TELOMERIZATION OF 3,3,3-TRIFLUOROPROP-1-ENE AND FUNCTIONALIZATION OF ITS TELOMERS

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Dedicated to our friend Professor Oldřich Paleta on the occasion of his 70th birthday in recognition of his outstanding contributions to the area of organofluorine chemistry.

The synthesis of four 3,3,3-trifluoroprop-1-ene telomers ($R_F(C_3H_3F_3)_nI$, n = 1, 2, R_F = n-C_6F_{13}- or $(CF_3)_2CF$-) and their allyl derivatives $R_F(C_3H_3F_3)_nCH_2CH{=}CH_2$ are presented. The allyl telomers were prepared by a three-step reaction. The first step involved the thermal and peroxide-induced bulk telomerization of 3,3,3-trifluoroprop-1-ene (TFP) with heptafluoro-2-iodopropane or tridecafluoro-6-iodohexane leading to monoadduct and diadduct, the ratio of which depends on the $R_0 = [R_FI]_0/[TFP]_0$ initial molar ratio and the reaction temperature. The amount of monoadduct increased up to 50–60% and of the diadduct to 25–30% at temperatures up to 180 °C (thermal-initiated) and 150 °C (initiated with di-*tert*-butyl peroxide, DTBP), R_0 up to 1.5. It was observed that the addition of the $(CF_3)_2CF^{\bullet}$ radical onto the $=CH_2$ of TFP was regioselective leading to selective formation of a single isomer in contrast to the addition of the n-$C_6F_{13}^{\bullet}$ radical. Then, the telomers reacted with allyl acetate yielding $R_F(C_3H_3F_3)_nCH_2CH(I)CH_2OCOCH_3$ (n = 1, 2) in 50–80% yields. The third step consisted of a deiododeacetatization of these iodoacetates into $R_F(C_3H_3F_3)_nCH_2{-}CH{=}CH_2$ (**C,n**) giving 50–80% yields. All the intermediates were characterized by ^1H, ^{19}F and products by ^{13}C NMR spectroscopy.

Keywords: 3,3,3-Trifluoroprop-1-ene; Radical additions; Perfluoroalkyl iodides; Thermal and peroxide telomerization; Fluoroallylic monomer; Fluorinated polymers; ^1H, ^{19}F and ^{13}C NMR spectroscopy.

Telomerization of 3,3,3-trifluoroprop-1-ene (TFP) with various transfer agents was pioneered by Haszeldine after its synthesis in 1951 by dehydroiodination of $CF_3CH_2CH_2I$ [1–3] (Table I). Various ways of initiat-

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TABLE I
Telomerization of 3,3,3-trifluoroprop-1-ene with different chain-transfer agents (or telogens) and initiators (experimental conditions and results)

Telogen	Initiator	Telomers	Ref.
CF_3I	UV/5 days	$CF_3[CH_2CH(CF_3)]_nI$ n = 1,2	2
CF_3I	225 °C/36 h	$CF_3[CH_2CH(CF_3)]_nI$ n = 1–3	2,3
CF_3I	UV/various T	normal and reverse monoadducts small amounts of n=2	4
$IC_6F_{12}I$	(t-BuO)$_2$/143 °C	$\{I[CH_2\text{-}CH(CF_3)]_nC_3F_6\text{-}\}_2$ n=1–3	5
Cl_3SiH	UV	$Cl_3Si[CH_2CH(CF_3)]_nH$ n=1,2	6
$(C_2H_5O)_2P(O)H$	(t-BuO)$_2$/130 °C	$(C_2H_5O)_2P(O)CH_2CH_2CF_3$ (39%)	7a
$(C_2H_5O)_2P(O)H$	(t-BuO)$_2$/140 °C	$H(TFP)_nP(O)(OC_2H_5)_2$ n=1–4	7b
THF	DTBP/140 °C	monoadduct (48%)	8
2-Me-1,3-dioxolane	$Fe(CO)_5$	2-Me-2,4-bis(TFP)dioxolane	9
CH_3SSCH_3	UV	$CH_3SCH_2CH(CF_3)SCH_3$	10
HBr	UV	$CF_3CH_2CH_2Br$	2
Cyclopentadiene	180 °C/72 h	exo/endo = 62:38	11
$CH_3OCOCH(CH_3)_2$	peroxides	$CH_3OCOC(CH_3)_2[CH_2CH(CF_3)]_nH$	12
$(CH_3)_2CHOH$	γ-rays (T < 90 °C)	$(CH_3)_2C(OH)[CH_2CH(CF_3)]_nH$ n=1,2	13
$C_6H_5CH_2Cl$	$Fe(CO)_5$	$C_6H_5CHX[CH_2CH(CF_3)]_nY$ n = 1,2; X = Cl, H; Y = H, Cl	14
CCl_4	$Fe(CO)_5$	$Cl_3C[CH_2CH(CF_3)]_nCl$ n = 1–3	15
CCl_4	$CuCl_2$/LiCl	$Cl_3C[CH_2CH(CF_3)]_nCl$ n = 1–7	16
$C_6H_5CH_2Br$	$Fe(CO)_5$	$C_6H_5CHX[CH_2CH(CF_3)]_nY$ n = 1,2; X = Br, H; Y = H, Br	17
$CHBr_3$	$Fe(CO)_5$/DMF	$Br_2CH[CH_2CH(CF_3)]_nBr$ n = 1–3	18
Br_2CHBr	DBP[a]	$XCBr_2[CH_2CH(CF_3)]_nY$ n = 1,2; X = Y = H or Br	18
$BrCH_2Br$	$Fe(CO)_5$	$BrCH_2[CH_2CH(CF_3)]_nBr$ n = 1,2	18
CBr_4	DBP[a]	$Br_3C[CH_2CH(CF_3)]_nBr$ n = 1–3	19

