (DCM/methanol = 8/2, v/v, *Fluka*) and recrystallization from DCM to obtain 5,10,15-tris(3-hydroxyphenyl)-20-[4-(5-aminopentylamino)tetrafluorophenyl]porphyrin (**2c)** (71.3 mg, 85,4 µmol, 54% yield) as a purple solid.

^{1}H NMR (CD_3OD, 500 MHz): δ = 9.25–8.62 (bs, 8H, β), 7.70–7.59 (m, 6H, 5,10,15-*meso*-2,6-Ar), 7.58–7.49 (m, 3H, 5,10,15-*meso*-5-Ar), 7.27–7.18 (m, 3H, 5,10,15-*meso*-4-Ar), 3.54 (t, ^3J(H,H) = 7.0 Hz, 2H, Ar_F-NHCH_2), 2.62 (t, ^3J(H,H) = 7.1 Hz, 2H, C$H_2$$NH_2$), 1.74 (quin, ^3J(H,H) = 7.4 Hz, 2H, Ar_F-NHCH$_2$CH_2), 1.55–1.44 ppm (m, 4H, CH_2CH_2CH$_2$$NH_2$). ^{13}C NMR ($CD_3OD$, 126 MHz): δ = 157.45, 157.39, 149.29, 147.39, 144.37, 144.24, 139.39, 128.77, 128.72, 127.44, 127.40, 123.34, 123.29, 122.80, 121.88, 116.19, 104.07, 46.45, 42.14, 32.70, 31.78, 25.10 ppm. ^{19}F NMR (CD_3OD, 376 MHz): δ = −143.80–(−144.17) (m, 2F, *m*-Ar_F), −163.38 ppm (d, ^3J(F,F) = 15.6 Hz, 2F, *o*-Ar_F). m.p.: > 300 °C. HRMS (ESI): calc. for $C_{49}H_{39}F_4N_6O_3^+$ ([M + H]$^+$): 835.3020; found: 835.3018. UV/Vis (Methanol): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 644 (2000), 588 (5000), 547 (6000), 512 (15 000), 415 nm (186 000).



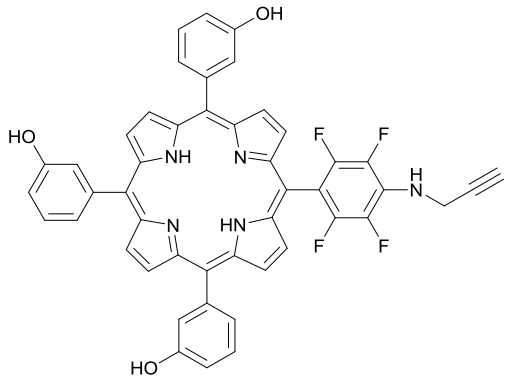
5,10,15-Tris(3-hydroxyphenyl)-20-[4-(6-aminohexylamino)tetrafluorophenyl]porphyrin (2d) In a 10 mL flask with magnetic stirrer 5,10,15-tris(3-hydroxyphenyl)-20-pentafluorophenylporphyrin (**1c**) (120 mg, 159 µmol) was dissolved in 4 mL of anhydrous DMSO (*Acros*) under argon. To the stirred solution 1,6-diaminohexane (98%, 3.60 mL, 2.99 g, 25.5 mmol) was added. The solution was stirred at 100 °C for 1 h. The crude product was diluted with 100 mL of ethyl acetate and washed twice with 150 mL of saturated NaCl-solution and twice with 150 mL of H_2O. Afterwards the organic layer was dried over Na_2SO_4. The crude product was evaporated to dryness and the remaining residue was purified by column chromatography (DCM/methanol = 8/2, v/v, *Fluka*) and recrystallization from DCM to obtain 5,10,15-tris(3-hydroxyphenyl)-20-[4-(6-aminohexylamino)tetrafluorophenyl]porphyrin (**2d**) (107 mg, 127 µmol, 79% yield) as a purple solid.

^{1}H NMR (CD_3OD, 500 MHz): δ = 8.96–8.92 (bs, 8H, β), 7.68–7.64 (m, 3H, 5,10,15-*meso*-2-Ar), 7.63 (t, ^3J(H,H) = 8.0 Hz, 3H, 5,10,15-*meso*-6-Ar), 7.543 (t, ^3J(H,H) = 7.7 Hz, 2H, 5,15-*meso*-5-Ar), 7.537 (t, ^3J(H,H) = 7.9 Hz, 1H, 10-*meso*-5-Ar), 7.24 (dd, ^3J(H,H) = 8.3, ^4J(H,H) = 1.6 Hz, 3H, 5,15-*meso*-4-Ar), 3.52 (t, ^3J(H,H) = 7.3 Hz, 2H, NHCH_2), 2.62 (t, ^3J(H,H) = 7.2 Hz, 2H, NHCH_2), 1.73 (quin, ^3J(H,H) = 7.3 Hz, 2H, NHCH$_2$CH_2), 1.52–1.31 ppm (m, 6H, NHCH$_2$CH_2CH_2CH_2). ^{13}C NMR (CD_3OD, 126 MHz): δ = 157.50, 157.43, 144.36, 144.24, 128.77, 128.72, 127.42, 127.38, 123.37, 123.32, 122.81, 121.88, 116.21, 104.08, 46.49, 42.15, 32.90, 31.92, 27.65 ppm. ^{19}F NMR (CD_3OD, 471 MHz): δ = −143.95 (d, ^3J(F,F) = 16.1 Hz, 2F, *m*-Ar$_F$), −163.40 ppm (d, ^3J(F,F) = 16.1 Hz, 2F, *o*-Ar$_F$). m.p.: > 300 °C. HRMS (ESI): calc. for $C_{50}H_{41}F_4N_6O_3^+$ ([M + H]$^+$): 849.3176; found: 849.3184. UV/Vis (Methanol): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 644 (2000), 588 (5000), 545 (6000), 512 (16 000), 415 nm (178 000).



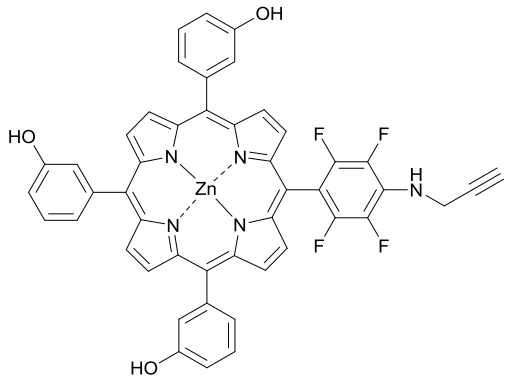
***N*-Boc protected 5,10,15-Tris(3-hydroxyphenyl)-20-[4-(6-aminopentylamino)tetrafluorophenyl]porphyrin (2e)** In a 10 mL flask with magnetic stirrer 5,10,15-tris(3-hydroxyphenyl)-20-pentafluorophenylporphyrin **1c** (49 mg, 65.1 µmol) was dissolved in 0.5 mL of anhydrous DMSO (*Acros*) under argon. To the stirred solution *N*-Boc-cadaverine (97%, 60 µL, 58 mg, 280 µmol) was added. The solution was stirred at 100 °C for 4 h. The crude product was diluted with 100 mL of ethyl acetate and washed three times with 50 mL of H_2O. Afterwards the organic layer was dried over Na_2SO_4. The crude product was evaporated to dryness and the remaining residue was purified by column chromatography (DCM/acetone = 9/1, v/v, *Machery-Nagel*) and recrystallization from DCM/*n*-hexane to obtain *N*-Boc protected 5,10,15-tris(3-hydroxyphenyl)-20-[4-(6-aminopentylamino)tetrafluorophenyl]porphyrin (**2e)** (42 mg, 127 µmol, 69% yield) as a purple solid.

^{1}H NMR (Acetone-D_6, 500 MHz): δ = 9.13–9.08 (m, 2H, 2,18-β), 9.02 (d, ^3J(H,H) = 4.5 Hz, 2H, 3,17-β), 8.99–8.94 (bs, 4H, 7,8,12,13-β), 8.83 (s, 3H, 5,10,15-*meso*-3-Ar-O*H*), 7.79–7.70 (m, 6H, 5,10,15-*meso*-2,6-Ar), 7.66–7.61 (m, 3H, 5,10,15-*meso*-5-Ar), 7.36–7.32 (m, 3H, 5,10,15-*meso*-4-Ar), 6.00 (s, 1H, N*H*), 5.66 (s, 1H, N*H*), 3.72 (t, ^3J(H,H) = 6.9 Hz, 2H, NHCH_2), 3.17 (t, ^3J(H,H) = 6.5 Hz, 2H, NHCH_2), 1.91 (quin, ^3J(H,H) = 7.3 Hz, 2H, NHCH$_2$CH_2), 1.68–1.55 ppm (m, 4H, NHCH$_2$CH_2CH_2), 1.43 (s, 9H, CH_3), −2.74 ppm (s, 2H, pyrrole-N*H*). ^{13}C NMR (Acetone-D_6, 126 MHz): δ = 156.85, 156.80, 148.91, 147.02, 144.03, 143.89, 139.08, 137.04, 132.21, 130.66, 128.69, 128.65, 127.29, 127.25, 122.91, 122.87, 122.31, 121.38, 116.01, 107.46, 103.79, 78.40, 46.45, 41.08, 35.26, 31.40, 30.72, 28.72, 24.79 ppm. ^{19}F NMR (Acetone-D_6, 471 MHz): δ = −143.34–(−143.51) (m, 2F, *m*-Ar_F), −162.44–(−162.61) (m, 2F, *o*-Ar_F). m.p.: 190 °C. HRMS (ESI): calc. for $C_{54}H_{47}F_4N_6O_5^+$ ([M + H]$^+$): 935.3544; found: 935.3536. UV/Vis (ethanol): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 645 (4000), 589 (8000), 546 (9000), 512 (25 000), 416 nm (445 000).



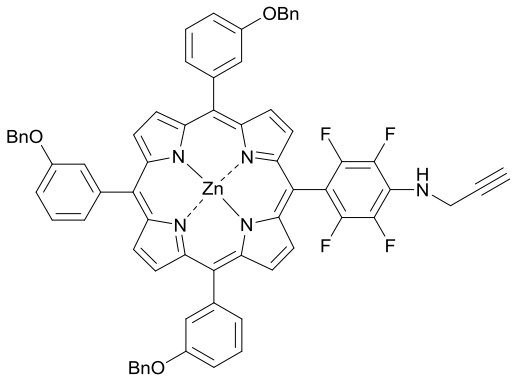
5,10,15-Tris(3-hydroxyphenyl)-20-[4-(prop-2-yn-1-ylamino)tetrafluorophenyl]porphyrin (2f) In a 10 mL flask with magnetic stirrer 5,10,15-tris(3-acetoxyphenyl)-20-pentafluorophenylporphyrin (**1a**) (203 mg, 231 µmol) was dissolved in 2 mL of anhydrous DMSO (*Roth*) under argon. Propargylamine (98%, 300 µL, 258 mg, 4.59 mmol) was added and the solution was stirred at 83 °C for 3 h. The crude product was diluted with 150 mL of ethyl acetate and washed three times with 30 mL of H_2O. Afterwards the organic layer was dried over Na_2SO_4. The crude product was evaporated to dryness and the remaining residue was purified by column chromatography (DCM/acetone = 9/1, v/v, *Machery-Nagel*) and recrystallization from DCM/*n*-hexane to obtain 5,10,15-tris(3-hydroxyphenyl)-20-[4-(prop-2-yn-1-ylamino)tetrafluorophenyl]porphyrin (**2f**) (170 mg, 216 µmol, 94% yield) as a purple solid.

^{1}H NMR (Acetone-D_6, 500 MHz): δ = 9.13–9.06 (m, 2H, 2,18-β), 9.03 (d, ^3J(H,H) = 4.8 Hz, 2H, 3,17-β), 9.00–8.92 (bs, 4H, 7,8,12,13-β), 8.87 (s, 3H, 5,10,15-*meso*-3-Ar-O*H*), 7.77 (t, ^4J(H,H) = 2.0 Hz, 2H, 5,15-*meso*-2-Ar), 7.76–7.71 (m, 4H, 10-*meso*-2-Ar + 5,10,15-*meso*-6-Ar), 7.66–7.61 (m, 3H, 5,10,15-*meso*-5-Ar), 7.36–7.32 (m, 3H, 5,10,15-*meso*-4-Ar), 6.15 (t, ^3J(H,H) = 7.2 Hz, 1H, Ar_F-N*H*), 4.49–4.46 (m, 2H, CH_2), 2.98 (t, ^4J(H,H) = 2.5 Hz, 1H, C≡C*H*), −2.75 ppm (s, 2H, pyrrole-N*H*). ^{13}C NMR (Acetone-D_6, 126 MHz): δ = 156.83, 156.78, 148.78, 146.83, 143.97, 143.82, 139.72, 137.82, 132.39, 129.38, 128.70, 128.65, 127.27, 127.23, 122.88, 122.84, 122.42, 121.45, 116.00, 109.58, 103.30, 81.88, 73.55, 35.75 ppm. ^{19}F NMR (Acetone-D_6, 471 MHz): δ = −142.99 (d, ^3J(F,F) = 20.5 Hz, 2F, *m*-Ar_F), −160.83 ppm (d, ^3J(F,F) = 19.3 Hz, 2F, *o*-Ar_F). m.p.: 135 °C. HRMS (ESI): calc. for $C_{47}H_{30}F_4N_5O_3^+$ ([M + H]$^+$): 788.2285 found: 788.2270. UV/Vis (Ethanol): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 645 (3000), 589 (5000), 546 (6000), 512 (17 000), 416 nm (283 000).



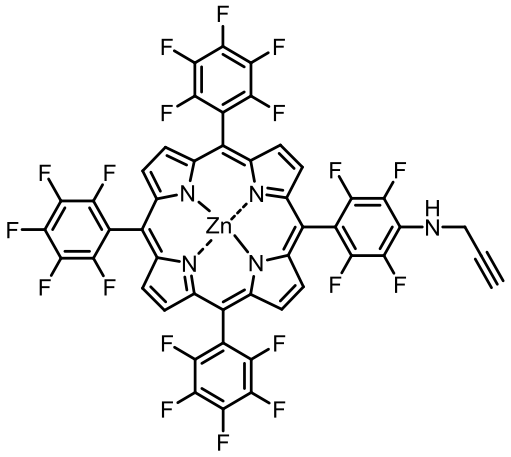
{5,10,15-Tris(3-hydroxyphenyl)-20-[4-(prop-2-yn-1-ylamino)tetrafluorophenyl]porphyrinato}-zinc(II) (2h) In a 25 mL flask with magnetic stirrer 5,10,15-tris(3-hydroxyphenyl)-20-[4-(prop-2-yn-1-ylamino)tetrafluorophenyl]porphyrin (**2f**) (181 mg, 230 µmol) was dissolved in 10 mL of methanol. A point of a spatula of sodium acetate and zinc acetate dihydrate (506 mg, 2.31 mmol) was added to the stirred solution. The solution was stirred for 1 h at RT. The crude product was diluted with 150 mL of ethyl acetate and washed three times with 50 mL of H_2O. Afterwards the organic layer was dried over Na_2SO_4 and the solution was evaporated to dryness. The crude product was purified by recrystallization from DCM/*n*-hexane to obtain {5,10,15-tris(3-hydroxyphenyl)-20-[4-(prop-2-yn-1-ylamino)tetrafluorophenyl]porphyrinato}-zinc(II) (**2h**) (186 mg, 219 µmol, 95% yield) as a pink solid.

^{1}H NMR (Acetone-D_6, 400 MHz): δ = 8.99 (s, 4H, 2,3,17,18-β), 8.97–8.91 (m, 4H, 7,8,12,13-β), 8.82–8.70 (bs, 3H, 5,10,15-*meso*-3-Ar-O*H*), 7.76–7.71 (m, 6H, 5,10,15-*meso*-2,6-Ar), 7.58 (t, ^3J(H,H) = 7.8 Hz, 3H, 5,10,15-*meso*-5-Ar), 7.287 (dd, ^3J(H,H) = 8.2 Hz; ^4J(H,H) = 1.2 Hz, 2H, 5,15-*meso*-4-Ar), 7.281 (dd, ^3J(H,H) = 8.1 Hz; ^4J(H,H) = 1.0 Hz, 1H, 10-*meso*-4-Ar), 6.04–5.94 (m, 1H, Ar_F-N*H*), 4.43–4.36 (m, 2H, CH_2), 2.95 ppm (t, ^4J(H,H) = 2.4 Hz, 1H, C≡C*H*). ^{13}C NMR (Acetone-D_6, 126 MHz): δ = 156.54, 156.51, 151.17, 151.05, 150.86, 150.69, 148.70, 146.81, 145.32, 145.25, 139.76, 137.84, 133.58, 132.74, 132.44, 130.93, 128.78, 128.73, 128.28, 128.25, 127.29, 122.91, 122.81, 121.82, 115.44, 111.25, 103.43, 81.91, 73.53, 35.81 ppm. ^{19}F NMR (Acetone-D_6, 471 MHz): δ = −142.68 (d, ^3J(F,F) = 22.9 Hz, 2F, *m*-Ar_F), −160.99 ppm (d, ^3J(F,F) = 20.7 Hz, 2F, *o*-Ar_F). m.p.: > 230 °C. HRMS (ESI): calc. for $C_{47}H_{27}F_4N_5O_3Zn^+$ ([M]$^+$): 849.1341 found: 849.1331. UV/Vis (Ethanol): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 597 (5000), 556 (20 000), 423 nm (435 000).



{5,10,15-Tris(3-benzyloxyphenyl)-20-[4-(prop-2-ynylamino)tetrafluorophenyl]porphyrinato}-zinc(II) (2i) In a 100 mL flask with magnetic stirrer 5,10,15-tris(3-benzyloxyphenyl)-20-[4-(prop-2-ynylamino)tetrafluorophenyl]porphyrin (**2g**) (444 mg, 420 µmol) was dissolved in 10 mL of DCM. A point of a spatula of sodium acetate and zinc acetate dihydrate (99.5%, 1.02 g, 4.60 mmol) were dissolved in 500 µL methanol and added to the stirred solution. The solution was stirred at RT for 18 h. The crude product was diluted with 70 mL of DCM and washed twice with 70 mL of H_2O. Afterwards the organic layer was dried over Na_2SO_4. The crude product was evaporated to dryness and the remaining residue was purified by column chromatography (DCM/*n*-hexane = 3/1, v/v, *Machery-Nagel*) and recrystallization from DCM/*n*-hexane to obtain {5,10,15-tris(3-benzyloxyphenyl)-20-[4-(prop-2-ynylamino)tetrafluorophenyl]-porphyrinato}-zinc(II) (**2i**) (343 mg, 306 µmol, 73% yield) as a pink solid.

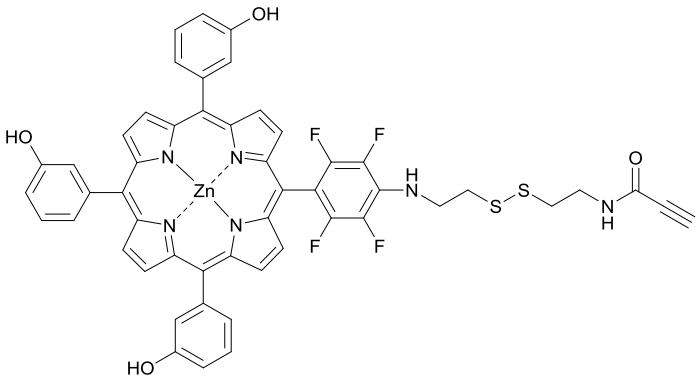
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 9.09–9.00 (m, 6H, 3,7,8,12,13,17-β), 8.77 (s, 2H, 2,18-β), 7.94–7.80 (m, 6H, Ar), 7.67–7.58 (m, 3H, Ar), 7.38–7.28 (m, 3H, Ar), 7.20–6.84 (m, 15H, Ar), 4.99–4.82 (m, 9H, CH_2 + Ar_F-N*H*), 1.95 ppm (s, 1H, C≡C*H*). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 157.06, 150.59, 150.15, 150.04, 149.91, 146.60, 144.72, 144.13, 144.04, 138.30, 136.69, 136.61, 133.24, 132.55, 132.25, 130.55, 128.27, 128.22, 128.16, 127.68, 127.62, 127.54, 127.29, 127.24, 127.20, 127.16, 122.31, 121.47, 121.43, 121.29, 114.76, 102.50, 78.61, 72.82, 70.04, 34.06 ppm. ^{19}F NMR ($CDCl_3$, 471 MHz): δ = −139.59–(−140.24) (m, 2F, *m*-Ar_F), −157.91–(−158.49) ppm (m, 2F, *o*-Ar_F). m.p.: 100 °C. HRMS (ESI): calc. for $C_{68}H_{45}F_4N_5O_3Zn^+$ ([M]$^+$): 1119.2750 found: 1119.2767. UV/Vis (DCM): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 584 (3000), 548 (20 000), 420 nm (296 000).



{5,10,15-Tris(pentafluorophenyl)-20-[4-(prop-2-ynylamino)tetrafluorophenyl]porphyrinato}-zinc(II) (4) In a 25 mL flask with magnetic stirrer {5,10,15,20-tetrakispentafluorophenylporphyrinato}-zinc(II) (**3**) (43.0 mg, 39.5 µmol) was dispensed in 5 mL of anhydrous DMSO (*Roth*) and 5 mL of anhydrous THF (*Acros*) under argon. Propargylamine (98%, 100 µL, 1.53 mmol) was added and the solution was stirred at 100 °C for 90 min. The crude product was diluted with 100 mL of DCM and washed three times with 30 mL of H_2O. Afterwards the organic layer was dried over Na_2SO_4. The crude product was evaporated to dryness and the remaining residue was purified by column chromatography (DCM/*n*-hexane = 2/1, v/v, *Machery-Nagel*) and recrystallization from DCM/methanol to obtain the main product {5,10,15-tris(pentafluorophenyl)-20-[4-(prop-2-ynylamino)tetrafluorophenyl]porphyrinato}-zinc(II) (**4)** (10.0 mg, 9.32 µmol, 22% yield) and the by-product {bis(pentafluorophenyl)-bis[4-(prop-2-ynylamino)tetrafluorophenyl]porphyrinato}-zinc(II) (*cis*/*trans* mixture) (8.0 mg, 7.22 µmol, 18% yield) as purple solids.

^{1}H NMR (Acetone-D_6, 500 MHz): δ = 9.26–9.22 (m, 6H, 3,7,8,12,13,17-β), 9.21–9.19 (m, 2H, 2,18-β), 6.11 (t, ^3J(H,H) = 7.0 Hz, 1H, Ar_F-N*H*), 4.47 (d, ^3J(H,H) = 7.2 Hz, 2H, NHCH_2), 2.95 ppm (t; ^4J(H,H) = 2.4 Hz, 1H, C≡C*H*). ^{13}C NMR (Acetone-D_6, 126 MHz): δ = 151.99, 151.22, 151.17, 151.12, 148.63, 146.69, 144.03, 142.04, 139.72, 137.73, 133.33, 133.00, 132.94, 132.83, 129.31, 117.77, 109.96, 106.70, 104.36, 104.17, 81.90, 73.50, 35.75 ppm. ^{19}F NMR (Acetone-D_6, 471 MHz): δ = −139.74 (dd, ^3J(F,F) = 24.1 Hz; ^4J(F,F) = 7.3 Hz, 2H, 5,10,15-*o*-Ar_F), −142.78–(−142.93) (m, 2F, 20-*m*-Ar_F), −156.32 (dd, ^3J(F,F) = 20.2 Hz; ^4J(F,F) = 9.6 Hz, 3H, 5,10,15-*p*-Ar_F), −160.95 (d, ^3J(F,F) = 16.1 Hz, 2F, *o*-Ar_F), −164.96–(−165.14) ppm (m, 6F, 5,10,15-*m*-Ar_F). m.p.: > 230 °C. HRMS (ESI): calc. for $C_{47}H_{12}F_{19}N_5Zn^+$ ($[M]^+$): 1071.0081 found: 1071.0035. UV/Vis (DCM): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 578 (4000), 544 (19 000), 415 nm (271 000).

{Bis(pentafluorophenyl)-bis[4-(prop-2-ynylamino)tetrafluorophenyl]porphyrinato}-zinc(II) (*cis*/*trans* mixture) ^{1}H NMR (Acetone-D_6, 250 MHz): δ = 9.35–9.08 (m, 8H, β), 6.17 (t, ^3J(H,H) = 7.0 Hz, 2H, ArF-N*H*), 4.48 (d, ^3J(H,H) = 6.0 Hz, 4H, NHCH_2), 2.97 ppm (s, 2H, C≡C*H*). HRMS (ESI): calc. for $C_{50}H_{17}F_{18}N_6Zn^+$ ([M + H]$^+$): 1107.0519 found: 1107.0469.



{5,10,15-Tris(3-hydroxyphenyl)-20-[2,3,5,6-tetrafluoro-4-(*N*-(2-((2-aminoethyl)disulfanyl)ethyl propyneamido))-phenyl]porphyrynato}-zinc(II) (5c) In a 10 mL flask with magnetic stirrer 5,10,15-tris(3-hydroxyphenyl)-20-[2,3,5,6-tetrafluoro-4-(*N*-(2-((2-aminoethyl)disulfanyl)ethyl-propyneamido))phenyl]porphyrin (**5b**) (56.0 mg, 59.8 µmol) was dissolved in 2 mL of methanol. A point of a spatula of sodium acetate and zinc acetate dihydrate (138 mg, 629 µmol) was added to the stirred solution. The solution was stirred for 30 min at RT. The crude product was dissolved in 100 mL of ethyl acetate and washed three times with 50 mL of H_2O. Afterwards the organic layer was dried over Na_2SO_4 and the solution was evaporated to dryness. The crude product was purified by recrystallization from DCM/*n*-hexane to obtain {5,10,15-tris-(3-hydroxyphenyl)-20-[2,3,5,6-tetrafluoro-4-(*N*-(2-((2-aminoethyl)disulfanyl)ethyl propyneamido))phenyl]porphyrinato}-zinc(II) (**5c**) (58.0 mg, 58.0 µmol, 97% yield) as a pink solid.

^{1}H NMR (Acetone-D_6, 700 MHz): δ = 9.02 (d, ^3J(H,H) = 4.5 Hz, 2H, 2,18-β), 8.98 (d, ^3J(H,H) = 4.5 Hz, 2H, 3,17-β), 8.95 (d, ^3J(H,H) = 4.5 Hz, 2H, 6,13-β), 8.94 (d, ^3J(H,H) = 4.5 Hz, 2H, 8,12-β), 8.91–8.87 (bs, 3H, 5,10,15-*meso*-3-Ar-O*H*), 8.10–8.07 (bs, 1H, N*H*C(O)), 7.72 (s, 3H, 5,10,15-*meso*-2-Ar), 7.69 (d, ^3J(H,H) = 7.2 Hz, 3H, 5,10,15-*meso*-6-Ar), 7.62–7.57 (m, 3H, 5,10,15-*meso*-5-Ar), 7.29 (dd, ^3J(H,H) = 8.6, ^4J(H,H) = 2.6 Hz, 3H, 5,10,15-*meso*-4-Ar), 5.79 (t, ^3J(H,H) = 6.6 Hz, 1H, Ar_F-NHCH_2), 4.01 (q, ^3J(H,H) = 6.8 Hz, 2H, Ar_F-NHCH_2CH_2), 3.67 (q, ^3J(H,H) = 6.5 Hz, 2H, CH_2NHC(O)), 3.52 (s, 1H, C≡C*H*), 3.25 (t, ^3J(H,H) = 6.7 Hz, 2H, Ar_F-NHCH_2CH_2), 3.01 ppm (t, ^3J(H,H) = 6.8 Hz, 2H,

C*H*$_2$CH$_2$NHC(O)). ^{13}C NMR (Acetone-D$_6$, 176 MHz): δ = 156.54, 156.52, 152.89, 151.17, 151.09, 150.82, 150.60, 148.55, 147.20, 145.39, 145.32, 138.85, 137.52, 133.44, 132.61, 132.32, 131.04, 129.32, 128.18, 128.15, 127.21, 122.88, 122.67, 121.68, 115.37, 109.94, 103.57, 78.66, 74.45, 45.49, 39.56, 39.42, 37.93 ppm. ^{19}F NMR (Acetone-D$_6$, 376 MHz): δ = −142.72 (d, ^3J(F,F) = 21.3 Hz, 2F, *m*-Ar$_F$), −161.99–(−162.12) ppm (m, 2F, *o*-Ar$_F$). m.p.: > 230 °C. HRMS (ESI): calc. for $C_{51}H_{34}F_4N_6O_4S_2Zn^+$ ([M]$^+$): 998.1311 found: 998.1294. UV/Vis (Ethanol): λ_{max} (ε [M^{-1}cm^{-1}]) = 597 (5000), 556 (18 000), 423 nm (411 000).

2. ^{1}H, ^{13}C, and ^{19}F-NMR of porphyrins **1d, 2a-i, 4, 5a-c, 6a-c, 8a-c, 9, 10a-d, 11, 13a-b**, and **14a-b**

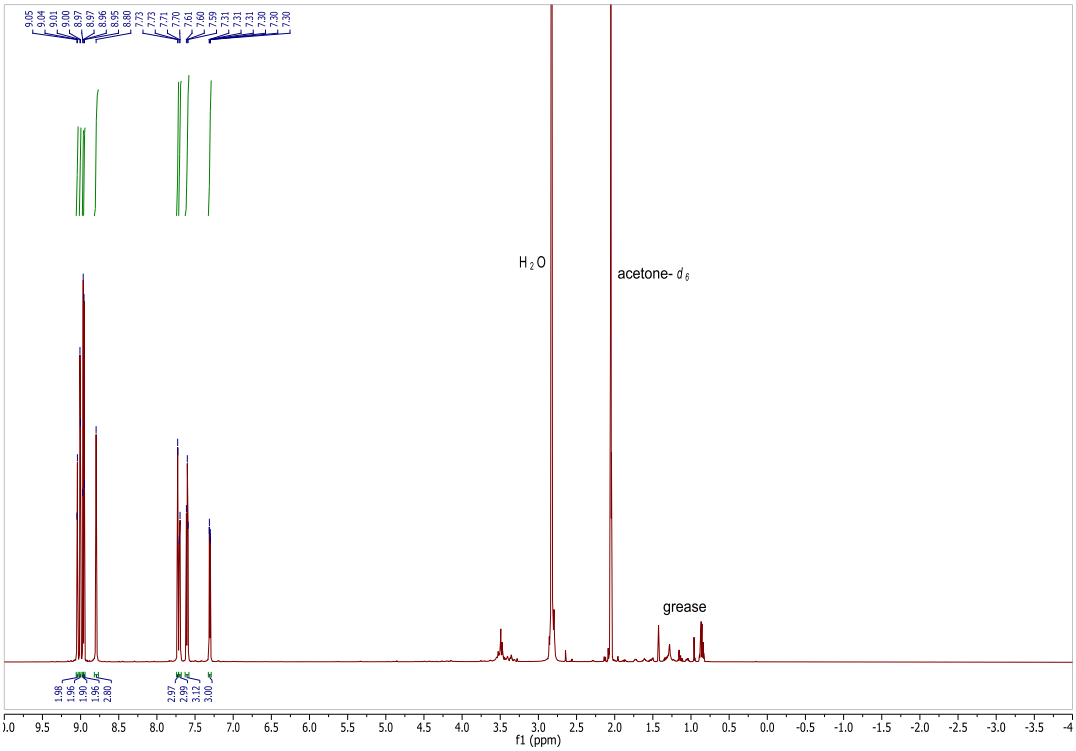


Figure 1. ^{1}H spectrum (*Bruker BioSpin* AVANCE700, 700 MHz, acetone-d_6) of porphyrin **1d**

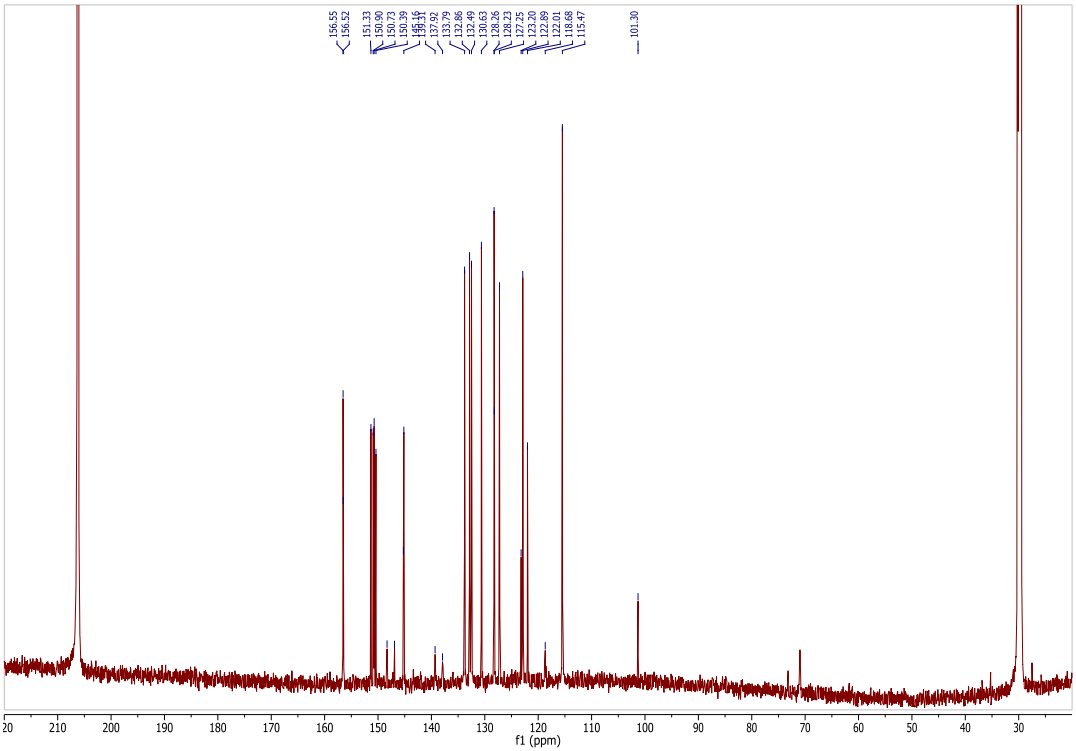


Figure 2. ^{13}C spectrum (*Bruker BioSpin* AVANCE700, 176 MHz, acetone-d_6) of porphyrin **1d**

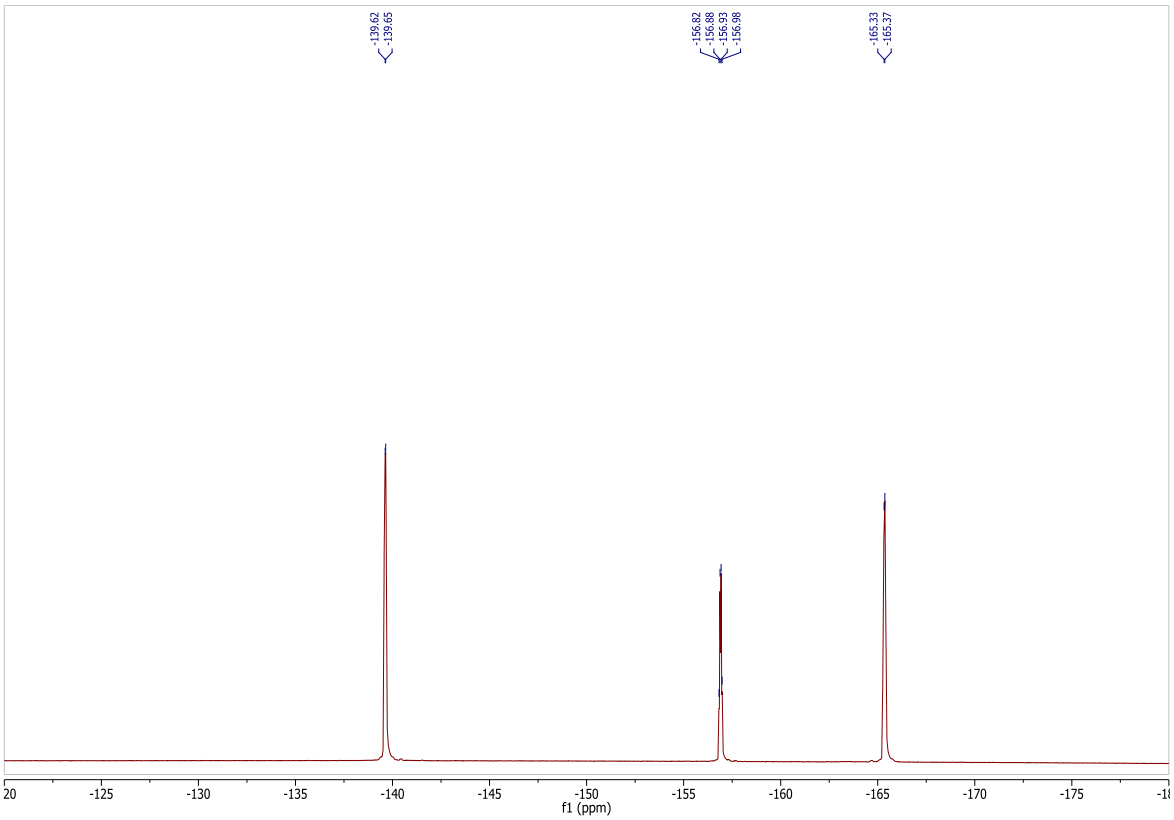


Figure 3. ^{19}F spectrum (*JEOL*^{TM} ECX 400, 376 MHz, acetone-d_6) of porphyrin **1d**

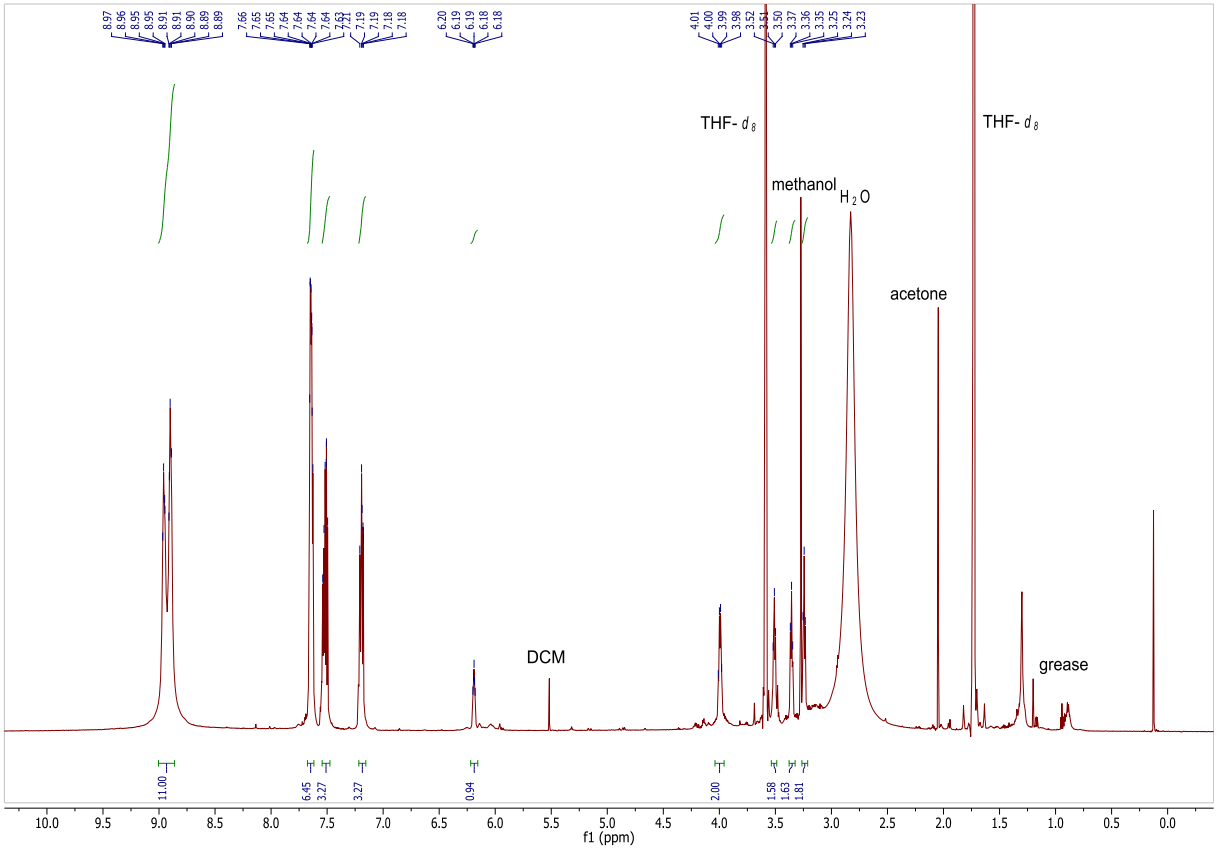


Figure 4. ^{1}H spectrum (*Bruker BioSpin* AVANCE700, 700 MHz, THF-d_8) of porphyrin **2a**

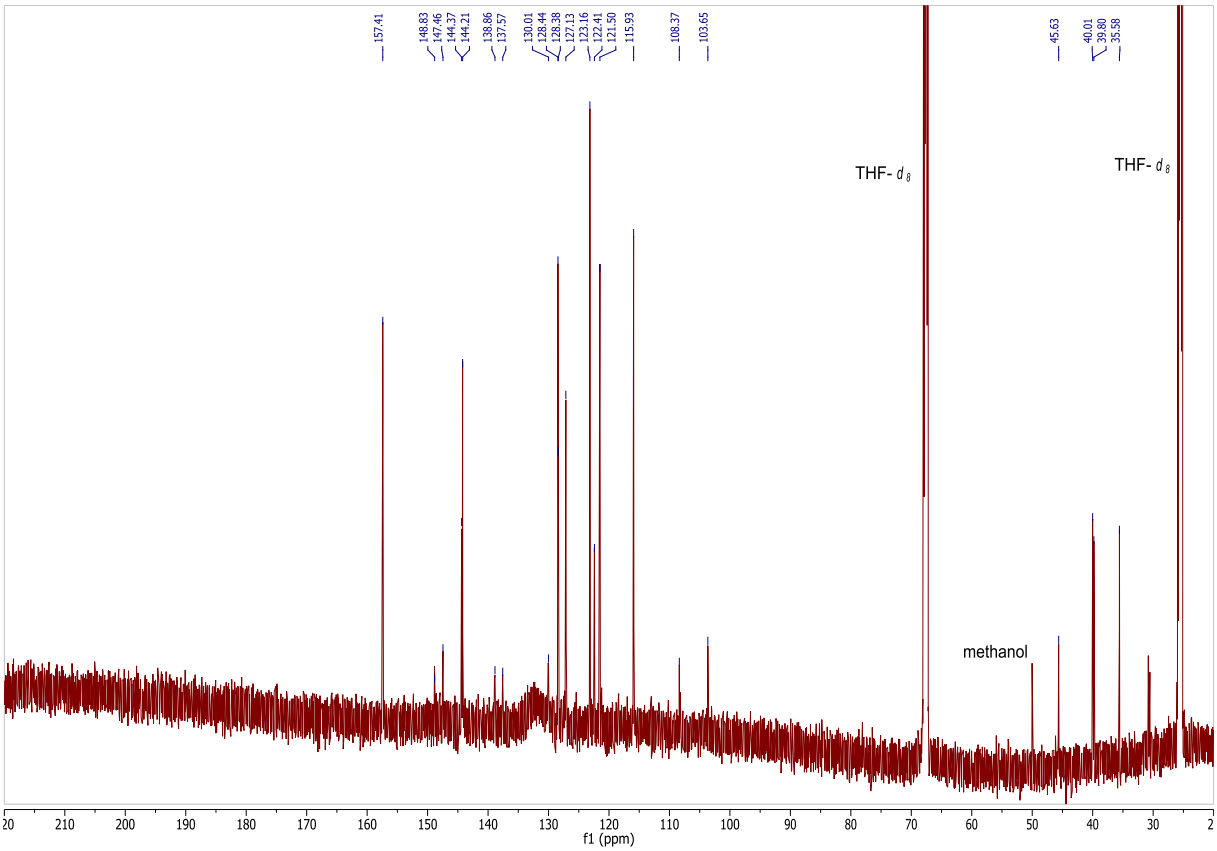


Figure 5. ^{13}C spectrum (*Bruker BioSpin* AVANCE700, 176 MHz, THF-d_8) of porphyrin **2a**

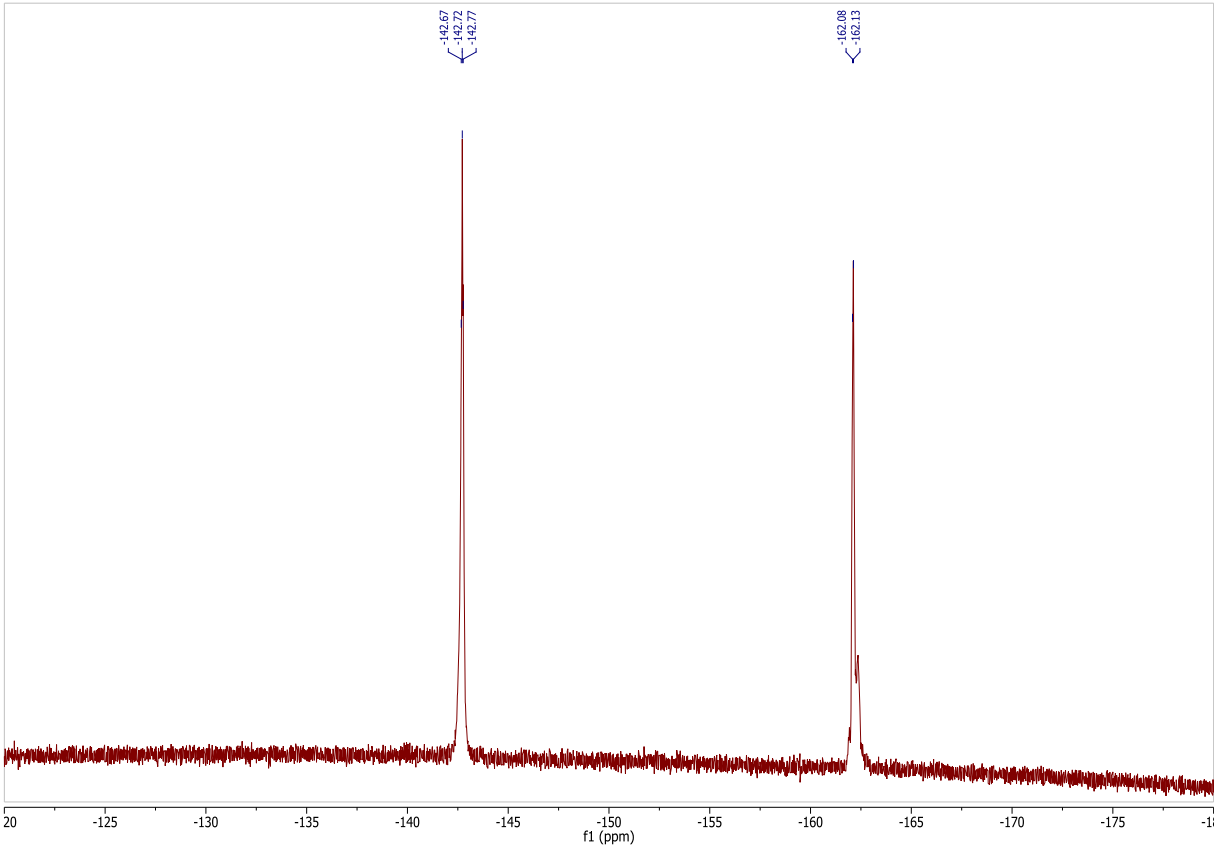


Figure 6. ^{19}F spectrum (*JEOL*^{TM} ECX 400, 376 MHz, THF-d_8) of porphyrin **2a**

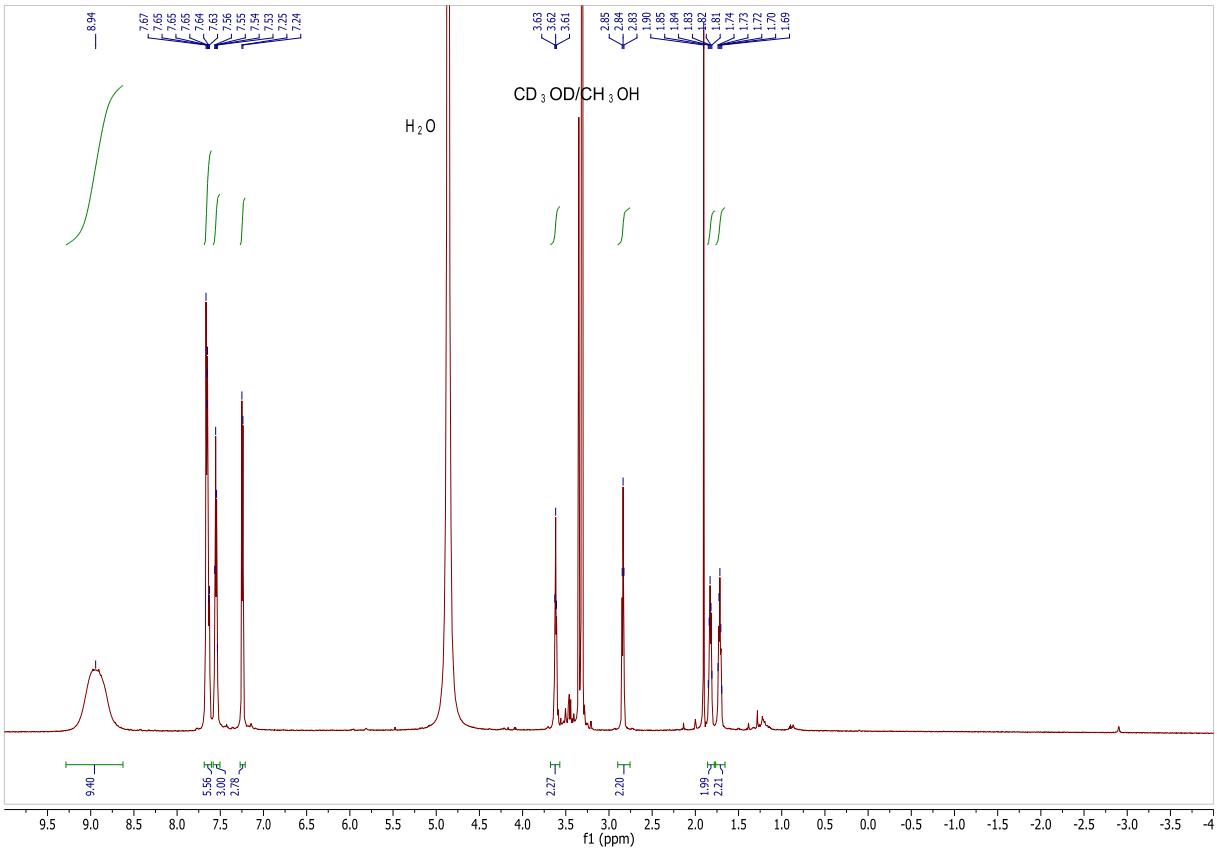


Figure 7. ^{1}H spectrum (*Bruker BioSpin* AVANCE700, 700 MHz, CD_3OD) of porphyrin **2b**

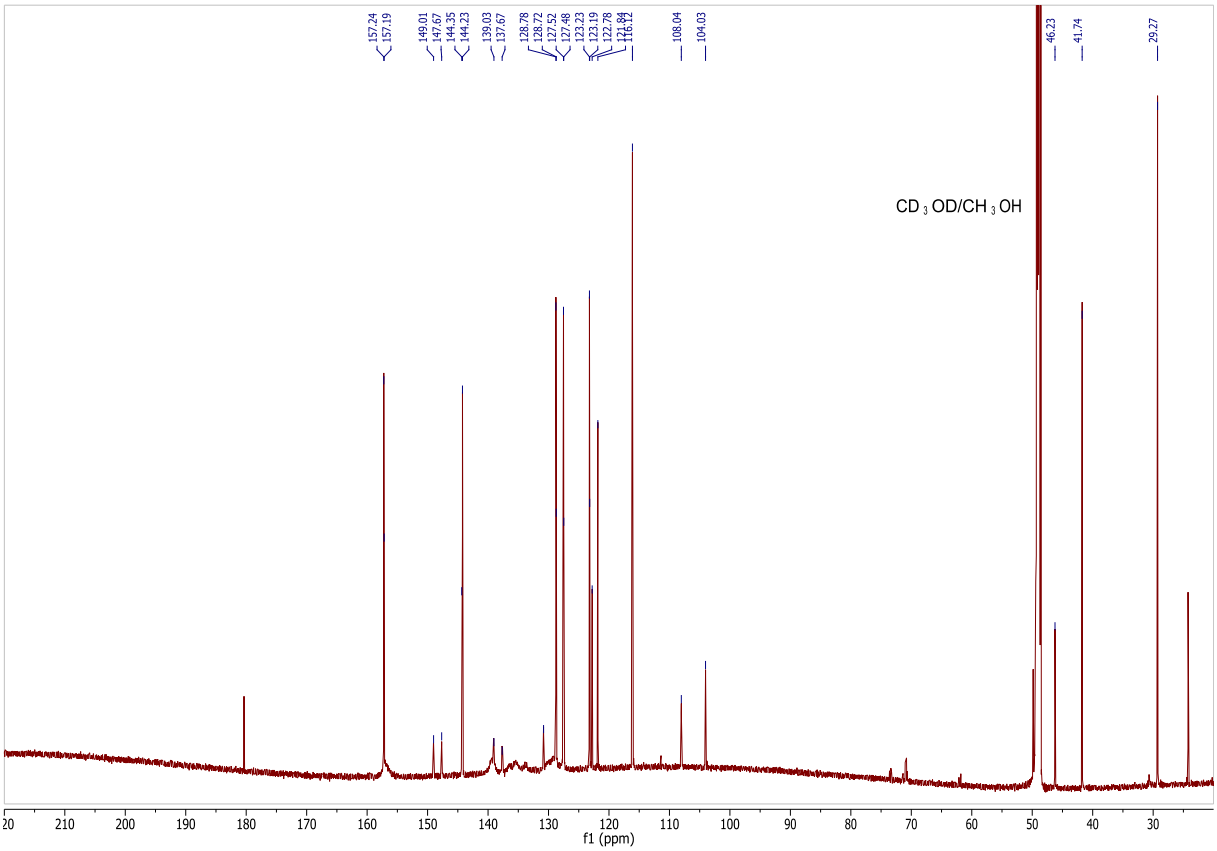


Figure 8. ^{13}C spectrum (*Bruker BioSpin* AVANCE700, 126 MHz, CD_3OD) of porphyrin **2b**

