

## Supporting Information

### Modulation of Acridinium Organophotoredox Catalysts Guided by Photophysical Studies

Christian Fischer,<sup>‡</sup> Christoph Kerzig,<sup>‡</sup> Bouthayna Zilate, Oliver S. Wenger\* and Christof Sparr\*  
Department of Chemistry, University of Basel, Basel CH-4056, Switzerland  
oliver.wenger@unibas.ch, christof.sparr@unibas.ch

#### Table of Contents:

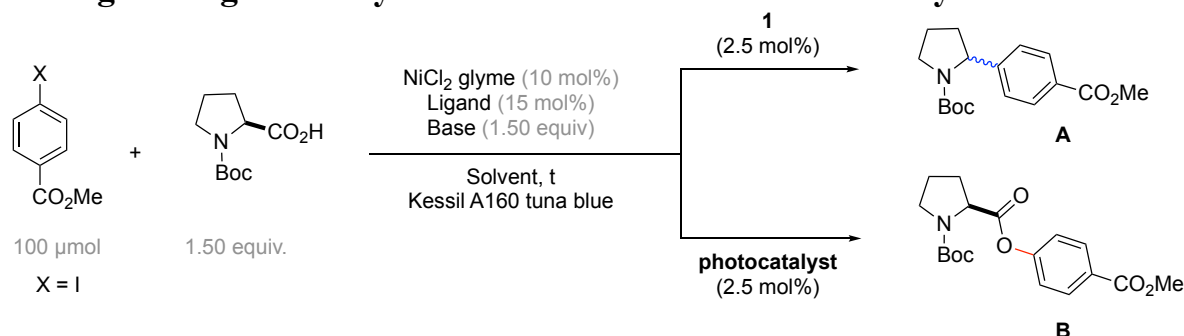
General Information	page S1 – page S2
Divergent Organocatalytic Photoredox and TTET Pathways	page S2 – page S4
DFT Calculations and Photophysical Properties of <b>1</b>	page S4 – page S6
Quenching Studies	page S6 – page S7
Precursor Synthesis	page S8 – page S11
Preparation of the Reagents <b>3a-e</b>	page S12
Direct Transformation of Esters into Acridinium Dyes <b>4a-4l</b>	page S12 – page S16
UV/VIS and Fluorescence Spectra	page S17 – page S28
Cyclic Voltammetry (CV)	page S29 – page S32
Emission Lifetime Determinations	page S33 – page S34
Quantum Mechanical Calculations of <b>4a-4l</b>	page S34
Organophotocatalytic Benchmarking Reactions	page S35 – page S37
Photostability Studies	page S38 – page S40
NMR Data	page S41 – page S61
ECD Spectroscopy	page S62 – page S63
HPLC Data	page S64 – page S82
References	page S83 – page S84

#### General Information

All reactions were carried out in dried glassware under an Ar atmosphere. *n*BuLi solution in hexanes was purchased from Acros Organics (Nr. 181271) and the concentration was determined by titration with 1,10-phenanthroline in THF against *s*BuOH according to Eastham and Watson<sup>[1]</sup>. Unless noted otherwise, all photoreactions were performed in a sealed *Biotage*<sup>®</sup> 2-5 mL microwave vial equipped with a 10 mm x 5 mm magnetic stir bar stirring at 1400 rpm. The vial was placed on a stirring plate laterally in 3 cm distance to a Kessil LED A160WE Tuna Blue, 40 W, adjusted to maximum intensity and white ( $\lambda_{\text{max}}$ : 464 nm). A sideward fan was used to keep ambient temperature (~30 °C). All starting materials and reaction solvents were purchased from

commercial sources and used without further purification. Solvents for extractions and column chromatography were technical grade. Analytical thin layer column chromatography (TLC) was performed on pre-coated Merck silica gel 60 F<sub>254</sub> plates (0.25 mm) and visualized by UV and VIS. Flash column chromatography was carried out on *Silicycle* SiliaFlash P60 (230–400 mesh) with  $\leq 0.4$  bar N<sub>2</sub> pressure. Concentration *in vacuo* was performed by rotary evaporation to  $\sim 10$  mbar at 40 °C and drying at high vacuum at  $10^{-2}$  mbar and RT. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a *Bruker Avance III* 500 MHz at 298 K in CDCl<sub>3</sub> supplied by *Cambridge Isotope Laboratories* (DLM-7TB-100S). Chemical shifts ( $\delta$ ) are reported in ppm relative to tetramethylsilane (0.00 ppm). The multiplicities are reported in Hz as: s = singlet, br = broad singlet, d = doublet, t = triplet, q = quartet and m = multiplet. Melting points were measured on a *Büchi M-565* melting point apparatus and are uncorrected. IR spectra were measured on a ATR *Varian Scimitar 800* FT-IR spectrometer and reported in cm<sup>-1</sup>. The intensities of the bands are reported as: w = weak, m = medium, s = strong. High-resolution mass spectrometry (HR-ESI) was performed by Dr. Heinz Nadig and Dr. Michael Pfeffer of the University of Basel on a *Bruker maXis 4G* QTOF ESI mass spectrometer. Cyclic Voltammetry was performed in dry, degassed 0.1 mol L<sup>-1</sup> tetra *n*butylammonium hexafluorophosphate in MeCN. Voltammograms were recorded with a *Versastat3-200* potentiostat from *Princeton Applied Research* employing a glassy carbon disk working electrode, SCE reference electrode and a silver wire counter electrode and a potential sweep rate of 0.1 Vs<sup>-1</sup>. The glassy carbon electrode and Ag wire were polished prior to measurement. UV/Vis spectroscopy was performed on a *Shimadzu UV-1650* PC spectrometer in acetonitrile using *Hellma* fluorescence cells (111-QS, light path: 10 mm). Molar absorption coefficients ( $\epsilon$ ) were determined at the wavelength of maximum absorbance ( $\lambda_{\text{abs}}$ ) and the full width at half maximum (FWHM) from the peak of maximum absorbance of a  $\sim 10$   $\mu\text{mol L}^{-1}$  dye solution. Steady-state emission spectroscopy was carried out with a *Fluorolog-3-22* instrument from *Horiba Jobin-Yvon*. Excitation occurred at the long-wavelength absorption band of the respective dye. All emission spectra were recorded in argon-saturated acetonitrile, and strongly diluted dye solutions ( $c < 15$   $\mu\text{mol L}^{-1}$ ) were used to avoid inner filter effects. All spectra so obtained were corrected for the wavelength-dependent sensitivity of the spectrometer. Additional emission spectra of the pure solvent at all excitation and detection conditions were measured to ensure the absence of stray light or impurity signals.

## Divergent Organocatalytic Photoredox and TTET Pathways



**Scheme S1:** Divergent Organocatalytic C-C and C-O Cross-Coupling Reactions

### General Procedure A:

According to a modified literature procedure.<sup>[2]</sup> Methyl 4-iodobenzoate (26.2 mg, 100  $\mu\text{mol}$ ), Boc-L-proline (32.3 mg, 150  $\mu\text{mol}$ ), NiCl<sub>2</sub>-ethylene glycol dimethyl ether complex (2.2 mg, 1.00 mol%), 2,2'-bipyridine (2.34 mg, 1.5 mol%), K<sub>2</sub>CO<sub>3</sub> (20.7 mg, 150  $\mu\text{mol}$ ) and photocatalyst (2.5 mol%, specified below) in dry DMF (volume specified below) was degassed by a stream of argon for 10 min. The reaction was performed with LED irradiation (Kessil A160 tuna blue) under argon atmosphere for the time specified below. The reaction mixture was diluted with H<sub>2</sub>O (20 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 15 mL). The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The yields were either determined by NMR analysis using 2,4,5-tetramethylbenzene as internal standard (ISTD) or by weight after column chromatography purification on silica gel with pentane: Et<sub>2</sub>O 8:1 to 4:1.

### Influence of Base:

#	Photocat.	Ligand	Base	Solvent	t	Yield A	Yield B	Remaining halide
1	1	2,2'-bpy	Cs <sub>2</sub> CO <sub>3</sub>	DMF (3 mL)	3 h	86%* <sup>[13]</sup>	-	-
2	1	2,2'-bpy	<i>i</i> PrNH <i>t</i> Bu	DMF (3 mL)	3 h	20%*	-	-
3	1	2,2'-bpy	K <sub>2</sub> CO <sub>3</sub>	DMF (6 mL)	3 h	82%*	-	-
4	Na <sub>2</sub> -Eosin Y	2,2'-bpy	Cs <sub>2</sub> CO <sub>3</sub>	DMF (3 mL)	3 h	-	14%	83%
5	Na <sub>2</sub> -Eosin Y	2,2'-bpy	<i>i</i> PrNH <i>t</i> Bu	DMF (3 mL)	3 h	-	39%	55%
6	Na <sub>2</sub> -Eosin Y	2,2'-bpy	K <sub>2</sub> CO <sub>3</sub>	DMF (3 mL)	3 h	-	30%	43%
7	-	2,2'-bpy	K <sub>2</sub> CO <sub>3</sub>	DMF (3 mL)	6 h	-	-	94%

\*Isolated yield.

## Influence of Dilution:

#	Photocat.	Ligand	Base	Solvent	t	Yield A	Yield B	Remaining halide
1	Na <sub>2</sub> -Eosin Y	2,2'-bpy	<i>i</i> PrNH <i>t</i> Bu	DMF (3 mL)	3 h	-	39%	55%
2	Na <sub>2</sub> -Eosin Y	2,2'-bpy	<i>i</i> PrNH <i>t</i> Bu	DMF (6 mL)	3 h	-	29%	66%
3	Na <sub>2</sub> -Eosin Y	2,2'-bpy	<i>i</i> PrNH <i>t</i> Bu	DMF (1 mL)	3 h	-	15%	82%

## Influence of the Organophotocatalyst:

#	Photocat.	Ligand	Base	Solvent	t	Yield A	Yield B	Remaining halide
1	Michler's Ketone	2,2'-bpy	K <sub>2</sub> CO <sub>3</sub>	DMF (3 mL)	6 h	-	59%	37%
2	Riboflavin	2,2'-bpy	K <sub>2</sub> CO <sub>3</sub>	DMF (3 mL)	6 h	5%	54%	20%
3	Rose Bengal	2,2'-bpy	K <sub>2</sub> CO <sub>3</sub>	DMF (3 mL)	6 h	-	21%	79%
4	Erythrosin	2,2'-bpy	K <sub>2</sub> CO <sub>3</sub>	DMF (3 mL)	6 h	-	38%	63%
5	Acridine Orange Base	2,2'-bpy	K <sub>2</sub> CO <sub>3</sub>	DMF (3 mL)	6 h	3%	78%	11%
6	4,4'-(OMe) <sub>2</sub> -Benzophenone	2,2'-bpy	K <sub>2</sub> CO <sub>3</sub>	DMF (3 mL)	6 h	-	13%	87%
7	Benzophenone	2,2'-bpy	K <sub>2</sub> CO <sub>3</sub>	DMF (3 mL)	6 h	-	17%	80%
8	3,6-Diamino-acridine HCl	2,2'-bpy	K <sub>2</sub> CO <sub>3</sub>	DMF (3 mL)	6 h	2%	57%	41%
9	Methylene Blue Hydrate	2,2'-bpy	K <sub>2</sub> CO <sub>3</sub>	DMF (3 mL)	6 h	-	81%	14%
10	9-Fluorenone	2,2'-bpy	K <sub>2</sub> CO <sub>3</sub>	DMF (3 mL)	6 h	5%	18%	71%
11	9H-Thioxanthene-9-one	2,2'-bpy	K <sub>2</sub> CO <sub>3</sub>	DMF (3 mL)	6 h	-	93%	-
12	Xanthone	2,2'-bpy	K <sub>2</sub> CO <sub>3</sub>	DMF (3 mL)	6 h	-	4%	97%
13	Cresyl Violet ClO <sub>4</sub> <sup>-</sup>	2,2'-bpy	K <sub>2</sub> CO <sub>3</sub>	DMF (3 mL)	6 h	-	3%	83%
14	Rhodamine B	2,2'-bpy	K <sub>2</sub> CO <sub>3</sub>	DMF (3 mL)	6 h	-	40%	58%
15	Nile Blue Cl <sup>-</sup>	2,2'-bpy	K <sub>2</sub> CO <sub>3</sub>	DMF (3 mL)	6 h	-	4%	93%
16	Rhodamine 6G	2,2'-bpy	K <sub>2</sub> CO <sub>3</sub>	DMF (3 mL)	6 h	5%	61%	25%
17	Fukuzumi's cat.	2,2'-bpy	K <sub>2</sub> CO <sub>3</sub>	DMF (3 mL)	6 h	-	-	84%
18	9-Mesityl-2,7-dimethyl-10-phenylacridinium tetrafluoroborate	2,2'-bpy	K <sub>2</sub> CO <sub>3</sub>	DMF (3 mL)	6 h	10%	16%	-

## Ligand Screening:

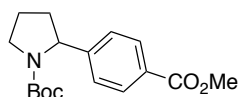
#	Photocat.	Ligand	Base	Solvent	t	Yield A	Yield B	Remaining halide
1	Na <sub>2</sub> -Eosin Y	2,2'-bpy	<i>i</i> PrNH <i>t</i> Bu	DMF (3 mL)	3 h	-	39%	55%
2	Na <sub>2</sub> -Eosin Y	dtbbpy	<i>i</i> PrNH <i>t</i> Bu	DMF (3 mL)	3 h	-	45%	52%
3	Na <sub>2</sub> -Eosin Y	1,10-phen	<i>i</i> PrNH <i>t</i> Bu	DMF (3 mL)	3 h	-	21%	77%
4	Na <sub>2</sub> -Eosin Y	dppf	<i>i</i> PrNH <i>t</i> Bu	DMF (3 mL)	3 h	-	-	-
5	Na <sub>2</sub> -Eosin Y	Box-Lig. <sup>a)</sup>	<i>i</i> PrNH <i>t</i> Bu	DMF (3 mL)	3 h	-	<4%	91%
6	Na <sub>2</sub> -Eosin Y	-	<i>i</i> PrNH <i>t</i> Bu	DMF (3 mL)	3 h	-	3%	93%

a) (+)-2,2'-Isopropylidenebis[(4*R*)-4-phenyl-2-oxazoline]

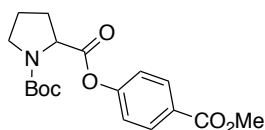
## Influence of the Reaction Time:

#	Photocat.	Ligand	Base	Solvent	t	Yield A	Yield B	Remaining halide
1	Na <sub>2</sub> -Eosin Y	dtbbpy	<i>i</i> PrNH <i>t</i> Bu	DMF (3 mL)	3 h	-	45%	52%
2	Na <sub>2</sub> -Eosin Y	2,2'-bpy	<i>i</i> PrNH <i>t</i> Bu	DMF (3 mL)	3 h	-	39%	55%
4	Na <sub>2</sub> -Eosin Y	2,2'-bpy	<i>i</i> PrNH <i>t</i> Bu	DMF (3 mL)	12 h	-	58%	38%
5	Na <sub>2</sub> -Eosin Y	dtbbpy	<i>i</i> PrNH <i>t</i> Bu	DMF (3 mL)	18 h	-	80%	6%
3	Na <sub>2</sub> -Eosin Y	2,2'-bpy	K <sub>2</sub> CO <sub>3</sub>	DMF (3 mL)	3 h	-	30%	43%
6	Na <sub>2</sub> -Eosin Y	dtbbpy	K <sub>2</sub> CO <sub>3</sub>	DMF (3 mL)	18 h	-	80%*	-
7	<b>Na<sub>2</sub>-Eosin Y</b>	<b>2,2'-bpy</b>	<b>K<sub>2</sub>CO<sub>3</sub></b>	<b>DMF (3 mL)</b>	<b>18 h</b>	-	<b>96%<sup>a)</sup></b>	-
8	Na <sub>2</sub> -Eosin Y	2,2'-bpy	K <sub>2</sub> CO <sub>3</sub>	DMF (3 mL)	6 h	-	59%	39%

\*Isolated yield. a) two lamps were used.

**tert-Butyl 2-(4-(methoxycarbonyl)phenyl)pyrrolidine-1-carboxylate (A):****A**

Colorless oil:  $R_f$  0.29 (pentane:Et<sub>2</sub>O 4:3); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) rotameric mixture:  $\delta$  = 7.97–7.99 (2H, m, C3'*H*, C5'*H*), 7.23–7.25 (2H, m, C2'*H*, C6'*H*), 4.98 and 4.80 (1H, 2 br, C2*H*), 3.91 (1H, s, CO<sub>2</sub>CH<sub>3</sub>), 3.51–3.66 (2H, m, C5*H*<sub>2</sub>), 2.30–2.38 (1H, m, C3*H*), 1.78–1.92 (3H, m, C3*H*, C4*H*<sub>2</sub>), 1.46 (3H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.17 (6H, s, C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) rotameric mixture, resonances of minor rotamer in parenthesis “{}”:  $\delta$  = 167.0 (CO<sub>2</sub>CH<sub>3</sub>), 154.4 (CO<sub>2</sub>*t*Bu), 150.6 {149.6} (C1'), {129.8} 129.6 (C3', C5'), 128.5 (C4'), 125.5 (C2', C6'), 79.5 (C(CH<sub>3</sub>)<sub>3</sub>), 61.2 {60.7} (C2), 52.0 (CO<sub>2</sub>CH<sub>3</sub>), {47.4} 47.2 (C5), 36.0 {34.8} (C3), {28.5} 28.2 (C(CH<sub>3</sub>)<sub>3</sub>), {23.6} 23.3 (C4); Analytical data is in agreement with literature data.<sup>[2b]</sup>

**1-(tert-Butyl) 2-(4-(methoxycarbonyl)phenyl) pyrrolidine-1,2-dicarboxylate (B):****B**

White solid (m.p. 72.8–74.6 °C):  $R_f$  0.29 (pentane:Et<sub>2</sub>O 4:3);  $\nu_{\max}$  (neat): 2979w, 1770w, 1706s, 1605w, 1392s, 1279s, 1162s, 1109s, 1015m, 923w, 874w, 765m, 698w; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) rotameric mixture:  $\delta$  = 8.05–8.10 (2H, m, C3'*H*, C5'*H*), 7.17–7.21 (2H, m, C2'*H*, C6'*H*), 4.52–4.54 and 4.45–4.47 (1H, m, C2*H*), 3.92 and 3.91 (3H, s, CO<sub>2</sub>CH<sub>3</sub>), 3.44–3.66 (2H, m, C5*H*<sub>2</sub>), 2.31–2.44 (1H, m, C3*H*<sub>2</sub>), 2.13–2.21 (1H, m, C3*H*<sub>2</sub>), 2.02–2.09 (1H, m, C4*H*<sub>2</sub>), 1.93–1.99 (1H, m, C4*H*<sub>2</sub>), 1.48 and 1.46 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) rotameric mixture, resonances of minor rotamer in parenthesis “{}”:  $\delta$  = {171.2} 171.1 (CO<sub>2</sub>Ar), {166.4} 166.2 (CO<sub>2</sub>CH<sub>3</sub>), {154.5} 154.2 (C1'), 153.7 (CO<sub>2</sub>*t*Bu), 131.3 {131.2} (C3', C5'), 127.9 {127.7} (C4'), {121.6} 121.2 (C2', C6'), 80.4 {80.2} (C(CH<sub>3</sub>)<sub>3</sub>), 59.2 {59.1} (C2), 52.3 {52.2} (CO<sub>2</sub>CH<sub>3</sub>), {46.7} 46.5 (C5), 31.1 {30.0} (C3), 28.4 (C(CH<sub>3</sub>)<sub>3</sub>), {24.6} 23.7 (C4); ESI-MS:  $m/z$  calcd. for C<sub>18</sub>H<sub>23</sub>NNaO<sub>5</sub><sup>+</sup> 372.1418 found 372.1423 [M+Na<sup>+</sup>]. e.r. = 99: 1, see HPLC Data.

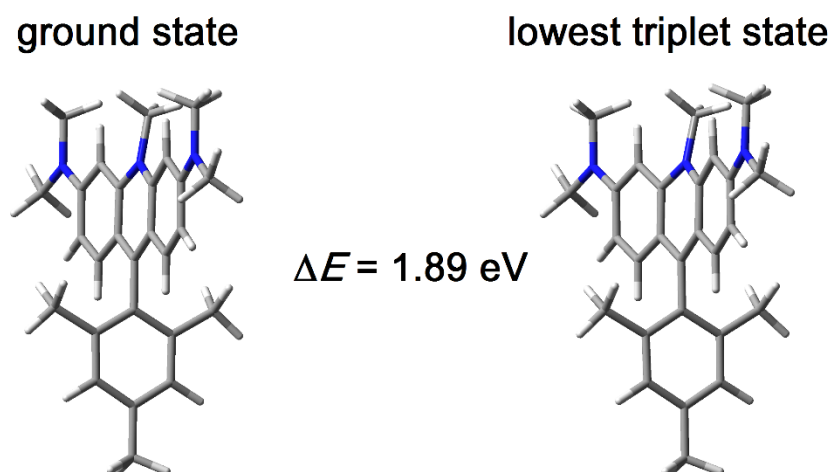
**DFT Calculations and Photophysical Properties of 1****1. DFT Calculations**

All DFT calculations were carried out with the Gaussian 09 package<sup>[3]</sup> using the B3LYP functional combined with the 6-31+G(d,p) basis set. The solvation model was IEFPCM with acetonitrile as solvent.

The geometry optimizations of the Fukuzumi catalyst and all acridinium dyes under study (see p. S34) were accompanied by frequency analyses. The optimized structures used for further investigations did not show negative vibrational frequencies, indicating convergence on minimum structures. The orbitals of the singlet ground states were obtained by additional single-point calculations with population analyses.

Starting from the energy-minimized singlet ground state geometries, the corresponding lowest triplet states were optimized. An example for the resulting singlet and triplet geometries is given in Figure S2 (compound **1**, the only discernible difference between both structures is the less planar acridinium moiety in the triplet state). The triplet state energies were determined simply by comparing the energies of both optimized structures for a given dye as exemplified in Figure S2 for compound **1**. The theoretical triplet energy of **1** so obtained (1.89 eV) is practically identical to the value determined by triplet-triplet energy transfer experiments (1.91 eV, see section 2. for details).





**Figure S2:** Optimized structures of the ground state as well as the lowest triplet state of **1** at the B3LYP/6-31+G(d,p) level of theory and the solvation model IEFPCM for acetonitrile, together with their energy difference. For details, see text.

## 2. Laser Flash Photolysis

All laser flash photolysis (LFP) studies with UVVis detection of transient species were carried out with the same setup as in a recent investigation.<sup>[4]</sup> Briefly, an LP920-KS apparatus (Edinburgh Instruments) equipped with a frequency-doubled Nd:YAG laser (Quantel Brilliant b, 532 nm output, ca. 10 ns pulse width) was employed; suitable optics were used to ensure homogeneous excitation in the detection volume; transient absorption spectra were monitored with an iCCD camera, single-wavelength kinetics using a photomultiplier tube.

The transient absorption (TA) spectrum of acridinium catalyst **1** in Ar-saturated acetonitrile upon 532 nm excitation is displayed in Fig. 2 of the main paper. After a detection delay time ensuring complete excited singlet decay (500 ns), the TA spectrum consists of a pronounced ground-state bleach centered at about 500 nm and broad absorption bands peaking at ~615 and ~400 nm. Both ground state bleach and new (positive) absorption signals decay monoexponentially with the same time constant (330  $\mu\text{s}$ ), as exemplified in the lower inset of Fig. 2. To identify the long-lived intermediate derived from **1**, we studied its reactivity towards aromatic hydrocarbons. In the presence of anthracene, we observed diffusion-controlled ( $k = 1.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) quenching and formation of the anthracene triplet with its characteristic spectrum<sup>[4,5]</sup> shown in the upper inset of Fig. 2. The only possible pathway leading to triplet anthracene formation is a triplet-triplet energy transfer (TTET) through the Dexter mechanism,<sup>[6,7]</sup> with the triplet state of **1** (**<sup>3</sup>1**) as triplet energy donor. Taking the known molar absorption coefficient of triplet anthracene in polar organic solvents (55000  $\text{M}^{-1} \text{ cm}^{-1}$  at 420 nm)<sup>[5]</sup> we determined the triplet anthracene concentration produced via TTET under conditions of quantitative energy transfer from **<sup>3</sup>1** (0.4 mM anthracene). The comparison of that quantity with the initial concentration of singlet-excited **1** generated by the green laser pulse (measured with  $[\text{Ru}(\text{bpy})_3]^{2+}$  in water using relative actinometry; see ref. <sup>[8]</sup> for a detailed description of that methodology) directly gave the triplet quantum yield of **1**, which amounts to 7%.

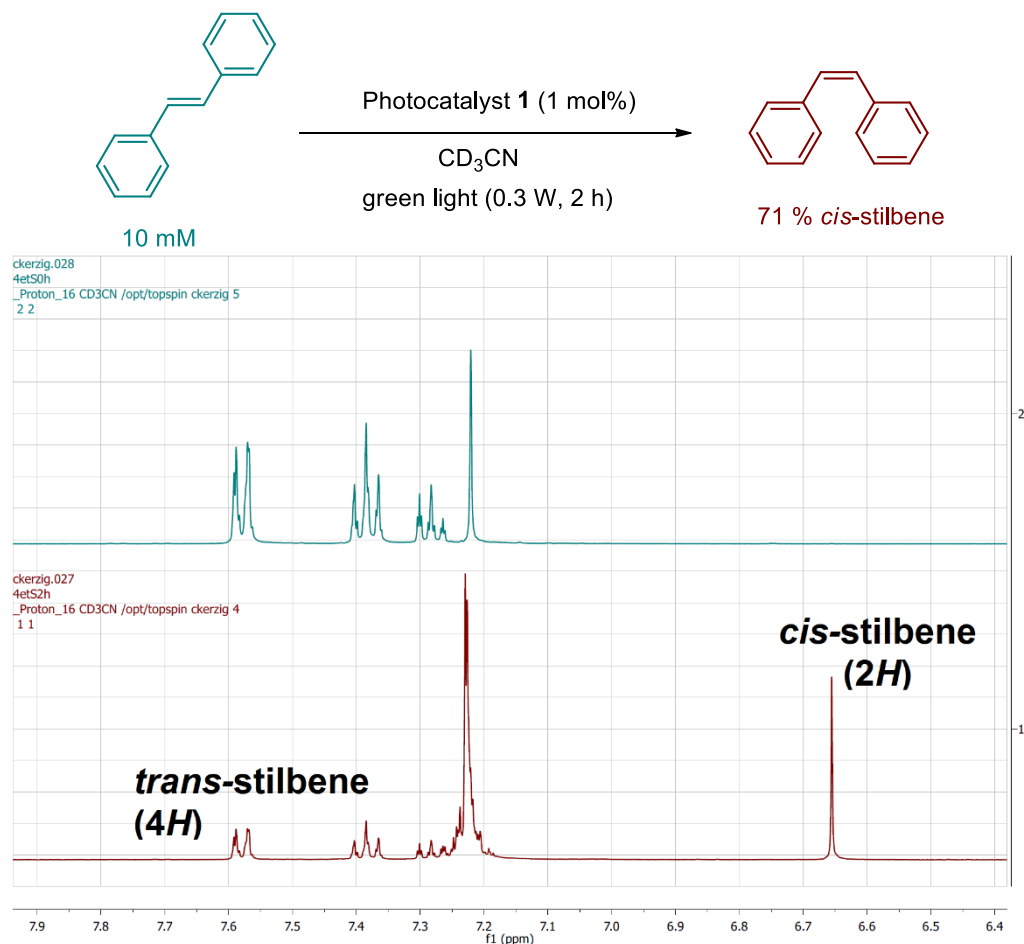
The observation of a diffusion-controlled TTET between **<sup>3</sup>1** and anthracene allows to set a lower limit for the triplet energy of the acridinium dye **1**, i.e., the triplet energy measured for anthracene (1.84 eV)<sup>[6]</sup>. Moreover, pyrene (triplet energy, 2.09 eV)<sup>[6]</sup> was employed as quencher. Quenching of **<sup>3</sup>1** and triplet pyrene<sup>[4,9]</sup> formation was indeed observed, but the TTET rate constant significantly decreases to about  $1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  (kinetic transient absorption measurements on the quenching rate constant were carried out with 615 nm detection of **<sup>3</sup>1**, because the pyrene triplet is practically transparent at that wavelength<sup>[9]</sup>). Using the well-established relation between TTET rate constants and donor-acceptor triplet energy differences,<sup>[7]</sup> we estimate the triplet energy of **1** to be  $1.91 \pm 0.02 \text{ eV}$ .

## 3. Stilbene Isomerization

The rather high triplet energy of catalyst **1**, combined with its long triplet lifetime and a noticeable triplet population quantum yield (7%, see above), encouraged us to test a typical triplet-sensitized photoreaction. The triplet state of *trans*-stilbene (2.13 eV) has a similar energy as the pyrene triplet (2.09 eV),<sup>[6]</sup> which we could already populate through a triplet-triplet energy transfer (section 2.), whereas the *cis*-stilbene triplet state (triplet energy, 2.35 eV)<sup>[6]</sup> cannot be generated with **1** as triplet energy donor for thermodynamic reasons. Therefore, we tested the feasibility of the triplet-sensitized *trans*-to-*cis* photoisomerization of stilbene<sup>[10,11]</sup> (Figure S3).

A solution of *trans*-stilbene (10 mM) and **1** (0.1 mM) in 3.0 mL  $\text{CD}_3\text{CN}$  was deoxygenated with argon for five minutes in a cuvette equipped with septum cap. The reaction mixture was irradiated with a 532 nm light source

(DPSS cw laser from Roithner Lasertechnik, 300 mW optical output, that light source was selected for comparability with the LFP measurements) at room temperature under water cooling. Conversion of *trans*- to *cis*-stilbene was monitored by  $^1\text{H}$  NMR spectroscopy (Figure S3). *Cis*-stilbene, whose NMR data are in agreement with those presented in ref. [12], is the only detectable product produced upon illumination, and we observed a *cis*-to-*trans* ratio of 2.4 (using the NMR integrals of the highlighted signals in the lower spectrum presented in Figure S3), corresponding to 71% yield of the desired *cis* isomer.



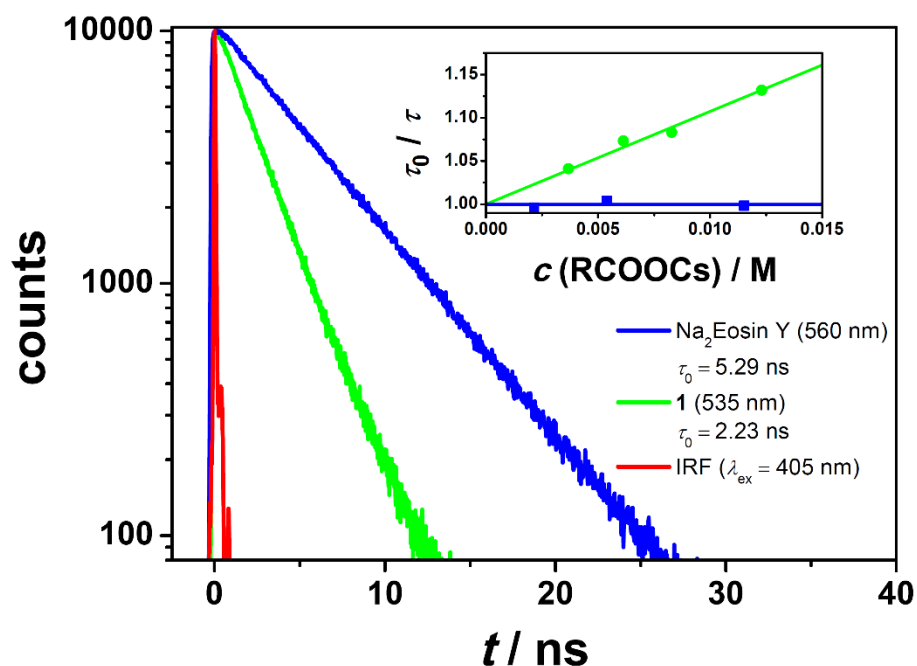
**Figure S3:**  $^1\text{H}$  NMR spectra (400 MHz) before (upper spectrum) and after (lower spectrum) the photoisomerization of *trans*-stilbene catalyzed by acridinium dye **1** under the conditions given at the reaction equation. The integrals of the aromatic signal of the *trans* isomer at 7.58 ppm and the olefinic protons of the *cis* form at 6.66 ppm have been used for quantification.

The results of that section clearly demonstrate that acridinium dyes can also catalyze triplet-sensitized reactions with attractive turnover numbers (71 under the conditions of Figure S3).

## Quenching Studies

Quenching studies were performed on a LifeSpec II apparatus (time-correlated single photon counting technique) from Edinburgh Instruments using picosecond pulsed diode lasers for excitation at either 405 nm (*ca.* 60 ps pulse width) or 473 nm (*ca.* 75 ps pulse width). Strongly diluted (< 50  $\mu\text{M}$ ) deoxygenated dye solutions were used for all measurements of this section. The emission traces were recorded with at least 3000 peak counts. Freshly prepared dye solutions (protected from light) have been used for all TCSPC experiments.

In addition to the Stern-Volmer quenching studies in DMF (Fig. 3 of the main paper), we investigated emission quenching of eosin Y and acridinium catalyst **1** in MeCN, using the cesium salt of Boc-L-proline as quencher (Figure S4).



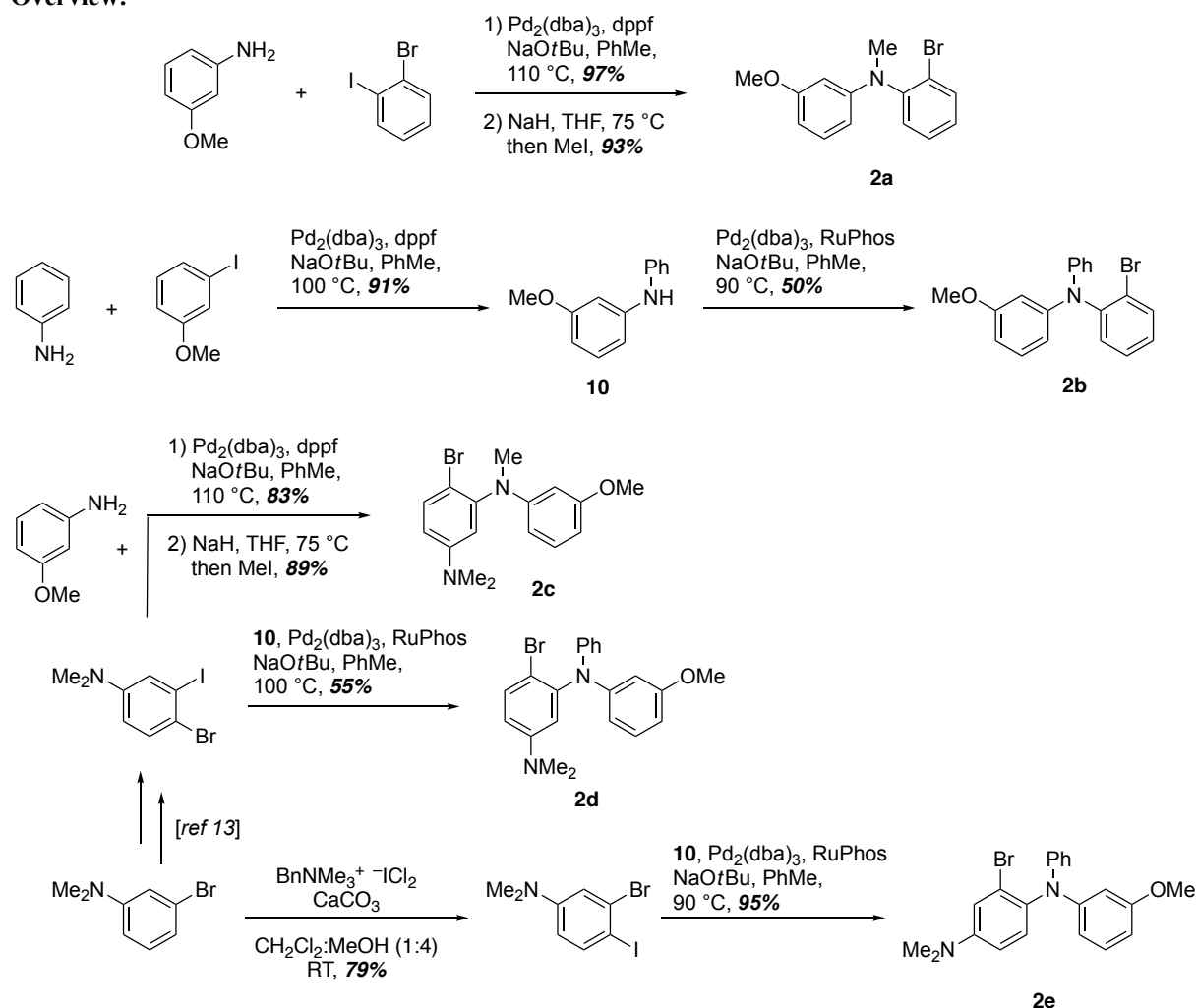
**Figure S4:** Fluorescence quenching studies of **1** and eosin Y in deoxygenated MeCN upon 405 nm excitation. Main plot, response function of the TCSPC instrument (IRF) and unquenched lifetimes of both emitters. Inset, Stern-Volmer plots using the Cs-salt of Boc-L-proline (RCOOCs) as quencher.

Rate constants for the quenching of singlet-excited **1** close to the diffusion limit ( $5.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and  $4.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  in DMF and MeCN, respectively) were obtained from the Stern-Volmer plots and the unquenched emission lifetimes (1.6 ns in DMF and 2.2 ns in MeCN). Quenching of excited eosin Y by Boc-L-proline is slower by a factor of at least 50 ( $< 1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  in both solvents). Considering the very similar oxidative power of the singlet-excited states of both fluorophores –  $E_{1/2}(\mathbf{1}^*/\mathbf{1}^-) = +1.25 \text{ V}^{[13]}$  and  $E_{1/2}(\text{eosin Y}^*/\text{eosin Y}^-) = +1.24 \text{ V}^{[14,15]}$  (both vs SCE). – the divergent rate constants for the oxidative decarboxylation, which requires a potential of +0.95 V vs SCE,<sup>[16]</sup> are highly surprising at first glance.

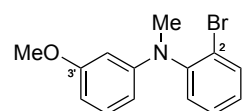
Coulomb interactions might provide an explanation for the substantially different kinetic reactivities of both singlet-excited organic dyes. Assuming complete dissociation of all salts in the polar organic solvents used as reaction medium (which is substantiated by the quenching rate constant independence of the carboxylate counter ion; see Fig. 3 of the main paper for details), and point charges for both the organic dyes (acridinium catalyst **1**, +1; eosin Y, -2) and the quencher (-1), the influence of Coulomb interactions on the quenching rate constants<sup>[17–19]</sup> can be estimated. With a typical reaction distance of 6 Å for electron transfer quenching and a relative solvent permittivity of 37.5, the Debye formula<sup>[17]</sup> predicts a 30-fold acceleration of the diffusion between **1** and our negatively charged quencher, whereas only a 3-fold deceleration for the diffusion-controlled reaction between eosin Y and the Boc-L-proline carboxylate can be estimated. In other words, Coulomb interactions could fully account for the observed quenching rate constant differences, leading to other main products in a photocatalytic reaction under otherwise identical conditions (see Scheme 1 of the main paper and corresponding text).

## Precursor Synthesis

## Overview:



Scheme S5: Overview of the synthesis of reagent precursor 2a-e.

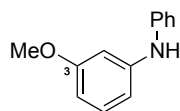
2-Bromo-*N*-(3-methoxyphenyl)-*N*-methylaniline (2a):

To a degassed mixture of tris(dibenzylideneacetone)dipalladium(0) (458 mg, 500  $\mu\text{mol}$ ), 1,1'-ferrocenediyl-bis(diphenylphosphine) (554 mg, 1.00 mmol) and sodium *tert*-butoxide (2.88 g, 30.0 mmol) in toluene (25 mL) at RT was added *m*-anisidine (2.24 mL, 20.0 mmol) and 1-bromo-2-iodobenzene (2.57 mL, 20.0 mmol). The mixture was stirred at  $110^\circ\text{C}$  for 12 h, then cooled to RT, diluted with water (200 mL), extracted with  $\text{CH}_2\text{Cl}_2$  (4 x 250 mL) and dried over  $\text{Na}_2\text{SO}_4$  and concentrated *in vacuo*. Column chromatography over silica gel with eluent pentane: $\text{CH}_2\text{Cl}_2$  1:1 to 1:2 gave 2-bromo-*N*-(3-methoxyphenyl)aniline as a yellowish oil (5.40 g, 97%):  $R_f$  0.53 ( $\text{CH}_2\text{Cl}_2$  100%);  $\nu_{\text{max}}$  (neat): 3395w, 2955w, 2833w, 1583s, 1512m, 1491s, 1467s, 1450m, 1306m, 1273m, 1196m, 1155s, 1042m, 1021m, 960w, 840w, 740s, 688m;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.52 (1H, dd,  $^3J$  8.0,  $^4J$  1.5, C3H), 7.29 (1H, dd,  $^3J$  8.2,  $^4J$  1.6, C6H), 7.19–7.14 (1H, m, C5'H), 7.15–7.18 (1H, m, C5H), 6.72–6.76 (2H, m, C4H, C6'H), 6.70–6.71 (1H, m, C2'H), 6.58 (1H, ddd,  $^3J$  8.3,  $^4J$  2.5, 0.8, C4'H), 6.06 (1H, br, NH), 3.79 (3H, s, OCH<sub>3</sub>);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  = 143.0 (C1'), 141.1 (C1), 133.0 (C3), 130.2 (C5'), 128.1 (C3), 121.2 (C4), 116.5 (C6), 112.5 (C2), 112.4 (C6'), 108.0 (C4'), 105.7 (C2'), 55.3 (OCH<sub>3</sub>); ESI-MS:  $m/z$  calcd. for  $\text{C}_{13}\text{H}_{13}\text{BrNO}^+$  278.0175 found 278.0176 [ $\text{M}+\text{H}^+$ ].

To a solution of 2-bromo-*N*-(3-methoxyphenyl)aniline (1.39 g, 5.00 mmol) in THF (15 mL) at RT was added sodium hydride (60% dispersion in mineral oil, 550 mg, 13.8 mmol). The suspension was heated to  $75^\circ\text{C}$  and stirred for 30 min at this

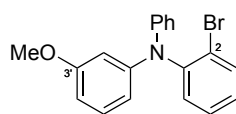
temperature. Iodomethane (0.716 mL, 11.5 mmol) was added within 5 min at 75 °C and the reaction mixture was continued to stir for 2 h at this temperature. The suspension was treated with water (20 mL) and extracted with Et<sub>2</sub>O (4 x 50 mL). The combined organic layer was washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. Column chromatography on silica gel with pentane 100% to pentane:CH<sub>2</sub>Cl<sub>2</sub> 1:1 gave 2-bromo-*N*-(3-methoxyphenyl)-*N*-methylaniline (**2a**) as a colorless oil (1.36 g, 93%): *R*<sub>f</sub> 0.61 (pentane:CH<sub>2</sub>Cl<sub>2</sub> 1:1); *v*<sub>max</sub> (neat): 2937w, 2833w, 1610s, 1577s, 1492s, 1464s, 1347w, 1278w, 1212s, 1168s, 1135m, 1039s, 931w, 828w, 755s, 730s, 687s; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.67 (1H, dd, <sup>3</sup>*J* 8.0, <sup>4</sup>*J* 1.4, C3*H*), 7.34 (1H, ddd, <sup>3</sup>*J* 7.9, 7.3, <sup>4</sup>*J* 1.5, C5*H*), 7.27 (1H, dd, <sup>3</sup>*J* 7.9, <sup>4</sup>*J* 1.7, C6*H*), 7.14 (1H, ddd, <sup>3</sup>*J* 8.0, 7.3, <sup>4</sup>*J* 1.7, C4*H*), 7.07–7.11 (1H, m, C5'*H*), 6.33 (1H, ddd, <sup>3</sup>*J* 8.1, <sup>4</sup>*J* 2.4, 0.7, C4'*H*), 6.17 (1H, ddd, <sup>3</sup>*J* 8.2, <sup>4</sup>*J* 2.4, 0.7, C6'*H*), 6.13 (1H, t, <sup>4</sup>*J* 2.4, C2'*H*), 3.74 (3H, s, OCH<sub>3</sub>), 3.22 (3H, s, NCH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  = 160.6 (C3'), 149.9 (C1'), 146.7 (C1), 134.1 (C3), 130.6 (C6), 129.6 (C5'), 128.9 (C5), 127.9 (C4), 124.3 (C2), 106.5 (C6'), 102.3 (C4'), 99.9 (C2'), 55.1 (OCH<sub>3</sub>), 39.0 (NCH<sub>3</sub>); ESI-MS: *m/z* calcd. for C<sub>14</sub>H<sub>15</sub>BrNO<sup>+</sup> 292.0332 found 292.0333 [M+H<sup>+</sup>].

### 3-Methoxy-*N*-phenylaniline (**10**):



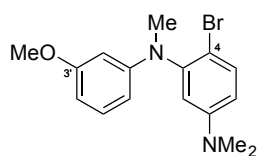
To a degassed mixture of tris(dibenzylideneacetone)dipalladium(0) (275 mg, 300  $\mu$ mol), 1,1'-ferrocenediyl-bis(diphenylphosphine) (333 mg, 600  $\mu$ mol) and sodium *tert*-butoxide (1.73 g, 18.0 mmol) in toluene (16 mL) at RT was added aniline (1.64 mL, 18.0 mmol) and 3-iodoanisole (1.43 mL, 12.0 mmol). The mixture was stirred at 100 °C for 1.5 h, then cooled to RT, diluted with water (120 mL), extracted with CH<sub>2</sub>Cl<sub>2</sub> (4 x 150 mL) and dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. Column chromatography over silica gel with eluent pentane:CH<sub>2</sub>Cl<sub>2</sub> 2:1 to 1:1 gave 3-methoxy-*N*-phenylaniline as a grey solid (2.18 g, 91%, m.p. 67.8–69.5 °C): *R*<sub>f</sub> 0.40 (pentane:CH<sub>2</sub>Cl<sub>2</sub> 1:1); *v*<sub>max</sub> (neat): 3380m, 3052w, 2998w, 2839w, 1585s, 1492s, 1451s, 1305m, 1263s, 1239m, 1200m, 1176m, 1157m, 1087w, 1033m, 953m, 895w, 834m, 779s, 738m, 688s; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.25–7.28 (2H, m, C3'*H*, C5'*H*), 7.15–7.18 (1H, m, C5*H*), 7.08–7.10 (2H, m, C2'*H*, C6'*H*), 6.92–6.96 (1H, m, C4'*H*), 6.63–6.66 (2H, m, C2'*H*, C6*H*), 6.47–6.49 (1H, m, C4*H*), 5.73 (1H, br, NH), 3.78 (3H, s, NCH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  = 160.7 (C3), 144.6 (C1), 142.8 (C1'), 130.1 (C5), 129.3 (C3', C5'), 121.3 (C4'), 118.4 (C2', C6'), 110.2 (C6), 106.2 (C4), 103.3 (C2), 55.2 (OCH<sub>3</sub>); ESI-MS: *m/z* calcd. for C<sub>13</sub>H<sub>14</sub>NO<sup>+</sup> 200.1070 found 200.1072 [M+H<sup>+</sup>].

### 2-Bromo-*N*-(3-methoxyphenyl)-*N*-phenylaniline (**2b**):



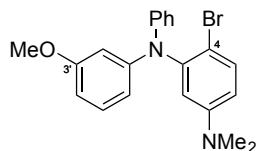
To a degassed mixture of tris(dibenzylideneacetone)dipalladium(0) (66.7 mg, 72.8  $\mu$ mol), 2-dicyclohexylphosphino-2',6'-diisopropoxybiphenyl (71.2 mg, 145  $\mu$ mol) and sodium *tert*-butoxide (421 mg, 4.38 mmol), 3-methoxy-*N*-phenylaniline (**10**, 578 mg, 2.90 mmol) in toluene (5.6 mL) was added 1-bromo-2-iodobenzene (447  $\mu$ L, 3.48 mmol) at RT. The mixture was stirred at 90 °C for 2.5 h, then cooled to RT, diluted with water (30 mL), extracted with CH<sub>2</sub>Cl<sub>2</sub> (4 x 40 mL) and dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. Column chromatography over silica gel with eluent pentane:CH<sub>2</sub>Cl<sub>2</sub> 2:1 gave 2-bromo-*N*-(3-methoxyphenyl)-*N*-phenylaniline (**2b**) as a yellowish oil (508 mg, 50%\*): *R*<sub>f</sub> 0.88 (pentane:CH<sub>2</sub>Cl<sub>2</sub> 1:1); *v*<sub>max</sub> (neat): 3059w, 2954w, 2834w, 1583s, 1486s, 1469s, 1309m, 1272m, 1222s, 1149s, 1046m, 1029m, 978w, 855w, 751s, 722m, 690s, 636w; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.63 (1H, dd, <sup>3</sup>*J* 8.0, <sup>4</sup>*J* 1.5, C3*H*), 7.29–7.33 (1H, m, C5*H*), 7.21–7.25 (3H, m, C6*H*, C3''*H*, C5''*H*), 7.09–7.14 (2H, m, C4*H*, C5'*H*), 6.96–7.02 (3H, m, C2''*H*, C4''*H*, C6''*H*), 6.51–6.55 (3H, m, C2'*H*, C4'*H*, C6'*H*), 3.71 (3H, s, OCH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  = 160.4 (C3'), 148.3 (C1'), 146.8 (C1''), 145.4 (C1), 134.5 (C3), 131.7 (C6), 129.6 (C5'), 129.0 (C3'', C5''), 128.8 (C5), 127.4 (C4), 123.8 (C2), 122.5 (C2'', C6''), 122.3 (C4''), 114.3 (C2'), 107.8 (C4'), 107.0 (C6'), 55.2 (OCH<sub>3</sub>); ESI-MS: *m/z* calcd. for C<sub>19</sub>H<sub>17</sub>BrNO<sup>+</sup> 354.0488 found 354.0494 [M+H<sup>+</sup>].

\* Column chromatography fractions containing a mixture of product and starting material were excluded and not repurified.

