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Synthesis and Emitting Properties of the Blue-Light Fluorophores Indolizino[3,4,5-*ab*]isoindole Derivatives

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Indolizino[3,4,5-*ab*]isoindoles **3a**–**3k** have been synthesized by [8+2] cycloaddition reactions of the corresponding indolizines **2a**–**2k** with benzyne in moderate yields. Cycloadditions of pyrrolo[2,1-*a*]isoquinolines **4a**–**4c** with benzyne gave the benzo[6,7]pyrrolizino[3,4,5-*ab*]isoquinolines **5a**–**5c**. Compounds **7** and **9** were similarly prepared by the reactions of 6*H*-[1]benzopyrano[3,4-*a*]indolizine-6-one (**6**) and 6*H*-[1]benzopyrano[3′,4′:3,4]pyrrolo[2,1-*a*]isoquinolin-6-one (**8**) with benzyne in 93 and 62 % yields, respectively. The electronic structures of these compounds have been calculated by the DFT method at the B3LYP/6-31G level. Compounds **3a**–**3j** fluoresce in the blue region (λ^{F}_{max} = 439–475 nm) with high quantum yields (Φ_F = 0.49–0.77 in ethanol). Compounds **5a**–**5c** and **9** are fluorescent in the green region with quantum yields of 0.44–0.77 in ethanol and compound **7** emits blue light with a quantum yield of 0.59. The electrochemical properties of these compounds have been investigated by cyclic voltammetry. Indolizino[3,4,5-*ab*]isoindoles without a substituent at C-2 (compounds **3a**, **3c**, **3d**) or with an alkyl substituent in the framework (**3i**, **3k**) undergo irreversible anodic oxidations and reversible cathodic reductions. Compounds **3e** and **3g** with an electron-withdrawing group at C-2, on the other hand, undergo quasi-reversible oxidations at 1.2–1.3 V (SCE) and reversible reductions at –1.5 to –1.9 V (SCE). Therefore, compounds **3e** and **3g** may be promising candidates to serve as blue-light emitters with both hole- and electron-transporting ability in monolayer OLED devices, while the other indolizino[3,4,5-*ab*]isoindoles (**3a**–**3d**, **3f**, **3h**–**3i**) are potential blue-light emitters with electron-transporting ability.

Introduction

Belonging to the general family of cyclazines and as *N*-bridged annulenes with 10 peripheral π electrons, pyrrolo[2,1,5-*cd*]indolizines, or [2,2,3]cyclazines following the naming system of Boekelheide[1] and Leaver[2] and their coworkers, have been drawing continuous research interest owing to their special electronic structures,[3] high fluorescence efficiency,[4] wide range of biological activity[5] and the fact that their partially hydrogenated frameworks have been found in several natural products.[6] In particular, their 1,2-benzannulated derivatives indolizino[3,4,5-*ab*]isoindoles have recently been found to be excellent fluorophores with high emission quantum yields and tunable colours in the blue and green region and may have promising applications as electroluminescence materials, sensors, etc.[7] Therefore, further investigation of their luminescence–structure relationship and other photophysical properties that have a bearing on their photoelectric functions is desirable. For this purpose, general and efficient synthetic methods leading to diverse structural modifications such as the introduction of functional groups at different ring positions and further annulation of the indolizino[3,4,5-*ab*]isoindole framework are needed.

Indolizino[3,4,5-*ab*]isoindoles are presently mainly prepared by the [2+12] cycloadditions of pyrido[2,1-*a*]isoindoles with electron-deficient alkynes and alkenes.[7–9,11] Therefore, they were prepared by the cycloaddition of 6-cyanopyrido[2,1-*a*]isoindoles with electron-deficient alkynes followed by the elimination of a hydrogen cyanide molecule[8a,11] or by the cycloaddition of pyrido[2,1-*a*]isoindoles with electron-deficient alkenes in the presence of dehydrogenation reagents such as chloranil, oxygen and sulfur.[7,9] These reactions have been mainly applied to the synthesis of 1- and 2-mono- or 1,2-disubstituted indolizino[3,4,5-*ab*]-isoindole derivatives and the starting pyrido[2,1-*a*]isoindoles need to be prepared by photoinduced cyclization of 1-benzyl-2-bromopyridinium bromide followed by deprotonation of the formed pyrido[2,1-*a*]isoindolinium bromide with sodium carbonate as base.[10] Matsumoto and Uchida have reported that indolizino[3,4,5-*ab*]isoindoles and their

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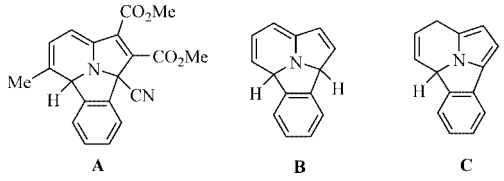
1,2-benzo- and 1,2:3,4-dibenzo-annulated derivatives can be prepared by consecutive cycloadditions of pyridinium or isoquinolinium dicyanomethylide with two benzynes.[8a,11] The benzyne precursor used in these reactions was 2-(phenyliodonio)benzoate and the yields of the benzo- and dibenzo-annulated indolizino[3,4,5-*ab*]isoindole products are in the range of 18–39%.[11] To the best of our knowledge, there has so far been no systematic investigation into the synthesis of indolizino[3,4,5-*ab*]isoindole derivatives by [8+2] cycloaddition reactions of benzyne with indolizines except for a single report in which the 1,2-benzannulated indolizino[3,4,5-*ab*]isoindole (benzo[1′,2′:1,2]indolizino-[3,4,5-*ab*]isoindole) was prepared by the [12+2] cycloaddition of benzyne with pyrido[2,1-*a*]isoindole in 6.6% yield with bromobenzene as the benzyne precursor.[7] We envisioned that the cycloadditions of the easily accessible substituted indolizines with benzyne generated from the 2-trimethylsilyl trifluoromethanesulfonate precursor **1**,[12] would provide a general and versatile synthesis of indolizino[3,4,5-*ab*]isoindole derivatives with different substitution patterns under mild conditions. Hence, we have synthesized a series of indolizino[3,4,5-*ab*]isoindole derivatives by this method and further investigated their fluorescence and electrochemical properties, as well as their electronic structure by molecular orbital calculations, because of their potential applications as blue and green light-emitting fluorophores and electroluminescent materials for OLED devices.[13]

Results and Discussion

Synthesis of Indolizino[3,4,5-*ab*]isoindoles (3a–3k) and Annulated Indolizino[3,4,5-*ab*]isoindoles (5, 7 and 9)

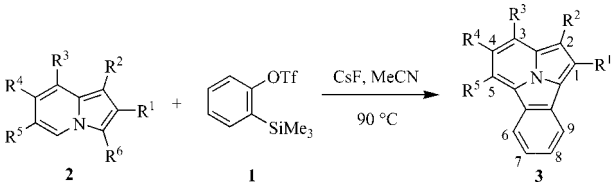
We first investigated the reactions of indolizines **2a**–**2k** with **1** as the benzyne precursor in the presence of cesium fluoride in acetonitrile and found that these reactions proceeded smoothly at reflux temperature to afford the desired indolizino[3,4,5-*ab*]isoindoles **3a**–**3k**, respectively, in 23–75% yields (Table 1).

