SYNTHESIS OF 2,5-DISUBSTITUTED 3-(4-CHLOROBENZOYL)-2,3-DIHYDRO-2-METHYL-1,3,4-THIADIAZOLE DERIVATIVES

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Abstract ——— 2-Substituted 3-(4-chlorobenzoyl)-2,3-dihydro-5-methylthio-1,3,4-thiadiazoles **(3)** were used as key intermediates to prepare 2,5-disubstituted 3-(4-chlorobenzoyl)-2,3-dihydro-1,3,4-thiadiazoles **(4)** and **(7)**.

We have previously reported that the reaction of aldehyde thiosemicarbazones and aldehyde methylthio(thiocarbonyl)hydrazones with acid chlorides gave 3-acyl-5-(acylamino)-2,3-dihydro-1,3,4-thiadiazoles[1] and 3-acetyl-2,3-dihydro-5-methylthio-1,3,4-thiadiazole,[2] respectively. We have also reported that nucleophilic substitution of the methylsulfinyl group of 3-acetyl-5-methylsulfinyl-2-phenyl-2,3-dihydro-1,3,4-thiadiazole gave 5-substituted 3-acetyl-2-phenyl-2,3-dihydro-1,3,4-thiadiazoles.[3]

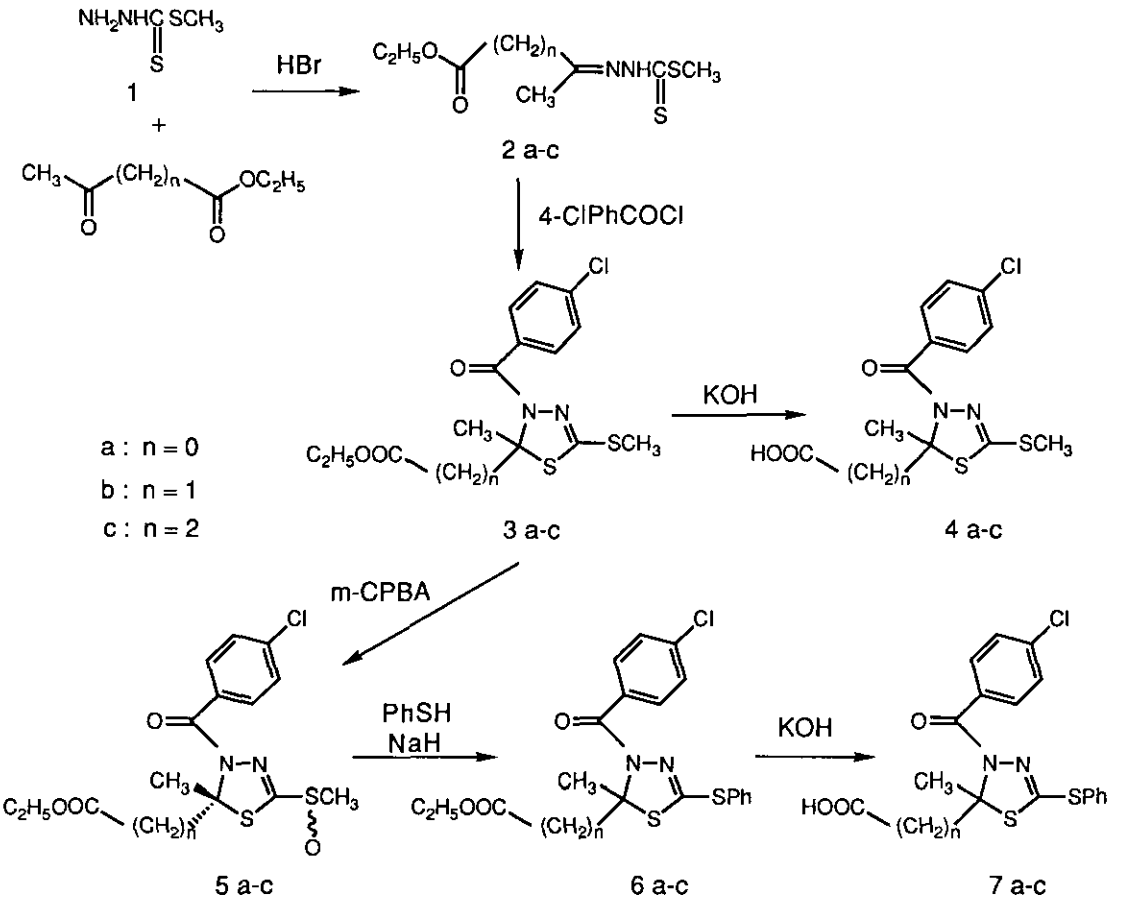
We now report the application of these methods for the synthesis of novel 2,3-dihydro-1,3,4-thiadiazole derivatives.

