Synthesis and Structure of novel 1 λ^4 ,2,6-Thiadiazines*Wibke E. Diederich and Manfred Haake***Table of Contents.**

Figure 4	¹ H NMR Spectrum of and ¹³ C NMR Spectrum of 17d	S3
Figure 5	¹³ C NMR Spectrum (APT) of 18a	S4
Figure 6	¹ H NMR Spectrum of 19a	S4
Figure 7	¹³ C NMR Spectrum of 20a	S5
Figure 8	¹ H NMR Spectrum and ¹³ C NMR Spectrum (APT) of 26a	S6
Figure 9	ORTEP of 26b	S7
Table 6	Crystallographic data of structure 26b	S7
Figure 10	¹³ C NMR Spectrum of 26h	S10
Figure 11	¹ H NMR Spectrum of 26k	S11
Figure 12	¹ H NMR Spectrum and ¹³ C NMR Spectrum of 29a	S12
Figure 13	¹ H NMR Spectrum of 29b	S13
Figure 14	ORTEP and Cell packing diagram of 29f	S14
Table 7	Crystallographic data of structure 29f	S14
Figure 15	¹ H NMR Spectrum of 30b	S18
Figure 16	ORTEP and Cell packing diagram of 30e	S19
Table 8	Crystallographic data of structure 30e	S19

Figure 17	^{13}C NMR Spectrum (APT) of 31a	S23
Figure 18	^{13}C NMR Spectrum of 31b	S23
Figure 19	^{13}C NMR Spectrum (APT) of 31f	S24
Figure 20	^1H NMR Spectrum and ^{13}C NMR Spectrum of 32a	S25
Figure 21	^{13}C NMR Spectrum of 5b	S26
Figure 22	ORTEP and Cell packing diagram of 5b	S26
Table 9	Crystallographic data of structure 5b	S27

Figure 4. ^1H NMR Spectrum (400 MHz, CDCl_3) and ^{13}C NMR Spectrum (100 MHz, CDCl_3) of **17d**

Figure 5. ¹³C NMR Spectrum (APT, 100 MHz, DMSO-d₆) of **18a**

Figure 6. ¹H NMR (400 MHz, DMSO-d₆) Spectrum of **19a** as mixture of diastereoisomers in a ratio of approximately 8:1 as determined by integration of the ¹H NMR. In expansion the AB system of the benzylic methylene signals as well as the dd of the protons attached to C4.

Figure 7. ^{13}C NMR Spectrum (400 MHz, CDCl_3) of **20a**

Figure 8. ^1H NMR Spectrum (400 MHz, CDCl_3) and ^{13}C NMR Spectrum (APT, 400 MHz, CDCl_3) of **26a** (tautomers). The tautomerism is indicated by the appearance of two additional doublets [3.32 Hz ($J = 20$ Hz) and 2.80 Hz ($J = 20$ Hz), in expansion] for the protons at C4 in the ^1H NMR spectrum. The ^{13}C NMR spectrum shows the corresponding methylene signal at about 40 ppm.

Figure 9. ORTEP of **26b**.**Table 6.** Crystallographic data of structure **26b**A. Crystal Data

Crystal Color, Habit	Clear, Rod
Crystal Dimensions	0.40 x 0.40 x 0.10 mm
Crystal System	monoclin
Space Group	$P2_1/c$, $Z = 4$
Lattice Parameters	$a = 531.4(3)$ pm
	$b = 2018.6(8)$ pm
	$c = 1040.4(7)$ pm
	$\alpha = 90^\circ$
	$\beta = 104.25(4)^\circ$
	$\gamma = 90^\circ$
Cell volume	$1081.7(10) \text{ \AA}^3$
Cell determination	25 reflections 13.9 to $22.3^\circ \theta$
Empirical Formula	$\text{C}_9\text{H}_{16}\text{N}_2\text{OS}$
Formula Weight	200.30 g/mol
F_{000}	432

