Supporting information for

Isoxazolidine-fused *meso*-tetraarylchlorins as key tools for the synthesis of mono- and bis-annulated chlorins

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Contents

Materials and Instrumentation.

Reagents and solvents were purchased as reagent-grade and used without further purification unless otherwise stated. Microwave irradiation experiments were carried out in a CEM Discovery Labmate circular single-mode cavity instrument (300 W max magnetron power output) from CEM Corporation. Flash chromatography was carried out using silica gel Merck (230-400 mesh).

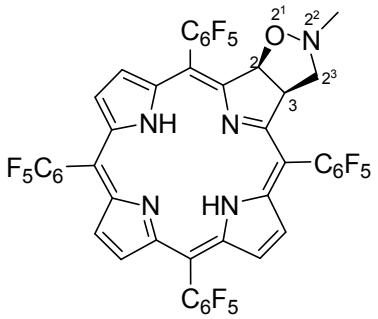
NMR spectra were recorded on a Bruker Avance III 400, operating at 400.15 MHz for proton, 376.46 MHz for fluorine and 100.62 MHz for carbon atoms, equipped with pulse gradient units, capable of producing magnetic field pulsed gradients in the z-direction of 50.0 G/cm. Two-dimensional $^{1}H/^{1}H$ correlation spectra (COSY), gradient selected $^{1}H/^{13}C$ heteronuclear single quantum coherence (HSQC) and $^{1}H/^{13}C$ heteronuclear multiple bond coherence (HMBC) spectra were acquired using the standard Bruker software. In most cases, both $CDCl_3$ and MeOD-d_4 were used as solvents for analysis in order to get as much information about the compounds.

High resolution MS analysis was carried out by electrospray ionization (ESI) in a LTQ-Orbitrap-XL instrument (Thermo Scientific) operated in the positive ionization mode with the following ESI source parameters: electrospray needle voltage +3 kV, sheath gas nitrogen 5, capillary temperature 275 °C, capillary voltage 37 V and tube lens voltage 120 V. Samples were dissolved in HPLC grade methanol to a final concentration of 5 $\mu g.ml^{-1}$ and were infused into the electrospray source using the mass spectrometer inbuilt syringe infusion pump at a flow rate of 10 $\mu l.min^{-1}$. Full scan positive mass spectra were acquired for *m/z* values between 200 and 2000 with resolution at *m/z* 400 set as 60000. MS/MS spectra were acquired using higher-energy collision dissociation (HCD) with 35% normalized collision energy, a precursor ion selection window of ±0.5 m/z and a resolution of 30000. MS and MS/MS spectra were recorded with Xcalibur (version 2.2).

Electronic absorption spectra were recorded on a Shimadzu–UV 3600 UV–Vis-NIR equipped with a Shimadzu TCC-Controller, at 25°C, in 1 cm cuvettes. Fluorescence measurements were performed with a Varian Cary Elipse Spectrofluorometer equipped with a constant-temperature multicell cell holder, at 25°C, with 5 mm slit width for excitation and emission in 1 cm cuvettes. All fluorescence spectra were recorded using the

maximum absorption wavelength as the excitation wavelength (λ_{exc}). To minimize reabsorption effects, the absorbance's sample values were kept below 0.1.

Synthesis of isoxazolidine-fused chlorin 2

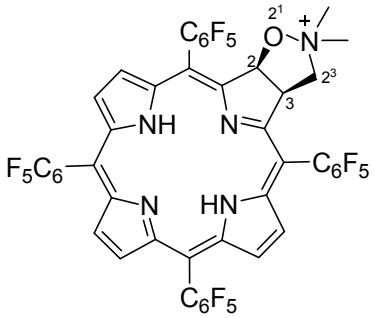


To a solution of *meso*-tetrakis(pentafluorophenyl)porphyrin **1** (50.0 mg, 0.05 mmol) in toluene (2 mL), was added the *N*-methyl hydroxylamine hydrochloride (25.0 mg, 0.30 mmol), paraformaldehyde (16.0 mg, 0.54 mmol) and K_2CO_3 (70.0 mg, 0.50 mmol). The resulting mixture was heated at 60 ˚C under a nitrogen atmosphere. Additional portions of *N*-methyl hydroxylamine hydrochloride, paraformaldehyde and K_2CO_3 were added after 6 h and 22 h. The mixture was maintained at 60 ºC until completed 30 h. After being cooled to room temperature, the reaction mixture was filtered to hold the carbonate residues and then it was purified by flash chromatography with a 1:1 mixture of dichloromethane/hexane. After the recovery of the low polarity starting porphyrin **1**, the expected chlorin **2** was then isolated. The last fractions were identified as bacteriochlorins (bisadducts), but these compounds were obtained in much lower amounts. Crystallization from dichloromethane/hexane afforded chlorin **2** (37 mg, 71% yield) as a green solid.

Chlorin 2: ^{1}H NMR (400 MHz, $CDCl_3$) δ: -1.91 (s br, 2H, N*H*), 2.57 (s, 3H, CH_3), 2.91-3.02 (m, 1H, H-2$^3_{cis}$), 3.44-3.52 (m, 1H, H-2$^3_{trans}$), 5.30-5.38 (m, 1H, H-3), 6.78-6.82 (m, 1H, H-2), 8.37-8.43 (m, 1H, H-β), 8.52 (br s, 3H, H-β), 8.72-8.77 (m, 2H, H-β); ^{1}H NMR (400 MHz, MeOD-d_4) δ: 2.59 (s, 3H, CH_3), 3.12-3.20 (m, 1H, H-2$^3_{cis}$), 3.44-3.51 (m, 1H, H-2$^3_{trans}$), 5.56-5.64 (m, 1H, H-3), 6.91-6.98 (m, 1H, H-2), 8.70 (br s, 3H, H-β), 8.76 (d, *J* 4.4, 3H, H-β), 9.02-9.07 (m, 2H, H-β); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -162.33 to -162.17 (m, 1F, F_{meta}-Ar); -161.55 to -161.48 (m, 4F, F_{meta}-Ar), -160.13 to -159.99 (m, 1F, F_{meta}-Ar), -160.10 to -160.25 (m, 1F, F_{meta}-Ar), -152.63 (t, *J* 20.0, 1F, F_{para}-Ar), -151.69 (t, *J* 20.0, 2F, F_{para}-Ar), -150.95 (t, *J* 20.0, 1F, F_{para}-Ar), -139.51 (d, *J* 20.0, 1F, F_{ortho}-Ar), -

137.03 to -136.81 (m, 4F, F_{ortho}-Ar), -136.60 (d, *J* 20.0, 1F, F_{ortho}-Ar), -135.42 (d, *J* 20.0, 1F, F_{ortho}-Ar), -134.44 (d, *J* 20.0, 1F, F_{ortho}-Ar), ^{19}F NMR (376 MHz, MeOD-d_4) δ: -166.11 to -166.00 (m, 1F, F_{meta}-Ar); -165.45 to -165.35 (m, 1F, F_{meta}-Ar), -165.19 to -164.99 (m, 4F, F_{meta}-Ar), -163.76 to -163.67 (m, 1F, F_{meta}-Ar), -163.36 (dt, *J* 22.6 and 7.5, 1F, F_{meta}-Ar), -156.77 (dd, *J* 22.6 and 18.8, 1F, F_{para}-Ar), -155.72 (t, *J* 18.8, 2F, F_{para}-Ar), -155.03 (t, *J* 18.8, 1F, F_{para}-Ar), -141.58 (d, *J* 18.8, 1F, F_{ortho}-Ar), -140.65 to -140.38 (m, 4F, F_{ortho}-Ar), -140.20 (dd, *J* 22.6 and 7.5, 1F, F_{ortho}-Ar), -138.90 (dd, *J* 22.6 and 7.5, 1F, F_{ortho}-Ar), -136.67 (dd, *J* 22.6 and 7.5, 1F, F_{ortho}-Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 44.9 (CH_3), 55.8 (C-3), 64.5 (C-2^3), 86.9 (C-2), 97.8, 107.3, 116.3, 124.7, 125.3, 126.2, 128.8, 129.0, 133.7, 136.2, 136.6, 137.1, 138.8, 139.7, 140.8, 141.5, 145.9, 148.4, 153.9, 154.1; ESI-HRMS: $[M+H]^+$ ($C_{46}H_{15}F_{20}N_5O+H^+$) *m/z*= 1034.1002 (Δm = -2.7 ppm); UV-Vis (MeOH) $\lambda_{max/nm}$ (ε) 398 (1.9 x 10^5), 499 (1.1 x 10^4), 525 (2.7 x 10^3), 594 (3.4 x 10^3), 646 (4.0 x 10^4).

Synthesis of cationic chlorin 3

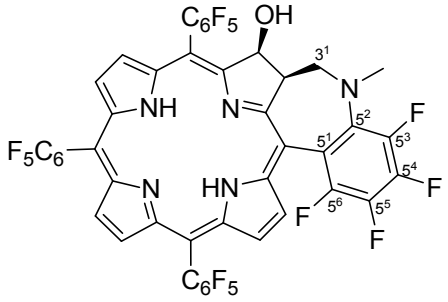


To a solution of chlorin **2** (45 mg, 0.04 mmol) in toluene (5 mL), methyl iodide (1.5 mL) was added dropwise and the mixture was heated at 40 ºC, under a nitrogen atmosphere, during 4 days. The reaction mixture was dropped into a 100 mL flask with hexane (5 mL) in order to precipitate the porphyrinic material. The precipitate was filtered and then dissolved in dichloromethane. The resulting residue was purified by preparative TLC using dichloromethane and then diclorometha/methanol (19:1) as the eluents. Chlorin **3** was isolated in 17% yield (7 mg). Porphyrin **1** (11 mg) was also recovered.

^{1}H NMR (400 MHz, $CDCl_3$) δ: -2.23 and -2.18 (2s, 2H, N*H*), 3.17 (s, 3H, $N^+(CH_3)_2$), 4.08 (s, 3H, $N^+(CH_3)_2$), 4.18-4.24 (m, 1H, H-2^3_{cis}), 5.58-5.66 (m, 1H, H-2^3_{trans}), 6.38-6.46 (m, 1H, H-3), 7.57-7.61 (m, 1H, H-2), 8.53-8.62 (m, 4H, H-β), 8.86-8.87 (m, 2H, H-β); ^{1}H NMR (400 MHz, MeOD-d_4) δ: 3.33 (s, 3H, $N^+(CH_3)_2$), 3.82 (s, 3H, $N^+(CH_3)_2$),

4.33 (dd, *J* 11.6 and 8.0, 1H, H-2^3_{cis}), 4.88-4.93 (m, 1H, H-2^3_{trans}), 6.29 (ddd, *J* 17.6, 8.4 and 8.0, 1H, H-3), 7.72 (d, *J* 8.4, 1H, H-2), 8.77-8.80 (m, 2H, H-β), 8.85 and 8.86 (2d, *J* 5.2, 2H, H-β), 9.15 (d, *J* 4.8, 2H, H-β); ^{19}F NMR (376 MHz, MeOD-d_4) δ: -164.97 to -164.78 (m, 4F, F_{meta}-Ar); -164.36 to -164.12 (m, 1F, F_{meta}-Ar), -163.97 to -163.76 (m, 1F, F_{meta}-Ar), -162.52 (ddd, *J* 26.3, 11.3 and 7.5, 2F, F_{meta}-Ar), -155.19 (t, *J* 18.8, 1F, F_{para}-Ar), -154.67 (t, *J* 18.8, 2F, F_{para}-Ar), -153.86 (t, *J* 18.8, 1F, F_{para}-Ar), -140.85 to -140.49 (m, 4F, F_{ortho}-Ar), -139.97 to -138.82 (m, 1F, F_{ortho}-Ar), -139.93 to -139.15 (m, 1F; F_{ortho}-Ar), -138.86 to -138.71 (m, 1F, F_{ortho}-Ar), -137.73 to -137.58 (m, 1F, F_{ortho}-Ar); ESI-HRMS: M^+ ($C_{47}H_{18}F_{20}N_5O^+$) *m/z* = 1048.1179 (Δm = -0.7 ppm). UV-Vis (MeOH) $\lambda_{max/nm}$ (ε) 420 (6.2 x 10^4), 509 (5.2 x 10^3), 552 (2.0 x 10^3), 595 (2.2 x 10^3), 650 (6.0 x 10^3).

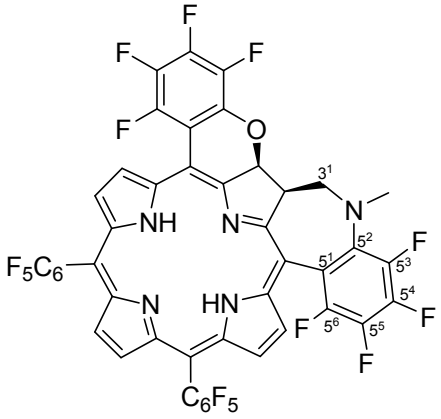
Synthesis of mono-annulated chlorin 4



To a mixture of chlorin **2** (16 mg, 0.014 mmol) and ethanol (2 mL) in a 10 mL Pyrex microwave vial was added cyclohexene (0.1 mL, 1 mmol), immediately followed by 10% (w/w) Pd/C (5.0 mg, 6.7 mol %). The reaction vial was sealed and the reaction mixture was subjected to microwave heating for 10 min (hold time) at 130 ºC, using 50 W of maximum power. The reaction mixture was filtered to remove the Pd/C and then subjected to flash chromatography (1:1 dichloromethane/hexane) to afford chlorin **4** as a brown solid (5 mg, 32% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: -1.81 and -1.68 (2s, 2H, N*H*), 2.93 (d, *J* 6.0, 3H, NCH_3), 3.73 (dd, *J* 12.8 and 10.4, 1H, H-3^1_{cis}), 4.01 (dd, *J* 10.4 and 6.8, 1H, H-3^1_{trans}), 4.82-4.84 (m, 1H, H-3), 6.99 (d, *J* 8.4, 1H, H-2), 8.41, 8.47 and 8.49 (3d, *J* 4.8, 3H, H-β), 8.69 (d, *J* 4.8, 1H, H-β), 8.74 (s, 2H, H-β); ^{1}H NMR (400 MHz, MeOD-d_4) δ: 2.95 (d, *J* 3.6, 3H, NCH_3), 3.80 (dd, *J* 8.4 and 7.2, 1H, H-3^1_{cis}), 3.99 (dd, *J* 7.2 and 4.8 Hz, 1H, H-3^1_{trans}), 4.89-4.90 (m, 1H, H-3), 6.95 (d, *J* 5.6, 1H, H-2), 8.61-8.65 (m, 3H, H-β), 8.86 (t, *J* 3.2, 1H, H-β), 8.94 and 8.97 (2d, *J* 3.2, 2H, H-β); ^{19}F NMR (376 MHz, $CDCl_3$) δ:

-162.84 (dd, *J* 22.6 and 18.8, 1F, F-5^5-Ar), -161.89 (ddd, *J* 24.4, 20.7 and 7.52, 1F, F$_{meta}$-Ar), -161.72 to -161.47 (m, 5F, F$_{meta}$-Ar), -154.29 (dd, *J* 22.6 and 18.8, 1F, F-5^4-Ar), -152.84 and -151.86 (2dd, *J* 22.6 and 18.8, 3F, F$_{para}$-Ar), -150.15 (dd, *J* 18.8 and 11.3, 1F, F-5^3-Ar), -140.14 (dd, *J* 22.6 and 7.5, 1F, F-5^6-Ar), -137.37 to -136.83 (m, 4F, F$_{ortho}$-Ar), -136.56 (dd, *J* 22.6 and 7.5, 1F, F$_{ortho}$-Ar); -134.42 (dd, *J* 26.3 and 7.5, 1F, F$_{ortho}$-Ar); ^{13}C NMR (100 MHz, MeOD-d$_4$) δ: 40.8 (CH$_3$), 48.2 (C-3), 60.4 (C-3^1), 76.3 (C-2), 98.1, 102.1, 105.0, 105.7, 123.5, 125.7, 127.6, 128.0, 132.0, 132.2, 134.9, 135.2, 139.5, 140.3, 152.5, 153.1, 166.8, 169.1; ESI-HRMS: $[M+H]^+$ ($C_{46}H_{16}F_{19}N_5O+H^+$) *m/z* = 1016.1106 (Δm = -1.8 ppm). UV-Vis (MeOH) $\lambda_{max/nm}$ (ε) 403 (5.5 x 10^4), 501 (5.6 x 10^3), 530 (3.0 x 10^3), 595 (2.9 x 10^3), 652 (1.4 x 10^4).

