Electrophilic Substitution of Monosubstituted Pyrenes

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Bromination and the Friedel–Crafts acetylation of monosubstituted pyrenes were examined. Acetylation of 1-acetyl- and 1-ethylpyrene occurred at the 8-, 6-, or 3-position, but the reaction of 1-methoxypyrene afforded only the 8- and 6-acetyl derivatives. By acetylation, 4-acetylpyrene yielded the 1- and 6-acetyl compounds, and 4-ethylpyrene gave the 6- and 8- derivatives. Also, 4-bromopyrene afforded the corresponding 8-, 6-, and 1-acetyl derivatives by the same reaction. Bromination of 1-ethyl- and 4-ethylpyrene yielded the 8- and 6-bromides, but the reaction of 1-nitro- and 1-bromopyrene took place at the 6-, 8-, or 3-position. The formation ratio of these regioisomers differs by the substituents. The regioselectivity on the acetylation accords in some degree with the prediction based on the ^{13}C NMR chemical shift of each position. The relative rates of these electrophilic substitutions correlate to the substituent constant, σ^+, of the substituent attached to the pyrene.

The chemistry of pyrene (**1**) is fairly well-known in polycyclic aromatic hydrocarbons (PAHs).[1,2] Recent studies of **1** and its derivatives are mainly focussed on application to electrically-conducting or photo-sensitive materials[3] and to hydrogen donor solvents in the coal liquefaction process.[4] Also, one of the current developments in the synthetic programs of **1** is the investigation of properties of these compounds as environmental mutagens.[5,6]

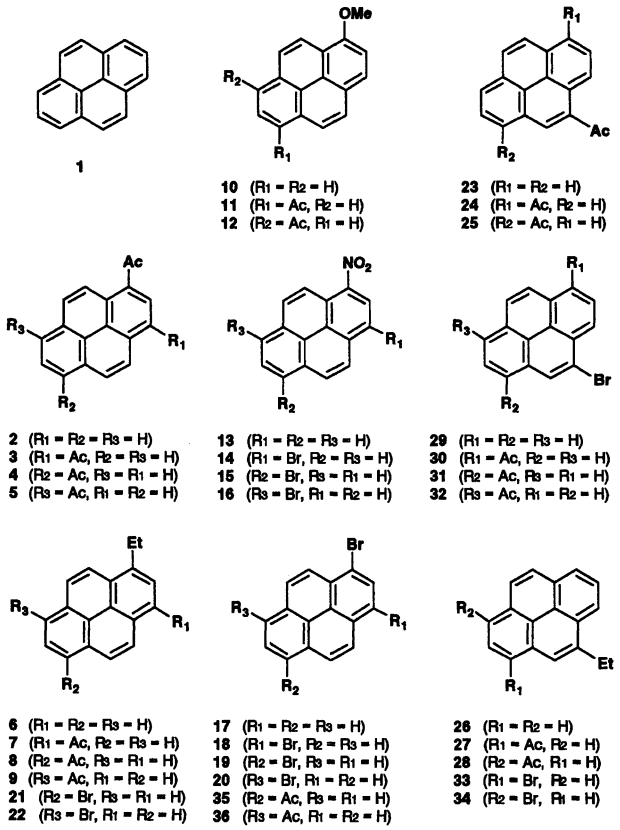
The electrophilic substitution of **1** is known to take place preferentially at the 1-position based both on the experimental results[2,7] and on the consideration of calculations of molecular orbitals.[8,9] The only exception is *t*-butylation.[10]

Electrophilic substitution of 1-substituted pyrene was reported to occur at the position 8, 6, or 3.[11—18] Traces of the 2- and 4-isomers were obtained in addition to the 8-, 6-, and 3-derivatives in the case of sulfonation.[16] In these reports, a fair amount (20—56%) of 1,3-disubstituted pyrenes was obtained in the reactions of sulfonation of 1-pyrenesulfonic acid,[16] nitration of 1-methylpyrene,[17] and protonation of 1-isopropylpyrene.[18] However, substitution at the 3-position of a 1-substituted pyrene has not been recognized in the other cases.[11—15] Likewise, bromination of **1** afforded no 1,3-dibromopyrene,[15] but the Friedel–Crafts acetylation[19] and isopropylation[20] of **1** yielded 1,3-disubstituted derivatives. Similar disagreement is known at the reaction of 4-substituted pyrene.[18]

This paper deals with the reaction of 1- and 4-substituted pyrene with electrophiles as part of a continuous program to investigate the syntheses and reactions of PAHs, to clarify the regioselectivity of the products and the relative rates of the reactions. The results described here may contribute to the syntheses of polysubstituted pyrenes and other PAHs.

Results

The Friedel–Crafts acetylation of 1-acetylpyrene (**2**) was done by adding acetyl chloride to a mixture of **2** and aluminum chloride in dichloromethane (see Scheme 1).



Scheme 1.

The HPLC analysis showed the formation of 1,3- (**3**) (yield, 34%), 1,6- (**4**) (26%), and 1,8-diacetylpyrene (**5**) (37%).[19] A similar reaction of 1-ethylpyrene (**6**) gave 1-acetyl-3-ethyl- (**7**) (19%, by HPLC), 1-acetyl-6-ethyl- (**8**) (29%), and 1-acetyl-8-ethylpyrene (**9**) (42%), in addition to recovered **6** (10%). Similarly, the reaction of 1-methoxypyrene (**10**) at −14 °C for 1 h afforded 1-acetyl-6-methoxy- (**11**) (22%) and 1-acetyl-8-methoxypyrene (**12**) (27%) with recovery (42%) of **10**. On the other hand, **10** was added to the complex of acetyl chloride and aluminum chloride at −14 °C for 15 min, giving **11** (46%) and **12** (54%). This means that the

Table 1. Electrophilic Substitution of Monosubstituted Pyrenes

Compd	Reaction conditions[a]	Isomer distribution[b] /%			
		Site 1	3	6	8
2	AcCl (2), $AlCl_3$ (4) CH_2Cl_2, 23—27 °C, 5.5 h		35(**3**)	27(**4**)	38(**5**)
17[c]	Ac_2O (4), $AlCl_3$ (4) CH_2Cl_2, 0 °C, 4 h	12(**2**)		35(**35**)	53(**36**)
6	AcCl (4), $AlCl_3$ (3.5) CH_2Cl_2, −5—−2 °C, 2 h		21(**7**)	32(**8**)	47(**9**)
10	AcCl (2.8), $AlCl_3$ (2.7) CH_2Cl_2, −14—−11 °C, 1 h			45(**11**)	55(**12**)
13	Br_2 (15.6), AcOH, 100 °C, 2.5 h		12(**14**)	60(**16**)	28(**16**)
13	Br_2 (1.2), CH_2Cl_2, r. t., 56 h		26(**14**)	40(**15**)	34(**16**)
17	Br_2 (1.2), CH_2Cl_2, r. t., 5.3 h		3(**18**)	53(**19**)	44(**20**)
6	Br_2 (1.2), Fe, CH_2Cl_2 −3—+3 °C, 5.5 h			46(**21**)	54(**22**)
23	AcCl (2.2), $AlCl_3$ (5.1) CH_2Cl_2, 40 °C, 1.25 h	83(**24**)		17(**25**)	
29	AcCl (1.1), $AlCl_3$ (4.8) CH_2Cl_2, 0 °C, 1 h	7(**30**)		39(**31**)	54(**32**)
26	AcCl (2.2), $AlCl_3$ (1.9) CH_2Cl_2, −15—−7 °C, 1.17 h			55(**27**)	45(**28**)
26	Br_2 (1.2), Fe, CH_2Cl_2 −1—+2 °C, 3 h			41(**33**)	59(**34**)

a) (): mole ratio to the substrate. b) (): product. c) Cited from Ref. 11.

procedure affects significantly to the reaction rate, but is not effective for regioselectivity in this system.