D_{calc}	1.230 Mg/m ³
$\mu(\text{CuK}\alpha)$	2.381 mm ⁻¹

B. Intensity Measurements

Diffractometer	Enraf Nonius CAD4
Radiation	CuK α (154.178 pm)
Temperature	213(2) K
θ -max	65.16°
Scan Type	ω -2 θ -scans
Scan Width	(1.50 + 0.14 tg θ)°
data collection software	CAD4 EXPRESS
Cell refinement	CAD4 Express
Data reduction	XCAD4 (Harms, 1997)

C. Structure Solution and Refinement

No of Reflections measured	total: 3742 unique: 1782 [$R_{int} = 0.0472$]
observed	1601 [$I > 2\sigma(I)$]
used	1782
extinction coefficient	$X = 0.0044(10)$ $F_C^* = F_C * k * [(1 + 0.001 * X * F_C^2 * \lambda^3) / \sin 2\theta]^{-1/4}$ k = overall scale factor
Absorption correction	semi empirical by ψ -scans
Max. and min. Transmission	0.9847 and 0.4204
largest e-Max and Min	0.649 and $-0.420 * 10^{30} \text{ e/m}^3$
Structure solution	Direct methods
Structure refinement	fullmatrix refinement on F^2
H-Atom refinement	riding model, calculated positions, fixed isotropic U s
Refinement programs	SHELXS-96 (Sheldrick, 1990) SHELXL (Sheldrick, 1996) SHELXTL
Data / Restraints / Parameter	1782 / 0 / 127

Least Square Weights	$w=1/[\sigma^2(F_o^2)+(0.0928P)^2+0.2865P]$; $P = (F_o^2+2F_c^2)/3$
Goodness-of-fit on F^2	1.110
R-Value all data on F^2	$wR_2 = 0.1526$
conventional R-Value [$I>2\sigma(I)$]	$R = 0.0536$

Bond lengths (pm)

atom	atom	distance	atom	atom	distance
S(1)	N(3)	161.5(2)	S(1)	N(2)	166.3(2)
S(1)	C(9)	180.6(3)	O(7)	C(4)	124.7(3)
C(4)	N(2)	137.9(3)	C(4)	C(5)	142.5(3)
N(3)	C(6)	135.6(3)	C(5)	C(6)	138.1(3)
C(9)	C(10)	151.7(3)	C(6)	C(8)	150.5(3)
C(10)	C(11)	150.8(5)	C(11)	C(12)	154.6(5)
C(12)	C(13)	149.8(5)			

Bond angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
N(3)	S(1)	N(2)	105.25(12)	N(3)	S(1)	C(9)	105.27(11)
N(2)	S(1)	C(9)	102.07(11)	O(7)	C(4)	N(2)	118.9(2)
O(7)	C(4)	C(5)	124.2(2)	N(2)	C(4)	C(5)	116.7(2)
C(6)	N(3)	S(1)	115.08(16)	C(6)	C(5)	C(4)	122.4(2)
C(10)	C(9)	S(1)	111.68(19)	N(3)	C(6)	C(5)	126.5(2)
N(3)	C(6)	C(8)	113.0(2)	C(5)	C(6)	C(8)	120.5(2)
C(4)	N(2)	S(1)	120.93(17)	C(11)	C(10)	C(9)	112.4(2)
C(10)	C(11)	C(12)	114.2(3)	C(13)	C(12)	C(11)	114.0(3)

Torsion angles (°)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
N(3)	S(1)	C(9)	C(10)	176.35(17)	N(3)	S(1)	N(2)	C(4)	-38.5(2)
O(7)	C(4)	C(5)	C(6)	-165.4(2)	N(2)	C(4)	C(5)	C(6)	9.2(4)
S(1)	C(9)	C(10)	C(11)	171.19(19)	S(1)	N(3)	C(6)	C(5)	-16.2(3)
S(1)	N(3)	C(6)	C(8)	166.43(18)	C(4)	C(5)	C(6)	N(3)	-10.2(4)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
O(7)	C(4)	N(2)	S(1)	-167.57(18)	C(9)	S(1)	N(3)	C(6)	-71.7(2)
N(2)	S(1)	C(9)	C(10)	66.6(2)	C(5)	C(4)	N(2)	S(1)	17.5(3)
C(4)	C(5)	C(6)	C(8)	167.0(2)	C(9)	S(1)	N(2)	C(4)	71.3(2)
C(9)	C(10)	C(11)	C(12)	-73.9(3)	N(2)	S(1)	N(3)	C(6)	35.7(2)
C(10)	C(11)	C(12)	C(13)	171.7(3)

Figure 10. ¹³C NMR Spectrum (125 MHz, CDCl₃) of **26h**

Figure 11. ¹H NMR Spectrum (400 MHz, DMSO-d₆) of **26k**. The α-methylen protons of the S-alkyl-substituent are diastereotopic due to their neighborhood to the chiral sulfur atom and therefore split up in the ¹H NMR Spectrum (AB system).

