SUPPORTING INFORMATION FOR

Conjugate Additions of *o*-Iodoanilines and Methyl Anthranilates to Acetylenic Sulfones. A New Route to Quinolones Including First Syntheses of Two Alkaloids from the Medicinal Herb *Ruta Chalepensis*

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Preparation of aniline 11a. Methyl 3-iodo-4-aminobenzoate (45.5 g, 164 mmol) was dissolved in formic acid (500 mL). The solution was refluxed for 4 h and volatile material was removed in vacuo to give 48.7 g (97 %) of **11a**, which was recrystallized from ethanol to afford white needles, mp 159-162 °C, obtained as a mixture of rotamers; IR (film) 1712, 1668 cm^{-1} ; ^1H NMR (400 MHz) major rotamer: δ 8.54 (s, 1 H), 8.46 (d, J = 1.5 Hz, 1 H), 8.42 (d, J = 8.6 Hz, 1 H), 8.00 (dd, J = 8.6, 1.5 Hz, 1 H), 7.74 (br, 1 H), 3.90 (s, 3 H); minor rotamer: δ 8.82 (d, J = 9.9 Hz), 8.49 (s), 7.26 (d, J = 9.9 Hz); ^{13}C NMR (100 MHz) major rotamer: δ 165.0, 158.9, 141.1, 140.3, 130.8, 127.4, 120.7, 87.8, 52.3; minor rotamer: 164.8, 161.0, 141.5, 141.4, 131.0, 128.0, 116.6, 88.5, 52.3; MS (EI) m/z (%) 305 (10, M^+), 276 (8), 246 (27), 218 (20), 178 (100). HRMS calcd. for $\text{C}_9\text{H}_8\text{INO}_3$: 304.9549. Found: 304.9571.

Preparation of aniline 11b. Methyl 3-iodo-4-aminobenzoate (669 mg, 2.41 mmol) was dissolved in 5 mL of acetic anhydride. Concentrated H_2SO_4 (0.1 mL) was added, and the solution was stirred for 15 min. The reaction mixture was diluted with ethyl acetate, then washed three times with water, and once with brine. The organic layer was dried and concentrated in vacuo. Recrystallization from ethanol gave 555 mg (72%) of **11b** as a fluffy white solid, mp 136-139 °C; IR (film) 1719, 1666 cm^{-1} ; ^1H NMR (400 MHz) δ 8.42 (d, J = 1.9 Hz, 1 H), 8.34 (d, J = 8.6 Hz, 1 H), 7.97 (dd, J = 8.6, 1.9 Hz, 1 H), 7.64 (br, 1 H), 3.88 (s, 3 H), 2.26 (s, 3 H); ^{13}C NMR (100 MHz) δ 168.3, 165.1, 142.0, 140.1, 130.7, 126.9, 120.2, 88.3, 52.2, 24.9; MS (EI) m/z (%) 319 (5, M^+), 276 (100), 246 (96), 192 (97). HRMS calcd. for $\text{C}_{10}\text{H}_{10}\text{INO}_3$: 318.9706. Found: 318.9709.

Preparation of aniline 12. Iodoaniline **11a** (305 mg, 1.00 mmol), triethylamine (0.14 mL, 1.0 mmol) and $\text{Pd}(\text{OAc})_2$ (22 mg, 0.1 mmol) were stirred in 30 mL of

methanol at 60 °C for 16 h in a Parr high-pressure reaction vessel under carbon monoxide at a pressure of 27 atm (400 psi). The apparatus was cooled to room temperature, vented, and the mixture was filtered, then concentrated in vacuo. Chromatography (hexanes-ethyl acetate, 4:1 to 2:1) gave 196 mg (83%) of **12** as a white solid, mp 131-133 °C; IR (film) 1722, 1699 cm^{-1} ; ^1H NMR (400 MHz) δ 8.73 (d, J = 8.6 Hz, 1 H), 8.64 (s, 1 H), 8.52 (s, 1 H), 8.12 (d, J = 8.6 Hz, 1 H), 3.92 (s, 3 H), 3.88 (s, 3 H); ^{13}C NMR (100 MHz) δ 167.8, 165.5, 159.6, 143.7, 135.4, 132.6, 124.5, 120.6, 114.7, 52.6, 52.2; MS (EI) m/z (%) 237 (4, M^+), 209 (77), 177 (65), 146 (100). HRMS calcd. for $\text{C}_{11}\text{H}_{11}\text{NO}_5$: 237.0637. Found: 237.0656.

Preparation of 5-[8-(*p*-Toluenesulfonyl)-7-octynyl]-1,2-(methylenedioxy)-benzene (16). A solution of 4-bromo-1,2-(methylenedioxy)benzene (2.000 g, 9.949 mmol) in 20 mL of THF was cooled to -78 °C. A solution of *tert*-butyllithium in pentane (1.7 M, 11.7 mL, 20 mmol) was added, and the resulting heterogeneous mixture was stirred for 15 min at -78 °C, then 10 minutes at -42 °C. The mixture was again cooled to -78 °C and 1-bromo-6-chlorohexane (1.48 mL, 9.95 mmol) was added. The mixture was stirred at room temperature for 1 h, then was partitioned between saturated $(\text{NH}_4)_2\text{SO}_4$ solution and dichloromethane. The aqueous layer was washed with dichloromethane and the combined organic layers were dried and concentrated in vacuo. The residue was dissolved in 25 mL of acetone and NaI (7.5 g, 50 mmol) was added. The mixture was refluxed for 2 d, then partitioned between water and ether. The aqueous layer was washed with ether, and the combined organic layers were dried and concentrated in vacuo. The residue of crude 4-(iodoethyl)-1,2-(methylenedioxy)benzene was redissolved in 5 mL of THF and 1.7 mL of HMPA.

A solution of *n*-butyllithium in hexane (2.41 M, 8.26 mL, 19.9 mmol) was added to a solution of trimethylsilylacetylene (2.81 mL, 19.9 mmol) in 10 mL of THF at 0 °C. The solution was warmed to room temperature for 15 min, then was transferred via cannula to the above solution of the alkyl iodide. The mixture was stirred for 2 d at room temperature, then was partitioned between water and ether. The aqueous layer was washed with ether and the combined organic layers were dried and concentrated in vacuo. The residue was redissolved in 20 mL of THF. A solution of tetrabutylammonium fluoride in THF (1.0 M, 20 mL, 20 mmol) was added and the solution was stirred for 30 min at room temperature, then was partitioned between water and ether. The aqueous layer was washed with ether and the combined organic layers were dried and concentrated in vacuo. Chromatography (hexanes-ethyl acetate, 40:1) gave 1.38 g (60%) of 5-(7-octynyl)-1,2-(methylenedioxy)benzene as a yellow oil, with properties in agreement with those reported in the literature via a different procedure [Clive, D. L. J.; Ardelean, E.-S. *J. Org. Chem.* **2001**, 66, 4841].

The above acetylene (2.26 g, 9.79 mmol) and *Se*-phenyl *p*-tolueneselenosulfonate (3.05 g, 9.80 mmol) were dissolved in 20 mL of chloroform and irradiated for 2 h in a Rayonet reactor equipped with six 300 nm lamps. The solvent was evaporated, and the residue was redissolved in 100 mL of chloroform. *m*-Chloroperbenzoic acid (4.4 g, ca. 77% purity, 20 mmol) was added in portions. The resulting mixture was stirred for 20 min, then was diluted to 250 mL with dichloromethane and washed twice with 500 mL of 5% NaOH solution. The aqueous extracts were each back-extracted twice with dichloromethane to ensure that the water-soluble selenoxide was not lost to the aqueous wash. The combined organic layers were dried and concentrated in vacuo. The residue

was dissolved in 300 mL of benzene, MgSO_4 (10 g) was added and the mixture was refluxed for 1 h, filtered to remove MgSO_4 and concentrated in vacuo. Chromatography (hexanes:ethyl acetate, 6:1 to 4:1) gave 2.70 g (72%) of **16** as a yellow oil, IR (film) 2198 cm^{-1} ; ^1H NMR (200 MHz) δ 7.88 (d, $J = 8.2\text{ Hz}$, 2 H), 7.35 (d, $J = 8.2\text{ Hz}$, 2 H), 6.72 (d, $J = 7.9\text{ Hz}$, 1 H), 6.64 (d, $J = 1.7\text{ Hz}$, 1 H), 6.58 (dd, $J = 7.9, 1.7\text{ Hz}$, 1 H), 5.90 (s, 2 H), 2.49 (t, $J = 7.4\text{ Hz}$, 2 H), 2.44 (s, 3 H), 2.34 (t, $J = 6.9\text{ Hz}$, 2 H), 1.62-1.44 (m, 4 H), 1.43-1.18 (m, 4 H); ^{13}C NMR (50 MHz) δ 147.4, 145.3, 144.9, 139.1, 136.2, 129.7, 127.1, 120.8, 108.6, 107.9, 100.6, 97.1, 78.4, 35.3, 31.2, 28.4, 28.2, 26.8, 21.5, 18.7; MS (EI) m/z (%) 384 (13, M^+), 147 (65), 135 (100). HRMS calcd. for $\text{C}_{22}\text{H}_{24}\text{O}_4\text{S}$: 384.1395. Found: 384.1384.

