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Preparation of a Family of 10-Hydroxybenzo[*h*]quinoline Analogues via a Modified Sanford Reaction and Their Excited State Intramolecular Proton Transfer Properties†

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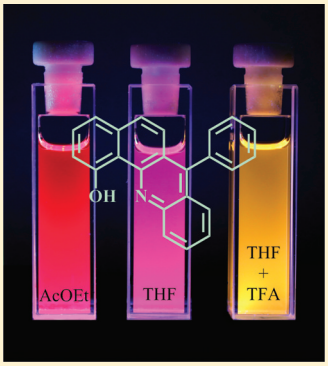
Supporting Information

ABSTRACT: We have developed a highly optimized methodology that allows for the oxidative acetoxylation of a sterically and electronically demanding library of analogues of benzo[*h*]quinoline. The optimal conditions for the insertion of an OAc group were identified after examining various reaction parameters (solvent, oxidant, catalyst, temperature, time). The conditions identified ($Pd(OAc)_2$, $PhI(OAc)_2$, MeCN, 150 °C, 16 h), combined with the hydrolysis of acetates, resulted in the formation of hydroxybenzoquinolines in 27−59% yield, whereas all previously published procedures were ineffective. This synthesis was compatible with diverse functionalities (ester, aldehyde, carbon−carbon triple bond) and, most importantly, worked for sterically hindered analogues as well as for compounds possessing electron-donating and electron-withdrawing substituents at various positions. All the obtained compounds demonstrated excited-state intramolecular proton transfer (ESIPT) manifesting as small fluorescence quantum yields and large Stokes shifts (8300−9660 cm^{-1}). The effect of structural variations in eight 10-hydroxybenzo[*h*]quinoline analogues on absorption and emission properties was studied in detail.



INTRODUCTION

Excited state intramolecular proton transfer (ESIPT)[1] has emerged in recent years as a most interesting phenomenon that can be utilized in the design of fluorescent sensors.[2] Compounds displaying ESIPT, such as benzoxazoles,[3] flavones,[4] imidazoles,[5] or anthraquinones,[6] possess a large Stokes shift, and hence many important applications have been found for them (such as laser dyes,[7] fluorescence recording,[8] ultraviolet stabilizers,[9] probes for solvation dynamics,[10] probes for biological environments,[11] and recently organic light-emitting devices[12]). 10-Hydroxybenzo[*h*]quinoline (HBQ)[13] constitutes one of the fundamental heterocyclic systems in which ESIPT occurs. Although this molecule has been used for a long time as a reagent in the preparation of optical filter agents in photographic emulsions, it was not until fundamental studies were carried out by Chou that ESIPT was recognized as the process responsible for its strongly bathochromically shifted fluorescence.[14] Detailed photophysical and theoretical studies of that molecule[15] showed very fast and solvent-independent ESIPT, but broader studies were hampered by considerable difficulties with the preparation of its more elaborate derivatives.[16] The recent discovery of coordination-assisted acetoxylation of derivatives and analogues of 2-phenylpyridine, made by Sanford and co-workers, opened up new possibilities.[17] Acetate derivatives of 10-hydroxybenzo[*h*]quinoline prepared in such a way can be easily hydrolyzed to the corresponding phenol. It is worth mentioning that in 6-, 7-, and 8-hydroxyquinolines, excited state proton transfer also occurs in intra- or intermolecular fashion.[18] These analogues of HBQ are known to be photoacids.[19] We envisioned that a combination of the rich chemistry of quinolines (and their benzoanalogues) with this modern tool could provide easy access to an almost unlimited variety of structural analogues of 10-hydroxybenzo[*h*]quinoline, which would allow studies on the structure−optical property relationship. The aim of this study was to explore this strategy to obtain a range of derivatives and investigate their fundamental optical properties. This in turn would allow us to address one of the most important issues regarding the ESIPT system, i.e., the wide tunability of chromophore absorption as well as proton transfer emission.

RESULTS AND DISCUSSION

As previously outlined, we designed a general approach toward derivatives and analogues of 10-hydroxybenzo[*h*]quinoline comprising a two-step strategy: (a) the synthesis of derivatives and analogues of benzo[*h*]quinoline and (b) their C−H acetoxylation followed by hydrolysis of the initially formed ester into a phenol. The investigation started from the synthesis of benzoacridine **3**,[20] which was performed via the Bernthsen reaction (Scheme 1).[21] We expected that linear fusion of benzo[*h*]quinoline with an additional benzene ring would lead to a bathochromic shift in both absorption and emission in the final product **4**. This compound was subjected to the original Sanford conditions ($PhI(OAc)_2$, $Pd(OAc)_2$, CH_3CN, 75 °C, 16 h), but conversion was very low, and the yield of product **4** was only 19% (Scheme 1, Table 1, entry 1) compared to 86% yield

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Scheme 1

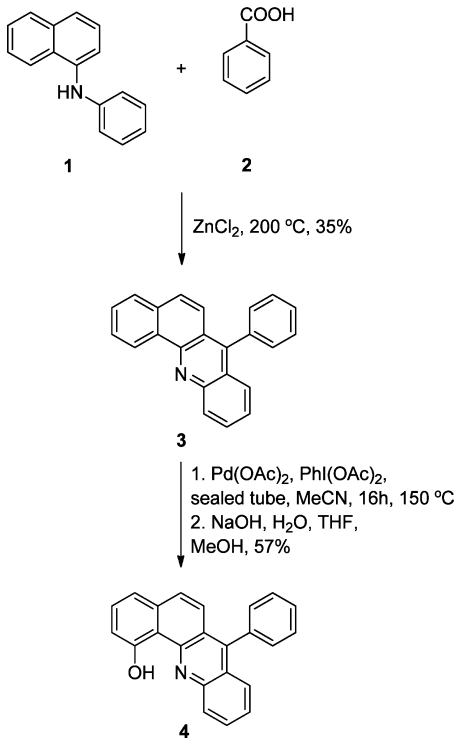


Table 1. Optimisation Studies for the Synthesis of Compound 4

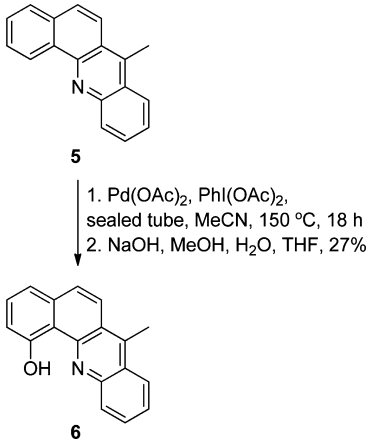
entry	solvent	temp (°C)	time (h)	catalyst, oxidant	yield of 4[a] (%)
1	CH_3CN	75	16	$Pd(OAc)_2$, $PhI(OAc)_2$	19
2	acetone	110	4	$Pd(OAc)_2$, $PhI(OAc)_2$	10
3	AcOH	120	20	$Pd(OAc)_2$, $PhI(OAc)_2$	<5
4	C_2H_5CN	100	16	$Pd(OAc)_2$, $PhI(OAc)_2$	<5
5	CH_3CN	130	48	$Cu(OAc)_2 \cdot H_2O$, O_2	trace
6	toluene, Ac_2O	145	24	$Cu(OAc)_2$	0
7	NMP	130	40	$[Rh(cod)Cl]_2$, CuI, $PCy_3 \cdot HBF_4$	Rh-complex with substrate
8	CH_3CN	100	24	AgOAc, $PhI(OAc)_2$	0
9	CH_3CN	90	24	$Mn(OAc)_3$, $PhI(OAc)_2$	0
10	CH_3CN	75	16	$Pd(OAc)_2$, $PhI(OCOCF_3)_2$	19
11	CH_3CN	150	16	$Pd(OAc)_2$, $PhI(OAc)_2$	57
12	dioxane	150	16	$Pd(OAc)_2$, $PhI(OAc)_2$	64

