Electronic Supplementary Material (ESI) for Chemical Communications

Molecular photoswitches based on spiroacridans

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Supporting Information

Full synthetic details pertaining to the preparations of new compounds, crystal data of **4a**, analysis of thermal back reactions (transient decay curves and absorption spectra).

General Methods

Commercially available chemicals and solvents (UVASOL, Merck) were used as received unless otherwise noted; solvents were dried according to standard procedures. Column chromatography (CC) was carried out on *200 mesh* silica gel (Merck) or on aluminium (III) oxide (90 standardized) (Merck). Melting points (m.p.) were determined with a Boetius heating microscope.

ESI mass spectroscopy was carried out on LTQ FT, Finnigan MAT (Bremen, Germany) equipped with an electrospray ion source (Thermo Electron).

NMR spectra were recorded on a Bruker DPX 300 (300 MHz), a Bruker Advance 400 (400 MHz) or a Bruker AMX 600 (600 MHz) spectrometers. The proton signals were attributed to the different subunits with the aid of two-dimensional NMR spectroscopy, such as C-H-COSY, H-H-COSY, and ROESY.

UV/Vis measurements were performed with a Shimadzu UV 2101 PC spectrometer.

Irradiation of the solutions were carried out with a conventional mercury arc (HBO 500) combined with a cut-off filter of 300 nm. Transient absorption spectra between 240 and 500 nm were recorded with the UV 2101 PC spectrometer using the fastest scan mode. A flash photolysis apparatus[1] was used in order to record transient absorption spectra of compounds **3_Za**, **3_Zb**, and **3_Zf**.

Quantum yield determination

Steady state photolysis experiments were carried out using a 500 W high pressure mercury lamp operated in conjunction with cut-off filter (300 nm). The solutions were irradiated in 1 cm quartz cuvettes. The integral quantum yields were calculated by the absorbance of the zwitterions at 360 nm recorded after an irradiation time of 5s. The concentration of **3_Z** was obtained by assuming the same ε-values for the zwitter-ion and the salt. 7-(4-dimethylaminophenyl)-cyclohepta-1,3,5-triene was used as a secondary actinometer ($\Phi_r^{313\ nm} = 0.45$, EtOH, 296 K)[2] in order to determine the intensity of incoming light.

The thermal reactions were followed by UV-Vis-spectroscopy using the kinetics-program of the spectrometer. The absorption decay curves were analysed by nonlinear regression fits (Origin 6.0, Microcal Software, Inc.).

ESR measurements

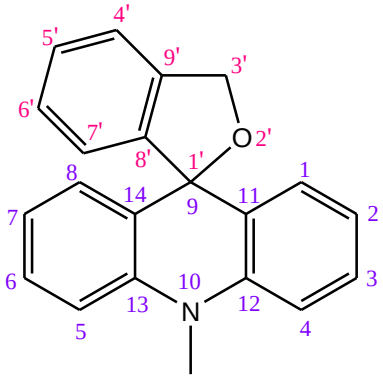
The solutions of **4a** in methanol or ethanol (0.001… 0.0001 M) were irradiated at 77 K with 290 nm wavelength light (HBO 500 lamp) for 5 min. The ESR measurements were subsequently performed on the X band spectrometer ERS 300 (ZWG/Magnetech Berlin, Germany) at 77 K.

Syntheses

General procedure for compounds 4a – d:

1 eq. of the corresponding alcohol **2** (ESI) in dry THF (50 mL) was cooled down to -78°C in an argon atmosphere and n-BuLi (1.6 M in n-hexane) (2 equ.) was added over 30 min. The resulting yellow suspension was stirred for 30 min. A solution of 10-methylacridin-9(10*H*)-one (1 eq) in dry THF (150 mL) was then added dropwise over 30 min. After stirring for 2 h at -78°C the orange solution was heated to room temperature and stirred overnight. After addition of water (3 mL) the suspension was filtrated. The organic phase was evaporated under reduced pressure. The remaining solid was purified by CC (SiO_2, BuOH/HOAc/H_2O 5mL:1mL:2mL; alternative eluent i-PrOH/HOAc/H_2O 7mL:1mL:3mL or MeOH/H_2O/aq NH_4Cl 30mL:6mL:0,1mL). The fractions containing the product were evaporated. The residue was dissolved in $CHCl_3$ and treated with NEt_3 until the solution became pale yellow. The solution was evaporated; and the residue was purified by CC (SiO_2, Et_2O/NEt_3 99mL:1mL; alternative eluent $CHCl_3$/NEt_3 19mL:1mL). The fractions containing the product were evaporated to provide a yellowish solid.

10-Methylspiro[acridan-9,1'-phthalan] 4a



According to the general procedure, from 2-bromobenzylalcohol **2a** (4 g, 21.4 mmol), n-BuLi (26.8 mL, 42.88 mmol) and 10-methylacridin-9(10*H*)-one (4.5 g, 21.4 mmol) **4a** was synthesized **(**3.3 g, 51%), m.p. 161-162°C. $C_{21}H_{17}NO$ (299.37): calcd. (%): C 84.25, H 5.72, N 4.68; found (%): C 84.03, H 6.11, N 4.51; HRMS (FTMS + c NSI): *m/z*: found 300.1382; calcd. for $[M+H]^+$ $[C_{21}H_{18}NO]^+$ 300.1383; UV-Vis (MeCN) λ/nm (ε/$cm^{-1}M^{-1}$): 287 (14200), 320 (sh).

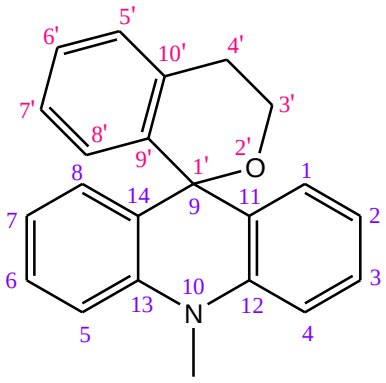
^{1}H-NMR (400 MHz, $CDCl_3$): 3.62 (s, 3H, N-CH_3), 5.20 (s, 2H, CH_2, H-3'), 6.88-6.95 (m, 2H, CH, H-3,6), 7.03 (dd, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.6 Hz, 2H, CH, H-4,5), 7.11-7.17 (m, 3H, CH, H-1,8,7'), 7.28-7.42 (m, 5H, CH, H-2,7,4',5',6').

(400 MHz, CD_3CN): 3.56 (s, 3H, N-CH_3), 5.31 (s, 2H, CH_2, H-3‘), 6.88-6.94 (m, 2H, CH, H-3,6), 6.98 (d, $^3J_{HH}$ = 7.7 Hz, 1H, CH, H-7‘), 7.14 (dd, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.6 Hz, 2H, CH, H-4,5), 7.17-7.23 (m, 3H, CH, H-1,8,6‘), 7.29-7.40 (m, 4H, CH, H-2,7,4‘,5‘).

^{13}C-NMR (100 MHz, $CDCl_3$): 33.5 (N-CH_3), 71.5 (CH_2, C-3‘), 86.8 (spiro C, C-9/1‘), 112.7 (CH, C-1,8), 120.2 (CH, C-3,6), 120.8 (CH, C-4‘), 124.3 (CH, C-7‘), 125.5 (C_q, C-11,14), 127.7 (CH, C-4,5), 127.9 (CH, C-6‘), 128.0 (CH, C-5‘), 128.6 (CH, C-2,7), 140.0 (C_q, C-8‘), 140.6 (C_q, C-9‘), 143.3 (C_q, C-12,13).

(100 MHz, CD_3CN): 33.9 (N-CH_3), 73.2 (CH_2, C-3‘), 87.0 (spiro C, C-9/1‘), 113.8 (CH, C-1,8), 121.1 (CH, C-3,6), 122.1 (CH, C-4‘), 123.6 (CH, C-7‘), 127.7 (CH, C-4,5), 127.8 (C_q, C-11,14), 128.9 (CH, C-6‘), 129.0 (CH, C-5‘), 129.4 (CH, C-2,7), 138.9 (C_q, C-8‘), 140.8 (C_q, C-9‘), 146.5 (C_q, C-12,13).

10-Methylspiro[acridan-9,1’-isochroman] 4b



According to the general procedure, from 2-bromophenethylalcohol **2b** (2 g, 10 mmol), n-BuLi (12.5 mL, 20 mmol) and 10-methylacridin-9(10*H*)-one (2.0 g, 9.56 mmol) **4b** was synthesized (1.92 g, 64%), m.p. 171-172°C. $C_{22}H_{19}NO$ (313.39): calcd. (%): C 84.31, H 6.11, N 4.47; found (%): C 84.00, H 6.45, N 4.17; HRMS (EI, 70 eV): *m/z*: found 313.1466; calcd. for $C_{22}H_{19}NO$ 313.1467; UV-Vis (MeCN), λ/nm (ε/$cm^{-1}M^{-1}$): 288 (16500), 318 (sh).

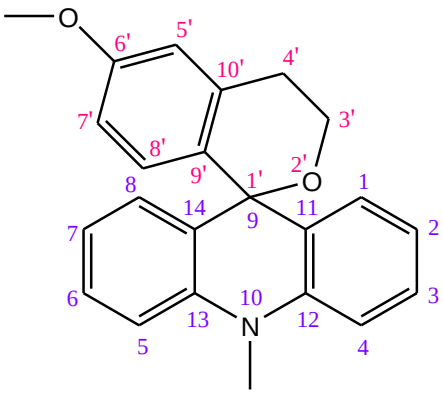
^{1}H-NMR (400 MHz, $CDCl_3$): 2.97 (t, $^3J_{HH}$ = 5.5 Hz, 2H, CH_2, H-4‘), 3.64 (s, 3H, N-CH_3), 3.76 (t, $^3J_{HH}$ = 5.5 Hz, 2H, CH_2, H-3‘), 6.85-6.93 (m, 4H, CH, H-3,4,5,6), 6.97 (d, $^3J_{HH}$ = 7.8 Hz, 1H, CH, H-8‘), 7.13-7.20 (m, 3H, CH, H-1,8,7‘), 7.26-7.33 (m, 2H, CH, H-5‘,6‘), 7.34-7.40 (m, 2H, CH, H-2,7).

(400 MHz, CD_3CN): 2.90 (t, $^3J_{HH}$ = 5.5 Hz, 2H, CH_2, H-4‘), 3.57 (s, 3H, N-CH_3), 3.62 (t, $^3J_{HH}$ = 5.5 Hz, 2H, CH_2, H-3‘), 6.76 (dd, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.6 Hz, 2H, CH, H-4,5), 6.80 (d, $^3J_{HH}$ = 7.8 Hz, 1H, CH, H-8‘), 6.82-6.88 (m, 2H, CH, H-3,6), 7.09-7.16 (m, 1H, CH, H-7‘), 7.21 (br d, $^3J_{HH}$ = 8.3 Hz, 2H, CH, H-1,8), 7.26-7.31 (m, 2H, CH, H-5‘,6‘), 7.34 (ddd, $^3J_{HH}$ = 8.3, 7.0 Hz, $^4J_{HH}$ = 1.6 Hz, 2H, CH, H-2,7).