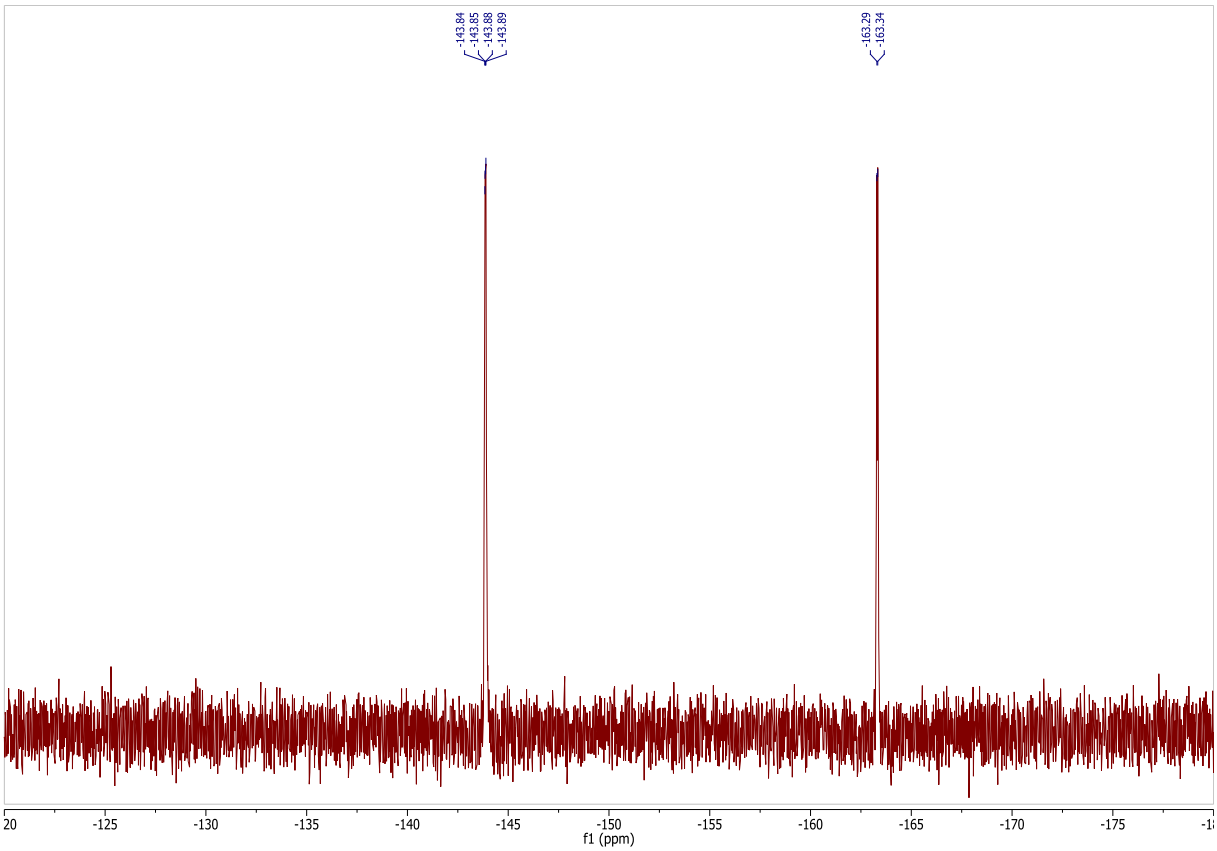


Figure 9. ^{19}F spectrum (*JEOL*^{TM} ECX 400, 376 MHz, CD_3OD) of porphyrin **2b**

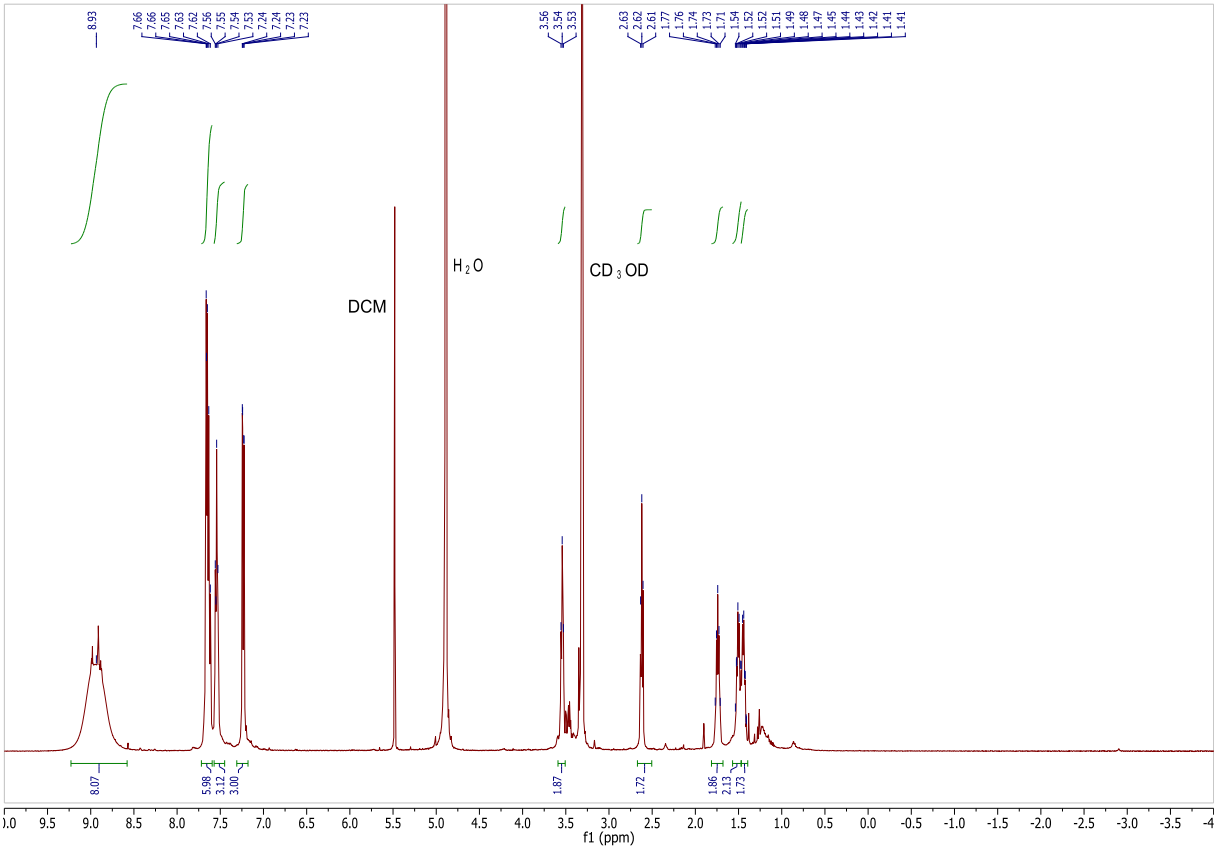


Figure 10. ^{1}H spectrum (*JEOL*^{TM} ECP 500, 500 MHz, CD_3OD) of porphyrin **2c**

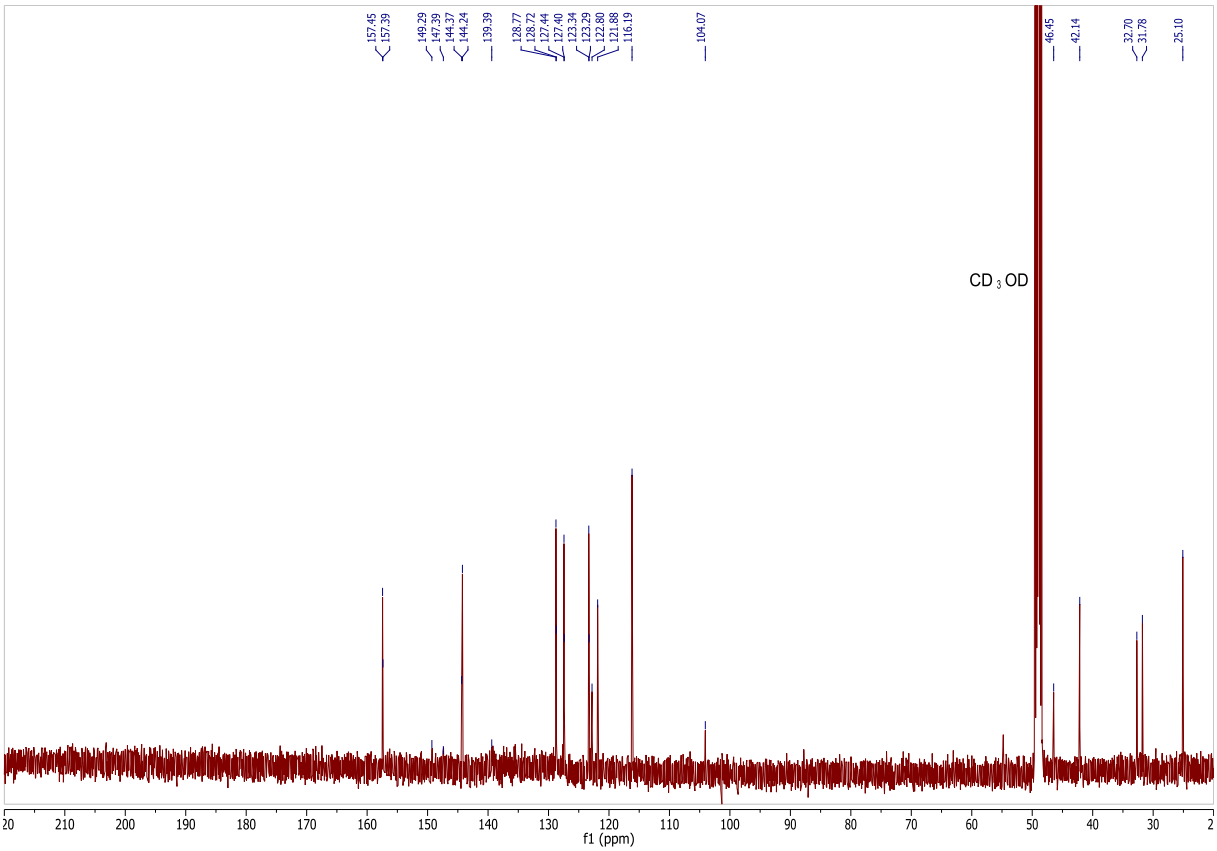


Figure 11. ^{13}C spectrum (*JEOL*^{TM} ECP 500, 126 MHz, CD_3OD) of porphyrin **2c**

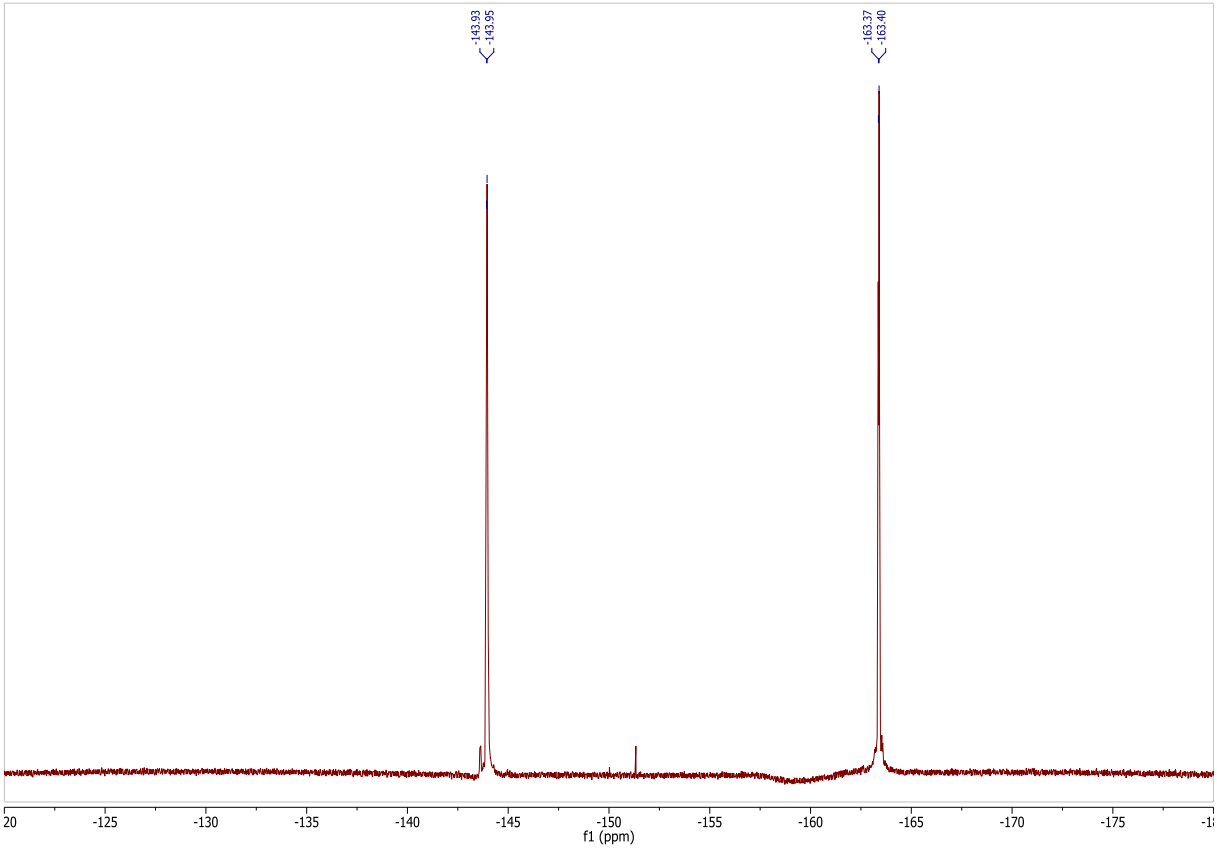


Figure 12. ^{19}F spectrum (*JEOL*^{TM} ECX 400, 376 MHz, CD_3OD) of porphyrin **2c**

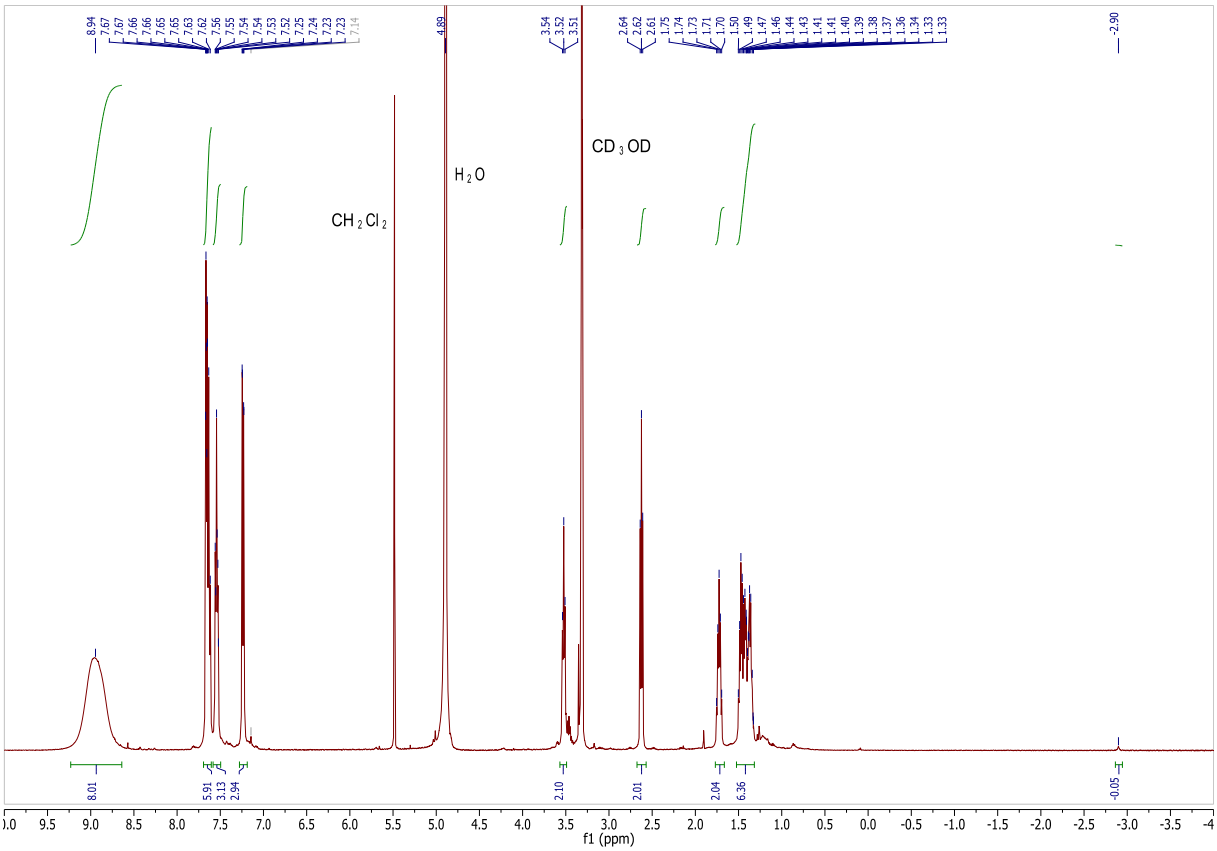


Figure 13. ^{1}H spectrum (*JEOL*^{TM} ECP 500, 500 MHz, CD_3OD) of porphyrin **2d**

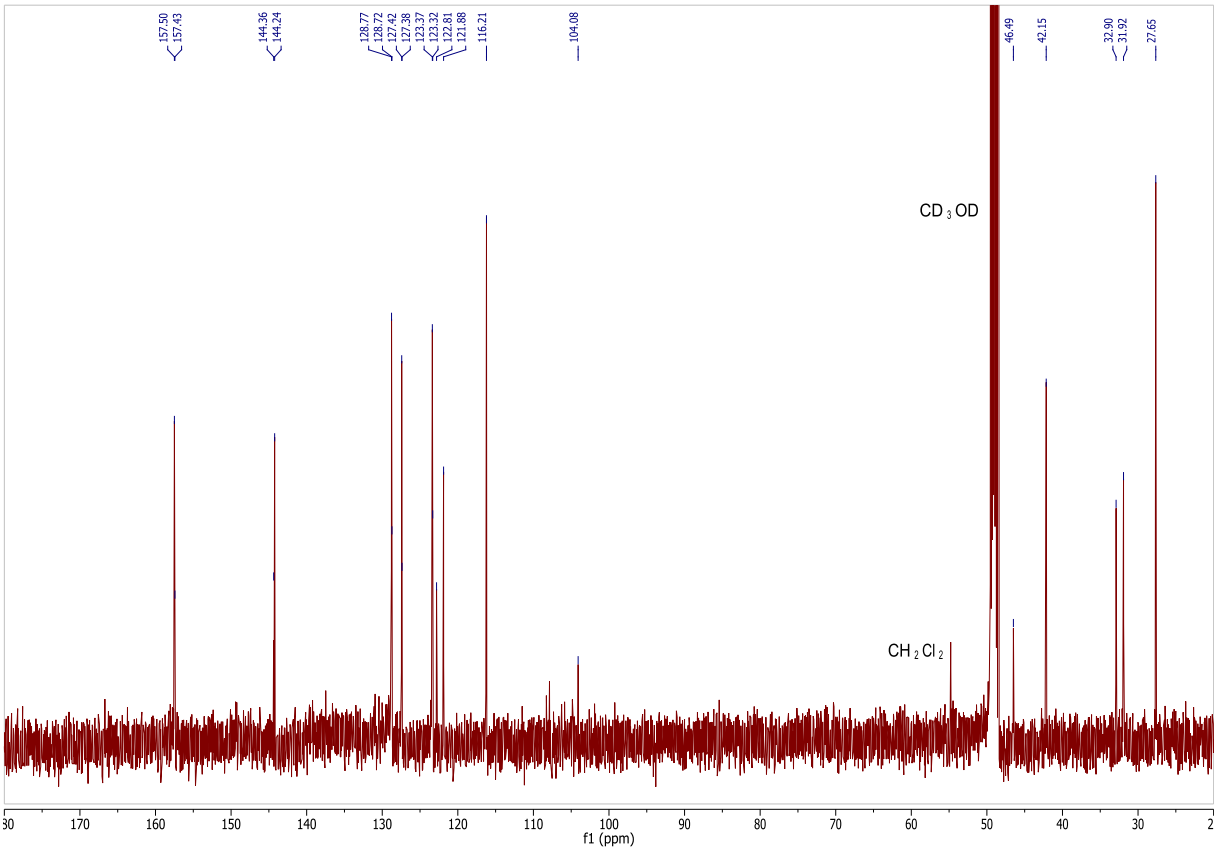


Figure 14. ^{13}C spectrum (*JEOL*^{TM} ECP 500, 126 MHz, CD_3OD) of porphyrin **2d**

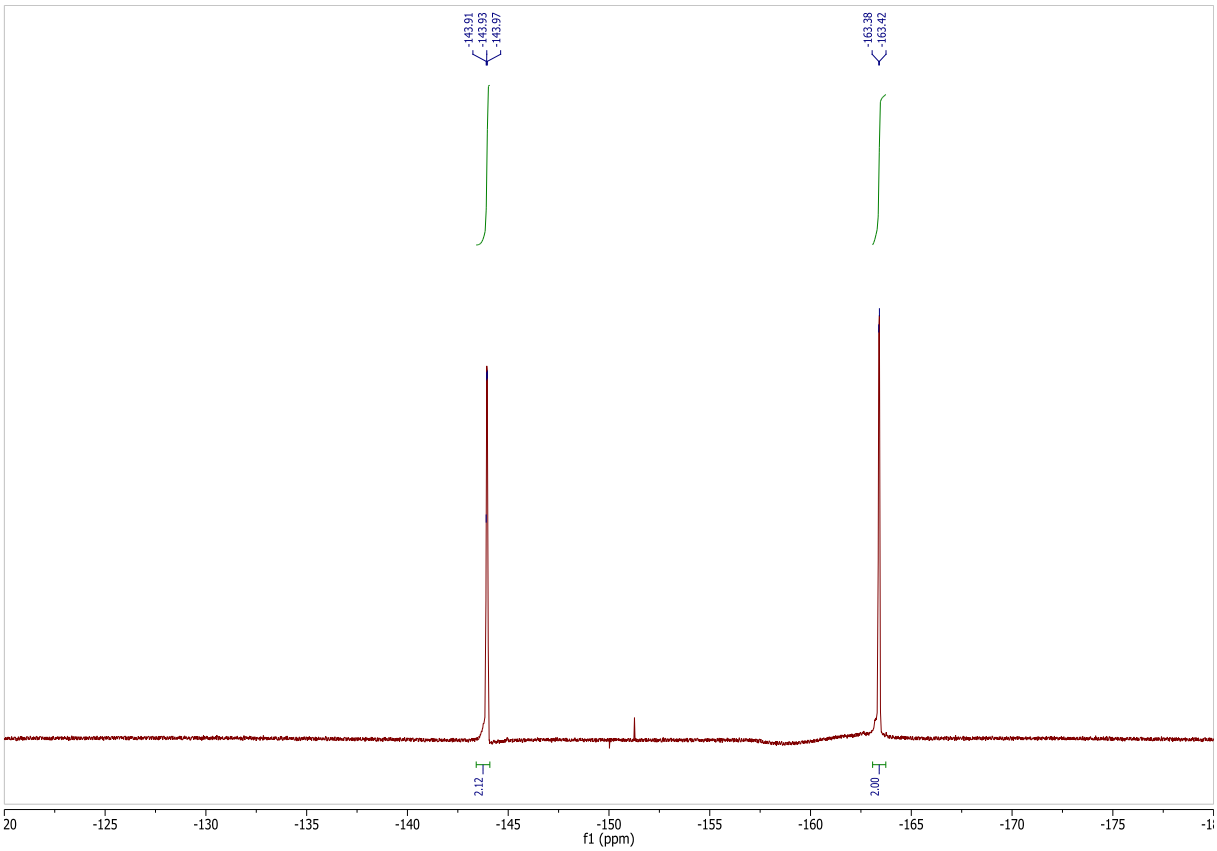


Figure 15. ^{19}F spectrum (*JEOL*^{TM} ECP 500, 471 MHz, CD_3OD) of porphyrin **2d**

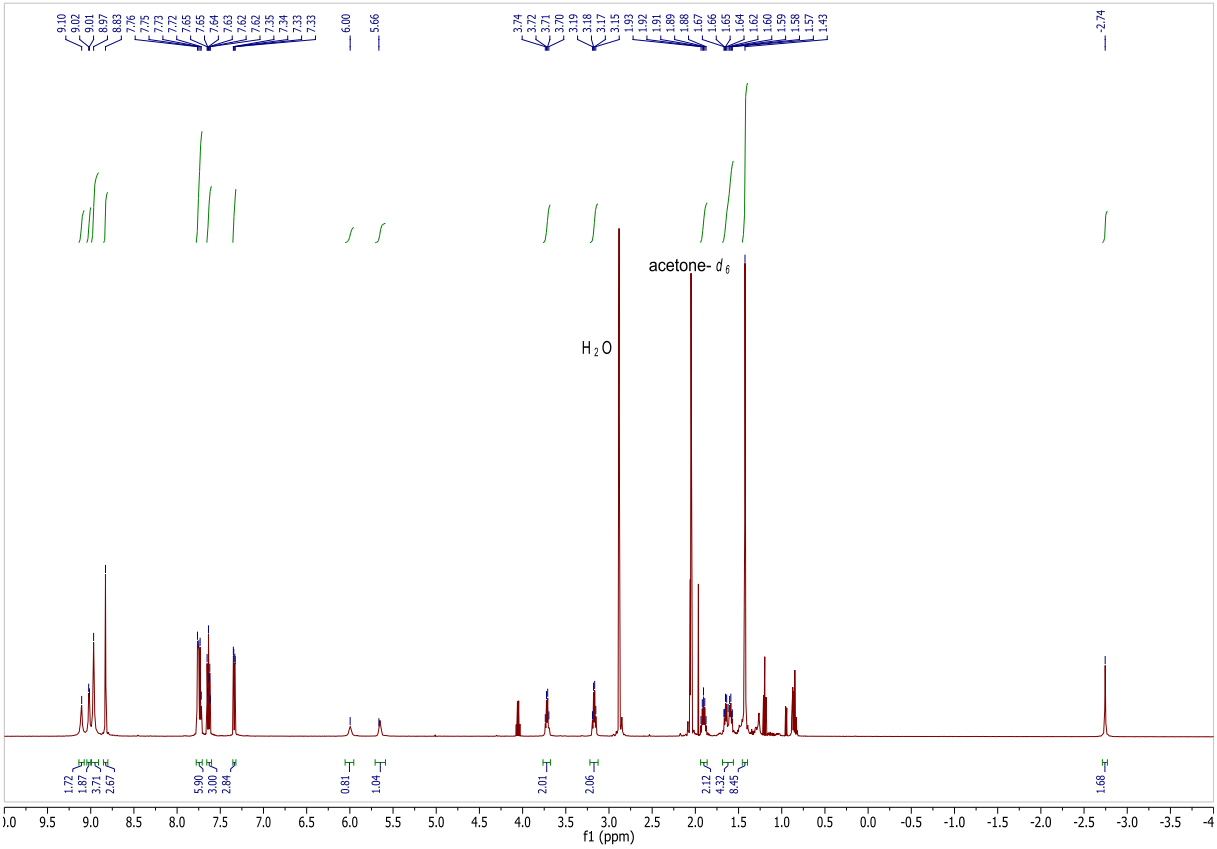


Figure 16. ^{1}H spectrum (*JEOL*^{TM} ECP 500, 500 MHz, acetone-d_6) of porphyrin **2e**

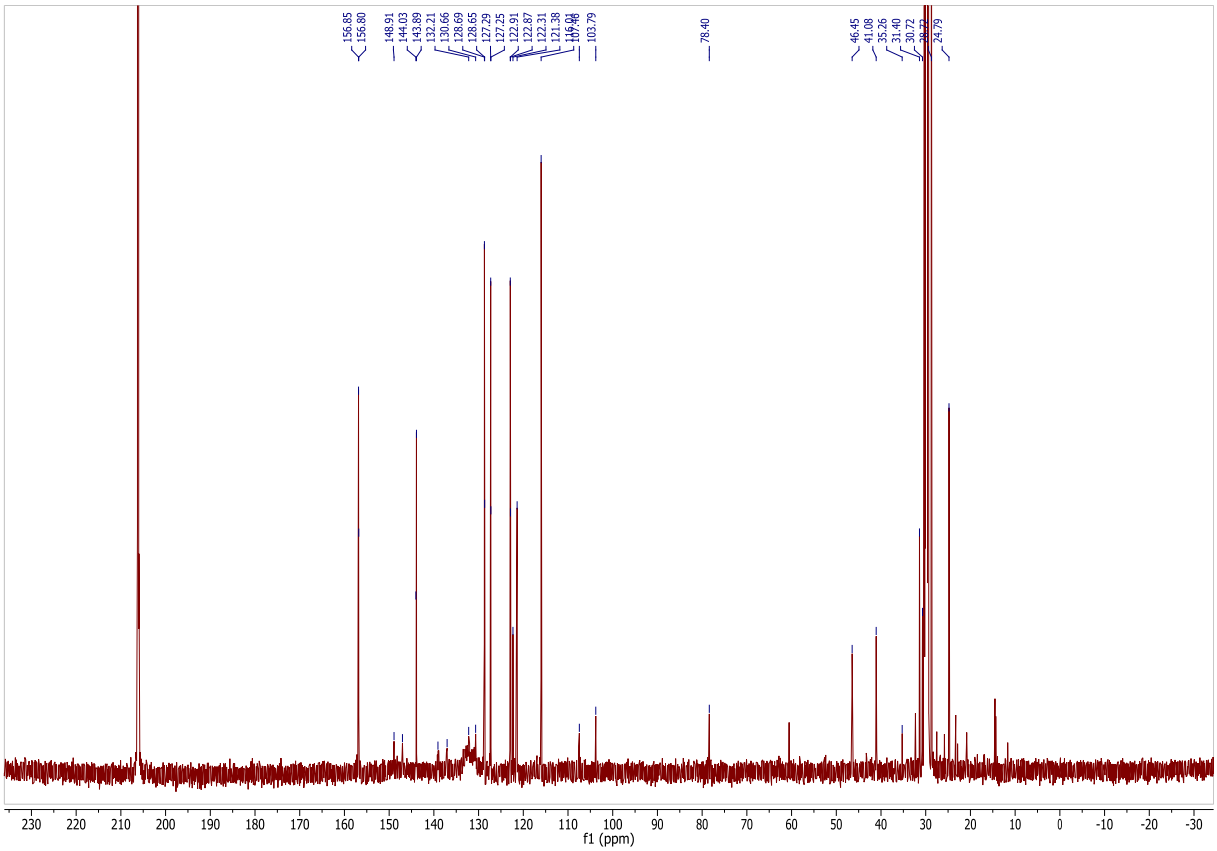


Figure 17. ^{13}C spectrum (*JEOL*^{TM} ECP 500, 126 MHz, acetone-d_6) of porphyrin **2e**

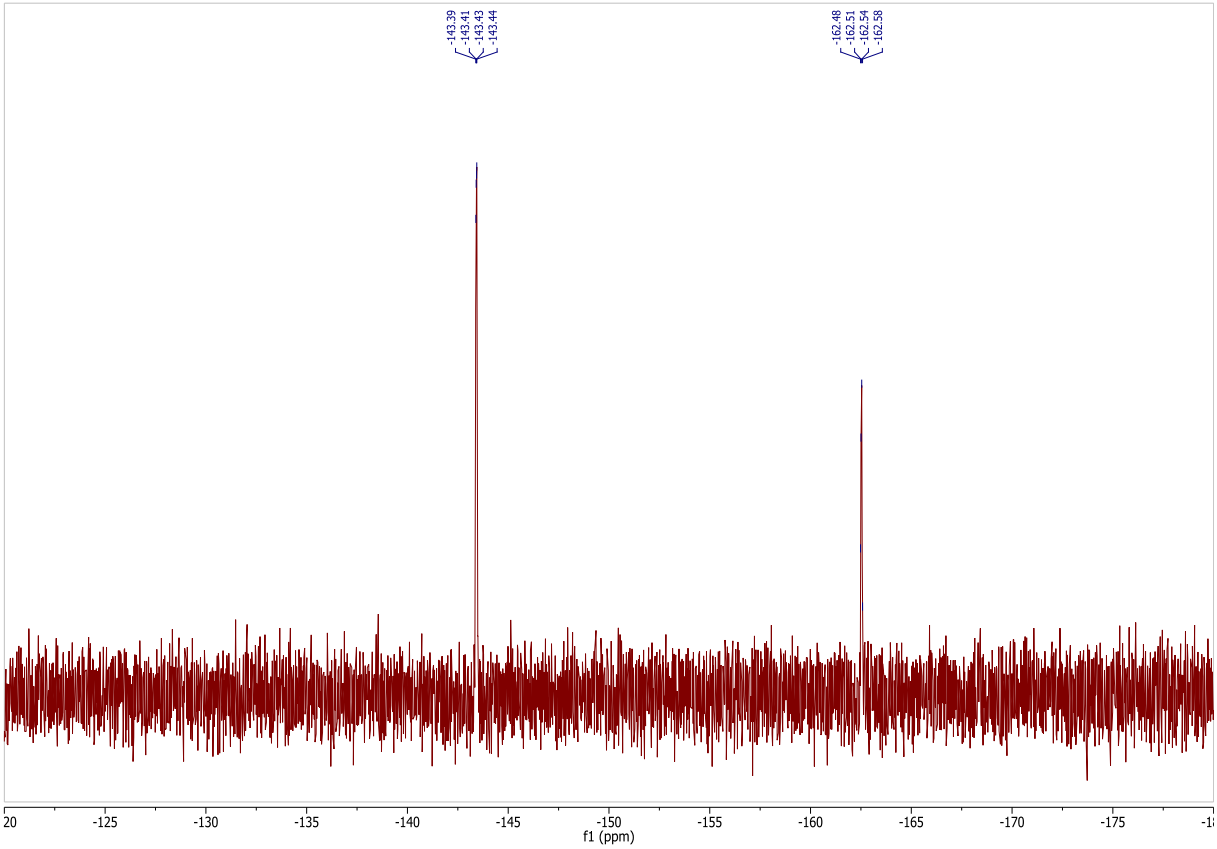


Figure 18. ^{19}F spectrum (*JEOL*^{TM} ECP 500, 471 MHz, acetone-d_6) of porphyrin **2e**

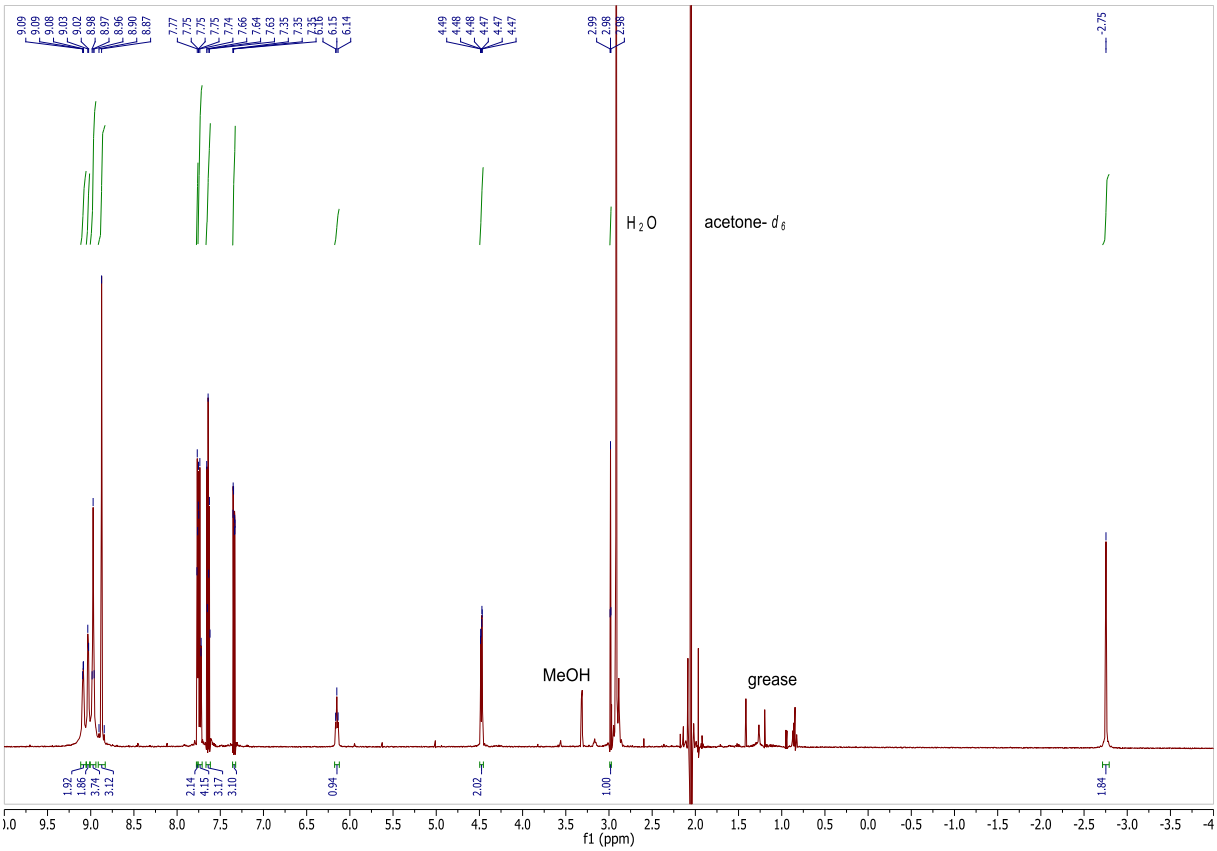


Figure 19. ^{1}H spectrum (*JEOL*^{TM} ECP 500, 500 MHz, acetone-d_6) of porphyrin **2f**

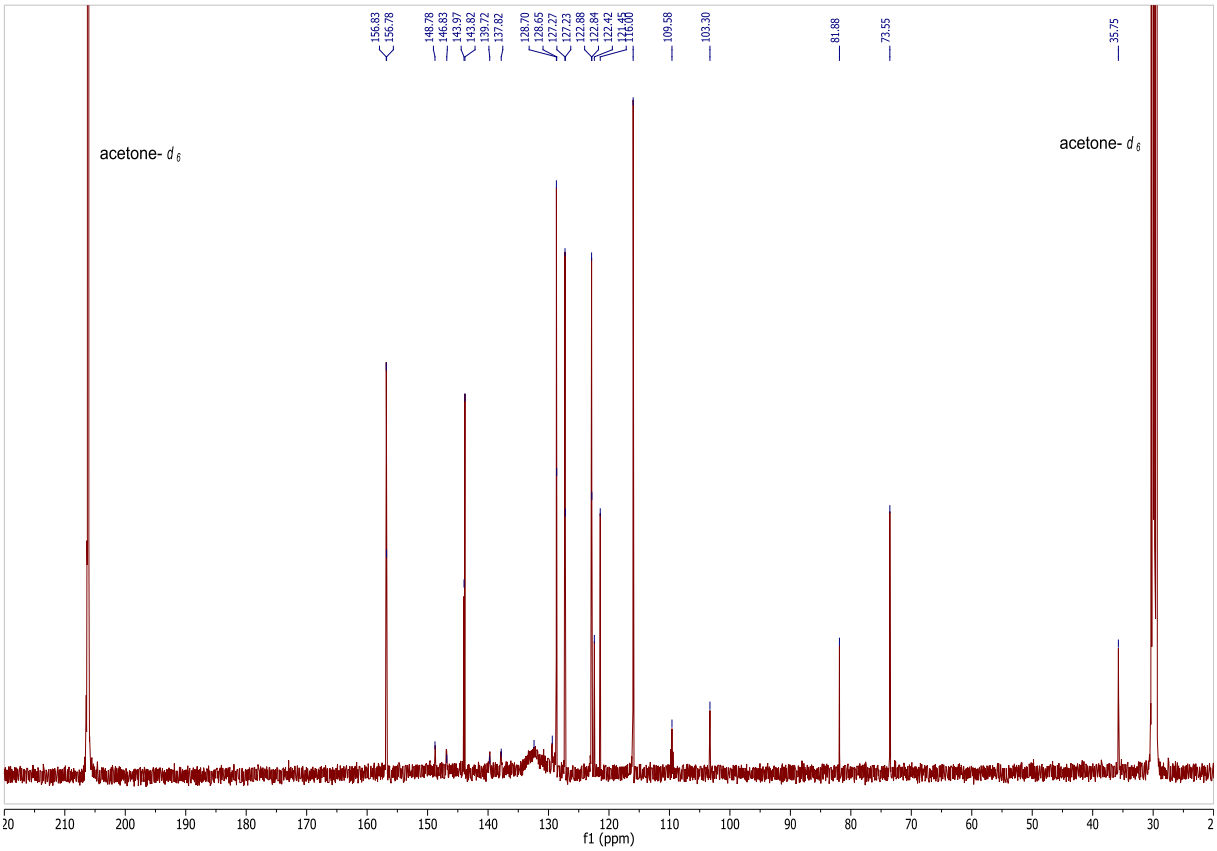


Figure 20. ^{13}C spectrum (*JEOL*^{TM} ECP 500, 126 MHz, acetone-d_6) of porphyrin **2f**

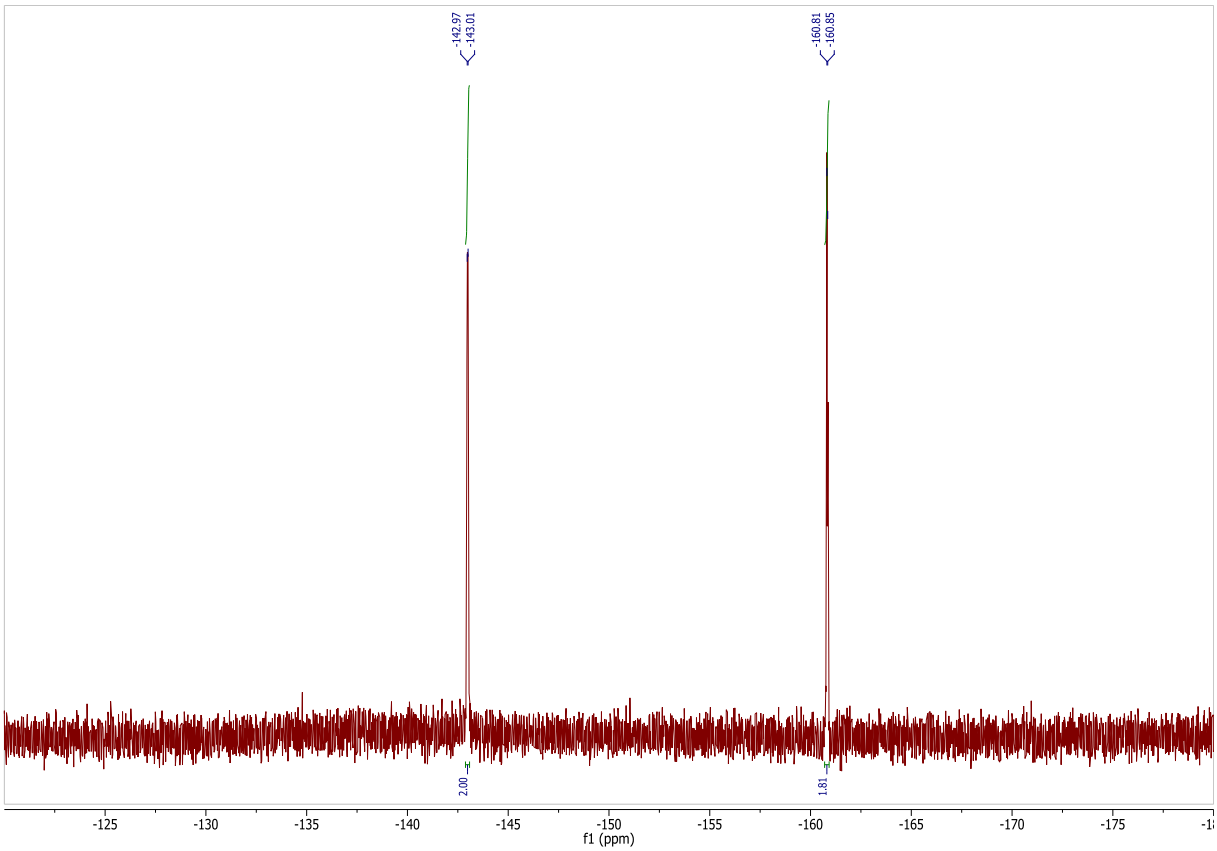


Figure 21. ^{19}F spectrum (*JEOL*^{TM} ECP 500, 471 MHz, acetone-d_6) of porphyrin **2f**

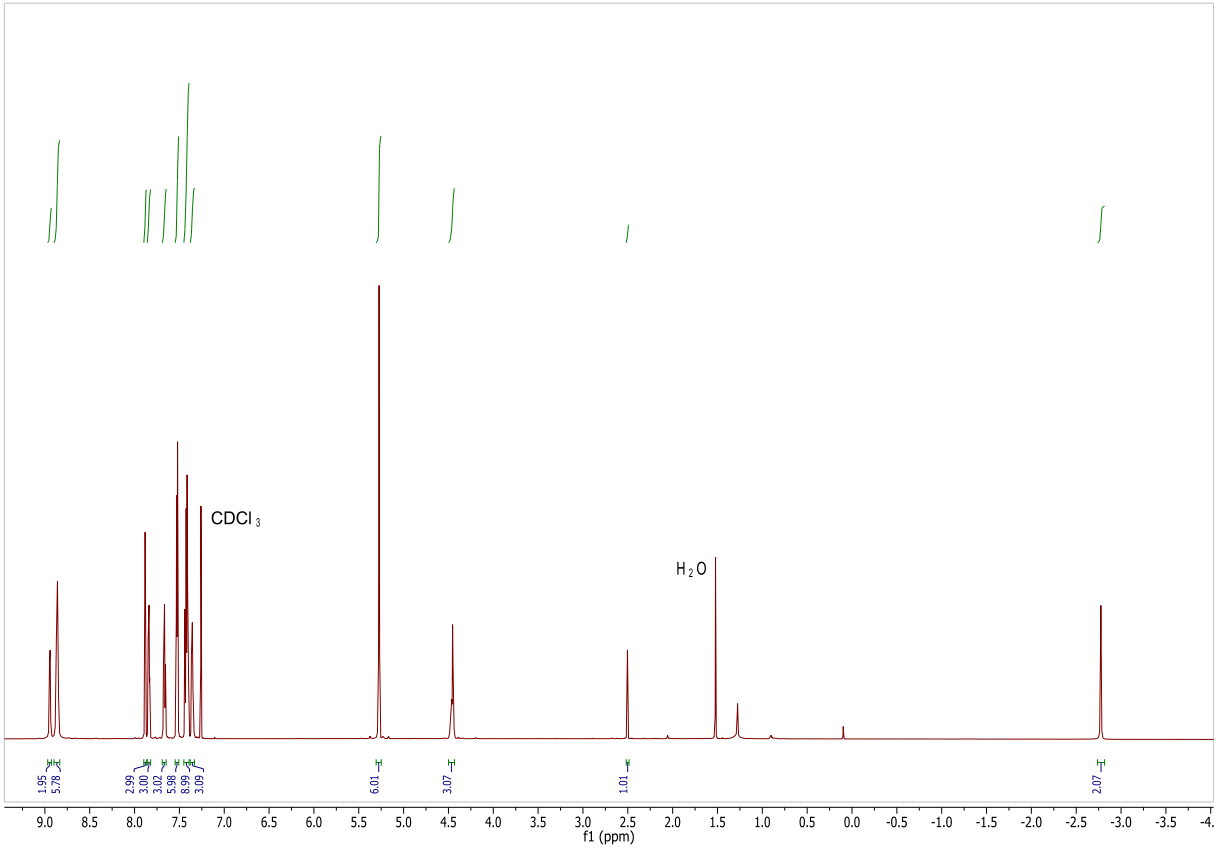


Figure 22. ^{1}H spectrum (*Bruker BioSpin* AVANCE700, 700 MHz, $CDCl_3$) of porphyrin **2g**

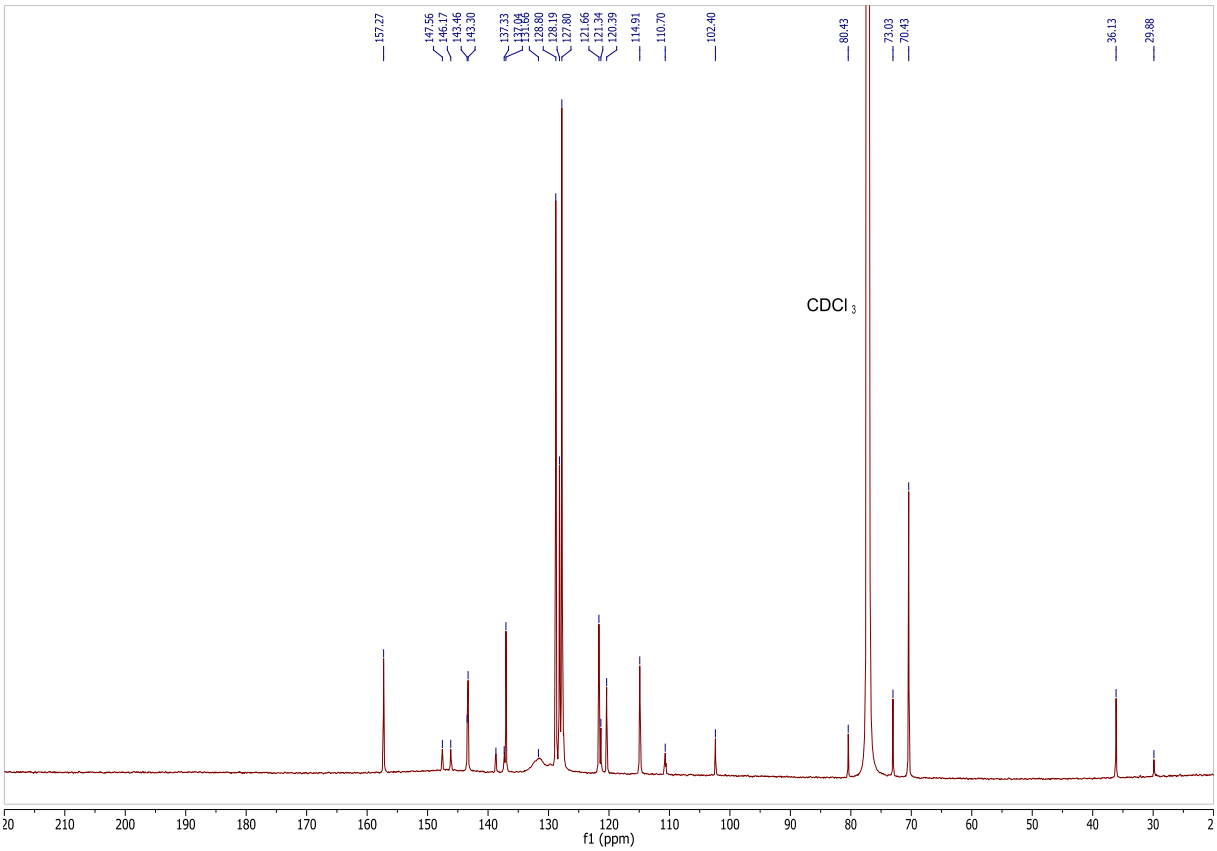


Figure 23. ^{13}C spectrum (*Bruker BioSpin* AVANCE700, 176 MHz, $CDCl_3$) of porphyrin **2g**

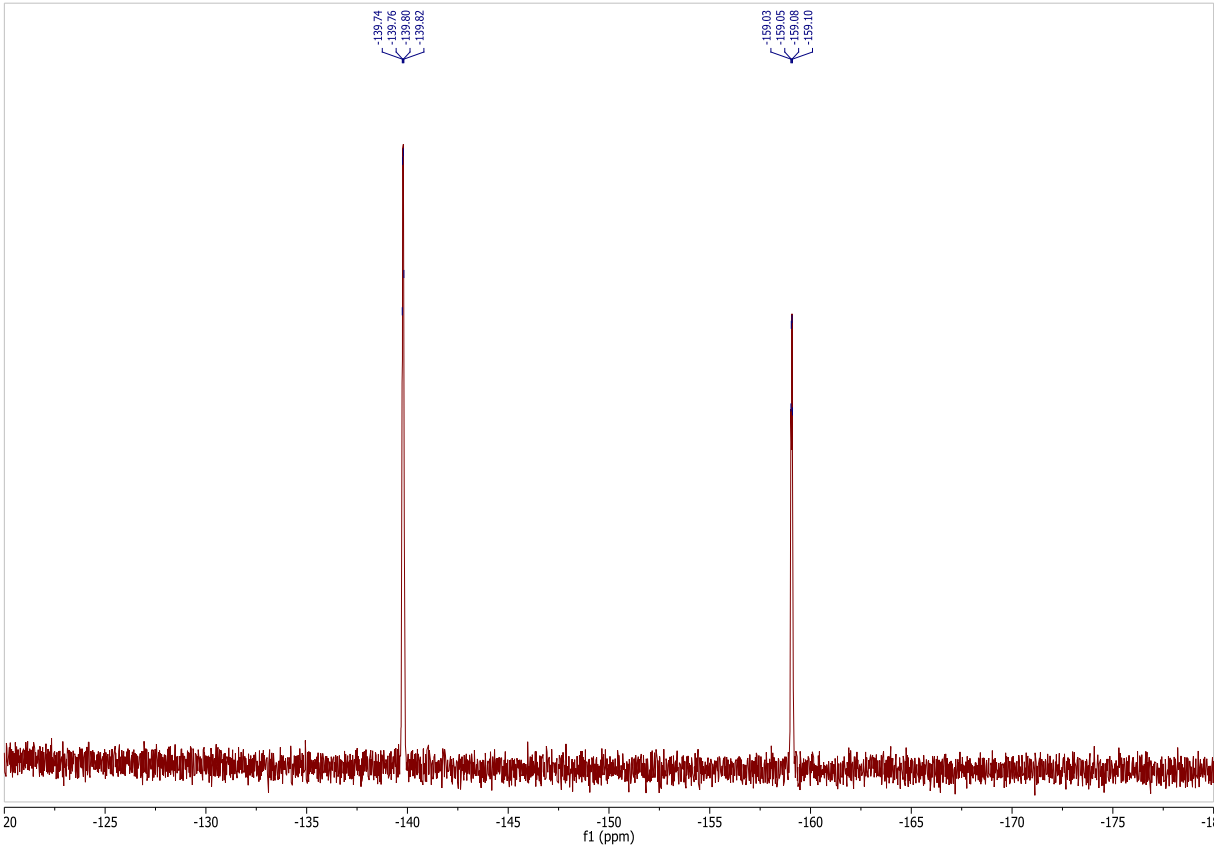


Figure 24. ^{19}F spectrum (*JEOL*^{TM} ECP 500, 471 MHz, $CDCl_3$) of porphyrin **2g**

