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Synthesis and Photophysical Studies of New Fluorescent Indole Derivatives Obtained from β-Bromodehydroamino Acids – Interaction with Fluoride Anions

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Several new indole derivatives were synthesised from β-brominated dehydroamino acids and arylboronic acids by using a strategy developed in our research group that involves a sequential Suzuki–Miyaura cross-coupling reaction and a metal-assisted C–N intramolecular cyclisation. The cyclised products were obtained either by direct cyclisation or by isomerisation followed by cyclisation. The photophysical properties of these compounds were studied in four solvents of different polarity (cyclohexane, diethyl ether, acetonitrile and ethanol). All these compounds have reasonably high fluorescence quantum yields (between 16 and 85 %) and show different solvent sensitivity in their fluorescence emission. These results indicate that the indole derivatives prepared are good candidates for fluorescent probes. The response of the new synthesised compounds towards fluoride ion (F^-) was evaluated. It was found that methyl 3-methyl-1*H*-dibenzo[*e*,*g*]indole-2-carboxylate, methyl 3-(phenanthren-9-yl)-1*H*-dibenzo[*e*,*g*]indole-2-carboxylate and methyl 1-(naphthalen-1-yl)-3*H*-benzo[*e*]indole-2-carboxylate showed significant spectral changes in fluorescence emission upon F^- addition with a decrease in intensity and the appearance of a new band at longer wavelengths. No detectable emission spectral changes were observed when several other anions were added to these compounds, which indicates their selectivity towards F^-.

Introduction

In our laboratories, we have been interested in the synthesis of new fluorescent indole derivatives as fluorescent probes for peptides and proteins. These compounds were obtained from brominated dehydroamino acids and aryl- or heteroarylboronated compounds by using a Suzuki–Miyaura cross coupling followed by a metal-mediated C–N intramolecular cyclisation developed in our research group.[1] Recently, we have used this strategy to synthesise a phenalenoindole and a pyrenylindole from a β-bromodehydrophenylalanine or a β-bromodehydroaminobutyric acid and pyren-1-boronic acid, respectively. The fluorescence properties of these compounds in solution and in lipid membranes showed their potential as fluorescent probes for biological systems.[2] In this work, we report the synthesis of several new compounds having the pyrrole unit fused with benzene, phenanthrene, 1,2-dihydroacenaphthylene and anthracene moieties to be studied as fluorescent probes and also to evaluate their behaviour in the presence of fluoride (F^-). Thus, several β,β-disubstituted dehydroamino acids were prepared in good to high yields from pure stereoisomers of a β-bromodehydroaminobutyric acid and a β-bromodehydrophenylalanine or a β,β-dibromodehydroalanine and arylboronic acids. These compounds were then treated with palladium and copper acetate to give the corresponding pyrrole-fused compounds. The photophysical properties of the latter were studied in several solvents. Since neutral F^- sensors usually have hydrogen-bonding units such as pyrrole, urea, amide or phenol in their recognition sites,[3] we decided to study the behaviour of the compounds prepared towards this anion. Due to the importance of F^- in biology, medicine, food and environmental sciences, as it is a common ingredient in anaesthetics, hypnotics, psychiatric drugs, several poisons and is a contaminant in water,[4] there is growing interest in the development of new molecules capable of selectively sensing F^- in solution. These molecules contain a binding site that interacts with the anion and a signaling subunit with the ability of converting the binding event into a readable signal.[5]

Results and Discussion

We treated the pure stereoisomers of a β-bromodehydroaminobutyric acid [(*Z*)- or (*E*)-**1**] and a β-bromodehydro-

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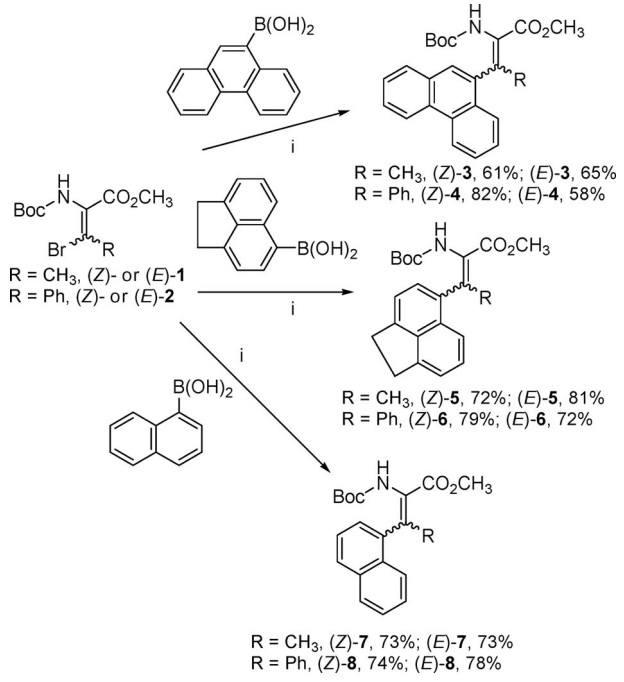
phenylalanine [(*Z*)- or (*E*)-**2**] with 9-phenanthracenylboronic acid, (1,2-dihydroacenaphthylen-5-yl)boronic acid or 1-naphthylboronic acid under Suzuki–Miyaura coupling conditions to afford in good yields the corresponding β-substituted dehydroamino acids (Scheme 1). We determined the stereochemistry of these compounds using NOE difference experiments by irradiating the α-NH and OCH_3 protons. In the case of the (*Z*) isomers, when we irradiated the OCH_3 protons, we observed an NOE enhancement on the β-CH_3 protons of dehydroaminobutyric acid derivatives or on the phenyl protons of dehydrophenylalanines. We confirmed the configuration of the (*E*) isomers by the observation of a positive NOE of the β-CH_3 or β-phenyl resonances when we irradiated the α-NH group. As reported by other authors and us also, it was possible to correlate the chemical shifts of the OCH_3, α-NH and β-CH_3 protons with the stereochemistry of the compounds.[6] Thus, we observed the NMR chemical shifts of the OCH_3 and β-CH_3 protons of the (*Z*) isomers of the dehydroaminobutyric acid derivatives at lower fields than those of the (*E*) isomers (Table 1). We also found this relation in the case of the OCH_3 protons of dehydrophenylalanines (Table 1). The α-NH resonances of all the (*Z*) isomers of β-aryldehydroaminobutyric acids and dehydrophenylalanines appeared at higher field than those of the (*E*) isomers. This is probably due to the shielding anisotropic effect of the aryl moiety.

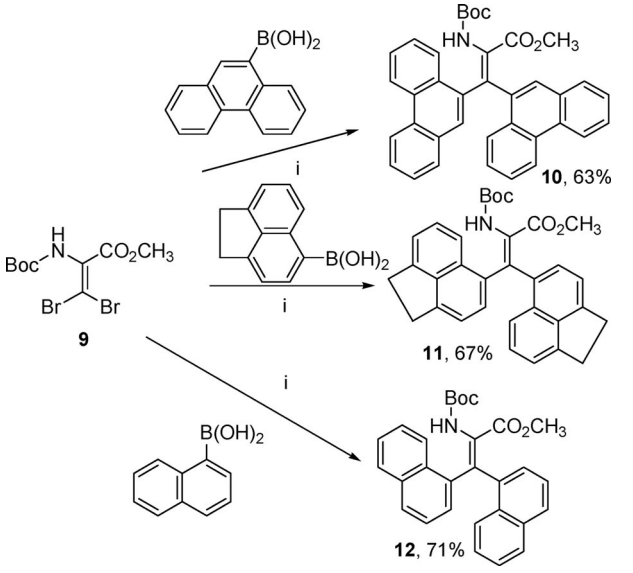


Scheme 1. Synthesis of β-aryldehydroaminobutyric acid and dehydrophenylalanine derivatives. (i) $PdCl_2dppf{\cdot}CH_2Cl_2$ (1:1) (10 mol-%); Cs_2CO_3 (1.4 equiv.); THF/H_2O (1:1).

When we used β,β-dibromodehydroalanine (**9**)[1a] as a substrate, we obtained the corresponding disubstituted dehydroalanines **10**–**12** in good yields (between 63 and 71%, Scheme 2).

Table 1. ^1H NMR chemical shifts of β-aryldehydroaminobutyric acid and dehydrophenylalanine derivatives in $CDCl_3$ (5×10^{-3} mol dm^{-3}).

Entry	Compound	δ [ppm] α-NH	OCH_3	β-CH_3
1	(*Z*)-**3**	5.61	3.95	2.38
2	(*E*)-**3**	6.28	3.24	2.27
3	(*Z*)-**4**	5.77	3.70	–
4	(*E*)-**4**	6.42	3.23	–
5	(*Z*)-**5**	5.56	3.91	2.32
6	(*E*)-**5**	6.16	3.30	2.23
7	(*Z*)-**6**	5.76	3.64	–
8	(*E*)-**6**	6.31	3.33	–
9	(*Z*)-**7**	5.48	3.92	2.32
10	(*E*)-**7**	6.22	3.25	2.24
11	(*Z*)-**8**	5.67	3.66	–
12	(*E*)-**8**	6.35	3.23	–



Scheme 2. Synthesis of β,β-diaryldehydroalanine derivatives. (i) $PdCl_2dppf{\cdot}CH_2Cl_2$ (1:1) (10 mol-%); Cs_2CO_3 (1.4 equiv.); THF/H_2O (1:1).

We then submitted some of these disubstituted dehydroamino acid derivatives (**3**–**12**) to a Pd/Cu-assisted C–N intramolecular cyclisation to afford the corresponding indole derivatives (Table 2). This reaction involved the electrophilic attack of Pd^{II} on the aromatic ring and a nucleophilic attack of N, forming a palladacycle.[1] The only products isolated from the cyclisation of (*Z*)-**4** and (*Z*)-**8** resulted from isomerisation followed by cyclisation giving **14** and **20**, respectively. Compounds (*E*)-**4** and (*E*)-**8** gave **14** and **20** in similar yields to those obtained by using (*Z*)-**4** and (*Z*)-**8** as starting materials. In the case of (*Z*)-**6**, although the major product (**17**, 52%) resulted from isomerisation followed by cyclisation, we also isolated **18** (13%) resulting from a direct cyclisation. In this case, the cyclisation of (*E*)-**6** afforded the same ratio of **17** and **18**.