[a]Isolated yields.

in the acetoxylation of benzo[*h*]quinoline itself.[17a] Apparently, steric hindrance caused by the presence of hydrogen from an additional benzene ring has a significant effect on the coordination abilities of the basic nitrogen atom. Disappointed with this result, we investigated the acetoxylation reaction in various solvents (CH_3COOH, C_2H_5CN, and acetone) to obtain even lower yields of product **4** (Table 1, entries 2–4). The utilization of other solvents (ethyl acetate and THF) did not bring any improvement to the reaction. We also investigated the model reaction under new conditions recently published recently by Yu with copper acetate as the catalyst and oxygen as the oxidant,[22,23] as well as with a catalytic system based on rhodium.[24] Although all these procedures were reported to work very well for 2-phenylpyridine, it turned out that they could not facilitate the key C–H activation in the case of benzoacridine **3**. We attempted to use salts of other metals like manganese or silver in order to induce the desired transformation with strikingly negative results (Table 1, entries 8 and 9). The replacement of PIDA with PIFA resulted in no formation of compound **4** (Table 1, entry 10). Finally, we decided to perform the reaction in CH_3CN at 150 °C using high-pressure glass tubes (Table 1, entry 11). Under these conditions, the reaction led to 57% yield of the desired product **4**. Although we subsequently found that slightly higher yield could be reached under analogous conditions in dioxane (Table 1, entry 12), we decided to use CH_3CN-based conditions because of their greater generality.

To test the generality and scope of the newly developed conditions, a broad variety of derivatives and analogues of benzo[*h*]quinoline possessing various functional groups (possibly influencing the rate of the Pd-catalyzed Sanford reaction) were designed. While designing these compounds, we also kept in mind the influence of structural alterations on the photophysical properties. Since our research was focused on hydroxy derivatives, the moderate stability of the initially formed acetates (on both silica and alumina) inclined us to hydrolyze them to the corresponding phenols without purification. In the course of this study, we found that the yield of hydrolysis was 90–95%. We synthesized the analogue of compound **3** possessing a methyl group in order to study the influence of replacement of the aromatic unit with an aliphatic unit at position 7 (Scheme 2). The benzoacridine **5** was

Scheme 2



prepared using a known two-step process comprised of the Ullmann and Friedel–Crafts reactions.[25] Acetoxylation of that compound led to the corresponding ester, which was transformed into phenol **6** without isolation, in 27% overall yield.

It is well-known that steric hindrance affects the coordination properties of various ligands. Since the single act of coordination of Pd^{2+} by the pyridine-type nitrogen atom is undoubtedly the first step of the mechanism[17] in the Sanford reaction, we found it of critical importance to study that effect. 8,9,10,11-Tetrafluorobenzo[*c*]acridine (**9**) was designed as a

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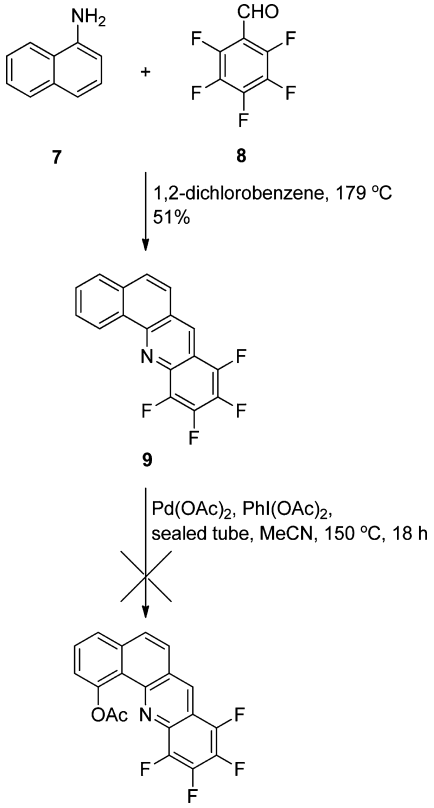
compound with not only considerable steric hindrance imparted by the fluorine atom at position 11, but also low electron density on the nitrogen atom due to the strong electron-withdrawing effect of the four fluorines (Scheme 3).

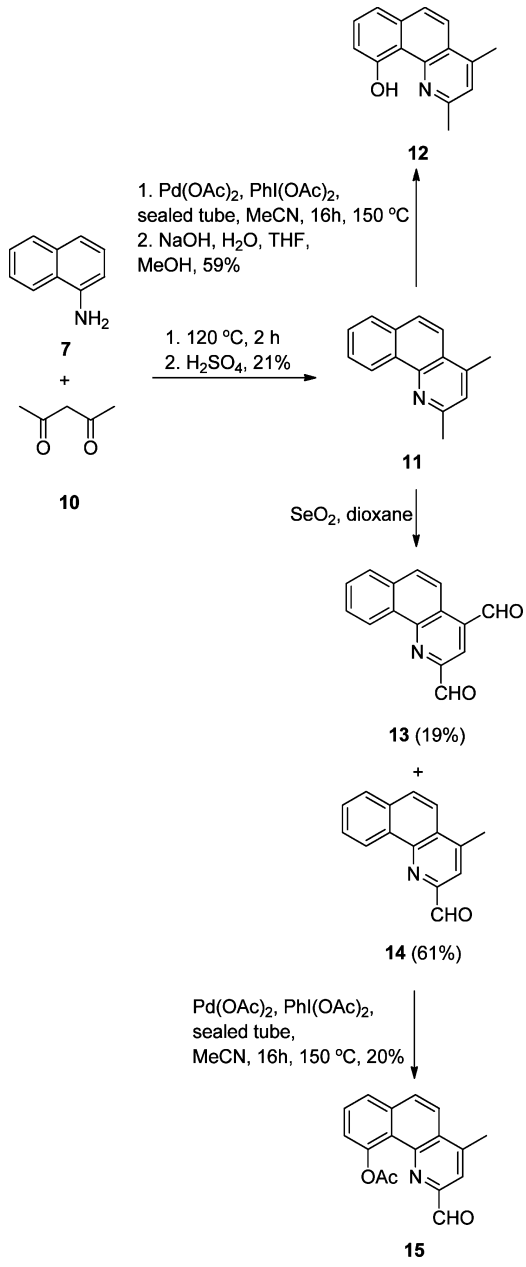
Scheme 3



The elegant synthesis of tetrafluoroquinolines from pentafluorobenzaldehyde (**8**) was developed in 1993 by Tipping and co-workers.[26] The preparation of benzoacridine **9** was obtained following this general procedure while replacing the aniline derivatives with 1-aminonaphthalene (**7**), furnishing the desired compound in 51% yield. Unfortunately, all attempts to acetoxylate this molecule under a variety of conditions (stated in Table 1) failed, and the substrate was quantitatively recovered (Scheme 3).

