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THE EFFECT OF THE ALKOXY GROUP AND THE STRUCTURE OF THE CYCLOALKENE ON 2+2 PHOTOCYCLOADDITION TO ALKOXY SUBSTITUTED PENTAFLUOROBENZENE

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ABSTRACT: The photoreaction of alkoxy substituted pentafluorobenzene with cycloalkenes in cyclohexane solution resulted in regioselective 2+2 cycloaddition to the 3,4 position of the arene. The stereochemistry of the products formed depended on the structure of the cycloalkene: only an anti 2+2 adduct was observed with cyclopentene, a syn 2+2 adduct with norbornene, while both syn and anti 2+2 cycloaddition took place with cycloheptene and cyclooctene. The magnitude of the alkoxy group had no influence on the course of the photochemical reaction.

In general, benzene and its substituted derivatives undergo ortho-, meta-, and para- cycloadditions[1]. The meta-cycloaddition is known to be the most usual of these photoreactions and is favoured when the difference betweeen the ionization potentials of the arene and the olefin is small, as proposed by Bryce-Smith's ΔIP rule[2]. The reaction begins with 1,3-closure of the excited singlet arene to give a biradical, which is then trapped by the olefin and forms the cycloadduct.

Whereas all the known photoreactions of olefins with donor-substituted benzenes show a type of selectivity similar to that of benzene, nevertheless ortho-cycloadditions with donor olefins are also observed when their oxidation potentials are extremely small[3]. Thus, anisole preferentially undergoes ortho-cycloadditions with acceptor olefins, such as acrylonitriles[4,5] and acrylates[4,5].

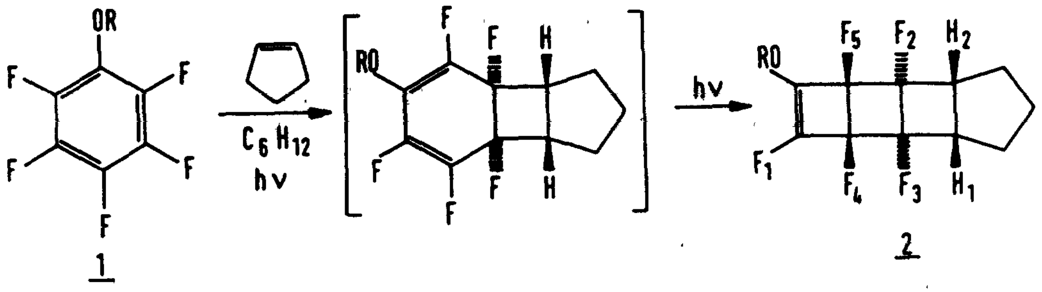
The advantage of fluorine as a substituent in investigations of phototransformations of organic molecules has been shown in several studies[6]. We have already shown that hexafluorobenzene reacted with various cycloalkenes when irradiation was carried out in a cyclohexane solution; however, the structure of the olefin played the major role in the stereochemistry of the 2+2 cycloaddition reaction[7].

We now report an investigation of the effect of alkoxy substituents in pentafluorobenzene on photocycloaddition reactions with cycloalkenes.

RESULTS AND DISCUSSION

A cyclohexane solution of cyclopentene (1 mmol) and pentafluoroanisole (1 mmol) was irradiated for forty hours in a Rayonet photochemical chamber reactor equipped with 253.7 nm lamps. The solvent was then evaporated and the crude reaction mixture analyzed by ^{19}F nmr spectroscopy and five signals at δ_F = -134(dm), -183.0(m), -184.0(m), -189.75(td), and -193.88(dd) ppm were observed. The product was purified by preparative glc and its mass spectrum, with the following fragments m/z 266 (M^+,20%), 198(94), 68(100), showed that the 1:1 adduct of pentafluoroanisole and cyclopentene was formed. On the basis of a comparison of the nmr, mass, and ir data of the product with the literature ones[7,8], we assigned the structure as 1,2,3,4,6-pentafluoro-4-methoxy-tetracyclo(5.4.0.$0^{2,5}$.$0^{7,11}$)undecen-3 (2) with the stereochemistry outlined in Scheme 1.

