Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Impact of cationic substituents in phenalen-1-one photosensitizers on antimicrobial photodynamic efficacy

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SUPPORTING INFORMATION

Selected Nuclear Magnetic Resonance (NMR) spectra of prepared compounds

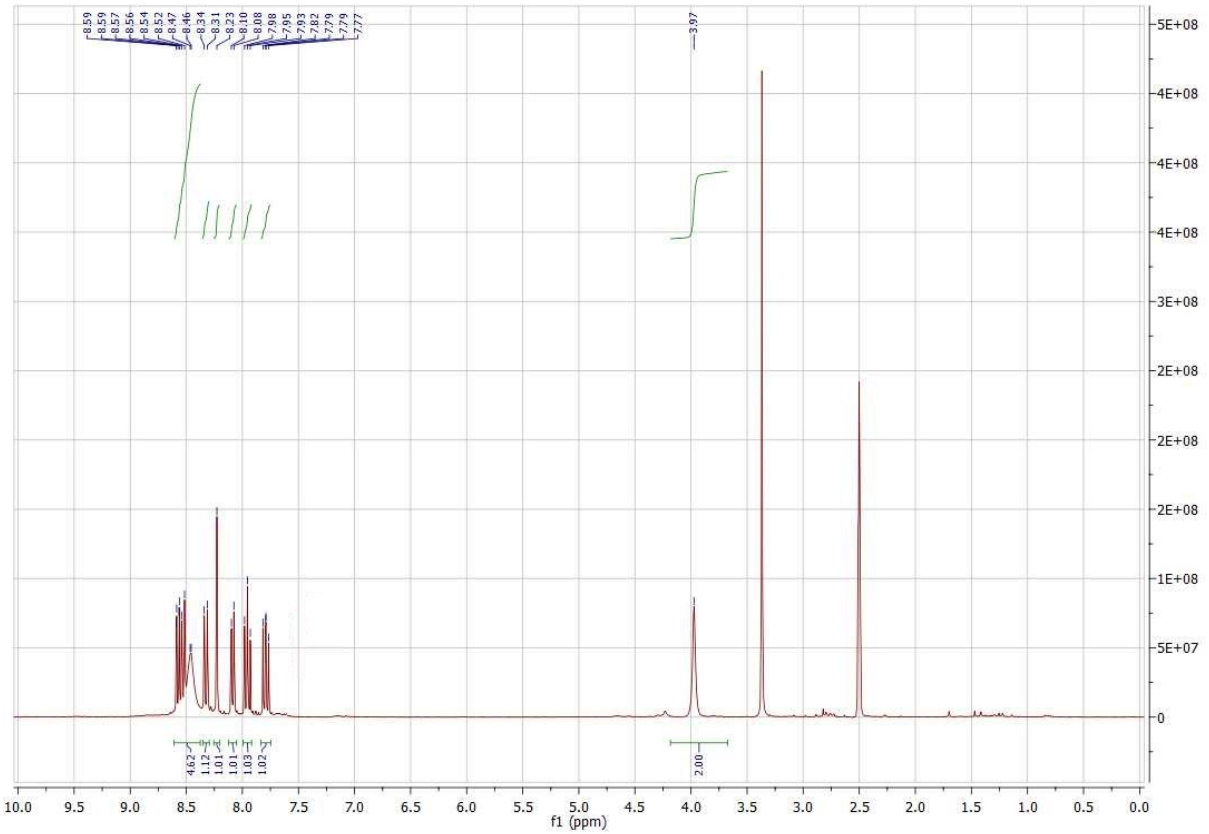


Figure S-1:[1]H-NMR spectrum of compound **2** DMSO-d6

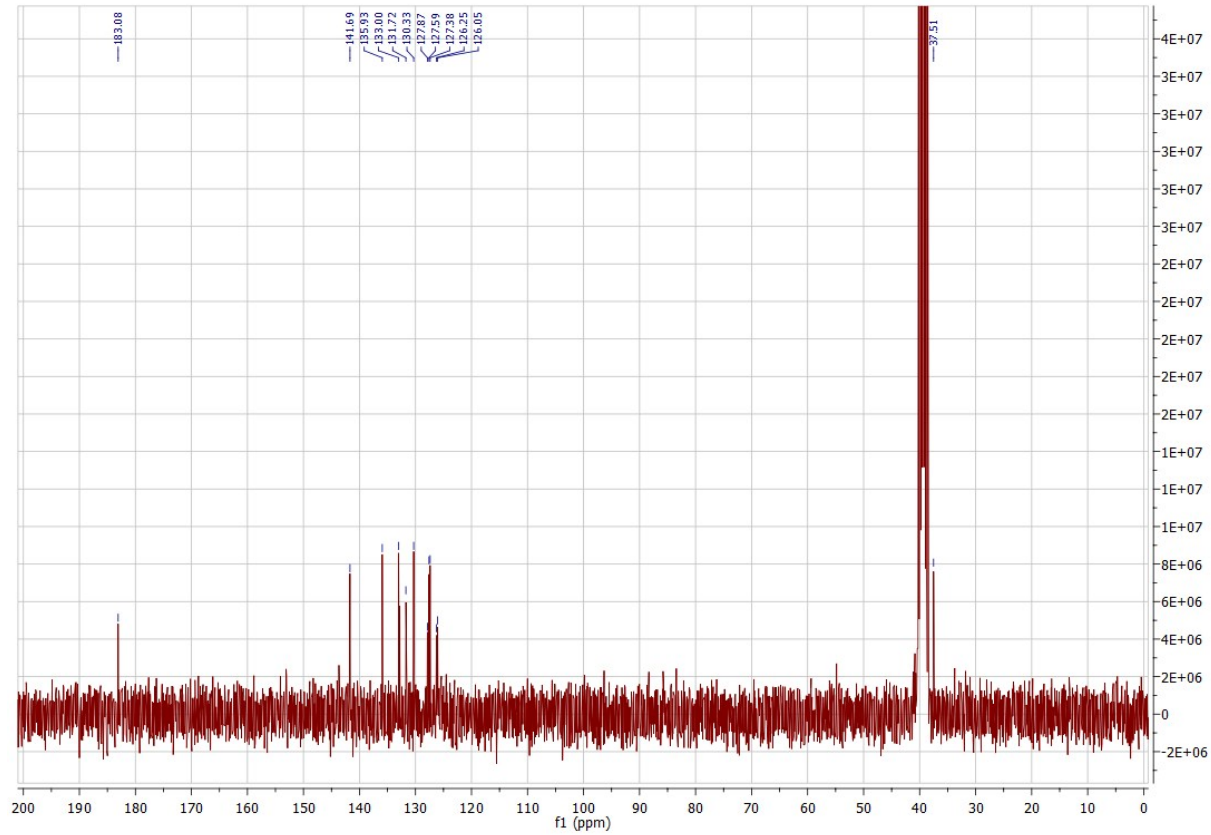


Figure S-2:[13]C-NMR spectrum of compound **2** in DMSO-d6

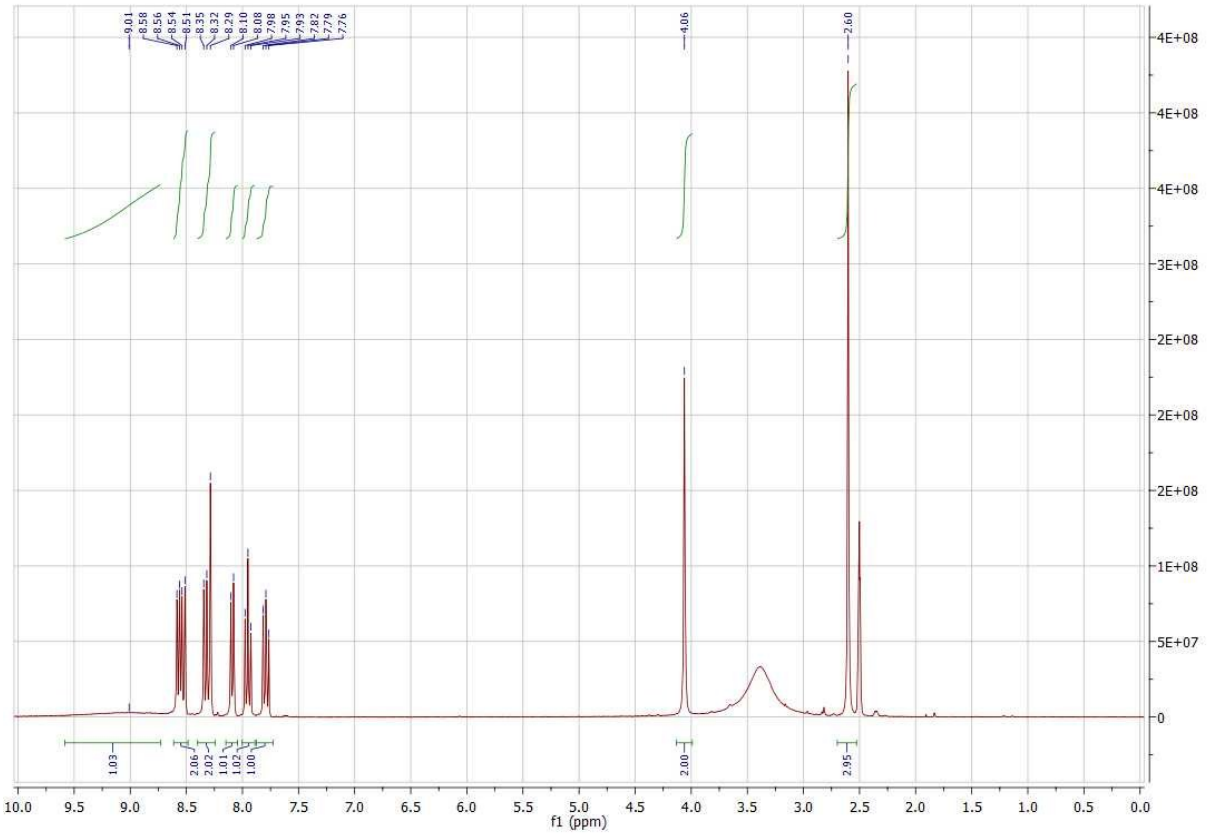


Figure S-3: ^{1}H-NMR spectrum of compound **3** in DMSO-d6

