Metal and Boron Derivatives of Fluorinated Cyclic 1,3-Dicarbonyl Compounds

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Starting from the corresponding cyclic 1,3-diketones or other precursors (cyclic ketones as well as lactones), several new salts and chelate complexes of fluorinated 1,3-dicarbonyls were obtained. Their preparative significance was demonstrated by straightforward syntheses of fluorinated pyrazoles, benzimidazoles and 1,7-ketoesters. The structure of a boron chelate of 2-(trifluoroacetyl)-cyclohexanone was investigated by X-ray diffraction.

Key words: Organofluorine Compounds, 1,3-Dicarbonyl Compounds, Salts, Chelates, Synthetic Application

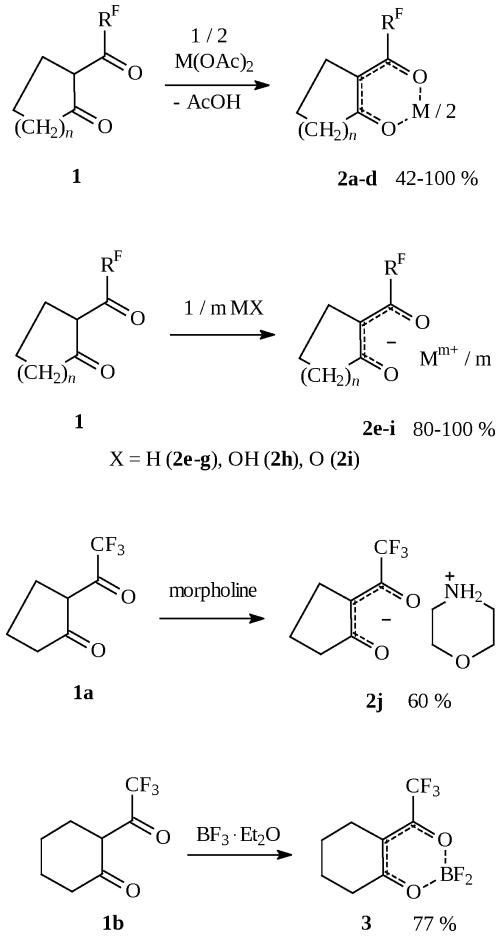
Introduction

Fluorinated compounds are the subject of growing interest due to their interdisciplinary significance and diverse practical uses [1]. Despite of great advances in organofluorine chemistry, the straightforward synthesis of target compounds remains a challenge for chemists [2]. Fluorinated 1,3-dicarbonyls are of special importance in this context: their versatility, high reactivity and preparative availability make them often the starting compounds of choice [3 – 5]. At the same time, fluorinated 1,3-dicarbonyl enolates (salts or complexes) [4 – 7] give frequently better results, when compared to the related 1,3-dicarbonyl compounds, and are as a rule more convenient in handling [5, 6, 8]. In this paper we report the synthesis and several striking synthetic applications of metal derivatives of *cyclic* fluorinated 1,3-dicarbonyl compounds which were collected in our groups during studies in this field [9 – 14].

Results and Discussion

The most famous members of the family of compounds under discussion are europium and praseodymium tris(3-fluoroacyl-(+)-camphorates), which are used in NMR spectroscopy as shift reagents [15, 16]. These chelates as well as derivatives of numerous *d* group metals could be synthesized from the corresponding chiral 1,3-diketone and metal salt [16, 17]. Synthesis of other related camphorates was achieved using barium bis(3-trifluoroacetyl-(+)-camphorate) as the starting compound [18]. As for practical applications, cyclic fluorinated 1,3-diketonates were used as catalysts in stereoselective reactions [17], as components of the bonded phase for the chromatographical separation of enantiomers [19], and as starting compounds in the synthesis of quinoline and phenanthridine derivatives [20].

We have synthesized the copper(II) and nickel(II) complexes of 2-(polyfluoroacyl)cycloalkanones **2a – d** *via* treatment of the 1,3-diketones **1** with the corresponding metal acetates (Scheme 1). Acetate salts were chosen because of their better solubility in organic solvents as compared to chlorides; besides that, the acidities of the starting 1,3-diketones and acetic acid are comparable [21] which facilitates the reaction.



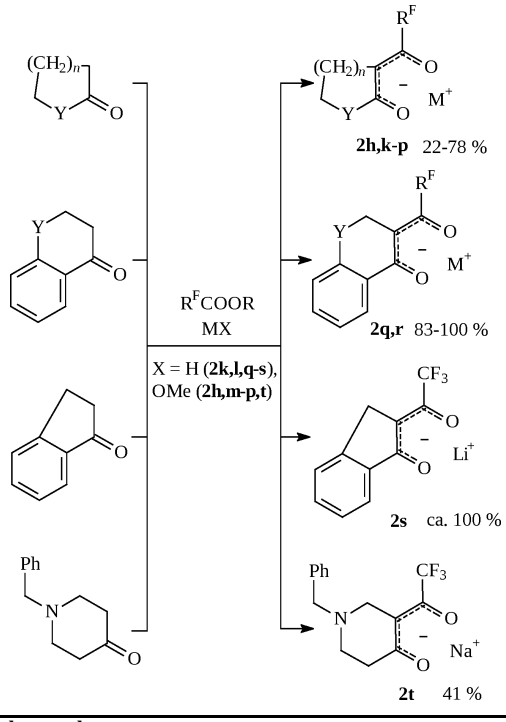
2	a	b	c	d	e	f	g	h	i
n	1	2	2	2	2	2	2	2	2
R^F	CF_3	CF_3	CF_3	CF_2CF_2H	CF_3	CF_2CF_2H	C_6F_{13}	CF_3	CF_3
M	Cu	Cu	Ni	Cu	Li	Li	Li	Na	Ba

Scheme 1.

Li, Na and Ba 2-(polyfluoroacyl)cyclohexanonates **2e – i** were obtained reacting the 1,3-diketone with a suitable base (Scheme 1). Additionally, the morpholinium salt of 2-(trifluoroacetyl)cyclopentanone **2j** was formed in 60 % yield in a similar reaction.

