Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Design of an amphiphilic porphyrin exhibiting high *in vitro* photocytotoxicity

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Supporting Information

Content

Characterization spectra

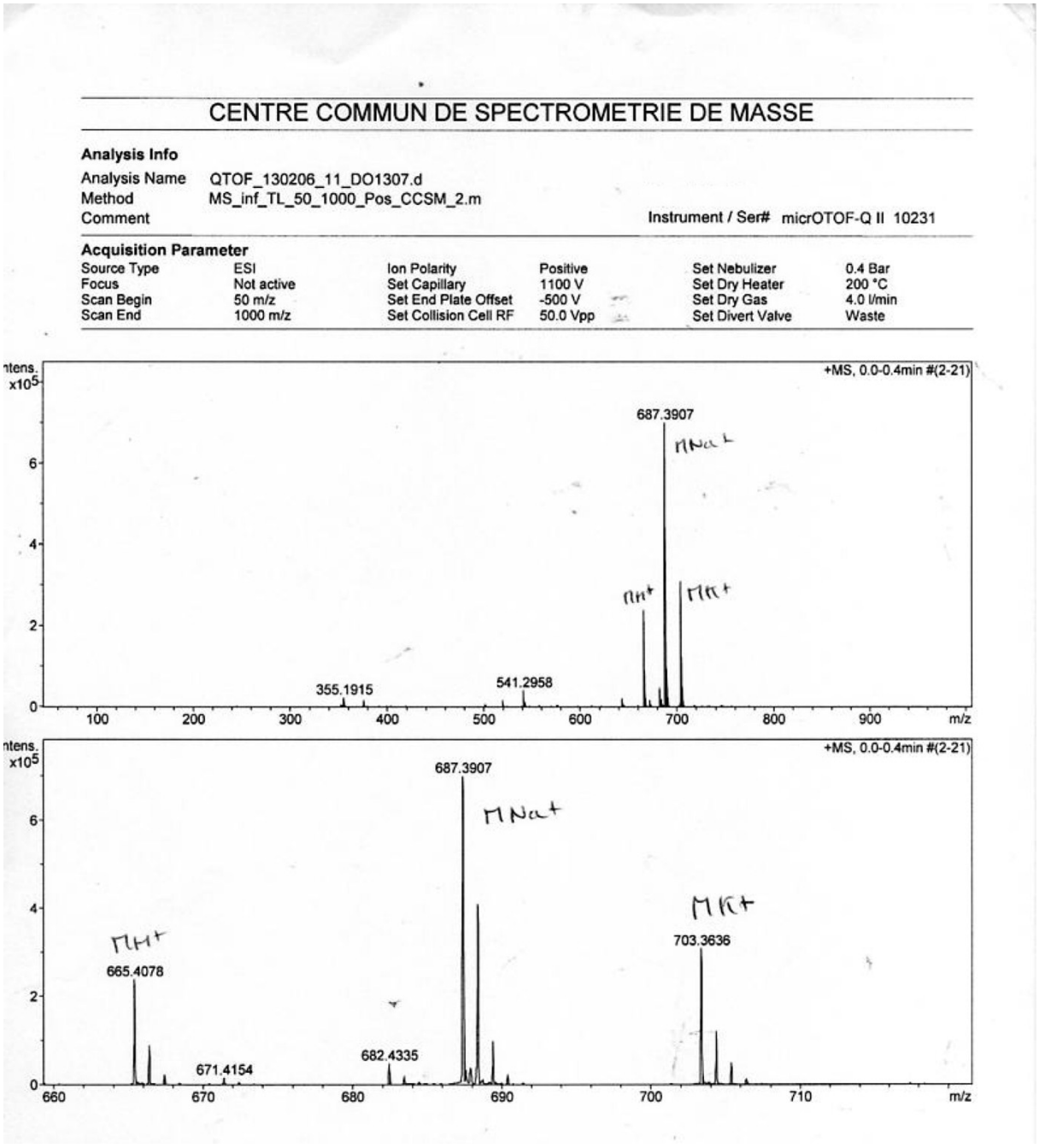


Figure S1 HRMS spectrum of **3**

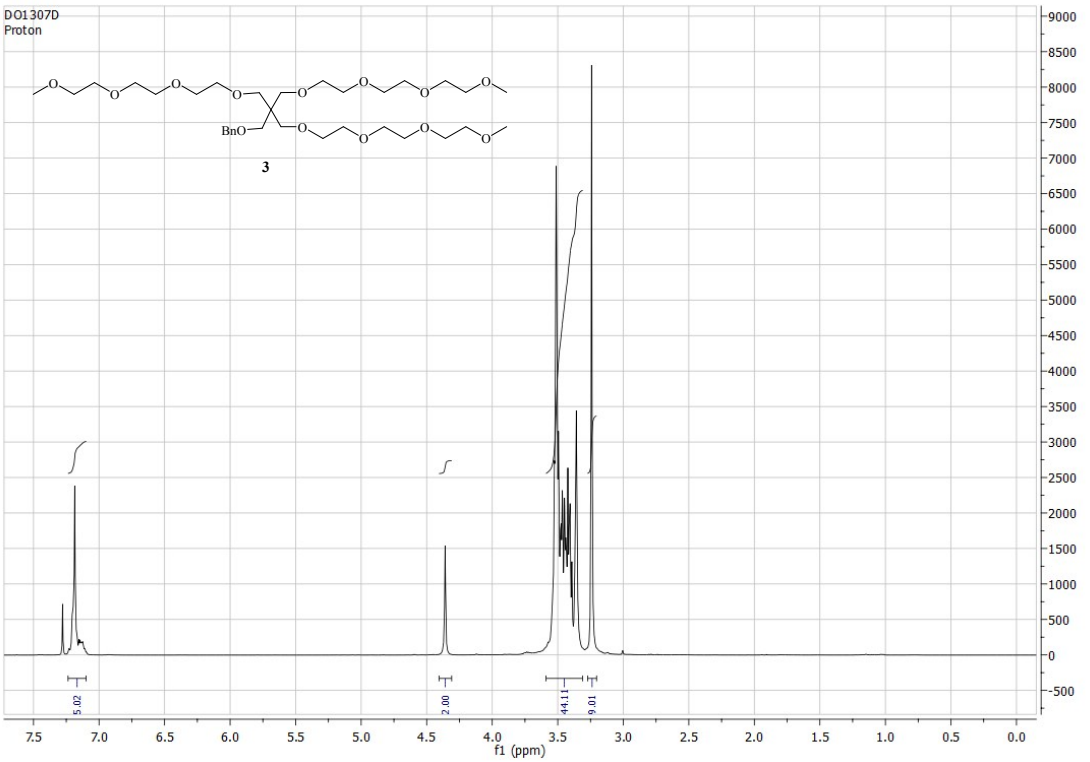


Figure S2 ^{1}H NMR spectrum of **3** (Bruker 300 MHz spectrometer, $CDCl_3$).

