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

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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 ($\Delta G^{\ddagger}$ values ranging from 85.0 to 137.1 kJ.mol^{-1} and above).

INTRODUCTION

Cationic helicenes, compounds that bear structural analogy to both triarylcarbenium ions[1] 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 ($\Delta G^{\ddagger}$ 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 physics[33] but also in analytical sciences[34-38] 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.

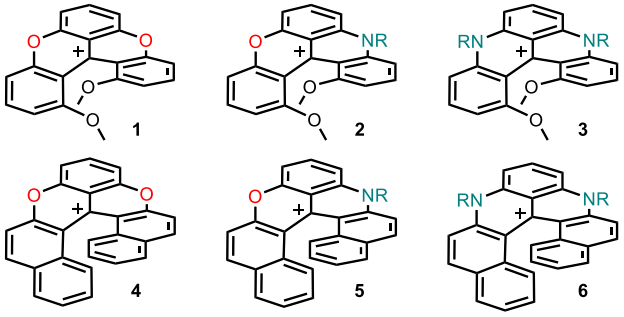


Figure 1. Dioxa, azaoxa and diaza [4] and [6]helicenes **1**-**6**.

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 ($\Delta G^{\ddagger}$ 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.

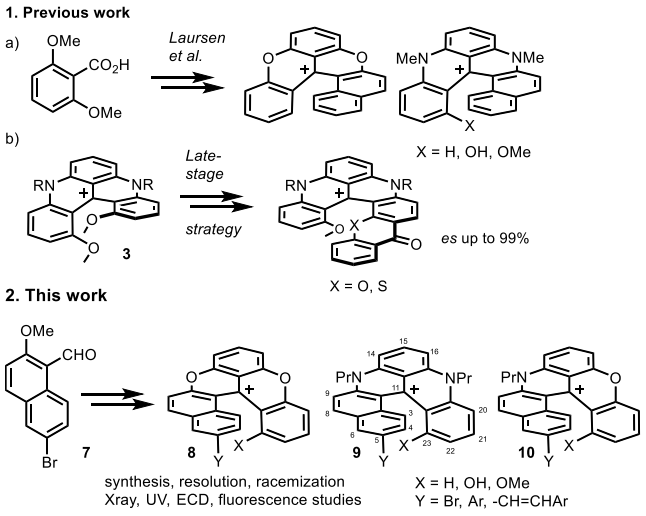


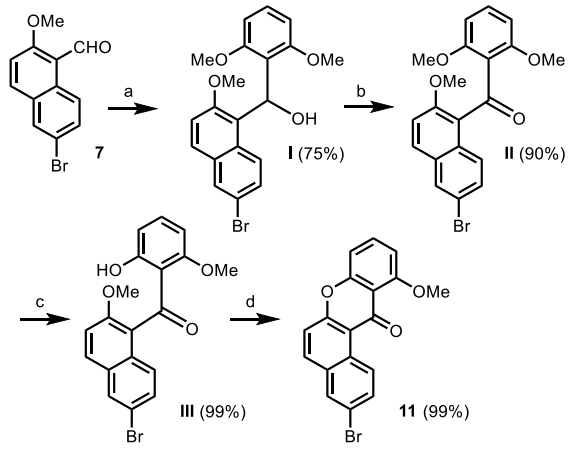
Figure 2. Synthesis of cationic [5]helicenes. The numbering of key helicene positions are indicated on compound **9**.

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.

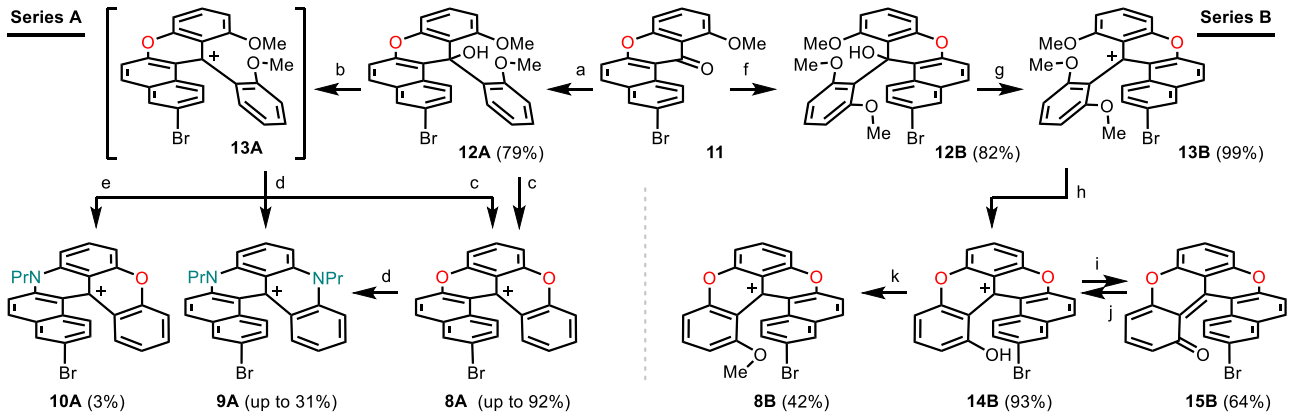
The starting material, 6-bromo-2-methoxy-1-naphthaldehyde **7** (Figure 2), was obtained according to the literature.[41] The reaction sequence follows strictly the procedure detailed for the synthesis of cationic [6]helicenes and it is hence presented only in Scheme 2 and detailed in the experimental section.[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 of (2-methoxyphenyl)lithium and (2,6-dimethoxyphenyl)lithium to ketone **11** required the activation of tetracyclic ketone with anhydrous $CeCl_3$[42] and reactions afforded the corresponding carbinols **12A** and **12B** in 79% and 82% respectively.

Scheme 2. Preparation of key substrate 11.



Reaction conditions: a) 1,3-dimethoxybenzene, *n*-BuLi, then **7**, THF, 25 °C, 24 h; b) DDQ, CH_2Cl_2, 20 °C, 24 h; c) BBr_3, CH_2Cl_2, -78 then 20 °C, 1 h; d) heating at 200 °C, 5h.

Scheme 1. Synthesis of a series of bromo-substituted [5]helicenes.