These products were fully characterized by spectral (^{1}H NMR, IR and MS) and analytical data. In their ^{1}H NMR spectra, all the ring protons absorb in the region of δ = 7.3–8.6 ppm, indicating the aromatic nature of the indolizino[3,4,5-*ab*]isoindole framework. In their mass spectra, in almost all cases except for **3j** and **3k**, there is a very strong molecular ion peak which often (for **3a**–**3d**, **3h**, **3i**) occurs as the base peak. The yields of the products were found to be dependent on the stability of the starting indolizines. Therefore, the low yield in the reaction of 2-phenylindolizine (**2a**) is largely caused by the low stability of this compound in solution upon heating. It is seen in Table 1 that the 3-cyanoindolizine **2j** gave a much higher yield of the cycloaddition product **3j** than all the other indolizines (**2a**–**2i**, **2k**) without a cyano in the 3-position. This shows that subsequent elimination of hydrogen cyanide from the primary cycloadduct **A** might be much more facile than the dehydrogenation of the primary cycloadduct **B** or its hydrogen-migrated isomer **C** formed in the reactions of 3-unsubstituted indolizines.[14]



For comparison, **3b**–**3d** were also synthesized with 1-aminobenzotriazole as the benzyne precursor with lead tetraacetate as the oxidation reagent.[15] These reactions invariably resulted in lower yields than obtained with **1** as the benzyne precursor (see Table 1, yields in parentheses).

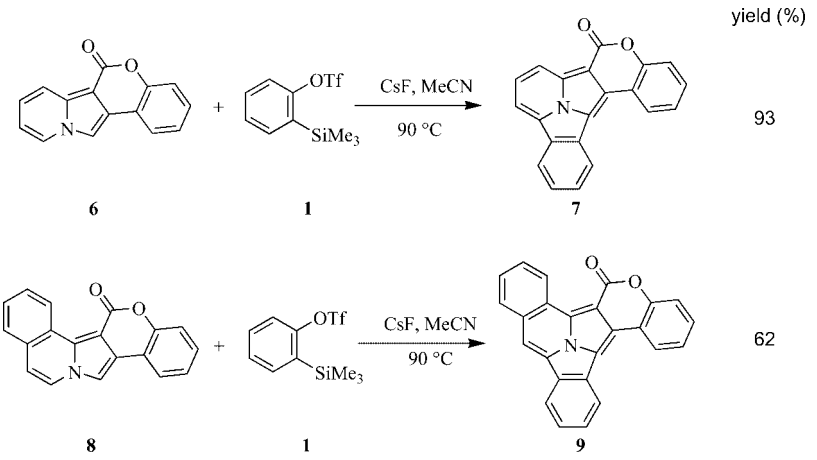
Table 1. Synthesis of indolizino[3,4,5-*ab*]isoindoles **3a**–**3k**.



2 1 3

R^1	R^2	R^3	R^4	R^5	R^6	Reagent	Product	Time[a] [h]	Yield[b,c] [%]
Ph	H	H	H	H	H	**2a**	**3a**	12	23
Ph	Me	H	H	H	H	**2b**	**3b**	7	49 (40)
Ph	H	Me	H	H	H	**2c**	**3c**	8	44 (18)
Ph	H	H	Me	H	H	**2d**	**3d**	8	55 (42)
H	CN	H	Me	H	H	**2e**	**3e**	7	51
H	CO_2Me	H	H	H	H	**2f**	**3f**	9	50
CO_2Me	CO_2Me	H	H	H	H	**2g**	**3g**	9	50
CO_2Et	CO_2Et	H	H	H	H	**2h**	**3h**	8	37
CO_2Et	CO_2Et	H	Me	H	H	**2i**	**3i**	8	30
CO_2Me	CO_2Me	H	H	Me	CN	**2j**	**3j**	10	75
Ph	PhCO	H	Me	H	H	**2k**	**3k**	8	51

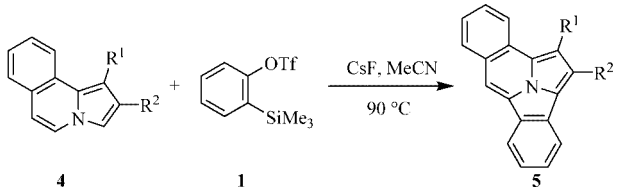
[a] Reaction time. [b] Isolated yield. [c] Yield in parentheses was obtained by using 1-aminobenzotriazole as benzyne precursor.



Scheme 1. Synthesis of annulated indolizino[3,4,5-*ab*]isoindoles **7** and **9**.

We then investigated the reactions of the pyrrolo[2,1-*a*]-isoquinolines **4a**–**4c** with benzyne. The starting materials **4a**–**4c** were prepared by the 1,3-dipolar cycloadditions of isoquinolinium carboxymethylide with the corresponding alkynes.[16] Their reactions with **1** under the same conditions as described above for the reactions of **2a**–**2k** with **1** gave the corresponding benzo[6,7]pyrrolizino[3,4,5-*ab*]isoquinolines **5a**–**5c** as red solids, respectively, in 52–60% yield (Table 2).

Table 2. Synthesis of indolizino[3,4,5-*ab*]isoindoles **5a**–**5c**.



4 1 5

R^1	R^2	Reagent	Product	Time[a] [h]	Yield[b] [%]
CO_2Me	H	**4a**	**5a**	8	60
CN	H	**4b**	**5b**	8	52
CO_2Et	CO_2Et	**4c**	**5c**	8	58

[a] Reaction time. [b] yield of isolated products.

Compounds **5a**–**5c** have strong molecular ion peaks in their MS spectra, with **5b** and **5c** having this peak as the base peak. To examine the influence of further annulation to the indolizino[3,4,5-*ab*]isoindole and the effect of incorporating another heterocycle which is itself a good fluorophore[17] into the π system, the reactions of 6*H*-[1]benzopyrano[3,4-*a*]indolizin-6-one (**6**)[16] and 6*H*-[1]benzopyrano-[3′,4′:3,4]pyrrolo[2,1-*a*]isoquinolin-6-one (**8**)[16] with **1** under the same conditions as described above were investigated. These reactions afforded **7** and **9**, respectively, in high yields (Scheme 1).

