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Quadricyclane—thermal cycloaddition to polyfluorinated carbonyl compounds A simple synthesis of polyfluorinated 3-oxatricyclo[4.2.1.$0^{2,5}$]non-7-enes

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Abstract

Quadricyclane (**1**) readily undergoes [2+2+2] cycloaddition reactions with electron-deficient fluorinated carbonyl compounds to give polyfluorinated 3-oxatricyclo[4.2.1.$0^{2,5}$]non-7-enes in high yields. Hexfluoroacetone, trifluoroacetyl chloride, methyl trifluoropyruvate, α-(fluorosulfonyl)difluoroacetyl fluoride, and bis(trifluoromethyl)ketene all react rapidly with **1**. Trifluoracetyl fluoride although less reactive, slowly interacts with **1** at ambient temperature. 1,1,1-Trifluoroacetone, trifluoroacetophenone, carbonyl fluoride, and $CF_3C(O)OC_6F_5$ require higher temperatures (60–90 °C) for reaction, and ethyl trifluoroacetate is unreactive at 90 °C. Heating **1** with the ethyl hemiacetal of trifluoroacetaldehyde gives the corresponding cycloadduct of $CF_3C(O)H$ in 44% yield.

The oxetane product from hexafluoroacetone is remarkably stable to both acids and bases, whereas the oxetanes with α-F or Cl leaving groups are sensitive to acid-catalyzed rearrangement.

Keywords: Quadricyclane; Thermal cycloaddition reactions; Hexafluoroacetone; Trifluoroacetyl fluoride; Carbonyl fluoride; Polyfluorinated carbonyl compounds trifluoracetaldehyde hemiacetal

1. Introduction

Thermal [2+2+2] cycloaddition reactions of quadricyclane (**1**) and olefins provide a simple and useful method for the synthesis of a variety of tricyclo[4.2.1.$0^{2,5}$]non-7-enes [1–6]. However, the cycloaddition of **1** with carbonyl compounds to form 3-oxa-tricyclo[4.2.1.$0^{2,5}$]non-7-enes is usually carried out under UV-irradiation (e.g. [7]). Exceptional cases of *thermal* cycloadditions of **1** across C=O bonds include the reactions with Moore's ketene (*t*-butylcyanoketene) [8] or diphenylketene [9], halogenated *p*-anils [10] or highly electrophilic ketones, such as $[CH_3O(O)C]_2$-C=O or $C_6H_5C(O)C(O)C(O)OCH_3$ [11,12]. Some activated ketones were also reported to give the corresponding cycloadducts with **1** under high pressure [11,12]. In the search of new monomers to prepare functional polymers for next generation microlithography [13–15] we found that perfluoroalkyl substituent has an unexpected and remarkable activating effect on carbonyl group and polyfluorinated carbonyl compounds are significantly more reactive towards **1** than any other reported carbonyl substrates.

2. Results and discussion

2.1. Reactions of *1* with carbonyl compounds

In sharp contrast to acetone, which does not react with **1** under ambient conditions (25 °C, 48 h), *hexafluoroacetone*

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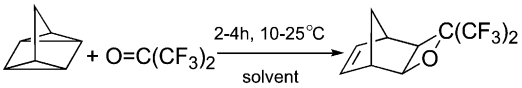
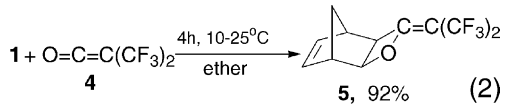
(**2**) reacts exothermally with **1** upon the addition of gaseous **2** into a solution of **1** in inert solvent (ether or dichloromethane) to give oxetane **3** in high yield (Eq. 1) [16]. In fact, dilution of the reaction mixture and slow addition of **2** are required to control the heat evolved from this reaction.



1 **2** **3**, >95% (1)

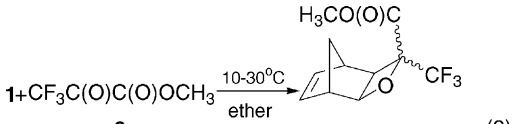
Compared with reported reactions of **1** with acrylates, which proceed only at elevated temperature and involve exclusively the C=C bond of acrylate [17,18], bis(trifluoromethyl)ketene (**4**) reacts with **1** selectively producing oxetane **5** (Eq. 2).



4 **5**, 92% (2)

This reactivity of **4** is analogous to that reported for bis(trifluoromethyl)thioketene which occurs regioselectively across the thioketene C=S bond [19]. Notably, the reactions of **1** with either **2** or **4** are both exceptionally clean (NMR) and give only one product (**3** or **5** respectively). Each oxetane product is a single isomer and, it is assumed based on literature data (e.g. [11]) that the oxetane rings in **3** and **5** have the *exo*-stereochemistry.

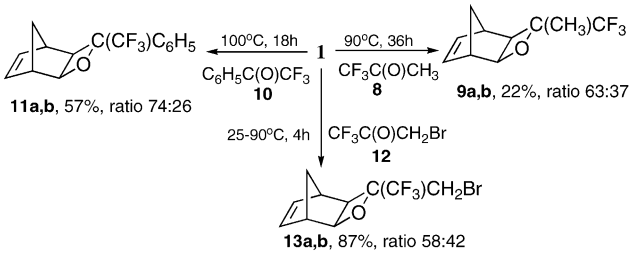
Methyl trifluoropyruvate (**6**) is significantly more reactive compared with $CH_3C(O)C(O)OC_2H_5$ (reported to react with **1** only at high pressure 800 MPa, 80 °C, 24 h [11]) and reacts with quadricyclane (**1**) *exothermally* (Eq. 3).



6 **7a,b**, 73% (3)
ratio of isomers 70:30

Although two isomeric oxetanes **7a,b** are formed in this reaction, only the carbonyl group adjacent to CF_3– is involved but not the carbonyl of ester (NMR). The significantly lower reactivity of the ester carbonyl is also consistent with the observation that no detectable amount of cycloadduct was observed in the reaction **1** and $CF_3C(O)OC_2H_5$ after 36 h at 90 °C by NMR. The reactivity of the carbonyl group varies significantly with the structure of fluorinated carbonyl reactant. For example, the reaction of trifluoroacetone (**8**) and **1** is slow at 90 °C, and gives a mixture of oxetanes **9a,b** in 22% yield (Scheme 1). However, the replacement of the electron donating methyl group in **8** by $–C_6H_5$ (compound **10**) or by $–CH_2Br$ (compound **12**) results in a shorter reaction time and higher yields of cycloadducts, **11a,b** and **13a,b** respectively (Scheme 1).

The difference in the reactivity between **10** and hydrocarbon counterpart – acetophenone – is amazing: $CH_3C(O)C_6H_5$ was reported to be completely inert towards **1** at elevated temperature and under high pressure – no reaction after 24 h at 900 mp and 80 °C [11] and is an

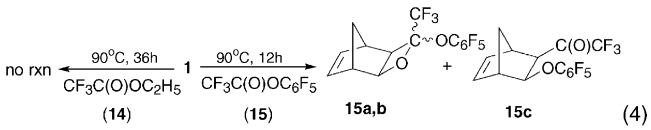


Scheme 1.

excellent example demonstrating the activation effect of a CF_3-substituent on the carbonyl group.

The formation of isomers in case of nonsymmetrical carbonyl compounds is the result of *syn*- versus *anti*-orientation of the two substituents relative to the methylene bridge of the norbornene fragment. The oxetane ring in each of the products is exclusively *exo*- within the limits of detection (NMR, see also discussion below).

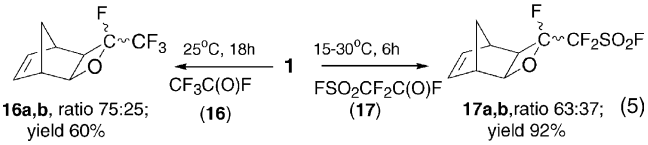
Although polyfluorinated esters are less reactive towards **1**, a similar dependence of the reactivity of C=O and degree of fluorination of the substrate is observed for esters of fluorinated acids. In contrast to the unreactivity of ethyltrifluoroacetate (**14**) at elevated temperature (90 °C, 36 h) pentafluorophenyl trifluoroacetate (**15**) rapidly reacts with **1** under similar conditions to give in high yield cycloadducts **15a,b** contaminated by small amount (5%) of isomeric byproduct (Eq. 4). Combined NMR, IR and mass spectroscopy data are in a good agreement with the structure **15c** assigned to this product (see also reaction of **20** and **1** below).



