Supporting Information

The Dermacozines and Light: A Novel Phenazine Semiquinone Radical based Photocatalytic System from the Deepest Oceanic Trench of the Earth

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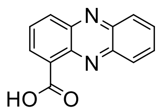
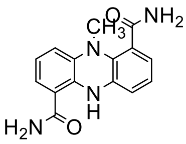
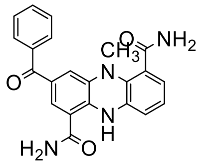


phenazine-1-carboxilic acid



Dermacozine A



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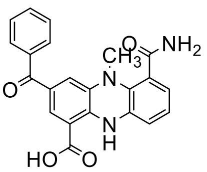

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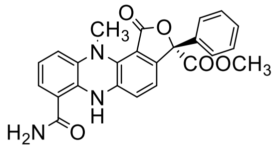

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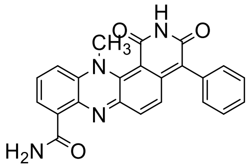

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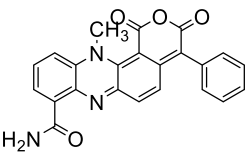

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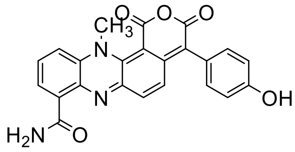

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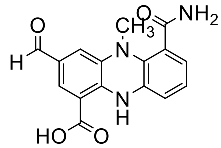

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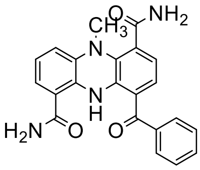
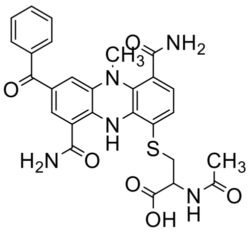


Dermacozine I



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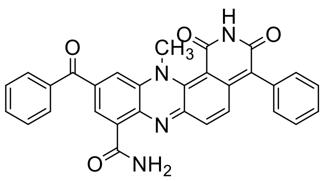

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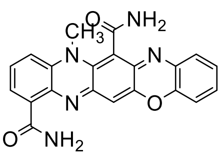
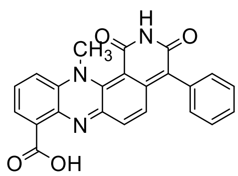
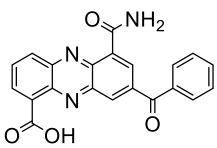


Dermacozine N



Dermacozine O



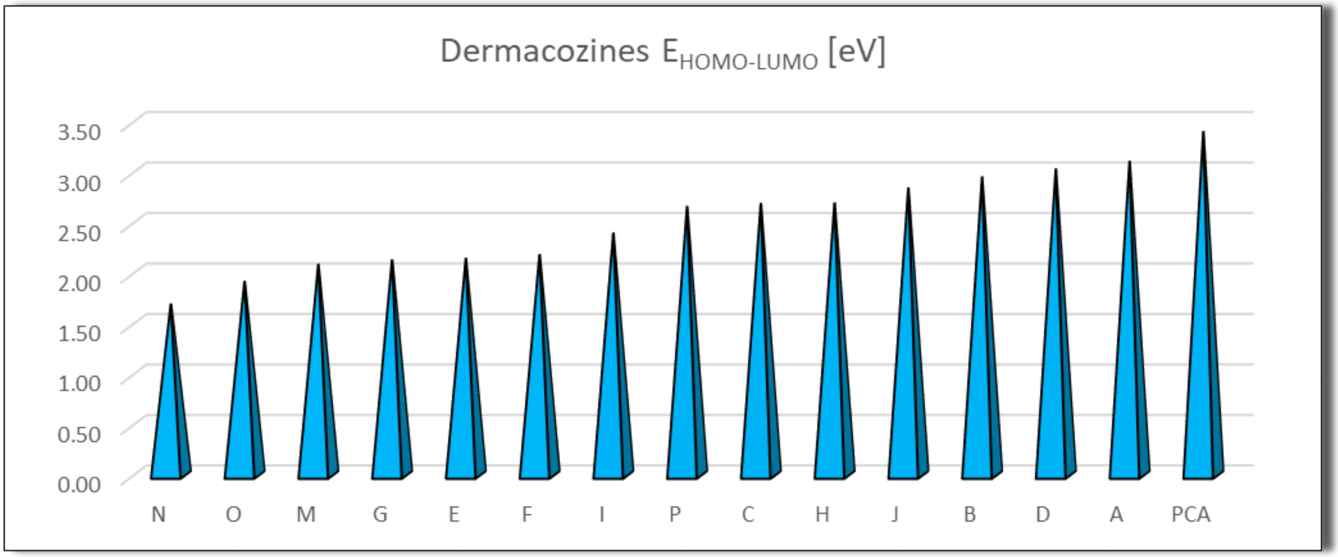
Dermacozine P

S1. Dermacozines isolated to date. [Ref.2,3,4,5]

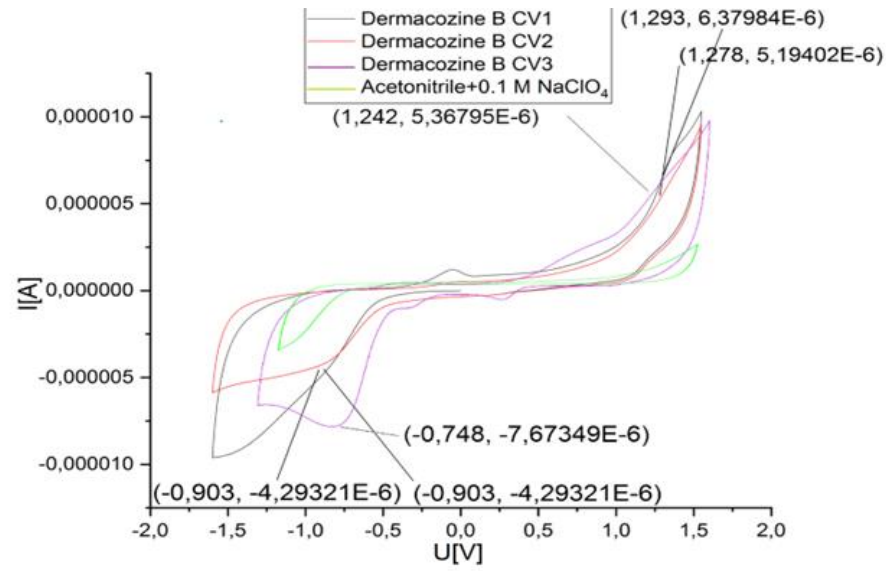
S2. Dermacozines, isolation (stationary phase: silica, mobile phase: 90% CH_2Cl_2-10% CH_3OH).

Dermacozine	Longest absorption maximum in the visible [nm]	Longest absorption maximum in the visible [m]	Calculated frequency [Hz]	$E_{optical\_gap\_calc\_Joules}$ [J]	$E_{optical\_gap\_calc\_eV}$[eV]
Dermacozine A	398	3.98E-07	7.53247E+14	4.99107E-19	3.12
Dermacozine B	419	4.19E-07	7.15495E+14	4.74092E-19	2.96
Dermacozine C	460	4.60E-07	6.51723E+14	4.31836E-19	2.70
Dermacozine D	408	4.08E-07	7.34785E+14	4.86874E-19	3.04
Dermacozine E	576	5.76E-07	5.20473E+14	3.44869E-19	2.15
Dermacozine F	566	5.66E-07	5.29669E+14	3.50962E-19	2.19
Dermacozine G	580	5.80E-07	5.16884E+14	3.42491E-19	2.14
Dermacozine H	459	4.59E-07	6.53143E+14	4.32777E-19	2.70
Dermacozine I	516	5.16E-07	5.80993E+14	3.84970E-19	2.40
Dermacozine J	435	4.35E-07	6.89178E+14	4.56654E-19	2.85
Dermacozine M	590	5.90E-07	5.08123E+14	3.36686E-19	2.10
Dermacozine N	729	7.29E-07	4.11238E+14	2.72489E-19	1.70
Dermacozine O	644	6.44E-07	4.65516E+14	3.08454E-19	1.93
Dermacozine P	465	4.65E-07	6.44715E+14	4.27193E-19	2.67
PCA	364	3.64E-07	8.23606E+14	5.45727E-19	3.41

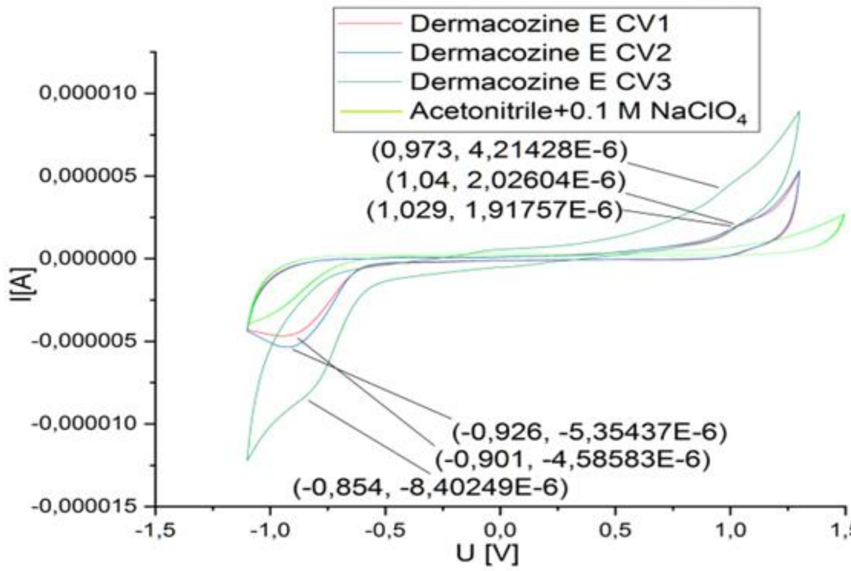
S3. UV-Vis measured Longest AMs of dermacozines (solvent: C_2H_5OH) in the visible EM radiation in [nm] [Ref.2,3,4,5], [m], [Hz], [J] and [eV].