Bromination of 1-nitropyrene (**13**) with bromine in acetic acid was reexamined by a method similar to that in the literature,[14] yielding 1-bromo-3-nitropyrene (**14**) (5%) in addition to 1-bromo-6-nitro- (**15**) (25%) and 1-bromo-8-nitropyrene (**16**) (12%). The bromination of **13** in dichloromethane at room temperature afforded **14**, **15**, and **16**, in yields of 19, 29, and 25%, respectively with recovered **13** (26%). A similar reaction of 1-bromopyrene (**17**) was confirmed to form 1,3-dibromo- (**18**), 1,6-dibromo- (**19**),[15] and 1,8-dibromopyrene (**20**),[15] in a ratio of 2—4, 52, 43%, respectively by means of ^{1}H NMR. The reaction of **6** with bromine in the presence of iron formed 1-bromo-6-ethyl- (**21**)[21] (36%) and 1-bromo-8-ethylpyrene (**22**)[21] (42%) with recovered **6** (22%), but no 1-bromo-3-ethyl isomer was detected.

The Friedel–Crafts acetylation of 4-acetylpyrene (**23**) gave 1,4-diacetyl- (**24**) and 3,5-diacetylpyrene (**25**) in 80 and 16% yields. A similar reaction of 4-ethylpyrene (**26**) afforded 3-acetyl-5-ethyl- (**27**) (54%) and 1-acetyl-5-ethylpyrene (**28**) (45%). On the other hand, the acylation of 4-bromopyrene (**29**) yielded 1-acetyl-4-bromo- (**30**) (7%), 3-acetyl-5-bromo- (**31**) (38%), and 1-acetyl-5-bromopyrene (**32**) (53%). Bromination of **26** with bromine occurred at the same positions as with acetylation, giving 3-bromo-5-ethyl- (**33**) (41%) and 1-bromo-5-ethylpyrene (**34**) (58%).

The ratio of isomer distribution of each reaction is summarized in Table 1 as the average value of plural trials. The result of acetylation of **17** is also cited from our previous paper;[11] this gave 1-acetyl-6-bromo- (**35**) (23%) and 1-acetyl-8-bromopyrene (**36**) (34%), in addition to ipso-attack product **2** (8%) and recovered **17** (12%).

The relative reactivity of these substrates was estimated by a competitive method using two of these reactants. The ratio of the rates of two substrates during the initial stage was calculated from the time-conversion relation based on the consumption of the reactants. This was used upon the assumption that the reaction mechanism of each reactant is the same as the others. However, the conditions might not be exactly valid, because the reaction conditions, for example reaction temperature, of a competitive reaction are not equal with those of others, to obtain an exact ratio in one competitive reaction. Table 2 shows the ratios of reaction rates (R) of substrates versus the rate (R_1) of **1**.

Discussion

The structures of these products were established by ^{1}H and ^{13}C NMR using homo- and hetero-COSY techniques. As an example, Fig. 1 shows the ^{13}C–^{1}H normal heteronuclear COSY spectrum (only the aromatic region) of **24**. The ^{1}H NMR signals (vertical axis of Fig. 1) are correlated by means of a COSY experiment (not shown). The correlations between H_5 (s) and H_6 (d), and between H_8 (d) and H_9 (d) are detected on a long-range COSY. The tertiary carbons of the ^{13}C NMR spectrum (horizontal axis) are assigned from the correlation with ^{1}H NMR signals in Fig. 1. The quaternary carbons are confirmed by the long-range hetero COSY spectrum in which the correlation through three bond

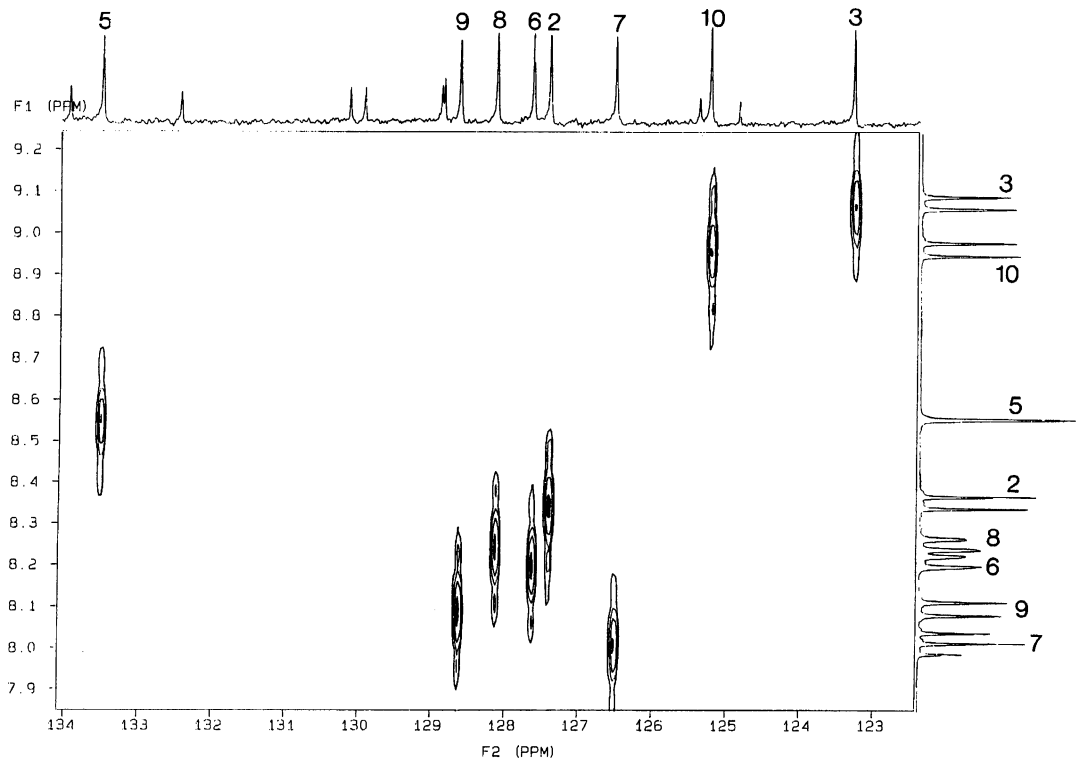


Fig. 1. Normal heteronuclear COSY spectrum of **24**.

Table 2. Relative Reactivities of Monosubstituted Pyrenes

Reaction	Compd	Reactivity[a)]	σ^+
Acetylation	**10**	4.41	−0.65
	6	2.16	−0.22
	17	0.35	+0.02
	2	0.13	+0.57
	26	1.89	−0.22
	29	0.60	+0.02
	23	0.35	+0.57
Bromination	**6**	4.07	−0.22
	17	0.20	+0.02
	13	0.024	+0.74
	26	2.10	−0.22

a) Ratio versus the reaction rate of **1**.

between ^{1}H and ^{13}C is enhanced, as is shown in Fig. 2. Carbon C_{10c} (δ=124.9) couples with the H_5, H_6, H_8, and H_9. Also, C_{10a} (δ=128.90) correlates with H_2 and H_9. Proton H_7 couples with C_{5a} (δ=128.87) and C_{8a} (δ=130.2), however, the C_{8a} couples also with H_{10}.

In the ^{1}H NMR spectra, the protons ortho and peri to the substituent resonate at lower fields than do the corresponding protons of the parent compounds, like other types of substituted pyrenes.[6,11,21)]

The substituent attached to **1** directly affects on the reaction rate of electrophilic substitution of monosubstituted pyrene (Table 2). A plot of logarithms of reactivity, or $\log(R/R_1)$, versus Brown σ^+ shows a first order relation in acetylations of 1- and 4-substituted pyrenes and bromination of 1-derivatives. The coefficient of correlation is 0.951 in the acetylation of 1-substituted pyrenes. The bromination is faster than the Friedel–Crafts acetylation, as in a benzene series. With acetylation, the reaction constant (ρ) of 4-substituted pyrenes is smaller than that of 1-substituted compounds. This suggests that the 4-substituent does not effectively influence the electrophilic reaction, unlike the 1-substituent.

