Chemistry

Melting points were recorded on a Büchi 530 melting point apparatus in open capillary tubes and are uncorrected. IR spectra were recorded as KBr pellets on a Perkin-Elmer 1750 FT-spectrophotometer. The ^{1}H-NMR spectra were taken on a Bruker AW-80 and AM-400 in DMSO-d_6; chemical shifts were reported in δ values (ppm). The abbreviation s = singulet, d = doublet, t = triplet, m = multiplet and b = broad were used throughout. Elemental analyses (C, H, N, S) were realized on a Carlo-Erba EA 1108-elemental analyzer and were within ± 0.4% of the theoretical values. All reactions were routinely checked by TLC on silica gel Merck 60F 254.

Compounds **2**, **3**, **4** and **5** were prepared as described by Cignarella and al (see reference 8).

3-Bromopyridine *N*-oxide (2)

Yield : 64 %; IR (KBr) : 3109 (C-H), 1595 (C=N), 1468 (C=C), 1292 (N-O) cm^{-1}

3-Bromo-4-nitropyridine *N*-oxide (3)

Yield : 69 % ; mp : 149-150 °C (lit mp: 152 °C[8]); IR (KBr) : 3099 (C-H), 1589 (C=N), 1552, 1338 (NO_2), 1295 (N-O), 643 (C-Br) cm^{-1}; ^{1}H-NMR (DMSO-d_6) : δ 8.1-8.3 (m, 2H, 5-H + 6-H), 8.75 (s, 1H, 2-H) ; Anal ($C_5H_3BrN_2O_3$) C, H, N, S.

4-Nitro-3-phenoxypyridine *N*-oxide (4)

Yield : 54 % ; mp : 108-109 °C (lit mp: 110°C[8]); IR (KBr) : 3109 (C-H), 1606 (C=N), 1507, 1313 (NO_2), 1219 (N-O) cm^{-1}; ^{1}H-NMR (DMSO-d_6) : δ 7.4-7.9 (m, 5H, H_{aro}), 8.2 (m, 1H, 5-H), 8.5 (m, 2H, 2-H + 6-H) ; Anal ($C_5H_3BrN_2O_3$) C, H, N, S.

4-Amino-3-phenoxypyridine (5)

Yield: 90%.

***N*-(3-Phenoxy-4-pyridinyl)methanesulfonamide (6)**

Anhydrous potassium carbonate (8.29 g, 60 mmol) was added to 4-amino-3-phenoxypyridine (1.82g, 10 mmol) dissolved in dry acetonitrile (112 mL). The suspension was stirred for 5 minutes and methanesulfonyl chloride (3.112 mL, 60 mmol) was added. The suspension was stirred for 12 h, filtered and the solvent evaporated under reduced pressure. The residue was taken up with a 10

% aqueous NaOH and the resulting solution was neutralized with 1N HCl to separate *N*-(3-phenoxy-4-pyridinyl)-methanesulfonamide as a white solid. Yield: 1.61g, 61 %; mp: 218-219 °C (lit mp: 220°C[8]); IR (KBr) : 2804, 2731, 2655 (N^+-H), 1637 (C=N), 1475 (C=C), 1347, 1117 (SO_2) cm^{-1}; 1H-NMR (DMSO-d_6) : δ 2.88 (s, 3H, SO_2CH_3), 6.97 (d, 2H, 2'-H + 6'-H), 7.12 (t, 1H, 4'-H), 7.38 (t, 2H, 3'-H' + 5'-H), 7.49 (d, 1H, 5-H), 8.10 (s, 2H, 2-H + 6-H), 11.87 (bs, N-*H*); Anal ($C_{12}H_{12}N_2O_3S$) C, H, N, S.

N-(3-Phenoxy-4-pyridinyl)trifluoromethanesulfonamide (7)

The title compound was obtained as described for **6** using trifluoromethanesulfonyl chloride instead of methanesulfonyl chloride. Yield : 80 % ; mp : 239 °C; IR (KBr) : 2807, 2728, 2648 (N^+-H), 1633 (C=N), 1473 (C=C), 1343, 1129 (SO_2) cm^{-1}; ^{1}H-NMR (DMSO-d_6) : δ 6.95 (d, 2H, 2'-H + 6'-H), 7.11 (t, 1H, 4'-H), 7.36 (t, 2H, 3'-H + 5'-H), 7.81 (d, 1H, 5-H), 8.30 (d, 1H, 6-H), 8.43 (s, 1H, 2-H), 13.90 (bs, N-*H*) ; Anal ($C_{12}H_9F_3N_2O_3S$) C, H, N, S.

