# Concise Synthesis of 3-Acetoxy-*N*,*N*-dialkylbenzo[*b*]thiophene-2-carboxamides from 2-Ethylsulfanylbenzoates

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**Abstract:** A convenient method for the synthesis of 3-acetoxy-*N*,*N*-dialkylbenzo[*b*]thiophene-2-carboxamides has been developed in three steps from 2-ethylsulfanylbenzoates using an interrupted Pummerer reaction of *N*,*N*-dialkyl-3-(2-ethylsulfinylphenyl)-3-oxopropanamides. Thus, treatment of these sulfinyl amides, prepared by the reaction of 2-ethylsulfanylbenzoates with lithium enolates of *N*,*N*-dialkylacetamides followed by oxidation of the resulting *N*,*N*-dialkyl-3-(2-ethylsulfanylphenyl)-3-oxopropanamides with sodium metaperiodate and acetic anhydride at 100 °C leads to the formation of the desired benzo[*b*]thiophenes.

**Key words:** 3-acetoxybenzo[*b*]thiophene-2-carboxamides, 2-ethylsulfanylbenzoates, interrupted Pummerer reaction, sulfoxides, acetic anhydride

We have recently described the synthesis of 3-arylbenzo[*b*]thiophenes by an interrupted Pummerer reaction of 2-ethylsulfinyl-α-arylstyrenes; the sulfoxides are heated in acetic anhydride at 100 °C to give the 3-arylbenzo[*b*]thiophenes in reasonable yields.[1] In this paper, we wish to report that the interrupted Pummerer reaction of *N*,*N*-dialkyl-3-(2-ethylsulfinylphenyl)-3-oxopropanamides, which can be easily prepared in two step from 2-sulfanylbenzoates, provides a concise route for the preparation of 3-acetoxy-*N*,*N*-dialkylbenzo[*b*]thiophene-2-carboxamides. Several methods for the preparation of 3-hydroxybenzo[*b*]thiophene-2-carboxic acid ester derivatives have already been reported[2] due to their biological utilities.[3] 3-Hydroxybenzo[*b*]thiophene-2-carboxamide derivatives are also of biological importance.[4] However, as far as we are aware, few general methods for the preparation of 3-hydroxybenzo[*b*]thiophene-2-carboxamide derivatives have been reported, though Lau et al. have demonstrated the formation of 3-hydroxy-*N*,*N*-dimethylbenzo[*b*]thiophene-2-carboxamide by a sodium hydroxide-catalyzed cyclization of *S*-(2-acetylphenyl)dimethylthiocarbamate.[5] Quite recently Steinmetz et al. have reported the synthesis of 3-hydroxy-*N*-methyl-*N*-phenylbenzo[*b*]thiophene-2-carboxamide from methyl 2-sulfanylbenzoate and 2-chloro-*N*-methyl-*N*-phenylbenzamide.[6] The present paper is the first report on the general synthesis of 3-hydroxybenzo[*b*]thiophene-2-carboxamide derivatives.

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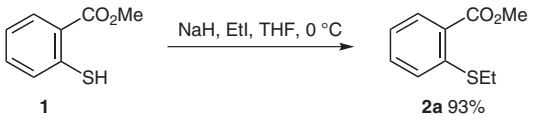
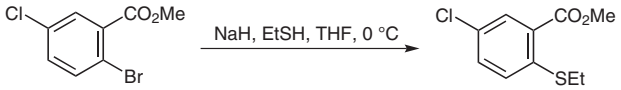
Two starting 2-sulfanylbenzoates were prepared as follows. First, S-ethylation of commercially available methyl 2-sulfanylbenzoate (**1**) with iodoethane in the presence of sodium hydride as a base gave methyl 2-ethylsulfanylbenzoate (**2a**) in 93% yield as depicted in Scheme 1. Then, 5-chloro-2-ethylsulfanylbenzoate (**2b**) was obtained in 80% yield by substitution of 2-bromo function of commercially available methyl 2-bromo-5-chlorobenzoate (**3**) with ethane thiolate, generated from ethanethiol and sodium hydride as shown in Scheme 2.



**1** **2a** 93%

**Scheme 1** Preparation of methyl 2-ethylsulfanylbenzoate (**2a**)

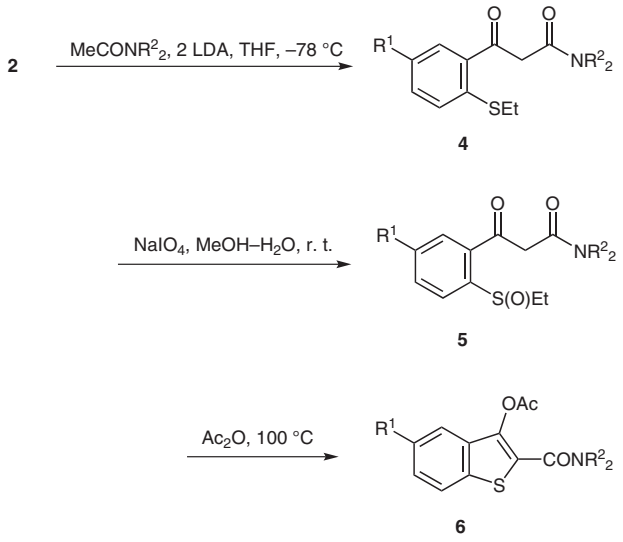


**3** **2b** 80%

**Scheme 2** Preparation of methyl 5-chloro-2-ethylsulfanylbenzoate (**2b**)

The procedure developed for the synthesis of *N*,*N*-dialkylbenzo[*b*]thiophene-2-carboxamides **6** from **2** is illustrated in Scheme 3. Thus, compounds **2** were readily converted into *N*,*N*-dialkyl-3-(2-ethylsulfanylphenyl)-3-oxopropanamides **4** in excellent yields on treatment with lithium enolates of *N*,*N*-dialkylacetamides in THF at –78 °C. Reaction of these sulfides with sodium metaperiodate in aqueous methanol at room temperature furnished the corresponding sulfoxides, *N*,*N*-dialkyl-3-(2-ethylsulfinylphenyl)-3-oxopropanamides **5**, in excellent yields as well. Subsequent cyclization of these substrates was carried out under the same conditions as previously described for the preparation of 3-arylbenzo[*b*]thiophenes (acetic anhydride, 100 °C). The cyclization occurred relative smoothly to afford the desired products **6** in fair yields as summarized in Table 1.

