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Reaction of 2-Methylene-1,3-dicarbonyl Compounds Containing a CF_3-Group with 1,3-Dienes

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Abstract—The Knoevenagel condensation of 1-substituted 4,4,4-trifluorobutan-1,3-diones with paraformaldehyde in the presence of cyclic and linear 1,3-dienes leads to Diels–Alder cycloadducts via in situ formation of the appropriate 2-methylene-1,3-dicarbonyl compounds **2**(**a**–**c**). In the reactions with linear 1,3-dienes, compounds **2**(**a**–**c**) react as dienophiles. In the case of the reactions with cyclic 1,3-dienes both normal and inverse demand Diels–Alder reactions take place.

Introduction

The chemistry of 1,1-disubstituted alkenes containing two electron withdrawing groups have received significant attention in recent years, compounds containing the sulfone,[1,2] sulfoxide,[3,4] cyano-[5,6] and carbonyl groups have been investigated. Due to the presence of two electron withdrawing groups these alkenes are very active Michael acceptors,[7] reacting with a wide range of 1,3-dienes[8] as well as with alkenes[9] and can act as *hetero*-dienes with alkyl-vinyl esters with the formation of dihydropyranes.[10] Many 1,1-disubstituted alkenes can be used as the perspective building blocks for the synthesis of natural products.

Introduction of fluorine into organic molecules often results in dramatic modification of their physical and chemical properties as well as of their biological activity profile.[11] It is not therefore surprising that the search for practical and high yielding methods for the preparation of fluorine-containing compounds has been an area of intensive activity in the past few decades.

CF_3-Ketones are known as valuable targets and their chemistry has been reviewed recently.[12,13] Study of the reactivity of the 2-methylene-1,3-dicarbonyl compounds containing trifluoroacetyl groups is an actual problem in organic synthesis due to the influence of the trifluoromethyl group on the reaction path as well as on the reactivity because of the very high electron withdrawing effect of the trifluoroacetyl moiety. Until recently no investigations had been done regarding the synthesis and reactivity of the 2-methylene-1,3-dicarbonyl compounds containing at least one CF_3CO group. Only the synthesis of trifluoroacetyl ethylene has been carried out, and it was found that this ketone dimerizes under the temperature of −30°C forming the Diels–Alder cycloadduct.[14]

We now report the investigation of the reactivity of the 2-methylene-1,3-dicarbonyl compounds containing the trifluoroacetyl group with various cyclic and linear 1,3-dienes. The experimental data obtained are in some cases unexpected, nevertheless, they are in good agreement with the frontier molecular orbital calculations made by the semi-empirical PM3 method.[15]

Results and Discussion

The Knoevenagel condensation of 1,3-dicarbonyl compounds with paraformaldehyde in the presence of various catalysts is a well known process.[16] For example, dialkyl methylidenemalonate can be prepared by this approach.[17] To study the reactivity of various 4,4,4-trifluoro-2-methylenebutane-1,3-diones (1-OEt, 1-Ph and 1-(2-thiophenyl) substituted) in the [2+4] cycloaddition reaction, we have investigated the Knoevenagel condensations of the substituted 4,4,4-trifluorobutan-1,3-diones with paraformaldehyde (Scheme 1) in the presence of cyclic and acyclic 1,3-dienes. The first step of the reaction is the formation of the corresponding 2-methylene-1,3-dicarbonyl compounds **2**(**a**–**c**). The next step is the Diels–Alder reaction. It should be noted that intermediate alkenes are very unstable and they cannot be isolated in pure form, however they are easily trapped with dienes. The reaction was carried out by heating a mixture of the diene, paraformaldehyde and 1,3-dione in a sealed tube at 100°C using acetic acid as solvent and $Cu(OAc)_2$ as catalyst.

Keywords: Diels–Alder reaction; *hetero*-dienes; α,β-unsaturated ketones; trifluoromethyl ketones; 2-methylene-1,3-dicarbonyl compounds.

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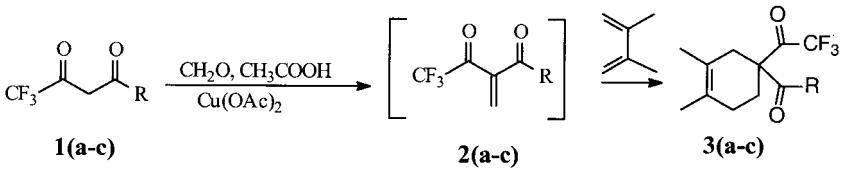


a: R = OEt
b: R = Ph
c: R = 2-Thienyl

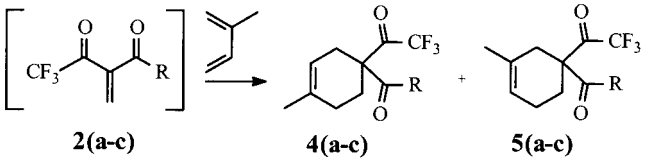
Scheme 1.

Table 1.

Products **3**	Yields (%)
a	67
b	57
c	59

cyclohexenes was formed. All three regents gave predominantly *para*-substituted products (Scheme 2, Table 2).

The reactions with cyclic 1,3-dienes such as cyclopentadiene and 1,3-cyclohexadiene proceed in a different way. The mixture of the normal Diels–Alder reaction products



a: R = OEt
b: R = Ph
c: R = 2-Thienyl

Scheme 2.

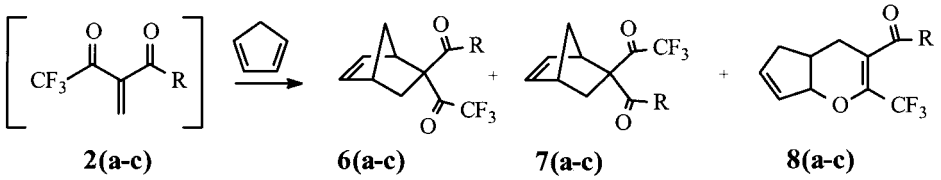
Table 2.

Products	Ratio of **4/5**[a] (%)	Yields (%)
a	83/17	68
b	86/14	57
c	90/10	63

[a] Ratio of isomers was determined by NMR spectroscopy.

We have performed for the first time the reaction of **2**(**a**–**c**) with acyclic dienes: 2,3-dimethylbut-1,3-diene and isoprene. The reaction with 2,3-dimethylbut-1,3-diene leads to the appropriate 1,1-disubstituted 3,4-dimethylcyclohex-3-ene (Scheme 1) in moderate yield (Table 1). In the case of the reaction with isoprene a mixture of *para*-**4**(**a**–**c**) and *meta*-isomers **5**(**a**–**c**) of the corresponding and products of inverse demand Diels–Alder reaction (due to the existence of the oxobut-1,3-diene fragment in the regents **2**)[15] were isolated (Scheme 3).