Alkali enolates of 1,3-dicarbonyl compounds are formed as intermediates in the course of Claisen-type condensations [6]. Indeed, salts **2h**, **k – t** could be synthesized directly from the corresponding cyclic ketone or lactone and fluorinated carboxylic acid esters in the presence of LiH and NaOMe, respectively (Scheme 2).

Taking into account that the 1,3-dicarbonyls are formed *via* acidic work-up of the crude reaction mixtures after Claisen-condensation [6], it is obvious that



2	k	l	m	n	o	p	q	r
Y	CH_2	CH_2	CH_2	O	O	O	O	S
n	2	2	2	1	1	2	–	–
R^F	CF_2H	C_3F_7	$CF(OMe)CF_3$	CF_2H	CF_3	CF_3	CF_3	C_2F_5
M	Li	Li	Na	Na	Na	Na	Li	Li

Scheme 2.

this approach to produce salts **2** is superior to that depicted in Scheme 1.

All the substances **2** are crystalline powders; as expected, the copper and nickel complexes are colored (see Experimental Section), but the residual salts are colorless. They are stable and can be stored in a sealed flask for months without any change. As reported [6b], isolation of compounds **2** in analytically pure form with satisfactory elemental analyses is quite difficult, therefore, some of them could be characterized only spectroscopically. The structure of the compounds **2** in [D_6]DMSO, [D_6]acetone, and [D_4]methanol solutions was studied by ^1H and ^{19}F NMR spectroscopy. Only *one* set of signals was always evident in the spectra of the 1,3-diketonates, verifying the presence of only one of two possible geometrical isomers at ambient temperature. An especially valuable information is provided by the $^5J_{F,H}$ splittings observed. This coupling results probably from the through-space interaction of the nuclei, and allows us to assign the *U*-structure to the enolone backbones [23].

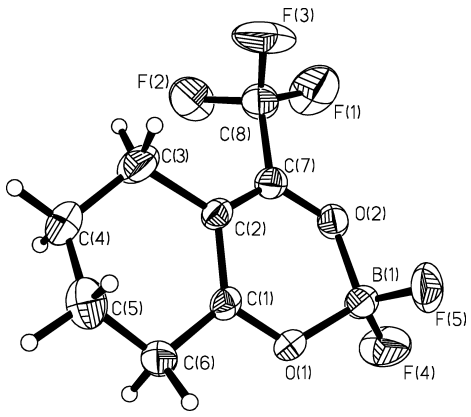


Fig. 1. Molecular structure of compound **3**, with displacement ellipsoids at the 50 % probability level. The alternative sites of the disordered tetramethylene moiety [atoms C(40) and C(50)] are not depicted for clarity reasons. Selected bond lengths of **3** (pm): C(1)–O(1) 129.0(4), C(1)–C(2) 141.3(4), C(1)–C(6) 147.0(5), C(2)–C(7) 136.2(5), C(2)–C(3) 152.0(4), C(7)–O(2) 130.3(4), B(1)–F(4) 134.6(5), B(1)–O(1) 148.2(5), B(1)–O(2) 149.8(4). Selected bond angles (deg): O(1)–C(1)–C(2) 121.4(3), O(1)–C(1)–C(6) 115.0(3), C(7)–C(2)–C(1) 115.8(3), C(7)–C(2)–C(3) 124.2(3), O(2)–C(7)–C(2) 125.4(3), O(2)–C(7)–C(8) 111.2(3), F(4)–B(1)–O(1) 109.4(3), F(4)–B(1)–O(2) 108.4(3), O(1)–B(1)–O(2) 109.0(3), C(1)–O(1)–B(1) 122.5(3), C(7)–O(2)–B(1) 118.9(3).

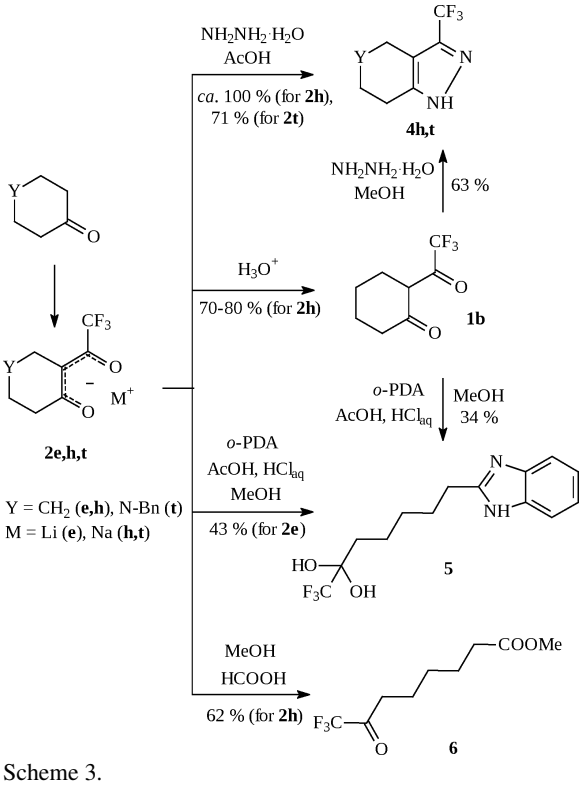
The boron chelate **3** was synthesized in 77 % yield *via* reaction of 2-(trifluoroacetyl)cyclohexanone (**1b**) with boron trifluoride ethyl etherate (Scheme 1).

An X-ray single crystal investigation of compound **3** revealed a bicyclic structure with a tetrahedrally four-coordinated boron atom (Fig. 1), in accordance with earlier findings for related compounds [24 – 27]. The boron atom is centrally located between both oxygen atoms [B(1)–O(1) 148.2(5) and B(1)–O(2) 149.8(4) pm]. The atoms C(3), C(6), C(1), C(2), C(7), O(1) and O(2) are almost co-planar (mean deviation from the plane 5.8 pm). The atoms C(4) and C(5) occupy positions on opposite sides of this plane (with 45.7 and 13.2 pm displacement, respectively) causing a twisted conformation of the carbocycle. There is a disorder at the carbocycle with two different conformations at both middle carbon atoms of the tetramethylene moiety. Similar to BF_2 derivatives of related cyclic 1,3-dicarbonyl compounds [26], the six-membered heterocycle of **3** adopts an envelope conformation with the boron atom 38.0 pm out of the mean plane. Interestingly, for the BF_2 chelates of benzoylacetones, the 1,3,2-dioxaborine ring was found to be nearly planar [27]. A special attention should be paid to the essential equalization of C(1)–O(1) and C(7)–O(2) [129.0(4) *vs.* 130.3(4) pm], and of C(1)–C(2) and C(2)–C(7) [141.3(4) *vs.* 136.2(5) pm] in **3**, compared to the "ideal" values for C=O, C–O, C=C, and C–C bonds [28]. This equalization is typical for highly delocalized keto-enol systems [28, 29]. The degree of electron density delocalization in the enolone backbone can be estimated by the degree of equalization of bond lengths, and the Q value (the sum of the differences of C=O, C–O and C=C, C–C bond lengths) of -6.4 in the case of **3** represents considerable delocalization ($Q = 0$ corresponds to complete delocalization, whereas $Q = \pm 32$ corresponds to a completely localized enolone system [28]).

