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Tetrahedron Letters
Tetrahedron Letters 46 (2005) 8889–8893

Amidine derivatives of α-arylglycines from *N*-(1-aryl-2,2,2-trichloroethyl)amides of arenesulfonic acids and secondary amines

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Received 19 July 2005; revised 6 October 2005; accepted 18 October 2005
Available online 4 November 2005

Abstract—The interaction of *N*-(1-aryl-2,2,2-trichloroethyl)amides of arenesulfonic acids with secondary amines or their salts in the presence of inorganic bases involves the formation of chloroaziridine intermediates. Depending upon the solvent and reagent ratio, the reaction results in *N*-[1-dialkylamino-2-chloro-2-arylethylidene]-, *N*-[2-dialkylamino-1-chloro-2-arylethylidene]-, *N*-[1,2-bis(dialkylamino)-2-arylethylidene]-, and *N*-(1,2-dioxo-2-arylethene)amides of arenesulfonic acids.

Among products containing an $RSO_2N{=}C{-}N$ fragment are some of the great practical importance. For example, chloral arenesulfonylimines react with secondary amines to afford arylsulfonylformamides—the effective flotation agents for ores of non-ferrous and rare metals.[1] Some amidines possess high biological activity and can be utilized as the building blocks for different drugs and insecticides.[2] Additionally, the N=C—N fragment is widely used in the synthesis of various nitrogen-containing acyclic and heterocyclic ensembles.[3] In this connection, the development of new approaches to these interesting structures is an important synthetic task.

Recently,[4] a new family of sulfonamidopolyhaloethylated aromatics and heteroaromatics **1** has been introduced as functionalized arenes containing pharmacophoric and synthetically attractive fragments: the polyhaloethyl group and the protected amino group. The synthetic importance of these compounds has been shown in the synthesis of biologically active N-protected α-arylglycines.[5]

In this letter, we report the unexpected formation of amidine derivatives of α-arylglycines from *N*-(1-aryl-2,2,2-trichloroethyl)amides **1a**–**g**.

Sulfonamides **1a**–**g** interact with an excess of a secondary amine or its salts in a dipolar aprotic medium in the presence of inorganic bases at 90–100 °C to give N^1-dialkyl-N^2-arylsulfonyl-(α-dialkylamino-α-aryl)acetamidines **6a**–**k** in moderate to good yields.[6] We suggest that the transformation proceeds as shown in Scheme 1.

$$ArSO_2NHCHCCl_2X \quad (Ar' \text{ on CH})$$

1

X= H, Hal, Ph
Ar= Ph, 4-MeC_6H_4, 4-ClC_6H_4, 2-$NO_2C_6H_4$, 3-$NO_2C_6H_4$, 4-$NO_2C_6H_4$
Ar'=Ph, 4-MeC_6H_4, 4-$HalC_6H_4$, 4-HOC_6H_4, 3,4-$(HO)_2C_6H_3$, 4-$MeOC_6H_4$, 4-$ROC(O)CH_2OC_6H_4$, 4-$ROC(O)CH_2SC_6H_4$, 1-naphthyl, 3-indolyl, 2-thienyl, 2-furyl, 2-pyrrolyl

Keywords: Amidines; Sulfonamides; Chloroaziridines; Secondary amines.
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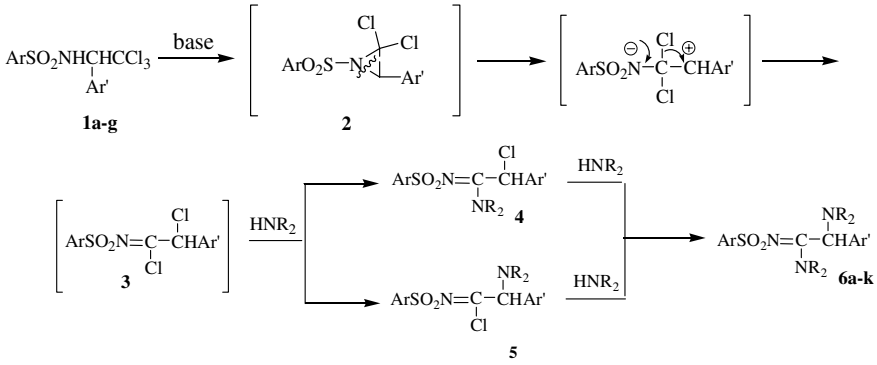
doi:10.1016/j.tetlet.2005.10.079



