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Perfluoroalkylations of Carbanions with (Perfluoroalkyl)phenyliodonium Triflates (FITS Reagents)

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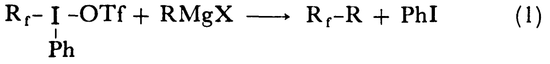
FITS reagents reacted with primary alkylmagnesium halides in THF at −78 °C to give the corresponding perfluoroalkyl(R_f)-alkanes in moderate to good yields. But an alkyl-lithium or -copper gave a poor yield of the R_f-product. The reaction of FITS with secondary or tertiary alkylmagnesium halides resulted in low yields of the products. Alkynyl-lithiums or -magnesium halides produced R_f-alkynes in favorable yields. The reaction with aryl or vinylmagnesium halide was complex and the yields of R_f derivatives were low. FITS also reacted smoothly with enolate anions of active methylene compounds such as 2-methyl-1,3-cyclopentanedione, ethyl 2-methylacetoacetate, and ethyl 2-oxocyclopentanecarboxylate in a polar solvent to afford *O*- and *C*-perfluoroalkylation products in moderate yields, ratios *O*-/*C*-Rf products depending on the reaction temperature. Anions of diethyl 2-methylmalonate and 2-nitropropane afforded *C*-R_f-compounds only.

There have been many investigations on perfluoroalkylations of organic compounds, but the perfluoroalkylations of carbanions have never been reported.[1)] This may be because it was very difficult to generate electrophilic perfluoroalkyl(R_f) species, since the R_f group has an extraordinary high electronegativity.[2)] We have developed (perfluoroalkyl)phenyliodonium triflates (FITS reagents) as useful electrophilic perfluoroalkylating agents[3,4)] and partly described the perfluoroalkylations of carbanions in the preliminary report.[5)] After that, *C*-perfluoroalkylations of *β*-diketones in liquid ammonia and of 2-nitropropyl anion with iodoperfluoroalkanes under irradiation were reported by L. M. Yagupol'skii's group[6)] and A. E. Feiring,[7)] respectively. This paper describes perfluoroalkylations of a variety of carbanions, and *O*- and *C*-perfluoroalkylations of active methylene compounds with FITS reagents.

Results and Discussion

Reaction of Grignard Reagents with FITS. FITS reacted with several kinds of Grignard reagents to give perfluoroalkyl derivatives in varying yields.



$$\underset{\text{FITS-}m}{R_f\text{-}\underset{\text{Ph}}{\text{I}}\text{-OTf}} + \text{RMgX} \longrightarrow \underset{\mathbf{1}}{R_f\text{-R}} + \underset{\mathbf{2}}{\text{PhI}} \qquad (1)$$

$(R_f{=}n\text{-}C_mF_{2m+1})$

Iodobenzene was formed in 70—95% isolated yield as another product. The reaction conditions of FITS-8 with octylmagnesium bromide are shown in Table 1. The best yield (52%) was obtained when FITS was added dropwise into a solution of an equivalent amount of the magnesium bromide in THF at −78 °C (Run 1). The reaction seemed to be fast, though the reaction mixture was stirred for 2 h. The reverse addition decreased the yield in some degree (Run 2) and there was no change in the yield at lower temperatures (Run 3). FITS-8 reacted with octylmagnesium chloride under the same conditions as in Run 1 to yield the product in a 58% yield. The yield was somewhat better than that of the bromide (52%). The results and reaction conditions of the reaction with several kinds of Grignard reagents are summarized in Table 2. No difference in reactivity among different carbon numbers of the *n*-R_f groups of FITS was observed. On the other hand, there was a significant difference between primary and secondary or tertiary Grignard reagents, and the secondary and tertiary reagents remarkably hindered the reaction (Run 6 and 7). Reactions of FITS-8 with Grignard reagents of sp^2 carbons, *p*-tolylmagnesium chloride and vinylmagnesium bromide, yielded complex mixtures, from which *p*-(perfluorooctyl)toluene and (perfluorooctyl)ethylene were isolated in low yields, respectively, along with a small amount of (perfluorooctyl)benzene. No formation of (perfluorooctyl)benzene