In the competitive acetylation between **10** and **1**, the value (4.41) of R_{10}/R_1 was obtained when a mixture of **1** and **10** was added to complexes of acetyl chloride and aluminum chloride. An unexpected value (0.39) was obtained by adding acetyl chloride to the mixture of **1**, **10**, and aluminum chloride. This is explained, in the latter procedure, by the electron-rich **10** complexes with aluminum chloride giving a black mixture and becoming a deactivated species. However, this does not influence the distribution of products (see Results section), unlike 2-methoxynaphthalene.[22)]

The brominations of **13** and **17** gave the 3-bromides in these experiments, despite the fact that these 3-bromides were not confirmed in the literature.[13—15)] The disagreement should be due only to the analytical method of the reaction mixture: They used IR spectra[13,14)] or separation by fractional recrystallization.[15)]

The relationship between the substituent occupying the 1-position and possibility of attack to the 3-position cannot be explained clearly. The results in Table 1 fit roughly to the generalization that the activating group activates positions 6 and 8 rather than the 3-position by electronic effects, giving mainly the 6- and 8-derivatives

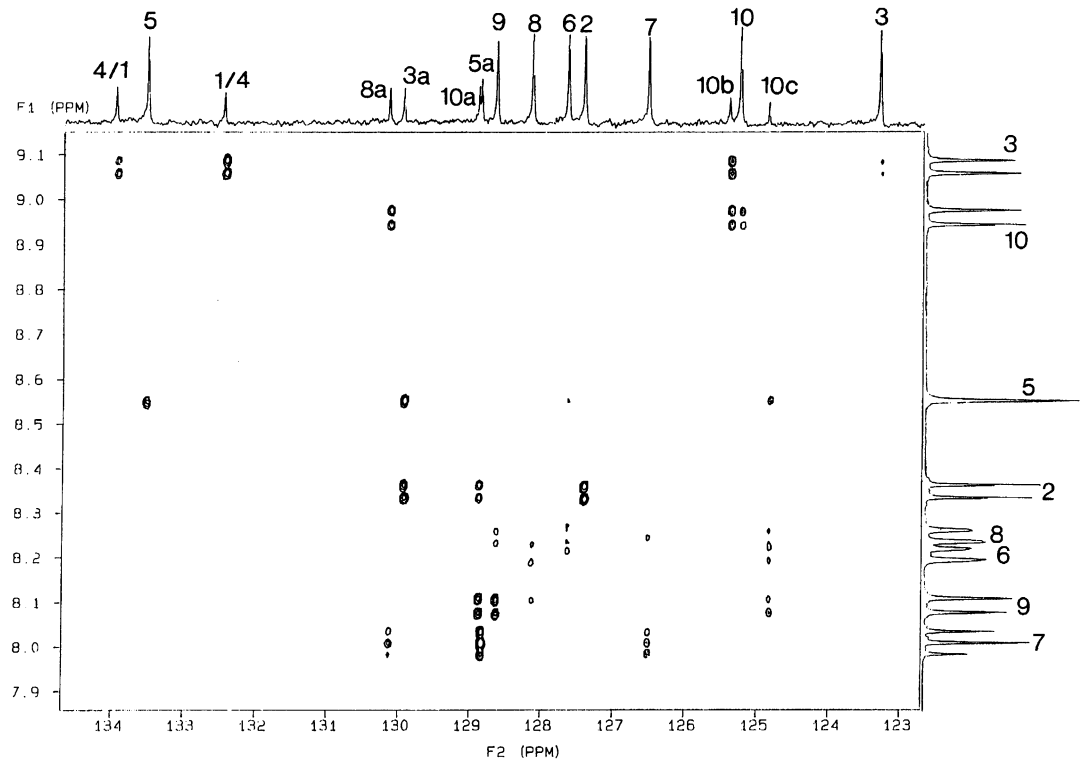


Fig. 2. Long-range heteronuclear COSY spectrum of **24**.

as in **10**. The deactivating group as in **2** acts in just the opposite way, giving the 3-derivative in addition to the 6- and 8-isomers. A similar explanation may be used for the 4-substituted pyrenes because the attack on the 3-position is inhibited by the steric hindrance due to peri-substituent.

The electron density at each carbon is calculated by the MNDO (modified neglect of diatomic overlap) method[9] and the CNDO/2 (complete neglect of differential overlap) procedure. The regioselectivity in the reaction accords outwardly with the calculated electron density of each position. For example, the acetylation of **6** occurs at the 8-, 6-, and 3-positions in a ratio of 47 : 32 : 21, and the HOMO electron density is 0.012, 0.011, and 0.005 larger than the unity (4.000) at the corresponding position, respectively, by CNDO/2. However, the differences among each of the densities are as small as the calculation error. Therefore, it is difficult to estimate the possibility of the attack at the 3-position of 1-substituted pyrene using calculated electron density.

The partial rate factor (f) of these reactants in acetylation is roughly estimated using the value "$f/6k$", where k is the relative reactivity of a monosubstituted pyrene with benzene, or $k = R/R_{\mathrm{PhH}}$. Table 3 indicates the ratio of partial rate factors of each position of reactant versus that of **1**, as the result of (value of isomer distribution)$\times(R/R_1)\times 4$. The ratio of the partial rate factor is only an apparent ratio. Table 3 is accompanied by the ^{13}C NMR chemical shifts of these positions. The substitution occurs more, except some cases, at the carbon showing a smaller $\Delta\delta$ value than others. Then, the regioselectivity of the reaction fits in some degree with the order of the ^{13}C NMR chemical shifts.

Table 3. Ratio of Partial Rate Factor in Acetylation

Compd	Ratio of partial rate factor[a] (^{13}C NMR chemical shift, δ in ppm)			
	Site 1	3	6	8
10		—	7.9	9.7
		(125.4)	(124.1)	(124.0)
6		1.8	2.8	4.1
		(124.8)	(124.6)	(124.5)
17	0.17[b]	—	0.49	0.74
	(119.8)	(125.4)	(125.6)	(125.4)
2		0.18	0.14	0.20
		(123.9)	(126.1)	(125.9)
26	—	—	4.2	3.4
	(124.8)	(121.1)	(124.2)	(124.4)
29	0.17	—	0.94	1.3
	(126.1)	(124.9)	(124.4)	(125.5)
23	1.2	—	0.24	—
	(125.8)	(124.4)	(126.4)	(127.2)

a) 1.0 for **1** (^{13}C NMR, $\delta = 125.2$). b) Ipso-attack product.

In conclusion, the rate of electrophilic substitution of monosubstituted pyrene should be expected from the σ^+ value of the substituent attached. Positions 8, 6, and 3 are reactive to the electrophiles. The order of the regioselectivity is some extent estimated based on the calculation or ^{13}C NMR, but it is difficult to predict the magnitude of the selectivity.

Experimental

The melting points are uncorrected. The column, Zorbax SIL (Du Pont, 4.6 mm i. d., 15 cm) was used for analytical HPLC (flow rate, 1 ml min^{-1}). The IR spectra (KBr pellets) were recorded with a JASCO IR Report-100. The UV-vis spectra (EtOH) were obtained with a Shimadzu UV-180. The ^1H and ^{13}C NMR spectra (0.7 ml $CDCl_3$) were recorded with a Varian VXR-300. The sample used was about 2 mg for ^1H NMR and 10—30 mg for ^{13}C NMR and 2D NMR spectra. The mass spectra were recorded with a Hitachi M-80 with a direct inlet and operated at an ionization voltage of 70 eV.

Materials. Compounds, **2**,[2,11] **6**,[2] **10**,[2,23] **13**,[2] **17**,[2,11] **23**,[12] **26**,[23] and **29**,[24] were obtained by the methods similar to the literatures.