The ^{19}F NMR spectrum of **3** features two signals of fluorinated moieties in a 3 : 2 intensity ratio. In addition to the signal of the CF_3 group ($\delta_F = -70.82$ ppm) two singlets of intensity 1 : 4 were found at -137.17 and -137.18 ppm, like for other 1,3,2-dioxaborines [25]. This pattern reflects the natural abundance of the two boron isotopes, the signal of the $^{10}BF_2$ moiety appearing at lower field.

Their availability and preparative handling convenience (when compared to the frequently liquid corresponding 1,3-dicarbonyls) are not the only advantageous features of compounds **2**. We have found that sometimes they are more synthetically preferable to the conjugated 1,3-dicarbonyls **1**. From the chemical point of view, the results of the reactions are mostly the same. As a rule, the reactions are carried out in acids as solvents, *i. e.*, the 1,3-dicarbonyl compounds are generated *in situ*. Nevertheless, the higher yields of products as well as the preparative facility prompt one to use compounds **2**.

Indeed, 2-hydroxy-2-(trifluoromethyl)pyrane is formed in a better yield starting from the sodium salt of α-(trifluoroacetyl)-δ-valerolactone than from the corresponding β-ketoester [13]. Cyclocondensation of 1,3-diketones with hydrazines is a conventional synthetic route to pyrazoles, *e. g.*, in the case **1b** the pyrazole **4h** is formed in less than 50 % overall yield (referring to the starting cyclohexanone [11, 22]). Use of sodium salt **2h** allowed us to obtain compound **4h** in 70 % overall yield in a very simple two-step reaction sequence (Scheme 3). In the case of sodium salt **2t** such direct comparison with the conjugated 1,3-diketone was not possible: its synthesis *via* acidification of **2t** failed, probably due to the presence of a basic center in the cyclic part of the molecule in addition to the acidic 1,3-dicarbonyl

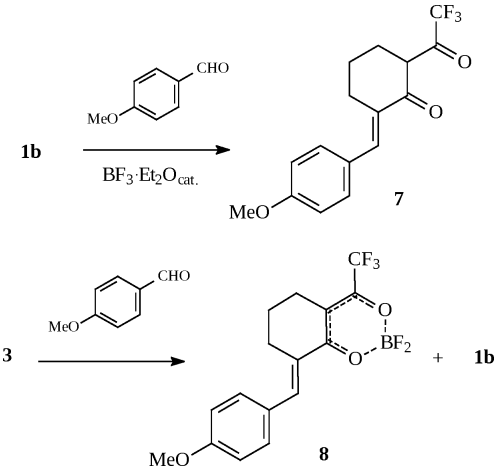


Scheme 3.

moiety. Treatment of an acetic acid solution of **2t** with hydrazine hydrate provided the bicyclic compound **4t** in 71 % yield (Scheme 3). In the framework of this synthetic methodology, the salt **2t** is indispensable for the preparation of **4t**.

Another advantageous example for the preparative application of enolates **2** is the ring opening of the 2-(trifluoroacetyl)cyclohexanone backbone upon treatment of the corresponding salt with *o*-phenylenediamine (*o*-PDA) or methanol under acidic conditions (Scheme 3). This procedure gives access to the highly promising [30] trifluoromethylated 1,7-ketoester **6** in a simple and convenient two-step procedure starting from cyclohexanone. In addition to the preparative advantages, in the case of the reaction with *o*-PDA the yield of the imidazole **5** was somewhat higher starting from salt **2e** rather than from 2-(trifluoroacetyl)cyclohexanone [10]: 43 *vs*. 34 %.

In order to elucidate the role of $BF_3 \cdot Et_2O$ in the course of the condensation of 1,3-diketones **1** with (het)aromatic aldehydes [12], we have studied the reaction of boron chelate **3** with anisaldehyde (Scheme 4). While the reaction of 1,3-diketone **1b** in the presence of catalytic amounts of $BF_3 \cdot Et_2O$ delivered the arylidene derivative **7** in 61 % yield [12], a mixture was obtained in the case of **3**, where both starting compounds (even after the reaction being maintained for 78 h), **1b** and 1,3,2-dioxaborine **8** (an insignificant amount) could be identified by ^1H and ^{19}F NMR spectroscopy. This fact indicates clearly that the Lewis acid activates the aldehyde toward nucleophilic attack of **1**, and that the formation of a boron chelate of type **3** is not a crucial step of the reaction.



Scheme 4.

Conclusion

In summary, a wide range of salts and chelate complexes of fluorinated cyclic 1,3-diketones and 1,3-ketoesters was prepared starting both from the corresponding 1,3-dicarbonyl compounds or from their precursors – cyclic ketones or lactones. The compounds obtained were shown to be promising reaction partners in organofluorine and heterocyclic chemistry. From the synthetic point of view, the alkali enolates are precursors of the corresponding 1,3-dicarbonyls, hence, their application instead of 1,3-dicarbonyls is methodologically reasonable and gives comparable results.

