Fluorinated Ketene Dithioacetals. 2. Synthesis of 2-Hydroperfluoro Acid Derivatives from Perfluoroketene Dithioacetals

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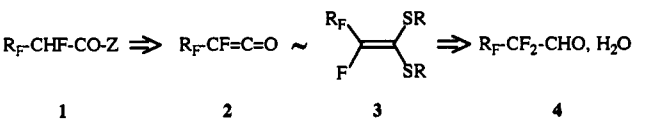
Perfluoroketene dithioacetals were prepared in high yields from perfluoroaldehyde hydrates via their thioacetalization ($TiCl_4/CH_2Cl_2$) followed by basic phase transfer catalyzed HF elimination. Acidic hydrolysis (CF_3CO_2H, H_2O) and then transesterification (EtOH, $Ti(OiPr)_4$) yielded *S*-alkyl 2-hydroperfluoro thioesters and ethyl 2-hydroperfluoro esters, respectively.

Alkyl 2-hydroperfluoro esters 1 (Z = OR, Scheme I) are very interesting fluorinated building blocks: due to the high lability of the α-proton, they react smoothly with amines,[1] and they can be considered as α,β-unsaturated perfluoro ester equivalents as well as α-hydro-β-keto-perfluoro ester equivalents.[2] Thus they were used as starting materials for the synthesis of fluorinated heterocycles.[3] Until now the usefulness of compounds 1 was limited by the lack of a general practical preparative method. We recently described a selective α-defluorination of perfluoro esters,[4] but this photoinduced electron transfer approach needed neat HMPA for the reaction medium and despite its generality it was not suitable for multigram-scale synthesis. 2-Hydroperfluoropropanoate derivatives were easily prepared from perfluoropropene,[5] but the application of the same methodology to the synthesis of ethyl 2-hydroperfluorobutanoate from perfluorobut-1-ene gave poor yields.[6] Furthermore, perfluorobut-1-ene is not commercially available.

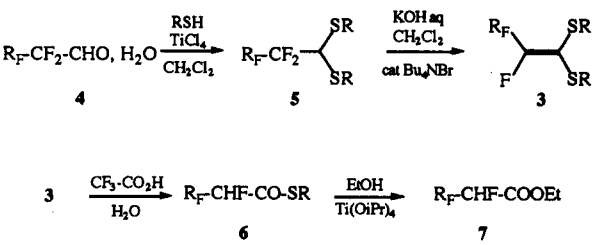
We have considered that 2-hydroperfluoro acid derivatives 1 could result from perfluoroketene 2 or an equivalent form of 2 (Scheme I). Ketene dithioacetals are versatile intermediates in classical organic chemistry,[7] but they are rarely used in organofluorine chemistry. α-(Trifluoromethyl)ketene dithioacetals[8] have recently been reported, but in the perfluoroketene dithioacetal series, which is the focus of the work reported here, only derivatives of difluoroketene have been described,[9] except for one case.[10]

We report in this paper a general synthesis of 2-hydroperfluoro acid derivatives (*S*-alkyl thioesters and alkyl esters) via perfluoroketene dithioacetals 3 from perfluoroaldehyde hydrates 4.

Scheme I



Scheme II



Results and Discussion

The reaction path employed is depicted in Scheme II. We first attempted to prepare **5b'** from perfluoropropanal hydrate (**4b**) and 1,3-propanedithiol, in either protic or Lewis acid medium. The reaction failed (concd H_2SO_4 or P_2O_5 + $Me_3SiOSiMe_3$, $ClCH_2CH_2Cl$) or gave poor yields (40% with BF_3·Et_2O in CH_2Cl_2), even using procedures described for the preparation of trifluoromethyl derivatives.[9] Much better results were obtained when titanium tetrachloride in methylene chloride was used. An excess (3 equiv) of this reagent was required to obtain **5b** in high yields. The efficiency of this reagent is presumably due to both its strong Lewis acid properties and its high dehydrating power with concomitant formation of hydrochloric acid. The reaction was general, and proved even more effective with ethanethiol which gave high yields of **5 (a–c)** (Table I).

