A Simple Strategy to Overcome Concentration Dependence of Photoswitching Properties in Donor-Acceptor Stenhouse Adducts

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1.0 UV-Vis spectroscopy

UV-Vis measurements were recorded using a Shimadzu UV-1800 spectrometer. Spectra were recorded over a range of 400 – 650 nm. The samples were irradiated from all directions using a 50 W, 650 K, full spectrum LED flood light, illuminating the samples inside a container with reflective mylar surfaces. A temperature of between 20 and 25°C was maintained throughout the irradiation of samples in each experiment. Samples were continuously irradiated and sequential measurements of the UV-Vis absorbance were taken. Cuvettes with a path length of 1 mm were used for all measurements. Thermal reversion of the photo-isomerisation was achieved through heating in the dark at 50°C. The interval time between measurements is shown in the individual absorption spectra of each compound. Samples were first dissolved in DMSO to create a 0.01 M solution, which was subsequently diluted with chloroform to the desired concentration. All of the final solutions that were measured through UV-Vis were in solutions of chloroform with 2% DMSO.

1.1 UV-Vis spectroscopy data for DASA 1

Individual absorption spetcra for DASA 1 in chloroform (2% DMSO) at each concentration reported. These spectra correspond with the data displayed in fig. 2 in the main text.
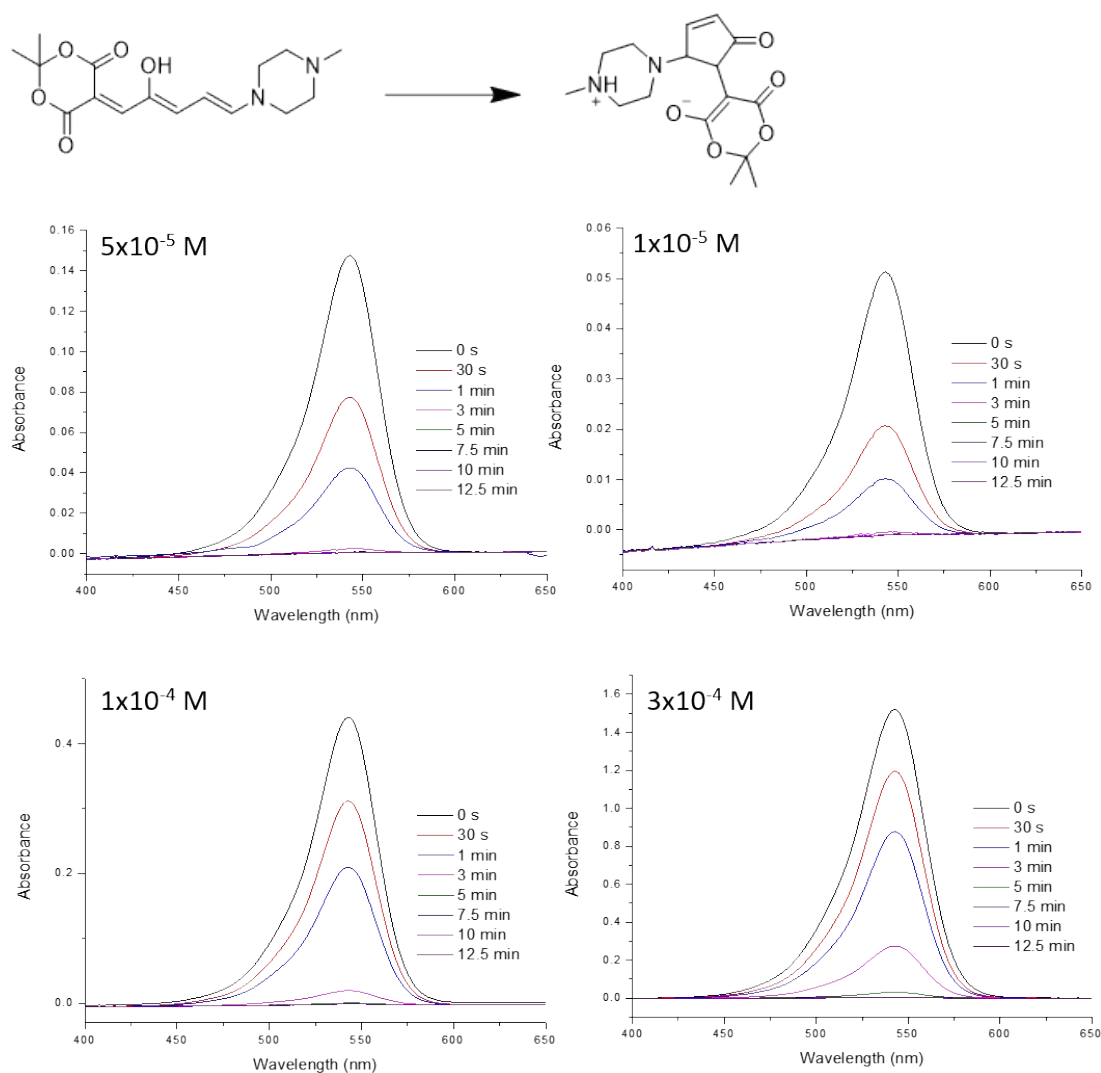

Figure S1. Absorption spectra for DASA 1 in chloroform (2% DMSO) at each concentration reported.

Absorption data for DASA 1 with absorbance plotted as a function of time, displaying the forward and reverse photoswitching reactions. Heating is required for full and fast recovery of the absorbance after irradiation.

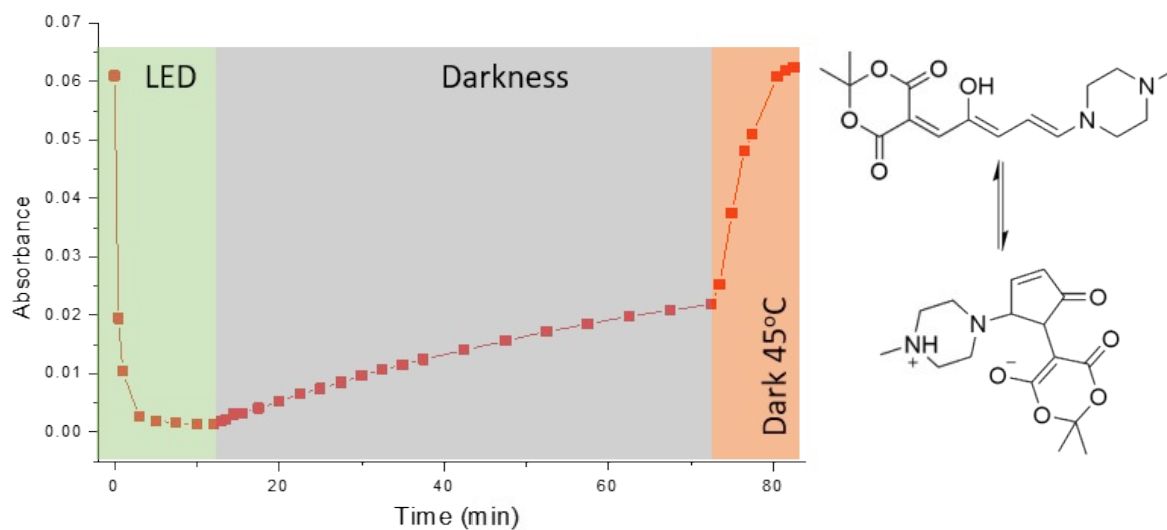*Figure S2. Plot displaying Absorbance as a function of time for DASA 1 for the forward and back photoswitching reactions in chloroform (2% DMSO), 10 μM.*

Figure S3. Absorption spectra for DASA 1 in pure chloroform at 100 μM (1x10-4 M). (a) Spectrum of the isomerisation from the linear to cyclized forms. (b) Spectrum of the reverse reaction from cyclized to linear. (c) Plot displaying absorbance as a function of time.

Figure S4. Absorption spectrum for DASA 1, in pure chloroform, 100 μM (1x10-4 M). Normalized absorbance plotted as a function of time over multiple photoswitching cycles. Minor variation in the irradiation time and recovery of absorbance are due to slight unavoidable variation in the temperature of the oven used to heat the samples over multiple cycles. The piperazine based DASAs showed more temperature sensitive behaviour than others with changes of >2 ℃ resulting in changes in the absorbance.

1.2 UV-Vis spectroscopy data for DASA 2

Individual absorption spetcra for DASA 2 in chloroform (2% DMSO) at each concentration reported. These spectra correspond with the data displayed in fig. 2 in the main text.

Figure S5. Absorption spectra for DASA 1 in chloroform (2% DMSO) at each concentration reported.

Absorption data for DASA 2 with absorbance plotted as a function of time, displaying the forward and reverse photoswitching reactions. Heating is required for full and fast recovery of the absorbance after irradiation.
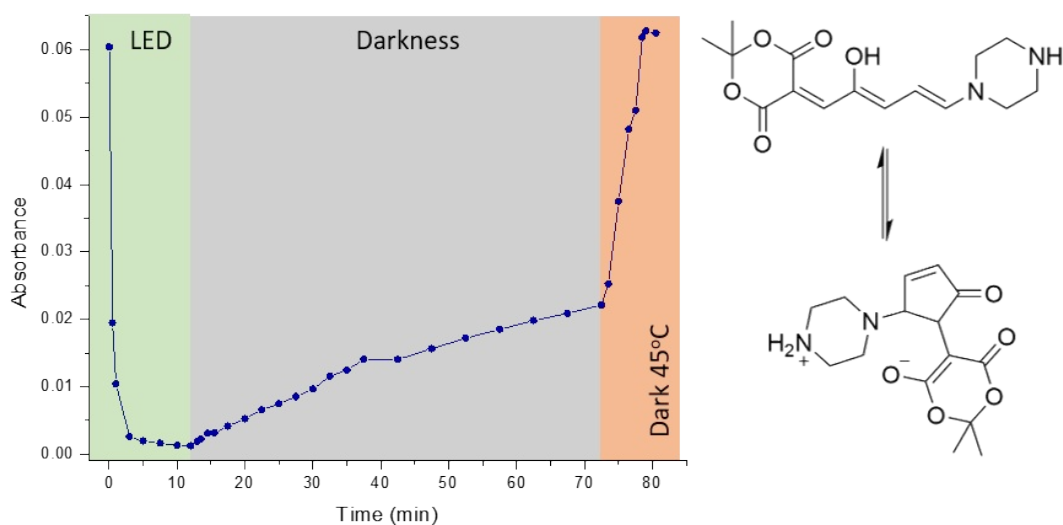
Figure S6. Plot displaying Absorbance as a function of time for DASA 2 for the forward and back photoswitching reactions in chloroform (2% DMSO), 10 µM.
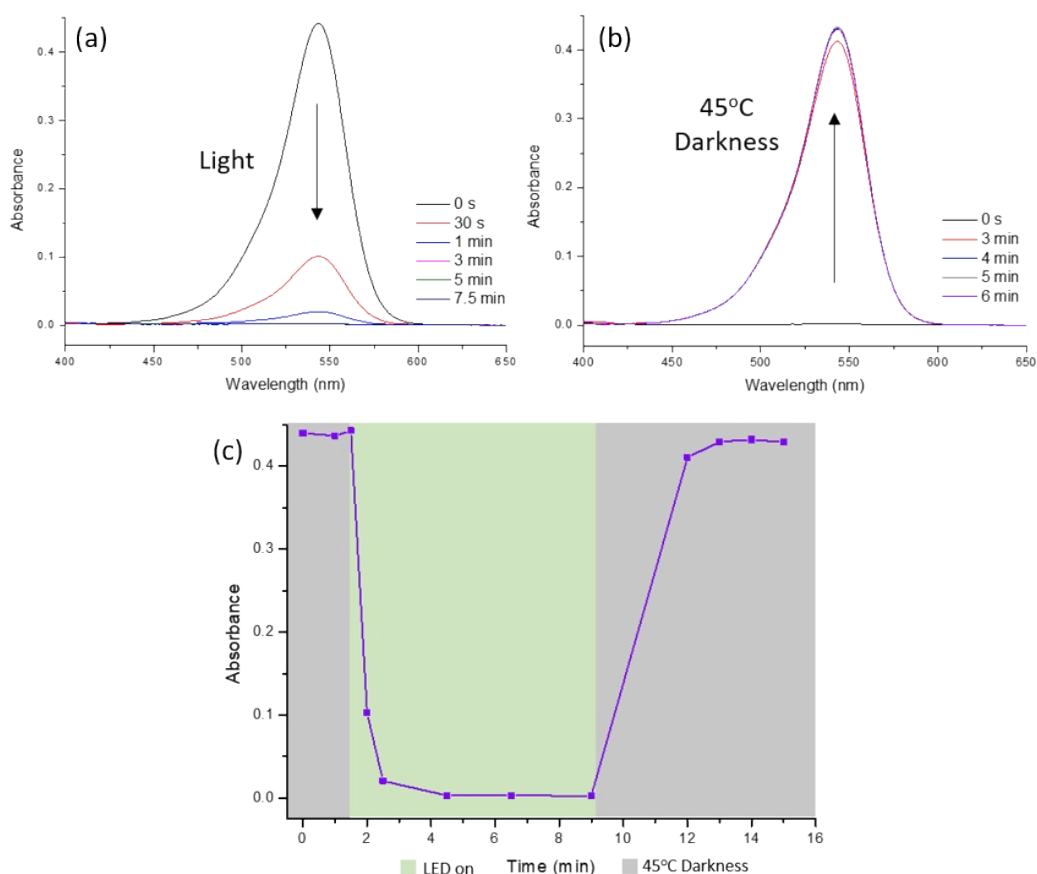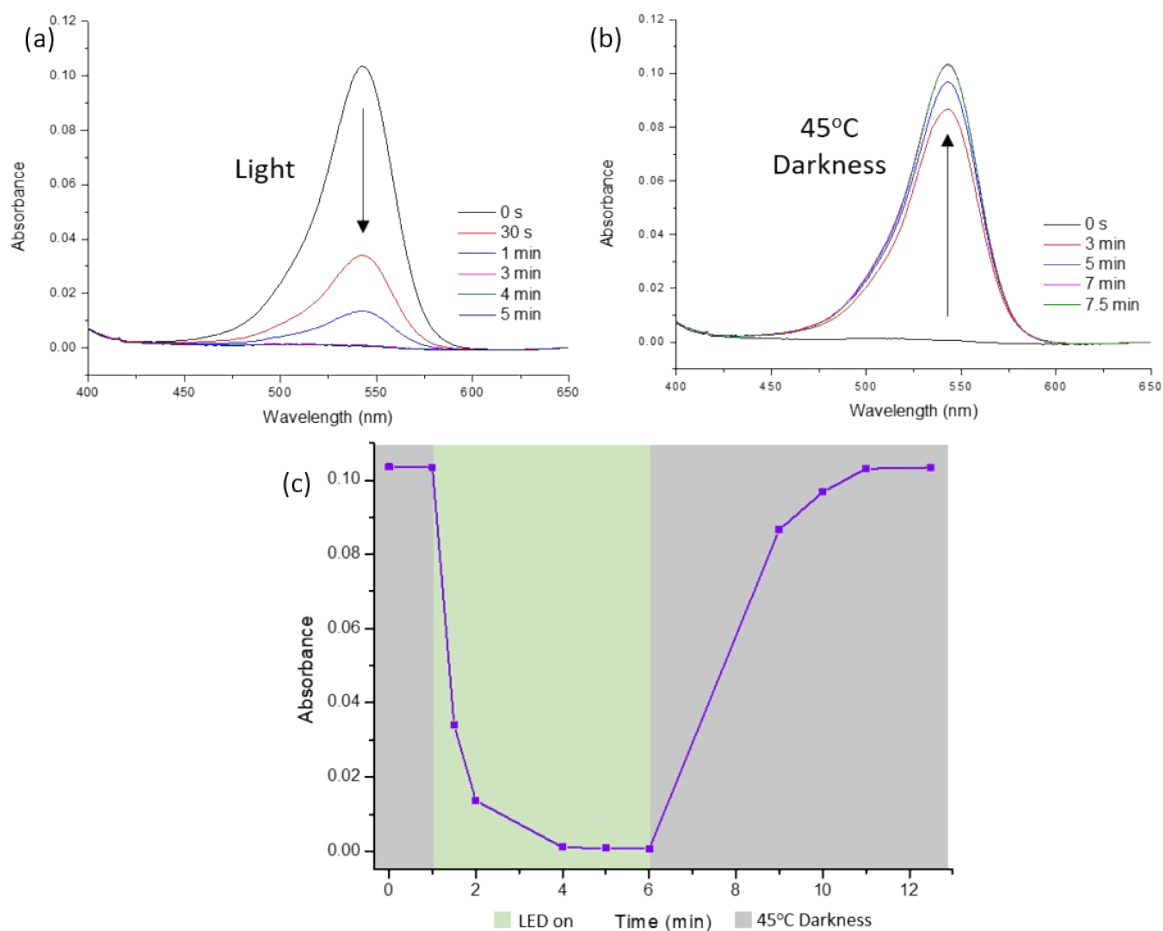

