Synthesis of 1,5-Bifunctional Organolithium Reagents by a Double Directed *ortho*-Metalation: Direct Transformation of Esters into 1,8-Dimethoxy-Acridinium Salts‡

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
Carboxylic Acid Ester;
Fluorophores;
Organometallic Reagents;
Directed *ortho*-Metalation;
Acridinium Salts;
Photoredox Catalysis

ABSTRACT

The impact of electronic and steric factors on the selectivity of the electrophilic aromatic substitution amounts to several limitations in accessing specific substitution patterns. Nucleophiles generated by directed metalation represent an effective alternative for the preparation of various distinctly substituted arenes and heterocyclic scaffolds to overcome these restraints. Herein, we report the direct synthesis of specifically substituted heterocyclic fluorophores from esters by the addition of 1,5-bifunctional organometallic reagents from a double directed *ortho*-metalation (dD*o*M). Bis(3-methoxylphenyl)amines were efficiently dilithiated und employed for the synthesis of 1,8-dimethoxy-acridinium salts with distinct photophysical and electrochemical properties. The individual reduction potentials, the water-solubility and the brightness of these new dyes promise different applications in catalysis, imaging and materials science.

1. Introduction

The possibility to adjust photophysical and electrochemical properties of luminescent metal complexes by variation of pyridine-based ligands crucially contributed to the advancement of photocatalysis in recent years.[1] In analogy, organic fluorophores would allow complementary and sustainable catalytic processes,[2] but are currently not accessible in similar variety despite substantial progress. As heterocyclic fluorophores are usually prepared by electrophilic aromatic substitution methods, their substitution pattern is typically governed by electronic and steric factors that limit the dye diversity.[3] Recently, we have investigated an alternative approach by the use of 1,5-bifunctional organometallic reagents from halogen–metal exchange reactions for the double addition to carboxylic acid esters.[4] Upon dehydration, this transformation enables the direct conversion of various esters into valuable heterocyclic fluorophores with high functional group tolerance.[5] However, the use of dimetallic reagents not only allows the direct transformation of stable and readily available carboxylic acid esters,[6] but would also provide a means to prepare heterocyclic compounds with a substitution pattern different to electrophilic aromatic substitution products of the same bis(3-methoxyphenyl)-amine precursors ***1*** (Figure 1 left).[7] More specifically, reagents prepared by a double directed *ortho*-metalation (dD*o*M) of bis(3-methoxyphenyl)-amines ***1*** would give rise to uncommonly substituted 1,8-dimethoxy acridinium salts ***4***, expected to exhibit distinct physical and chemical properties.[8] The resulting 1,8-substitution of the products from the double directed *ortho*-metalated reagent therefore provides a specific *peri*-relationship of the methoxy groups with the ester residue (R, Figure 1 right).

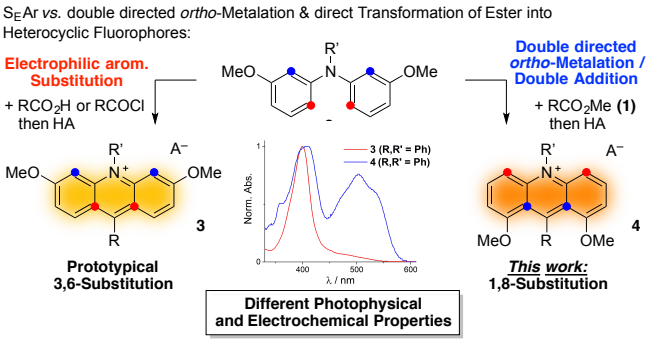

Figure 1. Varying substitution pattern from a common tertiary amine: electrophilic aromatic substitution and the double directed *ortho*-metalation for the direct transformation of esters into 1,8-dimethoxy acridinium salts with different photophysical and electrochemical properties.

‡ Dedicated to the memory of Sir Derek H. R. Barton FRS FRSE.

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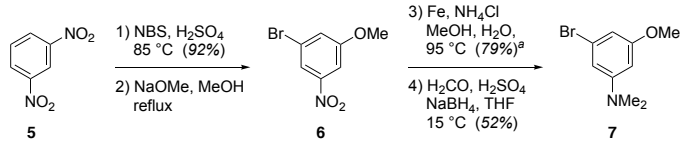
2. Results and Discussion

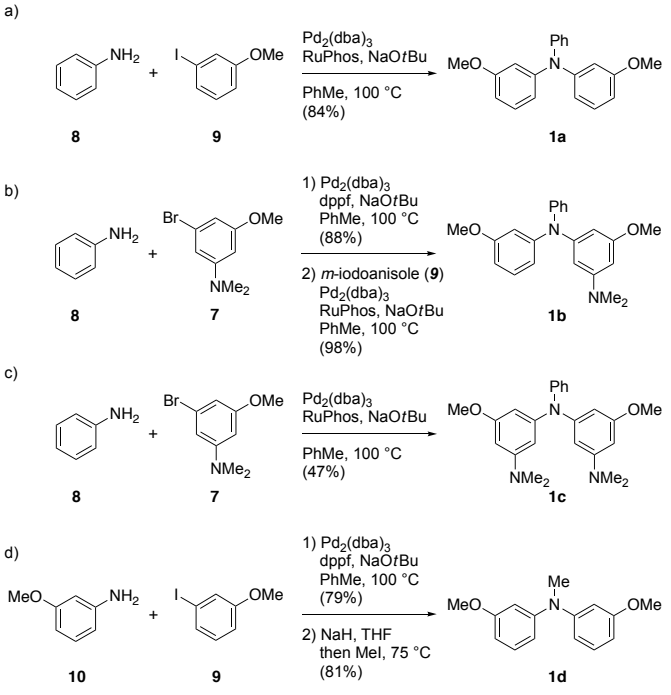
2.1. Synthesis of Tertiary Amine Precursors

To investigate the feasibility and applicability of this double directed *ortho*-metalation strategy, we anticipated a synthesis of tertiary bis(3-methoxyphenyl)-amines ***1*** from simple, commercially available building blocks. For further diversification, we prepared 3-bromo-5-methoxy-*N*,*N*-dimethyl-aniline (***7***) in four steps, involving a bromination of 1,3-dinitrobenzene using *N*-bromosuccinimide followed by nucleophilic aromatic substitution with sodium methoxide, reduction and dimethylation by reductive amination of the aniline (Scheme 1).[9] In the reductive amination step, the yield was improved by limiting the contact time of the aniline with formaldehyde in the acidic medium by the portionwise addition of a suspension of $NaBH_4$ and aniline in THF to the acidic aqueous formaldehyde solution.[10]



Scheme 1. Synthesis of arylbromide ***7***. ([a]Yield over two steps.)

Several tertiary amines were synthesized within one or two steps with aryl halides and anilines (Scheme 2), whereas the methoxy-residues were kept consistent as directed metalation group (DMG). Buchwald-Hartwig amination reactions allowed a high-yielding synthesis of secondary and tertiary amines by using $Pd_2(dba)_3$ with appropriate ligands (1,1′-bis(diphenyl-phosphino)ferrocene (dppf) for secondary amines and 2-dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl (RuPhos) for tertiary amines). Moreover, double amination gave direct access to the tertiary amine ***1a*** and ***1c*** in 84% and 47% yield, respectively. Alternatively, the secondary amine intermediates were either methylated with iodomethane in the presence of sodium hydride (***1d***, 81 % yield) or arylated to provide triarylamine ***1b*** in 98 % yield.



Scheme 2. Synthesis of various acridinium backbones ***1a-d***.

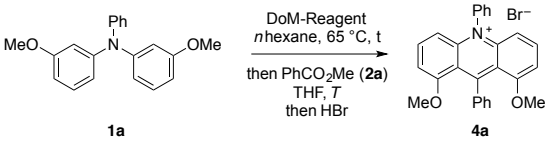
With the tertiary amine precurscors ***1a-d*** in hand, the reagent synthesis by a double directed *ortho*-metalation and the subsequent addition to carboxylic acid esters was investigated.