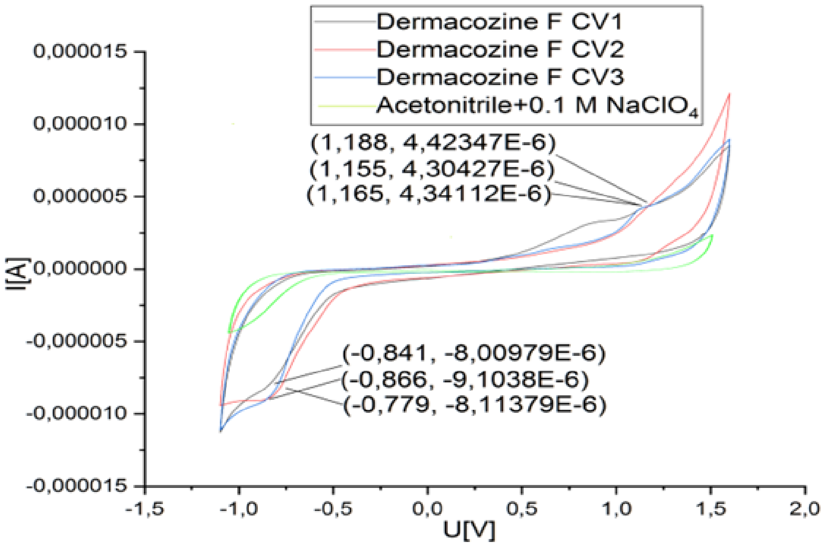
S4. Longest AMs of dermacozines in the visible EM (solvent: C_2H_5OH))[2,3,4,5] [eV].



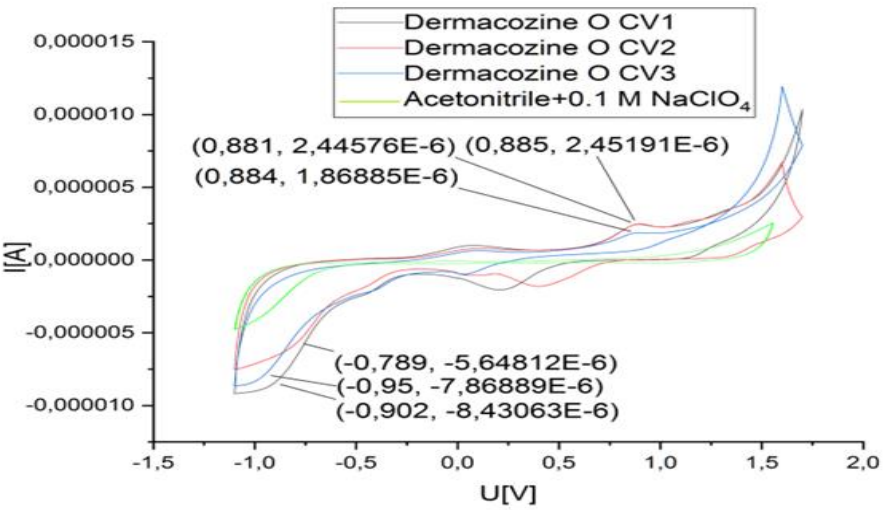
S5. Dermacozine B Cyclic Voltammetry measurements (0.1 M $NaClO_4$ in CH_3CN).



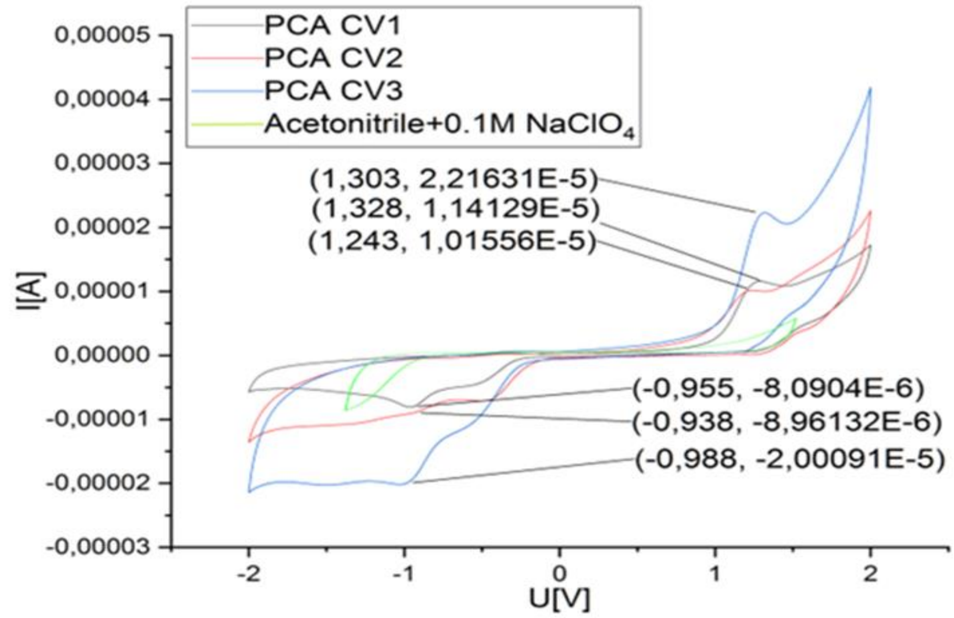
S6. Dermacozine E Cyclic Voltammetry measurements (0.1 M $NaClO_4$ in CH_3CN).



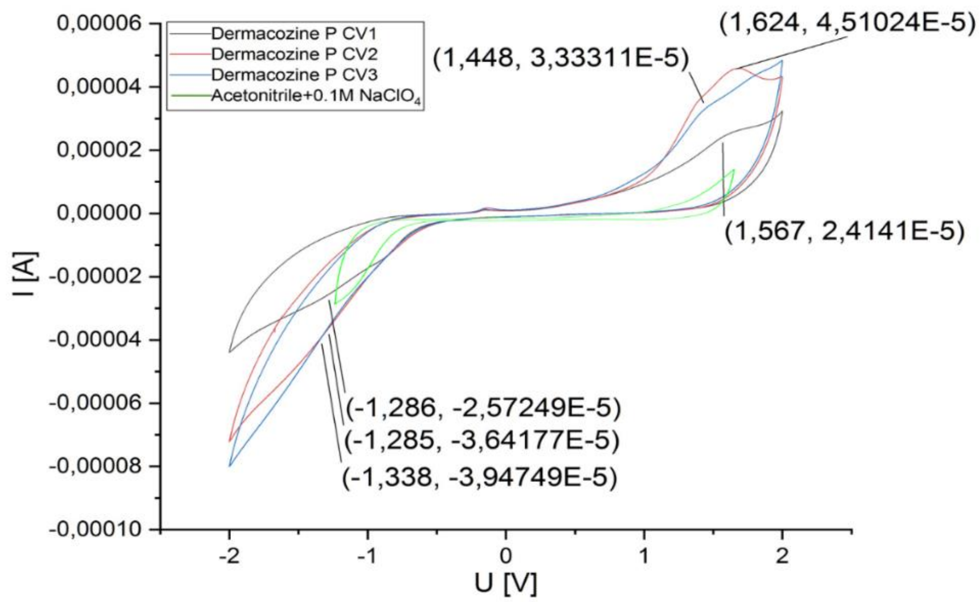
S7. Dermacozine F Cyclic Voltammetry measurements (0.1 M $NaClO_4$ in CH_3CN).



S8. Dermacozine O Cyclic Voltammetry measurements (0.1 M $NaClO_4$ in CH_3CN).



S9. PCA Cyclic Voltammetry measurements (0.1 M $NaClO_4$ in CH_3CN).

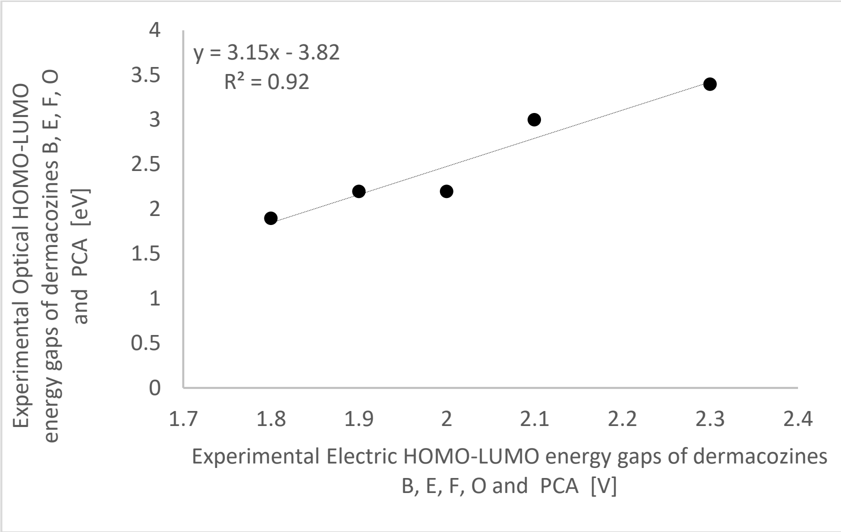


S10. Dermacozine P Cyclic Voltammetry measurements (0.1 M $NaClO_4$ in CH_3CN).