Figure S7. Absorption spectra for DASA 2 in pure chloroform at 100 µM (1x10-4 M). (a) Spectrum of the isomerisation from the linear to cyclized forms. (b) Spectrum of the reverse reaction from cyclized to linear. (c) Plot displaying absorbance as a function of time.
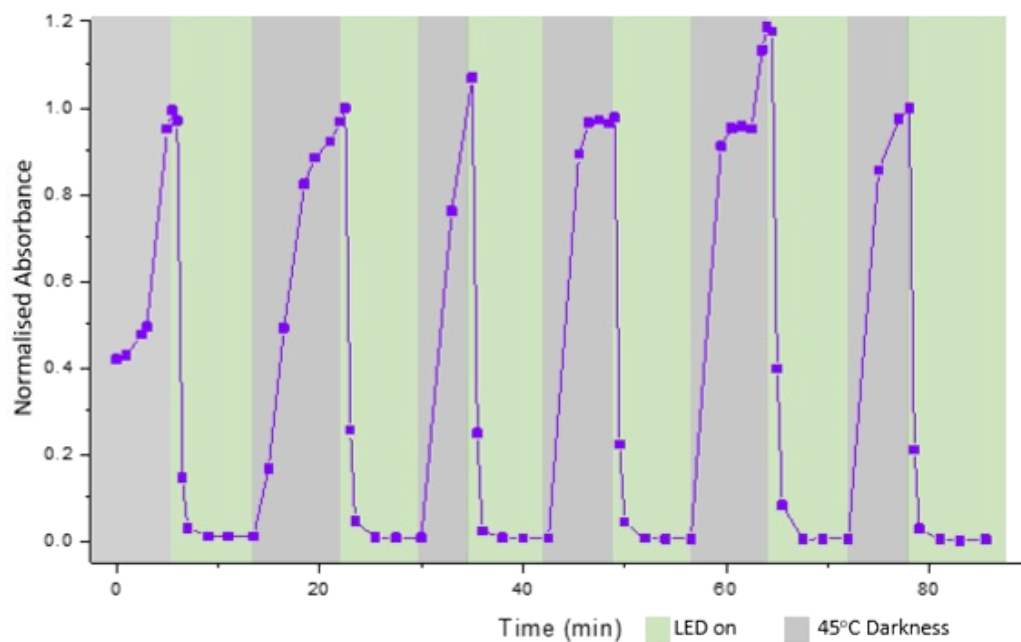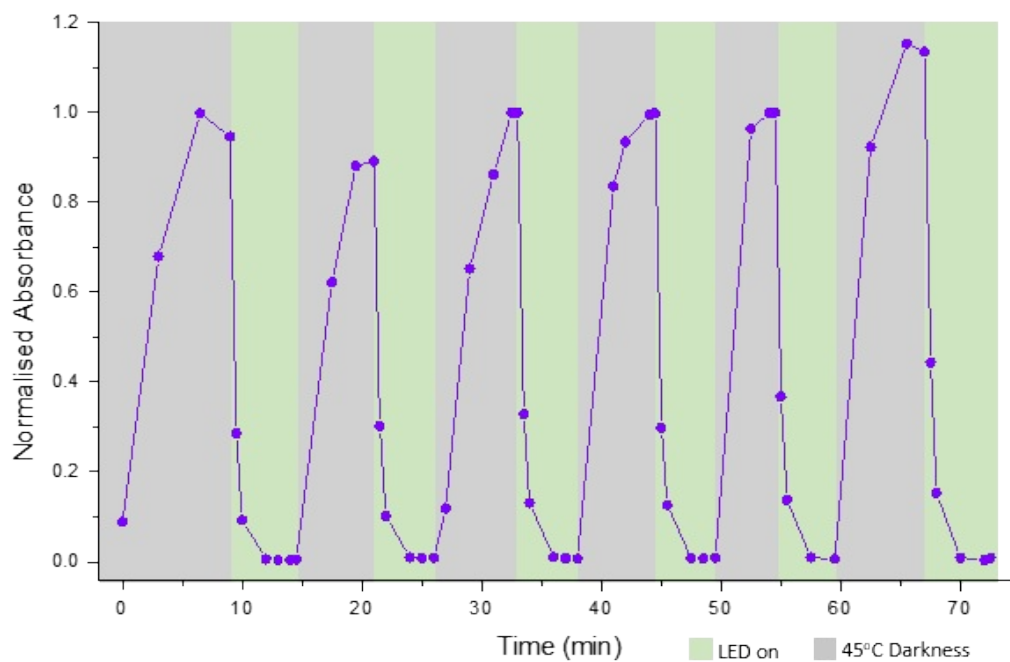
Figure S8. Absorption spectrum for DASA 2, in chloroform (2% DMSO), 100 μM (1x10-4 M). Normalized absorbance plotted as a function of time over multiple photoswitching cycles. Minor variation in the irradiation time and recovery of absorbance are due to slight changes in the temperature of the oven used to heat the samples over multiple cycles. The piperazine based DASAs showed more temperature sensitive behaviour than others with changes of >2 °C resulting in changes in the absorbance.

1.3 UV-Vis spectroscopy data for DASA 3

Individual absorption spetcra for DASA 3 in chloroform (2% DMSO) at each concentration reported. These spectra correspond with the data displayed in fig. 2 in the main text.
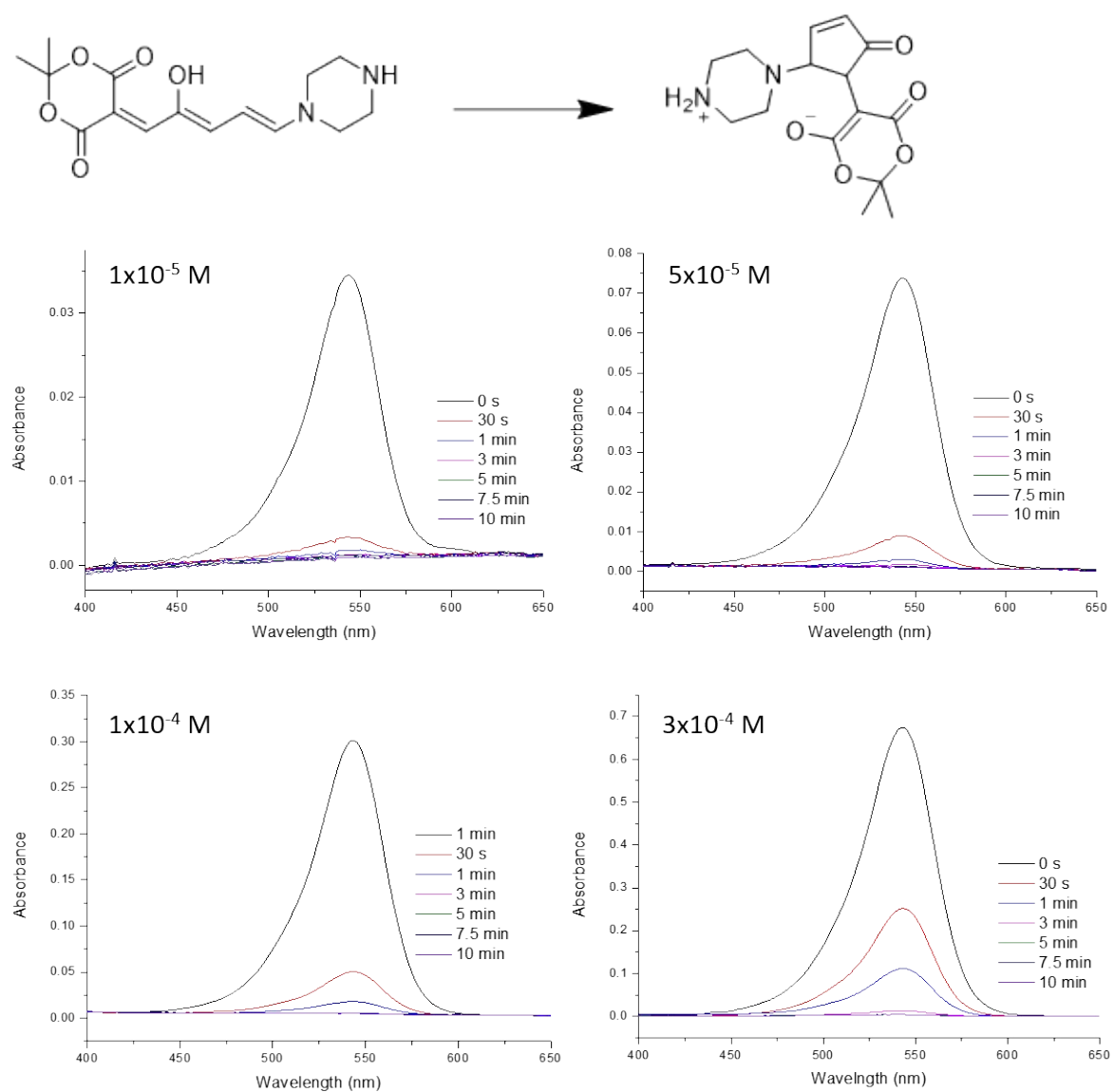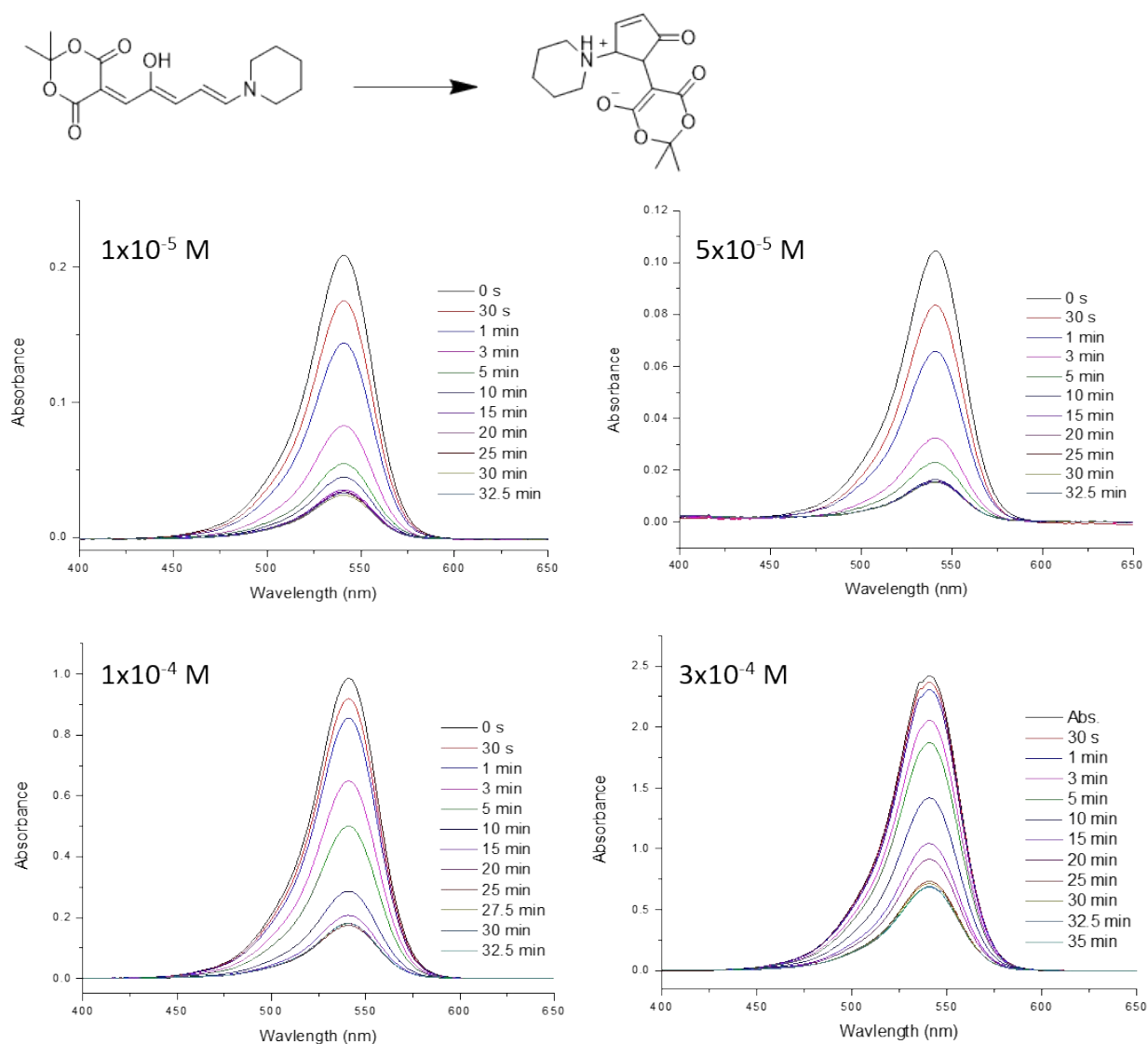

Figure S9. Absorption spectra for DASA 3 in chloroform (2% DMSO) at each concentration reported.

1.4 UV-Vis Spectroscopy data for DASA 4

Individual absorption spetcra for DASA 4 in chloroform (2% DMSO) at each concentration reported. These spectra correspond with the data displayed in fig. 2 in the main text.
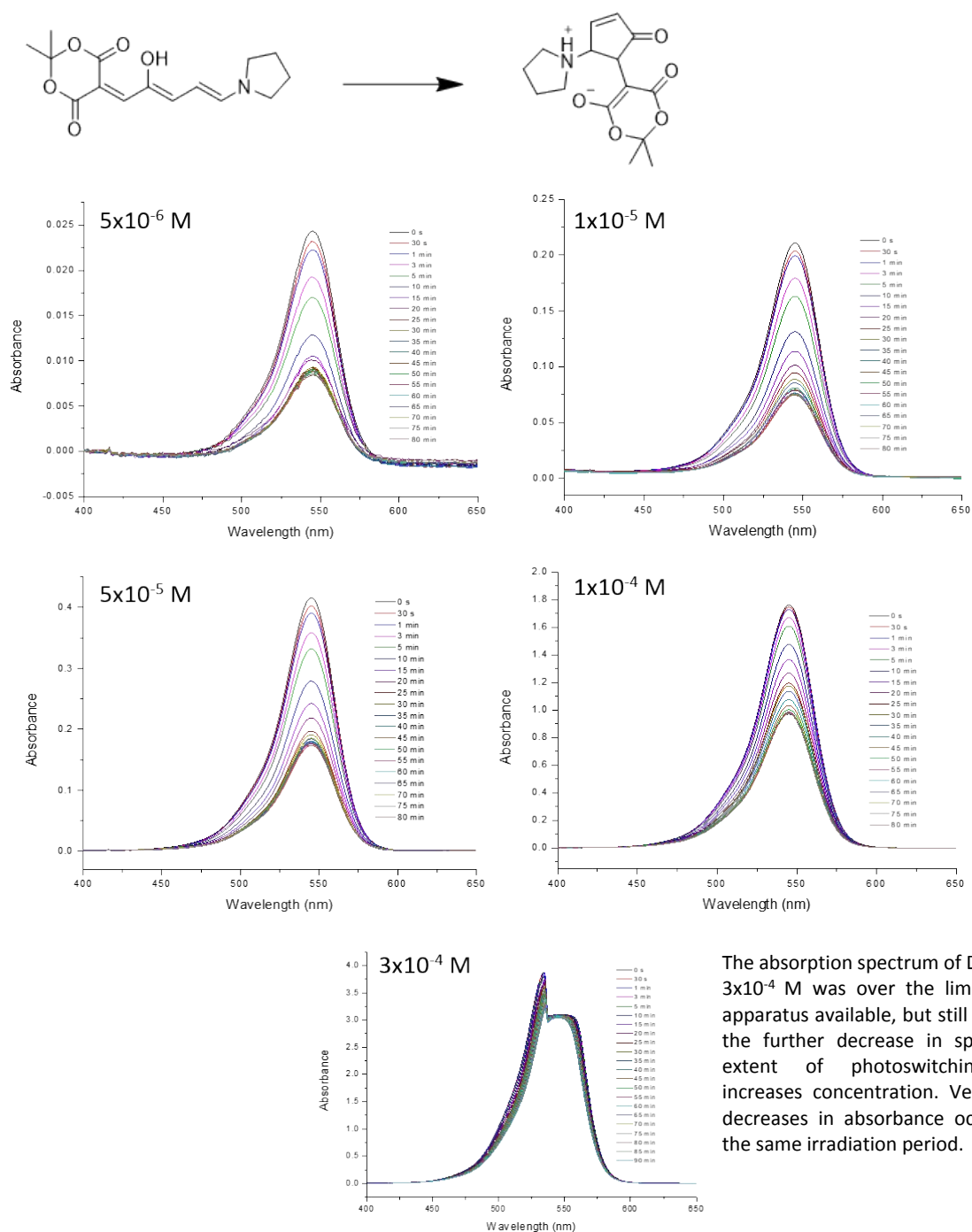
The absorption spectrum of DASA 3 at $3x10^{-4}$ M was over the limit of the apparatus available, but still indicates the further decrease in speed and extent of photoswitching with increases concentration. Very minor decreases in absorbance occur over the same irradiation period.

Figure S10. Absorption spectra for DASA 3 in chloroform (2% DMSO) at each concentration reported.

1.5 DASAs 3 and 4 photoswitching with Piperazine

In an effort to establish if the differences observed in concentration dependence could be attributed to the basicity of the Piperazine moiety, one equivalent of Piperazine was added to solutions of DASAs **3** and **4**. No changes to the extent of photoswitching (loss in absorbance at the PSS) were observed for either molecule. DASA **3** displayed identical switching behavior in both the presence and absence of 1 equiv. Piperazine, as shown in fig S11a, b. However, in the case of DASA **4**, the rate of photoswitching appeared to be slowed in the presence of Piperazine, and only 95% recovery of the absorbance was achieved, with no additional loss in absorbance upon irradiation, see fig S11c, d. Thus, inclusion of free Piperazine as an additive will not achieve the same negation of concentration dependence.
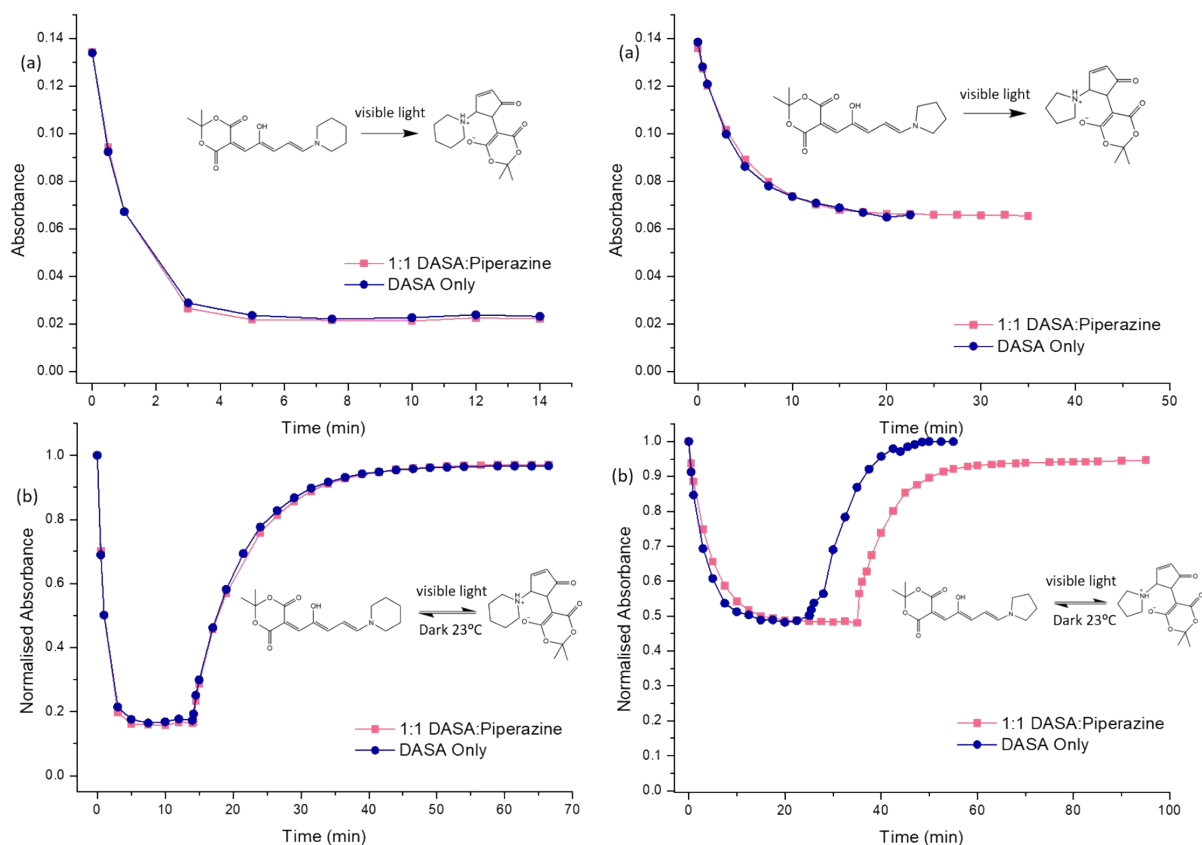
Figure S11. Absorption spectra for DASA 3 and 4 at 10 µM (1x10^{-5} M) in pure chloroform, showing data for solutions with Piperazine at a ratio of 1:1 with the DASA, and with no Piperazine added. (a) Plot of absorbance as a function of time for the isomerisation from the linear to cyclized form of DASA 3. (b) Plot of normalised as a function of time for the forward and reverse photoswitching process for DASA 3. (c) Plot of absorbance as a function of time for the isomerisation from the linear to cyclized form of DASA 4. (d) Plot of normalised as a function of time for the forward and reverse photoswitching process for DASA 4.