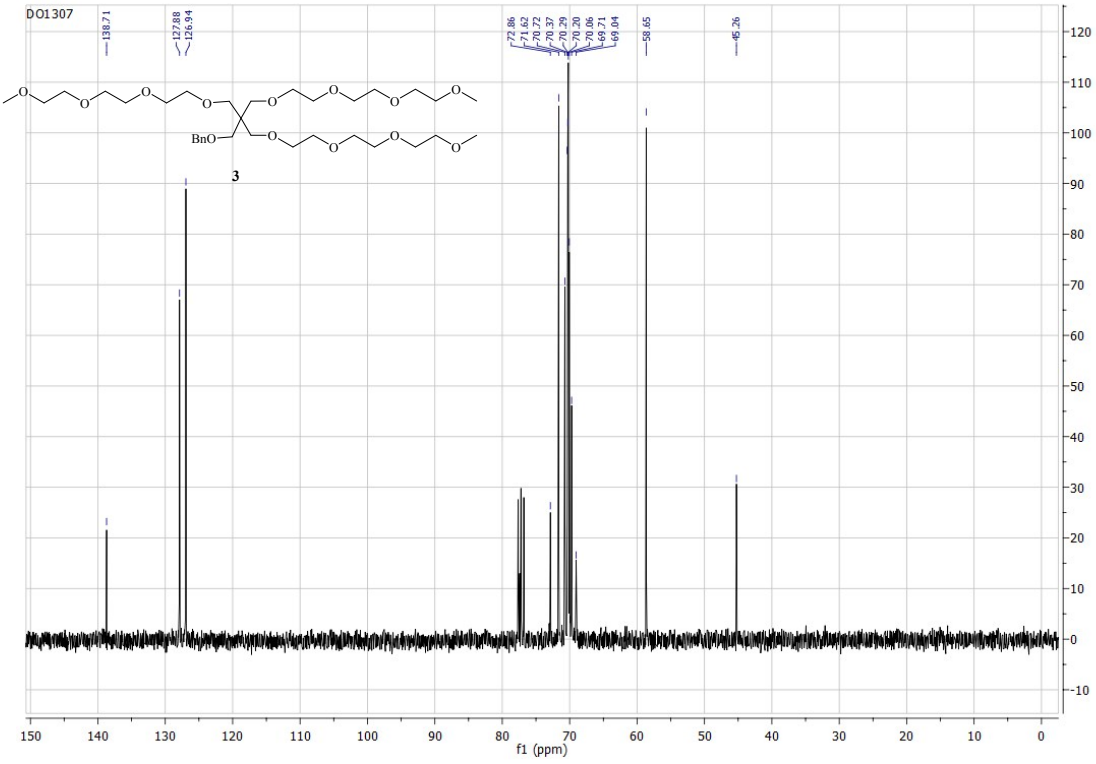


Figure S3 ^{13}C NMR spectrum of **3** (Bruker 300 MHz spectrometer, $CDCl_3$).

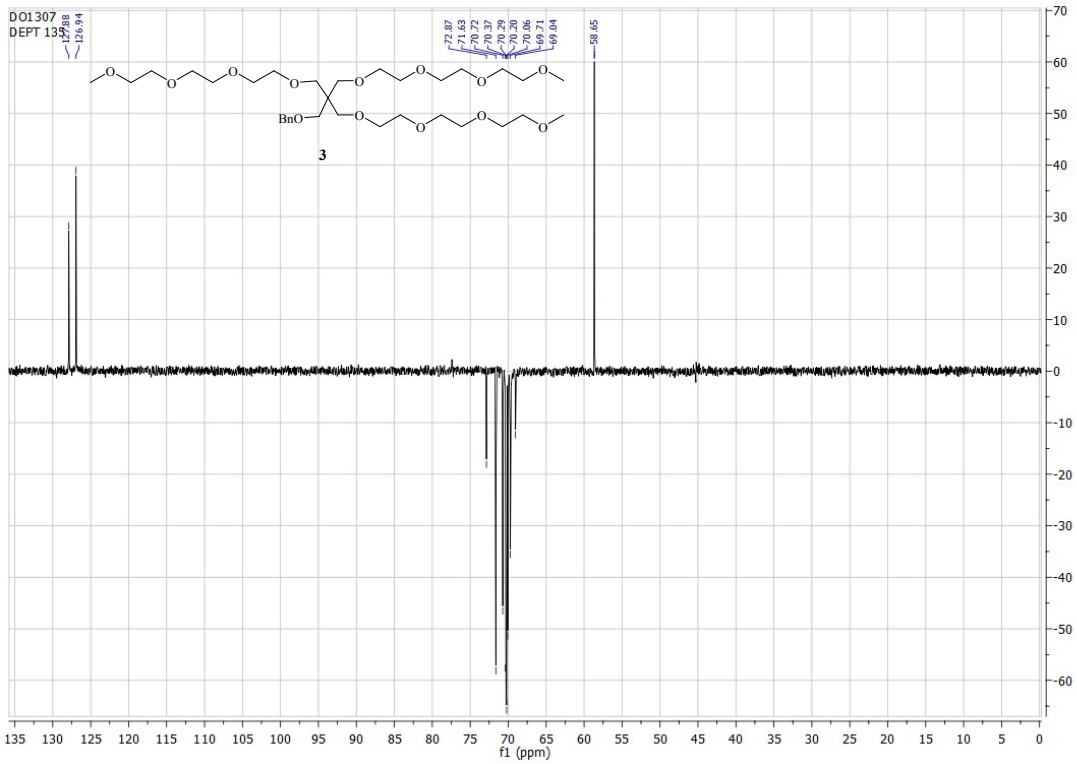


Figure S4 ^{13}C-DEPT NMR spectrum of **3** (Bruker 300 MHz spectrometer, $CDCl_3$).