Figure 12. ^1H NMR Spectrum (400 MHz, CDCl_3) and ^{13}C NMR Spectrum (125 MHz, CDCl_3) of **29a**

Figure 13. ^1H NMR Spectrum (400 MHz, CDCl_3) of **29b**. Shown in expansion is the quartet of the ethoxy substituent as well as the symmetrical multiplet of the protons of the α -methylene group of the S-alkyl-substituent.

Figure 14. ORTEP and cell packing diagram of **29f****Table 7.** Crystallographic data of structure **29f**

Experimental Details:

A. Crystal Data

Empirical Formula	C ₁₂ H ₁₇ F ₃ N ₂ OS
Formula Weight	294.33
Crystal Color, Habit	yellow, prism
Crystal Dimensions	0.35 x 0.35 x 0.40 mm
Crystal System	triclinic
Lattice Type	Primitive
No. of Reflections Used for Unit	
Cell Determination (2 θ range)	25 (78.4 - 80.0°)
Omega Scan Peak Width at Half-height	0.45°
Lattice Parameters	$a = 9.458(2)\text{\AA}$ $b = 10.362(3)\text{\AA}$ $c = 7.762(1)\text{\AA}$ $\alpha = 103.72(2)^\circ$ $\beta = 97.20(2)^\circ$

	$\gamma = 72.08(2)^\circ$
	$V = 702.1(3)\text{\AA}^3$
Space Group	$P\bar{1}$ (#2)
Z value	2
D_{calc}	1.392 g/cm ³
F_{000}	308.00
$\mu(\text{CuK}\alpha)$	23.37 cm ⁻¹

B. Intensity Measurements

Diffractometer	Rigaku AFC5R
Radiation	CuK α ($\lambda = 1.54178\text{ \AA}$) graphite monochromated
Attenuator	Ni foil (factors = 1.00, 3.41, 11.92, 40.89)
Take-off Angle	6.0°
Detector Aperture	9.0 mm horizontal 13.0 mm vertical
Crystal to Detector Distance	400 mm
Voltage, Current	0kV, 0mA
Temperature	20.0°C
Scan Type	ω -2 θ
Scan Rate	32.0°/min (in ω) (up to 4 scans)
Scan Width	$(1.42 + 0.30 \tan \theta)^\circ$
$2\theta_{max}$	120.3°
No. Of Reflections Measured	Total: 2246 Unique: 2097 ($R_{int} = 0.053$)
Corrections	Lorentz-polarization, Absorption (trans. Factors: 0.7289-1.0000)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\sum w(F_o - F_c)^2$

Least Squares Weights	$w = 1/[\sigma^2(\text{Fo})] = [\sigma_c^2(\text{Fo}) + (p^2/4) \text{Fo}^2]^{-1}$
p-factor	0.0020
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I > 3.00\sigma(I)$)	1881
No. Variables	172
Reflection/Parameter Ratio	10.94
Residuals: R; Rw	0.051; 0.048
Goodness of Fit Indicator	4.88
Max Shift/Error in Final Cycle	0.01
Maximum peak in Final Diff. Map	$0.54 \text{ e}^-/\text{\AA}^3$
Minimum peak in Final Diff. Map	$-0.40 \text{ e}^-/\text{\AA}^3$

Bond Lengths (Å)