Mechanistically, this cyclization process for the formation of 3-acetoxybenzo[*b*]thiophene-2-carboxamides **6** from 3-(2-ethylsulfinylphenyl)-3-oxopropanamides **5** appears to proceed as illustrated in Scheme 4. Thus, treatment of **5** with acetic anhydride generates an acetoxylated sulfo-




**Scheme 3** Preparation of 3-acetoxybenzo[*b*]thiophene-2-carboxamides **6** (for $R^1$ and $R^2$, see Table 1)

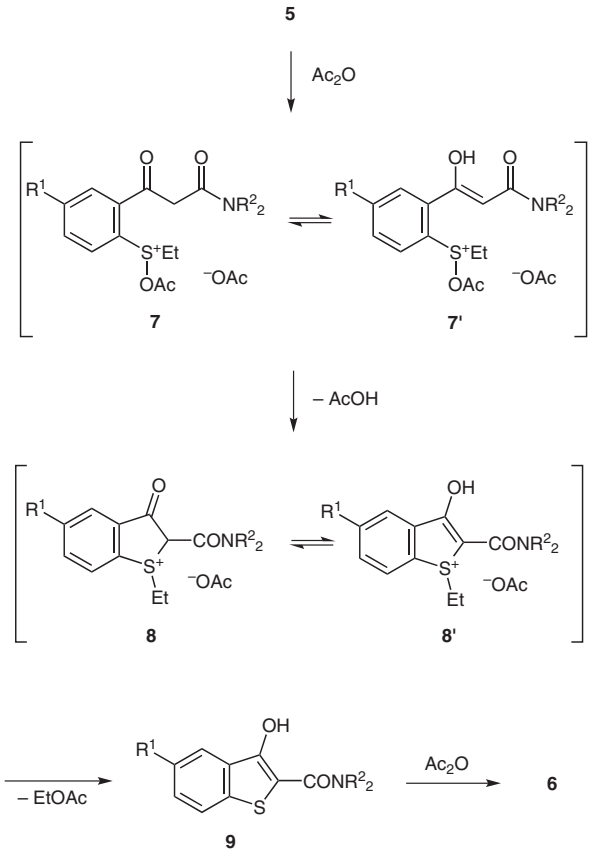
**Table 1** Preparation of 3-Acetoxybenzo[*b*]thiophene-2-carboxamides **6**

| Entry | **2** | $NR^2_2$ | **4** (Yield, %)[a] | **5** (Yield, %)[a] | **6** (Yield, %)[a] |
|---|---|---|---|---|---|
| 1 | **2a** | $NMe_2$ | **4a** (92) | **5a** (94) | **6a** (63) |
| 2 | **2a** | $NEt_2$ | **4b** (93) | **5b** (98) | **6b** (61) |
| 3 | **2a** | pyrrolidin-1-yl | **4c** (92) | **5c** (93) | **6c** (63) |
| 4 | **2a** | piperidin-1-yl | **4d** (94) | **5d** (91) | **6d** (62) |
| 5 | **2a** | morpholin-4-yl | **4e** (88) | **5e** (95) | **6e** (61) |
| 6 | **2b** | $NMe_2$ | **4f** (90) | **5f** (98) | **6f** (61) |
| 7 | **2b** | $NEt_2$ | **4g** (86) | **5g** (98) | **6g** (63) |
| 8 | **2b** | pyrrolidin-1-yl | **4h** (93) | **5h** (90) | **6h** (57) |
| 9 | **2b** | piperidin-1-yl | **4i** (93) | **5i** (89) | **6i** (54) |
| 10 | **2b** | morpholin-4-yl | **4j** (86) | **5j** (90) | **6j** (58) |

[a] Isolated yields. **4a–e**, **5a–e**, **6a–e**: $R^1$ = H; **4f–j**, **5f–j**, **6f–j**: $R^1$ = Cl.

nium ion intermediate **7**, which tautomerizes to its enol form **7′**. Trapping of the sulfonium ion center by the enol moiety of **7′** with a loss of acetic acid produces a 3-oxo-2,3-dihydrobenzothiophenium ion intermediate **8**, which tautomerizes to the 3-hydroxybenzothiophenium ion intermediate **8′**. Removal of ethyl acetate from this intermediate gives a 3-hydroxybenzo[*b*]thiophene-2-carboxamide precursor **9**, which is finally acetylated with acetic anhydride to lead to **6**.

In conclusion, we have demonstrated that 3-acetoxy-*N*,*N*-dialkylbenzo[*b*]thiophene-2-carboxamides, which are difficult to prepare by previous methods, can be conveniently synthesized from 2-ethylsulfanylbenzoates in three steps using an interrupted Pummerer reaction of *N*,*N*-dialkyl-3-(2-ethylsulfinylphenyl)-3-oxopropanamides as the key and final step. The ready availability of the starting materials and the ease of operations make the present method attractive.




**Scheme 4** Probable pathway to benzo[*b*]thiophene-2-carboxamides **6**

All melting points were obtained on a Laboratory Devices MEL-TEMP II melting apparatus and are uncorrected. IR spectra were recorded on a Shimadzu FTIR-8300 spectrophotometer. $^1$H NMR spectra were recorded in $CDCl_3$ using TMS as an internal reference on a JEOL ECP500 FT NMR spectrometer operating at 500 MHz or JEOL LA400FT NMR spectrometer operating at 400 MHz. $^{13}$C NMR spectra were measured in $CDCl_3$ using TMS as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 125 MHz. Low-resolution MS spectra (EI, 70 eV) were obtained by using a JEOL JMS AX505 HA spectrometer. TLC was carried out on a Merck Kieselgel 60 $PF_{254}$. Column chromatography was performed using Wako Gel C-200E. All of the organic solvents used in this study were dried over appropriate drying agents and distilled prior to use. BuLi was supplied by Asia Lithium Corporation. All other chemicals used in this study were commercially available. All of the reactions excluding the conversion of compounds **4** into **5** were carried out under argon.

**Methyl 2-(Ethylsulfanyl)benzoate (2a)[7]**

This compound was prepared by treating methyl 2-sulfanylbenzoate (**1**; 1.96 g, 10 mmol) with EtI (1.72 g, 11 mmol) in the presence of NaH (0.264 g, 11 mmol) in THF (24 mL) at 0 °C; yield: 1.82 g (93%); white solid; mp 29–30 °C (pentane) (Lit.[7] mp <30 °C). The spectral data (IR and $^1$H NMR) of this product were identical to those reported previously.[7]

**Methyl 3-Chloro-6-ethylsulfanylbenzoate (2b)**

This compound was prepared by treating methyl 2-bromo-5-chlorobenzoate (**3**; 2.5 g, 10 mmol) with NaSEt generated from EtSH

(0.744 g, 12 mmol) and NaH (0.288 g, 12 mmol) in DMF (12 mL) at 0 °C; yield: 1.84 g (80%); white solid; mp 55–58 °C (hexane).

IR (KBr): 1717 $cm^{-1}$.

$^1H$ NMR (400 MHz): δ = 1.38 (t, *J* = 7.3 Hz, 3 H), 2.94 (q, *J* = 7.3 Hz, 2 H), 3.92 (s, 3 H), 7.24 (d, *J* = 8.7 Hz, 1 H), 7.40 (dd, *J* = 8.7, 2.3 Hz, 1 H), 7.94 (d, *J* = 2.3 Hz, 1 H).

Anal. Calcd for $C_{10}H_{11}ClO_2S$: C, 52.06; H, 4.81. Found: C, 52.05; H, 4.82.