Crystal Structure of **1**

Experimental:

A colorless block crystal of $C_{14}H_{17}NO$ was coated with Paratone 8277 oil (Exxon) and mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo- $K\alpha$ radiation. Cell constants obtained from the refinement¹ of 2536 reflections in the range $1.0 < \theta < 27.5^\circ$ corresponded to a primitive monoclinic cell; details of crystal data and structure refinement have been provided in Table 1. The space group was uniquely determined from the systematic absences. The data were collected² at a temperature of 173(2) K using the ω and ϕ scans to a maximum θ value of 27.5° . The data were corrected for Lorentz and polarization effects and for absorption using multi-scan method¹. Since the crystal did not show any sign of decay during data collection a decay correction was deemed unnecessary.

The structure was solved by the direct methods³ and expanded using Fourier techniques⁴. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from a difference map, were included at geometrically idealized positions and were not refined. The final cycle of full-matrix least-squares refinement using SHELXL97⁵ converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors, $R = 0.042$ and $wR = 0.119$ (all data), respectively, and goodness of fit, $S = 1.03$. The weighting scheme was based on counting statistics and the final difference map was essentially featureless. The figures were plotted with the aid of ORTEPII⁶.

References:

1. Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307.
2. Hooft, R. (1998). *COLLECT*. Nonius BV, Delft. The Netherlands.
3. Altomare, A., Cascarano, M., Giacovazzo, C. & Guagliardi, A. (1993). *SIR92*. J. Appl. Cryst., **26**, 343
4. Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. & Smits, J.M.M. (1994). The *DIRDIF-94* program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.
5. Sheldrick, G.M. (1997). *SHELXL97*. University of Göttingen, Germany.
6. Johnson, C.K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Table 1. Crystal data and structure refinement for C₁₄H₁₇NO.

Empirical formula	C ₁₄ H ₁₇ NO
Formula weight	215.29
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	a = 11.4179(4) Å b = 8.2418(3) Å β = 105.2341(16)°. c = 12.7785(5) Å
Volume	1160.25(7) Å ³
Z	4
Density (calculated)	1.232 Mg/m ³
Absorption coefficient	0.077 mm ⁻¹
F(000)	464
Crystal size	0.20 x 0.20 x 0.18 mm ³
Theta range for data collection	3.0 to 27.5°.
Index ranges	-14 ≤ h ≤ 14, -10 ≤ k ≤ 10, -16 ≤ l ≤ 16
Reflections collected	4830
Independent reflections	2638 [R(int) = 0.023]
Observed data [I > 2σ(I)]	1896
Completeness to theta = 27.5°	99.0 %
Absorption correction	Multi-scan method
Max. and min. transmission	0.986 and 0.985
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2638 / 0 / 145
Goodness-of-fit on F ²	1.03
Final R indices [I > 2σ(I)]	R1 = 0.042, wR2 = 0.107
R indices (all data)	R1 = 0.066, wR2 = 0.119
Weighting scheme	w = 1/[σ ² (Fo ²) + (0.0655P) ² + 0.0733P] where P = (Fo ² + 2Fc ²)/3
(Δ/θ) _{max}	0.00
Largest diff. peak and hole	0.19 and -0.17 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{C}_{14}\text{H}_{17}\text{NO}$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
O(1)	3380(1)	3972(1)	4663(1)	32(1)
N(1)	3776(1)	2103(1)	1821(1)	25(1)
C(1)	2650(1)	2005(1)	2027(1)	24(1)
C(2)	1688(1)	1233(2)	1278(1)	31(1)
C(3)	574(1)	1132(2)	1491(1)	37(1)
C(4)	389(1)	1775(2)	2450(1)	39(1)
C(5)	1325(1)	2513(2)	3185(1)	33(1)
C(6)	2480(1)	2651(1)	2992(1)	25(1)
C(7)	3500(1)	3403(1)	3780(1)	26(1)
C(8)	4621(1)	3425(1)	3488(1)	26(1)
C(9)	4741(1)	2789(1)	2531(1)	24(1)
C(10)	5929(1)	2761(1)	2229(1)	26(1)
C(11)	5935(1)	3639(1)	1176(1)	26(1)
C(12)	7143(1)	3445(1)	897(1)	29(1)
C(13)	7219(1)	4381(2)	-111(1)	29(1)
C(14)	8395(1)	4080(2)	-426(1)	42(1)

Table 3. Bond lengths [$\text{\AA}$], angles [$^\circ$] and H-bonds [$\text{\AA}$ and $^\circ$] for $\text{C}_{14}\text{H}_{17}\text{NO}$.

O(1)-C(7)	1.2619(13)
N(1)-C(9)	1.3537(15)
N(1)-C(1)	1.3811(14)
C(1)-C(6)	1.4019(16)
C(1)-C(2)	1.4054(16)
C(2)-C(3)	1.3715(17)
C(3)-C(4)	1.4007(18)
C(4)-C(5)	1.3662(19)
C(5)-C(6)	1.4085(16)
C(6)-C(7)	1.4627(17)
C(7)-C(8)	1.4247(16)
C(8)-C(9)	1.3707(15)
C(9)-C(10)	1.5041(15)
C(10)-C(11)	1.5297(15)
C(11)-C(12)	1.5216(15)
C(12)-C(13)	1.5236(16)
C(13)-C(14)	1.5189(16)
C(9)-N(1)-C(1)	122.07(9)
N(1)-C(1)-C(6)	119.80(10)
N(1)-C(1)-C(2)	119.75(10)
C(6)-C(1)-C(2)	120.44(10)
C(3)-C(2)-C(1)	119.44(11)
C(2)-C(3)-C(4)	120.78(12)
C(5)-C(4)-C(3)	119.95(12)
C(4)-C(5)-C(6)	120.96(11)
C(1)-C(6)-C(5)	118.42(11)
C(1)-C(6)-C(7)	119.82(10)
C(5)-C(6)-C(7)	121.74(10)
O(1)-C(7)-C(8)	123.06(11)
O(1)-C(7)-C(6)	121.30(11)
C(8)-C(7)-C(6)	115.64(10)
C(9)-C(8)-C(7)	122.44(11)
N(1)-C(9)-C(8)	120.22(10)

N(1)-C(9)-C(10)	116.85(9)
C(8)-C(9)-C(10)	122.90(10)
C(9)-C(10)-C(11)	115.53(9)
C(12)-C(11)-C(10)	111.76(9)
C(11)-C(12)-C(13)	113.68(10)
C(14)-C(13)-C(12)	113.03(10)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(1)#1	0.88	1.99	2.8172(12)	157

Symmetry transformations used to generate equivalent atoms:

#1 x, -y+1/2, z-1/2

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{C}_{14}\text{H}_{17}\text{NO}$.

