

Eduardo Cortés Cortés\*[a][1], Rafael Sosa Mendoza [a], Maximiliano Santibáñez  
Gutiérrez [a], and Olivia García-Mellado de Cortés [b][a] Instituto de Química [2], Universidad Nacional Autónoma de México. Circuito Exterior, Ciudad  
Universitaria, Coyoacán 04510, México, D.F.[b] F.E.S., Cuautitlán-UNAM, Av. 1° de Mayo s/n, Campo 1, Cuautitlán Izcalli, Edo. de México 5470 México.  
Estancia Post-Doctoral, Instituto de Química, UNAM.

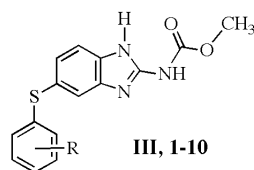
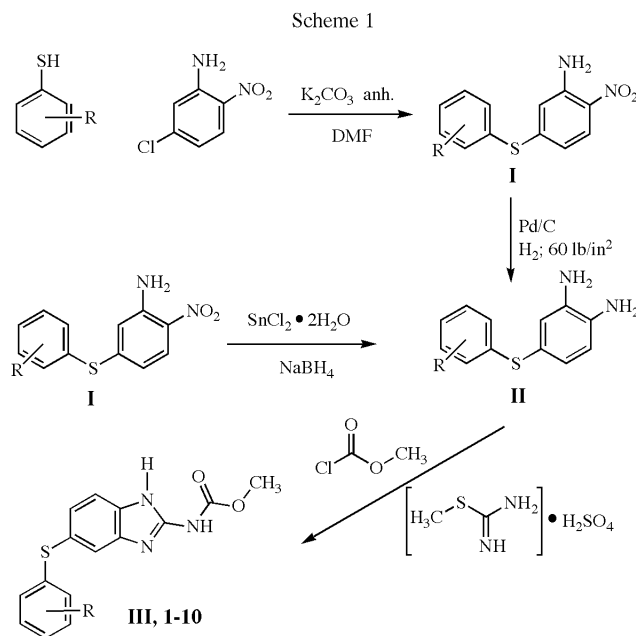
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The preparation and spectral properties of ten novel methyl 5-[(*o*-, *m*-, and *p*-substituted)-phenylthio]-2-benzimidazolecarbamates with possible pharmacological activity as anthelmintics is described; by condensation and cyclization between 5-methylthiours sulfate chloroformic acid methyl ester and 3,4-diaminophenyl-substituted-phenylthio ether dissolved in ethanol. The structures of all final products were corroborated by ir; <sup>1</sup>H-nmr, <sup>13</sup>C-nmr and ms.

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There have been many reports concerning pharmacological interest of benzimidazole carbamate derivatives as anthelmintics which have good efficacy against gastrointestinal nematodes of laboratory and domestic animals. The addition of a phenylthio group to a chemotherapeutically active molecule can considerably increase its efficacy [3-8]. Recently, it has been reported that benzimidazole anthelmintics are useful for the treatment of cryptococcal infection, including meningitis, in particular for AIDS patients [9].

In this report, we describe the synthesis of ten new derivatives of 2-benzimidazole carbamates **III**, **1-10** (Figure 1). The synthesis of these compounds was carried out by three steps as shown in Scheme I. The reaction of 5-chloro-2-nitroaniline was heated six hours under reflux in dimethylformamide anhydrous with the corresponding substituted-phenylthiol in the presence of anhydrous potassium carbonate.



- 1 H
- 2 *o*-OCH<sub>3</sub>
- 3 *m*-OCH<sub>3</sub>
- 4 *p*-OCH<sub>3</sub>
- 5 *o*-Br
- 6 *p*-Br
- 7 *m*-Cl
- 8 *p*-Cl
- 9 *o*-NH<sub>2</sub>
- 10 *p*-F

Figure 1

After cooling, the reaction mixture was diluted with water, the 3-amino-4-nitrophenyl-(*R*-phenyl-thio)ether, **I**, that had precipitated, was collected by filtration with suction; the corresponding derivatives have been obtained in 60-98%.