### 3-(2-Ethylsulfanylphenyl)-3-oxopropanamides 4; General Procedure

The respective ethylsulfanylbenzoate **2a**,**b** (1.0 mmol) was added to a stirred solution of the appropriate lithium enolate of *N*,*N*-dialkylacetamide (1.0 mmol), generated by the treatment of *N*,*N*-dialkylacetamides (1.0 mmol) with LDA (2.0 mmol) in THF (4 mL) at –78 °C. The reaction mixture was stirred at the same temperature for 30 min before sat. aq $NH_4Cl$ (10 mL) was added. The mixture was warmed to r.t. and extracted with EtOAc (3 × 10 mL). The combined extracts were washed with brine (10 mL) and dried ($Na_2SO_4$). Evaporation of the solvent gave a residue, which was purified by column chromatography on silica gel [$Et_2O$–hexane (1:2) or EtOAc–hexane (1:2)] to give **4**.

### 3-(2-Ethylsulfanylphenyl)-*N*,*N*-dimethyl-3-oxopropanamide (4a)

Pale-yellow solid; mp 64–69 °C (hexane–$Et_2O$); observed as a tautomeric mixture with the enol form in $CDCl_3$ (ca. 4:6).

IR (KBr): 3500–2500, 1622 $cm^{-1}$.

$^1H$ NMR (400 MHz): δ = 1.32 (t, *J* = 7.3 Hz, 1.8 H), 1.36 (t, *J* = 7.3 Hz, 1.2 H), 2.93 (q, *J* = 7.3 Hz, 0.8 H), 2.96 (q, *J* = 7.3 Hz, 1.2 H), 2.99 (s, 1.2 H), 3.05 (s, 3.6 H), 3.08 (s, 1.2 H), 4.11 (s, 0.8 H), 5.61 (s, 0.6 H), 7.16–7.24 (m, 1 H), 7.30–7.38 (m, 1.6 H), 7.43–7.50 (m, 1 H), 7.95 (dd, *J* = 7.7, 1.4 Hz, 0.4 H), 10.72 (br s, 0.6 H).

Anal. Calcd for $C_{13}H_{17}NO_2S$: C, 62.12; H, 6.82; N, 5.57. Found: C, 61.91; H, 6.71; N, 5.56.

### *N*,*N*-Diethyl-3-(2-ethylsulfanylphenyl)-3-oxopropanamide (4b)

Yellow oil; $R_f$ = 0.25 ($Et_2O$–hexane, 1:2); observed as a tautomeric mixture with the enol form in $CDCl_3$ (ca. 4:6).

IR (neat): 3500–2500, 1632 $cm^{-1}$.

$^1H$ NMR (500 MHz): δ = 1.11–1.37 (m, 9 H), 2.91–2.98 (m, 2 H), 3.34–3.48 (m, 4 H), 4.07 (s, 0.8 H), 5.56 (s, 0.6 H), 7.17–7.34 (m, 2.2 H), 7.37 (d, *J* = 8.2 Hz, 0.4 H), 7.44 (ddd, *J* = 8.2, 7.3, 1.4 Hz, 0.4 H), 7.50 (d, *J* = 7.8 Hz, 0.6 H), 7.97 (d, *J* = 7.8 Hz, 0.4 H), 10.76 (br s, 0.6 H).

Anal. Calcd for $C_{15}H_{21}NO_2S$: C, 64.48; H, 7.58; N, 5.01. Found: C, 64.39; H, 7.71; N, 4.90.

### 3-(2-Ethylsulfanylphenyl)-1-(pyrrolidin-1-yl)propane-1,3-dione (4c)

White solid; mp 87–89 °C (hexane); observed as a tautomeric mixture with the enol form in $CDCl_3$ (ca. 2:8).

IR (KBr): 3500–2500, 1626 $cm^{-1}$.

$^1H$ NMR (500 MHz): δ = 1.32 (t, *J* = 7.3 Hz, 2.4 H), 1.36 (t, *J* = 7.3 Hz, 0.6 H), 1.87–2.01 (m, 4 H), 2.94 (q, *J* = 7.3 Hz, 0.4 H), 2.96 (q, *J* = 7.3 Hz, 1.6 H), 3.45–3.57 (m, 4 H), 4.05 (s, 0.4 H), 5.47 (s, 0.8 H), 7.16–7.24 (m, 1 H), 7.32–7.33 (m, 1.6 H), 7.37 (d, *J* = 7.8 Hz, 0.2 H), 7.45 (ddd, *J* = 7.8, 7.3, 1.4 Hz, 0.2 H), 7.48 (dd, *J* = 7.8, 1.4 Hz, 0.8 H), 7.99 (dd, *J* = 7.8, 1.4 Hz, 0.2 H), 10.76 (br s, 0.8 H).

Anal. Calcd for $C_{15}H_{19}NO_2S$: C, 64.95; H, 6.90; N, 5.05. Found: C, 64.87; H, 7.17; N, 5.06.

### 3-(2-Ethylsulfanylphenyl)-1-(piperidin-1-yl)propane-1,3-dione (4d)

Pale-yellow oil; $R_f$ = 0.25 (EtOAc–hexane, 1:2); observed as a tautomeric mixture with the enol form in $CDCl_3$ (ca. 6:4).

IR (neat): 3500–2500, 1674, 1634 $cm^{-1}$.

$^1H$ NMR (500 MHz): δ = 1.32 (t, *J* = 7.3 Hz, 1.2 H), 1.36 (t, *J* = 7.3 Hz, 1.8 H), 1.53–1.68 (m, 6 H), 2.93 (q, *J* = 7.3 Hz, 1.2 H), 2.95 (q, *J* = 7.3 Hz, 0.8 H), 3.45–3.59 (m, 4 H), 4.11 (s, 1.2 H), 5.64 (s, 0.4 H), 7.16–7.23 (m, 1 H), 7.32–7.38 (1.4 H), 7.43–7.49 (m, 1 H), 7.97 (d, *J* = 7.8 Hz, 0.6 H), 10.89 (br s, 0.4 H).

Anal. Calcd for $C_{16}H_{21}NO_2S$: C, 65.95; H, 7.26; N, 4.81. Found: C, 65.96; H, 7.48; N, 4.75.

### 3-(2-Ethylsulfanylphenyl)-1-(morpholin-4-yl)propane-1,3-dione (4e)

White solid; mp 90–93 °C (hexane); observed as a tautomeric mixture with the enol form in $CDCl_3$ (ca. 8:2).

IR (KBr): 3500–2500, 1670, 1641, 1626 $cm^{-1}$.

$^1H$ NMR (500 MHz): δ = 1.32 (t, *J* = 7.3 Hz, 0.6 H), 1.36 (t, *J* = 7.3 Hz, 2.4 H), 2.94 (q, *J* = 7.3 Hz, 1.6 H), 2.97 (q, *J* = 7.3 Hz, 0.4 H), 3.55–3.72 (m, 8 H), 4.12 (s, 1.6 H), 5.60 (s, 0.2 H), 7.17–7.25 (m, 1.4 H), 7.38 (d, *J* = 7.3 Hz, 0.8 H), 7.45–7.50 (m, 1 H), 7.97 (dd, *J* = 7.8, 1.4 Hz, 0.8 H), 10.89 (br s, 0.2 H).

Anal. Calcd for $C_{15}H_{19}NO_3S$: C, 61.41; H, 6.53; N, 4.77. Found: C, 61.18; H, 6.58; N, 4.74.