The anisotropic displacement factor exponent takes the form:

$$-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$$

Atom	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
O(1)	41(1)	35(1)	22(1)	-2(1)	12(1)	3(1)
N(1)	28(1)	28(1)	20(1)	-1(1)	10(1)	-2(1)
C(1)	26(1)	26(1)	22(1)	5(1)	8(1)	0(1)
C(2)	33(1)	37(1)	22(1)	1(1)	8(1)	-4(1)
C(3)	29(1)	50(1)	30(1)	2(1)	4(1)	-7(1)
C(4)	27(1)	56(1)	36(1)	7(1)	12(1)	2(1)
C(5)	32(1)	40(1)	28(1)	4(1)	12(1)	6(1)
C(6)	29(1)	26(1)	22(1)	5(1)	8(1)	4(1)
C(7)	34(1)	22(1)	21(1)	4(1)	8(1)	3(1)
C(8)	31(1)	25(1)	21(1)	2(1)	4(1)	-2(1)
C(9)	28(1)	22(1)	24(1)	5(1)	7(1)	0(1)
C(10)	26(1)	28(1)	26(1)	2(1)	8(1)	-1(1)
C(11)	25(1)	29(1)	24(1)	-1(1)	8(1)	-2(1)
C(12)	26(1)	31(1)	30(1)	1(1)	9(1)	-1(1)
C(13)	28(1)	34(1)	28(1)	-2(1)	11(1)	-3(1)
C(14)	35(1)	55(1)	41(1)	6(1)	19(1)	0(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{C}_{14}\text{H}_{17}\text{NO}$.

Atom	x	y	z	U(eq)
H(1)	3868	1707	1208	30
H(2)	1809	785	629	37
H(3)	-80	621	983	44
H(4)	-386	1697	2589	47
H(5)	1195	2939	3836	39
H(8)	5311	3898	3975	31
H(10A)	6162	1615	2166	32
H(10B)	6558	3255	2828	32
H(11A)	5277	3198	576	31
H(11B)	5772	4807	1251	31
H(12A)	7280	2279	784	34
H(12B)	7802	3819	1520	34
H(13A)	6527	4066	-724	35
H(13B)	7146	5556	20	35
H(14A)	8390	4702	-1080	51
H(14B)	8468	2921	-568	51
H(14C)	9083	4422	168	51

Table 6. Torsion angles [$^{\circ}$] for C₁₄H₁₇NO.

C(9)-N(1)-C(1)-C(6)	0.96(16)
C(9)-N(1)-C(1)-C(2)	-177.93(10)
N(1)-C(1)-C(2)-C(3)	179.67(10)
C(6)-C(1)-C(2)-C(3)	0.78(17)
C(1)-C(2)-C(3)-C(4)	-0.63(19)
C(2)-C(3)-C(4)-C(5)	0.0(2)
C(3)-C(4)-C(5)-C(6)	0.44(19)
N(1)-C(1)-C(6)-C(5)	-179.21(9)
C(2)-C(1)-C(6)-C(5)	-0.33(16)
N(1)-C(1)-C(6)-C(7)	-0.89(16)
C(2)-C(1)-C(6)-C(7)	177.99(10)
C(4)-C(5)-C(6)-C(1)	-0.28(17)
C(4)-C(5)-C(6)-C(7)	-178.57(11)
C(1)-C(6)-C(7)-O(1)	-178.90(10)
C(5)-C(6)-C(7)-O(1)	-0.63(17)
C(1)-C(6)-C(7)-C(8)	0.33(15)
C(5)-C(6)-C(7)-C(8)	178.60(10)
O(1)-C(7)-C(8)-C(9)	179.40(10)
C(6)-C(7)-C(8)-C(9)	0.19(15)
C(1)-N(1)-C(9)-C(8)	-0.44(16)
C(1)-N(1)-C(9)-C(10)	177.64(9)
C(7)-C(8)-C(9)-N(1)	-0.15(16)
C(7)-C(8)-C(9)-C(10)	-178.11(9)
N(1)-C(9)-C(10)-C(11)	60.54(13)
C(8)-C(9)-C(10)-C(11)	-121.43(11)
C(9)-C(10)-C(11)-C(12)	-175.99(9)
C(10)-C(11)-C(12)-C(13)	-176.61(9)
C(11)-C(12)-C(13)-C(14)	-175.86(10)

Crystal Structure of **22**

Experimental:

A colorless plate crystal of $C_{21}H_{22}INO_6S$ was coated with Paratone 8277 oil (Exxon) and mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo- $K\alpha$ radiation. Cell constants obtained from the refinement¹ of 5049 reflections in the range $1.0 < \theta < 27.5^\circ$ corresponded to a primitive triclinic cell; details of crystal data and structure refinement have been provided in Table 1. The data were collected² at a temperature of 203(2) K using the ω and ϕ scans to a maximum θ value of 27.4° . The data were corrected for Lorentz and polarization effects and for absorption using multi-scan method¹. Since the crystal did not show any sign of decay during data collection a decay correction was deemed unnecessary.

The structure was solved by the direct methods³ and expanded using Fourier techniques⁴. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from a difference map, were included at geometrically idealized positions and were not refined. The final cycle of full-matrix least-squares refinement using SHELXL97⁵ converged (largest parameter shift was 0.001 times its esd) with unweighted and weighted agreement factors, $R = 0.040$ and $wR = 0.095$ (all data), respectively, and goodness of fit, $S = 0.96$. The weighting scheme was based on counting statistics and the final difference map was essentially featureless. The figures were plotted with the aid of ORTEPII⁶.

References:

7. Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307.
8. Hooft, R. (1998). *COLLECT*. Nonius BV, Delft. The Netherlands.
9. Altomare, A., Cascarano, M., Giacovazzo, C. & Guagliardi, A. (1993). *SIR92*. J. Appl. Cryst., **26**, 343
10. Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. & Smits, J.M.M. (1994). The *DIRDIF-94* program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.
11. Sheldrick, G.M. (1997). *SHELXL97*. University of Göttingen, Germany.
12. Johnson, C.K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Table 1. Crystal data and structure refinement for C₂₁H₂₂INO₆S.

Empirical formula	C ₂₁ H ₂₂ INO ₆ S
Formula weight	543.36
Temperature	203(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 9.5402(3) Å α = 106.4566(15)°. b = 11.6855(4) Å β = 104.8958(17)°. c = 11.8916(4) Å γ = 102.346(2)°.
Volume	1168.43(7) Å ³
Z	2
Density (calculated)	1.544 Mg/m ³
Absorption coefficient	1.50 mm ⁻¹
F(000)	544
Crystal size	0.18 x 0.15 x 0.08 mm ³
Theta range for data collection	1.90 to 27.4°.
Index ranges	-12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15
Reflections collected	9928
Independent reflections	5289 [R(int) = 0.047]
Observed data [I > 2σ(I)]	3379
Completeness to theta = 27.4°	99.1 %
Absorption correction	Multi-scan method
Max. and min. transmission	0.890 and 0.775
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5289 / 0 / 271
Goodness-of-fit on F ²	0.96
Final R indices [I > 2σ(I)]	R1 = 0.040, wR2 = 0.080
R indices (all data)	R1 = 0.089, wR2 = 0.095
Weighting scheme	w = 1/[σ ² (Fo ²) + (0.0425P) ²] where P = (Fo ² + 2Fc ²)/3
(Δ/θ) _{max}	0.001
Largest diff. peak and hole	0.64 and -0.67 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{C}_{21}\text{H}_{22}\text{INO}_6\text{S}$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
I(1)	11443(1)	6787(1)	1363(1)	43(1)
S(1)	6606(1)	3823(1)	3410(1)	29(1)
O(1)	12409(3)	10877(3)	6872(3)	53(1)
O(2)	13402(3)	11086(2)	5402(3)	48(1)
O(3)	7261(3)	4097(2)	641(2)	36(1)
O(4)	11021(3)	3347(3)	3253(2)	38(1)
O(5)	6233(3)	4871(2)	3156(3)	37(1)
O(6)	6666(3)	3697(3)	4589(2)	40(1)
N(1)	8951(3)	5487(3)	2484(3)	26(1)
C(1)	9839(4)	6749(3)	3297(3)	27(1)
C(2)	10937(4)	7492(3)	3001(3)	32(1)
C(3)	11779(4)	8700(3)	3810(3)	37(1)
C(4)	11565(4)	9182(3)	4938(3)	31(1)
C(5)	10479(4)	8440(3)	5243(3)	31(1)
C(6)	9616(4)	7240(3)	4422(3)	29(1)
C(7)	12485(4)	10464(4)	5852(4)	37(1)
C(8)	14374(5)	12349(4)	6222(4)	55(1)
C(9)	7832(4)	5187(4)	1355(3)	30(1)
C(10)	7327(5)	6229(4)	1059(4)	44(1)
C(11)	9281(4)	4494(3)	2881(3)	24(1)
C(12)	10747(4)	4288(4)	2780(3)	30(1)
C(13)	12392(5)	3093(5)	3161(5)	59(1)
C(14)	8369(4)	3780(3)	3258(3)	25(1)
C(15)	5312(4)	2420(3)	2233(3)	26(1)
C(16)	4607(4)	2435(4)	1073(3)	35(1)
C(17)	3591(4)	1323(4)	145(3)	37(1)
C(18)	3299(4)	220(4)	380(4)	34(1)
C(19)	4026(5)	228(4)	1542(4)	45(1)
C(20)	5047(4)	1331(4)	2480(4)	38(1)
C(21)	2180(5)	-975(4)	-640(4)	53(1)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for $\text{C}_{21}\text{H}_{22}\text{INO}_6\text{S}$.