^1H NMR of **6**: δ=1.49 (3H, t, J=7.6 Hz, Me), 3.39 (2H, q, J=7.6 Hz, CH_2), 7.89 (1H, d, J=7.8 Hz, H_2), 7.98 (1H, t, J=7.6 Hz, H_7), 8.01 (1H, d, J=9.0 Hz, H_4), 8.02 (1H, d, J=9.0 Hz, H_5), 8.10 (1H, d, J=9.3 Hz, H_9), 8.12 (1H, d, J=7.8 Hz, H_3), 8.15 (1H, d, J=7.6 Hz, H_6), 8.16 (1H, d, J=7.6 Hz, H_8), 8.30 (1H, d, J=9.3 Hz, H_{10}); ^{13}C NMR δ=16.3 (Me), 26.4 (CH_2), 123.2 (C_{10}), 124.5 (C_8), 124.6 (C_6), 124.8 (C_3), 124.9 (C_{10b}, C_{10c}), 125.6 (C_7), 126.2 (C_2), 126.3 (C_5), 127.0 (C_9), 127.4 (C_4), 128.3 (C_{10a}), 129.6 (C_{3a}), 130.8 (C_{8a}), 131.3 (C_{5a}), 138.4 (C_1).

^1H NMR of **10**:[23] δ=4.18 (3H, s, Me), 7.56 (1H, d, J=8.4 Hz, H_2), 7.89 (1H, d, J=9.0 Hz, H_5), 7.96 (1H, d, J=9.0 Hz, H_4), 7.96 (1H, t, J=7.6 Hz, H_7), 8.05 (1H, d, J=9.2 Hz, H_9), 8.09 (1H, d, J=7.6 Hz, H_6), 8.12 (1H, d, J=7.6 Hz, H_3), 8.13 (1H, d, J=7.6 Hz, H_8), 8.45 (1H, d, J=9.2 Hz, H_{10}); ^{13}C NMR δ=56.0 (Me), 108.0 (C_2), 120.1 (C_{3a}), 121.0 (C_{10}), 124.0 (C_8), 124.1 (C_6), 124.7 (C_5), 124.8 (C_{10a}), 125.1 (C_{10c}), 125.4 (C_3), 125.7 (C_{10b}), 126.0 (C_7), 126.3 (C_9), 127.1 (C_4), 131.6 (C_{5a}, C_{8a}), 153.5 (C_1).

^1H NMR of **13**: δ=8.14 (1H, d, J=9.0 Hz, H_4), 8.15 (1H, t, J=7.6 Hz, H_7), 8.20 (1H, d, J=8.5 Hz, H_3), 8.28 (1H, d, J=9.0 Hz, H_5), 8.35 (2H, d, J=7.6 Hz, H_6, H_8), 8.36 (1H, d, J=9.6 Hz, H_9), 8.70 (1H, d, J=8.5 Hz, H_2), 8.94 (1H, d, J=9.6 Hz, H_{10}); ^{13}C NMR δ=121.5 (C_{10}), 122.5 (C_2), 123.4 (C_{10b}), 124.0 (C_3), 124.6 (C_{10a}, C_{10b}), 126.8 (C_4), 127.0 (C_7, C_8), 127.5 (C_6), 129.9 (C_{8a}), 130.6 (C_5), 130.7 (C_{5a}), 131.3 (C_9), 134.9 (C_{3a}), 142.5 (C_1).

^1H NMR of **23**: δ=2.94 (3H, s, Me), 8.06 (1H, t, J=7.7 Hz, H_7), 8.07 (1H, d, J=9.1 Hz, H_9), 8.09 (1H, t, J=7.7 Hz, H_2), 8.11 (1H, d, J=9.1 Hz, H_{10}), 8.24 (1H, dd, J=7.7, 1.0 Hz, H_1), 8.28 (1H, d, J=7.7 Hz, H_6), 8.29 (1H, d, J=7.7 Hz, H_8), 8.60 (1H, s, H_5), 9.11 (1H, dd, J=7.7, 1.0 Hz, H_3); ^{13}C NMR δ=29.8 (Me), 124.4 (C_3), 125.2 (C_{10b}), 125.5 (C_{10c}), 125.8 (C_1), 126.1 (C_7), 126.4 (C_6), 126.6 (C_9), 126.7 (C_2), 127.2 (C_{3a}, C_8), 128.1 (C_{10}), 129.1 (C_{5a}), 130.9 (C_{8a}), 131.0 (C_{10a}), 131.6 (C_5), 134.8 (C_4), 201.6 (CO).

^1H NMR of **26**: δ=1.56 (3H, t, J=7.5 Hz, Me), 3.33 (2H, q, J=7.5 Hz, CH_2), 7.95 (1H, s, H_5), 7.98 (1H, t, J=8.0 Hz, H_7), 8.04 (1H, t, J=7.8 Hz, H_2), 8.08 (2H, s, H_9, H_{10}), 8.14 (2H, d, J=8.0 Hz, H_6, H_8), 8.19 (1H, dd, J=7.8, 1.1 Hz, H_1), 8.38 (1H, dd, J=7.8, 1.1 Hz, H_3); ^{13}C NMR δ=14.4 (Me), 26.2 (CH_2), 121.1 (C_3), 123.6 (C_{10c}), 124.2 (C_6), 124.4 (C_8), 124.8 (C_1), 124.9 (C_{10b}, C_5), 125.5 (C_2), 125.8 (C_7), 127.1 (C_{10}), 127.4 (C_9), 130.4 (C_{3a}), 130.8 (C_{8a}), 131.1 (C_{5a}), 131.5 (C_{10a}), 139.0 (C_4).

^1H NMR of **29**: δ=8.02 (1H, t, J=7.6 Hz, H_7), 8.10 (2H, s, H_9, H_{10}), 8.11 (1H, t, J=7.7 Hz, H_2), 8.13 (1H, dd, J=7.6, 1.2 Hz, H_6), 8.22 (1H, dd, J=7.6, 1.2 Hz, H_8), 8.26 (1H, dd, J=7.7, 1.1 Hz, H_1), 8.45 (1H, s, H_5), 8.60 (1H, dd, J=7.7, 1.1 Hz, H_3); ^{13}C NMR δ=122.3 (C_4), 123.6 (C_{10c}), 124.4 (C_6), 124.9 (C_3), 125.2 (C_{10b}), 125.5 (C_8), 126.1 (C_1), 126.2 (C_7), 126.3 (C_2), 127.3 (C_9, C_{10}), 129.6 (C_{3a}), 130.7 (C_5), 131.0 (C_{10a}), 131.1 (C_{8a}), 131.2 (C_{5a}).

Acetylation of 2. Anhydrous aluminum chloride (0.27 g, 2 mmol) was added to a solution of **2** (0.122 g, 0.5 mmol) in CH_2Cl_2 (10 ml). The AcCl (0.07 ml, 1 mmol) was added gradually over 30 min at r. t., and stirred for an additional 5 h. The reaction mixture was washed with water, dried over anhydrous Na_2SO_4, and diluted to 100 ml. To a part (1 ml) of the solution 9-fluorenone (retention volume, V_R=4.01 ml) was added as an internal standard, and analyzed by HPLC (mobile phase, hexane/THF=9/1); **3** (15.24 ml, sensitivity 3.23 mol/mol), **4** (14.71 ml, 3.58), and **5** (19.44 ml, 3.38) were confirmed. The reaction mixture of several trials was combined, chromatographed (Ph-H/hexane) with SiO_2, and each fraction was recrystallized from Ph-H/hexane giving **3**, **4**, and **5**.

3: Mp 184—186 °C (lit,[19] mp 184.5—185.5 °C); IR 1693 cm^{-1}; UV λ_{max} 378 (log ε 4.32), 287 (4.43), 248 nm (4.36); ^{13}C NMR δ=30.4 (Me), 123.9 (C_{10c}), 124.4 (C_4, C_{10}), 125.4 (C_{10b}), 126.8 (C_7), 127.4 (C_6, C_8), 127.5 (C_2), 130.3 (C_{5a}, C_{8a}), 131.2 (C_1, C_3), 131.6 (C_5, C_9), 131.7 (C_{3a}, C_{10a}), 201.5 (CO).

4: Mp 207—208 °C (lit,[19] mp 206.5—207.5 °C); IR 1682 cm^{-1}; UV λ_{max} 396 (log ε 4.15), 367 (4.41), 287 (4.47), 277 (4.27), 247 nm (4.55); ^{13}C NMR δ=30.4 (Me), 124.6 (C_{10b}, C_{10c}), 125.0 (C_3, C_8), 126.9 (C_5, C_{10}), 127.2 (C_2, C_7), 129.1 (C_4, C_9), 129.2 (C_{5a}, C_{10a}), 133.0 (C_{3a}, C_{8a}), 133.1 (C_1, C_6), 202.1 (CO).