SCHEME 1



R : $-CH_3$, $-CH_2CH_3$, $-CH(CH_3)_2$, $-C(CH_3)_3$

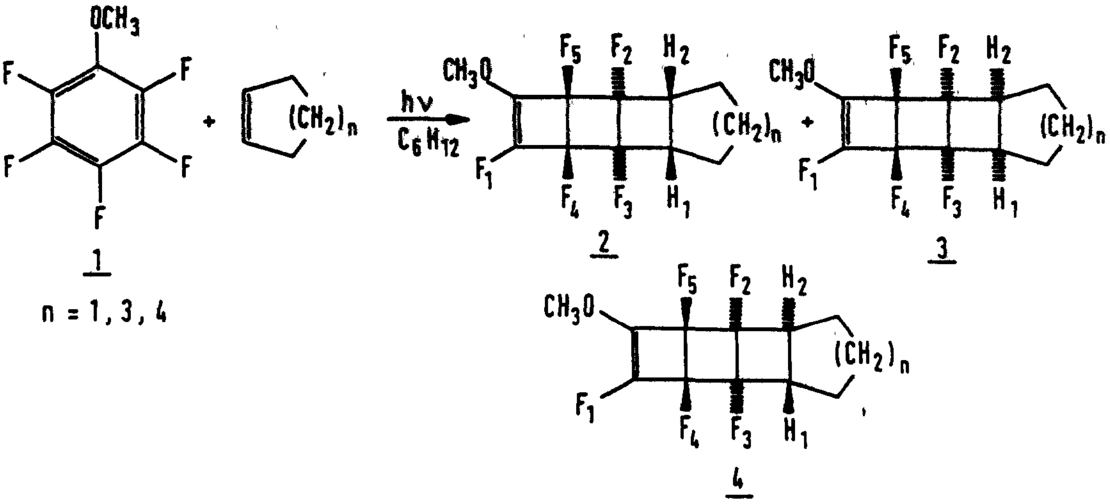
Reduction of the irradiation time from 40 hours to 3 hours led to only 30% conversion of pentafluoroanisole to two products, and besides 10% of product 2, 20% of a new product was formed, showing the following signals in its ^{19}F nmr spectrum: δ_F = -159.75, -165.0, -166.5, -187.5, -188.25 ppm. We were unable to isolate this product, but from comparison of the nmr data with the literature ones[7,8], and on the basis of its further phototransformation to product 2, we determined the structure of the product as 1,2,4,5,6-pentafluoro-3-methoxy-tricyclo(5.4.0.$0^{3,11}$)undecadiene-2,4, which was formed as the primary product by regio and stereoselective anti 2+2 photoaddition of cyclopentene to the 3,4 position in pentafluoroanisole (Scheme 1).

In order to study the effect of the size of the alkoxy group on the regio and stereoselectivity of 2+2 photoaddition of cyclopentene to alkoxy substituted pentafluorobenzene, we chose ethoxy, iso-propoxy, and tert-butoxy substituents. In all three cases the spectroscopic data of the products obtained were very similar to those of the product formed in cycloaddition between pentafluoroanisole and cyclopentene and we established that 2+2 cycloaddition occurred regioselectively and stereoselectively anti.

From the results obtained, we can conclude that the magnitude of the alkoxy group had no influence on the course of the photochemical reaction between alkoxy substituted pentafluorobenzene and cyclopentene, and that primarily formed 1,2,4,5,6-pentafluoro-3-methoxy-tricyclo(5.4.0.$0^{3,11}$)undecadiene-2,4 converted to product 2 in a very efficient secondary light-induced rearrangement (Scheme 1).

The effect of ring size of the cycloalkene on the course of photocycloaddition with pentafluoroanisole was then studied and cycloheptene and cyclooctene were chosen as substrates. Irradiations were carried out under the same reaction conditions: 2 mmols of cycloalkene and 1 mmol of pentafluoroanisole were

SCHEME 2



RELATIVE YIELDS

	2	3	4
1	100	/	/
3	64	16	20
4	34	38	28

Table: NMR data for 2, 3, and 4 (δ/ppm)