I(1)-C(2)	2.109(3)
S(1)-O(5)	1.435(3)
S(1)-O(6)	1.438(3)
S(1)-C(14)	1.747(3)
S(1)-C(15)	1.765(4)
O(1)-C(7)	1.199(4)
O(2)-C(7)	1.330(5)
O(2)-C(8)	1.457(4)
O(3)-C(9)	1.221(4)
O(4)-C(12)	1.411(4)
O(4)-C(13)	1.425(4)
N(1)-C(9)	1.378(4)
N(1)-C(11)	1.435(4)
N(1)-C(1)	1.437(4)
C(1)-C(6)	1.389(5)
C(1)-C(2)	1.396(5)
C(2)-C(3)	1.383(5)
C(3)-C(4)	1.385(5)
C(4)-C(5)	1.394(5)
C(4)-C(7)	1.491(5)
C(5)-C(6)	1.384(5)
C(9)-C(10)	1.498(5)
C(11)-C(14)	1.325(5)
C(11)-C(12)	1.497(5)
C(15)-C(20)	1.372(5)
C(15)-C(16)	1.378(5)
C(16)-C(17)	1.394(5)
C(17)-C(18)	1.380(5)
C(18)-C(19)	1.374(6)
C(18)-C(21)	1.516(5)
C(19)-C(20)	1.394(5)
O(5)-S(1)-O(6)	119.53(17)
O(5)-S(1)-C(14)	110.46(16)

O(6)-S(1)-C(14)	105.85(16)
O(5)-S(1)-C(15)	109.03(17)
O(6)-S(1)-C(15)	107.25(16)
C(14)-S(1)-C(15)	103.50(16)
C(7)-O(2)-C(8)	116.8(3)
C(12)-O(4)-C(13)	112.3(3)
C(9)-N(1)-C(11)	119.0(3)
C(9)-N(1)-C(1)	124.0(3)
C(11)-N(1)-C(1)	117.0(3)
C(6)-C(1)-C(2)	118.9(3)
C(6)-C(1)-N(1)	119.0(3)
C(2)-C(1)-N(1)	122.1(3)
C(3)-C(2)-C(1)	120.5(3)
C(3)-C(2)-I(1)	118.0(3)
C(1)-C(2)-I(1)	121.4(3)
C(2)-C(3)-C(4)	120.4(3)
C(3)-C(4)-C(5)	119.3(3)
C(3)-C(4)-C(7)	122.0(3)
C(5)-C(4)-C(7)	118.7(3)
C(6)-C(5)-C(4)	120.3(3)
C(5)-C(6)-C(1)	120.6(3)
O(1)-C(7)-O(2)	124.3(4)
O(1)-C(7)-C(4)	123.8(4)
O(2)-C(7)-C(4)	111.8(3)
O(3)-C(9)-N(1)	120.2(3)
O(3)-C(9)-C(10)	121.9(3)
N(1)-C(9)-C(10)	117.9(3)
C(14)-C(11)-N(1)	124.4(3)
C(14)-C(11)-C(12)	121.9(3)
N(1)-C(11)-C(12)	113.6(3)
O(4)-C(12)-C(11)	109.7(3)
C(11)-C(14)-S(1)	129.8(3)
C(20)-C(15)-C(16)	121.1(3)
C(20)-C(15)-S(1)	119.6(3)
C(16)-C(15)-S(1)	119.3(3)
C(15)-C(16)-C(17)	119.0(4)

C(18)-C(17)-C(16)	120.7(4)
C(19)-C(18)-C(17)	119.2(4)
C(19)-C(18)-C(21)	121.0(4)
C(17)-C(18)-C(21)	119.8(4)
C(18)-C(19)-C(20)	120.9(4)
C(15)-C(20)-C(19)	119.1(4)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{C}_{21}\text{H}_{22}\text{INO}_6\text{S}$.

The anisotropic displacement factor exponent takes the form:

$$-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$$

Atom	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
I(1)	53(1)	35(1)	31(1)	4(1)	21(1)	-6(1)
S(1)	25(1)	27(1)	33(1)	8(1)	12(1)	5(1)
O(1)	76(2)	35(2)	32(2)	1(1)	14(2)	6(2)
O(2)	50(2)	25(2)	51(2)	0(1)	16(2)	-5(1)
O(3)	39(2)	29(2)	27(1)	4(1)	8(1)	-1(1)
O(4)	37(2)	47(2)	51(2)	28(1)	25(1)	25(1)
O(5)	33(1)	24(2)	56(2)	12(1)	16(1)	13(1)
O(6)	41(2)	45(2)	30(1)	10(1)	17(1)	4(1)
N(1)	31(2)	20(2)	24(2)	7(1)	8(1)	2(1)
C(1)	29(2)	22(2)	24(2)	8(2)	5(2)	3(2)
C(2)	38(2)	25(2)	26(2)	6(2)	11(2)	2(2)
C(3)	45(2)	26(2)	36(2)	13(2)	15(2)	2(2)
C(4)	37(2)	22(2)	27(2)	7(2)	5(2)	6(2)
C(5)	40(2)	26(2)	24(2)	6(2)	8(2)	14(2)
C(6)	32(2)	27(2)	28(2)	12(2)	11(2)	10(2)
C(7)	42(2)	25(2)	36(2)	8(2)	4(2)	8(2)
C(8)	49(3)	24(2)	64(3)	-3(2)	11(2)	-6(2)
C(9)	31(2)	33(2)	25(2)	12(2)	10(2)	3(2)
C(10)	53(3)	39(3)	37(2)	19(2)	4(2)	15(2)
C(11)	24(2)	21(2)	20(2)	3(2)	6(2)	3(2)
C(12)	28(2)	31(2)	30(2)	9(2)	13(2)	6(2)
C(13)	44(3)	81(4)	77(3)	39(3)	33(3)	40(3)
C(14)	22(2)	28(2)	26(2)	11(2)	7(2)	10(2)
C(15)	21(2)	26(2)	32(2)	11(2)	13(2)	7(2)
C(16)	35(2)	36(2)	37(2)	17(2)	12(2)	9(2)
C(17)	36(2)	39(3)	26(2)	11(2)	2(2)	6(2)
C(18)	30(2)	26(2)	41(2)	5(2)	18(2)	5(2)
C(19)	55(3)	25(2)	48(3)	15(2)	14(2)	2(2)
C(20)	39(2)	37(3)	33(2)	14(2)	8(2)	4(2)
C(21)	54(3)	36(3)	49(3)	4(2)	10(2)	0(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{C}_{21}\text{H}_{22}\text{INO}_6\text{S}$.

Atom	x	y	z	U(eq)
H(3)	12500	9198	3594	44
H(5)	10333	8757	6009	37
H(6)	8872	6752	4628	34
H(8A)	14991	12707	5800	82
H(8B)	15033	12314	6975	82
H(8C)	13744	12867	6439	82
H(10A)	7917	7019	1736	66
H(10B)	6254	6077	957	66
H(10C)	7484	6266	295	66
H(12A)	10688	4033	1906	37
H(12B)	11589	5071	3253	37
H(13A)	12535	2444	3497	88
H(13B)	13250	3851	3631	88
H(13C)	12323	2811	2294	88
H(14)	8725	3155	3476	30
H(16)	4809	3183	908	42
H(17)	3098	1325	-648	44
H(19)	3833	-520	1706	54
H(20)	5546	1329	3271	46
H(21A)	1787	-803	-1391	79
H(21B)	1343	-1283	-372	79
H(21C)	2694	-1603	-808	79

Table 6. Torsion angles [$^{\circ}$] for $C_{21}H_{22}INO_6S$.