### 3-(5-Chloro-2-ethylsulfanylphenyl)-*N*,*N*-dimethyl-3-oxopropanamide (4f)

Yellow solid; mp 67–70 °C (hexane); observed as a tautomeric mixture with the enol form in $CDCl_3$ (ca. 5:5).

IR (KBr): 3500–2500, 1676, 1636 $cm^{-1}$.

$^1H$ NMR (500 MHz): δ = 1.31 (t, *J* = 7.3 Hz, 1.5 H), 1.34 (t, *J* = 7.3 Hz, 1.5 H), 2.92 (q, *J* = 7.3 Hz, 1 H), 2.93 (q, *J* = 7.3 Hz, 1 H), 2.99 (s, 1.5 H), 3.05 (s, 3 H), 3.08 (s, 1.5 H), 4.09 (s, 1 H), 5.61 (s, 0.5 H), 7.25 (d, *J* = 8.2 Hz, 0.5 H), 7.29 (dd, *J* = 8.7, 2.8 Hz, 0.5 H), 7.31 (d, *J* = 8.7 Hz, 0.5 H), 7.40 (dd, *J* = 8.2, 2.3 Hz, 0.5 H), 7.48 (d, *J* = 2.8 Hz, 0.5 H), 7.86 (d, *J* = 2.3 Hz, 0.5 H), 10.93 (br s, 0.5 H).

Anal. Calcd for $C_{13}H_{16}ClNO_2S$: C, 54.63; H, 5.64; N, 4.90. Found: C, 54.41; H, 5.84; N, 5.00.

### 3-(5-Chloro-2-ethylsulfanylphenyl)-*N*,*N*-diethyl-3-oxopropanamide (4g)

Pale-yellow solid; mp 76–78 °C (hexane); observed as a tautomeric mixture with the enol form in $CDCl_3$ (ca. 5:5).

IR (KBr): 3500–2500, 1674, 1620 $cm^{-1}$.

$^1H$ NMR (500 MHz): δ = 1.12–1.35 (m, 9 H), 2.89–2.96 (m, 2 H), 3.35–3.49 (m, 4 H), 4.04 (s, 1 H), 5.56 (s, 0.5 H), 7.25 (d, *J* = 8.2 Hz, 0.5 H), 7.28–7.31 (m, 1 H), 7.39 (dd, *J* = 8.2, 2.3 Hz, 0.5 H), 7.50 (d, *J* = 2.3 Hz, 0.5 H), 7.88 (d, *J* = 2.3 Hz, 0.5 H), 10.91 (br s, 0.5 H).

Anal. Calcd for $C_{15}H_{20}ClNO_2S$: C, 57.40; H, 6.42; N, 4.46. Found: C, 57.28; H, 6.41; N, 4.21.

### 1-(5-Chloro-2-ethylsulfanylphenyl)-3-(pyrrolidin-1-yl)propane-1,3-dione (4h)

Yellow solid; mp 83–85 °C (hexane); observed as a tautomeric mixture with the enol form in $CDCl_3$ (ca. 4:6).

IR (KBr): 3500–2500, 1624, 1603 $cm^{-1}$.

$^1H$ NMR (500 MHz): δ = 1.31 (t, *J* = 7.3 Hz, 1.8 H), 1.34 (t, *J* = 7.3 Hz, 1.2 H), 1.86–2.01 (m, 4 H), 2.91 (q, *J* = 7.3 Hz, 0.8 H), 2.94 (q, *J* = 7.3 Hz, 1.2 H), 3.45–3.57 (m, 4 H), 4.02 (s, 0.8 H), 5.48 (s, 0.6 H), 7.25 (d, *J* = 8.2 Hz, 0.6 H), 7.29 (dd, *J* = 8.2, 2.3 Hz, 0.6 H), 7.30

(d, $J$ = 8.2 Hz, 0.4 H), 7.40 (dd, $J$ = 8.2, 2.3 Hz, 0.4 H), 7.48 (d, $J$ = 2.3 Hz, 0.6 H), 7.91 (d, $J$ = 2.3 Hz, 0.4 H), 10.88 (br s, 0.6 H).

Anal. Calcd for $C_{15}H_{18}ClNO_2S$: C, 57.78; H, 5.82; N, 4.49. Found: C, 57.50; H, 5.80; N, 4.41.

**1-(5-Chloro-2-ethylsulfanylphenyl)-3-(piperidin-1-yl)propane-1,3-dione (4i)**

Yellow solid; mp 58–60 °C (hexane–$CH_2Cl_2$); observed as a tautomeric mixture with the enol form in $CDCl_3$ (ca. 6:4).

IR (KBr): 3500–2500, 1676, 1628 $cm^{-1}$.

$^1H$ NMR (500 MHz): δ = 1.31 (t, $J$ = 7.3 Hz, 1.2 H), 1.34 (t, $J$ = 7.3 Hz, 1.8 H), 1.56–1.69 (m, 6 H), 2.91 (q, $J$ = 7.3 Hz, 1.2 H), 2.93 (q, $J$ = 7.3 Hz, 0.8 H), 3.45 (t, $J$ = 5.0 Hz, 2 H), 3.58 (t, $J$ = 5.0 Hz, 2 H), 4.08 (s, 1.2 H), 5.63 (s, 0.4 H), 7.25 (d, $J$ = 8.7 Hz, 0.4 H), 7.29 (dd, $J$ = 8.7, 2.3 Hz, 0.4 H), 7.30 (d, $J$ = 8.7 Hz, 0.6 H), 7.40 (dd, $J$ = 8.7, 2.3 Hz, 0.6 H), 7.48 (d, $J$ = 2.3 Hz, 0.4 H), 7.88 (d, $J$ = 2.3 Hz, 0.6 H), 10.87 (br s, 0.4 H).

Anal. Calcd for $C_{16}H_{20}ClNO_2S$: C, 58.97; H, 6.19; N, 4.30. Found: C, 58.95; H, 6.40; N, 4.18.

**1-(5-Chloro-2-ethylsulfanylphenyl)-3-(morpholin-4-yl)propane-1,3-dione (4j)**

Beige solid; mp 96–99 °C (hexane–EtOAc); observed as a tautomeric mixture with the enol form in $CDCl_3$ (ca. 6:4).

IR (KBr): 3500–2500, 1672, 1651, 1638 $cm^{-1}$.

$^1H$ NMR (500 MHz): δ = 1.31 (t, $J$ = 7.3 Hz, 1.2 H), 1.35 (t, $J$ = 7.3 Hz, 1.8 H), 1.92 (q, $J$ = 7.3 Hz, 1.2 H), 2.94 (q, $J$ = 7.3 Hz, 0.8 H), 3.52–3.72 (m, 8 H), 4.09 (s, 1.2 H), 5.60 (s, 0.4 H), 7.25 (d, $J$ = 8.7 Hz, 0.4 H), 7.30 (dd, $J$ = 8.7, 2.3 Hz, 0.4 H), 7.31 (d, $J$ = 8.7 Hz, 0.6 H), 7.42 (dd, $J$ = 8.7, 2.3 Hz, 0.6 H), 7.48 (d, $J$ = 2.3 Hz, 0.4 H), 7.88 (d, $J$ = 2.3 Hz, 0.6 H), 10.91 (br s, 0.4 H).

