SYNTHESIS OF FUSED 3a,4-DIHYDRO-5a,*H*-BENZOFURO-[3,3a-*d*]ISOXAZOLES[1]

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Abstract - Reaction of 2-isoxazoline-2-oxides (**1**) with titanium tetrachloride afforded Diels-Alder dimers (**3**) of 3a,4-dihydro-5a,*H*-benzofuro[3,3a-*d*]isoxazoles (**2**). The stereochemistry of the dimer (**3a**) was confirmed by X-ray analysis. As an application of the Diels-Alder reaction, several fused 3a,4-dihydro-5a,*H*-benzofuro[3,3a-*d*]isoxazoles (**5**,**6**, and **7**) were synthesized by the reactions of **2** with acetylenic dienophiles.

Recently, we described new ring transformations of substituted 2-isoxazoline-2-oxides (**1**) to various heterocyclic ring systems such as fused furo[3,3a-*d*]isoxazoles,[2] monocyclic or fused 1,2-oxazines,[3] and benzofuro[2,3-*c*]tetrahydropyrans.[4] These transformations are mediated by Lewis acid ($TiCl_4$, $TiBr_4$ etc.), and the reaction course leading to the products depends on the type and site of substitution of **1**. Among the above ring transformation products, fused furo[3,3a-*d*]isoxazoles, such as benzofuro[3,3a-*d*]isoxazoles (**2**),[5] have a unique ring system which otherwise would be difficult to prepare. It is also important that **2** should have synthetic potential as the reactive cyclic dienes[6] or as isoxazolines.[7] We now report on the synthesis of a novel type of fused 3a,4-dihydro-5a,*H*-benzofuro[3,3a-*d*]isoxazoles (**5**,**6**, and

7) by Diels-Alder reaction of **2**.

The reaction of isoxazoline-2-oxide (**1 a**)[8] with excess $TiCl_4$ was previously shown to give **2 a** in 81 % yield by stirring for 30 min.[9] When the reaction time was extended to 18 hours, two additional products (**3 a**[10] ; 23 % and **4 a**; 21 %) were isolated after chromatographical separation. (Scheme 1)

The structures of **2a**, **3a**, and **4a** were deduced from spectroscopic data and confirmed by X-ray crystallography. Thus, **3 a** showed an [M^+] ion at *m/z* 626 corresponding to the molecular formula of $C_{26}H_{24}N_2O_{12}Cl_2$ expected for a dimer of **2 a**. The ^{1}H-nmr spectrum showed the presence of two olefinic hydrogens [δ_H 5.87, 6.10], two sets of coupled aliphatic methine hydrogens [δ_H 3.97, 4.54, J=7.0 Hz ; 4.04, 4.83, J=9.2 Hz], of which the coupling constants and chemical shifts are similar to those of a set of H-3a and H-4 of **2 a** [δ_H 4.21, 4.86, J=7.0 Hz], other six aliphatic methine hydrogens [δ_H 2.98, 3.20, 3.54, 3.67, 4.55, 4.74], in addition to four ester Me groups. (Table 1) These spectral data suggested that **3a** should be a Diels-Alder dimer of **2a**. This deduction was proved by a single crystal X-ray analysis of **3a**. A perspective drawing of the molecule of **3a** is illustrated in Figure 1. The structure of **3a** reveals that the molecule results from Diels-Alder dimerization of **2a**. Thus, the C(6)=C(7)-C(8)=C(9) and C(10)=C(11) moieties correspond *to diene and dienophile* compornents, respectively, in the Diels-Alder reaction for **3a**. The stereochemistry of **3a** was confirmed to be *endo* configuration, *i.e.*, as depicted in

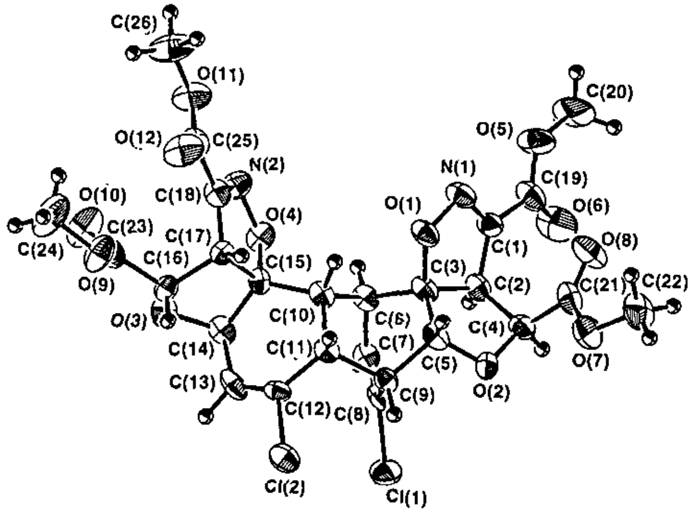
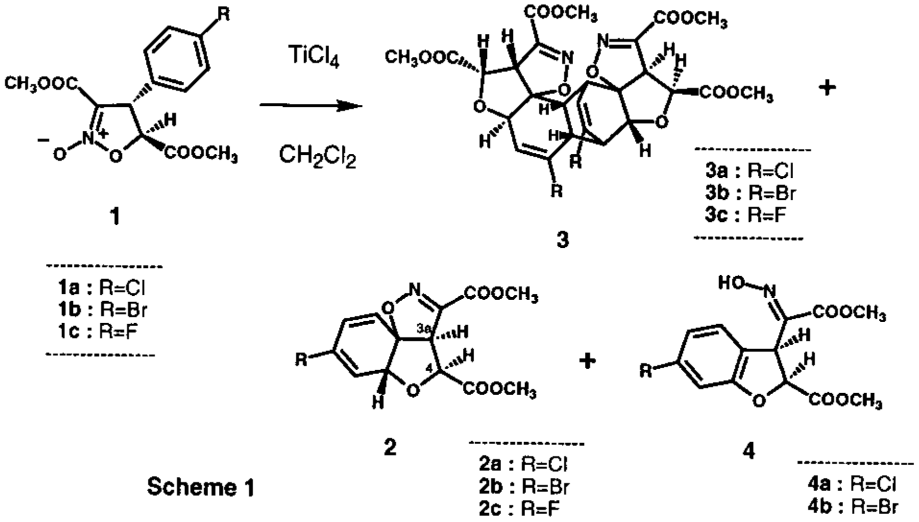


Figure 1 A Perspective Drawing of **3a**

Figure 1, the bulky cyclohexene ring C(10)-C(11)-C(12)-C(13)-C(14)-C(15) (dienophile component) is under the bridge C(6)-C(7)-C(8)-C(9) (diene). The molecule is also assigned to be *anti* π-facial diastereomer[6] with respect to the furan ring C(4)-C(2)-C(3)-C(5)-O(2), thus the addition of the dienophile forming C(10)-C(11) proceeds *via anti* to the diene forming cyclohexene ring C(5)-C(3)-C(6)-C(7)-C(8)-C(9). (Figure 1)



1

1a : R=Cl
1b : R=Br
1c : R=F

3

3a : R=Cl
3b : R=Br
3c : R=F

2

2a : R=Cl
2b : R=Br
2c : R=F

4

4a : R=Cl
4b : R=Br

Scheme 1

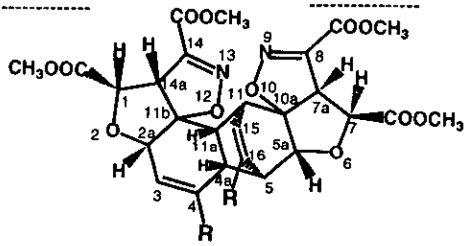


Table 1. Selected ^{1}H-Nmr Chemical Shifts and Coupling Constants for Compounds 3

	Chemical Shift (ppm)			Coupling Constant (Hz)			
	3a	3b	3c		3a	3b	3c
H-1	4.54 d	4.49 d	4.54 d	J(1,14a)	7.0	7.0	7.0
H-2a	4.55 d	4.56 d	4.56 d				
H-3	5.87 d	6.09 d	5.88 d	J(4a,11a)	9.0	9.0	9.0
H-4a	2.98 dd	3.08 dd	2.98 dd				
H-5	3.67 dd	3.97 dd	3.68 dd	J(7,7a)	9.2	9.2	9.2
H-5a	4.74 d	4.72 d	4.73 d				
H-7	4.83 d	4.83 d	4.83 d	J(4a,5)	3.0	3.0	3.0
H-7a	4.04 d	4.02 d	4.05 d				
H-11	3.54 dd	3.54 dd	3.54 dd	J(5,5a)	3.0	3.0	3.0
H-11a	3.20 dd	3.15 dd	3.20 dd				
H-14a	3.97 d	3.97 d	3.97 d	J(11,11a)	2.0	2.0	2.0
H-15	6.10 dd	6.37 dd	6.13 dd				