**4-Bromo-*N*<sup>3</sup>-(3-methoxyphenyl)-*N*<sup>1</sup>,*N*<sup>1</sup>,*N*<sup>3</sup>-trimethylbenzene-1,3-diamine (2c):**

To a degassed mixture of tris(dibenzylideneacetone)dipalladium(0) (45.8 mg, 50.0  $\mu$ mol), 1,1'-ferrocenediyl-bis(diphenylphosphine) (55.4 mg, 100  $\mu$ mol), sodium *tert*-butoxide (288 mg, 3.00 mmol) and 4-bromo-3-iodo-*N,N*-dimethylaniline<sup>[13]</sup> (652 mg, 2.00 mmol) in toluene (2.5 mL) was added *m*-anisidine (224  $\mu$ L, 2.00 mmol) at RT. The mixture was stirred at 110 °C for 12 h, then cooled to RT, diluted with water (8.0 mL), extracted with CH<sub>2</sub>Cl<sub>2</sub> (4 x 100 mL) and dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. Column chromatography over silica gel with eluent pentane:CH<sub>2</sub>Cl<sub>2</sub> 2:1 to 1:1 to 1:2 gave 4-bromo-*N*<sup>3</sup>-(3-methoxyphenyl)-*N*<sup>1</sup>,*N*<sup>1</sup>-dimethylbenzene-1,3-diamine as a brown oil (536 mg, 83%): *R*<sub>f</sub> 0.33 (pentane:CH<sub>2</sub>Cl<sub>2</sub> 1:1); *v*<sub>max</sub> (neat): 3394w, 2899w, 1588s, 1565s, 1491s, 1443m, 1355w, 1284m, 1238w, 1196m, 1153s, 1043m, 991w, 823m, 770m, 687m; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.32 (1H, d, <sup>3</sup>*J* 8.9, C5*H*), 7.18–7.21 (1H, m, C5'*H*), 6.73–6.76 (2H, m, C2'*H*, C6'*H*), 6.69 (1H, d, <sup>4</sup>*J* 2.9, C2*H*), 6.55 (1H, ddd, <sup>3</sup>*J* 8.2, <sup>4</sup>*J* 2.3, 1.0, C4'*H*), 6.20 (1H, dd, <sup>3</sup>*J* 8.9, <sup>4</sup>*J* 2.9, C6*H*), 5.98 (1H, br, *NH*), 3.78 (3H, s, OCH<sub>3</sub>), 2.88 (6H, s, N(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  = 160.7 (C3'), 150.6 (C1), 143.6 (C1'), 141.0 (C3), 132.8 (C5), 130.1 (C5'), 111.8 (C6'), 107.6 (C4'), 106.7 (C6), 104.8 (C2'), 101.3 (C2), 99.8 (C4), 55.3 (OCH<sub>3</sub>), 40.6 (N(CH<sub>3</sub>)<sub>2</sub>); ESI-MS: *m/z* calcd. for C<sub>15</sub>H<sub>18</sub>BrN<sub>2</sub>O<sup>+</sup> 321.0597 found 321.0603 [M+H<sup>+</sup>].

To a solution of 4-bromo-*N*<sup>3</sup>-(3-methoxyphenyl)-*N*<sup>1</sup>,*N*<sup>1</sup>-dimethylbenzene-1,3-diamine (225 mg, 700  $\mu$ mol) in THF (2.1 mL) at RT was added sodium hydride (60% dispersion in mineral oil, 77.0 mg, 1.93 mmol). The suspension was heated to 75 °C and stirred for 30 min at this temperature. Iodomethane (100  $\mu$ L, 1.61 mmol) was added within 5 min at 75 °C and the reaction mixture was continued to stir for 2 h at this temperature. The suspension was treated with water (2.8 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (4 x 13 mL). The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. Column chromatography on silica gel with pentane 100% to pentane:CH<sub>2</sub>Cl<sub>2</sub> 1:1 to 1:3 to 1:9 gave **2c** as a brownish solid (209 mg, 89%, m.p. 86.7–88.0 °C): *R*<sub>f</sub> 0.39 (pentane:CH<sub>2</sub>Cl<sub>2</sub> 1:1); *v*<sub>max</sub> (neat): 2998w, 2947w, 2893w, 2813w, 1614m, 1587m, 1575m, 1554m, 1492s, 1442m, 1364w, 1337m, 1297w, 1263w, 1217s, 1170s, 1125m, 1096w, 1048s, 973w, 826m, 813m, 751m, 683m; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.44 (1H, d, <sup>3</sup>*J* 8.9, C5*H*), 7.07–7.10 (1H, m, C5'*H*), 6.59 (1H, d, <sup>4</sup>*J* 3.1, C2*H*), 6.52 (1H, dd, <sup>3</sup>*J* 8.9, <sup>4</sup>*J* 3.0, C6*H*), 6.30 (1H, dd, <sup>3</sup>*J* 8.1, <sup>4</sup>*J* 2.1, C4'*H*), 6.18 (1H, dd, <sup>3</sup>*J* 8.2, <sup>4</sup>*J* 2.1, C6'*H*), 6.15–6.16 (1H, m, C2'*H*), 3.75 (3H, s, OCH<sub>3</sub>), 3.22 (3H, s, NCH<sub>3</sub>), 2.90 (6H, s, N(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  = 160.6 (C3'), 151.2 (C1), 150.0 (C1'), 146.6 (C3), 133.8 (C5), 129.6 (C5'), 114.0 (C2), 112.4 (C6), 109.7 (C4), 106.2 (C6'), 101.8 (C4'), 99.4 (C2'), 55.1 (OCH<sub>3</sub>), 40.5 (N(CH<sub>3</sub>)<sub>2</sub>), 38.9 (NCH<sub>3</sub>); ESI-MS: *m/z* calcd. for C<sub>16</sub>H<sub>20</sub>BrN<sub>2</sub>O<sup>+</sup> 335.0754 found 335.0760 [M+H<sup>+</sup>].

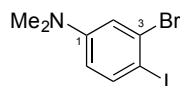
**4-Bromo-*N*<sup>3</sup>-(3-methoxyphenyl)-*N*<sup>1</sup>,*N*<sup>1</sup>-dimethyl-*N*<sup>3</sup>-phenylbenzene-1,3-diamine (2d):**

To a degassed mixture of tris(dibenzylideneacetone)dipalladium(0) (91.6 mg, 100  $\mu$ mol), 2-dicyclohexylphosphino-2',6'-diisopropoxybiphenyl (93.3 mg, 200  $\mu$ mol) and sodium *tert*-butoxide (580 mg, 6.04 mmol), 3-methoxy-*N*-phenylaniline (**10**, 797 mg, 4.00 mmol) and 4-bromo-3-iodo-*N,N*-dimethylaniline<sup>[2]</sup> (1.30 mg, 4.00 mmol) was added toluene (7.7 mL) at RT. The mixture was stirred at 100 °C for 3 h, cooled to RT, diluted with water (40 mL), extracted with CH<sub>2</sub>Cl<sub>2</sub> (4 x 85 mL) and dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. Column chromatography over silica gel with eluent pentane:CH<sub>2</sub>Cl<sub>2</sub> 2:1 to 1:1 to 1:2 gave **2d** as a brown oil (876 mg, 55%\*): *R*<sub>f</sub> 0.44 (pentane:CH<sub>2</sub>Cl<sub>2</sub> 1:1); *v*<sub>max</sub> (neat): 2935w, 1585s, 1555w, 1485s, 1445m, 1360w, 1305m, 1268m, 1220m, 1162m, 1146m, 1045m, 989w, 848w, 797w, 764w, 743m, 690s, 639w; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.41 (1H, d, <sup>3</sup>*J* 8.9, C5*H*), 7.20–7.23 (2H, m, C3''*H*, C5''*H*), 7.11 (1H, t, <sup>3</sup>*J* 8.1, C5'*H*), 7.04–7.05 (2H, m, C2''*H*, C6''*H*), 6.93–6.96 (1H, m, C6''*H*), 6.57–6.59 (1H, m, C6'*H*), 6.55–6.57 (2H, m, C2*H*, C2'*H*), 6.48–6.51 (2H, m, C6*H*, C4'*H*), 3.72 (3H, s, OCH<sub>3</sub>), 2.87 (6H, s, N(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  = 160.3 (C3'), 151.1 (C1), 148.2 (C1'), 146.7 (C1''), 145.3 (C3), 134.2 (C5), 129.5

(C5'), 128.9 (C3'', C5''), 122.1 (C2'', C6''), 121.8 (C4''), 115.3 (C2), 114.0 (C6'), 112.1 (C6), 109.7 (C4), 107.4 (C2'), 106.5 (C4'), 55.2 (OCH<sub>3</sub>), 40.5 (N(CH<sub>3</sub>)<sub>2</sub>); ESI-MS: m/z calcd. for C<sub>21</sub>H<sub>22</sub>BrN<sub>2</sub>O<sup>+</sup> 397.0910 found 397.0905 [M+H<sup>+</sup>].

\* Column chromatography fractions containing a mixture of product and starting material were excluded and not repurified.

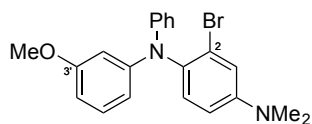
### 3-Bromo-4-iodo-*N,N*-dimethylaniline:



Prepared according to a modified literature procedure.<sup>[20]</sup> To a mixture of 3-bromo-*N,N*-dimethylaniline (0.857 mL, 6.00 mmol) and calcium carbonate (2.40 g, 24.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub>:MeOH (1:4, 120 mL) was added benzyltrimethylammonium dichloroiodate<sup>[21]</sup> (2.30 g, 6.60 mmol) at RT. The mixture was stirred at RT for 1 h, filtered and the filtrate was concentrated *in vacuo*, treated with aqueous sat. Na<sub>2</sub>SO<sub>3</sub> (30 mL), extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 80 mL) and dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo* to afford 3-bromo-4-iodo-*N,N*-dimethylaniline as a brown solid. Filtration over a plug of silica gel using eluent pentane:CH<sub>2</sub>Cl<sub>2</sub> 1:1, followed by recrystallization from *i*PrOH afforded 3-bromo-4-iodo-*N,N*-dimethylaniline as a yellowish solid (1.54 g, 79%, m.p. 76.8–78.6 °C): R<sub>f</sub> 0.86 (pentane:CH<sub>2</sub>Cl<sub>2</sub> 1:1); ν<sub>max</sub> (neat): 3082w, 2890m, 2814m, 1581s, 1496s, 1439s, 1365m, 1231s, 1177m, 1107m, 1066m, 981m, 956m, 825m, 793s, 664m; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 7.56 (1H, d, <sup>3</sup>J 9.2, C5H), 6.96 (1H, d, <sup>4</sup>J 2.9, C2H), 6.37 (1H, dd, <sup>3</sup>J 8.9, <sup>4</sup>J 2.9, C6H), 2.92 (12H, s, N(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ = 151.2 (C1), 139.8 (C5), 130.1 (C3), 116.3 (C2), 113.2 (C6), 83.0 (C4), 40.2 (N(CH<sub>3</sub>)<sub>2</sub>); ESI-MS: m/z calcd. for C<sub>8</sub>H<sub>10</sub>BrIN<sup>+</sup> 325.9036 found 325.9032 [M+H<sup>+</sup>].

**Caution:** 3-Bromo-4-iodo-*N,N*-dimethylaniline has limited stability under ambient conditions and is hence stored under argon in freezer at –20 °C or used immediately.

### 2-Bromo-*N*<sup>1</sup>-(3-methoxyphenyl)-*N*<sup>4</sup>,*N*<sup>4</sup>-dimethyl-*N*<sup>1</sup>-phenylbenzene-1,4-diamine (2e):



To a degassed mixture of tris(dibenzylideneacetone)dipalladium(0) (91.6 mg, 50.0 μmol), 2-dicyclohexylphosphino-2',6'-diisopropoxybiphenyl (98.2 mg, 100 μmol) and sodium *tert*-butoxide (288 mg, 1.50 mmol), 3-methoxy-*N*-phenylaniline (**10**, 399 mg, 2.00 mmol) and 4-bromo-3-iodo-*N,N*-dimethylaniline (782 mg, 2.40 mmol) was added toluene (4.0 mL) at RT. The mixture was stirred at 90 °C for 11 h, then cooled to RT, diluted with water (20 mL), extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 40 mL) and dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. Column chromatography over silica gel with eluent pentane:CH<sub>2</sub>Cl<sub>2</sub> 2:1 to 1:1 afforded **2e** as a yellow oil (755 mg, 95%): R<sub>f</sub> 0.63 (pentane:CH<sub>2</sub>Cl<sub>2</sub> 1:1); ν<sub>max</sub> (neat): 2935w, 1588s, 1488s, 1443m, 1313m, 1272m, 1225s, 1151s, 1050m, 957m, 907s, 831m, 728s, 691s, 628w; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 7.19–7.22 (2H, m, C3''H, C5''H), 7.11 (1H, d, <sup>3</sup>J 8.8, C6H), 7.10 (1H, t, <sup>3</sup>J 8.1, C5'H), 7.02–7.04 (2H, m, C2''H, C6''H), 6.95 (1H, d, <sup>4</sup>J 2.9, C3H), 6.90–6.93 (1H, m, C4''H), 6.66 (1H, dd, <sup>3</sup>J 8.8, <sup>4</sup>J 2.9, C5H), 6.54 (1H, t, <sup>4</sup>J 2.3, C2'H), 6.56 (1H, ddd, <sup>3</sup>J 8.1, <sup>4</sup>J 2.2, 0.8, C6'H), 6.46 (1H, ddd, <sup>3</sup>J 8.2, <sup>4</sup>J 2.4, 0.8, C4'H), 3.71 (3H, s, OCH<sub>3</sub>), 2.96 (6H, s, N(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ = 160.3 (C3'), 149.8 (C4), 148.6 (C1'), 147.0 (C1''), 133.5 (C1), 132.0 (C6), 129.5 (C5'), 128.9 (C3'', C5''), 125.3 (C2), 121.7 (C2'', C6''), 121.5 (C2'), 116.9 (C3), 113.4 (C6'), 112.8 (C5), 106.9 (C2'), 106.1 (C4'), 55.2 (OCH<sub>3</sub>), 40.5 (N(CH<sub>3</sub>)<sub>2</sub>); ESI-MS: m/z calcd. for C<sub>21</sub>H<sub>21</sub>BrN<sub>2</sub>O<sup>+</sup> 396.0832 found 396.0827 [M<sup>+</sup>].

## Preparation of the Reagents 3a-e

### General procedure B:

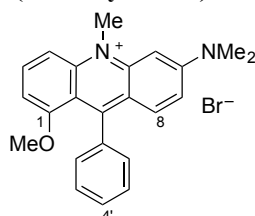
To a solution of tertiary amine **2a-e** (160  $\mu$ mol) in Et<sub>2</sub>O (200  $\mu$ L) and *n* hexane (2.0 mL) was added a solution of *n* butyllithium in hexanes (176  $\mu$ L, 1.49 mol L<sup>-1</sup>, 320  $\mu$ mol) at RT. The mixture was stirred 6 h at 65 °C. The reaction mixture was directly used in the next step.

## Direct Transformation of Esters into Acridinium Dyes 4a-l

### General procedure C:

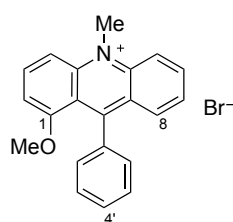
To the reaction mixture of the metalated aryl aniline in *n* hexane (160  $\mu$ mol) at -20 °C was added a solution of carboxylic acid ester (100  $\mu$ mol) in anhydrous THF (0.60 mL) and the reaction mixture was allowed to warm to RT over 12 h. Aqueous HBr (1.00 mL, 48%) was added, followed by water (20 mL) and the mixture was extracted by CHCl<sub>3</sub>:*i*PrOH solution (4  $\times$  10 mL; 85:15). The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated *in vacuo*. Column chromatography with 100% CH<sub>2</sub>Cl<sub>2</sub> to CH<sub>2</sub>Cl<sub>2</sub>:MeOH 100:2 to 100:3 to 100:4 to 100:5 (for compounds with NMe instead of NPh, up to 100:8 CH<sub>2</sub>Cl<sub>2</sub>:MeOH) afforded the product.

### 6-(Dimethylamino)-1-methoxy-10-methyl-9-phenylacridinium bromide salt 4a:



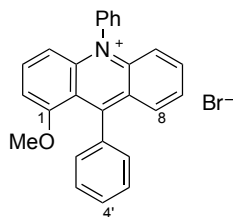
The compound was prepared according to the general procedure B and C, using 4-bromo-*N*<sup>3</sup>-(3-methoxyphenyl)-*N*<sup>1</sup>,*N*<sup>1</sup>,*N*<sup>3</sup>-trimethylbenzene-1,3-diamine (**2c**) (53.6 mg, 160  $\mu$ mol) and methyl benzoate (13.6 mg, 100  $\mu$ mol). Purification gave a brown red solid (41.3 mg, 98%, decomp. at 150 °C): *R*<sub>f</sub> 0.11 (CH<sub>2</sub>Cl<sub>2</sub>:MeOH 10:1);  $\nu_{\text{max}}$  (neat): 3406w, 2931w, 2169w, 1623s, 1599s, 1506s, 1470m, 1382m, 1344m, 1266s, 1248s, 1078m, 1027w, 925w, 810m, 707m, 635m; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.94 (1H, dd, <sup>3</sup>*J* 8.8, 8.3, C3*H*), 7.74 (1H, d, 9.0, C4*H*), 7.50–7.52 (3H, m, C3'*H*, C4'*H*, C5'*H*), 7.42 (1H, d, <sup>3</sup>*J* 9.9, C8*H*), 7.19–7.21 (3H, m, C5*H*, C2'*H*, C6'*H*), 7.11 (1H, dd, <sup>3</sup>*J* 9.9, <sup>4</sup>*J* 2.2, C7*H*), 6.81 (1H, d, <sup>3</sup>*J* 8.0, C2*H*), 4.72 (3H, s, NCH<sub>3</sub>), 3.50 (6H, br, N(CH<sub>3</sub>)<sub>2</sub>), 3.46 (3H, s, OCH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 159.3 (C1), 156.3 (C6), 154.6 (C9), 144.4 (C10a), 142.1 (C4a), 138.4 (C1'), 137.1 (C3), 132.1 (C8), 127.9 (C4'), 127.8 (C3', C5'), 127.5 (C2', C6'), 121.2 (C8a), 117.2 (C7), 115.0 (C9a), 109.1 (C4), 105.1 (C2), 93.8 (C5), 56.1 (OCH<sub>3</sub>), 41.6 (N(CH<sub>3</sub>)<sub>2</sub>), 39.9 (NCH<sub>3</sub>); ESI-MS: *m/z* calcd. for C<sub>23</sub>H<sub>23</sub>N<sub>2</sub>O<sup>+</sup> 343.1805 found 343.1804 [M<sup>+</sup>]. Absorption spectroscopy (in MeCN):  $\lambda_{\text{abs1}}$ : 506 nm;  $\lambda_{\text{abs2}}$ : 429 nm;  $\lambda_{\text{abs3}}$ : 289 nm;  $\epsilon_{\text{abs1}}$ : 1.0  $\cdot$  10<sup>4</sup> L cm<sup>-1</sup> mol<sup>-1</sup>;  $\epsilon_{\text{abs2}}$ : 1.5  $\cdot$  10<sup>4</sup> L cm<sup>-1</sup> mol<sup>-1</sup>;  $\epsilon_{\text{abs3}}$ : 3.1  $\cdot$  10<sup>4</sup> L cm<sup>-1</sup> mol<sup>-1</sup>;  $\lambda_{\text{em}}$ (exc 490): 575 nm; *E*<sub>0,0</sub>: 2.30 eV; Cyclic voltammetry (vs SCE): *E*<sub>1/2</sub>(P/P<sup>-</sup>): -0.83 V, *E*<sub>1/2</sub>(P<sup>+</sup>/P<sup>-</sup>): +1.47 V.

### 1-Methoxy-10-methyl-9-phenylacridinium bromide salt 4b:

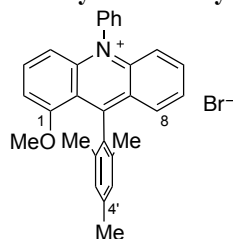


The compound was prepared according to the general procedure B and C, using 2-bromo-*N*-(3-methoxyphenyl)-*N*-methylaniline (**2a**) (46.7 mg, 160  $\mu$ mol) and methyl benzoate (13.6 mg, 100  $\mu$ mol). Purification gave a brown red solid (20.0 mg, 53%, decomp. at 160 °C): *R*<sub>f</sub> 0.06 (CH<sub>2</sub>Cl<sub>2</sub>:MeOH 10:1);  $\nu_{\text{max}}$  (neat): 3364w, 3012w, 1604s, 1577m, 1554m, 1516m, 1466s, 1355s, 1252s, 1176m, 1079m, 1017m, 925w, 762s, 699s, 660s; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.93 (1H, d, <sup>3</sup>*J* 9.2, C5*H*), 8.36–8.40 (3H, m, C3*H*, C4*H*, C6*H*), 7.82 (1H, dd, <sup>3</sup>*J* 8.7, <sup>4</sup>*J* 1.2, C8*H*), 7.71 (1H, dd, <sup>3</sup>*J* 8.6, 6.9, C7*H*), 7.58–7.60 (3H, m, C3'*H*, C4'*H*, C5'*H*), 7.26–7.30 (2H, m, C2'*H*, C6'*H*), 7.13 (1H, dd, <sup>3</sup>*J* 6.0, <sup>4</sup>*J* 2.6, C2*H*), 5.18 (3H, s, NCH<sub>3</sub>), 3.58 (3H, s, OCH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 160.6 (C9), 159.4 (C1), 142.7 (C4a), 141.2 (C3), 141.1 (C10a), 139.0 (C6), 137.6 (C1'), 130.4 (C8), 128.6 (C4'), 128.0 (C3', C5'), 127.3 (C7), 127.2 (C2', C6'), 126.5 (C8a), 119.2 (C9a), 119.1 (C5), 110.7 (C4), 106.6 (C2), 56.7 (OCH<sub>3</sub>), 41.5 (NCH<sub>3</sub>); ESI-MS: *m/z* calcd. for C<sub>21</sub>H<sub>18</sub>NO<sup>+</sup> 300.1383 found 300.1380 [M<sup>+</sup>]. Absorption spectroscopy (in MeCN):  $\lambda_{\text{abs1}}$ : 473 nm;  $\lambda_{\text{abs2}}$ : 362 nm;  $\lambda_{\text{abs3}}$ : 281 nm;  $\epsilon_{\text{abs1}}$ : 4.7  $\cdot$  10<sup>3</sup> L cm<sup>-1</sup> mol<sup>-1</sup>;  $\epsilon_{\text{abs2}}$ : 1.2  $\cdot$  10<sup>4</sup> L cm<sup>-1</sup> mol<sup>-1</sup>;  $\epsilon_{\text{abs3}}$ : 5.7  $\cdot$  10<sup>4</sup> L cm<sup>-1</sup> mol<sup>-1</sup>;  $\lambda_{\text{em}}$ (exc 490): 635 nm; *E*<sub>0,0</sub>: 2.29 eV; Cyclic voltammetry (vs SCE): *E*<sub>1/2</sub>(P/P<sup>-</sup>): -0.48 V; *E*<sub>1/2</sub>(P<sup>+</sup>/P<sup>-</sup>): +1.81 V.

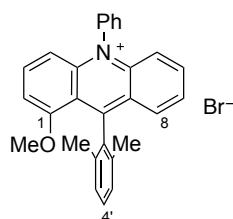


**1-Methoxy-9,10-diphenylacridinium bromide salt 4c:**

The compound was prepared according to the general procedure B and C, using 2-bromo-*N*-(3-methoxyphenyl)-*N*-phenylaniline (**2b**) (56.7mg, 160  $\mu$ mol) and methyl benzoate (13.6 mg, 100  $\mu$ mol). Purification gave a brown red solid (34.6 mg, 78%, decomp. at 135  $^{\circ}$ C):  $R_f$  0.21 ( $\text{CH}_2\text{Cl}_2$ :MeOH 10:1);  $\nu_{\text{max}}$  (neat): 2985w, 2161w, 1605m, 1578m, 1513m, 1468s, 1359m, 1273m, 1249s, 1197w, 1091s, 977w, 926w, 816w, 787s, 757s, 725s, 701s, 669m, 635w;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.14 (1H, dd,  $^3J$  9.1, 8.1, C3H), 8.10 (1H, ddd,  $^3J$  9.0, 6.8, 1.5, C6H), 7.91–7.94 (2H, m, C3''H, C5''H), 7.86–7.90 (2H, m, C8H, C4''H), 7.70–7.73 (3H, m, C7H, C2''H, 6''H), 7.60–7.63 (3H, m, C3'H, C4'H, C5'H), 7.43–7.45 (3H, m, C5H, C2'H, C6'H), 7.18 (1H, d,  $^3J$  8.0, C2H), 7.04 (1H, d,  $^3J$  8.6, C4H), 3.62 (3H, s, OCH<sub>3</sub>);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 162.7 (C9), 159.5 (C1), 143.3 (C4a), 141.5 (C10a), 141.2 (C3), 138.5 (C6), 137.5 (C1''), 137.3 (C1'), 131.9 (C4''), 131.8 (C3'', C5''), 130.5 (C8), 128.8 (C4'), 128.0 (C3', C5'), 127.9 (C2'', C6''), 127.6 (C7), 127.4 (C2', C6'), 126.5 (C8a), 119.4 (C9a), 119.1 (C5), 111.2 (C4), 107.1 (C2), 57.0 (OCH<sub>3</sub>); ESI-MS:  $m/z$  calcd. for  $\text{C}_{26}\text{H}_{20}\text{NO}^+$  362.1539 found 362.1543 [ $\text{M}^+$ ]. Absorption spectroscopy (in MeCN):  $\lambda_{\text{abs1}}$ : 479 nm;  $\lambda_{\text{abs2}}$ : 362 nm;  $\lambda_{\text{abs3}}$ : 282 nm;  $\epsilon_{\text{abs1}}$ :  $5.1 \cdot 10^3 \text{ L cm}^{-1} \text{ mol}^{-1}$ ;  $\epsilon_{\text{abs2}}$ :  $1.1 \cdot 10^4 \text{ L cm}^{-1} \text{ mol}^{-1}$ ;  $\epsilon_{\text{abs3}}$ :  $4.9 \cdot 10^4 \text{ L cm}^{-1} \text{ mol}^{-1}$ ;  $\lambda_{\text{em}}(\text{exc } 490)$ : 637 nm;  $E_{0,0}$ : 2.23 eV; Cyclic voltammetry (vs SCE):  $E_{1/2}(\text{P}/\text{P}^-)$ : -0.54 V;  $E_{1/2}(\text{P}^*/\text{P}^-)$ : +1.69 V.

**9-Mesityl-1-methoxy-10-phenylacridinium bromide salt 4d:**

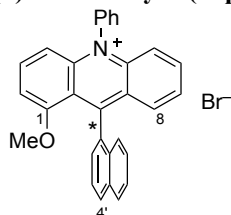
The compound was prepared according to the general procedure B and C, using 2-bromo-*N*-(3-methoxyphenyl)-*N*-phenylaniline (**2b**) (56.7mg, 160  $\mu$ mol) and methyl 2,4,6-trimethylbenzoate (17.8 mg, 100  $\mu$ mol). Purification gave a brown red solid (34.3 mg, 71%, decomp. at 139  $^{\circ}$ C):  $R_f$  0.21 ( $\text{CH}_2\text{Cl}_2$ :MeOH 10:1);  $\nu_{\text{max}}$  (neat): 3002w, 2913w, 2361w, 1609m, 1582m, 1549m, 1518m, 1462s, 1372m, 1265m, 1242s, 1189m, 1090s, 1034w, 983w, 846w, 808w, 770s, 736m, 702m, 672w, 629w;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.22 (1H, dd,  $^3J$  9.1, 8.1, C3H), 8.14 (1H, ddd,  $^3J$  9.0, 6.8,  $^4J$  1.6, C6H), 7.94–7.97 (2H, m, C3''H, C5''H), 7.88–7.91 (1H, m, C4''H), 7.80–7.82 (1H, m, C8H), 7.74 (1H, ddd,  $^3J$  9.0, 6.7,  $^4J$  1.0, C7H), 7.69–7.71 (2H, m, C2''H, C6''H), 7.48–7.49 (1H, m, C5H), 7.28–7.29 (1H, m, C2H), 7.07–7.09 (3H, m, C4H, C3'H, C5'H), 3.71 (3H, s, OCH<sub>3</sub>), 2.47 (3H, s, CH<sub>3</sub>), 1.81 (6H, s, 2 x CH<sub>3</sub>);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 164.3 (C9), 159.7 (C1), 143.1 (C4a), 141.5 (C3), 141.3 (C10a), 139.0 (C6), 138.7 (C4'), 137.3 (C1''), 133.9 (C1'), 133.6 (C2', C6'), 132.0 (C4''), 131.9 (C3'', C5''), 129.1 (C8), 128.3 (C3', C5'), 128.2 (C7), 127.9 (C2'', C6''), 125.5 (C8a), 119.6 (C9a), 119.5 (C5), 111.4 (C4), 107.1 (C2), 57.6 (OCH<sub>3</sub>), 21.2 (CH<sub>3</sub>), 20.4 (2 x CH<sub>3</sub>); ESI-MS:  $m/z$  calcd. for  $\text{C}_{29}\text{H}_{26}\text{NO}^+$  404.2009 found 404.2016 [ $\text{M}^+$ ]. Absorption spectroscopy (in MeCN):  $\lambda_{\text{abs1}}$ : 479 nm;  $\lambda_{\text{abs2}}$ : 360 nm;  $\lambda_{\text{abs3}}$ : 283 nm;  $\epsilon_{\text{abs1}}$ :  $5.9 \cdot 10^3 \text{ L cm}^{-1} \text{ mol}^{-1}$ ;  $\epsilon_{\text{abs2}}$ :  $1.3 \cdot 10^4 \text{ L cm}^{-1} \text{ mol}^{-1}$ ;  $\epsilon_{\text{abs3}}$ :  $5.5 \cdot 10^4 \text{ L cm}^{-1} \text{ mol}^{-1}$ ;  $\lambda_{\text{em}}(\text{exc } 490)$ : 632 nm;  $E_{0,0}$ : 2.25 eV; Cyclic voltammetry (vs SCE):  $E_{1/2}(\text{P}/\text{P}^-)$ : -0.57 V;  $E_{1/2}(\text{P}^*/\text{P}^-)$ : +1.68 V.

**9-(2,6-Dimethylphenyl)-1-methoxy-10-phenylacridinium bromide salt 4e:**

The compound was prepared according to the general procedure B and C, using 2-bromo-*N*-(3-methoxyphenyl)-*N*-phenylaniline (**2b**) (56.7mg, 160  $\mu$ mol) and methyl 2,6-dimethylbenzoate (16.4 mg, 100  $\mu$ mol). Purification gave a brown red solid (33.3 mg, 71%, decomp. at 139  $^{\circ}$ C):  $R_f$  0.14 ( $\text{CH}_2\text{Cl}_2$ :MeOH 10:1);  $\nu_{\text{max}}$  (neat): 3013w, 2361w, 1606m, 1582m, 1517m, 1466s, 1366m, 1271s, 1243m, 1197w, 1087s, 1030w, 977w, 771s, 738m, 701m, 670w, 626w;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.22 (1H, dd,  $^3J$  8.7, 8.4, C3H), 8.14 (1H, ddd,  $^3J$  9.2, 7.0,  $^4J$  1.5, C6H), 7.94–7.97 (2H, m, C3''H, C5''H), 7.88–7.91 (1H, m, C4''H), 7.78–7.80 (1H, m, C8H), 7.72–7.75 (3H, m, C7H, C2''H, C6''H), 7.51 (1H,  $^3J$  9.0, C5H), 7.41 (1H, t,  $^3J$  7.5, C4'H), 7.26–7.28 (3H, m, C2H, C3'H, C5'H), 7.10 (1H, d,  $^3J$  9.1, C4H), 3.69 (3H, s, OCH<sub>3</sub>), 1.86 (6H, s, 2 x CH<sub>3</sub>);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 163.6 (C9), 159.6 (C1), 143.2 (C4a), 141.6 (C3), 141.4 (C10a), 138.9 (C6), 137.3 (C1''), 136.8 (C1'), 133.8 (C2', C6'), 132.0 (C4''), 131.9 (C3'', C5''), 129.0 (C4'), 128.9 (C8), 128.3 (C7), 127.9 (C2'', C6''), 127.6 (C3', C5'), 125.2 (C8a), 119.6 (C5), 119.4 (C9a), 111.6 (C4), 107.1 (C2), 57.5 (OCH<sub>3</sub>), 20.6 (2 x CH<sub>3</sub>); ESI-MS:  $m/z$  calcd. for  $\text{C}_{28}\text{H}_{24}\text{NO}^+$  390.1852 found 390.1857 [ $\text{M}^+$ ]. Absorption spectroscopy (in MeCN):  $\lambda_{\text{abs1}}$ : 480 nm;  $\lambda_{\text{abs2}}$ : 360 nm;  $\lambda_{\text{abs3}}$ : 283 nm;  $\epsilon_{\text{abs1}}$ :  $4.1 \cdot 10^3 \text{ L cm}^{-1} \text{ mol}^{-1}$ ;  $\epsilon_{\text{abs2}}$ :  $9.7 \cdot 10^3 \text{ L cm}^{-1} \text{ mol}^{-1}$ ;  $\epsilon_{\text{abs3}}$ :  $4.4 \cdot 10^4 \text{ L cm}^{-1} \text{ mol}^{-1}$ ;

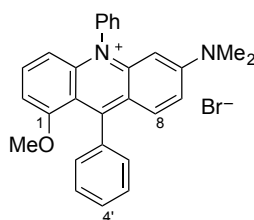
$\lambda_{\text{em}}(\text{exc } 490)$ : 634 nm;  $E_{0,0}$ : 2.25 eV; Cyclic voltammetry (vs SCE):  $E_{1/2}(\text{P}/\text{P}^-)$ :  $-0.56$  V;  $E_{1/2}(\text{P}^*/\text{P}^-)$ :  $+1.69$  V.

**( $\pm$ )-1-Methoxy-9-(naphthalen-1-yl)-10-phenylacridinium bromide salt 4f:**



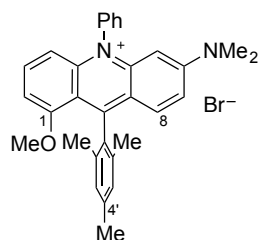
The compound was prepared according to the general procedure B and C, using 2-bromo-*N*-(3-methoxyphenyl)-*N*-phenylaniline (**2b**) (56.7 mg, 160  $\mu\text{mol}$ ) and methyl 1-naphthoate (18.6 mg, 100  $\mu\text{mol}$ ). Purification gave a brown red solid (36.6 mg, 74%, decomp. at 156  $^{\circ}\text{C}$ ):  $R_f$  0.22 ( $\text{CH}_2\text{Cl}_2$ :MeOH 10:1);  $\nu_{\text{max}}$  (neat): 3364w, 3003w, 2932w, 2361w, 1607m, 1581m, 1549w, 1519m, 1466s, 1367m, 1270m, 1248s, 1193w, 1089s, 1031w, 975w, 767s, 704s, 662w;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.12 (1H,  $^3J$  9.5, 8.0, C3H), 8.08–8.10 (1H, m, C4'H), 8.03–8.07 (2H, m, C6H, C5'H), 7.91–7.98 (2H, m, C3''H, C5''H), 7.88–7.90 (2H, m, C2''H, C6''H), 7.85–7.87 (1H, m, C4''H), 7.71–7.73 (1H, m, C8H), 7.68–7.70 (1H, m, C3'H), 7.58 (1H, dd,  $^3J$  6.6,  $^4J$  1.0, C7H), 7.56 (1H, ddd,  $^3J$  8.5, 7.5,  $^4J$  0.9, C6'H), 7.49–7.52 (2H, m, C5H, C2'H), 7.38–7.41 (1H, m, C7'H), 7.27 (1H,  $^3J$  8.6,  $^4J$  0.9, C8'H), 7.10 (1H,  $^3J$  9.0,  $^4J$  0.6, C4H), 7.06 (1H, d,  $^3J$  7.9, C2H), 3.26 (3H, s, OCH<sub>3</sub>);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 162.1 (C9), 159.2 (C1), 143.3 (C4a), 141.6 (C10a), 140.9 (C3), 138.5 (C6), 137.6 (C1''), 135.1 (C1'), 132.7 (C4'a), 131.9 (C3''), 131.8 (C5''), 131.7 (C4'), 131.5 (C8'a), 130.5 (C8), 129.1 (C4'), 128.4 (C5'), 128.2 (C2''), 128.0 (C6''), 127.5 (C7), 127.3 (C7'), 127.0 (C8a), 126.6 (C6'), 125.7 (C2'), 125.6 (C8'), 125.1 (C3'), 120.5 (C9a), 119.3 (C5), 111.4 (C4), 107.1 (C2), 56.9 (OCH<sub>3</sub>); ESI-MS:  $m/z$  calcd. for  $\text{C}_{30}\text{H}_{22}\text{NO}^+$  412.1696 found 412.1702 [ $\text{M}^+$ ]. Absorption spectroscopy (in MeCN):  $\lambda_{\text{abs1}}$ : 480 nm;  $\lambda_{\text{abs2}}$ : 362 nm;  $\lambda_{\text{abs3}}$ : 283 nm;  $\epsilon_{\text{abs1}}$ :  $5.4 \cdot 10^3$  L  $\text{cm}^{-1}$   $\text{mol}^{-1}$ ;  $\epsilon_{\text{abs2}}$ :  $1.2 \cdot 10^4$  L  $\text{cm}^{-1}$   $\text{mol}^{-1}$ ;  $\epsilon_{\text{abs3}}$ :  $5.8 \cdot 10^4$  L  $\text{cm}^{-1}$   $\text{mol}^{-1}$ ;  $\lambda_{\text{em}}(\text{exc } 490)$ : 635 nm;  $E_{0,0}$ : 2.26 eV; Cyclic voltammetry (vs SCE):  $E_{1/2}(\text{P}/\text{P}^-)$ :  $-0.53$  V;  $E_{1/2}(\text{P}^*/\text{P}^-)$ :  $+1.73$  V.

**6-(Dimethylamino)-1-methoxy-9,10-diphenylacridinium bromide salt 4g:**



The compound was prepared according to the general procedure B and C, using 4-bromo-*N*-(3-methoxyphenyl)-*N*<sup>1</sup>,*N*<sup>1</sup>-dimethyl-*N*<sup>3</sup>-phenylbenzene-1,3-diamine (**2d**) (63.6 mg, 160  $\mu\text{mol}$ ) and methyl benzoate (13.6 mg, 100  $\mu\text{mol}$ ). Purification gave a brown red solid (44.3 mg, 91%, decomp. at 105  $^{\circ}\text{C}$ ):  $R_f$  0.21 ( $\text{CH}_2\text{Cl}_2$ :MeOH 10:1);  $\nu_{\text{max}}$  (neat): 3371w, 2935w, 2165w, 1623m, 1597s, 1500s, 1431m, 1383m, 1343m, 1255s, 1213m, 1179m, 1096m, 1002w, 922m, 813w, 721s, 697s, 647w;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.88–7.91 (2H, m, C3''H, C5''H), 7.81–7.84 (1H, m, C4''H), 7.73 (1H, dd,  $^3J$  8.8, 8.2, C3H), 7.53–7.57 (3H, m, C3'H, C4'H, C5'H), 7.50 (1H, d,  $^3J$  9.9, C8H), 7.47–7.48 (2H, m, C2''H, C6''H), 7.30–7.32 (2H, m, C2'H, C6'H), 7.24 (1H, dd,  $^3J$  10,  $^4J$  2.5, C7H), 6.87 (1H, d,  $^3J$  8.0, C2H), 6.68 (1H, dd,  $^3J$  8.9,  $^4J$  0.6, C4H), 5.79 (1H, d,  $^4J$  2.4, C5H), 3.51 (3H, s, OCH<sub>3</sub>), 3.18 (6H, br, N(CH<sub>3</sub>)<sub>2</sub>);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 159.3 (C1), 156.4 (C9), 156.1 (C6), 144.9 (C10a), 142.3 (C4a), 137.9 (C1''), 137.0 (C3), 132.2 (C8), 132.0 (C3'', C5''), 131.3 (C4''), 128.2 (C4'), 128.0 (C3', C5'), 127.9 (C2'', C6''), 127.4 (C2', C6'), 121.0 (C8a), 117.8 (C7), 114.7 (C9a), 110.1 (C4), 105.7 (C2), 93.4 (C5), 56.4 (OCH<sub>3</sub>), 41.0 (N(CH<sub>3</sub>)<sub>2</sub>); ESI-MS:  $m/z$  calcd. for  $\text{C}_{28}\text{H}_{25}\text{N}_2\text{O}^+$  405.1961 found 405.1969 [ $\text{M}^+$ ]. Absorption spectroscopy (in MeCN):  $\lambda_{\text{abs1}}$ : 511 nm;  $\lambda_{\text{abs2}}$ : 488 nm;  $\lambda_{\text{abs3}}$ : 433 nm;  $\lambda_{\text{abs4}}$ : 292 nm;  $\epsilon_{\text{abs1}}$ :  $1.0 \cdot 10^4$  L  $\text{cm}^{-1}$   $\text{mol}^{-1}$ ;  $\epsilon_{\text{abs2}}$ :  $1.0 \cdot 10^4$  L  $\text{cm}^{-1}$   $\text{mol}^{-1}$ ;  $\epsilon_{\text{abs3}}$ :  $1.6 \cdot 10^4$  L  $\text{cm}^{-1}$   $\text{mol}^{-1}$ ;  $\epsilon_{\text{abs4}}$ :  $3.1 \cdot 10^4$  L  $\text{cm}^{-1}$   $\text{mol}^{-1}$ ;  $\lambda_{\text{em}}(\text{exc } 500)$ : 576 nm;  $E_{0,0}$ : 2.29 eV; Cyclic voltammetry (vs SCE):  $E_{1/2}(\text{P}/\text{P}^-)$ :  $-0.89$  V;  $E_{1/2}(\text{P}^*/\text{P}^-)$ :  $+1.40$  V.

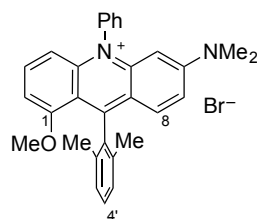
**6-(Dimethylamino)-9-mesityl-1-methoxy-10-phenylacridinium bromide salt 4h:**



The compound was prepared according to the general procedure B and C, using 4-bromo-*N*-(3-methoxyphenyl)-*N*<sup>1</sup>,*N*<sup>1</sup>-dimethyl-*N*<sup>3</sup>-phenylbenzene-1,3-diamine (**2d**) (63.6 mg, 160  $\mu\text{mol}$ ) and methyl 2,4,6-trimethylbenzoate (17.8 mg, 100  $\mu\text{mol}$ ). Purification gave a brown red solid (40.1 mg, 76%, decomp. at 106  $^{\circ}\text{C}$ ):  $R_f$  0.18 ( $\text{CH}_2\text{Cl}_2$ :MeOH 10:1);  $\nu_{\text{max}}$  (neat): 3380w, 2934w, 2360w, 1623m, 1597s, 1502s, 1473s, 1431s, 1383m, 1343m, 1255s, 1211m, 1094s, 916w, 813m, 794m, 687m, 647w;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.89–7.92 (2H, m, C3''H, C5''H), 7.81–7.84 (1H, m, C4''H), 7.74 (1H, dd,  $^3J$  8.9, 8.2, C3H), 7.48–7.50 (2H, m, C2''H, C6''H), 7.42 (1H, d,  $^3J$  9.9, C8H), 7.25 (1H, dd,  $^3J$  10,  $^4J$  2.4, C7H), 7.02 (2H, d,  $^4J$  0.5, C3'H, C5'H), 6.89 (1H, d,  $^3J$  7.8, C2H), 6.70 (1H, dd,  $^3J$  8.7,  $^4J$  0.9, C4H), 5.80 (1H, d,  $^4J$  2.4, C5H), 3.57

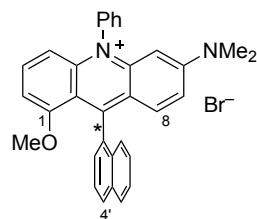
(3H, s, OCH<sub>3</sub>), 3.18 (6H, br, N(CH<sub>3</sub>)<sub>2</sub>), 2.43 (3H, s, CH<sub>3</sub>), 1.85 (6H, s, 2 x CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 159.7 (C1), 157.2 (C9), 156.3 (C6), 144.8 (C10a), 142.4 (C4a), 137.9 (C4'), 137.8 (C1''), 136.9 (C3), 134.3 (C1'), 133.7 (C2', C6'), 132.0 (C3'', C5''), 131.3 (C4''), 131.1 (C8), 128.0 (C3', C5'), 128.0 (C2'', C6''), 120.3 (C8a), 118.4 (C7), 114.8 (C9a), 110.3 (C4), 105.4 (C2), 93.6 (C5), 56.8 (OCH<sub>3</sub>), 41.0 (N(CH<sub>3</sub>)<sub>2</sub>), 21.2 (CH<sub>3</sub>), 20.2 (2 x CH<sub>3</sub>); ESI- MS: m/z calcd. for C<sub>31</sub>H<sub>31</sub>N<sub>2</sub>O<sup>+</sup> 447.2431 found 447.2439 [M<sup>+</sup>]. Absorption spectroscopy (in MeCN): λ<sub>abs1</sub>: 513 nm; λ<sub>abs2</sub>: 488 nm; λ<sub>abs3</sub>: 433 nm; λ<sub>abs4</sub>: 293 nm; ε<sub>abs1</sub>: 1.1·10<sup>4</sup> L cm<sup>-1</sup> mol<sup>-1</sup>; ε<sub>abs2</sub>: 1.0·10<sup>4</sup> L cm<sup>-1</sup> mol<sup>-1</sup>; ε<sub>abs3</sub>: 1.6·10<sup>4</sup> L cm<sup>-1</sup> mol<sup>-1</sup>; ε<sub>abs4</sub>: 3.4·10<sup>4</sup> L cm<sup>-1</sup> mol<sup>-1</sup>; λ<sub>em</sub>(exc 500): 573 nm; E<sub>0,0</sub>: 2.29 eV; Cyclic voltammetry (vs SCE): E<sub>1/2</sub>(P/P<sup>-</sup>): -0.89 V; E<sub>1/2</sub>(P<sup>+</sup>/P<sup>-</sup>): +1.40 V.

#### 6-(Dimethylamino)-9-(2,6-dimethylphenyl)-1-methoxy-10-phenylacridinium bromide salt 4i:

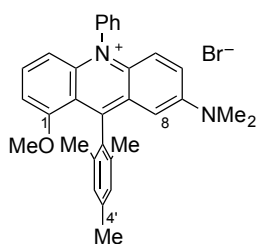


The compound was prepared according to the general procedure B and C, using 4-bromo-N<sup>3</sup>-(3-methoxyphenyl)-N<sup>1</sup>,N<sup>1</sup>-dimethyl-N<sup>3</sup>-phenylbenzene-1,3-diamine (**2d**) (63.6 mg, 160 μmol) and methyl 2,6-dimethylbenzoate (16.4 mg, 100 μmol). Purification gave a brown red solid (40.2 mg, 78%, decomp. at 121 °C): R<sub>f</sub> 0.18 (CH<sub>2</sub>Cl<sub>2</sub>:MeOH 10:1); ν<sub>max</sub> (neat): 3379w, 2925w, 2360w, 1623m, 1597s, 1503s, 1473s, 1431s, 1383m, 1343m, 1255s, 1211m, 1097s, 1002w, 966w, 915w, 764m, 702w, 685w; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.90–7.93 (2H, m, C3''H, C5''H), 7.83–7.85 (1H, m, C4''H), 7.74 (1H, dd, <sup>3</sup>J 8.9, 8.2, C3H), 7.50–7.52 (2H, m, C2''H, C6''H), 7.39 (1H, d, <sup>3</sup>J 9.7, C8H), 7.33 (1H, t, <sup>3</sup>J 7.6, C4'H), 7.26 (1H, dd, <sup>3</sup>J 9.9, <sup>4</sup>J 2.4, C7H), 7.21 (2H, d, <sup>3</sup>J 7.6, C3'H, C5'H), 6.88 (1H, d, <sup>3</sup>J 7.9, C2H), 6.72 (1H, <sup>3</sup>J 9.0, <sup>4</sup>J 0.7, C4H), 5.82 (1H, d, <sup>3</sup>J 2.4, C5H), 3.54 (3H, s, OCH<sub>3</sub>), 3.20 (6H, br, N(CH<sub>3</sub>)<sub>2</sub>), 1.90 (6H, s, 2 x CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 159.6 (C1), 156.6 (C9), 156.3 (C6), 144.9 (C10a), 142.5 (C4a), 137.8 (C1''), 137.3 (C1'), 136.9 (C3), 133.9 (C2', C6'), 132.1 (C3'', C5''), 131.3 (C4''), 130.9 (C8), 128.4 (C4'), 128.0 (C2'', C6''), 127.3 (C3', C5'), 120.1 (C8a), 118.5 (C7), 114.5 (C9a), 110.4 (C4), 105.4 (C2), 93.7 (C5), 56.8 (OCH<sub>3</sub>), 41.1 (N(CH<sub>3</sub>)<sub>2</sub>), 20.3 (2 x CH<sub>3</sub>); ESI- MS: m/z calcd. for C<sub>30</sub>H<sub>29</sub>N<sub>2</sub>O<sup>+</sup> 433.2274 found 433.2282 [M<sup>+</sup>]. Absorption spectroscopy (in MeCN): λ<sub>abs1</sub>: 514 nm; λ<sub>abs2</sub>: 489 nm; λ<sub>abs3</sub>: 433 nm; λ<sub>abs4</sub>: 293 nm; ε<sub>abs1</sub>: 1.1·10<sup>4</sup> L cm<sup>-1</sup> mol<sup>-1</sup>; ε<sub>abs2</sub>: 1.1·10<sup>4</sup> L cm<sup>-1</sup> mol<sup>-1</sup>; ε<sub>abs3</sub>: 1.6·10<sup>4</sup> L cm<sup>-1</sup> mol<sup>-1</sup>; ε<sub>abs4</sub>: 3.5·10<sup>4</sup> L cm<sup>-1</sup> mol<sup>-1</sup>; λ<sub>em</sub>(exc 500): 574 nm; E<sub>0,0</sub>: 2.29 eV; Cyclic voltammetry (vs SCE): E<sub>1/2</sub>(P/P<sup>-</sup>): -0.90 V; E<sub>1/2</sub>(P<sup>+</sup>/P<sup>-</sup>): +1.39 V.