Synthesis of bis-annulated chlorin 5

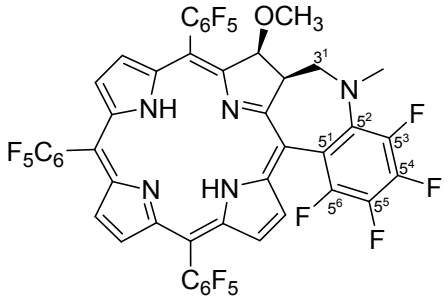


The chlorin **4** (12.3 mg, 0.012 mmol) was dissolved in dry THF (3 mL) and then an excess of NaH (4 mg of a 60% emulsion in mineral oil) was added. The reaction mixture was allowed to stir for 1.5 h at r.t. The reaction was quenched by slow addition of a concentrated aqueous NH_4Cl solution and the product was extracted with ethyl acetate. The organic phase was evaporated to dryness by rotary evaporation, and the residue was purified by flash chromatography using hexane/dichloromethane (1:1) as eluent to isolate chlorin **5** (11.1 mg, 92% yield)

Chlorin 5: ^{1}H NMR (400 MHz, $CDCl_3$) δ: -1.03 and -0.93 (2s, 2H, N*H*), 2.64 (d, *J* 5.6, 3H, NC*H*$_3$), 3.54-3.60 (m, 1H, H-3$^1_{cis}$), 4.21 (dd, *J* 10.5 and 6.4, 1H, H-3$^1_{trans}$), 5.05-5.12 (m, 1H, H-3), 6.70 (d, *J* 9.2, 1H, H-2), 8.41, 8.43 and 8.59 (3d, *J* 4.5, 3H, H-β), 8.64-8.65 (m, 2H, H-β), 8.82-8.84 (m, 1H, H-β); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -162.99 (t, *J*

20.7, 1F, F-5^5-Ar), -161.65 to -161.38 (m, 5F, F_{meta}-Ar), -159.06 (dd, *J* 20.7 and 7.5, 1F, F_{meta}-Ar), -154.06 (t, *J* 18.8, 2F, F-5^4-Ar and F_{ortho}-Ar), -151.77 and -151.71 (2t, *J* 20.7, 2F, F_{para}-Ar), -148.74 (dd, *J* 18.8 and 7.5, 1F, F-5^3-Ar), -138.98 (dd, *J* 22.6 and 7.5, 1F, F-5^6-Ar), -137.15 (dd, *J* 22.6 and 7.5, 1F, F_{ortho}-Ar), -137.04 to -136.96 (m, 2F, F_{ortho}-Ar), -136.57 and -136.46 (2dd, *J* 22.6 and 7.5, 2F, F_{ortho}-Ar); ^{13}C NMR extracted from the HSQC (100 MHz, $CDCl_3$) δ: 42.2 (CH_3), 48.2 (C-3), 58.8 (C-3^1), 86.4 (C-2), 123.5, 124.6, 126.7, 128.1, 132.2 (C-β); ESI-HRMS: $[M+H]^+$ ($C_{46}H_{15}F_{18}N_5O+H^+$) *m/z* = 996.1051 (Δm = -1.1 ppm). UV-Vis (MeOH) $\lambda_{max/nm}$ (ε) 418 (8.2 x 10^4), 512 (3.7 x 10^3), 550 (6.7 x 10^3), 602 (1.2 x 10^3), 664 (1.7 x 10^4).

Synthesis of methoxy chlorin 6



The chlorin **4** (12 mg, 0.012 mmol) was dissolved in dry THF (3 mL), under a nitrogen atmosphere. Methyl iodide (0.5 mL) was added dropwise and then an excess of NaH (4 mg of a 60% emulsion in mineral oil) was added. The reaction mixture was allowed to stir for 3 h at r.t. The reaction was quenched by slow addition of a concentrated aqueous NH_4Cl solution and the product was extracted with dichloromethane. The organic phase was evaporated to dryness by rotary evaporation, and the residue was purified via preparative TLC using hexane/dichloromethane (3:2) as the eluent to isolate chlorin **5** (higher R_f product, 8 mg, 67% yield) and chlorin **6** (2 mg, 16% yield).

Chlorin 6: ^{1}H NMR (400 MHz, $CDCl_3$) δ: -1.88 and -1.74 (2s, 2H, N*H*), 2.86 (d, *J* 6.0, 3H, NCH_3), 3.70-3.81 (m, 1H, H-3$^1_{cis}$), 3.80 (s, 3H, OCH_3), 3.85-3.95 (m, 1H, H-3$^1_{trans}$), 4.82-4.89 (m, 1H, H-3), 6.41 (d, *J* 8.4, 1H, H-2), 8.40, 8.47, 8.48 and 8.67 (4d, *J* 4.4, 4H, H-β), 8.72 (s, 2H, H-β); ^{19}F NMR (376 MHz, $CDCl_3$) -162.80 (dd, *J* 22.6 and 18.8, 1F, F-5^4-Ar), -162.60 to -162.32 (m, 1F, F_{meta}-Ar), -161.70 to -161.51 (m, 5F, F_{meta}-Ar), -154.34 (dd, *J* 22.6 and 18.8, 1F, F-5^3-Ar), -153.47 (dd, *J* 22.6 and 18.8, 1F, F_{para}-Ar), -

151.95 and -151.91 (2dd, *J* 22.6 and 18.8, 2F, F_{para}-Ar), -150.20 (dd, *J* 18.8 and 11.3, 1F, F-5^2-Ar), -140.14 (dd, *J* 22.6 and 7.5, 1F, F-5^5-Ar), -137.30 to -137.20 (m, 2F, F_{ortho}-Ar), -137.06 to -136.84 (m, 2F, F_{ortho}-Ar), -136.62 (dd, *J* 26.3 and 7.5, 1F, F_{ortho}-Ar), -133.71 (dd, *J* 26.3 and 7.5, 1F, F_{ortho}-Ar); ESI-HRMS: $[M+H]^+$ ($C_{47}H_{18}F_{19}N_5O+H^+$) *m/z* = 1030.1314 (Δm = 3.2 ppm). UV-Vis (MeOH) $\lambda_{max/nm}$ (ε) 405 (1.0 x 10^5), 499 (7.6 x 10^3), 529 (4.0 x 10^3), 591 (2.1 x 10^3), 652 (2.4 x 10^4).

Single-crystal X-ray diffraction

Single-crystals of compounds **2** and **5** were manually selected and mounted on the respective cryo-loop using viscous oil, with the assistance of a stereomicroscope. Diffraction data were collected at 180(2) K on a Bruker X8 Kappa APEX II Charge-Coupled Device (CCD) area-detector diffractometer controlled by the APEX2 software package (Mo K_α graphite-monochromated radiation, λ = 0.71073 Å; crystals positioned at 40 mm from the detector; 60 s of exposure time per image), and equipped with an Oxford Cryosystems Series 700. Images were processed with the software program SAINT+, and absorption correction was performed by the multi-scan semi-empirical method implemented in SADABS. The structure was solved by the direct methods of SHELXS-2014, and the non-hydrogen atoms were positioned from difference Fourier maps calculated by successive full-matrix least-squares refinement cycles on F^2 using SHELXL-97, and successfully refined with anisotropic displacement parameters.

Hydrogen atoms bound to carbon and nitrogen were placed at their idealized geometric positions using appropriate *HFIX* instructions in SHELXL, and included in the subsequent refinement cycles in riding-motion approximation with isotropic thermal displacements parameters (U_{iso}) fixed at 1.2 or 1.5 × U_{eq} of the parent atom.

In the crystal data of both compounds **2** and **5**, was found some additional electron density considerably dispersed as consequence of disordered solvent crystallization molecules (most probably hexane). Several attempts to locate and model these solvent molecules revealed to be ineffective, and the investigation for the total potential solvent area using the software package *PLATON,* confirmed unequivocally the occurrence of cavities with potential solvent accessible void volume. Therefore, the original data sets

were treated with the *SQUEEZE* subroutines to eliminate the contribution of these highly disordered molecules in the solvent-accessible volume.

Detailed information concerning the crystallographic data acquisitions and structure refinements are summarized in the Table S1.

Table S1 Data acquisition and structural refinement details for compounds **2** and **5**.

	2	**5**
Formula	$C_{46}H_{15}F_{20}N_5O$	$C_{46}H_{15}F_{18}N_5O$
Mr	1033.63	995.63
Crystal colour / shape	green / prism	black / plate
Crystal size /mm	0.20 × 0.15 × 0.09	0.25 × 0.17 × 0.01
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
a /Å	12.8835(11)	16.142(2)
b /Å	13.3978(11)	16.546(2)
c /Å	15.0065(12)	18.655(2)
α /°	74.581(4)	72.900(7)
β /°	88.333(4)	88.417(7)
γ /°	85.714(4)	85.613(6)
Volume /Å^3	2490.0(4)	4748.2(10)
Z	2	4
ρ_{calc} /g cm^{-3}	1.379	1.393
F(000)	1028	1984
μ /mm^{-1}	0.136	0.134
θ range /°	3.641 - 25.027	3.638 - 25.027
Reflections collected	46312	96687
Independent relections	8708 (R_{int} = 0.0499)	16701 (R_{int} = 0.0718)
Parameters (Restraints)	665 (0)	1251 (18)
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0570 wR_2 = 0.1443	R_1 = 0.0706 wR_2 = 0.1919
Final *R* indices (all data)	R_1 = 0.0920 wR_2 = 0.1585	R_1 = 0.1280 wR_2 = 0.2129

Min. and max. Residual electr. density /e Å^3	0.674 and −0.354	0.893 and −0.840

Crystallographic data (including structure factors) for the crystal structure of compounds **2** and **5** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication with references CCDC-1052565 and CCDC-1052566, respectively. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

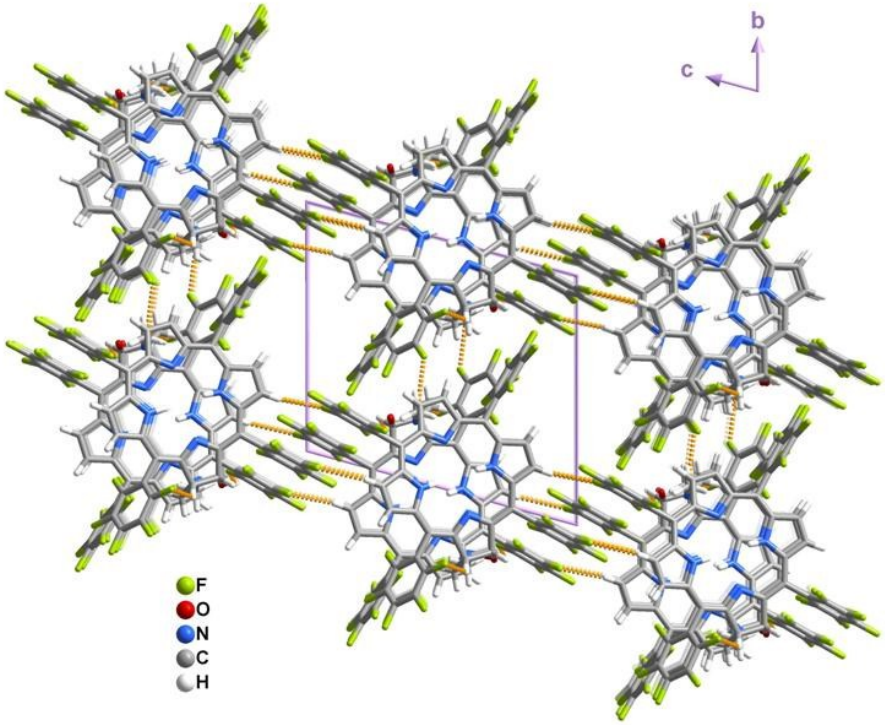


Figure S1 Crystal packing of the isoxazolidine-fused chlorin **2** viewed along the [0 1 1] direction of the unit cell, and with the C−H···F hydrogen bonds drawn as orange dashed lines.

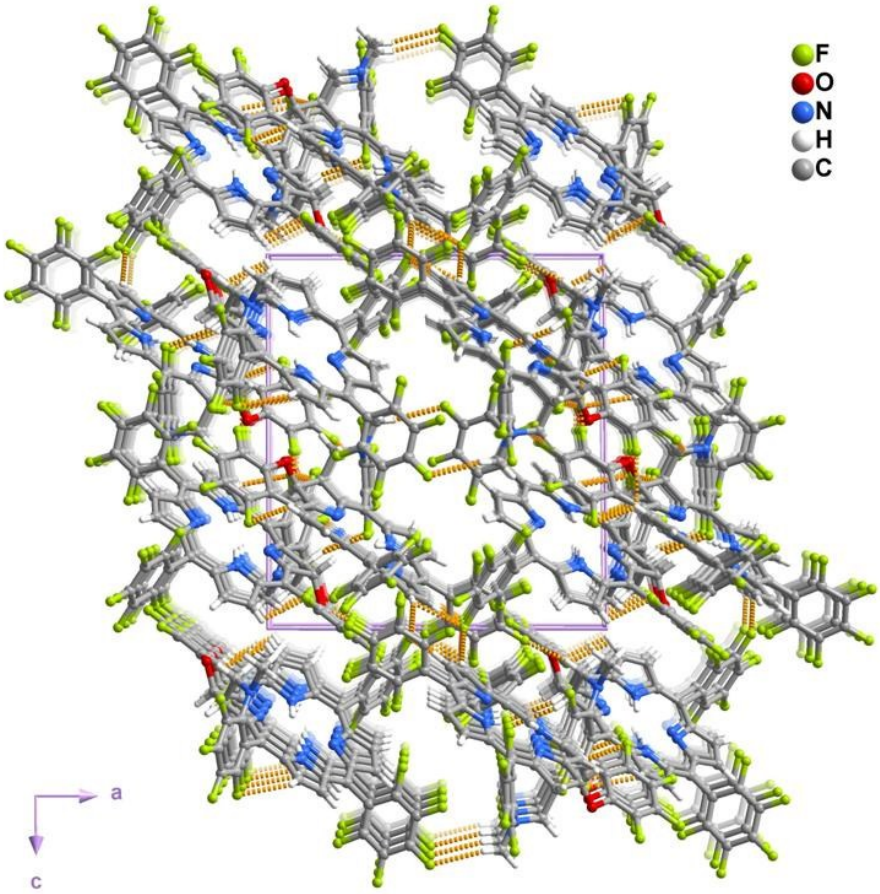


Figure S2. Crystal packing of the the bis-annulated chlorin **5** viewed along the [1 0 1] direction of the unit cell, showing the C−H···F hydrogen bonds represented as orange dashed lines.

