SYNTHESIS OF NOVEL HETEROCYCLE-FUSED FURO[3,4-*d*]-ISOXAZOLES *VIA* RING TRANSFORMATION OF 2-ISOXAZOLINE-2-OXIDES BY LEWIS ACID[1]

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Abstract - Reaction of five-membered heterocycle-substituted 2-isoxazoline-2-oxides (**2**, **3**, and **4**) with titanium tetrachloride afforded novel heterocycle-fused furo[3,4-*d*]isoxazoles (**5**, **6** and **7**), respectively. This transformation was applied to indole-substituted 2-isoxazoline-2-oxide (**8**) to give the corresponding fused furo[3,4-*d*]isoxazole (**9**) and indolo[2,3-*b*]-1-pyrroline-1-oxide (**10**).

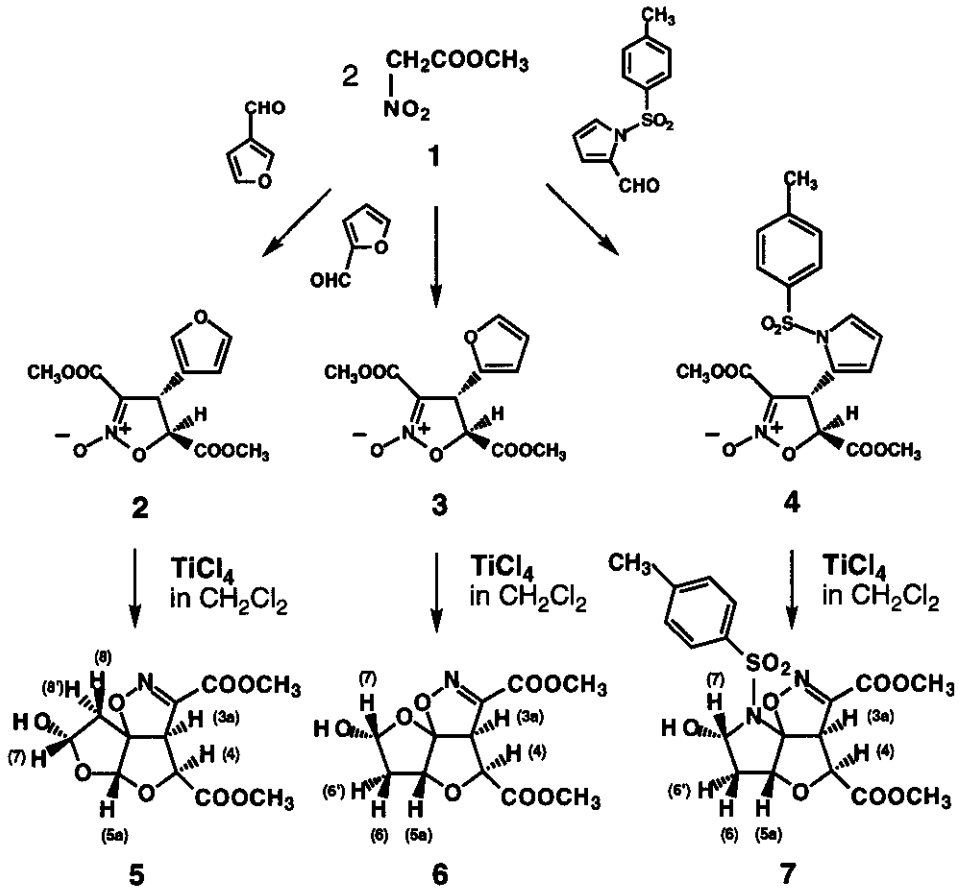
In continuation of our studies of the synthesis of benzofuro[3,4-*d*]isoxazole derivatives[2] through the ring transformation of 2-isoxazoline-2-oxides by Lewis acid,[3] we investigated the reaction of heterocycle-substituted 2-isoxazoline-2-oxides (**2**, **3**, **4**, and **8**) with titanium tetrachloride[4] and now report the preparation of heterocycle-fused furo[3,4-*d*]isoxazoles (**5**, **6**, **7**, and **9**), which are novel heterocyclic ring systems.

The heterocycle-substituted 2-isoxazoline-2-oxides (**2**, **3**, **4**, and **8**) were prepared by the reaction of the corresponding aldehydes, *i.e.*, 3-furaldehyde, 2-furaldehyde, 1-*p*-toluene-sulfonyl-2-pyrrolecarbaldehyde, and 1-*p*-toluenesulfonyl-2-indolecarbaldehyde, with two molar amount of methyl nitroacetate (**1**) in the presence of ammonium acetate.[5]

When furan-substituted 2-isoxazoline-2-oxides (**2** and **3**) were allowed to react with titanium tetrachloride at 0℃, tetrahydrofuran-fused furo[3,4-*d*]isoxazoles (**5** and **6**) were isolated from the reaction mixture in 33 and 28 % yields, respectively. Furthermore, pyrrole-substituted isoxazoline-2-oxide (**4**) reacted with titanium tetrachloride to afford the corresponding pyrrolidine-fused furo[3,4-*d*]isoxazole (**7**) in 40 % yield.

The structures of **5**, **6**, and **7** were deduced on the basis of ^{1}H-nmr analysis. The ^{1}H-nmr

spectral data of **6** are closely compatible with those of **5**. (Table 1) Both spectra showed the presence of a set of coupled aliphatic methine hydrogens (H-3a: δ 4.32, H-4: δ 5.23, $J_{3a,4}$=6.5 Hz for **5** ; H-3a: δ 4.20, H-4: δ 4.66, $J_{3a,4}$=6.3 Hz for **6**) and methylene hydrogens on a tetrahydrofuran ring (H-6 / H-6' for **6** or H-8 / H-8' for **5**) which were coupled with an adjacent hydrogen (H-7). H-5a appeared as a singlet at δ 5.95 in the ^{1}H-nmr spectrum of **5**, whereas, H-5a in that of **6** was observed at relatively high field (δ 4.98), and was coupled with methylene hydrogens (H-6 and H-6') on the furan ring ($J_{5a,6}$=8.0 Hz, $J_{5a,6'}$=5.0 Hz). The same coupling pattern of H-5a (δ 4.92) was observed in the ^{1}H-nmr spectrum of **7** ($J_{5a,6}$=7.0 Hz, $J_{5a,6'}$ =3.5 Hz).



Scheme 1

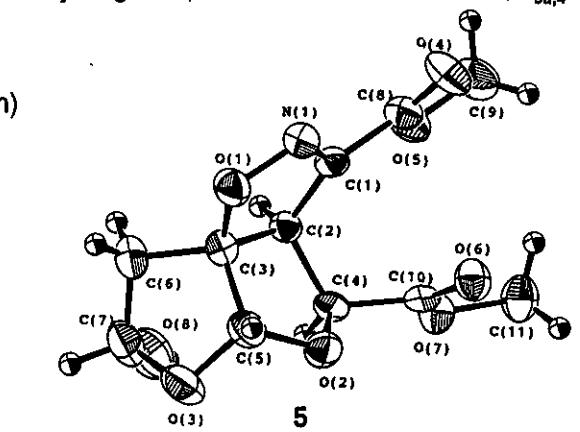
These spectral data suggested that both of **5** and **6** should have a furo[3,4-*d*]isoxazole ring system fused with another furan ring, but the fusion side between the two furan rings is

different each other. On the other hand, **7** should have a furo[3,4-*d*]isoxazole ring system fused with a pyrrolidine ring, and the fusion side between the furan and the pyrrolidine ring is *analogous to that of* **6**. *Finally, the structures of these compounds were determined by a* combination of this spectral deduction and single crystal X-ray analyses of **5** and **7**. The ORTEP drawings of **5** and **7** are shown in Figure 1, which shows that the ring systems are confirmed to be furo[2,3-*b*]furo[3,4-*d*]isoxazole for **5** and pyrrolo[3,2-*b*]furo[3,4-*d*]isoxazole for **7**. Both molecules have a hydroxyl group at 7-position *cis* to the H-3a and H-4. From the ^{1}H-nmr and X-ray crystallographic analyses, it is clear that **6** has furo[3,2-*b*]furo[3,4-*d*]-isoxazole ring system.