2.2. Synthesis of 1,5-Bifunctional Organolithium Reagents by a Double Directed ortho-Metalation

Owing to the expeditious one-step synthesis of amine ***1a***, the optimization parameters of the double directed *ortho*-metalation were investigated by the transformation of methyl benzoate (***2a***) into acridinium salt ***4a*** (Table 1).

Mainly the time for the directed *ortho*-metalation and the temperature for the direct ester transformation were found crucial and were examined in detail. As no metalation was observed at room temperature, the double directed *ortho*-metalation was performed at 65 °C throughout the optimization experiments. Furthermore, the reaction work-up by treatment with aq. HBr was kept consistent to uniformly form the corresponding acridinium bromide salt. Initially, three hours of metalation, followed by the addition of methyl benzoate at –20 °C and subsequent reaction at 65 °C over 12 hours followed by aq. HBr treatment led to the formation of 28% acridinium salt ***4a*** (Table 1, entry 1). An attempt to transmetalate lithium to magnesium under the same conditions to attenuate the reactivity of the 1,5-bifunctional organometallic reagent did not improve the yield (entry 2). However, by extending the metalation period to 6 hours and allowing the ester to react at either 65 °C or room temperature resulted in an increased product formation (40% and 43% yield, entries 3 & 4). Addition of Et_2O (~9 v/v %), to activate *n* BuLi to promote the lithiation[11] did not significantly change the reactivity (entry 5). Extending the metalation to 12 hours decreased product formation (32%, entry 6) and by an alternative lithiation with TMPLi (lithium tetramethylpiperidide) with or without transmetalation using a $MgCl_2$·LiCl solution, the formation of acridinium bromide salt ***4a*** was not observed.[12]

Table 1. Optimization of the double directed *ortho*-metalation (D*o*M) and *in situ* addition of carboxylic acid esters (***2***).[13]



Entry	DoM-Reagent	t	*T*	Isolated Yield
1	*n*BuLi	3 h	65 °C	28%
2	*n*BuLi[a]	3 h	65 °C	25%
3	*n*BuLi	6 h	65 °C	40%
4	*n*BuLi	6 h	RT	**43%**
5	*n*BuLi, Et_2O[b]	6 h	RT	39%
6	*n*BuLi	12 h	65 °C	32%
7	TMPLi[c]	1 h	RT	-

[a]After D*o*M, mixture was treated with $MgCl_2$·LiCl solution (in THF, 0.50 $molL^{-1}$, 0.64 mL) and then ester ***2*** (100 µmol) in THF (0.60 mL) at –20 °C; [b]Metalation in *n*hexane (2.0 mL) and Et_2O (0.20 mL); [c]Metalation performed in THF (0.50 mL) at –40 °C, followed by addition of Ester ***1*** (100 µmol) in THF (0.60 mL) and warmed to RT.

2.3. Direct Synthesis of 1,8-substituted Acridinium Dyes

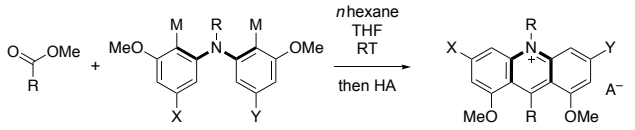
With the optimized conditions for the double directed *ortho*-metalation and ester to acridinium dye synthesis, we evaluated the dehydrative work-up with aqueous HBF_4 instead of hydrobromic acid, giving access to acridinium BF_4^- salt ***4a*** in similar yields (Table 2, entry 1). Furthermore, the scope of the double directed *ortho*-metalation and addition to methyl benzoate was studied with different tertiary amine precursors ***1a-d***. The presence of one or two NMe_2 moieties retards regioselective double lithiation. Nevertheless, acridinium dyes ***4b*** and ***4c*** could be synthesized in 26% and 35% yield, respectively (entry 2 & 3). By using amine ***1d*** and methyl benzoate, a higher efficiency in the transformation into acridinium bromide salt ***4d*** was observed (49% yield, entry 4). Whereas treatment of the reaction mixture with strong aqueous acids such as hydrobromic acid or HBF_4 promoted the elimination, treatment with ammonium chloride gave access to the intermediary 9,10-dihydroacridin-9-ol ***4e*** in 43%. The reactivity of the *N*-aryl-*N*-methylaniline ***1a*** was further investigated by varying the ester substrates. Both esters with an electron-withdrawing fluorine substituent (methyl 4-fluorobenzoate) or an electron-donating methoxy group (methyl *p*-anisate) yielded acridinium salts ***4f*** and ***4g*** in 41% and 39% respectively (entries 6 & 7). The sterically more demanding methyl 1-naphthoate was transformed into acridinium bromide salt ***4d*** in a yield of 57%.

2.4. Photophysical & Electrochemical Properties

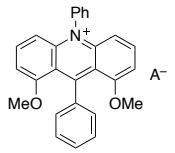
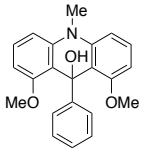
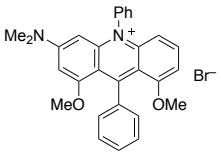
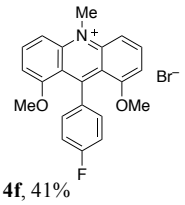
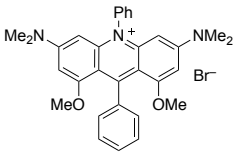
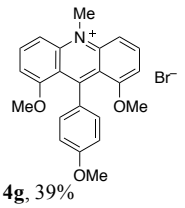
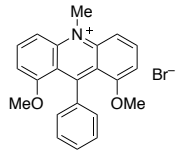
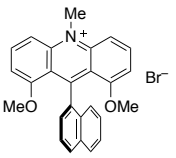
As the prepared acridinium salts ***4*** are characterized by an unusual substitution pattern, we studied the photophysical and electrochemical properties to assess their utility as fluorophores in imaging or photochemistry.

We therefore measured cyclic voltammetry and determined the absorption wavelength, molar attenuation coefficient, fluorescence emission wavelength and the fluorescent lifetime as well as the excitation energy $E_{0,0}$ to determine the reduction potential in the ground and excited state. In comparison to prototypical acridinium salts, both the absorption and emission of acridinium dyes ***4a-h*** are significantly red-shifted, exhibiting an average Stokes shift of larger than 70 nm (Table 3).

Table 2. Direct Transformation of Esters into 1,8-substituted acridinium dyes[a,b] and 9,10-dihydroacridin-9-ol.[c]



2 | **1a', R = Ph, X, Y = H**; **1b', R = Ph, X = H, Y = NMe_2**; **1c', R = Ph, X, Y = NMe_2**; **1d', R = Ph, X, Y = H** | **4a-h**

Entry	Product[d]	Entry	Product[d]
1	 **4a**, Br^-, 43%; BF_4^-, 44%[b]	5	 **4e**, 43%[c]
2	 **4b**, 26%	6	 **4f**, 41%
3	 **4c**, 35%	7	 **4g**, 39%
4	 **4d**, 49%	8	 **4h**, 57%

[a]Reactions performed with ***1*** (100 µmol) in THF (0.60 mL) and ***2a'-d'*** (M = Li; 160 µmol) for 12-14 h at RT followed by aqueous work-up (8.8 $molL^{-1}$, HBr); [b]Aqueous work-up using aq. HBF_4, 50%; [c]Aqueous work-up using aq. sat. NH_4Cl; [d]Yields of isolated products.

Table 3. Photophysical and Electrochemical Properties of Acridinium Dyes ***4a-4h***.

