Halogenation of Fluorinated 1,3,5-Triketones

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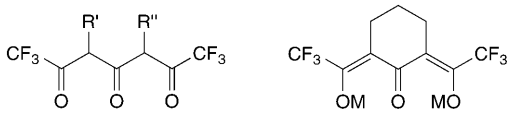
The behavior of linear and cyclic fluorinated 1,3,5-triketones and their metal derivatives towards common halogenating agents was examined, and optimal reaction conditions for the straightforward synthesis of mono-, di-, and tetrahalogenated products were found (*Schemes 1–3*). An aromatization through a double HBr elimination from an α,α'-dibrominated cyclohexanone was shown to be a promising synthetic route to 1,1′-(2-hydroxy-1,3-phenylene)bis[2,2,2-trifluoroethanones] (=2,6-bis(trifluoroacetyl)phenols; *Scheme 4*). Additionally, the 1,3,5-triketones prepared add readily H_2O or alcohols to produce novel bridged 2,6-dihydroxypyran-4-ones (*Scheme 2*). The structure of the obtained compounds **6a** and **7a** was confirmed by X-ray structure analysis.

Introduction. – Due to their polyfunctional nature and high reactivity, 1,3,5-triketones are versatile reaction partners in a variety of organic transformations [1], as well as valuable tridentate ligands in coordination chemistry [2]. The methods of preparation and synthetic applications are well documented [1–3]. However, little effort has been devoted to F-containing 1,3,5-triketones, although incorporation of F-atoms or fluorinated groups into organic compounds is known to induce dramatic consequences on their chemical reactivity, physical properties, and biological activity [4]. An excellent example of such a 'transformation' are fluorinated 1,3-dicarbonyl compounds. In this case, a significant change of the electron-density distribution results in peculiar tautomeric features (keto–enol, enol–enol) and in an unexpected behavior in the course of chemical reactions, when compared to nonfluorinated analogs [5]. Continuing our long-standing interest in the chemistry of fluorinated 1,3-diketones and 1,3-keto esters [6], we have started a research program dealing with related 1,3,5-triketones [7]. Given the synthetic importance of fluorinated 1,3-dicarbonyl compounds bearing an additional halogen atom in position 2 [8][9], we have explored reactions of bis(trifluoromethyl) triketones **1** and metal derivatives **2** with halogenating agents. The results obtained are presented herein.

Results and Discussion. – In spite of advances in the halogenation of 3-(polyfluoroalkyl)-substituted 1,3-keto esters [9], only scattered reports concerning related reactions of 1,3-diketones were published [10]. Elemental Br_2 was found to be unsuitable for selective bromination of 2-(trifluoroacetyl)cyclohexanone [10f][11]. On the other hand, *N*-bromosuccinimide (NBS) was efficient for the α-bromination of 4,4,4-tri-



1[1]) **2**

R' = R'' = H
R' + R'' = $(CH_2)_2$,
R' + R'' = $(CH_2)_3$,
R' + R'' = CH_2-CH(^{t}Bu)-CH_2

M = Li, Cu/2

fluoro-1-phenylbutane-1,3-dione [10d]. Therefore, it was reasonable to employ this reagent for our initial experiments.

Treatment of noncyclic 1,3,5-triketone **1a** with a 4-fold excess of NBS in $CHCl_3$ resulted in a complete bromination of both methylene moieties to afford **3** in a virtually quantitative yield (*Scheme 1*, *Entry 1*). Reactions of cyclohexanone derivative **1b** with 2 equiv. of NBS in CH_2Cl_2 and $CHCl_3$ proceeded smoothly to give 2,4-dibrominated 1,3,5-triketone **4a** as a mixture of *cis*- and *trans*-isomers (*Scheme 1*, *Entry 2*).

Attempts to convert **1a** with elemental Br_2 furnished only complex mixtures of several products – whatever molar amount of Br_2 was used (*Entry 3*). Tetrabrominated triketone **3** could be detected by ^{19}F-NMR spectroscopy in any case (δ(F) -67.2), but its yields were not satisfactory. By contrast, α,α'-dibromination of **1b** could be performed successfully with 2 equiv. of Br_2 in anhydrous $CHCl_3$ – similarly to the bromination of diethyl 2-oxocyclohexane-1,3-dicarboxylate [12]. The reaction (*Scheme 1*, *Entry 4*) proceeded with marked stereoselectivity in comparison to the brominations by NBS (*Entry 2*), the exclusive formation of *cis*-**4a** being observed (^{19}F-NMR monitoring of the reaction mixture). Use of the bis(lithium enolate) **2a** instead of the corresponding 1,3,5-triketone **1b** in this reaction appeared to be more convenient. In this case, evolution of gaseous HBr (*Entries 3* and *4*) did not take place, the only by-product was LiBr, and simple evaporation of the volatile materials allowed to isolate *cis*-**4a** in fair yield and purity (*Scheme 1*, *Entry 5*)

Chlorination of **1b** was also studied. Upon treatment with elemental Cl_2 or refluxing in SO_2Cl_2, α,α'-dichlorination was achieved (*Scheme 1*, *Entries 6* and *7*). Both transformations proceeded with similar stereoselectivity, the *cis*-**4b** being the predominant isomer. Noteworthy, in the case of SO_2Cl_2, the chemoselectivity can be directed easily. Carried out with **1b** in CH_2Cl_2 at room temperature, the reaction produced the mono-chlorinated 1,3,5-triketone **5b** in quantitative yield (*Scheme 1*, *Entry 8*). In contrast, the bromination of **1b** with 1 equiv. of Br_2 was not selective yielding both the monobrominated product **5a** and the dibromo derivative **4a** in a ratio of 81:10 (*Scheme 1*, *Entry 9*). I-Containing reagents were investigated to no avail. The 1,3,5-triketone **1b** and I_2 failed to react, and in the reactions with IBr and ICl, only intractable reaction mixtures were formed.

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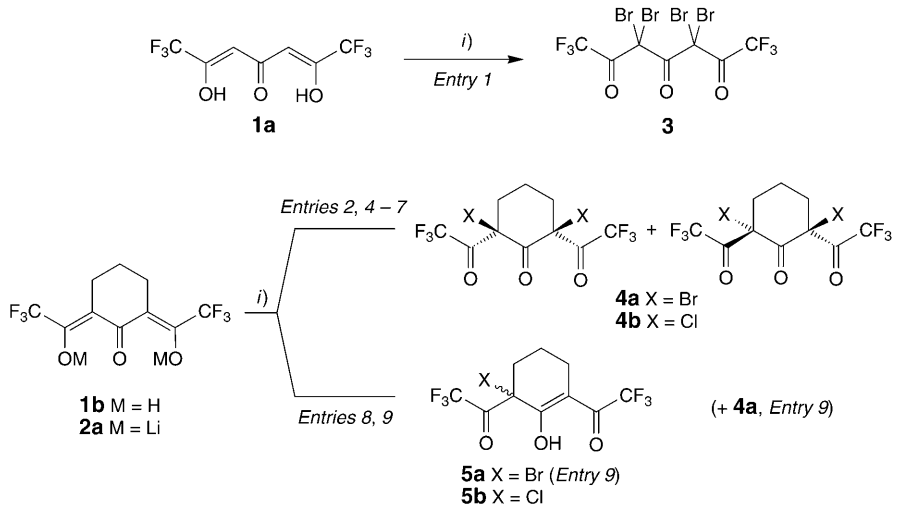
[1]) In the *General Part*, 1,3,5-triketones **1** are depicted as their major *U*-bis-enol tautomeric form [7].

Scheme 1



Entry	Substrate	*i)*			Product	Yield [%][a])
		Reagent	Solvent	Reaction temp.		
1	**1a**	NBS (4 equiv.)	$CHCl_3$	r.t.	**3**	81 (100)
2	**1b**	NBS (2 equiv.)	$CHCl_3$ or CH_2Cl_2	r.t.	**4a**, *cis*/*trans* 40:60	(100)
3	**1a**	Br_2 (1, 2 or 4 equiv.)	$CHCl_3$	r.t.	mixture	
4	**1b**	Br_2 (2 equiv.)	$CHCl_3$	r.t.	**4a**, *cis*/*trans* 100:0	83 (100)
5	**2a**	Br_2 (2 equiv.)	$CHCl_3$	r.t.	**4a**, *cis*/*trans* 100:0	74 (100)
6	**1b**	Cl_2 (2 equiv.)	$CHCl_3$	–196° → r.t.	**4b**, *cis*/*trans* 82:18	(100)
7	**1b**	SO_2Cl_2 (excess)		reflux	**4b**, *cis*/*trans* 82:18	97 (100)
8	**1b**	SO_2Cl_2 (2 equiv.)	CH_2Cl_2	r.t.	**5b**	97 (100)
9	**1b**	Br_2 (1 equiv.)	$CHCl_3$	r.t.	**5a**, *cis*-**4a**	(81, 10)

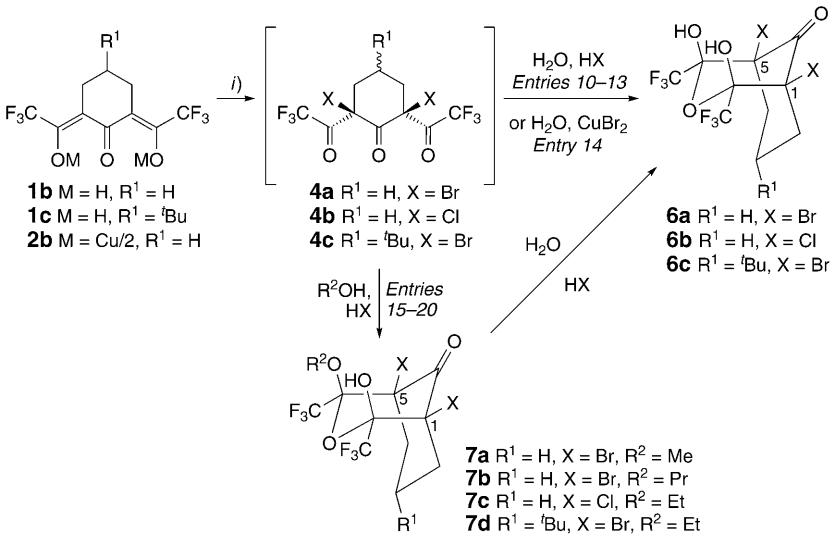
[a]) Isolated yield. In parentheses, virtual yield as determined by ^{19}F-NMR spectroscopy.