1.6 UV-Vis spectroscopy for DASA 5

Photoswitching of a diethyl amine based DASA for an example of a first generation DASA which undergoes very little photoswitching in chloroform, even in dilute solutions, after an extended period of irradiation from visible light. The reverse reaction of the photoswitching process is also shown, demonstrating the inefficiency of the reversibility of simple first generation DASAs.
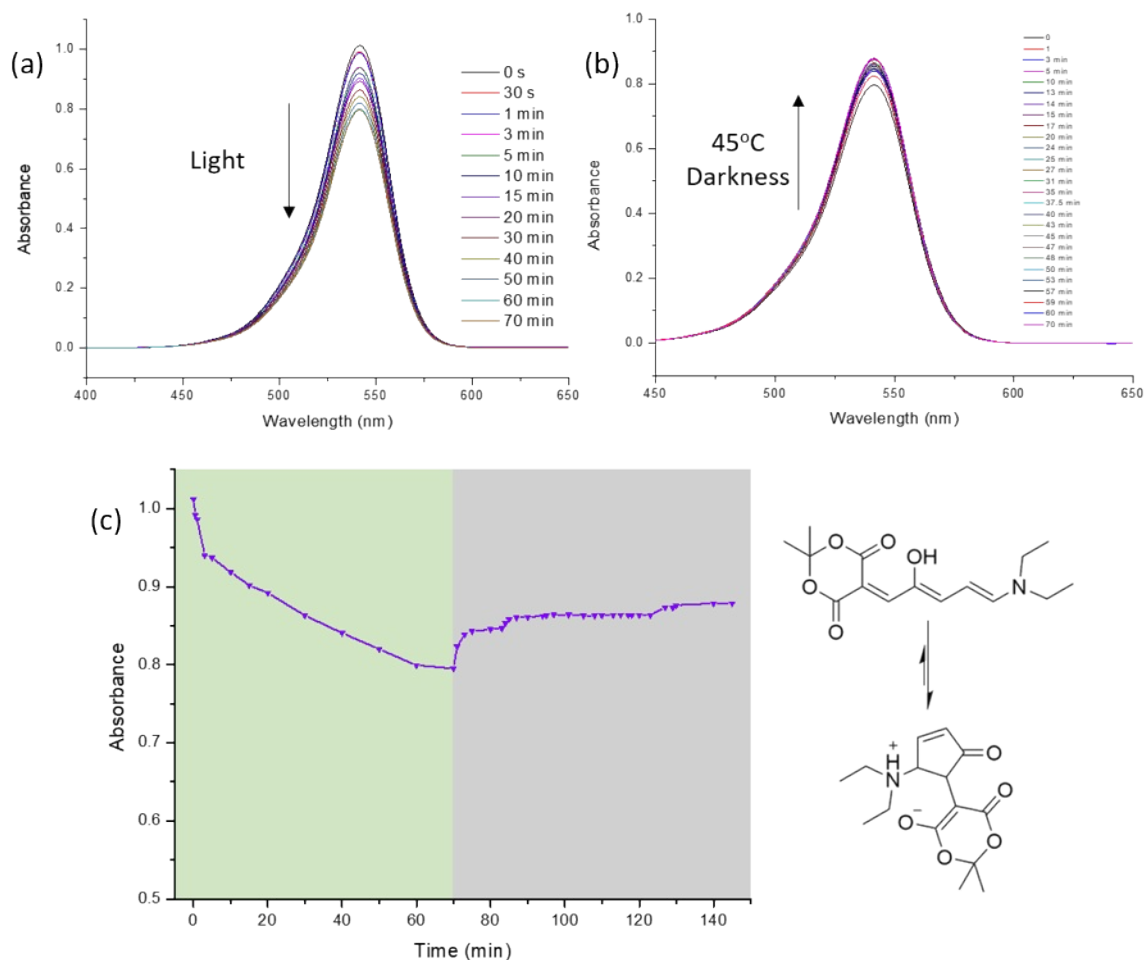
Figure S12. Absorption spectra for DASA 5 in pure chloroform at 60 µM (6x10-5 M). (a) Spectrum of the isomerisation from the linear to cyclized forms. (b) Spectrum of the reverse reaction from cyclized to linear. (c) Plot displaying absorbance as a function.

2 Synthetic Methods

All commercially obtained solvents and reagents were used without further purification.
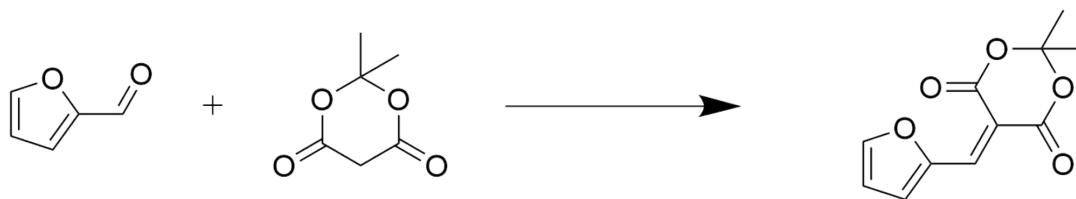
5-[(furan-2-yl)methylidene]-2,2-dimethyl-1,3-dioxane-4,6-dione: Prepared according to the literature procedure.[1] Meldrum's acid (10 mmol, 1.44 g) and furfural (10 mmol, 0.961 g) were mixed in water (30 mL) followed by heating to 70 °C and stirring for 2 hours. The solid obtained was filtered, vacuum dried and dissolved in dichloromethane (30 mL) followed by washing sequentially with saturated $NaHSO_3$ (30 mL), water (30 mL), $NaHCO_3$ (30 mL), and brine solution (30 mL). The organic layer was then dried over $MgSO_4$, filtered, and the solvent removed via rotary evaporation, yielding a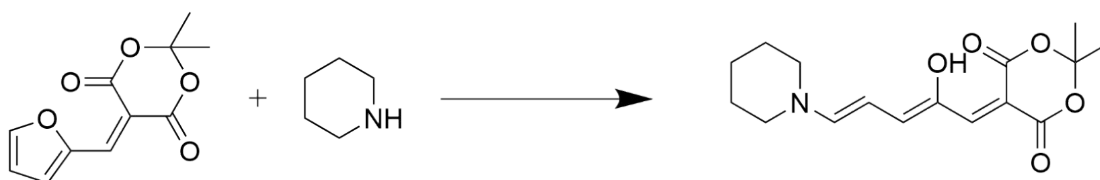 yellow powder (1.4 g, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (d, J = 3.9 Hz, 1H), 8.36 (s, 1H), 7.85 (dd, J = 0.5, 1.1 Hz, 1H) 6.75 (dq, J = 3.9, 0.7 Hz, 1H) 1.77 (s, 6H). ^{13}C NMR (100 MHz, 298 K, $CDCl_3$): δ 163.24, 160.1, 150.39, 150.24, 141.23, 128.09, 115.27,107.57, 104.51, 27.57.

(DASA 3) 5-[(2Z,4E)-2-hydroxy-5-(piperidin-1-yl)penta-2,4-dien-1-ylidene]-2,2-dimethyl-1,3-dioxane-4,6-dione: DASA **3** was prepared by literature procedure.[1] 5-[(furan-2-yl)methylidene]-2,2-dimethyl-1,3-dioxane-4,6-dione (0.3 g, 1.35 mmol) was dissolved in THF (5 mL) and left to stir. Piperidine (0.1149 g, 1.3 mmol) was added via micropipette, the reaction was left to stir at room temperature (23 °C) for 1 h followed by cooling to 0 °C for 20 min. The mixture was filtered and the resultant solid was washed with diethyl ether and further dried under vacuum yielding a red powder (0.3303 g, 79%). ^{1}H NMR (400 MHz CD_2Cl_2): δ 11.30 (s, 1H), 7.23 (d, J = 12.17 Hz, 1H), 6.84 (s, 1H), 6.74 (dd, J = 1.35, 12.42 Hz, 1H), 6.05 (t, J = 12.3 Hz, 1H), 3.47-3.51 (m, 4H), 1.67(s, 6H), 1.59 (s, 6H). ^{1}H NMR (400 MHz DMSO-d_6): δ 11.38 (s, 1H), 8.0 (d, J = 11.6, 1H), 7.11 (d, J = 11.6, 1H), 6.54 (s, 1H), 6.22 (t, J = 12.3), 3.71 (m, 4H), 1.67 (s, 6H), 1.58 (s, 6H). ^{13}C NMR (100 MHz, 298 K, DMSO-d_6): δ 161.88, 154.49, 143.53, 130.12, 104.98, 102.55, 85.24, 57.21, 48.55, 26.95, 26.46, 26.00, 23.35. LC-MS (ESI+) m/z 308.1, calculated [M+H]$^+$ [$C_{16}H_{21}NO_5$+H]$^+$ = 308.14.

(DASA 2) 5-[(2Z,4E)-2-hydroxy-5-(piperazin-1-yl)penta-2,4-dien-1-ylidene]-2,2-dimethyl-1,3-dioxane-4,6- (2): 5-[(furan-2-yl)methylidene]-2,2-dimethyl-1,3-dioxane-4,6-dione (0.5554 g, 2.5 mmol) was dissolved in chloroform (5 mL). To this solution piperazine (0.1895 g, 2.2 mmol) was added. The reaction mixture was stirred for 1 h, followed by cooling to 0 °C for 20 min. The mixture was filtered and the resultant solid was washed with diethyl ether and further dried under vacuum yielding

a dark purple powder (0.5833 g, 86%). ^{1}H NMR (400 MHz DMSO-d_6):δ 8.41 (s, 2H), 7.50 (dd, J = 5.77, 1.95 Hz, 1H), 6.20 (dd, J = 5.97, 1.83 Hz, 1H), 3.90 (d, J = 2.43 Hz, 1H), 3.14 (d, J = 2.9 Hz, 1H), 3.08 (t, J = 4.5 Hz,4H), 2.66 – 2.76 (m, 4H), 1.48 (s, 6H). ^{13}C NMR (100 MHz, 298 K, DMSO-d_6): δ 209.19, 160.47, 134.95, 99.95, 71.98, 71.71, 46.71, 44.89, 43.80, 40.65, 26.43, 26.63. LC-MS (ESI+) m/z 309, calculated [M+H]$^+$ [$C_{15}H_{20}NO_5$+H]$^+$ = 309.14.
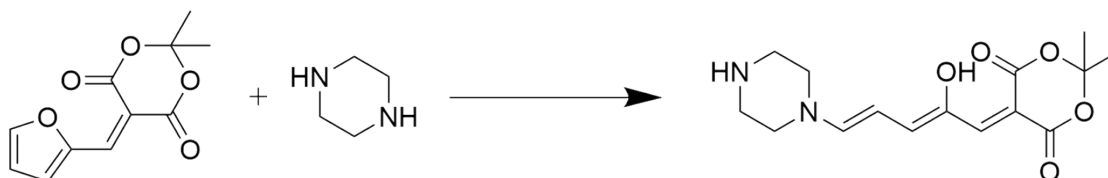

(DASA 4) 5-((2Z,4E)-2-Hydroxy-5-(pyrrolidin-1-yl)penta-2,4-dien-1-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione: DASA **4** was prepared by literature procedure.[1] 5-[(furan-2-yl)methylidene]-2,2-dimethyl-1,3-dioxane-4,6-dione (0.3 g, 1.35 mmol) was dissolved in THF (5 mL) and left to stir. Pyrrolidine (0.091g, 1.3 mmol) was added via micropipette, the reaction was left to stir at room temperature (23 °C) for 30 min followed by cooling to 0 °C for 20 min. The mixture was filtered and the resultant solid was washed with diethyl ether and further dried under vacuum yielding a red powder (0.2928 g, 77%). ^{1}H NMR (400 MHz CDCl$_3$) δ 11.41 (s, 1H), 7.42 (d, J = 12.30 Hz, 1H), 7.08 (s, 1H), 6.69 (d, J = 11.57 Hz, 1H), 5.96 (t, J = 12.3 Hz, 11H), 3.71 (m, 2H), 3.51 (m, 2H), 2.03-2.15 (m, 4H), 1.72 (s, 6H). ^{13}C NMR (100 MHz, 298 K, CDCl$_3$): δ 166.05, 164.24, 152.91, 149.15, 144.06, 138.65, 102.39, 89.88, 52.80, 47.41, 25.68, 24.00. LC-MS (ESI+) m/z 294.1, calculated [M+H]$^+$ [$C_{15}H_{19}NO_5$+H]$^+$ = 294.13.
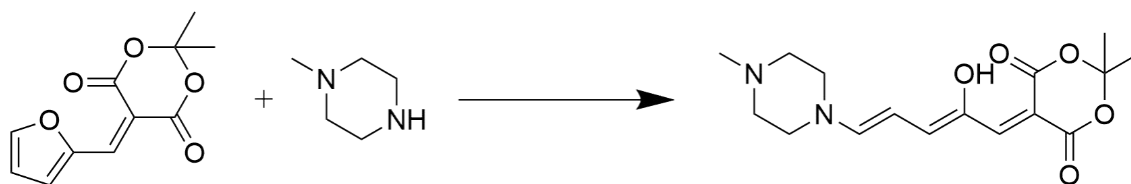

(DASA 1) 5-((2Z,4E)-2-hydroxy-5-(4-methylpiperazin-1-yl)penta-2,4-dien-1-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (1): 5-[(furan-2-yl)methylidene]-2,2-dimethyl-1,3-dioxane-4,6-dione (0.3 g, 1.35 mmol) was dissolved in minimal THF (≈ 5 mL). To this solution methyl piperazine (0.13 g, 1.3 mmol) was added. The reaction mixture was stirred for 1.5 h, followed by cooling to 0 °C for 20 min. The mixture was filtered and the resultant solid was washed with diethyl ether and further dried under vacuum yielding a crystalline magenta powder (0.2813 g, 67%). ^{1}H NMR (400 MHz CDCl$_3$) δ 11.38 (s, 1H), 7.17 (d, J = 12.42, 1H), 7.13 (s, 1H), 6.71 (d, J = 12.3 Hz, 1H), 6.08 (t, J = 12.3 Hz, 1H), 3.59 (s, 4H), 2.54 (s, 4H), 2.36 (s, 3H), 1.72 (s, 6H).
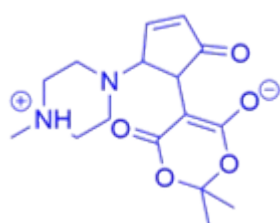
The NMR spectrum of DASA 1 in chloroform exhibits both the cyclopentanone and triene forms. The cyclopentanone isomer is assigned with blue letters to indicate which peaks correspond with which isomer.

¹H NMR (400 MHz CDCl₃) δ 7.4 (s, 1H) 6.35 (d, *J* = 4.26 Hz, 1H), 4.52 (s, 1H), 3.38 (m, 3H), 3.04 (m, 2H), 2.87 (m, 4H), 2.54 (s, 3H), 1.65 (s, 1H).

¹H NMR (400 MHz D₂O) δ 7.70 (dd, *J* = 6, 2.1, 1H), 6.4 (dd, *J* = 6, 1.9, 1H), 4.04 (m, 1H), 3.49 (m, 2H), 3.38 (d, *J* = 3, 1H), 3.06 - 3.17 (m, 4H), 2.84 (s, 1H), 2.75 (m, 1H), 1.6 (s, 6H). ¹³C NMR (100 MHz, 298 K, D₂O): δ 212.07, 162.10, 134.79, 103.43, 74.21, 70.64, 53.31, 43.59, 42.77. LC-MS (ESI+) *m/z* 323, calculated [M+H]⁺ [C₁₆H₂₂NO₅+H]⁺ = 332.15.

^{1}H NMR (400 MHz CDCl$_3$) δ 7.4 (s, 1H) 6.35 (d, *J* = 4.26 Hz, 1H), 4.52 (s, 1H), 3.38 (m, 3H), 3.04 (m, 2H), 2.87 (m, 4H), 2.54 (s, 3H), 1.65 (s, 1H).

^{1}H NMR (400 MHz D$_2$O) δ 7.70 (dd, *J* = 6, 2.1, 1H), 6.4 (dd, *J* = 6, 1.9, 1H), 4.04 (m, 1H), 3.49 (m, 2H), 3.38 (d, *J* = 3, 1H), 3.06 - 3.17 (m, 4H), 2.84 (s, 1H), 2.75 (m, 1H), 1.6 (s, 6H). ^{13}C NMR (100 MHz, 298 K, D$_2$O): δ 212.07, 162.10, 134.79, 103.43, 74.21, 70.64, 53.31, 43.59, 42.77. LC-MS (ESI+) *m/z* 323, calculated [M+H]$^+$ [C$_{16}$H$_{22}$NO$_5$+H]$^+$ = 332.15.

