Electrophilic Aromatic Substitution of 3-Alkoxy-6-alkyl-2-cyano-4,5,6a,11-tetraazabenzo[*a*]fluorene with Orthoesters

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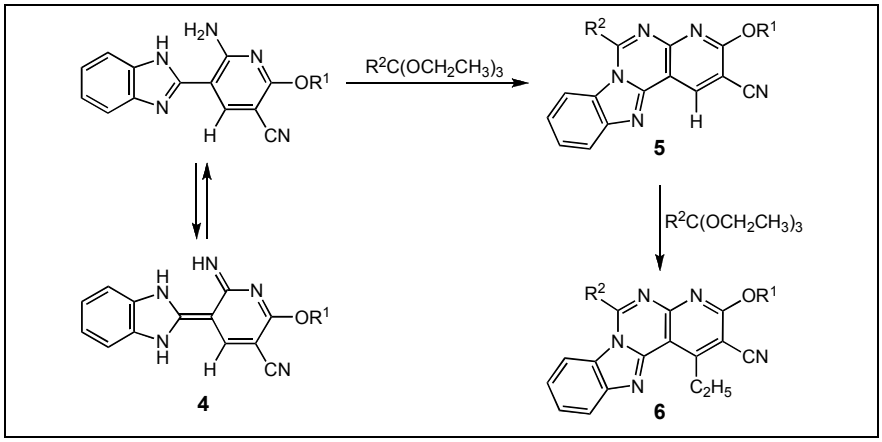

Fused tetracycles, 6-alkyl-3-alkoxy-2-cyano-4,5,6a,11-tetraazabenzo[*a*]fluorene derivatives (**5a**,**b**,**c**,**d**,**e**,**f**), are synthesized from 2-alkoxy-5-(benzimidazol-2-ylidene)-3-cyano-6-imino-5,6-dihydro-pyridines (**4b**,**c**), and when refluxed in ethyl orthoacetate or ethyl orthopropionate, the elecrophilic aromatic substitution occurs at the *ortho* position of the cyanopyridine ring in the fused tetracycles (**5b**,**c**,**e**,**f**) to afford 6-alkyl-3-alkoxy-2-cyano-1-ethyl-4,5,6a,11-tetraazabenzo[*a*]fluorenes(**6b**,**c**,**e**,**f**).

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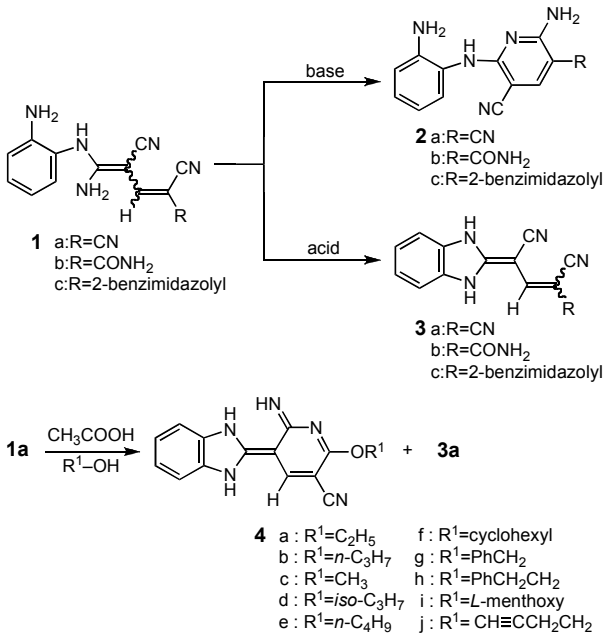
INTRODUCTION