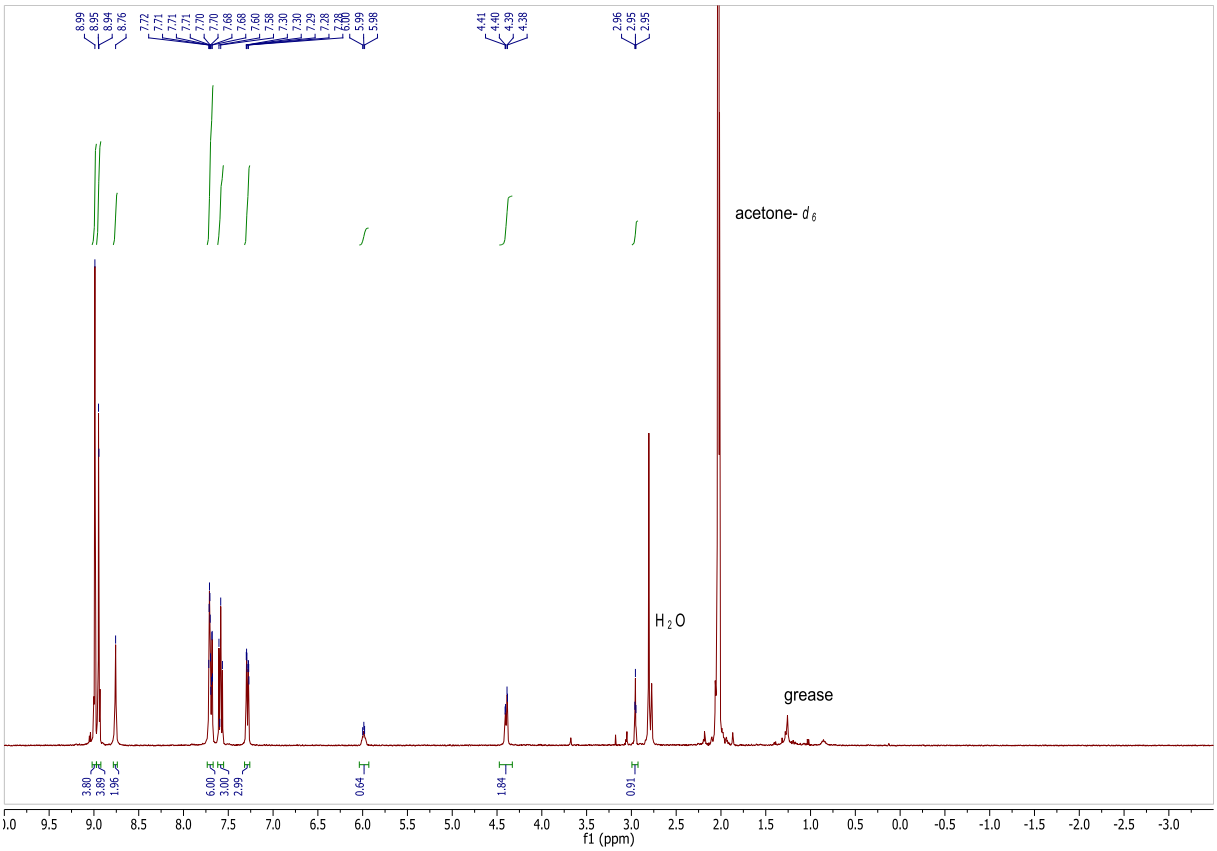


Figure 25. ^{1}H spectrum (*JEOL*^{TM} ECX 400, 400 MHz, acetone-d_6) of porphyrin **2h**

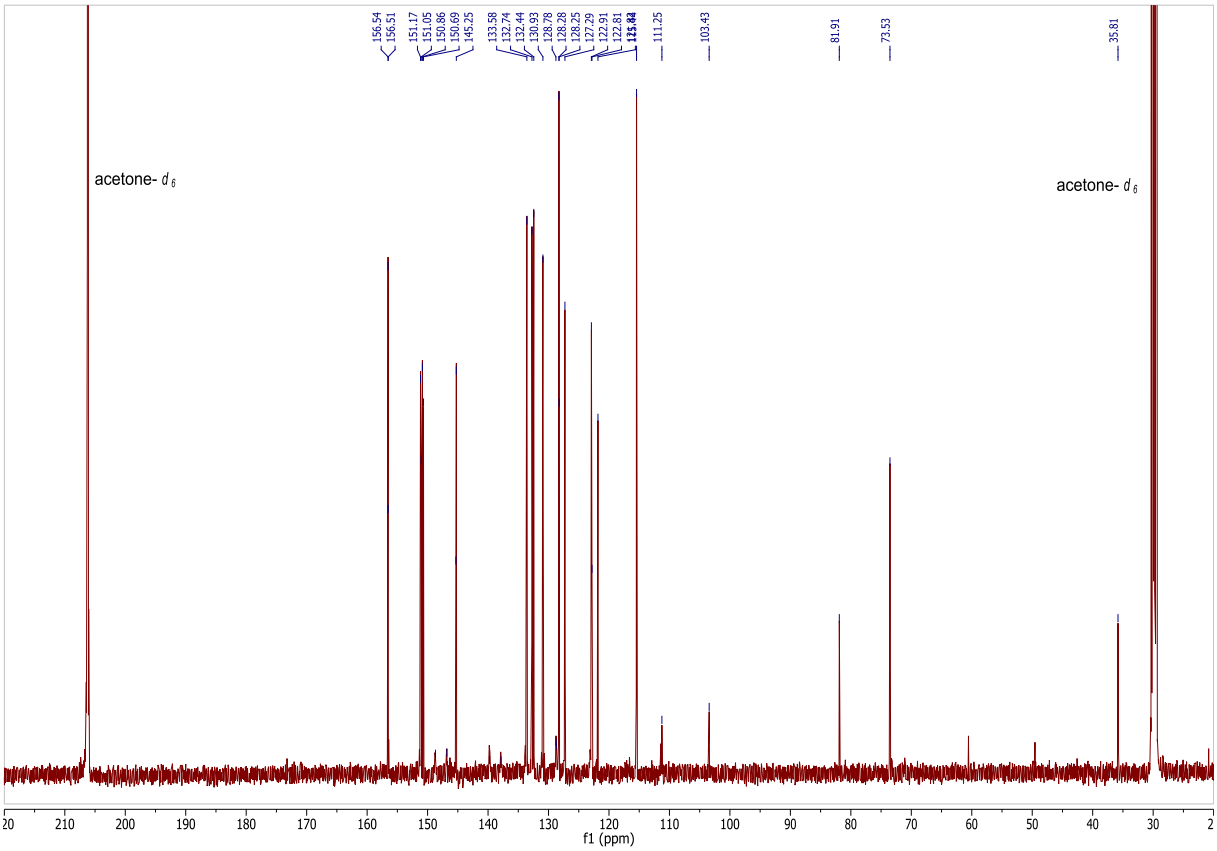


Figure 26. ^{13}C spectrum (*JEOL*^{TM} ECP 500, 126 MHz, acetone-d_6) of porphyrin **2h**

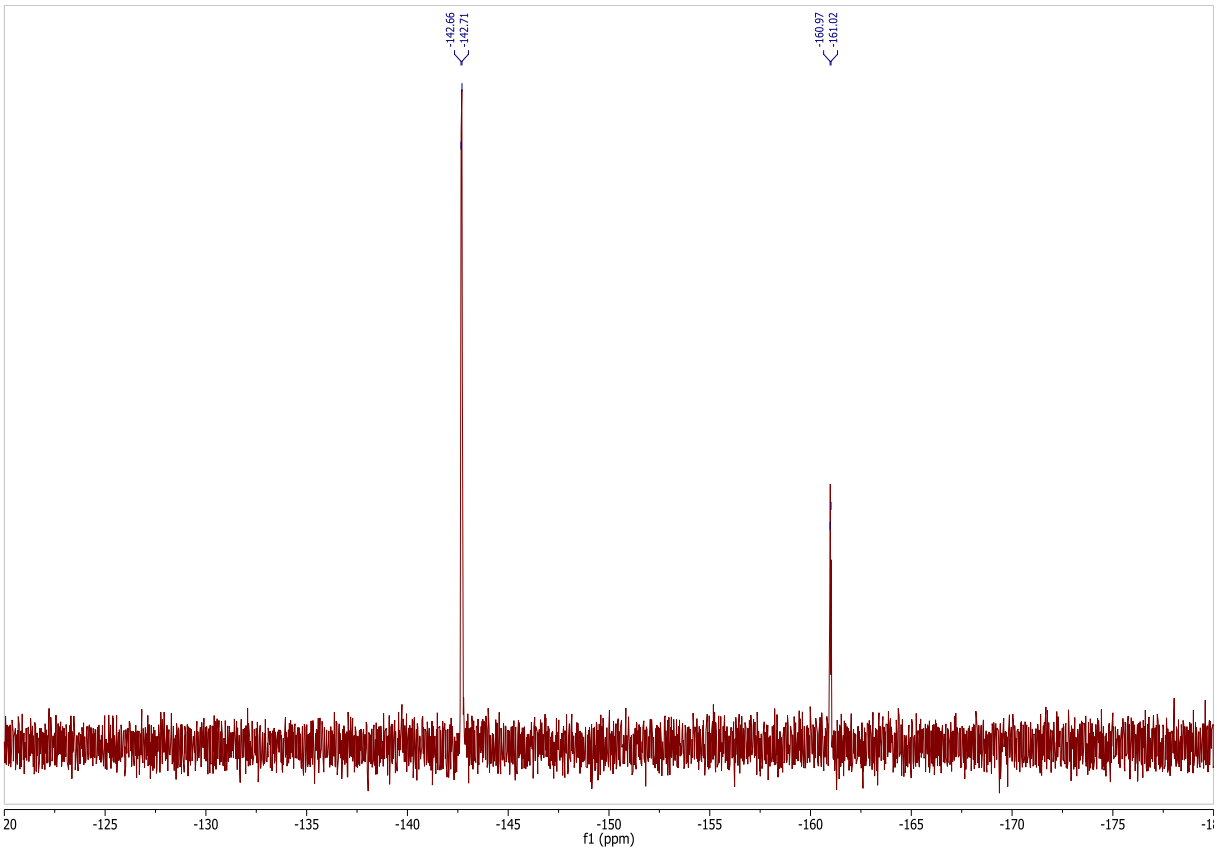


Figure 27. ^{19}F spectrum (*JEOL*^{TM} ECP 500, 471 MHz, acetone-d_6) of porphyrin **2h**

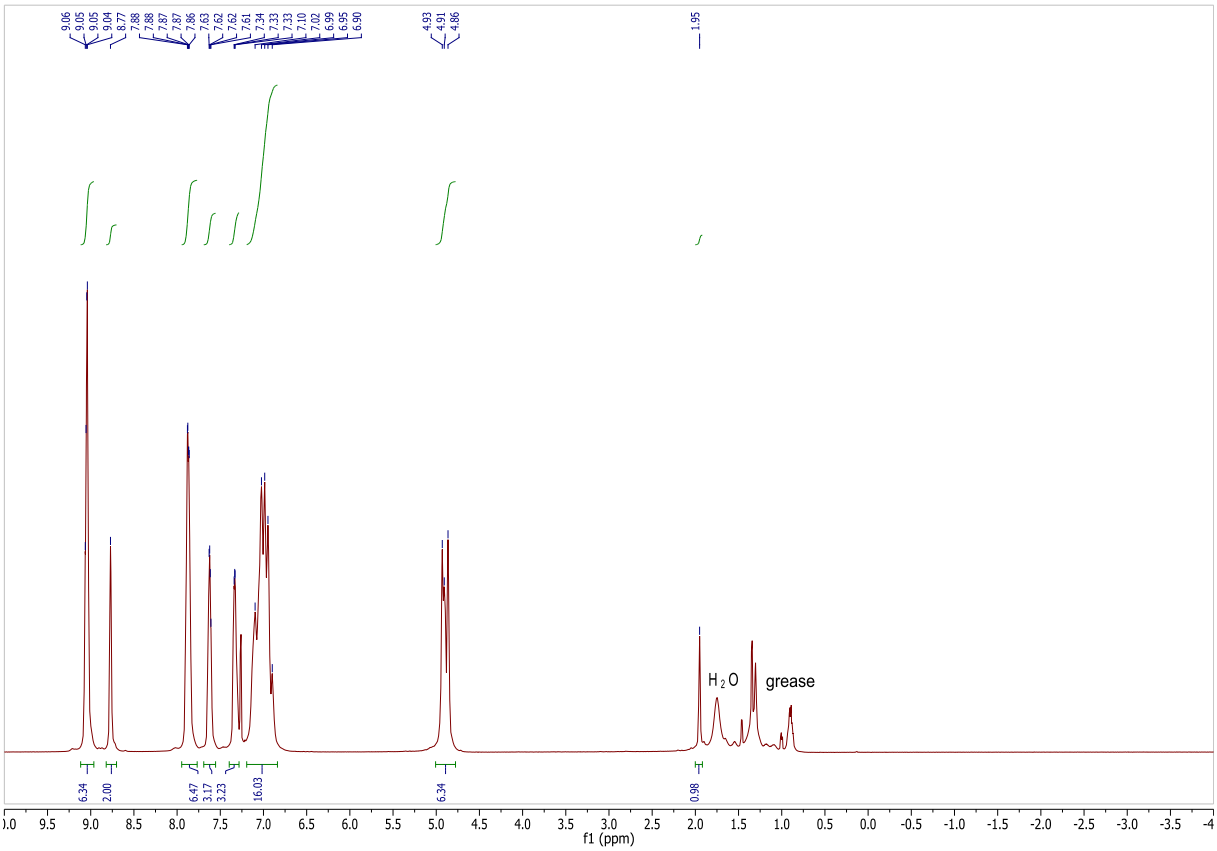


Figure 28. ^{1}H spectrum (*JEOL*^{TM} ECP 500, 500 MHz, $CDCl_3$) of porphyrin **2i**

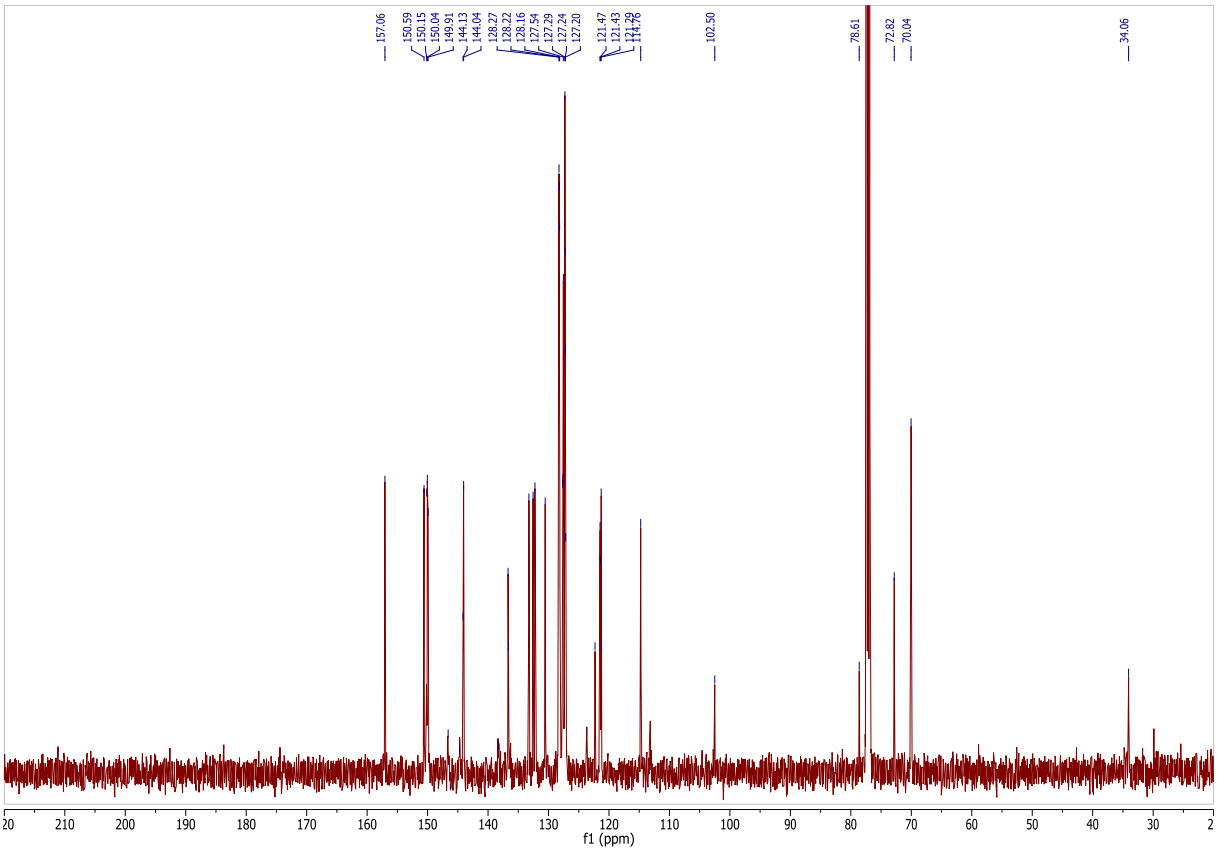


Figure 29. ^{13}C spectrum (*JEOL*^{TM} ECP 500, 126 MHz, $CDCl_3$) of porphyrin **2i**

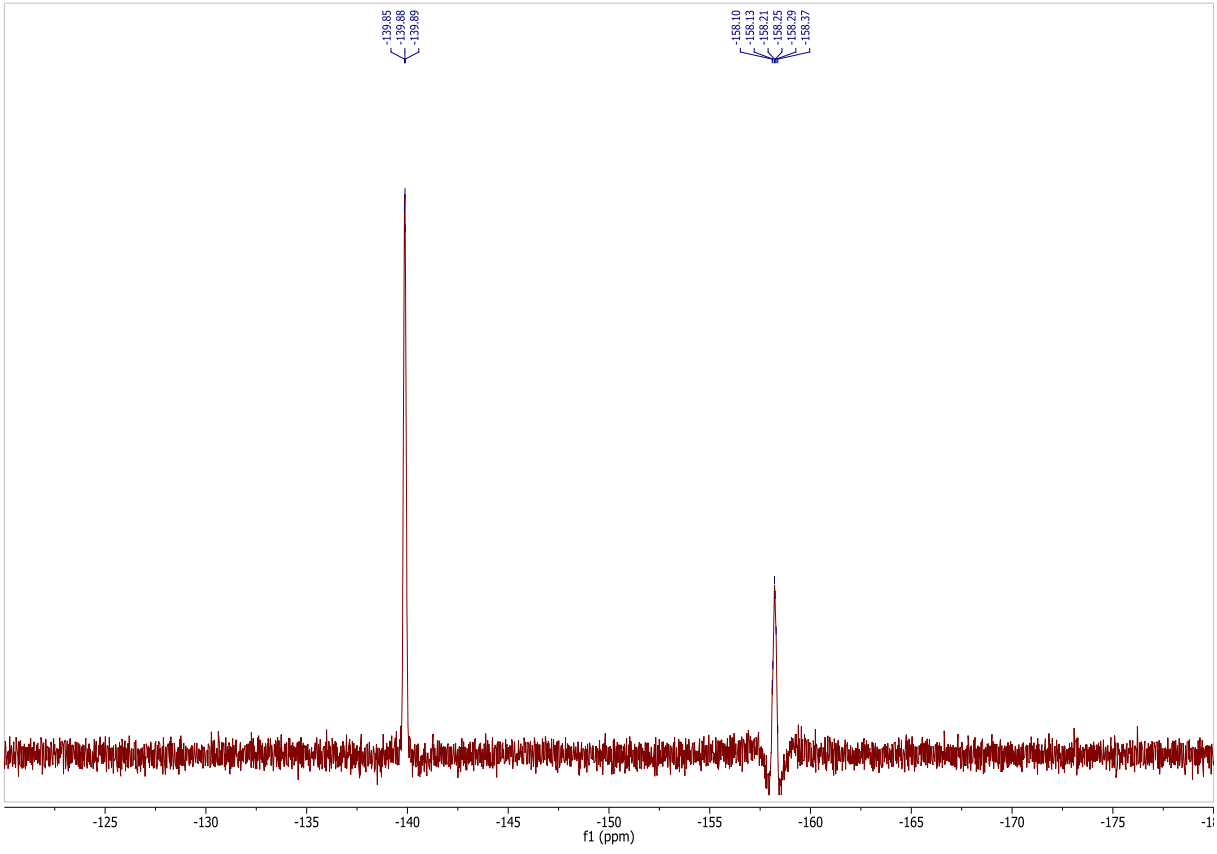


Figure 30. ^{19}F spectrum (*JEOL*^{TM} ECP 500, 471 MHz, $CDCl_3$) of porphyrin **2i**

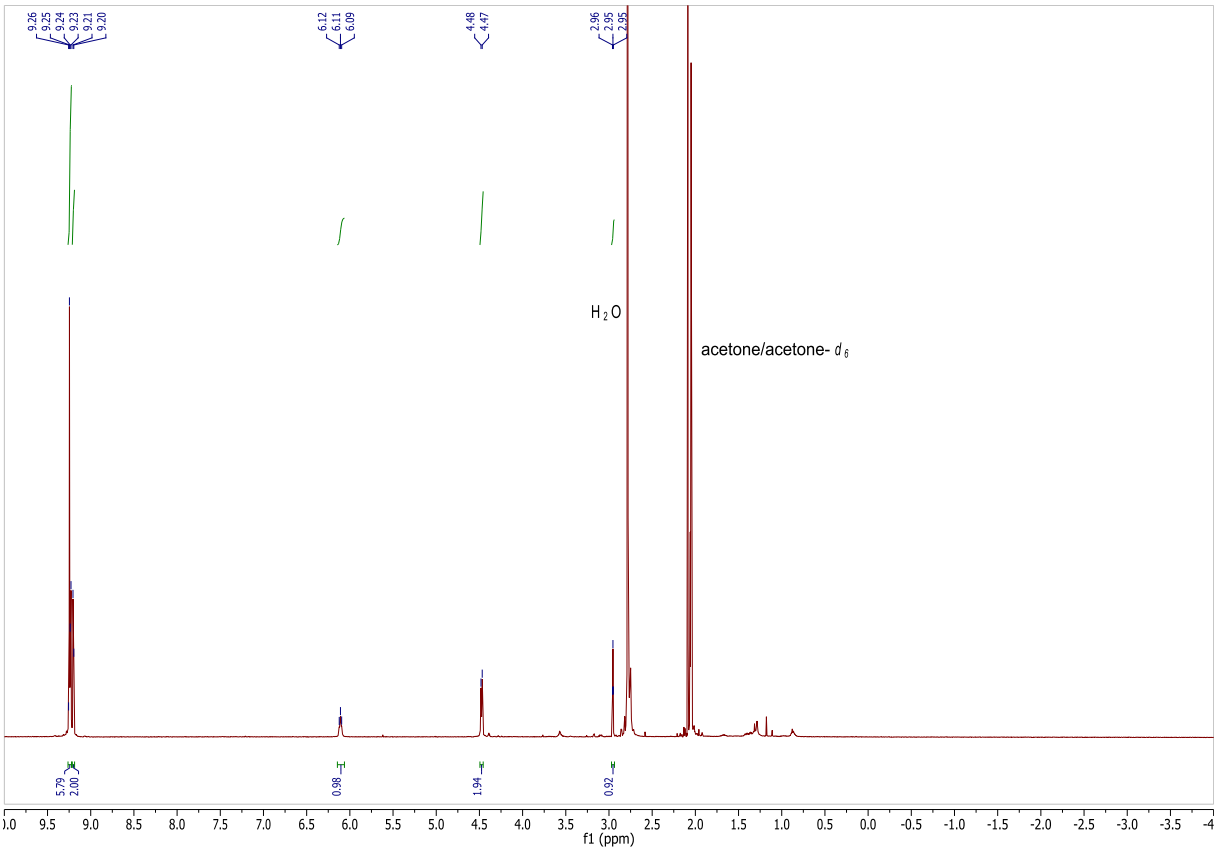


Figure 31. ^{1}H spectrum (*JEOL*^{TM} ECP 500, 500 MHz, acetone-d_6) of porphyrin **4**

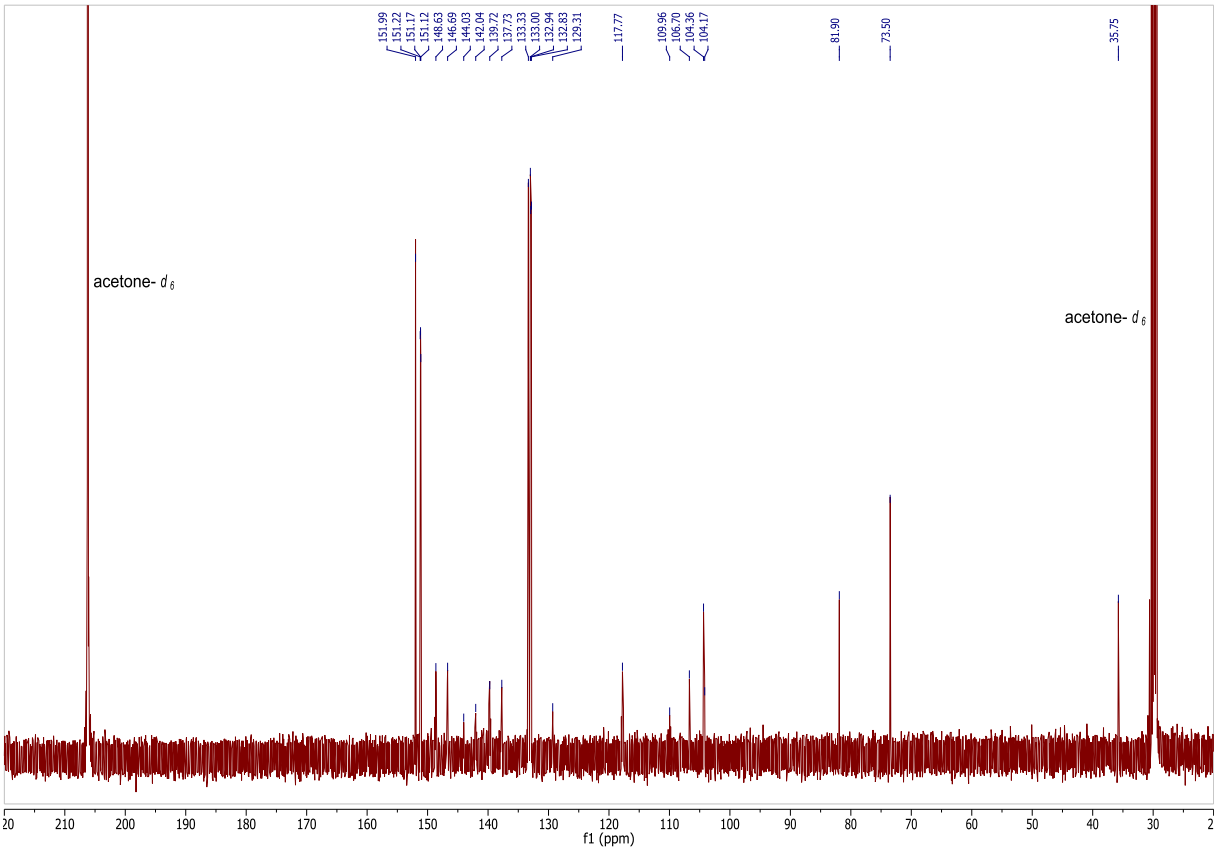


Figure 32. ^{13}C spectrum (*JEOL*^{TM} ECP 500, 126 MHz, acetone-d_6) of porphyrin **4**

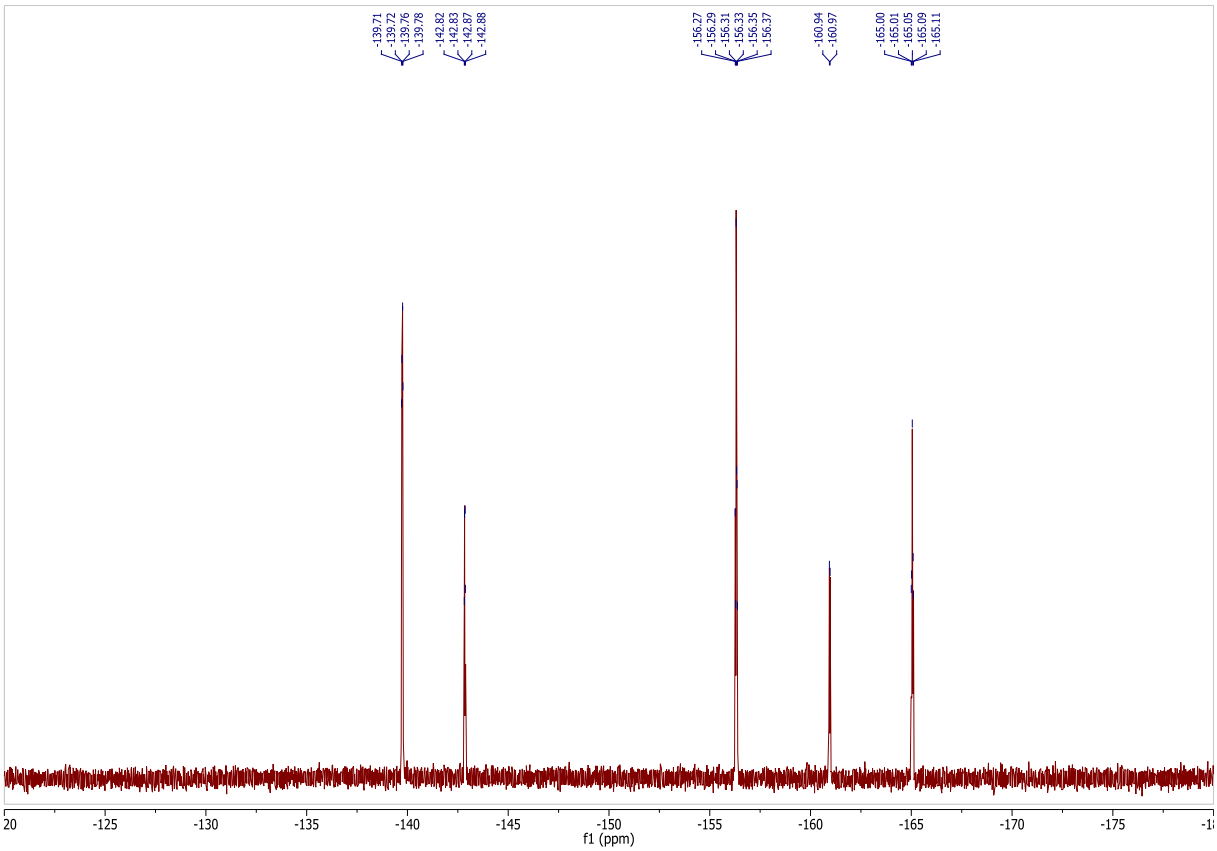


Figure 33. ^{19}F spectrum (*JEOL*^{TM} ECP 500, 471 MHz, acetone-d_6) of porphyrin **4**

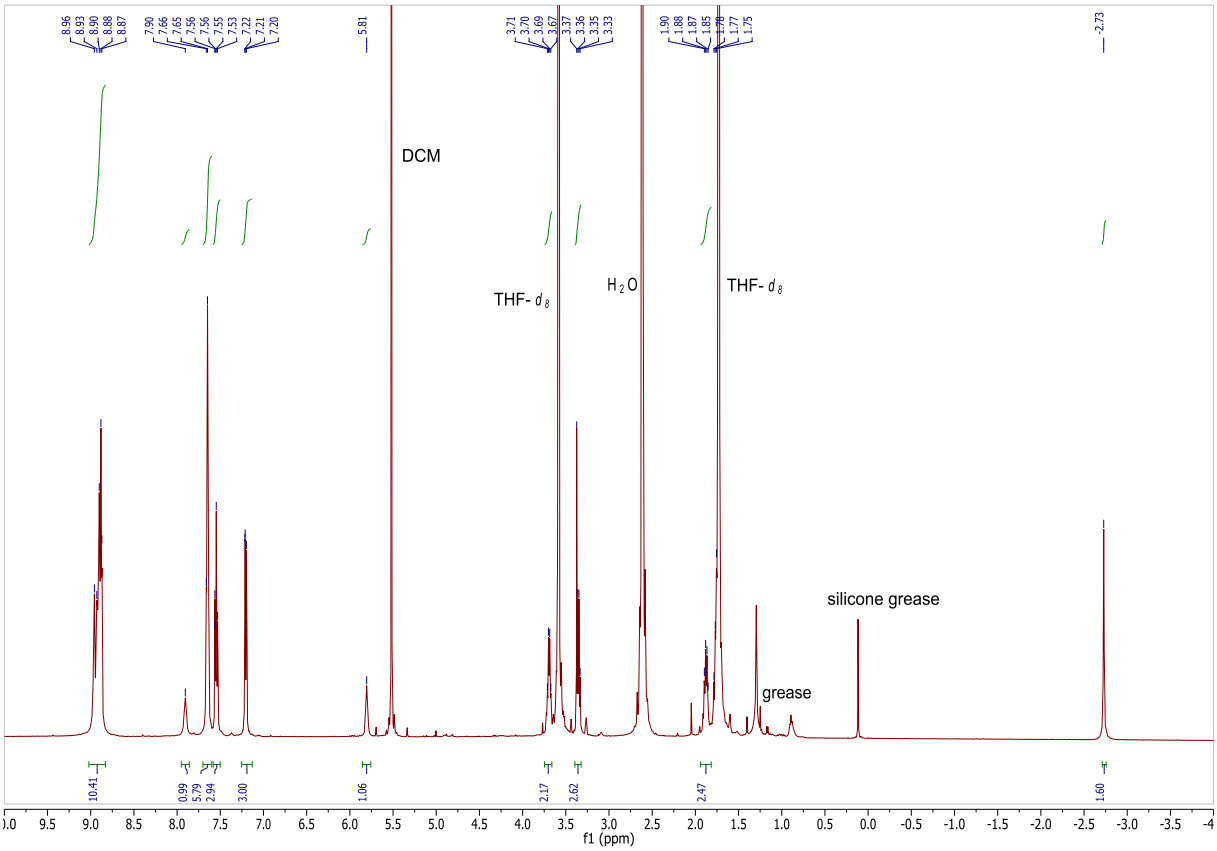


Figure 34. ^{1}H spectrum (*JEOL*^{TM} ECP 500, 500 MHz, THF-d_8) of porphyrin **5a**

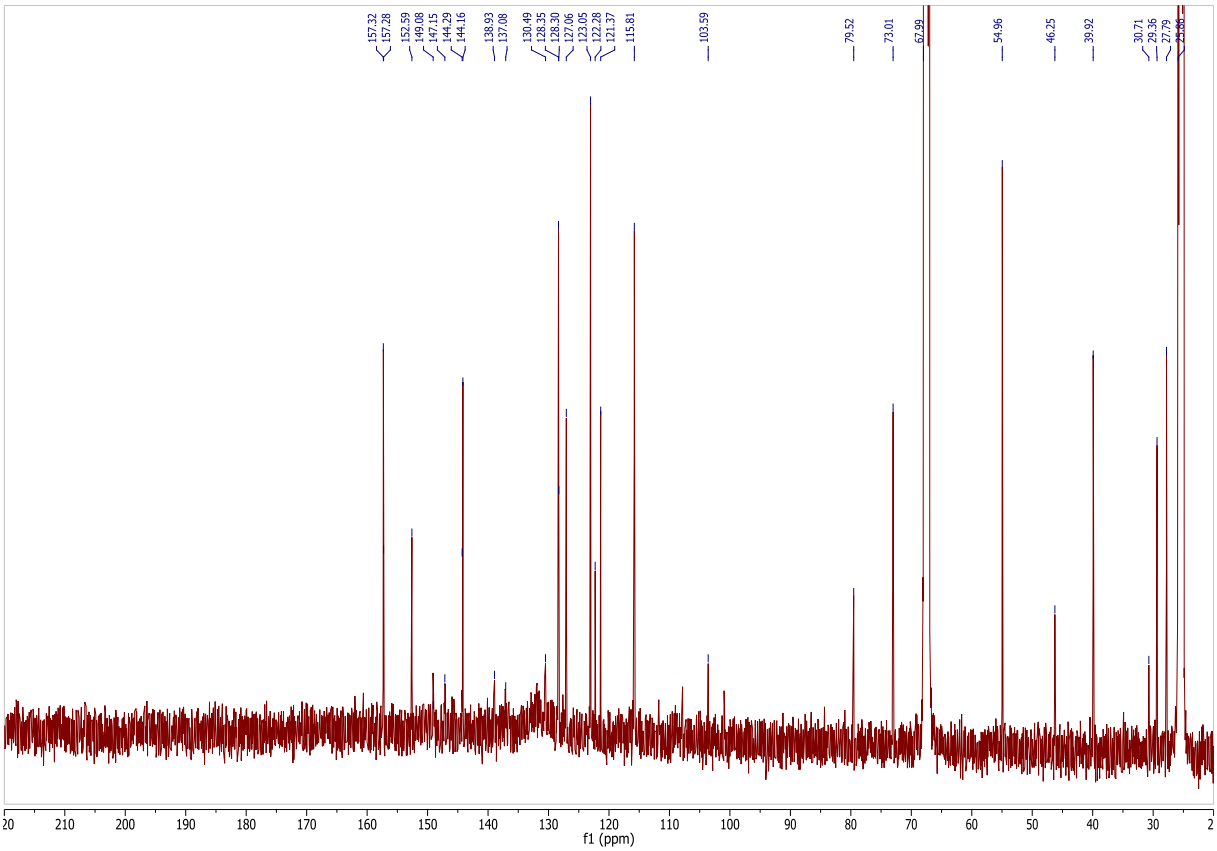


Figure 35. ^{13}C spectrum (*JEOL*^{TM} ECP 500, 126 MHz, THF-d_8) of porphyrin **5a**

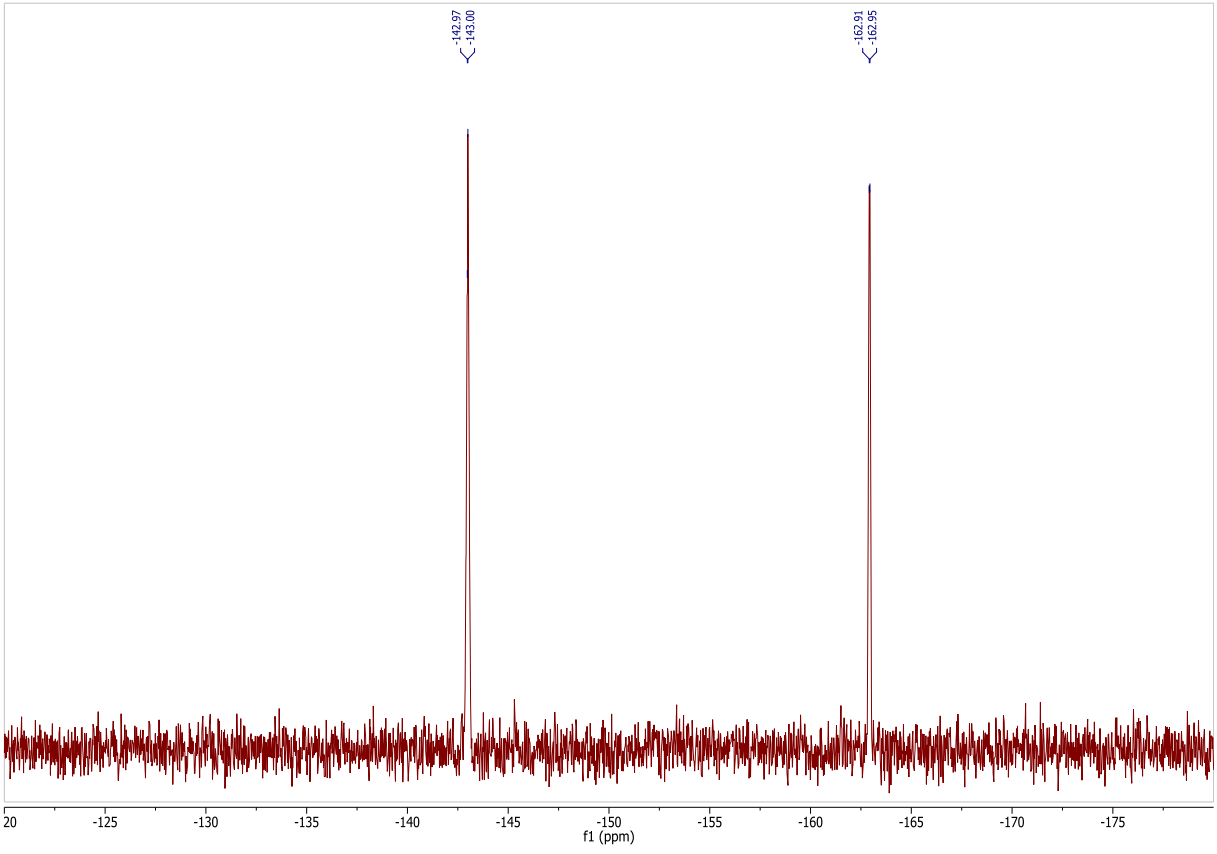


Figure 36. ^{19}F spectrum (*JEOL*^{TM} ECX 400, 376 MHz, THF-d_8) of porphyrin **5a**

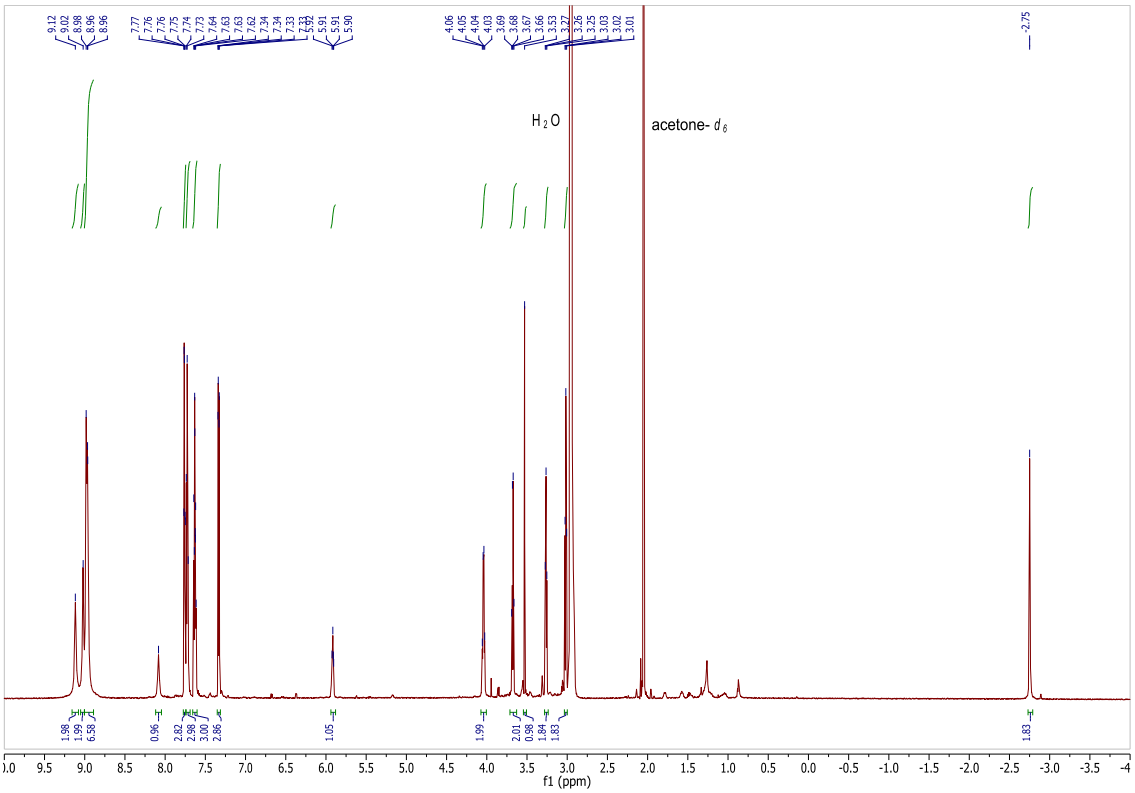


Figure 37. ^{1}H spectrum (*Bruker BioSpin* AVANCE700, 700 MHz, acetone-d_6) of porphyrin **5b**

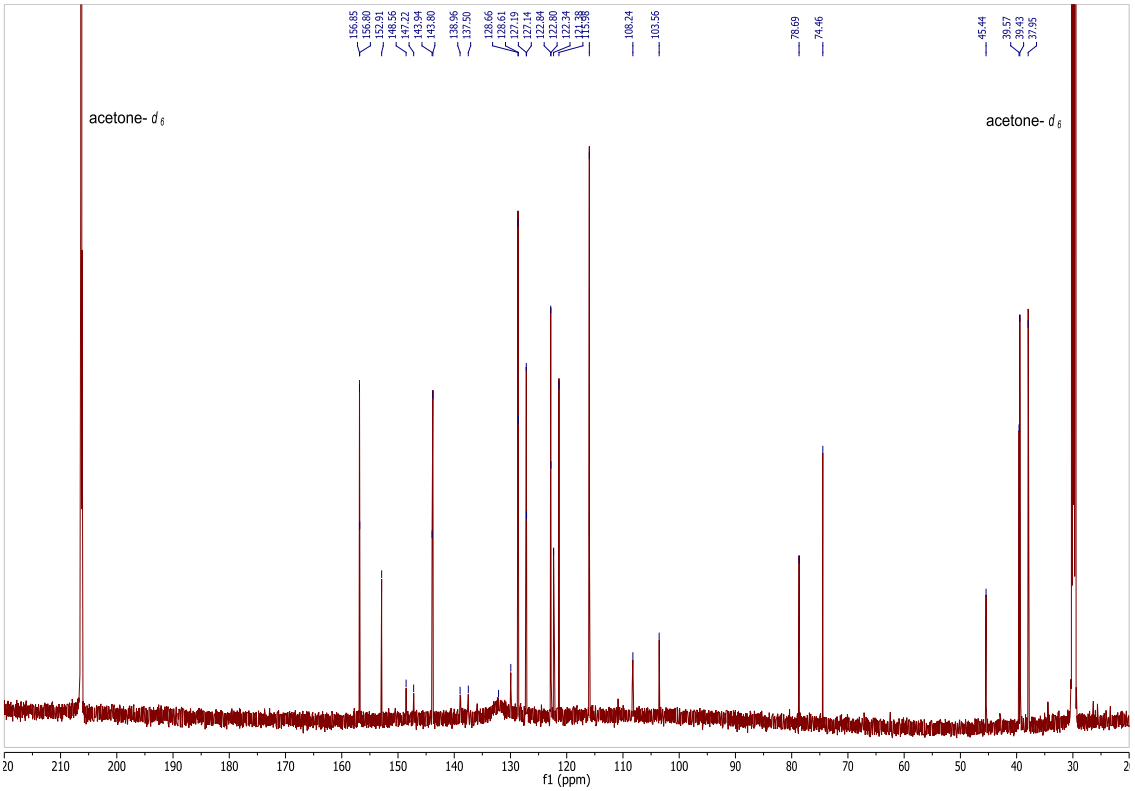


Figure 38. ^{13}C spectrum (*Bruker BioSpin* AVANCE700, 176 MHz, acetone-d_6) of porphyrin **5b**

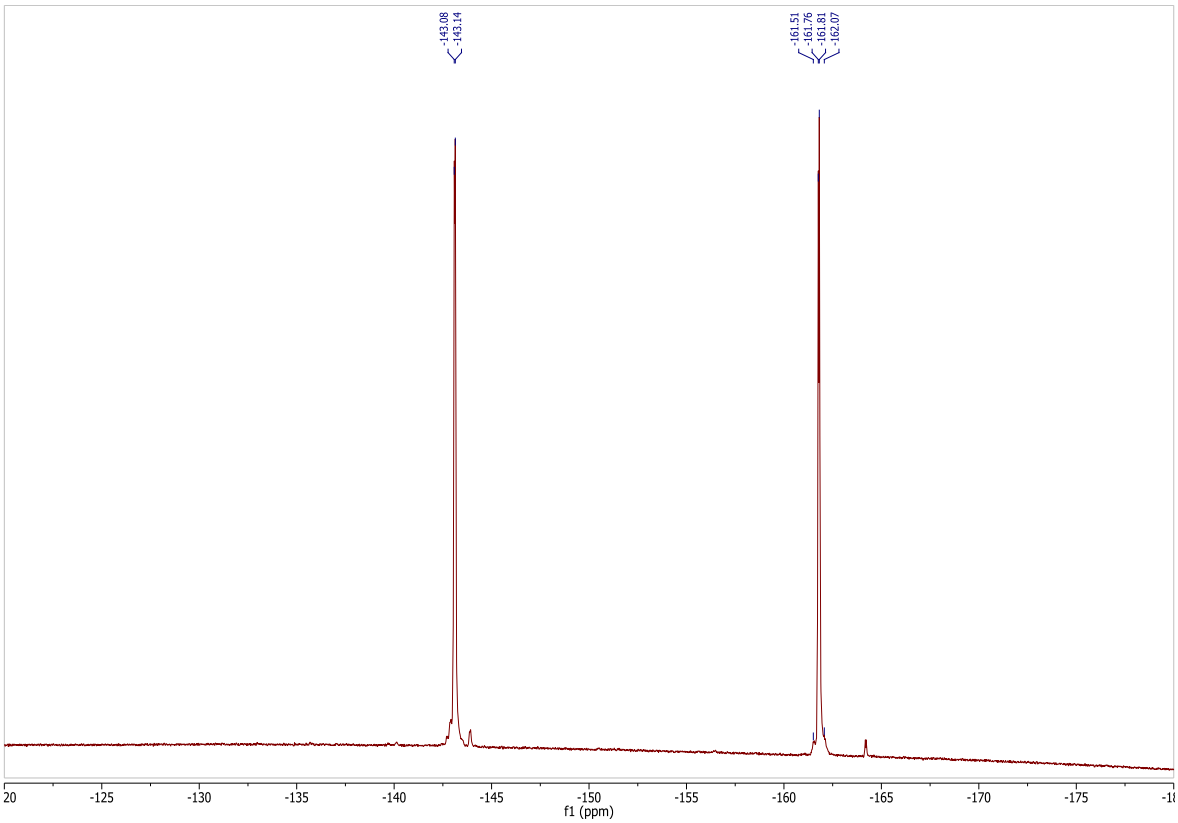


Figure 39. ^{19}F spectrum (*JEOL*^{TM} ECX 400, 376 MHz, acetone-d_6) of porphyrin **5b**

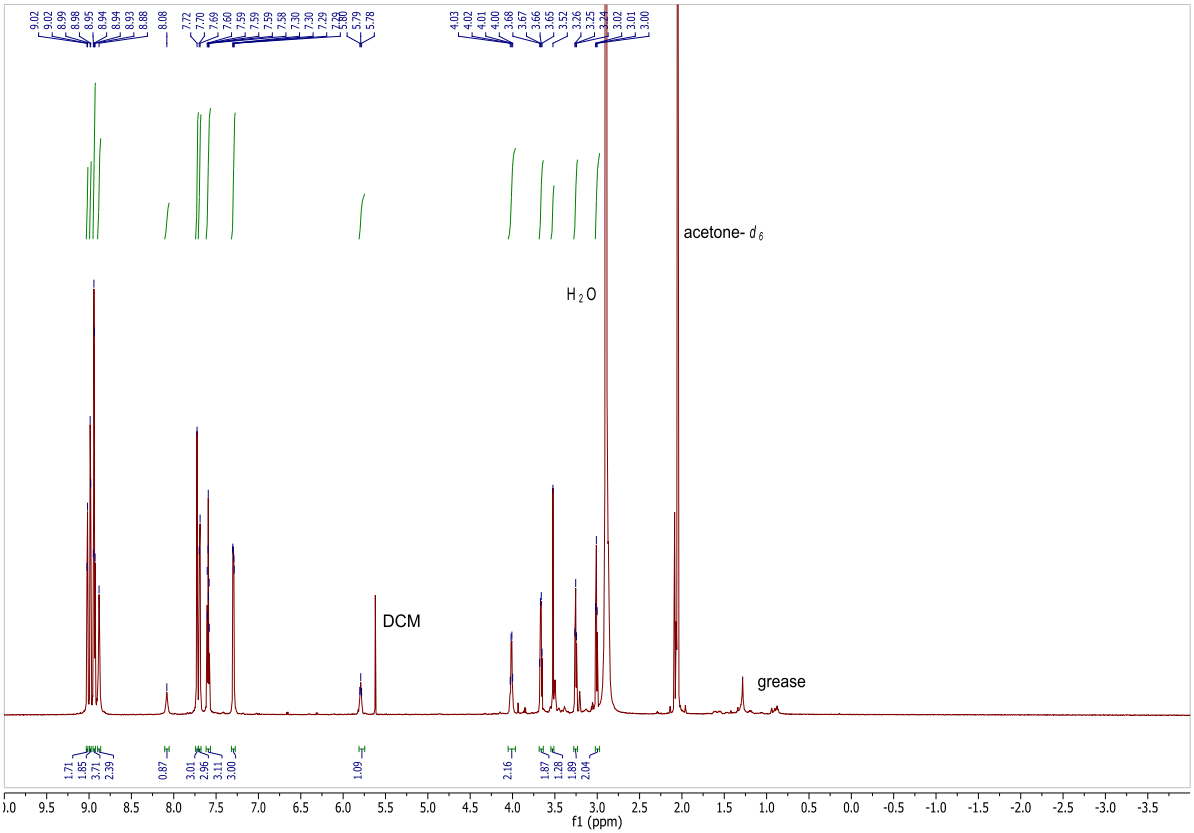


Figure 40. ^{1}H spectrum (*Bruker BioSpin* AVANCE700, 700 MHz, acetone-d_6) of porphyrin **5c**

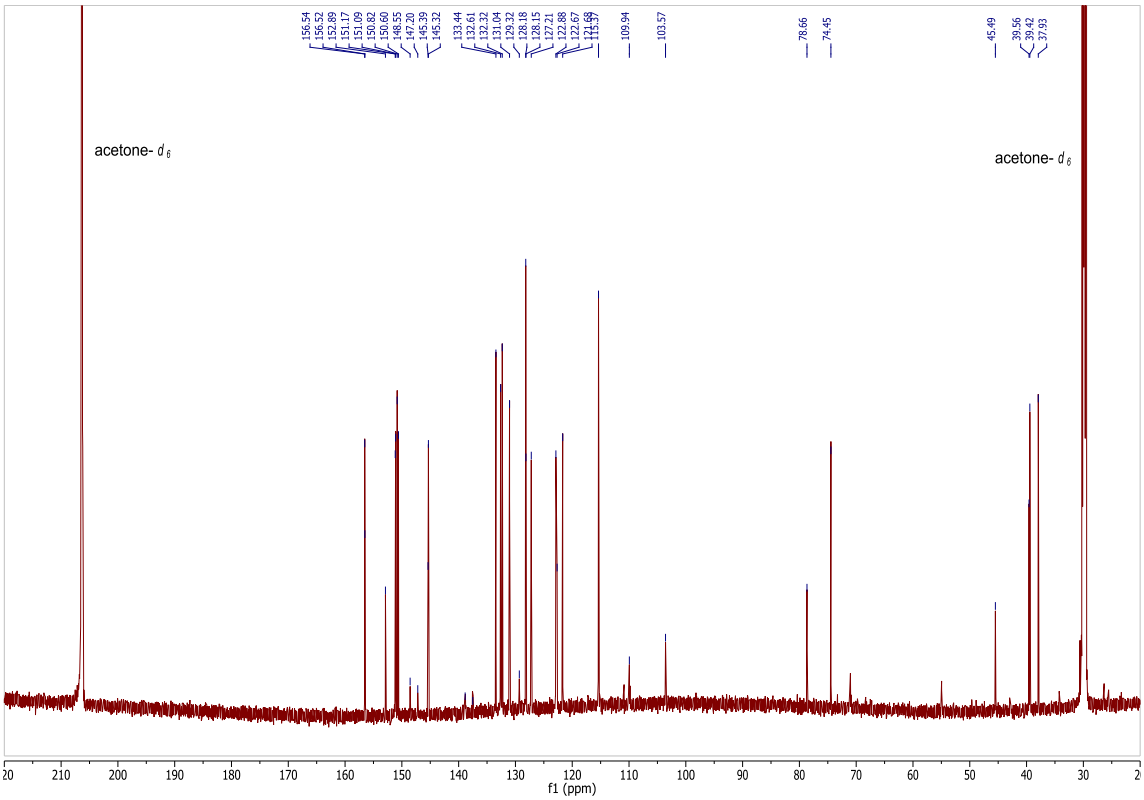


Figure 41. ^{13}C spectrum (*Bruker BioSpin* AVANCE700, 176 MHz, acetone-d_6) of porphyrin **5c**