1: Ar = 4-ClC_6H_4, Ar' = Ph (**a**), 4-MeC_6H_4 (**b**), 4-ClC_6H_4 (**c**), 4-FC_6H_4 (**d**), 4-HOC_6H_4 (**e**), 1-naphthyl (**f**)
Ar = 4-MeC_6H_4, Ar' = 4-MeC_6H_4 (**g**)
4 and **5** were isolated only for Ar =4-ClC_6H_4, Ar' =4-MeC_6H_4, R = *n*-Pr

6	Ar	Ar′	NR_2	Time (h)	Yield, %	Mp °C
a	4-ClC_6H_4	Ph	NEt_2	1	40	115 – 116
b	4-ClC_6H_4	4-MeC_6H_4	NEt_2	1	63	131 – 132
c	4-ClC_6H_4	4-ClC_6H_4	NEt_2	1	75	151 – 155
d	4-ClC_6H_4	4-FC_6H_4	NEt_2	1	38	76 – 80
e	4-ClC_6H_4	4-HOC_6H_4	NEt_2	1.5	15	73 – 75
f	4-ClC_6H_4	1-naphthyl	NEt_2	2	73	78 – 83
g[a]	4-ClC_6H_4	4-MeC_6H_4	NMe_2	3	32	138 – 141
h	4-ClC_6H_4	4-MeC_6H_4	N-*n*-Pr_2	1	62	144 – 145
i	4-ClC_6H_4	4-MeC_6H_4	$N(CH_2CH_2)_2O$	2	82	181 – 185
j	4-MeC_6H_4	4-MeC_6H_4	NEt_2	1	38	101 – 102
k	4-MeC_6H_4	4-MeC_6H_4	$N(CH_2CH_2)_2O$	2	45	159 – 160

[a] The hydrochloride of dimethylamine was used as the reagent.

Scheme 1.

The evidence for the mechanism of the process is as follows. The reaction of trichloroethylamide **1b** with 1 equiv of dipropylamine[7] in DMSO gives *N*-(1-dipropylamino-2-chloro-2-(4-methylphenyl)ethylidene)amide of 4-chlorobenzenesulfonic acid **4** (Fig. 1) in low yield as well as an isomeric product, the NMR, IR spectra, and elemental analysis of which correspond to *N*-(2-dipropylamino-1-chloro-2-(4-methylphenyl)ethylidene)amide of 4-chlorobenzenesulfonic acid **5**.

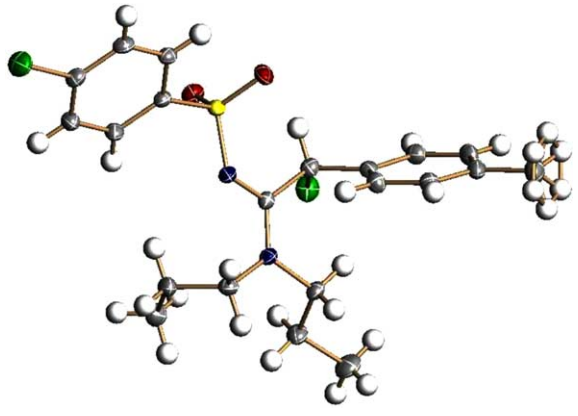
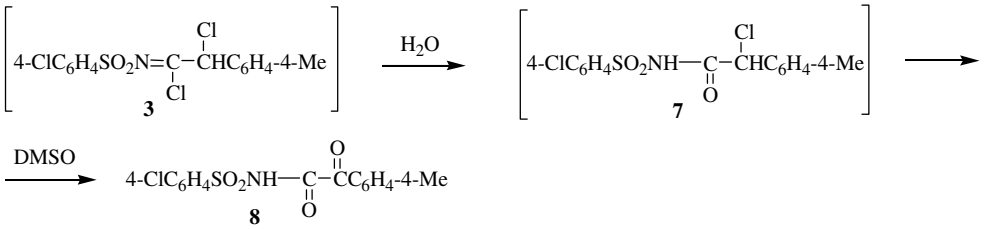