Molecular Structures of Compounds 3, 5, 7 and 9

DFT calculations have been shown to give structural parameters (bond lengths and angles) that well reproduce the X-ray crystallographic structures of many polycyclic heterocyclic compounds,[18] including some indolizino[3,4,5-*ab*]-isoindole derivatives.[7] We have carried out DFT calculations on compounds **3**, **5**, **7** and **9** at the B3LYP/6-31G level. The molecular geometry and frontier molecular orbital (FMO) properties of some representative compounds are given in the Supporting Information and the FMOs of compound **3a** are shown in Figure 1. Regarding the molecular structure, the calculations on compounds **3** gave results similar to those reported for some other indolizino[3,4,5-*ab*]isoindole derivatives,[7] showing that these polycyclic heterocycles with 14 peripheral π electrons can be viewed as consisting of two aromatic fragments: indolizine (10π electrons) and benzene (6π electrons). Compounds **5a**–**5c**, **7** and **9** have the same structural characteristics. Therefore, in **5a**–**5c**, the two C–C bonds (C7a–C7b and C11a–C11b) connecting the pyrrolo[2,1-*a*]isoquinoline ring with the benzene ring are significantly longer (1.45–1.47 Å) than normal C=C bonds (1.34 Å) and are similar to the length of C_{sp^2}–C_{sp^2} bonds that link two independent aromatic rings such as the bond between the two phenyls in biphenyl (1.49 Å).[19] Similarly, in **7** and **9**, the lengths of the two corresponding bonds linking the benzene ring with the annulated indolizine ring are 1.45–1.46 Å.

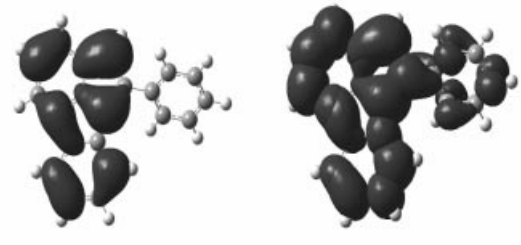


Figure 1. HOMO and LUMO of compound **3a** at the B3LYP /6-31G//B3LYP/6-31G level of theory.

Absorption and Fluorescence Spectral Properties of Compounds 3, 5, 7 and 9

The indolizino[3,4,5-*ab*]isoindoles **3a**–**3k** have similar UV/Vis spectra, with the longest wavelength absorption

Table 3. Absorption and fluorescence spectral properties and redox potentials of compounds **3**, **5**, **7** and **9**.

	λ^{A}_{max} [nm] (ε [10^4 L mol^{-1} cm^{-1}])	Stoke's shift: $\Delta\lambda$ [nm]	λ^{F}_{max}[a] [nm]	Φ_F[a]	τ_F[b] [ns]	E^{ox} [c] [V]	E^{red} [c] [V]
3a	284 (1.36), 406 (0.38), 431 (0.68)	14	445	0.49	18.0 ± 0.3	0.95	–2.03
3b	265 (6.35), 312 (2.30), 437 (0.71), 463 (0.88)	11	474	0.63	19.6 ± 0.1	0.77	–2.04/–2.13
3c	266 (5.53), 422 (0.66), 447 (0.81)	8	455	0.64	14.8 ± 0.1	0.84	–1.99/–2.13
3d	265 (6.77), 311 (2.72), 436 (0.84), 464 (0.98)	11	475	0.50		0.75	–2.02/–2.09
3e	265 (4.62), 296 (2.19), 410 (0.56), 432 (0.63)	15	447	0.51	16.7 ± 0.2	1.29/1.26	–1.81/–1.88
3f	268 (5.69), 321 (1.55), 405 (0.64), 430 (0.81)	9	439	0.52		not measured	
3g	269 (4.01), 312 (1.72), 425 (0.94), 442 (0.92)	22	464	0.77	11.5 ± 0.1	1.32/1.23	–1.55/–1.60
3h	269 (3.96), 312 (1.68), 425 (0.87), 440 (0.8)	26	466	0.60	11.7 ± 0.1	1.41	–1.54/–1.61
3i	272 (6.84), 430 (0.43), 447 (0.42)	26	473	0.72	13.0 ± 0.1	1.39	–1.56/–1.64
3j	268 (3.44), 425 (0.74), 444 (0.68)	18	462	0.69		not measured	
3k	265 (3.43), 352 (0.95), 422 (1.01), 446 (1.36)	18	464	0.01		1.23	–1.74/–1.77
5a	284 (5.29), 318 (5.07), 476 (1.01), 506 (1.69)	13	519	0.70	28.6 ± 0.3	0.96	–1.52/–1.59
5b	284 (3.64), 317 (2.83), 477 (0.49), 506 (0.83)	15	521	0.60	30 ± 1[d]	1.06	–1.44/–1.52
5c	286 (4.35), 319 (1.96), 513 (0.86)	43	556	0.44		1.07	–1.24/–1.32
7	278 (4.11), 343 (1.50), 413 (0.94), 439 (1.58)	6	445	0.59	6.5 ± 0.2[d]	1.38	–1.65/–1.71
9	325 (4.77), 391 (2.56), 475 (0.75), 509 (1.67)	9	518	0.77		1.08	–1.44

[a] Measured in EtOH. [b] Measured in MeCN. [c] There is also a small amount of 2nd exponential decay, but evaluation is not possible. The values given are τ_{eff}. [d] E^{ox} and E^{red} were measured in MeCN with a saturated calomel electrode (SCE) as the reference electrode. For irreversible redox processes, peak potentials are listed. For reversible and partly reversible processes, anodic and cathodic peaks are given.

maxima in the range of 405–447 nm (Table 3 and Figure 2 for **3a**; for the spectra of the other compounds, see the Supporting Information). Compounds **5a**–**5c**, which are 3,4-annulated indolizino[3,4,5-*ab*]isoindoles, have their longest wavelength absorption maxima red-shifted to the 506–513 nm region (Table 3). In contrast, annulation of the indolizino[3,4,5-*ab*]isoindoles at the 1,2-position by the coumarin ring resulted in no red shift of the absorption spectrum and compound **7** absorbs at a similar wavelength as **3a**–**3k**, with the longest wavelength absorption at 439 nm. In accord with this, the absorption spectrum of compound **9** displays no red shift, as compared with its unannulated counterpart **5**, and **9** has its longest λ absorption at 509 nm (Table 3).