3-Nitro-2-phenoxypyridine (9)

A 10% NaOH solution (8.53 mL, 120 mmol) was added to phenol (1.86 g, 20 mmol). The resulting solution was stirred for 5 minutes and evaporated under reduced pressure. The white solid was taken up with acetonitrile and heated with reflux. Then, 2-chloro-3-nitropyridine (1.58 g, 10 mmol) was added and the suspension was stirred at room temperature for 20 h. The mixture was filtered and the solvent was evaporated under reduced pressure. The solid was taken up with dichloromethane. The suspension was filtered and the filtrate was evaporated under reduced pressure. The solid was crystallized from methanol / water to afford 3-nitro-2-phenoxypyridine as a white solid. Yield :2.05 g, 95 % ; mp: 87-88 °C (lit mp : 94°C[9]) ; IR (KBr) : 3064 (C-H), 1606 (C=N), 1517, 1349 (NO_2) cm^{-1}; ^{1}H-NMR (DMSO-d_6) : δ 7.0-7.5 (m, 6H, H_{aro}+5-H), 8.25-8.55 (m, 2H, 4-H+ 6-H) ; Anal ($C_{11}H_8N_2O_3$) C, H, N, S ; C calcd : 61.11 % found 61.65 %.

3-Amino-2-phenoxypyridine (10)

3-Nitro-2-phenoxypyridine (2.16 g, 10 mmol) was dissolved in a mixture of glacial acetic acid / water 4 :1 (43 mL). The solution was heated with reflux and iron powder (4.32 g, 80 mmol) was added. The suspension was stirred and heated for 20 minutes with reflux and then filtered. Water was added to the filtrate and the solid which precipitated was filtered to afford 3-amino-2-

phenoxypyridine as a white solid. Yield: 1.73g, 93 % ; mp: 102-103 °C (lit mp :106°C[9]) ; IR (KBr) : 3471, 3335 (NH_2), 3059 (C-H), 1616 (C=N), 1490 , 1449 (C=C), 1227 (C-NH_2) cm^{-1}; ^{1}H-NMR (DMSO-d_6) : δ 5.1 (bs, 2H, N*H*$_2$, exchangeable), 6.6-7.5 (m, 8H, H_{aro}+ 4-H + 5-H + 6-H) ; Anal ($C_{11}H_{10}N_2O_3$) C, H, N, S; C calcd : 70.95 % found : 71.58 % C.

_N_-(2-Phenoxy-3-pyridinyl)methanesulfonimide (11)

Anhydrous potassium carbonate (13.8g, 100 mmol) and methanesulfonyl chloride (4.62 mL, 90 mmol) were added to a solution of 3-amino-2-phenoxypyridine (1.86g, 10 mmol) in acetonitrile (20 mL). The mixture was heated with reflux for 20 h and then filtered. The filtrate was evaporated under reduced pressure. The residue was crystallized from methanol / water to afford *N*-(2-phenoxy-3-pyridinyl)-methanesulfonimide as a white solid. Yield: 2.02 g, 59 % ; mp: 161-162 °C ; IR (KBr) : 3058 (C-H), 1582 (C=N), 1432 (C=C), 1358, 1160 (SO_2) cm^{-1}; ^{1}H-NMR (DMSO-d_6) : δ 3.5 (s, 6H, SO_2CH_3), 7.0-7.6 (m, 6H, H_{aro}+ 5-H), 8.0-8.1 (m, 2H, 4-H+ 6-H) ; Anal ($C_{13}H_{14}N_2O_5S_2$) C, H, N, S; C clacd : 45.60 % C found : 46.36 % C.

_N_-(2-Phenoxy-3-pyridinyl)methanesulfonamide (12)

N-(2-Phenoxy-3-pyridinyl)methanesulfonimide (3.42 g, 10 mmol) was suspended in a 50 % aqueous solution of potassium hydroxide (20 mL) and heated with reflux for 2 h. The mixture was filtered and the pH of the filtrate was adjusted to 6-7 with 1M HCl solution. The white solid which precipitated was collected by filtration to afford *N*-(2-phenoxy-3-pyridinyl)-methanesulfonamide. Yield: 2.40 g, 91 % ; mp: 130-131 °C ; IR (KBr) : 3226 (C-H), 1592 (C=N), 1489 (C=C), 1336, 1165 (SO_2) cm^{-1}; 1H-NMR (DMSO-d_6) : δ 3.15 (s, 3H, SO_2CH_3), 7.17 (m, 3H, 5-H + 2'-H + 6'-H), 7.25 (t, 1H, 4'-H), 7.45 (t, 2H, 3'-H + 5'-H), 7.83 (d, 1H, 4-H), 7.96 (d, 1H, 6-H), 9.64 (s, 1-H, N-*H*); Anal ($C_{12}H_{12}N_2O_3S$) C, H, N, S.

