

Supporting information

for

Enhancement of antiproliferative activity by phototautomerization of anthrylphenols

by

Marijeta Kralj,^{a*} Lidija Uzelac,^a Lily Wang,^b Peter Wan,^b Martina Tireli,^c Kata Mlinarić-Majerski,^c Ivo Piantanida,^c Nikola Basarić^{c*}

^a Department of Molecular Medicine, Ruđer Bošković Institute, Bijenička cesta 54, 10 000 Zagreb, Croatia. Fax: +385 1 4561 010; Tel: + 385 1 4571 235; E-mail: Marijeta.Kralj@irb.hr

^b Department of Chemistry, Box 3065, University of Victoria, Victoria, BC V8W 3V6, Canada.

^c Department of Organic Chemistry and Biochemistry, Ruđer Bošković Institute, Bijenička cesta 54, 10 000 Zagreb, Croatia. Fax: +385 1 4680 195; Tel: +385 12 4561 141; E-mail: nbasaric@irb.hr

Content

1. HPLC spectra after irradiation of 1 in the presence of nucleotides	S3
2. ^1H NMR spectrum after the irradiation of 1 in the presence of adenine	S6
3. ^1H NMR spectrum after the irradiation of 1 in the presence of glycine ethyl ester	S7
4. MS-MS apectra of photoproducts 10-12	S8
5. NMR spectra of 8	S11
6. UV-vis spectra of 1 in the presence of BSA	S13
7. Fluorescence spectra of 1 in the presence of BSA and DNA	S14
8. CD spectra	S17

1. HPLC spectra after irradiation of **1 in the presence of nucleotides**

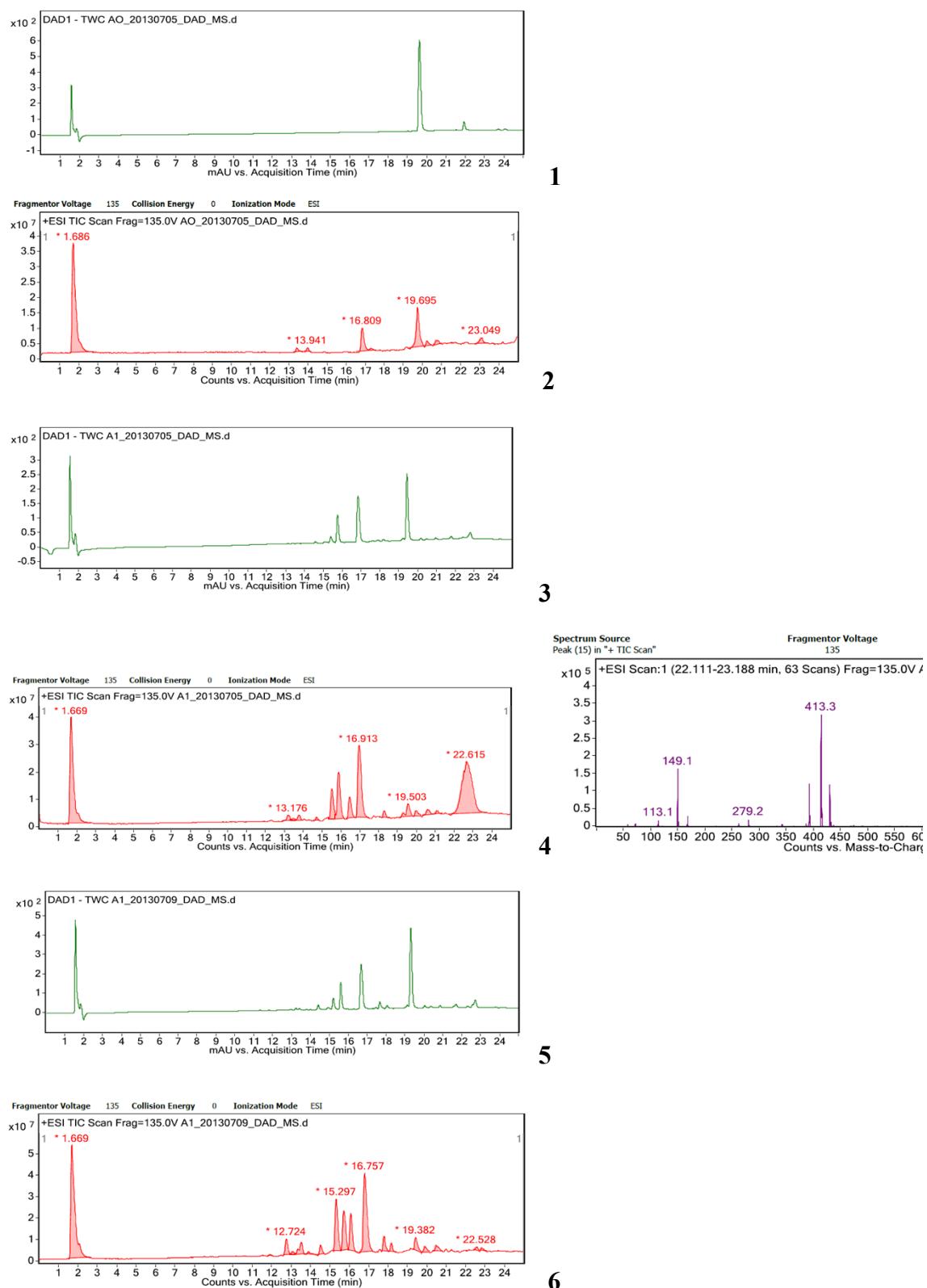


Fig. S1. HPLC chromatograms after irradiatio of **1** in the presence of adenine (Left: 1 and 2, before the irradiation; 3 and 4 after 1 h of irradation; bottom, 5 and 6 after standing at rt, right: MS of the fraction with rt 22-24 min).

