Supporting Information

Synthesis and Low Temperature Spectroscopic Observation of 1,3,5-Trioxane-2,4,6-Trione: The Cyclic Trimer of Carbon Dioxide.

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Discussion of Preparations of Compounds **2a** and **2b**.

A procedure for preparations of compound **2a** (Scheme 2, Route A) and **2b** (Scheme 3, Route A) is reported in a patent.[1] Repeated attempts to reproduce this synthesis of compounds **2a** and **2b** by Route A yielded no product. The procedure indicated in Scheme 2, Route B and described in the Experimental Section produced compound **2a** as supported by ^{1}H NMR, ^{13}C NMR, IR, UV, HMRS and elemental analysis entered above. The procedure in Reference 1 characterizes compound **2a** as a broad melting solid (Mp 54-62 °C) with supporting spectroscopic observation consisting of an observed disappearance of the **3a** reactant via its ^{1}H NMR resonance at 4.6 ppm assigned to the acetal proton and a fragment in the mass spectrum at m/e 70 ascribed to a dimethyl ketene decomposition product. No other reports of synthesis of either **2a** or **2b** are reported in the literature to the best of the authors' knowledge. As our synthesis of the hexamethyl-triolefin-trioxane **2a** by Route B was successful and its characterization differs from that reported in the referenced patent,[1] a brief discussion is given here with data provided in the Supporting Information. The ^{1}H NMR and ^{13}CNMR spectra of **2a** are presented in Figs. S1 and S2 respectively, and the observed chemical shifts are consistent with structural assignments for the resonances indicated in the Experimental Section. The IR spectrum of **2a** (Fig. S3) is particularly distinctive, and the 1726 cm^{-1} band is characteristic of the C=C bond in the ketene acetal functional group.[2-4] That this is not a carbonyl band is further confirmed by the absence of a carbonyl resonance at 195-220 ppm in the ^{13}C NMR spectrum. A vinyl ether functional group is just within the non-vacuum UV, and the spectrum of **2a** was obtained from a series of acetonitrile solutions over the range of 195 to 300 nm (Fig. S4). The spectrum maximum is at 210 nm with a molar extinction coefficient of 15,700 L/mole·cm. This result is in reasonably good agreement with that reported for the monofunctional methyl-vinylether (gas phase, λ_{max} =

211 nm ($\varepsilon = 2.2 \times 10^3$ L/mole·cm).[5] Finally, the issue of melting point of **2a** was of puzzling interest. It was reported to be a solid with a broad 54-62 °C melting point.[1] From our synthesis, this compound is a liquid. When slowly cooled to -20 °C or below, the compound appeared to form a glass rather than a polycrystalline mass. To observe its melting behavior, differential scanning calorimetry (DSC) was conducted over a -25 to 20 °C range at a 10 °C/min scan rate. Two heating cycles are depicted in Fig. S5. It appears to be a second order transition with maximum at -4 °C with an apparent melting range of about 15-20 °C. Such resistance to crystalizing from a compound with the degree of symmetry in structure **2a** is unexpected. It was conjectured that its six-membered ring structure might equilibrate readily between boat and chair conformations of comparable energy and possibly resist crystalline packing. Attempts to observe two such conformers by the temperature dependence of the methyl resonances in the ^{1}H NMR spectrum at -80 °C did not result in a change of the resonance line shape from that in Fig. S1.

References:

1. Boudakian, M. M.; Lapkin, M. *Substituted Trioxanes*. US Patent 3,560,526, 1971.
2. Mukaiyama, T.; Fujisawa, T.; Nohira, H.; Hyugaji, T. *J. Org. Chem.* **1962**, *27*, 3337-3340.
3. Graziano, M. L.; Scarpati, R. *J. Chem. Soc. Perkin Trans. I*, **1985**, 289-294.
4. Crevello, J. V.; Malik, R.; Lai, Y.-L. *J. Poly. Sci. A*, **1996**, *34*, 3091-3102.
5. Plankaert, A. A.; Doucet, J.; Sandorfy, C. *J. Chem. Phys*. **1974**, *60*, 4846-4853.