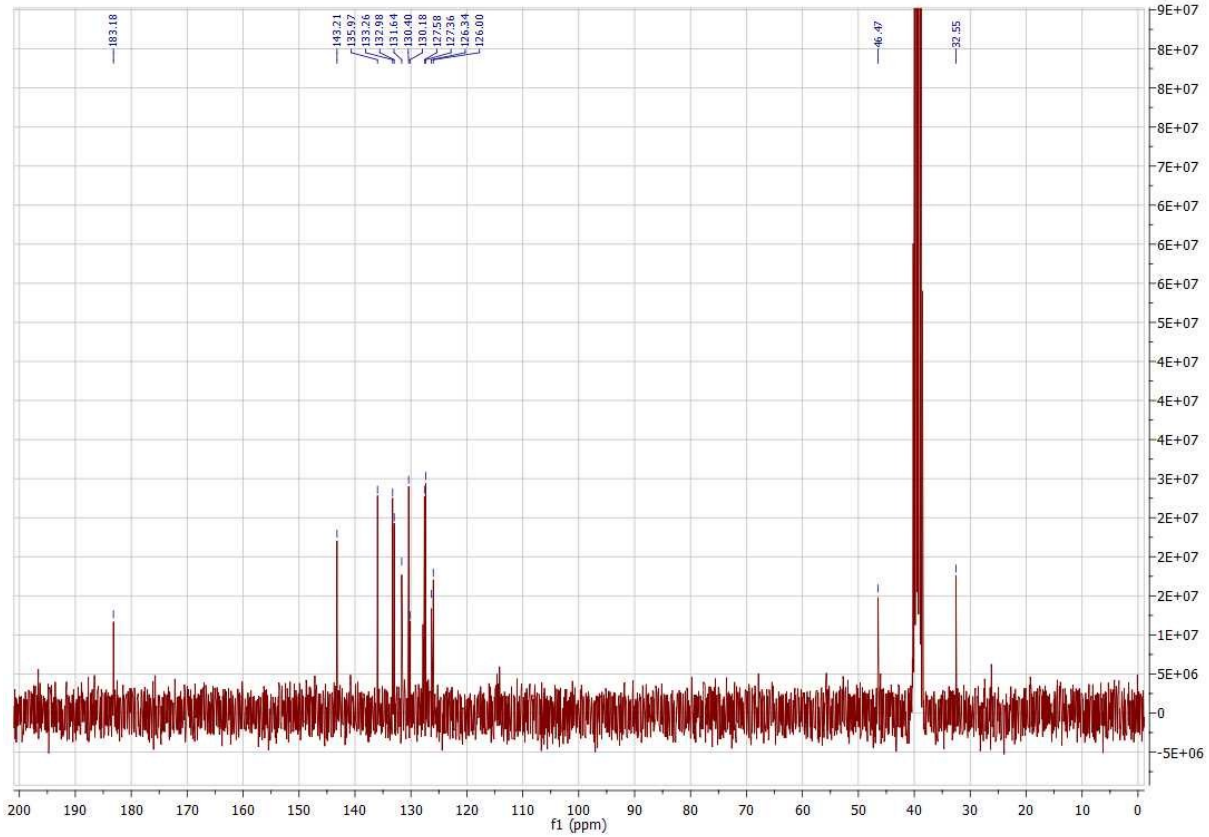


Figure S-4:[1]H-NMR spectrum of compound **3,** in DMSO-d6

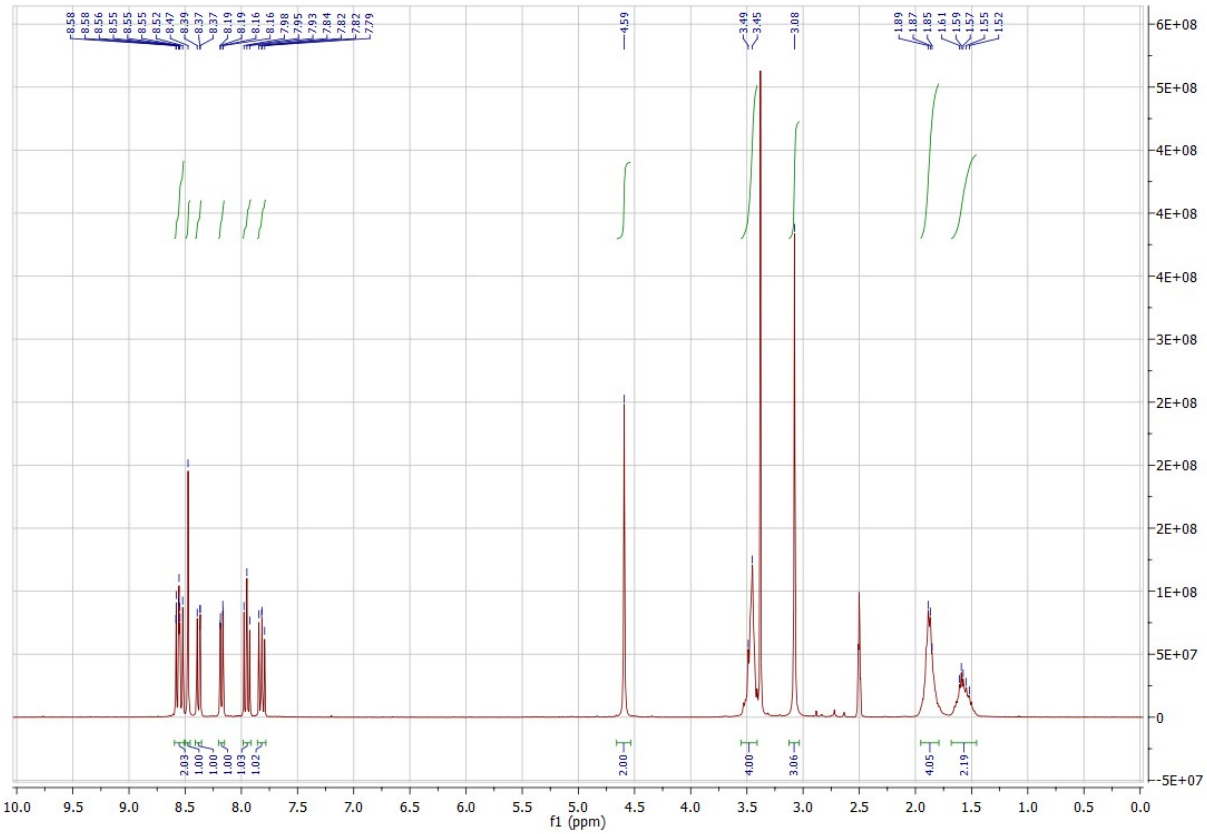


Figure S-5:[1]H-NMR spectrum of compound **4** in DMSO-d6

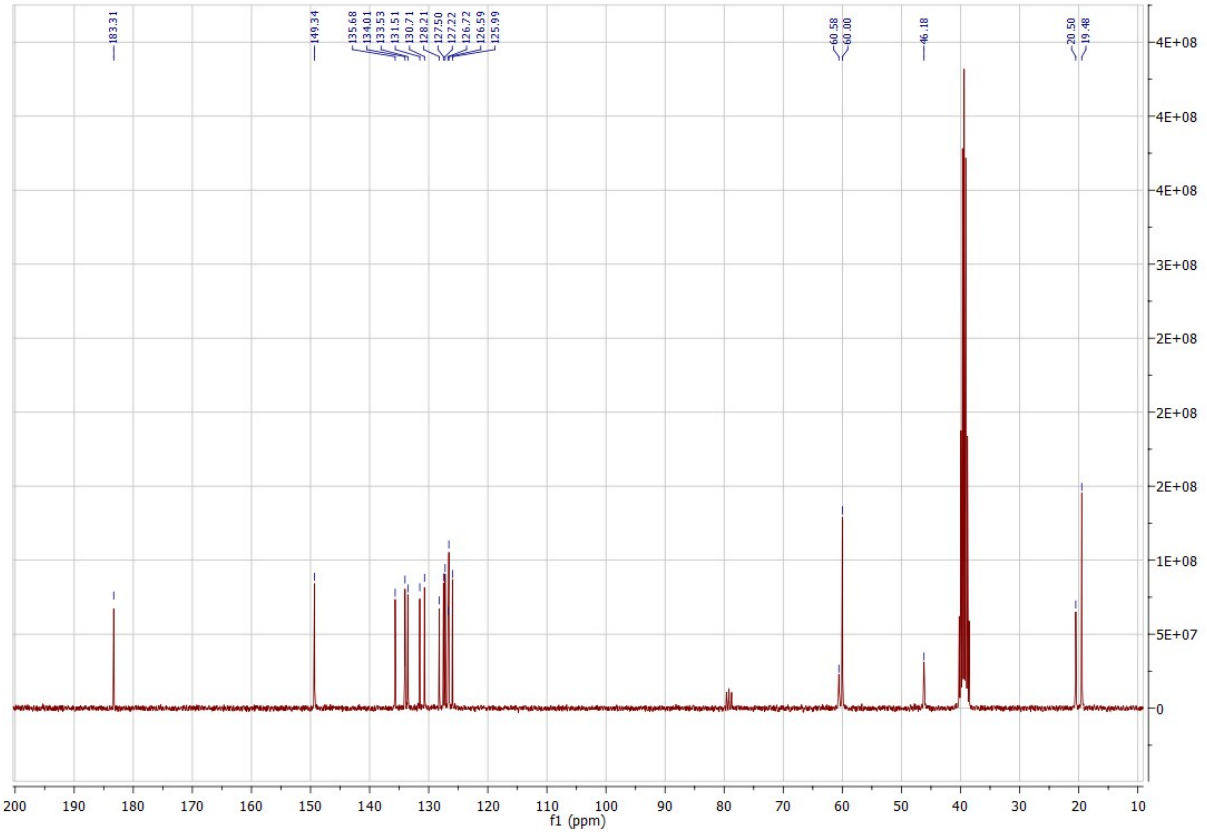


Figure S-6: ^{13}C-NMR spectrum of compound **4** in DMSO-d6

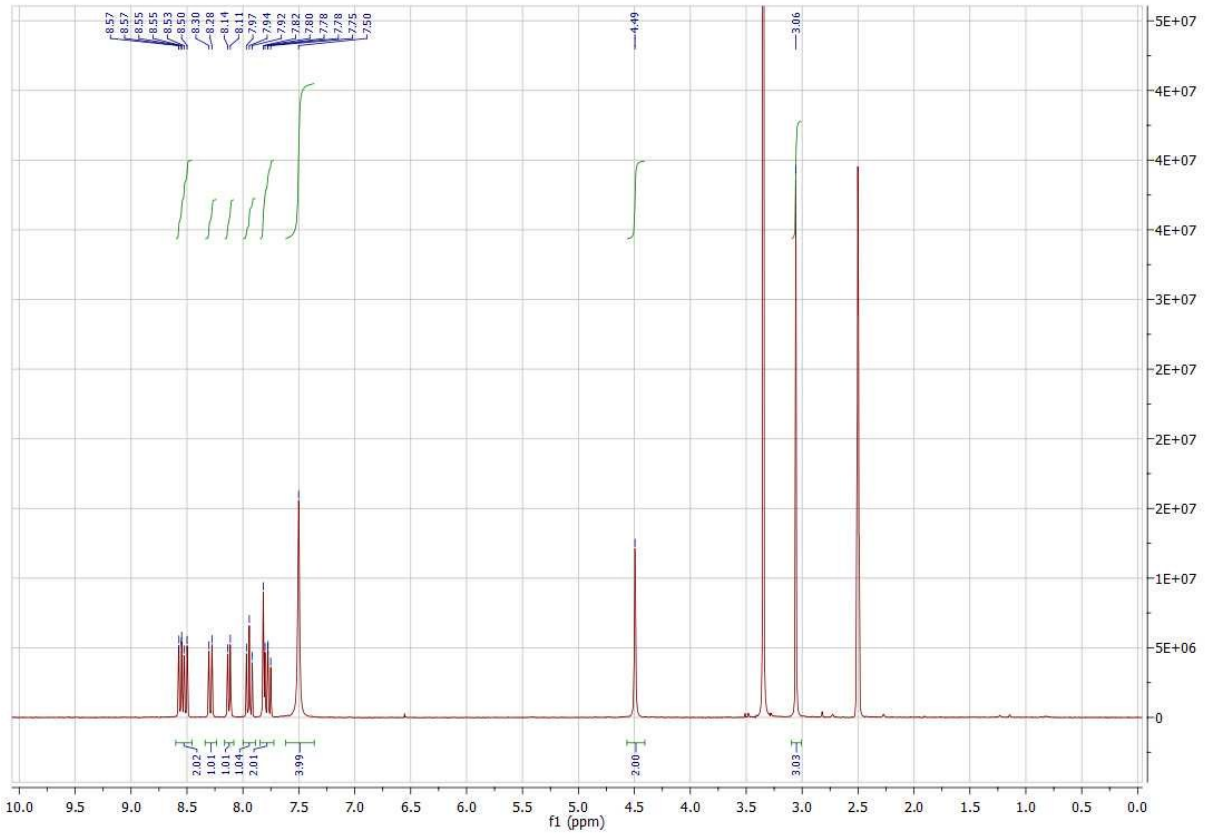