NMR spectra of isoxazolidine-fused chlorin 2

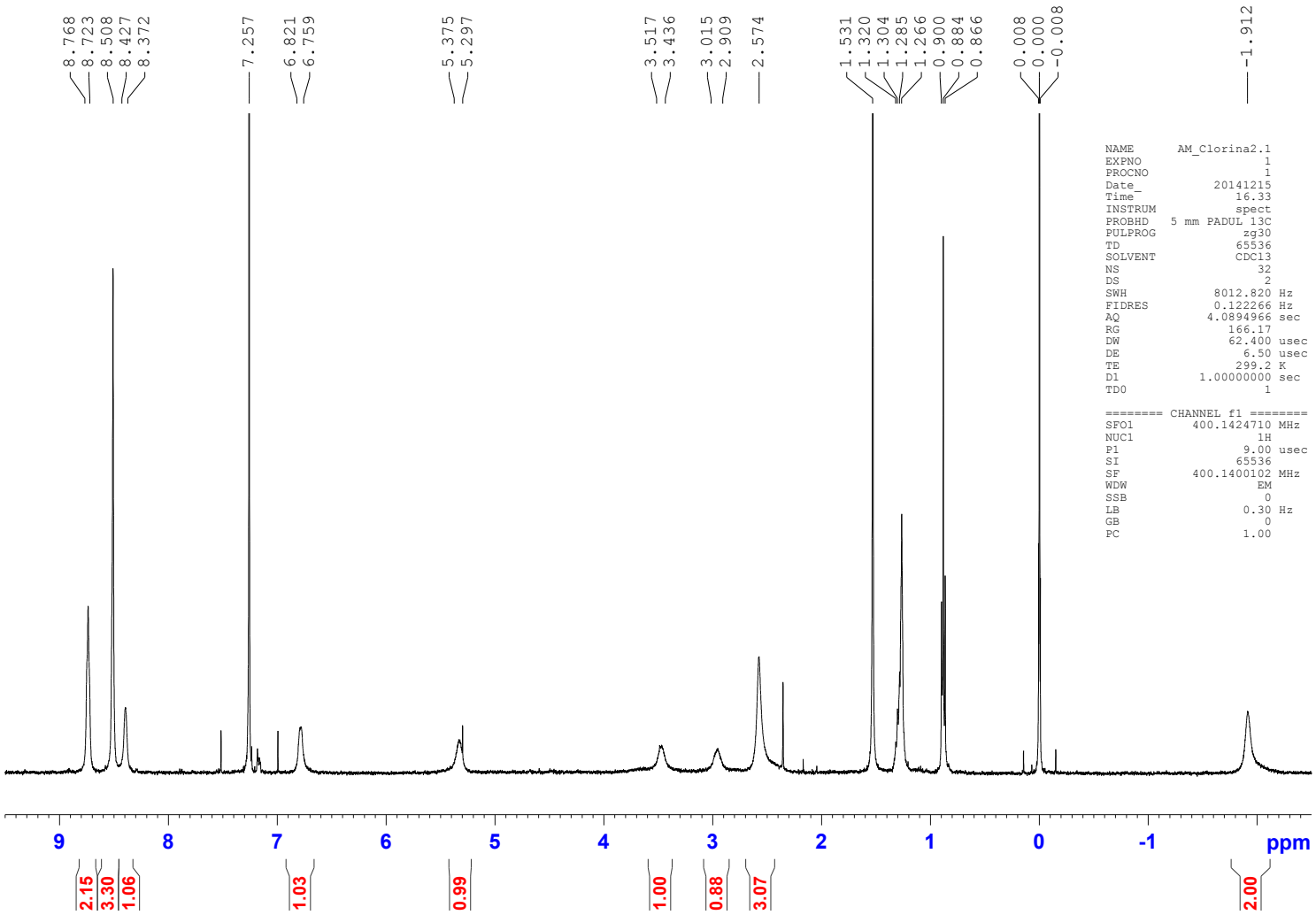


Figure S3. ^{1}H NMR spectrum of **2** (400 MHz, $CDCl_3$)

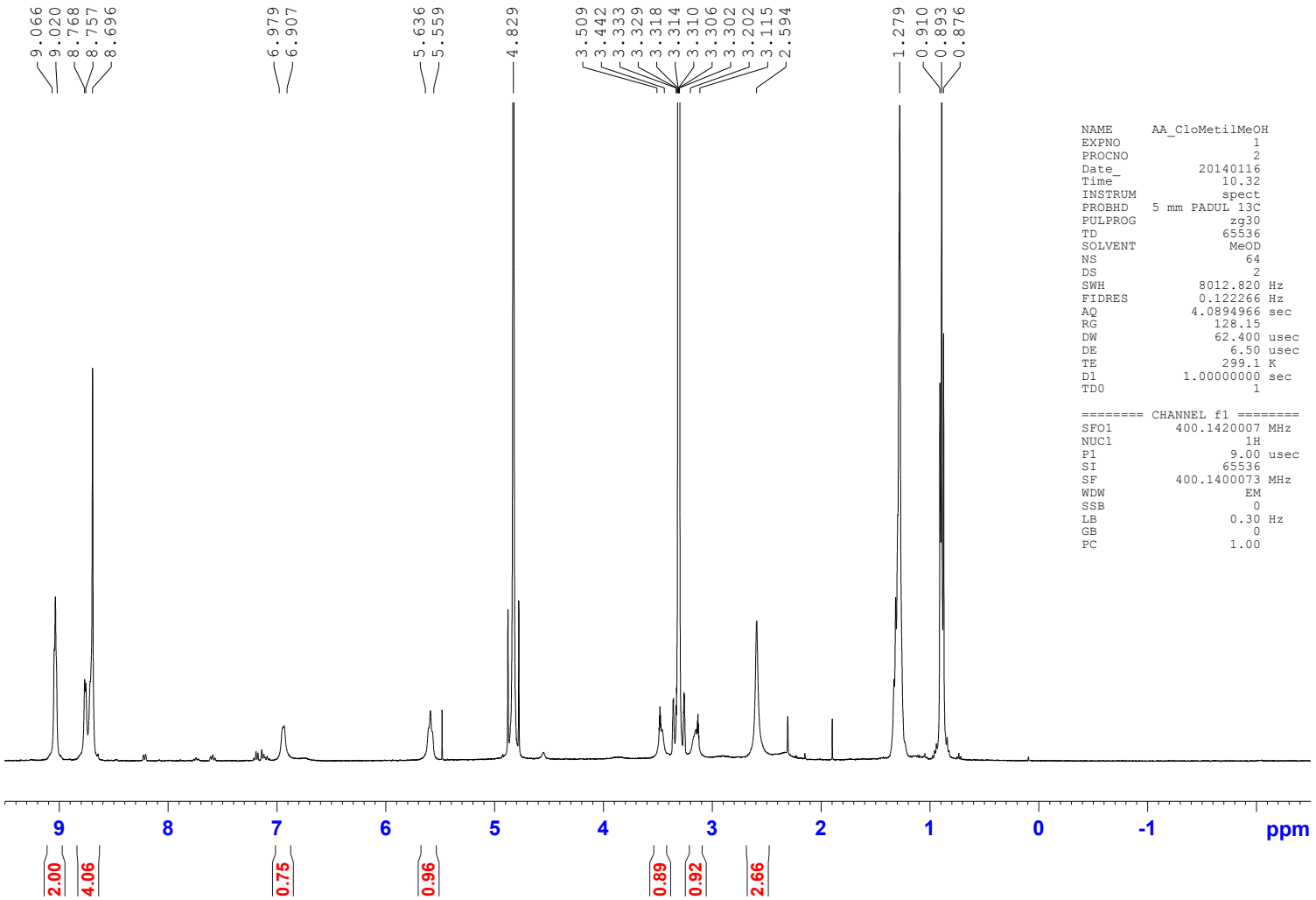


Figure S4. ^{1}H NMR spectrum of **2** (400 MHz, MeOD-d$_4$)

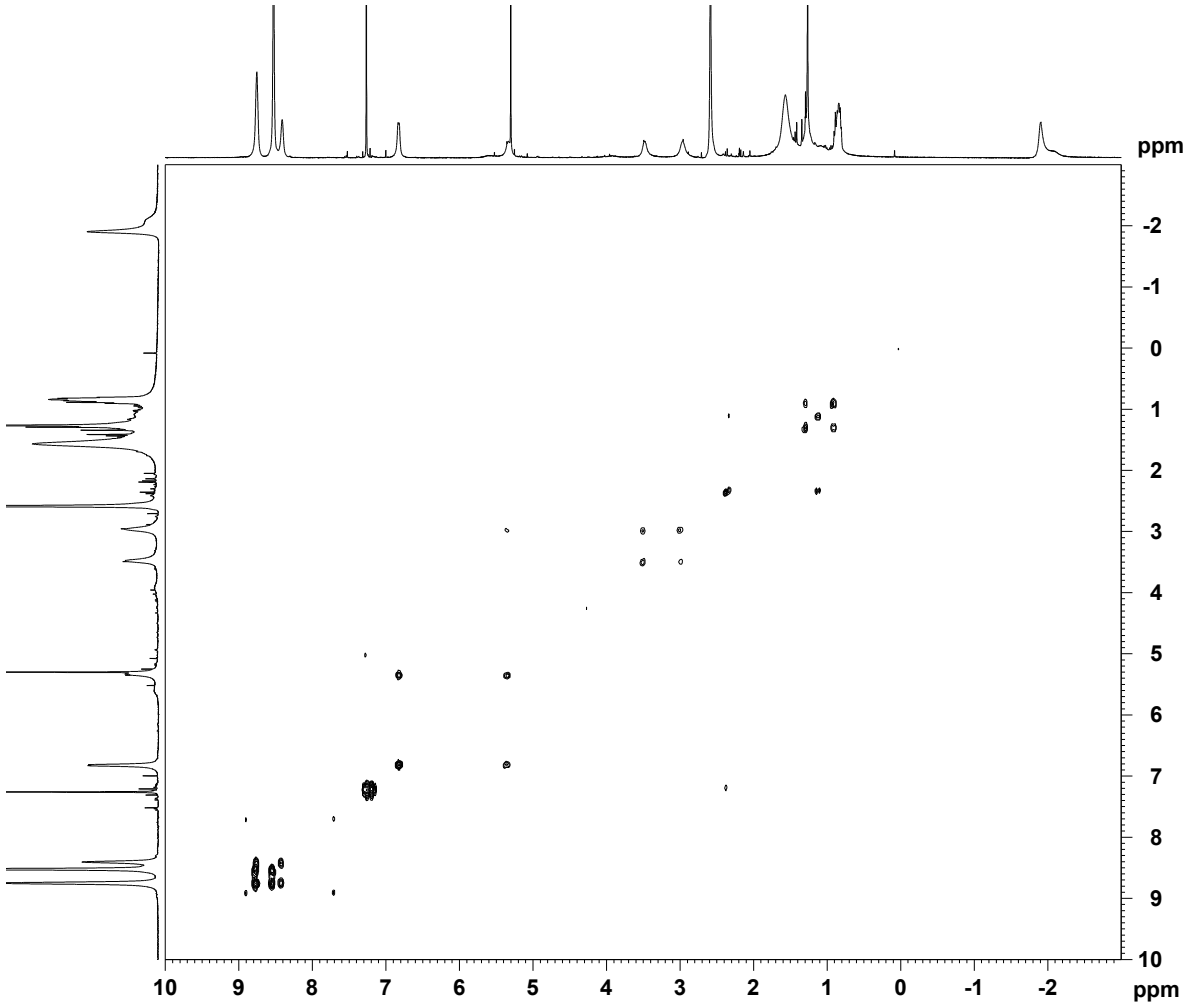


Figure S5. COSY of **2** ($CDCl_3$)

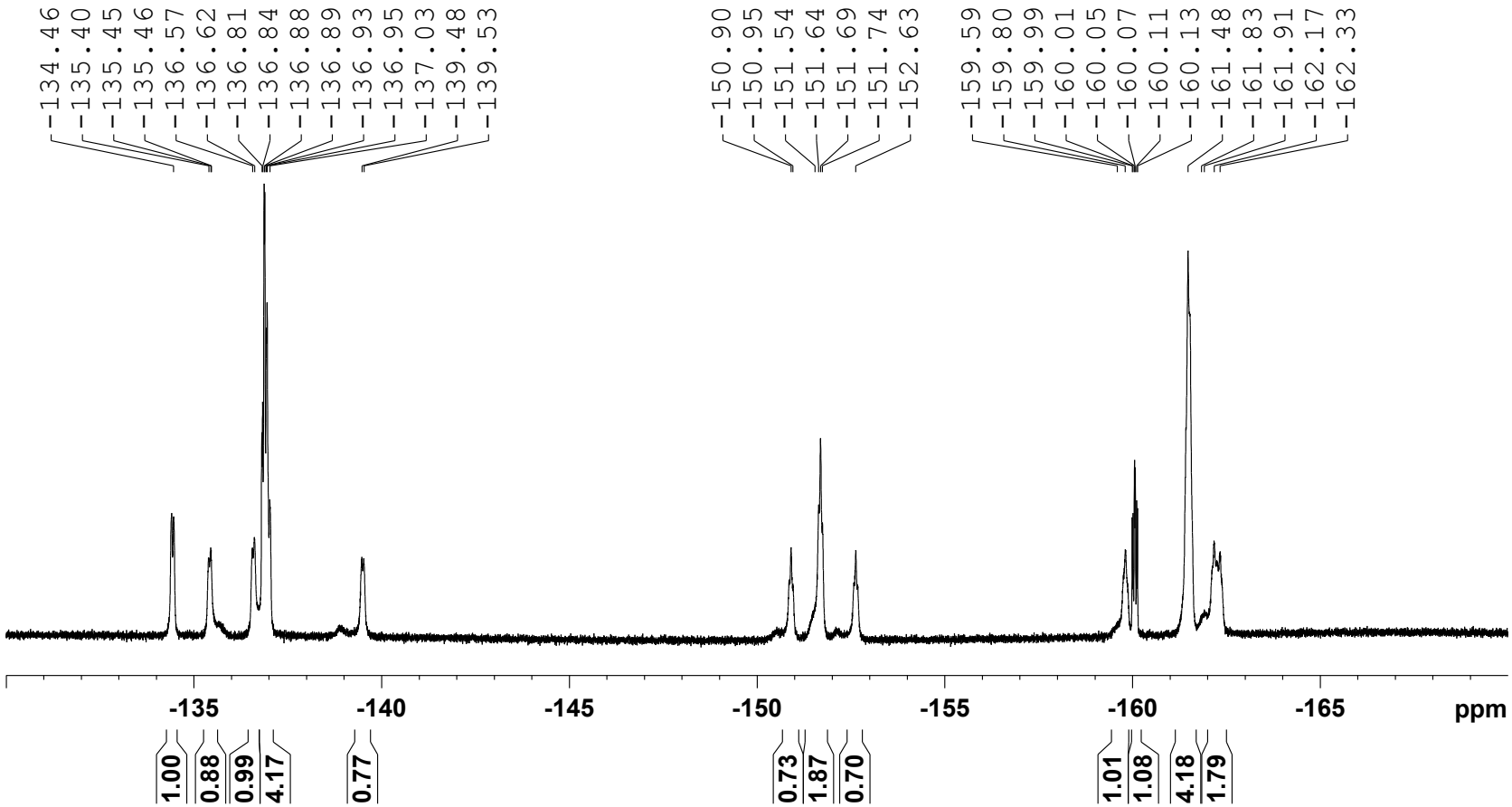


Figure S6. ^{19}F NMR spectrum of **2** (376 MHz, $CDCl_3$)

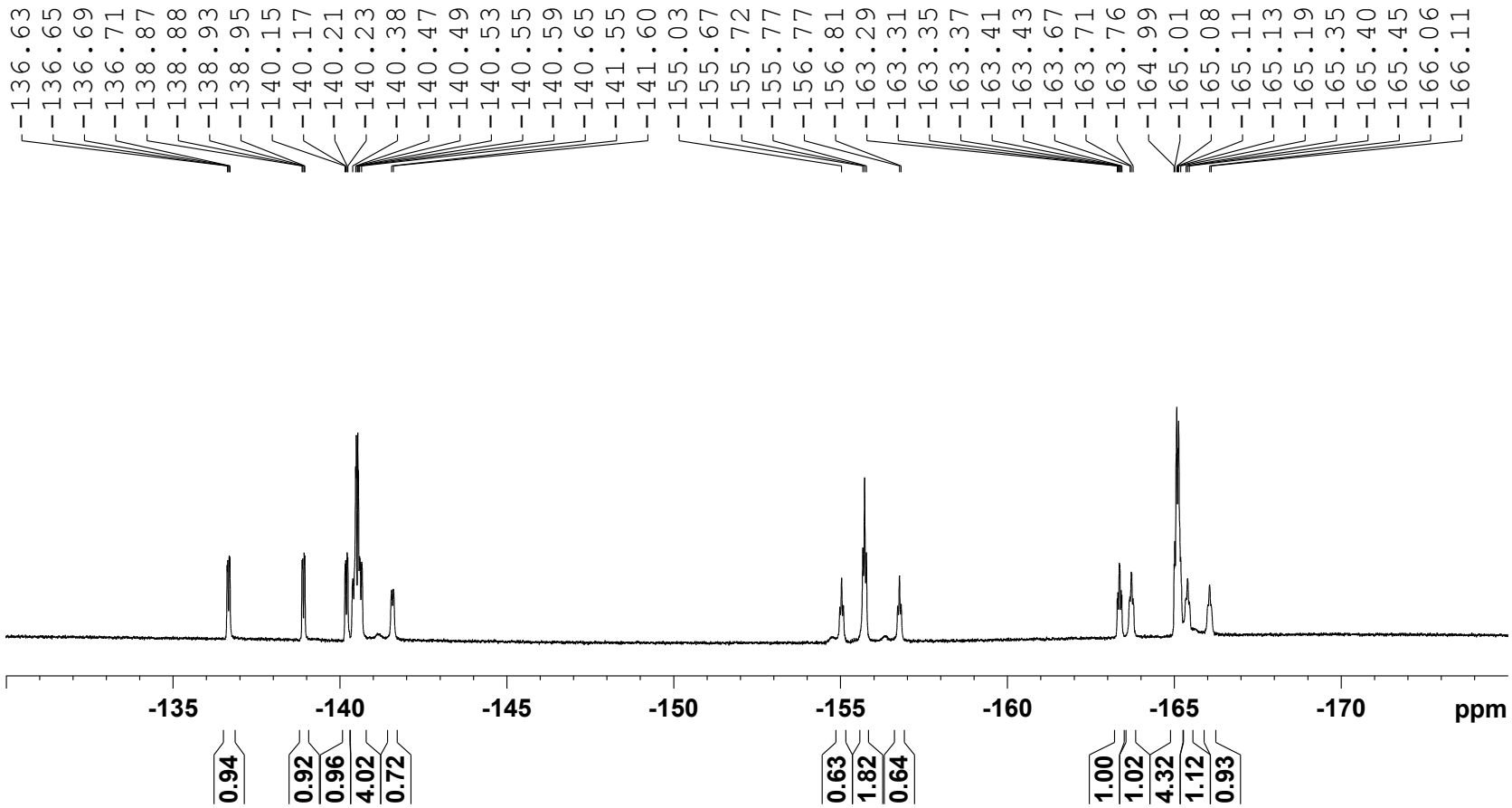


Figure S7. ^{19}F NMR spectrum of **2** (376 MHz, MeOD-d_4)