The formation of the *hetero*-Diels–Alder products is a rare type of cycloaddition of cyclic dienes with 1,1-diactivated alkenes. Cyclopentadiene is known as one of the most reactive dienes, nevertheless the significant amount of product **8** (which is the result of interaction between cyclopentadiene as a dienophile and trifluoroacetyl alkene as a *hetero*-diene) was obtained. Moreover the only type of reaction of cyclopentadiene with diketones **2b** and **2c** is the formation of pyrane derivatives. The reaction path depends upon the substituent in activated alkenes **2**. Diketone **2a** reacts with cyclopentadiene to form three possible isomers **6a**, **7a** and **8a**, with the predominance of **6a**. The reactions of **2**(**b**–**c**) with cyclopentadiene result



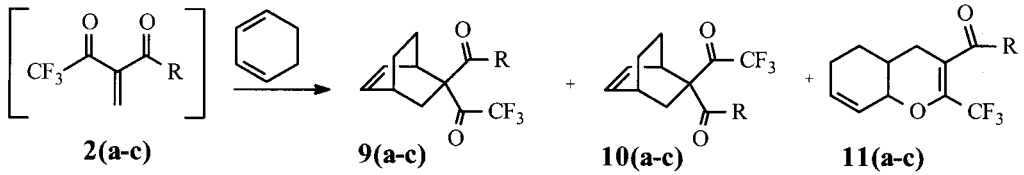
a: R = OEt
b: R = Ph
c: R = 2-Thienyl

Scheme 3.

Table 3.

Products	Ratio of isomers[a] **6/7/8** (%)	Isolated yields (%)
a	64/18/18	60
b	0/0/100	47
c	0/0/100	38

[a] Ratio of **6**(**a**–**c**)–**7**(**a**–**c**) isomers was determined by the NMR methods.



a: R = OEt
b: R = Ph
c: R = 2-Thienyl

Scheme 4.

Table 4.

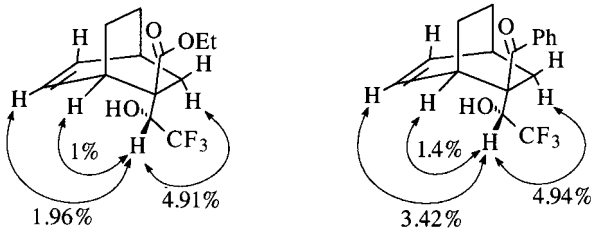
Products	Ratio of **9/10/11** (%)[a]	Isolated yields (%)
a	37/13/50	40% (**9a** and **10a**) and 40% (**11a**)
b	23/6/71	15% (**9b** and **10b**) and 37% (**11b**)
c	25/4/71	16% (**11b** and **11b**) and 41% (**11c**)

[a] Ratio of **9**(**a**–**c**)–**10**(**a**–**c**) isomers was determined by NMR methods.

only to the products of the *hetero*-Diels–Alder reactions **8**(**b**–**c**) and none of the normal Diels–Alder products were observed (Table 3).

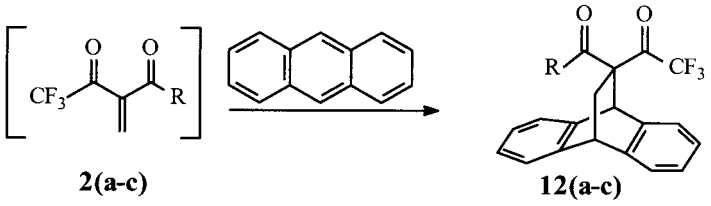
Considering the reaction of **2**(**a**–**c**) with cyclohex-1,3-diene (Scheme 4) a similar correlation takes place. The ratio of the cycloadducts of the normal Diels–Alder reaction **9**(**a**–**c**), **10**(**a**–**c**) and the products of the *hetero*-Diels–Alder reactions **11**(**a**–**c**) depends upon the substituent R (Table 4). In the case of more sterically hindered **2b** and **2c** pyrane derivative **11**(**b**–**c**) were preferentially isolated.

The orientation of the trifluoroacetyl group in the cycloadducts **9a/10a** and **9b/10b** was established by reduction of the products with lithium *t*-butoxy aluminum hydride to the corresponding alcohols. The resulting alcohols showed a NOE between the CF_3CH proton and the olefinic protons as expected.



The results of the NOE experiments show the stereochemistry of the main products **9a** and **9b** to have an *endo*-oriented CF_3CO group.

The reaction is sterically very sensitive. Studying the cycloaddition reaction with anthracene it was found that the yields of the products depend dramatically on the substituents of the reagent used. In the case of more hindered **2b** and **2c** (R=Ph or 2-thiophenyl) the corresponding products **12**(**b**–**c**) have been isolated in very poor yield while in the case of **2a** (R=OEt) the cycloadduct **12a** was isolated in 90% yield (Scheme 5, Table 5).



a: R = OEt
b: R = Ph
c: R = 2-Thienyl

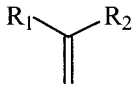
Scheme 5.

Table 5.

Products	Yields (%)
a	90
b	10
c	14

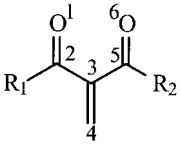
The reactions of **2a** with 9-methylanthracene and 9,10-dimethylanthracene proceed in a similar way to give the

Table 6.



Substituents R_1, R_2		LUMO (eV)
PhCO	CH_3CO	−0.67
PhCO	CF_3CO	−1.31
2-Thienoyl	CF_3CO	−1.36
COOEt	CF_3CO	−1.37
COOEt	CH_3CO	−0.73
CH_3CO	CH_3CO	−0.69
CN	COOEt	−0.91
COOEt	COOEt	−0.69
CN	CN	−1.11
$PhSO_2$	$PhSO_2$	−0.74
H	CF_3CO	−1.04
H	CN	−0.19
H	COOEt	−0.14
H	CHO	−0.19

Table 7.



Substituents R		LUMO coefficients at the atoms					
R_1	R_2	1	2	3	4	5	6
CF_3	OEt	−0.3848	0.4046	0.4119	−0.6621	0.1793	−0.1802
CH_3	OMe	−0.2998	0.3024	0.4754	−0.6810	0.2431	−0.2328
CF_3	Ph	−0.3727	0.3913	0.4101	−0.6579	0.2145	−0.2240
CH_3	Ph	−0.2856	0.2862	0.4648	−0.6685	0.2866	−0.2863

corresponding cycloadducts in high yield, in the case of 9-methylanthracene only *meta*-isomer was formed.

We have tried to explain the reactivity of the reagents **2** using semiempirical PM3 calculations. Frontier molecular orbital theory is one of the most successful approaches in the prediction of *regio*- and *endo–exo* selectivity for the Diels–Alder reactions.

The reaction of alkenes **2** with dienes is a diene HOMO–regent LUMO controlled process, both in the case of normal and inverse electron demand Diels–Alder cycloaddition. So the LUMO of the reagents **2**(**a**–**c**) has a very important value. We have calculated the LUMO for our new alkenes as well as for various 1,1-disubstituted and monosubstituted alkenes usually used as dienophiles. The results are given in Table 6. They show that there is dramatical difference between LUMO energies of CF_3 containing and non-fluorinated alkenes. The presence of the CF_3 group in the molecule results in the significant decreasing of the LUMO energy and CF_3 ketones are much more electron-deficient and reactive species. Usually these energies of standard dienophiles are about −0.2 to 1 eV, however the difference in LUMO between acrolein and trifluoromethyl analog is almost 0.8 eV (Table 6).