3 NMR Spectral Data

The NMR spectra were obtained using a Burker AV2 400 MHz or AVNEO 400 MHz spectrometer. The data was processed using ACD Labs software. NMR Chemical shift values are reported in parts per million (ppm) and calibrated to the centre of the residual solvent peak set (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet).
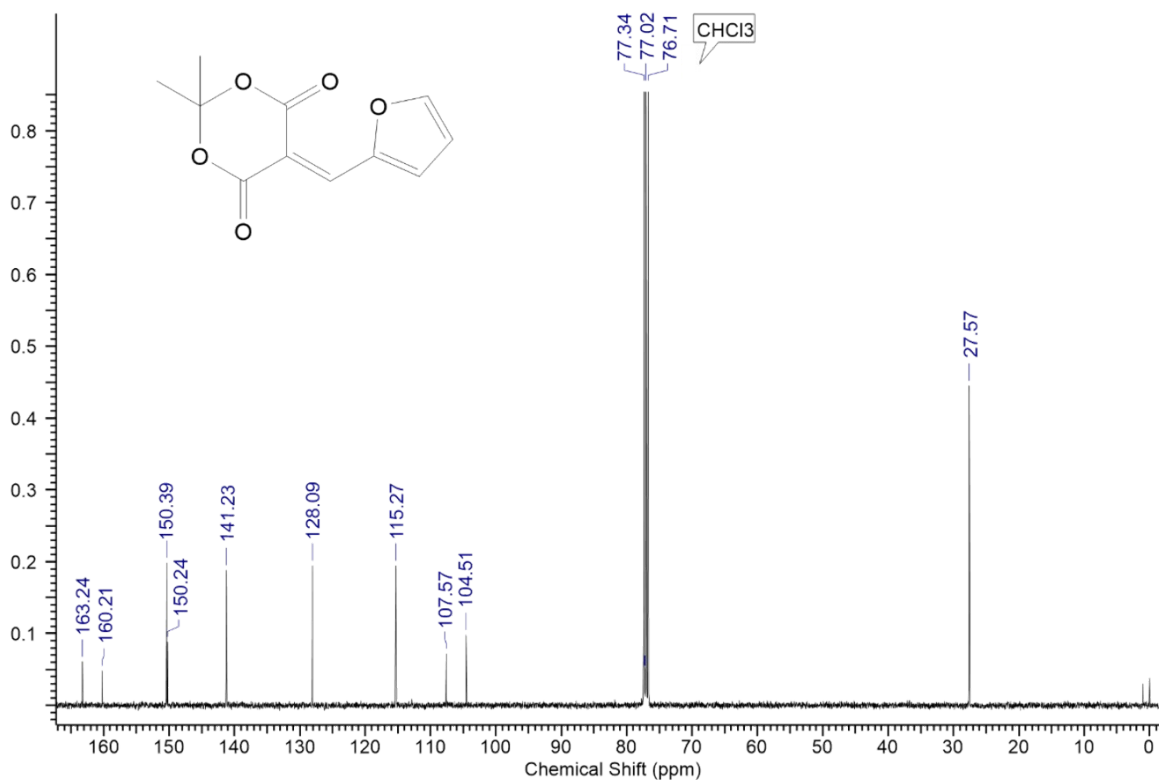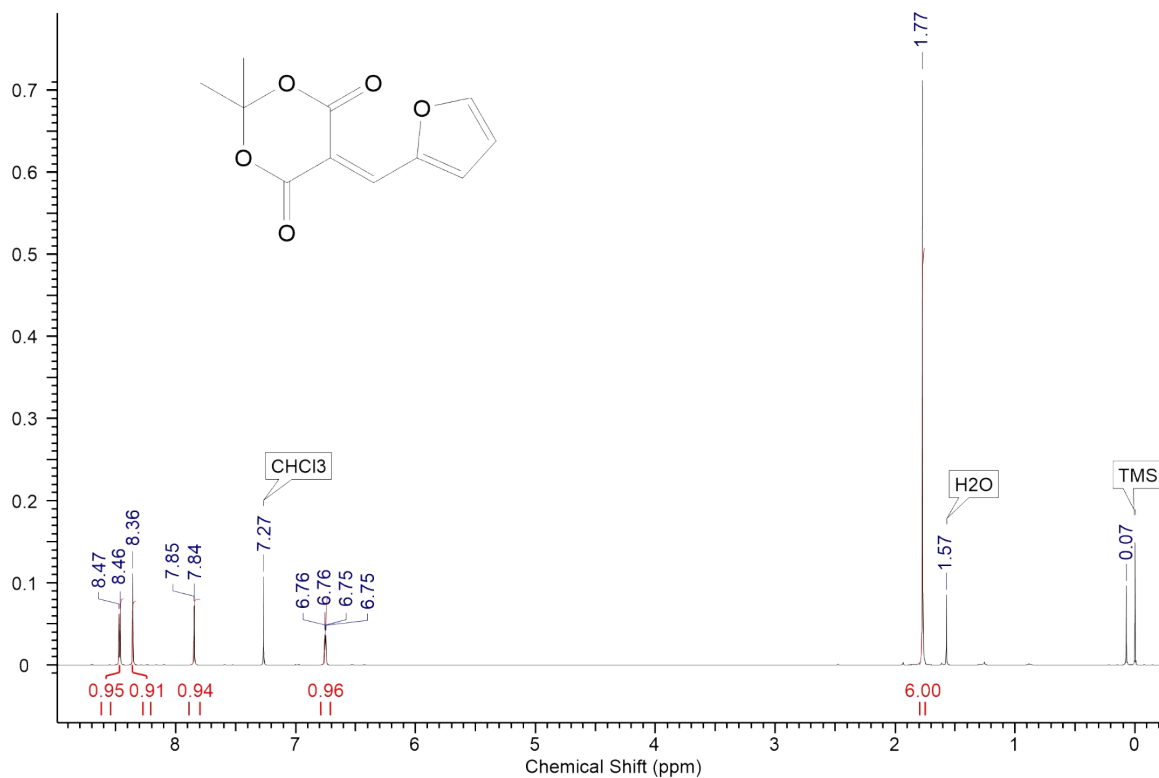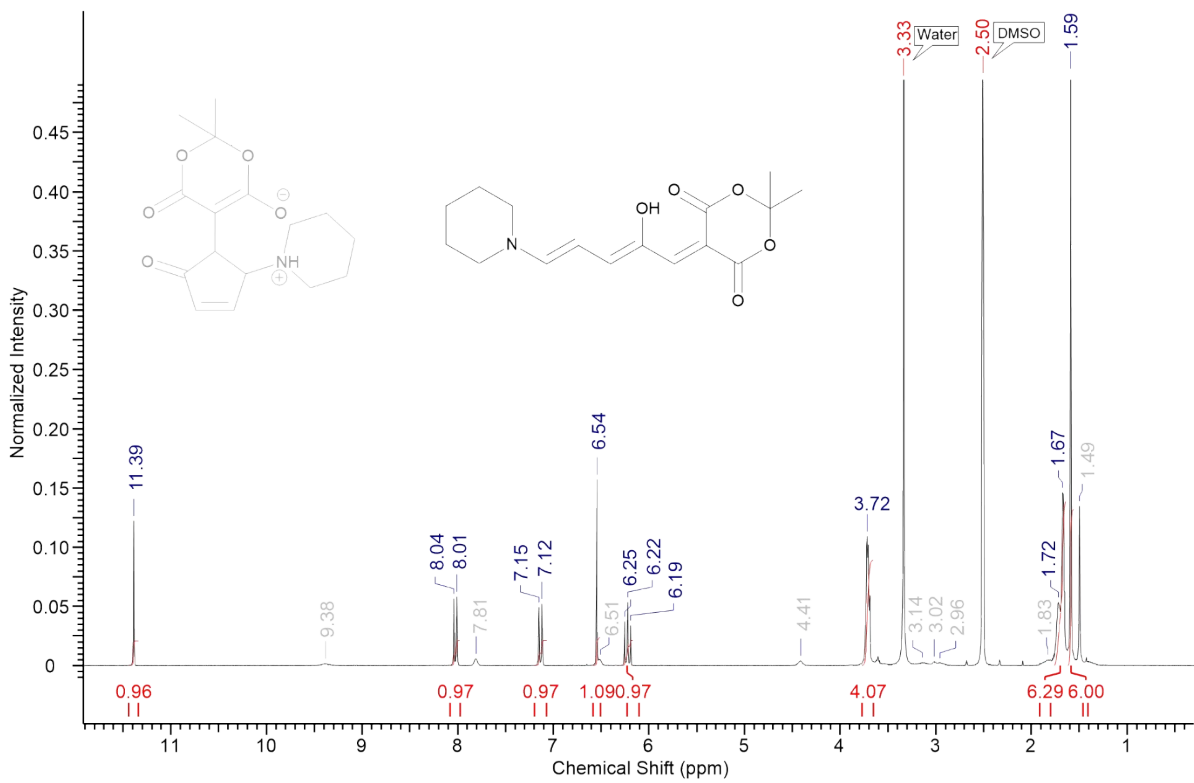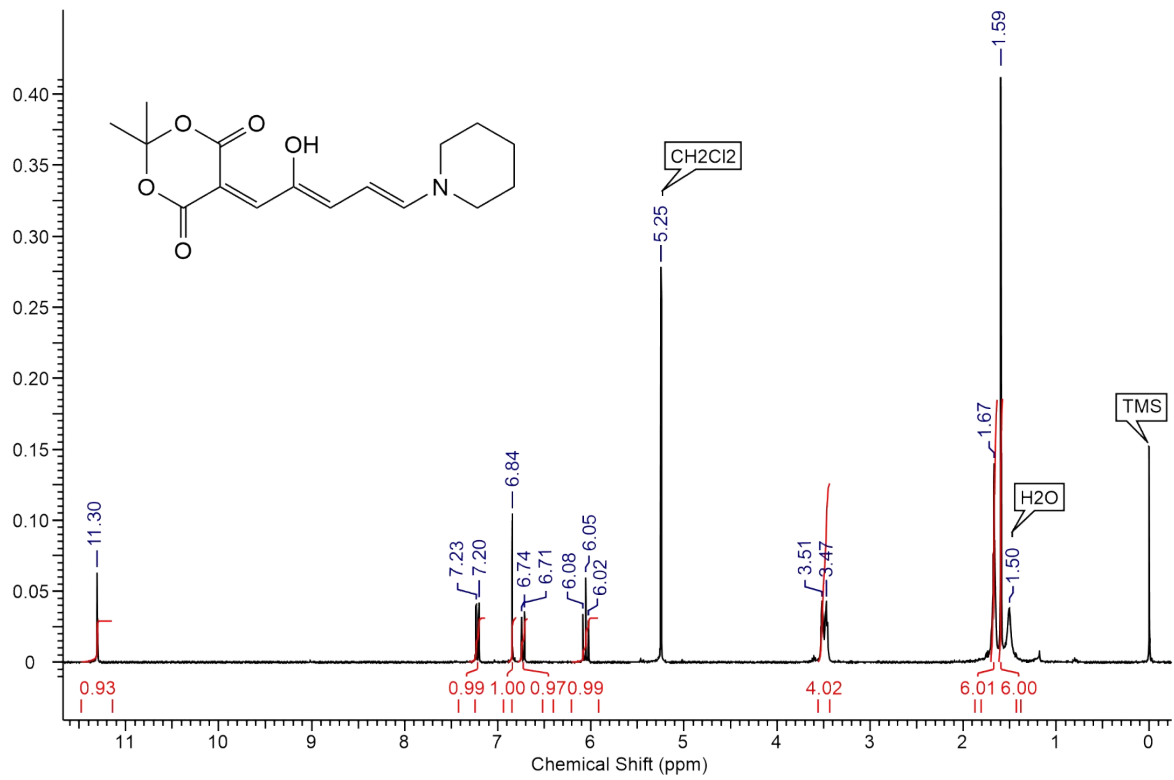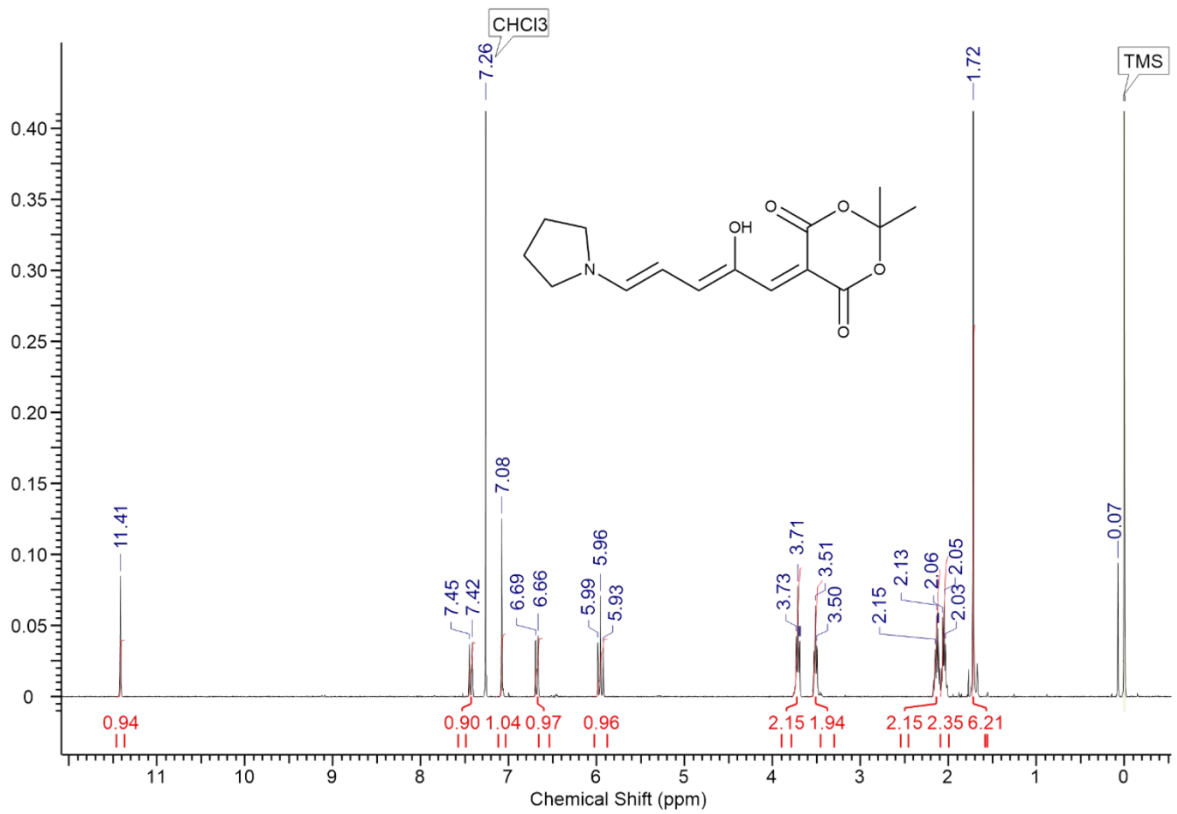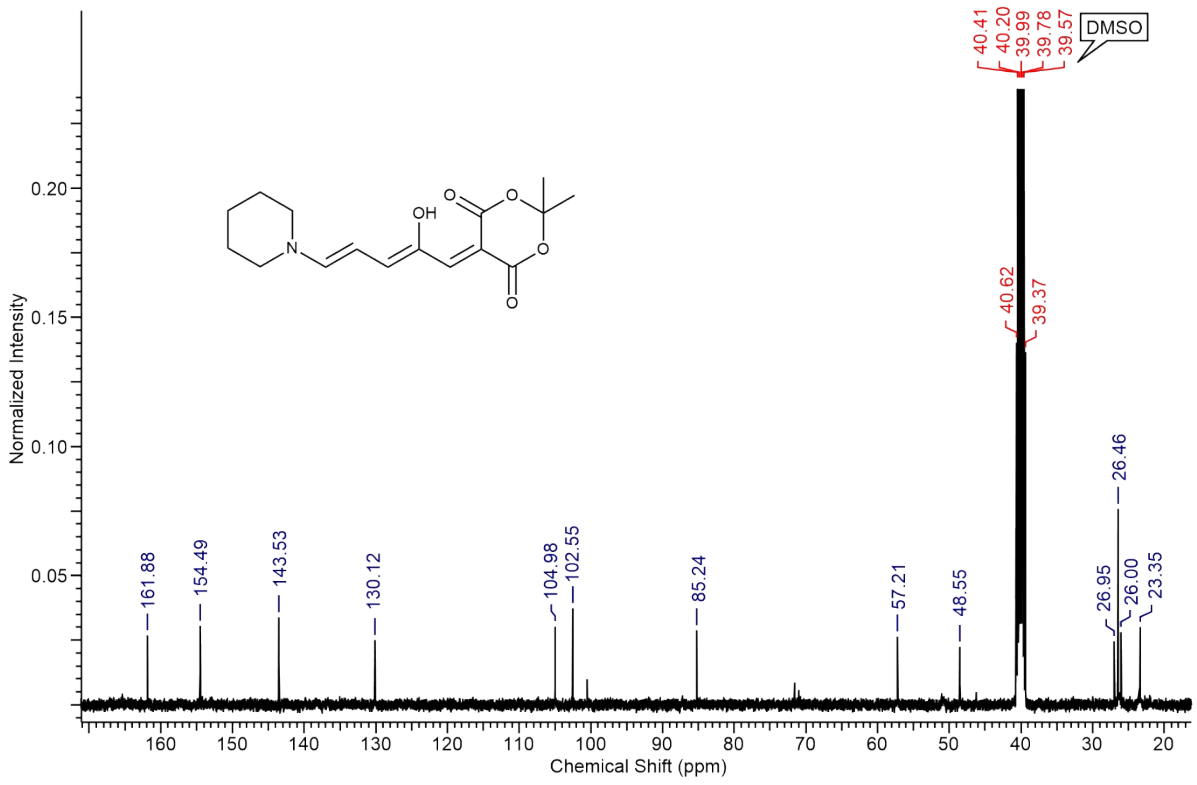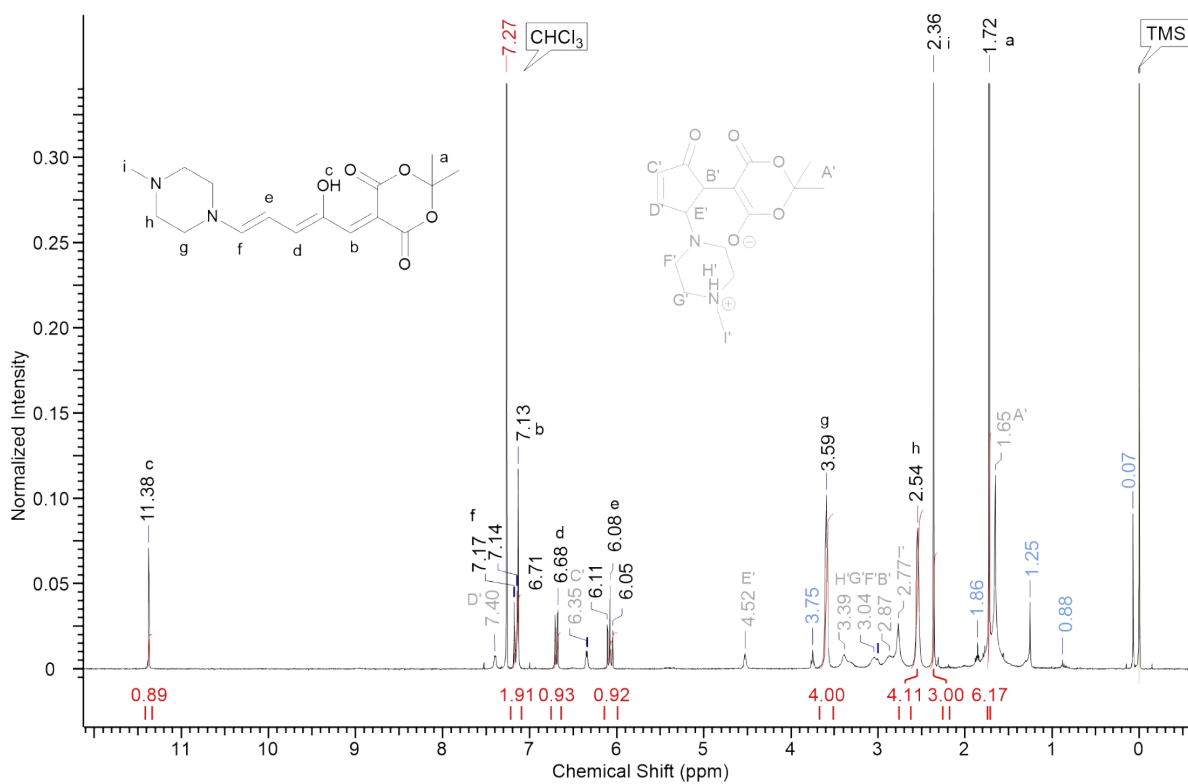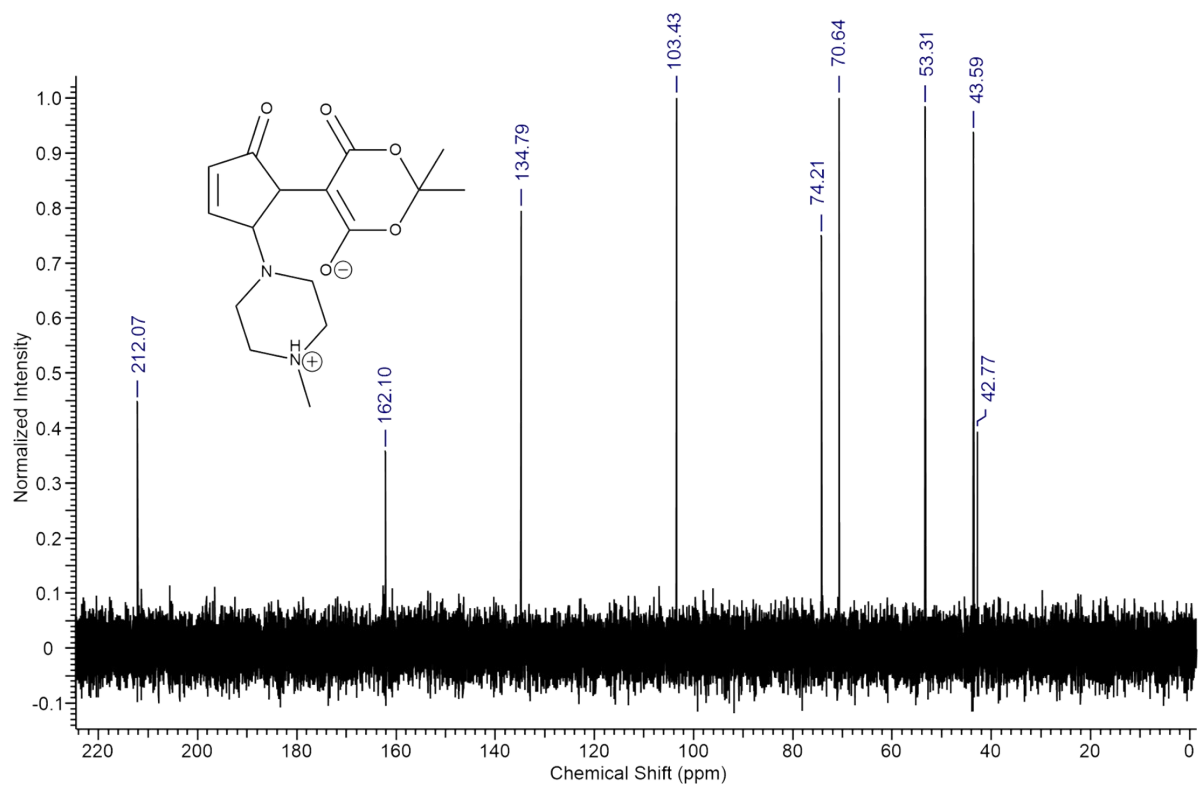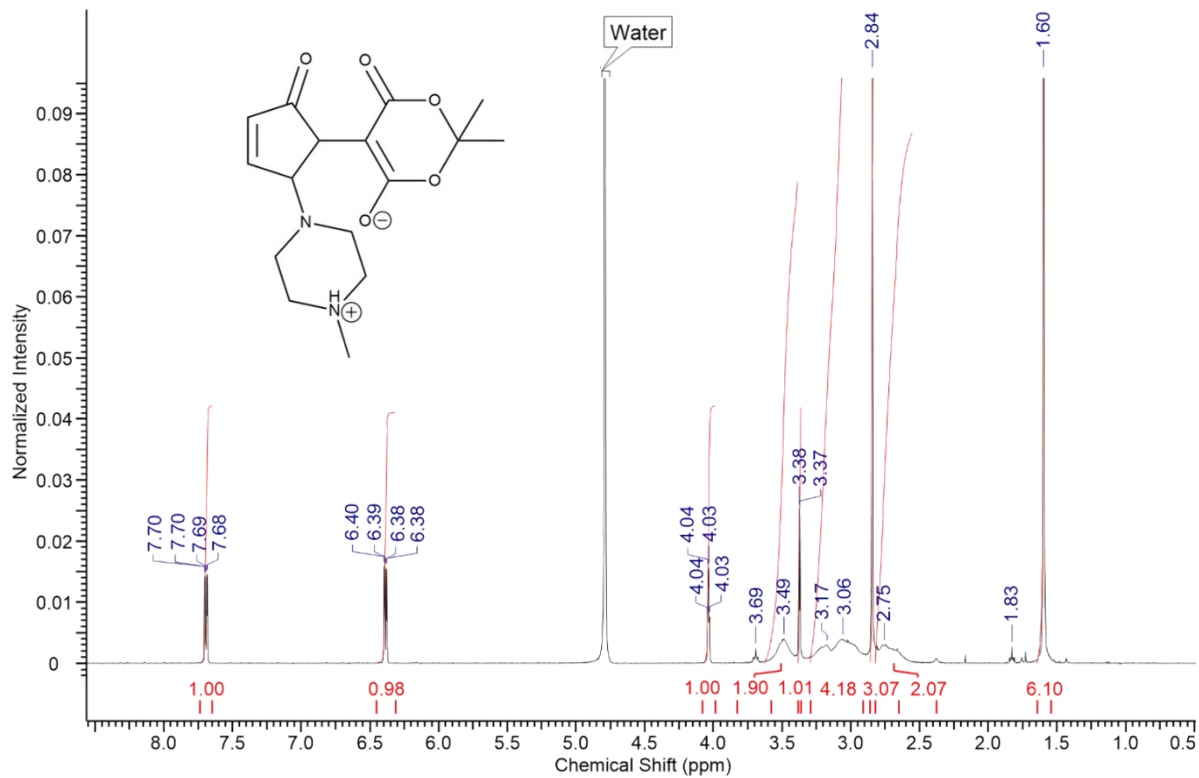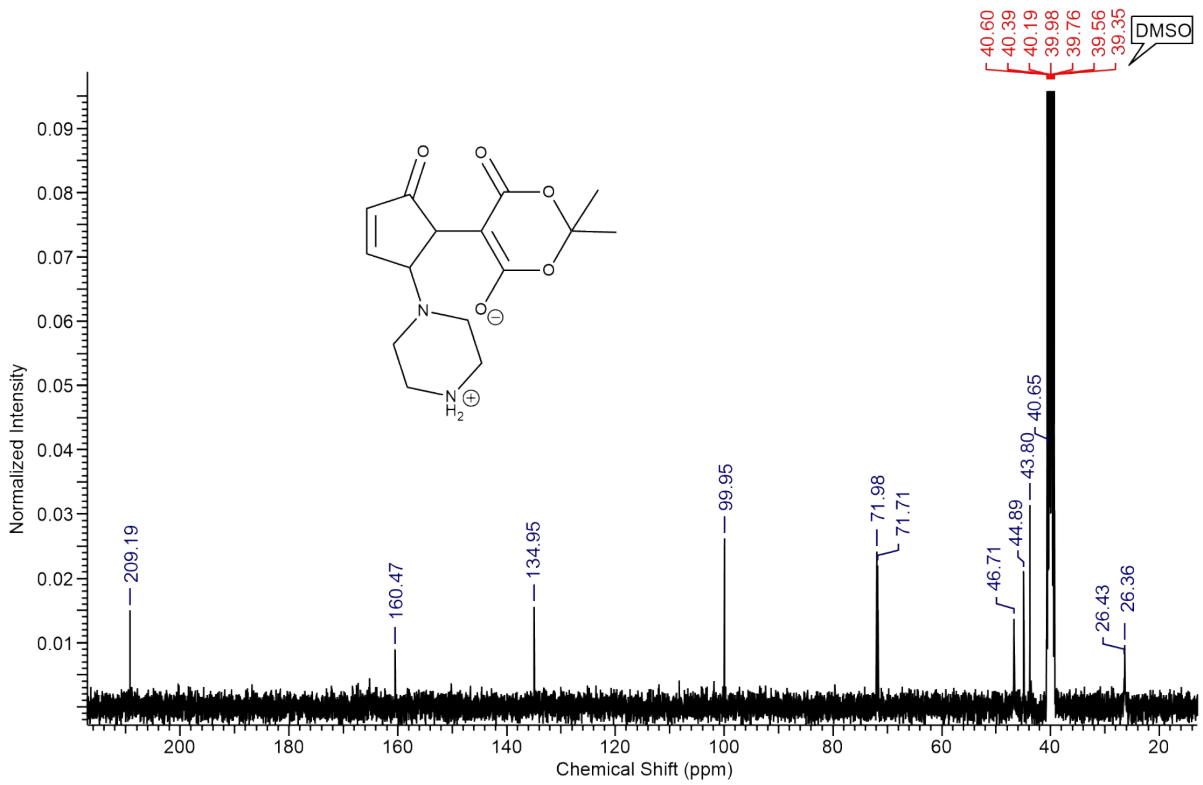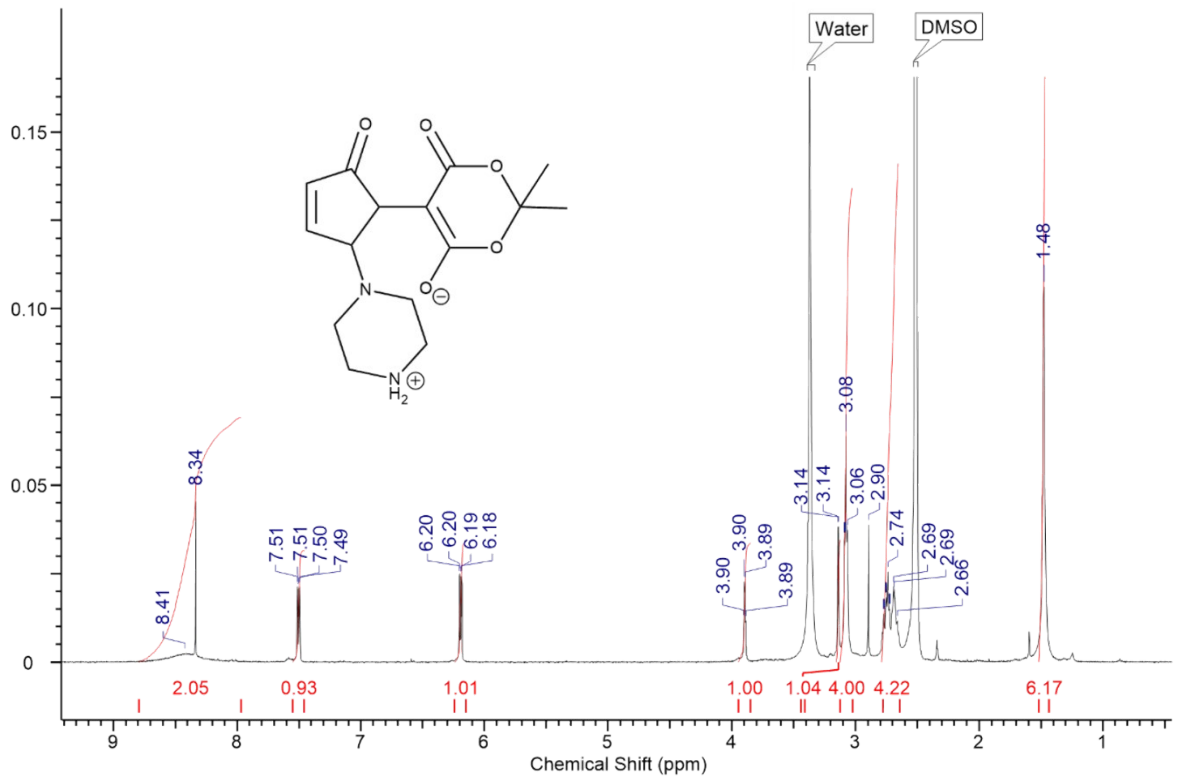
4 Single crystal X-ray diffraction (SCXRD)