In spite of the high electrophilicity of the terminal carbonyl groups (note, four or five halogen atoms are in α positions[2]), pure **3** and *cis*-**4a** are stable, nonhygroscopic substances and do not undergo any detectable hydration even after exposure for several days in an open flask, as confirmed by NMR spectroscopy. After dissolving in wet $CHCl_3$ and concentration of the solution, *cis*-**4a** remained unchanged, too. In this context, the result obtained from the repeated reaction of cyclohexanone **1b** with 2 equiv. of Br_2 seemed to be somewhat surprising. Instead of the expected **4a**, the bridged pyran-4-one **6a** was isolated in 49% yield after evaporation of the reaction mixture without vacuum (*Scheme 2*, *Entry 10*). From the structural point of view, compound **6a** can be considered as a cyclic hydrate of triketone *cis*-**4a** (related fluorinated cyclic/bridged compounds are described in [14]). Our initial assumption was that the solvent $CHCl_3$ was not dry enough, causing the hydration and cyclization of intermediary *cis*-**4a** already in the reaction vessel. However, during the reaction both in $CHCl_3$

[2]) The tendency of the highly halogenated ketones to add H_2O is well known [13], with hexafluoroacetone [13c] and methyl trifluoropyruvate (=methyl 3,3,3-trifluoro-2-oxopropanoate) [13d] as excellent examples.

distilled from P_2O_5 and in $CHCl_3$ of commercial quality (*Scheme 2*, *Entries 10* and *11*), only *cis*-**4a** was detected in the reaction mixture by ^{19}F-NMR spectroscopy (δ(F) −69.7). Its transformation to **6a** took place in both experiments *only on the final evaporation of the reaction mixture under air*. This fact suggests strongly that air moisture is responsible for the hydration step in $CHCl_3$ solution saturated by HBr, a by-product of the double bromination. Compound **4b** obtained by using either Cl_2 or SO_2Cl_2 behaves the same way, furnishing the pyran-4-one **6b** in 71 and 77% yield from **1b**, respectively (*Scheme 2*, *Entries 12* and *13*). The copper(II) complex **2b** appeared to be also reactive under the conditions described, giving rise to the corresponding bridged 3,5-dibromopyran-4-one **6a** in 83% yield, with $CuBr_2$ as by-product (S*cheme 2*, *Entry 14*). All the reactions (*Entries 10–14*) occur highly regioselectively, only *one* diastereoisomer could be observed, within the limits of NMR detection.

Scheme 2



Entry	Substrate	*i*)			Product	Isolated
		Reagent(s)	Solvent	Reaction temp.		yield [%]
10	**1b**	Br_2 (2 equiv.)[a])	$CHCl_3$ (dry)	r.t.	**6a**	49
11	**1b**	Br_2 (2 equiv.)[a])	$CHCl_3$ (moist)	r.t.	**6a**	81
12	**1b**	Cl_2 (2 equiv.)[a])	$CHCl_3$	−196° → r.t.	**6b**	71
13	**1b**	SO_2Cl_2 (excess)[a])		reflux	**6b**	77
14	**2b**	Br_2 (2 equiv.)[a])	$CHCl_3$	r.t.	**6a**	83
15	**1b**	Br_2 (2 equiv.), then MeOH[b])	$CHCl_3$	r.t.	**7a**	28
16	**1b**	Br_2 (2 equiv.), then MeOH[c])	$CHCl_3$	r.t.	**7a**, **6a**	5, 15
17	**1b**	Br_2 (2 equiv.), then MeOH[a])	$CHCl_3$	r.t.	**6a**	39
18	**1b**	Br_2 (2 equiv.), then PrOH[a])	$CHCl_3$	r.t.	**6a**	58
19	**1b**	Cl_2 (2 equiv.)[a])[c])	$CHCl_3$, EtOH	−196° → r.t.	**7c**, **6b**	36, 10
20	**1c**	Br_2 (2 equiv.)[b])[c])	$CHCl_3$, EtOH	r.t.	**7d**, **6c**	5, 8

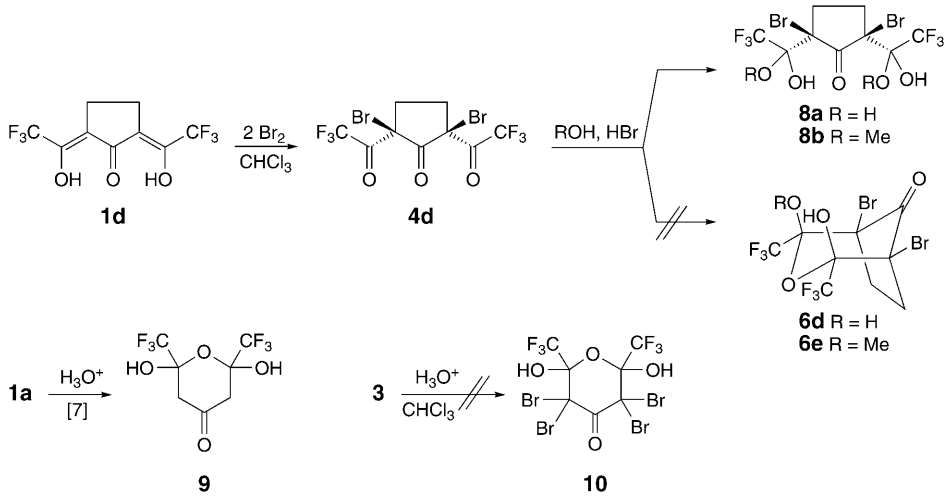
[a]) Workup: the mixture was evaporated without vacuum. [b]) Workup: the mixture was evaporated *in vacuo*. [c]) Workup: the crude product was recrystallized from moist toluene.

To pursue this point a little further, the dibromo derivative *cis*-**4a** (pre-generated from **1b** and Br_2) was treated *in situ* with an excess of dry MeOH. Subsequent concentration of the reaction mixture *in vacuo* gave the corresponding bridged adduct **7a** in 28% yield (*Scheme 2*, *Entry 15*). Interestingly, upon recrystallization of the crude product from wet toluene, both **6a** and **7a** could be isolated (*Scheme 2*, *Entry 16*). Formation of **6a** can be explained *via* a partial hydrolysis of **7a**. Indeed, for the MeOH and propan-1-ol adducts **7a**,**b** obtained *in situ* (established by ^{19}F-NMR spectroscopy), the complete conversion into **6a** was observed on exposure of the reaction mixture to atmospheric moisture (*Scheme 2*, *Entries 17* and *18*). It is worthy of mention that halogenation of cyclohexanones **1b**,**c** in the presence of EtOH also allowed to trap the intermediary *cis*-α,α'-dihalogenated compounds **4** (*Scheme 2*, *Entries 19* and *20*). Like the pyran-4-ones **6**, all the compounds **7** were formed as sole diastereoisomer.

Obviously, besides the enhanced electrophilicity of the terminal carbonyl moieties in **4**, there are two factors being critical for the cyclizations into compounds **6** or **7**. The first one is the necessity of an acid catalysis (HBr, HCl, or $CuBr_2$) for a double A_N sequence (addition of H_2O or alcohol followed by the pyran ring closure). The behavior of *cis*-**4a** in $CHCl_3$ solution acidified by 12% hydrochloric acid supports this last assumption. An equilibrium *cis*-**4a** $\rightleftharpoons$ **6a** was detected by ^{19}F-NMR spectroscopy (mol-ratio 64:36, respectively, after 16 h at room temperature). On the other hand, as mentioned, **3** and *cis*-**4a** did not add H_2O in a pure state. The second point is a sterical factor, where two requirements have to be fulfilled: *a*) a *cis*-structure of **4**, as well as *b*) the proximity of the terminal carbonyl groups in **4** are required for the successful cyclization. The importance of the second factor is clearly demonstrated by the reaction of cyclopentanone **1d** where the *monocyclic* bis(geminaldiol) derivative **8a** was formed as a sole product after the double bromination and hydration of the intermediary *cis*-**4d** (*Scheme 3*). Similarly, methanolysis of the reaction mixture resulted in an exclusive formation of *monocyclic* bis(hemi)ketal **8b** (*Scheme 3*). Additionally, no conversion was observed for the tetrabrominated compound **3** in a $CHCl_3$/aqueous HCl solution (*Scheme 3*), although transformation of starting **1a** into the corresponding 2,6-dihydroxypyran-4-one **9** was found to proceed smoothly (*Scheme 3*) [7][15]. There is little reason to doubt that the unfavorable structural features of the deduced product **10** are responsible for the lack of cyclization of **3** (*Scheme 3*). Indeed, two Br-atoms (*van-der-Waals* radii 190 pm) occupy inevitably the axial positions in **10** increasing significantly the conformational energy of the molecule (when 'chair' conformation is favored, similarly to **6a** and **7a** (see below, C(1)–C(5) distance *ca.* 251 pm), and other tetrahydro-4*H*-pyran-4-one [16] derivatives).