In a previous paper, [1] we studied a ring closure of 4-substituted 1-amino-1-(2-aminoanilino)-2,4-dicyano-buta-1,3-diene (**1**) from the standpoint of Baldwin's rule [2] (Scheme 1). Compound (**1**) was selectively cyclized to 3-substituted 2-amino-6-(2-amionoanilino)-5-cyanopyridine (**2**) or 2-substituted 4-(benzimidazol-2-ylidene)-2-pentenedinitrile (**3**) under basic or acidic conditions, respectively. Specifically, when 1-amino-1-(2-amino-anilino)-2,4,4-tricyanobuta-1,3-diene (**1a**) was heated in acetic acid in the presence of methanol, ethanol, *n*-propyl alcohol, isopropyl alcohol, *n*-butyl alcohol, cyclohexanol, benzyl alcohol, phenetyl alcohol, *L*-menthol, or 1-butyn-4-ol, 2-alkoxy-5-(benzimidazol-2-ylidene)-3-cyano-6-imino-5,6-dihydropyridines (**4a-j**) were obtained along with 4-(benzimidazol-2-ylidene)-2-cyano-2-pentene-dinitrile (**3a**).

Scheme 1



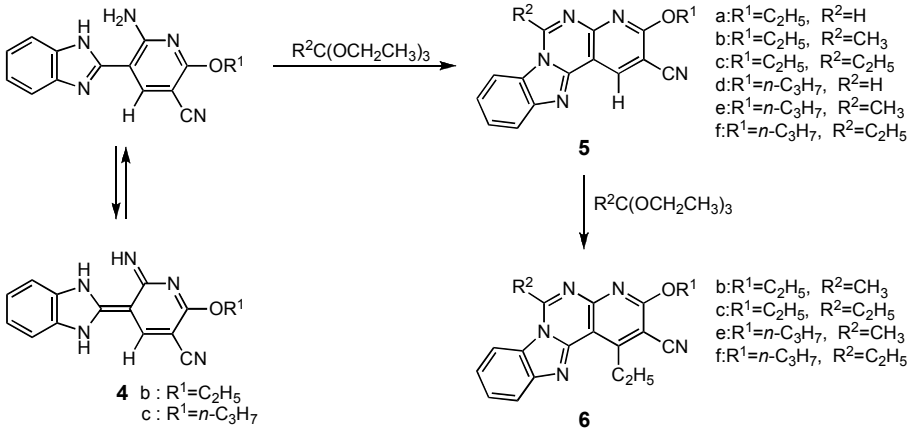
RESULTS AND DISCUSSION

In continuation of this study, we synthesized the fused tetracycles, 6-substituted 3-alkoxy-2-cyano-4,5,6a,11-tetraazabenzo[*a*]fluorenes (**5a-f**), by refluxing **4b,c** in triethyl orthoformate, triethyl orthoacetate, or triethyl orthopropionate, respectively (Scheme 2). When the reaction time was prolonged, compounds (**5b,c,e,f**) were gradually converted to 6-substituted 3-alkoxy-2-cyano-1-ethyl-4,5,6a,11-tetraazabenzo[*a*]fluorenes (**6b,c,e,f**),

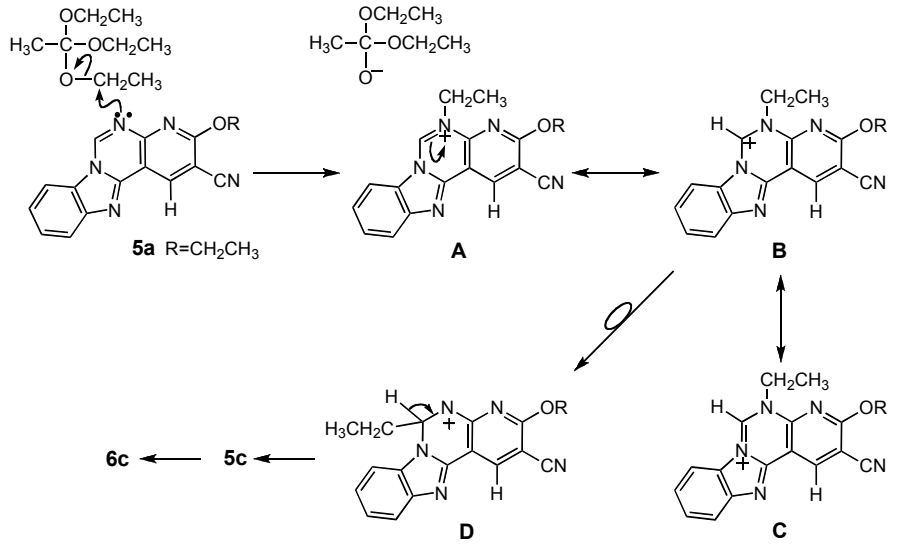
respectively. In fact, we confirmed that compounds (**5b**) were converted to **6b** in 12% yield by refluxing in triethyl orthoacetate. However, similar substitution reactions did not occur in both **5a** and **5d**. The electrophilic aromatic substitution of **5b,c,e,f** to **6b,c,e,f** is much more interesting because it is well known that 2- and 4-positions of pyridine are, in general, inactive against the substitution reaction due to the electron deficiency. Since the fused tetracycles (**5b,c,e,f**) have the electron-withdrawing group in the pyridine ring, the electrophilic aromatic substitutions at the pyridine ring might be much more difficult. This is why we studied the mechanisms of the substitution reactions.