Jones and Mathews[7] synthesised compounds similar to **15** with a 1*H*-dibenzo[*e*,*g*]indole moiety. The synthesis involved the formylation of a 9-bromophenanthrene followed

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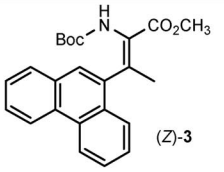
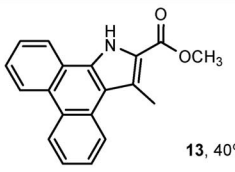
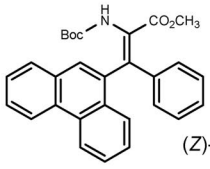
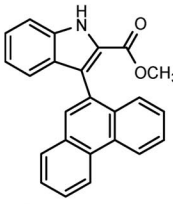
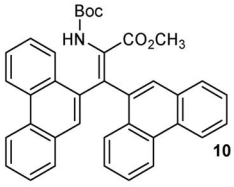
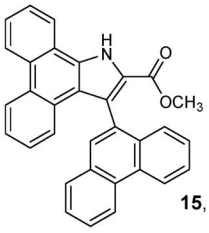
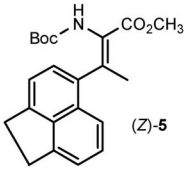
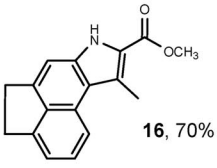
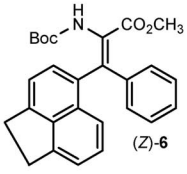
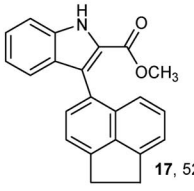
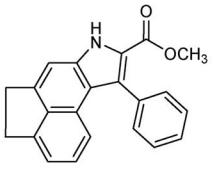
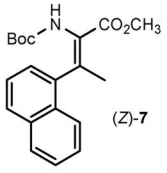
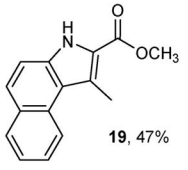
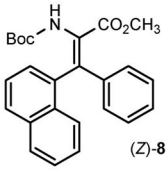
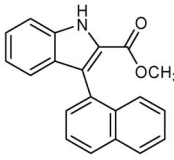
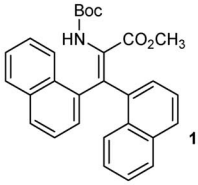
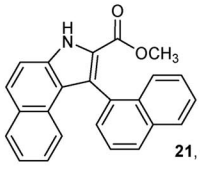
Table 2. Yields of the cyclisation products and ^{1}H NMR chemical shifts of the NH signals in [D_6]DMSO (5×10^{-3} mol dm^{-3}).

Dehydroamino acid	Cyclization products[a]	δ(NH) (in [D_6]DMSO)
 (*Z*)-**3**	 **13**, 40%	12.403
 (*Z*)-**4**	 **14**, 78%	12.165
 **10**	 **15**, 52%	13.030
 (*Z*)-**5**	 **16**, 70%	11.840
 (*Z*)-**6**	 **17**, 52% +  **18**, 13%	12.050 (**17**) 12.236 (**18**)
 (*Z*)-**7**	 **19**, 47%	12.029
 (*Z*)-**8**	 **20**, 87%	12.121
 **12**	 **21**, 86%	12.595

[a] Cyclisation conditions: $Pd(OAc)_2$ (50 mol-%), $Cu(OAc)_2 \cdot H_2O$ (3 equiv.), DMF, 160 °C, 3–4 h.

by the transformation of the aldehyde into an azidocinnamate using a Rees–Moody protocol. The latter gave the methyl 1*H*-dibenzo[*e*,*g*]indole-2-carboxylate by thermolysis.

We studied the absorption and fluorescence properties of **13**–**21** in four solvents of different polarity (cyclohexane, diethyl ether, acetonitrile and ethanol). The maximum ab-

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sorption (λ_{abs}) and emission wavelengths (λ_{em}), molar absorption coefficients (ε) and fluorescence quantum yields (Φ_F) of these indole derivatives are presented in Tables 3 and 4. The normalised absorption and fluorescence spectra of **13**–**21** are presented in Figures 1, 2 and 3.

All indole derivatives **13**–**21** presented relatively high molar absorption coefficients at the lowest energy maximum ($\varepsilon \geq 5.3 \times 10^3$ M^{-1} cm^{-1}) in all the solvents studied (Tables 3 and 4). The near-UV absorption of indole and its derivatives was attributed to two strongly overlapping π→π* transitions,[9–11] with an average ε value for unsubstituted indole of 5500 M^{-1} cm^{-1}.[12] A methyl carboxylate group is present in our compounds, and it is known that many carbonyl compounds present a low-lying n→π* state. The π→π* and n→π* electronic transitions can also be nearby in energy, resulting in state mixing.[13] The higher ε values observed here can be explained by a predominance of π→π* character in these compounds (Tables 3 and 4).

The absorption spectra of the indole derivatives **14**, **17** and **20** presented a broad and unstructured lowest-energy band, due to the strong conjugation of the indole moiety with the adjacent aromatic rings. A similar behaviour has

Table 3. Maximum absorption (λ_{abs}) and emission (λ_{em}) wavelengths, molar absorption coefficients (ε) and fluorescence quantum yields (Φ_F) for **13**–**16**.

Solvent	λ_{abs} [nm] (ε [10^4 M^{-1} cm^{-1}])				λ_{em} [nm]				Φ_F[a]			
	13	**14**	**15**	**16**	**13**	**14**	**15**	**16**	**13**	**14**	**15**	**16**
Cyclohexane	357 (0.53), 340 (0.49), 321 (1.44), 305 (1.32), 266 (4.46)	298 (2.47), 249 (6.27), 226 (5.14), 211 (5.50)	355 (0.75), 338 (0.75), 321 (1.66), 300 (2.36), 256 (8.36)	352 (2.34), 335 (1.56), 318 (1.38), 273 (2.00), 238 (2.71)	359, 377, 398	399	357, 375, 396, 416	353, 359, 372, 392	0.44	0.70	0.42	0.61
Diethyl ether	357 (0.55), 340 (0.51), 319 (1.52), 305 (1.43), 265 (4.68)	297 (2.71), 250 (6.62), 226 (6.58)	354 (0.76), 338 (0.75), 319 (1.68), 299 (2.31), 255 (7.87)	352 (2.37), 335 (1.64), 319 (1.39), 274 (2.31), 239 (2.63)	357, 376, 396	396	356, 374, 395, 414	353, 371, 391	0.44	0.68	0.37	0.56
Acetonitrile	355 (0.59), 338 (0.60), 318 (1.54), 303 (1.53), 265 (4.79)	297 (2.25), 248 (5.88), 226 (4.64), 211 (4.89)	354 (0.67), 337 (0.68), 317 (1.62), 300 (2.26), 255 (7.82)	351 (2.17), 335 (1.56), 318 (1.39), 273 (2.22), 238 (2.93)	361, 377, 395	401	358, 375, 394	356, 374, 392	0.36	0.55	0.16	0.59
Ethanol	357 (0.62), 340 (0.59), 320 (1.42), 305 (1.34), 265 (4.28)	298 (2.47), 249 (6.26), 227 (4.84), 210 (5.31)	355 (0.91), 338 (0.87), 320 (1.59), 300 (2.17), 256 (7.49)	352 (2.19), 336 (1.61), 320 (1.43), 275 (2.38), 239 (2.94)	361, 378, 398	417	357, 376, 395	362, 378	0.41	0.57	0.24	0.54

[a] Relative to 9,10-diphenylanthracene in ethanol (Φ = 0.95 at 25 °C).[8] The error was approximately 10%. Diethyl ether cut-off: 215 nm.

Table 4. Maximum absorption (λ_{abs}) and emission (λ_{em}) wavelengths, molar absorption coefficients (ε) and fluorescence quantum yields (Φ_F) for **17**–**21**.

Solvent	λ_{abs} [nm] (ε [10^4 M^{-1} cm^{-1}])					λ_{em} [nm]					Φ_F[a]					
	17	**18**	**19**	**20**	**21**	**17**	**18**	**19**	**20**	**21**	**17**	**18**	**19**	**20**	**21**	
Cyclohexane	294 (2.06), 224 (6.21)	352 (1.82), 336 (1.29), 316 (1.03), 374 (1.56), 237 (1.87), 223 (2.18)	345 (1.13), 322 (1.58), 308 (1.82), 270 (1.77), 233 (3.11)	291 (1.73), 219 (7.20)	344 (1.09), 328 (1.24), 304 (1.59), 283 (1.68), 223 (8.11)	399	355, 373, 393	346, 364, 382	393	347, 364, 383	0.53	0.85	0.59	0.60	0.72	
Diethyl ether	295 (1.99), 224 (5.75)	351 (2.06), 335 (1.53), 317 (1.27), 276 (2.49), 238 (3.06), 224 (4.17)	345 (1.18), 329 (1.71), 310 (1.89), 271 (2.24), 234 (3.03)	293 (1.67), 220 (6.28)	344 (1.11), 328 (1.33), 308 (1.57), 274 (1.84), 222 (7.73)	401	356, 374, 392	346, 364, 381	394	347, 364, 382	0.64	0.53	0.74	0.61	0.54	
Acetonitrile	296 (1.87), 224 (5.92)	351 (1.76), 335 (1.35), 317 (1.14), 275 (2.06), 237 (2.45), 222 (2.98)	343 (1.10), 327 (1.66), 310 (1.83), 270 (2.22), 233 (3.34)	293 (1.44), 220 (6.04)	343 (1.04), 327 (1.29), 308 (1.48), 275 (1.84), 222 (7.66)	426	364, 376	349, 366, 383	396	351, 366	0.70	0.64	0.48	0.71	0.39	
Ethanol	297 (2.04), 224 (6.29)	353 (1.53), 337 (1.18), 319 (1.00), 378 (1.80), 238 (1.96), 223 (2.23)	345 (1.06), 329 (1.64), 313 (1.68), 273 (2.10), 234 (3.00)	294 (1.68), 219 (6.99)	344 (1.30), 328 (1.60), 311 (1.78), 276 (2.29), 222 (9.12)	443	382	354, 369	411	357, 371	0.54	0.43	0.51	0.78	0.51	

[a] Relative to 9,10-diphenylanthracene in ethanol (Φ = 0.95 at 25 °C).[8] The error was approximately 10%. Diethyl ether cut-off: 215 nm.