Single crystal diffraction data were collected using an Oxford Diffraction SuperNova, using Cu Kα radiation (λ = 1.54413 Å) with an AtlasS2 detector. Crystals were kept at 100 K during data collection. Using Olex2,[2] the structures were solved with the ShelXT[3] structure solution program using direct methods and refined with the ShelXL[4] refinement package using least squares minimisation.

4.1 DASA 1 (chloroform solvate)
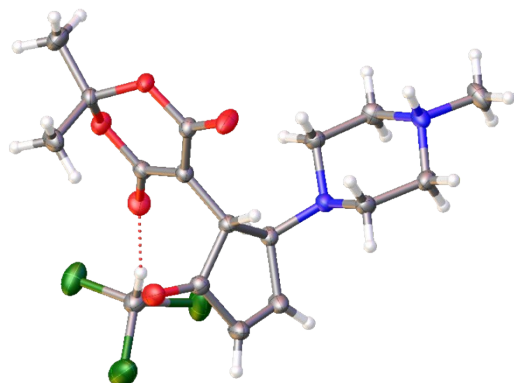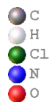
Crystal Data for DASA 1 (chloroform solvate): ($C_{17}H_{23}Cl_3N_2O_5$) (M =441.72 g/mol): triclinic, space group P-1 (no. 2), a = 10.0026(7) Å, b = 10.1400(9) Å, c = 10.8176(10) Å, α = 108.089(8)°, β = 96.421(7)°, γ = 92.493(6)°, V = 1032.86(15) Å^3, Z = 2, T = 150.00(10) K, μ(Cu Kα) = 4.285 mm^{-1}, $Dcalc$ = 1.420 g/cm^3, 7009 reflections measured (8.676° ≤ 2Θ ≤ 144.132°), 3933 unique (R_{int} = 0.0288, R_{sigma} = 0.0431) which were used in all calculations. The final R_1 was 0.0459 (I > 2σ(I)) and wR_2 was 0.1138 (all data).

4.2 DASA 1 (H$_2$O solvate)
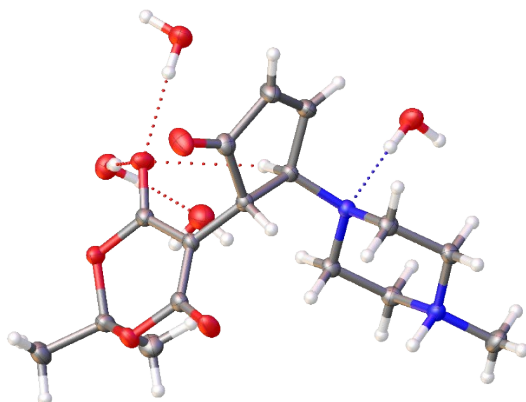
Crystal Data for DASA 1 (H$_2$O solvate): $C_{16}H_{30}N_2O_9$ (M =394.42 g/mol): monoclinic, space group P2$_1$/n (no. 14), a = 14.92326(18) Å, b = 8.57252(8) Å, c = 15.64663(18) Å, β = 94.0935(11)°, V = 1996.57(4) Å^3, Z = 4, T = 150.00(10) K, μ(Cu Kα) = 0.910 mm^{-1}, $Dcalc$ = 1.312 g/cm^3, 11588 reflections measured (7.91° ≤ 2Θ ≤ 143.974°), 3862 unique (R_{int} = 0.0205, R_{sigma} = 0.0183) which were used in all calculations. The final R_1 was 0.0344 (I > 2σ(I)) and wR_2 was 0.1325 (all data).

4.3 DASA 2 (H₂O solvate)
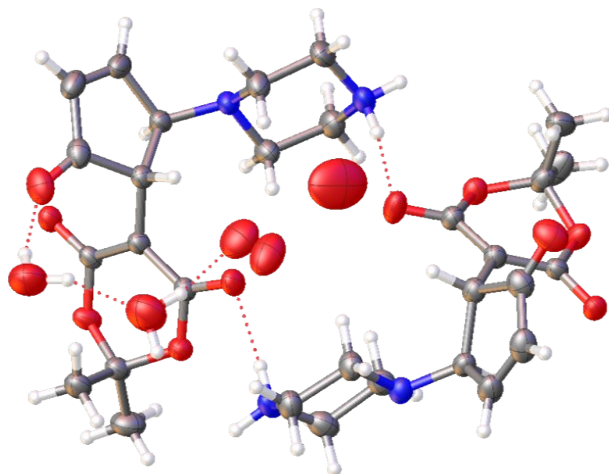
Crystal Data DASA 2 (H₂O solvate): $C_{30}H_{44}N_4O_{13.5}$ (M =676.69 g/mol): monoclinic, space group I2/a (no. 15), a = 18.9606(2) Å, b = 14.2438(2) Å, c = 25.8792(3) Å, β = 90.0200(10)°, V = 6989.22(15) Å^3, Z = 8, T = 200(2) K, µ(Cu Kα) = 0.861 mm^{-1}, $Dcalc$ = 1.286 g/cm^3, 25753 reflections measured (7.084° ≤ 2Θ ≤ 146.786°), 6929 unique (R_{int} = 0.0334, R_{sigma} = 0.0261) which were used in all calculations. The final R_1 was 0.0462 (I > 2σ(I)) and wR_2 was 0.1270 (all data).

4.4 DASA 4
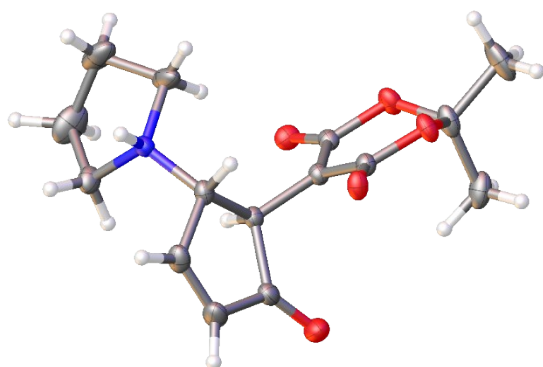
Crystal Data for DASA 4: $C_{15}H_{19}NO_5$ (M =293.31 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 7.9743(4) Å, b = 17.9548(7) Å, c = 10.8807(4) Å, β = 108.121(4)°, V = 1480.60(11) Å^3, Z = 4, T = 150(1) K, µ(Cu Kα) = 0.825 mm^{-1}, $Dcalc$ = 1.316 g/cm^3, 5777 reflections measured (9.852° ≤ 2Θ ≤ 143.996°), 2826 unique (R_{int} = 0.0402, R_{sigma} = 0.0489) which were used in all calculations. The final R_1 was 0.0415 (I > 2σ(I)) and wR_2 was 0.1314 (all data).