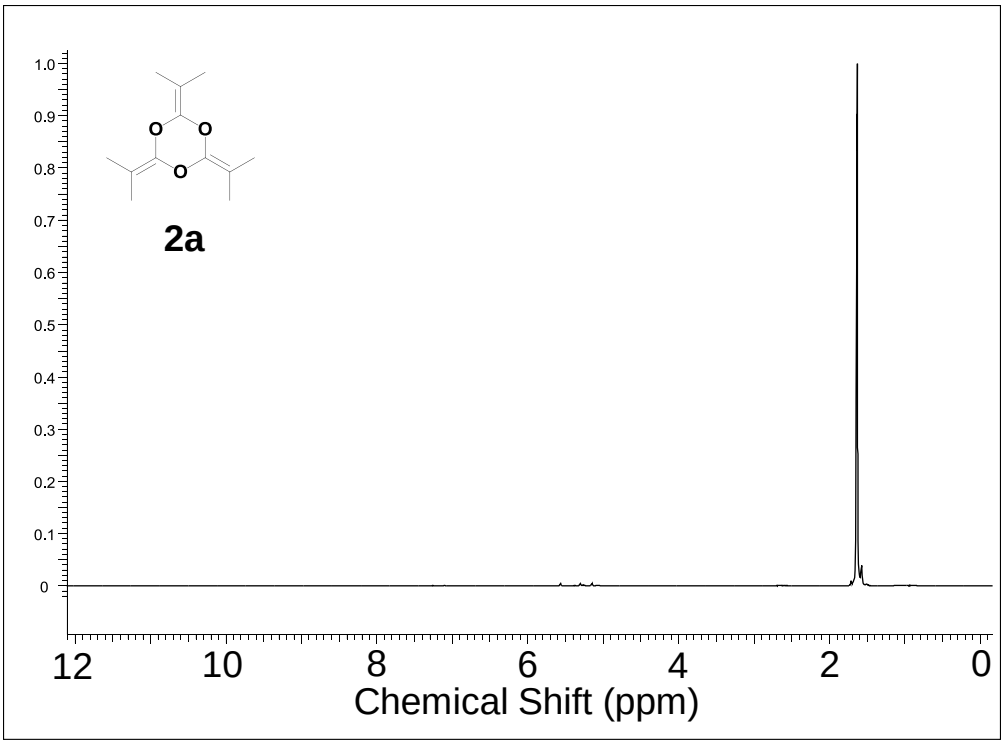

Fig. S1. ^{1}H NMR spectrum of triolefin-trioxane **2a** ($CDCl_3$, 300 Mhz).

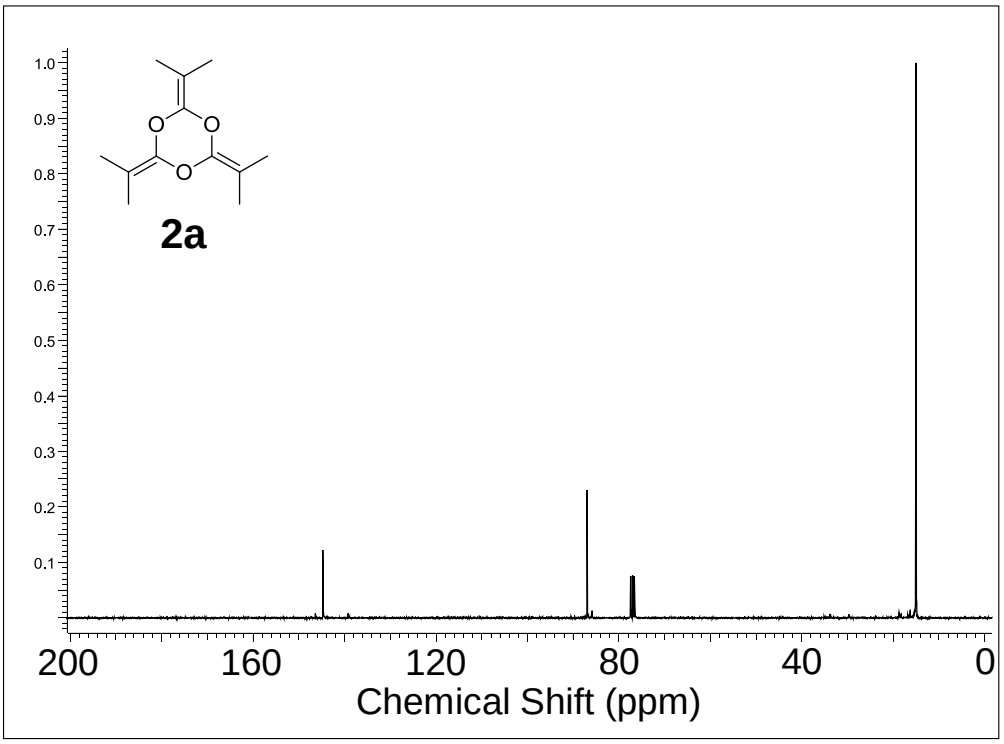

Fig. S2. ^{13}C NMR spectrum of triolefin-trioxane **2a** ($CDCl_3$, 75 Mhz).

