Supporting Information

for

Excited State Intramolecular Proton Transfer in Electron-Rich and Electron-Poor Derivatives of 10-Hydroxybenzo[*h*]quinoline

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SYNTHESIS

Conceptually, the simplest approaches towards π-expansion of a given chromophore can be realized *via* attachment of another aromatic unit *via* double bond, achieved by Knoevenagel or Wittig reaction. Derivatives and analogues of picolines are known to easily react with aromatic aldehydes.

We designed 4-methylbenzo[*h*]quinoline **1**[21] as a precursor of the expanded analogs *via* the Knoevenagel reaction. Its coordination-assisted acetoxylation (Sanford reaction) proceeded swiftly under conditions that we recently optimized[25] to give, after hydrolysis, phenol **2** (Scheme 1). Surprisingly, Knoevenagel reaction of compound **2** was not straightforward (Scheme 1). A variety of

classical conditions have been investigated such as TBAHS, NaOH, H_2O,[26] Ac_2O,[27a] or $ZnCl_2$.[27b] The most effective conditions were determined to be potassium *tert*-butoxide in anhydrous DMF.[28] Adducts **5** and **6** were obtained in the yields 15% and 38%, respectively. Derivative **6** was exceptionally problematic. This compound displayed strong yellow fluorescence but was stable neither on alumina nor on silica, which hampered its purification. Full conversion of substrate **1** was achieved only by using significant excesses of both aldehyde **4** and *t*-BuOK and the pure product **6** was obtained by extraction followed by crystallization. Acetoxylation of compounds **5** and **6** using the original conditions developed by Sanford[17a] failed. In the case of compound **5**, the use of modified conditions[25] proved successful and after hydrolysis phenol **7** was obtained in 20% yield. Unexpectedly, under identical reaction conditions, transformation of benzo[*h*]quinoline **6** followed a different pathway. *N*-Demethylated compound **8** was the only isolable product (Scheme 1).

The access to benzo[*h*]quinoline derivatives modified at the pyridine ring is limited to 19th century reactions, which usually also give substituents at position 2 that cause steric hindrance, which in turn affects the acetoxylation. To avoid this difficulty, we turned to the excellent method introduced by Wróbel.[22] Vicarious nucleophilic substitution[29] reactions on 1-nitronaphthalene followed by subsequent reactions gave access to 4-tosylbenzo[*h*]quinoline (**9**).

Compound **9** in turn underwent classical nucleophilic substitution giving derivatives **11** and **12** with opposite electronic effects (Scheme 2).

The electron-withdrawing tosyl substituent decreased the reactivity of substrate **9**, which, conversely, had a positive effect on the yield of the final product (Scheme 2). Under previously optimized reaction conditions, after 16 h, substantial conversion was achieved and we observed only the ester-type product which could be separated in a pure form from the reaction mixture. Subsequent hydrolysis afforded phenol **10** in 52% yield. Not surprisingly, the acetoxylation reaction of electron-rich derivative **12** can be easily realized under classical Sanford conditions[17a] in 26% yield (Scheme 2). After 1 h of conversion, however, the expected phenol **14** was isolated in only 26% yield, due to its instability and decomposition. The presence of the tosyl substituent accelerated the acetoxylation. Additionally, the

use of an excess of a catalyst accelerated the conversion, but at the same time had a negative effect on the yield. On the other hand, even after 15 h and reaction at 150 °C, 4-cyanobenzo[*h*]quinoline (**11**) was not 100% converted. Part of substrate **11** was recovered and product **13** was obtained in 77% yield. Excessive prolongation of the reaction time did not increase the conversion of substrate, but rather degraded the product (Scheme 2).

The nitration of benzo[*h*]quinoline has been reported to give four nitration products, namely 5-nitrobenzo[*h*]quinoline (**15**), 6-nitrobenzo[*h*]quinoline (**17**), 7-nitrobenzo[*h*]quinoline and 9-nitrobenzo[*h*]quinoline.[23] The nitro group usually quenches fluorescence, [30] but we questioned whether this would occur in a molecule that displays ESIPT. All four nitro-derivatives were submitted to the acetoxylation reaction (Schemes 3 and 4). Only **15** and **17** gave the desired products **16** and **18** (Schemes 3 and 4). The remaining regioisomers were totally inactive under these conditions.

