# Introduction of flavin anions into photoredox catalysis: Acid-base equilibria of lumichrome allows photoreductions with an anion of an elusive 10-unsubstituted isoalloxazine

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### S1. Materials and methods

Starting materials were purchased from Merck (Sigma-Aldrich) and Fluorochem. The solvents were purified and dried using standard procedures. Commercially obtained reagents were used as received without further purification unless otherwise stated. The compound structures were drawn and named using ChemDraw. Nuclear magnetic resonance (NMR) spectra were recorded in CD<sub>3</sub>CN, DMSO $d_6$ , DMF- $d_6$ , TFA- $d_3$  or in their mixtures on an Agilent 400-MR DDR2 (399.94 MHz for <sup>1</sup>H, 100.58 MHz for <sup>13</sup>C), JEOL-ECZL400G (400 MHz for <sup>1</sup>H, 101 MHz for <sup>13</sup>C), or Bruker Avance III 600 MHz (600 MHz for <sup>1</sup>H and 151 MHz for <sup>13</sup>C) at 298 K. Data for <sup>1</sup>H NMR are reported as follows: chemical shift ( $\delta$  ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, br = broad etc.), coupling constant (Hz), and integration. All NMR spectra were processed and assigned using MestreNova. High-resolution mass spectra were obtained on Q-Tof Micro (Waters), equipped with a quadrupole and time-of-flight (TOF) analyser and a multichannel plate (MCP) detector. GC-MS analysis were performed on gas chromatograph Trace Ultra (Themo Scientific) with a quadrupole mass spectrometer DSQ II (Thermo Scientific) equipped with DB-5ms capillary column (30 m x 0.25mm, film 0,25 um) or on gas chromatograph 7890 (Agilent) with an orbital trap mass spectrometer Exploris 240 (Thermo Scientific) equipped with DB-5ms capillary column (30 m x 0.25mm, film 0,25 um). SICRIT (Soft Ionization by Chemical Reaction In Transfer - Plasmion GmbH, Germany) was used in positive mode. The melting points were measured on a Boetius melting point apparatus and are not corrected. Photoredox catalysis was performed using Luxeon Star LED 470 nm (65 Im @ 700mA) with dominant peak wavelengths 460-485 nm in tempered aluminium block (for arrangement, see S3) and Luxeon Star LED 505 nm (76 lm @ 350mA) with dominant peak wavelengths 490-515 nm. UV-Vis absorption spectra were recorded on a UV-2550 spectrophotometer (Schimadzu). Steady-state emission spectra and fluorescence excitation spectra were recorded on a Jobin Yvon-SpexFluorolog 3-22 spectrofluorometer. Note that spectra were recorded using the same excitation and emission slits for uniform spectral resolution and sensitivity. Fluorescence lifetime measurements of all compounds were performed using the time-correlated single-photon counting (TCSPC) method. Decays were measured with the TCSPC Triple Illuminator as an accessory for the Fluorologs 3-22 steady-state spectrofluorometer that adds lifetime-capability in the time domain. The excitation source were NanoLED diodes ( $\lambda_{exc}$  = 368 nm and 389 nm) from IBH. The instrument in this hardware configuration is capable of measuring lifetimes as short as 400 ps. Deconvolution of fluorescence decay curves was performed using IBH Consultants software. The experimental uncertainties in the lifetimes are 10 %. Setup for UV-Vis transient absorption spectra measurements: The triplet states were generated and analysed using laser flash photolysis employing a nanosecond Q-switched Nd: YAG laser in combination with an optical parametric oscillator (OPO) operating at 470 nm; the laser pulse energy was kept around 0.5 mJ/pulse. The sample's solution was deoxygenated by bubbling argon for 15 min before measurements. Spectra were determined using kinetics collected between 350–700nm with a 10 nm interval. See ref.<sup>1</sup> for details. Electrochemical measurements (cyclic voltammetry) were managed by a computer driven potentiostat PGSTAT101 (Autolab-Metrohm) using NOVA 1.11 software, for details see Chapter 5.

**Quantum chemical calculations:** Geometries of all the structures were fully optimized to minima, confirmed by frequency calculations having no imaginary frequencies, using Gaussian 16 software<sup>2</sup> package employing a DFT method with a B3LYP functional in the calculation together with cc-pVTZ and aug-cc-pVTZ basis set. Acetonitrile as a solvent was approximated by CPCM method. Absorption spectra were calculated at the same level of theory using TD-DFT approach (the first 15 excited states were calculated). The optimized geometries were used for energy calculation. The energies were calculated at DFT-B3LYP level of theory together with cc-pVTZ and aug-cc-pVTZ basis set in Gaussian 16 software package. Acetonitrile as a solvent was simulated using CPCM approach. The NMR calculations were also performed using the NMR GIAO method at the same level of theory (DFT-B3LYP with cc-pVTZ and aug-cc-pVTZ basis set) and with acetonitrile as a solvent in the CPCM model

### S2. Synthesis and characterization of flavin derivatives

### **3-Methyllumichrome (1a-H)**



To the solution of 3,4-dimethylaniline (2.410 g, 19.88 mmol) in acetic acid (3.5 mL) acetic anhydride (3.5 ml, 31.74 mmol, 1.6 equiv.) was added. The reaction mixture was heated to reflux for 15 min and then added dropwise to water with ice. Precipitate (old pink color) was filtered off using Büchner funnel. The filtration cake was dissolved in acetic acid (6 mL) and added dropwise to the mixture of 65% nitric acid (12 ml, 266 mmol, 13 equiv.) and acetic acid (10 mL) cooled to +5 °C. The reaction mixture was allowed to warm to room temperature (90 min) and poured into water with ice (100 mL). Resulting precipitate was filtered off using Büchner funnel and washed with water (approximately 500 mL). After drying on air was obtained 2.337 g (56 %) of bright yellow crystals of 2-nitro-4,5-dimethylacetanilide (m.p. 99 – 103 °C, lit.<sup>3</sup> 101 - 104 °C)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.29 (s, 1H), 8.53 (s, 1H), 7.97 (s, 1H), 2.34 (s, 3H), 2.28 (s, 3H), 2.27 (d, J = 0.7 Hz, 3H).

HRMS APCI pos m/z for  $C_{10}H_{13}N_2O_3$  [M+H<sup>+</sup>] calculated 209.09027, found 209.09158.

2-Nitro-4,5-dimethylacetanilide was dissolved in 96% sulfuric acid (15 mL) and heated to 90 °C for 30 min. After cooling to r.t., the reaction mixture was poured dropwise on ice. The precipitated orange crystals were filtered off using Büchner funnel and dried on air. It was obtained 1.380 g (74 %) of 3,4-dimethyl-6-nitroaniline, m.p. 136 – 139 °C, lit.<sup>4</sup> 140-141 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.87 (s, 1H), 6.59 (s, 1H), 2.22 (s, 3H), 2.18 (s, 3H).

HRMS APCI pos m/z for  $C_8H_{11}N_2O_2$  [M+H<sup>+</sup>] calculated 167.08150, found 167.08138.

3,4-Dimethyl-6-nitroaniline (1.380 g, 8.30 mmol) was dissolved in acetic acid (60 mL) and palladium on carbon (10%, 0.150 g) was added. Hydrogen (balloon) was bubbled through the reaction mixture until the color disappear (20 hours). Residual of palladium was filtered off through celite and the filtrate was added to the hot solution of *N*-methylalloxane (1.310 g, 8.39 mmol) and boric acid (0.620 g, 10.03 mmol) in acetic acid (60 mL). Reaction mixture was stirred in dark at r.t. for 4 hours. Bright yellow crystals were filtered off through frit (S4), washed with diethyl ether (10 ml) and dried on vacuo. It was obtained 1.270 g (60 %) of **1a-H**, m.p. 354 - 359 °C.

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 12.12 (s, 1H), 7.95 – 7.91 (m, 1H), 7.73 – 7.68 (m, 1H), 3.29 (s, 3H), 2.48 (d, *J* = 1.0 Hz, 3H), 2.47 – 2.44 (m, 3H).

<sup>13</sup>C NMR (101 MHz, DMSO-*D*<sub>6</sub>) δ 160.46, 150.34, 145.16, 144.84, 141.78, 139.05, 138.58, 129.50, 128.75, 125.89, 27.74, 20.30, 19.67.

HRMS APCI pos m/z for  $C_{13}H_{13}N_4O_2$  [M+H<sup>+</sup>] calculated 257.10330, found 257.10336.

### 1-Methyllumichrome (3a-H)



Mixture of 3,4-dimethylaniline (0.900 g, 5.60 mmol) and 1-methyl-6-chlorouracil (2.410 g, 19.90 mmol) was heated to 150 °C under stopper with calcium chloride for 2 hours. To the cooled mixture, diethyl ether (30 mL) was added and the mixture was sonicated. Product was filtered off, washed with diethyl ether, methanol and again with diethyl ether. Filtrate was evaporated, diethyl ether was added (100 mL) and precipitated crystals were filtered off. Crystals were collected. It was obtained 1.390 g (99 %) of 1-methyl-6-(3,4-dimethylanilino)uracil, m.p. 316 - 320 °C.

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  10.62 (s, 1H), 7.20 (dd, J = 12.7, 8.1 Hz, 2H), 7.06 (d, J = 11.7 Hz, 3H), 7.03 (d, J = 2.3 Hz, 1H), 6.96 (dd, J = 7.9, 2.3 Hz, 1H), 4.39 (s, 1H), 2.22 (dd, J = 5.3, 2.8 Hz, 13H), 2.08 (s, 7H).

HRMS APCI pos m/z for  $C_{13}H_{16}N_3O_2$  [M+H<sup>+</sup>] calculated 246.12370, found 246.12352.