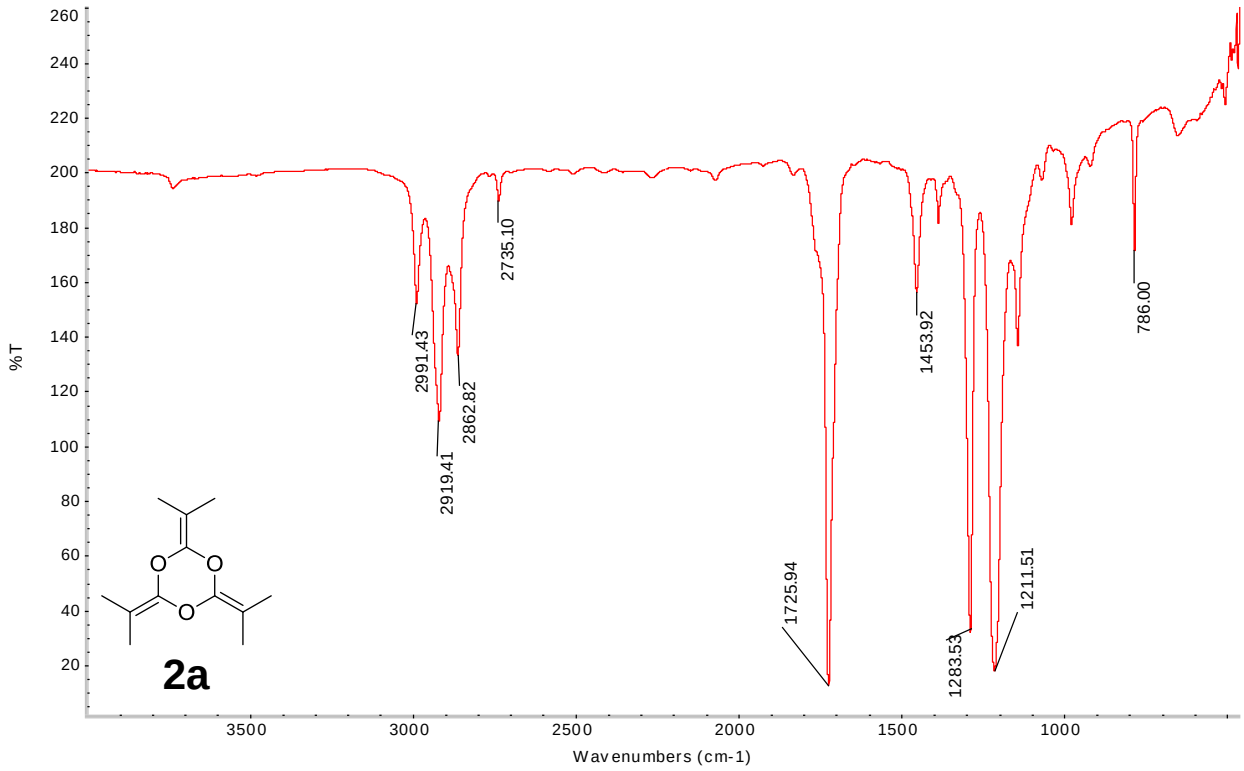

Fig. S3. Transmission FTIR spectrum of triolefin-trioxane **2a** liquid film supported on NaCl.

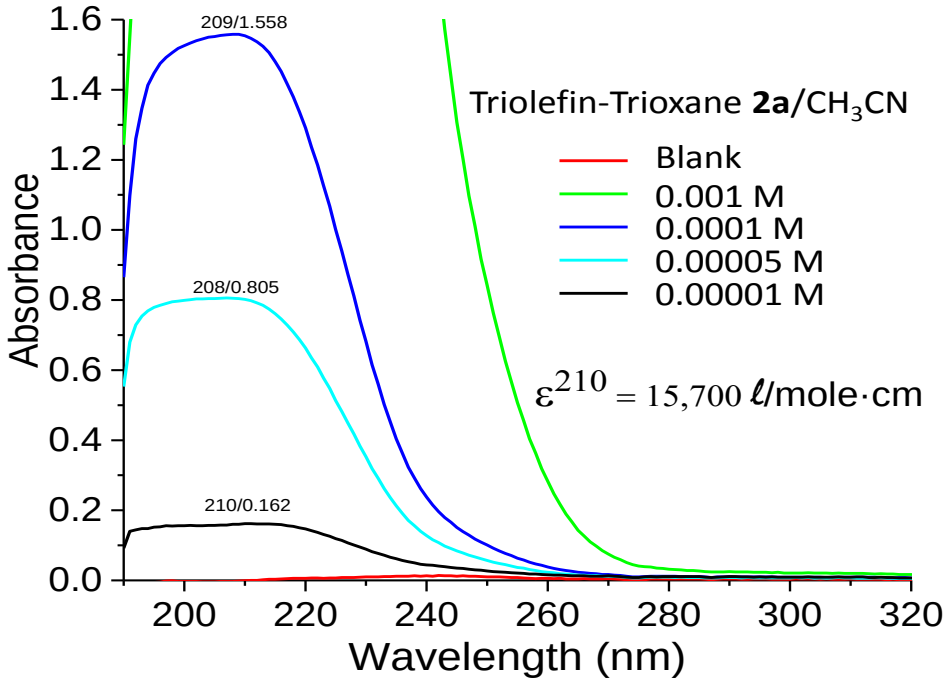

Fig. S4. UV spectrum of triolefin-trioxane **2a** in acetonitrile at various concentrations.

