Arenesulfonylheterocycles (I): Synthesis and Reactions of 2-Benzenesulfonyl-4,5-dichloropyridazin-3-ones with Amines

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Received July 24, 2001

The direct sulfonylation of 4,5-dichloropyridazin-3-ones with some benzenesulfonyl chlorides in the presence of base in tetrahydrofuran gave only the corresponding *N*-sulfonylated product. The reaction of 2-benzenesulfonyl-4,5-dichloropyridazin-3-ones with some aliphatic amines under neutral conditions afforded 5-alkylamino-2-benzenesulfonyl-4-chloropyridazin-3-ones and/or the corresponding *N*-alkylbenzenesulfonamides.

J. Heterocyclic Chem., **39**, 203 (2002).

In connection with our research program for the development of novel pyridazin-3-one derivatives as potential agrochemicals, we attempted to synthesize some new 2-benzenesulfonyl-5-(or 4-)alkylaminopyridazin-3-ones.

Dury [1] reported the synthesis of 2-(4-methylbenzenesulfonyl)-4,5-dichloropyridazin-3-one (**2g**) from 4 -methylbenzenesulfonylhydrazone of mucochloric acid. And Hamer *et al*. [2] also reported that treatment of 3,5-dichloro-2-pyridone with various benzenesulfonyl chlorides in the presence of triethylamine yielded both *O*- and *N*-sulfonylated products. *N/O*-Sulfonylation of 2-pyridone is due to the ambident anionic character of 2-pyridone under basic condition. Firstly, the synthesis of 2-(4-methylbenzenesulfonyl)-4,5-dichloropyridazin-3-one (**2g**) was carried out by the Dury's method. However, the preparation of the benzenesulfonylhydrazone of mucochloric acid was difficult and the overall yield was also low. Therefore, we investigated the direct sulfonylation of 4,5-dichloropyridazin-3-one (**1**) according to Hamer's method [2] and also the reaction of 2-benzenesulfonyl-4,5-chloropyridazin-3-ones **2** with various amines.

Therefore in this paper, we report the results of the direct sulfonylation of 4,5-dichloropyridazin-3-one (**1**) with various benzenesulfonyl chlorides and the reaction of 2-benzenesulfonyl-4,5-dichloropyridazin-3-ones with some aliphatic amines.

Pyridazin-3-ones are also the ambident anions under basic conditions [3,4]. The regioselectivity of the *N/O*-alkylation for a nitrogen heterocyclic ambident anion such as 2-pyridone and 3-pyridazinone depends on the nature of the base, the structure of alkyl halide, substituents on the heterocycles, reaction temperature and the solvent [5,6]. Similarly, the direct sulfonylation of pyridazin-3-ones under basic condition should furnish *N*- and/or *O*-sulfonylated products. However, to the best of our knowledge, the *N/O*-regioselectivity for the direct sulfonylation of 3-pyridazinone has not been reported. Therefore, we attempted the reaction of 4,5-dichloropyridazin-3-one (**1**) with benzenesulfonyl chloride under basic condition in order to examine the base effect.

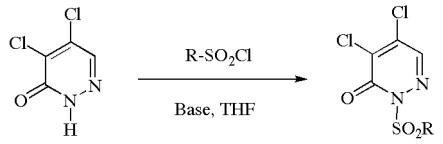
Reaction of compound **1** with 4-nitrobenzenesulfonyl chloride in the presence of various bases in tetrahydrofuran gave unexpectedly only 2-(4-nitrobenzenesulfonyl)-4,5-dichloropyridazin-3-one (**2j**) as *N*-sulfonylation product (Scheme I). *O*-Sulfonylation product was not detected by tlc monitoring during the reaction. The data of these experiments are summarised in Table 1. The rates of sulfonylation for 4,5-dichloropyridazin-3-one (**1**) were base dependent, whereas the base effect on the regioselectivity was not observed. The rate of *N*-sulfonylation using organic bases was faster than that of inorganic bases. Sulfonylation of **1** with 4-nitrobenzenesulfonyl chloride in the presence of potassium carbonate or pyridine at room temperature did not give the corresponding product, whereas the reaction was carried out at reflux temperature to afford the corresponding 2-sulfonyl derivative **2j** in 77% and 63% yield, respectively. 4-(*N*,*N*-Dimethylamino)pyridine was the most favourable base for *N*-sulfonylation of compound **1**.

N-Sulfonylation of **1** with various sulfonyl chlorides was also carried out in the presence of potassium carbonate or 4-(*N*,*N*-dimethylamino)pyridine representatively (Scheme I). The data of the reaction are summarised in Table 2. When potassium carbonate was used at reflux temperature in tetrahydrofuran, the corresponding 2-sulfonyl derivatives **2** were afforded in 51 – 98% yield except for **2l**, respectively. Compound **1** was not reacted with 2,4-dinitrobenzenesulfonyl chloride in the presence of potassium carbonate in tetrahydrofuran at reflux temperature. 2-Sulfonyl derivatives **2** were also furnished in good yield except for **2a** and **2l** when 4-(*N*,*N*-dimethylamino)pyridine was used at room temperature in tetrahydrofuran. The results of the sulfonylation for **1** under our condition are different from the sulfonylation of 2-pyridone [2], whereas

that is similar to the alkylation of **1** with alkyl halides in the presence of potassium carbonate [4,7]. According to Kim, *et al* [4], potassium ion in the potassium salt of **1** may be located in the proximity of oxygen because the electron density on oxygen of the carbonyl group is higher than that of nitrogen, at the 2-position in a free anion of **1**. Thus, *N*-sulfonylnation occurs predominantly in the sulfonylation of **1** in the presence of potassium carbonate. The structures of **2** were established by ir, nmr and elemental analyses. In the infrared spectra of **2**, the absorption bands of one amide carbonyl and SO_2 groups were detected. The proton magnetic resonance spectra showed the signals of one proton for C-6 of pyridazine ring, aromatic protons for phenyl ring and others.

We also investigated the reaction of some 2-benzenesulfonyl-4,5-dichloropyridazin-3-ones **2** with amines. Firstly, 2-benzenesulfonyl-4,5-dichloropyridazin-3-one (**2b**) was reacted with ethylamine to give 5-ethylamino-2-benzenesulfonyl-4-chloropyridazin-3-one (**4a**, 29%) and the corresponding *N*-ethylsulfonamide **5a** (63%). Reaction of **2b** with diethylamine, cyclohexylamine and piperidine also afforded 5-alkylamino-2-benzenesulfonylpyridazin-3-ones (**4b**, 46%; **4c**, 18%; **4d**, 11%) and *N*-alkylsulfonamide (**5b**, 49%; **5c**, 75%; **5d**, 88%), respectively. In order to examine the substituents and the substituted position effects for benzene ring of benzenesulfonyl-pyridazin-3-ones, compounds involving 4-substituted-benzenesulfonyl group **2g**, **2h** and **2j**, derivatives containing 2-substituted-benzenesulfonyl group **2c**, **2d** and **2e** or compound **2m** with 2,4,6-trimethylbenzenesulfonyl group was reacted with ethylamine, diethylamine, cyclohexylamine and piperidine under neutral conditions. Reaction of **2g** with ethylamine, diethylamine and cyclohexylamine gave the corresponding 5-alkylaminopyridazin-3-ones **4e** – **4g** and

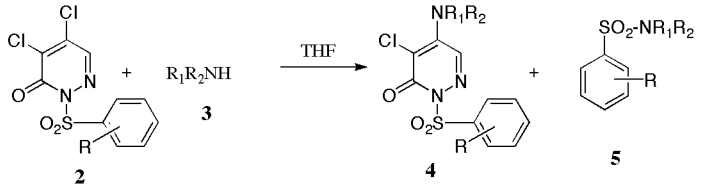
Scheme I



1 **2**

2	**a**	**b**	**c**	**d**	**e**	**f**
R	Me	Ph	2-CN-Ph	2-NO_2-Ph	2-Br-Ph	3-NO_2-Ph
2	**g**		**h**	**i**	**j**	**k**
R	4-Me-Ph		4--Cl-Ph	4-F-Ph	4-NO_2-Ph	2,5-Cl_2-Ph
2	**l**			**m**		
R	2,4-$(NO_2)_2$-Ph			2,4,6-$(Me)_3$-Ph		

Scheme II



2 **4** **5**

2	R
b	H
c	2-CN
d	2-NO_2
e	2-Br
g	4-Me
h	4-Cl
j	4-NO_2
m	2,4,6-$(Me)_3$

4	R	R^1	R^2
a	H	Et	H
b	H	Et	Et
c	H	C_6H_{11}	H
d	H	-$(CH_2)_5$-	
e	4-Me	Et	H
f	4-Me	Et	Et
g	4-Me	C_6H_{11}	H
h	4-Cl	Et	H
i	4-Cl	Et	Et
j	4-Cl	C_6H_{11}	H
k	4-Cl	-$(CH_2)_5$-	
l	4-NO_2	Et	H
m	4-NO_2	Et	Et
n	2-NO_2	Et	H
o	2-NO_2	Et	Et

4	R	R^1	R^2
p	2-NO_2	C_6H_{11}	H
q	2-NO_2	-$(CH_2)_5$-	
r	2-CN	Et	H
s	2-CN	Et	Et
t	2-CN	C_6H_{11}	H
u	2-CN	-$(CH_2)_5$-	
v	2-Br	Et	H
w	2-Br	Et	Et
x	2-Br	C_6H_{11}	H
y	2-Br	-$(CH_2)_5$-	
z	2,4,6-$(Me)_3$	Et	H
aa	2,4,6-$(Me)_3$	Et	Et
bb	2,4,6-$(Me)_3$	C_6H_{11}	H
cc	2,4,6-$(Me)_3$	-$(CH_2)_5$-	

5	R	R^1	R^2
a	H	Et	H
b	H	Et	Et
c	H	C_6H_{11}	H
d	H	-$(CH_2)_5$-	
e	4-Me	Et	H
f	4-Me	Et	Et
g	4-Me	C_6H_{11}	H
h	4-Me	-$(CH_2)_5$-	
i	4-Cl	Et	H
j	4-Cl	Et	Et
k	4-Cl	C_6H_{11}	H
l	4-Cl	-$(CH_2)_5$-	
m	4-NO_2	Et	H
n	4-NO_2	Et	Et
o	4-NO_2	C_6H_{11}	H
p	4-NO_2	-$(CH_2)_5$-	
q	2-NO_2	Et	H
r	2-NO_2	C_6H_{11}	H
s	2-CN	C_6H_{11}	H
t	2-CN	-$(CH_2)_5$-	

N-alkylsulfonamide **5e** – **5g**, treatment of **2g**, however, with piperidine afforded only *N*-piperidyl-4-methylbenzenesulfonamide (**5h**) in 90% yield. Reaction of **2h** with amines also gave 5-alkylaminopyridazin-3-ones **4h** - **4k** and *N*-alkylsulfonamide **5i** – **5l**. Compound **2j** was reacted with ethylamine or diethylamine to yield the corresponding 5-alkylaminopyridazin-3-ones **4l** – **4m** and *N*-alkylsulfonamide **5m** – **5n**, whereas treatment of **2j** with cyclohexylamine or piperidine gave only the corresponding *N*-alkylsulfonamide **5o** or **5p** in quantitative yield.