Atom	atom	distance	atom	atom	distance
S(1)	N(3)	1.664(2)	S(1)	N(4)	1.646(2)
S(1)	C(3)	1.824(3)	F(1)	C(1)	1.282(4)
F(2)	C(1)	1.296(4)	F(3)	C(1)	1.303(4)
O(2)	C(5)	1.341(3)	O(2)	C(6)	1.446(4)
N(3)	C(5)	1.307(4)	N(4)	C(13)	1.339(4)
C(1)	C(13)	1.500(4)	C(3)	C(7)	1.527(4)
C(3)	C(8)	1.517(4)	C(6)	C(9)	1.504(4)
C(4)	C(5)	1.407(4)	C(4)	C(13)	1.364(4)
C(7)	C(10)	1.512(4)	C(8)	C(12)	1.523(4)
C(11)	C(12)	1.515(5)	C(10)	C(11)	1.520(5)

Bond Angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
N(3)	S(1)	N(4)	109.8(1)	N(3)	S(1)	C(3)	101.9(1)
N(4)	S(1)	C(3)	103.5(1)	C(5)	O(2)	C(6)	117.5(2)
S(1)	N(3)	C(5)	114.4(2)	S(1)	N(4)	C(13)	113.3(2)
F(1)	C(1)	F(2)	106.5(4)	F(1)	C(1)	F(3)	105.2(4)
F(1)	C(1)	C(13)	114.8(3)	F(2)	C(1)	F(3)	104.4(4)
F(2)	C(1)	C(13)	111.8(3)	F(3)	C(1)	C(13)	113.3(3)

atom	atom	atom	angle	atom	atom	atom	angle
S(1)	C(3)	C(7)	109.2(2)	S(1)	C(3)	C(8)	109.3(2)
C(7)	C(3)	C(8)	111.4(3)	(5)	C(4)	C(13)	118.3(3)
O(2)	C(5)	N(3)	118.7(3)	(2)	C(6)	C(9)	107.1(3)
O(2)	C(5)	C(4)	114.2(3)	N(3)	C(5)	C(4)	126.9(3)
C(3)	C(7)	C(10)	111.2(3)	C(3)	C(8)	C(12)	110.6(3)
C(7)	C(10)	C(11)	111.8(3)	C(10)	C(11)	C(12)	110.6(3)
C(8)	C(12)	C(11)	111.6(3)	C(1)	C(13)	C(4)	118.9(3)
N(4)	C(13)	C(1)	112.7(3)	N(4)	C(13)	C(4)	128.2(3)

Torsion Angles (°)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
S(1)	N(3)	C(5)	O(2)	-173.6(2)	S(1)	N(3)	C(5)	C(4)	11.0(4)
S(1)	N(4)	C(13)	C(1)	174.3(2)	S(1)	N(4)	C(13)	C(4)	-11.2(4)
S(1)	C(3)	C(7)	C(10)	175.6(2)	S(1)	C(3)	C(8)	C(12)	-176.0(2)
F(1)	C(1)	C(13)	N(4)	-166.0(3)	F(1)	C(1)	C(13)	C(4)	18.9(5)
F(2)	C(1)	C(13)	N(4)	72.5(4)	F(2)	C(1)	C(13)	C(4)	-102.6(4)
F(3)	C(1)	C(13)	N(4)	-45.1(5)	F(3)	C(1)	C(13)	C(4)	139.8(4)
O(2)	C(5)	C(4)	C(13)	-164.5(3)	N(3)	S(1)	N(4)	C(13)	29.8(3)
N(3)	S(1)	C(3)	C(7)	59.2(2)	N(3)	S(1)	C(3)	C(8)	-178.8(2)
N(3)	C(5)	O(2)	C(6)	7.0(4)	N(3)	C(5)	C(4)	C(13)	11.0(5)
N(4)	S(1)	N(3)	C(5)	-30.0(3)	N(4)	S(1)	C(3)	C(7)	173.2(2)
N(4)	S(1)	C(3)	C(8)	-64.7(2)	N(4)	C(13)	C(4)	C(5)	-11.0(5)
C(1)	C(13)	C(4)	C(5)	163.2(3)	C(3)	S(1)	N(3)	C(5)	79.3(2)
C(3)	S(1)	N(4)	C(13)	-78.4(3)	C(3)	C(7)	C(10)	C(11)	-54.9(4)
C(3)	C(8)	C(12)	C(11)	56.3(4)	C(4)	C(5)	O(2)	C(6)	-177.1(3)
C(5)	O(2)	C(6)	C(9)	173.8(3)	C(7)	C(3)	C(8)	C(12)	-55.3(4)
C(7)	C(10)	C(11)	C(12)	55.5(4)	C(8)	C(3)	C(7)	C(10)	54.8(4)
C(8)	C(12)	C(11)	C(10)	-56.1(4)