Table 1. Reaction of FITS with Alkylmagnesium Bromide
FITS-8(1 equiv) + n-C_8H_{17}MgBr(1 equiv) ⟶ n-C_8F_{17}-C_8H_{17}

Run	Solv.	Temp/°C	Time/h	Yield/%[a)]
1	THF	−78	2	52
2[b)]	THF	−78	2	41
3	THF	−100	2	53
4	Et_2O	−78	2	43
5	Toluene	−78	2	29
6	Hexane	−78	2	23
7	THF–HMPA (95:5)[c)]	−78 −78→0	0.5 0.5	38

a) Isolated yields. b) Reverse addition; Grignard reagent was added to a mixture of FITS-8 in THF. c) HMPA=hexamethylphosphoric triamide.

Table 2. Reaction of FITS with Grignard Reagents
FITS-m + RMgX $\longrightarrow$ R-R$_f$ (R$_f$=n-C$_m$F$_{2m+1}$)

Run	FITS-m	RMgX	Temp/°C	Time/h	Yield/%
1	m=8	n-C_8H_{17}MgCl	−78	2	58[a]
2	m=8	n-$C_{12}H_{25}$MgCl	−78→−10	2	55[a]
3	m=6	n-$C_{12}H_{25}$MgCl	−78	2	50[a]
4	m=4	n-$C_{12}H_{25}$MgCl	−78	2	48[a]
5	m=3	n-$C_{12}H_{25}$MgCl	−78	2	55[a]
6	m=8	Cyclohexyl-MgCl	−78	2	10[a]
7	m=8	1-Adamantyl-MgCl	−78	2	9[a]
8	m=8	$PhCH_2$MgCl	−78	2	38[a]
9	m=3	$PhCH_2$MgCl	−78	1.5	63[b]
10	m=3	$PhCH_2$MgCl	−110	2	82[b]
11	m=2	p-Xylyl-MgCl	−78	1	58[b]
12	m=8	CH_2=$CHCH_2$MgBr	−30	2	40[b]
13	m=8	p-Tolyl-MgCl	−78	2	8[b](17)[d]
14	m=8	CH_2=CHMgBr	−78	2	8[c](2)[d]

a) Isolated yields. b) GLC yields. c) NMR yields. d) GLC yields of (perfluorooctyl)benzene.

Table 3. Effect of Metal in Organometallic Compounds
FITS-8 + R-M $\longrightarrow$ R-R$_f$

Run	R-M	Yield/%
1	n-C_8H_{17}MgCl	58
2	(n-$C_8H_{17})_2$CuMgBr	38
3	n-C_8H_{17}Cu	26
4	n-C_8H_{17}MgCl/cat. CuI	33
5	n-C_8H_{17}Li	9

was observed with sp^3 or sp carbon Grignard reagents.

We examined the reaction of FITS with other organometallic compounds and showed the results in Table 3. It is worth noting that the reaction with the lithium salt was complex and the yield was very low. Grignard reagents provided the best yield of all the organometallic compounds used.

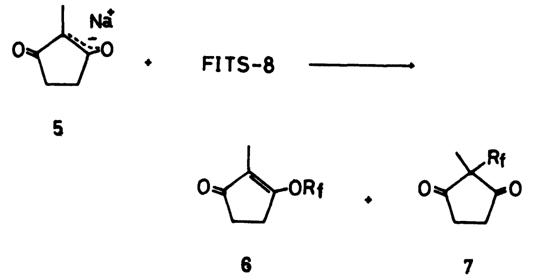
Reaction of Acetylides with FITS. FITS-8 reacted with an equimolar lithium salt of phenylacetylene in THF at −78 °C to give Rf-compound **4** (R=Ph) in favorable yield (Run 1 in Table 4).