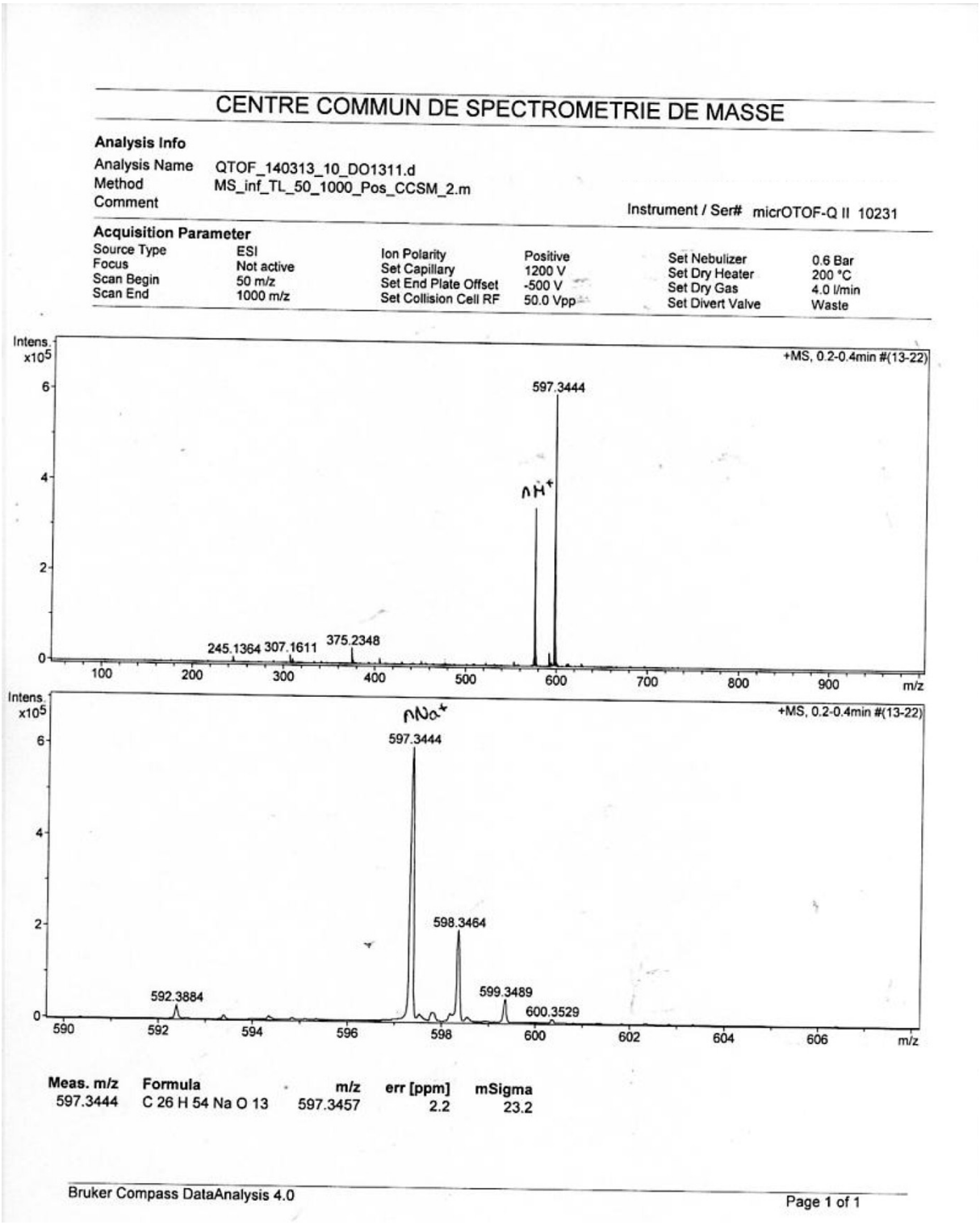


Figure S5 HRMS spectrum of **4**

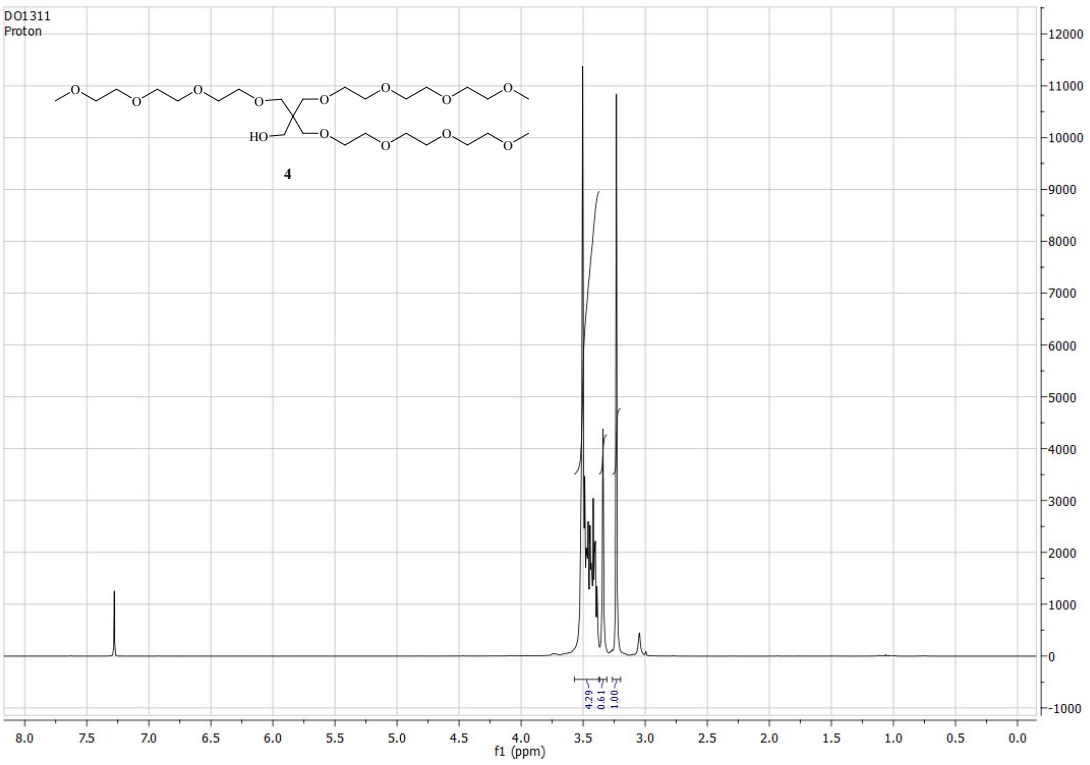


Figure S6 ^{1}H NMR spectrum of **4** (Bruker 300 MHz spectrometer, $CDCl_3$).

