# Synthesis of 2-*N*-(Benzo[*b*]thiophen-2-yl)benzo and heterofused-1,2,3-triazoles



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A novel efficient synthesis of 2-*N*-(benzo[*b*]thiophen-2-yl)benzo and heterofused-1,2,3-triazoles was achieved by the diazotisation of 2-amino-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile and ethyl-2-amino-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxylate and coupling with selected aromatic and heterocyclic amines followed by air oxidation in the presence of cupric acetate.

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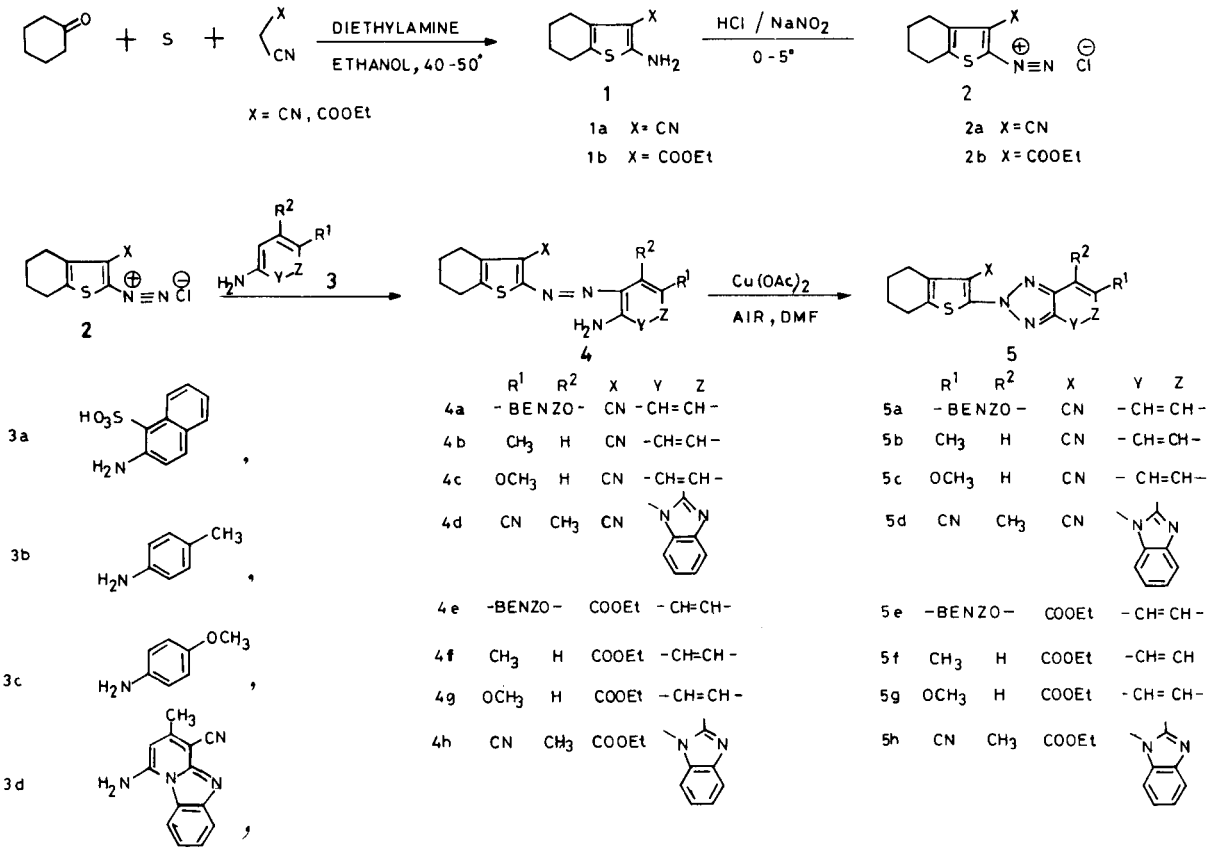
A fluorophoric heterocycle such as 1,2,3-triazole pendant to another heterocycle in a suitable position finds an exceedingly important place in some commercial fluorescent whiteners described in the patent literature [1-5]. Compounds with the 1,2,3-triazole ring system attract special attention on account of their strong fluorescence [6]. Some fused and pendant 1,2,3-triazolyl compounds have been reported by us previously [7-11]. We have also reported the synthesis of novel heterocyclic systems such as benzo[*b*]thiophenes [12], thiophene [13], benzopyrano-[3,4-*c*]pyridinone [14], pyrazolo[1,5-*a*]pyridines [15], thiazolo[4,5-*b*]quinoxalines [16] and their application as fluorescent brighteners and dyes. Several recent patents [17,18] describe the synthesis and technical importance of azobenzo[*b*]thiophene derivatives. Benzo[*b*]thiophene derivatives have been found to possess good medicinal and biological activities [19,20].