An ingenious use of vicarious nucleophilic aromatic substitution is based on the reaction of aryl acetonitriles with nitroarenes under conditions developed by Wróbel.[31] We employed this reaction to prepare benzophenanthridine derivative **21** (Scheme 5). The reaction was carried out with 2-(naphthalen-2-yl)acetonitrile (**19**) and 4-chloro-1-nitrobenzene (**20**). The product obtained in 20% yield was submitted to acetoxylation conditions and after hydrolysis gave hydroxyphenanthridine **22** in 46% yield.

EXPERIMENTAL SECTION

10-Hydroxy-4-methylbenzo[*h*]quinoline (2): A sealed tube was charged with 4-methylbenzo[*h*]quinoline (**1**) (67 mg, 0.37 mmol), $PhI(OAc)_2$ (234 mg, 0.69 mmol), $Pd(OAc)_2$ (1.6 mg, 0.007 mmol) and MeCN (3 mL). The mixture was stirred at 120 °C for 9 h. 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 mixture of two products (ester and phenol), which were collected together, was dissolved in MeOH and NaOH (5 eq.) was added. 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 with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and removed under vacuum. First crystallization (from hot MeCN) allowed various impurities to crystallize out (product stayed in the supernatant). After a second crystallization, from hot cyclohexane, a bright yellow product was obtained (17 mg, 22%); mp = 104-105 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ) 2.76 (s, 3H), 7.22 (dd, 1H, J_1=1.1 Hz, J_2=7.8 Hz), 7.37 (dd, 1H, J_1=0.6 Hz, J_2=4.7 Hz), 7.39 (dd, 1H, J_1=1.1 Hz, J_2=7.8 Hz), 7.60 (t, 1H, *J*=7.8), 7.78 (d, 2H, *J*=1.4), 8.65 (d, 1H, *J*=4.7), 15.28 (br.s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 19.3, 113.9, 116.2, 117.9, 120.6, 122.1, 125.5, 128.7, 129.7, 134.8, 144.3, 145.1, 147.8, 159.6; EI-HR found 209.0849 [$M^{\cdot+}$], calcd 209.0841 ($C_{14}H_{11}NO$); λ_{abs} (CH_2Cl_2, $\varepsilon\times10^{-3}$) 372 (9.8), 305 (6.9), 267 (24.3), 244 (68.8).

(*E*)-4-(4-(Trifluoromethyl)styryl)benzo[*h*]quinoline (5): The flask was charged under argon with 4-methylbenzo[*h*]quinoline (**1**) (199 mg, 1.03 mmol), 4-trifluoromethylbenzaldehyde (**3**) (161 μL, 1.24 mmol), *t*-BuOK (150 mg, 1.34 mmol) and dry DMF (1.2 mL). The mixture was stirred at 80 °C for 1 h, then at room temperature for 20 h. The residue was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and solvent was removed under vacuum. The remaining solid was chromatographed (DCVC, Al_2O_3, hexanes → AcOEt/hexanes 2:98). The pure product was obtained after crystallization from hot cyclohexane (55 mg, 15%); mp = 188-191 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ) 7.33 (d, 1H, *J*=16.1), 7.66-7.78 (m, 7H), 7.86-7.97 (m, 3H), 8.07 (d, 1H, *J*=9.1), 8.99 (d, 1H, *J*=4.6), 9.31-9.35 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 118.2, 120.7, 123.0, 124.1, 124.8, 125.1, 125.8, 125.8, 125.9, 125.9, 126.0, 127.2, 127.3, 127.7, 128.0, 128.4, 130.0, 130.2, 130.5, 130.7, 131.7, 133.3, 133.4, 140.0, 142.0, 147.0, 148.5; EI-HR found 349.1063 [$M^{\cdot+}$], calcd. 349.1078 ($C_{22}H_{14}NF_3$); λ_{abs} (CH_2Cl_2, $\varepsilon\times10^{-3}$) 323 (21.8), 285 (31.0), 245 (20.2).