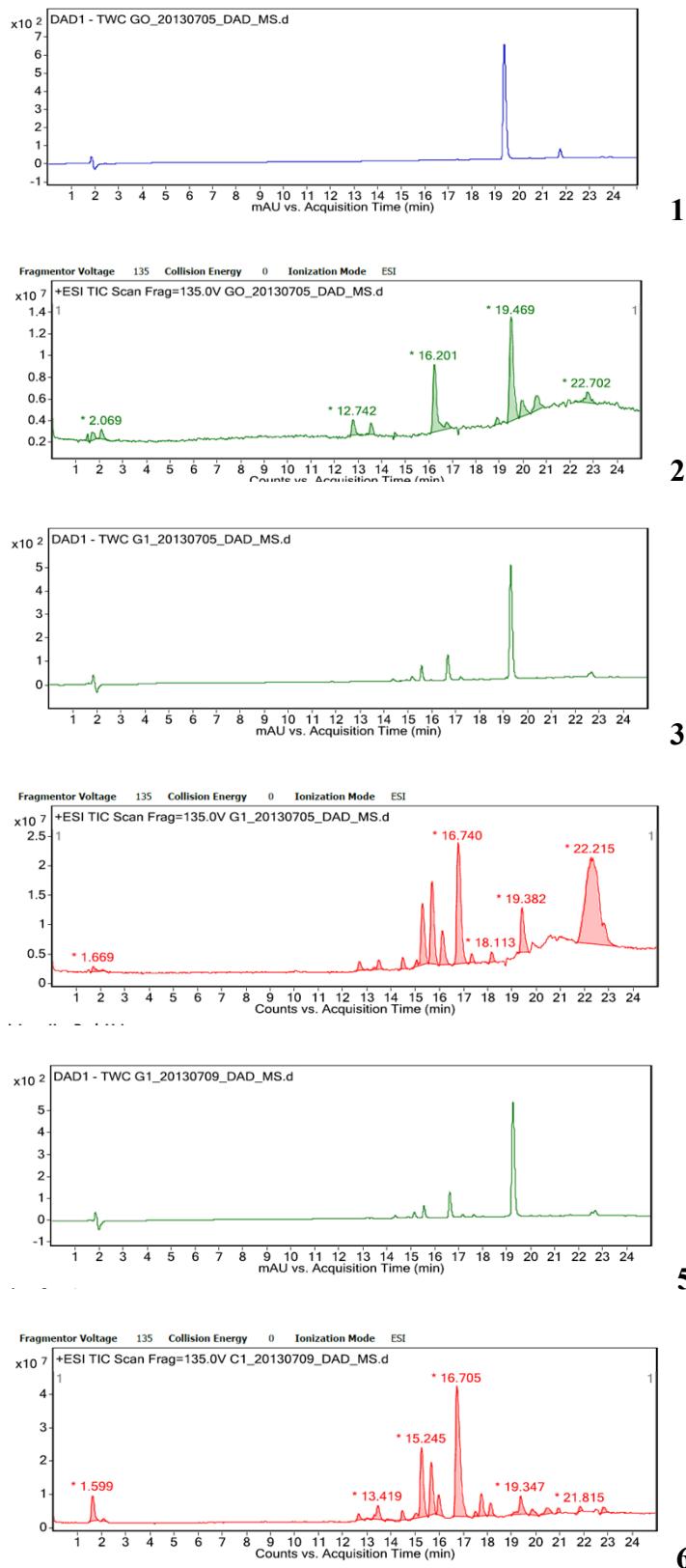
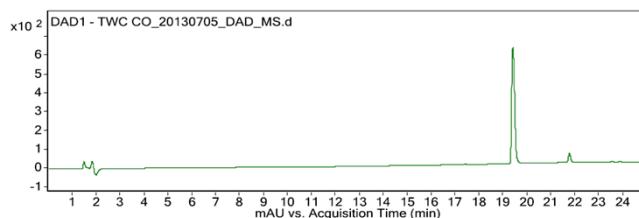
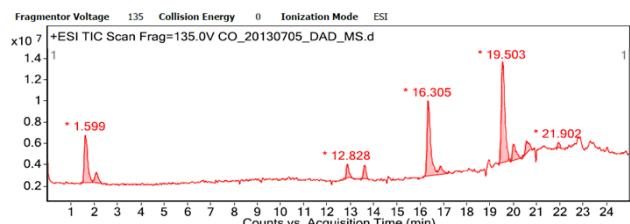


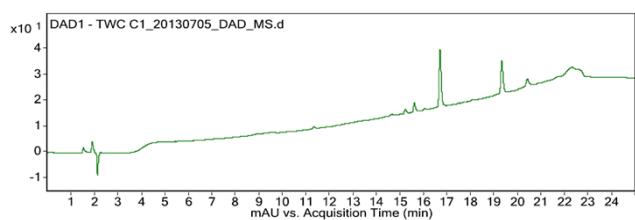
Fig. S2. HPLC chromatograms after irradiatio of **1** in the presence of guanine (1 and 2, before the irradiation; 3 and 4 after 1 h of irradiation; bottom, 5 and 6 after standing at rt).