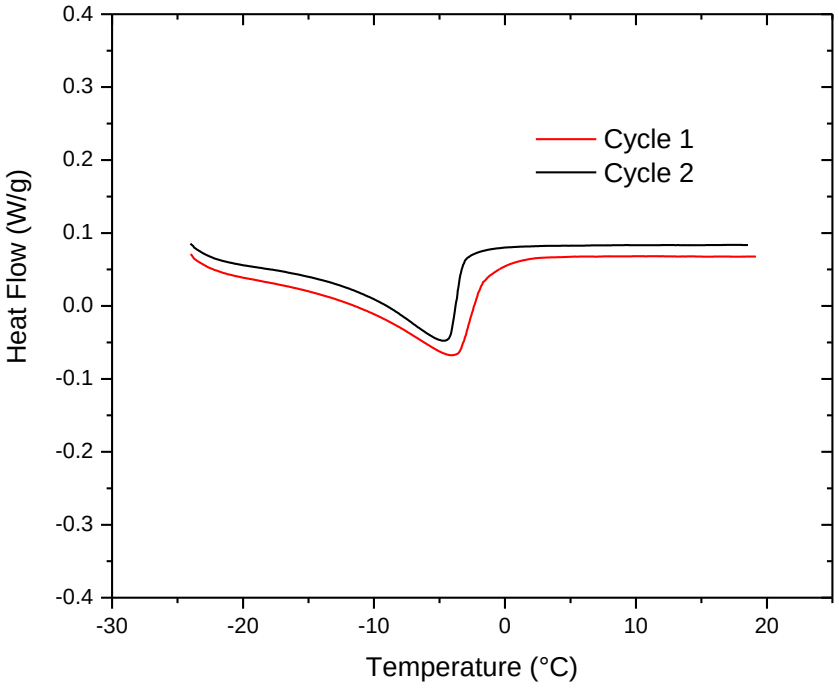

Fig. S5. DSC thermogram of triolefin-trioxane **2a** (two successive heating cycles, endotherm maximum -4 °C).

X-Ray Crystallography

Table S1. Crystal data and structure refinement for **2,4,6-tris(chloromethyl)-1,3,5-trioxane, 3b**

Identification code	SNOW001	
Empirical formula	$C_6H_9Cl_3O_3$	
Formula weight	235.48	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 8.2204(14) Å	α= 90°.
	b = 8.6550(15) Å	β= 90.139(2)°.
	c = 13.295(2) Å	γ = 90°.
Volume	945.9(3) $Å^3$	
Z	4	
Density (calculated)	1.653 Mg/m^3	
Absorption coefficient	0.933 mm^{-1}	
F(000)	480	
Crystal size	0.74 x 0.21 x 0.12 mm^3	
Theta range for data collection	2.81 to 26.51°.	
Index ranges	-10<=h<=9, -10<=k<=10, -16<=l<=16	
Reflections collected	8454	
Independent reflections	1954 [R_{int} = 0.0259]	
Completeness to theta = 26.51°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8963 and 0.5452	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1954 / 0 / 103	
Goodness-of-fit on F^2	1.074	
Final R indices [I>2sigma(I)]	R_1 = 0.0247, wR_2 = 0.0601	
R indices (all data)	R_1 = 0.0276, wR_2 = 0.0630	
Largest diff. peak and hole	0.264 and -0.356 e.$Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	8406(1)	3667(1)	7172(1)	19(1)
C(2)	7102(2)	3567(2)	6472(1)	18(1)
O(3)	5849(1)	4604(1)	6751(1)	19(1)
C(4)	5282(2)	4220(2)	7729(1)	18(1)
O(5)	6583(1)	4330(1)	8429(1)	19(1)
C(6)	7835(2)	3293(2)	8149(1)	18(1)
C(7)	7696(2)	4073(2)	5454(1)	22(1)
Cl(8)	9123(1)	2708(1)	4973(1)	30(1)
C(9)	4024(1)	5376(1)	8055(1)	22(1)
Cl(10)	2277(1)	5237(1)	7263(1)	34(1)
C(11)	9261(1)	3498(1)	8851(1)	22(1)
Cl(12)	8717(1)	2936(1)	10096(1)	26(1)

Table S3. Bond lengths [Å] and angles [°] for **3b**.

O(1)-C(6)	1.4198(17)	O(1)-C(2)	1.4204(17)
C(2)-O(3)	1.4161(17)	C(2)-C(7)	1.506(2)
C(2)-H(2)	1.0000	O(3)-C(4)	1.4217(17)
C(4)-O(5)	1.4193(17)	C(4)-C(9)	1.5035(15)
C(4)-H(4)	1.0000	O(5)-C(6)	1.4160(17)
C(6)-C(11)	1.5069(15)	C(6)-H(6)	1.0000
C(7)-Cl(8)	1.7842(15)	C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900	C(9)-Cl(10)	1.7828
C(9)-H(9A)	0.9900	C(9)-H(9B)	0.9900
C(11)-Cl(12)	1.7842	C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900		

C(6)-O(1)-C(2)	109.53(11)	O(3)-C(2)-O(1)	109.80(11)
O(3)-C(2)-C(7)	106.78(11)	O(1)-C(2)-C(7)	108.97(12)
O(3)-C(2)-H(2)	110.4	O(1)-C(2)-H(2)	110.4
C(7)-C(2)-H(2)	110.4	C(2)-O(3)-C(4)	109.35(10)
O(5)-C(4)-O(3)	109.67(11)	O(5)-C(4)-C(9)	106.49(10)
O(3)-C(4)-C(9)	109.60(10)	O(5)-C(4)-H(4)	110.3
O(3)-C(4)-H(4)	110.3	C(9)-C(4)-H(4)	110.3
C(6)-O(5)-C(4)	109.39(10)	O(5)-C(6)-O(1)	109.80(11)
O(5)-C(6)-C(11)	109.11(10)	O(1)-C(6)-C(11)	106.31(10)
O(5)-C(6)-H(6)	110.5	O(1)-C(6)-H(6)	110.5
C(11)-C(6)-H(6)	110.5	C(2)-C(7)-Cl(8)	110.17(10)
C(2)-C(7)-H(7A)	109.6	Cl(8)-C(7)-H(7A)	109.6

Table S3 (continued). Bond lengths [Å] and angles [°] for **3b**.