$$\text{FITS-}m + \underset{\mathbf{3}}{\text{R-C}\equiv\text{CM}} \longrightarrow \underset{\mathbf{4}}{\text{R-C}\equiv\text{C-R}_f} \qquad (2)$$

$$\text{M}=\text{Li, MgX}$$

Elevated temperature, excess of the lithium salt, or the reverse addition method resulted in lowering the yield (Runs 2, 3, and 4 in Table 4). Interestingly, it was found that β-(perfluorooctyl)styrene was formed in 11, 9, and 4% yields in Runs 2, 3, and 4, respectively, which was proved to be a 1:1 mixture of cis and trans isomers by comparison with authentic samples. At present the mechanism of the formation of the R$_f$-styrene is quite unclear. Table 5 shows the results of the reactions with several kinds of acetylides under similar conditions as in Run 1 in Table 4. It is interesting that there was no difference between the lithium salt and the magnesium chloride of phenylacetylene in contrast to the great difference between octyllithium and octylmagnesium chloride. Furthermore, it is worth noting that the acetylides (sp carbanions) afforded good yields of the products, while the reactions of vinyl or aryl anions (sp^2 carbanions) were complex and their yields were low.

Reaction of Enolate Anions of Active Methylene Compounds with FITS. FITS was allowed to react with sodium salt of 2-methyl-1,3-cyclopentanedione **5** in DMF at 0 °C for 3 h, giving *O*- and *C*-perfluoroalkylated compounds **6** and **7** in 26 and 7% yields, respectively. The ^{19}F chemical shifts of α-CF$_2$ groups clearly reflect the structural difference between **6** and **7**. The CF$_2$ group bonding to the oxygen atom in **6** appears at 80.1 ppm as a multiplet, while the CF$_2$ bonding to the carbon atom in **7** at 112.8 ppm. The effect of solvents and reaction temperature on the perfluoroalkylation was investigated and the results are summarized in Table 6. The reaction was exothermic and other products were tarry materials. Polar solvents such as DMF and DMSO were needed for the alkylation. The reaction at room temperature in DMF or DMSO afforded only the *O*-R$_f$-product **6**. With a lowering of the temperature, **6** decreased, while the *C*-R$_f$-product **7** increased. In hydrocarbon system, a similar temperature-dependent change of the ratios of *O*/*C*-alkylation was observed in butylation of an enolate anion of ethyl acetoacetate with butyl halides.[8] The above results are very different from the photo-reaction of β-diketones with iodoperfluoroalkanes in liquid



(3)

Table 4. Reaction of FITS with Lithium Phenylacetylide

$$\text{FITS-8} + \text{PhC}\equiv\text{CLi} \xrightarrow[\text{in THF}]{0.5\ \text{h}} \text{PhC}\equiv\text{C-C}_8\text{F}_{17}$$

Run	FITS-8	PhC≡CLi	Temp/°C	Yield/%
1	1 equiv	1 equiv	−78→−30	66
2[a)]	1 equiv	1 equiv	−78→−30	37(11)[b)]
3	1 equiv	1.5 equiv	−78→−30	35(9)[b)]
4	1 equiv	1 equiv	−40	47(4)[b)]

a) Reverse addition; Acetylide was added to a mixture of FITS-8 in THF. b) Figures in parentheses are the yields of β-(perfluorooctyl)styrene (cis/trans=1/1).

Table 5. Reaction of FITS with Acetylides

$$\text{FITS-}m + \text{R-C}\equiv\text{C-M} \xrightarrow[\text{in THF}]{} \text{R-C}\equiv\text{C-R}_f\ (\text{R}_f{=}n\text{-C}_m\text{F}_{2m+1})$$

Run	FITS-*m*	Acetylides	Temp/°C	Time/h	Yield/%
1	*m*=8	PhC≡CLi	−78→−30	0.5	66[a)]
2	*m*=6	PhC≡CLi	−78→−30	0.5	53[a)]
3	*m*=3	PhC≡CLi	−78→−30	0.5	44[b)]
4	*m*=2	PhC≡CLi	−78	1	56[b)]
5	*m*=2	PhC≡CMgCl[c)]	−78	1	58[b)]
6	*m*=8	n-$C_6H_{13}C\equiv CLi$	−78→−30	0.5	60[a)]
7	*m*=6	n-$C_6H_{13}C\equiv CLi$	−78	1	70[b)]
8[d)]	*m*=2	n-$C_6H_{13}C\equiv CLi$	0	1	50[a)]

a) Isolated yields. b) GLC yields. c) The magnesium chloride was prepared by treating phenylacetylene with a ethereal solution of benzylmagnesium chloride in THF. d) The reaction was carried out by adding an ethereal solution of 1-octynyllithium to a mixture of FITS-2 in pentane at 0 °C.