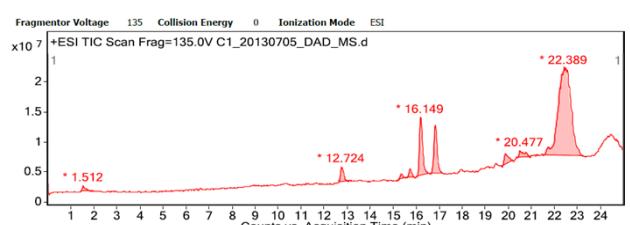
1



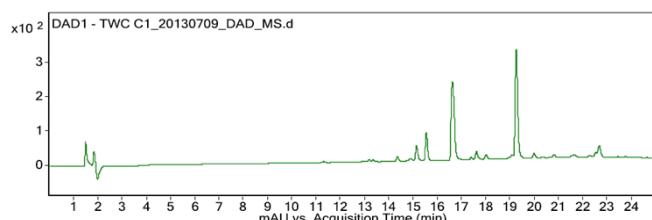
2



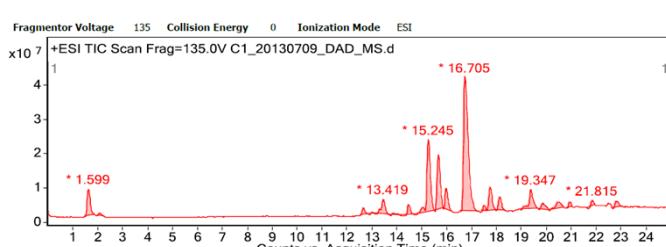
3



4



5

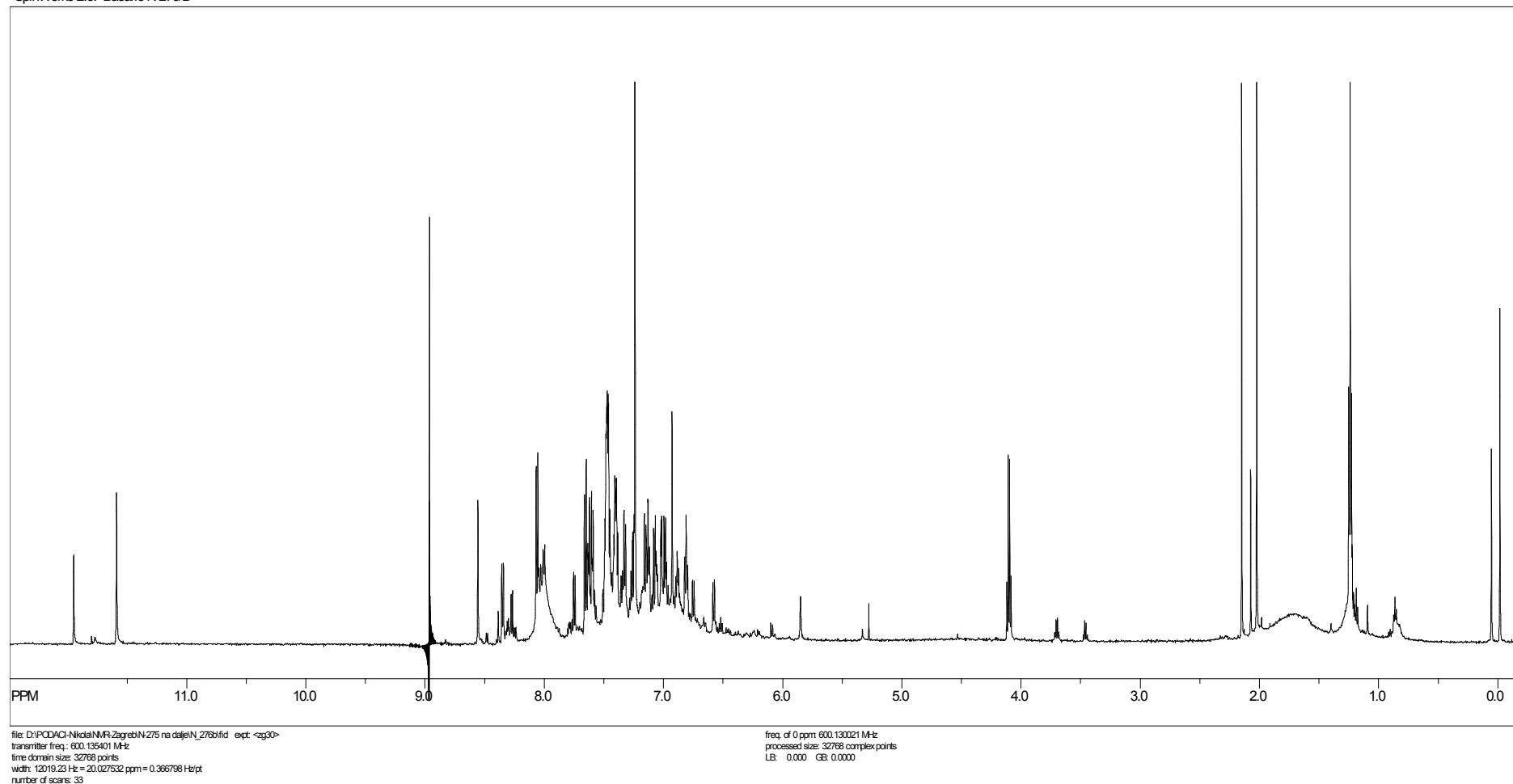


6

Fig. S3. HPLC chromatograms after irradiatio of **1** in the presence of cytosine (1 and 2, before the irradiation; 3 and 4 after 1 h of irradiation; bottom, 5 and 6 after standing at rt).

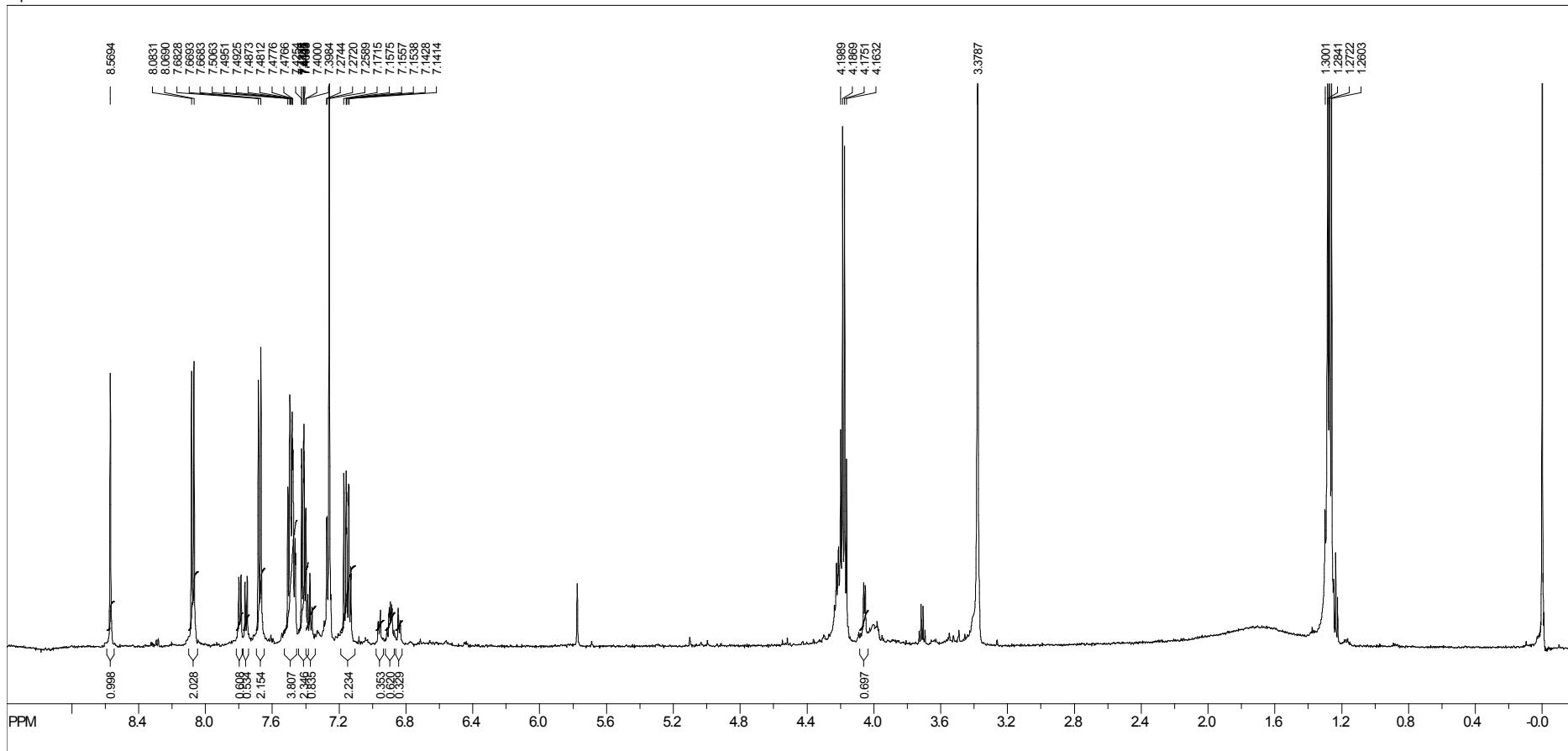
2. ^1H NMR spectrum after the irradiation of 1 in the presence of adenine