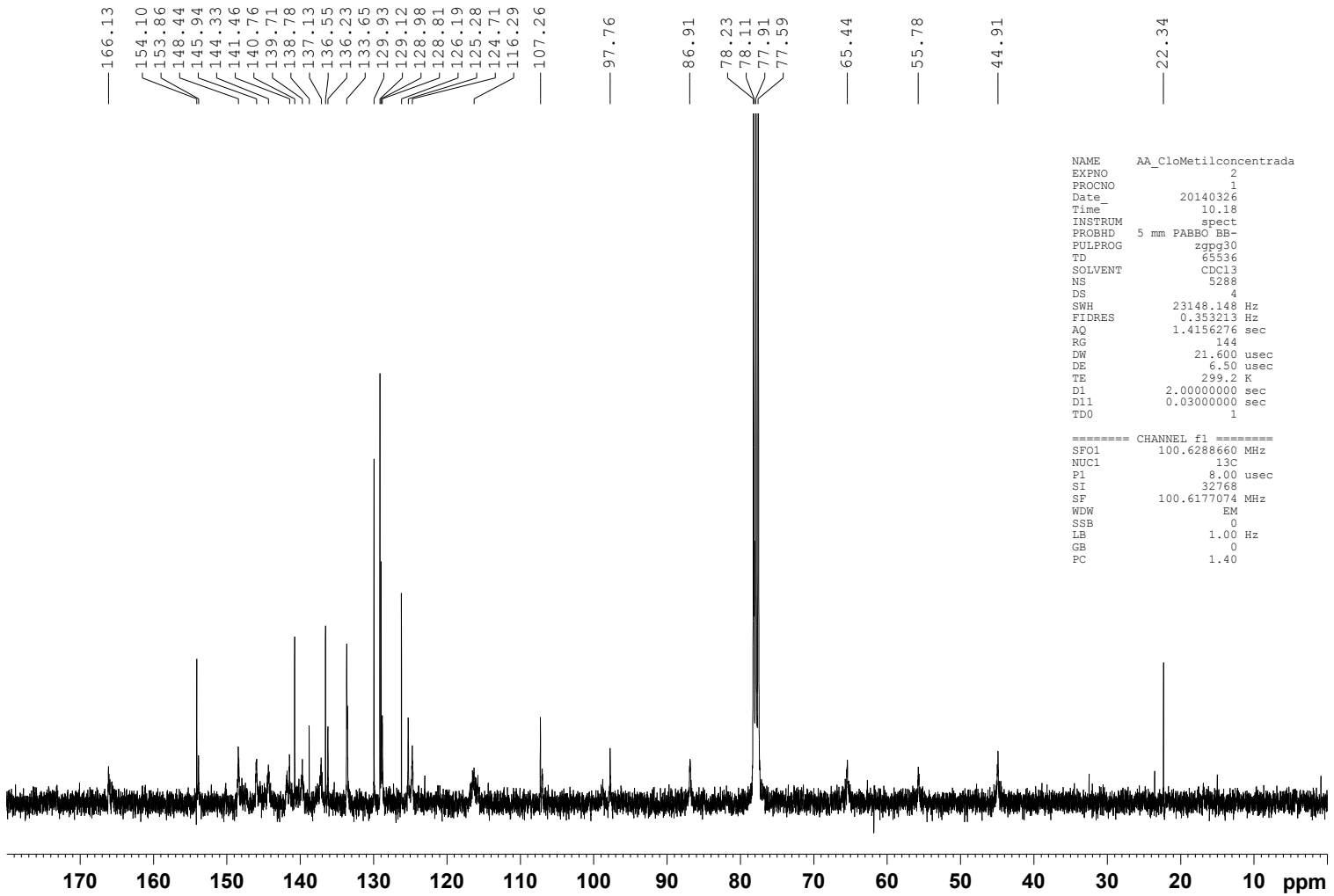


Figure S8. ^{13}C NMR spectrum of **2** (100 MHz, $CDCl_3$)

NMR spectra of cationic chlorin 3

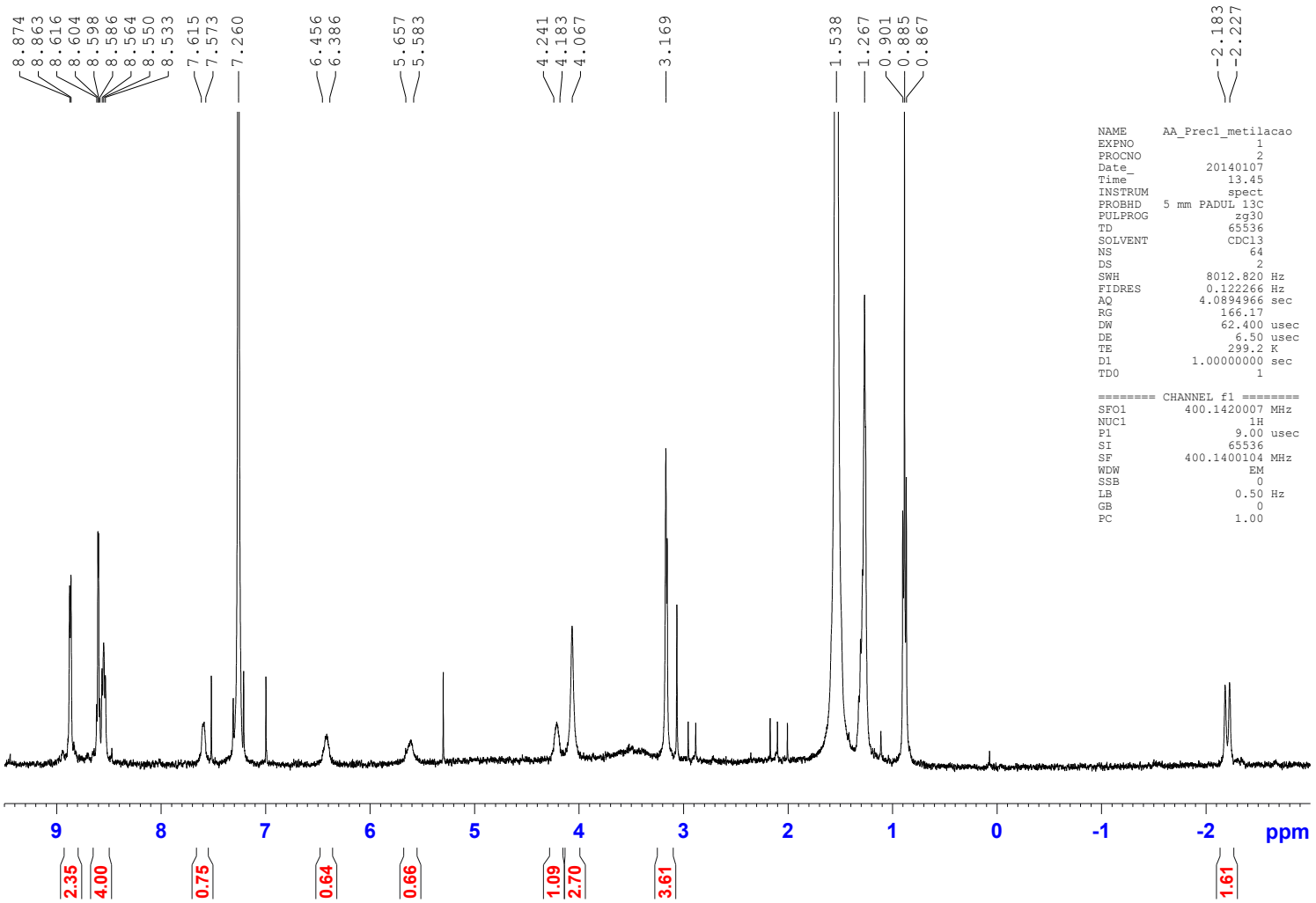


Figure S9. ^{1}H NMR spectrum of **3** (400 MHz, $CDCl_3$)

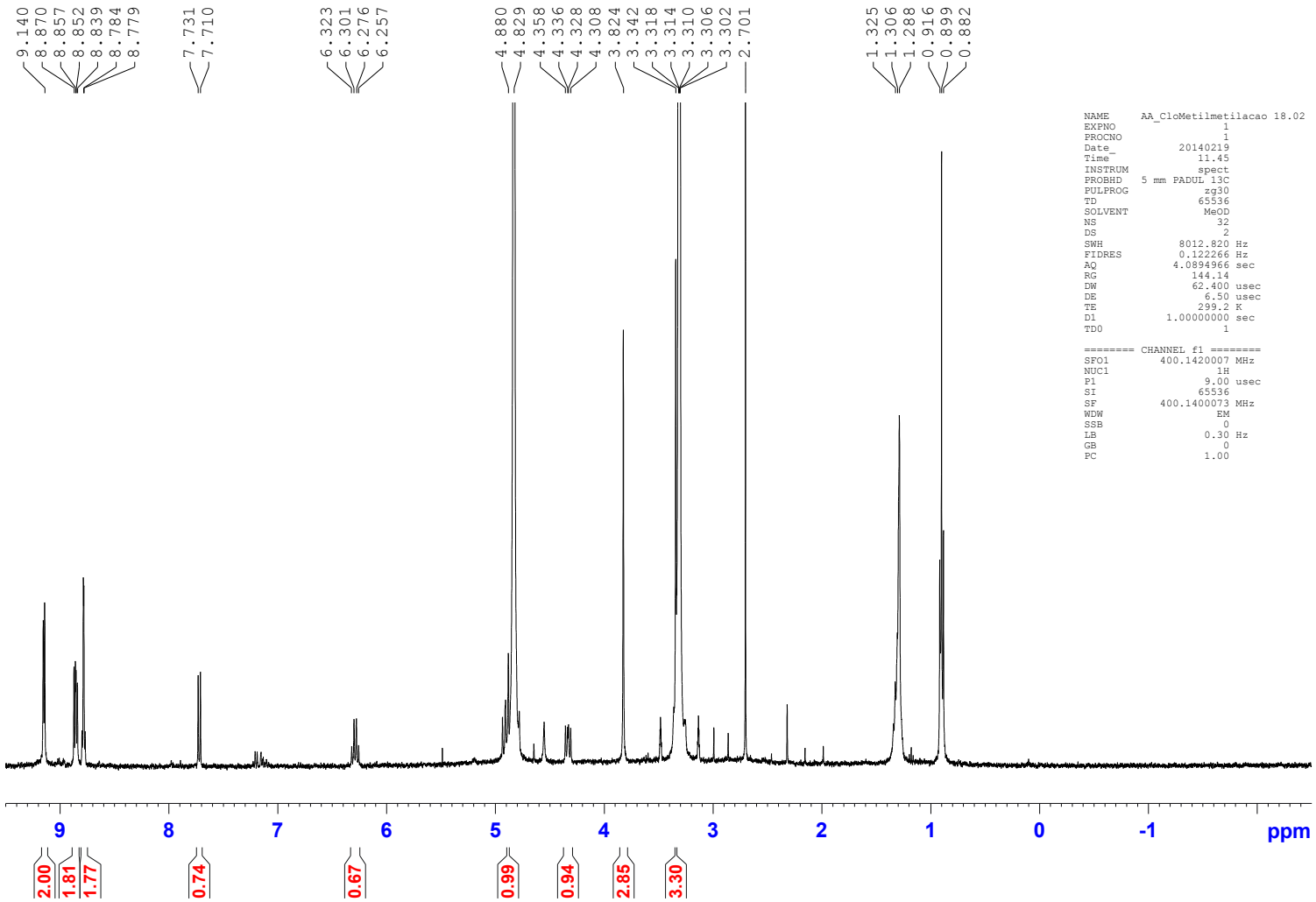


Figure S10. ^{1}H NMR spectrum of **3** (400 MHz, MeOD-d_4)

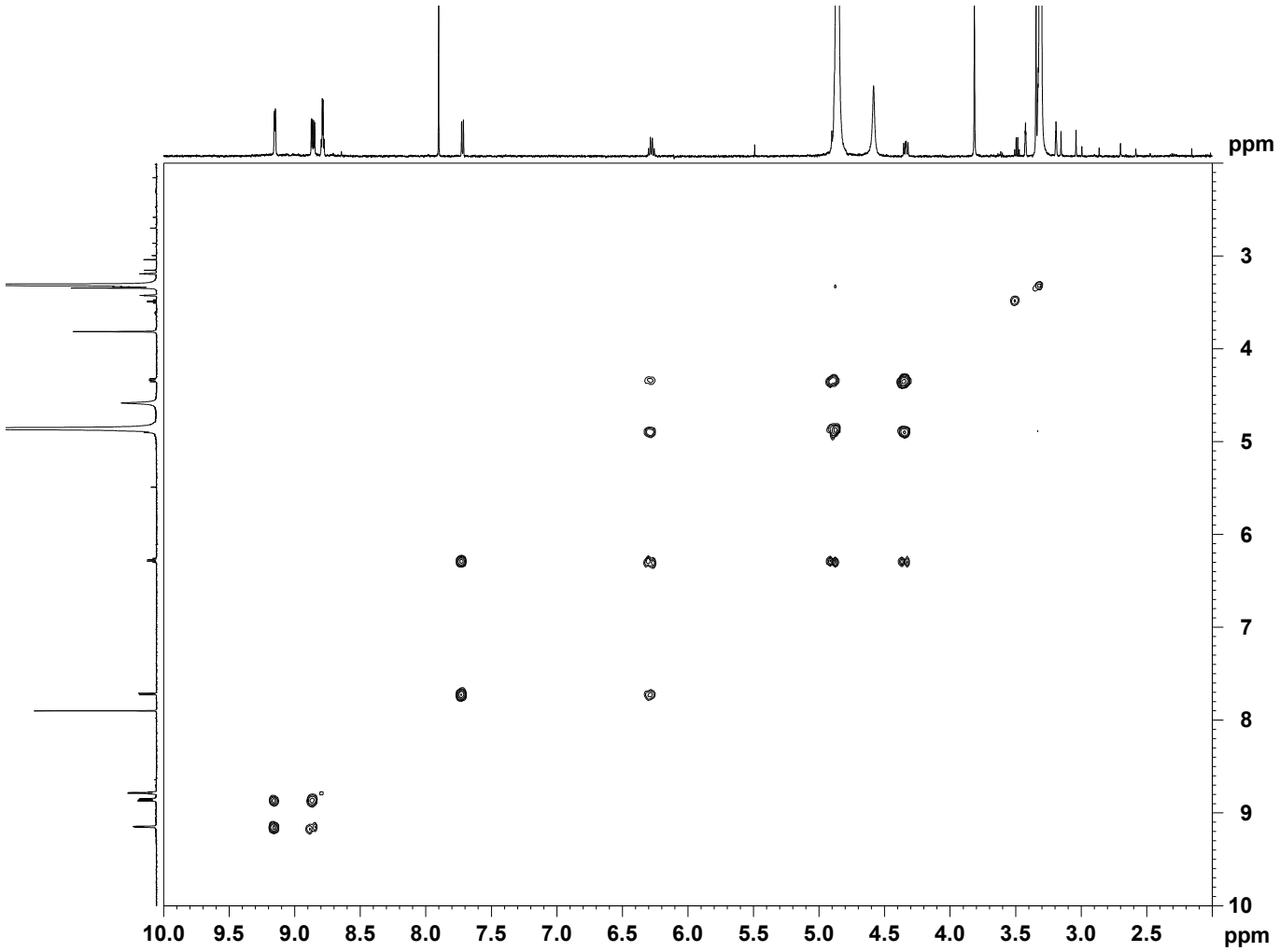


Figure S11. COSY of **3** (MeOD-d_4)

