Electronic supplementary materials for the paper

Synthesis, X-ray characterization and DFT calculations of a series of 3-substituted 4,5-dichloroisothiazole

by Irina A. Kolesnik,[a] Vladimir I. Potkin,[a] Mikhail S. Grigoriev,[b] Anton P. Novikov,[b] Rosa M. Gomila,[c] Alexandra. G. Podrezova,[d] Vadim V. Brazhkin,[e] Fedor I. Zubkov*[,d] and Antonio Frontera*[,c]

[a]*Institute of Physical Organic Chemistry of National Academy of Sciences of Belarus, 13 Surganov str., 220072 Minsk, Belarus. Email: irynakolesnik93@gmail.com*
[b]*Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 31 Bldg 4, Leninsky prosp., Moscow, 119071, Russian Federation. Email: mickgrig@mail.ru*
[c]*Department of Chemistry, Universidad de les Islas Baleares, Crta. de Valldemosa km 7.5, 07122 Palma de Mallorca (Baleares), Spain. Email: toni.frontera@uib.es*
[d]*Faculty of Science, Peoples' Friendship University of Russia (RUDN University), 6 Miklukho-Maklaya St., 117198 Moscow, Russian Federation. Email: fzubkov@sci.pfu.edu.ru*
[e]*Vereshchagin Institute for High Pressure Physics, Russian Academy of Sciences, Kaluzhskoe shosse 14, 108840 Troitsk, Moscow, Russian Federation. Email: brazhkin@hppi.troitsk.ru*

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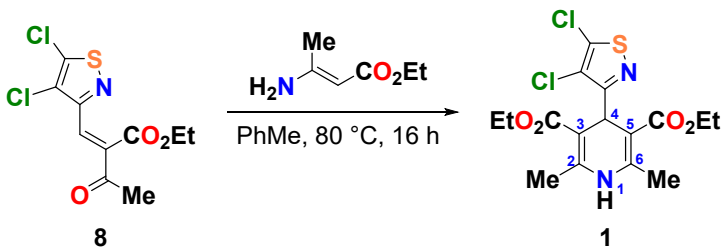
1. Synthetic details

All commercially available reagents and solvents (Acros Organics) were used without further purification. Values of the melting point were measured on Boetius apparatus and on a capillary point apparatus equipped with a digital thermometer (SMP 30) and were left unchanged. ^{1}H and ^{13}C NMR spectra were recorded on 500 (for ^{1}H), 125 (for ^{13}C) MHz spectrometers with TMS as an internal standard, using $CDCl_3$ as a solvent. Data for ^{1}H NMR spectra are reported as follows: chemical shift δ (ppm), referenced to TMS; multiplicities are indicated as the following: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; coupling constants (Hz) and integration. Data for ^{13}C NMR spectra are reported in terms of chemical shift δ (ppm) relative to residual solvent peaks. IR spectra were obtained in KBr pellets using an FTIR spectrometer Protege-460 (Nicolet). High-resolution MALDI mass spectra were obtained using a Bruker autoflex speed mass spectrometer equipped with a solid body UV-laser (λ = 355 nm) and operated in positive reflectron mode. Solutions of the analytes in CH_2Cl_2 (2 mg/mL) were mixed with a solution of 2,5-dihydrobeznoic acid in THF (2 mg/mL) and 1 μL of the mixtures were spotted on a steel target plate and air-dried. LC-ESI measurements were carried out on LCMS-8040 Triple quadrupole liquid chromatograph mass spectrometer (Shimadzu) and Kratos MS-30 mass spectrometer (EI, 70 eV). GC-MS studies were performed on an instrument Agilent 5975 inert MSD/6890 N Network GC System (EI ionization at 70 eV), HP-5MS capillary column 30 m × 0.25 mm, 5% PhMe Silicon stationary phase (0.25 mm), evaporator temperature 250 °C. HPLS-MS studies were performed using an Agilent 1200 liquid chromatograph with mass-selective detector Agilent 6410 Triple Quad with electrospray ionization (ESI+, scan mode – MS2). Column: Agilent ZORBAX Eclipse XDB-C18 (4.6 × 50 mm, 1.8 μm). Mobile phase – MeCN–H_2O+0.05% HCO_2H, gradient elution from 40 to 90% MeCN in 10 min. Elution rate 0.5 ml/min. Analytical TLC was performed on silica plates Sorbfil (visualization by I_2 vapors or 0.1 % $KMnO_4$ solution). All sample for XRD experiments were obtained by slow evaporation of methanol solutions at r.t.

Diethyl 4-(4,5-dichloroisothiazol-3-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1)



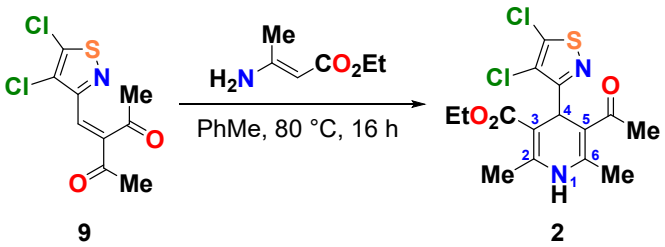
Scheme S1. Synthesis of compound **1**

A solution of compound **8** (0.61 mmol, 0.18 g) and methyl 3-aminocrotonate (0.73 mmol, 0.10 g) in toluene (5 mL) was stirred at 80 °C for 16 h. After cooling, the target product **1** was filtered off, washed with cold toluene (2 × 1 mL) and dried in vacuo.

Pale yellow powder (0.14 g, 0.35 mmol, 56%), m.p. 172.8–174.0 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 6.49 (1H, s, NH), 5.35 (1H, s, CH), 4.05–4.14 (4H, m, CH_2), 2.29 (6H, s, Me), 1.19 (6H, t, *J* = 7.1 Hz, $CH_2\underline{Me}$). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 173.3, 167.2, 146.2, 145.9, 123.3, 101.8, 60.1, 37.1, 19.6, 14.5 ppm. IR ν_{max}/cm^{-1} (KBr): 3282, 2979, 1705, 1698, 1499, 1200, 1091. GC-MS: found, *m/z*: 404 $[M]^+$. $C_{16}H_{18}Cl_2N_2O_4S$. Calculated, 404.0364.

Ethyl 5-acetyl-4-(4,5-dichloroisothiazol-3-yl)-2,6-dimethyl-1,4-dihydropyridine-3-carboxylate (2)



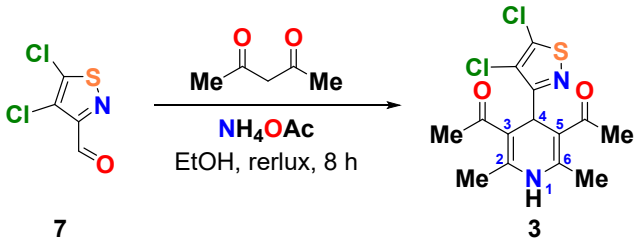
Scheme S2. Synthesis of compound **2**

A solution of compound **9** (0.72 mmol, 0.19 g) and methyl 3-aminocrotonate (0.72 mmol, 0.09 g) in toluene (5 mL) was stirred at 80 °C for 16 h. After cooling, the target product **2** was filtered off, washed with cold toluene (2 × 1 mL) and dried in vacuo.

Pale yellow powder (0.16 g, 0.43 mmol, 59%), m.p. 205–206 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 6.34 (1H, s, NH), 5.42 (1H, s, CH), 4.09–4.16 (2H, m, CH_2), 2.32 (3H, s, C(O)Me), 2.28 (6H, s, Me), 1.23 (3H, t, *J* = 7.1 Hz, $CH_2\underline{Me}$). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 197.7, 171.4, 167.1, 147.1, 145.6, 144.6, 122.7, 111.0, 101.7, 60.2, 38.2, 30.4, 20.6, 19.6, 14.6 ppm. IR ν_{max}/cm^{-1} (KBr): 3279, 2991, 1697, 1642, 1490, 1209, 1074. MS (ESI): found, *m/z*: 397.1 $[M+Na]^+$. $C_{15}H_{16}Cl_2N_2O_3S$. Calculated, 374.0259.