SpinWorks 2.3: Basaric N-276/B



3. ^1H NMR spectrum after the irradiation of 1 in the presence of glycine ethyl ester

SpinWorks 2.3: Basaric N316



file: D:\PODACI-Nikola\Measurements_Zagreb\NMR\Zagreb\N306 na dane\N316.1\fid expt: <zg30>

transmitter freq.: 600.135401 MHz

time domain size: 32768 points

width: 1219.23 Hz = 20.027532 ppm = 0.366798 Hz/pt

number of scans: 21

freq. of 0 ppm 600.130010 MHz

processed size: 32768 complex points

LB: 0.000 GB: 0.0000

4. MS-MS spectra of photoproducts 10-12

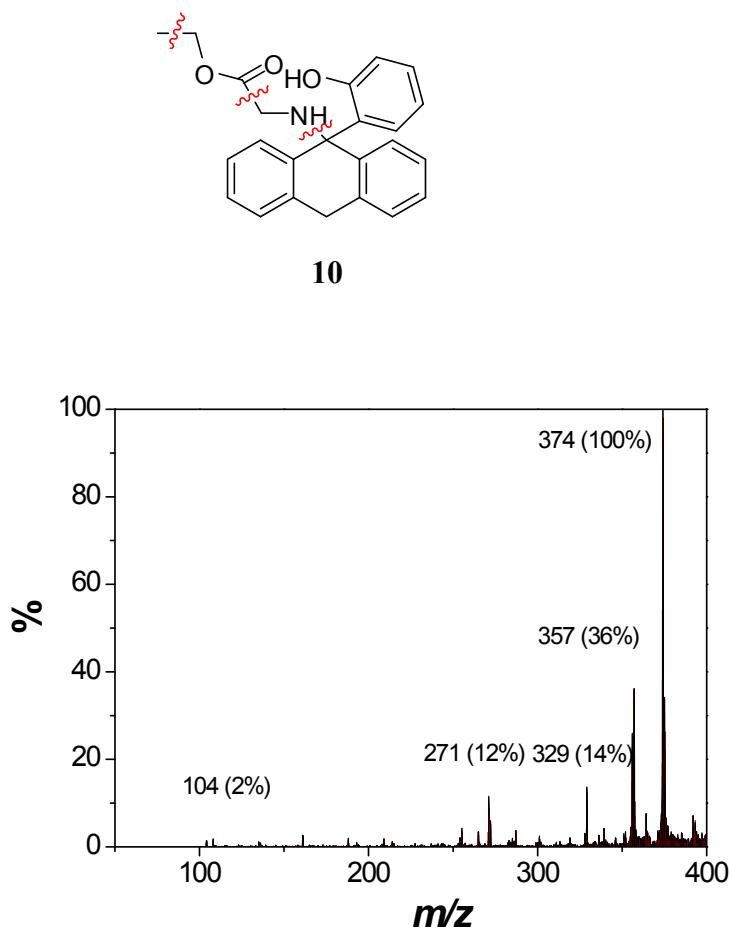
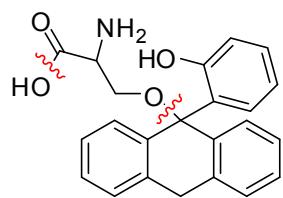


Fig S5. MS-MS spectrum of **10** obtained after the isolation of the molecular ion (m/z 374) and its fragmentation with 1 eV.



11

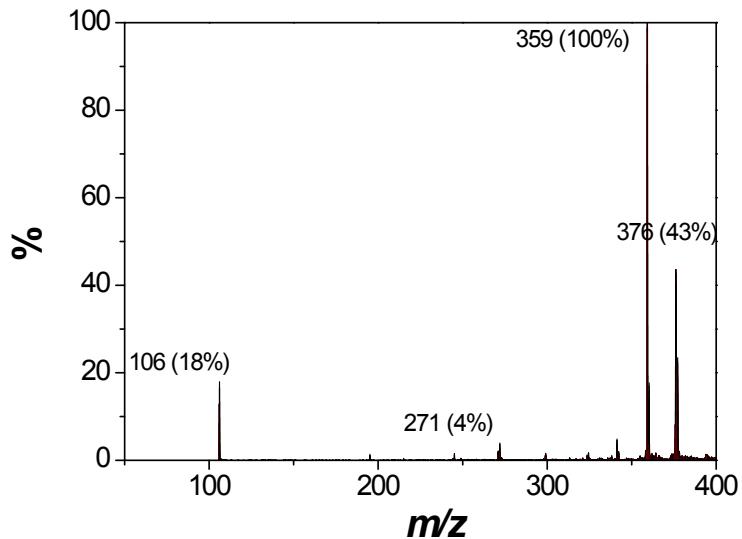
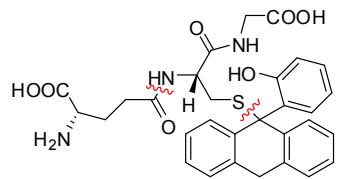


Fig S6. MS-MS spectrum of **11** obtained after the isolation of the molecular ion (m/z 376) and its fragmentation with 0.8 eV.