(*E*)-4-(4-(Dimethylamino)styryl)benzo[*h*]quinoline (6): The flask was charged under argon with 4-methylbenzo[*h*]quinoline (**1**) (100 mg, 0.52 mmol), 4-dimethylaminobenzaldehyde (**4**) (79 mg, 0.53 mmol), *t*-BuOK (67 mg, 0.6 mmol) and dry DMF (0.5 mL). The mixture was stirred at 80 °C for 1 h, then at room temperature for 20 h. The residue was extracted between CH_2Cl_2 and water. The organic

layer was washed by water, dried over Na_2SO_4 and solvent was removed under vacuum. The oily residue turned into crystals after a few minutes. These crystals were suspended in cyclohexane and filtered to obtained pure product (64 mg, 38%). *Important! - The compound is very unstable in contact with SiO_2 and Al_2O_3.* mp = 178-181 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ) 3.03 (s, 6H), 6.75 (d, 2H, *J*=8.8), 7.32 (d, 1H, *J*=15.9), 7.54 (d, 2H, *J*=8.7), 7.67-7.76 (m, 4H), 7.83 (d, 1H, *J*=9.1), 7.91 (d, 1H, *J*=7.3), 8.14 (d, 1H, *J*=9.1), 8.92 (d, 1H, *J*=4.8), 9.33 (d, 1H, *J*=8.1); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 40.3, 112.2, 117.2, 118.0, 121.1, 124.0, 124.8, 124.9, 127.0, 127.2, 127.6, 128.1, 128.5, 131.6, 133.3, 135.4, 144.0, 146.8, 148.1, 150.8; EI-HR found 324.1618 [$M^{\cdot+}$], calcd. 324.1626 ($C_{23}H_{20}N_2$); λ_{abs} (CH_2Cl_2, $\varepsilon\times10^{-3}$) 377 (9.5), 351 (9.8), 271 (29.7), 241 (38.7) nm.

(*E*)-4-(4-(Trifluoromethyl)styryl)-10-hydroxybenzo[*h*]quinoline (7): A sealed tube was charged with (*E*)-4-(4-(trifluoromethyl)styryl)benzo[*h*]quinoline **(5)** (27.5 mg, 0.079 mmol), $PhI(OAc)_2$ (51 mg, 0.16 mmol), $Pd(OAc)_2$ (4.3 mg, 0.0079 mmol) and MeCN (0.7 mL). The mixture was stirred at 100 °C for 4 h. The residue was transferred into a round-bottom flask, evaporated to dryness, dissolved in MeOH and filtered through Celite to remove an insoluble black solid. Then NaOH (5 eq.) was added to the 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 with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and removed under vacuum. The solid was chromatographed (DCVC, Al_2O_3, hexanes → hexanes/AcOEt 99:1, 98:2). The pure product was obtained after crystallization from hot cyclohexane (6.0 mg, 20%); mp = 162-163 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ) 7.27 (dd, 1H, J_1=0.9 Hz, J_2=8.0 Hz), 7.39 (d, 1H, *J*=16.2), 7.42 (d, 1H, *J*=7.1), 7.65 (t, 1H, *J*=7.9), 7.71 (d, 2H, *J*=8.3), 7.74-7.78 (m, 3H), 7.88 (d, 1H, *J*=9.3), 7.95 (d, 1H, *J*=16.2), 8.02 (d, 1H, *J*=9.2), 8.82 (d, 1H, *J*=5.1), 15.20 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 114.3, 116.1, 117.2, 118.0, 120.0, 122.9, 123.9, 125.1, 125.5, 125.9, 125.9, 125.9, 127.3, 129.4, 130.2, 130.5, 130.8, 134.4, 134.8, 139.7, 142.5, 144.5, 148.9, 159.7; EI-HR found 209.1023 [$M^{\cdot+}$], calcd. 209.1027 ($C_{22}H_{14}NO$); λ_{abs} (CH_2Cl_2, $\varepsilon\times10^{-3}$) 394 (7.5), 297 (18.5), 244 (29.9) nm.