[a] Dibenzoyl peroxide.

ing the telomerization were investigated. The photochemical or thermal addition of HBr and CF_3I to TFP yielded exclusively $CF_3CH_2CH_2Br$ and $CF_3[CH_2CH(CF_3)]_nCH_2CHICF_3$, respectively. Low et al.[4] investigated this reaction under UV radiation at various temperatures and obtained a mixture of normal and reverse isomers for the monoadduct. They observed that a higher proportion of products of reverse addition was formed at higher temperatures and the formation of higher adducts at ca. 175 °C. In addition for other transfer agents, diiodoperfluoroalkanes, silanes, phosphonates, disulfides react with TFP, yielding the monoadduct predominantly (Table I)[5–12].

Pertinent studies of TFP telomerization were performed by Russian teams using initiation with a peroxide or γ-rays (Table I). Terentev et al.[9] studied the cotelomerization of TFP with 2-methyl-1,3-dioxolane and obtained cyclic telomers accompanied by rearrangement of transient radical intermediates by 1,5-H migration. Zamyslov et al.[13] used C_1–C_4 alcohols as telogens in TFP telomerization under γ-irradiation to get different fluoroalcohols. Vasileva et al.[14–19] used different telogens such as $C_6H_5CH_2Cl$, CBr_4, $CHBr_3$, CH_2Br_2 (but not $CHCl_3$ and $CBrCl_3$) with the initiating system $Fe(CO)_5$–DMF or hexamethylphosphoramide (HMPA) (Table I). In the presence of $Fe(CO)_5$–DMF, a radical mechanism was proved to take place and chain transfer constants of the telogens involved in telomerizations were determined. Keim et al.[16] studied the transition-metal-catalyzed C–C coupling reaction of TFP with CCl_4 in the presence of copper salts and obtained new telomers.

Systematic studies of telomerization reactions of fluorinated monomers, in particular fluoroalkenes, with various transfer agents were performed by Ameduri and Boutevin, published in several papers[20] and more recently collected in a book[21].

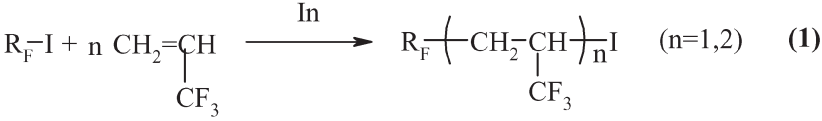
Two patents[22,23] of Pennsalt Chemical Corporation claim the production of fluorinated organic telomers by heating at 150–250 °C unsaturated fluorinated compounds with an R_FX telogen, where R_F and X are a perfluoroalkyl group and a halogen (Br or I), respectively. The degree of telomerization of the halogen-containing low-molecular-weight linear telomers ranged from 3 to 7. Rondestvedt[24] described the preparation of perfluoroalkyl iodide telomers with a general formula $R_F[C(R^1)_2CR^1R^2]_7I$ where R^1 = H or F, R^2 = H, F and R_F represents a perfluoroalkyl group containing 2–22 carbon atoms. A Japanese patent[25] claimed the synthesis of fluoroalkyl iodide telomers $C_nF_{2n+1}(CR^1R^2CRR^1)_mI$, where R = H, alkyl, R^1 = H, halogen, m = 2–6, n = 3–20, but the produced telomers were not characterized.

The aim of this work is to synthesize and to characterize 3,3,3-trifluoroprop-1-ene telomers (mostly mono- and diadducts) with perfluoroalkyl iodides R_FI (R_F = n-C_6F_{13} or $(CF_3)_2CF$) and their further modification to obtain new highly fluorinated monomers. The structure of the synthesized products, their main properties and telomerization mechanism were also studied.

RESULTS AND DISCUSSION

Telomerization of 3,3,3-Trifluoroprop-1-ene (TFP)

Any radical telomerization requires radicals; in this study, the TFP telomerization involves various initiating systems (thermal, photochemical (UV), radical, metal complexes) and a perfluoroalkyl iodide R_FI (preferably n-$C_6F_{13}I$ and i-C_3F_7I) as the telogen (or chain-transfer agent) as shown in Scheme 1.