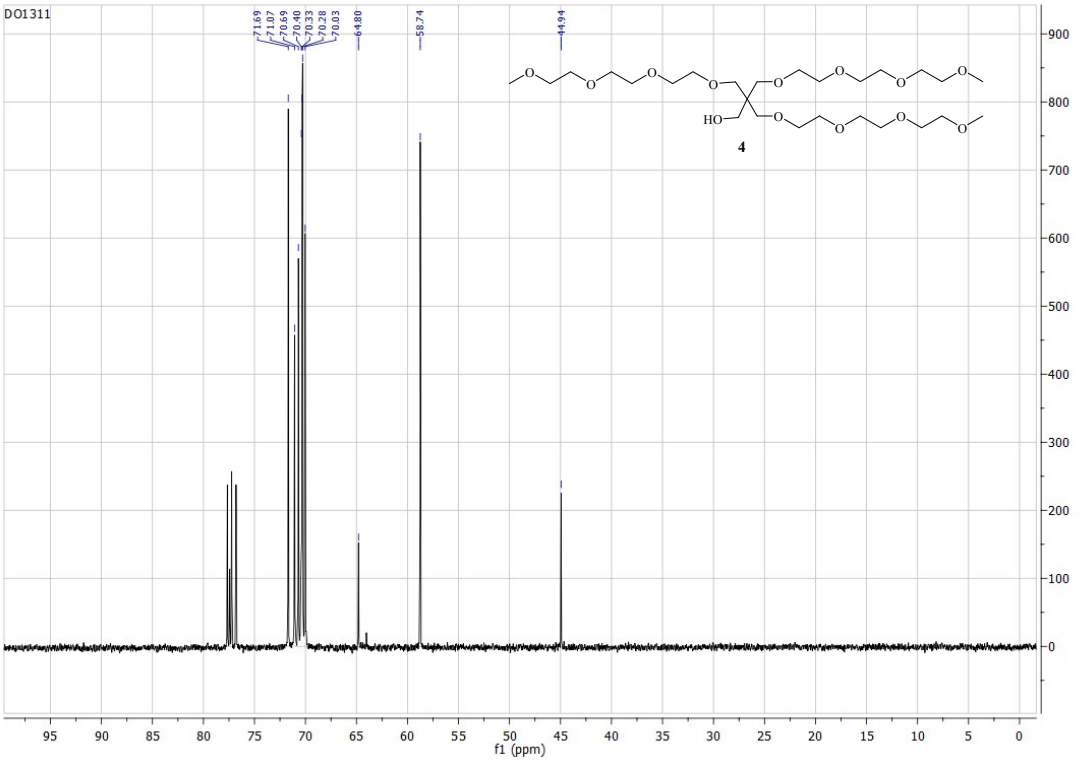


Figure S7 ^{13}C NMR spectrum of **4** (Bruker 300 MHz spectrometer, $CDCl_3$).