On the other hand, **4a** showed an [M$^+$] ion at m/z 313 corresponding to the molecular formula of $C_{13}H_{12}NO_6Cl_2$, which corresponds to that of monomer (**2a**). The ir and ^{1}H-nmr spectra exhibited the presence of oxime group and dihydrobenzofuran moiety in **4a**. The structure of **4a** was finally confirmed by X-ray analysis. A perspective drawing of the molecule of **4a** is illustrated in Figure 2. The molecule consists of a 2,3-dihydrobenzofuran ring with an oxime group which is *syn* to the 2,3-dihydrobenzofuran moiety, so that the molecule has the *E* configuration. This procedure was applied to **1b** (R=Br)[8] to afford **2b** (33 %), **3b** (22 %), and **4b** (24 %), however, in the case of **1c** (R=F),[8] only **2c** (32 %) and **3c** (26 %) were isolated. (Table 2, Method I) We also examined the synthesis of **3** directly from **2**. Thus, a solution of **2** in toluene was refluxed overnight to afford **3** in high yields. (Table 2, Method II) These results clearly show that the one-pot formation of **3** from **1** proceeds *via* the initial ring transformation into **2** *via* intermediate (**B**)[11] followed by the Lewis acid ($TiCl_4$) promoted Diels-Alder dimerization[6] *in situ* to give **3**. Formation of **4** can be postulated to occur *via* formation of 3*H*-indole-1-oxide

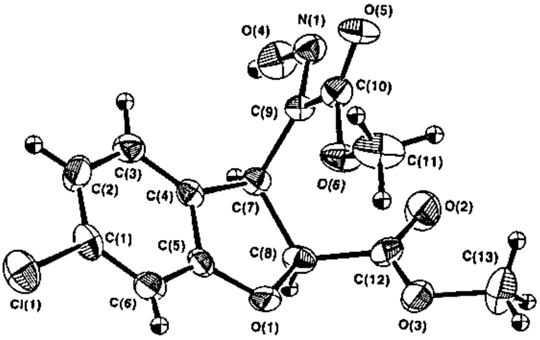
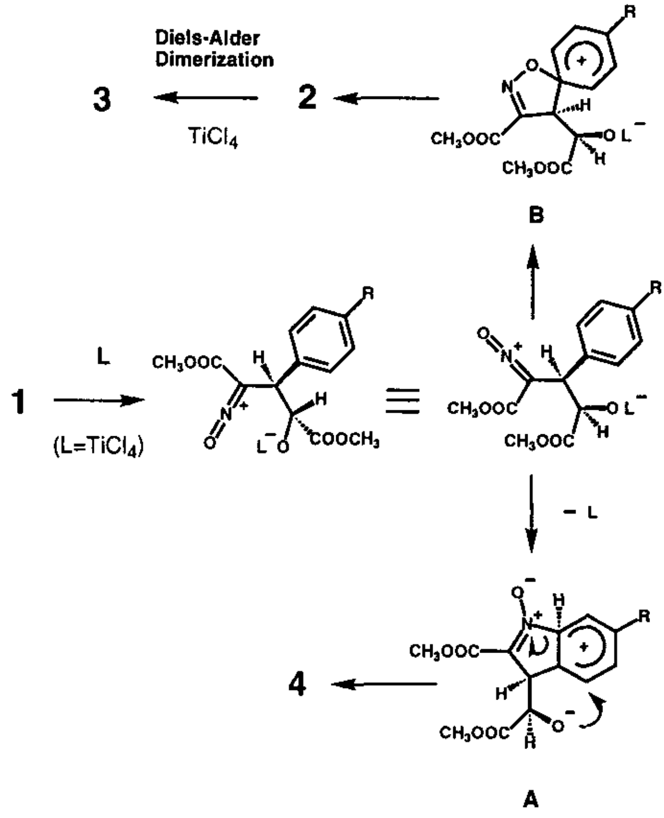


Figure 2 A Perspective Drawing of **4a**

Table 2 Yields and Physical Properties of the Compounds **2**, **3**, **4**, **5**, **6**, and **7**

Compd.	R	Yield (%) Method I	Yield (%) Method II	mp (°C)
2a	Cl	35	—	ref. 9
2b	Br	33	—	ref. 9
2c	F	32	—	ref. 9
3a	Cl	23	78	245–246
3b	Br	22	75	225–226
3c	F	26	72	273–276
4a	Cl	21	—	139–140
4b	Br	24	—	147–149
5a	Cl	43		118–119
5b	Br	42		131–133
5c	F	53		147–149
6a	Cl	30		146–148
6b	Br	28		syrup
6c	F	30		143–145
7a	Cl	67		syrup
7b	Br	65		syrup
7c	F	61		133–135

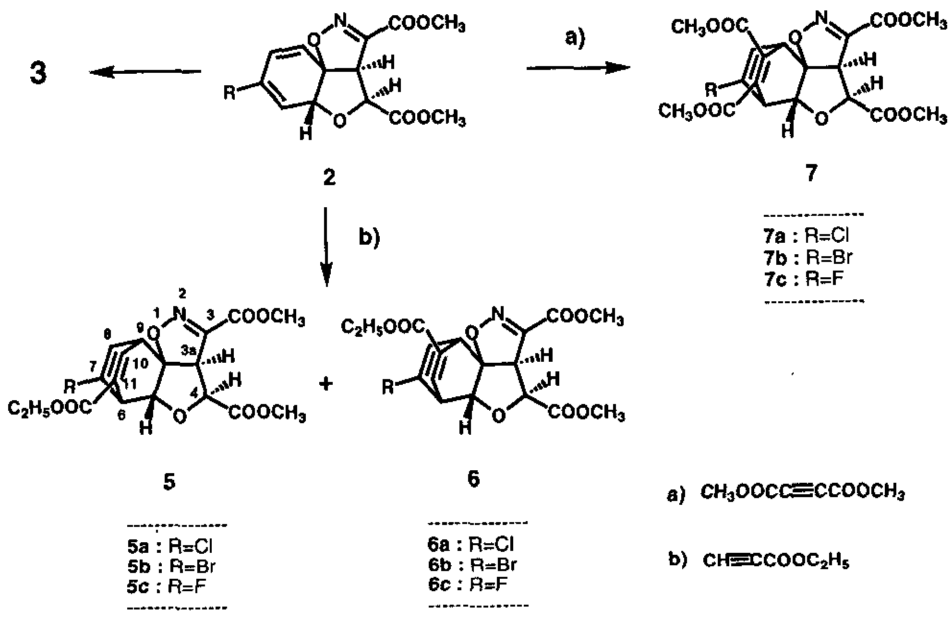
intermediate (**A**).[3c,4] Then, nucleophilic attack of negatively charged oxygen at the site *meta* to the substituent R in **A** causes formation of the furan ring and the subsequent cleavage of the C-N bond with protonation gives **4**. (Scheme 2) To an application of the dimerization, we examined Diels-Alder cycloaddition of **2** with acetylenic dienophiles such as ethyl propiolate and dimethyl acetylenedicarboxylate. The results are shown in Table 2. Both of dienophiles resulted to give the corresponding cycloadducts, thus ethyl propiolate afforded a pair of positional isomers (**5** and **6**), while dimethyl acetylenedicarboxylate gave **7**. (Scheme 3)



Scheme 2

The structures of the isomers **5** and **6** were distinguished on the basis of ^{1}H-nmr analysis. The ^{1}H-nmr spectral data of **5** were closely compatible with those of **6**, except for the coupling pattern of the H-6 and H-9 protons. Thus, in the ^{1}H-nmr spectrum of **5**, H-6 was not coupled with H-11 and H-9 was coupled with two olefinic protons (H-8 and H-10), while in that of **6**, H-6 and H-9 were coupled with H-11 and H-8, respectively. (Table 3) These results clearly show that the ester group is attached at C-11 for isomer (**5**), while at C-10 for isomer (**6**). This deduction was proved by X-ray analyses of **5a** and **6c**.