(E)-4-(4-(Methylamino)styryl)-10-hydroxybenzo[*h*]quinoline (8): A sealed tube was charged with (*E*)-4-(4-(dimethylamino)styryl)benzo[*h*]quinoline (**6**) (50 mg, 0.15 mmol), $PhI(OAc)_2$ (99 mg, 0.31 mmol), $Pd(OAc)_2$ (3.6 mg, 0.015 mmol) and dry dioxane (1.4 mL). The mixture was stirred at room temperature for 8 h. 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 95:5, 1:9) to give product (12.8 mg, 27%). The compound is not very stable in contact with SiO_2 and Al_2O_3. ^{1}H NMR (500 MHz, $CDCl_3$, δ) 2.90 (s, 3H), 6.65 (dd, 2H, J_1=1.9 Hz, J_2=6.7 Hz), 7.32 (d, 1H, *J*=16.0 Hz), 7.52 (dd, 2H, J_1=1.7 Hz, J_2=6.8 Hz), 7.65 (d, 1H, *J*=16.3 Hz), 7.77 – 7.68 (m, 3H), 7.85 (d, 1H, *J*=9.2 Hz), 7.91 (dd, 1H), 8.14 (d, 1H, *J*=9.2 Hz), 8.94 (d, 1H, *J*=4.8 Hz), 9.35 (d, 1H, *J*=8.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 30.5, 112.4, 117.2, 118.0, 121.0, 124.0, 124.9, 125.8, 127.1, 127.3, 127.6, 128.2, 128.5, 128.7, 131.2, 133.3, 135.7, 146.6, 147.9, 150.0; EI-HR found 310.1476 [$M^{\cdot+}$], calcd 310.1417 ($C_{22}H_{18}N_2$).

10-Hydroxy-4-tosylbenzo[*h*]quinoline (10): A sealed tube was charged with 4-tosylbenzo[*h*]quinoline (**9**) (47 mg, 0.14 mmol), $PhI(OAc)_2$ (90 mg, 0.28 mmol), $Pd(OAc)_2$ (0.6 mg, 0.0027 mmol) and MeCN (3 mL). The mixture was stirred at 75 °C for 15 h. The residue was transferred into a round-bottom flask, evaporated to dryness and dissolved in CH_2Cl_2. Aluminum oxide was added and solvent has been again evaporated to the dryness. The resulting solid was chromatographed (DCVC, Al_2O_3, hexanes → hexanes/AcOEt 8:2). The mixture of two products (ester and phenol) were collected and dissolved in MeOH/THF and NaOH (5 eq.) was added. 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 with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and removed under vacuum. The pure, bright yellow product was obtained after crystallization from hot cyclohexane (28.7 mg, 52%); mp = 179-180 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ) 2.38 (s, 3H), 7.27-7.35 (m, 3H), 7.42 (d, 1H, *J*=7.7 Hz), 7.66 (t, 1H, *J*=7.9), 7.87-7.95 (m, 3H), 8.32 (d, 1H, *J*=4.9), 8.50 (d, 1H, *J*=9.3), 9.03 (d, 1H, *J*=4.9), 14.41 (br.s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 21.6, 115.2,

115.5, 118.6, 119.8, 119.9, 121.7, 128.0, 130.1, 131.0, 131.9, 134.4, 137.0, 144.7, 145.2, 145.3, 149.8; EI-HR found 349.0769 [$M^{\cdot+}$], calcd. 349.0773 ($C_{20}H_{15}NO_3S$); λ_{abs} (CH_2Cl_2, $\varepsilon\times10^{-3}$) 402 (6.3), 248 (5.0) nm.

4-Cyanobenzo[*h*]quinoline (11): 4-Tosylbenzo[*h*]quinoline (**9**) (333 mg, 1 mmol) and tetraethylammonium cyanide (180 mg, 1.2 mmol) in dry DMF (5 mL) were stirred in a sealed tube at 60 °C for 48 h. After pouring into dil. NaCl solution (20 mL), the reaction mixture was extracted with ethyl acetate (3×20 mL), dried with Na_2SO_4 and evaporated. The residue was passed through a thin pad of silica gel to give product (196 mg, 96%); mp = 159-160 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ) 7.76 - 7.82 (m, 3H), 7.94 - 796 (m, 2H), 7.98 – 8.04 (m, 2H), 9.08 (d, 1H, *J*=4.6), 9.25 – 9.29 (m, 1H), ; ^{13}C NMR (125 MHz, $CDCl_3$, δ) 115.9, 118.1, 121.4, 124.5, 124.6, 125.0, 128.1, 128.1, 129.4, 130.9, 131.0, 133.6, 147.0, 148.0; EI-HR found 204.0682 [$M^{\cdot+}$], calcd. 204.0688 ($C_{14}H_8N_2$); λ_{abs} (CH_2Cl_2, $\varepsilon\times10^{-3}$) 370 (7.3), 353 (6.0), 278 (22.1), 256 (13.4), 238 (44.0) nm.