DERMACOZINE	OPTICAL GAP [EV] (EXP)	ELECTRIC GAP±SE [V] (EXP)	EXPERIMENTAL ANODIC POTENTIAL±SE [V] (AG ACETONITRILE) (EXP)	EXPERIMENTAL CATHODIC POTENTIAL±SE [V] (AG ACETONITRILE) (EXP)	SHE REFERENCED ANODIC POTENTIALS [V] (EXP)	SHE REFERENCED CATHODIC POTENTIALS [V] (EXP)	ESTIMATED ANODIC POTENTIALS BASED ON OPTICAL GAP – ELECTRIC HOMO EXPERIMENTAL RELATIONSHIP (R^2=0.73)±ME [V] $\mu_{Anodic}\,[\mathrm{V}] = \frac{E_{Optical}\,[\mathrm{eV}]+0.7}{3}$)±ME CALC (SHE)	ESTIMATED CATHODIC POTENTIALS FROM μ OF THE EXPERIMENTAL CATHODICPOTENTIALS [V]±ME CALC (SHE)
N	1,7						+0.8±0.01	-0.9±0.02
O	1,9	1.763±0.005	+0.883±0.001	-0.880±0.005	+0.848±0.003	-0.915±0.005	+0.9±0.01	-0.9±0.02
G	2,1						+1.0±0.01	-0.9±0.02
M	2,1						+1.0±0.01	-0.9±0.02
E	2,2	1.908±0.030	+1.014±0.021	-0.894±0.021	+0.979±0.021	-0.929±0.021	+1.0±0.01	-0.9±0.02
F	2,2	1.998±0.024	+1.169±0.010	-0.829±0.022	+1.134±0.010	-0.864±0.022	+1.0±0.01	-0.9±0.02
I	2,4						+1.1±0.01	-0.9±0.02
C	2,7						+1.1±0.01	-0.9±0.02
H	2,7						+1.1±0.01	-0.9±0.02
P	2,7	2.849±0.053*	+1.546±0.052*	-1.303±0.018*	+1.511±0.052*	-1.338±0.052*	+1.1±0.01	-0.9±0.02
J	2,9						+1.2±0.01	-0.9±0.02
B	3,0	2.122±0.054	+1.271±0.015	-0.851±0.052	+1.236±0.015	-0.886±0.052	+1.2±0.01	-0.9±0.02
D	3,0						+1.2±0.01	-0.9±0.02
A	3,1						+1.3±0.01	-0.9±0.02
PCA	3,4	2.252±0.029	+1.291±0.025	-0.960±0.015	+1.256±0.025	-0.995±0.015	+1.4±0.01	-0.9±0.02

S11. Measured anodic and cathodic potentials of dermacozines in 0.1 M $NaClO_4$ in CH_3CN±Standard Errors (SE) and calculated anodic and cathodic values±Mean Errors (ME) based on 13.a. linear regression (calculated anodic potentials) and arithmetic mean of measured cathodic potentials (μ)±ME. *Dermacozine P excluded from calculations as the cathodic and anodic current overlaps too much with the solvent decomposition.

NB: Since the errors of the AMs in Ethanol are not known, no standard propagation of error but mean error (ME) was given for calculated values. Whereas the measured potentials expressed as ± standard error (SE).

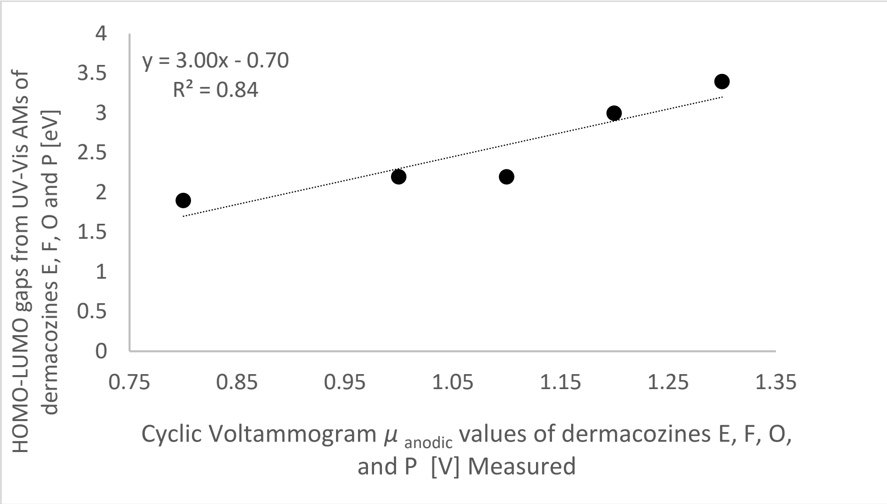


Dermacozine	**(x) Δ E electric [V]**	**(y) Δ E Optical [eV]**
PCA	2,3	3,4
B	2,1	3
E	1,9	2,2
F	2	2,2
O	1,8	1,9

S12.a. Dermacozine B, E, F, O and PCA`s experimental optical (Solvent: C_2H_5OH) and experimental electric HOMO-LUMO energy gaps (solvent: CH_3CN) correlation.

SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0,960027177							
R Square	0,92165218							
Adjusted R Square	0,89553624							
Standard Error	0,203903351							
Observations	5							
ANOVA								
	df	*SS*	*MS*	*F*	*Significance F*			
Regression	1	1,46727027	1,46727027	35,2907909	0,009535859			
Residual	3	0,12472973	0,041576577					
Total	4	1,592						
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95,0%*	*Upper 95,0%*
Intercept	-3,82027027	1,074519785	-3,555327993	0,037946247	-7,23987179	-0,40066875	-7,23987179	-0,40066875
X Variable 1	3,148648649	0,530021523	5,940605264	0,009535859	1,461883611	4,835413686	1,461883611	4,835413686

S12.b. Dermacozine B, E, F, O and PCA`s experimental optical [eV] (Solvent: C_2H_5OH) and experimental electric HOMO-LUMO energy gaps [V] (solvent: CH_3CN) multiple regression (Microsoft Excel).

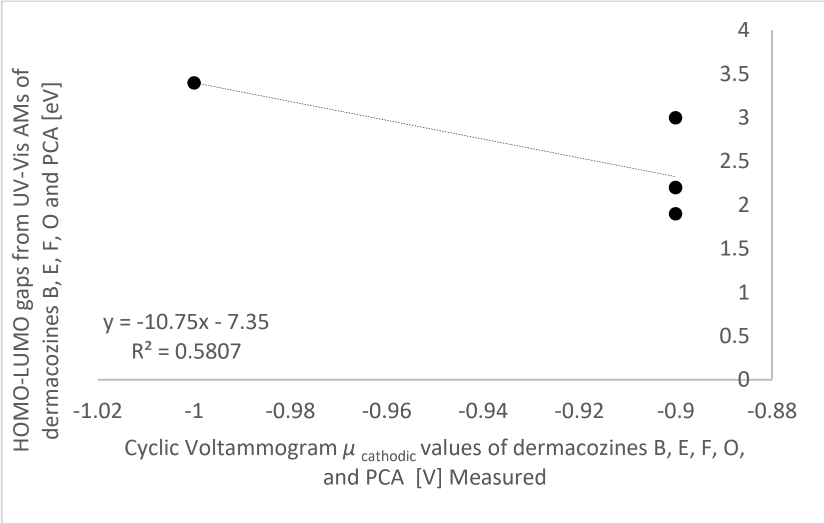


Dermacozine	**(x) Electric HOMO [V]**	**(y) Δ E Optical [eV]**
PCA	1,3	3,4
B	1,2	3
E	1	2,2
F	1,1	2,2
O	0,8	1,9

S13.a. Linear correlation between the experimental anodic potentials of dermacozine B, E, F, O and PCA [V] with Cyclic Voltammetry (solvent: CH_3CN) and the experimental optical HOMO-LUMO gaps measured with UV-Vis Spectroscopy (solvent C_2H_5OH) [eV].

SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0,914704005							
R Square	0,836683417							
Adjusted R Square	0,782244556							
Standard Error	0,294392029							
Observations	5							
ANOVA								
	df	*SS*	*MS*	*F*	*Significance F*			
Regression	1	1,332	1,332	15,36923077	0,029518265			
Residual	3	0,26	0,086666667					
Total	4	1,592						
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95,0%*	*Upper 95,0%*
Intercept	-0,7	0,836875355	-0,836444753	0,464292127	-3,363310883	1,963310883	-3,363310883	1,963310883
X Variable 1	3	0,765235641	3,920361051	0,029518265	0,564678663	5,435321337	0,564678663	5,435321337

S13.b. Multiple Regression (Microsoft Excel) between the experimental anodic potentials of dermacozine B, E, F, O and PCA [V] measured with Cyclic Voltammetry (solvent: CH_3CN) and the experimental optical HOMO-LUMO gaps measured with UV-Vis Spectroscopy (solvent C_2H_5OH) [eV].

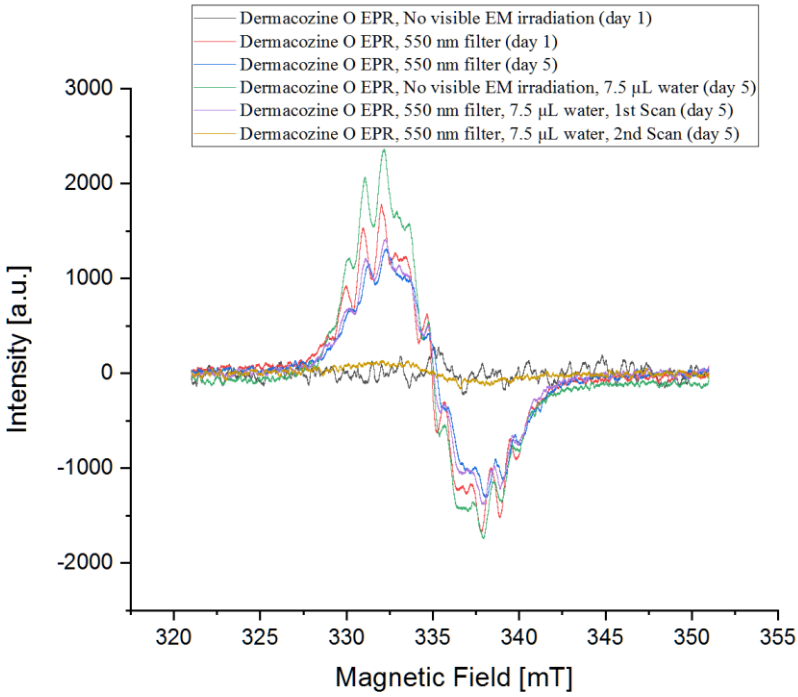


Dermacozine	(x) Electric LUMO [V]	(y) Δ E Optical [eV]
PCA	-1	3,4
B	-0,9	3
E	-0,9	2,2
F	-0,9	2,2
O	-0,9	1,9

