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Synthesis, Resolution, Configurational Stability and Properties of Cationic Functionalized [5]helicenes

Maya Marinova,^{†,‡} Simon Pascal,^{†,▽} Laure Guénée,[§] Céline Besnard,[§] Boris Shivachev,[∥] Kalina Kostova,[‡] Claudio Villani,[#] Roberta Franzini,[#] Vladimir Dimitrov,^{*‡} Jérôme Lacour^{*,†}

[†] Department of Organic Chemistry, University of Geneva, Quai Ernest Ansermet 30, CH-1211 Geneva 4, Switzerland.

[‡] Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev Str. 9, Sofia 1113, Bulgaria.

[§] Laboratory of Crystallography, University of Geneva, Quai Ernest Ansermet 24, CH-1211 Geneva 4, Switzerland.

Institute of Mineralogy and Crystallography "Acad. Ivan Kostov", Bulgarian Academy of Sciences, Acad. G. Bonchev Str. 107, Sofia 1113, Bulgaria.

[#] Dipartimento di Chimica e Tecnologie del Farmaco, Università "La Sapienza", 00185 Roma, Italy.

ABSTRACT: A straightforward approach to the synthesis of two different series of cationic [5]helicenes has been achieved including, in dioxa series, the possibility to introduce aromatic functional groups at the periphery of the helical structure. While photophysical study highlights that the introduction of aryl substituents at position 23 of the helical moieties has a negligible impact on the optical properties, styryl substituents allow a welcoming extension of the conjugation pathways. Finally, a redshift of the optical properties was evidenced upon introduction of nitrogen atoms in the helicene scaffold, leading to particularly good fluorescence efficiencies in the red domain for a helicenic dye. Detailed information on racemization kinetics was collected for the most stable species upon direct HPLC resolution or, when configurational lability was too high, through VT-HPLC analysis on chiral stationary phase (ΔG^{\ddagger} values ranging from 85.0 to 137.1 kJ.mol⁻¹ and above).



Cationic helicenes, compounds that bear structural analogy to both triarylcarbenium ions¹ and classical carbo or heterohelicenes,²⁻⁷ are strongly studied for their chemical and physical properties but also for their similarities to planar cationic triangulenes.⁸⁻¹² These compounds **1-6** (Figure 1),¹³ that exhibit the classical helical screw-shaped skeletons formed by *ortho*-fused aromatic rings, are chiral and can be separated as single M or P enantiomers (left and right-handedness) due to their high to very high configurational stabilities (ΔG^{\ddagger} 116.0 to 172.9 kJ/mol and 124.8 to >155 kJ/mol in [4] and [6]helicene series respectively).¹⁴⁻¹⁸ Not surprisingly, the barrier of racemization depends on size of the helical core (the larger the better) but also on the nature of the bridging heteroatoms and this property is, of course, not the only one being controlled by the dioxa,^{15, 19} azaoxa,^{17, 20} or diaza^{14, 16, 21} nature of the compounds.²² In fact, the modularity of the physical, electronic and chemical properties of these [4] and [6]helicenes^{16, 23-30} depends also on the heteroatoms and this has led to many applications from biology^{26, 31-} ³² to physics³³ but also in analytical sciences³⁴⁻³⁸ and in (chir)optical spectroscopy.³⁹⁻⁴⁰

Recently, late-stage regioselective functionalizations of compounds **3** and **6** have been achieved, extending further the possibility to address discrete properties in this series of compounds.^{16, 23, 26-28} However, only the most electron-rich



diaza skeletons can react under the electrophilic post-functionalization conditions.



Figure 1. Dioxa, azaoxa and diaza [4] and [6]helicenes 1-6.

Herein, to measure the effect of substituents on dioxa derivatives in particular but also, and importantly, to add to the cationic series many novel helical derivatives, care was taken to develop a modular (stepwise) approach to a series of cationic [5]helicenes (Figure 2). Previously, in the context of the preparation of new extended triangulenium ions, Laursen and collaborators reported the synthesis of four dioxa and diaza [5]helicene derivatives (Figure 2, a).¹² In another context, a series of cationic [5]derivatives was recently reported using a ring extension strategy starting from activated diaza [4]helicene **3** (Figure 2, b).²⁷ Here, starting by design with a pre-functionalized bromo-containing building block **7**, 17 new helicenes were prepared in the dioxa and diaza series predominantly, compounds **8** and **9** respectively. Azaoxa derivatives **10** were isolated in only minor quantities in one series although in a quantity sufficient for spectral characterization. The functional groups introduced by *Suzuki-Miyaura* cross-coupling reactions induce moderate but definite changes on the photophysical properties of the chromophores as demonstrated by absorption and fluorescence studies. Care was taken to attempt the enantiomeric separation of these moieties and determine the barriers of enantiomerization or racemization which were found to vary significantly (ΔG^{\ddagger} from 85.0 to 137.0 kJ/mol). Also, when possible, X-ray diffraction studies were performed to afford detailed structural information on the newly generated structures.





Figure 2. Synthesis of cationic [5]helicenes. The numbering of key helicene positions are indicated on compound 9.

RESULTS AND DISCUSSION

Synthesis. Access to the targeted [5]helicenes **8-10** was achieved by the making of a common synthetic intermediate, namely tetracyclic ketone **11** (Scheme 1). We used a modular route made of stepwise additions of aromatic subunits and controlled sequential ring closures, as summarized in Scheme 1.

The starting material, 6-bromo-2-methoxy-1-naphthaldehyde 7 (Figure 2), was obtained according to the literature.⁴¹ The reaction sequence follows strictly the procedure detailed for the synthesis of cationic [6]helicenes and it is hence detailed in the experimental section only (Scheme 5).¹⁶ Nevertheless, it was possible to synthesize 11 on a multigram scale in an overall yield of 63% over four steps, and this without any need for chromatographic purification of the synthetic intermediates between 7 and 11. With 11 in hand, reactions were performed with (2-methoxyphenyl)lithium and with (2,6-dimethoxyphenyl)lithium to generate two structurally similar yet different [5]helicene series (Scheme 1); series A containing on one hand a "naked" aromatic ring at a terminal end and, in the case of series **B**, a fused benzo ring with a methoxy group at position 23. In the latter case, the MeO substituent is ideally located inside the inner rim of the helical core to enforce stronger steric interactions between the extremities. Practically, to achieve high yields, the addition (2-methoxyphenyl)lithium and (2,6-dimethoxyof phenyl)lithium to ketone 11 required the activation of tetracyclic ketone with anhydrous CeCl₃⁴² and reactions afforded the corresponding carbinols 12A and 12B in 79% and 82% respectively.

From there, a different outcome was obtained in the two series. For series A (Scheme 1, left), treatment of 12A with 50% aqueous HBF₄ led to the partial formation of the corresponding carbenium derivative 13A. It was not possible to drive the reaction to completion and crude reactions of 13A always contained precursor **12A** in a typical 88:12 ratio.⁴³ It was nevertheless possible to perform the reaction on a multigram scale and the mixture 13A and 12A was isolated by precipitation and filtration without any need for chromatographic purification. Treatment of this combination in molten pyridinium hydrogen chloride led to the effective formation of cationic dioxa [5]helicene 8A (92%). Under the same conditions, the direct conversion of 12A to 8A was also possible albeit in a lower yield (61%). Starting from 13A, using a large excess of n-propylamine and benzoic acid, diaza [5]helicene 9A was synthesized in a low 16% yield. Under the same conditions but starting from already ring-closed dioxa 8A, the process was more efficient to yield 9A in 31%.





Reaction conditions: Series A: a) CeCl₃, THF, 25 °C, 24 h, then 2-methoxyphenyl lithium, 25 °C, 16 h, 79%; b) HBF₄ (50% aq. sol.), CH₂Cl₂, 25 °C, 2 h, (88% conv); c) Pyr•HCl, 225 °C, 2 min, 61% from **12A** and 92% from **13A**; d) 25 equiv NH₂Pr, 12.5 equiv PhCO₂H,

NMP, 140 °C, 12 h, 31% from **12A** and 16% from **13A**; e) 5 equiv PrNH₂, CH₃CN, reflux, 16 h, 3%. **Series B**: f) CeCl₃, THF, 25 °C, 24 h, (2,6-dimethoxyphenyl)lithium, 25 °C, 16 h, 82%; g) HBF₄ (50% aq. sol.), CH₂Cl₂, 25 °C, 2 h, 99%; h) Pyr·HCl, 225 °C, 2 min, 93%; i) NaHCO₃ sat aq. sol., 64%; j) 1 M HBF₄ aq. sol., 99%; k) K₂CO₃, DMF, MeI, 25 °C, 3 days, 42%.

Formation of azaoxa [5]helicene 10A turned out to be difficult on the other hand. Treatment of the combination of 13A and 12A with propylamine (5 equiv) under milder conditions generated little of the targeted product (3%); most of the reactivity being devoted to the formation of *leuco* adducts by direct nucleophilic attack of the amine to the central carbon atom. This reactivity probably indicates the stronger electrophilic nature of carbenium 13A.44 Interestingly azaoxa [5]helicene 10A was formed as a single regioisomer; the structure, which was being unambiguously determined by NMR spectroscopy (NOESY). In line with recent mechanistic hypotheses,⁴⁵ the amine attacks preferentially the tetracyclic moiety and not the appendant *p*-MeOPh ring that, due to its geometrical perpendicular orientation, is less conjugated to the carbenium moiety and less likely to undergo the S_NAr reactivity.

In series **B** (Scheme 1, right), starting from carbinol **12B**, the formation of the desired carbocation 13B was quantitative this time (99% yield). However, under standard conditions for the formation of dioxa helicenes,^{16, 45} deprotection of the terminal methoxy group occurred concomitantly with the ring closing formation. A similar behavior has been previously observed by Laursen and collaborators.¹² The resulting hydroxylated dioxa [5]helicene 14B was obtained in excellent yield (93%). Not surprisingly, this product isolated in its cationic form 14B undergoes a color change in solution from brown to green upon basification of the medium, corresponding to the conversion to the neutral dye 15B (64% vield after column chromatography). Its geometry, and the presence of an ortho-quinomethine type structure, was confirmed by X-ray diffraction analysis. The cliché will be detailed later together with that of other derivatives like 8A, 8B and 9A (see below). The formation of 15B is reversible and 14B is reformed by simple acidic treatment (yield 99%). Importantly, 14B reacted with MeI under basic conditions to afford the corresponding methoxy substituted dioxa [5]helicene 8B in 42% yield.

Also, with 13B in hand, it was possible to prepare desired diaza 9B and azaoxa 10B in moderate yields, up to 39% and 53% respectively (Scheme 2). The formation of these compounds was highly dependent on the reaction conditions. In fact, upon simple addition of propylamine to 13B in acetonitrile, *leuco* adduct **16B** forms immediately and precipitates. Its isolation by filtration (84% yield) afforded the possibility to obtain single crystals, which were analyzed by X-ray diffraction confirming hence the chemical nature of the adduct. With more forcing conditions (Scheme 2, b), diaza [5]helicene 9B was obtained in 39% yield along with minor hydroxylated 17B (5%) and amino 18B (2%) adducts. Using intermediate conditions (Scheme 2, c), a mixture of azaoxa [5]helicene 10B and its precursor 19B was obtained in 13% and 25% yields respectively; the latter derivative reacting quantitatively under basic conditions to form the desired ring-closed derivative. Combining the two steps in one-pot led, without surprise, to the most effective process to reach **10B** in 53% yield. Interestingly, on standing in CD₂Cl₂ solution, the cyclization of compound 19B into 10B occurs also

spontaneously. This reaction can be monitored in ¹H NMR spectroscopy and proceeds with ca. 30-40% conversion of **19B**, and a color change from yellow (**19B**) to pink (**10B**). Along with **16B** the structure of azaoxa [5]helicenes **10B** was determined by X-ray crystallography (*vide infra*).

Scheme 2. Synthesis of azaoxa and diaza [5]helicenes 9B and 10B and solid state structure of 16B.



Reaction conditions: a) 5 equiv PrNH₂, CH₃CN; b) 25 equiv PrNH₂, 12.5 equiv PhCO₂H, 25 $^{\circ}$ C, 5 days, then NMP, 90 $^{\circ}$ C, 5 h; c) 25 equiv PrNH₂, 25 $^{\circ}$ C, 2 days; d) NaHCO₃ sat. sol.

Finally, to measure primarily the effect of substituents on dioxa derivatives, care was taken to enlist the bromide substituent on the naphthyl ring of dioxa [5]helicene **8A** to extend the derivatives to choose for possible applications (Scheme 3). A series of *Suzuki-Miyaura* cross-coupling reactions were performed between **8A** and various aryl and styryl boronic acids to yield compounds **20a-20d** and **21a-21c** respectively. For derivatives **20**, yields were good to excellent (86-95%). For compounds **21a-21c**, conversion of **8A** to the products was excellent but the isolation of **21a-21c** through precipitation was more challenging than expected and reduced yields were obtained consequently (53-68%). Also, in one instance and using established conditions, it was possible to derive phenyl-substituted dioxa **20a** into the corresponding [5]helicene **22a** (43%). Scheme 3. Derivatization of [5]helicene 8A via *Suzuki-Miyaura* cross-coupling reactions.



Reaction conditions: a) Arylboronic acid, Pd(PPh₃)₄, K₂CO₃, 1,4-dioxane, 80 °C, 16 h; b) Styrylboronic acid, Pd(OAc)₂, PPh₃, 1,4-dioxane, 90 °C, 3 h; c) 25 equiv PrNH₂, 12.5 equiv PhCO₂H, 25 °C, 2 days, then NMP, 140 °C, 2 h.

Solid state analysis. Solid-state structures of cationic helicenes **8A**, **9A**, **8B**, **10B** and neutral adduct **15B** were studied by X-ray diffraction analyses (Figure 3, Figures S1-S7). Key structural features like helical pitches and dihedral angles are provided in Table 1 and the supporting information for **8A** (p. S96), **9A** (p. S100), **8B** (p. S98), **10B** (p. S102), and **15B** (p. S104). Unsurprisingly, the presence of methoxy groups on the inner rim of the helicenes (inside the fjord region) increases the helicity between series A and B (0.12 Å helical pitch expansion between **8A** and **8B**). Replacement of two oxygen by two nitrogen atoms in **9A** reduces the pitch by ca. 0.05 Å, this observation being in line with the augmented electronic stability and rigidity brought by the N atoms.



Figure 3. Stick view of the crystal structures of 8A, 9A, 8B, 10B and 15B.

Table 1. Key geometrical parameters for cationic helicenes 8A, 9A, 8B, 10B and quinomethine 15B.^a

Helicenes	Helical pitch [Å]	Helical angle [°]
dioxa 8A	2.94	37.5
diaza 9A	2.89	45

dioxa 8B	3.06	42.3
azaoxa 10B	3.08	51.4
quino 15B	3.04	43.6

^{*a*} The helical pitch is the distance between the first two overlapping atoms of the helicene (carbons 3 and 23, see Fig. 2). The helical angle defining the fjord region is a common descriptor for helicene scaffolds (dihedral angle between carbons 3-2-18-23, see SI, p. S110).

Resolution, CSP separation and configurational stability. As mentioned earlier, helicenes display attractive helical conformations due the repulsion of their termini and, consequently, it is of general interest to characterize these moieties as single enantiomers. Previously, the resolution of certain racemic cationic [4] and [6]helicenes was successfully achieved by an ion pairing strategy with enantiopure hexacoordinated phosphate anions.^{14, 16} However, as demonstrated in recent studies, ^{15, 17-18} the most general strategy for the resolution of racemic cationic helicenes is their transformation into neutral (reduced) adducts followed by a separation by mean of preparative chiral stationary phase (CSP) HPLC. As a consequence, [5]helicenes 8A, 9A, 10A, 8B, 9B and 10B were treated with NaBH₄ and NaBH₃CN (Table 2). With the more reactive NaBH4 reagent, reduction occurred in all cases and yielded triarylmethanes 23-25 in both series A and B. With milder cyanoborohydride, the hydride transfers only happened with more electrophilic dioxa 8 and azaoxa 10 cations; diaza [5]helicenes 9 being unreactive.46

Table 2. Diastereoselectivity upon treatment with NaBH₄ and NaBH₃CN.

Precursor	Product	Diastereoselectivity		
		NaBH ₄	NaBH ₃ CN	
8A	23A	>49:1	>49:1	
10A	24A	>49:1	81:19	
9A	25A	>49:1	n.r. ^a	
8B	23B	88:12	80:20	
10B	24B	60:40	14:86	
9B	25B	91:9	n.r. ^a	

^a No reaction occurs with NaBH₃CN.

In addition, as [5]helicenes **8-10** are devoid of local C_2 -symmetry and present diastereotopic faces for the central carbocationic centers,⁴⁷ reduced products **23-25** can be generated in two diastereomeric forms (Scheme 4). Of interest, and somewhat surprisingly in view of earlier results,¹⁷ better diastereomeric ratios (up to > 49:1, NMR) were obtained using NaBH₄ as hydride source instead of NaBH₃CN (Table 2).⁶ Selectivity ratios were also always higher in series **A** as compared to the **B** analogues. In fact, using NaBH₄ as reducing agent yielded **23A**, **24A** and **25A** as single diastereomers. In all instances, the configuration of the (predominant) diastereomers could be determined by ¹H NMR spectroscopy (NOESY, see SI, p. S81-S94) and confirmed by the X-ray structural analysis of the major diastereomer **24B** (reaction of **10B** with NaBH₃CN, see SI, p. S108).



From the solid-state structure of **24B** and that from previous studies,⁴⁷ it can be inferred that the reduced molecules do not adopt strict helical conformations anymore. On one side, four contiguous six-membered rings present an essentially planar arrangement in which the contained bridging atom is sp^2 hybridized (here atom X for series A which are the predominant diastereomers, except for the reduction of **10B** with NaBH₃CN, Scheme 4). On the other side, a strong bending of the backbone is enforced to compromise with the new carbon sp^3 center (and the repulsion of the methoxy substituent with naphthyl ring in series **B**). This has consequences on the other bridging atom (Y for series A) which pyramidalizes to account for the folding of the corresponding six-membered ring that most probably adopts an essentially boat-like conformation.