also compound (**5b**) could not be converted to **6b** under refluxing in triethyl orthoformate. These results indicate that both alkyl groups (methyl and ethyl) at 6-position of the fused tetracycles (**5**) and *C*-alkylated ortho-acid triethyl esters are essential for the ethylation at 1-position of **5** by the reaction of electrophilic aromatic substitution. Whereas **5a** was converted to **6c** under refluxing in triethyl orthoacetate in place of triethyl orthoformate (Scheme 3). Since both positions at 1 and 6 of **5a** are electron deficient, it is difficult for the ethyl group as electrophile to attack at those positions directly. The electrophile may just attack at 5 position giving rise to quaternary ions (**A**) instead, which are resonanced to (**B**)

Scheme 2



Scheme 3



It is worth noting that compounds (**5a**) and (**5d**) could not be converted to 2-cyano-1-ethyl-3-ethoxy-4,5,6a,11-tetraazabenzo[*a*]fluorene (**6a**) and 2-cyano-1-ethyl-3-propoxy-4,5,6a,11-tetraazabenzo[*a*]-fluorene (**6d**), respectively, under refluxing in triethyl orthoformate, and

and (**C**). The migration of the ethyl group at 5 position of **B** gives rise to ions (**D**), followed by the deprotonation provides **5c** which was converted to **6c** under refluxing in ethyl orthoacetate as described above. Thus the *C*-alkyl inductive effect of ortho-acid triethyl esters was also

reported in the studies of their hydrolytic rates. For example, the relative rates of hydrolysis of triethyl orthoacetate and orthopropionate are 38.5 and 24.3 times as fast as triethyl orthoformate, respectively [3]. When an electrophilic aromatic substitution is performed, two possibilities for the intermediary complex exist, namely, a π-complex and a σ-complex (arenium ions). Since electron-donating groups, in general, greatly tabilize σ-complexes but only slightly stabilize π-complexes [4], the electrophile in the substitution reactions of **5b,c,e,f** to **6b,c,e,f** might be directed to the *ipso* position [5] giving rise to arenium ions (**E**) for which it is able to write low-energy canonical forms, (**F**) and (**G**) (Scheme 4). In contrast, when the electrophile attacks at the *ortho* position to the cyano group, another arenium ions (**H**) is formed as a direct intermediary product, which also has a resonanced form (**I**). However, **I** is not a low-energy canonical form in which the benzene ring of **5b,c,e,f** has a complete sextet. Therefore, it may be reasonable that the ethylation of **5b,c,e,f** proceeds *via* the arenium ions (**E**) which can undergo a 1,2-migration [6] to provide the ions (**H**), followed by loss of the proton to give **6b,c,e,f**.