SCHEME 1
Radical telomerization of 3,3,3-trifluoroprop-1-ene (TFP) with perfluoroalkyl iodide (In, initiator)

Furthermore, the photochemical reaction and reactions of metal complexes were carried out under batch conditions in Carius tubes. Thermal and peroxide initiations were carried out under pressure, in autoclave; at temperature ranging from 60 to 180 °C depending on the initiators used (the reaction temperature was chosen as a temperature of which their half-life was close to 1 h). The initial telogen $[T]_0$/monomer $[M]_0$ molar ratio (R_0) varied from 0.25 to 1.50 and the reaction time ranged from 4 to 22 h. The main results are displayed in Table II.

The product mixture was analyzed by GC and, after distillation, the fractions were characterized by ^1H, ^{19}F and ^{13}C NMR. The yield of mono- (n = 1) and diadducts (n = 2), of normal and reverse-addition product ratios as a function of reaction conditions are also shown in Table II.

TABLE II
Radical telomerization of 3,3,3-trifluoroprop-1-ene with R_FI[a] as a telogen at different reaction conditions (batch operation)[b]

Run	Initiator	R_0	C_0	T °C	t_r h	P, bar		TFP conv. %	% by GC[c]		
						max	min		R_FI	**A,1**	**A,2**[d]
1	Thermal	0.25	–	160	20	39	34	36.8	52.8	26.2	21.0
2	Thermal	0.50	–	160	20	22	17	79.2	27.6	51.9	20.5
3	Thermal	0.50	–	180	22	30	11	73.4	2.4	65.9	31.2
4	Perkadox 16s	0.50	0.03	62	20	7	5	79.2	23.8	35.4	40.8
5	AIBN	0.50	0.03	82	18	10	7	79.2	17.4	38.8	42.0
6	Trigonox 101	0.50	0.03	134	6	16	0.6	89.6	3.7	19.1	63.8
7	DTBP	0.50	0.03	140	6	17	0.2	97.9	3.7	19.0	63.8
8	DTBP	0.50	0.03	143	4	19	0.8	94.3	9.6	21.1	66.6
9	DTBP	1.40	0.03	140	4	13	1.1	95.2	22.5	54.4	15.7
10	DTBP	0.40	0.03	140	4	25	2	96.8	2.9	3.7	47.4
11	DTBP	0.50	0.03	140	4	22	2	98.1	3.3	10.15	57.9
12	DTBP	0.75	0.03	145	4	20	3.0	93.8	6.8	34.1	49.0
13	DTBP	1.20	0.03	150	4	20	5.0	90.0	14.9	46.3	33.4
14	DTBP	1.40	0.03	150	4	21	3.5	95.0	12.6	54.1	28.6
15	DTBP	1.50	0.03	150	4	19	5.0	95.0	24.6	43.9	28.3
16	UV	1.40	–	30	24	–	–	75.2	27.8	38.2	21.6
17[f]	Fe^{3+}/benzoin	1.40	0.3	140	48	–	–	48.5	39.8	32.5	18.4

[a] R_F = n-C_6F_{13} (Runs 1–9, 16, 17) and $(CF_3)_2CF$ (Runs 10–15). [b] $R_0 = [R_FI]_0/[TFP]_0$; $C_0 = [In]_0/[TFP]$ (In, initiator). [c] The remaining part contained higher TFP telomers ($n > 2$). [d] **A,1** and **A,2** stand for $R_F(C_3H_3F_3)_1I$ and $R_F(C_3H_3F_3)_2I$, respectively. [e] Perkadox 16s, bis(4-*tert*-butylcyclohexyl)peroxydicarbonate; purity 95%. [f] $FeCl_3/C_6H_5CH(OH)COC_6H_5$ (1:1 mole/mole).

The most suitable initiators were: di-*tert*-butyl peroxide (DTBP) and 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane (Trigonox101). The yields (Y) of the diadducts were higher than 65% for R_0 = 0.5 and of monoadducts higher than 50% for R_0 = 1.4.

The structure of the telomers and the mechanism of radical telomerization of TFP were proved by NMR analysis. The NMR characteristics are detailed in Experimental. ^{19}F NMR spectrum of n-C_6F_{13}[$CH_2CH(CF_3)$]I as an example of monoadduct is shown in Fig. 1.

There was no signal at –59 ppm assigned to C**F**$_2$I end-groups of the reacted telogen. Two signals were observed in the range from –67 to –72 ppm. The first one, at –67.2 ppm (**b**, C**F**$_3$ of TFP), is related to the reverse addition (only 4.5 mole %). The major product (**a**, C**F**$_3$ of TFP at –70.2 ppm) has a structure with a normal addition (95.5 mole %). All other signals are assigned to the n-C_6F_{13} group of the telogen. The expected signal at –81.5 ppm (t, J = 9.5 Hz) is assigned to the α C**F**$_3$ of n-C_6F_{13}. The other signals are: λ (–113.7, m, C**F**$_2$$CH_2$), ε (–121.6, m, C**F**$_2$$CF_2CH_2$), δ (–122.8, m, $C_2F_5CF_2$C**F**$_2$), γ (–123.6, m, C_2F_5C**F**$_2$) and β (–126.6, m, CF_3C**F**$_2$).