C(9)-N(1)-C(1)-C(6)	110.7(4)
C(11)-N(1)-C(1)-C(6)	-70.1(4)
C(9)-N(1)-C(1)-C(2)	-70.3(5)
C(11)-N(1)-C(1)-C(2)	108.9(4)
C(6)-C(1)-C(2)-C(3)	-0.6(6)
N(1)-C(1)-C(2)-C(3)	-179.6(3)
C(6)-C(1)-C(2)-I(1)	176.4(3)
N(1)-C(1)-C(2)-I(1)	-2.6(5)
C(1)-C(2)-C(3)-C(4)	1.3(6)
I(1)-C(2)-C(3)-C(4)	-175.8(3)
C(2)-C(3)-C(4)-C(5)	-0.7(6)
C(2)-C(3)-C(4)-C(7)	178.0(4)
C(3)-C(4)-C(5)-C(6)	-0.5(6)
C(7)-C(4)-C(5)-C(6)	-179.3(3)
C(4)-C(5)-C(6)-C(1)	1.2(5)
C(2)-C(1)-C(6)-C(5)	-0.7(5)
N(1)-C(1)-C(6)-C(5)	178.3(3)
C(8)-O(2)-C(7)-O(1)	0.4(6)
C(8)-O(2)-C(7)-C(4)	-179.3(3)
C(3)-C(4)-C(7)-O(1)	-174.4(4)
C(5)-C(4)-C(7)-O(1)	4.3(6)
C(3)-C(4)-C(7)-O(2)	5.2(5)
C(5)-C(4)-C(7)-O(2)	-176.1(3)
C(11)-N(1)-C(9)-O(3)	-8.7(4)
C(1)-N(1)-C(9)-O(3)	170.5(3)
C(11)-N(1)-C(9)-C(10)	169.9(3)
C(1)-N(1)-C(9)-C(10)	-11.0(5)
C(9)-N(1)-C(11)-C(14)	-71.6(4)
C(1)-N(1)-C(11)-C(14)	109.2(4)
C(9)-N(1)-C(11)-C(12)	105.8(3)
C(1)-N(1)-C(11)-C(12)	-73.4(4)
C(13)-O(4)-C(12)-C(11)	179.0(3)
C(14)-C(11)-C(12)-O(4)	-5.8(5)
N(1)-C(11)-C(12)-O(4)	176.8(3)

N(1)-C(11)-C(14)-S(1)	-1.2(5)
C(12)-C(11)-C(14)-S(1)	-178.3(3)
O(5)-S(1)-C(14)-C(11)	-4.9(4)
O(6)-S(1)-C(14)-C(11)	-135.6(3)
C(15)-S(1)-C(14)-C(11)	111.7(3)
O(5)-S(1)-C(15)-C(20)	-155.7(3)
O(6)-S(1)-C(15)-C(20)	-25.0(3)
C(14)-S(1)-C(15)-C(20)	86.7(3)
O(5)-S(1)-C(15)-C(16)	25.5(3)
O(6)-S(1)-C(15)-C(16)	156.3(3)
C(14)-S(1)-C(15)-C(16)	-92.0(3)
C(20)-C(15)-C(16)-C(17)	1.1(5)
S(1)-C(15)-C(16)-C(17)	179.8(3)
C(15)-C(16)-C(17)-C(18)	-0.5(5)
C(16)-C(17)-C(18)-C(19)	-0.1(5)
C(16)-C(17)-C(18)-C(21)	179.5(4)
C(17)-C(18)-C(19)-C(20)	0.1(6)
C(21)-C(18)-C(19)-C(20)	-179.6(4)
C(16)-C(15)-C(20)-C(19)	-1.1(5)
S(1)-C(15)-C(20)-C(19)	-179.8(3)
C(18)-C(19)-C(20)-C(15)	0.5(6)

Crystal Structure of **31**

Experimental:

A colorless prismatic crystal of $C_{22}H_{21}NO_6S \cdot CH_2Cl_2$ was coated with Paratone 8277 oil (Exxon) and mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo-K α radiation. Cell constants obtained from the refinement¹ of 10644 reflections in the range $6.0 < \theta < 27.5^\circ$ corresponded to a primitive monoclinic cell; details of crystal data and structure refinement have been provided in Table 1. The data were collected² at a temperature of 173(2) K using the ω and ϕ scans to a maximum θ value of 27.5° . The data were corrected for Lorentz and polarization effects and for absorption using multi-scan method¹. Since the crystal did not show any sign of decay during data collection a decay correction was deemed unnecessary.

The structure was solved by the direct methods³ and expanded using Fourier techniques⁴. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions and were not refined. The final cycle of full-matrix least-squares refinement using SHELXL97⁵ converged with unweighted and weighted agreement factors, $R = 0.051$ and $wR = 0.107$ (all data), respectively, and goodness of fit, $S = 1.01$. The absolute structure was established by the Flack method⁶. The Flack parameter for the inverted structure was 0.89(7). Therefore, the inverted structure was rejected as the one present in the crystal. The weighting scheme was based on counting statistics and the final difference Fourier map was essentially featureless. The figures were plotted with the aid of ORTEPII⁷.

References:

13. Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307.
14. Hooft, R. (1998). *COLLECT*. Nonius BV, Delft. The Netherlands.
15. Altomare, A., Cascarano, M., Giacovazzo, C. & Guagliardi, A. (1993). *SIR92*. J. Appl. Cryst., **26**, 343
16. Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. & Smits, J.M.M. (1994). The *DIRDIF-94* program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.
17. Sheldrick, G.M. (1997). *SHELXL97*. University of Göttingen, Germany.
18. Flack, H. D. (1983). *Acta Cryst.* A39, 876.
19. Johnson, C.K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Table 1. Crystal data and structure refinement for $\text{C}_{22}\text{H}_{21}\text{NO}_6\text{S} \cdot \text{CH}_2\text{Cl}_2$.

Empirical formula	$\text{C}_{22}\text{H}_{21}\text{NO}_6\text{S} \cdot \text{CH}_2\text{Cl}_2$	
Formula weight	512.38	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	$a = 9.0459(13)$ Å	
	$b = 13.662(3)$ Å	$\beta = 91.610(13)^\circ$.
	$c = 9.4380(15)$ Å	
Volume	$1165.9(4)$ Å ³	
Z	2	
Density (calculated)	1.459 Mg/m ³	
Absorption coefficient	0.41 mm ⁻¹	
F(000)	532	
Crystal size	0.18 x 0.16 x 0.16 mm ³	
Theta range for data collection	6.0 to 27.5°.	
Index ranges	$-11 \leq h \leq 11$, $-17 \leq k \leq 17$, $-11 \leq l \leq 12$	
Reflections collected	10644	
Independent reflections	5070 [R(int) = 0.053]	
Completeness to $\theta = 27.5^\circ$	98.4 %	
Absorption correction	Multi-scan method	
Max. and min. transmission	0.937 and 0.930	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5070 / 1 / 298	
Goodness-of-fit on F^2	1.01	
Final R indices [$I > 2\sigma(I)$]	R1 = 0.051, wR2 = 0.095	
R indices (all data)	R1 = 0.093, wR2 = 0.107	
Absolute structure parameter	0.10(6)	
Largest diff. peak and hole	0.38 and -0.41 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{C}_{22}\text{H}_{21}\text{NO}_6\text{S} \cdot \text{CH}_2\text{Cl}_2$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
Cl(1)	2059(1)	-10083(1)	-13211(1)	64(1)
Cl(2)	3385(2)	-10397(1)	-15958(1)	85(1)
S(1)	-3842(1)	-8781(1)	-8767(1)	26(1)
O(1)	-7100(3)	-9903(2)	-9285(3)	37(1)
O(2)	-11443(3)	-7873(2)	-5037(3)	40(1)
O(3)	-11102(2)	-9345(2)	-6026(2)	35(1)
O(4)	-5726(2)	-5519(2)	-8189(2)	31(1)
O(5)	-4098(3)	-8195(2)	-7533(2)	34(1)
O(6)	-3566(2)	-9812(2)	-8597(2)	35(1)
N(1)	-6205(3)	-6983(2)	-9325(3)	23(1)
C(1)	-7328(3)	-7329(2)	-8436(3)	22(1)
C(2)	-8127(3)	-6707(2)	-7577(3)	28(1)
C(3)	-9219(3)	-7077(2)	-6741(3)	28(1)
C(4)	-9596(3)	-8059(2)	-6769(3)	25(1)
C(5)	-8818(3)	-8678(2)	-7627(3)	25(1)
C(6)	-7674(3)	-8333(2)	-8443(3)	23(1)
C(7)	-6797(3)	-9042(2)	-9237(3)	26(1)
C(8)	-5444(3)	-8646(2)	-9971(3)	24(1)
C(9)	-5679(3)	-7614(2)	-10430(3)	22(1)
C(10)	-5437(3)	-7268(2)	-11723(3)	26(1)
C(11)	-4797(4)	-7799(2)	-12945(3)	33(1)
C(12)	-5745(4)	-7671(3)	-14300(4)	44(1)
C(13)	-10802(4)	-8396(2)	-5860(3)	28(1)
C(14)	-12275(4)	-9722(3)	-5184(4)	40(1)
C(15)	-5465(3)	-6120(2)	-9100(3)	27(1)
C(16)	-2415(3)	-8251(2)	-9720(3)	25(1)
C(17)	-1728(3)	-8760(3)	-10780(3)	33(1)
C(18)	-697(4)	-8294(3)	-11580(4)	44(1)
C(19)	-354(4)	-7325(3)	-11375(4)	38(1)
C(20)	-1014(4)	-6838(3)	-10283(4)	38(1)