When this ring transformation was applied to indole-substituted 2-isoxazoline-2-oxide (**8**), two products (**9** and **10**) were obtained in 48 % and 15 % yields, respectively, after chromatographical separation. The structures of **9** and **10** were deduced from spectroscopic data and confirmed by X-ray crystallography. Thus, the ^{1}H-nmr spectrum of a product (**9**) showed the presence of coupled methine hydrogens (H-3a: δ 4.30, H-4: δ 4.82, $J_{3a,4}$=6.5

Table 1. ^{1}H-Nmr Chemical Shifts (ppm) and Coupling Constants for Compounds (**5**, **6**, and **7**)

	5	**6**	**7**
H-3a	4.32 d	4.20 d	4.98 d
H-4	5.23 d	4.66 d	5.31 d
H-5a	5.95 s	4.98 m	4.92 dd
H-6	------	2.36 m	2.22 m
H-6'	------	2.45 m	2.28 m
H-7	5.68 dd	5.85 dd	5.57 m
H-8	2.35 dd	------	-----
H-8'	2.72 dd	------	-----
$J_{3a,4}$	6.5	6.3	9.2
$J_{5a,6}$	----	8.0	7.0
$J_{5a,6'}$	----	5.0	3.5



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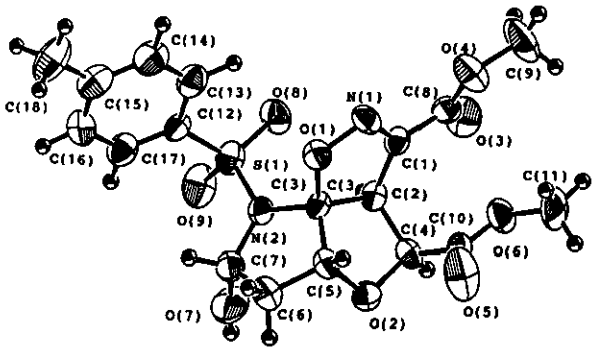

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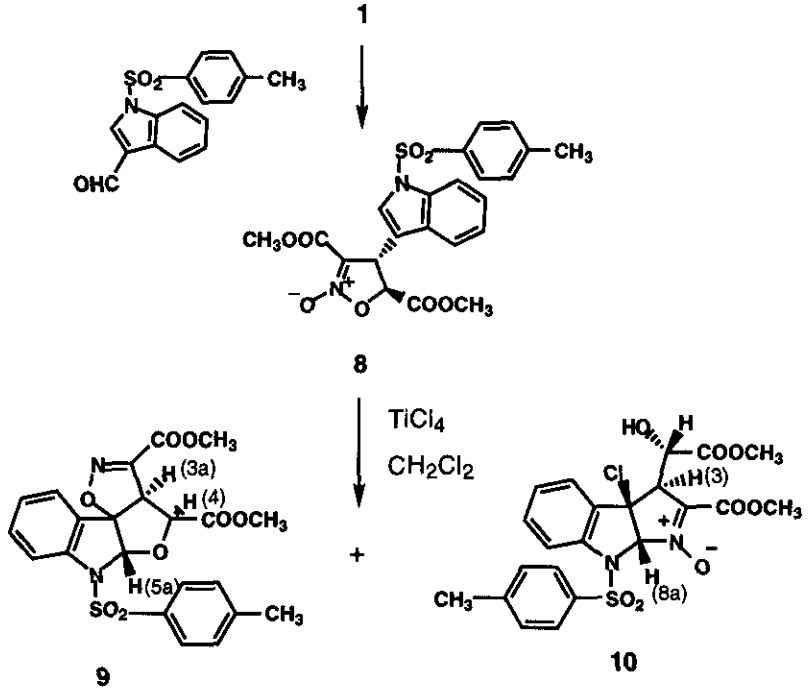
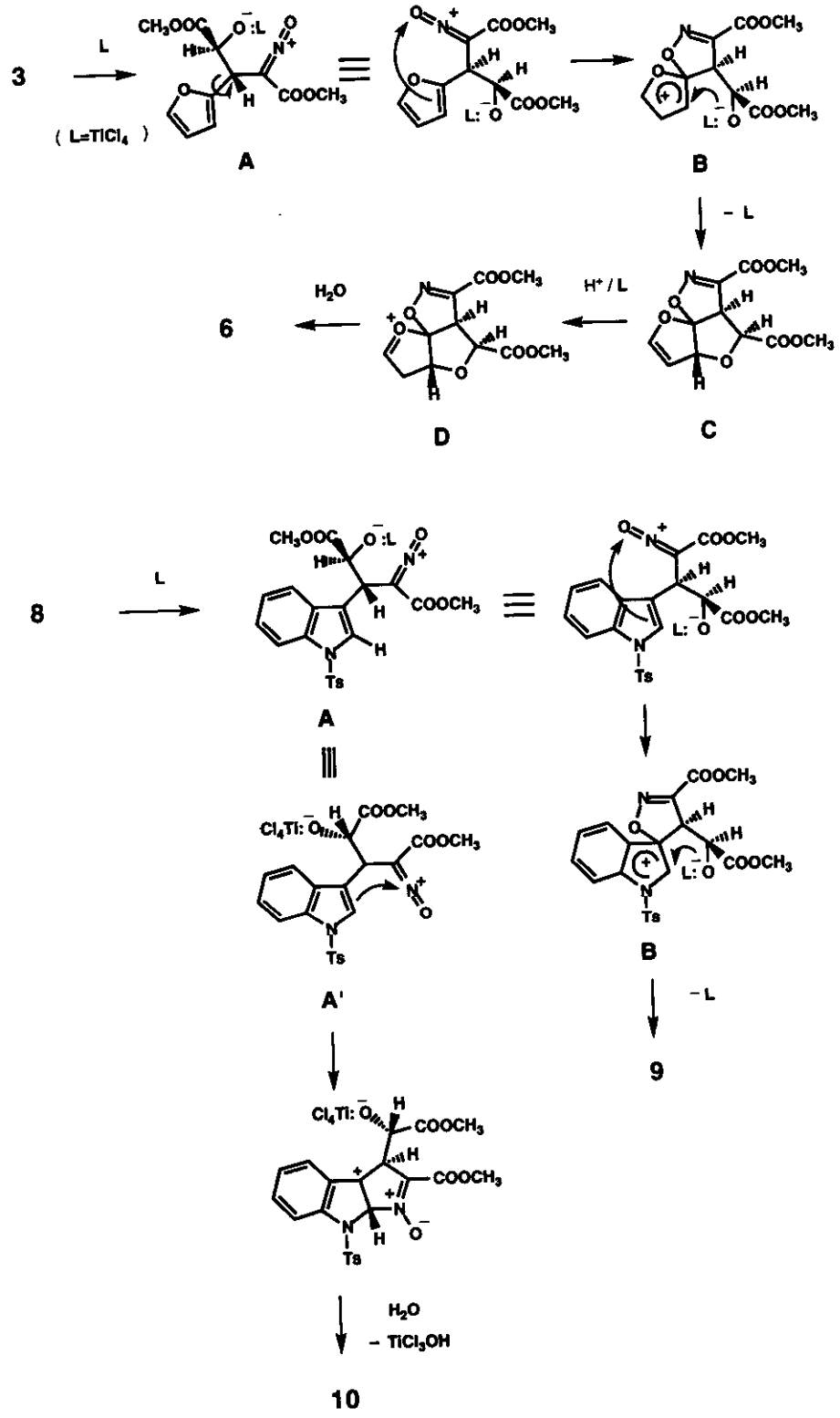
Figure 1. Perspective Drawings of Compounds (**5** and **7**)