^{1}H NMR spectra of both monoadducts show the presence of the characteristic quintet of the AB–X system: 4.8 ppm, C***H**-, $^3J_{HF}$ = $^3J_{HHA}$ ~15 Hz;

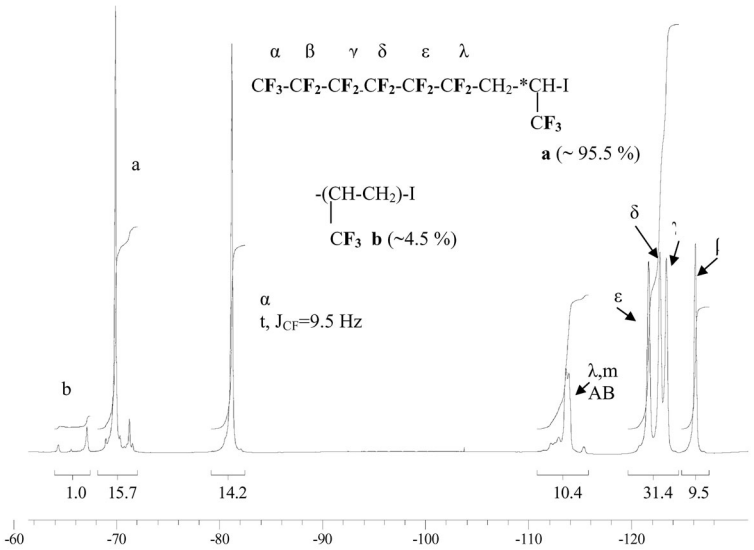


FIG. 1
^{19}F NMR spectrum (in $CDCl_3$) of n-$C_6F_{13}(C_3H_3F_3)$I monoadduct

$^3J_{HHB}$ = 7 Hz and a multiplet at 3.25–2.65 ppm, centered at 2.9 ppm (m, $\mathbf{H}_A$, $\mathbf{H}_B$ in AB system $R_FC\mathbf{H}_2$).

In addition, the ^{13}C NMR spectrum exhibits a quartet at 133.35, 127.88, 122.41, 116.93 ppm, assigned to $C\mathbf{F}_3$ ($^1J_{CF}$ = 275.4 Hz) and a triplet at 36.59, 36.17, 35.75 ppm for $C\mathbf{H}_2$ of TFP ($^3J_{CF}$ = 20.8 Hz). The quartet with negative intensity at 7.07, 6.42, 5.74, 5.06 ppm is assigned to asymmetric carbon C*H ($^2J_{CF}$ = 33.5 Hz) while that at –15.3 ppm is related to a reverse addition product (~3.0 mole %) of the CH_2I terminal group. Interestingly, the reverse monoadduct was not produced from i-C_3F_7I giving a more electrophilic and bulky perfluoroisopropyl radical, which hence reacted selectively at the CH_2 of TFP (more "nucleophilic" and less hindered than the =CH site).

NMR spectra of TFP diadducts of the n-$C_6F_{13}I$ telogen and those of $(CF_3)_2CFI$ are described in Experimental (Runs 2, 7 and 8, Table III) and DEPT ^{13}C NMR spectrum of $(CF_3)_2CFCH_2CH(CF_3)I$ monoadduct is illustrated in Fig. 2.

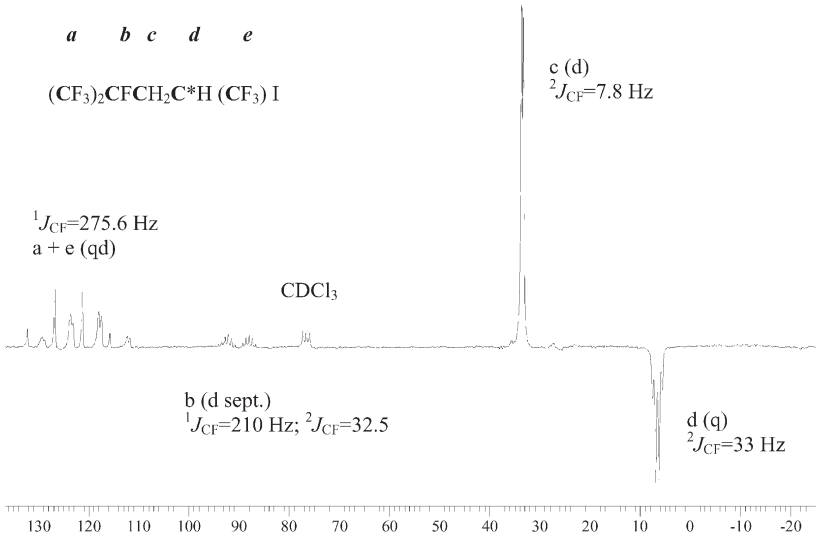
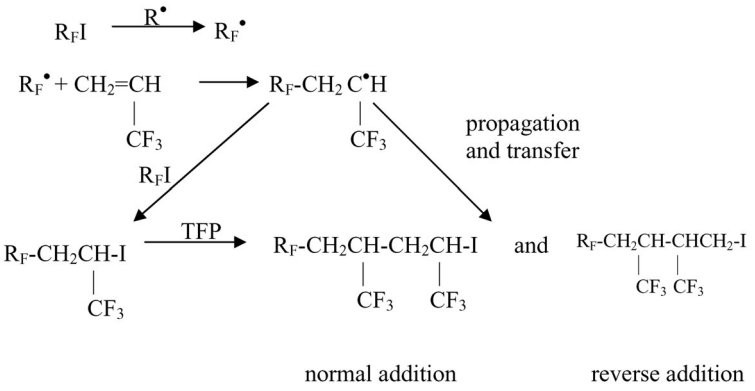