Entry	Compound	$\lambda_{abs,max}$[a]	ε_{max} [$L \cdot cm \cdot mol^{-1}$][a]	$\lambda_{em,max}$[a,b]	Stokes Shift	$E_{0,0}$[a]	$E_{1/2}(P/P^-)$[c]	$E_{1/2}(P^*/P^-)$[b]	$<\tau_F>$[a]
1	**4a-Br**$^-$	503 nm	$4.4 \cdot 10^3$	595 nm	92 nm	2.23 eV	–0.47 V	+1.76 V	3.1 ns
2	**4a-BF$_4^-$**	503 nm	$3.2 \cdot 10^3$	596 nm	93 nm	2.23 eV	–0.49 V	+1.74 V	3.4 ns
3	**4b**	501 nm	$8.6 \cdot 10^3$	584 nm	83 nm	2.25 eV	–0.94 V	+1.31 V	4.7 ns
4	**4c**	498 nm	$4.0 \cdot 10^4$	540 nm	42 nm	2.40 eV	–1.19 V	+1.21 V	4.4 ns
5	**4d**	497 nm	$4.4 \cdot 10^3$	576 nm	79 nm	2.33 eV	–0.52 V	+1.81 V	2.7 ns
6	**4f**	497 nm	$3.9 \cdot 10^3$	579 nm	82 nm	2.31 eV	–0.51 V	+1.80 V	3.0 ns
7	**4g**	494 nm	$4.5 \cdot 10^3$	567 nm	72 nm	2.30 eV	–0.62 V	+1.68 V	5.9 ns
8	**4h**	497 nm	$5.0 \cdot 10^3$	531 nm	34 nm	2.39 eV	–0.51 V	+1.88 V	4.1 ns

[a]from a 15 $\mu mol \cdot L^{-1}$ dye solution in acetonitrile. [b]Excited 10 nm below $\lambda_{max,abs}$. [c]Measured in dry, degassed 0.1 $mol \cdot L^{-1}$ *n* butylammonium hexafluorophosphate in acetonitrile against SCE.

All absorption spectra of ***4a-h***, except for $(NMe_2)_2$-acridinium dye ***4c,*** show two major signals corresponding to the absorption-signal of the arene and acridinium moiety. Similar to Fukuzumi's 9-mesityl-10-methylacridinium ($MesMeAcr^+$), the 1,8-substitution also promotes the perpendicular orientation of the two ring systems that limits their π-conjugation.[14] Furthermore, *N*-methyl to *N*-phenyl substitution was found not to influence the molar attenuation coefficient of ***4a*-Br$^-$**, ***4b***, ***4c*** and ***4d***. However, the higher the number of dimethylamino groups, the higher the coefficient. The reduction potential remains independent of the anion as well as the arene moiety, except for ***4g*** which is substituted by electron-rich anisole that decreases the ground-state reduction potential marginally. A higher number of dimethylamino groups at the acridinium of salts ***4b*** and ***4c*** furthermore decreases the reduction potential significantly, which is also reflected in the excited state reduction potential. Moreover, 1,8-dimethoxy substituted acridinium dyes possess excellent water solubility and fluorescence excited state lifetimes, which render these salts as promising photocatalysts.

3. Conclusion

A double directed *ortho*-metalation (dD*o*M) strategy giving access to reagents for the direct transformation of esters into 1,8-dimethoxy-acridinium salts with distinct photophysical and electrochemical properties is described. Starting from an identical tertiary amine motif, this method allows diverging from the substitution pattern obtained by electrophilic aromatic substitution reactions. Synthetic strategies that provide a means to modulate the properties of organic fluorophores would render organophotoredox catalysis more generally applicable and enable novel applications in imaging, sensing or materials science. Due to the unique photophysical and electrochemical properties and the excellent water-solubility, the products described in this article are part of a patent application.[15] Current studies on the application of the acridinium salts for photocatalysis will be reported in due course.

4. Experimental

4.1. Bis(3-methoxyphenyl)-amine Precursors Syntheses

4.1.1. 3-Bromo-5-methoxy-N,N-dimethylaniline (7)

Prepared according to modified literature procedures:[16a,b] To a solution of 1,3-dinitrobenzene (***5***) (20.2 g, 120 mmol) in conc. H_2SO_4 (95%, 0.24 L) at 85 °C was added *N*-bromosuccinimide (29.9 g, 168 mmol) portionwise over 1 h. The reaction was continued to stirr for 1 h at 85 °C, cooled and poured into ice water. The precipitate was filtered and washed with aq. sat. Na_2SO_3 and water to pH 7. The solid was dried in vacuo to give 1-bromo-3,5-dinitrobenzene as beige-yellow solid (27.3 g, 92%): R_f 0.60 (CH_2Cl_2 100%); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.00 (1H, t, ^4J 2.0, C4*H*), 8.71 (2H, d, ^4J 2.0, C2*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 148.9 (*C3*), 132.1 (*C2*), 123.9 (*C1*), 117.7 (*C4*). Analytical data is in agreement with literature.[16a]

To a solution of 1-bromo-3,5-dinitrobenzene (12.4 g, 50.0 mmol) in MeOH (0.50 L) was added sodium methoxide (21.6 g, 400 mmol) at RT and stirred 5 h at reflux. The mixture was adjusted to pH 6 with aq. HCl (1 molL^{-1}), filtered and the filtrate was concentrated in vacuo. The residue was filtered and washed with water to obtain 1-bromo-3-methoxy-5-nitrobenzene (***6***), which was directly used in the next step. R_f 0.83 (CH_2Cl_2 100%); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.96 (1H, t, ^4J 1.8, C6*H*), 7.68 (1H, t, ^4J 2.2, C2*H*), 7.37 (1H, dd, ^4J 2.1, 1.8, C4*H*), 3.89 (3H, s, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 160.6 (*C3*), 149.5 (*C5*), 123.9 (*C2*), 123.0 (*C1*), 107.8 (*C4*), 56.2 (O*C*H$_3$). Analytical data is in agreement with literature.[17a]

To a solution of 1-bromo-3-methoxy-5-nitrobenzene (***6***) (50.0 mmol) in MeOH:H_2O (1:1, 150 mL) was added carbonyl iron (250 mmol, 14.0 g) and ammonium chloride (21.4 g, 400 mmol) at RT and mixture was stirred at 95 °C for 2 h. The mixture was cooled to RT, adjusted to pH 8 with aq. sat. Na_2CO_3 and filtered over celite® (particle size 0.02-0.1 mm). The filtrate was concentrated in vacuo, aqueous residue diluted with H_2O (200 mL) and extracted with EtOAc (3 x 250 mL). The combined organic layer was dried over Na_2SO_4, concentrated and dried in vacuo to give 3-bromo-5-methoxyaniline as a dark solid (7.98 g, 79% over two steps). R_f 0.47 (CH_2Cl_2 100%); ^{1}H NMR (500 MHz, $CDCl_3$) δ= 6.46 (1H, t, ^4J 1.9), 6.44 (1H, t, ^4J 1.8) 6.13 (1H, t, ^4J 2.1), 3.74 (3H, s, OCH_3), 3.70 (2H, br, NH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 161.3 (*C5*), 148.6 (*C3*), 123.3 (*C1*), 110.9 (*C2*), 107.3 (*C6*), 99.9 (*C4*), 55.3 (O*C*H$_3$); Analytical data is in agreement with literature.[16c]

To a mixture of aq. formaldehyde (37 wt%, 4.47 mL, 60.0 mmol) in THF (15 mL) and aq. H_2SO_4 (3.0 molL^{-1}, 4.00 mL) in an open flask was added via dropping funnel a suspension of 3-bromo-5-methoxyaniline (3.03 g, 15.0 mmol) and $NaBH_4$ (1.70 g, 45.0 mmol) in THF (15 mL) over 1 h at 15 °C ±5 °C (inside temperature). After 30 min of stirring, pH 8 was adjusted with aq. sat. Na_2CO_3 and concentrated in vacuo. The residue was diluted with water (80 mL) extracted with CH_2Cl_2 (3 x 100 mL). The combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was suspended with CH_2Cl_2, filtered and the filtrate was concentrated in vacuo to give 3-bromo-5-methoxy-*N*,*N*-dimethylaniline (***7***) as an orange oil (1.81 g, 52%): R_f 0.81 (CH_2Cl_2 100%); ν_{max} (neat): 2935m, 2358w, 1604s, 1557s, 1495m, 1431m, 1358w, 1319w, 1276w, 1238m, 1149m, 1060m, 996m, 875w, 812w, 788m, 675w; ^{1}H NMR (500 MHz, $CDCl_3$) δ= 6.47 (1H, dd, ^4J 2.2, 1.7, C2*H*); 6.42 (1H, dd, ^4J 2.0, 1.7, C6*H*), 6.13 (1H, t, ^4J 2.2, C4*H*), 3.77 (3H, s, OCH_3), 2.92 (6H, s, N(CH_3)$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 161.1 (*C5*), 152.3 (*C3*), 123.5 (*C1*), 108.6 (*C2*), 104.7 (*C6*), 97.7 (*C4*), 55.4 (O*C*H$_3$), 40.4 (N(*C*H$_3$)$_2$); ESI-MS: m/z calcd. for $C_9H_{13}NO^+$ 230.0175 found 230.0173 [M+H$^+$].