X-Ray single-crystal investigation of compounds **6a** and **7a** revealed 'chair' conformations for both connected cycles (*Figure*, *Table*). In **6a**, the C(9) and O(3) atoms deviate from the plane of the other pyran-ring atoms by −73.9 and 57.1 pm, respectively; deviations of the C(9) and C(7) atoms from the plane of the other cyclohexanone-ring atoms are −74.2 and 60.5 pm, respectively. In **7a** the C(9) and O(3) atoms deviate from the plane of the other pyran-ring atoms by −75.0 and 57.2 pm, respectively; deviations of C(9) and C(7) atoms from the plane of the other cyclohexanone-ring atoms are −73.3 and 63.2 pm, respectively. The CF_3 substituents at the pyran ring of both compounds are equatorial and *cis* arranged, whereby the OH and MeO groups occupy axial positions (torsion angles C(9)–C(1)–C(2)–O(1) −68.6(3)°, C(9)–C(1)–C(2)–

Scheme 3



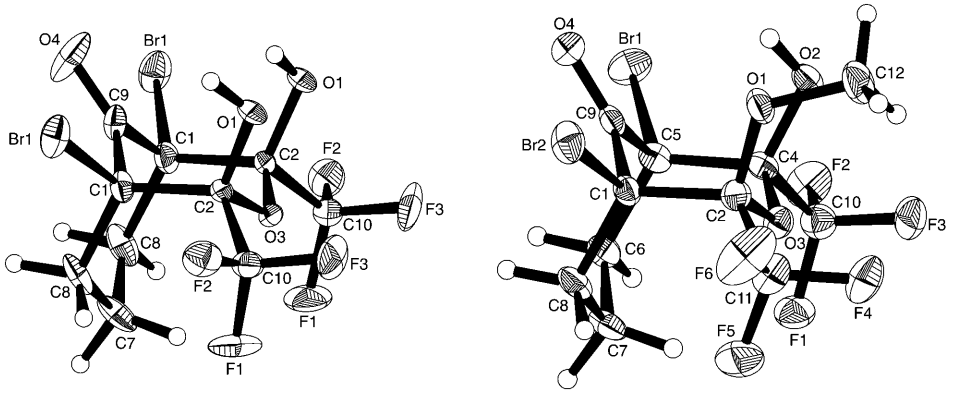
C(10) 169.4(3)° (for **6a**), and C(9)–C(1)–C(2)–O(1) 65.4(3)°, C(9)–C(1)–C(2)–C(11) –170.8(2)°, C(9)–C(5)–C(4)–O(2) –72.4(3)°, C(9)–C(5)–C(4)–C(10) 167.4(2)° (for **7a**)). In **6a**, one of the OH H-atoms is involved in intramolecular H-bonds to the second OH O-atom (O···O 280.4(4) pm, ∠O–H–O 125(5)°). In its turn, this second OH group forms an intermolecular H-bond to the C=O O-atom of the adjacent molecule (O(1)···O(4)′ 287.1(3) pm, ∠O–H–O 146(6)°). In **7a**, the proton of the OH group is involved in an intermolecular H-bond to the C=O O-atom of an adjacent molecule (O(1)···O(4)′ 281.1(3) pm, ∠O–H–O 153(2)°). These intermolecular O(1)–H···O(4)′ interactions cause the formation of molecular dimers in crystals of both **6a** and **7a**.

Table. *Principal Bond Lengths* [pm] *and Angles* [°] *for* **6a** *and* **7a**. For numbering, see *Figure.*

6a				**7a**			
C(1)–C(9)	152.9(4)	C(9)–C(1)–C(8)	107.2(3)	C(1)–C(9)	152.9(4)	C(9)–C(1)–C(8)	107.3(2)
C(1)–C(2)	155.8(4)	C(9)–C(1)–C(2)	106.1(2)	C(1)–C(2)	156.6(4)	C(9)–C(1)–C(2)	104.5(2)
C(2)–O(3)	141.5(3)	C(9)–C(1)–Br(1)	108.09(19)	C(2)–O(3)	142.1(3)	C(9)–C(1)–Br(2)	109.67(19)
O(3)–C(2)#1[a])	141.5(3)	O(1)–C(2)–O(3)	111.2(2)	O(3)–C(4)	142.6(3)	O(2)–C(4)–O(3)	112.9(2)
C(2)–O(1)	138.1(3)	O(1)–C(2)–C(10)	105.8(2)	C(2)–O(1)	137.8(3)	O(2)–C(4)–C(10)	104.2(2)
C(2)–C(10)	155.0(4)	C(7)–C(8)–C(1)	113.3(3)	C(2)–C(11)	155.3(4)	C(7)–C(8)–C(1)	113.2(3)
C(9)–O(4)	119.8(5)	C(2)#1–O(3)–C(2)	119.2(3)	C(9)–O(4)	119.7(3)	C(2)–O(3)–C(4)	119.1(2)
C(1)–Br(1)	195.9(3)	F(3)–C(10)–C(2)	109.8(2)	C(1)–Br(2)	195.0(3)	F(3)–C(10)–C(4)	109.4(2)
C(10)–F(1)	133.2(3)	F(3)–C(10)–F(2)	107.7(3)	C(10)–F(1)	132.7(4)	C(2)–O(1)–C(12)	119.8(2)

[a]) #1 $x, -y+\frac{1}{2}, z$.

Multinuclear NMR data of compounds **6** and **7**, collected for $CDCl_3$ and (D_6)acetone solutions, are consistent with the bridged bicyclic structure. ^{13}C-NMR Spectra are especially informative, with the signals for C(2) and C(4) found at δ *ca.*



6a **7a**

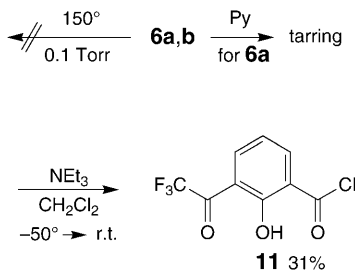
Figure. *Molecular structures of compounds* **6a** *and* **7a**. Thermal ellipsoids with 50% probability; arbitrary numberings. For **6a**, symmetry transformations used to generate equivalent atoms: #1 x, $-y+\frac{1}{2}$, z. For the principal bond lengths and bond angles, see the *Table*.

101, indicating their (hemi)ketal character. Only one set of signals was observed in all measured ^{1}H-, ^{13}C-, and ^{19}F-NMR spectra verifying the presence of only one diastereoisomer. We were not able to detect any ring–chain transformations for compounds **6** and **7** in $CDCl_3$ and (D_6)acetone solutions using NMR techniques. Obviously, the reason for such a stability of the cyclic hemiketal form (being reported earlier for other pyran derivatives with CF_3 and OH moieties in 2(6) positions [6d][7][14a–g]) is an electron-withdrawing influence of the CF_3 group [13]. Striking features of the NMR spectra of compounds **7a**,**c**,**d** are the ^5J(H,F) and ^4J(C,F) couplings which are helpful for the signal assignment. The NMR data of compound **5b** require special comments. In this case, only *one* tautomeric form, namely the enol, was obvious in the ^{1}H-, ^{13}C-, and ^{19}F-NMR spectra ($CDCl_3$ solution, 22°), as established by the OH resonance at δ(H) 14.05, as well as by the δ(C) values of the nuclei of the hydroxyenone backbone (δ 175.1, 104.7, and 182.8 for C(1), C(6) and CF_3C, resp.). Based on the ^4J(C,F) and ^5J(F,H) splittings observed, the *U*-structure of this backbone is suggested.

Pyran-4-ones **6a**,**b** are stable compounds. Being heated to 150° at 0.1 Torr for 30 min, they could be recovered without any detectable change. However, an attempt with pyridine resulted in a strong tarring. On the other hand, upon treatment of **4a** with Et_3N, 1,1′-(2-hydroxy-1,3-phenylene)bis[2,2,2-trifluoroethan-1-one] (=2,6-bis(trifluoroacetyl)phenol; **11**) was obtained in 31% yield (*Scheme 4*). The product is a valuable fluorinated building block being difficult to synthesize otherwise. Of course, reaction conditions have to be optimized; nevertheless, **4** and **5** are promising reaction partners, and this encouraging result stimulates us to continue the investigation.

Conclusion. – The halogenation of linear and cyclic F-containing 1,3,5-triketones and their metal salts was studied. Reaction conditions for the preparation of mono-, di-, and tetrahalogenated products were established. These compounds added H_2O and alcohols readily, and the subsequent cyclization provided novel bridged 2,6-dihy-

Scheme 4



droxy-4*H*-pyran-4-one derivatives. This ring closure is controlled by a complex interplay of electrophilicity of the terminal carbonyl moieties, their mutual sterical arrangement, and acid catalysis. A synthetic route to 2,6-bis(trifluoroacetyl)-substituted phenols *via* double HBr elimination from the α,α'-dibrominated cyclohexanone was discovered. Further evaluation of the synthetic potential of the obtained 1,3,5-triketones is under way, and the results will be published elsewhere.