Reaction conditions: **Series A**: a) $CeCl_3$, THF, 25 °C, 24 h, then 2-methoxyphenyl lithium, 25 °C, 16 h, 79%; b) HBF_4 (50% aq. sol.), CH_2Cl_2, 25 °C, 2 h, (88% conv); c) Pyr·HCl, 225 °C, 2 min, 61% from **12A** and 92% from **13A**; d) 25 equiv NH_2Pr, 12.5 equiv $PhCO_2H$, NMP, 140 °C, 12 h, 31% from **12A** and 16% from **13A**; e) 5 equiv $PrNH_2$, CH_3CN, reflux, 16 h, 3%. **Series B**: f) $CeCl_3$, THF, 25 °C, 24 h, (2,6-dimethoxyphenyl)lithium, 25 °C, 16 h, 82%; g) HBF_4 (50% aq. sol.), CH_2Cl_2, 25 °C, 2 h, 99%; h) Pyr·HCl, 225 °C, 2 min, 93%; i) $NaHCO_3$ sat aq. sol., 64%; j) 1 M HBF_4 aq. sol., 99%; k) K_2CO_3, DMF, MeI, 25 °C, 3 days, 42%.

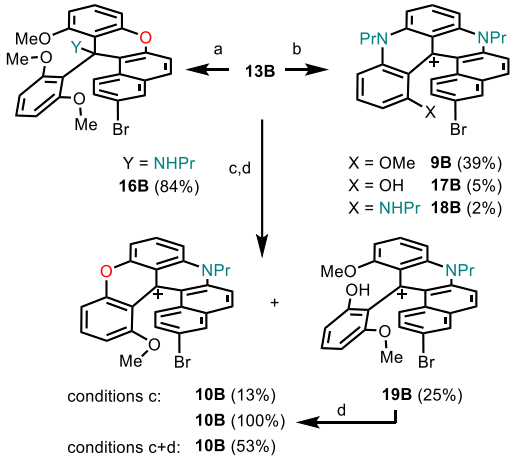
From there, a different outcome was obtained in the two series. For series **A** (Scheme 1, left), treatment of **12A** with 50% aqueous HBF_4 led to the partial formation of the corresponding carbenium derivative **13A**. It was not possible to drive the reaction to completion and crude reactions of **13A** always contained precursor **12A** in a typical 88:12 ratio.[43] It was nevertheless possible to perform the reaction on a multi-gram 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%.

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% yield 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 3). 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 3, 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 3, 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 CD_2Cl_2 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*).

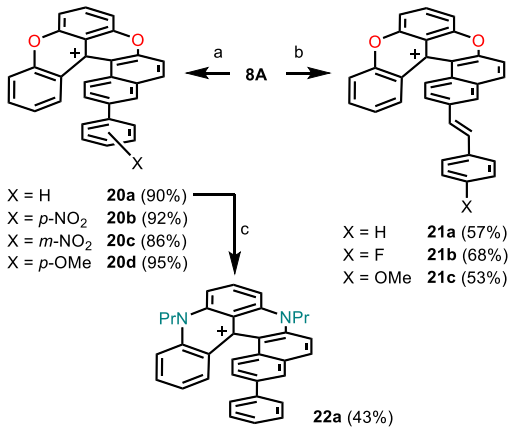
Scheme 3. Synthesis of azaoxa and diaza [5]helicenes 9B and 10B and solid state structure of 16B.



Reaction conditions: a) 5 equiv $PrNH_2$, CH_3CN; b) 25 equiv $PrNH_2$, 12.5 equiv $PhCO_2H$, 25 °C, 5 days, then NMP, 90 °C, 5 h; c) 25 equiv $PrNH_2$, 25 °C, 2 days; d) $NaHCO_3$ 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 4). 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 4. Derivatization of [5]helicene 8A via *Suzuki-Miyaura* cross-coupling reactions.



Reaction conditions: a) Arylboronic acid, $Pd(PPh_3)_4$, K_2CO_3, 1,4-dioxane, 80 °C, 16 h; b) Styrylboronic acid, $Pd(OAc)_2$, PPh_3, 1,4-dioxane, 90 °C, 3 h; c) 25 equiv $PrNH_2$, 12.5 equiv $PhCO_2H$, 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.

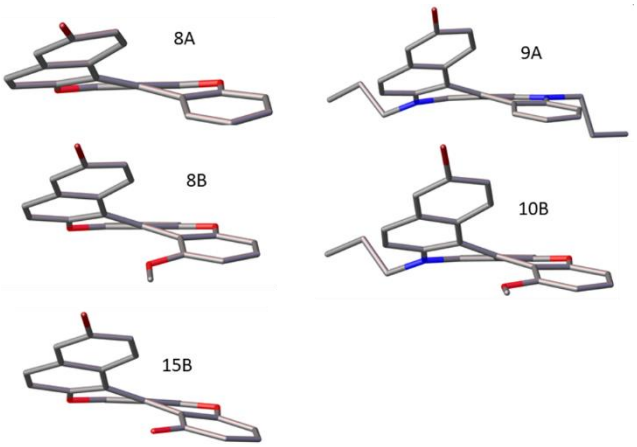


Figure 3. Stick view of the crystal structures of **8A**, **9A**, **8B**, **10B** and **15B**.

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 $NaBH_4$ and $NaBH_3CN$ (Table 2). With the more reactive $NaBH_4$ 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]

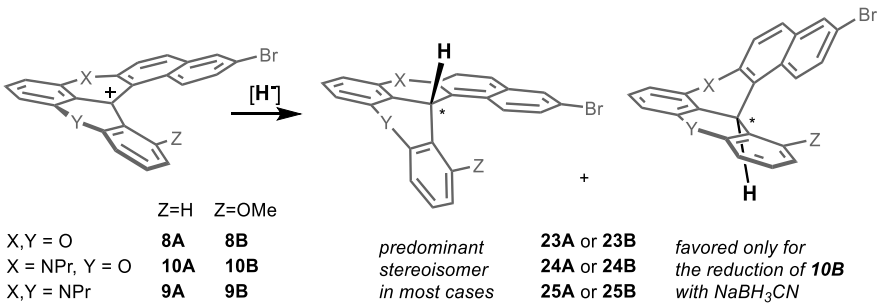
Table 2. Diastereoselectivity upon treatment with $NaBH_4$ and $NaBH_3CN$.

Precursor	Product	Diastereoselectivity	
		$NaBH_4$	$NaBH_3CN$
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 $NaBH_3CN$.

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 5). Of interest, and somewhat surprisingly in view of earlier results,[17] better diastereomeric ratios (up to > 49:1, NMR) were obtained using $NaBH_4$ as hydride source instead of $NaBH_3CN$ (Table 2).[6] Selectivity ratios were also always higher in series **A** as compared to the **B** analogues. In fact, using $NaBH_4$ 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 $NaBH_3CN$, see SI, p. S108).

Scheme 5. Diastereoselective reduction of [5]helicenes 8-10 and solid state structure of 24B.



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 $NaBH_3CN$, Scheme 5). 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)).