3,5-Diacetyl-4-(4,5-dichloroisothiazol-3-yl)-2,6-dimethyl-1,4-dihydropyridine) (3)



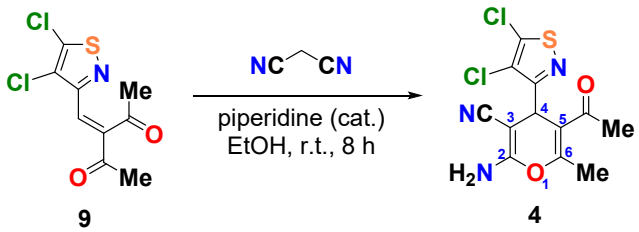
Scheme S3. Synthesis of compound **3**

A solution of ammonium acetate (1.00 mmol, 0.08 g), 4,5-dichloroisothiazole-3-carbaldehyde **7** (0.99 mmol, 0.18 g) and acetylacetone (2.00 mmol, 0.20 g) in ethanol (4 mL) was refluxed for 8 h. Then ethanol was evaporated and the crud product was recrystallized from methanol.

Yellow needles (0.17 g, 0.57 mmol, 58%), m.p. 191–192 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 6.24 (1H, s, NH), 5.50 (1H, s, CH), 2.32 (6H, s, C(O)Me), 2.30 (6H, s, Me). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 197.7, 169.7, 148.0, 144.3, 122.5, 110.6, 39.5, 30.3, 20.5 ppm. IR ν_{max}/cm^{-1} (KBr): 3296, 1625, 1592, 1384, 1218. MS (ESI): found, *m/z*: 367.1 $[M+Na]^+$. $C_{14}H_{14}Cl_2N_2O_2S$. Calculated, 344.0153.

5-Acetyl-2-amino-4-(4,5-dichloroisothiazol-3-yl)-6-methyl-4*H*-pyran-3-carbonitrile (4)



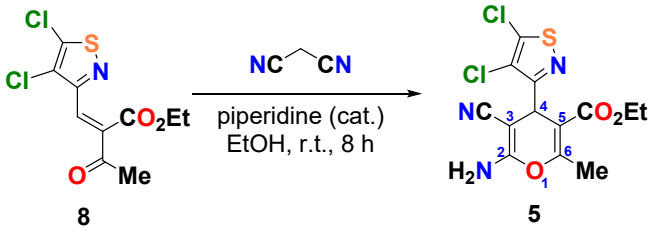
Scheme S4. Synthesis of compound **4**

A solution of one drop of piperidine, compound **9** (0.38 mmol, 0.1 g) and malononitrile (0.38 mmol, 24 μL) in ethanol (3 mL) was stirred at r.t. for 8 h. Then the resulting mixture was diluted with water (7 mL), the precipitate was filtered off, washed with 50% aqueous ethanol (2 × 1 mL) and dried in vacuo.

Creamy powder (0.08 g, 0.23 mmol, 62%), m.p. 155–156 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 4.94 (1H, q, *J* = 0.9 Hz, CH), 4.60 (2H, s, NH_2), 2.35 (3H, d, *J* = 0.9 Hz, C(O)Me), 2.19 (3H, s, Me). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 197.0, 166.6, 158.8, 157.5, 149.1, 118.1, 114.0, 112.7, 58.1, 36.6, 30.1, 19.2 ppm. IR ν_{max}/cm^{-1} (KBr): 3402, 3323, 2924, 2195, 2680, 1649, 1380, 1215. HPLC-MS, *m/z* (%): 352 $[M+Na]^+$. $C_{12}H_9Cl_2N_3O_2S$. Calculated, 328.9793.

Ethyl 2-amino-3-cyano-4-(4,5-dichloroisothiazol-3-yl)-6-methyl-4*H*-pyran-5-carboxylate (5)



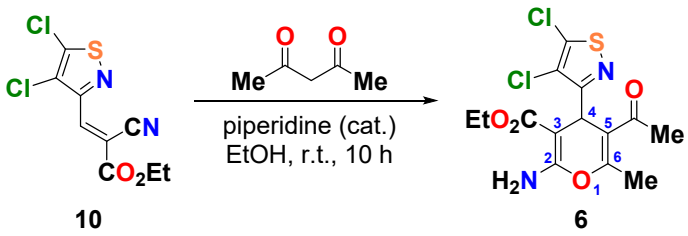
Scheme S5. Synthesis of compound **5**

A solution of one drop of piperidine, compound **8** (0.51 mmol, 0.15 g) and malononitrile (0.61 mmol, 39 μL) in ethanol (3 mL) was stirred at r.t. for 8 h. Then the resulting mixture was poured into water (10 mL) and extracted with diethyl ether (2 × 5 mL). Combined organic fractions was washed with water (2 × 5 mL) and dried over Na_2SO_4. After removing the solvent, the crude product **5** was recrystallized from methanol.

Creamy lamellar crystals (0.1 g, 0.28 mmol, 56%), m.p. 163–164 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 4.91 (1H, q, *J* = 0.7 Hz, CH), 4.70 (2H, s, NH_2), 3.99–4.11 (2H, m, CH_2), 2.42 (3H, d, *J* = 0.7 Hz, Me), 1.09 (3H, t, *J* = 7.1 Hz, CH_2Me). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 168.1, 165.3, 159.6, 158.9, 148.2, 122.5, 118.4, 104.9, 61.0, 58.3, 35.5, 18.7, 14.1 ppm. IR ν_{max}/cm^{-1} (KBr): 3371, 3178, 2990, 2194, 1694, 1683, 1608, 1267. MALDI-HRMS: found, *m/z*: 360 $[M+H]^+$. $C_{13}H_{11}Cl_2N_3O_3S$. Calculated, 358.9898.

Ethyl 5-acetyl-2-amino-4-(4,5-dichloroisothiazol-3-yl)-6-methyl-4*H*-pyran-3-carboxylate (6)



Scheme S6. Synthesis of compound **6**

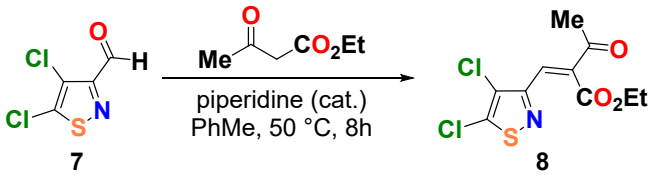
A solution of one drop of piperidine, compound **10** (0.97 mmol, 0.27 g) and acetylacetone (0.97 mmol, 100 μL) in ethanol (3 mL) was stirred at r.t. for 10 h. Then the resulting mixture was poured into water (10 mL) and extracted with diethyl ether (2 × 5 mL). Combined organic fractions were washed with

water (2 × 5 mL) and dried over Na_2SO_4. After removing the solvent, a crude product **6** was washed with cold methanol (2 × 1 mL) and dried in the air.

White powder (0.28 g, 0.74 mmol, 76%), m.p. 142–143 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 6.25 (2H, s, NH_2), 5.14 (1H, q, *J* = 0.7 Hz, CH), 4.04–4.14 (2H, m, CH_2), 2.30 (3H, s, C(O)Me), 2.29 (3H, d, *J* = 0.7 Hz, Me), 1.17 (3H, t, *J* = 7.1 Hz, CH_2Me). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 198.5, 169.4, 168.6, 159.4, 156.8, 147.5, 123.0, 115.5, 76.6, 59.9, 36.0, 30.54, 19.2, 14.6 ppm. IR ν_{max}/cm^{-1} (KBr): 3391, 3314, 3295, 2990, 1693, 1635, 1192. MS (ESI): *m/z*: 377 $[M+H]^+$. $C_{14}H_{14}Cl_2N_2O_4S$. Calculated, 376.0051.