FIG. 2
DEPT ^{13}C NMR spectrum (in $CDCl_3$) of $(CF_3)_2CF(C_3H_3F_3)I$ monoadduct

Mechanism of TFP Telomerization

Two alternatives of the mechanism can be proposed: the first one is the classical mechanism of telomerization in which the $R_FCH_2CH(CF_3)^\bullet$ radical produced may undergo either telogen transfer or initiate the propagation of TFP. In the latter case, the reverse addition product can be formed in the propagation step (Scheme 2).

However, a stepwise mechanism may operate in which $R_FCH_2CH(CF_3)I$ formed by R_FI transfer acts as a telogen in further telomerization of TFP as shown in Scheme 2.



SCHEME 2
Mechanism of radical telomerization of 3,3,3-trifluoroprop-1-ene (TFP) with perfluoroalkyl iodide (R_FI)

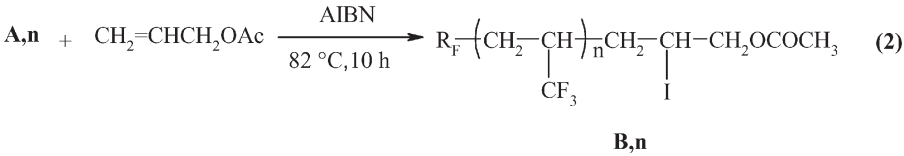
Synthesis of Iodoacetate Compounds of TFP Telomers, $R_F[CH_2CH(CF_3)]_nI$, n = 1, 2

This type of reactions was studied earlier[26] and more recently described[27].

Various peroxides such as dibenzoyl peroxide, *tert*-pentyl peroxypivalate, DTBP, AIBN, etc., can be used. Because of the great exothermicity of the reaction, the initiator used was of high importance; its activity is associated with its low decomposition temperature. It was previously observed that when the starting temperature was higher than 90 °C (e.g., when initiated with dibenzoyl peroxide) the reaction temperature rose to 160–180 °C and at such high temperature the produced ω-perfluoroiodoacetate undergoes a thermal rearrangement to $R_FCH_2CH(OAc)CH_2I$ [26,28].

To avoid such an undesired transformation, we chose AIBN as the initiator added[27]. In this case, no exotherm was observed and the GC yield in-

creased up to 80–82 or 75 wt.% after distillation. The main results are presented in Table III.



SCHEME 3
Radical addition of TFP telomers onto allyl acetate

TABLE III
Main reaction products and their characteristics

Run	Product	RT[a] min	B.p. °C	B.p. pressure mm Hg
1	n-$C_6F_{13}(C_3H_3F_3)I$ (A,1)	3.6	24–26 71–73	0.4 18–25
2	n-$C_6F_{13}(C_3H_3F_3)_2I$ (A,2)	5.5	29–31 100–105	0.2 18–25
3	n-$C_6F_{13}(C_3H_3F_3)CH_2CH(I)CH_2OCOCH_3$	11.5	70–72	0.1
4	n-$C_6F_{13}(C_3H_3F_3)_2CH_2CH(I)CH_2OCOCH_3$	13.4	110–115	0.05
5	n-$C_6F_{13}(C_3H_3F_3)CH_2CH=CH_2$	3.2	68–70 105–108	18–25 normal
6	n-$C_6F_{13}(C_3H_3F_3)_2CH_2CH=CH_2$	5.3	100–103	18–25
7	$(CF_3)_2C(F)C_3H_3F_3I$	1.5	100–110	normal
8	$(CF_3)_2C(F)(C_3H_3F_3)_2I$	3.2	65–70	18–25
9	$(CF_3)_2C(F)(C_3H_3F_3)CH_2CH(I)CH_2OCOCH_3$	8.2–8.9	115–120 65–70	18–25 1
10	$(CF_3)_2C(F)(C_3H_3F_3)_2CH_2CH(I)CH_2OCOCH_3$	10.8–11.1	78–84	0.1
11	$(CF_3)_2C(F)(C_3H_3F_3)CH_2CH=CH_2$	1.3–1.5	105–110	normal
12	$(CF_3)_2C(F)(C_3H_3F_3)_2CH_2CH=CH_2$	2.9–3.1	63–64	18–25

[a] RT, retention time; GC analysis: column OV1 (3% silicone grease on Chromosorb G), 2 m length, 0.30 cm diameter, 50–200 °C.

