

**A CONVENIENT SYNTHETIC METHOD FOR FLUORINE-CONTAINING BENZO[*h*]QUINOLINES FROM 2,4-BIS(TRIFLUOROACETYL)-1-NAPHTHYLAMINE AND KETONES**

Etsuji Okada,\* Norikado Tsukushi, Ting-Kai Huang, Hiroshi Tone, Nobuhiro Gotoh, Hiroshi Takeuchi, and Masaru Hojo

Department of Chemical Science and Engineering, Faculty of Engineering, Kobe University, Kobe 657, Japan

**Abstract** - 2,4-Bis(trifluoroacetyl)-1-naphthylamine (**1**) reacted easily with various ketones in the presence of aqueous ammonia or triethylamine to afford 6-trifluoroacetyl-4-trifluoromethylbenzo[*h*]quinolines (**2**) in moderate to excellent yields.

In recent years much attention has been paid to the development of new methodologies for the syntheses of many kinds of fluorine-containing heterocycles, since these compounds are now widely recognized as important organic materials showing interesting biological activities for their potential use in medicinal and agricultural scientific fields.<sup>1</sup> Previously, we reported that *N,N*-dimethyl-2,4-bis(trifluoroacetyl)-1-naphthylamine undergoes a novel aromatic nucleophilic substitution with various amines, thiols, and alcohols to give the corresponding 2,4-bis(trifluoroacetyl)-1-naphthylamines, sulfides, and ethers in high yields.<sup>2</sup> Later, we succeeded in applying this type of aromatic nucleophilic substitution and the related reactions to the simple syntheses of various naphthalene-fused heterocycles bearing trifluoromethyl groups.<sup>3</sup> In connection with these works, we found recently that 2,4-bis(trifluoroacetyl)-1-naphthylamine (**1**) reacted with various aldehydes in the presence of aqueous ammonia to yield fluorine-containing benzo[*h*]quinazolines<sup>4</sup> and further discovered an efficient access to 3-substituted 6-trifluoroacetyl-4-

trifluoromethylbenzo[*h*]quinolines through the ring forming reaction between *N*-propargyl derivative of **1** and *N*-, *S*- and *O*-nucleophiles.<sup>5</sup> As a part of our systematic research program on the simple syntheses of CF<sub>3</sub>-containing heterocycles, we now describe here the convenient synthesis of 2,3-disubstituted or 2-substituted 6-trifluoroacetyl-4-trifluoromethylbenzo[*h*]quinolines (**2**) by the reaction of **1** with various ketones in the presence of aqueous ammonia or triethylamine. These fluorine-containing benzoquinolines (**2**) are expected to show interesting pharmacological properties as antimicrobial agents and antitumor drugs.<sup>6</sup>

Reaction of **12a** with acetone in the presence of aqueous ammonia proceeded easily under mild conditions to give 6-trifluoroacetyl-4-trifluoromethyl-2-methylbenzo[*h*]quinoline (**2a**) in 87% yield without being accompanied by the corresponding benzo[*h*]quinazoline (**3a**) of which the formation we expected originally on the basis of the reaction of **1** with aldehydes (Table 1).<sup>4</sup> 2,2-Diethyl-6-trifluoroacetyl-4-trifluoromethyl-1,2-dihydrobenzo[*h*]quinazoline (**3b**), however, was formed in 51% yield with 42% yield of benzo[*h*]quinoline (**2b**) in the reaction with 3-pentanone. Separation of the **2b** - **3b** mixtures was easily effected

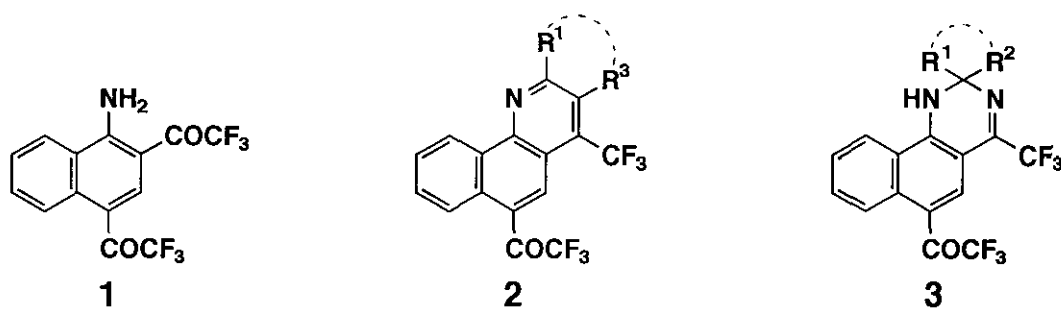


Table 1. Reaction of **1** with Ketones (R<sup>1</sup>COR<sup>2</sup>) in the Presence of Aqueous Ammonia<sup>a)</sup>

