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Synthesis of geminal-bis(trifluoromethyl)-substituted dienes, heterodienes, 7,7,7,8,8,8-hexafluoro-β-cyclocitral and -safranal

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Dedicated to Prof. Yoshiro Kobayashi on the occasion of his 75th birthday

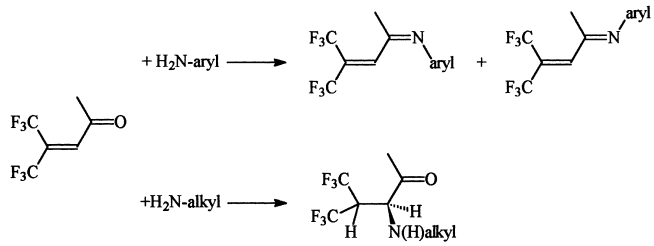
Abstract

Reaction of 5,5,5-trifluoro-4-(trifluoromethyl)penta-3-en-2-one (**1**) with *p*-toluene-sulfonylhydrazines under basic conditions provided anti-Michael addition products. Acid-catalyzed reactions yielded the expected hydrazones. In the absence of solvent the reaction of $(CH_3)_3SiCl$ with **1** gave the corresponding silylenolether (**3**), which did not yield cross condensation products with ketones. In the presence of $TiCl_4$ silylenolether (**3**) reacted at −78°C to give the corresponding nonadienone (**11**). Analogously at 20°C condensation with water elimination gave the pyran system (**12**). The yields of **11** and **12** were increased by adding $ZnCl_2$. It is interesting to note that trimethylsiloxycyclohexene reacted with **1** in a Mukaiyama-aldol-condensation to the corresponding cross condensation product **13**. Starting from $(CF_3)_2C{=}C(CN)_2$ and a mixture of (*E*/*Z*)-1,3-pentadiene the expected cyclohexene was formed. One of the two CN-groups was removed with NaOH in C_2H_5OH/H_2O. A second double bond was introduced in an allylic position of the hexene ring by bromination and elimination with $(C_2H_5)_3N$ to yield the diene. Reduction with DIBAlH provided the aldehyde 7,7,7,8,8,8-hexafluorosafranal. Hydrogenation of the C3–C4 double bond in the presence of palladium on a charcoal catalyst led to 7,7,7,8,8,8-hexafluoro-β-cyclocitral. X-ray structures of selected compounds are provided.

Keywords: Anti-Michael addition; Bis(trifluoromethyl)dienes; Condensation; Hydrazines; Disilylenolethers; Nonadienone; Substituted pyran; Cycloadditions; Bis(trifluoromethyl)-ethylene-1,1-carbodinitrile; Hexafluorosafranal; Selective hydrogenation; Hexafluoro-β-cyclocitral; X-ray structures

1. Introduction

Based on recent studies [1,2] and new reactions it could be shown that 5,5,5-trifluoro-4-trifluoromethylpent-3-en-2-one (**1**) is a versatile and highly reactive educt which provides new substances with interesting properties. Chemical reactivity differs substantially from the corresponding nonfluorinated pentaenone. It can be prepared almost quantitatively from $(CF_3)_2CO$ and $(C_5H_5)_3P{=}CHC(O)CH_3$ in the presence of hydroquinone without solvent [3]. Among the reactions studied it is interesting to note that **1** yields with ring-substituted aniline derivates, the corresponding stable bis-trifluoromethylated α,β-unsaturated imines as a mixture of *syn*- and *anti*-isomers and contrary to alkylamines the expected anti-Michael products are obtained quantitatively [1] as shown below.



With elemental bromine in CCl_4 **1** formed two brominated compounds $(CF_3)_2C{=}CH{-}C(O)CH_{3-n}Br_n$ (n=1,2) [2].

The aim of this paper is the investigation of the chemistry of **1** and the preparation of new precursors for the synthesis of 16,16,16,17,17,17-hexafluororetinals.

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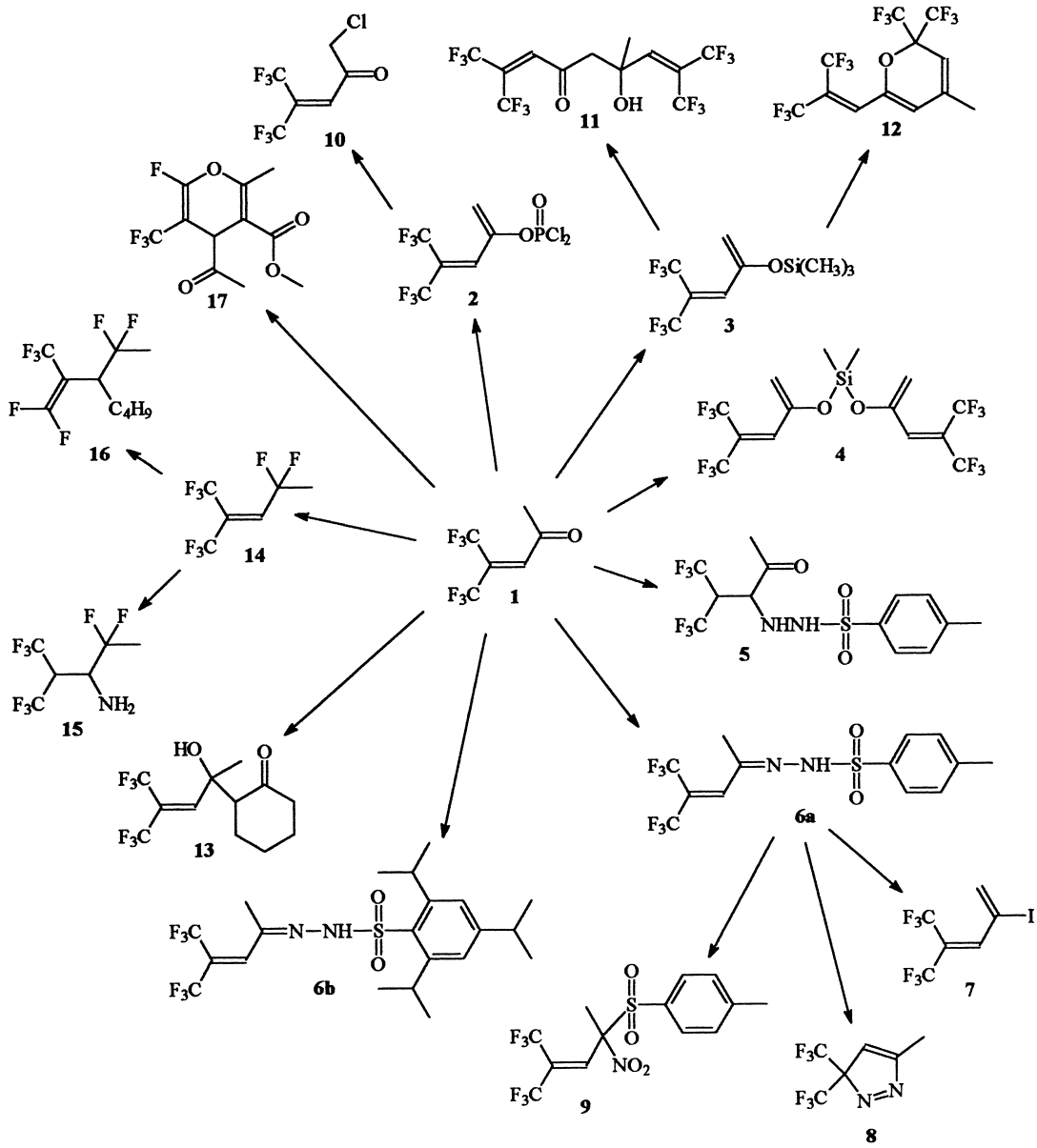


Scheme 1.

2. Results and discussion

The conversion of **1** with phosphoryl chloride and triethylamine without solvent leads to the diene 1,1,1-trifluoro-2-(trifluoromethyl)-penta-2,4-dienyl-(dichlorophosphoroacidester) (**2**), which was isolated and characterized. Similarly the silylenolethers 1,1,1-trifluoro-2-(trifluoromethyl)-4-(trimethylsiloxy)-penta-2,4-diene (**3**) and dimethyl-bis-(1,1,1-trifluoro-2-trifluoromethylpenta-2,4-dienyl-4-oxy)silane (**4**) are made by treating **1** with $(CH_3)_3SiCl$ or $(CH_3)_2SiCl_2$, respectively, in the precence of $(C_2H_5)_3N$ (see Scheme 1). Especially compounds **2** and **3** are reactive educts and are used for further investigations. The reactivity of **1** toward substituted arylsulfonylhydrazines depends on the pH-value of the medium. Under basic conditions 4-CH_3–$C_6H_5SO_2NHNH_2$ is added as a nucleophile to the C=C bond providing the anti-Michael addition product 1,1,1-trifluoro-2-(trifluoromethyl)-3-(*p*-toluene-sulfonylhydrazine)-pent-4-one (**5**). This type of addition was observed before with alkylamines [1].

The obtained X-ray structure of **5** (Fig. 1) shows an interesting detail. The two nitrogen atoms do not have the expected pyramidal structure as bond angles are moving toward planarity. This conclusion is confirmed by the nitrogen–nitrogen bond distance placed just between *d*(N–N) of a plane–plane and a plane–pyramidal structure as proved by the following figures.

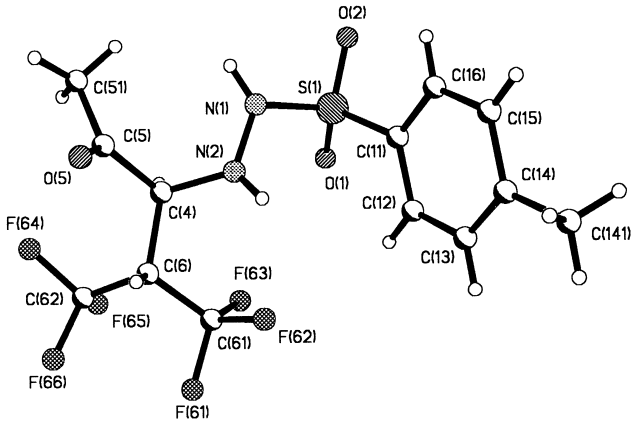


Fig. 1. X-ray structure of **5**.