^{13}C-NMR (100 MHz, $CDCl_3$): 29.4 (CH_2, C-4‘), 33.6 (N-CH_3), 58.4 (CH_2, C-3‘), 76.9 (spiro C, C-9/1‘), 112.6 (CH, C-1,8), 119.4 (CH, C-3,6), 125.6 (CH, C-7‘), 126.2 (C_q, C-11,14), 126.8 (CH, C-6‘), 128.2 (CH, C-5‘), 128.5 (CH, C-2,7), 130.0 (CH, C-4,5), 130.6 (CH, C-8‘), 136.6 (C_q, C-9‘), 138.1 (C_q, C-10‘), 141.0 (C_q, C-12,13).

(100 MHz, CD_3CN): 29.9 (CH_2, C-4‘), 34.1 (N-CH_3), 58.8 (CH_2, C-3‘), 77.4 (spiro C, C-9/1‘), 113.7 (CH, C-1,8), 120.1 (CH, C-3,6), 126.4 (CH, C-7‘), 127.2 (C_q, C-11,14), 127.7 (CH, C-6‘), 129.2 (CH, C-5‘), 129.5 (CH, C-2,7), 130.7 (CH, C-4,5), 131.0 (CH, C-8‘), 137.7 (C_q, C-9‘), 139.3 (C_q, C-10‘), 141.9 (C_q, C-12,13).

6’-Methoxy-10-methylspiro[acridan-9,1’-isochroman] 4c



According to the general procedure, from 2-bromo-5-methoxyphenethylalcohol **2c**[3] (3.35 g, 14.5 mmol), n-BuLi (19.94 mL, 31.9 mmol) and 10-methylacridin-9(10*H*)-one (3 g, 14.5 mmol) **4c** was synthesized (3.13 g, 63%); m.p. 225-226°C. HRMS (FTMS + c NSI): m/z: found 344.1646; calcd. for $[M+H]^+$ $[C_{23}H_{22}NO_2]^+$ 344.1645; UV-Vis (MeCN) λ/nm: 288, 318 (sh).

^{1}H-NMR (400 MHz, $CDCl_3$): 2.94 (t, $^3J_{HH}$ = 5.5 Hz, 2H, CH_2, H-4‘), 3.63 (s, 3H, N-CH_3), 3.74 (t, $^3J_{HH}$ = 5.5 Hz, 2H, CH_2, H-3‘), 3.88 (s, 3H, CH_3O), 6.75 (dd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 2.7 Hz, 1H, CH, H-7’), 6.80 (d, $^4J_{HH}$ = 2.7 Hz, 1H, CH, H-5’), 6.84-6.95 (m, 5H, CH, H-3,4,5,6,8’), 7.16 (br d, $^3J_{HH}$ = 8.3 Hz, 2H, CH, H-1,8), 7.36 (ddd, $^3J_{HH}$ = 8.3, 6.7 Hz, $^4J_{HH}$ = 2.1 Hz, 2H, CH, H-2,7).

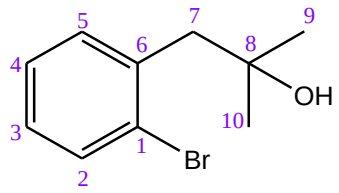
(400 MHz, CD_3CN): 2.90 (t, $^3J_{HH}$ = 5.5 Hz, 2H, CH_2, H-4‘), 3.59 (s, 3H, N-CH_3), 3.67 (t, $^3J_{HH}$ = 5.5 Hz, 2H, CH_2, H-3‘), 3.83 (s, 3H, CH_3O), 6.70 (dd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 2.7 Hz, 1H, CH, H-7’), 6.75-6.81 (m, 2H, H-5‘,8‘), 6.82-6.90 (m, 4H, CH, H-3,4,5,6), 7.14 (br d, $^3J_{HH}$ = 8.3 Hz, 2H, CH, H-1,8), 7.32 (ddd, $^3J_{HH}$ = 8.3, 6.5 Hz, $^4J_{HH}$ = 2.4 Hz, 2H, CH, H-2,7).

^{13}C-NMR (100 MHz, $CDCl_3$): 29.8 (CH_2, C-4‘), 33.6 (N-CH_3), 55.2 (CH_3O), 58.3 (CH_2, C-3‘), 76.7 (spiro C, C-9/1‘), 112.1 (CH, C-5’), 112.5 (CH, C-7’), 112.6 (CH, C-1,8), 119.4

(CH, C-3,6), 126.3 (C_q, C-11,14), 128.5 (CH, C-2,7), 129.9 (CH, C-4,5), 130.1 (C_q, C-9‘), 131.7 (CH, C-8’), 137.9 (C_q, C-10‘), 141.1 (C_q, C-12,13), 158.1 (C_q, C-6’).

(100 MHz, CD_3CN): 29.7 (CH_2, C-4‘), 33.6 (N-CH_3), 55.2 (CH_3O), 58.2 (CH_2, C-3‘), 76.6 (spiro C, C-9/1‘), 112.1 (CH, C-5’), 112.5 (CH, C-7’), 112.6 (CH, C-1,8), 119.3 (CH, C-3,6), 126.3 (C_q, C-11,14), 128.5 (CH, C-2,7), 129.9 (CH, C-4,5), 130.0 (C_q, C-9‘), 131.5 (CH, C-8’), 137.8 (C_q, C-10‘), 141.0 (C_q, C-12,13), 158.2 (C_q, C-6’).

1-(2-Bromophenyl)-2-methylpropan-2-ol 2d

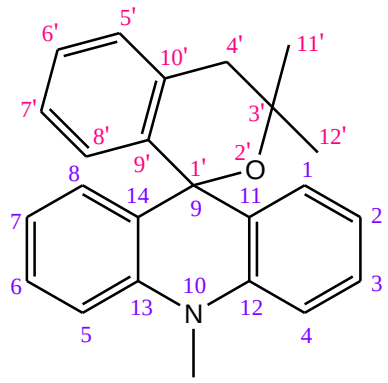


A solution of ethyl 2-(2-bromophenyl)acetate[4] (4.95 g, 20.36 mmol) in dry THF (50 mL) was added dropwise over 30 min to a stirred Grignard-solution of Mg (1.19 g, 48.9 mmol) and MeI (6.94 g, 48.9 mmol) in dry THF (50 mL). The reaction mixture was heated at reflux for 2 h. The solution was evaporated *in vacuo*. The residue was hydrolyzed with a saturated aqueous NH_4Cl solution und then extracted with diethyl ether (3x50 mL). The combined organic layers were washed with water and brine and then dried (Na_2SO_4). The solvent was removed and the crude product was purified by CC (Al_2O_3, $CHCl_3$) to give the alcohol (1.58 g, 34%) as colourless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): 1.25 (s, 6H, CH_3, H-9,10), 1.82 (s, 1H, OH), 2.98 (s, 2H, CH_2, H-7), 7.05 (dt, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, CH, H-3), 7.22 (dt, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, CH, H-4), 7.32 (dd, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, CH, H-5), 7.53 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, CH, H-2).

^{13}C-NMR (100 MHz, $CDCl_3$): 29.3 (CH_3, C-9,10), 47.8 (CH_2, C-7), 71.7 (C_q, C-8), 125.8 (C_q, C-1), 127.0 (CH, C-3), 128.0 (CH, C-4), 132.3 (CH, C-2), 132.9 (CH, C-5), 137.6 (C_q, C-6).

3’,3’-Dimethyl-10-methylspiro[acridan-9,1’-isochroman] 4d



According to the general procedure, from 1-(2-bromophenyl)-2-methylpropan-2-ol **2d** (1.5 g, 6.55 mmol), n-BuLi (8.5 mL, 13.6 mmol) and 10-methylacridin-9(10*H*)-one (1.37 g, 6.55 mmol) **4d** was synthesized (0.6 g, 27%), m.p. 153-155°C. $C_{24}H_{23}NO$ (341.45): calcd. (%): C 84.12, H 6.79, N 4.10; found (%): C 83.73, H 6.81, N 4.16; HRMS (EI, 70 eV): *m/z*: found 341.17794; calcd. for $C_{24}H_{23}NO$ 341.17796; UV-Vis (EtOH) λ/nm (ε/$cm^{-1}M^{-1}$): 287 (17640), 319 (sh).

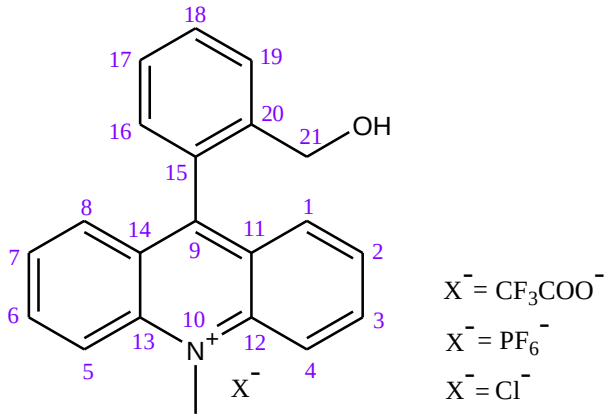
^{1}H-NMR (400 MHz, $CDCl_3$): 1.19 (s, 6H, CH_3, H-11',12'), 2.91 (s, 2H, CH_2, H-4'), 3.58 (s, 3H, N-CH_3), 6.83-6.91 (m, 2H, CH, H-3,6), 7.00 (br d, $^{3}J_{HH}$ = 7.8 Hz, 1H, CH, H-8'), 7.05-7.11 (m, 4H, CH, H-1,4,5,8), 7.11-7.16 (m, 1H, CH, H-7'), 7.18-7.22 (m, 1H, CH, H-5'), 7.22-7.32 (m, 3H, CH, H-2,7,6').

^{13}C-NMR (100 MHz, $CDCl_3$): 29.5 (CH_3, C-11',12'), 33.5 (N-CH_3), 41.7 (CH_2, C-4'), 72.6 (C_q, C-3'), 76.1 (spiro C, C-9/1'), 112.5 (CH, C-1,8), 119.6 (CH, C-3,6), 125.8 (CH, C-7'), 126.8 (CH, C-6'), 127.6 (CH, C-2,7), 128.2 (CH, C-4,5), 128.6 (CH, C-5'), 128.9 (C_q, C-11,14), 129.4 (CH, C-8'), 135.2 (C_q, C-9'), 137.8 (C_q, C-10'), 141.1 (C_q, C-12,13).

General procedure for compounds 3a – 3d:

The acridinium salts were prepared from the corresponding acridans by treating with an acid. If necessary, the crude products were purified by CC.