On the other hand, reaction of 2-(2-substituted-benzenesulfonyl)pyridazin-3-ones **2c** – **2e** with amines except for ethylamine (for **2d**), cyclohexylamine (for **2d** and **2c**) and piperidine (for **2c**) afforded only 5-alkylaminopyridazin-3-ones **4o**, **4q**, **4r**, **4s** and **4v** – **4y** in excellent yield. Amination of **2m** with ethylamine, diethylamine, cyclohexylamine or piperidine also gave the corresponding 5-alkylaminopyridazin-3-one derivatives **4z** – **4cc** in excellent yield, respectively. These results may be due to the *ortho*-substituent of 2-(benzenesulfonyl)pyridazin-3-ones **2**. The structures of 5-alkylaminopyridazin-3-ones and *N*-alkylbenzenesulfonamides were established by ir, nmr and elemental analyses. And the substituted position of alkylamino group for 5-alkylamino-4-chloropyridazin-3-ones was also confirmed by nuclear Overhauser enhancement. Representatively, irradiation of the proton at C6 of compound **4e** resulted in a 10.3 % nuclear Overhauser enhancement of the methylene protons of ethyl amino group at C5.

In the reaction of **2c** – **2e** and **2m** with aliphatic amines, the attack of amines on *N*-SO_2 bond was hindered by *o*-substituent of benzene ring. Therefore, the transfer of benzenesulfonyl group to aliphatic amines was more favourable with 2-(4-substituted-benzenesulfonyl)pyridazin-3-ones than with 2-(2-substituted- or 2,6-disubstituted-benzenesulfonyl)pyridazin-3-ones.

In conclusion, the product distribution for the reaction of 2-(benzenesulfonyl)-4,5-dichloropyridazin-3-ones **2** with aliphatic amines is dependent on the structure of amines,

Table 1

Reaction Conditions and Yields for Reaction of **1**with 4-Nitrobenzenesulfonylchloride in the Presence of Various Bases

Entry	Bases	Reaction Conditions		**2j**
		Times (h)	Temperature (°C)	(Isolated yield, %)
1	K_2CO_3	4	Reflux	77
2	Cs_2CO_3	5	r.t. [b]	75
3	NaH	50	r.t.	65
4	Et_3N	2	r.t.	92
5	DMAP [a]	0.17	r.t.	92
6	Pyridine	59	Reflux	63
7	*n*-BuLi	0.33	0	82

[a] DMAP = 4-(*N*,*N*-Dimethylamino)pyridine; [b] r.t. = Room temperature.

Table 2

Reaction Conditions and Yields for the Reaction of **1** with Sulfonyl Chlorides

R of RSO_2Cl	Reaction Conditions		Product
	Base	Time (h)	(Isolated yield, %)
Methyl	K_2CO_3	30	**2a** (65)
	DMAP [a]	2	**2a** (49) [b]
Phenyl	K_2CO_3	3	**2b** (73)
	DMAP	0.5	**2b** (81)
2-Cyanophenyl	K_2CO_3	4	**2c** (82)
	DMAP	1	**2c** (81)
2-Nitrophenyl	K_2CO_3	17	**2d** (80)
	DMAP	0.33	**2d** (91)
2-Bromophenyl	K_2CO_3	1	**2e** (98)
	DMAP	0.5	**2e** (96)
3-Nitrophenyl	K_2CO_3	14	**2f** (77)
	DMAP	0.5	**2f** (87)
4-Methylphenyl	K_2CO_3	4	**2g** (81)
	DMAP	2.5	**2g** (88)
4-Chlorophenyl	K_2CO_3	3.5	**2h** (87)
	DMAP	0.33	**2h** (93)
4-Fluorophenyl	K_2CO_3	4	**2i** (84)
	DMAP	1	**2i** (91)
4-Nitrophenyl	K_2CO_3	4	**2j** (77)
	DMAP [a]	0.17	**2j** (92)
2,5-Dichlorophenyl	K_2CO_3	2	**2k** (51)
	DMAP	0.08	**2k** (94)
2,4-Dinitrophenyl	K_2CO_3	—	No reaction
	Et_3N	2	**2l** (55) [c]
	DMAP	6	**2l** (26) [d]
2,4,6-Trimethylphenyl	K_2CO_3	6	**2m** (83)
	DMAP	1.5	**2m** (95)

[a] DMAP = 4-(*N*,*N*-Dimethylamino)pyridine: [b] The mole ratio of reagents **1**/sulfonyl chloride/base = 1: 2.5:2.5; [c] Reaction was carried out at room temperature; [d] The mole ratio of reagents: **1**/sulfonyl chloride/base = 1:3:3. Unreacted pyridazin-3-one was also isolated.

Table 3

Reagents, Reaction Times and Product Distributions for the Reaction of **2** with Various Aliphatic Amines Under Neutral Condition

	Reagents	Reaction Time (h)	Product (Isolated yield, %)	
2	Amines		5-Alkylamino-Pyridazinones	Sulfonamides
2b	Ethylamine	1.5	**4a** (29)	**5a** (63)
	Diethylamine	29	**4b** (46)	**5b** (49)
	Cyclohexylamine	10	**4c** (18)	**5c** (75)
	Piperidine	0.33	**4d** (11)	**5d** (88)
2g	Ethylamine	4	**4e** (53)	**5e** (35)
	Diethylamine	111	**4f** (71)	**5f** (24)
	Cyclohexylamine	12	**4g** (48)	**5g** (41)
	Piperidine	0.5	—	**5h** (90)
2h	Ethylamine	2	**4h** (23)	**5i** (65)
	Diethylamine	14	**4i** (86)	**5j** (14)
	Cyclohexylamine	1	**4j** (34)	**5k** (38)
	Piperidine	0.5	**4k** (15)	**5l** (55)
2j	Ethylamine	0.5	**4l** (8)	**5m** (61)
	Diethylamine	14	**4m** (54)	**5n** (28)
	Cyclohexylamine	1	—	**5o** (98)
	Piperidine	0.3	—	**5p** (98)

Table 3. (Continued)

	Reagents	Reaction Time (h)	Product (Isolated yield, %)	
2	Amines		5-Alkylamino-Pyridazinones	Sulfonamides
2d	Ethylamine	3	**4n** (68)	**5q** (27)
	Diethylamine	11	**4o** (94)	—
	Cyclohexylamine	7	**4p** (67)	**5r** (18)
	Piperidine	4	**4q** (98)	—
2c	Ethylamine	1.5	**4r** (80)	—
	Diethylamine	14	**4s** (97)	—
	Cyclohexylamine	11	**4t** (76)	**5s** (20)
	Piperidine	0.5	**4u** (63)	**5t** (32)
2e	Ethylamine	8	**4v** (86)	—
	Diethylamine	33	**4w** (89)	—
	Cyclohexylamine	18	**4x** (89)	—
	Piperidine	0.5	**4y** (95)	—
2m	Ethylamine	12	**4z** (93)	—
	Diethylamine	30	**4aa** (93)	—
	Cyclohexylamine	20	**4bb** (89)	—
	Piperidine	1.5	**4cc** (96)	—

the basicity of amines, the substituent of benzene ring and the substituted position of benzene ring. *N*-Sulfonylation of amine using 2-benzenesulfonylpyridazin-3-ones is also very interesting in the synthetic application for the *N*-protection of amine.

Further work including the application, the chemical transformation and a biological activity of these novel derivatives is under way in our laboratory.

EXPERIMENTAL

Melting points were determined with a Thomas-Hoover capillary apparatus and are uncorrected. Magnetic resonance spectra were obtained on a Brüker FT NMR-DRX 500 or Varian Inova 500 spectrometer and with chemical shift values reported in δ units (part per million) relative to an internal standard (tetramethylsilane). Infrared spectral data were obtained on a Hitachi 270-50 or Mattson Genesis Series FT-IR spectrophotometer. Elemental analyses were performed with a Perkin Elmer 240C.

2-(Benzenesulfonyl)-4,5-dichloropyridazin-3-ones **2**.

Method A.

A mixture of **1** (0.5 g, 3.05 mmoles), the corresponding sulfonyl chlorides (3.36 mmoles) and base (3.36 mmoles) and tetrahydrofuran (30 ml) was reacted at room temperature [for Cs_2CO_3, NaH, triethylamine and 4-(*N*,*N*-dimethylamino)pyridine] or at reflux temperature (for K_2CO_3 and pyridine) until compound **1** disappeared. After filtering the mixture, the filtrate was evaporated under reduced pressure. The resulting residue was applied to the top of an open-bed silica gel column (2.5 x 13cm). The column was eluted with methylene chloride. Fractions containing the product were combined and evaporated under reduced pressure to give compounds **2** .