Finally, with racemic 23A and 25A in hand, care was taken to separate the reduced derivatives into single enantiomers by semi-preparative HPLC on chiral stationary phase (Chiralpak IA or IB, hexane:THF, see p. S111 and S113). The efficiency of the resolution could be evidenced by the electronic circular dichroism (ECD) spectra of the separated fraction (*eg*, 23A, Figure 4, a). Subjected to air and light, enantiopure 23A and 25A spontaneously formed corresponding 8A and 9A (Figure 4, b), which were found to be prone to racemize. In fact, with (–)-9A, it was possible to determine the racemization barrier by ECD, monitoring a single wavelength every second (400 nm, see SI (p. S112 and S114)).



Figure 4. ECD spectra of compounds derived from the first and second eluted enantiomers of: a) reduced dioxa 23A; b) cationic

diaza [5]helicene **9A** generated from **25A** upon oxidation. Recorded in CH₂Cl₂ solutions (2.10⁻⁵ M) at 20 $^{\circ}$ C.

In fact, a moderate heating of DMSO solutions of (–)-9A to 32 °C was sufficient to start observing a decrease of the Cotton effect. After 1000 seconds, a 2% loss of enantiomeric purity was observed at that temperature. Samples were then heated at 40, 50, 60 and 70 °C and analyzed for the same period of time. The kinetic constants were calculated (e.g., k (343 K) 5.8 10⁻² min⁻¹) and the activation parameters determined (Δ H[‡] (343 K) 86.8 ± 1.6 kJ.mol⁻¹ and Δ S[‡] (343 K) –51.2 ± 1.3 J.K⁻¹.mol⁻¹). Not surprisingly, due to the absence of the inner rim substituent, the racemization barrier of (–)-9A (Δ G[‡] (343 K) 104.4 ± 1.1 kJ.mol⁻¹) is lower than that of the corresponding diaza [4] and [6]helicenes 3 and 6 (Δ G[‡] > 155 kJmol⁻¹).¹⁸

In view of the relatively low energy barrier for the racemization of **9A**, the more direct VT-HPLC analytical approach on chiral stationary phase was chosen to determine the enantiomerization kinetics of dioxa and azaoxa [5]helicenes 8A and 10A. Preliminary CSP HPLC experiments showed that single enantiomers of 8A and 10A were indeed prone to racemization at room temperature. Good enantioresolution of 8A were achieved lowering the column temperature between 5 °C and 10 °C, using an enantioselective HPLC column packed with an immobilized amylose derivative CSP (Chiralpak IA), and a mobile phase consisting of methanol containing 0.6% CF₃COOH and 0.4% Et₃N. At temperatures above 20 °C, a single broad peak was observed, due to fast on column enantiomerization. On the same column, 10A was nicely resolved even at room temperature, indicating a larger stereochemical stability compared to 8A. We used variable temperature dynamic high-performance liquid chromatography (DHPLC)⁴⁸⁻⁵⁰ on a chiral stationary phase (CSP) for the determination of the enantiomerization barriers. Then, computer simulations of the exchange broadened chromatograms were exploited to extract the apparent rate constants for the on-column M-P interconversion process, and from these values the corresponding free energy barriers of enantiomerization were calculated, whose averaged values are $\Box G^{\ddagger}_{av}$ 86.7 kJ.mol⁻¹ and $\Box G^{\ddagger}_{av}$ 95.3 kJ.mol⁻¹ for **8A** and 10A, respectively. These values correspond to racemization barriers $\Box G^{\ddagger}_{racem}$ 85.0 and 93.4 kJ.mol⁻¹ for **8A** and 10A.⁵¹ The complete set of experimental Gibbs free energy of enantiomerization $\Box G^{\ddagger}$ for **8A** and **10A** are gathered in Table S1.

Dye	Solvent	T (°C)	Enantiomeriza- tion ^b		Racemization	
			k	$\Box G^{\ddagger}$	k	$\Box G^{\ddagger}$
8A	Mix ^c	12	4.8 10 ⁻²	86.7	9.7 10 ^{-2 d}	85.0
8B	EtOH	70	4.7 10 ⁻³	111.5	9.4 10 ^{-3 d}	109.5
10A	Mix ^c	40	5.1 10 ⁻²	95.3	1.0 10 ^{-1 d}	93.4
10A	Mix ^c	46	8.9 10 ⁻²	95.7	1.8 10 ^{-1 d}	93.8
10B	DMSO	150	3.2 10 ⁻³	139.5	6.4 10 ^{-3 d}	137.1
9A	DMSO	70	n.d.	n.d.	5.8 10 ^{-2 d}	104.4
9B	DMSO	150	n.d.	n.d.	_ e	>155
15000 12500 a b 15000 b						

Table 3. Enantiomerization and racemization parameters ^a

Kinetic constants k in min⁻¹. Energies in kJ/mol. n.d. stands for not determined. ^b Average values. See Table S1 for values concerning each enantiomerization step. ^c Mix is the HPLC eluent composed of MeOH, CF3COOH 0.6%, Et3N 0.4 %. ^d Calculated using the following formula: k_{racemization} = 2 x $k_{\text{enantiomerization}}$ ^e No change in enantiomeric purity after 1h.

Helicene 8B and 10B gave no evidence of on-column interconversion at column temperatures as high as 60 °C, indicating a greater stereochemical stability. For these two helicenes, the energy barrier to interconversion was determined by isolating a single enantiomer by HPLC on CSP, and then incubating it in a solvent at high temperature and following its racemization by HPLC on a CSP. Racemization of the first eluted enantiomer of 8B was monitored in EtOH at 70 °C. The associated free energy barrier of enantiomerization is $\Box G^{\ddagger}$ 111.5 kJ.mol⁻¹ ($\Box G^{\ddagger}_{racem}$ 109.5 kJ.mol⁻¹). Analogously, the racemization of the first eluted enantiomer of 10B was monitored in DMSO at 150 °C,

display similar absorption maxima and intensities to their

parent dye 8A, regardless of the position of the nitro func-

tion. These observations suggest a weak electronic influence

of the nitrophenyl substituents in 20a-c, probably due to a

twist occurring around the Csp²-Csp² linked biaryl framework, which disadvantages the conjugation with the helicene

core. An electronic communication is however evidenced in

the case of the methoxyphenyl-containing dye 20d. The



Figure 5. Electronic absorption spectra of [5]helicenes in dichloromethane solution (10⁻⁵ M, 20 °C).

yielding a free energy barrier of enantiomerization $\Box G^{\ddagger}$ 139.5 kJ.mol⁻¹ ($\Box G^{\ddagger}_{racem}$ 137.1 kJ.mol⁻¹). Single enantiomers of 9B gave no evidence of racemization when heated at 150 °C in DMSO for 1 h. These overall results are summarized in Table 3.

Optical properties. The optical properties of the hetero[5]helicenes have been recorded in dichloromethane solution and the complete data are compiled in Table 4. The electronic absorption spectra are depicted in Figure 5, according to the heteroatom variations (a), the phenyl (b) or the styryl (c) substituents. The dioxa [5]helicene 8A displays a moderately intense absorption band centered in the yellow spectral range ($\lambda_{max} = 570$ nm) and a distinct higher energy transition located below 450 nm (Figure 5, a). The azaoxa [5]helicene 10A comparatively shows two blueshifted absorption maxima at 555 nm and 534 nm, characterized by lower molar extinction coefficients (ca. 6700 M⁻¹cm⁻¹) and a broader profile (full width at half maximum, fwhm ≈ 3300 cm^{-1} for **10A** and 2500 cm^{-1} for **8A**). Diaza [5]helicene **9A**, featuring two nitrogen atoms, exhibits the most redshifted absorption of this series with $\lambda_{max} = 622$ nm. Interestingly, when the bromine atom is replaced by a phenyl ring, the absorption transition undergoes moderate bathochromic and hypochromic shifts for dioxa [5]helicene 20a and only a bathochromic shift for the diaza analogue 22a (Figure 5, b). Both nitrophenyl-substituted dioxa [5]helicenes 20b-c

lower energy transition is in fact redshifted ($\lambda_{max} = 589 \text{ nm}$) and displays a broad and quasi-Gaussian profile (fwhm = 3300 cm⁻¹), suggesting the establishment of an internal charge transfer (ICT) from the methoxyphenyl moiety towards the electron-deficient cationic core. The extension of conjugation brought by the insertion of styryl derivatives in compounds 21a-c is confirmed by the non-negligible redshift of the absorption maxima within the 610-630 nm range (Figure 5, c). While **21a** and **21b**, respectively introducing styryl and p-fluorostyryl substituents exhibit comparable absorption transitions, compound 21c, featuring an electrondonating *p*-methoxy-styryl moiety presents the most redshifted absorption maximum of the whole series and a particularly broad absorption profile (fwhm = 3640 cm^{-1}) indicating a potentially stronger ICT compared to chromophore The emission properties of the [5]helicenes have been investigated in dichloromethane solution and the fluorescence

20d.

spectra of the emissive candidates are presented on Figure 6. Upon excitation of the lowest energetic absorption transition, compound 8A displays an emission centered at 610 nm with moderate quantum yield ($\Phi = 0.10$) and a lifetime of 3.9 ns. Despite its blue shifted absorption, the azaoxa analogue 10A shows a similar emission maximum although characterized by a higher quantum efficiency ($\Phi = 0.26$) and a relatively long fluorescence lifetime (ca. 10 ns) for an organic chromophore in the red spectral range. In the same series, the diaza [5]helicene 9A presents an emission band noticeably shifted to lower energy with a maximum peak at 658 nm. The fluorescence spectrum of phenyl-substituted dye 20a shows a particularly broad and redshifted transition compared to the functionalized compounds of the same series (**20b-c**), with a large Stokes shift of 2150 cm⁻¹, that can be most presumably assigned to an emissive ICT state. Diaza analogue 22a displays a sharp emission centered at 624 nm, characterized by a remarkable fluorescence quantum yield of 0.42, which is considered high for a red-emitting cationic helicene. Introduction of electron-withdrawing functions (20b-c) on the additional phenyl ring induces no noticeable modification of the fluorescence maxima compared to the precursor 8A ($\lambda_{em} \approx 610$ nm) but leads to a moderate increase of the fluorescence efficiency. On the contrary, the presence of an electron-donating substituent on the phenyl ring in 20d causes a quench of the fluorescence. No fluorescence was recorded for the styryl-containing dioxa [5]helicenes 21a-c. The possibility of non-radiative deexcitation via cis-trans photoisomerization of the double bond linker might explain the quenching of the fluorescence.



Figure 6. Normalized fluorescence spectra of [5]helicenes in dichloromethane solution (10^{-5} M, 20 °C).

 Table 4. Photophysical properties of [5]helicenes in dichloromethane.

Dye	λ_{max} (nm)	ϵ_{max} (M ⁻¹ cm ⁻¹)	λ_{em} (nm)	Φ	τ (ns)
8A	571	11,900	610	0.10	3.9
9A	623	11,600	658	0.31	9.7
10A	555	6,700	609	0.26	10.1
20a	578	10,300	660	0.18	7.5
20b	575	12,300	612	0.22	7.4

20c	572	12,600	607	0.25	7.9
20d	589	10,400	-	-	-
21a	613	10,100	-	-	-
21b	612	11,800	-	-	-
21c	634	10,600	-	-	-
22a	624	13,200	661	0.43	12

CONCLUSION

A straightforward approach to the synthesis of two different series of cationic [5]helicenes has been demonstrated including, in dioxa series, the possibility to introduce aromatic functional groups at the periphery of the helical structure. Photophysical study highlights however that the introduction of aryl substituents at the 23-position of the helical moieties has a negligible impact on the optical properties whereas styryl substituents allow a welcoming extension of the conjugation pathways. Finally, a redshift of the optical properties was evidenced upon introduction of nitrogen atoms in the helicene scaffold, leading to particularly good fluorescence efficiencies in the red domain for a helicene-derived chromophore. In terms of racemization, as it is customary in this family of cationic derivatives, diaza helicenes 9 were shown to be quite more configurationally stable than their azaoxa 10 and dioxa 8 analogues. In the classic [5]helicene series of type A, relatively small differences were however noted with ca. +8.4 kJ.mol⁻¹ of barrier energy for each introduction of a nitrogen atom. In series **B**, the influence of the extra methoxy group and of each bridging N-atom was however strongly felt since, for these configurationally stable derivatives, racemization occurred for dioxa 8B and azaoxa **10B** at 70 and 150 °C (G[‡] 109.2 and 137.2 kJ.mol⁻ ¹), respectively; the enantiomers of **9B** giving no evidence of racemization even at 150 °C for one hour.

EXPERIMENTAL SECTION

Synthetic Methods and Materials. Unless otherwise noted, all chemicals were used as received. Compound **7** was prepared according to reported procedures from commercially available 2-bromo-6-methoxynaphthalene.⁴¹ Propyl amine was distilled over Zn powder prior to use. HPLC solvents (analysis grade CHROMOSOLV Plus) from Sigma-Aldrich were used.

Spectroscopic Methods. NMR spectra were recorded on Brucker Avance II+ 600, AMX-500, AMX-400 and ARX-300 spectrometers at room temperature. ¹H NMR: chemical shifts were given in ppm relative to Me₄Si with solvent resonances used as internal standards (7.26 ppm for CDCl₃, 5.32 ppm for CD₂Cl₂ and 1.94 ppm for CD₃CN). ¹³C NMR chemicals shifts were given in ppm relative to Me₄Si with solvent resonances used as internal standards (77.1 ppm for CDCl₃, 53.8 ppm for CD₂Cl₂ and 118.26 ppm for CD₃CN). ¹H signals were reported as follows: chemical shift (δ) in ppm on the δ scale, multiplicity (s = singlet, brs = broad singlet, d = doublet, t = triplet, dd = doublet of doublet, m =multiplet, q = quartet), coupling constant (Hz), integration and identification. ¹³C{1H} NMR signals were reported as follows: chemical shift (δ) in ppm on the δ scale; assignments marked with (*) are tentative. The assignments of ¹H bering of the H and C, presented in the formulas, is arbitrary. IR spectra were recorded on a Perkin-Elmer 1650 FT-IR spectrometer using a diamond ATR Golden Gate sampling. Melting points (M.P.) were measured in open capillary tubes with a Buchi B-550 melting points apparatus and are uncorrected. Retardation factor (Rf) was measured on TLC Silicagel 60 F₂₅₄ Merck plates. Mass spectra were obtained on a spectrometer QSTAR pulsar (AB / MDS Sciex) by the Department of Mass Spectrometry of the University of Geneva. UV-vis-NIR absorption spectra were recorded on a JASCO V-650 spectrophotometer at 20 °C. HPLC analyses are performed at Agilent 1100, semi-preparative Chiralpak IA or IB $(0.46 \text{ cm} \times 25 \text{ cm})$. Detection was performed using DAD at 254.4. Retention times are given in minutes. Crystallography. All data were collected on an Agilent supernova dual source diffractometer equipped with an Atlas

and ${}^{13}C{1H}$ NMR signals were made on the basis of DEPT,

HSQC, HMBC, COSY and NOESY experiments. The num-

detector, using Cu K α radiation. Data reduction was carried out in the crysalis Pro Software.3 Structure solution was made using direct methods (Shelxs4 or sir20045) or chargeflipping (Superflip6). Refinements were carried out in ShexlL4 within the Olex27 software.

Fluorescence. Steady-state fluorescence spectra were measured using a Varian Cary 50 Eclipse spectrofluorimeter. All fluorescence spectra were corrected for the wavelength-dependent sensitivity of the detection.. Fluorescence quantum yields Φ were measured in diluted solution with an optical density lower than 0.1 using the following equation $\Phi x / \Phi r$ = $[Ar(\lambda)/Ax(\lambda)][nx2/nr2][Dx/Dr]$ where A is the absorbance at the excitation wavelength (λ), n the refractive index and D the integrated intensity. "r" and "x" stand for reference and sample. The fluorescence quantum yields were measured relative to Cresyl Violet in methanol ($\Phi f = 0.54$). Excitation of reference and sample compounds was performed at the same wavelength. Short luminescence decay was monitored with the TC-SPC Horiba apparatus using Ludox in distilled water to determine the instrumental response function used for deconvolution. Excitation was performed using a 570 nm NanoLED (peak wavelength: 573 nm; pulse duration: 1.5 ns), and the deconvolution was performed using the DAS6 fluorescence-decay analysis software.

Scheme 5. Preparation of key substrate 11.



Reaction conditions: a) 1,3-dimethoxybenzene, *n*-BuLi, then 7, THF, 25 °C, 24 h; b) DDQ, CH₂Cl₂, 20 °C, 24 h; c) BBr₃, CH₂Cl₂, -78 then 20 °C, 1 h; d) heating at 200 °C, 5h.