4.1.2. 3-methoxy-N-(3-methoxyphenyl)-N-phenylaniline (1a)

To a degassed mixture of $Pd_2(dba)_3$ (91.6 mg, 100 µmol), RuPhos (95%, 98.2 mg, 200 µmol) and sodium *t* butoxide (1.15 g, 12.0 mmol) in PhMe (20 mL) was added 3-iodoanisole (***9***) (1.00 mL, 8.40 mmol) and aniline (***8***) (0.365 mL, 4.00 mmol). The mixture was stirred at 100 °C for 14 h, then cooled to RT, diluted with water and extracted with CH_2Cl_2 (3 x 250 mL). The combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. Column chromatography over silica gel with eluent pentane:CH_2Cl_2 4:1 to 1:1 gave 3-methoxy-*N*-(3-methoxyphenyl)-*N*-phenylaniline (***1a***) as a brownish oil (1.02 g, 84%): R_f 0.53 (CH_2Cl_2 100%); ν_{max} (neat): 3391w, 3001w, 2954w, 2834w, 2339w, 1582s, 1484s, 1314m, 1273m, 1206s, 1158m, 1140m, 1043m, 982w, 849m, 766m, 747m, 690s; ^{1}H NMR (500 MHz, $CDCl_3$) δ= 7.22–7.26 (2H, m, C3*H*), 7.12–7.15 (2H, m, C5*H*), 7.09–7.11 (2H, m, C2'*H*), 6.99–7.03 (1H, m, C4'*H*), 6.66 (2H, ddd, ^3J 8.0, ^4J 2.1, 0.9, C6*H*), 6.63–6.64 (2H, m, C2*H*), 6.56 (2H, ddd, ^3J 8.2, ^4J 2.5, 0.8, C4*H*), 3.71 (6H, s, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 160.4 (*C3*), 149.0 (*C1*), 147.6 (*C1'*), 129.8 (*C5*), 129.2 (C3'), 124.7 (*C4'*), 123.0 (*C2'*), 116.7 (*C6*), 110.0 (*C2*), 108.2 (*C4*), 55.3 (O*C*H$_3$); ESI-MS: m/z calcd. for $C_{20}H_{20}NO_2^+$ 306.1489 found 306.1486 [M+H$^+$].

4.1.3. 5-Methoxy-N^1-(3-methoxyphenyl)-N^3,N^3-dimethyl-N^1-phenylbenzene-1,3-diamine (1b)

To a degassed mixture of tris(dibenzylideneacetone)dipalladium (19.5 mg, 21.3 µmol), 1,1'-bis(diphenylphosphino)ferrocene

(23.6 mg, 42.5 µmol) and sodium *t*butoxide (123 mg, 1.28 mmol) was added 3-bromo-5-methoxy-*N*,*N*-dimethylaniline (***7***) (196 mg, 0.850 mmol) in PhMe (1.1 mL) and aniline (***8***) (77.6 µL, 0.850 mmol) at RT and stirred 12 h at 100 °C. The mixture was diluted with H_2O (8.5 mL) and extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. Column chromatography on silica gel with pentane:CH_2Cl_2 2:1 to 1:1 gave 3-bromo-5-methoxy-*N*-phenylaniline as yellow oil (182 mg, 88%): R_f 0.25 (CH_2Cl_2 100%); ν_{max} (neat): 3381w, 2934w, 1583s, 1495m, 1305w, 1243w, 1155m, 1065w, 891w, 754m, 631s; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.24–7.27 (2H, m, C3'*H*), 7.08–7.10 (2H, m, C2H, C6*H*), 6.89–6.92 (1H, m, C4'*H*), 6.08–6.09 (1H, m, C6*H*), 6.06–6.07 (1H, m, C2*H*), 5.91–5.92 (1H, m, C4*H*), 5.66 (1H, br, N*H*), 3.76 (3H, s, OCH_3), 2.91 (6H, s, N(CH_3)$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 161.5 (*C5*), 152.6 (*C3*), 144.8 (*C1*), 143.3 (*C1'*), 129.3 (*C2'*), 120.8 (*C4'*), 118.1 (*C3'*), 95.5 (*C2*), 92.6 (*C4*), 92.5 (*C6*), 55.2 (OCH_3), 40.6 (N(CH_3)$_2$); ESI-MS: m/z calcd. for $C_{15}H_{19}N_2O^+$ 243.1492 found 243.1490 [M+H$^+$].

To a degassed mixture of $Pd_2(dba)_3$ (16.8 mg, 18.3 µmol), RuPhos (95%, 17.9 mg 36.5 µmol) and sodium *t*butoxide (106 mg, 1.10 mmol) was added 3-bromo-5-methoxy-*N*-phenylaniline (177 mg, 0.730 mmol) in PhMe (1.4 mL) and 3-iodoanisole (***9***) (87.2 µL, 0.730 mmol). The mixture was stirred at 100 °C for 14 h, then cooled to RT, diluted with water and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. Column chromatography over silica gel with eluent pentane:CH_2Cl_2 2:1 to 1:1 to 1:2 gave a brownish oil 5-methoxy-*N*^{1}-(3-methoxyphenyl)-*N*^{3},*N*^{3}-dimethyl-*N*^{1}-phenylbenzene-1,3-diamine (***1b***) (250 mg, 98%): R_f 0.58 (CH_2Cl_2 100%); ν_{max} (neat): 2934w, 1588s, 1489m, 1315w, 1304w, 1270m, 1244m, 1206m, 1165m, 1146m, 1064w, 813w, 697m; ^{1}H NMR (500 MHz, $CDCl_3$) δ= 7.21–7.24 (2H, m, C2"*H*, C4"*H*), 7.10–7.13 (3H, m, C5'*H*, C1"*H*, C6"*H*), 6.96–6.99 (1H, m, C3"*H*), 6.67–6.69 (1H, m, C6'*H*), 6.65–6.66 (1H, m, C2'*H*), 6.52–6.54 (1H, m, C4'*H*), 6.10–6.11 (1H, m, C2*H*), 6.03–6.04 (1H, m, C6*H*), 5.99–6.00 (1H, m, C4*H*), 3.71 (3H, s, C3'OCH_3), 3.69 (3H, s, C5OCH_3), 2.84 (6H, s, N(CH_3)$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 161.2 (C3'), 160.3 (C5), 152.2 (C3), 149.3 (C1), 149.2 (C1'), 147.8 (C1"), 129.5 (C5'), 129.0 (C3", C5") 124.3 (C2", C6"), 122.5 (C4"), 116.4 (C6'), 109.5 (C2'), 107.7 (C4'), 102.9 (C2), 99.3 (C6), 94.5 (C4), 55.2 (OCH_3), 55.2 (OCH_3), 40.6 (N(CH_3)$_2$); ESI-MS: m/z calcd. for $C_{22}H_{25}N_2O_2^+$ 349.1911 found 349.1909 [M+H$^+$].