C(2)-C(7)-H(7B)	109.6	Cl(8)-C(7)-H(7B)	109.6
H(7A)-C(7)-H(7B)	108.1	C(4)-C(9)-Cl(10)	109.78(6)
C(4)-C(9)-H(9A)	109.7	Cl(10)-C(9)-H(9A)	109.7
C(4)-C(9)-H(9B)	109.7	Cl(10)-C(9)-H(9B)	109.7
H(9A)-C(9)-H(9B)	108.2	C(6)-C(11)-Cl(12)	110.24(6)
C(6)-C(11)-H(11A)	109.6	Cl(12)-C(11)-H(11A)	109.6
C(6)-C(11)-H(11B)	109.6	Cl(12)-C(11)-H(11B)	109.6
H(11A)-C(11)-H(11B)	108.1		

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	16(1)	26(1)	15(1)	-2(1)	0(1)	0(1)
C(2)	16(1)	20(1)	17(1)	-2(1)	0(1)	0(1)
O(3)	17(1)	23(1)	15(1)	1(1)	2(1)	2(1)
C(4)	17(1)	22(1)	16(1)	1(1)	1(1)	-1(1)
O(5)	16(1)	23(1)	17(1)	-2(1)	-1(1)	3(1)
C(6)	18(1)	19(1)	17(1)	-1(1)	0(1)	1(1)
C(7)	22(1)	24(1)	19(1)	0(1)	4(1)	4(1)
Cl(8)	36(1)	34(1)	22(1)	0(1)	8(1)	12(1)
C(9)	19(1)	29(1)	19(1)	3(1)	2(1)	3(1)
Cl(10)	20(1)	54(1)	28(1)	4(1)	-2(1)	9(1)
C(11)	18(1)	29(1)	19(1)	-1(1)	0(1)	0(1)
Cl(12)	26(1)	35(1)	18(1)	-1(1)	-4(1)	0(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **3b**.

	x	y	z	U(eq)
H(2)	6675	2486	6441	21
H(4)	4814	3154	7733	22
H(6)	7433	2203	8170	22
H(7A)	8219	5100	5509	26
H(7B)	6763	4163	4985	26
H(9A)	4483	6432	8016	27
H(9B)	3711	5175	8762	27
H(11A)	9608	4594	8850	27
H(11B)	10185	2862	8616	27

Table S6. Torsion angles [°] for **3b**.

C(6)-O(1)-C(2)-O(3)	59.46(14)
C(6)-O(1)-C(2)-C(7)	176.09(11)
O(1)-C(2)-O(3)-C(4)	-59.65(14)
C(7)-C(2)-O(3)-C(4)	-177.65(11)
C(2)-O(3)-C(4)-O(5)	59.94(14)
C(2)-O(3)-C(4)-C(9)	176.51(10)
O(3)-C(4)-O(5)-C(6)	-59.98(14)
C(9)-C(4)-O(5)-C(6)	-178.49(10)
C(4)-O(5)-C(6)-O(1)	59.75(14)
C(4)-O(5)-C(6)-C(11)	175.89(10)
C(2)-O(1)-C(6)-O(5)	-59.47(14)
C(2)-O(1)-C(6)-C(11)	-177.36(9)
O(3)-C(2)-C(7)-Cl(8)	-173.49(9)
O(1)-C(2)-C(7)-Cl(8)	67.97(13)
O(5)-C(4)-C(9)-Cl(10)	-176.29(7)
O(3)-C(4)-C(9)-Cl(10)	65.15(10)
O(5)-C(6)-C(11)-Cl(12)	65.44(11)
O(1)-C(6)-C(11)-Cl(12)	-176.21(7)

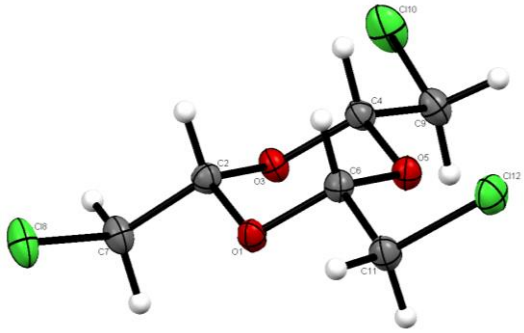

Fig. S6. Crystal structure of compound **3b** (displacement ellipsoid plot at 50% probability level).