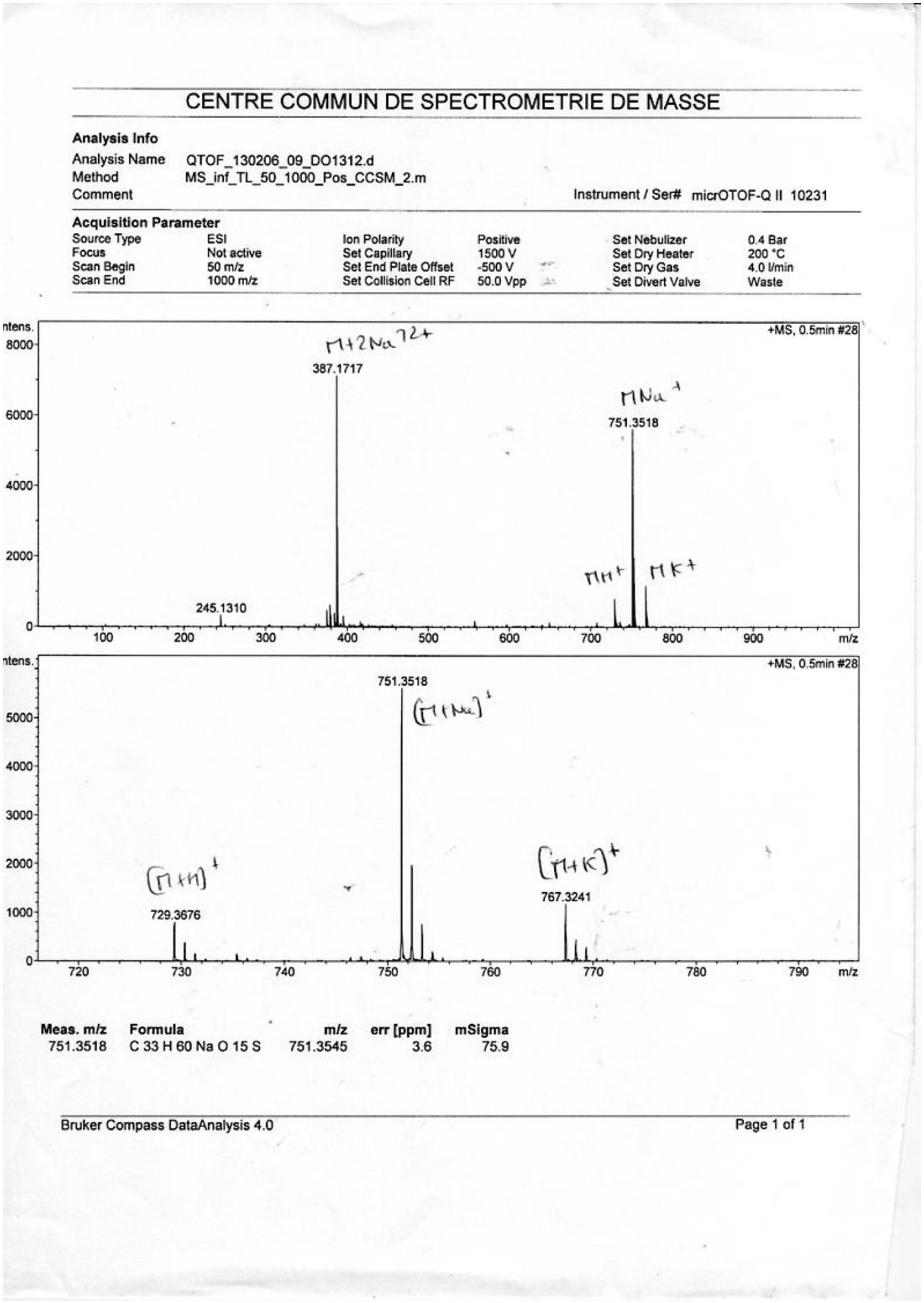


Figure S8 HRMS spectrum of **5**

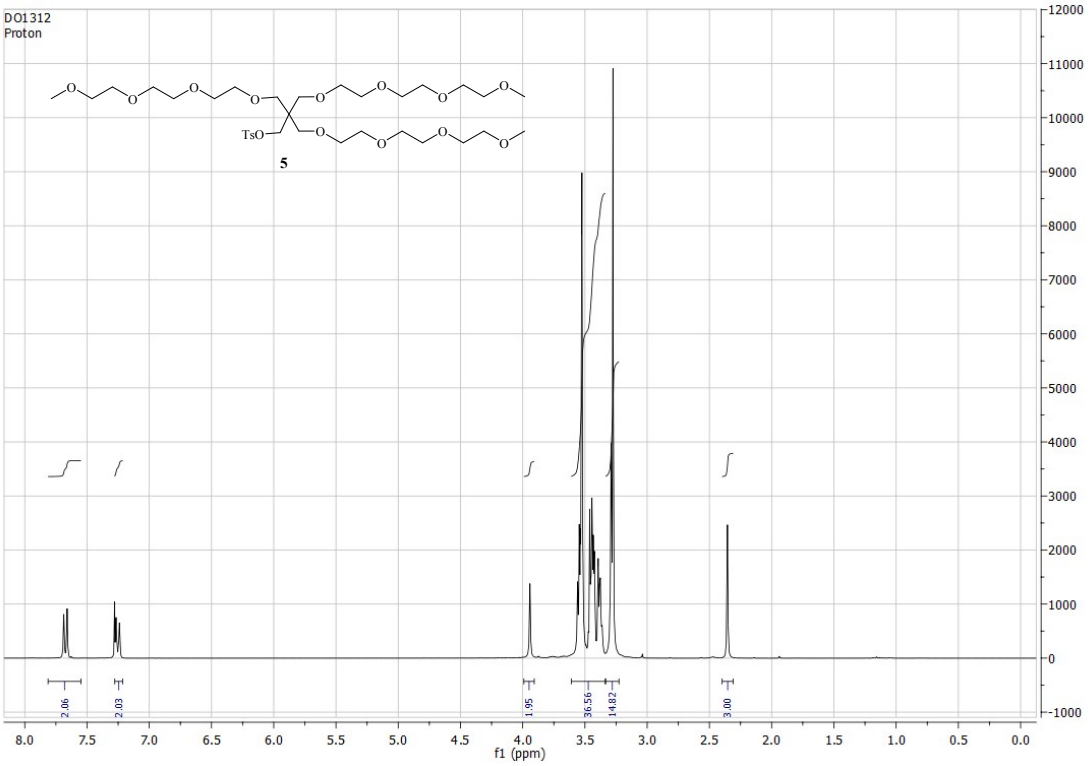


Figure S9 ^{1}H NMR spectrum of **5** (Bruker 300 MHz spectrometer, $CDCl_3$).

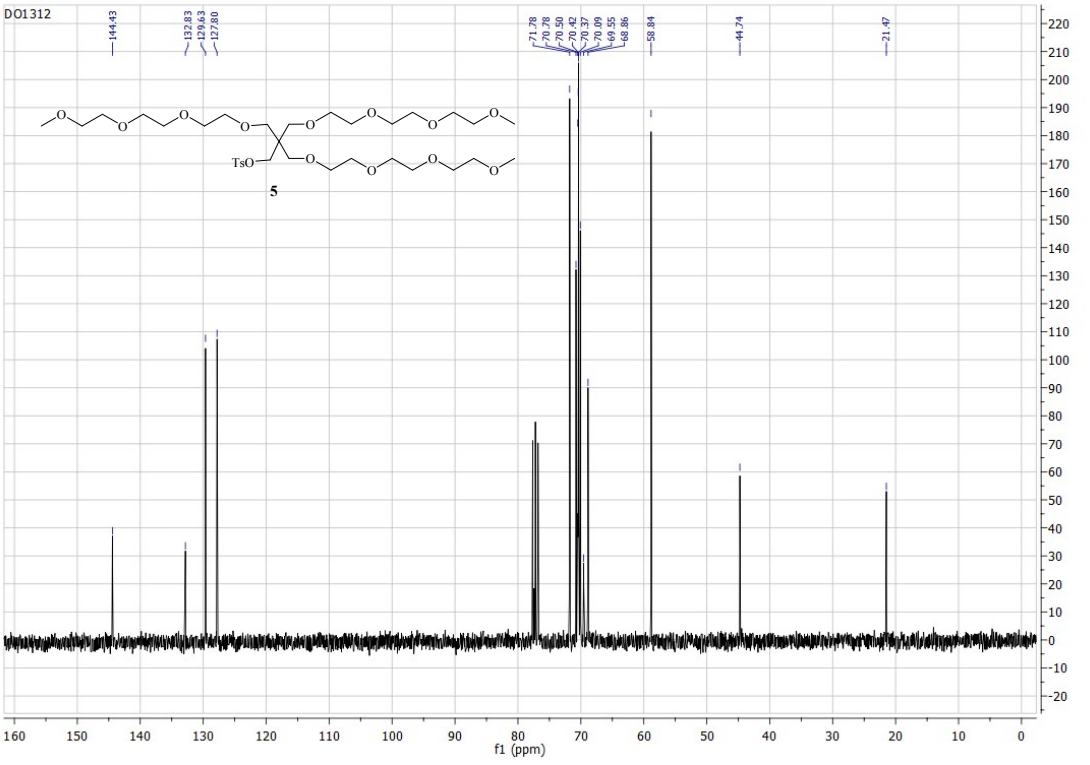


Figure S10 ^{13}C NMR spectrum of **5** (Bruker 300 MHz spectrometer, $CDCl_3$).

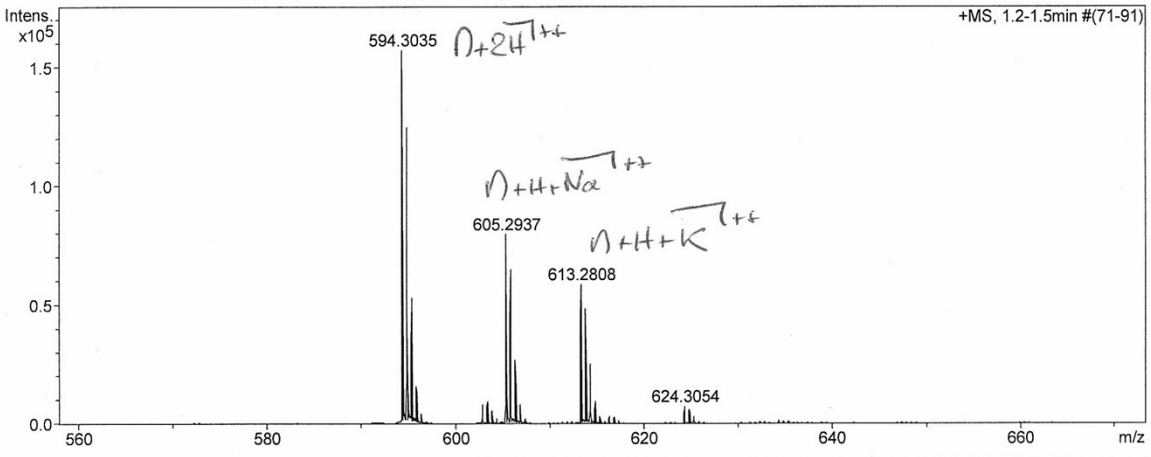
CENTRE COMMUN DE SPECTROMETRIE DE MASSE

Analysis Info

Analysis Name	QTOF_131122_07_DO1521.d
Method	MS_inf_TL_50_1000_Pos_CCSM_2.m
Comment	
Instrument / Ser#	micrOTOF-Q II 10231