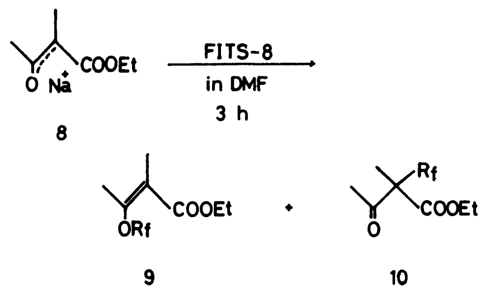
Table 6. Reaction of **5** with FITS-8[a)]

Run	Solv.	Temp/°C	Yield/%		Ratio
			6(*O*-R$_f$)	**7**(*C*-R$_f$)	**6**/**7**
1	DMF	R.t.	27	0	
2	DMF	0	26	7	3.7
3	DMF	−30	19	16	1.2
4	DMF	−55	7	31	0.23
5	DMSO	R.t.	20	0	
6	THF	−30	Trace	0	

a) Reaction time 3 h.

ammonia, which gave only *C*-R$_f$-products.[6)]

Similarly FITS reacted with enolate anions of β-keto esters **8** and its cyclic ester **11** in DMF at 0 °C to afford *C*-R$_f$-compounds **10** and **13** as major products along with a small amount of *O*-R$_f$-compounds **9** and **12**, respectively. Both the keto esters showed analogous behavior and it is in contrast to the case of the β-diketone **5** in which the *O*-product **6** was a main product at 0 °C. The *C*-products **10** and **13** increased further at lower temperatures.



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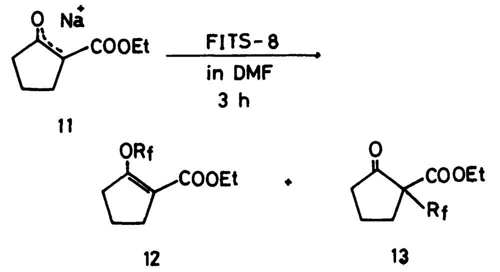
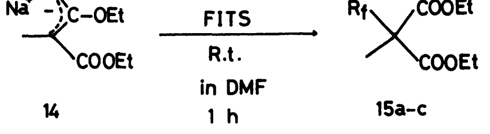


(5)

Temp/°C	9	10	12	13
0	8%	28%	8%	20%
−55	5%	36%	6%	29%

Sodium salt of diethyl 2-methylmalonate **14** reacted exothermically with FITS-8 at room temperature for 1 h to produce only a *C*-R$_f$-compound **15a** in a 24% yield. Other products were tarry materials, so their assignment was not made. In this reaction, the effect of the R$_f$ groups was examined by using FITS-8 and -3, and FITS(F)-3*i*[9)] (Eq. 6).



(6)

	R$_f$	Yield/%
15a	n-C_8F_{17}	24
15b	n-C_3F_7	20
15c	i-C_3F_7	3

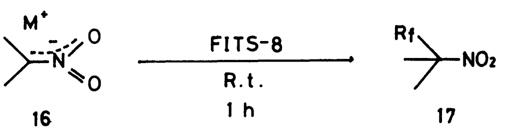
Table 7. Reaction of **16** with FITS-8[a]

Run	**16**	Solv.	Yield of **17**/%
1	M=Na	DMSO	43
2	M=Na	DMF	33
3	M=Na	Et_2O	22
4	M=Li	DMSO	49
5	M=Li	DMF	51
6	M=Li	Et_2O	18

a) Reaction time; 1 h, temp; room temperature.

Similar yields were obtained in the cases of FITS-8 and -3 having primary R_f, but FITS(F)-3*i* bearing perfluoroisopropyl group gave a very low yield of **15c**. Thus, the secondary R_f group strongly hindered the desired reaction.

The reaction of FITS-8 with 2-nitro-2-propanide anion **16** was run in several solvents at room temperature for 1 h. The reaction occurred exothermically and yielded 2-R_f-2-nitropropane **17** only in varying yields. The results are summarized in Table 7. Polar solvents gave better yields and the lithium salt in the polar solvents afforded somewhat better yields than the sodium salt.