The synthesis of model compounds of 2-*N*-(benzo[*b*]thiophen-2-yl]benzo and heterofused-1,2,3-triazoles **5a-5h** require diazotisation of **1** and coupling with selected aromatic and heterocyclic amino coupling components **3** to result in an orthoaminoaryl and hetarylazo derivatives **4**. The orthoaminoaryl and hetarylazo derivatives **4** on subsequent air oxidation in the presence of a cupric salt [5] yield 2-*N*-(benzo[*b*]thiophene-2-yl)benzo and heterofused-1,2,3-triazoles **5**.

SCHEME 1



We wish to report in this communication a facile synthesis of (2-*N*-(benzo[*b*]thiophen-2-yl)benzo and heterofused-1,2,3-triazoles **5** by a novel method. The key compounds such as 2-amino-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile **1a** and ethyl-2-amino-4,5,6,7-tetrahydrobenzo-[*b*]thiophene-3-carboxylate **1b** are synthesised by the condensation of cyclohexanone, sulfur and malononitrile or ethyl cyanoacetate, respectively following the Gewald synthesis [21].

The principle advantages of the key compounds used here are that the yields are high, the time of reaction is short, the procedure involved only one facile step, the work up is convenient and the starting materials are very easily prepared. The presence of a diazotisable amino group adjacent to electron withdrawing groups such as cyano and carbethoxy results in the deepening of hues of the dyes on polyester fibres and the hydrophobic nature of the tetrahydrobenzo structure is useful for better dispersability and dyeability.

In connection with our interest to study fluorescent properties of **5**, we have devised the following route for the efficient synthesis of **4**, a precursor of **5**. The striking fluorescent properties of **5** have found applications to whiten synthetic fibres. The sequence involved in the present synthesis consists of the diazotisation of **1** using hydrochloric acid and sodium nitrite and coupling with selected aromatic and heterocyclic amino coupling components **3**, such as tobias acid (2-aminonaphthalene-1-sulfonic acid), *p*-toluidine, *p*-anisidine and 1-amino-4-cyano-3-methylpyrido[1,2-*a*]benzimidazole [11], to give excellent yields 79-87% of orthoaminoaryl and hetarylazo compounds **4a-4h**. The compounds **4a-4h** were converted to **5a-5h** using cupric acetate, in refluxing *N,N*-dimethylformamide, in a current of bubbling air.

The fluorescent properties of the compounds have been studied and the wavelength of absorption maxima, fluorescence emission maxima and the values of the logarithms of the extinction coefficients are recorded. The application to synthetic fibres (polyester) resulted in moderate whitening of the fibres. The compounds **5a-5h** possessed bluish violet fluorescence in daylight in most of the organic solvents.

## EXPERIMENTAL

All melting points are uncorrected and are in °C. The infrared spectra were recorded on Perkin-Elmer Model 397 spectrophotometer in Nujol mull. The $^1$H nmr spectra were recorded on Varian-60 MHz instrument EM-360-L using TMS as internal standard and the chemical shifts are given in $\delta$ (ppm) scale. Mass spectra were recorded on a Varian Mat-311 instrument (70 eV). Absorption and fluorescence emission spectra in DMF solution were recorded on Beckman Model-25 spectrophotometer and Aminco Bowman Spectrophotofluorometer, respectively.

2-(2-Amino-1-naphthyl)azo-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile (**4a**).