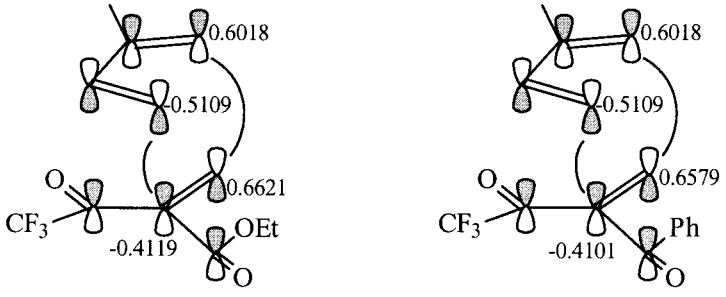
We have also tried to explain the *regio*- and *endo–exo* selectivity in the Diels–Alder reaction using the results of the calculations. *Regio*-selectivity in the interactions of **2**(**a**–**c**) with the isoprene, cyclopentadiene and cyclohexadiene can be considered from the LUMO orbital coefficient's point of view. For this reason LUMO coefficients were calculated by semiempirical PM3 method for **2**(**a**–**b**) as well as for dienes. The data obtained are given in Table 7.

The preferable formation of the *para*-isomers in the case of the reactions of **2**(**a**–**c**) with isoprene is in good agreement with *large–large* molecular orbitals overlapping in the transition state (Scheme 6).

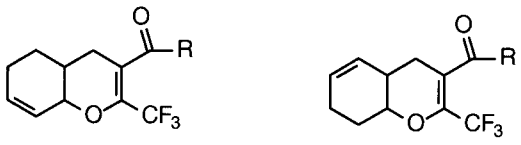
In the case of *hetero*-Diels–Alder reactions of **2**(**a**–**c**) with cyclic dienes the formation of the two *regio*-isomers is possible (Scheme 7).

Only isomers of type **11** were obtained, the *regio*-selectivity can be explained by the same *large–large* HOMO of diene-LUMO of the reagents overlapping in the transition state (Scheme 8).

Considering the LUMO of the **2**(**a**–**c**) we can see that LUMO coefficients at the oxygen of the trifluoroacetyl group are approximately two times greater than that of the oxygen of the neighboring carbonyl group, for this reason only the trifluoromethyl carbonyl group acts as an oxodiene component in the *hetero*-Diels–Alder reaction. As we have found in the reaction with cyclic 1,3-dienes the cycloadducts of normal Diels–Alder reaction have a preferably *endo*-oriented trifluoroacetyl moiety. It was difficult to predict such selectivity since we could not find any examples of similar reactions with cyclic dienes. Previously only cycloaddition reactions of β-alkoxy substituted CF_3 ketones with vinyl ethers have been described.[15] We

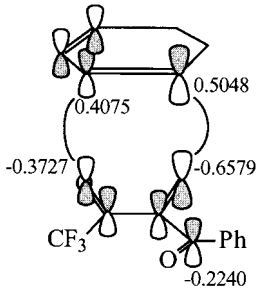


Scheme 6.

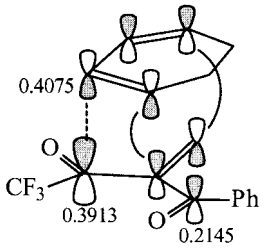


11(a-c)

Scheme 7.



Scheme 8.



Scheme 9.

propose that the *endo*-$COCF_3$ selectivity is connected with the secondary *p*-orbital interactions between π-system of the dienes and π-system of the carbonyl groups of the reagents. These interactions depend strongly upon the magnitude of the LUMO coefficients on the atoms of the carbonyl groups. Having two times greater LUMO coefficients at trifluoromethyl carbonyl group the secondary *p*-orbital interactions in the transition state are more probable between C_2 carbon of the reagents **2**(**a**–**c**) and π-system of the diene (Scheme 9) resulting in endo-$COCF_3$ stereochemistry.

The formation of pyrane derivatives can be explained also by sigmatropic rearrangement of normal Diels–Alder cycloadducts. To study this possibility we heated the mixtures of the products **9a/10a**, **6a/7a/8a**, **9b/10b** in acetic acid in the presence of $Cu(OAc)_2$. These mixtures do not undergo any change, we believe therefore that two parallel Diels–Alder reactions take place. Predominance of the *hetero*-Diels–Alder reactions in the case of **2**(**b**–**c**) is probably due to the aryl substituents in **2**(**b**–**c**) which destabilize the transition state for normal Diels–Alder reaction to give the more preferable *hetero*-Diels–Alder reaction (Scheme 9).

Thus we have investigated the preparation of 2-methylene-1,3-dicarbonyl compounds containing the CF_3-group and their reaction with different dienes have been studied. It was found that the 2-methylene-1,3-dicarbonyl compounds containing a CF_3 group are prone to react as oxo-butadienes to form *hetero*-Diels–Alder adducts. The chemo, regio and stereo-selectivity of the reaction was studied. The results were explained using semiempirical **PM3** calculations.

Experimental

NMR spectra were recorded on Varian VXR-400 spectrometers with TMS as an internal standard. The IR spectra were obtained with UR-20 spectrometer as films. All solvents used were dried and distilled according to standard procedures.

Preparation of Diels–Alder cycloadducts 3–11 (a–c)

The paraformaldehyde (0.3 g, 0.01 mol), copper (II) acetate (0.05 g, 0.28 mmol), acetic acid (1.125 ml, 0.02 mol), 1,3-diene (0.01 mol) and 1-substituted 4,4,4-trifluorobutan-1,3-dione (0.005 mol) were placed in the sealed tube (in the case of the reaction with anthracenes 2 ml of toluene was added and reactions were carried out at 110°C with stirring). The tube was shaken and then heated on a water bath for 3 h. Then the reaction mixture was evaporated under vacuum and the products were purified by column chromatography (10:1, hexane–diethylether).

3,4-Dimethyl-1-(2,2,2-trifluoroacetyl)-3-cyclohexene-1-carboxylic acid ethyl ester (3a). Yield 67% viscous oil. IR (ν, cm^{-1}): 1753 (C═O). ^1H NMR (δ ppm): 4.16 (q, 2H, CH_2-ethyl, $^3J_{HH}$=7.1 Hz), 2.53–2.40 (m, 2H), 2.30–2.20 (m, 1H), 2.20–2.03 (m, 1H), 2.02–1.97 (m, 2H), 1.62 (s, 3H, CH_3), 1.54 (s, 3H, CH_3), 1.24 (t, 3H, CH_3-ethyl, $^3J_{HH}$=7.1 Hz). ^{13}C NMR (δ ppm): 188.74 (q, C═O, CF_3CO, $^2J_{C-F}$=33.0 Hz), 170.10 (C═O), 124.64, 121.63, 115.74 (q, CF_3, $^1J_{C-F}$=290.0 Hz), 62.04, 56.25, 34.63, 27.88, 26.63, 18.69, 18.57, 13.76. Anal. Calcd for $C_{13}H_{17}O_3F_3$: C, 56.11; H, 6.16%. Found: C, 56.00; H, 6.44%.

1-(1-Benzoyl-3,4-dimethyl-3-cyclohexen-1-yl)-2,2,2-trifluoro-1-ethanone (3b). Yield 57% viscous oil. IR (ν, cm^{-1}): 1755 (CF_3CO), 1695 (C═O). ^1H NMR (δ ppm): 7.76–7.71 (m, 2H, arom.), 7.45–7.39 (m, 1H, arom.), 7.57–7.50 (m, 2H, arom.), 2.64–2.50 (m, 2H, CH_2), 2.44–2.30 (m, 2H, CH_2), 2.00–1.90 (m, 2H, CH_2), 1.68 (s, 3H, CH_3), 1.60 (s, 3H, CH_3). ^{13}C NMR (δ ppm): 194.80 (C═O), 191.60 (q, C═O, CF_3CO, $^2J_{C-F}$ 33.1 Hz), 135.87, 133.22, 128.80, 128.44, 124.65, 121.74, 115.60 (q, CF_3, $^1J_{C-F}$ 292.0 Hz), 61.00, 35.72, 27.69, 27.34, 18.73, 18.65. Anal. Calcd for $C_{17}H_{17}O_2F_3$: C, 65.80; H, 5.52%. Found: C, 66.00; H, 5.98%.