5: Mp 161—162 °C (lit,[19] mp 162—163 °C); IR 1668 cm^{-1}; UV λ_{max} 372 (log ε 4.35), 289 (4.38), 245 nm (4.52); ^{13}C NMR δ=30.5 (Me), 124.6 (C_{10b}, C_{10c}), 125.2 (C_3, C_6), 126.9 (C_9, C_{10}), 127.1 (C_2, C_7), 128.5 (C_{8a}, C_{10a}), 129.0 (C_4, C_5), 133.1 (C_1, C_8), 133.7 (C_{3a}, C_{5a}), 201.9 (CO).

Acetylation of 6. To a mixture of **6** (58 mg, 0.25 mmol), $AlCl_3$ (118 mg, 0.88 mmol) in CH_2Cl_2 (10 ml), AcCl (0.04 ml, 1.0 mmol) in CH_2Cl_2 (10 ml) was added at −5—−2 °C for 15 min, and the mixture was stirred at the same temperature for 1.75 h. The resulting mixture was analyzed by HPLC (hexane/THF=98/2). The residual portion was separated by preparative HPLC and each fraction was recrystallized from hexene.

7: Mp 124—125 °C (EtOH); IR 1671 cm^{-1}; UV λ_{max} 393 (log ε 3.98), 359 (4.28), 285 (4.37), 244 nm (4.54); ^1H NMR δ=1.52 (3H, t, J=7.6 Hz, Me), 2.92 (3H, s, Ac), 3.42 (2H, q, J=7.6 Hz, CH_2), 8.04 (1H, t, J=7.4 Hz, H_7), 8.16 (1H, d, J=9.4 Hz, H_9), 8.21 (1H, d, J=9.4 Hz, H_5), 8.23 (2H, d, J=7.4 Hz, H_6, H_8), 8.25 (1H, s, H_2), 8.31 (1H, d, J=9.4 Hz, H_4), 8.95 (1H, d, J=9.4 Hz, H_{10}); ^{13}C NMR δ=15.8 (Me), 26.6 (CH_2), 30.5 (Ac), 122.8 (C_4), 124.6 (C_{10c}), 124.8 (C_{10}), 125.3 (C_{10b}), 125.8 (C_6 or C_8), 125.9 (C_8 or C_6), 126.1 (C_7), 127.2 (C_2), 127.7 (C_{10a}), 128.6 (C_9), 129.3 (C_5), 130.7 (C_{8a}, C_{5a}), 131.3 (C_{3a}), 132.0 (C_1), 137.3 (C_3), 202.5 (CO); MS m/z 272 (M^+), 257, 243, 229, 228, 214, 200.

8: Mp 157—159 °C (EtOH); IR 1678 cm^{-1}; UV λ_{max} 369 (log ε 4.29), 287 (4.36), 243 nm (4.59); ^1H NMR δ=1.50 (3H, t, J=7.6 Hz, Me), 2.91 (3H, s, Ac), 3.41 (2H, q, J=7.6

Hz, CH_2), 7.95 (1H, d, J=7.9 Hz, H_7), 8.11 (1H, d, J=9.3 Hz, H_4), 8.16 (1H, d, J=8.1 Hz, H_3), 8.18 (1H, d, J=9.4 Hz, H_9), 8.20 (1H, d, J=7.9 Hz, H_8), 8.38 (1H, d, J=8.1 Hz, H_2), 8.42 (1H, d, J=9.3 Hz, H_5), 8.99 (1H, d, J=9.4 Hz, H_{10}); ^{13}C NMR δ=15.8 (Me), 26.6 (CH_2), 30.4 (Ac), 123.5 (C_3), 123.9 (C_{10}), 124.6 (C_{10c}), 125.3 (C_{10b}), 125.4 (C_5), 126.0 (C_8), 126.7 (C_4), 126.9, (C_2, C_7), 128.3 (C_{5a}), 129.0 (C_{8a}), 129.7 (C_{10a}), 129.8 (C_9), 131.7 (C_1), 133.7 (C_{3a}), 140.1 (C_6), 202.5 (CO); MS m/z 272 (M^+), 257, 243, 229, 228, 214, 200. Anal. Found: C, 87.76; H, 5.97%. Calcd for $C_{20}H_{16}O$: C, 88.20; H, 5.92%.

9: Mp 80—82 °C (EtOH); IR 1672 cm^{-1}; UV λ_{max} 394 (log ε 4.07), 361 (4.28), 286 (4.38), 244 nm (4.51); ^{1}H NMR δ=1.49 (3H, t, J=7.6 Hz, Me), 2.91 (3H, s, Ac), 3.42 (2H, q, J=7.6 Hz, CH_2), 7.95 (1H, d, J=7.8 Hz, H_7), 8.01 (1H, d, J=8.9 Hz, H_5), 8.13 (1H, d, J=8.9 Hz, H_4), 8.16 (1H, d, J=8.1 Hz, H_3), 8.19 (1H, d, J=7.8 Hz, H_6), 8.38 (1H, d, J=8.1 Hz, H_2), 8.47 (1H, d, J=9.8 Hz, H_9), 9.11 (1H, d, J=9.8 Hz, H_{10}); ^{13}C NMR δ=16.1 (Me), 26.5 (CH_2), 30.3 (Ac), 123.7 (C_3), 124.6 (C_{10}, C_{10c}), 125.3 (C_{10b}), 125.6 (C_9), 126.1 (C_4), 126.3 (C_6), 126.8 (C_7), 127.1 (C_2), 127.8 (C_{8a}), 129.3 (C_{10a}), 129.5 (C_{5a}), 129.7 (C_5), 131.4 (C_1), 134.3 (C_{3a}), 140.0 (C_8), 202.0 (CO); MS m/z 272 (M^+), 257, 243, 229, 228, 214, 200.

Acetylation of 10. A solution of AcCl (0.1 ml, 1.4 mmol) in CH_2Cl_2 (20 ml) was added to a mixture of **10** (116 mg, 0.5 mmol) and $AlCl_3$ (180 mg, 1.35 mmol) in CH_2Cl_2 (20 ml) at −14—−11 °C for 30 min, and stirred for 30 min. After identification of the components, **10**, **11**, and **12** by HPLC, the reaction mixture was separated by preparative HPLC.

11: Mp 167—168 °C (EtOH); IR 1671 cm^{-1}; UV λ_{max} 387 (log ε 4.30), 290 (4.26), 244 nm (4.68); ^{1}H NMR δ=2.90 (3H, s, Ac), 4.20 (3H, s, MeO), 7.61 (1H, d, J=8.5 Hz, H_7), 8.05 (1H, d, J=9.3 Hz, H_4), 8.10 (1H, d, J=8.2 Hz, H_3), 8.12 (1H, d, J=9.6 Hz, H_9), 8.21 (1H, d, J=8.5 Hz, H_8), 8.36 (1H, d, J=8.2 Hz, H_2), 8.59 (1H, d, J=9.3 Hz, H_5), 8.92 (1H, d, J=9.6 Hz, H_{10}); ^{13}C NMR δ=30.3 (Ac), 56.1 (MeO), 108.5 (C_7), 120.0 (C_{5a}), 122.4 (C_{10}), 123.0 (C_3), 123.3 (C_5), 124.5 (C_{8a}), 125.1 (C_{10b}), 125.3 (C_{10c}), 125.9 (C_4), 126.9 (C_8), 127.4 (C_2), 129.6 (C_9), 130.3 (C_{10a}), 130.9 (C_{3a}), 134.5 (C_1), 154.6 (C_6), 202.0 (CO); MS m/z 274 (M^+), 259, 231, 216. Anal. Found: C, 83.08; H, 5.35%. Calcd for $C_{19}H_{14}O_2$: C, 83.20; H, 5.15%.