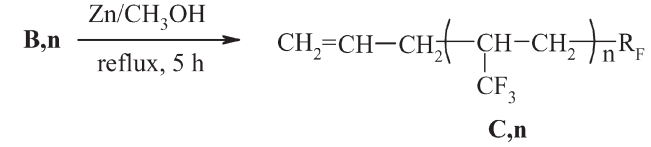
The structure of different iodoacetates was studied by ^{1}H and ^{19}F NMR spectroscopy (Runs 3, 4, 9 and 10 in Experimental). The signals at 4.2 ppm are assigned to protons of C**H**$_2$OAc groups of normal structure. However, the rearranged iodoacetate (the signal of C**H**OAc at 5.10 ppm) was not observed. The multiplet at 4.3–4.5 ppm is related to the C**H**I group, the multiplet of C**H**$_2$CHI at 2.1–2.2 ppm and a singlet at 2.02 ppm is attributed to C**H**$_3$ of the acetate. The other signals at 2.25–2.60 ppm (m, CFC**H**$_2$) and at 2.8–3.1 ppm (m, *C**H**(CF_3)) are assigned to TFP protons.

For the diadduct, ^{1}H NMR spectra are more complex due to a new multiplet in the range of 1.6–1.9 ppm (*C-C**H**$_2$-C*).

The ^{19}F NMR spectra are similar to those of the starting telomers.

Synthesis of Fluoroallylic Monomers CH_2=CH–$CH_2(C_3H_3F_3)_nR_F$

As described previously[27–29], fluorinated allyl monomers **C,n** can be obtained by deiododeacetatization reaction from **B,n** (Scheme 4).



(3)

SCHEME 4
Synthesis of fluorinated allylic monomers **C,n** by deiododeacetatization of **B,n**

The iodoacetate **B,n** was added to a two-fold excess of activated Zn in MeOH. The reaction was rather exothermic and was monitored by GC. The conversion of **B,n** was complete. The overall yield of the reaction product **C,n** was close to 75% after distillation.

Both allylic monomers with n-C_6F_{13} or $(CF_3)_2CF$ groups were characterized by ^{1}H and ^{19}F NMR spectroscopies. The ^{1}H NMR spectrum of $(CF_3)_2CFCH_2$–CH(CF_3)–CH_2CH=CH_2 exhibits two multiplets in the 5.0–5.4 and at 5.6–5.9 ppm regions, assigned to the protons of the double bond CH=C**H**$_2$ and CH_2=C**H** (Fig. 3). The multiplet at 2.6–3.0 ppm is related to the proton of asymmetric carbon, *C**H** (CF_3) and that at 2.2–2.6 ppm to both methylene protons of the C**H**$_2$CH=CH_2 and CFC**H**$_2$ structures.

The ^{13}C NMR spectrum also confirms the structure of the allylic monomers. Hence, the signals at 132.2 ppm (=C**H**, 1 C) and 119.4 ppm (s, CH=C**H**$_2$, 1 C) are assigned to both carbon atoms of the double bond. Both

quartets centered at 128 and 120 ppm are assigned to CF_3- of TFP ($^1J_{CF}$ = 279.7 Hz) and $(CF_3)_2$ of telogen ($^1J_{CF}$ = 284.7 Hz, $^2J_{CF}$ = 27.2 Hz), respectively. The doublet ($^1J_{CF}$ = 206.3 Hz) of septuplet ($^2J_{CF}$ = 32.0 Hz) centered at 90 ppm is characteristic of the CF group adjacent to both CF_3 end-groups while the quartet ($^2J_{CF}$ = 27.2 Hz) centered at 37.1 ppm is assigned to *CH (CF_3) group. The other signals are characteristic of the allyl carbon atoms with the doublet of $CFCH_2$, ($^2J_{CF}$ = 19.1 Hz) at 25.5 ppm. Of course, the ^{13}C NMR spectra of diadducts are more complex (see Experimental). The ^{19}F NMR spectra are similar to those of corresponding telomers and some of them were already discussed. The details of these spectra are presented in Experimental.