1-[3,4-Dimethyl-1-(2-thienylcarbonyl)-3-cyclohexen-1-yl]-2,2,2-trifluoro-1-ethanone (3c). Yield 59%, oil. IR (ν,(cm^{-1}): 1755 (CF_3CO), 1675 (C═O). ^1H NMR (δ ppm): 7.95 (dd, 1H, CH-arom, $^3J_{HH}$=5.0 Hz, $^4J_{HH}$=0.8 Hz), 7.75 (dd, 1H, CH-arom., $^3J_{HH}$=4.0 Hz, $^4J_{HH}$=0.8 Hz), 6.37 (dd, 1H, CH-arom., $^3J_{HH}$=5.0 Hz, $^3J_{HH}$=4.0 Hz), 2.90–2.80 (m, 2H, CH_2), 2.70–2.60 (m, 2H, CH_2), 2.40–2.20 (m, 2H, CH_2), 1.96 (s, 3H, CH_3), 1.86 (s, 3H, CH_3). ^{13}C NMR (δ ppm): 191.27 (q, C═O, CF_3CO, $^2J_{C-F}$=33.3 Hz), 186.67, 142.22, 135.00, 132.40,

128.47, 123.00 (q, CF_3, $^1J_{C-F}$=292.9 Hz), 124.65, 121.74, 60.95, 35.80, 27.92, 27.57, 18.81, 18.72. Anal. Calcd for $C_{15}H_{15}O_2F_3S$: C 56.95; H 4.78%. Found: C 57.35, 5.12%.

The reaction of **2a** with isoprene gave a mixture of isomers **4a** and **5a** (5:1), after purification. Yield 68%, viscous oil. Major isomer **4-methyl-1-(2,2,2-trifluoroacetyl)-3-cyclohexene-1-carboxylic acid ethyl ester (4a):** IR (ν,(cm^{-1}): 1753 (C=O). ^{1}H NMR (δ ppm): 5.33 (m, 1H, CH-vinyl), 4.16 (q, 2H, CH_2-ethyl, $^3J_{HH}$=7.2 Hz), 2.60–2.40 (m, 2H, CH_2), 2.30–2.05 (m, 2H, CH_2), 2.05–1.90 (m, 2H, CH_2), 1.60 (s, 3H, CH_3), 1.20 (t, 3H, CH_3-ethyl, $^3J_{HH}$=7.2 Hz). ^{13}C NMR (δ ppm): 188.74 (q, C=O, CF_3CO, $^2J_{C-F}$ 33.0 Hz), 170.08, 133.12, 116.53, 115.82 (q, CF_3, $^1J_{C-F}$=292.7 Hz), 62.08, 55.12, 28.91, 26.46, 26.36, 23.03, 13.7.

Minor isomer **3-methyl-1-(2,2,2-trifluoroacetyl)-3-cyclohexene-1-carboxylic acid ethyl ester 5a.** ^{1}H NMR (δ ppm): 2.41 (m, 2H, CH_2), 1.67 (s, 3H, CH_3). ^{13}C NMR (δ ppm): 169.99, 129.92, 119.00, 56.03, 33.21, 25.77, 23.14, 21.69. Other ^{1}H NMR, ^{13}C NMR signals are overlapped by the signals of major isomer. Anal. Calcd for the mixture of isomers $C_{13}H_{17}O_3F_3$: C, 54.54; H, 5.75%. Found: C, 54.17; H, 5.79%.

The reaction of **2b** with isoprene gave a mixture of isomers **4b** and **5b** (6:1), after purification. Yield 57%, viscous oil. Major isomer **1-(1-benzoyl-4-methyl-3-cyclohexen-1-yl)-2,2,2-trifluoro-1-ethanone (4b).** IR (ν, cm^{-1}): 1750 (CF_3CO), 1695 (C=O). ^{1}H NMR (δ ppm): 7.75–7.70 (m, 2H, arom.), 7.55–7.45 (m, 1H, arom.), 7.45–7.35 (m, 2H, arom.), 5.37 (m, 1H, CH-vinyl), 2.70–2.60 (m, 2H, CH_2), 2.50–2.30 (m, 2H, CH_2), 2.00–1.90 (m, 2H, CH_2), 1.61 (s, 3H, CH_3). ^{13}C NMR (δ ppm): 194.69, 191.40 (q, C=O, CF_3CO, $^2J_{C-F}$=33.1 Hz), 135.75, 133.15, 128.71, 128.35, 119.66, 116.66, 114.52 (q, CF_3, $^1J_{C-F}$=292.9 Hz), 60.96, 38.65, 30.00, 27.11, 22.87.

Minor isomer **1-(1-benzoyl-3-methyl-3-cyclohexen-1-yl)-2,2,2-trifluoro-1-ethanone (5b).** ^{1}H NMR (δ ppm): 7.70–7.65 (m, 2H, arom.), 2.58–2.50 (m, 2H, CH_2), 1.70 (s, 3H, CH_3). ^{13}C NMR (δ ppm): 194.46, 132.87, 60.80, 23.84. Other ^{1}H NMR, ^{13}C NMR signals are overlapped by the signals of major isomer. Anal. Calcd for the mixture of isomers $C_{16}H_{15}O_2F_3$: C, 64.86; H, 5.1%. Found: C, 65.36; H, 5.66%.

The reaction of **2c** with isoprene gave a mixture of isomers **4c** and **5c** (9:1), after purification. Total yield 63%, viscous oil. Major isomer **2,2,2-trifluoro-1-[4-methyl-1-thienylcarbonyl)-3-cyclohexen-1-yl]-1-ethanone (4c).** IR (ν, cm^{-1}): 1755 (CF_3CO), (C=O). ^{1}H NMR (δ ppm): 7.68 (dd, 1H, CH-arom., $^3J_{HH}$=5.0 Hz, $^4J_{HH}$=1.0 Hz), 7.47 (dd, 1H, CH-arom., $^3J_{HH}$=4.0 Hz, $^4J_{HH}$=1.0 Hz), 7.09 (dd, 1H, CH-arom., $^3J_{HH}$=5.0 Hz, $^3J_{HH}$=4.0 Hz), 5.41 (m, 1H, CH-vinyl), 2.80–2.60 (m, 2H, CH_2), 2.50–2.40 (m, 2H, CH_2), 2.20–1.96 (m, 2H, CH_2), 1.66 (s, 3H, CH_3). ^{13}C NMR (δ ppm): 191.30 (q, C=O, $COCF_3$, $^2J_{CF}$=33.4 Hz), 186.62, 142.27, 135.05, 132.43, 128.50, 119.78, 116.74, 115.50 (q, CF_3, $^1J_{CF}$=292.9 Hz), 60.88, 30.06, 27.27, 26.33, 23.05.