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.6 Bar
Focus	Not active	Set Capillary	1500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Collision Cell RF	400.0 Vpp	Set Divert Valve	Waste



Meas. m/z	Formula	m/z	err [ppm]	mSigma
594.3035	C 70 H 84 N 4 O 13	594.3012	-3.8	4.5

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Figure S11 HRMS spectrum of **7**

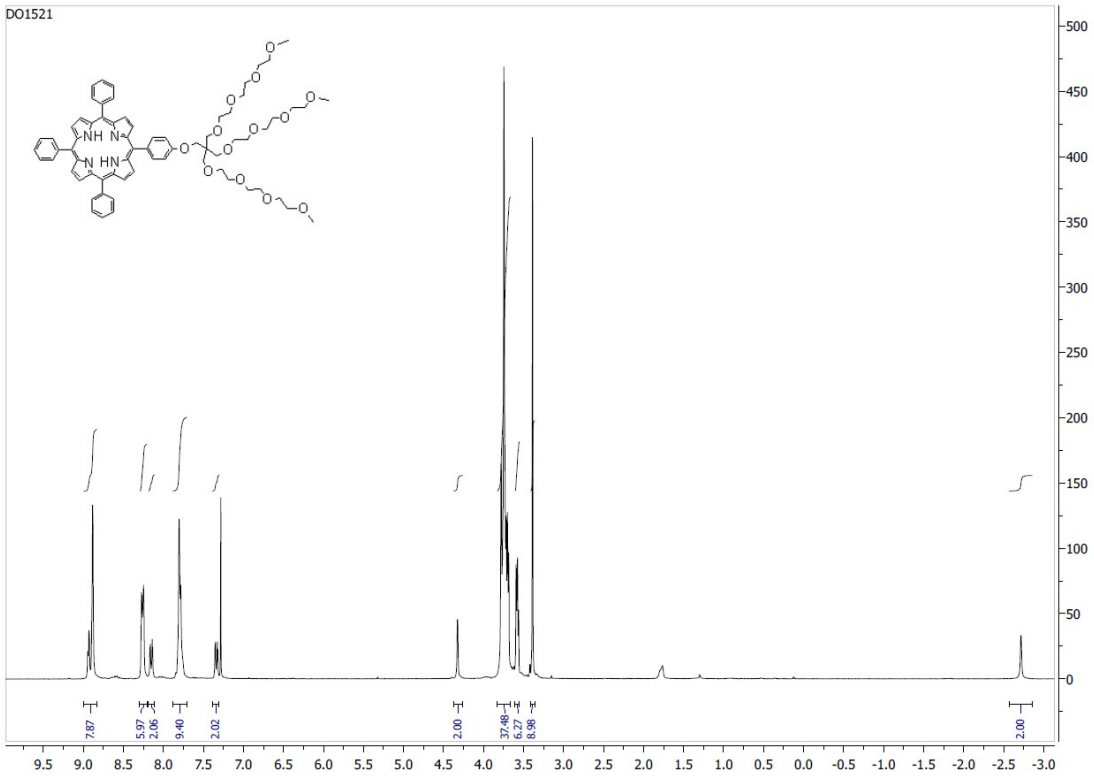

Figure S12 ^{1}H NMR spectrum of **7** (Bruker 300 MHz spectrometer, $CDCl_3$).

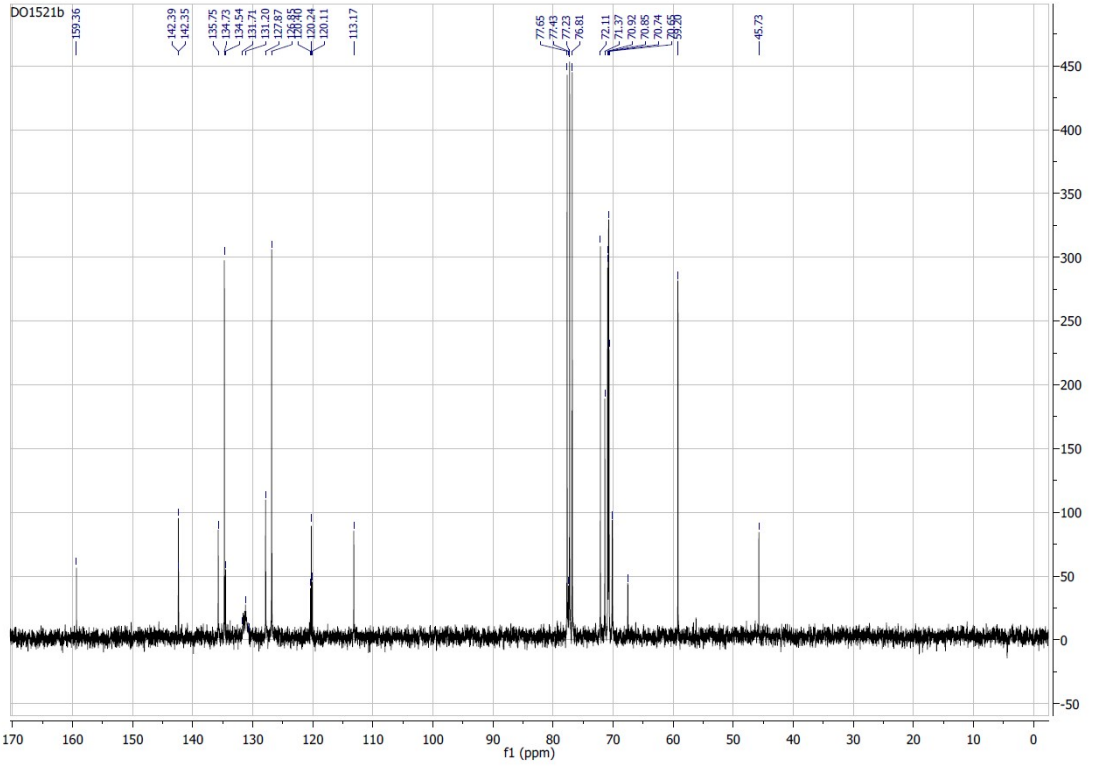

Figure S13 ^{13}C NMR spectrum of **7** (Bruker 300 MHz spectrometer, $CDCl_3$).

Photophysics and photochemistry

Table S1 Electronic absorption, fluorescence and singlet oxygen generation data for porphyrin **7** in chloroform. λ_{ex} : excitation wavelength, λ_{em} : emission wavelength, Φ_F: fluorescence quantum yield, τ_F: fluorescence lifetime, Φ_Δ: singlet oxygen quantum yield.