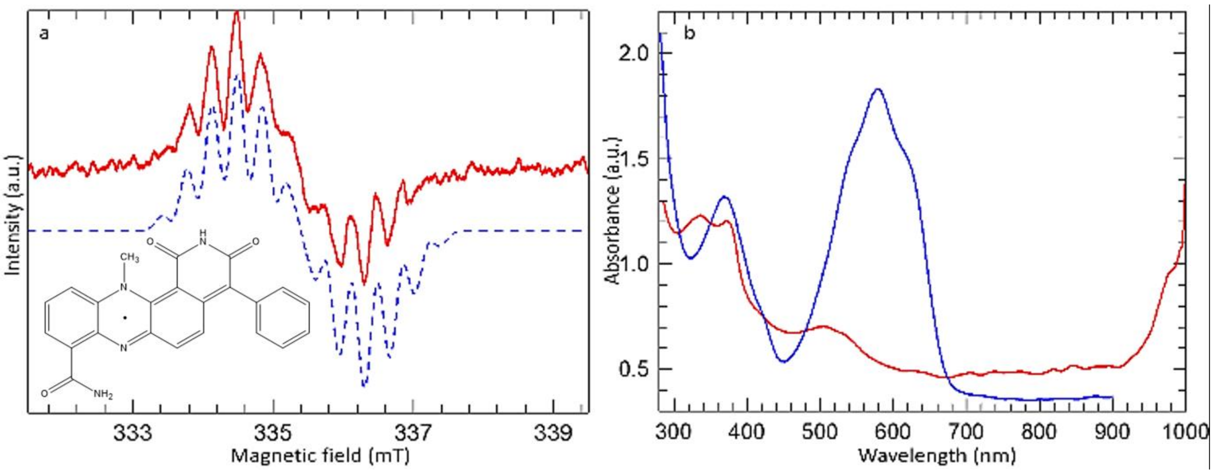
S14.a. Linear correlation between the cathodic potentials of dermacozine B, E, F, O and PCA [V] measured with Cyclic Voltammetry (solvent: CH_3CN) and the experimental optical HOMO-LUMO gaps measured with UV-Vis Spectroscopy (solvent C_2H_5OH) [eV].

SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0,762047295							
R Square	0,58071608							
Adjusted R Square	0,440954774							
Standard Error	0,471699057							
Observations	5							
ANOVA								
	df	*SS*	*MS*	*F*	*Significance F*			
Regression	1	0,9245	0,9245	4,15505618	0,134253828			
Residual	3	0,6675	0,2225					
Total	4	1,592						
	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95,0%*	*Upper 95,0%*
Intercept	-7,35	4,856439025	-1,513454604	0,227379012	-22,80535643	8,105356431	-22,8053564	8,105356431
X Variable 1	-10,75	5,273755777	-2,038395492	0,134253828	-27,53344459	6,033444589	-27,5334446	6,033444589

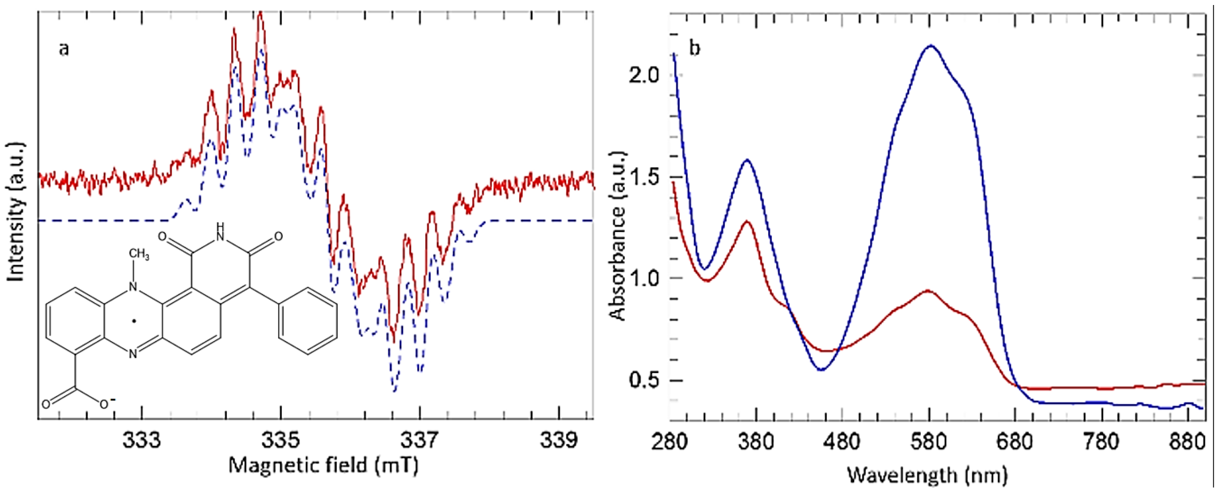
S14.b. Multiple regression (Microsoft Excel) between the experimental cathodic potentials of dermacozine B, E, F, O and PCA [V] measured with Cyclic Voltammetry (solvent: CH_3CN) and the experimental optical HOMO-LUMO gaps measured with UV-Vis Spectroscopy (solvent C_2H_5OH) [eV].



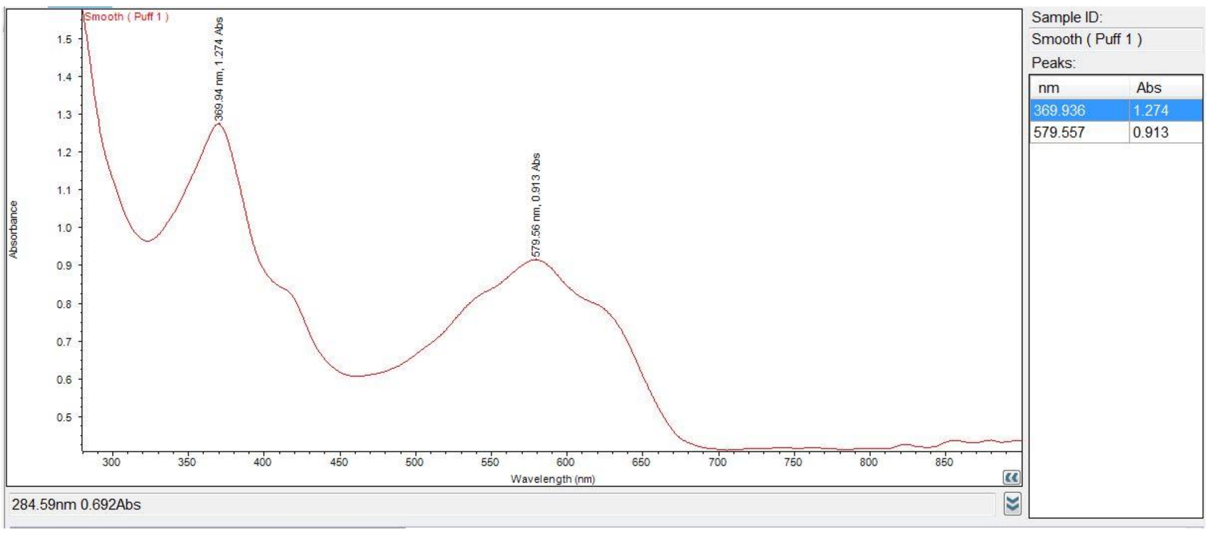
S15. Dermacozine O semiquinone radical`s reaction with water, EPR Spectroscopy, He atmosphere, 298 K, 550±50 nm filter in $CHCl_3$.



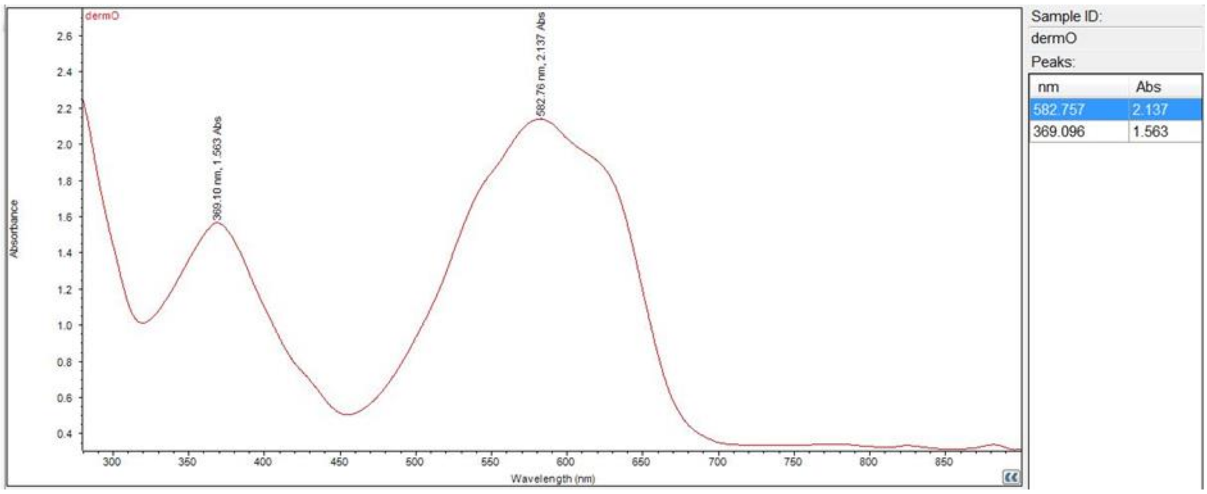
S16. Dermacozine E neutral semiquinone radical EPR (a) in chloroform (red line, experimetnal 550±50 nm filter, blue dashed line modelled EPR spectrum) and (b) UV Vis Spectrum before (blue) and after (red) the the dermacozine O semiquinone radical formed in chloroform (inlet: confirmed dermacozine E radical structure).