This different effect of the 1,2- (in compound **7**) and 3,4- (in compound **5**) annulations on the absorption wavelength may be rationalized in terms of the nature of the annulation groups. In **5**, the 3,4-positions are annulated by the electron-rich benzene ring, whose main effect is to extend the π-conjugation system to lead to a more dense distribution of the molecular orbitals and a decreased HOMO–LUMO energy gap. This situation is reflected in the smaller redox potential gaps for compounds **5a**–**5c** (oxidation–reduction potential gaps are 2.52, 2.54 and 2.35 eV for **5a**, **5b** and **5c**, respectively) than for compounds **3** (redox potential gaps in the range 2.81–2.99 eV). In contrast, compound **7** is derived from the annulation of the 1,2-positions of **3** by an electron-deficient coumarin ring which causes the simultaneous lowering of the HOMO and LUMO energy levels (both ionization potential and electron affinity are raised). As a result, the HOMO–LUMO gap in **7** is not much changed from that in **3**. In accord with this, the redox potential gap for **7** is close to those of compounds **3** (≈3 eV).

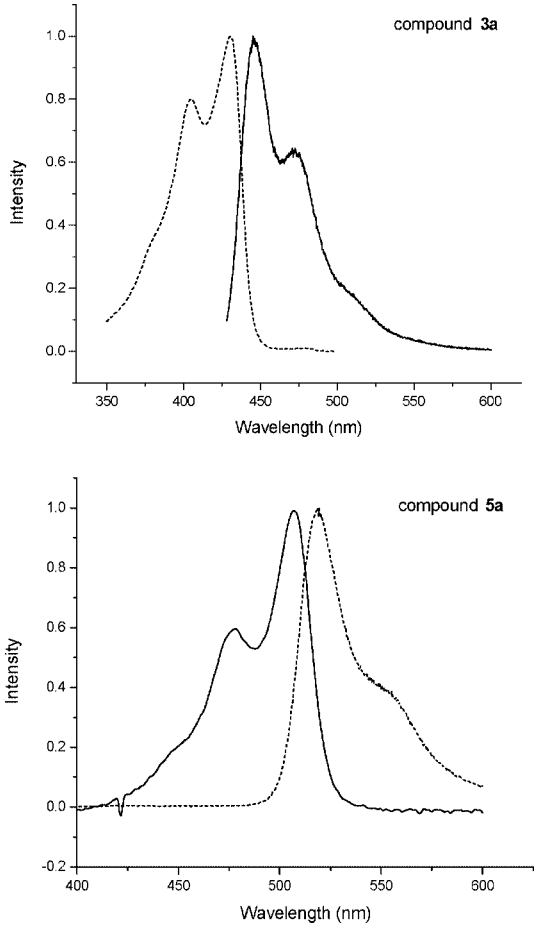


Figure 2. Normalized absorption and fluorescence spectra of **3a** and **5a**.

Compounds **3a**–**3k** are fluorescent in the region 439–475 nm (Table 3). Except for **3k**, all these compounds have high fluorescence quantum yields in the range of 0.49–0.77 in ethanol. For compound **3k**, the introduction of a benzoyl group at the C-2 atom resulted in a drastic decrease in fluorescence efficiency, making it behave as a typical aromatic

ketone with a Φ_F of 0.01. While compounds **3a**–**3k** emit in the blue region, the benzo[6,7]pyrrolizino[3,4,5-*ab*]isoquinolines **5a**–**5c** fluoresce in the green region with high quantum yields. Similar to the absorption spectra, compound **7** fluoresces at a similar wavelength as compounds **3a**–**3k** despite an extended π system in the former. In line with this, compound **9** fluoresces at a similar wavelength as compounds **5a**–**5c**.

The Stoke's shifts for most of the compounds (**3a**–**3f**, **5a**–**5b**, **7** and **9**) are small (≈10 nm). This, together with the good mirror-image relationship between the absorption and fluorescence spectra, indicates that these compounds have a rigid molecular framework that experiences only small geometry changes upon excitation. For compounds **3g**–**3k** and **5c**, the presence of bulky and conformationally flexible side-chains leads to a significantly larger Stoke's shift.

Fluorescence lifetimes for compounds **3a**–**3c**, **3e**, **3g**–**3i**, **5a**, **5b** and **7** have been measured and the results are given in Table 3. Compounds **3** have singlet lifetimes in the range 11–20 ns, similar to the fluorescence lifetimes of their ancestor indolizine compounds.[20]

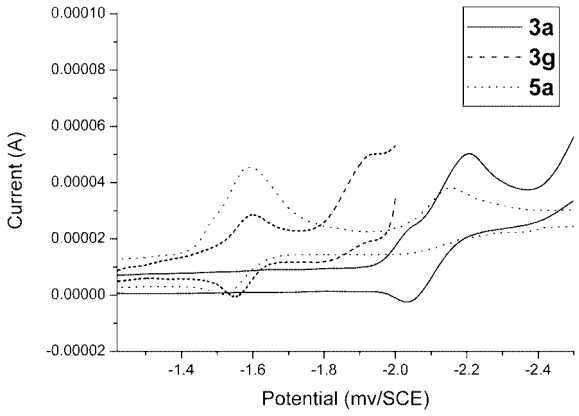


Figure 3. Cyclic voltammograms for compounds **3a**, **3g** and **5a**.

Electrochemical Properties

The oxidation and reduction potentials of the synthesized compounds have been measured by cyclic voltammetry to evaluate their potential as hole- and electron-transporting species. The results are summarized in Table 3.

For the indolizino[3,4,5-*ab*]isoindoles without a substituent at the C-2 atom, for example, compounds **3a**, **3c**, **3d**, the oxidations are irreversible without the corresponding radical-cation reduction peaks being observed during the cathodic scan, indicating an EC process at the anode. This behaviour is similar to the electrochemical oxidations of the indolizine derivatives in which the irreversible oxidation of the 1-unsubstituted indolizines was caused by the dimerization of the cation radicals to afford the 1,1′-biindolizines,[21,22] as evidenced by bulk electrolysis.[21] The oxidations of **3i** and **3k**, which have a methyl at the C-4 atom, are also irreversible. This is probably the result of facile deprotonation of the highly acidic cation radicals, as is often observed in methylarene cation radicals.[23] In contrast, the oxidations of compounds **3e** and **3g** with an electron-withdrawing group at C-2 are partially reversible with discernible cathodic peaks (Figure 3). In these cases, dimerization and alkyl deprotonation pathways of the cation radicals are blocked. The reductions for most of the indolizino[3,4,5-*ab*]-isoindoles are either reversible (**3a**, **3b** and **3g**) or partially reversible (**3c**, **3e**, **3h**, **3i** and **3k**), bespeaking the high stability of their anion radicals. The oxidations of compounds **5a**–**5c** are irreversible, but their reductions are reversible. For compounds **7** and **9**, both oxidations and reductions are irreversible.

