Supporting information:

Synthesis, Characterization and Optical Properties of New Tetrafluorenyl-Porphyrins Peripherally functionalized with Conjugated 2-Fluorenone Groups

Xu Zhang,[a] Zhipeng Sun,[a] Nicolas Richy,[a] Olivier Mongin,[a] Frédéric Paul,*[,a] Mireille Blanchard-Desce,*[,b] Christine O. Paul-Roth,*[,a]

[a] *Univ Rennes, INSA Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) – UMR 6226, F-35000 Rennes, France*

[b] *Université de Bordeaux, Institut des Sciences Moléculaires (CNRS UMR 5255), 33405 Talence, France*

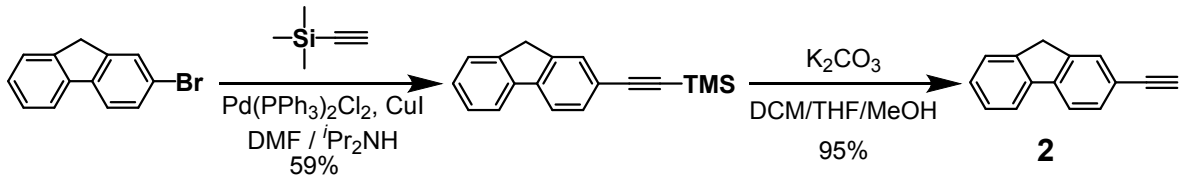
*Corresponding authors: christine.paul@insa-rennes.fr and frederic.paul@univ-rennes1.fr and mireille.blanchard-desce@u-bordeaux.fr

tel : (+33) (0) 2 23 23 63 72 fax: (+33) (0) 2 23 23 63 72

Contents:

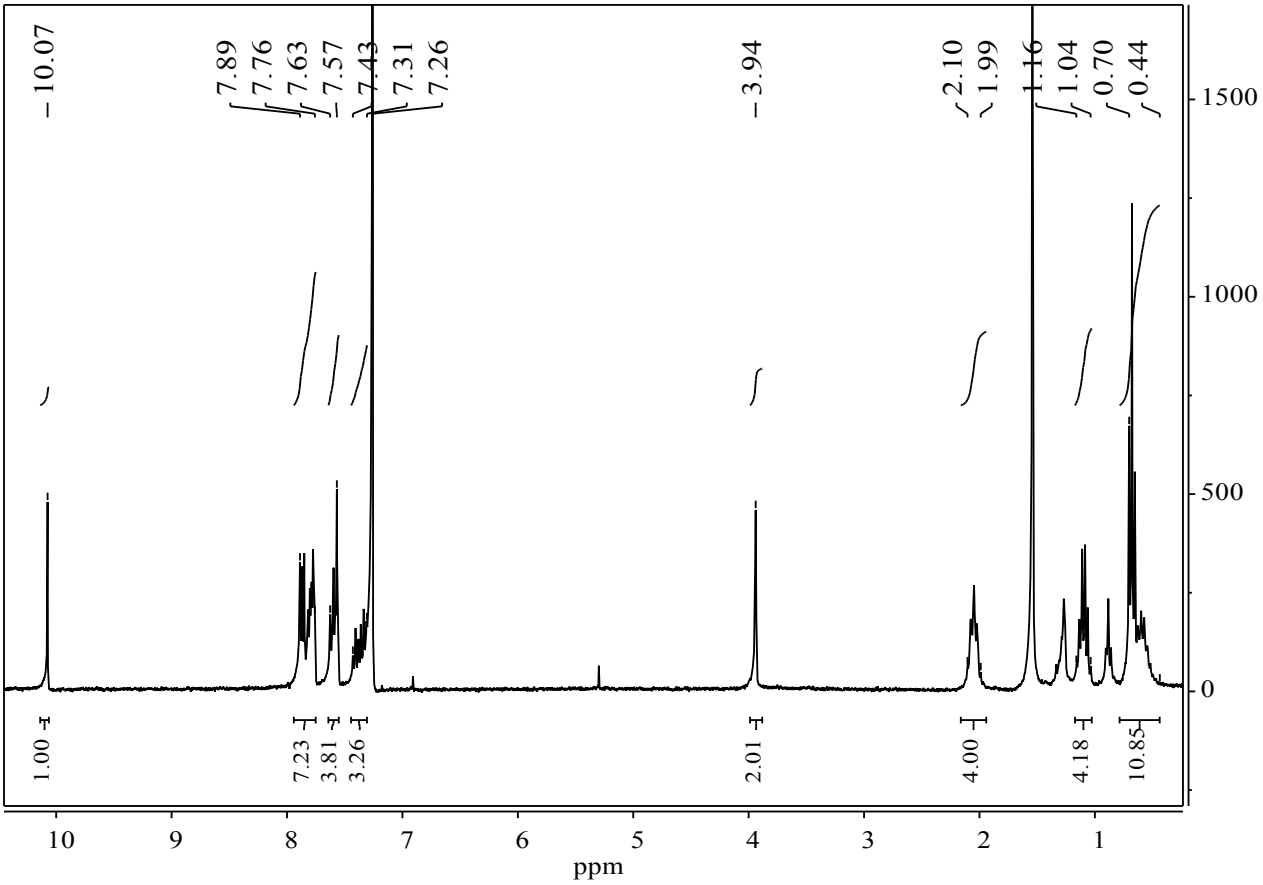
1. Synthesis of intermediate 2

This known compound **2**[7a] was obtained in two steps starting from commercial 2-bromofluorene with an overall the yield of 56%, as described below:



2. ^{1}H NMR Spectra of the difluorenyl aldehyde 3 and TFP1', TFOP2, TFOP2' and partial comparative ^{1}H NMR spectra of TFP1', and TFOP2, TFOP2' in THF-d_8 and labelization of the corresponding protons

Figure S1. ^{1}H NMR (400 MHz) of compound **3** in $CDCl_3$.