Selected bond angles of **5**:

N(2)–N(1)–S(1)	111.6°
N(2)–N(1)–H(1)	103.7°
S(1)–N(1)–H(1)	123°
N(1)–N(2)–C(4)	112.2°
N(1)–N(2)–H(2)	107°
C(4)–N(2)–N(1)	115°

Comparison of N–N bond distance in **5** *with literature data*:

N(1)–N(2) found	1.415 Å
$N_{pyramidal}$–$N_{pyramidal}$	1.425 Å [4]
$N_{pyramidal}$–N_{plane}	1.420 Å [4]
N_{plane}–N_{plane}	1.401 Å [4]

By changing the reaction conditions from basic to acid catalysis, the addition of a nucleophile could be prevented. **1** reacts with *p*-toluene-sulfonylhydrazine and 2,4,6-triisopropylbenzenesulfonylhydazine under acidic conditions to give the corresponding 1,1,1-trifluoro-2-(trifluoromethyl)-4-(*p*-toluene-sulfonylhydrazone)pent-2-ene (**6a**) and 1,1,1-trifluoro-2-(trifluoromethyl)-4-(2′,4′,6′-triisopropylbenzene-sulfonylhydrazone)pent-2-ene (**6b**) in almost quantitative yields.

Surprisingly the elucidated X-ray structures of **6a** and **b** (Figs. 2 and 3) prove that the C2=C3 and N=C double bonds

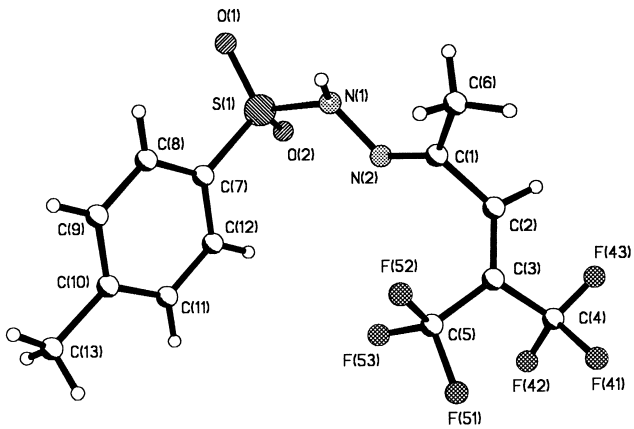


Fig. 2. X-ray structure of **6a**.

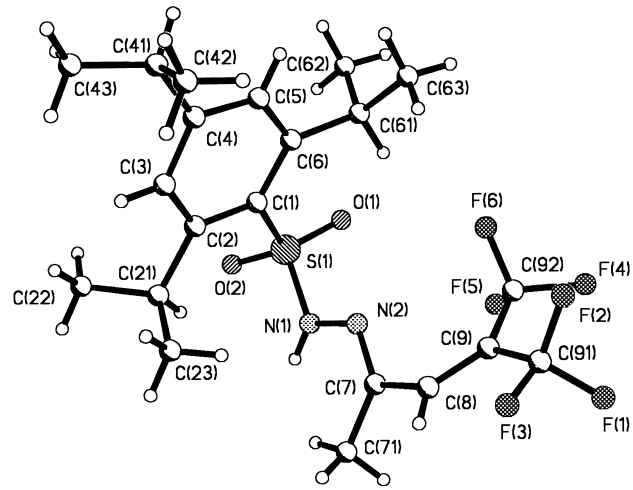


Fig. 3. X-ray structure of **6b**.

are not in the same plane. The torsional angles for **6a** and **b** are 70.1° and 41.2°, respectively. These θ angles show that both are not conjugated but **6a** less than **6b**. This conclusion is confirmed by considering bond lengths. The distances *d*(C1–C2) placed between *d*(N=C) and *d*(C2=C3) are more in the range of a nonconjugated system than those of a conjugated system as demonstrated by the following data. Therefore, it is concluded that the double bonds in both compounds are separated from each other.

Comparison of bond length:

	C–C (Å)	C=C (Å)
6a	1.475	1.315
6b	1.470	1.327
Conjugated system	1.455 [5]	1.330–1.345 [7,8]
Nonconjugated system	1.478 [6]	1.312–1.317 [9,10]

Both hydrazones **6a** and **b** react with triethylamine and iodine to give 1,1,1-trifluoro-2-(trifluoromethyl)-4-iodo-penta-2,4-diene (**7**).The main product in this reaction, however, is 5-methyl-3,3-bis-(trifluoromethyl)-3H-pyrazole (**8**). Better access to **8** is accomplished by treatment of **6a** with sodium hydroxide in a two phase system. The reaction between **6a** and nitrogen dioxide took an unexpected course. Surprisingly oxygen is not inserted but N_2-elimination is observed providing 5,5,5-trifluoro-2-nitro-4-trifluoromethyl-2-(4-toluenesulfonyl)-pent-3-ene (**9**) which could be recrystallized. An X-ray determination carried out on a single crystal (Fig. 4) proved the proposed structure.

The expected F/Cl-metathesis between diethylamino sulfurtrifluoride (DAST) and **2** unexpectedly did not give a fluorinated compound but 1,1,1-trifluoro-2-(trifluoromethyl)-5-chloro-pent-2-en-4-one (**10**). Such a result for a fluorination reaction was to our knowledge not observed before.

In Mukaiyama-aldol condensations, silylenolethers react smoothly with carbonyl compounds to give the correspond-

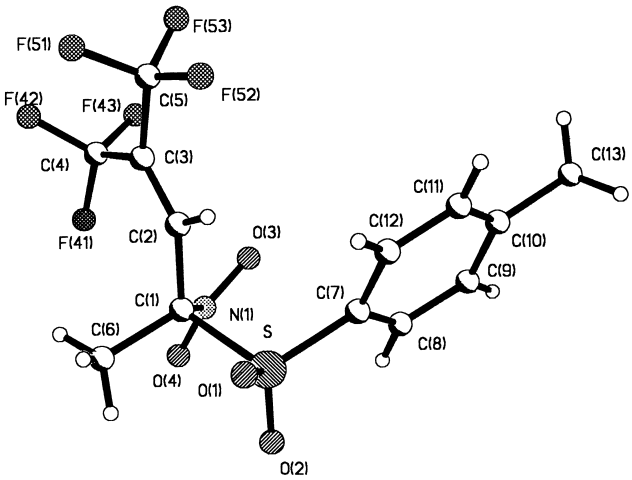


Fig. 4. X-ray structure of **9**.

ing cross-condensation products [11]. However, **3** does not perform with ketones the expected procedure. Under catalytic conditions self-condensation is substantially faster than reaction with the ketone. At −78°C the corresponding 1,1,1,9,9,9-hexafluoro-6-hydroxy-6-methyl-2,8-bis(trifluoromethyl)-nona-2,7-dien-4-one (**11**) is yielded and at room temperature under analogous catalytic conditions, water is eliminated and 4-methyl-2,2-bis-(trifluoromethyl)-6-(3,3,3-trifluoro-2-trifluoromethylpropenyl)-2H-pyran (**12**) is formed. The yield is increased by adding zinc chloride to the reaction mixture. In this context it is interesting to note that **1** reacts with 1-trimethylsilyloxycyclohexene in a Mukaiyama-aldol condensation to give the corresponding cross-condensation product 2-(4,4,4-trifluoro-1-hydroxy-1-methyl-3-trifluoromethylbut-2-enyl)cyclohexanone (**13**). Also in this case the yield could be increased by adding zinc chloride.

Conversion of **1** to a higher fluorinated alkene is accomplished by fluorination with sulfur tetrafluoride. In the presence of anhydrous HF as a catalyst and solvent 1,1,1,4,4-pentafluoro-2-trifluoromethylpent-2-ene (**14**) is provided.

Nucleophilic reagents such as NH_3 add on the C=C double bond of **14** according to anti-Michael addition as was shown before for **1** [1]. The preparation of 1,1,1,4,4-pentafluoro-2-trifluoromethyl-3-aminopentane (**15**) is accomplished by treating **14** with $NaNH_2$ in the presence of H_2O.

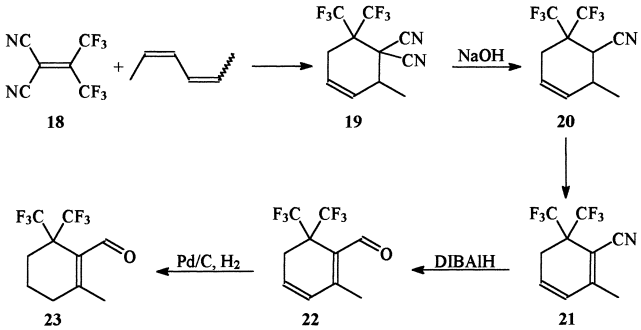
The reaction with nucleophilic *n*-butyl lithium leads to an addition of the butyl-moiety to the C=C bond but due to fluorine abstraction by lithium, the trifluoromethyl groups is defluorinated to a CF_2-group yielding 1,1-difluoro-2-trifluoromethyl-3-(1,1-difluoroethyl)hept-1-ene (**16**) (see Scheme 1).

The conversion of **1** with methyl acetoacetate in the presence of sodium hydride opens a new reaction pathway for the preparation of molecules which might show some biological and medical activities. The first step of this reaction is the anti-Michael addition of the nucleophile (α-metallated esther) in the 3-position of **1** followed by fluoride abstraction as shown for **16**. In the next step metallation in γ-position yields the enolate which attacks nucleophilically the olefinic CF_2-carbon forming 4-acetyl-2-fluoro-6-methyl-5-methoxycarbonyl-3-trifluoromethyl-pyran (**17**) by fluoride abstraction.