(4)

yield of mixture 76%, ratio **15a:15b:15c** - 82 :13 :5

Trifluoracetyl fluoride (**16**) is less active towards **1** than hexafluoroacetone (Eq. 1). The reaction proceeds slowly at ambient temperature to give cycloadduct **16a,b** in moderate yield (Eq. 5). More electrophilic α-(fluorosulfonyl)difluoroacetyl fluoride (**17**) reacts with **1** exothermally producing adduct **17a,b** in excellent yield.

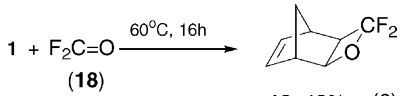


16a,b, ratio 75:25; yield 60% **17a,b**, ratio 63:37; yield 92% (5)

It should be pointed out that detailed NMR analysis of materials isolated in reaction of **1** with **16** or **17** revealed the presence in each cases of small amount (2–4%) of isomers of **16a,b** or **17a,b** respectively. Although the exact structure of the byproducts was not established, the presence of a norbornene fragment, –CFH-group (^1H and ^{19}F NMR) and weak absorption in the carbonyl region (1778 and 1761 cm^{-1} respectively) of both samples may be indicative of the formation of small amounts of 2,2,2-trifluoro-1-(3-

fluoro-bicyclo[2.2.1]hept-5-en-2-yl)-ethanone and 1,1-difluoro-2-(3-fluorobicyclo[2.2.1]hept-5-en-2-yl)-2-oxoethanesulfonyl fluoride respectively.

In contrast to hexafluoroacetone, COF_2 (**18**) is less reactive, giving at ambient temperature only trace of cycloadduct **19** (NMR). The yield of **19** although is significantly higher when the reaction is carried out at elevated temperature and autogenic pressure (Eq. 6).

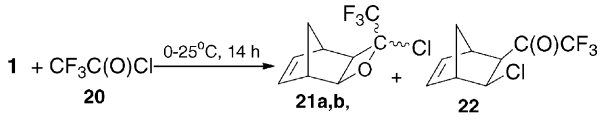


19, 48% (6)

The product isolated in this reaction contains a small amount of isomer (~2%, *endo*-isomer (?); ^{19}F NMR data see Section 3), along with isomeric **28a,b** (~1%, formed by rearrangement of **19**, see Eq. 13) and ~1% of unidentified compound (possibly, 3-fluoro-bicyclo[2.2.1]hept-5-ene-2-carbonyl fluoride). Relatively pure **19** (98%) was isolated by distillation under vacuum. **19** should be stored refrigerated, since its lifetime in glass vessel is limited to several days at ambient temperature. The combination of relatively low boiling point (see Table 1) and limited stability prevented the obtaining of reliable elemental analysis for **19**.

Moreover, the yield and the purity of **19** are greatly affected by reaction temperature. The experiment carried out at 100 °C in a Hastelloy reactor resulted in the formation of significant amount (up to 50%) of byproducts.

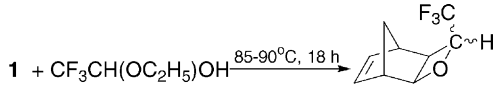
Trifluoroacetyl chloride (**20**) reacts with **1** exothermally giving a mixture of isomeric oxetanes **21a,b** however, in contrast to trifluoroacetyl fluoride (**16**) the major product in this case is the compound **22** (Eq. 7).



Ratio **21a** : **21b** : **22** = 30:17:50 (7)
yield of mixture = 90%;

It should be also pointed out that crude product along with **21a,b**, **22** was also contaminated by small amount (~3%) of unknown material. The crude reaction mixture was fractionated under vacuum and the fraction containing 78% of **22** was isolated. That allowed reliable characterization of this material by NMR. The structure of *exo*-5-chloro-*exo*-6-trifluoroacetylnorbonene-2 assigned to compound **22** is supported by the data of ^{1}H, ^{19}F, ^{13}C NMR (see also discussion below), IR spectroscopy and mass spectrometry.

Interestingly, the corresponding cycloadduct of $CF_3C(O)H$ and quadricyclane was obtained in the direct reaction of trifluoroacetaldehyde *ethylhemiacetal* (**23**) and **1** – refluxing the mixture of **23** and **1** led to the formation of cycloadducts **23a,b**.

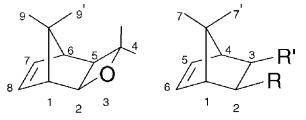


(8)

Ratio **23a** : **23b** = 88:12
yield 44%;

The structure of **23a,b** is in good agreement with ^{1}H, ^{13}C, ^{19}F and mass spectrometry data, but unfortunately, we were not able to obtain satisfactory elemental analysis.

With the exception of **19**, all new norbornenoxetanes are stable liquids at ambient temperature. The ^{19}F NMR spectrum of oxetane **19** exhibits two resonance of equal intensity around −60 and −70 ppm (J_{AB} = 112 Hz), typical for polyfluorinated oxetanes [20,21]. ^{1}H NMR spectra of oxetanes **7a,b**, **9a,b**, **11a,b**, **13a,b**, **15a,b**, **16a,b**, **17a,b**, **19**, **21a,b**, **23a,b** along with required number of resonances exhibit two signals of protons of the methylene bridge (H-9 and H-9′, see structure **9a**) which are well separated (Δ 0.2–0.9 ppm) and appear at 1.5–2.5 ppm as AB type quartet with geminal coupling constant J_{AB} = 9–11 Hz.



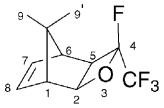
(9a) **(9b)**

Table 1
Reactions of **1** with polyfluorinated carbonyl compounds

Entry number	Reagents (mol)	Method	Solvent (mL)	Temperature (°C), time (h)	Product(s), yield (%)	bp (°C)/mmHg
1	**1**(0.35); **2**(.03)	B	CH_2Cl_2 (100)	10–25(2–4)	**3**(95)	67/21
2	**1**(0.33); **4**(0.35)[a]	B	Ether (100)	10–25(4)	**5**(92)	98–99/19
3	**1**(0.23); **6**(0.17)	B	Ether (60)	10–30(4)	**7a,b**(73[b])	119–121/19
4	**1**(0.074); **8**(0.07)	C		90(36)	**9a,b**(22[b])	72/14
5	**1**(0.11); **10**(0.1)	C		100(18)	**11a,b**(57[b])	81–83/0.1
6	**1**(0.32); **12**(0.31)[a]	B		25–90(4 h)	**13a,b**(87[b])	64–66/0.07
7	**1**(0.03); **15**(0.025)	C		105–100(9)	**15a,b,c**(76[b])	53–77/0.02
8	**1**(0.31); **16**(0.3)	B		25(18)	**16a,b**(60[b])	27–28/0.5
9	**1**(0.3); **17**(0.23)	B		15–30(6)	**17a,b**(92[b])	75–76/0.7
10	**1**(0.35); **18**(0.38)	A	Ether (100)	60(12)	**19**(48)	59–61/13
11	**1**(0.23); **20**(0.22)	B		15–30(4)	**21a,b**, **22**(90[b])	86–92/50
12	**1**(0.11); **23**(0.07)	B		85–90(18)	**23a,b**(44)	65–68/17

[a] Delayed exothermic reaction; temperature risen from 25 to 90 °C over ~1 h period.
[b] Yield of the mixture of isomers.