Compound **2a** has mp 162-164°; ir (potassium bromide): 3096, 3062, 3018, 2936, 1690, 1591, 1372, 1323, 1265, 1177, 1137, 1087, 969, 926, 812, 768, 622, 518 cm^{-1}; ^1H nmr (DMSO-d_6): δ 3.71 (s, 3H), 8.35 (s, 1H); ^{13}C nmr (DMSO-d_6): δ 41.0, 134.8, 136.8, 137.4, 154.7.

Anal. Calcd for $C_5H_4Cl_2N_2O_3S$: C, 24.71; H, 1.66; N, 11.52; S, 13.19. Found: C, 24.74; H, 1.67; N, 11.67; S, 13.27.

Compound **2b** has mp 197-199°; ir (potassium bromide): 3094, 3075, 1692, 1592, 1448, 1392, 1250, 1196, 1167, 1131, 1087, 922, 808, 763, 723, 685, 626, 572 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.59 (t, 2H, J = 7.7), 7.73 (t, 1H, J = 7.5), 7.89 (s, 1H), 8.18 (d, 2H, J = 8.1); ^{13}C nmr (deuteriochloroform): δ 129.3, 130.1, 135.4, 135.5, 136.2, 136.4, 137.8, 153.8.

Anal. Calcd for $C_{10}H_6Cl_2N_2O_3S$: C, 39.36; H, 1.98; N, 9.18; S, 10.51. Found: C, 39.45; H, 1.99; N, 9.32; S, 10.56.

Compound **2c** has mp 221-223°; ir (potassium bromide): 3099, 3054, 2229, 1680, 1590, 1395, 1267, 1193, 1145, 1087, 925, 811, 772, 688, 620, 575 cm^{-1}; ^1H nmr (DMSO-d_6): δ 8.03 (m, 2H), 8.20 (m, 1H), 8.32 (m, 1H), 8.46 (s, 1H); ^{13}C nmr (deuteriochloroform): δ 110.9, 114.7, 132.4, 133.8, 134.8, 135.8, 136.0, 136.6, 137.7, 137.8, 153.8.

Anal. Calcd for $C_{11}H_5Cl_2N_3O_3S$: C, 40.02; H, 1.53; N, 12.73; S, 9.71. Found: C, 40.15; H, 1.65; N, 12.79; S, 9.84.

Compound **2d** has mp 216-219°; ir (potassium bromide): 3102, 3049, 3022, 1678, 1588, 1536, 1445, 1401, 1361, 1313, 1264, 1197, 1147, 1086, 922, 812, 786 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.89 (m, 3H), 8.02 (s, 1H), 8.63 (m, 1H); ^{13}C nmr (deuteriochloroform): δ 125.1, 130.0, 132.6, 135.7, 136.1, 136.3, 136.6, 138.6, 148.5, 154.0.

Anal. Calcd for $C_{10}H_5Cl_2N_3O_5S$: C, 34.30; H, 1.44; N, 12.00; S, 9.16. Found: C, 34.42; H, 1.48; N, 12.22; S, 9.32.

Compound **2e** has mp 214-216°; ir (potassium bromide): 3095, 3004, 1691, 1589, 1571, 1448, 1432, 1382, 1256, 1183, 1141, 1087, 1026, 928, 885, 811, 769 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.54 (t, 1H, J = 7.4), 7.62 (t, 1H, J = 7.4), 7.73 (d, 1H, J = 7.9), 8.00 (s, 1H), 8.46 (d, 1H, J = 8.0); ^{13}C nmr (deuteriochloroform): δ 120.2, 128.1, 134.9, 135.4, 135.7,135.8, 136.1, 136.5, 138.5, 153.8.

Anal. Calcd for $C_{10}H_5Cl_2BrN_2O_3S$: C, 31.28; H, 1.31; N, 7.29; S, 8.35. Found: C, 31.32; H, 1.48; N, 7.36; S, 8.45.

Compound **2f** has mp 180-182°; ir (potassium bromide): 3104, 3062, 3024, 1690, 1595, 1530, 1428, 1389, 1347, 1261, 1194, 1142, 1087, 924, 876, 811, 739cm^{-1}; ^1H nmr (deuteriochloroform + DMSO-d_6): δ 7.94 (t, 1H, J = 8.1), 8.11 (s, 1H), 8.51 (m, 1H), 8.62 (m, 1H), 8.89 (t, 1H, J = 2.0); ^{13}C nmr (deuteriochloroform + DMSO-d_6): δ 119.8, 124.7, 125.9, 130.4, 130.6,132.0, 132.3, 133.1, 142.8, 148.7.

Anal. Calcd for $C_{10}H_5Cl_2N_3O_5S$: C, 34.30; H, 1.44; N, 12.00; S, 9.16. Found: C, 34.38; H, 1.58; N, 12.12; S, 9.22.

Compound **2g** has mp 183-185°; ir (potassium bromide): 3095, 3066, 2965, 2928, 1690, 1588, 1389, 1255, 1197, 1176, 1139, 1087, 920, 811, 671, 618, 559 cm^{-1}; ^1H nmr (DMSO-d_6): δ 2.43 (s, 3H), 7.51 (d, 2H, J = 8.2), 7.94 (d, 2H, J = 8.5), 8.35 (s, 1H); ^{13}C nmr (deuteriochloroform): δ 21.2, 129.4, 129.9, 132.2, 134.7, 137.3, 137.6, 146.8, 153.6.

Anal. Calcd for $C_{11}H_8Cl_2N_2O_3S$: C, 41.39; H, 2.53; N, 8.78; S, 10.05. Found: C, 41.52; H, 2.68; N, 8.90; S, 10.14.

Compound **2h** has mp 190-192°; ir (potassium bromide): 3097, 3064, 1707, 1589, 1474, 1393, 1253, 1190, 1123, 1091, 1012, 919, 810, 760, 643, 601, 556 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.56 (d, 2H, J = 8.7), 7.90 (s, 1H), 8.12 (d, 2H, J = 8.7); ^{13}C nmr (deuteriochloroform): δ 129.7, 131.6, 133.7, 136.3, 136.6, 138.0, 142.7, 153.9.

Anal. Calcd for $C_{10}H_5Cl_3N_2O_3S$: C, 35.37; H, 1.48; N, 8.25; S, 9.44. Found: C, 35.48; H, 1.58; N, 8.27; S, 9.52.

Compound **2i** has mp 175-177°; ir (potassium bromide): 3102, 3067, 1693, 1584, 1486, 1403, 1236, 1194, 1136, 1088, 917, 835, 817, 742, 673, 626, 561 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.27 (m, 2H), 7.91 (s, 1H), 8.22 (m, 2H); ^{13}C nmr (deuteriochloroform): δ 116.7, 116.8, 133.3, 133.4, 136.2, 136.6, 138.0, 153.9.

Anal. Calcd for $C_{10}H_5Cl_2FN_2O_3S$: C, 37.17; H, 1.56; N, 8.67; S, 9.92. Found: C, 37.32; H, 1.68; N, 8.71; S, 9.98.

Compound **2j** has mp 230-232°; ir (potassium bromide): 3105, 3066, 1703, 1591, 1546, 1396, 1351, 1314, 1251, 1192, 1113, 1089, 920, 857, 810, 744, 680, 640 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.94 (s, 1H), 8.41 (m, 4H); ^{13}C nmr (deuteriochloroform): δ 124.4, 131.6, 136.3, 137.2, 138.3, 140.9, 151.7, 153.9.

Anal. Calcd for $C_{10}H_5Cl_2N_3O_5S$: C, 34.30; H, 1.44; N, 12.00; S, 9.16. Found: C, 34.32; H, 1.48; N, 12.02; S, 9.12.

Compound **2k** has mp 182-184°; ir (potassium bromide): 3094, 3067, 1691, 1588, 1452, 1395, 1330, 1261, 1190, 1141, 1102, 1039, 923, 827, 740, 684, 629 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.45 (d, 1H, J = 8.5), 7.60 (d, 1H, J = 8.5), 8.00 (s, 1H), 8.38 (d, 1H, J = 2.5); ^{13}C nmr (deuteriochloroform): δ 130.6, 133.0, 133.8, 133.9, 135.4, 135.9, 136.2, 136.8, 138.5, 153.9.

Anal. Calcd for $C_{10}H_4Cl_4N_2O_3S$: C, 32.11; H, 1.08; N, 7.49; S, 8.57. Found: C, 32.22; H, 1.18; N, 7.60; S, 8.61.

Compound **2l** has mp 192-193°; ir (potassium bromide): 3127, 3104, 3088, 1691, 1587, 1555, 1538, 1391, 1348, 1260, 1186, 1140, 1103, 926, 753, 738, 663 cm^{-1}; ^1H nmr (deuteriochloroform): δ 8.06 (s, 1H), 8.67 (m, 2H), 8.85 (d, 1H, J = 9.3); ^{13}C nmr (deuteriochloroform): δ 120.4, 126.8, 135.1, 135.7, 137.3, 137.9, 139.1, 148.8, 151.3, 154.1.

Anal. Calcd for $C_{10}H_4Cl_2N_4O_7S$: C, 30.40; H, 1.02; N, 14.18; S, 8.12. Found: C, 30.54; H, 1.18; N, 14.22; S, 8.19.

Compound **2m** has mp 193-195°; ir (potassium bromide): 3100, 3062, 2982, 2944, 1690, 1592, 1459, 1372, 1256, 1191, 1141, 1088, 1034, 918, 859, 809, 673 cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.31 (s, 3H), 2.61 (s, 6H), 6.99 (s, 2H), 7.93 (s, 1H); ^{13}C nmr (deuteriochloroform): δ 130.3, 132.2, 135.5, 136.2, 137.9, 141.8, 145.4, 154.3.

Anal. Calcd for $C_{13}H_{12}Cl_2N_2O_3S$: C, 44.97; H, 3.48; N, 8.07; S, 9.24. Found: C, 44.99; H, 3.68; N, 8.12; S, 9.32.

Method B.