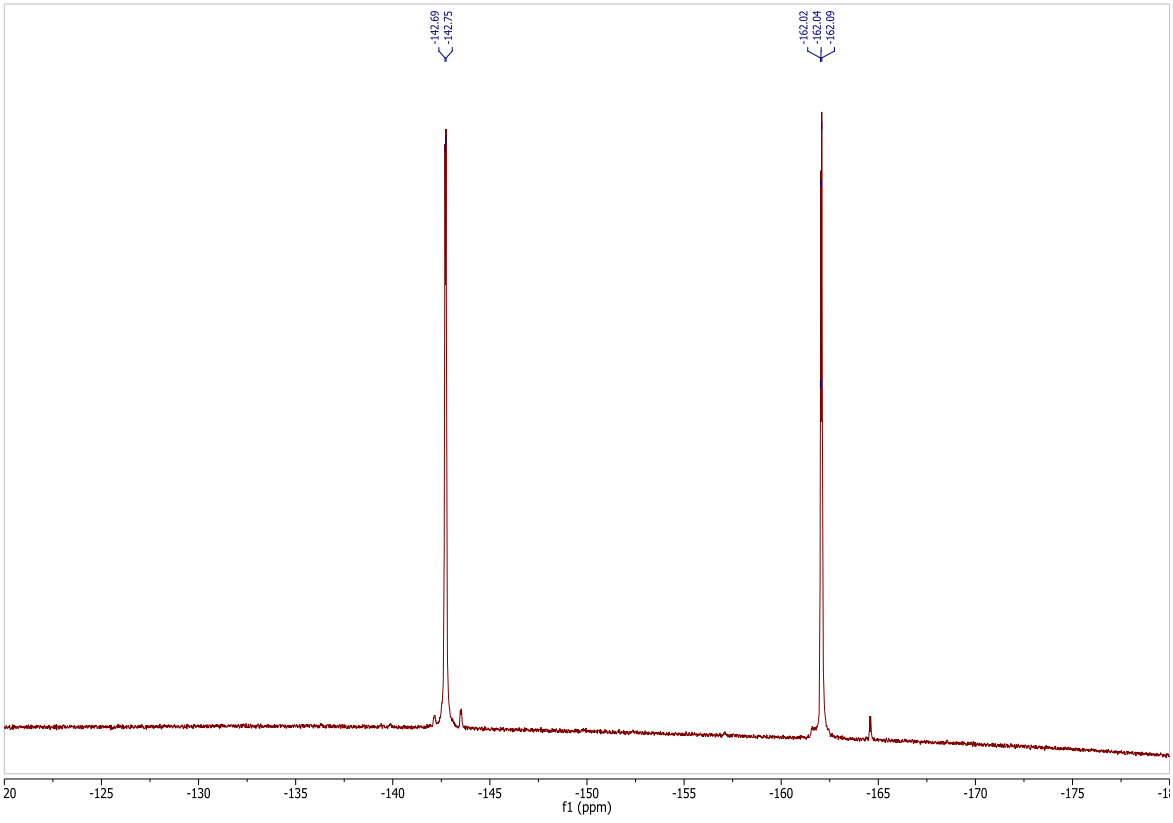


Figure 42. ^{19}F spectrum (*JEOL*^{TM} ECX 400, 376 MHz, acetone-d_6) of porphyrin **5c**

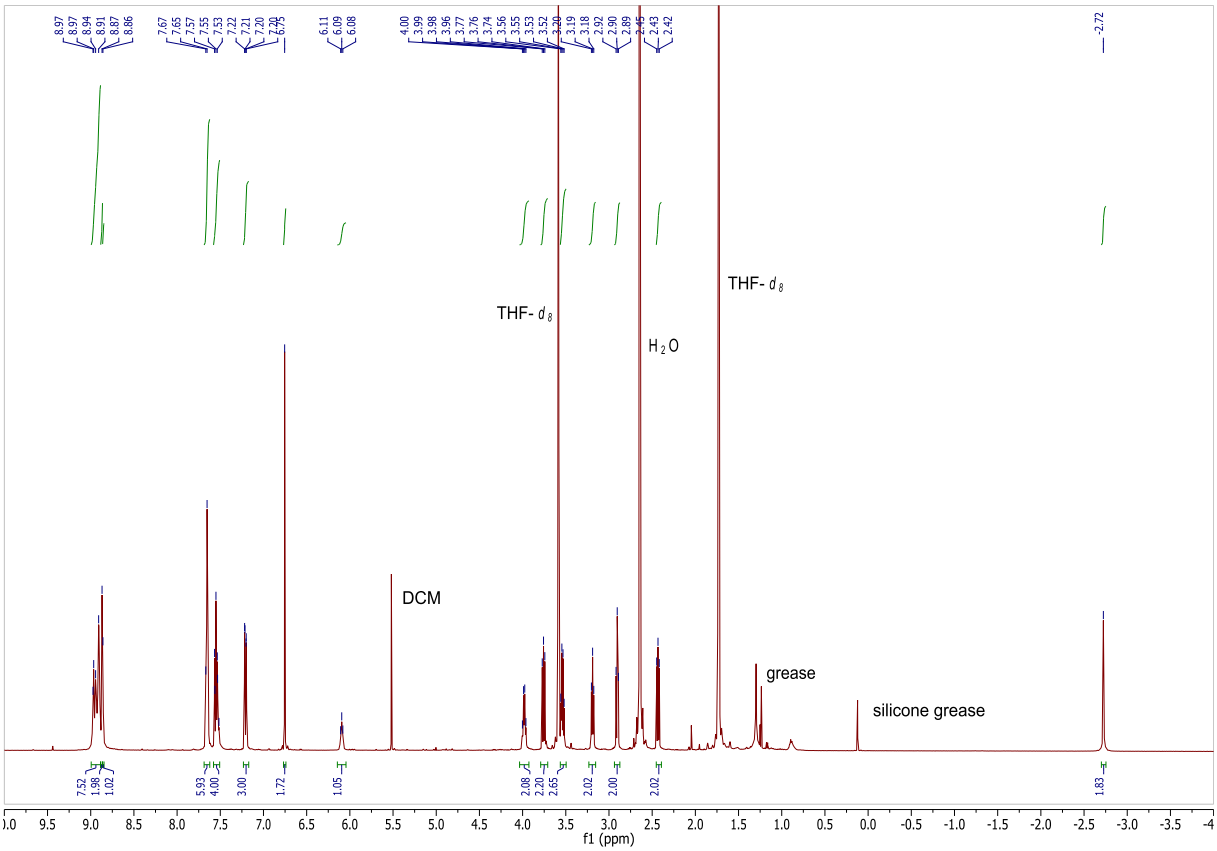


Figure 43. ^{1}H spectrum (*JEOL*^{TM} ECP 500, 500 MHz, THF-d_8) of porphyrin **6a**

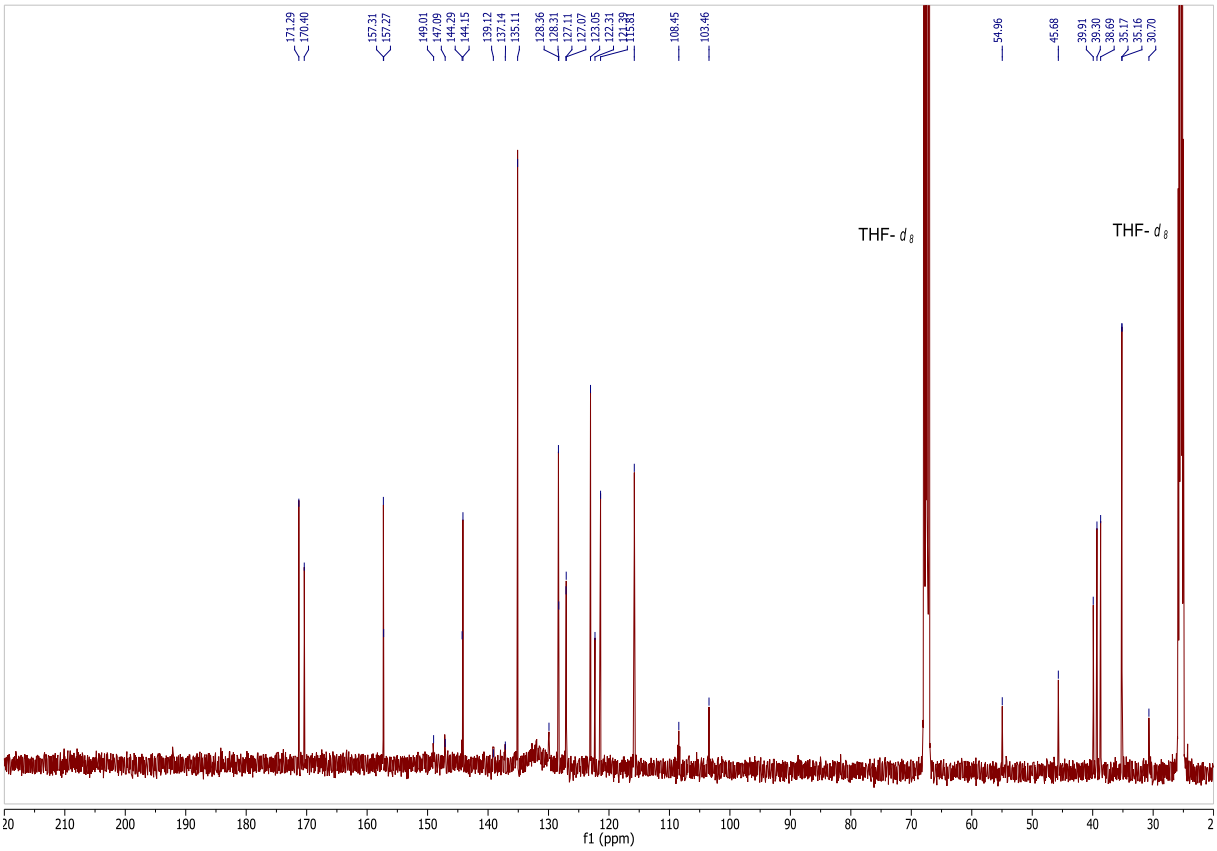


Figure 44. ^{13}C spectrum (*JEOL*^{TM} ECP 500, 126 MHz, THF-d_8) of porphyrin **6a**

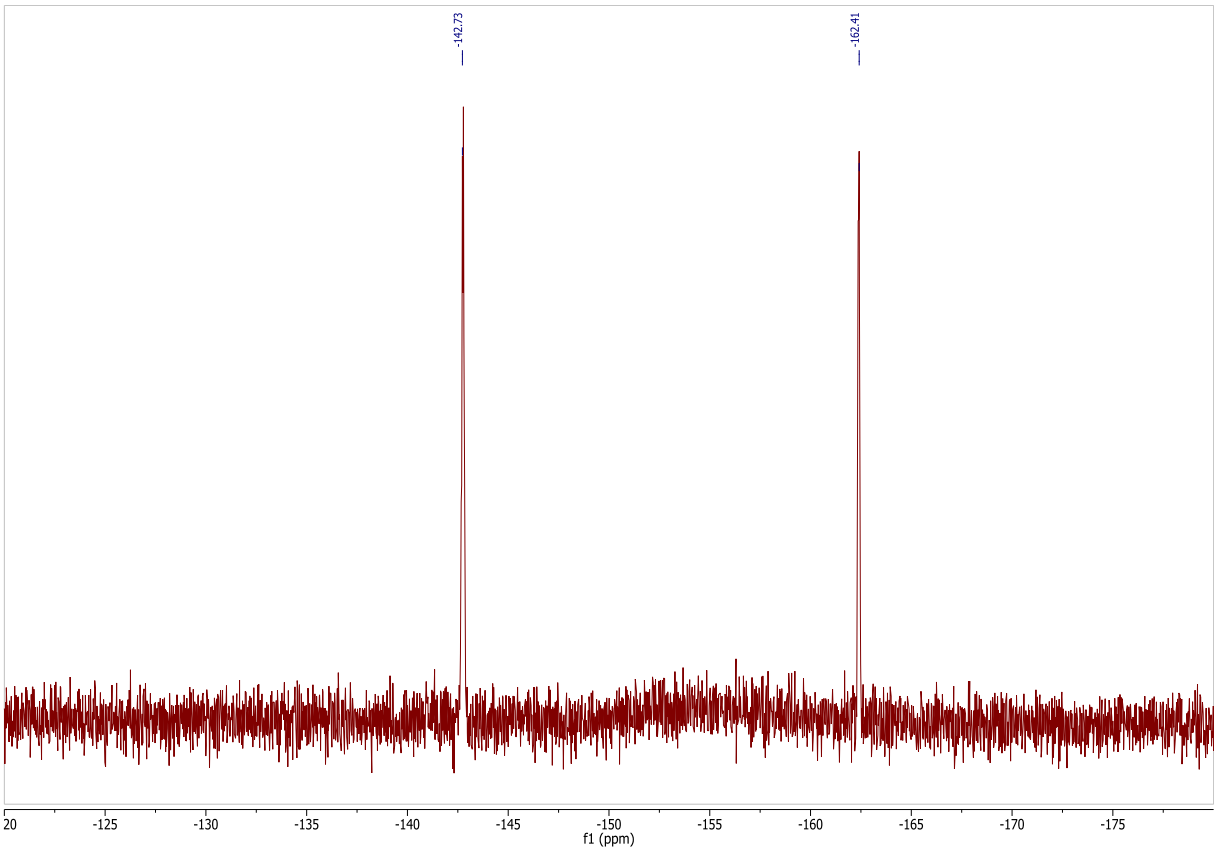


Figure 45. ^{19}F spectrum (*JEOL*^{TM} ECP 500, 471 MHz, THF-d_8) of porphyrin **6a**

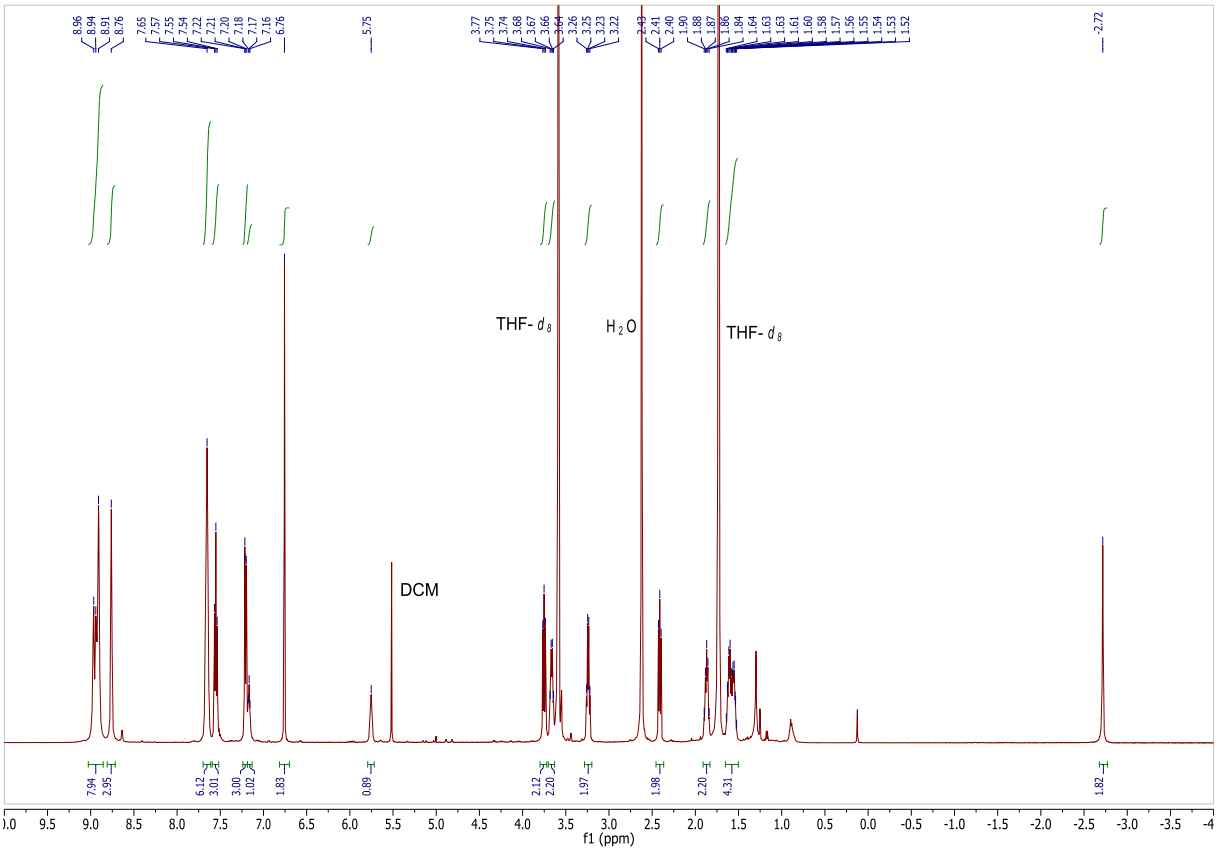


Figure 46. ^{1}H spectrum (*JEOL*^{TM} ECP 500, 500 MHz, THF-d_8) of porphyrin **6b**

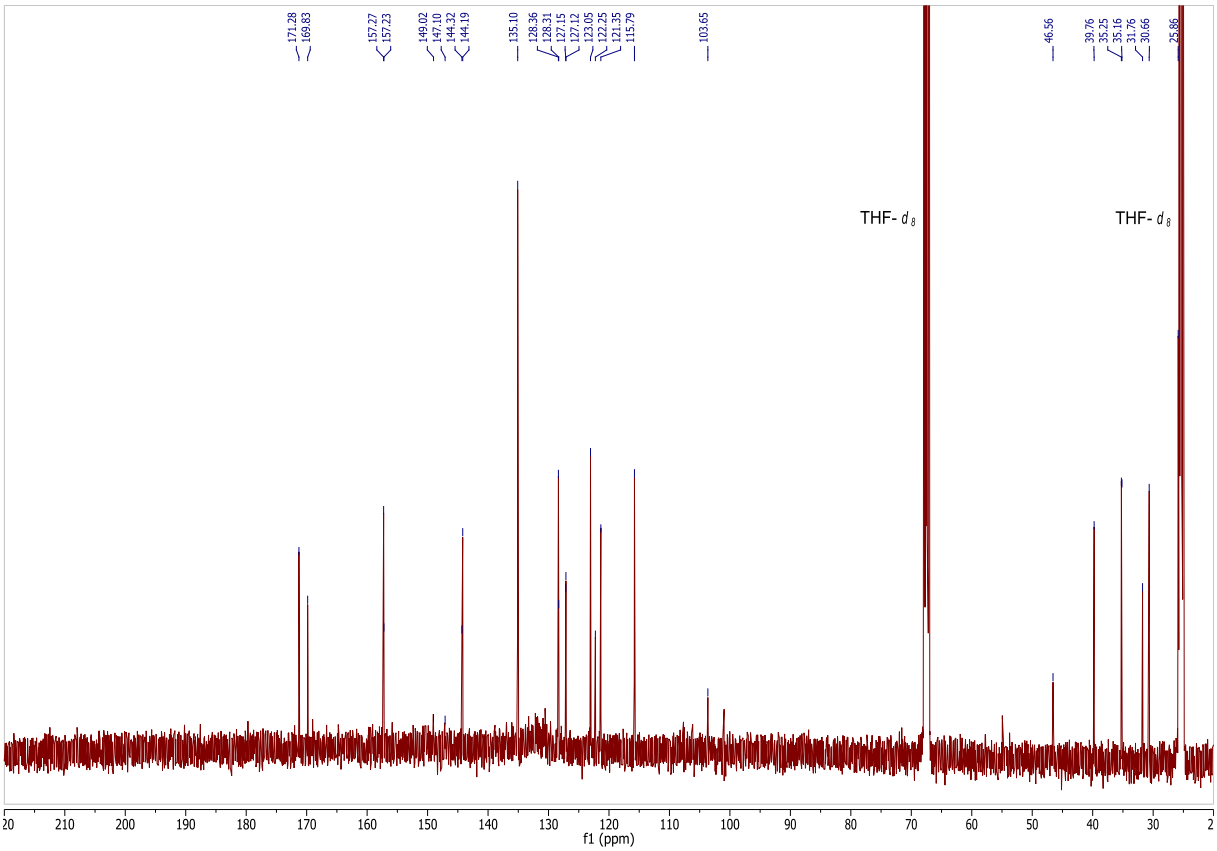


Figure 47. ^{13}C spectrum (*JEOL*^{TM} ECP 500, 126 MHz, THF-d_8) of porphyrin **6b**

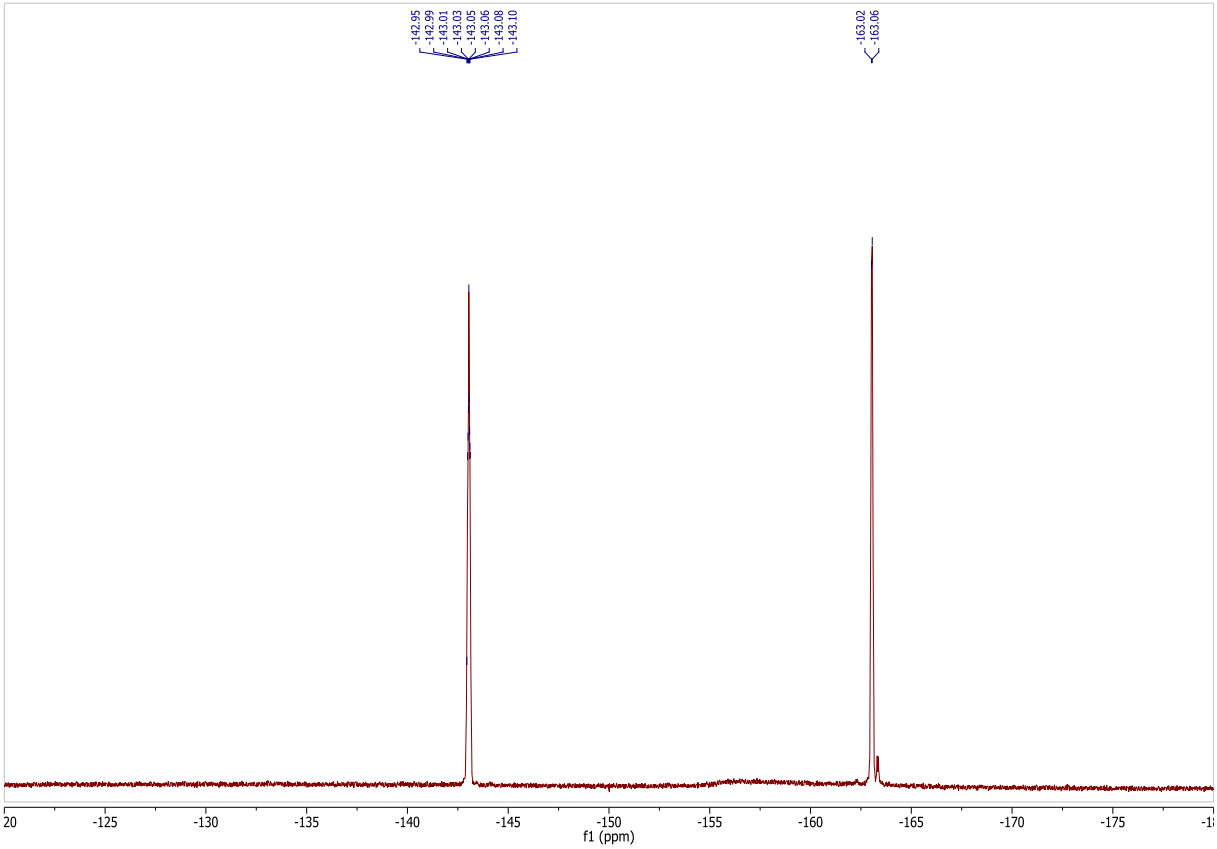


Figure 48. ^{19}F spectrum (*JEOL*^{TM} ECX 400, 376 MHz, THF-d_8) of porphyrin **6b**

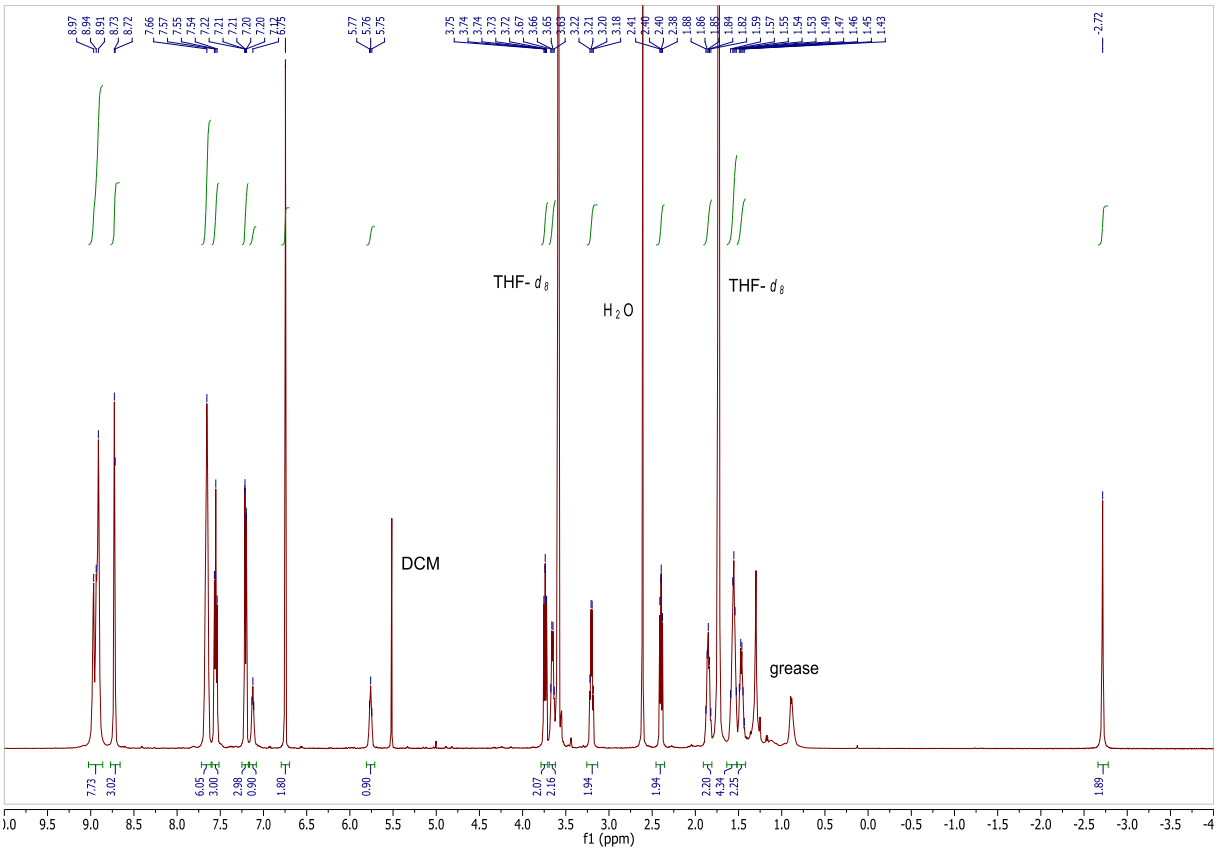


Figure 49. ^{1}H spectrum (*JEOL*^{TM} ECP 500, 500 MHz, THF-d_8) of porphyrin **6c**

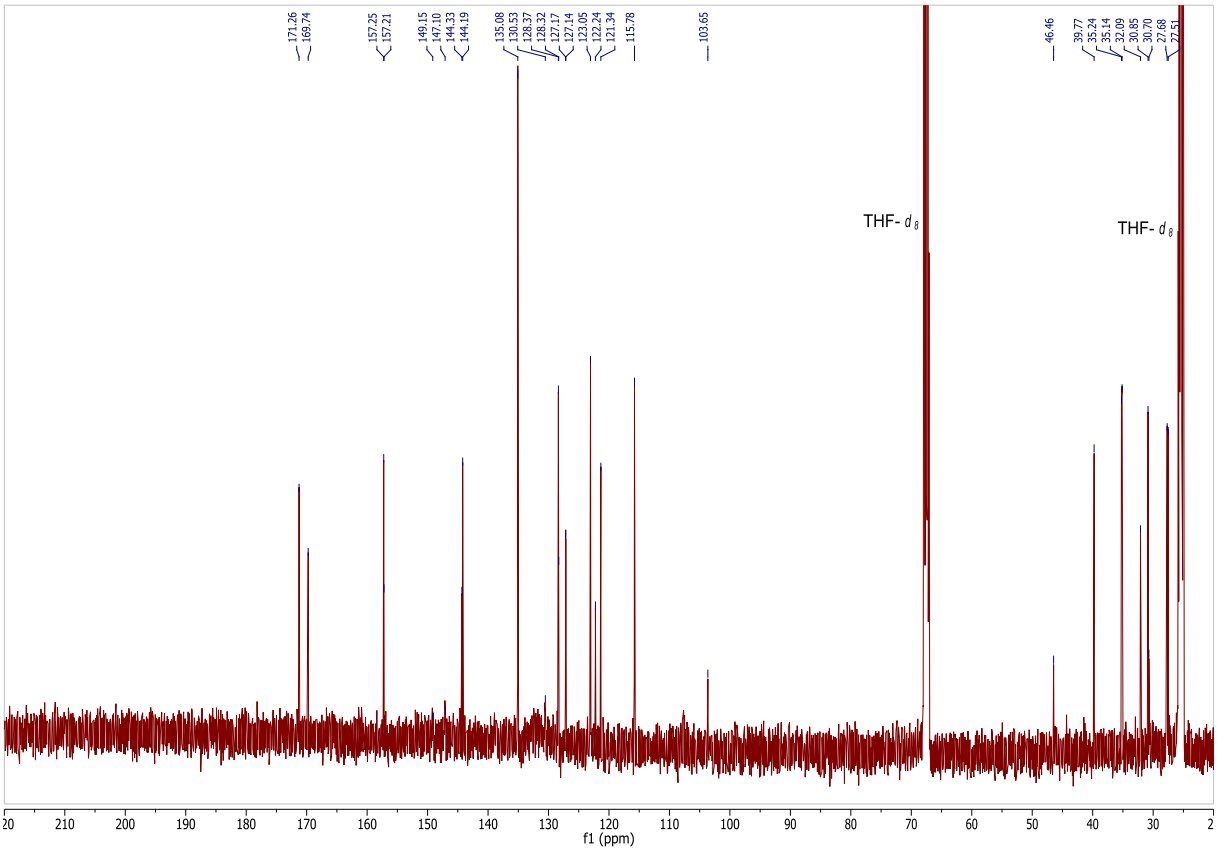


Figure 50. ^{13}C spectrum (*JEOL*^{TM} ECP 500, 126 MHz, THF-d_8) of porphyrin **6c**

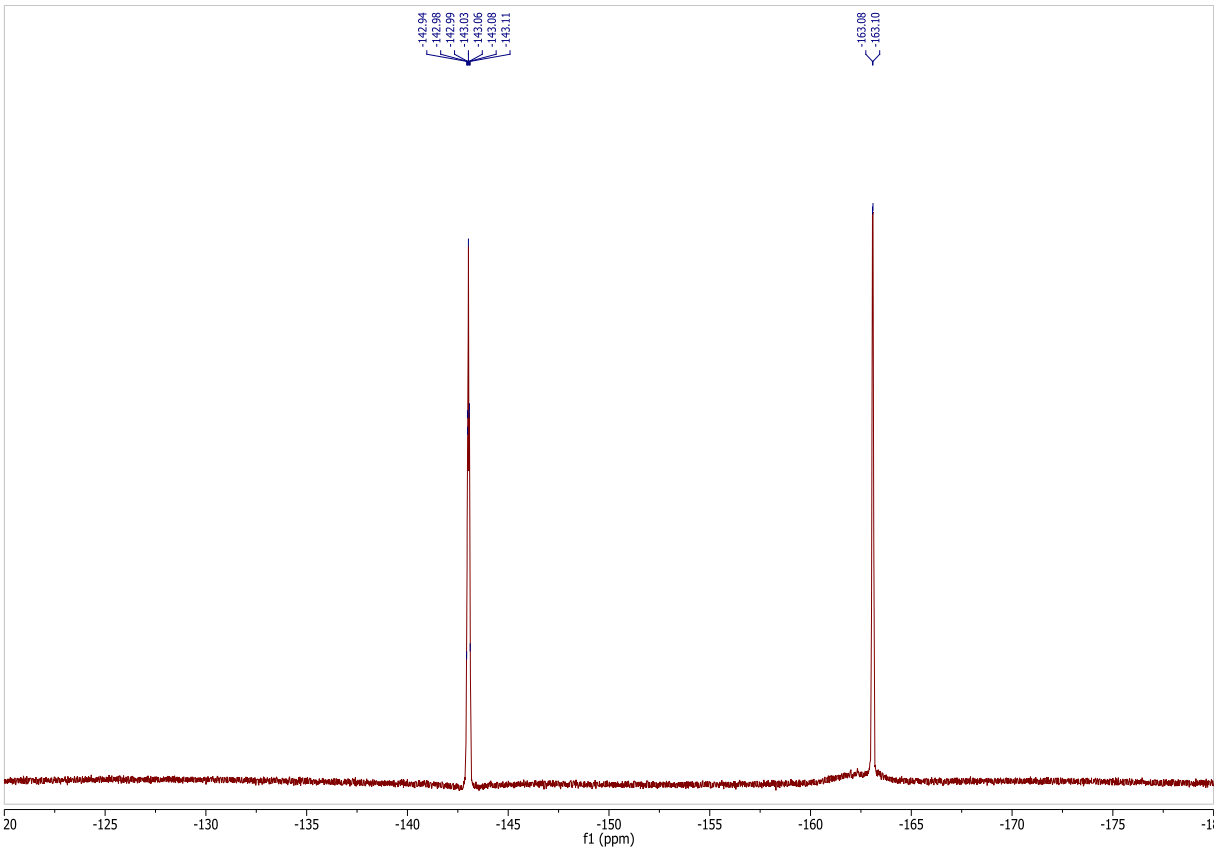


Figure 51. ^{19}F spectrum (*JEOL*^{TM} ECP 500, 471 MHz, THF-d_8) of porphyrin **6c**

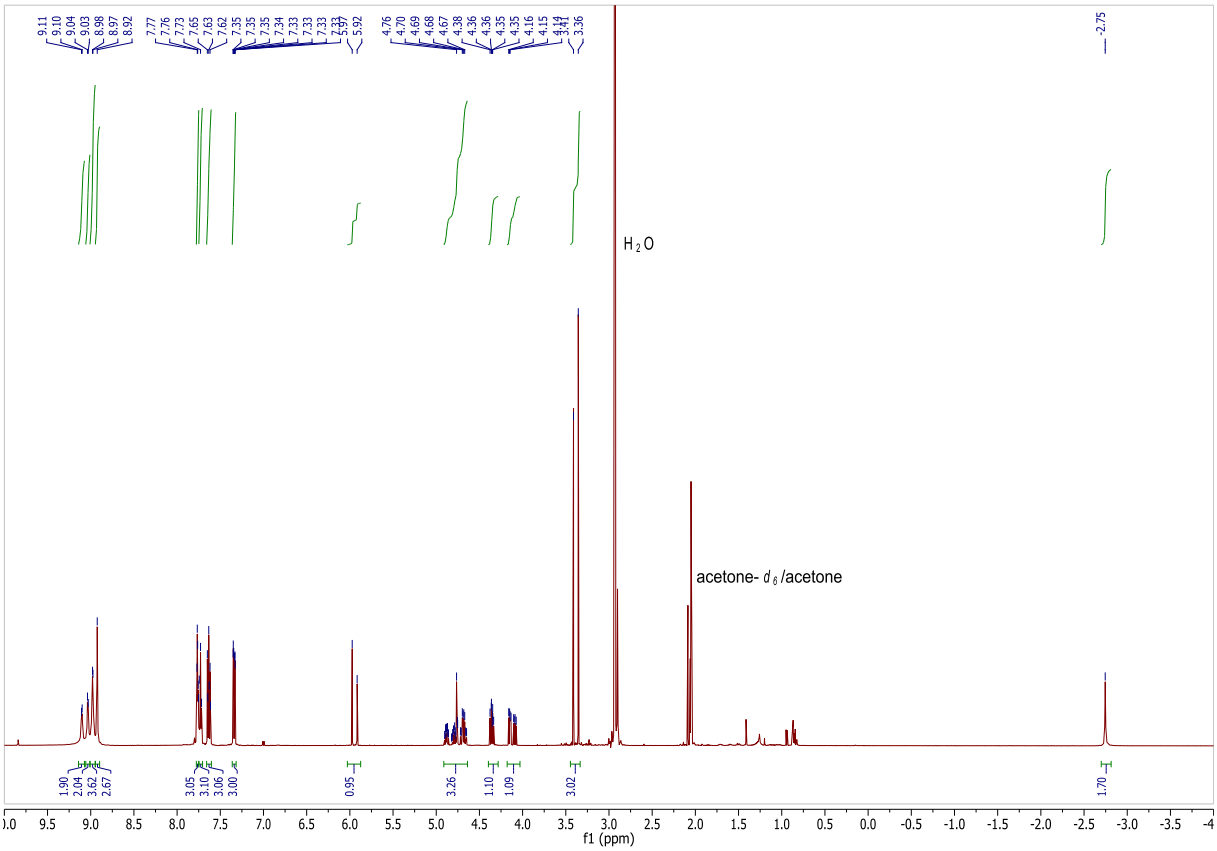


Figure 52. ^{1}H spectrum (*JEOL*^{TM} ECP 500, 500 MHz, acetone-d_6) of porphyrin **8a**

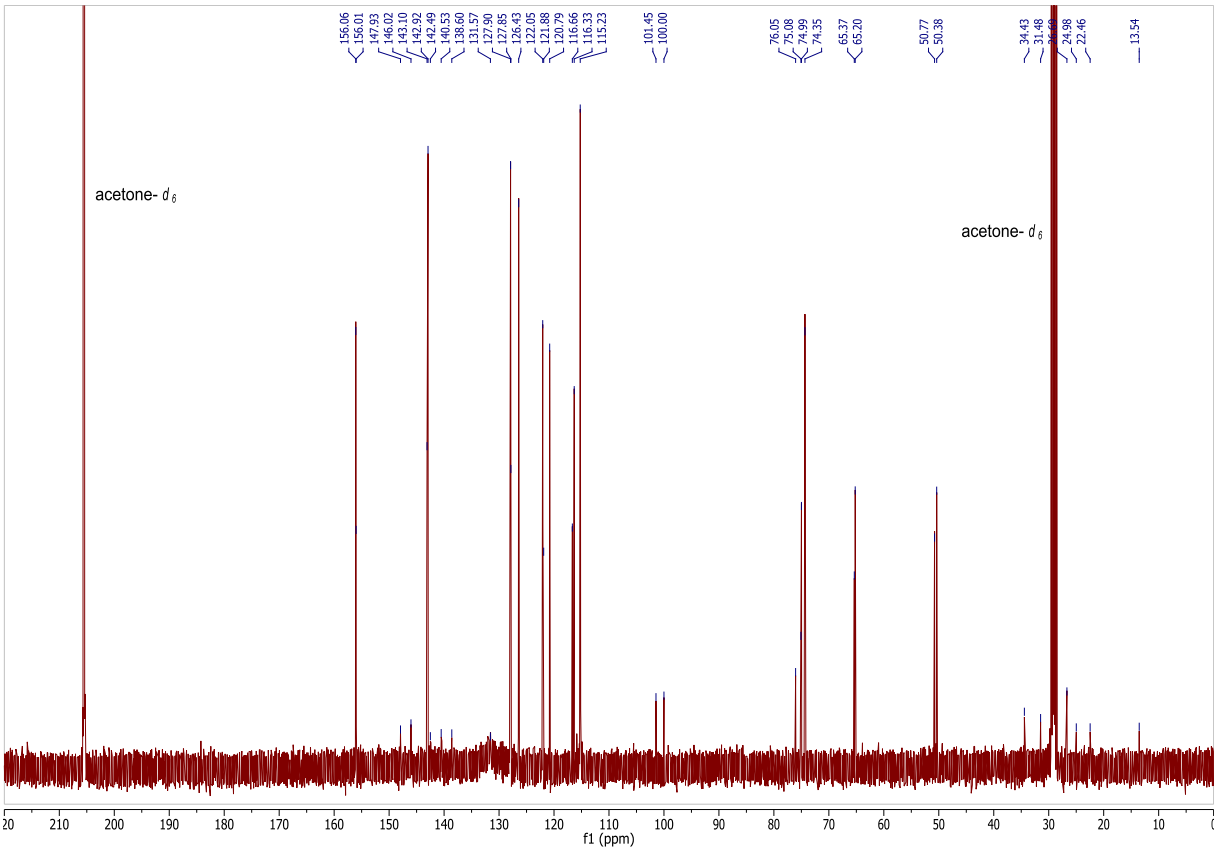


Figure 53. ^{13}C spectrum (*JEOL*^{TM} ECP 500, 126 MHz, acetone-d_6) of porphyrin **8a**

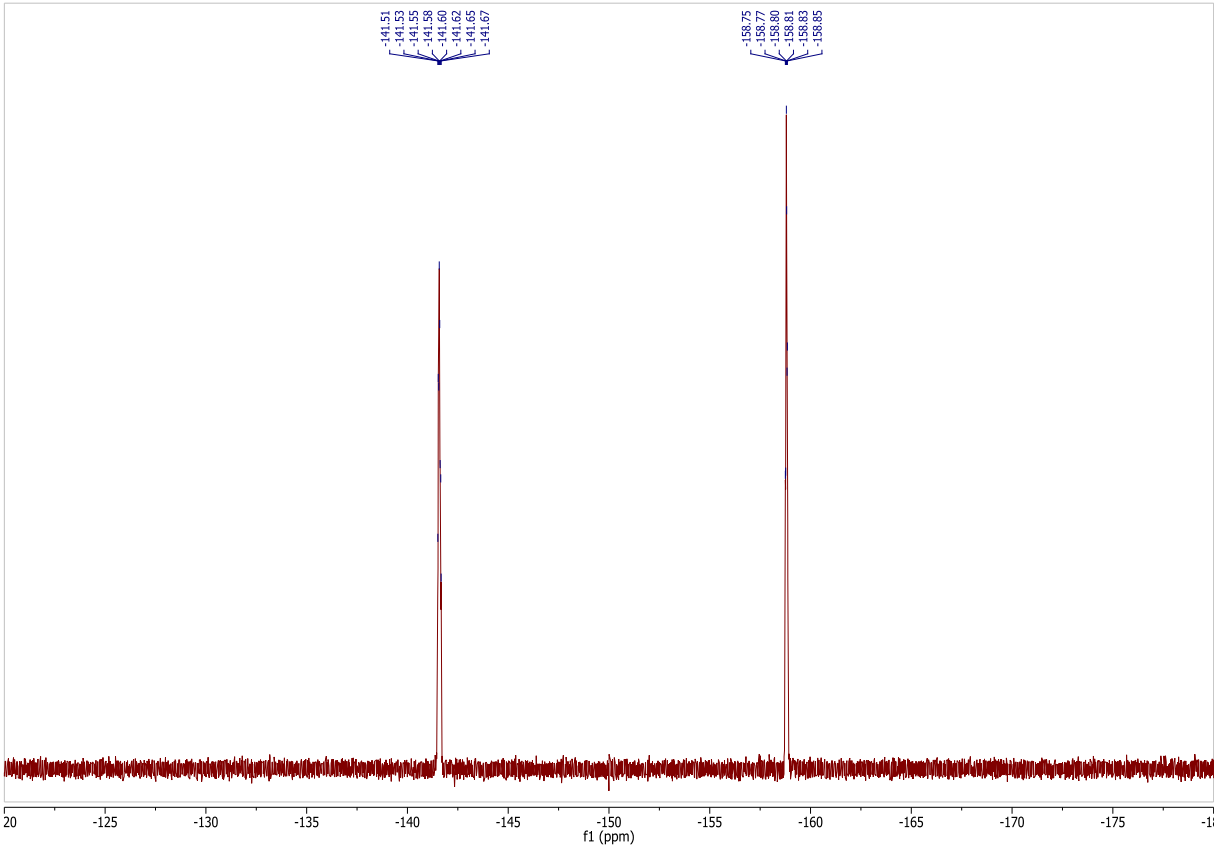


Figure 54. ^{19}F spectrum (*JEOL*^{TM} ECP 500, 471 MHz, acetone-d_6) of porphyrin **8a**

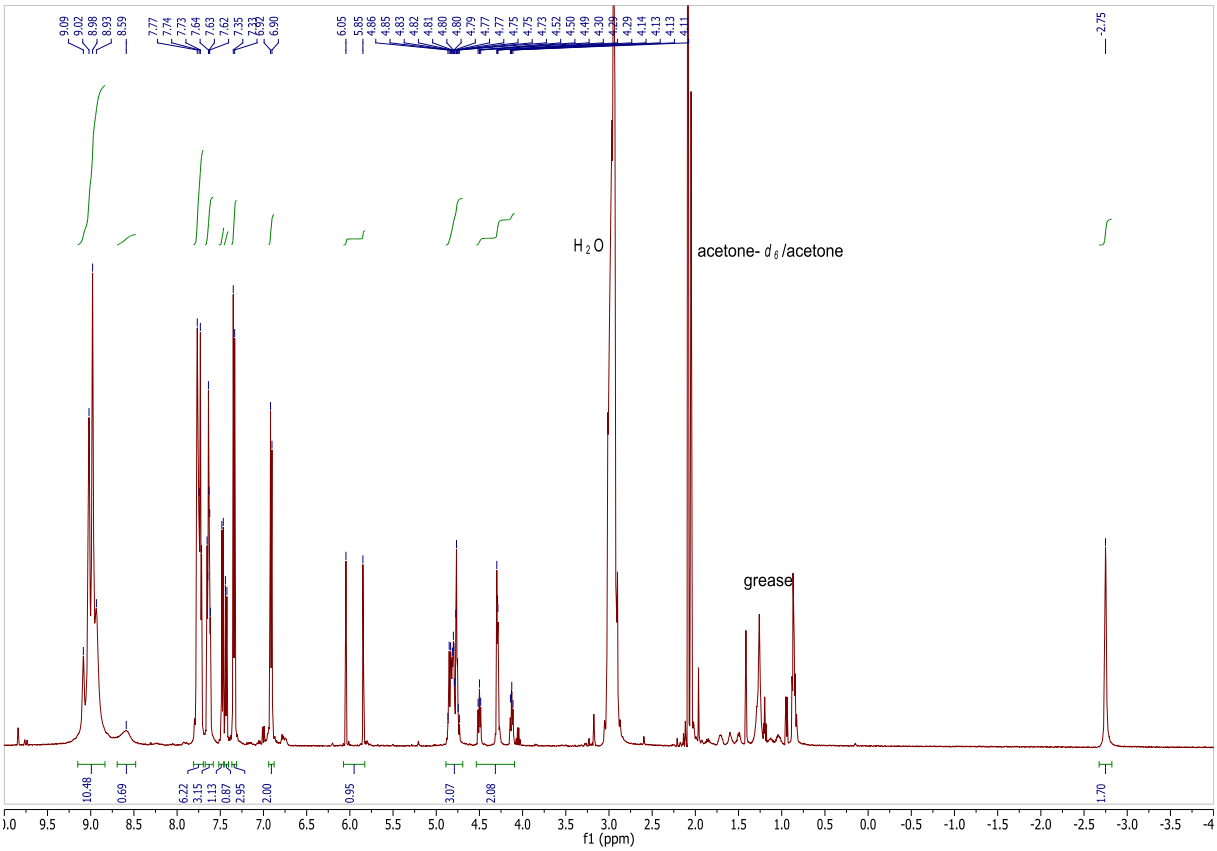


Figure 55. ^{1}H spectrum (*JEOL*^{TM} ECP 500, 500 MHz, acetone-d_6) of porphyrin **8b**

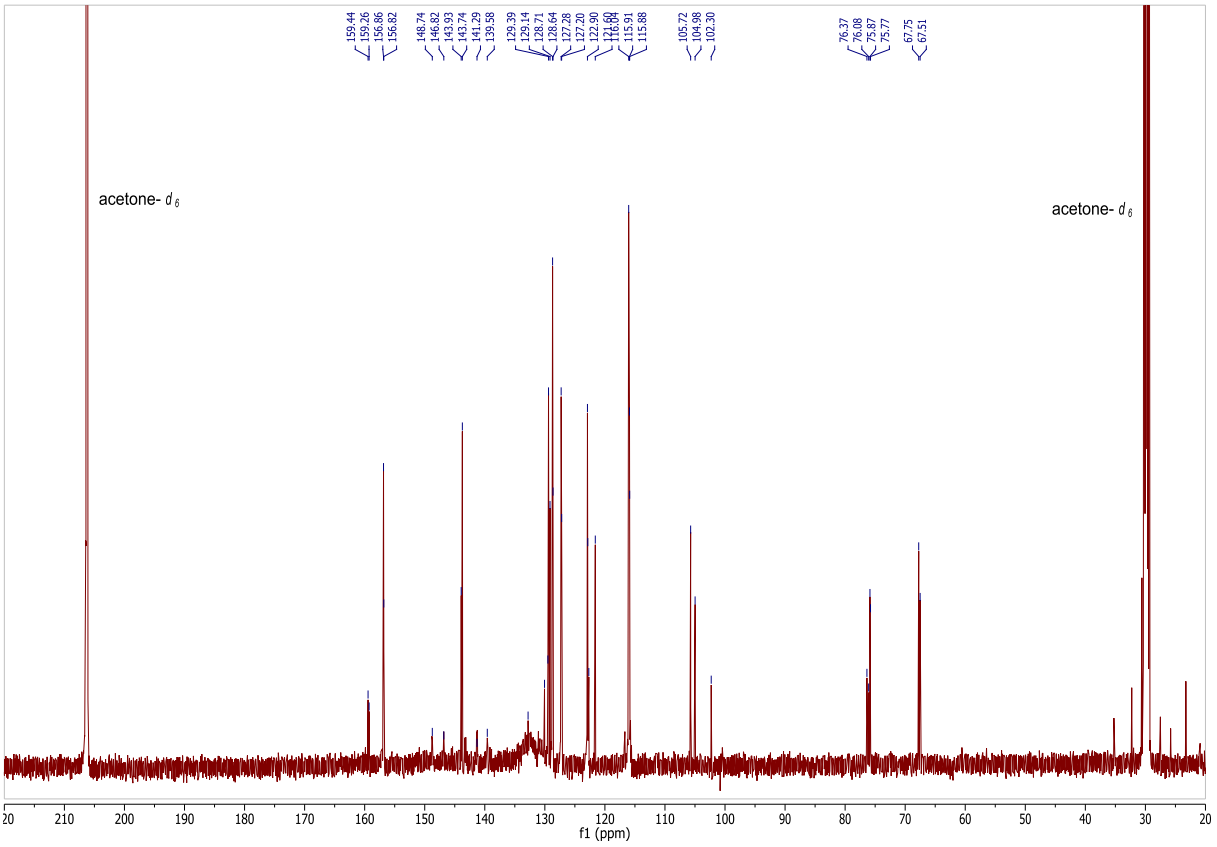


Figure 56. ^{13}C spectrum (*JEOL*^{TM} ECP 500, 126 MHz, acetone-d_6) of porphyrin **8b**

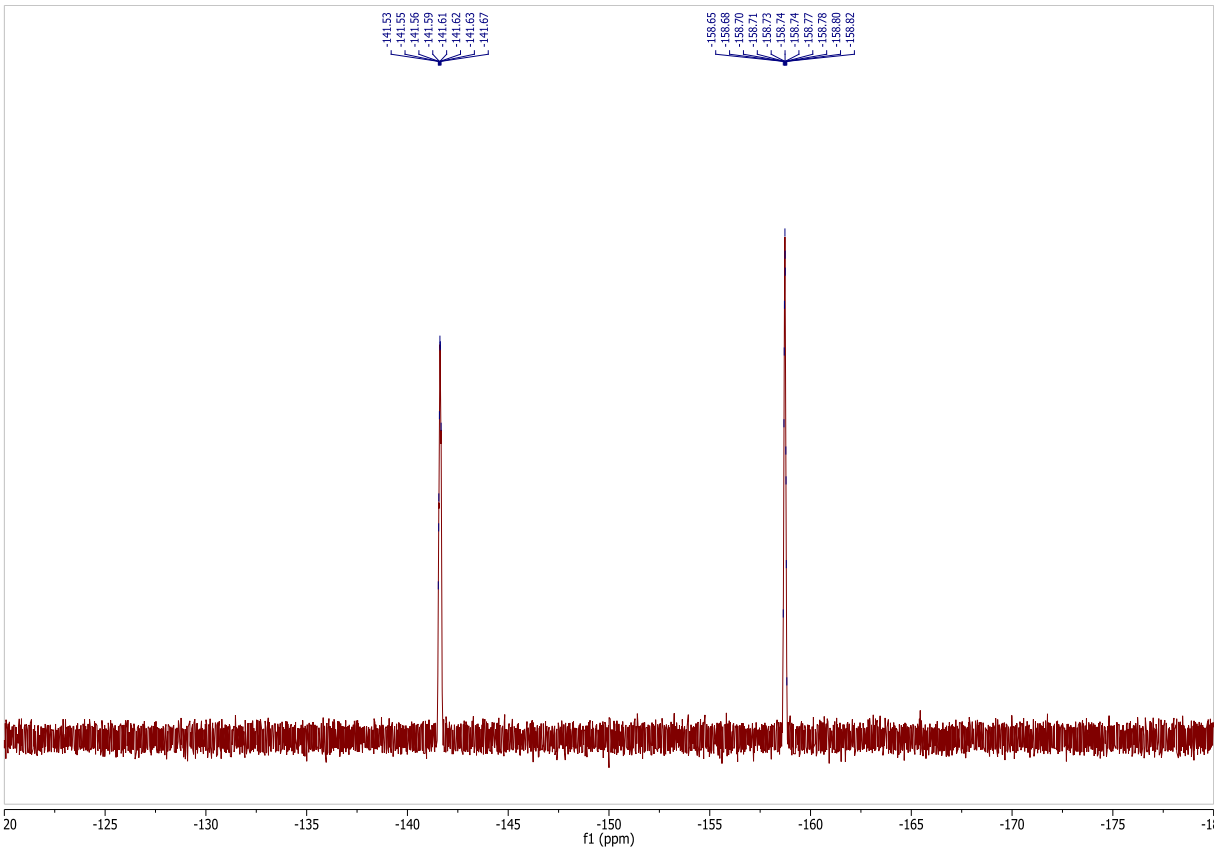


Figure 57. ^{19}F spectrum (*JEOL*^{TM} ECP 500, 471 MHz, acetone-d_6) of porphyrin **8b**