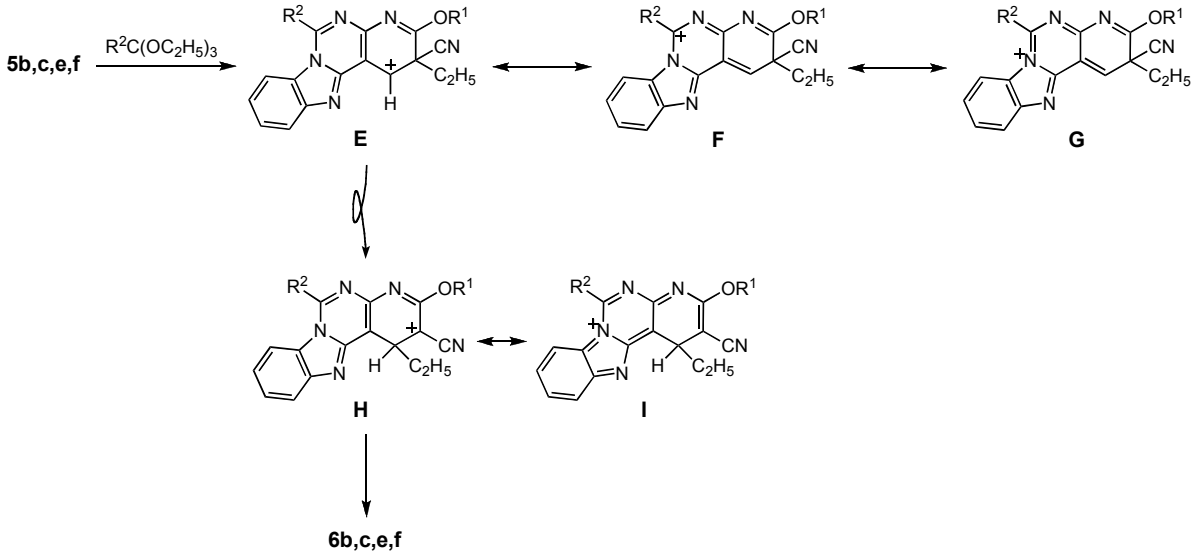
triethylorthopropionate. The key compound of the reaction is thought to be the intermediary arenium ions (**E**) which are formed through the *ipso*-attack of the electrophile.

EXPERIMENTAL

All melting points were determined on a Yazawa micro-melting point BY-2 apparatus and are uncorrected. The MS spectra were recorded using a JMS D-100. Elemental analyses were performed using a Perkin-Elmer 240B instrument. The IR spectra (potassium bromide) were recorded on a JASCO IRA-1 spectrophotometer, and all compounds showed the characteristic absorption bands at 2215-2230 cm^{-1} due to the cyano group. The NMR spectra were determined with a Varian VXR-300 spectrometer using deuteriodimethyl sulfoxide or deuteriochloroform as solvent and tetramethylsilane as the internal standard.

General Procedure for Synthesizing 3-Alkoxy-2-cyano-4,5,6a,11-tetraazabenzo[*a*]fluorene (5a,d). A suspension of **4b** (0.2 g, 0.72 mmol) in 30 mL (0.18 mol) of triethyl orthoformate was refluxed for 10 h. After having been allowed to cool, precipitates were filtered by suction filtration and recrystallized from ethanol/chloroform (1/1) to provide **5a** (73 mg, 35%): mp

Scheme 4



Meanwhile, no Friedel-Crafts ethylation of **5b** occurred using iodoethane and aluminum chloride in chloroform as solvent. This result might be interpreted as the reaction temperatures which depend on the reaction solvents used. The boiling points of all ortho-acid triethyl esters used here are above 142°C, which is much higher than those of iodoethane (b.p. 69~73°C) and chloroform (b.p. 60.5~61.5°C).