16 **17** (7)

FITS-8 was also treated with an enolate anion of acetophenone under several conditions to give a mixture of α-(perfluorooctyl)acetophenone and its dehydrofluorination product, 2-fluoro-2-(perfluoroheptyl)vinyl phenyl ketone in low yields (<17%). Therefore, the reaction of FITS with enol silyl ethers was much better as a synthetic method of α-(perfluoroalkyl) ketones because high yields were obtained and the reaction procedure was simple.[10]

Experimental

^{19}F Chemical shifts are given in ppm upfield from $CFCl_3$ as an internal standard. A gas chromatograph with a column of 10% SE-30 on Chromosorb WAW DMCS was used for the isolation or analysis of the products. FITS reagents were prepared by the method described previously.[3] Reaction solvents were purified and dried by the usual methods. All the reactions were done under argon atmosphere.

Note: FITS reagents decomposed soon in diethyl ether or sooner in THF at room temperature. Therefore, if necessary, FITS must be dissolved in the solvents at −78 °C.

Reaction of FITS with Grignard Reagents. Typical Procedure: Into a solution of 1.4 mmol of Grignard reagent (0.4—0.8 mmol ml^{-1} of THF or diethyl ether) in 13 ml of THF at −78 °C, was added 1.3 mmol of FITS reagent in several portions with stirring. After the reaction mixture was stirred at −78 °C for additional 2 h, it was quenched with aq ammonium chloride and extracted with pentane. The extract was dried with magnesium sulfate and concentrated. The desired R_f-compound was seperated from iodobenzene as another product by column chromatography of the residue on silica gel using pentane as an eluent and then distilled.

Grignard reagents were prepared from the halides in THF or diethyl ether by the usual method. The organocopper compounds used as shown in Table 3 were prepared by the methods reported.[11]

The reaction with Grignard reagents was carried out at different temperatures in different solvents as shown in Tables 1 and 2.

In the case of the reaction of FITS-8 with benzylmagnesium chloride, the residue resulting from the extraction with ether was treated with Raney Ni (W-2)[12] in ethanol to reduce iodobenzene to benzene, because it was difficult to seperate the R_f-product from iodobenzene by column chromatography or distillation. After the reduction, the resulting residue was distilled to give (1*H*, 1*H*-heptadecafluorononyl)benzene in a 38% yield.

The yields of the volatile R_f-products were determined by NMR or gas chromatography. Spectral data and elemental analyses of new compounds are summarized in Table 8.

Reaction of FITS with Acetylides. Typical Procedure: Into a solution of 1.32 mmol of an alkyne in 8 ml of THF at −78 °C, was dropwise added a solution of 1.32 mmol of butyllithium in 0.96 ml of hexane with stirring. The solution was stirred for additional 10 min and 1.32 mmol of FITS reagent was added in several portions into it at −78 °C. After the reaction mixture was stirred for additional 5 min at −78 °C, it was warmed to −30 °C for a period of 25 min, quenched with aq ammonium chloride, and extracted with pentane. The extract was dried with magnesium sulfate and concentrated. The residue was column-chromatographed on silica gel using pentane to give the R_f-alkyne. The yields of the volatile R_f-products were determined by NMR or gas chromatography of the concentrated extracts, as shown in Table 5. The spectral data and elemental analyses of the products are shown in Table 8.

Reaction of FITS with Enolate Anions 5, 8, 11, and 14. Typical Procedure: A solution of 2-methyl-1,3-cyclopentanedione (168 mg, 1.5 mmol) in 8 ml of DMF was added dropwise into a mixture of sodium hydride (1.7 mmol) and 5 ml of DMF with stirring. The reaction mixture was stirred for an additional 15 min at room temperature and cooled to −55 °C. Then FITS-8 (772 mg, 1 mmol) was added into the solution of the enolate anion. After an additional stirring for 3 h at −55 °C, the mixture was quenched with 3 mol dm^{-3} hydrochloric acid and extracted with ether. The organic layer was washed with water, dried with magnesium sulfate, and concentrated. Two isomers were separated by column chromatography on silica gel using a mixture of pentane and ether as an eluent and then each distillation gave 38 mg (7%) of **6** and 163 mg (31%) of **7**. Products **9** and **15c** were isolated by gas chromatography after column chromatography. Products **15a** and **15b** were isolated by column chromatography only. The results are shown in Table 6 and in Eqs. 4—6.

