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Interaction of Aryloxychlorocarbenes with Acetylenedicarboxylate: Novel Formation of Polyfunctional Butadienes and 8-Oxatricyclo[3.2.1.0^{2,4}]oct-6-enes

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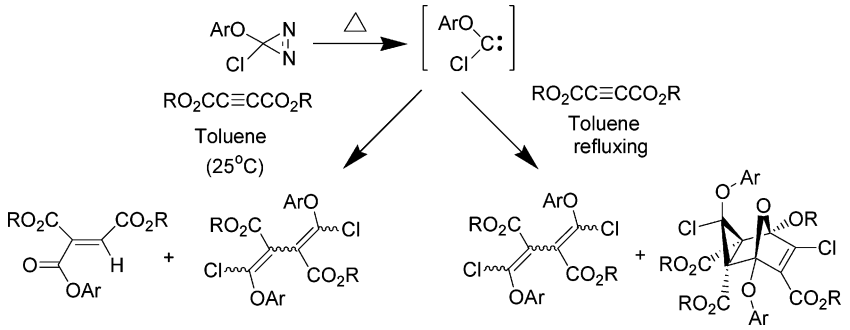

The interaction of aryloxychlorocarbenes with dialkyl acetylenedicarboxylates has been examined. Thermolyses of 3-aryloxy-3-chlorodiazirines in the presence of acetylenedicarboxylate resulted in the formation of unexpected polyfunctional 1,3-butadienes and 8-oxatricyclo[3.2.1.0^{2,4}]oct-6-enes or of 2-aryoxycarbonylmaleates dependent upon reaction conditions. This work confirmed the nucleophilicity of aryloxychlorocarbenes and underlined their synthetic potential.

Introduction

Nucleophilic and ambiphilic carbenes have attracted considerable attention in recent years due to their interesting chemistry and their potential application in organic synthesis.[1] The reactivity of chlorooxycarbenes should lie between that of the classical electrophilic carbenes such as dichlorocarbenes and nucleophilic carbenes, typified by dioxycarbenes. In fact, chlorooxycarbenes have been found to behave as ambiphilic carbenes. Moss and co-workers[2] have studied the chemistry of alkoxy- and aryloxychlorocarbenes and demonstrated experimentally and theoretically their ambiphilicity based on their relative reactivity with both electron-rich and electron-deficient alkenes to give cyclopropanes.[2] They also extensively investigated the fragmentation of alkoxychlorocarbenes, resulting in the formation of chloroalkanes, alkenes, etc.[3] Other groups such as those of Stevens[4] and Brueck[5] have also studied the reactivity of alkoxychlorocarbenes or phenyloxychlorocarbene toward differently substituted alkenes. All of those results have demonstrated that chlorooxycarbenes behave as ambiphiles in addition reactions to carbon−carbon double bonds to yield cyclopropanes. Although reactions between chlorooxycarbenes and different alkenes have been well documented, their reactivities to other electrophiles, such as electron-deficient alkynes and heterocumulenes, have not been reported.

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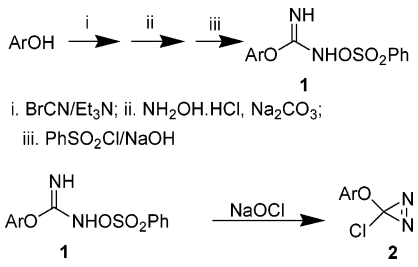
TABLE 1. Yields of *N*-Benzenesulfonyloxy-*O*-arylisoureas 1 and 3-Aryloxy-3-chlorodiazirines 2

Ar	1	yield (%)[a]	2	yield (%)[b]
Ph	**1a**	45	**2a**	30−45
4-MeC_6H_4	**1b**	42	**2b**	39−43
4-$MeOC_6H_4$	**1c**	48	**2c**	29−52
4-FC_6H_4	**1d**	38	**2d**	40−50
4-ClC_6H_4	**1e**	52	**2e**	31−57
4-BrC_6H_4	**1f**	40	**2f**	30−49
2,4-$Cl_2C_6H_3$	**1g**	35	**2g**	30−45
4-Cl-3,5-$Me_2C_6H_2$	**1h**	45	**2h**	30−39

[a] Overall yield in three steps from the corresponding phenols. [b] The isolated yield of diazirines is strongly dependent upon the ambient temperature because of the instability of the diazirines.

SCHEME 1



We have been interested in the chemistry of ambiphilic carbenes for some time.[1a] We herein explore the interaction of chlorooxycarbenes with diethyl acetylenedicarboxylate (DEAD) or dimethyl acetylenedicarboxylate (DMAD).

Results and Discussion

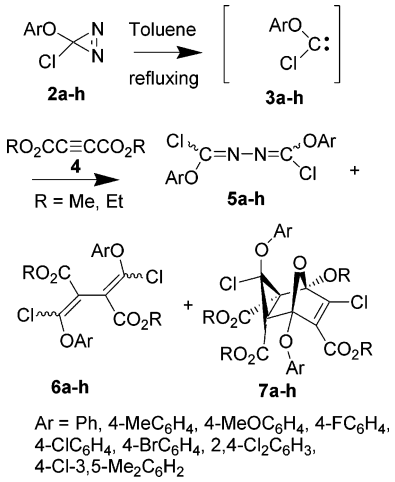
Although several methods for the generation of chlorooxycarbenes have been established, thermolysis or photolysis of alkoxy- or aryloxy-chlorodiazirines is the preferred approach to to give the corresponding chlorooxycarbene. Using the method of Moss,[2f,6] 3-aryloxy-3-chlorodiazirines **2** were obtained in 29−57%, by Graham[7] oxidation of *N*-benzenesulfonyloxy-*O*-arylisoureas **1** with NaOCl solution. The *N*-benzenesulfonyloxy-*O*-arylisoureas **1** were prepared from phenols and BrCN in three steps with an overall yield of 35−52%[2f,6] (Scheme 1 and Table 1). Thermolyses of 3-aryloxy-3-chlorodiazirines **2** in the presence of acetylenedicarboxylate (DEAD or DMAD) in refluxing toluene afforded a mixture of products, from which three types of products, **5**−**7**, were isolated (Scheme 2 and Table 2).

The products **5**, colorless crystals, were formed from the reaction of carbenes with their 3-aryloxy-3-chlorodiazirine precursors. Although all ^{1}H NMR and ^{13}C NMR spectra of the azines **5** indicated that each was a single isomer, their configuration could not be determined on the basis of spectroscopic data. Several similar 1,4-dialkoxy-1,4-dichloro-2,3-diazabuta-1,3-dienes have been reported from thermolysis of alkoxychlorodiazirines,[3b,4b] but to our knowledge, the 1,4-diaryoxy-1,4-dichloro-2,3-diazabuta-1,3-dienes **5** have not been found in the literature. It should be noted that the azines **5**, especially

TABLE 2. Products from Thermolysis of 3-Aryloxy-3-chlorodiazirines 2 with DEAD or DMAD in Refluxing Toluene

starting material			yield of product (%)		
2	X	**4**	**5**	**6**	**7**
a	H	DEAD	28	38	24
b	4-Me	DEAD	34	16	30
c	4-OMe	DEAD	28	21	31
d	4-F	DEAD	19	25	26
e	4-Cl	DEAD	21	29	37
f	4-Br	DEAD	19	31	30
g	2,4-Cl_2	DMAD	26	35	22
h	4-Cl-3,5-Me_2	DMAD	19	32	26

SCHEME 2



5a, were sensitive to water. They underwent partial hydrolysis during chromatography or recrystallization. Consequently, compound **5a** did not give satisfactory CHN analytical results.