Anal. Calcd for $C_{15}H_{18}ClNO_3S$: C, 54.96; H, 5.53; N, 4.27. Found: C, 54.94; H, 5.67; N, 4.22.

**3-(2-Ethylsulfinylphenyl)-*N*,*N*-dimethyl-3-oxopropanamides 5; General Procedure**

The amide **4** (0.80 mmol) was stirred with an equimolar amount of $NaIO_4$ (0.80 mmol) in aq MeOH (1:5, 6 mL) at r.t. overnight. After most of the MeOH was removed by evaporation, $H_2O$ (10 mL) was added and the mixture was extracted with EtOAc (3 × 10 mL). The combined extracts were washed with brine (10 mL) and dried ($Na_2SO_4$). Evaporation of the solvent gave a residue, which was purified by column chromatography on silica gel using the eluents indicated below to give **5**.

**3-(2-Ethylsulfinylphenyl)-*N*,*N*-dimethyl-3-oxopropanamide (5a)**

Pale-yellow oil; $R_f$ = 0.16 (THF–hexane, 1:2); observed as a tautomeric mixture with the enol form in $CDCl_3$ (ca. 7:3).

IR (neat): 3445, 1681, 1633, 1018 $cm^{-1}$.

$^1H$ NMR (500 MHz): δ = 1.28 (t, $J$ = 7.3 Hz, 0.9 H), 1.32 (t, $J$ = 7.3 Hz, 2.1 H), 2.69–2.80 (m, 2 H), 3.01 (s, 1.8 H), 3.068 (s, 2.1 H), 3.075 (s, 2.1 H), 4.05 (d, $J$ = 15.1 Hz, 0.7 H), 4.19 (d, $J$ = 15.1 Hz, 0.7 H), 5.66 (s, 0.3 H), 7.49 (ddd, $J$ = 7.8, 7.3, 1.4 Hz, 0.3 H), 7.58–7.66 (m, 1.3 H), 7.83 (ddd, $J$ = 7.8, 7.3, 1.4 Hz, 0.7 H), 8.10 (dd, $J$ = 7.8, 1.4 Hz, 0.7 H), 8.15 (dd, $J$ = 7.8, 1.4 Hz, 0.3 H), 8.32 (dd, $J$ = 7.8, 1.4 Hz, 0.7 H), 10.80 (br s, 0.3 H).

Anal. Calcd for $C_{13}H_{17}NO_3S$: C, 58.40; H, 6.41; N, 5.24. Found: C, 58.37; H, 6.46; N, 5.10.

***N*,*N*-Diethyl-3-(2-ethylsulfinylphenyl)3-oxopropanamide (5b)**

Yellow oil; $R_f$ = 0.26 (THF–hexane, 1:1); observed as a tautomeric mixture with the enol form in $CDCl_3$ (ca. 4:6).

IR (neat): 3474, 1682, 1634, 1018 $cm^{-1}$.

$^1H$ NMR (500 MHz): δ = 1.14, 1.22, 1.27, and 1.32 (4 t, $J$ = 7.3 Hz each, combined 9 H), 2.68–2.79 (m, 1 H), 3.16–3.23 (m, 1 H), 3.33–3.44 (m, 4 H), 3.97 (d, $J$ = 15.1 Hz, 0.4 H), 4.16 (d, $J$ = 15.1 Hz, 0.4 H), 5.59 (s, 0.6 H), 7.49 (ddd, $J$ = 7.8, 7.3, 1.4 Hz, 0.4 H), 7.58 (dd, $J$ = 7.8, 1.4 Hz, 0.4 H), 7.61–7.66 (m, 1 H), 7.82 (ddd, $J$ = 7.8, 7.3, 1.4 Hz, 0.6 H), 8.11 (dd, $J$ = 7.8, 1.4 Hz, 0.6 H), 8.15 (dd, $J$ = 7.8, 1.4 Hz, 0.4 H), 8.31 (dd, $J$ = 7.8, 1.4 Hz, 0.6 H), 10.83 (br s, 0.6 H).

Anal. Calcd for $C_{15}H_{21}NO_3S$: C, 60.99; H, 7.17; N, 4.74. Found: C, 60.88; H, 7.30; N, 4.64.

**3-(2-Ethylsulfinylphenyl)-1-(pyrrolidin-1-yl)propane-1,3-dione (5c)**

Yellow oil; $R_f$ = 0.50 (THF); observed as a tautomeric mixture with the enol form in $CDCl_3$ (ca. 7:3).

IR (neat): 3460, 1682, 1634, 1015 $cm^{-1}$.

$^1H$ NMR (500 MHz): δ = 1.28 (t, $J$ = 7.3 Hz, 0.9 H), 1.31 (t, $J$ = 7.3 Hz, 2.1 H), 1.84–2.04 (m, 4 H), 2.69–2.80 (m, 1 H), 3.16–3.24 (m, 1 H), 3.43–3.57 (m, 4 H), 3.96 (d, $J$ = 14.7 Hz, 0.7 H), 4.14 (d, $J$ = 14.7 Hz, 0.7 H), 5.51 (s, 0.3 H), 7.48 (ddd, $J$ = 7.8, 7.3, 1.4 Hz, 0.3 H), 7.58 (dd, $J$ = 7.8, 1.4 Hz, 0.3 H), 7.61–7.66 (m, 1 H), 7.83 (ddd, $J$ = 7.8, 7.3, 1.4 Hz, 0.7 H), 8.13–8.16 (m, 1 H), 8.31 (dd, $J$ = 7.8, 1.4 Hz, 0.7 H), 10.86 (br s, 0.3 H).

Anal. Calcd for $C_{15}H_{19}NO_3S$: C, 61.41; H, 6.53; N, 4.77. Found: C, 61.32; H, 6.54; N, 4.52.

**3-(2-Ethylsulfinylphenyl)-1-(piperidin-1-yl)propane-1,3-dione (5d)**

Pale-yellow oil; $R_f$ = 0.16 (EtOAc); observed as a tautomeric mixture with the enol form in $CDCl_3$ (ca. 8:2).

IR (neat): 3460, 1678, 1633, 1018 $cm^{-1}$.

$^1H$ NMR (500 MHz): δ = 1.28 (t, $J$ = 7.3 Hz, 0.6 H), 1.32 (t, $J$ = 7.3 Hz, 2.4 H), 1.52–1.66 (m, 6 H), 2.69–2.79 (m, 1 H), 3.16–3.23 (m, 1 H), 3.40–3.59 (m, 4 H), 4.05 (d, $J$ = 15.6 Hz, 0.8 H), 4.16 (d, $J$ = 15.6 Hz, 0.8 H), 5.69 (s, 0.2 H), 7.48 (ddd, $J$ = 7.8, 7.3, 1.4 Hz, 0.2 H), 7.58 (dd, $J$ = 7.8, 1.4 Hz, 0.2 H), 7.61–7.66 (m, 1 H), 7.83 (ddd, $J$ = 7.8, 7.3, 1.4 Hz, 0.8 H), 8.13 (dd, $J$ = 7.8, 1.4 Hz, 0.8 H), 8.15 (dd, $J$ = 7.8, 1.4 Hz, 0.2 H), 8.31 (dd, $J$ = 7.8, 1.4 Hz, 0.8 H), 10.92 (nr s, 0.2 H).