Experimental Section

General information: Melting and boiling points (m. p., b. p.) are uncorrected. NMR spectra, measured at 22 – 23 °C: Tesla BS-567A spectrometer [100.0 MHz (^1H)], Tesla BS-587A spectrometer [80.0 MHz (^1H)], Bruker DPX-200 spectrometer [200.1 (^1H), 188.3 MHz (^{19}F)]; chemical shifts (δ) in parts per million (ppm), coupling constants (J) in Hz, Me_4Si (^1H) and CCl_3F (^{19}F) as references. ^1H NMR chemical shifts in $CDCl_3$ solutions are referenced to the signal

at 7.25 ppm (residual $CHCl_3$), in [D_6]DMSO, [D_6]acetone, and CD_3OD to the central line of the solvent signal at δ = 2.50, 2.05 and 3.31 ppm, respectively. Mass spectra (FAB, Xe, 8 keV) were recorded on a Finnigan MAT-8200 spectrometer. Elemental analyses: Institute of Organic Synthesis, Ural Branch, Russian Academy of Sciences, Ekaterinburg, Russian Federation, and Mikroanalytisches Labor Beller, Göttingen, Germany. The IR spectra were recorded on a Specord-75 IR instrument on suspensions in Nujol (film). 2-(Trifluoroacetyl)cyclopentanone, 2-(trifluoroacetyl)cyclohexanone [21, 22], 2-(2,2,3,3-tetrafluoropropanoyl)cyclohexanone [9] and 2-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptanoyl)cyclohexanone [30] were prepared by a Claisen-type condensation of a cycloalkanone and a suitable fluorinated ester in the presence of NaOMe or LiH [6]. All other chemicals are commercially available and were used as purchased unless otherwise specified. Reactions in dried solvents (hexane distilled from phosphorus pentoxide, diethyl ether and benzene distilled from sodium/benzophenone ketyl) were performed in oven-dried glassware under a static nitrogen atmosphere.

*Copper(II) bis-[2-(trifluoroacetyl)cyclopentanonate] (**2a**)*

A mixture of cyclopentanone (15.0 g, 179 mmol) and trifluoroacetic acid ethyl ester (28.0 g, 200 mmol) was added dropwise to a well stirred suspension of potassium *tert*-butoxide (20.0 g, 179 mmol) in diethyl ether (250 mL). After the exothermic reaction, the brown homogeneous mixture was stirred at r. t. for 16 h, cooled to 0 °C, and treated with 10 % sulfuric acid (175 mL). The mixture was stirred for 10 min, and the organic layer was separated. After extraction with diethyl ether (3 × 15 mL) the combined organic layers were dried over $MgSO_4$ and concentrated to 80 mL. The solution of crude 2-(trifluoroacetyl)cyclopentanone **1a** was treated with a solution of $Cu(OAc)_2 \cdot H_2O$ (20.0 g, 100 mmol) in a mixture of acetic acid (50 mL) and water (250 mL). The mixture was stirred for 1 h and the organic layer was separated. After extraction with diethyl ether (4 × 30 mL) the combined organic layers were washed with water (20 mL) and evaporated. The solid residue was dissolved in ethanol, precipitated by addition of water at 0 °C and dried *in vacuo* to afford **2a** as a green powder, yield 16.5 g (44 %), m. p. 170 – 174 °C (lit.: 175 – 176 °C [22]).

*Copper(II) bis-[2-(trifluoroacetyl)cyclohexanonate] (**2b**)*

A solution of 2-(trifluoroacetyl)cyclohexanone **1b** (1.5 g, 7.7 mmol) in diethyl ether (20 mL) was added to a stirred solution of $Cu(OAc)_2 \cdot H_2O$ (0.8 g, 3.8 mmol) in water (25 mL). The mixture was stirred for 30 min at r. t., and the organic layer was separated. After extraction with diethyl ether (3 × 5 mL) the combined organic layers were washed with water (5 mL) and evaporated. The solid product was precipitated with water from the methanol solution twice and dried *in vacuo* to afford **2b** as a grayish-green powder, yield 1.7 g (*ca.* 100 %), m. p. 180 – 182 °C (lit.: 182 – 182.5 °C [22]). An analytical sample was recrystallized from methanol / water (1 : 1 by volume). – IR: ν = 1575 (conjugated C=O) cm^{-1}. – $C_{16}H_{16}CuF_6O_4$ (449.8): calcd. C 42.72, H 3.59, F 25.34; found C 42.88, H 3.58, F 25.78.

*Nickel(II) bis-[2-(trifluoroacetyl)cyclohexanonate] trihydrate (**2c**)*

A solution of **1b** (1.50 g, 7.7 mmol) in diethyl ether (10 mL) was added to a stirred solution of $Ni(OAc)_2 \cdot 4H_2O$ (0.94 g, 3.8 mmol) in water (10 mL). The mixture was stirred for 4 h at r. t., and the organic layer was separated. After extraction with diethyl ether (3 × 5 mL) the combined organic layers were washed with water (5 mL) and evaporated. The solid residue was precipitated with water from acetone solution and dried *in vacuo* to afford **2b** as a green powder, yield 0.70 g (42 %), m. p. 165 – 168 °C. An analytical sample was recrystallized from methanol / water (1 : 1 by volume). – IR: ν = 1590 (conjugated C=O), 3050 – 3650 (H_2O) cm^{-1}. – ^1H NMR (80.0 MHz, [D_6]DMSO): δ = −11.6, 0.4, 1.1, 11.3 (4 br.s, 4 × 2 H, $4CH_2$), 3.3 (br.s, 6 H, $3H_2O$). – $C_{16}H_{16}F_6NiO_4 \cdot 3H_2O$ (499.0): calcd. C 38.51, H 4.44, F 22.84; found C 38.85, H 4.19, F 22.49.

*Copper(II) bis-[2-(2,2,3,3-tetrafluoropropanoyl)cyclohexanonate] (**2d**)*

A solution of 2-(2,2,3,3-tetrafluoropropanoyl)cyclohexanone (1.0 g, 4.4 mmol) in diethyl ether (20 mL) was added to a stirred solution of $Cu(OAc)_2 \cdot H_2O$ (0.44 g, 2.2 mmol) in water (20 mL). The mixture was stirred for 30 min at r. t., and the organic layer was separated. After extraction with diethyl ether (3 × 5 mL) the combined organic layers were washed with water (5 mL) and evaporated. The solid residue was recrystallized from toluene to afford **2d** as a grayish-green powder, yield 0.80 g (71 %), m. p. 166.5 – 167.5 °C. – IR: ν = 1570 (conjugated C=O) cm^{-1}. – $C_{18}H_{18}CuF_8O_4$ (513.9): calcd. C 42.07, H 3.53, F 29.58; found C 42.51, H 3.39, F 29.97.