4.5 Extended Crystal Packing
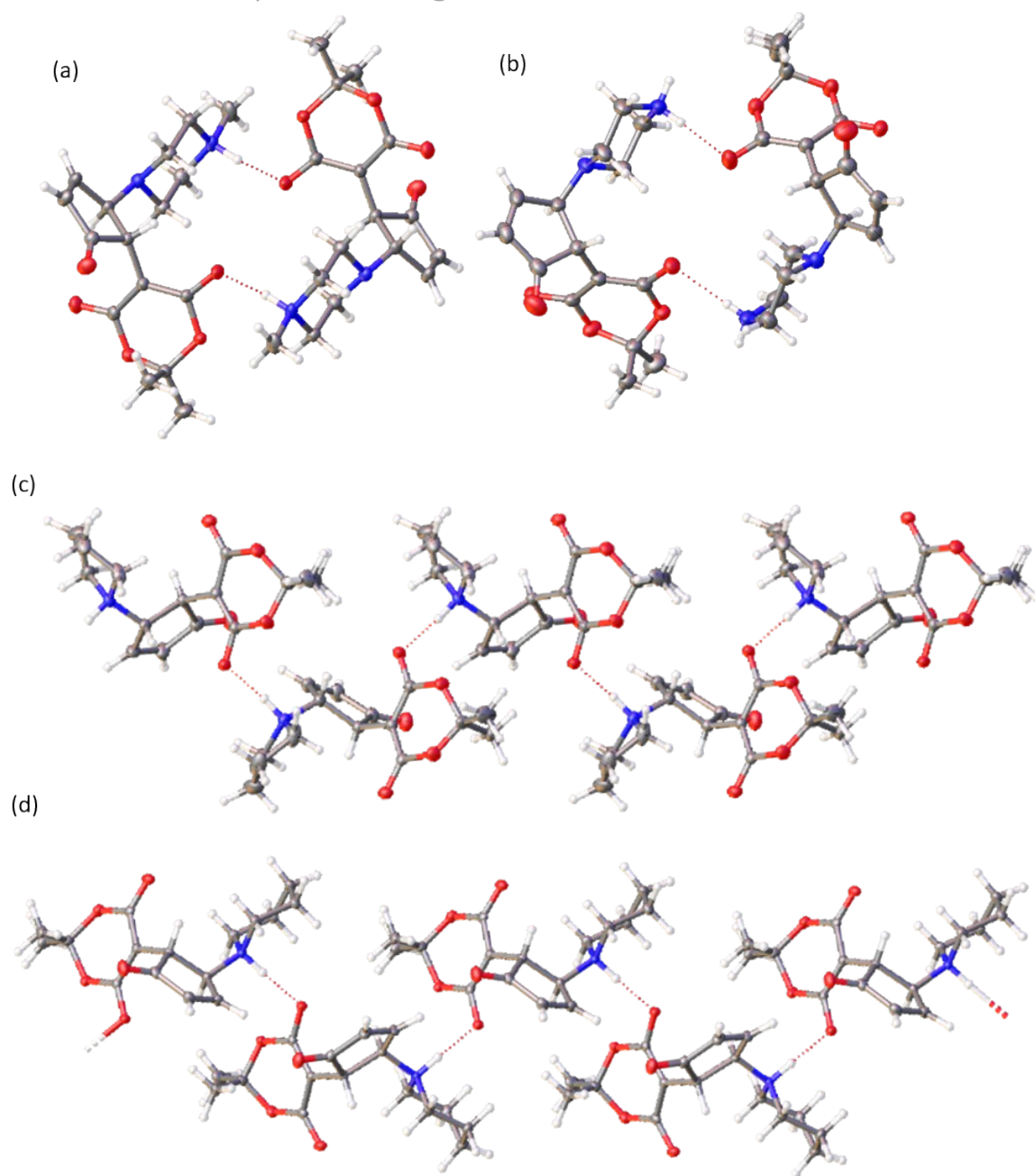
Figure S13. (a) Image from crystal structure of DASA 2 displaying dimer formed. (b) Image from crystal structure of DASA 1 displaying dimer formed. (c) Image from crystal structure of DASA 4 displaying chains formed in the extended lattice. (d) Image from crystal structure of DASA 3 displaying chains formed in the extended lattice.

5 Computational experiments

The initial minimum energy conformations of all molecules were assessed following extensive conformational searches and energy minimisations using the intrinsic molecular dynamics MM2 force field intrinsic to Chem3D, v15.0 (Perkin Elmer). All final conformations were modelled at the semi-empirical PM7 level (in $CHCl_3$, e=4.81, COSMO) using MOPAC2016[5] through the MOPAC Interface with Chem3D, v15.0 (Perkin Elmer). A typical input is as shown below. The co-ordinates for all minimum energy confirmations are given below.

PM7 CHARGE=0 EF EPS=4.81 GNORM=0.0001 LET SHIFT=80
DASA3_Linear_M#1

C	-11.0700 1	0.1166 1	3.7822 1
C	-9.9572 1	-0.3647 1	4.7191 1
C	-8.6857 1	0.4775 1	4.5267 1
N	-8.2756 1	0.4478 1	3.1087 1
C	-9.3063 1	0.9467 1	2.1821 1
C	-10.5852 1	0.1067 1	2.3295 1
C	-7.1366 1	-0.1127 1	2.7364 1
C	-6.6961 1	-0.2341 1	1.3994 1
C	-5.5008 1	-0.8378 1	1.0911 1
C	-5.0443 1	-0.9959 1	-0.2432 1
C	-3.8762 1	-1.6613 1	-0.5379 1
C	-3.2605 1	-1.9730 1	-1.7624 1
C	-3.7850 1	-1.7503 1	-3.0691 1
O	-2.9775 1	-2.0114 1	-4.1457 1
C	-1.5715 1	-2.0963 1	-3.9656 1
O	-1.2700 1	-2.8602 1	-2.8108 1
C	-2.0012 1	-2.6677 1	-1.6664 1
O	-1.5004 1	-3.1550 1	-0.6730 1
O	-4.9120 1	-1.4106 1	-3.4071 1
C	-0.9910 1	-0.7008 1	-3.8229 1
C	-1.0674 1	-2.9134 1	-5.1414 1
O	-5.8764 1	-0.4137 1	-1.1576 1
H	-11.9638 1	-0.5287 1	3.8908 1
H	-11.4030 1	1.1326 1	4.0705 1
H	-10.2853 1	-0.3021 1	5.7754 1
H	-9.7397 1	-1.4359 1	4.5375 1
H	-7.8662 1	0.1076 1	5.1836 1
H	-8.8707 1	1.5389 1	4.8216 1
H	-8.9441 1	0.9244 1	1.1271 1
H	-9.5102 1	2.0188 1	2.4195 1
H	-10.4019 1	-0.9333 1	1.9927 1
H	-11.3685 1	0.5064 1	1.6550 1
H	-6.4755 1	-0.4967 1	3.5442 1
H	-7.3188 1	0.1490 1	0.5864 1
H	-4.8594 1	-1.2302 1	1.8943 1
H	-3.3089 1	-2.0206 1	0.3513 1
H	-1.3817 1	-0.1759 1	-2.9409 1
H	0.1025 1	-0.7345 1	-3.7219 1
H	-1.2257 1	-0.0819 1	-4.7004 1
H	0.0194 1	-3.0623 1	-5.0834 1
H	-1.5354 1	-3.9088 1	-5.1689 1
H	-1.2957 1	-2.4176 1	-6.0951 1
H	-5.6516 1	-0.7339 1	-2.0827 1

5.1 DASA 1 modelling

(a)

-794.99 KJ mol^{-1}

(b)

-833.79 KJ mol^{-1}

(c)

-825.31 KJ mol^{-1}

(d)

-850.67 KJ mol^{-1}

(e)

-850.26 KJ mol^{-1}

Figure S14. (a) Chem3D model of triene form of DASA 1, and the value for the simulated heat of formation. (b-e) Chem3D models of possible cyclopentanone forms of DASA 1, and the values for the simulated heats of formation.
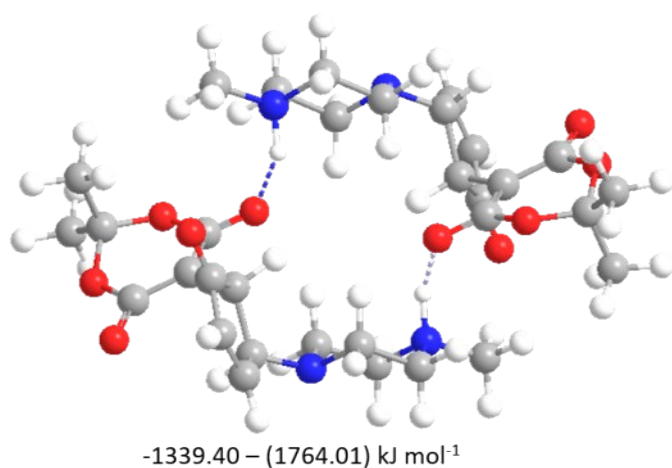
-1339.40 – (1764.01) kJ mol^{-1}

The calculated heats of formation for the modeled dimer fall in the range shown. Some calculations showed that the dimer is a lower energy conformation than two free molecules, but at not always. These are preliminary results and further higher-level calculations are ongoing.

Figure S15. (a) Chem3D model of cyclopentanone form of DASA 1 in the dimer conformation found in the crystal structure, also shown is the range of the heat of formation found for this dimer.

DASA 1: Cartesian co-ordinates for lowest energy minimised energy conformation in chloroform.

1	C	-14.561590550	5.252963156	1.501590571
2	C	-16.315824672	3.573563184	0.638726655
3	O	-13.212572497	1.039428131	0.638780487
4	O	-14.365816880	4.000596272	-2.821104552
5	C	-14.319691819	3.554222536	-1.663413309
6	O	-14.563729218	4.512315994	-0.717057411
7	C	-14.880229431	4.067790627	0.606215005
8	O	-14.002080513	3.037008465	1.007846754
9	C	-13.727519579	2.009459158	0.118577124
10	C	-12.233996888	0.732075723	-4.841855445
11	C	-13.207873640	1.792595456	-5.415988077
12	N	-12.918111798	3.174020821	-4.886864867
13	C	-11.467700726	3.280914901	-4.496160570
14	C	-11.204722048	2.349438367	-3.300116417
15	C	-14.011328701	2.254761250	-1.247657462
16	N	-11.701875402	0.967791352	-3.497470273
17	O	-15.972987687	0.015447915	-1.422625944
18	C	-14.842793046	-0.042646993	-1.828780456
19	C	-13.967595009	1.153908128	-2.222026573
20	C	-12.542030673	0.515918090	-2.381179985
21	C	-12.809412604	-0.977731031	-2.442771809
22	C	-14.066273717	-1.279752033	-2.089066116
23	C	-13.261462135	4.207889372	-5.913152978
24	H	-14.743889538	5.009271958	2.557386837
25	H	-13.507740238	5.551529086	1.409430335
26	H	-15.175067427	6.124480008	1.238781167
27	H	-17.013668894	4.352387126	0.305261777
28	H	-16.462223646	2.702277604	-0.017737307
29	H	-16.606496118	3.266548076	1.652525992
30	H	-11.350031661	0.645288242	-5.521444787
31	H	-12.733156167	-0.265790035	-4.877356236
32	H	-14.267435664	1.539427231	-5.178442861
33	H	-13.139964541	1.774624760	-6.527551069
34	H	-13.534261054	3.362670383	-3.983201198
35	H	-11.232150473	4.335467330	-4.219062449
36	H	-10.813787822	3.031508609	-5.359521696
37	H	-10.101844435	2.272140379	-3.134471388
38	H	-11.624777418	2.803031372	-2.368601680
39	H	-14.346839630	1.501126381	-3.213931583
40	H	-11.955353843	0.715128751	-1.432404629
41	H	-12.012131251	-1.651489270	-2.715215081
42	H	-14.519294718	-2.250115820	-1.989518303
43	H	-14.321665661	4.114080259	-6.217800546
44	H	-12.634278717	4.126659905	-6.816113770
45	H	-13.130556451	5.224503386	-5.493799559

5.2 DASA 2 modelling

(a)

-785.41 KJ mol^{-1}

(b)

-824.66 KJ mol^{-1}

(c)

-825.30 KJ mol^{-1}

(d)

-850.39 KJ mol^{-1}
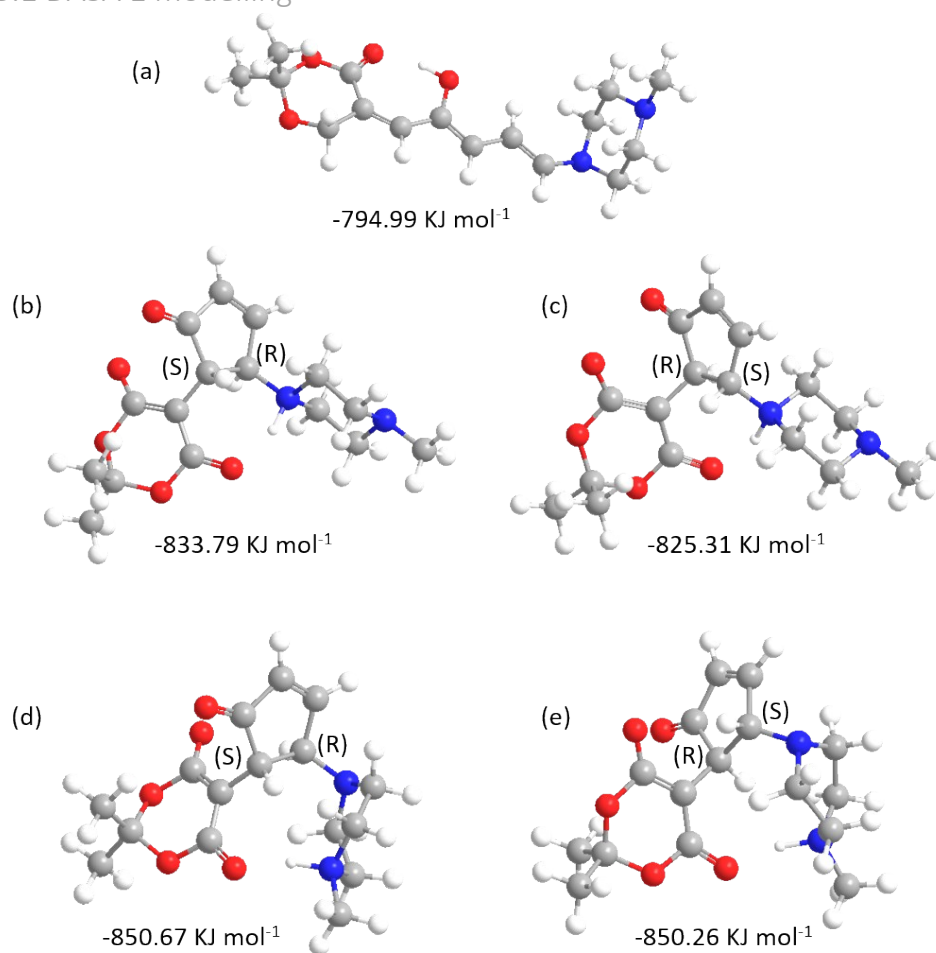
(e)

-836.81 KJ mol^{-1}

Figure S16. (a) Chem3D model of triene form of DASA 2, and the value for the simulated heat of formation. (b-e) Chem3D models of possible cyclopentanone forms of DASA 2, and the values for the simulated heats of formation.
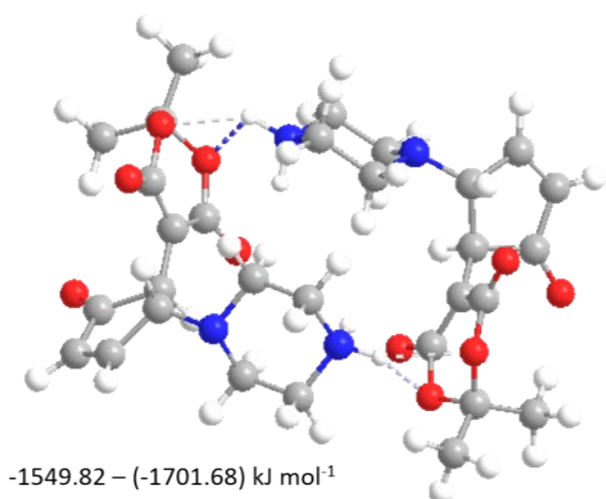
-1549.82 – (-1701.68) kJ mol^{-1}

The calculated heats of formation for the modeled dimer fall in the range shown. Some calculations showed that the dimer is a lower energy conformation than two free molecules, but at not always. These are preliminary results and further higher-level calculations are ongoing.

Figure S17. Chem3D model of cyclopentanone form of DASA 2 in the dimer conformation found in the crystal structure, the range of the simulated heats of formation of the dimer is also shown.

DASA 2: Cartesian co-ordinates for lowest energy minimised energy conformation in chloroform.