The resonance of the proton in the α-position to oxygen (H-2) appears at 4.3–4.9 ppm as a doublet (J_d = 4.0–5.5 Hz) coupled to the proton in the β-position to oxygen (H-5, at 2.4–2.6 ppm). All values are in good agreement with reported values of chemical shifts and coupling constants for nonfluorinated norbornenoxetanes [7,8,11]. It should be also pointed out that values of coupling constants between vicinal protons H-2 and H-3 of norbornenes **15c**, **22**, and **26** (see structure **9b**) are slightly higher (J = 7.2, 7.8 and 6.8 Hz, respectively), indicating *cis*-relationship of two protons, since *trans*-coupling constant is usually smaller (for example, values of coupling constant H-2/H-3 reported for large number of *exo*, *endo*-aryltiohalo-bicyclo[2.2.1]heptene-5-enes are in the range between 2.1 and 3.5 Hz [22]).



(16a) **(16b)**

The presence of two isomers in compounds **7a,b**, **9a,b**, **11a,b**, **13a,b**, **15a,b**, **16a,b**, **17a,b**, **21a,b**, **23a,b** is the result of different orientation of substituents at C-4 (structure **9a**) relative to the norbornene methylene bridge. It is reasonable to postulate on steric grounds that the major isomer in all these cases have the bulkiest substituent *anti*- to the norbornene methylene bridge. The aproof of this statement was obtained in 2D H-F HOESY (heteronuclear proton–fluorine 2D NOE) experiment carried out in case of compound **16a,b**. In major isomer **16a** an NOEs for F-4/H-9′ and CF_3-4/H-5 were observed indicating *syn*-orientation of F-4 in major isomer.

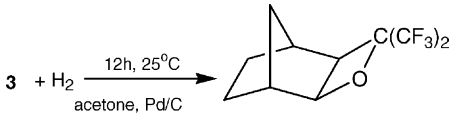
For minor isomer **16b** the confirmation of *anti*-orientation of F-4 and H-9′ was obtained, due to observed large NOEs between H-9′/CF_3-4, F-4/H-5 and H-4/H-2 (see Supplementary data for details). Therefore, the observed substantial four-bond coupling constant H-2/F-4 in **16a** (J = 12.5 Hz; similarly $J_{H2\text{-}F4}$ = 13.0 Hz in **17a**) is the coupling constant between *anti*-H-2 and *syn*-F-4 located on different sides of oxetane ring.

The ratio of isomers correlates well with the size of substituents and ranges widely from 58:42 for **13a,b** (containing CF_3- and CH_2Br groups at C-4), for substituents of similar size, to 88:12 for compounds **23a,b** bearing CF_3– and H– at C-4. The IR spectra of all oxetanes exhibit a band at 1430–1460 cm^{-1} of low or medium intensity, typical for polyfluorinated oxetanes [20]. Mass spectra of oxetanes **9a,b**, **19**, **21a,b**, **23a,b** contain a parent ion of low intensity along with high intensity masses 91 and 66, indicative of retro Diels–Alder type fragmentation as the major decomposition path.

The [2σ+2σ+2π] cycloadditions of quadricyclane with C=C double bonds are typically one-step concerted, regio- and stereospecific (*exo*) processes. For reactivity with C=O bonds, however, Jenner and co-workers [11,12] have reported that the carbonyl bond needs "drastic activation" by electron-withdrawing groups, and at least in the cases of $[CH_3O(O)C]_2C{=}O$ or $C_6H_5C(O)C(O)C(O)OCH_3$, the reactions are not concerted but most likely to involve radical–ion pair intermediates. The observed qualitative order of reactivity of our fluorinated carbonyl compounds toward quadricyclane indeed increases with the electron deficiency of the carbonyl group: $CF_3C(O)CF_3$ > $CF_3C(O)CH_2Br$ ≥ $CF_3C(O)C_6H_5$ > $CF_3C(O)CH_3$ >> $CF_3C(O)OC_2H_5$; $CF_3C(O)OC_6F_5$ >> $CF_3C(O)OC_2H_5$; $CF_3C(O)CF_3$ > $CF_3C(O)F$ > FC(O)F. The fact that $CF_3C(O)Cl$ is more reactive than $CF_3C(O)F$ and $CF_3C(O)CF_3$ > $CF_3C(O)F$ also is consistent with their relative electron-acceptor capacities [23]. Unfortunately, there are no experimental electron affinity data for these compounds, except for a lower limit value of 10.2 kcal/mol^{-1} for hexafluoroacetone [24]). The relatively fast, room temperature reactions all develop a transient yellow color upon mixing the quadricyclane and fluorinated carbonyl compound, which suggests formation of charge-transfer complexes [25] or radical–ion pairs [12], but much more than this circumstantial evidence needs to be adduced before a mechanism of cycloaddition can be established. The formation of by products **15c** and **22** in the reactions of **1** with $CF_3C(O)OC_6F_5$ and $CF_3C(O)Cl$ could be a result of competitive polar addition of the reagent $CF_3C(O)X$ to **1** through C–X bond (X = Cl or OC_6F_5).

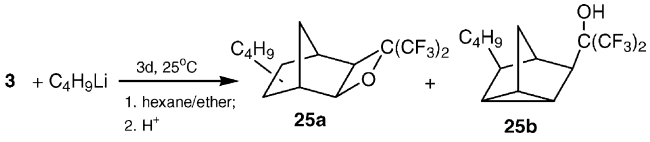
2.2. Selected reaction of norbornenoxetanes

The oxetane fragment in compound **3** is surprisingly stable. For example, Pd catalyzed addition of hydrogen proceeds selectively across the C=C bond of norbornene, but the strained oxetane fragment remains intact in this reaction (Eq. 9).



24,90% (9)

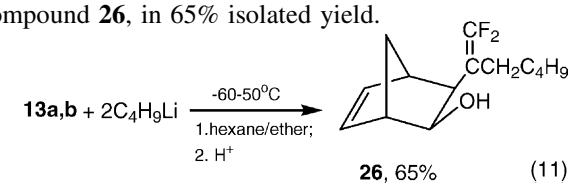
Compound **3** does not react at ambient temperature with potassium *t*-butoxide (DMF, 16 h), $NaBH_4$, or $NaB(Et)_3H$ (THF, reflux, 5 h). However, the reaction of **3** and C_4H_9Li slowly proceeds at ambient temperature to give, after hydrolysis, a mixture of **25a** and **25b** (Eq. 11).



yield 65%; ratio **25a**:**25b** 13:87 (10)

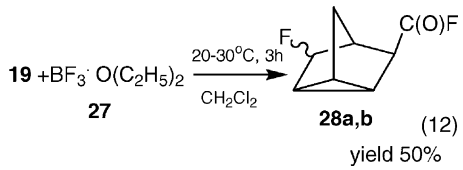
Based on NMR data, compounds **25a** and **25b** form in this reaction as a single isomer (possibly, having *exo*-, *exo*-orientation of both substituents), but NMR data were not sufficient to determine the exact position of butyl substituent in compound **25a** relative to the oxygen of oxetane ring.

Compared with **3**, the oxetane **13a,b** is much more active toward C_4H_9Li. The reaction between **13a,b** and two equivalents of C_4H_9Li rapidly proceeds at −60 to −40 °C to give compound **26**, in 65% isolated yield.

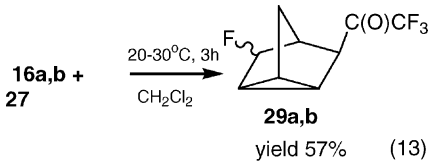


The ^{19}F NMR spectrum of **26** exhibits two doublets at −89.80 and −91.41 ppm with a coupling constant of 58 Hz. Chemical shifts and coupling constants of **26** are comparable to the corresponding values for fluorine substituents in the $=CF_2$ group of hexafluoropropene (δ = −82.8, −95.0, J = 58.3 Hz) [26]. The ^1H NMR spectrum of **26** although quite complex exhibits resonance of two nonequivalent protons of the methylene bridge at 1.63 and 1.84 ppm (AB quartet J = 9.0 Hz) and a proton adjacent to carbon bearing an –OH (H-2, structure **9b**), δ 3.88 ppm, coupled to H-3 (δ 2.34, J_d = 6.8 Hz). The value of the coupling constant suggests an *endo–endo* orientation of these two protons and therefore *exo–exo* relationship of two substituents. The ^{13}C {H} NMR spectrum contains the required number of signals (14, see Section 3) and four resonances of sp^2 carbons: two singlets at 133.19, 140.90 ppm (C=C of norbornene) and two multiplets at 88.26 (dd, J = 17.4, 11.6 Hz) and 153.42 (dd, J = 282.0, 285.0 Hz) ppm, assigned to the exocyclic double bond. IR spectrum exhibits an intensive band at 1735 cm^{-1} typical for fluorinated terminal double bond [27] and broad absorption of –OH centered at 3436 cm^{-1}. All these data are in good agreement with the structure **26**. The formation of compound **26** as a single isomer with *exo*-orientation of both substituents is in a good agreement with suggested *exo*-stereochemistry of **13a,b**.