_N_-Methyl-_N_-(4-nitro-2-phenoxyphenyl)methanesulfonamide (13)

N-(4-Nitro-2-phenoxyphenyl)methanesulfonamide (3 g, 9.7 mmol) was dissolved in acetonitrile (50 mL) and potassium carbonate (3.9 g, 28 mmol) was added. The suspension was stirred for 10 minutes and iodomethane (1 mL, 16 mmol) was added; the stirring was kept for 5 h. The solvent

was evaporated under reduced pressure. The residue was taken up with 20 mL of water and the solid was collected by filtration. The solid was crystallized from methanol / water to afford *N*-methyl-*N*-(4-nitro-2-phenoxyphenyl)methanesulfonamide as a yellow solid. Yield: 2.5 g, 77 % ; mp: 95-96 °C; IR (KBr) : 3082 (C-H), 1514 (NO_2), 1487 (C=C), 1344, 1144 (SO_2) cm^{-1}; ^{1}H-NMR (DMSO-d_6) : δ 3.07 (s, 3H, SO_2CH_3), 7.05-7.90 (m, 8H) ; Anal ($C_{14}H_{14}N_2O_5S$) C, H, N, S

Crystallographic analysis

Crystals of compounds **7** and **12** for X-ray analysis were prepared by growth under slow evaporation at room temperature of MeOH solution of each compound. Diffraction measurements were made on an Enraf-Nonius CAD-4 diffractometer by use of monochromatized Cu Kα radiation (λ = 1.54175). Unit cell parameters were obtained by a least-squares fit. Intensity data were collected by use of ω/2θ scan mode.

Crystal data for compound **7**: Empirical formula : $C_{12}H_9F_3N_2O_3S$; M_r: 318.27 ; Crystal system, space group: Monoclinic, P21/a ; Unit cell dimensions : a = 12.1950(10) alpha = 90. b = 7.8510(10) beta = 110.025(12). c = 14.480(3) gamma = 90 deg.; Volume: 302.5(3) $^{-3}$; Z, Calculated density: 4, 1.623 Mg/m^{-3} ; F(000) = 648; Theta range for data collection 3.25 to 71.89 deg.

Crystal data for compound **12**: Empirical formula: $C_{12}H_{12}N_2O_3S$; M_r: 264.30; Crystal system, space group: Monoclinic, P21/n; Unit cell dimensions: a = 9.800(5) alpha = 90.000(5). b = 8.143(5) beta = 93.099(5). c = 15.933(5) gamma = 90.000(5); Volume: 1269.6(11) ^{3}; Z, Calculated density: 4, 1.383 Mg/m^3; F(000) = 552; Theta range for data collection 5.18 to 71.84 deg.

Additional crystallographic informations for compound **7**

table 1. Crystal data and structure refinement for 7.

Identification code	cmfj8
Empirical formula	C12 H9 F3 N2 O3 S
Formula weight	318.27
Temperature	293(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, P21/a
Unit cell dimensions	a = 12.1950(10)A alpha = 90 deg. b = 7.8510(10)A beta = 110.025(12) deg. c = 14.480(3) A gamma = 90 deg.
Volume	1302.5(3) A^3
Z, Calculated density	4, 1.623 Mg/m^3
Absorption coefficient	2.704 mm^-1
F(000)	648
Crystal size	0.54 x 0.26 x 0.12 mm
Theta range for data collection	3.25 to 71.89 deg.
Index ranges	-15<=h<=0, -9<=k<=9, -16<=l<=17
Reflections collected / unique	5365 / 2550 [R(int) = 0.0282]
Completeness to 2theta = 71.89	92.9%
Absorption correction	Analytical
Max. and min. transmission	0.7373 and 0.3229
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2550 / 0 / 180
Goodness-of-fit on F^2	1.023
Final R indices [I>2sigma(I)]	R1 = 0.0450, wR2 = 0.1290
R indices (all data)	R1 = 0.0478, wR2 = 0.1325
Extinction coefficient	.0055(6)
Largest diff. peak and hole	.354 and -.421 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 7. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	6050(3)	2055(4)	-776(2)	73(1)
C(2)	6919(3)	1082(5)	-142(2)	76(1)
C(3)	6992(2)	881(4)	833(2)	60(1)
C(4)	6192(2)	1709(2)	1151(1)	39(1)
C(5)	5307(2)	2653(3)	522(2)	58(1)
C(6)	5242(3)	2820(4)	-453(2)	74(1)
O(7)	6339(1)	1487(2)	2147(1)	39(1)
C(8)	5582(2)	2340(2)	2503(1)	34(1)
C(9)	4618(2)	1508(2)	2541(2)	40(1)
N(10)	3869(1)	2293(2)	2893(1)	42(1)
C(11)	4043(2)	3906(3)	3208(2)	42(1)
C(12)	5007(2)	4793(2)	3210(1)	38(1)
C(13)	5842(2)	4020(2)	2873(1)	33(1)
N(14)	6874(1)	4680(2)	2859(1)	38(1)
S(15)	7309(1)	6532(1)	3209(1)	40(1)
O(16)	6436(2)	7796(2)	3090(1)	62(1)
O(17)	8267(2)	6886(2)	2885(1)	63(1)
C(18)	8030(2)	6341(4)	4545(2)	63(1)
F(19)	8717(2)	5010(3)	4776(1)	98(1)
F(20)	8655(2)	7720(3)	4886(2)	112(1)
F(21)	7257(2)	6195(3)	4994(1)	96(1)