2,4-Dimethylbenzo[*h*]quinoline (**11**) was another sterically hindered analogue that was designed for this study. This compound was synthesized following the classical Combes reaction (Scheme 4).[27] Acetoxylation at 150 °C followed by hydrolysis afforded the desired compound **12** in 59% yield. It is noteworthy to add that classical Sanford conditions gave product **12** in only 15% yield. Methylpyridines are known to be easily oxidizable to the corresponding aldehydes. Since the formyl group allows for an almost unlimited number of further chemical transformations, 2,4-dimethylbenzo[*h*]quinoline was oxidized using SeO_2, giving a mixture of two aldehydes (Scheme 4). The dialdehyde **13** (formed in 19% yield) was easily identified, but identification of the monoaldehyde **14** was only possible after obtaining X-ray quality crystals (Figure S1 in the Supporting Information). It was of interest to investigate if oxidative acetoxylation could be efficient in the presence of the easily oxidizable formyl group. It turned out that aldehyde **15** possessing the acetyloxy group could be prepared in 20% yield (Scheme 4).

Scheme 4



One of the most difficult regions of benzo[*h*]quinoline to functionalize is the middle ring. These positions of the molecule cannot be easy functionalized via electrophilic aromatic substitution (in contrast to the phenolic ring).[16] We approached this problem starting from 1-amino-4-bromonaphthalene (**16**) and performed the Skraup reaction with paraaldehyde (**17**) (Scheme 5).[28] Acetoxylation of the resulting bromobenzoquinoline **18** was straightforward and led directly to phenol **19**. Bromobenzoquinoline **18** was also subjected to both Buchwald–Hartwig amination as well as Sonogashira coupling (Scheme 5). Both reactions proceeded without problems, and products **20** and **21** were subsequently acetoxylated (Scheme 5). The reaction with amine **20** proceeded more efficiently in dioxane (see Table 1, entry 12), and in analogy to the previous example, hydrolysis occurred under acetoxylation conditions to give phenol **22**. The π-expanded analogue **21** was also smoothly acetoxylated under

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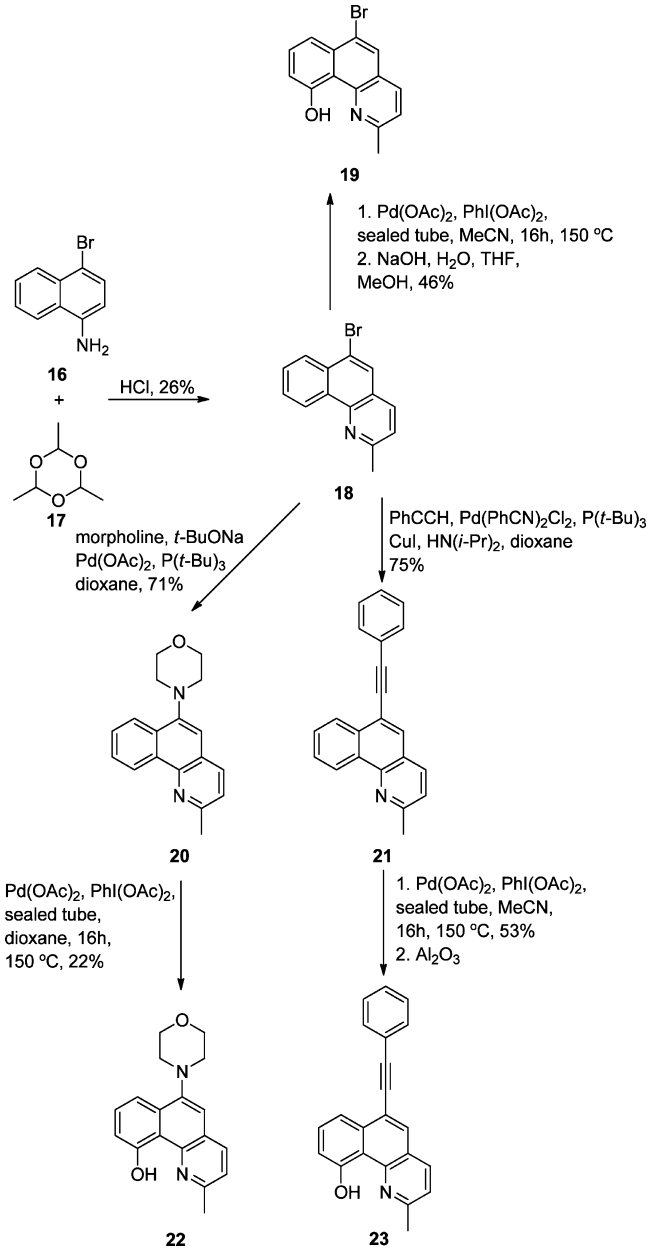
Scheme 5

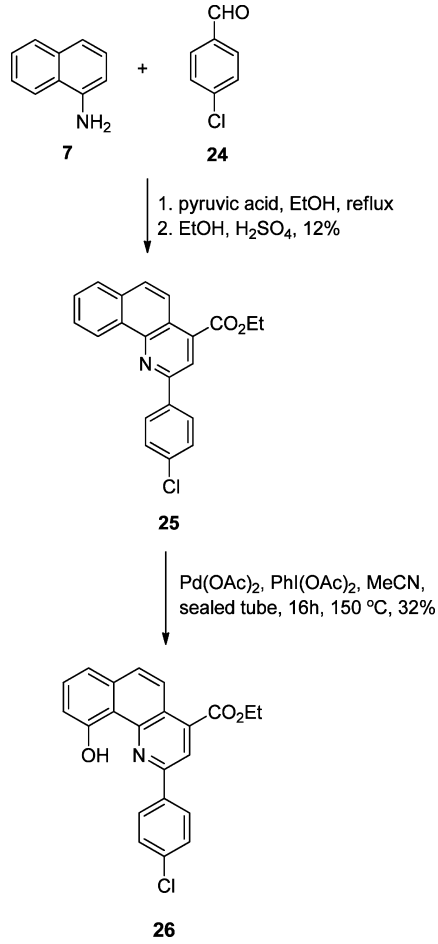


the previously identified high-temperature conditions, and the initially formed ester spontaneously hydrolyzed into the corresponding phenol **23** during chromatography. Such hydrolysis has been previously observed by Sanford and co-workers (at around 10%).[17a]

An elegant way to build a benzo[*h*]quinoline skeleton decorated with substituents at the pyridine ring proceeds via the Döbner reaction. Condensation of 1-aminonaphthalene (**7**) with pyruvic acid and 4-chlorobenzaldehyde (**24**) followed by esterification gave ester **25** in 12% yield (Scheme 6).[29] Subjecting this compound to the new conditions gave phenol **26** directly in 32% yield after chromatography. The attempts to hydrolyze the acetoxy compound under typical reaction conditions (NaOH, H_2O, and THF) resulted in the hydrolysis of both ester groups present in the molecule, giving an acid which could not be isolated.

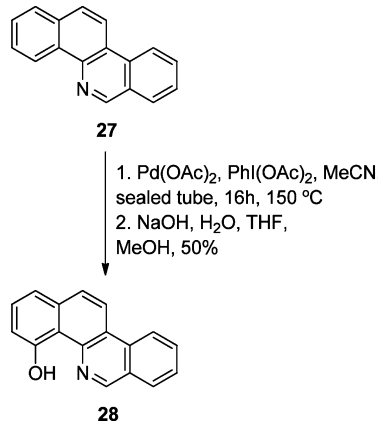
It was of particular interest to prepare the regioisomer of 10-hydroxybenzo[*c*]acridine with a nonlinear arrangement of the

Scheme 6



rings. Following a recently published procedure, we synthesized the required benzo[*c*]phenanthridine (**27**),[30] which was subsequently transformed into the required 4-hydroxybenzo-[*c*]phenanthridine (**28**) in 50% yield (Scheme 7).