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Experimental Part

1. *General*. All chemicals are commercially available and were used as purchased unless otherwise specified. Reactions in dried solvents (CH_2Cl_2 and $CHCl_3$ distilled from P_2O_5, $MeOCH_2CH_2OMe$ and THF from sodium/benzophenone ketyl) were performed in oven-dried glassware under a static N_2 atmosphere. Column chromatography (CC): Silica gel *60*, 320–630 mesh (*MP Biomedicals Germany GmbH*). M.p. and b.p.: uncorrected. NMR Spectra: *Bruker DPX-200* spectrometer; at 200.1 (^{1}H), 50.3 (^{13}C), or 188.3 MHz (^{19}F); δ in ppm, J in Hz, Me_4Si (^{1}H and ^{13}C) and CCl_3F (^{19}F) scales; δ(H) referenced to δ(H) 7.25 of residual $CHCl_3$ or to δ(H) 2.05 of the central line of (D_6)acetone; δ(C) referenced to δ(C) 77.0 ($CDCl_3$) and 29.9 ((D_6)acetone) of the central line of the solvent signal; δ(F) referenced to δ(F) -162.23 of hexafluorobenzene as internal standard; ^{19}F-NMR monitoring of samples from the reaction mixtures dissolved in $CHCl_3$ containing hexafluorobenzene as an internal reference (without lock); assignments of δ(H) and δ(C) of **6** and **7** by INEPT and DEPT135 experiments and by the ^5J(H,F) and ^4J(C,F) splittings; assignments of δ(F) of compounds **7** by comparison with δ(F) of the symmetrical **6**. MS (m/z, intensity (%)): EI (70 eV), *Finnigan MAT-8200* and *MAT-95* spectrometers; CI (NH_3 as reactant gas) and DCI (8 mA/s, NH_3 as reactant gas), *MAT-8200* spectrometer; ESI, *Bruker Esquire-LC* spectrometer. HR-MS: peak matching method, *Finnigan MAT-95* spectrometer. Elemental analyses: *Mikroanalytisches Beller Labor*, Göttingen, Germany.

X-Ray single-crystal determination for compounds **6a** and **7a** at $-100(2)^\circ$, *Siemens-P4* diffractometer with a graphite monochromated MoK_α radiation (λ 71.073 pm) and the low-temperature device *LT2*. The structures were solved by direct methods and refined by full-matrix least-squares at F^2 with the SHELXL-97 program package [17]. All non-H-atoms were refined anisotropically, the OH protons were refined isotropically, the positions of the other H-atoms were calculated as a riding model. For both compounds, absorption correction was carried out by using an empirical (DIFABS) method.

2. *Starting 1,3,5-Triketones and Metal Derivatives.* Compounds **1** were prepared by a double condensation of the corresponding ketone and ethyl trifluoroacetate with LiH as a base (**1a** and **1d**: in $MeOCH_2$-CH_2OMe as a solvent, according to [7] and [18a], resp.; **1b** [18] and **1c**: in THF as a solvent, according to [19]).

2.1. *4-(*tert*-Butyl)-2,6-bis(trifluoroacetyl)cyclohexanone* (**1c**). Yield 77%. Yellow liquid. B.p. 128–132°/20 Torr. In $CDCl_3$ at 22°, 75:14:11 mixture of the bis-enol, mono-enol, and monohydrate (*i.e.*, geminaldiol $R-C(OH)_2CF_3$), resp. (by ^{1}H-NMR; for details about tautomerism of fluorinated 1,3,5-triketones, see [7]). EI-MS: 346 (13, M^+), 331 (7, $[M-Me]^+$), 327 (4, $[M-F]^+$), 289 (6, $[M-C_4H_9]^+$); 277 (16, $[M-CF_3]^+$), 57 (100, $C_4H_9^+$), and other fragments. HR-MS: 346.1009 ($C_{14}H_{16}F_6O_3^+$, M^+; calc. 346.1004); −1.5 ppm (10.0), −0.5 mu (10.0), $R\approx10000$.

Data of Bis-enol **1c**: ^{1}H-NMR ($CDCl_3$): 0.94 (*s*, ^{t}Bu); 1.22–1.56 (*m*, 1 H); 2.01–2.15 (*m*, 2 H); 2.74–2.81 (*m*, 2 H); 14.58 (*q*, ^4J(H,F) = 1.9, 2 OH). ^{13}C-NMR ($CDCl_3$): 27.0 (*s*, Me); 24.2 (*q*, ^4J(C,F) = 2.8[3]), C(3), C(5)); 32.4 (*s*, Me_3C); 43.3 (*s*, C(4)); 109.0 (*s*, C(2), C(6)); 119.2 (*q*, ^1J(C,F) = 278.3, CF_3); 160.4 (*q*, ^2J(C,F) = 35.3, CF_3C); 195.9 (*s*, C(1)). ^{19}F-NMR ($CDCl_3$): −68.73 (*s*).

Data of Mono-enol **1c**: ^{1}H-NMR ($CDCl_3$): 0.91 (*s*, ^{t}Bu); 4.09 (*t*, ^3J(H,H) = 7.1, H–C(6)); 14.2 (br. *s*, OH); overlap of the other alicyclic CH signals by the corresponding resonances of the predominant tautomer. ^{19}F-NMR ($CDCl_3$): −76.88 (*s*, 3 F, (C=O)CF_3); −73.90 (*s*, 3 F, =C(OH)CF_3).

Data of Mono-hydrate **1c**·H_2O: ^{19}F-NMR ($CDCl_3$): −78.55 (*s*, $C(OH)_2CF_3$); −73.67 (*s*, =C(OH)-CF_3).

2.2. *2,6-Bis(trifluoroacetyl)cyclohexanone Dilithium Salt* (**2a**). According to [19]: 51% yield. Yellow powder. M.p. 250° (dec.). ^{1}H-NMR ((D$_6$)acetone): 1.51–1.68 (*m*, CH_2, 2 H); 2.34–2.51 (*m*, 2 CH_2, 4 H). ^{19}F-NMR ((D$_6$)acetone): −68.9 (*t*, ^5J(F,H) = 1.9[3])). ESI-MS (MeCN): 585 (100, $[2\,C_{10}H_6F_6O_3+Li+2\,H]^-$), 289 (80, $[C_{10}H_6F_6O_3+H]^-$), and other fragments.

2.3. *Bis[2,6-bis(trifluoroacetyl)cyclohexanone] Dicopper(2+) Salt* (**2b**). Dilithium salt **2a** (5.0 g, 16.6 mmol) was added to a sat. aq. $Cu(OAc)_2$ soln. (100 ml). The mixture was stirred for 24 h at r.t. The precipitated copper(2+) salt was filtered off, washed with H_2O (3 × 50 ml), and dried *in vacuo*. The solid was washed with hot $CHCl_3$ (3 × 20 ml), recrystallized from MeOH, and dried for 10 h at *ca.* 110°: **2b** (3.9 g, 66%). Dark green powder. M.p. >250° (dec.). Anal. calc. for $C_{20}H_{12}F_{12}O_6Cu_2$ (703.38(3)): C 34.15, H 1.72, F 32.4; found: C 33.98, H 1.84, F 32.3.

3. *Brominations with Br_2* (*Entries 3–5* and *9*). 3.1. cis-*2,6-Dibromo-2,6-bis(trifluoroacetyl)cyclohexanone cis*-**4a**; *Entries 4* and *5*). 3.1.1. *Entry 4*: Br_2 (0.64 g, 4.0 mmol) was added dropwise to a well stirred soln. of **1b** (0.52 g, 1.8 mmol) in dried $CHCl_3$ (8 ml). The mixture was stirred in a stoppered flask for 12 h at r.t. After opening the flask (caution, slight internal pressure due to HBr vapors), the volatile materials were removed *in vacuo*. The solid residue was recrystallized: *cis*-**4a** (0.67 g, 83%). Colorless crystals. M.p. 67–69° (petroleum ether (100–140°)). ^{1}H-NMR ($CDCl_3$): 2.07–2.19 (*m*, CH_2); 2.28–2.41 (*m*, 2 H); 2.85–2.98 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 19.6 (*s*, C(4)); 39.6 (*s*, C(3), C(5)); 65.2 (*s*, C(2), C(6)); 115.4 (*q*, ^1J(C,F) = 292.0, CF_3); 180.9 (*q*, ^2J(C,F) = 35.8, CF_3C); 188.3 (*s*, C(1)). ^{19}F-NMR ($CDCl_3$): −69.7 (*s*). EI-MS: 446 (18, M^+), 367 (24, $[M-Br]^+$), 218 (100, $[M-CF_3-2\,Br-H]^+$), 191 (60, $[M-CF_3CO-2\,Br]^+$), 69 (74, CF_3^+), and other fragments. HR-MS: 445.8600 (M^+, $C_{10}H_6{}^{79}Br_2F_6O_3$; calc. 445.8588); −2.8 ppm (10.0), −1.3 mu (10.0), $R\approx10000$.

3.1.2. *Entry 5*: Br_2 (3.2 g, 20 mmol) was added carefully to a well stirred suspension of **2a** (3.0 g, 10 mmol) in dried $CHCl_3$ (30 ml) causing an exothermic reaction. The mixture was stirred in a stoppered flask for 12 h at r.t. Petroleum ether (58–62°) (20 ml) was added to the suspension formed, the mixture cooled to −30°, and the precipitated LiBr filtered off. The filtrate was concentrated, and the solid residue recrystallized: *cis*-**4a** (3.3 g, 74%).

3.2. *Entry 3*: Br_2 (0.32 g, 2.0 mmol; 0.70 g, 4.3 mmol; 1.3 g, 8.1 mmol) was added dropwise to a well stirred soln. of **1a** (0.50 g, 2.0 mmol) in $CHCl_3$ (10 ml). The mixture was stirred in a stoppered flask for 40 h at r.t. After opening the flask (caution, slight internal pressure due to HBr vapors), the volatile mate-

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[3]) Confirming the *U*-structure of the C(O)–C–C(O)–C–C(O) or C(O)–C–C(O) fragment.

rials were evaporated. ^{19}F-NMR Investigation of the yellow oily residue revealed a complex mixture of products, with **3** as the only identifiable product (δ(F) −67.2 (*s*), see below, *4.1.*), at the complete conversion of starting **1a**.