Perspective drawings of the molecules of **5a** and **6c** are illustrated in Figures 3 and 4. The stereochemistry of **5 a** and **6 c** are assigned to be *anti* π-facial diastereomer[6] with respect to



Scheme 3

Table 3. Selected ^{1}H-Nmr Chemical Shifts and Coupling Constants for Compounds 5, 6, and 7

	Chemical Shift (ppm) / Coupling Constant (Hz)								
	5a	5b	5c	6a	6b	6c	7a	7b	7c
H-3a	3.89	3.99	4.00	3.99	3.99	3.98	3.99	3.99	4.01
H-4	5.03	5.02	5.07	5.02	5.02	5.04	5.03	5.02	5.06
H-5a	4.67	4.73	4.68	4.72	4.72	4.74	4.89	4.88	4.92
H-6	4.45	4.62	4.29	4.05	4.18	4.09	4.31	4.43	4.18
H-8	6.14	6.38	5.42	6.23	6.48	5.41	6.26	6.49	5.55
H-9	3.81	3.84	3.64	4.23	4.25	4.45	4.09	4.10	3.96
H-10	7.46	7.44	7.53	----	----	----	----	----	----
H-11	----	----	----	7.38	7.38	7.53	----	----	----
J(3a,4)	9.0	8.5	9.0	8.5	8.5	9.0	9.0	9.0	9.0
J(5a,6)	4.0	3.8	3.8	4.0	3.5	3.6	4.0	4.0	3.8
J(6,11)	---	---	---	6.0	6.5	6.0	---	---	---
J(8,9)	6.0	6.0	6.5	6.8	7.0	6.9	7.0	7.0	7.0
J(9,10)	6.0	6.0	6.0	---	---	---	---	---	---

the furan ring C(4)-C(2)-C(3)-C(5)-O(2), which is similar to the stereochemistry of ***3****.* Therefore, the addition of the dienophile forming C(10)-C(11) proceeds *via anti* to the diene forming cyclohexene ring C(5)-C(3)-C(6)-C(7)-C(8)-C(9).

In conclusion, this work emphasizes a novel facet of the 3a,4-dihydro-5a,*H*-benzofuro[3,3a-*d*]-isoxazole system which can act as a diene in Diels-Alder cycloaddition process to give novel bridged heterocyclic ring systems.

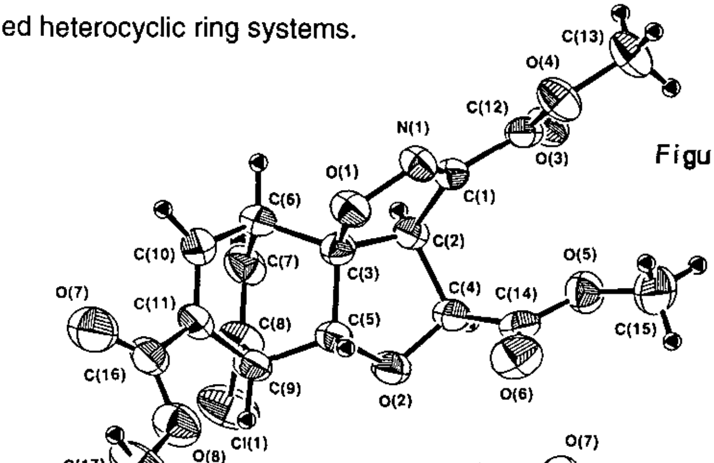


Figure 3 A Perspective Drawing of **5a**

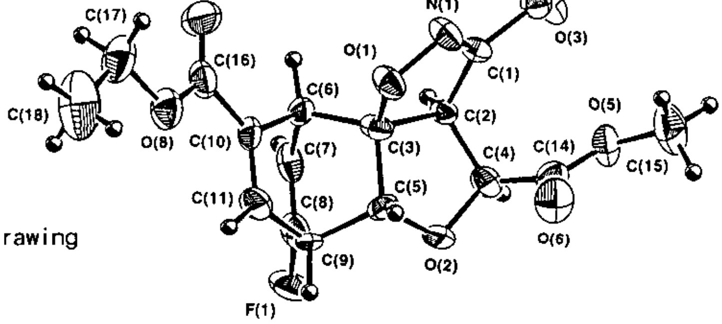


Figure 4 A Perspective Drawing of **6c**

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_3. Column chromatography was carried out on a silica gel(Kanto Kagaku Co. ; up to 100 mesh) column.

Tetramethyl 4,16-Dichloro-1,2a,4a,5,5a,7,7a,11,11a,14a-decahydro-5,11-ethenoisoxazolo[5''',4''':3',4']furo[2'',3'':7',8']naphtho[2',3':4,5]furo[3,4-*d*]-isoxazole-1,7,8,14-tetracarboxylate (3a) :

<Method I > To a solution of 313 mg (1.0 mmol) of 3,5-bis(methoxycarbonyl)-4-chlorophenyl-2-isoxazoline-2-oxide (**1a**) in 10 ml of dichloromethane was added 0.45 ml (4.0 mmol) of titanium tetrachloride at 0 ℃ and the reaction mixture was stirred at room temperature for 15 h. After the reaction mixture was quenched with 10% aqueous sodium carbonate and extracted with chloroform, separation by column chromatography on silica gel (hexane - ethyl acetate, 3:1) afforded **3a** (72 mg, 23%), dimethyl 7-chloro-3a,4-dihydro-5a,*H*-benzofuro[3,3a-*d*]isoxazole-3,4-dicarboxylate (**2 a**)[9] (108.5 mg, 35%), and (*E*)-6-chloro-2-methoxycarbonyl-3-methoxalyl-2,3-dihydrobenzofuran oxime (**4a**) (66 mg, 21%).

3 a : mp 245-246℃(chloroform-methanol). Ir ν (KBr)cm^{-1} : 1750(COOCH$_3$), 1620(C=N). Ms(m/z) : 626(M$^+$), 628(M$^+$+2). ^{1}H Nmr (CDCl$_3$, δ, ppm) : 2.98(dd, $J_{4a,11a}$=9.0 Hz, $J_{4a,5}$=3.0 Hz, 1H, H-4a), 3.20(dd, $J_{4a,11a}$=9.0 Hz, $J_{11,11a}$=2.0 Hz, 1H, H-11a), 3.54(dd, $J_{11,11a}$=2.0 Hz, $J_{11,15}$=7.0 Hz,1H, H-11), 3.65(s, 3H, CH$_3$), 3.67(dd, $J_{4a,5}$=3.0 Hz, $J_{5,5a}$=3.0 Hz, 1H, H-5), 3.69(s, 3H, CH$_3$). 3.84(s, 3H, CH$_3$), 3.88(s, 3H, CH$_3$), 3.97(d, $J_{1,14a}$=7.0 Hz, 1H, H-14a), 4.04(d, $J_{7,7a}$=9.2 Hz, 1H, H-7a), 4.54(d, $J_{1,14a}$=7.0 Hz, 1H, H-1), 4.55(d, $J_{2a,3}$=2.3 Hz,1H, H-2a), 4.74(d, $J_{5,5a}$=3.0 Hz, 1H, H-5a), 4.83(d, $J_{7,7a}$=9.2 Hz, 1H, H-7), 5.87(d, $J_{2a,3}$=2.3 Hz, 1H, H-3), 6.10(dd, $J_{11,15}$=7.0 Hz, $J_{5,15}$=2.5 Hz, 1H, H-15). *Anal.* Calcd for $C_{26}H_{24}N_2O_{12}Cl_2$: C, 49.78; H, 3.86; N, 4.47; Cl, 11.30. Found : C, 49.52; H, 4.07; N, 4.26; Cl, 11.86.

4 a : mp 139-140℃(ethyl acetate-hexane). Ir ν (KBr)cm^{-1} : 3300(N-OH), 1735(COOCH$_3$), 1610(C=N). Ms(m/z) : 313(M$^+$), 315(M$^+$+2). ^{1}H Nmr (CDCl$_3$, δ, ppm) : 3.73(s, 1H, CH$_3$), 3.77(s, 1H, CH$_3$), 5.42(d, $J_{2,3}$=11.0 Hz, 1H, H-3), 5.46(d, $J_{2,3}$=11.0 Hz, 1H, H-2), 6.90(d, $J_{4,5}$=11.0 Hz, 1H, H-4), 7.04(dd, $J_{4,5}$=11.0 Hz, $J_{5,7}$=2.0 Hz, 1H, H-5), 7.10(d, $J_{5,7}$=2.0 Hz, 1H, H-7). *Anal. Calcd for* $C_{13}H_{12}NO_6Cl$: C, 49.78; H, 3.86; N, 4.47; Cl, 11.30. Found : C, 49.66; H, 4.00; N, 4.31, Cl, 11.55.

<Method II > A solution of 500 mg of **2a** (1.6 mmol) in 5 ml of toluene was refluxed for 15 h. The reaction mixture was concentrated to dryness and purified by column chromatography on silica gel (hexane - ethyl acetate, 1:1) to afford 390 mg of **3a** (78%).