12: Mp 161—162 °C (EtOH); IR 1663 cm^{-1}; UV λ_{max} 361 (log ε 4.08), 286 (4.23), 242 nm (4.39); ^{1}H NMR δ=2.90 (3H, s, Ac), 4.20 (3H, s, MeO), 7.60 (1H, d, J=8.5 Hz, H_7), 7.90 (1H, d, J=9.0 Hz, H_4), 8.07 (1H, d, J=9.0 Hz, H_5), 8.09 (1H, d, J=8.1 Hz, H_3), 8.20 (1H, d, J=8.5 Hz, H_6), 8.38 (1H, d, J=8.1 Hz, H_2), 8.63 (1H, d, J=9.6 Hz, H_9), 9.10 (1H, d, J=9.6 Hz, H_{10}); ^{13}C NMR δ=30.3 (Ac), 56.1 (MeO), 108.2 (C_7), 119.8 (C_{8a}), 123.0 (C_3), 123.5 (C_9), 123.9 (C_{10}), 124.5 (C_4), 124.9 (C_{5a}), 125.2 (C_{10b}), 125.3 (C_{10c}), 127.1 (C_6), 127.7 (C_2), 129.5 (C_5), 130.2 (C_{10a}), 130.7 (C_{3a}), 134.8 (C_1), 154.5 (C_8), 201.8 (CO); MS m/z 274 (M^+), 259, 231, 216.

Acetylation of 23. A solution of AcCl (0.04 ml, 0.56 mmol) in CH_2Cl_2 (3 ml) was added to a mixture of **23** (61 mg, 0.25 mmol) and $AlCl_3$ (170 mg, 1.28 mmol) in CH_2Cl_2 (5 ml) at 40 °C for 15 min, and stirred for 1 h. After analysis of the mixture by HPLC, the reaction mixture was separated by column chromatography (PhH, SiO_2) to give **24** and **25**.

24: Mp 176—178 °C (PhH–hexane); IR 1670 cm^{-1}; UV λ_{max} 363 (log ε 4.21), 287 (4.28), 244 nm (4.49); ^{1}H NMR δ=2.92 (3H, s, 1-Ac), 2.96 (3H, s, 4-Ac), 8.11 (1H, t, J=7.6 Hz, H_7), 8.21 (1H, d, J=9.5 Hz, H_9), 8.33 (1H, d, J=7.6 Hz, H_6), 8.34 (1H, d, J=7.6 Hz, H_8), 8.44 (1H, d, J=8.5 Hz, H_2), 8.68 (1H, s, H_5), 9.04 (1H, d, J=9.5 Hz, H_{10}), 9.16 (1H, d, J=8.5 Hz, H_3); ^{13}C NMR δ=29.7 (4-Ac), 30.5 (1-Ac), 123.3 (C_3), 124.9 (C_{10c}), 125.3 (C_{10}), 125.4 (C_{10b}), 126.5 (C_7), 127.4 (C_2), 127.7 (C_6), 128.1 (C_8), 128.7 (C_9), 128.9 (C_{5a}, C_{10a}), 130.0 (C_{3a}), 130.2 (C_{8a}), 132.5 (C_1 or C_4), 133.5 (C_5), 134.0 (C_4 or C_1), 201.0 (4-CO), 202.1 (1-CO); MS m/z 286 (M^+), 271, 200. Anal. Found: C, 83.92; H, 4.96%. Calcd for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93%.

25: Mp 164—166 °C (PhH–hexane); IR 1668 cm^{-1}; UV λ_{max} 371 (log ε 3.91), 289 (4.06), 242 nm (4.16); ^{1}H NMR δ=2.96 (3H, s, 3-Ac), 2.97 (3H, s, 5-Ac), 8.08 (1H, d, J=9.0 Hz, H_{10}), 8.14 (1H, t, J=7.9 Hz, H_7), 8.21 (1H, d, J=9.0 Hz, H_9), 8.29 (1H, d, J=8.1 Hz, H_1), 8.31 (1H, dd, J=7.9, 0.9 Hz, H_8), 8.49 (1H, d, J=8.1 Hz, H_2), 9.15 (1H, dd, J=7.9, 0.9 Hz, H_6), 9.78 (1H, s, H_4); MS m/z 286 (M^+), 271, 200.

Acetylation of 26. A mixture of **26** (58 mg, 0.25 mmol) and $AlCl_3$ (65 mg, 0.49 mmol) in CH_2Cl_2 (10 ml) was allowed to react with a solution of AcCl (0.04 ml, 0.56 mmol) in CH_2Cl_2 (5 ml) at −15 °C for 10 min, and stirred for 1 h at −7 °C. After analysis of the mixture by HPLC, the reaction mixture was separated by column chromatography to afford **27** and **28**.

27: Mp 133—134 °C (hexane); IR 1672 cm^{-1}; UV λ_{max} 390 (log ε 4.02), 358 (4.30), 287 (4.44), 243 nm (4.56); ^{1}H NMR δ=1.56 (3H, t, J=7.5 Hz, Me), 2.92 (3H, s, Ac), 3.39 (2H, q, J=7.5 Hz, CH_2), 8.07 (1H, d, J=9.0 Hz, H_{10}), 8.10 (1H, t, J=7.8 Hz, H_7), 8.13 (1H, d, J=8.2 Hz, H_1), 8.18 (1H, d, J=9.0 Hz, H_9), 8.26 (1H, dd, J=7.8, 0.9 Hz, H_8), 8.38 (1H, d, J=8.2 Hz, H_2), 8.48 (1H, dd, J=7.8, 0.9 Hz, H_6), 8.96 (1H, s, H_4); ^{13}C NMR δ=14.7 (Me), 26.8 (CH_2), 30.5 (Ac), 122.3 (C_6), 122.8 (C_4), 123.2 (C_1), 124.0 (C_{10b}), 124.6 (C_{10c}), 126.0 (C_7), 126.2 (C_8), 126.8 (C_{10}), 127.0 (C_2), 129.5 (C_{3a}), 129.7 (C_9, C_{5a}), 131.3 (C_{10a}), 131.4 (C_{8a}), 133.7 (C_3), 141.9 (C_5), 202.3 (CO); MS m/z 272 (M^+), 257. Anal. Found: C, 88.20; H, 5.99%. Calcd for $C_{20}H_{16}O$: C, 88.20; H, 5.92%.

28: Mp 104—105 °C (hexane); IR 1664 cm^{-1}; UV λ_{max} 389 (log ε 4.02), 358 (4.33), 288 (4.47), 243 nm (4.52); ^{1}H NMR δ=1.57 (3H, t, J=7.5 Hz, Me), 2.91 (3H, s, Ac), 3.36 (2H, q, J=7.5 Hz, CH_2), 7.95 (1H, s, H_4), 8.09 (1H, t, J=7.7 Hz, H_7), 8.14 (1H, d, J=8.1 Hz, H_3), 8.23 (1H, d, J=9.4 Hz, H_9), 8.27 (1H, dd, J=7.7, 1.0 Hz, H_8), 8.40 (1H, d, J=8.1 Hz, H_2), 8.46 (1H, dd, J=7.7, 1.0 Hz, H_6), 9.09 (1H, d, J=9.4 Hz, H_{10}); ^{13}C NMR δ=14.3 (Me), 26.1 (CH_2), 30.3 (Ac), 122.3 (C_6), 123.4 (C_3), 123.9 (C_{10b}), 124.5 (C_{10c}), 124.7 (C_{10}), 124.8 (C_4), 125.9 (C_8), 126.0 (C_7), 127.3 (C_2), 129.3 (C_{10a}), 129.8 (C_9), 130.1 (C_{5a}), 130.8 (C_{8a}), 131.1 (C_{3a}), 134.1 (C_1), 141.6 (C_5), 202.0 (CO); MS m/z 272 (M^+), 257. Anal. Found: C, 88.01; H, 5.89%. Calcd for $C_{20}H_{16}O$: C, 88.20; H, 5.92%.

Acetylation of 29. A mixture of **29** (70 mg, 0.25 mmol) and $AlCl_3$ (160 mg, 1.2 mmol) in CH_2Cl_2 (8 ml) was mixed with a solution of AcCl (0.02 ml, 0.28 mmol) in CH_2Cl_2 (5 ml) at 0 °C for 30 min, and stirred for 1 h. After analysis of the mixture by HPLC, the reaction mixture was separated by preparative HPLC to afford **30**, **31**, and **32**.