Synthesis of (6-Bromo-2-methoxynaphthalen-1-yl)(2,6-dimethoxyphenyl)methanol (I)

To a solution of 1,3-dimethoxybenzene (15.9 mL, 121.5 mmol, 3 equiv) in dry THF (50 mL) was added dropwise n-BuLi (1.6M in hexane, 63.3 mL, 101.3 mmol, 2.5 equiv) at -78 °C under N₂ atmosphere. The reaction mixture was stirred for 2 h and allowed during this time to slowly warm to room temperature. Then the solution was cannulated into a premixed solution of activated 6-bromo-2-methoxy-1naphthaldehyde 7 (The activation was performed as follow: 6-bromo-2-methoxy-1-naphthaldehyde 7 (10.7 g, 40.5 mmol) and anhydrous CeCl₃ (12.0 g, 48.6 mmol, 1.3 equiv) were stirred in dry THF (80 mL) for 24 h at 25 °C). After stirring for 16 h, the reaction mixture was guenched with a minimum amount of water. The excess of solvent was evaporated under vacuum and the resulting mixture was extracted with CH₂Cl₂ (200 mL) and washed with water (2 x 200 mL). The organic layer was dried over Na₂SO₄ and the solvent evaporated under vacuum. The crude mixture was washed with Et₂O and after drying of the remaining residue, the desired compound was isolated as a colourless solid (12.2 g, 75%). M.P.: 183 °C. $\mathbf{R}_f = 0.23$ (Silica gel, CH₂Cl₂). ¹H **NMR** (500 MHz, CD_2Cl_2): δ 8.14 (dd, J = 9.2, 0.7 Hz, 1H, H-3), 7.90 (d, J = 2.2 Hz, 1H, H-6), 7.68 (d, J = 9.0 Hz, 1H, H-8), 7.46 (dd, J = 9.3, 2.2 Hz, 1H, H-4), 7.30 (d, J = 9.1 Hz, 1H, H-9), 7.17 (t, J = 8.3 Hz, 1H, H-15), 6.94 (d, J = 9.4 Hz, 1H, H-11), 6.56 (d, J = 8.4 Hz, 2H, H-14, H-16), 5.68 (d, J = 9.4 Hz, 1H, OH), 3.88 (s, 3H, H-20), 3.72 (s, 6H, H-18, H-19). ¹³C{1H} NMR (126 MHz, CD₂Cl₂): δ 158.4 (2C, C-13, C-17), 156.2 (C, C-10), 131.3* (C, C-1), 130.8* (C, C-7), 130.4 (CH, C-6), 129.5 (CH, C-4), 128.8 (CH, C-15), 128.4 (CH, C-8), 126.4 (CH, C-3), 125.8* (C, C-2), 120.4 (C, C-12), 117.2* (C, C-5), 116.1 (CH, C-9), 105.0 (2CH, C-14, C-16), 66.6 (C, C-11), 57.3 (CH₃, C-20), 56.2 (2CH₃, C-18, C-19). **IR** (neat, cm⁻¹): v 3523, 2935, 2896, 1586, 1496, 1455, 1266, 1236, 1173, 1104, 1045, 801. HRMS (ESI) m/z: $[M - OH]^+$ Calcd for C₂₀H₁₈BrO₃ 385.0434; Found 385.0431.

Synthesis of (6-Bromo-2-methoxynaphthalen-1-yl)(2,6-dimethoxyphenyl)methanone (II)

To a solution of I (12.2 g, 30.37 mmol) in CH_2Cl_2 (100 mL), 2,3-dichloro-5,6-dicyano-p-benzoquinone (8.3 g, 36.4 mmol, 1.2 equiv) was added under N₂ atmosphere at room temperature. The mixture was stirred for 24 h at room temperature. The reaction mixture was washed once with an aqueous solution of sodium hydroxide (1 M, 30 mL) and then so many times with water until the aqueous phase was colourless. The organic layer was dried over Na2SO4 and evaporated under vacuum, affording 11.0 g (90%) of the desired compound as a pale yellow powder. M.P.: 208 °C. Rf = 0.34 (Silica gel, CH₂Cl₂). ¹**H** NMR (500 MHz, CD₂Cl₂): δ 7.98-7.94 (m, 2H, H-3, H-6), 7.80 (d, J = 9.0, 0.6 Hz, 1H, H-8), 7.54 (dd, J = 9.2, 2.1 Hz, 1H, H-4), 7.30 (t, J = 8.4 Hz, 1H, H-15), 7.24 (d, J = 9.1 Hz, 1H, H-9), 6.57 (d, J = 8.4 Hz, 2H, H-14, H-16), 3.64 (s, 3H, H-20), 3.59 (2s, 6H, H-18, H-19. ¹³C{1H} NMR (126 MHz, CD₂Cl₂): δ 196.6 (C, C-11), 158.6 (2C, C-13, C-17), 156.3 (C, C-10), 131.5 (CH, C-15), 131.3 (CH, C-8), 130.7 (CH, C-4), 130.6* (C, C-5), 130.6* (C, C-7), 130.1 (CH, C-6), 127.5 (CH, C-3), 127.0* (C, C-1), 122.2 (C, C-12), 117.9* (C, C-2), 115.6 (CH, C-9), 104.7 (2CH, C-14, C-16), 57.3 (CH₃, C-20), 56.3 (2CH₃, C-18, C-19). **IR** (neat, cm⁻¹): v 2943, 1589, 1468, 1252, 1110. **HRMS (ESI)** m/z: [M + H]⁺ Calcd for C₂₀H₁₇BrO₄ 401.0383; Found: 401.0394.

Synthesis of (6-Bromo-2-methoxynaphthalen-1-yl)(2-hydroxy-6-methoxyphenyl)methanone (III)

To a solution of II (11 g, 27.3 mmol) in CH₂Cl₂ (90 mL) was added dropwise BBr₃ (1M solution in CH₂Cl₂, 27.3 mL, 1 equiv) at -78 °C under N2 atmosphere. After 30 min at this temperature, the reaction mixture was allowed to warm to room temperature and stirred for 1 h until completion of the reaction. Then it was quenched with 1M HCl. The solvent was evaporated under *vacuum* and the resulting mixture was extracted with CH₂Cl₂ (200 mL) and washed with water (2 x 200 mL). The organic layer was dried over Na₂SO₄ and evaporated under vacuum. The crude precipitate was washed with Et₂O to remove the impurities and after drying of the residue the desired compound was isolated as a yellow powder 10.5 g (>99%). M.P.: 148 °C; $\mathbf{R}_f = 0.69$ (Silica gel, CH₂Cl₂). ¹H NMR (500 MHz, CD₂Cl₂): δ 13.08 (s, 1H, OH), 8.00 (d, J = 2.0 Hz, 1H, H-6), 7.83 (d, J = 9.1 Hz, 1H, H-8), 7.45-7.38 (m, 3H, H-3, H-4, H-15), 7.36 (d, J = 9.1 Hz, 1H, H-9), 6.65 (dd, J = 8.4, 1.0 Hz, 1H, H-14), 6.25 (dd, J = 8.3, 0.7 Hz, 1H, H-16), 3.84 (s, 3H, H-20), 3.13 (s, 3H, H-18). ¹³C{1H} NMR (126 MHz, CD_2Cl_2): δ 201.2 (C, C-11), 165.3 (C, C-13), 162.2 (C, C-17), 153.2 (C, C-10), 137.9 (CH, C-15), 130.4 (CH, C-4), 130.4 (CH, C-6), 130.1* (C, C-7), 129.5 (CH, C-8), 129.4* (C, C-2), 127.7* (C, C-1), 125.7 (CH, C-3), 117.6 (C, C-5), 114.7 (CH, C-9), 113.1 (C, C-12), 110.9 (CH, C-16), 102.2 (CH, C-14), 57.0 (CH₃, C-20), 56.0 (CH₃, C-18). **IR** (neat, cm⁻¹): v 2944, 1583, 1497, 1455, 1339, 1231, 1180, 1089, 803. HRMS (ESI) m/z: [M + H]⁺ Calcd for C₁₉H₁₅BrO₄ 387.0227; Found 387.0227.

Synthesis of 3-Bromo-11-methoxy-12*H*-benzo[*a*]xanthen-12-one (11)

In an open flask, neat (6-bromo-2-methoxynaphthalen-1yl)(2-hydroxy-6-methoxy-phenyl)methanone III (10.5 g, 27.3 mmol) was heated at 200 °C for 5 h in a heat block for round bottom flask. The desired compound 11 was obtained quantitatively as an off-white powder 9.6 g (99%). M.P.: 233 °C; $\mathbf{R}_f = 0.42$ (Silica gel, CH₂Cl₂). ¹H NMR (500 MHz, CD₂Cl₂): δ 9.86 (dt, *J* = 9.3, 0.6 Hz, 1H, H-3), 8.07 (d, *J* = 2.3 Hz, 1H, H-6), 8.02 (dt, J = 9.0, 0.6 Hz, 1H, H-8), 7.80 (dd, J = 9.3, 2.2 Hz, 1H, H-4), 7.64 (t, J = 8.3 Hz, 1H, H-4)15), 7.56 (d, *J* = 9.1 Hz, 1H, H-9), 7.13 (dd, *J* = 8.4, 1.0 Hz, 1H, H-14), 6.89 (dd, J = 8.3, 0.9 Hz, 1H, H-16), 4.02 (s, 3H, H-18). ¹³C{1H} NMR (126 MHz, CD₂Cl₂): δ 178.1 (C, C-11), 160.9 (C, C-17), 157.1 (C, C-13), 156.5 (C, C-10), 135.2 (CH, C-8), 134.6 (CH, C-15), 132.5 (CH, C-4), 132.2* (C, C-2), 130.8 (CH, C-6), 130.0 (C, C-5), 129.0 (CH, C-3), 120.1* (C, C-7), 119.4 (CH, C-9), 116.2* (C, C-1), 114.4 (C, C-12), 109.9 (CH, C-14), 106.6 (CH, C-16), 56.8 (CH₃, C-18). **IR** (neat, cm⁻¹): v 2920, 1740, 1644, 1603, 1581, 1495, 1469, 1438, 1415, 1268, 1254, 1086, 1070, 903, 831, 782.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{11}BrO_3$ 354.9964; Found 354.9961.

Synthesis of 3-Bromo-11-methoxy-12-(2-methoxyphenvl)-12H-benzo[a]xanthen-12-ol (12A). To a solution of anisole (0.96 g, 8.44 mmol, 3 equiv) n-BuLi (1.6M in hexane, 4.4 mL, 7.03 mmol, 2.5 equiv) was added dropwise in dry THF (6 mL) under N₂ atmosphere at -78 °C. The reaction mixture was allowed to warm slowly to room temperature, stirred at this temperature for 3h and then it was cannulated into a premixed solution of activated ketone 5 (The activation was performed as follow: ketone **11** (1.00 g, 2.81 mmol) and anhydrous CeCl₃ (0.90 g, 3.66 mmol, 1.3 equiv) were stirred in dry THF (80 mL) for 24 h at 25 °C). After stirring for 16 h, the reaction mixture was quenched with a minimum amount of water. The solvent was evaporated under vacuum and the resulting mixture was dissolved in CH₂Cl₂ (200 mL) and washed with water (2 x 200 mL). The organic layer was dried over Na₂SO₄ and evaporated under vacuum. The crude precipitate was washed with Et₂O to remove some impurities and after drying the desired compound was isolated as a colourless solid 1.03 g (79%). M.P.: 225 °C. R_f = 0.55 (Silica gel, CH₂Cl₂). ¹**H** NMR (500 MHz, CD₂Cl₂): δ 8.54 (d, J = 9.3 Hz, 1H, H-3), 8.06 (d, J = 7.4 Hz, 1H, H-23), 7.85 (d, J = 2.2 Hz, 1H, H-6), 7.66 (d, J = 8.9 Hz, 1H, H-8), 7.34 (d, J= 8.9 Hz, 1H, H-9), 7.33 (dd, *J* = 9.3, 2.2 Hz, 1H, H-4), 7.25 (t, *J* = 8.2 Hz, 1H, H-15), 7.13 (ddd, *J* = 8.1, 7.4, 1.8 Hz, 1H, H-21), 7.05 (td, J = 7.6, 1.2 Hz, 1H, H-22), 6.87 (dd, J = 8.3, 1.0 Hz, 1H, H-14), 6.63 (dd, J = 8.1, 1.1 Hz, 1H, H-20), 6.60 (dd, J = 8.2, 0.9 Hz, 1H, H-16), 5.38 (s, 1H, OH), 3.69 (s, 3H, H-24), 3.25 (s, 3H, H-25). ¹³C{1H} NMR (125 MHz, CD₂Cl₂): δ 157.4 (C, C-17), 156.8 (C, C-19), 150.2 (C, C-13), 148.5 (C, C-10), 135.9 (C, C-18), 132.9* (C, C-7), 130.4 (CH, C-6), 130.3* (C, C-2), 129.4 (CH, C-8), 129.4 (CH, C-3), 129.1 (CH, C-9), 129.0 (CH, C-15), 128.6 (CH, C-21), 127.2 (CH, C-23), 119.7 (CH, C-22), 118.8 (CH, C-4), 117.5 (C, C-5), 117.0 (C, C-1), 115.4 (C, C-12), 113.0 (CH, C-20), 109.5 (CH, C-14), 106.5 (CH, C-16), 70.9 (CH, C-11), 56.2 (CH₃, C-24), 55.7 (CH₃, C-25). **IR** (neat, cm⁻¹): v 3544, 3113, 2952, 1612, 1588, 1478, 1383, 1281, 1269, 1250, 1086, 1062, 1024, 903, 795, 762. HRMS (ESI) m/z: [M -OH]⁺ Calcd for C₂₅H₁₈BrO₃ 445.0434; Found 445.0439.

Synthesis of 3-Bromo-11-methoxy-12-(2-methoxyphenyl)-12H-benzo[a]xanthen-12-ylium tetrafluoroborate (13A). Compound 12A (0.150 g, 0.281 mmol) was dissolved in CH₂Cl₂ (200 mL) and HBF₄ (0.5 mL, 50% aqueous solution) was added. After stirring for 2 h, the mixture was extracted with CH₂Cl₂, dried over Na₂SO₄ and evaporated under vacuum. The desired compound was isolated as a mixture of **13A**:**12A** = 88:12 as a red solid 0.175 g (88%). **M.P.:** 211 °C. ¹**H NMR** (600 MHz, CD₂Cl₂): δ 8.70 (d, J = 9.2 Hz, 1H, H-8), 8.42 (t, J = 8.5 Hz, 1H, H-15), 8.30 (d, J = 2.3 Hz, 1H, H-6), 8.19 (d, J = 9.2 Hz, 1H, H-9), 7.91 (dd, J = 8.6, 0.9 Hz, 1H, H-14), 7.75 (ddd, J = 8.4, 7.6, 1.7 Hz, 1H, H-22), 7.58 (dd, J = 9.3, 2.3 Hz, 1H, H-4), 7.32 (dt, J = 9.5, 2.4 Hz, 1H, H-3), 7.26 (ddd, 3H, H-16, H-20, H-21), 7.09-6.99 (m, 1H, H-23), 3.72 (s, 3H, H-24), 3.68 (s, 3H, H-25). ¹³C{1H} NMR (151 MHz, CD₂Cl₂): δ 170.1* (C, C-12), 161.4 (C, C-10), 161.0 (C, C-17), 155.3 (C, C-13), 155.2 (C, C-19), 147.4 (CH, C-8), 144.2 (CH, C-15), 134.2 (CH, C-4), 133.6 (CH, C-6), 133.3* (C, C-7), 132.6 (CH, C-22), 128.8 (CH, C-3), 128.3 (C, C-5), 127.2* (C, C-18), 125.8 (CH, C-23), 123.8* (C, C-2), 122.8 (CH, C-20), 121.6* (C, C-1), 119.0 (CH, C-9), 117.9* (C, C-11), 111.4 (CH, C-16), 110.4 (CH, C-14), 109.5 (CH, C-21), 57.4 (CH₃, C-25), 56.0 (CH₃, C-24). ¹⁹**F NMR** (282 MHz, CD₂Cl₂): δ –152.5, –152.5. **IR** (neat, cm⁻¹): v 3409, 2933, 1615, 1591, 1500, 1476, 1384, 1329, 1291, 1199, 1154, 1074, 1059, 895, 832, 753. **UV-Vis** (CH₂Cl₂, C = 2.10⁻⁵ M): λ_{max} (Log ε): 516 (3.83), 445 (4.23), 310 (4.52). **HRMS (ESI)** *m/z*: [M]⁺ Calcd for C₂₅H₁₈BrO₃ 445.0434; Found 445.0445.

Synthesis of 14-bromo-11bH-benzo[a]chromeno[2,3,4kl]xanthen-11b-ylium tetrafluoroborate (8A). Procedure **A:** In an open flask, pyridine hydrochloride (4 g, 100 equiv) was heated 30 min at 225 °C in a heat block for round bottom flask. Then compound 13A (250 mg, 0.47 mmol) was added in one portion, the mixture was stirred for 2 min at this temperature and then HBF₄ (30 mL, 1M aqueous solution) was added. The reaction mixture was extracted with CH₂Cl₂ (5 x 30 mL). The organic layer was dried over Na₂SO₄, evaporated under vacuum, washed with Et₂O and dried, yielding 0.209 mg (92%) of the desired compound 8A as a dark red solid. Procedure B: In an open flask, pyridine hydrochloride (1 g, 100 equiv) was heated 30 min at 225 °C using a heat block. Then the carbinol 12A (50 mg, 0.108 mmol) was added in one portion, the mixture was stirred for 5 min at this temperature and then HBF₄ (10 mL, 1M aqueous solution) was added. The reaction mixture was extracted with CH₂Cl₂ (5 x 30 mL). The organic layer was dried over Na₂SO₄, evaporated under *vacuum*, washed with Et₂O and dried, yielding 35 mg (61%) of the desired compound 8A as a dark red solid. M.P.: 303 °C (decomposition). ¹H NMR $(500 \text{ MHz}, \text{CD}_3\text{CN}): \delta 8.64 \text{ (d}, J = 9.2 \text{ Hz}, 1\text{H}, \text{H}-8), 8.51 \text{ (t},$ J = 8.4 Hz, 1H, H-15), 8.45 (d, J = 9.0 Hz, 1H, H-3), 8.41 (d, J = 2.1 Hz, 1H, H-6), 8.34 (dd, J = 8.5, 1.6 Hz, 1H, H-20), 8.18 (ddd, J = 8.7, 7.1, 1.5 Hz, 1H, H-22), 8.00-7.93 (m, 4H, H-9, H-14, H-16, H-23), 7.77 (dd, J = 9.0, 2.2 Hz, 1H, H-4), 7.53 (ddd, J = 8.3, 7.0, 1.2 Hz, 1H, H-21). ¹³C{1H} NMR (126 MHz, CD₃CN): δ 162.6 (C, C-10), 158.4 (C, C-19), 155.6 (C, C-11), 152.6 (C, C-13), 152.2 (C, C-17), 144.5 (CH, C-8), 142.1 (CH, C-22), 141.6 (CH, C-15), 134.0 (C, C-1), 133.0 (CH, C-4), 132.6 (CH, C-6), 131.5 (CH, C-20), 129.0 (C, C-5), 128.8 (CH, C-3), 126.8 (CH, C-21), 123.4* (C, C-2), 120.6 (CH, C-23), 119.9 (CH, C-9), 118.9 (C, C-18), 115.8* (C, C-7), 115.8* (C, C-12), 113.0 (CH, C-14), 112.1 (CH, C-16). ¹⁹F NMR (282 MHz, CD₃CN): δ-151.1, -151.1. **IR** (neat, cm⁻¹): v 3096, 1638, 1579, 1541, 1489. 1378, 1349, 1035, 775. UV-Vis (CH₂Cl₂, C = 2.10^{-5} M): λ_{max} (Log ε): 556 (4.01), 447 (3.83), 362 (4.07), 332 (4.08), 281 (4.08), 239 (4.67). HRMS (ESI) m/z: [M]⁺ Calcd for C₂₃H₁₂BrO₂ 399.0015; Found 399.0016.