The aldehyde **3** has four diagnostic signatures: (i) the aldehyde proton as a singlet, around 10 ppm, (ii) the aromatic protons located as multiplets in region 8.0-7.3 ppm and (iii) a singlet at 4.1 ppm corresponds to the two methylene protons H_e of non-substituted fluorenyl, (iv) the alkyl protons of the various butyl chains: H_a, H_b, H_c and H_d of the substituted fluorenyl around 2.2-0.5 ppm.

FigureS2. [1]H NMR (300 MHz) of compound **TFP1'** in THF-d_8.

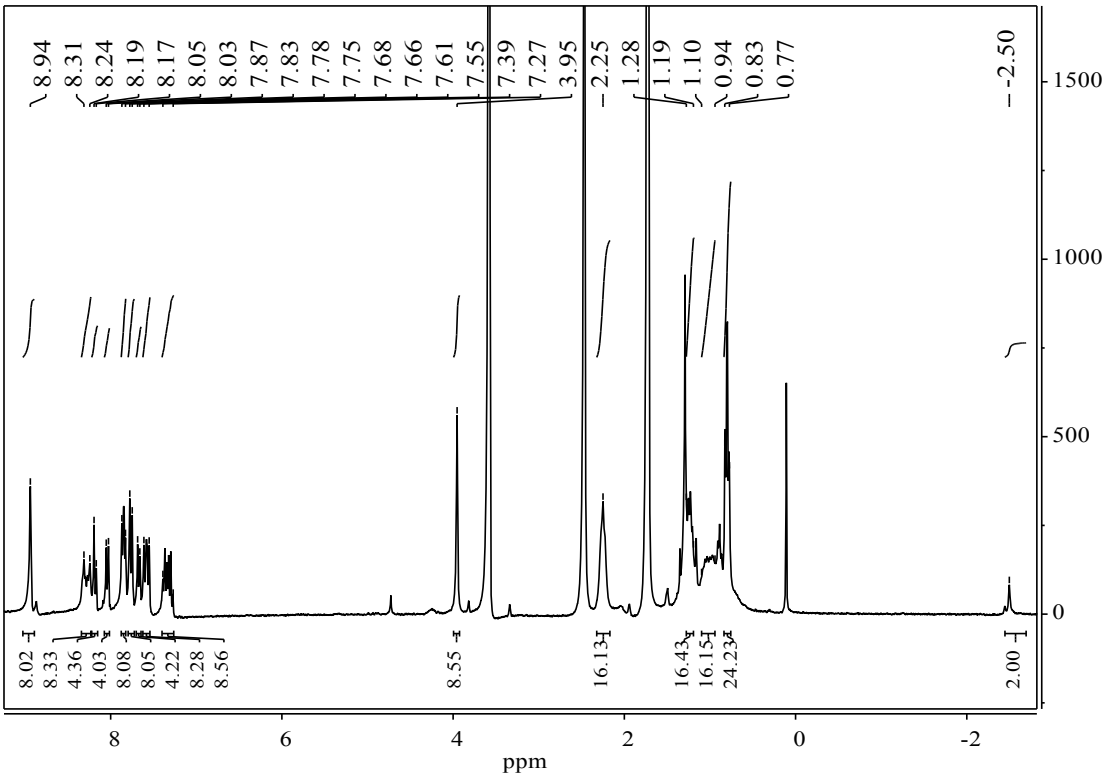


Figure S3. [1]H NMR (300 MHz) of compound **TFOP2'** in THF-d_8.