Minor isomer **2,2,2-trifluoro-1-[3-methyl-1-(2-thienylcarbonyl)-3-cyclohexen-1-yl]-1-ethanone (5c).** ^{1}H NMR (δ ppm): 7.68 (dd, 1H, CH-arom., $^3J_{HH}$=5.50 Hz, $^4J_{HH}$=1.02 Hz), 2.60–2.54 (m, 2H, CH_2), 2.40–2.34 (m, 2H, CH_2), 1.76 (s, 3H, CH_3). ^{13}C NMR (δ ppm): 187.90, 133.09, 61.00, 23.06. Other ^{1}H NMR, ^{13}C NMR signals are overlapped by the signals of major isomer. Anal. Calcd for the mixture of isomers $C_{14}H_{13}O_2F_3S$: C 55.62; H 4.33%. Found C 55.97; 4.59%.

The reaction of **2a** with cyclopentadiene gave a mixture of isomers **6a**, **7a**, **8a** (3.5:1:1) after purification. Total yield 60%, viscous oil. Main isomer **2-(2,2,2-trifluoroacetyl-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid ethyl ester (6a).** IR (ν, cm^{-1}): 1750 (C=O) C NMR (δ ppm): 6.24 (dd, 1H, CH-vinyl, $^3J_{HH}$=5.5 Hz, $^3J_{HH}$=3.0 Hz), 6.00 (dd, 1H, CH-vinyl, $^3J_{HH}$=5.6 Hz, $^3J_{HH}$=2.9 Hz), 4.20 (q, 2H, CH_2-ethyl, $^3J_{HH}$=7.2 Hz). 3.42 (s, 1H), 2.98 (s, 1H), 2.14–1.96 (m, 3H), 1.60–1.50 (m, 1H), 1.25 (t, 3H, CH_3-ethyl, $^3J_{HH}$=7.2 Hz). ^{13}C NMR (δ ppm):(187.50 (q, C=O, CF_3CO, $^2J_{CF}$=33.57 Hz), 170.58 (C=O), 139.96, 133.03, 62.05, 61.13, 49.59, 48.22, 41.73, 34.03, 13.62 or 13.56.

The signals of the minor isomers **7a**, **8a**: ^{1}H NMR (δ ppm): 6.37 (dd, 1H, CH-vinyl, $^3J_{HH}$=5.3 Hz, $^3J_{HH}$=2.8 Hz), 6.07 (m, 1H, CH-vinyl), 5.95 (dd, 1H, CH-vinyl, $^3J_{HH}$=5.2 Hz, $^3J_{HH}$=2.5 Hz), 5.84 (m, 1H, CH-vinyl), 5.15 (m, 1H), 3.52 (s, 1H), 3.04 (s, 1H). ^{13}C NMR (δ ppm): 168.27, 166.20, 140.24, 136.81, 131.65, 130.02, 85.42, 62.78, 62.10, 61.96, 49.11, 48.???, 43.05, 38.12, 35.65, 33.59, 25.82; 13.65, 13.62 or 13.56. Other ^{1}H NMR, ^{13}C NMR signals are overlapped by the signals of major isomer. Anal. Calcd for the mixture of isomers $C_{12}H_{13}O_3F_3$: C 54.96; H 5.00%. Found: C 55.38; H 5.32%.

[4,4a,5,7a-Tetrahydro-2-(trifluoromethyl)cyclopenta[*b*]-pyran-3-yl]phenylketone (8b). Yield 47%. IR (ν, cm^{-1}): 1671 (C=O). ^{1}H NMR (δ ppm):(7.90–7.80 (m, 2H, arom.), 7.60–7.40 (m, 3H, arom.), 6.13–6.08 (m, 1H), 5.09–5.88 (m, 1H), 5.28–5.22 (m, 1H), 2.92–2.82 (m, 1H), 2.64–2.50 (m, 2H), 2.34–2.16 (m, 2H). ^{13}C NMR (δ ppm): 194.54, 141.40 (q, $^2J_{CF}$=36.4 Hz), 136.73, 135.92, 133.69, 130.29, 129.14, 128.66, 119.50 (q, CF_3, $^1J_{CF}$=274.1 Hz), 119.28, 85.20, 38.40, 35.77, 35.76. Anal. Calcd for $C_{16}H_{13}O_2F_3$: C 65.30; H 4.42%. Found: C 65.36; 4.54%.

[4,4a,5,7a-Tetrahydro-2-(trifluoromethyl)cyclopenta[*b*]-pyran-3-yl]2-thienylketone (8c). Yield 38%. IR (ν, cm^{-1}): 1660 (C=O). ^{1}H NMR (δ ppm): 7.72 (dd, 1H, CH-arom., $^3J_{HH}$=4.9 Hz, $^4J_{HH}$=1.1 Hz), 7.59 (dd, 1H, CH-arom., $^3J_{HH}$=3.8 Hz, $^4J_{HH}$=1.1 Hz), 7.13 (dd, 1H, CH-arom., $^3J_{HH}$=4.9 Hz, $^3J_{HH}$=3.8 Hz), 6.15–6.05 (m, 1H, vinyl), 5.95–5.85 (m, 1H, vinyl), 5.25 (d, 1H, $^3J_{HH}$=7.4 Hz), 3.00–2.80 (m, 1H), 2.70–2.55 (m, 2H, CH_2), 2.40–2.20 (m, 2H, CH_2). ^{13}C NMR (δ ppm): 186.34, 140.91, 139.40 (q, $^2J_{CF}$=37.4 Hz), 135.25, 134.15, 131.40, 130.57, 128.25, 121.00 (q, CF_3, $^1J_{CF}$=275.5 Hz), 115.23, 83.87, 38.56, 32.36, 31.34. Anal. Calcd for $C_{14}H_{11}O_2F_3S$: C 55.99; H 3.69%. Found: C 55.77; H 3.21%.

Reaction of **2a** with cyclohexadiene leads to the formation of the mixture of isomers and **10a** (3:1, yield 40%) and **11a** (yield 40%). Major isomer *exo*-**2-(2,2,2-trifluoroacetyl)-bicyclo[2.2.2]oct-5-ene-2-carboxylic acid ethyl ester (9a).** colorless oil. IR (ν, cm^{-1}): 1750 (CF_3CO), 1720

(C═O). ^{1}H NMR (δ ppm): 6.35 (ddd, 1H, CH-vinyl, $^3J_{HH}$=6.4 Hz, $^3J_{HH}$=6.5 Hz, $^4J_{HH}$=1.2 Hz), 6.15 (m, 1H, CH-vinyl), 4.20 (dq, CH_2–ethyl, $^3J_{HH}$=7.1 Hz, $^2J_{HH}$= 21 Hz), 3.12–3/06 (m, 1H), 2.74–2.64 (m, 1H) 2.50 (dd, 1H, $^2J_{HH}$=13.5 Hz, $^3J_{HH}$=2.4 Hz), 1.80–1.50 (m, 3H), 1.25 (t, 3H, CH_3-ethyl, $^3J_{HH}$=7.1 Hz), 1.3–0.6 (m, 2H), ^{13}C NMR (δ ppm): 187.90 (q, C═O, CF_3CO $^2J_{C-F}$=32.5 Hz), 169.49, 133.65, 133.26, 115.38 (q, CF_3, $^1J_{C-F}$=294.6 Hz), 62.27, 61.26, 33.74, 32.08, 28.91, 22.68, 21.12, 13.8.