4-Morpholinobenzo[*h*]quinoline (12): 4-Tosylbenzo[*h*]quinoline (**9**) (2.52 g, 7.5 mmol) was heated with morpholine (25 mL) in a sealed tube at 150 °C for 6 days. The mixture was evaporated to dryness, the residue dissolved in CH_2Cl_2 (150 mL), washed with water (2×100 mL) and dried with Na_2SO_4. After evaporation of the solvent, the residue was chromatographed to give product (1.15 g, 58%); mp = 123-124 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ) 3.23 (t, 4H, *J*=4.6), 4.00 (t, 4H, *J*=4.6), 7.02 (d, 1H, *J*=5.2), 7.65 – 7.74 (m, 2H); 7.77 (d, 1H, *J*=9.0), 7.87 – 7.90 (m, 1H), 7.92 (d, 1H, *J*=9.0), 8.85 (d, 1H, *J*=5.0), 9.28 (dd, 1H, J_1=8.0, J_1=1.0); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 52.6×2, 66.9×2, 110.3, 120.6, 120.8, 124.8, 126.5, 127.0, 127.6, 128.1, 131.8, 133.3, 147.6, 149.2, 156.8; EI-HR found 264.1268 [$M^{\cdot+}$], calcd. 264.1263 ($C_{17}H_{16}N_2O$); λ_{abs} (CH_2Cl_2, $\varepsilon\times10^{-3}$) 348 (3.0), 312 (9.5), 263 (28.2) nm.

4-Cyano-10-hydroxybenzo[*h*]quinoline (13): A sealed tube was charged with 4-cyanobenzo[*h*]quinoline (**11**) (53 mg, 0.26 mmol), $PhI(OAc)_2$ (172 mg, 0.52 mmol), $Pd(OAc)_2$ (1.2 mg, 0.026 mmol) and MeCN (2.2 mL). The mixture was stirred at 150 °C for 15 h. The residue was transferred into a round-bottom flask, evaporated to dryness, dissolved in MeOH and filtered through Celite to remove an insoluble black solid. Then NaOH (5 eq.) was added to the 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 with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and solvent was removed under vacuum. The solid was chromatographed (DCVC, SiO_2, hexanes → hexanes/AcOEt 95:5, 9:1). The bright yellow product was obtained after crystallization from hot cyclohexane (36 mg, 77%); mp = 207-209 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ) 7.34 (dd, 1H, J_1=1.1 Hz, J_2=8.0 Hz), 7.50 (dd, 1H, J_1=1.0 Hz, J_2=7.8 Hz), 7.72 (t, 1H, J=7.9), 7.84 (d, 1H, J=4.8), 8.01 (q, 2H, J=9.0), 8.93 (d, 1H, J=4.8), 14.10 (br. s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 115.2, 115.4, 115.5,118.5, 118.9, 120.9, 123.4, 125.8, 131.3, 132.6, 125.0, 144.5, 148.9, 159.3; EI-HR found 220.0643 [$M^{\cdot+}$], calcd. 220.0637 ($C_{14}H_8N_2O$); λ_{abs} (CH_2Cl_2, $\varepsilon\times10^{-3}$) 408 (8.2), 293 (8.6), 250 (63.4) nm.

10-Hydroxy-4-morpholinobenzo[*h*]quinoline (14): A sealed tube was charged with 4-morpholinobenzo[*h*]quinoline (**12**) (70 mg, 0.26 mmol), $PhI(OAc)_2$ (167 mg, 0.52 mmol), $Pd(OAc)_2$ (5.8 mg, 0.026 mmol) and MeCN (1.2 mL). The mixture was stirred at 80 °C for 50 min. 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 95:5, 9:1). The mixture of two products (ester and phenol), which was collected, was dissolved in MeOH/THF and NaOH (5 eq.) was added. 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 with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and removed under vacuum. The bright yellow product was obtained after crystallization from hot cyclohexane (19 mg, 26%); mp = 171-173 °C; ^{1}H NMR (600 MHz, $CDCl_3$, δ) 3.27 (t, 4H, J=4.2), 4.00 (t, 4H, J=4.2), 7.04 (d, 1H, J=4.8), 7.18 (d, 1H, J=7.8), 7.37 (d, 1H, J=7.8), 7.58 (t, 1H, J=7.8), 7.74 (d, 1H, J=9.0), 7.81 (d, 1H, J=9.6), 8.65 (d, 1H, J=5.4), 15.35 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, δ) 52.5, 66.8, 109.3, 113.7, 116.6, 117.7, 119.9, 120.3, 127.6, 129.8, 134.8, 145.5, 149.5, 156.9, 159.6; EI-HR found 280.1203 [$M^{\cdot+}$], calcd. 280.1212 ($C_{17}H_{16}N_2O_2$); λ_{abs} (CH_2Cl_2, $\varepsilon\times10^{-3}$) 373 (8.7), 356 (7.0), 329 (7.6), 267 (13.9).