Table 3. Bond lengths [A] and angles [deg] for 7.

C(1)-C(6)	1.366(4)
C(1)-C(2)	1.372(5)
C(1)-H(1)	.9300
C(2)-C(3)	1.394(4)
C(2)-H(2)	.9300
C(3)-C(4)	1.376(3)
C(3)-H(3)	.9300
C(4)-C(5)	1.368(3)
C(4)-O(7)	1.401(2)
C(5)-C(6)	1.393(3)
C(5)-H(5)	.9300
C(6)-H(6)	.9300
O(7)-C(8)	1.375(2)
C(8)-C(9)	1.362(3)
C(8)-C(13)	1.418(2)
C(9)-N(10)	1.340(3)
C(9)-H(9)	.9300
N(10)-C(11)	1.338(3)
N(10)-H(10)	.85(3)
C(11)-C(12)	1.365(3)
C(11)-H(11)	.9300
C(12)-C(13)	1.409(2)
C(12)-H(12)	.9300
C(13)-N(14)	1.367(2)

N(14)-S(15)	1.571(2)
S(15)-O(16)	1.422(2)
S(15)-O(17)	1.427(2)
S(15)-C(18)	1.837(3)
C(18)-F(19)	1.309(3)
C(18)-F(20)	1.319(3)
C(18)-F(21)	1.320(3)

C(6)-C(1)-C(2)	119.9(2)
C(6)-C(1)-H(1)	120.0
C(2)-C(1)-H(1)	120.0
C(1)-C(2)-C(3)	120.5(3)
C(1)-C(2)-H(2)	119.8
C(3)-C(2)-H(2)	119.8
C(4)-C(3)-C(2)	118.7(3)
C(4)-C(3)-H(3)	120.7
C(2)-C(3)-H(3)	120.7
C(5)-C(4)-C(3)	121.4(2)
C(5)-C(4)-O(7)	123.2(2)
C(3)-C(4)-O(7)	115.4(2)
C(4)-C(5)-C(6)	118.9(2)
C(4)-C(5)-H(5)	120.5
C(6)-C(5)-H(5)	120.5
C(1)-C(6)-C(5)	120.6(3)
C(1)-C(6)-H(6)	119.7
C(5)-C(6)-H(6)	119.7
C(8)-O(7)-C(4)	117.28(14)
C(9)-C(8)-O(7)	118.7(2)
C(9)-C(8)-C(13)	121.0(2)
O(7)-C(8)-C(13)	120.2(2)
N(10)-C(9)-C(8)	120.3(2)
N(10)-C(9)-H(9)	119.8
C(8)-C(9)-H(9)	119.8
C(11)-N(10)-C(9)	121.1(2)
C(11)-N(10)-H(10)	120(2)
C(9)-N(10)-H(10)	119(2)
N(10)-C(11)-C(12)	121.3(2)
N(10)-C(11)-H(11)	119.3
C(12)-C(11)-H(11)	119.3
C(11)-C(12)-C(13)	120.2(2)
C(11)-C(12)-H(12)	119.9
C(13)-C(12)-H(12)	119.9
N(14)-C(13)-C(12)	128.3(2)
N(14)-C(13)-C(8)	115.8(2)
C(12)-C(13)-C(8)	115.9(2)
C(13)-N(14)-S(15)	123.87(13)
O(16)-S(15)-O(17)	119.23(11)
O(16)-S(15)-N(14)	116.76(9)
O(17)-S(15)-N(14)	107.39(9)
O(16)-S(15)-C(18)	104.60(12)
O(17)-S(15)-C(18)	102.22(12)
N(14)-S(15)-C(18)	104.50(11)
F(19)-C(18)-F(20)	108.8(2)
F(19)-C(18)-F(21)	107.9(3)
F(20)-C(18)-F(21)	107.8(2)
F(19)-C(18)-S(15)	111.6(2)
F(20)-C(18)-S(15)	109.5(2)
F(21)-C(18)-S(15)	111.2(2)