Minor isomer *endo*-**2-(2,2,2-trifluoroacetyl)-bicyclo[2.2.2]-oct-5-ene-2-carboxylic acid ethyl ester (10a).** ^{1}H NMR (δ ppm): 6.30 (ddd, 1H, CH-vinyl, $^3J_{HH}$=6.3 Hz, $^3J_{HH}$=6.4 Hz, $^4J_{HH}$=1.2 Hz), 2.36 (dd, 1H, $^2J_{HH}$=13.6 Hz, $^3J_{HH}$=2.5 Hz). Other ^{1}H NMR, ^{13}C NMR signals are overlapped by the signals of major isomer. Anal. Calcd for the mixture of the isomers $C_{13}H_{15}O_3F_3$: C, 56.52; H, 5.47%. Found: C, 56.42; H, 5.61%.

4a,5,6,8a-Tetrahydro-2-(trifluoromethyl)-4*H*-1-benzo-pyran-3-carboxylic acid ethyl ester (11a). Colorless oil. IR (ν, cm^{-1}): 1730 (C═O). ^{1}H NMR (δ ppm): 6.05–5.95 (m, CH vinyl), 5.90–5.80 (m, 1H, vinyl), 4.45 (t, 1H, $^3J_{HH}$=3.7 Hz), 4.20 (q, 2H, CH_2–ethyl, $^3J_{HH}$=7.1 Hz, 2.65–2.50 (m, 1H), 2.40–2.00 (m, 4H, CH_2), 1.80–1.50 (m, 2H, CH_2), 1.28 (t, 3H, CH_3–ethyl, $^3J_{HH}$=7.1 Hz). ^{13}C NMR (δ ppm): 167.01, 143.66 (q, $^2J_{C-F}$=36.1 Hz), 133.70, 124.40, 119.35 (CF_3, $^1J_{C-F}$=274.70 Hz), 108.41, 71.84, 61.26, 29.00, 27.11, 24.39, 22.95, 13.73. Anal. Calcd for $C_{13}H_{15}O_3F_3$: C, 56.32; H, 5.42%. Found: C, 56.42; H, 5.51%.

Reaction of **2b** with cyclohexadiene gave the mixture of isomers **9b** and **10b** (4:1, yield 15% and **11b** (yield 37%). Major isomer *endo*-**1-(2-benzoylbicyclo[2.2.2] oct-5-en-2-yl)-2,2,2-trifluoro-1-ethanone (9b).** colorless oil. IR (ν cm^{-1}): 1750 (CF_3CO), 1690 (C═O), ^{1}H NMR (δ ppm): 7.85–7.80 (m, 2H, CH-arom.), 7.60–7.50 (m, 1H, CH-arom.), 7.45–7.37 (m, 2H, CH-arom.), 6.38 (t, 1H, CH-vinyl, $^3J_{HH}$=6.9 Hz, $^3J_{HH}$=6.7 Hz), 6.28 (t, 1H, CH-vinyl, $^3J_{HH}$=6.9 Hz, $^3J_{HH}$=7.6 Hz), 3.60–3.50 (m, 1H), 2.70–2.60 (m, 1H), 2.63 (dd, 1H, $^2J_{HH}$=13.4 Hz, $^3J_{HH}$=2.2 Hz), 1.96 (d, 1H, $^2J_{HH}$=13.4 Hz), 1.75–1.55 (m, 2H), 1.30–1.18 (m, 2H). ^{13}C NMR (δ ppm): 193.00 (C═O), 191.80 (q, C═O, CF_3CO, $^2J_{C-F}$=32.80 Hz), 136.45, 134.40, 133.53, 132.37, 129.12, 128.81, 115.85 (q, CF_3, $^1J_{C-F}$=295.0 Hz), 66.80, 34.96, 32.42, 29.81, 22.91, 21.08.

Minor isomer *exo*-**1-(2-benzoylbicyclo[2.2.2]oct-5-en-2yl)-2,2,2-trifluoro-1-ethanone (10b).** ^{1}H NMR (δ ppm): 6.58–6.52 (m, 1H, CH-vinyl) 6.17–6.10 (m, 1H, CH-vinyl), 3.03 (dd, 1H, $^2J_{HH}$=13.3 Hz, $^3J_{HH}$=2.2 Hz). Other ^{1}H NMR, ^{13}C NMR signals are overlapped by the signals of major isomer. Anal. Calcd for the mixture of the isomers $C_{17}H_{15}O_2F_3$: C, 66.23; H, 4.90%. Found: C, 66.96; H, 5.16%.

[4a,5,6,8a-Tetrahydro-2-(trifluoromethyl)-4*H*-1-benzo-pyran-3-yl]phenylketone (11b). White solid, mp 76–78°C. IR (ν, cm^{-1}): 1670 (C═O). ^{1}H NMR (δ ppm): 7.92–7.87 (m, 2H, CH-arom.), 7.60–7.54 (m, 1H, CH-arom.), 7.50–7.43 (m, 2H, CH-arom.), 6.05–5.95 (m, 1H, CH-vinyl), 5.95–5.85 (m, 1H, CH-vinyl), 4.59–4.54 (m, 1H), 2.62–2.52 (m, 1H), 2.28–2.08 (m, 4H), 1.90–1.75 (m, 1H), 1.72–1.62 (m, 1H). ^{13}C NMR (δ ppm): 195.02, 137.58 (q, $^2J_{C-F}$ 35.7 Hz), 135.91, 133.76, 133.49, 124.96, 129.21, 128.79, 119.00 (q, CF_3, $^1J_{C-F}$=274.4 Hz), 71.55, 29.28, 28.40, 24.25, 23.29. Anal. Calcd for $C_{17}H_{15}O_2F_3$: C, 66.23; H, 4.90%. Found: C, 65.65; H, 5.81%.

Reaction of **2c** with the cyclohexadiene-1,3 gave the mixture of the isomers **9c** and **10c** (6:1, yield 16%) and **11c** (yield 41%). Main isomer *endo*-**2,2,2-trifluoro-1-[2-(2-thienylcarbonyl)bicyclo[2.2.2]oct-5-en-2-yl]-1-ethanone (9c).** colorless oil. IR (ν, cm^{-1}: 1755 (CF_3CO), 1650 (C═O). 1H NMR (δ ppm): 7.71 (dd, 1H, CH-arom., $^3J_{HH}$=5.0 Hz, $^4J_{HH}$=1.0 Hz), 7.51 (dd, 1H, CH-arom., $^3J_{HH}$=4.0 Hz, $^4J_{HH}$=0.9 Hz), 7.11 (dd, 1H, CH-arom., $^3J_{HH}$=5.0 Hz, $^3J_{HH}$=4.0 Hz), 6.42 (ddd, 1H, CH-vinyl, $^3J_{HH}$=6.4 Hz, $^3J_{HH}$=7.8 Hz, $^4J_{HH}$=1.1 Hz), 6.28 (t, 1H, CH-vinyl, $^3J_{HH}$=6.4 Hz, $^3J_{HH}$=7.8 Hz), 3.56–3.50 (m, 1H), 2.81 (dd, 1H, $^3J_{HH}$=2.34 Hz, $^2J_{HH}$=13.40 Hz, 2.81–2.72 (m, 1H), 1.82 (d, 1H, $^2J_{HH}$=13.4 Hz), 1.70–1.60 (m, 2H), 1.35–1.20 (m, 2H). ^{13}C NMR (δ ppm): 190.6 (q, C═O, $^2J_{C-F}$=32.7 Hz), 185.24, 143.05, 134.25, 133.18, 132.57, 135.35, 116.74, 115.50 (q, CF_3, $^1J_{CF}$=292.9 Hz), 67.41, 35.34, 29.41, 31.48, 22.45, 20.97.