This paper describes the synthesis of 2,5-disubstituted 3-(4-chlorobenzoyl)-2,3-dihydro-2-methyl-1,3,4-thiadiazoles **(4a-c)** and **(7a-c)**.

The synthesis of compounds **(4a-c)** and **(7a-c)** was achieved by starting with the key compounds **(3a-c)**. These were prepared by the reaction of 4-chlorobenzoyl chloride with the hydrazones **(2a-c)** obtained by the condensation of methylthio(thiocarbonyl)hydrazide **(1)** with ethyl pyruvate, ethyl acetoacetate, and ethyl levulinate, respectively.

Structure proof of **3a-c** was based upon satisfactory spectral data. In addition to correct molecular formula obtained by high-resolution mass spectrometry, the ^{13}C-nmr spectra clearly showed a

signal at 80.62-86.28 ppm which is assigned to the quaternary carbon in the 2,3-dihydro-1,3,4-thiadiazole ring.[4]



The first series of target compounds **(4a-c)** were then obtained by hydrolysis of **3a-c** with potassium hydroxide in aqueous methanol at room temperature. The second series **(7a-c)** were synthesized as shown in the Scheme. Starting with **3a-c**, 2,3-dihydro-5-methylsulfinyl-1,3,4-thiadiazoles **(5a-c)** were obtained by oxidation with 1.1 mol eq. of *m*-chloroperbenzoic acid (*m*-CPBA) at room temperature as diastereoisomeric mixtures in the ratio of 3:2. This ratio was determined by ^{1}H-nmr spectroscopy measuring the integrated intensities of the C-2 methyl signals at δ 2.20-2.32 ppm. Repeated attempts to obtain pure isomers by column chromatography were unsuccessful.

Nucleophilic substitution reactions of the diasteroisomeric mixture **(5a-c)** were examined, since the sulfinyl group is known to be a good leaving group.[3,5,6] Treatment of diastereomeric **5a-c** with thiophenol in tetrahydrofuran (THF) in the presence of sodium hydride at room temperature for 10 min gave the corresponding 5-phenylthio drivatives **(6a-c)** in moderate yields. These were hydrolyzed with potassium hydroxide in aqueous methanol to give the target carboxylic acids **(7a-c)**.

The analytical and spectral data of compounds **(6a-c)**, **(4a-c)** and **(7a-c)** are shown in Tables III and IV, respectively.

EXPERIMENTAL

Melting points were determined by the capillary method and are uncorrected. Ir spectra were recorded on a Hitachi 215 spectrophotometer. ^{1}H-Nmr spectra were measured with a JEOL JNM-PMX 60_{SI} spectrometer and ^{13}C-nmr spectra with a JEOL JMS FX-200 spectrometer using tetramethylsilane as an internal reference. Mass spectra were recorded on a JEOL D-300 instrument. Column chromatography was performed on silica gel (K-100-S, from Katayama Chemicals).