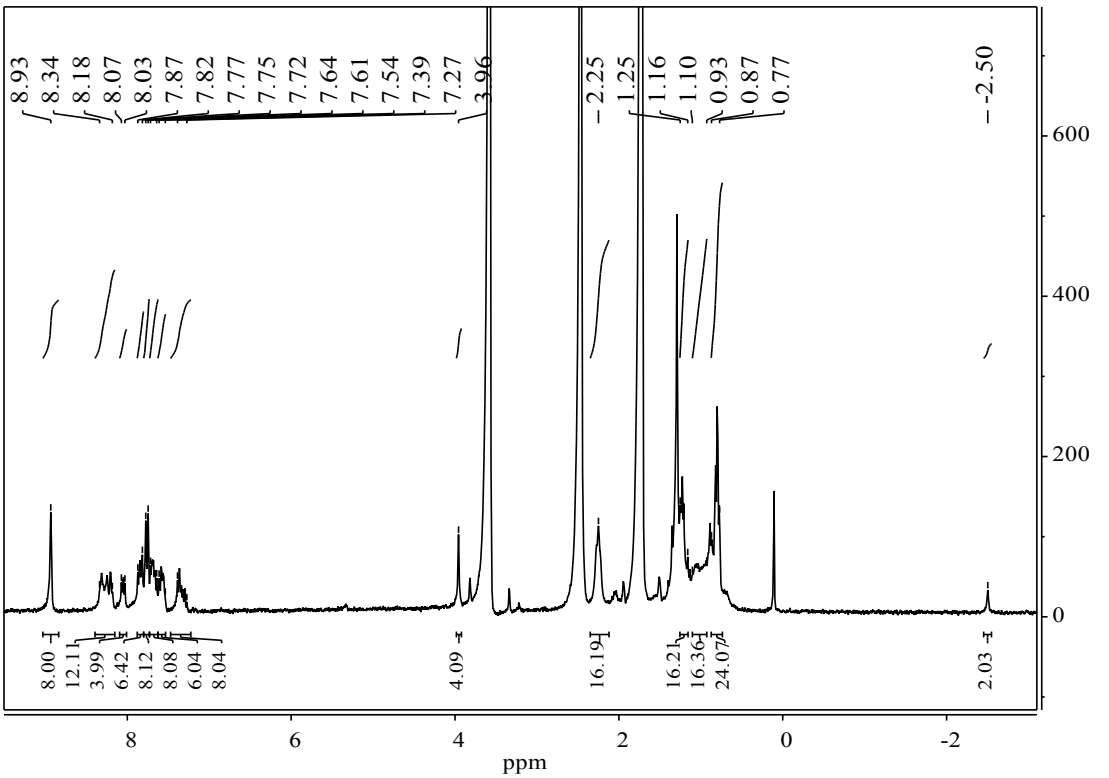
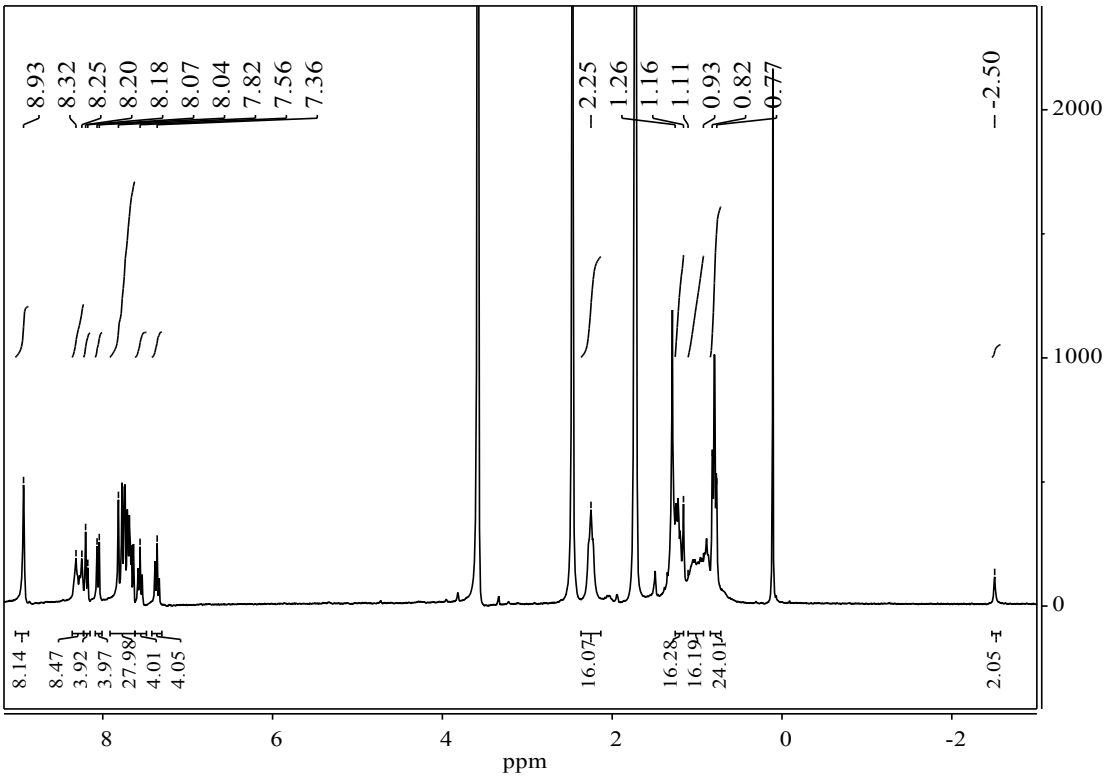
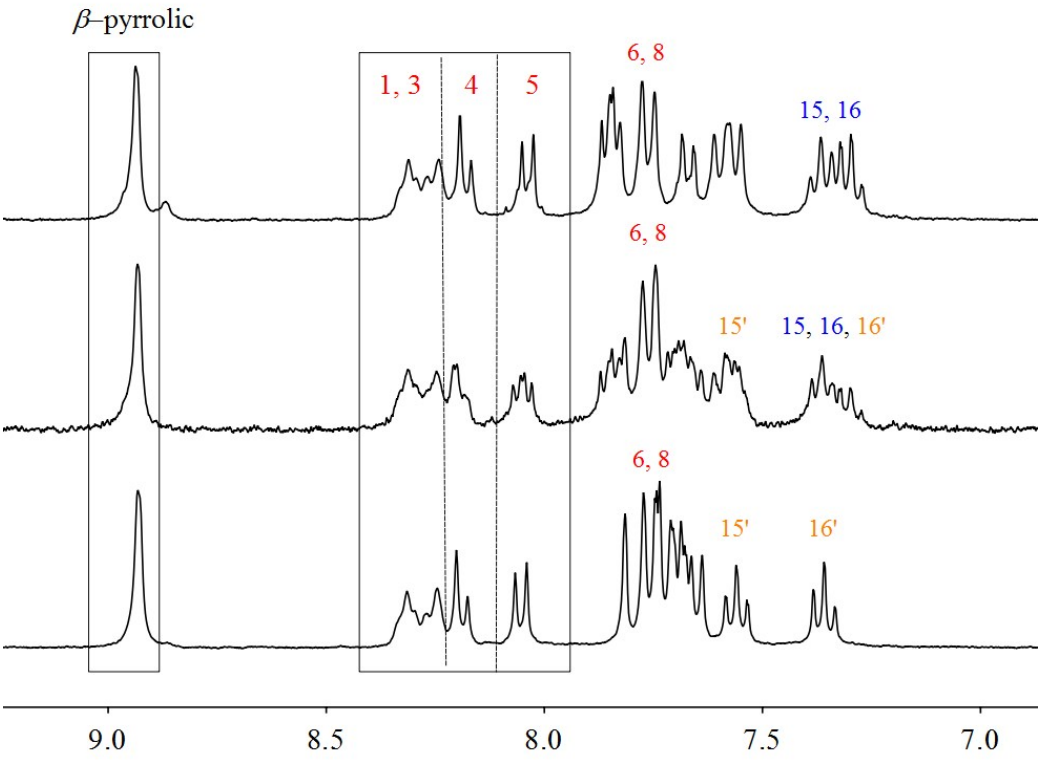


Figure S4. ^{1}H NMR (300 MHz) of compound **TFOP2** in THF-d_8.