The reduction potentials of compounds **7** and **9** are largely decided by the coumarin structural unit and are at slightly more negative values than that of coumarin itself (–1.35 V vs. SCE).[24] The irreversibility of the reductions of **7** and **9** are likely the result of the irreversible reduction of the coumarin ring which is known to cause dimerization to give the 4,4′-dimeric product.[24]

The redox potentials are sensitively influenced by the nature and the position of the substituents on the ring. Therefore, electron-withdrawing groups significantly raise the oxidation potential and make the reduction potential less negative, while electron-pushing groups have the reverse effect. The redox potentials are also strongly dependent on the position of the substituent in relation to the atomic coefficients in different ring positions in the HOMO and LUMO of the parent compound **3a**, as calculated by the DFT method at the B3LYP/6-31G level (Figure 1). Introduction of an electron-donating group (such as a methyl) at a ring position that has a large atomic coefficient in the HOMO (or LUMO) would lead to a decline in the oxidation potential (or a more negative reduction potential), while introducing an electron-withdrawing group at such a position has the reverse effect. However, the oxidation potentials seem to be more sensitive than the reduction potentials.

As a general rule, introducing an alkyl group at C-2 or, to a lesser extent, at C-4, would significantly lower the oxidation potential of the 1-phenylindolizino[3,4,5-*ab*]isoindoles, while placing an alkyl group at C-3 or C-5 would efficiently cause the reduction potentials to be more negative.

Compounds **5a**–**5c** are benzannulated indolizino[3,4,5-*ab*]isoindoles. Comparison of the oxidation potential of **9** with its benzannulated counterpart **5c** shows that the fusion of a benzene ring leads to a lowering of the oxidation potential by 0.33 eV.

The fusion of the electron-withdrawing coumarin ring at the 1,2-position in compound **7** results in an oxidation potential similar to **3g** and **3h**. Compound **9** has a much lower oxidation potential than **7** because of the further benzoannulation, **9** having an $E^{1}/_{2}$ value similar to compounds **5a**–**5c** with an electron-withdrawing group in the ring.

Conclusions

In summary, cycloadditions of indolizines and annulated indolizines with benzyne [generated from the precursor 2-(trimethylsilyl)phenyl triflate] provide a general and versatile one-pot synthesis of the indolizino[3,4,5-*ab*]isoindoles **3** and their 1,2- or 3,4-annulated and 1,2:3,4-bisannulated derivatives. By this method, 11 new indolizino[3,4,5-*ab*]isoindoles (**3a**–**3k**) and their 3,4-annulated (**5a**–**5c**), 1,2-annulated (**7**) as well as 1,2:3,4-bisannulated (**9**) derivatives have been synthesized in moderate to high yields. Compounds **3a**–**3i** are strong blue-light fluorophores that emit in the wavelength region of 439–475 nm with high quantum yields. In particular, for the indolizino[3,4,5-*ab*]isoindoles with an electron-withdrawing group at the C-2 atom (e.g., compounds **3e** and **3g**), their electrochemical redox processes are quasi-reversible or reversible in suitable potential regions (E^{ox} 1.2 to 1.3 V, E^{red} –1.5 to –1.9 V vs. SCE). This advantageous combination of fluorescence and electrochemical properties make them favourable candidates as blue-light emitters with both hole- and electron-transporting ability in monolayer OLED devices.[13] The other indolizino[3,4,5-*ab*]isoindoles (**3a**–**3d**, **3f**, **3h**, **3i** and **7**) may be tested as blue-light emitters with electron-transporting ability. In addition, compounds **5a**–**5c** and **9** are highly efficient fluorophores in the green region.

Experimental Section

General Methods: Melting points are uncorrected. ^{1}H NMR spectra were measured with a Bruker DPX 300 spectrometer at 300 MHz with $CDCl_3$ as solvent unless otherwise stated. The chemical shifts (δ) are reported in ppm relative to the residual deuteriated solvent signal and coupling constants (J) are given in Hz. ^{13}C NMR spectra were measured with a Bruker Avance 400 spectrometer at 100 MHz with $CDCl_3$ as solvent. IR spectra were recorded with a Shimadzu IR 440 spectrometer in KBr pellets. Mass spectra were recorded with a VG ZAB–HS spectrometer in the electron-impact ionization mode. Elemental analyses were performed with a Perkin–Elmer 240C analyzer.

Fluorescence and UV/Vis Spectroscopy: UV/Vis spectra were run on a Varian Cary 50 spectrophotometer. Fluorescence measurements were performed with a Varian Cary Elipse fluorospectrometer. Quantum yields were determined by using perylene in degassed cyclohexane as a standard (Φ = 0.94).[7] Lifetime measurements were carried out in acetonitrile by a modulation technique with a digital storage oscilloscope; the sample concentration was 2×10^{-5} M.

Cyclic Voltammetry: Cyclic voltammetry (CV) was performed with a three-electrode cell in acetonitrile solution with 0.1 M (nBu)$_4$N-ClO_4 as the supporting electrolyte. The scan rate was 100 mV/s. A Pt wire was used as the counter-electrode, glassy carbon was used as the working electrode and a saturated calomel electrode (SCE) was used as the reference electrode. The set-up was calibrated with potassium ferricyanide [$K_3Fe(CN)_6$] as the reference: E_p^{ox} = 0.226 V, E_p^{red} = 0.285 V vs. SCE[25] in 1 M KCl aqueous solution.

Computational Methods: The Gaussian 2003 series of programs[26] was used for all calculations. All molecules were fully optimized using the hybrid density functional B3LYP level of theory with the 6-31G basis set. All optimized structures were found to be planar by frequency analysis.

General Procedure for the Preparation of Compounds 3a–3k: A mixture of indolizine (**2a**–**2k**, 1.0 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**1**, 0.53 g, 2 mmol) and cesium fluoride (0.64 g, 4 mmol) in MeCN (20 mL) was heated at 90 °C for 7–12 h with magnetic stirring. The reaction was monitored by TLC. The solvent was removed in vacuo, the residue was poured into water, extracted with CH_2Cl_2 and then separated by flash chromatography on a silica gel column with petroleum ether (b.p. 60–90 °C)/ethyl acetate as eluent to give the product.