30: Mp 101—103 °C (EtOH); IR 1676 cm^{-1}; UV

λ_{max} 391 (log ε 3.89), 358 (4.28), 286 (4.42), 244 nm (4.57); ^{1}H NMR δ=2.93 (3H, s, Ac), 8.08 (1H, t, J=7.6 Hz, H_7), 8.20 (1H, dd, J=7.6, 1.2 Hz, H_6), 8.24 (1H, d, J=9.5 Hz, H_9), 8.30 (1H, d, J=7.6, 1.2 Hz, H_8), 8.46 (1H, d, J=8.4 Hz, H_2), 8.55 (1H, s, H_5), 8.65 (1H, d, J=8.4 Hz, H_3), 9.02 (1H, d, J=9.5 Hz, H_{10}); ^{13}C NMR δ=30.5 (Ac), 121.9, 123.2, 124.0 (C_3), 124.8 (C_{10}), 125.7, 125.8 (C_6), 126.6 (C_8), 126.8 (C_7), 127.2 (C_2), 129.2, 129.5 (C_9), 130.4, 131.0, 132.1, 132.8 (C_5), 133.0, 202.0 (CO); MS m/z 324, 322 (M^+), 309, 307, 281, 279, 200.

31: Mp 174—175 °C (EtOH); IR 1667 cm^{-1}; UV λ_{max} 390 (log ε 3.96), 358 (4.34), 287 (4.49), 244 nm (4.47); ^{1}H NMR δ=2.91 (3H, s, Ac), 8.10 (1H, d, J=8.7 Hz, H_{10}), 8.15 (1H, d, J=7.8 Hz, H_7), 8.20 (1H, d, J=8.7 Hz, H_9), 8.22 (1H, d, J=7.8 Hz, H_1), 8.32 (1H, dd, J=7.8, 1.1 Hz, H_8), 8.42 (1H, d, J=7.8 Hz, H_2), 8.69 (1H, dd, J=7.8, 1.1 Hz, H_6), 9.52 (1H, s, H_4); ^{13}C NMR δ=30.2 (Ac), 123.9 (C_{10b}), 124.4 (C_1), 124.7 (C_{10c}), 125.8 (C_5), 126.1 (C_6), 126.8 (C_7), 126.9 (C_{10}), 127.4 (C_8), 127.5 (C_2), 128.6 (C_4), 129.1 (C_{5a}), 129.2 (C_{3a}), 129.5 (C_9), 130.7 (C_3), 130.9 (C_{8a}), 133.8 (C_{10a}), 201.3 (CO); MS m/z 324, 322 (M^+), 309, 307, 281, 279, 200. Anal. Found: C, 66.84; H, 3.47%. Calcd for $C_{18}H_{11}OBr$: C, 66.90; H, 3.43%.

32: Mp 124—125 °C (EtOH); IR 1672 cm^{-1}; UV λ_{max} 389 (log ε 3.91), 358 (4.35), 286 (4.48), 243 nm (4.54); ^{1}H NMR δ=2.91 (3H, s, Ac), 8.13 (1H, d, J=8.1 Hz, H_3), 8.15 (1H, t, J=7.8 Hz, H_7), 8.25 (1H, d, J=9.4 Hz, H_9), 8.33 (1H, dd, J=7.8, 1.1 Hz, H_8), 8.41 (1H, d, J=8.1 Hz, H_2), 8.46 (1H, s, H_4), 8.68 (1H, dd, J=7.8, 1.1 Hz, H_6), 9.05 (1H, d, J=9.4 Hz, H_{10}); ^{13}C NMR δ=30.4 (Ac), 120.8 (C_5), 123.4 (C_3), 124.0 (C_{10b}), 124.9 (C_{10}), 125.0 (C_{10c}), 126.3 (C_6), 126.9 (C_7), 127.2 (C_8), 127.4 (C_2), 129.4 (C_{10a}), 129.6 (C_{5a}, C_9), 130.4 (C_4), 130.5 (C_{8a}), 132.4 (C_1), 133.8 (C_{3a}), 201.9 (CO); MS m/z 324, 322 (M^+), 309, 307, 281, 279, 200. Anal. Found: C, 67.10; H, 3.50%. Calcd for $C_{18}H_{11}OBr$: C, 66.90; H, 3.43%.

Bromination of 13. To a solution of **13** (124 mg, 0.5 mmol) in CH_2Cl_2 (15 ml), Br_2 (0.6 mmol) in CH_2Cl_2 (12 ml) was added at r. t. for 3 h, and the mixture was stirred for 53 h. The reaction mixture was washed with water, dried over anhydrous Na_2SO_4, and diluted to 100 ml. To a part (1 ml) of the solution anthraquinone (as internal standard, retention volume, V_R=15.40 ml) was added, and analyzed by HPLC (mobile phase, hexane/THF=99/1); **14** (6.79 ml, sensitivity 1.86 mol/mol), **15** (7.49 ml, 1.97), and **16** (12.37 ml, 2.73) were confirmed. The residual portion was separated by preparative HPLC and each fraction was recrystallized from hexane to give **14**, **15**, and **16**.

14: Mp 238—240 °C (MeCN) (lit,[25] mp 157—158 °C); IR 1510, 1331 cm^{-1}; UV (MeCN) λ_{max} 411 (log ε 4.05), 377 (4.04), 291 (4.17), 237 nm (4.62); ^{1}H NMR δ=8.18 (1H, t, J=7.6 Hz, H_7), 8.36 (1H, d, J=7.6 Hz, H_6), 8.36 (1H, d, J=9.6 Hz, H_5), 8.38 (1H, d, J=9.2 Hz, H_9), 8.40 (1H, d, J=7.6 Hz, H_8), 8.52 (1H, d, J=9.2 Hz, H_{10}), 8.87 (1H, d, J=9.6 Hz, H_4), 8.95 (1H, s, H_2); MS m/z 327, 325 (M^+), 297, 295, 200. Anal. Found: C, 59.07; H, 2.64; N, 4.21%. Calcd for $C_{16}H_8O_2NBr$: C, 58.92; H, 2.47; N, 4.29%.

15: Mp 259—260 °C (MeCN) (lit,[14] mp 248—250 °C); IR 1504, 1331 cm^{-1}; UV (MeCN) λ_{max} 401 (log ε 4.15), 380 (4.14), 288 (4.16), 241 nm (4.69); ^{1}H NMR δ=8.18 (1H, d, J=8.2 Hz, H_3), 8.23 (1H, d, J=9.4 Hz, H_9), 8.26 (1H, d, J=8.7 Hz, H_8), 8.31 (1H, d, J=10.0 Hz, H_4), 8.38 (1H, d, J=8.2 Hz, H_2), 8.66 (1H, d, J=9.4 Hz, H_{10}), 8.71 (1H, d, J=8.7 Hz, H_7), 8.92 (1H, d, J=10.0 Hz, H_5); MS m/z 327, 325 (M^+), 297, 295, 281, 279, 200. Anal. Found: C, 58.86; H, 2.62; N, 4.42%. Calcd for $C_{16}H_8O_2NBr$: C, 58.92; H, 2.47; N, 4.29%.

16: Mp 250—251 °C (MeCN) (lit,[14] mp 242—243 °C); IR 1511, 1332 cm^{-1}; UV (MeCN) λ_{max} 403 (log ε 4.11), 378 (4.12), 290 (4.21), 236 nm (4.69); ^{1}H NMR δ=8.14 (1H, d, J=8.8 Hz, H_5), 8.17 (1H, d, J=8.4 Hz, H_3), 8.22 (1H, d, J=8.8 Hz, H_4), 8.24 (1H, d, J=8.5 Hz, H_6), 8.36 (1H, d, J=8.4 Hz, H_2), 8.70 (1H, d, J=9.8 Hz, H_{10}), 8.71 (1H, d, J=8.5 Hz, H_7), 8.99 (1H, d, J=9.8 Hz, H_9); MS m/z 327, 325 (M^+), 297, 295, 281, 279, 200. Anal. Found: C, 59.16; H, 2.72; N, 4.34%. Calcd for $C_{16}H_8O_2NBr$: C, 58.92; H, 2.47; N, 4.29%.