9-(2-(Hydroxymethyl)phenyl)-10-methylacridinium salt 3a



$X^- = CF_3COO^-$

$X^- = PF_6^-$

$X^- = Cl^-$

The corresponding acridinium trifluoroacetate was quantitatively obtained from **4a** and trifluoroacetic acid. The corresponding acridinium hexafluorophosphate was quantitatively obtained from **4a** by treating the crude acridan with HPF_6 (60% in water) and by further purification of the product by CC (SiO_2, MeCN/H_2O/NH_4PF_6 80mL:2mL:0.1g), m.p.183-184°C. The corresponding acridinium chloride was quantitatively obtained from **4a** by

treating the crude acridan with HPF_6 and by purification of the product by CC (SiO_2, MeOH/H_2O/aq NH_4Cl 30mL:6mL:0,1mL).

HRMS **(**FTMS + c NSI): *m/z*: found 300.1383; calcd. for M^+ $[C_{21}H_{18}NO]^+$ 300.1388; UV-Vis (MeCN) λ/nm (ε/$cm^{-1}M^{-1}$): 260, 361 (15430), 423 (4850).

^{1}H-NMR (400 MHz, CD_3CN), $M^+CF_3COO^-$: 4.13 (s, 2H, CH_2, H-21), 4.84 (s, 3H, N-CH_3), 7.31 (br d, $^3J_{HH}$ = 7.6 Hz, 1H, CH, H-16), 7.62 (dt, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, CH, H-17), 7.73-7.78 (m, 1H, CH, H-18), 7.79-7.85 (m, 3H, CH, H-2,7,19), 7.89 (dd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 1.7 Hz, 2H, CH, H-1,8), 8.38 (ddd, $^3J_{HH}$ = 9.3, 6.6 Hz, $^4J_{HH}$ = 1.7 Hz, 2H, CH, H-3,6), 8.61 (d, $^3J_{HH}$ = 9.3 Hz, 2H, CH, H-4,5).

(400 MHz, CD_3CN), $M^+PF_6^-$: 4.63 (s, 2H, CH_2, H-21), 4.86 (s, 3H, N-CH_3), 7.39 (d, $^3J_{HH}$ = 7.5 Hz, 1H, CH, H-16), 7.68-7.74 (m, 1H, CH, H-17), 7.77-7.81 (m, 2H, CH, H-18,19), 7.82-7.89 (m, 4H, CH, H-1,2,7,8), 8.39 (ddd, $^3J_{HH}$ = 9.3, 5.7 Hz, $^4J_{HH}$ = 2.6 Hz, 2H, CH, H-3,6), 8.63 (d, $^3J_{HH}$ = 9.3 Hz, 2H, CH, H-4,5).

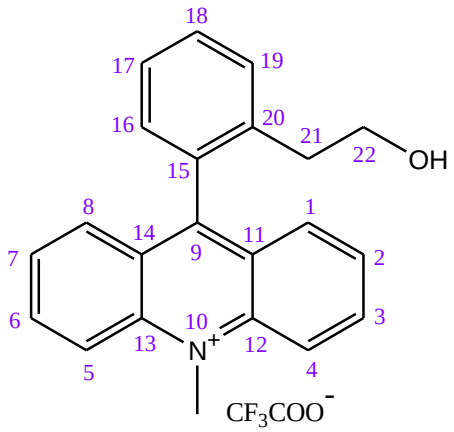
(400 MHz, CD_3CN), M^+Cl^- : 4.62 (s, 2H, CH_2, H-21), 4.93 (s, 3H, N-CH_3), 7.38 (d, $^3J_{HH}$ = 7.4 Hz, 1H, CH, H-16), 7.66-7.74 (m, 1H, CH, H-17), 7.75-7-81 (m, 2H, CH, H-18,19), 7.81-7.88 (m, 4H, CH, H-1,2,7,8), 8.35-8.44 (m, 2H, CH, H-3,6), 8.75 (d, $^3J_{HH}$ = 9.3 Hz, 2H, CH, H-4,5).

^{13}C-NMR (100 MHz, CD_3CN), $M^+CF_3COO^-$: 39.6 (N-CH_3), 62.5 (CH_2, C-21), 119.4 (CH, C-4,5), 127.2 (C_q, C-11,14), 128.5 (CH, C-17), 128.7 (CH, C-2,7), 129.1 (CH, C-19), 130.5 (CH, C-16), 130.9 (CH, C-1,8), 131.3 (CH, C-18), 132.6 (C_q, C-15), 139.7 (CH, C-3,6), 141.3 (C_q, C-20), 142.5 (C_q, C-12,13), 160.1 (C_q, C-9).

(100 MHz, CD_3CN), $M^+PF_6^-$: 39.7 (N-CH_3), 64.6 (CH_2, C-21), 119.5 (CH, C-4,5), 127.2 (C_q, C-11,14), 128.9 (CH, C-2,7), 129.8 (CH, C-17), 130.8 (CH, C-1,8), 130.9 (CH, C-19), 131.0 (CH, C-16), 131.5 (CH, C-18), 133.9 (C_q, C-15), 135.8 (C_q, C-20), 139.8 (CH, C-3,6), 142.5 (C_q, C-12,13), 161.0 (C_q, C-9).

(100 MHz, CD_3CN), M^+Cl^- : 40.1 (N-CH_3), 64.6 (CH_2, C-21), 119.8 (CH, C-4,5), 127.2 (C_q, C-11,14), 128.9 (CH, C-2,7), 129.7 (CH, C-17), 130.7 (CH, C-1,8), 130.8 (CH, C-19), 131.0 (CH, C-16), 131.4 (CH, C-18), 133.9 (C_q, C-15), 135.7 (C_q, C-20), 139.7 (CH, C-3,6), 142.5 (C_q, C-12,13), 160.8 (C_q, C-9).

9-(2-Hydroxyethylphenyl)-10-methylacridinium trifluoroacetate 3b



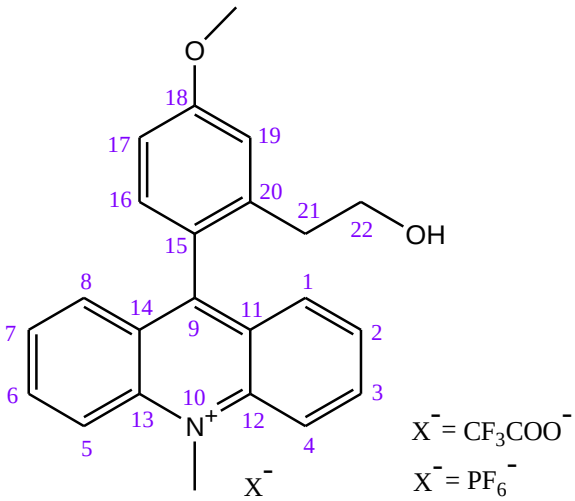
The corresponding acridinium trifluoroacetate was quantitatively obtained from **4b** and trifluoroacetic acid, HRMS (p ESI) m/z: found 314.1538; calcd. for $[M\text{-}CF_3COO^-]^+$ $[C_{22}H_{20}NO]^+$ 314.1545.

UV-Vis (MeCN) λ/nm (ε/$cm^{-1}M^{-1}$): 258, 361 (15400), 423 (4860).

^{1}H-NMR (400 MHz, CD_3CN), $M^+CF_3COO^-$: 2.35 (t, $^3J_{HH}$ = 7.0 Hz, 2H, CH_2, H-21), 2.67 (br s, 1H, OH), 3.25 (t, $^3J_{HH}$ = 7.0 Hz, 2H, CH_2, H-22), 4.86 (s, 3H, N-CH_3), 7.29 (d, $^3J_{HH}$ = 7.6 Hz, 1H, CH, H-16), 7.50-7.56 (m, 1H, CH, H-17), 7.65-7.70 (m, 2H, CH, H-18,19), 7.78-7.83 (m, 2H, CH, H-2,7), 7.89 (br d, $^3J_{HH}$ = 8.7 Hz, 2H, CH, H-1,8), 8.31-8.38 (m, 2H, CH, H-3,6), 8.64 (d, $^3J_{HH}$ = 9.2 Hz, 2H, CH, H-4,5).

^{13}C-NMR (100 MHz, CD_3CN), $M^+CF_3COO^-$: 37.6 (CH_2, C-21), 39.8 (N-CH_3), 62.5 (CH_2, C-22), 119.7 (CH, C-4,5), 127.2 (CH, C-17), 127.5 (C_q, C-11,14), 128.6 (CH, C-2,7), 130.5 (CH, C-19), 130.9 (CH, C-1,8), 131.1 (CH, C-16), 131.5 (CH, C-18), 134.1 (C_q, C-15), 139.4 (CH, C-3,6), 139.6 (C_q, C-20), 142.7 (C_q, C-12,13), 162.4 (C_q, C-9).

9-(2-(2-Hydroxyethyl)-4-methoxyphenyl)-10-methylacridinium salt 3c



The corresponding acridinium trifluoroacetate was quantitatively obtained from **4c** and trifluoroacetic acid. The corresponding acridinium hexafluorophosphate was quantitatively obtained from **4c** by treating the crude acridan with HPF_6 (60% in water), purification of the product by CC (SiO_2, MeOH/H_2O/aq NH_4Cl 30mL:6mL:0,1mL) and the following counter ion exchange by treating the acridinium chloride with 10 ml water and an excess of NH_4PF_6. The precipitated acridinium hexafluorophosphate was filtered and dried.

HRMS (p ESI) m/z: found 344.1646; calcd. for $[M\text{-}CF_3COO^-]^+$ $[C_{23}H_{22}NO_2]^+$ 344.1645.

UV-Vis (MeCN) λ/nm: 261, 360, 428.

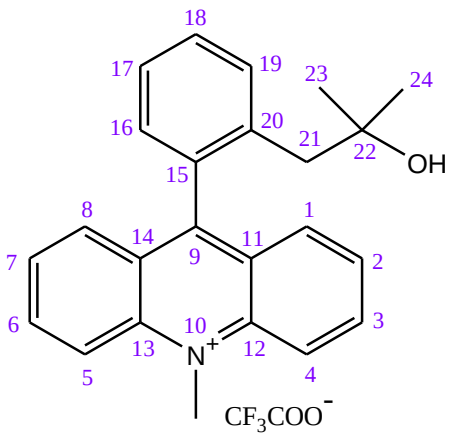
^{1}H-NMR (400 MHz, CD_3CN), $M^+PF_6^-$: 2.32 (t, $^3J_{HH}$ = 6.7 Hz, 2H, CH_2, H-21), 2.40 (br s, 1H, OH), 3.31-3.39 (m, 2H, CH_2, H-22), 3.95 (s, 3H, CH_3O), 4.83 (s, 3H, N-CH_3), 7.11 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 2.5 Hz, 1H, CH, H-17), 7.19 (d, $^3J_{HH}$ = 8.5 Hz, 1H, CH, H-16), 7.23 (d, $^4J_{HH}$ = 2.5 Hz, 1H, CH, H-19), 7.84 (ddd, $^3J_{HH}$ = 8.7, 6.7 Hz, $^4J_{HH}$ = 0.8 Hz, 2H, CH, H-2,7), 7.97 (dd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 1.5 Hz, 2H, CH, H-1,8), 8.37 (ddd, $^3J_{HH}$ = 9.3, 6.7 Hz, $^4J_{HH}$ = 1.5 Hz, 2H, CH, H-3,6), 8.60 (d, $^3J_{HH}$ = 9.3 Hz, 2H, CH, H-4,5).