*Lithium 1,3-diketonates **2k**, **l**, **q** – **s**. General Procedure A*

To a mechanically stirred suspension of lithium hydride (1.44 g, 0.18 mol) in hexane (for **2k**, 170 mL) or benzene (for **2l**, **q** – **s**, 300 – 500 mL) a mixture of ketone (0.16 mol) and fluorinated carboxylic acid ester (**2k**: HCF_2COOMe, **2l**: C_3F_7COOMe, 0.18 mol) or a solution of ketone (0.16 mol) and fluorinated carboxylic acid ester (**2q**, **s**: CF_3COOEt, **2r**: C_2F_5COOMe, 0.18 mmol) in benzene (50 – 300 mL) was added dropwise within 1 h. Several drops of dried methanol or ethanol, respectively, were added to start an exothermic

reaction (reflux condenser). The mixture was stirred either at ambient temperature (**2k**: for 48 h), or heated to reflux (**2l**: for 3 h, **2q**: 20 h, **2r**: 16 h, **2s**: 2 h) followed by stirring for further several hours (**2l**: for 16 h, **2q**: 1 h, **2r**: 1 h, **2s**: 12 h) at ambient temperature. The precipitate was filtered off, washed with pentane (2 × 70 mL) and dried *in vacuo* to afford salts **2** (**2k**,**l**,**s**: white powders, **2q**,**r**: yellow powders).

*Lithium 2-(difluoroacetyl)cyclohexanonate (**2k**)*

Yield: 75 %, m. p. > 230 °C (dec.) – IR: ν = 1610 (conjugated C=O) cm^{-1}. – ^1H NMR (100.0 MHz, CD_3OD): δ = 1.41 – 2.82 (m, 8 H, $4CH_2$), 5.70 (t, $^2J_{H,F}$ = 55.6 Hz, 1 H, CF_2H).

*Lithium 2-(perfluorobutanoyl)cyclohexanonate (**2l**)*

Yield: 75 % [after recrystallization from toluene / THF (3 : 1 by volume)], m. p. > 280 °C (dec.) – IR: ν = 1605 (conjugated C=O) cm^{-1}. – ^1H NMR (80.0 MHz, [D_6]DMSO): δ = 1.45 – 1.81 (m, 4 H, $2CH_2$), 1.99 – 2.48 (m, 4 H, $2CH_2$). – $C_{10}H_8F_7LiO_2$ (300.1): calcd. C 40.02, H 2.69, F 44.31; found C 40.43, H 2.43, F, 44.03.

*Lithium 3-(trifluoroacetyl)chromanonate (**2q**)*

Yield: 83 %, m. p. > 230 °C. – ^1H NMR (200.1 MHz, [D_6]acetone): δ = 4.98 (s, 2 H, CH_2), 6.88 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H, 8-H), 6.99 (dd, $^3J_{H,H} \approx 7.3$, $^3J_{H,H} \approx 7.3$ Hz, 1 H, 6-H), 7.39 (ddd, $^3J_{H,H}$ = 8.3, $^3J_{H,H}$ = 7.1, $^4J_{H,H}$ = 1.0 Hz, 1 H, 7-H), 7.89 (dd, $^3J_{H,H}$ = 7.8, $^4J_{H,H}$ = 2.0 Hz, 1 H, 5-H). – ^{19}F NMR (188.3 MHz, [D_6]acetone): δ = −71.0 (t, $^5J_{F,H}$ = 1.4 Hz).

*Lithium 3-(pentafluoropropanoyl)thiochromanonate (**2r**)*

Yield: *ca.* 100 %, m. p. > 230 °C. – ^1H NMR (200.1 MHz, [D_6]acetone): δ = 3.85 (t, $^5J_{H,F}$ = 1.4 Hz, 2 H, CH_2), 7.19 (ddd, $^3J_{H,H}$ = 7.7, $^3J_{H,H}$ = 5.7, $^4J_{H,H}$ = 2.8 Hz, 1 H, 6(7)-H), 7.24 – 7.35 (m, 2 H, 7(6), 8-H), 8.03 (ddd, $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.4, $^5J_{H,H}$ = 0.8 Hz, 1 H, 5-H). – ^{19}F NMR (188.3 MHz, [D_6]acetone): δ = −114.5 (t, $^5J_{F,H}$ = 1.3 Hz, 2 F, CF_2), −82.6 (s, 3 F, CF_3).

*Lithium 3-(trifluoroacetyl)indanonate (**2s**)*

Yield: *ca.* 100 %, m. p. > 220 °C. – ^1H NMR (200.1 MHz, [D_6]acetone + [D_6]DMSO, 4 + 1 by volume): δ = 3.73 (q, $^5J_{H,F}$ = 1.5 Hz, 2 H, CH_2), 7.32 – 7.41 (m, 1 H, Ar-H), 7.45 – 7.51 (m, 2 H, Ar-H), 7.69 (unresolv. ddd, $^3J_{H,H}$ = 7.4 Hz, 1 H, 7-H). – ^{19}F NMR (188.3 MHz, [D_6]acetone + [D_6]DMSO, 4 + 1 by volume): δ = −73.5 (t, $^5J_{F,H}$ = 1.2 Hz).

*Lithium 1,3-diketonates **2e** – **g**. General Procedure B*

A solution of the 2-(polyfluoroacyl)cyclohexanone **1** (30 mmol) in benzene (5 mL) was added carefully to a well stirred suspension of finely powdered LiH (0.25 g, 30 mmol) in benzene (15 mL). The mixture was stirred for 1 h at r. t., the precipitate was filtered off, washed with hexane (10 mL) and dried *in vacuo* to afford salts **2e** – **g** as white powders.