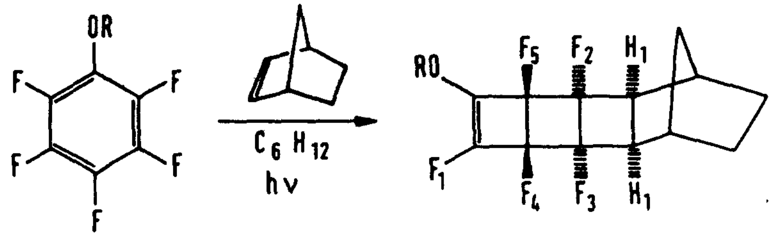
Compound	n	F1	F2	F3	F4	F5
2	1	-134.0 (dm)	-183.0 (m)	-184.0 (m)	-189.75 (td)	-193.88 (dd)
	3	-129.75 (dm)	-177.0 (m)	-177.75 (m)	-183.75 (td)	-187.5 (dd)
	4	-129.75 (dm)	-178.87 (tm)	-180.0 (tm)	-185.25 (td)	-189.0 (dd)
3	3	-130.5 (dm)	-157.47 (m)	-158.17 (m)	-177.6 (m)	-181.78 (m)
	4	-130.5 (dm)	-158.25 (m)	-159.0 (m)	-178.5 (tm)	-183.0 (dm)
4	3	-128.25 (dm)	-153.37 (m)	-183.25 (m)	-183.86 (m)	-183.17 (dm)
	4	-129.75 (dm)	-154.5 (m)	-181.5 (m)	-185.25 (m)	-185.0 (dd)

dissolved in 18 ml of cyclohexane, and the solutions were irradiated at λ = 253.7 nm for 60 hours. ^{19}F nmr spectra of the crude reaction mixture obtained with cyclooctene showed several signals corresponding to three products in the ratio of 34:38:28. The separation of the products was carried out by preparative glc, using FFAP as a stationary phase. The product with the lower retention time showed five signals in its ^{19}F nmr spectrum (Table) and in its mass spectrum a signal at m/z 308 corresponding to the 1:1 adduct of pentafluoroanisole and cyclooctene. The structure and the stereochemistry of the product was determined on the basis of its spectroscopic data. From the ^{19}F nmr spectrum we determined that the signal at δ = -129.75 ppm corresponded to a fluorine atom bonded to an sp^2 carbon atom in the cyclobutene ring, the signal at δ = - 181.5 ppm corresponded to a fluorine atom in the cyclobutane ring, being in anti position to a hydrogen atom, while the signal at δ = -154.5 ppm indicated the syn position of the fluorine and hydrogen atoms. We assigned the structure as 1,2,3,5,6-pentafluoro-4-methoxy-tetracyclo(8.4.0.0^{2,5}0^{7,14}) tetradecene-3 (4) (Scheme 2).

The structure of the other two products was also determined on the basis of their nmr, ir, and mass data, and by comparison with data previously published in the literature^{7,8} (Scheme 2, Table). We also studied the photoreaction of pentafluoroanisole and cycloheptene. After 60 hours irradiation, the ^{19}F nmr spectrum of the crude reaction mixture indicated the presence of three products in the ratio of 64:16:20, which were separated by preparative glc and the pure product 2 and a mixture of products 3 and 4 was obtained (Scheme 2, Table). We tried to separate products 3 and 4, using several types of chromatographic methods, but we were unsuccessful.

As we determined that the ring size of cycloalkene had an influence on the stereochemistry of the products formed, and that the increase in size resulted in diminished anti 2+2 cycloaddition, we also studied the reaction with a bicyclic alkene, i.e. norbornene. A 60 hour irradiation of a cyclohexane solution of 1 mmol of pentafluoroanisole and 2 mmols of norbornene led to 84% conversion, with only one product formed, its structure and the stereochemistry being assigned on the basis of ^{19}F and ^{1}H nmr spectra and by comparison of its spectroscopic data to those previously known^{7,8} (Scheme 3).

SCHEME 3



1 5

R : — CH$_3$, — CH$_2$CH$_3$

In order to determine the influence of the structure of the alkoxy substituted pentafluorobenzene on the course of reaction with norbornene, ethoxy pentafluorobenzene was also used as substrate. From the results obtained we concluded that the magnitude of the alkoxy group had only an influence on the degree of conversion (75%), while no change in reaction course and the stereochemistry of the products formed was observed.