3.3. *Entry 9*: Br_2 (0.07 g, 0.45 mmol) was added to a well stirred soln. of **1b** (0.13 g, 0.45 mmol) in $CHCl_3$ (2 ml). The mixture was stirred in a stoppered flask for 10 h at r.t. After opening the flask (caution, slight internal pressure due to HBr vapors), the mixture was analyzed by ^{19}F-NMR to reveal **5a** (δ(F) −71.1 (*s*, 3 F), −73.9 (*s*, 3 F)), and *cis*-**4a** (δ(F) −69.7 (*s*)) as the only identifiable products, at 87% conversion of starting **1b**.

4. *Brominations Using NBS* (*Entries 1* and *2*). 4.1. *3,3,5,5-Tetrabromo-1,1,1,7,7,7-heptafluoroheptane-2,4,6-trione* (**3***; Entry 1*). NBS (0.88 g, 4.9 mmol) was added to a stirred soln. of **1a** (0.30 g, 1.2 mmol) in $CHCl_3$ (15 ml). After the mixture was stirred in a stoppered flask for 18 h at r.t., the volatile materials were evaporated *in vacuo*, and the solid residue was carefully washed with hot petroleum ether (58–62°) (2×20 ml). The combined liquid phases were concentrated to afford **3** (0.55 g, 81%) as a white solid. An anal. sample was obtained by recrystallization from petroleum ether (58–62°): Colorless crystals. M.p. 83–84°. ^{13}C-NMR ($CDCl_3$): 52.3 (*s*, C(3), C(5)); 114.6 (*q*, ^1J(C,F) = 292.4, C(1), C(7)); 174.4 (*q*, ^2J(C,F) = 37.3, C(2), C(6)); 181.8 (*s*, C(4)). ^{19}F-NMR ($CDCl_3$): −67.24 (*s*). EI-MS: 562 (<1, M^+), 465 (<1, $[M-CF_3CO]^+$), 295 (40, $CF_3C(O)CBr_2CO^+$), 267 (32, $CF_3C(O)CBr_2^+$), 97 (14, CF_3CO^+), 69 (100, CF_3^+), and other fragments. Anal. calc. for $C_7Br_4F_6O_3$ (565.68(2)): C 14.86, H 0.0, F 20.2; found: C 14.92, H <0.30, F 20.0.

4.2. cis/trans-*2,6-Dibromo-2,6-bis(trifluoroacetyl)cyclohexanone* (*cis*/*trans*-**4a** mixture; *Entry 2*). NBS (0.29 g, 1.6 mmol) was added to a stirred soln. of **1b** (0.23 g, 0.8 mmol) in $CHCl_3$ (10 ml) or CH_2Cl_2 (5 ml). The mixture was stirred in a stoppered flask (in $CHCl_3$ for 4 h; in CH_2Cl_2 for 14 h) at r.t. ^{19}F-NMR Investigation of the pale yellow liquid revealed two products: *cis*-**4a** (δ(F) −69.7 (*s*)) and *trans*-**4a** (δ(F) −70.2 (*s*)), ratio 40:60, at complete conversion of starting **2b**.

5. *Chlorinations* (*Entries 6–8*). 5.1. cis/trans-*2,6-Dichloro-2,6-bis(trifluoroacetyl)cyclohexanone* (*cis*/*trans*-**4b** mixture; *Entries 6* and *7*). 5.1.1. *Entry 7*: The 1,3,5-triketone **1b** (1.0 g, 3.4 mmol) was dissolved in freshly distilled SO_2Cl_2 (6 ml) and the soln. heated to reflux for 16 h. The volatile materials were removed *in vacuo*: anal. pure *cis*/*trans*-**4b** 82:18 (by ^{19}F-NMR) (1.2 g, 97%). Colorless needles. M.p. 37–42°. ^{1}H-NMR ($CDCl_3$): 1.92–2.91 (*m*). EI-MS: 358 (2, M^+), 262 (24, $[M-CF_3CO+H]^+$), 227 (16, $[M-CF_3CO-Cl+H]^+$), 165 (100, $[M-2\,CF_3CO+H]^+$), 129 (28, $[M-2\,CF_3CO-Cl]^+$), 69 (46, CF_3^+), and other fragments. HR-MS: 357.9596 (M^+, $C_{10}H_6{}^{35}Cl_2F_6O_3^+$; calc. 357.9598); 0.5 ppm (10.0), 0.2 mu (10.0), $R \approx 10000$.

Data of cis-**4b**: ^{13}C-NMR ($CDCl_3$): 16.5 (*s*, C(4)); 37.9 (*s*, C(3), C(5)); 71.3 (*s*, C(2), C(6)); 115.1 (*q*, ^1J(C,F) = 291.5, CF_3); 183.3 (*q*, ^2J(C,F) = 36.3, CF_3C); 194.2 (*s*, C(1)). ^{19}F-NMR ($CDCl_3$): −71.08 (*s*).

Data of trans-**4b**: ^{13}C-NMR ($CDCl_3$): 17.9 (*s*, C(4)); 38.7 (*s*, C(3), C(5); 72.6 (*s*, C(2), C(6)); 115.3 (*q*, ^1J(C,F) = 292.0, CF_3); 180.7 (*q*, ^2J(C,F) = 37.7, CF_3C); 189.2 (*s*, C(1)). ^{19}F-NMR ($CDCl_3$): −71.13 (*s*).

5.1.2. *Entry 6*: A soln. of **1b** (0.26 g, 0.9 mmol) in dried $CHCl_3$ (6 ml) was placed in a thick-walled glass ampoule equipped with a *Teflon* tap. Then Cl_2 (0.14 g, 2.0 mmol) was condensed into the evacuated ampoule at liq.-N_2 temp. The mixture was gradually allowed to warm and stirred for 16 h at r.t. The formed pale yellow soln. was analyzed by ^{19}F-NMR to reveal two products: *cis*-**4b** and *trans*-**4a**, ratio 82:18, at complete conversion of starting **1b**.

5.2. *2-Chloro-2,6-bis(trifluoroacetyl)cyclohexanone* (**5b**; *Entry 8*). Freshly distilled SO_2Cl_2 (0.74 g, 5.5 mmol) was added dropwise to a stirred soln. of **1b** (0.73 g, 2.5 mmol) in dried CH_2Cl_2 (15 ml). The mixture was stirred for 40 h at r.t., the volatile materials were removed *in vacuo*: anal. pure **5b** (0.79 g, 97%). Pale yellow oil. ^{1}H-NMR ($CDCl_3$): 1.92–2.16 (*m*, 2 H); 2.20–2.42 (*m*, 2 H); 2.46–2.64 (*m*, 1 H); 2.67–2.84 (*m*, 1 H); 14.05 (*s*, 1 H, OH). ^{13}C-NMR ($CDCl_3$): 17.6 (*s*, C(4)); 21.0 (*q*, ^4J(C,F) = 2.9[3]), C(5)); 33.5 (*s*, C(3)); 71.2 (*s*, C(2)); 104.7 (*s*, C(6)); 115.4 (*q*, ^1J(C,F) = 292.9, CF_3); 116.5 (*q*, ^1J(C,F) = 287.2, CF_3); 175.1 (*s*, C(1)); 182.8 (*q*, ^2J(C,F) = 36.0, CF_3C); 184.0 (*q*, ^2J(C,F) = 35.5, CF_3C). ^{19}F-NMR ($CDCl_3$): −74.06 (*t*, ^5J(F,H) = 1.1[3]), C(OH)CF_3); −71.69 (*s*, C(O)CF_3). EI-MS: 324 (60, M^+), 289 (48, $[M-Cl]^+$), 255 (68, $[M-CF_3]^+$), 227 (80, $[M-CF_3CO]^+$), 191 (100, $[M-CF_3CO-Cl-H]^+$), 69 (64, CF_3^+), and other fragments. HR-MS: 323.9985 (M^+, $C_{10}H_7{}^{35}ClF_6O_3^+$; calc. 323.9988); 1.0 ppm (10.0), 0.3 mu (10.0), $R \approx 10000$.

6. *Bridged Pyran-4-ones* **6** *and* **7**. 6.1. *(1*RS,*2*SR,*4*RS,*5*SR*)-1,5-Dibromo-2,4-dihydroxy-2,4-bis(trifluoromethyl)-3-oxabicyclo[3.3.1]nonan-9-one* (**6a**; *Entries 10*, *11*, *14*, *17*, and *18*). 6.1.1. *Entries 10* and

11: Br_2 (0.16 g, 1.00 mmol) was added dropwise to a well stirred soln. of **1b** (0.13 g, 0.45 mmol) in $CHCl_3$ (2 ml; dried (*Entry 10*) or of commercial quality (*Entry 11*)). The mixture was stirred in a stoppered flask for 14 h at r.t. After opening the flask (caution, slight internal pressure due to HBr vapors) the content was concentrated without vacuum. The solid residue was recrystallized: **6a** (*Entry 10*: 0.10 g, 49%; *Entry 11*: 0.17 g, 81%). Off-white crystals. M.p. 112–116° (toluene). ^{1}H-NMR ($CDCl_3$): 1.55–1.75 (*m*, 1 H); 2.38–2.50 (*m*, 3 H); 2.94–3.10 (*m*, 2 H); 4.1 (br. *s*, 2 OH). ^{13}C-NMR ($CDCl_3$): 23.0 (*s*, C(7)); 42.6 (*s*, C(6), C(8)); 70.1 (*s*, C(1), C(5)); 100.6 (*q*, ^2J(C,F) = 33.1, C(2), C(4)); 120.6 (*q*, ^1J(C,F) = 289.9, CF_3); 188.8 (*s*, C(9)). ^{19}F-NMR ($CDCl_3$): −78.69 (*s*). EI-MS: 446 (4, $[M-H_2O]^+$), 367 (3, $[M-H_2O-Br]^+$), 349 (19, $[M-H_2O-CF_3CO]^+$), 270 (100, $[M-Br-CF_3CO-H_2O]^+$), 69 (58, CF_3^+), and other fragments. DCI-MS (pos.): 482 (4, $[M+NH_4]^+$), 210 (100, $[M-CF_3CO-2\,Br+H]^+$), 69 (24, CF_3^+), and other fragments. DCI-MS (neg.): 463 (12, $[M-H]^-$), 385 (19, $[M-Br]^-$), 367 (29, $[M-Br-H_2O]^-$), 113 (100), 79 (12, Br^-), and other fragments. HR-MS: 445.8597 ($[M-H_2O]^+$, $C_{10}H_6{}^{79}Br_2F_6O_3^+$; calc. 445.8588); −1.9 ppm (10.0), −0.9 mu (5.0), $R \approx 10000$.