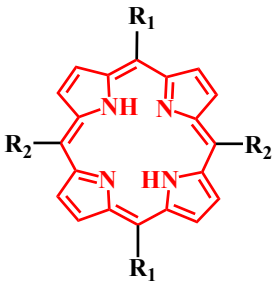


In the comparative partial spectra of aromatic zone, the protons of fluorenyl substituted by two butyl chains (red colored fluorenyl units), near the porphyrin shielding cone, are clearly recognized at low field by the peaks ranged in 8.4-8.0 ppm region. The peaks, strongly overlapped in 7.9-7.5 region, correspond to the protons of the fluorenone (orange colored fluorenyl units, see Fig. S5), including the doublets identifying H_6 and H_8, but the external protons H_{15}, $H_{15'}$, H_{16} and $H_{16'}$ are identified by the triplets ranged from 7.6 to 7.2 ppm, particularly remarkable are $H_{15'}$ and $H_{16'}$ of fluorenone units of **TFOP2**, the last two protons are characterized by two isolated triplets at 7.56 and 7.36 ppm. As expected, for all these porphyrins, the *β*-pyrrolic protons are identified as the lowest field singlet, around 8.9 ppm, integrating for eight protons. Correspondingly, the singlets, present at 3.9 ppm corresponding to the CH_2 group (or H_{18} in SI) for non-oxidized **TFP1'** and partially oxidized **TFOP2'**, progressively disappear upon increasing substitution of 9-protons by oxygen atoms.

Figure S5. Partial comparative ^{1}H NMR spectra (400 MHz) of **TFP1'**, **TFOP2** and **TFOP2'** in THF-d_8, and labelization of the corresponding protons.



Protons labelling:

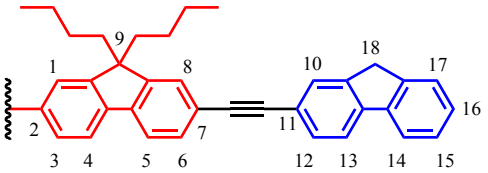


TFP1':
$R_1 = R_2$ = FlF

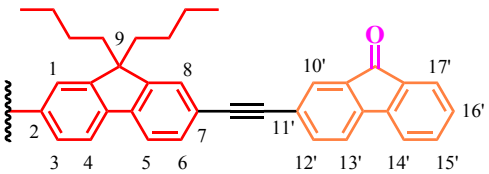
TFOP2':
R_1 = FlF; R_2 = FlFO

TFOP2:
$R_1 = R_2$ = FlFO

FlF :



FlFO :



3. ^{1}H NMR spectra of intermediate compounds 2-TMS and 2

Figure S6. ^{1}H NMR (400 MHz) of compound **2-TMS** in $CDCl_3$.

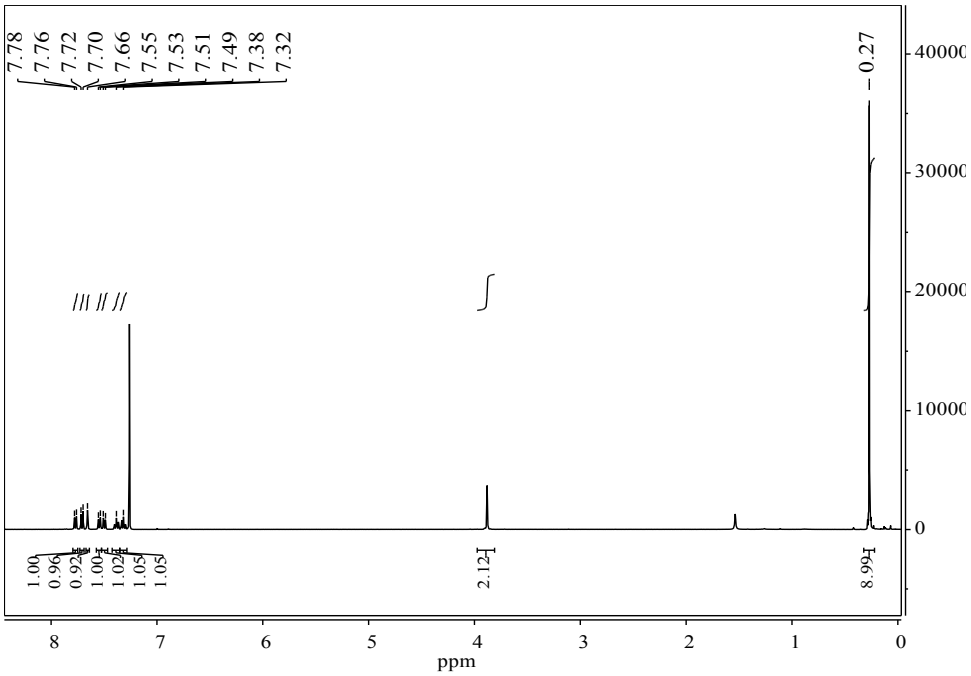
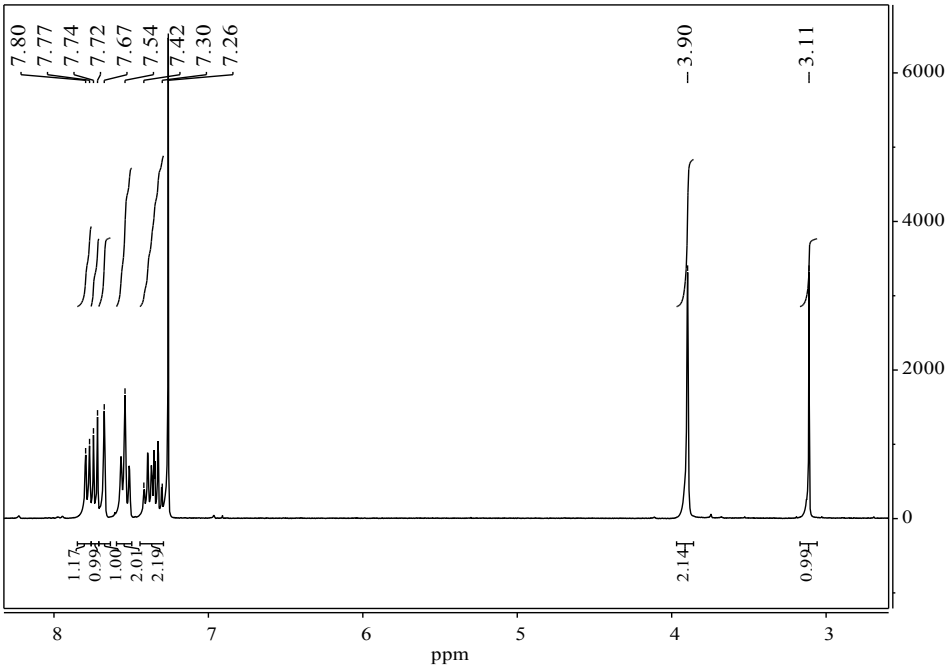