Synthesis

14-Bromo-3in 11b(3H)

propylbenzo[*a*]chromeno[2,3,4-*kl*]acridin-11b(3*H*)ylium tetrafluoroborate (10A). To a solution of 13A (100 mg, 0.187 mmol, 1equiv) in acetonitrile (50 mL) propyl amine (0.09 ml, 1.125 mmol, 6 equiv) was added under N_2 atmosphere and the reaction mixture was refluxed for 48 h heat in an oil bath. During this time a colorless solid was formed, filtered and identified as compound 9 (see below).

of

The solution was evaporated, the residue was dissolved in CH₂Cl₂ and washed with HBF₄ (30 mL, 1M aqueous solution). The organic phase was evaporated to dryness and the residue purified by column chromatography on silica gel using CH₂Cl₂/CH₃OH = 100:1. Compound 10A was isolated as a pink powder, 3.4 mg (3%). M.P.: 124 °C. $R_f = 0.19$ (Silica gel, CH₂Cl₂/MeOH, 98:2). ¹H NMR (500 MHz, CD_2Cl_2 : δ 8.47 (d, J = 9.6 Hz, 1H, H-8), 8.40 (d, J = 8.9 Hz, 1H, H-3), 8.35 (t, J = 8.6 Hz, 1H, H-15), 8.23 (d, J = 2.1 Hz, 1H, H-6), 8.14 (d, J = 9.7 Hz, 1H, H-9), 7.98 (dd, J = 8.3, 1.5 Hz, 1H, H-20), 7.96 (d, J = 8.9 Hz, 1H, H-14), 7.84 (ddd, J = 8.6, 7.1, 1.5 Hz, 1H, H-22), 7.78 (dd, J = 8.1, 0.5 Hz, 1H, H-16), 7.70 (dd, J = 8.5, 0.9 Hz, 1H, H-23), 7.60 (dd, J = 8.9, 2.1 Hz, 1H, H-4), 7.28 (ddd, J = 8.3, 7.1, 1.2 Hz, 1H, H-21), 5.06 (ddd, J = 16.7, 10.6, 6.3 Hz, 1H, H_a-24), 4.88 (td, *J* = 10.1, 5.6 Hz, 1H, H_b-24), 2.25-2.13 (m, 2H, H-25), 1.28 (dd, J = 14.4, 6.9 Hz, 3H, H-26). ¹³C{1H} NMR (126 MHz, CD₂Cl₂): δ ¹³C{1H} NMR (126 MHz, CD₂Cl₂) δ: 155.2 (C, C-19), 151.3 (C, C-17), 145.3 (C, C-10), 145.2 (C, C-13), 141.2 (CH, C-8), 137.9 (CH, C-15), 138.0* (C, C-11), 137.7 (CH, C-22), 132.4 (C, C-1), 131.9 (CH, C-4), 131.7 (CH, C-6), 130.2 (CH, C-20), 128.5 (CH, C-3), 128.3 (C, C-5), 125.5 (CH, C-21), 124.0* (C, C-7), 119.7 (CH, C-23), 118.7* (C, C-18), 117.8* (C, C-2), 117.6 (C, C-12), 116.6 (CH, C-9), 111.5 (CH, C-16), 110.5 (CH, C-14), 52.9 (CH₂, C-24), 22.0 (CH₂, C-25), 11.2 (CH₃, C-26). ¹⁹F NMR (282 MHz, CD₂Cl₂): δ -151.2, -151.2. **IR** (neat, cm⁻¹): v 3075, 2928, 1628, 1583, 1547, 1531, 1491, 1350, 1145, 1057, 832, 776, 728. UV-Vis (CH₂Cl₂, C = 2.10⁻⁵ M): λ_{max} (Log ϵ): 556 (4.01), 447(3.83), 362 (4.07), 332 (4.08), 281 (4.67). HRMS (ESI) *m/z*: [M]⁺ Calcd for C₂₆H₁₉BrNO 440.0645; Found 440.0649.

Synthesis of 14-bromo-3.7-dipropyl-3.7-dihydro-11bHbenzo[a]quinolino[2,3,4-kl]acridin-11b-ylium tetrafluoroborate (9A). To a mixture of compound 8A (100 mg, 0.205 mmol), benzoic acid (313 mg, 2.56 mmol, 12.5 equiv) and NMP (0.5 mL) freshly distilled propyl amine (25 equiv, 5.13 mmol) was added in a glass vessel under N₂ atmosphere. The reaction mixture was heated in an oil bath at 140 °C for 22 h. The mixture was dissolved in CH₂Cl₂ washed with HBF_4 (1M aqueous solution, 2 x 5 mL). The organic phase was separated, dried over Na2SO4 and evaporated under vacuum. The crude material was washed with Et₂O (3 x 50 mL). After purification by column chromatography on silica gel using $CH_2Cl_2/MeOH = 98:2$ the desired product 9A (36 mg, 31%) was isolated as an amorphous blue powder. M.P.: 124 °C. $\mathbf{R}_f = 0.29$ (Silica gel, CH₂Cl₂/MeOH, 98:2). ¹H NMR (500 MHz, CD₂Cl₂): δ 8.35-8.28 (m, 2H, H-8, H-15), 8.15 (d, J = 2.1 Hz, 1H, H-6), 7.96 (dd, J = 8.9, 7.2 Hz, 2H, H-9, H-23), 7.92-7.84 (m, 3H, H-22, H-3, H-20), 7.60 (dd, 2H, J = 8.6, 1.7 Hz, H-14, H-16), 7.45 (dd, J = 9.0, 2.1 Hz, 1H, H-4), 7.27 (ddd, *J* = 8.2, 6.8, 1.1 Hz, 1H, H-21), 4.81 (ddd, J = 15.4, 11.2, 5.8 Hz, 1H, H_a-24), 4.72 (ddd, J =15.3, 11.5, 5.5 Hz, 1H, Ha-27), 4.54 (tdd, *J* = 15.5, 11.1, 5.3 Hz, 2H, H_b-24, H_b-27), 2.27-2.06 (m, 4H, H-25, H-28), 1.33-1.22 (m, 6H, H-26, H-29). ¹³C{1H} NMR (126 MHz, CD2Cl2): 8 145.4 (C, C-10), 143.3 (C, C-19), 141.4 (C, C-11), 139.2 (C, C-13), 139.1 (C, C-17), 138.2 (CH, C-8), 137.3 (CH, C-15), 136.9 (CH, C-22), 131.8 (C, C-1), 131.4 (CH, C-6), 131.2 (CH, C-4), 131.1 (CH, C-20), 129.5 (C, C- 5), 126.7 (CH, C-3), 124.0 (CH, C-21), 121.8* (C, C-7), 120.4 (C, C-12), 119.9* (C, C-18), 117.3 (CH, C-23), 116.1 (CH, C-9), 115.0* (C, C-2), 106.7 (CH, C-16), 106.1 (CH, C-14), 52.0 (CH₂, C-24), 51.6 (CH₂, C-27), 20.9 (CH₂, C-25), 20.0 (CH₂, C-28), 11.3 (CH₃, C-29), 11.2 (CH₃, C-26). ¹⁹**F NMR** (282 MHz, CD₂Cl₂): δ –151.2, –151.3. **IR** (neat, cm⁻¹): v 2962, 2927, 2881, 1610, 1584, 1548, 1499, 1343, 1248, 1176, 1051, 908, 881, 761. **UV-Vis** (CH₂Cl₂, C = 2.10⁻⁵ M): λ_{max} (Log ε): 616 (3.94), 372 (4.00), 285 (4.45), 238 (4.61). **HRMS (ESI)** *m/z*: [M]⁺ Calcd for C₂₉H₂₆BrN₂ 481.1274; Found 481.1289.

Synthesis of 3-bromo-12-(2,6-dimethoxyphenyl)-11methoxy-12H-benzo[a]xanthen-12-ol (12B). To a solution of dimethoxybenzene (1.1 mL, 8.44 mmol, 3 equiv), n-BuLi (1.6M in hexane, 4.4 mL, 7.03 mmol, 2.5 equiv) was added dropwise in dry THF (6 mL) under N2 atmosphere at -78 °C. The reaction mixture was allowed to warm slowly to room temperature and stirred for 3 h. Then the solution was cannulated into a premixed solution of activated ketone 11 (The activation was performed as follow: ketone 11 (1.00 g, 2.81 mmol), and anhydrous CeCl₃ (0.90 g, 3.66 mmol, 1.3 equiv) were stirred in dry THF (80 mL) for 24 h at 25 °C). After stirring for 16h, the reaction mixture was quenched with a minimum amount of water. The solvent was evaporated under vacuum and the resulting mixture was dissolved in CH₂Cl₂ (200 mL) and washed with water (2 x 200 mL). The organic layer was dried over Na2SO4 and evaporated under vacuum. The crude mixture was washed with Et₂O and after drying the desired compound 12B was isolated as a colorless solid 1.125 g (82%). M.P.: 254 °C. ¹H NMR (500 MHz, CD_2Cl_2 : δ 8.45 (d, J = 9.3 Hz, 1H, H-3), 7.86 (d, J = 2.2 Hz, 1H, H-6), 7.64 (d, J = 8.9 Hz, 1H, H-8), 7.41-7.34 (m, 1H, H-4), 7.31 (d, *J* = 8.9 Hz, 1H, H-9), 7.21 (t, *J* = 8.2 Hz, 1H, H-15), 7.09 (t, J = 8.3 Hz, 1H, H-21), 6.92 (s, 1H, C-OH), 6.81 (dd, J = 8.3, 1.0 Hz, 1H, H-14), 6.70 (br s, 1H, H-20),6.61 (dd, *J* = 8.2, 0.8 Hz, 1H, H-16), 6.29 (br s, 1H, H-22), 4.18 (br s, 3H, H-25), 3.71 (s, 3H, H-24), 3.06 (br s, 3H, H-26). ¹³C{1H} NMR (126 MHz, CD₂Cl₂): δ 158.0 (3C, C-17, C-19, C-23), 149.7 (C, C-13), 148.3 (C, C-10), 132.7 (C, C-2), 130.6 (C, C-7)*, 130.5 (CH, C-6), 130.5 (2CH, C-20*, C-22*), 129.0 (CH, C-4), 128.9 (CH, C-8), 128.7 (CH, C-21), 128.5 (CH, C-15), 128.4 (CH, C-3), 123.5 (C, C-18), 119.2 (C, C-1), 118.7 (CH, C-9), 117.6 (C, C-12)*, 117.3 (C, C-5)*, 108.8 (CH, C-14), 106.3 (CH, C-16), 71.8 (C, C-11), 56.1 (CH₃, C-25), 56.5 (CH₃, C-24), 56.1 (CH₃, C-26). IR (neat, cm⁻¹): v 3494, 2933, 2841, 1630, 1590, 1468, 1393, 1353, 1301, 1254, 1090, 1025, 1006 cm⁻¹. HRMS (ESI) m/z: $[M - OH]^+$ Calcd for C₂₆H₂₀BrO₄ 475.0540; Found 475.0550.

Synthesis of 3-bromo-12-(2,6-dimethoxyphenyl)-11methoxy-12*H*-benzo[*a*]xanthen-12-ylium tetrafluoroborate (13B). Compound 12B (1.13 g, 2.28 mmol) was dissolved in CH₂Cl₂ (200 mL) and HBF₄ (6 ml, 2.66 equiv, 50% aqueous solution) was added. After stirring for 2 h, the mixture was extracted with CH₂Cl₂, dried over Na₂SO₄ and evaporated under *vacuum*. The desired compound 13B was isolated as a brown solid 1.33 g (99%). M.P.: 256 °C (decomposition). ¹H NMR (500 MHz, CD₂Cl₂): δ 8.68 (d, *J* = 9.2 Hz, 1H, H-8), 8.39 (t, *J* = 8.4 Hz, 1H, H-15), 8.30 (d, *J* = 1.9 Hz, 1H, H-6), 8.17 (d, J = 9.2 Hz, 1H, H-9), 7.89 (dd, J = 8.6, 0.9 Hz, 1H, H-14), 7.71 (t, J = 8.5 Hz, 1H, H-21), 7.68-7.59 (m, 2H, H-3, H-4), 7.29-7.20 (m, 1H, H-16), 6.87 (d, J = 8.5 Hz, 2H, H-20, H-22), 3.71 (s, 3H, H-24), 3.56 (s, 3H6H, H-25, H-26). ¹³C{1H} NMR (126 MHz, CD₂Cl₂): δ 169.2 (C, C-11), 161.6 (C, C-10), 161.5 (C, C-13), 155.9 (C, C-17), 155.7 (2C, C-19, C-23), 147.4 (CH, C-8), 144.2 (CH, C-15), 134.9 (CH, C-4), 133.9 (CH, C-6), 133.9 (CH, C-21), 133.5 (C, C-1), 128.9 (C, C-5), 128.0 (CH, C-3), 124.2 (C, C-2), 122.4 (C, C-7), 119.4 (CH, C-9), 118.8 (C, C-12), 115.8 (C, C-18), 110.8 (CH, C-14), 109.7 (CH, C-16), 105.5 (2CH, C-20, C-22), 57.9 (CH₃, C-24), 56.6 (2CH₃, C-25, C-26). ¹⁹F NMR (282 MHz, CD₂Cl₂): δ -153.2, -153.2. IR (neat, cm⁻¹): v 3300, 2932, 1612, 1588, 1504, 1476, 1432, 1380, 1287, 1260, 1106, 1065, 901, 808, 785, 752 cm⁻¹. UV-**Vis** (CH₂Cl₂, c = 2.10⁻⁵ M): λ_{max} (Log ϵ): 504(3.95), 428 (4.39), 307 (4.64), 207 (4.99). HRMS (ESI) m/z: [M]⁺ Calcd for C₂₆H₂₀BrO₄ 475.0540; Found 475.0541.

Synthesis 14-bromo-11-hydroxy-11bHof benzo[a]chromeno[2,3,4-kl]xanthen-11b-ylium tetrafluoroborate (14B). In an open flask, pyridine hydrochloride (2 g, 50 equiv) was heated 30 min at 225 °C in a heat block for round bottom flask. Then compound 13B (200 mg, 0.355 mmol) was added in one portion and the mixture was stirred for 2 min at this temperature and then HBF₄ (30 mL, 1M aqueous solution) was added. The reaction mixture was extracted with CH₂Cl₂ (5 x 30 mL). The organic layer was dried over Na₂SO₄, evaporated under *vacuum*, washed with Et₂O and dried, yielding 167 mg (93%) of the desired compound **14B** as a brown solid. **M.P.:** 256 °C (decomposition). ¹**H NMR** (500 MHz, CD₃CN): δ 8.57-8.50 (d, 1H, H-8), 8.39 (t, J = 8.4 Hz, 1H, H-15), 8.32 (d, J = 2.1 Hz, 1H, H-6), 8.15(d, J = 9.0 Hz, 1H, H-3), 7.99 (t, J = 8.3 Hz, 1H, H-21), 7.93-7.87 (m, 2H, H-9, H-16), 7.84 (dd, J = 8.4, 0.8 Hz, 1H, H-14), 7.74 (dd, J = 9.0, 2.1 Hz, 1H, H-4), 7.35 (dd, J = 8.4, 1.0 Hz, 1H, H-22), 6.89 (dd, J = 8.2, 1.0 Hz, 1H, H-20). ¹³C{1H} NMR (126 MHz, CD₃CN): δ 161.8 (C, C-10), 159.5 (C, C-19), 159.0 (C, C-23), 152.7 (C, C-18), 152.2 (C, C-13), 151.9 (C, C-17), 144.0 (CH, C-8), 142.9 (CH, C-21), 140.4 (CH, C-15), 133.0 (CH, C-4), 132.2 (CH, C-6), 132.0 (C, C-7), 130.3 (C, C-5), 127.8 (CH, C-3), 122.8 (C, C-2), 119.5 (CH, C-9), 117.1 (C, C-1)*, 116.1 (C, C-12)*, 113.6 (CH, C-22), 112.5 (CH, C-16), 112.2 (C, C-11), 111.9 (CH, C-14), 109.8 (CH, C-20). IR (neat, cm⁻¹): v 2956, 2922, 2857, 1605, 1581, 1503, 1462, 1378, 1344, 1267, 1241, 1056, 908, 810, 785 cm⁻¹. ¹⁹F NMR (282 MHz, CD₃CN): δ -151.1, -151.1 **HRMS** (ESI) m/z: $[M]^+$ Calcd for C₂₃H₁₂BrO₃ 414.9964; Found 414.9951.

Synthesis of 14-bromo-11*H*-benzo[*a*]chromeno[2,3,4*kl*]xanthen-11-one (15B). Compound 14B (50 mg, 0.099 mmol) was dissolved in CH₂Cl₂ (100 mL) and NaHCO₃ (saturated solution in water) was added. After extraction with CH₂Cl₂, the organic layer was dried over Na₂SO₄ and evaporated under *vacuum*. The residue was purified by column chromatography on silica gel using CH₂Cl₂/MeOH = 99:1. The desired compound **15B** was isolated as a dark green solid 26 mg (64%). **M.P.:** 365 °C (decomposition). ¹H NMR (500 MHz, CD₂Cl₂): δ 8.07-8.00 (m, 3H, H-3, H-6, H-8), 7.70 (t, *J* = 8.3 Hz, 1H, H-15), 7.60-7.54 (m, 2H, H-4, H-9),

7.29 (m, 2H, H-14, H-21), 7.21 (dd, J = 8.1, 0.9 Hz, 1H, H-16), 6.21 (dd, J = 9.4, 1.0 Hz, 1H, H-22), 6.15 (dd, J = 7.4, 1.0 Hz, 1H, H-20). ¹³C{1H} NMR (126 MHz, CD₂Cl₂): δ 180.2 (C, C-23), 156.9 (C, C-10), 155.2 (C, C-19), 152.3 (C, C-13), 150.0 (C, C-17), 139.1 (C, C-11), 138.7 (CH, C-21), 136.5 (CH, C-8), 133.8 (CH, C-15), 131.0 (C, C-7), 130.8 (C, C-4), 130.7 (CH, C-6), 128.6 (C, C-1), 128.3 (CH, C-3), 121.7 (CH, C-22), 120.1 (C, C-5), 119.4 (C, C-18), 118.9 (CH, C-9), 113.5 (C, C-2), 113.2 (C, C-12), 110.5 (CH, C-16), 110.0 (CH, C-14), 97.5 (CH, C-20). **IR** (neat, cm⁻¹): v 2924, 2853, 1718, 1620, 1585, 1519, 1502, 1471, 1438, 1334, 1240, 1194, 1151, 1063, 1028, 911, 873, 807, 776, 754 cm⁻¹. UV-Vis (CH₂Cl₂, c = 2.10^{-5} M): λ_{max} (Log ϵ): 654 (3.81), 461 (4.26), 339 (4.26), 308 (4.31), 254 (4.39). **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for C₂₃H₁₁BrO₃ 414.9964; Found 414.9968.