12

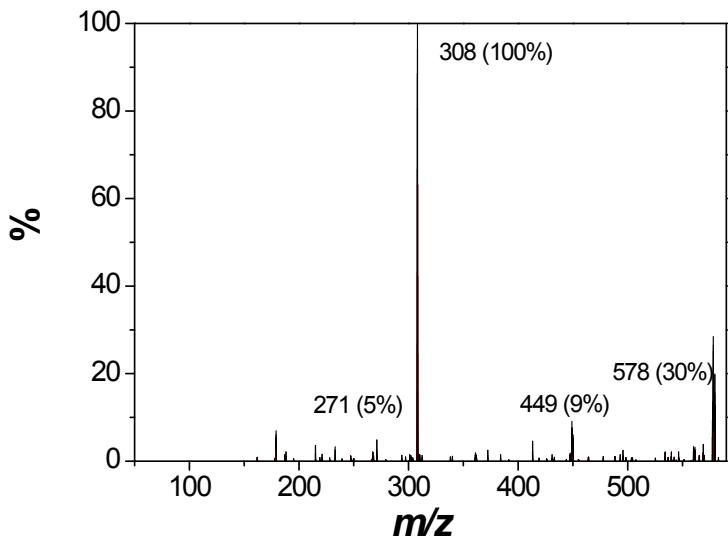
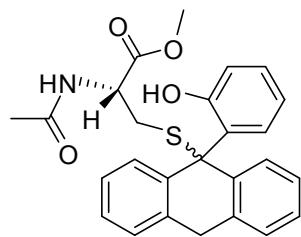


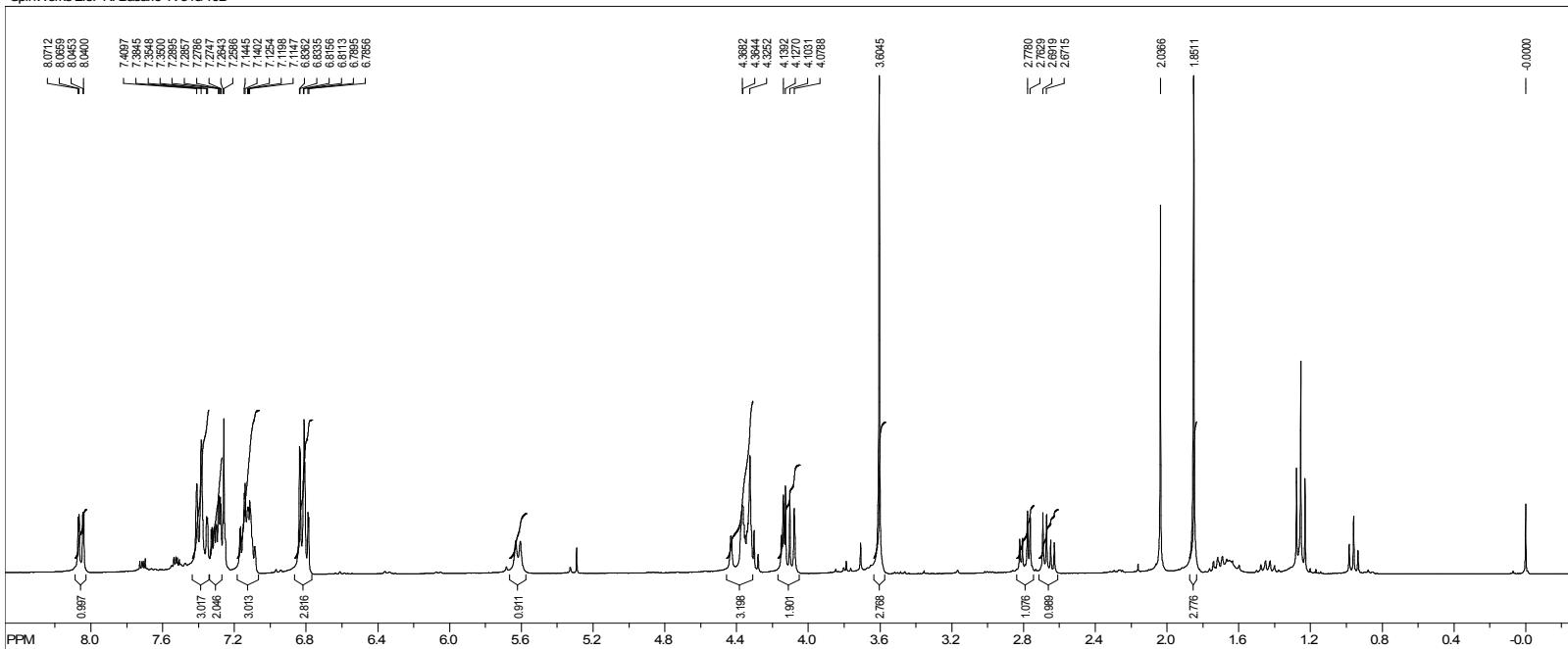
Fig S7. MS-MS spectrum of **12** obtained after the isolation of the molecular ion (m/z 578) and its fragmentation in the source with 0.8 eV.