There is a clear correlation between the stability and the structure of norbornenoxetanes. Among oxetanes **3**, **16a,b** and **19**, compound **3** is the most stable – it can be stored for a long time without any decomposition at ambient temperature; distilled **16a,b** stored in a glass bottle for several months at ambient temperature turned dark brown, but the NMR spectra remained unchanged. By contrast, compound **19** completely decomposed over a one week period when kept in glass vessel at ambient temperature. The stability also correlates with the reactivity of all three toward acids. In sharp contrast to compound **3**, which is stable to the action of Lewis acids [boron trifluoride etherate (**27**) or TaF_5, 25 °C, 16 h) oxetanes **16a,b** and **19** are quite sensitive. For example, the addition of **19** to the solution of **27** in CH_2Cl_2 results in an exothermic rearrangement with the formation of a mixture of two isomeric nortricyclanes **28a,b** (Eq. 13).



NMR and GC/MS analysis of the crude reaction mixture revealed the presence of a small amount (∼5%) of isomeric byproducts (possibly, 3-fluoro-bicyclo[2.2.1]hept-5-ene-2-*exo*-carbonyl fluoride). Compound **16a,b** behaves similarly. Although the reaction with **27** is not as exothermic it leads to a mixture of nortricyclanes **29a,b** (Eq. 13) contaminated by small amount (∼2%, NMR, GC/MS) of isomeric byproducts [likely to be 2,2,2-trifluoro-1-(3-fluoro-bicyclo[2.2.1]hept-5-en-2-yl)-ethanone].



3. Experimental

^1H and ^{19}F NMR spectra were recorded on Brucker DRX-400 (400.5524 and 376.8485 MHz respectively) instruments using $CFCl_3$ as an internal standard and $CDCl_3$ as a lock solvent. ^1H NMR spectra of compounds **3**, **5**, **16a,b**, **17a,b**, **19**, **22**, **23a,b** and **26** were recorded on Brucker DRX-500 (499.87 MHz), values of major proton coupling constants for compounds **3**, **5**, **16a,b**, **17a,b**, **19** were confirmed in homonuclear ^1H COSY experiments; for compounds **23a,b** and **26** – in ^1H selective homodecoupling experiments. Values of major (>5 Hz) proton–fluorine coupling constants in compounds **16a,b** and **17a,b** were confirmed in ^{19}F {H} experiments. The 2D ^{19}F-^1H HOESY spectra (^{19}F observed) for mixture of compounds 16a,b was performed on a 400 MHz Varian Inova spectrometer where ^{19}F appears at 376.284 MHz; more details and spectrum can be found in Supplementary material (see Appendix A).

Separation isomers of compounds **7a,b**, **9a,b**, **11a,b**, **13a,b**, **15a,b**, **16a,b**, **17a,b**, **21a,b**, **23a,b** was not attempted in this study and they were characterized in mixtures by NMR, which in some cases due to overlap of signals could effect the accuracy of signal assignments and determination of values of coupling constants. IR spectra were recorded on a Perkin-Elmer 1600 FT spectrometer as liquid films (KCl plates). Moisture sensitive materials were handled in a glove box. GC and GC/MS analysis were carried out on HP-6890 instrument, using HP FFAP capillary column and either TCD (GC) or mass selective detector (GS/MS) respectively.

Compounds **2**, **12**, **15**, **16** (Synquest), **17** (DuPont), **8**, **10**, **14**, **18**, **20**, butyl lithium (**2M** solution in pentane) (Aldrich) were purchased and used without further purification. Quadricyclane (**1**) was prepared by photochemical isomerization of norbornadiene [28] using *t*-butyl methyl ether as a solvent. For all reactions quadricyclane of 90–95% purity [remainder – norbornadiene (5–8%) and solvent (2–3%)] was used. Molar ratio of reagent are calculated based on 100% **1** (Table 1). Compounds **4** [29] and **6** [30] was prepared according literature procedures. All other chemicals and solvents were obtained commercially and used as received.

Caution! Both hexafluoroacetone and carbonyl fluoride are toxic materials that should be handled properly and by trained personnel only. We did not experience any problems during this study, but some reactions of **1** with polyfluorinated carbonyl compounds are highly exothermic and should be carried out under conditions allowing control of the heat evolving during reaction.

*3.1. Reactions of **1** with polyfluorinated carbonyl compounds*

3.1.1. Method A

In a 400 mL Hastelloy shaker tube, the solution 35 g (0.36 mol) of **1** in 100 mL of dry ether was added. The reactor was cooled down, evacuated, charged with carbonyl fluoride (25 g, 0.38 mol) was kept under autogenic pressure at 60 °C for 12 h. The reaction vessel was unloaded. The solvent was removed under vacuum and the liquid residue was distilled under reduced pressure. The reaction conditions and ratio of reactants are given in Table 1.

3.1.2. Method B

The carbonyl compound (0.1–0.3 mol) was slowly added (either as a gas or liquid) to a well agitated solution of **1** (0.1–0.3 mol) in CH_2Cl_2 or ether solvent, placed in a three-neck round bottom flask equipped with dry-ice condenser, thermometer and either inlet tube or additional funnel. The addition was started at 10 °C and carried out with the rate that allowed the internal temperature to be kept at 20–30 °C. After the addition of carbonyl compound, the reaction mixture was agitated at ambient temperature. the solvent was removed under vacuum and the residue was distilled under reduced pressure. The reaction conditions and ratio of reactants are given in Table 1.

3.1.3. Method C

A glass sample vial (20 mL) was charged with the mixture of **1** (0.05–0.1 mol; 10–20% excess) and the corresponding substrate (0.03–0.08 mol), sealed and kept at 80–110 °C for the period of time indicated in Table 1. The product was isolated by vacuum distillation of the crude reaction mixture. The reaction conditions and ratio of reactants are given in Table 1.

*3.1.4. 4,4-Bis(trifluoromethyl)-3-oxa-tricyclo[4.2.1.0^{2,5}]non-7-ene (**3**)*

Exo-isomer; ^{1}H NMR ($CDCl_3$): δ 1.53(1H, d, J = 9.6 Hz), 2.42(1H, d, J = 9.6 Hz), 2.60(1H, d pent., J = 4.9, 0.9 Hz), 3.21(1H, m), 3.24(1H, m), 4.75(1H, d, J = 4.9 Hz), 5.92(1H, dd, J = 5.7, 3.4 Hz), 6.31(1H, dd, J = 5.7, 3.0 Hz); ^{13}C(neat, {H}): δ 41.30(q, J = 4.0 Hz), 41.90, 42.20, 45.20, 80.50 (sept. J = 31.0 Hz), 83.84, 122.00(q, J = 286 Hz), 122.70(q, J = 285 Hz), 132.30, 140.60. ^{19}F NMR ($CDCl_3$): δ −69.12(3F, q, J = 10.3 Hz), −78.63(3F, q, J = 10.3 Hz). IR: 1462 (w) cm^{-1}. Anal. calc. for $C_{10}H_8F_6O$: C, 46.5, H, 3.1, F, 44.2. Found: C, 46.3, H, 3.0, F, 44.3.