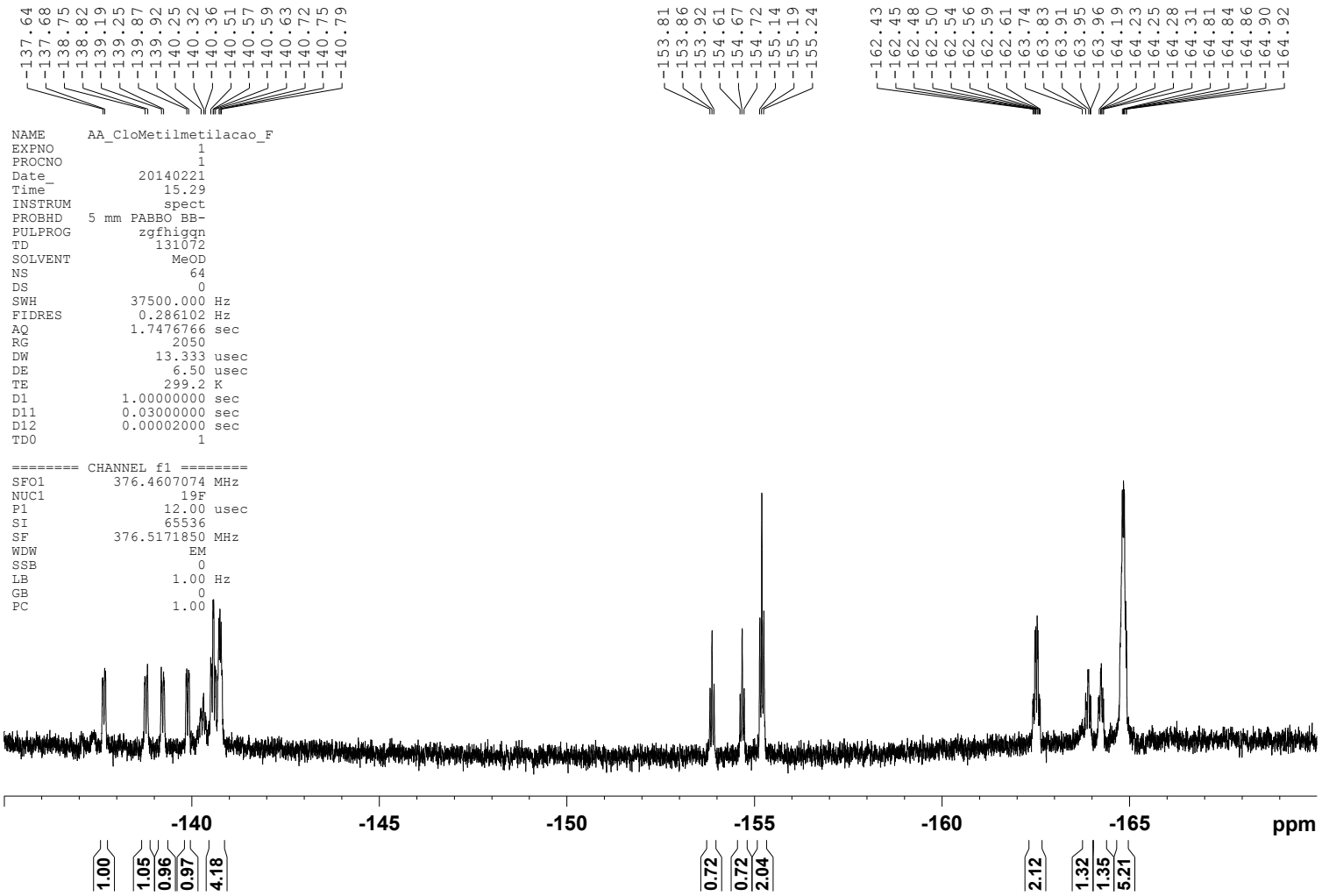


Figure S12. ^{19}F NMR spectrum of **3** (376 MHz, MeOD-d_4)

NMR spectra of mono-annulated 4

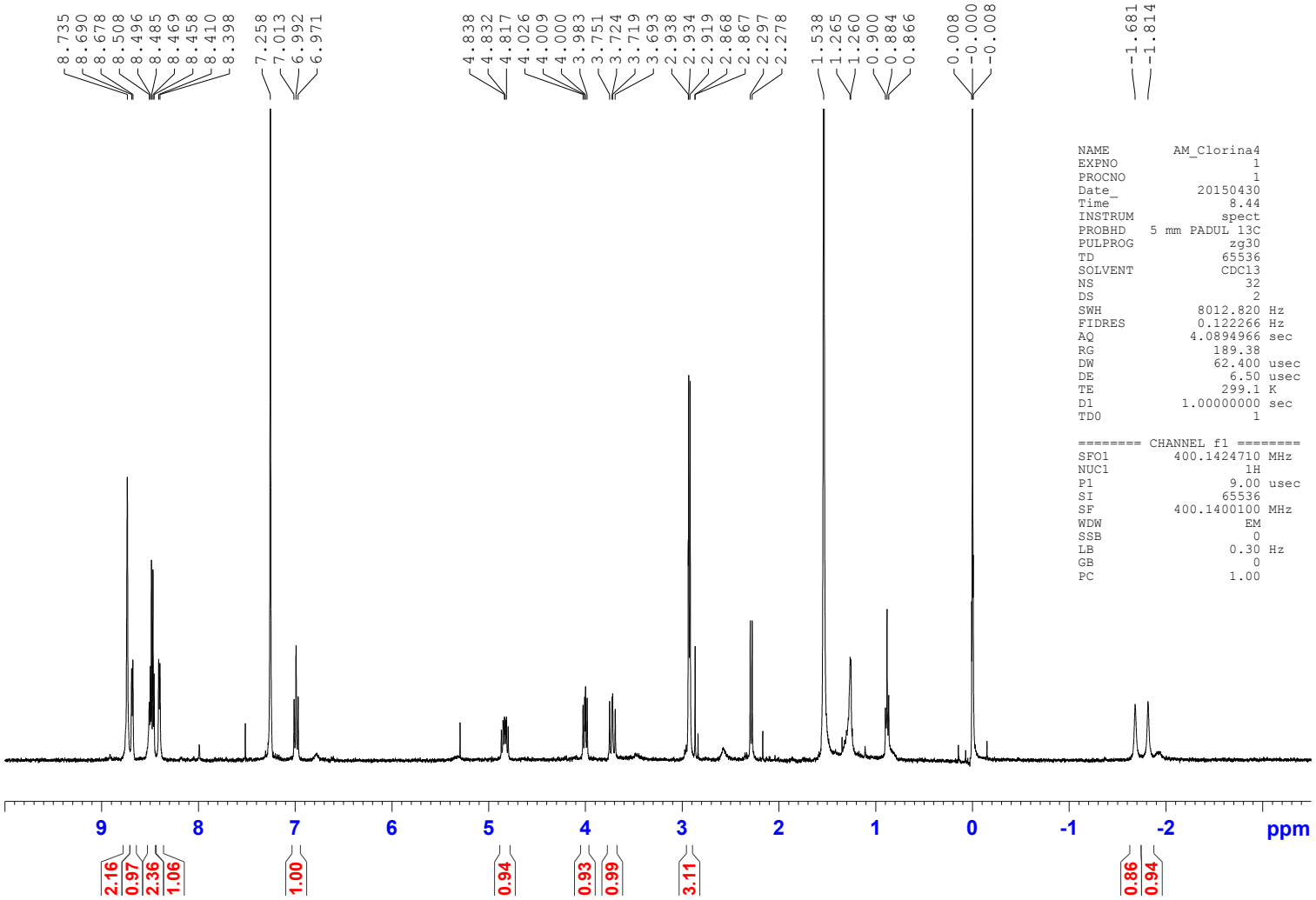


Figure S13. ^{1}H NMR spectrum of **4** (400 MHz, $CDCl_3$)

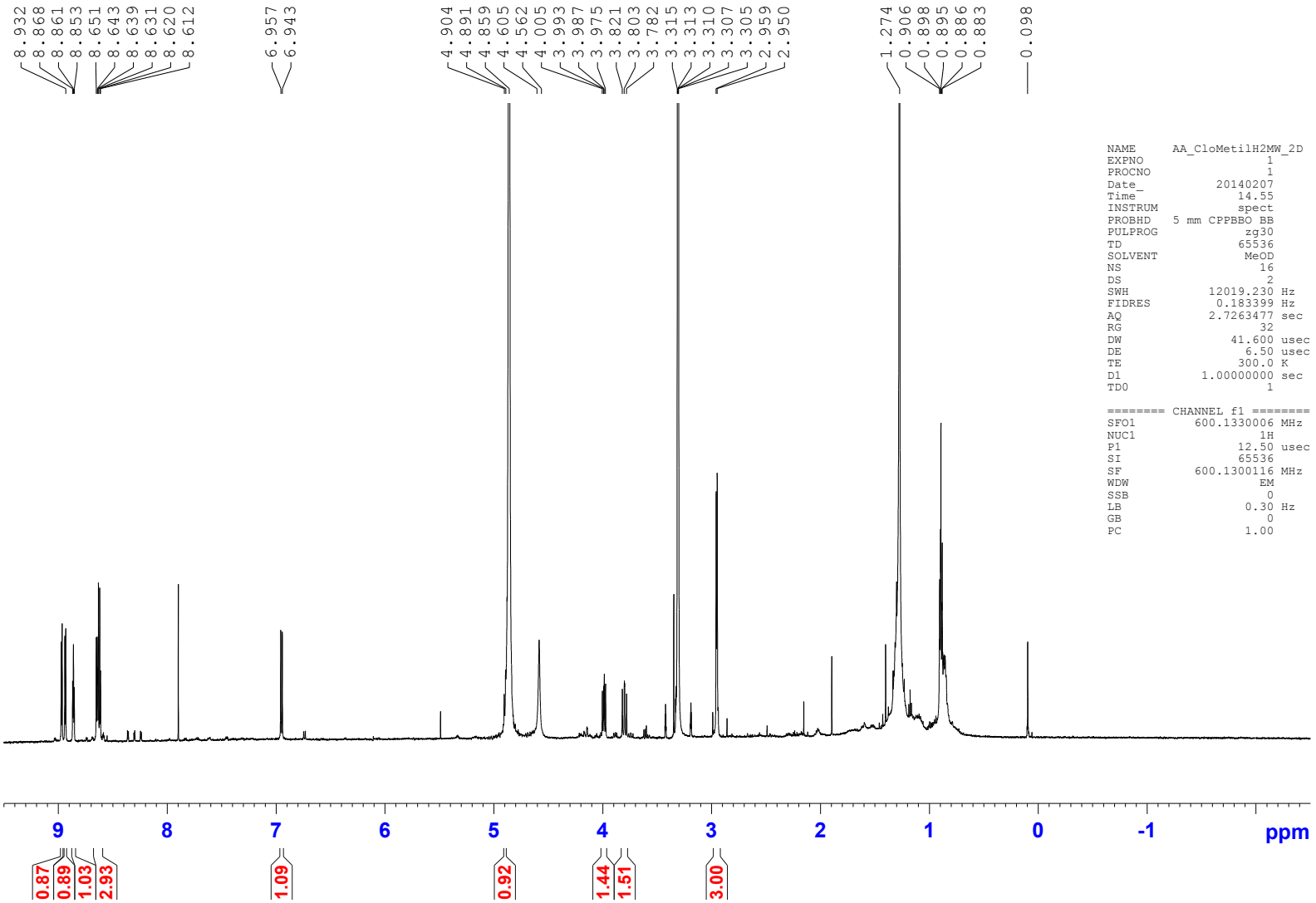


Figure S14. ^{1}H NMR spectrum of **4** (400 MHz, MeOD-d_4)

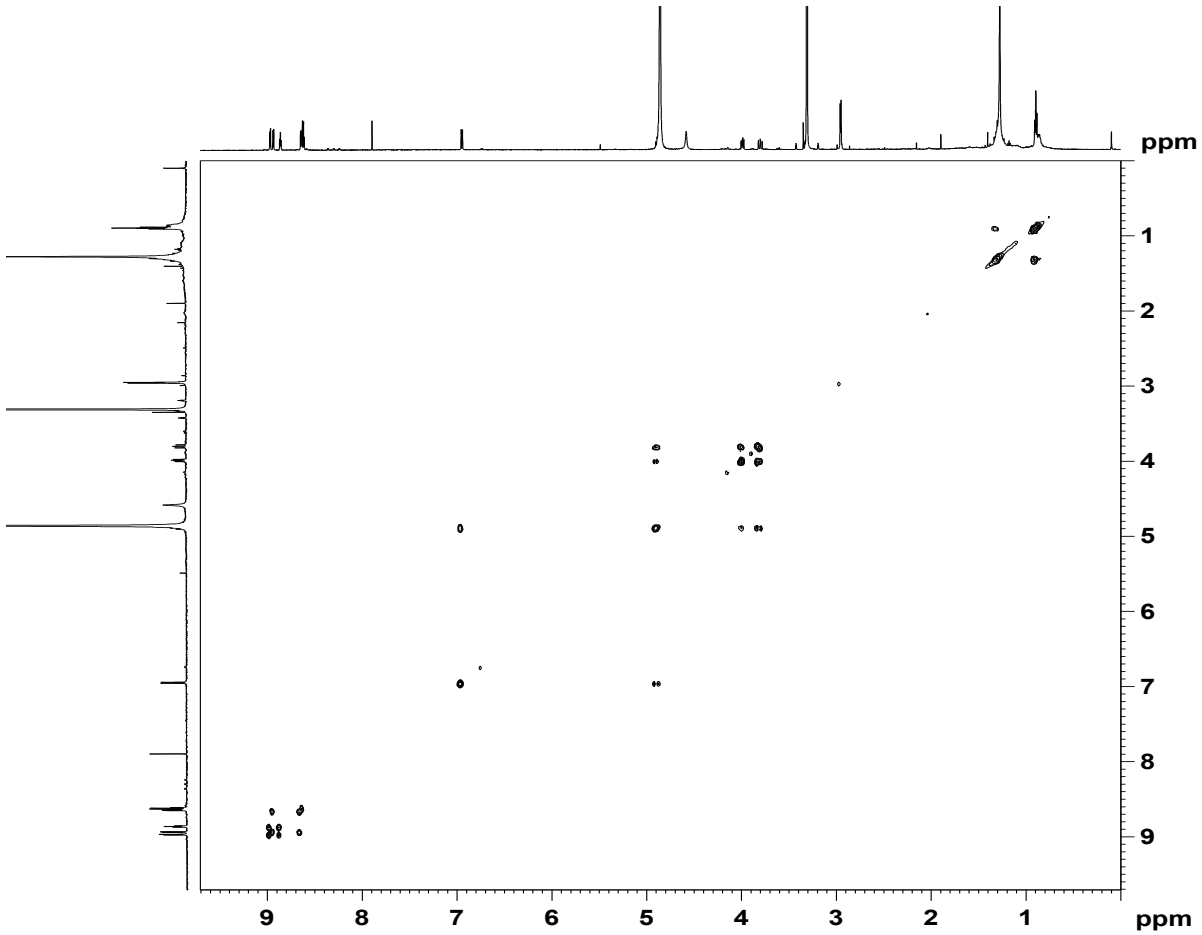


Figure S15. COSY of **4** (MeOD-d_4)