To the mixture of anilinouracil (1.390 g, 5.60 mmol) and acetic acid (30 mL), sodium nitrite (1.89 g, 26.40 mmol) was added. The mixture was stirred at r.t. for 2 hours and after addition of water (20 mL), the mixture was stirred 10 minutes. Precipitated crystals were filtered off through Büchner funnel and washed with diethyl ether. It was obtained 0.990 g of orange crystals as mixture of alloxazine and alloxazinium-*N*-oxide (3:1, according <sup>1</sup>H NMR).

Part (0.275 g) of the mixture of alloxazin and alloxazinium-*N*-oxide was dissolved in the mixture of solvents DMF (8 mL) and acetic acid (45 mL). Palladium on carbon was added (10%, 70 mg) and the mixture was stirred under hydrogen (6 atm) in autoclave at r.t. for 46 hours. The reaction mixture was heated until dissolving all solids and palladium on carbon was filtered off. After evaporation of solvents, it was obtained 0.255 g (64 %) of **3a-H**, m.p. 338-342 °C, lit.<sup>5</sup> >300 °C.

<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN / DMSO- $d_6$ )  $\delta$  11.49 (s, 1H), 7.93 (d, J = 1.3 Hz, 1H), 7.77 (s, 1H), 3.59 (s, 3H), 2.51 (d, J = 1.0 Hz, 3H), 2.48 (d, J = 1.1 Hz, 3H).

<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) δ 7.93 (d, *J* = 1.2 Hz, 1H), 7.80 (d, *J* = 1.2 Hz, 1H), 3.52 (s, 3H), 2.48 (s, 3H), 2.46 (d, *J* = 1.0 Hz, 3H).

<sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>) δ 159.73, 150.31, 146.61, 144.85, 141.00, 139.22, 137.60, 130.73, 128.56, 126.33, 28.27, 20.21, 19.62.

HRMS APCI pos m/z for  $C_{13}H_{13}N_4O_2$  [M+H<sup>+</sup>] calculated 257.10330, found 257.10294.

### Lumiflavin (7,8,10-trimethylisoalloxazine, 4a-H)



Lumiflavin **4a-H** was obtained starting from 3,4-dimethyl-6-nitroaniline using procedure described in literature.<sup>6</sup>

M.p. > 370 °C.

<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN) δ 10.73 (s, 1H), 7.88 (s, 1H), 7.64 (s, 1H), 3.98 (s, 3H), 2.52 (s, 3H), 2.41 (s, 3H).

<sup>13</sup>C NMR (151 MHz, CD<sub>3</sub>CN / DMSO-*d*<sub>6</sub>) δ 161.07, 156.67, 154.38, 138.10, 134.91, 132.87, 132.16, 117.09, 32.62, 21.12, 19.24.

HRMS APCI pos m/z for  $C_{13}H_{13}N_4O_2$  [M+H<sup>+</sup>] calculated 257.10330, found 257.10355.

### 1,3-Dimethyllumichrome (5a)



Lumichrome (0.080 g, 0.33 mmol) was dissolved in dry DMF (4 mL), potassium carbonate (0.300 g, 2.17 mmol) and methyl iodide (0.270 g, 0.525 mmol) were added. The mixture was stirred under argon atmosphere for 2 hours, then poured into water and extracted with ethyl acetate. Combined extracts were washed with water, brine and dried over magnesium sulfate. After evaporation of solvent was obtained 0.090 g (99 %) of 1,3-dimethyllumichrome, m.p. 242 - 245 °C, lit.<sup>7</sup> 246 - 248 °C.

<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN / DMSO- $d_6$ )  $\delta$  7.94 (d, J = 1.3 Hz, 1H), 7.79 – 7.76 (m, 1H), 3.68 (d, J = 0.5 Hz, 3H), 3.43 (d, J = 0.5 Hz, 3H), 2.52 (d, J = 1.0 Hz, 4H), 2.51 – 2.48 (m, 4H).

<sup>13</sup>C NMR (151 MHz, CD<sub>3</sub>CN / DMSO-*d*<sub>6</sub>) δ 160.84, 151.81, 146.53, 146.47, 142.74, 140.77, 139.44, 130.56, 129.68, 127.35, 29.67, 29.09, 20.75, 20.09.

HRMS APCI pos m/z for  $C_{14}H_{15}N_4O_2$  [M+H<sup>+</sup>] calculated 271.11895, found 271.11838.

### Lumichrome



To the mixture of 1,2-dimethyl-4,5-dinitrobenzene (0.600 g, 3.06 mmol) in acetic acid (20 mL), palladium on carbon (10%, 160 mg) was added. The mixture was stirred under hydrogen atmosphere (balloon) for 24 hours. Palladium on carbon was filtered off through celite, washed with acetic acid and filtrate was immediately added to the hot solution of alloxane hydrate (0.490 g, 3.06 mmol, 1 equiv.) and boric acid (0.208 g, 3.36 mmol, 1.1 equiv.) in acetic acid (30 mL). The mixture was stirred at r.t. in

dark overnight. Precipitated orange crystals were filtered off through frit (S4), washed with acetic acid and diethyl ether. It was obtained 0.580 g (78 %) of lumichrome, m.p. 358 - 362°C., lit.<sup>7</sup> 368 – 370 °C. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN / DMSO- $D_6$ )  $\delta$  11.32 (s, 2H), 7.90 (s, 1H), 7.69 (s, 1H), 2.50 (s, 3H), 2.47 (d, J = 1.0 Hz, 3H).

<sup>13</sup>C NMR (151 MHz, CD<sub>3</sub>CN / DMSO-*D*<sub>6</sub>) δ 161.84, 151.13, 147.53, 146.19, 143.09, 140.38, 139.87, 130.99, 129.81, 126.94, 20.68, 20.04.

HRMS APCI pos m/z for  $C_{12}H_{11}N_4O_2$  [M+H<sup>+</sup>] calculated 243.08765, found 243.08786.

### S3. Photoredox catalysis - experimental



### **Dehalogenation – inert conditions**

Substrate (0.038 mmol), alloxazine or flavin derivative (10 mol%;  $4 \times 10^{-3}$  mmol),  $\gamma$ -terpinene (2 equiv.; 0.076 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (2 equiv.; 0.076 mmol) were suspended in DMF (0.5 mL), placed into vial or Schlenk tube and bubbled with argon or degassed using the freeze-pump-thaw technique (3 × 5 min), respectively. The reaction mixture was stirred and irradiated with LED 470 nm (65 lm @ 700mA) or LED 505 nm for 3-bromo-*9H*-fluoren-9-one at 25 °C for 16 h. Conversion was determined by GC-MS.

### **Dehalogenation – under air**

4-Bromobenzonitrile (0.038 mmol), alloxazine derivative (10 mol%;  $4 \times 10^{-3}$  mmol),  $\gamma$ -terpinene (2 equiv.; 0.076 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (2 equiv.; 0.076 mmol) were suspended in DMF (0.5 mL) and placed into vial. The reaction mixture was stirred and irradiated with LED 470 nm (65 lm @ 700mA) at 25 °C for 16 h. Conversion was determined by GC-MS.

### **Dehalogenation – other bases**



4-Bromobenzonitrile (0.038 mmol), **1a-H** (10 mol%;  $4 \times 10^{-3}$  mmol),  $\gamma$ -terpinene (2 equiv.; 0.076 mmol), and CsOAc or TBAH<sub>2</sub>PO<sub>4</sub> (2 equiv.; 0.076 mmol), were dissolved/suspended in DMF (0.5 mL), placed into vial or Schlenk tube and bubbled with argon or degassed using the freeze-pump-thaw technique (3 × 5 min), respectively. The reaction mixture was stirred and irradiated with LED 470 nm (65 lm @ 700mA) at 25 °C for 16 h. Conversion was determined by GC-MS.

### Coupling with P(OMe)<sub>3</sub> – inert conditions



4-Bromobenzonitrile (0.038 mmol), trimethyl phosphite (5 equiv.; 0.190 mmol), **1a-H** (10 mol%;  $4 \times 10^{-3}$  mmol),  $\gamma$ -terpinene (2 equiv.; 0.076 mmol), and  $Cs_2CO_3$  (2 equiv.; 0.076 mmol), were suspended in DMF (0.5 mL), placed into vial or Schlenk tube and bubbled with argon or degassed using the freeze-pump-thaw technique (3 × 5 min). The reaction mixture was stirred and irradiated at 470 nm (65 lm @ 700mA) at 25 °C for 48 h. Conversion was determined by GC-MS.

### Coupling with P(OMe)<sub>3</sub> – under air

4-Bromobenzonitrile (0.038 mmol), trimethyl phosphite (5 equiv.; 0.190 mmol), **1a-H** (10 mol%;  $4 \times 10^{-3}$  mmol),  $\gamma$ -terpinene (2 equiv.; 0.076 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (2 equiv.; 0.076 mmol) were suspended in DMF (0.5 mL) and placed into vial. The reaction mixture was stirred and irradiated at 470 nm (65 lm @ 700mA) at 25 °C for 48 h. Conversion was determined by GC-MS.



FigureS3.1 Typical set-up of photochemical experiment

# S4. UV-Vis, fluorescence and excitation spectra, fluorescence lifetime and UV-Vis transient absorption spectra measurements

Anions of 3-methyllumichrome (**1a-H**), 1-methyllumichrome (**3a-H**) and lumiflavin (**4a-H**) were obtained *in situ*, adding salt tetrabutylammonium acetate (TBAOAc). TBAOAc was of  $\geq$  99% of purity and was from Sigma-Aldrich. Before use, TBAOAc was dried under vacuum and stored in a desiccator. Flavin derivatives were dissolved in dry acetonitrile (ACN). Only freshly prepared solutions were used in order to minimize possible photolytic reactions or hydrolysis. All experiments were carried out at room temperature.



**Figure S4.1**. The absorption spectra of lumiflavin (**4a-H**) in ACN (8.49×10<sup>-6</sup> M) with TBAOAc.



**Figure S4.2.** The emission spectra of lumiflavin (**4a-H**) in ACN (8.49×10<sup>-6</sup> M) with TBAOAc, excited at  $\lambda$  = 393 nm.