Ethyl 2-[(4,5-dichloroisothiazol-3-yl)methylene]-3-oxobutanoate (8)



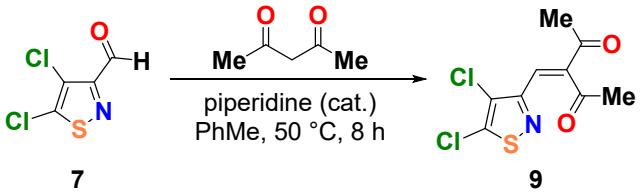
Scheme S7. Synthesis of compound **8**

A solution of one drop of piperidine, compound **7** (1.65 mmol, 0.30 g) and acetoacetic ester (1.65 mmol, 210 μL) in toluene (15 mL) was stirred at 50 °C for 8 h. Then the resulting mixture was washed with a diluted HCl solution (1 × 10 mL), water (1 × 10 mL), a sat. solution of $NaHCO_3$ (1 × 10 mL) and dried over Na_2SO_4. After removing the solvent, the crude product **8** was recrystallized from hexane.

Creamy powder (0.39 g, 1.32 mmol, 80%), m.p. 88–89 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.47 (1H, s, CH), 4.37 (2H, q, *J* = 7.2 Hz, CH_2), 2.44 (3H, s, C(O)Me), 1.32 (3H, t, *J* = 7.2 Hz, CH_2Me). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 193.8, 166.8, 157.7, 149.1, 138.3, 126.7, 125.5, 62.1, 27.0, 14.1 ppm. IR ν_{max}/cm^{-1} (KBr): 3448, 3324, 2987, 1736, 1669, 1356, 1321, 1222. GC-MS: found, *m/z*: 293 $[M]^+$. $C_{10}H_9Cl_2NO_3S$. Calculated, 293.0.

3-[(4,5-Dichloroisothiazol-3-yl)methylene]pentane-2,4-dione (9)



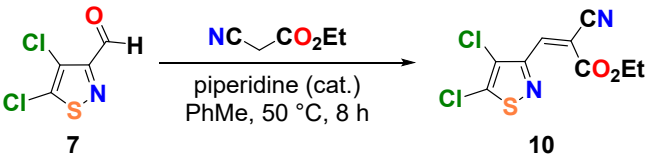
Scheme S8. Synthesis of compound **9**

A solution of one drop of piperidine, compound **7** (1.10 mmol, 0.20 g) and acetylacetone (1.15 mmol, 114 μL) in toluene (5 mL) and the reaction mixture was stirred at 50 °C for 8 h. Then the resulting mixture was washed with a diluted HCl solution (1 × 10 mL), water (1 × 10 mL), a sat. solution of $NaHCO_3$ (1 × 10 mL) and dried over Na_2SO_4. After removing the solvent, the crude product **9** was recrystallized from hexane.

Yellowish lamellar crystals (0.26 g, 0.99 mmol, 90%), m.p. 92–94 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.32 (1H, s, CH), 2.44 (3H, s, Me), 2.43 (3H, s, Me). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 203.6, 195.9, 157.8, 149.4, 146.6, 125.2, 125.1, 31.4, 26.8 ppm. IR ν_{max}/cm^{-1} (KBr): 3400, 3304, 2925, 1711, 1663, 1360, 1319, 1176. GC-MS: found, *m/z*: 263 $[M]^+$. $C_9H_7Cl_2NO_2S$. Calculated, 263.0.

Ehyl 2-cyano-3-(4,5-dichloroisothiazol-3-yl)acrylate (10)



Scheme S9. Synthesis of compound **10**

A solution of one drop of piperidine, compound **7** (2.80 mmol, 0.51 g) and ethyl cyanoacetate (2.80 mmol, 300 μL) in toluene (10 mL) and the reaction mixture was stirred at 50 °C for 8 h. Then the resulting mixture was washed with a diluted HCl solution (1 × 10 mL), water (1 × 10 mL), a sat. solution of $NaHCO_3$ (1 × 10 mL) and dried over Na_2SO_4. After removing the solvent, the crude product **10** was recrystallized from hexane.

Creamy needles (0.73 g, 2.63 mmol, 94%), m.p. 84–85 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.19 (1H, s, CH), 4.42 (2H, q, *J* = 7.1 Hz, CH_2), 1.41 (3H, t, *J* = 7.1 Hz, Me). ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 195.9, 161.5, 156.0, 150.3, 140.1, 114.1, 109.6, 63.6, 14.3

ppm. IR ν_{max}/cm^{-1} (KBr): 3428, 3000, 2229, 1724, 1368, 1327, 1257, 1001, 1086. GC-MS: found, *m/z*: 276 $[M]^+$. $C_9H_6Cl_2N_2O_2S$. Calculated, 276.0.

2. XRD part

The crystal structure of heterocycles **2**, **3**, **5** and **6** was determined by X-ray structural analysis using an automatic four-circle area-detector diffractometer Bruker KAPPA APEX II with MoKα radiation. The crystal structure **1** and **4** was determined by X-ray structural analysis using XtaLAB Synergy, Dualflex, HyPix with CuKα radiation. The cell parameters of **2**, **3**, **5** and **6** were refined over the entire data set, together with data reduction using SAINT-Plus software.[1] Absorption corrections of **2**, **3**, **5** and **6** were introduced using the SADABS program.[2] The structures were solved using the SHELXT-2018/2 program[3] and refined by full-matrix least squares on F^2 in the anisotropic approximation for all non-hydrogen atoms (SHELXL-2018/3).[4] The C-H bonded hydrogen atoms were placed in geometrically calculated positions and refined in an idealized geometry with isotropic temperature factors equal to 1.2*U*eq(C) for CH and CH_2-groups, and 1.5*U*eq(C) for CH_3-groups. The N-H bonded atoms were objectively located from the difference Fourier synthesis and refined with isotropic temperature factors equal to 1.2*U*eq(N) for NH and NH_2-groups. The orientation of CH_3-groups was refined. Structures **3** and **6** were refined as inversion twins. Tables and figures for the structures were generated using Olex2.[5]

Crystal data, data collection, and structure refinement details are summarized in Table 1 (see the main part of the paper). All other crystallographic parameters of the structures are indicated below in Tables S1−S24. The atomic coordinates were deposited at the Cambridge Crystallographic Data Centre (CCDC).[6] CCDC numbers are 2213501−2213504 for **2**, **3**, **5**, **6**, correspondingly and 2243955−2243956 for **1** and **4**.

1. Bruker AXS Inc.: Madison, WI, U. SAINT, V8.40B 2020.
2. L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, *J. Appl. Crystallogr*., 2015, **48**, 3–10.
3. G. M. Sheldrick, *Acta Crystallogr*. *A*, 2015, **A71**, 3–8.
4. G. M. Sheldrick, *Acta Crystallogr. C*, 2015, **C71**, 3–8.
5. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr*., 2009, **42**, 339–341.