High yield conversion to the corresponding perfluoroketene dithioacetal **3** was cleanly performed by elimination of hydrogen fluoride with aqueous potassium hydroxide/methylene chloride in a phase transfer catalysis procedure. Compounds **3** are very stable. Their hydrolysis required refluxing in a strong acidic medium (CF_3CO_2H, H_2O) and yielded the corresponding *S*-alkyl thioester **6** (SR = SEt for **6b** and **6c**; SR = $S(CH_2)_3SH$ for **6b'** and **6c'**). Compounds **6** remained unchanged even after a long reflux period in aqueous or ethanolic acid. Base-induced transesterification is disfavored here due to the preferred reaction with the acidic α-proton.

Transesterification was achieved by refluxing **6** (R = Et) in ethanol with titanium tetraisopropoxide as a catalyst.[11] This procedure was applied only to thioethyl

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Table I. Products and Yields

		product: yield (%)							
R_F	$(SR)_2$	R_FCF_2-$CH(SR)_2$		$R_FCF{=}C(SR)_2$		R_FCHF-COSR		R_FCHF-CO_2Et	
F	$(SEt)_2$	**5a**:	73	**3a**:	97				
CF_3	$(SEt)_2$	**5b**:	83	**3b**:	80	**6b**:	98	**7b**:	60[a]
CF_3	$S(CH_2)_3S$	**5b'**:	50[a]	**3b'**:	80	**6b'**:	90		
C_2F_5	$(SEt)_2$	**5c**:	90	**3c**:	91	**6c**:	95	**7c**:	61[a]
C_2F_5	$S(CH_2)_3S$	**5c'**:	78	**3c'**:	89	**6c'**:	74		

[a] Not optimized.

derivatives, the volatility of ethanethiol being able to favor the equilibrium toward the *O*-ester. The reaction was slow but very clean and quantitative according to chromatographic and NMR analysis. However, some product was lost during the isolation procedure, and pure isolated **7** was obtained in 60% yield, which is certainly improvable. It seems that this reaction is the first example of *S*- to *O*-alkyl transesterification by $Ti(OiPr)_4$ catalysis.

Conclusion

We have developed an effective general methodology for the synthesis of 2-hydroperfluoro acid derivatives. It is limited only by the availability of perfluoroaldehyde hydrates, which are commercial compounds up to the C_4 homolog. Higher homologs need to be prepared, for example, by $LiAlH_4$ reduction of perfluoro acids or their esters[12] or by formylation of perfluoroalkyl iodides with DMF/AIBN.[13]

Perfluoroketene dithioacetals and 2-hydroperfluoro acid derivatives are potentially useful intermediates for other applications which are under investigation.

Experimental Section

For general experimental information, see ref 8. In most of the ^{13}C NMR spectra, signals due to CF_3 and/or CF_2 carbons were lost in the base line and are not mentioned. Reagents were used as received: perfluoroaldehyde hydrates were purchased from Lancaster, and ethanethiol and 1,3-propanedithiol were purchased from Aldrich. Methylene chloride was distilled over calcium hydride. Dithioacetalization were performed under an inert atmosphere using a syringe-cap technique owing to the moisture-sensitive titanium chloride and the ill-smelling thiols. All reactions were performed under a well-ventilated hood.

Perfluoroaldehyde Dithioacetals (5). General Procedure. A solution of the perfluoroaldehyde hydrate (0.05 mol) in CH_2Cl_2 (100 mL) was introduced in a flask equipped with a condenser and an addition funnel. Ethanethiol (0.1 mol, 6.2 g) or 1,3-propanedithiol (0.05 mol, 5.4 g) was added to the flask via a syringe, and the mixture was cooled to −20 °C. A solution of $TiCl_4$ (0.15 mol, 28.4 g) in CH_2Cl_2 (20 mL) was added dropwise, with magnetic stirring. The reaction mixture became orange, was stirred at room temperature for 2 h, and was cooled to 0 °C. Water (1 volume) was added, and the organic layer was decanted and dried over $MgSO_4$. Solvent was removed by distillation (rotatory evaporator for dithiane derivatives, at atmospheric pressure for diethylthio derivatives). The dithioacetal was purified by silica gel chromatography (petroleum ether/CH_2Cl_2; 80/20 for dithiane derivatives, 95/5 for diethylthio derivatives) for small-scale preparations or distilled for large-scale preparations. Yields are reported in Table I. Compound **5a** has been described.[9]

Bis(ethylthio)(pentafluoroethyl)methane (5b): bp = 75 °C (24 mmHg); ^1H NMR δ 1.29 (t, *J* = 7 Hz, 6 H), 2.79 (m, 4 H), 4.13 (t, *J* = 15 Hz, 1 H); ^{13}C NMR δ 13.9 (CH_2CH_3), 25.8 (CH_2CH_3), 50.2 (t, *J* = 25 Hz, *C*H); ^{19}F NMR δ −80.5 (s, 3 F), −111.8 (d, *J* = 15 Hz, 2 F); MS *m/z* (%) 254 (M^+, 60), 193 (100). Anal. Calcd for $C_7H_{11}F_5S_2$: C, 33.07; H, 4.36. Found: C, 33.06; H, 4.47.