Compound **1** (0.5 g, 3.05 mmoles) and 4-nitrobenzenesulfonyl chlorides (0.74 g, 3.36 mmoles) were dissolved in tetrahydrofuran (30 ml). *n*-Butyllithium (3.36 mmoles, 1.6 *M* solution in hexane) was added to the solution. And the mixture was then stirred at 0° until compound **1** disappeared. After adding ice water (10 ml) with stirring at room temperature, the product was extracted with methylene chloride (80 ml). The extract was dried over anhydrous magnesium sulfate. The solution was filtered and evaporated under reduced pressure. The resulting residue was recrystallized from ethyl acetate to give compound **2j**.

Reaction of Compounds 2 with Aliphatic Amines Under Neutral Condition.

To a solution of **2** (1 equivalent) in tetrahydrofuran (30 ml) was added amine (2 equivalents). The mixture was stirred at 20-22° until **2** disappeared. After filtering the mixture, the filtrate was evaporated under reduced pressure. The resulting residue was applied to the top of an open-bed silica gel column (2.5 x 6 - 13 cm). The column was eluted with methylene chloride or ethyl acetate/*n*-hexane (1:2, v/v). Fractions containing 5-alkyl- amino-2-(substituted-benzenesulfonyl)pyridazin-3-ones **4** or *N*-alkylbenzenesulfonamides **5** were combined and evaporated under reduced pressure to afford the corresponding product, respectively.

Compound **4a** has mp 177-178°; R_f = 0.24 (methylene chloride); ir (potassium bromide): 3393, 3361, 3087, 2977, 2939, 2878, 1663, 1625, 1543, 1447, 1373, 1327, 1189, 1092, 816, 732 cm^{-1} [8]; ^1H nmr (deuteriochloroform): δ 1.34 (t, 3H, J = 7.2), 3.46 (m, 2H), 4.97 (bs, NH, D_2O exchangeable), 7.54 (m, 2H), 7.66 (m, 1H), 7.78 (s, 1H), 8.16 (m, 2H); ^{13}C nmr (deuteriochloroform): δ 15.4, 38.3, 106.3, 127.7, 129.0, 129.8, 134.7, 136.8, 144.2, 155.2.

Anal. Calcd for $C_{12}H_{12}ClN_3O_3S$: C, 45.94; H, 3.85; N, 13.39; S, 10.22. Found: C, 45.97; H, 3.93; N, 13.41; S, 10.32.

Compound **4b** has mp 176-177°; R_f = 0.45 (methylene chloride); ir (potassium bromide): 3098, 3013, 2984, 2931, 2913, 2872, 1660, 1606, 1531, 1486, 1469, 1449, 1372, 1345, 1306, 1259, 1187, 1142, 1074, 891, 848 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.27 (t, 6H, J = 7.1), 3.54 (q, 4H, J = 7.1), 7.54 (m, 2H), 7.64 (m, 1H), 7.73 (s, 1H), 8.17 (m, 2H); ^{13}C nmr (deuteriochloroform): δ 14.2, 45.7, 108.4, 128.9, 129.8, 131.6, 134.6, 136.8, 145.5, 156.3.

Anal. Calcd for $C_{14}H_{16}ClN_3O_3S$: C, 49.19; H, 4.72; N, 12.29; S, 9.38. Found: C, 49.21; H, 4.83; N, 12.42; S, 9.42.

Compound **4c** has mp 183-184°; R_f = 0.43 (methylene chloride); ir (potassium bromide): 3430, 3375, 3100, 2955, 2875, 1675, 1635, 1545, 1460, 1440, 1390, 1355, 1199, 1183, 1120, 1100, 970, 900, 820, 735 cm^{-1} [8]; ^1H nmr (deuteriochloroform):δ 1.38 (m, 4H), 1.66 (m, 2H), 1.78 (m, 2H), 2.01 (m, 2H), 3.51 (m, 1H), 4.84 (d, NH, J = 8.0, D_2O exchangeable), 7.53 (m, 2H), 7.66 (m, 1H), 7.76 (s, 1H), 8.17 (m, 1H); ^{13}C nmr (deuteriochloroform): δ 24.6, 25.1, 33.8, 52.1, 106.3, 127.9, 128.9, 129.8, 134.7, 136.8, 143.5, 155.2.

Anal. Calcd for $C_{16}H_{18}N_3ClO_3S$: C, 52.24; H, 4.93; N, 11.42; S, 8.72. Found: C, 52.35; H, 5.02; N, 11.53; S, 8.81.

Compound **4d** has mp 161-163°; R_f = 0.45 (methylene chloride); ir (potassium bromide): 3079, 2936, 2845, 1661, 1598, 1510, 1450, 1420, 1364, 1338, 1279, 1251, 1175, 1143, 1091, 1004 cm^{-1}; ^1H nmr (deuteriochloroform):δ 1.70 (m, 6H), 3.46 (m, 4H), 7.53 (m, 2H), 7.65 (m, 1H), 7.74 (s, 1H), 8.17 (m, 2H); ^{13}C nmr (deuteriochloroform): δ 23.7, 26.2, 50.4, 112.8, 129.0, 129.8, 132.8, 134.7, 136.7, 147.5, 156.3.

Anal. Calcd for $C_{15}H_{16}N_3ClO_3S$: C, 50.92; H, 4.56; N, 11.88; S, 9.06. Found: C, 50.97; H, 4.62; N, 11.96; S, 9.21.

Compound **4e** has mp 191-192°; R_f = 0.21 (ethyl acetate/*n*-hexane = 1:2, v/v); ir (potassium bromide): 3398, 3092, 2974, 2930, 2877, 1667, 1625, 1542, 1445, 1372, 1329, 1191, 1174, 1092, 822, 675, 633 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.34 (t, 3H, J = 7.2), 2.43 (s, 3H), 3.45 (m, 2H), 4.90 (bs, NH, D_2O exchangeable), 7.33 (d, 2H, J = 8.4), 7.76 (s, 1H), 8.05 (d, 2H, J = 8.4); ^{13}C nmr (deuteriochloroform): δ 15.3, 21.8, 38.3, 106.6, 127.3, 129.6, 129.9, 133.7, 144.1, 146.1, 155.2.

Anal. Calcd for $C_{13}H_{14}ClN_3O_3S$: C, 47.63; H, 4.30; N, 12.82; S, 9.78. Found: C, 47.66; H, 4.32; N, 12.92; S, 9.82.

Compound **4f** has mp 169-171°; R_f = 0.22 (ethyl acetate/*n*-hexane = 1:2, v/v);ir (potassium bromide): 3100, 3000, 2950, 2875, 1660, 1610, 1530, 1500, 1470, 1450, 1420, 1380, 1360, 1320, 1300, 1280, 1260, 1200, 1180, 1140, 1120, 1090, 1080, 1050, 1000, 880, 850 cm^{-1}; ^1H nmr (DMSO-d_6): δ 1.18 (t, 6H, J = 7.0), 2.42 (s, 3H), 3.57 (t, 4H, J = 7.0), 7.47 (d, 2H, J = 8.2), 7.89 (d, 2H, J = 8.3), 8.08 (s, 1H); ^{13}C nmr (DMSO-d_6): δ 14.4,

21.5, 45.7, 105.2, 129.3, 130.1, 133.2, 134.0, 145.8, 146.3, 156.0.

Anal. Calcd for $C_{15}H_{18}ClN_3O_3S$: C, 50.63; H, 5.10; N, 11.81; S, 9.01. Found: C, 50.77; H, 5.28; N, 11.78; S, 9.12.

Compound **4g** has mp 164-166°; R_f = 0.25 (ethyl acetate/*n*-hexane = 1:2, v/v);ir (potassium bromide): 3420, 2960, 2880, 1690, 1640, 1610, 1560, 1465, 1395, 1205, 1190, 1125, 1105, 1050, 960, 835, 740 cm^{-1}; ^1H nmr (DMSO-d_6): δ 1.07 (m, 1H), 1.37 (m, 4H), 1.59 (d, 1H, J = 13.0), 1.70 (d, 2H, J = 13.0), 1.80 (d, 2H, J = 11.0), 2.40 (s, 3H), 3.71 (m, 1H), 6.78 (d, NH, J = 8.0, D_2O exchangeable), 7.46 (d, 2H, J = 8.0), 7.87 (d, 2H, J = 8.5), 8.23 (s, 1H); ^{13}C nmr (DMSO-d_6): δ 21.8, 24.4, 25.1, 33.8, 52.1, 106.3, 127.7, 129.6, 129.9, 133.8, 143.4, 146.0, 155.2.

Anal. Calcd for $C_{17}H_{20}ClN_3O_3S$: C, 53.47; H, 5.28; N, 11.00; S, 8.40. Found: C, 53.52; H, 5.40; N, 11.22; S, 8.45.

Compound **4h** has mp 183-185°; R_f = 0.48 (ethyl acetate/*n*-hexane = 1:2, v/v); ir (potassium bromide): 3377, 3094, 2966, 2937, 2976, 1666, 1622, 1538, 1470, 1438, 1384, 1326, 1276, 1191, 1147, 1090, 1030, 1009 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.35 (t, 3H, J = 7.2), 3.46 (m, 2H), 4.97 (bs, NH, D_2O exchangeable), 7.51 (d, 2H, J = 8.8), 7.78 (s, 1H), 8.11 (d, 2H, J = 8.8); ^{13}C nmr (deuteriochloroform): δ 15.3, 38.3, 106.3, 127.8, 129.3, 131.3, 135.1, 141.7, 144.2, 155.2.

Anal. Calcd for $C_{12}H_{11}Cl_2N_3O_3S$: C, 41.39; H, 3.18; N, 12.07; S, 9.21. Found: C, 41.52; H, 3.38; N, 12.22; S, 9.32.