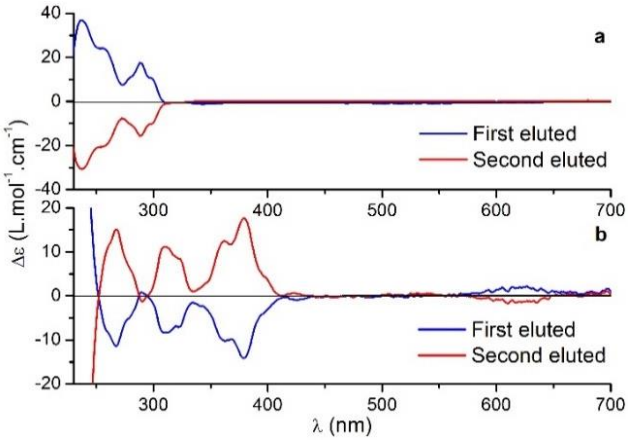


Figure 4. ECD spectra of compounds derived from the first and second eluted enantiomers of: a) reduced dioxa **23A**; b) cationic diaza [5]helicene **9A** generated from **25A** upon oxidation. Recorded in CH_2Cl_2 solutions (2.10^{-5} M) at 20 °C.

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 ($\Delta H^{\ddagger}$ (343 K) 86.8 ± 1.6 $kJ.mol^{-1}$ and $\Delta S^{\ddagger}$ (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** ($\Delta G^{\ddagger}$ (343 K) 104.4 ± 1.1 $kJ.mol^{-1}$) is lower than that of the corresponding diaza [4] and [6]helicenes **3** and **6** ($\Delta G^{\ddagger} > 155$ $kJmol^{-1}$).[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% CF_3COOH and 0.4% Et_3N. 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 $\Delta G^{\ddagger}_{av}$ 86.7 $kJ.mol^{-1}$ and $\Delta G^{\ddagger}_{av}$ 95.3 $kJ.mol^{-1}$ for **8A** and **10A**, respectively. These values correspond to racemization barriers $\Delta G^{\ddagger}_{racem}$ 85.0 and 93.4 $kJ.mol^{-1}$ for **8A** and **10A**.[51] The complete set of experimental Gibbs free energy of enantiomerization $\Delta G^{\ddagger}$ for **8A** and **10A** are gathered in Table S1.

Table 3. Enantiomerization and racemization parameters [a]

Dye	Solvent	T (°C)	Enantiomerization [b]		Racemization	
			k	$\Delta G^{\ddagger}$	k	$\Delta G^{\ddagger}$

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

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, CF_3COOH 0.6%, Et_3N 0.4 %. [d] Calculated using the following formula: $k_{racemization} = 2 \times k_{enantiomerization}$ [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 $\Delta G^{\ddagger}$ 111.5 kJ.mol^{-1} ($\Delta G^{\ddagger}_{racem}$ 109.5 kJ.mol^{-1}). Analogously, the racemization of the first eluted enantiomer of **10B** was monitored in DMSO at 150 °C,

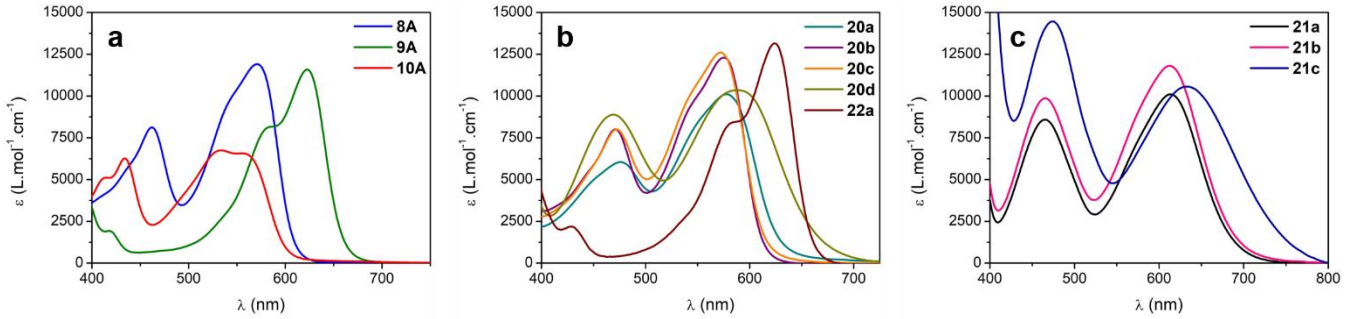


Figure 5. Electronic absorption spectra of [5]helicenes in dichloromethane solution (10^{-5} M, 20 °C).

yielding a free energy barrier of enantiomerization $\Delta G^{\ddagger}$ 139.5 kJ.mol^{-1} ($\Delta G^{\ddagger}_{racem}$ 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 (λ_{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^{-1}cm^{-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 λ_{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** display similar absorption maxima and intensities to their parent dye **8A**, regardless of the position of the nitro function. These observations suggest a weak electronic influence of the nitrophenyl substituents in **20a-c**, probably due to a twist occurring around the Csp^2-Csp^2 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 lower energy transition is in fact redshifted (λ_{max} = 589 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 electron-donating *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 **20d**.

The emission properties of the [5]helicenes have been investigated in dichloromethane solution and the fluorescence 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 (Φ = 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 (Φ = 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.

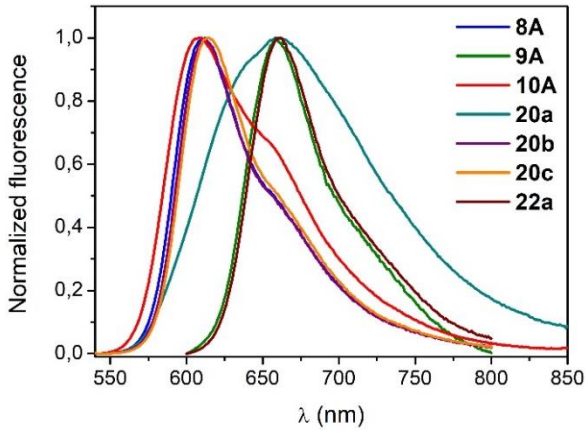


Figure 6. Normalized fluorescence spectra of [5]helicenes in dichloromethane solution (10^{-5} M, 20 °C).