In conclusion, the electrophilic aromatic substitution at the 1-position of the tetraazabenzo[*a*]fluorene (**5b,c,e,f**) was accomplished with triethyl orthoacetate and

313~315°C; ^{1}H-NMR: 9.63 (s, 1H, CH), 8.86 (s, 1H, CH), 7.63 (m, 2H, arom), 7.23 (m, 2H, arom), 4.53 (q, 2H, CH_2, *J*=7 Hz), 1.37 (t, 3H, CH_3, *J*=7 Hz). ^{13}C-NMR: 162.97 (CH), 144.52, 142.95 (CH), 141.51, 126.43, 123.32, 122.50 (2C, arom), 119.35, 115.41 (2C, arom), 112.44, 108.67, 64.05 (CH_2), 63.89, 14.18 (CH_3); MS m/z 289 (M^+); Anal. Calcd for $C_{16}H_{11}N_5O•1/8H_2O$: C, 65.92; H, 3.89; N, 24.06. Found: C, 66.08; H, 3.93; N, 24.06. **5d** (81 mg, 39%): mp >310 °C; ^{1}H-NMR: 10.00 (s, 1H, CH), 9.34 (s, 1H, CH), 8.41 (m, 1H, arom), 7.93 (m, 1H, arom), 7.50~7.63 (m, 2H, arom), 4.52 (t, 2H, $OCH_2CH_2CH_3$, *J*=6.5 Hz), 1.84 (q, 2H, $OCH_2CH_2CH_3$, *J*=7 Hz), 1.03 (t, 3H, $OCH_2CH_2CH_3$, *J*=7.3 Hz); MS m/z 303 (M^+); Anal.

Calcd for $C_{17}H_{13}N_5O•1/8H_2O$: C, 66.82; H, 4.37; N, 22.92. Found: 67.03; H, 4.41; N, 22.58

2-Cyano-3-ethoxy-6-methyl-4,5,6a,11-tetraazabenzo[*a*]-fluorene (5b) and 2-Cyano-3-ethoxy-1-ethyl-6-methyl-4,5,6a, 11-tetraazabenzo[*a*]fluorene (6b). Method A. A suspension of **4b** (0.15 g, 0.54 mmol) in 20 mL (0.109 mol) of triethyl orthoacetate was refluxed for 5 h. After having been allowed to cool, precipitates were filtered by suction filtration and purified by silica gel column chromatography (chloroform) to provide pure **5b** (55 mg, 34%): mp 286-287 ˚C [recrystallized from ethanol/chloroform(1/1)]; ^{1}H-NMR: 9.29 (s, 1H, CH), 8.26 (d, 1H, arom, J=8.5 Hz), 7.93 (d, 1H, arom, J=8 Hz), 7.60 (m, 1H, arom), 7.52 (m, 1H, arom), 4.59 (q, 2H, CH_2CH_3, J=7.2 Hz), 3.12 (s, 3H, CH_3), 1.44 (t, 3H, CH_2CH_3, J=7 Hz). ^{13}C-NMR: 163.84, 155.72, 153.52, 146.03, 144.24 (arom), 141.41 (=CH), 128.96 (arom), 126.05 (CH, arom), 123.34 (CH, arom), 119.39 (CH, arom), 115.59 (CH, arom), 114.78, 107.13, 63.94 (OCH_2CH_3), 24.12 (CH_3), 14.19 (OCH_2CH_3); MS m/z 303 (M^+); Anal. Calcd for $C_{17}H_{13}N_5O•1/4H_2O$: C, 66.33; H, 4.42; N, 22.75. Found: C, 66.39, H, 4.48; N, 22.69.