Both the ^{1}H NMR and the MS spectra of products **6** suggested that they were derived from one acetylenedicarboxylate molecule and two carbene moieties. Diphenoxycarbene has been reported to react with DEAD to give a bicyclobutane.[8] In the case of **6**, however, the lack of any signals between 75 and 95 ppm for quaternary aliphatic carbons in the ^{13}C NMR spectra ruled out the bicyclobutane structure **9**. Combining the ^{13}C NMR and other spectral data, the products were concluded to be polysubstituted 1,3-butadiene **6**, which could be generated from thermal rearrangement of **9** (Scheme 3). (Note: We found that the aryloxy (chloro) substituted aliphatic carbons appeared at around 86 ppm in their ^{13}C NMR spectra; see, for example, the spectroscopic data of compounds **7**.)

The addition of carbene **3** to cyclopropene **8** could lead to the formation of three diastereomeric bicyclobutane intermediates, **9-I**, **9-II**, and **9-III**. Each of these could then rearrange with retention of configuration into the corresponding (*Z*,*Z*), (*Z*,*E*), or (*E*,*E*)-isomer of 1,3-butadiene **6** (Scheme 4). The ^{1}H NMR spectra showed that each of the products **6b**−**6g** was indeed a mixture of three isomers, whereas **6a** apparently contained a tiny amount of a fourth component, possibly a conformational isomer or its precursor **9a**. The separation of the isomers of the

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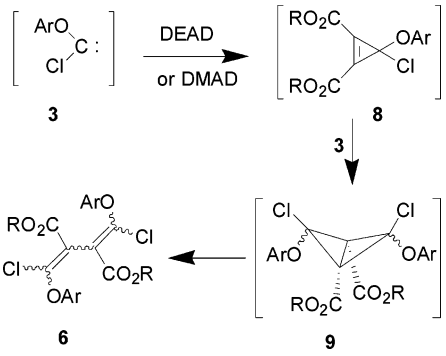
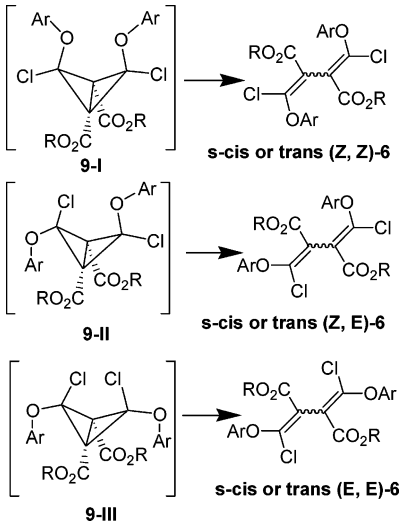
SCHEME 3



SCHEME 4



oily products **6a**−**6g** was attempted but was unsuccessful. In fact, the isomers underwent interconversion during attempted chromatographic separation. Immediately upon isolation, the major component of **6** was a symmetrical molecule [(*Z*,*Z*) or (*E*,*E*)-isomer] according to the ^{1}H NMR spectra. However, it partially converted into a nonsymmetric and another symmetrical isomer after further attempted purification by column chromatography. Among all the reactions examined, only the one between 4-chloro-3,5-dimethylphenoxychlorocarbene **3h** and DMAD gave a crystalline product **6h**. Although a tiny amount of **6h** converted into other isomers during chromatography, fortunately, **6h** was easily isolated from the mixture by recrystallization. A single-crystal X-ray diffraction study showed that the major isomer of **6h** was the (*Z*,*Z*)-isomer, with the two carbon−carbon double bonds being almost orthogonal (see Supporting Information).

To throw light on the preferred isomer of product **6**, we calculated the relative energies of the isomers of intermediate **9h** and products **6f** and **6h** on the basis of the B3LYP/6-31G* [9] optimized structures (Tables 3 and 4). It is not surprising that the **9h-I** has the lowest energy, having the weakest dipolar repulsion between the two oxygen atoms compared to that between oxygen and chlorine atom in **9-II** or two chlorines in **9-III** (Figure 1). The initially formed (*Z*,*Z*)-isomer of **6,** which was derived from the predominant isomer **9-I,** was therefore a kinetic product. It was noticed that the computational optimized structure of the *cis*-(*Z*,*Z*)-isomer of **6**, which is

TABLE 3. Total and Relative Energies of Stationary Structures 9h

structure	total energy (au)	relative energy (kcal/mol)
9h-I	−3219.8589	0.00
9h-II	−3219.8586	0.13
9h-III	−3219.8535	3.36

TABLE 4. Total Energies, Relative Energies, and Dihedral Angles of Carbon−Carbon Double Bond π-Systems of Stationary Structures

structure	total energy (au)	relative energy (kcal/mol)	dihedral angle of double bond (deg)
trans-(*Z*,*Z*)-**6f**	−7364.2889	1.69	90.56
cis-(*Z*,*Z*)-**6f**	−7364.2868	3.03	−73.66
trans-(*Z*,*E*)-**6f**	−7364.2916	0.00	86.86
cis-(*Z*,*E*)-**6f**	−7364.2896	1.26	−83.20
trans-(*E*,*E*)-**6f**	−7364.2897	1.20	96.99
cis-(*E*,*E*)-**6f**	−7364.2912	0.26	−99.12
trans-(*Z*,*Z*)-**6h**	−3219.9080	1.51	91.31
cis-(*Z*,*Z*)-**6h**	−3219.9061	2.75	−76.81
trans-(*Z*,*E*)-**6h**	−3219.9105	0.00	87.00
cis-(*Z*,*E*)-**6h**	−3219.90849	1.23	−84.01
trans-(*E*,*E*)-**6h**	−3219.90847	1.24	95.08
cis-(*E*,*E*)-**6h**	−3219.9101	0.21	−99.50

exemplified by **6h** in Figure 2, is very similar to the single-crystal structure of (*Z*,*Z*)-**6h**. The dihedral angles of the two double bonds in all of the isomers are around 90°. The calculated relative energy of the geometrical isomer followed the order *cis*-(*Z*,*Z*) > *trans*-(*Z*,*Z*) > *trans*-(*E*,*E*) ≈ *cis*-(*Z*,*E*) > *cis*-(*E*,*E*) > *trans*-(*Z*,*E*), clarifying the observed interconversion of the isomers of product **6**. The (*Z*,*Z*)-isomer of **6** was formed predominantly in the reaction, which partly converted into more stable (*Z*,*E*)- and (*E*,*E*)-products on silica gel column.

The most intriguing product from the interaction of the carbenes with acetylenedicarboxylate was compound **7**. These products displayed three distinct carbonyl absorptions in their IR spectra. Both ^{1}H NMR and ^{13}C NMR spectra showed four nonequivalent alkoxy groups and two nonequivalent aryl rings. Combining the spectroscopic information and CHN analytical results, the compound **7** was the adduct of two aryloxychlorocarbenes and two acetylenedicarboxylate molecules. Although spectral data did not allow full verification of the structure, X-ray diffraction studies unambiguously confirmed that the compound **7** (X = Br) was a polysubstituted 8-oxatricyclo[3.2.2.0^{2,4}]oct-6-ene (see Supporting Information).