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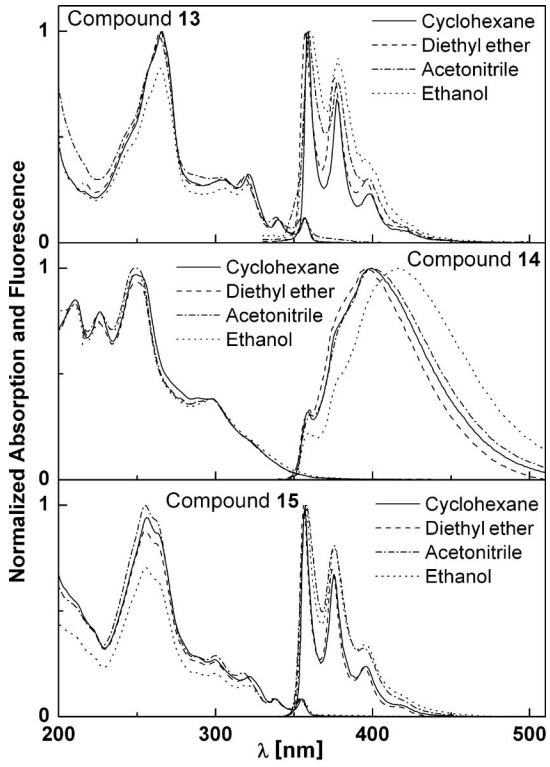

Figure 1. Normalised absorption (in the lowest energy peak) and fluorescence spectra of solutions (2×10^{-5} M for absorption and 2×10^{-6} M for fluorescence) of **13**–**15**, in several solvents.

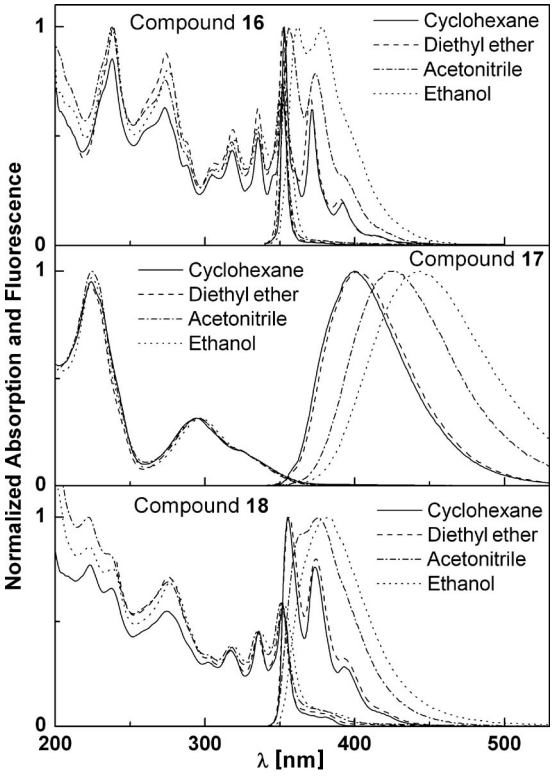

Figure 2. Normalised absorption (in the lowest energy peak) and fluorescence spectra of solutions (2×10^{-5} M for absorption and 2×10^{-6} M for fluorescence) of **16**–**18**, in several solvents.

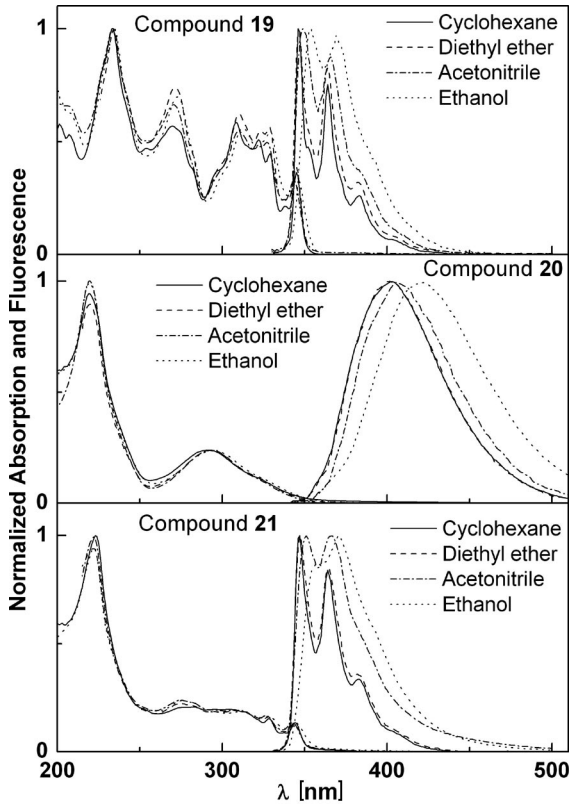

Figure 3. Normalised absorption (in the lowest energy peak) and fluorescence spectra of solutions (2×10^{-5} M for absorption and 2×10^{-6} M for fluorescence) of **19**–**21**, in several solvents.

previously been observed in a pyrenylindole-2-carboxylate compound.[2] All other compounds, which had the indole moiety condensed in an extended aromatic system, presented a structured absorption spectrum in the lower-energy region, as observed for a phenalenoindole[2] and pyrene[2,1-*b*]pyrrole derivatives.[14]

The fluorescence spectra of indoles **14**, **17** and **20** were mainly unstructured bands, with large Stokes' shifts and appreciable solvatochromic behaviour, typical of the charge-transfer (CT) character of the excited state, even in nonpolar solvents. The influence of the solvent on the absorption spectral shape was negligible. The effect on the emission spectra was more pronounced for **17**, where the spectral shift between cyclohexane and ethanol was 44 nm. We observed a similar behaviour due to a high CT character of the excited state for a pyrenylindole-2-carboxylate.[2] Compound **14** exhibited a slightly structured emission and a small peak on the higher-energy side (at 359 nm), indicating that there was a small contribution from the locally excited (LE) state.

All the other compounds (**13**, **15**, **16**, **18**, **19** and **21**), displayed fluorescence spectra with well-defined vibrational structure, especially in solvents of low polarity (Figures 1, 2 and 3). Compounds **13** and **15** had similar absorption and fluorescence spectra (Figure 1), with a low influence of the solvent on the emission spectra. This behaviour indicates that the substituent attached to the dibenzo[*e*,*g*]indole-2-

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carboxylate moiety (a methyl group in **13** and a phenanthracenyl group in **15**) had a small contribution to the lowest excited state.

We observed a pronounced loss of vibrational structure in polar solvents for **18** and **21** (Figures 2 and 3), indicating the CT character of the excited state in polar solvents. The effect was more significant in ethanol, probably due to contribution of hydrogen bonding from this protic solvent, through the α-NH group (donor) or carboxylate group (acceptor). The extension of the conjugation by the substitution of a methyl group (**16** and **19**) by an aromatic moiety (**18** and **21**, respectively) provides a significant increase in excited-state CT character.

All compounds had reasonable to high fluorescence quantum yields in almost all the solvents studied (Tables 3 and 4), attaining 70–80% in some cases. We observed the lowest Φ_F values (between 16 and 42%) for **15**, which is the largest molecule with seven aromatic rings and showed a predominance of the nonradiative pathways of deactivation. The generally high fluorescence quantum yields of these new indole derivatives and the different solvent sensitivity of their fluorescence emission make them good candidates for fluorescent probes.

It has been established that compounds containing pyrrole, urea, amide, amine or phenol units can act as F^- sensors.[3] We also evaluated the response of **13**–**21** toward F^- ions. We performed fluorescence titration experiments on 5×10^{-6} M solutions in acetonitrile with the incremental addition of F^- (as the tetrabutylammonium salt). We observed significant spectral changes in emission upon F^- addition for **13**, **15** and **21** (Figures 4, 5 and 6), especially for **13** and **15**. The emission spectrum of each compound decreased in intensity, and a new unstructured band appeared at longer wavelengths (maximum at ca. 465 nm for **13**, 515 nm for **15** and ca. 510 nm for **21**). In all cases, we observed a clear isoemissive point [at 423 nm for **13** (Figure 4), 432 nm for **15** (Figure 5) and 440 nm for **21** (Figure 6)]. Compounds **13** and **15** exhibited noticeable spectral changes at intervals of 10 and 5 equiv. of F^-, respectively (Figures 4 and 5), whereas for **21**, the spectral changes were significantly smaller (Figure 6). The addition of F^- to solutions of **13** and **15** led to an intensely coloured fluorescence (blue and green, respectively) upon irradiation with near-UV light (see the Supporting Information).

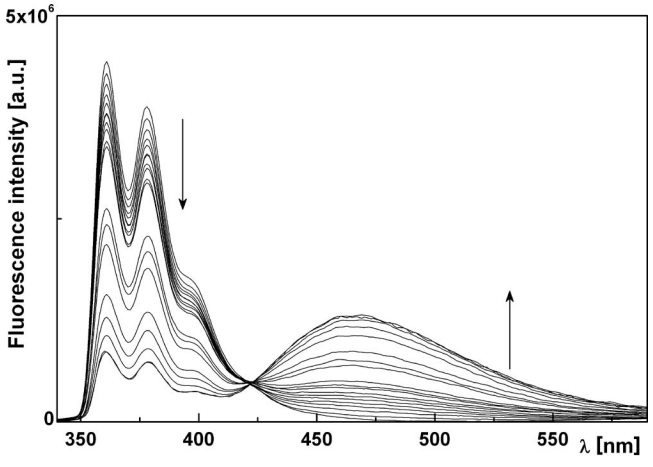

Figure 4. Fluorescence emission spectra (λ_{ex} = 325 nm) of **13** (5×10^{-6} M in acetonitrile) in the presence of different amounts of F^- (0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 150, 200, 250, 300, 350, 400, 450 and 500 equiv.).