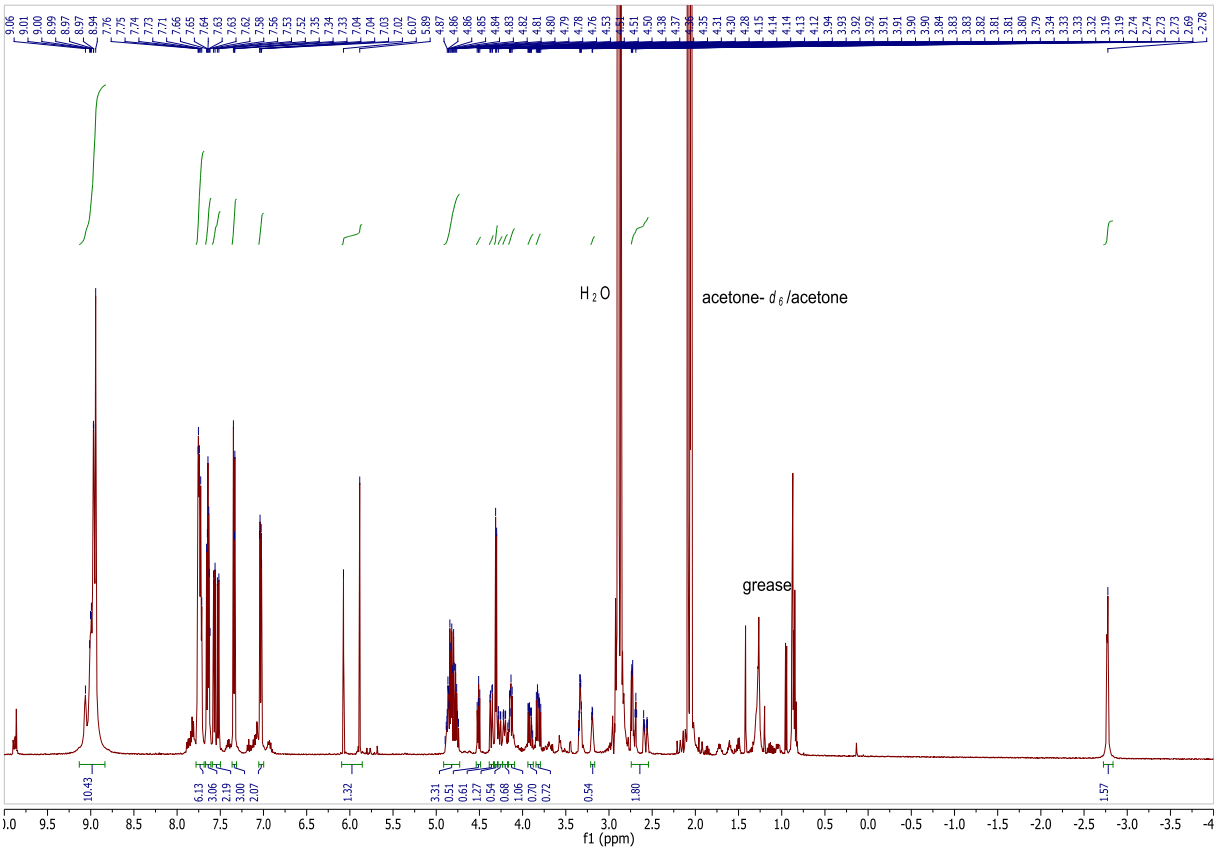


Figure 58. ^{1}H spectrum (*JEOL*^{TM} ECP 500, 500 MHz, acetone-d_6) of porphyrin **8c**

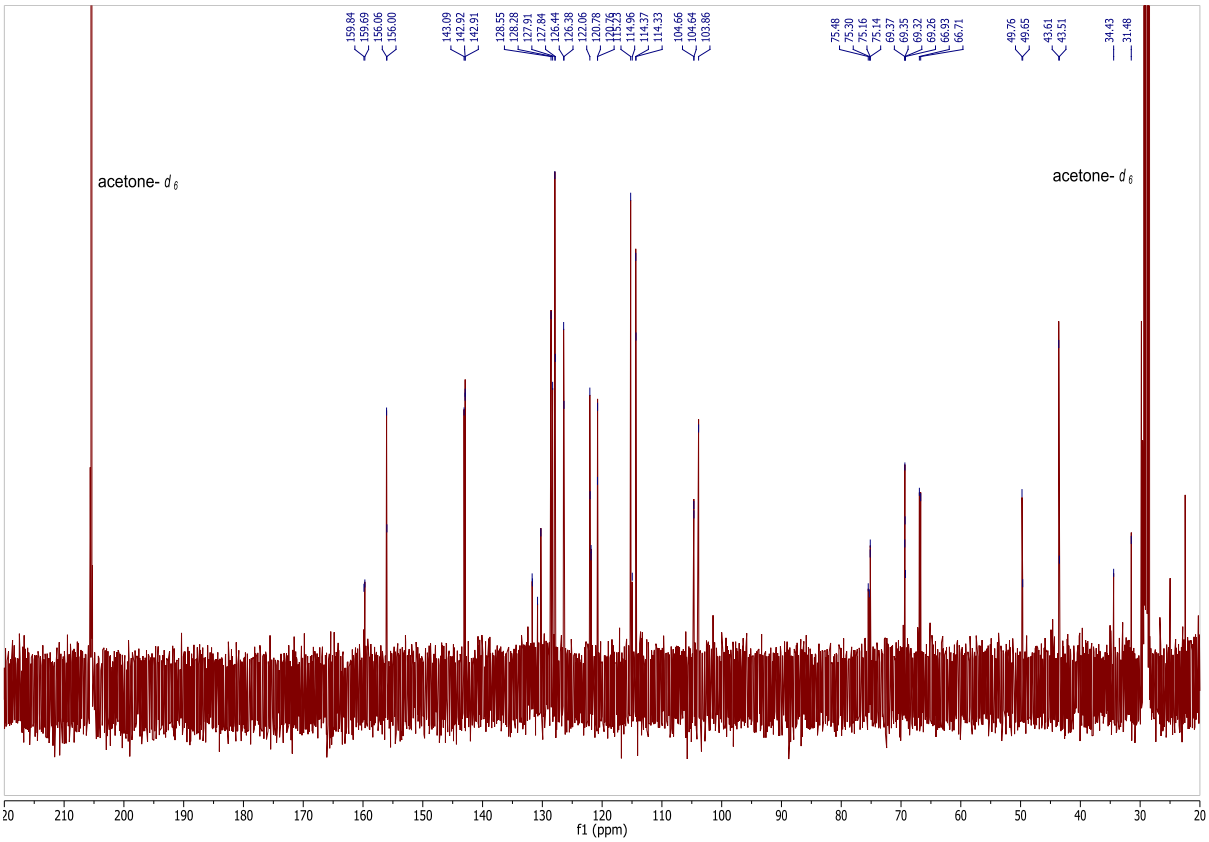


Figure 59. ^{13}C spectrum (*JEOL*^{TM} ECP 500, 126 MHz, acetone-d_6) of porphyrin **8c**

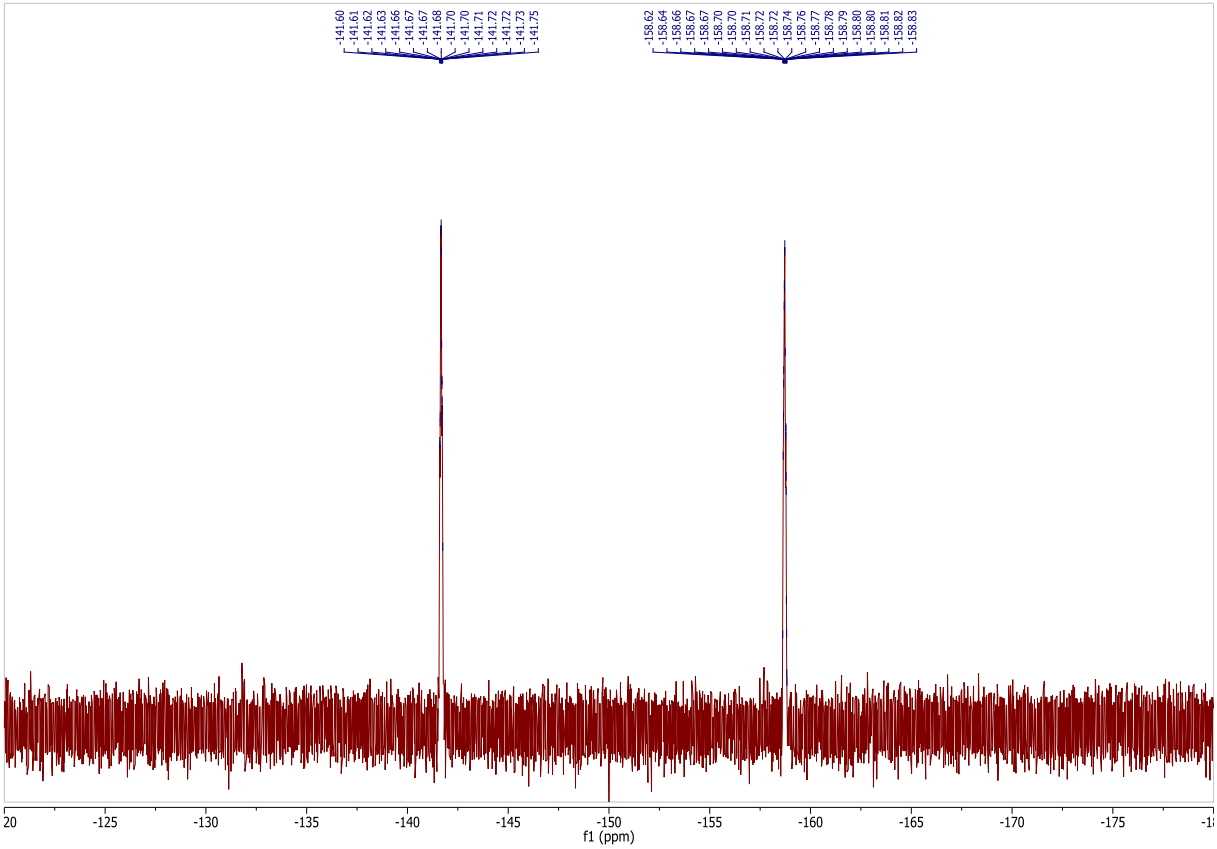


Figure 60. ^{19}F spectrum (*JEOL*^{TM} ECP 500, 471 MHz, acetone-d_6) of porphyrin **8c**

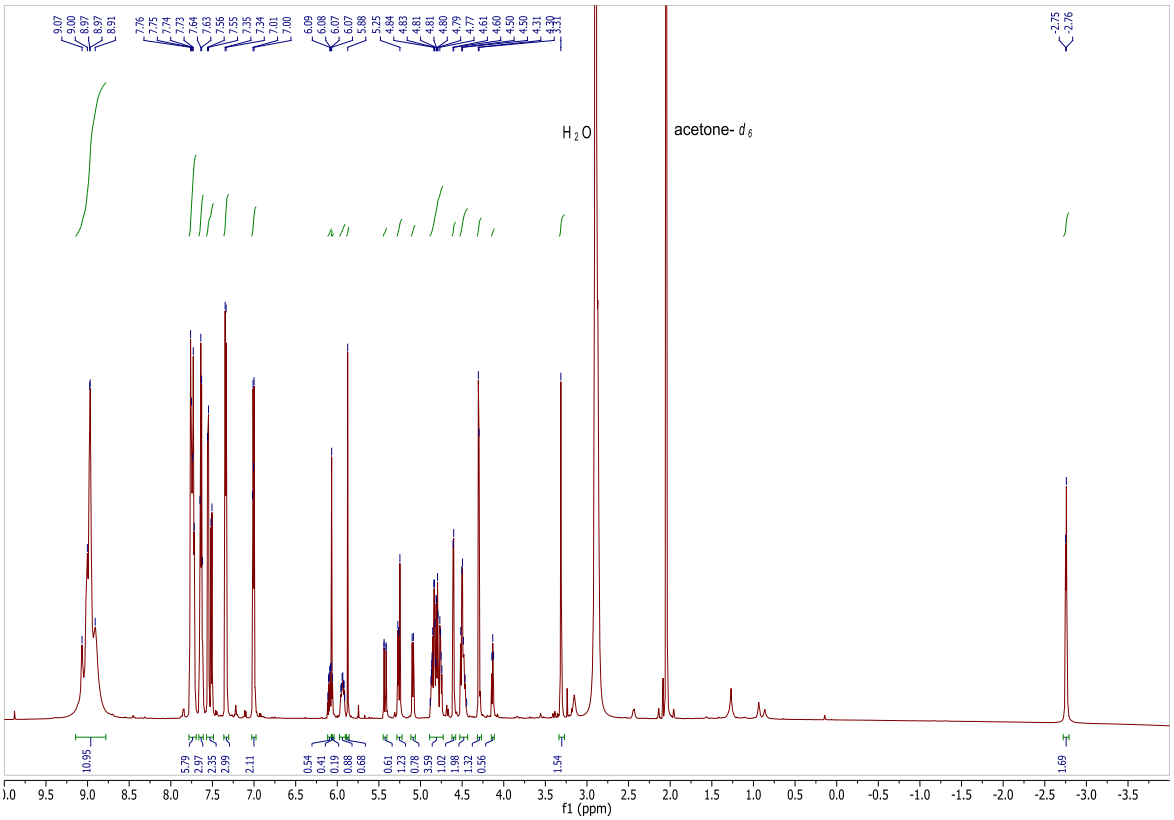


Figure 61. ^{1}H spectrum (*Bruker BioSpin* AVANCE700, 700 MHz, acetone-d_6) of porphyrin **9**

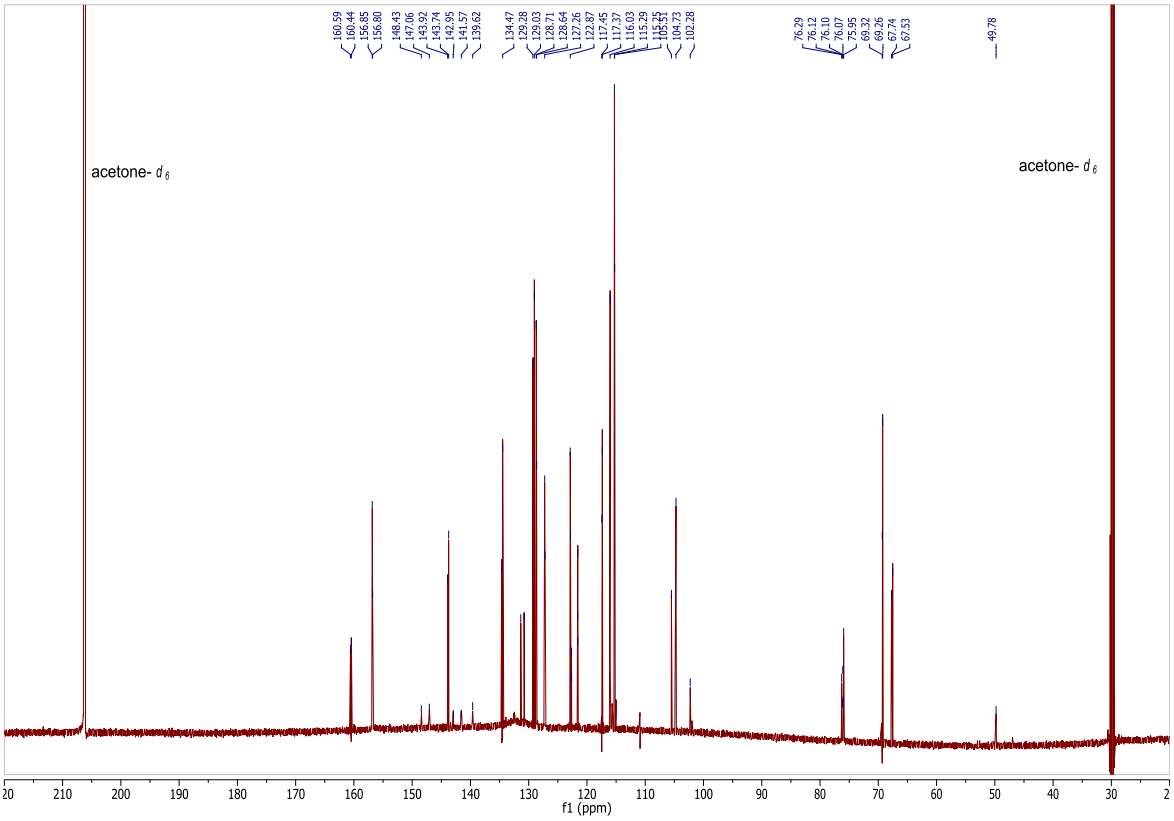


Figure 62. ^{13}C spectrum (*Bruker BioSpin* AVANCE700, 176 MHz, acetone-d_6) of porphyrin **9**

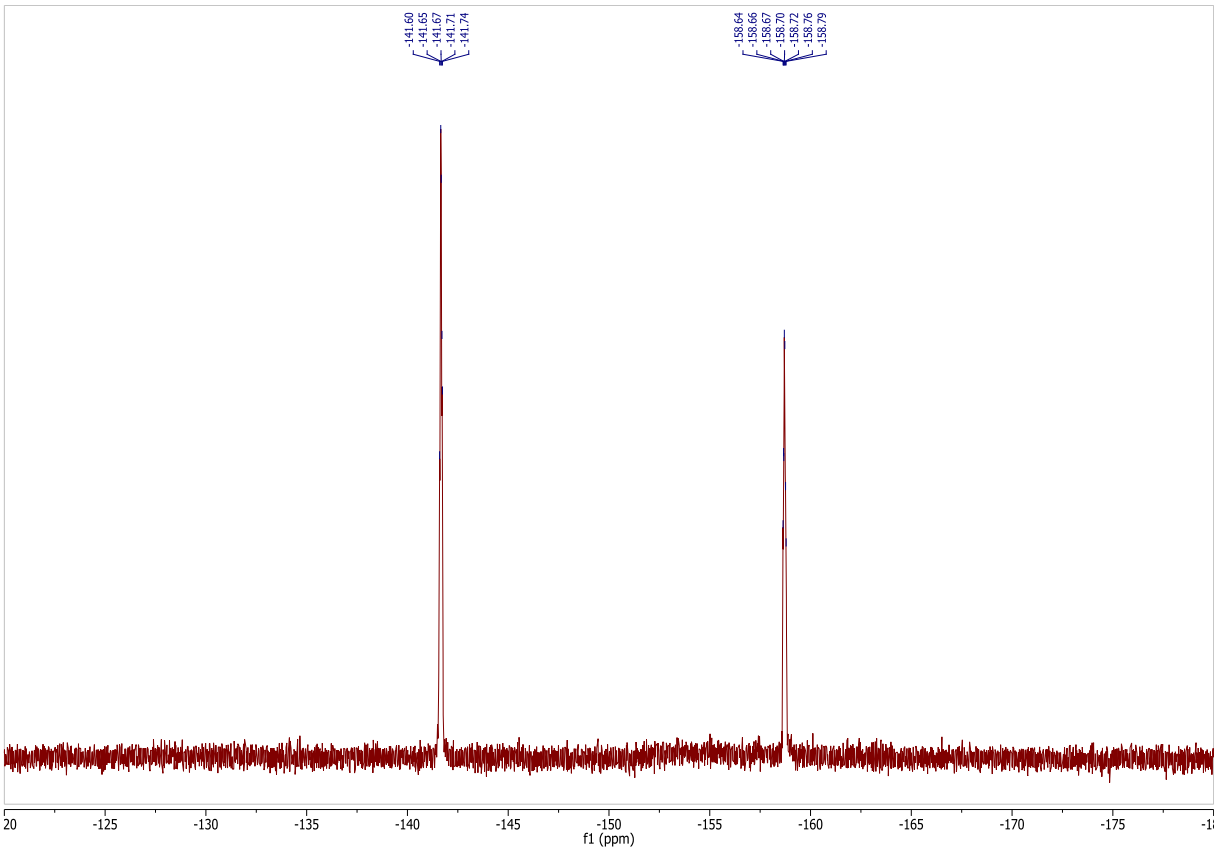


Figure 63. ^{19}F spectrum (*JEOL*^{TM} ECP 500, 471 MHz, acetone-d_6) of porphyrin **9**

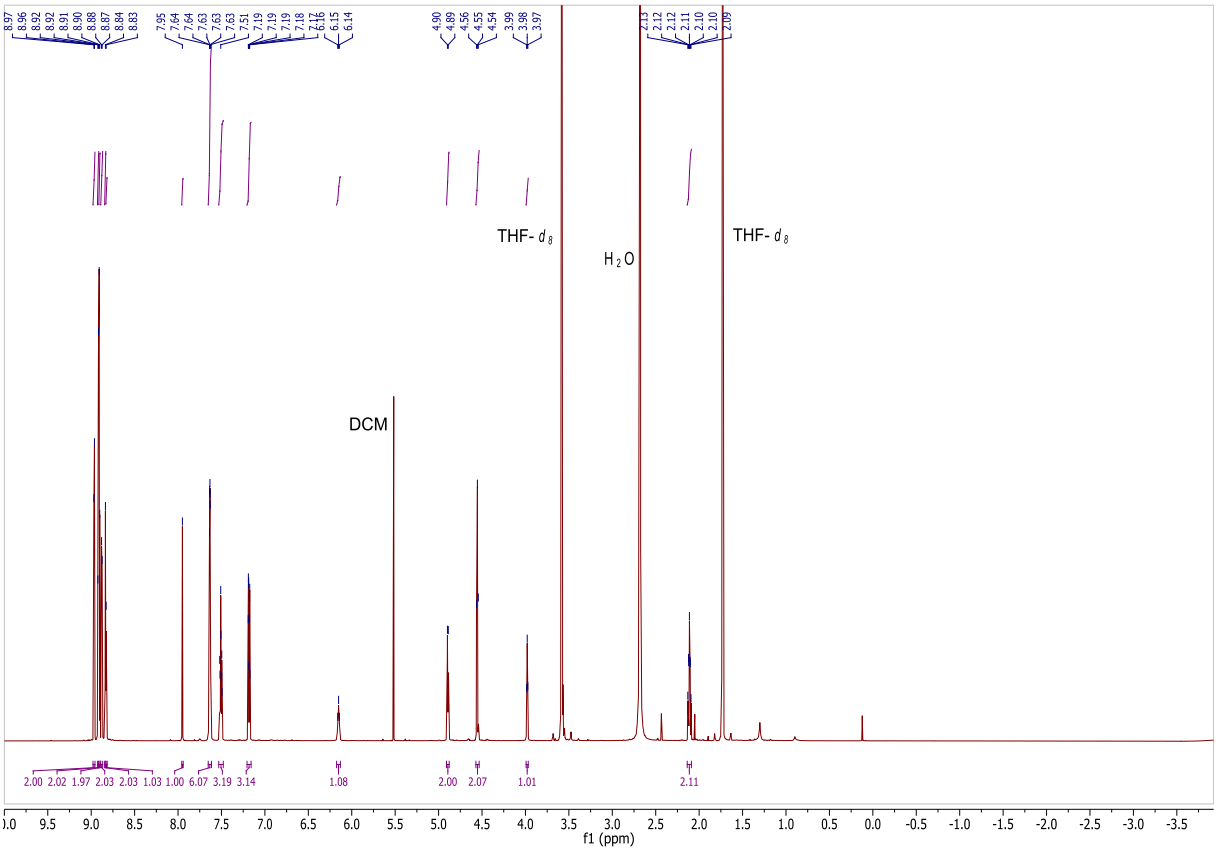


Figure 64. ^{1}H spectrum (*Bruker BioSpin* AVANCE700, 700 MHz, THF-d_8) of porphyrin **10a**

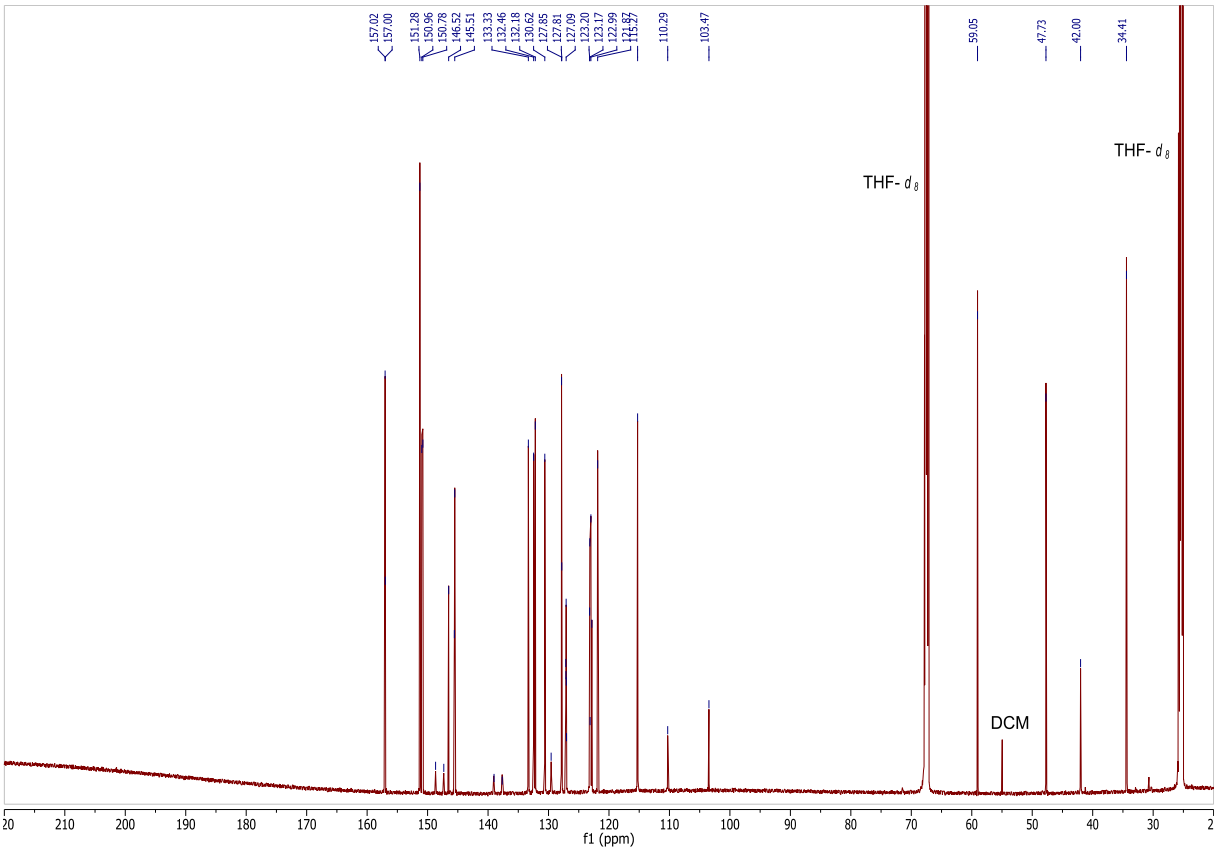


Figure 65. ^{13}C spectrum (*Bruker BioSpin* AVANCE700, 176 MHz, THF-d_8) of porphyrin **10a**

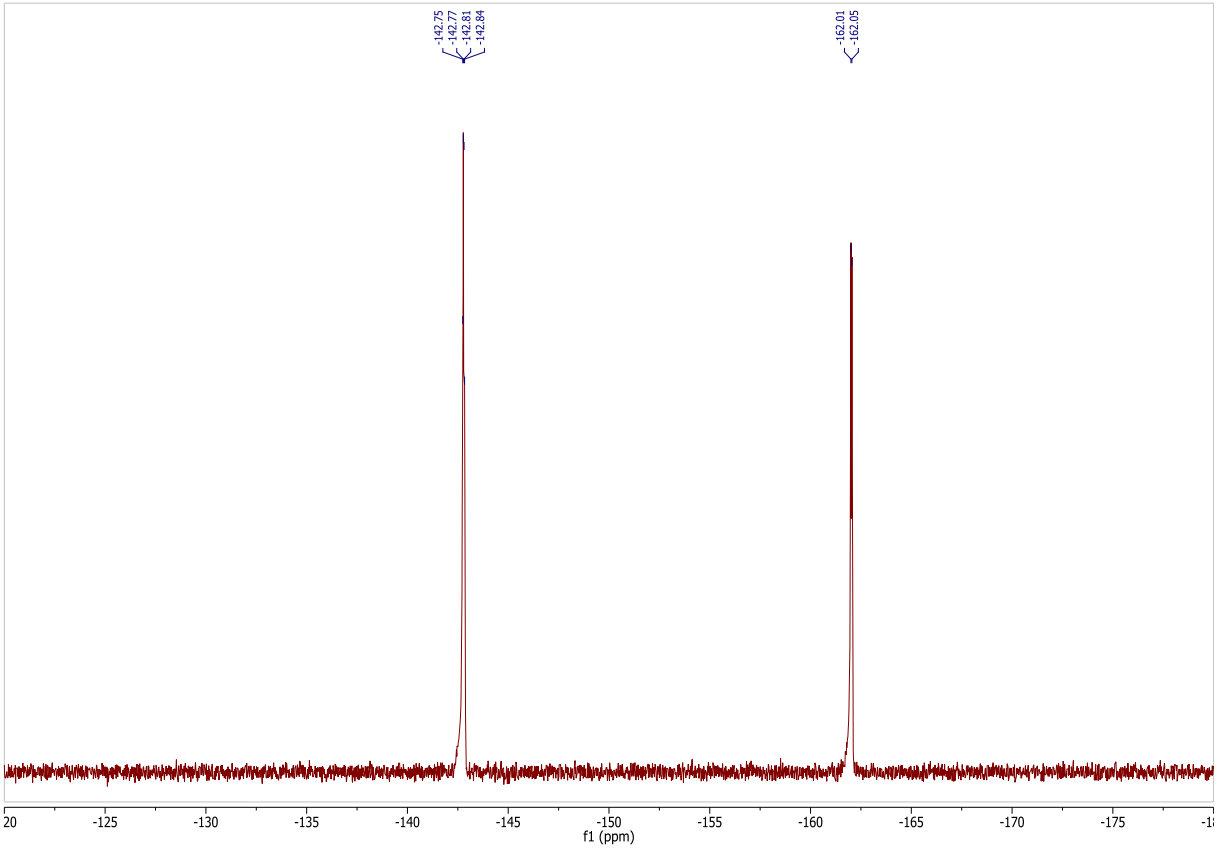


Figure 66. ^{19}F spectrum (*JEOL*^{TM} ECX 400, 376 MHz, THF-d_8) of porphyrin **10a**

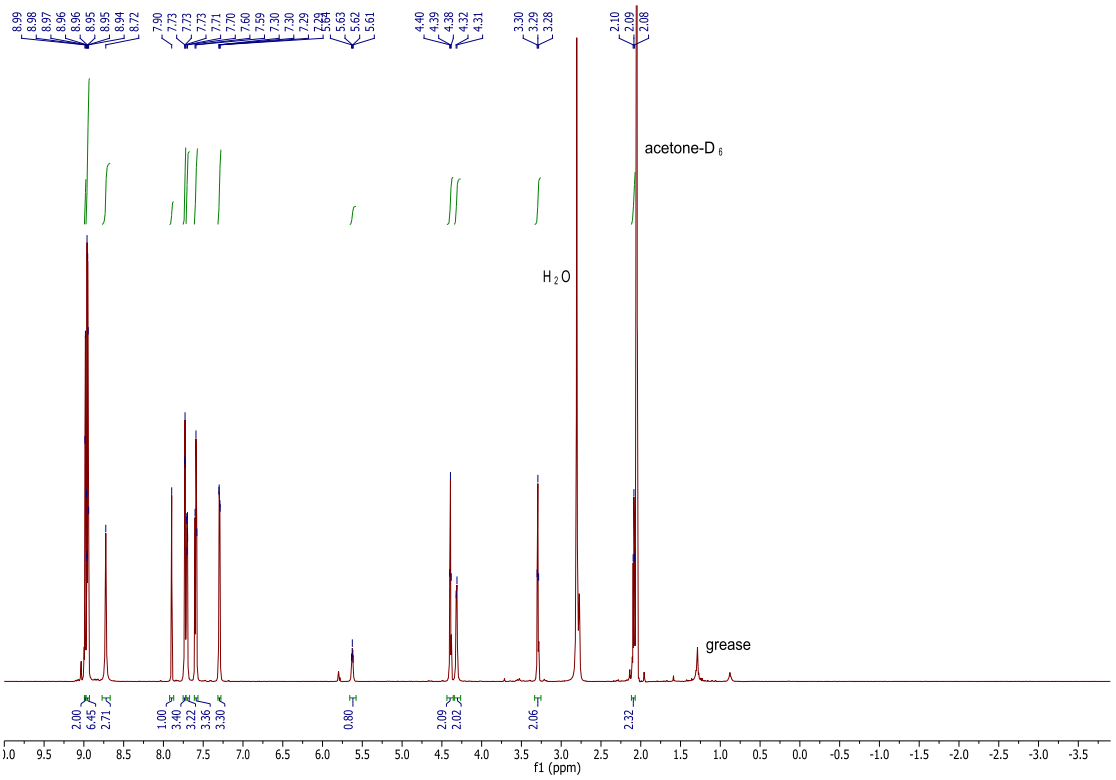


Figure 67. ^{1}H spectrum (*Bruker BioSpin* AVANCE700, 700 MHz, acetone-d_6) of porphyrin **10b**

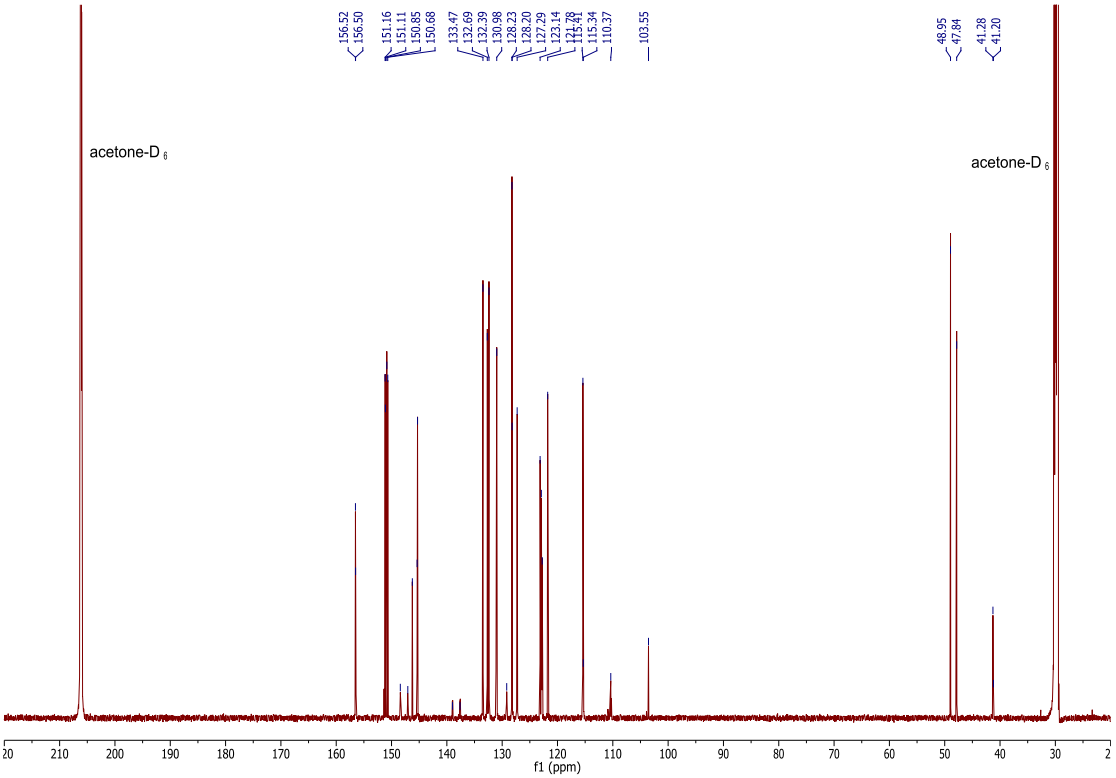


Figure 68. ^{13}C spectrum (*Bruker BioSpin* AVANCE700, 176 MHz, acetone-d_6) of porphyrin **10b**

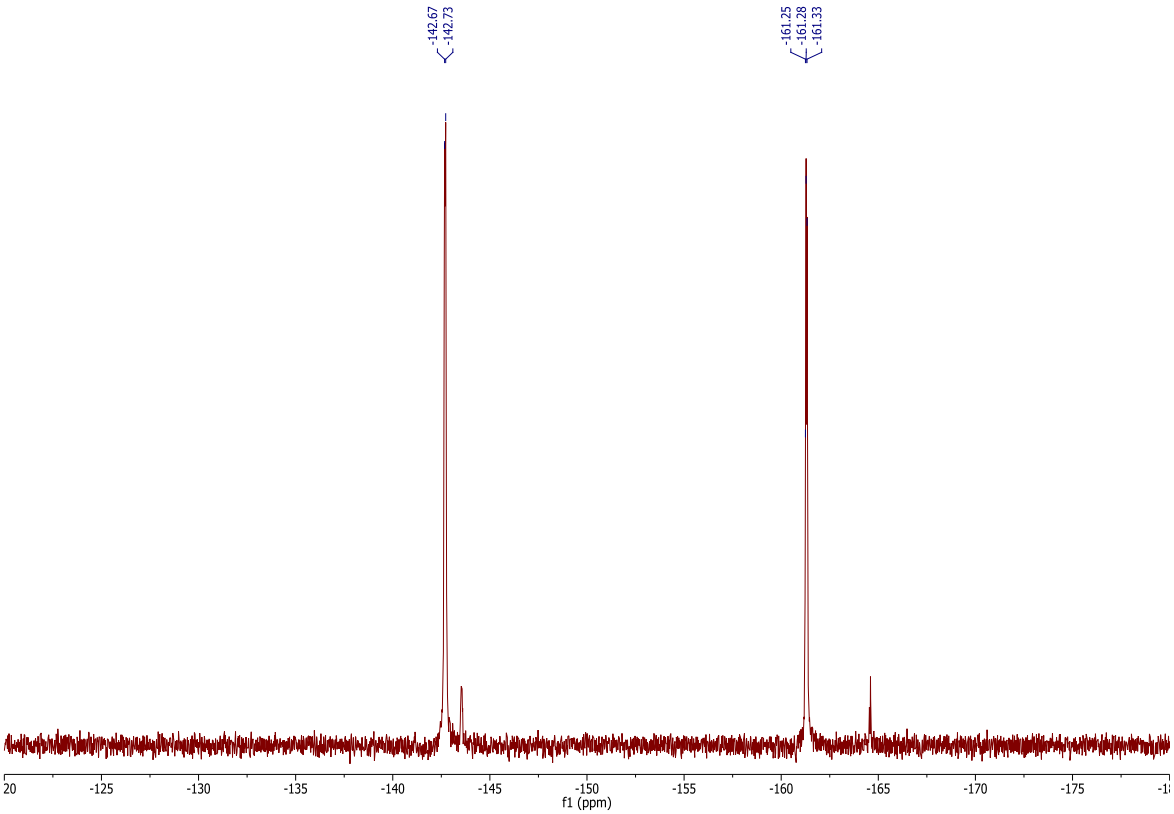


Figure 69. ^{19}F spectrum (*JEOL*^{TM} ECP 500, 471 MHz, acetone-d_6) of porphyrin **10b**

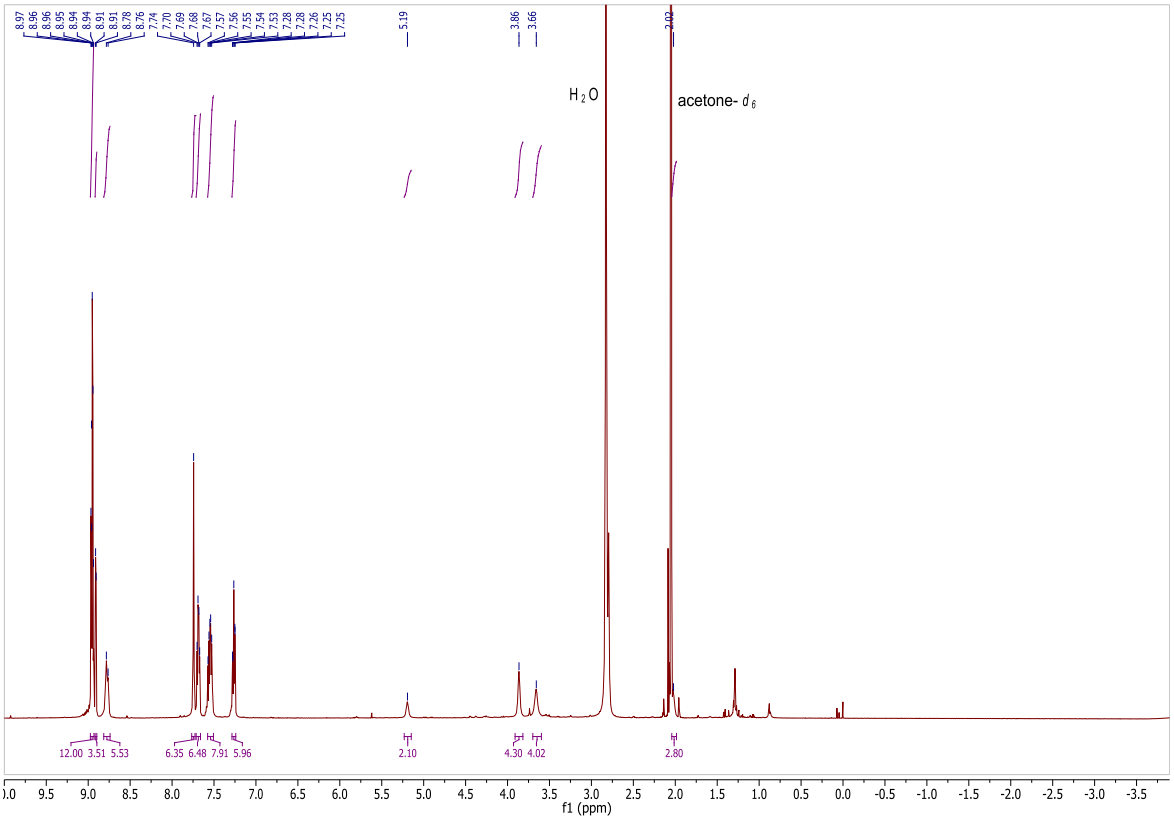


Figure 70. ^{1}H spectrum (*Bruker BioSpin* AVANCE700, 700 MHz, acetone-d_6) of porphyrin **10c**

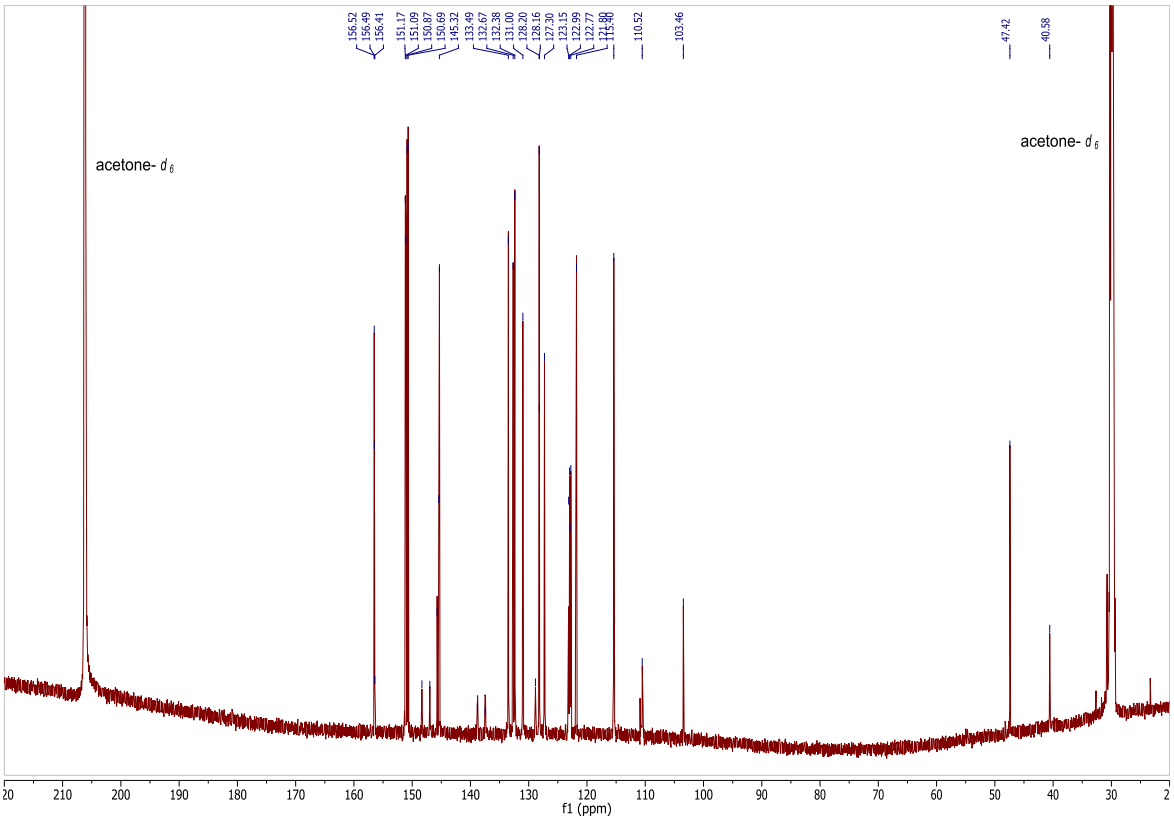


Figure 71. ^{13}C spectrum (*Bruker BioSpin* AVANCE700, 176 MHz, acetone-d_6) of porphyrin **10c**

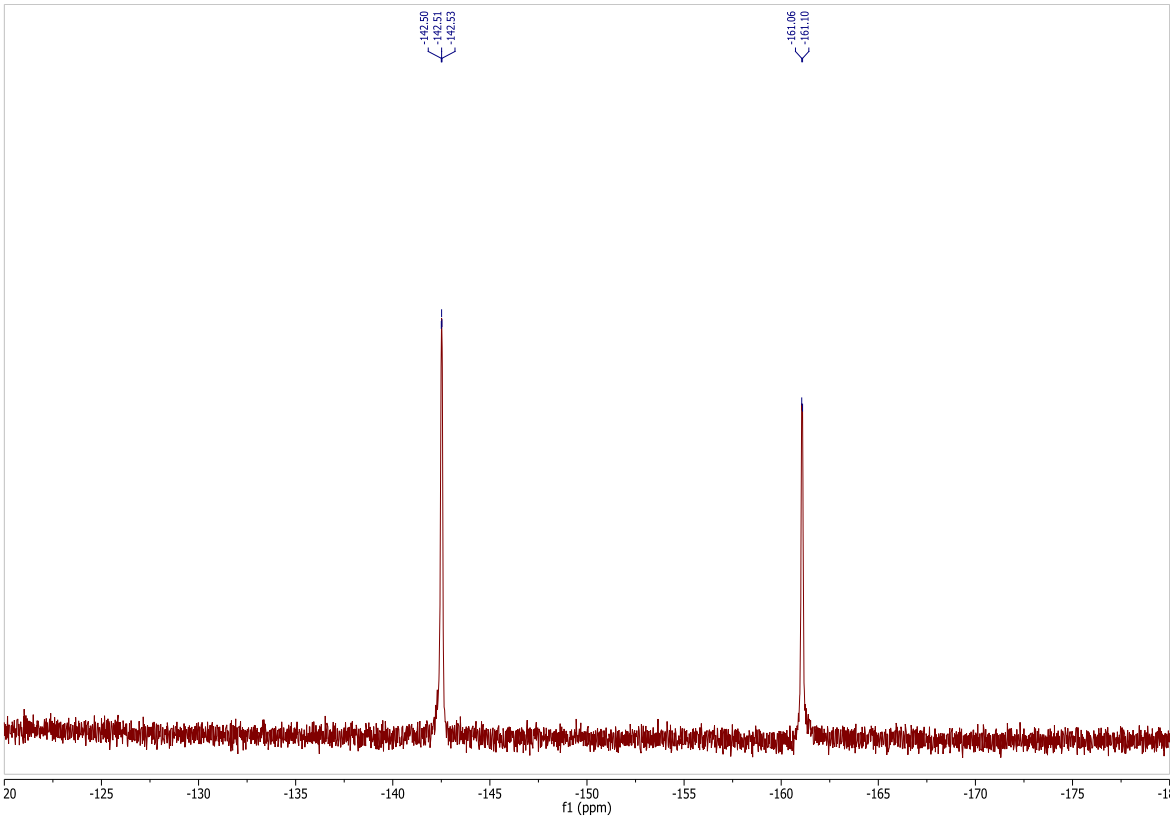


Figure 72. ^{19}F spectrum (*JEOL*^{TM} ECX 400, 376 MHz, acetone-d_6) of porphyrin **10c**

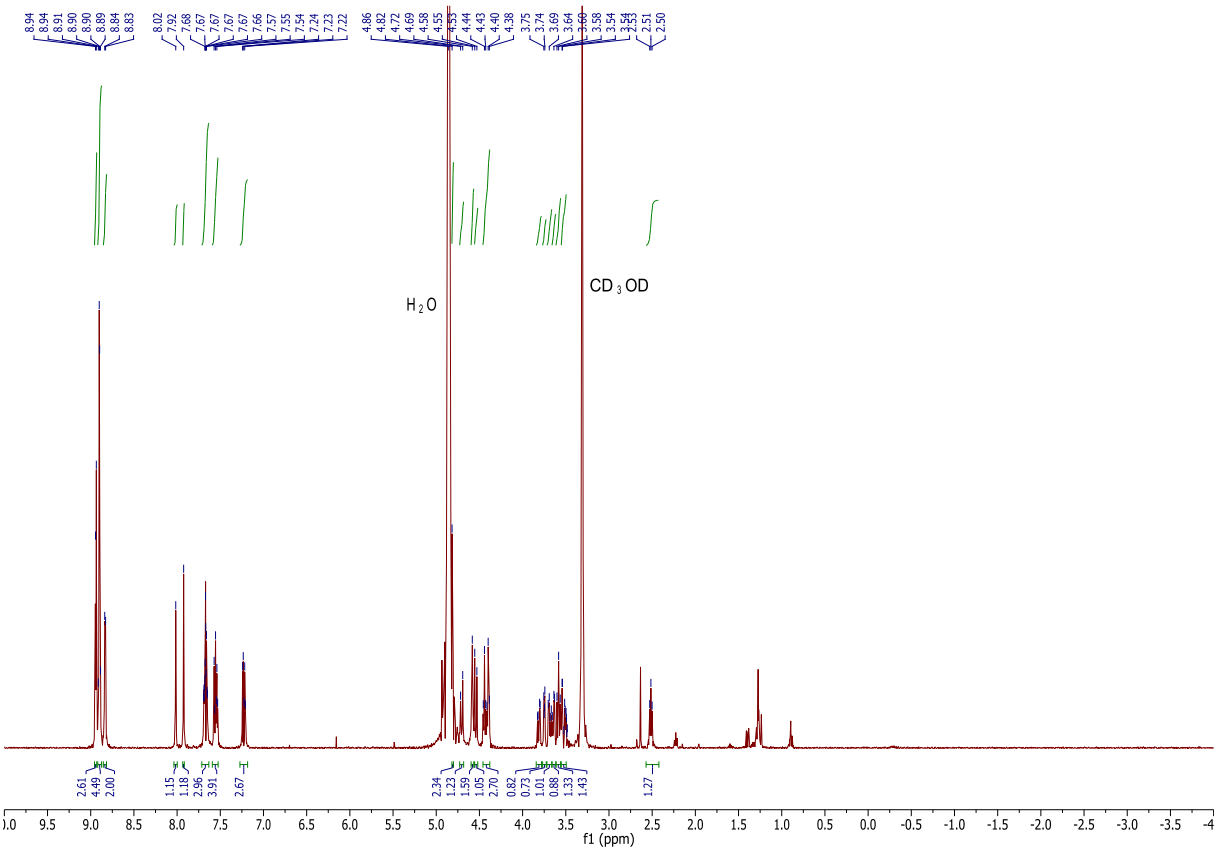


Figure 73. ^{1}H spectrum (*JEOL*^{TM} ECP 500, 500 MHz, CD_3OD) of porphyrin **10d**

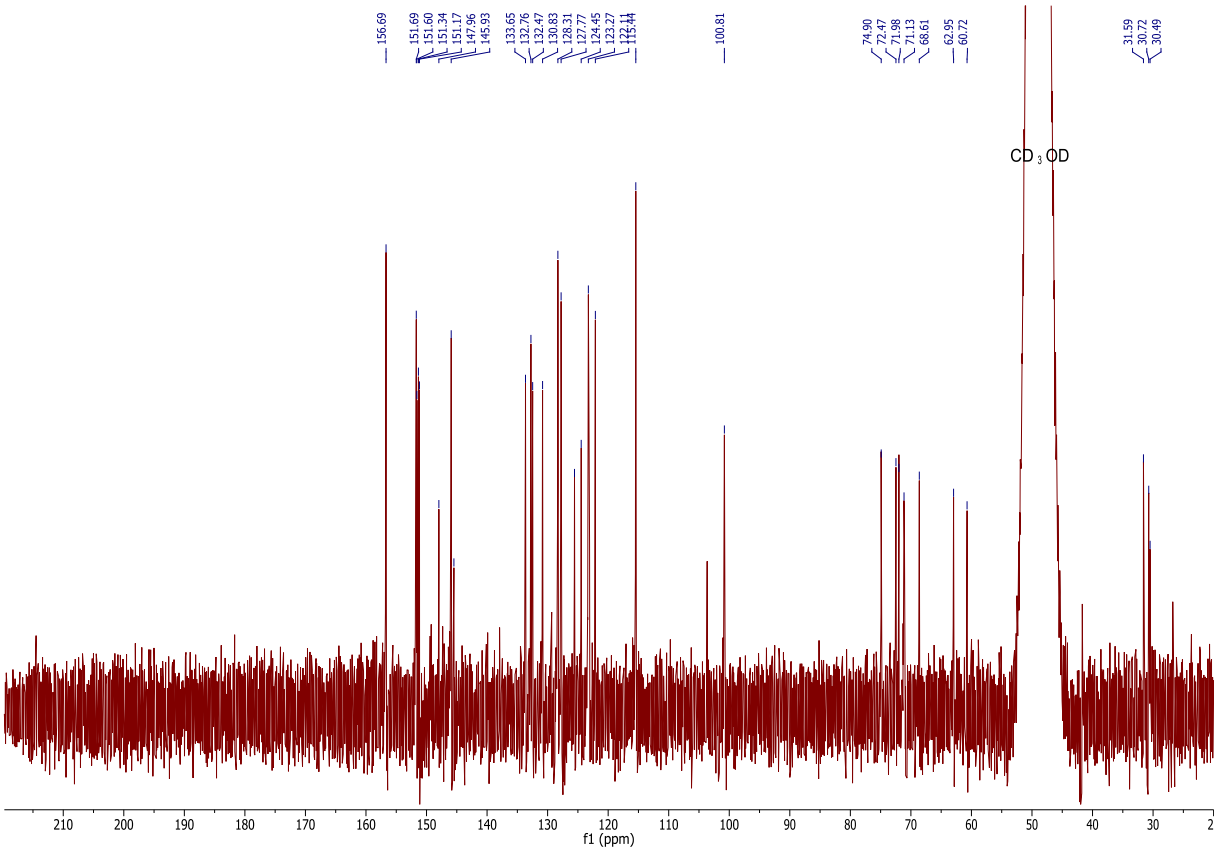


Figure 74. ^{13}C spectrum (*JEOL*^{TM} ECP 500, 126 MHz, CD_3OD) of porphyrin **10d**