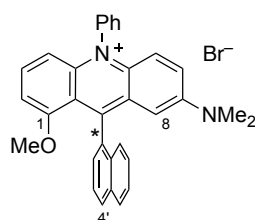
#### (±)-6-(Dimethylamino)-1-methoxy-9-(naphthalen-1-yl)-10-phenylacridinium bromide salt 4j:



The compound was prepared according to the general procedure B and C, using 4-bromo-N<sup>3</sup>-(3-methoxyphenyl)-N<sup>1</sup>,N<sup>1</sup>-dimethyl-N<sup>3</sup>-phenylbenzene-1,3-diamine (**2d**) (63.6 mg, 160 μmol) and methyl 1-naphthoate (18.6 mg, 100 μmol). Purification gave a brown red solid (50.6 mg, 95%, decomp. at 154 °C): R<sub>f</sub> 0.18 (CH<sub>2</sub>Cl<sub>2</sub>:MeOH 10:1); ν<sub>max</sub> (neat): 3385w, 2934w, 2361w, 1624m, 1597s, 1503s, 1473s, 1430s, 1385m, 1361m, 1254s, 1211s, 1178m, 1097s, 1029w, 922w, 785s, 703m, 690m; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 8.03–8.05 (1H, m, C4'H), 8.01–8.02 (1H, m, C5'H), 7.91–7.96 (2H, m, C3''H, C5''H), 7.82–7.85 (1H, m, C4''H), 7.72 (1H, dd, <sup>3</sup>J 8.9, 8.2, C3H), 7.65 (1H, dd, <sup>3</sup>J 7.7, 7.0, C3'H), 7.59–7.61 (1H, m, C2''H), 7.53–7.56 (2H, m, C6'H, C6''H), 7.38 (1H, ddd, <sup>3</sup>J 8.5, 7.7, <sup>4</sup>J 1.1, C7'H), 7.35 (1H, dd, <sup>3</sup>J 6.8, <sup>4</sup>J 1.0, C2'H), 7.35 (1H, d, <sup>3</sup>J 10, C8H), 7.25 (1H, dd, <sup>3</sup>J 8.2, <sup>4</sup>J 0.6, C8'H), 7.11 (1H, dd, <sup>3</sup>J 10, <sup>4</sup>J 2.4, C7H), 6.77 (1H, d, <sup>3</sup>J 8.0, C2H), 6.74 (1H, dd, <sup>3</sup>J 8.8, <sup>4</sup>J 0.5, C4H), 5.85 (1H, d, <sup>3</sup>J 2.4, C5H), 3.16 (6H, br, N(CH<sub>3</sub>)<sub>2</sub>), 3.13 (3H, s, OCH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 159.2 (C1), 156.3 (C6), 155.4 (C9), 145.0 (C10a), 142.3 (C4a), 137.9 (C1''), 136.9 (C3), 135.6 (C1'), 132.9 (C4'a), 132.2 (C8), 132.2 (C3''), 132.1 (C5''), 131.6 (C8'a), 131.3 (C4''), 128.7 (C4'), 128.5 (C5'), 128.0 (C2''), 128.0 (C6''), 127.0 (C7'), 126.4 (C6'), 125.3 (C2'), 125.1 (C8'), 125.1 (C3'), 121.6 (C8a), 117.9 (C7), 115.6 (C9a), 110.3 (C4), 105.8 (C2), 93.5 (C5), 56.4 (OCH<sub>3</sub>), 41.0 (N(CH<sub>3</sub>)<sub>2</sub>); ESI- MS: m/z calcd. for C<sub>32</sub>H<sub>27</sub>N<sub>2</sub>O<sup>+</sup> 455.2118 found 455.2122 [M<sup>+</sup>]. Absorption spectroscopy (in MeCN): λ<sub>abs1</sub>: 516 nm; λ<sub>abs2</sub>: 491 nm; λ<sub>abs3</sub>: 433 nm; λ<sub>abs4</sub>: 294 nm; ε<sub>abs1</sub>: 1.1·10<sup>4</sup> L cm<sup>-1</sup> mol<sup>-1</sup>; ε<sub>abs2</sub>: 1.1·10<sup>4</sup> L cm<sup>-1</sup> mol<sup>-1</sup>; ε<sub>abs3</sub>: 1.6·10<sup>4</sup> L cm<sup>-1</sup> mol<sup>-1</sup>; ε<sub>abs4</sub>: 4.0·10<sup>4</sup> L cm<sup>-1</sup> mol<sup>-1</sup>; λ<sub>em</sub>(exc 500): 578 nm; E<sub>0,0</sub>: 2.27 eV; Cyclic voltammetry (vs SCE): E<sub>1/2</sub>(P/P<sup>-</sup>): -0.87 V; E<sub>1/2</sub>(P<sup>+</sup>/P<sup>-</sup>): +1.40 V.

**7-(Dimethylamino)-9-mesityl-1-methoxy-10-phenylacridinium bromide salt 4k:**

The compound was prepared according to the general procedure B and C, using 2-bromo-*N*<sup>1</sup>-(3-methoxyphenyl)-*N*<sup>4</sup>,*N*<sup>4</sup>-dimethyl-*N*<sup>1</sup>-phenylbenzene-1,4-diamine (**2e**) (63.6 mg, 160 μmol) and methyl 2,4,6-trimethylbenzoate (17.8 mg, 100 μmol). Purification gave a brown red solid (41.2 mg, 78%, decomp. at 143 °C): *R*<sub>f</sub> 0.24 (CH<sub>2</sub>Cl<sub>2</sub>:MeOH 10:1); *v*<sub>max</sub> (neat): 3380w, 2919w, 2361w, 1617s, 1573m, 1518m, 1490m, 1455m, 1359s, 1267s, 1209s, 1088s, 979w, 924w, 816m, 764s, 726m, 702m, 635w; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.92–7.95 (2H, m, C3''H, C5''H), 7.84–7.90 (3H, m, C3H, C6H, C4''H), 7.57–7.59 (2H, m, C2''H, C6''H), 7.37 (1H, d, <sup>3</sup>J 9.8, C5H), 7.06 (2H, d, <sup>4</sup>J 0.5, C3'H, C5'H), 7.01 (1H, d, <sup>3</sup>J 7.9, C2H), 6.93 (1H, dd, <sup>3</sup>J 9.1, <sup>4</sup>J 0.5, C4H), 6.44 (1H, d, <sup>3</sup>J 2.9, C8H), 3.63 (3H, s, OCH<sub>3</sub>), 2.99 (6H, s, N(CH<sub>3</sub>)<sub>2</sub>), 2.45 (3H, s, CH<sub>3</sub>), 1.83 (6H, s, 2 x CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 158.5 (C1), 157.3 (C9), 148.8 (C7), 140.0 (C4a), 138.0 (C4'), 137.5 (C1''), 137.1 (C3), 135.5 (C10a), 134.6 (C1'), 133.3 (C2', C6'), 131.8 (C4''), 131.8 (C3'', C5''), 129.2 (C6), 128.3 (C3', C5'), 128.2 (C8a), 127.7 (C2'', C6''), 120.2 (C5), 119.7 (C9a), 111.4 (C4), 105.8 (C2), 101.5 (C8), 57.0 (OCH<sub>3</sub>), 40.2 (N(CH<sub>3</sub>)<sub>2</sub>), 21.3 (CH<sub>3</sub>), 20.1 (2 x CH<sub>3</sub>); ESI- MS: *m/z* calcd. for C<sub>31</sub>H<sub>31</sub>N<sub>2</sub>O<sup>+</sup> 447.2431 found 447.2439 [M<sup>+</sup>]. Absorption spectroscopy (in MeCN): λ<sub>abs1</sub>: 583 nm; λ<sub>abs2</sub>: 412 nm; λ<sub>abs3</sub>: 318 nm; ε<sub>abs1</sub>: 5.6·10<sup>3</sup> L cm<sup>-1</sup> mol<sup>-1</sup>; ε<sub>abs2</sub>: 2.5·10<sup>3</sup> L cm<sup>-1</sup> mol<sup>-1</sup>; ε<sub>abs3</sub>: 3.1·10<sup>4</sup> L cm<sup>-1</sup> mol<sup>-1</sup>; λ<sub>em</sub>(exc 570): 723 nm; E<sub>0,0</sub>: 1.94 eV; Cyclic voltammetry (vs SCE): E<sub>1/2</sub>(P/P<sup>+</sup>): -0.71 V; E<sub>1/2</sub>(P<sup>+</sup>/P): +1.23 V.

**(±)-7-(Dimethylamino)-1-methoxy-9-(naphthalen-1-yl)-10-phenylacridinium bromide salt 4l:**

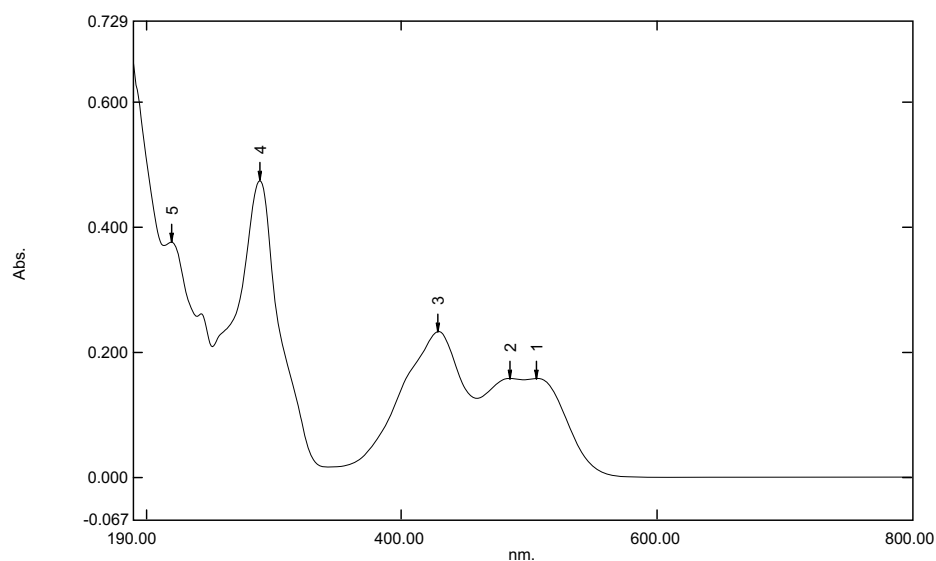
The compound was prepared according to the general procedure B and C, using 2-bromo-*N*<sup>1</sup>-(3-methoxyphenyl)-*N*<sup>4</sup>,*N*<sup>4</sup>-dimethyl-*N*<sup>1</sup>-phenylbenzene-1,4-diamine (**2e**) (63.6 mg, 160 μmol) and methyl 1-naphthoate (18.6 mg, 100 μmol). Purification gave a brown red solid (50.1 mg, 94%, decomp. at 113 °C): *R*<sub>f</sub> 0.20 (CH<sub>2</sub>Cl<sub>2</sub>:MeOH 10:1); *v*<sub>max</sub> (neat): 3365w, 3002w, 2934w, 2361w, 1619m, 1573m, 1518m, 1490m, 1456m, 1361s, 1267s, 1207s, 1169m, 1089m, 976w, 924w, 782s, 692m; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 8.05–8.07 (1H, m, C4'H), 8.02–8.03 (1H, m, C5'H), 7.91–7.98 (2H, m, C3''H, C5''H), 7.88–7.90 (1H, m, C4''H), 7.82–7.85 (2H, m, C3H, C6H), 7.66–7.73 (3H, m, C3'H, C2''H, C6''H), 7.53–7.56 (1H, m, C6'H), 7.42 (1H, dd, <sup>3</sup>J 7.0, <sup>4</sup>J 0.9, C2'H), 7.39 (1H, d, <sup>3</sup>J 10, C5H), 7.37 (1H, <sup>3</sup>J 8.2, 7.5, <sup>4</sup>J 1.3, C7'H), 7.23–7.25 (1H, m, C8'H), 6.97 (1H, d, <sup>3</sup>J 9.5, C4H), 6.89 (1H, d, <sup>3</sup>J 8.0, C2H), 6.33 (1H, d, <sup>4</sup>J 2.9, C8H), 3.21 (3H, s, OCH<sub>3</sub>), 2.81 (6H, s, N(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 158.1 (C1), 155.1 (C9), 148.3 (C7), 140.1 (C4a), 137.6 (C1''), 137.0 (C3), 136.1 (C1'), 135.8 (C10a), 132.9 (C4'a), 131.8 (C3'', C5''), 131.7 (C4''), 131.0 (C8'a), 129.5 (C8a), 129.2 (C6), 128.7 (C4'), 128.5 (C5'), 127.8 (C2''), 127.8 (C6''), 127.0 (C7'), 126.4 (C6'), 125.3 (C3'), 125.1 (C8'), 125.0 (C2'), 120.4 (C9a), 120.0 (C5), 111.4 (C4), 106.3 (C2), 103.4 (C8), 56.6 (OCH<sub>3</sub>), 40.0 (N(CH<sub>3</sub>)<sub>2</sub>); ESI- MS: *m/z* calcd. for C<sub>32</sub>H<sub>27</sub>N<sub>2</sub>O<sup>+</sup> 455.2118 found 455.2120 [M<sup>+</sup>]. Absorption spectroscopy (in MeCN): λ<sub>abs1</sub>: 590 nm; λ<sub>abs2</sub>: 419 nm; λ<sub>abs3</sub>: 317 nm; ε<sub>abs1</sub>: 5.8·10<sup>3</sup> L cm<sup>-1</sup> mol<sup>-1</sup>; ε<sub>abs2</sub>: 2.7·10<sup>3</sup> L cm<sup>-1</sup> mol<sup>-1</sup>; ε<sub>abs3</sub>: 3.2·10<sup>4</sup> L cm<sup>-1</sup> mol<sup>-1</sup>; λ<sub>em</sub>(exc 580): 755 nm; E<sub>0,0</sub>: 1.87 eV; Cyclic voltammetry (vs SCE): E<sub>1/2</sub>(P/P<sup>+</sup>): -0.68 V; E<sub>1/2</sub>(P<sup>+</sup>/P): +1.19 V.

Compounds **4a-l** are part of a filed patent (C. Fischer, C. Sparr. EP 17/188,288).

## UV/VIS and Fluorescence Spectra

### 6-(Dimethylamino)-1-methoxy-10-methyl-9-phenylacridinium bromide salt 4a

#### UV/Vis Spectroscopy:



Measurement Properties  
 Wavelength Range (nm.): 190.00 to 800.00  
 Scan Speed: Medium  
 Sampling Interval: 1.0  
 Auto Sampling Interval: Disabled  
 Scan Mode: Single

Sample Preparation Properties  
 Weight: 0.643 mg  
 Volume: 100 mL  
 Dilution: -  
 Path Length: 1.00 cm  
 Additional Information: CF952P in Acetonitrile

Instrument Properties  
 Instrument Type: UV-1600 Series  
 Measuring Mode: Absorbance  
 Slit Width: 2.0 nm  
 Light Source Change Wavelength: 340.8 nm  
 S/R Exchange: Normal

Attachment Properties  
 Attachment: None  
 FWHM: 81.5 nm

No.	P/V	Wavelength	Abs.	Description
1	⊕	506.00	0.158	
2	⊕	485.00	0.158	
3	⊕	429.00	0.233	
4	⊕	289.00	0.474	
5	⊕	220.00	0.376	
6	⊕	597.00	-0.000	
7	⊕	495.00	0.155	
8	⊕	459.00	0.126	
9	⊕	340.00	0.016	
10	⊕	252.00	0.208	
11	⊕	214.00	0.370	

#### Fluorescence Spectroscopy:

Excitation Wavelength: 490 nm

Excitation Slit Width: 5 nm

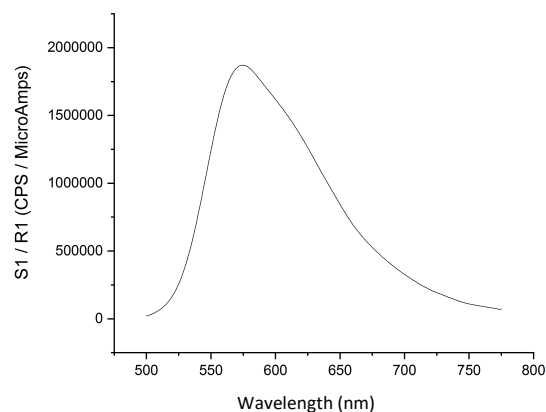
Emission Slit Width: 2 nm

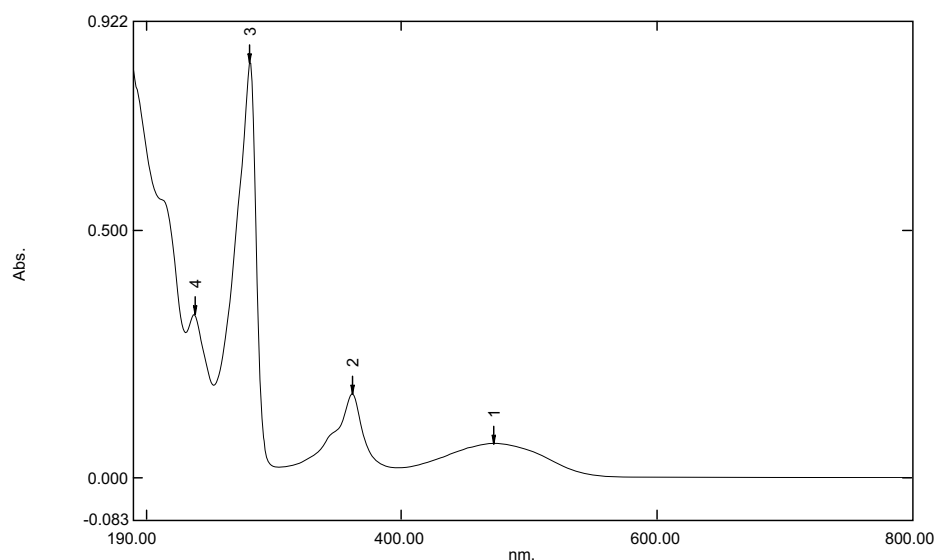
Integration Time: 0.2 s

Solvent: MeCN

$\lambda_{em}$ : 575 nm

FWHM: 100 nm



**1-Methoxy-10-methyl-9-phenylacridinium bromide salt 4b**UV/Vis Spectroscopy:

Measurement Properties  
Wavelength Range (nm.): 190.00 to 800.00  
Scan Speed: Medium  
Sampling Interval: 1.0  
Auto Sampling Interval: Disabled  
Scan Mode: Single

Sample Preparation Properties  
Weight: 0.563 mg  
Volume: 100 mL  
Dilution: -  
Path Length: 1.00 cm  
Additional Information: CF931P in Acetonitrile

Instrument Properties  
Instrument Type: UV-1600 Series  
Measuring Mode: Absorbance  
Slit Width: 2.0 nm  
Light Source Change Wavelength: 340.8 nm  
S/R Exchange: Normal

Attachment Properties  
Attachment: None  
FWHM: 90.3 nm

No.	P/V	Wavelength	Abs.	Description
1	⊕	473.00	0.070	
2	⊕	362.00	0.170	
3	⊕	281.00	0.839	
4	⊕	238.00	0.329	
5	⊕	609.00	0.001	
6	⊕	397.00	0.020	
7	⊕	304.00	0.021	
8	⊕	253.00	0.187	
9	⊕	231.00	0.293	

Fluorescence Spectroscopy:

Excitation Wavelength: 490 nm

Excitation Slit Width: 5 nm

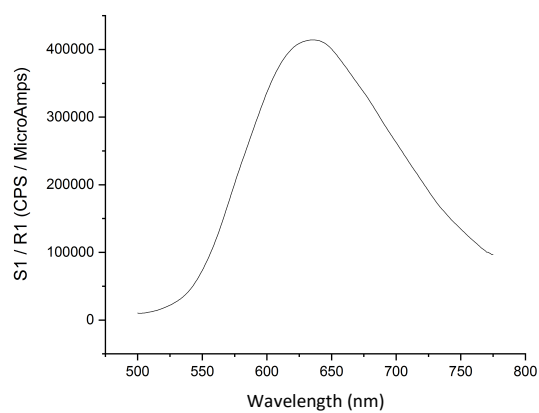
Emission Slit Width: 2 nm

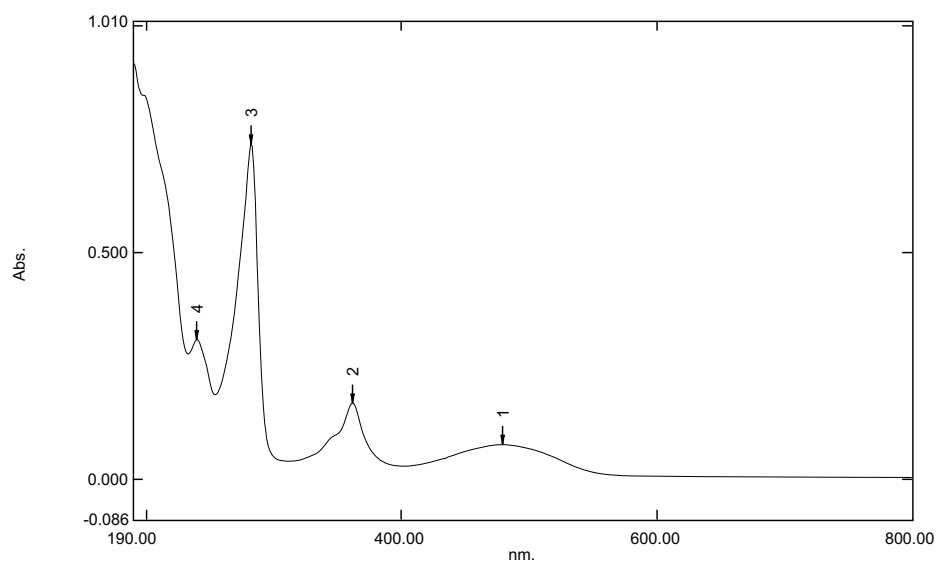
Integration Time: 0.2 s

Solvent: MeCN

$\lambda_{em}$ : 635 nm

FWHM: 143 nm



**1-Methoxy-9,10-diphenylacridinium bromide salt 4c**UV/Vis Spectroscopy:

Measurement Properties  
Wavelength Range (nm.): 190.00 to 800.00  
Scan Speed: Medium  
Sampling Interval: 1.0  
Auto Sampling Interval: Disabled  
Scan Mode: Single

Sample Preparation Properties  
Weight: 0.671 mg  
Volume: 100 mL  
Dilution: -  
Path Length: 1.00 cm  
Additional Information: CF1201P in Acetonitrile

No.	P/V	Wavelength	Abs.	Description
1	⊕	479.00	0.078	
2	⊕	362.00	0.169	
3	⊕	282.00	0.740	
4	⊕	240.00	0.309	
5	⊕	626.00	0.007	
6	⊕	402.00	0.030	
7	⊕	312.00	0.041	
8	⊕	254.00	0.188	
9	⊕	233.00	0.277	

Instrument Properties  
Instrument Type: UV-1600 Series  
Measuring Mode: Absorbance  
Slit Width: 2.0 nm  
Light Source Change Wavelength: 340.8 nm  
S/R Exchange: Normal

Attachment Properties  
Attachment: None  
FWHM: 106 nm

Fluorescence Spectroscopy:

Excitation Wavelength: 490 nm

Excitation Slit Width: 5 nm

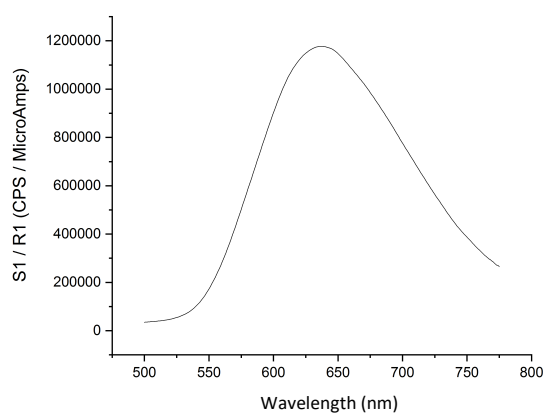
Emission Slit Width: 2 nm

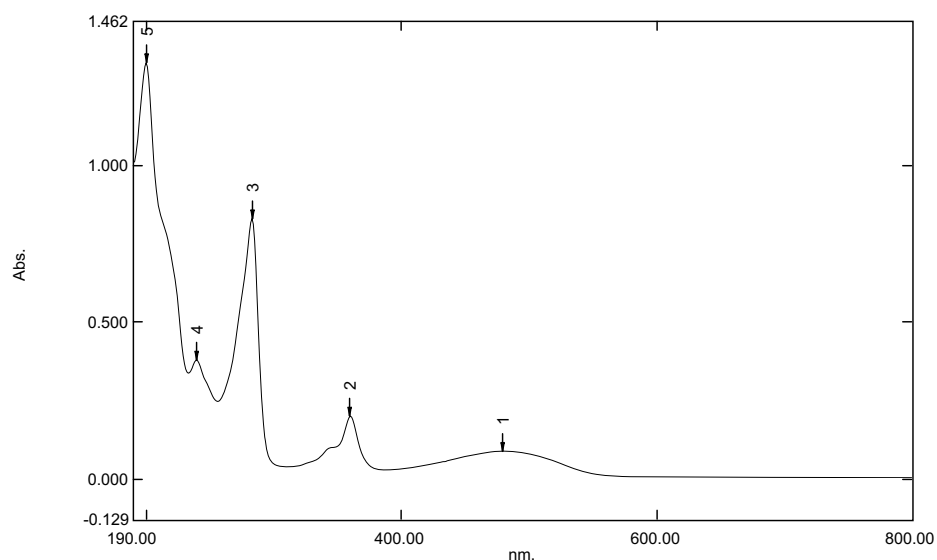
Integration Time: 0.2 s

Solvent: MeCN

 $\lambda_{em}$ : 637 nm

FWHM: 142 nm



**9-Mesityl-1-methoxy-10-phenylacridinium bromide salt 4d**UV/Vis Spectroscopy:

Measurement Properties  
Wavelength Range (nm.): 190.00 to 800.00  
Scan Speed: Medium  
Sampling Interval: 1.0  
Auto Sampling Interval: Disabled  
Scan Mode: Single

Sample Preparation Properties  
Weight: 0.728 mg  
Volume: 100 mL  
Dilution: -  
Path Length: 1.00 cm  
Additional Information: CF1200P in Acetonitrile

No.	P/V	Wavelength	Abs.	Description
1	⊕	479.00	0.089	
2	⊕	360.00	0.200	
3	⊕	283.00	0.831	
4	⊕	240.00	0.378	
5	⊕	200.00	1.329	
6	⊕	601.00	0.006	
7	⊕	387.00	0.028	
8	⊕	309.00	0.038	
9	⊕	256.00	0.247	
10	⊕	233.00	0.337	

Instrument Properties  
Instrument Type: UV-1600 Series  
Measuring Mode: Absorbance  
Slit Width: 2.0 nm  
Light Source Change Wavelength: 340.8 nm  
S/R Exchange: Normal

Attachment Properties  
Attachment: None  
FWHM: 107 nm

Fluorescence Spectroscopy:

Excitation Wavelength: 490 nm

Excitation Slit Width: 5 nm

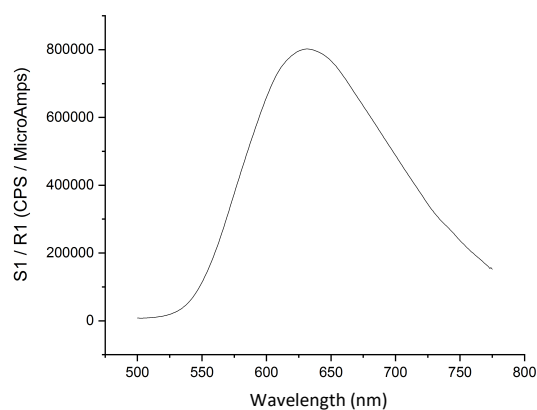
Emission Slit Width: 2 nm

Integration Time: 0.2 s

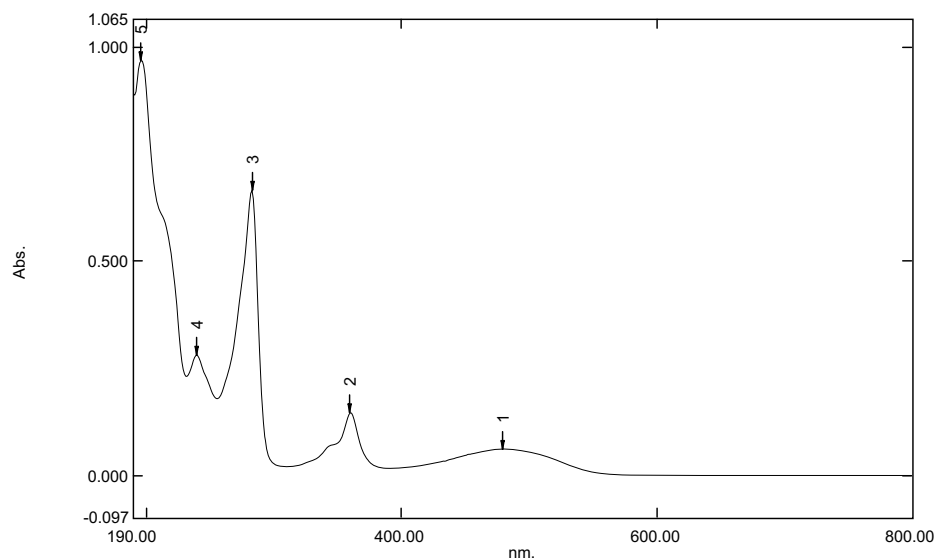
Solvent: MeCN

 $\lambda_{em}$ : 632 nm

FWHM: 138 nm





**9-(2,6-Dimethylphenyl)-1-methoxy-10-phenylacridinium bromide salt 4e**UV/Vis Spectroscopy:

Measurement Properties  
Wavelength Range (nm.): 190.00 to 800.00  
Scan Speed: Medium  
Sampling Interval: 1.0  
Auto Sampling Interval: Disabled  
Scan Mode: Single

Sample Preparation Properties  
Weight: 0.709 mg  
Volume: 100 mL  
Dilution: -  
Path Length: 1.00 cm  
Additional Information: CF1219P in Acetonitrile

No.	P/V	Wavelength	Abs.	Description
1	⊕	480.00	0.062	
2	⊕	360.00	0.146	
3	⊕	283.00	0.665	
4	⊕	240.00	0.281	
5	⊕	196.00	0.968	
6	⊕	589.00	0.001	
7	⊕	391.00	0.017	
8	⊕	309.00	0.021	
9	⊕	256.00	0.180	
10	⊕	232.00	0.232	

Instrument Properties  
Instrument Type: UV-1600 Series  
Measuring Mode: Absorbance  
Slit Width: 2.0 nm  
Light Source Change Wavelength: 340.8 nm  
S/R Exchange: Normal

Attachment Properties  
Attachment: None  
FWHM: 98.0 nm

Fluorescence Spectroscopy:

Excitation Wavelength: 490 nm

Excitation Slit Width: 5 nm

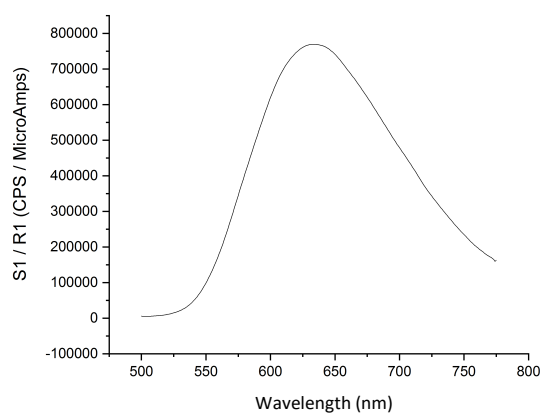
Emission Slit Width: 2 nm

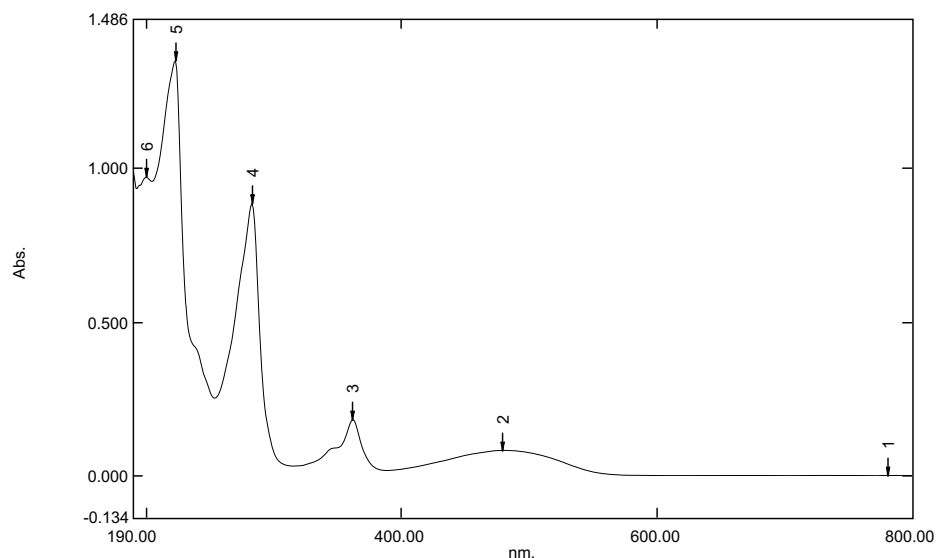
Integration Time: 0.2 s

Solvent: MeCN

 $\lambda_{em}$ : 634 nm

FWHM: 139 nm



**(±)-1-Methoxy-9-(naphthalen-1-yl)-10-phenylacridinium bromide salt 4f**UV/Vis Spectroscopy:

Measurement Properties  
Wavelength Range (nm.): 190.00 to 800.00  
Scan Speed: Medium  
Sampling Interval: 1.0  
Auto Sampling Interval: Disabled  
Scan Mode: Single

Sample Preparation Properties  
Weight: 0.302 mg  
Volume: 10 mL  
Dilution: 4 fold  
Path Length: 1.00 cm  
Additional Information: CF1251P rac in Acetonitrile

Instrument Properties  
Instrument Type: UV-1600 Series  
Measuring Mode: Absorbance  
Slit Width: 2.0 nm  
Light Source Change Wavelength: 340.8 nm  
S/R Exchange: Normal

Attachment Properties  
Attachment: None  
FWHM: 104 nm

No.	P/V	Wavelength	Abs.	Description
1	⊕	782.00	0.002	
2	⊕	480.00	0.083	
3	⊕	362.00	0.183	
4	⊕	283.00	0.886	
5	⊕	223.00	1.351	
6	⊕	200.00	0.971	
7	⊕	618.00	0.001	
8	⊕	391.00	0.017	
9	⊕	318.00	0.032	
10	⊕	254.00	0.253	
11	⊕	204.00	0.958	

Fluorescence Spectroscopy:

Excitation Wavelength: 490 nm

Excitation Slit Width: 6 nm

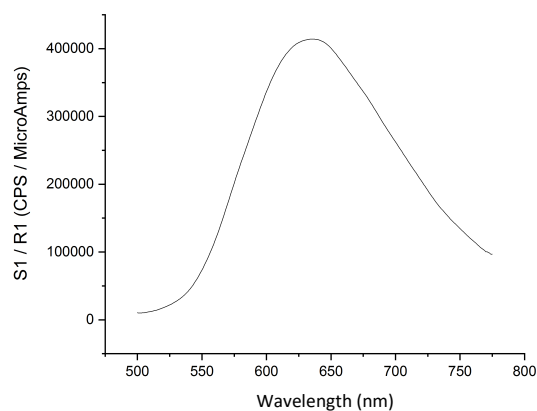
Emission Slit Width: 2 nm

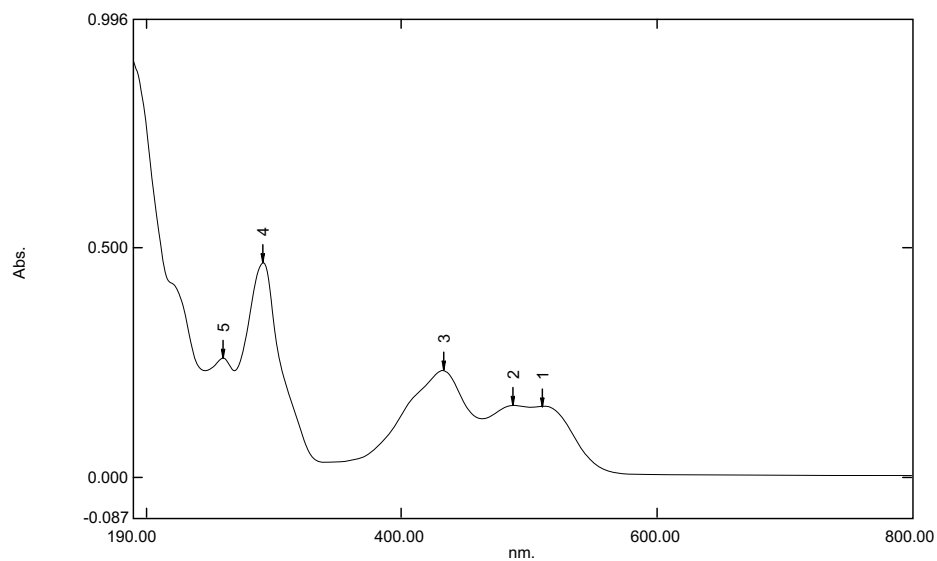
Integration Time: 0.2 s

Solvent: MeCN

 $\lambda_{em}$ : 635 nm

FWHM: 143 nm



**6-(Dimethylamino)-1-methoxy-9,10-diphenylacridinium bromide salt 4g**UV/Vis Spectroscopy:

Measurement Properties  
Wavelength Range (nm.): 190.00 to 800.00  
Scan Speed: Medium  
Sampling Interval: 1.0  
Auto Sampling Interval: Disabled  
Scan Mode: Single

Sample Preparation Properties  
Weight: 0.722 mg  
Volume: 100 mL  
Dilution: -  
Path Length: 1.00 cm  
Additional Information: CF1164P in Acetonitrile

Instrument Properties  
Instrument Type: UV-1600 Series  
Measuring Mode: Absorbance  
Slit Width: 2.0 nm  
Light Source Change Wavelength: 340.8 nm  
S/R Exchange: Normal

Attachment Properties  
Attachment: None  
FWHM: 84.6 nm

No.	P/V	Wavelength	Abs.	Description
1	⊕	511.00	0.154	
2	⊕	488.00	0.156	
3	⊕	433.00	0.232	
4	⊕	292.00	0.466	
5	⊕	260.00	0.259	
6	⊕	608.00	0.005	
7	⊕	501.00	0.152	
8	⊕	464.00	0.127	
9	⊕	342.00	0.032	
10	⊕	269.00	0.231	
11	⊕	246.00	0.231	

Fluorescence Spectroscopy:

Excitation Wavelength: 500 nm

Excitation Slit Width: 4 nm

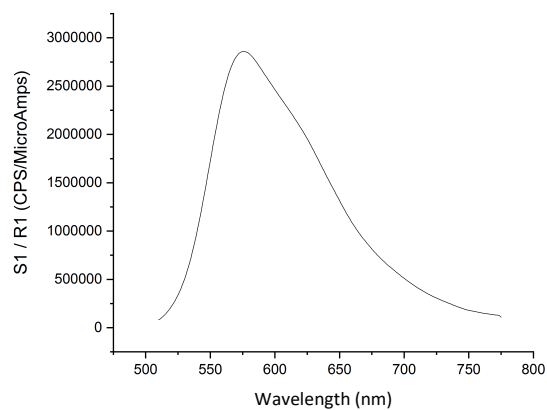
Emission Slit Width: 2 nm

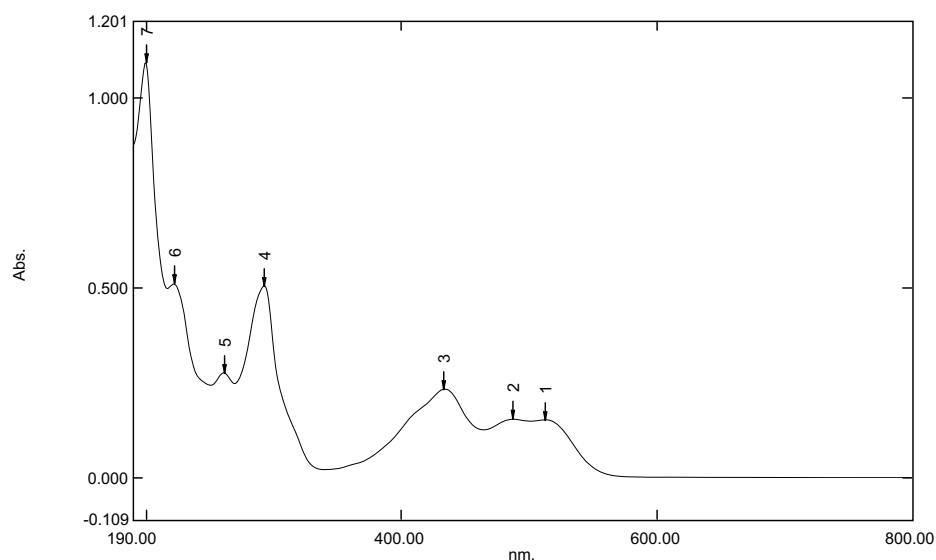
Integration Time: 0.2 s

Solvent: MeCN

 $\lambda_{em}$ : 576 nm

FWHM: 99 nm



**6-(Dimethylamino)-9-mesityl-1-methoxy-10-phenylacridinium bromide salt 4h**UV/Vis Spectroscopy:

Measurement Properties  
 Wavelength Range (nm.): 190.00 to 800.00  
 Scan Speed: Medium  
 Sampling Interval: 1.0  
 Auto Sampling Interval: Disabled  
 Scan Mode: Single

Sample Preparation Properties  
 Weight: 0.792 mg  
 Volume: 100 mL  
 Dilution: -  
 Path Length: 1.00 cm  
 Additional Information: CF1163P in Acetonitrile

Instrument Properties  
 Instrument Type: UV-1600 Series  
 Measuring Mode: Absorbance  
 Slit Width: 2.0 nm  
 Light Source Change Wavelength: 340.8 nm  
 S/R Exchange: Normal

Attachment Properties  
 Attachment: None  
 FWHM: 75.0 nm

No.	P/V	Wavelength	Abs.	Description
1	⊕	513.00	0.153	
2	⊕	488.00	0.154	
3	⊕	433.00	0.233	
4	⊕	293.00	0.505	
5	⊕	261.00	0.276	
6	⊕	222.00	0.510	
7	⊕	200.00	1.092	
8	⊕	592.00	0.002	
9	⊕	501.00	0.149	
10	⊕	464.00	0.126	
11	⊕	338.00	0.022	
12	⊕	269.00	0.248	
13	⊕	250.00	0.244	
14	⊕	217.00	0.499	

Fluorescence Spectroscopy:

Excitation Wavelength: 500 nm

Excitation Slit Width: 4 nm

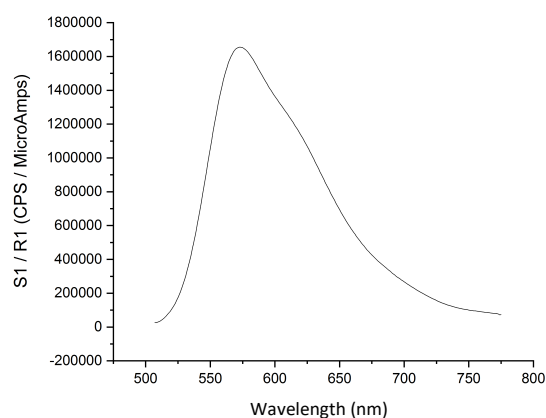
Emission Slit Width: 2 nm

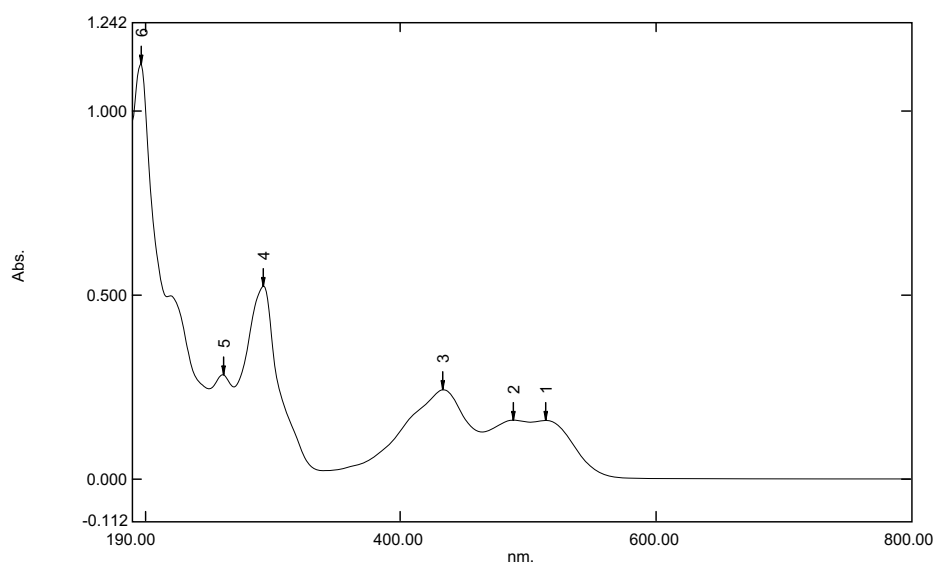
Integration Time: 0.2 s

Solvent: MeCN

 $\lambda_{em}$ : 573 nm

FWHM: 95 nm

**6-(Dimethylamino)-9-(2,6-dimethylphenyl)-1-methoxy-10-phenylacridinium bromide 4i**

UV/Vis Spectroscopy:

Measurement Properties  
Wavelength Range (nm.): 190.00 to 800.00  
Scan Speed: Medium  
Sampling Interval: 1.0  
Auto Sampling Interval: Disabled  
Scan Mode: Single

Sample Preparation Properties  
Weight: 0.773 mg  
Volume: 100 mL  
Dilution: -  
Path Length: 1.00 cm  
Additional Information: CF1220P in Acetonitrile

Instrument Properties  
Instrument Type: UV-1600 Series  
Measuring Mode: Absorbance  
Slit Width: 2.0 nm  
Light Source Change Wavelength: 340.8 nm  
S/R Exchange: Normal

Attachment Properties  
Attachment: None  
FWHM: 79.1 nm

No.	P/V	Wavelength	Abs.	Description
1	⊕	514.00	0.160	
2	⊕	489.00	0.161	
3	⊕	433.00	0.243	
4	⊕	293.00	0.526	
5	⊕	261.00	0.284	
6	⊕	197.00	1.129	
7	⊖	602.00	0.002	
8	⊖	501.00	0.155	
9	⊖	464.00	0.129	
10	⊖	339.00	0.023	
11	⊖	270.00	0.251	
12	⊖	250.00	0.246	

Fluorescence Spectroscopy:

Excitation Wavelength: 500 nm

Excitation Slit Width: 5 nm

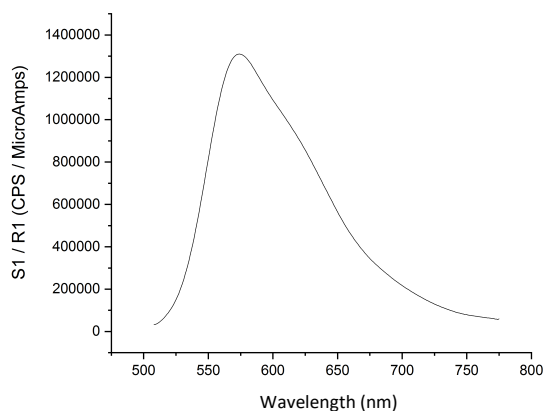
Emission Slit Width: 2 nm

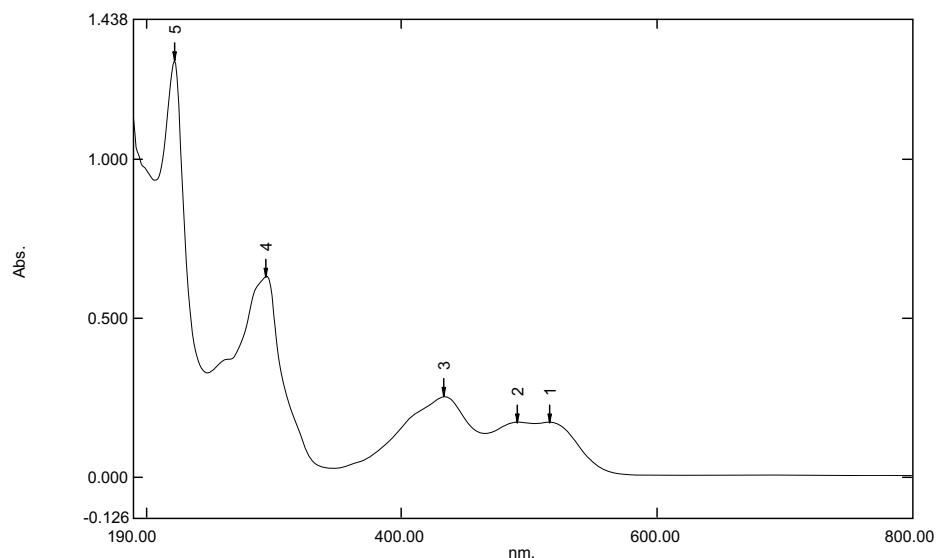
Integration Time: 0.2 s

Solvent: MeCN

$\lambda_{em}$ : 574 nm

FWHM: 98 nm



**(±)-6-(Dimethylamino)-1-methoxy-9-(naphthalen-1-yl)-10-phenylacridinium bromide salt 4j**UV/Vis Spectroscopy:

Measurement Properties  
Wavelength Range (nm.): 190.00 to 800.00  
Scan Speed: Medium  
Sampling Interval: 1.0  
Auto Sampling Interval: Disabled  
Scan Mode: Single

Sample Preparation Properties  
Weight: 0.338 mg  
Volume: 10 mL  
Dilution: 4 fold  
Path Length: 1.00 cm  
Additional Information: CF1252P rac in Acetonitrile

Instrument Properties  
Instrument Type: UV-1600 Series  
Measuring Mode: Absorbance  
Slit Width: 2.0 nm  
Light Source Change Wavelength: 340.8 nm  
S/R Exchange: Normal