Reaction of FITS with 16. Typical Procedure: Sodium or lithium 2-nitro-2-propanide was prepared according to the method described in the literature.[13] FITS-8 (1.33 mmol) was added into a solution of **16** (2.00 mmol) in 10 ml of DMF at room temperature with stirring. After an additional stirring for 1 h, some water was added into the reaction mixture and the mixture was extracted with ether. The post-

Table 8. Properties of Products

Compd[a]	Bp(θ_b/°C)/mmHg[b] [Mp (θ_m/°C)]	^{1}H-NMR (δ, in $CDCl_3$)	^{19}F-NMR (in $CDCl_3$)	IR (Method)	m/z	Anal (%) Found (Calcd)	
						C	H
2							
n-C_8H_{17}-R_{f_8}	95—7/1.5	0.90(3H, m), 1.30 (12H, m),1.80—2.20(2H, m)	80.3(3F, m), 112.5 (2F, m), 120.0(8F, m), 121.9(2F, m), 124.5 (2F, m)	—	532 (M$^+$)	36.38 (36.10)	3.36 (3.22)
n-$C_{12}H_{25}$-R_{f_8}	160/6[b]	0.90(3H, m), 1.30 (20H, m), 1.80—2.30(2H, m)	81.5(3F, t, J=10 Hz), 114.8(2F, m), 122.3 (6F, m), 123.2(2F, m), 124.0(2F, m), 126.6 (2F, m)	—	—	—	—
n-$C_{12}H_{25}$-R_{f_6}	170/25[b]	0.90(3H, m), 1.30 (20H, m),1.80—2.30(2H, m)	81.9(3F, t, J=10 Hz), 114.8(2F, m), 122.4 (2F, m), 123.4(2F, m), 124.0(2F, m), 126.7 (2F, m)	—	488 (M$^+$)	44.31 (44.27)	5.11 (5.16)
n-$C_{12}H_{25}$-R_{f_4}	150/25[b]	0.90(3H, m), 1.30 (20H, m), 1.80—2.30(2H, m)	81.7(3F, t, J=10 Hz), 115.0(2F, m), 125.0 (2F, m), 126.6(2F, m)	—	388 (M$^+$)	49.54 (49.48)	6.57 (6.49)
n-$C_{12}H_{25}$-R_{f_3}	200/30[b]	0.90(3H, m), 1.30 (20H, m), 1.80—2.30(2H, m)	81.3(3F, t, J=10 Hz), 115.8(2F, m), 128.4 (2F, s)	—	—	—	—
R_{f_8}-Cyclohexane	120/20[b]	0.90—1.40(5H, m), 1.40—2.20 (6H, m)	81.4(3F, t, J=10 Hz), 118.5(2F, m), 121.0 (2F, m), 122.3(6F, m) 123.1(2F, m), 126.6 (2F, m)	—	501 (M$^+$−1)	33.23 (33.48)	2.09 (2.21)
1-R_{f_8}-Adamantane	[54—55]	1.74(6H, m), 1.94 (6H, m), 2.08 (3H, m)	81.4(3F, t, J=10 Hz), 118.6(2F, m), 122.2 (8F, m), 123.1(2F, m), 126.6(2F, m)	—	554 (M$^+$)	39.09 (38.93)	2.69 (2.90)
$PhCH_2$-R_{f_8}	100/0.3[b] [37.5—38.5]	3.30(2H, t, J=18 Hz), 7.10—7.45 (5H, m)	81.4(3F, t, J=10 Hz), 110.8(2F, t, J=15 Hz), 121.7(2F, m), 122.4(6F, m), 123.2(2F, m), 126.6 (2F, m)	—	510 (M$^+$)	35.28 (35.31)	1.26 (1.38)
$PhCH_2$-R_{f_3}	Oil	3.28(2H, tt, J=18.9, 1.5 Hz), 7.25 (5H, bs)	81.05(3F, t, J=10 Hz), 114.3(2F, m) 127.6 (2F, m)	—	260 (M$^+$)	—	—
p-Xylyl-R_{f_2}	[13—15]	2.30(3H, s), 3.30 (2H, t, J=18 Hz), 7.20(4H, s)	85.1(3F, s), 117.3 (2F, t, J=18 Hz)	—	224 (M$^+$)	53.54 (53.58)	4.07 (4.05)
CH_2=$CHCH_2$-R_{f_8}	130/140	2.82(2H, dt, J=6, 18 Hz), 5.03—5.45 (2H, m), 5.55—6.03(1H, m)	81.3(3F, t, J=10 Hz), 113.6(2F, m), 122.4 (6F, m), 123.5(4F, m), 126.6(2F, m)	1650(C=C) (neat)	460 (M$^+$)	—	—
4							
PhC≡C-R_{f_8}	120/2[b]	7.20—7.65(5H, m)	81.4(3F, t, J=10 Hz), 97.5(2F, m), 121.4 (2F, m), 122.2(4F, m), 122.9(4F, m), 126.5 (2F, m)	2250(C≡C) (neat)	520 (M$^+$)	36.74 (36.94)	0.97 (0.97)