Figure 1. X-ray structure of compound **4** and the atom-numbering scheme. The hydrogen atoms are drawn to an arbitrary size. Crystal data: $C_{21}H_{26}Cl_2N_2O_2S$, MW = 441.40, T = 297(2) K, triclinic, P-1, a = 8.9141(11), b = 9.5091(15), c = 14.138(2) Å, V = 1072.5(3) Å^3, Z = 2, D_{calcd} = 1.367 mg m^{-3}, λ(MoK$_\alpha$) = 0.71073 Å, μ = 0.420 mm^{-1}, F(000) = 464, 4097 unique observed reflections, R_1 = 0.0399, S = 1.029.

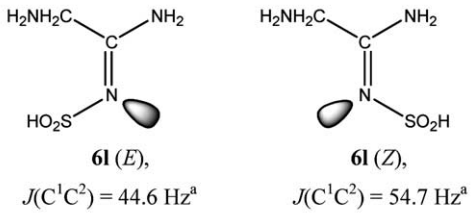
Additionally, the use of DMSO[7] instead of DMF results in the formation of *N*-[1,2-dioxo-2-(4-methylphenyl)-ethyl]amide of 4-chlorophenylsulfonic acid **8**. The dicarbonyl compound **8** could be formed from intermediate **3** by hydrolysis with water present in the solvent or by interaction of the inorganic base with the starting sulfonamide **1b**, followed by oxidation of intermediate amide **7** as shown in Scheme 2. Dimethylsulfoxide could act here as an oxidant in a Kornblum-type oxidation.

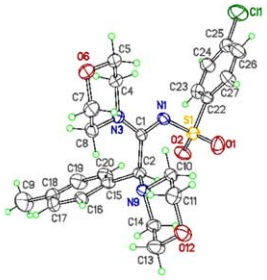
The ^{1}H and ^{13}C NMR signals of compounds **4**–**6** and **8** were assigned using $^{13}C_{jmod}$, $^{13}C_{rggd}$, 2D HSQC, and NOESY experiments ($CDCl_3$, Bruker DPX 400). It is noteworthy that in both the ^{1}H and ^{13}C NMR spectra of compounds **6a**–**g**, the alkyl fragments of one dialkylamino group were equivalent, whereas the alkyl groups of the other dialkylamino group (probably, N=C—$NAlk_2$) were non-equivalent.

It is well known that the lone electron pair of azomethine nitrogen atom in an —N=C(1)—C(2) moiety has a profound influence on the spin–spin coupling constants $J(C^1C^2)$ of the adjacent carbon–carbon bonds,



Scheme 2.





6i (*E*)

Compound	**6a**	**6b**	**6c**	**6e**	**6h**	**6i**	**6j**	**6k**
$J(C^1C^2)$, Hz[b]	44.7	45.3	45.1	45.1	45.9	44.4	44.7	45.0

[a]calculated at the SOPPA/Huz-III level
[b]measured by means of the INADEQUATE pulse sequence in $CDCl_3$ at 300 K

Figure 2. Configurations, $J(C^1C^2)$ data, salient X-ray structure **6i** and the atom-numbering scheme. Crystal data: $C_{23}H_{28}ClN_3O_4S$, MW = 447.99, $T = 297(2)$ K, monoclinic, *Cc*, $a = 14.729(7)$, $b = 24.834(13)$, $c = 7.754(6)$ Å, $V = 2444(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.299$ mg m^{-3}, $\lambda(MoK_\alpha) = 0.71073$ Å, $\mu = 0.275$ mm^{-1}, $F(000) = 1008$, 2221 unique observed reflections, $R_1 = 0.0690$, $S = 0.951$.