Attachment Properties  
Attachment: None  
FWHM: 85.1 nm

No.	P/V	Wavelength	Abs.	Description
1	⊕	516.00	0.172	
2	⊕	491.00	0.173	
3	⊕	433.00	0.252	
4	⊕	294.00	0.631	
5	⊕	222.00	1.308	
6	⊕	590.00	0.006	
7	⊕	504.00	0.168	
8	⊕	465.00	0.137	
9	⊕	347.00	0.027	
10	⊕	248.00	0.328	
11	⊕	206.00	0.933	

Fluorescence Spectroscopy:

Excitation Wavelength: 500 nm

Excitation Slit Width: 5 nm

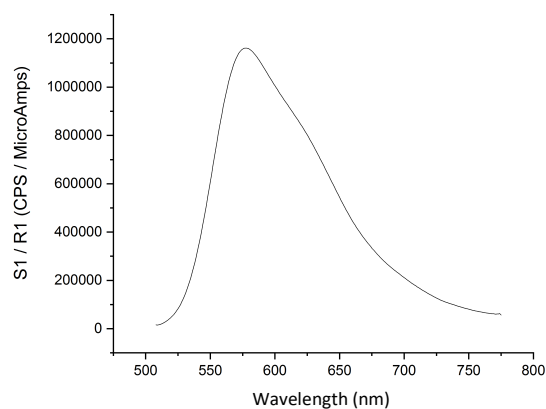
Emission Slit Width: 2 nm

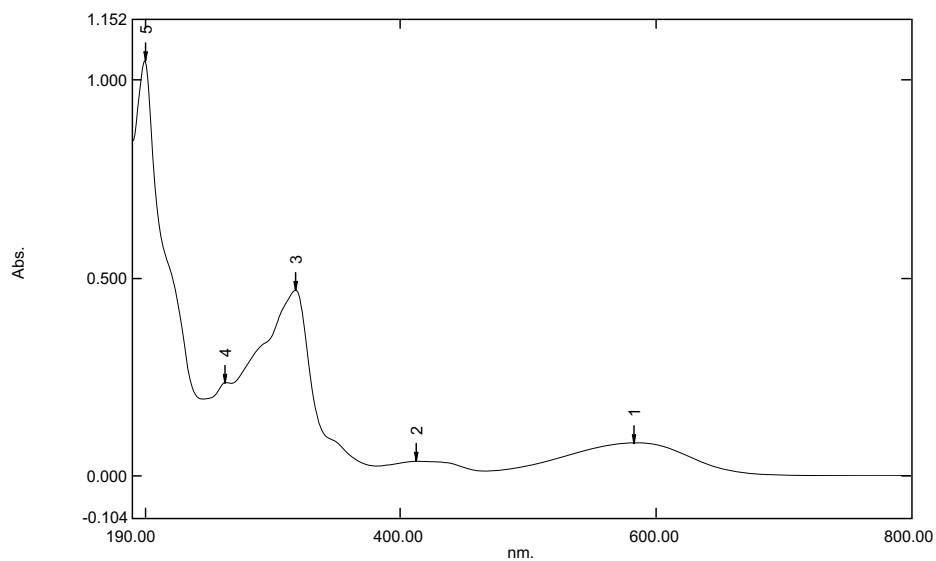
Integration Time: 0.2 s

Solvent: MeCN

 $\lambda_{em}$ : 578 nm

FWHM: 98 nm



**7-(Dimethylamino)-9-mesityl-1-methoxy-10-phenylacridinium bromide salt 4k**UV/Vis Spectroscopy:

Measurement Properties  
Wavelength Range (nm.): 190.00 to 800.00  
Scan Speed: Medium  
Sampling Interval: 1.0  
Auto Sampling Interval: Disabled  
Scan Mode: Single

Sample Preparation Properties  
Weight: 0.793 mg  
Volume: 100 mL  
Dilution: -  
Path Length: 1.00 cm  
Additional Information: CF1230P in Acetonitrile

No.	P/V	Wavelength	Abs.	Description
1	⊕	583.00	0.084	
2	⊕	412.00	0.037	
3	⊕	318.00	0.469	
4	⊕	263.00	0.236	
5	⊕	200.00	1.047	
6	⊕	772.00	0.001	
7	⊕	465.00	0.012	
8	⊕	381.00	0.025	
9	⊕	268.00	0.234	
10	⊕	245.00	0.194	

Instrument Properties  
Instrument Type: UV-1600 Series  
Measuring Mode: Absorbance  
Slit Width: 2.0 nm  
Light Source Change Wavelength: 340.8 nm  
S/R Exchange: Normal

Attachment Properties  
Attachment: None  
FWHM: 111 nm

Fluorescence Spectroscopy:

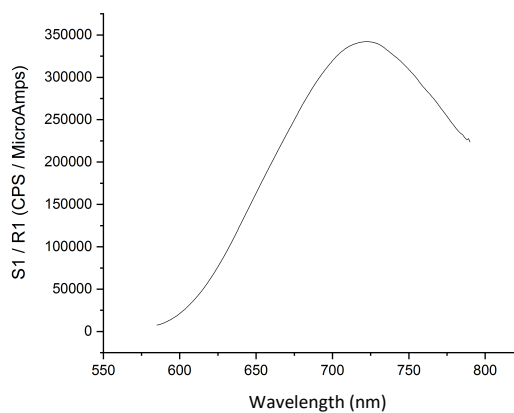
Excitation Wavelength: 570 nm

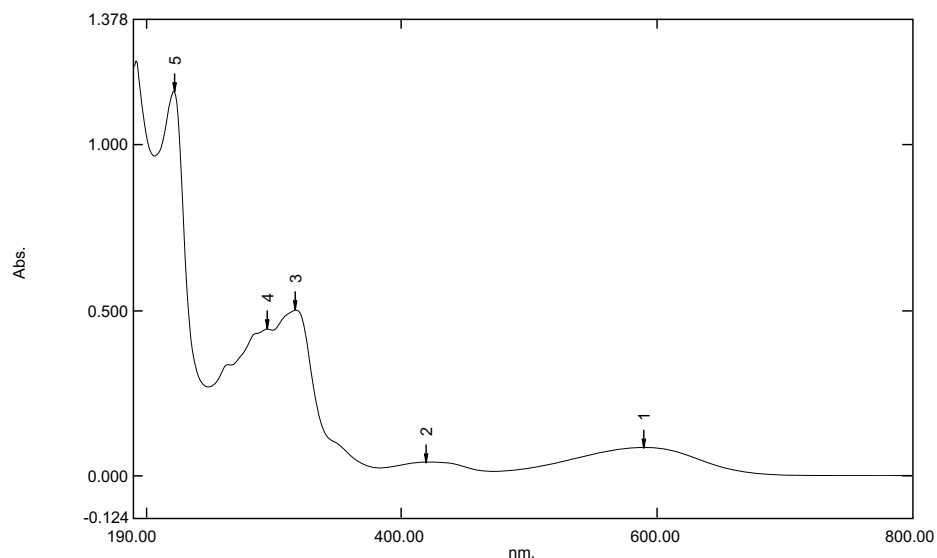
Excitation Slit Width: 8 nm

Emission Slit Width: 2 nm

Integration Time: 0.4 s

Solvent: MeCN

 $\lambda_{em}$ : 723 nmFWHM:  $\approx$  140 nm

**(±)-7-(Dimethylamino)-1-methoxy-9-(naphthalen-1-yl)-10-phenylacridinium bromide salt 4I**UV/Vis Spectroscopy:

Measurement Properties  
Wavelength Range (nm.): 190.00 to 800.00  
Scan Speed: Medium  
Sampling Interval: 1.0  
Auto Sampling Interval: Disabled  
Scan Mode: Single

Sample Preparation Properties  
Weight: 0.334 mg  
Volume: 10 mL  
Dilution: 3 fold  
Path Length: 1.00 cm  
Additional Information: CF1253P rac in Acetonitrile

Instrument Properties  
Instrument Type: UV-1600 Series  
Measuring Mode: Absorbance  
Slit Width: 2.0 nm  
Light Source Change Wavelength: 340.8 nm  
S/R Exchange: Normal

Attachment Properties  
Attachment: None  
FWHM: 112 nm

No.	P/V	Wavelength	Abs.	Description
1	⊕	590.00	0.086	
2	⊕	419.00	0.042	
3	⊕	317.00	0.500	
4	⊕	295.00	0.443	
5	⊕	222.00	1.161	
6	⊕	725.00	0.001	
7	⊕	472.00	0.014	
8	⊕	381.00	0.024	
9	⊕	299.00	0.440	
10	⊕	249.00	0.269	
11	⊕	206.00	0.966	

Fluorescence Spectroscopy:

Excitation Wavelength: 580 nm

Excitation Slit Width: 10 nm

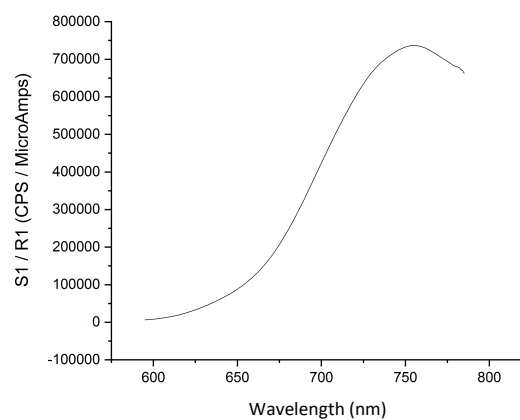
Emission Slit Width: 3 nm

Integration Time: 0.4 s

Solvent: MeCN

$\lambda_{em}$ : 755 nm

FWHM:  $\approx$  122 nm

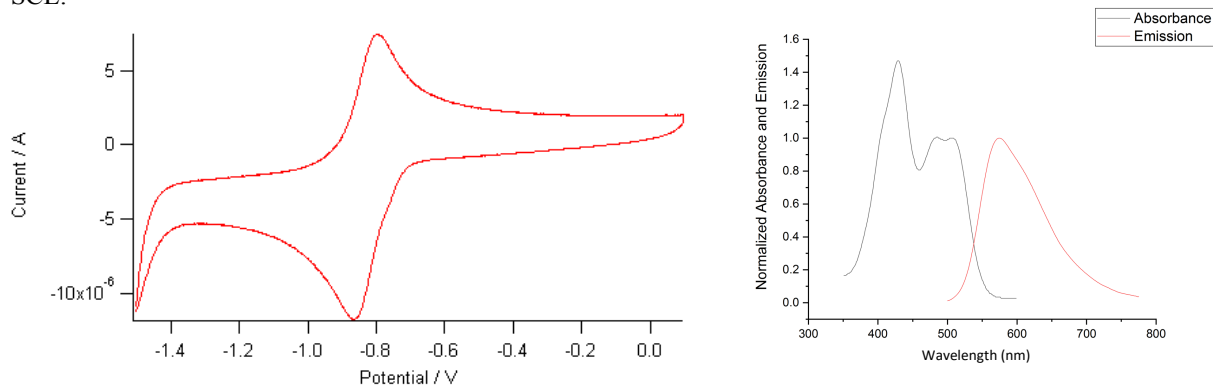




## Cyclic Voltammetry (CV)

### 6-(Dimethylamino)-1-methoxy-10-methyl-9-phenylacridinium bromide salt **4a**:

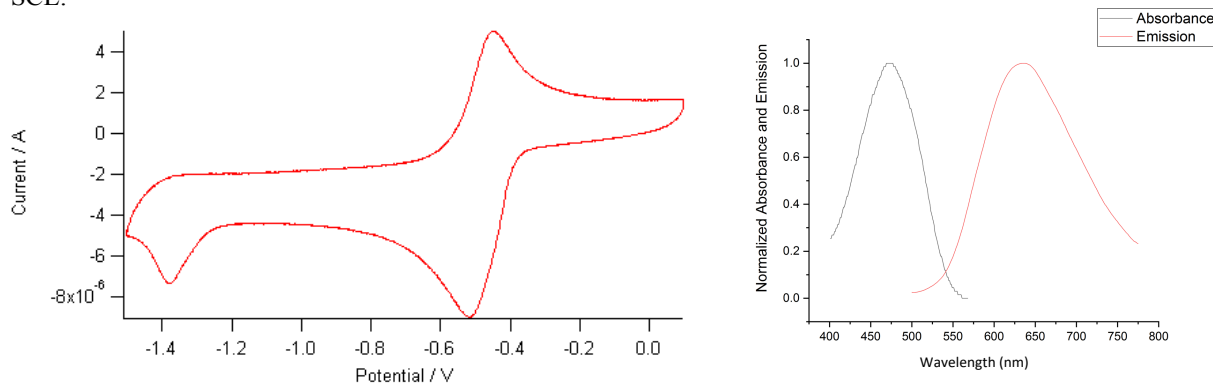
Cyclic voltammogram of acridinium dye **4a** shows a ground state reduction potential  $E_{1/2}(P/P^-)$  of  $-0.83$  V against SCE.



The excitation energy ( $E_{0,0}$ ) of acridinium dye **4a** is  $538$  nm or  $2.30$  eV. Resulting in an excited state reduction potential  $E_{1/2}(P^*/P^-)$  of  $+1.47$  V.

### 1-Methoxy-10-methyl-9-phenylacridinium bromide salt **4b**:

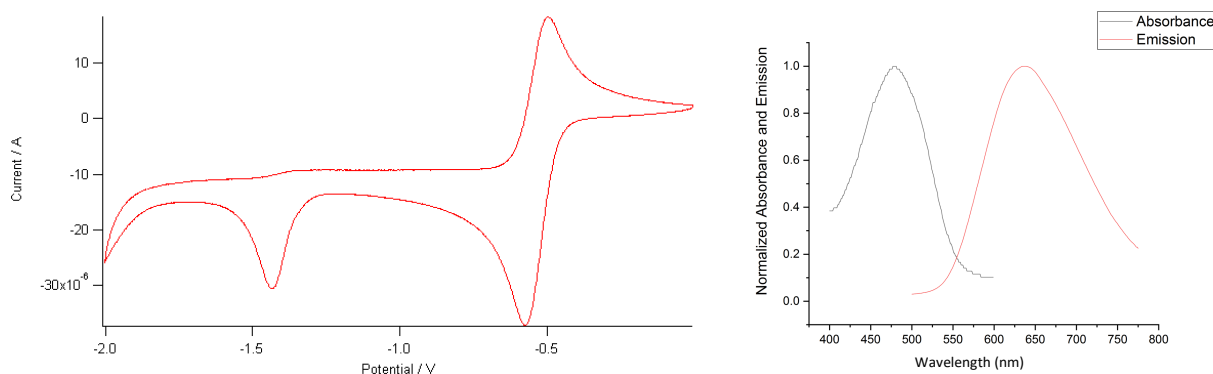
Cyclic voltammogram of acridinium dye **4b** shows a ground state reduction potential  $E_{1/2}(P/P^-)$  of  $-0.48$  V against SCE.



The excitation energy ( $E_{0,0}$ ) of acridinium dye **4b** is  $541$  nm or  $2.29$  eV. Resulting in an excited state reduction potential  $E_{1/2}(P^*/P^-)$  of  $+1.81$  V.

### 1-Methoxy-9,10-diphenylacridinium bromide salt **4c**:

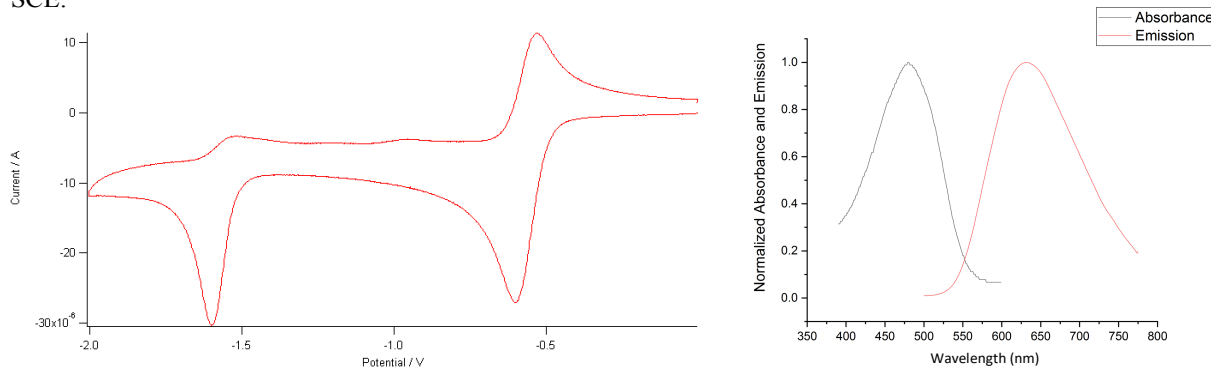
Cyclic voltammogram of acridinium dye **4c** shows a ground state reduction potential  $E_{1/2}(P/P^-)$  of  $-0.54$  V against SCE.



The excitation energy ( $E_{0,0}$ ) of acridinium dye **4c** is  $555$  nm or  $2.23$  eV. Resulting in an excited state reduction potential  $E_{1/2}(P^*/P^-)$  of  $+1.69$  V.

### 9-Mesityl-1-methoxy-10-phenylacridinium bromide salt **4d**:

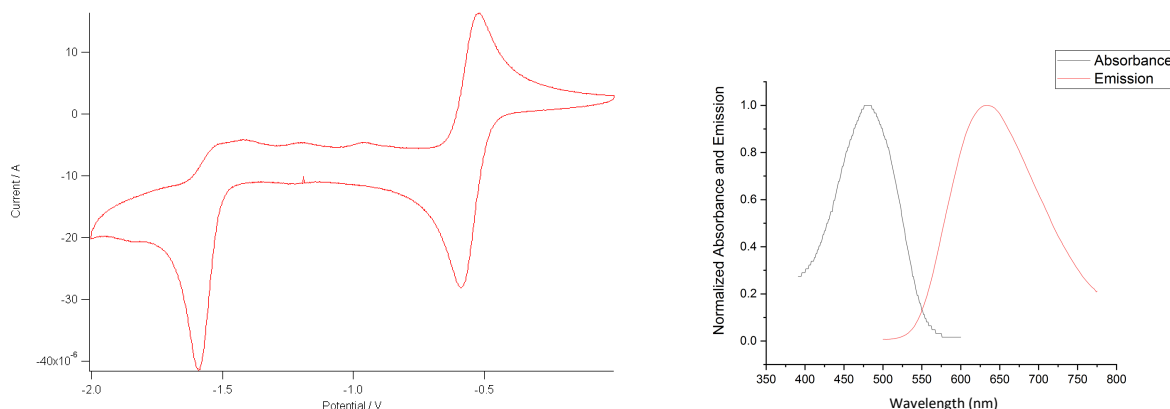
Cyclic voltammogram of acridinium dye **4d** shows a ground state reduction potential  $E_{1/2}(P/P^-)$  of  $-0.57$  V against SCE.



The excitation energy ( $E_{0,0}$ ) of acridinium dye **4d** is  $552$  nm or  $2.25$  eV. Resulting in an excited state reduction potential  $E_{1/2}(P^*/P^-)$  of  $+1.68$  V.

**9-(2,6-Dimethylphenyl)-1-methoxy-10-phenylacridinium bromide salt 4e:**

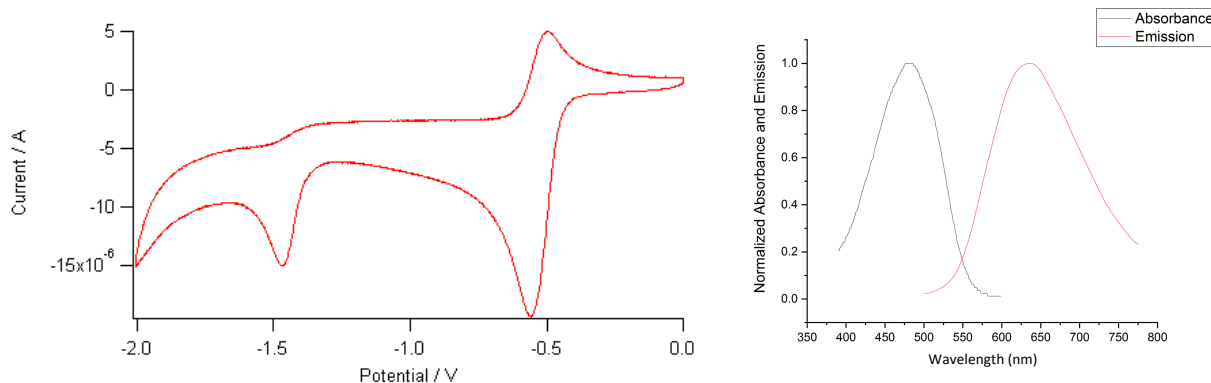
Cyclic voltammogram of acridinium dye **4e** shows a ground state reduction potential  $E_{1/2}(P/P^-)$  of  $-0.56$  V against SCE.



The excitation energy ( $E_{0,0}$ ) of acridinium dye **4e** is  $550$  nm or  $2.25$  eV. Resulting in an excited state reduction potential  $E_{1/2}(P^*/P^-)$  of  $+1.69$  V.

**( $\pm$ )-1-Methoxy-9-(naphthalen-1-yl)-10-phenylacridinium bromide salt 4f:**

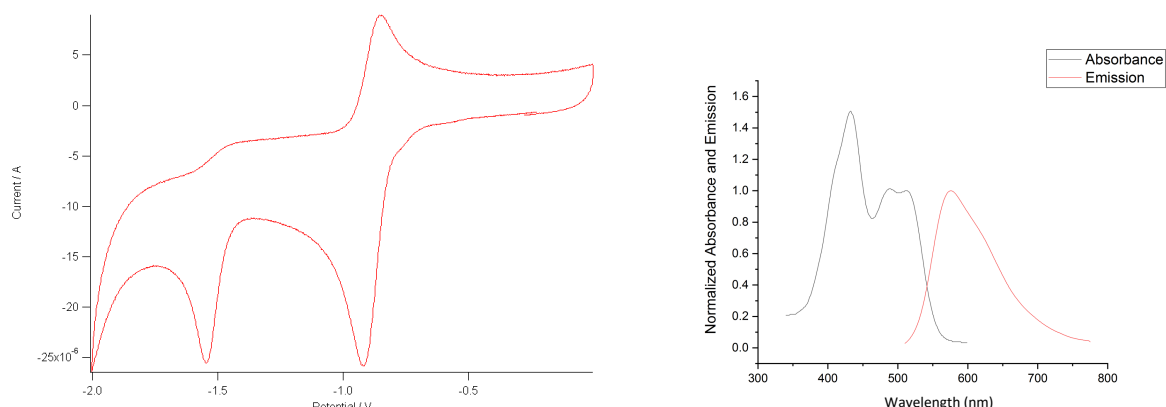
Cyclic voltammogram of acridinium dye **4f** shows a ground state reduction potential  $E_{1/2}(P/P^-)$  of  $-0.53$  V against SCE.



The excitation energy ( $E_{0,0}$ ) of acridinium dye **4f** is  $549$  nm or  $2.26$  eV. Resulting in an excited state reduction potential  $E_{1/2}(P^*/P^-)$  of  $+1.73$  V.

**6-(Dimethylamino)-1-methoxy-9,10-diphenylacridinium bromide salt 4g:**

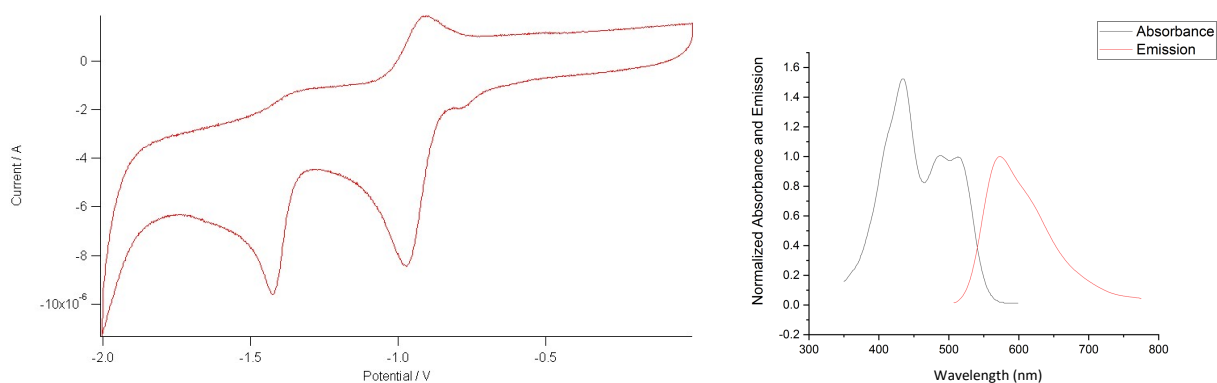
Cyclic voltammogram of acridinium dye **4g** shows a ground state reduction potential  $E_{1/2}(P/P^-)$  of  $-0.89$  V against SCE.



The excitation energy ( $E_{0,0}$ ) of acridinium dye **4g** is  $542$  nm or  $2.29$  eV. Resulting in an excited state reduction potential  $E_{1/2}(P^*/P^-)$  of  $+1.40$  V.

**6-(Dimethylamino)-9-mesityl-1-methoxy-10-phenylacridinium bromide salt 4h:**

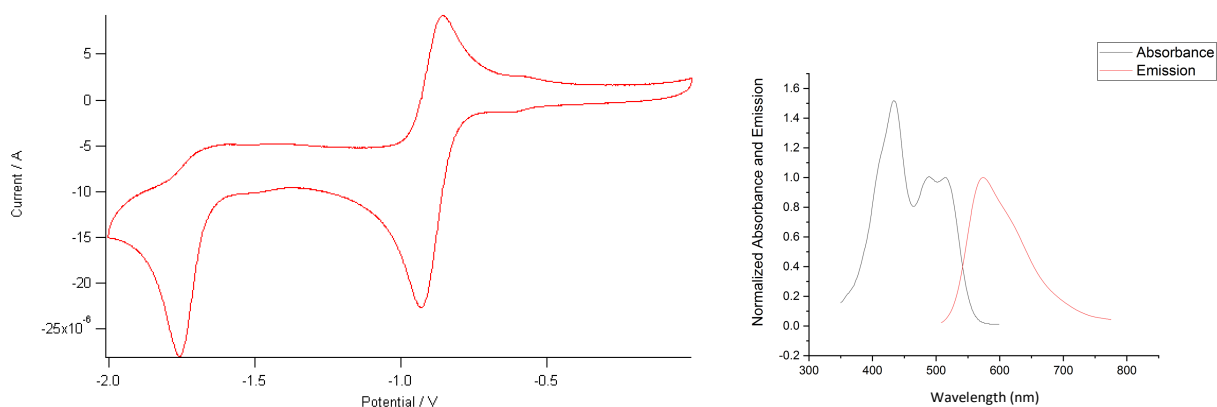
Cyclic voltammogram of acridinium dye **4h** shows a ground state reduction potential  $E_{1/2}(P/P^-)$  of  $-0.89$  V against SCE.



The excitation energy ( $E_{0,0}$ ) of acridinium dye **4h** is  $541$  nm or  $2.29$  eV. Resulting in an excited state reduction potential  $E_{1/2}(P^*/P^-)$  of  $+1.40$  V.

**6-(Dimethylamino)-9-(2,6-dimethylphenyl)-1-methoxy-10-phenylacridinium bromide 4i:**

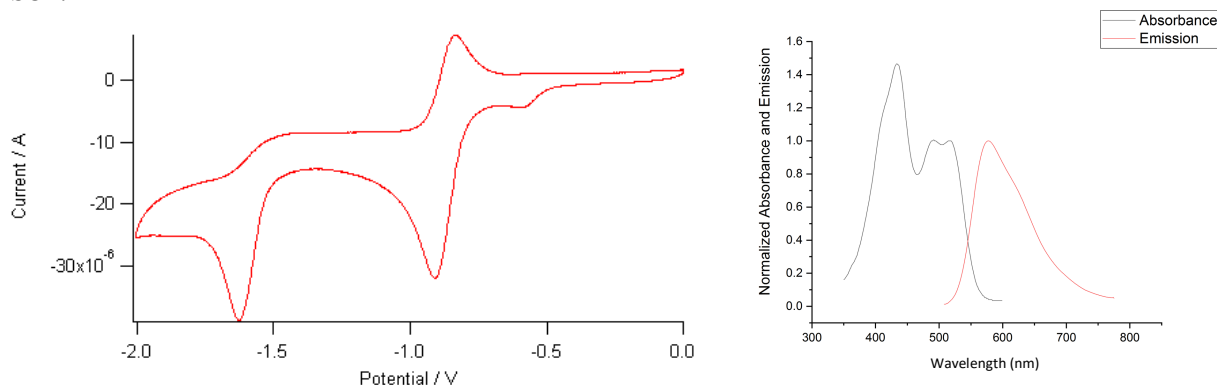
Cyclic voltammogram of acridinium dye **4i** shows a ground state reduction potential  $E_{1/2}(P/P^-)$  of  $-0.90$  V against SCE.



The excitation energy ( $E_{0,0}$ ) of acridinium dye **4i** is  $541$  nm or  $2.29$  eV. Resulting in an excited state reduction potential  $E_{1/2}(P^*/P^-)$  of  $+1.39$  V.

**(±)-6-(Dimethylamino)-1-methoxy-9-(naphthalen-1-yl)-10-phenylacridinium bromide salt 4j:**

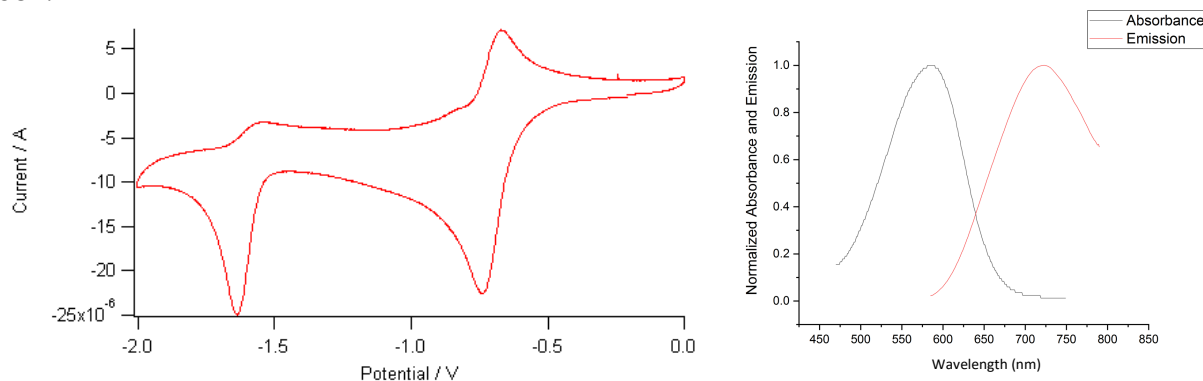
Cyclic voltammogram of acridinium dye **4j** shows a ground state reduction potential  $E_{1/2}(P/P^-)$  of  $-0.87$  V against SCE.



The excitation energy ( $E_{0,0}$ ) of acridinium dye **4j** is 545 nm or 2.27 eV. Resulting in an excited state reduction potential  $E_{1/2}(P^*/P^-)$  of +1.40 V.

**7-(Dimethylamino)-9-mesityl-1-methoxy-10-phenylacridinium bromide salt **4k**:**

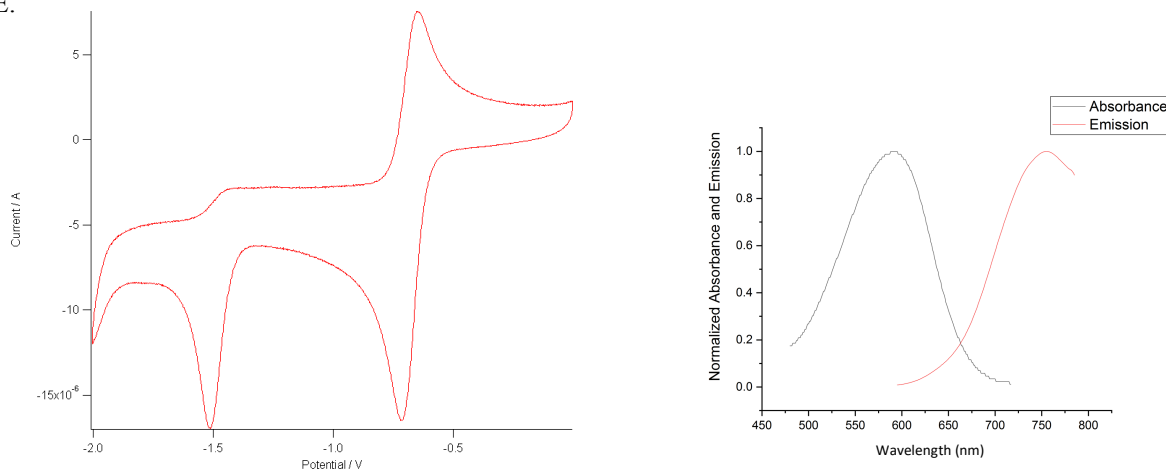
Cyclic voltammogram of acridinium dye **4k** shows a ground state reduction potential  $E_{1/2}(P/P^-)$  of  $-0.71$  V against SCE.



The excitation energy ( $E_{0,0}$ ) of acridinium dye **4k** is 640 nm or 1.94 eV. Resulting in an excited state reduction potential  $E_{1/2}(P^*/P^-)$  of +1.23 V.

**(±)-7-(Dimethylamino)-1-methoxy-9-(naphthalen-1-yl)-10-phenylacridinium bromide salt **4l**:**

Cyclic voltammogram of acridinium dye **4l** shows a ground state reduction potential  $E_{1/2}(P/P^-)$  of  $-0.68$  V against SCE.

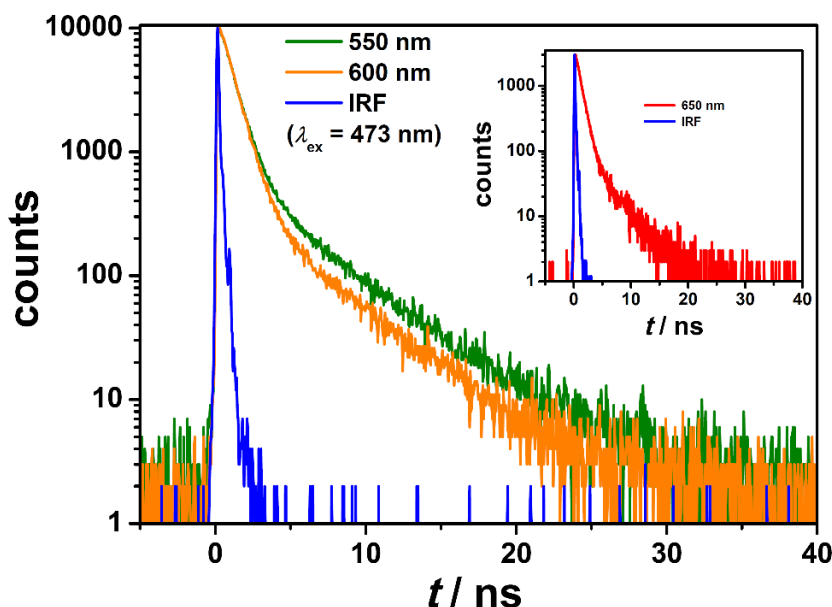


The excitation energy ( $E_{0,0}$ ) of acridinium dye **4l** is 663 nm or 1.87 eV. Resulting in an excited state reduction potential  $E_{1/2}(P^*/P^-)$  of +1.19 V.

## Emission Lifetime Determinations

Excited singlet lifetime investigations were carried out with the same methodology as described for the quenching studies presented on page S6.

Emission lifetimes of acridinium dyes **4a-l** were measured monitoring the emission decay using at least two detection wavelengths to obtain reliable results. An example of the TCSPC measurements for compound **4a** is displayed in Figure S6.



**Figure S6:** Fluorescence lifetime determination of **4a** in deoxygenated MeCN upon pulsed 473 nm excitation. Emission traces were recorded at 550 nm, 600 nm (main plot) as well as 650 nm (inset), together with the instrument response function of the TCSPC apparatus. See text for further details.

Emission decay traces were fitted with a minimum number of lifetimes required for a satisfactory decay analysis. The emission lifetime results so obtained have been compiled in Table S1 and are summarized in Table 2 of the main paper.

**Table S1:** Emission lifetimes of the acridinium dyes in deoxygenated MeCN determined from TCSPC experiments upon 473 nm excitation. **a)** Relative contribution of a respective lifetime to the multiexponential fit given in brackets.

Dye	Fluorescence lifetime / ns <sup>a</sup>		
	Detection wavelength 1	Detection wavelength 2	Detection wavelength 3
<b>4a</b>	550 nm: <b>0.9</b> (47%), <b>4.5</b> (53%)	600 nm: <b>0.9</b> (60%), <b>4.6</b> (40%)	650 nm: <b>0.9</b> (67%), <b>4.1</b> (33%)
<b>4b</b>	515 nm: <b>2.7</b> (29%), <b>17.5</b> (71%)	600 nm: <b>1.0</b> (53%), <b>3.3</b> (28%), <b>17.0</b> (19%)	-
<b>4c</b>	570 nm: <b>1.1</b> (41%), <b>10.1</b> (59%)	605 nm: <b>1.0</b> (79%), <b>9.7</b> (21%)	675 nm: <b>1.0</b> (100%)
<b>4d</b>	580 nm: <b>1.4</b> (78%), <b>12.2</b> (22%)	600 nm: <b>1.4</b> (91%), <b>12.0</b> (9%)	660 nm: <b>1.4</b> (100%)
<b>4e</b>	515 nm: <b>3.3</b> (20%), <b>16.8</b> (80%)	600 nm: <b>1.2</b> (91%), <b>3.3</b> (9%)	-
<b>4f</b>	605 nm: <b>1.0</b> (47%), <b>4.5</b> (53%)	650 nm: <b>0.9</b> (65%), <b>4.4</b> (35%)	-
<b>4g</b>	570 nm: <b>1.0</b> (48%), <b>6.9</b> (52%)	650 nm: <b>1.0</b> (45%), <b>6.9</b> (55%)	-
<b>4h</b>	565 nm: <b>1.0</b> (61%), <b>6.6</b> (39%)	670 nm: <b>1.1</b> (61%), <b>6.9</b> (39%)	-
<b>4i</b>	565 nm: <b>1.0</b> (60%), <b>7.3</b> (40%)	650 nm: <b>1.1</b> (32%), <b>7.1</b> (68%)	-
<b>4j</b>	570 nm: <b>1.0</b> (58%), <b>6.1</b> (42%)	650 nm: <b>1.0</b> (63%), <b>6.2</b> (37%)	-
<b>4k</b>	635 nm: <b>1.6</b> (20%), <b>5.9</b> (80%)	675 nm: <b>1.3</b> (11%), <b>4.7</b> (89%)	-
<b>4l</b>	670 nm: <b>0.8</b> (40%), <b>4.9</b> (60%)	700 nm: <b>0.9</b> (31%), <b>5.0</b> (69%)	-

The following results support the absence of emissive impurities: (a) Prior to our lifetime measurements, purity of all compounds has been confirmed by HPLC analysis and <sup>1</sup>H NMR spectroscopy. (b) When we carried out the very same lifetime measurement several times (same dye solution), identical results were obtained, indicating perfect photostability during our measurements. Our kinetic measurements thus establish the multiexponential

nature of the emission decays of the novel acridinium dyes. These results are also in line with steady-state emission spectra recorded with shorter excitation wavelengths than shown on SI pages S17-S28 (the 473 nm laser used for kinetic emission spectroscopy does not selectively excite the long-wavelength absorption bands of all acridinium dyes), which usually show more than one emission maximum or at least a shoulder in the spectrum, suggesting that dual emission occurs. Similar observations have also been made for other (sometimes unsymmetrically substituted) acridinium dyes.<sup>[22,27]</sup>

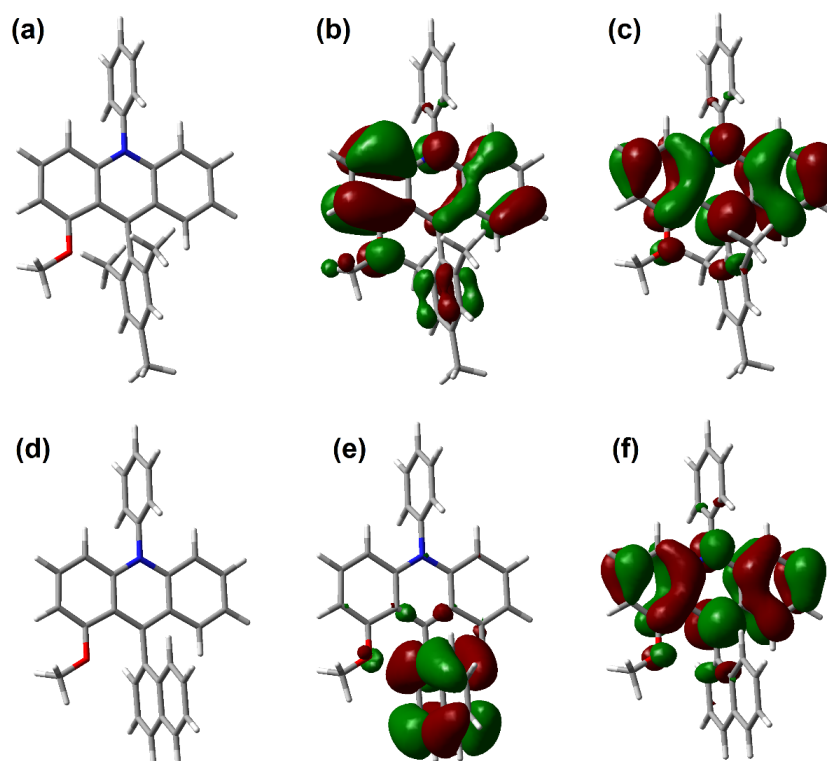
## Quantum Mechanical Calculations of 4a-4l

These DFT calculations were carried out as described for organocatalyst **1** (see p. S4).

The agreement between theoretical calculations and experimental results for the acridinium ion **1** triplet energy, and the fact that similar DFT calculations have already proven very successful for the estimation of triplet energies,<sup>[9,28,29]</sup> prompted us to calculate this quantity for all novel acridinium dyes with the same methodology as in Figure S2. These results are included in Table 2 of the main paper.

We limited our orbital analysis to the frontier orbitals, since they usually determine the excited-state reactivity of a respective dye. Depending on the electron-donating ability of the substituent at the central carbon atom (naphthyl > mesityl > vic.-*m*-xylyl > phenyl) and the degree of donor substitution at the acridinium core, different HOMO-LUMO transition types result. Charge-transfer (CT) transitions between an aryl-localized HOMO and an acridinium-localized LUMO, which populate an excited state comprising a formal aryl radical cation and a neutral acridinium radical, play a role when rather electron poor acridinium moieties are combined with rather electron rich aryl substituents, as our calculations on all acridinium dyes suggest (see Table 2 of the main paper). A similar behavior was calculated and experimentally observed for Fukuzumi's catalyst (see Fig. 1 of the main paper and ref. <sup>[30]</sup>). However, our calculations predict a pure  $\pi$ - $\pi^*$  transition for most of the novel acridinium dyes (an example is given for compound **1** in Fig. 1 of the main paper).

The frontier orbitals of **4d** and **4f** have been collected in Figure S7. They illustrate how the orbital picture for a mixed CT/ $\pi$ - $\pi^*$  HOMO-LUMO transition (**4d**) and a quasi-pure CT transition (**4f**) look like.



**Figure S7:** DFT-optimized ground-state structures of **4d** (a) and **4f** (d) and their computed frontier orbitals. Panels (b) and (e) display the corresponding HOMOs, whereas (c) and (f) show the LUMOs. Further explanations, see text.

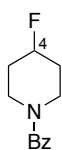
## Organophotocatalytic Benchmarking Reactions

### 1. Decarboxylative Fluorination

#### General Procedure D:

Prepared according to a modified literature procedure.<sup>[33]</sup> To a mixture of 1-chloromethyl-4-fluoro-1,4-diazonia-bicyclo[2.2.2]octane bis(tetrafluoroborate) (106 mg, 300  $\mu$ mol), sodium hydrogen phosphate (28.4 mg, 200  $\mu$ mol) and photocatalyst (2.5 mol%, *see table below*) in MeCN:H<sub>2</sub>O (1:1, 2.0 mL) was added carboxylic acid (100  $\mu$ mol) and was degassed by a stream of argon for 10 min. The reaction was performed under argon atmosphere with a 40 W blue LED for the time specified below.<sup>[32]</sup> The reaction mixture was twice treated with EtOAc (5 mL) and concentrated *in vacuo*. Purification (*specified below*) afforded fluorinated products in the yields indicated in the tables.

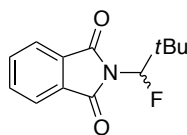
#### (4-Fluoropiperidin-1-yl)(phenyl)methanone (6a):



The compound was prepared according to the general procedure D, using 1-benzoyl-piperidine-4-carboxylic acid<sup>[34]</sup> (**5a**, 23.3 mg, 100  $\mu$ mol) and 6 h of irradiation. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, mixed with silica gel (1 g), concentrated *in vacuo* and the residue was column chromatographed over silica gel with eluent pentane:Et<sub>2</sub>O 2:1 to 1:2 to afford the product as a colorless oil: *R<sub>f</sub>* 0.21 (pentane:Et<sub>2</sub>O 1:2); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.39–7.42 (5H, m, C<sub>6</sub>H<sub>5</sub>), 4.84–4.97 (1H, m, C4H), 3.64–4.02 (2H, m, C2H<sub>2</sub>), 3.43–3.56 (2H, m, C6H<sub>2</sub>), 1.72–1.95 (4H, m, C3H<sub>2</sub>, C5H<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 170.5 (C=O), 135.9 (C1'), 129.7 (C4'), 128.6 (C3', C5'), 126.8 (C2', C6'), 87.7 (<sup>1</sup>*J*<sub>CF</sub> 171, C-F), 43.6 (C6), 38.1 (C2), 31.8 (C3), 31.0 (C5); <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>): –183.2; Analytical data is in agreement with literature.<sup>[33]</sup>

Photocatalyst	Yield of 6a
<b>4d</b> (1.21 mg, 2.5 mol%)	66% (13.6 mg)
<b>4e</b> (1.18 mg, 2.5 mol%)	58% (12.0 mg)
<b>4h</b> (1.32 mg, 2.5 mol%)	75% (15.6 mg)
<b>4i</b> (1.28 mg, 2.5 mol%)	<b>78% (16.1 mg)</b>
<b>4k</b> (1.32 mg, 2.5 mol%)	56% (11.5 mg)
<b>1</b> (1.20 mg, 2.5 mol%)	<b>80% (16.6 mg)</b>
9-Mesityl-2,7-dimethyl-10-phenylacridinium tetrafluoroborate (1.45 mg, 2.5 mol%)	52% (10.8 mg)
Fukuzumi (998 $\mu$ g, 2.5 mol%)	47% (9.79 mg)
4CzIPN (1.97 mg, 2.5 mol%)	65% (13.5 mg)

#### (±)-2-(1-Fluoro-2,2-dimethylpropyl)isoindoline-1,3-dione (6b):



The compound was prepared according to the general procedure D, using (*S*)-2-(1,3-dioxoisoindolin-2-yl)-3,3-dimethylbutanoic acid<sup>[35]</sup> (**5b**, 26.1 mg, 100  $\mu$ mol) and 3 h or 6 h of irradiation. The residue was filtered over a plug of silica gel with CH<sub>2</sub>Cl<sub>2</sub> affording the product as a white solid: *R<sub>f</sub>* 0.38 (pentane:CH<sub>2</sub>Cl<sub>2</sub> 1:1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.89–7.90 (2H, m, C5H, C8H), 7.76–7.79 (2H, m, C6H, C7H), 5.91 (1H, d, <sup>1</sup>*J*<sub>HF</sub> 44, CHF), 1.12 (9H, d, <sup>3</sup>*J* 1.1, C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 167.0 (C1, C3), 134.5 (C6, C7), 131.6 (C4, C9), 123.7 (C5, C8), 98.4 (<sup>1</sup>*J*<sub>CF</sub> 211, C-F), 37.2 (<sup>2</sup>*J*<sub>CF</sub> 23.4, C(CH<sub>3</sub>)<sub>3</sub>), 25.6 (<sup>3</sup>*J*<sub>CF</sub> 3.4, C(CH<sub>3</sub>)<sub>3</sub>); <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>): –173.0; Analytical data is in agreement with literature.<sup>[33]</sup>

Photocatalyst	Yield of <b>6b</b>	
<b>4d</b> (1.21 mg, 2.5 mol%)	90% (21.2 mg) <sup>a</sup> ;	94% (22.1 mg) <sup>b</sup>
<b>4e</b> (1.18 mg, 2.5 mol%)	<b>93% (21.9 mg)<sup>a</sup>;</b>	
<b>4h</b> (1.32 mg, 2.5 mol%)	83% (19.4 mg) <sup>a</sup> ;	88% (20.7 mg) <sup>b</sup>
<b>4i</b> (1.28 mg, 2.5 mol%)	86% (20.3 mg) <sup>a</sup> ;	88% (20.8 mg) <sup>b</sup>
<b>4k</b> (1.32 mg, 2.5 mol%)	89% (20.9 mg) <sup>a</sup>	
<b>(S<sub>a</sub>)-4f</b> (985 µg, 2.5 mol%) <sup>c</sup>	<b>94% (17.7 mg)<sup>a,c,d</sup></b>	
<b>1</b> (1.20 mg, 2.5 mol%)	85% (20.0 mg) <sup>a</sup>	
9-Mesityl-2,7-dimethyl-10-phenylacridinium tetrafluoroborate (1.45 mg, 2.5 mol%)	89% (21.0 mg) <sup>a</sup>	
Fukuzumi (998 µg, 2.5 mol%)	90% (21.2 mg) <sup>a</sup>	
4CzIPN (1.97 mg, 2.5 mol%)	84% (19.8 mg) <sup>a</sup>	

**a)** 3 h reaction time; **b)** 6 h reaction time; **c)** 80 µmol scale reaction; **d)** Product was obtained as a 1:1 enantiomer mixture, analyzed via HPLC on a Chiralcel® OD-H column (4.6 mm x 150 mm; 5 µm; Art. Nr. 14324) using a 1.0 mL/min flow of *n* heptane/*i* PrOH 95:5: 6.5 and 8.1 min.