Anal. Calcd for $C_{16}H_{21}NO_3S$: C, 62.51; H, 6.89; N, 4.56. Found: C, 62.42; H, 7.01; N, 4.55.

**3-(2-Ethylsulfinylphenyl)-1-(morpholin-4-yl)propane-1,3-dione (5e)**

Yellow oil; $R_f$ = 0.67 (THF–hexane, 2:1); observed as a tautomeric mixture with the enol form in $CDCl_3$ (ca. 8:2).

IR (neat): 3460, 1678, 1634, 1017 $cm^{-1}$.

$^1H$ NMR (500 MHz): δ = 1.28 (t, $J$ = 7.3 Hz, 0.6 H), 1.32 (t, $J$ = 7.3 Hz, 2.4 H), 2.69–2.79 (m, 1 H), 3.14–3.22 (m, 1 H), 3.49–3.75 (m, 8 H), 4.07 (d, $J$ = 15.1 Hz, 0.8 H), 4.18 (d, $J$ = 15.1 Hz, 0.8 H), 5.65 (s, 0.2 H), 7.49 (ddd, $J$ = 7.8, 7.3, 1.4 Hz, 0.2 H), 7.58 (dd, 7.8, 1.4 Hz, 0.2 H), 7.64 (ddd, $J$ = 7.8, 7.3, 1.4 Hz, 0.8 H), 7.66 (ddd, $J$ = 7.8, 7.3, 1.4 Hz, 0.2 H), 7.85 (ddd, $J$ = 7.8, 7.3, 1.4 Hz, 0.8 H), 8.12 (dd, $J$ = 7.8, 1.4 Hz, 0.8 H), 8.15 (dd, $J$ = 7.8, 1.4 Hz, 0.2 H), 8.32 (dd, $J$ = 7.8, 1.4 Hz, 0.8 H), 10.89 (br s, 0.2 H).

Anal. Calcd for $C_{15}H_{19}NO_4S$: C, 58.23; H, 6.19; N, 4.53. Found: C, 58.19; H, 6.20; N, 4.38.

**3-(5-Chloro-2-ethylsulfinylphenyl)-*N*,*N*-dimethyl-3-oxopropanamide (5f)**

Yellow oil; $R_f$ = 0.30 (THF–hexane, 1:1); observed as a tautomeric mixture with the enol form in $CDCl_3$ (ca. 5:5).

IR (neat): 3360, 1683, 1643, 1605, 1022 $cm^{-1}$.

$^1$H NMR (500 MHz): δ = 1.27 (t, *J* = 7.3 Hz, 1.5 H), 1.31 (t, *J* = 7.3 Hz, 1.5 H), 2.68–2.79 (m, 1 H), 3.01 (s, 1.5 H), 3.08 (br s, 4.5 H), 3.14–3.23 (m, 1 H), 3.99 (d, *J* = 15.6 Hz, 0.5 H), 4.15 (d, *J* = 15.6 Hz, 0.5 H), 5.64 (s, 0.5 H), 7.56 (d, *J* = 2.3 Hz, 0.5 H), 7.61 (dd, *J* = 8.2, 2.3 Hz, 0.5 H), 7.78 (dd, *J* = 8.2, 2.3 Hz, 0.5 H), 8.02 (d, *J* = 1.8 Hz, 0.5 H), 8.09 (d, *J* = 8.2 Hz, 0.5 H), 8.24 (d, *J* = 8.2 Hz, 0.5 H), 10.88 (br s, 0.5 H).

Anal. Calcd for $C_{13}H_{16}ClNO_3S$: C, 51.74; H, 5.34; N, 4.64. Found: C, 51.52; H, 5.34; N, 4.53.

**3-(5-Chloro-2-ethylsulfinylphenyl)-*N*,*N*-diethyl-3-oxopropanamide (5g)**

Pale-yellow oil; $R_f$ = 0.34 (EtOAc–hexane, 5:1); observed as a tautomeric mixture with the enol form in $CDCl_3$ (ca. 4:6).

IR (neat): 3422, 1684, 1634, 1022 cm$^{-1}$.

$^1$H NMR (500 MHz): δ = 1.25, 1.26, 1.27, and 1.30 (4t, *J* = 7.3 Hz each, combined 9 H), 2.69–2.80 (m, 1 H), 3.17–3.23 (m, 1 H), 3.35–3.48 (m, 4 H), 3.93 (d, *J* = 15.1 Hz, 0.4 H), 4.13 (d, *J* = 15.1 Hz, 0.4 H), 5.57 (s, 0.6 H), 7.55 (d, *J* = 1.8 Hz, 0.6 H), 7.60 (dd, *J* = 8.2, 1.8 Hz, 0.6 H), 7.77 (dd, *J* = 8.2, 1.8 Hz, 0.4 H), 8.03 (d, *J* = 1.8 Hz, 0.4 H), 8.09 (d, *J* = 8.2 Hz, 0.6 H), 8.24 (d, *J* = 8.2 Hz, 0.4 H), 10.92 (br s, 0.6 H).

Anal. Calcd for $C_{15}H_{20}ClNO_3S$: C, 54.62; H, 6.11; N, 4.25. Found: C, 54.58; H, 6.12; N, 4.24.

**1-(5-Chloro-2-ethylsulfinylphenyl)-3-(pyrrolidin-1-yl)propane-1,3-dione (5h)**

Yellow oil; $R_f$ = 0.30 (THF–hexane, 1:1); observed as a tautomeric mixture with the enol form in $CDCl_3$ (ca. 4:6).

IR (neat): 3325, 1682, 1634, 1022 cm$^{-1}$.

$^1$H NMR (500 MHz): δ = 1.27 (t, *J* = 7.3 Hz, 1.8 H), 1.30 (t, *J* = 7.3 Hz, 1.2 H), 1.92–2.06 (m, 4 H), 2.70–2.78 (m, 1 H), 3.16–3.22 (m, 1 H), 3.47–3.56 (m, 4 H), 3.91 (d, *J* = 14.7 Hz, 0.4 H), 4.11 (d, *J* = 14.7 Hz, 0.4 H), 5.51 (s, 0.6 H), 7.56 (d, *J* = 2.3 Hz, 0.6 H), 7.60 (dd, *J* = 8.2, 2.3 Hz, 0.6 H), 7.78 (dd, *J* = 8.2, 2.3 Hz, 0.4 H), 8.07 (d, *J* = 2.3 Hz, 0.4 H), 8.09 (d, *J* = 8.2 Hz, 0.6 H), 8.24 (d, *J* = 8.2 Hz, 0.4 H), 10.90 (br s, 0.6 H).

Anal. Calcd for $C_{15}H_{18}ClNO_3S$: C, 54.96; H, 5.53; N, 4.27. Found: C, 54.95; H, 5.54; N, 4.24.