Ethyl pyruvate methylthio(thiocarbonyl)hydrazone (2a)

Compound **(2a)** was prepared by *literature method*.[7]

Ethyl acetoacetate methylthio(thiocarbonyl)hydrazone (2b)

Compound **(2b)** was prepared by literature method.[8]

Ethyl levulinate methylthio(thiocarbonyl)hydrazone (2c)

A *mixture* of **1** (3.38 g, 27.70 mmol), ethyl levulinate (3.94 ml, 27.77 mmol), and 47 % hydrobromic acid (1 drop) in EtOH (60 ml) was stirred at room temperature for 1.5 h. The resulting precipitate was collected by filtration and recrystallized from EtOH to give **2c** (4.27 g, 62 %); mp 99-100 °C. Ir(KBr) 3220 (NH), 1725 (CO) cm^{-1}. ^{1}H-Nmr($CDCl_3$) δ 1.32 (3H, t, *J*=7 Hz, $CH_2C\underline{H}_3$), 2.00 (3H, s, CH_3), 2.65 (3H, s, SCH_3), 2.74 (4H, s, CH_2CH_2), 4.22 (2H, q, *J*=7 Hz, $C\underline{H}_2CH_3$), 9.89 (1H, br s, NH). Ms *m/z* 248 (M^+). *Anal.* Calcd for $C_9H_{16}N_2O_2S_2$: C,43.52; H,6.49; N,11.28. Found: C,43.42; H,6.56; N,11.29.

Reaction of 2a-c with 4-Chlorobenzoyl Chloride

A solution of 4-chlorobenzoyl chloride (0.58 ml, 4.56 mmol) in $CHCl_3$ (4 ml) was added to a stirred solution of **2a** (500 mg, 2.27 mmol) in $CHCl_3$ (20 ml) at room temperature. After being refluxed for 4 h, the mixture was concentrated under reduced pressure. The residue was chromatographed on silica gel to give 3-(4-chlorobenzoyl)-2-ethoxycarbonyl-2,3-dihydro-2-methyl-5-methylthio-1,3,4-thiadiazole **3a** (679 mg, 83 %) as an oil. 2-Substituted 3-(4-chlorobenzoyl)-2,3-dihydro-2-methyl-5-methylthio-1,3,4-thiadiazoles **(3b)** and **(3c)** were prepared in a similar manner to that described for compound **(3a)**. Yields and analytical and spectral data for compounds **(3a-c)** are given in Tables I and II.

Hydrolysis of 3a-c

A solution of 85 % KOH (899 mg, 13.62 mmol) in water (20 ml) was added to a stirred solution of **3a** (1.63 g, 4.55 mmol) in MeOH (50 ml) at room temperature. After being stirred for 6 h, the mixture was acidified with 10 % HCl, and extracted with ethyl acetate. The combined extracts were washed with brine, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was recrystallized from isopropyl ether to give 3-(4-chlorobenzoyl)-2,3-dihydro-2-hydroxycarbonyl-2-methyl-5-methylthio-1,3,4-thiadiazole **4a** (1.29 g, 86 %). 2-Substituted 3-(4-chlorobenzoyl)-2,3-dihydro-2-methyl-5-methylthio-1,3,4-thiadiazoles **(4b)** and **(4c)** were prepared in a similar manner to that described for compound **(4a)**. Yields, melting points, recrystallization solvents, and analytical and spectral data for compounds **(4a-c)** are given in Table IV.

3-(4-Chlorobenzoyl)-2-ethoxycarbonyl-2,3-dihydro-2-methyl-5-methylsulfinyl-1,3,4-thiadiazole (5a)