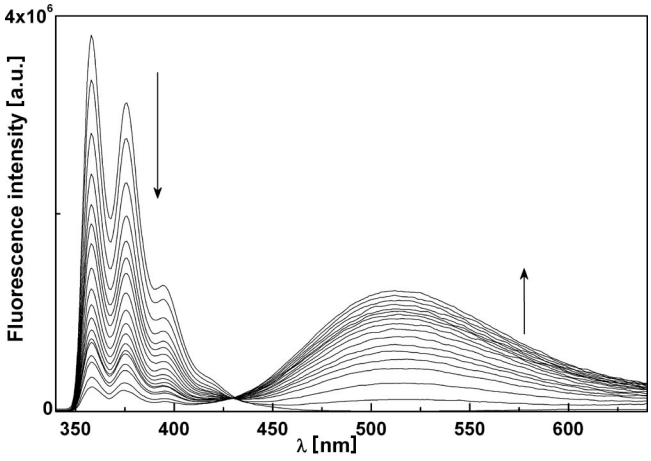

Figure 5. Fluorescence emission spectra (λ_{ex} = 335 nm) of **15** (5×10^{-6} M in acetonitrile) in the presence of different amounts of F^- (0, 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 80, 90, 100, 130, 150, 200 and 250 equiv.).

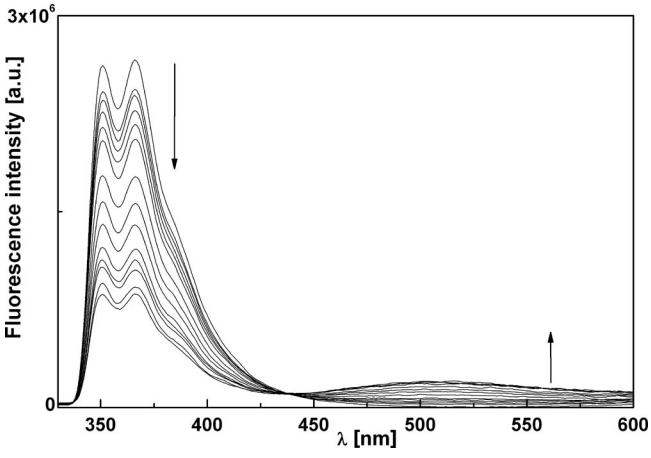

Figure 6. Fluorescence emission spectra (λ_{ex} = 325 nm) of **21** (5×10^{-6} M in acetonitrile) in the presence of different amounts of F^- (0, 20, 40, 60, 80, 100, 150, 200, 250, 300, 350, 400, 450 and 500 equiv.).

The corresponding UV/Vis absorption titrations caused smaller spectral changes, but we observed clear changes for larger amounts of F^-, with the appearance of a new band in the higher-wavelength region of the absorption spectrum (see the Supporting Information). The excitation spectrum obtained at the compound emission region was always very

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similar to the absorption spectrum in the absence of F^-. The excitation spectrum recorded at the maximum of the new fluorescence band (where the compound emission is negligible) also resembled the absorption spectrum (for the same F^- content), considering that the latter has a contribution from the pure compound absorption (see the Supporting Information).

We observed no detectable emission spectral changes with F^- addition to indoles **14**, **16**–**18** and **20**. For **19**, we detected a small new emission band in the presence of F^-, but only with large amounts of the anion (≥300 equiv.), and changes with further increases of F^- content were negligible.

The ^1H NMR spectra in [D_6]DMSO of **13** and **15** showed the appearance of a triplet at $\delta \approx 16$ ppm, characteristic of the FHF moiety formed upon the addition of 2 equiv. of F^-.[15] This clearly shows that the mechanism of F^- recognition was the deprotonation of the indole group by the F^- ion in the ground state. This explains why in these new compounds the F^- recognition is stronger for compounds with a higher NH chemical shift (**13**, **15** and **21**; see Table 2). The higher NH acidity in these three compounds can facilitate the hydrogen abstraction process and the formation of the FHF species.

The formation of a compound anion also justifies the anomalously large spectral shifts between the compound emission (first peak) and the new fluorescence band[16] (104 nm for **13**, 157 nm for **15** and 159 nm for **21**). The fluorescence titration of a solution of **15** with OH^- in acetonitrile revealed similar spectral changes as those observed with F^- (see the Supporting Information), with the new unstructured band arising at the same emission wavelengths (maximum at 515 nm), indicating that this new emission is due to an indole **15** anion. The absorption spectra in the presence of OH^- and F^- were also roughly similar (see the Supporting Information), pointing to the formation of identical species in the ground state, in the presence of either of the two anions. A similar behaviour was reported for the pyreno[2,1-*b*]pyrrole interaction with F^- and OH^- in acetonitrile.[16] Intermolecular excited-state proton-transfer processes have been reported in several indoles, with strong hydrogen bonding with polar solvent molecules leading to ion-pair formation.[17] However, in our new indole derivatives, the proton abstraction from the NH group occurred in the ground state (for an F^- amount above 2 equiv.).

To examine the F^- selectivity of these compounds, we performed fluorescence titrations of solutions of **13**, **15** and **21** in acetonitrile with various anions (Cl^-, Br^-, HSO_4^- and CH_3COO^- as the tetrabutylammonium salts). For each of the compounds, we observed no emission spectral changes for any of these anions, demonstrating the selectivity for F^-. Figure 7 displays the ratio of the maximum emission intensities at the new band ($I_{compound–F^-}$) and first peak ($I_{compound}$) for the several anions tested. The corresponding intensity ratio for the free compounds (without anion) at the same wavelengths is shown for comparison. The high electronegativity and basicity of F^- may justify this selectivity.

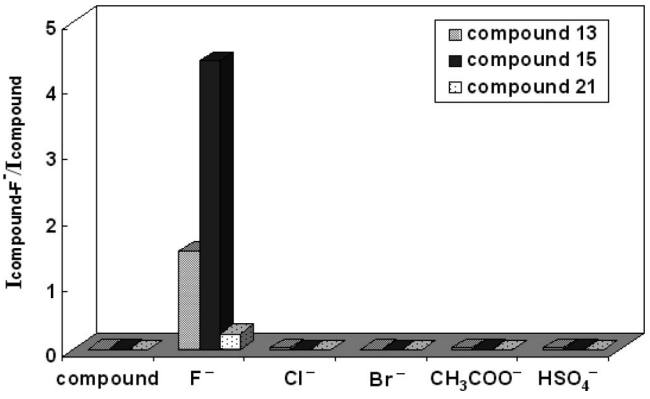

Figure 7. Response of **13**, **15** and **21** to different anions in fluorescence titrations.

Conclusions

Several new pyrrole-fused compounds were prepared in good yields from brominated dehydroamino acids and arylboronic acids by a Suzuki–Miyaura cross coupling followed by a Pd/Cu-mediated C–N intramolecular cyclisation. As expected, the Suzuki products maintained the stereochemistry of the β-brominated dehydroamino acid starting material. The cyclisation of (*Z*)-β-aryldehydrophenylalanines gave mainly the product that results from isomerisation followed by cyclisation.

The photophysical properties of the new indole derivatives were studied in four solvents of different polarity. All compounds showed reasonably high quantum yields in all solvents (16–85%) and different solvent sensitivity of their fluorescence emission, which indicated their potential use as fluorescent probes.

Of all the compounds prepared, three (**13**, **15** and **21**) showed significant spectral changes in the fluorescence emission upon F^- addition with a decrease in intensity and the appearance of a new band at longer wavelengths. Selectivity tests performed with other anions (Cl^-, Br^-, HSO_4^- and CH_3COO^-) revealed no emission spectral changes, indicating a selectivity of these compounds towards F^-.

Experimental Section

Materials and Methods: Melting points [°C] were determined with a Gallenkamp apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance II$^+$ spectrometer at 400 and 100.6 MHz, respectively. Chemical shifts and coupling constants are given in ppm and Hz, respectively. ^1H-^{13}C heteronuclear correlations, HMQC, HMBC and NOE experiments were also performed. HRMS (EI or ESI) data were recorded by the mass spectrometry service of the University of Vigo, Spain. Elemental analysis was performed with a LECO CHNS 932 elemental analyser. The reactions were monitored by thin layer chromatography (TLC). Column chromatography was performed on Macherey–Nagel silica gel (230–400 mesh). Petroleum ether refers to the fraction that boils at 40–60 °C. When a solvent gradient was used, polarity was increased from that of neat petroleum ether with diethyl ether in 10% steps until the isolation of the product. $PdCl_2$dppf·CH_2Cl_2

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(1:1) refers to [1,1′-bis(diphenylphosphanyl)ferrocene]dichloridopalladium(II)–dichloromethane complex adduct.

Synthesis of (*Z*)-1, (*E*)-1, (*Z*)-2, (*E*)-2 and 9: The synthesis of these compounds is described elsewhere.[18–20]

General Procedure for the Synthesis of β-Substituted Dehydroamino Acid Derivatives: To a solution of the β-bromodehydroamino acid derivative in THF/H_2O (1:1) (0.05 M) boronic acid (1.5 or 5 equiv.), $PdCl_2dppf{\cdot}CH_2Cl_2$ (1:1) (10 mol-%) and Cs_2CO_3 (1.4 equiv.) were added. The reaction mixture was heated at 90 °C, and the reaction was monitored by TLC until all of the β-bromodehydroamino acid was consumed (1–3 h). The solvent was removed under reduced pressure, and the residue was dissolved in ethyl acetate (100 mL). The organic layer was washed with water and brine (2 × 30 mL each), dried with $MgSO_4$, and the solvent was removed. The residue was submitted to column chromatography.

Methyl (*Z*)-2-(*tert*-Butoxycarbonylamino)-3-(phenanthracen-9-yl)-but-2-enoate [(*Z*)-3]: Compound (*Z*)-**3** was prepared from (*Z*)-**1** (0.5 mmol, 147 mg) and 9-phenanthracenylboronic acid according to the general procedure described above and with heating for 1 h. Column chromatography with diethyl ether/petroleum ether (1:4) gave (*Z*)-**3** (120 mg, 61%) as a white solid. M.p. 159.0–160.0 °C (from diethyl ether/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27 (s, 9 H, CH_3 Boc), 2.38 (s, 3 H, CH_3), 3.95 (s, 3 H, OCH_3), 5.61 (br. s, 1 H, NH), 7.59–7.73 (m, 5 H, ArH), 7.89 (d, *J* = 8.0 Hz, 2 H ArH), 8.72 (d, *J* = 8.4 Hz, 1 H, ArH), 8.77 (d, *J* = 8.0 Hz, 1 H, ArH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.03 (CH_3), 27.98 [C(CH_3)$_3$], 52.08 (OCH_3), 80.67 [O*C*(CH_3)$_3$], 122.58 (CH), 123.22 (CH), 125.28 (CH), 125.53 (CH), 126.06 (C), 126.95 (CH), 127.05 (CH), 127.06 (CH), 127.30 (CH), 128.48 (C), 128.64 (CH), 130.10 (C), 130.77 (C), 131.38 (C), 131.93 (C), 136.22 (C), 152.96 (C=O), 165.54 (C=O) ppm. HRMS (micrOTOF): calcd. for $C_{24}H_{26}NO_4$ [M + H]$^+$ 392.18618; found 392.18563.