Besides **1**, 2,2-bis(trifluoromethyl)-ethylene-1,1-dicarbonitrile (**18**) is an active and versatile synthon [15]. It reacts with normal dienes as dienophile in Diels–Alder reactions providing corresponding cyclohexenes and in some cases the reaction rate is higher than the one of tetracyanoethylene, an extremely strong dienophile. With (*E*)-1,3-pentadiene **18** forms 90% 1,1-bis(trifluoromethyl)-5-methyl-6,6-dicyano-cyclohex-3-ene (**19**) [16]. The yield can be increased to 97% by using a slight excess of (*E*/*Z*)-mixture and extending the reaction time from 10 to 15 min at 0°C. In order to use **19** as a precursor for the synthesis of 16,16,16,17,17,17-hexafluoro-retinal, the double bond has to be shifted from position 3 to 5 and one nitrile group has to be eliminated. The latter is accomplished by stirring **19** at 22°C (5 days) with a solution of NaOH ethanol/water (2:1) providing (5-*R*,6-*S*/5-*S*,6-*R*)-1,1-bis(trifluoro-methyl)-5-methyl-6-cyanocyclohex-3-ene (**20**) in 97% yield. The shift of the double bond is possible by bromination with *N*-bromosuccinimide substituting an allylic position and afterwards eliminating HBr with $(C_2H_5)_3N$ yielding 1,1-bis(trifluoromethyl)-5-methyl-6-cyanocyclohexa-3,5-diene (**21**). Starting from **21** new hexafluorinated natural products can be obtained, e.g. by reduction with diisobutylaluminiumhydride (DIBAlH) 7,7,7,8,8,8-hexafluorosafranal (**22**) is obtained. The C3–C4 double bond is selectively removed by hydrogenation with palladium on charcoal as a catalyst providing another hexafluorinated natural product 7,7,7,8,8,8-hexafluoro-β-cyclocitral (**23**). Both compounds are made on a preparative scale and are available for further synthetic investigations. Especially **23** has the fully functionalized ring system of 16,16,16,17,17,17-hexafluororetinal and can be used as a starting material for the preparation of such compounds. For the second time — after 2-methyl-6,6-bis(trifluoromethyl)cyclohexanone failed to lead to hexafluororetinals [3] – there is a good chance to sythesize the target molecules. Molecular structures and reaction pathways for the molecules described are shown below. The crystal structure gave proof of the introduction of a second double bond in 5,6-position as the distances of *d*(C2–C3)=1.35 Å and *d*(C4–C5)=1.33 Å are in the range of C=C bonds in cyclic systems Scheme 2.

3. Experimental

Volatile compounds were handled in a vacuum line. Solvents were distilled before use and dried according to published procedures [12]. Melting points (not corrected) were determined using a Dr. Tottoli apparatus; elemental



Scheme 2.

microanalyses were carried out with a Carlo-Erba-Elemental Analyzer Model 1106. IR spectra were recorded using a Bruker Vektor 22 and Bruker FT-IR-spectrometer IFS 85; ^{1}H and ^{19}F NMR spectra were recorded with a Bruker WP 80 PFT spectrometer; ^{13}C NMR spectra were obtained using Bruker WM 250 PFT- and AM 400 PFT-NMR-spectrometers; ^{31}P NMR spectra were obtained using Bruker WM 250 PFT-NMR spectrometer. As reference standards, TMS was used for ^{1}H and ^{13}C spectra (internal), fluorotrichloromethane for ^{19}F NMR spectra (internal) and phosphoric acid for ^{31}P spectra (external). Mass spectra of solids were recorded from electron ionization (EI, 70 eV) with a Varian MAT-CH 7 instrument; mass spectra of liquids were obtained with a HP-gaschromatograph 5890 with a 12.5 m capillary column covered with OV1 and an HP MS Engine 5989 A and electron ionization (EI, 70 eV). X-ray structural analyses were carried out with a Siemens P4 diffractometer, graphite-monochromated Mo-Kα radiation, ω-Scans. The structures were solved using direct methods [13] and refined against F_o^2 by full-matrix least squares [14]. Hydrogen atoms were placed at calculated positions and allowed to ride on their parent atoms. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre.[1]

3.1. Syntheses

3.1.1. 1,1,1-Trifluoro-2-(trifluoromethyl)penta-2,4-dienyl-dichlorophosphoroacid ester (**2**)

1.48 g (9.6 mmol) phosphoryl chloride, 1.98 g (9.6 mmol) of **1** and 0.97 g (9.6 mmol) triethylamine were condensed in an evacuated 100 ml Carius tube with Young ventil. After 20 h at RT, 2.33 g (7.2 mmol; 75%) of **2** were isolated by distillation in vacuo (10^{-3} torr). (b.p. 127°C, 77 torr).

R (film) υ (cm^{-1}): 3136 (w), 3058 (m), 2362 (w), 1664 (C=C) (m), 1605 (s), 1398 (m), 1371 (m), 1275 (m), 1226 (m), 1168(vvs), 1022 (s), 985 (m), 936 (s), 805 (w), 758 (w), 730 (s), 593 (vvs), 541 (w), 531 (w), 508 (m), 487 (w). ^{1}H NMR ($CDCl_3$) δ: 5.54 (dd, 1H, ^{2}J(H,H)=3.5 Hz, ^{4}J(H,H)=3.5 Hz); 5.86 (dd, 1H, ^{2}J(H,H)=3.5 Hz, ^{4}J(H,H)=3.5 Hz); 6.89 (bs, 1H) ppm. ^{13}C NMR ($CDCl_3$) δ: 115.17 (t, ^{1}J(C,H)=166.8 Hz); 119.69 (dq, ^{3}J(C,H)=11.4 Hz, ^{1}J(C,F)=274.6 Hz); 120.69 (q, ^{1}J(C,F)=274.6 Hz); 122.83 (d, ^{2}J(C,H)=66.7 Hz); 134.03 (d, ^{1}J(C,H)=162.1 Hz); 145.16 (s) ppm. ^{19}F NMR ($CDCl_3$) δ: −57.04 (q, ^{4}J(F,F)=7.8 Hz); −64.38 (q, ^{4}J(F,F)=7.8 Hz) (F,F)=7.8 Hz) ppm. ^{31}P NMR ($CDCl_3$) δ: 3.67 (s) ppm. MS, *m/z* (%): 326 (M^+/1), 324 (M^+/9), 322 (M^+/14), 287 (1), 285 (8), 283 (11), 269(2), 267 (6), 255 (2), 253 (4), 235 (1), 233 (2), 191 (4), 189 (2), 188 (14), 187 (2), 185 (2), 170 (1), 169 (23), 168 (6), 163 (5), 158 (2), 157 (4), 138 (18), 137 (2), 136 (71), 135 (100), 134 (8), 133 (11), 121 (3), 120 (4), 119 (67), 117 (27), 103 (5), 101 (14), 100 (4), 99 (17), 89 (8), 88 (4), 77 (4), 75 (24), 69 (41), 57 (11), 51 (15), 50 (8), 47 (29). $C_6H_3Cl_2F_6O_2P$ (322.91) calculated: C, 22.3; H, 0.9; Cl 21.9. Found: C, 22.7; H, 1.1; Cl, 18.9.

3.1.2. 1,1,1-Trifluoro-2-(trifluoromethyl)-4-(trimethylsiloxy)penta-2,4-diene (**3**)

0.70 g (6.4 mmol) of trimethylsilylchloride 1.32 g (6.4 mmol) of **1** and 0.65 g (6.4 mmol) of triethylamine were condensed in an evacuated 100 ml Carius tube with Young ventil. After 20 h at RT, 1.75 g (6.2 mmol; 97%) of **3** were isolated by distillation in vacuo (10^{-3} torr). (b.p. 147°C).

IR (film) υ (cm^{-1}): 2967 (m), 1651 (C=C) (s), 1598 (vs), 1426 (w), 1395 (m), 1329 (m), 1282 (m), 1227 (m), 1166 (vvs), 1033 (s), 982 (s), 926 (s), 852 (vvs), 755 (m), 734 (m), 695 (w), 644 (m), 605 (w), 537 (w), 517 (m). ^{1}H NMR ($CDCl_3$) δ: 0.24 (s, 9H); 4.79 (s, 2H); 6.80 (s,1H) ppm. ^{13}C NMR ($CDCl_3$) δ: 0 (q, ^{1}J(C,H)=118.2 Hz); 106.47 (t, ^{1}J(C,H)=161.1 Hz); 118.89 (m); 118.98 (dq, ^{3}J(C,H)=13.3 Hz, ^{1}J(C,F)=274.6 Hz); 121.81 (dq, ^{3}J(C,H)=5.7 Hz, ^{1}J(C,F)=272.7 Hz); 140.20 (d, ^{1}J(C,H)=148.7 Hz); 150.80 (s) ppm. ^{19}F NMR ($CDCl_3$) δ: −55.52 (q, ^{4}J(F,F)=7.8 Hz); −64.10 (q, ^{4}J(F,F)=7.8 Hz) ppm. MS, *m/z* (%): 278 (18/M^+), 209 (14), 186 (4), 168 (6), 167 (82), 158 (11), 146 (12), 139 (59), 120 (3), 119 (8), 117 (2), 113 (2), 101 (4), 89 (6), 81 (6), 79 (6), 78 (8), 77 (100), 75 (18), 74 (6), 73 (63), 72 (6), 71 (2), 69 (8), 65 (6), 64 (11), 59 (2), 57 (4), 51 (5), 49 (18), 47 (12). $C_9H_{12}F_6OSi$ (278.16): C, 38.8; H, 4.3. Found: C, 38.4; H, 4.0.

3.1.3. Dimethyl-bis-(1,1,1-trifluoro-2-trifluoromethylpenta-2,4-dienyl-4-oxysilane (**4**)

0.70 g (5.4 mmol) of dimethylsilyldichloride, 2.22 g (10.8 mmol) of **1** and 1.09 g (10.8 mmol) of triethylamine were condensed in an evacuated 100 ml Carius tube with Young ventil. After 20 h at RT, 2.15 g (4.6 mmol; 85%) of **4** were isolated by distillation in vacuo(10^{-3} torr). (b.p. decomposition).

IR (film) υ (cm^{-1}): 2978 (w), 1653 (m), 1599 (m), 1396 (m), 1326 (s), 1282 (s), 1227 (s), 1164 (s), 1037 (m), 983

[1]Copies of the data (deposition numbers CCDC-) may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk).

(m), 930 (s), 845 (m), 726 (w), 671 (w), 635 (w), 515 (w), 481 (w). ^{1}H NMR ($CDCl_3$) δ: 0.58 (s, 6H); 5.02 (s, 4H); 6.82 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$) δ: 1.58 (q, ^1J(C,H)=122.0 Hz); 108.71 (t, ^1J(C,H)=162.1 Hz); 119.36 (m); 120.33 (q, ^1J(C,F)=274.6 Hz); 121.57 (q, ^1J(C,F)=267.0 Hz); 138.92 (d, ^1J(C,H)=158.3 Hz); 149.29 (s); 149.29 (s) ppm. ^{19}F NMR ($CDCl_3$) δ: −55.39 (q, ^4J(F,F)=7.8 Hz); −64.20 (q, ^4J(F,F)=7.8 Hz) ppm. MS, *m/z* (%): 468 (2/M$^+$), 449 (1), 402 (1), 373 (1), 353 (2), 352 (2), 333 (2), 305 (8), 283 (5), 277 (13), 265 (2), 257 (8), 238 (6), 215 (15), 189 (21), 181 (32), 167 (48), 165 (7), 163 (6), 157 (4), 145 (12), 140 (39), 135 (13), 119 (14), 100 (4), 88 (8), 83 (29), 79 (13), 78 (8), 77 (100), 75 (21), 69 (15), 50 (8). 49 (16), 47 (12). $C_{14}H_{12}F_{12}O_2Si$ (468.20) calculated: C, 35.8; H, 2.5. Found: C, 33.3; H, 2.7.