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C(21)	-2043(3)	-7289(2)	-9447(4)	31(1)
C(22)	692(4)	-6797(4)	-12327(5)	62(1)
C(23)	3209(5)	-10817(3)	-14251(4)	51(1)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for $\text{C}_{22}\text{H}_{21}\text{NO}_6\text{S} \cdot \text{CH}_2\text{Cl}_2$.

Cl(1)-C(23)	1.763(4)
Cl(2)-C(23)	1.722(4)
S(1)-O(5)	1.437(2)
S(1)-O(6)	1.438(2)
S(1)-C(16)	1.750(3)
S(1)-C(8)	1.826(3)
O(1)-C(7)	1.208(3)
O(2)-C(13)	1.215(4)
O(3)-C(13)	1.334(4)
O(3)-C(14)	1.438(4)
O(4)-C(15)	1.216(4)
N(1)-C(15)	1.370(4)
N(1)-C(1)	1.416(4)
N(1)-C(9)	1.444(4)
C(1)-C(2)	1.391(4)
C(1)-C(6)	1.407(4)
C(2)-C(3)	1.378(4)
C(3)-C(4)	1.385(4)
C(4)-C(5)	1.378(4)
C(4)-C(13)	1.479(4)
C(5)-C(6)	1.390(4)
C(6)-C(7)	1.471(4)
C(7)-C(8)	1.523(4)
C(8)-C(9)	1.489(4)
C(9)-C(10)	1.332(4)
C(10)-C(11)	1.493(4)
C(11)-C(12)	1.530(5)
C(16)-C(21)	1.380(4)
C(16)-C(17)	1.381(4)
C(17)-C(18)	1.373(5)
C(18)-C(19)	1.372(5)
C(19)-C(20)	1.377(5)
C(19)-C(22)	1.506(5)
C(20)-C(21)	1.382(5)

O(5)-S(1)-O(6)	119.08(14)
O(5)-S(1)-C(16)	108.90(14)
O(6)-S(1)-C(16)	109.52(14)
O(5)-S(1)-C(8)	107.74(13)
O(6)-S(1)-C(8)	107.51(13)
C(16)-S(1)-C(8)	102.85(14)
C(13)-O(3)-C(14)	115.7(3)
C(15)-N(1)-C(1)	123.4(3)
C(15)-N(1)-C(9)	117.1(2)
C(1)-N(1)-C(9)	119.0(2)
C(2)-C(1)-C(6)	118.6(3)
C(2)-C(1)-N(1)	122.3(3)
C(6)-C(1)-N(1)	119.0(3)
C(3)-C(2)-C(1)	120.2(3)
C(2)-C(3)-C(4)	121.6(3)
C(5)-C(4)-C(3)	118.4(3)
C(5)-C(4)-C(13)	123.2(3)
C(3)-C(4)-C(13)	118.4(3)
C(4)-C(5)-C(6)	121.2(3)
C(5)-C(6)-C(1)	119.8(3)
C(5)-C(6)-C(7)	118.6(3)
C(1)-C(6)-C(7)	121.5(3)
O(1)-C(7)-C(6)	122.4(3)
O(1)-C(7)-C(8)	120.9(3)
C(6)-C(7)-C(8)	116.7(2)
C(9)-C(8)-C(7)	111.1(2)
C(9)-C(8)-S(1)	112.4(2)
C(7)-C(8)-S(1)	108.3(2)
C(10)-C(9)-N(1)	121.1(3)
C(10)-C(9)-C(8)	125.2(3)
N(1)-C(9)-C(8)	113.7(2)
C(9)-C(10)-C(11)	127.8(3)
C(10)-C(11)-C(12)	111.7(3)
O(2)-C(13)-O(3)	123.2(3)
O(2)-C(13)-C(4)	124.1(3)

O(3)-C(13)-C(4)	112.7(3)
O(4)-C(15)-N(1)	125.9(3)
C(21)-C(16)-C(17)	120.2(3)
C(21)-C(16)-S(1)	118.5(2)
C(17)-C(16)-S(1)	121.2(2)
C(18)-C(17)-C(16)	119.4(3)
C(17)-C(18)-C(19)	121.7(3)
C(18)-C(19)-C(20)	118.1(3)
C(18)-C(19)-C(22)	121.4(4)
C(20)-C(19)-C(22)	120.5(4)
C(19)-C(20)-C(21)	121.7(3)
C(16)-C(21)-C(20)	118.8(3)
Cl(2)-C(23)-Cl(1)	113.7(2)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{C}_{22}\text{H}_{21}\text{NO}_6\text{S}$
 $\cdot \text{CH}_2\text{Cl}_2$. The anisotropic displacement factor exponent takes the form:

$$-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$$

Atom	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Cl(1)	66(1)	54(1)	74(1)	-8(1)	25(1)	-3(1)
Cl(2)	130(1)	74(1)	53(1)	27(1)	23(1)	42(1)
S(1)	31(1)	24(1)	22(1)	1(1)	1(1)	1(1)
O(1)	45(1)	20(1)	47(2)	-6(1)	18(1)	-1(1)
O(2)	45(2)	40(1)	37(2)	-2(1)	16(1)	-1(1)
O(3)	33(1)	29(1)	43(2)	4(1)	10(1)	-3(1)
O(4)	43(1)	20(1)	31(1)	-6(1)	4(1)	-3(1)
O(5)	41(1)	39(1)	21(1)	-3(1)	3(1)	1(1)
O(6)	43(1)	26(1)	36(1)	9(1)	-5(1)	3(1)
N(1)	31(1)	19(1)	20(1)	1(1)	4(1)	-1(1)
C(1)	24(2)	23(1)	20(2)	0(1)	-2(1)	0(1)
C(2)	34(2)	20(2)	31(2)	1(1)	4(2)	-3(1)
C(3)	30(2)	28(2)	27(2)	-5(1)	4(1)	3(1)
C(4)	24(2)	28(2)	23(2)	0(1)	0(1)	4(1)
C(5)	27(2)	23(2)	25(2)	-1(1)	0(1)	-2(1)
C(6)	26(2)	23(2)	21(2)	1(1)	-1(1)	-1(1)
C(7)	32(2)	20(2)	24(2)	-2(1)	0(1)	0(1)
C(8)	32(2)	22(2)	17(2)	-2(1)	2(1)	-1(1)
C(9)	24(2)	21(2)	22(2)	0(1)	4(1)	1(1)
C(10)	28(2)	24(2)	26(2)	3(1)	5(1)	4(1)
C(11)	41(2)	32(2)	26(2)	6(1)	12(2)	7(2)
C(12)	53(2)	50(2)	29(2)	-3(2)	10(2)	6(2)
C(13)	28(2)	31(2)	26(2)	3(1)	-2(1)	3(1)
C(14)	38(2)	40(2)	43(2)	11(2)	9(2)	-4(2)
C(15)	30(2)	19(2)	33(2)	6(1)	-1(1)	-3(1)
C(16)	23(2)	29(2)	24(2)	0(1)	-2(1)	0(1)
C(17)	31(2)	34(2)	35(2)	-8(2)	5(2)	-1(2)
C(18)	29(2)	65(3)	39(2)	-9(2)	10(2)	3(2)
C(19)	24(2)	50(2)	38(2)	9(2)	-2(2)	0(2)
C(20)	28(2)	34(2)	53(2)	5(2)	-2(2)	-1(2)

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C(21)	27(2)	26(2)	40(2)	0(2)	2(2)	1(1)
C(22)	33(2)	88(3)	63(3)	14(2)	4(2)	-11(2)
C(23)	64(3)	45(2)	43(2)	5(2)	3(2)	0(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{C}_{22}\text{H}_{21}\text{NO}_6\text{S} \cdot \text{CH}_2\text{Cl}_2$.