Scheme 7



The spectral characteristics of products **4**, **6**, **12**, **19**, **22**, **23**, **26**, and **28** were then examined and compared to those of the parent 10-hydroxybenzo[*h*]quinoline (Table 2). The most notable feature was that ESIPT occurred in all compounds studied, and emission was only observed from the excited state of the keto form. According to expectations, the bathochromic

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Table 2. Spectroscopic Properties of Compounds 4, 6, 12, 19, 22, 23, 26, and 28

compound	solvent	λ_{abs}/nm	λ_{em}/nm	Φ_{fl}[a]	Stokes shift (cm^{-1})
HBQ	CH_3CN	370	625	0.003	11000
4	CH_3CN	418	642	<0.001	8300
6	CH_2Cl_2	414	632	0.001	8300
12	CH_3CN	371	573	0.004	9500
19	CH_3CN	375	578	0.002	9370
22	CH_3CN	379	575	0.002	9000
23	CH_3CN	381	603	0.001	9660
26	CH_2Cl_2	409	*b*	*b*	
28	CH_2Cl_2	382	*b*	*b*	

[a]Determined in MeCN using quinine sulfate in 0.05 M H_2SO_4 as a standard. [b]Below the detection limit.

shift of absorption was visible when going from simple derivatives of benzo[*h*]quinoline to the π-expanded analogues (Table 2, Figure 2, λ_{max} (**12**) = 371 nm, λ_{max} (**4**) = 418 nm). It is well-established that angular fusion of a benzene ring to a given chromophore usually does not lead to significant bathochromic shift of absorption.[31] Accordingly, the comparison of derivatives of benzo[*h*]quinoline with derivative of benzo[*c*]phenantridine (i.e., **12** → **28**) reveals almost no bathochromic shift (Table 2).

Fluorescence quantum yields of products **4**, **6**, **12**, **19**, **22**, and **23** were found to be very low (0.1−0.4) in CH_3CN. For compounds **26** and **28**, these values were nonmeasurable (Table 2). Fluorescence spectra were obtained by exciting the molecules at 480 nm. When compared to the parent HBQ, the Stokes shift of all its substituted derivatives was lower (11 000 cm^{-1} for HBQ and 9000−9660 cm^{-1} for compounds **12**, **19**, **22**, and **23** in CH_3CN). The difference had its origin in the emission values, which were significantly hypsochromically shifted, whereas absorption remained at the same place, even for the π-expanded compound **23**. For both hydroxybenzoacridines **4** and **6**, the Stokes shift was even lower (8300 cm^{-1}). Absorption of compound **4** was bathochromically shifted versus HBQ (~45 nm); however, emission was shifted only slightly (Table 2). An addition of an excess of strong acid (TFA) to the solution of dye **4** resulted in hypsochromic shift of emission combined with sharp increase in Φ_{fl} (see the abstract graphic).

In conclusion, we have developed versatile conditions for the coordination-assisted C−H acetoxylation of benzo[*h*]quinoline derivatives, which work for sterically hindered substrates. This critical development significantly broadens the scope of substrates that can be functionalized using the Sanford reaction, and it gives access to a variety of derivatives and analogues of 10-hydroxybenzo[*h*]quinoline. Both steric hindrance and electron density were found to be critical factors influencing the Sanford reaction. Regardless of the type of structural modification (π-expansion of the chromophore in various ways, strong electron-donating and electron-withdrawing substituents), all compounds displayed excited state intramolecular proton transfer, which was reflected in a large Stokes shift. A detailed study of the optical properties of the phenolic products allowed us to observe that substitution of 10-hydroxybenzoquinolines led to a decrease in the Stokes shift while maintaining the same fluorescence quantum yields. Even smaller Stokes shifts were displayed by the π-expanded analogues. We found that chemical modifications resulted in significantly altered spectroscopic properties relative to the parent 10-hydroxybenzo[*h*]quinoline, such as red-shifted absorption and emission maxima. In the future, derivatives of HBQ can find applications as fluorophores or emitters in analogy to well-known complexes of 8-hydroxyquinolines.[32]

EXPERIMENTAL SECTION

All chemicals were used as received unless otherwise noted. Reagent-grade solvents (CH_2Cl_2, hexanes) were distilled prior to use. All reported ^1H NMR and ^{13}C NMR spectra were collected using 600, 500, 400, or 200 MHz spectrometers. Chemical shifts (δ ppm) were determined with TMS as the internal reference; *J*-values are given in Hz. The UV−vis absorption spectra were recorded in CH_2Cl_2 or TFA. The absorption wavelengths are reported in nm with the extinction coefficient in M^{-1} cm^{-1} in brackets. The melting points of compounds were determined using a capillary-type apparatus. Chromatography was performed on silica (230−400 mesh) or neutral alumina. Dry column vacuum chromatography (DCVC)[33] was performed on preparative thin-layer chromatography alumina. The mass spectra were obtained via field desorption MS (FD-MS), electrospray ionization (ESI-MS), and electron impact MS (EI-MS). Compounds

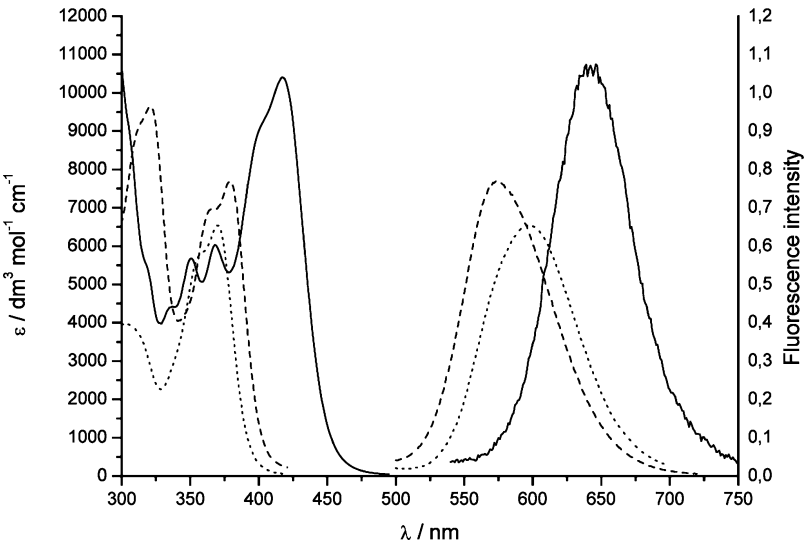

Figure 2. Absorption and emission of compounds **4** (solid line), **22** (dashed line), and **HBQ** (dotted line).

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3,[20] **5**,[25] **11**,[27] **18**,[28] **25**,[29] and **27**[30] were prepared according to the literature procedures. A spectrophotometer and a spectrofluorimeter were used to acquire the absorption and emission spectra. Spectrophotometric-grade solvents were used without further purification.