Entry	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	$\frac{R^1COR^2}{\text{equiv.}}$	Temp (°C)	Time (h)	Product	Yield (%)
1	Me	Me	H	3	30	48	<b>2a</b>	87
2	Et	Et	Me	5	100 <sup>b)</sup>	24	<b>2b/3b</b>	42/51
3	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	CH <sub>2</sub>	1.2	rt	24	<b>2c</b>	90
4	C <sub>3</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	CH <sub>2</sub>	5	50	24	<b>2d/3d</b>	40/53
5	C <sub>4</sub> H <sub>8</sub>	C <sub>2</sub> H <sub>4</sub>	CH <sub>2</sub>	2	50	24	<b>2e</b>	89
6	Et	Me	H	5	50	24	<b>2f/3f</b>	65/12 <sup>c)</sup>
7	<i>i</i> -Pr	Me	H	5	50	48	<b>2g/3g</b>	84/6
8	Ph	Me	H	5	50	96	<b>2h</b>	92

a) Molar ratio, [**1**] / [NH<sub>3</sub>]=1 / 1.2 ; MeCN was used as a solvent. b) In a sealed tube with PrCN as a solvent. c) With 13% yield of **2f** (R<sup>1</sup>=R<sup>3</sup>=Me).

by chromatography. Next, we examined the reaction of **1** with cyclic ketones in order to synthesize benzo-*[h]*quinolines fused by cycloalkane rings. In the cases of cyclopentanone and cycloheptanone, the desired benzo-*[h]*quinolines (**2c,e**) were exclusively obtained in high yields. However, **1** reacted with cyclohexanone to provide spiro type of benzoquinazoline (**3d**) predominantly. Further, the present reaction was applicable to some unsymmetrical ketones, such as 2-butanone and 3-methyl-2-butanone. In both cases, the desired benzoquinolines (**2f,g**) were obtained in 65-84% yields, together with small amounts of benzoquinazolines (**3f,g**). It is of interest that 13% yield of 2,3-dimethyl derivative (**2f'**) was generated in the reaction with 2-butanone. Quite similarly, reaction of **1** with acetophenone proceeded easily to give selectively 2-phenyl derivative of benzo-*[h]*quinoline (**2h**) in 92% yield. For the sake of avoiding the formation of benzoquinazolines (**3b,d,f,g**), we tried to replace ammonia by triethylamine as a base in the present reaction (Table 2). Expectedly, in the reaction of **1** with 3-pentanone in the presence of

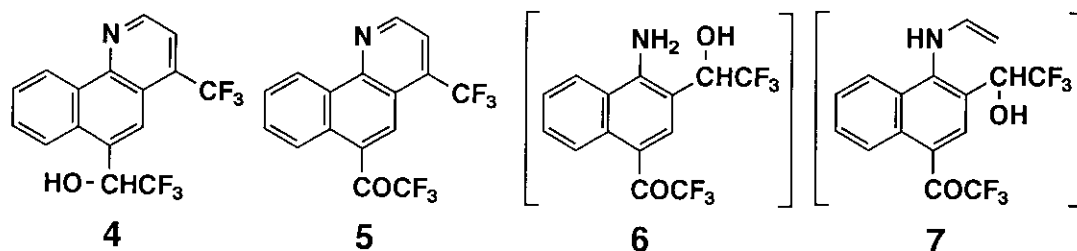
Table 2. Reaction of **1** with Ketones ( $R^1COR^2$ ) in the Presence of Triethylamine<sup>a)</sup>