5. NMR spectra of 8

¹H NMR (300 MHz, CDCl₃) of **8**



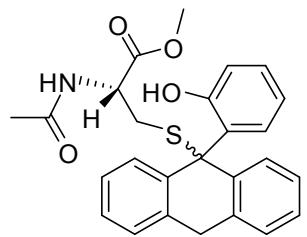
SpinWorks 2.3: N. Basaric N-313/10B



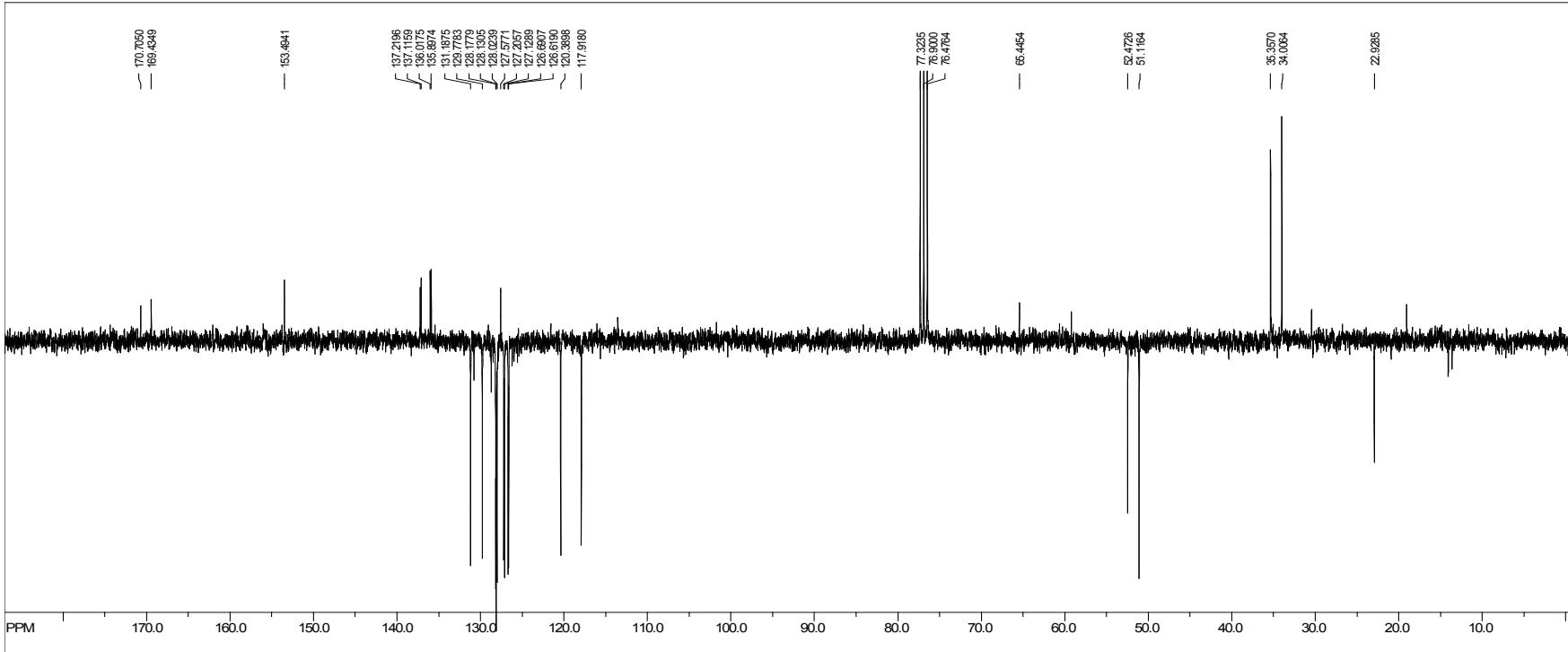
file: D:\DODAC-NicolaNMR Zagreb\N-306 na dane\N-313-10_TLO3.fid expt: <g30>
transmitter freq.: 300.132701 MHz
time domain size: 32768 points
width: 6172.84 Hz = 20.567034 ppm = 0.188380 Hz/pt
number of scans: 27

freq. of 0 ppm: 300.130007 MHz
processed size: 32768 complex points
LB: 0.000 GB: 0.000

¹³C NMR (75 MHz, CDCl₃) of **8**



SpinWorks 2.3: N. Basaric N-313/10B



file: D:\PODaci-NikolaNMR-Zagreb\N-306 na dajte\basaric_n31310bept1\fid expt: <jmod>
transmitter freq: 75.475295 MHz
time domain size: 65536 points
width: 17086.61 Hz = 238.207995 ppm = 0.274439 Hz/pt
number of scans: 845

freq. of 0 ppm: 75.467768 MHz
processed size: 32768 complex points
LB: 1.000 GB: 0.0000

6. UV-vis spectra of **1 in the presence of BSA**

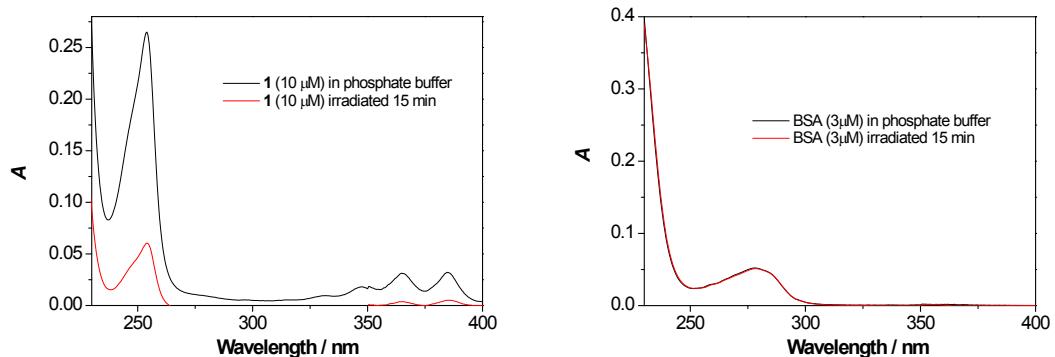


Fig S8. UV-vis spectra of **1** ($c = 10 \mu\text{M}$, left) and BSA ($c = 3 \mu\text{M}$, right), in phosphate buffer (pH = 7, 1 mM), before and after the irradiation (Luzchem, $8 \times 350 \text{ nm}$, 15 min).

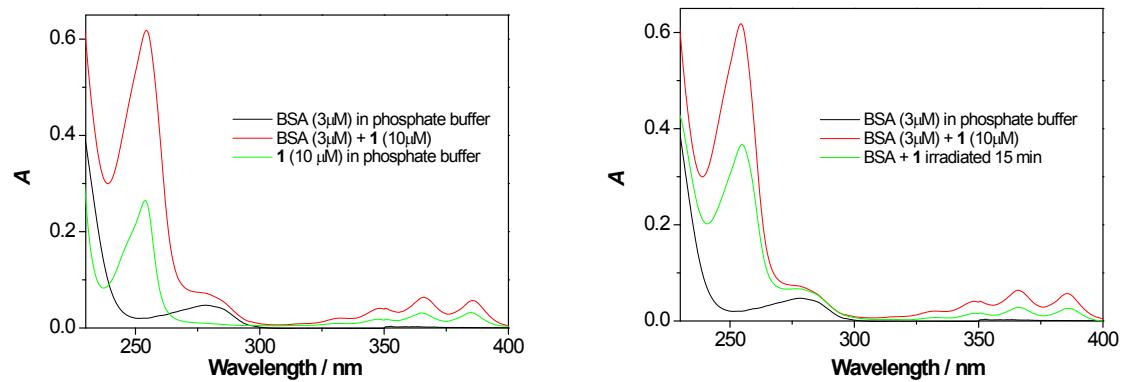


Fig S9. UV-vis spectra of **1** ($c = 10 \mu\text{M}$), BSA ($c = 3 \mu\text{M}$, right) in phosphate buffer (pH = 7, 1 mM), and their mixture (left), before and after the irradiation (Luzchem, $8 \times 350 \text{ nm}$, 15 min, right).