X-Ray Crystal-Structure Analysis of **6a**[4]). Single crystal, crystallized from toluene. Colorless prisms; $C_{10}H_8Br_2F_6O_4$ (465.98); $0.35\times0.35\times0.3$ mm^3, orthorombic *Pnma* with $a = 704.60(10)$, $b = 1541.1(3)$, $c = 1207.8(2)$ pm; $V = 1.3115(4)$ nm^3, $D = 2.360$ g·cm^{-3}, $Z = 4$; difference electron density 0.565 and −0.888 e·Å^{-3}. Index range $-9 \le h \le 1$, $-20 \le k \le 20$, $-15 \le l \le 15$, 2θ range 2.64 to 27.50°, reflections measured 6823, unique reflections 1557 (R(int) = 0.0383). Completeness to $\theta_{max} = 27.50°$: 99.9%, data/restraints/parameter 1557/2/117. Goodness-of-fit on F^2 1.087; final R values ($I > 2\sigma(I)$): $R_1 = 0.0315$, $wR_2 = 0.0693$; R value (all reflections): $R_1 = 0.0467$, $wR_2 = 0.0754$.

6.1.2. *Entry 14*: A soln. of Br_2 (1.61 g, 10.1 mmol) in $CHCl_3$ (5 ml) was added in one portion to a well stirred suspension of **2b** (1.76 g, 2.5 mmol) in $CHCl_3$ (10 ml). The mixture was stirred in a stoppered flask for 12 h at r.t. Then the mixture was treated with Et_2O (20 ml), the aq. phase extracted with Et_2O (3 × 10 ml), the combined extract concentrated without vacuum, and the solid residue recrystallized to afford **6a** (1.93 g, 83%).

6.1.3. *Entries 17* and *18*: Br_2 (0.64 g, 4.0 mmol) was added dropwise to a well stirred soln. of **1b** (0.52 g, 1.8 mmol) in dried $CHCl_3$ (8 ml). The mixture was stirred in a stoppered flask for 12 h at r.t. After opening the flask (caution, slight internal pressure due to HBr vapors), the content was treated with dried MeOH (8 ml, *Entry 17*) or propan-1-ol (2 ml, *Entry 18*). After stirring at r.t. (*Entry 17*: for 4 h; *Entry 18*: for 20 h), the mixture was analyzed by ^{19}F-NMR to reveal the corresponding alcohol adducts **7a**,**b** as the only products (**7a**: δ(F) −78.7 (*s*, CF_3) and −71.4 (*s*, CF_3); **7b**: δ(F) −78.3 (*s*, CF_3) and −71.4 (*s*, CF_3)). The soln. was concentrated without vacuum, and the solid residue recrystallized from toluene: **6a** (*Entry 17*: 0.34 g, 39%; *Entry 18*: 0.50 g, 58%).

6.2. *(1*RS*,2*SR*,4*RS*,5*SR*)-1,5-Dichloro-2,4-dihydroxy-2,4-bis(trifluoromethyl)-3-oxabicyclo[3.3.1]-nonan-9-one* (**6b**; *Entries 12* and *13*). 6.2.1. *Entry 12*: A soln. of **1b** (0.26 g, 0.9 mmol) in dried $CHCl_3$ (6 ml) was placed in a thick-walled glass ampoule equipped with a *Teflon* tap, and then Cl_2 (0.14 g, 2.0 mmol) was condensed into the evacuated ampoule at liq.-N_2 temp. The mixture was gradually allowed to warm and stirred for 16 h at r.t. The resulting pale yellow soln. was concentrated without vacuum, and the solid residue was recrystallized to afford **6b** (0.24 g, 71%). Off-white crystals. M.p. 140° (toluene). ^{1}H-NMR ($CDCl_3$): 1.56–1.99 (*m*, 1 H); 2.18–2.53 (*m*, 3 H); 2.79–2.97 (*m*, 2 H); 4.3 (br. *s*, 2 OH). ^{1}H-NMR ((D$_6$)acetone): 1.79–1.91 (*m*, 1 H); 2.27–2.46 (*m*, 3 H); 2.89–3.24 (*m*, 2 H); 7.4 (br. *s*, 2 OH). ^{13}C-NMR ($CDCl_3$): 21.0 (*s*, C(7)); 41.0 (*s*, C(6), C(8)); 76.0 (*s*, C(1), C(5)); 100.5 (*q*, ^2J(C,F) = 33.4, C(2), C(4)); 120.5 (*q*, ^1J(C,F) = 289.2, CF_3); 189.6 (*s*, C(9)). ^{13}C-NMR ((D$_6$)acetone): 22.0 (*s*, C(7)); 42.2 (*s*, C(6), C(8)); 77.2 (*s*, C(1), C(5)); 101.6 (*q*, ^2J(C,F) = 32.5, C(2), C(4)); 122.3 (*q*, ^1J(C,F) = 289.6, CF_3); 190.2 (*s*, C(9)). ^{19}F-NMR ($CDCl_3$): −79.16 (*s*). ^{19}F-NMR ((D$_6$)acetone): −77.78 (*s*). EI-MS: 262 (14, $[M-CF_3COOH]^+$), 227 (10, $[M-CF_3COOH-Cl]^+$), 165 (100, $[M-CF_3COOH-CF_3CO]^+$), 129

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[4]) CCDC-618481 and CCDC-618480 contain the supplementary crystallographic data (excluding structure factors) for the structures **6a** and **7a**, resp. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif from the *Cambridge Crystallographic Data Centre*.

(27, $[M-CF_3COOH-CF_3CO-HCl]^+$), 69 (44, CF_3^+), and other fragments. CI-MS (neg.): 375 (14, $[M-H]^-$), 261 (10, $[M-CF_3COOH-H]^-$), 227 (100, $[M-CF_3COOH-Cl]^-$), and other fragments. Anal. calc. for $C_{10}H_8Cl_2F_6O_4$ (377.06(7)): C 31.85, H 2.14; found: C 31.74, H 2.24.

6.2.2. *Entry 13*: The 1,3,5-triketone **1b** (0.40 g, 1.4 mmol) was dissolved in freshly distilled SO_2Cl_2 (2 ml). After heating to reflux for 1 h, the mixture was concentrated under air, and the solid residue was recrystallized: **6b** (0.40 g, 77%).

6.3. *(1*RS*,2*SR*,4*RS*,5*SR*)-1,5-Dibromo-2-hydroxy-4-methoxy-2,4-bis(trifluoromethyl)-3-oxabicyclo-[3.3.1]nonan-9-one* (**7a**; *Entries 15* and *16*). 6.3.1. *Entry 15*: Br_2 (0.16 g, 1.0 mmol) was added dropwise to a well stirred soln. of **1b** (0.13 g, 0.45 mmol) in dried $CHCl_3$ (2 ml). The mixture was stirred in a stoppered flask for 12 h at r.t. After opening the flask (caution, slight internal pressure due to HBr vapors), dry MeOH (2 ml) was added, and the mixture was stirred for additional 4 h at r.t. The volatile materials were removed *in vacuo*. The resulting oily residue was dissolved in dry toluene (1 ml) and the soln. left to crystallize at −35°. The precipitate formed was filtered off and dried: **7a** (60 mg, 28%). Colorless prisms. M.p. 116–122° (toluene). ^{1}H-NMR ($CDCl_3$): 1.54–1.70 (*m*, 1 H); 2.31–2.52 (*m*, 3 H); 2.97–3.14 (*m*, 2 H); 3.52 (*q*, ^5J(H,F) = 2.6, Me); 3.79 (*s*, OH). ^{13}C-NMR ($CDCl_3$): 23.1 (*s*, C(7)); 42.9 (*s*, C(8)); 43.4 (*q*, ^4J(C,F) = 3.3, C(6)); 54.8 (*q*, ^4J(C,F) = 2.9, Me); 69.9 (*s*, C(1)); 73.1 (*s*, C(5)); 99.9 (*q*, ^2J(C,F) = 33.1, C(2)); 102.5 (*q*, ^2J(C,F) = 31.4, C(4)); 120.7 (*q*, ^1J(C,F) = 289.5, *C*F_3–C(2)); 120.7 (*q*, ^1J(C,F) = 294.0, *C*F_3–C(4)); 188.2 (*s*, C(9)). ^{19}F-NMR ($CDCl_3$): −78.65 (*s*, CF_3–C(2)); −71.38 (*q*, ^5J(F,H) = 2.6, CF_3–C(4)). EI-MS: 446 (2, $[M-MeOH]^+$), 409 (1, $[M-CF_3]^+$), 367 (4, $[M-MeOH-Br]^+$), 350 (8, $[M-CF_3COOMe]^+$), 285 (36, $[M-CF_3COOH-Br]^+$), 271 (100, $[M-CF_3COOMe-Br]^+$), 69 (40, CF_3^+), and other fragments. CI-MS (pos.): 496 (23, $[M+NH_4]^+$), 382 (28, $[M-CF_3CO+H]^+$), 208 (100), 69 (51, CF_3^+), and other fragments. CI-MS (neg.): 557 (6, $[M+Br]^-$), 478 (4, M^-), 477 (4, $[M-H]^-$), 446 (1, $[M-MeOH]^-$), 399 (5, $[M-Br]^-$), 365 (14, $[M-CF_3COO]^-$), 349 (8, $[M-CF_3COOMe-H]^-$), 286 (100, $[M-CF_3COO-Br]^-$), 79 (21, Br^-), and other fragments. HR-MS: 556.8029 ($[M+Br]^-$, $C_{11}H_{10}{}^{79}Br_3F_6O_4^-$; calc. 556.8033); 0.8 ppm (10.0), 0.5 mu (10.0), $R \approx 3600$.