*4.1.4. N^1-(3-(dimethylamino)-5-methoxyphenyl)-5-methoxy-N^3,N^3-dimethyl-N^1-phenylbenzene-1,3-diamine (**1c**)*

To a degassed mixture of 3-bromo-5-methoxy-*N*,*N*-dimethylaniline (***7***) (920 mg, 4.00 mmol), RuPhos (95%, 98.2 mg, 200 µmol), $Pd_2(dba)_3$ (91.6 mg, 100 µmol) and sodium *t*butoxide (577 mg, 6.00 mmol) in PhMe (10 mL) at RT was added aniline (***8***) (183 µL, 2.00 mmol). The mixture was stirred at 100 °C for 12 h, then cooled to RT, diluted with water and extracted with CH_2Cl_2 (3 x 150 mL). The combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. Column chromatography over silica gel with eluent pentane:CH_2Cl_2 3:1 to 1:1 to 100% CH_2Cl_2 gave *N*^{1}-(3-(dimethylamino)-5-methoxyphenyl)-5-methoxy-*N*^{3},*N*^{3}-dimethyl-*N*^{1}-phenylbenzene-1,3-diamine (1***c***) (365 mg, 47%,[18] m.p. 118.8-120.6 °C) as a beige solid: R_f 0.53 (pentane:CH_2Cl_2 1:1); ν_{max} (neat): 2934w, 2339w, 1578s, 1491m, 1447m, 1297w, 1269m, 1242w, 1202w, 1173w, 1146m, 1066m, 765m, 712m, 630m; ^{1}H NMR (500 MHz, $CDCl_3$) δ= 7.18–7.22 (2H, m, C3'*H*), 7.11–7.13 (2H, m, C2'*H*), 6.93–6.97 (1H, m, C4'*H*), 6.14 (2H, t, ^4J 2.0, C2*H*), 6.06 (2H, t, ^4J 2.0, C6*H*), 5.97 (2H, t, ^4J 1.9, C4*H*), 3.69 (6H, s, 2 x OCH_3), 2.84 (12H, s, 2 x N(CH_3)$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 161.1 (C5), 152.1 (C3), 149.4 (C1), 148.0 (C1'), 128.8 (C3'), 124.2 (C2'), 122.1 (C4'), 102.6 (C2), 98.9 (C6), 94.2 (C4), 55.2 (OCH_3), 40.7 (2 x N(CH_3)$_2$); ESI-MS: m/z calcd. for $C_{24}H_{30}N_3O_2^+$ 392.2333 found 392.2330 [M+H$^+$].

*4.1.5. 3-Methoxy-N-(3-methoxyphenyl)-N-methylaniline (**1d**)*

Prepared according to modified literature procedures:[19] To a degassed mixture of tris(dibenzylideneacetone)dipalladium(0) (458 mg, 0.500 mmol), 1,1'-bis(diphenyl-phosphino)ferrocene (554 mg, 1.00 mmol) and sodium *t* butoxide (2.88 g, 30.0 mmol) in PhMe (25 mL) was added 3-iodoanisole (***9***) (2.38 mL, 20.0 mmol) and *m*-anisidine (***10***) (2.24 mL, 20.0 mmol) at RT and stirred 14 h at 110 °C. The mixture was diluted with H_2O (200 mL) and extracted with CH_2Cl_2 (3 x 250 mL). The combined organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. Column chromatography on silica gel with pentane:CH_2Cl_2 1:1 to 1:2 gave bis(3-methoxyphenyl)amine as yellow oil (3.60 g, 79%): R_f 0.53 (CH_2Cl_2 100%); ν_{max} (neat): 3389w, 2955w, 2836w, 2359w, 1593s, 1492m, 1273w, 1209m, 1158m, 1045w, 968w, 835w, 765w, 687w; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.17 (2H, t, ^3J 8.1, C5*H*), 6.67 (2H, ddd, ^3J 8.1, ^4J 2.2, 0.9, C6*H*), 6.65–6.66 (2H, m, C2*H*), 6.49 (2H, ddd, ^3J 8.2, ^4J 2.4, 0.9, C4*H*), 5.71 (1H, br, N*H*), 3.78 (6H, s, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 160.7 (*C3*), 144.3 (*C1*), 130.1 (*C5*), 110.6 (*C6*), 106.5 (*C4*), 103.8 (*C2*), 55.2 (OCH_3); ESI-MS: m/z calcd. for $C_{14}H_{16}NO_2^+$ 230.1176 found 230.1175 [M+H$^+$].

To a solution of bis(3-methoxyphenyl)amine (1.15 g, 5.00 mmol) in THF (20 mL) at RT was added sodium hydride (60% dispersion in mineral oil, 550 mg, 13.8 mmol). The suspension was heated to 75 °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_2O (3 x 65 mL). The combined organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. Column chromatography on silica gel with pentane:CH_2Cl_2 3:1 to 1:1 gave 3-methoxy-*N*-(3-methoxyphenyl)-*N*-methylaniline (***1d***) as a yellowish oil (979 mg, 81%): R_f 0.64 (CH_2Cl_2 100%); ν_{max} (neat): 2938w, 2834w, 2338w, 1589s, 1489s, 1347w, 1279w, 1221m, 1169w, 1122w, 1046w, 766s, 708w, 631s; ^{1}H NMR (500 MHz, $CDCl_3$) δ= 7.15–7.19 (2H, m, C5*H*), 6.62 (2H, ddd, ^3J 8.1, ^4J 2.2, 0.8, C6*H*), 6.57–6.58 (2H, m, C2*H*), 6.52 (2H, ddd, ^3J 8.2, ^4J 2.5, 0.8, C4*H*), 3.76 (6H, s, OCH_3), 3.29 (3H, s, NCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 160.5 *(C3)*, 150.2 (*C1*), 129.8 (*C5*), 113.3 (*C6*), 106.7 (*C4*), 106.6 (*C2*), 55.2 (OCH_3), 40.3 (NCH_3); ESI-MS: m/z calcd. for $C_{15}H_{18}NO_2^+$ 244.1332 found 244.1330 [M+H$^+$].

4.2. General Procedure A: Double directed ortho-Metalation

To a solution of bis(3-methoxyphenyl)-amine ***1a-d*** (160 µmol) in *n* hexane (2.0 mL) was added a solution of *n* butyllithium in hexanes (176 µL, 1.49 molL^{-1}, 320 µmol) at RT. The mixture was stirred 6 h at 65 °C. The reaction mixture was directly used in the next step.

4.3. General Procedure B: Ester to Acridinium Transformation

To the reaction mixture of the metalated aryl aniline ***1a'-d'*** in *n*hexane (160 µmol) at –20 °C was added a solution of carboxylic acid ester (***1***) (100 µmol) in anhydrous THF (0.60 mL) and the reaction mixture was allowed to warm to RT over 12 h or 14 h (indicated individually). Aqueous HBr (1.00 mL, 48%) was added, followed by water (20 mL) and the mixture was

extracted by $CHCl_3$:*i*PrOH solution (4 x 10 mL; 85:15). The combined organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. Column chromatography with 100% CH_2Cl_2 to CH_2Cl_2:MeOH 100:2 to 100:5 to 100:8 to 100:9 gave the product.

4.4. Synthesis of Acridinium Dyes and 9,10-Dihydroacridin-9-ols

*4.4.1. 1,8-Dimethoxy-9,10-diphenylacridinium bromide salt (**4a-Br**$^-$)*

The compound was prepared according to the general procedure A and B using 3-methoxy-*N*-(3-methoxyphenyl)-*N*-phenylaniline (***1a***) (48.9 mg, 160 µmol) and methyl benzoate (13.6 mg, 100 µmol) and was stirred 12 h at RT. Purification gave a brown red solid (20.1 mg, 43%, HPLC purity: 95.2%;[19] decomp. at 115 °C): R_f 0.19 (CH_2Cl_2:MeOH 10:1); ν_{max} (neat): 2999w, 1586s, 1462s, 1363m, 1265s, 1248s, 1198w, 1082s, 982w, 925w, 811m, 758s, 738s, 696s, 655m; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.02 (2H, t, ^3J 8.4, C3*H*, C6*H*), 7.89–7.91 (2H, m, C3"*H*, C5"*H*), 7.83–7.86 (1H, m, C4"*H*), 7.64–7.66 (2H, m, C2"*H*, C6"*H*), 7.44–7.50 (3H, m, C3'*H*, C4'*H*, C5'*H*), 7.33–7.34 (2H, m, C2'*H*, C6'*H*), 7.03 (2H, d, ^3J 7.9, C2*H*, C7*H*), 6.92 (2H, dd, ^3J 8.9, ^4J 0.6, C4*H*, C5*H*), 3.52 (6H, s, 2 x OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.3 (*C9*), 160.2 (*C1*, *C8*), 142.8 (*C4a*, *C10a*), 141.3 (*C1'*), 140.4 (*C3*, *C6*), 138.4 (*C1"*), 131.8 (*C3"*, *C5"*), 131.6 (*C4"*), 127.9 (*C2"*, *C6"*), 127.2 (*C4'*), 126.9 (*C3'*, *C5'*), 125.7 (*C2'*, *C6'*), 119.1 (*C8a*, *C9a*), 110.9 (*C4*, *C5*), 107.1 (*C2*, *C7*), 56.9 (2 x OCH_3); ESI-MS: m/z calcd. for $C_{27}H_{22}NO_2^+$ 392.1645 found 392.1648 [M$^+$]. Luminescence spectroscopy (in MeCN): λ_{abs1}: 503 nm; λ_{abs2}: 409 nm; ε_{abs1}: $4.4\cdot10^3$ L·cm·mol^{-1}; ε_{abs2}: $5.8\cdot10^3$ L·cm·mol^{-1}, λ_{em}(exc 493): 595 nm; λ_{em}(exc 399): 591 nm; Stokes shift: 92 nm; $E_{0,0}$: 2.23 eV; $<\tau_F>$: 3.1 ns; Cyclic voltammetry (vs SCE): $E_{1/2}(P^*/P^-)$: +1.76 V, $E_{1/2}(P/P^-)$: –0.47 V.