The products **7** are apparently the Diels−Alder adducts of the initial two products of the 1:1 interaction of the

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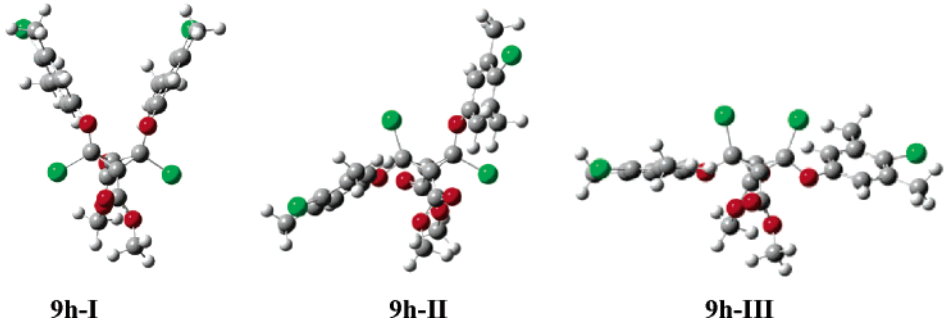


FIGURE 1. Computational optimized stationary structures of the three isomers of intermediate **9h**.

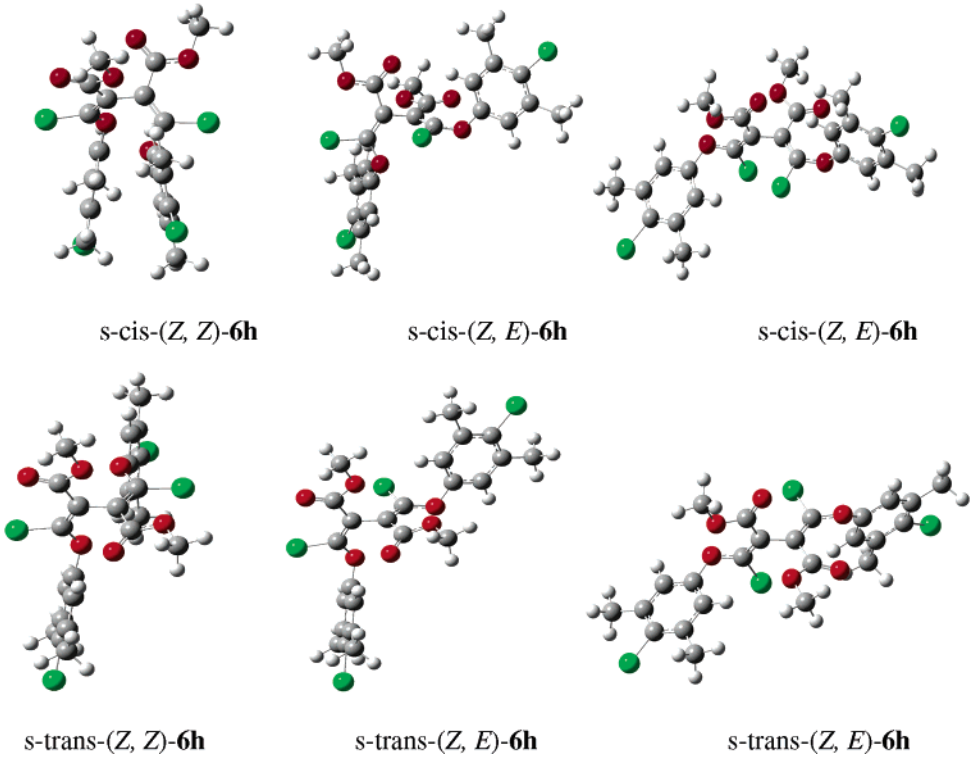


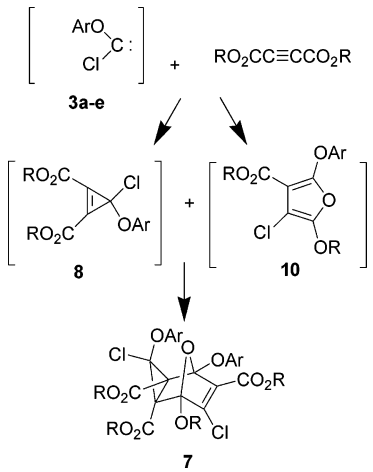
FIGURE 2. Computational optimized stationary structures of configurational and conformational isomers of **6h**.

carbene and DEAD (DMAD). These two initial products are the cyclopropene **8** and furan **10**, although in no case were these intermediates isolated (Scheme 5). A reasonable mechanism for the formation of intermediate **10** involves the isomerization of cyclopropenes **8** to **12** via a cyclopropenium ion **11** followed by the rearrangement of **12** to furans **10** (Scheme 6).

It is not surprising that compound **7f** is an *endo* Diels–Alder cycloaddition product. Actually, only one isomer of **7** was found in the mixture of products. It is also noteworthy that the aryloxy group rather than the chlorine atom on the three-membered ring is close to the oxygen bridge. The preponderance of this configuration is due to the dipolar repulsion between the oxygen and chlorine atoms and to the steric hindrance between the alkoxycarbonyls and the aryloxy group.

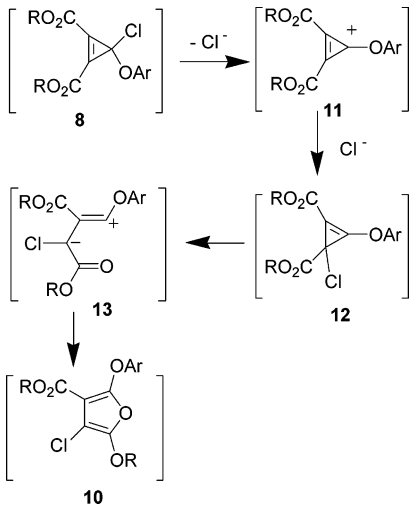
To isolate the intermediates, we performed the photolyses of the diazirines with DEAD at a lower temperature. At 25 °C no significant product was found except those compounds derived from decomposition or polymerization of starting materials. Using diazirine **2** and

SCHEME 5

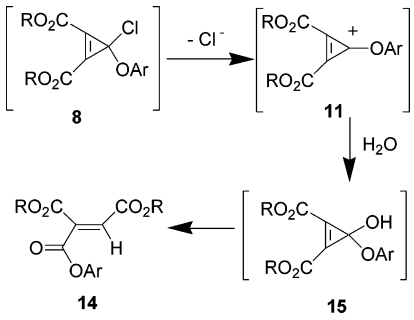


DEAD at 25–30 °C for 48 h gave a new product **14**, isolated along with compound **5** and **6**. Spectral data suggested that the compound **14** was a diethyl aryloxy-

SCHEME 6



SCHEME 7



carbonylmaleate, with ^{1}H NOE studies supporting the maleate configuration. The formation of **14** probably resulted from the hydrolysis of cyclopropene **8** (Scheme 7). The formation of **7** in refluxing toluene but **14** at room temperature can be best explained by the thermally induced rearrangement of **8** into furan **10** followed by the Diels−Alder reaction of **10** with **8**, which also required an elevated temperature. Any intermediate **8** that did not rearrange to **10** during the reaction presumably hydrolyzed to **14** during workup or chromatography. The formation of *E*-configuration product further supports this reaction pathway.