7. Fluorescence spectra of **1 in the presence of BSA and DNA**

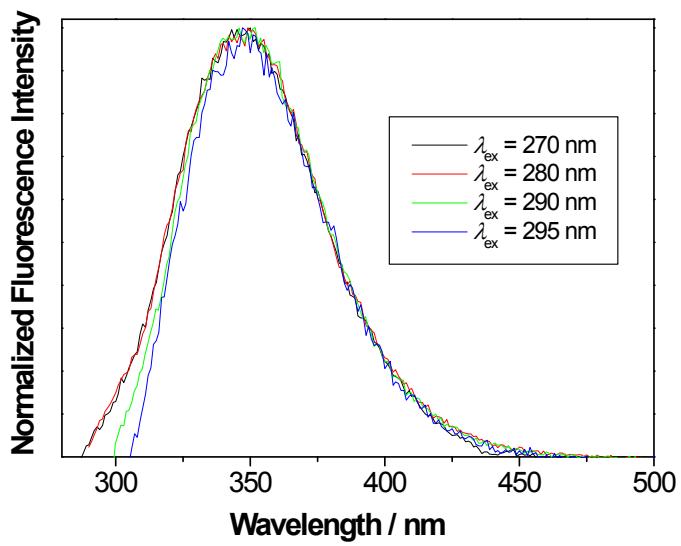


Fig S10. Normalized fluorescence spectra of BSA ($c = 3 \mu\text{M}$) in phosphate buffer (pH = 7, $c = 1 \text{ mM}$) at different excitation wavelengths.

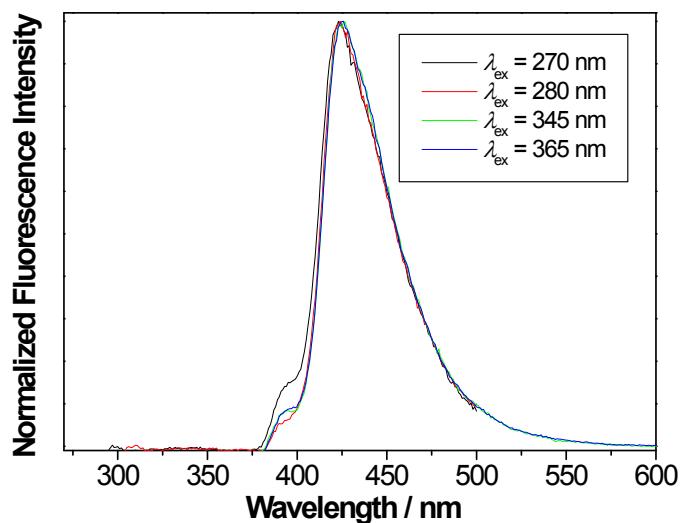


Fig S11. Normalized fluorescence spectra of **1** ($c = 10 \mu\text{M}$) in phosphate buffer (pH = 7, $c = 1 \text{ mM}$) at different excitation wavelengths.

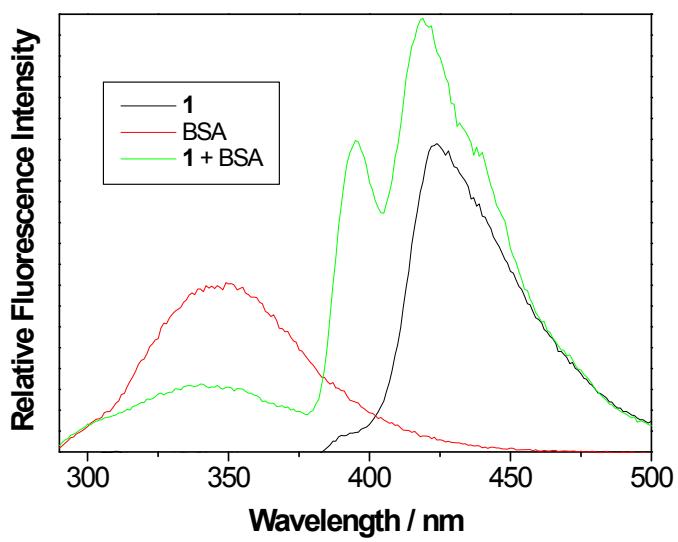


Fig S 12. Fluorescence spectra ($\lambda_{\text{ex}} = 280 \text{ nm}$) of **1** ($c = 10 \mu\text{M}$), BSA ($c = 3 \mu\text{M}$), and their corresponding mixture in phosphate buffer (pH = 7, $c = 1 \text{ mM}$).

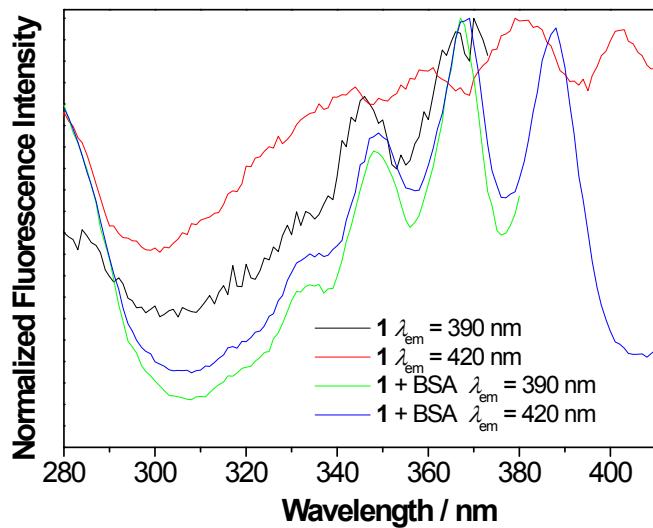


Fig S13. Normalized excitation spectra ($\lambda_{\text{em}} = 390 \text{ nm}$ and $\lambda_{\text{em}} = 420 \text{ nm}$) of **1** ($c = 10 \mu\text{M}$), with and without BSA ($c = 3 \mu\text{M}$) in phosphate buffer (pH = 7, $c = 1 \text{ mM}$).