**Figure S4.3.** Fluorescence excitation spectra of (A) **1a-H** (8.49×10<sup>-6</sup> M) with TBAOAc (observed at  $\lambda_{Em}$  = 440 nm), (B) **1a-H** (8.49×10<sup>-6</sup> M) with TBAOAc (observed at  $\lambda_{Em}$  = 540 nm), and (C) **3a-H** (1.24×10<sup>-5</sup> M) with TBAOAc (observed at  $\lambda_{Em}$  = 450 nm).

### Fluorescence lifetime quenching

The measurements were conducted in the presence of varying concentrations of the quencher. Excitation was achieved using a LED diode with a nominal wavelength of 455 nm (actual wavelength 449nm) and fluorescence emission was monitored at 540 nm. The data illustrate the effect of quencher concentration on the fluorescence lifetime of **1a-H**.

**Table S4.1** Fluorescence lifetime measurement of **1a-H** in dimethylformamide (DMF) containing tetrabutylammonium acetate (TBAOAc, 29 mM) and 4-bromobenzonitrile (**6a**) in different concentrations.

В

c( <b>6a</b> )	τ
[M]	[ns]
0	8.66
0.076	8.62
0.092	8.58
0.112	8.49
0.131	8.46
0.168	8.45
0.201	8.43
0.232	8.38
0.261	8.37
0.288	8.33

 $\begin{aligned} \tau_0 / \tau = 1 + k_q \tau_0 [Q] \\ 1 / \tau = 1 / \tau_0 + k_q [Q] \\ k_q = 1.64 \times 10^7 M^{-1} s^{-1} \end{aligned}$ 

Α









**Figure S4.4.** Absorption spectra of **1a-H** in DMF in the presence of TBAOAc (29 mM) at different concentration of 4-bromobenzonitrile (**6a**) as a quencher (A). Linear plot of  $1/\tau_f$  versus quencher concentration [Q] (B). Fluorescence decay of **1a-H** in the presence of TBAOAc (29 mM) at different concentration of **6a** as a quencher (C).

c( <b>6f</b> )	τ
[M]	[ns]
0	8.48
3.32	7.48
6.60	6.63
9.85	5.92
13.07	5.40
16.26	4.91
19.42	4.56
22.54	4.24
25.64	3.96
28.71	3.71
31.75	3.50
60.61	2.32

 Table S4.2 Fluorescence lifetime measurement of 1a-H in dimethylformamide (DMF) containing

 tetrabutylammonium acetate (TBAOAc, 29 mM) and 1-bromo-4-nitrobenzene (6f) at different concentrations.

В

 $\tau_0/\tau = 1 + k_q \tau_0[Q]$  $1/\tau = 1/\tau_0 + k_q[Q]$ 

k<sub>q</sub> =5.21×10<sup>9</sup>M<sup>-1</sup>s<sup>-1</sup>

Α

С

5 c(1-Br-4-NO<sub>2</sub>Ph mol L<sup>-1</sup> 4 - 0 (1a<sup>-</sup>) - 3.32 - 6.60 - 9.85 - 13.07 - 16.26 - 19.42 - 22.54 - 25.64 - 28.71 - 31.75 - 60.61 Absorbance 3 2 1 0. 300 350 400 450 500 550  $\lambda$  / nm





**Figure S4.5.** Absorption spectra of **1a-H** in DMF in the presence of TBAOAc (29 mM) at different concentration of 1-bromo-4-nitrobenzene (**6f**) as a quencher (A). Linear plot of  $1/\tau_f$  versus quencher concentration [Q] (B). Fluorescence decay of **1a-H** in the presence of TBAOAc (29 mM) at different concentration of **6f** as a quencher (C).

**Table S4.3** Fluorescence lifetime measurement of **1a-H** in dimethylformamide (DMF) containing tetrabutylammonium acetate (TBAOAc, 29 mM) and 1-bromo-9-H-fluoren-9-one (**6e**) in different concentrations.

В

c( <b>6e</b> )	τ
[M]	[ns]
0	8.48
3.32	7.42
6.60	6.58
9.85	5.93
13.07	5.46
16.26	5.06
19.42	4.70
22.54	4.37
25.64	4.28
28.71	3.92
31.75	3.73
60.61	2.57

 $\tau_0/\tau=1 + k_q \tau_0[Q]$ 

 $1/\tau = 1/\tau_0 + k_q[Q]$ 

k<sub>q</sub> =4.47×10<sup>9</sup>M<sup>-1</sup>s<sup>-1</sup>





**Figure S4.6.** Absorption spectra of **1a-H** in DMF in the presence of TBAOAc (29 mM) at different concentration of 1-bromo-9-H-fluorene-9-one (**6e**) as a quencher (A). Linear plot of  $1/\tau_f$  versus quencher concentration [Q] (B). Fluorescence decay of **1a-H** in the presence of TBAOAc (29 mM) at different concentration of **6e** as a quencher (C).

**Triplet lifetime quenching in DMF** 



**Figure S4.7.** Absorption spectra of **1a-H** in the presence of TBAOAc (29 mM) at varying concentration of 1-bromo-4-nitrobenzene (**6f**) (A). Triplet decay of **1a-H** in the presence of TBAOAc at different concentration of **6f**, monitored at 530nm with laser excitation at 470 nm. Notably, multiexponential decay is due to triplet-triplet annihilation in the first microseconds followed by triplet population decay over tens of microseconds. (B). Linear plot of  $1/\tau_t$  versus quencher **6f** concentration [Q] (C). The transient absorption spectra of **1a-H** at different time delays, wavelength of excitation 405 nm (D). The transient absorption spectra of **1a-H** with TBAOAc at different time delays, wavelength of excitation 470 nm (E). The transient absorption spectra of **1a-H** with TBAOAc at different time delays, may elength of excitation 470 nm (E). The transient absorption spectra of **1a-H** with TBAOAc at different time delays, wavelength of excitation 470 nm (F).



**Figure S4.8.** Absorption spectra of **1a-H** in the presence of TBAOAc (29 mM) at varying concentration of 1-bromo-9H-fluorene-9-one (**6e**) (A). Triplet decay of **1a-H** with TBAOAc at different concentration of **6e**, monitored at 530nm with laser excitation at 470 nm. Notably, multiexponential decay is due to triplet-triplet anihilation in the first microseconds followed by triplet population decay over tens of microseconds. (B). Linear plot of  $1/\tau_t$  versus quencher **6e** concentration [Q] (C).

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### Triplet lifetime of anion formed from 1a-H in DMF under argon and air

**Figure S4.9.** Transient absorption spectra of **1a-H** with TBAOAc (29 mM) **under argon** (A) and triplet decay at 530 nm with laser excitation at 470 nm (B);  $\tau_T = 57.3 \ \mu$ s (short component of 2.32  $\mu$ s is due to triplet-triplet annihilation). Transient absorption spectra of **1a-H** with TBAOAc (29 mM) **under air** (C) and triplet decay at 530 nm with laser excitation at 470 nm;  $\tau_T = 1.81 \ \mu$ s (D). Laser power energy 0.5 mJ.

### Experiments aimed at triplet anion photophysics characterization: $\Phi_{ISC}$ , $\varepsilon_{max}(T_1, 520 \text{ nm})$

### **Relative actinometry**

Comparative experiment using Ru(bpy)<sub>3</sub><sup>2+</sup> was performed for two solutions:

sample 1: solution of anion in DMF

sample 2: solution of  $Ru(bpy)_3^{2+}$  in  $H_2O$ 

Both samples were prepared with the same absorption at excitation wavelength:

A(470 nm, 1 cm)=0.30.

Transient absorption experiment was executed in row: sample 1, sample 2. The laser pulse energy 0.5 mJ. The obtained initial amplitudes signals are:

 $\Delta A(Ru(bpy)_{3}^{2+}, 450 \text{ nm}) = -0.01866 \text{ (dominated by S}_{0} \text{ bleaching)}$ 

 $\Delta A(anion, 520 \text{ nm}) = 0.0069$  (the band peak of triplet-triplet anion absorption).

Accordingly with literature<sup>8</sup> for Ru(bpy)<sub>3</sub><sup>2+</sup>, the difference in the epsilon values at 450 nm of the triplet excited state and ground state state is  $\Delta \varepsilon$  (Ru(bpy)<sub>3</sub><sup>2+</sup>, 450nm) = -1.0 ×10<sup>4</sup> M<sup>-1</sup>cm<sup>-1</sup> (accuracy 9 %).

This allows us to estimate the  $\epsilon_{T1}$ (anion, 520 nm)× $\Phi_{ISC}$  from following equation:

$$\varepsilon_{T1}(anion, 520 nm) \times \Phi_{ISC} = \frac{\Delta A(anion T_1, 520 nm) \times \Delta \varepsilon(Ru(bpy)_3^{2+}, 450 nm)}{\Delta A(Ru(bpy)_3^{2+}, 450 nm)} \approx 3700 M^{-1} cm^{-1}$$

With accuracy of about 15 %.

Since anion fluorescence quantum yield  $\Phi_f$  is 0.26, it is clear that expected value  $\Phi_{ISC}$  is, at best, limited to 1-0.26 = 0.74, thus  $\varepsilon_{T1}(anion, 520 nm) \ge \frac{3700}{0.74} = 5000 M^{-1} cm^{-1}$ .

### Triplet-triplet energy transfer from anion-T<sub>1</sub> to retinol-T<sub>1</sub>

Experiment was performed for the mixture anion and retinol in DMF, deoxygenated by 15 min Ar bubbling. As the excitation wavelength 470 nm was chosen for a selective excitation of the anion (retinol shows an absorption band peaking at 329 nm in DMF).

In transient absorption experiment, at delay of 300 ns a positive band is observed, peaking at 520 nm, corresponding to  $T_1$  state of anion ( $T_1 \rightarrow T_n$ , Figure 1A).