1-Phenylindolizino[3,4,5-*ab*]isoindole (3a): Yield: 61 mg (23%), yellow solid from petroleum ether (b.p. 60–90 °C)/ethyl acetate, m.p. 75–76 °C. IR (KBr): $\tilde{\nu}$ = 1604, 1497, 751 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.33 (s, 1 H), 7.47 (t, J = 7.4 Hz, 1 H), 7.56 (t, J = 7.6 Hz, 1 H), 7.63 (t, J = 7.6 Hz, 2 H), 7.73 (t, J = 6.9 Hz, 2 H), 8.06 (d, J = 8.3 Hz, 1 H), 8.11 (dd, J = 7.1, 1.7 Hz, 3 H), 8.43 (d, J = 8.1 Hz, 1 H), 8.49 (d, J = 8.0 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 104.3, 108.2, 115.4, 115.7, 120.0, 120.2, 123.0, 123.1, 127.8, 128.4, 129.0, 129.1, 129.4, 130.1, 131.8, 136.6 ppm. MS: m/z (%) = 267 (100) [M]$^+$, 191 (3), 132 (12), 94 (7). $C_{20}H_{13}N$ (267.10): calcd. C 89.86, H 4.90, N 5.24; found C 89.70, H 4.98, N 5.34.

2-Methyl-1-phenylindolizino[3,4,5-*ab*]isoindole (3b): Yield: 138 mg (49%), yellow solid from petroleum ether (b.p. 60–90 °C)/ethyl acetate, m.p. 97–99 °C. IR (KBr): $\tilde{\nu}$ = 3044, 2962, 1600, 1523, 769, 742 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.84 (s, 3 H), 7.46–7.54 (m, 2 H), 7.62–7.72 (m, 4 H), 7.93 (dd, J = 8.2, 1.2 Hz, 2 H), 8.07 (d, J = 8.2 Hz, 1 H), 8.12 (d, J = 7.3 Hz, 1 H), 8.23 (d, J = 8.1 Hz, 1 H), 8.47 (d, J = 8.0 Hz, 1 H) ppm. MS: m/z (%) = 281 (100) [M]$^+$, 252 (16), 204 (14), 139 (15), 114 (12), 77 (14). $C_{21}H_{15}N$ (281.12): calcd. C 89.65, H 5.37, N 4.98; found C 89.47, H 5.32, N 4.81.

3-Methyl-1-phenylindolizino[3,4,5-*ab*]isoindole (3c): Yield: 127 mg (44%), yellow solid from petroleum ether (b.p. 60–90 °C)/ethyl acetate, m.p. 131–132 °C. IR (KBr): $\tilde{\nu}$ = 2923, 2852, 1603, 1495, 746 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.94 (s, 1 H), 7.32 (s, 1 H), 7.47 (t, J = 7.8 Hz, 2 H), 7.54 (t, J = 7.6 Hz, 1 H), 7.64 (t, J = 7.6 Hz, 2 H), 7.70 (t, J = 7.6 Hz, 1 H), 7.97 (d, J = 7.4 Hz, 1 H), 8.12 (d, J = 7.4 Hz, 2 H), 8.42 (dd, J = 8.1, 2.7 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 17.9, 102.6, 108.0, 119.5, 119.6, 120.4, 122.2, 122.7, 125.9, 126.5, 127.3, 127.5, 128.6, 129.0, 129.3, 129.6, 130.4, 136.4 ppm. MS: m/z (%) = 281 (100) [M]$^+$, 204 (7.6), 189 (2.4), 132 (4.9). $C_{21}H_{15}N$ (281.12): calcd. C 89.65, H 5.37, N 4.98; found C 89.74, H 5.45, N 5.02.

4-Methyl-1-phenylindolizino[3,4,5-*ab*]isoindole (3d): Yield: 154 mg (55%), yellow solid from petroleum ether (b.p. 60–90 °C)/ethyl acetate, m.p. 123–126 °C. IR (KBr): $\tilde{\nu}$ = 3060, 2909, 1603, 1514, 746 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 2.84 (s, 3 H), 7.45–7.54 (m, 2 H), 7.62 (t, J = 7.5 Hz, 2 H), 7.70 (td, J = 7.6, 0.9 Hz, 2 H), 7.84 (s, 1 H), 7.93 (s, 1 H), 8.09 (dd, J = 8.3, 1.2 Hz, 2 H), 8.39 (d, J = 8.2 Hz, 1 H), 8.43 (d, J = 8.0 Hz, 1 H) ppm. MS: m/z (%) = 281 (100) [M]$^+$, 252 (12), 207 (11), 139 (28), 113 (15), 44 (13). $C_{21}H_{15}N$ (281.12): calcd. C 89.65, H 5.37, N 4.98; found C 89.52, H 5.22, N 4.78.

4-Methylindolizino[3,4,5-*ab*]isoindole-2-carbonitrile (3e): Yield: 117 mg (51%), yellow solid from petroleum ether (b.p. 60–90 °C)/ethyl acetate, m.p. 124–125 °C. IR (KBr): $\tilde{\nu}$ = 2928, 2853, 2206, 1616, 1519, 727 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.85 (s, 3 H), 7.60 (t, J = 7.6 Hz, 1 H), 7.72–7.78 (m, 2 H), 7.94 (s, 1 H), 7.97 (s, 1 H), 8.15 (d, J = 8.0 Hz, 1 H), 8.35 (d, J = 7.9 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 23.8, 111.7, 114.9, 115.8, 117.7,

120.7, 123.2, 125.2, 129.7, 130.7, 136.1 ppm. MS: *m*/*z* (%) = 230 (24) $[M]^+$, 204 (7), 165 (3), 149 (100), 57 (48). $C_{16}H_{10}N_2$ (230.08): calcd. C 83.46, H 4.38, N 12.17; found C 83.37, H 4.42, N 12.20.

Methyl Indolizino[3,4,5-*ab*]isoindole-2-carboxylate (3f): Yield: 124 mg (50%), yellow solid from petroleum ether (b.p. 60–90 °C)/ethyl acetate, m.p. 116–117 °C (ref.[7] 118–119 °C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.04 (s, 3 H), 7.59 (t, *J* = 7.6 Hz, 1 H), 7.76 (t, *J* = 7.2 Hz, 1 H), 7.91 (t, *J* = 7.8 Hz, 1 H), 8.12 (d, *J* = 7.6 Hz, 1 H), 8.13 (s, 1 H), 8.21 (d, *J* = 8.0 Hz, 1 H), 8.41 (d, *J* = 8.0 Hz, 1 H), 8.50 (d, *J* = 8.4 Hz, 1 H) ppm.