Method B. A suspension of **4b** (0.15 g, 0.54 mmol) in 20 mL (0.109 mol) of triethyl orthoacetate was refluxed for 13 h. After having been allowed to cool, precipitates were filtered by suction filtration and purified by silica gel column chromatography (chloroform) to provide **5b** (27 mg, 15%) and **6b** (19 mg, 10%): mp 296-298 ˚C [recrystallized from ethanol/ chloroform (1/1)]; ^{1}H-NMR: 8.02 (m, 2H, arom), 7.61 (m, 1H, arom), 7.50 (m, 1H, arom), 4.70 (q, 2H, OCH_2CH_3, *J*=7.1 Hz), 3.96 (q, 2H, CH_2CH_3, *J*=7.3 Hz), 3.27 (s, 3H, CH_3), 1.52 (t, 3H,OCH_2CH_3, *J*=7 Hz), 1.45 (t, 3H, CH_2CH_3, *J*=7.5 Hz). ^{13}C-NMR: 164.44, 162.96, 154.22, 153.88, 146.04, 145.11 (arom), 128.11 (arom), 126.75 (CH, arom), 123.66 (CH, arom), 120.75 (CH, arom), 114.07 (CH, arom), 106.32, 97.95, 76.57, 64.20 (OCH_2CH_3), 26.93 (CH_2CH_3), 24.62 (CH_3), 14.39 (OCH_2CH_3), 13.97 (CH_2CH_3); MS m/z 331 (M^+); Anal. Calcd for $C_{19}H_{17}N_5O•1/4H_2O$: C, 67.94; H, 5.25; N, 20.85. Found: C, 67.87; H, 5.24; N, 20.61.

2-Cyano-3-ethoxy-6-ethyl-4,5,6a,11-tetraazabenzo[*a*]fluor-ene (5c). A suspension of **4b** (0.2 g, 0.72 mmol) in 20 mL (0.0994 mol) of triethyl orthopropionate was refluxed for 12 h. After having been allowed to cool, precipitates were collected by suction filtration and purified by silica gel column chromatography (chloroform) to provide pure **5c** (74 mg, 33%): mp 268-270 ˚C [recrystallized from ethanol/chloroform (1/1)]; ^{1}H-NMR: 9.31 (s, 1H, CH), 8.26 (m, 1H, arom), 7.94 (m, 1H, arom), 7.61 (m, 1H, arom), 7.52 (m, 1H, arom), 4.61 (q, 2H, CH_2CH_3, *J*=7 Hz), 3.57 (q, 2H, CH_2CH_3, *J*=7.2 Hz), 1.49 (t, 3H, CH_2CH_3, *J*=7 Hz), 1.44 (t, 3H, CH_2CH_3, *J*=7 Hz). ^{13}C-NMR: 194.11, 163.92, 159.21, 153.44, 144.30, 141.45, 128.62, 125.99, 123.37, 119.45, 115.90, 114.82, 109.92, 64.00, 29.08, 14.22, 9.67; MS m/z 317 (M^+); Anal. Calcd for $C_{18}H_{15}N_5O$: C, 68.13; H, 4.76; N, 22.07. Found: C, 68.23; H, 4.82; N, 21.87.

2-Cyano-3-ethoxy-1,6-diethyl-4,5,6a,11-tetraazabenzo[*a*]-fluorine (6c). A suspension of **4b** (0.2 g, 0.72 mmol) in 20 mL (0.0994 mol) of triethyl orthopropionate was refluxed for 24 h. After having been allowed to cool, precipitates were collected by suction filtration and purified by silica gel column chromatography (chloroform) to provide **6c** (87 mg, 35%): mp 261 ˚C [recrystallized from ethanol/chloroform (1/1)]; ^{1}H-NMR: 7.98 (dd ,2H, arom, *J*=8.8 Hz, 8.8 Hz), 7.59 (dt, 1H, arom, *J*=1 Hz, 7 Hz), 7.49 (dt, 1H, arom, *J*=1 Hz, 7 Hz), 4.70 (q, 2H, OCH_2CH_3, *J*=7 Hz), 3.94 (q, 2H, 1-CH_2CH_3, *J*=7.3 Hz), 3.53 (q, 2H, 6-CH_2CH_3, *J*=7.3 Hz), 1.63 (t, 3H, 6-CH_2CH_3, *J*=7.5 Hz), 1.52 (t, 3H, OCH_2CH_3, *J*=7 Hz), 1.43 (t, 3H, 1-CH_2CH_3, *J*=7.3 Hz). ^{13}C-NMR: 164.44 (3), 162.89 (1), 157.93 (6), 154.27, 146.26, 145.12 (6b or 10a), 127.43 (6b or 10a), 126.12 (8 or 9), 123.67 (8 or 9), 120.72 (7 or 10), 114.36 (7 or 10), 114.20, 106.30, 97.81, 64.12 (OCH_2CH_3), 29.67 (6-CH_2CH_3), 26.91 (1-CH_2CH_3), 14.36 (OCH_2CH_3), 13.93 (1-CH_2CH_3), 10.43 (6-CH_2CH_3); MS m/z 345 (M^+); Anal. Calcd for $C_{20}H_{19}N_5O$: C, 69.55; H, 5.54; N, 20.28. Found: C, 69.30; H, 5.51; N, 20.15.