10-Hydroxy-6-nitrobenzo[*h*]quinoline (16): A sealed tube was charged with 6-nitrobenzo[*h*]quinoline (**15**) (100 mg, 0.45 mmol), $PhI(OAc)_2$ (290 mg, 0.9 mmol), $Pd(OAc)_2$ (10.1 mg, 0.045 mmol) and MeCN (2.1 mL). The mixture was stirred at 150 °C for 18 h. 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 95:5). The mixture of two products (ester and phenol), which was collected together, was dissolved in MeOH/THF and NaOH (5 eq.) was added. 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 with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and removed under vacuum. The pure product was obtained (81 mg, 75%); ^{1}H NMR (500 MHz, $CDCl_3$, δ) 7.21 (dd, 1H, J_1=0.6 Hz, J_2=8.1 Hz), 7.66-7.72 (m, 2H), 8.30 (d, 1H, J=8.4 Hz), 8.95-9.01 (m, 2H), 14.88 (s, 1H), 12.95 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 111.7, 113.6, 114.9, 119.1, 121.5, 126.8, 127.3, 132.4, 135.2, 149.8, 150.7, 155.4, 159.4; EI-HR found 240.0534 [$M^{\cdot+}$], calcd. 240.0535 ($C_{13}H_8N_2O_3$); λ_{abs} (CH_2Cl_2, $\varepsilon\times10^{-3}$) 339 (7.7), 239 (26.9) nm.

10-Hydroxy-7-nitrobenzo[*h*]quinoline (18): A sealed tube was charged with 7-nitrobenzo[*h*]quinoline (**17**) (805 mg, 3.6 mmol), $PhI(OAc)_2$ (2.3 g, 7.2 mmol), $Pd(OAc)_2$ (80.7 mg, 0.36 mmol) and MeCN (14 mL). The mixture was stirred at 150 °C for 20 h. 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 95:5). The pure product was obtained after crystallization from toluene/cyclohexane (131 mg, 17%); mp = 200-201 °C; ^{1}H NMR (600 MHz, $CDCl_3$, δ) 7.21 (d, 1H, J=9.2 Hz), 7.72 (dd, 1H, J_1=4.8 Hz, J_2=8.1 Hz), 7.92 (d, 1H, J=9.5 Hz), 8.39 (dd, 1H, J_1=1.5 Hz, J_2=8.1 Hz), 8.51 (dd, 1H, J_1=4.4 Hz, J_2=8.8 Hz), 8.87 (d, 1H, J=9.2 Hz), 8.92 (dd, 1H, J_1=1.8 Hz, J_2=4.8 Hz), 16.57 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, δ) 113.3, 115.1, 122.8, 122.8, 123.4, 123.8, 125.8, 128.5, 128.8, 129.4, 137.0, 137.2, 145.8, 137.1, 165.7; EI-HR found 240.0534 [$M^{\cdot+}$], calcd. 240.0535 ($C_{13}H_8N_2O_3$); λ_{abs} (CH_2Cl_2 $\varepsilon\times10^{-3}$) 371 (12.5), 264 (15.2).