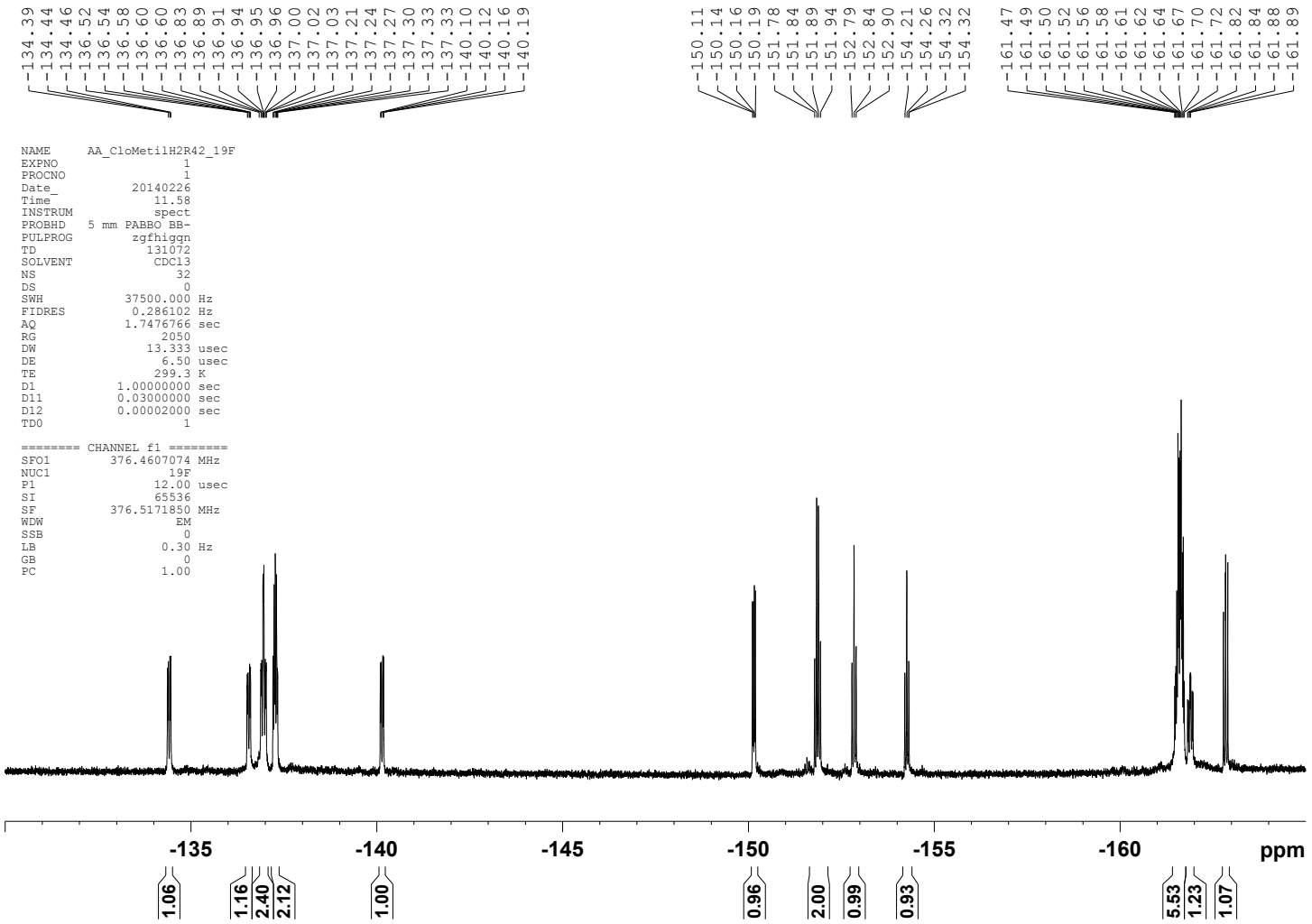


Figure S16. ^{19}F NMR spectrum of **4** (376 MHz, $CDCl_3$)

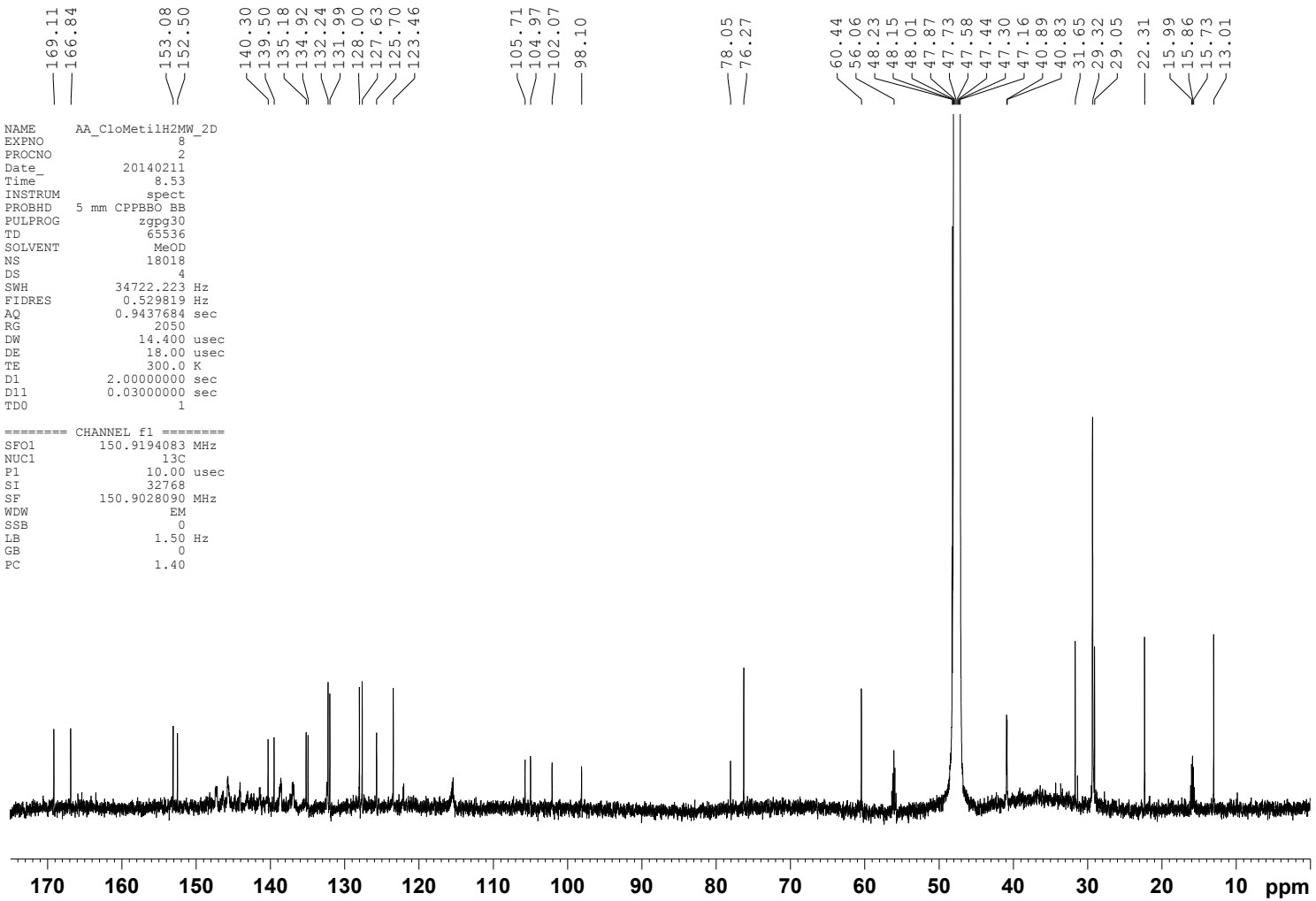


Figure S17. ^{13}C NMR spectrum of **4** (100 MHz, MeOD-d_4)

NMR spectra of bis-annulated chlorin 5

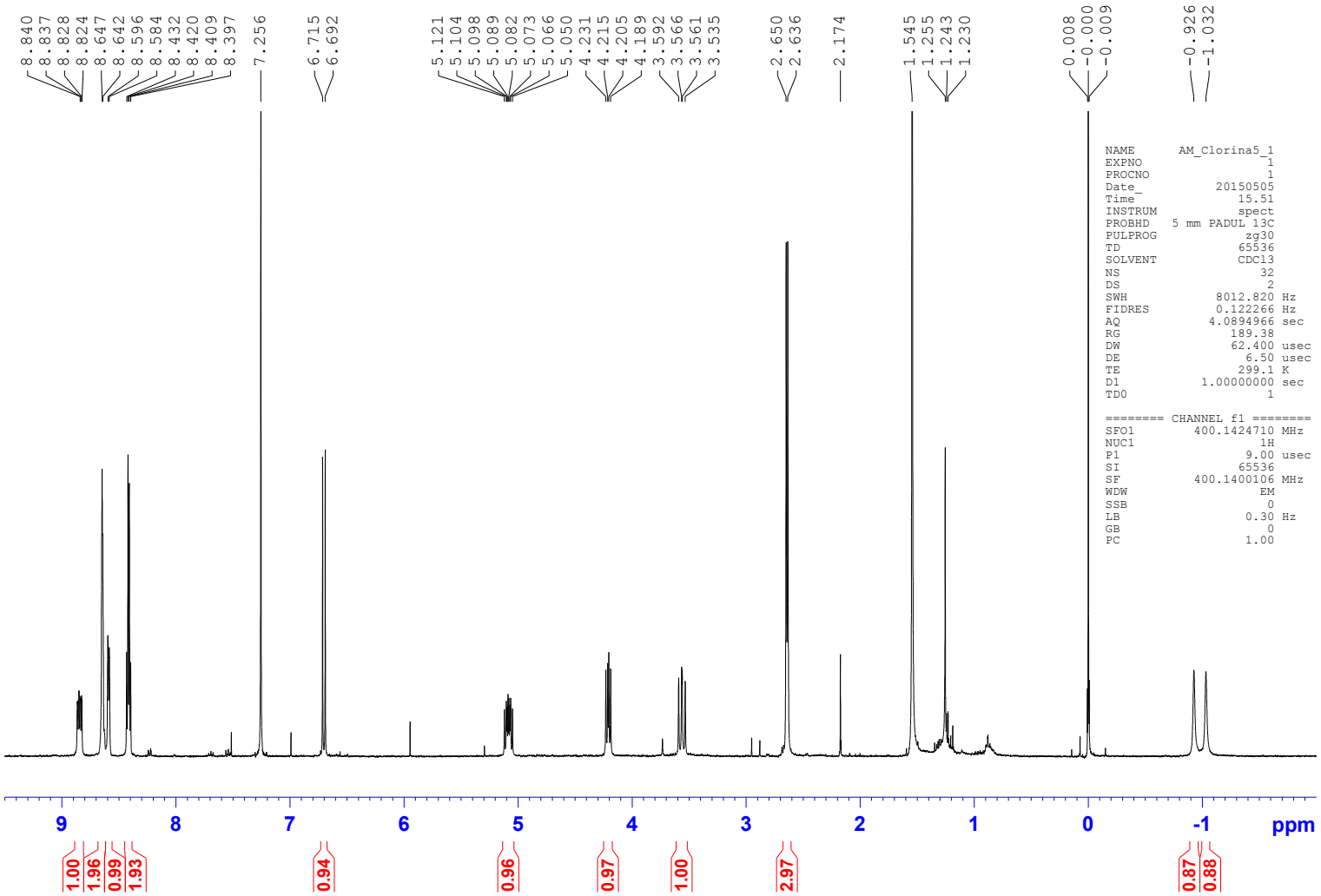


Figure S18. ^{1}H NMR spectrum of **5** (400 MHz, $CDCl_3$)

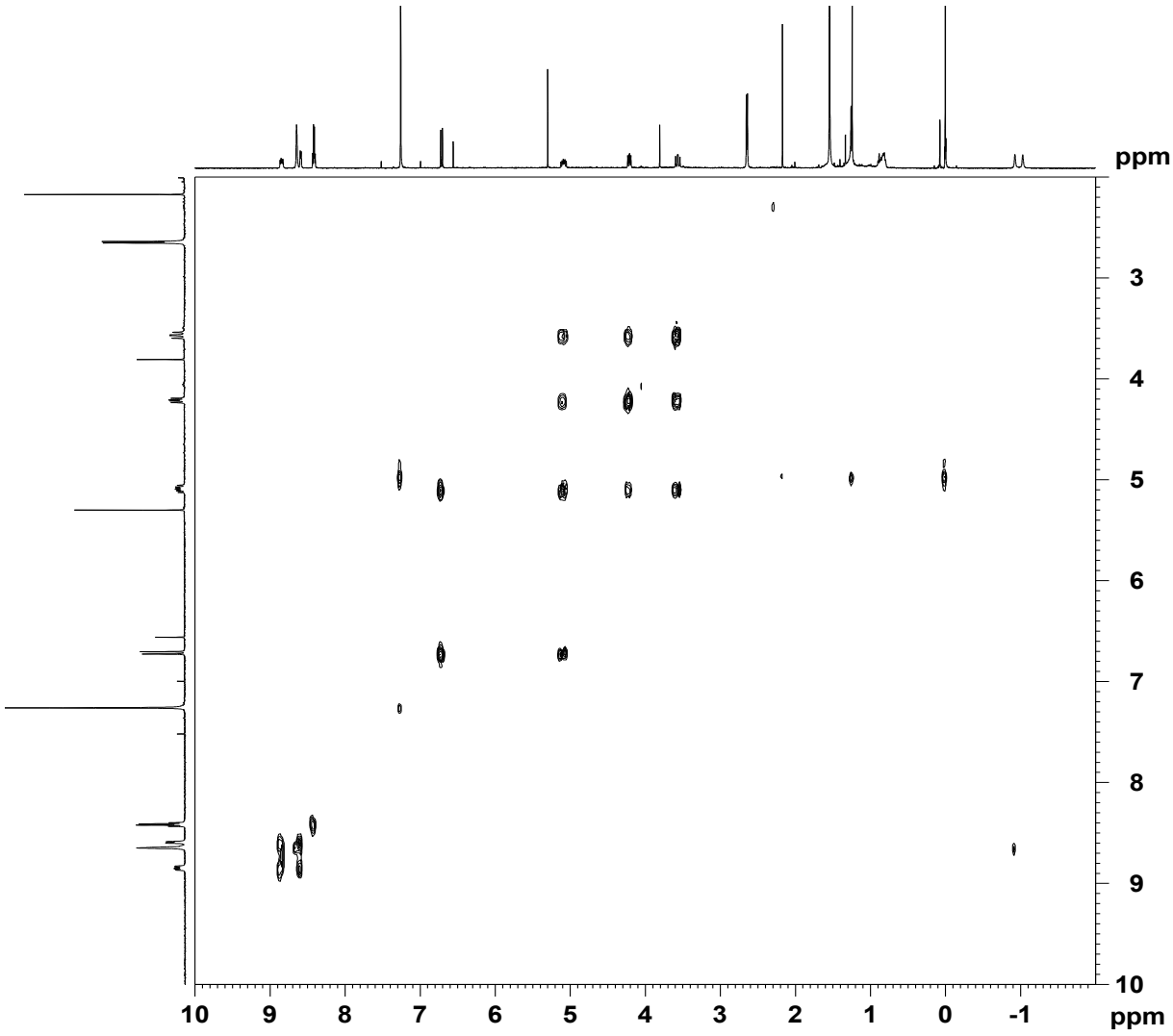


Figure S19. COSY of **5** ($CDCl_3$)

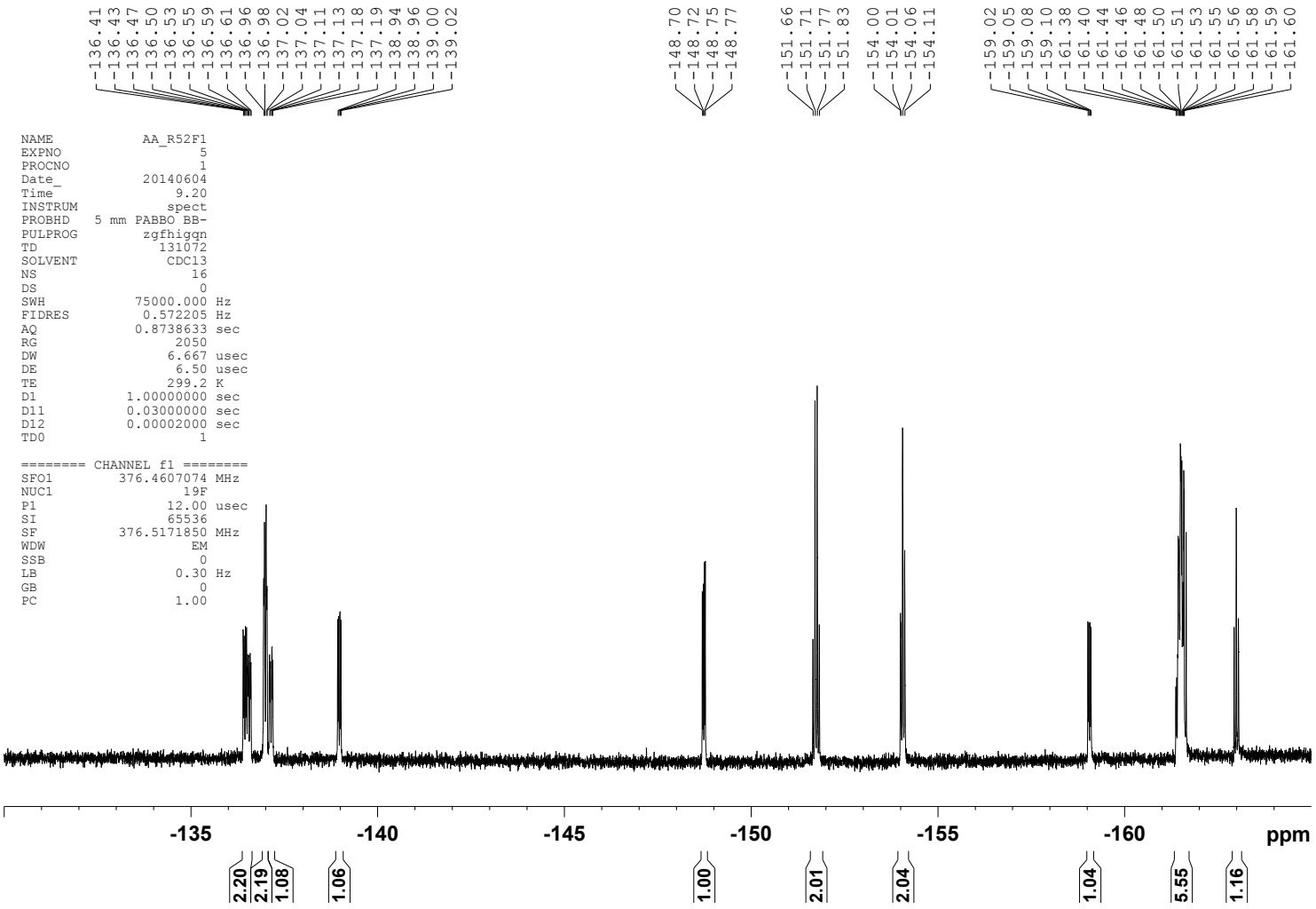


Figure S20. ^{19}F NMR spectrum of **5** (376 MHz, $CDCl_3$)