Entry	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Temp (°C)	Time (d)	Product	Yield (%)
1	Et	Et	Me	50	14	<b>2b</b>	56 <sup>b)</sup>
2	Et	Et	Me	60	10	<b>2b/4</b>	55/19
3	Et	Et	Me	82	5	<b>2b/4</b>	49/32
4	C <sub>3</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	CH <sub>2</sub>	50	10	<b>2d</b>	71
5	Et	Me	H	50	4	<b>2f</b>	60 <sup>c)</sup>
6	<i>i</i> -Pr	Me	H	50	10	<b>2g</b>	67

a) Molar ratio, [1] / [R<sup>1</sup>COR<sup>2</sup>] / [Et<sub>3</sub>N]=1 / 5 / 5 ; MeCN was used as a solvent. b) With 20% yield of Substrate **1**. c) With 14% yield of **2f'** (R<sup>1</sup>=R<sup>3</sup>=Me).

triethylamine at 50 °C for 14 d, the desired benzoquinoline (**2b**) was merely obtained in 56% yield without any formation of benzoquinazoline (**3b**) a nitrogen atom of which arose from ammonia as a base, although 20% of unreacted substrate (**1**) was recovered. Similarly, reactions with cyclohexanone, 2-butanone, and 3-methyl-2-butanone gave the desired benzoquinolines (**2d,f,g**) selectively in 60 - 71% yields. All reactions using triethylamine as a base required more forced reaction conditions than ammonia. Consequently aqueous ammonia is considered to be a better base-catalyst than triethylamine in the present synthetic method for benzo-*[h]*quinolines (**2**). Next, we examined to carry out the reaction of **1** with 3-pentanone at higher temperature (60 and 82 °C) for completing of the reaction, and the desired

benzoquinoline (**2b**) was obtained in 49 - 55% yields with no recovery of substrate (**1**). Interestingly, the unexpected 2,3-unsubstituted benzoquinoline (**4**) was newly formed in 19 - 32% yields. The yield of **4** gradually increased with elevating the reaction temperature. The reaction of **1** with triethylamine without 3-pentanone was undertaken for obtaining the information on the mechanism for the formation of **4**. The run at reflux temperature (90 °C) for 48 h afforded **4** and **5**, considered as a **4**'s precursor, in 32% and 40% yields, respectively. Prolonged (5 d) heating resulted in yielding **4** as a sole product in 66% yield. A speculated reaction mechanism for the formation of **4** is as follows: reduction of **1** by triethylamine is thermally induced to provide amino alcohol (**6**) and *N,N*-diethylvinylamine. Nucleophilic attack of amino group of **6** to the olefinic carbon of *N,N*-diethylvinylamine and subsequent elimination of diethylamine take place to afford intermediary *N*-vinyl derivative (**7**). The formation of **5** is achieved by the ring closure accompanied by dehydration and dehydrogenation in **7**. Finally, trifluoroacetyl group of **5** is reduced again by triethylamine to yield alcohol (**4**). To the best of our knowledge, there have been no reports that triethylamine reduces carbonyl compounds.<sup>7</sup>



The structures of all new compounds (**2-5**) were determined on the basis of their <sup>1</sup>H-NMR and IR spectra, together with elemental analyses.

Thus, the present method provides a facile and convenient access to 2,3-disubstituted or 2-substituted 6-trifluoroacetyl-4-trifluoromethylbenzo[*h*]quinolines which are not easily obtained by other methods. Further utilization of **1** as a useful synthetic block for the preparation of various fluorine-containing naphthalene-fused heterocycles which are potentially medicinally active are now under investigation and will be presented elsewhere.

## EXPERIMENTAL

All melting points were determined on an electrothermal digital melting point apparatus and are

uncorrected. IR spectra were recorded on a Hitachi EPI-G3 spectrophotometer.  $^1\text{H-NMR}$  spectra were obtained with JEOL PMX 60SI instrument using  $\text{CDCl}_3$  as a solvent unless otherwise indicated. All chemical shifts are reported in ppm downfield from internal tetramethylsilane; coupling constants (J) are given in Hz. Elemental analyses were performed by the Microanalyses Center of Kyoto University. Chromatographic separations were carried out on a silica gel column (Wakogel C-200; 100-200 mesh). All reagents were obtained commercially and used without further purification. Final purification of all products for elemental analyses was done by recrystallization.