2-(Pentafluoroethyl)-1,3-dithiane (5b'): oil; ^1H NMR δ 1.79–2.22 (m, 2 H), 2.58–2.61 (m, 2 H), 3.10–3.25 (m, 2 H), 3.91 (t, *J* = 16 Hz, 1 H); ^{13}C NMR δ 23.9 ($SCH_2CH_2CH_2S$), 25.8 ($SCH_2CH_2CH_2S$), 39.1 (t, *J* = 25 Hz, *C*H), 120.8 (qt, *J* = 375 Hz, *J* = 53 Hz, *C*F_3); ^{19}F NMR δ −80.3 (s, 3 F), −110.0 (d, *J* = 16 Hz, 2 F); MS *m/z* (%) 238 (M^+, 47), 119 (100). Anal. Calcd for $C_6H_7F_5S_2$: C, 30.25; H, 2.96. Found: C, 30.13; H, 2.76.

Bis(ethylthio)(heptafluoropropyl)methane (5c): bp = 83 °C (17 mmHg); ^1H NMR δ 1.29 (t, *J* = 7 Hz, 3 H), 2.79 (m, 2 H), 4.21 (t, *J* = 15 Hz, 1 H); ^{13}C NMR δ 13.8 (CH_2CH_3), 25.7 (CH_2CH_3), 50.6 (t, *J* = 25 Hz, *C*H); ^{19}F NMR δ −81.2 (t, *J* = 11 Hz, 3 F), −108.7 (m, 2 F), −123.5 (m, 2 F); MS *m/z* (%) 304 (M^+, 42), 243 (100). Anal. Calcd for $C_8H_{11}F_7S_2$: C, 31.58; H, 3.64. Found: C, 31.67; H, 3.48.

2-(Heptafluoropropyl)-1,3-dithiane (5c'): oil; ^1H NMR δ 1.96–2.22 (m, 2 H), 2.62 (m, 2 H), 3.17 (m, 2 H), 3.95 (t, *J* = 16 Hz, 1 H); ^{13}C NMR δ 23.9 ($SCH_2CH_2CH_2S$), 25.8 ($SCH_2CH_2CH_2S$), 39.2 (t, *J* = 26 Hz, *C*H), 109.5 (ts, *J* = 267 Hz, *J* = 37 Hz, CF_3CF_2), 117.8 (qt, *J* = 288 Hz, *J* = 35 Hz, *C*F_3), 117.6 (tt, *J* = 260 Hz, *J* = 30 Hz, $C_2F_5CF_2$); ^{19}F NMR δ −81.4 (t, *J* = 10 Hz, 3 F), −106.7 (m, 2 F), −123.4 (m, 2 F); MS *m/z* (%) 288 (M^+, 20), 119 (100). Anal. Calcd for $C_7H_7F_7S_2$: C, 29.16; H, 2.44. Found: C, 29.43; H, 2.49.

Perfluoroketene Dithioacetals (3). General Procedure. A solution of the perfluoroaldehyde dithioacetal **5** (0.05 mol) in CH_2Cl_2 (50 mL) and 3 M KOH (50 mL), with a catalytic amount of tetrabutylammonium bromide (0.5 g), was magnetically stirred at room temperature for 2 h. The organic layer was decanted, washed with water, and dried over $MgSO_4$. Solvent was removed by distillation (rotary evaporator for dithiane derivatives; at atmospheric pressure for diethylthio derivatives). Purification was performed by silica gel chromatography (petroleum ether/CH_2Cl_2, 95/5) or distillation. Yields are reported in Table I. Compound **3a** has been described.[9]