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for 7. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	110(2)	64(2)	58(1)	-17(1)	45(2)	-25(2)
C(2)	70(2)	99(2)	75(2)	-39(2)	45(2)	-20(2)
C(3)	45(1)	74(2)	64(1)	-23(1)	22(1)	-1(1)
C(5)	70(2)	54(1)	54(1)	2(1)	26(1)	14(1)
C(6)	109(2)	60(2)	52(1)	4(1)	28(1)	11(2)
O(7)	34(1)	38(1)	48(1)	-2(1)	16(1)	5(1)
C(9)	35(1)	37(1)	49(1)	-1(1)	14(1)	-4(1)
N(10)	30(1)	45(1)	54(1)	2(1)	17(1)	-5(1)
C(11)	31(1)	48(1)	49(1)	0(1)	17(1)	3(1)
C(12)	31(1)	37(1)	48(1)	-3(1)	14(1)	1(1)
N(14)	31(1)	34(1)	53(1)	-5(1)	19(1)	-3(1)
S(15)	40(1)	32(1)	53(1)	-3(1)	21(1)	-7(1)
O(16)	64(1)	35(1)	89(1)	4(1)	30(1)	6(1)
O(17)	65(1)	56(1)	83(1)	-12(1)	45(1)	-25(1)
C(18)	57(1)	67(2)	60(1)	-15(1)	13(1)	-12(1)
F(19)	80(1)	111(2)	79(1)	11(1)	-4(1)	21(1)
F(20)	122(2)	112(2)	87(1)	-45(1)	17(1)	-59(1)
F(21)	100(1)	135(2)	62(1)	-5(1)	42(1)	-13(1)

Table 5. Torsion angles [deg] for 7.

C(6)-C(1)-C(2)-C(3)	-.7(4)
C(1)-C(2)-C(3)-C(4)	-1.5(4)
C(2)-C(3)-C(4)-C(5)	2.9(4)
C(2)-C(3)-C(4)-O(7)	-178.2(2)
C(3)-C(4)-C(5)-C(6)	-2.1(4)
O(7)-C(4)-C(5)-C(6)	179.1(2)
C(2)-C(1)-C(6)-C(5)	1.5(5)
C(4)-C(5)-C(6)-C(1)	-.1(4)
C(5)-C(4)-O(7)-C(8)	-3.3(3)
C(3)-C(4)-O(7)-C(8)	177.8(2)
C(4)-O(7)-C(8)-C(9)	95.4(2)
C(4)-O(7)-C(8)-C(13)	-88.2(2)
O(7)-C(8)-C(9)-N(10)	179.3(2)
C(13)-C(8)-C(9)-N(10)	2.9(3)
C(8)-C(9)-N(10)-C(11)	.4(3)
C(9)-N(10)-C(11)-C(12)	-2.1(3)
N(10)-C(11)-C(12)-C(13)	.3(3)
C(11)-C(12)-C(13)-N(14)	-177.0(2)
C(11)-C(12)-C(13)-C(8)	2.7(3)
C(9)-C(8)-C(13)-N(14)	175.5(2)
O(7)-C(8)-C(13)-N(14)	-.9(2)
C(9)-C(8)-C(13)-C(12)	-4.3(3)
O(7)-C(8)-C(13)-C(12)	179.3(2)
C(12)-C(13)-N(14)-S(15)	-1.9(3)
C(8)-C(13)-N(14)-S(15)	178.29(13)
C(13)-N(14)-S(15)-O(16)	-30.3(2)
C(13)-N(14)-S(15)-O(17)	-167.3(2)

C(13)-N(14)-S(15)-C(18)	84.6(2)
O(16)-S(15)-C(18)-F(19)	168.6(2)
O(17)-S(15)-C(18)-F(19)	-66.4(2)
N(14)-S(15)-C(18)-F(19)	45.4(2)
O(16)-S(15)-C(18)-F(20)	-70.9(2)
O(17)-S(15)-C(18)-F(20)	54.1(2)
N(14)-S(15)-C(18)-F(20)	165.9(2)
O(16)-S(15)-C(18)-F(21)	48.1(2)
O(17)-S(15)-C(18)-F(21)	173.1(2)
N(14)-S(15)-C(18)-F(21)	-75.1(2)

Additional crystallographic informations for compound **12**

Table 1. Crystal data and structure refinement for **12**.