## 2. Oxidative [3+2] Cycloaddition

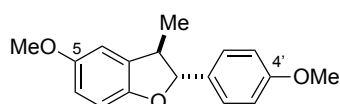
### General Procedure E:

Prepared according to a modified literature procedure.<sup>[31]</sup> To a mixture of *trans*-anethol (**8**, 19.3 mg, 130 µmol), ammonium peroxydisulfate (45.6 mg, 200 µmol) photocatalyst (2.5 mol%, *see table below*) in MeCN (3.0 mL) was added *p*-hydroxyanisole (**7**, 12.4 mg, 100 µmol) and was degassed by a stream of argon for 10 min. The reaction was performed under argon atmosphere with a 40 W blue LED for the time specified below.<sup>[32]</sup> The reaction mixture was filtered over silica gel and rinsed with EtOAc. The filtrate was concentrated *in vacuo*, dissolved in CH<sub>2</sub>Cl<sub>2</sub>, mixed with silica gel (1 g), concentrated *in vacuo* and the residue was column chromatographed over silica gel with cyclohexane:EtOAc 50:1-50:3 as eluent to afford cycloadducts in the yields indicated in the table.

Photocatalyst	Yield of <b>±9</b>	
<b>4d</b> (1.21 mg, 2.5 mol%)	43% (9.18 mg) <sup>a</sup> ;	19% (5.15 mg) <sup>b</sup>
<b>4e</b> (1.18 mg, 2.5 mol%)	55% (14.9 mg) <sup>a</sup>	
<b>4h</b> (1.32 mg, 2.5 mol%)	<b>77% (20.8 mg)<sup>a</sup>;</b>	33% (8.80 mg) <sup>b</sup>
<b>4i</b> (1.28 mg, 2.5 mol%)	57% (15.5 mg) <sup>a</sup> ;	31% (8.47 mg) <sup>b</sup>
<b>4k</b> (1.32 mg, 2.5 mol%)	37% (9.99 mg) <sup>a</sup>	
<b>(±)-4j</b> (1.34 µg, 2.5 mol%)	61% (16.4 mg) <sup>a,c,d</sup>	
<b>1</b> (1.20 mg, 2.5 mol%)	53% (14.2 mg) <sup>a</sup>	
9-Mesityl-2,7-dimethyl-10-phenylacridinium tetrafluoroborate (1.45 mg, 2.5 mol%)	71% (19.1 mg) <sup>a</sup>	
Fukuzumi (998 µg, 2.5 mol%)	45% (12.2 mg) <sup>a</sup>	
4CzIPN (1.97 mg, 2.5 mol%)	59% (15.9 mg) <sup>a</sup>	

**a)** 40 h reaction time; **b)** 24 h reaction time; **c)** 20 µmol scale reaction performed with enantioenriched **4j**; **d)** Product was obtained as racemic mixture, analyzed via HPLC on a Chiralcel® OD-H column (4.6 mm x 150 mm; 5 µm; Art. Nr. 14324) using a 1.0 mL/min flow of *n* heptane/*i* PrOH 95:5: 6.8 and 9.0 min.

### (±)-5-Methoxy-2-(4-methoxyphenyl)-3-methyl-2,3-dihydrobenzofuran (±**9**):



The compound was prepared according to the general procedure E to afford the product as a colorless oil: *R<sub>f</sub>* 0.29 (*n* hexane:EtOAc 5:1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.35–7.37 (2H, m, C2'*H*, C6'*H*), 6.90–6.92 (2H, m, C3'*H*, C5'*H*), 6.72–6.76 (1H, m, C4*H*), 6.69–6.72 (2H, m, C6*H*, C7*H*), 5.08 (1H, d, <sup>3</sup>*J* 9.0, C1*H*), 3.82 (3H, s, C4'*OCH*<sub>3</sub>), 3.78 (3H, s, C5*OCH*<sub>3</sub>), 3.38–3.44 (1H,



m, C2H), 1.38 (3H, d,  $^3J$  6.8, CH<sub>3</sub>);  $^{13}\text{C}$  NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 159.6 (C4'), 154.4 (C5), 153.3 (C8), 133.1 (C3), 132.7 (C1'), 127.7 (C2', C6'), 114.0 (C3', C5'), 112.9 (C6), 110.0 (C7), 109.4 (C4), 92.6 (C1), 56.1 (C4'OCH<sub>3</sub>), 55.3 (C5OCH<sub>3</sub>), 45.7 (C2), 17.6 (CH<sub>3</sub>); Analytical data is in agreement with literature.<sup>[31]</sup>

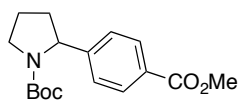
### 3. Divergent Organocatalytic Photoredox and TTET Pathways using Acridinium Salts

Carried out according to the General Procedure A described on pages S2-S4.

Photocatalyst	Yield of A	Yield of B
<b>1</b> (1.20 mg, 2.5 mol%) <sup>[13]</sup>	<b>86%</b>	-
<b>4d</b> (1.21 mg, 2.5 mol%) <sup>a,b</sup>	-	3%
<b>4e</b> (1.18 mg, 2.5 mol%) <sup>a,b</sup>	-	9%
<b>4h</b> (1.32 mg, 2.5 mol%) <sup>a,b</sup>	57%	5%
<b>4i</b> (1.28 mg, 2.5 mol%) <sup>a,b</sup>	75%	6%
<b>4k</b> (1.32 mg, 2.5 mol%) <sup>a,b</sup>	-	8%

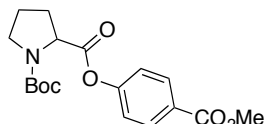
a) 6 h reaction time; b) in 3.0 mL DMF

#### *tert*-Butyl 2-(4-(methoxycarbonyl)phenyl)pyrrolidine-1-carboxylate (A):



Details about the preparation and characterization of this compound are described on pages S2-S4.

#### 1-(*tert*-Butyl) 2-(4-(methoxycarbonyl)phenyl) pyrrolidine-1,2-dicarboxylate (B):



Details about the preparation and characterization of this compound are described on pages S2-S4.

### 4. Stilbene Isomerizations

A solution of *trans*-stilbene (10 mM) and acridinium photocatalyst (0.1 mM, 1.0 mol%) in CD<sub>3</sub>CN (1.0 mL) was deoxygenated with argon for five minutes in a microwave tube. The mixture was irradiated with a Kessil A160 tuna blue lamp at room temperature for 1h. The conversion of *trans*- to *cis*-stilbene was monitored by  $^1\text{H}$  NMR spectroscopy. *cis*-Stilbene was detected as the only product produced upon illumination.

Photocatalyst	Yield of <i>cis</i>	Photocatalyst	Yield of <i>cis</i>
<b>1</b>	78%	<b>4h</b>	72%
<b>4a</b>	47%	<b>4i</b>	70%
<b>4b</b>	17%	<b>4j</b>	54%
<b>4c</b>	37%	<b>4k</b>	<b>84%</b>
<b>4d</b>	36%	<b>4l</b>	77%
<b>4e</b>	16%	<b>9-Mesityl-2,7-dimethyl-10-phenylacridinium tetrafluoroborate</b>	28%
<b>4f</b>	45%		
<b>4g</b>	41%	<b>Fukuzumi catalyst</b>	18%

With photocatalyst **1**, the previous results with green light (pages S5 and S6) were confirmed with a 78% yield for *cis*-stilbene. Notably, acridinium salts with a high  $E_T$  and relatively low  $E_{1/2}$  ( $P^*/P^-$ ) show mostly good *cis*-stilbene yields, while strongly oxidizing catalysts may promote stilbene radical cation formation through a photoinduced electron transfer<sup>[38]</sup> leading to lower yields for *cis*-stilbene. The interesting mechanistic details of the isomerization and competing back-isomerization processes, particularly for catalysts with low  $E_T$  and  $E_{1/2}$  ( $P^*/P^-$ ), are under current investigation in our laboratories and will be reported in due course.

## Photostability Studies

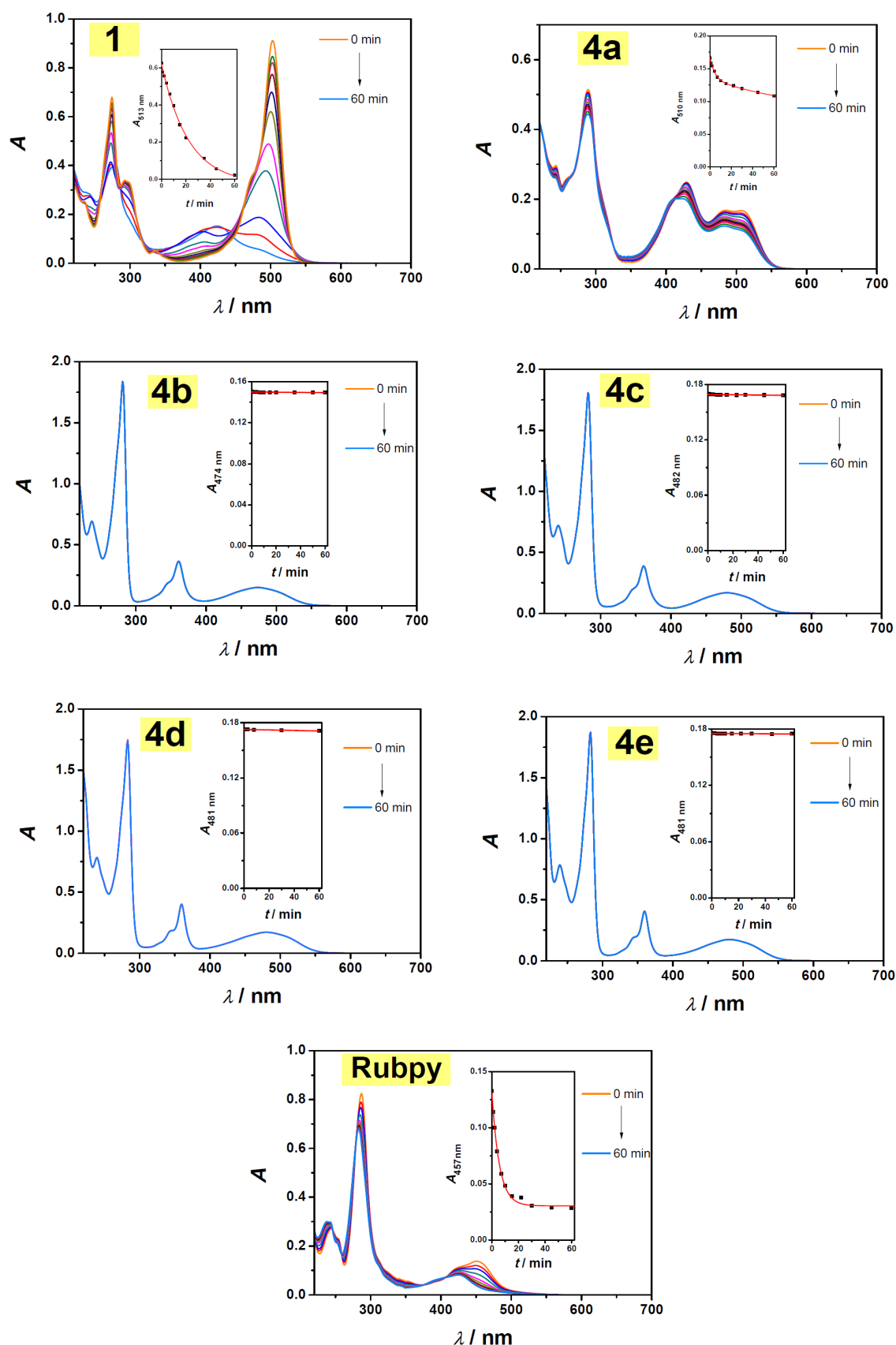
Several strategies to avoid acridinium catalyst bleaching by nucleophilic attack or radical addition during photoredox applications have already been identified.<sup>[22, 36, 37]</sup> In contrast, relatively little is known about the inherent photostability of acridinium dyes,<sup>[23]</sup> which we regard as a subject of equal importance. To address this issue, we irradiated strongly diluted (~10 to ~30  $\mu$ M) solutions of six acridinium dyes in the absence of dissolved oxygen, and monitored their UVVis absorption spectra over one hour of irradiation. The following conditions allowed us to compare their intrinsic photostabilities:

(i) 4 mL cuvettes containing 3 mL of deoxygenated acetonitrile and the respective dye were irradiated in the sample chamber of our UVVis spectrometer (Figure S8) with a 455 nm LED from Thorlabs (M455L3-C1), whose position and optical output power (500 mW) remained constant during all photostability measurements, (ii) the absorptions of the irradiated solutions at the peak emission wavelength (455 nm) were always 0.14 (a significantly higher absorption would cause heating of the solution, a much lower absorption would result in a poor detection sensitivity). Our setup thus makes sure that the same amount of light is absorbed by all dye solutions laying the grounds for (semi-)quantitative stability comparisons.



**Figure S8:** Setup used for photostability studies. Cuvettes with deoxygenated solutions were irradiated with a collimated 455 nm LED (M455L3-C1, Thorlabs) in the sample chamber of the Cary 5000 spectrophotometer (from Varian). The cuvette holder permits LED illumination of the whole UVVis detection volume at right angle to the detection beam. For clarity, the LED power was significantly reduced in the left part of the figure. Further details are given in the text.

The results for compound **1** (DMesMeAcr), the novel acridinium dyes **4a-e** and  $[\text{Ru}(\text{bpy})_3]^{2+}$  (reference) are summarized in Figure S9.

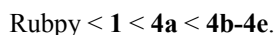


**Figure S9:** Comparative stability of six acridinium dyes and [Ru(bpy)<sub>3</sub>]<sup>2+</sup> (Rubpy) upon illumination with a blue LED (using the setup shown in Figure S8) in argon-saturated acetonitrile. Main plots, UV-Vis absorption spectra measured after the illumination times given in the corresponding insets. The illuminations were stopped for 2 minutes while the absorption spectra were detected. For further explanations, see text.

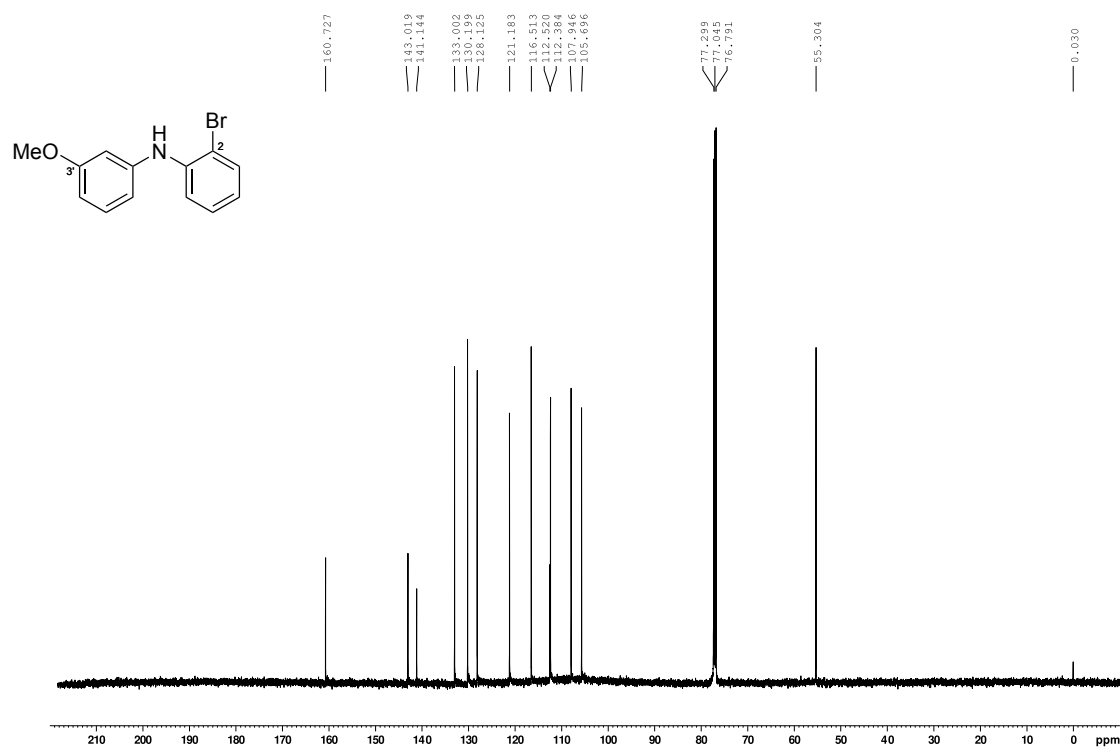
Under our standardized conditions, the photodecomposition of **1** is practically completed within one hour of irradiation, whereas photodegradation of **4a** is still ongoing. The absence of clear isosbestic points and the

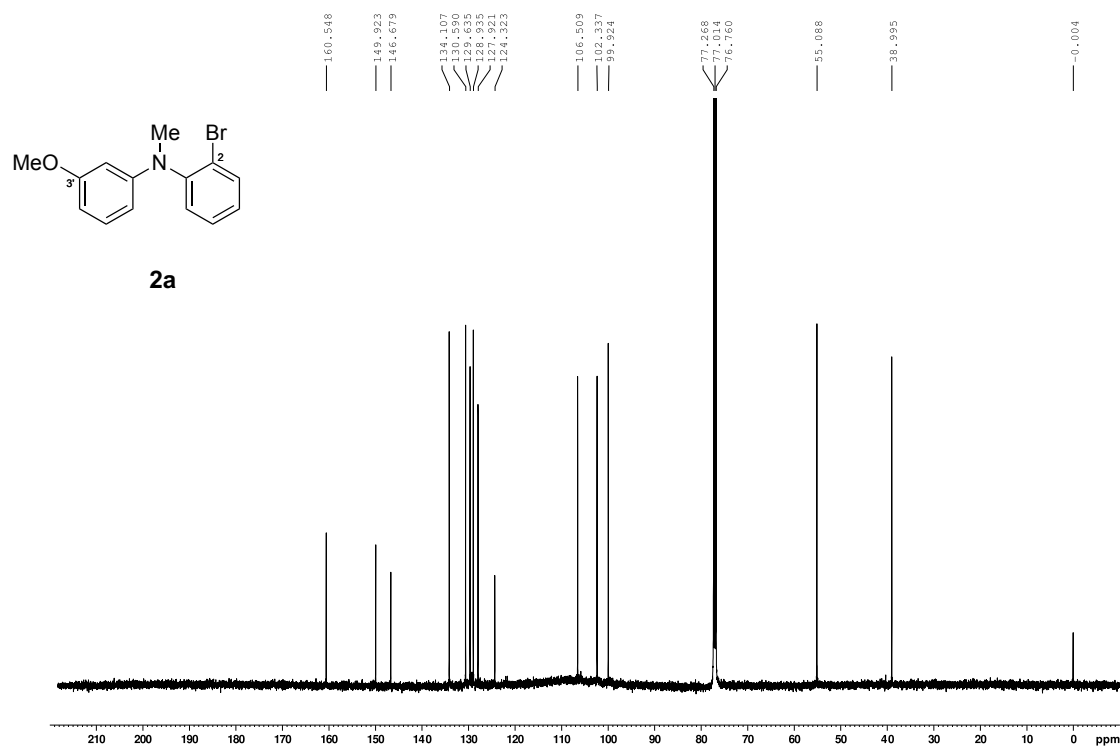
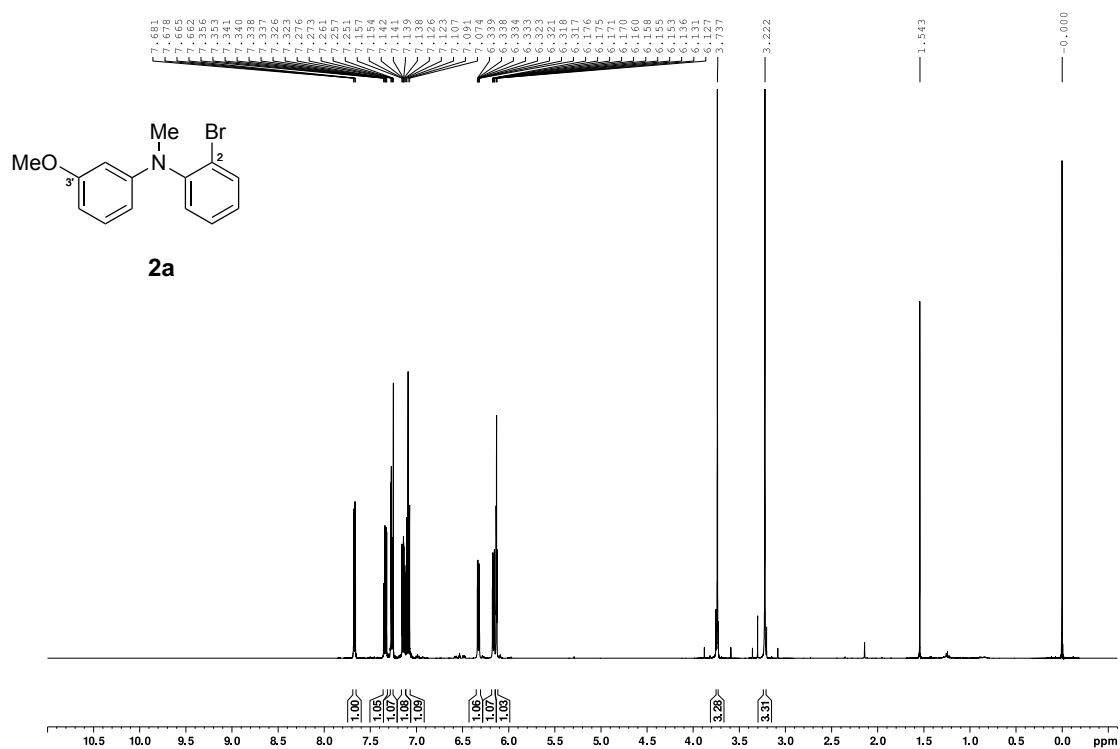
degradation kinetics (monitored at the wavelengths of maximum absorption changes in the course of irradiation, see the corresponding insets in Figure S9) suggest that photodecomposition is a stepwise process for both compounds. The UVVis absorption spectra of acridinium dyes **4b-e** in our photostability assay, however, are virtually identical to those of the respective freshly prepared solutions – the maximum relative absorption decrease is less than 2%. We regard it as very unlikely that decomposition product(s) and acridinium catalysts have the very same UVVis absorption spectrum and, in addition, the characteristic emission colors of **4b-e**, which can even be observed with the naked eye, do not alter upon irradiation. Therefore, we conclude that **4b-e** are almost completely stable under our irradiation conditions (Figures S8 and S9).

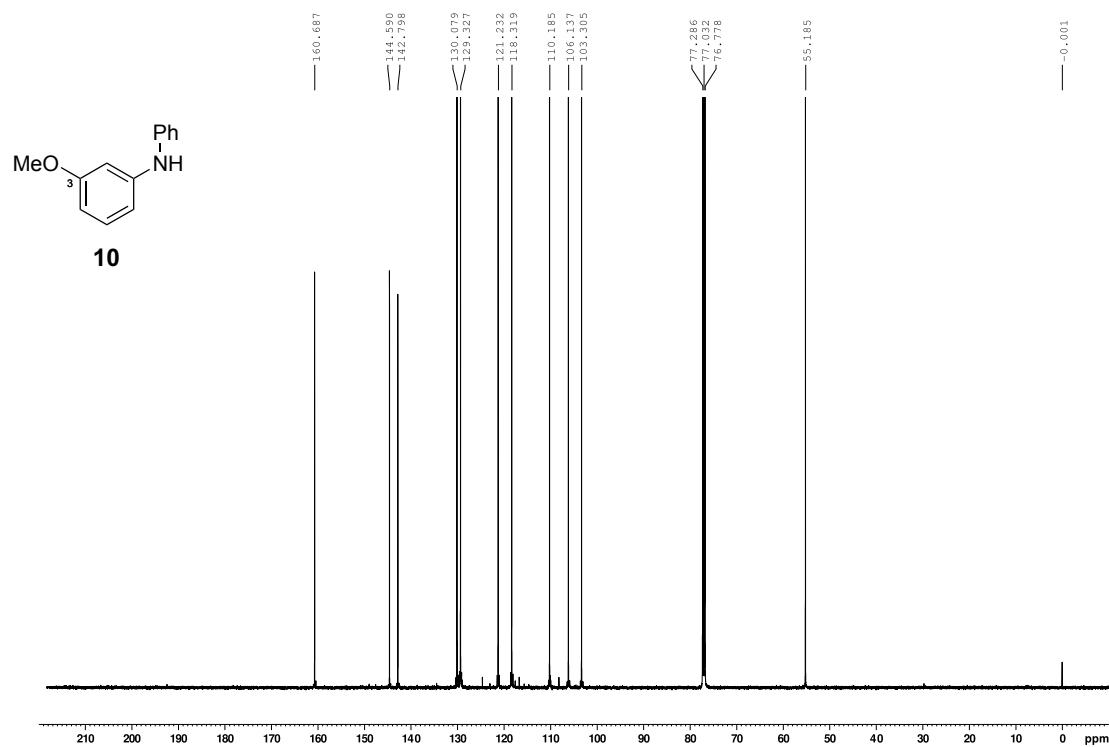
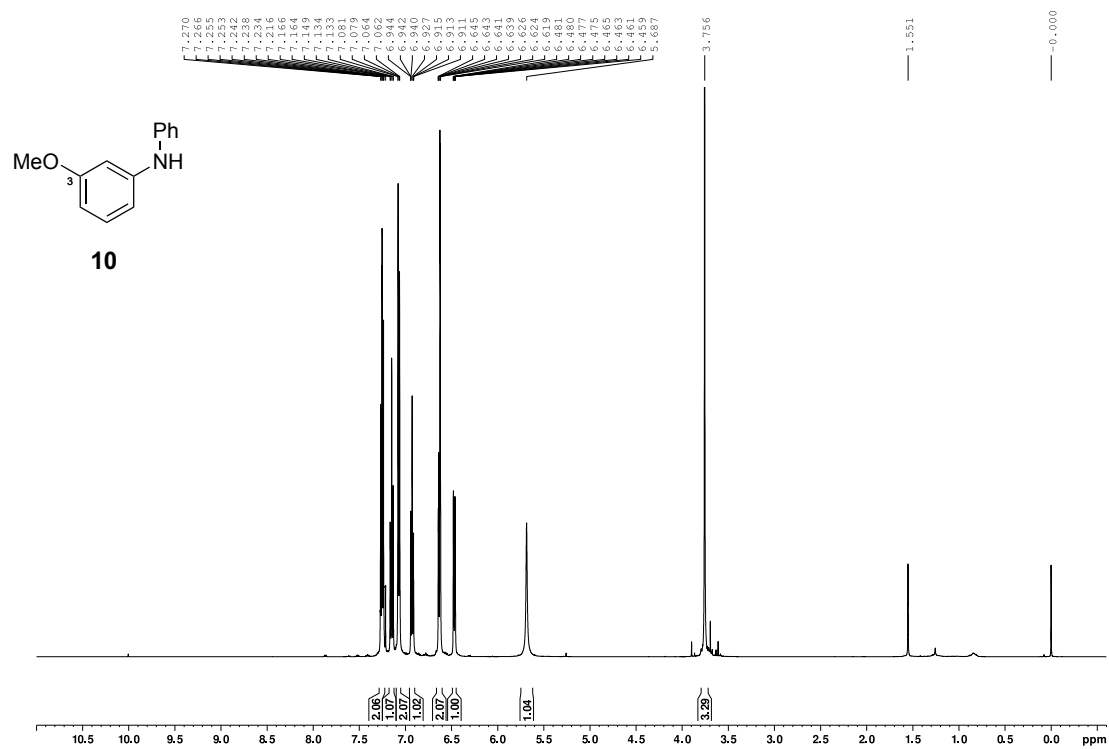
To compare our photostability results obtained for the six acridinium dyes to that of a widely-used reference compound, we investigated the complex [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (Rubpy), which is able to catalyze numerous photoredox reactions efficiently,<sup>[24–26]</sup> under the very same experimental conditions (Figure S8 and S9). After 30 minutes of blue light irradiation (455 nm, 500 mW), the UVVis spectrum of the Rubpy decomposition product(s) (in deoxygenated acetonitrile) does not change anymore, indicating that photodecomposition is even faster than for the least stable acridinium dye (**1**). Although the UVVis spectral changes presented in Figure S9 does not permit a quantitative analysis owing to spectral overlaps of starting materials and decomposition products, the kinetics of photodecomposition (insets of Figure S9) allow the following ordering regarding the inherent photostability, with Rubpy being least stable:

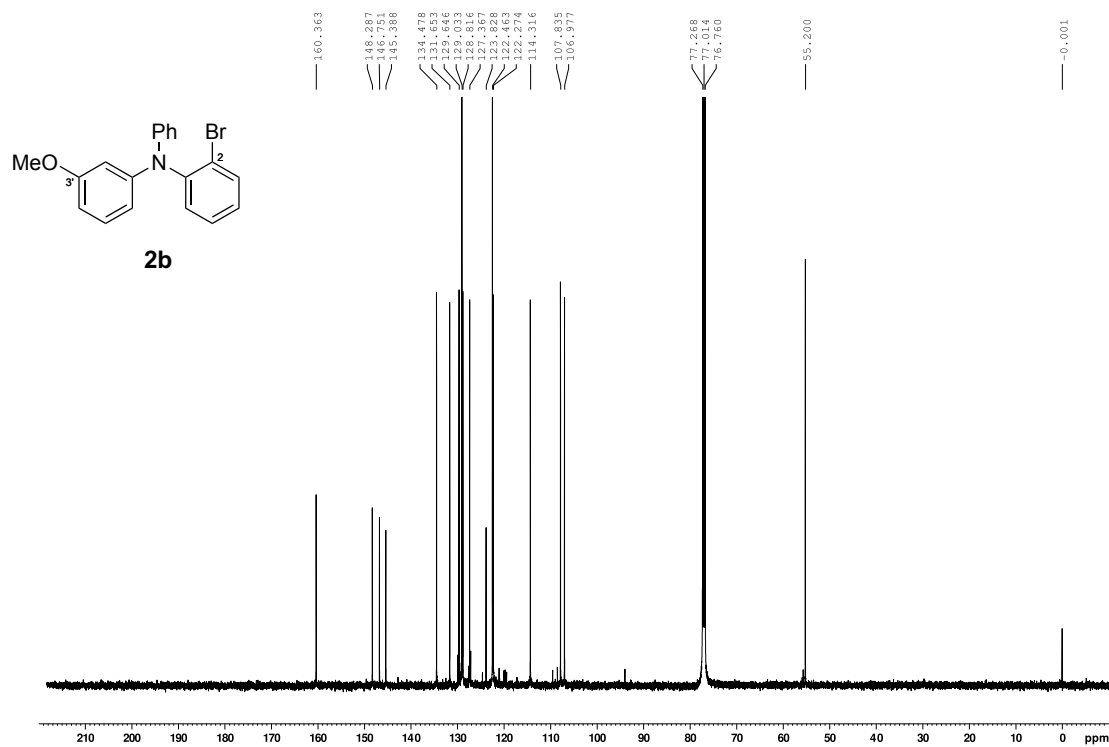
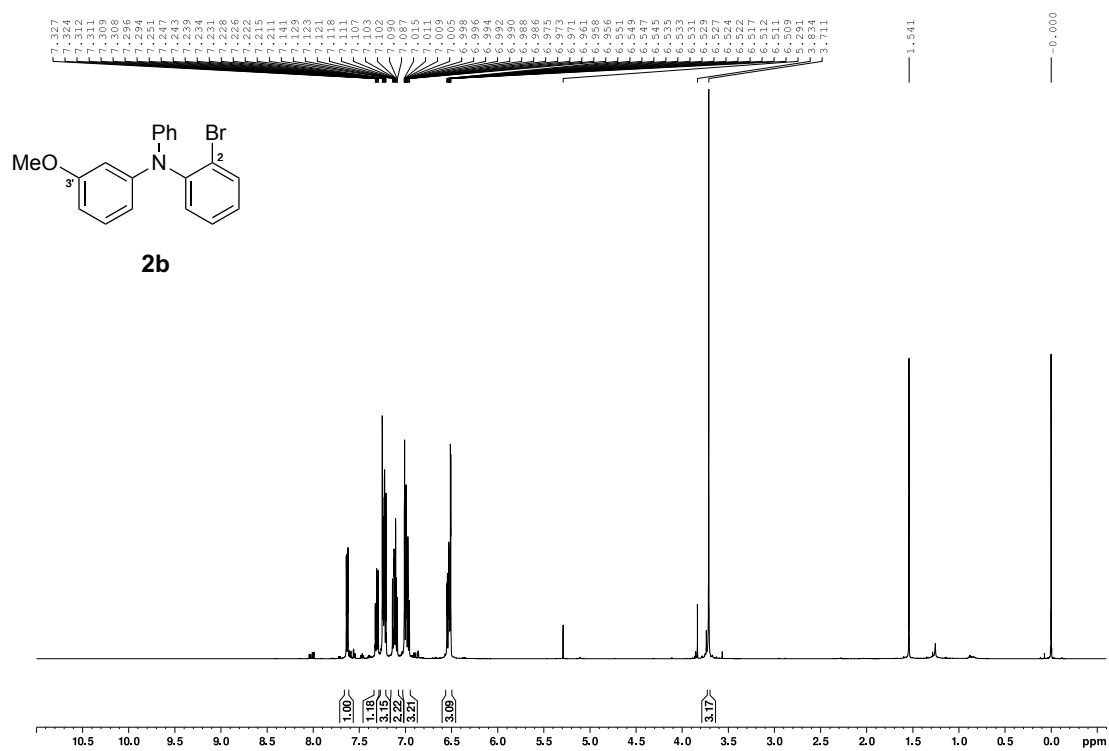


According to our results, the only structural element promoting fast photodegradation of the acridinium dyes in strongly diluted and deoxygenated acetonitrile solution is the -NMe<sub>2</sub> group (see Table 1 of the main paper for the structures of compounds **1** and **4a**). Dealkylation at the central nitrogen atom seems to be not detrimental to the intrinsic photostability, as the comparable photostability results for **4b** (N-Me) and **4c** (N-Ph) clearly show.

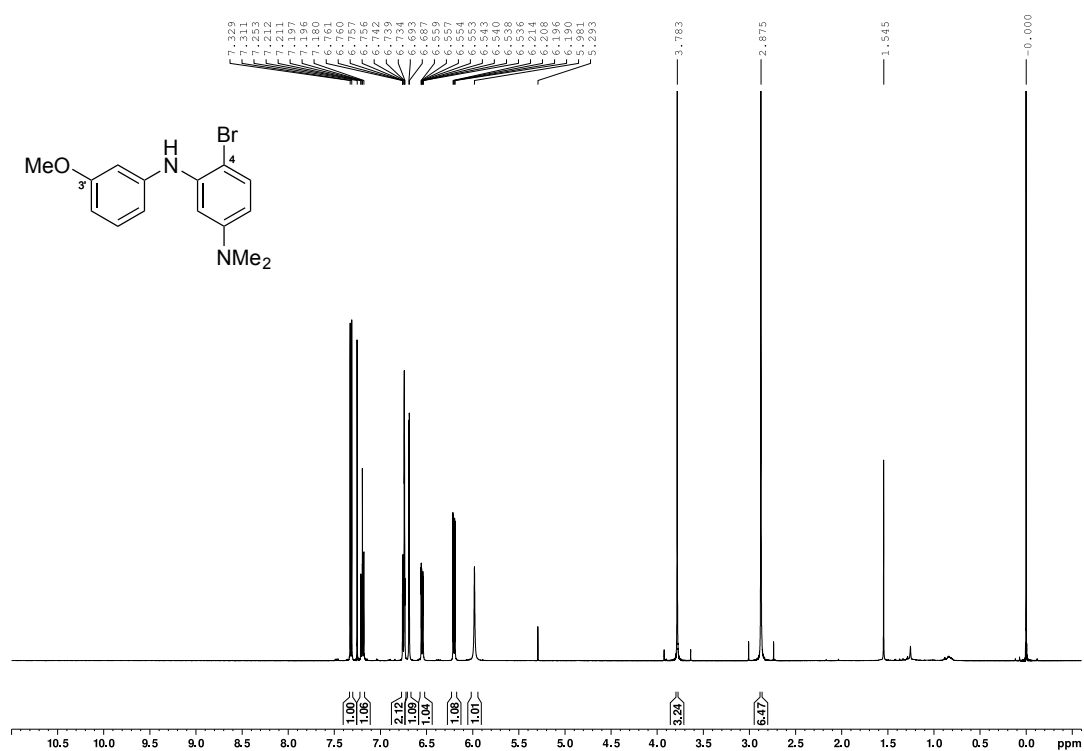


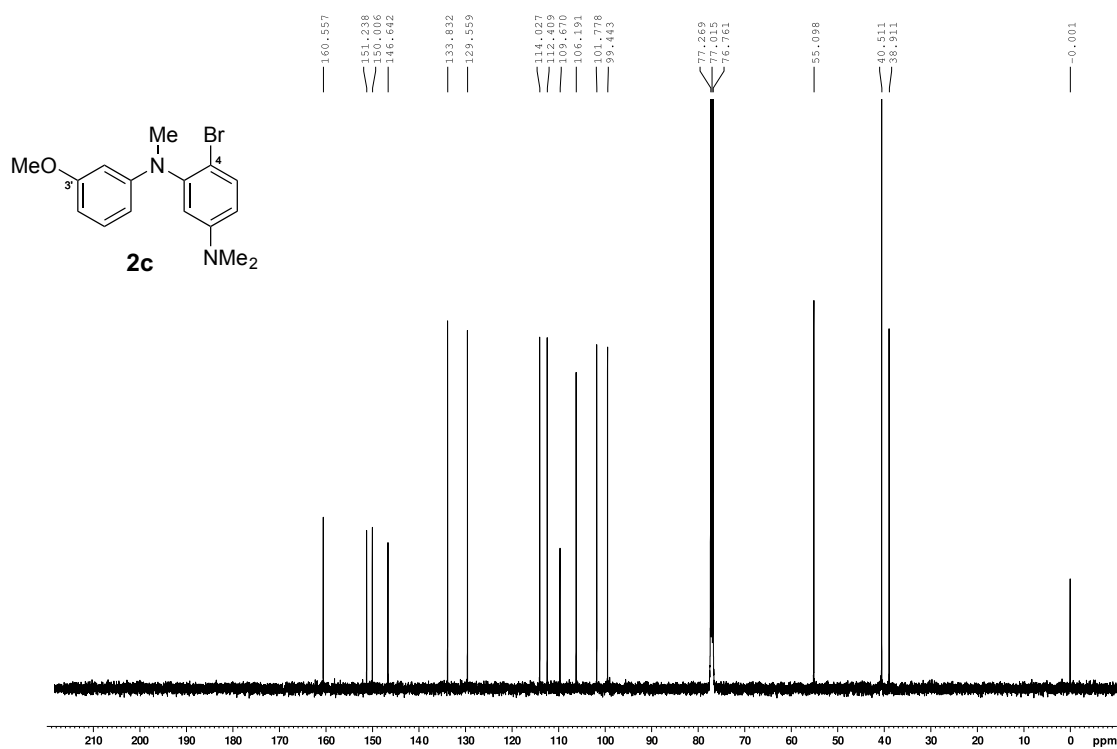
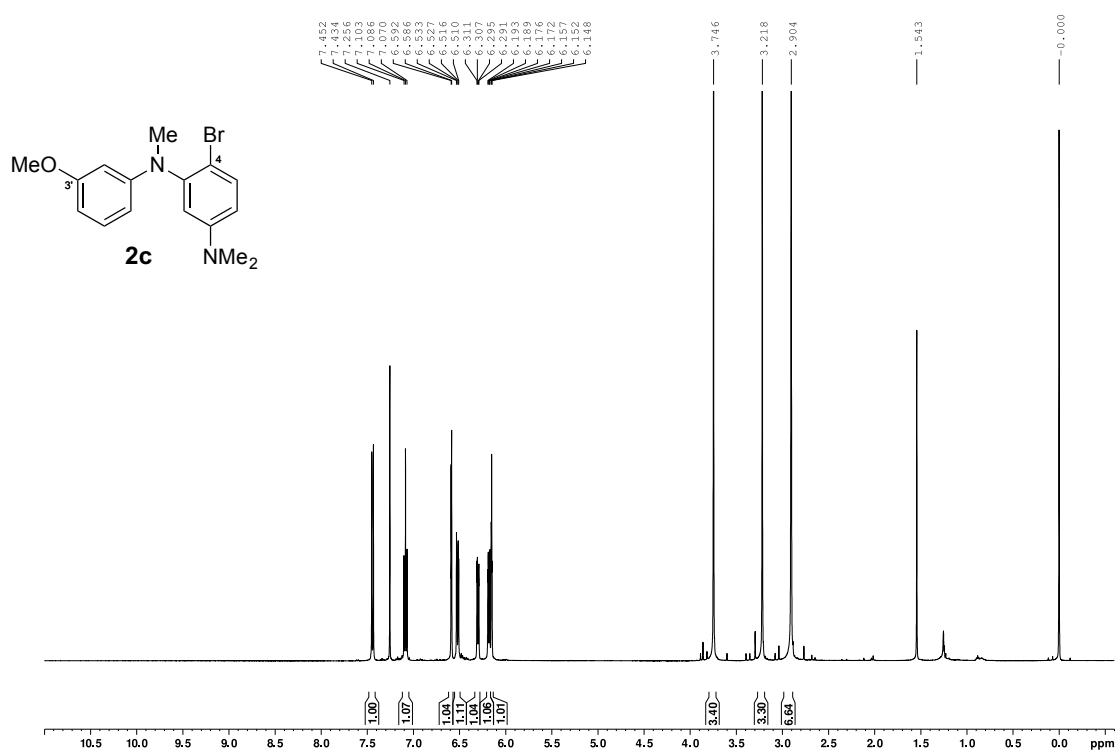


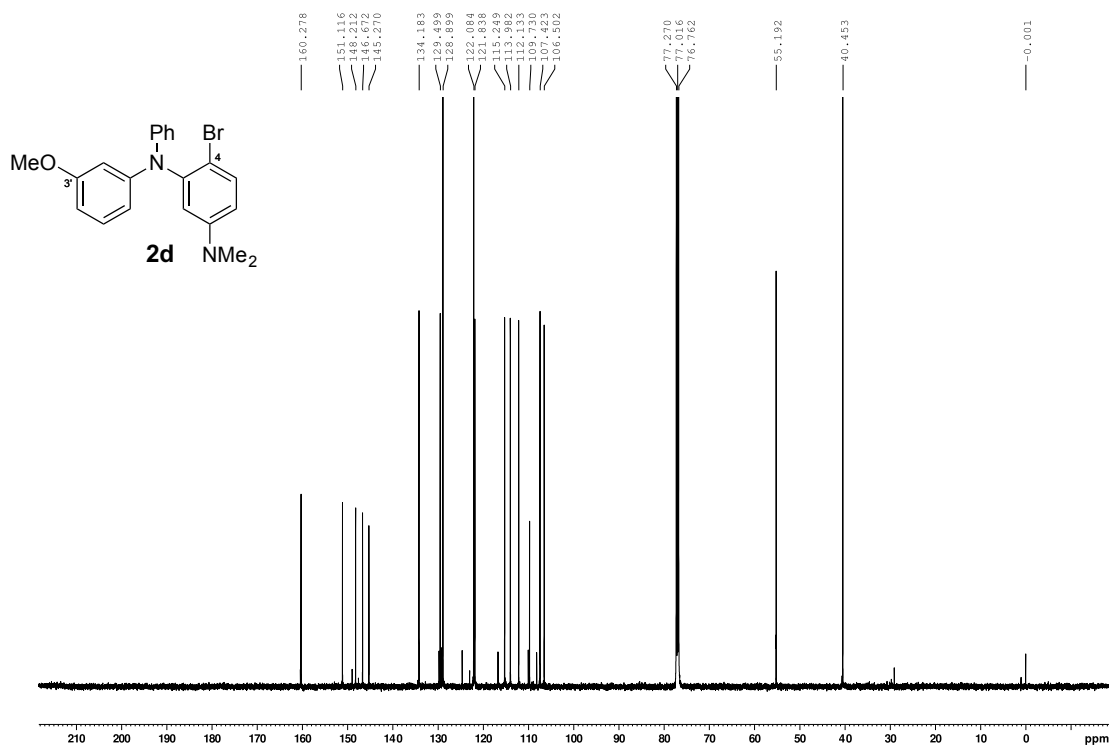
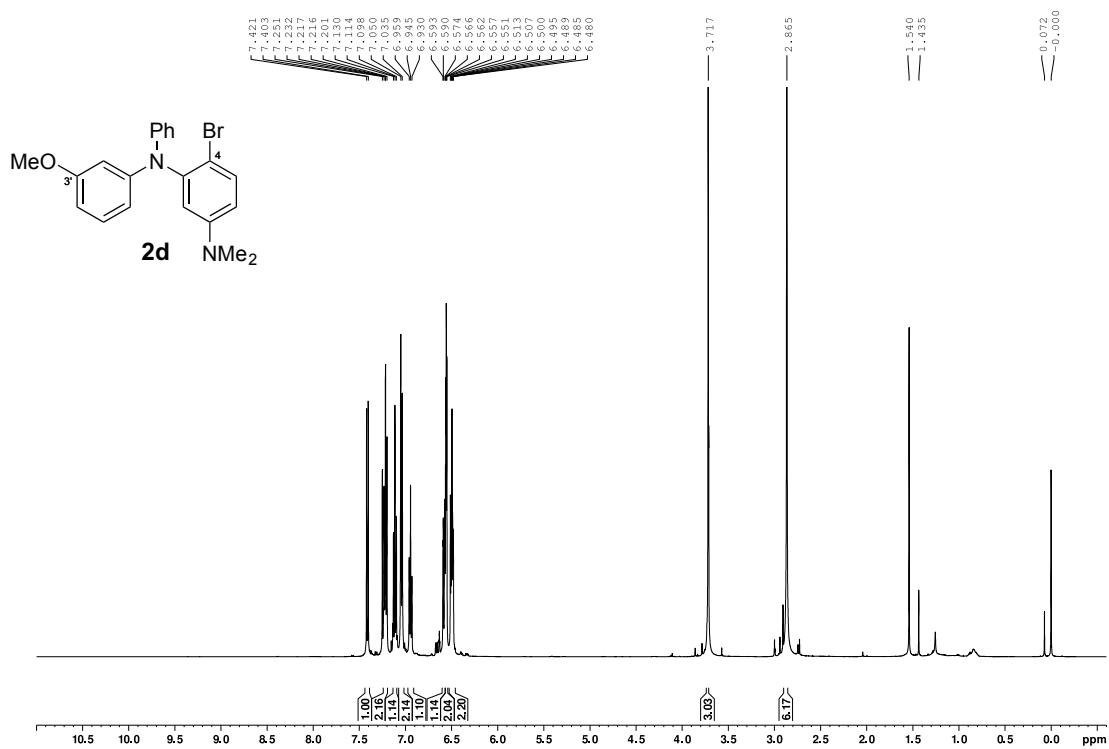


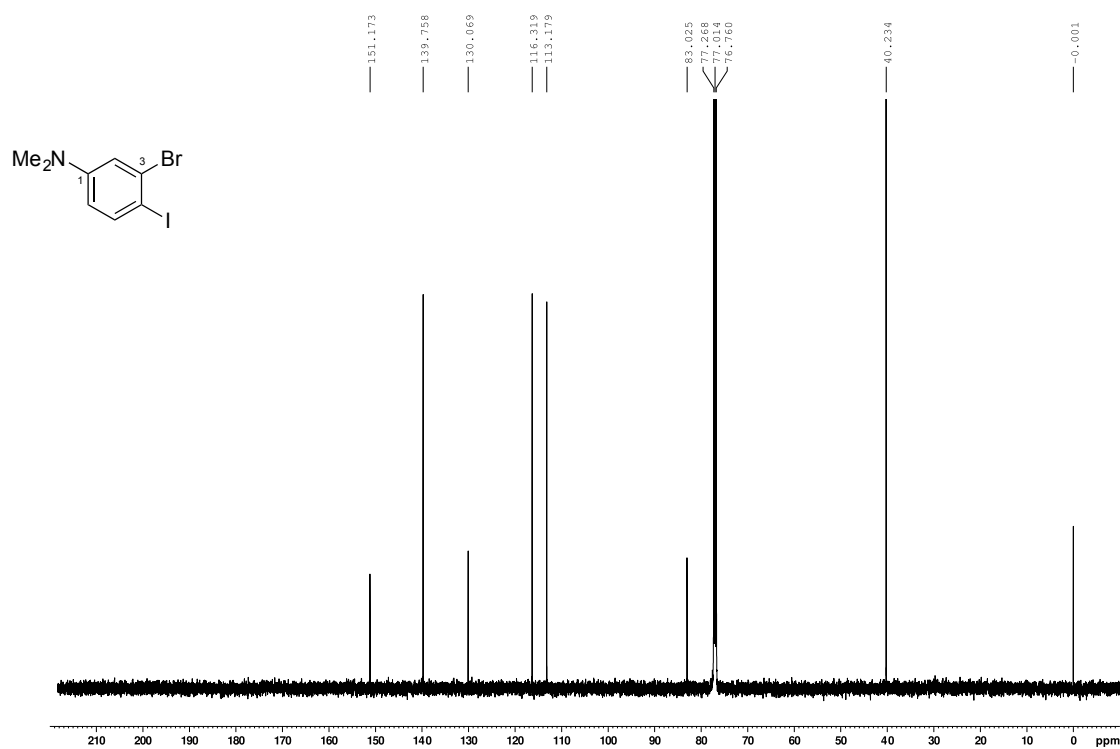
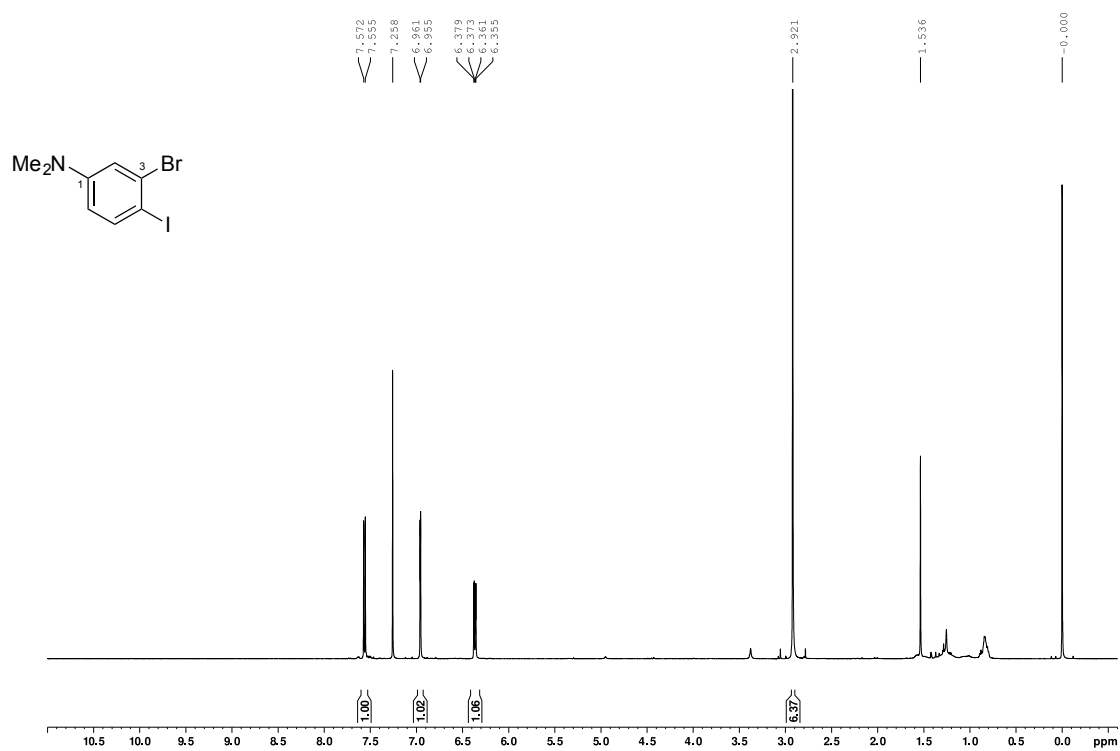