**1-(5-Chloro-2-ethylsulfinylphenyl)-3-(piperidin-1-yl)propane-1,3-dione (5i)**

Pale-yellow oil; $R_f$ = 0.30 (EtOAc–hexane, 1:2); observed as a tautomeric mixture with the enol form in $CDCl_3$ (ca. 6:4).

IR (neat): 3420, 1683, 1634, 1020 cm$^{-1}$.

$^1$H NMR (500 MHz): δ = 1.27 (t, *J* = 7.3 Hz, 1.2 H), 1.30 (t, *J* = 7.3 Hz, 1.8 H), 1.56–1.71 (m, 6 H), 2.69–2.80 (m, 1 H), 3.15–3.23 (m, 1 H), 3.40–3.60 (m, 4 H), 3.99 (d, *J* = 15.1 Hz, 0.6 H), 4.12 (d, *J* = 15.1 Hz, 0.6 H), 5.68 (s, 0.4 H), 7.56 (d, *J* = 1.8 Hz, 0.4 H), 7.60 (dd, *J* = 8.7, 1.8 Hz, 0.4 H), 7.78 (dd, *J* = 8.2, 2.3 Hz, 0.6 H), 8.04 (d, *J* = 2.3 Hz, 0.6 H), 8.08 (d, *J* = 8.7 Hz, 0.4 H), 8.24 (d, *J* = 8.2 Hz, 0.6 H), 10.87 (br s, 0.4 H).

Anal. Calcd for $C_{16}H_{20}ClNO_3S$: C, 56.21; H, 5.90; N, 4.10. Found: C, 56.18; H, 5.90; N, 4.08.

**1-(5-Chloro-2-ethylsulfinylphenyl)-3-(morpholin-4-yl)propane-1,3-dione (5j)**

Pale-yellow oil; $R_f$ = 0.41 (EtOAc); observed as a tautomeric mixture with the enol form in $CDCl_3$ (ca. 6:4).

IR (neat): 3420, 1682, 1639, 1020 cm$^{-1}$.

$^1$H NMR (500 MHz): δ = 1.27 (t, *J* = 7.3 Hz, 1.2 H), 1.31 (t, *J* = 7.3 Hz, 1.8 H), 2.70–2.80 (m, 1 H), 3.13–3.21 (m, 1 H), 3.49–3.76 (m, 8 H), 4.02 (d, *J* = 15.1 Hz, 0.6 H), 4.15 (d, *J* = 15.1 Hz, 0.6 H), 5.64 (s, 0.4 H), 7.55 (d, *J* = 1.8 Hz, 0.4 H), 7.61 (dd, *J* = 8.2, 1.8 Hz, 0.4 H), 7.80 (dd, *J* = 8.7, 1.8 Hz, 0.6 H), 8.05 (d, *J* = 1.8 Hz, 0.6 H), 8.09 (d, *J* = 8.2 Hz, 0.4 H), 8.25 (d, *J* = 8.7 Hz, 0.6 H), 10.91 (br s, 0.4 H).

Anal. Calcd for $C_{15}H_{18}ClNO_4S$: C, 52.40; H, 5.28; N, 4.07. Found: C, 52.29; H, 5.26; N, 4.07.

**3-Acetoxy-*N*,*N*-dimethylbenzo[*b*]thiophene-2-carboxamide (6a); Typical Procedure**

A solution of **5a** (0.17 g, 0.63 mmol) in $Ac_2O$ (2 mL) was heated at 100 °C under stirring until the disappearance of **5a** had been confirmed by TLC analyses ($SiO_2$; THF–hexane, 1:2). After cooling, excess $Ac_2O$ was removed under reduced pressure, and the residue was purified by preparative TLC on silica gel to give **6a** (0.10 g, 63%) as a pale-orange oil; $R_f$ = 0.21 (THF–hexane, 1:2).

IR (neat): 1778, 1633 cm$^{-1}$.

$^1$H NMR (500 MHz): δ = 2.39 (s, 3 H), 3.11 (s, 6 H), 7.38–7.44 (m, 2 H), 7.58–7.62 (m, 1 H), 7.76–7.80 (m, 1 H).

$^{13}$C NMR: δ = 20.6, 35.5, 121.3, 122.7, 122.8, 124.9, 126.3, 132.0, 136.4, 138.9, 163.2, 168.0.

MS: *m*/*z* (%) = 263 (8.7, [M$^+$]), 221 (100).

Anal. Calcd for $C_{13}H_{13}NO_3S$: C, 59.30; H, 4.98; N, 5.32. Found: C, 59.27; H, 5.01; N, 5.16.

**3-Acetoxy-*N*,*N*-diethylbenzo[*b*]thiophene-2-carboxamide (6b)**

Beige oil; $R_f$ = 0.12 (THF–hexane, 1:3).

IR (neat): 1778, 1634 cm$^{-1}$.

$^1$H NMR (500 MHz): δ = 1.21 (t, *J* = 7.3 Hz, 6 H), 2.37 (s, 3 H), 3.50 (q, *J* = 7.3 Hz, 4 H), 7.39–7.43 (m, 2 H), 7.59–7.62 (m, 1 H), 7.76–7.79 (m, 1 H).

$^{13}$C NMR: δ = 13.9, 20.6, 41.8, 121.2, 122.7, 122.8, 124.9, 126.2, 132.0, 136.1, 138.8, 162.4, 168.1.

MS: *m*/*z* (%) = 291 (9.2, [M$^+$]), 249 (100).

Anal. Calcd for $C_{15}H_{17}NO_3S$: C, 61.83; H, 5.88; N, 4.81. Found: C, 61.62; H, 5.90; N, 4.69.

**2-(Pyrrolidin-1-ylcarbonyl)benzo[*b*]thiophen-3-yl Acetate (6c)**

Pale-yellow oil; $R_f$ = 0.18 (EtOAc–hexane, 1:2).

IR (neat): 1775, 1623 cm$^{-1}$.

$^1$H NMR (500 MHz): δ = 1.94 (br s, 4 H), 2.40 (s, 3 H), 3.61–3.64 (m, 4 H), 7.39–7.44 (m, 2 H), 7.63–7.65 (m, 1 H), 7.76–7.78 (m, 1 H).

$^{13}$C NMR: δ = 20.8, 24.4, 46.4, 121.3, 122.7, 122.9, 124.9, 126.4, 132.1, 136.2, 139.7, 161.5, 168.1.

MS: *m*/*z* (%) = 289 (7.0, [M$^+$]), 247 (100).

Anal. Calcd for $C_{15}H_{15}NO_3S$: C, 62.26; H, 5.23; N, 4.84. Found: C, 62.25; H, 5.31; N, 4.78.

**2-(Piperidin-1-ylcarbonyl)benzo[*b*]thiophen-3-yl Acetate (6d)**

Beige oil; $R_f$ = 0.22 (EtOAc–hexane, 1:3).

IR (neat): 1778, 1634 cm$^{-1}$.

$^1$H NMR (500 MHz): δ = 1.58–1.68 (m, 6 H), 2.40 (s, 3 H), 3.60 (br, 4 H), 7.39–7.43 (m, 2 H), 7.57–7.60 (m, 1 H), 7.66–7.78 (m, 1 H).