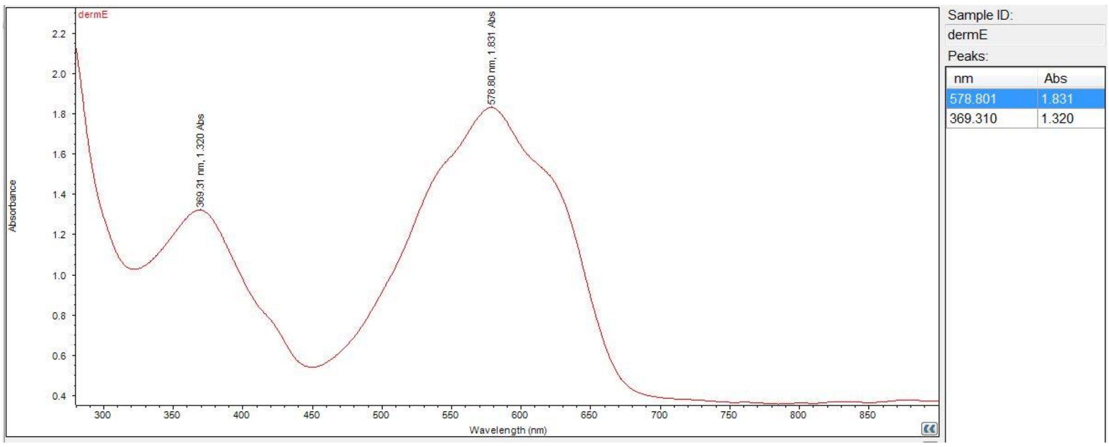
S17. Dermacozine O neutral semiquinone radical EPR (a) in chloroform (red line, experimetnal 550±50 nm filter, blue dashed line modelled EPR spectrum) and (b) UV Vis Spectrum before and after the the dermacozine O semiquinone radical formed in chloroform (inlet: confirmed dermacozine O radical structure).



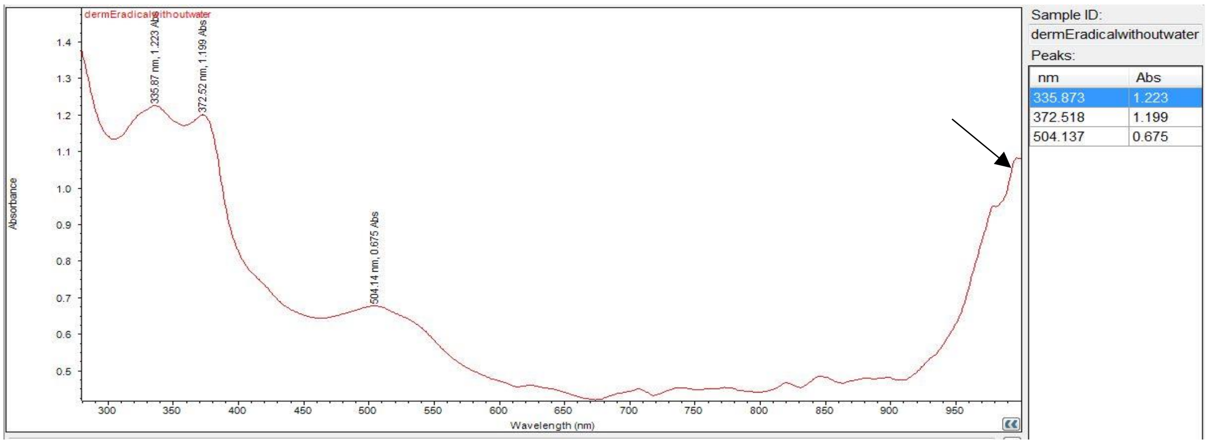
S18. Dermacozine O radical UV-Vis Spectrum in $CHCl_3$.



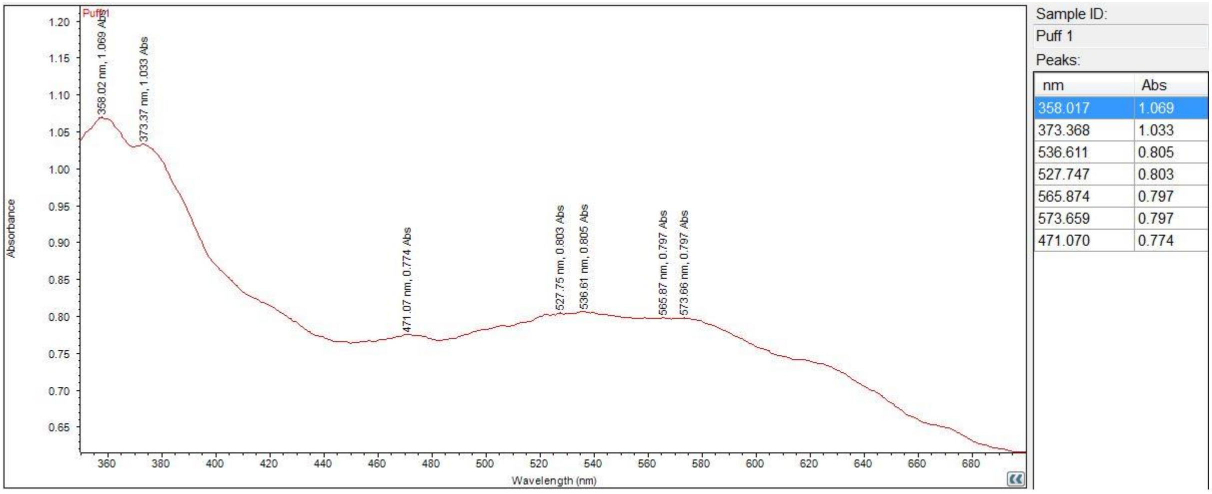
S19. Dermacozine O UV-Vis Spectrum in $CHCl_3$.



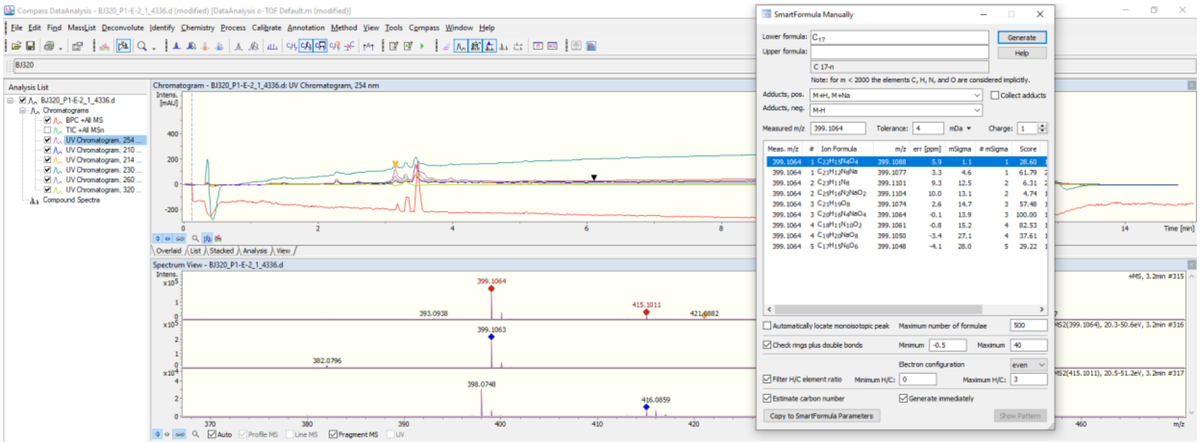
S20. Dermacozine E UV-Vis Spectrum in $CHCl_3$ (solution is blue).



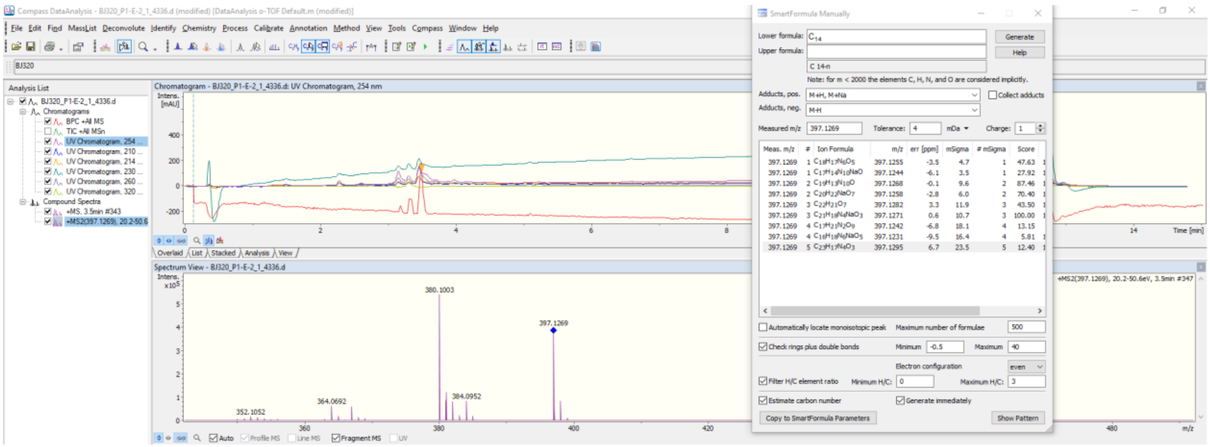
S21. Dermacozine E UV-Vis Spectrum, after EPR and with 550 nm filter irradiation, in $CHCl_3$ (solution is orange), a near infrared band (arrow) appeared at ~1000 nm, 298 K.



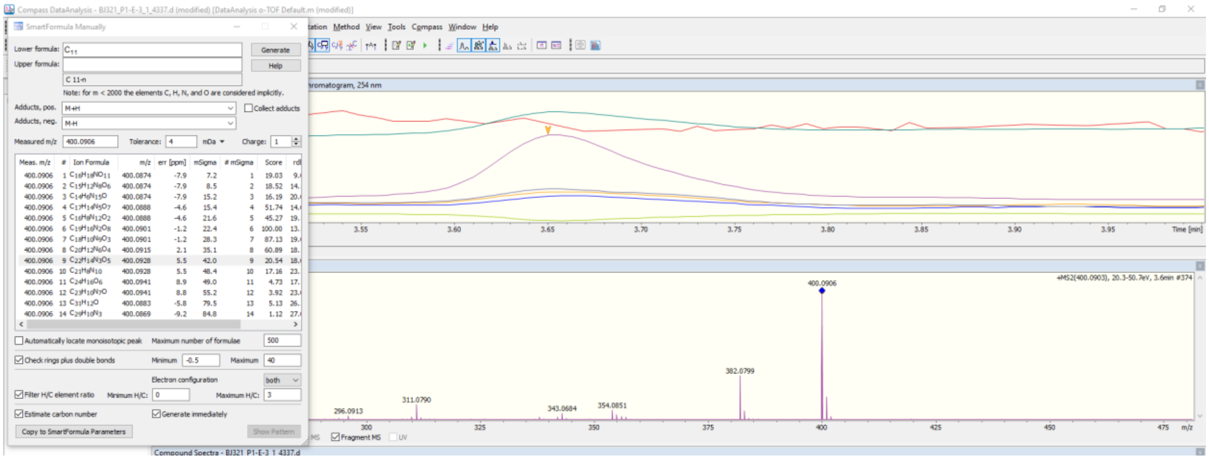
S22. Dermacozine E UV-Vis Spectrum, after EPR and with 550 nm filter irradiation, in CH_3OH (colour of the solution changed to blue from orange), 298 K.