(400 MHz, $CDCl_3$), $M^+CF_3COO^-$: 2.56 (t, $^3J_{HH}$ = 6.8 Hz, 2H, CH_2, H-21), 3.97 (s, 3H, CH_3O), 4.16 (t, $^3J_{HH}$ = 6.8 Hz, 2H, CH_2, H-22), 4.90 (s, 3H, N-CH_3), 7.11-7.24 (m, 3H, CH, H-16,17,19), 7.82-7.88 (m, 2H, CH, H-2,7), 7.98 (br d, $^3J_{HH}$ = 8.7 Hz, 2H, CH, H-1,8), 8.34-8.41 (m, 2H, CH, H-3,6), 8.54 (d, $^3J_{HH}$ = 9.3 Hz, 2H, CH, H-4,5).

^{13}C-NMR (100 MHz, CD_3CN), $M^+PF_6^-$: 37.3 (CH_2, C-21), 39.5 (N-CH_3), 56.2 (CH_3O), 62.5 (CH_2, C-22), 113.0 (CH, C-17), 116.7 (CH, C-19), 119.4 (CH, C-4,5), 126.1 (C_q, C-15), 127.8 (C_q, C-11,14), 128.6 (CH, C-2,7), 131.1 (CH, C-1,8), 132.1 (CH, C-16), 139.6 (CH, C-3,6), 141.1 (C_q, C-20), 142.6 (C_q, C-12,13), 162.1 (C_q, C-9), 163.1 (C_q, C-18).

(100 MHz, $CDCl_3$), $M^+CF_3COO^-$: 31.9 (CH_2, C-21), 38.3 (N-CH_3), 55.5 (CH_3O), 66.5 (CH_2, C-22), 113.5 (CH, C-17), 115.8 (CH, C-19), 118.0 (CH, C-4,5), 124.4 (C_q, C-15), 126.8 (C_q, C-11,14), 128.5 (CH, C-2,7), 130.1 (CH, C-1,8), 131.7 (CH, C-16), 136.5 (C_q, C-20), 139.6 (CH, C-3,6), 141.3 (C_q, C-12,13), 159.9 (C_q, C-9), 161.6 (C_q, C-18).

9-[2-(2-Hydroxy-2-methylpropyl)phenyl]-10-methylacridinium trifluoroacetate 3d



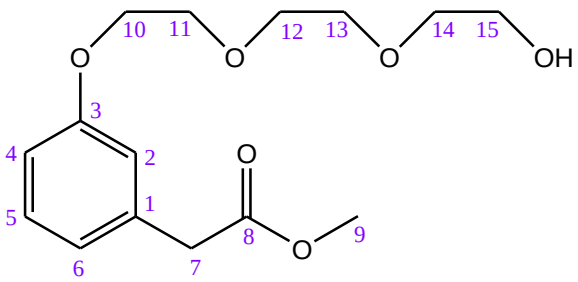
The corresponding acridinium trifluoroacetate was quantitatively obtained from **4d** and trifluoroacetic acid. HRMS (p-ESI) m/z: found 342.1862; calcd. for $[M\text{-}CF_3COO^-]^+$ $[C_{24}H_{24}NO]^+$ 342.1858.

UV-Vis (EtOH) λ/nm (ε/$cm^{-1}M^{-1}$): 259, 361 (15580), 426 (5600).

^{1}H-NMR (400 MHz, $CDCl_3$), $M^+CF_3COO^-$: 0.99 (s, 6H, CH_3, H-23,24), 2.54 (s, 2H, CH_2, H-21), 4.87 (s, 3H, N-CH_3), 7.28 (d, $^3J_{HH}$ = 7.5 Hz, 1H, CH, H-16), 7.56-7.62 (m, 1H, CH, H-17), 7.67-7.75 (m, 2H, CH, H-18,19), 7.82 (dd, $^3J_{HH}$ = 8.7, 6.8 Hz, 2H, CH, H-2,7), 8.01 (dd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 1.0 Hz, 2H, CH, H-1,8), 8.34 (ddd, $^3J_{HH}$ = 9.2, 6.8 Hz, $^4J_{HH}$ = 1.3 Hz, 2H, CH, H-3,6), 8.48 (d, $^3J_{HH}$ = 9.2 Hz, 2H, CH, H-4,5).

^{13}C-NMR (100 MHz, $CDCl_3$), $M^+CF_3COO^-$: 28.3 (CH_3, C-23,24), 38.1 (N-CH_3), 45.6 (CH_2, C-21), 74.6 (C_q, C-22), 117.7 (CH, C-4,5), 126.3 (C_q, C-11,14), 127.5 (CH, C-17), 128.2 (CH, C-2,7), 130.7 (CH, C-1,8), 130.8 (CH, C-16,19), 132.4 (CH, C-18), 133.1 (C_q, C-15), 136.3 (C_q, C-20), 139.4 (CH, C-3,6), 141.4 (C_q, C-12,13), 159.7 (C_q, C-9).

Methyl 2-{3-[2-(2-(2-hydroxyethoxy)ethoxy)ethoxy]phenyl}acetate

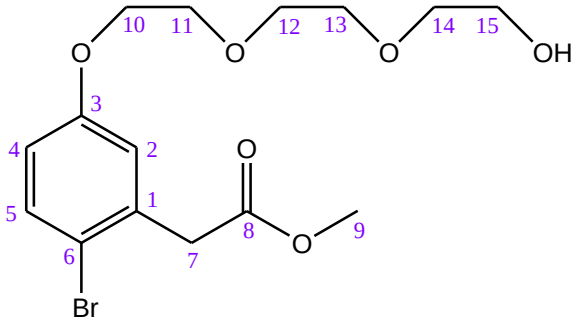


To methyl 2-(3-hydroxyphenyl)acetate (13.23 g, 79.6 mmol) dissolved in dry MeCN (200 mL) NaH (3.5 g, 60% in oil) was added. The reaction mixture was heated at reflux for 40 min. Triethylenglycolmonotosylate (24.2 g, 79.6 mmol) was then added. The resulting mixture was heated at reflux for 23 h. The solvent was removed *in vacuo* and the residue was treated with dichloromethane and water. The separated organic layer was washed with water and brine. The aqueous phase was extracted with dichloromethane. The combined organic layers were dried over $MgSO_4$. The solvent was removed and the crude product was purified by CC (SiO_2, n-hexane/ethyl acetate 1:1→ n-hexane/ethyl acetate 1:2→ ethyl acetate) to afford a clear yellowish oil (10.4 g, 44%). $C_{15}H_{22}O_6$ (298.33): calcd. (%): C 60.39, H 7.43; found (%): C 60.48, H 7.58; HRMS (FTMS + p ESI): *m/z*: found 299.1490; calcd. for $[M+H]^+$ $[C_{15}H_{23}O_6]^+$ 299.1489; found 316.1756; calcd. for $[M+NH_4]^+$ $[C_{15}H_{26}NO_6]^+$ 316.1755; found 321.1310; calcd. for $[M+Na]^+$ $[C_{15}H_{22}O_6Na]^+$ 321.1309; found 337.1049; calcd. for $[M+K]^+$ $[C_{15}H_{22}O_6K]^+$ 337.1048.

^{1}H-NMR (400 MHz, $CDCl_3$): 2.82 (br s, 1H, OH), 3.57 (s, 2H, CH_2, H-7), 3.58-3.61 (m, 2H, OCH_2, H-15), 3.64-3.73 (m, 9H, CH_3, OCH_2, H-9,12,13,14), 3.81-3.85 (m, 2H, OCH_2, H-11), 4.08-4.13 (m, 2H, OCH_2, H-10), 6.78-6.87 (m, 3H, CH, H-2,4,6), 7.20 (t, $^{3}J_{HH}$ = 8.1 Hz, 1H, CH, H-5).

^{13}C-NMR (100 MHz, $CDCl_3$): 41.1 (CH_2, C-7), 52.0 (CH_3, C-9), 61.6 (OCH_2), 67.2 (OCH_2, C-10), 69.6 (OCH_2, C-11), 70.2 (OCH_2), 70.7 (OCH_2), 72.4 (OCH_2, C-15), 113.2, 115.5, 121.7 (CH, C-2,4,6), 129.4 (CH, C-5), 135.2 (C_q, C-1), 158.7 (C_q, C-3), 171.8 (C_q, C-8).

Methyl {2-[2-bromo-5-(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)phenyl]}acetate[5]



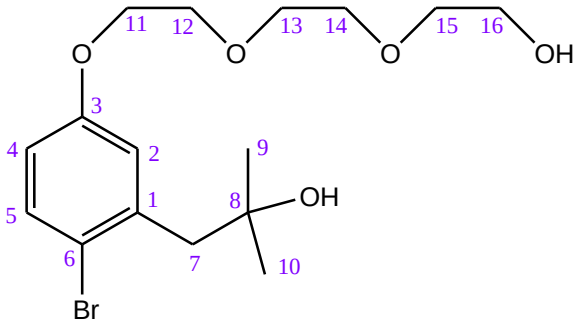
A solution of *tert*-butylhydroperoxide (70% aq.; 2.78 g, 30.84 mmol) was added to a cooled (0^{o}C) mixture of HBr (48% aq.; 3.76 g, 46.5 mmol) in methanol (100 mL). The resulting mixture was stirred for 5 min at 0^{o}C. To this cold solution, methyl 2-{3-[2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)phenyl]}acetate (9.2 g, 30.84 mmol) in cold methanol (30 mL) was added, and the mixture was stirred for 40 min at 0^{o}C and then heated at reflux for 20 h. Upon the completion of the reaction (TLC, SiO_2, *tert*-butylmethylether) the solvent was removed *in vacuo* and water (100 mL) was added to the residue and then extracted with dichloromethane (3x200 ml). The combined organic layers were washed with water, brine and dried over $MgSO_4$. On evaporation of solvent the crude product (11.9 g, 96%) was obtained as clear yellowish oil and found to be pure by TLC and NMR-spectroscopy.

HRMS (FTMS + p ESI): *m/z*: found 377.0589; calcd. for $[M+H]^+$ $[C_{15}H_{22}BrO_6]^+$ 377.0594; found 394.0858; calcd. for $[M+NH_4]^+$ $[C_{15}H_{25}BrNO_6]^+$ 394.0860; found 399.0412; calcd. for $[M+Na]^+$ $[C_{15}H_{21}BrO_6Na]^+$ 399.0414; found 415.0153; calcd. for $[M+K]^+$ $[C_{15}H_{21}BrO_6K]^+$ 415.0153.