To a solution of 100 ml of concentrated hydrochloric acid, was dissolved 8.9 g (0.05 mole) of 2-amino-4,5,6,7-tetrahydrobenzo[*b*]-thiophene-3-carbonitrile **1a** by warming and the solution was then cooled to 0-5°. With vigorous stirring 3.45 g (0.05 mole) of sodium nitrite in 10 ml water was gradually added to this solution in about 2 hours at 0-5°. The reaction mixture was stirred for a further 1 hour, maintaining the temperature at 0-5°. The excess of nitrous acid was decomposed by addition of urea. The clear diazonium salt solution was slowly added to 11.15 g (0.05 mole) of tobias acid **3a** in 50 ml of acetic acid at 0°. The *p*H of the reaction mixture was maintained at 4-5 throughout the coupling period by addition of sodium carbonate in portions for 2 hours at 0°. After the addition of the diazonium salt was over, the reaction mixture was stirred for a further period of 5 hours and the partially separated dye was completely precipitated by neutralisation. The dye was filtered, washed with water and dried. Recrystallisation from ethanol yielded 13.44 g (81%) of **4a** as pink crystalline solid, mp 219°.

*Anal.* Calcd. for $C_{19}H_{16}N_4S$: C, 68.67; H, 4.81; N, 16.86; S, 9.63. Found: C, 68.71; H, 4.58; N, 16.64; S, 9.71.

2-(2-Amino-5-methylphenyl)azo-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile (**4b**).

The same procedure as described for **4a** was applied except *p*-toluidine **3b** was used in place of **3a**, yielding 2-(2-amino-5-methylphenyl)azo-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile **4b**, recrystallised from ethanol to yield 12.87 g, (87%) of **4b**, mp 187°.

*Anal.* Calcd. for $C_{16}H_{16}N_4S$: C, 64.86; H, 5.40; N, 18.91; S, 10.81. Found: C, 64.98; H, 5.24; N, 18.99; S, 10.91.

2-(2-Amino-5-methoxyphenyl)azo-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile (**4c**).

The same procedure as described for **4a** was applied except *p*-anisidine **3c** was used in place of **3a**, yielding 2-(2-amino-5-methoxyphenyl)azo-4,5,6,7-tetrahydro[*b*]thiophene-3-carbonitrile **4c**, recrystallised from benzene to yield 12.79 g (82%) of **4c** mp 261°.

*Anal.* Calcd. for $C_{16}H_{16}N_4OS$: C, 61.53; H, 5.12; N, 17.94; S, 10.25. Found: C, 61.46; H, 5.02; N, 17.80; S, 10.11.

2-(2-Amino-5-cyano-4-methylpyrido[1,2-*a*]benzimidazol-3-yl)azo-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile (**4d**).

The same procedure as described for **4a** was applied except 1-amino-4-cyano-3-methylpyrido[1,2-*a*]benzimidazole **3d** was used in place of **3a**, yielding 2-(2-amino-5-cyano-4-methylpyrido[1,2-*a*]-benzimidazol-3-yl)azo-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile **4d**, recrystallised from acetic acid to yield 16.23 g (79%) of **4d**, mp 311°.

*Anal.* Calcd. for $C_{22}H_{17}N_7S$: C, 64.23; H, 4.13; N, 23.84; S, 7.78. Found: C, 64.18; H, 4.09; N, 23.76; S, 7.81.

Ethyl 2-(2-Amino-1-naphthyl)azo-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxylate (**4e**).

To a solution of 100 ml of concentrated hydrochloric acid, was dissolved 11.25 g (0.05 mole) of ethyl-2-amino-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxylate **1b** by warming and the solution was then cooled to 0-5°. With vigorous stirring 3.45 g (0.05 mole) of sodium nitrite in 10 ml water was gradually added to this solution in about 3 hours at 0-5°. The reaction mixture was stirred for a further 2 hours, maintaining the temperature at 0-5°. The ex-

cess of nitrous acid was decomposed by addition of urea. The clear diazonium salt solution was slowly added to 11.15 g (0.05 mole) of tobias acid **3a** in 50 ml of acetic acid at 0°. The *p*H of the reaction mixture was maintained at 4-5 throughout the coupling period by addition of sodium carbonate in portions for 2 hours at 0°. After the addition of the diazonium salt was over, the reaction mixture was stirred for a further period of 5 hours and the partially separated dye was completely precipitated by neutralisation. The dye was filtered, washed with water and dried. Recrystallisation from ethanol yielded 15.91 g (84%) of **4e**, mp 194°.

*Anal.* Calcd. for $C_{21}H_{21}N_3O_2S$: C, 66.49; H, 5.54; N, 11.08; S, 8.44. Found: C, 66.41; H, 5.49; N, 11.02; S, 8.35.

Ethyl-2-(2-Amino-5-methylphenyl)azo-4,5,6,7-tetrahydrobenzo[*b*]-thiophene-3-carboxylate (**4f**).