To prepare the 3,4-diaminophenyl-(substituted-phenylthio) ethers we followed two routes.

#### Route 1.

This route was used only when the *R*-substituents are (*o*-, *m*-, *p*-) CH<sub>3</sub>O- and H-. The 3-amino-4-nitrophenyl-(substituted-phenylthio)ether was hydrogenated in ethanol in presence of Pd/C 10% under a pressure of 60 pounds/inch<sup>2</sup> at room temperature, the catalyst was then removed by filtration and the solution was evaporated under reduced

pressure. The 3,4-diaminophenyl-(substituted-phenylthio)-ethers have been obtained in 80-98% yield.

#### Route 2.

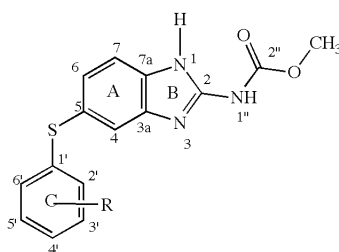
This route was used only when the R-substituents are Cl, Br, NH<sub>2</sub>, and F. The 3-amino-4-nitrophenyl-(substituted-phenylthio)ether was dissolved in ethanol, subsequently, was added stannous chloride, sodium borohydride and the mixture was stirred and heated at 60-80 °C for three hours. After the reaction mixture was cooled with ice-water, subsequently washed with cold water and aqueous sodium hydroxide solution, until neutral pH was attained. The ethanol was evaporated *in vacuo* and the residue was filtered, the solution was extracted with dichloromethane and dried with anhydrous sodium sulfate and evaporated to obtain the 3,4-diaminophenyl-(substituted-phenylthio)ethers in 60-90% yield.

The S-methylthiourea sulfate was dissolved in water and then methyl chloroformate and an aqueous sodium

hydroxide solution were added dropwise, while stirring at a temperature of 5-8°, in the mixture cooled with ice-water. After been stirred for forty minutes, the reaction mixture was neutralized with glacial acetic acid solution and the 3,4-diaminophenyl-(substituted-phenylthio)-ether dissolved in ethanol and the mixture was stirred and heated at 95° for twenty four hours, during this time methylmercaptan was removed. After having allowed the entire reaction mixture to cool with ice-water, the methyl 5-[(*o*-, *m*-, *p*-substituted)phenylthio]-2-benzimidazolecarbamate that had formed was collected by suction filtration to yield **III, 1-10** (57-90%).

The infrared spectrum of compounds **1-10** displayed absorptions at 3342-3397 cm<sup>-1</sup> for N-H stretching, at 2835-2625 cm<sup>-1</sup> for NH-CO stretching, at 1721-1698 cm<sup>-1</sup> for C=O stretching, at 1657-1627 cm<sup>-1</sup> for C=N stretching, at 1206-1264 cm<sup>-1</sup> for C-O stretching, at 1196-1127 cm<sup>-1</sup> and 1024-1006 cm<sup>-1</sup> for C-N stretching and the corresponding absorptions for the R-substituent. In the <sup>1</sup>H-nmr