Hz), which suggests that **9** has furo[3,4-*d*]isoxazole ring system. On the other hand, in the case of **10** methine hydrogens appeared at relatively low field (δ 4.13 and δ 6.47), and the coupling constant was much smaller than that of **9** (2.0 Hz). The ORTEP drawings of **9** and **10** are shown in Figure 2. As can be seen, **9** has indolo[2,3-*b*]furo[3,4-*d*]isoxazole ring system, while, the structure of **10** was confirmed to be 3a-chloroindolo[2,3-*b*]furo[3,4-*d*]-1-pyrroline-1-oxide.



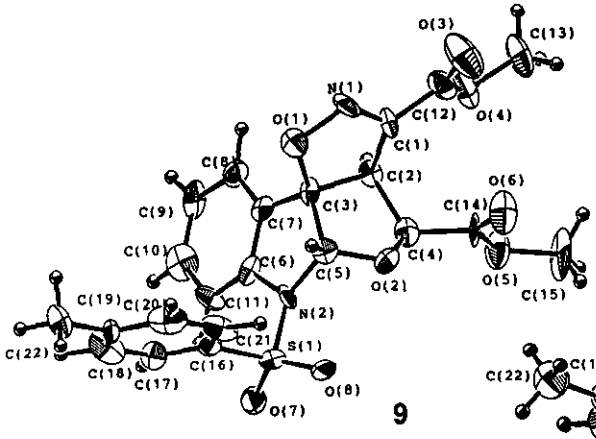
Scheme 2

The postulated mechanism of the formation of **6**, **9**, and **10** are illustrated in Scheme 3. The initial electrophilic attack of the Lewis acid on **3** causes N-O bond cleavage to give an ionic intermediate (**A**), which cyclizes through intramolecular *ipso*-attack[6] by oxygen atom of nitrosonium function to afford a spiro-intermediate (**B**). Then nucleophilic attack of negative oxygen ion to the furan ring gives a tricyclic intermediate (**C**), which is protonated (→**D**) and followed by hydration under acidic condition to afford **6**.[7] Analogous mechanism can be deduced for the formation of **9**, except for the acid-catalysed hydration process. On the other hand, intramolecular electrophilic attack of nitrosonium function at C-2 of the indole ring in the intermediate (**A'**), and subsequent chlorination with titanium tetrachloride gives the minor



Scheme 3

product (**10**). Compounds (**5**, **6**, **7**, and **9**) have a unique ring system which otherwise would be difficult to prepare, and may be applicable to synthesis of biologically active natural compounds containing furan or indole rings. Furthermore, it should be noted that compound (**10**) could be regarded as a new indole alkaloid and biological studies of **10** are in progress.



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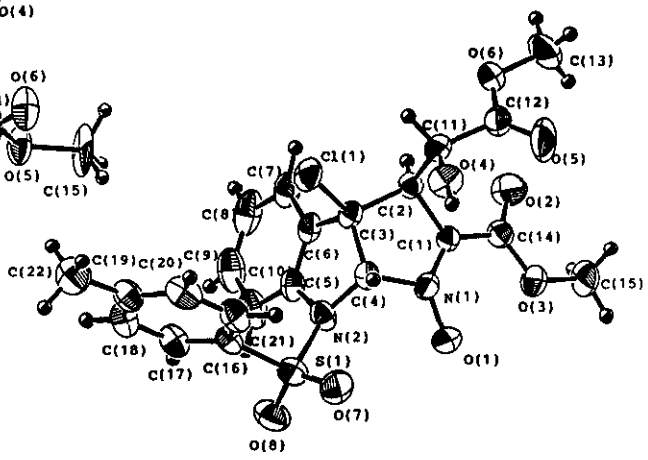

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Figure 2. Perspective Drawings of Compounds (**9** and **10**)

EXPERIMENTAL

Melting points were measured with a Yanaco MP apparatus and are uncorrected. Spectral data were recorded on the following instruments : Jasco IR-810(ir), JMS DX-300(ms), and Varian EM-390, XL-400, and VXR-300(^{1}H-nmr), JEOL PFT-100 and Varian XL-400(^{13}C-nmr). Tetramethylsilane was used as an internal standard for nmr measurement in chloroform-d. Column chromatography was carried out on a silica gel(Kanto Kagaku Co. ; up to 100 mesh) column.

3,5-Bis(methoxycarbonyl)-4-(3-furyl)-2-isoxazoline-2-oxide (2) : To a solution of 3-furaldehyde (1.35 ml , 15.6 mmol) in 10 ml of dimethylformaldehyde (DMF) was added methyl nitroacetate (**1**) (3.714 g, 31.2 mmol) and ammonium acetate (1.203 g, 15.6 mmol), and the mixture was stirred at room temperature for 15 h. The reaction mixture was poured into 900 ml of ice-water and extracted with toluene (3×300 ml). The extract was dried over anhydrous Na_2SO_4 and concentrated to dryness. The crude product (3.873 g) was

recrystallized from ethyl acetate-hexane to afford **2** (3.64 g, 87 %) as colorless needles: mp 104-106℃. Ir ν (KBr)cm^{-1} : 1760($COOCH_3$), 1740($COOCH_3$),1635(C=N). Ms(m/z) : 269 (M^+). ^1H Nmr ($CDCl_3$, δ, ppm) : 3.80(s, 3H, ester CH_3), 3.86(s, 3H, ester CH_3), 4.85(d, $J_{4,5}$=3.0 Hz, 1H, H-4), 4.93(d, $J_{4,5}$=3.0 Hz, 1H, H-5), 6.42(d, $J_{4',5'}$=2.0 Hz, 1H, H-4' (furan ring)), 7.44(d, $J_{4',5'}$=2,0 Hz, 1H, H-5' (furan ring)), 7.48(s, 1H, H-2' (furan ring)). *Anal.* Calcd for $C_{11}H_{11}NO_7$: C, 49.07; H, 4.12; N, 5.20. Found : C, 48.88; H, 4.03; N, 5.33.

The same procedure was applied to prepare **3** and **4** from 2-furaldehyde and *N-p*-toluene-sulfonyl-2-pyrrolecarbaldehyde, respectively.