9-Chloro-7-cyanobenzo[*c*]acridine (21): To a stirred solution of 2-(naphthalen-2-yl)acetonitrile (**19**) (254 mg, 1.52 mmol), 4-chloro-1-nitrobenzene (**20**) (315 mg, 2 mmol) and triethylamine (1.5 mL, ca. 10 mmol) in dry THF (10 mL) under an argon atmosphere at -78 °C, a solution of potassium *t*-butoxide (270 mg, 2.4 mmol) was added. The mixture was stirred for 5 min at -78 °C and chlorotrimethylsilane (1.3 mL, ca. 10 mmol) was added. The cooling bath was removed and the mixture was stirred at rt overnight. After pouring into satd. NH_4Cl solution (50 mL), extraction with ethyl acetate (3×50 mL), drying of the extracts with Na_2SO_4 and evaporation of the solvent, the residue was chromatographed (SiO_2, hexanes/toluene 10:1 to 3:1) to give product (88 mg, 20%); mp = 233 – 236 °C (ethyl acetate); ^{1}H NMR (500 MHz, THF, δ) 7.82 – 7.85 (m, 2H), 7.95 (dd, 1H, J_1=2.3, J_2=9.2 Hz), 8.07 – 8.13 (m, 1H), 8.00 – 8.04 (m, 2H), 8.35 (dd, 1H, J_1=0.4 Hz, J_2=2.3 Hz), 8.42 (dd, 1H, J_1=0.4 Hz, J_2=9.2 Hz), 9.40 – 9.43 (m, 1H); ^{13}C NMR (125 MHz, THF, δ) 114.9, 115.2, 122.7, 124.3, 126.0, 127.0, 127.2, 129.3, 129.4, 131.1, 131.9, 132.6, 133.2, 133.5, 134.6, 135.8, 146.1, 148.3; EI-HR found 288.0446 [$M^{\cdot+}$], calcd. 288.0454 ($C_{18}H_9N_2{}^{35}Cl$); λ_{abs} (CH_2Cl_2 $\varepsilon\times10^{-3}$) 415 (14.6), 393 (14.1), 294 (62.0), 288 (61.3), 264 (23.6), 253 (25.1), 240 (38.8).

9-Chloro-7-cyano-10-hydroxybenzo[*c*]acridine (22): A sealed tube was charged with 9-chloro-7-cyanobenzo[*c*]acridine (**21**) (36.2 mg, 0.125 mmol), $PhI(OAc)_2$ (80.8 mg, 0.25 mmol), $Pd(OAc)_2$ (2.5 mg, 0.0112 mmol) and MeCN (1 mL). The mixture was stirred at 150 °C for 3.5 h. 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 1:99 → hexanes/CH_2Cl_2 4:1, 3:1). The mixture of two products (ester and phenol), which was collected, was dissolved in MeOH/THF and NaOH (5 eq.) was added. 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 with CH_2Cl_2 and water. The organic layer was dried over Na_2SO_4 and solvent removed under vacuum. The resulting product suspended in hot AcOEt and after filtration pure phenol **22** was obtained (17.5 mg, 46%); mp = 295-296 °C; ^{1}H NMR (500 MHz, $CDCl_3$, δ) 7.37 (d, 1H, *J*=7.5 Hz), 7.44 (d, 1H, *J*=7.4 Hz), 7.74 (t, 1H, *J*=7.5

Hz), 7.88 (d, 1H, *J*=9.0 Hz), 7.95 (d, 1H, *J*=9.3 Hz), 8.02 (d, 1H, *J*=9.3 Hz), 8.28 (d, 1H, *J*=9.0 Hz), 14.69 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 113.8, 114.1, 114.4, 117.0, 119.7, 121.4, 123.8, 125.3, 127.4, 129.8, 132.2, 132.6, 134.0, 134.5, 135.3, 141.8, 150.0, 160.4; EI-HR found 304.0410 [$M^{\cdot+}$], calcd. 304.0403 ($C_{18}H_9N_2O^{35}Cl$); λ_{abs} (CH_2Cl_2, $\varepsilon\times10^{-3}$) 461 (10.2), 401 (5.3), 381 (4.1), 273 (48.9) nm.

Optical studies measurements

Steady state absorption spectra were measured by Shimadzu UV-3600 spectrophotometer. Corrected emission spectra were acquired by Fluorolog 3 fluorimeter (SPEX Inc.), with excitation at 328-409 nm, depending on the compound. Emission quantum yields of **2**, **14** and **18** was determine using Rhodamine 6G as a standard. The quantum yields of other compounds were too low to use a highly emissive standard, therefore **14** was used as the standard for other compounds. Emission decays were measured using two methods, femtosecond up-conversion and picosecond time correlated single photon counting (TCSPC). The up-conversion instrument has been described elsewhere.[24] In brief, the excitation wavelengths were 380-400 nm, the time resolution was approximately 150 fs, and emission decays was measured at three wavelengths when was possible: at the expected emission maximum of the enol-form and close to the maximum and at the red sides of the keto-form emission band. The longest delay time is limited by 1.2 ns for the up-conversion instrument. Therefore the samples with emission lifetime longer than few hundredths of picoseconds were also measured using TCSPC instrumentation described elsewhere.[24] In brief, the samples were excited with a pulsed diode laser at 405 nm, the emission detection range was 450-840 nm, and the time resolution was 60-70 ps.

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