Table 1  
<sup>13</sup>C NMR Spectral Data for Compounds **1-10**



**III, 1-10**

Compounds R	<b>1</b> H	<b>2</b> <i>o</i> -OCH <sub>3</sub>	<b>3</b> <i>m</i> -OCH <sub>3</sub>	<b>4</b> <i>p</i> -OCH <sub>3</sub>	<b>5</b> <i>o</i> -Br	<b>6</b> <i>p</i> -Br	<b>8</b> <i>p</i> -Cl	<b>9</b> <i>o</i> -NH <sub>2</sub>	<b>10</b> <i>p</i> -F
C-2	148.3	149.0	154.4	148.0	148.4	148.2	148.2	147.9	154.7
C-3a	137.2	137.0	138.0	137.0	138.0	137.0	135.0	139.0	137.0
C-4	119.1	120.0	119.5	116.3	119.9	119.2	116.2	129.3	118.0
C-5	123.5	124.2	122.9	127.0	121.9	122.5	122.6	122.5	125.6
C-6	126.8	128.0	126.8	124.4	126.7	126.7	127.0	121.4	126.1
C-7	114.9	114.1	114.4	114.5	115.3	114.8	114.0	113.1	112.5
C-7a	137.0	137.0	137.5	136.0	137.0	136.0	134.1	138.5	136.0
C-1'	138.4	127.9	148.5	126.9	140.5	138.2	137.8	127.9	133.0 (d) <sup>4</sup> J <sub>C-F</sub> =3.3
C-2'	127.6	156.0	114.3	132.6	119.0	131.7	129.1	153.5	130.3 (d) <sup>3</sup> J <sub>C-F</sub> =7.7
C-3'	129.1	110.2	159.4	115.1	127.1	129.2	128.9	114.1	115.3 (d) <sup>2</sup> J <sub>C-F</sub> =21.8
C-4'	125.8	127.0	119.4	158.7	126.6	118.4	130.3	129.3	160.8 (d) <sup>1</sup> J <sub>C-F</sub> =243.6
C-5'	129.0	121.8	129.4	115.0	128.2	129.0	128.0	116.5	115.3 (d) <sup>2</sup> J <sub>C-F</sub> =21.8
C-6'	127.0	128.2	109.1	132.0	132.6	131.0	129.0	135.1	130.3 (d) <sup>3</sup> J <sub>C-F</sub> =7.7
C=O	154.5	155.8	154.3	154.6	154.4	154.4	154.4	154.5	154.6
OCH <sub>3</sub>	52.5	52.2	52.1	52.5	52.5	52.3	52.6	51.8	52.5
R	-	56.0	54.7	55.2	-	-	-	-	-

Note: The numbering of the phenyl ring is only for the assignment of the chemical shifts of the carbon in <sup>13</sup>C nmr spectra.

spectra of derivatives **1-10** the presence of two broad proton signals at  $\delta$  11.8-11.6 that exchanges with deuterium oxide was consistent with the presence of two amine groups. One other proton signal at  $\delta$  7.5-7.4 as a doublet was assigned to the proton joined to C-7. The other one-proton signal at  $\delta$  7.6-7.3, a doublet was assigned to the proton joined to C-4. The presence of a one-proton doublet of doublets signal at  $\delta$  7.3-7.0 was consistent with the presence of the proton joined to C-6.

The aromatic protons appeared as a multiplet and an AA'BB' system at  $\delta$  7.6-6.6. A three proton signal at  $\delta$  3.8-3.7 as a singlet was assigned to the methoxy protons joined to C-2" of the ester group, and the signals for the R-substituents.

The  $^{13}\text{C}$ -nmr spectra of the compounds **1-10** are given in Table 1. The signals were confirmed by using HETCOR; LONG RANGE HETCOR, FLOCK, COSY and NOESY nmr experiments operating at 300 and 500 MHz.

The mass spectra of compounds **1-10** exhibit a stable molecular ion that is the base peak in most of the compounds analyzed. The main fragmentation was consistent with the assigned structures.

The relative abundance of the principal fragment ions in the compounds **1-10** have some common features and the proposed fragmentation pathways leading to the formation of a number of important daughter ions have been confirmed by the corresponding parent ion spectra in collision-induced dissociation experiments. The elemental composition of the molecular ion was determined by exact mass measurements. The important fragment ions are:  $\text{M}^+$ ;  $[\text{M}-32]^+$ ;  $[\text{M}-33]^+$ ;  $[\text{M}-58]^+$ ;  $[\text{M}-59]^+$   $m/z$  266; 239, 224; 211, 190; 171 and 109.