Figure S-7: ^{1}H-NMR spectra of compound **5** in DMSO-d6

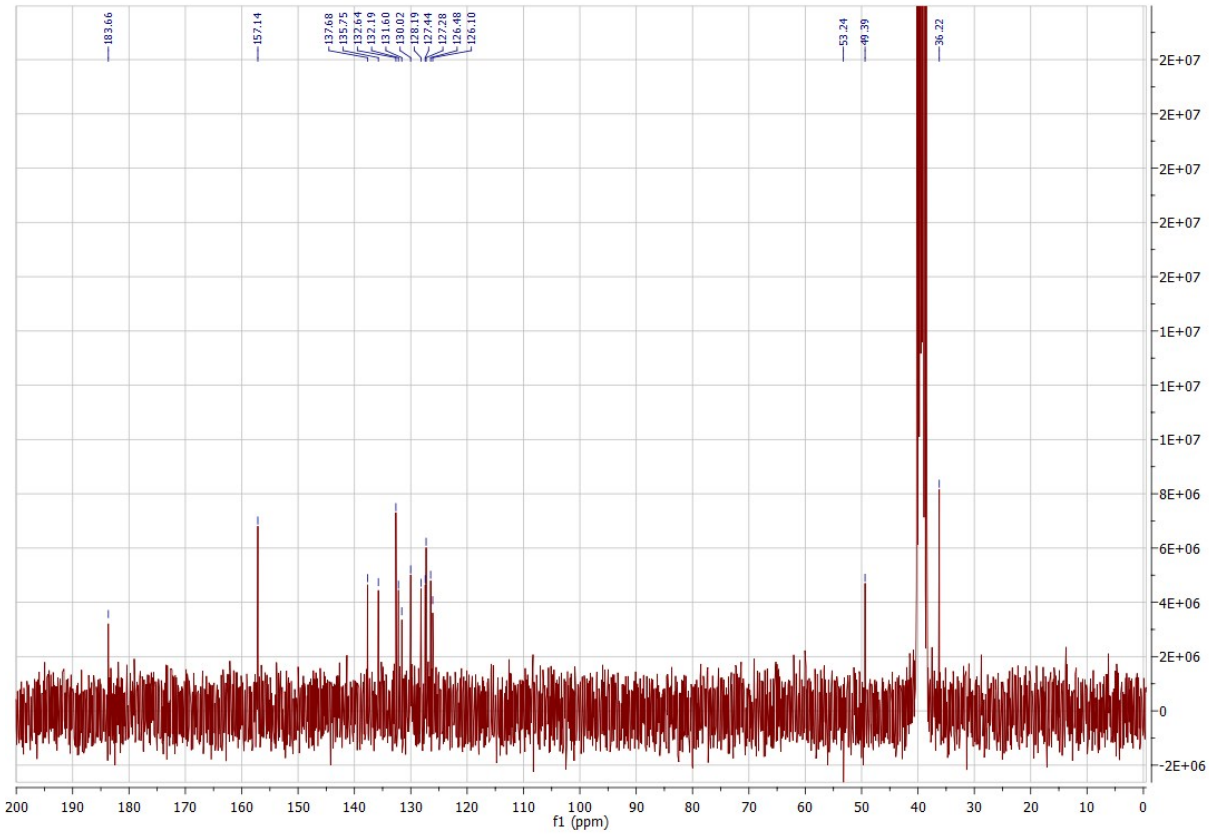


Figure S-8:[13]C-NMR spectrum of compound **5** in DMSO-d6

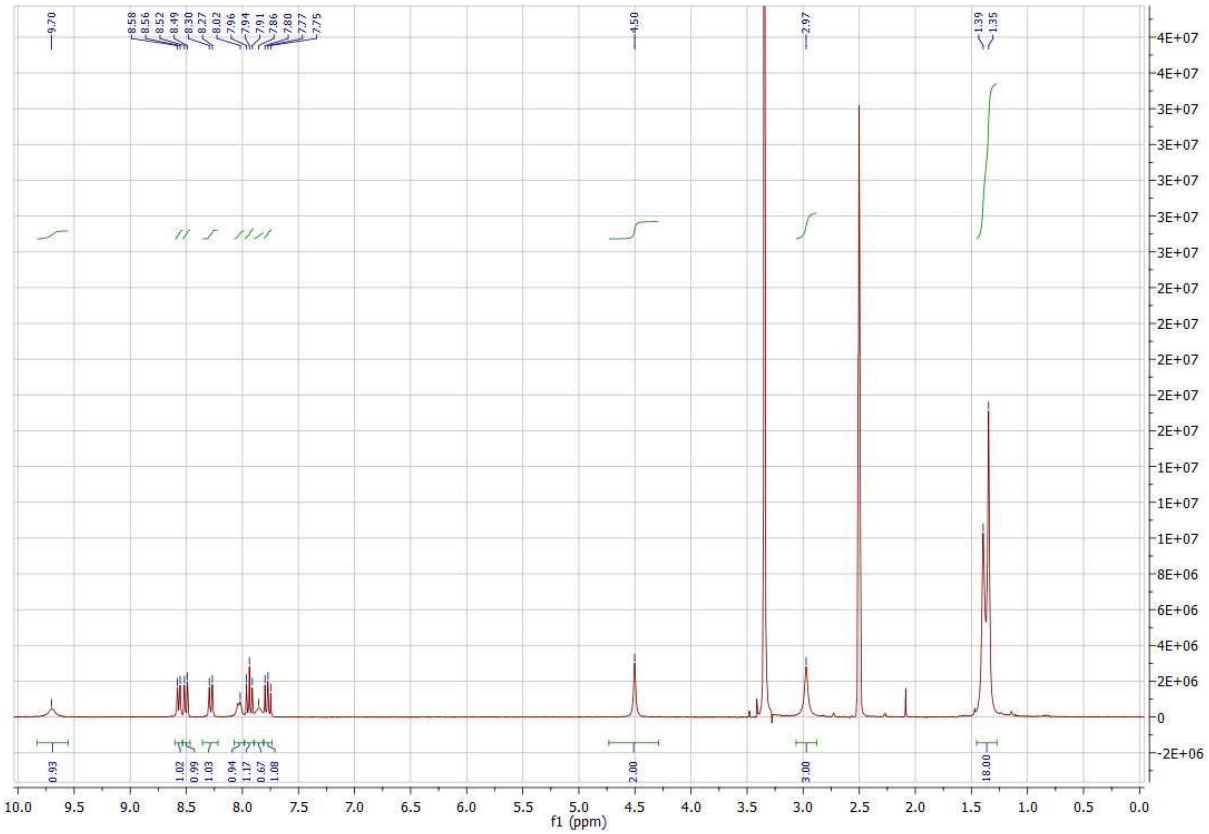


Figure S-9:[1]H-NMR spectra of compound **8** in DMSO-d6

Photophysical Characterisation