3.1.4. 1,1,1-Trifluoro-2-(trifluoromethyl)-3-(p-toluenesulfonylhydrazine)-pent-4-one (**5**)

To a solution of 2.00 g (9.7 mmol) of **1** and 1.8 g (9.7 mmol) of *p*-toluene-sulfonylhydrazine in acetonitrile (20 ml) placed in a 50 ml flask were added 0.25 ml triethylamine. After 20 h at RT the solvent was removed in vacuo (10^{-3} torr) and 3.72 g (9.5 mmol; 98%) **5** was obtained. (m.p. 135°C).

IR (KBr-pellet) υ (cm^{-1}): 3278 (w), 3231 (N–H) (w), 1716 (C=O) (w), 1600 (w), 1373 (w), 1335 (w), 1292 (w), 1259 (w), 1224 (w), 1184 (w), 1164 (w), 1088 (w), 872 (w), 811 (w), 725 (w), 697 (w), 667 (w), 550 (w), 533 (w), 487 (w) ^{1}H NMR ($CDCl_3$) δ: 2.23 (s, 3H); 2.37 (s, 3H); 3.57 (dspt, 1H, ^3J(H,H)=3.0 Hz, ^3J(F,H)=7.8 Hz); 6.20 (d, 1H, ^3J(H,H)=3.0 Hz); 7.27 (d, 2H, ^1J(H,H)=8.0 Hz); 7.70 (d, 2H, ^1J(H,H)=8.5 Hz) ppm. ^{13}C NMR ($CDCl_3$) δ: 21.97 (q, ^1J(C,H)=128.7 Hz); 27.47 (q, ^1J(C,H)=128.7 Hz); 49.25 (dspt, ^1J(C,H)=125.0 Hz, ^2J(C,F)=23.9 Hz); 67.14 (d, ^1J(C,H)=141.5 Hz); 128.72 (d, ^1J(C,H)=147.0 Hz); 129.39 (q, ^1J(C,F)=307.0 Hz); 130.12 (d, ^1J(C,H)=136.0 Hz); 134.38 (s); 144.98 (s); 203.12 (s) ppm. ^{19}F NMR ($CDCl_3$) δ: −62.11 (dq, ^3J(F,H)=7.8 Hz, ^4J(F,F)=7.8 Hz); −64.33 (dq, ^3J(F,H)=7.8 Hz, ^4J(F,F)=7.8 Hz) ppm. MS, *m/z* (%): 392 (M$^+$/1), 351 (1), 350 (3), 349 (21), 278 (6), 246 (3), 237 (9), 195 (16), 193 (4), 172 (4), 171 (10), 159 (2), 158 (3), 157 (30), 156 (9), 155 (30), 150 (8), 141 (9), 140 (7), 139 (53), 134 (5), 133 (11), 131 (6), 129 (3), 108 (11), 107 (10), 93 (9), 92 (31), 91 (81), 89 (10), 86 (39), 79 (9), 78 (4), 77 (16), 65 (47), 59 (8), 58 (17), 51 (13), 45 (13), 44 (23), 43 (100), 42 (12), 41 (11), 40 (27), 30 (20), 29 (19), 28 (38), 27 (17). $C_{13}H_{14}F_6N_2O_3S$ (392.16) calculated: C, 39.7; H, 3.5; N, 7.1; S, 8.1. Found: C, 40.7; H, 3.8; N, 7.7; S, 8.9.

Crystal data: $C_{13}H_{14}F_6N_2O_3S$, M=392.32, monoclinic, space group $P2_1/n$, a=15.134(4), b=5.184(2), c=21.537(6) Å, β=99.173(7), U=1668.0(10) Å^3, Z=4, F(000)=800, D_c=1.562 Mg m^{-3}, μ(Mo-Kα)=0.272 mm^{-1}. Colorless tablet (0.56×0.26×0.11 mm), 2167 unique reflections ($2\theta_{max}$=55°) of which 1007 had $I\geq2\sigma(I)$. Terminal reliability indices were R_1=0.063 [$I\geq2\sigma(I)$], wR_2=0.176 (all data) for 235 refined parameters, S=0.808, $\Delta\rho_{max}$=0.55 e Å^{-3}, $\Delta\rho_{min}$=−0.50 e Å^{-3}, CCDC Nr. 410331.

3.1.5. 1,1,1-Trifluoro-2-(trifluoromethyl)-4-(p-toluenesulfonylhydrazone)pent-2-ene (**6a**)

To a solution of 8.00 g (38.8 mmol) of **1** and 7.22 g (38.8 mmol) of *p*-toluene-sulfonylhydrazine in acetonitrile (100 ml) placed in a 250 ml flask was added 2 ml concentrated hydrochloric acid. After 20 h at RT the solvent was removed in vacuo and 14.22 g (38.0 mmol; 98%) of **6a** was obtained. (m.p. 146°C).

IR (KBr-pellet) υ (cm^{-1}): 3233 (N–H) (w), 1683 (w), 1598 (w), 1395 (w), 1344 (w), 1298 (w), 1217 (w), 1160 (m), 1073 (w), 967 (w), 906 (w), 921 (w), 906 (w), 858 (m), 816 (m), 722 (m), 705 (w), 674 (m), 611 (w), 550 (m), 508 (w), 437 (w). ^{1}H NMR ($CDCl_3$) δ: 1.98 (s, 3H); 1.98 (s, 3H); 7.01 (s, 1H); 7.32 (d, 2H, ^3J(H,H)=8.2 Hz); 7.82 (d, 2H, ^3J(H,H)=8.2 Hz); 8.47 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$) δ: 16.52 (q, ^1J(C,H)=129.7 Hz); 21.51 (q, ^1J(C,H)=127.7 Hz); 128.79 (d, ^1J(C,H)=165.9 Hz); 130.38 (d, ^1J(C,H)=156.4 Hz); 136.60 (s); 143.15 (d,^1J(C,H)=165.93); 145.51 (s); 148.45 (s) ppm. ^{19}F NMR ($CDCl_3$) δ: −58.11 (q, ^4J(F,F)=7.8 Hz); −64.04 (dq, ^4J(F,H)=1.4 Hz, ^4J(F,F)=7.8 Hz) ppm. MS, *m/z* (%): 374 (M$^+$/6), 278 (1), 242 (2), 199 (17), 190 (15), 158 (3), 157 (33), 156 (9), 155 (30), 140 (7), 139 (22), 121 (18), 101 (12), 93 (9), 92 (39), 91 (100), 77 (8), 69 (17), 65, (38), 63 (9), 58 (2), 57 (3), 52 (3), 51 (12), 41 (5), 39 (20), 29 (5), 28 (8), 27 (4). $C_{13}H_{12}F_6N_2O_2S$ (374.31) calculated: C, 41.7; H, 3.2; N, 7.4; S, 8.5. Found: C, 41.9; H, 3.4; N, 7.7; S, 8.3.

Crystal data: $C_{13}H_{12}F_6N_2O_2S$, M=374.31, triclinic, space group $P\bar{1}$, a=7.105(3), b=8.447(3), c=14.215(5) Å, α=84.63(3), β=88.35(3), γ=69.27(3)°, U=794.4(5) Å^3, Z=2, F(000)=380, D_c=1.565 Mg m^{-3}, μ(Mo-Kα)=0.277 mm^{-1}. Colorless tablet (0.76×0.25 ×0.22 mm), 2767 unique reflections ($2\theta_{max}$=50°) of which 1893 had $I\geq2\sigma(I)$. Terminal reliability indices were R_1=0.078 [$I\geq2\sigma(I)$], wR_2=0.240 (all data) for 235 refined parameters, S=0.993, $\Delta\rho_{max}$=0.497 e Å^{-3}, $\Delta\rho_{min}$=−0.471 e Å^{-3}, CCDC Nr. 410329.

3.1.6. 1,1,1-Trifluoro-2-(trifluoromethyl)-4-(2′,4′,6′-triisopropylbenzenesulfonylhydrazone)pent-2-ene (**6b**)

To a solution of 8.00 g (38.8 mmol) of **1** and 11.7 g (38.8 mmol) of 2,4,6-triisopropylbenzenesulfonylhydrazine in acetonitrile (100 ml) placed in a 250 ml flask was added 2 ml concentrated hydrochloric acid. After 20 h at RT the solvent was removed and 14.22 g (38.0 mmol; 98%) of **6b** was obtained. (m.p. 77°C).

IR (KBr-pellet) υ (cm^{-1}): 3256 (N–H) (w), 2964 (w), 2120 (w), 1684 (w), 1601 (w), 1385 (m), 1306 (w), 1212 (w), 1165 (w), 1098 (w), 908 (w), 857 (w), 723 (w), 667 (m), 591 (w), 513 (w), 457 (w). ^{1}H NMR ($CDCl_3$) δ: 1.23 (d, 18H, ^3J(H,H)=6.7 Hz); 1.99 (s, 3H); 2.90 (spt, 2H, ^3J(H,H)=6.7 Hz); 4.18 (spt, 1H, ^3J(H,H)=6.7 Hz); 6.96

(s, 1H); 7.17 (s, 2H); 8.67 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$) δ: 14.74 (q, ^1J(C,H)=129.7 Hz); 23.35 (q, ^1J(C,H)=127.8 Hz); 23.35 (q, ^1J(C,H)=127.8 Hz); 24.50 (q, ^1J(C,H)=127.8 Hz); 29.78 (d, ^1J(C,H)=127.8 Hz); 34.14 (d, ^1J(C,H)=133.5 Hz); 123.84 (d, ^1J(C,H)=156.4); 130.24 (s); 140.67 (d, ^1J(C,H)=158.3); 143.94 (s); 151.43 (s); 153.95 (s) ppm. ^{19}F NMR ($CDCl_3$) δ: −57.93 (q, ^4J(F,F)=7.8 Hz); −64.51 (q, ^4J(F,F)=7.8 Hz). MS, *m/z* (%): 283 (17), 282 (6), 269 (7), 267 (20), 267 (100), 266 (50), 251 (15), 249 (6), 232 (4), 218 (9), 204 (5), 203 (14), 202 (12), 191 (4), 190 (4), 189 (11), 188 (6), 187 (26), 175 (19), 173 (7), 161 (10), 160 (5), 159 (14), 149 (9), 145 (12), 132 (8), 130 (9), 129 (10), 128 (12), 119 (14), 117 (14), 115 (11), 104 (14), 90 (27), 77 (8), 69 (6), 65 (6), 64 (5), 60 (12), 52 (5), 44 (95), 42 (32), 28 (27). $C_{21}H_{29}F_6N_2O_2S$ (487.52) calculated: C, 51.8; H, 5.7; N, 5.7; S, 6.5. Found: C, 52.2; H, 6.1; N, 5.8; S, 7.0.