Bis(ethylthio)(1,2,2,2-tetrafluoroethylidene)methane (3b): bp = 81 °C (24 mmHg); ^1H NMR δ 1.25 (t, *J* = 7 Hz, 3 H), 1.27 (t, *J* = 7 Hz, 3 H), 2.75–2.94 (m, 4 H); ^{13}C NMR δ 14.3 (CH_3), 14.8 (CH_3), 26.9 (CH_2), 27.9 (CH_2), 123.1 (d, *J* = 20 Hz, CF=*C*), 146.7 (dq, *J* = 245 Hz, *J* = 36 Hz, *C*F=C); ^{19}F NMR δ −63.1 (d, *J* = 8 Hz, 3 F), −103.3 (q, *J* = 8 Hz, 1 F); IR 1610, 1315, 1190, 1145; MS *m/z* (%) 234 (M^+, 60), 203 (70), 71 (100). Anal. Calcd for $C_7H_{10}F_4S_2$: C, 35.89; H, 4.30. Found: C, 35.90; H, 4.17.

2-(1,2,2,2-Tetrafluoroethylidene)-1,3-dithiane (3b'): oil; ^1H NMR δ 2.18 (qu, *J* = 7 Hz, 2 H), 2.96 (td, *J* = 7 Hz, *J* = 2 Hz, 2 H), 3.03 (t, *J* = 7 Hz, 2 H); ^{13}C NMR δ 23.4, 23.6, 26.9 ($S(CH_2)_3S$), 109.0 (tqu, *J* = 261 Hz, *J* = 39 Hz, *C*F_2), 118.5 (qt, *J* = 289 Hz, *J* = 40 Hz, *C*F_3), 128.8 (d, *J* = 21 Hz, CF=*C*), 137.5 (dt, *J* = 249 Hz, *J* = 29 Hz, *C*F=C); ^{19}F NMR δ −65.7 (d, *J* = 11 Hz, 3 F), −119.1 (q, *J* = 11 Hz, 1 F); IR 1600, 1200; MS *m/z* (%) 218 (M^+, 100), 144 (53), 74 (68). Anal. Calcd for $C_6H_6F_4S_2$: C, 33.02; H, 2.77. Found: C, 33.03; H, 2.80.

Bis(ethylthio)(1,2,2,3,3,3-hexafluoropropylidene)methane (3c): bp = 92 °C (27 mmHg); ^1H NMR δ 1.25 (t, *J* = 7 Hz, 3 H), 1.27 (t, *J* = 7 Hz, 3 H), 2.77–2.95 (m, 4 H); ^{13}C NMR δ 14.3 (CH_3), 14.65 (CH_3), 27.2 (CH_2), 28.1 (CH_2), 118.4 (dt, *J* = 287 Hz, *J* = 38 Hz, -*C*F_3), 126.6 (d, *J* = 20 Hz, CF=*C*), 145.2 (dt, *J* = 264 Hz, *J* = 26 Hz, *C*F=C); ^{19}F NMR δ −84.1 (t, *J* = 5 Hz, 3 F), −101.7 (m, 1 F), −112.5 (dm, *J* = 12.5 Hz, 2 F); IR 1605, 1330, 1190, 1145; MS *m/z* (%) 284 (M^+, 77), 255 (100), 125 (99). Anal. Calcd for $C_8H_{10}F_6S_2$: C, 33.80; H, 3.55. Found: C, 34.06; H, 3.30.

2-(1,2,2,3,3,3-Hexafluoropropylidene)-1,3-dithiane (3c'): oil; ^1H NMR δ 2.19 (qu, *J* = 7 Hz, 2 H), 2.98 (td, *J* = 7 Hz, 2 H), 3.02 (t, *J* = 7 Hz, 2 H); ^{13}C NMR δ 23.5, 27.0, 27.8 ($S(CH_2)_3S$), 109.0 (tq, *J* = 261 Hz, *J* = 39 Hz, *C*F_2), 118.5 (qt, *J* = 289 Hz, *J* = 40 Hz, *C*F_3), 128.7 (d, *J* = 21 Hz, CF=*C*), 137.6 (dt, *J* = 249 Hz, *J* = 28.5 Hz, *C*F=C); ^{19}F NMR δ −84.4 (dt, *J* = 6 Hz, *J* = 4 Hz, 3 F), −114.8 (dq, *J* = 9 Hz, *J* = 3 Hz, 2 F), −117.6 (m, 1 F); IR 1600, 1200–1230; MS *m/z* (%) 268 (M^+, 39), 199 (100), 125 (90). Anal. Calcd for $C_7H_6F_4S_2$: C, 31.34; H, 2.25. Found: C, 31.22; H, 1.98.