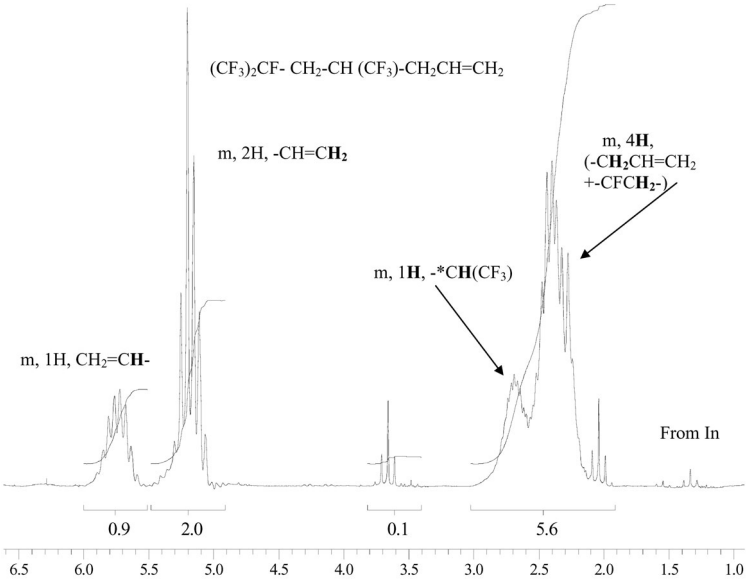


FIG. 3
^{1}H NMR spectrum (in $CDCl_3$) of $(CF_3)_2CFCH_2CH(CF_3)CH_2CH=CH_2$ (In, initiator)

CONCLUSION

This work described the synthesis of four new highly fluorinated telomers based on 3,3,3-trifluoroprop-1-ene (*n* = 1 and 2) and their functionalization to obtain allylic monomers containing TFP unit(s), by a three-step reaction for further applications. The first step involved a simple bulk addition of perfluoroalkyl iodide R_FI (R_F = n-C_6F_{13} or i-C_3F_7) onto TFP and showed that

DTBP at 150 °C was a suitable initiator to get 50–60% yield for n = 1 or 2 depending on the R_0 ratio. For n-$C_6F_{13}I$ as the telogen, both normal and reverse additions took place, but no reverse addition product was obtained with i-C_3F_7I. The second step involved radical addition of $R_F(C_3H_3F_3)_nI$ onto allyl acetate using AIBN initiator added portionwise. The thermal rearrangement was not observed, and the yield was satisfactory (50–80%). In the third step, the deiododeacetatization took place to produce allylic fluorine-containing monomer in 50–80% yield. All the compounds synthesized were characterized by GC and ^1H, ^{19}F and ^{13}C NMR spectroscopies. The obtained products could be suitable intermediates in preparation of new fluorinated products utilized as coating materials, surfactants, block copolymers, hybrid fluorosilicones.

EXPERIMENTAL

Reactants

3,3,3-Trifluoroprop-1-ene (TFP) and heptafluoro-2-iodopropane (i-C_3F_7I) were kindly supplied by the Great Lakes Chemical Corporation (now Chemtura, West Lafayette (IN), U.S.A.), tridecafluoro-6-iodohexane (n-$C_6F_{13}I$) by Elf Atochem (Pierre Benite, France), 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane (Trigonox101) by Akzo Nobel, acetonitrile by SDS, AIBN and di-*tert*-butyl peroxide (DTBP) by Aldrich, and were used as received.

Apparatus

After reaction and evaporation of the solvent, the product mixture was analyzed by gas chromatography (GC) using a Delsi apparatus (model 330) equipped with an SE 30 column, 2 m × 30 mm (i.d.). The nitrogen pressure at the inlet of the column was maintained at 1 bar and the detector and injector temperatures were 240 and 235 °C, respectively. The temperature programmer started from 50 °C and reached 200 °C at a heating rate of 10 °C/min. The GC apparatus was connected to a Hewlett–Packard integrator (model 3390).

The structures of the telomers were determined by NMR spectroscopy at room temperature. ^1H, ^{19}F and ^{13}C NMR spectra were recorded on a Bruker AC-250 or Bruker 400 MHz instruments using deuterated chloroform or acetone and tetramethylsilane and $CFCl_3$ as the solvent and internal references, respectively. Chemical shifts, δ, are given in ppm, coupling constants, J, in Hz. The experimental conditions for recording ^1H (or ^{19}F) NMR spectra were the following: flip angle 90° (30°), acquisition time 4.5 s (0.7 s), pulse delay 2 s (5 s), 36 (64) scans and pulse width 5 μs for ^{19}F NMR. Abbreviations used: s, singlet; d, doublet; t, triplet; q, quartet; qn, quintet; sex, sextet; sept, septuplet; m, multiplet; er, erythro; tr, threo.

Telomerization of TFP with R_FI to Obtain $R_F(TFP)_nI$

In a 160- or 500-ml Hastelloy autoclave equipped with a manometer, a magnetic stirrer, and safety valve, R_FI and the initiator (in amounts depending on initial molar ratios R_0 and C_0) were introduced and purged with Ar for 15 min. The reactor was closed and checked for the

leak at 30 bar of N_2. The reactor was placed in acetone/liquid nitrogen to cool the contents. Then, 5–7 vacuum-Ar cycles were applied to remove oxygen from the liquid. The required amount of TFP, depending on the R_0 was condensed in the autoclave. The autoclave was heated up to 150 °C and the telomerization was carried out at 150 ± 5 °C for 4 h. According to the TFP amount, the pressure was increased and pressure and temperature were recorded during the reaction. A sharp decrease in the pressure at almost constant temperature (150 °C) for the first hour and then a small pressure change were observed. After the reaction stopped, the autoclave was cooled and then placed in an ice bath. The unreacted monomer was expelled by purging and the conversion of telomerization was determined by double weighing (ca. 90–95%). The crude product was analyzed by GC and then washed with a saturated solution of $Na_2S_2O_5$ in aqueous NaOH to remove the iodine produced. The reaction mixture was distilled to separate the adducts. The retention time (RT) and boiling point (b.p.) of the products are listed in Table III.