Crystal data: $C_{21}H_{29}F_6N_2O_2S$, M=487.52, triclinic, space group $P\bar{1}$, a=7.255(2), b=12.894(5), c=13.196(5) Å, α=74.66(2), β=82.07(2), γ=84.99(2)°, U=1177.4(7) Å^3, Z=2, F(000)=510, D_c 1.375 Mg m^{-3}, μ(Mo-Kα)=0.205 mm^{-1}. Colorless tablet (0.7×0.5×0.7 mm), 3041 unique reflections ($2\theta_{max}$=45°) of which 2281 had $I \geq 2\sigma(I)$. Terminal reliability indices were R_1=0.051 [$I \geq 2\sigma(I)$], wR_2=0.131 [all data] for 284 refined parameters, S=0.908, $\Delta\rho_{max}$=0.350 e Å^{-3}, $\Delta\rho_{min}$=−0.496 e Å^{-3} CCDC Nr. 104485.

3.1.7. 1,1,1-Trifluoro-2-(trifluoromethyl)-4-iodopenta-2,4-diene (**7**)

To a solution of 1.00 g (2.7 mmol) of **6a** and 0.68 g (2.7 mmol) iodine in diethylether (10 ml) placed in a 20 ml flask was added 0.27 g (2.7 mmol) triethylamine. **7** could only be characterized by GC-MS analysis. MS, *m/z* (%): 316 (M$^+$/93), 190 (5), 189 (100), 169 (40), 167 (32), 139 (19), 127 (22), 120 (6), 119 (26), 101 (13), 99 (14), 77 (10), 75 (18), 70 (6), 69 (29), 58 (13), 50 (21).

3.1.8. 5-Methyl-3,3-bis-(trifluoromethyl)-3H-pyrazole (**8**)

To a solution of 5.00 g (13.3 mmol) of **6a** in diethyl ether (50 ml) placed in a 250 ml flask was added 50 ml of a sodium carbonate solution (10%). After seven days at RT the mixture was extracted twice with diethyl ether. The combined organic layers were dried ($MgSO_4$). 1.44 g (6.6 mmol; 50%) of **8** was obtained by distillation. (b.p. 121°C).

IR (film) υ (cm^{-1}): 3124 (m), 2967 (w), 1645 (m), 1473 (m), 1443 (m), 1385 (m), 1368 (w), 1308 (w), 1217 (m), 1173 (vs), 1117 (m), 1064 (w), 1008 (w), 979 (s), 931 (w), 912 (m), 844 (m), 801 (m), 753 (m), 737 (m), 721 (s), 650 (vvs), 542 (s), 449 (s). ^{1}H NMR ($CDCl_3$) δ: 2.55 (d, 3H, ^4J(H,H)=1.6 Hz); 6.43 (q, 1H, ^4J(H,H)=1.6 Hz) ppm. ^{13}C NMR ($CDCl_3$) δ: 12.92 (q, ^1J(CH)=129.7 Hz); 100.91 (dq, ^2J(C,H)=9.5 Hz, ^2J(C,F)=28.6 Hz); 119.75 (q, ^1J(C,F)=284.1 Hz); 121.56 (d, ^1J(C,H)=185.0 Hz); 164.02 (s) ppm. ^{19}F NMR ($CDCl_3$) δ: −67.28 (s) ppm. MS, *m/z* (%): 218 (M$^+$/1), 191 (3), 190 (59), 189 (3), 172 (1), 171 (2), 169 (9), 163 (1), 157 (1), 156 (2), 152 (1), 151 (22), 150 (6), 145 (7), 140 (7), 139 (11), 137 (3), 126 (4), 125 (4), 122 (4), 121 (78), 120 (5), 119 (12), 113 (2), 112 (1), 102 (9), 101 (100), 99 (7), 96 (1), 95 (13), 94 (2), 93 (3), 90 (7), 89 (3), 88 (3), 81 (3), 80 (2), 78 (5), 77 (10), 76 (5), 75 (39), 71 (9), 70 (8), 69 (71), 59 (6), 58 (5), 57 (16), 53 (1), 52 (10), 51 (17), 50 (17), 49 (3). $C_6H_4F_6N_2$ (218.06) calculated: C, 33.0; H, 1.8; N, 12.8. Found: C, 33.2; H, 2.1; N, 12.7.

3.1.9. 5,5,5-Trifluoro-2-nitro-4-trifluoromethyl-2-(4-toluenesulfonyl)-pent-3-ene (**9**)

To 2.00 g (5.3 mmol) of **6a** placed in a evacuated 100 ml Carius tube with Young ventil were added 0.73 g (15.8 mmol) nitrogen dioxide. After 20 h at RT all volatile reaction products were removed in vacuo (10^{-3} torr). The remaining product was purified by recrystallization from tetrachloromethane. 0.90 g (2.3 mmol; 43%) of **9** was obtained. (m.p. 84°C).

IR (KBr-pellet) υ (cm^{-1}): 3441 (w), 2368 (w), 1683 (C=C) (w), 1596 (w), 1565 (N=O) (w), 1449 (w), 1416 (w), 1384 (w), 1340 (w), 1299 (w), 1263 (w), 1197 (w), 1159 (w), 1077 (w), 1040 (w), 1016 (w), 985 (w), 941 (w), 896 (w), 850 (w), 821 (w), 810 (w), 716 (w), 704 (w), 682 (w), 668 (w), 621 (w), 591 (w), 577 (w), 558 (w), 543 (w), 517 (w), 501 (w), 480 (w), 472 (w). ^{1}H NMR ($CDCl_3$) δ: 2.17 (s, 3H); 2.50 (s, 3H); 7.32 (s, 1H); 7.41 (d, 2H, ^3J (H,H)=8.5 Hz); 7.71 (d, 2H, ^3J (H,H)=8.5 Hz) ppm. ^{13}C NMR ($CDCl_3$) δ: 21.43 (q, ^1J(C,H)=125.8 Hz); 21.90 (q, ^1J(C,H)=126.8 Hz); 105.52 (m); 127.14 (q, ^1J(C,F)=268.9 Hz); 130.38 (d, ^1J(C,H)=160.2 Hz); 131.50 (q, ^1J(C,F)=268.9 Hz); 132.02 (d, ^1J(C,H)=167.8 Hz); 136.36 (d, ^1J(C,H)=164.03 Hz); 139.51 (s); 143.94 (s); 150.06 (s) ppm. ^{19}F NMR ($CDCl_3$) δ: −60.12 (q, ^4J(F,F)=7.8 Hz); −64.60 (dq, ^4J(F,H)=1.2 Hz, ^4J(F,F)=7.8 Hz) ppm. MS, *m/z* (%): 157 (5), 156 (8), 155 (90), 139 (14), 121 (4), 92 (10), 91 (100), 65 (21), 51 (4), 49 (9), 30 (6). $C_{13}H_{11}F_6NO_4S$ (391.15) calculated: C, 39.8; H, 2.8; N, 3.5; S, 8.2. Found: C, 39.6; H, 2.8; N, 3.3; S, 8.3.

Crystal data: $C_{13}H_{11}F_6NO_4S$, M=391.29, monoclinic, ace group $P2_1/c$, a=12.153(2), b=10.994(2), c=12.464(3) Å, β=100.36(2), U=1637.3(6) Å^3, Z=4, F(000) = 792, D_c=1.587 Mg m^{-3}, μ(Mo-Kα)= 0.280 mm^{-1}. Colorless tablet (0.66×0.42×0.26 mm), 2856 unique reflections ($2\theta_{max}$=50°) of which 1564 had $I \geq 2\sigma(I)$. Terminal reliability indices were R_1=0.061 ($I \geq 2\sigma(I)$), wR_2=0.174 (all data) for 228 refined parameters, S=1.013, $\Delta\rho_{max}$=0.441 e Å^{-3}, $\Delta\rho_{min}$=−0.272 e Å^{-3}, CCDC Nr. 410330.

3.1.10. 1,1,1-Trifluoro-2-(trifluoromethyl)-5-chloro-pent-2-en-4-one (**10**)

To 2.00 g (6.2 mmol) of **2** placed in a 50 ml two-necked flask equipped with a septum and drying tube were added 0.83 g (6.2 mmol) of dimethylamino sulfur trifluoride at −40°C. The mixture was slowly warmed to RT and stirred

for another 2 h. Then water (10 ml) and diethyl ether (10 ml) were added. The mixture was extracted twice with diethyl ether. The combined organic layers were dried ($MgSO_4$). After removing the solvent in vacuo (10^{-3} torr) 0.34 g (1.4 mmol; 23%) of **10** was obtained. (b.p. decomposition).