*Lithium 2-(trifluoroacetyl)cyclohexanonate (**2e**)*

Yield 83 % [after recrystallization from toluene / acetone (3 : 1 by volume)], m. p. > 250 °C (dec.) – IR: ν = 1610 (conjugated C=O) cm^{-1}. – ^1H NMR (200.1 MHz, [D_6]DMSO): δ = 1.40 – 1.80 (m, 4 H, $2CH_2$), 2.12 (t, $^3J_{H,H}$ = 5.9 Hz, 2 H, CH_2), 2.35 – 2.45 (m, 2 H, CH_2). – ^{19}F NMR (188.3 MHz, [D_6]DMSO): δ = −69.68 (s, $^5J_{F,H}$ = 1.6 Hz). – $C_8H_8F_3LiO_2 \cdot 1/3\ H_2O$ (206.1): calcd. C 46.62, H 4.24; found C 46.72, H 4.05.

*Lithium 2-(2,2,3,3-tetrafluoropropanoyl)cyclohexanonate (**2f**)*

Yield: *ca.* 100 %, m. p. 240 – 242 °C (dec.) – IR: ν = 1610 (conjugated C=O) cm^{-1}. – ^1H NMR (100.0 MHz, [D_6]acetone): δ = 1.49 – 1.73 (m, 4 H, $2CH_2$), 2.18 – 2.34, 2.45 – 2.68 (both m, 2 × 2 H, $2CH_2$), 6.44 (tt, $^2J_{H,F}$ = 53.1, $^3J_{H,F}$ = 5.9 Hz, 1 H, CF_2H).

*Lithium 2-(perfluoroheptanoyl)cyclohexanonate (**2g**)*

Yield: *ca.* 100 %, m. p. > 220 °C (dec.) – IR: ν = 1610 (conjugated C=O) cm^{-1}. – ^1H NMR (100.0 MHz, [D_6]acetone): δ = 1.49 – 1.72 (m, 4 H, $2CH_2$), 2.16 – 2.36, 2.42 – 2.63 (both m, 2 × 2 H, $2CH_2$).

*Barium bis-[2-(trifluoroacetyl)cyclohexanonate] (**2i**)*

To a solution of **1b** (1.5 g, 7.7 mmol) in diethyl ether (20 mL) barium oxide (0.6 g, 3.8 mmol) was added. The mixture was stirred for 30 min at r. t., and the solvent was removed *in vacuo* to leave **2i** as a white solid, yield 2.0 g (*ca.* 100 %), m. p. > 250 °C. – IR: ν = 1610 (conjugated C=O) cm^{-1}. – ^1H NMR (100.0 MHz, CD_3OD): δ = 1.61 – 1.72, 2.16 – 2.46 (both m, 2 × 4 H, $4CH_2$). – $C_{16}H_{16}BaF_6O_4$ (523.6): calcd. C 36.70, H 3.08, F 21.77; found C 36.72, H 3.30, F 21.86.

*Sodium salts **2h**, **m** – **p**, **t**. General Procedure A*

To a well stirred suspension of sodium methoxide (5.4 g, 0.1 mol) in diethyl ether (250 mL) a mixture of cyclic ketone or lactone (0.1 mol) and fluorinated ester (**2h**, **o**, **p**, **t**: CF_3COOEt, **2m**: $CF_3CF(OMe)COOMe$, **2n**: HCF_2COOMe, 0.1 mmol) was added dropwise within 30 min. The mixture was either stirred at ambient temperature for 20 h and then heated to reflux for 16 h (**2m**), or heated to reflux (**2n**: for 12 h, **2o**: for 7 h) followed by stirring for further several h (**2n**: 1 h, **2o**: 16 h), or stirred at r. t. for 20 h (**2h**, **p**, **t**).

The reaction mixture was cooled to −30 °C. The solid was separated [by filtration (**2h**, **m**, **o**, **p**, **t**) or decantation (**2n**)], washed with pentane (2 × 70 mL) and dried *in vacuo* to afford salts **2h**, **m** – **p**, **t** as white powders.

*Sodium 2-(trifluoroacetyl)cyclohexanonate (**2h**)*

Yield: 70 %, m. p. 294 – 296 °C (dec.) – IR: ν = 1615 (conjugated C=O) cm^{-1}. – ^1H NMR (200.1 MHz, [D$_6$]acetone): δ = 1.47 – 1.71 (m, 4 H, 2CH$_2$), 2.14 (t, $^3J_{H,H}$ = 6.1 Hz, 2 H, CH$_2$), 2.36 – 2.51 (m, 2 H, CH$_2$). – ^{19}F NMR (188.3 MHz, [D$_6$]acetone): δ = −71.2 s. – $C_8H_8F_3NaO_2 \cdot 1/3\ H_2O$ (222.1): calcd. C 43.26, H 3.93; found C 43.25, H 4.10.

*Sodium 2-(2,3,3,3-tetrafluoro-2-methoxypropanoyl)cyclohexanonate (**2m**)*

Yield: 22 %, m. p. 228 – 230 °C (dec.) – ^1H NMR (200.1 MHz, [D$_6$]DMSO): δ = 1.39 – 1.65 (m, 4 H, 2CH$_2$), 2.04 (t, $^3J_{H,H}$ = 6.8 Hz, 2 H, CH$_2$), 2.36 – 2.48 (m, 2 H, CH$_2$), 3.44 (s, 3 H, Me). – ^{19}F NMR (188.3 MHz, [D$_6$]DMSO): δ = −126.8 (s, 1 F, *CF), −80.0 (s, 3 F, CF$_3$). – MS (FAB, 4-NO$_2$-C$_6$H$_4$-CH$_2$OH (NBA), negative): *m/z* (%) = 255 (20) [A]$^-$, 153 (100) [NBA]$^-$. – $C_{10}H_{11}F_4NaO_3$ (278.2): calcd. C 43.18, H 3.99, F 27.32; found C 43.05, H 3.89, F 27.20.

*Sodium α-(difluoroacetyl)-γ-butyrolactonate (**2n**)*

Yield: 78 %, m. p. > 240 °C. – ^1H NMR (200.1 MHz, [D$_6$]DMSO): δ = 2.57 – 2.65 (m, 2 H, CH$_2$), 3.98 (t, $^3J_{H,H}$ = 8.1 Hz, 2 H, OCH$_2$), 7.07 (t, $^2J_{H,F}$ = 56.7 Hz, 1 H, CF$_2$H). – ^{19}F NMR (188.3 MHz, [D$_6$]DMSO): δ = −126.8 (d, $^2J_{F,H}$ = 56.9 Hz). – MS (FAB, glycerine, negative): *m/z* (%) = 163 (58) [A]$^-$, 135 (100) [A–CO]$^-$.