**Reaction of 2,4-Bis(trifluoroacetyl)-1-naphthylamine (1) with Ketones; General Procedure:**

**In the Presence of Ammonia :** To a solution of **1**<sup>2a</sup> (335 mg, 1 mmol) in MeCN (5 mL) were added the appropriate ketone (1.2 - 5 mmol) and aqueous ammonia (28 wt.%, 73 mg, 1.2 mmol). The mixture was stirred at rt - 100 °C for 24 - 96 h, the solvent was removed under reduced pressure, and  $\text{CH}_2\text{Cl}_2$  (50 mL) was added to the residue. This solution was washed with  $\text{H}_2\text{O}$  (100 mL) and dried ( $\text{Na}_2\text{SO}_4$ ). The solvent was evaporated and the crude product was chromatographed using hexane/benzene (1:1) for **2a-h**, benzene/EtOAc (3:1) for **3b,g**, benzene/EtOAc (7:1) for **3f**, and hexane/benzene (1:3) for **3d** as eluent. The reaction of **1** with 3-pentanone was run in a sealed tube with PrCN as a solvent (see Table 1).

**In the Presence of Triethylamine :** To a solution of **1** (335 mg, 1 mmol) in MeCN (5 mL) were added the appropriate ketone (5 mmol) and triethylamine (506 mg, 5 mmol). The mixture was stirred at 50 - 82 (reflux) °C for 4 - 14 d. Following work-up and purification were carried out in a similar manner as above (see Table 2).

**2a:** mp 107-108 °C (hexane); IR (KBr) 1714, 1604, 1514  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  9.35 (dd, 1H, J=3, 6, H-7), 8.77-8.40 (br, 2H, H-5, -10), 7.85-7.62 (m, 3H, H-3, -8, -9), 2.90 (s, 3H,  $\text{CH}_3$ ). Anal. Calcd for  $\text{C}_{17}\text{H}_9\text{NOF}_6$ : C, 57.15; H, 2.54; N, 3.92. Found: C, 56.97; H, 2.46; N, 3.98.

**2b:** mp 148-149 °C (hexane); IR (KBr) 1712, 1580, 1510  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  9.30 (dd, 1H, J=3, 6, H-7), 8.73-8.39 (m, 2H, H-5, -10), 7.80-7.52 (m, 2H, H-8, -9), 3.01 (q, 2H, J=7,  $\text{CH}_2\text{CH}_3$ ), 2.61 (q, 3H,  $J_{\text{HF}}=3$ ,  $\text{CH}_3$ ), 1.58 (q, 3H, J=6,  $\text{CH}_2\text{CH}_3$ ). Anal. Calcd for  $\text{C}_{19}\text{H}_{13}\text{NOF}_6$ : C, 59.23; H, 3.40; N, 3.64. Found: C, 59.30; H, 3.38; N, 3.60.

**2c:** mp 157-158 °C (hexane/ $\text{CHCl}_3$ ); IR (KBr) 1713, 1602, 1575, 1517  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  9.33-8.98 (m, 1H, H-7), 8.71-8.35 (m, 2H, H-5, -10), 7.81-7.44 (m, 2H, H-8, -9), 3.51-3.08 (m, 4H,  $\text{CH}_2$ ), 2.48-

1.97 (m, 2H, CH<sub>2</sub>). Anal. Calcd for C<sub>19</sub>H<sub>11</sub>NOF<sub>6</sub>: C, 59.54; H, 2.89; N, 3.65. Found: C, 59.51; H, 2.84; N, 3.61.

**2d**: mp 111-112 °C (hexane/benzene); IR (KBr) 1706, 1602, 1572, 1510 cm<sup>-1</sup>; <sup>1</sup>H-NMR 9.20 (dd, 1H, J=3, 6, H-7), 8.68-8.33 (m, 2H, H-5, -10), 8.05-7.60 (m, 2H, H-8, -9), 3.57-2.90 (br, 4H, CH<sub>2</sub>), 2.20-1.80 (br m, 4H, CH<sub>2</sub>). Anal. Calcd for C<sub>20</sub>H<sub>13</sub>NOF<sub>6</sub>: C, 60.46; H, 3.30; N, 3.53. Found: C, 60.45; H, 3.19; N, 3.62.