Compound **4i** has mp 170-172°; R_f = 0.21 (ethyl acetate/*n*-hexane = 1:2, v/v); ir (potassium bromide): 3092, 2982, 2964, 2934, 2871, 1644, 1604, 1529, 1497, 1468, 1393, 1350, 1317, 1270, 1257, 1196, 1081, 1067, 1007 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.27 (t, 6H, J = 3.3), 3.56 (m, 4H), 7.51 (d, 2H, J = 8.8), 7.73 (s, 1H), 8.12 (d, 2H, J = 8.8); ^{13}C nmr (deuteriochloroform): δ 13.3, 45.8, 108.3, 129.3, 131.4, 131.8, 135.1, 141.6, 145.6, 156.3.

Anal. Calcd for $C_{14}H_{15}Cl_2N_3O_3S$: C, 44.69; H, 4.02; N, 11.17; S, 8.52. Found: C, 44.73; H, 4.12; N, 11.22; S, 8.65.

Compound **4j** has mp 180-182°; R_f = 0.61 (ethyl acetate/*n*-hexane = 1:2, v/v); ir (potassium bromide): 3400, 3100, 2950, 2870, 1680, 1635, 1595, 1550, 1480, 1445, 1400, 1380, 1340, 1290, 1180, 1100, 1020, 1070 cm^{-1}; ^1H nmr (DMSO-d_6): δ 1.08 (m, 1H), 1.36 (m, 4H), 1.58 (d, 1H, J = 13.0), 1.69 (d, 2H, J = 13.5), 1.80 (d, 2H, J = 10.5), 3.72 (m, 1H), 6.84 (d, NH, J = 8.0, D_2O exchangeable), 7.73 (d, 2H, J = 9.0), 7.99 (d, 2H, J = 8.5), 8.26 (s, 1H); ^{13}C nmr (deuteriochloroform): δ 24.4, 25.1, 33.8, 52.1, 106.2, 128.1, 129.3, 131.3, 135.2, 141.6, 143.5, 155.2.

Anal. Calcd for $C_{16}H_{17}Cl_2N_3O_3S$: C, 47.77; H, 4.26; N, 10.45; S, 7.97. Found: C, 47.79; H, 4.29; N, 10.52; S, 8.02.

Compound **4k** has mp 164-166°; R_f = 0.37 (ethyl acetate/*n*-hexane = 1:2, v/v); ir (potassium bromide): 3130, 3070, 3000, 2950, 2850, 1660, 1600, 1520, 1445, 1380, 1280, 1260, 1180, 1125, 1175, 1000, 940, 870, 755 cm^{-1}; ^1H nmr (DMSO-d6): δ 1.61 (s, 6H), 3.50 (m, 4H), 7.76 (d, 2H, J = 8.5), 8.01 (d, 2H, J = 8.5), 8.17 (s, 1H); ^{13}C nmr (DMSO-d_6): δ 23.2, 25.8, 49.7, 108.4, 129.5, 130.7, 134.5, 135.2, 140.1, 147.4, 155.4.

Anal. Calcd for $C_{15}H_{15}Cl_2N_3O_3S$: C, 46.40; H, 3.89; N, 10.82; S, 8.26. Found: C, 46.37; H, 3.92; N, 10.91; S, 8.28.

Compound **4l** has mp 202-204°; R_f = 0.10 (methylene chloride); ir (potassium bromide): 3310, 3114, 2980, 2936, 1656, 1622, 1529, 1435, 1347, 1326, 1193, 1104, 1008, 854, 742, 680, 633 cm^{-1}; ^1H nmr (DMSO-d_6): δ 1.17 (t, 3H, J = 7.0, 6.9), 3.46 (m, 2H), 7.43 (bs, NH, D_2O exchangeable), 8.25 (d, 2H, J = 9.0), 8.28 (s, 1H), 8.44 (d, 2H, J = 9.0); 13C nmr (DMSO-d_6): δ 15.5, 37.3, 101.9, 124.4, 130.3, 130.7, 142.0, 144.9, 150.8, 154.5.

Anal. Calcd for $C_{12}H_{11}ClN_4O_5S$: C, 40.17; H, 3.09; N, 15.62; S, 8.94. Found: C, 40.21; H, 3.12; N, 15.54; S, 8.87.

Compound **4m** has mp 163-164°; R_f = 0.18 (ethyl acetate/*n*-hexane = 1:2, v/v); ir (potassium bromide): 3130, 3000, 2950, 2890, 1665, 1620, 1545, 1480, 1390, 1360, 1320, 1280, 1245, 1200, 1100, 1060, 865, 820 cm^{-1}; ^1H nmr (DMSO-d_6): δ 1.20 (t, 6H, J = 7.0, 7.0), 3.60 (t, 4H, J = 7.0), 8.17 (s, 1H), 8.28 (d, 2H, J = 8.8), 8.46 (d, 2H, J = 7.1); ^{13}C nmr (DMSO-d_6): δ 14.5, 45.8, 104.5, 124.9, 130.9, 134.2, 142.2, 145.9, 151.3, 155.9.

Anal. Calcd for $C_{14}H_{15}ClN_4O_5S$: C, 43.47; H, 3.91; N, 14.48; S, 8.29. Found: C, 43.51; H, 3.88; N, 14.51; S, 8.34.

Compound **4n** has mp 216-217°; R_f = 0.30 (ethyl acetate/*n*-hexane = 1:1, v/v); ir (potassium bromide): 3365, 3102, 2987, 2942, 2892, 1660, 1622, 1548, 1440, 1378, 1361, 1328, 1186, 11500, 1125, 1095 cm^{-1}; ^1H nmr (DMSO-d_6): δ 1.27 (t, 3H, J = 7.2), 3.53 (m, 2H), 7.08 (bs, NH, D_2O exchangeable), 7.94 (m, 3H), 8.11 (s, 1H), 8.45 (d, 1H, J = 0.6); ^{13}C nmr (DMSO-d_6): δ 15.5, 37.8, 102.9, 124.7, 130.3, 132.2, 134.5, 134.6, 136.0, 145.0, 147.9, 154.8.

Anal. Calcd for $C_{12}H_{11}ClN_4O_5S$: C, 40.17; H, 3.09; N, 15.62; S, 8.94. Found: C, 40.21; H, 3.13; N, 15.66; S, 9.02.

Compound **4o** has mp 164-165°; R_f = 0.18 (ethyl acetate/*n*-hexane = 1:2, v/v); ir (potassium bromide): 3100, 3000, 2950, 2900, 1660, 1610, 1540, 1500, 1480, 1460, 1390, 1350, 1310, 1270, 1190, 1150, 1130, 1090 cm^{-1}; ^1H nmr (DMSO-d_6): δ 1.21 (t, 6H, J = 7.0), 3.63 (m, 4H), 8.07 (m, 2H), 8.10 (d, 1H, J = 7.8), 8.22 (s, 1H), 8.36 (d, 1H, J = 7.8); ^{13}C nmr (DMSO-d_6): δ 14.5, 46.0, 104.3, 125.4, 129.8, 133.1, 133.5, 143.2, 137.0, 146.0, 147.9, 155.7.

Anal. Calcd for $C_{14}H_{15}ClN_4O_5S$: C, 43.47; H, 3.91; N, 14.48; S, 8.29. Found: C, 43.51; H, 3.98; N, 14.52; S, 8.32.

Compound **4p** has mp 204-205°; R_f = 0.15 (ethyl acetate/*n*-hexane = 1:2, v/v); ir (potassium bromide): 3380, 3100, 3082, 2931, 2860, 1655, 1618, 1538, 1432, 1380, 1358, 1312, 1183, 1123, 1107, 1030, 959, 821 cm^{-1}; ^1H nmr (DMSO-d_6): δ 1.09 (m, 1H), 1.40 (m, 4H), 1.60 (d, 1H, J = 13.0), 1.72 (d, 2H, J = 13.0), 1.83 (d, 2H, J = 10.0), 3.79 (m, 1H), 6.99 (bs, NH, D_2O exchangeable), 8.05 (m, 3H), 8.35 (d, 1H, J = 7.5), 8.37 (s, 1H); ^{13}C nmr (DMSO-d_6): δ 24.9, 25.2, 33.1, 52.3, 102.1, 125.4, 130.8, 133.1, 134.2, 137.0, 144.8, 147.9, 154.9.

Anal. Calcd for $C_{16}H_{17}ClN_4O_5S$: C, 46.55; H, 4.15; N, 13.57; S, 7.77. Found: C, 46.61; H, 4.21; N, 13.62; S, 7.82.

Compound **4q** has mp 178-180°; R_f = 0.19 (ethyl acetate/*n*-hexane = 1:2, v/v); ir (potassium bromide): 3093, 3017, 2940, 2859, 1646, 1605, 1539, 1446, 1377, 1356, 1292, 1280, 1181, 1123, 1088, 999 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.75 (m, 6H), 3. 55 (m, 4H), 7.85 (m, 3H), 7.87 (s, 1H), 8.66 (m, 1H); ^{13}C nmr (deuteriochloroform): δ 23.9, 26.2, 50.5, 111.4, 124.7, 131.2, 132.4, 132.9, 135.5, 135.8, 147.8, 148.3, 156.4.

Anal. Calcd for $C_{15}H_{15}ClN_4O_5S$: C, 45.17; H, 3.79; N, 14.05; S, 8.04. Found: C, 45.21; H, 3.82; N, 14.10; S, 8.11.

Compound **4r** has mp 200-202°; R_f = 0.21 (ethyl acetate/*n*-hexane = 1:1, v/v); ir (potassium bromide): 3374, 3097, 3071, 2979, 2929, 2234, 1658, 1619, 1542, 1473, 1446, 1375, 1331, 1277, 1189, 1131, 1105, 1089 cm^{-1}; ^1H nmr (deuteriochloroform + DMSO-d_6): δ 1.28 (t, 3H, J = 7.2), 3.52 (m, 2H), 6.87 (bs, NH, D_2O exchangeable), 7.90 (m, 3H), 8.07 (s, 1H), 8.33 (d, 1H, J = 8.0); ^{13}C nmr (deuteriochloroform + DMSO-d_6): δ 15.5, 37.9, 103.3, 110.7, 114.7, 131.8, 131.9, 133.1, 134.5, 135.3, 139.4, 144.9, 155.1.