To increase the selective formation of the products, optimization was carried out by varying the ratio of starting materials, solvent, and reaction temperature. It was found that three different rations of starting materials (**2**:**4** = 2:1, 1:1, 1:2) gave similar yields of products **6** and **7**, even though they were a [2 + 1] and a [2 + 2] adduct of carbene to acetylenedicarboxylate, respectively. In contrast, the outcomes of the reaction seemed strongly dependent upon both solvent and reaction temperature. When the reaction was performed in refluxing toluene or xylene, product **5**, **6**, and **7** were obtained in similar yields. However, if the starting materials were refluxed in benzene or dichloroethane or stirred in toluene at ambient temperature, products **5**, **6**, and **14** were isolated. 1,2-Dimethoxyethane, 1,4-dioxane, or 1,1,2,2-tetrachloroethane were inefficient solvents for this reaction. (Table 5)

In summary, we have examined the reaction between aryloxychlorocarbenes and DEAD (or DMAD) and found more direct evidence for the nucleophilicity of aryloxychlorocarbenes. More importantly, this work has provided a new route to the synthesis of polysubstituted 1,3-butadienes and polysubstituted 8-oxatricyclo [3.2.1.0^{2,4}]-oct-6-ene derivatives, which are not easily prepared by other synthetic methods.

TABLE 5. Thermolysis of 3-Aryloxy-3-chlorodiazirines 2 in the Presence of DEAD under Different Conditions

			yield (%)			
2	solvent	temp (°C)	**5**	**6**	**7**	**14**
2a	toluene	25	18	25		12
2a	benzene	80	23	23		16
2a	toluene	110	28	38	24	
2a	xylene	140	16	28	27	
2a	dichloroethane	82	22	31		19
2a	tetrachloroethane	140				
2a	ethylene glycol dimethyl ether	80	18			
2a	1,4-dioxane	100				
2e	toluene	25	27	25		13
2e	benzene	80	24	30		13
2e	dichloroethane	82	23	27		15
2f	benzene	80	22	29		19

Experimental Section

N-Benzenesulfonyloxy-*O*-arylisoureas **1** and 3-aryloxy-3-chlorodiazirines **2** were prepared according to the method of Moss et al.[2f,6]

General Procedure for the Reaction of 3-Aryloxy-3-chlorodiazirines 2 with DEAD (or DMAD). A mixture of 3-aryloxy-3-chlorodiazirines **2** (4 mmol) and DEAD (or DMAD) (4 mmol) in toluene (or other solvent) (50 mL) was heated under reflux for 15 h under an argon atmosphere. After removal of the solvent under reduced pressure, the products **5**, **6**, and **7** or **14** (see Tables 2 and 4) were isolated by chromatography on silica gel, eluting with a mixture of petroleum ether (60−90 °C) and ethyl acetate (10:1 to 4:1).

1,4-Diphenoxy-1,4-dichloro-2,3-diazabuta-1,3-dienes (5a). Colorless crystals; mp 68−69 °C; IR υ (cm^{-1}) 1627, 1577; ^{1}H NMR δ (ppm) 7.43 (d, J = 7.9 Hz, 4H), 7.26−7.29 (m, 6H); ^{13}C NMR δ (ppm) 153.4, 147.1, 129.6, 126.1, 120.5; TOF MS-EI 215 (100)/217 (40), 373 (15%, M$^+$ − Cl)/ 275 (5).

1,4-Bis-4-methylphenoxy-1,4-dichloro-2,3-diazabuta-1,3-dienes (5b). Colorless crystals; mp 98−100 °C; IR υ (cm^{-1}) 1630, 1595; ^{1}H NMR δ (ppm) 7.20 (d, J = 8.3 Hz, 4H), 7.14 (d, J = 8.5 Hz, 4H), 2.38 (s, 6H); ^{13}C NMR δ (ppm) 151.3, 147.0, 135.8, 130.2, 120.2, 20.9; Maldi-TOF MS 337 (M$^+$ + 1). Anal. Calcd for $C_{16}H_{14}Cl_2N_2O_2$: C, 56.99; H, 4.19; N, 8.31. Found: C, 57.12; H, 4.13; N, 8.64.

1,4-Bis-4-methoxyphenoxy-1,4-dichloro-2,3-diazabuta-1,3-dienes (5c). Colorless crystals; mp 100−101 °C; IR υ (cm^{-1}) 1633, 1602; ^{1}H NMR δ (ppm) 7.19 (d, J = 9.1 Hz, 2H), 6.91 (d, J = 9.1 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR δ (ppm) 157.4, 147.4, 147.0, 121.4, 114.4, 55.6; TOF MS-EI 245 (100)/247 (50), 333 (12%, M$^+$ − Cl)/ 335 (4). Anal. Calcd for $C_{16}H_{14}Cl_2N_2O_4$: C, 52.05; H, 3.82; N, 7.59. Found: C, 52.04; H, 3.86; N, 7.50.

1,4-Bis-4-fluorophenoxy-1,4-dichloro-2,3-diazabuta-1,3-dienes (5d) colorless crystals; mp 111−112 °C; IR υ (cm^{-1}) 1630, 1592; ^{1}H NMR δ (ppm) 7.22−7.25 (m, 4H), 7.10 (t, J = 8.2 Hz, 4H); ^{13}C NMR δ (ppm) 161.3, 159.3, 149.1, 147.6, 122.1 (d), 116.3, 116.1; MS (FAB) 345 (M + 1). Anal. Calcd for $C_{14}H_8Cl_2F_2N_2O_2$: C, 48.69; H, 2.33, N, 8.11. Found: C, 48.73; H, 2.43. N, 8.12.

1,4-Bis-4-chlorophenoxy-1,4-dichloro-2,3-diazabuta-1,3-dienes (5e). Colorless crystals; mp 171−173 °C; IR υ (cm^{-1}) 1632, 1581; ^{1}H NMR δ (ppm) 7.38 (d, J = 8.9 Hz, 4H), 7.22 (d, J = 8.9 Hz, 4H); ^{13}C NMR δ (ppm) 151.7, 147.4, 131.5, 19.6, 121.9; TOF MS-EI 249 (100)/251 (99), 341 (20%, M$^+$ −

Cl)/ 343 (18). Anal. Calcd for $C_{14}H_8Cl_4N_2O_2$: C, 44.48; H, 2.13; N, 7.41. Found: C, 44.46; H, 2.42; N, 7.26.

1,4-Bis-4-bromophenoxy-1,4-dichloro-2,3-diazabuta-1,3-dienes (5f). Colorless crystals; mp 176−178 °C; IR υ (cm^{-1}) 1634, 1575; ^1H NMR δ (ppm) 7.53 (d, J = 8.9 Hz, 4H), 7.17 (d, J = 8.9 Hz, 4H); ^{13}C NMR δ (ppm) 152.3, 147.3, 132.6, 122.3, 119.2; N-Maldi-TOF MS 463 ($M^+ - 1$). Anal. Calcd for $C_{14}H_8Br_2Cl_2N_2O_2$: C, 36.01; H, 1.73; N, 6.00. Found: C, 36.12; H, 1.73; N, 5.96.