^{1}H-NMR (400 MHz, $CDCl_3$): 2.55 (br s, 1H, OH), 3.56-3.60 (m, 2H, OCH_2, H-15), 3.64-3.71 (m, 9H, CH_3, OCH_2, H-9,12,13,14), 3.72 (s, 2H, CH_2, H-7), 3.80-3.84 (m, 2H, OCH_2, H-11), 4.05-4.09 (m, 2H, OCH_2, H-10), 6.70 (dd, $^{3}J_{HH}$ = 8.8 Hz, $^{4}J_{HH}$ = 3.0 Hz, 1H, CH, H-4), 6.85 (d, $^{4}J_{HH}$ = 3.0 Hz, 1H, CH, H-2), 7.40 (d, $^{3}J_{HH}$ = 8.8 Hz, 1H, CH, H-5).

^{13}C-NMR (100 MHz, $CDCl_3$): 41.5 (CH_2, C-7), 52.1 (CH_3, C-9), 61.6 (OCH_2), 67.5 (OCH_2, C-10), 69.5 (OCH_2, C-11), 70.2 (OCH_2), 70.7 (OCH_2), 72.4 (OCH_2, C-15), 115.1 (CH, C-4), 115.5 (C_q, C-6), 117.8 (CH, C-2), 133.2 (CH, C-5), 134.9 (C_q, C-1), 157.9 (C_q, C-3), 170.8 (C_q, C-8).

1-[2-Bromo-5-(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)phenyl]-2-methylpropan-2-ol

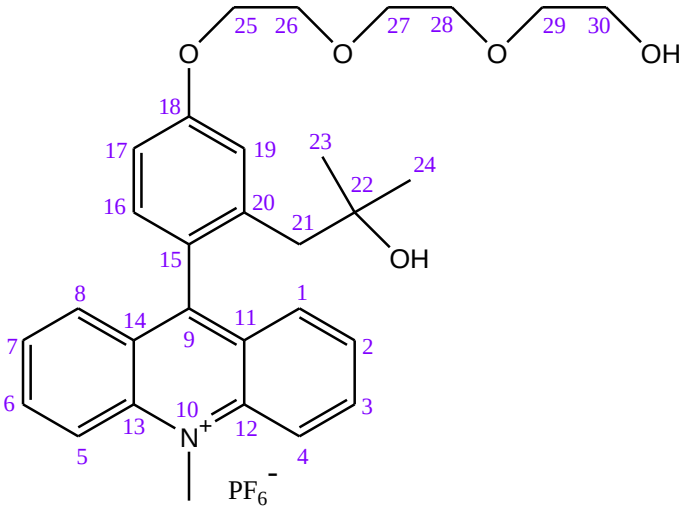


Methylmagnesium iodide (3.0 M solution in diethylether) (34.4 mL, 103.04 mmol) was added dropwise over 30 min to a stirred solution of methyl 2-[2-bromo-5-(2-(2-(2-hydroxyethoxy)-ethoxy)ethoxy)phenyl]acetate (11.11 g, 29.44 mmol) in dry THF (200 mL) in an argon atmosphere. The reaction mixture was heated under reflux for 4 h. The solvent was removed *in vacuo*. The residue was hydrolyzed with a saturated aqueous NH_4Cl solution und then extracted with dichloromethane (2x100 mL). The combined organic layers were washed with water and brine and then dried over $MgSO_4$. The solution was evaporated and the crude product was purified by CC (SiO_2, n-hexane/acetone 1:1) to give **2e** (5.88 g, 53%) as clear yellow oil. HRMS (FTMS +p ESI): *m/z*: found 377.0964; calcd. for $[M+H]^+$ $[C_{16}H_{26}BrO_5]^+$ 377.0958; found 394.1224; calcd. for $[M+NH_4]^+$ $[C_{16}H_{29}BrNO_5]^+$ 394.1224; found 399.0779; calcd. for $[M+Na]^+$ $[C_{16}H_{25}BrO_5Na]^+$ 399.0778; found 415.0519; calcd. for $[M+K]^+$ $[C_{16}H_{25}BrO_5K]^+$ 415.0517.

^{1}H-NMR (400 MHz, $CDCl_3$): 1.24 (s, 6H, CH_3, H-9,10), 2.57 (br s, 2H, OH), 2.92 (s, 2H, CH_2, H-7), 3.55-3.59 (m, 2H, OCH_2, H-16), 3.63-3.70 (m, 6H, OCH_2, H-13,14,15), 3.79-3.83 (m, 2H, OCH_2, H-12), 4.06-4.10 (m, 2H, OCH_2, H-11), 6.67 (dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 3.1 Hz, 1H, CH, H-4), 6.94 (d, $^4J_{HH}$ = 3.1 Hz, 1H, CH, H-2), 7.39 (d, $^3J_{HH}$ = 8.8 Hz, 1H, CH, H-5).

^{13}C-NMR (100 MHz, $CDCl_3$): 29.3 (CH_3, C-9,10), 47.9 (CH_2, C-7), 61.5 (OCH_2), 67.5 (OCH_2, C-11), 69.6 (OCH_2, C-12), 70.2 (OCH_2), 70.7 (OCH_2), 71.6 (C_q, C-8), 72.4 (OCH_2, C-16), 114.5 (CH, C-4), 116.6 (C_q, C-6), 118.4 (CH, C-2), 133.3 (CH, C-5), 138.6 (C_q, C-1), 157.5 (C_q, C-3).

9-{2-[2-Hydroxy-2-methylpropyl]-4-(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)phenyl}-10-methylacridinium hexafluorophosphate 3e



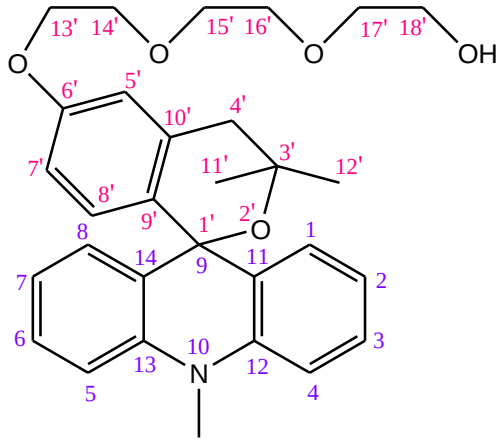
A solution of 1-(2-bromo-5-(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)phenyl)-2-methylpropan-2-ol (5.75 g, 15.24 mmol) in dry THF (150 mL) was cooled down to -78°C in an argon atmosphere. n-Butyllithium (1.6 M in n-hexane; 28.6 mL, 45.72 mmol) was added dropwise over 30 min. The resulting orange solution was stirred for 30 min. 10-Methylacridin-9(10*H*)-one (3.19 g, 15.24 mmol) dissolved in dry THF (200 mL) was then slowly added. The reaction mixture was stirred for 1 h at -78°C. After stirring for 72 h at room temperature, water (5 mL) was added. The solvent was removed *in vacuo.* The residue was dissolved in chloroform/acetone/water 3:1:1 and acidified with HOAc. Impurities were removed by CC (SiO_2, chloroform). The product remained at the start and was separated together with the column material. Water was added. The suspension was extracted with chloroform/triethylamine 9:1. The combined organic layers were dried ($MgSO_4$) and evaporated. The remaining solid was purified by CC (SiO_2, acetonitrile/ethylacetate/ cyclohexane/NH_4PF_6 40mL:20mL:10mL:0.05g). The yellow fractions containing the product were evaporated. The residue was dissolved in water (70 mL) and then extracted with dichloromethane (3x50 mL). The combined dichloromethane solutions were dried over $MgSO_4$. The solvent was removed to provide **3e** as orange resin (3.05 g, 32%). $C_{30}H_{36}F_6NO_5P$ (635.57): calcd. (%): C 56.69, H 5.71, N 2.20; found (%): C 56.12, H 6.06, N 1.76; HRMS (FTMS + p ESI): *m/z*: found 490.2584; calcd. for M^+ $[C_{30}H_{36}NO_5]^+$ 490.2588; UV-Vis (MeCN) λ/nm: 258, 358, 432.

^{1}H-NMR (400 MHz, CD_3CN), **$M^+PF_6^-$** : 0.78 (s, 6H, CH_3, H-23,24), 2.35 (s, 2H, CH_2, H-21), 2.82 (t, $^3J_{HH}$ = 5.7 Hz, 1H, OH), 3.51-3.55 (m, 2H, OCH_2, H-29), 3.59-3.67 (m, 4H,

OCH_2, H-28,30), 3.68-3.73 (m, 2H, OCH_2, H-27), 3.86-3.91 (m, 2H, OCH_2, H-26), 4.25-4.30 (m, 2H, OCH_2, H-25), 4.82 (s, 3H, N-CH_3), 7.12 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 2.6 Hz, 1H, CH, H-17), 7.20 (d, $^3J_{HH}$ = 8.5 Hz, 1H, CH, H-16), 7.39 (d, $^4J_{HH}$ = 2.5 Hz, 1H, CH, H-19), 7.81 (ddd, $^3J_{HH}$ = 8.7, 6.7 Hz, $^4J_{HH}$ = 0.8 Hz, 2H, CH, H-2,7), 8.04 (dd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 1.5 Hz, 2H, CH, H-1,8), 8.35 (ddd, $^3J_{HH}$ = 9.2, 6.7 Hz, $^4J_{HH}$ = 1.5 Hz, 2H, CH, H-3,6), 8.57 (d, $^3J_{HH}$ = 9.2 Hz, 2H, CH, H-4,5).

^{13}C-NMR (100 MHz, CD_3CN), **$M^+PF_6^-$** : 29.8 (CH_3, C-23,24), 39.5 (N-CH_3), 46.8 (CH_2, C-21), 61.9 (OCH_2, C-30), 68.7 (OCH_2, C-25), 70.2 (OCH_2, C-26), 71.0 (OCH_2, C-28), 71.3 (C_q, C-22), 71.4 (OCH_2, C-27), 73.3 (OCH_2, C-29), 113.5 (CH, C-17), 119.1 (CH, C-19), 119.3 (CH, C-4,5), 127.0 (C_q, C-15), 127.7 (C_q, C-11,14), 128.3 (CH, C-2,7), 131.7 (CH, C-1,8), 132.8 (CH, C-16), 139.4 (CH, C-3,6), 141.0 (C_q, C-20), 142.6 (C_q, C-12,13), 160.7 (C_q, C-9), 163.5 (C_q, C-18).

3',3'-Dimethyl-6'-(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)-10-methylspiro[acridan-9,1'-isochroman] 4e

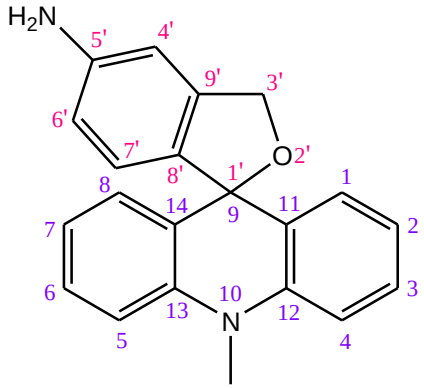


3e (3 g, 4.72 mmol) dissolved in water (10 mL) was extracted with $CHCl_3$/Et_3N 9:1 (2x10 mL). The combined organic layers were dried over $MgSO_4$. The solution was then evaporated and the residue was purified by CC (SiO_2, diethylether/Et_3N, 9:1) to give **4e (**2.02 g, 88%) as yellow, viscous oil. HRMS (FTMS + p ESI): *m/z*: found 490.2584; calcd. for $[M+H]^+$ $[C_{30}H_{36}NO_5]^+$ 490.2588; UV-Vis (MeCN) λ/nm: 284, 316 (sh).