EXPERIMENTAL

Preparative experiments were carried out with a Rayonet Model RPR 100 with RPR 253.7 nm lamps. Ir spectra were recorded using a Perkin-Elmer 727 B instrument, and ^{1}H and ^{19}F NMR spectra on a Jeol JNM-PS-100 spectrometer in $CDCl_3$ or CCl_4 solution with Me_4Si or CCl_3F as an internal reference. Mass spectra and high resolution measurements were taken on a CEC 21-110 spectrometer. Tlc was carried out on Merck PSC Fertigplatten F 254, and glc on a Varian Aerograph, Model 1800.

The starting materials pentafluoroanisole, cyclopentene, cycloheptene, cyclooctene and norbornene were commerically available and were purified before use. Ethoxy pentafluorobenzene[9], iso-propoxy pentafluorobenzene[10] and tert-butoxy pentafluorobenzene[10] were prepared by known procedures. Cyclohexane was purified and distilled before use.

Photocycloaddition Reactions of Alkoxy Pentafluorobenzene with Cycloalkenes: General Procedure

A cyclohexane solution (18 ml) of alkene (1 or 2 mmols) and the alkoxy pentafluorobenzene (1 mmol) was irradiated at λ 253.7 nm for various times (3-60 hours), the solvent evaporated under reduced pressure, the crude reaction mixture analysed by ^{19}F nmr spectroscopy, and separated by preparative glc or tlc.

Reaction of Pentafluoroanisole with Cyclopentene

Pentafluoroanisole: 1 mmol; cyclopentene: 1 mmol; irradiation time: 40 h; the product was purified by preparative glc (30% FFAP on CHROM A/W, T = 160°C), and 173 mg(65%) of liquid product **2** was isolated. ^{1}H NMR (CCl_4) δ = 2.0 (6H,m,CH_2), 3.1 (2H,m,H-1,H-2), 4.0 ppm (3H,s,OCH_3), ^{19}F NMR (CCl_4) δ = -134 (1F,d,J = 16 Hz,F-1), -183 (1F,m,F-2), -184 (1F,m,F-3), -189.75 (1F,td,J = 16,7.5 Hz,F-4), -193.88 ppm (1F,dd,J = 19,7.5 Hz,F-5), mass spectra m/z (relative intensity): M^+ 266(20), 198(94), 184(33), 155(16), 99(20), 68(100), 67(63). Found: m/z 266.0730, Calcd. for $C_{12}H_{11}OF_5$ M, 266.0730.

Reaction of Ethoxy Pentafluorobenzene with Cyclopentene

Ethoxy pentafluorobenzene: 1 mmol; cyclopentene: 1 mmol; irradiation time: 40 hours; the product was purified by preparative glc (30% FFAP on CHROM A/W, T = 160°C) and 140 mg(50 %) of liquid product **2** was isolated.

^{1}H NMR (CCl_4) δ = 1.4 (3H,t,J = 7.5 Hz,CH_3), 1.8 (6H,m,CH_2), 3.04 (2H,m,H-1,H-2), 4.2 ppm (2H,q,J = 7.5 Hz, OCH_2), ^{19}F NMR (CCl_4) δ = -131.2 (1F,d,J = 16 Hz,F-1), -179.6 (1F,m,F-2), -180.5 (1F,m,F-3), -185.8 (1F,td,J = 16,7.5 Hz,F-4), -190 ppm (1F,dd,J = 19,7.5 Hz,F-5), mass spectra m/z (relative intensity): M^+ 280(3), 260(10), 185(13), 184(100), 58(80), 57(45). Found: m/z 280.0881, Calcd. for $C_{13}H_{13}OF_5$: M, 280.0886.

Reaction of iso-Propoxy Pentafluorobenzene with Cyclopentene

iso-Propoxy pentafluorobenzene: 1 mmol; cyclopentene: 1 mmol; irradiation time: 40 hours; the product was purified by preparative glc (30% FFAP on CHROM A/W, T = 160°C) and 165 mg(56%) of liquid product 2 was isolated.

^{1}H NMR (CCl_4) δ = 1.45 (6H,dd,J = 6,3 Hz, CH_3), 1.8 (6H,m, CH_2), 3.04 (2H,m,H-1,H-2), 4.5 ppm (1H,m,CH), ^{19}F NMR (CCl_4) δ = -131.2 (1F,d,J = 16 Hz,F-1), -182.25 (1F,m,F-2), -183 (1F,m,F-3), -187.5 (1F,td,J = 16,7.5 Hz,F-4), -192.7 ppm (1F,dd,J = 19,7.5 Hz, F-5), mass spectra m/z (relative intensity): M^+ 294(1), 232(17), 184(21), 58(100). Found m/z 294.1060, Calcd. for $C_{14}H_{15}OF_5$: M, 294.1043.