1,4-Bis-2,4-dichlorophenoxy-1,4-dichloro-2,3-diazabuta-1,3-dienes (5g). Colorless crystals; mp 132−133 °C; IR υ (cm^{-1}) 1615, 1581, 1473; ^1H NMR δ (ppm) 7.49 (2H, d, J = 2.3 Hz), 7.30 (2H, dd, J = 8.7 and 2.3 Hz), 7.24 (2H, d, J = 8.7 Hz); ^{13}C NMR δ (ppm) 147.9, 147.1, 132.4, 130.4, 128.0, 127.4, 123.8; MS (EI) 133 (100)/135(65), 283 (25)/285 (35)/287 (15), 409 (20)/411(30)/413 (20), 444 (M^+, 3)/446 (5)/448 (4). Anal. Calcd for $C_{14}H_6Cl_6N_2O_2$: C, 37.62; H, 1.35; N, 6.27. Found: C, 37.71; H, 1.44; N, 5.95.

1,4-Bis-(4-chloro-3,5-dimethylphenoxy)-1,4-dichloro-2,3-diazabuta-1,3-dienes (5h). Colorless crystals; mp 142−143 °C; IR υ (cm^{-1}) 1628, 1582, 1469; ^1H NMR δ (ppm) 7.02 (s, 4H), 2.40 (s, 12H); ^{13}C NMR δ (ppm) 150.9, 146.9, 137.7, 131.9, 120.1, 20.9; TOF MS 379, 433 ($M^+ + 1$)/435/437. Anal. Calcd for $C_{18}H_{16}Cl_4N_2O_2$: C, 49.80; H, 3.71; N, 6.32. Found: C, 49.84; H, 3.84; N, 6.32.

Diethyl 1,4-Dichloro-1,4-diphenoxy-1,3-butadiene-2,3-dicarboxylate (6a). Colorless oil; a mixture of four isomers, IR (film) υ (cm^{-1}) 1730, 1614, 1585; ^1H NMR δ (ppm) major asymmetric isomer: 7.36 (t, J = 7.8 Hz, 4H), 7.22 (t, J = 7.5 Hz, 2H), 7.04 (d, J = 8.5 Hz, 4H), 4.25 (q, J = 7.1 Hz, 4H), 1.32 (t, J = 7.1 Hz, 6H). A mixture of four isomers: 7.31−7.41 (m, 6.0H), 7.16−7.26 (m, 1.0H), 7.14 (t, J = 8.0 Hz, 1.2H), 7.07 (t, J = 8.5 Hz, 1.8H), 4.40 (q, J = 7.1 Hz, 0.3H), 4.33−4.35 (m, 1.2H), 4.23−4.27 (m, 1.6H), 4.15 (q, J = 7.1 Hz, 0.9H), 1.38−1.42 (m, 2.05H), 1.35 (t, J = 7.1 Hz, 1.35H), 1.24 (t, J = 7.1 Hz, 1.05H), 1.14(t, J = 7.1 Hz, 1.35H). ^{13}C NMR δ (ppm) a mixture of four isomers: 164.3, 163.8, 163.0, 162.5, 154.9, 153.7, 153.2, 151.6, 150.8, 148.6, 130.9, 129.8, 129.7, 129.6, 129.5, 126.4, 125.4, 125.2, 124.7, 124.5, 121.4, 119.5, 119.4, 119.3, 117.7, 117.4, 115.0 111.5, 62.7, 62.0, 61.4, 61.35, 61.3, 61.2, 14.2 (d) 14.1, 14.0 (d). HRMS (FAB) calcd for $C_{22}H_{21}Cl_2O_6$ 451.0710 (M + 1), found 451.0709.

Diethyl 1,4-Dichloro-1,4-bis(4-methylphenoxy)-1,3-butadiene-2,3-dicarboxylate (6b). Colorless oil; a mixture of three isomers, IR (film) υ (cm^{-1}) 1730, 1590; ^1H NMR δ (ppm) major symmetric isomer: 7.15 (d, J = 8.3 Hz, 4H), 6.93 (d, J = 8.5 Hz, 4H), 4.25 (q, J = 7.1 Hz, 4H), 2.37 (s, 6H), 1.31 (t, J = 7.1 Hz, 6H). A mixture of three isomers: 7.18−7.20 (m, 1.4H), 7.15 (d, J = 8.3 Hz, 1.9H), 7.12 (d, J = 8.4 Hz, 0.7H), 7.07 (d, J = 8.6 Hz, 0.7H), 7.01 (d, J = 8.6 Hz, 0.7H), 6.96 (d, J = 8.6 Hz, 0.7H), 6.93 (d, J = 8.5 Hz, 1.9H), 4.31 (q, J = 7.1 Hz, 0.7H), 4.25 (q, J = 7.1 Hz, 2.6H), 4.16 (q, J = 7.1 Hz, 0.7H), 2.39 (s, 1.05H), 2.37 (s, 3.9H), 2.27 (s, 1.05H), 1.37 (t, J = 7.1 Hz, 1.05H), 1.31 (t, J = 7.1 Hz, 3.9H), 1.25 (t, J = 7.1 Hz, 1.05H), 1.17 (t, J = 7.1 Hz, 1.05H). ^{13}C NMR δ (ppm) a mixture of three isomers: 164.4, 163.1, 162.6, 152.8, 151.9, 151.5, 151.1, 148.9, 135.1, 134.9, 134.5, 134.1, 130.3, 130.2, 130.0 129.7, 129.0, 128.8, 128.5, 128.3, 126.5, 119.5, 119.4, 119.3, 117.9, 117.7, 117.3, 111.6, 110.9, 61.3, 61.25, 61.2, 61.1, 20.9, 20.8, 20.7, 20.6, 14.2, 14.1, 14.0, 13.9. HRMS (FAB) calcd for $C_{24}H_{25}Cl_2O_6$ 479.1023 (M + 1), found 479.1027.

Diethyl 1,4-Dichloro-1,4-bis(4-methoxyphenoxy)-1,3-butadiene-2,3-dicarboxylate (6c). Colorless oil; a mixture of three isomers, IR (film) υ (cm^{-1}) 1727, 1615, 1592. ^1H NMR δ (ppm) major symmetric isomer: 6.97 (d, J = 9.0 Hz, 4H), 6.86 (d, J = 9.0 Hz, 4H), 4.25 (q, J = 7.1 Hz, 4H), 3.82 (s, 6H), 1.31 (t, J = 7.1 Hz, 6H). A mixture of three isomers: 7.11 (d, J = 9.0 Hz, 0.4H), 7.02−7.05 (m, 1.2H), 6.97 (d, J = 9.0 Hz, 1.2H), 6.88−6.92 (m, 1.2H), 6.85−6.87 (m, 3H), 4.31 (q, J = 7.1 Hz, 0.6H), 4.25 (q, J = 7.1 Hz, 2.8H), 4.18 (q, J = 7.1 Hz, 2.8H), 3.83 (s, 0.9H), 3.82 (s, 3.3H), 3.81 (s, 0.9H), 1.36 (t, J = 7.1 Hz, 0.9H), 1.31 (t, J = 7.1 Hz, 3.3H). 1.26 (t, J = 7.2 Hz, 0.9H), 1.19 (t, J = 7.1 Hz, 0.9H). ^{13}C NMR δ (ppm) a mixture of three isomers: 164.5, 164.0, 163.3, 157.0, 156.8, 156.6, 149.2, 148.5, 147.2, 129.4, 120.9, 120.7, 119.2, 118.8, 114.7, 114.6, 114.5, 114.4, 110.3, 61.3, 61.1, 61.2, 61.1, 55.6, 14.2, 14.1 (d). HRMS (FAB) calcd for $C_{24}H_{25}Cl_2O_8$ 511.0921 (M + 1), found 511.0917.