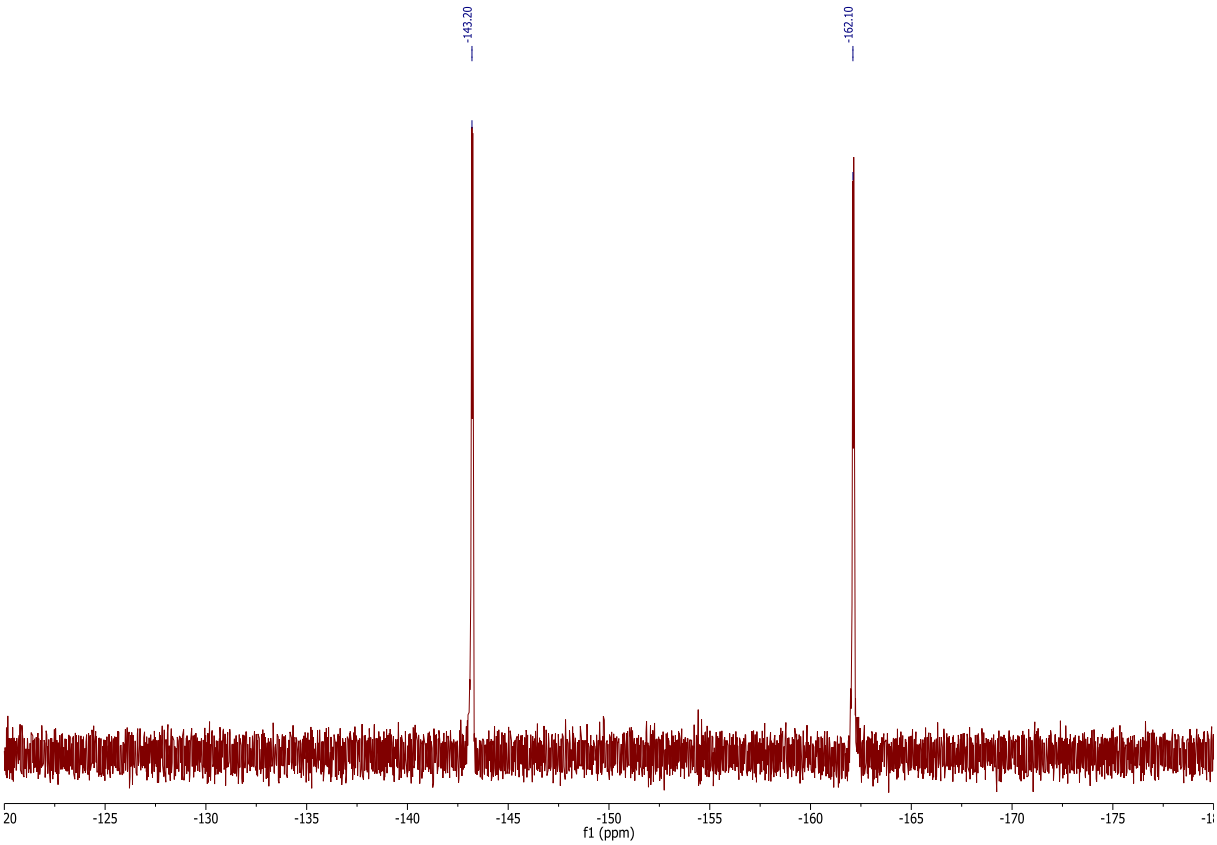


Figure 75. ^{19}F spectrum (*JEOL*^{TM} ECX 400, 376 MHz, CD_3OD) of porphyrin **10d**

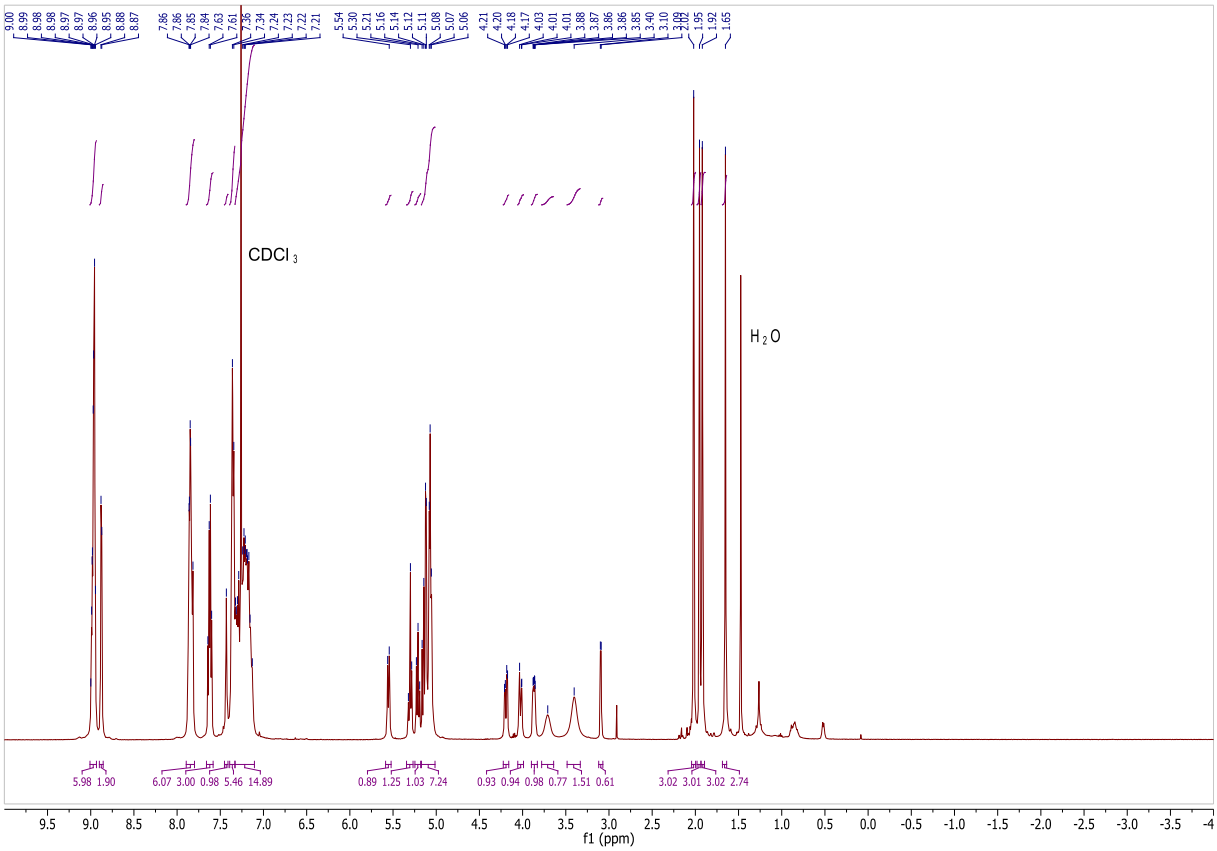


Figure 76. ^{1}H spectrum (*JEOL*^{TM} ECP 500, 500 MHz, $CDCl_3$) of porphyrin **11**

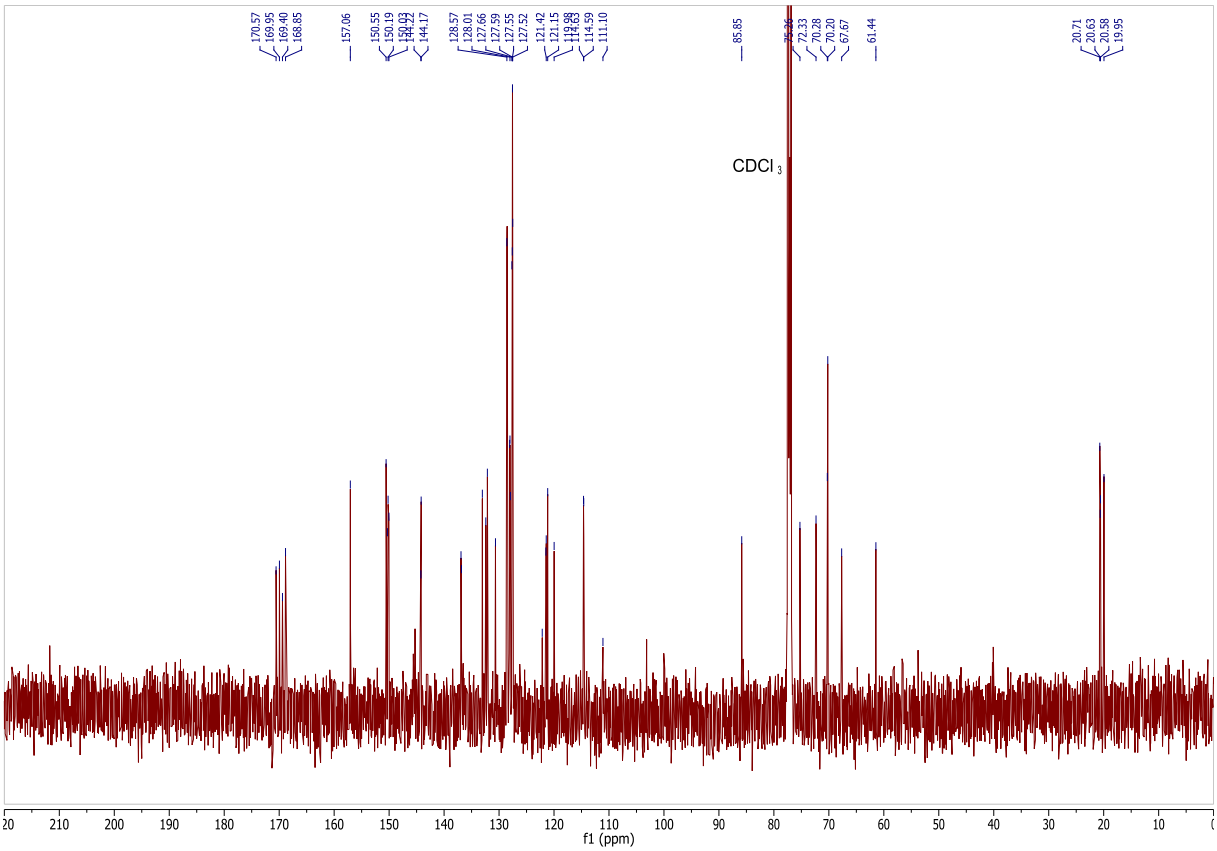


Figure 77. ^{13}C spectrum (*JEOL*^{TM} ECP 500, 126 MHz, $CDCl_3$) of porphyrin **11**

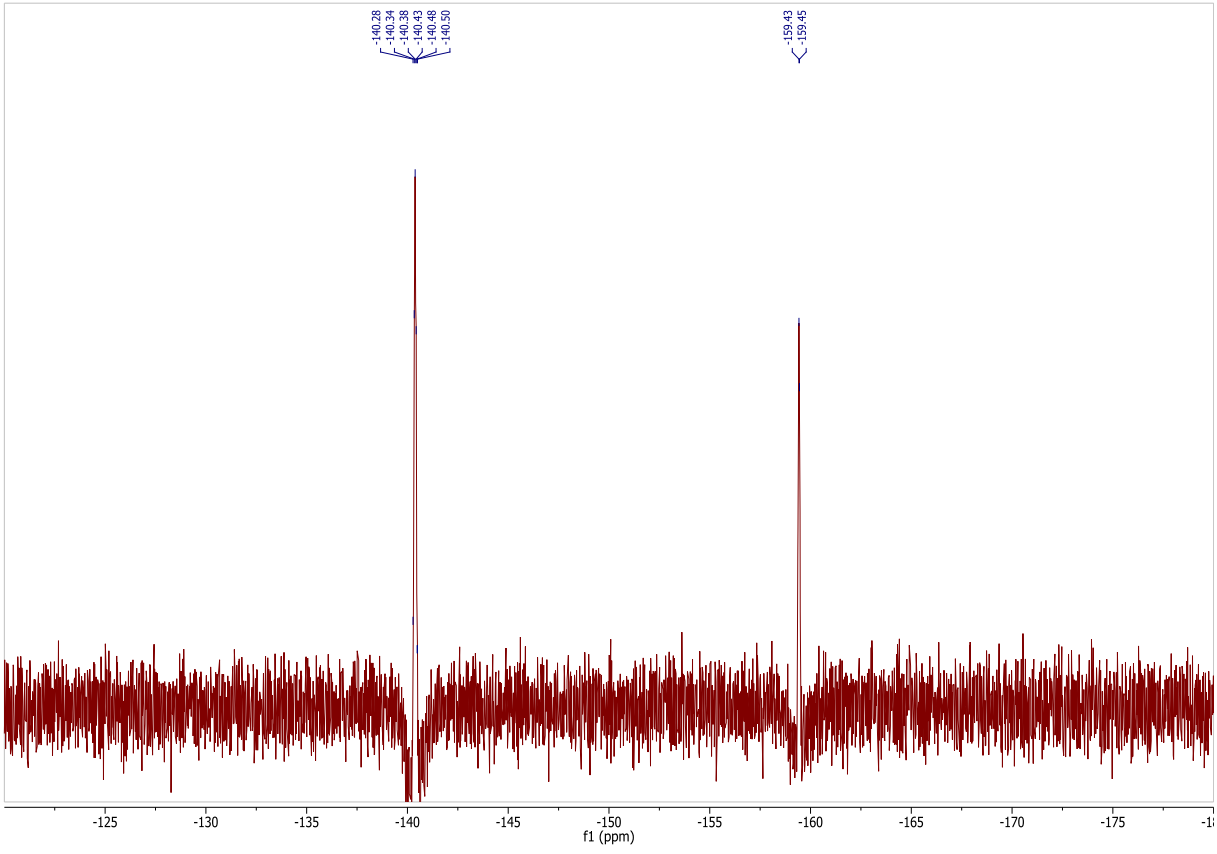


Figure 78. ^{19}F spectrum (*JEOL*^{TM} ECP 500, 471 MHz, $CDCl_3$) of porphyrin **11**

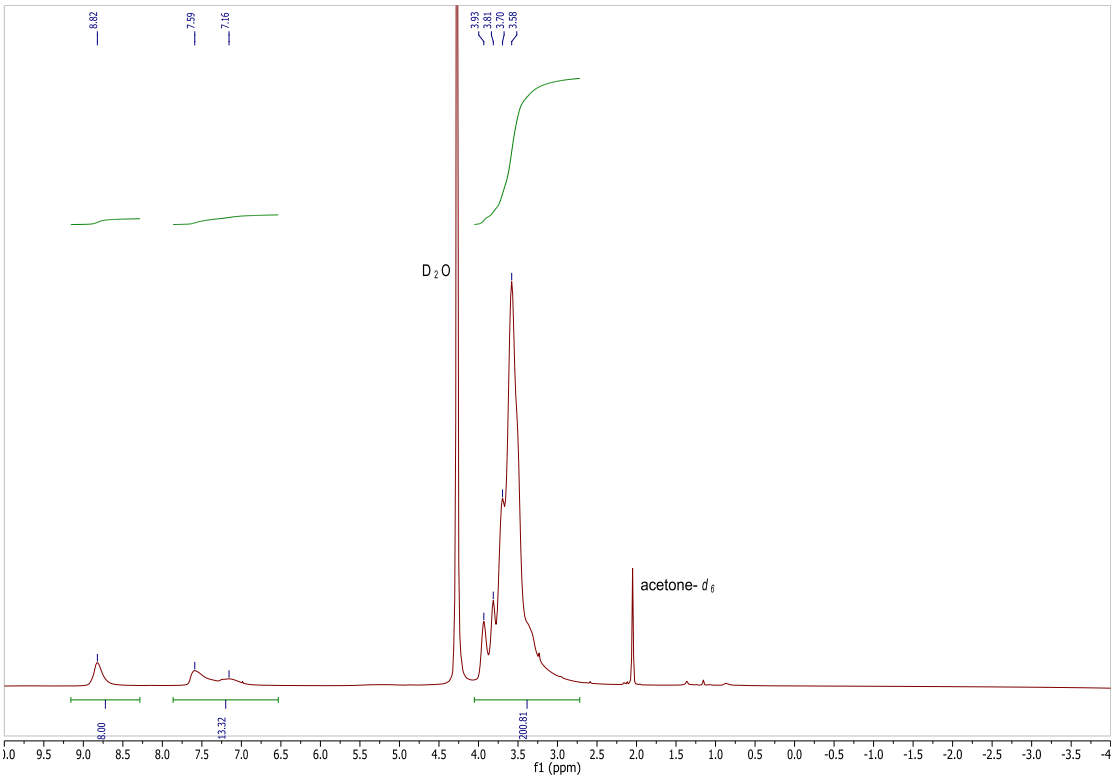


Figure 79. ^{1}H spectrum (*Bruker BioSpin* AVANCE700, 700 MHz, acetone-d_6/D_2O = 5/1, v/v) of conjugate **13a**

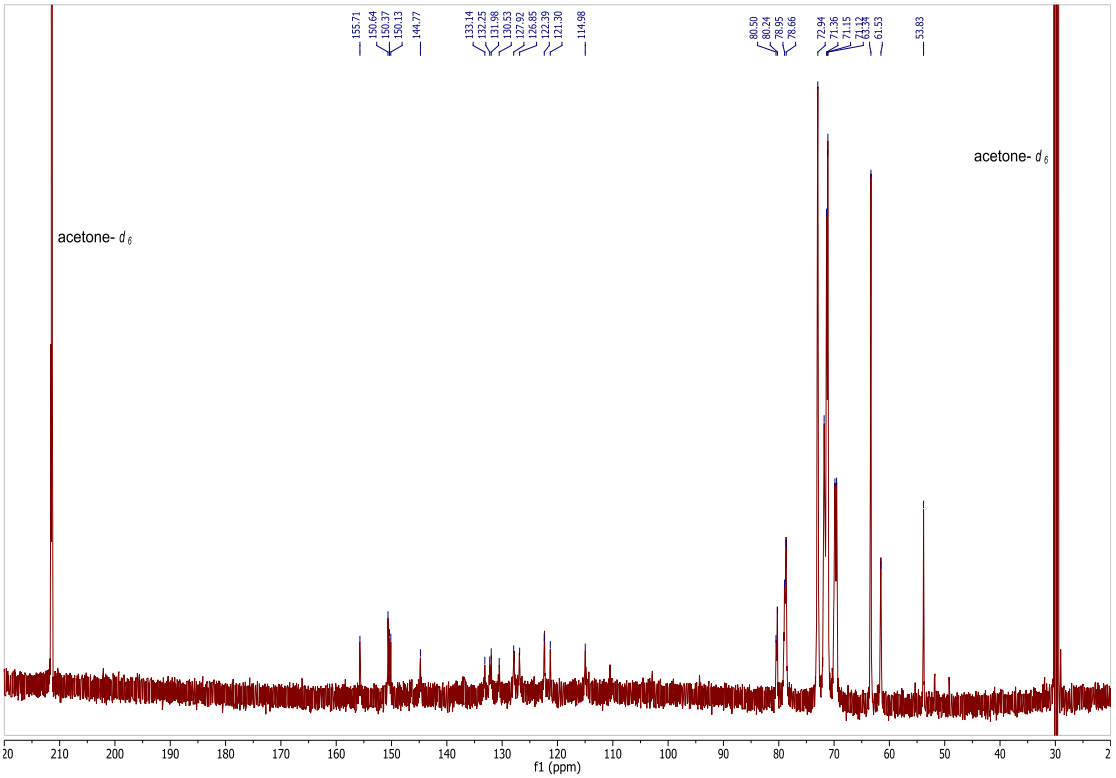


Figure 80. ^{13}C spectrum (*Bruker BioSpin* AVANCE700, 176 MHz, acetone-d_6/D_2O = 5/1, v/v) of conjugate **13a**

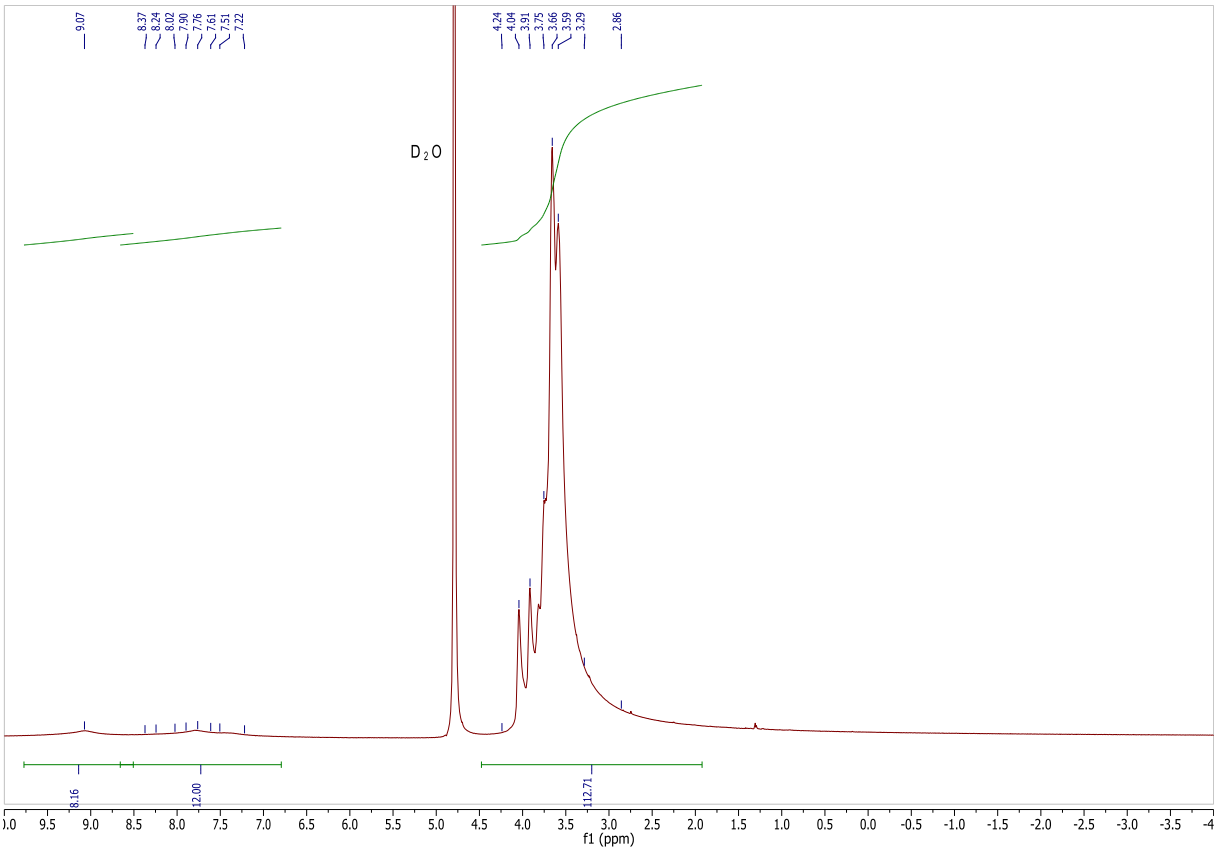


Figure 81. ^{1}H spectrum (*Bruker BioSpin* AVANCE700, 700 MHz, D_2O) of conjugate **13b**

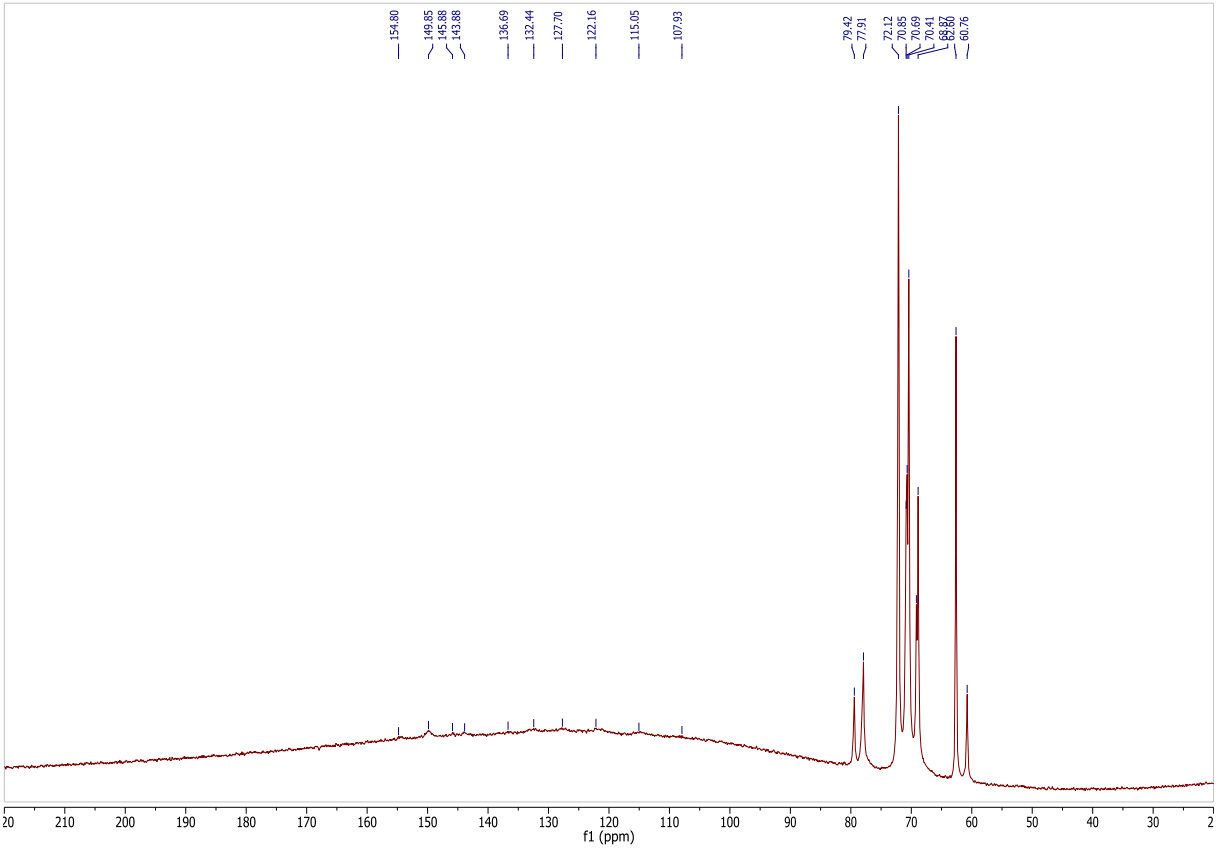


Figure 82. ^{13}C spectrum (*Bruker BioSpin* AVANCE700, 176 MHz, D_2O) of conjugate **13b**

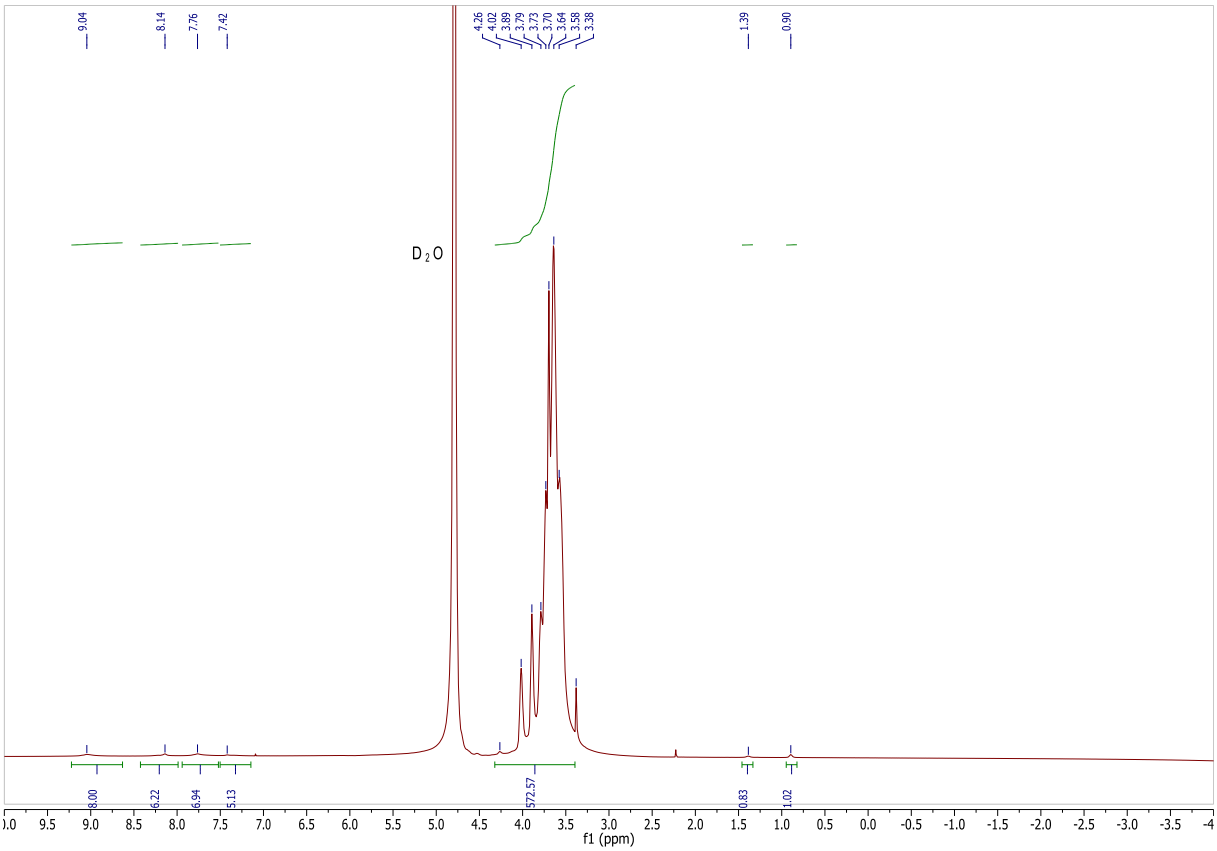


Figure 83. ^{1}H spectrum (*Bruker BioSpin* AVANCE700, 700 MHz, D_2O) of conjugate **14a**

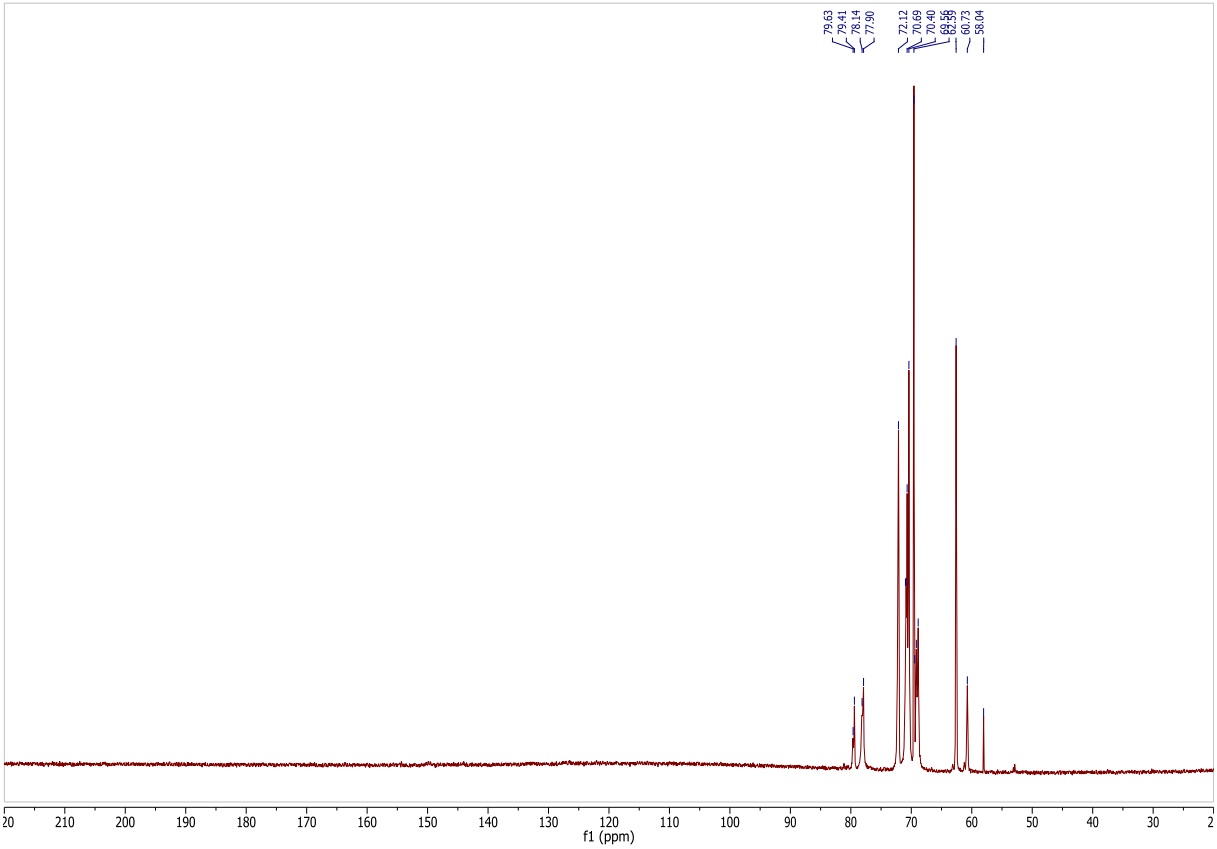


Figure 84. ^{13}C spectrum (*Bruker BioSpin* AVANCE700, 176 MHz, D_2O) of conjugate **14a**

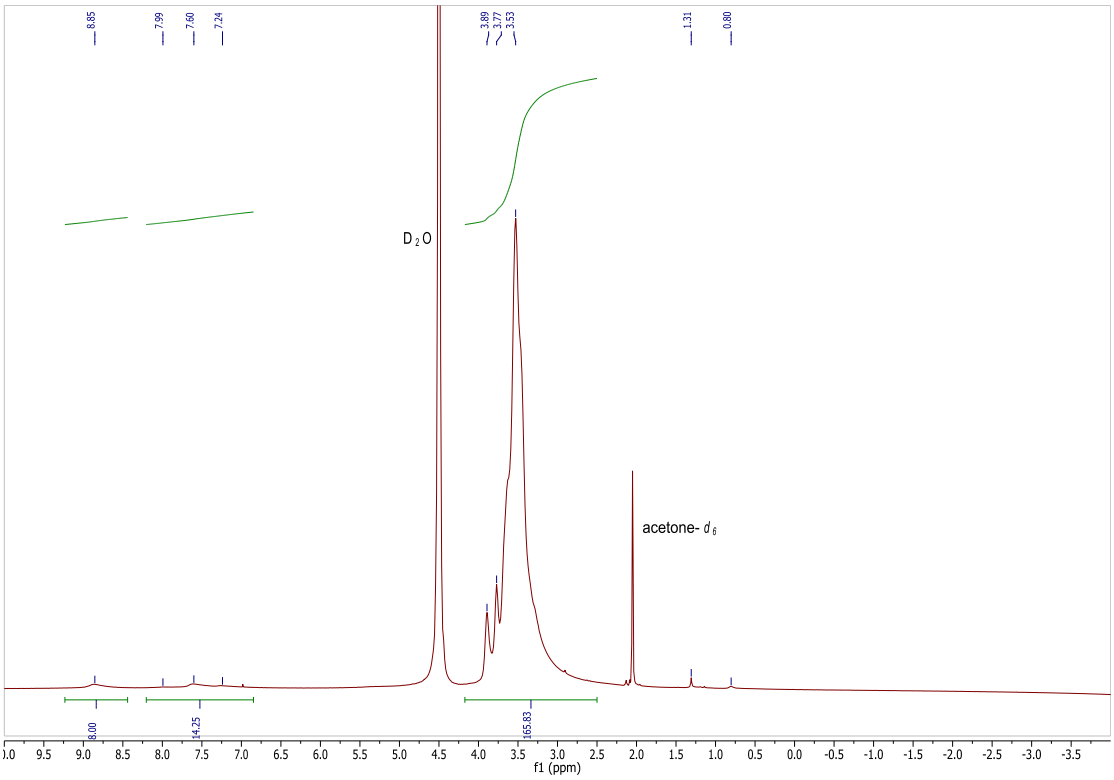


Figure 85. ^{1}H spectrum (*Bruker BioSpin* AVANCE700, 176 MHz, acetone-d_6/D_2O = 5/1, v/v) of conjugate **14b**

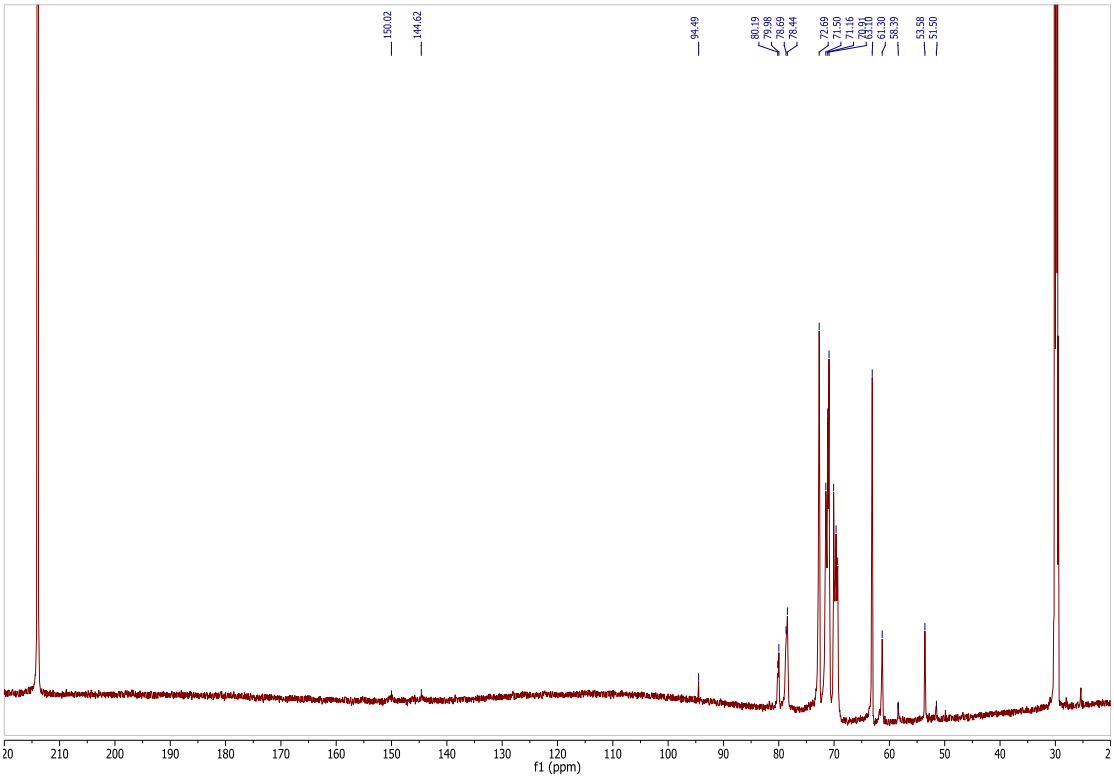


Figure 86. ^{13}C spectrum (*Bruker BioSpin* AVANCE700, 176 MHz, acetone-d_6/D_2O = 5/1, v/v) of conjugate **14b**