*4.4.2. 1,8-Dimethoxy-9,10-diphenylacridinium tetrafluoroborate salt (**4a-BF**$_4^-$)*

The compound was prepared according to the general procedure A and B using 3-methoxy-*N*-(3-methoxyphenyl)-*N*-phenylaniline (***1a***) (48.9 mg, 160 µmol) and methyl benzoate (13.6 mg, 100 µmol) and was stirred 12 h at RT and treated with aq. HBF_4 (50%, 1.00 mL) instead of aq. HBr. Purification gave a brown red solid (21.3 mg, 44%, HPLC purity: 97.2%; decomp. at 140 °C): R_f 0.28 (CH_2Cl_2:MeOH 10:1); ν_{max} (neat): 3060w, 2938w, 1581m, 1501m, 1464m, 1434m, 1362m, 1266s, 1198w, 1048s, 910w, 819w, 748s, 698m; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.94 (2H, dd, ^3J 8.9, 8.1, C3*H*, C6*H*), 7.82–7.88 (3H, m, C3"*H*, C4"*H*, C5"*H*), 7.55–7.56 (2H, m, C2"*H*, C6"*H*), 7.42–7.48 (3H, m, C3'*H*, C4'*H*, C5'*H*), 7.31–7.33 (2H, m, C2'*H*, C6'*H*), 6.98 (2H, d, ^3J 8.0, C2*H*, C7*H*), 6.89 (2H, d, ^3J 9.0, C4*H*, C5*H*), 3.49 (6H, s, 2 x OCH_3); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 163.4 (*C9*), 160.2 (*C1*, *C8*), 142.7 (*C4a*, *C10a*), 141.4 (*C1'*), 140.9 (*C3*, *C6*), 138.4 (*C1"*), 131.7 (*C3"*, *C5"*), 131.5 (*C4"*), 127.8 (*C2"*, *C6"*), 127.1 (*C4'*), 126.9 (*C3'*, *C5'*), 125.6 (*C2'*, *C6'*), 119.1 (*C8a*, *C9a*), 110.8 (*C4*, *C5*), 106.9 (*C2*, *C7*), 56.7 (2 x OCH_3); ^{19}F NMR (235 MHz, $CDCl_3$): –154.5; ESI-MS: m/z calcd. for $C_{27}H_{22}NO_2^+$ 392.1645 found 392.1649 [M$^+$]. Luminescence spectroscopy (in MeCN): λ_{abs1}: 503 nm; λ_{abs2}: 409 nm; ε_{abs1}: $3.2\cdot10^3$ L·cm·mol^{-1}; ε_{abs2}: $4.2\cdot10^3$ L·cm·mol^{-1}, λ_{em}(exc 493): 596 nm; λ_{em}(exc 399): 592 nm; Stokes shift: 93 nm; $E_{0,0}$: 2.23 eV; $<\tau_F>$: 3.4 ns; Cyclic voltammetry (vs SCE): $E_{1/2}(P^*/P^-)$: +1.74 V, $E_{1/2}(P/P^-)$: –0.49 V.

*4.4.3. 3-(Dimethylamino)-1,8-dimethoxy-9,10-diphenylacridinium bromide salt (**4b**)*

The compound was prepared according to the general procedure A and B using 5-methoxy-N^1-(3-methoxyphenyl)-N^3,N^3-dimethyl-N^1-phenylbenzene-1,3-diamine (***1b***) (55.8 mg, 160 µmol) and methyl benzoate (13.6 mg, 100 µmol) and was stirred 14 h at RT. Purification gave a brown red solid (13.6 mg, 26%, HPLC purity: 94.7%;[19] decomp. at 117 °C): R_f 0.18 (CH_2Cl_2:MeOH 10:1); ν_{max} (neat): 3387w, 2926m, 2361m, 2178w, 1623s, 1597s, 1501s, 1428s, 1373m, 1349m, 1295m, 1255s, 1182m, 1096s, 973m, 921m, 806w, 771m, 723s, 697s, 652w; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.84–7.87 (2H, m, C3"H, C5"H), 7.76–7.79 (1H, m, C4"H), 7.58 (1H, dd, ^3J 8.6, 8.3, C6H), 7.38–7.43 (5H, m, C3'H, C4'H, C5'H, C2"H, C6"H), 7.20 (2H, dd, ^3J 7.5, ^4J 1.3, C2'H, C6'H), 6.71 (1H, d, ^3J 8.0, C7H), 6.51 (1H, d, ^3J 8.6, C5H), 6.41 (1H, d, ^4J 1.1, C2*H*), 5.42 (1H, d, ^4J 1.1, C4H), 3.52 (3H, s, OCH_3), 3.38 (3H, s, OCH_3), 3.19 (6H, br, N(CH_3)$_2$); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.3 (*C1*), 160.0 (*C8*), 157.3 (*C3*), 156.1 (*C9*), 145.4 (*C4a*), 142.0 (*C10a*), 141.6 (*C1'*), 138.7 (*C1"*), 136.2 (*C6*), 132.0 (*C3"*, *C5"*), 131.0 (*C4"*), 128.0 (*C2"*, *C6"*), 126.8 (*C3'*, *C5'*), 126.7 (*C4'*), 125.9 (*C2'*, *C6'*), 115.5 (*C9a*), 114.7 (*C8a*), 109.6 (*C5*), 105.7 (*C7*), 95.8 (*C2*), 89.1 (*C4*), 57.0 (C1OCH_3), 56.3 (C8OCH_3), 41.3 (N(*C*H_3)$_2$); ESI-MS: m/z calcd. for $C_{29}H_{27}N_2O_2^+$ 435.2067 found 435.2073 [M$^+$]. Luminescence spectroscopy (in MeCN): λ_{abs1}: 501 nm; λ_{abs2}: 430 nm; ε_{abs1}: $8.6\cdot10^3$ L·cm·mol^{-1}; ε_{abs2}: $1.6\cdot10^4$ L·cm·mol^{-1}, λ_{em}(exc 491): 584 nm; λ_{em}(exc 420): 589 nm; Stokes shift: 83 nm; $E_{0,0}$: 2.25 eV; $<\tau_F>$: 4.7 ns; Cyclic voltammetry (vs SCE): $E_{1/2}(P^*/P^-)$: +1.31 V, $E_{1/2}(P/P^-)$: –0.94 V.