*Sodium α-(trifluoroacetyl)-γ-butyrolactonate (**2o**)*

Yield: 51 % [after recrystallization from hexane-ethanol (4 + 1 by volume)], m. p. > 220 °C (subl.) – ^1H NMR (200.1 MHz, [D$_6$]acetone): δ = 2.86 – 2.94 (m, 2 H, CH$_2$), 4.10 (t, $^3J_{H,H}$ = 7.8 Hz, 2 H, OCH$_2$). – ^{19}F NMR (188.3 MHz, [D$_6$]acetone): δ = −73.0 (t, $^5J_{F,H}$ = 2.2 Hz). – $C_6H_4F_3O_3Na \cdot 1/3\ H_2O$ (210.1): calcd. C 34.30, H 2.23, F 27.13; found C 34.46, H 2.68, F 27.00.

*Sodium α-(trifluoroacetyl)-δ-valerolactonate (**2p**)*

Yield: 78 % [after recrystallization from ethanol-acetone (4 + 1 by volume)], m. p. > 240 °C. – ^1H NMR (200.1 MHz, [D$_6$]acetone): δ = 1.58 – 1.84, 2.32 – 2.57 (both m, 2 × 2 H, 2CH$_2$), 3.90 – 4.12 (m, 2 H, OCH$_2$). – ^{19}F NMR (188.3 MHz, [D$_6$]acetone): δ = −69.6 s.

*Sodium 1-benzyl-3-(trifluoroacetyl)piperidin-4-onate (**2t**)*

Yield: 41 %, m. p. > 230 °C. – ^1H NMR (200.1 MHz, [D$_6$]acetone): δ = 2.24 (t, $^3J_{H,H}$ = 6.4 Hz, 2 H, CH$_2$), 2.55 (t, $^3J_{H,H}$ = 6.1 Hz, 2 H, CH$_2$), 3.35, 3.57 (both s, 2 × 2 H, 2CH$_2$), 7.17 – 7.39 (m, 5 H, Ph). – ^{19}F NMR (188.3 MHz, [D$_6$]acetone): δ = −71.8 (t, $^5J_{F,H}$ = 1.4 Hz). – ^{19}F NMR (188.3 MHz, CDCl$_3$): δ = −72.3 br.s.

*Sodium salt **2h**. Procedure B*

To a solution of **1b** (1.0 g, 5.2 mmol) in diethyl ether (10 mL) finely powdered sodium hydroxide (0.2 g, 5.2 mmol) was added. The mixture was stirred for 30 min at r. t., and the solvent was removed *in vacuo*. The white solid left was recrystallized from hexane / acetone (1 : 1 by volume) to afford **2h**, yield 0.9 g (80 %).

*Morpholinium 2-(trifluoroacetyl)cyclopentanonate (**2j**)*

To a well stirred solution of **1a** (1.0 g, 5.6 mmol) in hexane (10 mL) a solution of morpholine (0.49 g, 5.6 mmol) in hexane (5 mL) was added carefully at 0 °C. After stirring for 30 min at this temperature the precipitate was filtered off, washed with cold hexane (2 × 5 mL) and dried *in vacuo* to afford **2j** as colorless crystals (yield 0.90 g, 60 %), m. p. 66 – 67 °C. – ^1H NMR (200.1 MHz, CDCl$_3$): δ = 1.76 – 1.96 (m, 2 H, CH$_2$), 2.24 (t, $^3J_{H,H}$ = 8.0 Hz, 2 H, CH$_2$), 2.68 – 2.80 (m, 2 H, CH$_2$), 3.07, 3.71 (both t, $^3J_{H,H}$ = 4.4 Hz, 2 × 4 H, 4CH$_2$), 9.5 (br.s, 2 H, NH$_2$). – ^{19}F NMR (188.3 MHz, CDCl$_3$): δ = −74.01 s.

*5,6,7,8-Tetrahydro-4-(trifluoromethyl)benzo-[d]-1,3,2-dioxaborine (**3**)*

To a well stirred solution of **1b** (1.94 g, 10 mmol) in CH$_2$Cl$_2$ (40 mL) BF$_3$·Et$_2$O (1.41 g, 10 mmol) as added carefully at r. t. After stirring for 10 min the solvent was removed *in vacuo*. The residue (a brown oil which solidified over night) was purified by recrystallization from heptane to afford **3** as colorless crystals, yield 1.85 g (77 %), m. p. 94 – 95 °C. – IR: ν = 1595 (conjugated C=O) cm^{-1}. – ^1H NMR (200.1 MHz, CDCl$_3$): δ = 1.74 – 1.95 (m, 4 H, 2CH$_2$), 2.62 (t, $^3J_{H,H}$ = 5.6 Hz, 2 H, CH$_2$), 2.79 (t, $^3J_{H,H}$ = 6.4 Hz, 2 H, CH$_2$). – ^{19}F NMR (188.3 MHz, CDCl$_3$): δ = −137.18, −137.17 (both s, 4 : 1 integral ratio, 2 F, BF$_2$), −70.82 (t, $^5J_{F,H}$ = 1.5 Hz, 3 F, CF$_3$). – $C_8H_8BF_5O_2$ (242.0): calcd. C 39.71, H 3.33, F 39.26; found C 39.87, H 3.11, F 39.60.

*4,5,6,7-Tetrahydro-3-trifluoromethyl-1H-indazole (**4h**)*

To a stirred solution of **2h** (3.2 g, 15 mmol) in glacial acetic acid (20 mL) 98 % hydrazine hydrate (1.2 g, 24 mmol) was added carefully. The mixture was stirred at 65 °C (bath temperature) for 16 h. The reaction mixture (a colorless solution) was concentrated *in vacuo* to 3/4 of its volume, and the residue was mixed with water (50 mL). The white precipitate was filtered off, washed with water (15 mL) and air-dried to afford 3.0 g (*ca.* 100 %) of analytically pure pyrazole **4h** [11].