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 ($\Delta G^{\ddagger}$ 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. ^{1}H NMR: chemical shifts were given in ppm relative to Me_4Si with solvent resonances used as internal standards (7.26 ppm for $CDCl_3$, 5.32 ppm for CD_2Cl_2 and 1.94 ppm for CD_3CN). ^{13}C NMR chemicals shifts were given in ppm relative to Me_4Si with solvent resonances used as internal standards (77.1 ppm for $CDCl_3$, 53.8 ppm for CD_2Cl_2 and 118.26 ppm for CD_3CN). ^{1}H 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. $^{13}C\{1H\}$ NMR signals were reported as follows: chemical shift (δ) in ppm on the δ scale; assignments marked with (*) are tentative. The assignments of ^{1}H and $^{13}C\{1H\}$ NMR signals were made on the basis of DEPT, HSQC, HMBC, COSY and NOESY experiments. The numbering 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 (R*f*) was measured on TLC Silicagel 60 F_{254} 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 cm × 25 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 detector, using Cu Kα radiation. Data reduction was carried out in the crysalis Pro Software.3 Structure solution was made using

direct methods (Shelxs4 or sir20045) or charge-flipping (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 Φx/ Φr = [Ar(λ)/Ax(λ)][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 (Φ*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.

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 N_2 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-1-naphthaldehyde **7** (The activation was performed as follow: 6-bromo-2-methoxy-1-naphthaldehyde **7** (10.7 g, 40.5 mmol) and anhydrous $CeCl_3$ (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 quenched with a minimum amount of water. The excess of solvent was evaporated under *vacuum* and the resulting mixture was extracted with CH_2Cl_2 (200 mL) and washed with water (2 x 200 mL). The organic layer was dried over Na_2SO_4 and the solvent evaporated under *vacuum*. The crude mixture was washed with Et_2O 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, CH_2Cl_2). **^{1}H 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). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): 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 (CH_3, C-20), 56.2 ($2CH_3$, C-18, C-19). **IR** (neat, cm^{-1}): ν 3523, 2935, 2896, 1586, 1496, 1455, 1266, 1236, 1173, 1104, 1045, 801. **HRMS (ESI) *m/z*:** $[M - OH]^+$ Calcd for $C_{20}H_{18}BrO_3$ 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 N_2 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 Na_2SO_4 and evaporated under *vacuum*, affording 11.0 g (90%) of the desired compound as a pale yellow powder. **M.P.:** 208 °C. $\mathbf{R_f}$ = 0.34 (Silica gel, CH_2Cl_2). **^{1}H NMR** (500 MHz, CD_2Cl_2): 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. **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): 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 (CH_3, C-20), 56.3 ($2CH_3$, C-18, C-19). **IR** (neat, cm^{-1}): ν 2943, 1589, 1468, 1252, 1110. **HRMS (ESI) *m/z*:** $[M + H]^+$ Calcd for $C_{20}H_{17}BrO_4$ 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 CH_2Cl_2 (90 mL) was added dropwise BBr_3 (1M solution in CH_2Cl_2, 27.3 mL, 1 equiv) at -78 °C under N_2 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 CH_2Cl_2 (200 mL) and washed with water (2 x 200 mL). The organic layer was dried over Na_2SO_4 and evaporated under *vacuum*. The crude precipitate was washed with Et_2O 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, CH_2Cl_2). **^{1}H NMR** (500 MHz, CD_2Cl_2): 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). **^{13}C{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 (CH_3, C-20), 56.0 (CH_3, C-18). **IR** (neat, cm^{-1}): ν 2944, 1583, 1497, 1455, 1339, 1231, 1180, 1089, 803. **HRMS (ESI) *m/z*:** $[M + H]^+$ Calcd for $C_{19}H_{15}BrO_4$ 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-1-yl)(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, CH_2Cl_2). **^{1}H NMR** (500 MHz, CD_2Cl_2): 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-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). **^{13}C{1H} NMR** (126 MHz,

CD_2Cl_2): 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 (CH_3, C-18). **IR** (neat, cm^{-1}): ν 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-methoxyphenyl)-12*H*-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 N_2 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 $CeCl_3$ (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 CH_2Cl_2 (200 mL) and washed with water (2 x 200 mL). The organic layer was dried over Na_2SO_4 and evaporated under *vacuum*. The crude precipitate was washed with Et_2O to remove some impurities and after drying the desired compound was isolated as a colourless solid 1.03 g (79%). **M.P.:** 225 °C. $\mathbf{R}_f$ = 0.55 (Silica gel, CH_2Cl_2). **^{1}H NMR** (500 MHz, CD_2Cl_2): 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). **^{13}C{1H} NMR** (125 MHz, CD_2Cl_2): 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 (CH_3, C-24), 55.7 (CH_3, C-25). **IR** (neat, cm^{-1}): ν 3544, 3113, 2952, 1612, 1588, 1478, 1383, 1281, 1269, 1250, 1086, 1062, 1024, 903, 795, 762. **HRMS (ESI) *m/z*:** $[M - OH]^+$ Calcd for $C_{25}H_{18}BrO_3$ 445.0434; Found 445.0439.

Synthesis of 3-Bromo-11-methoxy-12-(2-methoxyphenyl)-12*H*-benzo[*a*]xanthen-12-ylium tetrafluoroborate (13A). Compound **12A** (0.150 g, 0.281 mmol) was dissolved in CH_2Cl_2 (200 mL) and HBF_4 (0.5 mL, 50% aqueous solution) was added. After stirring for 2 h, the mixture was extracted with CH_2Cl_2, dried over Na_2SO_4 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, CD_2Cl_2): 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). **^{13}C{1H} NMR** (151 MHz, CD_2Cl_2): 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 (CH_3, C-25), 56.0 (CH_3, C-24). **^{19}F NMR** (282 MHz, CD_2Cl_2): δ –152.5, –152.5. **IR** (neat, cm^{-1}): ν 3409, 2933, 1615, 1591, 1500, 1476, 1384, 1329, 1291, 1199, 1154, 1074, 1059, 895, 832, 753. **UV-Vis** (CH_2Cl_2, 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 $C_{25}H_{18}BrO_3$ 445.0434; Found 445.0445.

Synthesis of 14-bromo-11b*H*-benzo[*a*]chromeno[2,3,4-*kl*]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 HBF_4 (30 mL, 1M aqueous solution) was added. The reaction mixture was extracted with CH_2Cl_2 (5 x 30 mL). The organic layer was dried over Na_2SO_4, evaporated under *vacuum*, washed with Et_2O 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 HBF_4 (10 mL, 1M aqueous solution) was added. The reaction mixture was extracted with CH_2Cl_2 (5 x 30 mL). The organic layer was dried over Na_2SO_4, evaporated under *vacuum*, washed with Et_2O and dried, yielding 35 mg (61%) of the desired compound **8A** as a dark red solid. **M.P.:** 303 °C (decomposition). **^{1}H NMR** (500 MHz, CD_3CN): δ 8.64 (d, *J* = 9.2 Hz, 1H, H-8), 8.51 (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). **^{13}C{1H} NMR** (126 MHz, CD_3CN): 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). **^{19}F NMR** (282 MHz, CD_3CN): δ –151.1, –151.1. **IR** (neat, cm^{-1}): ν 3096, 1638, 1579, 1541, 1489, 1378, 1349, 1035, 775. **UV-Vis** (CH_2Cl_2, 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 $C_{23}H_{12}BrO_2$ 399.0015; Found 399.0016.