3,5-Bis(methoxycarbonyl)-4-(2-furyl)-2-isoxazoline-2-oxide (3) : Yield 71 %. mp 103-105℃. (ethyl acetate-hexane). Ir ν (KBr)cm^{-1} : 1750($COOCH_3$), 1710($COOCH_3$), 1640(C=N). Ms(m/z) : 269 (M^+). ^1H Nmr ($CDCl_3$, δ, ppm) : 3.80(s, 3H, ester CH_3), 3.87(s, 3H, ester CH_3), 5.03(d, $J_{4,5}$=3.0 Hz, 1H, H-4), 5.07(d, $J_{4,5}$=3.0 Hz, 1H, H-5), 6.33(d, $J_{3',4'}$=3.5 Hz, 1H, H-3'), 6.37(m, 1H, H-4'), 7.41(d, $J_{4',5'}$=1.5 Hz, 1H, H-5'). *Anal.* Calcd for $C_{11}H_{11}NO_7$: C, 49.07; H, 4.12; N, 5.20. Found : C, 49.01; H, 4.14; N, 5.12.

3,5-Bis(methoxycarbonyl)-4-[3-(1-*p*-toluenesulfonyl)pyrrolyl]-2-isoxazoline-2-oxide (4) : Yield 59%. mp 147-150℃ (ethyl acetate-hexane). Ir ν (KBr)cm^{-1} : 1740 ($COOCH_3$), 1635(C=N). Ms(m/z) : 422 (M^+). ^1H Nmr ($CDCl_3$, δ, ppm) : 2.44(s, 3H, CH_3), 3.58(s, 3H, ester CH_3), 3.90(s, 3H, ester CH_3), 4.88(d, $J_{4,5}$=2.0 Hz, 1H, H-4), 5.44(d, $J_{4,5}$=2.0 Hz, 1H, H-5), 6.16(dd, $J_{3',4'}$=3.5 Hz, $J_{3,5}$=2.0 Hz, 1H, H-3'), 6.27(dd, $J_{3',4'}$=3.5 Hz, $J_{4,5}$=3.0 Hz, 1H, H-4'), 7.35(m, 1H, H-5'), 7.36(d, J=8.5 Hz, 2H, phenyl proton), 7.74(d, J=8.5 Hz, 2H, phenyl proton). *Anal.* Calcd for $C_{18}H_{18}N_2O_8S$: C, 51.18; H, 4.27; N, 6.64. Found : C, 51.30; H, 4.30; N, 6.54.

Dimethyl 7-Hydroxy-3a,4,7,8-tetrahydro-5a*H*-furo[2,3-*b*]furo[3,4-*d*]isoxazole-3,4-dicarboxylate (5) : Titanium tetrachloride (0.6 ml, 5.64 mmol) was added to a solution of **2** (500 mg, 1.86 mmol) in 20 ml of dichloromethane at 0 ℃, and the mixture was stirred at 0℃ for 1.5 h. The reaction mixture was poured into 100 ml of water and neutrallized with aqueous 10% Na_2CO_3 and extracted with dichloromethane (3×60 ml). The extract was washed with water (3×60 ml), dried over anhydrous Na_2SO_4, and concentrated to dryness. The residual syrup was applied to a silica gel column and eluted with ethyl acetate-hexane (1:1, v/v) to give **5** (176 mg, 33%). mp 134-136℃ (ethyl acetate-hexane). Ir ν (KBr)cm^{-1} : 3500(OH), 1740($COOCH_3$), 1590(C=N). Ms(m/z) : 287 (M^+). ^1H Nmr ($CDCl_3$, δ, ppm) :

2.35(d, $J_{7,8'}$=14.0 Hz, 1H, H-8'), 2.72(m, 1H, H-8), 3.45(s, 1H, OH), 3.75(s, 3H, ester CH_3), 3.86(s, 3H, ester CH_3), 4.32(d, $J_{3a,4}$=6.5 Hz, 1H, H-3a), 5.23(d, $J_{3a,4}$=6.5 Hz, 1H, H-4), 5.68(m, 1H, H-7), 5.95(s, 1H, H-5a). *Anal.* Calcd for $C_{11}H_{13}NO_8$: C, 46.00; H, 4.56; N, 4.88. Found : C, 46.17; H, 4.58; N, 4.72. The same procedure was applied to synthesize **6** and **7** from **3** and **4**, respectively.

Dimethyl 7-Hydroxy-3a,4,6,7-tetrahydro-5a*H*-furo[3,2-*b*]furo[3,4-*d*]isoxazole-3,4-dicarboxylate (6) : Yield 28%. mp 96-98℃ (ethyl acetate-hexane). Ir ν (KBr)cm^{-1} : 3425(OH), 1730($COOCH_3$), 1570(C=N). Ms(m/z) : 287 (M^+). ^{1}H Nmr ($CDCl_3$, δ, ppm) : 2.36(m, 1H, H-6), 2.45(m, 1H, H-6'), 3.84(s, 3H, ester CH_3), 3.86(s, 3H, ester CH_3), 4.20(d, $J_{3a,4}$ =6.3 Hz, 1H, H-3a), 4.66(d, $J_{3a,4}$ =6.3 Hz, 1H, H-4), 4.98(dd, $J_{5a,6}$ =8.0 Hz, $J_{5a,6'}$=5.0 Hz, 1H, H-5a), 5.85(m, 1H, H-7). *Anal.* Calcd for $C_{11}H_{13}NO_8$: C, 46.00; H, 4.56; N, 4.88. Found : C, 46.01; H, 4.56; N, 4.88.

Dimethyl 7-Hydroxy-3a,4,6,7-tetrahydro-8-*p*-toluenesulfonyl-5a*H*-pyrrolo-[3,2-*b*]furo[3,4-*d*]isoxazole-3,4-dicarboxylate (7) : Yield 40%. mp 178-180℃ (ethyl acetate-hexane). Ir ν (KBr)cm^{-1} : 3560(OH), 1740($COOCH_3$), 1570(C=N). Ms(m/z) : 440 (M^+). ^{1}H Nmr ($CDCl_3$, δ, ppm) : 2.22(m, 1H, H-6), 2.28(m, 1H, H-6'), 2.43(s, 3H, CH_3), 3.70(s, 3H, ester CH_3), 3.94(s, 3H, ester CH_3), 4.92(dd, $J_{5a,6}$ =7.0 Hz, $J_{5a,6'}$=3.5 Hz, 1H, H-5a), 4.98(d, $J_{3a,4}$ =9.2 Hz, 1H, H-3a), 5.31(d, $J_{3a,4}$ =9.2 Hz, 1H, H-4), 5.57(m, 1H, H-7), 7.32(d, J=8.5 Hz, 2H, phenyl protons), 7.81(d, J=8.5 Hz, 2H, phenyl protons). *Anal.* Calcd for $C_{18}H_{20}N_2O_9S$: C, 49.09; H, 5.00; N, 6.36. Found : C, 48.93; H, 4.72; N, 6.74.