^{1}H-NMR (400 MHz, $CDCl_3$): 1.17 (s, 6H, CH_3, H-11',12'), 2.52 (br s, 1H, OH), 2.85 (s, 2H, CH_2, H-4'), 3.58 (s, 3H, N-CH_3), 3.61-3.65 (m, 2H, OCH_2, H-18'), 3.69-3.77 (m, 6H, OCH_2, H-15',16',17'), 3.86-3.91 (m, 2H, OCH_2, H-14'), 4.13-4.19 (m, 2H, OCH_2, H-13'), 6.72 (dd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 2.7 Hz, 1H, CH, H-7'), 6.76 (d, $^4J_{HH}$ = 2.6 Hz, 1H, CH, H-5'), 6.84-6.90 (m, 3H, CH, H-3,6,8'), 7.05-7.11 (m, 4H, CH, H-1,4,5,8), 7.24-7.30 (m, 2H, CH, H-2,7).

^{13}C-NMR (100 MHz, $CDCl_3$): 29.5 (CH_3, C-11',12'), 33.5 (N-CH_3), 42.0 (CH_2, C-4'), 61.7 (OCH_2), 67.2 (OCH_2, C-13'), 69.7 (OCH_2, C-14'), 70.4 (OCH_2), 70.8 (OCH_2), 72.4 (OCH_2, C-18'), 72.5 (C_q, C-3'), 75.9 (spiro C, C-9/1'), 112.4 (CH, C-1,8), 112.5 (CH, C-7'), 113.8 (CH, C-5'), 119.6 (CH, C-3,6), 127.5 (CH, C-2,7), 128.1 (CH, C-4,5), 129.1 (C_q, C-11,14), 130.2 (C_q, C-9'), 130.6 (CH, C-8'), 136.6 (C_q, C-10'), 141.1 (C_q, C-12,13), 157.4 (C_q, C-6').

5'-Amino-10-methylspiro[acridan-9,1'-phthalan] 4f

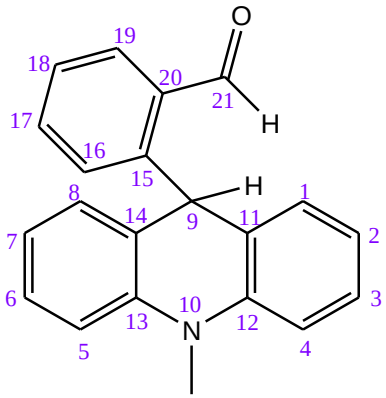


A mixture of 10-methylacridiniumiodide (3 g, 9.34 mmol), 3-aminobenzylalcohol (2.42 g, 19.65 mmol) and S_8 (0.87 g, 27.14 mmol) was heated for 2 h at 140°C. The cooled melt was extracted with diethyl ether (4x25 mL) and CCl_4 (2x25 mL) in order to remove sulfur. The resulting residue, dissolved in methanol and acidified with HPF_6, was purified by CC (SiO_2, i-PrOH/HOAc/H_2O 7mL:1mL:3mL). The red colored fractions were collected. After removing of the solvents, the residue was dissolved in $CHCl_3$/dichloromethane and treated with triethylamine until the color changed from red to yellow. The solvents were removed *in vacuo* and the residue was purified by CC (SiO_2, Et_2O/NEt_3 99mL:1mL) to give **4f** as yellow solid (1.11 g, 38 %), m.p. 68-70°C. HRMS (c-NSI): *m/z*: found 315.1488; calcd.for $[M+H]^+$ $[C_{21}H_{19}N_2O]^+$ 315.1492; UV-Vis (MeCN) λ/nm: 287, 320 (sh).

^{1}H-NMR (400 MHz, $CDCl_3$): 3.60 (s, 3H, N-CH_3), 3.74 (br s, 2H, NH_2), 5.05 (s, 2H, CH_2, H-3'), 6.58-6.67 (m, 2H, CH, H-4',6'), 6.85-6.99 (m, 3H, CH, H-3,6,7'), 7.04-7.19 (m, 4H, CH, H-1,4,5,8), 7.29-7.39 (m, 2H, CH, H-2,7).

^{13}C-NMR (100 MHz, $CDCl_3$): 33.3 (N-CH_3), 70.9 (CH_2, C-3'), 86.4 (spiro C, C-9/1'), 106.4 (CH, C-4'), 112.6 (CH, C-1,8), 115.2 (CH, C-6'), 120.0 (CH, C-3,6), 125.0 (CH, C-7'), 125.6 (C_q, C-11,14), 127.7 (CH, C-4,5), 128.4 (CH, C-2,7), 133.0 (C_q, C-8'), 140.7 (C_q, C-9'), 141.9 (C_q, C-12,13), 146.6 (C_q, C-5').

2-(10-Methyl-9,10-dihydroacridin-9-yl)benzaldehyde 7a

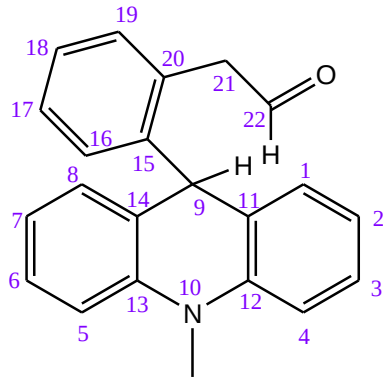


4a (0.15 g, 0.5 mmol) in methanol (120 mL) was placed into several preparative quartz cuvettes and irradiated for 60 min in a *Rayonet* RPR 100 photochemical reactor equipped with 12 lamps RPR 3000 (300 nm) and a *Rayonet* RMA-500 merry-go-round apparatus. The solution was evaporated and the resulting residue was purified by preparative TLC (*Merck* PLC silica gel 60 F_{254}, 2 mm) (BuOH/HOAc/H_2O 5mL:1mL: 2mL). The layer containing the product was removed and extracted with $CHCl_3$. After filtration the solution was concentrated under reduced pressure and purified by a second preparative TLC (*Merck* PLC silica gel 60 F_{254}, 2 mm) (cyclohexane/ ethylacetate 10:1). The layer containing the product was removed and extracted with $CHCl_3$. After filtration, the solution was evaporated *in vacuo* to afford **7a** (0.06 g, 40%). HRMS (FTMS + p ESI): *m/z*: found 298.1221; calcd. for $[M\text{-}H^-]^+$ $[C_{21}H_{16}NO]^+$ 298.1226; UV-Vis (MeCN) λ/nm: 293.

^{1}H-NMR (400 MHz, $CDCl_3$): 3.48 (s, 3H, N-CH_3), 6.27 (s, 1H, CH, H-9), 6.83 (dt, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.0 Hz, 2H, CH, H-3,6), 6.91-7.00 (m, 4H, CH, H-1,4,5,8), 7.19-7.25 (m, 2H, CH, H-2,7), 7.36-7.44 (m, 2H, CH, H-16,18), 7.49 (dt, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, CH, H-17), 7.91 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, CH, H-19), 10.32 (s, 1H, COH, H-21).

^{13}C-NMR (100 MHz, $CDCl_3$): 33.3 (N-CH_3), 42.7 (CH, C-9), 112.4 (CH, C-1,8), 120.7 (CH, C-3,6), 127.2 (CH, C-18), 127.3 (C_q, C-11,14), 127.5 (CH, C-2,7), 128.3 (CH, C-4,5), 131.7 (CH, C-16), 132.0 (CH, C-19), 133.1 (C_q, C-20), 134.4 (CH, C-17), 142.0 (C_q, C-12,13), 147.0 (C_q, C-15), 192.6 (C_q, C-21).

2-[2-(10-methyl-9,10-dihydroacridin-9-yl)phenyl]acetaldehyde 7b



4b (0.025 g, 0.08 mmol) dissolved in methanol (6 mL) was placed into a preparative quartz cuvette and irradiated for 55 min in a *Rayonet* RPR 100 photochemical reactor equipped with 12 lamps RPR 3000 (300 nm) and a *Rayonet* RMA-500 merry-go-round apparatus. The solution was evaporated and the resulting residue was dissolved in $CDCl_3$ in order to record the NMR spectra of the mixture, which consists of only **4b** and **7b**.

^{1}H-NMR (400 MHz, $CDCl_3$): 3.46 (s, 3H, N-CH_3), 3.63 (d, $^3J_{HH}$ = 2.1 Hz, 2H, CH_2, H-21), 5.36 (s, 1H, CH, H-9), 6.72 (br d, $^3J_{HH}$ = 7.5 Hz, 2H, CH, H-4,5), 6.77 (dt, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.0 Hz, 2H, CH, H-3,6), 6.93 (d, $^3J_{HH}$ = 8.3 Hz, 2H, CH, H-1,8), 7.12-7.39 (m, 6H, CH, H-2,7,16,17,18,19), 9.37 (t, $^3J_{HH}$ = 2.1 Hz, 1H, COH, H-22).

^{13}C-NMR (100 MHz, $CDCl_3$): 33.4 (N-CH_3), 45.5 (CH_2, C-21), 48.2 (CH, C-9), 112.2 (CH, C-1,8), 120.4 (CH, C-3,6), 126.6 (CH, C-18), 127.4 (CH, C-2,7), 127.5 (C_q, C-11,14), 127.8 (CH, C-4,5), 128.1 (CH, C-17), 131.4 (C_q, C-15), 132.0, 132.3 (CH, C-16,19), 142.0 (C_q, C-12,13), 142.5 (C_q, C-20), 199.4 (C_q, C-22).

Crystal structure determinations[6]

Compound **4a** was obtained in monocrystalline form by slow evaporating of the saturated diethylether solution.

Data collection for **4a** was performed at 100 K on a Stoe IPDS 2T diffractometer using Mo-K_α radiation (λ = 0.71073 Å) and a sealed tube generator with graphite monochromator as radiation source. The structure was solved by direct methods and refined by full matrix least-squares procedures based on F^2 with all measured reflections[7,8]. All non-hydrogen atoms were refined anisotropically. H atoms were introduced in their idealized positions and refined as riding.