providing an unambiguous guide to the configurational assignment at the C=N group.[8] Based on the experimental values of $J(C^1C^2)$ of compounds **6** (~45 Hz, Fig. 2), it was absolutely clear that they were all *E*/*Z* isomers. Comparison of the experimental $J(C^1C^2)$ values with those calculated at the SOPPA level (second-order polarization propagator approach),[9] with the Huz-III basis set in the various isomers of the model *N*-sulfonylamidine **6l**, as well as the X-ray data of compound **6i** (Fig. 2), provide an unambiguous *E*-configurational assignment to the C=N bond of amidines **6**.

Attempts to isolate dichloroaziridines **2** or imidoylchlorides **3**, to confirm their intermediacy in the reaction, gave no positive results. However, there is indirect evidence that chloroaziridine structures can be formed by intramolecular cyclization of polychloroethylamides of arenesulfonic acids. Thus, we succeeded in synthesizing chloroaziridines **9a**,**b** (Fig. 3), using *N*-(2-phenyl-2,2-dichloroethyl)amides of 4-chlorobenzenesulfonic acid **1h**,**i** as starting reagents (Scheme 3).[10]

The molecule of compound **9b** has a 'propeller' structure: the angles between the planes of the aromatic rings C(16)–C(21), C(9)–C(14), C(3)–C(8), and the plane of the aziridine are 97.4°, 92.5°, and 100°, respectively. The planes of the sulfonic group O(1)–S(1)–O(2) and the aromatic ring C(3)–C(8) are parallel. The sum of the valence angles at nitrogen is 301.4° suggesting that the nitrogen atom is pyramidal.

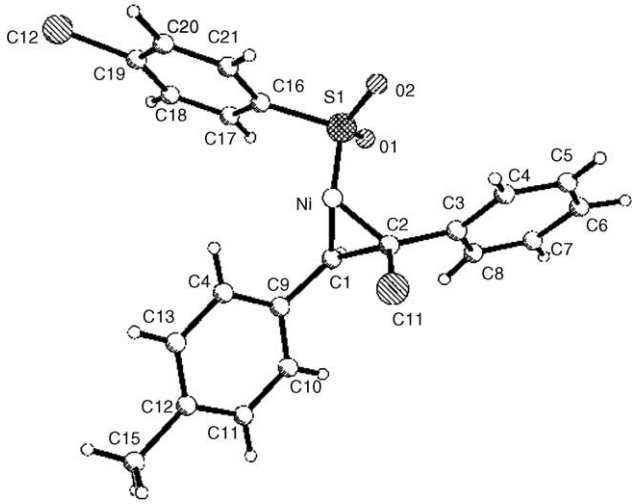
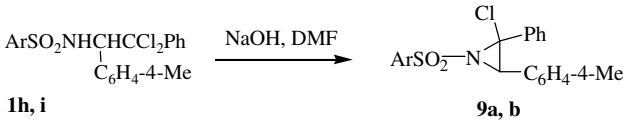


Figure 3. X-ray structure of chloroaziridine **9b** and the atom-numbering scheme. Crystal data: $C_{21}H_{17}Cl_2NO_2S$, MW = 418.32, $T = 293(2)$ K, monoclinic, $P2_1/n$, $a = 6.223(1)$, $b = 21.477(15)$, $c = 15.197(2)$ Å, $V = 2006.0(5)$ Å^3, $Z = 4$, $D_{calcd} = 1.385$ mg m^{-3}, $\lambda(MoK_\alpha) = 0.71073$ Å, $\mu = 0.444$ mm^{-1}, $F(000) = 864$, 2082 unique observed reflections, $R_1 = 0.0399$, $S = 1.031$.

Crystallographic data (excluding structure factors) for the structures in this letter have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 282927 (for **6i**), 282928 (for **4**), and 283870 (for **9b**). Copies



1h, i **9a, b**

Ar = Ph (**1h**, **9a**), 4-ClC_6H_4(**1i**,**9b**)

Scheme 3.

of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

The compounds **4**–**6**, **8**, and **9** are colorless or faintly colored crystalline substances. They are soluble in the most organic solvents, but insoluble in water.