Diethyl 1,4-Dichloro-1,4-bis(4-fluorophenoxy)-1,3-butadiene-2,3-dicarboxylate (6d). Colorless oil; a mixture of isomers, IR (film) υ (cm^{-1}) 1732, 1601, 1501, 1456; ^1H NMR δ (ppm): 6.98−7.39 (m, 8H), 4.37 (q, J = 7.1 Hz, 0.2H), 4.33 (q, J = 7.1 Hz, 0.6H), 4.26 (q, J = 7.1 Hz, 2.6H), 4.17 (q, J = 7.1 Hz, 0.4H), 4.17 (q, J = 7.1 Hz, 0.2H), 1.40 (t, J = 7.2 Hz, 0.3H), 1.36 (t, J = 6.9 Hz, 1.2H), 1.31 (t, J = 7.1 Hz, 3.0H), 1.27 (t, J = 7.1 Hz, 0.3H), 1.25 (t, J = 7.1 Hz, 1.2H), 1.17 (t, J = 7.1 Hz, 0.6H); ^{13}C NMR δ (ppm) 164.2, 163.6, 163.0, 162.4, 161.0, 160.9, 160.7, 151.6, 150.7, 149.4, 148.6, 142.7, 131.0, 129.5, 128.7, 128.4, 128.3, 127.2, 123.8, 122.9, 122.3, 121.2, 121.1, 121.0, 120.9, 119.3, 119.2, 119.0, 118.9, 116.5 (d), 116.4, 116.3, 116.2, 116.1, 114.9, 111.3, 62.8, 62.1, 61.5, 61.4, 61.3, 60.8, 14.2, 14.1, 14.0, 13.9. HRMS (FAB) calcd for $C_{22}H_{19}Cl_2F_2O_6$ 487.0521 (M + 1), found 487.0526.

Diethyl 1,4-Dichloro-1,4-bis(4-chlorophenoxy)-1,3-butadiene-2,3-dicarboxylate (6e). Colorless oil; a mixture of three isomers, IR (film) υ (cm^{-1}) 1725, 1612, 1584, 1485; ^1H NMR δ (ppm) major symmetric isomer: 7.31 (d, J = 9.0 Hz, 4H), 6.95 (d, J = 9.0 Hz, 4H), 4.23 (q, J = 7.1 Hz, 4H), 1.29 (t, J = 7.1 Hz, 6H). A mixture of three isomers: 7.35 (d, J = 9.1 Hz, 1.6H), 7.31 (d, J = 9.0 Hz, 1.4H), 7.27 (d, J = 9.0 Hz, 1H), 7.10 (d, J = 9.0 Hz, 0.8H), 7.05 (d, J = 9.0 Hz, 0.8H), 6.98 (d, J = 9.0 Hz, 1.0H), 6.95 (d, J = 9.0 Hz, 1.4H), 4.32 (q, J = 7.1 Hz, 0.8H), 4.21−4.25 (m, 2.4H), 4.13 (q, J = 7.1 Hz, 0.8H), 1.35 (t, J = 7.1 Hz, 1.5H), 1.29 (t, J = 7.1 Hz, 2.1H), 1.22 (t, J = 7.1 Hz, 1.2H), 1.14 (t, J = 7.1 Hz, 1.2H). ^{13}C NMR δ (ppm) a mixture of three isomers: 164.0, 163.5, 162.7, 162.2, 153.4, 153.3, 152.7, 152.0, 151.2, 148.2, 130.9, 130.7, 130.1, 129.9, 129.8, 129.7, 129.6, 129.0, 120.8, 120.6, 119.0, 118.6, 115.7, 115.3, 111.9, 61.6, 61.5 (d), 61.4, 14.2, 14.1, 14.0, 13.9. HRMS (FAB) calcd for $C_{22}H_{19}Cl_4O_6$ 518.9930 (M + 1), found 518.9935.

Diethyl 1,4-Dichloro-1,4-bis(4-bromophenoxy)-1,3-butadiene-2,3-dicarboxylate (6f). Colorless oil; a mixture of three isomers, IR (film) υ (cm^{-1}) 1732, 1615, 1579, 1482; ^1H NMR δ (ppm) major symmetric isomer: 7.47 (d, J = 8.9 Hz, 4H), 6.91 (d, J = 8.9 Hz, 4H), 4.25 (q, J = 7.1 Hz, 4H), 1.31 (t, J = 7.1 Hz, 6H). A mixture of the other two isomers: 7.52 (d, J = 8.9 Hz, 6H), 7.45 (d, J = 8.9 Hz, 2H), 7.06 (d, J = 8.9 Hz, 4H), 7.01 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 9.0 Hz, 2H), 4.34 (q, J = 7.2 Hz, 2H), 4.24 (q, J = 7.1 Hz, 4H), 4.15 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H), 1.24 (t, J = 7.1 Hz, 6H), 1.15 (t, J = 7.1 Hz, 3H). ^{13}C NMR δ (ppm) a mixture of isomers: 163.4, 162.7, 153.9, 153.8, 152.7, 152.6, 151.1, 132.8, 132.8, 132.7, 124.6, 123.0, 121.2, 119.4, 119.2, 119.0, 117.6, 117.4, 115.8, 61.6, 61.5 (d), 14.2, 14.1, 14.0. HRMS (FAB) calcd for $C_{22}H_{19}Br_2Cl_2O_6$ 606.8921 (M + 1), found 606.8907

Dimethyl 1,4-Dichloro-1,4-bis(2,4-dichlorophenoxy)-1,3-butadiene-2,3-dicarboxylate (6g). Colorless oil; asymmetric isomer, IR υ (cm^{-1}) 1734, 1658, 1608, 1580, 1474; ^1H NMR δ (ppm) 7.50 (d, J = 2.4 Hz, 1H,), 7.31 (d, J = 2.4 Hz, 1H), 7.08−7.13 (m, 4H), 3.85 (s, 3H), 3.70 (s, 3H). A mixture of isomers: IR υ (cm^{-1}) 1734, 1604, 1577, 1473; ^1H NMR δ (ppm) 7.49 (d, J = 2.4 Hz, 1H), 7.46−7.48 (m, 3H), 7.22−7.30 (m, 4H), 7.08 (d, J = 8.5 Hz, 1H), 7.05 (d, J = 8.7 Hz, 3H), 3.86 (s, 3H), 3.81 (s, 6H), 3.73 (s, 3H). ^{13}C NMR δ (ppm) a mixture of isomers: 164.3, 163.9, 162.9, 151.7, 150.6, 149.2, 149.0, 147.9, 147.7, 131.9, 131.7, 130.6, 130.5 (d), 128.0 (d), 127.9, 127.2, 127.1, 125.6, 122.5, 122.4, 120.2, 119.6, 113.6, 110.7, 110.0, 52.6, 52.5. HRMS (FAB) calcd for $C_{20}H_{13}Cl_6O_6$ 558.8838 (M + 1), found 558.8835.