Methyl (*E*)-2-(*tert*-Butoxycarbonylamino)-3-(phenanthracen-9-yl)-but-2-enoate [(*E*)-3]: Compound (*E*)-**3** was prepared from (*E*)-**1** (0.5 mmol, 147 mg) and 9-phenanthracenylboronic acid according to the general procedure described above and with heating for 1 h. Column chromatography with diethyl ether/petroleum ether (1:3) gave (*E*)-**3** (128 mg, 65%) as a white solid. M.p. 143.0–144.0 °C (from diethyl ether/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.57 (s, 9 H, CH_3 Boc), 2.27 (s, 3 H, CH_3), 3.24 (s, 3 H, OCH_3), 6.28 (br. s, 1 H, NH), 7.46 (s, 1 H, ArH), 7.56–7.69 (m, 4 H, ArH), 7.83 (dd, *J* = 7.8, 1.2 Hz, 1 H, ArH), 7.94 (d, *J* = 8.0 Hz, 1 H, ArH), 8.68 (d, *J* = 8.4 Hz, 1 H, ArH), 8.73 (d, *J* = 8.4 Hz, 1 H, ArH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 22.32 (CH_3), 28.28 [C(CH_3)$_3$], 51.63 (OCH_3), 80.75 [O*C*(CH_3)$_3$], 122.51 (CH), 122.86 (CH), 124.18 (CH), 125.33 (C), 126.11 (CH), 126.46 (CH), 126.62 (CH), 126.76 (CH), 128.50 (CH), 129.88 (C), 130.32 (C), 131.43 (C), 138.20 (C), 140.93 (C), 153.41 (C=O), 165.11 (C=O) ppm. HRMS (micrOTOF): calcd. for $C_{24}H_{26}NO_4$ [M + H]$^+$ 392.18618; found 392.18563.

Methyl (*Z*)-2-(*tert*-Butoxycarbonylamino)-3-(phenanthracen-9-yl)-3-phenylacrylate [(*Z*)-4]: Compound (*Z*)-**4** was prepared from (*Z*)-**2** (0.50 mmol, 178 mg) and 9-phenanthracenylboronic acid according to the general procedure described above and with heating for 1 h. Column chromatography with diethyl ether/petroleum ether (1:3) gave (*Z*)-**4** (185 mg, 82%) as a white solid. M.p. 168.0–169.0 °C (from diethyl ether/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.33 (s, 9 H, CH_3 Boc), 3.70 (s, 3 H, OCH_3), 5.77 (br. s, 1 H, NH), 7.26–7.30 (m, 5 H, ArH), 7.60–7.65 (m, 3 H, ArH), 7.69–7.74 (m, 2 H, ArH), 7.85 (d, *J* = 7.6 Hz, 1 H, ArH), 8.12 (d, *J* = 8.4 Hz, 1 H, ArH), 8.74 (d, *J* = 8.0 Hz, 1 H, ArH), 8.78 (d, *J* = 8.0 Hz, 1 H, ArH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 27.99 [C(CH_3)$_3$], 52.22 (OCH_3), 81.27 [O*C*(CH_3)$_3$], 122.58 (CH), 123.11 (CH), 125.85 (CH), 126.95 (CH), 127.06 (CH), 127.36 (CH), 127.44 (CH), 127.84 (CH), 127.90 (C), 128.18 (CH), 128.34 (CH), 128.87 (CH), 129.01 (CH), 129.41 (C), 130.36 (C), 130.80 (C), 131.29 (C), 134.50 (C), 139.44 (C), 152.50 (C=O), 166.27 (C=O) ppm. HRMS (micrOTOF): calcd. for $C_{29}H_{28}NO_4$ [M + H]$^+$ 454.20183; found 454.20128.

Methyl (*E*)-2-(*tert*-Butoxycarbonylamino)-3-(phenanthracen-9-yl)-3-phenylacrylate [(*E*)-4]: Compound (*E*)-**4** was prepared from (*E*)-**2** (0.50 mmol, 178 mg) and 9-phenanthracenylboronic acid according to the general procedure described above and with heating for 2 h. Column chromatography with diethyl ether/petroleum ether (1:4) gave (*E*)-**4** (132 mg, 58%) as a white solid. M.p. 173.0–174.0 °C (from diethyl ether/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.52 (s, 9 H, CH_3 Boc), 3.23 (s, 3 H, OCH_3), 6.42 (br. s, 1 H, NH), 7.24–7.28 (m, 1 H, ArH), 7.31–7.35 (m, 2 H, ArH), 7.42–7.49 (m, 3 H, ArH), 7.57–7.69 (m, 4 H, ArH), 7.88–7.94 (m, 2 H, ArH), 8.67 (d, *J* = 8.4 Hz, 2 H, ArH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 28.17 [C(CH_3)$_3$], 51.82 (OCH_3), 81.36 [O*C*(CH_3)$_3$], 122.49 (CH), 122.63 (CH), 126.46 (CH), 126.62 (CH), 126.71 (CH), 126.91 (CH), 127.16 (CH), 127.75 (C), 128.02 (CH), 128.30 (CH), 128.70 (CH), 128.83 (CH), 129.03 (CH), 130.37 (C), 130.58 (C), 130.74 (C), 131.17 (C), 132.32 (C), 135.76 (C), 137.65 (C), 152.86 (C=O), 166.12 (C=O) ppm. HRMS (micrOTOF): calcd. for $C_{29}H_{27}NNaO_4$ [M]$^+$ 476.18378; found 476.18323.

Methyl (*Z*)-2-(*tert*-Butoxycarbonylamino)-(1,2-dihydroacenaphthylen-5-yl)but-2-enoate [(*Z*)-5]: Compound (*Z*)-**5** was prepared from (*Z*)-**1** (0.5 mmol, 147 mg) and (1,2-dihydroacenaphthylen-5-yl)boronic acid according to the general procedure described above and with heating for 1 h. Column chromatography with diethyl ether/petroleum ether (3:7) gave (*Z*)-**5** (133 mg, 72%) as a white solid. M.p. 106–107 °C (from diethyl ether/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 (s, 9 H, CH_3 Boc), 2.32 (s, 3 H, CH_3), 3.43 (s, 4 H, 2 CH_2), 3.91 (s, 3 H, OCH_3), 5.56 (br. s, 1 H, NH), 7.25–7.33 (m, 3 H, ArH), 7.43–7.49 (m, 2 H, ArH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.15 (CH_3), 28.04 [C(CH_3)$_3$], 30.11 (CH_2), 30.44 (CH_2), 51.96 (OCH_3), 80.50 [O*C*(CH_3)$_3$], 119.15 (CH), 119.74 (CH), 119.94 (CH), 125.36 (C), 126.91 (CH), 128.00 (C), 128.61 (CH), 131.53 (C), 132.74 (C), 139.50 (C), 146.44 (C), 146.53 (C), 153.10 (C=O), 165.76 (C=O) ppm. $C_{22}H_{25}NO_4$ (367.44): calcd. C 71.91, H 6.86, N 3.81; found C 71.46, H 6.34, N 3.75.

Methyl (*E*)-2-(*tert*-Butoxycarbonylamino)-(1,2-dihydroacenaphthylen-5-yl)but-2-enoate [(*E*)-5]: Compound (*E*)-**5** was prepared from (*E*)-**1** (0.5 mmol, 147 mg) and (1,2-dihydroacenaphthylen-5-yl)boronic acid according to the general procedure described above and with heating for 1 h. Column chromatography with diethyl ether/petroleum ether (3:7) gave (*E*)-**5** (149 mg, 81%) as a white solid. M.p. 131.0–132.0 °C (from diethyl ether/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.53 (s, 9 H, CH_3 Boc), 2.23 (s, 3 H, CH_3), 3.03 (s, 3 H, OCH_3), 3.40 (s, 4 H, 2 CH_2), 6.16 (br. s, 1 H, NH), 7.17 (d, *J* = 7.2 Hz, 1 H, ArH), 7.22–7.28 (m, 2 H, ArH), 7.40–7.45 (m, 1 H, ArH), 7.54 (d, *J* = 8.1 Hz, 1 H, ArH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 22.42 (CH_3), 28.28 [C(CH_3)$_3$], 30.07 (CH_2), 30.48 (CH_2), 51.63 (OCH_3), 80.62 [O*C*(CH_3)$_3$], 118.70 (CH), 119.28 (CH), 120.29 (CH), 124.86 (C), 125.83 (CH), 127.96 (CH), 129.02 (C), 134.68 (C), 139.19 (C), 140.46 (C), 145.44 (C), 146.12 (C), 153.41 (C=O), 165.21 (C=O) ppm. $C_{22}H_{25}NO_4$ (367.44): calcd. C 71.91, H 6.86, N 3.81; found C 71.97, H 6.48, N 3.74.

Methyl (*Z*)-2-(*tert*-Butoxycarbonylamino)-3-phenyl-3-(1,2-dihydroacenaphthylen-5-yl)acrylate [(*Z*)-6]: Compound (*Z*)-**6** was prepared

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from (*Z*)-**2** (0.5 mmol, 178 mg) and (1,2-dihydroacenaphthylen-5-yl)boronic acid according to the general procedure described above and with heating for 1.5 h. Column chromatography with diethyl ether/petroleum ether (1:3) gave (*Z*)-**6** (170 mg, 79%) as a white solid. M.p. 160.0–161.0 °C (from diethyl ether/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.37 (s, 9 H, CH_3 Boc), 3.41–3.46 (m, 4 H, 2 CH_2), 3.64 (s, 3 H, OCH_3), 5.76 (br. s, 1 H, NH), 7.17–7.21 (m, 3 H, ArH), 7.24–7.28 (m, 4 H, ArH), 7.32 (d, J = 6.8 Hz, 1 H, ArH), 7.44 (t, J = 7.6 Hz, 1 H, ArH), 7.60 (d, J = 8.4 Hz, 1 H, ArH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 28.03 [C(CH_3)$_3$], 30.17 (CH_2), 30.42 (CH_2), 52.06 (OCH_3), 80.98 [O*C*(CH_3)$_3$], 119.22 (CH), 119.73 (CH), 120.45 (CH), 126.92 (C), 127.64 (C), 128.03 (CH), 128.61 (CH), 128.81 (CH), 129.05 (C), 130.40 (CH), 131.15 (C), 139.54 (C), 140.32 (C), 146.42 (C), 147.24 (C), 152.76 (C=O), 166.51 (C=O) ppm. HRMS (micrOTOF): calcd. for $C_{27}H_{28}NO_4$ [M + H]$^+$ 430.20183; found 430.20128.