14-bromo-11-methoxy-11bH-**Synthesis** of benzo[*a*]chromeno[2,3,4-*kl*]xanthen-11b-ylium tetrafluoro-borate (8B). To a solution of dioxa [5]helicene 14B (20 mg, 0.040 mmol, 1equiv) in DMF (4 mL) K₂CO₃ (22 mg, 0.200 mmol, 5 equiv) was added under N₂ atmosphere. The reaction mixture was stirred for 1 h and after that CH₃I (0.075 ml, 1.20 mmol 30 equiv) was added. The reaction mixture was stirred for 3 days at 25 °C. The solution was evaporated, the residue was dissolved with CH₂Cl₂ and stirred with HBF4 (3 mL, 50% aqueous solution) under Rayonet UV light. The reaction mixture was extracted with CH₂Cl₂ and precipitated with Et₂O. The solid was dissolved in acetonitrile and NaBH₃CN (12.5 mg, 5 equiv) was added. The crude mixture was evaporated to dryness and the residue purified by column chromatography on silica gel using pen $tane/Et_2O = 97:3$. The neutral compound was dissolved in CH₂Cl₂ and HBF₄ (3 mL, 50% aqueous solution) was added and the reaction mixture was stirred under Rayonet UV light for 30 min. After extraction with CH₂Cl₂, the organic layer was dried over Na₂SO₄ and evaporated under *vacuum* to give compound 8B (8.6 mg, 42%) as a dark red powder. M.P.: 281-283°C (decomposition). ¹H NMR (500 MHz, CD₃CN): δ 8.57 (d, J = 9.1 Hz, 1H, H-8), 8.43 (t, J = 8.4 Hz, 1H, H-15), 8.37 (d, J = 2.0 Hz, 1H, H-6), 8.15 (t, J = 8.4 Hz, 1H, H-21), 8.08 (d, J = 9.0 Hz, 1H, H-3), 7.97 – 7.91 (m, 2H, H-9, H-14), 7.89 (dd, J = 8.4, 0.7 Hz, 1H, H-16), 7.76 (dd, J = 9.0, 2.1 Hz, 1H, H-4), 7.49 (dd, J = 8.5, 0.8 Hz, 1H, H-20), 7.06 (d, J = 8.3 Hz, 1H, H-22), 3.29 (s, 3H, H-24). ¹³C{1H} NMR (126 MHz, CD₃CN): δ 161.8 (C, C-10), 160.1 (C, C-23), 159.4 (C, C-19), 152.6 (C, C-18), 152.0 (C, C-13), 151.9 (C-17), 144.2 (CH, C-8), 143.2 (CH, C-21), 140.5 (CH, C-15), 133.1 (CH, C-4), 132.5 (CH, C-6), 132.1 (C, C-7), 130.2 (C, C-5), 127.0 (CH, C-3), 122.8 (C, C-2), 119.6 (CH, C-9), 117.2 (C, C-1), 116.3 (C, C-12), 112.5 (CH, C-14), 112.4 (C, C-11), 112.1 (CH, C-16), 111.3 (CH, C-22), 109.0 (CH, C-20), 56.8 (CH₃, C-24). ¹⁹F NMR (282 MHz, CD₂Cl₂): δ -151.9, -151.9. **IR** (neat, cm⁻¹): v 3088, 2925, 1637, 1602, 1582, 1508, 1473, 1381, 1348, 1286, 1228, 1197, 1053, 812, 776 cm⁻¹. UV-Vis (CH₂Cl₂, c = 10⁻⁵M): λ_{max} (Log ε): 575 (3.77), 488 (3.88), 439 (3.93), 356 (3.80), 318 (4.13), 286 (4.05). HRMS (ESI) *m/z*: [M]⁺ Calcd for C₂₄H₁₄BrO₃ 429.0121; Found 429.0126.

Synthesis of 3-bromo-12-(2,6-dimethoxyphenyl)-11methoxy-N-propyl-12*H*-benzo[*a*]xanthen-12-amine

(16B). To a solution of 13B (50 mg, 0.089 mmol, 1 equiv) in acetonitrile (10 mL) propyl amine (0.04 ml, 0.534 mmol, 6 equiv) was added. After 5 min colourless solid was formed, filtered and identified as compound 16B (40 mg, 84%). M.P.: 144-146°C. ¹H NMR (500 MHz, CD₃CN): δ 9.04 (d, J = 9.4 Hz, 1H, H-3), 7.78 (d, J = 2.2 Hz, 1H, H-6), 7.56 (m, 1H, H-8), 7.24 (dd, J = 9.4, 2.2 Hz, 1H, H-4), 7.21 (d, J= 8.8 Hz, 1H, H-9), 7.14 (t, J = 8.2 Hz, 1H, H-15), 7.04 (t, J = 8.3 Hz, 1H, H-21), 6.72 (dd, J = 8.2, 1.1 Hz, 1H, H-21)14), 6.66 (dd, J = 8.5, 1.2 Hz, 1H, H-20), 6.54 (dd, J = 8.1, 1.1 Hz, 1H, H-16), 6.23 (dd, J = 8.2, 1.2 Hz, 1H, H-22), 4.24 (s, NH), 4.10 (s, 3H, H-25), 3.62 (s, 3H, H-24), 2.98 (s, 3H, H-26), 2.02 – 1.90 (m, 1H, H-27), 1.80 (dt, J = 10.5, 6.6 Hz, 1H, H-27), 1.21 (qd, J = 6.6, 1.2 Hz, 2H, H-28), 0.67 (t, J = 7.4 Hz, 3H, H-29). ¹³C{1H} NMR (126 MHz, CD₂Cl₂): δ 158.9 (C, C-19), 158.7 (C, C-23), 157.8 (C, C-17), 151.5 (C, C-13), 149.7 (C, C-10), 132.7 (C, C-2), 130.8 (C, C-7), 130.1 (CH, C-3), 129.9 (CH, C-6), 128.4 (CH, C-8), 128.1 (CH, C-21), 127.9 (CH, C-4), 127.6 (CH, C-15), 125.3 (C, C-18), 119.4 (C, C-1), 118.1 (CH, C-9), 117.1 (C, C-5), 115.9 (C, C-12), 108.2 (CH, C-14), 107.6 (CH, C-20), 106.2 (CH, C-16), 105.6 (CH, C-22), 61.2 (C, C-11), 56.6 (CH₃, C-25), 56.1 (CH₃, C-24), 56.0 (CH₃, C-26), 45.9 (CH₂, C-27), 24.2 (CH₂, C-28), 12.1 (CH₃, C-29). **IR** (neat, cm⁻¹): v 3300, 2932, 1612, 1588, 1504, 1476, 1432, 1380, 1287, 1260, 1106, 1065, 901, 808, 785, 752 cm⁻¹. HRMS (ESI) *m/z*: [M - NHPr]⁺ Calcd for C₂₆H₂₀BrO₄ 475.0540; Found 475.0542. Synthesis of 3-bromo-12-(2-hydroxy-6-methoxyphenyl)-11-methoxy-7-propyl-7,12-dihydrobenzo[a]-acridin-12vlium tetrafluoroborate (19B). The mixture of the compound 13B (100 mg, 0.177 mmol) and freshly distilled propyl amine (0.44 ml, 5.26 mmol, 45 equiv) was stirred at room temperature for 2 days. The crude mixture was dissolved in CH_2Cl_2 and washed with HBF₄ (1 M aqueous solution, 2 x 5mL). The organic phase was separated, dried over Na₂SO₄ and evaporated under vacuum. The residue was purified by column chromatography on silica gel using CH₂Cl₂/MeOH = 98:2. It was isolated product 19B (31 mg, 25%) as a yellow powder along with product 10B (15 mg, 13%). Data for 19B: M.P.: 191 °C (decomposition). ¹H NMR (500 MHz, CD₂Cl₂): δ 8.37 (d, J = 9.6 Hz, 1H, H-8), 8.18 (dd, J = 9.0, 8.1 Hz, 1H, H-15), 8.14 (d, J = 2.3 Hz, 1H, H-6), 8.06 (d, J = 9.7 Hz, 1H. H-9), 7.81 (d, J = 8.9 Hz, 1H, H-14), 7.74 (d, J = 9.3 Hz, 1H, H-3), 7.49-7.43 (m, 2H, H-4, H-21), 7.15 (d, J = 8.0 Hz, 1H, H-16), 6.80 (dd, J = 8.3, 0.6 Hz, 1H, H-20), 6.66 (d, J = 8.3 Hz, 1H, H-22), 6.58 (s, 1H, OH), 5.11-5.03 (m, 2H, H-26), 3.67 (s, 3H, H-24), 3.44 (s, 3H, H-25), 2.33 (dd, J = 16.9, 7.6 Hz, 2H, H-27), 1.36 (t, J = 7.4 Hz, 3H, H-28). ¹³C{1H} NMR (126 MHz, CD₂Cl₂): δ 161.0 (C, C-17), 156.6 (C, C-19), 153.5 (C, C-23), 153.3 (C, C-11), 143.7 (C, C-10), 141.6 (CH, C-8), 140.3 (C, C-13), 138.8 (CH, C-15), 132.7 (2CH, C-4, C-21), 132.2 (CH, C-6), 132.0 (CH, C-3), 129.6 (2C, C-2, C-7), 125.4 (C, C-1), 123.6 (C, C-5), 121.3 (C, C-12), 116.9 (C, C-18), 116.4 (CH, C-9), 110.4 (CH, C-20), 109.0 (CH, C-14), 108.2 (CH, C-22), 103.8 (CH, C-16), 57.5 (CH₃, C-24), 56.2 (CH₃, C-25), 54.7 (CH₂, C-26), 22.5 (CH₂, C-27), 11.2 (CH₃, C-28). ¹⁹F NMR (282 MHz, CD₂Cl₂): δ –151.6, –151.7. IR (neat, cm⁻¹): v 3401, 2941, 2350, 1609, 1591, 1517, 1469, 1344, 1265, 1148, 1078, 780,

748 cm⁻¹. UV-Vis (CH₂Cl₂, c = 2.10⁻⁵ M): λ_{max} (Log ε): 404

(4.14), 324 (4.53), 304 (4.60). HRMS (ESI) *m*/*z*: [M]⁺ Calcd for C₂₈H₂₅BrNO₃ 502.1012; Found 502.0996.

Svnthesis 14-bromo-11-methoxy-3of propylbenzo[a]chromeno[2,3,4-kl]acridin-11b(3H)ylium tetrafluoroborate (10B). The mixture of the compound 13B (100 mg, 0.177 mmol) and freshly distilled propyl amine (0.37 ml, 4.44 mmol, 25 equiv) was stirred at room temperature for 3 days. After that, CH₃CN was added and the reaction mixture was reflux for 15 min heat in an oil bath. The crude was purified by column chromatography on silica gel using $CH_2Cl_2/MeOH = 95:5$. The desired product 10B (52 mg, 53%) was isolated as a pink powder. M.P.: 146 °C (decomposition). ¹H NMR (500 MHz, CD₂Cl₂): δ 8.43 (d, J = 9.6 Hz, 1H, H-8), 8.29 (dd, J = 8.9, 8.1 Hz, 1H, H-)15), 8.21 (d, J = 2.1 Hz, 1H, H-6), 8.12 (m, 2H, H-3, H-9), 7.96 (d, J = 8.8 Hz, 1H, H-14), 7.82 (t, J = 8.3 Hz, 1H, H-21), 7.72 (dd, J = 8.0, 0.7 Hz, 1H, H-16), 7.57 (dd, J = 8.9, 2.1 Hz, 1H, H-4), 7.30 (dd, J = 8.4, 1.0 Hz, 1H, H-20), 6.78 (dd, J = 8.4, 0.9 Hz, 1H, H-22), 5.05 (ddd, J = 15.3, 10.8, 6.2 Hz, 1H, H_a-24), 4.87 (ddd, J = 15.9, 10.7, 6.0 Hz, 1H, H_b-24), 3.18 (s, 3H, H-27), 2.26-2.13 (m, 2H, H-25), 1.29 (t, J = 7.4 Hz, 6H, H-26). ¹³C{1H} NMR (126 MHz, CD₂Cl₂): δ 157.7 (C, C-23), 156.6 (C, C-19), 150.9 (C, C-17), 144.5 (C, C-10), 142.0 (C, C-11), 141.1 (CH, C-8), 138.3 (CH, C-21), 137.5 (C, C-13), 137.0 (CH, C-15), 132.0 (CH, C-4), 131.4 (CH, C-6), 130.4 (C, C-2), 130.3 (C, C-7), 125.4 (CH, C-3), 123.2 (C, C-5), 119.5 (C, C-1), 118.5 (C, C-12), 116.4 (CH, C-9), 111.1 (CH, C-14), 110.6 (CH, C-20), 110.4 (CH, C-16), 107.7 (CH, C-22), 55.6 (CH₃, C-27), 30.1 (CH₂, C-24), 22.1 (CH₂, C-25), 11.2 (CH₃, C-26). In this case (C18) was not detected neither on ¹³C, HSQC or HMBS. ¹⁹F NMR (282 MHz, CD₂Cl₂): δ –151.0, –151.1. **IR** (neat, cm⁻¹): v 2967, 2925, 1627, 1587, 1528, 1474, 1390, 1349, 1259, 1189, 1047, 955, 883, 809, 779, 708, 675 cm⁻¹. UV-Vis (CH₂Cl₂, c $= 2.10^{-5}$ M): λ_{max} (Log ε): 529 (3.73), 411 (3.78), 335 (4.24), 265 (4.36). HRMS (ESI) m/z: [M]⁺ Calcd for C₂₇H₂₁BrNO₂ 470.0750; Found 470.0742.

Synthesis of substituted diaza [5]helicenes. The mixture of compound 13B (150 mg, 0.266 mmol), benzoic acid (406 mg, 3.33 mmol, 12.5 equiv) and freshly distilled propyl amine (0.55 ml, 6.66 mmol, 25 equiv) was stirred at room temperature for 5 days. After that, NMP (1mL) was added and the reaction mixture was heated at 90 °C for 5 h in an oil bath. The mixture was dissolved in CH2Cl2 washed with HBF₄ (1M aqueous solution, 2 x 15mL). The organic phase was separated, dried over Na2SO4 and evaporated under vacuum. The crude material was washed three times with 50 ml Et₂O. The crude was purified by column chromatography on silica gel using $CH_2Cl_2/MeOH = 98:2$. After that the isolated compounds were dissolved in CH₂Cl₂ and washed with 1M KPF_6 to exchange the anion. The residue was purified by column chromatography on silica gel using CH₂Cl₂/Me₂CO = 97:3. The products **9B** (62 mg, 39%) and **17B** (8 mg, 5%) were isolated as amorphous blue solids. The mother liquor from the precipitation with ether was evaporated under vacuum, after that dissolved in CH₂Cl₂ and washed NaHCO₃ (three times) after that again with 1M HBF₄. The crude material was washed three times with 50 ml Et₂O. After that the isolated compound was dissolved in CH₂Cl₂ and washed with 1M KPF₆ to exchange the anion. The residue was

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purified by column chromatography on silica gel using $CH_2Cl_2/Me_2CO=98:2$. The product **18B** (4 mg, 2%) was isolated as an amorphous purple solid.

14-bromo-11-methoxy-3,7-dipropyl-3,7-dihydro-11bHbenzo[a]quinolino[2,3,4-kl]acridin-11b-ylium tetrafluoroborate (9B). M.P.: 165 °C (decomposition). ¹H NMR (500 MHz, CD₂Cl₂): δ 8.29-8.24 (m, 2H, H-8, H-15), 8.15 (d, *J* = 2.1 Hz, 1H, H-6), 7.97-7.93 (m, 1H, H-21), 7.93-7.89 (m, 1H, H-9), 7.79 (d, *J* = 9.0 Hz, 1H, H-3), 7.62 (d, *J* = 8.5 Hz, 1H, H-14), 7.56 (d, *J* = 8.5 Hz, 1H, H-16), 7.46 (dd, *J* = 9.0, 2.1 Hz, 1H, H-4), 7.43 (d, J = 8.8 Hz, 1H, H-20), 6.71 (d, J = 8.0 Hz, 1H, H-22), 4.82 (ddd, *J* = 15.3, 11.5, 5.7 Hz, 1H, H_{a} -25), 4.65 (m, 1H, H_{a} -28), 4.58 (q, J = 5.3, 4.7 Hz, 1H, H_{b} -25), 4.42 (td, J = 11.0, 10.5, 5.7 Hz, 1H, H_b-28), 3.06 (s, 3H, H-24), 2.28 - 2.10 (m, 4H, H-26, H-29), 1.31-1.25 (m, 6H, H-27, H-30). ¹³C{1H} NMR (126 MHz, CD₂Cl₂): δ 158.0 (C, C-23), 143.0 (C, C-11), 142.1 (C, C-19), 141.8 (C, C-10), 139.0 (C, C-13), 138.6 (C, C-17), 137.9 (CH, C-8), 137.8 (CH, C-9), 136.5 (CH, C-15), 131.6 (CH, C-4), 131.1 (CH, C-6), 131.1 (C, C-5), 130.0 (C, C-2), 123.2 (CH, C-3), 121.5 (C, C-7), 121.0 (C, C-12), 118.0 (C, C-1), 116.0 (CH, C-21), 112.3 (C, C-18), 108.6 (CH, C-20), 106.4 (CH, C-14), 106.1 (CH, C-16), 105.1 (CH, C-22), 55.3 (CH₃, C-24), 52.3 (CH₂, C-25), 52.1 (CH₂, C-28), 21.1 (CH₂, C-26), 20.0 (CH₂, C-29), 11.3 (CH₃, C-27)*, 11.2 (CH₃, C-30)*. ¹⁹F NMR (282 MHz, CD_2Cl_2) δ –152.5, –152.5. IR (neat, cm⁻¹): v 2971, 2931, 2881, 1605, 1580, 1548, 1524, 1342, 1260, 1178, 1162, 1054, 777, 756 cm⁻¹. UV-Vis (CH₂Cl₂, c = 2.10⁻ ⁵M): λ_{max} (Log ε): 621 (4.30), 367 (4.42), 306 (4.38), 282 (4.63). HRMS (ESI) m/z: [M]⁺ Calcd for C₃₀H₂₈BrN₂O 511.1380; Found 511.1367.