Table S7. Crystal data and structure refinement for **2,4,6-tris(2-chloropropan-2-yl)-1,3,5-trioxane, 3a**

Identification code	SNOW002	
Empirical formula	$C_{12}H_{21}Cl_3O_3$	
Formula weight	319.64	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.5632(6) Å	α= 90°.
	b = 6.0365(4) Å	β= 91.120(2)°.
	c = 27.2812(17) Å	γ = 90°.
Volume	1574.60(17) $Å^3$	
Z	4	
Density (calculated)	1.348 Mg/m^3	
Absorption coefficient	0.580 mm^{-1}	
F(000)	672	
Crystal size	0.39 x 0.37 x 0.25 mm^3	
Theta range for data collection	1.49 to 26.47°.	
Index ranges	-11<=h<=11, -7<=k<=7, -32<=l<=34	
Reflections collected	14512	
Independent reflections	3238 [R_{int} = 0.0302]	
Completeness to theta = 26.47°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8686 and 0.8054	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3238 / 1 / 170	
Goodness-of-fit on F^2	1.066	
Final R indices [I>2sigma(I)]	R_1 = 0.0407, wR_2 = 0.1106	
R indices (all data)	R_1 = 0.0467, wR_2 = 0.1151	
Largest diff. peak and hole	1.102 and -0.823 e.$Å^{-3}$	

Table S8. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2 x\ 10^3$) for **3a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	4309(1)	9619(2)	8351(1)	18(1)
C(2)	4829(2)	8447(3)	8765(1)	18(1)
O(3)	3747(1)	8100(2)	9104(1)	19(1)
C(4)	2623(2)	6945(3)	8876(1)	18(1)
O(5)	2102(1)	8164(2)	8471(1)	19(1)
C(6)	3174(2)	8481(3)	8128(1)	17(1)
C(7)	6020(2)	9739(3)	9006(1)	21(1)
Cl(8)	5356(1)	12436(1)	9186(1)	32(1)
C(9)	7194(2)	10105(4)	8642(1)	30(1)
C(10)	6541(2)	8553(4)	9464(1)	29(1)
C(11)	1489(2)	6700(3)	9260(1)	21(1)
Cl(12)	107(1)	5060(1)	8967(1)	30(1)
C(13)	864(2)	8928(4)	9403(1)	26(1)
C(14)	2057(2)	5401(4)	9696(1)	31(1)
C(15)	2587(1)	9908(3)	7713(1)	19(1)
Cl(16)	3873(1)	9893(1)	7237(1)	30(1)
C(17)	2286(3)	12317(6)	7870(1)	20
C(18)	1249(3)	8831(5)	7492(1)	20
Cl'	1192(4)	8299(7)	7423(2)	42(2)
C(17')	2069(18)	12370(30)	7942(6)	20
C(18')	3710(20)	10210(40)	7362(7)	20

Table S9. Bond lengths [Å] and angles [°] for **3a**.

O(1)-C(6)	1.412(2)	O(1)-C(2)	1.414(2)
C(2)-O(3)	1.417(2)	C(2)-C(7)	1.520(3)
C(2)-H(2)	0.9800	O(3)-C(4)	1.415(2)
C(4)-O(5)	1.409(2)	C(4)-C(11)	1.531(3)
C(4)-H(4)	0.9800	O(5)-C(6)	1.415(2)
C(6)-C(15)	1.521(3)	C(6)-H(6)	0.9800
C(7)-C(10)	1.517(3)	C(7)-C(9)	1.530(3)
C(7)-Cl(8)	1.818(2)	C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600	C(9)-H(9C)	0.9600
C(10)-H(10A)	0.9600	C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600	C(11)-C(14)	1.516(3)
C(11)-C(13)	1.525(3)	C(11)-Cl(12)	1.824(2)
C(13)-H(13A)	0.9600	C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600	C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600	C(14)-H(14C)	0.9600

Table S9 continued. Bond lengths [Å] and angles [°] for **3a**.

C(15)-C(18')	1.46(2)	C(15)-C(17)	1.544(4)
C(15)-C(18)	1.547(3)	C(15)-C(17')	1.690(17)
C(15)-Cl(16)	1.8058(16)	C(15)-Cl'	1.8200
C(17)-H(17A)	0.9600	C(17)-H(17B)	0.9600
C(17)-H(17C)	0.9600	C(18)-H(18A)	0.9600
C(18)-H(18B)	0.9600	C(18)-H(18C)	0.9600
C(17')-H(17D)	0.9600	C(17')-H(17E)	0.9600
C(17')-H(17F)	0.9600	C(18')-H(18D)	0.9600
C(18')-H(18E)	0.9600	C(18')-H(18F)	0.9600
C(6)-O(1)-C(2)	110.80(14)	O(1)-C(2)-O(3)	110.24(14)
O(1)-C(2)-C(7)	109.76(15)	O(3)-C(2)-C(7)	110.07(15)
O(1)-C(2)-H(2)	108.9	O(3)-C(2)-H(2)	108.9
C(7)-C(2)-H(2)	108.9	C(4)-O(3)-C(2)	110.03(14)
O(5)-C(4)-O(3)	109.99(15)	O(5)-C(4)-C(11)	110.03(15)
O(3)-C(4)-C(11)	106.72(15)	O(5)-C(4)-H(4)	110.0
O(3)-C(4)-H(4)	110.0	C(11)-C(4)-H(4)	110.0
C(4)-O(5)-C(6)	109.78(14)	O(1)-C(6)-O(5)	110.02(14)
O(1)-C(6)-C(15)	108.29(14)	O(5)-C(6)-C(15)	107.88(13)
O(1)-C(6)-H(6)	110.2	O(5)-C(6)-H(6)	110.2
C(15)-C(6)-H(6)	110.2	C(10)-C(7)-C(2)	110.26(17)
C(10)-C(7)-C(9)	111.72(17)	C(2)-C(7)-C(9)	110.23(17)
C(10)-C(7)-Cl(8)	108.14(15)	C(2)-C(7)-Cl(8)	108.28(13)
C(9)-C(7)-Cl(8)	108.10(14)	C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5	H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5	H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5	C(7)-C(10)-H(10A)	109.5
C(7)-C(10)-H(10B)	109.5	H(10A)-C(10)-H(10B)	109.5
C(7)-C(10)-H(10C)	109.5	H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5	C(14)-C(11)-C(13)	113.10(17)
C(14)-C(11)-C(4)	109.86(17)	C(13)-C(11)-C(4)	112.11(17)
C(14)-C(11)-Cl(12)	107.98(15)	C(13)-C(11)-Cl(12)	107.85(14)
C(4)-C(11)-Cl(12)	105.57(13)	C(11)-C(13)-H(13A)	109.5
C(11)-C(13)-H(13B)	109.5	H(13A)-C(13)-H(13B)	109.5
C(11)-C(13)-H(13C)	109.5	H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5	C(11)-C(14)-H(14A)	109.5
C(11)-C(14)-H(14B)	109.5	H(14A)-C(14)-H(14B)	109.5
C(11)-C(14)-H(14C)	109.5	H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5	C(18')-C(15)-C(6)	106.9(9)
C(18')-C(15)-C(17)	102.0(8)	C(6)-C(15)-C(17)	113.31(19)
C(18')-C(15)-C(18)	114.1(9)	C(6)-C(15)-C(18)	110.01(17)
C(17)-C(15)-C(18)	110.24(18)	C(18')-C(15)-C(17')	110.9(10)
C(6)-C(15)-C(17')	109.3(6)	C(17)-C(15)-C(17')	8.9(6)
C(18)-C(15)-C(17')	105.5(7)	C(18')-C(15)-Cl(16)	8.7(8)
C(6)-C(15)-Cl(16)	106.60(9)	C(17)-C(15)-Cl(16)	109.70(14)
C(18)-C(15)-Cl(16)	106.70(15)	C(17')-C(15)-Cl(16)	118.6(5)