	λ_{abs} (nm)	log ε	λ_{em} (nm)[a]	Φ_F (%)[a,b]	τ_F (ns)	Φ_Δ (%)[d]
Soret	419	5.61	653 / 719	11	7.76[c]	76
Q^{IV}	516	4.23				
Q^{III}	552	3.94				
Q^{II}	591	3.75				
Q^{I}	646	3.65				

[a] λ_{exc} = 515 nm;

[b] using TPP in $CHCl_3$ as a reference (Φ_F = 0.11);

[c] λ_{exc} = 490 nm (Q^{IV});

[d] λ_{exc}= 420 nm, using phenalenone in $CHCl_3$ as reference (Φ_Δ= 0.98)[1]

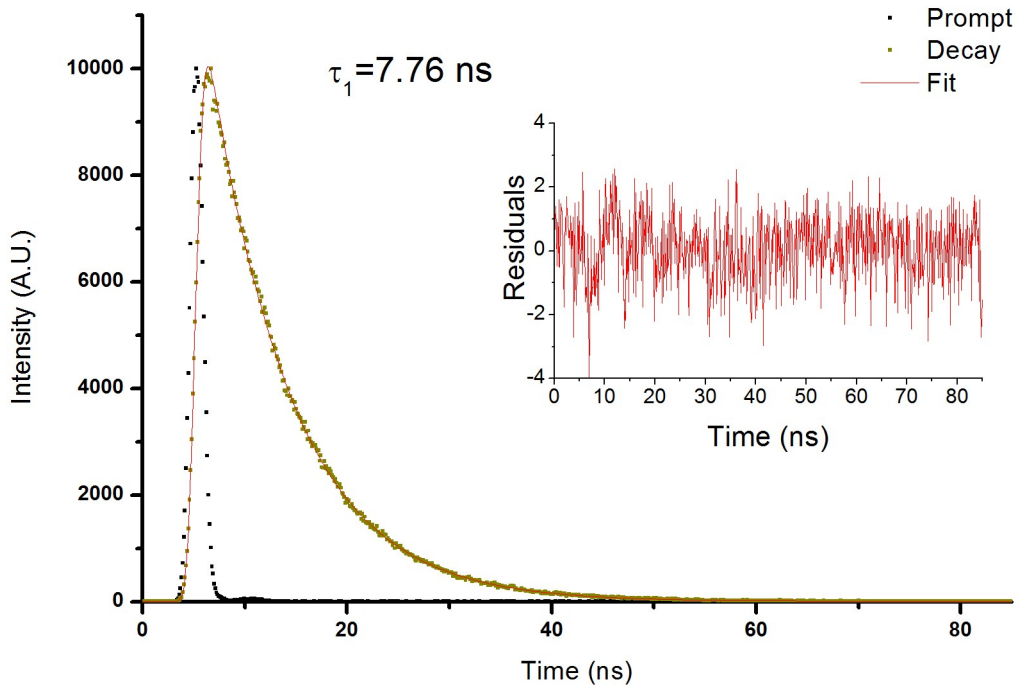

Figure S14 Time resolved fluorescence decay of **7** in $CHCl_3$ with the excitation source at λ_{exc}=490 nm while monitored at λ_{em}=725 nm. Inset: residual values after fitting.

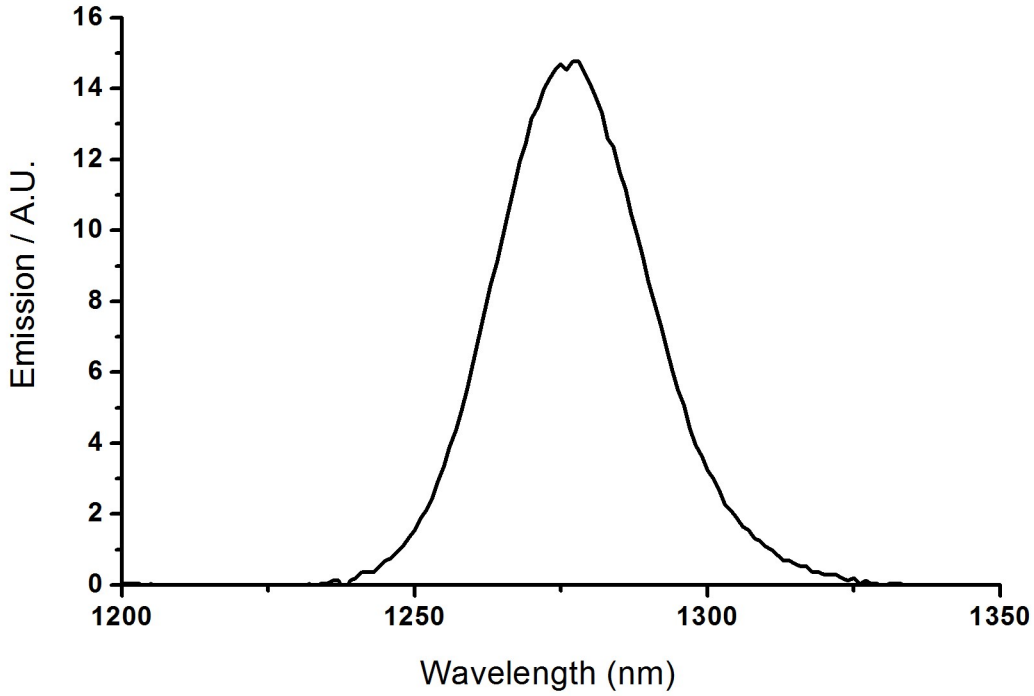

Figure S15 Singlet oxygen phosphorescence signal measured after excitation at λ_{exc}=420 nm.