**2e**: mp 132-133 °C (hexane); IR (KBr) 1717, 1599, 1575, 1511 cm<sup>-1</sup>; <sup>1</sup>H-NMR 9.30-9.00 (m, 1H, H-7), 8.87 (br s, 1H, H-5), 8.59-8.31 (m, 1H, H-10), 7.70-7.41 (m, 2H, H-8, -9), 3.63-2.76 (br, 4H, CH<sub>2</sub>), 1.86 (br s, 6H, CH<sub>2</sub>). Anal. Calcd for C<sub>21</sub>H<sub>15</sub>NOF<sub>6</sub>: C, 61.32; H, 3.68; N, 3.41. Found: C, 61.43; H, 3.62; N, 3.46.

**2f**: mp 106-107 °C (hexane); IR (KBr) 1714, 1605, 1514 cm<sup>-1</sup>; <sup>1</sup>H-NMR 9.45-9.14 (m, 1H, H-7), 8.73-8.35 (m, 2H, H-5, -10), 7.80-7.50 (m, 3H, H-3, -8, -9), 3.15 (q, 2H, J=7, CH<sub>2</sub>), 1.52 (t, 3H, J=7, CH<sub>3</sub>). Anal. Calcd for C<sub>18</sub>H<sub>11</sub>NOF<sub>6</sub>: C, 58.23; H, 2.99; N, 3.77. Found: C, 58.33; H, 2.71; N, 3.68.

**2f'**: mp 119-120 °C (hexane); IR (KBr) 1709, 1602, 1585, 1514 cm<sup>-1</sup>; <sup>1</sup>H-NMR 9.41-9.03 (m, 1H, H-7), 8.67-8.35 (m, 2H, H-5, -10), 7.80-7.47 (m, 2H, H-8, -9), 2.80 (s, 3H, CH<sub>3</sub>-2), 2.57 (q, 3H, J<sub>HF</sub>=3, CH<sub>3</sub>-3). Anal. Calcd for C<sub>18</sub>H<sub>11</sub>NOF<sub>6</sub>: C, 58.23; H, 2.99; N, 3.77. Found: C, 57.99; H, 3.16; N, 3.87.

**2g**: mp 100-101 °C (hexane/benzene); IR (KBr) 1717, 1604, 1565, 1511 cm<sup>-1</sup>; <sup>1</sup>H-NMR 9.45-9.29 (m, 1H, H-7), 8.62-8.41 (m, 2H, H-5, -10), 7.81-7.52 (m, 3H, H-3, -8, -9), 3.45 (heptuplet, 1H, J=7, CH), 1.51 (d, 6H, J=7, CH<sub>3</sub>). Anal. Calcd for C<sub>19</sub>H<sub>13</sub>NOF<sub>6</sub>: C, 59.23; H, 3.40; N, 3.64. Found: C, 59.36; H, 3.28; N, 3.63.

**2h**: mp 148-149 °C (hexane); IR (KBr) 1715, 1595, 1558, 1509 cm<sup>-1</sup>; <sup>1</sup>H-NMR 9.36-9.19 (m, 1H, H-7), 8.63-8.40 (m, 2H, H-5, -10), 8.19-8.03 (m, 3H, H-3, C<sub>6</sub>H<sub>5</sub>), 7.78-7.33 (m, 5H, H-8, -9, C<sub>6</sub>H<sub>5</sub>). Anal. Calcd for C<sub>22</sub>H<sub>11</sub>NOF<sub>6</sub>: C, 63.02; H, 2.64; N, 3.34. Found: C, 62.75; H, 2.50; N, 3.63.

**3b**: mp 130-131 °C (hexane/CH<sub>2</sub>Cl<sub>2</sub>); IR (KBr) 3385, 3350, 1646, 1618, 1595, 1511 cm<sup>-1</sup>; <sup>1</sup>H-NMR 9.30-9.14 (dd, 1H, J=2, 4, H-7), 8.35 (br s, 1H, H-5), 7.97-7.50 (m, 3H, H-8, -9, -10), 5.43 (br s, 1H, NH), 2.27-1.50 (m, 4H, CH<sub>2</sub>CH<sub>3</sub>), 1.01 (t, 6H, J=7, CH<sub>2</sub>CH<sub>3</sub>). Anal. Calcd for C<sub>19</sub>H<sub>16</sub>N<sub>2</sub>F<sub>6</sub>O: C, 56.72; H, 4.01; N, 6.96. Found: C, 56.70; H, 3.97; N, 7.02.