## EXPERIMENTAL

The ir spectra were recorded on a Nicolet Magna TR-750 spectrophotometer. The  $^1\text{H}$ -nmr spectra were recorded on a Varian Unity 300 spectrometer operating at 300 MHz and the  $^{13}\text{C}$ -nmr spectra were recorded on a Varian Unity 500 spectrometer operating at 125 MHz in deuteriochloroform solution containing tetramethylsilane as the internal standard with chemical shifts  $\delta$  (ppm) expressed downfield from tetramethylsilane. The mass spectra were measured on a JEOL JMS-AC505 and JEOL MS-SX 102A high-resolution mass spectrometer with accurate mass determination of the molecular ion and the principal fragment ions, using the direct inlet system. The spectra were recorded by electron impact at an ionization chamber temperature of  $190^\circ$  and ionizing electron energy of 70 eV.

Compounds **I** and **II** were prepared following methods developed by us, with modifications [9-10].

General Procedure for the Synthesis of the Methyl 5-[(*o*-, *m*-, and *p*-substituted)phenylthio)-2-benzimidazolecarbamates, **III, 1-10**.

S-Methylthiourea sulfate ( $1.25 \times 10^{-3}$  mole) was dissolved in water (3.0 ml) and then chloroformic acid methyl ester ( $2.4 \times 10^{-3}$  mole) and 25% aqueous sodium hydroxide solution (10 ml) were added dropwise, while stirring at a temperature of  $3^\circ$  to  $6^\circ$

cooling with an ice-water bath. After having stirred for forty minutes the reaction mixture was combined with aqueous glacial acetic acid solution (0.6 ml of glacial acetic acid in 5.0 ml of water) at room temperature and subsequently was added the 3,4-diaminophenyl-phenyl-substituted-phenylthio ether ( $1.0 \times 10^{-3}$  mole) dissolved in ethanol (5.0 ml). The mixture was stirred and heated at  $95^\circ$  for twenty four hours, during which time methylmercaptan separated. The entire reaction mixture was cooled with ice-water, then the methyl 5-[(*o*-, *m*-, and *p*-substituted)phenylthio)-2-benzimidazolecarbamate that had formed was collected by filtration to yield **II, 1-10** (57-90%).

### Methyl-5-phenylthio-2-benzimidazolecarbamate (**1**).

This compound was obtained as whitish needles in 88% yield, mp  $298^\circ$ ; ir (chloroform):  $\nu$  NH 3339; NH-CO 2850-2667; C=O 1709; C=N 1630; C-O 1273 and 1098; C-N 1194 and 1130  $\text{cm}^{-1}$ .  $^1\text{H}$ -nmr (deuteriochloroform):  $\delta$  3.71 (s, 3H,  $\text{COOCH}_3$ ), 7.1 (dd, 1H,  $J=2.1, 8.1$  Hz, 6-H), 7.1 (dd, 2H,  $J=1.2, 8.4$  Hz, 2'-H and 6'-H), 7.14 (dt, 1H,  $J=1.2, 7.2$  Hz, 4'-H), 7.26 (dt, 2H,  $J=1.3, 7.5$  Hz, 3'-H and 5'-H), 7.4 (d, 1H,  $J=8.4$  Hz, 7-H), 11.8 (bs, 2H, N-H, deuterium oxide exchangeable); ms:  $m/z$  299 ( $\text{M}^+$ ); 301 [ $\text{M}+2$ ] $^+$ .

Anal. Calcd. for  $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}_2\text{S}$ : C, 60.18; H, 4.38; N, 14.04. Found. C, 60.29, H, 4.45; N, 14.13.

### Methyl-5-(*o*-methoxy phenylthio)-2-benzimidazolecarbamate (**2**).

This compound was obtained as whitish needles in 57% yield, mp  $198^\circ$ ; ir (chloroform):  $\nu$  NH 3396, NH-CO 2835-2625, C=O 1729, C=N 1647, C-O 1271 and 1068, C-N 1190 and 1024  $\text{cm}^{-1}$ .  $^1\text{H}$ -nmr (deuteriochloroform):  $\delta$  3.85 (s, 3H,  $\text{COOCH}_3$ ); 3.9 (s, 3H,  $-\text{OCH}_3$ ), 6.8 (dt, 1H,  $J=1.3, 7.5$  Hz, 5'-H), 6.82 (dd, 1H,  $J=1.2, 8.3$  Hz, 6'-H), 6.86 (dd, 1H,  $J=1.2, 8.1$  Hz, 3'-H), 7.12 (dt, 1H,  $J=1.4, 8.1$  Hz, 4'-H), 7.31 (dd, 1H,  $J=1.2, 8.4$  Hz, 6-H), 7.5 (d, 1H,  $J=8.4$  Hz, 7-H), 7.67 (d, 1H,  $J=1.4$  Hz, 4-H), 11.8 (bs, 2H, N-H, deuterium oxide exchangeable), ms:  $m/z$  329 ( $\text{M}^+$ ), 331 [ $\text{M}+2$ ] $^+$ .