Identification code	cmfj2
Empirical formula	C12 H12 N2 O3 S
Formula weight	264.30
Temperature	293(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, P21/n
Unit cell dimensions	a = 9.800(5) A alpha = 90.000(5) deg. b = 8.143(5) A beta = 93.099(5) deg. c = 15.933(5) A gamma = 90.000(5) deg.
Volume	1269.6(11) A^3
Z, Calculated density	4, 1.383 Mg/m^3
Absorption coefficient	2.305 mm^-1
F(000)	552
Crystal size	0.50 x 0.29 x 0.14 mm
Theta range for data collection	5.18 to 71.84 deg.
Index ranges	-10<=h<=12, -10<=k<=0, -19<=l<=19
Reflections collected / unique	4409 / 2490 [R(int) = 0.0163]
Completeness to 2theta = 71.84	93.0%
Absorption correction	Analytical
Max. and min. transmission	0.7385 and 0.3920
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2490 / 0 / 168
Goodness-of-fit on F^2	1.424
Final R indices [I>2sigma(I)]	R1 = 0.0383, wR2 = 0.1498
R indices (all data)	R1 = 0.0406, wR2 = 0.1543
Extinction coefficient	.035(3)
Largest diff. peak and hole	.308 and -.334 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **12**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	7059(2)	-1441(3)	2652(2)	91(1)
C(2)	7120(2)	-1418(3)	1804(2)	89(1)
C(3)	6219(2)	-493(2)	1317(1)	68(1)
C(4)	5238(2)	393(2)	1704(1)	54(1)
C(5)	5144(2)	387(2)	2558(1)	63(1)
C(6)	6089(2)	-552(3)	3040(1)	79(1)
O(7)	4436(1)	1431(2)	1190(1)	81(1)
C(8)	3057(1)	1258(2)	1113(1)	53(1)
N(9)	2446(1)	7(2)	1444(1)	62(1)
C(10)	1075(2)	-65(2)	1325(1)	64(1)
C(11)	325(2)	1079(2)	880(1)	67(1)
C(12)	1000(2)	2367(2)	505(1)	62(1)
C(13)	2395(1)	2484(2)	627(1)	50(1)
N(14)	3175(1)	3719(2)	244(1)	56(1)
S(15)	3030(1)	5653(1)	515(1)	52(1)
O(16)	1617(1)	6024(2)	533(1)	70(1)
O(17)	3847(1)	6542(2)	-46(1)	74(1)
C(18)	3761(2)	5847(3)	1534(1)	74(1)

Table 3. Bond lengths [A] and angles [deg] for **12**.

C(1)-C(2)	1.355(4)
C(1)-C(6)	1.369(4)
C(1)-H(1)	.9300
C(2)-C(3)	1.369(3)
C(2)-H(2)	.9300
C(3)-C(4)	1.374(2)
C(3)-H(3)	.9300
C(4)-C(5)	1.368(2)
C(4)-O(7)	1.391(2)
C(5)-C(6)	1.398(3)
C(5)-H(5)	.9300
C(6)-H(6)	.9300
O(7)-C(8)	1.359(2)
C(8)-N(9)	1.307(2)
C(8)-C(13)	1.401(2)
N(9)-C(10)	1.349(2)
C(10)-C(11)	1.361(3)
C(10)-H(10)	.9300
C(11)-C(12)	1.392(3)
C(11)-H(11)	.9300
C(12)-C(13)	1.374(2)
C(12)-H(12)	.9300
C(13)-N(14)	1.421(2)
N(14)-S(15)	1.641(2)
N(14)-H(14)	.96(2)
S(15)-O(16)	1.4193(13)
S(15)-O(17)	1.4278(13)
S(15)-C(18)	1.746(2)
C(18)-H(18A)	.9600