1	C	-6.885314871	2.458325194	-0.726199344
2	C	-8.176918122	2.201183856	-0.478805247
3	C	-8.406726816	0.751966743	-0.093761158
4	C	-6.964744235	0.197225875	0.182499363
5	C	-6.059335139	1.255784239	-0.459533023
6	O	-4.881095176	1.139421307	-0.671118006
7	N	-9.416297354	0.616896891	0.963596081
8	C	-6.733138079	-1.156169444	-0.342441588
9	C	-9.850370322	-0.788240918	1.145523911
10	C	-9.744333142	-1.289982626	2.595648228
11	N	-8.387044127	-0.941594586	3.148102153
12	C	-8.228602378	0.554973134	3.244060861
13	C	-9.124962865	1.302281598	2.225261074
14	C	-6.842265215	-1.415650095	-1.729867528
15	O	-6.343844575	-2.630950245	-2.176838821
16	C	-5.421196263	-3.316273143	-1.354674119
17	O	-5.902481088	-3.365130563	-0.006422014
18	C	-6.389681318	-2.200616142	0.525579604
19	O	-6.505625985	-2.243286938	1.759185636
20	O	-7.369079691	-0.752842735	-2.602245471
21	C	-4.071467113	-2.620709987	-1.386129653
22	C	-5.433017219	-4.758971997	-1.829993036
23	H	-6.437778743	3.375607652	-1.068626774
24	H	-9.017826466	2.873441353	-0.555800848
25	H	-8.821782089	0.221705765	-1.005806681
26	H	-6.744801100	0.228512792	1.279105050
27	H	-10.918278952	-0.837732811	0.818782101
28	H	-9.288486829	-1.475730332	0.465476624
29	H	-9.882347630	-2.396484281	2.634811400
30	H	-10.540155103	-0.853146360	3.237561534
31	H	-7.620933177	-1.359305399	2.498845877
32	H	-8.254862738	-1.374850487	4.083896417
33	H	-7.151998536	0.808332217	3.098300326
34	H	-8.478909524	0.893905675	4.274357030
35	H	-10.112035392	1.524515245	2.702231017
36	H	-8.669906567	2.299286951	2.012284792
37	H	-3.350969832	-3.115901883	-0.723384033
38	H	-3.654025190	-2.617347475	-2.402825352
39	H	-4.143057558	-1.570811480	-1.062830408
40	H	-4.748198984	-5.377580037	-1.233012885
41	H	-6.435364827	-5.201429556	-1.745691517
42	H	-5.128746182	-4.826449865	-2.883066707

(a)

-849.82 KJ mol^{-1}

(b)

(S) (R)

-886.72 KJ mol^{-1}

(c)

(R) (S)

-896.47 KJ mol^{-1}

(d)

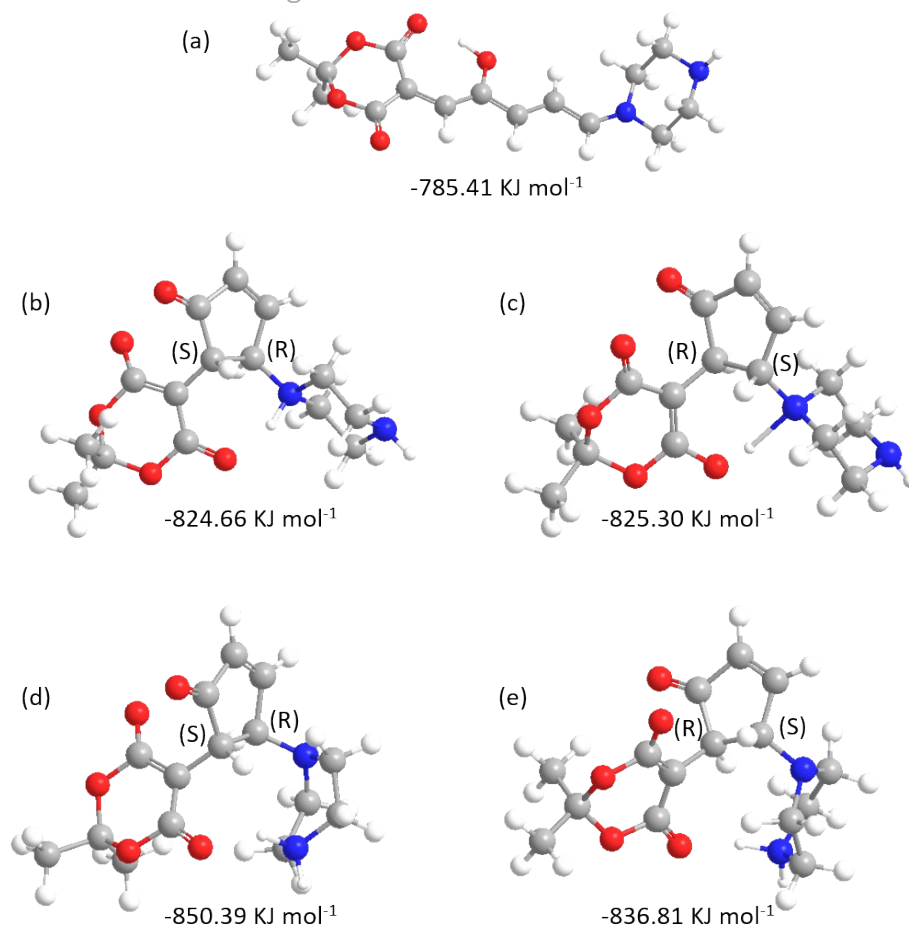*Figure S18. (a) Chem3D model of triene form of DASA 3, and the value for the simulated heat of formation. (b,c) Chem3D models of possible cyclized forms of DASA 3, and the values for the simulated heats of formation. (d) Chem3D model of cyclized form of DASA 3 in the chain-like conformation found in the crystal structure.*

DASA 3: Cartesian co-ordinates for lowest energy minimised energy conformation in chloroform.

1	C	5.362370107	1.866160188	-1.051934154
2	C	4.459366671	0.975548837	-0.621073248
3	C	5.094664704	-0.061791201	0.268877042
4	C	6.507701057	0.525439436	0.628419029
5	C	6.694150072	1.628710505	-0.415190231
6	O	7.693865106	2.256792772	-0.618681245
7	N	4.362688600	-0.422434349	1.539425821
8	C	7.509404521	-0.545359845	0.666362446
9	C	3.777573443	0.790935619	2.226818781
10	C	3.176554755	0.369306503	3.569115926
11	C	2.089740281	-0.689341242	3.363527220
12	C	2.650413968	-1.883869239	2.587166626
13	C	3.268033995	-1.430200292	1.263012950
14	C	7.522259593	-1.390001425	1.791527489
15	O	8.549149451	-2.277456479	1.939947167
16	C	9.708496985	-2.099525948	1.116304159
17	O	9.345309969	-1.776815682	-0.208394500
18	C	8.361115251	-0.821188567	-0.425138663
19	O	8.326768452	-0.404268947	-1.565257941
20	O	6.652909054	-1.470464062	2.667596826
21	C	10.348698182	-3.475815629	1.045554744
22	C	10.568781147	-0.995418316	1.706967579
23	H	5.223372143	2.677960142	-1.746989199
24	H	3.414774013	0.913861102	-0.882992074
25	H	5.240792122	-1.011959274	-0.326497290
26	H	6.475845003	1.043939858	1.628187162
27	H	5.106597928	-0.879015402	2.196054899
28	H	3.005151911	1.258179183	1.576338756
29	H	4.578322819	1.552273468	2.374920868
30	H	3.964004845	-0.012116625	4.252428336
31	H	2.757787521	1.258846336	4.083425780
32	H	1.692193415	-1.023318081	4.342481251
33	H	1.222332409	-0.254450504	2.830194405
34	H	3.396711384	-2.428162904	3.203408880
35	H	1.849447332	-2.625363012	2.387112432
36	H	3.703916368	-2.299941605	0.715881515
37	H	2.500691812	-0.979321282	0.596392645
38	H	11.256581516	-3.456552164	0.426910079
39	H	10.620835202	-3.837473150	2.046205007
40	H	9.663724827	-4.213171944	0.603462934
41	H	11.481443513	-0.846779462	1.113610126
42	H	10.036827032	-0.033672241	1.731993602
43	H	10.866840856	-1.230736379	2.736760656

(a)

-830.12 KJ mol^{-1}

(b)

(S) (R)

-853.51 KJ mol^{-1}

(c)

(R) (S)

-860.36 KJ mol^{-1}

(d)

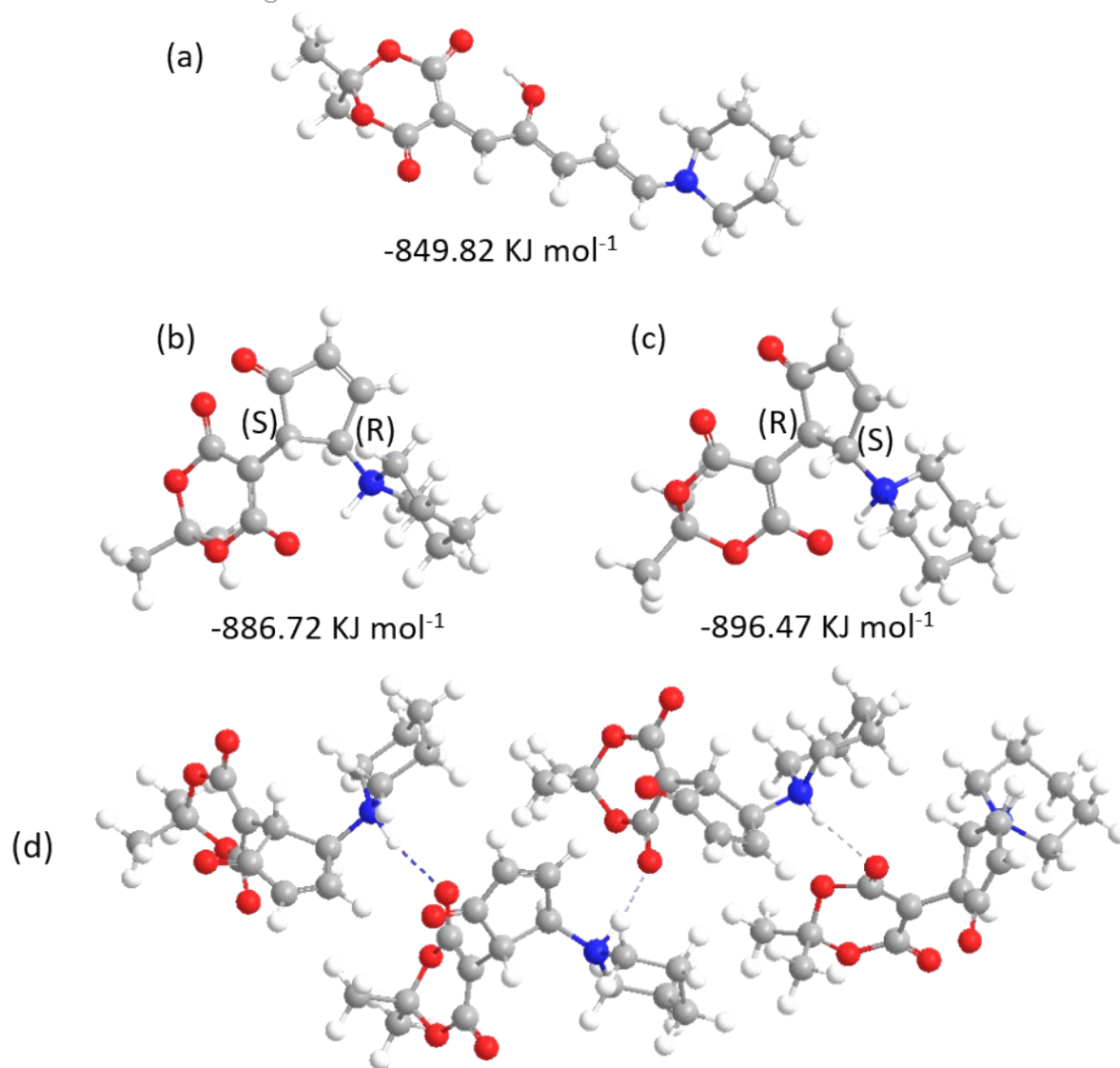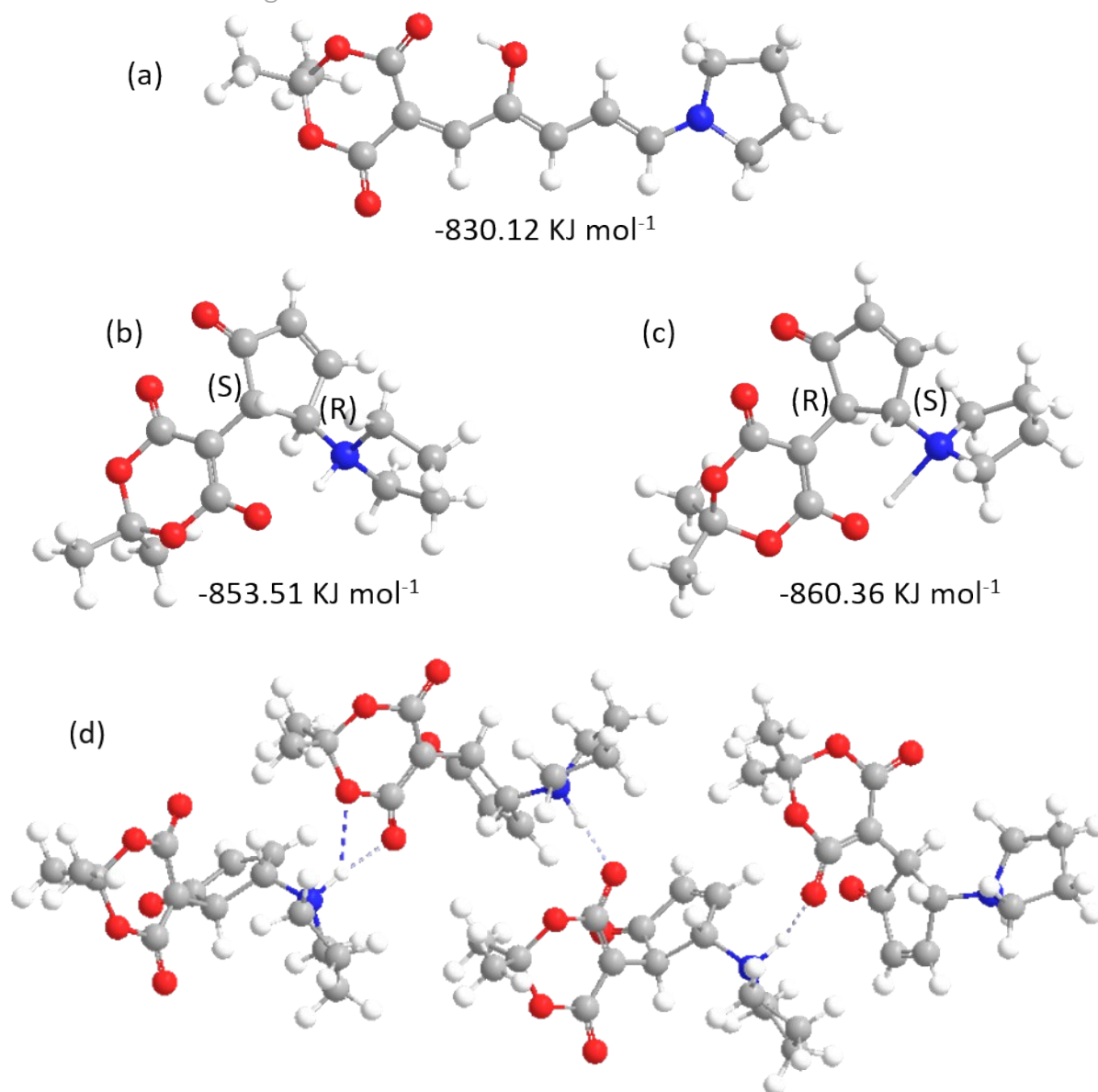*Figure S19. (a) Chem3D model of triene form of DASA 4, and the value for the simulated heat of formation. (b,c) Chem3D models of possible cyclopentanone forms of DASA 4, and the values for the simulated heats of formation. (d) Chem3D model of cyclized form of DASA **4** in the chain-like conformation found in the crystal structure.*

DASA 4: Cartesian co-ordinates for lowest energy minimised energy conformation in chloroform.

|				
1	C	-10.281976697	2.430672618	-0.739969538
2	C	-11.240939380	1.572071006	-0.369898609
3	C	-10.662318550	0.373941161	0.338822223
4	C	-9.181291833	0.780220154	0.673584371
5	C	-8.948167019	1.997020025	-0.224119679
6	O	-7.906977837	2.562777122	-0.401465583
7	N	-11.348348063	-0.082210306	1.603877179
8	C	-8.284912233	-0.368728901	0.501492639
9	C	-8.314164304	-1.374762011	1.484015700
10	O	-7.367159287	-2.356501229	1.455783375
11	C	-6.221650330	-2.152839088	0.616899494
12	O	-6.596392934	-1.604181953	-0.627058195
13	C	-7.494793183	-0.544814117	-0.655416919
14	O	-7.523504742	0.043275806	-1.717152732
15	O	-9.161673877	-1.515172628	2.376706821
16	C	-5.709203886	-3.550898299	0.314121915
17	C	-5.248771188	-1.227915072	1.328035418
18	C	-12.618992189	-0.854802372	1.313328161
19	C	-13.786675102	0.122409414	1.477642593
20	C	-13.246631061	1.324003068	2.269719354
21	C	-11.753562814	1.066878966	2.504635604
22	H	-10.380353596	3.337258990	-1.314117969
23	H	-12.300291234	1.636265106	-0.562596847
24	H	-10.646544333	-0.500773456	-0.376467451
25	H	-9.107038206	1.156452136	1.733004985
26	H	-10.619162815	-0.722939308	2.110116142
27	H	-6.473492732	-4.155495980	-0.194587171
28	H	-4.828746222	-3.512963937	-0.342461243
29	H	-5.429794559	-4.079087608	1.235343219
30	H	-4.341272523	-1.073597810	0.728020653
31	H	-5.688506653	-0.237563101	1.513278105
32	H	-4.948009004	-1.638661910	2.300521066
33	H	-12.691287275	-1.698230947	2.037084365
34	H	-12.583738375	-1.309587099	0.300433632
35	H	-14.191467472	0.439350162	0.498405730
36	H	-14.635994636	-0.356567402	1.999508713
37	H	-13.782772974	1.448351177	3.228928044
38	H	-13.413257938	2.269620753	1.720805302
39	H	-11.136542112	1.967660497	2.300229174
40	H	-11.553129572	0.776101181	3.560555888

(a)

(b)
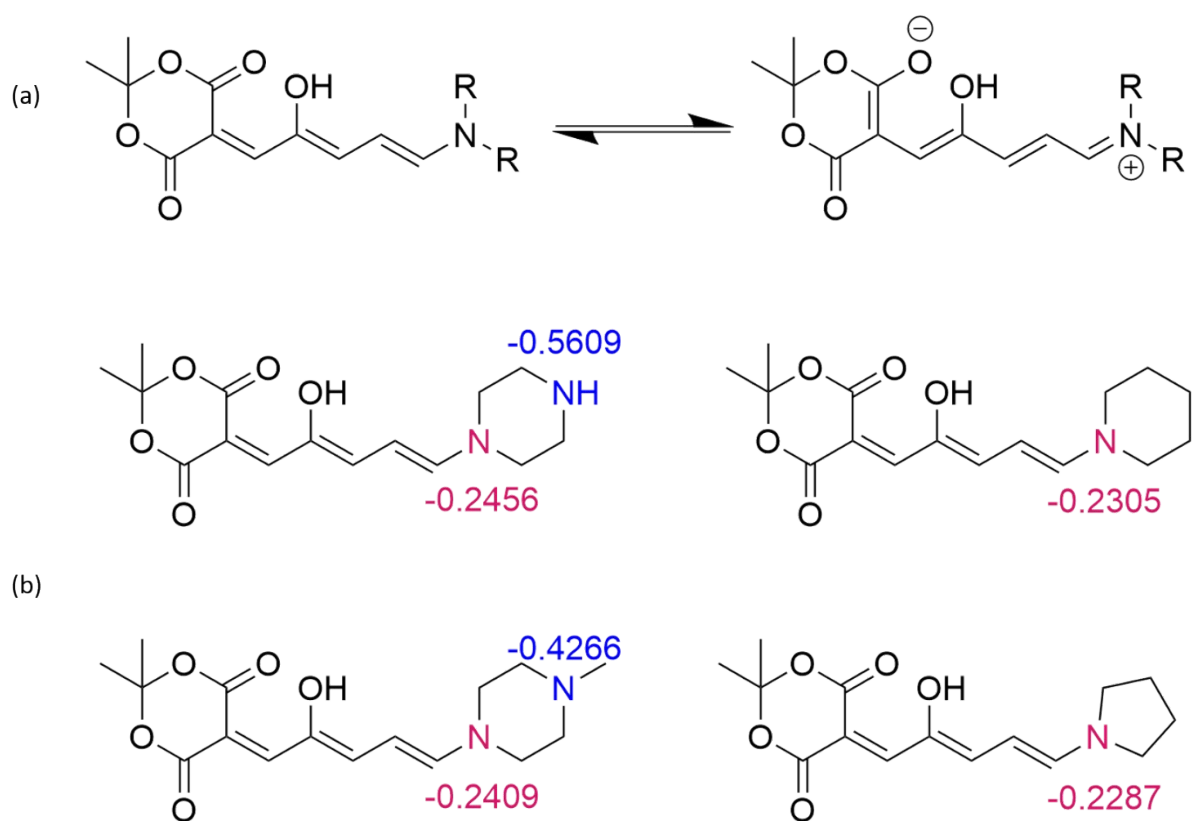
Figure S20. (a) Structural representation of the polarization of the triene moiety. (b) Skeletal structures of DASAs 1 – 4 with the charge on the nitrogen atoms shown.