Methyl (*E*)-2-(*tert*-Butoxycarbonylamino)-3-(1,2-dihydroacenaphthylen-5-yl)-3-phenylacrylate [(*E*)-6]: Compound (*E*)-**6** was prepared from (*E*)-**2** (0.5 mmol, 178 mg) and (1,2-dihydroacenaphthylen-5-yl)boronic acid according to the general procedure described above and with heating for 2 h. Column chromatography with diethyl ether/petroleum ether (1:4) gave (*E*)-**6** (154 mg, 72%) as a white solid. M.p. 157.0–158.0 °C (from diethyl ether/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.48 (s, 9 H, CH_3 Boc), 3.33 (s, 3 H, OCH_3), 3.39 (s, 4 H, 2 CH_2), 6.31 (br. s, 1 H, NH), 7.23–7.38 (m, 10 H, ArH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 28.17 [C(CH_3)$_3$], 30.06 (CH_2), 30.44 (CH_2), 51.82 (OCH_3), 81.13 [O*C*(CH_3)$_3$], 118.61 (CH), 119.29 (CH), 120.98 (CH), 126.95 (C), 127.92 (CH), 128.05 (C), 128.12 (CH), 128.74 (CH), 129.21 (CH), 129.25 (CH), 130.24 (C), 132.54 (C), 138.68 (C), 139.48 (C), 145.94 (C), 146.54 (C), 152.94 (C=O), 166.31 (C=O) ppm. HRMS (EI): calcd. for $C_{27}H_{27}NNaO_4$ [M]$^+$ 452.18323; found 452.18279.

Methyl (*Z*)-2-(*tert*-Butoxycarbonylamino)-3-(naphthalen-1-yl)but-2-enoate [(*Z*)-7]: Compound (*Z*)-**7** was prepared from (*Z*)-**1** (0.5 mmol, 147 mg) and (naphthalen-1-yl)boronic acid according to the general procedure described above and with heating for 1 h. Column chromatography with diethyl ether/petroleum ether (3:7) gave (*Z*)-**7** (125 mg, 73%) as a white solid. M.p. 88.0–89.0 °C (from diethyl ether/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.30 (s, 9 H, CH_3 Boc), 2.32 (s, 3 H, CH_3), 3.92 (s, 3 H, OCH_3), 5.48 (br. s, 1 H, NH), 7.30 (s, 1 H, ArH), 7.49–7.52 (m, 3 H, ArH), 7.78–7.85 (m, 2 H, ArH), 7.88–7.90 (m, 1 H, ArH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.19 (CH_3), 27.99 [C(CH_3)$_3$], 52.03 (OCH_3), 82.57 [O*C*(CH_3)$_3$], 124.55 (CH), 124.83 (CH), 125.66 (CH), 125.72 (C), 126.26 (CH), 126.82 (CH), 128.24 (CH), 128.61 (CH), 129.48 (C), 132.16 (C), 133.83 (C), 137.51 (C), 152.95 (C=O), 165.58 (C=O) ppm. $C_{20}H_{23}NO_4$ (341.40): calcd. C 70.36, H 6.79, N 4.10; found C 70.32, H 6.80, N 4.07.

Methyl (*E*)-2-(*tert*-Butoxycarbonylamino)-3-(naphthalen-1-yl)but-2-enoate [(*E*)-7]: Compound (*E*)-**8** was prepared from (*E*)-**1** (1.0 mmol, 294 mg) and (naphthalen-1-yl)boronic acid according to the general procedure described above and with heating for 1 h. Column chromatography with diethyl ether/petroleum ether (3:7) gave (*E*)-**7** (250 mg, 73%) as a white solid. M.p. 79.0–80.0 °C (from diethyl ether/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.55 (s, 9 H, CH_3 Boc), 2.24 (s, 3 H, CH_3), 3.25 (s, 3 H, OCH_3), 6.22 (br. s, 1 H, NH), 7.20 (d, J = 6.8 Hz, 1 H, ArH), 7.40–7.49 (m, 3 H, ArH), 7.77 (d, J = 8.4 Hz, 1 H, ArH), 7.84–7.88 (m, 2 H, ArH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 22.59 (CH_3), 28.27 [C(CH_3)$_3$], 51.56 (OCH_3), 80.70 [O*C*(CH_3)$_3$], 123.80 (CH), 125.15 (CH), 125.27 (CH), 125.74 (CH), 126.13 (CH), 127.42 (CH), 128.22 (CH), 130.58 (C), 133.41 (C), 139.49 (C), 141.11 (C), 150.47 (C), 153.36 (C=O), 165.04 (C=O) ppm. HRMS (EI): calcd. for $C_{20}H_{23}NNaO_4$ [M]$^+$ 364.15193; found 364.15159.

Methyl (*Z*)-2-(*tert*-Butoxycarbonylamino)-3-(naphthalen-1-yl)-3-phenylacrylate [(*Z*)-8]: Compound (*Z*)-**8** was prepared from (*Z*)-**2** (0.5 mmol, 178 mg) and (naphthalen-1-yl)boronic acid according to the general procedure described above and with heating for 1 h. Column chromatography with diethyl ether/petroleum ether (1:2) gave (*Z*)-**8** (149 mg, 74%) as a white solid. M.p. 165.0–166.0 °C (from diethyl ether/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.35 (s, 9 H, CH_3 Boc), 3.66 (s, 3 H, OCH_3), 5.67 (br. s, 1 H, NH), 7.18–7.30 (m, 6 H, ArH), 7.47–7.54 (m, 3 H, ArH), 7.86–7.92 (m, 2 H, ArH), 8.02 (d, J = 8.0 Hz, 1 H, ArH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 28.00 [C(CH_3)$_3$], 52.14 (OCH_3), 81.17 [O*C*(CH_3)$_3$], 125.07 (CH), 125.62 (CH), 126.27 (CH), 127.06 (CH), 127.57 (C), 127.75 (CH), 128.12 (CH), 128.36 (CH), 128.56 (CH), 128.89 (CH), 130.57 (C), 133.90 (C), 135.66 (C), 139.74 (C), 152.53 (C=O), 166.30 (C=O) ppm. HRMS (micrOTOF): calcd. for $C_{25}H_{26}NO_4$ [M + H]$^+$ 404.18618; found 404.18563.

Methyl (*E*)-2-(*tert*-Butoxycarbonylamino)-3-(naphthalen-1-yl)-3-phenylacrylate [(*E*)-8]: Compound (*E*)-**8** was prepared from (*E*)-**2** (0.5 mmol, 178 mg) and (naphthalen-1-yl)boronic acid according to the general procedure described above and with heating for 1 h. Column chromatography with diethyl ether/petroleum ether (1:2) gave (*E*)-**8** (157 mg, 78%) as a white solid. M.p. 155.0–156.0 °C (from diethyl ether/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.48 (s, 9 H, CH_3 Boc), 3.23 (s, 3 H, OCH_3), 6.35 (br. s, 1 H, NH), 7.24–7.46 (m, 9 H, ArH), 7.80–7.85 (m, 3 H, ArH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 28.20 [C(CH_3)$_3$], 51.74 (OCH_3), 81.17 [O*C*(CH_3)$_3$], 124.99 (CH), 125.76 (CH), 126.06 (CH), 126.15 (CH), 127.33 (CH), 127.54 (C), 128.12 (CH), 128.22 (CH), 128.44 (CH), 128.81 (CH), 129.04 (CH), 131.85 (C), 132.48 (C), 133.71 (C), 137.10 (C), 138.24 (C), 152.89 (C=O), 166.06 (C=O) ppm. $C_{25}H_{25}NO_4$ (403.47): calcd. C 74.42, H 6.25, N 3.47; found C 74.52, H 6.07, N 3.43.

Methyl 2-(*tert*-Butoxycarbonylamino)-3,3-bis(phenanthracen-9-yl)-acrylate (10): Compound **10** was prepared from **9** (0.5 mmol, 178.4 mg) and 9-phenanthracenylboronic acid (5 equiv., 2.5 mmol) according to the general procedure described above and with heating for 2 h. Column chromatography with diethyl ether/petroleum ether (1:3) gave **10** (175 mg, 63%) as a white solid. M.p. 212.0–213.0 °C (from ethyl acetate/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.37 (s, 9 H, CH_3 Boc), 3.36 (s, 3 H, OMe), 5.84 (br. s, 1 H, NH), 7.17–7.21 (m, 1 H, ArH), 7.45–7.54 (m, 3 H, ArH), 7.59–7.80 (m, 8 H, ArH), 7.89–7.91 (m, 2 H, ArH), 8.00–8.02 (m, 1 H, ArH), 8.64–8.70 (m, 2 H, ArH), 8.81–8.83 (m, 1 H, ArH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 28.06 [(CH_3)$_3$C], 52.13 (OCH_3), 81.21 [(CH_3)$_3$*C*], 122.40 (CH), 122.57 (CH), 122.70 (CH), 123.57 (CH), 126.27 (CH), 126.56 (CH), 126.75 (CH), 126.83 (CH), 126.89 (CH), 126.93 (CH), 127.01 (CH), 127.11 (CH), 127.52 (CH), 128.05 (CH), 128.82 (CH), 128.97 (CH), 128.70 (CH), 129.70 (CH), 129.80 (C), 130.13 (C), 130.19 (C), 130.45 (C), 130.54 (C), 130.60 (C), 130.69 (C), 130.94 (C), 131.29 (C), 132.95 (C), 135.71 (C), 136.82 (C), 152.74 (C=O), 166.22 (C=O) ppm. HRMS (micrO-TOF): calcd. for $C_{37}H_{32}NO_4$ [M + H]$^+$ 554.23313; found 554.23258.