Minor isomer *exo*-**2,2,2-trifluoro-1-[2-(2-thienylcarbonyl)bicyclo[2.2.2]oct-5-en-2yl]-1-ethanone (10c).** ^{1}H NMR (δ ppm): 7.67 (dd, 1H, CH-arom., $^3J_{HH}$=5.0 Hz, $^4J_{HH}$=1.0 Hz), 6.53–6.48 (m, 1H, CH-vinyl), 6.23–6.17 (m, 1H, CH-vinyl). Other ^{1}H NMR, ^{13}C NMR signals are overlapped by the signals of major isomer. Anal. Calcd for $C_{15}H_{13}O_2F_3S$: C 57.32; H 4.17%. Found: C 57.59; 4.36%.

[4a,5,6,8a-Tetrahydro-2-(trifluoromethyl)-4H-1-benzo-pyran-3-yl]2-thienylketo (11c). White solid, mp 81–83°C. IR (ν, cm^{-1}): 1663 (C═O). ^{1}H NMR (δ ppm): 7.71 (dd, 1H, CH-arom., $^3J_{HH}$=5.0 Hz, $^4J_{HH}$=1.1 Hz), 7.61 (dd, 1H, CH-arom., $^3J_{HH}$=3.8 Hz, $^4J_{HH}$=1.1 Hz) 7.14 (dd, 1H, CH-arom., $^3J_{HH}$=5.0 Hz, $^3J_{HH}$=3.8 Hz), 6.08–6.00 (m, 1H, CH-vinyl), 5.92–5.86 (m, 1H, CH-vinyl), 4.56 (s, 1H), 2.70–2.60 (m, 1H), 2.30–2.10 (m, 4H), 1.90–1.76 (m, 1H), 1.76–1.64 (m, 1H). ^{13}C NMR (δ ppm): 187.28, 143.53, 138.00 (q, $^2J_{C-F}$=35.7 Hz), 135.25, 134.22, 133.58, 128.35, 124.85, 119.50 (q, CF_3, $^1J_{C-F}$=273.0 Hz), 114.85, 71.63, 29.27, 28.56, 24.23, 23.25. Anal. Calcd for $C_{15}H_{13}O_2F_3S$: C 57.32; H 4.17%. Found: C 57.33; 4.14%.

15-(2,2,2-Trifluoroacetyl)-tetracyclo[6.6.2.0^{2,7}.0^{9,14}]hexa-deca-2,4,6,9,11,13-hexaene-15-carboxylic acid ethyl ester (12a). White solid, mp 68–70°C, yield 90%. IR (ν, cm^{-1}): 1770 (CF_3CO), 1710 (C═O). ^{1}H NMR (δ ppm): 7.5–7.0 (m, 8H, CH-arom.), 4.97 (s, 1H), 4.42 (t, 1H, $^3J_{HH}$=2.8 Hz), 4.05 (q, 2H, CH_2-ethyl, $^3J_{HH}$=7.1), 2.72 (dd, 1H, $^3J_{HH}$=2.8 Hz, $^2J_{HH}$=13.2 Hz) 2.20 (d, 1H, $^2J_{HH}$=13.2 Hz), 1.16 (3H, CH_3-ethyl, $^3J_{HH}$=7.1 Hz). ^{13}C NMR (δ ppm): 187.12 (q, C═O, $^2J_{C-F}$=37.4 Hz), 167.69, 143.45, 143.03, 138.81, 138.50, 126.83, 126.54, 126.46, 125.94, 125.91, 124.63, 123.63, 122.96, 115.26 (q, CF_3, $^1J_{C-F}$=294.5 Hz), 62.09, 62.48, 48.51, 43.40, 34.23, 13.72. Anal. Calcd for $C_{21}H_{17}O_3F_3$: C 67.38; H 4.58%. Found: C 67.25; H 4.48%.

1-(15-Benzoyltetracyclo[6.6.2.0^{2,7}.0^{9,14}]hexadeca-2,4,6,9, 11,13-hexaen-15-yl)-2,2,2-trifluoro-1-ethanone (12b). White

solid, mp 171–173°C, yield 10%. IR (ν, cm^{-1}): 1765 (CF_3CO), 1695 (C=O). ^1H NMR (δ ppm): 7.60–7.55, 7.47–7.40, 7.40–7.35, 7.35–7.25, 7.20, (m, 13H, CH-arom), 5.35 (s, 1H), 4.39 (t, 1H, $^3J_{HH}$=3.0 Hz, $^3J_{HH}$=2.6), 3.20 (dd, 1H, $^2J_{HH}$=12.9 Hz, $^3J_{HH}$=3.0 Hz), 2.40 (dd, 1H, $^2J_{HH}$=12.9 Hz, $^3J_{HH}$=2.6 Hz). ^{13}C NMR (δ ppm): 191.60, 189.60 (q, C=O, $^2J_{C-F}$=34.0 Hz), 143.62, 143.55, 139.25, 138.31, 135.62, 135.44, 128.86, 128.68, 127.03, 126.91, 126.45, 126.11, 125.80, 125.20, 123.64, 122.91, 69.00, 48.79, 43.95, 35.79. Anal. Calcd for $C_{25}H_{17}F_3O_2$: C 73.89; H 4.22%. Found: C 74.00; H 4.30%.

2,2,2-Trifluoro-1-[15-(2-thienylcarbonyl)tetracyclo-[6.6.2.0^{2,7}.0^{9,14}]hexadeca-2,4,6,10,12-pentaen-15-yl]-1-ethanone (12c). Yellow solid, mp 174–175°C, yield 14% (ν, cm^{-1}): 1750 (CF_3CO), 1670 (C=O). ^1H NMR (δ ppm): 7.60 (dd, 1H, CH-arom., $^3J_{HH}$=5.0 Hz, $^4J_{HH}$=0.8 Hz), 7.39 (d, 1H, CH-arom., $^3J_{HH}$=4.0 Hz), 7.32–7.25, 7.25–7.2, 7.12–7.02 (m, 9H, CH-arom.); 5.35 (s, 1H), 4.41 (t, 1H, $^3J_{HH}$=2.7 Hz), 2.83 (dd, 1H, $^2J_{HH}$=12.9 Hz, $^3J_{HH}$=2.8 Hz), 2.63 (dd, 1H, $^2J_{HH}$=12.9 Hz, $^3J_{HH}$=2.6 Hz). ^{13}C NMR (δ (ppm): 189.50 (q, C=O, $^2J_{C-F}$=34.0 Hz), 184, 143.58, 143.43, 142.54, 138.78, 138.34, 135.29, 132.68, 128.34, 126.88, 126.59, 126.44, 126.05, 125.93, 125.53, 123.51, 123.13, 116.00 (q, CF_3, $^1J_{C-F}$=294.6 Hz), 68.63, 48.87, 43.76, 35.18. Anal. Calcd for $C_{23}H_{15}F_3O_2S$: C 66.98; H 3.67%. Found: C 67.09; H 3.75%.