*5-Benzyl-4,5,6,7-tetrahydro-3-(trifluoromethyl)pyrazolo-[4,3-c]-pyridine (**4t**)*

To a stirred solution of **2t** (10.0 g, 33 mmol) in glacial acetic acid (200 mL) 98 % hydrazine hydrate (3.7 g, 74 mmol) was added carefully. The mixture was stirred at 55 °C (bath temperature) for 20 h to give a colorless solution which was concentrated *in vacuo*. The oily residue was dissolved in water (300 mL) and treated with 10 % NaOH solution to pH = 12. After extraction with CH_2Cl_2 (5 × 30 mL) the combined organic layers were washed with brine (20 mL), dried over $MgSO_4$ and the solvents evaporated. The oily residue solidified to give a practically pure pyrazole **4t** as yellowish waxy crystals, yield 6.5 g, (71 %). – ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 2.76 (s, 4 H, $2CH_2$), 3.61, 3.73 (both s, 2 × 2 H, $2CH_2$), 7.27 – 7.38 (m, 5 H, Ph), 12.3 (br.s, 1 H, NH). – ^{19}F NMR (188.3 MHz, $CDCl_3$): δ = −61.71 s. – $C_{14}H_{14}F_3N_3$ (281.3): calcd. C 59.78, H 5.02; found C 59.89, H 5.17.

*2-(7,7,7-Trifluoro-6-oxoheptyl)benzimidazole hydrate (**5**)*

To a stirred mixture of **2e** (2.6 g, 13 mmol) and *ortho*-phenylenediamine (1.5 g, 14 mmol) in methanol (20 mL) acetic acid (2 mL) was added. After stirring for 5 min conc. hydrochloric acid (10 mL) was added, and the mixture was stirred for further 20 h. The resulting yellow solution with a white precipitate was poured into water (150 mL) and treated with 33 % NaOH solution carefully until pH = 10 was reached. The precipitate was filtered off, washed with water (20 mL) and dried. Recrystallization from toluene / ethyl acetate (10 : 1 by volume) afforded **5**, yield 1.7 g (43 %) as a greyish powder [10].

*Methyl 8,8,8-trifluoro-7-oxooctanonate (**6**)*

To a stirred suspension of **2h** (6.6 g, 31 mmol) in dried methanol (50 mL) 98 % formic acid (0.98 g, 21 mmol) was added. The reaction mixture was stirred at r. t. for 24 h, poured onto water (200 mL) and treated with 10 % H_2SO_4 to pH = 5. After extraction with CH_2Cl_2 (5 × 25 mL) the combined organic layers were dried over $MgSO_4$ and the solvent evaporated. The residue was distilled to afford ketoester **6** as a pale yellow liquid, yield 4.35 g (62 %), b. p. 210 – 214 °C (760 Torr). – ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.28 – 1.41 (m, 2 H, CH_2), 1.54 – 1.73 (m, 4 H, $2CH_2$), 2.28, 2.69 (both t, $^3J_{H,H}$ = 7.3 Hz, 2 × 2 H, $2CH_2$), 3.62 (3, 3 H, Me). – ^{19}F NMR (188.3 MHz, $CDCl_3$): δ = −79.83 s. – $C_9H_{13}F_3O_3$ (226.2): calcd. C 47.79, H 5.79; found C 47.50, H 5.55.

*Reaction of **3** with anisaldehyde*

To a stirred solution of **3** (0.80 g, 3.3 mmol) in diethyl ether anisaldehyde (0.45 g, 3.3 mmol) was added carefully. The mixture was stirred in a sealed flask at r. t. for 78 h. After evaporation of the volatiles *in vacuo* the waxy residue was investigated by ^{1}H and ^{19}F NMR to reveal a mixture (in 48 : 19 : 19 : 14 molar ratio, respectively) of anisaldehyde, **3**, 2-(trifluoroacetyl)cyclohexanone (**1b**) [21, 22], and 5,6,7,8-tetrahydro-2,2-difluoro-4-trifluoromethyl-8-(*E*)-(*p*-methoxybenzylidene)benzo[*d*]-1,3,2-dioxaborine **8**: ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.7 – 1.8, 2.5 – 2.7 (both m, 2 × 2 H, $2CH_2$), 2.85 (t, $^3J_{H,H}$ = 6.0 Hz, 2 H, CH_2), 3.88 (s, 3 H, OMe), 6.99, 7.60 (dd, AA′BB′ system, $J_{A,B}$ = $J_{A',B'}$ = 8.8 Hz, 4 H, Ar), 8.3 (unresolv. t, 1 H, =CH). – ^{19}F NMR (188.3 MHz, $CDCl_3$): δ = −140.46, −140.45 (both s, 4 : 1 integral ratio, 2 F, BF_2), −69.73 (s, 3 F, CF_3).

*X-Ray structure determination of **3***

Siemens-P4 diffractometer with graphite-monochromatized MoK_α radiation (λ = 71.073 pm) and the low-temperature device LT2. Diffraction-quality single crystals of **3** (colorless scales, 0.80 × 0.50 × 0.15 mm^3) were selected from an analytic sample; data collection at −100(2) °C. The structure was solved by Direct Methods and refined by full-matrix least-squares on F^2 with the SHELXL-97 program package [31]. All non-H atoms were refined anisotropically. The positions of the hydrogen atoms were calculated as a riding model.

Crystal and structure determination data: $C_8H_8BF_3O_2$ (241.95); monoclinic space group $P2_1/c$ with a = 1294.3(8), b = 765.3(7), c = 962.5(16) pm, β = 94.83(8)°, V = 0.9500(19) nm^3, D = 1.692 g cm^{-3}, Z = 4. Index ranges $-15 \le h \le 15$, $-9 \le k \le 1$, $-11 \le l \le 11$, 2θ range 3.10 – 24.99°, 3943 collected reflections, 1667 independent reflections, R_{int} = 0.0626, completeness to θ_{max} = 24.99°: 99.9 %. Data/restraints/parameters 1667/0/165, goodness-of-fit (F^2) 0.991, final R indices [$I \ge 2\sigma(I)$]: R_1 = 0.0573, wR_2 = 0.1442; R indices (all data): R_1 = 0.0957, wR_2 = 0.1646, residual difference electron density 0.261 and −0.275 e Å^{-3}.

CCDC 718414 contains the supplementary crystallographic data for compound **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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