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***S*-Alkyl 2-Hydroperfluoro Thioesters 6. General Procedure.** A solution of the ketene dithioacetal **3** (0.03 mol) in trifluoroacetic acid (50 mL) and water (5 mL) was refluxed for 2 h, then diluted with water (50 mL), and extracted with CH_2Cl_2 (2 × 50 mL). After the same workup as above, the *S*-ethyl derivatives were purified by distillation, while the *S*-mercaptopropyl derivatives were purified by silica gel chromatography (petroleum ether/CH_2Cl_2, 70/30). Yields are reported in Table I.

***S*-Ethyl 2,3,3,3-tetrafluoropropanethioate (6b)**: bp = 102 °C (1 atm); ^{1}H NMR δ 1.32 (t, J = 7 Hz, 3 H), 3.03 (q, J = 7 Hz, 2 H), 5.07 (dq, J = 47 Hz, J = 7 Hz, 1 H); ^{13}C NMR δ 13.7 (CH_2CH_3), 23.0 (CH_2CH_3), 88.8 (dq, J = 203 Hz, J = 34 Hz, *C*HF), 119.6 (qd, J = 283 Hz, J = 25.5 Hz, CF_3), 190.7 (d, J = 27 Hz, *C*(O)); ^{19}F NMR δ −76.4 (dd, J = 12 Hz, J = 7 Hz, 3 F), −202.8 (dq, J = 47 Hz, J = 12 Hz, 1 F); IR 1680, 1260, 1150, 1130; MS m/z (%) 190 (M^+, 68), 129 (46), 101 (82), 89 (100). Anal. Calcd for $C_5H_6F_4OS$: C, 31.58; H, 3.18. Found: C, 31.78; H, 3.16.

***S*-(3-Mercaptopropyl) 2,3,3,3-tetrafluoropropanethioate (6b′)**: oil; ^{1}H NMR δ 1.40 (t, J = 8 Hz, S*H*), 1.85–2.20 (m, 2 H), 2.55–2.70 (m, 2 H), 3.05–3.18 (m, 2 H), 5.10 (dm, J = 46 Hz, C*H*F); ^{13}C NMR δ 23.1, 26.8, 31.5 ($S(CH_2)_3S$), 88.6 (dq, J = 203 Hz, J = 34 Hz, *C*HF), 120.0 (qd, J = 282 Hz, J = 26 Hz, CF_3), 190.7 (d, J = 27 Hz, *C*(O)); ^{19}F NMR δ −76.3 (t, J = 7 Hz, 3 F), −202.8 (m, 1 F); IR 1690, 1270, 1130, 1160; MS m/z (%) 237 (M + 1, 8), 235 (78), 106 (100). Anal. Calcd for $C_6H_8F_4OS_2$: C, 30.51; H, 3.41. Found: C, 30.56; H, 3.31.

***S*-Ethyl 2,3,3,4,4,4-hexafluorobutanethioate (6c)**: bp = 120 °C (1 atm); ^{1}H NMR δ 1.32 (t, J = 7 Hz, CH_2CH_3), 3.03 (q, J = 7 Hz, CH_2CH_3), 5.19 (ddd, J = 46 Hz, J = 16 Hz, J = 6 Hz, C*H*F); ^{13}C NMR δ 13.9 (CH_2CH_3), 23.3 (CH_2CH_3), 88.2 (dt, J = 203 Hz, J = 28 Hz, *C*HF), 118.0 (qt, J = 287 Hz, J = 33 Hz, CF_3), 190.6 (d, J = 28 Hz, *C*(O)); ^{19}F NMR δ −82.6 (s, 3 F), −122.7 (ddd, J = 286 Hz, J = 12 Hz, J = 6 Hz, 1 Fβ), −128.2 (ddd, J = 286 Hz, J = 16 Hz, J = 15 Hz, 1 Fβ), −203.5 (m, Fα); IR 1680, 1200–1230; MS m/z (%) 240 (M^+, 58), 129 (62), 83 (65), 59 (100). Anal. Calcd for $C_6H_6F_6OS$: C, 30.01; H, 2.52. Found: C, 30.11; H, 2.45.

