Electronic Supplementary Material (ESI) for RSC Medicinal Chemistry. This journal is © The Royal Society of Chemistry 2021

## Supporting Information

## Novel fluorinated ring-fused chlorins as promising PDT agents against melanoma and esophagus cancer

Nelson A. M. Pereira,<sup>1</sup> Mafalda Laranjo,<sup>2,3,4</sup> Bruno F. O. Nascimento,<sup>1</sup> João C. S. Simões,<sup>1,2</sup> João Pina,<sup>1</sup> Bruna D. P. Costa,<sup>1,2</sup> Gonçalo Brites,<sup>2</sup> João Braz,<sup>1,2</sup> J. Sérgio Seixas de Melo,<sup>1</sup> Marta Piñeiro,<sup>1</sup> Maria Filomena Botelho,<sup>2,3,4</sup> Teresa M. V. D. Pinho e Melo<sup>1</sup>\*

<sup>1</sup>University of Coimbra, Coimbra Chemistry Centre (CQC) and Department of Chemistry, 3004-535 Coimbra, Portugal <sup>2</sup>University of Coimbra, Institute of Biophysics and Institute for Clinical and Biomedical Research (iCBR), area of Environment Genetics and Oncobiology (CIMAGO), Faculty of Medicine, 3000-548 Coimbra, Portugal <sup>3</sup>University of Coimbra, Center for Innovative Biomedicine and Biotechnology (CIBB), 3000-548 Coimbra, Portugal <sup>4</sup>Clinical and Academic Centre of Coimbra, 3000-548 Coimbra, Portugal

\*tmelo@ci.uc.pt

## **Table of contents**

| I.  | NMR Spectra of Compounds 4-8.                | S2 |
|-----|--|----|
| II. | Photophysical Spectra of Chlorins 4 and 6-8. | S9 |



Figure S1. (a) <sup>1</sup>H NMR spectrum (top) and (b) <sup>19</sup>F NMR spectrum (bottom) of porphyrin 5 in DMSO- $d_6$ .



Figure S2. (a) <sup>1</sup>H NMR spectrum (top) and (b) <sup>19</sup>F NMR spectrum (bottom) of chlorin 4 in CDCl<sub>3</sub>.



Figure S2. (c) <sup>13</sup>C NMR spectrum of chlorin 4 in CDCl<sub>3</sub>.



Figure S3. (a) <sup>1</sup>H NMR spectrum (top) and (b) <sup>19</sup>F NMR spectrum (bottom) of chlorin 6 in CDCl<sub>3</sub>.



Figure S4. (a) <sup>1</sup>H NMR spectrum (top) and (b) <sup>19</sup>F NMR spectrum (bottom) of chlorin 7 in CDCl<sub>3</sub>.





Figure S5. (a) <sup>1</sup>H NMR spectrum (top) and (b) <sup>19</sup>F NMR spectrum (bottom) of chlorin 8 in CD<sub>4</sub>O.



**Figure S6.** Room temperature time-resolved triplet-singlet difference absorption spectra for chlorins **4** and **6-8** in deaerated DMSO solutions, measured at various times after 355 nm nanosecond laser flash spectroscopy (12, 24, 40, 80, 120 and 160 µs delay after flash).



**Figure S7-** Plots of the initial phosphorescence of singlet oxygen at 1270 nm as a function of laser intensity together with the best fits to the linear part of the curve for the reference compound, *meso*-tetraphenylporphyrin (TPP), and chlorins **4**, **6** and **7** in air saturated toluene and dimethyl sulfoxide solutions, respectively, at 293 K.