Figure S7. ^{1}H NMR (400 MHz) of compound **2** in $CDCl_3$.



4. $^{13}C\{^1H\}$ NMR spectra of TFP1' and TFOP2

Figure S8. $^{13}C\{^1H\}$ NMR (100 MHz) of compound **TFP1'** in $CDCl_3$.

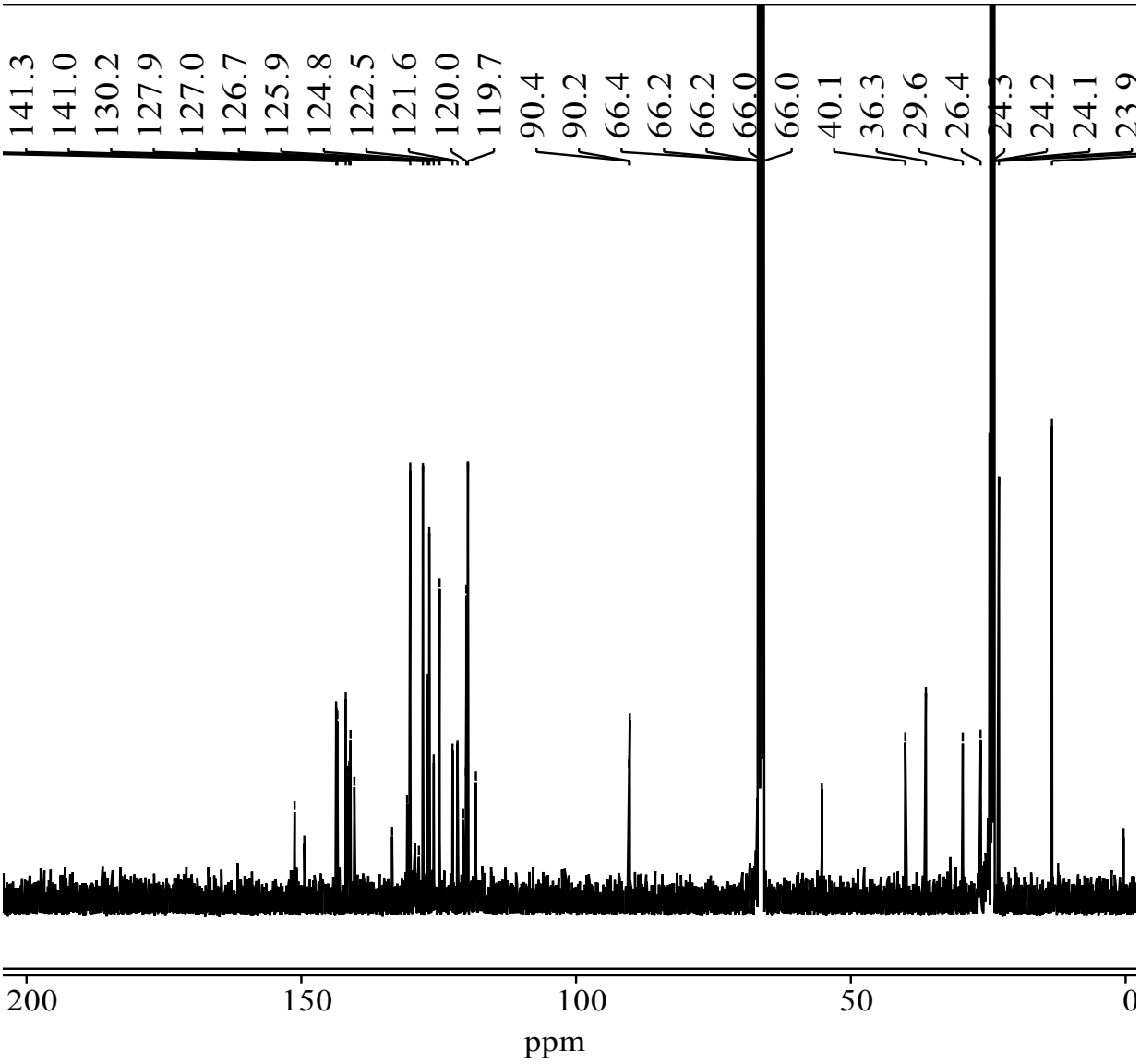