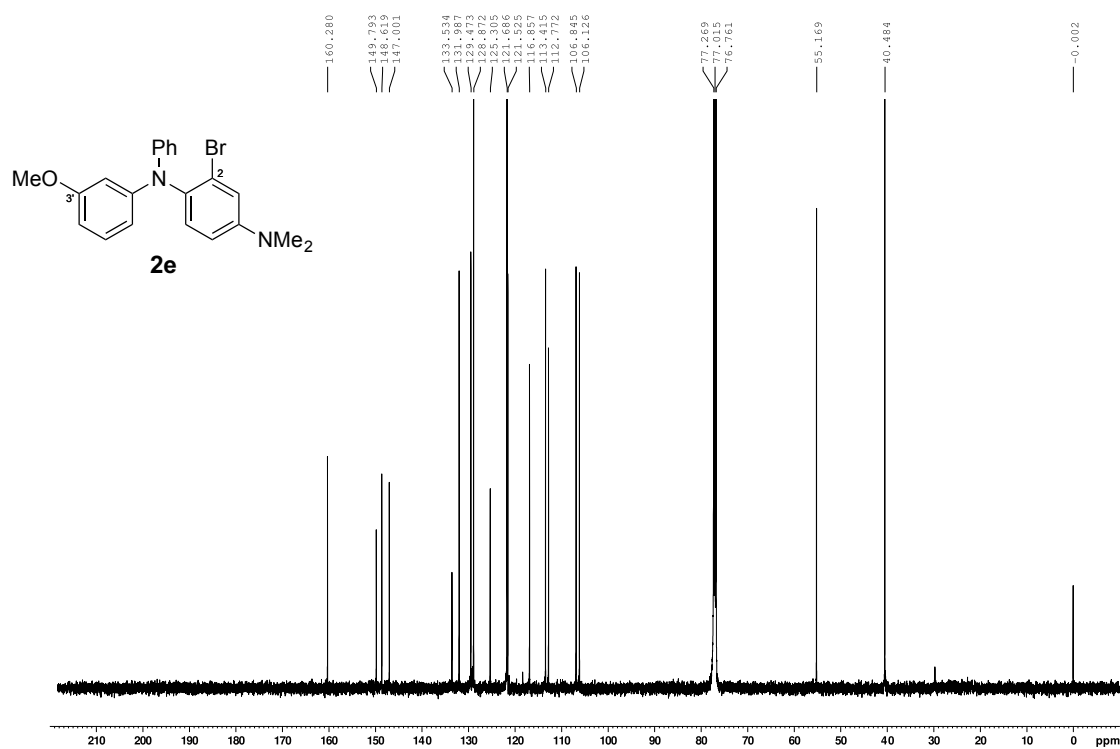
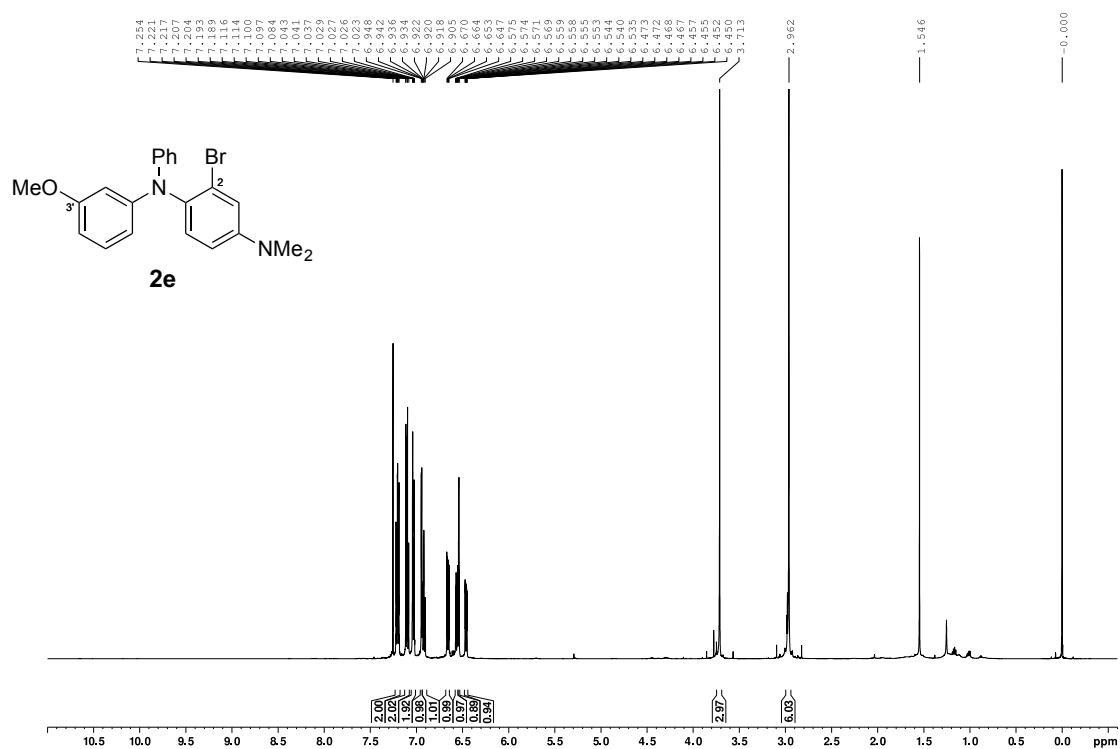


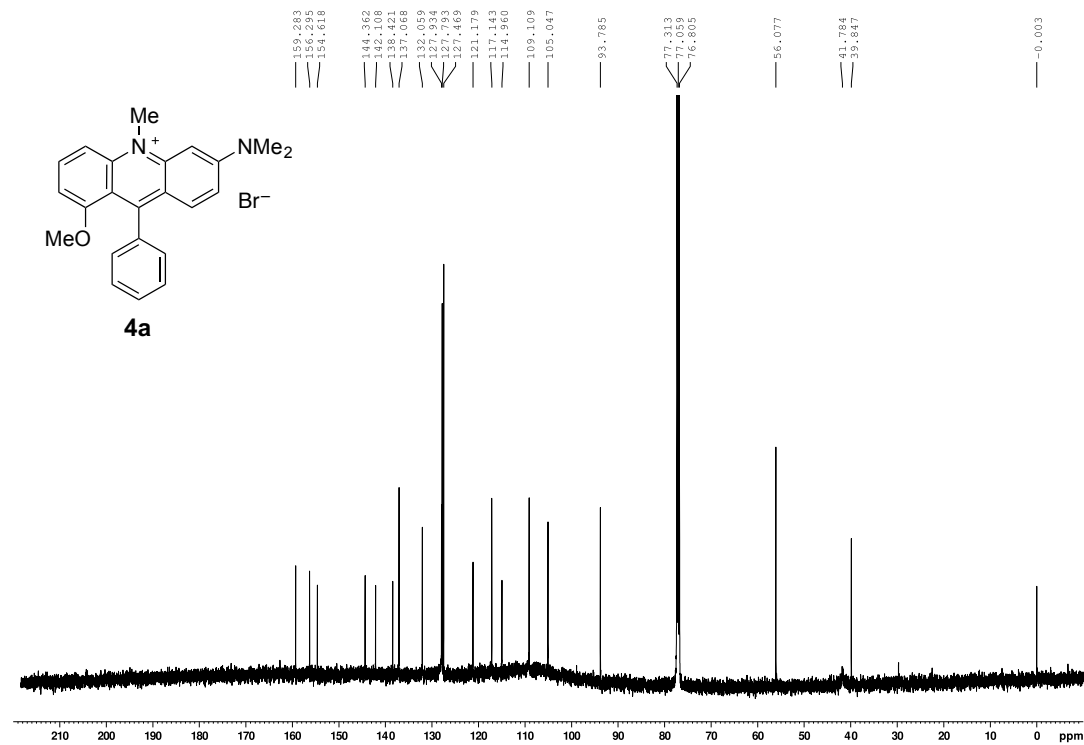
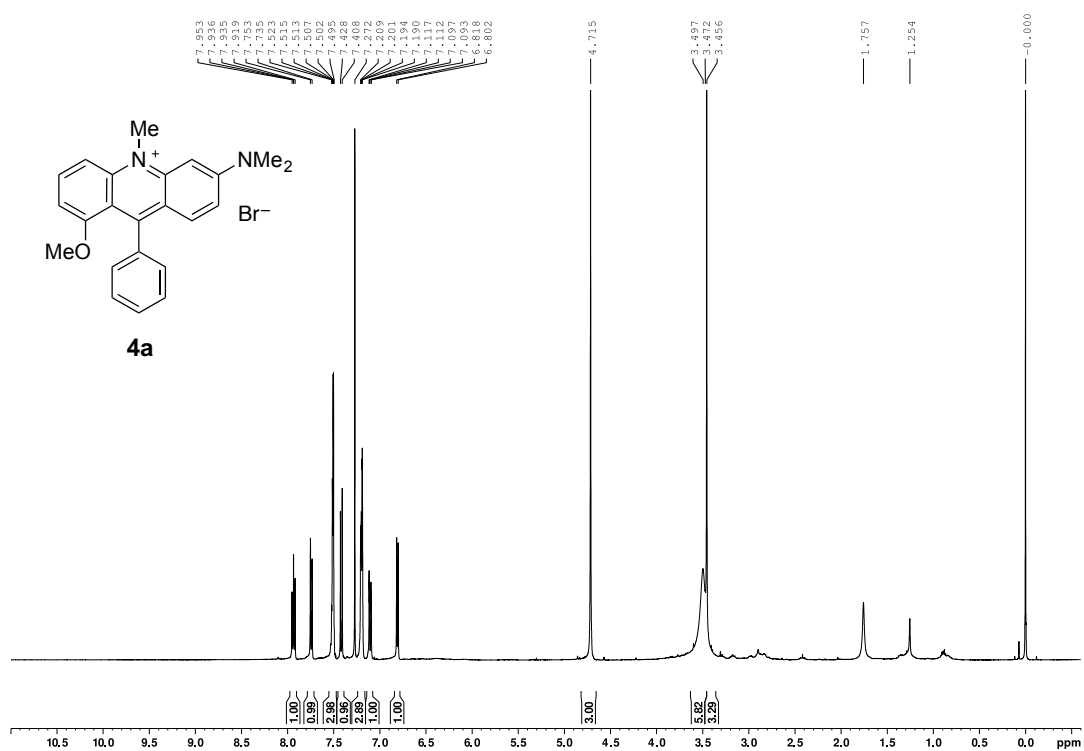


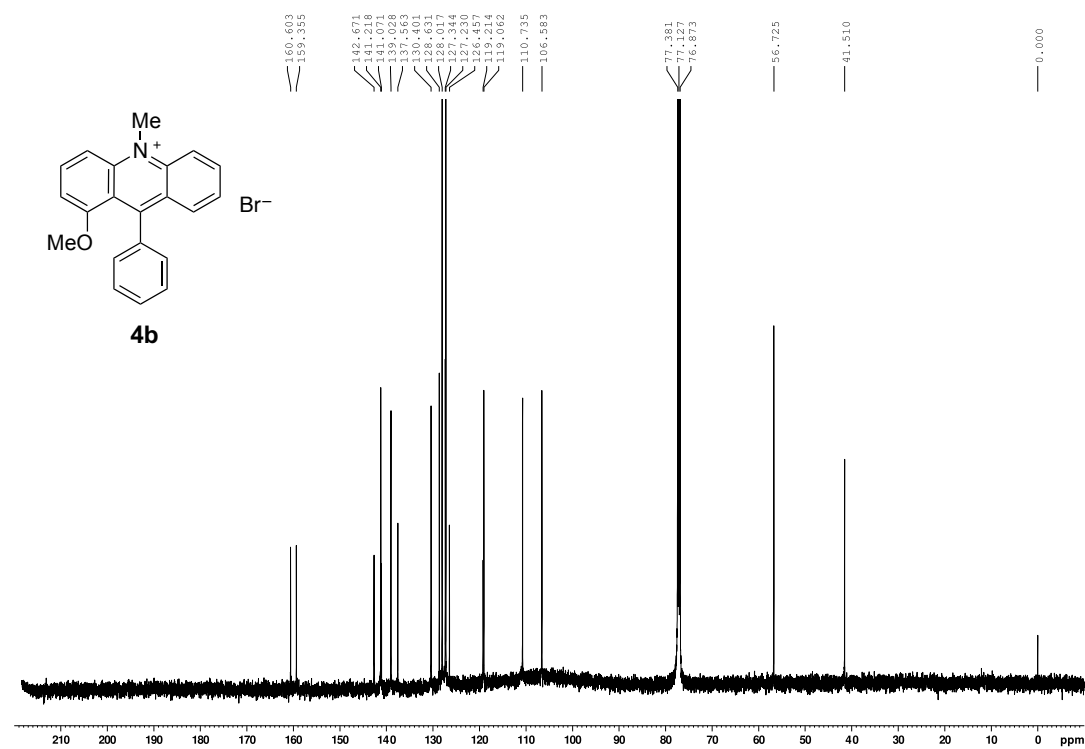
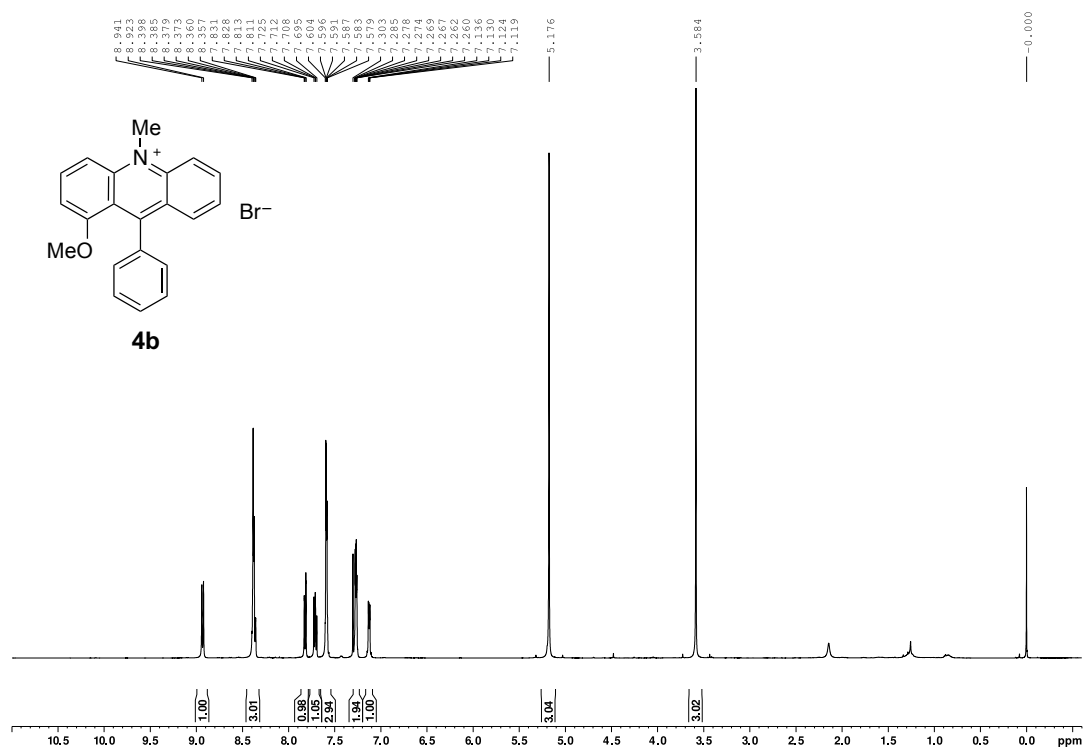


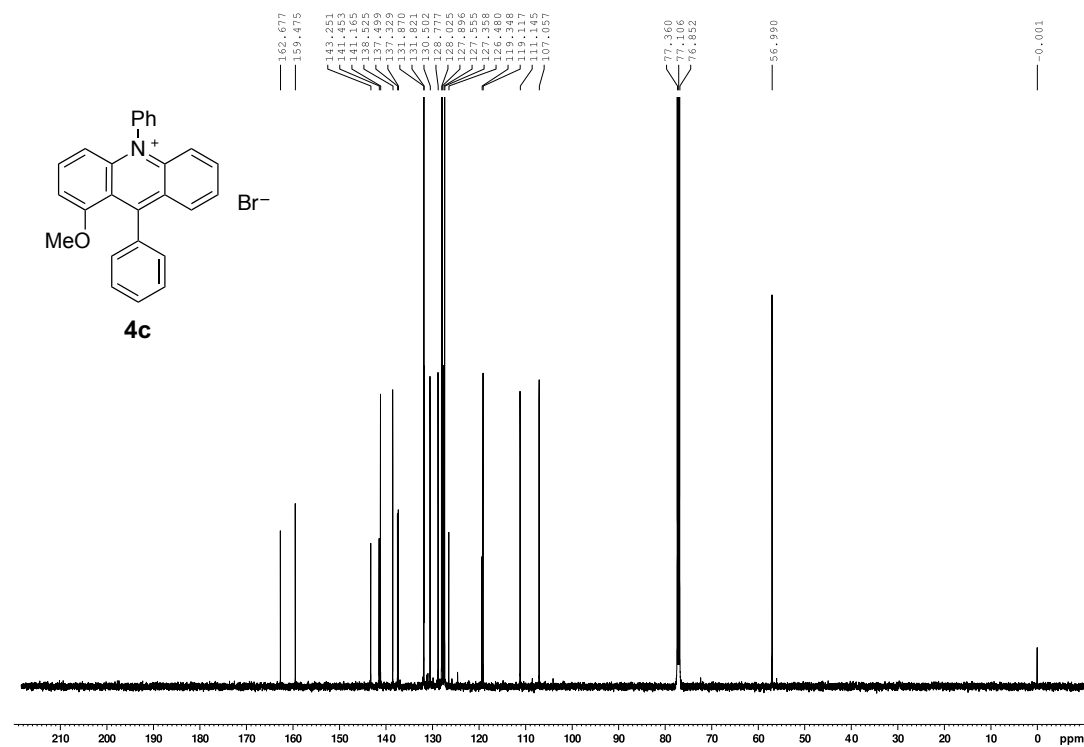
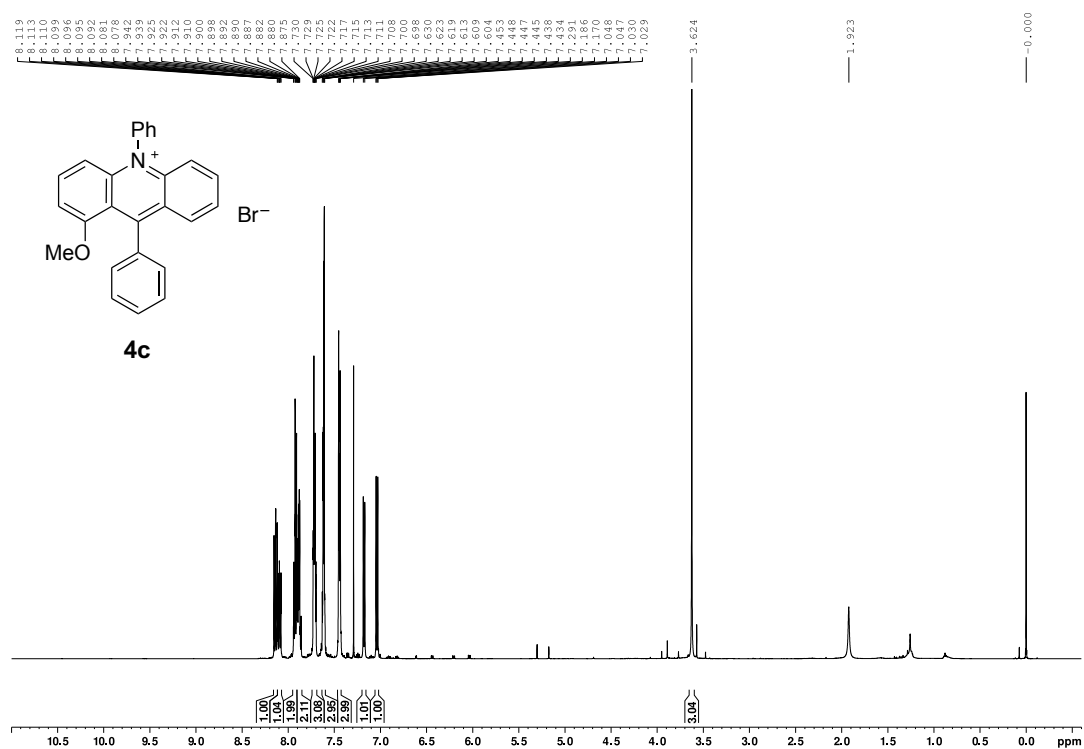




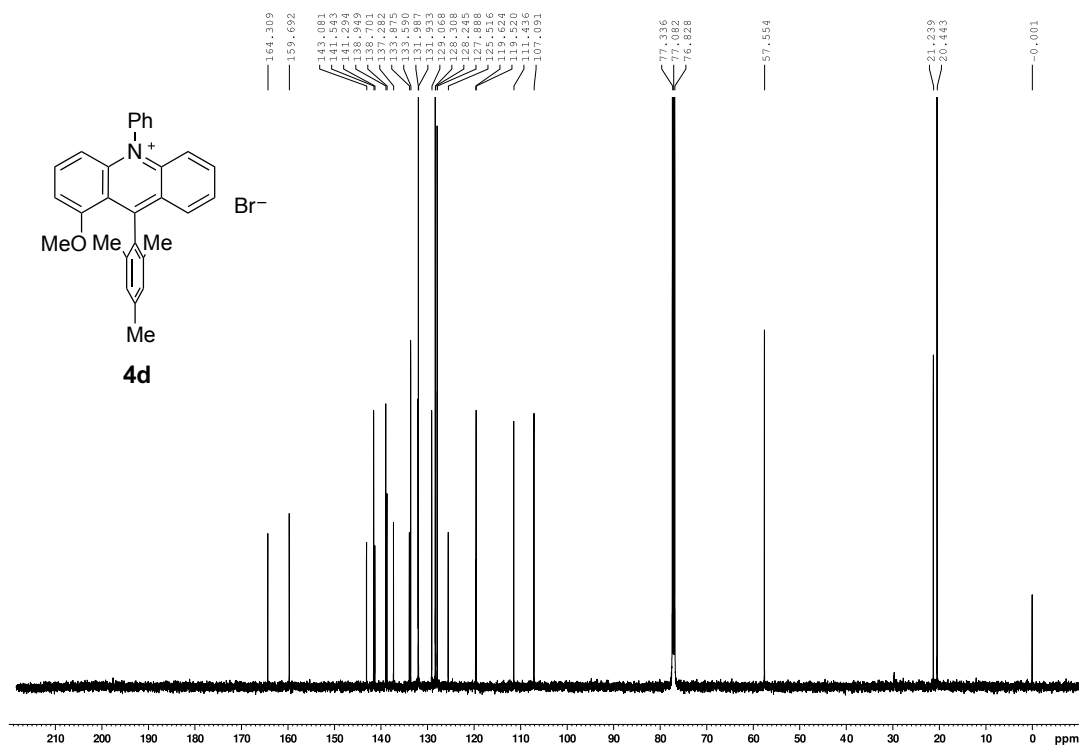
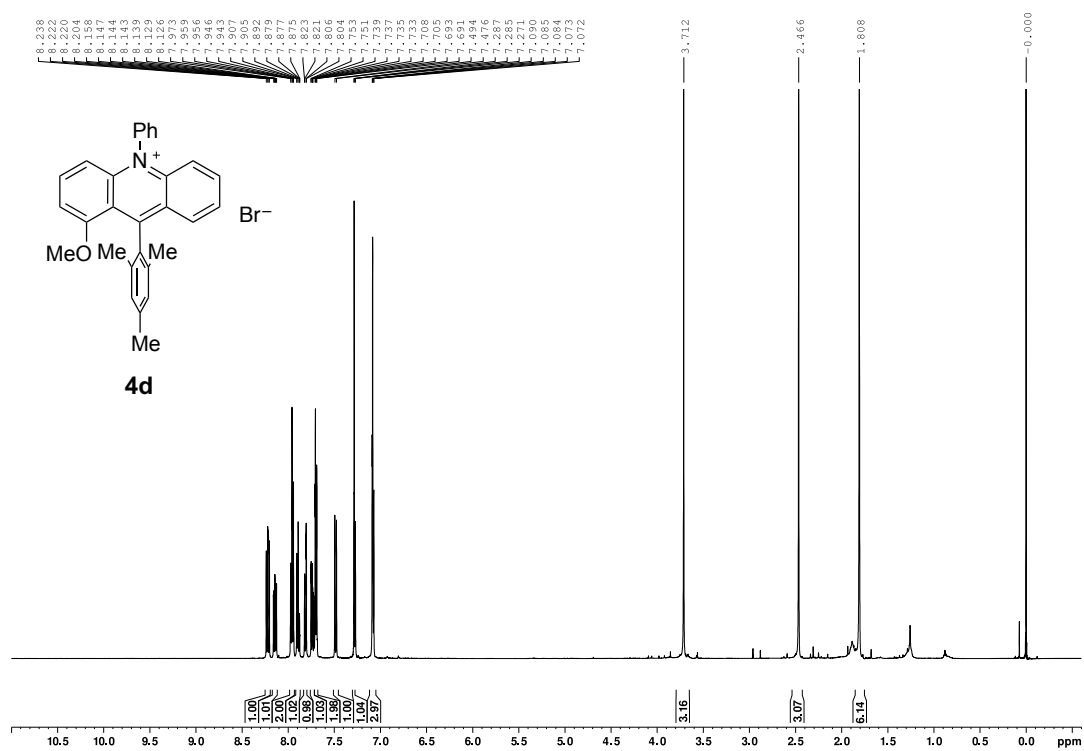


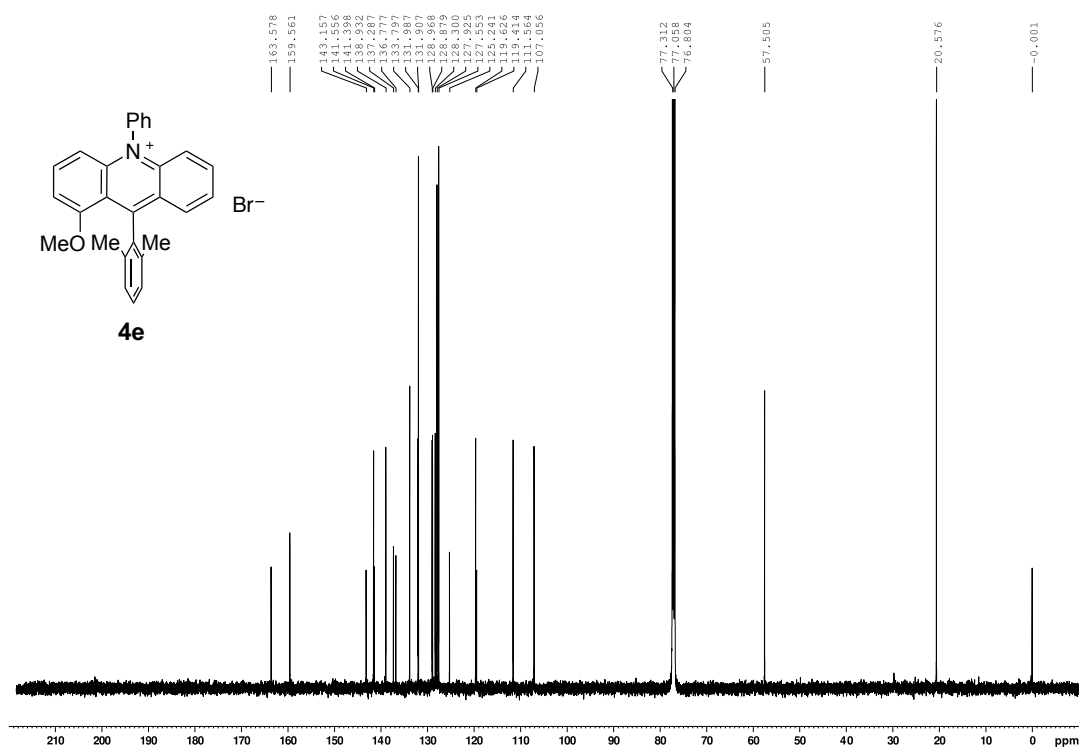
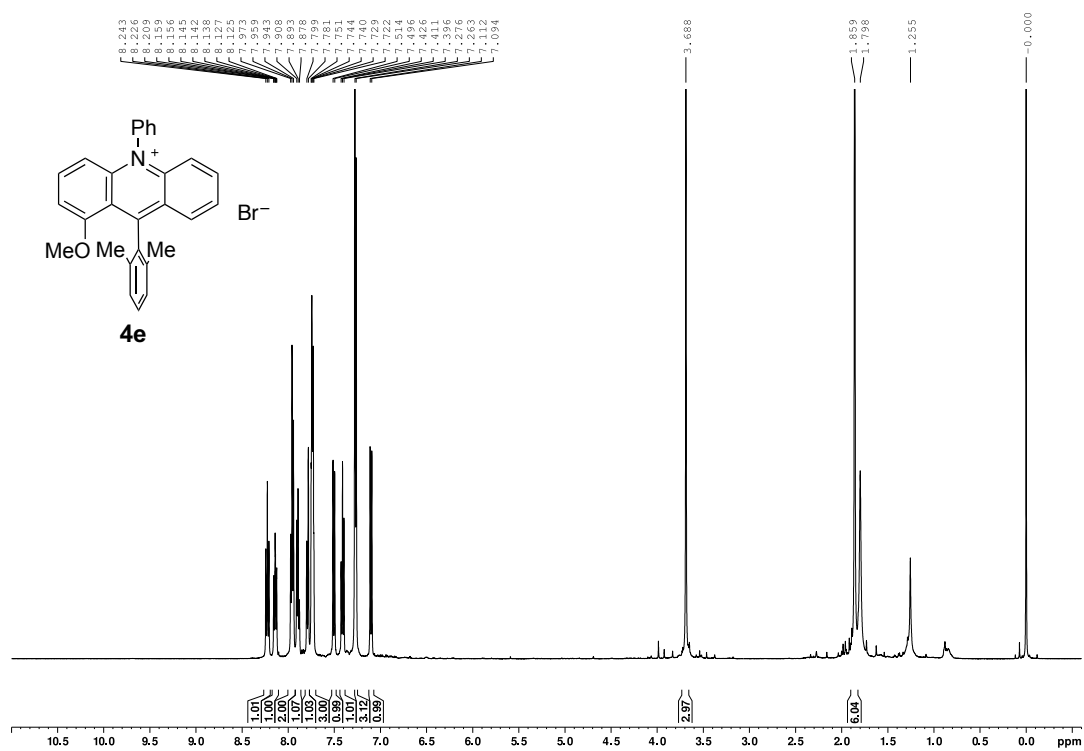


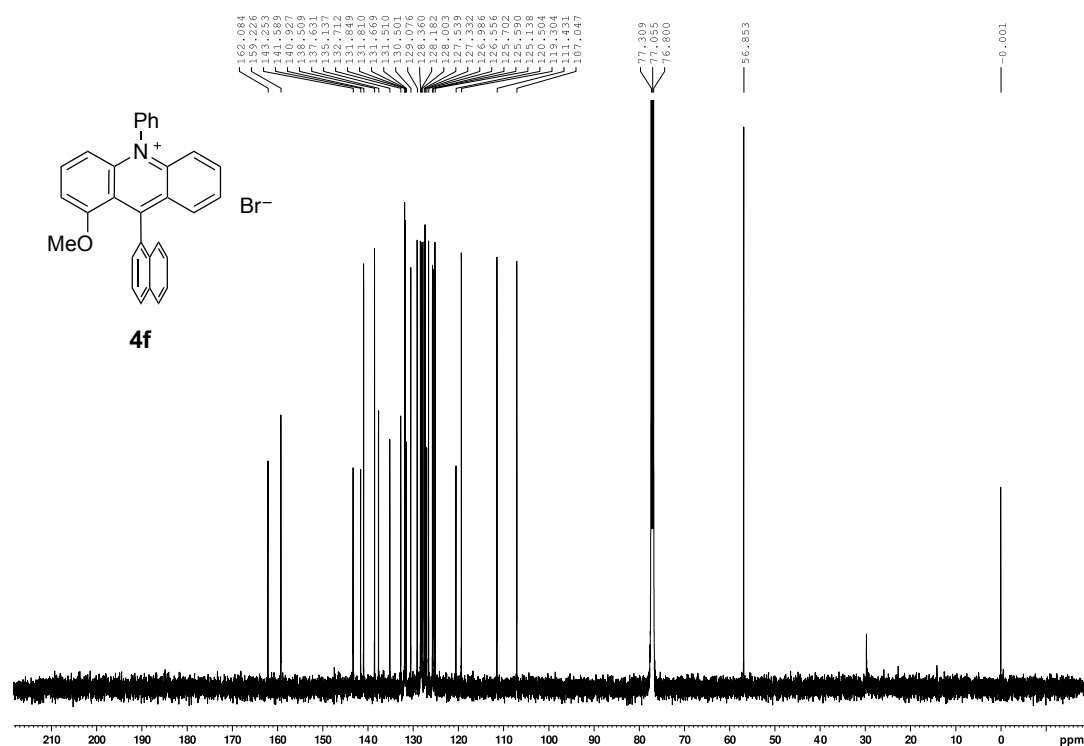
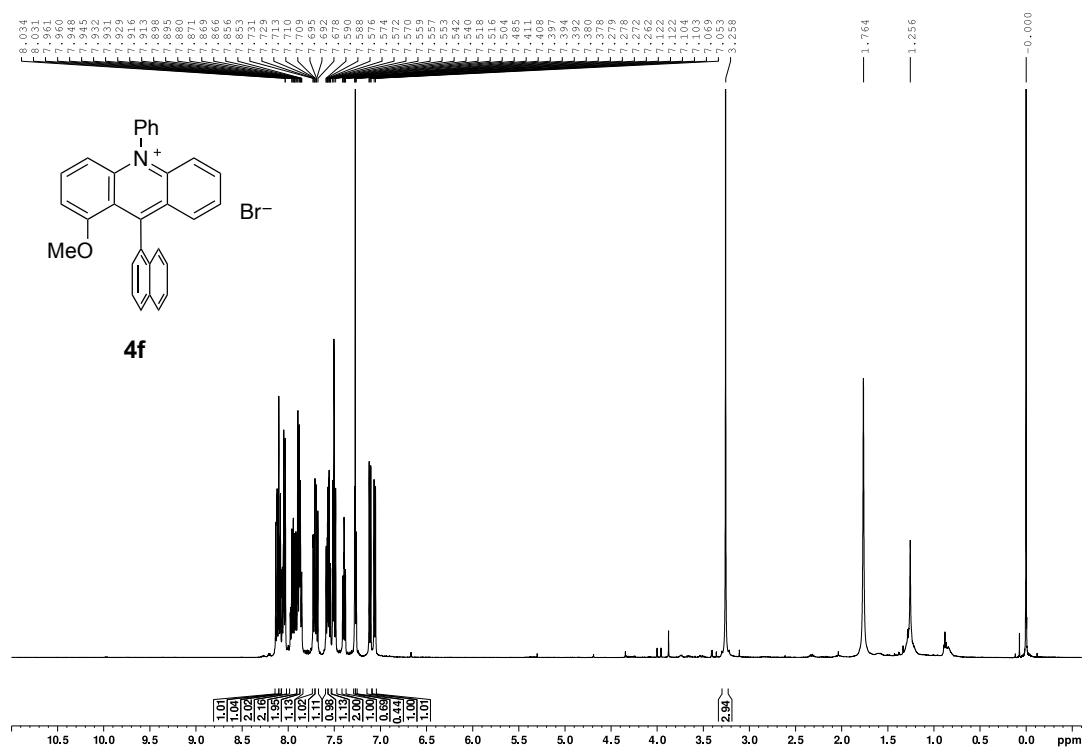


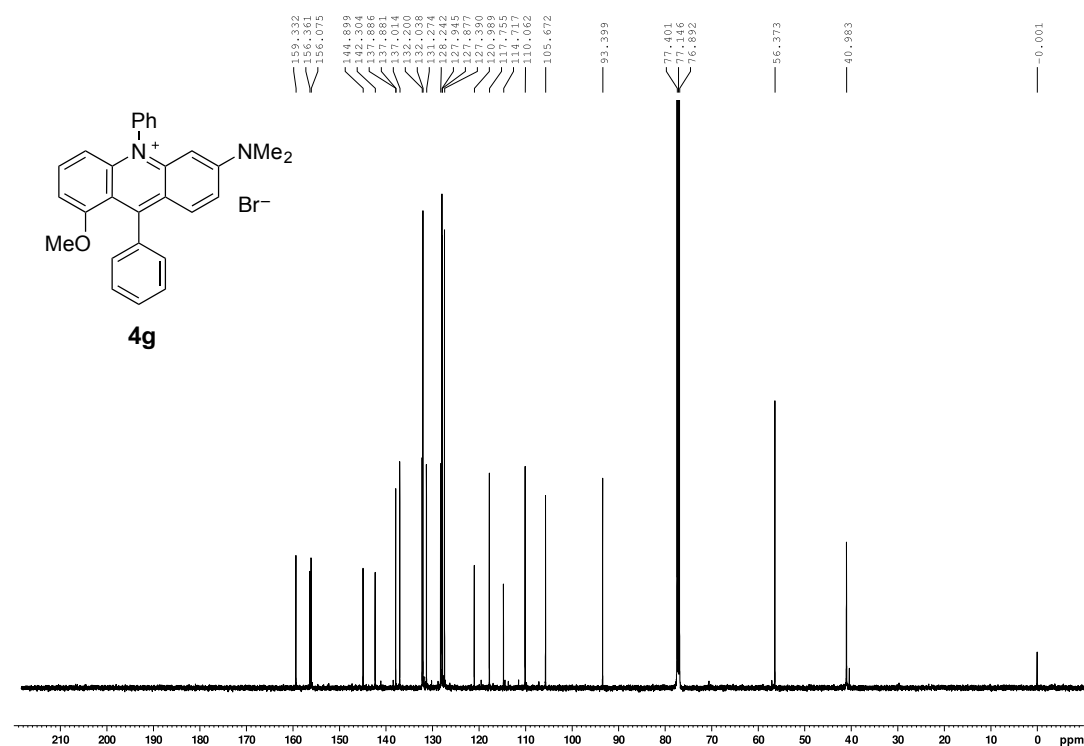
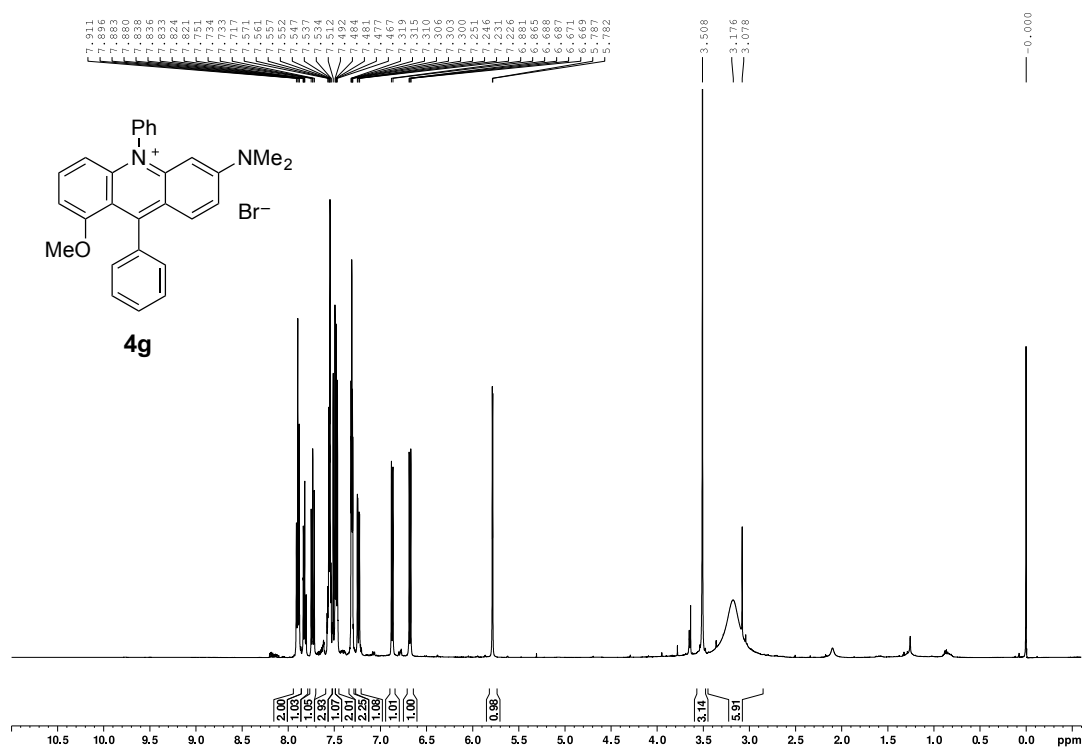


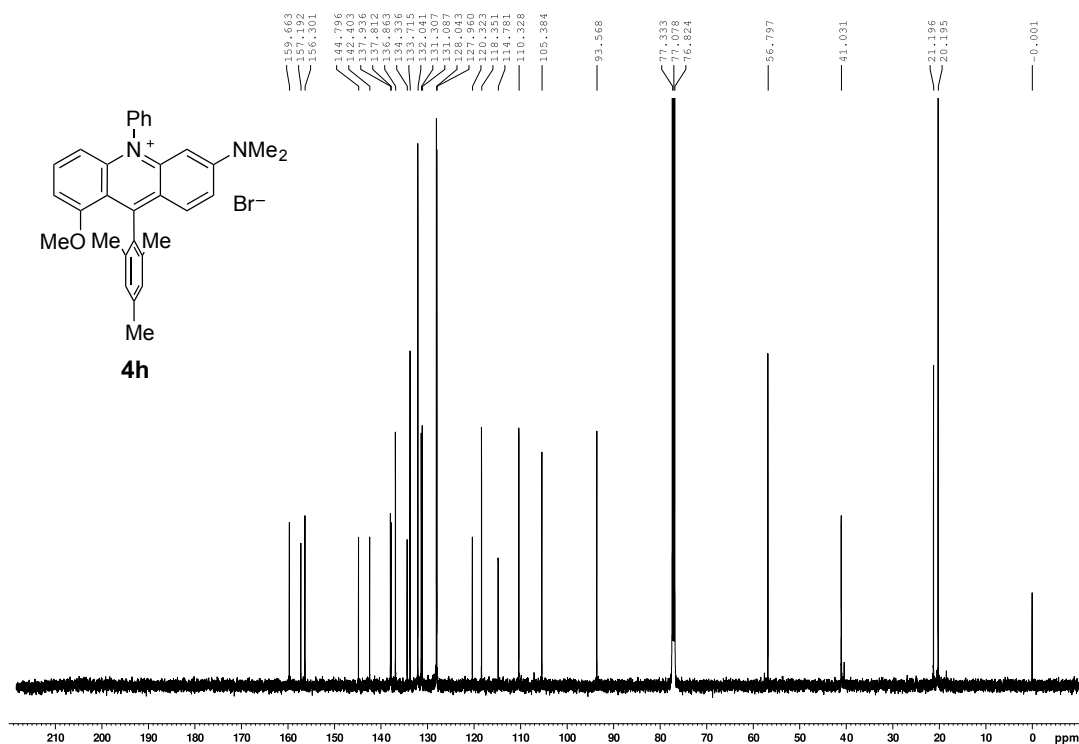
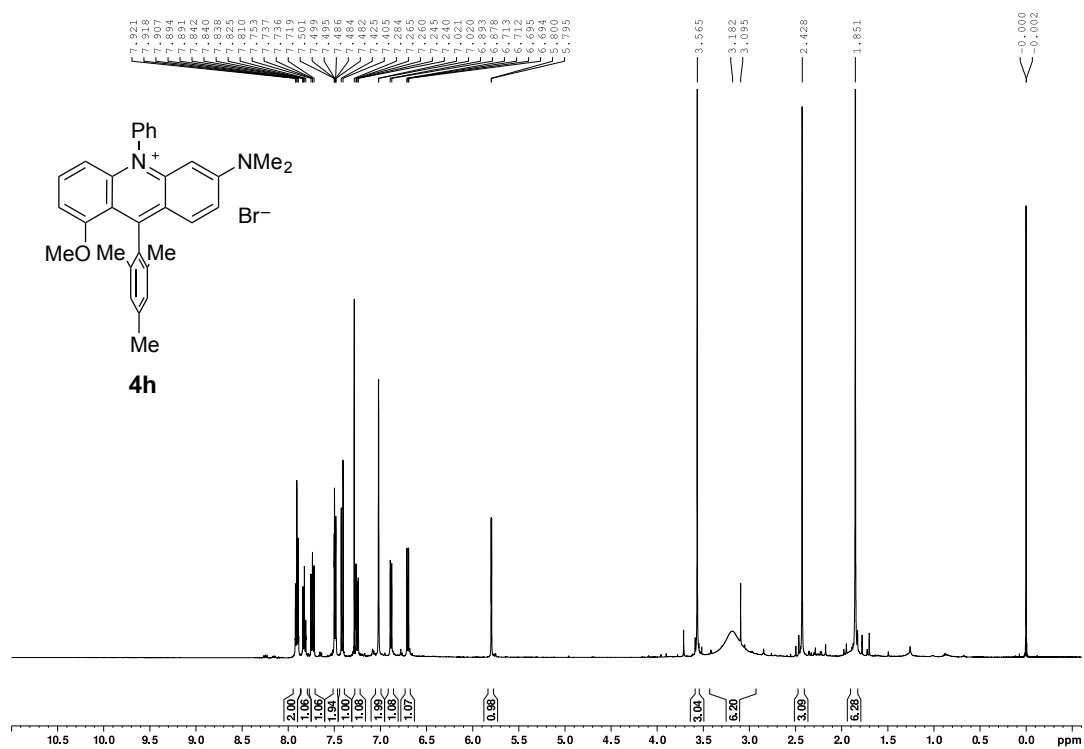


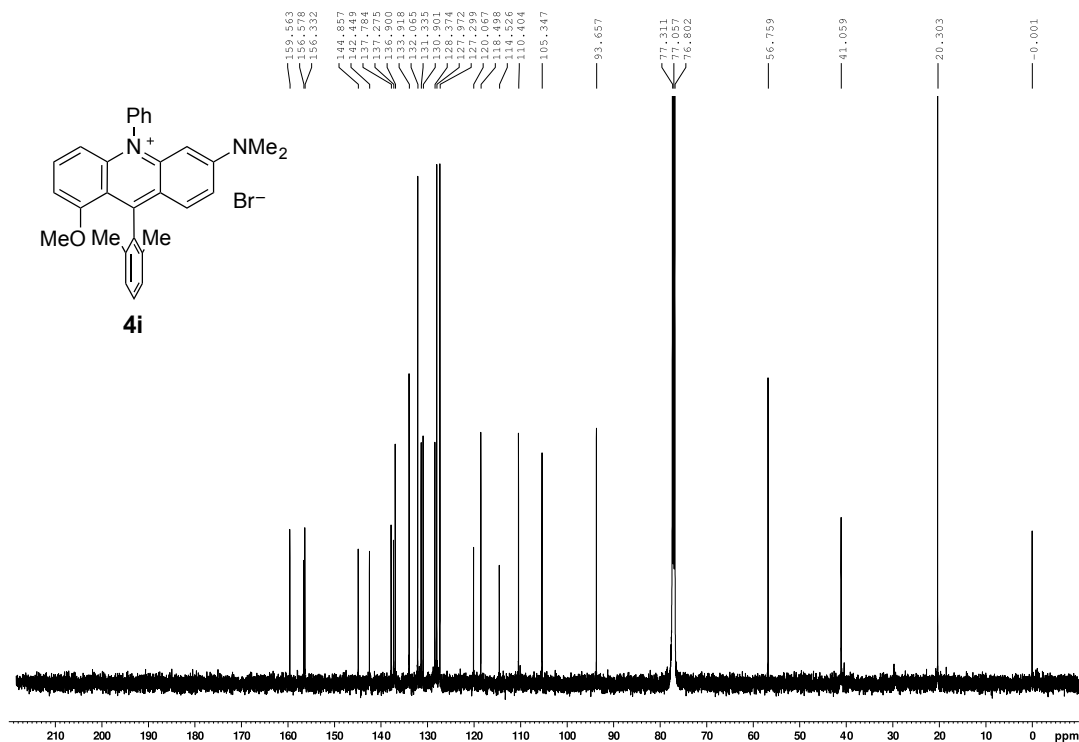
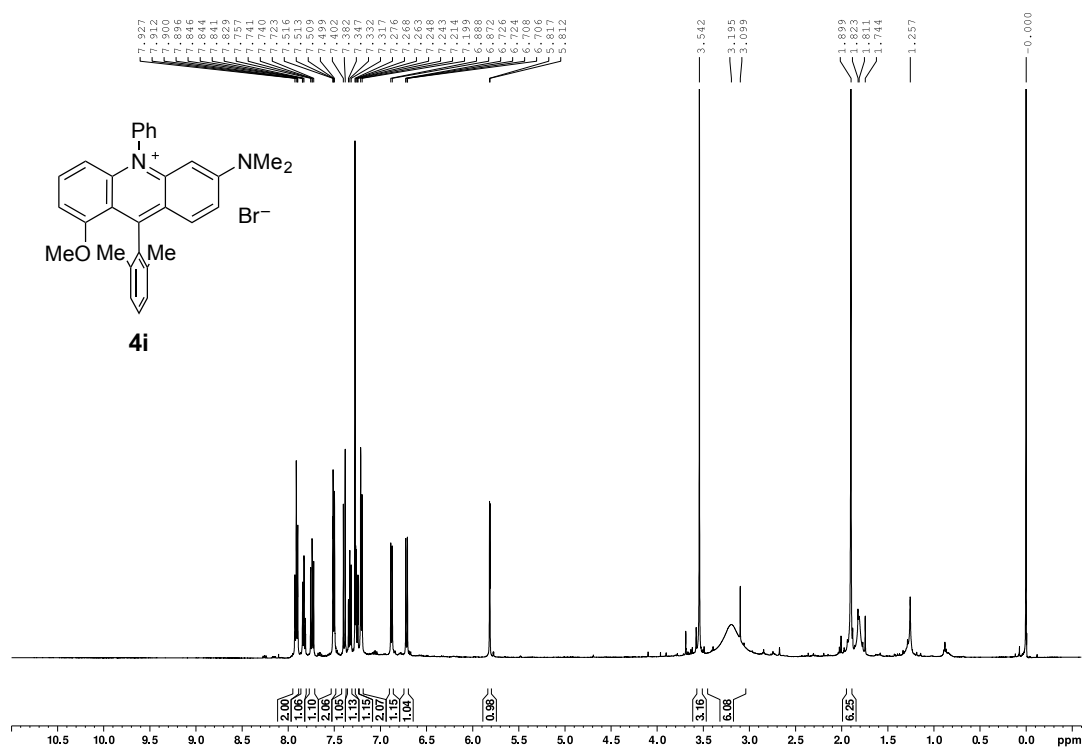