The same procedure as described for **4e** was applied except *p*-toluidine **3b** was used in place of **3a**, yielding ethyl-2-(2-amino-5-methylphenyl)azo-4,5,6,7-tetrahydrobenzo[**b**]thiophene-3-carboxylate **4f**, recrystallised from benzene to yield 13.72 g (80%) of **4f**, mp 254°.

*Anal.* Calcd. for $C_{18}H_{21}N_3O_2S$: C, 62.97; H, 6.12; N, 12.24; S, 9.32. Found: C, 62.99; H, 6.20; N, 12.13; S, 9.21.

Ethyl 2-(2-Amino-5-methoxyphenyl)azo-4,5,6,7-tetrahydrobenzo-[*b*]thiophene-3-carboxylate (**4g**).

The same procedure as described for **4e** was applied except *p*-anisidine **3c** was used in place of **3a**, yielding ethyl 2-(2-amino-5-methoxyphenyl)azo-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxylate **4g**, recrystallised from benzene to yield 15.43 g (86%) of **4g**, mp 287°.

*Anal.* Calcd. for $C_{18}H_{21}N_3O_3S$: C, 60.16; H, 5.84; N, 11.69; S, 8.91. Found: C, 60.06; H, 5.81; N, 11.60; S, 8.87.

Ethyl 2-(2-Amino-5-cyano-4-methylpyrido[1,2-*a*]benzimidazol-3-yl)azo-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxylate (**4h**).

The same procedure as described for **4e** was applied except 1-amino-4-cyano-3-methylpyrido[1,2-*a*]benzimidazole **3d** was used in place of **3a** yielding ethyl 2-(2-amino-5-cyano-4-methylpyrido-[1,2-*a*]benzimidazol-3-yl)azo-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxylate **4h**, recrystallised from acetic acid to yield 18.77 g (82%) of **4h**, mp 357°.

*Anal.* Calcd. for $C_{24}H_{22}N_6O_2S$: C, 62.88; H, 4.80; N, 18.34; S, 6.98. Found: C, 62.71; H, 4.69; N, 18.31; S, 6.92.

2-*N*-(3-Cyano-4,5,6,7-tetrahydrobenzo[*b*]thiophen-2-yl)naphtho-[1,2-*d*]-1,2,3-triazole (**5a**).

To a solution of 1.66 g (0.005 mole) of **4a** in 15 ml of *N,N*-dimethylformamide was added 1 g (0.0052 mole) of cupric acetate. The reaction mixture was brought to reflux temperature. Air was continuously bubbled through the reaction mixture and the reflux was continued for 4 hours. The reaction mixture was cooled and then added to 100 ml of 5% ice cold hydrochloric acid with constant stirring. The precipitated solid was filtered, washed with water, dried and recrystallised from DMF to yield 1.17 g (71%) of **5a** as a white crystalline solid, mp >360°; ir (nujol): 2220 $cm^{-1}$; $^1H$ nmr (dimethyl sulfoxide-$d_6$): $\delta$ 1.6-2.03 (m, 4H, 2H-5, 2H-6), 2.26-2.90 (m, 4H, 2H-4, 2H-7), 7.16-8.36 (m, 6H, aromatic H-9, H-10, H-11, H-12, H-13, H-14); ms: m/z 330 ($M^+$); $\lambda$ max absorption 386 nm, $\lambda$ max emission 439 nm, log $\epsilon$ 4.41.

*Anal.* Calcd. for $C_{19}H_{14}N_4S$: C, 69.09; H, 4.24; N, 16.96; S, 9.69. Found: C, 69.01; H, 4.18; N, 17.00; S, 9.63.

2-*N*-(3-Cyano-4,5,6,7-tetrahydrobenzo[*b*]thiophen-2-yl)-5-methylbenzo[*d*]-1,2,3-triazole (**5b**).

The same procedure as described for the oxidation of **4a** to **5a** was applied to the oxidation of **4b**, yielding 2-*N*-(3-cyano-4,5,6,7-tetrahydrobenzo[*b*]thiophen-2-yl)-5-methylbenzo[*d*]-1,2,3-triazole **5b**, recrystallised from DMF to yield 0.94 g (64%) of **5b**, mp 291°; ir (nujol): 2220 $cm^{-1}$; $^1H$ nmr (dimethyl sulfoxide-$d_6$): $\delta$ 1.6-2.0 (m, 4H, 2H-5, 2H-6), 2.33-2.8 (m, 4H, 2H-4, 2H-7), 7.7-8.36 (m, 3H, aromatic, H-9, H-10, H-12), 3.86 (s, 3H, $CH_3$); ms: m/z 294 ($M^+$); $\lambda$ max absorption 367 nm, $\lambda$ max emission 432 nm, log $\epsilon$ 4.16.