IR (film) υ (cm^{-1}): 3029 (m), 2944 (w), 1808 (w), 1729 (C=O) (s), 1676 (C=C) (w), 1383 (m), 1285 (m), 1222 (w), 1176 (vvs), 1044 (w), 1013 (w), 991 (s), 905 (m), 836 (w), 786 (m), 717 (m), 702 (w), 650 (m), 530 (w), 478 (m). ^{1}H NMR ($CDCl_3$) δ: 4.22 (s, 2H); 7.16 (q, 1H, ^4J(H,F)=1.1 Hz) ppm. ^{13}C NMR ($CDCl_3$) δ: 47.16 (t, ^1J(C,H)=152.5 Hz); 119.83 (q, ^1J(C,F)=276.5 Hz); 119.55 (q, ^1J(C,F)=276.5Hz); 126.42 (m); 138.16 (d, ^1J(C,H)=167.8 Hz); 191.59 (s) ppm. ^{19}F NMR ($CDCl_3$) δ: −60.72 (q, ^4J(F,F)=7.8 Hz); −65.52 (dq, ^4J(C,H)=1.1 Hz, ^4J(F,F)=7.8 Hz) ppm. MS, *m/z* (%): 240 (M^+/1), 212 (1), 195 (2), 193 (6), 192 (6), 191 (100), 174 (2), 173 (10), 172 (1), 170 (6), 164 (2), 163 (48), 157 (12), 144 (1), 142 (2), 140 (4), 137 (4), 121 (2), 113 (4), 95 (2), 94 (2), 93 (4), 77 (4), 76 (3), 75 (48), 69 (51), 57 (3), 56 (4), 53 (3), 51 (18), 49 (27), 48 (3). $C_6H_3ClF_6O$ (240.50) calculated: C, 29.9; H, 1.2; Cl, 14.7. Found: C, 29.8; H, 1.1; Cl, 13.1.

3.1.11. 1,1,1,9,9,9-Hexafluoro-6-hydroxy-6-methyl-2,8-bis(trifluoromethyl)nona-2,7-dien-4-one (**11**)

To 1.00 g (3.6 mmol) of **3** and 0.98 g (7.2 mmol) of zinc chloride in dichloromethane (20 ml) placed in a −196°C cooled evacuated 100 ml Carius tube with Young ventil were condensed 0.72 g (3.8 mmol) titanium tetrachloride. The mixture was warmed to −78°C and stirred for 20 h. Then 20 ml of sodium carbonate solution (5%) were added. The organic layer was dried ($MgSO_4$). The volatile substances were removed in vacuo (10^{-3} torr). The remaining product was purified by column chromatography. (Si60; 63–200 μm; eluent: petroleum ether 40–60/chloroform 20:1). 0.58 g (1.4 mmol; 78%) of **11** was obtained. (b.p. decomposition).

IR (film) υ (cm^{-1}): 3537 (O–H) (s), 2990 (m), 2360 (m), 1785 (w), 1718 (C=O) (s), 1675 (C=C) (m), 1639 (w), 1262 (s), 995 (m), 904 (m), 855 (w), 826 (w), 775 (w), 719 (m), 680 (m), 649 (m), 493 (m). ^{1}H NMR ($CDCl_3$) δ: 1.45 (s, 3H); 2.95 (d, 1H, ^2J (H,H)=18.1 Hz); 3.09 (d, 1H, ^2J (H,H)=18.1 Hz); 6.72 (q, 1H, ^4J(F,H)=0.9 Hz); 6.90 (q, 1H, 3-CH, ^4J(F,H)=1.2 Hz) ppm. ^{13}C NMR ($CDCl_3$) δ: 26.96 (q, ^1J(C,H)=129.5 Hz); 53.45 (t, ^1J(C,H)=128.8 Hz); 71.07 (s); 120.04 (q, ^1J(C,F)=275.9 Hz); 120.17 (q, ^1J(C,F)=275.9 Hz); 120.81 (q, ^1J(C,F)=274.3 Hz); 120.95 (q, ^1J(C,F)=274.3 Hz); 125.68 (spt, ^2J(C,F)=30.7 Hz); 125.72 (spt, ^1J (C.F)=30.7 Hz); 139.33 (d, ^1J(C,H)=163.4 Hz); 149.98 (d, ^1J(C,H)=157.5 Hz); 197.34 (s) ppm. ^{19}F NMR ($CDCl_3$) δ: −55.76 (q, ^4J(F,F)=8.0 Hz); −60.35 (q, ^4J(F,F)=6.5 Hz); −64.91 (dq, ^4J(F,H)=1.2 Hz, ^4J(F,H)=8.0 Hz); −65.65 (dq, ^4J(F,H)=0.9 Hz, ^4J(F,H)=6.5 Hz) ppm. MS, *m/z* (%): 412 (M^+/1), 397 (5), 375 (3), 326 (2), 325 (16), 305 (1), 257 (1), 207 (8), 206 (22), 192 (5), 191 (100), 189 (24), 188 (8), 163 (55), 162 (8), 159 (19), 141 (5), 139 (20), 113 (5), 94 (7), 75 (39), 69 (38), 64 (4), 57 (3), 51 (10). $C_{12}H_8F_{12}O_2$ (412.10) calculated: C, 34.9; H, 1.9. Found: C, 34.6; H, 1.9.

3.1.12. 4-Methyl-2,2-bis-(trifluoromethyl)-6-(3,3,3-trifluoro-2-trifluoromethylpropenyl)-2H-pyran (**12**)

To 1.00 g (3.6 mmol) of **3** and 0.98 g (7.2 mmol) of zinc chloride in dichloromethane (20 ml) placed in a −196°C cooled evacuated 100 ml Carius tube with Young ventil were condensed 0.72 g (3.8 mmol) titanium tetrachloride. The mixture was warmed to RT and stirred for 20 h. Then 20 ml of 5% sodium carbonate solution was added. The organic layer was dried ($MgSO_4$). The volatile substances were removed in vacuo (10^{-3} torr). The remaining product was purified by column chromatography. (Si60; 63–200 μm; eluent: petroleum ether 40–60/chloroform 20:1). 0.58 g (1.4 mmol; 78%) of **12** was obtained. (b.p. decomposition).

IR (film) υ (cm^{-1}): 3093 (w), 2994 (w), 2931 (m), 2866 (w), 1676 (m), 1639 (C=C) (vvs), 1579 (m), 1454 (w), 1442 (m), 1411 (s), 1388 (m), 1172 (vvs), 1078 (s), 975 (vs), 954 (w), 921 (s), 843 (m), 826 (w), 795 (vs), 749 (vs), 726 (m), 714 (vs), 664 (s), 646 (m), 583 (w), 567 (w), 554 (w), 534 (w), 525 (m), 488 (m). ^{1}H NMR ($CDCl_3$) δ: 1.95 (s, 3H); 5.33 (s, 1H); 5.68 (s, 1H); 6.65 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$) δ: 20.37 (q, ^1J(C,H)=128.7 Hz); 80.91 (dspt, ^2J(C,H)=7.3 Hz, ^2J(C,F)=33.1 Hz); 106.38 (d, ^1J(C,H)=172.81 Hz); 114.38 (d, ^1J(C,H)=167.29 Hz); 120.11 (q, ^1J(C,F)=273.9 Hz); 120.15 (spt, ^2J(C,F)=31.2 Hz); 120.23 (q, ^1J(C,F)=273.9 Hz); 121.27 (q, ^1J(C,F)=288.6 Hz); 132.38 (d, ^1J(C,H)=167.1 Hz); 136.96 (s); 145.16 (s) ppm. ^{19}F NMR ($CDCl_3$) δ: −56.94 (q, ^4J(F,F)=7.8 Hz); −64.30 (q, ^4J(F,F)=7.8 Hz); −78.90 (s) ppm. MS, *m/z* (%): 394 (M^+/14), 374 (12), 373 (7), 354 (3), 347 (3), 346 (2), 327 (3), 326 (13), 325 (100), 307 (4), 306 (3), 305 (10), 287 (3), 285 (7), 277 (7), 257 (13), 236 (7), 230 (5), 227 (3), 220 (3), 192 (3), 191 (49), 178 (13), 169 (5), 163 (38), 145 (10), 132 (6), 113 (6), 112 (7), 101 (3), 99 (3), 95 (8), 75 (24), 73 (10), 69 (42), 51 (15). $C_{12}H_6F_{12}O$ (394.11) calculated: C, 36.5; H, 1.5. Found: C, 36.3; H, 1.7.

3.1.13. 2-(4,4,4-Trifluoro-1-hydroxy-1-methyl-3-trifluoromethylbut-2-enyl)cyclohexanone (**13**)

To 2.00 g (9.7 mmol) of **1**, 1.65 g (9.7 mmol) of 1-trimethylsiloxycyclohexene and 2.64 g (19.4 mmol) of zinc chloride in dichloromethane (20 ml) placed in a −196°C cooled evacuated 100 ml Carius tube with Young ventil, 3.68 g (19.4 mmol) titanium tetrachloride was condensed. The mixture was warmed to −78°C and stirred for 20 h. Then 20 ml of sodium carbonate solution (5%) was added. The organic layer was dried ($MgSO_4$). The volatile substances were removed in vacuo (10^{-3} torr). The residue was purified by column chromatography (Si 60; 63–200 μm; eluent: petroleum ether 40–60/chloroform 20:1). 1.97 g (6.4 mmol; 67%) of **13** was obtained. (b.p. decomposition).

IR (film) υ (cm^{-1}): 3519 (m), 2942 (s), 2867 (m), 1701 (s), 1667 (w), 1452 (m), 1403 (m), 1366 (w), 1301 (m), 1236 (m), 1165 (vvs), 1047 (w), 978 (m), 950 (w), 903 (w), 841 (w), 813 (w), 759 (m), 721 (m), 657 (m), 563 (m), 517 (w), 440 (w), 428 (w). ^{1}H NMR ($CDCl_3$) δ: 1.27 (s, 3H); 1.5–2.6 (m, 9H); 6.82 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$) δ: 23.67 (q, ^1J(C,H)=126.8 Hz); 24.94 (t, ^1J(C,H)=128.7 Hz); 28.10 (t, ^1J(C,H)=128.7 Hz); 28.52 (t, ^1J(C,H)=130.1 Hz); 42.92 (t, ^1J(C,H)=125.0 Hz); 59.96 (d, ^1J(C,H)=126.85 Hz); 72.66 (s); 120.74 (q, ^1J(C,F)=273.9 Hz); 121.43 (q, ^1J(C,F)= 272.0 Hz); 124.30 (m); 154.14 (d, ^1J(C,H)=156.2 Hz); 214.02 (s) ppm. ^{19}F NMR ($CDCl_3$) δ: −55.50 (q, ^4J(F,F) =7.8 Hz); −64.40 (q, ^4J 4J(F,F)=7.8 Hz) ppm. MS, *m/z* (%): 304 (M^+/3), 289 (1), 257 (1), 243 (1), 217 (6), 208 (3), 207 (5), 206 (1), 199 (3), 191 (22), 187 (14), 163 (20), 159 (13), 145 (3), 141 (3), 139 (14), 125 (6), 99 (13), 98 (100), 97 (21), 95 (8), 83 (37), 81 (8), 80 (3), 79 (6), 77 (23), 71 (8), 70 (56), 69 (38), 63 (6), 57 (6), 56 (10), 55 (76), 54 (6), 53 (6), 50 (8). $C_{12}H_{14}F_6O_2$ (304.10) calculated: C, 47.3; H, 4.6. Found: C, 47.3; H, 4.9.