Figure 15. ¹H NMR Spectrum (400 MHz, CD₃OD) of **30b**. The ddd splitting of each of the protons of the α-CH₂ group of the S-alkyl-substituent as well as the two pseudo sextets of the protons of the methylen group of the N-CH₂CH₃ substituent are shown in expansion.

Figure 16. ORTEP and cell packing diagram of **30e****Table 8.** Crystallographic data of structure **30e**

Experimental Details

A. Crystal Data

Empirical Formula	C ₁₂ H ₁₇ F ₃ N ₂ OS
Formula Weight	294.33
Crystal Color, Habit	Clear, Rod
Crystal Dimensions	0.30 x 0.25 x 0.20 mm
Crystal System	orthorhombic
Lattice Type	Primitive
No. of Reflections Used for Unit	
Cell Determination (2 θ range)	25 (73.2 - 79.9°)
Omega Scan Peak Width at Half-height	0.19°
Lattice Parameters	a = 9.599(1) Å b = 16.839(1) Å c = 8.705(1) Å V = 1407.1(3) Å ³
Space Group	Pna2 ₁ (#33)
Z value	4
D _{calc}	1.389 g/cm ³

F_{000}	616.00
$\mu(\text{CuK}\alpha)$	23.32 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku AFC5R
Radiation	CuK α ($\lambda = 1.54178 \text{ \AA}$)
	Graphite monochromated
Attenuator	Ni foil (factors = 1.00, 3.41, 11.92, 40.89)
Take-off Angle	6.0°
Detector Aperture	9.0 mm horizontal, 13.0 mm vertical
Crystal to Detector Distance	400 mm
Voltage, Current	0kV, 0mA
Temperature	23.0°C
Scan Type	ω -2 θ
Scan Rate	$32.0^\circ/\text{min}$ (in ω) (up to 4 scans)
Scan Width	$(1.26 + 0.30 \tan \theta)^\circ$
$2\theta_{\text{max}}$	120.5°
No. Of Reflections Measured	Total: 1257
Corrections	Lorentz-polarization
	Absorption
	(trans. Factors: 0.8168 – 1.0000)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\sum w(F_o - F_c)^2$
Least Squares Weights	$w = 1/[\sigma^2(F_o)] = [\sigma_c^2(F_o) + (p^2/4) F_o^2]^{-1}$
p-factor	0.0300
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I > 3.00\sigma(I)$)	1055
No. Variables	0
Residuals: R; Rw	0.052; 0.073

Goodness of Fit Indicator	2.32
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.30 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.24 e ⁻ /Å ³

Bond Lengths (Å)

atom	atom	distance	atom	atom	distance
S(1)	N(3)	2(2)	S(1)	N(4)	2(2)
S(1)	C(13)	2(2)	F(1)	C(9)	1(4)
F(2)	C(9)	1(1)	F(3)	C(9)	1(3)
O(1)	C(1)	1(4)	N(3)	C(1)	1(4)
N(3)	C(10)	1.6(6)	N(4)	C(4)	1(4)
C(1)	C(14)	2(1)	C(2)	C(5)	2(2)
C(2)	C(11)	2(2)	C(4)	C(9)	1(2)
C(4)	C(14)	1(4)	C(5)	C(13)	2(2)
C(6)	C(7)	2(2)	C(6)	C(13)	1(2)
C(7)	C(11)	2(2)	C(10)	C(12)	2(2)