Anal. Calcd for $C_{13}H_{11}ClN_4O_3S$: C, 46.09; H, 3.27; N, 16.54; S, 9.47. Found: C, 46.14; H, 3.31; N, 16.48; S, 9.51.

Compound **4s** has mp 183-185°; R_f = 0.27 (ethyl acetate/*n*-hexane = 1:2, v/v); ir (potassium bromide): 3104, 3080, 3022, 2976, 2934, 2232, 1650, 1606, 1538, 1486, 1446, 1422, 1384, 1308, 1275, 1180, 1148, 1075 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.30 (t, 6H, J = 7.1), 3.60 (m, 4H), 7.77 (t, 1H, J = 7.6), 7.84 (m, 2H), 7.86 (s, 1H), 8.46 (d, 1H, J = 9.4); ^{13}C nmr (deuteriochloroform): δ 14.3, 45.9, 107.1, 110.8, 114.9, 132.2, 132.7, 133.1, 134.2, 135.2, 139.9, 145.8, 156.4.

Anal. Calcd for $C_{15}H_{15}ClN_4O_3S$: C, 49.11; H, 4.12; N, 15.27; S, 8.74. Found: C, 49.023; H, 4.21; N, 15.31; S, 8.81.

Compound **4t** has mp 211-213°; R_f = 0.22 (ethyl acetate/*n*-hexane = 1:2, v/v); ir (potassium bromide): 3380, 3354, 3094, 3026, 2934, 2855, 2234, 1667, 1621, 1542, 1434, 1381, 1341, 1188, 1133, 1105, 1087, 818 cm^{-1}[7]; ^1H nmr (deuteriochloroform): δ 1.26 (m, 1H), 1.39 (m, 4H), 1.69 (m, 1H), 1.82 (m, 2H), 2.03 (m, 2H), 3.57 (m, 1H), 4.96 (d, NH, J = 8.1, D_2O exchangeable), 7.76 (t, 1H, J = 7.7), 7.83 (m, 2H), 7.91 (s, 1H), 8.46 (d, 1H, J = 8.0); ^{13}C nmr (deuteriochloroform): δ 24.4, 25.1, 33.8, 52.3, 105.3, 110.8, 114.8, 128.5, 132.7, 133.0, 134.2, 135.1, 140.0, 143.9, 155.3.

Anal. Calcd for $C_{17}H_{17}ClN_4O_3S$: C, 51.97; H, 4.36; N, 14.26; S, 8.16. Found: C, 51.98; H, 4.39; N, 14.27; S, 8.21.

Compound **4u** has mp 198-199°; R_f = 0.17 (methylene chloride); ir (potassium bromide): 3098, 3069, 3022, 2930, 2864, 2233, 1645, 1602, 1529, 1473, 1448, 1374, 1292, 1275, 1185, 1131, 1085, 999 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.72 (d, 6H, J = 1.1), 3.53 (d, 4H, J = 5.3), 7.77 (m, 1H), 7.84 (m, 2H), 7.88 (s, 1H), 8.46 (d, 1H, J = 9.4); ^{13}C nmr (deuteriochloroform): δ 23.8, 26.2, 50.5, 110.8, 114.8, 132.8, 133.0, 133.5, 134.3, 135.1, 139.8, 147.8, 156.5.

Anal. Calcd for $C_{16}H_{15}ClN_4O_3S$: C, 50.73; H, 3.99; N, 14.79; S, 8.46. Found: C, 50.68; H, 4.03; N, 14.85; S, 8.55.

Compound **4v** has mp 203-205°; R_f = 0.20 (ethyl acetate/*n*-hexane = 1:2, v/v); ir (potassium bromide): 3363, 3143, 3073, 2994, 2944, 2878, 1658, 1620, 1570, 1544, 1447, 1370, 1327, 1284, 1183, 1133, 1091, 1022 cm^{-1}; ^1H nmr (deuteriochloroform + DMSO-d_6): δ 1.29 (t, 3H, J = 7.2), 3.51 (m, 2H), 6.80 (bs, NH, D_2O exchangeable), 7.56 (m, 1H), 7.62 (m, 1H), 7.74 (m, 1H), 8.03 (s, 1H), 8.34 (d, 1H, J = 8.0); ^{13}C nmr (deuteriochloroform + DMSO-d_6): δ 15.5, 37.9, 103.4, 119.3, 127.8, 133.5, 135.1, 135.3, 136.2, 137.3, 144.8, 154.9.

Anal. Calcd for $C_{12}H_{11}ClBrN_3O_3S$: C, 36.71; H, 2.82; N, 10.70; S, 8.17. Found: C, 36.64; H, 2.84; N, 10.72; S, 8.15.

Compound **4w** has mp 152-153°; R_f = 0.22 (ethyl acetate/*n*-hexane = 1:2, v/v); ir (potassium bromide): 3068, 2974, 2935, 2874, 1657, 1601, 1526, 1467, 1450, 1371, 1342, 1315, 1273, 1181, 1145, 1081, 1024, 850 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.30 (t, 6H, J = 7.1), 3.58 (m, 4H), 7.47 (t, 1H, J = 7.7), 7.56 (t, 1H, J = 7.7), 7.68 (d, 1H, J = 7.9), 7.82 (s, 1H), 8.46 (d, 1H, J = 8.0); ^{13}C nmr (deuteriochloroform): δ 14.3, 45.8, 107.9, 119.9, 127.9, 131.7, 134.5, 135.1, 135.2, 137.2, 145.7, 156.2.

Anal. Calcd for $C_{14}H_{15}ClBrN_3O_3S$: C, 39.97; H, 3.59; N, 9.99; S, 7.62. Found: C, 39.96; H, 3.63; N, 9.91; S, 7.66.

Compound **4x** has mp 219-220°; R_f = 0.21 (ethyl acetate/*n*-hexane = 1:2, v/v); ir (potassium bromide): 3336, 3085, 2933, 2850, 1649, 1613, 1541, 1433, 1371, 1336, 1182, 1134, 1105, 1025, 818, 769 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.24 (m, 1H), 1.40 (m, 4H), 1.68 (m, 1H), 1.82 (m, 2H), 2.03 (m, 2H), 3.56 (m, 1H), 4.91 (d, NH, J = 8.0, D_2O exchangeable), 7.46 (t, 1H, J = 7.8), 7.56 (t, 1H, J = 7.5), 7.67 (d, 1H, J =7.9), 7.86 (s, 1H), 8.45 (m, 1H); ^{13}C nmr (deuteriochloroform): δ 24.4, 25.1, 33.8, 52.2, 105.7, 119.9, 127.8, 127.9, 134.4, 135.1, 135.2, 137.2, 143.7, 155.1.

Anal. Calcd for $C_{16}H_{17}ClBrN_3O_3S$: C, 43.02; H, 3.84; N, 9.41; S, 7.18. Found: C, 43.08; H, 3.88; N, 9.36; S, 7.24.

Compound **4y** has mp 217-218°; R_f = 0.23 (ethyl acetate/*n*-hexane = 1:2, v/v); ir (potassium bromide): 3089, 2999, 2938, 2857, 1642, 1605, 1569, 1530, 1448, 1423, 1371, 1280, 1255, 1183, 1082, 1023, 998, 826 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.72 (m, 6H), 3.51 (m, 4H), 7.48 (t, 1H, J = 7.7), 7.56 (t, 1H, J = 7.7), 7.68 (d, 1H, J = 7.9), 7.84 (s, 1H), 8.45 (d, 1H, J = 8.0); ^{13}C nmr (deuteriochloroform): δ 23.9, 26.2, 50.4, 111.8, 119.9, 127.9, 132.9, 134.4, 135.1, 135.3, 137.1, 147.7, 156.2.

Anal. Calcd for $C_{15}H_{15}ClBrN_3O_3S$: C, 41.63; H, 3.49; N, 9.71; S, 7.41. Found: C, 41.59; H, 3.54; N, 9.66; S, 7.44.

Compound **4z** has mp 189-191°; ir (potassium bromide): 3399, 3062, 3025, 2985, 2939, 2872, 1660, 1614, 1538, 1445, 1403, 1367, 1323, 1272, 1195, 1174, 1135, 1104, 1078, 1010 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.35 (t, 3H, J = 7.3), 2.28 (s, 3H), 2.60 (s, 6H), 3.47 (m, 2H), 4.93 (t, NH, J = 4.9, D_2O exchangeable), 6.94 (s, 2H), 7.79 (s, 1H); ^{13}C nmr (deuteriochloroform): δ 15.3, 21.1, 22.6, 38.3, 106.5, 126.6, 131.7, 132.0, 141.2, 144.2, 144.4, 155.6.

Anal. Calcd for $C_{15}H_{18}ClN_3O_3S$: C, 50.63; H, 5.10; N, 11.81; S, 9.01. Found: C, 56.74; H, 5.32; N, 11.96; S, 9.27.

Compound **4aa** has mp 181-183°; ir (potassium bromide): 3087, 2974, 2934, 2875, 1659, 1643, 1601, 1525, 1469, 1449, 1403, 1368, 1303, 1274, 1179, 1143, 1074, 1056 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.28 (t, 6H, J =7.1), 2.28 (s, 3H), 2.61 (s, 6H), 3.56 (m, 4H), 6.95 (s, 2H), 7.75 (s, 1H); ^{13}C nmr (deuteriochloroform): δ 14.2, 21.1, 22.7, 45.7, 109.0, 130.7, 131.7, 132.0, 141.2, 144.3, 145.6, 156.7

Anal. Calcd for $C_{17}H_{22}ClN_3O_3S$: C, 53.19; H, 5.78; N, 10.95; S, 8.35. Found: C, 53.25; H, 5.83; N, 11.01; S, 8.41.