As an another experiment, bromine (0.2 ml, 7.8 mmol) was added to **13** (124 mg, 0.5 mmol) in AcOH (8 ml) at 100 °C for 30 min, and the mixture was stirred at 100 °C for an additional 2 h.

Bromination of 17. To a solution of **17** (70 mg, 0.25 mmol) in CH_2Cl_2 (8 ml), Br_2 (0.3 mmol) in CH_2Cl_2 (8 ml) was added at r. t. for 20 min, and the mixture was stirred for an additional 5 h. The reaction mixture was treated as usual, and submitted to ^{1}H NMR. The spectrum showed the characteristic signals of **18** at δ=8.41 (2H, d, J=9.0 Hz, H_4, H_{10}) and 8.53 (1H, s, H_2), in addition to the authentic signals at δ=8.45 (d, H_{10} of **17**), 8.48 (d, H_5, H_{10} of **19**), and 8.56 (s, H_9, H_{10} of **20**). The amounts of **18**, **19**, and **20** were determined from ratio of the area of these signals. The residual portion was separated by fractional recrystallization from hexane to give **19** and **20**.

19: Mp 230—231 °C (PhH) (lit,[15] mp 230—231 °C); UV λ_{max} 383 (log ε 3.04), 361 (3.94), 353 (4.73), 336 (4.54), 321 (4.13), 280 (4.68), 269 (4.41), 259 (4.04), 246 (4.80), 236 nm (4.61); ^{1}H NMR δ=8.08 (2H, d, J=8.3 Hz, H_3, H_8), 8.15 (2H, d, J=9.3 Hz, H_4, H_9), 8.22 (2H, d, J=8.3 Hz, H_2, H_7), 8.48 (2H, d, J=9.3 Hz, H_5, H_{10}); MS m/z 362, 360, 358 (M^+).

20: Mp 210—211 °C (PhH) (lit,[15] mp 210—211 °C); UV λ_{max} 383 (log ε 2.93), 355 (4.64), 338 (4.47), 323 (4.09), 307 (3.69), 281 (4.63), 270 (4.37), 260 (4.05), 245 nm (4.74); ^{1}H NMR δ=8.06 (2H, s, H_4, H_5), 8.06 (2H, d, J=8.2 Hz, H_3, H_6), 8.28 (2H, d, J=8.2 Hz, H_2, H_7), 8.56 (2H, s, H_9, H_{10}); ^{13}C NMR δ=120.4 (C_1, C_8), 125.1 (C_{10b}, C_{10c}), 126.1 (C_3, C_6), 127.3 (C_4, C_5), 127.4 (C_9, C_{10}), 129.4 (C_{8a}, C_{10a}), 130.5 (C_{3a}, C_{5a}), 130.6 (C_2, C_7); MS m/z 362, 360, 358 (M^+).

Bromination of 6. To a solution of **6** (115 mg, 0.5 mmol) in CH_2Cl_2 (15 ml) in the presence of Fe (15 mg), Br_2 (0.6 mmol) in CH_2Cl_2 (10 ml) was added at −3—3 °C for 5.5 h. The reaction mixture was treated as usual, and determined the amounts of **6**, **21**, and **22**, using ^{1}H NMR by comparison with the literature.[21]

Bromination of 26. To a mixture of **26** (115 mg, 0.5 mmol) and Fe (30 mg) in CH_2Cl_2 (10 ml), Br_2 (0.6 mmol) in CH_2Cl_2 (6 ml) was added at −1—2 °C for 3 h. The reaction mixture was treated as usual, and determined the amounts of **26**, **33**, and **34** using ^{1}H NMR. The residual part was treated with preparative HPLC (hexane) to afford **33** and **34**.

33: Mp 132—133 °C (EtOH); UV λ_{max} 378 (log ε 2.85), 348 (4.61), 331 (4.47), 317 (4.12), 279 (4.66), 268 (4.42), 244

nm (4.83); ^{1}H NMR δ=1.58 (3H, t, J=7.5 Hz, Me), 3.38 (2H, q, J=7.5 Hz, CH_2), 7.97 (1H, d, J=8.2 Hz, H_1), 8.02 (1H, d, J=8.9 Hz, H_{10}), 8.08 (1H, d, J=7.8 Hz, H_7), 8.10 (1H, d, J=8.9 Hz, H_9), 8.22 (1H, d, J=8.2 Hz, H_2), 8.23 (1H, dd, J=7.8, 0.9 Hz, H_8), 8.31 (1H, s, H_4), 8.44 (1H, dd, J=7.8, 0.9 Hz, H_6); ^{13}C NMR δ=14.5 (Me), 26.6 (CH_2), 119.4 (C_3), 121.7 (C_6), 123.7 (C_4), 124.4, 124.7 (C_1), 124.8, 125.5 (C_8), 126.1 (C_7), 126.8 (C_{10}), 127.7 (C_9), 129.4, 129.9 (C_2), 130.1, 130.3, 131.5, 141.0 (C_5); MS m/z 310, 308 (M^+), 295, 293. Anal. Found: C, 69.83; H, 4.39%. Calcd for $C_{18}H_{13}Br$: C, 69.92; H, 4.23%.

34: Mp 88—90 °C (EtOH); UV λ_{max} 378 (log ε 2.94), 347 (4.60), 330 (4.45), 316 (4.10), 279 (4.64), 268 (4.41), 245 nm (4.80); ^{1}H NMR δ=1.56 (3H, t, J=7.4 Hz, Me), 3.32 (2H, q, J=7.4 Hz, CH_2), 7.90 (1H, s, H_4), 7.98 (1H, d, J=8.2 Hz, H_3), 8.08 (1H, t, J=7.8 Hz, H_7), 8.18 (1H, d, J=9.3 Hz, H_9), 8.22 (1H, d, J=8.2 Hz, H_2), 8.24 (1H, dd, J=7.8, 1.0 Hz, H_8), 8.42 (1H, dd, J=7.8, 1.0 Hz, H_6), 8.44 (1H, d, J=9.3 Hz, H_{10}); ^{13}C NMR δ=14.2 (Me), 26.2 (CH_2), 119.0 (C_1), 121.8 (C_6), 124.3, 124.6 (C_4), 124.8, 125.0 (C_3), 125.3 (C_8), 125.6 (C_{10}), 126.1 (C_7), 129.0 (C_9), 129.3, 129.9 (C_2), 130.5, 130.6, 131.3, 139.4 (C_5); MS m/z 310, 308 (M^+), 295, 293. Anal. Found: C, 69.87; H, 4.43%. Calcd for $C_{18}H_{13}Br$: C, 69.92; H, 4.23%.

Competitive Acetylation. Acetyl chloride (0.02 ml, 0.28 mmol) was added at once to a stirred mixture of **2** (12.2 mg, 0.05 mmol), **23** (12.2 mg, 0.05 mmol), $AlCl_3$ (76.6 mg, 0.57 mmol), and hexacosane (10.0 mg, as internal standard) in CH_2Cl_2 (5 ml) at r. t. A small portion of the mixture was taken out at one min intervals and analyzed by GLPC. Each of the conversions was plotted and the ratio of the reaction rates of **2** and **23** at time=0 was calculated from each slope, giving 0.37 for **2/23**. The average ratio of several trials was 0.37/1.00 for **2/23**.

Similarly, the combination of **1/10**, **1/17**, **1/23**, **1/29**, **2/6**, and **23/26** was examined.

Competitive Bromination. Bromine (0.04 mmol) was added at once to a stirred mixture of **1** (20.2 mg, 0.1 mmol), **13** (24.7 mg, 0.1 mmol), and nitrobenzene (19.0 mg, 0.15 mmol, as an internal standard) in CH_2Cl_2 (40 ml) at −8 °C. The reaction mixture was analyzed by HPLC giving the ratio of 0.024/1.00 for **13/1**. The other sets, **1/6**, **1/26**, **13/17**, were also examined.

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