14-bromo-11-hydroxy-3,7-dipropyl-3,7-dihydro-11bHbenzo[a]quinolino[2,3,4-kl]acridin-11b-ylium tetrafluoroborate (17B). M.P. 183 °C (decomposition). ¹H NMR (500 MHz, CD₂Cl₂): δ 8.25 – 8.19 (m, 1H, H-8), 8.17 (m, 1H, H-15), 8.05 (d, J = 2.2 Hz, 1H, H-6), 7.89 (d, J = 9.1 Hz, 1H, H-3), 7.85 (d, J = 9.6 Hz, 1H, H-9), 7.76 (m, 1H, H-21), 7.53 (d, J = 8.6 Hz, 1H, H-16), 7.47 - 7.39 (m, 2H, H-4. H-14),7.25 (d, J = 8.7 Hz, 1H, H-20), 6.73 (br s, 1H, H-22), 4.76 $(td, J = 11.5, 11.0, 5.8 Hz, 1H, H_a-24), 4.56 (m, 2H, H_b-24)$ H_a -27), 4.35 (td, J = 10.4, 5.6 Hz, 1H, H_b -27), 2.27 – 2.12 (m, 4H, H-25, H-28), 1.32 – 1.22 (m, 6H, H-26, H-29). ¹³C{1H} NMR (126 MHz, CD₂Cl₂): δ 156.9 (C, C-11)*, 142.7 (C, C-23), 142.6 (C, C-19), 141.9 (C, C-10), 139.1 (C, C-13), 138.5 (C, C-17), 137.9 (2CH, C-8, C-21), 136.0 (CH, C-15), 131.7 (CH, C-4), 131.2 (C, C-7), 130.9 (CH, C-6), 130.1 (C, C-1), 123.5 (CH, C-3), 121.6 (C, C-5), 120.6 (C, C-12), 117.9 (C, C-2), 115.6 (CH, C-9), 112.3 (C, C-18), 110.7 (CH, C-22), 106.6 (CH, C-20), 105.8 (CH, C-14), 105.4 (CH, C-16), 52.4 (CH₂, C-24), 51.9 (CH₂, C-27), 21.0 (CH₂, C-25), 19.8 (CH₂, C-28), 11.3 (CH₃, C-26*), 11.3 (CH₃, C-29*). ¹⁹F NMR (282 MHz, CD₂Cl₂): δ –151.4, -151.5. IR (neat, cm⁻¹): v 3377, 2929, 1607, 1583, 1526, 1504, 1544, 1260, 1176, 1160, 1067, 778, 754 cm⁻¹. UV-Vis $(CH_2Cl_2, c = 2.10^{-5}M): \lambda_{max} (Log \epsilon): 623 (4.00), 368 (4.14),$ 281 (4.41). HRMS (ESI) m/z: [M]+ Calcd for C₂₉H₂₆BrN₂O 497.1207; Found 497.1223.

14-bromo-3,7-dipropyl-11-(propylamino)-3,7-dihydro-11b*H*-benzo[*a*]quinolino[2,3,4-*kl*]acridin-11b-ylium

tetrafluoroborate (18B). M.P.: 137-140 °C (decomposition). ¹H NMR (500 MHz, CD₂Cl₂): δ 8.24 (d, J = 9.5 Hz, 1H. H-8), 8.18 (t, J = 8.5 Hz, 1H, H-15), 8.11 (d, J = 2.0 Hz, 1H, H-6), 7.97 (d, *J* = 9.5 Hz, 1H, H-9), 7.94 (d, *J* = 9.1 Hz, 1H, H-3), 7.76 (t, *J* = 8.4 Hz, 1H, H-21), 7.53 (d, *J* = 8.5 Hz, 1H, H-14), 7.49 (d, J = 8.5 Hz, 1H, H-16), 7.44 (dd, J = 9.1, 2.1 Hz, 1H, H-4), 6.95 (d, J = 8.5 Hz, 1H, H-22), 6.37 (d, J = 8.2 Hz, 1H, H-20), 4.85 – 4.77 (m, 1H, Ha-27), 4.62 – 4.54 (m, 1H, H_{b} -27), 4.52 – 4.46 (m, 1H, H_{a} -24), 4.42 – 4.30 (m, 1H, H_b -24), 2.70 (dq, J = 8.4, 6.3 Hz, 1H, H_a -30), 2.45 – 2.36 (m, 1H, H_b-30), 2.26 - 2.08 (m, 4H, H-25, H-28), 1.29 (t, J = 7.4Hz, 3H, H-29), 1.25 (t, J = 7.3 Hz, 3H, H-26), 0.82 (dt, J = 14.7, 7.2 Hz, 2H, H-31), 0.53 (t, J = 7.4 Hz, 3H, H-32). ¹³C{1H} NMR (126 MHz, CD₂Cl₂): δ 148.3 (C, C-23), 142.8 (C, C-11), 142.7 (C, C-10), 142.1 (C, C-19), 138.9 (d, C-21), 138.9 (C, C-13), 138.4 (C, C-17), 137.2 (CH, C-8), 135.9 (CH, C-15), 131.6 (CH, C-4), 131.0 (CH, C-6), 130.4 (C, C-2), 128.8 (C, C-5), 123.1 (CH, C-3), 121.8 (C, C-7), 120.6 (C, C-12), 117.4 (CH, C-9), 113.6 (C, C-1), 109.5 (C, C-18), 106.3 (CH, C-16), 105.6 (CH, C-14), 103.6 (CH, C-22), 101.9 (CH, C-20), 52.4 (CH₂, C-27), 51.8 (CH₂, C-24), 45.6 (CH₂, C-30), 21.7 (CH₂, C-28), 21.0 (CH₂, C-31), 19.8 (CH₂, C-25), 11.3 (CH₃, C-29), 11.3 (CH₃, C-26), 11.2 (CH₃, C-32). ¹⁹F NMR (282 MHz, CD₂Cl₂): δ –152.3, –152.3. IR (neat, cm⁻¹): v 3393, 2947, 1677, 1612, 1588, 1521, 1494, 1333, 1275, 1162, 1054, 874, 824, 754 cm⁻¹. UV-Vis $(CH_2Cl_2, c = 2.10^{-5}M): \lambda_{max} (Log \epsilon): 639 (3.85), 571 (4.03),$ 368 (4.19), 315 (4.29), 280 (4.49). HRMS (ESI) m/z: [M]+ Calcd for C₃₂H₃₃BrN₃ 538.1852; Found 538.1827.

General procedure for *Suzuki* coupling reactions. In a Schlenk flask, Pd(PPh₃)₄ (0.1 equiv) and the appropriate boronic acid (1.25 equiv) were added to a solution of compound **8** in 1,4-dioxane (4 mL) under N₂ atmosphere. To this mixture K₂CO₃ (4 equiv) dissolved in water (2 mL) was added. The reaction mixture was stirred for 16 h at 80 °C in an oil bath. After completion of the reaction, the crude mixture was cooled down to room temperature, diluted with CH₂Cl₂ (5 mL), and washed with HBF₄ (15 mL, 1M aqueous solution). The organic layer was dried, evaporated and the residue washed with Et₂O to give the corresponding product.

Synthesis of 14-Phenyl-11bH-benzo[a]chromeno[2,3,4kl]xanthen-11b-ylium tetrafluoroborate (20a). Following the general procedure for Suzuki coupling, compound 8A (50 mg, 0,103 mmol, 1 equiv), phenyl boronic acid (16 mg, 0.129 mmol, 1.25 equiv), Pd(PPh₃)₄ (12 mg, 0.0103 mmol, 0.1 equiv) and K₂CO₃ (57 mg, 0.410 mmol, 4 equiv) were stirred. After work up the desired compound 20a (44.5 mg, 90%) was isolated as purple solid. M.P.: 298 °C (decomposition). ¹**H NMR** (500 MHz, CD₃CN): δ 8.78 (d, *J* = 9.1 Hz, 1H, H-8), 8.66 (d, J = 8.7 Hz, 1H, C-3), 8.50 (t. J = 8.4 Hz, 1H, H-15); 8.48 (d, 1H, H-6), 8.45 (dd, *J* = 8.4, 1.6 Hz, 1H, H-20), 8.17 (ddd, J = 8.5, 7.0, 1.5 Hz, 1H, H-22), 8.01-7.93 (m, 5H, H-4, H-9, H-14, H-16, H-23), 7.88 (d 2H, J = 7.4, H-25, H-29), 7.58 (t, 2H, J = 7.4, H-26, H-28), 7.55-7.46 (m , 2H, H-21, H-27). ¹³C{1H} NMR (126 MHz, CD₃CN): δ 162.9 (C, C-10), 158.3 (C, C-19), 155.2 (C, C-11), 152.5 (C, C-13), 152.3 (C, C-17), 146.3 (CH, C-8), 142.4 (C, C-24), 141.9 (CH, C-22), 141.2 (CH, C-15), 139.7 (C, C-5), 133.3* (C, C-7), 131.5 (CH, C-20), 130.3 (2CH, C-26, C-28), 129.6 (CH, C-4), 129.1* (C, C-2), 129.1 (CH, C-27), 128.1 (2CH, C-25, C-29), 128.1 (CH, C-6), 127.7 (CH, C-3), 126.6 (CH, C-21), 120.6 (CH, C-23), 119.0 (CH, C-9), 119.0 (C, C-18), 116.0* (C, C-12), 115.6* (C, C-1), 112.9 (CH, C-14), 112.0 (CH, C-16). ¹⁹**F NMR** (282 MHz, CH₃CN): δ –151.0, –151.1. **IR** (neat, cm⁻¹): v 3086, 2920, 1638, 1580, 1496, 1376, 1346, 1052, 771, 699. **UV-Vis** (CH₂Cl₂, C = 2.10⁻⁵ M): λ_{max} (Log ϵ): 570 (3.93), 463 (3.69), 338 (4.15), 264 (4.64). **HRMS (ESI)** *m*/*z*: [M]⁺ Calcd for C₂₉H₁₇O₂ 397.1223; Found 397.1224.

Synthesis of 14-(4-Nitrophenvl)-11bHbenzo[a]chromeno[2,3,4-kl]xanthen-11b-ylium tetra**fluoroborate** (20b). Following the general procedure for Suzuki coupling, compound 8A (50 mg, 0.103 mmol, 1 equiv), 4-Nitrophenylboronic acid (21 mg, 0.129 mmol, 1.25 equiv), Pd(PPh₃)₄ (12 mg, 0.0103 mmol, 0.1 equiv) and K₂CO₃ (57 mg, 0.410 mmol, 4 equiv) were stirred. After work up the desired compound 20b (49.6 mg, 92%) was isolated as red solid. M.P.: 253 °C (decomposition). ¹H NMR (500 MHz, CD₃CN): δ 8.77 (d, J = 9.1 Hz, 1H, H-8), 8.64 (d, J = 8.7 Hz, 1H, H-3), 8.53-8.47 (m, 2H, H-6, H-15), 8.40-8.33 (m, 3H, H-20, H-26, H-28), 8.17 (ddd, J = 8.7, 7.1, 1.5 Hz, 1H, H-22), 8.06-8.01 (m, 2H, H-25, H-29), 8.00-7.92 (m, 5H, H-4, H-9, H-14, H-16, H-23), 7.51 (ddd, J = 8.3, 7.0, 1.2 Hz, 1H, H-21). ¹³C{1H} NMR (126 MHz, CD₃CN): δ 163.0 (C, C-10), 158.4 (C, C-19), 155.4 (C, C-11), 152.5 (C, C-13), 152.2 (C, C-17), 148.8 (C, C-27), 146.1 (CH, C-8), 146.0 (C, C-24), 142.1 (CH, C-22), 141.5 (CH, C-15), 139.8 (C, C-5), 133.1 (C, C-1), 131.5 (CH, C-20), 130.0* (C, C-7), 129.1 (CH, C-6), 129.1 (2CH, C-25, C-29), 128.9 (CH, C-4), 127.9 (CH, C-3), 126.7 (CH, C-21), 125.3 (2CH, C-26, C-28), 120.6 (CH, C-23), 119.4 (CH, C-9), 118.9* (C, C-18), 115.8* (C, C-2), 115.6* (C, C-12), 113.0 (CH, C-14), 112.1 (CH, C-16). ¹⁹F NMR (282 MHz, CD₃CN): δ -151.1, -151.2. **IR** (neat, cm⁻¹): v 3089, 1638, 1579, 1498, 1376, 1343, 1277, 1241, 1052, 841, 772. UV-Vis (CH_2Cl_2 , C = 2.10⁻⁵ M): λ_{max} (Log ε): 563 (4.08), 457 (3.88), 341 (4.52), 268 (4.34). HRMS (ESI) m/z: [M]⁺ Calcd for C₂₉H₁₆NO₄ 442.1074; Found 442.1069.

Synthesis of 14-(3-Nitrophenyl)-11bHbenzo[a]chromeno[2,3,4-kl]xanthen-11b-ylium tetrafluoroborate (20c). Following the general procedure for Suzuki coupling, compound 8A (40 mg, 0.082 mmol, 1 equiv), 3-Nitrophenvl boronic acid (17 mg, 0.103 mmol, 1.25 equiv), Pd(PPh3)₄ (9 mg, 0.008 mmol, 0.1 equiv) and K₂CO₃ (45 mg, 0.410 mmol, 4 equiv) were stirred. After work up the desired compound **20c** (36.8 mg, 86%) was isolated as red solid. M.P.: 254 °C (decomposition). ¹H NMR (500 MHz, CD₃CN): δ 8.80 (d, J = 9.1 Hz, 1H, H-8), 8.70-8.65 (m, 2H, H-25, H-3), 8.56 (d, J = 2.0 Hz, 1H, H-6), 8.51 (t, J = 8.4 Hz, 1H, H-15), 8.42 (dd, J = 8.5, 1.5 Hz, 1H, H-20), 8.31 (ddd, *J* = 8.2, 2.3, 1.0 Hz, 1H, H-27), 8.25 (ddd, *J* = 7.8, 1.8, 1.0 Hz, 1H, H-29), 8.19 (ddd, J = 8.7, 7.1, 1.6 Hz, 1H, H-22), 8.02 (dd, J = 8.8, 2.1 Hz, 1H, H-4), 8.00-7.95 (m, 4H, H-9, H-14, H-16, H-23), 7.81 (t, J = 8.0 Hz, 1H, H-28), 7.25 (t, 1H, H-21). ¹³C{1H} NMR (126 MHz, CD₃CN): δ 163.0 (C, C-10), 158.4 (C, C-19), 155.4 (C, C-11), 152.5 (C, C-13), 152.2 (C, C-17), 150.0 (C, C-26), 146.1 (CH, C-8), 146.1 (C, C-7)*, 142.0 (CH, C-22), 141.4 (CH, C-15), 139.9 (C, C-24), 134.3 (CH, C-27), 133.2 (C, C-1), 131.5 (2CH, C-20, C-28), 129.8 (C, C-5), 128.9 (CH, C-4), 128.8 (CH, C-6), 128.0 (CH, C-3), 126.7 (CH, C-21), 124.1 (CH, C-29), 122.8 (CH, C-25), 120.6 (CH, C-23), 119.3 (CH, C-9), 119.0 (C, C-18), 115.8* (C, C-12), 115.7* (C, C-2), 113.0 (CH, C-14), 112.1 (CH, C-16). ¹⁹**F** NMR (282 MHz, CD₃CN): δ -151.1, -151.2. **IR** (neat, cm⁻¹): v 3083, 2925, 2852, 1741, 1637, 1601, 1580, 1496, 1374, 1347, 1281, 1243, 1053, 769, 735. **UV-Vis** (CH₂Cl₂, C = 2.10⁻⁵ M): λ_{max} (Log ϵ): 563 (3.99), 458 (3.77), 361 (3.99), 334 (4.22), 268 (4.52). **HRMS (ESI)** *m/z*: [M]⁺ Calcd for C₂₉H₁₆NO₄ 442.1074; Found 442.1084.