Table S9 continued. Bond lengths [Å] and angles [°] for **3a**.

C(18')-C(15)-Cl'	108.8(9)	C(6)-C(15)-Cl'	106.2(2)
C(17)-C(15)-Cl'	118.9(2)	C(18)-C(15)-Cl'	8.9(2)
C(17')-C(15)-Cl'	114.4(7)	Cl(16)-C(15)-Cl'	100.82(19)
C(15)-C(17)-H(17A)	109.5	C(15)-C(17)-H(17B)	109.5
C(15)-C(17)-H(17C)	109.5	C(15)-C(18)-H(18A)	109.5
C(15)-C(18)-H(18B)	109.5	C(15)-C(18)-H(18C)	109.5
C(15)-C(17')-H(17D)	109.5	C(15)-C(17')-H(17E)	109.5
H(17D)-C(17')-H(17E)	109.5	C(15)-C(17')-H(17F)	109.5
H(17D)-C(17')-H(17F)	109.5	H(17E)-C(17')-H(17F)	109.5
C(15)-C(18')-H(18D)	109.5	C(15)-C(18')-H(18E)	109.5
H(18D)-C(18')-H(18E)	109.5	C(15)-C(18')-H(18F)	109.5
H(18D)-C(18')-H(18F)	109.5	H(18E)-C(18')-H(18F)	109.5

Table S10. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	16(1)	22(1)	18(1)	4(1)	-3(1)	-2(1)
C(2)	17(1)	20(1)	18(1)	3(1)	0(1)	2(1)
O(3)	17(1)	23(1)	17(1)	0(1)	0(1)	-2(1)
C(4)	18(1)	17(1)	19(1)	1(1)	0(1)	0(1)
O(5)	15(1)	24(1)	18(1)	2(1)	0(1)	-1(1)
C(6)	15(1)	19(1)	17(1)	-1(1)	1(1)	-1(1)
C(7)	18(1)	20(1)	23(1)	1(1)	-2(1)	1(1)
Cl(8)	34(1)	22(1)	40(1)	-6(1)	-8(1)	1(1)
C(9)	19(1)	38(1)	31(1)	5(1)	-2(1)	-5(1)
C(10)	26(1)	34(1)	26(1)	4(1)	-9(1)	-1(1)
C(11)	19(1)	24(1)	20(1)	0(1)	2(1)	-4(1)
Cl(12)	24(1)	32(1)	33(1)	-2(1)	3(1)	-9(1)
C(13)	24(1)	28(1)	27(1)	-8(1)	6(1)	0(1)
C(14)	27(1)	40(1)	25(1)	10(1)	3(1)	-2(1)
C(15)	18(1)	21(1)	18(1)	1(1)	1(1)	-1(1)
Cl(16)	29(1)	37(1)	23(1)	5(1)	4(1)	0(1)

Table S11. Hydrogen coordinates ($x10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for **3a**.