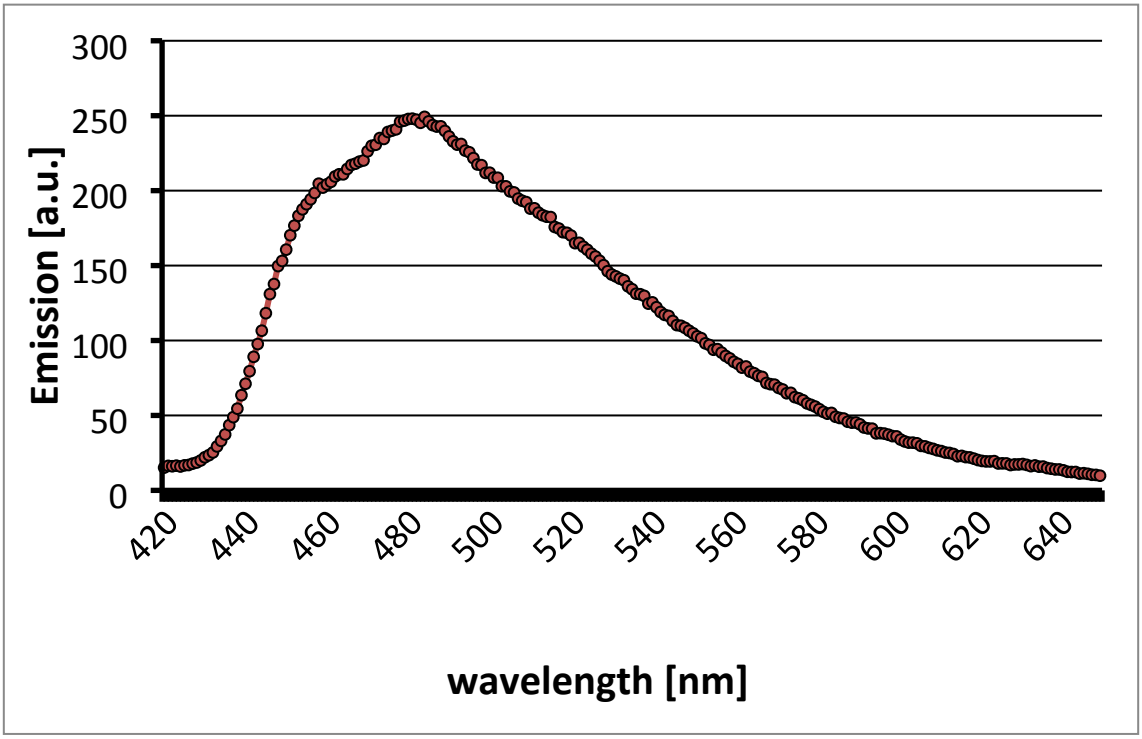


Figure S-10: Emission spectrum of compound **5** in H_2O; c = 60 µM

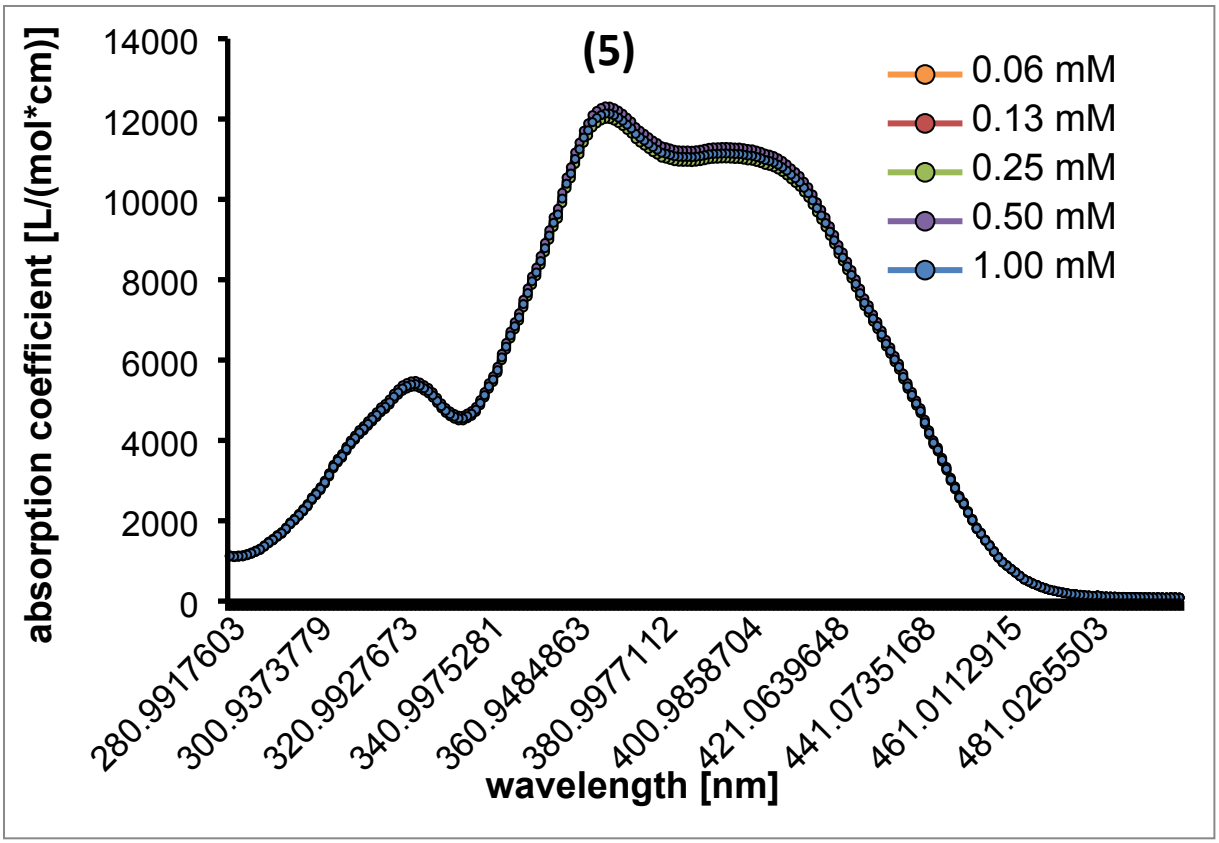
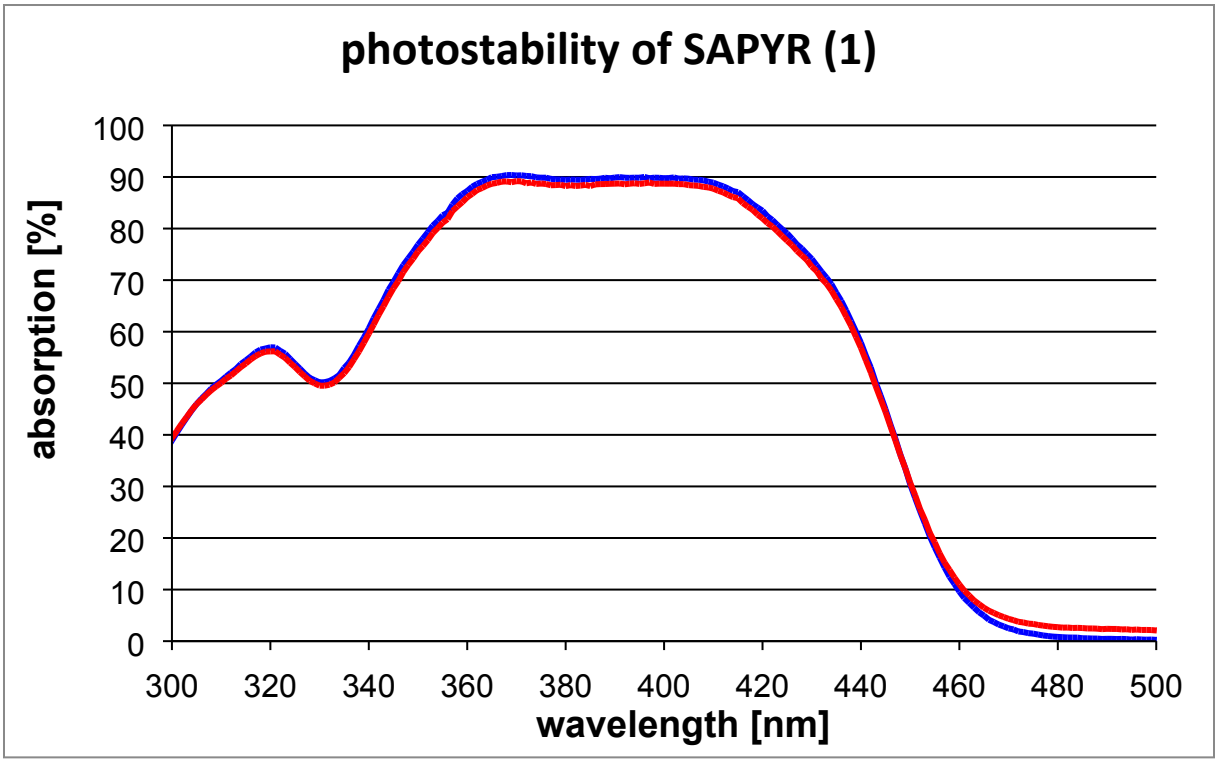
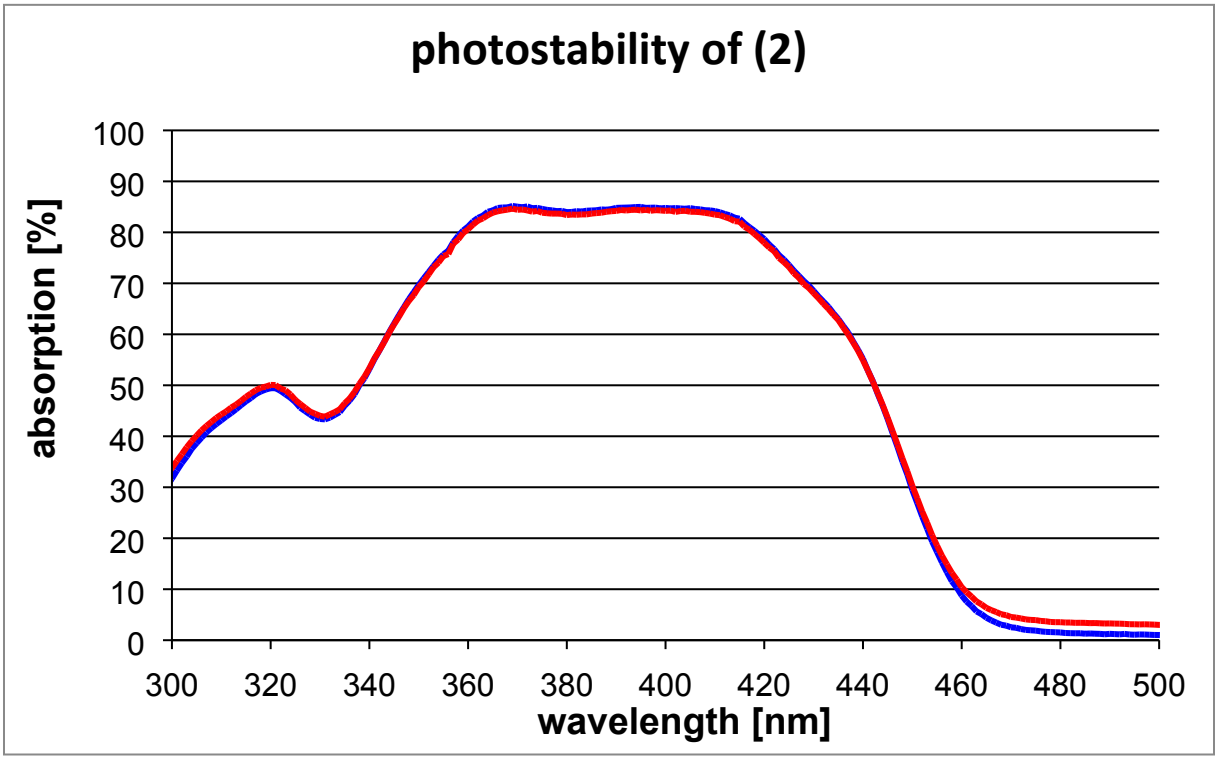
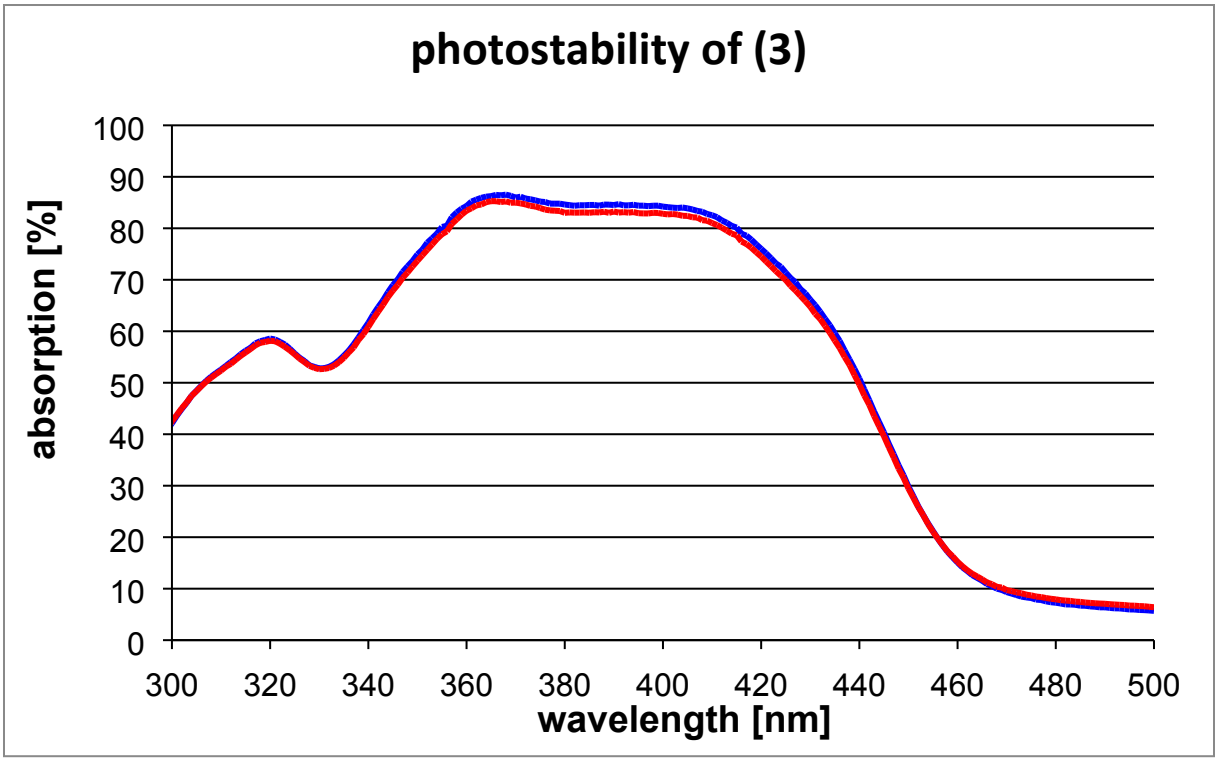
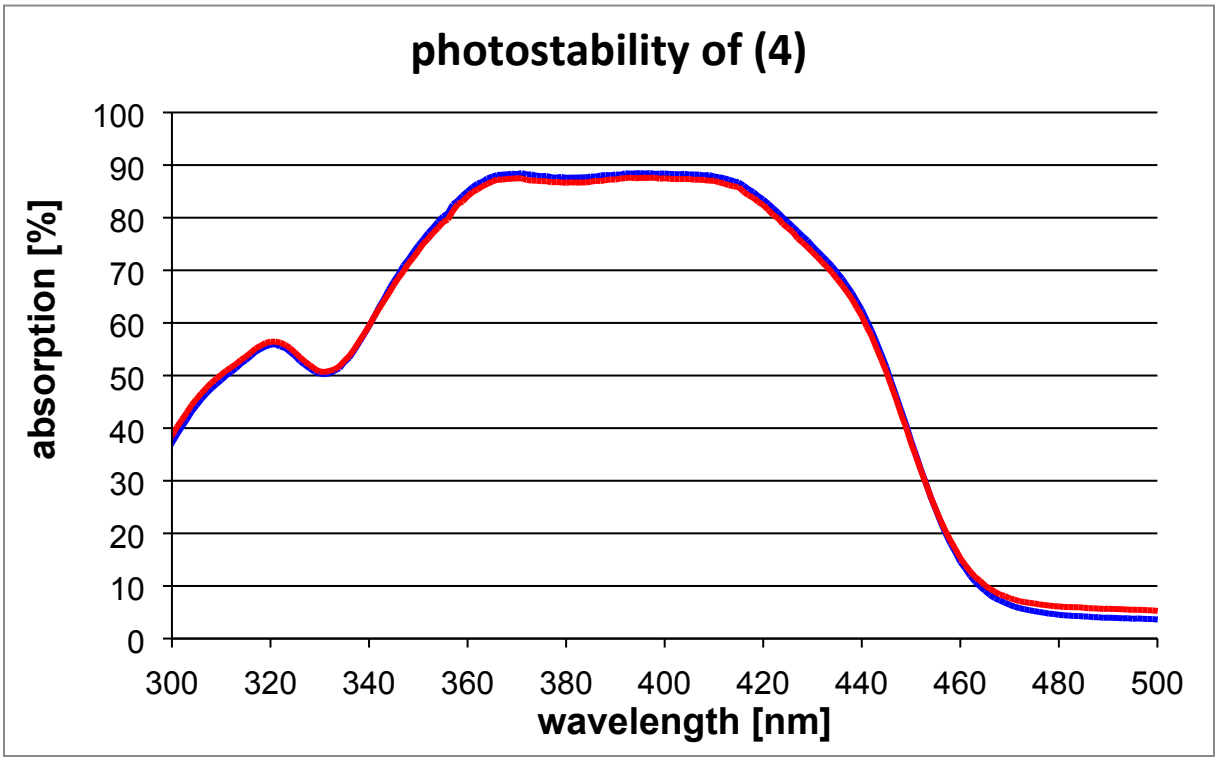