7-Phenylbenzo[*c*]acridine.[20] (**3**): mp 141−143 °C (lit.[20] 140 °C); ^{1}H NMR (500 MHz, $CDCl_3$, δ) 7.42−7.48 (m, 4H), 7.53−7.62 (m, 4H), 7.67−7.73 (m, 2H), 7.76−7.83 (m, 3H), 8.43 (d, 1H, J = 9.5), 9.60 (d, 1H, J = 9.6); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 123.1, 124.0, 125.5, 125.8, 125.9, 126.5, 127.2, 127.4, 127.7, 128.2, 128.4, 129.1, 129.3, 129.9, 130.5, 131.6, 133.6, 136.3, 146.1, 147.3, 147.4; EI-HR found 305.1202 [M^+], calcd. 305.1204 ($C_{23}H_{15}N$); λ_{abs} (cyclohexane) 389, 368, 350, 336; λ_{em} (cyclohexane) 395, 417 nm; IR (KBr) 3051, 1492, 750 cm^{-1}.

8,9,10,11-Tetrafluorobenzo[*c*]acridine (9). A two-neck round-bottom flask (100 mL) was charged with pentafluorobenzaldehyde (**8**) (864 μL, 7 mmol), 1-aminonaphthalene (**7**) (2.0 g, 14 mmol), and 1,2-dichlorobenzene (30 mL). The reaction was heated under reflux for 2.5 h under argon. Subsequently, the reaction mixture was allowed to cool, which led to product crystallization. Yellow crystals were filtered and rinsed with hot AcOEt. The pure compound was obtained after heating the crude product in AcOEt, followed by filtration (1.07 g, 51%): mp 257−260 °C; ^{1}H NMR (500 MHz, CF_3COOD, δ) 8.00−8.25 (m, 5H), 9.16 (d, 1H, J = 9.4), 9.81 (s, 1H), 11.50 (s, 1H); ^{13}C NMR (125 MHz, CF_3COOD, δ) 110.8, 112.7, 113.1, 113.5, 114.4, 114.6, 114.9, 115.3, 115.7, 117.6, 120.4, 123.4, 123.5, 126.8, 129.8, 130.2, 132.5, 135.6, 137.4, 141.0, 142.3; ^{19}F NMR (470 MHz, CF_3COOD, δ) −155.46 (t, 1F, J = 15.5), −152.16 (t, 1F, J = 16.2), −144.48−(−144.36) (m, 1F), −138.22−(−138.10) (m, 1F); EI-HR found 301.0504 [M^+], calcd. 301.0515 ($C_{17}H_7NF_4$); λ_{abs} (cyclohexane) 390, 370, 278 nm; λ_{em} (cyclohexane) 441, 417, 395 nm; IR (KBr) 3078, 1592, 1492, 1026, 756 cm^{-1}.

2,4-Dimethylbenzo[*h*]quinoline.[27] (**11**): mp 128−130 °C (lit.[27] 126 °C); ^{1}H NMR (500 MHz, $CDCl_3$, δ) 2.69 (s, 3H), 2.77 (s, 3H), 7.22 (s, 1H), 7.62−7.71 (m, 2H), 7.75 (d, 1H, J = 9.1 Hz), 7.83−7.89 (m, 2H), 9.35 (d, 1H, J = 8.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 18.9, 25.3, 121.2, 123.2, 123.7, 124.8, 126.2, 126.6, 127.5, 127.7, 131.7, 133.4, 143.9, 145.7, 157.2; EI-HR found 207.1057 [M^+], calcd. 207.1048 ($C_{15}H_{13}N$); λ_{abs} (CH_2Cl_2, $\varepsilon \times 10^{-3}$) 348 (3.9), 332 (3.3), 317 (1.9), 299 (8.9), 268 (26.5), 245 (38.7) nm; λ_{em} (cyclohexane) 353, 369, 387, 410 nm; (KBr) 3058, 1498, 741 cm^{-1}. Anal. Calcd for $C_{15}H_{13}N$: C, 86.92%; H, 6.32%; N, 6.76%. Found: C, 87.14%; H, 6.34%; N, 6.48%.

Oxidation of 2,4-Dimethylbenzo[*h*]quinoline using SeO_2. 2,4-Dimethylbenzo[*h*]quinoline (**11**) (500 mg, 2.4 mmol) and SeO_2 (1.2 g) were heated under reflux in 1,4-dioxane (25 mL) for 38 h. The residue was filtered through Celite, and the solvent was removed under reduced pressure. The solid thus obtained was dissolved in hot AcOEt, and then silica gel was added, and the solvent was evaporated to dryness. The solid was chromatographed (SiO_2, CH_2Cl_2/hexanes 1:4, 2:3, 1:1), resulting in the separation of two products. The pure products were obtained after crystallization from hot AcOEt: monoaldehyde **14** (326 mg, 61%) and dialdehyde **13** (67 mg, 19%). 4-Methyl-2-formylbenzo[*h*]quinoline (**14**): mp 154−156 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ) 2.77 (s, 3H), 7.69−7.81 (m, 2H), 7.85−7.96 (m, 4H), 9.40 (dd, 1H, J_1 = 1.0 Hz, J_2 = 2.0 Hz), 10.29 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 19.21, 119.3, 121.0, 124.9, 127.7, 127.8, 128.4, 128.6, 130.2, 131.2, 133.4, 145.3, 146.0, 150.5, 194.4; EI-HR found 221.0848 [M^+], calcd. 221.0841 ($C_{15}H_{11}NO$); λ_{abs} (cyclohexane) 358, 341, 336, 323, 285, 258 nm; IR (KBr) 3065, 2841, 1694, 763 cm^{-1}. 2,4-Diformylbenzo[*h*]quinoline (**13**): mp 176−178 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ) 7.79−7.87 (m, 2H), 7.96−7.80 (m, 1H), 8.12 (d, 1H, J = 9.2), 8.50 (s, 1H), 8.93 (d, 1H, J = 9.2), 9.41−9.44 (m, 1H), 10.40 (s, 1H), 10.60 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 120.9, 122.2, 125.0, 125.3, 128.0, 128.4, 129.6, 131.1, 133.4, 133.6, 137.5, 147.8, 151.2, 192.4, 192.9; EI-HR found 235.0639 [M^+], calcd. 235.0633 ($C_{15}H_9NO_2$); IR (KBr) 3055, 2852, 1698, 769 cm^{-1}. Anal. Calcd for $C_{15}H_9NO_2$: C, 76.59%, H, 3.86%, N, 5.95%. Found: C, 76.30%; H, 3.97%; N, 5.91%.

6-Bromo-2-methylbenzo[*h*]quinoline. (**18**): mp 101−103 °C (lit.[28] 99−100 °C); ^{1}H NMR (400 MHz, $CDCl_3$, δ) 2.81 (s, 3H), 7.36 (d, 1H, J = 8.2 Hz), 7.72−7.80 (m, 2H), 7.94 (d, 1H, J = 8.3 Hz), 7.99 (s, 1H), 8.27−8.33 (m, 1H), 9.34−9.39 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, δ) 25.4, 121.2, 122.7, 124.5, 124.6, 127.3, 127.5, 128.6, 128.8, 131.9, 132.3, 135.0, 145.2, 158.2; EI-HR found 270.9994 [M^+], calcd. 270.9997 ($C_{14}H_{10}N^{79}Br$); λ_{abs} (CH_2Cl_2, $\varepsilon \times 10^{-3}$) 352 (4.5), 336 (3.9), 321 (2.0), 302 (10.0), 290 (9.7), 269 (24.2), 246 (37.1) nm; λ_{em} (cyclohexane) 359, 374, 395, 416 nm. Anal. Calcd for $C_{14}H_{10}NBr$: C, 61.79%; H, 3.70%; N, 5.15%. Found: C, 61.71%; H, 3.68%; N, 5.12%.