A solution of 80 % *m*-CPBA (1.08 g, 5.01 mmol) in $CHCl_3$ (25 ml) was added dropwise to a stirred solution of **3a** (1.63 g, 4.55 mmol) in $CHCl_3$ (30 ml) at room temperature. After being stirred at room temperature for 1 h, the mixture was neutralized with 5 % aqueous sodium hydrogen carbonate and extracted with $CHCl_3$. The combined extracts were washed with brine, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was chromatographed on a silica gel column to give 2,3-dihydro-1,3,4-thiadiazole **(5a)** as an inseparable diastereomeric mixture (1.47 g, 86 %). Ir(neat) 1750, 1740, 1665, 1655 (CO), 1090, 1070 (SO) cm^{-1}. Major isomer; ^{1}H-nmr($CDCl_3$) δ 1.31 (3H, t, *J*=7 Hz, $CH_2C\underline{H}_3$), 2.27 (3H, s, CH_3), 2.97 (3H, s, $SOCH_3$), 4.39 (2H, q, *J*=7 Hz, $C\underline{H}_2CH_3$), 7.38 (2H, dd, *J*=3, 9 Hz, ArH), 7.73 (2H, dd, *J*=3, 9 Hz, ArH). Minor isomer; ^{1}H-

nmr($CDCl_3$) δ 1.31 (3H, t, *J*=7 Hz, $CH_2C\underline{H}_3$), 2.32 (3H, s, CH_3), 2.93 (3H, s, $SOCH_3$), 4.39 (2H, q, *J*=7 Hz, $C\underline{H}_2CH_3$), 7.38 (2H, dd, *J*=3, 9 Hz, ArH), 7.73 (2H, dd, *J*=3, 9 Hz, ArH). Ms *m/z* 374, 376 (M^+). Calcd for $C_{14}H_{15}N_2O_4ClS_2$ 374.0161, Found 374.0148.

3-(4-Chlorobenzoyl)-2-ethoxycarbonylmethyl-2,3-dihydro-2-methyl-5-methylsulfinyl-1,3,4-thiadiazole (5b)

Compound **(5b)** was prepared from **3b** (1.26 g, 3.38 mmol) and 80 % *m*-CPBA (800 mg, 3.71 mmol) in a similar manner to that described for compound **(5a)**. Yield 1.15 g (88 %). Ir(neat) 1735, 1725, 1665, 1655 (CO), 1090, 1075 (SO) cm^{-1}. Major isomer; ^{1}H-nmr($CDCl_3$) δ 1.28 (3H, t, *J*=7 Hz, $CH_2C\underline{H}_3$), 2.21 (3H, s, CH_3), 2.90 (3H, s, $SOCH_3$), 3.63 (2H, d, *J*=9 Hz, CH_2), 4.20 (2H, q, *J*=7 Hz, $C\underline{H}_2CH_3$), 7.32 (2H, dd, *J*=3, 9 Hz, ArH), 7.62 (2H, dd, *J*=3, 9 Hz, ArH). Minor isomer; ^{1}H-nmr($CDCl_3$) δ 1.28 (3H, t, *J*=7 Hz, $CH_2C\underline{H}_3$), 2.25 (3H, s, CH_3), 2.90 (3H, s, $SOCH_3$), 3.61 (2H, d, *J*=7 Hz, CH_2), 4.17 (2H, q, *J*=7 Hz, $C\underline{H}_2CH_3$), 7.32 (2H, dd, *J*=3, 9 Hz, ArH), 7.62 (2H, dd, *J*=3, 9 Hz, ArH). Ms m/z 388, 390 (M^+). Calcd for $C_{15}H_{17}N_2O_4ClS_2$ 388.0324, Found 388.0298.

3-(4-Chlorobenzoyl)-2-ethoxycarbonylethyl-2,3-dihydro-2-methyl-5-methylsulfinyl-1,3,4-thiadiazole (5c)