Figure S-11: Absorption spectra of (**5**) within a concentration range of 60 – 1000 µM in H_2O; the graphs show no dimerisation in this concentration range.


photostability of SAPYR (1)
absorption [%]
100
90
80
70
60
50
40
30
20
10
0
300
320
340
360
380
400
420
440
460
480
500
wavelength [nm]


photostability of (2)
absorption [%]
100
90
80
70
60
50
40
30
20
10
0
300
320
340
360
380
400
420
440
460
480
500
wavelength [nm]


photostability of (3)
absorption [%]
100
90
80
70
60
50
40
30
20
10
0
300
320
340
360
380
400
420
440
460
480
500
wavelength [nm]


photostability of (4)
absorption [%]
100
90
80
70
60
50
40
30
20
10
0
300
320
340
360
380
400
420
440
460
480
500
wavelength [nm]

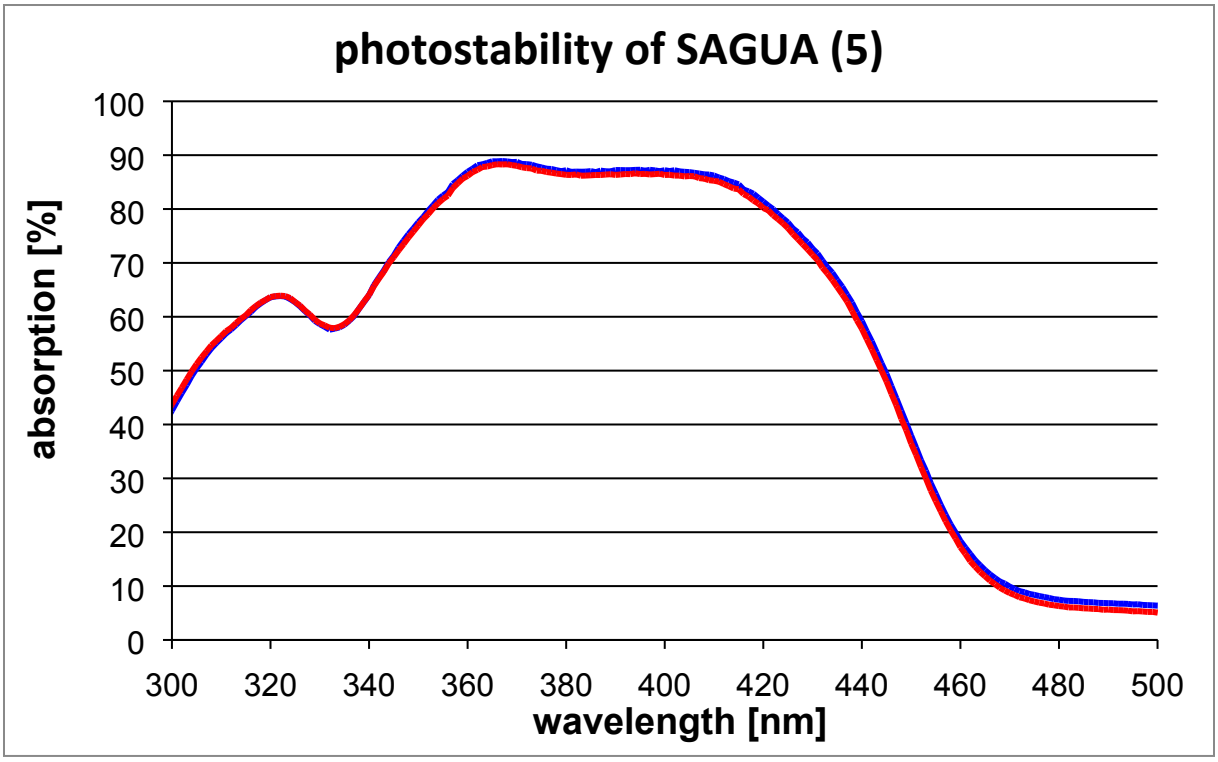


Figure S-12: Photostability measurements of PN derivatives in a quartz cuvette with an irradiation at 400 nm with 6 J laser energy (10 mW for 10 min); In all cases, the blue spectrum shows the absorption before irradiation, while the red spectrum shows absorption after irradiation. All compounds show no photobleaching under the conditions used.

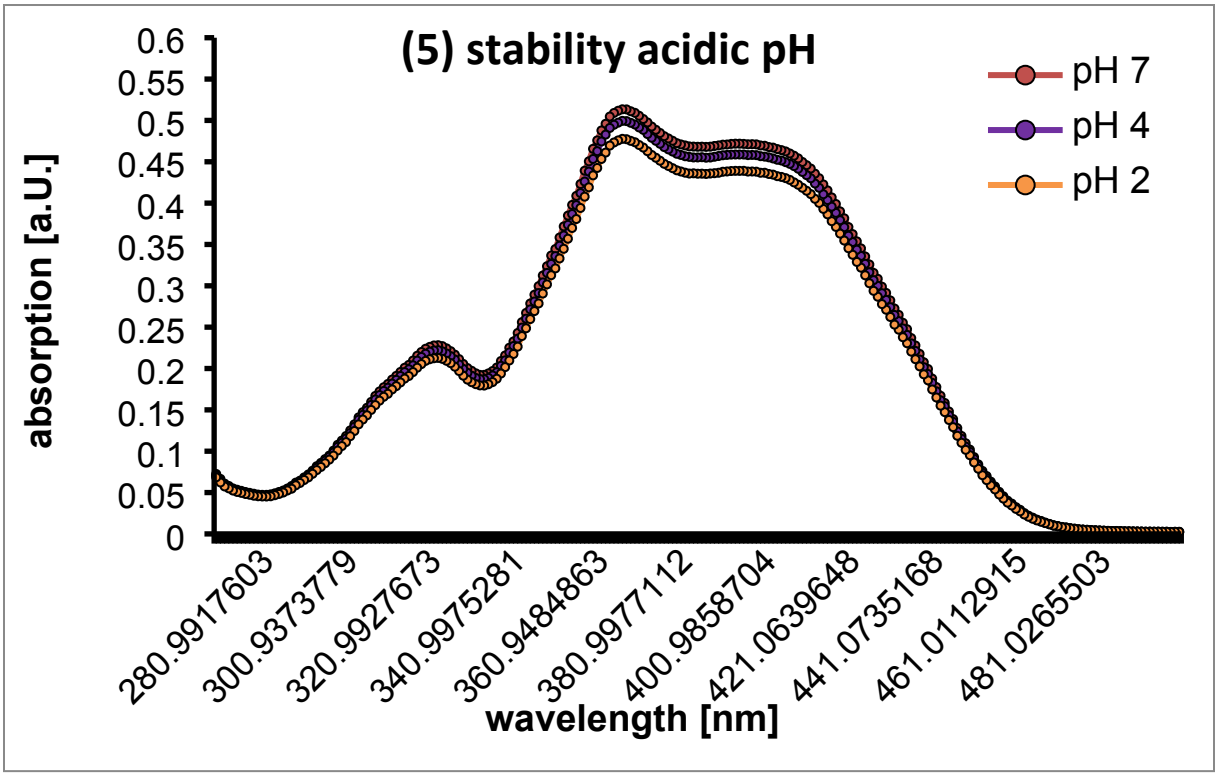


Figure S-13: pH stability of (**5**) in acidic medium after 20 mins; c = 60 µM, in water or dilute aqueous hydrochloric acid, respectively. The derivative is perfectly stable up to pH = 2