Figure 1. (A) UV-vis transient absorption spectra determined for mixture of anion and retinol in DMF deoxygenated solution in time windows (A) 300 ns–15  $\mu$ s and (B) 18–150  $\mu$ s. Excitation at 470 nm, 0.5 mJ per pulse, c(anion) = 1.3 × 10<sup>-4</sup> M, c(retinol) = 2.8 × 10<sup>-5</sup> M.

In time-window from 300 ns to 15  $\mu$ s (Figure 1A) a decay of population of anion in the T<sub>1</sub> state takes place, and the rise of the band peaking at 400 nm, corresponding to retinol in the T<sub>1</sub> triplet state, occurs. Triplet-triplet energy takes place. Over a longer time-window, from 18 to 150  $\mu$ s (Figure 1B), positive band at 400 nm undergoes a decay. It is related to decay of retinol population in the T<sub>1</sub> state.

Triplet-triplet energy transfer from anion to retinol is also confirmed by shortening of the triplet state lifetime of anion upon going from a pure deoxygenated anion solution ( $\tau = 32.3 \,\mu$ s, amplitude averaged lifetime) to the mixture of anion with retinol ( $\tau = 6.8 \,\mu$ s, amplitude averaged lifetime). Amplitude

averaged lifetimes ( $\tau = \frac{A_1 \tau_1 + A_2 \tau_2}{A_1 + A_2}$ ) were calculated to take into account a biexponential character of the kinetics.

To estimate the efficiency  $\Phi_{T \rightarrow T}$  for triplet-triplet energy process:

 $\Phi_{T \to T} = k_{T \to T} / (k_{T \to T} + k_0) = 0.82$ 

Where:

the rate k<sub>0</sub> corresponds to the decay of triplet of anion in a pure argon-saturated DMF

 $(k_0=1/32.3 \ \mu s)$ , and

 $k_{T \rightarrow T}$  is the rate of the triplet-triplet energy transfer in the presence of retinol

 $(k_{T \to T} + k_0 = 1/6.8 \ \mu s).$ 

Let us estimate the molar absorption coefficient  $\varepsilon_{T1}(anion, 520 nm)$ .

The kinetics at 520 nm shows a decrease in  $\Delta A$  amplitude by 0.0084 (triplet anion population, Figure 1A). This is accompanied by the rise of band at 400 nm with amplitude of 0.00987 (triplet retinol population).

The molar absorption coefficient for retinol in the triplet state is  $\epsilon$ (retinol T<sub>1</sub>, 400nm)  $\approx 6.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  (see ref.<sup>9</sup>).

These findings lead us to following equation:

$$\varepsilon_{T1}(anion, 520 nm) = \frac{\varepsilon(\operatorname{retinol} T_1, 400 nm) \times \Delta A(anion T_1, 520 nm) \times \Phi_{T \to T}}{\Delta A(\operatorname{retinol} T_1, 400 nm)}$$
$$= \frac{6.6 \times 10^4 \times 0.0084 \times 0.82}{0.00987} \approx 46000 \, M^{-1} cm^{-1}$$

Since the comparative experiment lead to

 $\varepsilon_{T1}(anion, 520 nm) \times \Phi_{ISC} \approx 3700 M^{-1} cm^{-1}$ 

### The resulting $\Phi_{ISC}$ is close to 0.08.

The accuracy in that estimation is not high, taking into account all assumptions undertaken. Further studies should be performed to bring us more accurate characterization of photophysics for the triplet anion.

### S5. CV measurements

An undivided 10 ml cell with three-electrode system: work - GCE  $\phi$  3 mm, reference - SCE, auxiliary - Pt plate, scan rate 100 mV·s<sup>-1</sup> in ACN deoxygenated by argon. 0.1 mol L<sup>-1</sup>. Tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as the supporting electrolyte; samples concentrations 0.5 x 10<sup>-3</sup> mol L<sup>-1</sup>. The concentration of added base change from 0.25·10<sup>-3</sup> mol L<sup>-1</sup> to 25·10<sup>-3</sup> mol L<sup>-1</sup>. The maximum concentration of added base (TBAOAc, respective TBAH<sub>2</sub>PO<sub>4</sub>, 25·10<sup>-3</sup> mol L<sup>-1</sup>) correspond to 50 equivalents.



**Figure S5.1** Cyclic voltammograms of (A) **4a-H** and (B) **5a** in the absence and in the presence of TBAOAc (50 equiv.). Data obtained in acetonitrile in the presence of TBAPF<sub>6</sub> ( $c = 0.1 \text{ mol } L^{-1}$ ) using glassy carbon working, saturated calomel reference and platinum auxiliary electrodes.

### S6. Estimation of $E^*_{ox}$ of $2a^-$ in singlet excited state

 $E^*_{ox}$  of **2a**<sup>-</sup> in single excited state was estimated from ground state redox potential ( $E_{p/2} = 1.02$  V; i.e. value from CV measurement of **1a-H** in the presence of TBAOAc) and the value  $E^{0-0} = 2.52$  eV corresponding to intersection of the normalized absorption and emission bands (see Figure S6.1).



$$E^*_{\text{ox}}(2a) = E_{p/2} - E^{0-0} = 1.02 - 2.52 = -1.5 \text{ V}$$

Figure S6.1 Normalized UV-VIS and fluorescence spectra of anion 2a<sup>-</sup>.

# S7. Experimental and theoretical NMR data in the presence of base

### NMR analysis of mixture 3-methyllumichrome (1a-H) with tetrabutylammonium acetate in mixture of solvents $CD_3CN/DMSO-d_6 85/15$

Stock solution (c = 17 mM) of **1a-H** was prepared from 6.58 mg of 3-methyllumichrome (**1a-H**) and 1500  $\mu$ l of DMSO-*d*<sub>6</sub>. Stock solution (c = 34 mM) of tetrabutylammonium acetate (TBAOAc) was prepared from 30.50 mg of TBAOAc and 3000  $\mu$ l of CD<sub>3</sub>CN. Into NMR tube was added solution of flavine, TBAOAc and CD<sub>3</sub>CN in different ratio.

	1:0	1:0.5	1:1	1:2	1.3	1:4	1:5	1:6	1:7	1:8	1.9	1:10	1:100
V(1a-H)	100	100	100	100	100	100	100	100	100	100	100	100	
c(1a-H)	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.7
V(TBAOAc)	0	25	50	100	150	200	250	300	350	400	450	500	
C(TBAOAc)	0	1.2	2.4	4.8	7.2	9.6	12.0	14.4	16.8	19.2	21.6	24	300
V(CD₃CN)	600	575	550	500	450	400	350	300	250	200	150	100	
ppm	7.918	7.901	7.864	7.847	7.837	7.833	7.820	7.816	7.815	7.806	7.807	7.815	7.749
ppm	7.702	7.687	7.653	7.637	7.628	7.624	7.612	7.609	7.618	7.600	7.608	7.600	7.547
ppm	2.499	2.493	2.479	2.472	2.468	2.467	2.462	2.460	2.461	2.457	2.457	2.461	2.432
pm	2.476	2.470	2.456	2.452	2.447	2.446	2.440	2.438	2.438	2.435	2.436	2.437	2.411

**Table S7.1** Preparation and NMR analysis of mixture **1a-H** with TBAOAc



Figure S7.1 Changes in chemical shifts of aromatic protons H6 and H9 after addition of TBAOAc



Figure S7.2 Changes in chemical shifts of aromatic protons H6 and H9 after addition of TBAOAc

### NMR analysis of mixture 3-methyllumichrome (1a-H) with tetrabutylammonium dihydrogenphosphate in mixture of solvents $CD_3CN/DMSO-d_6$ 85/15.

Stock solution (c = 17.5 mM) of **1a-H** was prepared from 6.75 mg of 3-methyllumichrome (**1a-H**) and 1500  $\mu$ l of DMSO-*d*<sub>6</sub>. Stock solution (c = 36 mM) of tetrabutylammonium dihydrogenphosphate (TBAH<sub>2</sub>PO<sub>4</sub>) was prepared from 36.70 mg of TBAH<sub>2</sub>PO<sub>4</sub> and 3000  $\mu$ l of CD<sub>3</sub>CN. Into NMR tube was added solution of flavine, TBAH<sub>2</sub>PO<sub>4</sub> and CD<sub>3</sub>CN in different ratio.

				,									
	1:0	1:0.5	1:1	1:2	1.3	1:4	1:5	1:6	1:7	1:8	1.9	1:10	1:85
V(1a-H)	100	100	100	100	100	100	100	100	100	100	100	100	
c(1a-H)	2.5	2.5ř	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	
V(TBAH <sub>2</sub> PO <sub>4</sub> )	0	25	50	100	150	200	250	300	350	400	450	500	
C(TBAH <sub>2</sub> PO <sub>4</sub> )	0	1.25	2.5	5.1	7.7	10.3	12.85	15.4	18.0	20.6	23.1	25.7	210.4
V(CD <sub>3</sub> CN)	600	575	550	500	450	400	350	300	250	200	150	100	
ppm	7.918	7.890	7.863	7.827	7.799	7.778	7.765	7.750	7.738	7.730	7.724	7.719	7.652
ppm	7.702	7.676	7.652	7.619	7.595	7.575	7.563	7.549	7.538	7.531	7.525	7.520	7.449
ppm	2.500	2.488	2.479	2.466	2.457	2.448	2.444	2.438	2.433	2.430	2.428	2.426	2.395
ppm	2.476	2.465	2.456	2.443	2.433	2.426	2.420	2.415	2.410	2.407	2.405	2.403	2.373

Table S7.2 Preparation and NMR analysis of mixture 1a-H with TBAH<sub>2</sub>PO<sub>4</sub>



Figure S7.3 Changes in chemical shifts of aromatic protons H6 and H9 after addition of TBAH<sub>2</sub>PO<sub>4</sub>.



Figure S7.4 Changes in chemical shifts of aromatic protons H6 and H9 after addition of TBAH<sub>2</sub>PO<sub>4</sub>.