Dimethyl 1,4-Dichloro-1,4-bis(4-chloro-3,5-dimethylphenoxy)-1,3-butadiene-2,3-dicarboxylate (6h). Colorless crystals; mp 179−180 °C; IR υ (cm^{-1}) 1730, 1628, 1598, 1583, 1468; ^1H NMR δ (ppm) 7.21 (s, 4H), 3.79 (s, 6H), 2.34 (s, 12H); ^{13}C NMR δ (ppm) 164.6, 151.0, 148.7, 137.7, 131.0, 118.9, 111.0,

52.3, 20.8; TOF-MS 511(M^+ − Cl)/513, 569(M + Na^+)/571/573. Anal. Calcd for $C_{24}H_{22}Cl_4O_6$: C 52.58, H 4.05. Found: C 52.74, H 4.15.

Triethyl 3,7-Dichloro-1-ethoxy-3,5-diphenoxy-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene-2,4,6-tricarboxylate (7a). Colorless crystals; mp 68−69 °C; IR υ (cm^{-1}) 1745, 1734, 1720, 1616, 1592; ^{1}H NMR δ (ppm) 7.47 (d, J = 7.9 Hz, 2H), 7.35 (t, J = 7.37 Hz, 2H), 7.17 (t, J = 7.8 Hz, 2H), 7.09 (t, J = 7.3 Hz, 1H), 7.00 (t, J = 7.3 Hz, 1H), 6.92 (d, J = 7.8 Hz, 2H), 4.41−4.43 (m, 1H), 4.34−4.37 (m, 2H), 4.24−4.26 (m, 1H), 4.09 (q, J = 7.0 Hz, 2H), 4.00 (q, J = 7.0 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H), 1.37 (t, J = 7.0 Hz, 3H), 1.28 (t, J = 7.0 Hz, 3H), 1.01 (t, J = 7.0 Hz, 3H); ^{13}C NMR δ (ppm) 162.0, 160.0, 154.6, 154.2, 152.0, 137.7, 129.4, 129.1, 129.0, 123.6, 123.2, 118.3, 117.2, 107.4, 105.9, 86.1, 64.8, 62.3, 62.2, 61.0, 59.1, 54.6, 15.1, 14.0, 13.9, 13.7; MS (EI) 463 (100), 585 (90, M^+ − Cl)/587 (30). Anal. Calcd for $C_{30}H_{30}Cl_2O_{10}$: C 57.98, H 4.87. Found: C 58.04, H 4.93.

Triethyl 3,7-Dichloro-1-ethoxy-3,5-bis(4-methylphenoxy)-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene-2,4,6-tricarboxylate (7b). Colorless crystals; mp 80−82 °C; IR υ (cm^{-1}) 1749, 1740, 1720, 1621, 1509; ^{1}H NMR δ (ppm) 7.36 (d, J = 8.6 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 6.95 (d, J = 8.4 Hz, 2H), 6.81 (d, J = 8.6 Hz, 2H), 4.39−4.41 (m, 1H), 4.32−4.36 (m, 2H), 4.24−4.28 (m, 1H), 4.07 (q, J = 7.3 Hz, 2H), 4.02 (q, J = 7.1 Hz, 2H), 2.30 (s, 3H), 2.24 (s, 3H), 1.38 (t, J = 7.2 Hz, 3H), 1.36 (t, J = 7.2 Hz, 3H), 1.29 (t, J = 7.0 Hz, 3H), 1.06 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ (ppm) 162.1, 162.0, 152.5, 152.1, 151.9, 137.7, 133.0, 132.6, 129.5, 129.4, 118.4, 117.1, 107.3, 106.1, 86.4, 64.8, 62.2, 62.1, 60.9, 59.2, 54.6, 20.6, 20.6, 15.1, 14.0, 13.9, 13.8;. MS (EI) 106 (100), 613 (45, M^+ − Cl)/615 (10). Anal. Calcd for $C_{32}H_{34}Cl_2O_{10}$: C 59.17, H 5.27. Found: C 59.00, H 5.22.

Triethyl 3,7-Dichloro-1-ethoxy-3,5-bis(4-methoxyphenoxy)-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene-2,4,6-tricarboxylate (7c). Colorless oil; IR υ (cm^{-1}) 1736, 1725, 1612, 1507; ^{1}H NMR δ (ppm) 7.40 (d, J = 9.1 Hz, 2H), 6.89 (d, J = 9.0 Hz, 2H), 6.88 (d, J = 9.0 Hz, 2H), 6.69 (d, J = 9.1 Hz, 2H), 4.38−4.41 (m, 1H), 4.32−4.36 (m, 2H), 4.24−4.28 (m, 1H), 4.07 (q, J = 7.1 Hz, 4H), 3.78 (s, 3H), 3.73 (s, 3H), 1.37 (t, J = 7.0 Hz, 3H), 1.36 (t, J = 7.0 Hz, 3H), 1.28 (t, J = 7.0 Hz, 3H), 1.11 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ (ppm) 162.1, 162.0, 160.2, 155.9, 155.6, 151.9, 148.3, 148.2, 137.8, 120.0, 118.1 114.2, 114.0, 107.3, 106.4, 86.7, 64.7, 62.2, 62.1, 61.0, 59.1, 55.6, 55.5, 54.8, 15.1, 14.0, 13.9, 13.8. HRMS (FAB) calcd for $C_{32}H_{35}Cl_2O_{12}$ 681.1500 (M + 1), found 681.1520.

Triethyl 3,7-Dichloro-1-ethoxy-3,5-bis(4-fluorophenoxy)-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene-2,4,6-tricarboxylate (7d). Colorless crystals; mp 83−84 °C; IR υ (cm^{-1}) 1745, 1735, 1721, 1614, 1505; ^{1}H NMR δ (ppm) 7.39−7.42 (m, 2H), 6.88−6.92 (m, 4H), 4.37−4.41 (m, 1H), 4.33−4.36 (m, 2H), 4.25−4.27 (m, 1H), 4.05 (m, 4H), 1.37 (t, J 7.1, 6H), 1.29 (t, J 7.0, 3H), 1.09 (t, J 7.1, 3H); ^{13}C NMR δ (ppm) 161.8, 159.9, 159.8, 158.0, 157.9, 152.2, 150.4, 150.2, 137.3, 120.1, 120.0, 118.4, 118.3, 115.7, 115.6, 115.5, 115.4, 107.4, 106.1, 86.4, 64.9, 62.4, 62.3, 61.1, 58.8, 55.8, 54.9, 15.0, 14.0, 13.9, 13.8; MS (EI) 112 (100), 621 (25, M^+ − Cl)/623 (10). Anal. Calcd for $C_{30}H_{28}Cl_2F_2O_{10}$: C 54.81, H 4.29. Found: C 54.86, H 4.55.

Triethyl 3,7-Dichloro-1-ethoxy-3,5-bis(4-chlorophenoxy)-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene-2,4,6-tricarboxylate (7e). Colorless crystals; mp 126−128 °C; IR υ (cm^{-1}) 1747, 1736, 1723, 1622, 1489; ^{1}H NMR δ (ppm) 7.38 (d, J = 8.8 Hz, 2H), 7.29 (d, J = 8.8 Hz, 2H), 7.15 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 4.39−4.43 (m, 1H), 4.33−4.38 (m, 2H), 4.24−4.27 (m, 1H), 4.05 (q, J = 7.4 Hz, 4H), 1.37 (t, J = 7.1 Hz, 6H), 1.30 (t, J = 7.0 Hz, 3H), 1.07 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ (ppm) 161.7, 159.8, 152.9, 152.8, 152.3, 137.2, 129.1, 129.0, 128.9, 128.5, 119.7 118.5, 107.5, 105.8, 86.2, 64.9, 62.4, 62.3, 61.1, 58.7, 54.8, 15.0, 14.0, 13.9, 13.8; MS (EI) 128 (100), 653 (15, M^+ − 1)/655 (17). Anal. Calcd for $C_{30}H_{28}Cl_4O_{10}$: C 52.19, H 4.09. Found: C 52.67, H 4.03.