3,5-Bis(methoxycarbonyl)-4-(1-*p*-toluenesulfonyl)indolyl-2-isoxazoline-2-oxide (8) : To a solution of 1-*p*-toluenesulfonyl-3-indolealdehyde (460 mg , 1.5 mmol) in 45 ml of dimethylformaldehyde (DMF) was added **1** (372 mg, 3.1 mmol) and ammonium acetate (120.5 mg, 1.6 mmol), and the mixture was stirred at room temperature for 15 h. The reaction mixture was poured into 100 ml of ice-water and extracted with toluene (3×100 ml). The extract was dried over anhydrous Na_2SO_4 and concentrated to dryness. The crude product (979.8 mg) was recrystallized from ethyl acetate to afford **8** (534 mg, 75 %) as colorless needles: mp 181.5-183℃. Ir ν (KBr)cm^{-1} : 1758($COOCH_3$), 1735($COOCH_3$), 1620(C=N). Ms(m/z) : 472 (M^+). ^{1}H Nmr ($CDCl_3$, δ, ppm) : 2.35(s, 3H, CH_3), 3.73(s, 3H, ester CH_3), 3.91(s, 3H, ester CH_3), 4.98(d, $J_{4,5}$=3.0 Hz, 1H, H-4), 5.13(d, $J_{4,5}$=3.0 Hz, 1H, H-5), 7.2-8.05(m, 9H, aromatic protons). *Anal.* Calcd for $C_{22}H_{20}N_2O_8S$: C, 55.92; H, 4.27; N, 5.93. Found : C,

55.81; H, 4.30; N, 5.88.

Reaction of 8 with Titanium Tetrachloride : Titanium tetrachloride (1.40 ml, 12.8 mmol) was added to a solution of **8** (1.60 g, 3.2 mmol) in 80 ml of dichloromethane at 0 ℃, and the mixture was stirred at 0℃ for 1.5 h. The reaction mixture was poured into 500 ml of water and neutrallized with aqueous 10% Na_2CO_3 and extracted with dichloromethane (3× 150 ml). The extract was washed with water (3×100 ml), dried over anhydrous Na_2SO_4, and concentrated to dryness. The residual syrup (1.60 g) was applied to a silica gel column and eluted with ethyl acetate-hexane (1:3, v/v) to give dimethyl 3a,4-dihydro-6-*p*-toluenesulfonyl-5a*H*-indolo[2,3-*b*]furo[3,4-*d*]isoxazole-3,4-dicarboxylate (**9**) (800 mg, 48%) and methyl 3a-chloro-α-hydroxy-2-methoxycarbonyl-1-oxido-8-*p*-toluenesulfonylindolo[2,3-*b*]-1-pyrroline-3-acetate (**10**) (244 mg, 15%).

9 : mp 86.0-88.0℃ (benzene-petroleum ether). Ir ν (KBr)cm^{-1} : 1750($COOCH_3$), 1610(C=N). Ms(m/z) : 472 (M^+). ^{1}H Nmr ($CDCl_3$, δ, ppm) : 2.40(s, 3H, CH_3), 3.76(s, 3H, ester CH_3), 3.89(s, 3H, ester CH_3), 4.30(d, $J_{3a,4}$=6.5 Hz, 1H, H-3a), 4.82(d, $J_{3a,4}$=6.5 Hz, 1H, H-4), 6.25(s, 1H, H-5a), 7.20-7.80(m, 8H, aromatic protons). *Anal.* Calcd for $C_{22}H_{20}N_2O_8S$: C, 55.92; H, 4.27; N, 5.93. Found : C, 55.98; H, 4.58; N, 5.54.

10 : mp 190.0-192.0℃ (ethyl acetate-hexane). Ir ν (KBr)cm^{-1} : 3475(OH), 1700($COOCH_3$), 1610(C=N). Ms(m/z) : 508 (M^+). ^{1}H Nmr ($CDCl_3$, δ, ppm) : 2.39(s, 3H, CH_3), 3.31(d, $J_{OH,\alpha}$=6.0 Hz, 1H, OH), 3.74(s, 3H, ester CH_3), 3.90(s, 3H, ester CH_3), 4.13(d, $J_{3,\alpha}$=2.0 Hz, 1H, H-3), 5.08(dd, $J_{3,\alpha}$=2.0 Hz, $J_{OH,\alpha}$=6.0 Hz, 1H, H-3'), 6.46(s, 1H, H-8a), 7.12-7.40(m, 4H, H-4, H-5, H-6, and H-7), 7.28(d, J=8.5 Hz, 2H, tosyl-H), 7.92(d, J=8.5 Hz, 2H, tosyl-H). *Anal.* Calcd for $C_{22}H_{21}N_2O_8ClS$: C, 51.96; H, 4.13; N, 5.51; Cl, 6.98; S, 6.30. Found : C, 51.77; H, 4.16; N, 5.68; Cl, 6.89; S, 6.33.

X-Ray Analyses of 5, 7, 9, and 10

X-Ray structure analyses of **5**, **7**, **9**, and **10** were carried out on a Rigaku AFC-5R diffractometer, and the cell parameters and the intensity data were measured with graphite monochromated Cu Kα(λ=1.54179 Å) radiation at 23℃. The crystal data are summarized in Table 2. The structures were solved by the direct method using the program MITHRIL (C. J. Gilmore : MITHRIL, an integrated direct method computer program, *J. Appl. Cryst.*, 1984, **17**, 42, Univ. of Glasgow, Scotland). The parameters of non-hydrogen atoms were refined by the

full-matrix least-squares method with anisotropic temperature factors. The hydrogen atoms were located from a difference Fourier synthesis, and refined only the temperature factors isotropically. The positional parameters for **5**, **7**, **9**, and **10** are listed in Tables 3~6, respectively. The selected bond lengths, bond angles torsion angles for **5**, **7**, **9**, and **10** are listed in Tables 7~10. In the case of **9**, a pair of enantiomer was solved as a unit. The positional parameters for both of them are listed in Table 5, but only one of them is depicted in Figure 2.

Table 2 Crystallographic Data for Compounds (**5**, **7**, **9**, and **10**)

	5	**7**	**9**	**10**
Formula	$C_{11}H_{13}NO_8$	$C_{18}H_{20}N_2O_9S$	$C_{22}H_{20}N_2O_8S$	$C_{22}H_{21}N_2ClO_8S$
F_w	287.23	440.42	472.47	508.93
Crystal dimensions (mm)	0.2×0.1×0.4	0.2×0.2×0.2	0.2×0.2×0.3	0.2×0.3×0.2
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	*P*1	$P2_1/a$	$P2_1/n$	$P2_1/n$
Lattice parameters				
a/Å	8.870 (1)	14.965 (1)	10.796 (4)	12.210 (1)
b/Å	12.159 (1)	8.529 (1)	30.556 (8)	14.616 (2)
c/Å	6.0696 (6)	16.417 (2)	13.565 (4)	13.151 (1)
α/deg	102.08 (1)	———	———	———
β/deg	90.59 (1)	109.415 (7)	99.93 (2)	102.037 (7)
γ/deg	71.110 (8)	———	———	———
V/Å^3	604.5 (1)	1976.1 (4)	4408 (4)	2295.4 (4)
Z	2	4	8	4
Dc/gcm^{-3}	1.578	1.480	1.424	1.473
μ(Cu $K\alpha$)/cm^{-1}	11.40	19.07	17.18	27.70
$2\theta_{max}$/deg	140.0	140.2	110.1	140.2
No. of Observation	1513	1616	1591	2734
No. of Variables	181	271	595	351
R	0.049	0.066	0.060	0.047