	x	y	z	U(eq)
H(2)	5183	7006	8658	22
H(4)	2936	5481	8768	22
H(6)	3486	7050	8001	21
H(9A)	7581	8701	8551	44
H(9B)	7911	11005	8792	44
H(9C)	6825	10839	8355	44
H(10A)	6867	7102	9379	43
H(10B)	5792	8423	9692	43
H(10C)	7294	9381	9613	43
H(13A)	1579	9840	9550	40
H(13B)	130	8696	9633	40
H(13C)	489	9649	9116	40
H(14A)	2785	6236	9857	46
H(14B)	2427	4013	9585	46
H(14C)	1317	5129	9921	46
H(17A)	1609	12318	8125	30
H(17B)	1926	13135	7593	30
H(17C)	3135	12995	7988	30
H(18A)	527	8838	7732	30
H(18B)	1448	7332	7399	30
H(18C)	943	9654	7209	30
H(17D)	1074	12360	7981	30
H(17E)	2317	13535	7720	30
H(17F)	2523	12618	8254	30
H(18D)	4172	8815	7311	30
H(18E)	4372	11266	7489	30
H(18F)	3323	10731	7057	30

Table S12. Torsion angles [°] for **3a**.

C(6)-O(1)-C(2)-O(3)	-56.95(19)
C(6)-O(1)-C(2)-C(7)	-178.34(15)
O(1)-C(2)-O(3)-C(4)	57.35(19)
C(7)-C(2)-O(3)-C(4)	178.56(15)
C(2)-O(3)-C(4)-O(5)	-59.05(19)
C(2)-O(3)-C(4)-C(11)	-178.37(15)
O(3)-C(4)-O(5)-C(6)	59.79(19)
C(11)-C(4)-O(5)-C(6)	177.07(15)
C(2)-O(1)-C(6)-O(5)	57.70(19)
C(2)-O(1)-C(6)-C(15)	175.38(13)
C(4)-O(5)-C(6)-O(1)	-58.95(19)

Table S12 continued. Torsion angles [°] for **3a**.

C(4)-O(5)-C(6)-C(15)	-176.90(14)
O(1)-C(2)-C(7)-C(10)	177.34(16)
O(3)-C(2)-C(7)-C(10)	55.8(2)
O(1)-C(2)-C(7)-C(9)	-58.8(2)
O(3)-C(2)-C(7)-C(9)	179.65(16)
O(1)-C(2)-C(7)-Cl(8)	59.21(17)
O(3)-C(2)-C(7)-Cl(8)	-62.29(17)
O(5)-C(4)-C(11)-C(14)	-179.67(17)
O(3)-C(4)-C(11)-C(14)	-60.4(2)
O(5)-C(4)-C(11)-C(13)	-53.0(2)
O(3)-C(4)-C(11)-C(13)	66.3(2)
O(5)-C(4)-C(11)-Cl(12)	64.14(17)
O(3)-C(4)-C(11)-Cl(12)	-176.56(12)
O(1)-C(6)-C(15)-C(18')	61.2(9)
O(5)-C(6)-C(15)-C(18')	-179.7(9)
O(1)-C(6)-C(15)-C(17)	-50.42(19)
O(5)-C(6)-C(15)-C(17)	68.63(19)
O(1)-C(6)-C(15)-C(18)	-174.33(16)
O(5)-C(6)-C(15)-C(18)	-55.3(2)
O(1)-C(6)-C(15)-C(17')	-58.9(6)
O(5)-C(6)-C(15)-C(17')	60.1(6)
O(1)-C(6)-C(15)-Cl(16)	70.34(16)
O(5)-C(6)-C(15)-Cl(16)	-170.61(12)
O(1)-C(6)-C(15)-Cl'	177.2(2)
O(5)-C(6)-C(15)-Cl'	-63.7(2)

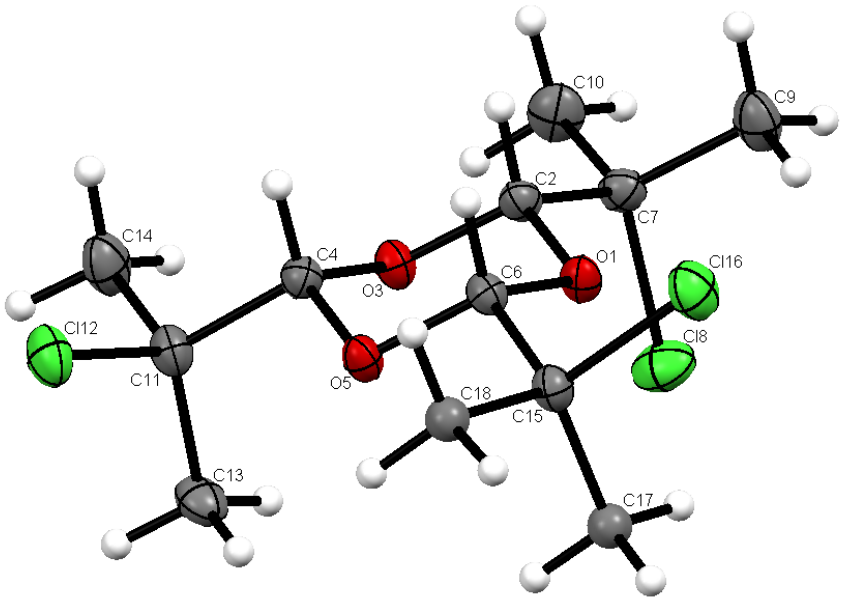

Fig. S7. Crystal structure of compound **3a** (displacement ellipsoid plot at 50% probability level).