Synthesis of 14-Bromo-3-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). The solution was evaporated, the residue was dissolved in CH_2Cl_2 and washed with HBF_4 (30 mL, 1M aqueous solution). The organic phase was evaporated to dryness and the residue purified by column chromatography on silica gel using CH_2Cl_2/CH_3OH = 100:1. Compound **10A** was isolated as a pink powder, 3.4 mg (3%). **M.P.:** 124 °C. $\mathbf{R}_f$ = 0.19 (Silica gel, CH_2Cl_2/MeOH, 98:2). **^{1}H 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). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ ^{13}C{1H} NMR (126 MHz, CD_2Cl_2) 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 (CH_2, C-24), 22.0 (CH_2, C-25), 11.2 (CH_3, C-26). **^{19}F NMR** (282 MHz, CD_2Cl_2): δ −151.2, −151.2. **IR** (neat, cm^{-1}): ν 3075, 2928, 1628, 1583, 1547, 1531, 1491, 1350, 1145, 1057, 832, 776, 728. **UV-Vis** (CH_2Cl_2, 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 $C_{26}H_{19}BrNO$ 440.0645; Found 440.0649.

Synthesis of 14-bromo-3,7-dipropyl-3,7-dihydro-11b*H*-benzo[*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 N_2 atmosphere. The reaction mixture was heated in an oil bath at 140 °C for 22 h. The mixture was dissolved in CH_2Cl_2 washed with HBF_4 (1M aqueous solution, 2 x 5 mL). The organic phase was separated, dried over Na_2SO_4 and evaporated under *vacuum*. The crude material was washed with Et_2O (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. **R_f** = 0.29 (Silica gel, CH_2Cl_2/MeOH, 98:2). **^{1}H NMR** (500 MHz, CD_2Cl_2): 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, H_a-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). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): δ 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 (CH_2, C-24), 51.6 (CH_2, C-27), 20.9 (CH_2, C-25), 20.0 (CH_2, C-28), 11.3 (CH_3, C-29), 11.2 (CH_3, C-26). **^{19}F NMR** (282 MHz, CD_2Cl_2): δ −151.2, −151.3. **IR** (neat, cm^{-1}): ν 2962, 2927, 2881, 1610, 1584, 1548, 1499, 1343, 1248, 1176, 1051, 908, 881, 761. **UV-Vis** (CH_2Cl_2, 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 $C_{29}H_{26}BrN_2$ 481.1274; Found 481.1289.

Synthesis of 3-bromo-12-(2,6-dimethoxyphenyl)-11-methoxy-12*H*-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 N_2 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 $CeCl_3$ (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 CH_2Cl_2 (200 mL) and washed with water (2 x 200 mL). The organic layer was dried over Na_2SO_4 and evaporated under *vacuum*. The crude mixture was washed with Et_2O and after drying the desired compound **12B** was isolated as a colorless solid 1.125 g (82%). **M.P.:** 254 °C. **^{1}H 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). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): 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 (CH_3, C-25), 56.5 (CH_3, C-24), 56.1 (CH_3, C-26). **IR** (neat, cm^{-1}): ν 3494, 2933, 2841, 1630, 1590, 1468, 1393, 1353, 1301, 1254, 1090, 1025, 1006 cm^{-1}. **HRMS (ESI) *m/z*:** $[M - OH]^+$ Calcd for $C_{26}H_{20}BrO_4$ 475.0540; Found 475.0550.

Synthesis of 3-bromo-12-(2,6-dimethoxyphenyl)-11-methoxy-12*H*-benzo[*a*]xanthen-12-ylium tetrafluoroborate (13B). Compound **12B** (1.13 g, 2.28 mmol) was dissolved in CH_2Cl_2 (200 mL) and HBF_4 (6 ml, 2.66 equiv, 50% aqueous solution) was added. After stirring for 2 h, the mixture was extracted with CH_2Cl_2, dried over Na_2SO_4 and evaporated under *vacuum*. The desired compound **13B** was isolated as a brown solid 1.33 g (99%). **M.P.:** 256 °C (decomposition). **^{1}H NMR** (500 MHz, CD_2Cl_2): 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, 6H, H-25, H-26). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): 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 (CH_3, C-24), 56.6 (2CH_3, C-25, C-26). **^{19}F NMR** (282 MHz, CD_2Cl_2): δ −153.2, −153.2. **IR** (neat, cm^{-1}): ν 3300, 2932, 1612, 1588, 1504, 1476, 1432, 1380, 1287, 1260, 1106, 1065, 901, 808, 785, 752 cm^{-1}. **UV-Vis** (CH_2Cl_2, 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 $C_{26}H_{20}BrO_4$ 475.0540; Found 475.0541.

Synthesis of 14-bromo-11-hydroxy-11b*H*-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 HBF_4 (30 mL, 1M aqueous solution) was added. The reaction mixture was extracted with CH_2Cl_2 (5 x 30 mL). The organic layer was dried over Na_2SO_4, evaporated under *vacuum*, washed with Et_2O 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, CD_3CN): 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). **^{13}C{1H} NMR** (126 MHz, CD_3CN): 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}): ν 2956, 2922, 2857, 1605, 1581, 1503, 1462, 1378, 1344, 1267, 1241, 1056, 908, 810, 785 cm^{-1}. **^{19}F NMR** (282 MHz, CD_3CN): δ –151.1, –151.1 **HRMS (ESI) *m/z*:** $[M]^+$ Calcd for $C_{23}H_{12}BrO_3$ 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 CH_2Cl_2 (100 mL) and $NaHCO_3$ (saturated solution in water) was added. After extraction with CH_2Cl_2, the organic layer was dried over Na_2SO_4 and evaporated under *vacuum*. The residue was purified by column chromatography on silica gel using CH_2Cl_2/MeOH = 99:1. The desired compound **15B** was isolated as a dark green solid 26 mg (64%). **M.P.:** 365 °C (decomposition). **^{1}H NMR** (500 MHz, CD_2Cl_2): 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). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): 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}): ν 2924, 2853, 1718, 1620, 1585, 1519, 1502, 1471, 1438, 1334, 1240, 1194, 1151, 1063, 1028, 911, 873, 807, 776, 754 cm^{-1}. **UV-Vis** (CH_2Cl_2, 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 $C_{23}H_{11}BrO_3$ 414.9964; Found 414.9968.