3.1.14. 1,1,1,4,4-Pentafluoro-2-trifluoromethylpent-2-ene (**14**)

To 20.00 g (97 mmol) of **1** and 10 g of anhydrous hydrogen fluoride placed in a −196°C cooled evacuated 200 ml autoclave, 16 g (148 mmol) of sulfurtetrafluoride was condensed. The mixture was warmed to 20°C and stirred for 18 h. Then the autoclave was cooled to −78°C, opened and 150 g ice was added to the reaction mixture. The organic layer was washed with 20 ml of sodium carbonate solution (10%) and dried ($MgSO_4$). After distillation 14 g (61 mmol 63%) of **14** was obtained. (b.p. 79°C).

IR (film) υ (cm^{-1}): 3049 (w), 1694 (w), 1391 (vs), 1301 (vs), 1265 (vvs), 1218 (vs), 1187 (vvs), 984 (s), 955 (s), 934 (s), 897 (s), 723 (s), 656 (s), 593 (s), 541 (s), 526 (s). ^{1}H NMR ($CDCl_3$) δ: 1.82 (t, 3H, ^3J(H,F)=18.1 Hz); 6.71 (t, 1H, ^3J(H,F)=12.6 Hz). ^{13}C NMR ($CDCl_3$) δ: 23.87 (tq, ^1J(C,H)=129 Hz, ^2J(C,F)=28 Hz); 118.06 (tm, ^1J(C,F)= 239 Hz); 119.34 (dq, ^1J(C,F)=275 Hz, ^3J(C,H)=8 Hz); 120.30 (dq, ^1J(C,F)=268 Hz, ^3J(C,H)=13 Hz); 126.26 (dm, ^2J(C,H)=4 Hz); 139.69 (dt, ^1J(C,H)=166 Hz, ^2J(C,F)=28 Hz). ^{19}F NMR ($CDCl_3$) δ: −59.03 (tq, ^4J(F,F)=7.6 Hz, ^5J(F,F)=14.4 Hz); −65.83 (dtq, ^4J(F,H) =7.4 Hz, ^4J(F,F)=7.6 Hz, ^5J(F,F)=1.5 Hz); −87.30 (dqqq, ^3J(F,H)=12.6 Hz, ^3J(F,H)=18.1 Hz, ^5J(F,F)=1.5 Hz, ^5J(F,F)=28 Hz) ppm. MS, *m/z* (%): 213 (100), 208 (23), 189 (48), 169 (14), 163 (50), 159 (75), 139 (31), 119 (6), 113 (19), 69 (36), 65 (58). $C_6H_4F_8$ (228.08) calculated: C, 31.5; H, 1.8. Found: C, 31.8; H, 2.0.

3.1.15. 1,1,1,4,4-Pentafluoro-2-trifluoromethyl-3-aminopentane (**15**)

To 5.00 g (22 mmol) of **14** and 1.7 g (22 mmol) of sodium amide placed in a 50 ml Carius tube with Young ventil, 0.8 g (44 mmol) of water was added. The Carius tube was closed and heated for 15 min to 100°C. The volatile substances were distilled in vacuo (10^{-3} torr) and dried ($MgSO_4$). 2.25 g (9.1 mmol; 45%) **15** was obtained by distillation. (b.p. 120°C).

IR (film) υ (cm^{-1}): 3454 (w), 3380 (w), 3013 (w), 2976 (w), 1738 (w), 1630 (w), 1406 (s), 1391 (s), 1314 (vs), 1279 (vs), 1225 (vs), 1176 (vvs), 1113 (vs), 1006 (w), 897 (s), 821 (w), 735 (w), 713 (w), 638(w), 603 (w), 551 (w), 541 (w), 515 (w), 458 (w). ^{1}H NMR ($CDCl_3$) δ: 1.59 (m); 1.78 (t, 3H, ^3J(H,F)=18.8 Hz); 3.48 (m); 3.50 (m). ^{13}C NMR ($CDCl_3$) δ: 21.17 (tq, ^1J(C,H)=129 Hz, ^2J(C,F)=27 Hz); 47.37 (ddsep, ^1J(C,H)=128 Hz; ^2J(C,H)=4 Hz; ^2J(C,F)=26 Hz); (C,F)=26 Hz); 54.11 (dt, ^1J(C,H)=136 Hz, ^2J(C,F)= 27 Hz); 122.63 (t, ^1J(C,F)=245 Hz); 122.91 (q, ^1J(C,F)= 279 Hz); 123.74 (q, ^1J(C,F)=280 Hz). ^{19}F NMR ($CDCl_3$) δ: −60.58 (ddq, ^3J(F,H)=2.0 Hz, ^5J(F,F)=16.6 Hz, ^4J(F,F)= 9.3 Hz); −67.39 (dq, ^3J(F,H)=7.3 Hz, ^4J(F,F)=9.3 Hz); −95.84 (ddq,^3J(F,H)=3.0 Hz, ^2J(F,F)=247.8 Hz, ^3J(F,H)= 18.8 Hz); −106.13 (ddqq, ^3J(F,H)=16.0 Hz, ^2J(F,F)= 247.8 Hz, ^3J(F,H)=18.8 Hz, ^5J(F,F)=16.6 Hz) ppm. MS, *m/z* (%): 246 (M^+/1), 226 (3), 206 (2), 180 (100), 160 (8), 140 (2), 94 (28), 74 (16), 69 (8), 65 (8). $C_6Hd_7F_8N$ (245.11) calculated: C, 29.3; H, 2.8; N, 5.7. Found: C, 29 2; H, 2 8; N, 6.2.

3.1.16. 1,1-Difluoro-2-trifluoromethyl-3-(1,1-difluoroethyl)hept-1-ene (**16**)

To 5.00 g (22 mmol) of **14** placed in a −78°C cooled 50 ml two-necked flask equipped with a septum and drying tube, 13.7 ml (22 mmol) of a 1.6 M butyllithium solution in *n*-hexane was added. The mixture was slowly warmed to 20°C. The volatile substances were distilled in vacuo (10^{-3} torr) in a −196°C cooled trap and purified by preparative gas chromatography (Perkin-Elmer F 21; stationary phase OV 17, 100°C). 0.5 g (1.8 mmol; 8%) **16** was obtained. (b.p. decomposition).

IR (solution in $CDCl_3$ with $CDCl_3$ as reference) υ (cm^{-1}): 2962 (s), 2932 (s), 2875 (s), 1734 (vvs), 1539 (w), 1456 (s), 1138 (vvs), 1033 (s). ^{1}H NMR ($CDCl_3$) δ: 0.92 (t, 3H, ^3J (H,H)=6.9 Hz); 1.33 (m, 2H); 1.35 (m, 2H), 1.63 (t, 3H, ^3J(H,F)=18.6 Hz); 1.77 (dt, 2H, ^3J (H,H)= 6.9 Hz, ^3J (H,H)=6.9 Hz); 2.78 (m, 1H). ^{13}C NMR ($CDCl_3$) δ: 13.71 (q, ^1J(C,H)=124 Hz); 22.11 (tq, ^1J(C,H)=128 Hz, ^2J(C,F)=28 Hz); 22.11 (t, ^1J(C,H)=124 Hz); 25.20 (t, ^1J(C,H)=129 Hz); 29.24 (t, ^1J(C,H)=124 Hz); 43.52 (dt, ^1J(C,H)=129 Hz, ^2J(C,F)=28 Hz); 85.18 (m); 122.83 (q, ^1J(C,F)=272 Hz); 123.30 (t, ^1J(C,F)=242 Hz); 157.93 (t, ^1J(C,F)=302 Hz). ^{19}F NMR ($CDCl_3$) δ: −59.43 (m); −69.83 (m); −73.05 (m); −93.55 (m) ppm. MS, *m/z* (%): 266 (M^+/1), 246 (3), 201 (5), 181 (82), 159 (98), 145 (58), 115 (7), 113 (19), 95 (12), 69 (12), 65 (100), 57 (65). $C_{10}H_{13}F_7$ (266.19) calculated: C, 45.1; H, 4.8. Found: C, 45.2; H, 4.9.

3.1.17. 4-Acetyl-2-fluoro-6-methyl-5-methoxycarbonyl-3-trifluoromethylpyran (**17**)

To 0.98 g (20 mmol) of a sodium hydride suspension (50%) placed in a 50 ml two-necked flask equipped with a

septum and drying tube, 50 ml THF and slowly 1.15 ml (10 mmol) methyl acetoacetate were added. Then 2.10 g (10 mmol) of **1** was added and the reaction mixture was stirred at RT for 20 h. The reaction was stopped by adding 10 ml diluted hydrochloric acid and the mixture the mixture was extracted twice with diethylether. The combined organic layers were dried (Na_2SO_4). The volatile substances were removed by rotation evaporator. The obtained product was purified by distillation in vacuo (10^{-3} torr). 1.68 g (5.9 mmol; 58%) **17** was obtained. (b.p. 46°C, 10^{-2} torr).

IR (film) υ (cm^{-1}): 2959 (s), 1746 (C=O) (vs), 1655 (s), 1438 (s), 1373 (vs), 1248 (vs), 1215 (vs), 1184(vs), 1127 (vs), 1079 (vs), 1014 (vs), 772 (w). ^{1}H NMR ($CDCl_3$) δ: 2.23 (s, 3H), 2.31 (s, 3H), 3.76 (s, 3H), 4.34 (d, 1H, ^4J(H,F)=6.4 Hz). ^{13}C NMR ($CDCl_3$) δ: 18.02 (q, ^1J(C,H)=129.7 Hz), 28.60 (q, ^1J(C,H)=127.8 Hz), 45.04 (d, ^1J(C,H)=141.1 Hz), 52.04 (q, ^1J(C,H)=146.9 Hz), 81.00 (ddq, ^2J (C;F)=36.2 Hz, ^2J(C,F)=13.4 Hz, ^2J(C,H) =7.63 Hz), 105.47 (s), 122.59 (q, ^1J(C,F)=273.2 Hz), 155.08 (d, ^1J(C,F)=271.1 Hz), 160.21 (s), 165.15 (s), 205.85 (s). ^{19}F NMR ($CDCl_3$) δ: −60.17 (d, ^4J(F,F)= 20.3 Hz), −86.21 (qd, ^4J(F,F)=20.3 Hz, ^4J(F,H)=6.4 Hz) ppm. MS, *m/z* (%): 282 (M^+/1), 251 (11), 239 (100), 219 (49), 207 (10), 199 (17), 191 (13), 163 (21), 161 (8), 151 (7), 132 (7), 113 (6), 101 (8), 83 (14), 69 (4), 63 (4), 59 (44). $C_{11}H_{10}F_4O_4$ (282.19) calculated: C, 46.8; H, 3.6. Found: C, 45.7; H, 3.7.