$^{13}$C NMR: δ = 20.7, 25.8, 29.9, 47.7, 121.2, 122.8, 122.8, 124.9, 126.2, 132.1, 136.3, 138.7, 161.6, 168.0.

MS: *m*/*z* (%) = 303 (6.5, [M$^+$]), 261 (100).

Anal. Calcd for $C_{16}H_{17}NO_3S$: C, 63.34; H, 5.65; N, 4.62. Found: C, 63.17; H, 5.68; N, 4.50.

**2-(Morpholin-4-ylcarbonyl)benzo[*b*]thiophen-3-yl Acetate (6e)**
Yellow oil; $R_f$ = 0.73 (THF–pentane, 1:1).

IR (neat): 1778, 1634 $cm^{-1}$.

$^1H$ NMR (500 MHz): δ = 2.41 (s, 3 H), 3.69–3.76 (m, 8 H), 7.40–7.46 (m, 2 H), 7.61–7.63 (m, 1 H), 7.77–7.79 (m, 1 H).

$^{13}C$ NMR: δ = 20.7, 49.1, 57.2, 121.3, 121.5, 122.8, 126.0, 126.5, 132.0, 136.4, 139.2, 162.1, 167.8.

MS: *m*/*z* (%) = 305 (9.6, [$M^+$]), 263 (100).

Anal. Calcd for $C_{15}H_{15}NO_4S$: C, 59.00; H, 4.95; N, 4.59. Found: C, 58.86; H, 5.13; N, 4.53.

**3-Acetoxy-5-chloro-*N*,*N*-dimethylbenzo[*b*]thiophene-2-carboxamide (6f)**
Pale-yellow oil; $R_f$ = 0.36 (THF–hexane, 1:1).

IR (neat): 1778, 1636 $cm^{-1}$.

$^1H$ NMR (500 MHz): δ = 2.40 (s, 3 H), 3.10 (s, 6 H), 7.38 (dd, *J* = 8.7, 1.8 Hz, 1 H), 7.58 (d, *J* = 1.8 Hz, 1 H), 7.69 (d, *J* = 8.7 Hz, 1 H).

$^{13}C$ NMR: δ = 20.6, 38.7, 121.0, 123.9, 124.6, 126.9, 131.5, 133.2, 134.5, 138.0, 162.7, 167.8.

MS: *m*/*z* (%) = 297 (8.4, [$M^+$]), 255 (100).

Anal. Calcd for $C_{13}H_{12}ClNO_3S$: C, 52.44; H, 4.06; N, 4.70. Found: C, 52.32; H, 4.14; N, 4.65.

**3-Acetoxy-5-chloro-*N*,*N*-diethylbenzo[*b*]thiophene-2-carboxamide (6g)**
Yellow oil; $R_f$ = 0.36 (EtOAc–hexane, 1:2).

IR (neat): 1780, 1633 $cm^{-1}$.

$^1H$ NMR (400 MHz): δ = 1.21 (t, *J* = 7.3 Hz, 6 H), 2.38 (s, 3 H), 3.49 (br s, 4 H), 7.38 (dd, *J* = 8.3, 2.0 Hz, 1 H), 7.59 (d, *J* = 2.0 Hz, 1 H), 7.69 (d, *J* = 8.3 Hz, 1 H).

$^{13}C$ NMR: δ = 14.3, 20.5, 39.5, 120.8, 123.8, 124.8, 126.7, 131.4, 133.2, 134.1, 137.9, 161.9, 167.9.

MS: *m*/*z* (%) = 325 (7.3, [$M^+$]), 283 (100).

Anal. Calcd for $C_{15}H_{16}ClNO_3S$: C, 55.30; H, 4.95; N, 4.30. Found: C, 55.11; H, 5.03; N, 4.25.

**5-Chloro-2-(pyrrolidin-1-ylcarbonyl)benzo[*b*]thiophen-3-yl Acetate (6h)**
Pale-yellow solid; mp 95–97 °C (hexane).

IR (KBr): 1778, 1626 $cm^{-1}$.

$^1H$ NMR (500 MHz): δ = 1.95 (br s, 4 H), 2.40 (s, 3 H), 3.61 (br s, 4 H), 7.39 (dd, *J* = 8.7, 1.8 Hz, 1 H), 7.61 (d, *J* = 1.8 Hz, 1 H), 7.69 (d, *J* = 8.7 Hz, 1 H).

$^{13}C$ NMR: δ = 20.7, 26.2, 48.8, 121.0, 123.8, 124.9, 127.0, 131.4, 133.3, 134.2, 138.7, 161.0, 167.9.

MS: *m*/*z* (%) = 323 (10, [$M^+$]), 281 (100).

Anal. Calcd for $C_{15}H_{14}ClNO_3S$: C, 55.64; H, 4.36; N, 4.33. Found: C, 55.59; H, 4.47; N, 7.18.

**5-Chloro-2-(piperidin-1-ylcarbonyl)benzo[*b*]thiophen-3-yl Acetate (6i)**
Pale-yellow oil; $R_f$ = 0.30 (EtOAc–$C_6H_6$, 1:10).

IR (neat): 1778, 1634 $cm^{-1}$.

$^1H$ NMR (500 MHz): δ = 1.62–1.70 (m, 6 H), 2.40 (s, 3 H), 3.58 (br s, 4 H), 7.38 (dd, *J* = 8.7, 1.8 Hz, 1 H), 7.57 (d, *J* = 1.8 Hz, 1 H), 7.69 (d, *J* = 8.7 Hz, 1 H).

$^{13}C$ NMR: δ = 20.6, 23.7, 26.5, 35.5, 121.2, 122.7, 122.8, 124.9, 126.2, 132.1, 136.1, 138.8, 162.4, 168.1.

MS: *m*/*z* (%) = 337 (4.4, [$M^+$]), 295 (100).

Anal. Calcd for $C_{16}H_{16}ClNO_3S$: C, 56.89; H, 4.77; N, 4.15. Found: C, 56.95; H, 5.05; N, 4.12.

**5-Chloro-2-(morpholin-1-ylcarbonyl)benzo[*b*]thiophen-3-yl Acetate (6j)**
Pale-yellow oil; $R_f$ = 0.30 (EtOAc–hexane, 2:3).

IR (neat): 1780, 1636 $cm^{-1}$.

$^1H$ NMR (500 MHz): δ = 2.42 (s, 3 H), 3.68–3.72 (m, 8 H), 7.40 (dd, *J* = 8.7, 1.8 Hz, 1 H), 7.60 (d, *J* = 1.8 Hz, 1 H), 7.70 (d, *J* = 8.7 Hz, 1 H).

$^{13}C$ NMR: δ = 20.6, 50.1, 58.8, 121.0, 123.4, 123.9, 127.1, 131.6, 133.2, 134.4, 138.3, 161.6, 167.7.

MS: *m*/*z* (%) = 339 (4.0, [$M^+$]), 297 (100).

Anal. Calcd for $C_{15}H_{14}ClNO_4S$: C, 53.02; H, 4.15; N, 4.12. Found: C, 52.92; H, 4.15; N, 3.94.

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