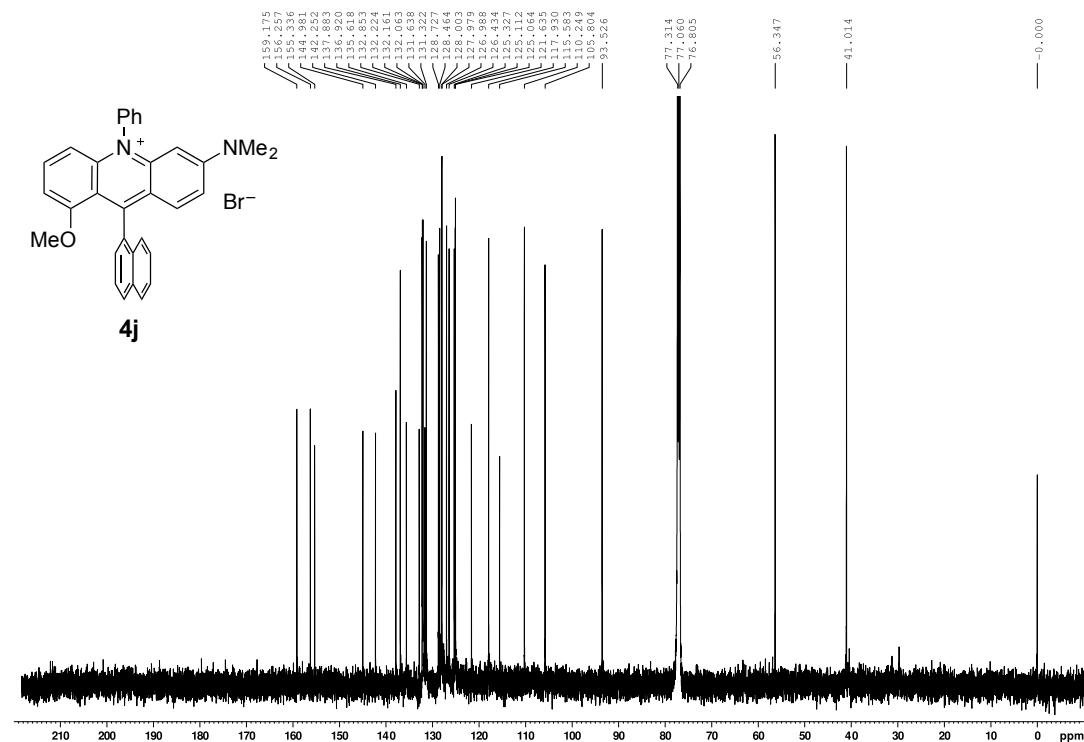
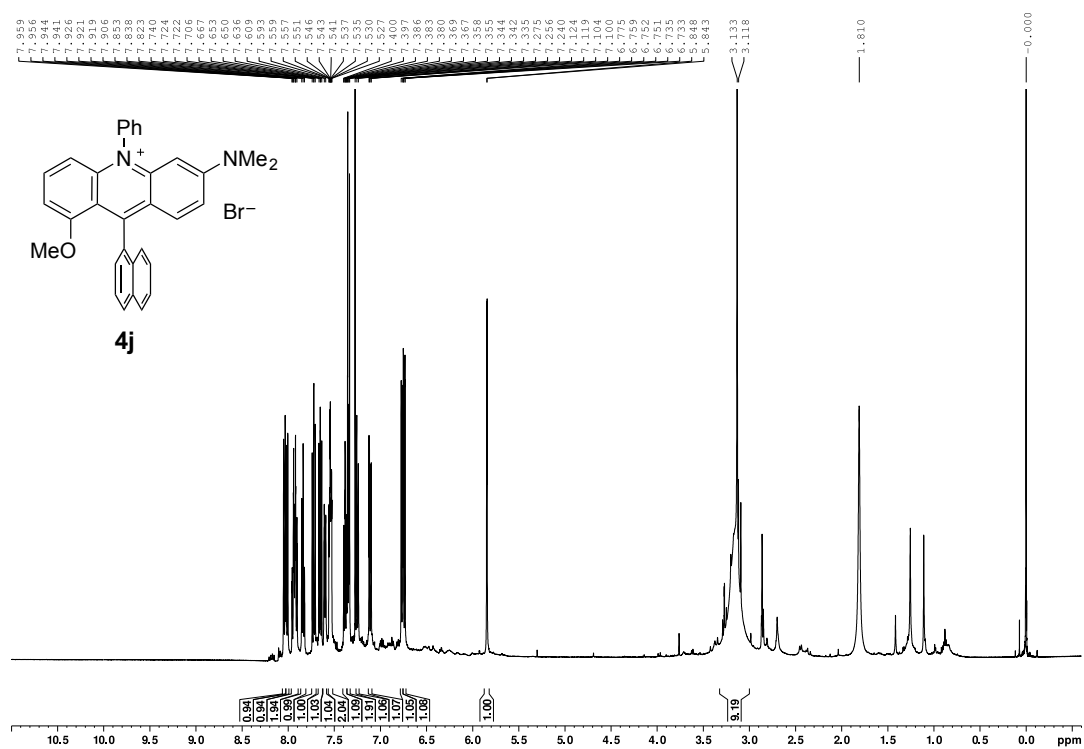


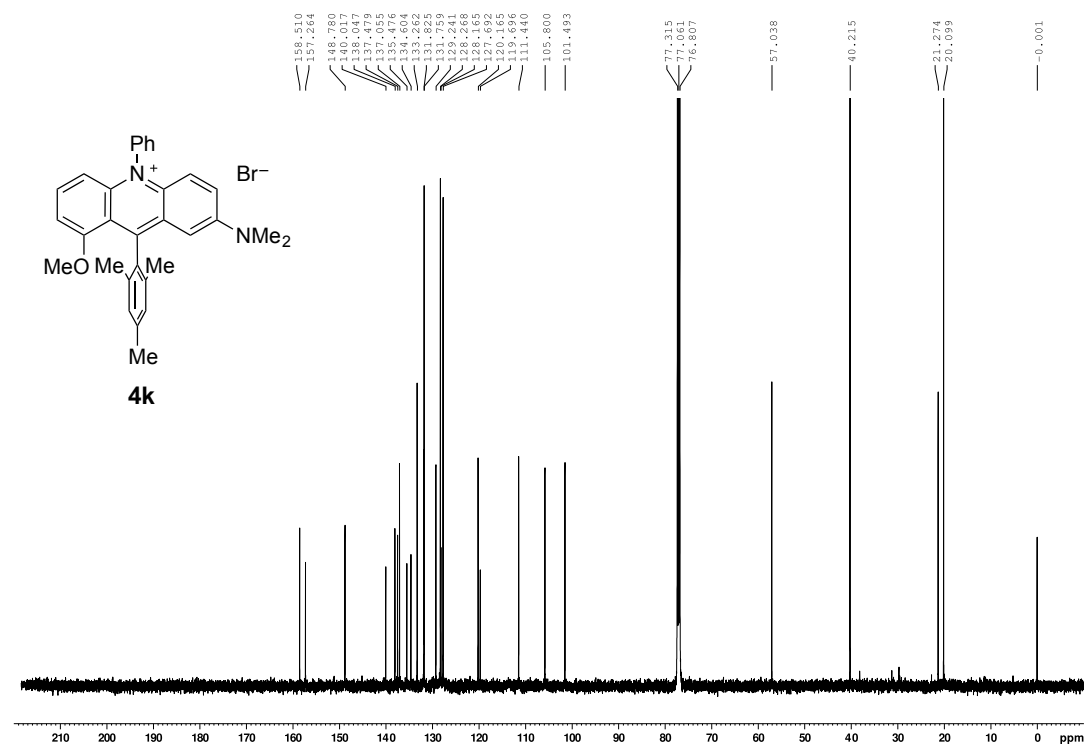
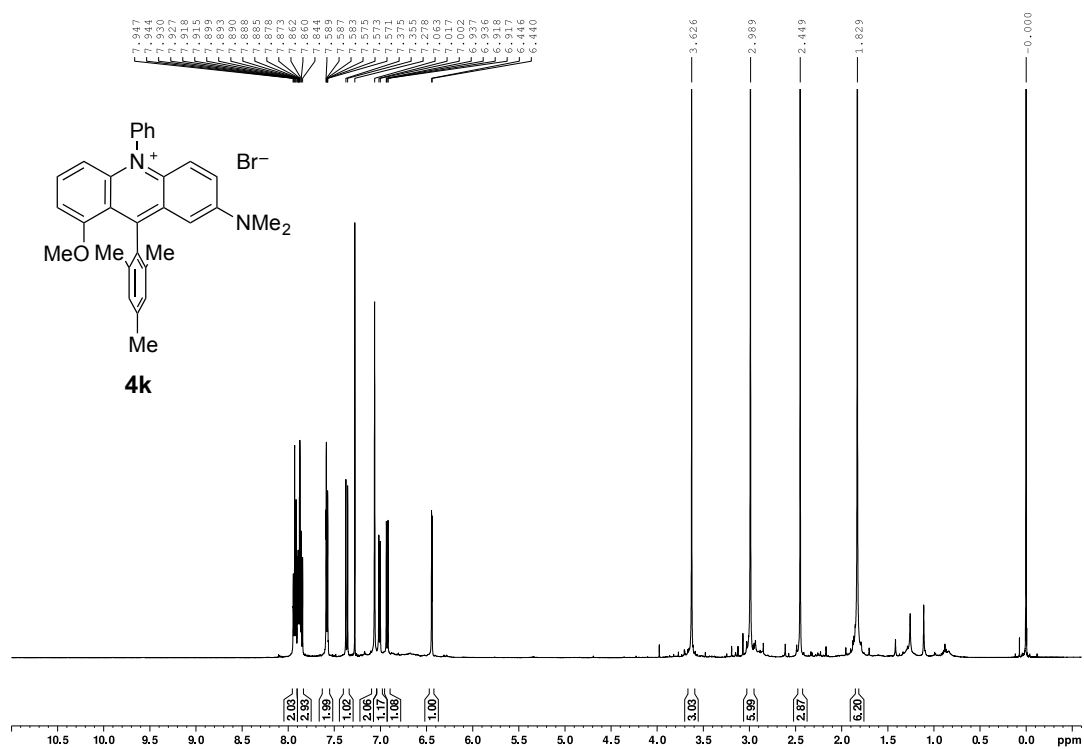




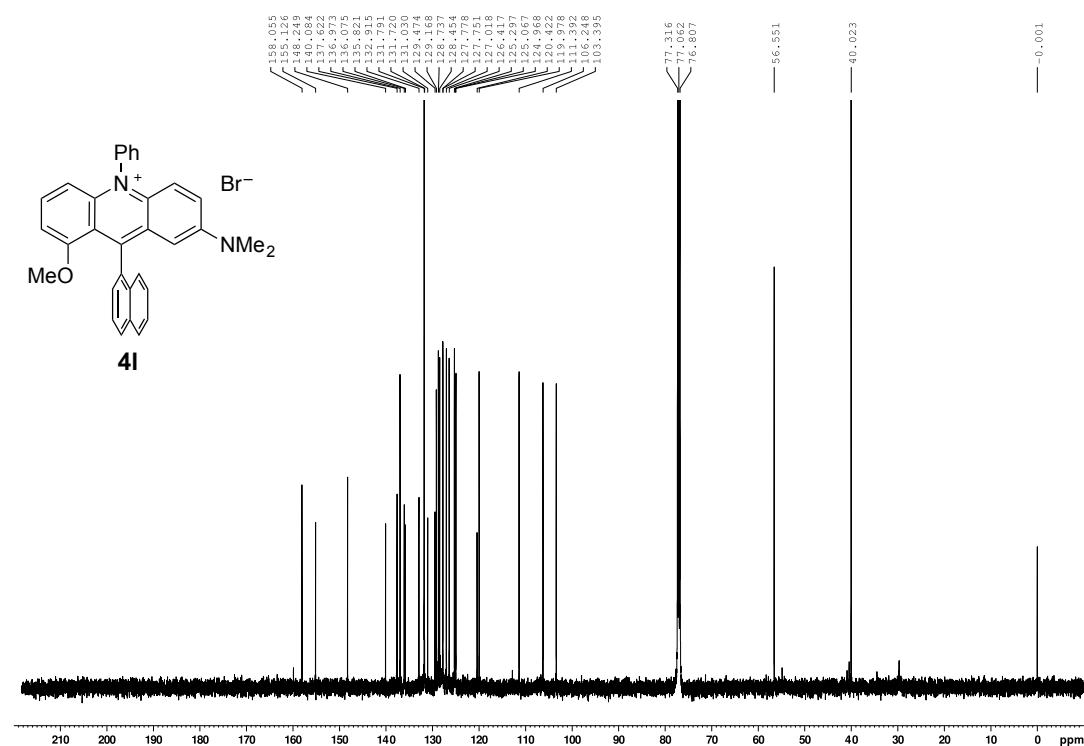
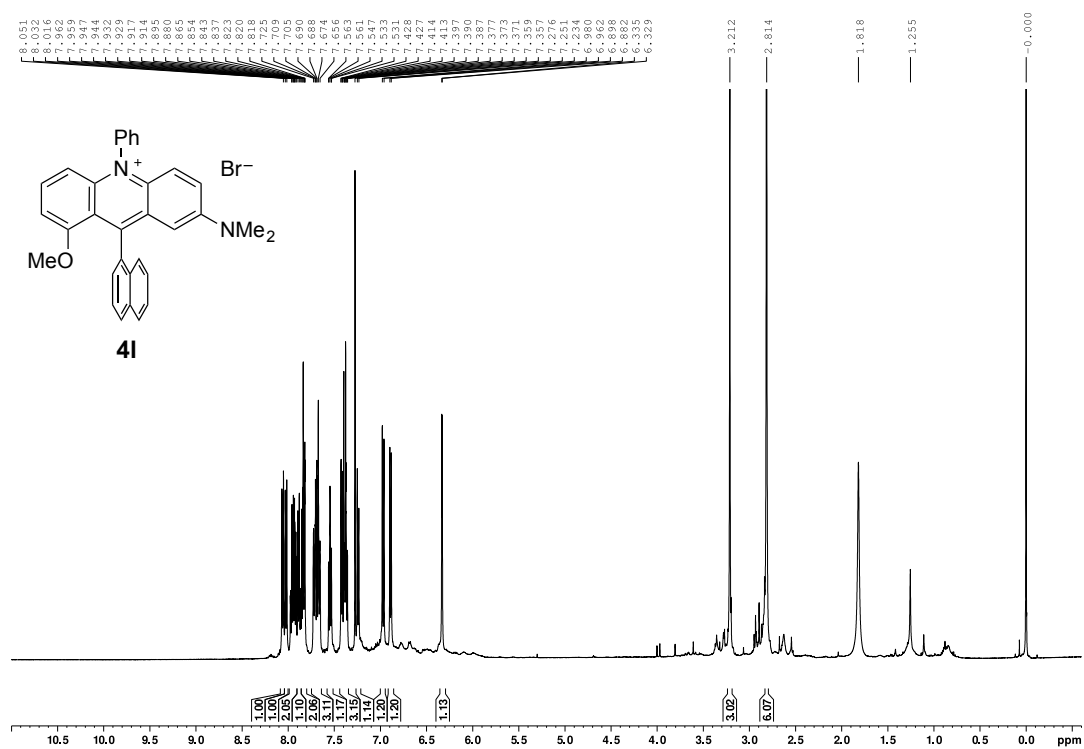










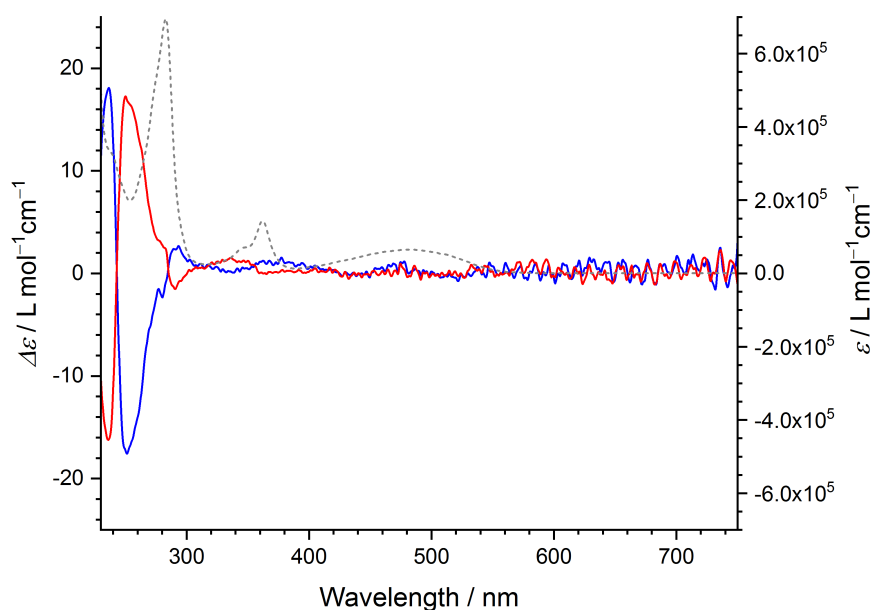


## ECD Spectroscopy

Atropisomeric dyes were reduced to their *leuco*-forms, separated on chiral HPLC columns (parameters specified below) into their enantiomers, oxidized and the barrier of rotation and ECD spectra were investigated, as described previously.<sup>[39,40]</sup>

### (±)-1-Methoxy-9-(naphthalen-1-yl)-10-phenylacridinium bromide salt **4f**:

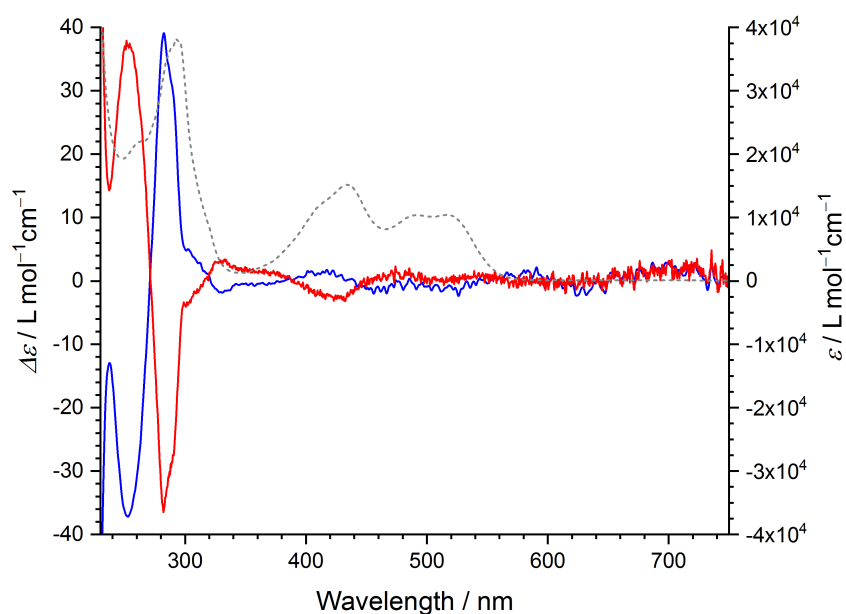
Separated on a Chiralpak® IC-3 column (4.6 mm x 250 mm; 3 µm; Art. Nr. 83525) using a 1.0 mL/min flow of *n*heptane/*i*PrOH 97:3: 4.3 and 5.0 min.  $\Delta G^\ddagger_{333K} \approx 107 \text{ kJmol}^{-1}$



**Figure S1:** ECD spectroscopy of both enantiomers of **4f** (red and blue, y-axis:  $\Delta\epsilon$ ) and the corresponding UV/VIS absorption spectrum (dashed grey lines, y-axis:  $\epsilon$ ).

### (±)-6-(Dimethylamino)-1-methoxy-9-(naphthalen-1-yl)-10-phenylacridinium bromide salt **4j**:

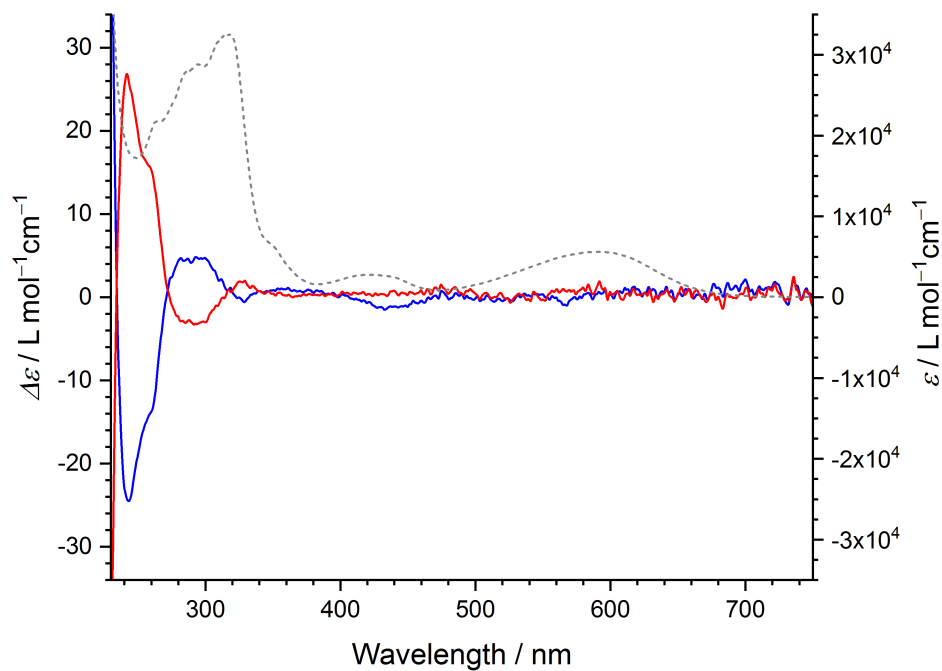
Separated on a Chiralpak® AD-H column (4.6 mm x 250 mm; 5 µm; Art. Nr. 19325) using a 1.0 mL/min flow of *n*heptane/*i*PrOH 97:3: 6.6 and 8.2 min.  $\Delta G^\ddagger_{403K} \approx 130 \text{ kJmol}^{-1}$



**Figure S2:** ECD spectroscopy of both enantiomers of **4j** (red and blue, y-axis:  $\Delta\epsilon$ ) and the corresponding UV/VIS absorption spectrum (dashed grey lines, y-axis:  $\epsilon$ ).

**(±)-7-(Dimethylamino)-1-methoxy-9-(naphthalen-1-yl)-10-phenylacridinium bromide salt 4l:**

Separated on a Chiralpak<sup>®</sup> AD-H column (4.6 mm x 250 mm; 5  $\mu$ m; Art. Nr. 19325) using a 1.0 mL/min flow of *n*heptane/*i*PrOH 95:5: 6.5 and 7.4 min.  $\Delta G^\ddagger_{423K} \approx 135$  kJmol<sup>-1</sup>

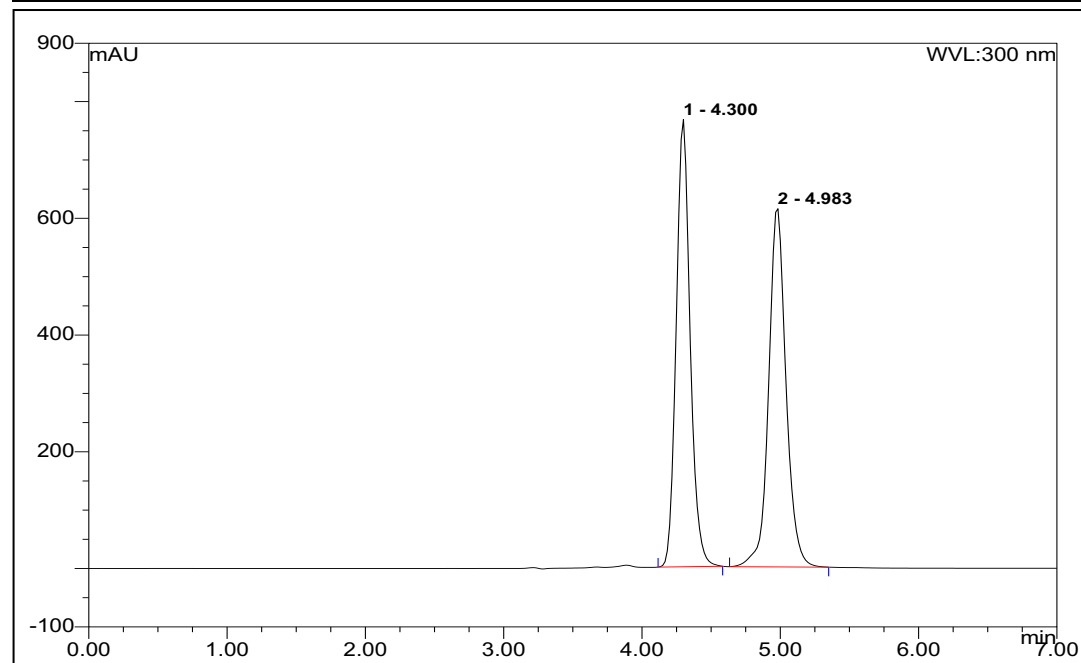


**Figure S3:** ECD spectroscopy of both enantiomers of **4l** (red and blue, y-axis:  $\Delta\epsilon$ ) and the corresponding UV/VIS absorption spectrum (dashed grey lines, y-axis:  $\epsilon$ ).

## HPLC Data

**(±)-1-Methoxy-9-(naphthalen-1-yl)-10-phenylacridinium *Leuco*-form 4f-*leuco*:**

Sample Name:	CF1251P leuco	Injection Volume:	2.0
Vial Number:	BE1	Channel:	UV_VIS_4
Sample Type:	unknown	Wavelength:	300.0
Control Program:	IC-3_hep_ipr_97_3_7min	Bandwidth:	4
Quantif. Method:	default	Dilution Factor:	1.0000
Recording Time:	07.08.18 08:39	Sample Weight:	1.0000
Run Time (min):	7.00	Sample Amount:	1.0000

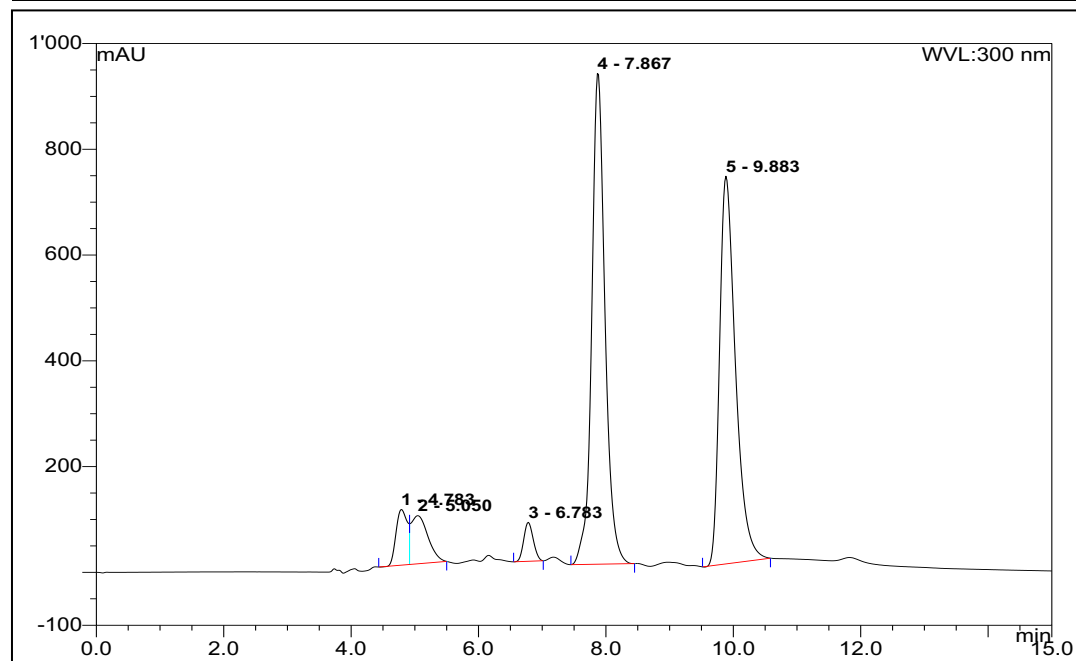


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	4.30	<b>4f-<i>leuco</i></b>	766.408	89.560	50.03	BMB*
2	4.98	<b>4f-<i>leuco</i></b>	613.769	89.454	49.97	BMB*
<b>Total:</b>			1380.178	179.013	100.00	

Analyzed on a Chiralpak<sup>®</sup> IC-3 column (4.6 mm x 250 mm; 3 µm; Art. Nr. 83525) using a 1.0 mL/min flow of *n*heptane/*i*PrOH 97:3.

**(±)-6-(Dimethylamino)-1-methoxy-9-(naphthalen-1-yl)-10-phenylacridinium *Leuco*-form 4j-*leuco*:**

Sample Name:	CF1252P leuco	Injection Volume:	90.0
Vial Number:	BD1	Channel:	UV_VIS_4
Sample Type:	unknown	Wavelength:	300.0
Control Program:	AD-H_hep_ipr_97_3_15min	Bandwidth:	4
Quantif. Method:	default	Dilution Factor:	1.0000
Recording Time:	08.08.18 13:29	Sample Weight:	1.0000
Run Time (min):	15.00	Sample Amount:	1.0000

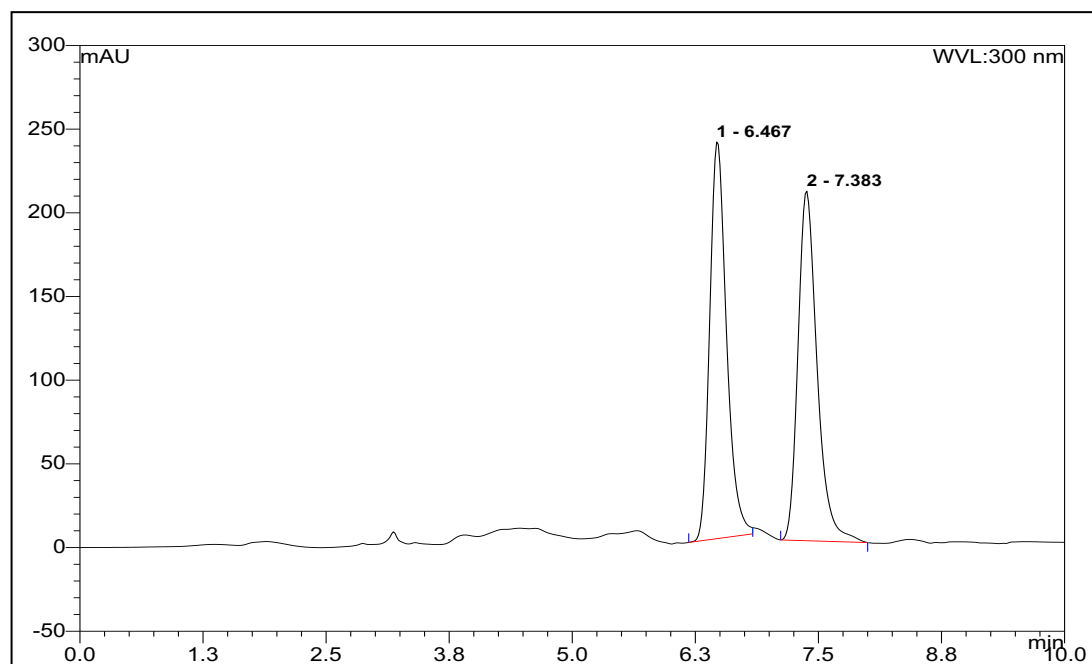


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	4.78	n.a.	105.341	21.732	4.36	BM *
2	5.05	n.a.	90.976	27.956	5.61	MB*
3	6.78	n.a.	73.655	12.753	2.56	BMB*
4	7.87	<b>4j-<i>leuco</i></b>	927.966	223.954	44.92	BMB*
5	9.88	<b>4j-<i>leuco</i></b>	733.137	212.157	42.55	BMB*
<b>Total:</b>			1931.076	498.553	100.00	

Analyzed on a Chiralpak® AD-H column (4.6 mm x 250 mm; 5 µm; Art. Nr. 19325) using a 1.0 mL/min flow of *n*heptane/*i*PrOH 97:3.

**(±)-7-(Dimethylamino)-1-methoxy-9-(naphthalen-1-yl)-10-phenylacridinium *Leuco*-form 4I-*leuco*:**

Sample Name:	CF1253P leuco rac	Injection Volume:	1.0
Vial Number:	GE4	Channel:	UV_VIS_4
Sample Type:	unknown	Wavelength:	300.0
Control Program:	AD-H_hep_ipr_95_5_10min	Bandwidth:	4
Quantif. Method:	default	Dilution Factor:	1.0000
Recording Time:	19.08.18 14:31	Sample Weight:	1.0000
Run Time (min):	10.00	Sample Amount:	1.0000

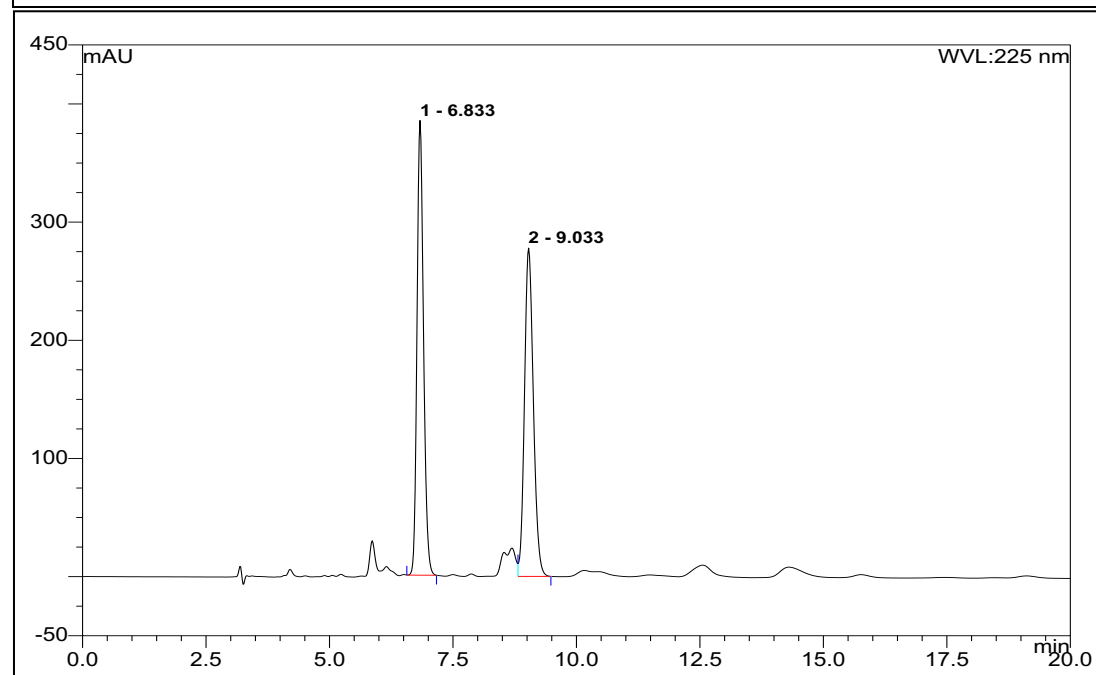


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	6.47	4I- <i>leuco</i>	237.106	47.040	50.01	BM *
2	7.38	4I- <i>leuco</i>	208.935	47.027	49.99	BMB*
Total:			446.042	94.067	100.00	

Analyzed on a Chiralpak<sup>®</sup> AD-H column (4.6 mm x 250 mm; 5 µm; Art. Nr. 19325) using a 1.0 mL/min flow of *n*-heptane/*i*PrOH 95:5.

**(±)-2-(1-Fluoro-2,2-dimethylpropyl)isoindoline-1,3-dione (±6b):**

Sample Name:	CF1308C	Injection Volume:	5.0
Vial Number:	RD6	Channel:	UV_VIS_1
Sample Type:	unknown	Wavelength:	225.0
Control Program:	OD-H_hep_ipr_95_5_20min	Bandwidth:	4
Quantif. Method:	default	Dilution Factor:	1.0000
Recording Time:	12.08.18 18:23	Sample Weight:	1.0000
Run Time (min):	20.00	Sample Amount:	1.0000

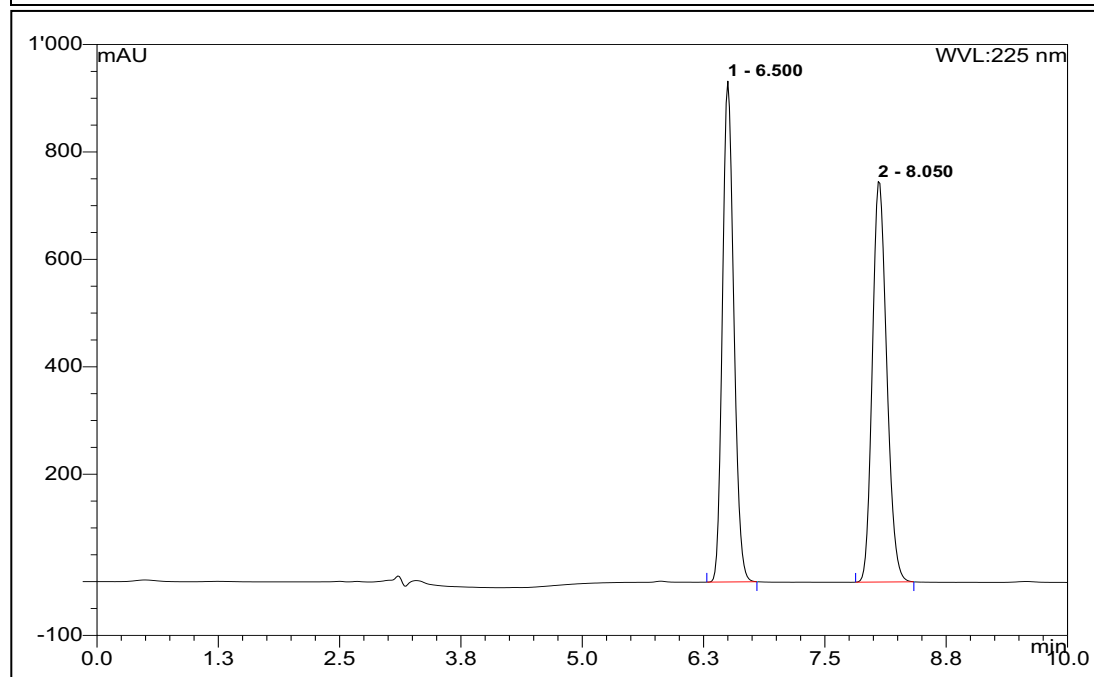


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	6.83	n.a.	384.761	58.854	50.39	BMB*
2	9.03	n.a.	277.843	57.938	49.61	MB*
<b>Total:</b>			662.604	116.792	100.00	

Analyzed on a Chiralcel® OD-H column (4.6 mm x 150 mm; 5 µm; Art. Nr. 14324) using a 1.0 mL/min flow of *n*heptane/*i*PrOH 95:5.

**(±)-5-Methoxy-2-(4-methoxyphenyl)-3-methyl-2,3-dihydrobenzofuran (±9):**

Sample Name:	CF1303P	Injection Volume:	5.0
Vial Number:	BE4	Channel:	UV_VIS_1
Sample Type:	unknown	Wavelength:	225.0
Control Program:	OD-H_hep_ipr_95_5_10min	Bandwidth:	4
Quantif. Method:	default	Dilution Factor:	1.0000
Recording Time:	07.08.18 21:13	Sample Weight:	1.0000
Run Time (min):	10.00	Sample Amount:	1.0000



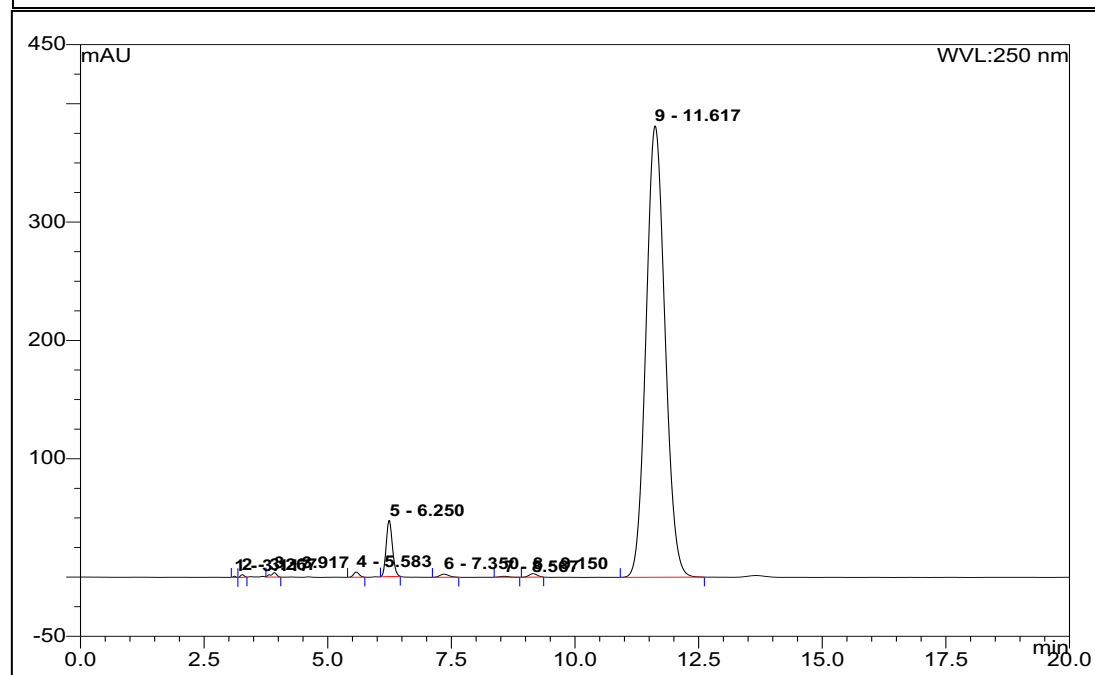
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	6.50	n.a.	932.501	126.537	49.58	BMB*
2	8.05	n.a.	745.629	128.674	50.42	BMB*
<b>Total:</b>			1678.130	255.211	100.00	

Analyzed on a Chiralcel® OD-H column (4.6 mm x 150 mm; 5 µm; Art. Nr. 14324) using a 1.0 mL/min flow of *n*heptane/*i*PrOH 95:5.



**1-(*tert*-Butyl) 2-(4-(methoxycarbonyl)phenyl) pyrrolidine-1,2-dicarboxylate (B):**

Sample Name:	CF1159-1P	Injection Volume:	40.0
Vial Number:	RD6	Channel:	UV_VIS_2
Sample Type:	unknown	Wavelength:	250.0
Control Program:	AD-H_hep_ipr_90_10_20min	Bandwidth:	4
Quantif. Method:	default	Dilution Factor:	1.0000
Recording Time:	01.03.18 11:36	Sample Weight:	1.0000
Run Time (min):	20.00	Sample Amount:	1.0000



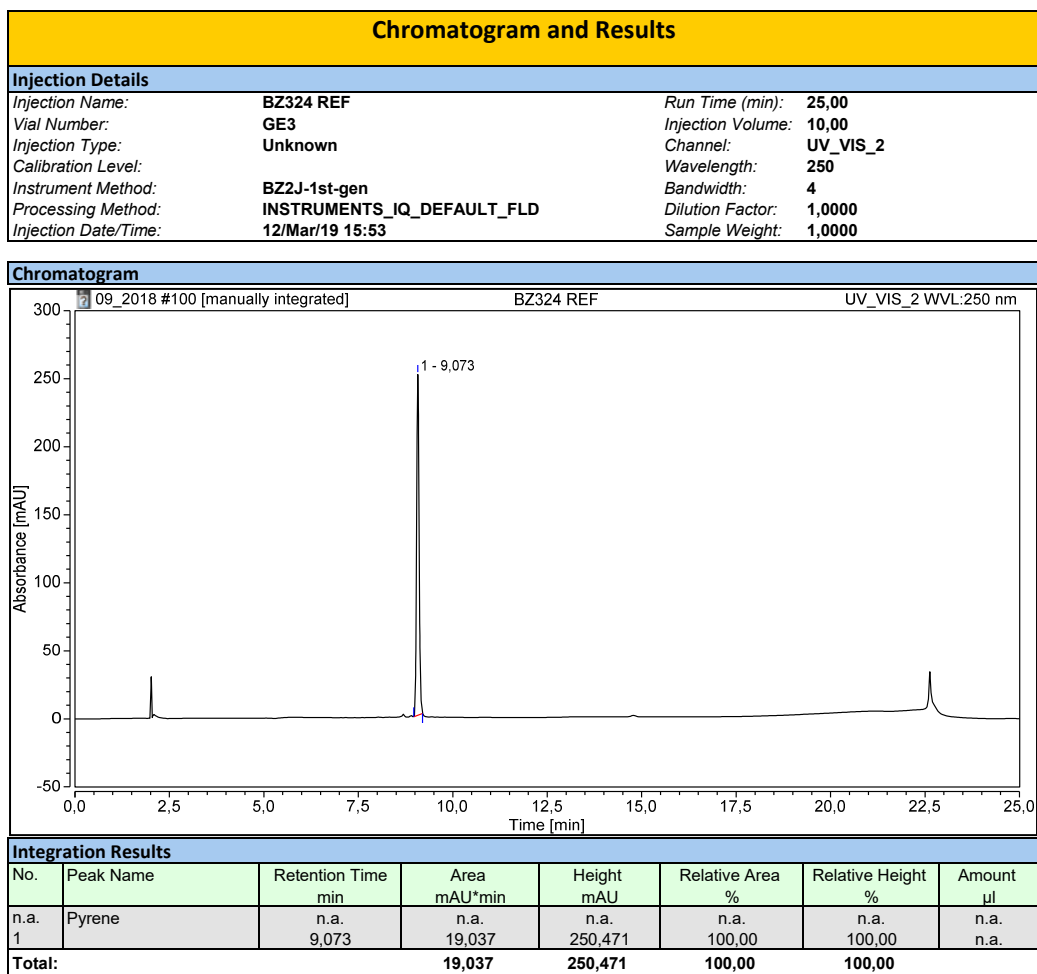
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Type
1	3.12	n.a.	1.022	0.060	0.03	BMB*
2	3.27	n.a.	2.250	0.191	0.11	bMB*
3	3.92	n.a.	3.699	0.507	0.28	BMB*
4	5.58	n.a.	4.357	0.578	0.32	BMB*
5	6.25	n.a.	47.398	6.972	3.89	BMB*
6	7.35	n.a.	2.640	0.558	0.31	BMB*
7	8.57	( <i>R</i> )-Prod	0.773	0.155	0.09	BMB*
8	9.15	n.a.	2.908	0.559	0.31	BMB*
9	11.62	( <i>S</i> )-Prod	381.483	169.504	94.65	BMB*
<b>Total:</b>			446.531	179.084	100.00	

Analyzed on a Chiralpak® AD-H column (4.6 mm x 250 mm; 5 µm; Art. Nr. 19325) using a 1.0 mL/min flow of *n*-heptane/*i*PrOH 90:10.