*3.1.5. 4-(2,2,2-Trifluoro-1-trifluoromethyl-ethylidene-3-oxa-tricyclo[4.2.1.0^{2,5}]non-7-ene (**5**)*

Exo-isomer; ^{1}H NMR ($CDCl_3$): δ 1.78(1H, d, J = 9.4 Hz), 1.92(1H, d, J = 9.4 Hz), 3.08(1H, s), 3.29(1H, s), 3.43(1H, d, J = 4.5 Hz), 4.92(1H, d, J = 4.5 Hz), 6.02(1H, dd, J = 3.0, 5.7 Hz), 6.38(1H, dd, J = 3.0, 5.7). ^{13}C(neat, {^{1}H}): δ 40.26, 41.59(s), 44.87, 47.56, 87.36, 92.63 (sept. J = 34.0 Hz), 122.62(q, J = 272.0 Hz), 123.3(q, J = 270.0 Hz), 131.72, 139.71, 175.86 (m). ^{19}F NMR ($CDCl_3$): δ −58.07(3F, m), −58.15(3F, m). IR: 1687(s), 1456 (w) cm^{-1}. Anal. calc. for $C_{11}H_8F_6O$: C, 48.9, H, 3.0, F, 42.2. Found: C, 48.6, H, 2.9, F, 42.6.

*3.1.6. 4-Trifluoromethyl-3-oxa-tricyclo[4.2.1.0^{2,5}]non-7-ene-4-carboxylic acid methyl ester (**7a,b**)*

Mixture of two isomers, ratio 70:30. Major isomer: ^{1}H NMR ($CDCl_3$): δ 1.50(1H, d, J = 10.9 Hz), 1.83(1H, d, J = 10.9 Hz), 2.71(1H, m), 3.08(1H, s), 3.12(1H, s), 3.86(3H, s), 4.55(1H, m, J_d ∼5 Hz), 5.92(1H, dd, J = 3.4, 5.7 Hz), 6.22(1H, dd, J = 3.4, 5.7 Hz); ^{19}F NMR ($CDCl_3$): δ −80.00 (s); minor isomer: ^{1}H NMR ($CDCl_3$): δ 1.50(1H, d, J = 11.0 Hz), 2.43(1H, d, J = 11.0 Hz), 2.55(1H, d, J ∼5 Hz), 3.17(1H, s), 3.22(1H, s), 3.87(3H, s), 4.63(1H, d, J ∼5 Hz), 5.92(1H, dd, J = 3.4, 5.7 Hz), 6.30(1H, dd, J = 3.4, 5.7 Hz); ^{19}F NMR ($CDCl_3$): δ −69.21 (s). IR (mixture of isomers): 1754(s), 1436 (d, m) cm^{-1}. Anal. (mixture of isomers) calc. for $C_{11}H_{11}F_3O_3$: C, 53.2, H, 4.5, F, 23.0. Found: C, 53.0, H, 4.6, F, 23.0.

*3.1.7. 4-Methyl-4-trifluoromethyl-3-oxa-tricyclo[4.2.1.0^{2,5}]non-7-ene (**9a,b**)*

Mixture of two isomers, ratio 63:37. Major isomer: ^{1}H NMR ($CDCl_3$): δ 1.39(3H, q, J = 1.1 Hz), 1.59(1H, d, J = 9.2 Hz), 2.25(1H, d, J = 9.4 Hz), 2.43(1H, d, J = 5.0 Hz), 2.91(1H, m), 3.10(1H,m) 4.59(1H, d pent., J = 5.0, 1.0 Hz), 5.90(1H, dd, J = 3.4, 5.7 Hz), 6.23(1H, dd, 3.0, 5.7 Hz); ^{19}F NMR ($CDCl_3$): δ −82.06(s). Minor isomer: ^{1}H NMR ($CDCl_3$): δ 1.50(1H, d, J = 9.4 Hz), 1.65(3H, q, J = 1.1 Hz), 2.18(1H, d, J = 5.0 Hz), 2.52(1H, d, J = 9.4 Hz), 3.00(2H, s), 4.53(1H, d, J = 5.0 Hz), 5.85(1H, dd, J = 3.4, 5.7 Hz), 6.27(1H,dd, J = 3.4, 5.7 Hz); ^{19}F NMR ($CDCl_3$): δ −72.33 (s). IR (mixture of isomers): 1457 (m) cm^{-1}. GC/MS (*m/e,* major): 204(M^+, $C_{10}H_{11}F_3O^+$), 91($C_7H_7^+$), 66 ($C_5H_5^+$).

*3.1.8. 4-Phenyl-4-trifluoromethyl-3-oxa-tricyclo[4.2.1.0^{2,5}]non-7-ene (**11a,b**)*

Mixture of two isomers, ratio 74:26. Major isomer: ^{1}H NMR ($CDCl_3$): δ 1.19(1H, d, J = 9.4 Hz), 1.61(1H, d; J = 9.4 Hz), 2.80(1H, m), 2.85(1H, d, J = 4.9 Hz), 3.07(1H, m), 4.76(1H, d, J = 4.9 Hz), 5.93(1H, dd, J = 3.4, 5.7 Hz), 6.23(1H, dd, J = 3.4, 5.7 Hz), 7.37(5H, m); ^{19}F NMR ($CDCl_3$): δ −84.57(s). Minor isomer: 1.59(1H, d, J = 9.8 Hz), 2.51(1H, d; J = 4.9 Hz), 2.75(1H, d, J = 9.8 Hz), 3.19(1H, m), 3.33(1H, m), 4.72(1H, d, J = 4.9 Hz), 5.85(1H, dd, J = 3.0, 5.7 Hz), 6.32(1H, dd, J = 3.0, 5.7 Hz), 7.37(3H,

m), 7.62(2H, d, J = 7.6 Hz); ^{19}F NMR ($CDCl_3$): δ −75.62 (s). IR: 1498(w), 1450(m) cm^{-1}. Anal. (mixture of isomers) calc. for $C_{15}H_{13}F_3O$: C, 67.7; H, 4.9; F, 21.4. Found: C, 67.6; H, 4.8; F, 21.3.

*3.1.9. 4-Bromomethyl-4-trifluoromethyl-3-oxa-tricyclo[4.2.1.0^{2,5}]non-7-ene (**13a,b**)*

Mixture of two isomers, ratio 58:42. Major isomer: ^{1}H NMR ($CDCl_3$): δ 1.66(1H, d, J = 9.4 Hz), 2.13(1H, d, J = 9.4 Hz), 2.51(1H, d m, J = 4.9, 1.9 Hz), 3.18(2H, m), 3.62(2H, s), 4.62(1H, d, J = 4.9 Hz), 5.93(1H, dd, J = 3.4, 5.7 Hz), 6.28(1H, dd, J = 3.0, 5.7 Hz). ^{19}F NMR ($CDCl_3$): δ −80.28 (s). Minor isomer: 1.54(1H, d, J = 9.8 Hz), 2.49(1H, d, J = 9.8 Hz), 2.51(1H, d, J = 4.9), 3.13(1H, m), 3.18(1H, m), 3.67(1H, dq, J = 11.3, 1.5 Hz), 3.80(1H, d, J = 11.3 Hz), 4.59(1H, dd, J = 4.9, 1.5 Hz), 5.90(1H, dd, J = 3.4, 5.7 Hz), 6.32(1H, dd, J = 3.0, 5.7 Hz). ^{19}F NMR ($CDCl_3$): δ −69.17 (s). IR (mixture of isomers): 1430 (w), 1462(w) cm^{-1}. Anal. (mixture of isomers) calc. for $C_{10}H_{10}BrF_3O$: C, 42.4; H, 3.6; F, 20.1. Found: C, 41.9; H, 3.4; F, 20.0.

*3.1.10. 4-Pentafluorophenoxy-4-trifluoromethyl-3-oxa-tricyclo[4.2.1.0^{2,5}]non-7-ene (**15a,b**)*

Crude reaction mixture (26 g) was subjected to distillation under reduced pressure (0.02 mmHg) using a 60 cm long spinning band column. Seven fractions were collected and analyzed by NMR:

Fraction 1: 2.2 g; bp 53–58 °C, **15a**, 62.4%, 15b; 33.3%, **15c**, 4.3%;

Fraction 2: 5.3 g; bp 58–59 °C, **15a**, 73.7%, 15b; 23.5%, **15c**, 2.5%;

Fraction 3: 5.9 g; bp 59–60 °C, **15a**, 82.6%, 15b; 13.2%, **15c**, 4.2%;

Fraction 4: 1.4 g; bp 60–67 °C, **15a**, 82.2%, **15b**, 13.6%, **15c**, 4.2%;

Fraction 5: 1.6 g; bp 67–68 °C, **15a**, 89%, **15b**, 5.4%, **15c**, 5.1%;

Fraction 6: 1.9 g; bp 67–76 °C, **15a**, 91%, **15b**, 3.2%, **15c**, 5.8%;

Fraction 7: 1.3 g; bp 76–77 °C, **15a**, 91%, **15b**, 1.0%, **15c**, 8.0%;

Total, fractions 1–7: 19.6 g; yield of the mixture 76%.