Taking into account the feasibility of the experiment and the accessibility of amidotrichloroethylated aromatics **1** the route to amidine derivatives of α-arylglycines **6** and to chloroaziridines **9** described is of special attractiveness and calls for further development.

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6. General procedure for the synthesis of **6a**–**k**: The *N*-(1-aryl-2,2,2-trichloroethyl)amide of an arenesulfonic acid (10 mmol), potassium carbonate (5.52 g, 40 mmol), and dialkylamine or dialkylamine hydrochloride (40 mmol) were stirred in DMF (20–25 ml) at 90–100 °C for 1–3 h. The reaction mixture was cooled to room temperature and mixed with water (25 ml). The insoluble part was separated from the water, dried in vacuo with P_2O_5, quickly washed with cold diethyl ether (2 × 1 ml), and recrystallized from hexane to give colorless crystals or a yellow gum, which gave a solid product on standing for several weeks. For reaction times, yields and mp see Scheme 1.

Compound **6a**: IR (KBr, cm^{-1}): 1125, 1270 (SO_2), 1545 (N=C–N), 2700–2970 (C–H_{Alk}). ^1H NMR (400 MHz, $CDCl_3$): 0.33, 0.98, 1.10, 2.67, 2.91, 3.08, 3.38, 4.39 (m, 20H, $4C_2H_5$), 6.05 (s, 1H, Ar′C*H*N), 7.23, 7.32, 7.61 (m, 5H, C_6H_5), 7.41, 7.93 (AA′BB′, 4H, 4-ClC_6H_4). ^{13}C NMR (100.6 MHz, $CDCl_3$): 10.95, 11.40, 12.18, 42.99, 43.73 (C_2H_5), 67.96 (Ar′*C*HN), 127.60, 128.66, 137.33, 143.58 (4-ClC_6H_4), 127.28, 128.19, 128.48, 137.25 (Ph), 164.66 (N=C). Anal. Calcd for $C_{22}H_{30}ClN_3O_2S$: C, 60.60; H, 6.94; Cl, 8.13; N, 9.64; S, 7.35. Found: C, 60.76; H, 6.90; Cl, 8.38; N, 9.71; S, 7.48.

Compound **6b**: IR (KBr, cm^{-1}): 1125, 1270 (SO_2), 1540 (N=C–N), 2730–2980 (C–H_{Alk}). ^1H NMR (400 MHz, $CDCl_3$): 0.41, 0.98, 1.08, 2.66, 2.89, 3.10, 3.18, 3.39, 4.41 (m, 20H, $4C_2H_5$), 2.31 (s, 3H, $CH_3C_6H_4$), 6.00 (s, 1H, Ar′C*H*N), 7.12, 7.48 (AA′BB′, 4H, 4-MeC_6H_4), 7.39, 7.90 (AA′BB′, 4H, 4-ClC_6H_4). ^{13}C NMR (100.6 MHz, $CDCl_3$): 10.95, 11.27, 12.30, 42.94, 43.62, 43.70 (C_2H_5), 21.05 ($CH_3C_6H_4$), 67.77 (Ar′*C*HN), 127.55, 128.61, 137.24, 143.54 (4-ClC_6H_4), 128.13, 129.12, 133.99, 136.94 (MeC_6H_4), 164.92 (N=C). Anal. Calcd for $C_{23}H_{32}ClN_3O_2S$: C, 61.38; H, 7.17; Cl, 7.88; N, 9.34; S, 7.12. Found: C, 61.47; H, 7.11; Cl, 7.98; N, 9.57; S, 7.36.