Elavina darivativa	nnm	nnm	nnm	nnm
3-Methyllumichrome (1a-H)	2.476	2.500	7.701	7.917
3-Methyllumichrome ( <b>1a-H</b> ) + IBAOAc	2.429	2.451	7.588	7.793
3-Methyllumichrome ( <b>1a-H</b> ) + TBAOAc + CF <sub>3</sub> COOD	2.474	2.497	7.699	7.913
3-Methyllumichrome ( <b>1a-H</b> ) + TBAH <sub>2</sub> PO <sub>4</sub>	2.400	2.423	7.511	7.710
3-Methyllumichrome ( <b>1a-H</b> ) + TBAH <sub>2</sub> PO <sub>4</sub> + CF <sub>3</sub> COOD	2.479	2.502	7.706	7.920
3-Methyllumichrome ( <b>1a-H</b> ) + TBAOH	2.392	2.415	7.499	7.703
3-Methyllumichrome (1a-H) + excess of TBAOAc	2.411	2.432	7.547	7.749
3-Methyllumichrome (1a-H) + excess of TBAH <sub>2</sub> PO <sub>4</sub>	2.373	2.395	7.449	7.652
3-Methyllumichrome ( <b>1a-H</b> ) + TBAOAc in DMF- $D_6$	2.427	2.449	7.532	7.753
3-Methyllumichrome ( <b>1a-H</b> ) + TBAOAc + CF <sub>3</sub> COOD in	2.515	2.538	7.740	7.950
DMF-D <sub>6</sub>				
3-Methyllumichrome (1a-H) in CD <sub>3</sub> CN	2.502	2.525	7.714	7.947
3-Methyllumichrome ( <b>1a-H</b> ) in DMSO- <i>d</i> <sub>6</sub>	2.454	2.478	7.705	7.930
3-Methyllumichrome (1a-H) in CD <sub>3</sub> COOD	2.550	2.590	7.903	8.087
3-Methyllumichrome ( <b>1a-H</b> ) in DMF-D <sub>6</sub>	2.517	2.539	7.742	7.955
1-Methyllumichrome ( <b>3a-H</b> )	2.484	2.514	7.768	7.929
1-Methyllumichrome ( <b>3a-H</b> ) + TBAOAc	2.470	2.497	7.728	7.902
1-Methyllumichrome ( <b>3a-H</b> ) + TBAOAc + CF <sub>3</sub> COOD	2.483	2.513	7.767	7.929
1-Methyllumichrome ( <b>3a-H</b> ) + TBAH <sub>2</sub> PO <sub>4</sub>	2.453	2.478	7.673	7.863
1-Methyllumichrome ( <b>3a-H</b> ) + TBAH <sub>2</sub> PO <sub>4</sub> + CF <sub>3</sub> COOD	2.481	2.511	7.753	7.917
1-Methyllumichrome ( <b>3a-H</b> ) + TBAOH	2.436	2.457	7.637	7.844
1-Methyllumichrome ( <b>3a-H</b> ) + NaH	n.v.	n.v.	7.625	7.856
Lumiflavin ( <b>4a-H</b> )	2.413	2.516	7.642	7.881
Lumiflavin ( <b>4a-H</b> ) + TBAOAc	2.412	2.515	7.645	7.879
Lumiflavin (4a-H) + TBAOAc + CF <sub>3</sub> COOD	2.413	2.517	7.646	7.882
Lumiflavin ( <b>4a-H</b> ) + TBAH <sub>2</sub> PO <sub>4</sub>	2.411	2.517	7.647	7.881
Lumiflavin ( <b>4a-H</b> ) + TBAOH	Aduct and	decompo	sition	
1,3-Dimethyllumichrome (5a)	2.493	2.522	7.776	7.944
1,3-Dimethyllumichrome (5a) + TBAOAc	2.486	2.515	7.776	7.937
1,3-Dimethyllumichrome ( <b>5a</b> ) + TBAOAc + CF <sub>3</sub> COOD	2.492	2.516	7.779	7.941
1,3-Dimethyllumichrome ( <b>5a</b> ) + TBAH <sub>2</sub> PO <sub>4</sub>	2.482	2.511	7.765	7.930
1,3-Dimethyllumichrome ( <b>5a</b> )+ TBAH <sub>2</sub> PO <sub>4</sub> + CF <sub>3</sub> COOD	2.484	2.512	7.766	7.931
1,3-Dimethyllumichrome ( <b>5a</b> )+ TBAOH – ADUCT!	2.109	2.133	6.591	6.812
Lumichrome	2.469	2.495	7.689	7.901

**Table S7.3:** Chemical shifts of selected protons ( $C^7$ -CH<sub>3</sub>,  $C^8$ -CH<sub>3</sub>,  $H^6$ ,  $H^9$ ) of flavin derivatives in mixture of solvents CD<sub>3</sub>CN/DMSO-*d*<sub>6</sub> 85/15 or in common solvents after addition of base (and acid).



**Figure S7.5** NMR spectra of flavin and formation of their anions after addition of TBAOAc, TBAH<sub>2</sub>PO<sub>4</sub> or TBAOH.

		17		
	ppm	ppm	ppm	ppm
3-Methyllumichrome <b>1a-H</b>	2.476	2.499	7.702	7.918
+ TBAOAc	2.429	2.451	7.588	7.793
+ TBAOAc + CF <sub>3</sub> COOD	2.474	2.497	7.699	7.913
+ excess (100 eq) TBAOAc	2.411	2.432	7.546	7.749
+ NaOH	2.467	2.490	7.680	7.899
+ NaOH + CF <sub>3</sub> COOD	2.479	2.502	7.708	7.926
+ TBAHCO₃	2.474	2.298	7.700	7.912
+ TBAHCO <sub>3</sub> + CF <sub>3</sub> COOD	2.474	2.499	7.702	7.914
+ DBU	2.392	2.413	7.473	7.693
+ DBU + $CF_3COOD$	2.477	2.500	7.703	7.916
+ K <sub>2</sub> CO <sub>3</sub>	2.455	2.479	7.655	7.867
$+ K_2CO_3 + CF_3COOD$	2.475	2.499	7.703	7.919
+ NaH	2.387	2.408	7.484	7.710
+ NaH + CF₃COOD	2.478	2.508	7.710	7.941
+ TBAH <sub>2</sub> PO <sub>4</sub>	2.400	2.423	7.511	7.710
+ TBAH <sub>2</sub> PO <sub>4</sub> + CF <sub>3</sub> COOD	2.479	2.502	7.706	7.920
+excess (85 eq) TBAH <sub>2</sub> PO <sub>4</sub>	2.373	2.395	7.449	7.652
+ TBAOH	2.392	2.415	7.499	7.703

**Table S7.4:** Changes in chemical shift 3-methyllumichrome (1a-H) in mixture of solvents  $CD_3CN/DMSO$ *d*<sub>6</sub> 85/15 after addition of different bases (10 eq) and CF<sub>3</sub>COOD (10 eq).



**Figure S7.6** Changes in chemical shifts of aromatic protons H6 and H6 of 3-methyllumichrome (**1a-H**) after addition of different bases and  $CF_3COOD$ .

	1a-H		1a <sup>-</sup>		2a-H		За-Н		3a <sup>-</sup>		4a-H		4a <sup>-</sup>	
	isotropic (shielding constant)	sigma (chemical shift)												
TMS	31.7369													
H <sup>6</sup>	23.4623	8.2746	23.793	7.9439	23.5404	8.1965	23.4604	8.2765	23.6383	8.0986	23.5485	8.1884	23.7998	7.9371
H <sup>7</sup>	23.6817	8.0552	24.0339	7.703	24.1789	7.558	23.5878	8.1491	23.8006	7.9363	23.9368	7.8001	24.2554	7.4815
N <sup>1</sup> -CH <sub>3</sub>							29.0408	2.6961	29.123	2.6139				
N <sup>1</sup> -CH <sub>3</sub>							29.0954	2.6415	29.2074	2.5295				
N <sup>1</sup> -CH <sub>3</sub>							29.0407	2.6962	29.1232	2.6137				
N <sup>3</sup> -CH <sub>3</sub>	27.3091	4.4278	27.1245	4.6124	27.2646	4.4723								
N <sup>3</sup> -CH <sub>3</sub>	28.6593	3.0776	28.8716	2.8653	28.7607	2.9762								
N <sup>3</sup> -CH <sub>3</sub>	28.6611	3.0758	28.8715	2.8654	28.7626	2.9743								
N <sup>10</sup> -CH <sub>3</sub>											29.0444	2.6925	29.1599	2.577
N <sup>10</sup> -CH <sub>3</sub>											29.1153	2.6216	29.2597	2.4772
N <sup>10</sup> -CH <sub>3</sub>											29.0446	2.6923	29.1599	2.577
C <sup>8</sup> -CH <sub>3</sub>	29.0544	2.6825	29.1682	2.5687	29.0981	2.6388	29.0878	2.6491	29.1535	2.5834	29.1832	2.5537	29.2647	2.4722
C <sup>8</sup> -CH <sub>3</sub>	29.1154	2.6215	29.2699	2.467	29.1969	2.54	29.0878	2.6491	29.1537	2.5832	29.1834	2.5535	29.2648	2.4721
C <sup>8</sup> -CH <sub>3</sub>	29.0548	2.6821	29.1684	2.5685	29.098	2.6389	29.1164	2.6205	29.2131	2.5238	29.2073	2.5296	29.33	2.4069
C <sup>7</sup> -CH <sub>3</sub>	29.0945	2.6424	29.1982	2.5387	29.1897	2.5472	28.4337	3.3032	28.7001	3.0368	28.3682	3.3687	28.7133	3.0236
C <sup>7</sup> -CH <sub>3</sub>	29.095	2.6419	29.1982	2.5387	29.1898	2.5471	28.4338	3.3031	28.6993	3.0376	28.3692	3.3677	28.7139	3.023
C <sup>7</sup> -CH <sub>3</sub>	29.1263	2.6106	29.284	2.4529	29.2129	2.524	27.1606	4.5763	26.9696	4.7673	25.9269	5.81	26.0117	5.7252
N <sup>1</sup> -H	23.8598	7.8771												
N <sup>3</sup> -H							23.8013	7.9356			23.9056	7.8313		
N <sup>10</sup> -H					22.6767	9.0602								