*Anal.* Calcd. for $C_{16}H_{14}H_4S$: C, 65.30; H, 4.76; N, 19.04; S, 10.88. Found: C, 65.41; H, 4.89; N, 19.00; S, 10.81.

2-*N*-(3-Cyano-4,5,6,7-tetrahydrobenzo[*b*]thiophen-2-yl)-5-methoxybenzo[*d*]-1,2,3-triazole (**5c**).

The same procedure as described for the oxidation of **4a** to **5a** was applied to the oxidation of **4c**, yielding 2-*N*-(3-cyano-4,5,6,7-tetrahydrobenzo[*b*]thiophen-2-yl)-5-methoxybenzo[*d*]-1,2,3-triazole **5c**, recrystallised from DMF to yield 0.94 g (61%) of **5c**, mp 349°; ir (nujol): 2210 $cm^{-1}$; $^1H$ nmr (dimethyl sulfoxide-$d_6$): $\delta$ 1.7-2.06 (m, 4H, 2H-5, 2H-6), 2.31-2.85 (m, 4H, 2H-4, 2H-7), 7.75-8.30 (m, 3H, aromatic, H-9, H-10, H-12), 4.1 (s, 3H, $OCH_3$); ms: m/z 310 ($M^+$); $\lambda$ max absorption 371 nm, $\lambda$ max emission 443 nm, log $\epsilon$ 4.30.

*Anal.* Calcd. for $C_{16}H_{14}N_4OS$: C, 61.93; H, 4.51; N, 18.06; S, 10.32. Found: C, 61.88; H, 4.46; N, 18.01; S, 10.21.

2-*N*-(3-Cyano-4,5,6,7-tetrahydrobenzo[*b*]thiophen-2-yl)-5-cyano-4-methylbenzimidazolo[1′,2′:1,6]pyrido[2,3-*d*]-1,2,3-triazole (**5d**).

The same procedure as described for the oxidation of **4a** to **5a** was applied to the oxidation of **4d**, yielding 2-*N*-(3-cyano-4,5,6,7-tetrahydrobenzo[*b*]thiophen-2-yl)-5-cyano-4-methylbenzimidazolo[1′,2′:1,6]pyrido[2,3-*d*]-1,2,3-triazole **5d**, recrystallised from DMF to yield 1.18 g (58%) of **5d**, mp >360°; ir (nujol): 2200 $cm^{-1}$; ms: m/z 409 ($M^+$); $\lambda$ max absorption 397 nm, $\lambda$ max emission 461 nm, log $\epsilon$ 4.49.

*Anal.* Calcd. for $C_{22}H_{15}N_7S$: C, 64.54; H, 3.66; N, 23.96; S, 7.82. Found: C,64.51; H, 3.60; N, 24.00; S, 7.69.

2-*N*-(3-Carbethoxy-4,5,6,7-tetrahydrobenzo[*b*]thiophen-2-yl)naphtho[1,2-*d*]-1,2,3-triazole (**5e**).

The same procedure as described for the oxidation of **4a** to **5a** was applied to the oxidation of **4e**, yielding 2-*N*-(3-carbethoxy-4,5,6,7-tetrahydrobenzo[*b*]thiophen-2-yl)naphtho[1,2-*d*]-1,2,3-triazole **5e**, recrystallised from DMF to yield 1.39 g (74%) of **5e**, mp 264°; ir (nujol): 1700 $cm^{-1}$; $^1H$ nmr (dimethyl sulfoxide-$d_6$); $\delta$ 1.61-2.02 (m, 4H, 2H-5, 2H-6), 2.24-2.98 (m, 4H, 2H-4, 2H-7), 7.10-8.24 (m, 6H, aromatic, H-9, H-10, H-11, H-12, H-13, H-14), 1.1 (t, 3H, $CH_3$), 4.3 (q, 2H, $CH_2$); ms: m/z 377 ($M^+$); $\lambda$ max absorption 379 nm, $\lambda$ max emission 434 nm, log $\epsilon$ 4.21.