Compounds **15a,b**: major isomer: ^{1}H NMR ($CDCl_3$): δ 1.58(1H, d, J = 9.8 Hz), 2.32(1H, d, J = 9.8 Hz), 2.73(1H, d J = 4.5 Hz), 3.16(1H, m), 3.21(1H, m), 4.38(1H, d, J = 4.5 Hz), 5.89(1H, dd, J = 3.0, 5.7 Hz), 6.36(1H, dd, J = 3.0, 5.7 Hz); ^{19}F NMR ($CDCl_3$): δ −77.48(3F, t, J = 5.8 Hz), −151.27(2F,m), −159.22(1F,t, J = 21.6 Hz), −163.21(2F,m); minor isomer: ^{1}H NMR ($CDCl_3$): δ 1.58(1H, d, J = 9.8 Hz), 2.45(1H, d, J = 9.8 Hz), 2.83(1H, dm, J = 4.9 Hz), 3.16(1H) 3.21(1H, m) 4.42(1H, dm, J = 4.9 Hz), 5.98(1H, dd, J = 3.4, 5.7Hz), 6.32(1H, dd, J = 3.0, 5.7 Hz). ^{19}F NMR ($CDCl_3$): δ −82.89(3F, t, J = 7.1 Hz), −150.39(2F,m), −160.0(1F,t, 21.6 Hz), −164.03(F, m). **15c**: ^{1}H NMR ($CDCl_3$): δ 1.83(1H, dm, J = 9.4, 1.8 Hz), 2.34(1H, d, J = 9.4 Hz), 2.92(1H, m), 3.21(1H, m), 3.25(1H, dd, J = 7.6, 2.3 Hz), 4.85(1H, dm, J = 7.6, 0.8 Hz), 6.08(1H, dd, J = 3.0, 5.7 Hz), 6.30(1H, dd, J = 3.0, 5.7 Hz); ^{19}F NMR ($CDCl_3$): δ −79.51(3F, t, J = 4.5 Hz), −154.93(2F, dm, J = 22.6 Hz), −161.68(1F, tt, J = 22.0, 1.9 Hz), −162.92(2F, m); IR (mixture of isomers): 1761 (w), 1518(s), 1468(s) cm^{-1}. Anal. (mixture of isomers) calc. for $C_{15}H_8F_8O_2$: C, 48.4; H, 2.2; F, 40.8. Found: C, 48.7; H, 2.0; F, 41.0.

*3.1.11. 4-Fluoro-4-trifluoromethyl-3-oxa-tricyclo[4.2.1.0^{2,5}]non-7-ene (**16a,b**)*

Mixture of isomers **16a,b**, contaminated by small amount of unidentified isomeric material (NMR, GC/MS, possibly 2,2,2-trifluoro-1-(3-fluoro-bicyclo[2.2.1]hept-5-en-2-yl)-ethanone), ratio 74:24:2 respectively. **16a,b**: major isomer: ^{1}H NMR ($CDCl_3$): δ 1.61(1H, d, J = 10 Hz), 2.30(1H, d, J = 9.4 Hz), 2.78(1H, ddt, J = 7.9, 4.8, 1.5 Hz), 3.12(1H, m, J = 3.2 Hz), 3.20(1H, m, J = 3.4 Hz), 4.35(1H, ddt, J = 12.5, 4.8, 1.4 Hz), 5.97(1H, dd, J = 3.0, 5.7, Hz), 6.31(1H, dd, J = 3.4, 5.7, Hz); ^{19}F NMR ($CDCl_3$): δ −87.64(3F,d; J = 3.2, Hz), −126.61(1F, ddq; J = 12.5, 7.9, 3.2 Hz). Minor: ^{1}H NMR ($CDCl_3$): δ 1.61(1H, d, J = 10.0 Hz), 2.25(1H, d, J = 10.0 Hz), 2.62(1H, ddt, J = 12.1, 4.1, 1.5 Hz), 3.12(1H, m), 3.24(1H, m), 4.86(1H, d pent., J = 4.1, 1.1 Hz), 5.96(1H, dd, J = 3.0, 5.7Hz), 6.36(1H, dd, J = 3.4, 5.7 Hz). ^{19}F NMR ($CDCl_3$): δ −80.10(3F, d, J = 1.1 Hz), −103.84(1F, dm, J = 12.1, 1.9 Hz). IR (mixture of isomers): 1768 (w), 1463(w) cm^{-1}. Anal. (mixture of isomers) calc. for $C_9H_8F_4O$: C, 51.93; H, 3.87; F, 36.51. Found: C, 51.64; H, 3.78; F, 36.35.

*3.1.12. Difluoro-(4-fluoro-3-oxa-tricyclo[4.2.1.0^{2,5}]non-7-en-4-yl)-methanesulfonyl fluoride (**17a,b**)*

Isolated mixture of **17a** and **17b** was contaminated by unidentified isomeric material (∼3%, NMR, GC/MS, possibly 1,1-difluoro-2-(3-fluoro-bicyclo[2.2.1]hept-5-en-2-yl)-2-oxo-ethanesulfonyl fluoride), ratio 66:30:4. **17a,b** major: ^{1}H NMR ($CDCl_3$): δ 1.66(1H, d, J = 10.2 Hz), 2.30(1H, d, J = 10.2 Hz), 2.95(1H, ddq, J = 8.0, 4.5, 1.1 Hz), 3.17(1H, m, J = 1.1 Hz), 3.25(1H, m, J = 1.5 Hz), 4.46(1H, ddt, J = 13.0, 4.5, 1.1 Hz), 5.95(1H, dd, J = 3.4, 5.7Hz), 6.3(1H, dd, J = 3.0, 5.7, Hz); ^{19}F NMR ($CDCl_3$): δ 45.20(1F,dt, J = 11.4, 5.7 Hz), −111.15(1F,ddt, J = 247.0, 6.5, 3.9 Hz), −113.50(1F, ddd, J = 247.0, 5.2, 3.9 Hz), −119.17(1F, qt, J = 13.0, 10.7 Hz). Minor isomer: ^{1}H NMR ($CDCl_3$): ^{1}H NMR ($CDCl_3$): 1.66(1H), 2.21(1H, d, J = 10.2 Hz), 2.75(1H, ddt, J = 12.0, 4.2, 1.1 Hz), 3.20(1H, s), 3.30(1H, m, J = 1.3 Hz), 4.96(1H, d pent., J = 4.1, 1.5 Hz), 5.95(1H, dd, J = 5.7, 3.0 Hz), 6.39(1H, dd, J = 5.7, 3.0 Hz). ^{19}F NMR ($CDCl_3$): δ 43.11(1F, dt, 11.0, 4.7 Hz), −95.83(1F, t, J = 12.0 Hz), −104.6(1F, dd, J = 246.0, 5.2 Hz), −107.50(1F, dt, J = 246.0, 4.2 Hz). IR (mixture of isomers): 1443(w) cm^{-1}. Anal. (mixture of isomers) calc. for $C_9H_8F_4O_3S$: C, 39.7, H, 3.0;. Found: C, 39.5, H, 2.8.