 Table S7.5
 Theoretical NMR chemical shifts calculated using GIAO/B3LYP/cc-pVTZ (with solvent - acetonitrile)



**Figure S7.7** Visualization of theoretical chemical shift of aromatic protons H<sup>6</sup> and H<sup>9</sup> GIAO/B3LYP/cc-pVTZ (with solvent - acetonitrile)

	1a-H		1a <sup>-</sup>		2a-H		За-Н		3a⁻		4a-H		4a⁻	
	isotropic (shielding constant)	sigma (chemical shift)												
TMS	31.7369													
H <sup>6</sup>	23.4371	8.2998	24.0536	7.6833	23.59	8.1469	23.4334	8.3035	23.8034	7.9335	23.5857	8.1512	24.0843	7.6526
H <sup>9</sup>	23.7968	7.9401	24.2957	7.4412	24.7464	6.9905	23.7168	8.0201	24.1716	7.5653	24.4386	7.2983	25.116	6.6209
N <sup>1</sup> -CH <sub>3</sub>							28.5709	3.166	29.0462	2.6907				
N <sup>1</sup> -CH <sub>3</sub>							28.5708	3.1661	29.0467	2.6902				
N <sup>1</sup> -CH <sub>3</sub>							27.0164	4.7205	26.6123	5.1246				
N <sup>3</sup> -CH <sub>3</sub>	27.2621	4.4748	26.9345	4.8024	27.1797	4.5572								
N <sup>3</sup> -CH <sub>3</sub>	28.7171	3.0198	29.1058	2.6311	28.8384	2.8985								
N <sup>3</sup> -CH <sub>3</sub>	28.7191	3.0178	29.1077	2.6292	28.8392	2.8977								
N <sup>10</sup> -CH <sub>3</sub>											28.8326	2.9043	29.5071	2.2298
N <sup>10</sup> -CH <sub>3</sub>											28.8334	2.9035	29.5072	2.2297
N <sup>10</sup> -CH <sub>3</sub>											25.57	6.1669	25.4437	6.2932
C <sup>8</sup> -CH <sub>3</sub>	29.1614	2.5755	29.4097	2.3272	29.2256	2.5113	29.1467	2.5902	29.3478	2.3891	29.1686	2.5683	29.4166	2.3203
C <sup>8</sup> -CH <sub>3</sub>	29.2225	2.5144	29.4933	2.2436	29.4334	2.3035	29.2075	2.5294	29.4624	2.2745	29.3495	2.3874	29.6384	2.0985
C <sup>8</sup> -CH <sub>3</sub>	29.1618	2.5751	29.4101	2.3268	29.2256	2.5113	29.1467	2.5902	29.3478	2.3891	29.1685	2.5684	29.4168	2.3201
C <sup>7-</sup> CH <sub>3</sub>	29.2011	2.5358	29.3936	2.3433	29.3293	2.4076	29.1948	2.5421	29.3685	2.3684	29.3174	2.4195	29.5183	2.2186
C <sup>7</sup> -CH <sub>3</sub>	29.2015	2.5354	29.394	2.3429	29.3296	2.4073	29.1949	2.542	29.3685	2.3684	29.3181	2.4188	29.5177	2.2192
C <sup>7</sup> -CH <sub>3</sub>	29.1803	2.5566	29.4957	2.2412	29.2963	2.4406	29.1697	2.5672	29.391	2.3459	29.2855	2.4514	29.5399	2.197
N <sup>1</sup> -H	24.3606	7.3763												
N <sup>3</sup> -H							24.2241	7.5128			24.2745	7.4624		
N <sup>10</sup> -H					23.7653	7.9716								

 Table S7.6 Theoretical NMR chemical shift calculated using GIAO/B3LYP/aug-CC-pVZT (without solvent – acetonitrile)



**Figure S7.8** Visualization of theoretical chemical shift of aromatic protons  $H^6$  and  $H^9$  GIAO/B3LYP/aug-cc-pVTZ (without solvent - acetonitrile)

	1a-H		1a <sup>-</sup>		2a-H		За-Н		3a <sup>-</sup>		4a-H		4a⁻	
	isotropic (shielding constant)	sigma (chemical shift)												
TMS	31.7315													
H <sup>6</sup>	23.3959	8.3356	23.6896	8.0419	23.4571	8.2744	23.3995	8.332	23.5497	8.1818	23.4573	8.2742	23.6641	8.0674
H <sup>9</sup>	23.6155	8.116	23.9384	7.7931	24.1025	7.629	23.4949	8.2366	23.6736	8.0579	23.8444	7.8871	24.1178	7.6137
N <sup>1</sup> -CH <sub>3</sub>							28.351	3.3805	28.5503	3.1812				
N <sup>1</sup> -CH <sub>3</sub>							28.351	3.3805	28.5505	3.181				
N <sup>1</sup> -CH <sub>3</sub>							27.0748	4.6567	26.874	4.8575				
N <sup>3</sup> -CH <sub>3</sub>	27.2166	4.5149	27.01	4.7215	27.1659	4.5656								
N <sup>3</sup> -CH <sub>3</sub>	28.5926	3.1389	28.7536	2.9779	28.6844	3.0471								
N <sup>3</sup> -CH <sub>3</sub>	28.5916	3.1399	28.7524	2.9791	28.6792	3.0523								
N <sup>10</sup> -CH <sub>3</sub>											28.2786	3.4529	28.5722	3.1593
N <sup>10</sup> -CH <sub>3</sub>											28.2789	3.4526	28.5733	3.1582
N <sup>10</sup> -CH <sub>3</sub>											25.8366	5.8949	25.903	5.8285
C <sup>8</sup> -CH <sub>3</sub>	29.0236	2.7079	29.1282	2.6033	29.0612	2.6703	29.0062	2.7253	29.0798	2.6517	29.003	2.7285	29.1052	2.6263
C <sup>8</sup> -CH <sub>3</sub>	29.0752	2.6563	29.2196	2.5119	29.147	2.5845	29.0473	2.6842	29.1466	2.5849	29.0665	2.665	29.1931	2.5384
C <sup>8</sup> -CH <sub>3</sub>	29.0233	2.7082	29.1288	2.6027	29.061	2.6705	29.0061	2.7254	29.0797	2.6518	29.0031	2.7284	29.1052	2.6263
C <sup>7-</sup> CH <sub>3</sub>	29.0669	2.6646	29.1607	2.5708	29.1568	2.5747	29.0556	2.6759	29.1142	2.6173	29.1484	2.5831	29.2177	2.5138
C <sup>7</sup> -CH <sub>3</sub>	29.0667	2.6648	29.1609	2.5706	29.1566	2.5749	29.0556	2.6759	29.1141	2.6174	29.1483	2.5832	29.218	2.5135
C <sup>7</sup> -CH <sub>3</sub>	29.0893	2.6422	29.2314	2.5001	29.1678	2.5637	29.0785	2.653	29.1617	2.5698	29.1594	2.5721	29.2647	2.4668
N <sup>1</sup> -H	23.5899	8.1416												
N <sup>3</sup> -H							23.5247	8.2068			23.5591	8.1724		
N <sup>10</sup> -H					22.4269	9.3046								

 Table S7.7 Theoretical NMR chemical shift calculated using GIAO/B3LYP/aug-cc-pVZT (with solvent - acetonitrile)



Figure S7.9 Visualization of theoretical chemical shift of aromatic protons  $H^6$  and  $H^9$  GIAO/B3LYP/aug-cc-pVTZ (with solvent - acetonitrile)

### S8. Photoredox catalysis – analysis of reaction mixtures

Analysis were performed by GC-MS analysis. The results are ordered according to entries in Table 1 and Scheme 1.





Apex KT	% Area		
8.33	5.1	$C_7H_5N$	103
12.59	94.9	$C_7H_4BrN$	181































Table S8.1 Calibration of mass spectroscopy analysis of 3-bromo-9H-fluoren-9-one debromination

7d:6d	7d	6d	6d	6d	6d and 7d	7d/(6d and 7d)	7d
	m/z	m/z	m/z	sum	sum	ratio	%
	180.06	255.9714	259.9697				
1:0	2200000	16000	16000	32000	2232000	0.985663	100
1:1	1400000	835000	840000	1675000	3075000	0.455285	50
10:1	2200000	196000	200000	396000	2596000	0.847458	90.9
1:10	242000	724000	730000	1454000	1696000	0.142689	9.1
0:1	96000	820000	800000	1620000	1716000	0.055944	0
EZ133-	13600000	47000000	47000000	94000000	107600000	0.126394	9.115525
blank							
EZ133-1	15600000	2600000	2500000	5100000	20700000	0.753623	78.2361

![](_page_42_Figure_4.jpeg)

y = 110.1975x - 4.8131

![](_page_42_Figure_6.jpeg)

![](_page_42_Figure_7.jpeg)

Figure S8.2 3-Bromo-9H-fluoren-9-one debromination analysis

### Data on phosphonylations (related to Scheme 1)

![](_page_43_Figure_1.jpeg)

![](_page_44_Figure_0.jpeg)

Apex RT	% Area		MW Da
8.37	4.58	$C_7H_5N$	103
12.61	61.67	$C_7H_4BrN$	181
17.78	33.75	$C_9H_{10}NO_3P$	211

![](_page_45_Figure_0.jpeg)

![](_page_46_Figure_0.jpeg)

Figure S9.1 <sup>1</sup>H and <sup>13</sup>C NMR spectra of 3-methyllumichrome (3,7,8-trimethylalloxazine (1a-H))

![](_page_47_Figure_0.jpeg)

Figure S9.2 <sup>1</sup>H and <sup>13</sup>C NMR spectra of 1-methyllumichrome (1,7,8-trimethylalloxazine (3a-H))

![](_page_48_Figure_0.jpeg)

Figure S9.3 <sup>1</sup>H and <sup>13</sup>C NMR spectra of lumiflavine (7,8,10-trimethylisoalloxazine (4a-H))

![](_page_49_Figure_0.jpeg)

Figure S9.4 <sup>1</sup>H and <sup>13</sup>C NMR spectra of 1.3-dimethyllumichrome (1,3,7,8-tetramethylalloxazine (5a))

![](_page_50_Figure_0.jpeg)

Figure S9.5 <sup>1</sup>H and <sup>13</sup>C NMR spectra of lumichrome (7,8-dimethylalloxazine)

S10. Natural population analysis data for anions

![](_page_51_Figure_1.jpeg)

**Figure S10.1** The atomic charge distribution for an anion formed from **1a-H** based on NBO (Natural Bond Orbital) analysis.