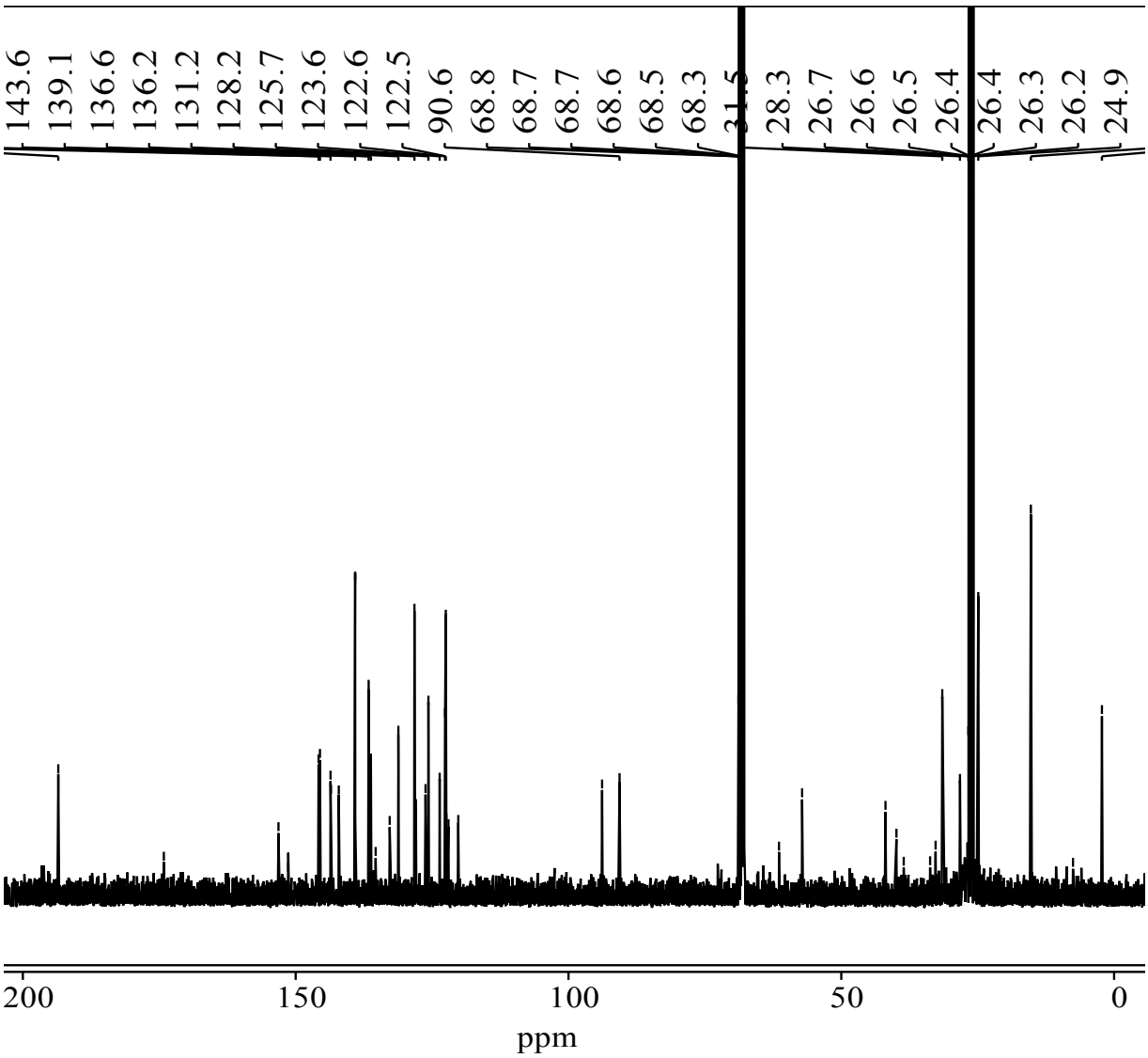


Figure S9. $^{13}C\{^{1}H\}$ NMR (100 MHz) of compound **TFOP2** in $CDCl_3$.



5. Mass spectra of TFP1', TFOP2 and TFOP2'

Figure S10. (a) HRMS-ESI and (b) HRMS-MALDI (positive mode) of **TFP1'**.