3.1.18. (5-R,6-S/5-S,6-R)-1,1-bis(trifluoromethyl)-5-methyl-6-cyanocyclohex-3-ene (**20**)

15.0 g (53.2 mmol) of 1,1-bis(trifluoromethyl)-5-methyl-6,6-dicyano-cyclohex-3-en (**19**) was dissolved in 30 ml ethanol and cooled to 0°C. A solution of 10.0 g (250 mmol) sodium hydroxide in 15 ml water was slowly added. The yellow mixture was stirred for five days at 22°C, forming slowly a white precipitate. The precipitate was filtered off and washed with water. The crude product was purified by sublimation (100°C, 15 mbar). Pure **20** (13.26 g, 51.6 mmol; 97.0%) was obtained as a white solid melting at 93°C.

IR (KBr-pellet) υ (cm^{-1}): 2982 (w), 2247 (CN) (s), 1463 (w), 1369 (w), 1277 (s), 1223 (s), 1200 (vs), 1188 (vs), 1160 (s), 1127 (s), 1095 (s), 1072 (s), 1058 (s), 993 (w), 972 (w), 935 (w), 874 (w), 856 (w), 801 (w), 718 (s), 697 (s), 669 (w). ^{1}H NMR ($CDCl_3$) δ: 1.30 (d, 3H, ^3J (H,H)=6.7 Hz), 2.41 (d, 1H, ^2J (H,H)=18.6 Hz), 2.55 (d, 1H, ^2J (H,H)= 18.6 Hz), 2.58–2.68 (m, 1H), 2.73 (d, 1H, ^2J (H,H)= 11.0), 5.59–5.65 (m, 2H). ^{13}C NMR ($CDCl_3$) δ: 19.54 (q, ^1J (C;H)=127.8 Hz), 25.54 (t, ^1J(C,H)=131.6 Hz), 31.03 (d, ^1J(C,H)=135.4 Hz), 34.36 (d, ^1J(C,H)=137.3 Hz), 51.13 (sep, ^2J(C,F)=26.7 Hz), 116.48 (d, ^2J(C,H)=9.5 Hz), (C,H)=9.5 Hz), 120.70 (ddd, ^1J C,H)=164.0 Hz, ^2J(C,H)= 12.4 Hz, ^2J(C,H)=6.6 Hz), 123.98 (q, ^1J(C,F)=286.1 Hz), 130.34 (d, ^1J (C.H)=164.0 Hz). ^{19}F NMR ($CDCl_3$) δ: −67.98 (q, ^4J(F,F)=9.8 Hz), −71.90 (q, ^4J(F,F)=9.8 Hz) ppm. MS, *m/z* (%): 257 (M^+/37), 242 (32), 230 (21), 188 (43), 161 (53), 141 (19), 69 (43), 68 (100), 67 (38), 53 (26). $C_{10}H_9F_6N$ (257.18) calculated: C, 46.7; H, 3.5; N, 5.4. Found: C, 45.8; H, 3.8; N, 5.7.

3.1.19. 1,1-Bis(trifluoromethyl)-5-methyl-6-cyanocyclohexa-3,5-diene (**21**)

4.5 g (17.5 mmol) of **20** and 3.6 g (20.2 mmol) of *N*-bromosuccinimide were dissolved in 50 ml carbon terachloride and refluxed for 3 h. The white succinimide was filtered off and the orange solution was cooled to 0°C. 2.5 ml of triethylamine was added and the mixture was stirred for 1 h at 0°C. The reaction was quenched by 15 ml of diluted hydrochloric acid. After 30 min the organic phase is separated and washed two times with water. The solvent is removed under reduced pressure and 5.1 g of an orange oil was obtained. This oil is a complex mixture of educt, product and some monobromo and dibromo derivatives. 1 ml of petroleum ether 40–60 was added and the mixture was stored overnight at −18°C. Now the solids **20** and **21** were filtered off and purified by sublimation (100°C, 15 mbar) and separated by MPLC (petroleum ether 40–60/ chloroform 100:1). Pure **20** (1.39 g, 5.4 mmol, 31%) and **21** (1.42 g, 5.6 mmol, 32%, 63% of conversation) were obtained. **21** is a white solid melting at 78°C.

IR (KBr-pellet) υ (cm^{-1}): 2214 (CN) (w), 1651 (w), 1579 (w), 1437 (w), 1282 (vs), 1226 (vs), 1152 (s), 1008 (s), 988 (s), 972 (s), 960 (w), 878 (w), 835 (w), 779 (s), 735 (w), 719 (vw), 703 (vw), 529 (vw). ^{1}H NMR ($CDCl_3$) δ: 2.23 (s, 3H), 2.83 (d, 2H, ^3J (H,H)=2.7 Hz), 6.05–6.20 (m, 2H). ^{13}C NMR ($CDCl_3$) δ: 24.19 (q, ^1J(C,H)=129.7 Hz), 51.02 (sep, ^2J(C,F)=31.2 Hz), 94.07 (s), 115.48 (s), 124.00 (q, ^1J(C,F)=286.1 Hz), 125.65 (d, ^1J(C,H)= 162.1 Hz), 129.49 (d, ^1J(C,H)=167.8 Hz), 155.78 (s). ^{19}F NMR ($CDCl_3$) δ: −71.96 (s) ppm. MS, *m/z* (%): 255(M^+/37), 240 (1), 234 (1), 186 (100), 184 (11), 166 (75), 152 (4), 116 (13), 69 (43), 51 (7).

3.1.20. 1,1-Bis(trifluoromethyl)-6-formyl-5-methyl-cyclohexa-3,5-diene or 7,7,7,8,8,8-hexafluorosafranal (**22**)

0.5 g (1.96 mmol) of **21** was dissolved in 5 ml *n*-hexane at −35°C in an argon atmosphere. 29 ml (29 mmol, 15 equivalents) of a 1 M solution of diisobutylaluminiumhydride was added via syringe and stirred for 6 h at −35°C. The reaction was quenched by addition of 5 ml ethyl acetate. After warm up to 0°C 15 ml diethylether and 20 ml diluted sulfuric acid were added and stirred for another 30 min. The organic phase was separated and washed two times with brine. The solvents were removed under reduced pressure and the crude yellow liquid was purified by chromatography (petroleum ether 40–60/ethyl acetate 100:1). **22** (354 mg, 1.37 mol, 70%) was obtained as a colorless liquid boiling at 99°C/15 torr.

IR (film) υ (cm^{-1}): 1691 (s), 1651 (w), 1553 (s), 1432 (s), 1305 (w), 1270 (vs), 1193 (vs), 1133 (s), 1011 (s), 733 (s), 103 (w). ^{1}H NMR ($CDCl_3$) δ: 2.19 (s, 3H), 2.76 (bs, 2H),

5.95 (bs, 2H), 9.79 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 21.80 (q, ^1J(C,H)=124.0 Hz), 26.78 (t, ^1J(C,H)=135.4 Hz), 51.74 (sep, ^2J(C,F)=26.7 Hz), 102.97 (d, ^1J(C,H)=165.9 Hz), 118.33 (d, ^2J(C,H)=24.8 Hz), 124.94 (q, ^1J(C,F)= 286.1 Hz), 129.61 (td, ^1J(C,H)=167.8 Hz, ^2J(C,H)= 7.6 Hz), 151.51 (s), 190.18 (d, ^1J(C,H)=181.2 Hz). ^{19}F NMR ($CDCl_3$) δ: −69.56 (s) ppm. MS, *m/z* (%): 258 (M^+/80), 239 (3), 209 (3), 189 (3), 187 (2), 169 (12), 161 (50), 145 (9), 141 (100), 119 (8), 109 (9), 101 (10), 91 (20), 69 (15), 65 (19), 51 (17).

3.1.21. *1,1-Bis(trifluoromethyl)-6-formyl-5-methyl-cyclohex-5-ene or 7,7,7,8,8,8-hexa-fluoro-β-cyclocitral (**23**)*

0.20 g (0.78 mmol) of **22** was dissolved in 20 ml methylene chloride and 0.20 g of palladium (10%) on charcoal was added. The mixture was stirred for 20 h in a hydrogen atmosphere at 22°C/1 bar. The charcoal was filtered off and the solvent removed under reduced pressure. The remaining yellow oil was purified by chromatography (petroleum ether 40–60/acetic acid ethylester 20:1). Pure **23** (0.174 g, 0.67 mmol, 86%) was obtained as a colorless liquid boiling at 101°C, 15 torr.

IR (film) υ (cm^{-1}): 2977 (s), 1702 (C=O) (vs), 1601 (vs), 1458 (s), 1422 (s), 1379 (s), 1355 (s), 1264(vs), 1206 (vs), 1178 (s), 1148 (s), 1080 (w), 992 (s), 976 (s), 930 (s), 917 (s), 734 (s), 718 (w). ^{1}H NMR ($CDCl_3$) δ: 1.54–2.34 (m, 6H), 2.09 (s, 3H). ^{13}C NMR ($CDCl_3$) δ: 16.84 (t, ^1J(C,H)=127.8 Hz), 23.53 (q, ^1J(C,H)=128.1 Hz), 25.30 (t, ^1J(C,H)=137.3 Hz), 33.56 (t, ^1J(C,H)=124.0 Hz), 51.95 (m), 123.02 (d, ^2J(C,H)=17.2 Hz), 124.83 (q, ^1J(C,F)= 288.0 Hz), 160.24 (s), 191.53 (d, ^1J(C,H)=179.3 Hz). ^{19}F NMR ($CDCl_3$) δ: −67.39 (s) ppm. MS, *m/z* (%): 260 (M^+/100), 245 (19), 231 (18), 225 (16), 191 (19), 171 (30), 163 (25), 143 (24), 141 (19), 127 (17), 123 (15), 115 (11), 95 (9), 79 (13), 77 (15), 69 (14), 65 (20), 51 (14), 47 (13).

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