Compound **(5c)** was prepared from **3c** (2.22 g, 5.74 mmol) and 80 % *m*-CPBA (1.36 g, 6.30 mmol) in a similar manner to that described for compound **(5a)**. Yield 2.07 g (90 %). Ir(neat) 1740, 1730, 1665, 1660 (CO), 1090, 1075 (SO) cm^{-1}. Major isomer; ^{1}H-nmr($CDCl_3$) δ 1.26 (3H, t, *J*=7 Hz, $CH_2C\underline{H}_3$), 2.26 (3H, s, CH_3), 2.92 (3H, s, $SOCH_3$), 1.90-3.54 (4H, m, CH_2CH_2), 4.20 (2H, q, *J*=7 Hz, $C\underline{H}_2CH_3$), 7.39 (2H, dd, *J*=3, 9 Hz, ArH), 7.70 (2H, dd, *J*=3, 9 Hz, ArH). Minor isomer; ^{1}H-nmr($CDCl_3$) δ 1.26 (3H, t, *J*=7 Hz, $CH_2C\underline{H}_3$), 2.20 (3H, s, CH_3), 2.92 (3H, s, $SOCH_3$), 1.90-3.54 (4H, m, CH_2CH_2), 4.20 (2H, q, *J*=7 Hz, $C\underline{H}_2CH_3$), 7.39 (2H, dd, *J*=3, 9 Hz, ArH), 7.70 (2H, dd, *J*=3, 9 Hz, ArH). Ms *m/z* 402, 404 (M^+). Calcd for $C_{16}H_{19}N_2O_4ClS_2$ 402.0475, Found 402.0447.

Reaction of 5a-c with Thiophenol in the Presence of Sodium Hydride

A suspension of sodium hydride (178 mg, 4.45 mmol, 60 % dispersion in oil, washed with ether) in anhydrous THF (10 ml) was added dropwise to a stirred solution of thiophenol (0.46 ml, 4.48 mmol) in anhydrous THF (10 ml) at 0 °C. After being stirred at room temperature for 10 min, the mixture was treated dropwise with a solution of **5a** (1.67 g, 4.46 mmol) in anhydrous THF (30 ml). After 1 h at room temperature, the mixture was neutralized with aqueous acetic acid and extracted with $CHCl_3$. The combined extracts were washed with brine, dried over anhydrous Na_2SO_4, and

evaporated under reduced pressure. The residue was chromatographed on a silica gel column to give 3-(4-chlorobenzoyl)-2-ethoxycarbonyl-2,3-dihydro-2-methyl-5-phenylthio-1,3,4-thiadiazole **(6a)** (1.25 g, 67 %) as an oil. 2-Substituted 3-(4-chlorobenzoyl)-2,3-dihydro-2-methyl-5-phenylthio-1,3,4-thiadiazoles **(6b)** and **(6c)** were prepared in a similar manner to that described for compound **(6a)**. Yields and analytical and spectral data for compounds **(6a-c)** are given in Table III.

Hydrolysis of 6a-c

3-(4-Chlorobenzoyl)-2,3-dihydro-2-hydroxycarbonyl-2-methyl-5-phenylthio-1,3,4-thiadiazole **(7a)** was prepared from **6a** (1.12 g, 2.66 mmol) and 85 % KOH (528 mg, 8.00 mmol) in a similar manner to that described for compound **(4a)**. Yield 764 mg (73 %). 2-Substituted 3-(4-chlorobenzoyl)-2,3-dihydro-2-methyl-5-phenylthio-1,3,4-thiadiazoles **(7b)** and **(7c)** were prepared in a similar manner to that described for compound **(4a)**. Yields, melting points, recrystallization solvents, and analytical and spectral data for compounds **(7a-c)** are given in Table IV.

Table I. Spectral data for **3a-c**

Compd No.	Yield (%)	Ir cm^{-1} (neat) CO	Formula	Analysis[a] Calcd(Found)	Ms *m/z* (M^+)
3a	83	1740 1645	$C_{14}H_{15}N_2O_3ClS_2$	358.0212 (358.0201)	358 360
3b	84	1730 1645	$C_{15}H_{17}N_2O_3ClS_2$	372.0369 (372.0386)	372 374
3c	98	1730 1640	$C_{16}H_{19}N_2O_3ClS_2$	386.0526 (386.0495)	386 388

[a] Determined by high-resolution mass spectrometry. Upper figure, Calcd for M^+; lower figure found.

Table II. ^{1}H-Nmr and ^{13}C-nmr spectral data for **3a-c**.