Tetramethyl 4,16-Dibromo-1,2a,4a,5,5a,7,7a,11,11a,14a-decahydro-5,11-ethenoisoxazolo[5''',4''':3',4']furo[2'',3'':7',8']naphtho[2',3':4,5]furo[3,4-*d*]-isoxazole-1,7,8,14-tetracarboxylate (3b) : Yield : 22% (Method I), 75% (Method II). mp 225-226℃(chloroform-methanol). Ir ν (KBr)cm^{-1} : 1755(COOCH$_3$), 1620(C=N). Ms(m/z) : 714(M$^+$), 716(M$^+$+2). ^{1}H Nmr (CDCl$_3$, δ, ppm) : 3.08(dd, $J_{4a,11a}$=9.0 Hz, $J_{4a,5}$=3.0 Hz, 1H, H-4a), 3.15(dd, $J_{4a,11a}$=9.0 Hz, $J_{11,11a}$=2.0 Hz, 1H, H-11a), 3.54(dd, $J_{11,11a}$=2.0 Hz, $J_{11,15}$=7.0 Hz, 1H, H-11), 3.66(s, 3H, CH$_3$), 3.70(s, 3H, CH$_3$), 3.84(s, 3H, CH$_3$), 3.89(s, 3H, CH$_3$), 3.97(dd, $J_{4a,5}$=3.0 Hz, $J_{5,5a}$=3.0 Hz, 1H, H-5), 3.97(d, $J_{1,14a}$=7.0 Hz, 1H, H-14a), 4.02(d, $J_{7,7a}$=9.2 Hz, 1H, H-7a), 4.49(d, $J_{1,14a}$=7.0 Hz, 1H, H-1), 4.56(d, $J_{2a,3}$=2.3 Hz,1H, H-2a), 4.72(d, $J_{5,5a}$=3.0 Hz, 1H, H-5a), 4.83(d, $J_{7,7a}$=9.2 Hz, 1H, H-7), 6.09(d, $J_{2a,3}$=2.3 Hz, 1H, H-3), 6.37(dd, $J_{11,15}$=7.0 Hz, $J_{5,15}$=2.5 Hz, 1H, H-15). *Anal.* Calcd for $C_{26}H_{24}N_2O_{12}Br_2$: C, 43.60; H, 3.38; N, 3.91; Br, 22.31. Found : C, 43.89; H, 3.50; N, 3.85; Br, 22.43.

(*E*)-6-Bromo-2-methoxycarbonyl-3-methoxalyl-2,3-dihydrobenzofuran Oxime (4b) : Yield : 24% (Method I). mp 147-149℃(ethyl acetate-hexane). Ir ν (KBr)cm^{-1} : 3300(N-OH), 1735(COOCH$_3$), 1610(C=N). Ms(m/z) : 357(M$^+$). ^{1}H Nmr (CDCl$_3$, δ, ppm) : 3.74(s, 1H, CH$_3$), 3.76(s, 1H, CH$_3$), 5.43(d, $J_{2,3}$=11.0 Hz, 1H, H-3), 5.49(d, $J_{2,3}$=11.0 Hz, 1H, H-2), 6.90(d, $J_{4,5}$=11.0 Hz, 1H, H-4), 7.02(dd, $J_{4,5}$=11.0 Hz, $J_{5,7}$=2.0 Hz, 1H, H-5), 7.09(d, $J_{5,7}$=2.0 Hz, 1H, H-7). *Anal.* Calcd for $C_{13}H_{12}NO_6Br$: C, 43.60; H, 3.38; N, 3.91; Br, 22.31. Found : C, 43.43; H, 3.29; N, 3.89; Br, 22.59.

Tetramethyl 4,16-Difluoro-1,2a,4a,5,5a,7,7a,11,11a,14a-decahydro-5,11-ethenoisoxazolo[5''',4''':3',4']furo[2'',3'':7',8']naphtho[2',3':4,5]furo[3,4-*d*]-isoxazole-1,7,8,14-tetracarboxylate (3c) : Yield : 26% (Method I), 72% (Method II).

mp 273-276℃(chloroform-methanol). Ir ν (KBr)cm^{-1} : 1750(COOCH$_3$), 1620(C=N). Ms(m/z) : 594(M$^+$). ^{1}H Nmr (CDCl$_3$, δ, ppm) : 2.98(dd, $J_{4a,11a}$=9.0 Hz, $J_{4a,5}$=3.0 Hz, 1H, H-4a), 3.20(dd, $J_{4a,11a}$=9.0 Hz, $J_{11,11a}$=2.0 Hz, 1H, H-11a), 3.54(dd, $J_{11,11a}$=2.0 Hz, $J_{11,15}$=7.0 Hz,1H, H-11), 3.63(s, 3H, CH$_3$), 3.68(dd, $J_{4a,5}$=3.0 Hz, $J_{5,5a}$=3.0 Hz, 1H, H-5), 3.69(s, 3H, CH$_3$), 3.84(s, 3H, CH$_3$), 3.88(s, 3H, CH$_3$), 3.97(d, $J_{1,14a}$=7.0 Hz, 1H, H-14a), 4.05(d, $J_{7,7a}$=9.2 Hz, 1H, H-7a), 4.54(d, $J_{1,14a}$=7.0 Hz, 1H, H-1), 4.56(d, $J_{2a,3}$=2.3 Hz,1H, H-2a), 4.73(d, $J_{5,5a}$=3.0 Hz, 1H, H-5a), 4.83(d, $J_{7,7a}$=9.2 Hz, 1H, H-7), 5.88(d, $J_{2a,3}$=2.3 Hz, 1H, H-3), 6.13(dd, $J_{11,15}$=7.0 Hz, $J_{5,15}$=2.5 Hz, 1H, H-15). *Anal.* Calcd for $C_{26}H_{24}N_2O_{12}F_2$: C, 52.25; H, 3.23; N, 4.71. Found : C, 52.16; H, 3.33; N, 4.59.

Diels-Alder Cycloaddition of 2 with Ethyl Propiolate

-------- General Procedure

A mixture of 0.64 mmol of **2** and 2.27 ml (22.4 mmol) of ethyl propiolate was refluxed for 21 h. After ethyl propiolate was removed under reduced pressure, the residue was purified by column chromatography on silica gel (hexane - ethyl acetate, 3:1) to afford **5** and **6**.

Dimethyl 7-Chloro-11-ethoxycarbonyl-3a,4,6,9-tetrahydro-5a,*H*-6,9-ethenobenzofuro[3,3a-*d*]isoxazole-3,4-dicarboxylate (5a) : Yield : 43%.

mp 118-119℃(ethyl acetate-hexane). Ir ν (KBr)cm^{-1} : 1745(COOCH$_3$), 1705(COOCH$_3$), 1580(C=N). Ms(m/z) : 412(M$^+$). ^{1}H Nmr (CDCl$_3$, δ, ppm) : 1.33(t, J=7.0 Hz, 3H, $CH_2C\underline{H_3}$), 3.63(s, 3H, COOCH$_3$), 3.81(dd, $J_{8,9}$=6.0 Hz, $J_{9,10}$=6.0 Hz, 1H, H-9), 3.84(s, 3H, COOCH$_3$), 3.89 (d, $J_{3a,4}$=9.0 Hz, 1H, H-3a), 4.23(q, J=7.0 Hz, 2H, $C\underline{H_2}CH_3$), 4.45(d, $J_{5a,6}$=4.0 Hz, 1H, H-6), 4.67(d, $J_{5a,6}$=4.0 Hz, 1H, H-5a), 5.03(d, $J_{3a,4}$=9.0 Hz, 1H, H-4), 6.14(d, $J_{8,9}$=6.0 Hz, 1H, H-8), 7.46(d, $J_{9,10}$=6.0 Hz, 1H, H-10). *Anal.* Calcd for $C_{18}H_{18}NO_8Cl$: C, 52.49; H, 4.41; N, 3.40 ; Cl, 8.63. Found : C, 52.41; H, 4.38; N, 3.29; Cl, 8.60.

Dimethyl 7-Chloro-10-ethoxycarbonyl-3a,4,6,9-tetrahydro-5a,*H*-6,9-ethenobenzofuro[3,3a-*d*]isoxazole-3,4-dicarboxylate (6a) : Yield : 30%.

mp 146-148℃(ethyl acetate-hexane). Ir ν (KBr)cm^{-1} : 1715($COOCH_3$), 1715($COOCH_3$), 1580(C=N). Ms(m/z) : 412(M^+). ^{1}H Nmr ($CDCl_3$, δ, ppm) : 1.29(t, J=7.0 Hz, 3H, $CH_2C\underline{H}_3$), 3.65(s, 3H, $COOCH_3$), 3.87(s, 3H, $COOCH_3$), 3.99(d, $J_{3a,4}$=8.5 Hz, 1H, H-3a), 4.05(dd, $J_{5a,6}$=4.0 Hz, $J_{6,11}$=6.0 Hz, 1H, H-6), 4.22(q, J=7.0 Hz, 2H, $C\underline{H}_2CH_3$), 4.23(d, $J_{8,9}$=6.8 Hz,1H, H-9), 4.72(d, $J_{5a,6}$=4.0 Hz, 1H, H-5a), 5.02(d, $J_{3a,4}$=8.5 Hz, 1H, H-4), 6.23(d, $J_{8,9}$=6.8 Hz, 1H, H-8), 7.38(d, $J_{6,11}$=6.0 Hz, 1H, H-11). *Anal.* Calcd for $C_{18}H_{18}NO_8Cl$: C, 52.49; H, 4.41; N, 3.40 ; Cl, 8.63. Found : C, 52.43; H, 4.44; N, 3.22; Cl, 8.43.