6. C. R. Groom, I. J. Bruno, M. P. Lightfoot and S. C. Ward, *Acta Crystallogr. B*, 2016, **72**, 171–179.

Table S1. Bond Lengths for **1.**

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Cl1	C11	1.7098(16)		C1	C2	1.505(2)
Cl2	C12	1.7007(16)		C2	C3	1.357(2)
S1	N2	1.6569(14)		C3	C4	1.530(2)
S1	C12	1.7051(17)		C3	C7	1.472(2)
O1	C7	1.211(2)		C4	C5	1.529(2)
O2	C7	1.357(2)		C4	C10	1.520(2)
O2	C8	1.4501(19)		C5	C6	1.355(2)
O3	C13	1.212(2)		C5	C13	1.471(2)
O4	C13	1.3545(19)		C6	C16	1.504(2)
O4	C14	1.4533(19)		C8	C9	1.512(3)
N1	C2	1.379(2)		C10	C11	1.431(2)
N1	C6	1.376(2)		C11	C12	1.367(2)
N2	C10	1.322(2)		C14	C15	1.508(2)

Table S2. Bond Angles for **1.**

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
N2	S1	C12	94.13(7)		C5	C6	C16	127.50(14)
C7	O2	C8	116.69(13)		O1	C7	O2	122.56(15)
C13	O4	C14	114.02(13)		O1	C7	C3	127.83(15)
C6	N1	C2	124.15(14)		O2	C7	C3	109.60(13)
C10	N2	S1	111.29(11)		O2	C8	C9	109.91(14)
N1	C2	C1	112.78(14)		N2	C10	C4	119.43(13)
C3	C2	N1	119.96(14)		N2	C10	C11	113.97(14)
C3	C2	C1	127.23(15)		C11	C10	C4	126.59(14)
C2	C3	C4	120.86(14)		C10	C11	Cl1	125.81(12)
C2	C3	C7	121.37(14)		C12	C11	Cl1	123.04(13)
C7	C3	C4	117.63(13)		C12	C11	C10	111.13(14)
C5	C4	C3	111.86(13)		Cl2	C12	S1	123.01(10)
C10	C4	C3	109.62(12)		C11	C12	Cl2	127.50(13)
C10	C4	C5	110.60(12)		C11	C12	S1	109.48(12)
C6	C5	C4	121.07(14)		O3	C13	O4	121.65(14)
C6	C5	C13	120.62(14)		O3	C13	C5	126.68(15)
C13	C5	C4	118.25(13)		O4	C13	C5	111.67(13)
N1	C6	C16	112.78(14)		O4	C14	C15	108.16(14)
C5	C6	N1	119.69(14)					

Table S3. Hydrogen Bonds for **1.**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1	H1	N2[1]	0.90(2)	2.10(2)	3.000(2)	178(2)
C1	H1B	O1	0.98	2.16	2.866(2)	127

C16	H16B	O3	0.98	2.33	2.827(2)	111

[1]2-X,1-Y,1-Z

Table S4. Torsion Angles for **1.**

A	B	C	D	Angle/°		A	B	C	D	Angle/°
Cl1	C11	C12	Cl2	0.6(2)		C4	C5	C13	O3	175.07(15)
Cl1	C11	C12	S1	179.14(9)		C4	C5	C13	O4	-5.3(2)
S1	N2	C10	C4	-178.14(11)		C4	C10	C11	Cl1	-0.7(2)
S1	N2	C10	C11	0.38(17)		C4	C10	C11	C12	177.60(14)
N1	C2	C3	C4	-2.3(2)		C5	C4	C10	N2	-62.28(17)
N1	C2	C3	C7	-177.85(13)		C5	C4	C10	C11	119.41(16)
N2	S1	C12	Cl2	178.10(11)		C6	N1	C2	C1	169.59(14)
N2	S1	C12	C11	-0.53(13)		C6	N1	C2	C3	-8.6(2)
N2	C10	C11	Cl1	-179.07(11)		C6	C5	C13	O3	-7.5(3)
N2	C10	C11	C12	-0.79(19)		C6	C5	C13	O4	172.10(14)
C1	C2	C3	C4	179.78(14)		C7	O2	C8	C9	86.51(18)
C1	C2	C3	C7	4.2(2)		C7	C3	C4	C5	-170.48(13)
C2	N1	C6	C5	5.7(2)		C7	C3	C4	C10	66.46(17)
C2	N1	C6	C16	-172.48(14)		C8	O2	C7	O1	6.7(2)
C2	C3	C4	C5	13.8(2)		C8	O2	C7	C3	-171.85(13)
C2	C3	C4	C10	-109.26(16)		C10	C4	C5	C6	105.77(16)
C2	C3	C7	O1	0.7(3)		C10	C4	C5	C13	-76.84(17)
C2	C3	C7	O2	179.14(14)		C10	C11	C12	Cl2	-177.75(12)
C3	C4	C5	C6	-16.7(2)		C10	C11	C12	S1	0.81(17)
C3	C4	C5	C13	160.66(13)		C12	S1	N2	C10	0.08(12)
C3	C4	C10	N2	61.53(18)		C13	O4	C14	C15	175.84(14)
C3	C4	C10	C11	-116.79(16)		C13	C5	C6	N1	-169.32(14)
C4	C3	C7	O1	-175.04(16)		C13	C5	C6	C16	8.5(2)
C4	C3	C7	O2	3.45(19)		C14	O4	C13	O3	6.8(2)
C4	C5	C6	N1	8.0(2)		C14	O4	C13	C5	-172.84(14)
C4	C5	C6	C16	-174.16(15)						

Table S5. Bond Lengths for **2**.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Cl1	C16	1.703(4)		C2	C7	1.501(4)
Cl2	C15	1.720(3)		C3	C4	1.528(4)
S1	N2	1.651(3)		C3	C8	1.456(4)
S1	C16	1.709(3)		C4	C5	1.523(4)
O1	C8	1.245(3)		C4	C14	1.512(5)
O2	C10	1.222(4)		C5	C6	1.363(4)
O3	C10	1.359(4)		C5	C10	1.467(4)
O3	C11	1.458(4)		C6	C13	1.498(4)

N1	C2	1.370(4)		C8	C9	1.504(5)
N1	C6	1.379(4)		C11	C12	1.509(5)
N2	C14	1.329(4)		C14	C15	1.442(4)
C2	C3	1.371(4)		C15	C16	1.357(5)

Table S6. Bond Angles for **2.**

Atom	**Atom**	**Atom**	**Angle/°**		**Atom**	**Atom**	**Atom**	**Angle/°**
N2	S1	C16	94.65(15)		C5	C6	C13	127.5(3)
C10	O3	C11	115.1(2)		O1	C8	C3	118.9(3)
C2	N1	C6	124.2(2)		O1	C8	C9	118.2(3)
C14	N2	S1	111.1(2)		C3	C8	C9	122.9(3)
N1	C2	C3	118.0(3)		O2	C10	O3	121.6(3)
N1	C2	C7	113.4(2)		O2	C10	C5	127.4(3)
C3	C2	C7	128.6(3)		O3	C10	C5	110.9(3)
C2	C3	C4	118.4(2)		O3	C11	C12	107.9(3)
C2	C3	C8	124.8(3)		N2	C14	C4	119.2(3)
C8	C3	C4	116.8(2)		N2	C14	C15	113.5(3)
C5	C4	C3	110.0(3)		C15	C14	C4	127.4(3)
C14	C4	C3	111.1(3)		C14	C15	Cl2	124.9(3)
C14	C4	C5	110.5(3)		C16	C15	Cl2	123.5(3)
C6	C5	C4	118.2(3)		C16	C15	C14	111.6(3)
C6	C5	C10	122.1(3)		Cl1	C16	S1	122.9(2)
C10	C5	C4	119.3(3)		C15	C16	Cl1	127.9(2)
N1	C6	C13	113.5(2)		C15	C16	S1	109.2(2)
C5	C6	N1	118.9(3)					

Table S7. Hydrogen Bonds for **2.**

D	**H**	**A**	**d(D-H)/Å**	**d(H-A)/Å**	**d(D-A)/Å**	**D-H-A/°**
N1	H1	O1[1]	0.80(3)	2.05(3)	2.819(3)	162(4)