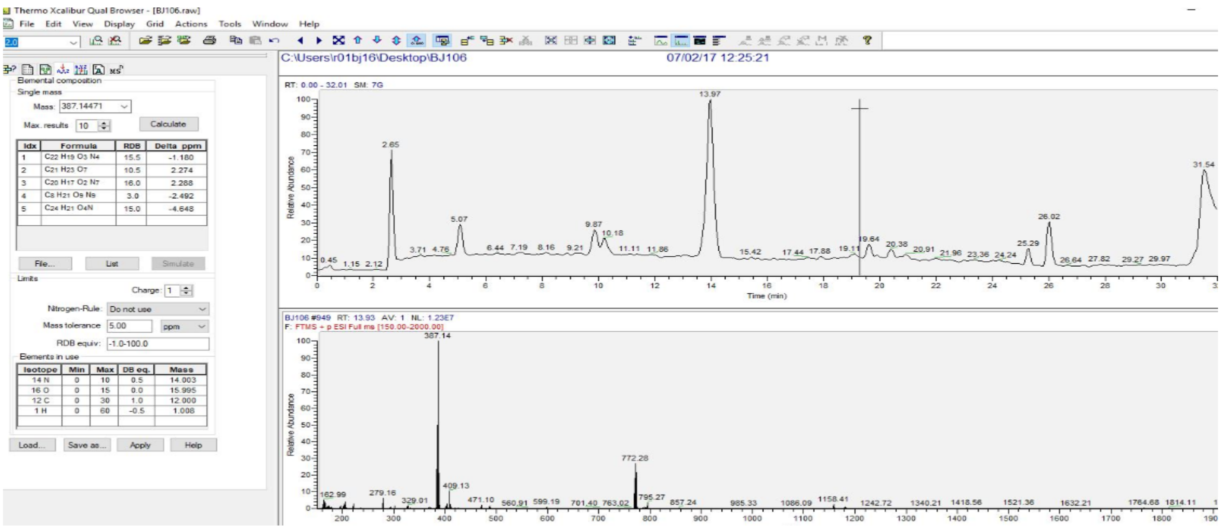
S23. Dermacozine E (LC)-HR-(ESI)-MS^n after irradiation and EPR in CH_3OH.



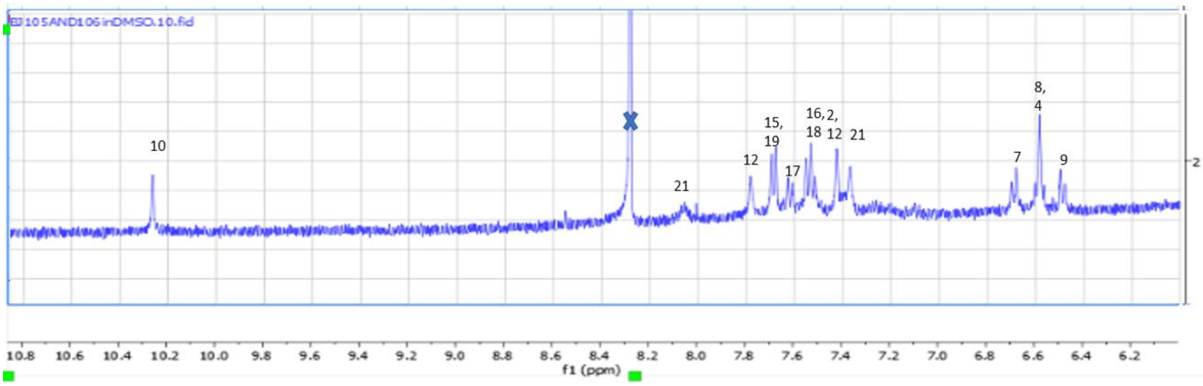
S24. Dermacozine E dimer (LC)-HR-(ESI)-MS^n after irradiation dissociated in CH_3OH and dermacozine E is detectable again.



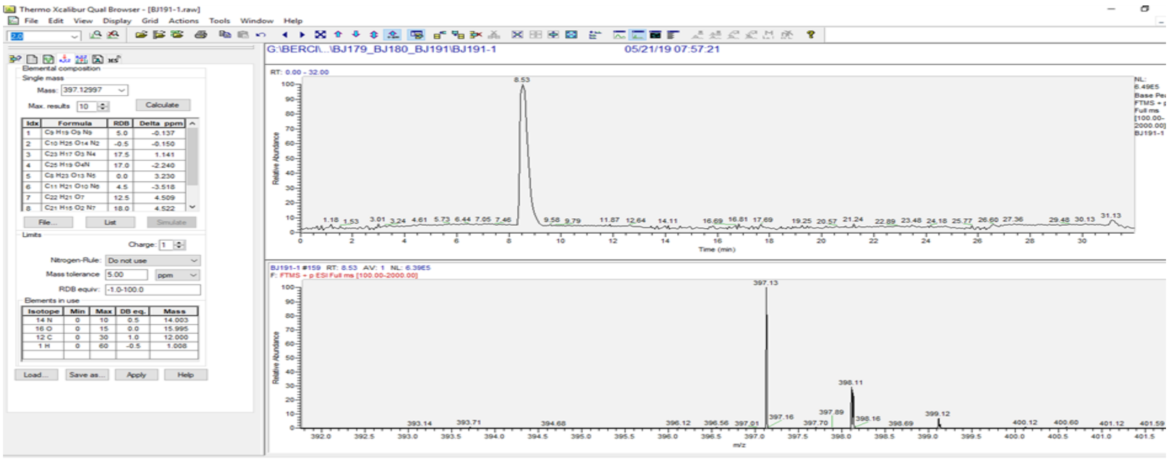
S25. Dermacozine O (LC)-HR-(ESI)-MS^n after irradiation and EPR in CH_3OH.



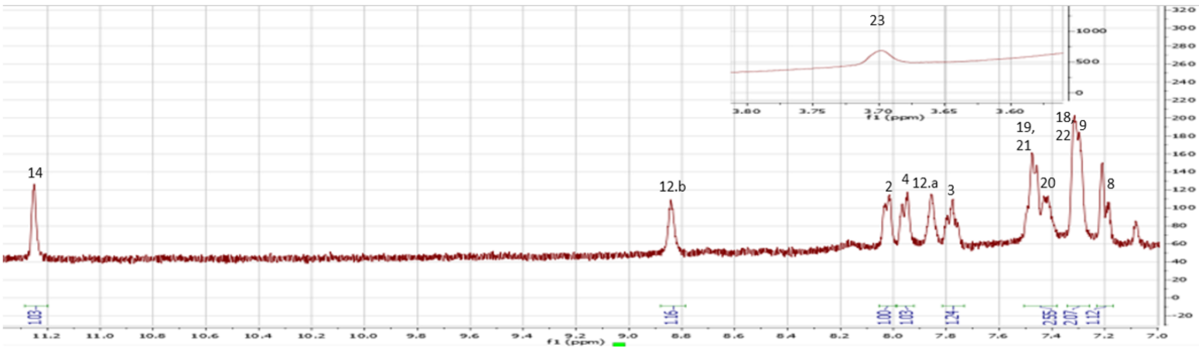
S26. LC MS Mass Spectrometry Chromatogram of Dermacozine B (Orbitrap)



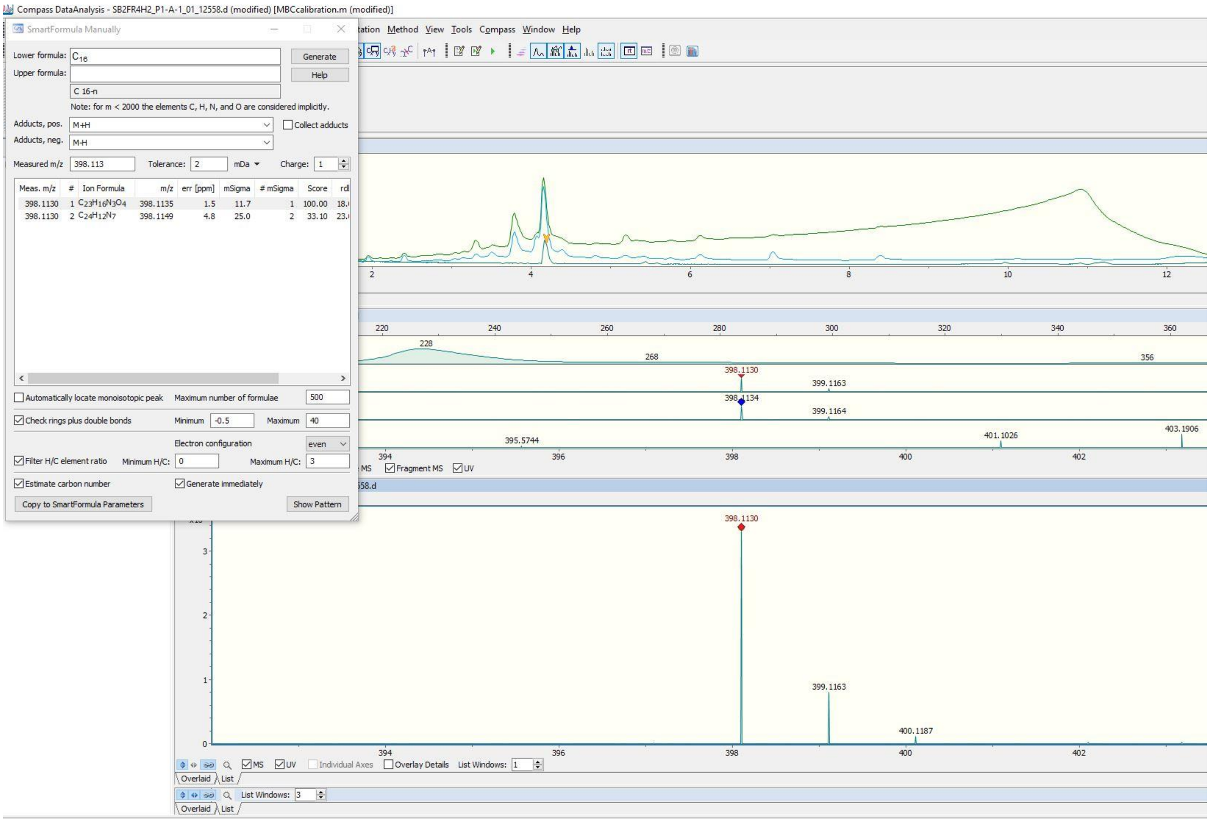
S27. Dermacozine B 1D [1]H NMR Spectrum in DMSO-d_6 400 MHz (x: contaminant)