Atom	x	y	z	U(eq)
H(2)	-7919	-6025	-7567	34
H(3)	-9727	-6647	-6130	34
H(5)	-9067	-9353	-7661	30
H(8)	-5277	-9053	-10833	29
H(10)	-5704	-6605	-11887	31
H(11A)	-4718	-8504	-12715	40
H(11B)	-3788	-7549	-13105	40
H(12A)	-5296	-8032	-15076	52
H(12B)	-5803	-6974	-14545	52
H(12C)	-6741	-7924	-14148	52
H(14A)	-12412	-10420	-5385	48
H(14B)	-13193	-9369	-5418	48
H(14C)	-12018	-9633	-4177	48
H(15)	-4676	-5977	-9711	33
H(17)	-1966	-9428	-10955	40
H(18)	-209	-8651	-12293	53
H(20)	-755	-6176	-10099	46
H(21)	-2487	-6942	-8697	37
H(22A)	799	-6116	-12014	74
H(22B)	298	-6812	-13304	74
H(22C)	1660	-7120	-12280	74
H(23A)	4203	-10850	-13787	61
H(23B)	2803	-11490	-14286	61

Table 6. Torsion angles [$^{\circ}$] for $C_{22}H_{21}NO_6S \cdot CH_2Cl_2$.

C(15)-N(1)-C(1)-C(2)	22.6(4)
C(9)-N(1)-C(1)-C(2)	-164.9(3)
C(15)-N(1)-C(1)-C(6)	-158.8(3)
C(9)-N(1)-C(1)-C(6)	13.7(4)
C(6)-C(1)-C(2)-C(3)	0.8(4)
N(1)-C(1)-C(2)-C(3)	179.4(3)
C(1)-C(2)-C(3)-C(4)	-2.7(5)
C(2)-C(3)-C(4)-C(5)	2.1(5)
C(2)-C(3)-C(4)-C(13)	-178.8(3)
C(3)-C(4)-C(5)-C(6)	0.4(4)
C(13)-C(4)-C(5)-C(6)	-178.7(3)
C(4)-C(5)-C(6)-C(1)	-2.1(4)
C(4)-C(5)-C(6)-C(7)	174.5(3)
C(2)-C(1)-C(6)-C(5)	1.5(4)
N(1)-C(1)-C(6)-C(5)	-177.1(3)
C(2)-C(1)-C(6)-C(7)	-175.1(3)
N(1)-C(1)-C(6)-C(7)	6.3(4)
C(5)-C(6)-C(7)-O(1)	5.3(5)
C(1)-C(6)-C(7)-O(1)	-178.1(3)
C(5)-C(6)-C(7)-C(8)	-172.9(3)
C(1)-C(6)-C(7)-C(8)	3.7(4)
O(1)-C(7)-C(8)-C(9)	150.4(3)
C(6)-C(7)-C(8)-C(9)	-31.3(4)
O(1)-C(7)-C(8)-S(1)	-85.7(3)
C(6)-C(7)-C(8)-S(1)	92.6(3)
O(5)-S(1)-C(8)-C(9)	60.6(2)
O(6)-S(1)-C(8)-C(9)	-169.9(2)
C(16)-S(1)-C(8)-C(9)	-54.4(2)
O(5)-S(1)-C(8)-C(7)	-62.6(2)
O(6)-S(1)-C(8)-C(7)	66.9(2)
C(16)-S(1)-C(8)-C(7)	-177.5(2)
C(15)-N(1)-C(9)-C(10)	-49.9(4)
C(1)-N(1)-C(9)-C(10)	137.1(3)
C(15)-N(1)-C(9)-C(8)	129.9(3)

C(1)-N(1)-C(9)-C(8)	-43.1(4)
C(7)-C(8)-C(9)-C(10)	-130.0(3)
S(1)-C(8)-C(9)-C(10)	108.4(3)
C(7)-C(8)-C(9)-N(1)	50.2(3)
S(1)-C(8)-C(9)-N(1)	-71.3(3)
N(1)-C(9)-C(10)-C(11)	175.2(3)
C(8)-C(9)-C(10)-C(11)	-4.5(5)
C(9)-C(10)-C(11)-C(12)	130.5(4)
C(14)-O(3)-C(13)-O(2)	1.4(5)
C(14)-O(3)-C(13)-C(4)	-179.4(3)
C(5)-C(4)-C(13)-O(2)	175.6(3)
C(3)-C(4)-C(13)-O(2)	-3.5(5)
C(5)-C(4)-C(13)-O(3)	-3.6(4)
C(3)-C(4)-C(13)-O(3)	177.3(3)
C(1)-N(1)-C(15)-O(4)	-4.9(5)
C(9)-N(1)-C(15)-O(4)	-177.6(3)
O(5)-S(1)-C(16)-C(21)	-17.5(3)
O(6)-S(1)-C(16)-C(21)	-149.3(2)
C(8)-S(1)-C(16)-C(21)	96.6(3)
O(5)-S(1)-C(16)-C(17)	166.2(2)
O(6)-S(1)-C(16)-C(17)	34.4(3)
C(8)-S(1)-C(16)-C(17)	-79.7(3)
C(21)-C(16)-C(17)-C(18)	-1.5(5)
S(1)-C(16)-C(17)-C(18)	174.7(3)
C(16)-C(17)-C(18)-C(19)	-1.5(5)
C(17)-C(18)-C(19)-C(20)	3.6(5)
C(17)-C(18)-C(19)-C(22)	-175.4(3)
C(18)-C(19)-C(20)-C(21)	-2.8(5)
C(22)-C(19)-C(20)-C(21)	176.2(3)
C(17)-C(16)-C(21)-C(20)	2.2(5)
S(1)-C(16)-C(21)-C(20)	-174.1(2)
C(19)-C(20)-C(21)-C(16)	0.0(5)