Compound **4bb** has mp 217-219°; ir (potassium bromide): 3349, 3025, 2930, 2856, 1667, 1613, 1536, 1429, 1402, 1340, 1315, 1285, 1193, 1171, 1141, 1112, 1086, 1030 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.34 (m, 5H), 1.68 (m, 1H), 1.81 (m, 2H), 2.02 (m, 2H), 2.28 (s, 3H), 2.61 (s, 6H), 3.53 (m, 1H), 4.83 (d, NH, J = 8.1, D_2O exchangeable), 6.94 (s, 2H), 7.78 (s, 1H); ^{13}C nmr (deuteriochloroform): δ 21.2, 22.6, 24.4, 25.1, 33.8, 52.1, 106.5, 126.8, 131.8, 132.0, 141.2, 143.5, 144.3, 155.6.

Anal. Calcd for $C_{19}H_{24}ClN_3O_3S$: C, 55.67; H, 5.90; N, 10.25; S, 7.82. Found: C, 55.78; H, 6.11; N, 10.43; S, 7.94.

Compound **4cc** has mp 190-191°; ir (potassium bromide): 3027, 2973, 2935, 2858, 1659, 1600, 1523, 1452, 1369, 1289, 1189, 1175, 1080, 1027, 1004 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.70 (s, 6H), 2.89 (s, 3H), 2.61 (s, 6H), 3.47 (s, 4H), 6.95 (s, 2H), 7.76 (s, 1H); ^{13}C nmr (deuteriochloroform): δ 21.2, 22.7, 23.9, 26.2, 50.4, 113.3, 131.6, 131.9, 132.0, 141.3, 144.4, 147.7, 156.7.

Anal. Calcd for $C_{18}H_{22}ClN_3O_3S$: C, 54.61; H, 5.60; N, 10.61; S, 8.10. Found: C, 56.62; H, 5.81; N, 10.74; S, 8.30.

Compound **5a** is a liquid; R_f = 0.41 (methylene chloride); ir (sodium chloride): 3281, 3066, 2981, 2938, 2878, 1478, 1447, 1427, 1324, 1160, 1094, 1063, 948, 755 cm^{-1}; ^1H nmr (deuteriochloroform):δ 1.09 (t, 3H, J = 7.2), 3.01 (m, 2H), 4.96 (t, NH, J = 4.9, D_2O exchangeable), 7.51 (m, 2H), 7.56 (m, 1H), 7.88 (m, 2H); ^{13}C nmr (deuteriochloroform): d 15.0, 38.3, 127.1, 129.1, 132.6, 140.0.

Anal. Calcd for $C_8H_{11}NO_2S$: C, 51.87; H, 5.99; N, 7.56; S, 17.31. Found: C, 51.90; H, 6.12; N, 7.76; S, 17.45.

Compound **5b** is a liquid; R_f = 0.64 (methylene chloride); ir (sodium chloride): 3066, 2977, 2938, 2876, 1467, 1447, 1384, 1333, 1201, 1158, 1091, 1017, 934, 759, 732, 692 cm^{-1}; ^1H nmr (deuteriochloroform):δ 1.12 (t, 6H, J = 7.2), 3.24 (q, 4H, J = 7.2), 7.49 (m, 3H), 7.81 (m, 2H); ^{13}C nmr (deuteriochloroform): δ 14.1, 42.1, 127.0, 129.0, 132.3, 140.5.

Anal. Calcd for $C_{10}H_{15}NO_2S$: C, 56.31; H, 7.09; N, 6.57; S, 15.03. Found: C, 56.43; H, 7.34; N, 6.87; S, 15.23.

Compound **5c** is a liquid; R_f = 0.52 (methylene chloride); ir (sodium chloride): 3278, 3065, 2933, 2856, 1448, 1324, 1263, 1160, 1094, 1081, 993, 914, 884, 756 cm^{-1}; ^1H nmr (deuteriochloroform):δ 1.18 (m, 5H), 1.45 (m, 1H), 1.62 (m, 2H), 1.73 (m, 2H), 3.14 (m, 1H), 5.11 (d, NH, J = 7.6, D_2O exchangeable), 7.52 (m, 3H), 7.91 (m, 2H); ^{13}C nmr (deuteriochloroform): δ 24.6, 25.1, 33.8, 52.7, 126.9, 129.0, 132.4, 141.6.

Anal. Calcd for $C_{12}H_{17}NO_2S$: C, 60.22; H, 7.16; N, 5.85; S, 13.40. Found: C, 60.34; H, 7.34; N, 5.98; S, 13.52.

Compound **5d** has mp 86-87°; R_f = 0.77 (methylene chloride); ir (potassium bromide): 3057, 2946, 2928, 2840, 1478, 1446, 1360, 1336, 1276, 1166, 1094, 1051, 932, 740, 690 cm^{-1}; ^1H nmr (deuteriochloroform):δ 1.42 (m, 2H), 1.63 (m, 4H), 3.99 (m, 4H), 7.52 (m, 2H), 7.59 (m, 1H), 7.75 (2, 2H); ^{13}C nmr (deuteriochloroform): δ 23.5, 25.2, 46.9, 127.6, 128.9, 132.6, 136.4.

Anal. Calcd for $C_{11}H_{15}NO_2S$: C, 58.64; H, 6.71; N, 6.22; S, 14.23. Found: C, 58.76; H, 6.90; N, 6.30; S, 14.35.

Compound **5e** has mp 63–65°; R_f = 0.41 (ethyl acetate/*n*-hexane = 1:2, v/v); ir (potassium bromide): 3262, 3049, 2974, 2929, 2884, 1579, 1495, 1451, 1420, 1319, 1291, 1159, 1120, 1057, 950, 811, 707 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.10 (t, 3H, J = 7.2), 2.43 (s, 3H), 3.16 (m, 2H), 4.47 (bs, NH, D_2O exchangeable), 7.31 (d, 2H, J = 8.3), 7.75 (d, 2H, J = 8.2); ^{13}C nmr (deuteriochloroform): δ 15.1, 21.5, 38.3, 127.2, 129.7, 137.1, 143.4.

Anal. Calcd for $C_9H_{13}NO_2S$: C, 54.25; H, 6.58; N, 7.03; S, 16.09. Found: C, 54.28; H, 6.45; N, 7.02; S, 16.05.

Compound **5f** has mp 43-44°; R_f = 0.66 (ethyl acetate/*n*-hexane = 1:2, v/v); ir (potassium bromide): 3075, 3010, 2960, 2800, 1605, 1500, 1480, 1400, 1350, 1310, 1215, 1190, 1165, 1100, 1030, 945, 820, 790, 725, 705, 650 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.12 (t, 6H, J = 7.1), 2.41 (s, 3H), 3.22 (m, 4H), 7.28 (d, 2H, J = 8.0), 7.69 (d, 2H, J = 8.2); ^{13}C nmr (deuteriochloroform): δ 14.2, 21.5, 42.0, 127.1, 130.0, 137.5, 142.9.

Anal. Calcd for $C_{11}H_{17}NO_2S$: C, 58.12; H, 7.54; N, 6.16; S, 14.11. Found: C, 58.14; H, 7.55; N, 6.15; S, 14.12.

Compound **5g** has mp 78-80°; R_f = 0.57 (ethyl acetate/*n*-hexane = 1:2, v/v); ir (potassium bromide): 3310, 2983, 2850, 1600, 1550, 1495, 1455, 1425, 1380, 1325, 1290, 1280, 1160, 1090, 1075, 990, 910, 880, 840, 810, 700, 665 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.18 (m, 5H), 1.49 (m, 1H), 1.62 (m, 2H), 1.74 (m, 2H), 2.42 (s, 3H), 3.12 (m, 1H), 4.77 (d, 1H, J = 7.5), 7.29 (d, 2H, J = 8.3), 7.78 (d, 2H, J = 8.2); ^{13}C nmr (deuteriochloroform): δ 21.5, 24.6, 25.2, 33.9, 52.6, 127.0, 129.6, 138.6, 143.1.

Anal. Calcd for $C_{13}H_{19}NO_2S$: C, 61.63; H, 7.56; N, 5.53; S, 12.66. Found: C, 61.62; H, 7.58; N, 5.57; S, 12.68.

Compound **5h** has mp 96-98°; R_f = 0.64 (ethyl acetate/*n*-hexane = 1:2, v/v); ir (potassium bromide): 3060, 2960, 2850, 1605, 1500, 1475, 1460, 1405, 1350, 1330, 1315, 1280, 1220, 1180, 1095, 1055, 1045, 930 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.41 (m, 2H), 1.64 (m, 4H), 2.43 (s, 3H), 2.96 (t, 4H, J = 10.1), 7.31 (d, 2H, J = 8.0), 7.63 (d, 2H, J = 8.1); ^{13}C nmr (deuteriochloroform): δ 21.5, 23.5, 25.2, 46.9, 76.8, 77.0, 77.3, 127.7, 129.5, 133.4, 143.3.

Anal. Calcd for $C_{12}H_{17}NO_2S$: C, 60.22; H, 7.16; N, 5.85; S, 13.40. Found: C, 60.25; H, 7.19; N, 5.89; S, 13.54.

Compound **5i** has mp 70-71°; R_f = 0.64 (ethyl acetate/*n*-hexane = 1:2, v/v); ir (potassium bromide): 3276, 3086, 3070, 2989, 2939, 2898, 1585, 1475, 1451, 1429, 1394, 1327, 1276, 1163, 1090, 1054, 1011 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.10 (t, 3H, J = 7.5), 3.00 (m, 2H), 4.80 (bs, NH, D_2O exchangeable), 7.49 (d, 2H, J = 9.0), 7.82 (d, 2H, J = 8.5); ^{13}C nmr (deuteriochloroform): δ 15.1, 38.3, 128.6, 129.4, 138.7, 139.1.

Anal. Calcd for $C_8H_{10}ClNO_2S$: C, 43.74; H, 4.59; N, 6.38; S, 14.60. Found: C, 43.77; H, 4.61; N, 6.47; S, 14.62.

Compound **5j** is a liquid; R_f = 0.60 (ethyl acetate/*n*-hexane = 1:2, v/v); ir (sodium chloride): 3092, 2977, 2938, 2876, 1585, 1475, 1385, 1337, 1201, 1158, 1093, 1013, 935, 758, 687 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.13 (t, 6H, J = 6.5), 3.24 (m, 4H), 7.47 (d, 2H, J = 8.5), 7.75 (d, 2H, J = 9.0); ^{13}C nmr (deuteriochloroform): δ 14.5, 42.5, 127.9, 128.8, 139.0, 139.5.