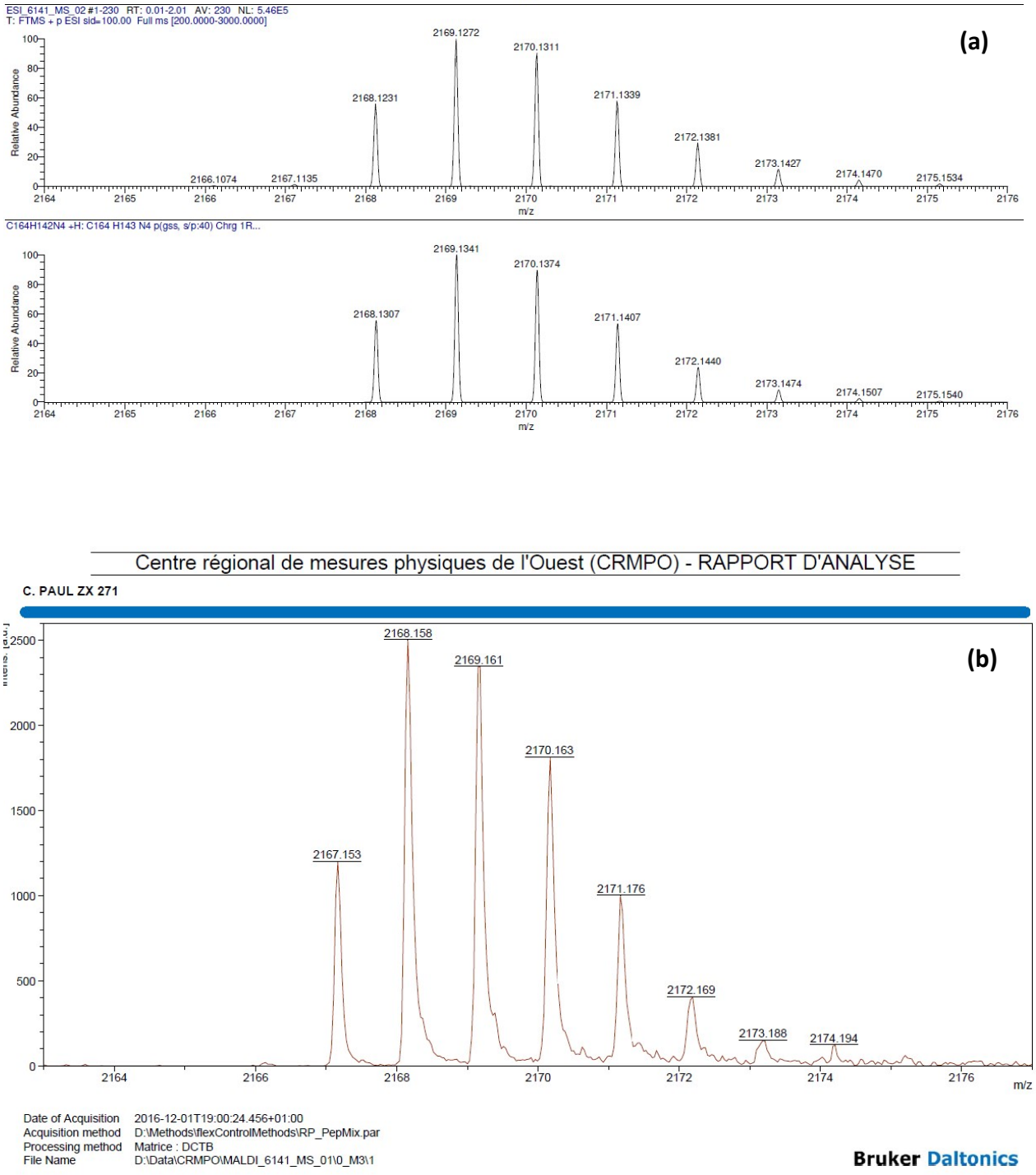


Figure S11. HRMS-ESI (positive mode) of **TFOP2'**.