Natural Population				n			
Atom	No		Natural Natural Charge	Core	Valence	Rydberg	Total
	С	1	-0.18657	1.99906	4.16753	0.01999	6.18657
	С	2	0.09038	1.99905	3.88146	0.02911	5.90962
	С	3	0.10623	1.99914	3.84291	0.05172	5.89377
	С	4	-0.10470	1.99906	4.09301	0.01262	6.10470
	С	5	-0.06976	1.99921	4.01122	0.05933	6.06976
	С	6	-0.03169	1.99908	4.00959	0.02303	6.03169
	Н	7	0.20773	0.00000	0.78753	0.00474	0.79227
	Н	8	0.19870	0.00000	0.79122	0.01007	0.80130
	С	9	0.04137	1.99902	3.93066	0.02895	5.95863
	С	10	0.34558	1.99915	3.62040	0.03487	5.65442
	Ν	11	-0.48015	1.99941	5.44202	0.03872	7.48015
	С	12	0.63069	1.99929	3.33400	0.03602	5.36931
	С	13	0.74767	1.99938	3.21073	0.04222	5.25233
	Ν	14	-0.65107	1.99936	5.61198	0.03973	7.65107
	Ν	15	-0.46154	1.99933	5.43695	0.02526	7.46154
	0	16	-0.66417	1.99979	6.63891	0.02547	8.66417
	0	17	-0.72821	1.99979	6.70307	0.02535	8.72821
	С	18	-0.38239	1.99940	4.36740	0.01558	6.38239
	Н	19	0.22849	0.00000	0.76879	0.00272	0.77151
	Н	20	0.20241	0.00000	0.79485	0.00274	0.79759
	Н	21	0.20243	0.00000	0.79483	0.00274	0.79757
	С	22	-0.53776	1.99918	4.51858	0.02000	6.53776
	Н	23	0.20859	0.00000	0.78613	0.00528	0.79141
	Н	24	0.20289	0.00000	0.79182	0.00528	0.79711
	Н	25	0.20858	0.00000	0.78613	0.00528	0.79142
	С	26	-0.58945	1.99918	4.57721	0.01307	6.58945
	Н	27	0.21176	0.00000	0.78466	0.00358	0.78824
	Н	28	0.21176	0.00000	0.78466	0.00358	0.78824
	Н	29	0.21046	0.00000	0.78675	0.00279	0.78954
	N	30	-0.36706	1.99941	5.33717	0.03047	7.36706
* [	 Fotal	 L *	-0.99877	37.98627	95.39218	0.62031	133.99877

 Table S10.1 Summary of natural population analysis for anion formed from 1a-H

![](_page_52_Figure_0.jpeg)

**Figure S10.2** The atomic charge distribution for an anion formed from **3a-H** based on NBO (Natural Bond Orbital) analysis

		Natural		Natural Pop	ulation	
Atom	No	Charge	Core	Valence	Rydberg	Total
С	1	-0.18613	1.99906	4.16701	0.02006	6.18613
С	2	0.05383	1.99912	3.90064	0.04641	5.94617
С	3	0.27954	1.99909	3.67916	0.04222	5.72046
С	4	-0.19517	1.99915	4.15753	0.03848	6.19517
С	5	-0.00833	1.99913	3.97821	0.03099	6.00833
С	6	-0.01585	1.99907	3.99398	0.02281	6.01585
Н	7	0.20988	0.00000	0.78580	0.00433	0.79012
Н	8	0.20115	0.00000	0.79177	0.00708	0.79885
С	9	0.06843	1.99901	3.90121	0.03135	5.93157
С	10	0.37363	1.99911	3.59642	0.03084	5.62637
N	11	-0.51948	1.99944	5.45812	0.06192	7.51948
С	12	0.57774	1.99932	3.37714	0.04581	5.42226
С	13	0.75321	1.99939	3.20479	0.04261	5.24679
N	14	-0.44374	1.99931	5.41657	0.02786	7.44374
N	15	-0.68359	1.99936	5.64353	0.04069	7.68359
0	16	-0.70892	1.99980	6.68423	0.02489	8.70892
0	17	-0.72009	1.99979	6.69495	0.02536	8.72009
С	18	-0.60958	1.99942	4.59803	0.01213	6.60958
Н	19	0.21805	0.00000	0.77921	0.00275	0.78195
Н	20	0.21335	0.00000	0.78387	0.00277	0.78665
Н	21	0.21804	0.00000	0.77921	0.00275	0.78196
С	22	-0.60573	1.99942	4.59484	0.01147	6.60573
Н	23	0.21590	0.00000	0.78162	0.00248	0.78410
Н	24	0.21590	0.00000	0.78162	0.00248	0.78410
Н	25	0.21373	0.00000	0.78403	0.00224	0.78627
N	26	-0.36752	1.99940	5.33741	0.03070	7.36752
С	27	-0.37876	1.99940	4.36468	0.01468	6.37876
Н	28	0.20116	0.00000	0.79586	0.00298	0.79884
Н	29	0.20116	0.00000	0.79586	0.00298	0.79884
Н	30	0.22886	0.00000	0.76847	0.00268	0.77114
===================================	=== 1 *	-0.99934	37.98678	= 95.37577	0.63679	==================================

Table S10.2 Summary	of natural	population	analysis for	anion for	ned from <b>3</b>	a-H

![](_page_53_Figure_0.jpeg)

**Figure S10.3** The atomic charge distribution for an anion formed from **4a-H** based on NBO (Natural Bond Orbital) analysis

		Natural	Natural Population			
Atom	No	Charge	Core	Valence	Rydberg	Total
C	1	-0.15053	1.99917	4.11343	0.03793	6.15053
С	2	0.06118	1.99905	3.90101	0.03876	5.93882
С	3	0.15448	1.99902	3.80975	0.03675	5.84552
С	4	-0.24811	1.99906	4.22993	0.01911	6.24811
С	5	-0.01821	1.99918	3.96954	0.04950	6.01821
С	6	0.05002	1.99914	3.88595	0.06489	5.94998
Н	7	0.21356	0.0000	0.78161	0.00482	0.78644
Н	8	0.22096	0.00000	0.77637	0.00267	0.77904
С	9	0.08756	1.99904	3.88072	0.03269	5.91244
С	10	0.37762	1.99915	3.58291	0.04032	5.62238
N	11	-0.26667	1.99931	5.23301	0.03436	7.26667
С	12	0.56657	1.99933	3.38699	0.04712	5.43343
С	13	0.71696	1.99944	3.23875	0.04484	5.28304
N	14	-0.61885	1.99933	5.58912	0.03041	7.61885
N	15	-0.69452	1.99937	5.65388	0.04127	7.69452
0	16	-0.72036	1.99980	6.69567	0.02489	8.72036
0	17	-0.72264	1.99979	6.69736	0.02549	8.72264
С	18	-0.61073	1.99942	4.59840	0.01292	6.61073
Н	19	0.22103	0.0000	0.77655	0.00242	0.77897
Н	20	0.21406	0.0000	0.78341	0.00252	0.78594
Н	21	0.22104	0.00000	0.77655	0.00242	0.77896
С	22	-0.57625	1.99950	4.54983	0.02692	6.57625
Н	23	0.20469	0.00000	0.78883	0.00647	0.79531
Н	24	0.20469	0.00000	0.78883	0.00647	0.79531
Н	25	0.20867	0.00000	0.78664	0.00469	0.79133
N	26	-0.35221	1.99940	5.32153	0.03129	7.35221
С	27	-0.40888	1.99943	4.38796	0.02149	6.40888
Н	28	0.21135	0.00000	0.78618	0.00247	0.78865
Н	29	0.21135	0.00000	0.78618	0.00247	0.78865
Н	30	0.24310	0.00000	0.75258	0.00432	0.75690
* Tota	.1 *	-0.99906	37.98691	95.30947	0.70268	133.99906

Table S10.3         Summary of natural population analysis for anion formed	d from <b>4a-H</b>
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### S11. Cartesian coordinates

Cartesian coordinates (in Å) of the ground state singlet equilibrium structure of anion from **1a-H**.