Bond Angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
N(3)	S(1)	N(4)	105.4	N(3)	S(1)	C(13)	101.2
N(4)	S(1)	C(13)	106.0	S(1)	N(3)	C(1)	128.8(9)
S(1)	N(3)	C(10)	118.5	C(1)	N(3)	C(10)	112.8(6)
S(1)	N(4)	C(4)	111.2	O(1)	C(1)	N(3)	129.9
O(1)	C(1)	C(14)	118.5	N(3)	C(1)	C(14)	109.6(9)
C(5)	C(2)	C(11)	111.8	C(9)	C(4)	C(14)	114.8
N(4)	C(4)	C(9)	110.7	N(4)	C(4)	C(14)	134.2
C(2)	C(5)	C(13)	106.5	C(7)	C(6)	C(13)	108.4
C(6)	C(7)	C(11)	106.0	N(3)	C(10)	C(12)	109.4
F(1)	C(9)	F(2)	104.1	F(1)	C(9)	F(3)	106.5
F(1)	C(9)	C(4)	115.9	F(2)	C(9)	F(3)	97.0
F(2)	C(9)	C(4)	115.6	F(3)	C(9)	C(4)	115.6

C(2)	C(11)	C(7)	108.6	C(5)	C(13)	C(6)	112.4
atom	atom	atom	angle	atom	atom	atom	angle
S(1)	C(13)	C(5)	103.8	S(1)	C(13)	C(6)	103.5
C(1)	C(14)	C(4)	115.9				

Torsion Angles (°)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
S(1)	N(3)	C(1)	O(1)	154.6	S(1)	N(3)	C(1)	C(14)	-8.7
S(1)	N(3)	C(10)	C(12)	114.6(5)	S(1)	N(4)	C(4)	C(9)	-169.7(9)
S(1)	N(4)	C(4)	C(14)	3.8	S(1)	C(13)	C(5)	C(2)	-173.3(4)
S(1)	C(13)	C(6)	C(7)	177.6	F(1)	C(9)	C(4)	N(4)	-79.3
F(1)	C(9)	C(4)	C(14)	105.9(8)	F(2)	C(9)	C(4)	N(4)	42.8(5)
F(2)	C(9)	C(4)	C(14)	-132.0	F(3)	C(9)	C(4)	N(4)	155.0
F(3)	C(9)	C(4)	C(14)	-19.8	O(1)	C(1)	N(3)	C(10)	-26.5
O(1)	C(1)	C(14)	C(4)	171.3(2)	N(3)	S(1)	N(4)	C(4)	-31.0(2)
N(3)	S(1)	C(13)	C(5)	-57.8(8)	N(3)	S(1)	C(13)	C(6)	-175.4
N(3)	C(1)	C(14)	C(4)	-23.2	N(4)	S(1)	N(3)	C(1)	35.9
N(4)	S(1)	N(3)	C(10)	-143.0(7)	N(4)	S(1)	C(13)	C(5)	-167.7(5)
N(4)	S(1)	C(13)	C(6)	74.8	N(4)	C(4)	C(14)	C(1)	27.9
C(1)	N(3)	S(1)	C(13)	-74.4	C(1)	N(3)	C(10)	C(12)	-64.5
C(1)	C(14)	C(4)	C(9)	-159(5)	C(2)	C(5)	C(13)	C(6)	-62.2(8)
C(2)	C(11)	C(7)	C(6)	58.9	C(4)	N(4)	S(1)	C(13)	75.9
C(5)	C(2)	C(11)	C(7)	-59.6(9)	C(5)	C(13)	C(6)	C(7)	66.2
C(10)	N(3)	S(1)	C(13)	106.7	C(10)	N(3)	C(1)	C(14)	170.2(2)
C(11)	C(2)	C(5)	C(13)	57.2(5)	C(11)	C(7)	C(6)	C(13)	-63.1(5)

Figure 17. ^{13}C NMR Spectrum (APT, 125 MHz, CDCl_3) of **31a**

Figure 18. ^{13}C NMR Spectrum (125 MHz, CDCl_3) of **31b**

Figure 19. ^{13}C NMR Spectrum (APT, 125 MHz, CDCl_3) of **31f**

Figure 20. ^1H NMR Spectrum (500 MHz, CDCl_3) and ^{13}C NMR Spectrum (125 MHz, CDCl_3) of **32a**