Table 3 Positional Parameters and Their Estimated Standard Deviations for **5**

Atom	*x*	*y*	*z*	B_{eq}
O(1)	0.2857(3)	0.1807(2)	−0.1215(4)	3.4(2)
O(2)	0.2415(3)	0.4226(2)	0.2711(4)	3.1(1)
O(3)	−0.0184(3)	0.4217(2)	0.1953(5)	4.0(2)
O(4)	0.7542(3)	0.0808(3)	0.0689(5)	4.3(2)
O(5)	0.6325(3)	0.1011(2)	0.4042(4)	3.3(2)
O(6)	0.5588(3)	0.3641(2)	0.3916(4)	3.4(2)
O(7)	0.4568(3)	0.3616(2)	0.7268(4)	3.1(2)
O(8)	−0.0408(3)	0.3278(3)	0.4846(5)	4.6(2)
N(1)	0.4487(3)	0.1376(3)	−0.0900(5)	3.0(2)
C(1)	0.4702(4)	0.1581(3)	0.1210(6)	2.4(2)

Table 3 continued

Atom	x	y	z	B_{eq}
C(2)	0.3211(4)	0.2176(3)	0.2743(6)	2.3(2)
C(3)	0.1984(4)	0.2421(3)	0.0942(6)	2.7(2)
C(4)	0.3005(4)	0.3426(3)	0.4197(6)	2.5(2)
C(5)	0.1442(4)	0.3777(3)	0.1156(6)	3.0(2)
C(6)	0.0440(4)	0.2153(4)	0.1114(7)	3.7(2)
C(7)	- 0.0655(4)	0.3298(4)	0.2582(8)	4.0(3)
C(8)	0.6366(4)	0.1092(3)	0.1889(6)	2.8(2)
C(9)	0.7855(5)	0.0515(4)	0.4940(7)	4.4(3)
C(10)	0.4538(4)	0.3585(3)	0.5070(6)	2.5(2)
C(11)	0.6055(5)	0.3627(4)	0.8279(7)	4.1(3)

Table 4 Positional Parameters and Their Estimated Standard Deviations for 7

Atom	x	y	z	B_{eq}
S(1)	0.5267(1)	0.2968(3)	0.7403(1)	3.9(1)
O(1)	0.3142(3)	0.3408(6)	0.7248(3)	3.6(2)
O(2)	0.3958(3)	0.3989(6)	0.9506(3)	3.9(2)
O(3)	0.3711(4)	0.8586(7)	0.7567(4)	5.7(3)
O(4)	0.2280(4)	0.7911(7)	0.6676(4)	5.7(3)
O(5)	0.2212(4)	0.5250(7)	0.9232(5)	7.0(4)
O(6)	0.2629(4)	0.7454(6)	0.8776(3)	4.6(3)
O(7)	0.5787(4)	0.1800(7)	0.9430(3)	6.1(3)
O(8)	0.4953(4)	0.4450(6)	0.6993(3)	4.5(3)
O(9)	0.6258(3)	0.2716(6)	0.7871(4)	5.6(3)
N(1)	0.2820(4)	0.4922(8)	0.6933(4)	3.7(3)
N(2)	0.4721(4)	0.2693(7)	0.8105(4)	3.4(3)
C(1)	0.3271(5)	0.597(1)	0.7473(5)	3.0(4)
C(2)	0.3965(5)	0.5345(9)	0.8260(5)	3.0(3)
C(3)	0.3886(5)	0.3578(8)	0.8099(5)	2.8(3)
C(4)	0.3780(5)	0.5501(8)	0.9128(5)	3.3(4)
C(5)	0.3620(5)	0.288(1)	0.8824(5)	3.3(3)
C(6)	0.4117(5)	0.134(1)	0.9043(5)	4.2(4)
C(7)	0.4978(5)	0.143(1)	0.8743(5)	3.7(4)
C(8)	0.3117(6)	0.761(1)	0.7246(5)	3.5(4)
C(9)	0.2072(7)	0.953(1)	0.6445(7)	8.0(6)
C(10)	0.2776(6)	0.601(1)	0.9050(6)	3.6(4)
C(11)	0.1737(6)	0.817(1)	0.8713(6)	6.4(5)
C(12)	0.4885(5)	0.146(1)	0.6652(5)	3.3(4)
C(13)	0.4111(6)	0.168(1)	0.5922(6)	4.3(4)
C(14)	0.3785(6)	0.045(1)	0.5350(6)	5.1(5)
C(15)	0.4213(6)	- 0.100(1)	0.5499(6)	4.8(5)
C(16)	0.5006(7)	- 0.117(1)	0.6240(6)	5.2(5)
C(17)	0.5344(5)	0.007(1)	0.6801(5)	4.4(4)
C(18)	0.3841(6)	- 0.236(1)	0.4918(6)	7.2(6)

Table 5 Positional Parameters and Their Estimated Standard Deviations for **9**

Atom	*x*	*y*	*z*	B_{eq}
S(1)	0.1059(5)	0.1227(2)	0.8878(4)	3.2(3)
S(2)	0.5850(5)	− 0.0915(2)	1.4721(4)	4.2(3)
O(1)	0.106(1)	0.0780(4)	1.224(1)	4.6(7)
O(2)	− 0.061(1)	0.1505(5)	1.0734(9)	4.4(7)
O(3)	− 0.179(1)	0.1028(5)	1.374(1)	6.4(9)
O(4)	− 0.104(2)	0.1720(6)	1.391(1)	10(1)
O(5)	− 0.241(1)	0.1869(5)	1.167(1)	9(1)
O(6)	− 0.108(1)	0.2400(5)	1.222(1)	8(1)
O(7)	0.171(1)	0.1534(3)	0.8364(7)	3.9(7)
O(8)	− 0.028(1)	0.1175(3)	0.8586(7)	4.4(7)
O(9)	0.469(1)	− 0.1514(4)	1.1397(9)	4.3(7)
O(10)	0.409(1)	− 0.1757(4)	1.3655(8)	4.9(8)
O(11)	0.128(1)	− 0.2308(4)	1.114(1)	5.5(8)
O(12)	0.284(1)	− 0.2727(5)	1.080(1)	9(1)
O(13)	0.110(1)	− 0.2032(4)	1.374(1)	6.2(8)
O(14)	0.255(1)	− 0.2500(4)	1.340(1)	7(1)
O(15)	0.539(1)	− 0.0539(4)	1.5210(8)	5.2(8)
O(16)	0.605(1)	− 0.1334(3)	1.5217(7)	4.7(7)
N(1)	0.012(2)	0.0814(5)	1.284(1)	5(1)
N(2)	0.129(1)	0.1372(4)	1.007(1)	2.8(8)
N(3)	0.419(1)	− 0.1935(5)	1.107(1)	4(1)
N(4)	0.477(1)	− 0.0999(5)	1.137(1)	2.9(8)
C(1)	− 0.016(2)	0.1225(7)	1.287(1)	4(1)
C(2)	0.052(2)	0.1558(7)	1.233(1)	4(1)
C(3)	0.117(2)	0.1210(6)	1.178(1)	3(1)
C(4)	− 0.024(2)	0.1839(6)	1.152(2)	4(1)
C(5)	0.038(2)	0.1221(6)	1.070(1)	4(1)
C(6)	0.255(2)	0.1405(5)	1.063(1)	2(1)
C(7)	0.249(2)	0.1298(5)	1.162(1)	3(1)
C(8)	0.354(2)	0.1302(5)	1.233(1)	3(1)
C(9)	0.470(2)	0.1408(7)	1.207(1)	5(1)
C(10)	0.470(2)	0.1501(6)	1.106(2)	4(1)
C(11)	0.365(2)	0.1512(6)	1.032(1)	4(1)
C(12)	− 0.109(3)	0.1366(8)	1.358(2)	6(2)
C(13)	− 0.267(2)	0.1119(7)	1.440(1)	10(2)
C(14)	− 0.143(2)	0.2033(8)	1.177(2)	6(1)
C(15)	− 0.204(2)	0.2647(7)	1.257(2)	10(2)
C(16)	0.172(2)	0.0702(6)	0.883(1)	3(1)
C(17)	0.298(2)	0.0647(7)	0.871(1)	4(1)
C(18)	0.347(2)	0.0258(7)	0.861(2)	5(1)
C(19)	0.277(2)	− 0.0121(7)	0.868(1)	5(1)
C(20)	0.153(2)	− 0.0068(7)	0.884(1)	5(1)
C(21)	0.101(2)	0.0350(7)	0.888(1)	4(1)
C(22)	0.332(2)	− 0.0541(6)	0.857(1)	8(1)
C(23)	0.321(2)	− 0.2006(6)	1.145(1)	3(1)
C(24)	0.285(1)	− 0.1628(5)	1.207(1)	3(1)
C(25)	0.40292)	− 0.1337(6)	1.214(1)	3(1)
C(26)	0.282(2)	− 0.1728(6)	1.317(2)	4(1)
C(27)	0.475(2)	− 0.1430(7)	1.323(1)	3(1)
C(28)	0.427(2)	− 0.0666(7)	1.302(2)	3(1)
C(29)	0.382(2)	− 0.0863(7)	1.210(2)	4(1)