5.6 Density functional theory calculations

All density functional theory (DFT) calculations were run using the GAMESS-US code 5 Dec 2014 (R1).[6] All minimum energy confirmations and frequencies were determined at the B3-LYP/6-31+G(d) level of theory[7,8] at 298.15 K starting with minimum energy confirmations determined by the PM7 calculations. Single-point energy calculations were conducted at the B3LYP/6-311++G(d,p), BMK/aug-cc-pVTZ,[9] and M06-2X/aug-cc-pVTZ[10] levels of theory using unrestricted wave functions. DFT-D3 dispersion corrections were utilised in all cases.[11,12] Cartesian coordinates and energies are given below.

TRIENE FORM
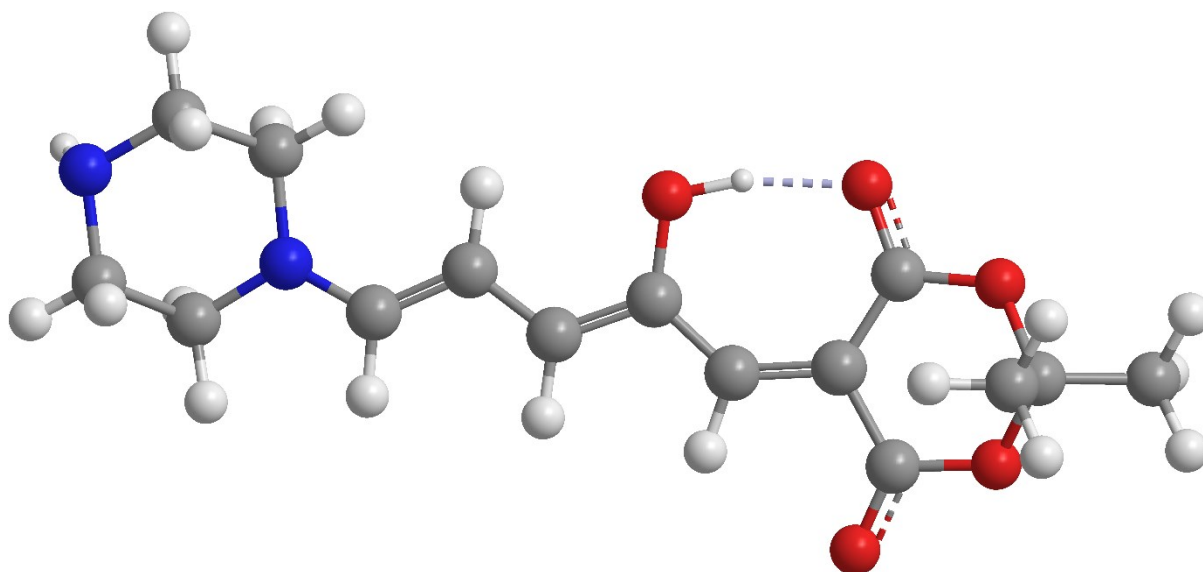

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ATOM   CHARGE       X             Y             Z
-----------------------------------------------------------
C       6.0   0.3407979170   2.5463022177   5.3931700752
C       6.0  -0.5792309646   1.9376939307   4.3194114926
N       7.0  -0.3284686796   0.4942162276   4.1936922638
C       6.0  -0.3879564405  -0.2434572202   5.4673213028
C       6.0   0.5314813976   0.4078928636   6.5131965006
C       6.0  -0.2204005868  -0.1504274046   3.0282080688
C       6.0  -0.2876669063   0.3800067537   1.7401748930
C       6.0  -0.1672712243  -0.4608041538   0.6281805858
C       6.0  -0.2544887222  -0.0272438555  -0.7064808227
O       8.0  -0.4140835599   1.3114537893  -0.9069020905
C       6.0  -0.1899412863  -0.9943023678  -1.7177931390
C       6.0  -0.2609887648  -0.9529979404  -3.1276343150
C       6.0  -0.2137390000  -2.2507279906  -3.8021425658
O       8.0  -0.2348894910  -2.2432200703  -5.1736187487
C       6.0   0.1738373412  -1.0587926100  -5.8714585825
O       8.0  -0.4482435712   0.1024758812  -5.2798988325
C       6.0  -0.4761055184   0.2329100436  -3.9266260727
O       8.0  -0.2176970036  -3.3431627557  -3.2485508765
O       8.0  -0.7364621258   1.3691047610  -3.5034518620
C       6.0   1.6938080347  -0.9139460383  -5.8336696289
```

```
C      6.0 -0.3858239603 -1.1686558905 -7.2780740691
N      7.0  0.2952494500  1.8451086839  6.6786595897
H      1.0  0.0624389982  3.5951892013  5.5444372060
H      1.0  1.3765784566  2.5269809344  5.0303295179
H      1.0 -1.6353677123  2.0860005587  4.5896679732
H      1.0 -0.4056543752  2.4272874119  3.3597916761
H      1.0 -0.0927904778 -1.2820460043  5.2867180352
H      1.0 -1.4283134873 -0.2410106970  5.8245941803
H      1.0  1.5783966790  0.2649375905  6.2163957405
H      1.0  0.3881357216 -0.0932824790  7.4772204091
H      1.0 -0.0609822293 -1.2235650022  3.1284697850
H      1.0 -0.4554748890  1.4364027536  1.5681288488
H      1.0 -0.0026250659 -1.5239048502  0.7875997536
H      1.0 -0.5684869498  1.4774785614 -1.8757989505
H      1.0 -0.0674779125 -2.0061265633 -1.3403352886
H      1.0  2.0680444665 -0.8241698304 -4.8084023403
H      1.0  2.1582426585 -1.7936040308 -6.2916736403
H      1.0  1.9987194020 -0.0239919912 -6.3936104376
H      1.0 -1.4766280709 -1.2549940845 -7.2430621039
H      1.0 -0.1166479425 -0.2813239078 -7.8595112874
H      1.0  0.0250393304 -2.0529401167 -7.7752739054
H      1.0 -0.6003629351  2.0061856906  7.1380116617
```

CYCLOPENTANONE form: N1 protonated (cyclopentanone N1)
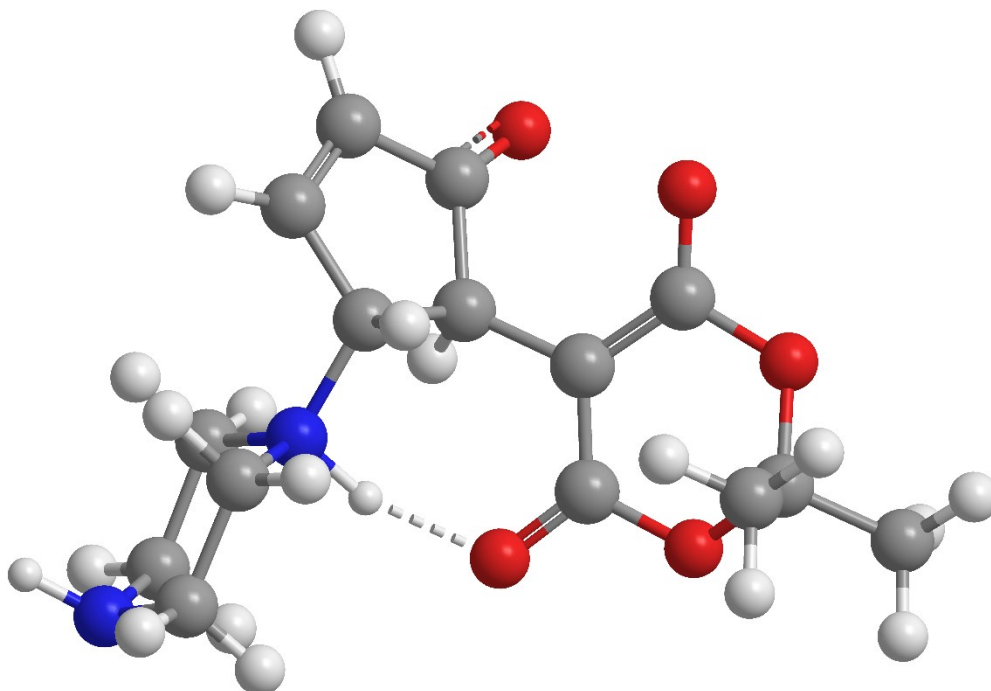

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ATOM  CHARGE     X          Y          Z
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C      6.0  1.4527413843  0.1899972858  0.0199538057
C      6.0  1.4473011662 -1.0299650223  0.7226450172
```

O	8.0	2.5968635554	-1.4477930731	1.3414758650
C	6.0	3.5805743637	-0.4460025824	1.6899373421
O	8.0	3.7283070592	0.5294330324	0.6544014942
C	6.0	2.5825066982	1.0532165995	0.0523065033
O	8.0	0.4539342411	-1.7994921268	0.8270190437
O	8.0	2.6754673811	2.1852641606	-0.4211512236
C	6.0	0.1754197040	0.5317465362	-0.7048912883
C	6.0	0.1826698261	1.5258965680	-1.8803012472
C	6.0	-1.0346753633	2.3687730054	-1.7521023267
C	6.0	-1.7307989362	2.0449932574	-0.6497760110
C	6.0	-0.9892950303	1.0312355503	0.1871598329
O	8.0	0.9618427102	1.5297872483	-2.8168586819
N	7.0	-1.7999629583	-0.1570871486	0.7112361155
C	6.0	-2.5340029516	0.1379270038	1.9964201803
C	6.0	-2.7480353406	-0.7831092958	-0.2863009291
C	6.0	-3.3476799012	-2.0607859370	0.3208114418
C	6.0	4.9099263408	-1.1738846516	1.7983072001
C	6.0	3.1592638349	0.2338590718	2.9936259218
C	6.0	-3.1635985700	-1.1474321035	2.5510531282
H	1.0	-4.9025837603	-1.3367887464	1.4614864121
H	1.0	-0.1616145770	-0.3995899887	-1.1865260786
H	1.0	-1.3035741986	3.1190137115	-2.4895468474
H	1.0	-2.6669788122	2.5047393967	-0.3431447629
H	1.0	-0.5918595442	1.5082454946	1.0894435663
H	1.0	-3.2974338201	0.8922074927	1.7767675819
H	1.0	-1.8165897307	0.5641365704	2.7033714612
H	1.0	-2.1927692789	-1.0068495497	-1.1999557880
H	1.0	-3.5258481942	-0.0481520213	-0.5155468394
H	1.0	-4.0471358003	-2.4964105569	-0.3995833788
H	1.0	-2.5465105627	-2.7963003138	0.4735457808
H	1.0	5.1594303869	-1.6416880333	0.8403265018
H	1.0	5.7034923163	-0.4673559201	2.0629897681
H	1.0	4.8584804607	-1.9498609135	2.5692291924
H	1.0	3.0788911612	-0.5061631094	3.7971295133
H	1.0	3.9038365030	0.9848332631	3.2790106997
H	1.0	2.1911263936	0.7347858294	2.8847704126
H	1.0	-3.7350236408	-0.8949616409	3.4497515627
H	1.0	-2.3644453608	-1.8352905985	2.8600070434
N	7.0	-4.0279010204	-1.8453675815	1.5981254369
H	1.0	-1.0478281339	-0.8751501630	0.9000375780

Cyclopentanone form: N2 protonated (cyclopentanone N2)
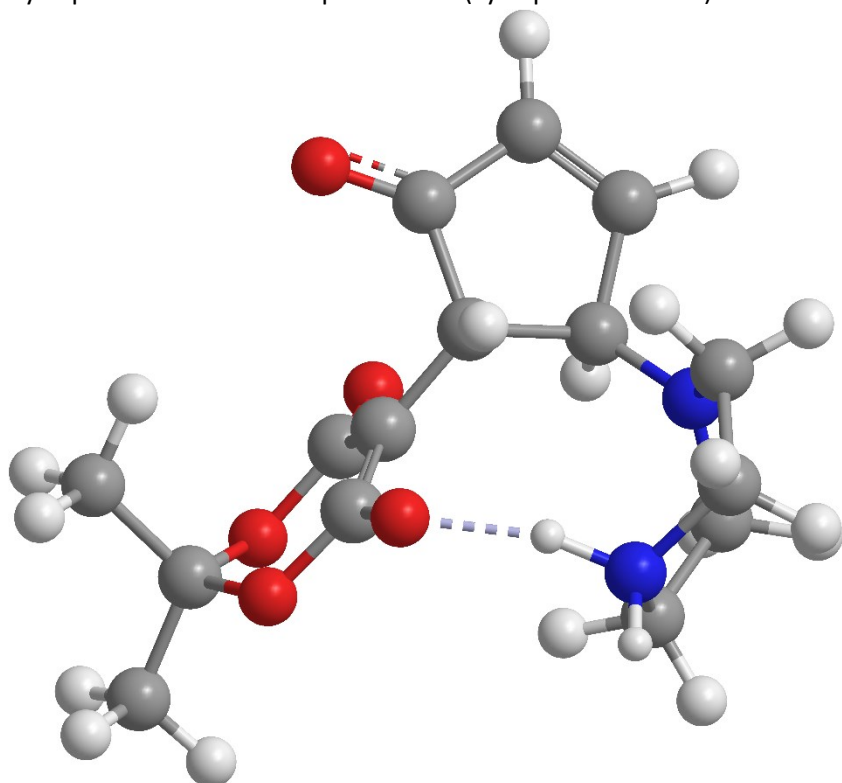

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ATOM   CHARGE      X            Y            Z
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C      6.0  -0.1103320000   0.3255567933   1.0238343108
C      6.0  -1.1425928782  -0.1228312231   1.8973770511
O      8.0  -0.7896672104  -1.0612786158   2.8574014383
C      6.0   0.5910884110  -1.1322290198   3.2413704984
O      8.0   1.4357468952  -1.1645521556   2.0715850678
C      6.0   1.1558883141  -0.2780508304   1.0578273404
O      8.0  -2.3350042484   0.1912590657   1.8371985921
O      8.0   2.0784697736  -0.1362452723   0.2063142288
C      6.0  -0.4191208340   1.3701673220  -0.0073867602
C      6.0  -0.9530194935   2.7115845825   0.5345915291
C      6.0  -1.8925458086   3.2537592481  -0.4666054844
C      6.0  -2.1302476342   2.3323885620  -1.4165240487
C      6.0  -1.4382814440   1.0110805086  -1.1484900483
O      8.0  -0.6272415738   3.2419353394   1.5895838695
N      7.0  -0.9495446861   0.3588216196  -2.3618896502
C      6.0   0.1591034749   0.9569356812  -3.1085675127
C      6.0  -1.0509419170  -1.0838628872  -2.4989546663
C      6.0   0.1930998644  -1.8423154877  -1.9925783486
C      6.0   0.7756472990  -2.4712205368   3.9363017548
C      6.0   0.9625730638   0.0558309213   4.1300972823
C      6.0   1.2669334629  -0.0690627784  -3.4202190493
N      7.0   1.4387738575  -1.0135917466  -2.2643300545
H      1.0   0.5297325472   1.6402389739  -0.4895381815
H      1.0  -2.3213473374   4.2491503658  -0.3947755328
H      1.0  -2.7795743742   2.4628010392  -2.2797104465
```

H	1.0	-2.1851222912	0.3332548178	-0.7166116986		
H	1.0	0.5837469779	1.7904747889	-2.5381964602		
H	1.0	-0.1760113716	1.3785810222	-4.0695031236		
H	1.0	-1.9291682156	-1.4484345661	-1.9577226940		
H	1.0	-1.2194491156	-1.3324772029	-3.5565946279		
H	1.0	0.3064081506	-2.8061291048	-2.4971019340		
H	1.0	0.1653647061	-2.0125122364	-0.9150495052		
H	1.0	0.5082298592	-3.2871247753	3.2567428825		
H	1.0	1.8181023935	-2.5964801855	4.2472102673		
H	1.0	0.1353511991	-2.5251542715	4.8226179500		
H	1.0	0.8360659531	1.0059338936	3.6026260475		
H	1.0	0.3224207845	0.0640329411	5.0187588574		
H	1.0	2.0064563776	-0.0302927332	4.4508781738		
H	1.0	2.2260232399	0.4200730974	-3.6066012083		
H	1.0	1.0197525603	-0.6732078258	-4.2969542935		
H	1.0	2.2395355836	-1.6301616318	-2.4370672239		
H	1.0	1.6898819266	-0.5014412529	-1.367887439		

	B3LYP/6-311++G(d,p)-D3 CHCl3					
	E_{tot} (Hartrees)	E_{tot} (kJ mol^{-1})	ΔE	ΔH	ΔG	ΔS
Triene	-1069.014786	-2806697.916	964.127	966.606	777.931	632.819
Cyclopentanone N1	-1069.013997	-2806695.843	965.19	967.669	787.424	604.544
Cyclopentanone N2	-1069.022238	-2806717.479	965.063	967.542	785.939	609.1
	ΔG C–N1 to C–N2	-23.120				

	M06-2X/aug-cc-pVTZ-D3 CHCl3					
	E_{tot} (Hartrees)	E_{tot} (kJ mol^{-1})	ΔE	ΔH	ΔG	ΔS
Triene	-1069.29	-2807412	964.127	966.606	777.931	632.819
Cyclopentanone N1	-1069.3	-2807443	965.19	967.669	787.424	604.544
Cyclopentanone N2	-1069.32	-2807489	965.063	967.542	785.939	609.1
	ΔG C–N1 to C–N2	-47.513				

	BMK/aug-cc-pVTZ-D3 CHCl3					
	Etot (Hartrees)	E_{tot} (kJ mol^{-1})	ΔE	ΔH	ΔG	ΔS
Triene	-1069.06	-2806808	964.127	966.606	777.931	632.819
Cyclopentanone N1	-1069.07	-2806853	965.19	967.669	787.424	604.544
Cyclopentanone N2	-1069.08	-2806865	965.063	967.542	785.939	609.1
	ΔG C–N1 to C–N2	-13.2394				

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