Figure 21. ^{13}C NMR Spectrum (125 MHz, DMSO-d_6) of **5b**

Figure 22. ORTEP and cell packing diagram of **5b**

Table 9. Crystallographic data of structure **5b**

Experimental Details

A. Crystal Data

Empirical Formula	C ₁₇ H ₂₀ F ₃ N ₃ S
Formula Weight	355.42
Crystal Color,Habit	clear, prism
Crystal Dimensions	0.25 x 0.25 x 0.25 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit	
Cell Determination (2 θ range)	25 (71.7 – 79.3°)
Omega Scan Peak Width at Half-height	0.21°
Lattice Parameters	a = 10.143(4) Å b = 15.162(3) Å c = 12.170(2) Å β = 104.88(2)° V = 1808.8(7) Å ³
Space Group	P2 ₁ /c (#14)
Z value	4
D _{calc}	1.305 g/cm ³
F ₀₀₀	744.00
μ (CuK α)	18.85 cm ⁻¹

B. Intensity Measurements

Diffractometer	Rigaku AFC5R
Radiation	CuK α (λ = 1.54178 Å) Graphite monochromated
Attenuator	Ni foil (factors = 1.00, 3.41, 11.92, 40.89)
Take-off Angle	6.0°

Detector Aperture	9.0 mm horizontal 13.0 mm vertical
Crystal to Detector Distance	400 mm
Voltage, Current	0kV, 0mA
Temperature	23.0°C
Scan Type	ω -2 θ
Scan Rate	32.0°/min (in ω) (up to 4 scans)
Scan Width	$(1.47 + 0.30 \tan \theta)^\circ$
$2\theta_{\max}$	120.3°
No. Of Reflections Measured	Total: 3008 Unique: 2831 ($R_{\text{int}} = 0.102$)
Corrections	Lorentz-polarization Absorption (trans. Factors: 0.8689-0.9957)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\sum w(F_o - F_c)^2$
Least Squares Weights	$w = 1/[\sigma^2(F_o)] = [\sigma_c^2(F_o) + (p^2/4) F_o^2]^{-1}$
p-factor	0.0090
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I > 3.00\sigma(I)$)	2024
No. Variables	217
Reflection/Parameter Ratio	9.33
Residuals: R; Rw	0.099; 0.112
Goodness of Fit Indicator	5.22
Max Shift/Error in Final Cycle	0.02
Maximum peak in Final Diff. Map	0.63 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.68 e ⁻ /Å ³

Bond Lengths (Å)

atom	atom	distance	atom	atom	distance
S(1)	N(1)	1.649(5)	S(1)	N(2)	1.637(6)
S(1)	C(10)	1.819(7)	F(1)	C(14)	1.31(1)
F(2)	C(14)	1.32(1)	F(3)	C(14)	1.32(1)
N(1)	C(1)	1.371(9)	N(2)	C(4)	1.365(9)
N(3)	C(1)	1.335(8)	N(3)	C(7)	1.449(9)
C(1)	C(6)	1.407(9)	C(4)	C(14)	1.46(1)
C(2)	C(7)	1.537(9)	C(2)	C(9)	1.37(1)
C(2)	C(11)	1.37(1)	C(4)	C(6)	1.357(9)
C(9)	C(12)	1.40(1)	C(11)	C(16)	1.39(1)
C(10)	C(15)	1.52(1)	C(10)	C(17)	1.53(1)
C(12)	C(13)	1.35(1)	C(13)	C(16)	1.39(1)
C(15)	C(18)	1.49(1)	C(17)	C(20)	1.49(1)
C(18)	C(19)	1.52(1)	C(19)	C(20)	1.51(1)