C(18)-H(18B)	.9600
C(18)-H(18C)	.9600
C(2)-C(1)-C(6)	120.8(2)
C(2)-C(1)-H(1)	119.6
C(6)-C(1)-H(1)	119.6
C(1)-C(2)-C(3)	120.7(2)
C(1)-C(2)-H(2)	119.7
C(3)-C(2)-H(2)	119.7
C(2)-C(3)-C(4)	118.7(2)
C(2)-C(3)-H(3)	120.7
C(4)-C(3)-H(3)	120.7
C(5)-C(4)-C(3)	122.1(2)
C(5)-C(4)-O(7)	121.4(2)
C(3)-C(4)-O(7)	116.2(2)
C(4)-C(5)-C(6)	118.0(2)
C(4)-C(5)-H(5)	121.0
C(6)-C(5)-H(5)	121.0
C(1)-C(6)-C(5)	119.8(2)
C(1)-C(6)-H(6)	120.1
C(5)-C(6)-H(6)	120.1
C(8)-O(7)-C(4)	121.21(12)
N(9)-C(8)-O(7)	121.27(13)
N(9)-C(8)-C(13)	124.79(14)
O(7)-C(8)-C(13)	113.89(13)
C(8)-N(9)-C(10)	116.84(14)
N(9)-C(10)-C(11)	123.3(2)
N(9)-C(10)-H(10)	118.3
C(11)-C(10)-H(10)	118.3
C(10)-C(11)-C(12)	118.9(2)
C(10)-C(11)-H(11)	120.5
C(12)-C(11)-H(11)	120.5
C(13)-C(12)-C(11)	118.9(2)
C(13)-C(12)-H(12)	120.5
C(11)-C(12)-H(12)	120.5
C(12)-C(13)-C(8)	117.14(14)
C(12)-C(13)-N(14)	122.85(13)
C(8)-C(13)-N(14)	119.90(13)
C(13)-N(14)-S(15)	120.68(10)
C(13)-N(14)-H(14)	112(2)
S(15)-N(14)-H(14)	113(2)
O(16)-S(15)-O(17)	119.02(8)
O(16)-S(15)-N(14)	107.93(8)
O(17)-S(15)-N(14)	105.21(8)
O(16)-S(15)-C(18)	108.28(9)
O(17)-S(15)-C(18)	108.67(9)
N(14)-S(15)-C(18)	107.14(8)
S(15)-C(18)-H(18A)	109.5
S(15)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
S(15)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **12**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	67(1)	83(1)	120(2)	37(1)	-14(1)	12(1)
C(2)	71(1)	77(1)	119(2)	15(1)	12(1)	25(1)
C(3)	65(1)	69(1)	70(1)	-3(1)	6(1)	7(1)
C(4)	45(1)	46(1)	70(1)	15(1)	-1(1)	-1(1)
C(5)	63(1)	55(1)	73(1)	4(1)	15(1)	-3(1)
C(6)	82(1)	85(1)	68(1)	22(1)	-10(1)	-21(1)
O(7)	46(1)	87(1)	110(1)	54(1)	4(1)	5(1)
C(8)	48(1)	56(1)	54(1)	5(1)	3(1)	4(1)
N(9)	57(1)	59(1)	68(1)	9(1)	1(1)	-2(1)
C(10)	58(1)	58(1)	75(1)	-5(1)	2(1)	-11(1)
C(11)	52(1)	64(1)	84(1)	-13(1)	-5(1)	-4(1)
C(12)	55(1)	60(1)	68(1)	-5(1)	-8(1)	7(1)
C(13)	51(1)	51(1)	48(1)	-2(1)	4(1)	7(1)
N(14)	56(1)	56(1)	56(1)	7(1)	10(1)	13(1)
S(15)	47(1)	53(1)	56(1)	13(1)	4(1)	9(1)
O(16)	50(1)	61(1)	98(1)	3(1)	-2(1)	14(1)
O(17)	73(1)	68(1)	82(1)	30(1)	22(1)	11(1)
C(18)	80(1)	77(1)	64(1)	2(1)	-6(1)	-8(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **12**.

	x	y	z	U(eq)
H(1)	7684	-2067	2974	109
H(2)	7780	-2037	1550	106
H(3)	6270	-465	736	82
H(5)	4471	990	2810	76
H(6)	6058	-573	3622	95
H(10)	618	-941	1558	77
H(11)	-623	1002	829	80
H(12)	514	3135	177	74
H(14)	4100(2)	3390(3)	186(15)	89(7)
H(18A)	4714	5576	1536	111
H(18B)	3311	5115	1902	111
H(18C)	3658	6957	1723	111

Table 6. Torsion angles [deg] for **12**.