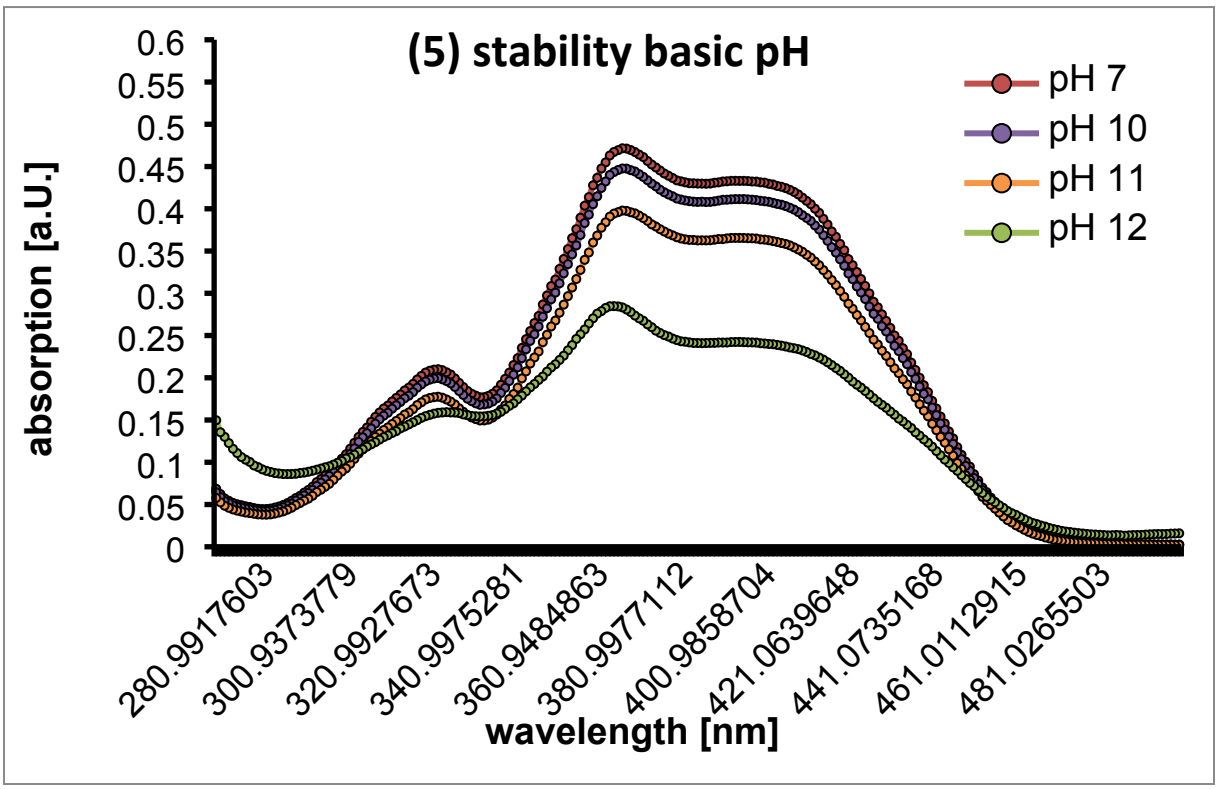


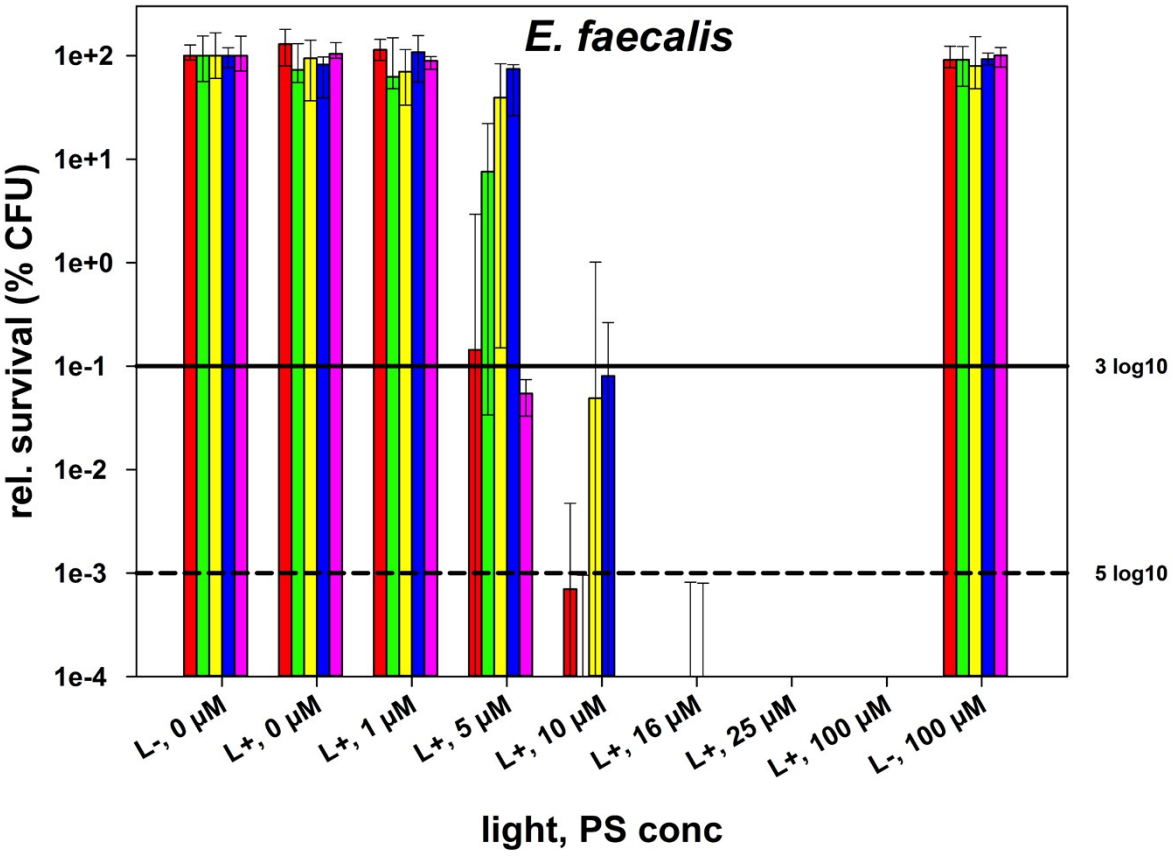
Figure S-14: pH stability of (**5**) in basic medium after 20 mins; c = 50 µM, in water or TRIS-buffer 50 mM, respectively. Decomposition begins at pH = 11