*Anal.* Calcd. for $C_{21}H_{19}N_3O_2S$: C, 66.84; H, 5.03; N, 11.14; S, 8.48. Found: C, 66.91; H, 5.00; N, 11.08; S, 8.42.

2-*N*-(3-Carbethoxy-4,5,6,7-tetrahydrobenzo[*b*]thiophen-2-yl)-5-methylbenzo[*d*]-1,2,3-triazole (**5f**).

The same procedure as described for the oxidation of **4a** to **5a** was applied to the oxidation of **4f**, yielding 2-*N*-(3-carbethoxy-4,5,6,7-tetrahydrobenzo[*b*]thiophen-2-yl)-5-methylbenzo[*d*]-1,2,3-triazole **5f**, recrystallised from DMF to yield 1.17 g (69%) of **5f**, mp >360°; ir (nujol): 1670 $cm^{-1}$; $^1H$ nmr (dimethyl sulfoxide-

$d_6$): δ 1.63-2.04 (m, 4H, 2H-5, 2H-6), δ 2.30-2.9 (m, 4H, 2H-4, 2H-7), δ 7.61-8.40 (m, 3H, aromatic, H-9, H-10, H-12), δ 3.84 (s, 3H, $CH_3$), δ 1.4 (t, 3H, $CH_3$, δ 4.2 (q, 2H, $CH_2$); ms: m/z 341 ($M^+$); λ max absorption 374 nm, λ max emission 426 nm, log ε 4.19.

*Anal.* Calcd. for $C_{18}H_{19}N_3O_2S$: C, 63.34; H, 5.57; N, 12.31; S, 9.38. Found: C, 63.48; H, 5.71; N, 12.24; S, 9.31.

2-*N*-(3-Carbethoxy-4,5,6,7-tetrahydrobenzo[*b*]thiophen-2-yl)-5-methoxybenzo[*d*]-1,2,3-triazole (**5g**).

The same procedure as described for the oxidation of **4a** to **5a** was applied to the oxidation of **4g**, yielding 2-*N*-(3-carbethoxy-4,5,6,7-tetrahydrobenzo[*b*]thiophen-2-yl)-5-methoxybenzo[*b*]-1,2,3-triazole **5g**, recrystallised from DMF to yield 1.12 g (63%) of **5g**, mp 347°; ir (nujol): 1690 $cm^{-1}$; $^1H$ nmr (dimethyl sulfoxide-$d_6$): 1.61-2.07 (m, 4H, 2H-5, 2H-6), 2.36-2.91 (m, 4H, 2H-4, 2H-7), 7.20-8.29 (m, 3H, aromatic, H-9, H-10, H-12), δ 4.1 (s, 3H, $OCH_3$), δ 1.4 (t, 3H, $CH_3$), 4.4 (q, 2H, $CH_2$); ms: m/z 357 ($M^+$); λ max absorption 369 nm, λ max emission 429 nm, log ε 4.26.

*Anal.* Calcd. for $C_{18}H_{19}N_3O_3S$:C, 60.50; H, 5.32; N, 11.76; S, 8.96. Found: C, 60.61; H, 5.44; N, 11.71; S, 8.88.

2-*N*-(3-Carbethoxy-4,5,6,7-tetrahydrobenzo[*b*]thiophen-2-yl)-5-cyano-4-methylbenzimidazolo[1′,2′:1,6]pyrido[2,3-*d*]-1,2,3-triazole (**5h**).

The same procedure as described for the oxidation of **4a** to **5a** was applied to the oxidation of **4h** yielding 2-*N*-(3-carbethoxy-4,5,6,7-tetrahydrobenzo[*b*]thiophen-2-yl)-5-cyano-4-methylbenzimidazolo[1′,2′:1,6]pyrido[2,3-*d*]-1,2,3-triazole **5h**, recrystallised from DMF to yield 1.39 g (61%) of **5h**, mp >360°; ir (nujol): 1670, 2200 $cm^{-1}$; λ max absorption 382 nm, λ max emission 456 nm, log ε 4.35.

*Anal.* Calcd. for $C_{24}H_{20}N_6O_2S$: C, 63.15; H, 4.38; N, 18.42; S, 7.01. Found: C, 63.02; H, 4.29; N, 18.38; S, 7.08.

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