Triethyl 3,7-Dichloro-1-ethoxy-3,5-bis(4-bromophenoxy)-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene-2,4,6-tricarboxylate (7f). Colorless crystals; mp 129−130 °C; IR υ (cm^{-1}) 1746, 1736, 1723, 1624, 1486; ^{1}H NMR δ (ppm) 7.44 (d, J = 9.0 Hz, 2H), 7.33 (d, J = 9.0 Hz, 2H), 7.30 (d, J = 9.0 Hz, 2H), 6.80 (d, J = 8.9 Hz, 2H), 4.39−4.42 (m,1H), 4.33−4.37 (m, 2H), 4.23−4.26 (m, 1H), 4.06 (q, J = 7.3 Hz, 4H), 1.37 (t, J = 7.1 Hz, 6H), 1.30 (t, J = 7.0 Hz, 3H), 1.07 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ (ppm) 161.7, 159.8, 153.5, 153.4, 152.3, 137.2, 132.1, 132.0, 120.0, 119.0 116.5, 116.1, 107.5, 105.8, 86.1, 65.0, 62.5, 62.4, 61.2, 14.5, 14.0, 13.9, 13.8. MS (EI) 49 (100), 172 (75)/174 (70), 741 (6, M^+ − Cl)/743 (12)/745 (8). Anal. Calcd for $C_{30}H_{28}Br_2Cl_2O_{10}$: C 46.24, H 3.62. Found: C 46.56, H 3.81.

Trimethyl 3,7-Dichloro-1-methoxy-3,5-bis(2,4-dichlorophenoxy)-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene-2,4,6-tricarboxylate (7g). Colorless crystals; mp 175−176 °C; IR υ (cm^{-1}) 1741, 1732, 1615, 1480; ^{1}H NMR δ (ppm) 8.05 (d, J = 8.6 Hz, 1H), 7.34 (m, 3H), 7.06 (d, J = 9.0 Hz, 1H), 7.02 (dd, J = 9.0 and 2.2 Hz, 1H), 4.01 (s, 3H), 3.90 (s, 6H), 3.54 (s, 3H); ^{13}C NMR δ (ppm) 162.0, 159.6, 153.2, 149.3, 148.3, 135.8, 130.2, 129.8, 129.1, 128.8, 127.8, 127.4, 125.8, 125.2, 124.0, 118.4, 117.9, 108.0, 106.2, 85.6, 60.4, 59.2, 56.3, 53.3, 51.9; MS (EI) 350 (78)/352 (70), 539 (48)/541 (100)/543 (50), 665 (5, M^+ − Cl)/667 (7)/669 (7)/671(6). Anal. Calcd for $C_{26}H_{18}Cl_6O_{10}$: C 44.41, H 2.58. Found: C 44.60, H 2.90.

Trimethyl 3,7-Dichloro-1-methoxy-3,5-bis(4-dichloro-3,5-dimethylphenoxy)-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene-2,4,6-tricarboxylate (7h). Mp 189−190 °C; IR υ (cm^{-1}) 1744, 1734, 1726, 1621, 1591, 1470; ^{1}H NMR δ (ppm) 7.22 (s, 2H), 6.52 (s, 2H), 3.88 (s, 6H), 3.84 (s, 3H), 3.65 (s, 3H), 2.40 (s, 6H), 2.26 (s, 6H); ^{13}C NMR δ (ppm) 162.5, 162.4, 160.4, 151.7, 151.6, 151.5, 137.4, 137.0, 129.7, 129.2, 118.3, 117.0, 107.8 105.7, 86.0, 59.5, 55.9, 54.3, 53.1, 53.0, 52.0, 20.9, 20.4; MS-EI 343 (35)/345 (57)/347 (10), 533 (100)/535(40)/537(10), 653 (10, M^+ − Cl)/ 655 (6)/657 (8). Anal. Calcd for $C_{30}H_{28}Cl_4O_{10}$: C 52.20, H 4.09. Found: C 52.54, H 4.30.

Diethyl 2-Phenoxycarbonylmaleate (14a). Colorless oil; IR υ (cm^{-1}) 1732, 1716, 1639, 1490; ^{1}H NMR δ (ppm) 7.33 (t, J = 8.3 Hz, 2H), 7.11 (t, J = 7.4 Hz, 1H), 6.99 (d, J = 7.9 Hz, 2H), 6.55 (s, 1H), 4.26 (q, J = 7.1 Hz, 2H), 4.17 (q, J = 7.1 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H), 1.21 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ (ppm) 183.1, 167.2, 165.0, 163.0, 161.8, 130.3, 129.7, 126.5, 123.9, 120.8, 117.2, 116.5, 100.6, 63.0, 61.3, 13.9, 13.8; MS (EI) 77 (95), 95 (100), 191 (60), 293 (20%, M + 1); HRMS (FAB) calcd for $C_{15}H_{17}O_6$ (M + 1) 293.1020, found 293.1023.

Diethyl 2-(4-Chlorophenoxycarbonyl)maleate (14e). Colorless oil; IR υ (cm^{-1}) 1732, 1714, 1637, 1590, 1487.^{1}H NMR δ (ppm) 7.28 (d, J = 8.9 Hz, 2H), 6.94 (d, J = 8.9 Hz, 2H), 6.63 (s, 1H), 4.31 (q, J = 7.1 Hz, 2H), 4.19 (q, J = 7.1 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H), 1.23 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ (ppm) 182.5, 162.7, 161.7, 154.8, 151.8, 130.5, 129.7, 128.9, 122.2, 118.7, 117.7, 101.3, 63.1, 61.5, 14.0, 13.9; HRMS (FAB) calcd for $C_{15}H_{16}ClO_6$ (M + 1) 327.0630, found 327.0626.

Diethyl 2-(4-Bromophenoxycarbonyl)maleate (14f). Colorless oil; IR υ (cm^{-1}) 1732, 1713, 1639, 1582, 1483; ^{1}H NMR δ (ppm) 7.43 (d, J = 8.9 Hz, 2H), 6.89 (d, J = 8.9 Hz, 2H), 6.64 (s, 1H), 4.31 (q, J = 7.1 Hz, 2H), 4.19 (q, J = 7.1 Hz 2H), 1.32 (t, J = 7.1 Hz, 3H), 1.22 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ (ppm) 182.5, 162.7, 161.7, 155.3, 151.7, 133.4, 118.8, 118.1, 116.3, 63.2, 61.5, 14.0, 13.9; MS (EI) 69 (100), 269 (30)/271 (28), 371 (10%, M + 1)/373 (10); HRMS (FAB) calcd for $C_{15}H_{16}BrO_6$ (M + 1) 371.0125, found 371.0129.

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Supporting Information Available: Experimental procedures for preparation of**1a**−**h** and **2a**−**h**; full characterization for **1b**−**h**; IR data of **2a**−**h**; ^{1}H NMR and ^{13}C NMR spectrum of **6a**−**h** and **7a**−**h**; ORTEP drawings of single-crystal structures of compound **6h** and **7f**; and single-crystal data of **6h** and **7f** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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