[1]-1+X,+Y,+Z

Table S8. Torsion Angles for **2.**

A	**B**	**C**	**D**	**Angle/°**		**A**	**B**	**C**	**D**	**Angle/°**
Cl2	C15	C16	Cl1	1.0(5)		C4	C5	C10	O2	174.2(3)
Cl2	C15	C16	S1	179.71(18)		C4	C5	C10	O3	-5.2(4)
S1	N2	C14	C4	-178.9(2)		C4	C14	C15	Cl2	-0.5(5)
S1	N2	C14	C15	0.4(3)		C4	C14	C15	C16	178.5(3)
N1	C2	C3	C4	-14.2(5)		C5	C4	C14	N2	-52.1(4)
N1	C2	C3	C8	162.8(3)		C5	C4	C14	C15	128.7(3)
N2	S1	C16	Cl1	178.4(2)		C6	N1	C2	C3	-14.9(5)
N2	S1	C16	C15	-0.4(3)		C6	N1	C2	C7	164.4(3)

N2	C14	C15	Cl2	-179.8(2)		C6	C5	C10	O2	1.1(6)
N2	C14	C15	C16	-0.7(4)		C6	C5	C10	O3	-178.2(3)
C2	N1	C6	C5	17.7(5)		C7	C2	C3	C4	166.7(3)
C2	N1	C6	C13	-160.5(3)		C7	C2	C3	C8	-16.3(6)
C2	C3	C4	C5	36.2(4)		C8	C3	C4	C5	-141.0(3)
C2	C3	C4	C14	-86.4(3)		C8	C3	C4	C14	96.4(3)
C2	C3	C8	O1	174.4(3)		C10	O3	C11	C12	-175.4(3)
C2	C3	C8	C9	-8.9(5)		C10	C5	C6	N1	-177.9(3)
C3	C4	C5	C6	-33.4(4)		C10	C5	C6	C13	0.0(6)
C3	C4	C5	C10	153.2(3)		C11	O3	C10	O2	-2.2(5)
C3	C4	C14	N2	70.3(3)		C11	O3	C10	C5	177.2(3)
C3	C4	C14	C15	-108.9(3)		C14	C4	C5	C6	89.6(4)
C4	C3	C8	O1	-8.6(5)		C14	C4	C5	C10	-83.7(3)
C4	C3	C8	C9	168.1(3)		C14	C15	C16	Cl1	-178.0(2)
C4	C5	C6	N1	9.0(5)		C14	C15	C16	S1	0.7(3)
C4	C5	C6	C13	-173.1(3)		C16	S1	N2	C14	0.0(3)

Table S9. Bond Lengths for **3.**

Atom	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**
Cl1	C14	1.719(5)		Cl21	C34	1.707(5)
Cl2	C15	1.705(5)		Cl22	C35	1.697(5)
S1	N2	1.656(4)		S21	N22	1.657(4)
S1	C15	1.707(5)		S21	C35	1.717(5)
O1	C8	1.233(5)		O21	C28	1.234(5)
O2	C10	1.228(6)		O22	C30	1.225(5)
N1	C2	1.370(6)		N21	C22	1.366(6)
N1	C6	1.391(6)		N21	C26	1.382(6)
N2	C13	1.325(6)		N22	C33	1.320(5)
C2	C3	1.369(6)		C22	C23	1.369(6)
C2	C7	1.498(6)		C22	C27	1.505(6)
C3	C4	1.517(6)		C23	C24	1.515(6)
C3	C8	1.460(6)		C23	C28	1.464(6)
C4	C5	1.523(6)		C24	C25	1.514(6)
C4	C13	1.522(6)		C24	C33	1.521(6)
C5	C6	1.350(6)		C25	C26	1.370(6)
C5	C10	1.470(6)		C25	C30	1.471(7)
C6	C12	1.508(6)		C26	C32	1.502(6)
C8	C9	1.505(6)		C28	C29	1.499(6)
C10	C11	1.497(7)		C30	C31	1.504(6)
C13	C14	1.424(6)		C33	C34	1.422(6)
C14	C15	1.356(6)		C34	C35	1.368(7)

Table S10. Bond Angles for **3.**

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
N2	S1	C15	94.5(2)		N22	S21	C35	94.3(2)
C2	N1	C6	125.0(4)		C22	N21	C26	124.7(4)
C13	N2	S1	110.3(3)		C33	N22	S21	110.6(4)
N1	C2	C7	113.2(4)		N21	C22	C23	118.3(4)
C3	C2	N1	117.8(4)		N21	C22	C27	113.0(4)
C3	C2	C7	129.0(4)		C23	C22	C27	128.7(4)
C2	C3	C4	118.1(4)		C22	C23	C24	118.2(4)
C2	C3	C8	126.0(4)		C22	C23	C28	126.0(4)
C8	C3	C4	115.8(4)		C28	C23	C24	115.7(4)
C3	C4	C5	112.0(4)		C23	C24	C33	110.5(4)
C3	C4	C13	110.0(4)		C25	C24	C23	112.4(4)
C13	C4	C5	110.6(3)		C25	C24	C33	110.8(3)
C6	C5	C4	118.5(4)		C26	C25	C24	118.2(4)
C6	C5	C10	127.7(4)		C26	C25	C30	127.7(4)
C10	C5	C4	113.6(4)		C30	C25	C24	114.0(4)
N1	C6	C12	112.6(4)		N21	C26	C32	113.0(4)
C5	C6	N1	118.5(4)		C25	C26	N21	118.8(4)
C5	C6	C12	128.8(4)		C25	C26	C32	128.2(4)
O1	C8	C3	118.9(4)		O21	C28	C23	118.5(4)
O1	C8	C9	117.8(4)		O21	C28	C29	117.7(4)
C3	C8	C9	123.2(4)		C23	C28	C29	123.7(4)
O2	C10	C5	118.5(4)		O22	C30	C25	118.1(4)
O2	C10	C11	118.2(4)		O22	C30	C31	118.8(4)
C5	C10	C11	123.3(4)		C25	C30	C31	123.1(4)
N2	C13	C4	119.4(4)		N22	C33	C24	119.1(4)
N2	C13	C14	114.5(5)		N22	C33	C34	114.9(5)
C14	C13	C4	126.1(4)		C34	C33	C24	125.9(4)
C13	C14	Cl1	125.5(4)		C33	C34	Cl21	126.9(4)
C15	C14	Cl1	123.0(4)		C35	C34	Cl21	121.9(4)
C15	C14	C13	111.5(4)		C35	C34	C33	111.2(4)
Cl2	C15	S1	124.2(3)		Cl22	C35	S21	123.3(3)
C14	C15	Cl2	126.6(4)		C34	C35	Cl22	127.8(4)
C14	C15	S1	109.1(3)		C34	C35	S21	108.9(4)

Table S11. Hydrogen Bonds for **3.**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1	H1	O1[1]	0.80(3)	2.04(4)	2.825(5)	169(5)
C4	H4A	Cl1	1.00	2.82	3.325(4)	111.8
C11	H11C	O22[2]	0.98	2.58	3.554(6)	171.4
N21	H21	O21[1]	0.79(3)	2.09(4)	2.871(5)	170(5)
C27	H27B	O21[1]	0.98	2.56	3.403(5)	144.6
C31	H31C	O2[3]	0.98	2.57	3.546(6)	178.6