Table 5 continued

Atom	x	y	z	B_{eq}
C(30)	0.320(2)	- 0.0619(7)	1.132(1)	4(1)
C(31)	0.305(2)	- 0.0175(7)	1.147(2)	5(1)
C(32)	0.349(2)	0.0011(7)	1.241(2)	5(1)
C(33)	0.411(2)	- 0.0235(7)	1.319(1)	491)
C(34)	0.247(2)	- 0.2391(7)	1.107(2)	5(1)
C(35)	0.038(2)	- 0.2651(7)	1.082(2)	8(1)
C(36)	0.216(2)	- 0.2132(6)	1.343(2)	5(1)
C(37)	0.038(2)	- 0.2371(7)	1.407(2)	10(2)
C(38)	0.729(2)	- 0.0768(8)	1.434(1)	4(1)
C(39)	0.820(2)	- 0.1090(6)	1.423(1)	5(1)
C(40)	0.930(2)	- 0.0938(9)	1.394(1)	6(1)
C(41)	0.949(2)	- 0.0495(8)	1.382(1)	5(1)
C(42)	0.856(2)	- 0.0206(7)	1.392(2)	6(1)
C(43)	0.745(2)	- 0.0324(6)	1.417(1)	4(1)
C(44)	1.077(2)	- 0.0375(6)	1.355(1)	6(1)

Table 6 Positional Parameters and Their Estimated Standard Deviations for **10**

Atom	x	y	z	B_{eq}
Cl(1)	0.37741(9)	0.47798(7)	0.57426(8)	4.97(5)
S(1)	0.1122(1)	0.60664(7)	0.33037(9)	4.47(5)
O(1)	- 0.0101(2)	0.3879(2)	0.3814(2)	5.4(1)
O(2)	0.1518(3)	0.1397(2)	0.4630(3)	6.5(2)
O(3)	- 0.0166(2)	0.2030(2)	0.4102(2)	4.9(1)
O(4)	0.2049(2)	0.3757(2)	0.6780(2)	5.1(1)
O(5)	0.1589(3)	0.1997(2)	0.7057(3)	8.8(2)
O(6)	0.3216(2)	0.1562(2)	0.6726(2)	4.9(1)
O(7)	0.0304(2)	0.6171(2)	0.3933(2)	6.0(2)
O(8)	0.0804(2)	0.6134(2)	0.2202(2)	6.1(2)
N(1)	0.0882(3)	0.3745(2)	0.4312(2)	3.7(1)
N(2)	0.1631(3)	0.5022(2)	0.3554(2)	3.8(1)
C(1)	0.1398(3)	0.2979(3)	0.4665(3)	3.4(2)
C(2)	0.2570(3)	0.3148(3)	0.5243(3)	3.4(2)
C(3)	0.2808(3)	0.4102(2)	0.4829(3)	3.4(2)
C(4)	0.1664(3)	0.4565(3)	0.4520(3)	3.5(2)
C(5)	0.2519(3)	0.4655(3)	0.3107(3)	3.9(2)
C(6)	0.3185(3)	0.4091(2)	0.3821(3)	3.7(2)
C(7)	0.4080(4)	0.3637(3)	0.3553(4)	5.0(2)
C(8)	0.4274(5)	0.3773(4)	0.2572(5)	6.4(3)
C(9)	0.3597(5)	0.4350(4)	0.1881(5)	6.5(3)
C(10)	0.2708(5)	0.4800(3)	0.2121(4)	5.1(2)
C(11)	0.2705(3)	0.3097(3)	0.6419(3)	4.0(2)
C(12)	0.2430(4)	0.2155(3)	0.6784(3)	4.7(2)
C(13)	0.3002(4)	0.0633(3)	0.6973(4)	7.6(3)
C(14)	0.0924(3)	0.2059(3)	0.4479(3)	4.0(2)
C(15)	- 0.0656(4)	0.1137(3)	0.3924(3)	6.0(2)
C(16)	0.2235(3)	0.6814(2)	0.3733(3)	3.8(2)

Table 6 continued

Atom	x	y	z	B_{eq}
C(17)	0.2909(4)	0.7086(3)	0.3072(4)	4.6(2)
C(18)	0.3757(4)	0.7701(3)	0.3410(4)	4.9(2)
C(19)	0.3943(4)	0.8064(3)	0.4407(4)	4.7(2)
C(20)	0.3281(4)	0.7755(3)	0.5059(4)	5.3(2)
C(21)	0.2422(4)	0.7138(3)	0.4752(4)	4.7(2)
C(22)	0.4814(4)	0.8780(3)	0.4736(4)	6.8(3)

Table 7 Selected Bond Lengths, Bond Angles, and Torsion Angles of **5**

Bond Length (Å)		Bond Angle (°)		Torsion Angle (°)	
O(1)–N(1)	1.396 (3)	O(1)–N(1)–C(1)	109.2 (3)	O(1)–N(1)–C(1)–C(2)	1.6 (4)
O(1)–C(3)	1.452 (4)	O(1)–C(3)–C(2)	105.8 (3)	O(1)–N(1)–C(1)–C(8)	175.0 (3)
O(2)–C(4)	1.436 (4)	O(2)–C(4)–C(2)	105.0 (3)	O(1)–C(3)–C(2)–C(1)	8.3 (3)
O(2)–C(5)	1.417 (4)	O(2)–C(5)–C(3)	107.3 (3)	O(1)–C(3)–C(2)–C(4)	128.9 (3)
O(3)–C(5)	1.416 (4)	O(3)–C(5)–C(3)	106.3 (3)	O(1)–C(3)–C(6)–C(7)	– 148.1 (3)
O(3)–C(7)	1.434 (5)	N(1)–O(1)–C(3)	109.7 (3)	O(2)–C(5)–C(3)–C(6)	133.7 (3)
N(1)–C(1)	1.277 (4)	C(1)–C(2)–C(3)	98.9 (3)	O(3)–C(5)–C(3)–C(6)	13.7 (4)
C(1)–C(2)	1.504 (4)	C(2)–C(3)–C(5)	105.0 (3)	O(3)–C(7)–C(6)–C(3)	– 34.6 (4)
C(2)–C(3)	1.540 (4)	C(3)–C(6)–C(7)	102.5 (3)	C(1)–C(2)–C(3)–C(5)	– 108.6 (3)
C(3)–C(5)	1.537 (5)	C(4)–O(2)–C(5)	109.1 (3)	C(2)–C(4)–O(2)–C(5)	32.9 (3)
C(3)–C(6)	1.517 (5)	C(5)–O(3)–C(7)	110.7 (3)	C(3)–C(5)–O(2)–C(4)	– 25.1 (4)
C(6)–C(7)	1.516 (6)	C(5)–C(3)–C(6)	104.1 (3)	C(5)–C(3)–C(6)–C(7)	– 29.2 (4)