Compound **6c**: ^{13}C NMR (100.6 MHz, $CDCl_3$): 10.88, 11.25, 12.36, 42.81, 43.64, 43.74 (C_2H_5), 67.59 (Ar′*C*HN), 127.60, 128.75, 137.53, 143.38 (4-ClC_6H_4), 128.70, 129.72, 133.22, 135.91 (4-ClC_6H_4), 164.10 (N=C). ^{15}N NMR (40.5 MHz, $CDCl_3$, NO_2CH_3): −152.3 (=N), −240.5 (=C–NEt_2), −333.1 (Ar′CHNEt_2).

Compound **6d**: ^1H NMR (400 MHz, $CDCl_3$): 0.41, 0.97, 1.09, 2.68, 2.83, 3.08, 3.17, 3.36, 4.38 (m, 20H, $4C_2H_5$), 5.98 (s, 1H, Ar′C*H*N), 7.43, 7.90 (AA′BB′, 4H, 4-ClC_6H_4), 7.09, 7.62 (m, 4H, 4-FC_6H_4).

Compound **6e**: ^{13}C NMR (100.6 MHz, $CDCl_3$): 10.83, 11.22, 12.29, 42.78, 43.61, 43.69 (C_2H_5), 67.55 (Ar′*C*HN), 127.36, 128.55, 137.21, 143.36 (4-ClC_6H_4), 115.53, 128.66, 129.55, 156.17 (4-HOC_6H_4), 165.26 (N=C). ^{15}N NMR (40.5 MHz, $CDCl_3$, NO_2CH_3): −166.5 (=N), −239.2 (=C–NEt_2), −332.7 (Ar′CHNEt_2).

Compound **6f**: ^{13}C NMR (100.6 MHz, $CDCl_3$): 11.67, 12.45, 12.63, 44.53, 44.69 (C_2H_5), 64.05 (Ar′*C*HN), 127.34, 128.87, 136.78, 143.38 (4-ClC_6H_4), 124.11, 125.21, 125.89, 126.45, 126.52, 128.15, 128.90, 132.60, 132.83, 133.93 (1-naphthyl), 167.20 (N=C). ^{15}N NMR (40.5 MHz, $CDCl_3$, NO_2CH_3): −168.7 (=N), −238.1 (=C–NEt_2), −334.4 (Ar′CHNEt_2).

Compound **6g**: ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.08 ($CH_3C_6H_4$), 38.89, 40.59, 43.89 (NCH_3), 71.88 (Ar′*C*HN), 127.68, 128.68, 137.44, 143.45 (4-ClC_6H_4), 128.33, 129.02, 132.73, 137.24 (4-$CH_3C_6H_4$), 165.77 (N=C).

Compound **6h**: ^{13}C NMR (100.6 MHz, $CDCl_3$): 10.76, 11.50, 11.94, 19.16, 20.08, 50.62, 51.36, 52.67 (C_3H_7), 21.08 ($CH_3C_6H_4$), 68.36 (Ar′*C*HN), 127.62, 128.62, 137.33, 143.74 (4-ClC_6H_4), 128.05,129.08, 134.43, 137.00 (4-$CH_3C_6H_4$), 164.93 (N=C). ^{15}N NMR (40.5 MHz, $CDCl_3$, NO_2CH_3): −166.7 (=N), −244.2 (=C–NPr_2), −337.8 (Ar′CHNPr_2).

Compound **6i**: ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.02 ($CH_3C_6H_4$), 46.25, 47.63, 52.15, 65.93, 66.89 ($N(CH_2CH_2)_2O$), 70.52 (Ar*C*H), 127.72, 128.77, 137.76, 142.78 (4-ClC_6H_4), 127.90, 129.39, 131.84, 137.70 (4-$CH_3C_6H_4$), 163.92 (N=C). ^{15}N NMR (40.5 MHz, $CDCl_3$, NO_2CH_3): −159.5 (=N), −256.1 (=C–N), −330.2 (ArCH–N).

Compound **6j**: ^{13}C NMR (100.6 MHz, $CDCl_3$): 11.07, 11.48, 12.39, 42.87, 43.64, 43.74 (C_2H_5), 21.14, 21.52 ($CH_3C_6H_4$), 67.59 (Ar′*C*HN), 126.13, 129.10, 141.55, 142.28 (4-$CH_3C_6H_4$), 128.21, 129.10, 134.36, 136.81 (4-$CH_3C_6H_4$), 164.70 (N=C).