Table 8. (Continued)

Compd[a]	Bp(θ_b/°C)/mmHg[b] [Mp (θ_m/°C)]	^{1}H-NMR (δ, in $CDCl_3$)	^{19}F-NMR (in $CDCl_3$)	IR (Method)	m/z	Anal (%) Found (Calcd)	
						C	H
PhC≡C-R_{f_6}	140/25[b]	7.15—7.80(5H, m)	81.5(3F, t, J=10 Hz), 97.5(2F, m), 121.6 (2F, m), 123.0(4F, m), 126.5(2F, m)	2250(C≡C) (neat)	420 (M^+)	40.15 (40.02)	1.15 (1.20)
PhC≡C-R_{f_3}	135/110[b]	7.4(5H, m)	80.7(3F, tt, J=8.5, 0.5Hz), 98.7(2F, tq, J=8.5, 6.0Hz), 127.3 (2F, tq, J=6.0, 0.5Hz)	2240(C≡C) (neat)	270 (M^+)	49.20 (48.91)	1.90 (1.87)
PhC≡C-R_{f_2}	Oil	7.3—7.7(5H, m)	85.8(3F, t, J=4.5 Hz), 101.6(2F, q, J= 4.5Hz)	2250(C≡C) (neat)	220 (M^+)	54.47 (54.56)	2.23 (2.29)
n-$C_6H_{13}C\equiv C$-R_{f_8}	Oil	0.90(3H, m), 1.20—1.75(8H, m), 2.33(2H, m)	81.5(3F, t, J=10 Hz), 96.6(2F, m), 121.5 (2F, m), 122.3(4F, m), 123.1(4F, m), 126.6(2F, m)	2340(C≡C) (neat)	527 (M^+-1)	36.32 (36.38)	2.41 (2.48)
n-$C_6H_{13}C\equiv C$-R_{f_6}	Oil	0.8—1.0(3H, m), 1.1—1.7(8H, m), 2.30(2H, t, J= 6 Hz)	81.4(3F, t, J=10 Hz), 96.6(2F, m), 121.8 (2F, m), 123.2(4F, m), 126.6(2F, m)	2250(C≡C) (neat)	429((M^++1) 427(M^+-1)	39.35 (39.27)	3.08 (3.06)
n-$C_6H_{13}C\equiv C$-R_{f_2}	Oil	0.87(3H, t, J= 6 Hz), 1.00—1.78 (8H, m), 2.00—2.45(2H, m)	86.1(3F, t, J=2 Hz), 100.9(2F, q, J=2 Hz)	2260(C≡C) (neat)	213 (M^+-CH_3)	—	—
6	160/14	1.60(3H, s), 2.47—2.70(2H, m), 2.70—3.00(2H, m)	80.1(2F, m), 81.4 (3F, t, J=10Hz), 122.4(6F, m), 123.3 (2F, m), 125.6(2F, m), 126.8(2F, m)	1730(C=O), 1690(C=C) (neat)	530 (M^+)	31.63 (31.71)	1.25 (1.33)
7	150/11 [44.5—45.5]	1.48(3H, s), 2.90(4H, m)	81.3(3F, t, J=10Hz), 112.8(2F, m), 117.4 (2F, m), 122.4(6F, m), 123.4(2F, m), 126.8(2F, m)	1740(C=O) (KBr)	530 (M^+)	31.77 (31.71)	1.37 (1.33)
9	Oil	1.33(3H, t, J=7Hz), 1.88(3H, s), 2.36 (3H, m), 4.26(2H, q, J=7Hz)	80.1(2F, bs), 81.3 (3F, t, J=10Hz), 122.4(6F, m), 123.3 (2F, m), 125.5(2F, m), 126.7(2F, m)	1730(C=O), 1670(C=C) (neat)	562 (M^+)	31.83 (32.04)	1.75 (1.94)
10	180/14	1.30(3H, t, J=7Hz), 1.63(3H, s), 2.33 (3H, s), 4.28(2H, q, J=7Hz)	81.4(3F, t, J=10Hz), 108.8(2F, m), 116.8 (2F, m), 122.3(6F, m), 123.3(2F, m), 126.8(2F, m)	1760(ester), 1740(C=O) (neat)	563 (M^++1)	32.01 (32.04)	1.97 (1.97)
12	170/15	1.25(3H, t, J=7Hz), 1.83—2.20(2H, m), 2.50—2.90(4H, m), 4.18(2H, q, J=7Hz)	80.7(2F, bs), 81.3 (3F, t, J=10Hz), 122.5(6F, m), 123.3 (2F, m), 125.5(2F, m), 126.7(2F, m)	1710(C=O), 1670(C=C) (neat)	575 (M^++1)	33.29 (33.46)	1.78 (1.90)
13	190/15 [54]	1.30(3H, t, J=7Hz), 1.80—3.00(6H, m), 4.27(2H, q, J=7Hz)	81.3(3F, t, J=10Hz), 109.0(1F, AB system, J=295Hz, FA), 111.9 (1F, AB system J=295Hz, FB), 118.0(2F, m), 122.4 (6F, m), 123.2(F, m), 126.7(2F, m)	1760(ester), 1740(C=O) (KBr)	574 (M^+)	33.68 (33.46)	2.07 (1.90)