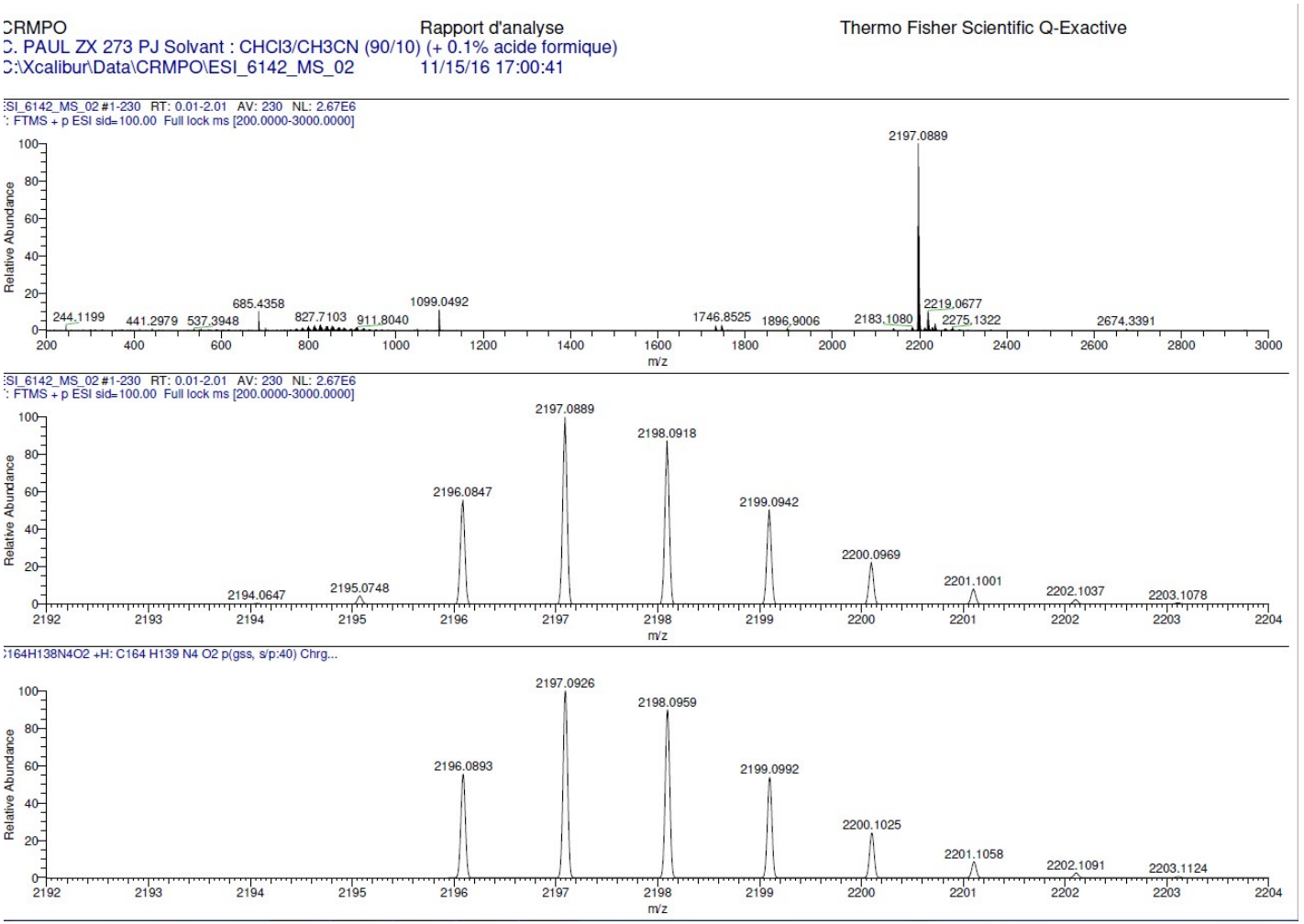
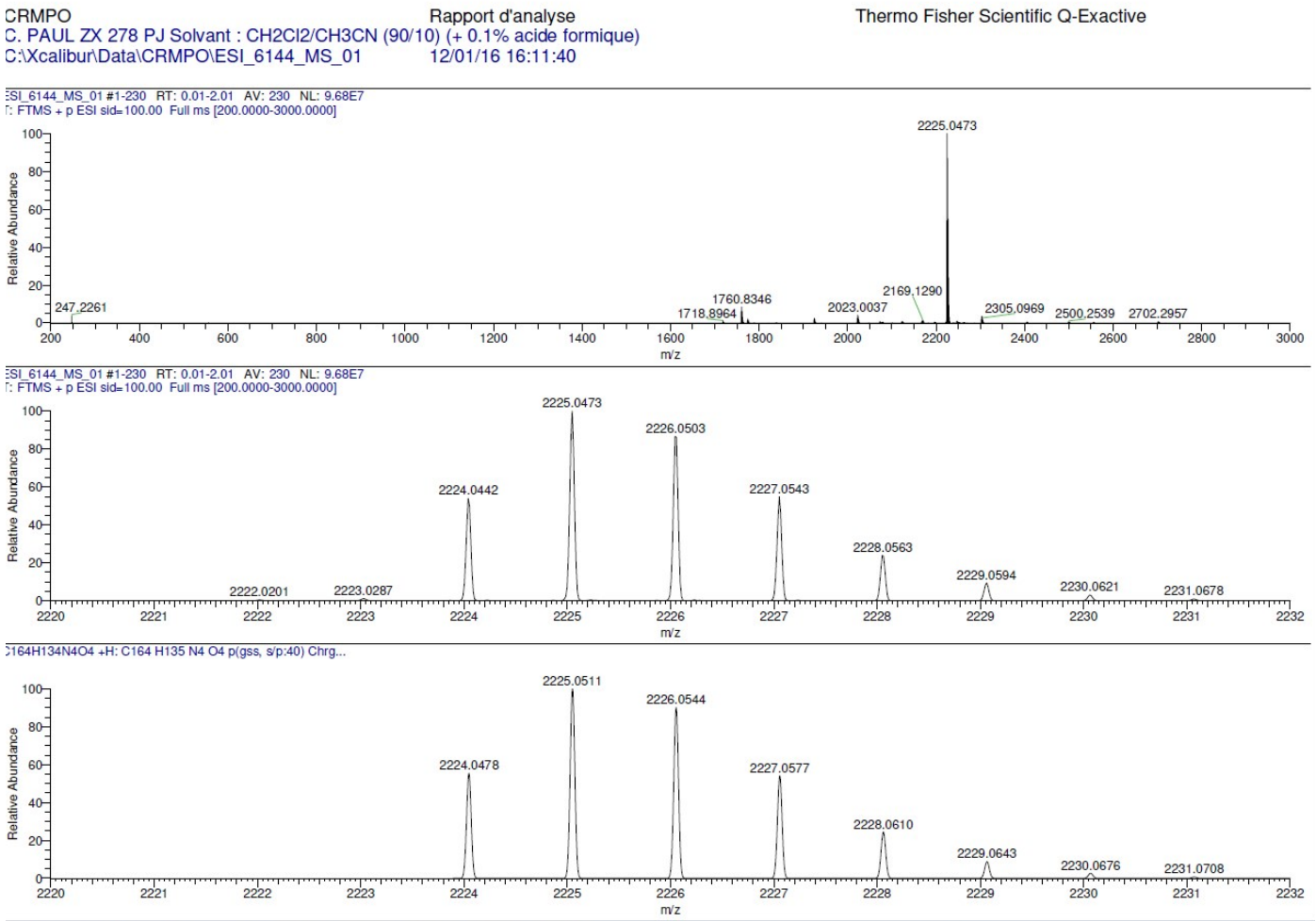


Figure S12. HRMS-ESI (positive mode) of **TFOP2**.



6. Complementary fluorescence data for TFP1', TFOP2 and TFOP2'

Figure S13. Emission spectra of **TFP1'** and **TFOP2-2'** in CH_2Cl_2 (500-820 nm) excited in their arm-based absorption (380 nm).