Compound **6k**: ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.11, 21.43 ($CH_3C_6H_4$), 46.23, 47.65, 52.12, 65.92, 66.86 ($N(CH_2CH_2)_2O$), 70.07 (Ar′*C*HN), 126.28, 129.40, 141.54, 142.12 (4-$CH_3C_6H_4$), 127.97, 129.20, 132.16, 137.56 (4-$CH_3C_6H_4$), 163.78 (N=C). ^{15}N NMR (40.5 MHz, $CDCl_3$, NO_2CH_3): −157.3 (=N), −257.3 (=C−N), −330.4 (Ar′CH–N).

7. Procedure for the synthesis of **4**, **5**, and **8**: Amide **1b** (4.13 g, 10 mmol), Na_2CO_3 (2.12 g, 20 mmol), dipropylamine (1.37 ml, 10 mmol), and dimethylsulfoxide (25–30 ml) were stirred for 1.5 h at 90 °C. The reaction mixture was cooled to room temperature and mixed with water (25–30 ml). The mixture was filtered and the filtrate was acidified with hydrochloric acid to pH = 6–7. The precipitated oxoamide **8** was filtered off, dried, and recrystallized from CCl_4. The water-insoluble mass was dried under vacuum, quickly washed with cold diethyl ether (2 × 1 ml), and dissolved in CCl_4. The remaining insoluble in CCl_4 solid, was imidoyl chloride **5**. Crystals of amidine **4** were precipitated from CCl_4 after standing the solution for 20 h.

   Compound **4**. Yield 0.80 g (18%), mp 140–141 °C. IR (KBr, cm^{-1}): 1120, 1260 (SO_2), 1520–1590 (br, N=C), 2800–2950 (C–H_{Alk}). ^{1}H NMR (400 MHz, $CDCl_3$): 0.52, 0.80, 1.25–1.60, 2.98–3.33 (m, 14H, $N(C_3H_7)_2$), 2.34 (s, 3H, $CH_3C_6H_4$), 7.29 (s, 1H, 4-MeC_6H_4CHCl), 7.17, 7.31 (AA′BB′, 4H, 4-MeC_6H_4), 7.43, 7.89 (AA′BB′, 4H, 4-ClC_6H_4). ^{13}C NMR (100.6 MHz, $CDCl_3$): 10.83, 11.38, 19.58, 20.63, 50.89, 51.32 ($N(C_3H_7)_2$), 21.12 ($CH_3C_6H_4$), 54.91 (Ar′*C*HCl), 125.49, 129.50, 131.44, 137.88 (4-MeC_6H_4), 127.74, 128.79, 138.23, 142.20 (4-ClC_6H_4), 162.24 (N=C).

   Compound **5**. Yield 0.09 g (2%), mp 198–201 °C (dec). IR (KBr, cm^{-1}): 1120, 1280 (SO_2), 1520–1590 (N=C), 2800–2950 (C–H_{Alk}). ^{1}H NMR (400 MHz, $CDCl_3$): 0.82 (t, 6H, CH_3, $J = 7.2$ Hz), 1.58 (m, 4H, CH_2), 2.69 and 2.89 (m, 4H, NCH_2), 2.36 (s, 3H, $CH_3C_6H_4$), 4.64 (s, 1H, Ar′*C*HNR_2), 7.09, 7.19 (AA′BB′, 4H, 4-MeC_6H_4), 7.28, 7.76 (AA′BB′, 4H, 4-ClC_6H_4). ^{13}C NMR (100.6 MHz, $CDCl_3$): 11.11, 17.97, 52.72 ($N(C_3H_7)_2$), 21.21 ($CH_3C_6H_4$), 72.28 (Ar′*C*HCl), 127.84, 129.65, 130.46, 138.00 (4-MeC_6H_4), 128.43, 129.46, 139.69, 140.81(4-ClC_6H_4), 170.17 (N=C). Anal. Calcd for $C_{21}H_{26}Cl_2N_2O_2S$: C, 57.14; H, 5.94; Cl, 16.06; N, 6.35; S, 7.26. Found: C, 57.28; H, 5.91; Cl, 16.21; N, 6.49; S, 7.41.