Reaction of tert-Butoxy Pentafluorobenzene with Cyclopentene

tert-Butoxy pentafluorobenzene: 1 mmol; cyclopentene: 1 mmol; irradiation time: 40 hours; the product was purified by preparative glc (30% FFAP on CHROM A/W, T = 180°C) and 147 mg(48%) of liquid product 2 was isolated.

^{1}H NMR (CCl_4) δ = 1.42 (9H,s,CH_3), 1.8 (6H,m,CH_2), 3.08 ppm (2H,m,H-1,H-2), ^{19}F NMR (CCl_4) δ = -125.4 (1F,d,J = 16Hz,F-1), -182.6 (1F,m,F-2), -183.4 (1F,m,F-3), -188.4 (1F,td,J = 16,7.5 Hz,F-4), -193 ppm (1F,dd,J = 19,7.5 Hz,F-5), mass spectra m/z (relative intensity): M^+ 308(1), 119(11), 117(11), 67(17), 57(100). Found m/z 308.1208, Calcd. for $C_{15}H_{17}OF_5$: M, 308.1199.

Reaction of Pentafluoroanisole with Cyclooctene

Pentafluoroanisole: 1 mmol; cyclooctene: 2 mmols; irradiation time: 60 hours; the products were separated by preparative glc (10% FFAP on CHROM A/W, T = 180°C) and 45 mg(14.6%) of 2, 85 mg(27.6%) of 3 and 52 mg(17%) of 4 were isolated.

Spectroscopic data of product 2

Ir 800, 900, 1100, 1330, 1440, 1710 cm^{-1}, ^{1}H NMR (CCl_4) δ = 1.06-2.06 (12H,m,CH_2), 2.64 (2H,m,H-1,H-2), 3.88 ppm (3H,s,OCH_3), ^{19}F NMR (CCl_4) δ = -129.75 (1F,dm,J = 15 Hz,F-1), -178.87 (1F,tm,J = 19.5 Hz,F-2), -180.0 (1F,tm, J = 19.5 Hz,F-3), -185.25 (1F,td,J = 19.5,7.5 Hz,F-4), -189.0 ppm (1F,dd,J = 19.5,7.5 Hz,F-5), mass spectra m/z (relative intensity): M^+ 308(10), 288(8), 206(22), 198(22), 193(13), 110(40), 95(24), 82(100), 81(47), 69(13), 68(30), 67(68). Found m/z 308.1191, Calcd. for $C_{15}H_{17}OF_5$: M, 308.1199.

Spectroscopic data of product 3

Ir 810, 910, 1100, 1335, 1720 cm^{-1}, ^{1}H NMR (CCl_4) δ = 1.05-2.1 (12H,m,CH_2), 2.8 (2H,m,H-1,H-2), 3.87 ppm (3H,s,OCH_3), ^{19}F NMR (CCl_4) δ = -130 (1F,dm,J = 15 Hz,F-1), -158.25 (1F,m,F-2), -159.0 (1F,m,F-3), -178.5 (1F,tm,J = 18 Hz,F-4), -183.0 ppm (1F,dm,J = 18 Hz,F-5), mass spectra m/z (relative intensity): M^+ 308(9), 288(9), 206(23), 198(18), 193(12), 110(50), 95(29), 82(100), 81(47), 69(15), 68(29), 67(59). Found m/z 308.1195, Calcd. for $C_{15}H_{17}OF_5$: M, 308.1199.

Spectroscopic data of product 4

Ir 800, 900, 1100, 1330, 1440, 1710 cm^{-1}, ^{1}H NMR (CCl_4) δ = 1.06-2.12 (12H,m,CH_2), 2.57 (2H,m,H-1,H-2), 3.91 ppm (3H,s,OCH_3), ^{19}F NMR (CCl_4) δ = -129.75 (1F,dm,J = 15 Hz, F-1), -154.5 (1F,m,F-2), -181.5 (1F,m,F-3), -185.25 (1F,m,F-4), -185.0 ppm (1F,dd,J = 18,7.5 Hz,F-5), mass spectra m/z (relative intensity): M$^+$ 308(11), 288(8), 206(21), 198(19), 193(16), 183(11), 163(11), 110(35), 82(95), 81(54), 69(16), 68(30), 67(54), 58(32), 55(35), 54(40), 43(100). Found m/z 308.1197, Calcd. for $C_{15}H_{17}OF_5$: M, 308.1199.