X-Ray Crystal-Structure Analysis of **7a**[4]). Single crystal, crystallized from toluene. Colorless prisms; $C_{11}H_{10}Br_2F_6O_4$ (480.01); $0.5 \times 0.4 \times 0.4$ mm^3, monoclinic $P2_1/c$ with $a = 1217.9(2)$, $b = 776.30(10)$, $c = 1645.7(2)$ pm, $\beta = 109.760(10)°$; $V = 1.4643(4)$ nm^3, $D = 2.177$ g·cm^{-3}, $Z = 4$; difference electron density 0.515 and −0.536 e·Å^{-3}. Index range $-1 \le h \le 15$, $-10 \le k \le 1$, $-21 \le l \le 21$, 2θ range 2.63 to 27.50°, reflections measured 4408, unique reflections 3331 (R(int) = 0.0231). Completeness to $\theta_{max} = 27.50°$: 99.3%, data/restraints/parameter 3331/0/213. Goodness-of-fit on F^2 1.034; final R values ($I > 2\sigma(I)$): $R_1 = 0.0321$, $wR_2 = 0.0643$; R value (all reflections): $R_1 = 0.0483$, $wR_2 = 0.0695$.

6.3.2. *Entry 16*: Br_2 (0.16 g, 1.0 mmol) was added dropwise to a well stirred soln. of **1b** (0.13 g, 0.45 mmol) in dried $CHCl_3$ (2 ml). The mixture was stirred in a stoppered flask for 11 h at r.t. After opening the flask (caution, slight internal pressure due to HBr vapors), dry MeOH (4 ml) was added, and the mixture was stirred for additional 8 h at r.t. The volatile materials were removed *in vacuo*, and **7a** (10 mg, 5%) and **6a** (30 mg, 15%) were obtained by a fractional recrystallization of the solid residue from toluene.

6.4. *(1*RS*,2*SR*,4*RS*,5*SR*)-1,5-Dichloro-4-ethoxy-2-hydroxy-2,4-bis(trifluoromethyl)-3-oxabicyclo-[3.3.1]nonan-9-one* (**7c**; *Entry 19*). A mixture of **1b** (0.26 g, 0.9 mmol), dried EtOH (0.10 g), and dried $CHCl_3$ (6 ml) was placed in a thick-walled glass ampoule equipped with a *Teflon* tap, and then Cl_2 (0.14 g, 2.0 mmol) was condensed into the evacuated ampoule at liq.-N_2 temp. The mixture was gradually allowed to warm and stirred for 14 h at r.t. The resulting colorless soln. was concentrated without vacuum, and the solid residue was recrystallized from toluene to afford a mixture of two kinds of crystals who could be easily separated mechanically: **6b** (30 mg, 10%; off-white crystals) and **7c** (130 mg, 36%; colorless prisms). **7c**: M.p. 130–150°. ^{1}H-NMR ($CDCl_3$): 1.12 (*t*, ^3J(H,H) = 6.8, Me); 1.68–1.85 (*m*, 1 H); 2.09–2.53 (*m*, 3 H); 2.80–3.02 (*m*, 2 H); 3.70–3.88 (*m*, 1 H, CH_2O); 3.85 (*s*, OH); 3.90–4.08 (*m*, 1 H, CH_2O). ^{13}C-NMR ($CDCl_3$): 14.5 (*s*, Me); 21.0 (*s*, C(7)); 41.2 (*s*, C(8)); 41.8 (*q*, ^4J(C,F) = 3.3, C(6)); 63.0 (*q*, ^4J(C,F) = 2.8, CH_2O); 99.6 (*q*, ^2J(C,F) = 33.0, C(2)); 102.3 (*q*, ^2J(C,F) = 32.5, C(4)); 120.8 (*q*, ^1J(C,F) = 289.2, *C*F_3–C(2)); 120.8 (*q*, ^1J(C,F) = 293.9, *C*F_3–C(4)); 189.3 (*s*, C(9)); probably, the signals of C(1) and C(5) are overlapped by the resonance of the solvent. ^{19}F-NMR ($CDCl_3$): −79.20 (*s*, CF_3–C(2)); −72.00 (*m*, CF_3–C(4)). EI-MS: 262 (15, $[M-CF_3COOC_2H_5]^+$), 227 (11, $[M-CF_3COOC_2H_5-Cl]^+$), 165 (100, $[M-CF_3COOC_2H_5-CF_3CO]^+$), 129 (12,

$[M-CF_3COOC_2H_5-CF_3CO-HCl]^+$), 69 (15, CF_3^+), 29 (34, $C_2H_5^+$), and other fragments. CI-MS (pos.): 422 (100, $[M+NH_4]^+$), 386 (9, $[M+NH_4-HCl]^+$), 308 (30, $[M+NH_4-CF_3COOH]^+$), and other fragments. Anal. calc. for $C_{12}H_{12}Cl_2F_6O_4$ (405.12(0)): C 35.58, H 2.99; found: C 35.70, H 2.89.

6.5. *(1*RS*,2*SR*,4*RS*,5*SR*)-1,5-Dibromo-7-(*tert*-butyl)-4-ethoxy-2-hydroxy-2,4-bis(trifluoromethyl)-3-oxabicyclo[3.3.1]nonan-9-one* (**7d**) *and (1*RS*,2*SR*,4*RS*,5*SR*)-1,5-Dibromo-7-(*tert*-butyl)-2,4-dihydroxy-2,4-bis(trifluoromethyl)-3-oxabicyclo[3.3.1]nonan-9-one* (**6c**; *Entry 20*). Dried EtOH (2 ml) was added to a soln. of **1c** (0.50 g, 1.4 mmol) in $CHCl_3$ (15 ml), followed by Br_2 (0.51 g, 3.2 mmol). The mixture was stirred in a stoppered flask for 18 h at r.t. The volatile materials were evaporated, and **7d** (40 mg, 5%) and **6c** (60 mg, 8%) were obtained by fractional recrystallization of the solid residue from toluene/petroleum ether (100–140°) 1:5.

Data of **7d**: Colorless crystals. M.p. 161–162°. ^{1}H-NMR ((D$_6$)acetone): 0.92 (*s*, ^{t}Bu); 1.06 (*t*, ^3J(H,H) = 6.8, Me); 2.12–2.37 (*m*, 2 H); 2.41–2.61 (*s*, 1 H); 2.86–3.11 (*m*, 2 H); 3.65–3.83 (*m*, 1 H, CH_2O); 3.95–4.10 (*m*, 1 H, CH_2O); 7.89 (*s*, OH). ^{13}C-NMR ((D$_6$)acetone): 14.9 (*s*, *Me*CH$_2$); 27.2 (*s*, *Me*$_3$C); 33.1 (*s*, Me$_3$*C*); 43.6 (*s*, C(7)); 45.4 (*s*, C(8)); 45.8 (*q*, ^4J(C,F) = 3.3, C(6)); 63.3 (*q*, ^4J(C,F) = 1.9, CH_2O); 71.8 (*s*, C(1)); 72.3 (*s*, C(5)); 101.9 (*q*, ^2J(C,F) = 32.0, C(2)); 102.9 (*q*, ^2J(C,F) = 30.6, C(4)); 122.2 (*q*, ^1J(C,F) = 294.3, *C*F$_3$–C(4)); 122.3 (*q*, ^1J(C,F) = 290.1, *C*F$_3$–C(2)); 188.5 (*s*, C(9)). ^{19}F-NMR ((D$_6$)acetone): −77.93 (*s*, CF$_3$–C(2)); −71.84 (*s*, CF$_3$–C(4)). EI-MS: 327 (14, $[M-CF_3COOC_2H_5-Br]^+$), 247 (5, $[M-CF_3COOC_2H_5-Br-HBr]^+$), 69 (7, CF_3^+), 57 (100, $C_4H_9^+$), and other fragments. CI-MS (pos.): 566 (55, $[M+NH_4]^+$), 452 (10, $[M-CF_3CO+H]^+$), 372 (4, $[M-CF_3CO-Br]^+$), 355 (7, $[M-CF_3CO-Br-OH]^+$), 264 (10, $[M-C_2H_5-CF_3CO-2\ Br]^+$), and other fragments. CI-MS (neg.): 627 (3, $[M+Br]^-$), 548 (2, M^-), 547 (2, $[M-H]^-$), 423 (22, $[M-Br-C_2H_5OH]^-$), 388 (75, $[M-2\ HBr]^-$), 342 (100, $[M-2\ HBr-C_2H_5OH]^-$), 331 (95, $[M-2\ HBr-C_4H_9]^-$), 322 (45, $[M-2\ HBr-C_2H_5OH-HF]^-$), 113 (40, CF_3COO^-), 79 (76, Br^-), and other fragments. HR-MS: 327.0219 ($[M-CF_3COOC_2H_5-Br]^+$, $C_{12}H_{15}{}^{79}BrF_3O_2^+$; calc. 327.0208); −3.6 ppm (10.0), −1.2 mu (10.0), $R \approx 10000$.