Table 1: Experimental X-ray diffraction parameters and crystal data for **4a**

	4a
Empirical formula	$C_{21}H_{17}NO$
Formula mass	299.36
Crystal habit, color	Fragment, light brown
Crystal dim. (mm)	0.42 x 0.46 x 0.48
Crystal system	Triclinic
Space Group	*P*-1
a [Å]	10.6160(5)
b [Å]	12.2924(6)
c [Å]	12.6394(6)
α [°]	77.384(4)
β [°]	72.856(4)
γ [°]	72.749(4)
V [Å^3]	1489.62(12)
Z	4
D [g.cm^{-1}]	1.335
F000	632
μ(Mo-K_α) [cm^{-1}]	0.082
T [K]	100(2)
θ range	3.33- 29.59
Refl. collected	20471
Unique refl.	6831
R_{int}	0.0437
Reflections used	6831
Parameters refined	417
R_1	0.0371
wR_2	0.0954
GooF	1.058
Diff. peak/ hole [e/Å^3]	-.25/ .28

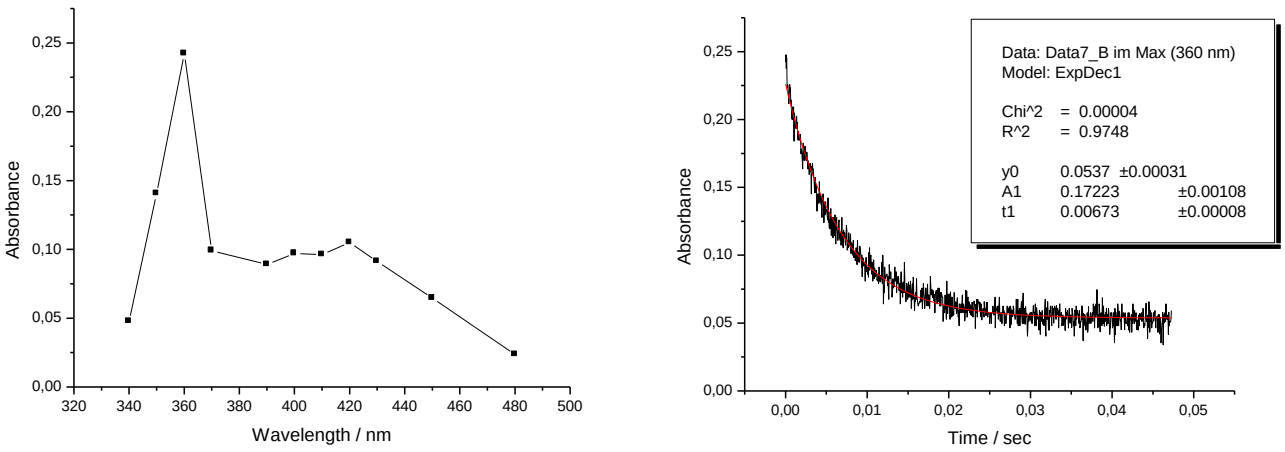


Figure S1. Transient absorption spectra observed during flash photolysis (μs-flash, cut off 330 nm) of a solution of **4a** in methanol (left panel) and the corresponding decay curve of the transient absorption at 360 nm (right).

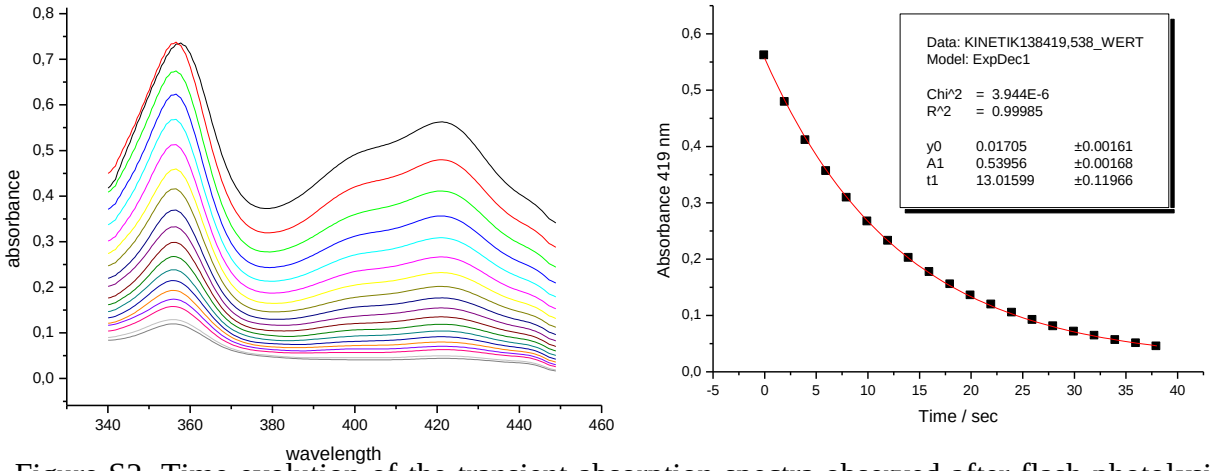


Figure S2. Time evolution of the transient absorption spectra observed after flash photolysis (μs-flash, cut off 330 nm) of a solution of **4b** in methanol (left panel) and the corresponding decay curve of the transient absorption at 419 nm (right).

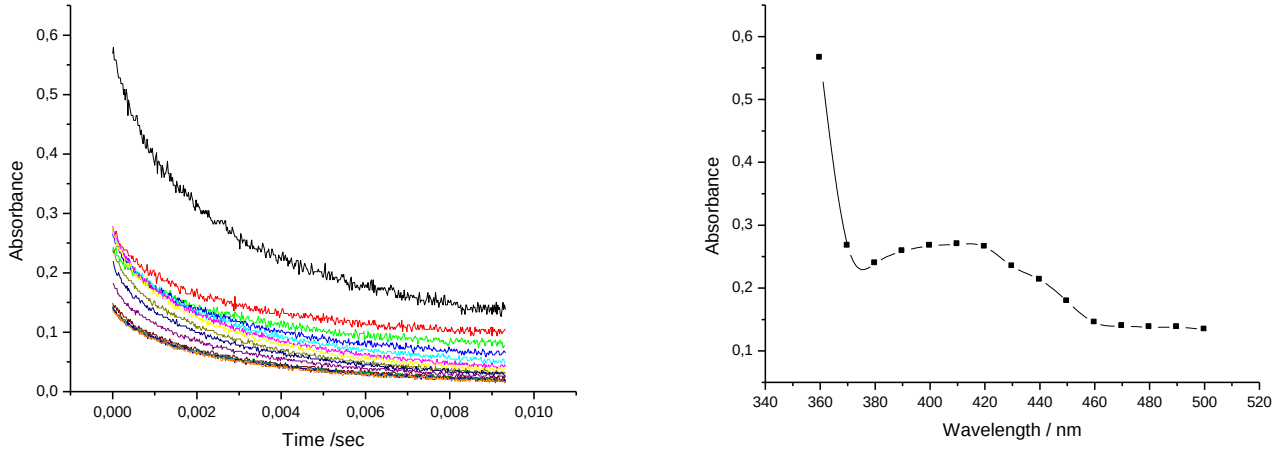


Figure S3. Decay curves of the transient absorption at different wavelengths of a solution of **4f** in methanol (left) recorded after flash photolysis (μs-flash, cut off 330 nm) and the corresponding transient absorption spectrum (right).

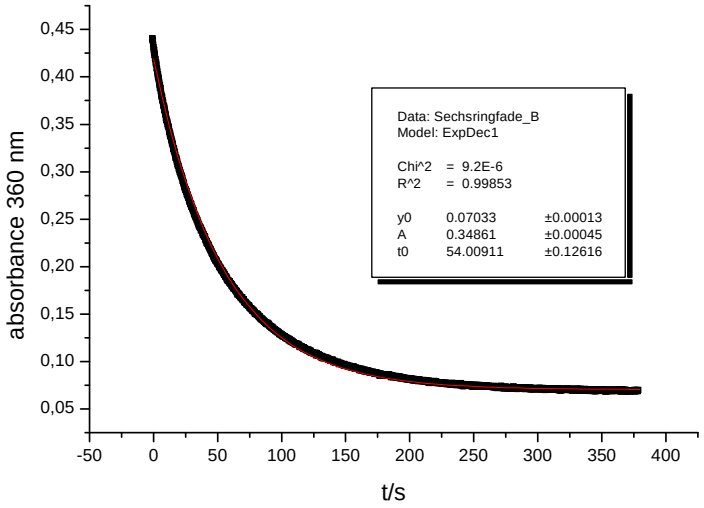


Figure S4. Decay curve of the absorbance at 360 nm recorded after irradiation of compound **4e** for 5 s (HBO 500; filter 300 nm) in acetonitrile/methanol 4:1 solution. Turnover 23%.

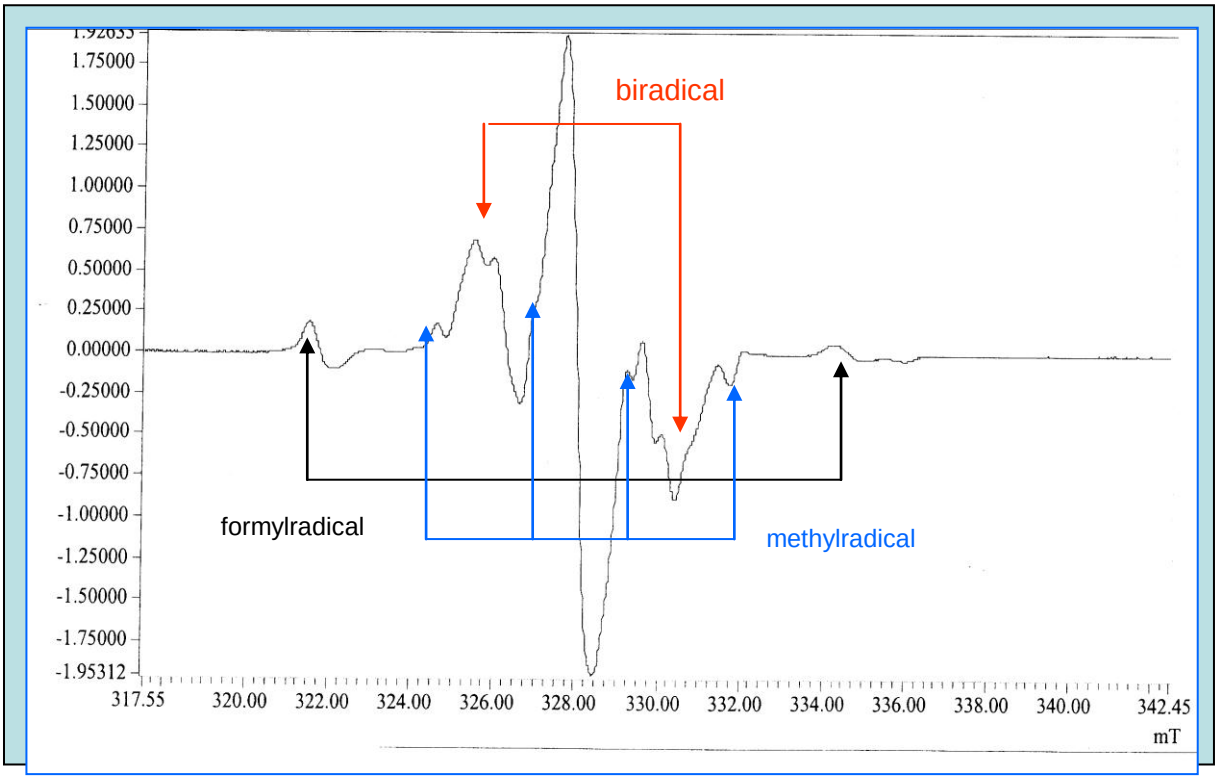


Figure S5. ESR-spectrum obtained after irradiation of **4a** in methanol solution at 77 K.