Reaction of Pentafluoroanisole with Cycloheptene

Pentafluoroanisole: 1 mmol; cycloheptene: 2 mmols; irradiation time: 60 hours; the reaction mixture was separated by preparative glc (10% FFAP on CHROM A/W, T = 180°C) and 108 mg (37%) of oily product 2, and 78 mg(26 %) of an oily mixture containing 3 and 4 was isolated.

Spectroscopic data of product 2

^{1}H NMR (CCl_4) δ = 1.0-2.1 (10H,m,CH_2), 2.79 (2H,m,H-1,H-2), 3.88 ppm (3H,s,OCH_3), ^{19}F NMR (CCl_4) δ = -129.75 (1F,dm,J = 15 Hz,F-1), -177.0 (1F,m,F-2), -177.75 (1F,m,F-3), -183.75 (1F,td,J = 21,9 Hz,F-4), -187.5 ppm (1F,dd,J = 21,9 Hz,F-5), mass spectra m/z (relative intensity): M$^+$ 294(8), 274(8), 206(21), 198(30), 96(86), 81(100), 68(63), 67(92). Found m/z 294.1040, Calcd. for $C_{14}H_{15}OF_5$: M, 294.1043.

Reaction of Pentafluoroanisole with Norbornene

Pentafluoroanisole: 1 mmol; norbornene: 2 mmols; irradiation time: 60 hours; the product was purified by preparative tlc (activated Al_2O_3, mobile phase: petroleum ether) and by crystallization from methanol and 96 mg(33%) of white crystalline product 5, mp 90-92°C, was isolated.

Spectroscopic data of product 5

Ir 720, 1050, 1100, 1230, 1715 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ = 1.0-1.9 (6H,m,norbornene's CH), 2.45 (2H, broad singlet, CH_2 bridge), 2.67 (2H,dt, J = 24,6 Hz; J_{FH} = 24 Hz, H-1,H-2), 3.84 ppm (3H,s,OCH_3), ^{19}F NMR ($CDCl_3$) δ = -143.25 (1F,dm,J = 12 Hz,F-1), -168.75 (1F,m,F-2), -169.5 (1F,m,F-3), -184.5 (1F,tm,J = 15 Hz,F-4), -189.75 ppm (1F,dm,J = 15 Hz,F-5), mass spectra m/z (relative intensity): M$^+$ 292(7), 224(10), 94(10), 79(9), 67(15), 66(100). Found m/z 292.0881, Calcd. for $C_{14}H_{13}OF_5$: M, 292.0886.

Reaction of Ethoxy Pentafluorobenzene with Norbornene

Ethoxy pentafluorobenzene: 1 mmol; norbornene: 2 mmols; irradiation time: 60 hours; the product was purified by preparative tlc (activated Al_2O_3, mobile phase: petroleum ether) and by crystallization from methanol and 105 mg(34%) of white crystalline product 5 (mp 58-60°C) was isolated.

Spectroscopic data of product 5

Ir 740, 880, 1050, 1105, 1230, 1320, 1720 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ = 1.06-2.1 (6H,m,norbornene's CH), 1.42 (3H,t,J = 7.5 Hz, CH_3), 2.72 (2H, broad singlet, CH_2 bridge), 2.92 (2H,dt,J = 27,6 Hz; J_{FH} = 27 Hz, H-1,H-2), 4.5 ppm (2H,q,J = 7.5 Hz,OCH_2), ^{19}F NMR ($CDCl_3$) δ = -143.25 (1F,dm,J = 12 Hz,F-1), -168.75 (1F,m,F-2), -169.5 (1F,m,F-3), -184.1 (1F,m,F-4), -189.75 ppm (1F,dm,J = 18 Hz, F-5), mass spectra m/z (relative intensity): M$^+$ 306(7), 278(3), 210(12), 192(9), 184(22), 94(20), 79(21), 77(12), 67(35), 66(100). Found m/z 306.1049, Calcd. for $C_{15}H_{15}OF_5$: M, 306.1043.

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