[1]-1+X,+Y,+Z; [2]1-X,1/2+Y,2-Z; [3]1-X,-1/2+Y,2-Z

Table S12. Torsion Angles for **3.**

A	B	C	D	Angle/°		A	B	C	D	Angle/°
Cl1	C14	C15	Cl2	2.6(6)		Cl21	C34	C35	Cl22	1.6(6)
Cl1	C14	C15	S1	-179.6(3)		Cl21	C34	C35	S21	-178.8(3)
S1	N2	C13	C4	179.0(3)		S21	N22	C33	C24	-179.3(3)
S1	N2	C13	C14	-0.4(5)		S21	N22	C33	C34	0.1(5)
N1	C2	C3	C4	15.4(6)		N21	C22	C23	C24	-14.5(6)
N1	C2	C3	C8	-159.9(5)		N21	C22	C23	C28	164.3(5)
N2	S1	C15	Cl2	178.2(3)		N22	S21	C35	Cl22	179.9(3)
N2	S1	C15	C14	0.4(3)		N22	S21	C35	C34	0.3(4)
N2	C13	C14	Cl1	179.7(3)		N22	C33	C34	Cl21	178.6(3)
N2	C13	C14	C15	0.8(6)		N22	C33	C34	C35	0.1(6)
C2	N1	C6	C5	-17.3(7)		C22	N21	C26	C25	17.2(7)
C2	N1	C6	C12	160.0(4)		C22	N21	C26	C32	-161.4(4)
C2	C3	C4	C5	-34.2(5)		C22	C23	C24	C25	32.8(6)
C2	C3	C4	C13	89.3(5)		C22	C23	C24	C33	-91.6(5)
C2	C3	C8	O1	169.4(5)		C22	C23	C28	O21	-178.8(5)
C2	C3	C8	C9	-8.3(7)		C22	C23	C28	C29	-0.1(8)
C3	C4	C5	C6	28.9(6)		C23	C24	C25	C26	-27.5(6)
C3	C4	C5	C10	-155.0(4)		C23	C24	C25	C30	156.6(4)
C3	C4	C13	N2	-71.0(5)		C23	C24	C33	N22	72.0(5)
C3	C4	C13	C14	108.4(5)		C23	C24	C33	C34	-107.3(5)
C4	C3	C8	O1	-6.1(7)		C24	C23	C28	O21	0.0(7)
C4	C3	C8	C9	176.3(4)		C24	C23	C28	C29	178.7(4)
C4	C5	C6	N1	-5.3(6)		C24	C25	C26	N21	4.6(6)
C4	C5	C6	C12	177.9(4)		C24	C25	C26	C32	-177.0(4)
C4	C5	C10	O2	2.1(6)		C24	C25	C30	O22	-1.8(6)
C4	C5	C10	C11	-175.6(4)		C24	C25	C30	C31	176.9(4)
C4	C13	C14	Cl1	0.2(7)		C24	C33	C34	Cl21	-2.0(7)
C4	C13	C14	C15	-178.6(4)		C24	C33	C34	C35	179.5(4)
C5	C4	C13	N2	53.2(5)		C25	C24	C33	N22	-53.3(5)
C5	C4	C13	C14	-127.4(5)		C25	C24	C33	C34	127.4(4)
C6	N1	C2	C3	11.8(7)		C26	N21	C22	C23	-11.9(7)
C6	N1	C2	C7	-167.4(4)		C26	N21	C22	C27	165.9(4)
C6	C5	C10	O2	177.8(5)		C26	C25	C30	O22	-177.2(5)
C6	C5	C10	C11	0.0(7)		C26	C25	C30	C31	1.5(8)
C7	C2	C3	C4	-165.5(5)		C27	C22	C23	C24	168.0(5)
C7	C2	C3	C8	19.1(8)		C27	C22	C23	C28	-13.2(8)
C8	C3	C4	C5	141.6(4)		C28	C23	C24	C25	-146.1(4)
C8	C3	C4	C13	-94.9(5)		C28	C23	C24	C33	89.5(5)
C10	C5	C6	N1	179.3(4)		C30	C25	C26	N21	179.9(4)
C10	C5	C6	C12	2.4(8)		C30	C25	C26	C32	-1.7(8)

C13	C4	C5	C6	-94.3(5)		C33	C24	C25	C26	96.7(5)
C13	C4	C5	C10	81.9(5)		C33	C24	C25	C30	-79.2(5)
C13	C14	C15	Cl2	-178.5(4)		C33	C34	C35	Cl22	-179.8(4)
C13	C14	C15	S1	-0.7(5)		C33	C34	C35	S21	-0.2(5)
C15	S1	N2	C13	0.0(3)		C35	S21	N22	C33	-0.2(3)

Table S13. Bond Lengths for **4.**

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Cl1	C8	1.7155(15)		C2	C3	1.363(2)
Cl2	C9	1.7031(16)		C3	C4	1.515(2)
S1	N3	1.6490(14)		C4	C5	1.514(2)
S1	C9	1.7056(16)		C4	C7	1.519(2)
O1	C2	1.3638(19)		C5	C6	1.344(2)
O1	C6	1.3873(18)		C5	C10	1.488(2)
O2	C10	1.222(2)		C6	C12	1.499(2)
N1	C2	1.336(2)		C7	C8	1.424(2)
N2	C1	1.153(2)		C8	C9	1.365(2)
N3	C7	1.326(2)		C10	C11	1.501(2)
C1	C3	1.416(2)				

Table S14. Bond Angles for **4.**

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
N3	S1	C9	94.76(7)		O1	C6	C12	107.54(13)
C2	O1	C6	120.58(12)		C5	C6	O1	122.12(14)
C7	N3	S1	110.46(11)		C5	C6	C12	130.34(14)
N2	C1	C3	178.58(17)		N3	C7	C4	120.19(13)
N1	C2	O1	110.87(13)		N3	C7	C8	114.60(14)
N1	C2	C3	127.94(15)		C8	C7	C4	125.03(14)
C3	C2	O1	121.19(14)		C7	C8	Cl1	124.33(12)
C1	C3	C4	118.47(13)		C9	C8	Cl1	124.42(13)
C2	C3	C1	119.09(14)		C9	C8	C7	111.13(14)
C2	C3	C4	121.92(14)		Cl2	C9	S1	123.32(10)
C3	C4	C7	109.58(12)		C8	C9	Cl2	127.63(13)
C5	C4	C3	110.57(12)		C8	C9	S1	109.03(12)
C5	C4	C7	109.79(12)		O2	C10	C5	117.94(14)
C6	C5	C4	121.48(14)		O2	C10	C11	118.86(14)
C6	C5	C10	125.60(14)		C5	C10	C11	123.15(14)
C10	C5	C4	112.90(13)					

Table S15. Hydrogen Bonds for **4.**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1	H1A	O2[1]	0.88(3)	2.11(3)	2.984(2)	172(2)

N1	H1B	N2[2]	0.82(3)	2.28(3)	3.088(2)	168(2)

[1]1+X,+Y,+Z; [2]1-X,1-Y,2-Z

Table S16. Torsion Angles for **4.**

A	B	C	D	Angle/°		A	B	C	D	Angle/°
Cl1	C8	C9	Cl2	3.5(2)		C3	C4	C7	C8	-86.44(17)
Cl1	C8	C9	S1	-175.24(9)		C4	C5	C6	O1	3.6(2)
S1	N3	C7	C4	-174.74(11)		C4	C5	C6	C12	-175.96(15)
S1	N3	C7	C8	0.72(17)		C4	C5	C10	O2	-14.2(2)
O1	C2	C3	C1	-177.12(13)		C4	C5	C10	C11	163.16(15)
O1	C2	C3	C4	-5.5(2)		C4	C7	C8	Cl1	-9.7(2)
N1	C2	C3	C1	3.3(3)		C4	C7	C8	C9	174.03(14)
N1	C2	C3	C4	174.91(15)		C5	C4	C7	N3	-33.11(18)
N3	S1	C9	Cl2	-179.38(10)		C5	C4	C7	C8	151.94(14)
N3	S1	C9	C8	-0.59(12)		C6	O1	C2	N1	172.93(13)
N3	C7	C8	Cl1	175.11(11)		C6	O1	C2	C3	-6.7(2)
N3	C7	C8	C9	-1.2(2)		C6	C5	C10	O2	167.22(16)
C1	C3	C4	C5	-173.48(13)		C6	C5	C10	C11	-15.4(3)
C1	C3	C4	C7	65.37(17)		C7	C4	C5	C6	107.16(16)
C2	O1	C6	C5	7.7(2)		C7	C4	C5	C10	-71.51(16)
C2	O1	C6	C12	-172.61(13)		C7	C8	C9	Cl2	179.77(11)
C2	C3	C4	C5	14.9(2)		C7	C8	C9	S1	1.05(17)
C2	C3	C4	C7	-106.25(16)		C9	S1	N3	C7	-0.08(12)
C3	C4	C5	C6	-13.9(2)		C10	C5	C6	O1	-177.92(14)
C3	C4	C5	C10	167.46(12)		C10	C5	C6	C12	2.5(3)
C3	C4	C7	N3	88.52(16)						