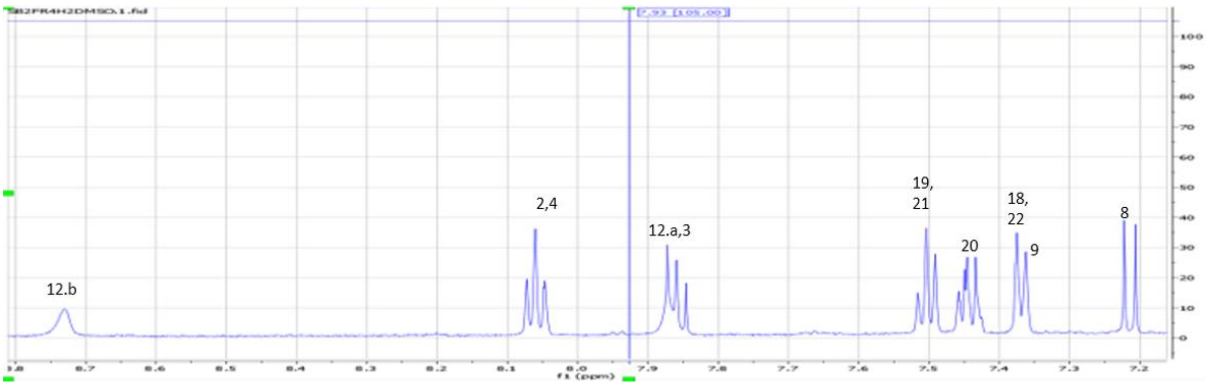
S28. LC MS Mass Spectrometry Chromatogram of Dermacozine E (Orbitrap)



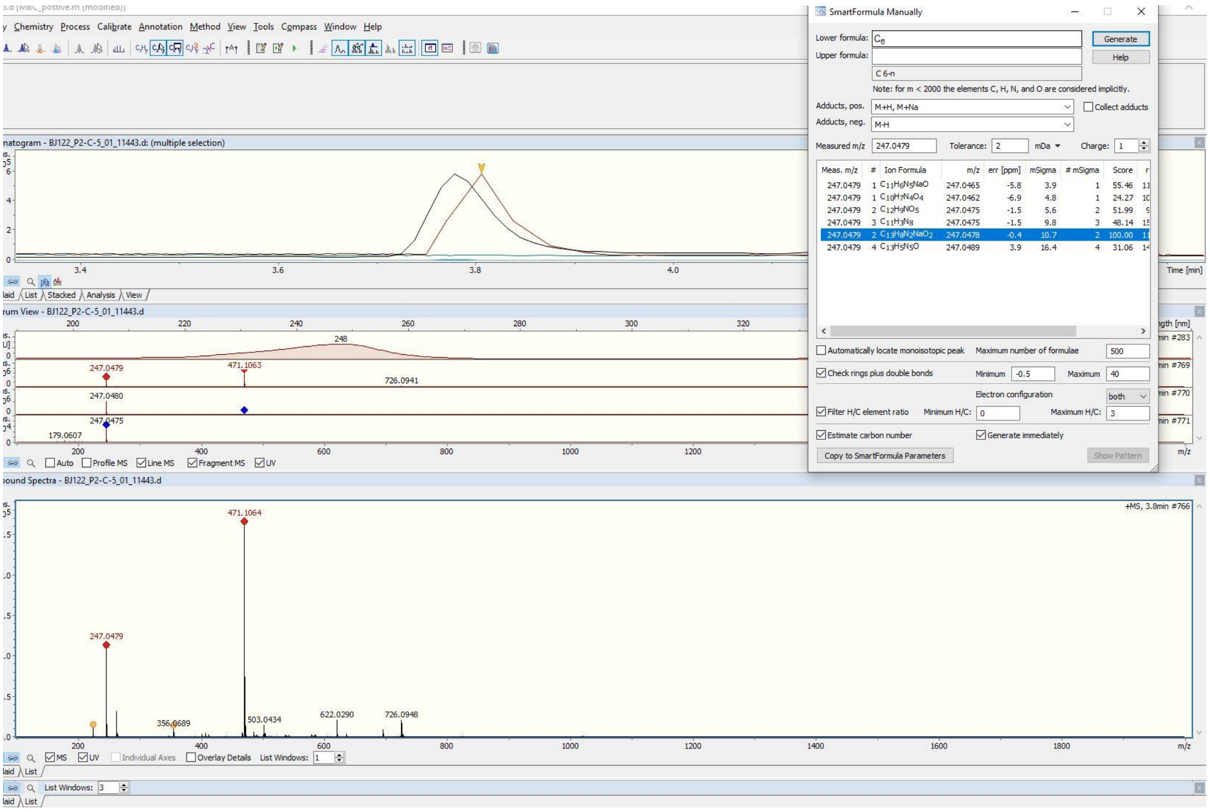
S29. Dermacozine E 1D ^{1}H NMR Spectrum in DMSO-d_6 400 MHz



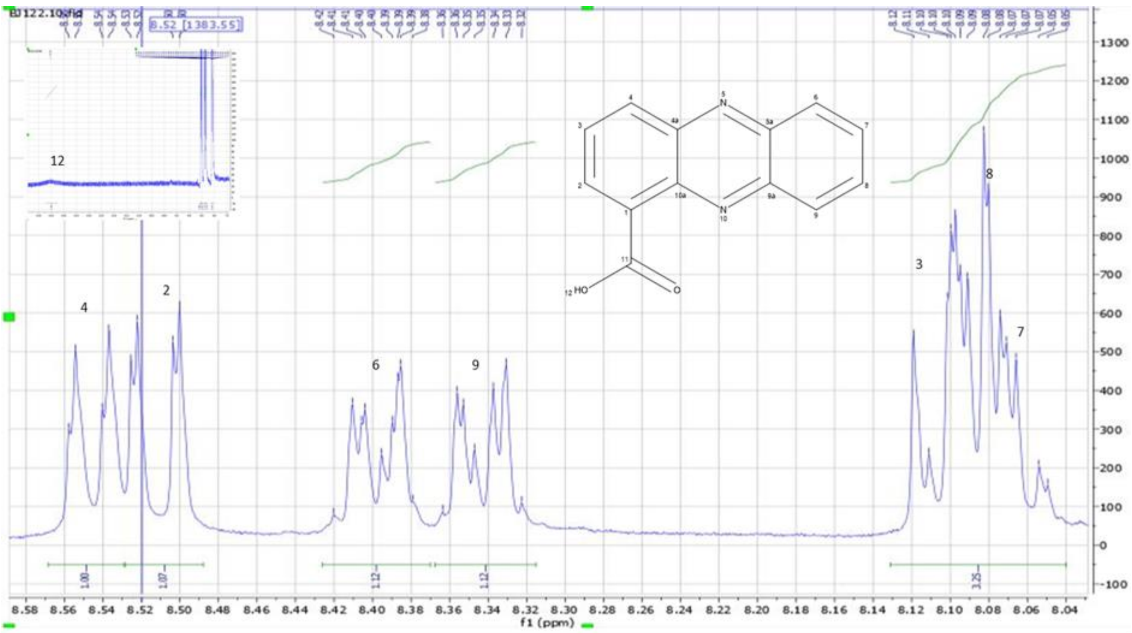
S30. LC MS Mass Spectrometry Chromatogram of Dermacozine F (qToF)



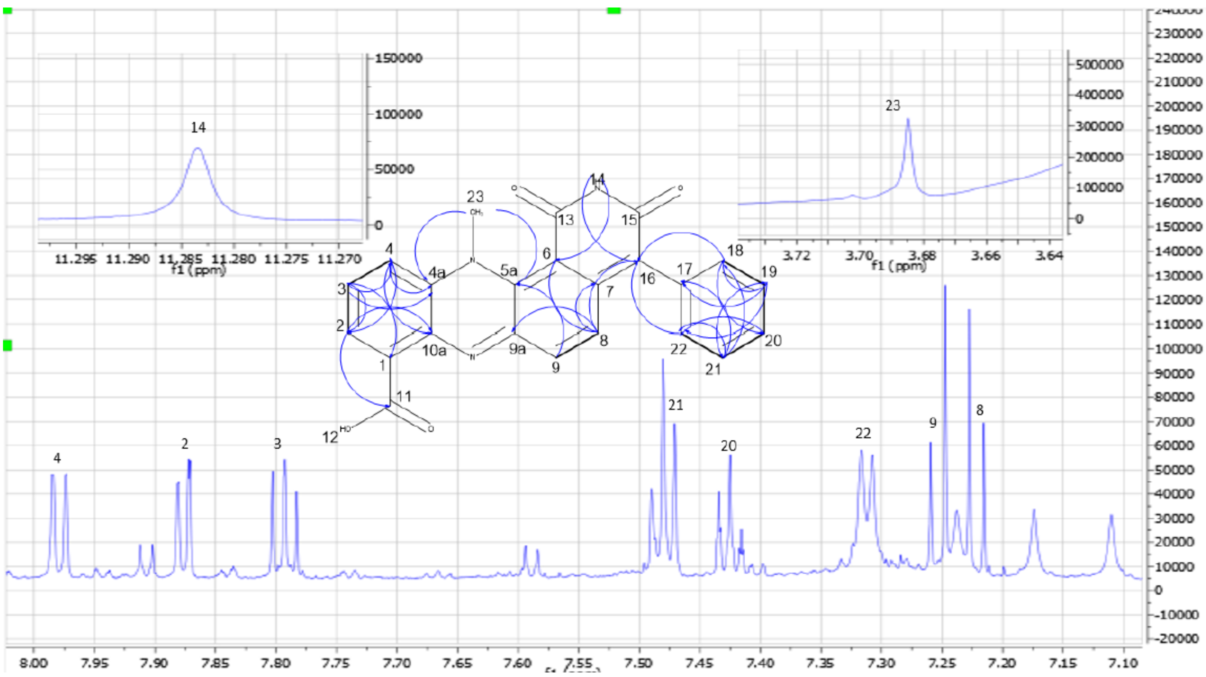
S31. Dermacozine F 1D ^{1}H NMR Spectrum in DMSO-d_6 400 MHz