2-Methyl-6-morpholinebenzo[*h*]quinoline (20). 6-Bromo-2-methylbenzo[*h*]quinoline (**18**) (500 mg, 1.8 mmol), morpholine (0.39 mL, 4.5 mol), $Pd(OAc)_2$ (50 mg, 0.22 mmol), P(*t*-Bu)$_3$ (0.9 mL, 0.25 M in dioxane), *t*-BuONa (0.3 g, 3.1 mmol), and dioxane (14 mL) were heated under nitrogen in a Schlenk flask at room temperature for 48 h. The residue was filtered through a small pad of Celite, dissolved in CH_2Cl_2, evaporated to dryness, and purified by column chromatography (DCVC, Al_2O_3, hexanes → CH_2Cl_2/hexanes 5:95, 1:9, 2:8). The pure product was obtained after crystallization (AcOEt/hexanes) as white crystals (357 mg, 71%): mp 127−128 °C; ^{1}H NMR (600 MHz, $CDCl_3$, δ) 2.80 (s, 3H), 3.17 (s, 4H), 4.00 (t, 4H, J = 4.4), 7.16 (s, 1H), 7.34 (d, 1H, J = 7.9), 7.66−7.72 (m, 2H), 7.96 (d, 1H, J = 6.5), 8.23−8.26 (m, 1H), 9.35 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, δ) 25.2, 53.4, 67.4, 112.1, 122.3, 123.4, 124.5, 125.0, 126.8, 127.7, 130.2, 132.5, 135.1, 143.8, 147.4, 156.2; EI-HR found 278.1412 [M^+], calcd. 278.1419 ($C_{18}H_{18}N_2O$); λ_{abs} (CH_2Cl_2, $\varepsilon \times 10^{-3}$) 356 (3.5), 340 (3.8), 309 (8.8), 272 (19.6), 241 (47.3) nm; λ_{em} (cyclohexane) 411 nm; IR (KBr) 3052, 2824, 1596, 1119, 775 cm^{-1}.

2-Methyl-6-(phenylacetylenyl)benzo[*h*]quinoline (21). Pd(PhCN)$_2$Cl$_2$ (5.2 mg, 0.014 mmol), 6-bromo-2-methylbenzo[*h*]quinoline (**18**) (100 mg, 0.450 mmol), and CuI (1.7 mg, 0.009 mmol; stored under argon) were added to a dry Schlenk flask, which was then purged with argon and charged with dioxane (0.9 mL). P(*t*-Bu)$_3$ (117 μL of a 0.25 M solution in dioxane; 0.028 mmol), HN(*i*-Pr)$_2$ (76 μL, 0.540 mmol), and phenylacetylene (82 μL, 0.750 mmol) were added via a syringe to the stirred reaction mixture. During the reaction, the progress of which was followed by TLC, precipitation of [H_2N(*i*-Pr)$_2$]Br was observed. After 4 h (at which point the aryl bromide had been consumed), the reaction mixture was diluted with AcOEt, filtered through a small pad of silica gel (with AcOEt rinsing), concentrated, and purified by flash chromatography (SiO_2, CH_2Cl_2/hexanes 1:9). The pure product was obtained after crystallization from hot cyclohexane (99 mg, 75%): mp 134−136 °C; ^{1}H NMR (600 MHz, $CDCl_3$, δ) 2.84 (s, 3H), 7.36−7.45 (m, 4H), 7.65−7.70 (m, 2H), 7.72−7.82 (m, 2H), 7.98 (s, 1H), 8.02 (d, 1H), 8.46−8.53 (m, 1H), 9.33−9.40 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, δ) 25.5, 87.3, 94.2, 119.5, 122.6, 123.2, 123.5, 124.6, 126.2, 127.2, 128.4, 128.5, 128.5, 130.0, 131.1, 131.7, 132.9, 135.7, 145.8, 158.6; EI-HR found 293.1217 [M^+], calcd. 293.1204 ($C_{22}H_{15}N$); λ_{abs} (CH_2Cl_2, $\varepsilon \times 10^{-3}$) 362 (8.1), 345 (16.4), 322 (27.6), 278 (32.1), 246 (39.8) nm; λ_{em} (cyclohexane + a few drops of CH_2Cl_2) 408, 388, 369 nm; IR (KBr) 3054, 2923, 2201, 1279, 759 cm^{-1}. Anal. Calcd for $C_{22}H_{15}N$: C, 90.07%; H, 5.15%; N, 4.77%. Found: C, 90.04%; H, 5.01%; N, 4.64%.

General Procedure for Acetoxylation of Benzo[*h*]quinolines and Their Analogues. A sealed tube was charged with the benzo[*h*]quinoline-type substrate (0.6 mmol), PhI(OAc)$_2$ (397 mg, 1.2 mmol), $Pd(OAc)_2$ (3.7 mg, 0.0115 mmol), and MeCN (4.8 mL). The mixture was stirred at 150 °C for 16 h. The residue was moved to a round-bottom flask, evaporated to dryness, dissolved in MeOH/THF, and filtered through Celite to remove an insoluble black solid. Subsequently, solid NaOH (1.0 g, 25 mmol) was added to the transparent solution. After stirring at room temperature for a few hours, the mixture was acidified with 10% HCl to neutral pH (the solvent was removed under reduced pressure) and extracted between CH_2Cl_2 and water. The organic layer was dried over dry Na_2SO_4 and removed under vacuum. The details of purification are given in each case as follows.

1-Hydroxy-7-phenylbenzo[*c*]acridine (4). A sealed tube was charged with 7-phenylbenzo[*c*]acridine (**3**) (51 mg, 0.166 mmol),

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$PhI(OAc)_2$ (107 mg, 0.33 mmol), $Pd(OAc)_2$ (3.7 mg, 0.0166 mmol), and 1,4-dioxane (1.4 mL). The mixture was stirred at 150 °C for 16 h. The residue was moved into a round-bottom flask, evaporated to dryness, dissolved in MeOH/THF, and filtered through Celite to remove an insoluble black solid. Then, a slight excess of NaOH was added to the clear solution. After stirring at room temperature for a few hours, the mixture was acidified with 10% HCl to neutral pH (the solvent was removed under reduced pressure) and extracted between CH_2Cl_2 and water. The organic layer was dried over dry Na_2SO_4 and removed under vacuum. The solid was chromatographed (DCVC, Al_2O_3, hexanes → hexanes/CH_2Cl_2 99:1, 98:2, 96:4). The pure product was obtained after crystallization from hot cyclohexane (34 mg, 64%): mp 218−221 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ) 7.32 (d, 2H, J = 7.6), 7.39 (d, 1H, J = 9.4), 7.43−7.45 (m, 2H), 7.53 (ddd, 1H, J_1 = 1.2, Hz, J_2 = 6.7 Hz, J_3 = 7.3 Hz), 7.50 (d, 1H, J = 9.4), 7.59−7.67 (m, 4H), 7.70−7.74 (m, 1H), 7.80−7.85 (m, 1H), 8.30 (d, 1H, J = 8.5), 16.10 (br. s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 115.1, 115.2, 118.2, 123.2, 123.3, 125.3, 126.1, 126.7, 127.5, 128.6, 128.6, 128.7, 130.2, 130.3, 131.0, 135.0, 135.6, 143.6, 146.9, 149.9, 160.9; EI-HR found 321.1167 [M^+], calcd. 321.1154 ($C_{23}H_{15}NO$); λ_{abs} (CH_2Cl_2, $\varepsilon \times 10^{-3}$) 420 (10.4), 370 (6.4), 352 (5.9), 269 (45.8) nm; λ_{em} (acetonitrile) 642 nm; IR (KBr) 3041,1465, 754 cm^{-1}.