Data of **6c**: Colorless prisms. M.p. 130–131°. ^{1}H-NMR ((D$_6$)acetone): 0.93 (*s*, ^{t}Bu); 2.17–2.37 (*m*, 2 H); 2.45–2.68 (*s*, 1 H); 2.84–3.03 (*m*, 2 H); 7.37 (*s*, 2 OH). ^{13}C-NMR ((D$_6$)acetone): 27.2 (*s*, *Me*$_3$C); 33.2 (*s*, Me$_3$*C*); 43.6 (*s*, C(7)); 45.1 (*s*, C(6), C(8)); 71.3 (*s*, C(1), C(5)); 101.8 (*q*, ^2J(C,F) = 32.5, C(2), C(4)); 122.3 (*q*, ^1J(C,F) = 289.6, CF_3); 189.2 (*s*, C(9)). ^{19}F-NMR ((D$_6$)acetone): −78.51 (*s*). EI-MS: 406 (1, $[M-CF_3COOH]^+$), 327 (9, $[M-CF_3COOH-Br]^+$), 309 (2, $[M-CF_3COOH-CF_3CO]^+$), 69 (6, CF_3^+), 57 (100, $C_4H_9^+$), and other fragments. CI-MS (pos.): 538 (5, $[M+NH_4]^+$), 425 (55, $[M-CF_3CO+H]^+$), 344 (90, $[M-CF_3CO-Br]^+$), 264 (90, $[M-CF_3CO-2\ Br-H]^+$), and other fragments. CI-MS (neg.): 519 (1, $[M-H]^-$), 405 (16, $[M-H-CF_3COOH]^-$), 326 (35, $[M-CF_3COOH-HBr]^-$), 113 (100, CF_3COO^-), 79 (62, Br^-), and other fragments. HR-MS: 327.0216 ($[M-CF_3COOH-Br]^+$, $C_{12}H_{15}{}^{79}BrF_3O_2^+$; calc. 327.0208); −2.6 ppm (10.0), −0.8 mu (10.0), $R \approx 10000$.

7. *Cyclopentanone Derivatives* **8**. 7.1. cis-*2,5-Dibromo-2,5-bis(2,2,2-trifluoro-1,1-dihydroxyethyl)cyclopentanone* (**8a**). A soln. of Br_2 (1.61 g, 10.1 mmol) in $CHCl_3$ (5 ml) was added in one portion to a well stirred soln. of **1d** (1.38 g, 5.0 mmol) in $CHCl_3$ (5 ml). The mixture was stirred in a stoppered flask for 24 h at r.t. After opening the flask (caution, slight internal pressure due to HBr vapors), the content was slowly concentrated without vacuum. The solid residue was recrystallized: **8a** (1.74 g, 74%). Colorless crystals. M.p. 105–110° ($CHCl_3$). ^{1}H-NMR ($CDCl_3$): 2.39–2.50, 2.86–2.96 (2*m*, 2 × 2 H, 2 CH_2); 3.8, 5.3 (2 br. *s*, 2 × 2 H, 4 OH). ^{13}C-NMR ($CDCl_3$): 33.4 (*s*, C(3), C(4)); 60.1 (*s*, C(2), C(5)); 93.8 (*q*, ^2J(C,F) = 32.3, CF_3*C*); 121.4 (*q*, ^1J(C,F) = 288.3, CF_3); 206.5 (*s*, C(1)). ^{19}F-NMR ($CDCl_3$): −80.31 (*s*). EI-MS: 468 (9, M^+), 432 (15, $[M-2\ H_2O]^+$), 370 (42, $[M-H_2O-HBr]^+$), 353 (35, $[M-2\ H_2O-Br]^+$), 325 (78, $[M-2\ H_2O-Br-CO]^+$), 273 (100, $[M-H_2O-HBr-CF_3CO]^+$), and other fragments. Anal. calc. for $C_9H_8Br_2F_6O_5$ (469.95 (7)): C 23.00, H 1.72, F 24.3, Br 34.01; found: C 23.02, H 1.74, F 24.2, Br 34.04.

7.2. cis-*2,5-Dibromo-2,5-bis(2,2,2-trifluoro-1-hydroxy-1-methoxyethyl)cyclopentanone* (**8b**). A soln. of Br_2 (0.58 g, 3.63 mmol) in dried $CHCl_3$ (3 ml) was added in one portion to a well stirred soln. of **1d** (0.5 g, 1.81 mmol) in dried $CHCl_3$ (3 ml). The mixture was stirred in a stoppered flask for 24 h at r.t. After opening the flask (caution, slight internal pressure due to HBr vapors), dry MeOH (5 ml) was added, and the mixture was stirred for additional 12 h at r.t. The volatile materials were removed *in vacuo*. The solid residue was recrystallized: **8b** (0.39 g, 43%). White crystals. M.p. 144–145° (hexane).

^{1}H-NMR ($CDCl_3$): 2.32–2.41, 2.88–2.97 (2*m*, 2×2 H, 2 CH_2); 3.53 (*q*, ^5J(H,F) = 1.2, 2 MeO); 5.05 (*q*, ^4J(H,F) = 1.0, 2 OH). ^{13}C-NMR ($CDCl_3$): 33.0 (*m*, C(3), C(4)); 52.4 (*q*, ^4J(C,F) = 1.7, MeO); 60.7 (*s*, C(2), C(5)); 95.4 (*q*, ^2J(C,F) = 31.6, CF_3C); 121.8 (*q*, ^1J(C,F) = 291.1, CF_3); 208.1 (*s*, C(1)). ^{19}F-NMR ($CDCl_3$): −76.55 (*m*). Anal. calc. for $C_{11}H_{12}Br_2F_6O_5$ (498.01(0)): C 26.53, H 2.43, F 22.9, Br 32.09; found: C 26.58, H 2.47, F 22.9, Br 32.10.

8. *1,1′-(2-Hydroxy-1,3-phenylene)bis[2,2,2-trifluoroethan-1-one]* (= *2,6-Bis(trifluoroacetyl)phenol*; **11**). Dry Et_3N (0.24 g, 2.3 mmol) was added dropwise at −50° to a soln. of **4a** (0.35 g, 0.8 mmol) in dried CH_2Cl_2 (5 ml). The mixture was allowed to reach r.t. After stirring for 24 h, H_2O (40 ml) was added, and the mixture was acidified with 12% HCl soln. to pH 1 and extracted with CH_2Cl_2 (5×10 ml). The combined org. phase was dried ($MgSO_4$) and concentrated and the crude product purified by CC ($CHCl_3$): **11** (70 mg, 31%). Yellow oil (^{19}F-NMR: containing *ca.* 20% of mono-hydrate), *i.e.*, geminal diol R−C(OH)$_2$CF$_3$. EI-MS: 286 (16, M^+), 217 (100, $[M-CF_3]^+$), 147 (46, $[M-2\,CF_3-H]^+$), and other fragments. HR-MS: 286.0069 (M^+, $C_{10}H_4F_6O_3$; calc. 286.0065); −1.4 ppm (10.0), −0.4 mu (10.0), $R \approx 10000$.

Data of **11**. ^{1}H-NMR ($CDCl_3$): 7.18 (*t*, ^3J(H,H) = 7.8, H−C(4)); 8.10 (*d*, H−C(3), H−C(5)); 11.90 (*s*, OH). ^{13}C-NMR ($CDCl_3$): 115.9 (*q*, ^1J(C,F) = 290.1, CF_3); 118.7 (*s*, C(4)); 120.0 (*s*, C(2), C(6)); 138.5 (*q*, ^4J(C,F) = 2.8^3), C(3), C(5)); 164.1 (*s*, C(1)); 182.8 (*q*, ^2J(C,F) = 37.2, C=O). ^{19}F-NMR ($CDCl_3$): −72.78 (*s*).

Data of Mono-hydrate **11**·H_2O: ^{1}H-NMR ($CDCl_3$): 2.1, 4.8 (2 br. *s*, 2×1 H, 2 OH); 7.17 (*t*, ^3J(H,H) = 7.8, H−C(4)); 7.96 (*dm*, 1 H); 8.10 (*m*, 1 H); 12.19 (*s*, 1 H, OH). ^{13}C-NMR ($CDCl_3$): 93.5 (*q*, ^2J(C,F) = 33.9, C(OH)$_2$); 122.8 (*q*, ^1J(C,F) ≈ 290, CF_3); 120.7 (*s*, C(2)); 133.0 (*q*, ^3J(C,F) = 3.8, C(6)); 135.0 (*q*, ^4J(C,F) = 2.8^3), C(3)); 139.9 (*s*, C(5)); 161.1 (*s*, C(1)); 185.2 (*q*, ^2J(C,F) = 36.7, C=O); the signals of the second CF_3 group and C(4) could not be found. ^{19}F-NMR ($CDCl_3$): −85.97 (*s*, $CF_3C(OH)_2$); −70.68 (*d*, ^5J(F,H) = 2.0^3), CF_3C=O).

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