Synthesis of 14-bromo-11-methoxy-11b*H*-benzo[*a*]chromeno[2,3,4-*kl*]xanthen-11b-ylium tetrafluoroborate (8B). To a solution of dioxa [5]helicene **14B** (20 mg, 0.040 mmol, 1equiv) in DMF (4 mL) K_2CO_3 (22 mg, 0.200 mmol, 5 equiv) was added under N_2 atmosphere. The reaction mixture was stirred for 1 h and after that CH_3I (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 CH_2Cl_2 and stirred with HBF_4 (3 mL, 50% aqueous solution) under Rayonet UV light. The reaction mixture was extracted with CH_2Cl_2 and precipitated with Et_2O. The solid was dissolved in acetonitrile and $NaBH_3CN$ (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 pentane/Et_2O = 97:3. The neutral compound was dissolved in CH_2Cl_2 and HBF_4 (3 mL, 50% aqueous solution) was added and the reaction mixture was stirred under Rayonet UV light for 30 min. After extraction with CH_2Cl_2, the organic layer was dried over Na_2SO_4 and evaporated under *vacuum* to give compound **8B** (8.6 mg, 42%) as a dark red powder. **M.P.:** 281-283°C (decomposition). **^{1}H NMR** (500 MHz, CD_3CN): 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). **^{13}C{1H} NMR** (126 MHz, CD_3CN): 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 (CH_3, C-24). **^{19}F NMR** (282 MHz, CD_2Cl_2): δ –151.9, –151.9. **IR** (neat, cm^{-1}): ν 3088, 2925, 1637, 1602, 1582, 1508, 1473, 1381, 1348, 1286, 1228, 1197, 1053, 812, 776 cm^{-1}. **UV-Vis** (CH_2Cl_2, c = 10^{-5}M): 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 $C_{24}H_{14}BrO_3$ 429.0121; Found 429.0126.

Synthesis of 3-bromo-12-(2,6-dimethoxyphenyl)-11-methoxy-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. **^{1}H NMR** (500 MHz, CD_3CN): 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-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). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): 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 (CH_3, C-25), 56.1 (CH_3, C-24), 56.0 (CH_3, C-26), 45.9 (CH_2, C-27), 24.2 (CH_2, C-28), 12.1 (CH_3, C-29). **IR** (neat, cm^{-1}): ν 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 $C_{26}H_{20}BrO_4$ 475.0540; Found 475.0542.

Synthesis of 3-bromo-12-(2-hydroxy-6-methoxyphenyl)-11-methoxy-7-propyl-7,12-dihydrobenzo[*a*]-acridin-12-ylium 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 HBF_4 (1 M aqueous solution, 2 x 5mL). The organic phase was separated, dried over Na_2SO_4 and evaporated under *vacuum*. The residue was purified by column chromatography on silica gel using CH_2Cl_2/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). ^{1}H NMR (500 MHz, CD_2Cl_2): 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). ^{13}C{1H} NMR (126 MHz, CD_2Cl_2): 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 (CH_3, C-24), 56.2 (CH_3, C-25), 54.7 (CH_2, C-26), 22.5 (CH_2, C-27), 11.2 (CH_3, C-28). ^{19}F NMR (282 MHz, CD_2Cl_2): δ –151.6, –151.7. IR (neat, cm^{-1}): ν 3401, 2941, 2350, 1609, 1591, 1517, 1469, 1344, 1265, 1148, 1078, 780, 748 cm^{-1}. UV-Vis (CH_2Cl_2, 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 $C_{28}H_{25}BrNO_3$ 502.1012; Found 502.0996.

Synthesis of 14-bromo-11-methoxy-3-propylbenzo[*a*]chromeno[2,3,4-*kl*]acridin-11b(3*H*)-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, CH_3CN 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)**. ^{1}H NMR** (500 MHz, CD_2Cl_2): 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). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): 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 (CH_3, C-27), 30.1 (CH_2, C-24), 22.1 (CH_2, C-25), 11.2 (CH_3, C-26). In this case (C18) was not detected neither on ^{13}C, HSQC or HMBS. **^{19}F NMR** (282 MHz, CD_2Cl_2): δ **–**151.0, –151.1. **IR** (neat, cm^{-1}): ν 2967, 2925, 1627, 1587, 1528, 1474, 1390, 1349, 1259, 1189, 1047, 955, 883, 809, 779, 708, 675 cm^{-1}. **UV-Vis** (CH_2Cl_2, 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 $C_{27}H_{21}BrNO_2$ 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 CH_2Cl_2 washed with HBF_4 (1M aqueous solution, 2 x 15mL). The organic phase was separated, dried over Na_2SO_4 and evaporated under *vacuum*. The crude material was washed three times with 50 ml Et_2O. 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 CH_2Cl_2 and washed with 1M KPF_6 to exchange the anion. The residue was purified by column chromatography on silica gel using CH_2Cl_2/Me_2CO = 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 CH_2Cl_2 and washed $NaHCO_3$ (three times), after that again with 1M HBF_4. The crude material was washed three times with 50 ml Et_2O. After that the isolated compound was dissolved in CH_2Cl_2 and washed with 1M KPF_6 to exchange the anion. The residue was 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-11b*H*-benzo[a]quinolino[2,3,4-*kl*]acridin-11b-ylium tetrafluoroborate (9B). M.P.: 165 °C (decomposition). ^{1}H NMR (500 MHz, CD_2Cl_2): 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). ^{13}C{1H} NMR (126 MHz, CD_2Cl_2): 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 (CH_3, C-24), 52.3 (CH_2, C-25), 52.1 (CH_2, C-28), 21.1 (CH_2, C-26), 20.0 (CH_2, C-29), 11.3 (CH_3, C-27)*, 11.2 (CH_3, C-30)*. ^{19}F NMR (282 MHz, CD_2Cl_2) δ –152.5, –152.5. IR (neat, cm^{-1}): ν 2971, 2931, 2881, 1605, 1580, 1548, 1524, 1342, 1260, 1178, 1162, 1054, 777, 756 cm^{-1}. UV-Vis (CH_2Cl_2, c = 2.10^{-5}M): λ_{max} (Log ε): 621 (4.30), 367 (4.42), 306 (4.38), 282 (4.63). HRMS (ESI) *m/z*: $[M]^+$ Calcd for $C_{30}H_{28}BrN_2O$ 511.1380; Found 511.1367.