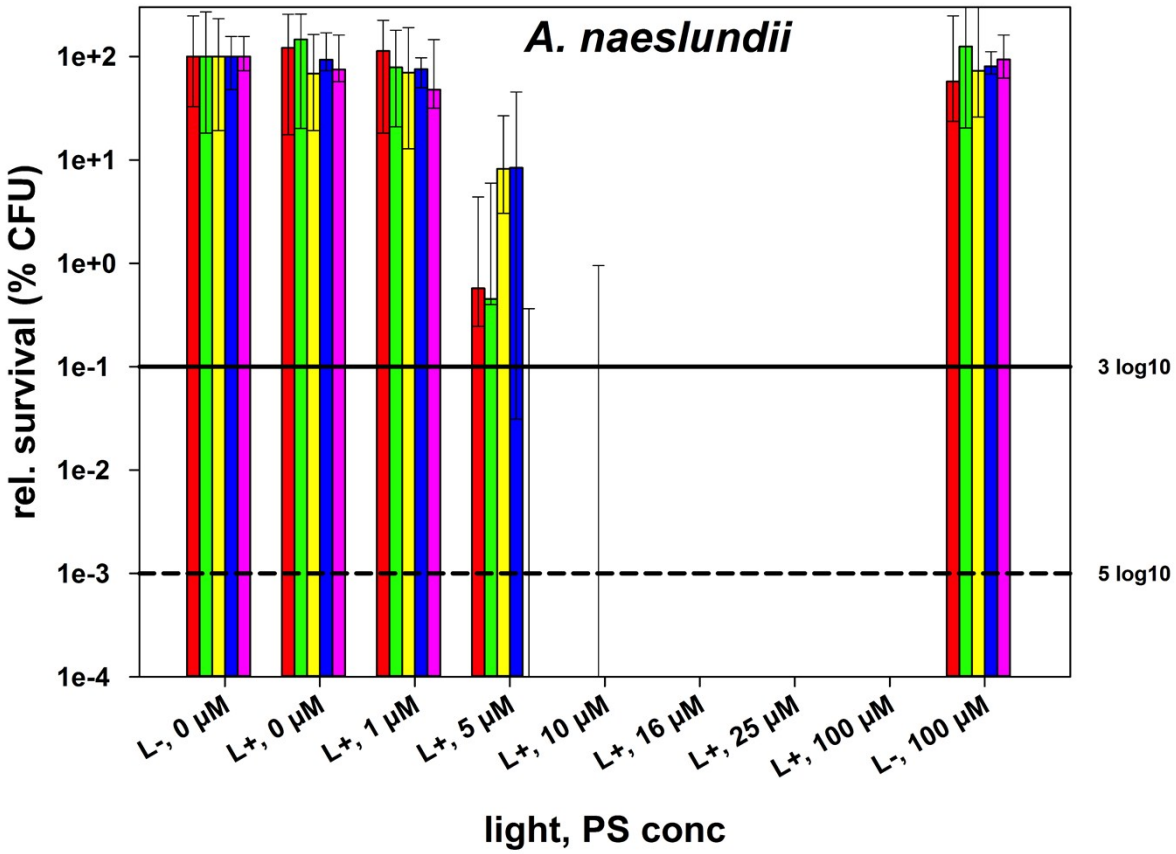
Antimicrobial Activity Data

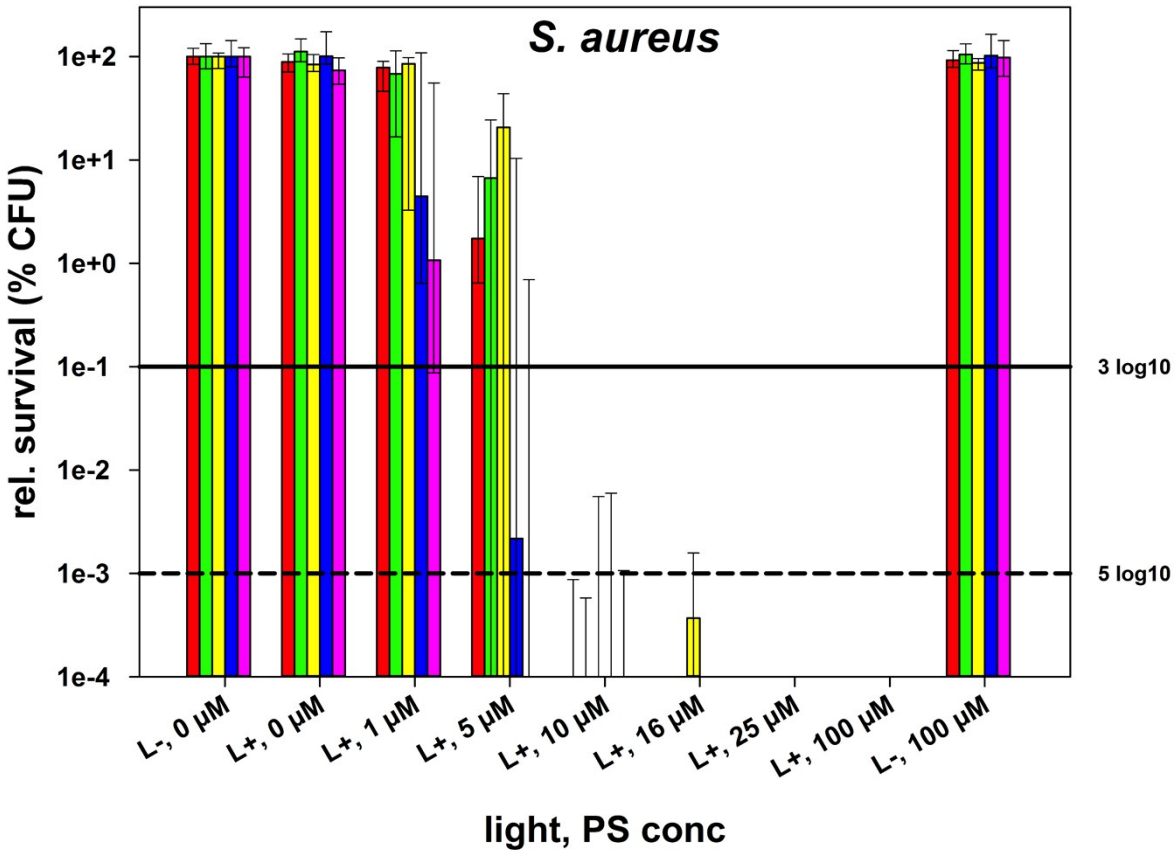
Photodynamic treatment was performed with all 1H-phenalen-1-one derivatives described in this study (**1** – **5**) using a blue light emitting prototype light source (BlueV, Waldmann, Villingen-Schwenningen, Germany) with an output-intensity of 20 mW/cm^2. Irradiation of the samples was from below, with direct contact to the bottom of the well plates containing the suspensions, wherefore diffusion of light due to surface tensions in the samples could be excluded. Irradiation was for 60 s, applying a light dose of 1.2 J/cm^2.

Surviving colonies were counted 24h (*E. faecalis*, *S. aureus* and *E. coli*) or 48 h (*S. mutans*, *A. naeslundii*) later. Relative survival rates were calculated with untreated control groups (L-, 0 µM, without irradiation) being setted as 100%. Horizontal and dashed lines mean reductions of 99.9% (3 $\log_{10}$ steps) and 99.999% (5 $\log_{10}$ steps), respectively.

L+: samples were irradiated; CFU: colony forming units; red column: SAPYR (**1**); green column: (**2**); yellow column: (**3**); blue column: (**4**); pink column: SAGUA (**5**) (n=6 experiments: medians including 25% and 75 % quartiles)




A. naeslundii
rel. survival (% CFU)
1e+2
1e+1
1e+0
1e-1
1e-2
1e-3
1e-4
3 log10
5 log10
L-, 0 µM
L+, 0 µM
L+, 1 µM
L+, 5 µM
L+, 10 µM
L+, 16 µM
L+, 25 µM
L+, 100 µM
L-, 100 µM
light, PS conc


S. aureus
rel. survival (% CFU)
1e+2
1e+1
1e+0
1e-1
1e-2
1e-3
1e-4
3 log10
5 log10
L-, 0 µM
L+, 0 µM
L+, 1 µM
L+, 5 µM
L+, 10 µM
L+, 16 µM
L+, 25 µM
L+, 100 µM
L-, 100 µM
light, PS conc

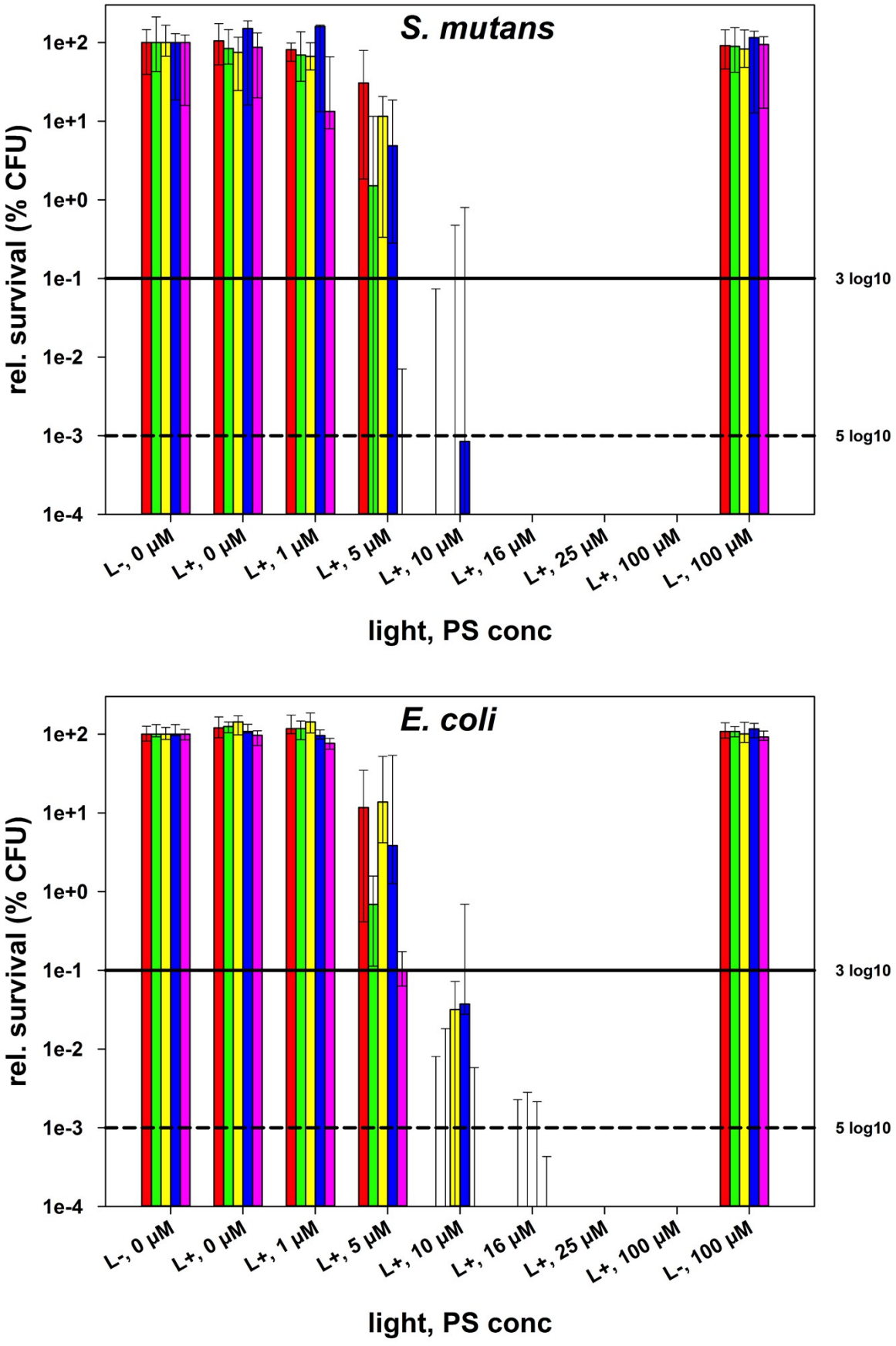


Figure S-15: Photodynamic inactivation of *E. faecalis*, *A. naeslundii*, *S.mutans*, *S. aureus* and *E. coli* by 1H-phenalen-1-one derivatives **1** – **5**