*4.4.4. 3,6-Bis(dimethylamino)-1,8-dimethoxy-9,10-diphenylacridinium bromide salt (**4c**)*

The compound was prepared according to the general procedure A and B using N^1-(3-(dimethylamino)-5-methoxyphenyl)-5-methoxy-N^3,N^3-dimethyl-N^1-phenylbenzene-1,3-diamine (***1c***) (62.6 mg, 160 µmol) in *n* hexane:Et_2O (2.2 mL, 10:1) and methyl benzoate (13.6 mg, 100 µmol) and was stirred 14 h at RT. Purification gave a brown red solid (19.7 mg, 35%, HPLC purity: 78.7%;[19] decomp. at 148 °C): R_f 0.17 (CH_2Cl_2:MeOH 10:1); ν_{max} (neat): 2925w, 2360w, 2166w, 1599s, 1490m, 1433w, 1333m, 1254s, 975w, 923w, 781m, 630w; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.82–7.85 (2H, m), 7.73–7.76 (1H, m), 7.38–7.40 (4H, m, C2'*H*, C6'*H*, C2"*H*, C6"*H*), 7.33–7.36 (1H, m), 7.17–7.18 (2H, m), 6.07 (2H, d, ^4J 1.9, C2*H*, C7*H*), 5.36 (2H, d, ^4J 1.8, C4*H*, C5*H*), 3.38 (6H, s, 2 x OCH_3), 3.00 (12H, s, 2 x N(CH_3)$_2$); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.3 (C1, C8), 155.4 (C3, C6), 154.6, 144.9 (C4a, C5a), 142.2 (C9), 139.2, 131.9, 130.6, 128.1, 126.7, 126.3, 126.0, 109.8 (C8a, C9a), 93.3 (C2, C7), 89.5 (C4, C5), 56.1 (OCH_3), 40.3 (N(*C*H_3)$_2$); ESI-MS: m/z calcd. for $C_{31}H_{32}N_3O_2^+$ 478.2489 found 478.2495 [M$^+$]. Luminescence spectroscopy (in MeCN): λ_{abs}: 498 nm; ε_{abs}: $4.0\cdot10^4$ L·cm·mol^{-1}; λ_{em}(exc 488): 540 nm; Stokes shift: 42 nm; $E_{0,0}$: 2.40 eV; $<\tau_F>$: 4.4 ns; Cyclic voltammetry (vs SCE): $E_{1/2}(P^*/P^-)$: +1.21 V, $E_{1/2}(P/P^-)$: –1.19 V.

*4.4.1. 1,8-Dimethoxy-10-methyl-9-phenylacridinium bromide salt (**4d**)*

The compound was prepared according to the general procedure A and B using 3-methoxy-*N*-(3-methoxyphenyl)-*N*-methylaniline (***1d***) (38.9 mg, 160 µmol) and methyl benzoate (13.6 mg, 100 µmol) and was stirred 12 h at RT. Purification gave a brown red solid (19.9 mg, 49%, HPLC purity: 98.6%; decomp. at 150 °C): R_f 0.12 (CH_2Cl_2:MeOH 10:1); ν_{max} (neat): 3411w, 1606m, 1504m, 1465m, 1345m, 1260s, 1168m, 1072m, 926w, 816m, 729s, 699s, 632m; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.24–8.28 (2H, m, C4*H*, C5*H*), 8.26–8.30 (2H, m, C3*H*, C6*H*), 7.42–7.46 (3H, m, C3'*H*, C4'*H*, C5'*H*), 7.15–7.17 (2H, m, C2'*H*, C6'*H*), 7.01 (2H, dd, ^3J 7.2, ^4J 1.2, C2*H*, C7*H*), 5.02 (3H, s, NCH_3), 3.48 (6H, s, 2 x OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.1 (*C9*), 160.1 (*C1*, *C8*), 142.3 (*C4a*, *C10a*), 141.4 (*C1'*), 140.8 (*C3*, *C6*), 127.1 (*C4'*), 126.8 (*C3'*, *C5'*), 125.6 (*C2'*, *C6'*), 119.1 (*C8a*, *C9a*), 110.2 (*C4*, *C5*), 106.8 (*C2*, *C7*), 56.6 (2 x OCH_3), 42.3 (NCH_3); ESI-MS: m/z calcd. for $C_{22}H_{20}NO_2^+$ 330.1489 found 330.1494 [M$^+$]. Luminescence spectroscopy (in MeCN): λ_{abs1}: 497 nm; λ_{abs2}: 403

nm; ε_{abs1}: $4.4 \cdot 10^3$ L·cm·mol^{-1}; ε_{abs2}: $6.7 \cdot 10^3$ L·cm·mol^{-1}, λ_{em}(exc 487): 576 nm; λ_{em}(exc 393): 586 nm; Stokes shift: 79 nm; $E_{0,0}$: 2.33 eV; $<\tau_F>$: 2.7 ns; Cyclic voltammetry (vs SCE): $E_{1/2}(P^*/P^-)$: +1.81 V, $E_{1/2}(P/P^-)$: –0.52 V.

*4.4.2. 1,8-Dimethoxy-10-methyl-9-phenyl-9,10-dihydroacridin-9-ol (**4e**)*

The compound was prepared according to the general procedure A using using 3-methoxy-*N*-(3-methoxyphenyl)-*N*-methylaniline (***1d***) (38.9 mg, 160 µmol). To the metalated aniline in *n*hexane (160 µmol) at –20 °C was added a solution of methyl benzoate (13.6 mg, 100 µmol) in anhydrous THF (0.60 mL) and the reaction mixture was allowed to warm to RT over 12 h. Aqueous saturated NH_4Cl (1.00 mL) was added, followed by water (20 mL) and the mixture was extracted by CH_2Cl_2 (4 x 10 mL). The combined organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. Recrystallization from hexane:toluene (7.0 mL, 5:3) gave a dark grey solid (19.9 mg, 43%, m.p. 171.5-173.9 °C): ν_{max} (neat): 3514w, 1596s, 1470s, 1374w, 1251m, 1171w, 1081s, 1020w, 908w, 773s, 725s, 631m; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33–7.35 (2H, m, C2'*H*, C6'*H*), 7.21 (2H, t, ^3J 8.3, C3*H*, C6*H*), 7.13–7.16 (2H, m, C3'*H*, C5'*H*), 7.01–7.04 (1H, C4'*H*), 6.70 (2H, dd, ^3J 8.4, ^4J 0.5, C4*H*, C5*H*), 6.44 (2H, dd, ^3J 8.2, ^4J 0.6, C2*H*, C7*H*), 5.17 (1H, s, O*H*), 3.53 (3H, s, NCH_3), 3.51 (6H, s, 2 x OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.3 (*C1*, *C8*), 150.8 (*C1'*), 139.4 (*C4a*, *C10a*), 128.8 (*C3*, *C6*), 126.1 (*C3'*, *C5'*), 125.9 (*C2'*, *C6'*), 125.0 (*C4'*), 117.0 (*C8a*, *C9a*), 106.4 (*C4*, *C5*), 105.0 (*C2*, *C7*), 72.6 (*C9*), 55.9 (2 x OCH$_3$), 35.2 (NCH$_3$). ESI-MS: m/z calcd. for $C_{22}H_{21}NNaO_3^+$ 370.1419 found 370.1418 [MNa^+].

*4.4.3. 9-(4-Fluorophenyl)-1,8-dimethoxy-10-methylacridinium bromide salt (**4f**)*