8-Methyl-15-(2,2,2-trifluoroacetyl)tetracyclo[6.6.2.0^{2,7}.0^{9,14}]-hexadeca-2,4,6,9,11,13-hexaene-15-carboxylic acid ethyl ester (13). White solid, mp 84–85°C, yield 80%. IR (ν, cm^{-1}): 1750 (C=O). ^1H NMR (δ ppm): 7.50–7.00 (m, 8H, CH-arom.), 4.93 (s, 1H), 4.00 (q 2H, CH_2-ethyl, $^3J_{HH}$=7.1 Hz), 2.50 (d, 1H, $^2J_{HH}$=13.1 Hz), 2.00 (d, 1H, $^2J_{HH}$=13.1 Hz), 1.97 (s, 3H), 1.12 (t, 3H, CH_3-ethyl, $^3J_{HH}$=7.1 Hz). ^{13}C NMR (δ ppm): 187.02 (q, C=O, CF_3CO, $^2J_{C-F}$=33.8 Hz), 167.74, 145.64, 145.28, 139.30, 139.01, 126.77, 126.44, 126.32, 125.79, 125.77, 124.68, 121.10, 120.32, 115.35 (q, CF_3, $^1J_{C-F}$=294.4 Hz), 63.16, 62.53, 48.64, 40.82, 42.20, 17.18, 13.77. Anal. Calcd for $C_{22}H_{19}O_3F_3$: C 68.04%; H 4.93%. Found: C 67.89%; H 4.72%.

1,8-Dimethyl-15-(2,2,2-trifluoroacetyl)tetracyclo[6.6.2.0^{2,7}.0^{9,14}]hexadeca-2,4,6,9,11,13-hexaene-15-carboxylic acid ethyl ester (14). Yellow solid, mp 107–108°C, yield 70%. IR (ν, cm^{-1}): 1770 (CF_3CO), 1710 (C=O). ^1H NMR (δ ppm): 7.60–7.00 (m, 8H, CH-arom.), 4.04 (q, 2H, CH_2-ethyl, $^3J_{HH}$=7.2 Hz), 2.54 (d, 1H, $^2J_{HH}$=13.2 Hz), 2.16 (s, 3H), 1.96 (s, 3H), 1.10 3H, CH_3-ethyl, $^3J_{HH}$=7.2 Hz). ^{13}C NMR (δ ppm): 186.84 (q, C=O, $^2J_{C-F}$=31.7 Hz), 168.35, 145.73, 145.25, 142.33, 142.00, 126.35, 125.95, 125.68, 125.58, 123.97, 122.31, 120.42, 120.18, 115.02 (q, CF_3, $^1J_{C-F}$=295.6 Hz), 63.70, 62.21, 46.86, 44.03, 40.92, 17.67, 13.98, 13.60. Anal. Calcd for $C_{23}H_{21}O_3F_3$: C 68.65%; H 5.26%. Found: C 68.96%; H 5.48%.

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References

1. De Lucchi, O.; Lucchini, V.; Pasquato, L.; Zamai, M.; Modena, G. *Gazz. Chim. Ital.* **1984**, *114*, 293–295.
2. Hoffman, H. M. R.; Weichert, A. *J. Org. Chem.* **1991**, *56*, 4098.
3. Carretero, J. C.; Garcia Ruano, J. L.; Martin Cabrejas, L. M. *Tetrahedron: Asymmetry* **1997**, *8*, 2215.
4. Hayes, P.; Dujardin, G.; Maignan, C. *Tetrahedron Lett.* **1996**, *37*, 3687.
5. Westfahl, J. C.; Gresham, T. L. *J. Am. Chem. Soc.* **1954**, *76*, 1076.
6. Ardis, A. E.; Averill, S. J.; Gilbert, H.; Miller, F. F.; Schmidt, R. F.; Stewart, F. D.; Trumbull, H. L. *J. Am. Chem. Soc.* **1950**, 1305.
7. (a) Gololobov, Y. G.; Kolomnikova, G. D.; Krylova, T. O. *Tetrahedron Lett.* **1994**, *35*, 1751. (b) Hoffman, H. M. R.; Gassner, A.; Eggert, U. *Chem. Ber.* **1991**, *124*, 2475. (c) Kandror, I. I.; Galkina, M. A.; Bragina, I. O.; Lavrukhin, B. D.; Belokon, Yu. N.; Gololobov, Yu. G. *Bull. Russ. Acad. Sci. Div. Chem. Sci. (Engl. Transl.)* **1992**, *41*:10.2, 1928–1930. (d) Kolomnikova, G. L.; Krylova, T. O.; Gololobov, Yu. G. *Russ. J. Gen. Chem.* **1993**, *63* (3.2), 506–508. (e) Kolomnikova, G. D.; Krylova, T. O.; Chernoglazova, I. V.; Petrovskii, P. V.; Gololobov, Yu. G. *Russ. Chem. Bl.* **1993**, *42*, 7, 1188–1190.
8. (a) Samuilov, Ya. D.; Bukharov, S. V.; Konovalov, A. I. *J. Org. Chem. USSR (Engl. Transl.)* **1981**, *17*, 1, 109–115. (b) Samuilov, Ya. D.; Bukharov, S. V.; Konovalov, A. I. *J. Org. Chem. USSR (Engl. Transl.)* **1981**, *17*, 11, 2135–2139. (c) Tolstikov, G. A.; Shul'ts, E. E.; Safarova, G. M.; Spirikhin, L. V.; Panasenko, A. A. *J. Org. Chem. USSR (Eng. Transl.)* **1990**, *26*, 6, 1110–1119. (d) Yamauchi, M.; Honda, Y.; Matsuki, N.; Watanabe, T.; Date, K.; Hiramatsu, H. *J. Org. Chem.* **1996**, *61*, 2719. (e) Zia-Ebrahimi, M.; Huffman, G. W. *Synthesis* **1996**, 215. (f) Buzinkai, J. F.; Hrubowchak, D. M.; Smith, F. X. *Tetrahedron Lett.* **1985**, *26*, 3195. (g) Corey, E. J.; Munroe, J. E. *J. Am. Chem. Soc.* **1992**, *104*, 6189.
9. Snider, B. B.; Phillips, G. B. *J. Org. Chem. Soc.* **1981**, 2563.
10. (a) Yamauchi, M.; Katayama, S.; Baba, S.; Watanabe, T. *J. Chem. Soc. Perkin Trans. 1* **1990**, 3041. (b) Yamauchi, M.; Katayama, S.; Baba, S.; Watanabe, T. *J. Chem. Soc., Chem. Commun.* **1983**, 281.
11. *Selective Fluorination in Organic and Bioorganic Chemistry*; Welch, J. T., Ed.; ACS Symposium Series 456: Washington, DC, 1991.
12. (a) Nenajdenko, V. G.; Sanin, A. V.; Balenkova, E. S. *Russ. Chem. Rev.* **1999**, *6*, 437. (b) Nenajdenko, V. G.; Sanin, A. V.; Balenkova, E. S. *Molecules* **1997**, *2*, 186.
13. Begue, J.-P.; Bonnet-Delpon, D. *Tetrahedron* **1991**, *47*, 3207.
14. (a) Tordeux, M.; Wakselman, C. *J. Fluor. Chem.* **1982**, *20*, 301. (b) Von Werner, K.; Gisser, A. *J. Fluor. Chem.* **1977**, *10*, 387.
15. Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209.
16. (a) Bachman, G. B.; Tanner, H. A. *J. Org. Chem.* **1939**, *4*, 493. (b) Ballesteros, P.; Roberts, B. W.; Wong, J. *J. Org. Chem.* **1983**, *48*, 3603. (c) De Keyser, J. L.; De Cock, C. J. C.; Poupaert, J. H.; Dumont, P. *J. Org. Chem.* **1988**, *53*, 4859.
17. (a) Hojo, M.; Masuda, R.; Okada, E. *Synthesis* **1990**, No. 4, 347. (b) Hojo, M.; Masuda, R.; Okada, E. *Synthesis* **1989**, No. 3, 215.