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O=Cc1cc(OC(=O)C)cc(NC(=O)C1=CC=C(C=C1)C2=CC=CC=C2C3=CC=CC=C3C4=CC=CC=C4C5=CC=CC=C5C6=CC=CC=C6C7=CC=CC=C7C8=CC=CC=C8C9=CC=CC=C9C10=CC=CC=C10C11=CC=CC=C11C12=CC=CC=C12C13=CC=CC=C13C14=CC=CC=C14C15=CC=CC=C15C16=CC=CC=C16C17=CC=CC=C17C18=CC=CC=C18C19=CC=CC=C19C20=CC=CC=C20C21=CC=CC=C21C22=CC=CC=C22C23=CC=CC=C23C24=CC=CC=C24C25=CC=CC=C25C26=CC=CC=C26C27=CC=CC=C27C28=CC=CC=C28C29=CC=CC=C29C30=CC=CC=C30C31=CC=CC=C31C32=CC=CC=C32C33=CC=CC=C33C34=CC=CC=C34C35=CC=CC=C35C36=CC=CC=C36C37=CC=CC=C37C38=CC=CC=C38C39=CC=CC=C39C40=CC=CC=C40C41=CC=CC=C41C42=CC=CC=C42C43=CC=CC=C43C44=CC=CC=C44C45=CC=CC=C45C46=CC=CC=C46C47=CC=CC=C47C48=CC=CC=C48C49=CC=CC=C49C50=CC=CC=C50C51=CC=CC=C51C52=CC=CC=C52C53=CC=CC=C53C54=CC=CC=C54C55=CC=CC=C55C56=CC=CC=C56C57=CC=CC=C57C58=CC=CC=C58C59=CC=CC=C59C60=CC=CC=C60C61=CC=CC=C61C62=CC=CC=C62C63=CC=CC=C63C64=CC=CC=C64C65=CC=CC=C65C66=CC=CC=C66C67=CC=CC=C67C68=CC=CC=C68C69=CC=CC=C69C70=CC=CC=C70C71=CC=CC=C71C72=CC=CC=C72C73=CC=CC=C73C74=CC=CC=C74C75=CC=CC=C75C76=CC=CC=C76C77=CC=CC=C77C78=CC=CC=C78C79=CC=CC=C79C80=CC=CC=C80C81=CC=CC=C81C82=CC=CC=C82C83=CC=CC=C83C84=CC=CC=C84C85=CC=CC=C85C86=CC=CC=C86C87=CC=CC=C87C88=CC=CC=C88C89=CC=CC=C89C90=CC=CC=C90C91=CC=CC=C91C92=CC=CC=C92C93=CC=CC=C93C94=CC=CC=C94C95=CC=CC=C95C96=CC=CC=C96C97=CC=CC=C97C98=CC=CC=C98C99=CC=CC=C99C100=CC=CC=C100C101=CC=CC=C101C102=CC=CC=C102C103=CC=CC=C103C104=CC=CC=C104C105=CC=CC=C105C106=CC=CC=C106C107=CC=CC=C107C108=CC=CC=C108C109=CC=CC=C109C110=CC=CC=C110C111=CC=CC=C111C112=CC=CC=C112C113=CC=CC=C113C114=CC=CC=C114C115=CC=CC=C115C116=CC=CC=C116C117=CC=CC=C117C118=CC=CC=C118C119=CC=CC=C119C120=CC=CC=C120C121=CC=CC=C121C122=CC=CC=C122C123=CC=CC=C123C124=CC=CC=C124C125=CC=CC=C125C126=CC=CC=C126C127=CC=CC=C127C128=CC=CC=C128C129=CC=CC=C129C130=CC=CC=C130C131=CC=CC=C131C132=CC=CC=C132C133=CC=CC=C133C134=CC=CC=C134C135=CC=CC=C135C136=CC=CC=C136C137=CC=CC=C137C138=CC=CC=C138C139=CC=CC=C139C140=CC=CC=C140C141=CC=CC=C141C142=CC=CC=C142C143=CC=CC=C143C144=CC=CC=C144C145=CC=CC=C145C146=CC=CC=C146C147=CC=CC=C147C148=CC=CC=C148C149=CC=CC=C149C150=CC=CC=C150C151=CC=CC=C151C152=CC=CC=C152C153=CC=CC=C153C154=CC=CC=C154C155=CC=CC=C155C156=CC=CC=C156C157=CC=CC=C157C158=CC=CC=C158C159=CC=CC=C159C160=CC=CC=C160C161=CC=CC=C161C162=CC=CC=C162C163=CC=CC=C163C164=CC=CC=C164C165=CC=CC=C165C166=CC=CC=C166C167=CC=CC=C167C168=CC=CC=C168C169=CC=CC=C169C170=CC=CC=C170C171=CC=CC=C171C172=CC=CC=C172C173=CC=CC=C173C174=CC=CC=C174C175=CC=CC=C175C176=CC=CC=C176C177=CC=CC=C177C178=CC=CC=C178C179=CC=CC=C179C180=CC=CC=C180C181=CC=CC=C181C182=CC=CC=C182C183=CC=CC=C183C184=CC=CC=C184C185=CC=CC=C185C186=CC=CC=C186C187=CC=CC=C187C188=CC=CC=C188C189=CC=CC=C189C190=CC=CC=C190C191=CC=CC=C191C192=CC=CC=C192C193=CC=CC=C193C194=CC=CC=C194C195=CC=CC=C195C196=CC=CC=C196C197=CC=CC=C197C198=CC=CC=C198C199=CC=CC=C199C200=CC=CC=C200C201=CC=CC=C201C202=CC=CC=C202C203=CC=CC=C203C204=CC=CC=C204C205=CC=CC=C205C206=CC=CC=C206C207=CC=CC=C207C208=CC=CC=C208C209=CC=CC=C209C210=CC=CC=C210C211=CC=CC=C211C212=CC=CC=C212C213=CC=CC=C213C214=CC=CC=C214C215=CC=CC=C215C216=CC=CC=C216C217=CC=CC=C217C218=CC=CC=C218C219=CC=CC=C219C220=CC=CC=C220C221=CC=CC=C221C222=CC=CC=C222C223=CC=CC=C223C224=CC=CC=C224C225=CC=CC=C225C226=CC=CC=C226C227=CC=CC=C227C228=CC=CC=C228C229=CC=CC=C229C230=CC=CC=C230C231=CC=CC=C231C232=CC=CC=C232C233=CC=CC=C233C234=CC=CC=C234C235=CC=CC=C235C236=CC=CC=C236C237=CC=CC=C237C238=CC=CC=C238C239=CC=CC=C239C240=CC=CC=C240C241=CC=CC=C241C242=CC=CC=C242C243=CC=CC=C243C244=CC=CC=C244C245=CC=CC=C245C246=CC=CC=C246C247=CC=CC=C247C248=CC=CC=C248C249=CC=CC=C249C250=CC=CC=C250C251=CC=CC=C251C252=CC=CC=C252C253=CC=CC=C253C254=CC=CC=C254C255=CC=CC=C255C256=CC=CC=C256C257=CC=CC=C257C258=CC=CC=C258C259=CC=CC=C259C260=CC=CC=C260C261=CC=CC=C261C262=CC=CC=C262C263=CC=CC=C263C264=CC=CC=C264C265=CC=CC=C265C266=CC=CC=C266C267=CC=CC=C267C268=CC=CC=C268C269=CC=CC=C269C270=CC=CC=C270C271=CC=CC=C271C272=CC=CC=C272C273=CC=CC=C273C274=CC=CC=C274C275=CC=CC=C275C276=CC=CC=C276C277=CC=CC=C277C278=CC=CC=C278C279=CC=CC=C279C280=CC=CC=C280C281=CC=CC=C281C282=CC=CC=C282C283=CC=CC=C283C284=CC=CC=C284C285=CC=CC=C285C286=CC=CC=C286C287=CC=CC=C287C288=CC=CC=C288C289=CC=CC=C289C290=CC=CC=C290C291=CC=CC=C291C292=CC=CC=C292C293=CC=CC=C293C294=CC=CC=C294C295=CC=CC=C295C296=CC=CC=C296C297=CC=CC=C297C298=CC=CC=C298C299=CC=CC=C299C300=CC=CC=C300C301=CC=CC=C301C302=CC=CC=C302C303=CC=CC=C303C304=CC=CC=C304C305=CC=CC=C305C306=CC=CC=C306C307=CC=CC=C307C308=CC=CC=C308C309=CC=CC=C309C310=CC=CC=C310C311=CC=CC=C311C312=CC=CC=C312C313=CC=CC=C313C314=CC=CC=C314C315=CC=CC=C315C316=CC=CC=C316C317=CC=CC=C317C318=CC=CC=C318C319=CC=CC=C319C320=CC=CC=C320C321=CC=CC=C321C322=CC=CC=C322C323=CC=CC=C323C324=CC=CC=C324C325=CC=CC=C325C326=CC=CC=C326C327=CC=CC=C327C328=CC=CC=C328C329=CC=CC=C329C330=CC=CC=C330C331=CC=CC=C331C332=CC=CC=C332C333=CC=CC=C333C334=CC=CC=C334C335=CC=CC=C335C336=CC=CC=C336C337=CC=CC=C337C338=CC=CC=C338C339=CC=CC=C339C340=CC=CC=C340C341=CC=CC=C341C342=CC=CC=C342C343=CC=CC=C343C344=CC=CC=C344C345=CC=CC=C345C346=CC=CC=C346C347=CC=CC=C347C348=CC=CC=C348C349=CC=CC=C349C350=CC=CC=C350C351=CC=CC=C351C352=CC=CC=C352C353=CC=CC=C353C354=CC=CC=C354C355=CC=CC=C355C356=CC=CC=C356C357=CC=CC=C

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