1-Hydroxy-7-methylbenzo[*c*]acridine (6). 7-Methylbenzo[*c*]-acridine (**5**) (50 mg, 0.2 mmol), $PhI(OAc)_2$ (129 mg, 0.4 mmol), and $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) were reacted according to the general procedure. The solid was chromatographed (DCVC, Al_2O_3, hexanes → hexanes/AcOEt 97:3). The product was suspended in a mixture of MeOH/cyclohexane, then filtered to obtain pure crystals (15 mg, 27%): mp 211−214 °C; ^{1}H NMR (600 MHz, $CDCl_3$, δ) 3.03 (s, 3H), 7.25−7.30 (m, 2H), 7.58−7.62 (m, 3H), 7.75−7.80 (m, 1H), 7.82 (d, 1H, J = 9.3), 8.31 (d, 1H, J = 8.6), 8.20 (d, 1H, J = 5.6), 16.18 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, δ) 14.0, 115.1, 118.0, 118.2, 121.3, 123.2, 124.3, 125.3, 125.9, 127.7, 128.4, 130.0, 130.8, 134.8, 142.2, 142.8, 149.1, 160.8; EI-HR found 259.0991 [M^+], calcd. 259.0997 ($C_{18}H_{13}NO$); λ_{abs} (CH_2Cl_2, $\varepsilon \times 10^{-3}$) 417 (8.4), 367 (5.6), 350 (5.4), 334 (4.6), 268 (44.3), 247 (25.7) nm; λ_{em} (acetonitrile) 632 nm; IR (KBr) 3049, 2961, 1603, 1283, 819 cm^{-1}.

10-Hydroxy-2,4-dimethylbenzo[*h*]quinoline (12). 2,4-Dimethylbenzo[*h*]quinoline (**11**) (124 mg, 0.6 mmol), $PhI(OAc)_2$ (397 mg, 1.2 mmol), $Pd(OAc)_2$ (3.7 mg, 0.0115 mmol) were reacted according to the general procedure. The solid was chromatographed (DCVC, Al_2O_3, hexanes → hexanes/CH_2Cl_2 9:1). The pure product was obtained after crystallization from hot cyclohexane (80 mg, 59%): mp 124−126 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ) 2.70 (s, 3H), 2.73 (s, 3H), 7.17−7.22 (m, 2H), 7.36 (dd, 1H, J_1 = 1.0 Hz, J_2 = 7.8 Hz), 7.57 (t, 1H, J = 7.8), 7.74 (s, 2H), 15.57 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 19.2, 24.2, 113.4, 116.1, 117.7, 120.6, 122.4, 123.3, 127.6, 129.5, 135.0, 145.1, 147.3, 153.8, 159.8; EI-HR found 223.0992 [M^+], calcd. 223.0997 ($C_{15}H_{13}NO$); λ_{abs} (CH_2Cl_2, $\varepsilon \times 10^{-3}$) 372 (9.8), 305 (6.8), 267 (24.3), 244 (68.8) nm; λ_{em} (acetonitrile) 573 nm; IR (KBr) 3042, 2970, 1597, 1274, 826 cm^{-1}. Anal. Calcd for $C_{15}H_{13}NO$: C, 80.69%; H, 5.87%; N, 6.27%. Found: C, 80.37%; H, 5.91%; N, 6.23%.

10-Acetoxy-4-methyl-2-formylbenzo[*h*]quinoline (15). 4-Methyl-2-formylbenzo[*h*]quinoline (**14**) (57 mg, 0.26 mmol), $PhI(OAc)_2$ (167 mg, 0.52 mmol), and $Pd(OAc)_2$ (5.8 mg, 0.026 mmol) were reacted according to the general procedure. The residue was moved into the round-bottom flask, evaporated to dryness, and dissolved in CH_2Cl_2. Aluminum oxide was added to this solution and again evaporated to dryness. The solid was chromatographed (DCVC, Al_2O_3, hexanes → hexanes/AcOEt 95:5, 1:9). The pure product was obtained after crystallization from hot cyclohexane (12,3 mg, 20%): mp 109−111 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ) 2.60 (s, 3H), 2.81 (s, 3H), 7.47 (d, 1H, J_1 = 7.5 Hz), 7.47 (t, 1H, J = 7.8 Hz), 7.89 (d, 1H, J = 7.8 Hz), 7.95−8.01 (m, 3H), 10.26 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 19.7, 22.1, 119.7, 121.9, 123.2, 123.9, 127.1, 128.8, 129.5, 130.7, 135.9, 145.3, 145.5, 148.8, 150.1, 170.3, 193.4; ESI-HR found 302.0800 [M + Na^+], calcd. 302.0788 ($C_{17}H_{13}NO_3Na$); IR (KBr) 3049, 2924, 2825, 1696, 1206, 754 cm^{-1}.

6-Bromo-10-hydroxy-2-methylbenzo[*h*]quinoline (19). 6-Bromo-2-methylbenzo[*h*]quinoline (**18**) (60 mg, 0.22 mmol), $PhI(OAc)_2$ (142 mg, 0.44 mmol), and $Pd(OAc)_2$ (2.5 mg, 0.011 mmol) were reacted according to the general procedure. The solid was chromatographed (DCVC, Al_2O_3, hexanes → hexanes/AcOEt 98:2). The pure product was obtained after crystallization from hot cyclohexane (29 mg, 46%): mp 165−167 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ) 2.80 (s, 3H), 7.31 (dd, 1H, J_1 = 1.0 Hz, J_2 = 8.0 Hz), 7.39 (d, 1H, J = 8.2 Hz), 7.68 (t, 1H, J = 8.0 Hz), 7.80 (dd, 1H, J_1 = 1.0 Hz, J_2 = 8.2 Hz), 8.03 (d, 1H, J = 8.1 Hz), 8.42 (dd, 1H, J_1 = 1.3 Hz, J_2 = 8.3 Hz), 15.41 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 24.4, 115.0, 116.1, 117.8, 121.8, 123.0, 124.0, 127.9, 130.6, 133.2, 135.9, 146.7, 154.9, 159.7; EI-HR found 286.9933 [M^+], calcd. 286.9946 ($C_{14}H_{10}NO^{79}Br$); λ_{abs} (CH_2Cl_2, $\varepsilon \times 10^{-3}$) 378 (7.2), 363 (6.3), 319 (5.0), 249 (41.5), 241 (43.6) nm; λ_{em} (acetonitrile) 578 nm; IR (KBr) 3436, 3056, 2922, 2538, 1593, 1419, 1270, 891 cm^{-1}.