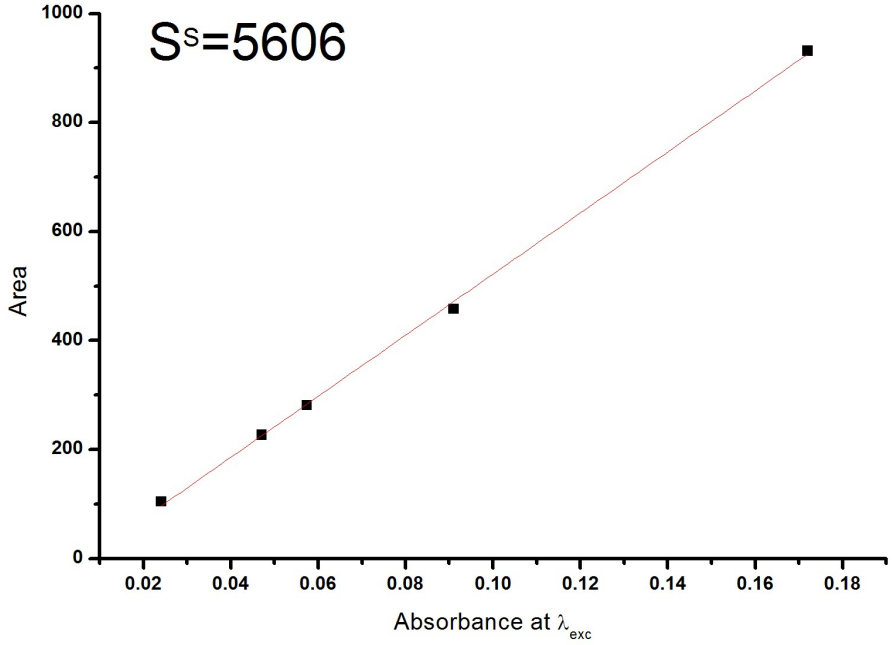

Figure S16 Plot of the integrated area under the $^1O_2$ emission spectrum *vs* the absorbance at λ_{exc}=420 nm for various solution of compound **7** in $CHCl_3$. The slops S^S was used for the determination of Φ_Δ the singlet oxygen generation quantum yield according to equation (1).

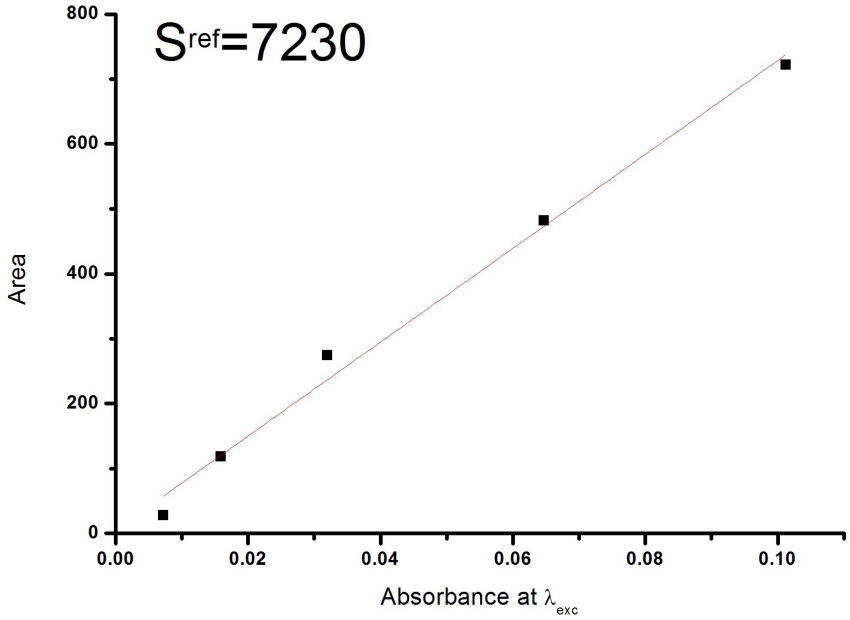

Figure S17 Plot of the integrated area under the $^1O_2$ emission spectrum *vs* the absorbance at λ_{exc}=420 nm for various solution of phenalenone in $CHCl_3$. The slope S^{ref} was used for the determination of Φ_Δ the singlet oxygen generation quantum yield according to equation (1).

Biological experiments

Table S2 Preparation of the final concentration solutions of porphyrin **7**, from DMSO stock solutions. For each experiment, a final volume of 4.5 mL (duplicate by plate, one plate for dark cytotoxicity and another one for the photo cytotoxicity) for each final concentration was prepared in culture medium and 1 mL was replaced in each well.

DMSO control cells were treated in duplicate with the following percentage of DMSO 0.3 %, 0.15 % and 0.075 %.

Concentration of **7** in stock solution (mM)	10	1	1	1	0.1	0.1
Volume of stock solution (µL)	3.375	13.5	6.75	3.375	13.5	6.75
Final volume (mL)	4.5	4.5	4.5	4.5	4.5	4.5
Final concentration of **7** (µM)	7.5	3	1.5	0.75	0.3	0.15
DMSO (%, v/v)	0.075	0.3	0.15	0.075	0.3	0.15

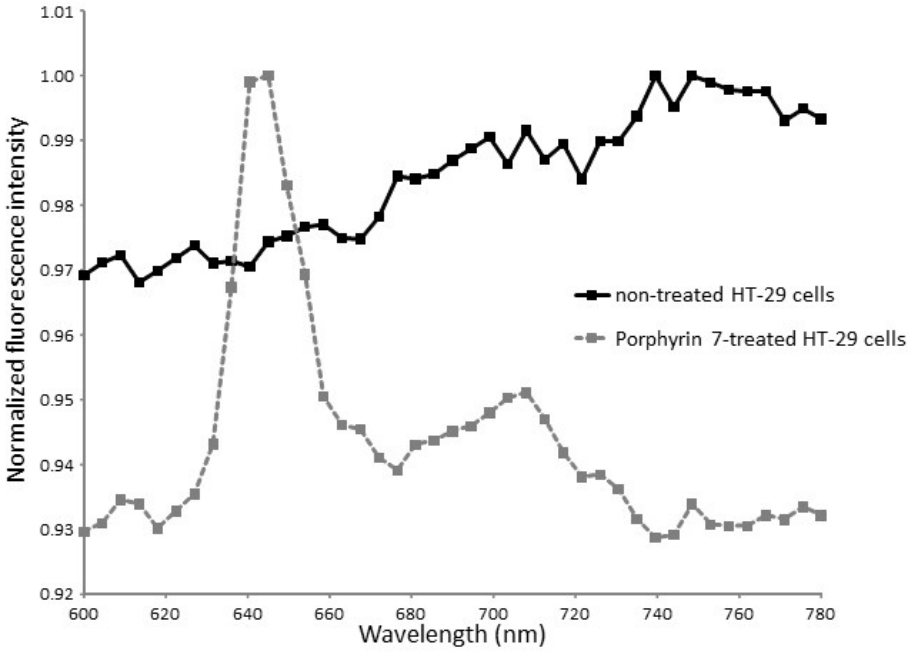

Figure S18 Wide field fluorescence emission spectra of non-treated HT-29 cells (black) and porphyrin **7** treated HT-29 cells (grey). Spectra were acquired at 514 nm and fluorescence emission was recorded between 600 and 780 nm with a step size of 4.5 nm. The fluorescence intensity was normalized relatively to the maximum of each spectrum. The fluorescence emission spectra of treated cells showed the specific spectrum of the porphyrin **7** while the non-treated HT-29 spectrum is linear.

Reference

[1] Schmidt, R.; Tanielian, C.; Dunsbach, R.; Wolff, C. Phenalenone, a universal reference compound for the determination of quantum yields of singlet oxygen $O_2(1\Delta g)$ sensitization. *J. Photochem. Photobiol. A: Chem.* **1994**, 79, 11-17.