Dimethyl 7-Bromo-11-ethoxycarbonyl-3a,4,6,9-tetrahydro-5a,*H*-6,9-ethenobenzofuro[3,3a-*d*]isoxazole-3,4-dicarboxylate (5b) : Yield : 42%.
mp 131-133℃(ethyl acetate-hexane). Ir ν (KBr)cm^{-1} : 1770($COOCH_3$), 1720($COOCH_3$), 1580(C=N). Ms(m/z) : 456(M^+), 458(M^++2). ^{1}H Nmr ($CDCl_3$, δ, ppm) : 1.32(t, J=7.0 Hz, 3H, $CH_2C\underline{H}_3$), 3.66(s, 3H, $COOCH_3$), 3.84(dd, $J_{8,9}$=6.0 Hz, $J_{9,10}$=6.0 Hz, 1H, H-9), 3.88(s, 3H, $COOCH_3$), 3.99(d, $J_{3a,4}$=8.5 Hz, 1H, H-3a), 4.25(q, J=7.0 Hz, 2H, $C\underline{H}_2CH_3$), 4.62(d, $J_{5a,6}$=3.8 Hz, 1H, H-6), 4.73(d, $J_{5a,6}$=3.8 Hz, 1H, H-5a), 5.02(d, $J_{3a,4}$=8.5 Hz, 1H, H-4), 6.38(d, $J_{8,9}$=6.0 Hz, 1H, H-8), 7.44(d, $J_{9,10}$=6.0 Hz, 1H, H-10). *Anal.* Calcd for $C_{18}H_{18}NO_8Br$: C, 47.38; H, 3.98; N, 3.07 ; Br, 17.51. Found : C, 47.28; H, 4.00; N, 3.06; Br, 17.27.

Dimethyl 7-Bromo-10-ethoxycarbonyl-3a,4,6,9-tetrahydro-5a,*H*-6,9-ethenobenzofuro[3,3a-*d*]isoxazole-3,4-dicarboxylate (6b) : Yield : 28%.
A syrup. Ir ν (KBr)cm^{-1} : 1760($COOCH_3$), 1720($COOCH_3$), 1590(C=N). Ms(m/z) : 456(M^+), 458(M^++2).. ^{1}H Nmr ($CDCl_3$, δ, ppm) : 1.29(t, J=7.0 Hz, 3H, $CH_2C\underline{H}_3$), 3.66(s, 3H, $COOCH_3$), 3.88(s, 3H, $COOCH_3$), 3.99(d, $J_{3a,4}$=8.5 Hz, 1H, H-3a), 4.18(dd, $J_{5a,6}$=3.5 Hz, $J_{6,11}$=6.5 Hz, 1H, H-6), 4.22(q, J=7.0 Hz, 2H, $C\underline{H}_2CH_3$), 4.25(d, $J_{8,9}$=7.0 Hz,1H, H-9), 4.72(d, $J_{5a,6}$=3.5 Hz, 1H, H-5a), 5.02(d, $J_{3a,4}$=8.5 Hz, 1H, H-4), 6.48(d, $J_{8,9}$=7.0 Hz, 1H, H-8), 7.38(d, $J_{6,11}$=6.5 Hz, 1H, H-11). *Anal.* Calcd for $C_{18}H_{18}NO_8Br$: C, 47.38; H, 3.98; N, 3.07; Br, 17.51. Found : C, 47.60; H, 4.18; N, 3.00; Br, 17.19.

Dimethyl 11-Ethoxycarbonyl-7-fluoro-3a,4,6,9-tetrahydro-5a*H*-6,9-ethenobenzofuro[3,3a-*d*]isoxazole-3,4-dicarboxylate (5c) : Yield : 53%. mp 147-149°C (ethyl acetate-hexane). Ir ν (KBr)cm^{-1} : 1745(COOCH$_3$), 1730(COOCH$_3$), 1580(C=N). Ms(m/z) : 395(M$^+$). ^{1}H Nmr (CDCl$_3$, δ, ppm) : 1.30(t, J=7.0 Hz, 3H, CH$_2$C$\underline{H_3}$), 3.63(s, 3H, COOCH$_3$), 3.64(dd, $J_{8,9}$=6.5 Hz, $J_{9,10}$=6.0 Hz, 1H, H-9), 3.85(s, 3H, COOCH$_3$), 4.00(d, $J_{3a,4}$=9.0 Hz, 1H, H-3a), 4.22(q, J=7.0 Hz, 2H, C$\underline{H_2}$CH$_3$), 4.29(d, $J_{5a,6}$=3.8 Hz, 1H, H-6), 4.68(d, $J_{5a,6}$=3.8 Hz, 1H, H-5a), 5.07(d, $J_{3a,4}$=9.0 Hz, 1H, H-4), 5.42(d, $J_{8,9}$=6.5 Hz, 1H, H-8), 7.53(d, $J_{9,10}$=6.0 Hz, 1H, H-10). *Anal.* Calcd for $C_{18}H_{18}NO_8F$: C, 54.66; H, 4.59; N, 3.54. Found : C, 54.77; H, 4.60; N, 3.66.

Dimethyl 10-Ethoxycarbonyl-7-fluoro-3a,4,6,9-tetrahydro-5a,*H*-6,9-ethenobenzofuro[3,3a-*d*]isoxazole-3,4-dicarboxylate (6c) : Yield : 30%. mp 143-145°C (ethyl acetate-hexane). Ir ν (KBr)cm^{-1} : 1745(COOCH$_3$), 1715(COOCH$_3$), 1580(C=N). Ms(m/z) : 395(M$^+$). ^{1}H Nmr (CDCl$_3$, δ, ppm) : 1.29(t, J=7.0 Hz, 3H, CH$_2$C$\underline{H_3}$), 3.63 (s, 3H, COOCH$_3$), 3.87(s, 3H, COOCH$_3$), 3.98(d, $J_{3a,4}$=9.0 Hz, 1H, H-3a), 4.09(dd, $J_{5a,6}$=3.6 Hz, $J_{6,11}$=6.0 Hz, 1H, H-6), 4.23(q, J=7.0 Hz, 2H, C$\underline{H_2}$CH$_3$), 4.45(d, $J_{8,9}$=6.9 Hz, 1H, H-9), 4.74(d, $J_{5a,6}$=3.6 Hz, 1H, H-5a), 5.04(d, $J_{3a,4}$=9.0 Hz, 1H, H-4), 5.41(d, $J_{8,9}$=6.9 Hz, 1H, H-8), 7.53(d, $J_{6,11}$=6.0 Hz, 1H, H-11). *Anal.* Calcd for $C_{18}H_{18}NO_8F$: C, 54.66; H, 4.59; N, 3.54. Found : C, 54.73; H, 4.71; N, 3.69.

Diels-Alder Cycloaddition of 2 with Dimethyl Acetylenedicarboxylate -------- General Procedure

A mixture of 0.48 mmol of **2** and 2.06 ml (16.7 mmol) of dimethyl acetylenedicarboxylate was refluxed for 2 h. After dimethyl acetylenedicarboxylate was removed under reduced pressure, the residue was purified by column chromatography on silica gel (hexane - ethyl acetate, 3:1) to afford **7**.

Dimethyl 7-Chloro-10,11-bis(methoxycarbonyl)-3a,4,6,9-tetrahydro-5a,*H*-6,9-

ethenobenzofuro[3,3a-*d*]isoxazole-3,4-dicarboxylate (7a) : Yield : 67%. A syrup. Ir ν (KBr)cm^{-1} : 1730(COOCH$_3$), 1580(C=N). Ms(m/z) : 456(M$^+$). ^{1}H Nmr (CDCl$_3$, δ, ppm) : 3.67(s, 3H, COOCH$_3$), 3.81(s, 3H, COOCH$_3$), 3.84(s, 3H, COOCH$_3$), 3.89(s, 3H, COOCH$_3$), 3.99(d, $J_{3a,4}$=9.0 Hz, 1H, H-3a), 4.09(d, $J_{8,9}$=7.0 Hz, 1H, H-9), 4.31(d, $J_{5a,6}$=4.0 Hz, 1H, H-6), 4.89(d, $J_{5a,6}$=4.0 Hz, 1H, H-5a), 5.03(d, $J_{3a,4}$=9.0 Hz, 1H, H-4), 6.26(d, $J_{8,9}$=7.0 Hz, 1H, H-8). *Anal.* Calcd for $C_{19}H_{18}NO_{10}Cl$: C, 50.01; H, 3.98; N, 3.07. Found : C, 50.21; H, 3.89; N, 2.99.