*3.1.13. Exo-4,4-difluoro-3-oxa-tricyclo[4.2.1.0^{2,5}]non-7-ene (**19**)*

Sample contained 2% of isomer [^{19}F ($CDCl_3$): δ −62.1(1F,dm; 152 Hz), −81.1(1F, dm; 152 Hz, *endo*-isomer?] and ~5% of two unidentified materials isomeric to **19** (GC/MS). **19**: ^{1}H NMR ($CDCl_3$): δ 1.63(1H, d, J = 9.8 Hz), 2.12(1H, d, J = 9.8 Hz), 2.90(1H, qt, J = 4.9, 1.5 Hz), 3.05(1H, m, J = 0.8 Hz), 3.21(1H, sept, J = 1.3 Hz), 4.35(1H, ddq, J = 12.8, 4.9, 1.5 Hz), 6.01(1H, dd, J = 3.0, 5.7 Hz), 6.31(1H, dd, J = 3.4, 5.7 Hz); ^{19}F NMR ($CDCl_3$): δ −61.11(1F,dd; 112.0, 5.0 Hz), −70.81(1F, ddd, J = 112.0, 12.8, 2.9 Hz). ^{13}C(neat, {^{1}H}): δ 38.49(d, J = 5 Hz), 40.60(dd, J = 3.5, 1.5 Hz), 44.21(d, J = 4Hz), 48.40(dd, J = 26, 29 Hz), 74.30(dd, J = 5.0, 3.0 Hz), 122.87(dd, J = 384, 289 Hz), 132.56, 139.96. IR: 1837(w), 1439(w) cm^{-1}. GC/MS (*m/e*, major): 158 (M^+, $C_8H_8F_2O^+$), 129($C_6H_3F_2O^+$), 109, 92($C_7H_8^+$), 66($C_5H_5^+$).

*3.1.14. Reaction of **1** with **20***

Gaseous **20** (36 g, 0.27 mol) was slowly added to 25 g of **1** (95%) placed in three-neck round bottomed flask equipped with a thermometer, and dry ice condenser at 0–10 °C over a 30 min period. The reaction mixture was kept at 0–10° for 1 h after addition was finished, warmed up to ambient temperature and left agitated overnight. The crude reaction mixture was the subject of distillation under reduced pressure (26 mmHg) using a 60 cm spinning band column. Five fractions were collected and analyzed by NMR:

Fraction 1: 12.0 g; bp 53–54 °C, **21a**, 55%, **21b**, 15.9%, 22, 26.2%, unknown, 2.9%;

Fraction 2: 17.0 g; bp 55–56 °C, **21a**, 41.2%, **21b**, 18.3%, **22**, 37.5%, unknown, 3.0%;

Fraction 3: 6.8 g; bp 55–56 °C, **21a**, 27.8%, **21b**, 19.1%, **22**, 50.2%, unknown, 2.9%;

Fraction 4: 5.0 g; bp 56–60 °C, **21a**, 18.6%, **21b**, 17.7%, 22; 60.6%, unknown, 2.7%;

Fraction 5: 8.0 g; bp 60–63 °C, **21a**, 5.7%, **21b**, 13%, **22**, 78.3%, unknown, 3.0%;

Total, fractions 1–5: 48.8 g; yield of the mixture 80%.

21a,b, major isomer: ^{1}H NMR ($CDCl_3$): δ 1.45(1H, d, J = 10.0 Hz), 2.28(1H, d, J = 10.0 Hz), 2.61(1H, dt, J = 4.6, 1.2 Hz) 2.86(1H, m), 2.93(1H, m), 4.32(1H,dt, J = 4.6, 1.4 Hz), 5.72(1H, dd, J = 3.2, 5.7 Hz), 6.05(1H, dd, J = 3.2, 5.7 Hz); ^{19}F NMR ($CDCl_3$): δ −84.08 (s); minor isomer: ^{1}H NMR ($CDCl_3$): δ 1.36(1H, d, J = 10.0 Hz), 2.08(1H, d, J = 10.0 Hz), 2.62(1H, dt, J = 4.9, 1.2 Hz) 2.90(1H, m), 2.98(1H, m), 4.72(1H, dm, J = 4.9, 1.2 Hz), 5.72(1H, dd, J = 3.2, 6.0 Hz), 6.05(1H, dd, J = 3.2, 6.0 Hz); ^{19}F NMR ($CDCl_3$): δ −76.00(s).

22: δ 1.62(1H, d pent., J = 9.6, 1.9 Hz), 2.08(1H, dm J = 9.6, 1.5 Hz), 2.87(1H, m), 2.91(1H, m), 2.94(1H, dd, 7.8, 1.8 Hz), 3.99(1H, ddd, J = 7.8, 1.8, 0.7 Hz), 5.99(1H, dd, J = 3.4, 5.7 Hz), 6.11(1H, dd, J = 3.4, 5.7 Hz); ^{19}F NMR ($CDCl_3$): δ −79.26 (s); ^{13}C {H}(neat): δ 43.00, 43.61, 49.46, 51.06, 56.54, 113.95 (q, 293 Hz), 134.69, 138.77, 189.19 (q, J = 34.9 Hz); IR (fraction 5): 1761 (s), 1457(m) cm^{-1}; fraction 1: 1761 (m), 1457(m) cm^{-1}. GC/MS (*m/e*, mixture of isomers): 224 (M^+, $C_9H_8ClF_3O^+$).

*3.1.15. 4-Trifluoromethyl-3-oxa-tricyclo[4.2.1.0^{2,5}]non-7-ene (**23a,b**)*

Mixture of two isomers, ratio 88:12. Major isomer: δ 1.61(1H, d pent., J = 9.7, 1.4 Hz), 2.04(1H, dt, J = 9.7, 1.6 Hz), 2.48(1H, octet, J = 5.3, 3.4, 1.6 Hz), 2.84(1H, m), 3.04(1H, m), 4.07(1H, qd, J = 6.8, 3.4 Hz), 4.53(1H, d, 5.3 Hz), 5.8 (1H, dd, J = 5.7, 3.5Hz), 6.22(1H, dd, J = 5.7, 3.0 Hz); ^{19}F NMR ($CDCl_3$): δ −81.24(3F, d, 6.8 Hz); ^{13}C {H}(neat): 38.22(m), 41.0, 41.55, 46.57, 75.76(q, 33 Hz), 84.17, 125.13 (q, 278 Hz), 131.61, 139.38; minor isomer δ: 1.44(1H, d, J = 9.6 Hz), 2.38(1H, dm J = 9.6 Hz), 2.42(1H, dd, 5.5, 6.2 Hz), 3.04(2H), 4.56(1H, d, 5.5 Hz), 4.82(1H, qd, 9.0, 6.2 Hz), 5.8(1H, dd, J = 5.7, 3.0 Hz), 6.28(1H, dd, J = 5.7, 3.0 Hz); ^{19}F NMR ($CDCl_3$): δ −73.11(3F, d, 9.0 Hz); ^{13}C {H}(neat): 39.50(m), 41.66, 45.83, 73.88(q, 35.0 Hz), 81.93, 124.90 (q, 281.0 Hz), 131.81, 140.97, 142.40. IR (mixture of isomers): 1460(w) cm^{-1}; GC/MS (*m/e*, mixture of isomers): 190 (M^+, $C_9H_9F_3O^+$).

3.2. Reactions of norbonenoxetanes

*3.2.1. Hydrogenation of **3***

A 400 mL Hastelloy shaker tube was loaded with the solution of 75 g (0.29 mol) of **3** in 100 mL of acetone and 1 g of Pd on carbon (5 wt.%, Aldrich). The reaction vessel was evacuated at −40 °C, and kept with agitation at ambient temperature under constant pressure of hydrogen (300 psi) for 12 h. The reactor was unloaded and the crude reaction mixture was filtered through Celite^R. The solvent was removed under vacuum and the product was distilled under vacuum to give 68 g (90%) of 24, bp 64–65/2.5 mmHg. ^{1}H NMR ($CDCl_3$): δ 0.95(1H,t, J = 8.3 Hz), 1.1(1H, t, J = 8.3 Hz), 1.45(1H, d, J = 9.6 Hz), 1.60(2H, m), 2.38(1H, s), 2.48(1H, d, J = 9.6 Hz), 2.55(1H, s), 2.60(1H, d, J = 4.9 Hz), 4.91(1H, d, J = 4.9 Hz); ^{19}F NMR ($CDCl_3$): δ −70.13(3F,q, J = 9.6 Hz),−79.36(3F, q, J = 9.6 Hz). IR: 1484(w), 1456(w) cm^{-1}. Anal. calc. for $C_{10}H_{10}F_6O$: C, 46.2; H, 3.9; F, 43.8. Found: C, 45.7; H, 3.7; F, 44.0.