Methyl 2-(*tert*-Butoxycarbonylamino)-3,3-bis(1,2-dihydroacenaphthen-5-yl)acrylate (11): Compound **11** was prepared from **9** (0.25 mmol, 89.2 mg) and 1,2-dihydroacenaphthylen-5-ylboronic acid (5 equiv., 1.25 mmol) according to the general procedure described above and with heating for 2 h. Column chromatography with diethyl ether/petroleum ether (1:3) gave **11** (85 mg, 67%) as a white solid. M.p. 121.0–122.0 °C (from ethyl acetate/*n*-hexane). ^{1}H

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NMR (400 MHz, [D$_6$]DMSO): δ = 1.34 (s, 9 H, CH$_3$ Boc), 3.25 (s, 3 H, OCH$_3$), 3.29–3.39 (m, 4 H, 2 CH$_2$), 7.00 (d, J = 7.2 Hz, 1 H, ArH), 7.13–7.25 (m, 6 H, ArH), 7.34 (d, J = 6.8 Hz, 1 H, ArH), 7.47 (t, J = 8.4 Hz, 1 H, ArH), 7.74 (d, J = 8.0 Hz, 1 H, ArH), 8.10 (br. s, 1 H, NH) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]DMSO): δ = 27.59 [C(*C*H$_3$)$_3$], 29.22 (CH$_2$), 29.61 (CH$_2$), 50.66 (OCH$_3$), 78.88 [O*C*(CH$_3$)$_3$], 118.31 (CH), 118.63 (CH), 118.77 (CH), 118.81 (CH), 119.87 (CH), 120.31 (CH), 127.37 (CH), 127.77 (CH), 127.92 (C), 128.18 (CH), 128.23 (C), 129.67 (C), 129.74 (CH), 132.08 (C), 132.98 (C), 134.13 (C), 138.59 (C), 145.33 (C), 145.43 (C), 145.79 (C), 153.00 (C=O), 165.57 (C=O) ppm. HRMS (micrOTOF): calcd. for $C_{33}H_{32}NO_4$ [M + H]$^+$ 506.23313; found 506.23258.

Methyl 2-(*tert*-Butoxycarbonylamino)-3,3-bis(naphthalen-1-yl)acrylate (12): Compound **12** was prepared from **9** (0.5 mmol, 178 mg) and (naphthalen-1-yl)boronic acid (5 equiv.) according to the general procedure described above and with heating for 2 h. Column chromatography with diethyl ether/petroleum ether (1:2) gave **12** (160 mg, 71%) as a white solid. M.p. 194.0–195.0 °C (from ethyl acetate/petroleum ether). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.38 (s, 9 H, CH$_3$ Boc), 3.36 (s, 3 H, OCH$_3$), 5.78 (br. s, 1 H, NH), 7.12–7.18 (m, 1 H, ArH), 7.28–7.36 (m, 3 H, ArH), 7.46–7.50 (m, 2 H, ArH), 7.53–7.69 (m, 2 H, ArH), 7.72–7.88 (m, 4 H, ArH), 7.93 (d, J = 7.6 Hz, 1 H, ArH), 8.41 (d, J = 7.2 Hz, 1 H, ArH) ppm. ^{13}C NMR (100.6 MHz, CDCl$_3$): δ = 28.03 [C(*C*H$_3$)$_3$], 51.90 (OCH$_3$), 81.15 [O*C*(CH$_3$)$_3$], 124.90 (CH), 125.34 (CH), 125.54 (CH), 125.77 (CH), 126.06 (CH), 126.20 (CH), 126.51 (CH), 127.29 (CH), 127.34 (CH), 127.60 (CH), 128.15 (CH), 128.78 (CH), 129.12 (CH), 129.23 (CH), 129.27 (C), 129.51 (C), 132.00 (C), 133.78 (C), 133.90 (C), 134.72 (C), 136.61 (C), 138.05 (C), 152.82 (C=O), 166.16 (C=O) ppm. HRMS (micrOTOF): calcd. for $C_{29}H_{28}NO_4$ [M + H]$^+$ 454.20183; found 454.20128.

General Procedure for the Intramolecular Cyclisation: To a solution of the β-substituted or β,β-disubstituted dehydroamino acid derivatives in DMF, Pd(OAc)$_2$ (50 mol-%) and Cu(OAc)$_2$·H$_2$O (3 equiv.) were added, and the mixture was heated at 160 °C (the reaction was moniored by TLC). Ethyl acetate (50 mL) was then added, and the organic layer was washed with water and brine (2 × 30 mL, each), dried with MgSO$_4$, and the solvent was removed.

Methyl 3-Methyl-1*H*-dibenzo[*e*,*g*]indole-2-carboxylate (13): Compound **13** was prepared from (*Z*)-**3** (0.29 mmol, 112 mg) according to the general procedure described above and with heating for 6 h. Column chromatography with diethyl ether/petroleum ether (1:4) afforded **13** (33.4 mg, 40%) as a white solid. M.p. 212.0–213.0 °C (from ethyl acetate/petroleum ether). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.05 (s, 3 H, CH$_3$), 4.01 (s, 3 H, OCH$_3$), 7.55–7.59 (m, 1 H, ArH), 7.62–7.68 (m, 3 H, ArH), 8.06–8.08 (m, 1 H, ArH), 8.53 (d, J = 8.4 Hz, 1 H, ArH), 8.67–8.70 (m, 2 H, ArH), 9.56 (br. s, 1 H, NH) ppm. ^{13}C NMR (100.6 MHz, CDCl$_3$): δ = 51.60 (OCH$_3$), 119.50 (C), 120.59 (CH), 121.29 (C), 122.37 (C), 123.66 (CH), 123.78 (CH), 123.90 (CH and C), 124.33 (CH), 126.46 (CH), 126.91 (CH), 127.13 (CH), 127.77 (C), 129.96 (C), 130.01 (C), 130.67 (C), 162.71 (C=O) ppm. $C_{19}H_{15}NO_2$ (289.33): calcd. C 78.87, H 5.23, N 4.84; found C 78.75, H 5.32, N 4.32.

Methyl 3-(Phenanthren-9-yl)-1*H*-indole-2-carboxylate (14): Compound **14** was prepared from (*Z*)-**4** (0.5 mmol, 227 mg) according to the general procedure described above and with heating for 4 h. Crystallization (diethyl ether/petroleum ether) gave **14** (137 mg, 78%) as a white solid. M.p. 102.0–103.0 °C (from diethyl ether/petroleum ether). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.59 (s, 3 H, OCH$_3$), 7.11 (t, J = 7.6 Hz, 1 H, ArH), 7.36–7.49 (m, 3 H, ArH), 7.54 (d, J = 8.4 Hz, 1 H, ArH), 7.63–7.74 (m, 4 H, ArH), 7.84 (s, 1 H, ArH), 7.92 (d, J = 7.2 Hz, 1 H, ArH), 8.81 (t, J = 7.6 Hz, 2 H, ArH), 9.46 (br. s, 1 H, NH) ppm. ^{13}C NMR (100.6 MHz, CDCl$_3$): δ = 51.74 (OCH$_3$), 111.81 (CH), 120.84 (CH), 121.89 (C), 121.98 (CH), 122.54 (CH), 122.67 (CH), 124.43 (C), 125.86 (CH), 126.24 (CH), 126.29 (CH), 126.56 (CH), 126.58 (CH), 126.88 (CH), 128.64 (CH), 128.99 (CH), 129.03 (C), 130.25 (C), 130.32 (C), 130.39 (C), 131.61 (C), 131.85 (C), 135.89 (C), 162.58 (C=O) ppm. HRMS (micrOTOF): calcd. for $C_{24}H_{18}NO_2$ [M + H]$^+$ 352.13375; found 352.13321.

Methyl 3-(Phenanthren-9-yl)-1*H*-dibenzo[*e*,*g*]indole-2-carboxylate (15): Compound **15** was prepared from **10** (0.32 mmol, 175 mg) according to the general procedure described above and with heating for 4 h (110 mg, 52%). Column chromatography with diethyl ether/petroleum ether (1:3) afforded **15** as a white solid. M.p. 260.0–261.0 °C (from ethyl acetate/petroleum ether). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.55 (s, 3 H, OCH$_3$), 7.00 (t, J = 8 Hz, 1 H, ArH), 7.35–7.41 (m, 3 H, ArH), 7.65–7.77 (m, 6 H, ArH), 7.91 (s, 1 H, ArH), 7.88 (d, J = 8 Hz, 1 H, ArH), 8.24–8.26 (m, 1 H, ArH), 8.61 (d, J = 8 Hz, 1 H, ArH), 8.70–8.73 (m, 1 H, ArH), 8.86 (d, J = 8.4 Hz, 2 H, ArH), 10.05 (br. s, 1 H, NH) ppm. ^{13}C NMR (100.6 MHz, CDCl$_3$): δ = 51.71 (OCH$_3$), 120.33 (C), 120.78 (CH), 122.37 (C), 122.70 (CH), 122.81 (CH), 122.95 (C), 123.30 (CH), 123.94 (CH), 124.04 (CH), 124.66 (CH), 124.84 (C), 126.53 (CH), 126.62 (CH), 126.66 (CH), 126.72 (CH), 126.73 (CH), 126.78 (CH), 127.06 (CH), 127.14 (CH), 127.85 (C), 128.50 (CH), 128.73 (C), 128.89 (CH), 130.21 (C), 130.49 (C), 130.63 (C), 131.92 (C), 131.98 (C), 132.39 (C), 162.14 (C=O) ppm. HRMS (micrOTOF): calcd. for $C_{32}H_{22}NO_4$ [M + H]$^+$ 452.16505; found 452.16451.