**3,6-Bis(dimethylamino)-9-mesityl-10-methylacridinium bromide (1):**

Instrument:RP\_HPLC Sequence:09\_2018

Page 1 of 1



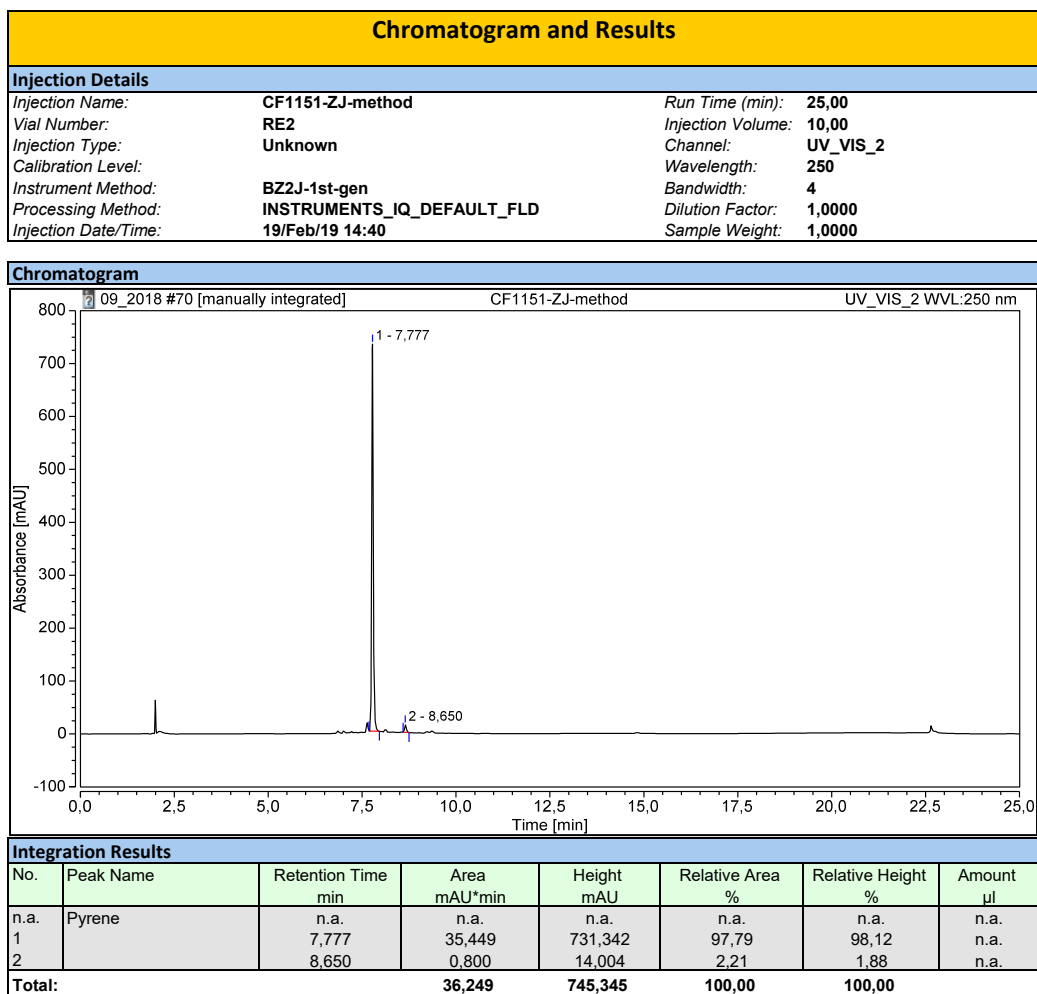
Default/Integration

Chromeleon (c) Dionex  
Version 7.2.7.10369

**6-(Dimethylamino)-1-methoxy-10-methyl-9-phenylacridinium bromide (4a):**

Instrument:RP\_HPLC Sequence:09\_2018

Page 1 of 1



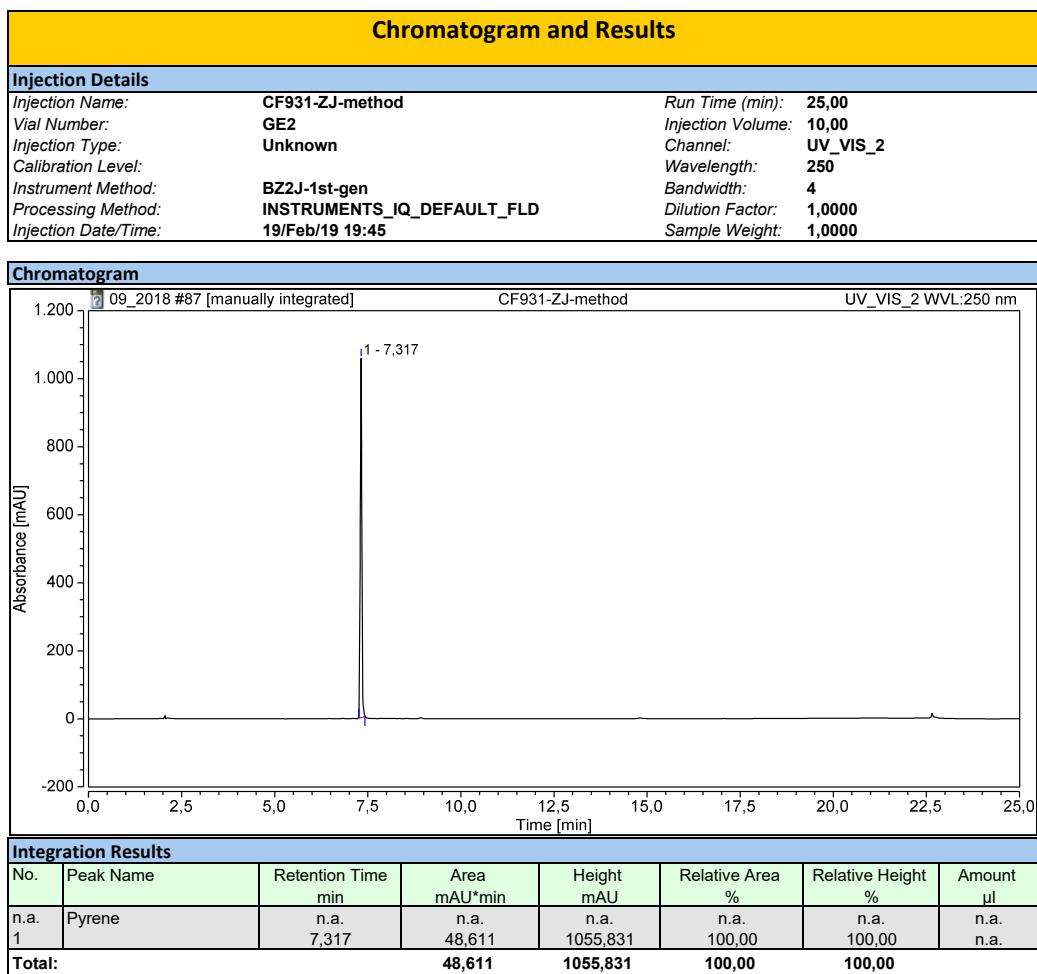
Default/Integration

Chromeleon (c) Dionex  
Version 7.2.7.10369

**1-Methoxy-10-methyl-9-phenylacridinium bromide (4b):**

Instrument:RP\_HPLC Sequence:09\_2018

Page 1 of 1



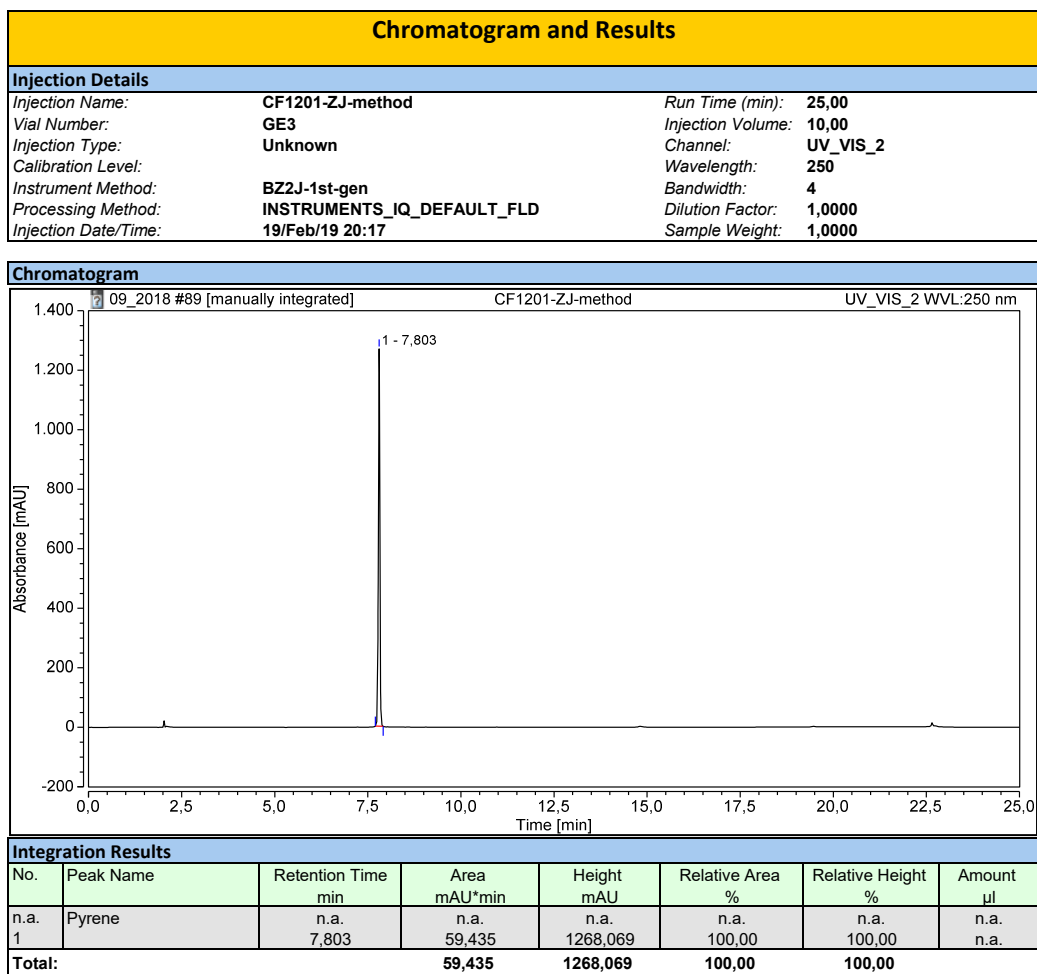
Default/Integration

Chromeleon (c) Dionex  
Version 7.2.7.10369

**1-Methoxy-9,10-diphenylacridinium bromide (4c):**

Instrument:RP\_HPLC Sequence:09\_2018

Page 1 of 1



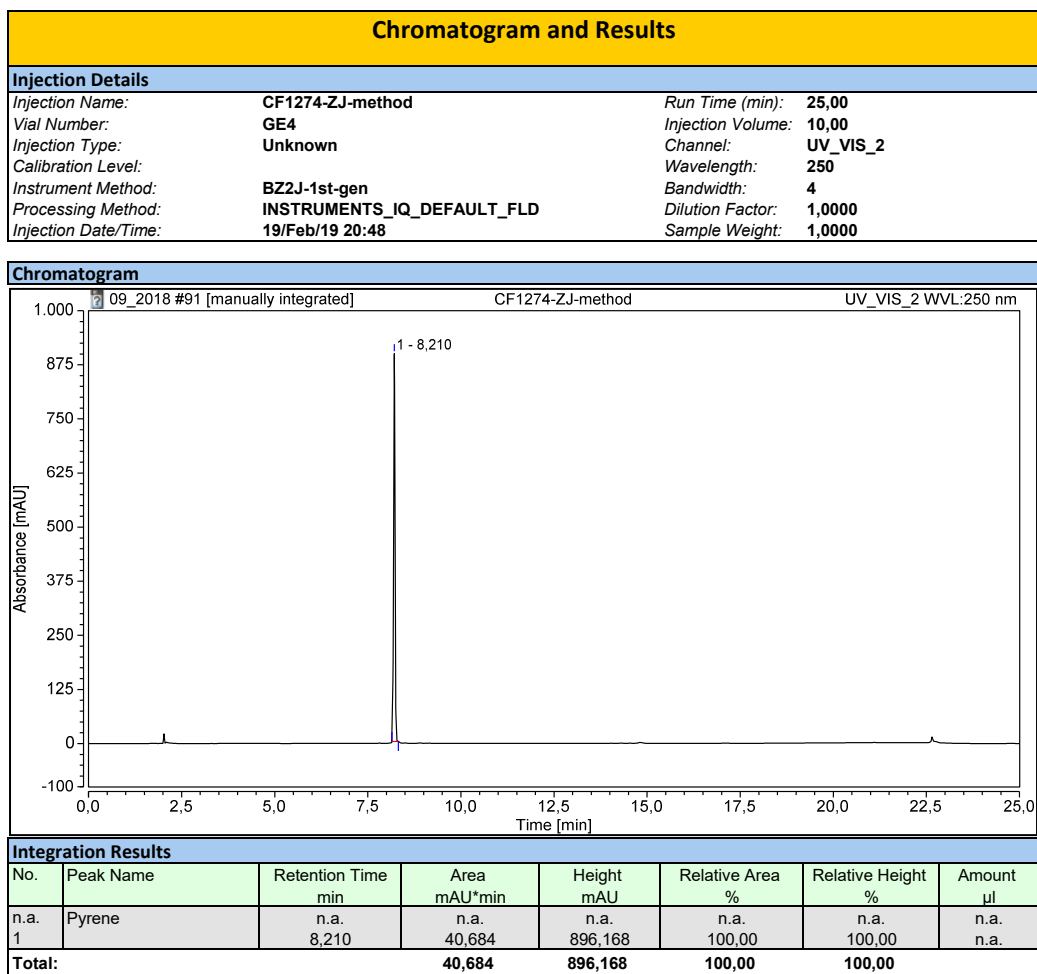
Default/Integration

Chromeleon (c) Dionex  
Version 7.2.7.10369

**9-Mesityl-1-methoxy-10-phenylacridinium bromide (4d):**

Instrument:RP\_HPLC Sequence:09\_2018

Page 1 of 1



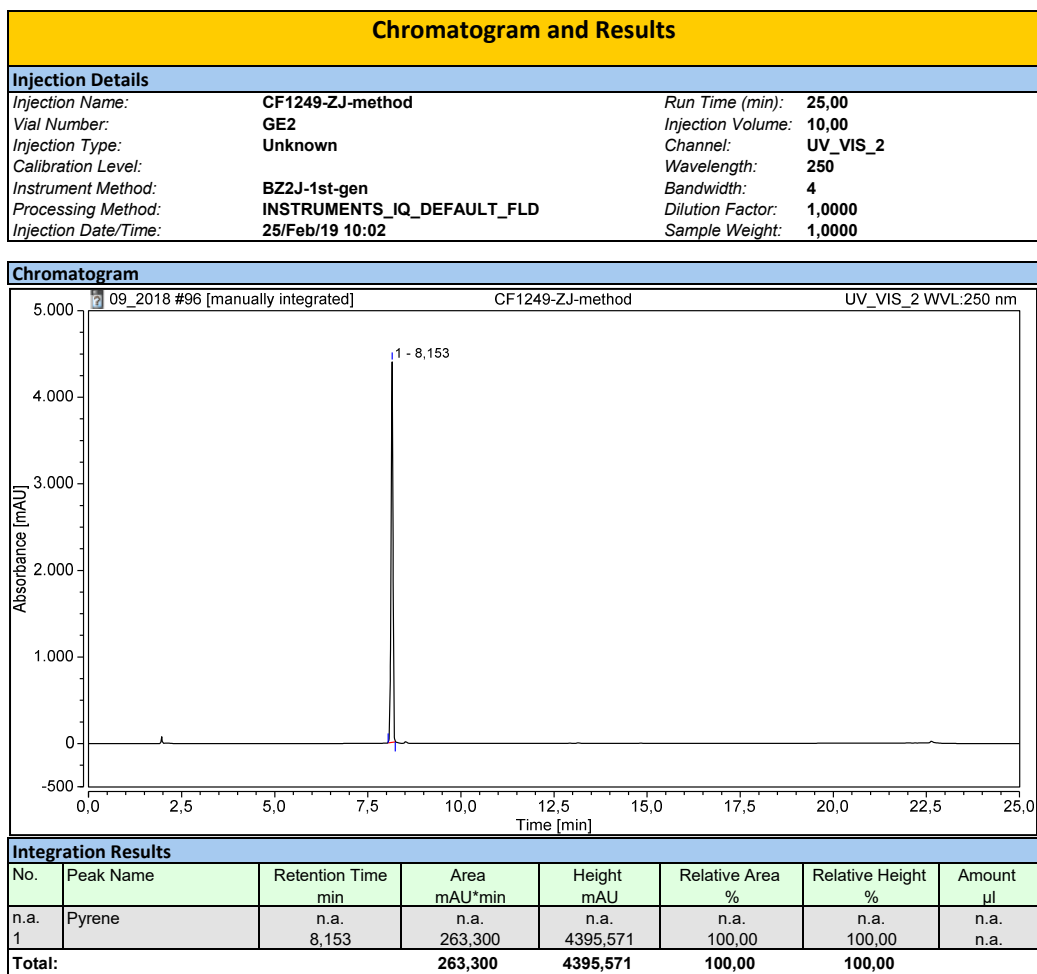
Default/Integration

Chromeleon (c) Dionex  
Version 7.2.7.10369

**9-(2,6-Dimethylphenyl)-1-methoxy-10-phenylacridinium bromide (4e):**

Instrument:RP\_HPLC Sequence:09\_2018

Page 1 of 1



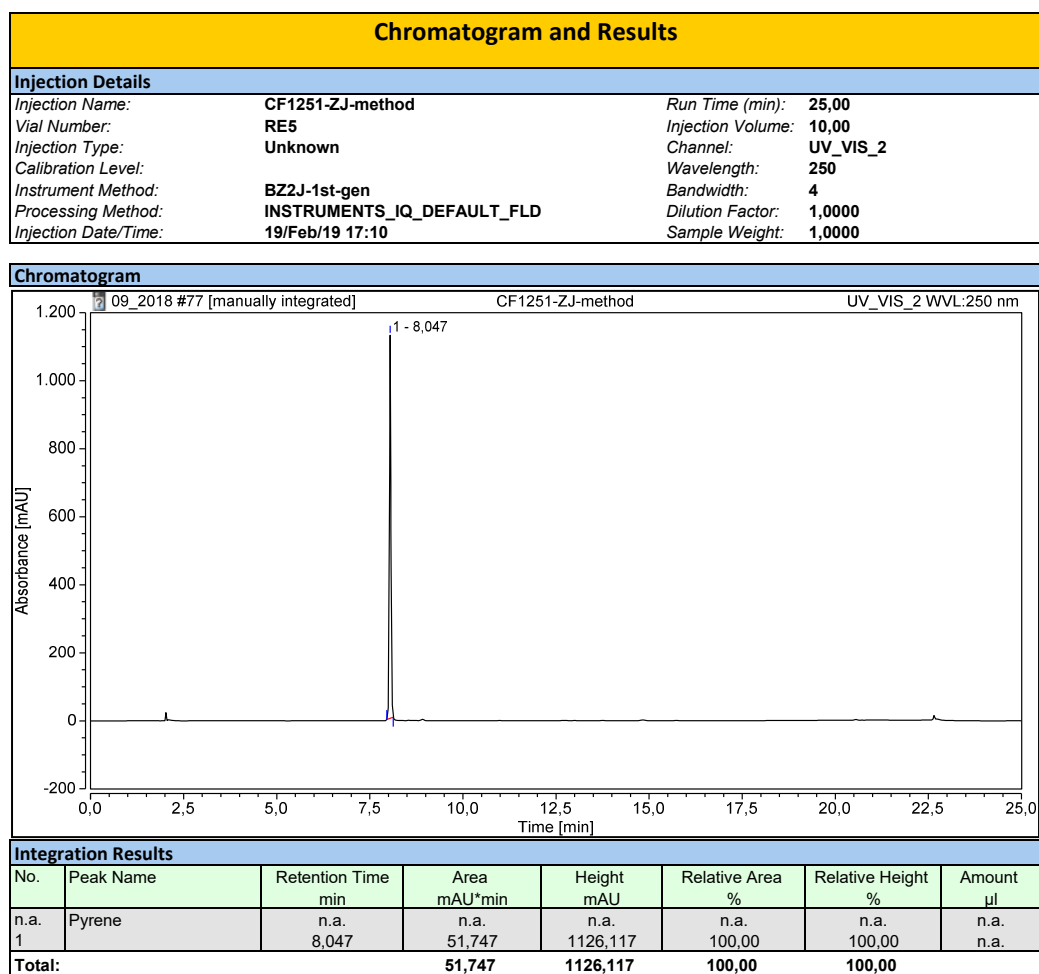
Default/Integration

Chromeleon (c) Dionex  
Version 7.2.7.10369

**1-Methoxy-9-(naphthalen-1-yl)-10-phenylacridinium bromide (4f):**

Instrument:RP\_HPLC Sequence:09\_2018

Page 1 of 1



Default/Integration

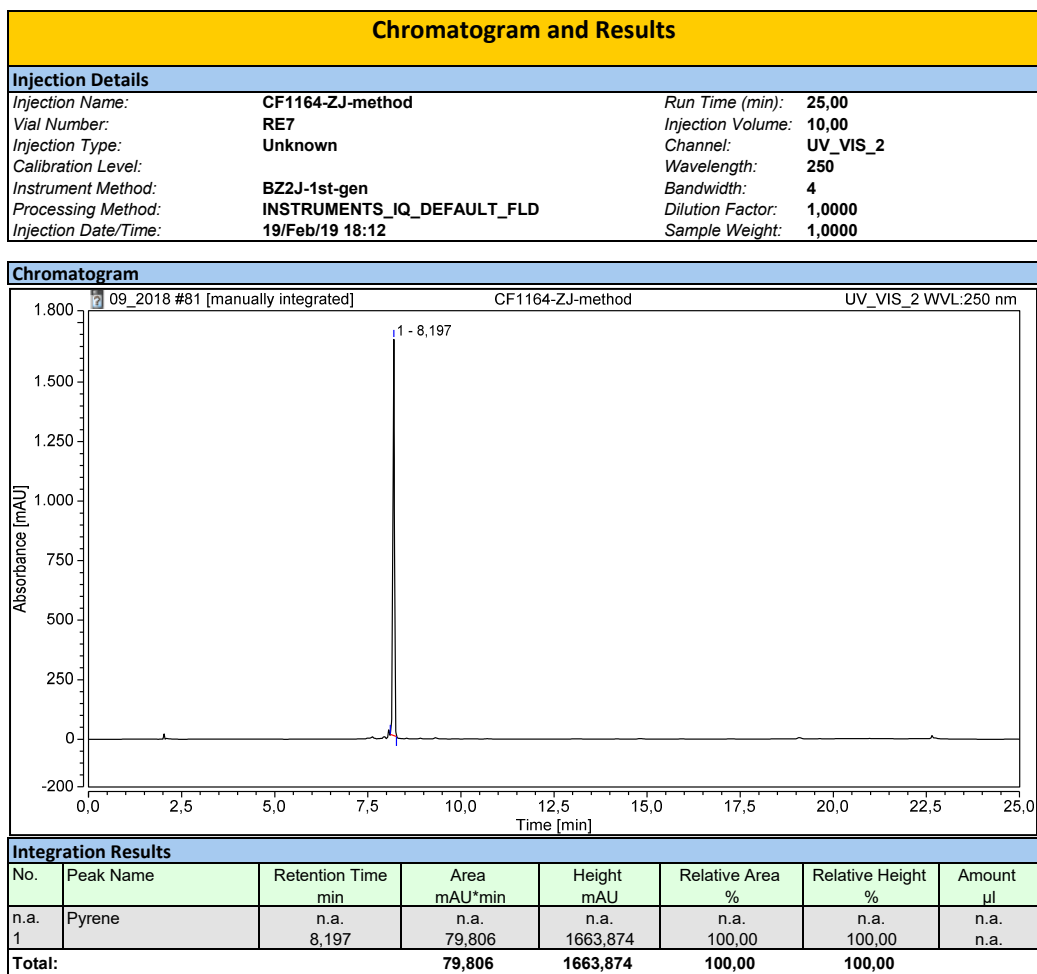
Chromeleon (c) Dionex  
Version 7.2.7.10369



**6-(Dimethylamino)-1-methoxy-9,10-diphenylacridinium bromide (4g):**

Instrument:RP\_HPLC Sequence:09\_2018

Page 1 of 1



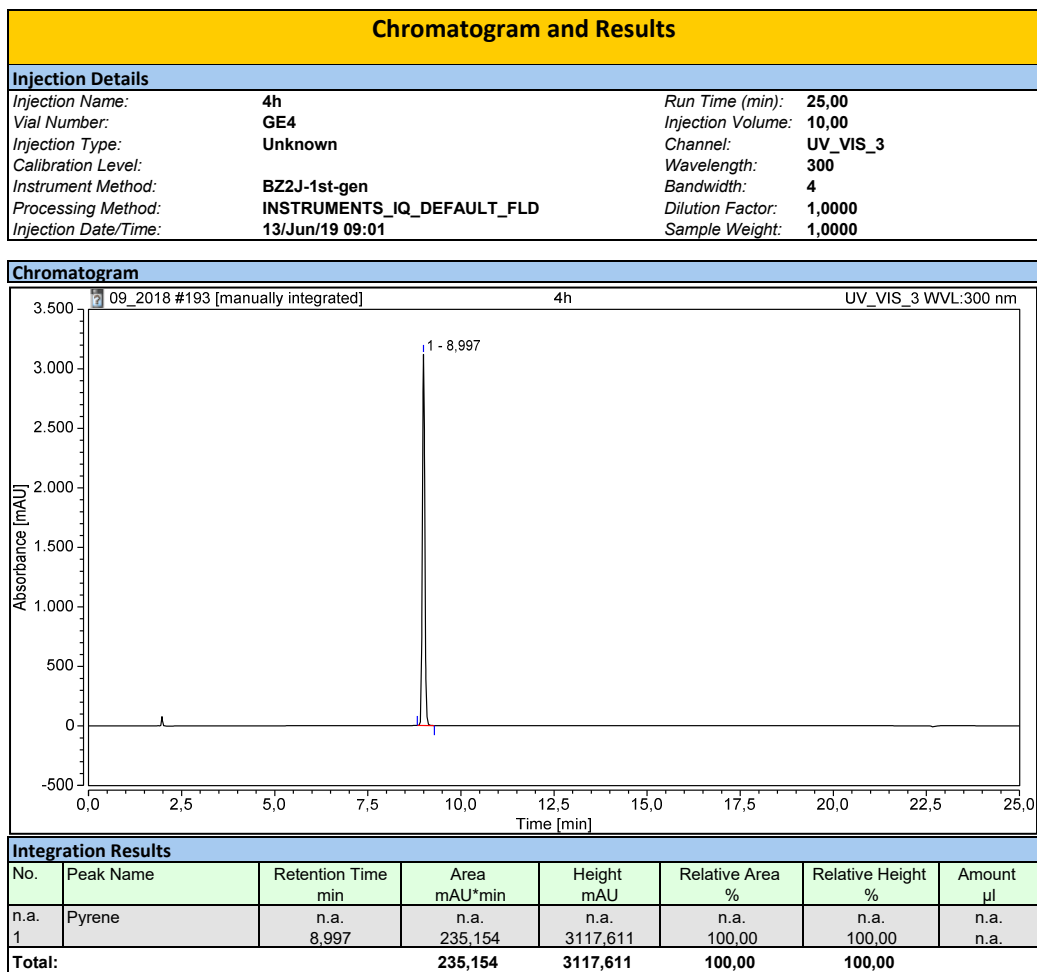
Default/Integration

Chromeleon (c) Dionex  
Version 7.2.7.10369

**6-(Dimethylamino)-9-mesityl-1-methoxy-10-phenylacridinium bromide (4h):**

Instrument:RP\_HPLC Sequence:09\_2018

Page 1 of 1



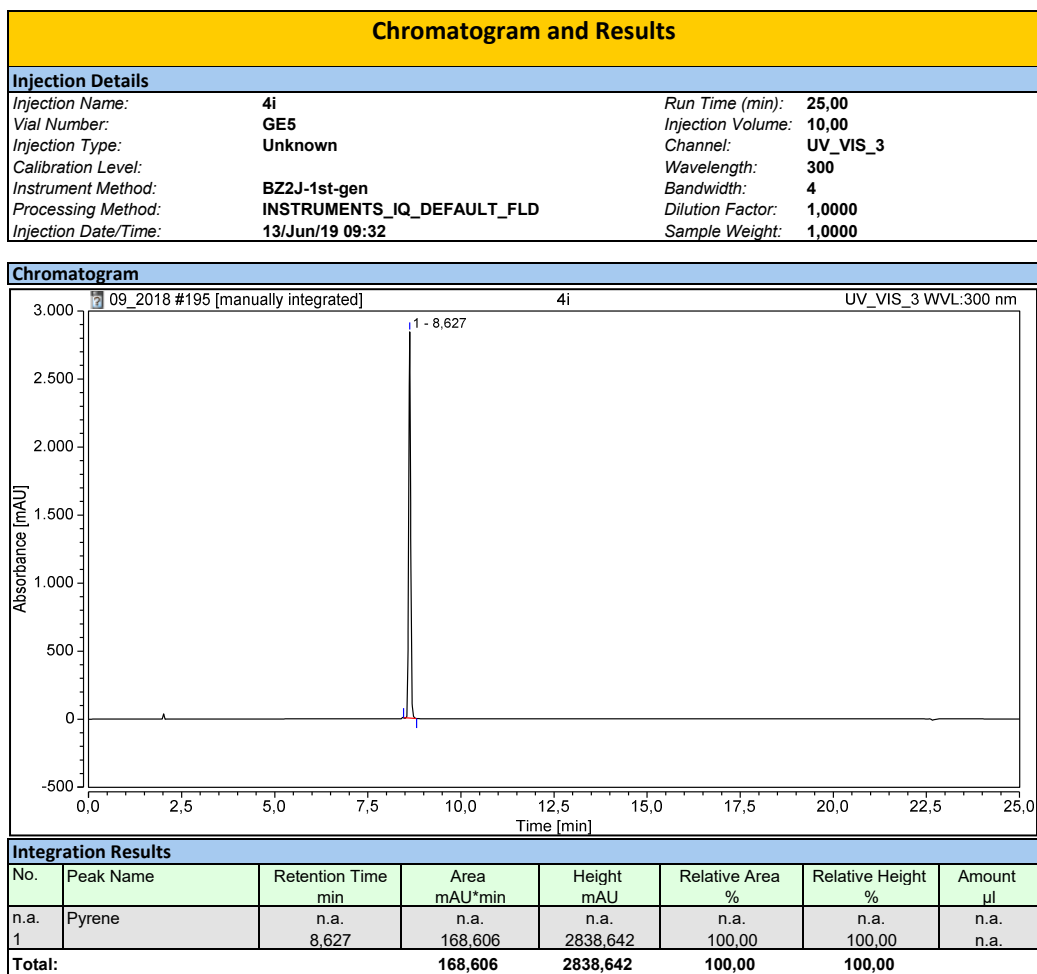
Default/Integration

Chromeleon (c) Dionex  
Version 7.2.7.10369

**6-(Dimethylamino)-9-(2,6-dimethylphenyl)-1-methoxy-10-phenylacridinium bromide (4i):**

Instrument:RP\_HPLC Sequence:09\_2018

Page 1 of 1



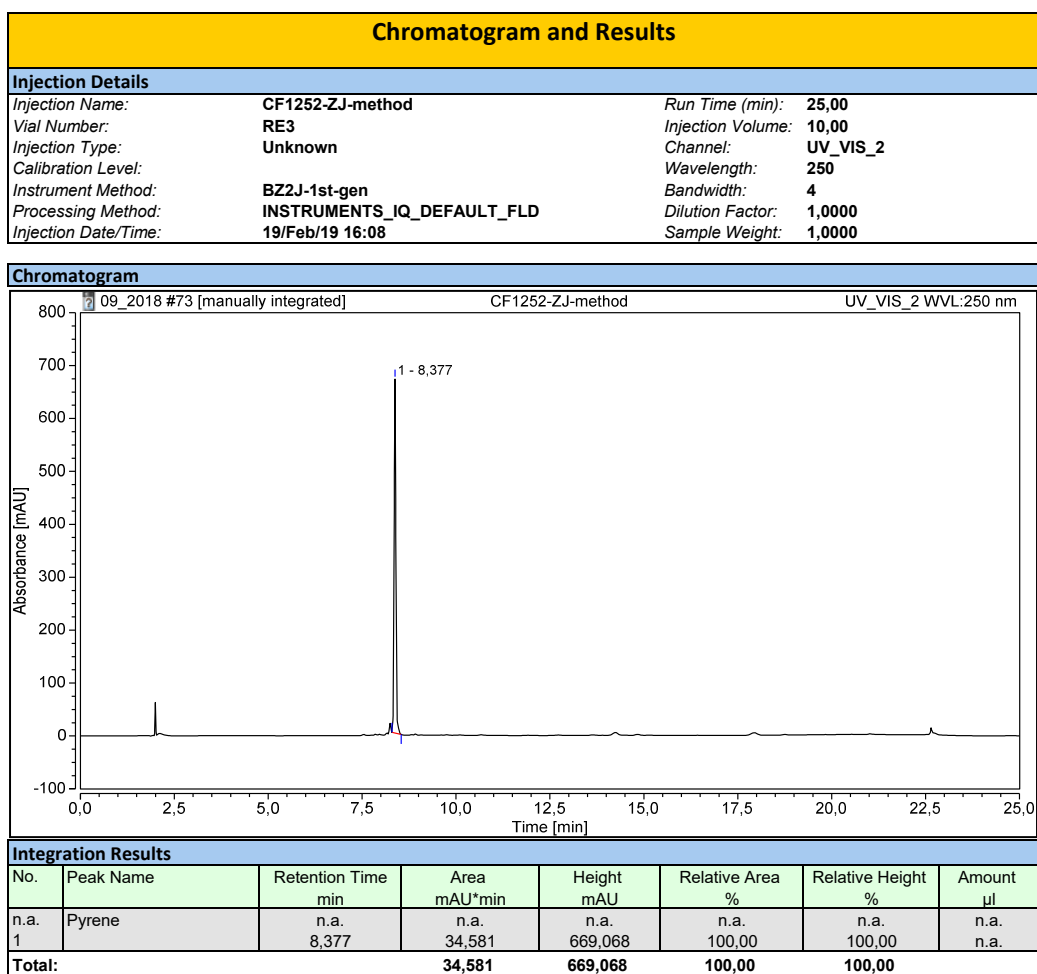
Default/Integration

Chromeleon (c) Dionex  
Version 7.2.7.10369

**6-(Dimethylamino)-1-methoxy-9-(naphthalen-1-yl)-10-phenylacridinium bromide (4j):**

Instrument:RP\_HPLC Sequence:09\_2018

Page 1 of 1



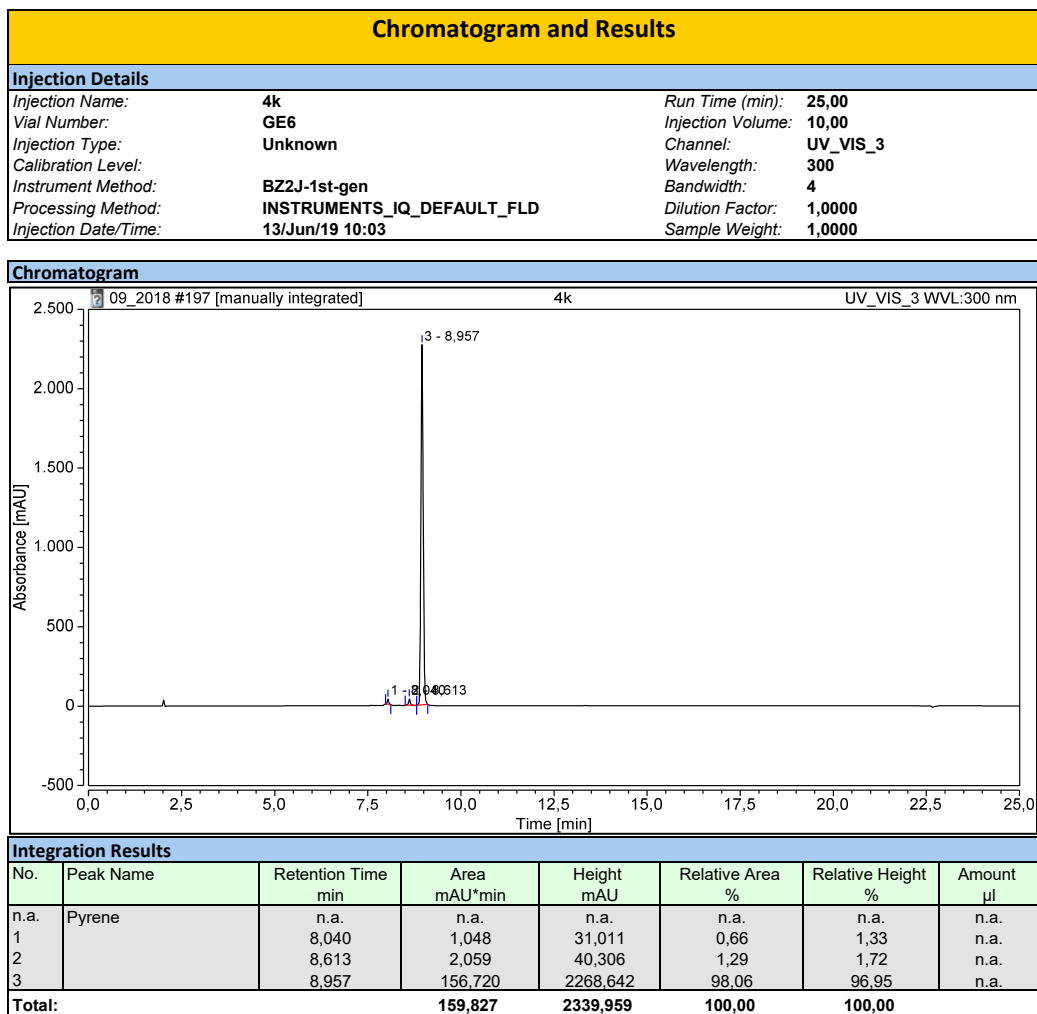
Default/Integration

Chromeleon (c) Dionex  
Version 7.2.7.10369

**7-(Dimethylamino)-9-mesityl-1-methoxy-10-phenylacridinium bromide (4k):**

Instrument:RP\_HPLC Sequence:09\_2018

Page 1 of 1



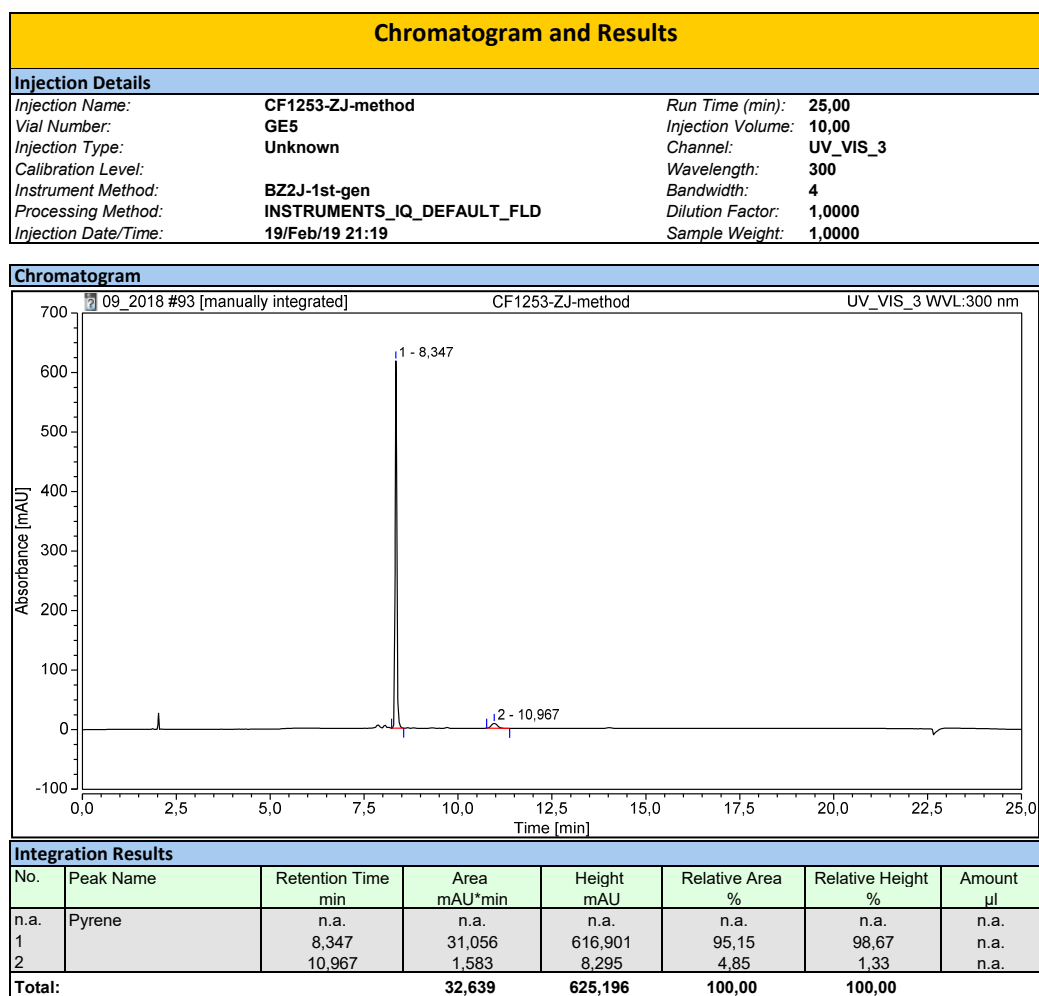
Default/Integration

Chromeleon (c) Dionex  
Version 7.2.7.10369

**7-(Dimethylamino)-1-methoxy-9-(naphthalen-1-yl)-10-phenylacridinium bromide (4l):**

Instrument:RP\_HPLC Sequence:09\_2018

Page 1 of 1



Default/Integration

Chromeleon (c) Dionex  
Version 7.2.7.10369

## References

- [1] Watson, S. C.; Eastham, J. F. Colored Indicators for Simple Direct Titration of Magnesium and Lithium Reagents. *J. Organometal. Chem.* **1967**, *9*, 165–168.
- [2] Zuo, Z.; Ahneman, D. T.; Chu, L.; Terrett, J. A.; Doyle, A. G.; MacMillan, D. W. C. Merging Photoredox with Nickel Catalysis: Coupling of a  $\alpha$ -Carboxyl  $sp^3$ -Carbons with Aryl Halides. *Science* **2014**, *345*, 437–440; see also Ref. [16].
- [3] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09 Revision B.01, **2010**.
- [4] Kerzig, C.; Wenger, O. S. Sensitized Triplet-Triplet Annihilation Upconversion in Water and its Application to Photochemical Transformations. *Chem. Sci.* **2018**, *9*, 6670–6678.
- [5] Yoshimura, A.; Hoffman, M. Z.; Sun, H. An Evaluation of the Excited State Absorption Spectrum of  $Ru(bpy)_3^{2+}$  in Aqueous and Acetonitrile Solutions. *J. Photochem. Photobiol. Chem.* **1993**, *70*, 29–33.
- [6] Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T. *Handbook of Photochemistry*, CRC/Taylor & Francis, Boca Raton, **2006**.
- [7] Klán, P.; Wirz, J. *Photochemistry of Organic Compounds: From Concepts to Practice*, Wiley, Chichester, West Sussex, U.K., **2009**.
- [8] Kerzig, C.; Guo, X.; Wenger, O. S. Unexpected Hydrated Electron Source for Preparative Visible-Light Driven Photoredox Catalysis. *J. Am. Chem. Soc.* **2019**, *141*, 2122–2127.
- [9] Kerzig, C.; Goez, M. Combining Energy and Electron Transfer in a Supramolecular Environment for the "Green" Generation and Utilization of Hydrated Electrons through Photoredox Catalysis. *Chem. Sci.* **2016**, *7*, 3862–3868.
- [10] Wrighton, M.; Markham, J. Quenching of the Luminescent State of tris(2,2'-bipyridine) Ruthenium(II) by Electronic Energy Transfer. *J. Phys. Chem.* **1973**, *77*, 3042–3044.
- [11] Saltiel, J.; Hammond, G. S. Mechanisms of Photochemical Reactions in Solution. XVII. *cis-trans* Isomerization of the Stilbenes by Excitation Transfer from Low Energy Sensitizers. *J. Am. Chem. Soc.* **1963**, *85*, 2515–2516.
- [12] Pape, F.; Thiel, N. O.; Teichert, J. F. Z-Selective Copper(I)-Catalyzed Alkynes Semihydrogen with Tethered Cu-Alkoxide Complexes. *Chem. - Eur. J.* **2015**, *21*, 15934–15938.
- [13] Fischer, C.; Sparr, C. Direct Transformation of Esters into Heterocyclic Fluorophores. *Angew. Chem. Int. Ed.* **2018**, *57*, 2436–2440.
- [14] Reckenthäler, M.; Griesbeck, A. G. Photoredox Catalysis for Organic Syntheses. *Adv. Synth. Catal.* **2013**, *355*, 2727–2744.
- [15] Hari, D. P.; König, B. Synthetic Applications of Eosin Y in Photoredox Catalysis. *Chem Commun* **2014**, *50*, 6688–6699.
- [16] Luo, J.; Zhang, J. Donor-Acceptor Fluorophores for Visible-Light-Promoted Organic Synthesis: Photoredox/Ni Dual Catalytic  $C(sp^3)$ - $C(sp^2)$  Cross-Coupling. *ACS Catalysis* **2016**, *6*, 873–877.
- [17] Debye, P. Reaction Rates in Ionic Solutions. *Trans. Electrochem. Soc.* **1942**, *82*, 265–272.
- [18] Kerzig, C.; Goez, M. Generating Hydrated Electrons through Photoredox Catalysis with 9-Anthrolate. *Phys. Chem. Chem. Phys.* **2015**, *17*, 13829–13836.
- [19] Kerzig, C.; Hoffmann, M.; Goez, M. Resveratrol Radical Repair by Vitamin C at the Micelle-Water Interface: Unexpected Reaction Rates Explained by Ion-Dipole. *Chem. - Eur. J.* **2018**, *24*, 3038–3044.
- [20] Lee, S. H.; Jang, B.-B.; Kafafi, Z. H. Highly Fluorescent Solid-State Asymmetric Spirosilabifluorene Derivatives. *J. Am. Chem. Soc.* **2005**, *127*, 9071–9078.
- [21] Commercially available under CAS Registry Number: [114971-52-7] or for preparation see: Kajigaeshi, S.; Kakinami, T.; Yamasaki, H.; Fujisaki, S.; Kondo, M.; Okamoto, T. Iodination of Phenols by Use of benzyltrimethylammonium Dichloriodate(1-). *Chem. Lett.* **1987**, *16*, 2109–2112.
- [22] White, A.; Wang, L.; Nicewicz, D. Synthesis and Characterization of Acridinium Dyes for Photoredox Catalysis. *Synlett* **2019**, DOI 10.1055/s-0037-1611744.
- [23] Benniston, A. C.; Elliott, K. J.; Harrington, R. W.; Clegg, W. On the Photochemical Stability of the 9-Mesityl-10-Methylacridinium Cation. *Eur. J. Org. Chem.* **2009**, *2009*, 253–258.
- [24] Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. Visible Light Photoredox Catalysis with Transition Metal Complexes: Application in Organic Synthesis. *Chem. Rev.* **2013**, *113*, 5322–5363.

- [25] Xi, Y.; Yi, H.; Lei, A. Synthetic Applications of Photoredox Catalysis with Visible Light. *Org. Biomol. Chem.* **2013**, *11*, 2387.
- [26] Koike, T.; Akita, M. Visible-Light Radical Designed by Ru- and Ir-based Photoredox Catalysis. *Inorg Chem Front* **2014**, *1*, 562–576.
- [27] Joshi-Pangu, A.; Lévesque, F.; Roth, H. G.; Oliver, S. F.; Campeau, L.-C.; Nicewicz, D.; DiRocco, D. A. Acridinium-Based Photocatalysts: A Sustainable Option in Photoredox Catalysis. *J. Org. Chem.* **2016**, *81*, 7244–7249.
- [28] Blum, T. R.; Miller, Z. D.; Bates, D. M.; Guzei, I. A.; Yoon, T. P. Enantioselective Photochemistry through Lewis Acid-Catalyzed Triplet Energy Transfer. *Science* **2016**, *354*, 1391–1395.
- [29] Gray, V.; Dreos, A.; Erhart, P.; Albinsson, B.; Moth-Poulsen, K.; Abrahamsson, M. Loss Channels in Triplet-Triplet Annihilation Photon Upconversion: Importance of Annihilator Singlet and Triplet Surface Shapes. *Phys. Chem. Chem. Phys.* **2017**, *19*, 10931–10939.
- [30] Fukuzumi, S.; Kotani, H.; Ohkubo, K.; Ogo, S.; Tkachenko, N. V.; Lemmetyinen, H. Electron-Transfer State of 9-Mesityl-10-Methylacridinium Ion with a Much Longer Lifetime and Higher Energy Than That of the Natural Photosynthetic Reaction Center. *J. Am. Chem. Soc.* **2004**, *126*, 1600–1601.
- [31] Blum, T. R.; Zhu, Y.; Nordeen, S. A.; Yoon, T. P. Photocatalytic Synthesis of Dihydrobenzofurans by Oxidative [3+2] Cycloaddition of Phenols. *Angew. Chem. Int. Ed.* **2014**, *53*, 11056–11059.
- [32] See General Information for more details.
- [33] Ventre, S.; Petronijevic, F. R.; MacMillan, D. W. C. Decarboxylative Fluorination of Aliphatic Carboxylic Acids via Photoredox Catalysis. *J. Am. Chem. Soc.* **2015**, *137*, 5654–5657.
- [34] Prepared according to: Ventre, S.; Petronijevic, F. R.; MacMillan, D. W. C. Decarboxylative Fluorination of Aliphatic Carboxylic Acids via Photoredox Catalysis. *J. Am. Chem. Soc.* **2015**, *137*, 5654–5657.
- [35] Prepared according to: Bourhani, Z.; Malkov, A. V. Ligand-Accelerated Vanadium-Catalysed Epoxidation in Water. *Chem. Commun.* **2005**, 4592–4594.
- [36] Wilger, D. J.; Grandjean, J.-M. M.; Lammert, T. R.; Nicewicz, D. A. The Direct Anti-Markovnikov Addition of Mineral Acids to Styrenes. *Nat. Chem.* **2014**, *6*, 720–726.
- [37] Romero, N. A.; Nicewicz, D. A. Organic Photoredox Catalysis. *Chem. Rev.* **2016**, *116*, 10075–10166.
- [38] a) Kuriyama, Y.; Arai, T.; Sakuragi, H.; Tokumaru, K. Direct Observation of cis-to-trans Conversion of Olefin Radical Cations. Electron Transfer-Induced Isomerization of Stilbene Derivatives. *Chem. Phys. Lett.* **1990**, *173*, 253; b) Fukuzumi, S.; Ohkubo, K. Organic Synthetic Transformations Using Organic Dyes as Photoredox Catalysts. *Org. Biomol. Chem.* **2014**, *12*, 6059; c) Miranda, M. A.; Garcia, H. 2,4,6-Triphenylpyrylium Tetrafluoroborate as an Electron-Transfer Photosensitizer. *Chem. Rev.* **1994**, *94*, 1063.
- [39] Fischer, C.; Sparr, C. Configurationally Stable Atropisomeric Acridinium Fluorophores. *Synlett* **2018**, *29*, 2176–2180.
- [40] (a) Lotter, D.; Neuburger, M.; Rickhaus, M.; Häussinger, D.; Sparr, C. Stereoselective Arene-Forming Aldol Condensation: Synthesis of Configurationally Stable Oligo-1,2-Naphthylenes. *Angew. Chem. Int. Ed.* **2016**, *55*, 2920–2923; (b) Rickhaus, M.; Jundt, L.; Mayor, M. Determining Inversion Barriers in Atrop-Isomers - A Tutorial for Organic Chemists. *Chimia* **2016**, *70*, 192–202.