NMR spectra of methoxy chlorin 6

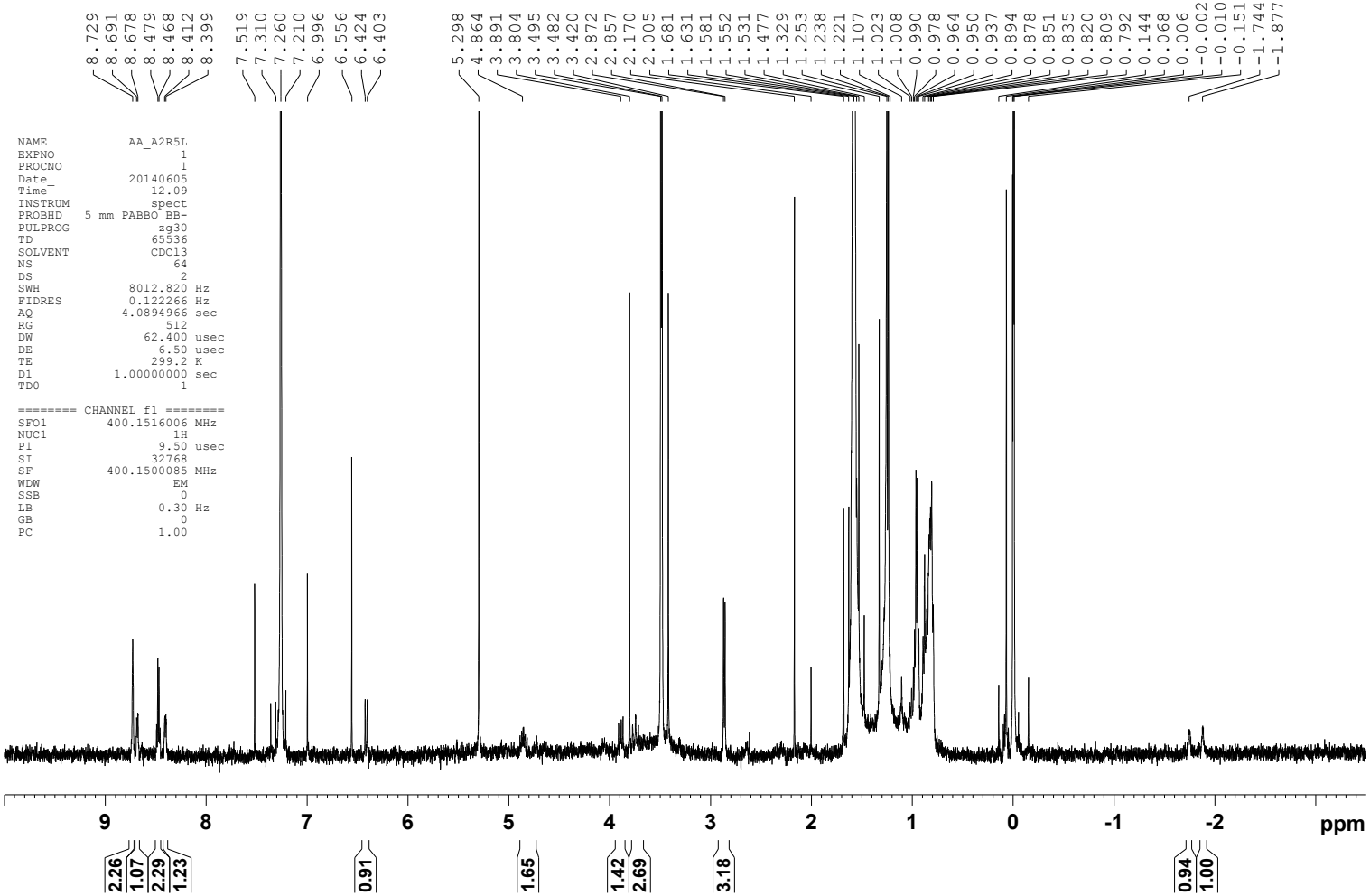


Figure S21. ^{1}H NMR spectrum of **6** (400 MHz, $CDCl_3$)

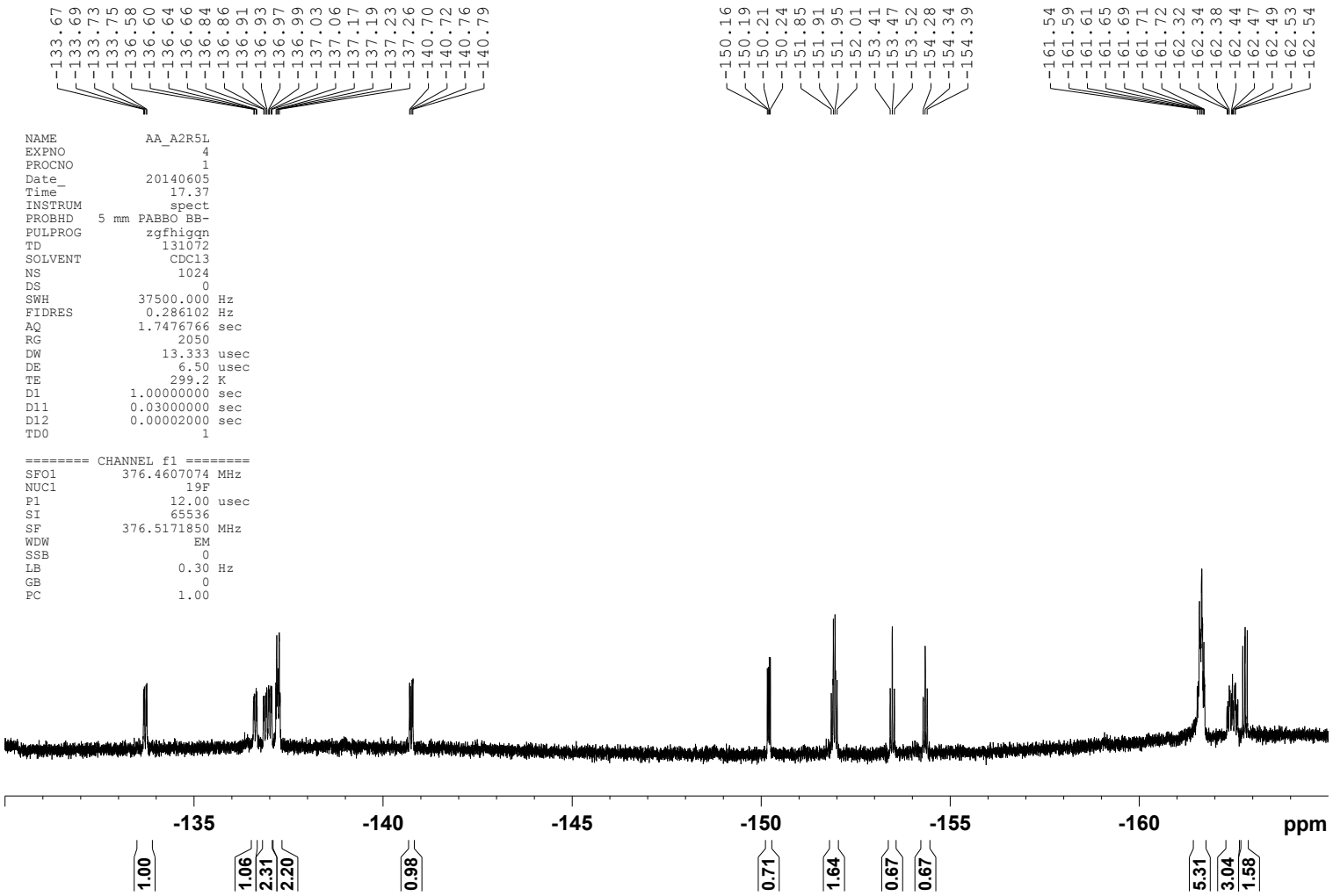


Figure S22. ^{19}F NMR spectrum of **6** (376 MHz, $CDCl_3$)

Comparison NMR spectra

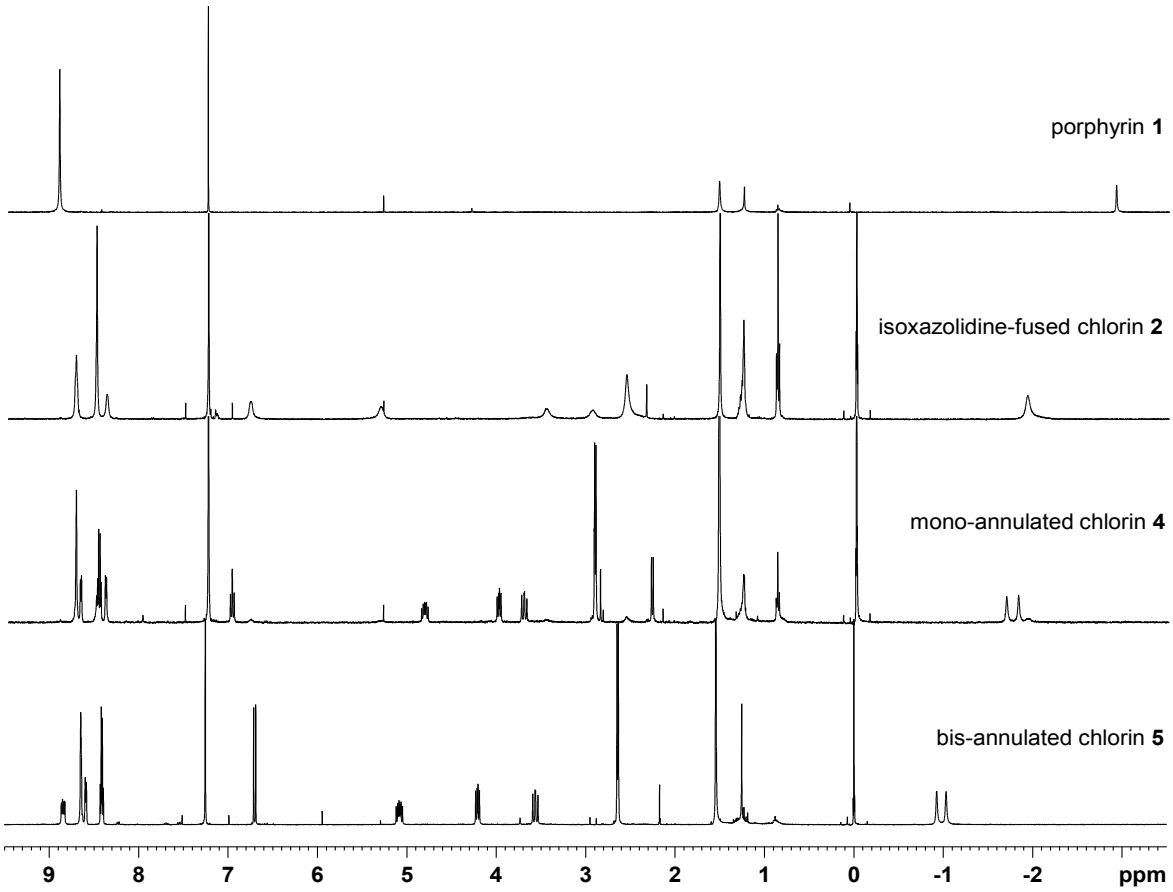


Figure S23. Comparison of ^{1}H NMR spectra of porphyrin **1** and chlorins **2, 4** and **5**, in $CDCl_3$.

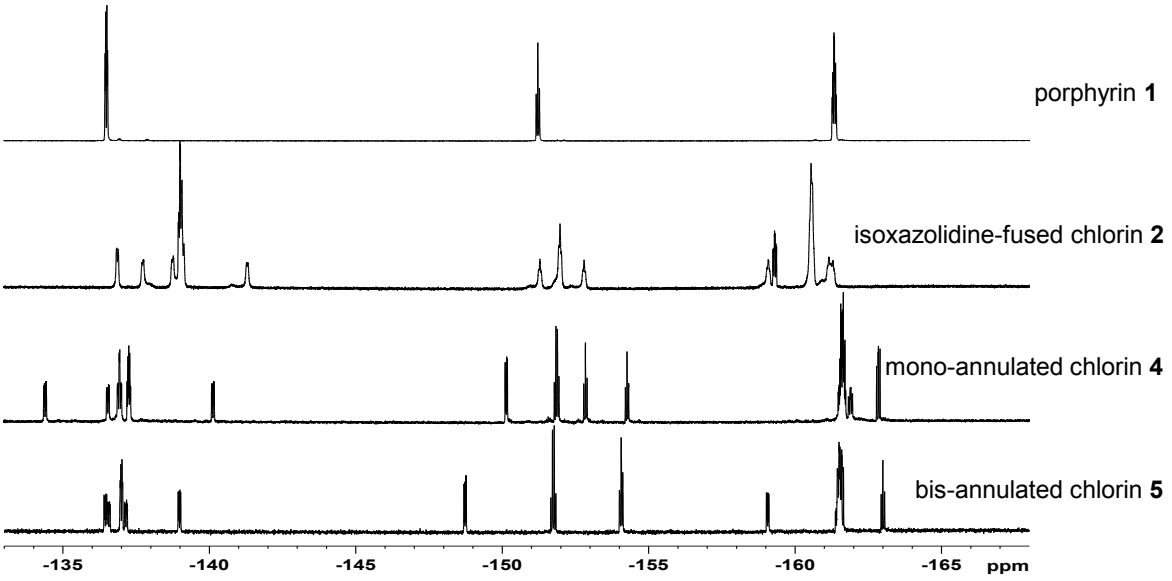


Figure S24. Comparison of ^{19}F NMR spectra of porphyrin **1** and chlorins **2, 4** and **5** in $CDCl_3$.