***S*-(3-Mercaptopropyl) 2,3,3,4,4,4-hexafluorobutanethioate (6c′)**: oil; ^{1}H NMR δ 1.40 (t, J = 8 Hz, S*H*), 1.75 (qu, J = 8 Hz, 2 H), 2.62 (q, J = 8 Hz, 2 H), 3.15 (t, J = 8 Hz, 2 H), 5.20 (ddd, J = 47 Hz, J = 17 Hz, J = 5 Hz, C*H*F); ^{13}C NMR δ 23.2, 27.0, 32.8 ($S(CH_2)_3S$), 88.2 (dt, J = 203 Hz, J = 27 Hz, *C*HF), 190.5 (d, J = 27 Hz, *C*(O)); ^{19}F NMR δ −82.7 (d, J = 9 Hz, 3 F), −122.7 (ddd, J = 285 Hz, J = 14 Hz, J = 5 Hz, 1 Fβ), −128.2 (dm, J = 285 Hz, 1 Fβ), −203.7 (m, 1 Fα); IR 1685, 1200–1230; MS m/z (%) 287 (M + 1, 1), 269 (100). Anal. Calcd for $C_7H_8F_6OS_2$: C, 29.37; H, 2.82. Found: C, 29.39; H, 2.55.

Ethyl 2-Hydroperfluoro Esters (7). General Procedure. To a solution of *S*-ethyl 2-hydroperfluoro thioester (0.01 mol) in absolute ethanol (10 mL) was added $Ti(OiPr)_4$ (0.005 mol, 1.4 g). The mixture was refluxed until complete conversion was observed by ^{19}F NMR (evolution of the signal of α-fluorine; 24–48 h). Hydrolysis with HCl (0.2 N) at 0 °C was followed by extraction with CH_2Cl_2 (3 × 10 mL). The organic layer was dried over $MgSO_4$. The solvent and then the product were distilled at atmospheric pressure. Yields are reported in Table I.

Ethyl 2,3,3,3-tetrafluoropropanoate (7b): bp = 100 °C (1 atm) (lit.[14] bp 107–108 °C); ^{1}H NMR δ 1.35 (t, J = 7 Hz, 3 H), 4.38 (qd, J = 7 Hz, J = 1 Hz, 2 H), 5.11 (dq, J = 46 Hz, J = 6.5 Hz, 1 H); ^{13}C NMR δ 13.8 (CH_2CH_3), 63.2 (CH_2CH_3), 83.9 (dq, J = 200 Hz, J = 35 Hz, *C*HF), 120.2 (qd, J = 281 Hz, J = 25 Hz, CF_3), 161.8 (d, J = 23 Hz, *C*(O)); ^{19}F NMR δ −76.5 (dd, J = 12 Hz, J = 6.5 Hz, 3 F), −204.7 to −205.2 (m, 1 F); IR 1755, 1200–1230, 1150; MS m/z (%) 174 (M^+, 2), 129 (100), 101 (78), 69 (56), 51 (73).

Ethyl 2,3,3,4,4,4-hexafluorobutanoate (7c): bp = 106 °C (1 atm) (lit.[15] bp 118–120 °C); ^{1}H NMR δ 1.35 (t, J = 7 Hz, 3 H), 4.38 (qd, J = 7 Hz, J = 1 Hz, 2 H), 5.23 (ddd, J = 46 Hz, J = 16 Hz, J = 6 Hz, 1 H); ^{13}C NMR δ 13.7 (CH_2CH_3), 63.3 (CH_2CH_3), 88.7 (dt, J = 197 Hz, J = 29.5 Hz, *C*HF), 161.7 (d, J = 24 Hz, *C*(O)); ^{19}F NMR δ −82.8 (d, J = 9 Hz, 3 F), −122.3 (ddd, J = 287 Hz, J = 12 Hz, J = 6 Hz, 1 Fβ), −127.3 (ddd, J = 287 Hz, J = 16 Hz, J = 11 Hz, 1 Fβ), −205.9 (m, Fα); IR 1765, 1200–1240, 1310, 1015; MS m/z (%) 224 (M^+, 10), 109 (100), 81 (90). Anal. Calcd for $C_6H_6F_6O_2$: C, 32.16; H, 2.78. Found: C, 32.12; H, 2.50.

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