Dimethyl 7-Bromo-10,11-bis(methoxycarbonyl)-3a,4,6,9-tetrahydro-5a,*H*-6,9-ethenobenzofuro[3,3a-*d*]isoxazole-3,4-dicarboxylate (7b) : Yield : 65%. A syrup. Ir ν (KBr)cm^{-1} : 1730(COOCH$_3$), 1580(C=N). Ms(m/z) : 500(M$^+$), 502(M$^+$+2). ^{1}H Nmr (CDCl$_3$, δ, ppm) : 3.66(s, 3H, COOCH$_3$), 3.80(s, 3H, COOCH$_3$), 3.84(s, 3H, COOCH$_3$), 3.88(s, 3H, COOCH$_3$), 3.99(d, $J_{3a,4}$=9.0 Hz, 1H, H-3a), 4.10(d, $J_{8,9}$=7.0 Hz, 1H, H-9), 4.43(d, $J_{5a,6}$=4.0 Hz, 1H, H-6), 4.88(d, $J_{5a,6}$=4.0 Hz, 1H, H-5a), 5.02(d, $J_{3a,4}$=9.0 Hz, 1H, H-4), 6.49(d, $J_{8,9}$=7.0 Hz, 1H, H-8). *Anal.* Calcd for $C_{19}H_{18}NO_{10}Br$: C, 45.58; H, 3.63; N, 2.80. Found : C, 45.33; H, 3.60; N, 3.01.

Dimethyl 7-Fluoro-10,11-bis(methoxycarbonyl)-3a,4,6,9-tetrahydro-5a,*H*-6,9-ethenobenzofuro[3,3a-*d*]isoxazole-3,4-dicarboxylate (7c) : Yield : 61%. mp 133-135℃(ethyl acetate-hexane). Ir ν (KBr)cm^{-1} : 1730(COOCH$_3$), 1580(C=N). Ms(m/z) : 440(M$^+$). ^{1}H Nmr (CDCl$_3$, δ, ppm) : 3.66(s, 3H, COOCH$_3$), 3.80(s, 3H, COOCH$_3$), 3.83(s, 3H, COOCH$_3$), 3.89(s, 3H, COOCH$_3$), 3.96(d, $J_{8,9}$=7.0 Hz, 1H, H-9), 4.01(d, $J_{3a,4}$=9.0 Hz, 1H, H-3a), 4.18(d, $J_{5a,6}$=3.8 Hz, 1H, H-6), 4.92(d, $J_{5a,6}$=3.8 Hz, 1H, H-5a), 5.06(d, $J_{3a,4}$=9.0 Hz, 1H, H-4), 5.55(d, $J_{8,9}$=7.0 Hz, 1H, H-8). *Anal.* Calcd for $C_{19}H_{18}NO_{10}F$: C, 51.94; H, 4.13; N, 3.19; F, 4.32. Found : C, 51.87; H, 4.17; N, 3.09; F, 4.03.

X-Ray Analyses of 3a, 4a, 5a, and 6c

X-Ray structure analyses of **3a**, **4a**, **5a**, and **6c** 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 4. 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 **3a**, **4a**, **5a**, and **6c** are listed in Tables 5, 6, 7, and 8, respectively. The selected bond lengths, bond angles, and torsion angles for **3a**, **4a**, **5a**, and **6c** are listed in Tables 9, 10, 11 and 12, respectively. In the case of **3a**, a pair of enantiomer was solved as a unit. The positional parameters for both of them are listed in Table 5, in which Cl(3), Cl(4), O(13)-O(24), N(3), N(4), and C(27)-C(52) are another pairs to Cl(1), Cl(2), O(1)-O(12), N(1), N(2), and C(1)-C(26), respectively.

Table 4 Crystallographic Data for Compounds (**3a**, **4a**, **5a**, and **6c**)

	3a	4a	5a	6c
Formula	$C_{26}H_{24}N_2Cl_2O_{12}$	$C_{13}H_{12}NClO_6$	$C_{18}H_{18}NClO_8$	$C_{18}H_{18}NFO_8$
F_W	627.39	313.69	411.80	395.34
Crystal dimensions (mm)	0.2×0.2×0.2	0.1×0.2×0.2	0.3×0.1×0.1	0.2×0.1×0.4
Crystal system	triclinic	orthorhombic	monoclinic	monoclinic
Space group	$P\bar{1}$	*Pbca*	*C2/c*	$P2_1/n$
Lattice parameters				
a/Å	13.174 (4)	28.622 (4)	32.561 (9)	15.790 (5)
b/Å	19.400 (7)	12.767 (4)	6.860 (5)	6.811 (6)
c/Å	10.751 (3)	7.565 (3)	19.688 (6)	18.513 (5)
α/deg	94.66 (3)	——	——	——
β/deg	90.70 (2)	——	120.13 (2)	111.31 (2)
γ/deg	80.30 (3)	——	——	——
$V/Å^3$	2699 (2)	2764 (2)	3803 (6)	1855 (2)
Z	4	8	8	4
Dc/gcm^{-3}	1.544	1.507	1.438	1.416
$\mu(Cu\ K\alpha)/cm^{-1}$	28.02	27.36	22.01	9.79
$2\theta_{max}/deg$	139.9	139.8	139.9	140.0
No. of Observation	3744	1418	2001	1216
No. of Variables	757	202	253	253
R (*Rw*)	0.055 (0.042)	0.067 (0.065)	0.065 (0.063)	0.077 (0.066)

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

Atom	*x*	*y*	*z*	B_{eq}
Cl(1)	0.9222(2)	0.0721(1)	1.0682(2)	4.2(1)
Cl(2)	0.6729(2)	0.0416(1)	1.1972(2)	3.9(1)
Cl(3)	0.4213(2)	0.0621(1)	0.3336(2)	5.1(1)
Cl(4)	0.1739(2)	0.0345(1)	0.1780(2)	4.0(1)
O(1)	0.6780(4)	0.3496(3)	1.0606(5)	3.3(3)
O(2)	0.8840(4)	0.2531(3)	1.1933(5)	3.5(3)
O(3)	0.4798(4)	0.0930(3)	0.8149(4)	3.4(3)
O(4)	0.5535(4)	0.2271(3)	0.7878(4)	3.1(3)
O(5)	0.8121(4)	0.4977(3)	0.9104(6)	5.4(4)
O(6)	0.9571(5)	0.4196(3)	0.9067(6)	6.1(4)
O(7)	0.9247(4)	0.3598(3)	1.3506(3)	4.5(4)
O(8)	0.9862(5)	0.4341(3)	1.2017(5)	5.3(4)
O(9)	0.2333(4)	0.1311(3)	0.9444(5)	4.4(4)
O(10)	0.2776(4)	0.1333(3)	0.7441(5)	5.1(4)
O(11)	0.2651(4)	0.3375(3)	0.7693(5)	4.6(4)
O(12)	0.2335(4)	0.2899(3)	0.9468(5)	5.1(4)
O(13)	0.1826(4)	0.3445(3)	0.3896(5)	3.2(3)
O(14)	0.3913(4)	0.2462(3)	0.2386(5)	3.9(3)
O(15)	−0.0151(4)	0.0914(3)	0.5728(5)	3.8(3)
O(16)	0.0586(4)	0.2259(3)	0.6323(4)	3.3(3)
O(17)	0.3122(4)	0.4938(3)	0.5883(6)	5.7(4)
O(18)	0.4567(5)	0.4173(3)	0.5765(6)	6.0(4)
O(19)	0.4233(4)	0.3546(3)	0.1151(5)	4.6(4)
O(20)	0.4003(5)	0.4289(3)	0.2842(5)	5.8(4)
O(21)	−0.2661(5)	0.1252(4)	0.4588(5)	7.2(5)
O(22)	−0.2148(4)	0.1367(3)	0.6556(5)	5.6(4)
O(23)	−0.2290(4)	0.3367(3)	0.6759(5)	5.0(4)
O(24)	−0.2651(5)	0.2866(4)	0.4879(6)	5.9(4)
N(1)	0.7126(5)	0.4063(3)	1.0098(6)	3.5(4)
N(2)	0.4568(5)	0.2680(3)	0.7697(6)	3.5(4)
N(3)	0.2159(5)	0.4018(3)	0.4583(6)	3.4(4)
N(4)	−0.0371(5)	0.2675(3)	0.6585(6)	3.7(4)
C(1)	0.8088(6)	0.3889(4)	0.9890(7)	3.0(5)
C(2)	0.8549(6)	0.3171(4)	1.0211(7)	2.9(5)
C(3)	0.7579(6)	0.2872(4)	1.0457(7)	2.8(5)
C(4)	0.9166(6)	0.3102(4)	1.1453(8)	3.2(5)
C(5)	0.7778(6)	0.2528(4)	1.1701(7)	2.7(4)
C(6)	0.7253(6)	0.2348(4)	0.9455(6)	2.5(4)
C(7)	0.8095(6)	0.1713(4)	0.9366(7)	2.8(5)
C(8)	0.8281(6)	0.1438(4)	1.0429(8)	2.6(4)
C(9)	0.7623(6)	0.1767(4)	1.1525(6)	2.5(4)
C(10)	0.6228(6)	0.2179(4)	0.9974(7)	2.6(4)