Table 8 Selected Bond Lengths, Bond Angles, and Torsion Angles of **7**

Bond Length (Å)		Bond Angle (°)		Torsion Angle (°)	
O(1)–N(1)	1.415 (7)	O(1)–N(1)–C(1)	110.2 (6)	O(1)–N(1)–C(1)–C(2)	– 1.4 (9)
O(1)–C(3)	1.475 (8)	O(1)–C(3)–C(2)	104.6 (5)	O(1)–N(1)–C(1)–C(8)	174.3 (6)
O(2)–C(4)	1.417 (8)	O(2)–C(4)–C(2)	105.1 (6)	O(1)–C(3)–C(2)–C(1)	– 1.2 (7)
O(2)–C(5)	1.426 (8)	O(2)–C(5)–C(3)	103.8 (6)	O(1)–C(3)–C(2)–C(4)	123.2 (5)
N(1)–C(1)	1.281 (8)	N(1)–C(1)–C(2)	114.5 (7)	O(1)–C(3)–N(2)–C(7)	– 118.1 (6)
N(2)–C(3)	1.458 (8)	N(2)–C(3)–C(5)	104.0 (6)	O(2)–C(5)–C(3)–N(2)	102.3 (6)
N(2)–C(7)	1.461 (9)	N(2)–C(7)–C(6)	102.5 (6)	N(2)–C(3)–C(5)–C(6)	– 16.5 (7)
C(1)–C(2)	1.462 (9)	C(1)–C(2)–C(3)	102.4 (6)	C(1)–C(2)–C(3)–C(5)	– 121.4 (6)
C(2)–C(3)	1.528 (9)	C(2)–C(3)–C(5)	106.4 (6)	C(2)–C(4)–O(2)–C(5)	– 37.4 (7)
C(3)–C(5)	1.500 (9)	C(3)–N(2)–C(7)	114.0 (6)	C(3)–N(2)–C(7)–C(6)	10.8 (8)
C(5)–C(6)	1.487 (9)	C(3)–C(2)–C(4)	102.6 (6)	C(3)–C(5)–O(2)–C(4)	39.1 (7
C(6)–C(7)	1.526 (9)	C(5)–C(6)–C(7)	106.8 (7)	C(5)–C(3)–N(2)–C(7)	3.2 (8)

Table 9 Selected Bond Lengths, Bond Angles, and Torsion Angles of **9**

Bond Length (Å)		Bond Angle (°)		Torsion Angle (°)	
S(1)–N(2)	1.65 (1)	O(1)–N(1)–C(1)	107 (2)	O(1)–N(1)–C(1)–C(2)	– 1 (3)
O(1)–N(1)	1.41 (2)	O(1)–C(3)–C(2)	110 (2)	O(1)–N(1)–C(1)–C(12)	– 174 (2)
O(1)–C(3)	1.47 (2)	O(2)–C(4)–C(2)	100 (1)	O(1)–C(3)–C(2)–C(1)	– 14 (2)
O(2)–C(4)	1.48 (2)	O(2)–C(5)–C(3)	107 (1)	O(1)–C(3)–C(2)–C(4)	– 136 (2)
O(2)–C(5)	1.38 (2)	N(1)–C(1)–C(2)	119 (2)	O(1)–C(3)–C(7)–C(6)	126 (2)
N(1)–C(1)	1.30 (2)	N(2)–C(5)–C(3)	104 (1)	O(2)–C(5)–C(3)–C(7)	– 128 (2)
N(2)–C(5)	1.49 (2)	N(2)–C(6)–C(7)	107 (2)	N(2)–C(5)–C(3)–C(7)	– 7 (2)
N(2)–C(6)	1.44 (2)	C(1)–C(2)–C(3)	94 (2)	N(2)–C(6)–C(7)–C(3)	– 3 (2)
C(1)–C(2)	1.52 (2)	C(2)–C(3)–C(5)	103 (2)	C(1)–C(2)–C(3)–C(5)	103 (2)
C(2)–C(3)	1.53 (2)	C(3)–C(2)–C(4)	106 (2)	C(2)–C(4)–O(2)–C(5)	– 39 (2)
C(3)–C(5)	1.56 (2)	C(3)–C(7)–C(6)	113 (2)	C(3)–C(5)–O(2)–C(4)	28 (2)
C(3)–C(7)	1.50 (2)	C(5)–N(2)–C(6)	112 (1)	C(5)–C(3)–C(7)–C(6)	6 (2)

Table 10 Selected Bond Lengths, Bond Angles, and Torsion Angles of **10**

Bond Length (Å)		Bond Angle (°)		Torsion Angle (°)	
Cl(1)–C(3)	1.796 (3)	Cl(1)–C(3)–C(2)	114.1 (3)	Cl(1)–C(3)–C(2)–C(1)	150.1 (3)
S(1)–N(2)	1.656 (3)	O(1)–N(1)–C(1)	130.4 (3)	Cl(1)–C(3)–C(6)–C(5)	– 104.8 (3)
O(1)–N(1)	1.258 (3)	O(4)–C(11)–C(2)	111.2 (3)	S(1)–N(2)–C(4)–C(3)	– 136.8 (3)
O(4)–C(11)	1.320 (4)	N(1)–C(1)–C(2)	112.0 (3)	S(1)–N(2)–C(5)–C(10)	– 36.1 (5)
N(1)–C(1)	1.320 (4)	N(1)–C(4)–C(3)	101.7 (3)	O(4)–C(11)–C(2)–C(1)	– 61.1 (4)
N(1)–C(4)	1.521 (4)	N(2)–C(4)–C(3)	107.4 (3)	N(1)–C(1)–C(2)–C(3)	– 20.2 (4)
N(2)–C(4)	1.428 (4)	N(2)–C(5)–C(6)	109.3 (3)	N(1)–C(4)–C(3)–C(2)	– 24.7 (4)
N(2)–C(5)	1.441 (4)	C(1)–C(2)–C(3)	101.5 (3)	N(1)–C(4)–N(2)–C(5)	– 92.3 (3)
C(1)–C(2)	1.495 (3)	C(2)–C(3)–C(4)	105.4 (3)	C(1)–C(2)–C(3)–C(4)	27.2 (4)
C(2)–C(3)	1.546 (5)	C(3)–C(2)–C(11)	114.4 (3)	C(2)–C(1)–N(1)–C(4)	4.7 (4)
C(2)–C(11)	1.524 (5)	C(3)–C(6)–C(5)	110.6 (3)	C(2)–C(3)–C(6)–C(7)	– 55.8 (5)
C(3)–C(4)	1.529 (5)	C(4)–N(2)–C(5)	107.7 (3)	C(4)–C(3)–C(6)–C(5)	13.1 (4)

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