14-bromo-11-hydroxy-3,7-dipropyl-3,7-dihydro-11b*H*-benzo[*a*]quinolino[2,3,4-*kl*]acridin-11b-ylium tetrafluoroborate (17B). M.P. 183 °C (decomposition). ^{1}H NMR (500 MHz, CD_2Cl_2): 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). ^{13}C{1H} NMR (126 MHz, CD_2Cl_2): 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 (CH_2, C-24), 51.9 (CH_2, C-27), 21.0 (CH_2, C-25), 19.8 (CH_2, C-28), 11.3 (CH_3, C-26*), 11.3 (CH_3, C-29*). ^{19}F NMR (282 MHz, CD_2Cl_2): δ –151.4, –151.5. IR (neat, cm^{-1}): ν 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): λ_{max} (Log ε): 623 (4.00), 368 (4.14), 281 (4.41). HRMS (ESI) *m/z*: $[M]^+$ Calcd for $C_{29}H_{26}BrN_2O$ 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). ^{1}H NMR (500 MHz, CD_2Cl_2): 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, H_a-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* = 7.4 Hz, 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). ^{13}C{1H} NMR (126 MHz, CD_2Cl_2): 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 (CH_2, C-27), 51.8 (CH_2, C-24), 45.6 (CH_2, C-30), 21.7 (CH_2, C-28), 21.0 (CH_2, C-31), 19.8 (CH_2, C-25), 11.3 (CH_3, C-29), 11.3 (CH_3, C-26), 11.2 (CH_3, C-32). ^{19}F NMR (282 MHz, CD_2Cl_2): δ –152.3, –152.3. IR (neat, cm^{-1}): ν 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): λ_{max} (Log ε): 639 (3.85), 571 (4.03), 368 (4.19), 315 (4.29), 280 (4.49). HRMS (ESI) *m/z*: $[M]^+$ Calcd for $C_{32}H_{33}BrN_3$ 538.1852; Found 538.1827.

General procedure for *Suzuki* coupling reactions. In a Schlenk flask, $Pd(PPh_3)_4$ (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 N_2 atmosphere. To this mixture K_2CO_3 (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 CH_2Cl_2 (5 mL), and washed with HBF_4 (15 mL, 1M aqueous solution). The organic layer was dried, evaporated and the residue washed with Et_2O to give the corresponding product.

Synthesis of 14-Phenyl-11b*H*-benzo[*a*]chromeno[2,3,4-*kl*]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), $Pd(PPh_3)_4$ (12 mg, 0.0103 mmol, 0.1 equiv) and K_2CO_3 (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, CD_3CN): 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). **^{13}C{1H} NMR** (126 MHz, CD_3CN): 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, CH_3CN): δ –151.0, –151.1. **IR** (neat, cm^{-1}): ν 3086, 2920, 1638, 1580, 1496, 1376, 1346, 1052, 771, 699. **UV-Vis** (CH_2Cl_2, 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 $C_{29}H_{17}O_2$ 397.1223; Found 397.1224.

Synthesis of 14-(4-Nitrophenyl)-11b*H*-benzo[*a*]chromeno[2,3,4-*kl*]xanthen-11b-ylium tetrafluoroborate (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), $Pd(PPh_3)_4$ (12 mg, 0.0103 mmol, 0.1 equiv) and K_2CO_3 (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). **^{1}H NMR** (500 MHz, CD_3CN): 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). **^{13}C{1H} NMR** (126 MHz, CD_3CN): 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). **^{19}F NMR** (282 MHz, CD_3CN): δ –151.1, –151.2. **IR** (neat, cm^{-1}): ν 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 $C_{29}H_{16}NO_4$ 442.1074; Found 442.1069.

Synthesis of 14-(3-Nitrophenyl)-11b*H*-benzo[*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-Nitrophenyl boronic acid (17 mg, 0.103 mmol, 1.25 equiv), $Pd(PPh3)_4$ (9 mg, 0.008 mmol, 0.1 equiv) and K_2CO_3 (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). **^{1}H NMR** (500 MHz, CD_3CN): 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). **^{13}C{1H} NMR** (126 MHz, CD_3CN): 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, CD_3CN): δ **–**151.1, –151.2. **IR** (neat, cm^{-1}): ν 3083, 2925, 2852, 1741, 1637, 1601, 1580, 1496, 1374, 1347, 1281, 1243, 1053, 769, 735. **UV-Vis** (CH_2Cl_2, 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 $C_{29}H_{16}NO_4$ 442.1074; Found 442.1084.

Synthesis of 14-(4-Methoxyphenyl)-11b*H*-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), $Pd(PPh_3)_4$ (12 mg, 0.0103 mmol, 0.1 equiv) and K_2CO_3 (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). **^{1}H NMR** (400 MHz, CD_3CN): 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). **^{13}C{1H} NMR** (101 MHz, CD_3CN): 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 (CH_3, C-30). **^{19}F NMR** (282 MHz, CH_3CN): δ –151.1, –151.2. **IR** (neat, cm^{-1}): ν 3077, 2926, 2858, 1637, 1603, 1580, 1498, 1374, 1348, 1279, 1250, 1183, 1054, 833, 777, 731. **UV-Vis** (CH_2Cl_2, 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 $C_{30}H_{19}O_3$ 427.1329; Found 427.1325.

General procedure for *Suzuki* coupling with styryl boronic acids. In a Schlenk flask PPh_3 (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 N_2 atmosphere. To this mixture K_2CO_3 (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 CH_2Cl_2 and washed with HBF_4 (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 Et_2O (2 x 30 mL) to give the corresponding product.

Synthesis of (*E*)-14-styryl-11b*H*-benzo[*a*]chromeno[2,3,4-*kl*]xanthen-11b-ylium tetrafluoroborate (21a). Following the general procedure for *Suzuki* 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 K_2CO_3 (57 mg, 0.410 mmol, 4 equiv) were stirred. After work up the desired compound **21a** (30 mg, 57%) was isolated as blue-green solid. **M.P.:** 205 °C (decomposition). **^{1}H NMR** (500 MHz, CD_3CN): 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). **^{13}C{1H} NMR** (126 MHz, CD_3CN): 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). **^{19}F NMR** (282 MHz, CD_3CN): δ –151.06, –151.11. **IR** (neat, cm^{-1}): ν 3540, 2925, 2857, 1638, 1601, 1579, 1498, 1374, 1347, 1275, 1157, 1059, 792, 755, 697. **UV-Vis** (CH_2Cl_2, 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 $C_{31}H_{19}O_2$ 423.1380; Found 423.1371.