   Compound **8**. Yield 0.5 g (15%), mp 147–150 °C. IR (KBr, cm^{-1}): 1160, 1350 (SO_2), 1660 (ArC=O), 1720 (NC=O), 3220 (NH). ^{1}H NMR (400 MHz, $CDCl_3$): 2.41 (s, 3H, $CH_3C_6H_4$), 7.25, 7.53 (AA′BB′, 4H, 4-MeC_6H_4), 8.07, 8.16 (AA′BB′, 4H, 4-ClC_6H_4), 9.73 (br s, 1H, NH). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.97 ($CH_3C_6H_4$), 129.18, 131.60, 134.20 (4-MeC_6H_4), 129.21, 130.08, 141.25, 147.16 (4-ClC_6H_4), 158.25 (NC=O), 183.06 (Ar*C*=O). Anal. Calcd for $C_{15}H_{12}ClNO_4S$: C, 53.34; H, 3.58; Cl, 10.50; N, 4.15; S, 9.49. Found: C, 53.41; H, 3.52; Cl, 10.31; N, 4.23; S, 9.60.

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10. Procedure for the synthesis of **9**: Amide **1h**,**i** (5 mmol), NaOH or Na_2CO_3 (20 mmol) and DMF (10–15 ml) were stirred for 0.5 h at room temperature. The reaction mixture was mixed with water (10 ml). The resulting precipitate was filtered off, dried and recrystallized from CCl_4.

    Compound **9a**. Yield 0.48 g (25%), mp 121–123 °C. IR (KBr, cm^{-1}): 1160, 1330 (SO_2), 1580 (C=C arom.), 2910 (C–H_{Alk}). ^{1}H NMR (400 MHz, $CDCl_3$): 2.27 (s, 3H, CH_3), 4.75 (s, 1H, CH^3), 7.11, 7.24 (AA′BB′, 4H, 4-MeC_6H_4), 7.39, 7.41, 7.77 (m, 10H, $2C_6H_5$). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.17 ($CH_3C_6H_4$), 51.15 (C^3), 72.51 (C^2), 128.28, 128.35, 128.84, 129.30, 129.41, 129.58, 129.77, 130.58, 134.44, 135.75, 138.98, 139.05 (Ar). Anal. Calcd for $C_{21}H_{18}ClNO_2S$: C, 65.70; H, 4.73; Cl, 9.24; N, 3.65; S, 8.35. Found: C, 65.58; H, 4.65; Cl, 9.01; N, 3.72; S, 8.40.

    Compound **9b**. Yield 1.22 g (60%), mp 125–128 °C. IR (KBr, cm^{-1}): 1160, 1330 (SO_2), 1590 (C=C arom.), 2910 (C–H_{Alk}). ^{1}H NMR (400 MHz, $CDCl_3$): 2.33 (s, 3H, CH_3), 4.64 (s, 1H, CH^3), 7.13, 7.40 (AA′BB′, 4H, 4-MeC_6H_4), 7.41, 7.71 (AA′BB′, 4H, 4-ClC_6H_4), 7.38, 7.63, 7.73 (m, 5H, C_6H_5). ^{13}C NMR (100.6 MHz, $CDCl_3$): 21.34 ($CH_3C_6H_4$), 51.12 (C^3), 72.06 (C^2), 127.63, 128.23, 128.53, 128.95, 129.26, 129.41, 129.47, 130.38, 134.88, 137.19, 138.97, 140.50 (Ar). Anal. Calcd for $C_{21}H_{17}Cl_2NO_2S$: C, 60.29; H, 4.10; Cl, 16.95; N, 3.35; S, 7.66. Found: C, 60.12; H, 4.03; Cl, 17.09; N, 3.51; S, 9.83.