3. ESI-MS of porphyrins **1d, 2a-i, 4, 5a-c, 6a-c, 8a-c, 9, 10a-d,** and **11**

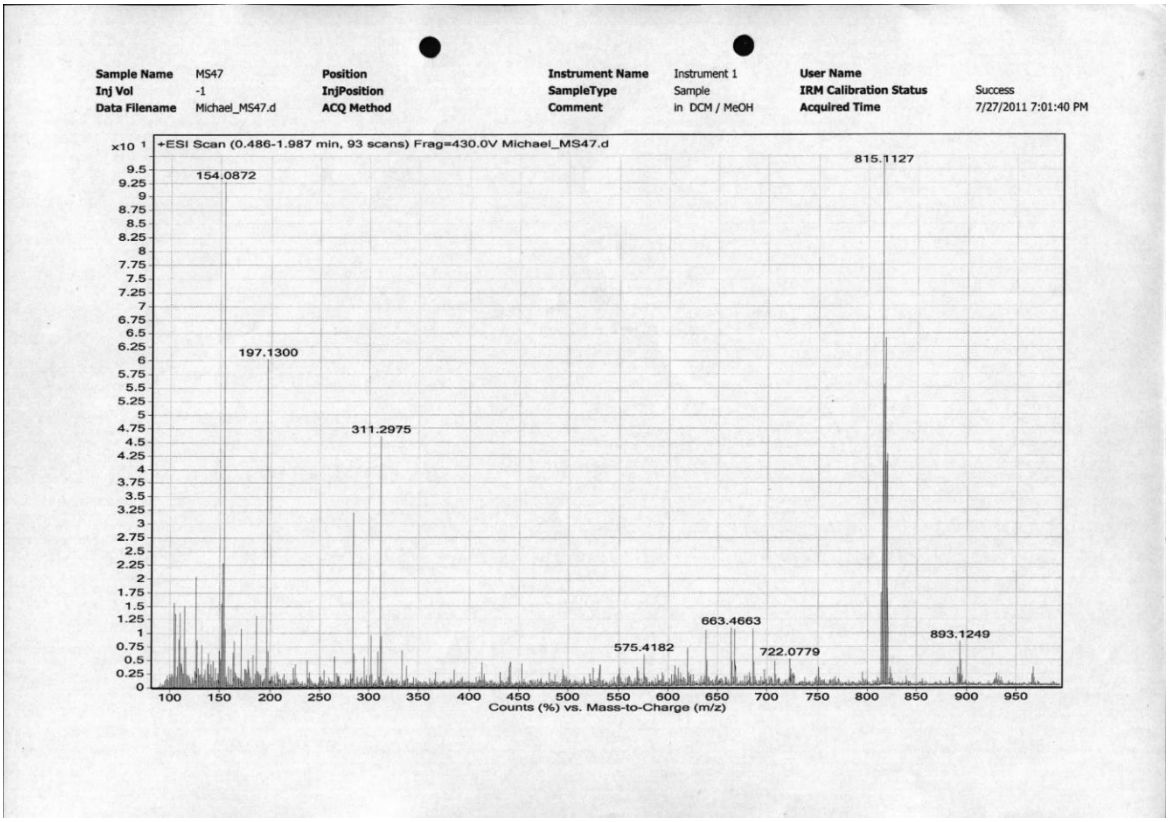


Figure 87. HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **1d**

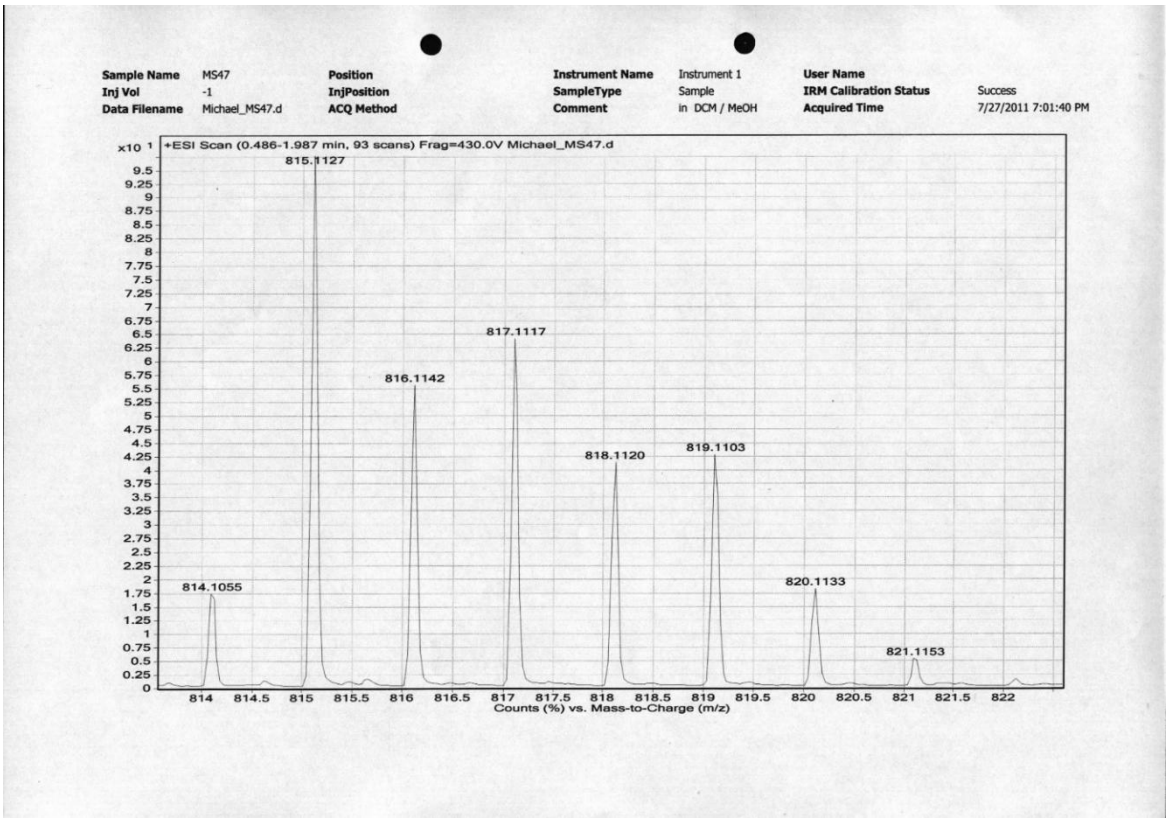


Figure 88. Zoomed HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **1d**

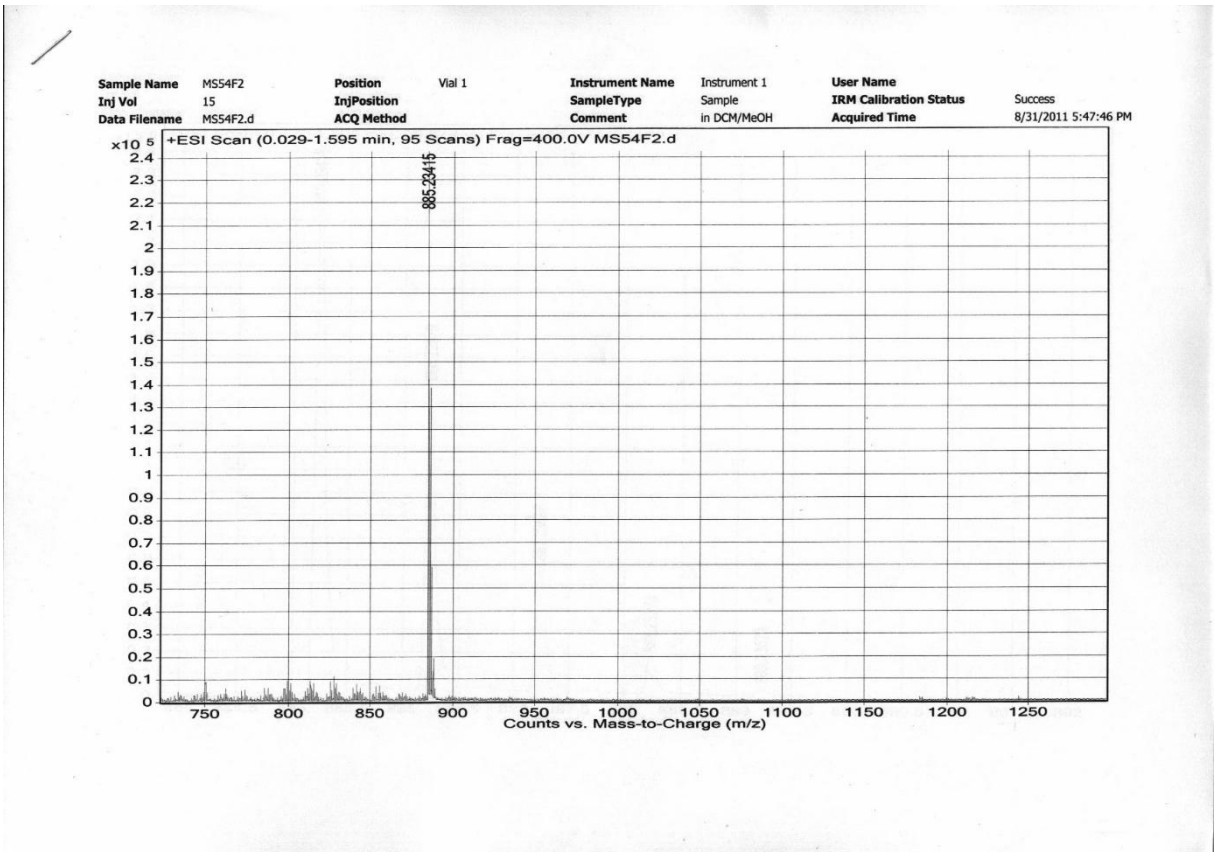


Figure 89. HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **2a**

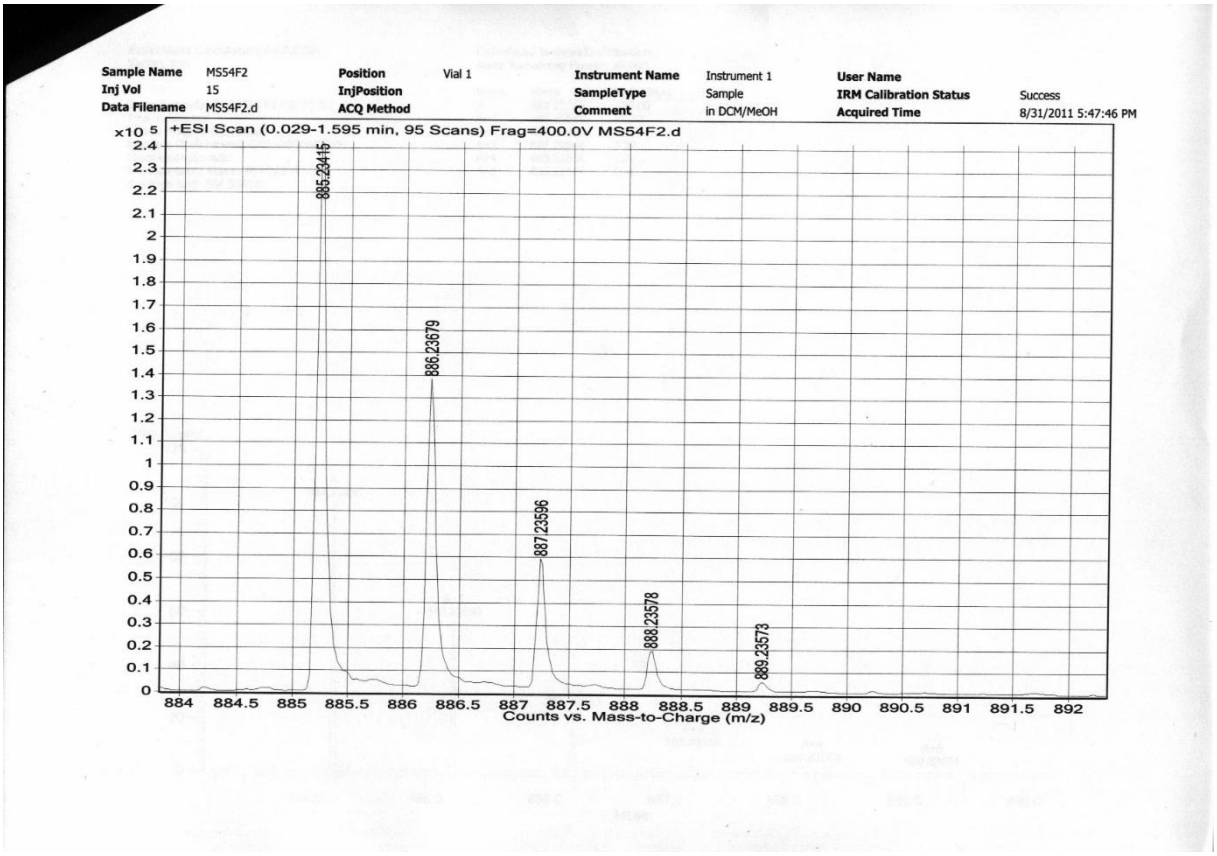


Figure 90. Zoomed HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **2a**

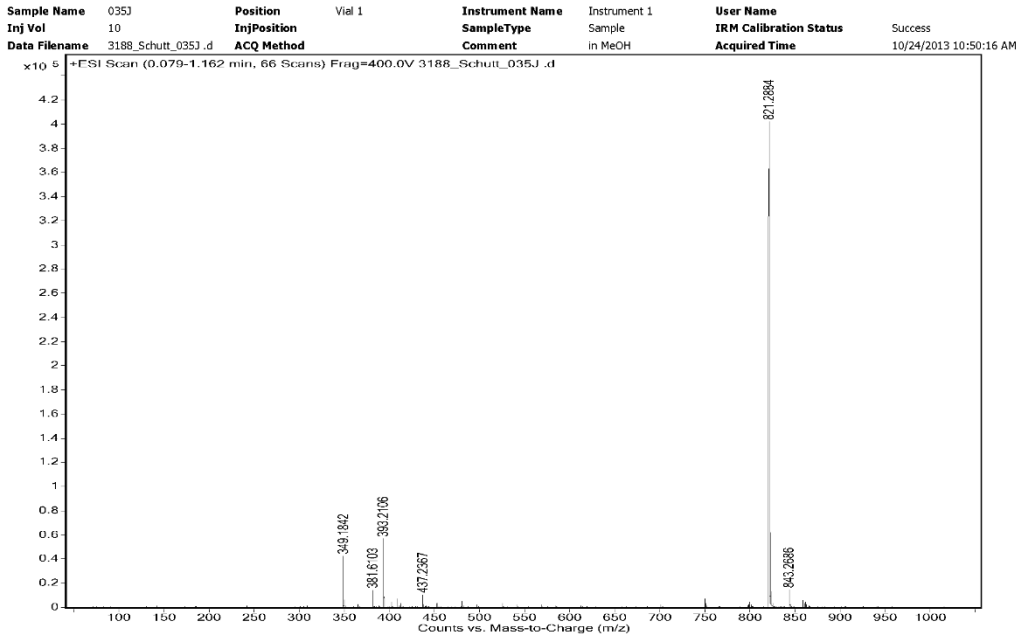


Figure 91. HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **2b**

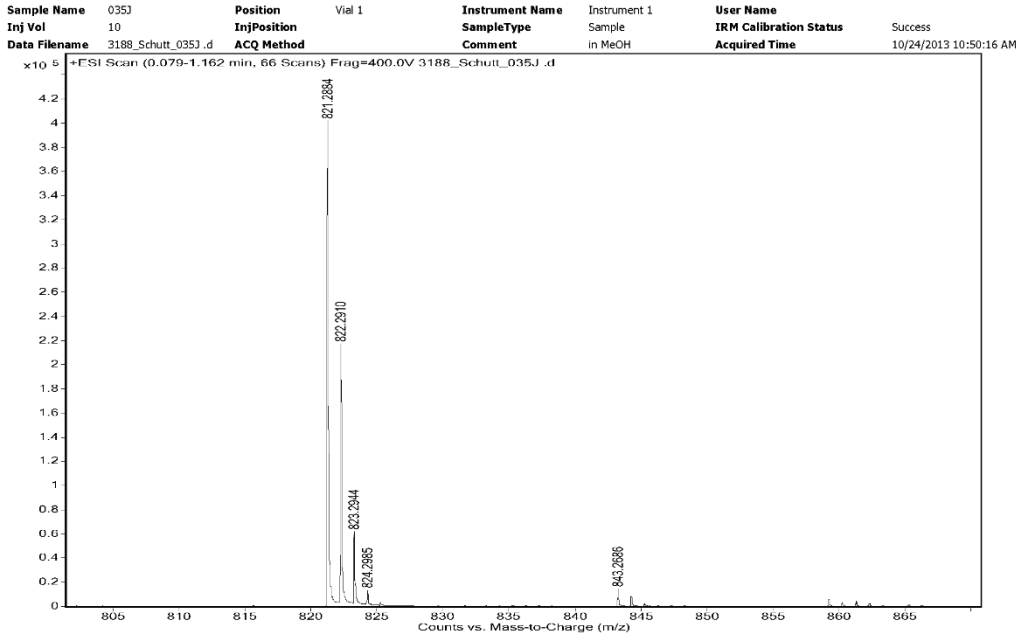


Figure 92. Zoomed HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **2b**

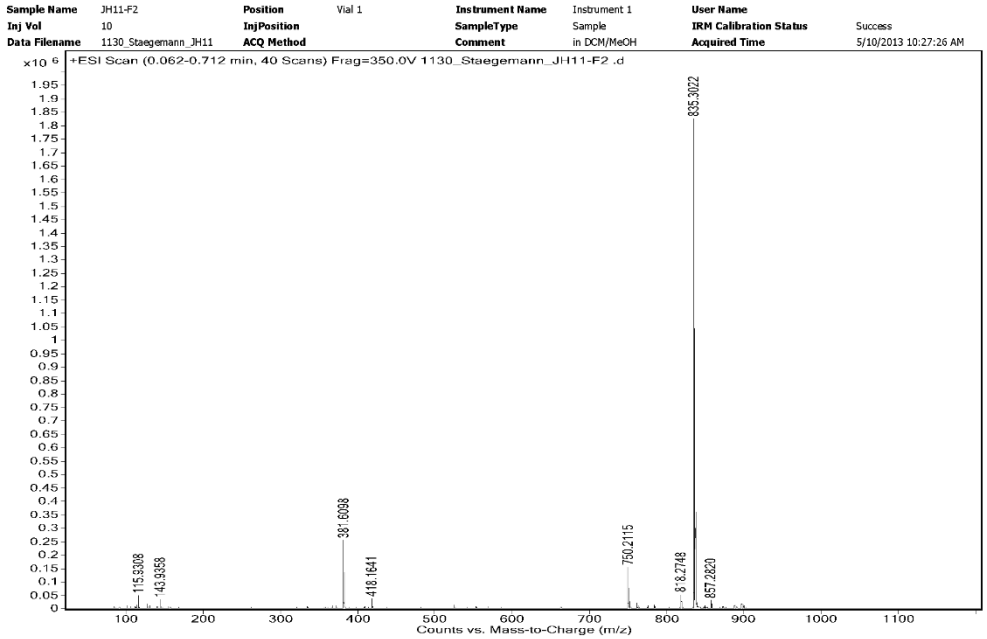


Figure 93. HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **2c**

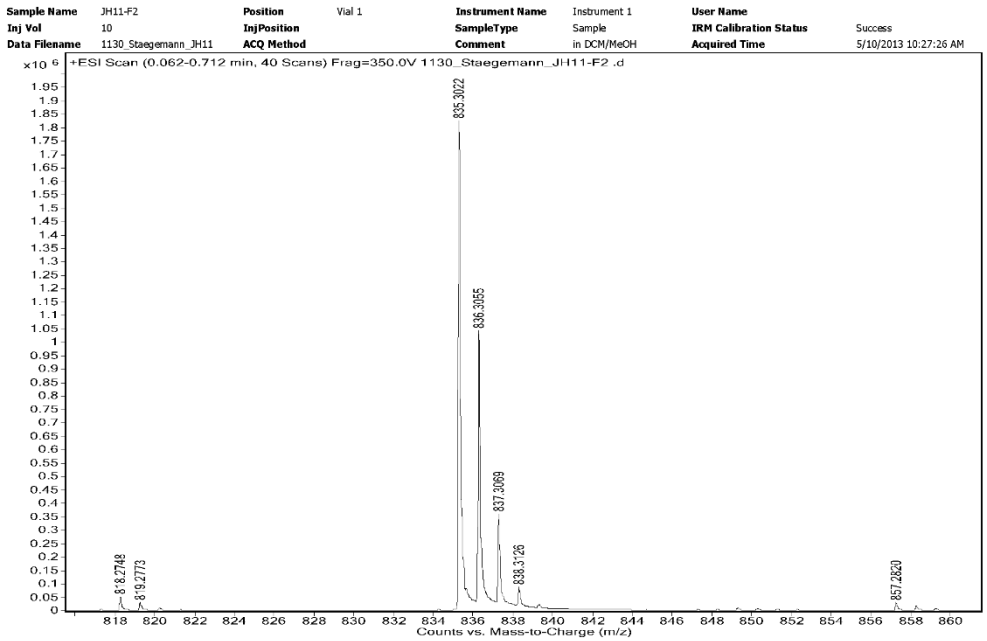


Figure 94. Zoomed HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **2c**

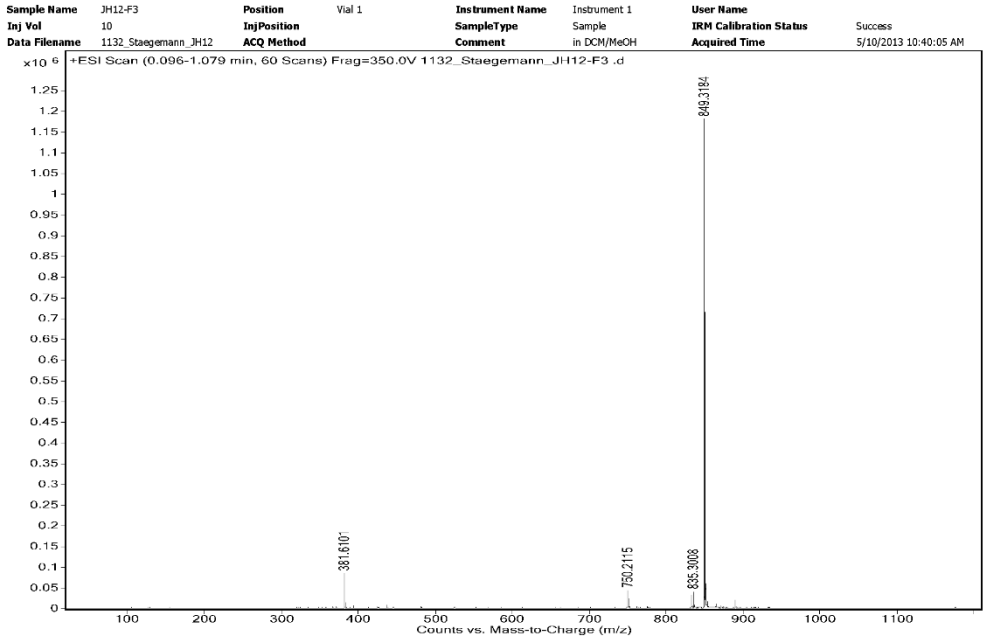


Figure 95. HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **2d**

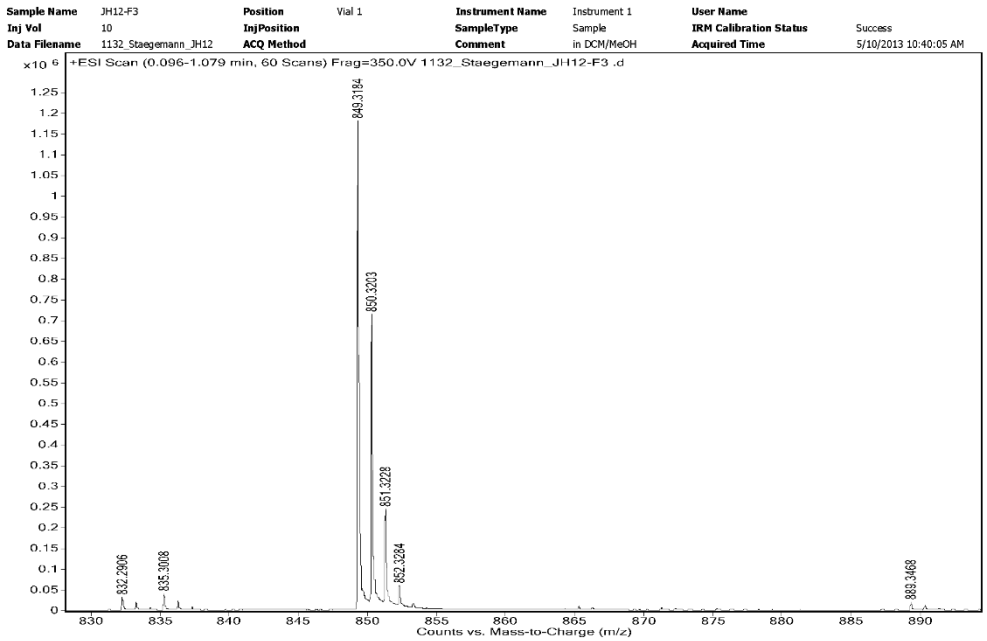


Figure 96. Zoomed HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **2d**

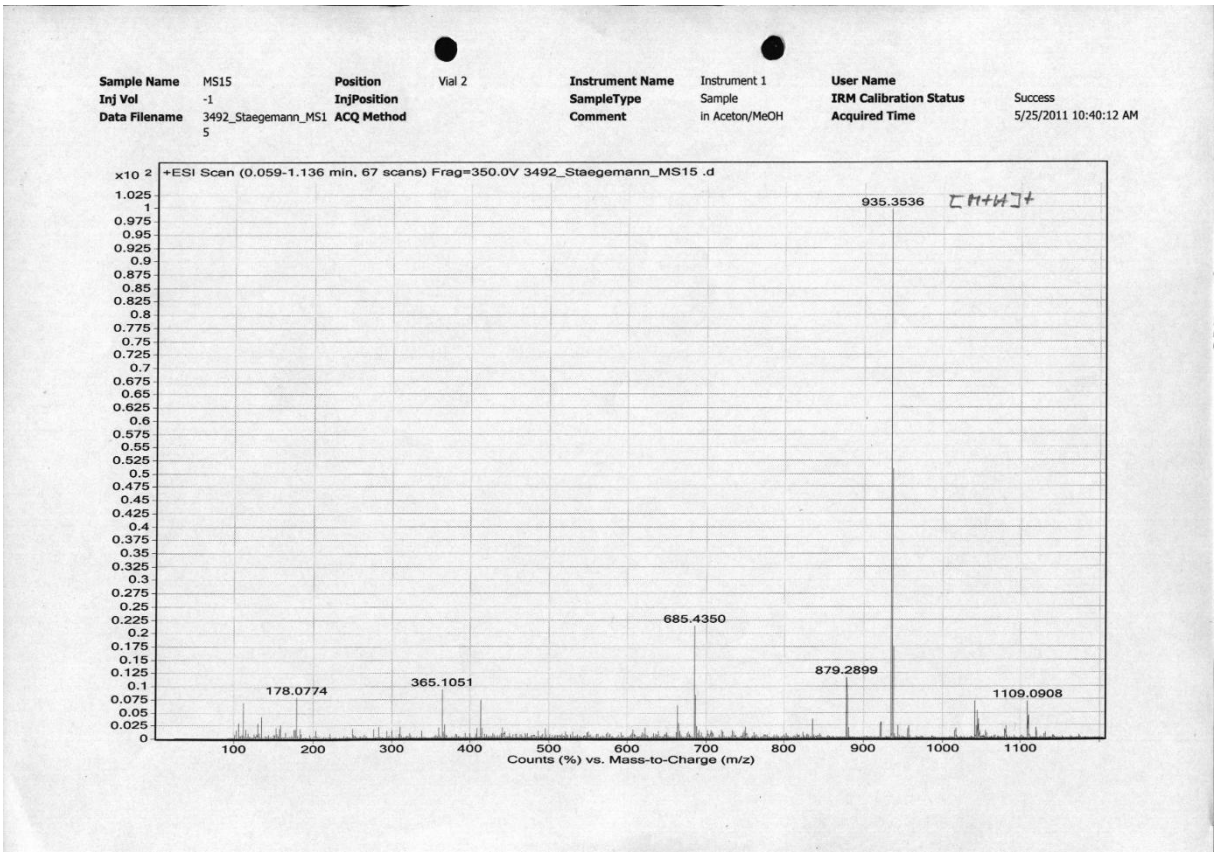


Figure 97. HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **2e**

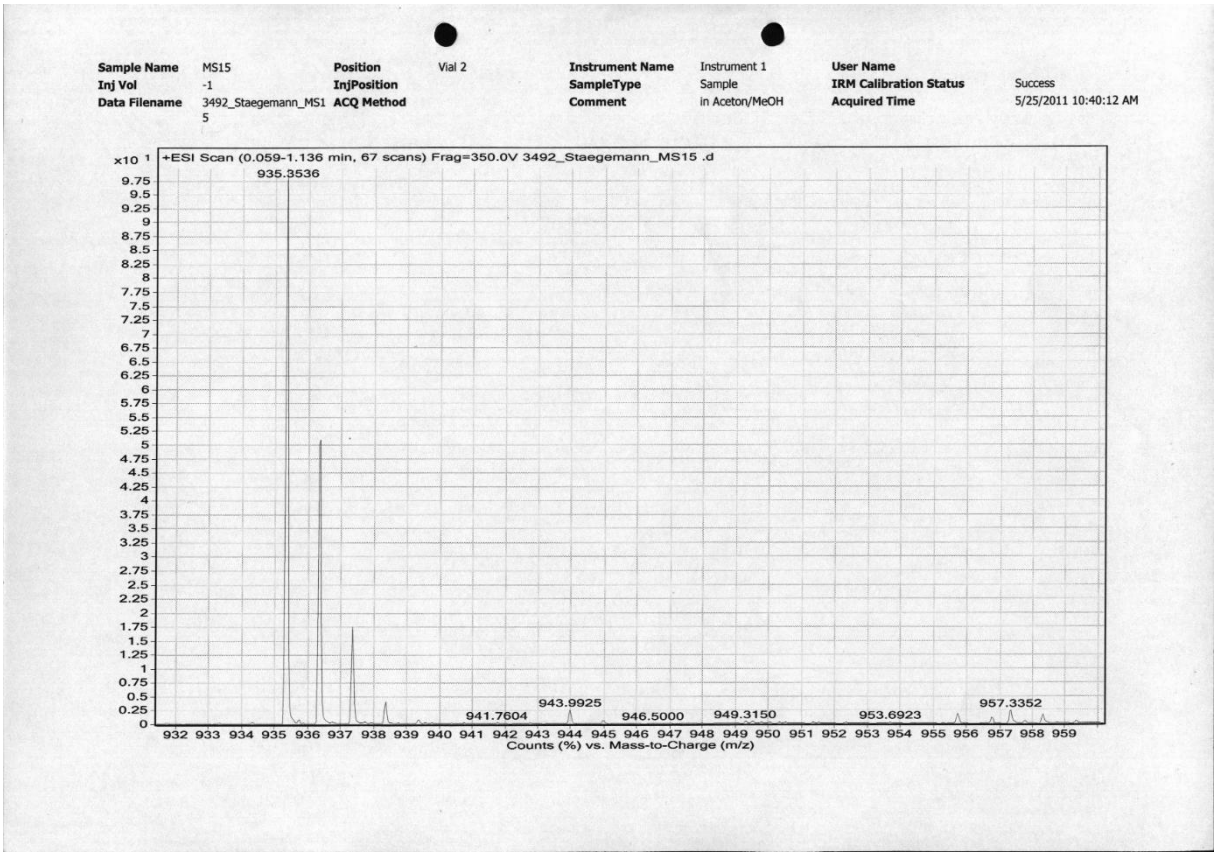


Figure 98. Zoomed HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **2e**

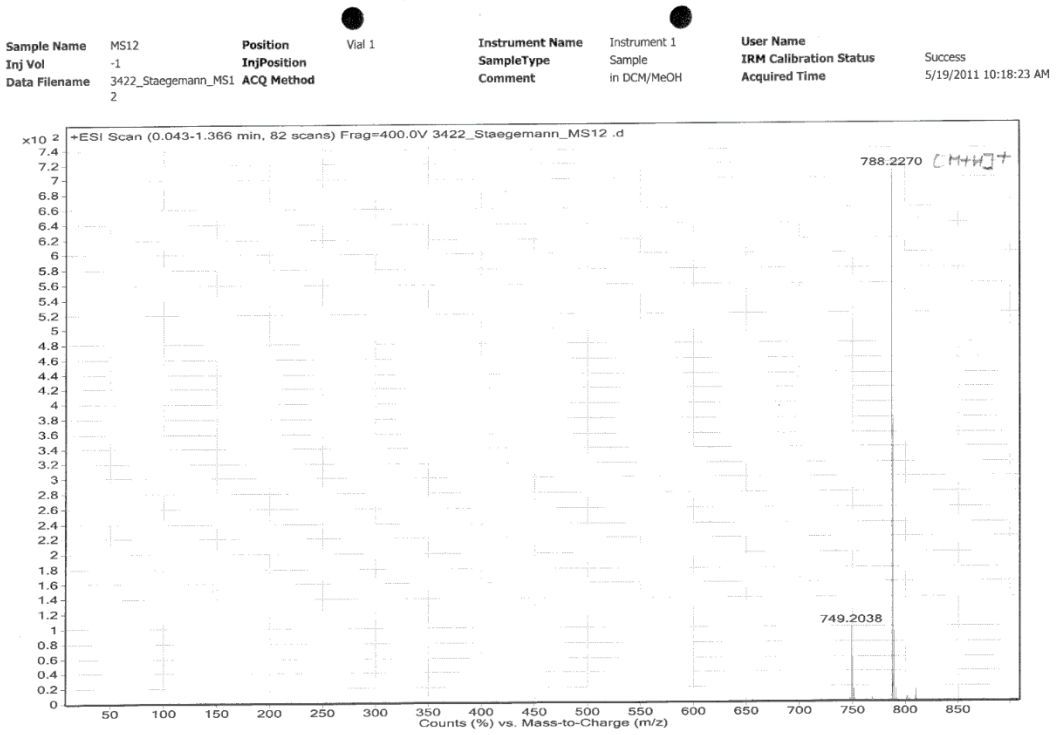


Figure 99. HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **2f**

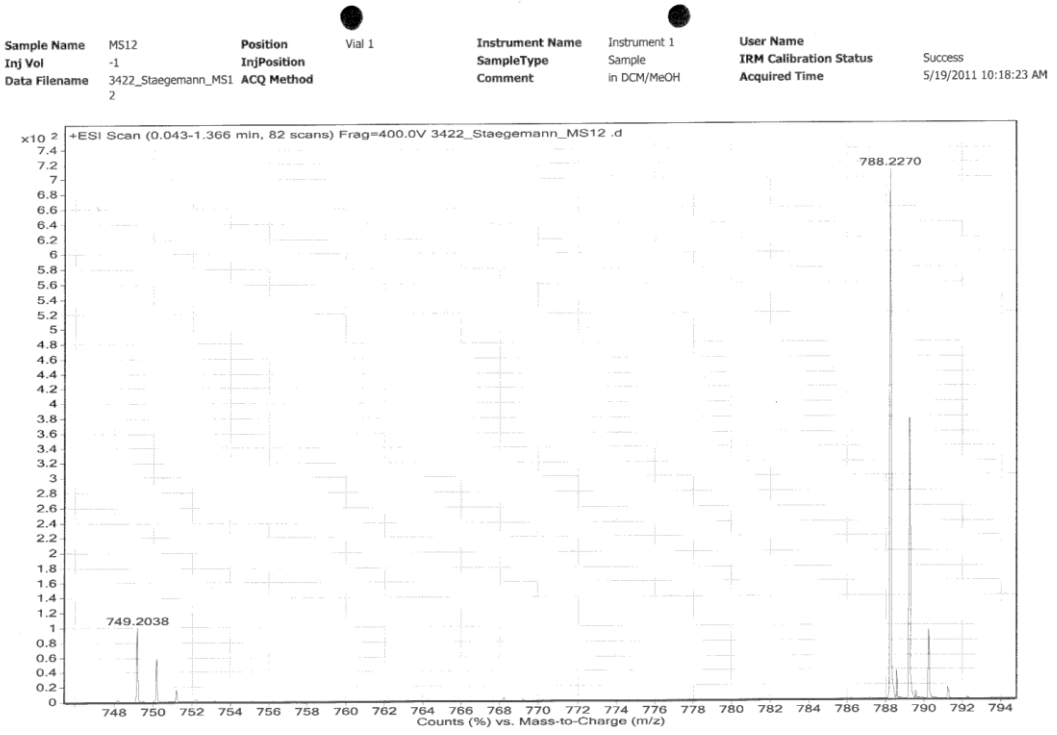


Figure 100. Zoomed HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **2f**

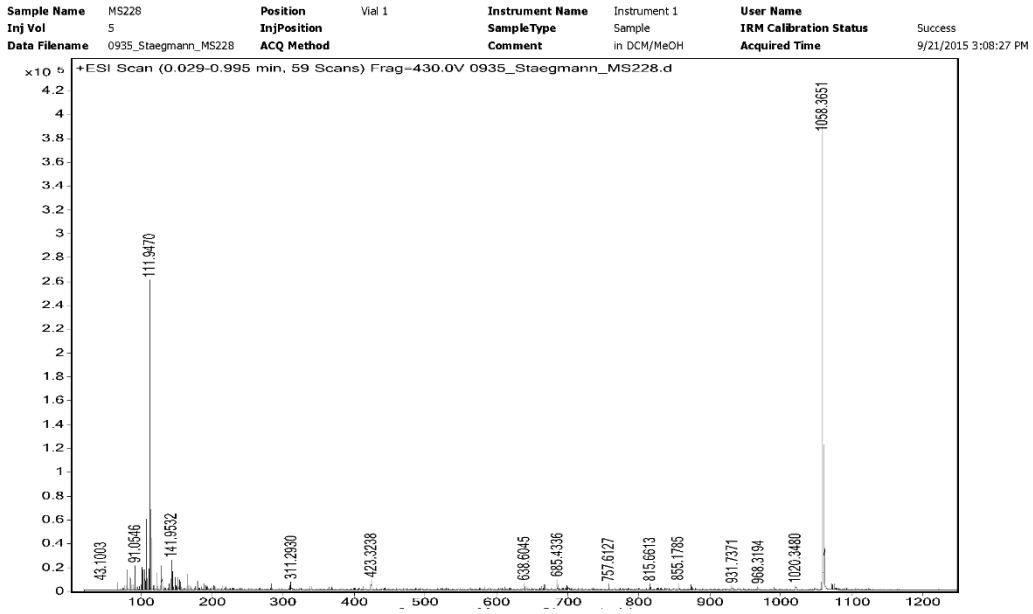


Figure 101. HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **2g**

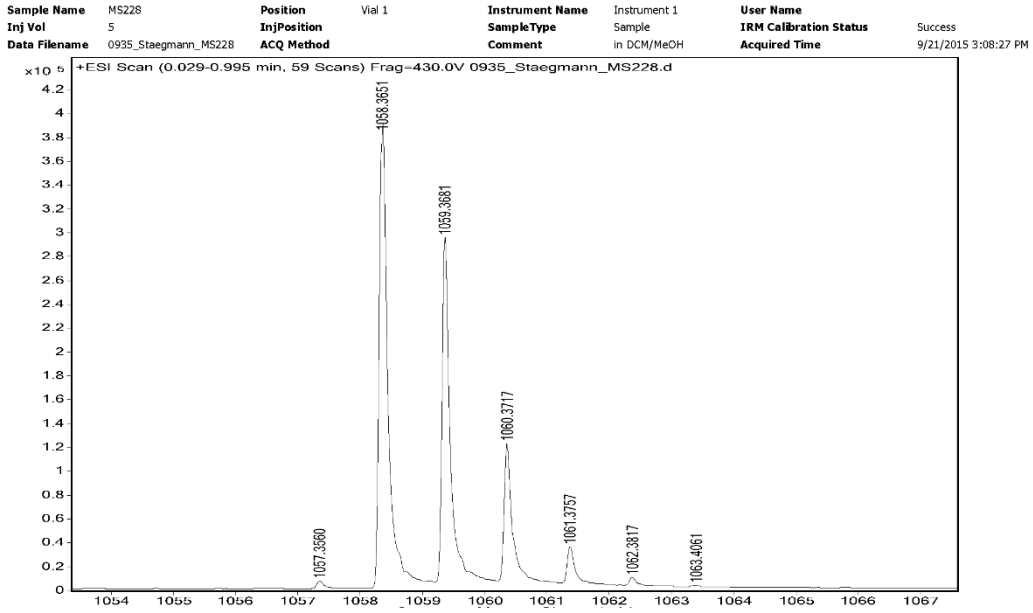


Figure 102. Zoomed HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **2g**

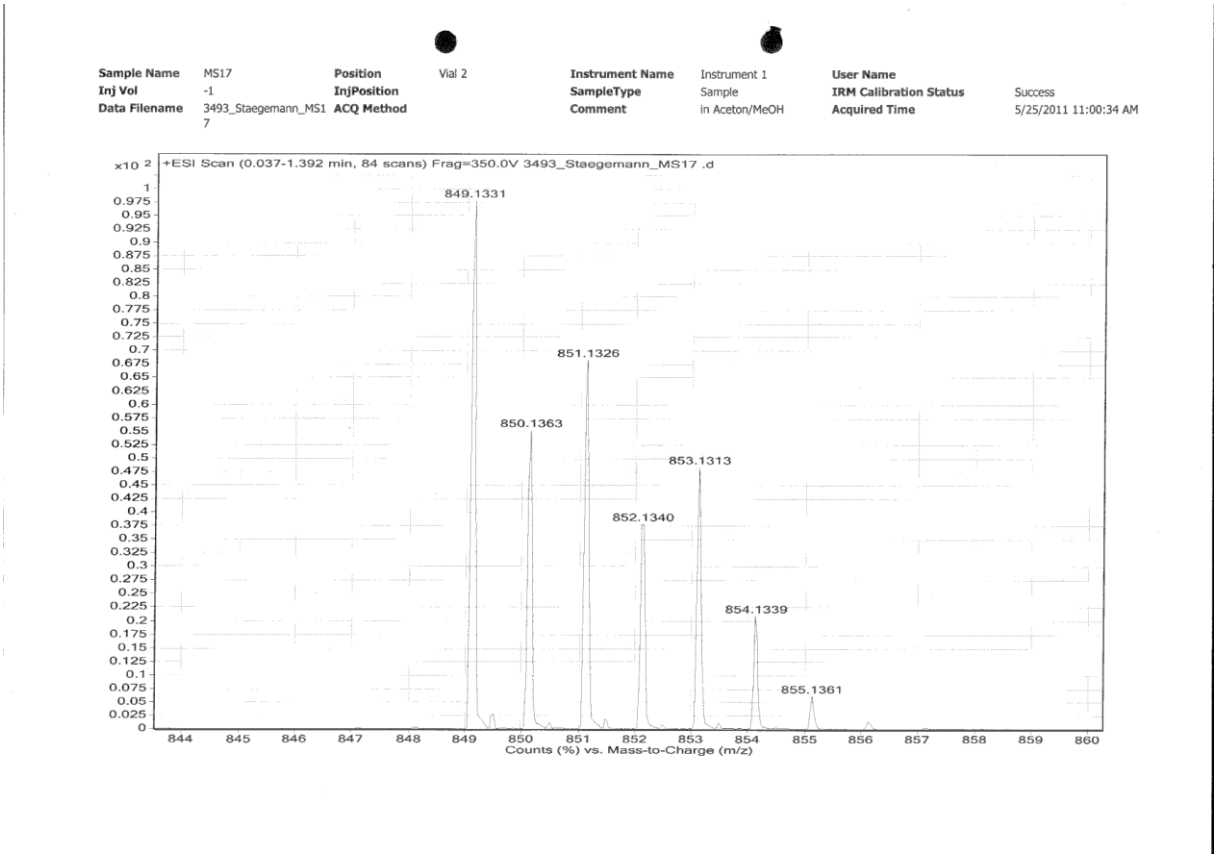


Figure 103. HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **2h**

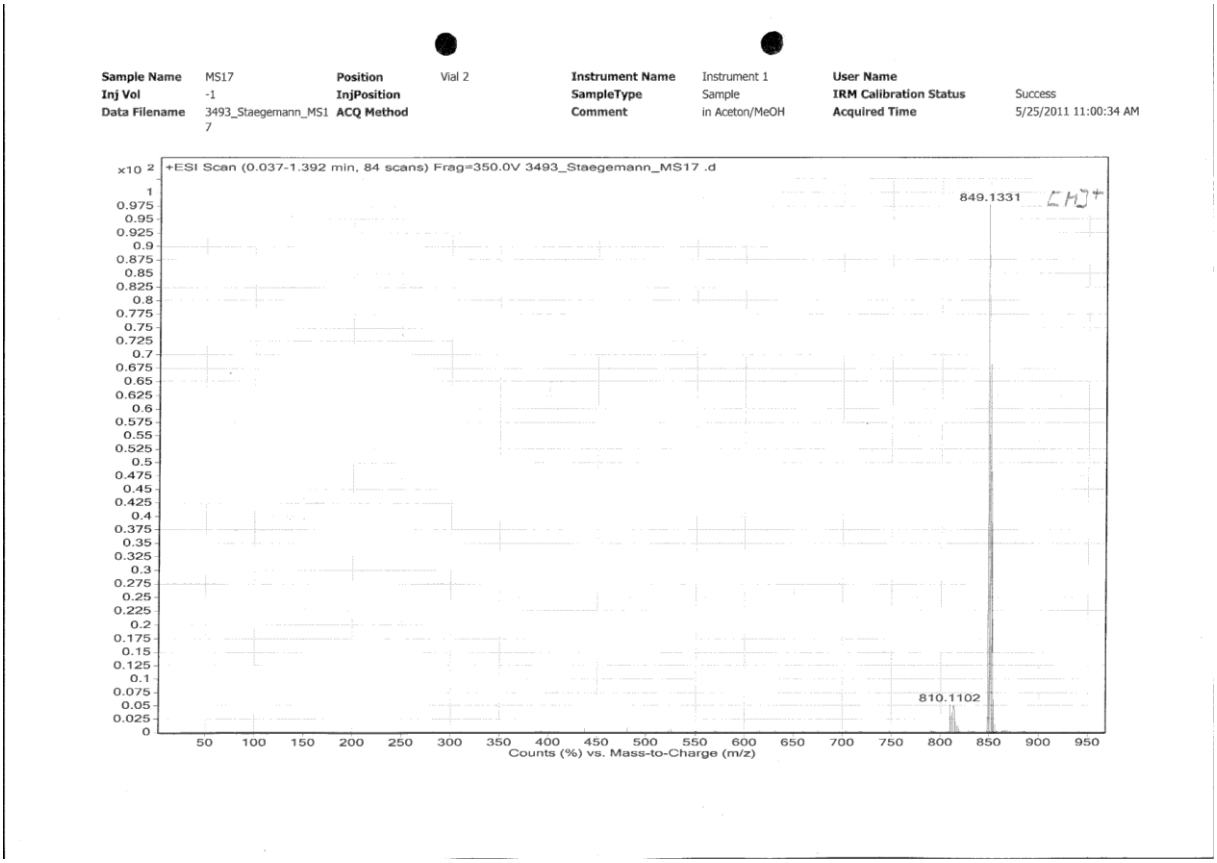


Figure 104. Zoomed HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **2h**

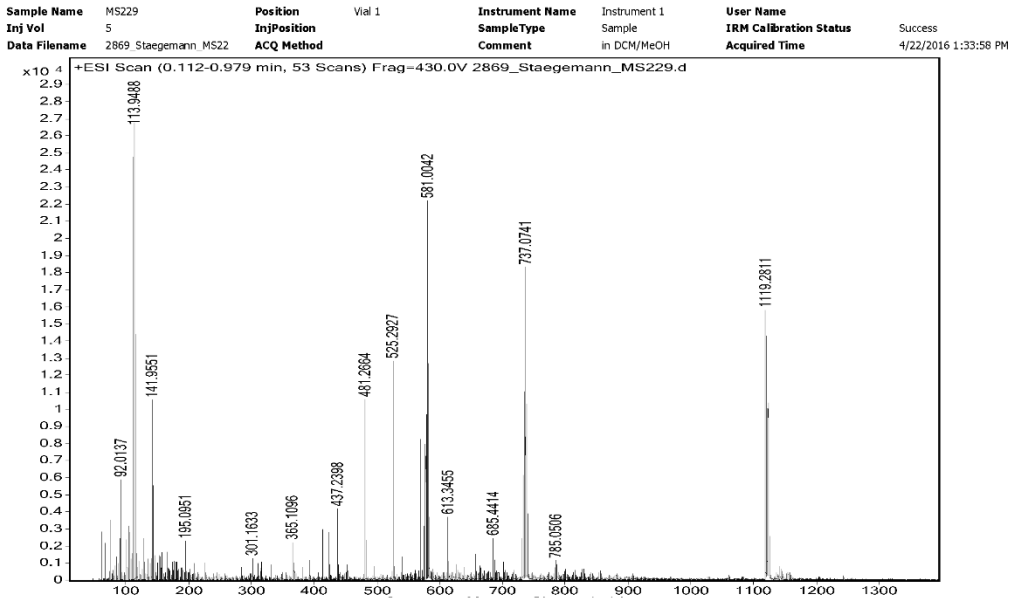


Figure 105. HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **2i**

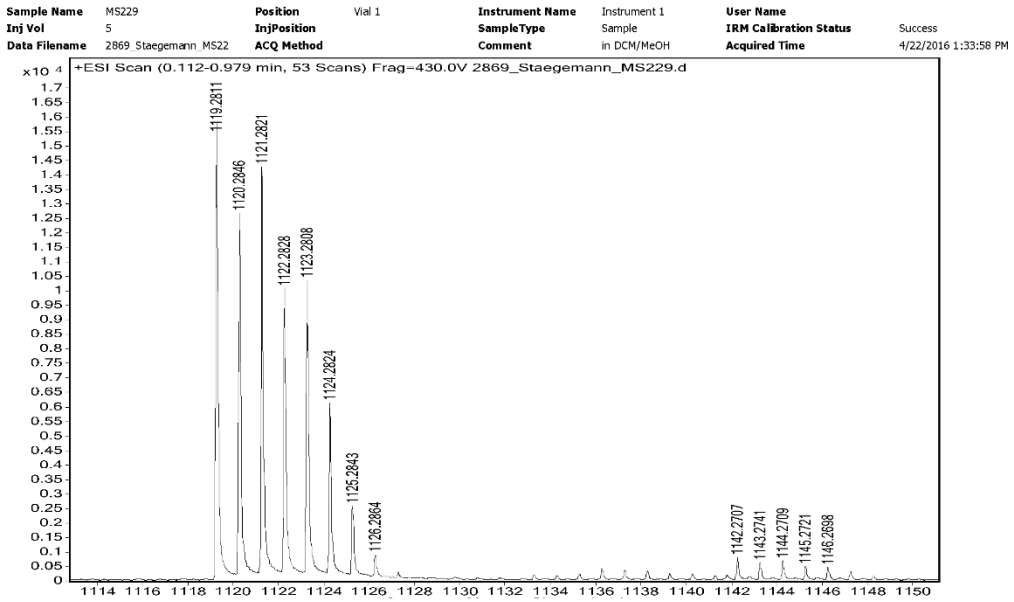


Figure 106. Zoomed HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **2i**

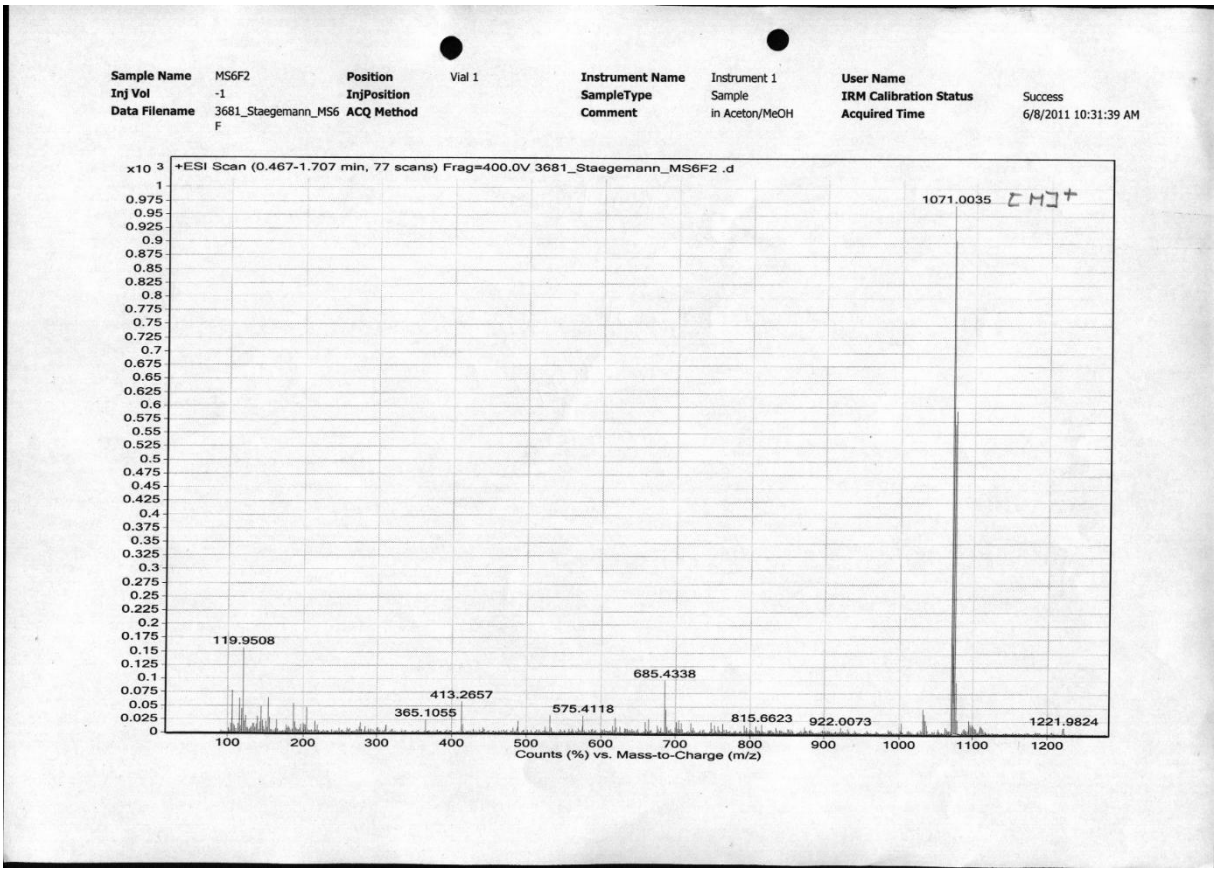


Figure 107. HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **4**

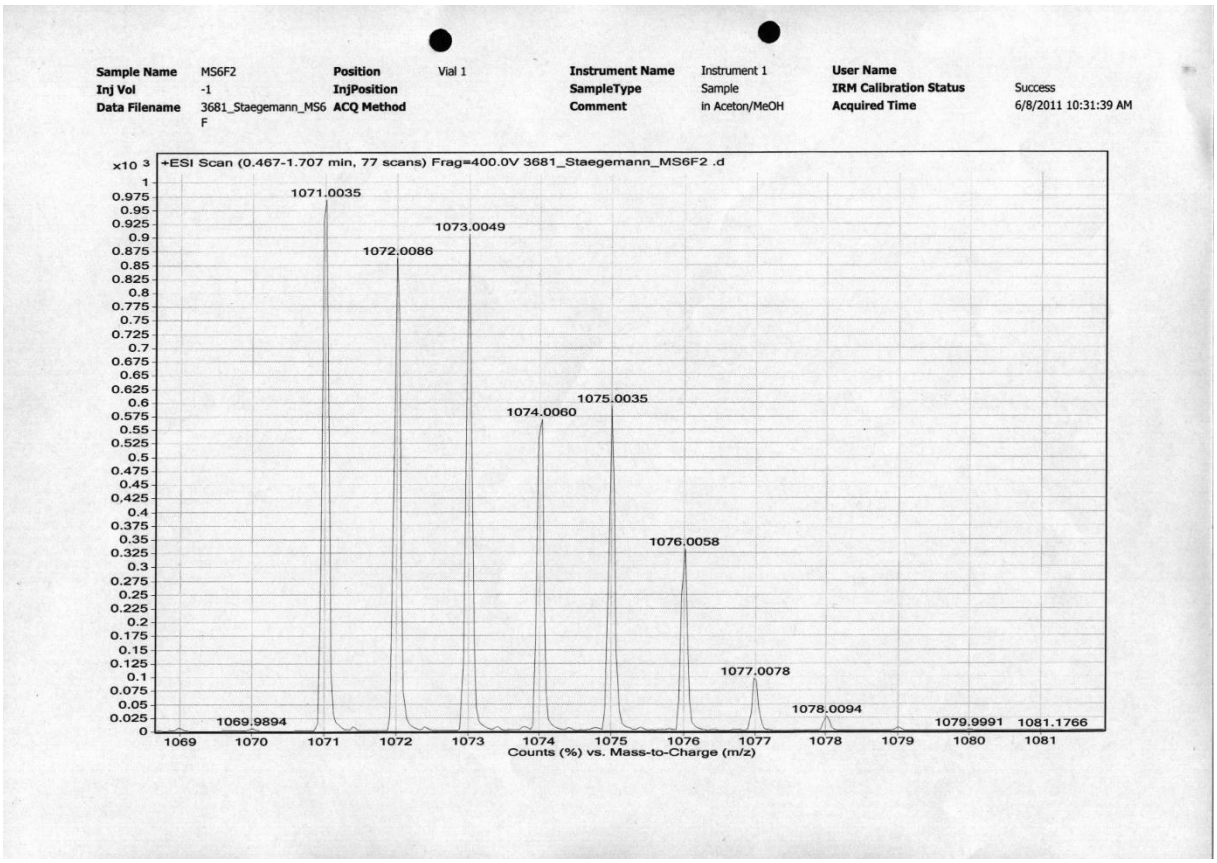


Figure 108. Zoomed HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **4**

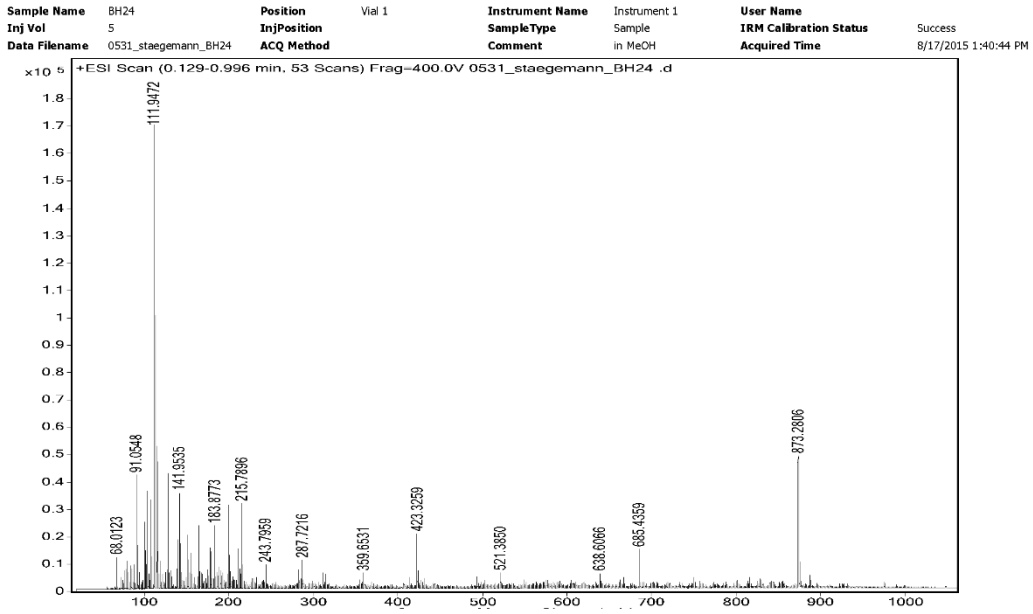


Figure 109. HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **5a**

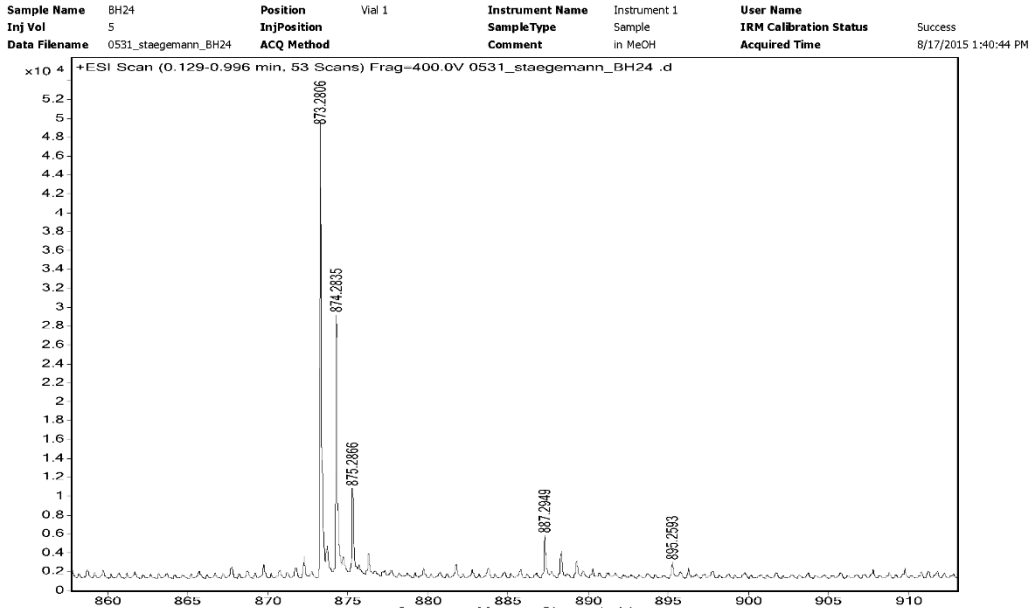


Figure 110. Zoomed HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **5a**

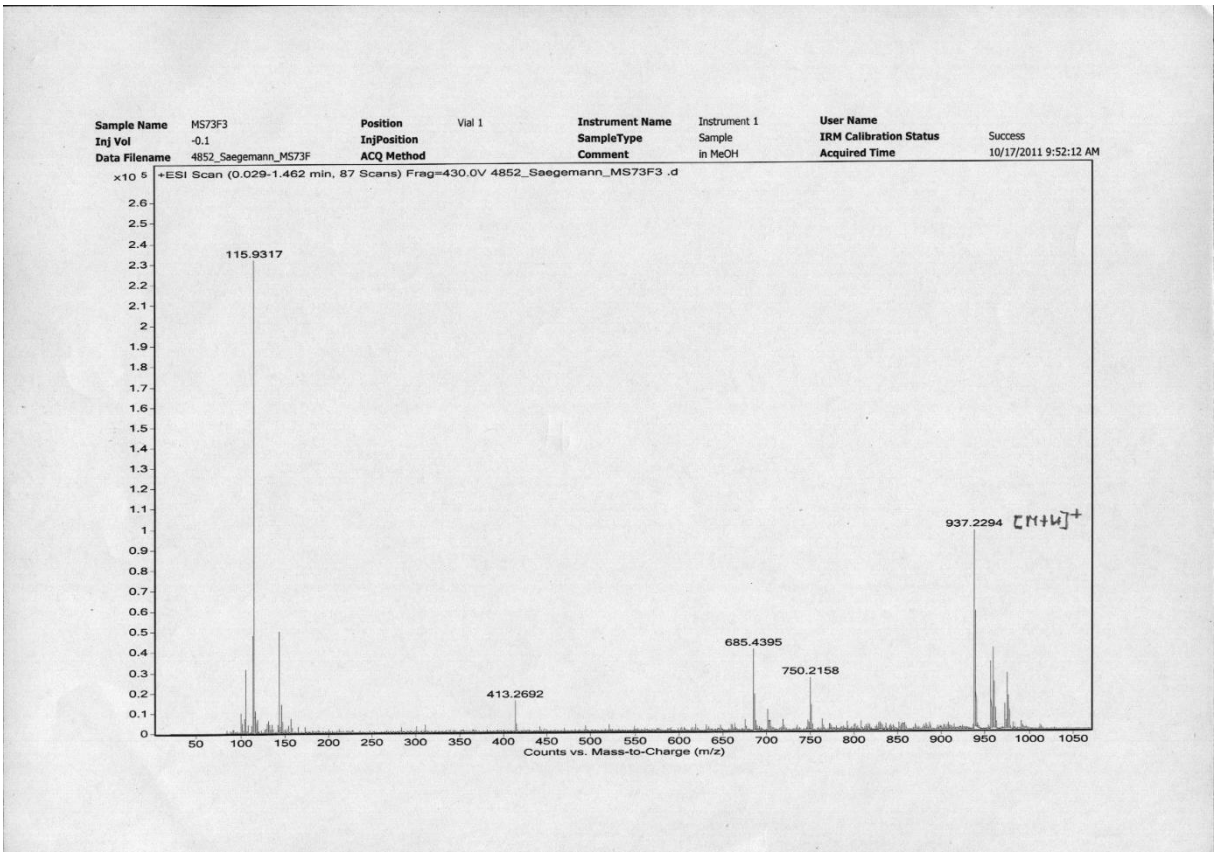


Figure 111. HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **5b**

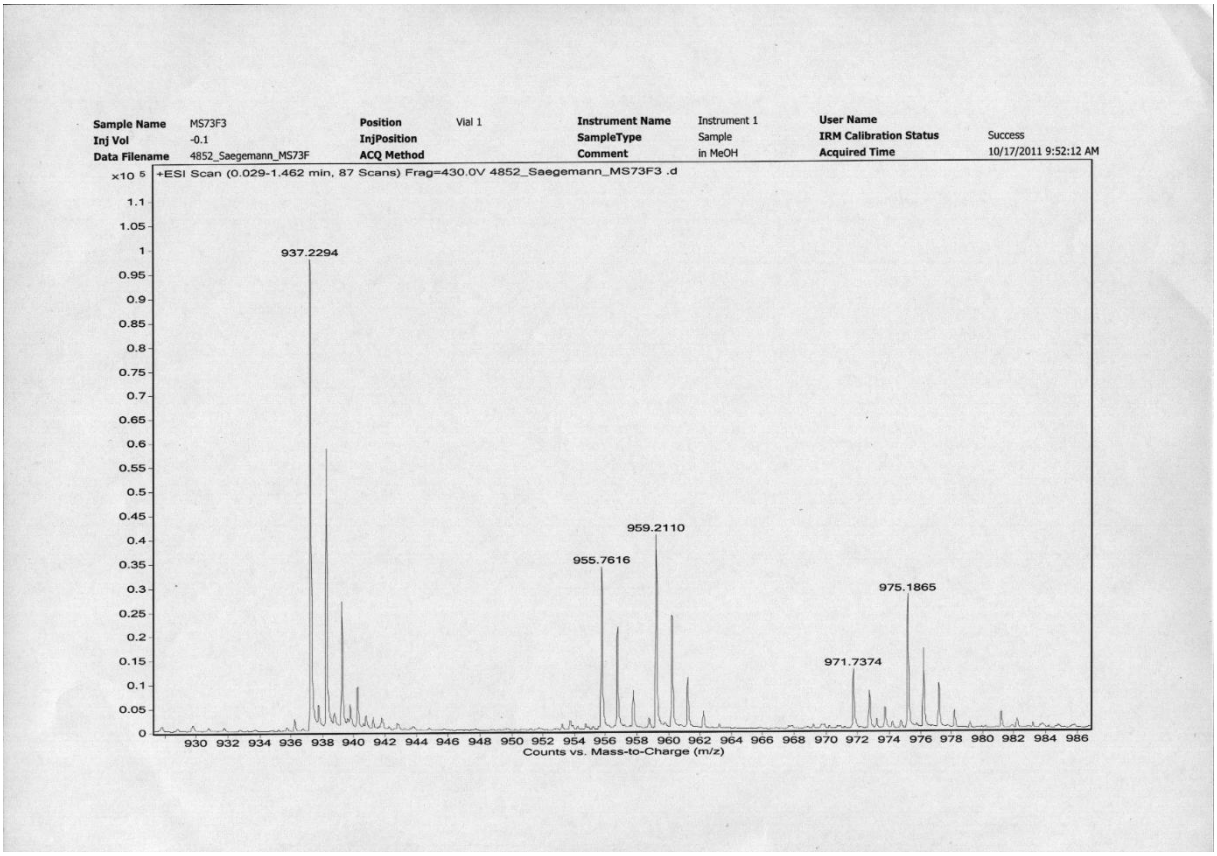