Bond Angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
N(1)	S(1)	N(2)	111.7(3)	n(1)	S(1)	C(10)	103.2(3)
N(2)	S(1)	C(10)	104.6(3)	S(1)	N(1)	C(1)	112.8(5)
S(1)	N(2)	C(4)	113.3(5)	C(1)	N(3)	C(7)	124.9(7)
N(1)	C(1)	N(3)	114.6(7)	N(1)	C(1)	C(6)	125.9(6)
N(3)	C(1)	C(6)	119.4(7)	C(7)	C(2)	C(9)	120.0(8)
C(7)	C(2)	C(11)	120.9(8)	C(9)	C(2)	C(11)	129.2(8)
N(2)	C(4)	C(6)	126.9(7)	N(2)	C(4)	C(14)	112.2(7)
C(6)	C(4)	C(14)	120.8(8)	C(1)	C(6)	C(4)	120.1(7)
N(3)	C(7)	C(2)	111.3(6)	C(2)	C(9)	C(12)	120.7(9)
S(1)	C(10)	C(15)	108.0(6)	S(1)	C(10)	C(17)	109.7(6)
C(15)	C(10)	C(17)	113.0(7)	C(2)	C(11)	C(16)	120.3(9)
C(9)	C(12)	C(13)	120.3(9)	C(12)	C(13)	C(16)	119.7(9)
F(1)	C(14)	F(2)	104.8(9)	F(1)	C(14)	F(3)	103.5(8)
F(1)	C(14)	C(4)	115.0(8)	F(2)	C(14)	f(3)	104.6(8)
F(2)	C(14)	C(4)	113.3(8)	F(3)	C(14)	C(4)	114.4(9)

atom	atom	atom	angle	atom	atom	atom	angle
C(10)	C(15)	C(18)	112.1(8)	C(11)	C(16)	C(13)	119.9(9)
C(10)	C(17)	C820)	112.6(7)	C(15)	C(18)	C(19)	112.5(9)
C(18)	C(19)	C(20)	110.9(8)	C(7)	C(20)	C819)	113.0(8)

Torsion Angles (°)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
S(1)	N(1)	C(1)	N(3)	-173.2(5)	S(1)	N(1)	C(1)	C(6)	11.8(9)
S(1)	N(2)	C(4)	C(6)	-13(1)	S(1)	N(2)	C(4)	C(14)	170.9(6)
S(1)	C(10)	C(15)	C(18)	171.2(8)	S(1)	C(10)	C(17)	C(20)	-169.6(7)
F(1)	C(14)	C(4)	N(2)	179.6(8)	F(1)	C(14)	C(4)	C(6)	3(1)
F(2)	C(14)	C(4)	N(2)	59(1)	F(2)	C(14)	C(4)	C(6)	-118(1)
F(3)	C(14)	C(4)	N(2)	-61(1)	F(3)	C(14)	C(4)	C(6)	122.5(9)
N(1)	S(1)	N(2)	C(4)	31.5(6)	N(1)	S(1)	C(10)	C(15)	60.7(7)
N(1)	S(1)	C(10)	C(17)	-175.8(6)	N(1)	C(1)	N(3)	C(7)	6(1)
N(1)	C(1)	C(6)	C(4)	10(1)	N(2)	S(1)	N(1)	C(1)	-30.9(6)
N(2)	S(1)	C810)	C(15)	177.6(6)	N(2)	S(1)	C(10)	C(17)	-58.9(7)
N(2)	C(4)	C(6)	C(1)	-10(1)	N(3)	C(1)	C(6)	C(4)	-164.9(7)
N(3)	C(7)	C(2)	C(9)	-134.3(8)	N(3)	C(7)	C(2)	C(11)	46(1)
C(1)	N(1)	S(1)	C(10)	80.8(5)	C(1)	N(3)	C(7)	C(2)	68(1)
C(1)	C(6)	C(4)	C(14)	166.7(8)	C(2)	C(9)	C(12)	C(13)	-1(1)
C(2)	C(11)	C(16)	C(13)	0(2)	C(4)	N(2)	S(1)	C(10)	-79.4(6)
C(6)	C(1)	N(3)	C(7)	-178.2(7)	C(7)	C(2)	C(9)	C(12)	-179.5(7)
C(7)	C(2)	C(11)	C(16)	-179.9(8)	C(9)	C(2)	C(11)	C(16)	0(1)
C(9)	C(12)	C(13)	C(16)	0(2)	C(10)	C(15)	C(18)	C(19)	-53(1)
C(10)	C(17)	C(20)	C(19)	52(1)	C(11)	C(2)	C(9)	C(12)	1(1)
C(11)	C(16)	C(13)	C(12)	0(2)	C(15)	C(10)	C(17)	C(20)	-49(1)
C(15)	C(18)	C(19)	C(20)	55(1)	C(17)	C(10)	C(15)	C(18)	50(1)
C(17)	C(20)	C(19)	C(18)	-54(1)					