С	-2.406395	1.359199	-0.000116
С	-1.204684	0.612161	0.000027
С	-1.264716	-0.813869	0.000167
С	-2.543762	-1.423617	0.000278
С	-3.701528	-0.684512	0.000106
С	-3.635269	0.750106	-0.000127
Н	-2.327054	2.438991	-0.000213
Н	-2.585626	-2.505283	0.000508
С	1.068619	0.494604	0.000050
С	1.032212	-0.944853	0.000075
Ν	-0.150574	-1.570651	0.000187
С	2.386743	1.164149	0.000098
С	3.358700	-1.120323	-0.000199
Ν	2.150098	-1.696631	-0.000033
Ν	3.464448	0.313704	0.000161
0	2.533211	2.385448	0.000158
0	4.416942	-1.766559	-0.000646
С	4.788431	0.933833	0.000214
Н	5.526391	0.142924	0.000719
Н	4.908837	1.560233	-0.882473
Н	4.908387	1.561003	0.882395
С	-5.037483	-1.375001	0.000139
Н	-5.627856	-1.097644	-0.875902
Н	-4.918492	-2.456553	0.000471
Н	-5.628254	-1.097055	0.875680
С	-4.896701	1.570250	-0.000386
Н	-5.513143	1.357533	-0.876664
Н	-5.513496	1.357733	0.875657
Н	-4.667365	2.634181	-0.000506
Ν	-0.010908	1.242157	0.000011

### Cartesian coordinates (in Å) of the ground state singlet equilibrium structure of **1a-H**.

С	-2.435661	-1.368890	-0.000053
С	-1.231071	-0.627081	-0.000011
С	-1.293964	0.801253	0.000028
С	-2.559312	1.422880	0.000006
С	-3.719935	0.686561	-0.000038
С	-3.658506	-0.749538	-0.000068
Η	-2.361799	-2.448208	-0.000073
Н	-2.593861	2.504026	0.000036
С	1.043238	-0.526480	0.000031
С	0.970684	0.890120	0.000035
Ν	-0.164365	1.546811	0.000051
С	2.369575	-1.188418	0.000081
С	3.407094	1.061477	0.000001
Ν	2.146832	1.602561	0.000000
Ν	3.470499	-0.334739	-0.000059
0	2.521137	-2.396391	0.000191
0	4.400385	1.767781	0.00004

С	4.793913	-0.968118	-0.000178
Н	5.542190	-0.186796	-0.000844
Н	4.901136	-1.591043	0.884554
Н	4.900476	-1.591970	-0.884313
Н	2.096032	2.610987	0.000082
С	-5.051521	1.380791	0.000011
Н	-5.641165	1.102401	0.875884
Н	-4.929819	2.461568	-0.000119
Н	-5.641336	1.102181	-0.875676
С	-4.923785	-1.560809	-0.000041
Н	-5.536706	-1.340580	0.876303
Н	-5.536909	-1.340350	-0.876181
Н	-4.702620	-2.625920	-0.000193
Ν	-0.043294	-1.264618	0.000030

### Cartesian coordinates (in Å) of the ground state singlet equilibrium structure of $\mbox{2a-H}.$

С	-2.405274	-1.368265	0.000072
С	-1.216673	-0.612790	0.000115
С	-1.312599	0.799293	0.000059
С	-2.563308	1.417056	-0.000065
С	-3.720318	0.658476	-0.000112
С	-3.642773	-0.767302	-0.000017
Н	-2.312631	-2.445690	0.000116
Н	-2.623252	2.497237	-0.000155
С	1.076642	-0.517277	0.000190
С	1.081531	0.924912	0.000145
Ν	-0.141265	1.509080	0.000099
С	2.401796	-1.185743	0.000170
С	3.383049	1.092656	0.000095
Ν	2.149995	1.679991	0.000193
Ν	3.480893	-0.328451	-0.000268
0	2.540315	-2.399210	0.000428
0	4.410996	1.757699	0.000313
С	4.807842	-0.950531	-0.000872
Н	5.548345	-0.162314	-0.003769
Н	4.924111	-1.572977	0.884040
Н	4.921190	-1.576950	-0.883297
С	-5.055903	1.342087	-0.000312
Н	-5.642013	1.055836	0.875317
Н	-4.946381	2.423923	-0.000380
Н	-5.641770	1.055677	-0.876055
С	-4.895055	-1.599152	-0.000011
Н	-5.511184	-1.390208	0.876711
Н	-5.511382	-1.389941	-0.876525
Н	-4.655817	-2.660292	-0.000176
Ν	-0.007872	-1.235500	0.000181
Н	-0.165688	2.521432	0.000074

Cartesian coordinates (in Å) of the ground state singlet equilibrium structure of anion from  $\mbox{\bf 3a-H}.$ 

С	-2.393936	-1.364772	0.000058
С	-1.118360	-0.757369	-0.000050
С	-1.024555	0.660755	-0.000197
С	-2.217611	1.415235	-0.000165
С	-3.453716	0.811129	-0.000040
С	-3.547311	-0.619010	0.000065
Н	-2.437250	-2.446387	0.000163
Н	-2.135726	2.494453	-0.000216
С	1.163505	-0.916327	-0.000078
С	1.252000	0.514008	-0.000114
Ν	0.180463	1.281488	-0.000235
С	2.433219	-1.711304	-0.000070
С	3.673464	0.316231	0.000144
Ν	2.492200	1.100441	-0.000026
Ν	3.595062	-1.034007	0.000060
0	2.388693	-2.953290	-0.000196
0	4.761423	0.908508	0.000364
С	-4.702737	1.648341	0.000049
Н	-5.320590	1.439306	0.876000
Н	-4.462471	2.709507	-0.000107
Н	-5.320857	1.439087	-0.875659
С	-4.892162	-1.293370	0.000249
Н	-5.480390	-1.012198	0.876479
Н	-5.480536	-1.012353	-0.875937
Н	-4.783340	-2.376152	0.000336
Ν	0.001530	-1.520475	-0.000025
С	2.581433	2.558369	0.000014
Н	2.092853	2.968447	-0.882762
Н	2.092597	2.968459	0.882628
Н	3.630617	2.822452	0.000135

### Cartesian coordinates (in Å) of the ground state singlet equilibrium structure of $\mbox{\bf 3a-H}.$

С	-2.426442	-1.375742	0.000019
С	-1.149692	-0.767631	0.00008
С	-1.054310	0.655895	0.000012
С	-2.243519	1.413076	-0.00003
С	-3.478027	0.807916	-0.000004
С	-3.574381	-0.626114	0.000022
Н	-2.470527	-2.456708	0.000022
Н	-2.159706	2.491515	-0.000019
С	1.124996	-0.912201	-0.000005
С	1.219401	0.511923	0.000011
Ν	0.149909	1.272874	0.000017
С	2.360674	-1.726148	-0.000019
С	3.640213	0.417439	0.00002
Ν	2.462248	1.133423	0.000016
Ν	3.511175	-0.965172	-0.000011
0	2.405263	-2.942377	-0.000037
0	4.746331	0.930526	0.00000
С	-4.725827	1.643457	-0.000069
Н	-5.342494	1.430902	0.875610
Н	-4.487242	2.704558	-0.000042
Н	-5.342360	1.430927	-0.875855

С	-4.920780	-1.294023	0.000043
Н	-5.505952	-1.007956	0.876369
Н	-5.506051	-1.007858	-0.876182
Н	-4.817201	-2.376907	-0.000017
Ν	-0.035437	-1.524923	-0.00004
С	2.525556	2.598359	0.000022
Н	2.029389	2.989650	-0.884593
Н	2.029420	2.989647	0.884658
Н	3.569320	2.884016	0.00006
Н	4.388220	-1.467613	-0.000018

Cartesian coordinates (in Å) of the ground state singlet equilibrium structure of anion from  $\mbox{4a-H}.$ 

С	-2.128338	-1.491367	0.000089
С	-0.912857	-0.787373	-0.000035
С	-0.935762	0.624298	-0.000102
С	-2.173921	1.278947	-0.000092
С	-3.365178	0.569203	-0.000022
С	-3.348744	-0.849905	0.000119
Н	-2.073624	-2.571972	0.000127
Н	-2.215843	2.356720	-0.000131
С	1.380588	-0.832464	-0.000051
С	1.463329	0.620322	-0.000014
Ν	0.267643	1.304482	-0.000186
С	2.694731	-1.568328	-0.000163
С	3.780797	0.528750	0.000231
Ν	2.590335	1.268919	0.000197
Ν	3.818558	-0.839495	-0.000019
0	2.690972	-2.813726	-0.000402
0	4.843824	1.176905	0.000509
С	-4.670693	1.313813	-0.000035
Η	-5.270815	1.057507	0.875650
Н	-4.511936	2.390033	0.000089
Н	-5.270635	1.057678	-0.875892
С	-4.630016	-1.638549	0.000335
Н	-5.240021	-1.410679	0.877062
Н	-5.240541	-1.410471	-0.875950
Н	-4.427358	-2.707757	0.000183
Ν	0.263034	-1.486431	-0.000081
С	0.272822	2.769019	-0.000316
Н	-0.234746	3.142395	-0.888187
Н	-0.233476	3.142602	0.888217
Н	1.303075	3.097989	-0.001066

Cartesian coordinates (in Å) of the ground state singlet equilibrium structure of **4a-H**.

С	-2.164315	1.500543	-0.000033
С	-0.945907	0.794363	0.000012
С	-0.965069	-0.622117	0.000034
С	-2.200227	-1.279175	0.000041
С	-3.389614	-0.569068	-0.000002
С	-3.377886	0.855475	-0.000061
Н	-2.109267	2.580543	-0.000064
Н	-2.242700	-2.356271	0.000074
С	1.337257	0.823435	0.000046

С	1.427866	-0.622279	0.00000
Ν	0.238841	-1.300104	0.000050
С	2.616198	1.584694	0.000080
С	3.741024	-0.628160	-0.000098
Ν	2.556110	-1.297222	-0.000063
Ν	3.722369	0.777736	-0.000022
0	2.693669	2.801766	0.000174
0	4.830594	-1.190485	-0.000194
С	-4.692956	-1.312694	0.000042
Н	-5.291363	-1.052707	-0.875529
Н	-4.535778	-2.388640	0.000037
Н	-5.291284	-1.052689	0.875661
С	-4.662366	1.635963	-0.000155
Н	-5.269547	1.401956	-0.876782
Н	-5.269580	1.402103	0.876492
Н	-4.466021	2.705922	-0.000240
Ν	0.220382	1.485333	0.000037
С	0.238136	-2.769493	0.000116
Н	-0.272489	-3.132676	0.889258
Н	-0.272159	-3.132768	-0.889181
Н	1.264455	-3.107327	0.000330
Н	4.624870	1.233202	-0.000039

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