Table S17. Bond Lengths for **5.**

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Cl1	C13	1.713(3)		C2	C3	1.358(4)
Cl2	C14	1.703(3)		C3	C4	1.521(4)
S1	N1	1.659(2)		C3	C11	1.412(4)
S1	C14	1.704(3)		C4	C5	1.511(4)
O1	C2	1.360(3)		C4	C12	1.524(3)
O1	C6	1.382(3)		C5	C6	1.337(3)
O2	C7	1.206(3)		C5	C7	1.479(4)
O3	C7	1.342(3)		C6	C10	1.487(4)
O3	C8	1.452(3)		C8	C9	1.507(4)
N1	C12	1.313(3)		C12	C13	1.423(4)
N2	C2	1.336(3)		C13	C14	1.368(4)
N3	C11	1.154(4)				

Table S18. Bond Angles for **5.**

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
N1	S1	C14	94.03(12)		C5	C6	O1	121.6(3)
C2	O1	C6	120.8(2)		C5	C6	C10	130.8(2)
C7	O3	C8	115.6(2)		O2	C7	O3	123.5(3)
C12	N1	S1	111.02(19)		O2	C7	C5	122.6(3)
N2	C2	O1	110.0(2)		O3	C7	C5	113.9(2)
N2	C2	C3	128.2(3)		O3	C8	C9	106.2(2)
C3	C2	O1	121.8(2)		N3	C11	C3	179.3(3)
C2	C3	C4	122.1(3)		N1	C12	C4	121.0(2)
C2	C3	C11	118.0(2)		N1	C12	C13	114.7(2)
C11	C3	C4	119.7(2)		C13	C12	C4	124.3(2)
C3	C4	C12	110.7(2)		C12	C13	Cl1	125.0(2)
C5	C4	C3	110.1(2)		C14	C13	Cl1	124.1(2)
C5	C4	C12	112.2(2)		C14	C13	C12	110.9(2)
C6	C5	C4	123.1(2)		Cl2	C14	S1	124.54(16)
C6	C5	C7	124.1(3)		C13	C14	Cl2	126.0(2)
C7	C5	C4	112.8(2)		C13	C14	S1	109.4(2)
O1	C6	C10	107.6(2)					

Table S19. Hydrogen Bonds for **5.**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N2	H2A	N3[1]	0.84(3)	2.22(3)	3.056(4)	169(3)
N2	H2B	N1[2]	0.89(3)	2.19(3)	3.069(3)	170(3)
C4	H4A	Cl1	1.00	2.74	3.269(3)	113.6
C10	H10B	N3[3]	0.98	2.57	3.532(4)	166.5

[1]1-X,2-Y,2-Z; [2]1-X,1-Y,2-Z; [3]+X,-1+Y,+Z

Table S20. Torsion Angles for **5.**

A	B	C	D	Angle/°		A	B	C	D	Angle/°
Cl1	C13	C14	Cl2	-1.6(4)		C4	C5	C7	O2	-0.4(4)
Cl1	C13	C14	S1	-179.65(17)		C4	C5	C7	O3	179.8(2)
S1	N1	C12	C4	-177.8(2)		C4	C12	C13	Cl1	-2.4(4)
S1	N1	C12	C13	0.5(3)		C4	C12	C13	C14	178.0(3)
O1	C2	C3	C4	-3.5(4)		C5	C4	C12	N1	-55.3(3)
O1	C2	C3	C11	-180.0(2)		C5	C4	C12	C13	126.5(3)
N1	S1	C14	Cl2	-177.75(19)		C6	O1	C2	N2	177.2(2)
N1	S1	C14	C13	0.3(2)		C6	O1	C2	C3	-1.5(4)
N1	C12	C13	Cl1	179.3(2)		C6	C5	C7	O2	179.0(3)
N1	C12	C13	C14	-0.3(4)		C6	C5	C7	O3	-0.8(4)
N2	C2	C3	C4	178.1(3)		C7	O3	C8	C9	177.5(2)

N2	C2	C3	C11	1.6(4)		C7	C5	C6	O1	-177.5(2)
C2	O1	C6	C5	2.4(4)		C7	C5	C6	C10	2.6(5)
C2	O1	C6	C10	-177.7(2)		C8	O3	C7	O2	1.4(4)
C2	C3	C4	C5	6.7(4)		C8	O3	C7	C5	-178.8(2)
C2	C3	C4	C12	-117.9(3)		C11	C3	C4	C5	-176.8(2)
C3	C4	C5	C6	-6.0(4)		C11	C3	C4	C12	58.6(3)
C3	C4	C5	C7	173.4(2)		C12	C4	C5	C6	117.8(3)
C3	C4	C12	N1	68.1(3)		C12	C4	C5	C7	-62.8(3)
C3	C4	C12	C13	-110.1(3)		C12	C13	C14	Cl2	178.0(2)
C4	C5	C6	O1	1.9(4)		C12	C13	C14	S1	0.0(3)
C4	C5	C6	C10	-178.1(3)		C14	S1	N1	C12	-0.5(2)

Table S21. Bond Lengths for **6.**

Atom	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**
Cl1	C11	1.710(3)		Cl21	C31	1.714(3)
Cl2	C12	1.703(3)		Cl22	C32	1.706(3)
S1	N2	1.653(2)		S21	N22	1.650(2)
S1	C12	1.704(3)		S21	C32	1.703(3)
O1	C2	1.384(3)		O21	C22	1.383(3)
O1	C6	1.366(3)		O21	C26	1.375(3)
O2	C8	1.227(3)		O22	C28	1.220(3)
O3	C13	1.221(3)		O23	C33	1.227(3)
O4	C13	1.358(3)		O24	C33	1.351(3)
O4	C14	1.453(3)		O24	C34	1.460(3)
N1	C6	1.346(3)		N21	C26	1.342(4)
N2	C10	1.312(3)		N22	C30	1.316(3)
C2	C3	1.343(4)		C22	C23	1.342(4)
C2	C7	1.491(4)		C22	C27	1.497(4)
C3	C4	1.515(4)		C23	C24	1.522(4)
C3	C8	1.478(4)		C23	C28	1.489(4)
C4	C5	1.508(4)		C24	C25	1.518(4)
C4	C10	1.521(3)		C24	C30	1.516(4)
C5	C6	1.362(4)		C25	C26	1.353(4)
C5	C13	1.452(4)		C25	C33	1.449(4)
C8	C9	1.502(4)		C28	C29	1.508(4)
C10	C11	1.433(3)		C30	C31	1.426(4)
C11	C12	1.365(4)		C31	C32	1.361(4)
C14	C15	1.510(4)		C34	C35	1.491(4)

Table S22. Bond Angles for **6.**

Atom	**Atom**	**Atom**	**Angle/°**		**Atom**	**Atom**	**Atom**	**Angle/°**
N2	S1	C12	94.53(13)		N22	S21	C32	94.30(13)
C6	O1	C2	119.9(2)		C26	O21	C22	119.6(2)