Anal. Calcd. For  $\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}_3\text{S}$ : C, 58.34; H, 4.59; N, 12.76. Found. C, 58.22; H, 4.67, N, 12.64.

### Methyl-5-(*m*-methoxyphenylthio)-2-benzimidazolecarbamate (**3**).

This compound was obtained as whitish needles in 88% yield, mp  $180^\circ$ , ir (chloroform):  $\nu$  NH 3342, NH-CO 2840-2674, C=O 1706; C=N 1632, C-O 1266 and 1060, C-N 1143 and 1020  $\text{cm}^{-1}$ .  $^1\text{H}$ -nmr (deuteriochloroform):  $\delta$  3.7 (s, 3H,  $\text{COOCH}_3$ ), 3.8 (s, 3H,  $\text{OCH}_3$ ), 6.61 (d, 1H,  $J=1.7$  Hz, 2'-H), 6.67 (dd, 1H,  $J=1.4, 7.9$  Hz, 4'-H), 6.69 (dd, 1H,  $J=1.4, 7.9$  Hz, 6'-H), 7.1 (5, 1H,  $J=8.9$  Hz, 5'-H), 7.2 (dd, 1H,  $J=1.6, 8.2$  Hz, 6-H), 7.5 (d, 1H,  $J=8.2$  Hz, 7-H), 7.6 (d, 1H,  $J=1.4$  Hz, 4-H), 11.7 (bs, 2H, N-H, deuterium oxide exchangeable); ms:  $m/z$  329 ( $\text{M}^+$ ), 331 [ $\text{M}+2$ ] $^+$ .

Anal. Calcd. For  $\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}_3\text{S}$ : C, 58.34; H, 4.59; N, 12.76. Found: C, 58.45; H, 4.46; N, 12.84.

### Methyl-5-(*p*-methoxy phenylthio)-2-benzimidazolecarbamate (**4**).

This compound was obtained as whitish needles in 67% yield, mp  $223^\circ$ , ir (chloroform):  $\nu$  NH 3359; NH-CO 2835-2670; C=O 1716; C=N 1642; C-O 1267 and 1065; C-N 1193 and 1015  $\text{cm}^{-1}$ .  $^1\text{H}$ -nmr (deuteriochloroform):  $\delta$  3.73 (s, 3H,  $\text{COOCH}_3$ ), 3.74 (s, 3H,  $\text{OCH}_3$ ), 6.91 and 7.25 (AA'BB', 4H,  $J=8.7$  Hz, phenyl protons of "C" ring); 7.06 (dd, 1H,  $J=1.8, 8.1$  Hz, 6-H), 7.34 (d, 1H,  $J=1.5$  Hz, 4-H); 7.35 (d, 1H,  $J=8.4$  Hz, 7-H); 11.7 (bs, 2H, N-H, deuterium oxide exchangeable). ms:  $m/z$  329 ( $\text{M}^+$ ); 331 [ $\text{M}+2$ ] $^+$ .

Anal. Calcd. For  $\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}_3\text{S}$ : C, 58.34; H, 4.59; N, 12.76. Found: C, 58.43; H, 4.68; N, 12.87.

Methyl-5-(*o*-bromo phenylthio)-2-benzimidazolecarbamate (**5**).