The compound was prepared according to the general procedure A and B using 3-methoxy-*N*-(3-methoxyphenyl)-*N*-methylaniline (***1d***) (38.9 mg, 160 µmol) and methyl 4-fluorobenzoate (15.4 mg, 100 µmol) and was stirred 12 h at RT. Purification gave a brown red solid (17.5 mg, 41%, HPLC purity: 96.1%; decomp. at 130 °C): R_f 0.13 (CH_2Cl_2:MeOH 10:1); ν_{max} (neat): 3379w, 1606m, 1579m, 1508s, 1462s, 1348m, 1259s, 1219m, 1167m, 1072m, 1025w, 919m, 833m, 816m, 770m, 723m,635s; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.27–8.29 (4H, m, C3*H*, C4*H*, C5*H*, C6*H*), 7.16–7.17 (4H, m, C2'*H*, C3'*H*, C5'*H*, C6'*H*), 7.04 (2H, dd, ^3J 5.9, ^4J 2.9, C2*H*, C7*H*), 5.03 (3H, s, NCH_3), 3.54 (6H, s, 2 x OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.0 ($^1J_{CF}$ 247 Hz, *C*F), 159.9 (*C9*), 159.8 (*C1*, *C8*), 142.3 (*C4a*, *C10a*), 140.8 (*C3*, *C6*), 137.3 ($^4J_{CF}$ 3.6 Hz, *C1'*), 127.6 ($^3J_{CF}$ 8.0 Hz, *C2'*, *C6'*), 119.2 (*C8a*, *C9a*), 114.0 ($^2J_{CF}$ 21.8 Hz, *C3'*, *C5'*), 110.5 (*C4*, *C5*), 106.9 (*C2*, *C7*), 56.7 (2 x OCH$_3$), 42.5 (NCH$_3$); ^{19}F NMR (235 MHz, $CDCl_3$): 114.7; ESI-MS: m/z calcd. for $C_{22}H_{19}FNO_2^+$ 348.1394 found 348.1397 [M^+]. Luminescence spectroscopy (in MeCN): λ_{abs1}: 497 nm; λ_{abs2}: 395 nm; ε_{abs1}: $3.9 \cdot 10^3$ L·cm·mol^{-1}; ε_{abs2}: $6.3 \cdot 10^3$ L·cm·mol^{-1}, λ_{em}(exc 487): 579 nm; λ_{em}(exc 385): 581 nm; Stokes shift: 82 nm; $E_{0,0}$: 2.31 eV; $<\tau_F>$: 3.0 ns; Cyclic voltammetry (vs SCE): $E_{1/2}(P^*/P^-)$: +1.80 V, $E_{1/2}(P/P^-)$: –0.51 V.

*4.4.4. 1,8-Dimethoxy-9-(4-methoxyphenyl)-10-methylacridinium bromide salt (**4g**)*

The compound was prepared according to the general procedure A and B using 3-methoxy-*N*-(3-methoxyphenyl)-*N*-methylaniline (***1d***) (38.9 mg, 160 µmol) and methyl 4-methoxybenzoate (16.6 mg, 100 µmol) and was stirred 12 h at RT. Purification gave a brown red solid (17.2 mg, 39%, HPLC purity: 96.3%; decomp. at 130 °C): R_f 0.15 (CH_2Cl_2:MeOH 10:1); ν_{max} (neat): 3375w, 2993w, 1606m, 1577m, 1509m, 1461m, 1346m, 1240s, 1165s, 1032m, 814m, 765s, 734w, 647m, 635w; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.22–8.28 (4H, m, C3*H*, C4*H*, C5*H*, C6*H*), 7.06–7.09 (2H, m, C2'*H*, C6'*H*), 7.02 (2H, dd, ^3J 7.6, ^4J 0.9, C2*H*, C7*H*), 6.98–7.00 (2H, m, C3'*H*, C5'*H*), 5.00 (3H, s, NCH_3), 3.93 (3H, s, OCH_3), 3.55 (6H, s, 2 x OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.6 (*C9*), 160.2 (*C1*, *C8*), 158.9 (*C4'*), 142.3 (*C4a*, *C10a*), 140.6 (*C3*, *C6*), 133.7 (*C1'*), 127.2 (*C2'*, *C6'*), 119.5 (*C8a*, *C9a*), 112.4 *C3'*, *C5'*), 110.1 (*C4*, *C5*), 106.8 (*C2*, *C7*), 56.8 (2 x OCH$_3$), 55.5 (OCH$_3$), 42.3 (NCH$_3$); ESI-MS: m/z calcd. for $C_{23}H_{22}NO_3^+$ 360.1594 found 360.1595 [M^+]. Luminescence spectroscopy (in MeCN): λ_{abs1}: 494 nm; λ_{abs2}: 399 nm; ε_{abs1}: $4.5 \cdot 10^3$ L·cm·mol^{-1}; ε_{abs2}: $7.0 \cdot 10^3$ L·cm·mol^{-1}, λ_{em}(exc 485): 567 nm; λ_{em}(exc 389): 569 nm; Stokes shift: 72 nm; $E_{0,0}$: 2.30 eV; $<\tau_F>$: 5.9 ns; Cyclic voltammetry (vs SCE): $E_{1/2}(P^*/P^-)$: +1.68 V, $E_{1/2}(P/P^-)$: –0.62 V.

*4.4.5. 1,8-Dimethoxy-10-methyl-9-(naphthalen-1-yl)acridinium bromide salt (**4h**)*

The compound was prepared according to the general procedure A and B using 3-methoxy-*N*-(3-methoxyphenyl)-*N*-methylaniline (***1d***) (38.9 mg, 160 µmol) and methyl 1-naphthoate (18.6 mg, 100 µmol) and was stirred 12 h at RT. Purification gave a brown red solid (26.0 mg, 57%, HPLC purity: 95.7%;[19] decomp. at 120 °C): R_f 0.01 (CH_2Cl_2:MeOH 10:1); ν_{max} (neat): 3462w, 3396w, 1608m, 1577m, 1503m, 1458s, 1348m, 1258s, 1161m, 1065s, 1015w, 950w, 800m, 762s, 647 w; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.36–8.38 (2H, m, C3*H*, C6*H*), 8.24–8.27 (2H, m, C4*H*, C5*H*), 7.97–7.98 (1H, m, C5'*H*), 7.91–7.93 (1H, m, C4'*H*), 7.49–7.52 (2H, m, C3'*H*, C6'*H*), 7.32 (1H, ddd, ^3J 8.2, 7.5, ^4J 1.2, C7'*H*), 7.19 (1H, dd, ^3J 8.2, ^4J 0.7, C8'*H*), 6.96 (1H, dd, ^3J 7.0, ^4J 1.0, C2'*H*), 6.88 (2H, d, ^3J 8.0, C2*H*, C7*H*), 5.14 (3H, s, NCH_3), 3.08 (6H, s, 2 x OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.2 (*C9*), 159.7 (*C1*, *C8*), 142.4 (*C4a*, *C10a*), 140.6 (*C4*, *C5*), 139.9 (*C4a'*), 132.1 (*C1'*), 131.9 (*C8a'*), 128.1 (*C5'*), 127.4 (*C4'*), 126.3 (*C7'*), 125.8 (*C3'*), 125.0 (*C8'*), 124.9 (*C6'*), 121.8 (*C2'*), 120.0 (*C8a*, *C9a*), 110.7 (*C3*, *C6*), 106.8 (*C2*, *C7*), 56.4 (2 x OCH$_3$), 42.5 (NCH$_3$); ESI-MS: m/z calcd. for $C_{26}H_{22}NO_2^+$ 380.1645 found 380.1648 [M^+]. Luminescence spectroscopy (in MeCN): $\boldsymbol{\lambda}_{abs1}$: 497 nm; $\boldsymbol{\lambda}_{abs2}$: 394 nm; $\boldsymbol{\varepsilon}_{abs1}$: $5.0 \cdot 10^3$ L·cm·mol^{-1}; $\boldsymbol{\varepsilon}_{abs2}$: $7.6 \cdot 10^3$ L·cm·mol^{-1}, $\boldsymbol{\lambda}_{em}$(exc 487): 531 nm; $\boldsymbol{\lambda}_{em}$(exc 384): 580 nm; Stokes shift: 34 nm; $E_{0,0}$: 2.39 eV; $<\boldsymbol{\tau}_F>$: 4.1 ns; Cyclic voltammetry (vs SCE): $E_{1/2}(P^*/P^-)$: +1.88 V, $E_{1/2}(P/P^-)$: –0.51 V.

Acknowledgments

We gratefully acknowledge the Swiss National Science Foundation (BSSGI0-155902/1), the University of Basel, the NCCR Molecular Systems Engineering for generous financial support and PD Dr. D. Häussinger for assistance with NMR spectroscopy. We thank Prof. O. S. Wenger, Prof. M. Mayor, Prof. E. C. Constable and Prof. C. E. Housecroft for the use of their equipment for acquiring photophysical and electrochemical data and Dr. C. Kerzig, Dr. X. Guo for helpful discussions.

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18. Alongside the desired product, mono-coupled 5-methoxy-N^1,N^1-dimethyl-N^3-phenylbenzene-1,3-diamine (129 mg, 27%) was isolated as a dark oil. Analytical data is in agreement with the intermediate of ***1b***.
19. Aliquote was additionally purified for analytical purposes by reversed phase semi-prep HPLC.