C(6)-C(1)-C(2)-C(3)	.6(4)
C(1)-C(2)-C(3)-C(4)	-1.0(3)
C(2)-C(3)-C(4)-C(5)	.5(3)
C(2)-C(3)-C(4)-O(7)	174.0(2)
C(3)-C(4)-C(5)-C(6)	.3(2)
O(7)-C(4)-C(5)-C(6)	-172.9(2)
C(2)-C(1)-C(6)-C(5)	.2(3)

C(4)-C(5)-C(6)-C(1)	-.7(3)
C(5)-C(4)-O(7)-C(8)	-65.6(2)
C(3)-C(4)-O(7)-C(8)	120.8(2)
C(4)-O(7)-C(8)-N(9)	-7.6(3)
C(4)-O(7)-C(8)-C(13)	175.0(2)
O(7)-C(8)-N(9)-C(10)	-179.3(2)
C(13)-C(8)-N(9)-C(10)	-2.1(2)
C(8)-N(9)-C(10)-C(11)	.4(3)
N(9)-C(10)-C(11)-C(12)	2.1(3)
C(10)-C(11)-C(12)-C(13)	-3.0(2)
C(11)-C(12)-C(13)-C(8)	1.5(2)
C(11)-C(12)-C(13)-N(14)	177.6(2)
N(9)-C(8)-C(13)-C(12)	1.1(2)
O(7)-C(8)-C(13)-C(12)	178.50(13)
N(9)-C(8)-C(13)-N(14)	-175.08(14)
O(7)-C(8)-C(13)-N(14)	2.3(2)
C(12)-C(13)-N(14)-S(15)	67.9(2)
C(8)-C(13)-N(14)-S(15)	-116.12(14)
C(13)-N(14)-S(15)-O(16)	-46.55(14)
C(13)-N(14)-S(15)-O(17)	-174.60(12)
C(13)-N(14)-S(15)-C(18)	69.86(14)

Table 7. Hydrogen-bonds for **12** [A and deg.].

Type	Donor --- H....Acceptor	d(H...A)	d(D...A)	<(DHA)
Intra	N(14) -- H(14) .. O(7)	2.27	2.659(3)	103.4
	N(14) -- H(14) .. O(17)	2.04	2.961(3)	162

Additional information : elemental analyses

Compound **3**

$C_5H_3N_2O_3Br$

Theoretical : 27.42 % C, 12.79 % N, 1.38 % H, 0 % S.

Found : 27.66 % C, 12.59 % N, 1.40 % H, 0 % S.

Compound **4**

$C_5H_3N_2O_3Br$

Theoretical : 58.89 % C, 12.06 % N, 3.47 % H, 0 % S.

Found : 58.64 % C, 11.99 % N, 3.50 % H, 0 % S.

Compound **6**

$C_{12}H_{12}N_2O_3S$

Theoretical : 54.53 % C, 10.59 % N, 4.57 % H, 12.13 % S.

Found : 54.52 % C, 10.52 % N, 4.96 % H, 11.77 % S.

Compound **7**

$C_{12}H_9N_2O_3SF_3$

Theoretical : 45.28 % C, 8.80 % N, 2.85 % H, 10.07 % S.

Found : 45.55 % C, 8.89 % N, 2.84 % H, 9.90 % S.

Compound **9**

$C_{11}H_8N_2O_3$

Theoretical : 61.11 % C, 12.95 % N, 3.72 % H, 0 % S.

Found : 61.65 % C, 13.06 % N, 3.79 % H, 0 % S.

Compound **10**

$C_{11}H_{10}N_2O_3$

Theoretical : 70.95 % C, 15.04 % N, 5.41 % H, 0 % S.

Found : 71.58 % C, 15.19 % N, 4.97 % H, 0 % S.

Compound **11**

$C_{13}H_{14}N_2O_5S_2$

Theoretical : 45.60 % C, 8.18 % N, 4.12 % H, 18.72 % S.

Found : 46.36 % C, 8.41 % N, 4.09 % H, 18.51 % S.

Compound **12**

$C_{12}H_{12}N_2O_3S$

Theoretical : 54.53 % C, 10.59 % N, 4.57 % H, 12.13 % S.

Found : 54.52 % C, 10.58 % N, 4.56 % H, 11.69 % S.

Compound **13**

$C_{14}H_{14}N_2O_5S$

Theoretical : 52.16 % C, 8.69 % N, 4.37 % H, 9.94 % S.

Found : 51.77 % C, 8.68 N, 4.50 % H, 9.58 % S.