Figure 112. Zoomed HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **5b**

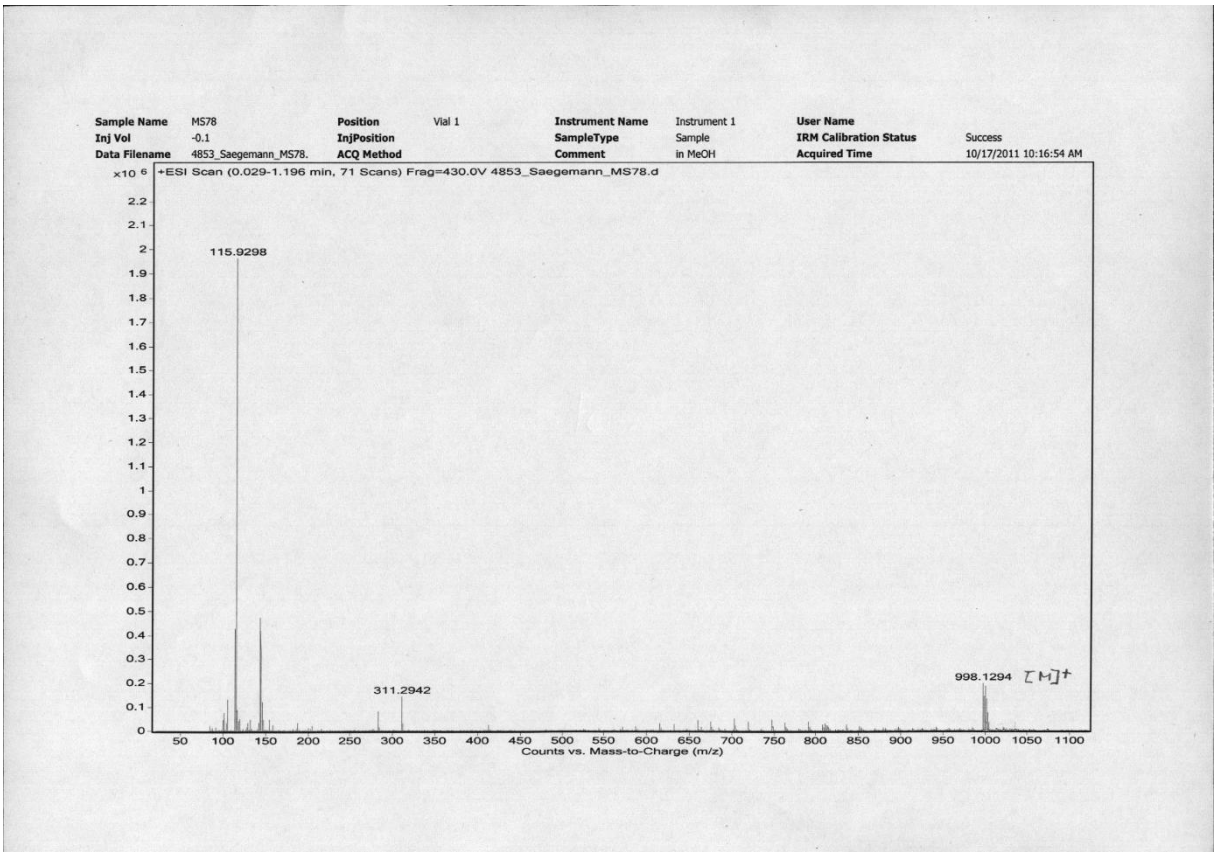


Figure 113. HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **5c**

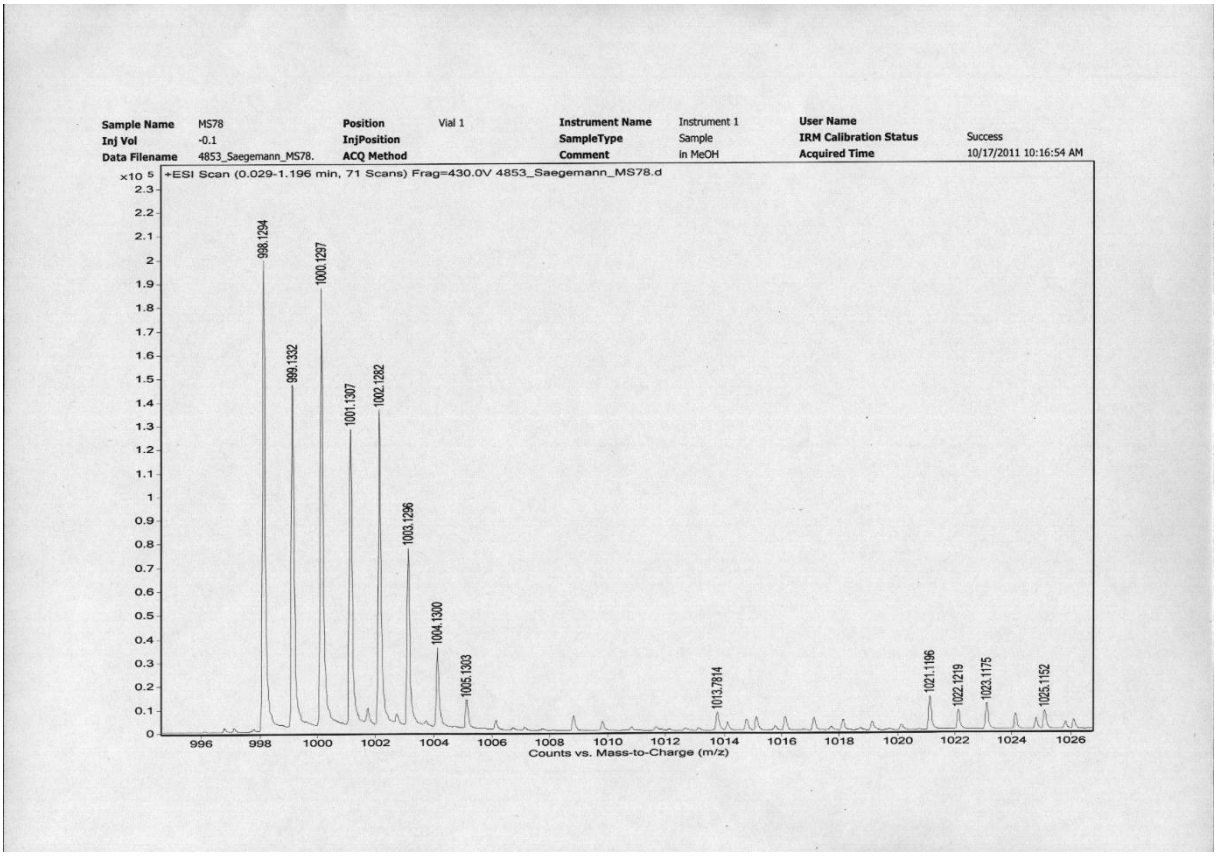


Figure 114. Zoomed HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **5c**

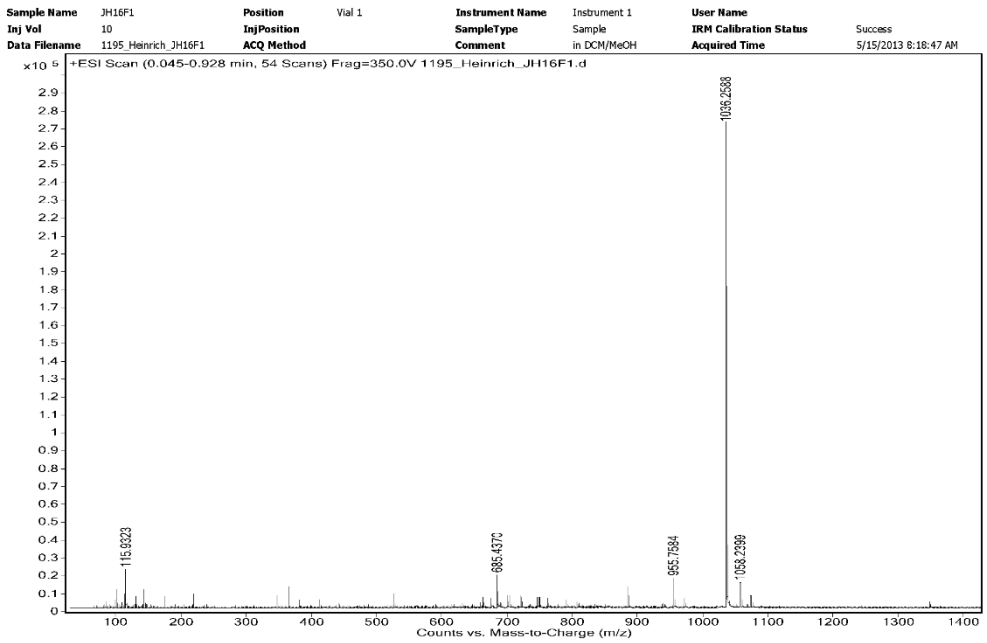


Figure 115. HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **6a**

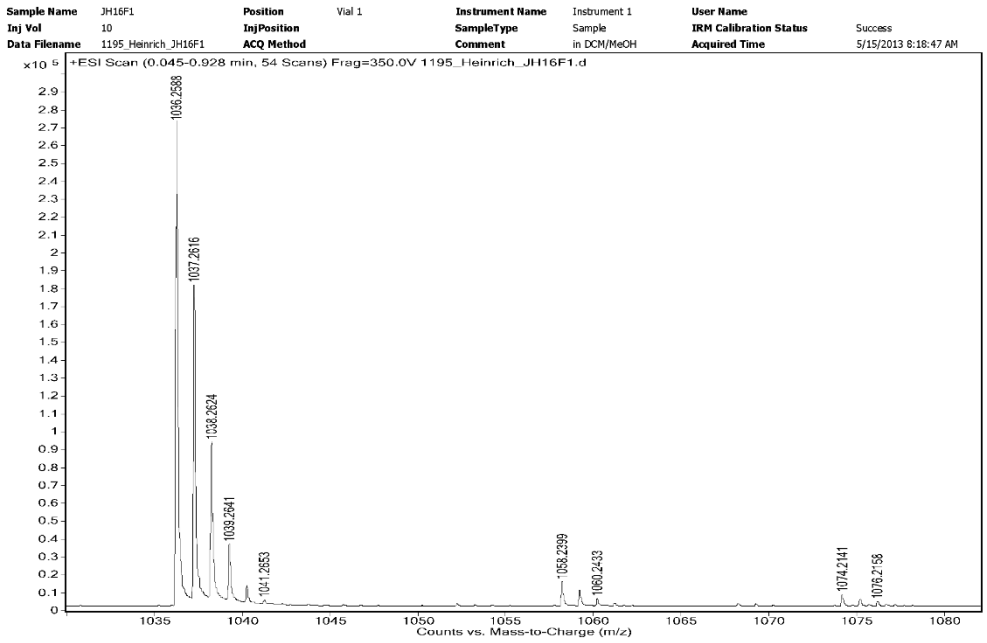


Figure 116. Zoomed HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **6a**

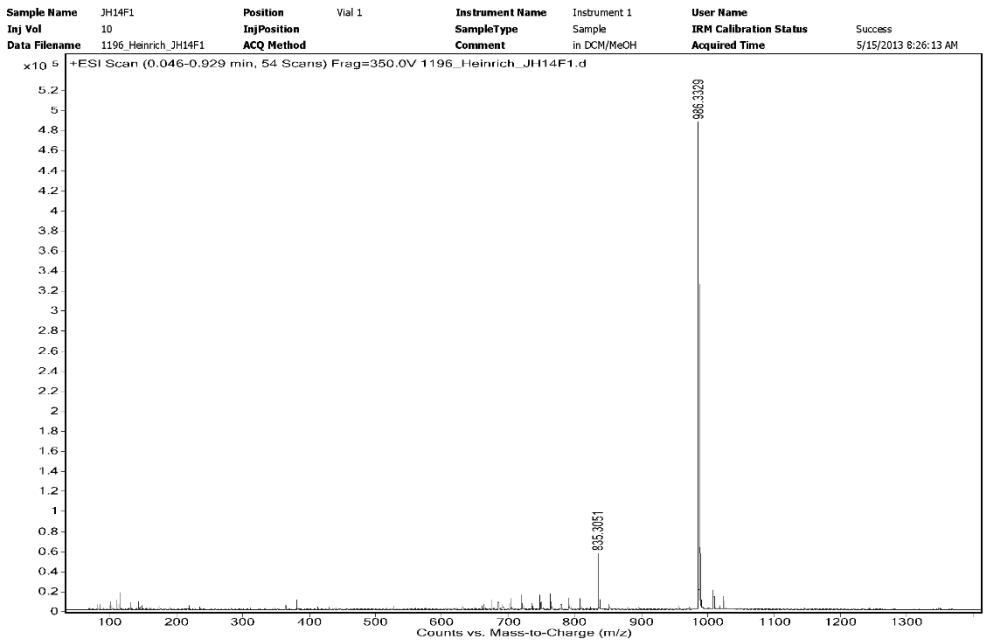


Figure 117. HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **6b**

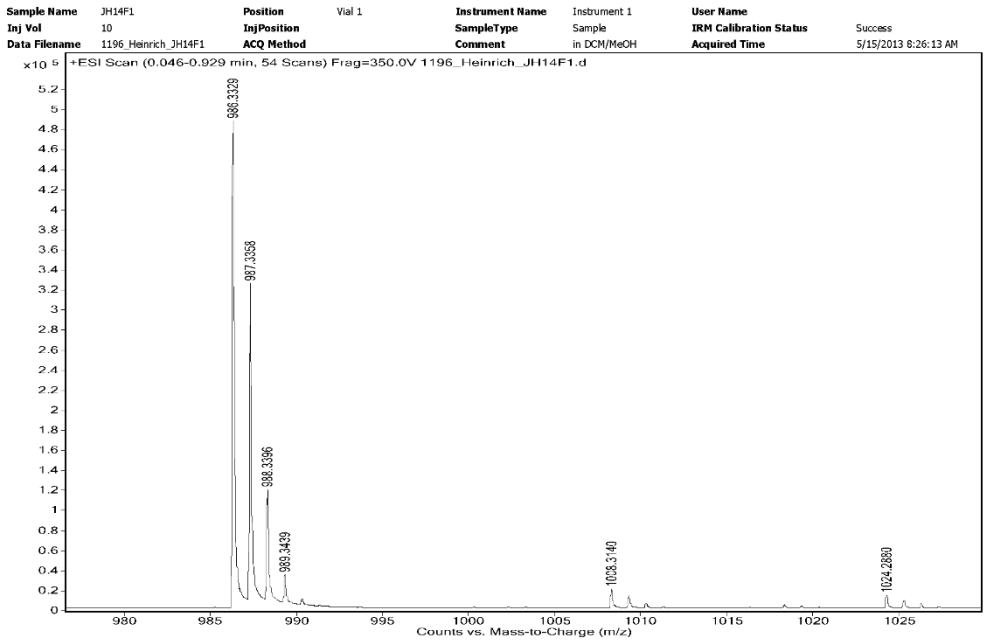


Figure 118. Zoomed HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **6b**

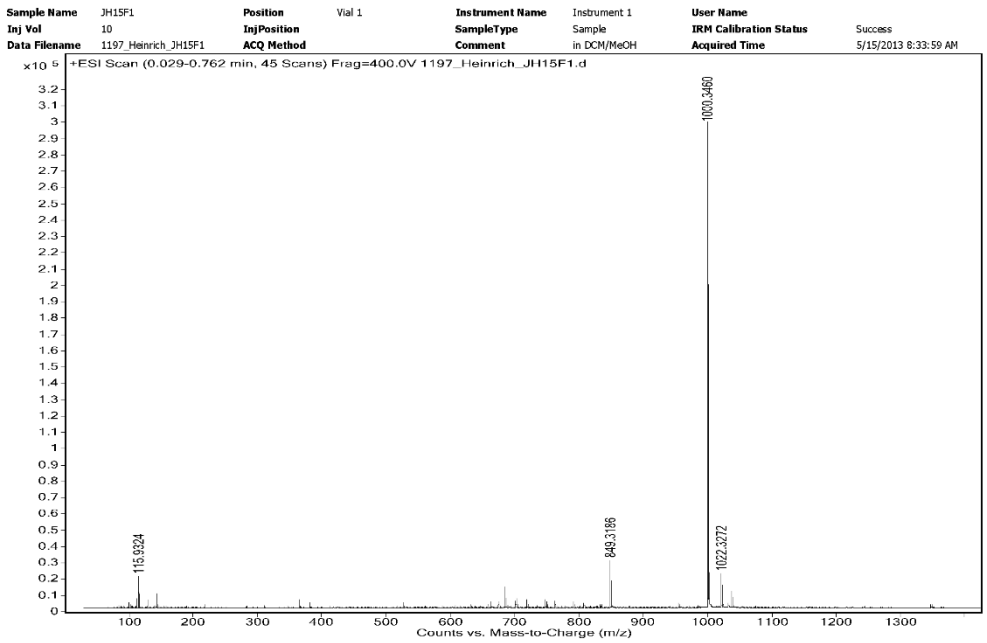


Figure 119. HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **6c**

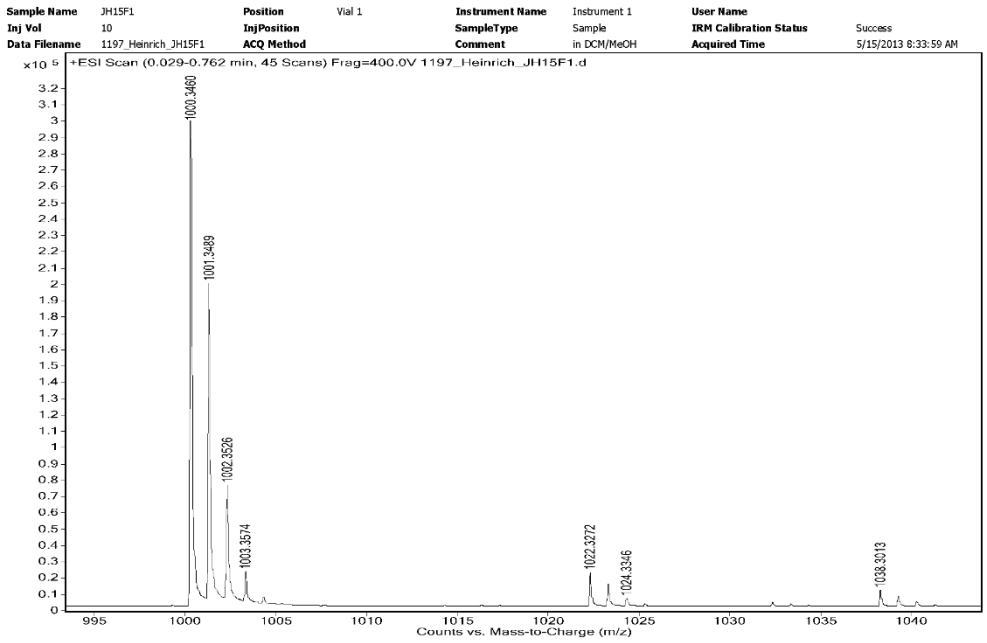


Figure 120. Zoomed HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **6c**

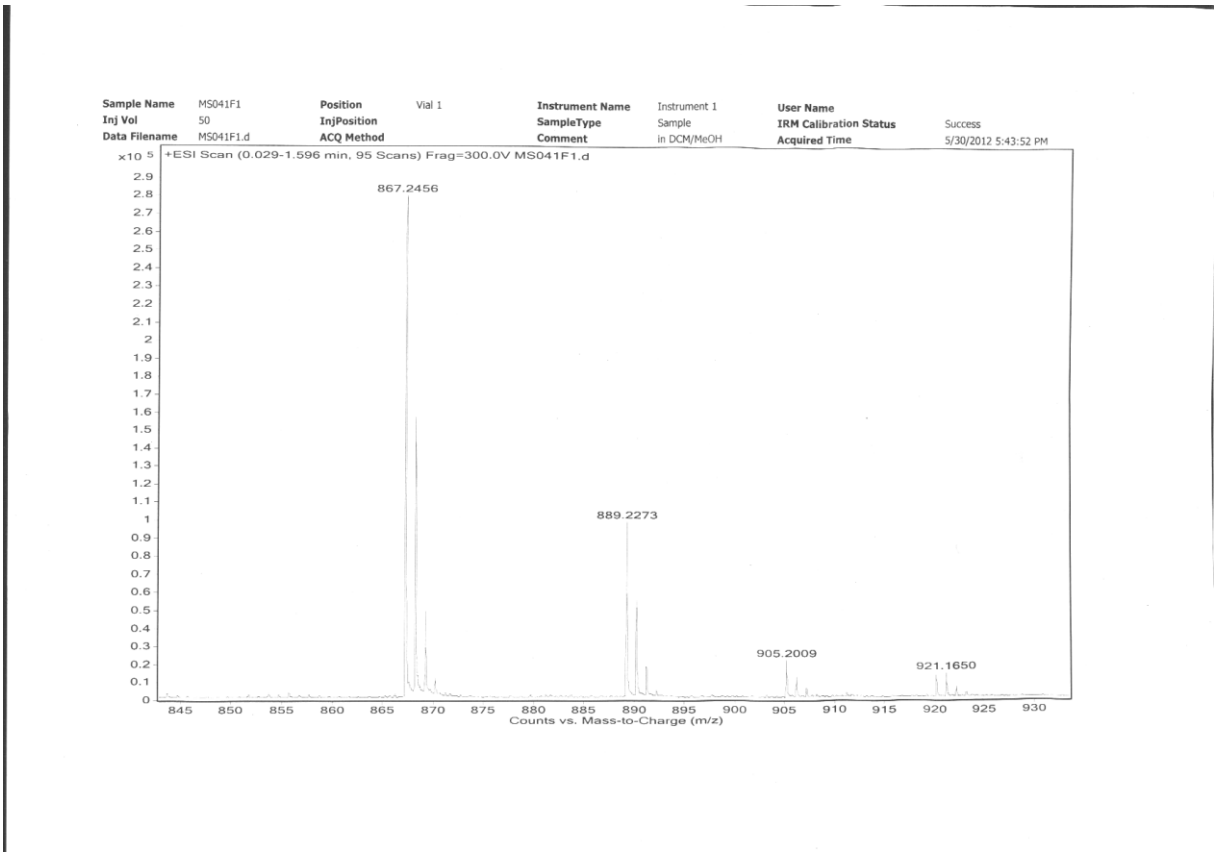


Figure 121. HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **8a**

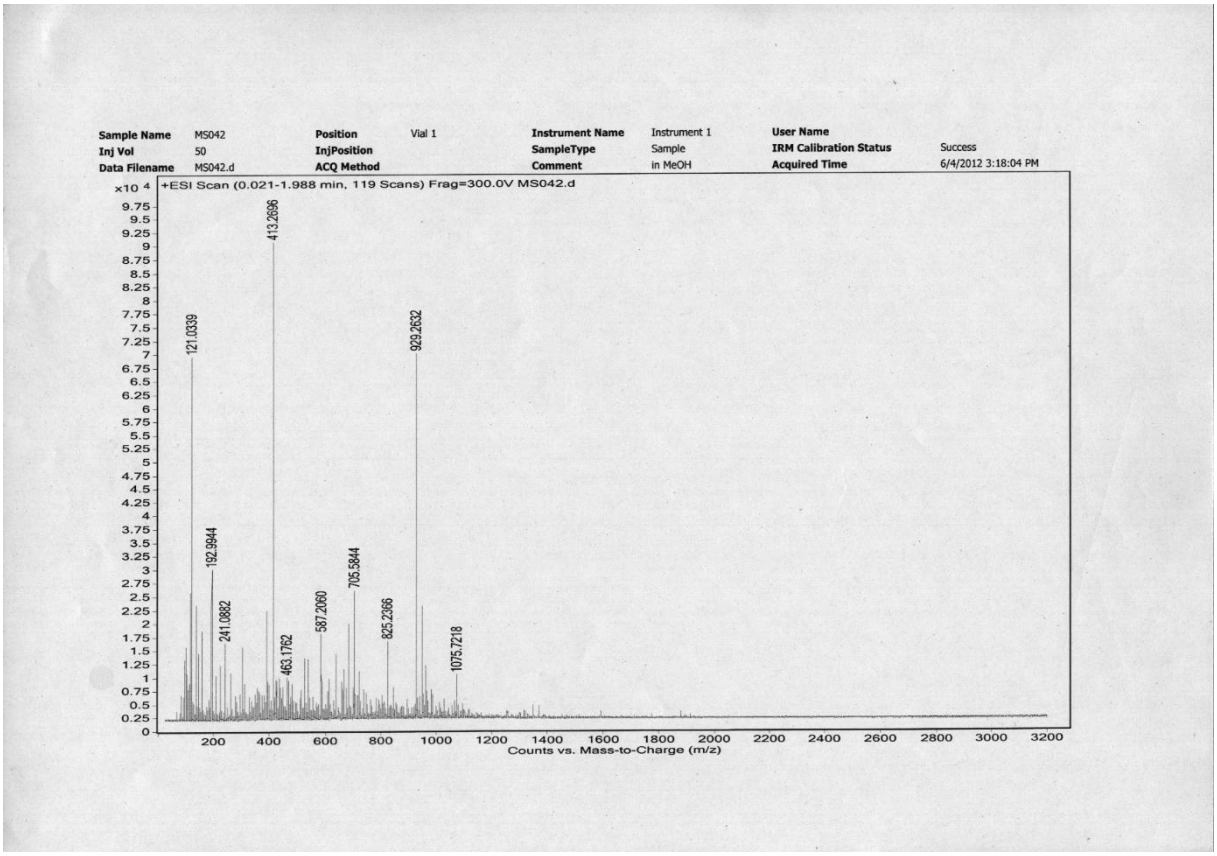


Figure 122. HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **8b**

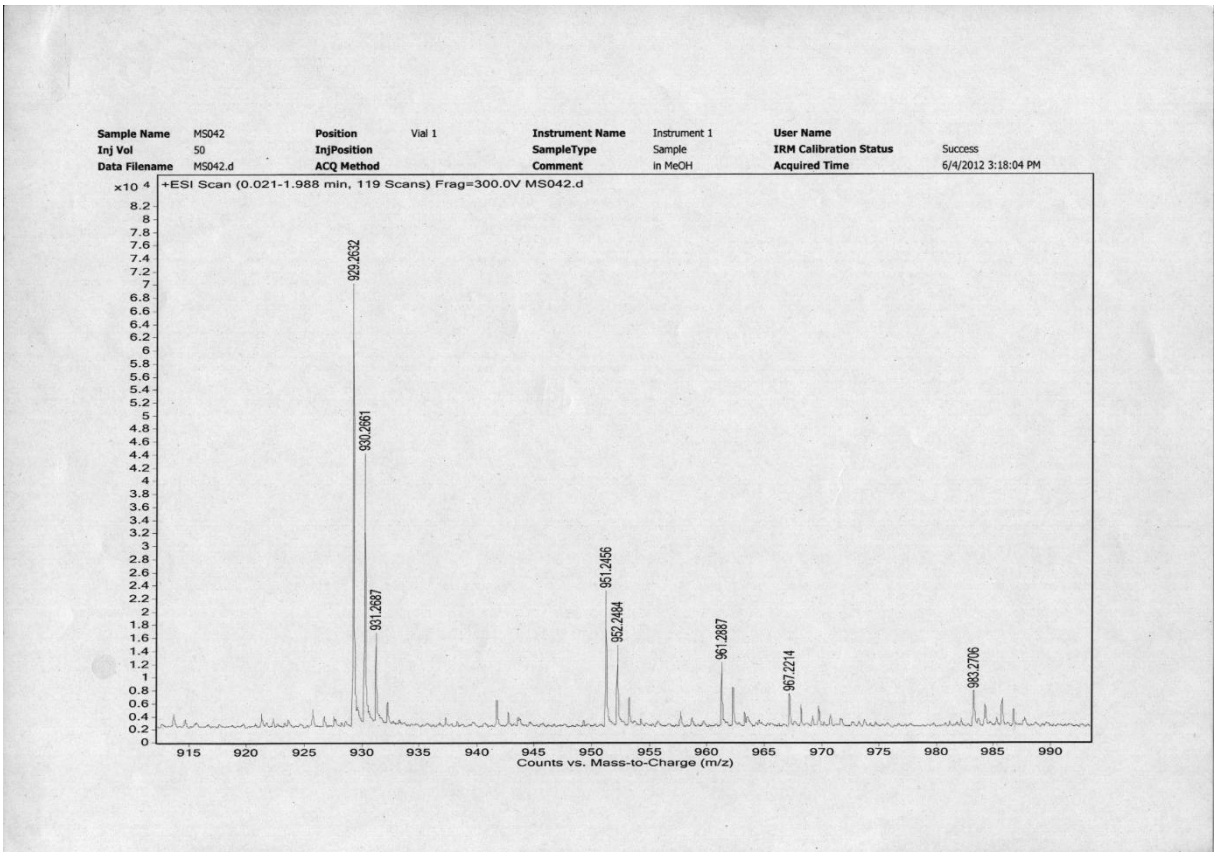


Figure 123. Zoomed HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **8b**

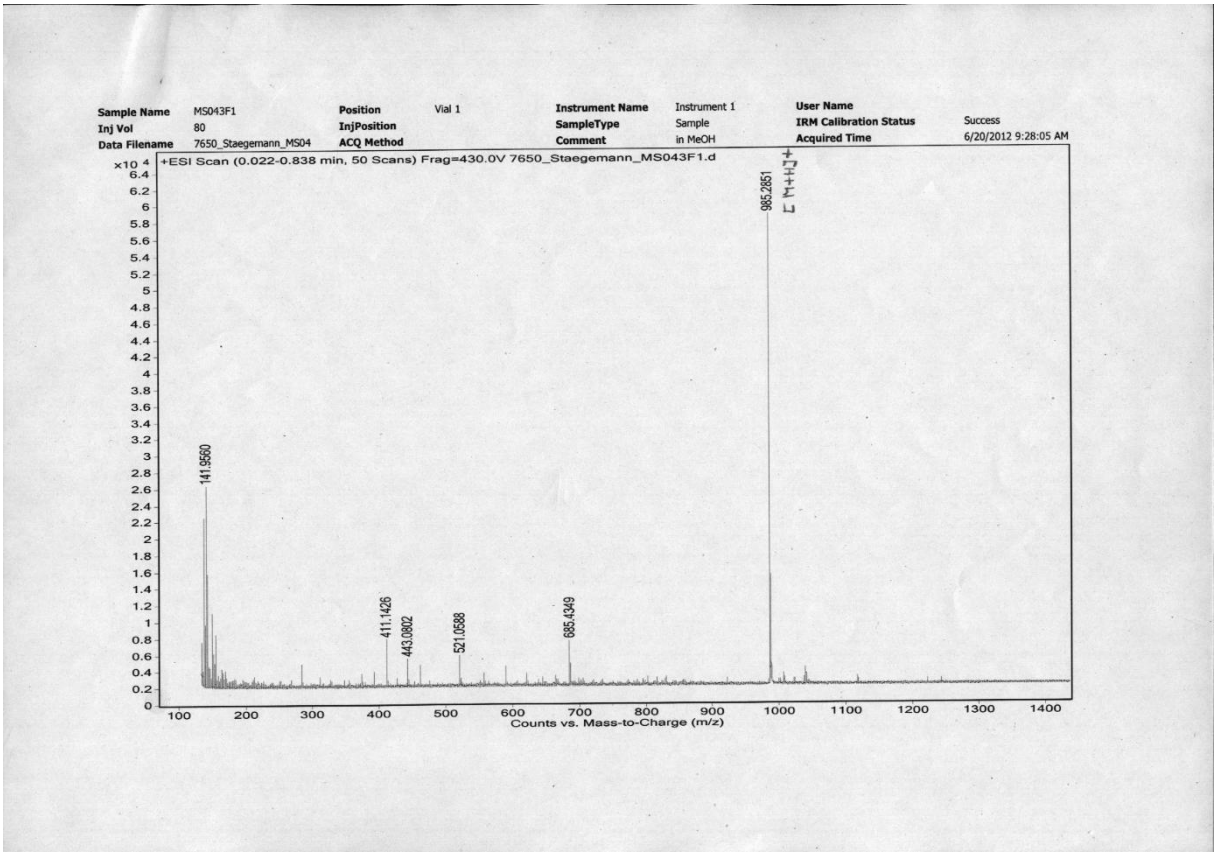


Figure 124. HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **8c**

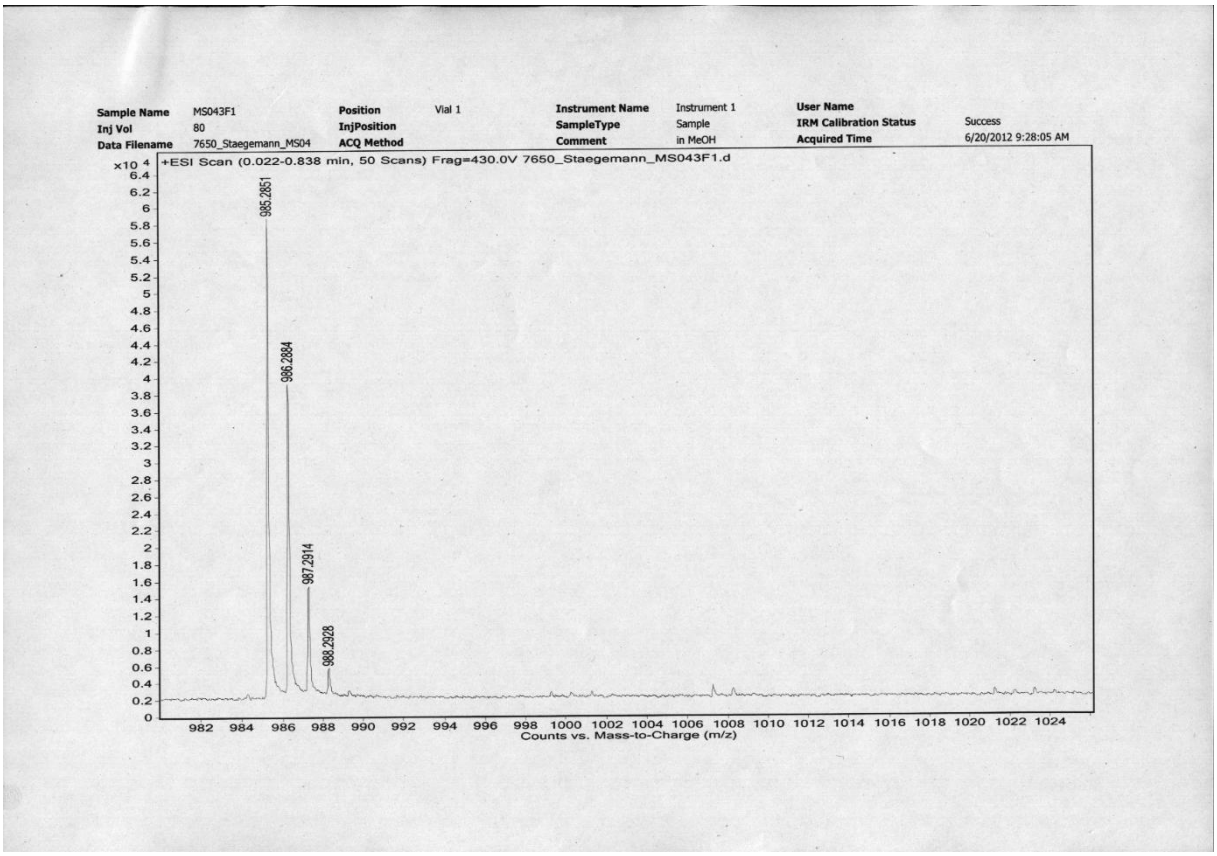


Figure 125. Zoomed HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **8c**

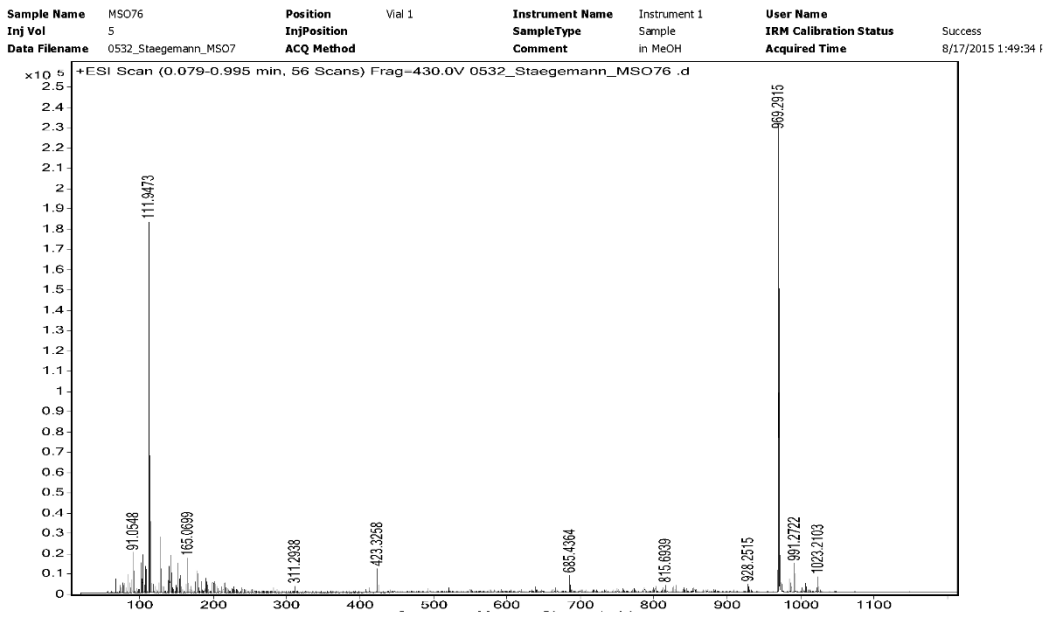


Figure 126. HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **9**

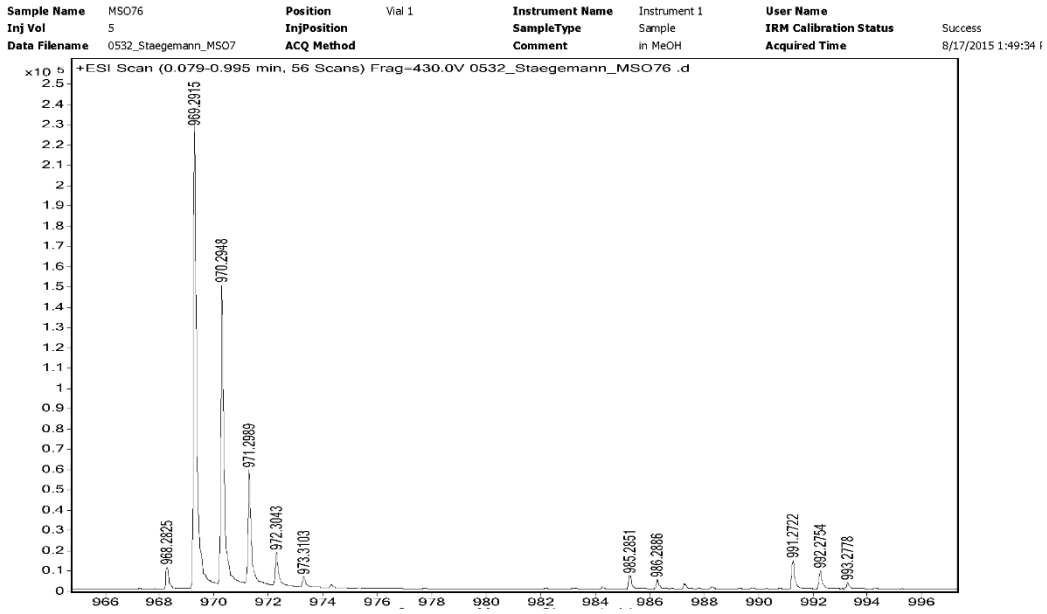


Figure 127. Zoomed HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **9**

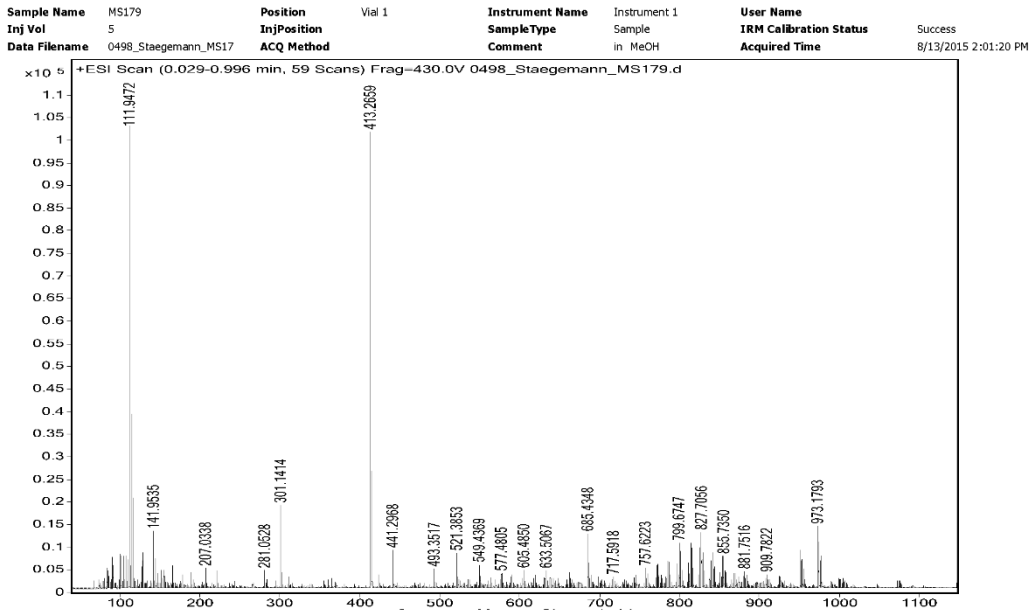


Figure 128. HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **10a**

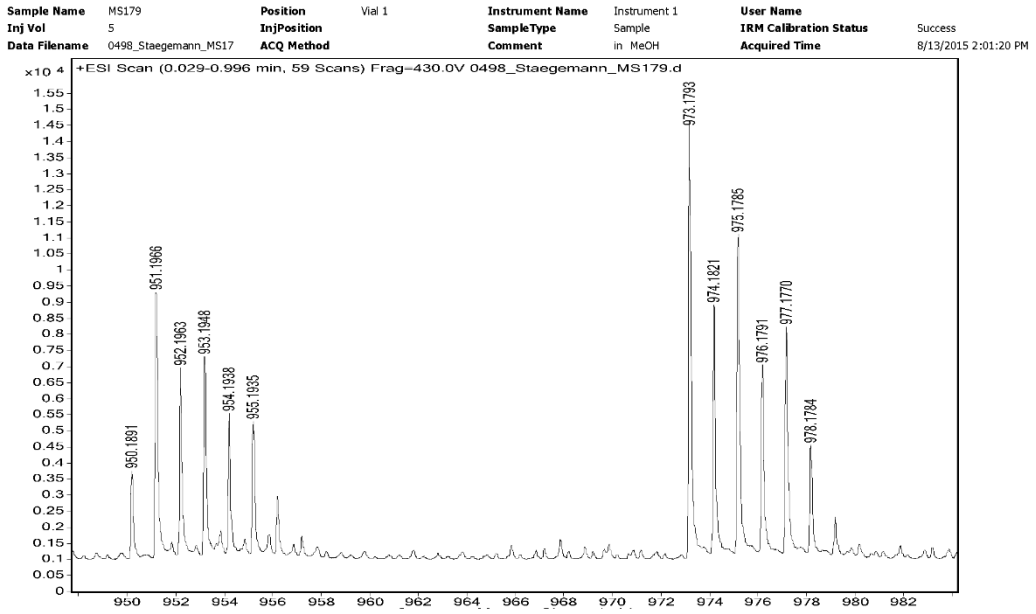


Figure 129. Zoomed HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **10a**

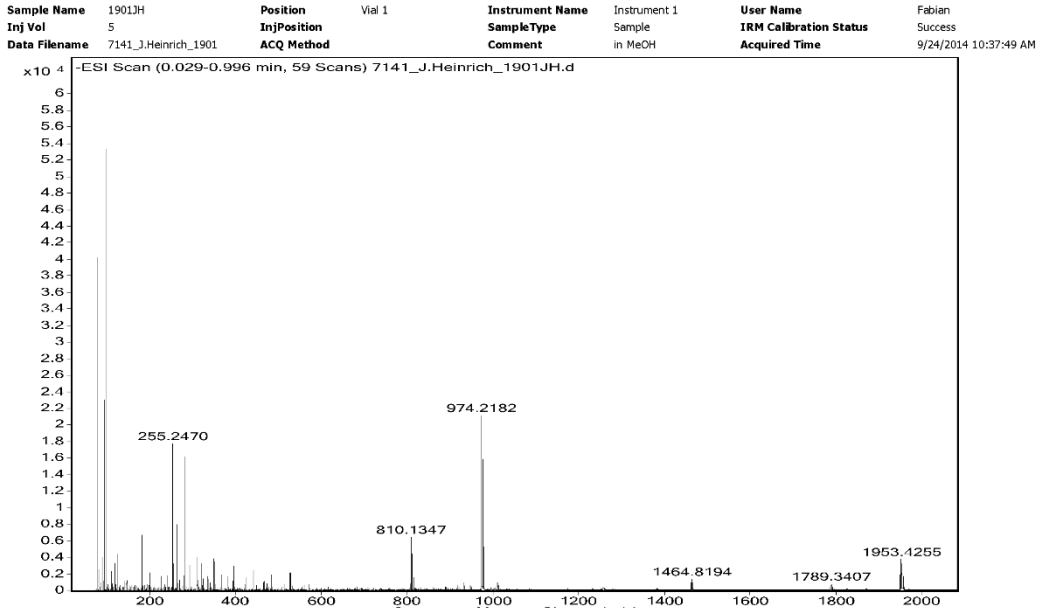


Figure 130. HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **10b**

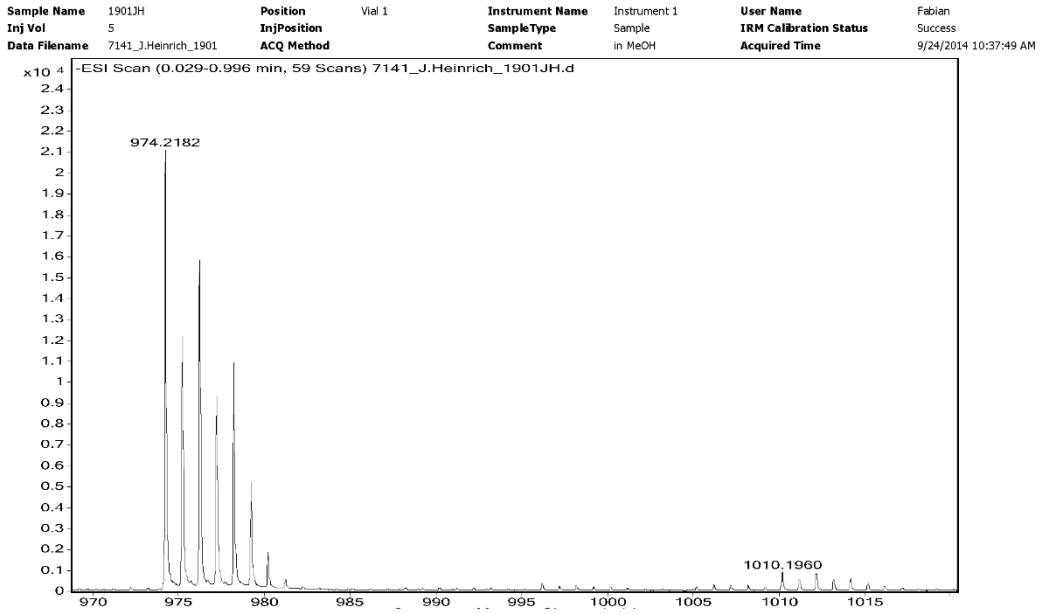


Figure 131. Zoomed HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **10b**

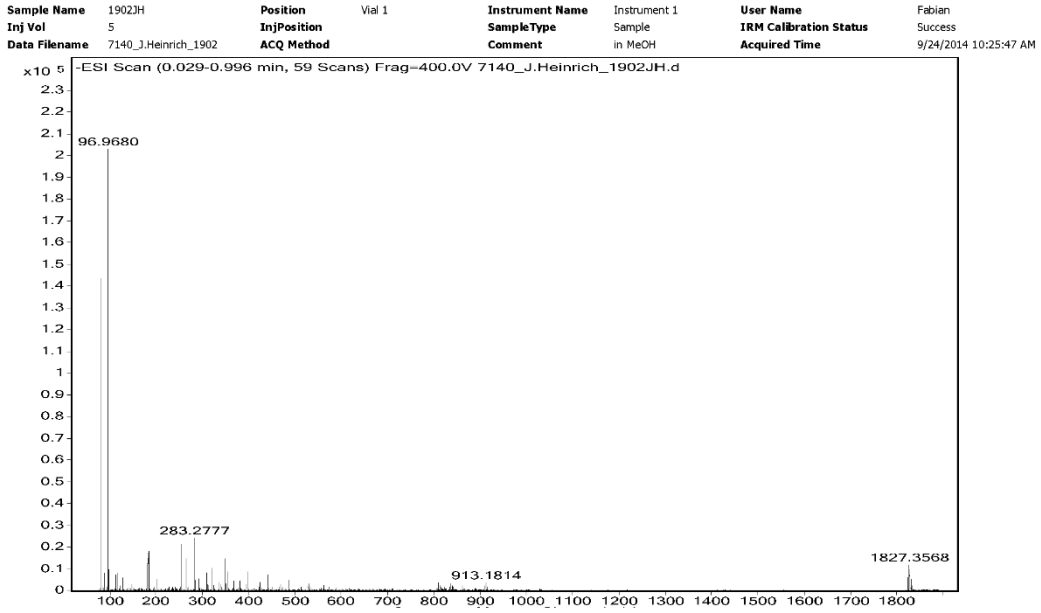


Figure 132. HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **10c**

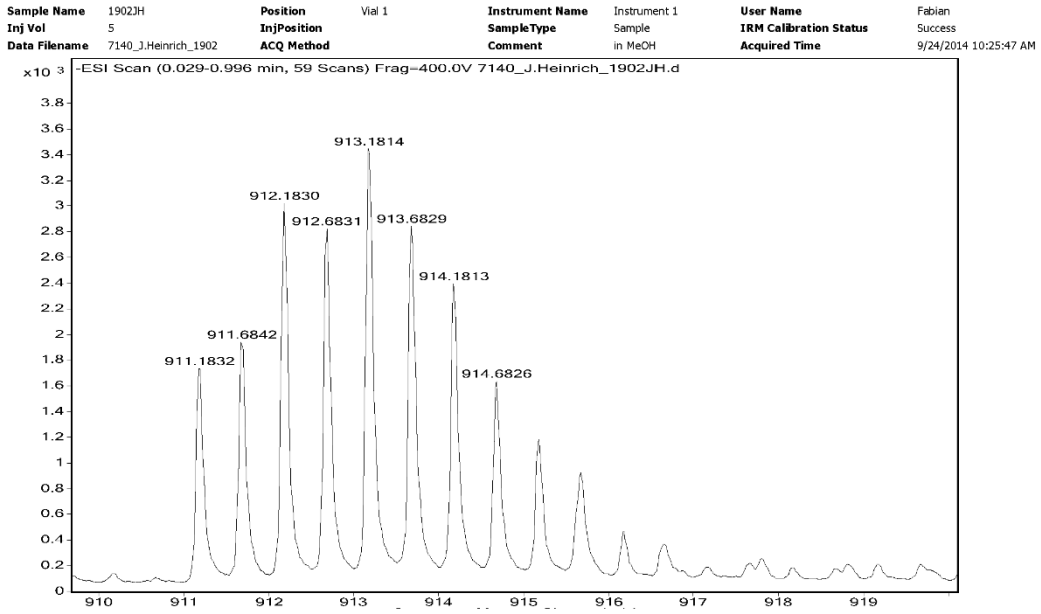


Figure 133. Zoomed HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **10c**

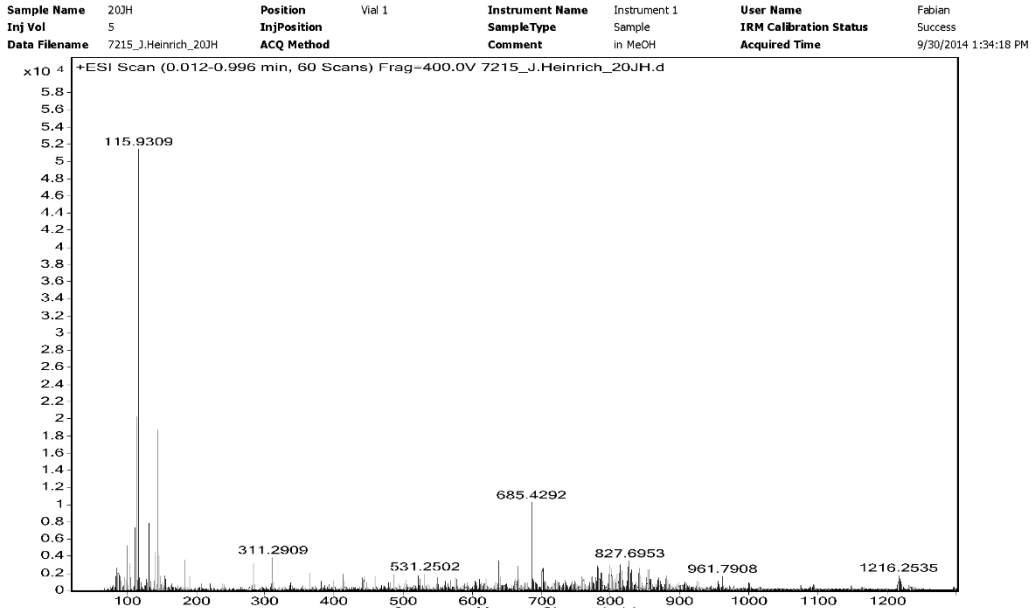


Figure 134. HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **10d**

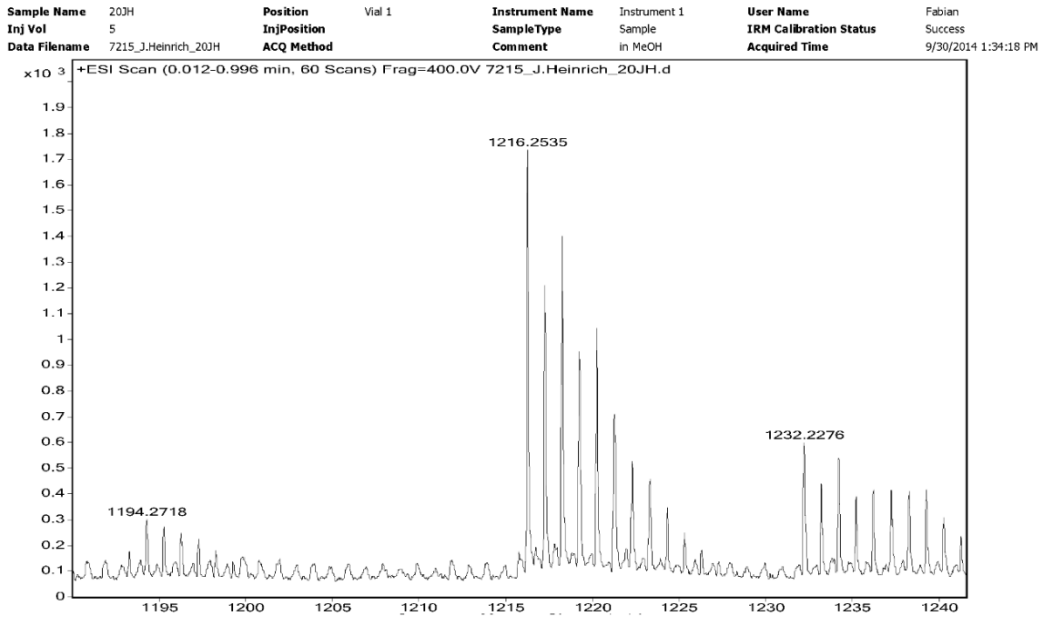


Figure 135. Zoomed HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **10d**

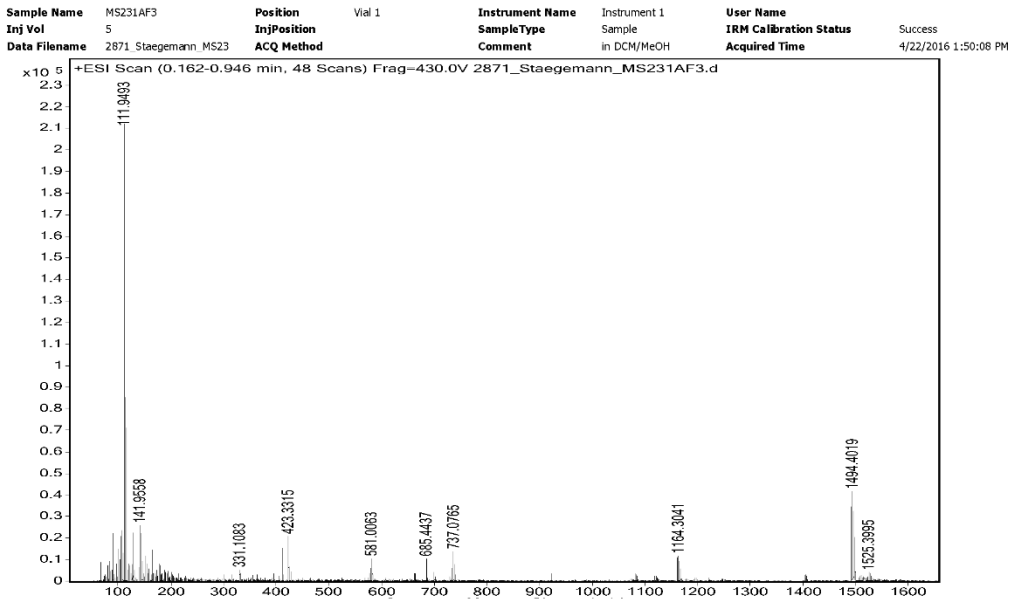


Figure 136. HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **11**

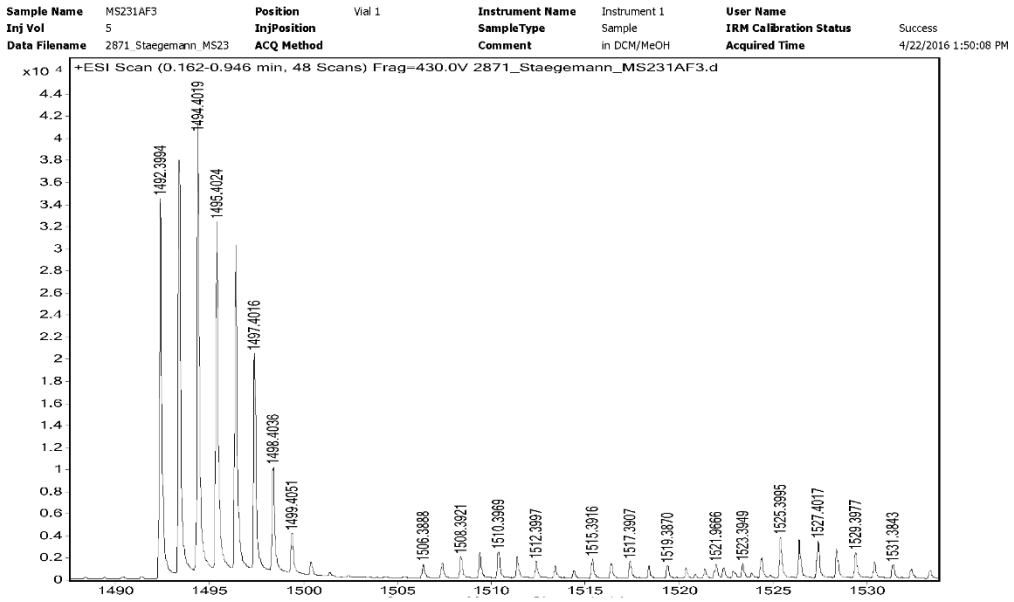


Figure 137. Zoomed HRMS spectrum (Agilent 6210, *Agilent Technologies*) of porphyrin **11**