Table 5 continued

Atom	*x*	*y*	*z*	B_{eq}
C(11)	0.6483(6)	0.1717(4)	1.1103(6)	2.4(4)
C(12)	0.6376(6)	0.0972(4)	1.0757(7)	2.6(4)
C(13)	0.6116(6)	0.0691(4)	0.9688(8)	3.1(5)
C(14)	0.5776(6)	0.1104(4)	0.8600(7)	3.0(5)
C(15)	0.5524(6)	0.1884(4)	0.9006(7)	2.4(4)
C(16)	0.4075(6)	0.1276(4)	0.9052(7)	2.6(4)
C(17)	0.4374(5)	0.2005(4)	0.9377(6)	2.4(4)
C(18)	0.3950(6)	0.2543(4)	0.8512(7)	3.1(5)
C(19)	0.8676(7)	0.4371(5)	0.9288(8)	3.9(6)
C(20)	0.8631(7)	0.5463(5)	0.850(1)	7.1(7)
C(21)	0.9098(7)	0.3756(5)	1.2326(9)	3.6(5)
C(22)	0.9326(7)	0.4187(4)	1.4406(8)	5.2(6)
C(23)	0.2971(7)	0.1304(4)	0.8499(8)	3.6(5)
C(24)	0.1258(6)	0.1403(6)	0.9068(8)	6.2(7)
C(25)	0.2861(7)	0.2968(5)	0.860(1)	3.8(5)
C(26)	0.1627(7)	0.3803(5)	0.7780(9)	6.1(6)
C(27)	0.3110(6)	0.3852(4)	0.4806(7)	2.8(5)
C(28)	0.3591(6)	0.3133(4)	0.4318(7)	2.7(4)
C(29)	0.2630(6)	0.2832(4)	0.3928(7)	2.7(4)
C(30)	0.4212(6)	0.3047(4)	0.3078(7)	3.0(5)
C(31)	0.2835(6)	0.2457(4)	0.2630(7)	3.1(5)
C(32)	0.2280(6)	0.2318(4)	0.4813(6)	2.7(4)
C(33)	0.3117(6)	0.1682(4)	0.4809(7)	3.0(5)
C(34)	0.3325(6)	0.1375(4)	0.3692(8)	3.1(5)
C(35)	0.2684(6)	0.1686(4)	0.2635(7)	2.9(5)
C(36)	0.1267(5)	0.2139(4)	0.4201(6)	2.4(4)
C(37)	0.1565(5)	0.1655(4)	0.2980(6)	2.5(4)
C(38)	0.1423(6)	0.0913(4)	0.3107(7)	3.0(5)
C(39)	0.1135(6)	0.0644(4)	0.4102(8)	3.3(5)
C(40)	0.0811(6)	0.1086(4)	0.5302(7)	3.4(5)
C(41)	0.0561(6)	0.1855(4)	0.5104(7)	2.5(4)
C(42)	- 0.0901(6)	0.1250(4)	0.4907(7)	3.3(5)
C(43)	- 0.0600(5)	0.1972(4)	0.4749(6)	2.7(4)
C(44)	- 0.1016(6)	0.2529(4)	0.5740(8)	3.1(5)
C(45)	0.3678(8)	0.4332(5)	0.5526(8)	3.7(6)
C(46)	0.3628(8)	0.5426(5)	0.664(1)	7.4(7)
C(47)	0.4118(6)	0.3693(5)	0.2371(9)	3.4(5)
C(48)	0.4287(7)	0.4138(5)	0.0412(8)	5.6(6)
C(49)	- 0.1969(7)	0.1290(5)	0.5463(9)	4.1(6)
C(50)	- 0.3728(7)	0.1359(7)	0.500(1)	10.2(9)
C(51)	- 0.2082(7)	0.2936(5)	0.572(1)	4.2(6)
C(52)	- 0.3317(7)	0.3797(5)	0.6783(9)	7.0(7)

Table 6 Positional Parameters and Their Estimated Standard Deviations for **4a**

Atom	*x*	*y*	*z*	B_{eq}
Cl(1)	0.54732(7)	0.2041(2)	0.9626(3)	5.0(1)
O(1)	0.3861(1)	0.2080(3)	0.6756(6)	3.2(2)
O(2)	0.2839(2)	0.0664(4)	0.5421(7)	4.7(3)
O(3)	0.2950(2)	0.2063(4)	0.7166(7)	4.0(3)
O(4)	0.3655(2)	- 0.1553(4)	0.3954(7)	4.1(3)
O(5)	0.3367(2)	- 0.1401(4)	0.9172(6)	3.8(3)
O(6)	0.3482(2)	0.0329(3)	0.8993(6)	3.5(3)
N(1)	0.3530(2)	- 0.1513(4)	0.5714(8)	3.2(3)
C(1)	0.5013(2)	0.1480(6)	0.846(1)	3.2(4)
C(2)	0.5057(3)	0.0471(6)	0.788(1)	3.7(4)
C(3)	0.4695(3)	0.0014(6)	0.691(1)	3.2(4)
C(4)	0.4306(2)	0.0590(5)	0.6566(8)	2.3(3)
C(5)	0.4267(2)	0.1598(5)	0.716(1)	2.6(3)
C(6)	0.4622(3)	0.2065(7)	0.813(1)	3.4(4)
C(7)	0.3863(2)	0.0302(5)	0.5611(9)	2.5(3)
C(8)	0.3601(2)	0.1374(5)	0.561(1)	2.9(3)
C(9)	0.3623(2)	- 0.0633(5)	0.642(1)	2.5(3)
C(10)	0.3475(2)	- 0.0643(6)	0.837(1)	2.9(3)
C(11)	0.3324(3)	0.0430(6)	1.083(1)	5.0(5)
C(12)	0.3088(3)	0.1305(5)	0.606(1)	3.3(4)
C(13)	0.2461(3)	0.2026(7)	0.768(1)	5.8(5)

Table 7 Positional Parameters and Their Estimated Standard Deviations for **5a**

Atom	*x*	*y*	*z*	B_{eq}
Cl(1)	0.06598(7)	0.8977(3)	0.7634(1)	8.0(1)
O(1)	0.1355(1)	0.7373(6)	1.0919(2)	4.5(2)
O(2)	0.1408(1)	0.5903(6)	0.9295(2)	5.0(2)
O(3)	0.2855(1)	0.8873(6)	1.1541(2)	4.9(2)
O(4)	0.2764(1)	0.7288(6)	1.2458(2)	5.4(2)
O(5)	0.2595(1)	0.4874(6)	1.0737(2)	5.2(2)
O(6)	0.1935(2)	0.3194(7)	1.0426(3)	6.5(2)
O(7)	- 0.0396(2)	0.7360(9)	0.9230(3)	8.5(3)
O(8)	- 0.0136(1)	0.5003(8)	0.8765(2)	6.3(2)
N(1)	0.1828(2)	0.7415(7)	1.1517(2)	4.0(2)
C(1)	0.2093(2)	0.7829(8)	1.1241(3)	3.5(2)
C(2)	0.1831(2)	0.8086(8)	1.0358(3)	3.5(2)
C(3)	0.1324(2)	0.7975(8)	1.0174(3)	3.7(2)
C(4)	0.1876(2)	0.6358(9)	0.987393)	3.8(2)
C(5)	0.1084(2)	0.6361(8)	0.9545(3)	3.9(2)
C(6)	0.1010(2)	0.981(1)	0.9883(3)	4.6(3)
C(7)	0.0965(2)	1.033(1)	0.9100(4)	5.2(3)

Table 7 continued

Atom	x	y	z	B_{eq}
C(8)	0.0757(2)	0.892(1)	0.8586(3)	5.1(3)
C(9)	0.0620(2)	0.711(1)	0.8864(3)	4.3(3)
C(10)	0.0531(2)	0.916(1)	0.9747(3)	5.1(3)
C(11)	0.0327(2)	0.755(1)	0.9224(3)	4.6(3)
C(12)	0.2608(2)	0.8059(9)	1.1745(3)	3.9(3)
C(13)	0.3273(2)	0.749(1)	1.3002(3)	6.3(3)
C(14)	0.2129(2)	0.462(1)	1.0365(3)	4.0(3)
C(15)	0.2895(3)	0.341(1)	1.1290(4)	7.1(4)
C(16)	-0.0103(2)	0.675(1)	0.9088(4)	5.4(3)
C(17)	-0.0532(3)	0.375(1)	0.8605(4)	8.9(5)
C(18)	-0.0889(3)	0.382(1)	0.7807(5)	10.3(5)