C13	O4	C14	114.8(2)		C33	O24	C34	117.9(2)
C10	N2	S1	110.64(18)		C30	N22	S21	110.63(18)
O1	C2	C7	107.8(2)		O21	C22	C27	107.9(2)
C3	C2	O1	120.9(2)		C23	C22	O21	121.3(2)
C3	C2	C7	131.3(3)		C23	C22	C27	130.8(3)
C2	C3	C4	119.9(2)		C22	C23	C24	120.9(2)
C2	C3	C8	125.8(3)		C22	C23	C28	124.2(2)
C8	C3	C4	114.3(2)		C28	C23	C24	114.9(2)
C3	C4	C10	109.2(2)		C25	C24	C23	109.7(2)
C5	C4	C3	110.7(2)		C30	C24	C23	109.0(2)
C5	C4	C10	111.1(2)		C30	C24	C25	110.9(2)
C6	C5	C4	119.4(2)		C26	C25	C24	120.2(2)
C6	C5	C13	119.5(2)		C26	C25	C33	119.5(2)
C13	C5	C4	121.1(2)		C33	C25	C24	120.1(2)
N1	C6	O1	110.4(2)		N21	C26	O21	110.2(2)
N1	C6	C5	128.3(3)		N21	C26	C25	127.9(3)
C5	C6	O1	121.3(2)		C25	C26	O21	121.9(2)
O2	C8	C3	117.7(2)		O22	C28	C23	118.6(2)
O2	C8	C9	119.2(3)		O22	C28	C29	119.3(3)
C3	C8	C9	123.0(2)		C23	C28	C29	122.0(2)
N2	C10	C4	119.4(2)		N22	C30	C24	118.8(2)
N2	C10	C11	115.0(2)		N22	C30	C31	115.0(2)
C11	C10	C4	125.7(2)		C31	C30	C24	126.3(2)
C10	C11	Cl1	125.3(2)		C30	C31	Cl21	125.6(2)
C12	C11	Cl1	124.2(2)		C32	C31	Cl21	124.0(2)
C12	C11	C10	110.5(2)		C32	C31	C30	110.5(2)
Cl2	C12	S1	122.64(17)		S21	C32	Cl22	122.46(17)
C11	C12	Cl2	128.0(2)		C31	C32	Cl22	127.9(2)
C11	C12	S1	109.4(2)		C31	C32	S21	109.6(2)
O3	C13	O4	122.3(2)		O23	C33	O24	122.9(3)
O3	C13	C5	126.0(2)		O23	C33	C25	125.5(3)
O4	C13	C5	111.7(2)		O24	C33	C25	111.7(2)
O4	C14	C15	107.8(2)		O24	C34	C35	110.5(2)

Table S23. Hydrogen Bonds for **6.**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1	H1A	O3	0.89(3)	2.10(3)	2.741(3)	128(3)
N1	H1B	N2[1]	0.83(3)	2.57(3)	3.324(4)	152(3)
C4	H4A	Cl1	1.00	2.80	3.311(3)	112.2
N21	H21A	O23	0.84(4)	2.05(3)	2.710(4)	135(3)
N21	H21B	O2	0.79(3)	2.22(3)	2.989(3)	162(4)
C24	H24A	Cl21	1.00	2.83	3.323(3)	111.4
C27	H27B	N22[2]	0.98	2.60	3.351(3)	133.9
C29	H29A	S1[3]	0.98	2.82	3.767(3)	163.0

C35	H35C	O23[4]	0.98	2.54	3.311(4)	135.5

[1]1-X,-1/2+Y,2-Z; [2]1-X,1/2+Y,1-Z; [3]1-X,-1/2+Y,1-Z; [4]2-X,-1/2+Y,1-Z

Table S24. Torsion Angles for **6.**

A	B	C	D	Angle/°		A	B	C	D	Angle/°
Cl1	C11	C12	Cl2	2.6(4)		Cl21	C31	C32	Cl22	-2.4(4)
Cl1	C11	C12	S1	-178.71(14)		Cl21	C31	C32	S21	-179.46(15)
S1	N2	C10	C4	178.03(18)		S21	N22	C30	C24	-179.56(19)
S1	N2	C10	C11	-1.2(3)		S21	N22	C30	C31	0.2(3)
O1	C2	C3	C4	-7.8(4)		O21	C22	C23	C24	7.9(4)
O1	C2	C3	C8	175.0(2)		O21	C22	C23	C28	-174.6(2)
N2	S1	C12	Cl2	177.90(17)		N22	S21	C32	Cl22	-176.50(18)
N2	S1	C12	C11	-0.9(2)		N22	S21	C32	C31	0.7(2)
N2	C10	C11	Cl1	179.59(19)		N22	C30	C31	Cl21	179.1(2)
N2	C10	C11	C12	0.5(3)		N22	C30	C31	C32	0.3(3)
C2	O1	C6	N1	-162.0(2)		C22	O21	C26	N21	165.0(2)
C2	O1	C6	C5	19.4(4)		C22	O21	C26	C25	-15.5(4)
C2	C3	C4	C5	26.9(3)		C22	C23	C24	C25	-24.6(3)
C2	C3	C4	C10	-95.7(3)		C22	C23	C24	C30	97.0(3)
C2	C3	C8	O2	167.7(3)		C22	C23	C28	O22	-162.2(3)
C2	C3	C8	C9	-15.2(4)		C22	C23	C28	C29	20.8(4)
C3	C4	C5	C6	-24.4(3)		C23	C24	C25	C26	22.7(3)
C3	C4	C5	C13	157.8(2)		C23	C24	C25	C33	-161.9(2)
C3	C4	C10	N2	60.2(3)		C23	C24	C30	N22	-61.2(3)
C3	C4	C10	C11	-120.7(3)		C23	C24	C30	C31	119.1(3)
C4	C3	C8	O2	-9.6(4)		C24	C23	C28	O22	15.5(4)
C4	C3	C8	C9	167.4(2)		C24	C23	C28	C29	-161.5(2)
C4	C5	C6	O1	2.8(4)		C24	C25	C26	O21	-4.3(4)
C4	C5	C6	N1	-175.5(3)		C24	C25	C26	N21	175.1(3)
C4	C5	C13	O3	175.2(3)		C24	C25	C33	O23	-175.7(2)
C4	C5	C13	O4	-4.6(4)		C24	C25	C33	O24	4.9(3)
C4	C10	C11	Cl1	0.4(4)		C24	C30	C31	Cl21	-1.2(4)
C4	C10	C11	C12	-178.6(2)		C24	C30	C31	C32	-179.9(2)
C5	C4	C10	N2	-62.2(3)		C25	C24	C30	N22	59.7(3)
C5	C4	C10	C11	116.9(3)		C25	C24	C30	C31	-120.0(3)
C6	O1	C2	C3	-16.8(4)		C26	O21	C22	C23	13.6(4)
C6	O1	C2	C7	165.1(2)		C26	O21	C22	C27	-168.3(2)
C6	C5	C13	O3	-2.6(4)		C26	C25	C33	O23	-0.2(4)
C6	C5	C13	O4	177.6(2)		C26	C25	C33	O24	-179.6(2)
C7	C2	C3	C4	169.8(3)		C27	C22	C23	C24	-169.6(3)
C7	C2	C3	C8	-7.4(5)		C27	C22	C23	C28	7.9(5)
C8	C3	C4	C5	-155.5(2)		C28	C23	C24	C25	157.7(2)
C8	C3	C4	C10	81.9(3)		C28	C23	C24	C30	-80.7(3)

C10	C4	C5	C6	97.1(3)		C30	C24	C25	C26	-97.8(3)
C10	C4	C5	C13	-80.6(3)		C30	C24	C25	C33	77.6(3)
C10	C11	C12	Cl2	-178.3(2)		C30	C31	C32	Cl22	176.3(2)
C10	C11	C12	S1	0.4(3)		C30	C31	C32	S21	-0.7(3)
C12	S1	N2	C10	1.2(2)		C32	S21	N22	C30	-0.5(2)
C13	O4	C14	C15	175.7(2)		C33	O24	C34	C35	114.3(3)
C13	C5	C6	O1	-179.4(2)		C33	C25	C26	O21	-179.7(2)
C13	C5	C6	N1	2.3(4)		C33	C25	C26	N21	-0.4(4)
C14	O4	C13	O3	0.0(4)		C34	O24	C33	O23	-5.6(4)
C14	O4	C13	C5	179.8(2)		C34	O24	C33	C25	173.8(2)