Dimethyl Indolizino[3,4,5-*ab*]isoindole-1,2-dicarboxylate (3g): Yield: 154 mg (50%), yellow solid from petroleum ether (b.p. 60–90 °C)/ethyl acetate, m.p. 182–184 °C (ref.[7] 182–183 °C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.06 (s, 3 H), 4.19 (s, 3 H), 7.65 (t, *J* = 7.6 Hz, 1 H), 7.78 (t, *J* = 7.6 Hz, 1 H), 7.90 (t, *J* = 7.9 Hz, 1 H), 8.09 (d, *J* = 7.2 Hz, 1 H), 8.37 (d, *J* = 7.9 Hz, 1 H), 8.45 (d, *J* = 7.7 Hz, 1 H), 8.47 (d, *J* = 8.0 Hz, 1 H) ppm.

Diethyl Indolizino[3,4,5-*ab*]isoindole-1,2-dicarboxylate (3h): Yield: 124 mg (37%), yellow solid from petroleum ether (b.p. 60–90 °C)/ethyl acetate, m.p. 60–61 °C. IR (KBr): $\tilde{\nu}$ = 3056, 2979, 2900, 1718, 1690, 1494 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.52 (t, *J* = 7.1 Hz, 3 H), 1.58 (t, *J* = 7.2 Hz, 3 H), 4.52 (q, *J* = 7.1 Hz, 2 H), 4.65 (q, *J* = 7.1 Hz, 2 H), 7.62 (t, *J* = 7.6 Hz, 1 H), 7.76 (t, *J* = 7.6 Hz, 1 H), 7.86 (t, *J* = 7.9 Hz, 1 H), 8.05 (d, *J* = 7.1 Hz, 1 H), 8.34 (d, *J* = 7.6 Hz, 1 H), 8.44 (d, *J* = 8.4 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 14.5, 14.6, 60.4, 61.5, 109.4, 110.0, 118.5, 119.0, 122.1, 122.5, 124.2, 124.8, 125.5, 129.3, 129.6, 129.9, 130.1, 130.7, 164.0, 164.8 ppm. MS: *m*/*z* (%) = 335 (100) $[M]^+$, 290 (26), 262 (70), 190 (40). $C_{20}H_{17}NO_4$ (335.12): calcd. C 71.63, H 4.18, N 5.11; found C 70.52, H 4.69, N 4.98.

Diethyl 4-Methylindolizino[3,4,5-*ab*]isoindole-1,2-dicarboxylate (3i): Yield: 105 mg (30%), yellow solid from petroleum ether (b.p. 60–90 °C)/ethyl acetate, m.p. 136–137 °C. IR (KBr): $\tilde{\nu}$ = 2977, 2905, 1736, 1690, 1495 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.51 (t, *J* = 7.1 Hz, 3 H), 1.57 (t, *J* = 7.1 Hz, 3 H), 2.83 (s, 3 H), 4.51 (q, *J* = 7.1 Hz, 2 H), 4.64 (q, *J* = 7.1 Hz, 2 H), 7.60 (t, *J* = 7.6 Hz, 1 H), 7.74 (t, *J* = 7.6 Hz, 1 H), 7.91 (s, 1 H), 8.26 (s, 1 H), 8.32 (d, *J* = 7.9 Hz, 1 H), 8.43 (d, *J* = 8.0 Hz, 2 H) ppm. MS: *m*/*z* (%) = 349 (100) $[M]^+$, 276 (36), 249 (20), 204 (30). $C_{21}H_{19}NO_4$ (349.13): calcd. C 72.19, H 5.48, N 4.01; found C 72.02, H 5.56, N 3.92.

Dimethyl 5-Methylindolizino[3,4,5-*ab*]isoindole-1,2-dicarboxylate (3j): Yield: 241 mg (75%), yellow solid from petroleum ether (b.p. 60–90 °C)/ethyl acetate, m.p. 128–129 °C. IR (KBr): $\tilde{\nu}$ = 2923, 2851, 1731, 1703, 1599, 1488 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.94 (s, 3 H), 4.06 (s, 3 H), 4.14 (s, 3 H), 7.57 (dd, *J* = 7.3, 0.8 Hz, 1 H), 7.63 (td, *J* = 7.6, 0.9 Hz, 1 H), 7.75 (td, *J* = 7.6, 1.0 Hz, 1 H), 7.98 (d, *J* = 7.3 Hz, 1 H), 8.34 (d, *J* = 7.9 Hz, 1 H), 8.53 (d, *J* = 8.0 Hz, 1 H) ppm. MS: *m*/*z* (%) = 321 (24) $[M]^+$, 289 (35), 271 (100), 231 (19), 204 (29), 57 (47). $C_{19}H_{15}NO_4$ (321.10): calcd. C 71.02, H 4.71, N 4.36; found C 70.91, H 4.83, N 4.35.

(4-Methyl-1-phenylindolizino[3,4,5-*ab*]isoindol-2-yl)phenylmethanone (3k): Yield: 196 mg (51%), yellow solid from petroleum ether (b.p. 60–90 °C)/ethyl acetate, m.p. 93–95 °C. IR (KBr): $\tilde{\nu}$ = 3055, 2949, 1732, 1493, 1387 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.82 (s, 3 H), 7.18–7.36 (m, 6 H), 7.53–7.72 (m, 6 H), 7.96 (s, 1 H), 8.12–8.14 (m, 2 H), 8.38 (d, *J* = 7.7 Hz, 1 H) ppm. MS: *m*/*z* (%) = 385 (2.4) $[M]^+$, 203 (10), 163 (20), 112 (100), 85 (26). $C_{28}H_{19}NO$ (385.15): calcd. C 87.25, H 4.97, N 3.63; found C 87.05, H 5.17, N 3.56.

General Procedure for the Preparation of Compounds 5a–5c: A mixture of indolizine (**4a**–**4c**, 1.0 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**1**, 0.53 g, 2 mmol) and cesium fluoride (0.64 g, 4 mmol) in MeCN (20 mL) was heated at 90 °C for 8 h with magnetic stirring. The reaction was monitored by TLC. The solvent was removed in vacuo, the residue poured into water, extracted with CH_2Cl_2 and then separated by flash chromatography on a silica gel column with petroleum ether (b.p. 60–90 °C)/ethyl acetate as eluent to give the product.

Methyl Benzo[6,7]pyrrolizino[3,4,5-*ab*]isoquinoline-2-carboxylate (5a): Yield: 179 mg (60%), red solid from petroleum ether (b.p. 60–90 °C)/ethyl acetate, m.p. 157–159 °C. IR (KBr): $\tilde{\nu}$ = 2949, 1698, 1603, 1513 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.10 (s, 3 H), 7.61–7.76 (m, 3 H), 7.80 (t, *J* = 7.2 Hz, 1 H), 8.28 (t, *J* = 8.9 Hz, 2 H), 8.40 (s, 1 H), 8.73 (d, *J* = 8.1 Hz, 1 H), 8.85 (d, *J* = 8.8 Hz, 1 H), 8.88 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 51.4, 110.7, 115.6, 120.1, 120.3, 120.6, 120.8, 123.0, 123.2, 123.7, 123.8, 125.6, 127.3, 127.4, 128.4, 128.5, 128.7, 129.9, 130.0 ppm. MS: *m*/*z* (%) = 299 (90) $[M]^+$, 268 (48), 240 (100), 213 (23), 120 (31), 11 (38). $C_{20}H_{13}NO_2$ (299.09): calcd. C 80.25, H 4.38, N 4.68; found C 80.26, H 4.26, N 4.59.