Table 8 Positional Parameters and Their Estimated Standard Deviations for **6c**

Atom	x	y	z	B_{eq}
F(1)	0.2979(4)	1.160(1)	0.9389(3)	5.6(3)
O(1)	-0.0421(4)	0.975(1)	0.7274(4)	4.1(4)
O(2)	0.1199(4)	0.835(1)	0.9020(4)	4.3(4)
O(3)	-0.1692(5)	1.131(1)	0.9023(4)	4.1(4)
O(4)	-0.2586(4)	0.965(1)	0.7971(4)	4.8(4)
O(5)	-0.0784(5)	0.727(1)	0.9426(4)	4.5(4)
O(6)	-0.0186(6)	0.560(1)	0.8681(5)	5.7(5)
O(7)	0.0086(6)	1.373(2)	0.6166(5)	7.8(6)
O(8)	0.1030(5)	1.169(1)	0.5866(4)	5.2(4)
N(1)	-0.1251(5)	0.979(1)	0.7394(5)	4.2(5)
C(1)	-0.1072(6)	1.019(2)	0.8123(6)	3.0(5)
C(2)	-0.0076(6)	1.049(2)	0.8606(5)	2.6(5)
C(3)	0.0330(6)	1.039(2)	0.7955(6)	3.3(5)
C(4)	0.0394(7)	0.886(2)	0.9171(6)	4.0(6)
C(5)	0.1060(7)	0.880(2)	0.8213(6)	3.3(5)
C(6)	0.0739(7)	1.233(2)	0.7778(6)	3.4(5)
C(7)	0.1540(8)	1.285(2)	0.8500(6)	3.7(6)
C(8)	0.2186(9)	1.151(2)	0.8740(8)	4.7(7)
C(9)	0.1977(7)	0.976(2)	0.8227(7)	4.3(6)
C(10)	0.1074(7)	1.165(2)	0.7128(6)	3.3(6)
C(11)	0.1716(7)	1.028(2)	0.7378(7)	4.3(6)
C(12)	-0.1831(7)	1.045(2)	0.8423(7)	3.5(6)
C(13)	-0.3344(7)	0.985(2)	0.8230(7)	7.0(7)
C(14)	-0.0206(8)	0.702(2)	0.9060(7)	4.0(6)
C(15)	-0.1481(9)	0.581(2)	0.9313(8)	7.0(8)
C(16)	0.0679(8)	1.255(2)	0.6354(7)	4.6(7)
C(17)	0.0676(8)	1.243(2)	0.5071(7)	6.5(8)
C(18)	0.124(1)	1.145(3)	0.4685(7)	10(1)

Table 9 Selected Bond Lengths, Bond Angles, and Torsion Angles of **3a**

Bond Length (A)		Bond Angle (°)		Torsion Angle (°)	
O(1)-N(1)	1.409 (7)	O(1)-N(1)-C(1)	107.9 (6)	O(1)-N(1)-C(1)-C(2)	0.7 (9)
O(1)-C(3)	1.464 (8)	N(1)-O(1)-C(3)	109.6 (5)	O(4)-N(2)-C(18)-C(17)	- 1.4 (9)
O(4)-N(2)	1.404 (7)	O(4)-N(2)-C(18)	108.1 (6)	N(1)-O(1)-C(3)-C(2)	18.0 (7)
O(4)-C(15)	1.480 (8)	N(2)-O(4)-C(15)	110.4 (5)	N(2)-O(4)-C(15)-C(17)	9.4 (7)
N(1)-C(1)	1.274 (8)	C(3)-C(6)-C(7)	107.0 (6)	C(3)-C(6)-C(7)-C(8)	56.6 (8)
C(3)-C(5)	1.543 (9)	C(3)-C(6)-C(10)	103.8 (6)	C(3)-C(5)-C(9)-C(8)	52.6 (8)
C(3)-C(6)	1.530 (9)	C(5)-C(9)-C(8)	106.3 (6)	C(3)-C(5)-C(9)-C(11)	- 60.7 (8)
C(6)-C(7)	1.51 (1)	C(5)-C(9)-C(11)	110.8 (6)	C(3)-C(6)-C(10)-C(11)	- 71.9 (7)
C(7)-C(8)	1.303 (9)	C(6)-C(7)-C(8)	112.8 (7)	C(6)-C(3)-C(5)-C(9)	2.0 (9)
C(8)-C(9)	1.504 (9)	C(7)-C(8)-C(9)	117.3 (7)	C(6)-C(10)-C(11)-C(9)	15.2 (7)
C(10)-C(11)	1.567 (9)	C(11)-C(12)-C(13)	128.5 (7)	C(10)-C(11)-C(12)-C(13)	0 (1)
C(12)-C(13)	1.299 (9)	C(12)-C(13)-C(14)	123.4 (7)	C(11)-C(12)-C(13)-C(14)	- 6 (1)

Table 10 Selected Bond Lengths, Bond Angles, and Torsion Angles of **4a**

Bond Length (A)		Bond Angle (°)		Torsion Angle (°)	
Cl(1)-C(1)	1.741 (7)	O(1)-C(5)-C(4)	115.1 (6)	O(1)-C(5)-C(4)-C(7)	- 0.5 (8)
O(1)-C(5)	1.351 (7)	O(1)-C(8)-C(7)	107.9 (6)	O(1)-C(8)-C(7)-C(4)	0.7 (9)
O(1)-C(8)	1.455 (7)	O(4)-N(1)-C(9)	112.4 (6)	O(4)-N(1)-C(9)-C(7)	- 9.3 (6)
O(4)-N(1)	1.380 (7)	C(5)-O(1)-C(8)	107.0 (5)	N(1)-C(9)-C(7)-C(4)	- 119.4 (8)
N(1)-C(9)	1.271 (8)	C(4)-C(7)-C(8)	101.0 (5)	C(5)-O(1)-C(8)-C(7)	9.5 (7)
C(7)-C(8)	1.562 (8)	C(7)-C(9)-C(10)	121.4 (6)	C(5)-C(4)-C(7)-C(8)	6.0 (7)

Table 11 Selected Bond Lengths, Bond Angles, and Torsion Angles of **5a**

Bond Length (A)		Bond Angle (°)		Torsion Angle (°)	
O(1)-N(1)	1.392 (5)	O(1)-N(1)-C(1)	110.3 (4)	O(1)-N(1)-C(1)-C(2)	- 2.0 (7)
O(1)-C(3)	1.478 (6)	N(1)-O(1)-C(3)	109.2 (4)	N(1)-O(1)-C(3)-C(2)	8.4 (6)
N(1)-C(1)	1.260 (6)	C(3)-C(6)-C(7)	105.0 (5)	C(3)-C(6)-C(7)-C(8)	- 60.0 (7)
C(3)-C(5)	1.548 (7)	C(3)-C(6)-C(10)	106.0 (5)	C(3)-C(5)-C(9)-C(8)	- 57.1 (6)
C(3)-C(6)	1.540 (7)	C(5)-C(9)-C(8)	105.4 (5)	C(3)-C(5)-C(9)-C(11)	56.1 (6)
C(6)-C(7)	1.512 (8)	C(5)-C(9)-C(11)	104.7 (5)	C(3)-C(6)-C(10)-C(11)	61.7 (7)
C(7)-C(8)	1.322 (7)	C(6)-C(7)-C(8)	115.0 (5)	C(6)-C(3)-C(5)-C(9)	- 0.9 (7)
C(8)-C(9)	1.513 (7)	C(7)-C(8)-C(9)	113.1 (5)	C(6)-C(10)-C(11)-C(9)	- 1.7 (8)
C(10)-C(11)	1.316 (8)				

Table 12 Selected Bond Lengths, Bond Angles, and Torsion Angles of **6c**

Bond Length (A)		Bond Angle (°)		Torsion Angle (°)	
O(1)-N(1)	1.39 (1)	O(1)-N(1)-C(1)	107.6 (8)	O(1)-N(1)-C(1)-C(2)	0 (1)
O(1)-C(3)	1.45 (1)	N(1)-O(1)-C(3)	111.8 (7)	N(1)-O(1)-C(3)-C(2)	10 (1)
N(1)-C(1)	1.30 (1)	C(3)-C(6)-C(7)	106.8 (9)	C(3)-C(6)-C(7)-C(8)	58 (1)
C(3)-C(5)	1.53 (1)	C(3)-C(6)-C(10)	101.5 (9)	C(3)-C(5)-C(9)-C(8)	56 (1)
C(3)-C(6)	1.55 (1)	C(5)-C(9)-C(8)	109.4 (9)	C(3)-C(5)-C(9)-C(11)	- 63 (1)
C(6)-C(7)	1.51 (1)	C(5)-C(9)-C(11)	100.3 (9)	C(3)-C(6)-C(10)-C(11)	- 63 (1)
C(7)-C(8)	1.32 (1)	C(6)-C(7)-C(8)	116 (1)	C(6)-C(3)-C(5)-C(9)	2 (1)
C(8)-C(9)	1.48 (2)	C(7)-C(8)-C(9)	112 (1)	C(6)-C(10)-C(11)-C(9)	- 2 (2)
C(10)-C(11)	1.33 (1)				

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