Methyl 9-Methyl-5,7-dihydro-4*H*-indeno[7,1-*ef*]indole-8-carboxylate (16): Compound **16** was prepared from (*Z*)-**5** (0.27 mmol, 100 mg) according to the general procedure described above and with heating for 4 h. Crystallization (ethyl acetate/petroleum ether) gave **16** (50 mg, 70%) as a white solid. M.p. 240.0–241.0 °C (from ethyl acetate/petroleum ether). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.00 (s, 3 H, CH$_3$), 3.39–3.46 (dd, J = 7.6 Hz, 4 H, 2 CH$_2$), 3.97 (s, 3 H, OCH$_3$), 7.21 (s, 1 H, ArH), 7.31 (d, J = 7.2 Hz, 1 H, ArH), 7.56 (t, J = 7.6 Hz, 1 H, ArH), 8.14 (d, J = 8.0 Hz, 1 H, ArH), 8.97 (br. s, 1 H, NH) ppm. ^{13}C NMR (100.6 MHz, CDCl$_3$): δ = 12.77 (CH$_3$), 29.58 (CH$_2$), 31.01 (CH$_2$), 51.43 (OCH$_3$), 106.03 (CH), 118.32 (CH), 119.05 (CH), 119.60 (C), 120.57 (C), 127.95 (C), 128.37 (CH), 135.78 (C), 136.14 (C), 145.64 (C), 146.23 (C), 162.95 (C=O) ppm. $C_{17}H_{15}NO_2$ (265.31): calcd. C 76.96, H 5.70, N 5.28; found C 76.55, H 5.36, N 4.99.

Methyl 3-(1,2-Dihydroacenaphthylen-5-yl)-1*H*-indole-2-carboxylate (17) and Methyl 9-phenyl-5,7-dihydro-4*H*-indeno[7,1-*ef*]indole-8-carboxylate (18): A mixture (4:1) of **17/18** was obtained by applying the general procedure described above to (*Z*)-**6** (0.35 mmol, 150 mg) and heating for 4 h (79 mg, 65%). Column chromatography with diethyl ether/petroleum ether (1:3) afforded **17** as a white solid. M.p. 220.0–221.0 °C (from ethyl acetate/petroleum ether). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.49 (s, 4 H, 2 CH$_2$), 3.65 (s, 3 H, OCH$_3$), 7.09 (t, J = 7.8 Hz, 1 H, ArH), 7.27–7.34 (m, 3 H, ArH), 7.36–7.40 (m, 3 H, ArH), 7.49–7.54 (m, 2 H, ArH), 9.11 (br. s, 1 H, NH) ppm. ^{13}C NMR (100.6 MHz, CDCl$_3$): δ = 30.21 (CH$_2$), 30.55 (CH$_2$), 51.70 (OCH$_3$), 111.66 (CH), 118.81 (CH), 119.02 (CH), 120.64 (CH), 121.35 (CH), 122.08 (C), 122.27 (CH), 123.82 (C), 125.79 (CH), 126.54 (C), 127.52 (CH), 128.83 (C), 130.19 (CH), 130.94 (C), 135.77 (C), 139.36 (C), 145.85 (C), 146.00 (C), 162.46 (C=O) ppm. HRMS (micrOTOF): calcd. for $C_{22}H_{18}NO_2$ [M + H]$^+$ 328.13375; found 328.13321. Compound **18** was also isolated as white solid. M.p. 203.0–204.0 °C (from ethyl acetate/petroleum ether). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.43 (s, 4 H, 2 CH$_2$), 3.75 (s, 3 H, OCH$_3$), 7.22–7.24 (m, 3 H, ArH), 7.29 (s, 1 H,

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ArH), 7.47–7.55 (m, 5 H, ArH), 9.21 (br. s, 1 H, NH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 29.63 (CH_2), 30.96 (CH_2), 51.49 (OCH_3), 105.87 (CH), 118.63 (CH), 118.96 (CH), 119.28 (C), 120.73 (C), 126.83 (C), 127.16 (C), 127.41 (CH), 128.01 (CH), 128.16 (CH), 130.31 (CH), 135.68 (C), 135.72 (C), 135.96 (C), 145.95 (C), 146.06 (C), 162.26 (C=O) ppm. HRMS (micrOTOF): calcd. for $C_{22}H_{18}NO_4$ $[M + H]^+$ 328.13375; found 328.133321.

Methyl 1-Methyl-3*H*-benzo[*e*]indole-2-carboxylate (19): Compound **19** was prepared from (*Z*)-**7** (0.29 mmol, 112 mg) according to the general procedure described above and with heating for 6 h. Column chromatography with diethyl ether/petroleum ether (1:4) afforded **19** (33.4 mg, 47%) as a white solid. M.p. 212.0–213.0 °C (from ethyl acetate/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.07 (s, 3 H, CH_3), 3.99 (s, 3 H, OCH_3), 7.45–7.49 (m, 2 H, ArH), 7.60–7.64 (m, 1 H, ArH), 7.70 (d, *J* = 9.2 Hz, 1 H, ArH), 7.91–7.93 (m, 1 H, ArH), 8.55 (d, *J* = 8.0 Hz, 1 H, ArH), 9.56 (br. s, 1 H, NH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 51.58 (OCH_3), 112.92 (CH), 121.48 (C), 121.54 (C), 122.93 (C), 123.18 (CH), 123.63 (CH), 126.61 (CH), 127.58 (CH), 129.14 (CH), 129.88 (C), 130.20 (C), 133.58 (C), 162.86 (C=O) ppm. HRMS (EI): calcd. for $C_{15}H_{14}NO_2$ $[M + H]^+$ 240.10191; found 240.10180.

Methyl 3-(Naphthalen-1-yl)-1*H*-indole-2-carboxylate (20): Compound **20** was prepared from (*Z*)-**8** (0.30 mmol, 120 mg) according to the general procedure described above and with heating for 3 h. Crystallization from diethyl ether/petroleum ether gave **20** (78 mg, 87%) as a white solid. M.p. 168.0–169.0 °C (from ethyl acetate/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.62 (s, 3 H, OCH_3), 7.10 (t, *J* = 7.6 Hz, 1 H, ArH), 7.27–7.42 (m, 3 H, ArH), 7.47–7.61 (m, 4 H, ArH), 7.66 (d, *J* = 8.4 Hz, 1 H, ArH), 7.94 (d, *J* = 8.0 Hz, 2 H, ArH), 9.32 (br. s, 1 H, NH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 51.73 (OCH_3), 111.76 (CH), 120.80 (CH), 122.08 (CH), 122.15 (C), 124.12 (C), 125.15 (CH), 125.55 (CH), 125.65 (CH), 125.84 (CH), 126.23 (CH), 127.88 (CH), 128.12 (CH), 128.45 (CH), 128.93 (C), 131.53 (C), 132.69 (C), 133.56 (C), 135.77 (C), 162.52 (C=O) ppm. HRMS (micrOTOF): calcd. for $C_{20}H_{16}NO_4$ $[M + H]^+$ 302.11810; found 302.11756.

Methyl 1-(Naphthalen-1-yl)-3*H*-benzo[*e*]indole-2-carboxylate (21): Compound **21** was prepared from **12** (0.30 mmol, 120 mg) according to the general procedure described above and with heating for 3 h. Crystallization from diethyl ether/petroleum ether gave **21** (144 mg, 86%) as a white solid. M.p. 194.0–195.0 °C (from ethyl acetate/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.56 (s, 3 H, OCH_3), 7.04 (t, *J* = 7.6 Hz, 1 H, ArH), 7.14 (d, *J* = 8.0 Hz, 1 H, ArH), 7.25–7.32 (m, 2 H, ArH), 7.48 (t, *J* = 7.2 Hz, 1 H, ArH), 7.56–7.67 (m, 4 H, ArH), 7.77 (d, *J* = 8.8 Hz, 1 H, ArH), 7.85 (d, *J* = 8.0 Hz, 1 H, ArH), 7.98 (d, *J* = 8.4 Hz, 1 H, ArH), 8.02 (d, *J* = 7.6 Hz, 1 H, ArH), 9.78 (br. s, 1 H, NH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 51.61 (OCH_3), 112.91 (CH), 122.04 (C), 122.88 (C), 123.03 (CH), 123.88 (CH), 123.95 (C), 125.52 (CH), 125.74 (CH), 126.03 (CH), 126.47 (CH), 127.85 (CH), 128.01 (CH), 128.13 (CH), 128.75 (CH), 129.10 (C), 129.93 (C), 132.87 (C), 133.49 (C), 133.61 (C), 133.72 (C), 162.31 (C=O) ppm. $C_{24}H_{17}NO_2$ (351.38): calcd. C 82.03, H 4.88, N 3.99; found C 81.64, H 4.46, N 4.29.

Spectroscopic Measurements: All solutions were prepared by using spectroscopy-grade solvents. Absorption spectra were recorded with a Shimadzu UV-3101PC UV/Vis/NIR spectrophotometer. Fluorescence measurements were performed with a Spex Fluorolog 3 spectrofluorimeter, equipped with double monochromators in both excitation and emission and a temperature-controlled cuvette holder. Fluorescence spectra were corrected for the instrumental response of the system.

Fluorescence Quantum Yields: For fluorescence quantum yield determinations, the solutions were bubbled with ultrapure nitrogen for 40 min before measurement. The fluorescence quantum yields (Φ_s) were determined by the standard method [Equation (1)].[21,22] 9,10-Diphenylanthracene in ethanol (Φ_r = 0.95[10]) was the reference.

$$\Phi_s = \frac{A_r F_s n_s^2}{A_s F_r n_r^2} \Phi_r \quad (1)$$

where *A* is the absorbance at the excitation wavelength, *F* the integrated emission area and *n* the refraction index of the solvents used. Subscripts refer to the reference (r) or sample (s) compound.

Fluorescence and UV/Vis Absorption Titrations: Stock solutions (5×10^{-6} M) were prepared by using spectroscopy-grade acetonitrile. Solutions of tetrabutylammonium fluoride, tetrabutylammonium chloride, tetrabutylammonium bromide, tetrabutylammonium hydrogen sulfate and tetrabutylammonium acetate were prepared at 1×10^{-2} M. The solution containing the fluorescent compound (2 mL of stock solution) was placed in a quartz cell (10.0 mm width), and the tetrabutylammonium salt solution was introduced in an incremental fashion. The corresponding absorption and fluorescence spectra were recorded at 25 °C and were corrected for dilution.

Supporting Information (see footnote on the first page of this article): Several figures including the emission observed from a solution of **13** and **15** and of **13** + F^- and **15** + F^- in acetonitrile, under irradiation with 340 nm light; the normalised absorption of **13** and **15** (5×10^{-6} M in acetonitrile) and excitation spectrum of **13** and **15** + 500 equiv. of F^-; the fluorescence emission spectra (λ_{ex} = 335 nm) of **15** (5×10^{-6} M in acetonitrile) in the presence of different amounts of OH^- (0, 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 80 and 90 equiv.) and the absorption of **15** (5×10^{-6} M in acetonitrile) in the absence and presence of OH^- (90 equiv.).

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