Benzo[6,7]pyrrolizino[3,4,5-*ab*]isoquinoline-2-carbonitrile (5b): Yield: 138 mg (52%), red solid from petroleum ether (b.p. 60–90 °C)/ethyl acetate, m.p. 170–172 °C. IR (KBr): $\tilde{\nu}$ = 2206, 1729, 1514, 747 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.70–7.84 (m, 3 H), 7.90 (t, *J* = 7.6 Hz, 1 H), 8.25 (s, 1 H), 8.35 (t, *J* = 9.0 Hz, 2 H), 8.68 (s, 1 H), 8.83 (d, *J* = 8.0 Hz, 1 H), 8.96 (d, *J* = 8.6 Hz, 1 H) ppm. MS: *m*/*z* (%) = 266 (100) $[M]^+$, 238 (11), 149 (9), 133 (7). $C_{19}H_{10}N_2$ (266.08): calcd. C 85.70, H 3.79, N 10.52; found C 85.63, H 4.06, N 10.31.

Diethyl Benzo[6,7]pyrrolizino[3,4,5-*ab*]isoquinoline-1,2-dicarboxylate (5c): Yield: 223 mg (58%), red solid from petroleum ether (b.p. 60–90 °C)/ethyl acetate, m.p. 130–131 °C. IR (KBr): $\tilde{\nu}$ = 2980, 1732, 1704 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.57 (t, *J* = 6.2 Hz, 3 H), 1.62 (t, *J* = 6.2 Hz, 3 H), 4.59 (q, *J* = 7.1 Hz, 2 H), 4.71 (q, *J* = 7.1 Hz, 2 H), 7.68–7.88 (m, 4 H), 8.34 (d, *J* = 8.5 Hz, 1 H), 8.51 (d, *J* = 7.9 Hz, 1 H), 8.80 (d, *J* = 8.0 Hz, 1 H), 8.91 (d, *J* = 8.5 Hz, 1 H), 9.03 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 14.5, 14.6, 60.5, 61.8, 109.0, 117.4, 120.8, 121.1, 121.6, 122.8, 123.5, 123.6, 123.9, 124.8, 125.8, 127.8, 128.1, 128.3, 129.1, 129.9, 130.5, 164.0, 165.0 ppm. MS: *m*/*z* (%) = 385 (100) $[M]^+$, 313 (22), 285 (42), 240 (48). $C_{24}H_{19}NO_4$ (385.13): calcd. C 74.79, H 4.97, N 3.63; found C 74.76, H 5.23, N 3.56.

Preparation of Compound 7: A mixture of 6*H*-[1]benzopyrano[3,4-*a*]indolizine-6-one (**6**, 1.0 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**1**, 0.53 g, 2 mmol) and cesium fluoride (0.64 g, 4 mmol) in MeCN (20 mL) was heated at 90 °C for 5 h with magnetic stirring. The reaction was monitored by TLC. A yellow precipitate was collected and washed with ethyl acetate to give the product.

6*H*-[1]Benzopyrano[3′,4′:1,2]indolizino[3,4,5-*ab*]isoindole-6-one (7): Yield: 287 mg (93%), yellow solid from petroleum ether (b.p. 60–90 °C)/ethyl acetate, m.p. 269–271 °C. IR (KBr): $\tilde{\nu}$ = 1716 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.49–7.60 (m, 3 H), 7.67 (t, *J* = 7.7 Hz, 1 H), 7.87 (t, *J* = 7.6 Hz, 1 H), 8.04 (t, *J* = 7.9 Hz, 1 H), 8.26 (d, *J* = 7.5 Hz, 1 H), 8.45–8.51 (m, 3 H), 8.63 (d, *J* = 8.2 Hz, 1 H) ppm. MS: *m*/*z* (%) = 309 (34) $[M]^+$, 252 (16), 44 (100). $C_{21}H_{11}NO_2$ (309.08): calcd. C 81.54, H 3.58, N 4.53; found C 80.97, H 3.71, N 4.45.

Preparation of Compound 9: A mixture of 6*H*-[1]benzopyrano-[3′,4′:3,4]pyrrolo[2,1-*a*]isoquinolin-6-one (**8**, 1.0 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**1**, 0.53 g, 2 mmol) and cesium fluoride (0.64 g, 4 mmol) in MeCN (20 mL) was heated at

90 °C for 8 h with magnetic stirring. The reaction was monitored by TLC. The solvent was removed in vacuo, the residue poured into water, extracted with CH_2Cl_2, the solvent removed in vacuo and the residue separated by flash chromatography on a silica gel column with petroleum ether (b.p. 60–90 °C)/ethyl acetate as eluent to give the product.

6*H*-[1]Benzopyrano[3′,4′:1,2]benzo[6,7]pyrrolizino[3,4,5-*ab*]isoquinoline-6-one (9): Yield: 223 mg (62%), yellow solid from petroleum ether (b.p. 60–90 °C)/ethyl acetate, m.p. 247–248 °C. IR (KBr): $\tilde{\nu}$ = 1727, 1610, 1400, 741 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.53–7.70 (m, 4 H), 7.79 (t, J = 7.9 Hz, 1 H), 7.83 (t, J = 7.8 Hz, 1 H), 7.92 (t, J = 7.4 Hz, 1 H), 8.35 (d, J = 8.3 Hz, 1 H), 8.47–8.50 (m, 2 H), 8.78 (d, J = 8.3 Hz, 1 H), 8.92 (d, J = 8.6 Hz, 1 H), 8.96 (s, 1 H) ppm. MS: *m*/*z* (%) = 359 (100) $[M]^+$, 302 (9), 180 (1), 138 (2). $C_{25}H_{13}NO_2$ (359.09): calcd. C 83.55, H 3.65, N 3.90; found C 83.16, H 3.92, N 3.79.

Supporting Information (see also the footnote on the first page of this article): Absorption and fluorescence spectra, ^1H- and ^{13}C-NMR spectra of compounds **3a**–**3k**, **5a**–**5c**, **7**, **9**. Calculated results (DFT method at the B3LYP/6-31G level) for compounds **3a**, **3b**, **3c**, **3d**, **5a**, **7**, **9**.

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