This compound was obtained as brownish needles in 58% yield. mp > 300°; ir (chloroform):  $\nu$  NH 3397; NH-CO 2854-2650; C=O 1721; C=N 1657; C-O 1278 and 1100; C-N 1196, 1011  $\text{cm}^{-1}$ ;  $^1\text{H}$ -nmr (deuteriochloroform):  $\delta$  3.76 (s, 3H,  $\text{COOCH}_3$ ); 6.58 (dd, 1H,  $J=1.4, 8.1$  Hz, 3'-H); 7.04 (dt, 1H,  $J=1.3, 8.1$  Hz, 4'-H); 7.18 (dt, 1H,  $J=1.3, 8.1$  Hz, 5'-H); 7.23 (dd, 1H,  $J=1.4, 8.4$  Hz, 6-H); 7.51 (d, 1H,  $J=8.4$  Hz, 7-H); 7.58 (d, 1H,  $J=1.5$  Hz, 4-H); 7.59 (dd, 1H,  $J=1.4, 7.8$  Hz, 6'-H); 11.8 (bs, 2H, N-H, deuterium oxide exchangeable). ms:  $m/z$  377 ( $\text{M}^+$ ), 379 [ $\text{M}+2$ ] $^+$ , 381 [ $\text{M}+4$ ] $^+$ .

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{12}\text{BrN}_3\text{O}_2\text{S}$ : C, 47.63; H, 3.20, N, 11.11. Found: C, 47.72, H, 3.12; N, 11.18.

Methyl-5-(*p*-bromophenylthio)-2-benzimidazolecarbamate (**6**).

This compound was obtained as brownish needles in 90% yield; mp 230°; ir (chloroform):  $\nu$  NH 3376; NH-CO 2855-2674, C=O 1698; C=N 1648; C-O 1272 and 1104, C-N 1198 and 1006  $\text{cm}^{-1}$ ;  $^1\text{H}$ -nmr (deuteriochloroform)  $\delta$  3.76 (s, 3H,  $\text{COOCH}_3$ ), 7.04 and 7.44 (AA'BB', 4H  $J=8.4$  Hz, phenyl protons of "C" ring), 7.2 (dd, 1H,  $J=1.4, 8.1$  Hz, 6-H), 7.45 (d, 1H,  $J=8.4$  Hz, 7-H), 7.53 (d, 1H,  $J=1.5$  Hz, 4-H), 11.6 (bs, 2H, N-H, deuterium oxide exchangeable); ms:  $m/z$  377 ( $\text{M}^+$ ); 379 [ $\text{M}+2$ ] $^+$ , 381 [ $\text{M}+4$ ] $^+$ .

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{12}\text{BrN}_3\text{O}_2$ : C, 47.63, H, 3.2, N, 11.11. Found: C, 47.48; H, 3.10; N, 11.01.

Methyl-5-(*m*-chlorophenylthio)-2-benzimidazolecarbamate (**7**).

This compound was obtained as brownish needles in 60%; mp 215°, ir (KBr):  $\nu$  NH 3346, NH-CO 2840-2655, C=O 1708, C=N 1649; C-O 1274 and 1095, C-N 1144 and 1005  $\text{cm}^{-1}$ ;  $^1\text{H}$ -nmr (deuteriochloroform): it was not possible to obtain the spectrum, because it is not soluble; ms:  $m/z$  333 ( $\text{M}^+$ ); 335 [ $\text{M}+2$ ] $^+$ ; 337 [ $\text{M}+4$ ] $^+$ .

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{12}\text{ClN}_3\text{O}_2\text{S}$ : C, 53.97; H, 3.62, N, 12.59. Found: C, 53.83; H, 3.70; N, 12.45.

Methyl-5-(*p*-chlorophenylthio)-2-benzimidazolecarbamate (**8**).