Anal. Calcd for $C_{10}H_{14}ClNO_2S$: C, 48.48; H, 5.70; N, 5.65; S, 12.94. Found: C, 48.57; H, 5.84; N, 5.75; S, 12.97.

Compound **5k** has mp 102-104°; R_f = 0.61 (ethyl acetate/*n*-hexane = 1:2, v/v); ir (potassium bromide): 3390, 3100, 2960, 2890, 1600, 1590, 1490, 1460, 1410, 1360, 1340, 1290, 1200, 1160, 1100, 1010, 930 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.18 (m, 5H), 1.47 (m, 1H), 1.64 (m, 2H), 1.75 (m, 2H), 3.14 (m, 1H), 4.81 (d, NH, J = 7.3, D_2O exchangeable), 7.47 (m, 2H), 7.83 (d, 2H, J = 8.1); ^{13}C nmr (deuteriochloroform): δ 24.6, 25.1, 33.9, 52.8, 128.4, 129.3, 138.9, 140.2

Anal. Calcd for $C_{12}H_{16}ClNO_2S$: C, 52.64; H, 5.89; N, 5.12; S, 11.71. Found: C, 52.74; H, 5.91; N, 5.14; S, 11.74.

Compound **5l** has mp 96-98°; R_f = 0.66 (ethyl acetate/*n*-hexane = 1:2, v/v); ir (potassium bromide): 3100, 3000, 2950, 2850, 1595, 1580, 1480, 1460, 1400, 1360, 1340, 1280, 1230, 1170, 1100, 1050, 1010 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.43 (m, 2H), 1.64 (m, 4H), 2.99 (m, 4H), 7.50 (m, 2H), 7.69 (m, 2H); ^{13}C nmr (deuteriochloroform): δ 23.5, 25.2, 46.9, 76.8, 77.1, 77.3, 129.1, 129.3, 135.1, 139.1.

Anal. Calcd for $C_{11}H_{14}ClNO_2S$: C, 50.86; H, 5.43; N, 5.39; S, 12.34. Found: C, 50.88; H, 5.48; N, 5.46; S, 12.45.

Compound **5m** has mp 102-103°; R_f = 0.23 (methylene chloride); ir (potassium bromide): 3262, 3106, 2967, 2862, 1607, 1524, 1477, 1435, 1346, 1310, 1162, 1087, 1057, 1013, 949, 855, 798, 740, 638 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.15 (t, 3H, J = 7.5), 3.09 (m, 2H), 4.85 (t, NH, J = 5.6, D_2O exchangeable), 8.07 (d, 2H, J = 8.9), 8.37 (d, 2H, J = 8.9); ^{13}C nmr (deuteriochloroform): δ 15.2, 38.5, 124.4, 128.3, 146.1, 150.1.

Anal. Calcd for $C_8H_{10}N_2O_4S$: C, 41.73; H, 4.38; N, 12.17; S, 13.93. Found: C, 41.87; H, 4.48; N, 12.22; S, 14.00.

Compound **5n** has mp 131-132°; R_f = 0.47 (ethyl acetate/*n*-hexane = 1:2, v/v); ir (potassium bromide): 3120, 3000, 2950, 2880, 1615, 1540, 1475, 1350, 1315, 1205, 1165, 1090, 1025, 945, 860, 750, 700 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.16 (t, 6H, J = 7.2), 3.30 (t, 4H, J = 7.2), 8.00 (d, 2H, J = 8.7), 8.35 (d, 2H, J = 8.7); ^{13}C nmr (deuteriochloroform): δ 14,2, 42.2, 124.4, 128.1, 146.6, 149.9

Anal. Calcd for $C_{10}H_{14}N_2O_4S$: C, 46.50; H, 5.46; N, 10.85; S, 12.41. Found: C, 46.62; H, 5.58; N, 10.94; S, 12.32.

Compound **5o** has mp 135-137°; R_f = 0.55 (ethyl acetate/*n*-hexane = 1:2, v/v); ir (potassium bromide): 3288, 3124, 2946, 2929, 2856, 1609, 1526, 1448, 1349, 1333, 1299, 1159, 1073,

857, 740, 683, 625 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.20 (m, 5H), 1.54 (m, 1H), 1.65 (m, 2H), 1.77 (m, 2H), 3.22 (m, 1H), 4.89 (d, NH, J = 7.7, D_2O exchangeable), 8.09 (d, 2H, J = 7.3), 8.36 (d, 2H, J = 7.1); ^{13}C nmr (deuteriochloroform): δ 24.6, 25.0, 34.0, 53.2, 124.4, 128.2, 147.5, 150.0.

Anal. Calcd for $C_{12}H_{16}N_2O_4S$: C, 50.69; H, 5.67; N, 9.85; S, 11.28. Found: C, 50.78; H, 5.78; N, 9.98; S, 11.31.

Compound **5p** has mp 168-170°; R_f = 0.50 (ethyl acetate/*n*-hexane = 1:2, v/v); ir (potassium bromide): 3113, 2949, 2934, 2852, 1607, 1530, 1471, 1345, 1310, 1175, 1091, 1052, 939, 856, 747, 706 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.46 (m, 2H), 1.66 (m, 4H), 3.06 (t, 4H, J = 5.5), 7.95 (m, 2H), 8.37 (m, 2H); ^{13}C nmr (deuteriochloroform): δ 23.4, 25.2, 46.9, 76.8, 77.1, 77.3, 124.3, 128.8, 142.8, 150.1.

Anal. Calcd for $C_{11}H_{14}N_2O_4S$: C, 48.88; H, 5.22; N, 10.36; S, 11.86. Found: C, 48.96; H, 5.34; N, 10.41; S, 11.97.

Compound **5q** has mp 98-100°; R_f = 0.37 (ethyl acetate/*n*-hexane = 1:1, v/v); ir (potassium bromide): 3333, 3099, 2982, 2939, 2900, 1594, 1538, 1470, 1442, 1407, 1358, 1335, 1281, 1164, 1120, 1101, 1066, 949 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.18 (t, 3H, J = 3.7), 3.17 (m, 2H), 5.21 (s, 1H), 7.74 (m, 2H), 7.86 (m, 1H), 8.15 (m, 1H); ^{13}C nmr (deuteriochloroform): δ 15.2, 38.9, 125.4, 131.1, 132.8, 133.5, 133.9, 148.2.

Anal. Calcd for $C_8H_{10}N_2O_4S$: C, 41.73; H, 4.38; N, 12.17; S, 13.93. Found: C, 41.86; H, 4.46; N, 12.32; S, 13.98.

Compound **5r** has mp 81-82°; R_f = 0.48 (ethyl acetate/*n*-hexane = 1:2, v/v); ir (potassium bromide): 3306, 3099, 2934, 2957, 1595, 1543, 1435, 1369, 1333, 1165, 1127, 1071, 887, 787, 743 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.15 (m, 1H), 1.27 (m, 4H), 1.54 (m, 1H), 1.66 (m, 2H), 1.81 (m, 2H), 3.36 (m, 1H), 5.21 (d, NH, J = 7.45, D_2O exchangeable), 7.73 (m, 2H), 7.86 (m, 1H), 8.17 (m, 1H); ^{13}C nmr (deuteriochloroform): δ 24.6, 25.1, 33.8, 53.6, 125.4, 130.7, 132.9, 133.3, 135.4, 147.9.

Anal. Calcd for $C_{12}H_{16}N_2O_4S$: C, 50.69; H, 5.67; N, 9.85; S, 11.28. Found: C, 50.72; H, 5.81; N, 9.96; S, 11.35.

Compound **5s** is a liquid; R_f = 0.41 (ethyl acetate/*n*-hexane = 1:2, v/v); ir (sodium chloride): 3292, 3098, 3070, 2933, 2857, 2232, 1612, 1569, 1450, 1338, 1297, 1265, 1165, 1130, 1073, 997, 916 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.20 (m, 5H), 1.52 (d, 1H, J = 13.0), 1.66 (m, 2H), 1.76 (m, 2H), 3.23 (m, 1H), 5.15 (d, NH, J = 8.0, D_2O exchangeable), 7.69 (t, 1H, J = 7.5), 7.75 (m, 1H), 7.86 (m, 1H), 8.16 (m, 1H); ^{13}C nmr (deuteriochloroform): δ 23.6, 24.0, 32.8, 52.1, 108.9, 115.3, 128.4, 131.4, 132.1, 133.9, 143.6.

Anal. Calcd for $C_{13}H_{16}N_2O_2S$: C, 59.07; H, 6.10; N, 10.60; S, 12.13. Found: C, 59.11; H, 6.28; N, 10.76; S, 12.15.

Compound **5t** is a liquid; R_f = 0.39 (methylene chloride); ir (sodium chloride): 3096, 2942, 2856, 2231, 1586, 1568, 1469, 1444, 1363, 1346, 1280, 1216, 1174, 1129, 1069, 1051, 935, 772 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.52 (m, 2H), 1.66 (m, 4H), 3.22 (m, 4H), 7.72 (m, 1H), 7.78 (m, 1H), 7.89 (m, 1H), 8.03 (m, 1H); ^{13}C nmr (deuteriochloroform): δ 23.5, 25.3, 46.8, 110.9, 116.4, 130.3, 132.6, 133.0, 135.6, 140.6.

Anal. Calcd for $C_{12}H_{14}N_2O_2S$: C, 57.58; H, 5.64; N, 11.19; S, 12.81. Found: C, 57.62; H, 5.77; N, 11.32; S, 12.97.

Acknowledgments.

This work was supported by Korea Research Foundation Grant (KRF-2000-015-DP0251).

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[8] The infrared spectrum of this compound showed the absorption bands of two NH. This is due to the hydrogen bond between NH and Cl at C-4 position [9].

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