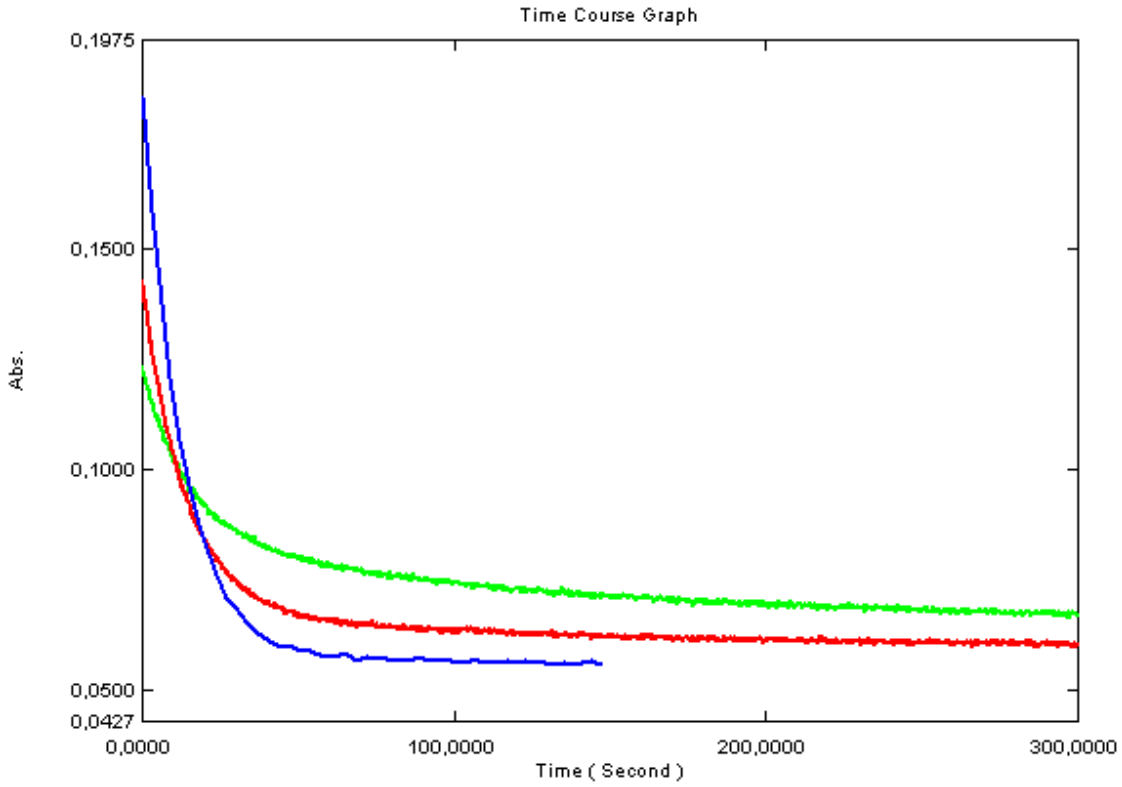


Figure S 6 Decay curves of the absorbance at 360 nm of compound **4b** in methanol solution after repeated irradiations (5 s) with light of the wavelength > 300 nm: blue – first irradiation; red – second irradiation; green – third irradiation

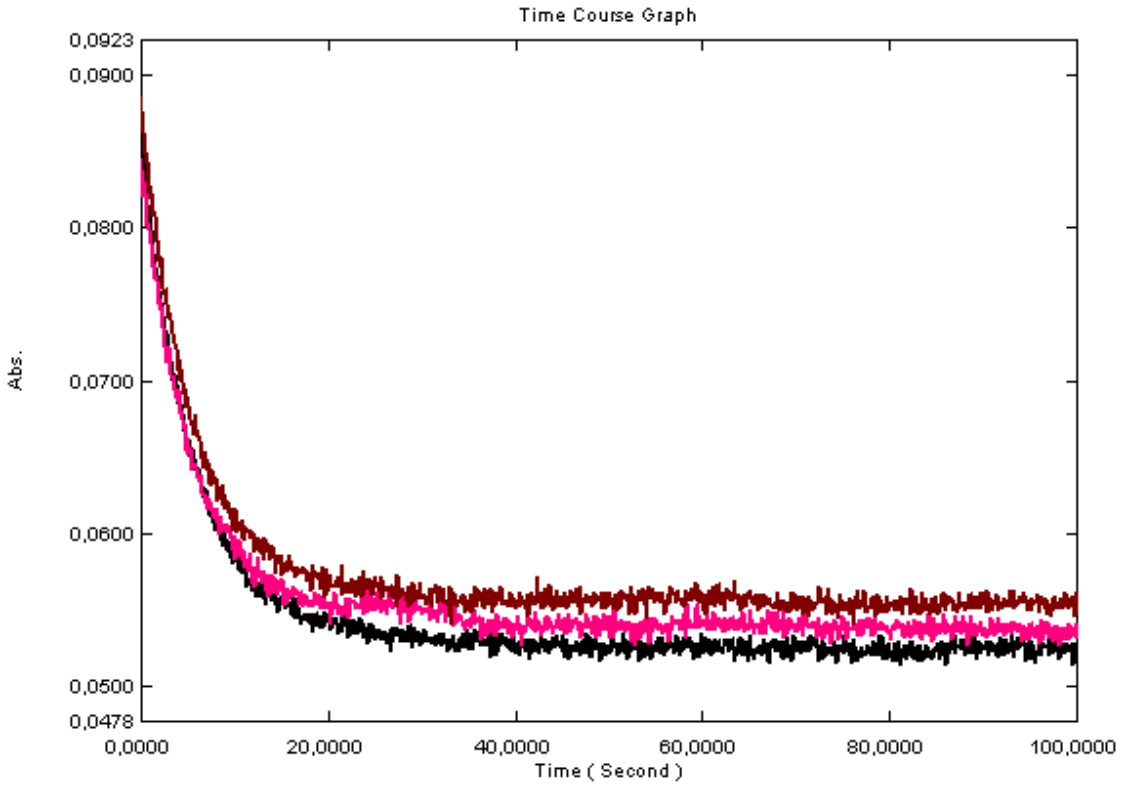


Figure S 7 Decay curves of the absorbance at 360 nm of compound **4d** in methanol solution after repeated irradiations (5 s) with light of the wavelength > 300 nm: red – first irradiation; black – fourth irradiation; brown – tenth irradiation

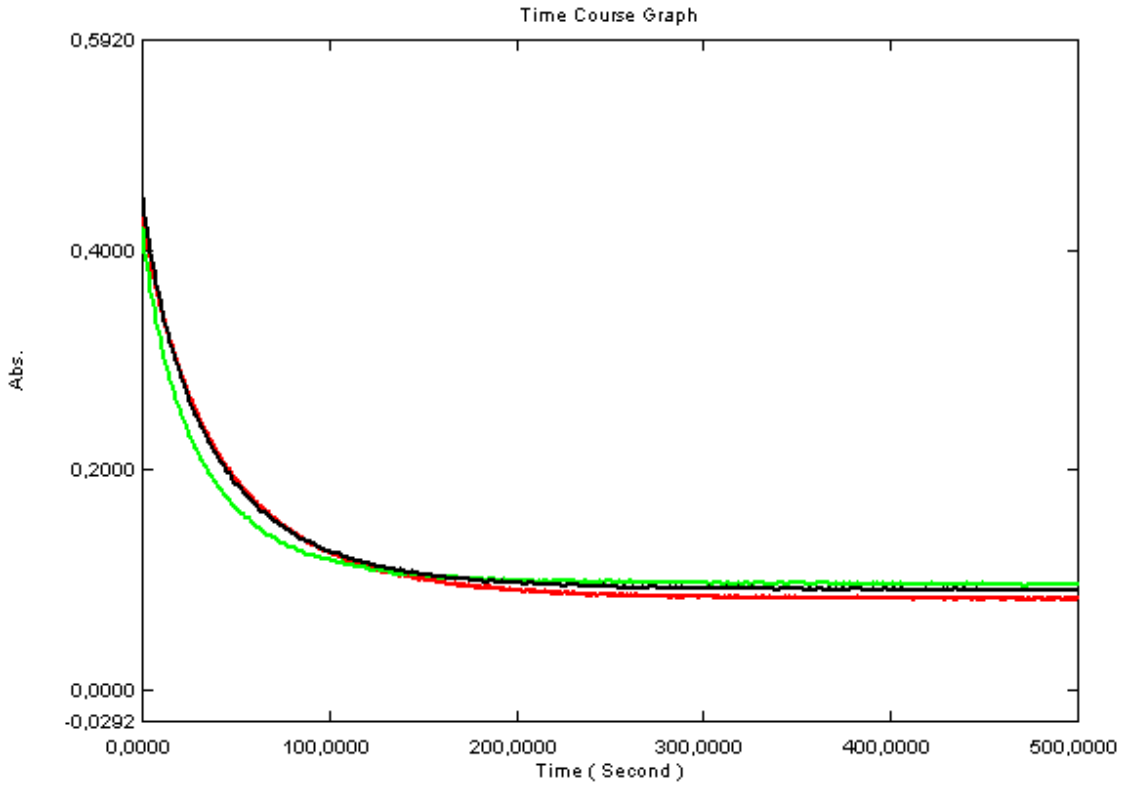


Figure S 8 Decay curves of the absorbance at 360 nm of compound **4e** in MeCN/MeOH (4:1) solution after repeated irradiations (5 s) with light of the wavelength > 300 nm: red – first irradiation; black – tenth irradiation; green – fifteenth irradiation.

References

(1) The apparatus is described in: S. Schmidt-Schäffer, L. Grubert, U. W. Grummt, K. Buck and W. Abraham, *Eur. J. Org. Chem.* **2006**, 378-398.
(2) W. Abraham, H. Otto and D. Kreysig, *J. Photochem.* **1981**, *16*, 261-266.
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(5) The method of regioselective bromination of aromatic compounds with an aqueous *tert*-butylhydroperoxide and a hydrohalic acid is described in: N.B. Barhate, A.S. Gajare, R.D. Wakharkar and A.V. Bedekar, *Tetrahedron Letters* **1998**, *39*, 6349-6350 and N.B. Barhate, A.S. Gajare, R.D. Wakharkar and A.V. Bedekar, *Tetrahedron* **1999**, *55*, 11127-11142.
(6) We express our sincere thanks to Dr. Beatrice Braun (Humboldt-University, Berlin) for these measurements.
(7) A.L. Spek, *J. Appl. Cryst.* **2003**, *36*, 7-13.
(8) G.M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112.