This compound was obtained as brownish needles in 61%, mp 225°, ir (chloroform):  $\nu$  NH 3372; NH-CO 2847-2640; C=O 1702, C=N 1649; C-O 1275 and 1102, C-N 1127 and 1020  $\text{cm}^{-1}$ ;  $^1\text{H}$ -nmr (deuteriochloroform):  $\delta$  3.75 (s, 3H,  $\text{COOCH}_3$ ); 7.08 and 7.32 (AA'BB', 4H,  $J=8.7$  Hz, phenyl protons of "C" ring); 7.2 (dd, 1H,  $J=1.7, 8.1$  Hz 6-H); 7.46 (d, 1H,  $J=8.4$  Hz, 7-H); 7.53 (d, 1H,  $J=1.5$  Hz, 4-H); 11.7 (bs, 2H, N-H, deuterium oxide exchangeable); ms:  $m/z$  333 ( $\text{M}^+$ ); 335 [ $\text{M}+2$ ] $^+$ ; 337 [ $\text{M}+4$ ] $^+$ .

*Anal.* Calcd. For  $\text{C}_{15}\text{H}_{12}\text{ClN}_3\text{O}_2\text{S}$ : C, 53.97; H, 3.62; N, 12.59. Found: C, 54.08; H, 3.56; N, 12.71

Methyl-5-(*o*-amine phenylthio)-2-benzimidazolecarbamate (**9**).

This compound was obtained as brownish needles in 60% yield, mp 245°; ir (chloroform):  $\nu$  NH 3462 and 3334; NH-CO

2848-2670; C=O 1707; C=N 1628; C-O 1278 and 1099; C-N 1137 and 980  $\text{cm}^{-1}$ .  $^1\text{H}$ -nmr (deuteriochloroform):  $\delta$  3.75 (s, 3H,  $\text{COOCH}_3$ ); 6.64 (dt, 1H,  $J=1.5, 7.5$  Hz, 5'-H); 6.8 (dd, 1H,  $J=1.2, 8.1$  Hz, 3'-H); 7.03 (dd, 1H,  $J=1.6, 8.2$  Hz, 6-H); 7.15 (dt, 1H,  $J=1.5, 7.6$  Hz, 4'-H); 7.27 (d, 1H,  $J=1.5$  Hz, 4-H); 7.37 (d, 1H,  $J=8.4$  Hz, 7-H); 7.38 (dd, 1H,  $J=1.8, 7.6$  Hz, 6'-H); 11.8 (bs, 2H, N-H, deuterium oxide exchangeable); ms:  $m/z$  314 ( $\text{M}^+$ ); 316 [ $\text{M}+2$ ] $^+$ .

*Anal.* Calcd. For  $\text{C}_{15}\text{H}_{14}\text{N}_4\text{O}_2\text{S}$ : C, 57.31; H, 4.49; N, 17.83. Found: C, 57.19; H, 4.37; N, 17.93.

Methyl-5-(*p*-fluorophenylthio)-2-benzimidazolecarbamate (**10**).

This compound was obtained as brownish needles in 80% yield; mp 187°; ir (chloroform):  $\nu$  NH 3343; NH-CO 2856-2680; C=O 1705; C=N 1639; C-O 1275 and 1127; C-N 1135 and 1010  $\text{cm}^{-1}$ ;  $^1\text{H}$ -nmr (deuteriochloroform):  $\delta$  3.85 (s, 3H,  $\text{COOCH}_3$ ), 6.95 and 7.22 (AA'BB', 4H,  $J_{\text{H-H}}=8.7$  Hz;  $J_{\text{H-F}}=8.4$  Hz, 3'-H and 5'-H;  $J_{\text{H-H}}=9.1$  Hz;  $J_{\text{H-F}}=5.4$  Hz, 2'-H and 6'-H); 7.23 (dd, 1H,  $J=1.5, 7.9$  Hz, 6-H); 7.45 (d, 1H,  $J=7.5$  Hz, 7-H); 7.6 (d, 1H,  $J=1.5$  Hz, 4-H); 11.8 (bs, 2H, N-H, deuterium oxide exchangeable); ms:  $m/z$  317 ( $\text{M}^+$ ); 319 [ $\text{M}+2$ ] $^+$ .

*Anal.* Calcd. For  $\text{C}_{15}\text{H}_{12}\text{FN}_3\text{O}_2\text{S}$ : C, 56.77; H, 3.81; N, 13.24. Found: C, 56.60; H, 3.88; N, 13.15.

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