S32. LC MS Mass Spectrometry Chromatogram of PCA (qToF)

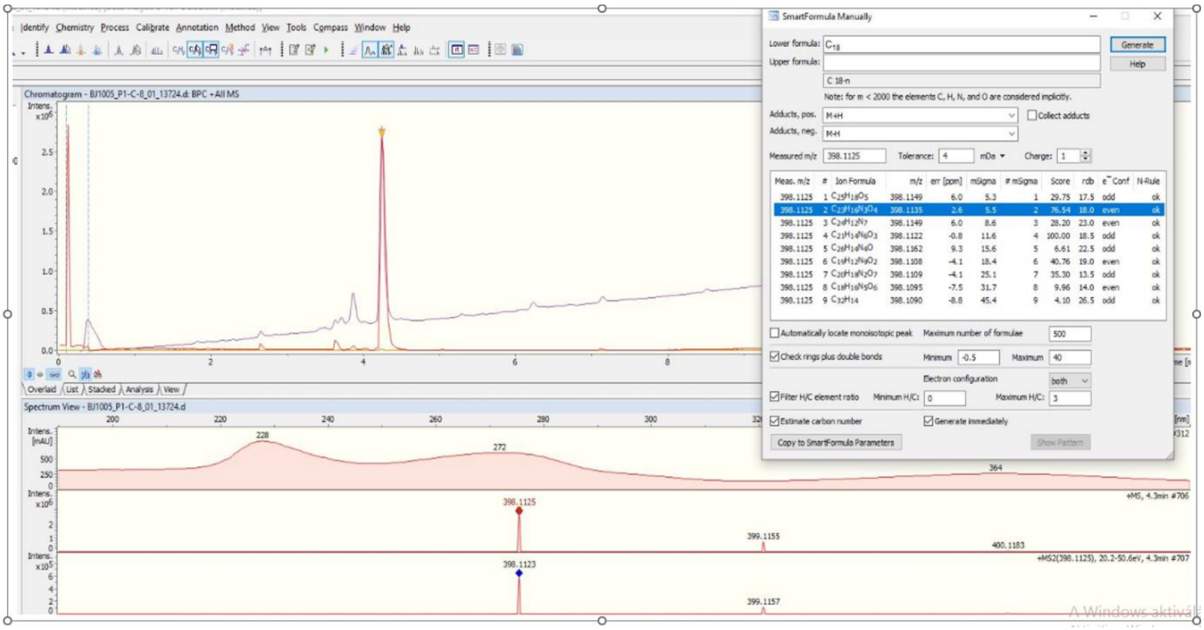


S33. PCA 1D ^{1}H NMR Spectrum in DMSO-d_6 400 MHz



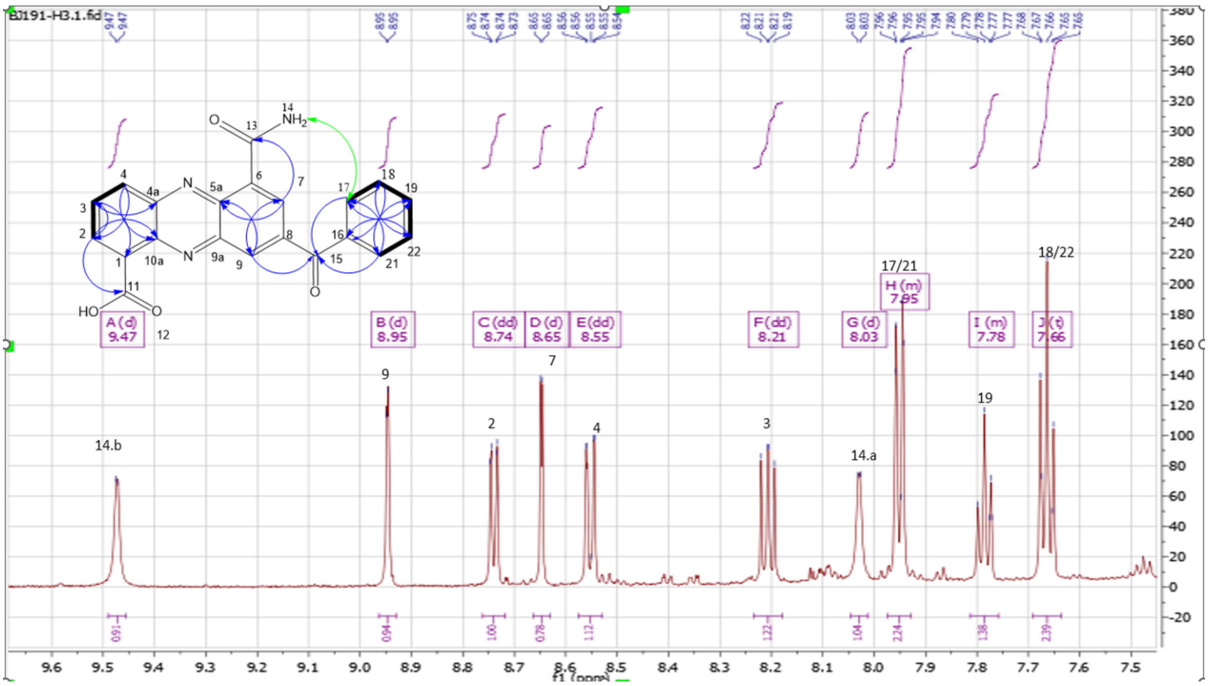
S34. Dermacozine O 1D ^{1}H NMR Spectrum in DMSO-d_6 400 MHz

(† N.B. Identical spectral data of dermacozine O and P appearing in SI which have already been published in Reference [5]. However, for clarity and for completeness the authors present them in the SI with appropriate citation).



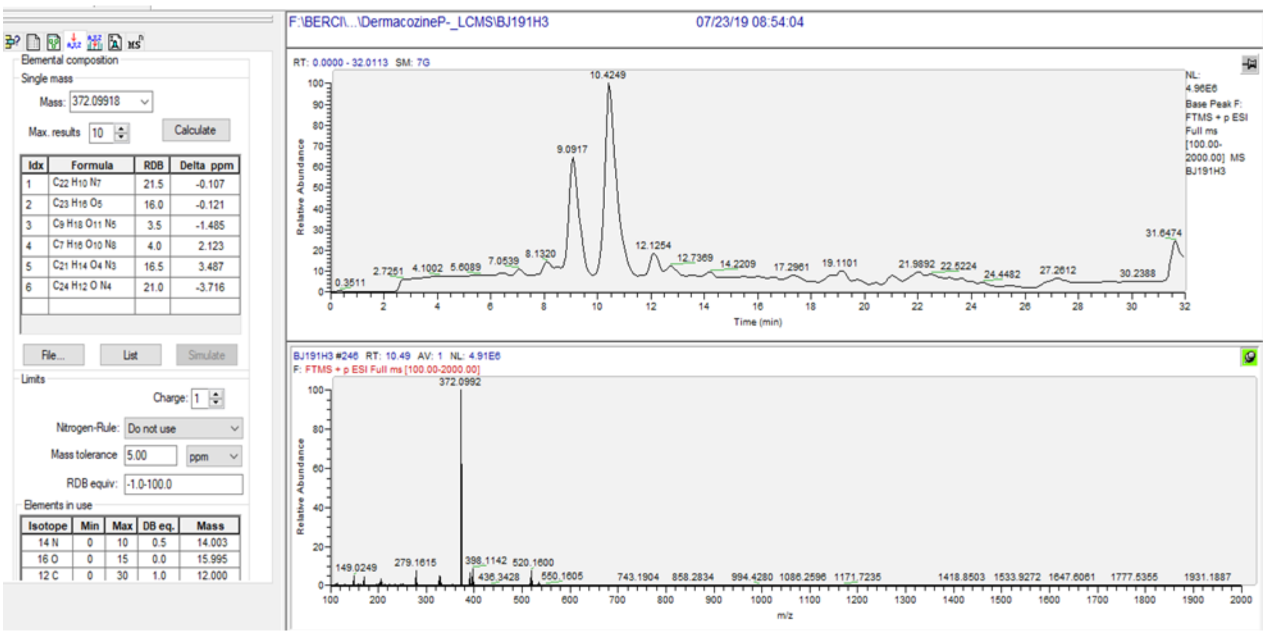
S35. LC MS Mass Spectrometry Chromatogram of Dermacozine O (qToF)

(† N.B. Identical spectral data of dermacozine O and P appearing in SI which have already been published in Reference [5]. However, for clarity and for completeness the authors present them in the SI with appropriate citation).



S36. Dermacozine P 1D ^{1}H NMR Spectrum in DMSO-d_6 400 MHz

(† N.B. Identical spectral data of dermacozine O and P appearing in SI which have already been published in Reference [5]. However, for clarity and for completeness the authors present them in the SI with appropriate citation).



S37. LC MS Mass Spectrometry Chromatogram of Dermacozine P (Orbitrap)

(† N.B. Identical spectral data of dermacozine O and P appearing in SI which have already been published in Reference [5]. However, for clarity and for completeness the authors present them in the SI with appropriate citation).