Synthesis 14-(4-Methoxyphenyl)-11bHof benzo[a]chromeno[2,3,4-kl]xanthen-11b-ylium tetrafluoroborate (20d). Following the general procedure for Suzuki coupling, compound 8A (50 mg, 0.103 mmol, 1 equiv), 4-Methoxyphenyl boronic acid (19 mg, 0.129 mmol, 1.25 equiv), Pd(PPh₃)₄ (12 mg, 0.0103 mmol, 0.1 equiv) and K₂CO₃ (57 mg, 0.410 mmol, 4 equiv) were stirred. After work up the desired compound 20d (50.1 mg, 95%) was isolated as purple solid. M.P.: 182 °C (decomposition). ¹H **NMR** (400 MHz, CD₃CN): δ 8.76 (d, J = 9.2 Hz, 1H, H-8), 8.62 (d, J = 8.8 Hz, 1H, H-3), 8.49 (t, J = 8.5 Hz, 1H, H-15),8.46-8.38 (m, 2H, H-20, H-6), 8.16 (t, J = 1.6 Hz, 1H, H-22), 7.99-7.91 (m, 5H, H-4, H-9, H-14, H-16, H-23), 7.86-7.77 (m, 2H, H-26, H-28), 7.51 (ddd, J = 8.3, 7.1, 1.2 Hz, 1H, H-21), 7.17-7.07 (m, 2H, H-25, H-29), 3.88 (s, 3H, H-30). ¹³C{1H} NMR (101 MHz, CD₃CN): δ 162.7 (C, C-10), 161.2 (C, C-27), 158.2 (C, C-19), 154.9 (C, C-11), 152.4 (C, C-13), 152.2 (C, C-17), 146.3 (CH, C-8), 142.0 (C, C-24), 141.8 (CH, C-22), 141.1 (CH, C-15), 133.3 (C, C-1), 131.8 (C, C-5), 131.4 (CH, C-20), 129.2 (2CH, C-26, C-28), 128.6 (CH, C-4), 128.4* (C, C-7), 127.6 (CH, C-3), 127.2 (CH, C-6), 126.5 (CH, C-21), 120.6 (CH, C-23), 118.9 (C, C-18), 118.8 (CH, C-9), 116.0* (C, C-2), 115.6 (2CH, C-25, C-29) 115.5* (C, C-12), 112.8 (CH, C-14), 112.0 (CH, C-16), 56.1 (CH₃, C-30). ¹⁹F NMR (282 MHz, CH₃CN): δ -151.1, -151.2. **IR** (neat, cm⁻¹): v 3077, 2926, 2858, 1637, 1603. 1580, 1498, 1374, 1348, 1279, 1250, 1183, 1054, 833, 777, 731. UV-Vis (CH₂Cl₂, C = 2.10⁻⁵ M): λ_{max} (Log ϵ): 581 (3.90), 456 (3.72), 340 (4.23), 269 (4.60). HRMS (ESI) m/z: [M]⁺ Calcd for C₃₀H₁₉O₃ 427.1329; Found 427.1325.

General procedure for *Suzuki* coupling with styryl boronic acids. In a Schlenk flask PPh₃ (0.3 equiv), Pd(OAc)₂ (0.1 equiv), and the appropriate styryl boronic acid (5 equiv) were added to a solution of compound **8A** in 1,4-dioxane (2 mL) under N₂ atmosphere. To this mixture K₂CO₃ (5 equiv) dissolved in water (2 mL) was added. The reaction mixture was stirred for 3 h at 90 °C in an oil bath. After completion of the reaction, the crude mixture was cooled down to room temperature, extracted with CH₂Cl₂ and washed with HBF₄ (15 mL, 1M aqueous solution). The organic layer was evaporated to dryness to remove all volatiles. The residue was washed with toluene (3 x 20 mL) and Et₂O (2 x 30 mL) to give the corresponding product.

Synthesisof(E)-14-styryl-11bH-benzo[a]chromeno[2,3,4-kl]xanthen-11b-yliumtetra-fluoroborate (21a). Following the general procedure for Su-zuki coupling, compound 8A (50 mg, 0103 mmol, 1 equiv),

(E)-styryl boronic acid (75 mg, 0.129 mmol, 1.25 equiv), Pd(OAc)₂ (12 mg, 0.0103 mmol, 0.1 equiv) and K₂CO₃ (57 mg, 0.410 mmol, 4 equiv) were stirred. After work up the desired compound 21a (30 mg, 57%) was isolated as bluegreen solid. M.P.: 205 °C (decomposition). ¹H NMR (500 MHz, CD₃CN): δ 8.70 (d, J = 9.2 Hz, 1H, H-8), 8.55 (d, J =8.8 Hz, 1H, H-3), 8.48 (t, J = 8.4 Hz, 1H, H-15), 8.42 (d, J = 8.5 Hz, 1H, H-20), 8.25 (s, 1H, H-6), 8.16 (ddd, J = 8.7, 7.1, 1.6 Hz, 1H, H-22), 7.99-7.88 (m, 4H, H-9, H-14, H-16, H-23), 7.87 (d, J = 8.9, 1H, H-4) 7.65 (d, J = 7.5 Hz, 2H, H-27, H-31), 7.52 (ddd, J = 8.3, 7.1, 1.2 Hz, 1H, H-21), 7.43 (m, 4H, H-24, H-25, H-28, H-30), 7.39-7.31 (m, 1H, H-29). ¹³C{1H} NMR (126 MHz, CD₃CN): δ 162.8 (C, C-10), 158.3 (C, C-11), 154.9 (C, C-19), 152.5 (C, C-13), 152.2 (C, C-17), 146.2 (CH, C-8), 141.9 (CH, C-22), 141.2 (CH, C-15), 139.6 (C, C-5), 137.7 (C, C-26), 133.3 (C, C-1), 132.6 (CH, C-24), 131.5 (CH, C-20), 129.9 (2CH, C-27, C-31), 129.4 (CH, C-25), 129.2* (C, C-7), 128.4 (CH, C-6), 127.8 (2CH, C-28, C-30), 127.7 (CH, C-29), 127.7 (CH, C-3), 127.6 (CH, C-4), 126.6 (CH, C-21), 120.6 (CH, C-23), 118.9 (C, C-18), 118.3 (CH, C-9), 116.2* (C, C-2), 115.6* (C, C-12), 112.8 (CH, C-14), 112.0 (CH, C-16). ¹⁹F NMR (282 MHz, CD₃CN): δ –151.06, –151.11. **IR** (neat, cm⁻¹): v 3540, 2925, 2857, 1638, 1601, 1579, 1498, 1374, 1347, 1275, 1157, 1059, 792, 755, 697. UV-Vis (CH₂Cl₂, C = 2.10⁻⁵ M): λ_{max} (Log ε): 613 (4.00), 465 (3.95), 353 (4.54). HRMS (ESI) m/z: [M]⁺ Calcd for C₃₁H₁₉O₂ 423.1380; Found 423.1371.

Synthesis of (E)-14-(4-fluorostyryl)-11bHbenzo[a]chromeno[2,3,4-kl]xanthen-11b-ylium tetrafluoroborate (21b). Following the general procedure for Suzuki coupling, compound 8A (50 mg, 0103 mmol, 1 equiv), 4-Fluoro-*trans-β*-styrylboronic acid pinacol ester (127 mg, 0.513 mmol, 5 equiv), Pd(OAc)₂ (8 mg, 0.0307 mmol, 0.3 equiv), PPh₃ (2 mg, 0.0103 mmol, 0.1 equiv) and K₂CO₃ (71 mg, 0.513 mmol, 5 equiv) were stirred. After work up the desired compound 21b (37 mg, 68%) was isolated as bluegreen solid. M.P.: 194 °C (decomposition). ¹H NMR (500 MHz, CD₃CN): δ 8.57 (d, *J* = 9.1 Hz, 1H, H-8), 8.46-8.40 (m, 2H, H-15, H-3), 8.30 (dd, J = 8.5, 1.5 Hz, 1H, H-20), 8.16-8.11 (m, 1H, H-22), 8.05 (d, J = 1.8 Hz, 1H, H-6), 7.92-7.87 (m, 3H, H-14, H-16, H-23), 7.82 (d, J = 9.1 Hz, 1H, H-9), 7.76 (dd, J = 8.8, 1.9 Hz, 1H, H-4), 7.58-7.53 (m, 2H, H-27, H-31), 7.48 (ddd, J = 8.2, 6.9, 1.1 Hz, 1H, H-21), 7.28 (d, *J* = 16.4 Hz, 1H, H-24), 7.17 (d, *J* = 16.4 Hz, 1H, H-25), 7.11 (t, J = 8.8 Hz, 2H, H-28, H-30). ¹³C{1H} NMR (126) MHz, CD₃CN): δ 163.5 (d, C, ${}^{1}J_{C-F}$ = 246.7 Hz, C-29), 162.5 (C, C-10), 158.1 (C, C-19), 154.6 (C, C-11), 152.3 (C, C-13), 152.0 (C, C-17), 146.1 (CH, C-8), 141.9 (CH, C-22), 141.2 (CH, C-15), 139.2 (C, C-5), 134.0 (C, C-26), 133.1 (C, C-1), 131.3 (CH, C-20), 131.1 (CH, C-24), 129.6 (d, 2CH, ${}^{3}J_{C-F} = 8.6$ Hz, C-27, C-31), 128.9* (C, C-7), 128.2 (CH, C-6), 127.5 (2CH, C-4, C-3), 127.4 (CH, C-25), 126.5 (CH, C-21), 120.6 (CH, C-23), 118.9 (CH, C-9), 118.8 (C, C-18), 116.6 (d, 2CH, ${}^{2}J_{C-F} = 22$ Hz, C-28, C-30), 115.9* (C, C-2), 115.3* (C, C-12), 112.9 (CH, C-14), 112.1 (CH, C-16). ¹⁹F NMR (282 MHz, CD₂Cl₂): δ -113.9, -151.0, -151.04. IR (neat, cm⁻¹): v 3315, 2929, 1634, 1581, 1503, 1376, 1350, 1278, 1228, 1159, 1057, 974, 773. UV-Vis (CH₂Cl₂, C = 2.10⁻⁵ M): λ_{max} (Log ε): 612 (4.07), 465 (4.01), 352 (4.60). **HRMS (ESI)** m/z: [M]⁺ Calcd for C₃₁H₁₈FO₂ 441.1285; Found 441.1276.

Synthesis (E)-14-(4-methoxystyryl)-11bHof benzo[a]chromeno[2,3,4-kl]xanthen-11b-ylium tetrafluoroborate (21c). Following the general procedure for Su*zuki* coupling, compound **8A** (50 mg, 0.103 mmol, 1 equiv), 4-Methoxy-trans- β -styrylboronic acid pinacol ester (0.133) mg, 0.513 mmol, 5 equiv), Pd(OAc)₂ (8 mg, 0.0307 mmol, 0.3 equiv), PPh₃ (2 mg, 0.0103 mmol, 0.1 equiv) and K₂CO₃ (71 mg, 0.513 mmol, 5 equiv) was stirred. After work up the desired compound 21c (29 mg, 53%) was isolated as dark green solid. M.P.: 206 °C (decomposition). ¹H NMR (500 MHz, CD₃CN): δ 8.69 (d, J = 9.1 Hz, 1H, H-8), 8.53 (d, J =8.8 Hz, 1H, H-3), 8.47 (t, J = 8.4 Hz, 1H, H-15), 8.42 (d, J = 8.5, 1.6 Hz, 1H, H-20), 8.20 (d, J = 1.8 Hz, 1H, H-6), 8.16 (t, 1H, H-22), 7.97-7.90 (m, 4H, H-9, H-14, H-16, H-23), 7.88 (dd, J = 8.9, 1.9 Hz, 1H, H-4), 7.61-7.55 (m, 2H, H-27, H-31), 7.54-7.49 (m, 1H, H-21), 7.41 (d, J = 16.4 Hz, 1H, H-24), 7.26 (d, J = 16.4 Hz, 1H, H-25), 7.02-6.95 (m, 2H, H-28, H-30), 3.83 (s, 3H, H-32). ¹³C{1H} NMR (126 MHz, CD₃CN): δ 162.5 (C, C-10), 161.0 (C, C-29), 158.1 (C, C-11), 154.6 (C, C-19), 152.3 (C, C-13), 152.0 (C, C-17), 146.1 (CH, C-8), 141.8 (CH, C-22), 141.0 (CH, C-15), 139.8 (C, C-5), 133.2 (C, C-1), 132.1 (CH, C-24), 131.3 (CH, C-20), 130.1 (C, C-26), 129.1 (2CH, C-27, C-31), 128.6* (C, C-7), 127.8 (CH, C-6), 127.5 (CH, C-3), 127.3 (CH, C-4), 126.4 (CH, C-21), 125.2 (CH, C-25), 120.6 (CH, C-23), 118.9 (CH, C-18), 118.8 (CH, C-9), 116.0* (C, C-2), 115.4* (C, C-12), 115.2 (2CH, C-28, C-30), 112.8 (CH, C-14), 112.0 (CH, C-16), 56.0 (C, C-32). ¹⁹F NMR (282 MHz, CD₂Cl₂): δ -151.0, -151.1. **IR** (neat, cm⁻¹): v 3072, 2933, 1636, 1600, 1580, 1508, 1495, 1345, 1243, 1176, 1047, 1034, 972, 763. **UV-Vis** (CH₂Cl₂, C = 2.10⁻⁵ M): λ_{max} (Log ε): 634 (4.02), 474 (4.14), 358 (4.71). HRMS (ESI) m/z: [M]⁺ Calcd for C₃₂H₂₁O₃ 453.1485; Found 453.1486.

Synthesis of 14-Phenyl-3,7-dipropyl-3,7-dihydro-11bHbenzo[a]quinolino[2,3,4-kl]acridin-11b-ylium tetrafluoroborate (22a). To a mixture of compound 20a (0.020 mg, 0.041 mmol), benzoic acid (63 mg, 0.516 mmol, 12.5 equiv) and NMP (0.5 mL) freshly distilled propyl amine (0.085 mL, 1.03 mmol, 25 equiv) was added in a glass vessel under N2 atmosphere. The reaction mixture was stirred at room temperature for 3 days and after that heated at 140 °C for 2 h using an oil bath. The mixture was dissolved in CH₂Cl₂ and washed with HBF₄ (1 M aqueous solution, 2 x 5 mL). The organic phase was dried over Na₂SO₄ and evaporated under vacuum. The resulting crude material was washed with Et_2O (3 x 10 mL). After purification by column chromatography on silica gel using $CH_2Cl_2/MeOH = 98:2$, the desired product 22a (10 mg, 43%) was isolated as an amorphous blue powder. M.P.: 153 °C; $\mathbf{R}_f = 0.67$ (Silica gel, CH₂Cl₂/MeOH, 98:2). ¹H NMR (500 MHz, CD₂Cl₂): δ 8.48 (d, J = 9.4 Hz, 1H, H-8), 8.29 (t, J = 10.5, 6.5 Hz, 1H, H-15), 8.22 (d, J = 1.9 Hz, 1H, H-6), 8.13 (d, J = 8.8 Hz, 1H, H-3), 8.01 (d, J = 7.3 Hz, 1H, H-23), 7.98-7.92 (m, 2H, H-9, H-22), 7.90 (d, J = 8.4 Hz, 1H, H-20), 7.76 (dt, J = 8.2, 1.7 Hz, 2H, H-25, H-29), 7.68-7.64 (m, 1H, H-4), 7.59 (dd, J = 8.4, 6.7 Hz, 2H, H-14, H-16), 7.55-7.50 (m, 2H, H-26, H-28), 7.47-7.40 (m, 1H, H-27), 7.30-7.23 (m, 1H, H-21), 4.84 (ddd, J = 16.7, 11.2, 5.8 Hz, 1H, H_a-30), 4.72 (ddd, J =

16.8, 11.5, 5.5 Hz, 1H, H_a-33), 4.62-4.46 (m, 2H, H_b-30, H_b-33), 2.28-2.08 (m, 4H, 2H-31, 2H-34), 1.33-1.23 (m, 6H, 3H-32, 3H-34). ¹³C{1H} NMR (126 MHz, CD₂Cl₂): δ 145.4 (C, C-11), 143.4 (C, C-10), 141.4 (C, C-19), 141.0 (C, C-24), 139.9 (CH, C-8), 139.6 (C, C-17), 139.3 (C, C-13), 139.1* (C, C-2), 137.0 (CH, C-15), 136.7 (CH, C-22), 131.6 (CH, C-23), 131.0 (C, C-1), 129.8 (C, C-5), 129.5 (2CH, C-26, C-28), 128.6 (CH, C-27), 127.4 (2CH, C-25, C-29), 127.4 (CH, C-4), 126.6 (CH, C-6), 125.8 (CH, C-3), 123.8 (CH, C-21), 120.3 (C, C-12), 120.0 (C, C-18), 117.1 (CH, C-20), 115.4* (C, C-7), 115.0 (CH, C-9), 106.4 (CH, C-14), 106.0 (CH, C-16), 52.1 (CH₂, C-30), 51.5 (CH₂, C-33), 20.9 (CH₂, C-31), 20.0 (CH₂, C-34), 11.3 (CH₃, C-32), 11.2 (CH₃, C-35). ¹⁹F NMR (282 MHz, CD₂Cl₂): δ –152.46, –152.47. **IR** (neat, cm⁻¹): v 2924, 2852, 1609, 1575, 1553, 1500, 1460. 1342, 1246, 1177, 1038, 890, 812, 759, 697, 628. UV-Vis $(CH_2Cl_2, C = 2.10^{-5} M): \lambda_{max} (Log \epsilon): 624 (3.89), 429 (3.11),$ 379 (3.93), 289 (4.34). HRMS (ESI) m/z: [M]⁺ Calcd for C₃₅H₃₁N₂ 479.2482; Found 479.2462.

Synthesis of 14-Bromo-11bH-benzo[a]chromeno[2,3,4kl]xanthene (23A). To a solution of 8A (35 mg, 0.087 mmol, 1 equiv) in acetonitrile (10 mL) NaBH₄ (10 mg, 0.264 mmol, 3 equiv) was added and the mixture was stirred for 5 min at 25 °C. in absence of light. The solvent was evaporated under *vacuum*, the residue was dissolved in CH₂Cl₂ and washed with water. The organic layer was dried over Na₂SO₄ and evaporated under vacuum. The neutral product 23A (20 mg, 70%) was isolated as a colorless solid and the two enantiomers were isolated in pure form by preparative CSP HPLC (see below). ¹**H** NMR (500 MHz, CD_2Cl_2): δ 8.05 (d, J = 2.2 Hz, 1H, H-6), 7.79 (d, J = 8.9 Hz, 1H, H-8), 7.65 (d, J = 9.0 Hz, 1H, H-3), 7.52 (dd, J = 9.0, 2.1 Hz, 1H, H-4), 7.35 (d, J = 9.0 Hz, 1H, H-9), 7.30 (dd, J = 8.1, 1.3 Hz, 1H, H-20), 7.26-7.19 (m, 2H, H-15, H-21), 6.98 (d, J = 8.0 Hz, 1H, H-14), 6.93 (td, J = 7.5, 1.4 Hz, 1H, H-22), 6.86 (d, J =8.2 Hz, 1H, H-16), 6.78 (dt, J = 7.8, 1.4 Hz, 1H, H-23), 5.47 (s, 1H, H-11). ¹³C{1H} NMR (126 MHz, CD₂Cl₂): δ 157.0 (C, C-17), 156.6 (C, C-19), 150.4 (C, C-10), 149.1 (C, C-13), 132.1 (C, C-1), 131.8 (C, C-5), 130.8 (CH, C-6), 129.9 (CH, C-4), 129.6* (C, C-18), 129.4 (CH, C-8), 128.3 (CH, C-15), 127.6 (CH, C-22), 126.9 (CH, C-3), 126.5 (CH, C-23), 123.6 (CH, C-21), 120.1 (CH, C-9), 118.6* (C, C-7), 117.7 (CH, C-20), 111.1 (CH, C-14), 111.0 (C, C-12), 110.8 (CH, C-16), 110.7* (C, C-2), 30.5 (CH, C-11).