Table S1. ^{1}H NMR spectra data for synthesized chlorins **2**, **3**, **4**, **5** and **6**, in $CDCl_3$.

chlorins	pyrrolic β-H	β-H [C(sp^3)]	CH_2	CH_3	NH
2	8.37-8.43 (m), 8.52 (br s), 8.72-8.77 (m)	5.30-5.38 (m), 6.78-6.82 (m)	2.91-3.02 (m), 3.44-3.52 (m)	2.57 (s)	-1.91 (s br)
3	8.53-8.62 (m), 8.86-8.87 (m)	6.38-6.46 (m), 7.57-7.61 (m)	4.18-4.24 (m), 5.58-5.66 (m)	3.17 (s) 4.08 (s)	-2.23 (s) -2.18 (s)
4	8.41, 8.47 and 8.49 (3d, *J* 4.8), 8.69 (d, *J* 4.8), 8.74 (s)	4.82-4.84 (m), 6.99 (d, *J* 8.4)	3.73 (dd, *J* 12.8 and 10.4), 4.01 (dd, *J* 10.4 and 6.8)	2.93 (d, *J* 6.0)	-1.81 (s) -1.68 (s)
5	8.41, 8.43 and 8.59 (3d, *J* 4.5), 8.64-8.65 (m), 8.82-8.84 (m)	5.05-5.12 (m), 6.70 (d, *J* 9.2)	3.54-3.60 (m), 4.21 (dd, *J* 10.5 and 6.4)	2.64 (d, *J* 5.6)	-1.03 (s) -0.93 (s)
6	8.40, 8.47, 8.48 and 8.67 (4d, *J* 4.4), 8.72 (s)	4.82-4.89 (m), 6.41 (d, *J* 8.4)	3.70-3.81 (m), 3.85-3.95 (m)	2.86 (d, *J* 6.0) 3.80 (s, OCH_3)	-1.88 (s) -1.74 (s)

MS spectra

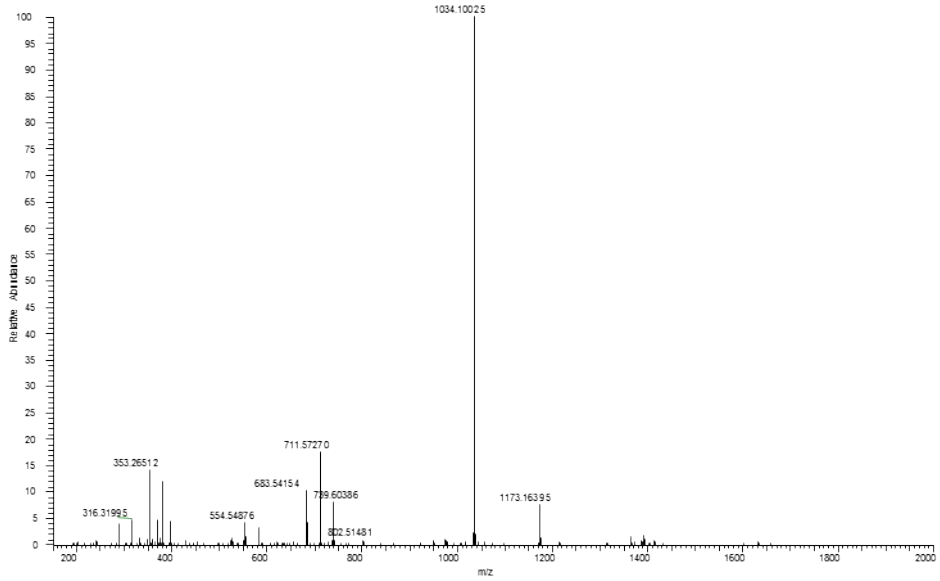


Figure S25. MS spectrum of isoxazolidine-fused chlorin **2**

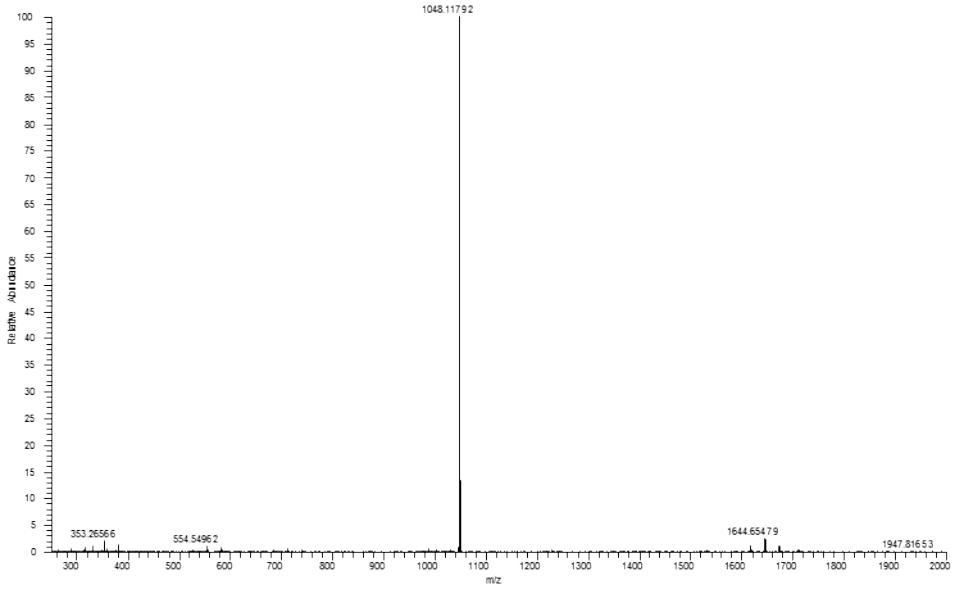


Figure S26. MS spectrum of cationic chlorin **3**

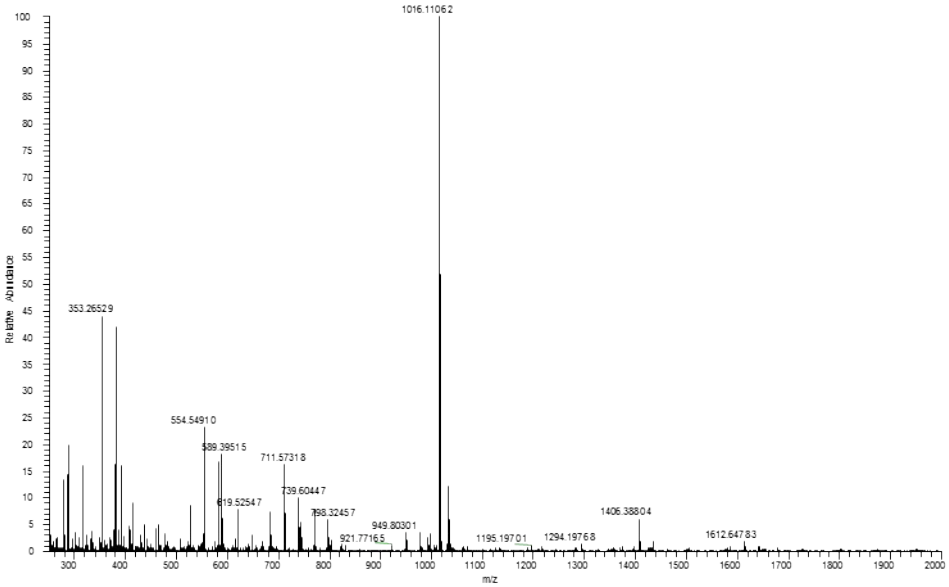


Figure S27. MS spectrum of mono-annulated chlorin **4**

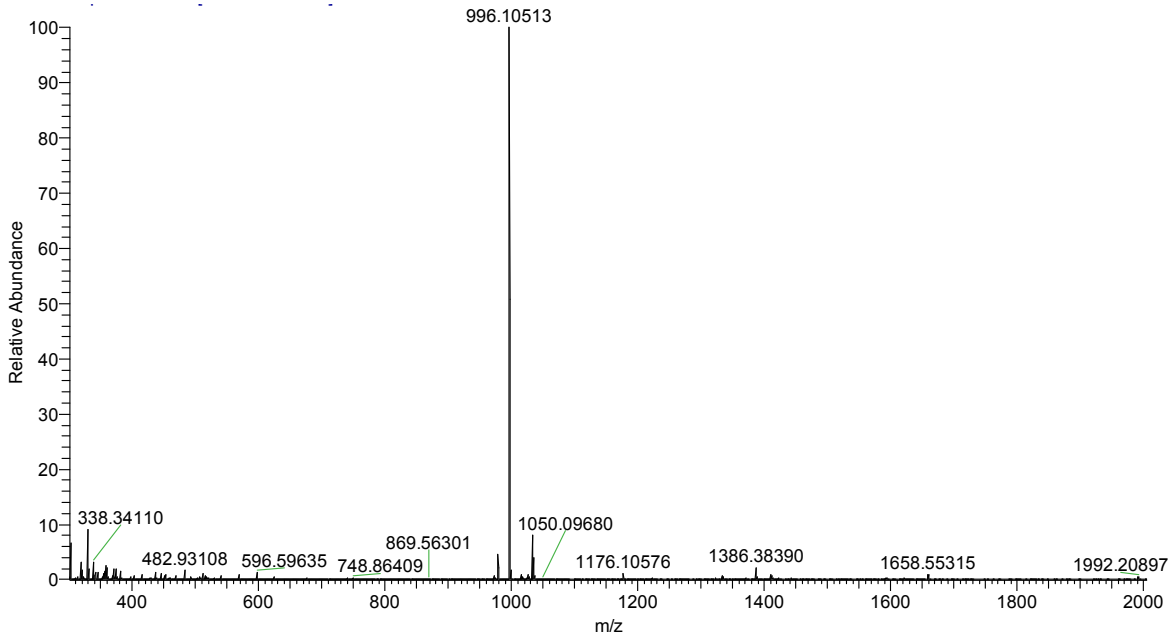


Figure S28. MS spectrum of bis-annulated chlorin **5**

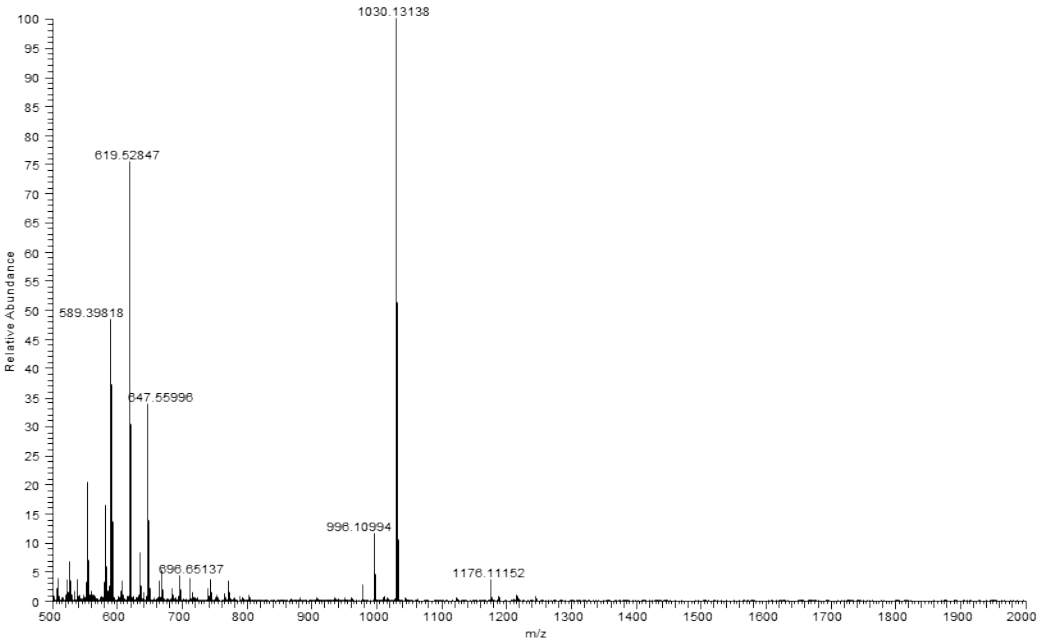


Figure S29. MS spectrum of methoxy chlorin **6**

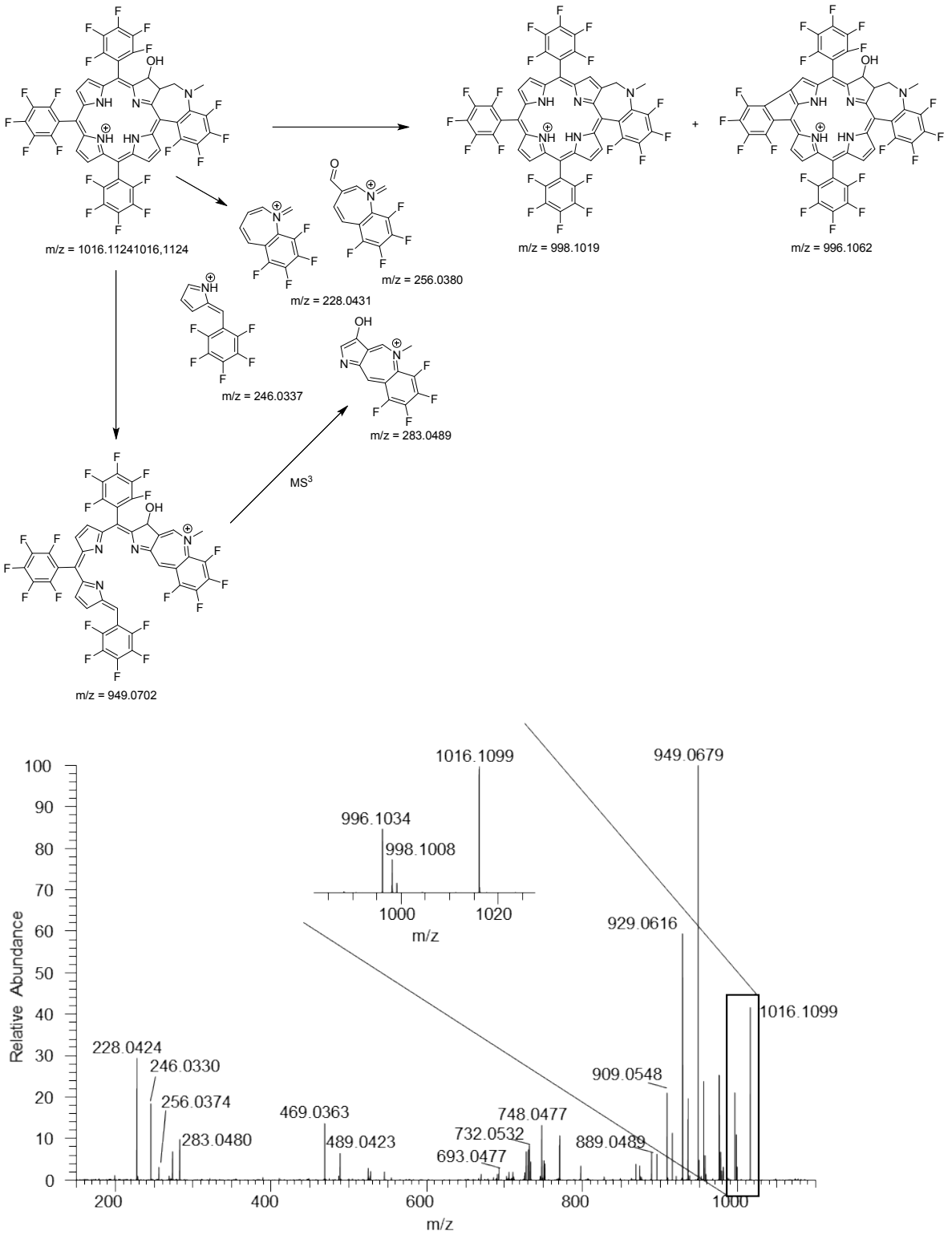


Figure S30. HCD-MS/MS spectrum and fragmentation pathways of mono-annulated chlorin **4**.

Absorption spectra data

Table S2. Absorption spectra data for synthesized compounds **1**, **2**, **3**, **4**, **5** and **6**, in methanol

compound	Absorption λ_{max}[nm] (ε [M^{-1} cm^{-1}])				
	B(0,0)	**Qy(1,0)**	**Qy(0,0)**	**Qx(1,0)**	**Qx(0,0)**
1	409 (1.6 x 10^5)	505 (1.9 x 10^4)	533 (2.3 x 10^3)	580 (5.6 x 10^3)	654 (1.0 x 10^3)
2	398 (1.9 x 10^5)	499 (1.1 x 10^4)	525 (2.7 x 10^3)	594 (3.4 x 10^3)	646 (4.0 x 10^4)
3	420 (6.2 x 10^4)	509 (5.2 x 10^3)	552 (2.0 x 10^3)	595 (2.2 x 10^3)	650 (6.0 x 10^3)
4	403 (5.5 x 10^4)	501 (5.6 x 10^3)	530 (3.0 x 10^3)	595 (2.9 x 10^3)	652 (1.4 x 10^4)
5	418 (8.2 x 10^4)	512 (3.7 x 10^3)	550 (6.7 x 10^3)	602 (1.2 x 10^3)	664 (1.7 x 10^4)
6	405 (1.0 x 10^5)	499 (7.6 x 10^3)	529 (4.0 x 10^3)	591 (2.1 x 10^3)	652 (2.4 x 10^4)

Fluorescence quantum yields

The fluorescence quantum yields φ_{F_x} of the synthetized chlorins were estimated from the emission and absorption spectra by a comparative method [S1] using the following equation,

$$\varphi_{F_x} = \left(\frac{A_s}{A_x}\right)\left(\frac{F_x}{F_s}\right)\left(\frac{n_x}{n_s}\right)^2\varphi_{F_s}$$

Where F_x and F_s are the integrated fluorescence intensities of the chlorins and the standard, A_x and A_s are the absorbances of chlorins and the standard at the excitation wavelength and φ_{F_s} the quantum yield of the standard sample. Free-base tetraphenylporphyrin (H_2TPP, φ_{F_s} = 0.11 in toluene)[S2] was used as standard for the determination of the chlorins quantum yield.

References

S1. N. C. Maiti and M. Ravikanth, *J. Chem. Soc.Faraday Trans.* 1996, **92**, 1095-1100.

S2. I. Gupta and M. Ravikanth, *J. Chem. Sci.* 2005, **117**, 161–166.