*3.2.2. Reaction of **3** with butyl lithium*

To the solution of 10 g (0.038 mol) of **3** in 50 mL of dry THF 20 mL of a 2 M solution of butyl lithium in pentane was slowly added at −40 °C. The reaction mixture was warm up to ambient temperature and agitated for 2 days. The reaction mixture was diluted with 200 mL of saturated solution of NH_4Cl, extracted with CH_2Cl_2, combined organic layer was washed with water (200 mL × 2), dried over $MgSO_4$, solvent was removed under vacuum and crude product was distilled under vacuum to give 6g (65%) of **25a,b**, bp 92–92.5/0.65 mmHg (ratio **25a:25b** – 13:87). **25a**: ^{1}H NMR ($CDCl_3$): δ 0.75(3H, t), 1.10–1.20(9H, m), 1.49(1H), 2.14(1H, s), 2.36(1H, d, J = 11.5 Hz), 2.53(1H, s), 2.58(1H, d, J = 4.2 Hz), 4.85(1H, d, J = 4.2 Hz); ^{19}F

NMR ($CDCl_3$): δ −70.20(3F, q, J = 10.0Hz), −79.25(3F, q, J = 10.0 Hz). **25b**: ^{1}H NMR ($CDCl_3$): δ 0.75(3H, t), 1.10–1.20(9H, m), 1.40(1H, d, J = 11.0 Hz), 1.52(1H, t, J = 5.7 Hz), 1.65(1H, d, J = 11.0 Hz), 1.94(1H, m), 2.02(1H, s), 2.90(1H, s); ^{19}F NMR ($CDCl_3$): δ −73.90(3F, qd, J = 11.0, 2.6 Hz), −77.71(3F, qd, J = 11.0, 1.9 Hz). IR (mixture isomers): 3567 (OH), 1467 cm^{-1}. Anal. calc. for $C_{14}H_{18}F_6O$: C, 53.2; H, 5.7; F, 36.0. Found: C, 53.0; H, 5.4; F, 36.2.

3.2.3. Reaction of *13a,b* with butyl lithium

To the solution of 13 g (0.068 mol) of **13a,b** in 100 mL of dry ether, 70 mL of a 2 M solution of butyl lithium in pentane was added drop wise at −60 to −50 °C. The reaction mixture was stirred at −50 °C for 1 h, brought to ambient temperature and kept agitated for 3 h. It was poured slowly into 500 mL of saturated solution of NH_4Cl, extracted with CH_2Cl_2, the combined organic layer was washed with water (300 mL × 2), dried over $MgSO_4$, solvent was removed under vacuum and crude product was distilled under vacuum to give 10.5 g (65%) of 26; bp 92–93/0.65 mmHg. ^{1}H NMR ($CDCl_3$): δ 0.87(3H, t, J = 6.6 Hz), 1.27(4H, m), 1.42(2H,m), 1.59(1H, d, J = 9.0 Hz), 1.70(1H, br. s), 1.84(1H, d, J = 9.0 Hz), 1.86(1H, m) 2.05(1H, m), 2.34(1H, dq, J = 6.8, 2.3Hz), 2.77(1H, m), 2.82(1H, m), 3.88(1H, dt, J = 6.8, 1.1 Hz), 6.00(1H, dd, J = 3.0, 5.7 Hz), 6.36(1H, J = 3.0, 5.7 Hz); ^{19}F NMR ($CDCl_3$): δ −89.80(1F, dq, J = 53.7; 2.6 Hz), −91.41(3F, d, J = 53.7 Hz). ^{13}C {H} (neat): 21.80, 26.50, 27.57, 31.12, 39.87, 42.50, 43.46(d), 44.18, 48.46, 71.47, 88.26 (dd, J = 17.4, 11.6 Hz), 133.19, 140.90, 153.42 (dd, J = 282.0, 285.0 Hz). IR: 3436(OH, m), 1735(s), 1462(w) cm^{-1}. GC/MS (*m/e*, major): 242 (M^+, $C_{14}H_{20}F_2O^+$), 176($C_9H_{14}F_2O^+$), 120($C_5H_6F_2O^+$).

3.2.4. Isomerization of *19* by action of *27*

Compound **27** (0.5 g, 0.0035 mol) of was dissolved in 20 mL of CH_2Cl_2 and 7 g (0.044 mol) of **19** was added to this solution with the rate varied to maintain the internal temperature <30 °C (∼30 min). The reaction mixture was agitated at ambient temperature for 3 h, diluted with 300 mL of water and extracted with 50 mL of CH_2Cl_2. Organic layer was separated, dried over $MgSO_4$, solvent was removed under vacuum and the residue (6.8 g) distilled under vacuum to give 3.5 g of liquid bp 73–74/10 mmHg **28a,b** [ratio 60:40, containing ∼5% of two unidentified materials isomeric to **28a,b** (GC/MS)]. **28a,b**: major isomer: ^{1}H NMR ($CDCl_3$): δ 1.43(1H, m), 1.49(2H, m), 1.58(1H, t, J = 4.5 Hz), 1.67(1H, t, J = 4.8 Hz), 2.33(1H, s), 3.22(1H, s), 4.73(1H, d, J = 58.0 Hz); ^{19}F NMR ($CDCl_3$): δ 45.40(1F, s), −197.51(1F, d, J = 58 Hz); minor isomer: ^{1}H NMR ($CDCl_3$): δ 1.39(1H, dm, J = 10.7 Hz), 1.49(2H, m), 1.95(1H, d, J = 10.7 Hz), 2.40(1H, s), 2.58(1H, m, J = 1.5 Hz), 2.58(1H, m, J = 1.5 Hz), 4.62(1H, d, t, J = 57.7 Hz); ^{19}F NMR ($CDCl_3$): δ 41.98(1F, s), −194.57(1F, d, J = 57.7 Hz). IR (mixture of isomers): 1838(s) cm^{-1}. GC/MS (mixture of isomers; *m/e*, major): 158 (M^+, $C_8H_8F_2O^+$), 138($C_8H_7FO^+$), 118($C_8H_6O^+$), 109($C_6H_2FO^+$), 99($C_6H_2O^+$), 91($C_7H_7^+$).

3.2.5. Isomerization of *15a,b* by action of *27*

The reaction was carried under similar conditions using 0.5 g of 27(0.0035 mol) and 10 g (0.048 mol) of **15a,b** and 30 mL of CH_2Cl_2. After vacuum distillation it was isolated 5.8 g (57%) of **29a,b** (ratio 62:38), bp 67–69/14 mmHg, contaminated with ∼2% of two unidentified materials isomeric to **29a,b** (GC/MS).

29a,b: major isomer: ^{1}H NMR ($CDCl_3$): δ 1.46(1H, tt, J = 9.9, 1.2 Hz), 1.58(2H, m), 1.65(1H, tm, J = 5.0, 1.1 Hz), 1.73(1H, m, J = 5.0 Hz), 1.83(1H, t, J = 5.0 Hz), 2.59(1H, s), 4.92(1H, dt, J = 57.8, 2 Hz); ^{19}F NMR ($CDCl_3$): δ −78.00(3F, s), −197.30(1F,d, 57.8 Hz); minor isomer: ^{1}H NMR ($CDCl_3$): δ 1.45(1H, dt, J = 11.0, 1.2 Hz), 1.58(3H, m), 2.03(1H, dq, J = 11.2, 1.2 Hz), 2.63(1H, s), 2.95(1H, s), 4.83(1H, dt, J = 56.7, 2.0 Hz); ^{19}F NMR ($CDCl_3$): δ −77.71(3F,s), −193.58(1F, d, J = 56.7Hz). IR (mixture of isomers): 1757(s) cm^{-1}. GC/MS (mixture of isomers; *m/e*): 208 (M^+, $C_9H_8F_4O^+$), 188($C_9H_7F_3O^+$), 109($C_6H_2FO^+$), 91($C_7H_7^+$).

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Appendix A. Supplementary material

Parameters of 2D H-F HOESY experiment for compounds **16a,b** can be found in the on-line version, at doi:10.1016/j.jfluchem.2004.06.011.

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