10-Hydroxy-2-methyl-6-morpholinebenzo[*h*]quinoline (22). 6-Morpholino-2-methylbenzo[*h*]quinoline (**20**) (100 mg, 0.36 mmol), $PhI(OAc)_2$ (162 mg, 0.72 mmol), and $Pd(OAc)_2$ (8 mg, 0.036 mmol) were reacted according to the general procedure but in 1,4-dioxane (3 mL). The solid was chromatographed (DCVC, Al_2O_3, hexanes → hexanes/AcOEt 98:2). The pure product was obtained after crystallization from hot cyclohexane (23 mg, 22%): mp 176−177 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ) 2.78 (s, 3H), 3.17 (br. s, 4H), 4.00 (t, 4H, J = 4.5 Hz), 7.13 (s, 1H), 7.26 (d, 1H, J = 6.1 Hz), 7.36 (d, 1H, J = 8.2 Hz), 7.61 (t, 1H, J = 8.0 Hz), 7.74 (d, 1H, J = 8.0), 8.06 (d, 1H, J = 8.2), 15.54 (br. s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 24.1, 53.3, 67.3, 111.4, 113.7, 114.0, 116.6, 121.4, 124.5, 129.6, 131.8, 135.9, 145.2, 148.8, 152.6, 160.2; ESI-HR found 295.1454 [M + H^+], calcd. 295.1441 ($C_{18}H_{19}N_2O_2$); λ_{abs} (CH_2Cl_2, $\varepsilon \times 10^{-3}$) 381 (7.7), 323 (9.3), 268 (18.2), 248 (41.1) nm; λ_{em} (acetonitrile) 574 nm; IR (KBr) 3039, 2956, 2541, 1528, 1116 cm^{-1}.

10-Hydroxy-2-methyl-6-(phenylacetylenyl)benzo[*h*]-quinoline (23). A sealed tube was charged with 6-phenylacetylenyl-2-methylbenzo[*h*]quinoline (**21**) (73.5 mg, 0.25 mmol), $PhI(OAc)_2$ (161 mg, 0.5 mmol), $Pd(OAc)_2$ (1.12 mg, 0.005 mmol), and MeCN (2.1 mL). The mixture was stirred at 150 °C for 4.5 h. The residue was moved into a round-bottom flask, evaporated to dryness, and dissolved in CH_2Cl_2. Aluminum oxide was added to this solution and again evaporated to dryness. The solid was chromatographed (DCVC, Al_2O_3, hexanes → hexanes/CH_2Cl_2 95:5, 1:9). The pure, bright-yellow product was obtained after crystallization from hot EtOH (41 mg, 53%): mp 161−163 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ) 2.82 (s, 3H), 7.33 (d, 1H, J = 7.8 Hz), 7.38−7.43 (m, 4H), 7.64−7.69 (m, 2H), 7.70 (d, 1H, J = 8.0), 7.89 (s, 1H), 7.99 (d, 1H, J = 7.7) 8.10 (d, 1H, J = 8.2), 15.28 (br. s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 24.4, 87.2, 94.8, 114.5, 115.2, 116.6, 121.3, 121.7, 123.0, 123.5, 128.5, 128.7, 128.9, 130.4, 131.8, 134.3, 136.8, 146.8, 155.0, 159.6; EI-HR found 309.1148 [M^+], calcd. 309.1154 ($C_{22}H_{15}NO$); λ_{abs} (CH_2Cl_2, $\varepsilon \times 10^{-3}$) 594 (0.1), 385 (9.7), 345 (14.8), 280 (30.8), 249 (43.2) nm; λ_{em} (CH_2Cl_2) 612 nm, (acetonitrile) 602 nm; IR (KBr) 3056, 2918, 2197, 1271, 754 cm^{-1}.

Ethyl 2-(4-Chlorophenyl)-10-hydroxybenzo[*h*]quinoline-4-carboxylate (26). Ethyl 2-(4-chlorophenyl)-benzo[*h*]quinoline-4-carboxylate (**25**) (70 mg, 0.19 mmol), $PhI(OAc)_2$ (125 mg, 0.39 mmol), and $Pd(OAc)_2$ (4.3 mg, 0.019 mmol) were reacted according to the general procedure. The residue was transferred into a round-bottom flask, evaporated to dryness, and dissolved in CH_2Cl_2. Aluminum oxide was added to this solution and again evaporated to dryness. The solid was chromatographed (DCVC, Al_2O_3, hexanes → hexanes/AcOEt 98:2). The pure product **26** was obtained after crystallization from hot cyclohexane (23 mg, 32%): mp 157−159 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ) 1.53 (t, 3H, J = 7.2), 4.57 (q, 2H, J = 7.1), 7.28 (dd, 1H, J_1 = 1.0 Hz, J_2 = 8.0 Hz), 7.41 (d, 1H, J = 7.2), 7.54 (d, 2H, J = 8.4), 7.65 (t, 1H, J = 7.8), 7.86 (d, 1H, J = 9.5), 8.01 (d, 2H, J = 8.4), 8.35 (s, 1H), 8.49 (d, 1H, J = 9.1), 15.06 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 14.3, 62.4, 114.6, 115.4, 118.5, 118.9, 121.6, 123.1, 128.4, 129.6, 130.6, 130.8, 124.8, 135.7, 136.5, 136.6, 149.1, 151.5, 159.2, 165.9; EI-HR found 377.0813 [M^+], calcd. 377.0819 ($C_{22}H_{16}NO_3{}^{35}Cl$); λ_{abs} (CH_2Cl_2, $\varepsilon \times 10^{-3}$) 409 (9.8), 306 (20.4), 266 (28.6), 244 (39.2) nm; IR (KBr) 3063, 2922, 2201, 1279, 771 cm^{-1}.

4-Hydroxybenzo[c]phenanthridine (28). Benzo[*c*]-phenanthridine (**27**) (100 mg, 0.44 mmol), $PhI(OAc)_2$ (281 mg, 0.88 mmol), and $Pd(OAc)_2$ (9.9 mg, 0.044 mmol) were reacted according to the general procedure. The residue was moved into a round-bottom flask, evaporated to dryness, and dissolved in CH_2Cl_2. Aluminum oxide was added to this solution and again evaporated to dryness. The solid was chromatographed (DCVC, Al_2O_3, hexanes → hexanes/AcOEt 99:1, 95:5). The pure product was obtained after crystallization from hot cyclohexane (52 mg, 48%): mp 166−167 °C; ^{1}H NMR (600 MHz, $CDCl_3$, δ) 7.22 (dd, 1H, J_1 = 1.0 Hz, J_2 = 7.8 Hz), 7.46 (d, 1H, J = 7.5), 7.59 (t, 1H, J = 7.8), 7.70−7.74 (m, 1H), 7.91 (ddd, 1H, J_1 = 1.2, Hz, J_2 = 6.8 Hz, J_3 = 8.5 Hz), 7.98 (d, 1H, J = 9.0), 8.12 (d, 1H, J = 8.0), 8.41 (d, 1H, J = 9.0), 8.63 (d, 1H, J = 8.5), 14.90 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, δ) 113.3, 117.3, 118.0, 119.3, 120.8, 122.2, 125.7, 127.3, 128.5, 129.0, 129.2, 131.6, 132.6, 134.8, 142.6, 148.4, 158.8; EI-HR found 245.0838 [M^+], calcd. 245.0841 ($C_{17}H_{11}NO$); λ_{abs} (CH_2Cl_2, $\varepsilon \times 10^{-3}$) 382 (8.0), 259 (54.2) nm; IR (KBr) 3038, 2923, 2545, 1272, 748 cm^{-1}.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H NMR and ^{13}C NMR spectra of compounds **3**−**4**, **6**, **9**, **11**−**15**, **18**−**23**, **26**, and **28** as well as X-ray structure of compound **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ DEDICATION

†Dedicated to Dr. Lucia Flamigni on occasion of her 60th birthday.

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