**3d**: mp 167-168 °C (hexane/CHCl<sub>3</sub>); IR (KBr) 3425, 1655, 1615, 1597, 1565, 1515 cm<sup>-1</sup>; <sup>1</sup>H-NMR

9.23-8.90 (dd, 1H,  $J=2, 4$ , H-7), 8.27 (br s, 1H, H-5), 7.93-7.13 (m, 3H, H-8, -9, -10), 5.63 (br s, 1H, NH), 2.50-0.90 (br, 10H, CH<sub>2</sub>). Anal. Calcd for C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>OF<sub>6</sub>: C, 57.97; H, 3.89; N, 6.76. Found: C, 57.69; H, 4.09; N, 6.82.

**3f**: mp 125-126 °C (hexane/CHCl<sub>3</sub>); IR (KBr) 3342, 1639, 1618, 1584, 1529, 1512 cm<sup>-1</sup>; <sup>1</sup>H-NMR 9.20-8.87 (m, 1H, H-7), 8.23 (br s, 1H, H-5), 7.93-7.30 (m, 3H, H-8, -9, -10), 5.50-5.20 (br, 1H, NH), 2.21-1.63 (m, 5H, CH<sub>2</sub>CH<sub>3</sub>, CH<sub>3</sub>), 1.00 (t, 3H,  $J=7$ , CH<sub>2</sub>CH<sub>3</sub>). Anal. Calcd for C<sub>18</sub>H<sub>14</sub>N<sub>2</sub>OF<sub>6</sub>: C, 55.68; H, 3.63; N, 7.21. Found: C, 56.06; H, 3.56; N, 6.90.

**3g**: mp 129-130 °C (hexane/CHCl<sub>3</sub>); IR (KBr) 3443, 1675, 1654, 1618, 1599, 1566, 1517 cm<sup>-1</sup>; <sup>1</sup>H-NMR 9.27-9.03 (m, 1H, H-7), 8.35 (br s, 1H, H-5), 8.00-7.37 (m, 3H, H-8, -9, -10), 5.50 (br s, 1H, NH), 2.12 (heptuplet, 1H,  $J=7$ , CH(CH<sub>3</sub>)<sub>2</sub>), 1.61 (s, 3H, CH<sub>3</sub>), 1.08 (d, 6H,  $J=7$ , CH(CH<sub>3</sub>)<sub>2</sub>). Anal. Calcd for C<sub>19</sub>H<sub>16</sub>N<sub>2</sub>OF<sub>6</sub>: C, 56.72; H, 4.01; N, 6.96. Found: C, 56.65; H, 4.01; N, 6.95.

**Reaction of 1 with Triethylamine**: A solution of **1** (335 mg, 1 mmol) in Et<sub>3</sub>N (3.4 mL, 24.4 mmol) was refluxed with stirring for 48 h. Evaporation and subsequent chromatography using hexane/EtOAc (9/1) as an eluent gave **4** (110 mg, 32%) and **5** (137 mg, 40%).

**4**: mp 130-131 °C (hexane/CHCl<sub>3</sub>); IR (KBr) 3300, 1593 cm<sup>-1</sup>; <sup>1</sup>H-NMR 9.11 (dd, 1H,  $J=3,6$ , H-7), 8.92 (d, 1H,  $J=5$ , H-2), 8.25-7.42 (m, 5H, H-3, -5, -8, -9, -10), 5.84 (q, 1H,  $J_{HF}=7$ , CHCF<sub>3</sub>), 5.32-4.30 (br, 1H, OH). Anal. Calcd for C<sub>16</sub>H<sub>9</sub>NOF<sub>6</sub>: C, 55.66; H, 2.63; N, 4.06. Found: C, 55.41; H, 2.92; N, 4.02.

**5**: mp 134-135 °C (hexane/EtOAc); IR (KBr) 1708, 1598, 1522 cm<sup>-1</sup>; <sup>1</sup>H-NMR 9.33 (dd, 1H,  $J=3, 6$ , H-7), 9.16 (d, 1H,  $J=5$ , H-2), 8.75-8.40 (m, 2H, H-5, -10), 7.91-7.63 (m, 3H, H-3, -8, -9). Anal. Calcd for C<sub>16</sub>H<sub>7</sub>NOF<sub>6</sub>: C, 55.99; H, 2.06; N, 4.08. Found: C, 55.73; H, 2.31; N, 4.39.

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