Synthesis 14-Bromo-3-propyl-3,11b-dihydroof benzo[a]chromeno[2,3,4-kl]acridine (24A). To the solution of 10A (3.3 mg, 0.0062 mmol 1 equiv) in acetonitrile (5 ml) NaBH₄ (1.1 mg, 0.031 mmol, 5 equiv) was added and the mixture was stirred for 5 min at 25 °C. in absence of light. The solvent was evaporated under vacuum, the residue was dissolved in CH2Cl2 and washed with water. The organic layer was dried over Na₂SO₄ and evaporated under vacuum. The neutral product 24A was isolated as a colorless solid. ¹**H** NMR (500 MHz, CD₂Cl₂): δ 7.95 (d, J = 2.1 Hz, 1H, H-6), 7.77 (d, J = 9.2 Hz, 1H, H-8), 7.47 (d, J = 9.1 Hz, 1H, H-3), 7.38 (dd, J = 9.1, 2.1 Hz, 1H, H-4), 7.35 (d, J = 9.2 Hz, 1H, H-9), 7.26 (dd, *J* = 8.1, 1.3 Hz, 1H, H-20), 7.22 -7.11 (m, 2H, H-15, H-21), 6.87 (td, J = 7.5, 1.3 Hz, 1H, H-22), 6.80 (dd, J = 8.0, 0.8 Hz, 1H, H-16), 6.64 (dd, J = 8.3, 0.9 Hz, 1H, H-14), 6.58 (dt, J = 7.7, 1.3 Hz, 1H, H-23), 5.72 (s, 1H, H-11), 3.86 (ddd, J = 16.4, 10.6, 6.2 Hz, 1H, H_a-24), 3.72 (ddd, J = 16.2, 10.6, 6.0 Hz, 1H, H_b-24), 1.87 – 1.77 (m, 2H, H-25), 1.07 (t, J = 7.4 Hz, 3H, H-26). ¹³C{1H} NMR (126 MHz, CD₂Cl₂): δ 157.1 (C, C-17), 156.2 (C-19), 139.7 (C-10), 139.2 (C, C-13), 132.0 (C, C-7), 131.6 (C, C-18), 130.2 (CH, C-6), 130.0 (C, C-1), 129.6 (CH, C-4), 128.8 (CH, C-8), 128.1 (CH, C-15), 127.1 (CH, C-22), 126.4 (CH, C-23), 125.9 (CH, C-3), 123.1 (CH, C-21), 117.3 (CH, C-20), 116.8 (CH, C-9), 116.8 (C, C-5), 112.1 (C, C-12), 110.1 (C, C-2), 108.6 (CH, C-14), 107.7 (CH, C-16), 53.8 (CH, C-11), 48.5 (CH₂, C-24), 20.5 (CH₂, C-25), 11.1 (CH₃, C-26).

Synthesis of 14-Bromo-3,7-dipropyl-7,11b-dihydro-3Hbenzo[a]quinolino[2,3,4-kl]acridine (25A). To a solution of **9A** (12 mg, 0.015 mmol, 1 equiv) in acetonitrile (5 mL) NaBH₄ (2 mg, 0.045 mmol, 3 equiv) was added and the mixture was stirred for 5 min at 25 °C. in absence of light. The solvent was evaporated under vacuum, the residue was dissolved in CH₂Cl₂ and washed with water. The organic layer was dried over Na₂SO₄ and evaporated under vacuum. The neutral product 25A (6 mg, 60%) was isolated as a colorless solid and the two enantiomers were isolated in pure form by preparative CSP HPLC (see below). ¹H NMR (500 MHz, CD_2Cl_2 : δ 7.94 (d, J = 2.0 Hz, 1H, H-6), 7.75 (d, J = 9.2 Hz, 1H, H-8), 7.39-7.31 (m, 3H, H-3, H-4, H-9), 7.15-7.08 (m, 3H, H-15, H-20, H-22), 6.77-6.70 (m, 1H, H-21), 6.65 (d, J = 8.0 Hz, 1H, H-16), 6.55 (d, J = 8.2 Hz, 1H, H-14), 6.46-6.40 (m, 1H, H-23), 5.15 (s, 1H, H-11), 3.95 (m, 2H, H-27), 3.87 (m, 1H, Ha-24), 3.72 (m, 1H, Hb-24), 1.96 (m, 2H, H-28), 1.82 (m, 2H, H-25), 1.10-1.04 (m, 6H, H-26, H-29). ¹³C{1H} NMR (126 MHz, CD₂Cl₂): δ 145.9 (C, C-17), 144.6 (C, C-19), 140.0 (C, C-10), 138.6 (C, C-13), 132.1 (C, C-1), 131.1 (C, C-5), 130.1 (CH, C-6), 129.9* (C, C-7), 129.5 (CH, C-8), 128.4 (CH, C-15), 127.1 (CH, C-22), 125.9 (CH, C-3), 125.9 (CH, C-4), 125.5 (CH, C-23), 120.8 (CH, C-21), 116.8 (CH, C-9), 116.5* (C, C-18), 113.9 (CH, C-20), 111.7 (C, C-12), 110.9* (C, C-2), 106.1 (CH, C-14), 105.7 (CH, C-16), 48.6 (CH₂, C-24), 47.4 (CH₂, C-27), 36.0 (CH, C-11), 21.2 (CH₂, C-28), 20.5 (CH₂, C-25), 11.7* (CH₃, C-29), 11.0* (CH₃, C-26).

14-bromo-11-methoxy-11bH-Synthesis of benzo[a]chromeno[2,3,4-kl]xanthene (23B). To the solution of **8B** (4 mg, 0.0077 mmol, 1 equiv) in ethanol (5 ml) NaBH₄ (0.8 mg, 0.023 mmol, 3 equiv) was added and the mixture was stirred for 5 min at 25 °C. in absence of light. The solvent was evaporated under vacuum, the residue was dissolved in CH₂Cl₂ and washed with water. The organic layer was dried over Na₂SO₄ and evaporated under vacuum. The neutral product 23B (3.3 mg, 99%) was isolated as a colorless solid as a mixture of two diastereoisomers in ratio 88:12. Data for 23B (major diastereoisomer): ¹H NMR (500 MHz, CD_2Cl_2): δ 8.01 (d, J = 2.1 Hz, 1H, H-6), 7.78 – 7.70 (m, 1H, H-8), 7.63 (d, J = 9.0 Hz, 1H, H-3), 7.51 (dd, J =9.0, 2.1 Hz, 1H, H-4), 7.31 (d, J = 8.9 Hz, 1H, H-9), 7.21 (m, 2H, H-15, H-21), 6.97 (m, 2H, H-14, H-20), 6.88 (dd, J = 8.2, 0.9 Hz, 1H, H-16), 6.56 (dd, *J* = 8.4, 1.0 Hz, 1H, H-22), 5.47 (s, 1H, H-11), 2.90 (s, 3H, H-24). ¹³C{1H} NMR (126 MHz, CD₂Cl₂): δ 158.5 (C, C-13), 157.0 (C, C-23), 156.9 (C, C-17), 149.2 (C, C-10), 149.0 (C, C-19), 134.3 (C, C-1)*, 131.2 (C, C-7)*, 130.2 (CH, C-6), 129.3 (CH, C-4), 128.6 (CH, C-8), 128.1 (CH, C-21), 127.9 (CH, C-15), 126.7

(CH, C-3), 119.5 (CH, C-9), 118.0 (C, C-5), 117.9 (C, C-18), 113.1 (C, C-2)*, 112.4 (C, C-12), 110.9 (CH, C-20), 110.7 (CH, C-16), 110.5 (CH, C-14), 110.3 (CH, C-14), 108.1 (CH, C-22), 30.1 (CH₃, C-24).

Synthesis of 14-bromo-11-methoxy-3-propyl-3,11*b*-dihydrobenzo[a]chromeno[2,3,4-*kl*]acridine (24B). To the solution of 10B (18 mg, 0.032 mmol, 1 equiv) in ethanol (5 ml) NaBH₄ (6 mg, 0.161 mmol, 5 equiv) was added and the mixture was stirred for 5 min at 25 °C. in absence of light. The solvent was evaporated under *vacuum*, the residue was dissolved in CH₂Cl₂ and washed with water. The organic layer was dried over Na₂SO₄ and evaporated under *vacuum*. The residue was purified by column chromatography (eluent: pentane/Et₂O = 99:1) in absent of light. The both diastereoisomers 24B major (7.6 mg, 51%) and 24B minor (2 mg, 13%) were isolated in pure form and characterized by NMRexperiments. In the case of 24B major was performed X-ray analysis on monocrystal. Data for 24B major ((*p*)-(*R*)-14bromo-11-methoxy-3-propyl-3,11*b*-dihydro-

benzo[a]chromeno[2,3,4-kl]acridine): ¹H NMR (500 MHz, CD₂Cl₂): δ 7.92 (d, J = 2.1 Hz, 1H, H-6), 7.71 (d, J = 9.2 Hz, 1H, H-8), 7.50 (d, J = 9.1 Hz, 1H, H-3), 7.39 (dd, J = 9.1, 2.2 Hz, 1H, H-4), 7.31 (d, J = 9.2 Hz, 1H, H-9), 7.15 (m, *J* = 8.1, 1.8, 0.7 Hz, 2H, H-15, H-21), 6.95 (dd, *J* = 8.1, 1.0 Hz, 1H, H-20), 6.78 (dd, J = 8.0, 0.8 Hz, 1H, H-16), 6.67-6.62 (m, 1H, H-14), 6.50 (dd, J = 8.3, 1.0 Hz, 1H, H-22),5.69 (C, 1H, H-11), 3.90 (ddd, J = 16.4, 10.7, 6.0 Hz, 1H, H_a -25), 3.73 (ddd, J = 16.2, 10.7, 5.9 Hz, 1H, H_b -25), 2.85 (C, 3H, H-24), 1.83 (dddd, J = 15.1, 13.5, 10.7, 7.6 Hz, 2H, H-26), 1.07 (t, J = 7.4 Hz, 3H, H-27). ¹³C{1H} NMR (126) MHz, CD₂Cl₂): δ 158.1 (C, C-23), 157.0 (C, C-19), 156.9 (C, C-17), 139.2 (C, C-13), 138.2 (C, C-10), 134.3 (C, C-1), 129.8 (CH, C-6), 129.4 (C, C-2), 129.2 (CH, C-4), 128.0 (CH, C-8), 127.9 (CH, C-15), 127.5 (CH, C-21), 125.3 (CH, C-3), 119.7 (C, C-18), 116.4 (CH, C-9), 116.4 (C, C-7), 113.5 (C, C-12), 112.8 (C, C-5), 110.3 (CH, C-20), 108.2 (CH, C-23), 108.2 (CH, C-16), 107.7 (CH, C-14), 55.6 (CH, C-11), 48.5 (CH₂, C-25) 32.4 (CH₃, C-24), 20.5 (CH₂, C-26), 11.1 (CH₃, C-27). Data for **24B minor** ((*m*)-(*R*)-14-bromo-11-methoxy-3-propyl-3,11b-dihydro-

benzo[a]chromeno[2,3,4-kl]acridine): ¹H NMR (500 MHz, CD₂Cl₂): δ 7.86 (d, J = 2.2 Hz, 1H, H-6), 7.61 (d, J = 8.9 Hz, 1H, H-8), 7.50 (d, J = 9.0 Hz, 1H, H-9), 7.44 (d, J = 9.4 Hz, 1H, H-3), 7.40 (t, J = 8.3 Hz, 1H, H-21), 7.14 (td, J = 8.1, 0.7 Hz, 1H, H-15), 7.08 (dd, J = 9.4, 2.2 Hz, 1H, H-4), 6.85 (dd, J = 8.3, 1.0 Hz, 1H, H-20), 6.82-6.78 (m, 1H, H-14), 6.72 (dd, J = 8.1, 0.8 Hz, 1H, H-16), 6.68 (dd, J =8.2, 1.0 Hz, 1H, H-22), 4.68 (s, 1H, H-11), 4.15-4.02 (m, 2H, H-25), 3.51 (s, 3H, H-24), 1.97 (d, J = 7.3 Hz, 2H, H-26), 1.06 (t, J = 7.4 Hz, 3H, H-27). ¹³C{1H} NMR (126 MHz, CD₂Cl₂): δ 159.9 (C, C-23), 153.2 (C, C-19), 149.0 (C, C-17), 145.9 (C, C-13), 143.1 (C, C-10), 131.4 (C, C-2), 130.3 (C, C-5), 130.1 (CH, C-6), 129.7 (CH, C-21), 128.4 (CH, C-4), 126.9 (CH, C-15), 125.9 (CH, C-8), 124.7 (CH, C-3), 120.6 (C, C-1), 116.6 (CH, C-9), 116.4 (C, C-7), 111.7 (C, C-12), 110.4 (C, C-18), 110.2 (CH, C-20), 108.6 (CH, C-16), 108.1 (CH, C-14), 104.9 (CH, C-23), 55.8 (CH₃, C-24), 48.2 (CH₂, C-25), 21.7 (CH₂, C-26), 11.7 (CH₃, C-27).

Synthesis of 14-bromo-11-methoxy-3,7-dipropyl-7,11*b*-dihydro-3*H*-benzo[*a*]quinolino[2,3,4-*kl*]acridine (25B).

To the solution of **9B** (5.6 mg, 0.001 mmol, 1 equiv) in ethanol (5 ml) NaBH₄ (1.1 mg, 0.003 mmol) was added. The mixture was stirred for 5 min at 25 °C. in absence of light. The solvent was evaporated under vacuum, the residue was dissolved in CH₂Cl₂ and washed with water. The organic layer was dried over Na₂SO₄ and evaporated under vacuum. The neutral product 25B was isolated as a colorless solid as a mixture of two diastereoisomer in ratio 91:9. Data for 25B (major diastereoisomer): ¹H NMR (500 MHz, CD_2Cl_2): δ 7.91 (d, *J* = 2.2 Hz, 1H, H-6), 7.69 (d, *J* = 9.0 Hz, 1H, H-8), 7.45 (d, J = 9.1 Hz, 1H, H-3), 7.39 - 7.25 (m, 2H, H-4, H-9), 7.10 (m, 2H, H-15, H-21), 6.79 (dd, J = 8.3, 0.9 Hz, 1H, H-20), 6.63 (d, J = 8.0 Hz, 1H, H-16), 6.55 (d, J = 8.2 Hz, 1H, H-14), 6.38 (dd, J = 8.2, 0.9 Hz, 1H, H-22), 5.08 (s, 1H, H-11), 3.98 - 3.86 (m, 3H, 2H-28, H_a-25), 3.77 (dd, J = 10.3, 5.9 Hz, 1H, H_b-25), 2.78 (s, 3H, H-24), 2.00 – 1.90 (m, 2H, H-29), 1.86 - 1.76 (m, 2H, H-26), 1.05 (q, J = 7.4 Hz, 6H, H-27, H-30). ¹³C{1H} NMR (126 MHz, CD₂Cl₂): δ 156.8 (C, C-23), 146.6 (C, C-19), 145.7 (C-17), 138.6 (C, C-13), 138.1 (C, C-10), 134.0 (C, C-1), 129.8 (CH, C-6), 129.4 (C, C-7), 129.1 (CH, C-4), 127.3 (CH, C-8), 126.8 (CH, C-15), 126.5 (CH, C-21), 125.0 (CH, C-3), 118.0 (C, C-18), 116.5 (CH, C-9), 116.1 (C, C-5), 114.6 (C, C-2), 113.1 (C, C-12), 107.4 (CH, C-20), 106.2 (CH, C-16), 105.9 (CH, C-14), 105.7 (CH, C-22), 55.7 (CH₃, C-24), 48.4 (CH₂, C-25), 47.9 (CH₂, C-28), 35.1 (CH, C-11), 21.3 (CH₂, C-29), 20.3 (CH₂, C-26), 11.7 (CH₂, C-27)*, 11.1 (CH₂, C-30)*.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXX. It contains ¹H NMR, ¹³C NMR, ¹⁹F NMR, NOESY and HRMS spectra of the compounds, X-ray data, additional data relative to enantiomers separation, ECD spectra and racemization barrier determination (PDF). CCDC 2017329-2017335 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures. In addition, the dataset for this arfound the following ticle can be at DOI: 10.26037/yareta:jbrucdsj5nentl4mjqehwtcycu. It will be preserved for 10 years.

AUTHOR INFORMATION

Corresponding Author

* V.D.: <u>vdim@orgchm.bas.bg</u>

* J.L.: jerome.lacour@unige.ch

Present Addresses

^vS.P. is currently at CINaM, Aix-Marseille Univ, UMR CNRS 7325, Campus de Luminy, 13288 Marseille Cedex 9, France.

ORCID

Maya Marinova: 0000-0001-8635-0973 Simon Pascal: 0000-0001-8387-494X Laure Guénée: 0000-0002-2136-0510 Céline Besnard: 0000-0001-5699-9675 Boris Shivachev: 0000-0001-8765-6536 Kalina Kostova: 0000-0002-6406-7680 Claudio Villani: 0000-0002-3253-3608 Roberta Franzini: 0000-0002-5735-7399 Vladimir Dimitrov: 0000-0002-9668-9388 Jérôme Lacour: 0000-0001-6247-8059

Notes

The authors declare no competing financial interest.

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