Conversion of 5b to 6b. A suspension of **5b** (30 mg 0.099 mmol) in 7 mL (38.15 mmol) of triethyl orthoacetate was refluxed for 12 h. The solution was concentrated under a reduced pressure, and precipitates were purified by silica gel column chromatography (chloroform) to provide 6b in 12% yield (4 mg, 0.012 mmol).

Conversion of 5a to 6c. A suspension of **5a** (30 mg, 0.104 mmol) in 7 mL (38.15 mmol) of triethyl orthoacetate was refluxed for 11 h. The solution was concentrated under a reduced pressure, and precipitates were purified by silica gel colum chromatography (chloroform) to provide 6c in 11% yield (4 mg, 0.0116 mmol).

General Procedure for Synthesizing 6-Alkyl-2-cyano-3-propoxy-4,5,6a,11-tetraazabenzo[*a*]fluorine (5e,f) and 1,6-Alkyl-2-cyano-3-propoxy-4,5,6a,11-tetraazabenzo[*a*]fluorine (6e,f). A suspension of **4c** (0.15 g, 0.51 mmol) in 20 mL (0.109 mol) of triethyl orthoacetate was refluxed for 14 h. After having been allowed to cool, precipitates were collected by suction filtration and purified by silica gel column chrom-atography (chloroform) to provide **5e** (37 mg, 23%): mp 255 ˚C [recrystallized from chloroform/ethanol (1/1)]; ^{1}H-NMR: 9.29 (s, 1H, CH), 8.26 (m, 1H, arom), 7.94 (m, 1H, arom), 7.61 (m, 1H, arom), 7.52 (m, 1H, arom), 4.49 (t, 2H, $OCH_2CH_2CH_3$, *J*=6.5 Hz), 3.20 (s, 3H, CH_3), 1.83 (tq, 2H, $OCH_2CH_2CH_3$, *J*=7 Hz, 7 Hz), 1.02 (t, 3H, $OCH_2CH_2CH_3$, *J*=7.5 Hz). ^{13}C-NMR: 163.97, 155.71, 153.51, 146.03, 144.24, 142.63, 141.39, 128.96, 126.05, 124.19, 123.35, 119.38, 115.59, 114.71, 107.16, 104.42, 96.06, 95.64, 69.28, 24.11, 21.55, 10.21; MS m/z 317 (M^+); Anal. Calcd for $C_{18}H_{15}N_5O$: C, 68.13; H, 4.76; N, 22.07. Found: C, 67.96; H, 4.82; N, 21.87 and **6e** (2.3 mg, 2.3%): mp 206-208 ˚C; ^{1}H-NMR: 8.25 (d, 1H, arom, *J*=8.5 Hz), 7.93 (d, 1H, arom, *J*=8 Hz), 7.53 (m, 1H, arom), 7.49 (m, 1H, arom), 4.45 (t, 2H, $OCH_2CH_2CH_3$, *J*=7.5 Hz), 3.80 (q, 2H, 1-CH_2CH_3, *J*=7.5 Hz), 2.46 (s, 3H, 6-CH_3), 1.82 (tq, 2H, $OCH_2CH_2CH_3$, *J*=7 Hz, 7 Hz), 1.33 (t, 3H, 1-CH_2CH_3, *J*=7.5 Hz), 1.02 (t, 3H, $OCH_2CH_2CH_3$, *J*=7.3 Hz). ^{13}C-NMR: 170.08, 163.80 (3), 161.49, 154.29, 146.51, 144.36 (6b or 10a), 127.91 (6b or 10a), 125.79 (CH, arom), 123.42 (CH, arom), 119.65 (CH, arom), 115.30 (CH, arom), 114.46, 105.1, 95.1, 68.83 ($OCH_2CH_2CH_3$), 26.26 (1-CH_2CH_3), 21.66 ($OCH_2CH_2CH_3$), 20.08 (6-CH_3), 13.77 (1-CH_2CH_3), 10.31 ($OCH_2CH_2CH_3$); MS m/z 345 (M^+); Anal. Calcd for $C_{20}H_{19}N_5O$: C, 69.55; H, 5.54; N, 20.28. Found: C, 69.53; H, 5.98; N, 19.80. **5f** (108 mg, 59%): mp 261-263 ˚C; ^{1}H-NMR:9.25 (s, 1H, CH), 8.23 (d, 1H, arom, *J*=8.5 Hz), 7.92 (d, 1H, arom, *J*=8 Hz), 7.59 (t, 1H, arom, *J*=7.7 Hz), 7.50 (t, 1H, arom, *J*=7.7 Hz), 4.50 (t, 2H, $OCH_2CH_2CH_3$, *J*=6.5 Hz), 3.54 (q, 2H,CH_2CH_3, *J*=7.2 Hz), 1.84 (m, 2H, $OCH_2CH_2CH_3$), 1.48 (t, 3H, CH_2CH_3, *J*=7 Hz), 1.03 (t, 3H, $OCH_2CH_2CH_3$, *J*=7.5 Hz). ^{13}C-NMR: 163.95, 159.05, 153.32, 146.02, 144.22 (arom), 141.26 (=CH), 128.50 (arom), 125.91 (CH, arom), 123.33 (CH, arom), 119.38 (CH, arom), 115.77 (CH, arom), 114.63, 107.11, 96.05, 69.28 ($CH_2CH_2CH_3$), 28.99 (CH_2CH_3), 21.53