Synthesis of (*E*)-14-(4-fluorostyryl)-11b*H*-benzo[*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), PPh_3 (2 mg, 0.0103 mmol, 0.1 equiv) and K_2CO_3 (71 mg, 0.513 mmol, 5 equiv) were stirred. After work up the desired compound **21b** (37 mg, 68%) was isolated as blue-green solid. **M.P.:** 194 °C (decomposition). **^{1}H NMR** (500 MHz, CD_3CN): 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). **^{13}C{1H} NMR** (126 MHz, CD_3CN): δ 163.5 (d, C, $^1J_{C-F}$ = 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, $^3J_{C-F}$ = 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, $^2J_{C-F}$ = 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). **^{19}F NMR** (282 MHz, CD_2Cl_2): δ –113.9, **–**151.0, –151.04. **IR** (neat, cm^{-1}): ν 3315, 2929, 1634, 1581, 1503, 1376, 1350, 1278, 1228, 1159, 1057, 974, 773. **UV-Vis** (CH_2Cl_2, 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 $C_{31}H_{18}FO_2$ 441.1285; Found 441.1276.

Synthesis of (*E*)-14-(4-methoxystyryl)-11b*H*-benzo[*a*]chromeno[2,3,4-*kl*]xanthen-11b-ylium tetrafluoroborate (21c). Following the general procedure for *Suzuki* 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), PPh_3 (2 mg, 0.0103 mmol, 0.1 equiv) and K_2CO_3 (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). **^{1}H NMR** (500 MHz, CD_3CN): 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). **^{13}C{1H} NMR** (126 MHz, CD_3CN): 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). **^{19}F NMR** (282 MHz, CD_2Cl_2): δ –151.0, –151.1. **IR** (neat, cm^{-1}): ν 3072, 2933, 1636, 1600, 1580, 1508, 1495, 1345, 1243, 1176, 1047, 1034, 972, 763. **UV-Vis** (CH_2Cl_2, 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 $C_{32}H_{21}O_3$ 453.1485; Found 453.1486.

Synthesis of 14-Phenyl-3,7-dipropyl-3,7-dihydro-11b*H*-benzo[*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 N_2 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 CH_2Cl_2 and washed with HBF_4 (1 M aqueous solution, 2 x 5 mL). The organic phase was dried over Na_2SO_4 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; **R_f** =0.67 (Silica gel, CH_2Cl_2/MeOH, 98:2). **^{1}H NMR** (500 MHz, CD_2Cl_2): 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). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): 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 (CH_2, C-30), 51.5 (CH_2, C-33), 20.9 (CH_2, C-31), 20.0 (CH_2, C-34), 11.3 (CH_3, C-32), 11.2 (CH_3, C-35). **^{19}F NMR** (282 MHz, CD_2Cl_2): δ –152.46, –152.47. **IR** (neat, cm^{-1}): ν 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): λ_{max} (Log ε): 624 (3.89), 429 (3.11), 379 (3.93), 289 (4.34). **HRMS (ESI) *m/z*:** $[M]^+$ Calcd for $C_{35}H_{31}N_2$ 479.2482; Found 479.2462.

Synthesis of 14-Bromo-11b*H*-benzo[*a*]chromeno[2,3,4-*kl*]xanthene (23A). To a solution of **8A** (35 mg, 0.087 mmol, 1 equiv) in acetonitrile (10 mL) $NaBH_4$ (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 CH_2Cl_2 and washed with water. The organic layer was dried over Na_2SO_4 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). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): 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 of 14-Bromo-3-propyl-3,11b-dihydrobenzo[*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) $NaBH_4$ (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 CH_2Cl_2 and washed with water. The organic layer was dried over Na_2SO_4 and evaporated under *vacuum*. The neutral product **24A** was isolated as a colorless solid. **^{1}H NMR** (500 MHz, CD_2Cl_2): 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). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): 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 (CH_2, C-24), 20.5 (CH_2, C-25), 11.1 (CH_3, C-26).

Synthesis of 14-Bromo-3,7-dipropyl-7,11b-dihydro-3*H*-benzo[*a*]quinolino[2,3,4-*kl*]acridine (25A). To a solution of **9A** (12 mg, 0.015 mmol, 1 equiv) in acetonitrile (5 mL) $NaBH_4$ (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 CH_2Cl_2 and washed with water. The organic layer was dried over

Na_2SO_4 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). **^{1}H 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, H_a-24), 3.72 (m, 1H, H_b-24), 1.96 (m, 2H, H-28), 1.82 (m, 2H, H-25), 1.10-1.04 (m, 6H, H-26, H-29). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): 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 (CH_2, C-24), 47.4 (CH_2, C-27), 36.0 (CH, C-11), 21.2 (CH_2, C-28), 20.5 (CH_2, C-25), 11.7* (CH_3, C-29), 11.0* (CH_3, C-26).

Synthesis of 14-bromo-11-methoxy-11b*H*-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) $NaBH_4$ (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 CH_2Cl_2 and washed with water. The organic layer was dried over Na_2SO_4 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): **^{1}H 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). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): 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 (CH_3, 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) $NaBH_4$ (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 CH_2Cl_2 and washed with water. The organic layer was dried over Na_2SO_4 and evaporated under *vacuum*. The residue was purified by column chromatography (eluent: pentane/Et_2O = 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 NMR-experiments. In the case of **24B major** was performed X-ray analysis on monocrystal. Data for **24B major ((*p*)-(*R*)-14-bromo-11-methoxy-3-propyl-3,11*b*-dihydrobenzo[*a*]chromeno[2,3,4-*kl*]acridine)**: **^{1}H NMR** (500 MHz, CD_2Cl_2): 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). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): 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 (CH_2, C-25) 32.4 (CH_3, C-24), 20.5 (CH_2, C-26), 11.1 (CH_3, C-27). Data for **24B minor ((*m*)-(*R*)-14-bromo-11-methoxy-3-propyl-3,11*b*-dihydrobenzo[a]chromeno[2,3,4-*kl*]acridine)**: **^{1}H NMR** (500 MHz, CD_2Cl_2): 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). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): 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 (CH_3, C-24), 48.2 (CH_2, C-25), 21.7 (CH_2, C-26), 11.7 (CH_3, 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) $NaBH_4$ (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 CH_2Cl_2 and washed with water. The organic layer was dried over Na_2SO_4 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): **^{1}H 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). **^{13}C{1H} NMR** (126 MHz, CD_2Cl_2): 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 (CH_3, C-24), 48.4 (CH_2, C-25), 47.9 (CH_2, C-28), 35.1 (CH, C-11), 21.3 (CH_2, C-29), 20.3 (CH_2, C-26), 11.7 (CH_2, C-27)*, 11.1 (CH_2, C-30)*.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXX. It contains ^{1}H NMR, ^{13}C NMR, ^{19}F 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 article can be found at the following DOI: 10.26037/yareta:jbrucdsj5nentl4mjqehwtcycu. It will be preserved for 10 years.

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Notes

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SYNOPSIS TOC