Compd No.	^{1}H-Nmr ($CDCl_3$)δ (*J*=Hz)	^{13}C-Nmr ($CDCl_3$)δ
3a	1.32(3H,t,*J*=7,$CH_2\underline{CH_3}$),2.25(3H,s,CH_3), 2.53(3H,s,SCH_3),4.32(2H,q,*J*=7,$C\underline{H_2}CH_3$), 7.35(2H,dd,*J*=3,9,ArH),7.83(2H,dd,*J*=3,9, ArH)	13.99(q,$CH_2\underline{C}H_3$),15.62(q,SCH_3),24.73(q,CH_3), 62.60(t,$\underline{C}H_2CH_3$),80.62(s,C-2),127.80(d),131.08(d), 132.56(s),137.32(s)(aromatic C),148.13(s,C-5), 165.59(s,CO),168.27(s,CO)
3b	1.26(3H,t,*J*=7,$CH_2\underline{CH_3}$),2.19(3H,s,CH_3), 2.44(3H,s,SCH_3),3.67(2H,d,*J*=8,CH_2), 4.21(2H,q,*J*=7,$C\underline{H_2}CH_3$),7.35(2H,dd, *J*=3,9,ArH),7.74(2H,dd,*J*=3,9,ArH)	14.10(q,$CH_2\underline{C}H_3$),15.21(q,SCH_3),27.48(q,CH_3), 44.09(t,CH_2),60.91(t,$\underline{C}H_2CH_3$),82.20(s,C-2),127.60 (d),130.81(d),134.23(s),136.71(s)(aromatic C), 149.94(s,C-5),166.44(s,CO),169.71(s,CO)

Table II (Continued). ^{1}H-Nmr and ^{13}C-nmr spectral data for **3a-c**.

Compd No.	^{1}H-Nmr ($CDCl_3$)δ (J=Hz)	^{13}C-Nmr ($CDCl_3$)δ
3c	1.26(3H,t,J=7,$CH_2\underline{C}H_3$),2.19(3H,s,CH_3), 2.45(3H,s,SCH_3),2.23-3.45(4H,m,CH_2CH_2), 4.20(2H,q,J=7,$C\underline{H}_2CH_3$),7.37(2H,dd,J= 3,9,ArH),7.75(2H,dd,J=3,9,ArH)	14.16(q,$CH_2\underline{C}H_3$),15.24(q,SCH_3),28.18(q,CH_3), 30.37(t,CH_2CH_2),34.37(t,CH_2CH_2),60.56(t,$\underline{C}H_2CH_3$), 86.28(s,C-2),127.60(d),130.84(d),134.05(s),136.74 (s)(aromatic C),148.45(s,C-5),166.03(s,CO),172.10 (s,CO)

Table III. Spectral data for **6a-c**.

Compd No.	Yield (%)	Ir cm^{-1} (neat) CO	^{1}H-Nmr ($CDCl_3$)δ (J=Hz)	Formula	Analysis[a] Calcd(Found)	Ms *m/z* (M^+)
6a	67	1755 1660	1.33(3H,t,J=7,$CH_2C\underline{H}_3$),2.19(3H,s,CH_3), 4.33(2H,q,J=7,$C\underline{H}_2CH_3$),7.34(2H,dd,J=3,9, ArH),7.82(2H,dd,J=3,9,ArH),7.24-7.98 (5H,m,ArH)	$C_{19}H_{17}N_2O_3ClS_2$	420.0369 (420.0367)	420 422
6b	57	1735 1650	1.24(3H,t,J=7,$CH_2C\underline{H}_3$),2.15(3H,s,CH_3), 3.66(2H,d,J=6,CH_2),4.21(2H,q,J=7, $C\underline{H}_2CH_3$),7.19-7.70(9H,m,ArH)	$C_{20}H_{19}N_2O_3ClS_2$	434.0526 (434.0548)	434 436
6c	82	1740 1655	1.22(3H,t,J=7,$CH_2C\underline{H}_3$),2.09(3H,s,CH_3), 2.04-3.33(4H,m,CH_2CH_2),4.15(2H,q,J=7, $C\underline{H}_2CH_3$),7.08-7.85(9H,m,ArH)	$C_{21}H_{21}N_2O_3ClS_2$	448.0682 (448.0686)	448 450

[a] Determined by high-resolution mass spectrometry. Upper figure, Calcd for M^+; lower figure found.