Table 8. (Continued)

Compd[a]	Bp[b](θ_b/°C) [Mp (θ_m/°C)]	^{1}H-NMR (δ, in CDCl$_3$)	^{19}F-NMR (in CDCl$_3$)	IR (Method)	m/z	Anal (%) Found (Calcd)		
						C	H	
15a	Oil	1.30(6H, t, J=6Hz), 1.73(3H, s), 4.20 (4H, q, J=6Hz)	81.3(3F, t, J=10Hz, 109.4(2F, m), 116.5 (2F, m), 122.3(6F, m), 123.2(2F, m), 126.6(2F, m)	1750(ester) (KBr)	592 (M$^+$)	32.32 (32.45)	2.13 (2.21)	
15b	Oil	1.30(6H, t, J=6Hz), 1.70(3H, s), 4.25 (4H, q, J=6Hz)	81.7(3F, t, J=10Hz), 110.0(2F, m), 120.8 (2F, t, J=5Hz)	1750(ester) (KBr)	342 (M$^+$)	38.52 (38.61)	3.72 (3.83)	
15c	Oil	1.30(6H, t, J=6Hz), 1.75(3H, s), 4.23 (4H, q, J=6Hz)	70.0(6F, s), 173.4 (1F, s)	1750(ester) (neat)	342 (M$^+$)	—	—	
						C	H	N
17	[73—74]	1.83(6H, s)	81.5(3F, t, J=10Hz), 115.6(2F, m), 118.6 (2F, m), 122.2(6F, m), 123.3(2F, m), 126.7 (2F, m)	1560(NO$_2$) 1345(NO$_2$) (KBr)	461 (M$^+$$-NO_2$)	25.76 (26.05)	1.25 (1.19)	2.72 (2.76)

a) R_{fm}=n-C_mF_{2m+1}. b) Bath temperature °C/mmHg. Distillation was carried out by using a glass tube oven.

treatment was carried out in a similar manner as above. Column chromatography of the resulting residue on silica gel gave **17** as crystals. The results are summarized in Table 7.

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