($CH_2CH_2CH_3$), 10.16 ($CH_2CH_2CH_3$), 9.57 (CH_2CH_3); MS m/z 331 (M^+); Anal. Calcd for $C_{19}H_{17}N_5O$: C, 68.87; H, 5.17; N, 21.13. Found: C, 68.54; H, 5.31; N, 20.77. **6f** (8 mg, 4%): mp 216-218 °C; ^{1}H-NMR: 8.03 (d, 1H, arom, *J*=8 Hz), 8.01 (d, 1H, arom, *J*=8 Hz), 7.62 (m, 1H, arom), 7.52 (m, 1H, arom), 4.62 (t, 2H, $OCH_2CH_2CH_3$, *J*=6.5 Hz), 3.98 (q, 2H, 1-CH_2CH_3, *J*=7.5 Hz), 3.57 (q, 2H, 6-CH_2CH_3, *J*=7.5 Hz), 1.95 (tq, 2H, $OCH_2CH_2CH_3$, *J*=7.3 Hz,7.3 Hz), 1.66 (t, 3H, 6-CH_2CH_3, *J*=7.5 Hz), 1.47 (t,3H,1-CH_2CH_3,*J*=7.5 Hz), 1.13 (t,3H, $OCH_2CH_2CH_3$, *J*=7.5 Hz). ^{13}C-NMR: 164.61 (3), 162.91 (1), 157.95 (6), 154.30, 146.30, 145.15 (6b or 10a), 127.47 (6b or 10a), 126.12 (CH, arom), 123.69 (CH, arom), 120.75 (CH, arom), 114.38 (CH, arom), 114.15, 106.35, 97.87, 69.74 ($OCH_2CH_2CH_3$), 26.94 (1-CH_2CH_3), 22.11 ($OCH_2CH_2CH_3$), 13.97 (1-CH_2CH_3), 10.45 (2C, 3,6-CH_3); MS m/z 359 (M^+); *Anal.* Calcd for $C_{21}H_{21}N_5O$: C, 70.18; H, 5.89; N, 19.48. Found: C, 69.86; H, 5.84; N, 19.17.

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