Table IV. Spectral data for **4a-c** and **7a-c**.

Compd No.	Yield (%)	mp(°C) (a)	Ir cm^{-1} (KBr) OH	Ir cm^{-1} (KBr) CO	^{1}H-Nmr (DMSO-d_6)δ (J=Hz)	Formula	Analysis Calcd(Found) C	H	N	Ms *m/z* (M^+)
4a	86	161-163 (isopropyl ether)	3100-2600	1750 1605	2.14(3H,s,CH_3),2.53(3H,s, SCH_3),7.49(2H,dd,J=3,9, ArH),7.80(2H,dd,J=3,9,ArH) 11.00-14.00(1H,br s,COOH)	$C_{12}H_{11}N_2O_3ClS_2$	43.57 (43.73	3.35 3.38	8.47 8.33)	330 332
4b	47	137-139 (50%MeOH)	3100-2600	1710 1645	2.07(3H,s,CH_3),2.46(3H,s, SCH_3),3.67(2H,d,J=8,CH_2), 7.51(2H,dd,J=3,9,ArH), 7.76(2H,dd,J=3,9,ArH), 10.00-12.50(1H,br s,COOH)	$C_{13}H_{13}N_2O_3ClS_2$	45.28 (45.32	3.80 3.80	8.12 8.11)	344 346
4c	76	142-143 (50%EtOH)	3200-2500	1710 1640	2.14(3H,s,CH_3),2.48(3H,s, SCH_3),2.25-3.12(4H,m, CH_2CH_2),7.50(2H,dd,J=3,9, ArH),7.77(2H,dd,J=3,9, ArH),12.40(1H,br s,COOH)	$C_{14}H_{15}N_2O_3ClS_2$	46.86 (46.87	4.21 4.11	7.81 7.72)	358 360

[a] Solvent of recrystallization

Table IV(Continued). Spectral data for **4a-c** and **7a-c**.

Compd No.	Yield (%)	mp(°C) (a)	Ir cm^{-1} (KBr) OH	Ir cm^{-1} (KBr) CO	^{1}H-Nmr (DMSO-d_6)δ (J=Hz)	Formula	Analysis Calcd(Found) C	H	N	Ms *m/z* (M^+)
7a	73	165-166 (50%EtOH)	3100-2600	1755 1600	2.11(3H,s,CH_3),7.45(2H,dd, J=3,9,ArH),7.72(2H,dd,J=3,9,ArH),7.45-7.75(5H,m, ArH),9.50-13.50(1H,br s, COOH)	$C_{17}H_{13}N_2O_3ClS_2$	51.97 (52.08	3.34 3.16	7.13 7.11)	392 394
7b	60	134-136 (50%EtOH)	3100-2600	1725 1610	2.03(3H,s,CH_3),3.58(2H,d, J=6,CH_2),7.33-7.69(7H,m, ArH),7.96(2H,dd,J=3,9,ArH), 10.00-12.50(1H,br s,COOH)	$C_{18}H_{15}N_2O_3ClS_2$	51.13 (52.18	3.72 3.59	6.88 6.84)	406 408
7c	41		3200-2600	1710[b] 1640	2.06(3H,s,CH_3),1.91-2.90 (4H,m,CH_2CH_2),7.28-7.82 (9H,m,ArH),10.50-13.00(1H, br s,COOH)	$C_{19}H_{17}N_2O_3ClS_2$	420.0369[c] (420.0365)			420 422

[a] Solvent of recrystallization
[b] Neat
[c] Determined by high-resolution mass spectrometry. Upper figure, Calcd for M^+; lower figure found.

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