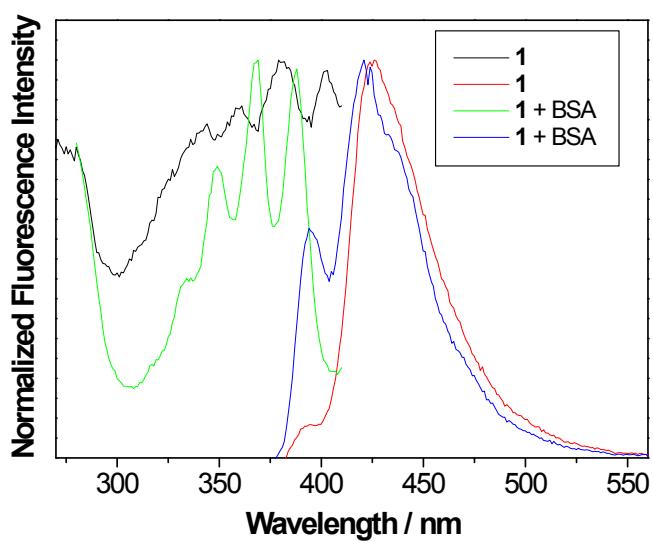


Fig S14. Normalized excitation ($\lambda_{\text{em}} = 420 \text{ nm}$) and emission ($\lambda_{\text{ex}} = 345 \text{ nm}$) spectra of **1** ($c = 10 \mu\text{M}$), with and without BSA ($c = 3 \mu\text{M}$) in phosphate buffer (pH = 7, $c = 1 \text{ mM}$).

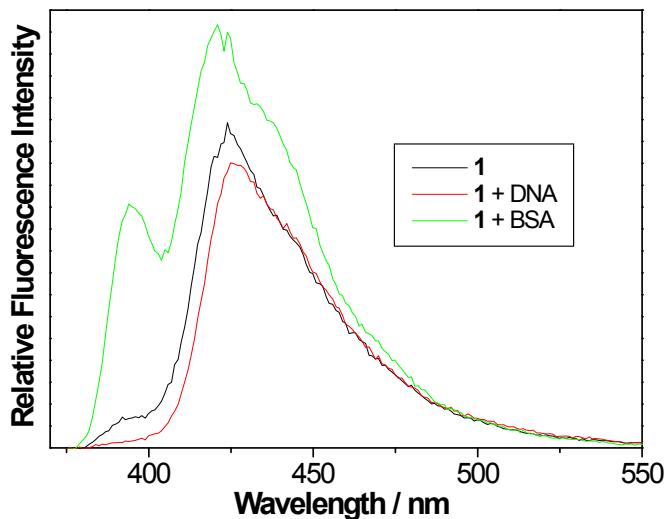


Fig S15. Fluorescence spectra ($\lambda_{\text{ex}} = 345 \text{ nm}$) of **1** ($c = 10 \mu\text{M}$), in the presence of ct-DNA ($c = 100 \mu\text{M}$) or BSA ($c = 3 \mu\text{M}$) in aqueous cacodylate buffer (pH = 7, 50 mM).

8. CD Spectra

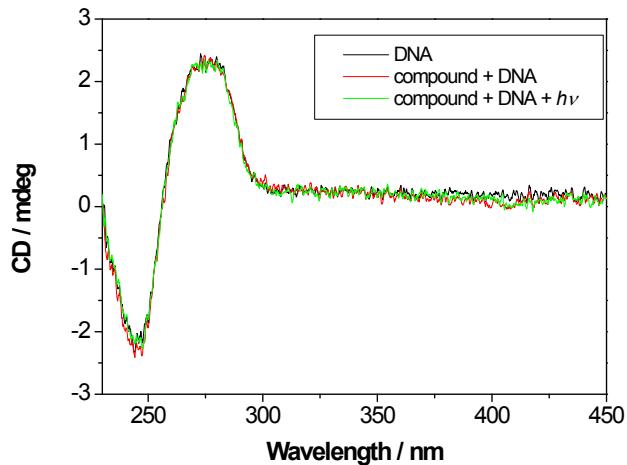


Fig S16. CD spectra of **1** ($c = 1 \times 10^{-5}$ M), ct-DNA ($c = 4 \times 10^{-5}$ M) in H_2O before and after the irradiation in Luzchem (8×350 nm, 15 min).

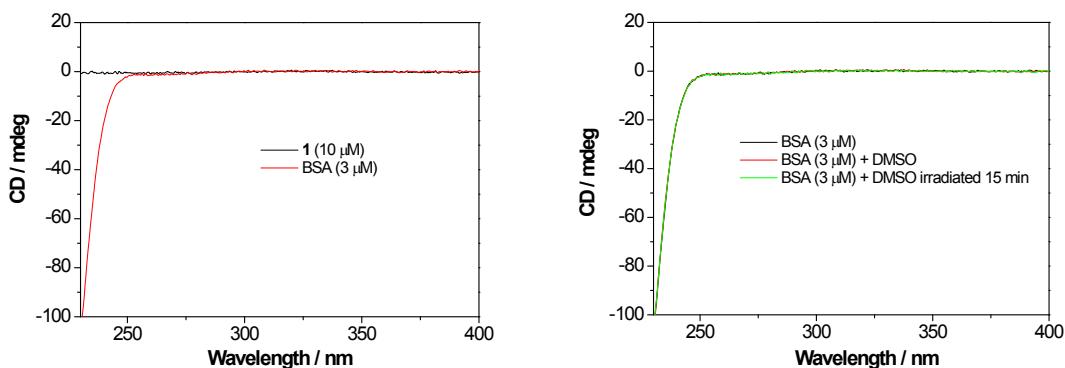


Fig S17. CD spectra of **1** ($c = 1 \times 10^{-5}$ M) and BSA ($c = 3 \times 10^{-6}$ M) in phosphate buffer (pH = 7, 1mM, left), and BSA ($c = 3 \times 10^{-6}$ M) in phosphate buffer (pH = 7, 1mM) in the presence of DMSO, before and after the irradiation (Luzchem, 8×350 nm, 15 min; right).

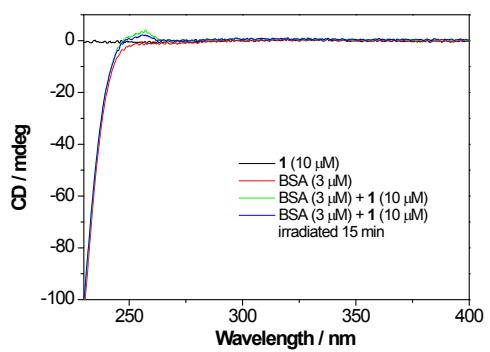


Fig S18. CD spectra of **1** ($c = 1 \times 10^{-5}$ M) and BSA ($c = 3 \times 10^{-6}$ M) in phosphate buffer (pH = 7, 1 mM) before and after the irradiation in Luzchem (8 \times 350 nm, 15 min).