Run 1. Monoadduct: n-$C_6F_{13}(C_3H_3F_3)$I; 2-iodo-2H,3H,3H-perfluorononane – normal adduct (96%), 1-iodo-1H,1H,2H-2-(trifluoromethyl)perfluorooctane – reverse adduct (4%). ^{19}F NMR (acetone-d_6) (Fig. 1): –67.2 (**b**, C**F**$_3$ of TFP, reverse adduct); –70.2 (**a**, C**F**$_3$ of TFP, normal adduct, 3 F); –81.5 (t, J = 9.5, C**F**$_3$ of n-C_6F_{13}I, α, 3 F); –113.7 (m, C**F**$_2$CH$_2$, λ, 2 F); –121.6 (m, C**F**$_2$CF$_2$CH$_2$, ε, 2 F); –122.8 (m, $C_2F_5CF_2$C**F**$_2$, δ, 2 F); –123.6 (m, C_2F_5C**F**$_2$, γ, 2 F); –126.6 (m, CF_3C**F**$_2$, β, 2 F). ^{1}H NMR (acetone-d_6): 4.8 (qn, AB–X system, C*-**H**, $^3J_{HF}$ = $^3J_{HHA}$ ~ 15; $^3J_{HHB}$ = 7), 3.25–2.65, 2.9 (m, **H**$_A$, **H**$_B$ in AB system R$_F$C**H**$_2$, 2 H). ^{13}C NMR (acetone-d_6): 133.35, 127.88, 122.41, 116.93 (q, C**F**$_3$, $^1J_{CF}$ = 275.4); 36.59, 36.17, 35.75 (t, C**H**$_2$, $^3J_{CF}$ = 20.8); 7.07, 6.42, 5.74, 5.06 (q, negative intensity C*H, $^2J_{CF}$ = 33.5); –15.3 (C**H**$_2$I), ~2.5% reverse adduct.

Run 7. Monoadduct: $(CF_3)_2CF(C_3H_3F_3)$I; 2-iodo-2H,3H,3H-4-(trifluoromethyl)perfluoropentane. ^{19}F NMR (CDCl$_3$): –71.3 (m, C**F**$_3$ of TFP, 3 F); –77.7 and –78.5 (d t, (C**F**$_3$)$_2$, 6 F); –188.9 (t, C**F**, 1 F). ^{1}H NMR (CDCl$_3$): 2.75–3.40 (m, C**H**$_2$, 2 H); 4.3–4.7 (m, *C**H**, 1 H). ^{13}C NMR (CDCl$_3$) (Fig. 2): 132.1, 126.7, 121.2, 115.7 (q, C**F**$_3$ of TFP, $^1J_{CF}$ = 275.6, 1 C); 129.2, 123.5, 117.9, 112.2 (q of d, (C**F**$_3$)$_2$-, $^1J_{CF}$ = 285.04, $^2J_{CF}$ = 25.3, 2 C); 92.08–87.91 (d of sept, C(F), $^1J_{CF}$ = 210, $^2J_{CF}$ = 32.5, 1 C); 33.6–33.2 (d, C**H**$_2$ of TFP, $^2J_{CF}$ = 17.8, 1 C); 7.5, 6.8, 6.2, 5.5 (q, C**H**(CF$_3$), $^2J_{CF}$ = 33.0, 1 C).

Run 2. Diadduct: n-$C_6F_{13}(C_3H_3F_3)_2$I; 2-iodo-2H,3H,3H,4H,5H,5H-4-(trifluoromethyl)perfluoroundecane – normal adduct (72%), 1-iodo-1H,1H,2H,3H,4H,4H-2,3-bis(trifluoromethyl)perfluorodecane – reverse adduct (28%). ^{19}F NMR (CDCl$_3$): –68.8 (s, CH(C**F**$_3$)I, reverse, b, 3 F); –71.4 (CH$_2$-C*H(C**F**$_3$)-CH$_2$, normal, a, 3 F); –69.6 and –72.2 (C*H(C**F**$_3$)-C*H(C**F**$_3$), 6 F); –81.2 (t, J = 9.5, α, C**F**$_3$, 3 F); –113.7 (m, C**F**$_2$CH$_2$, λ, 2 F); –121.6 (m, C**F**$_2$CF$_2$CH$_2$, ε, 2 F); –122.8 (m, $C_2F_5CF_2$C**F**, δ, 2 F); –123.6 (m, C_2F_5C**F**$_2$, γ, 2 F); –126.6 (m, CF_3C**F**$_2$, β, 2 F). ^{1}H NMR (CDCl$_3$): 2.18–2.28 (t, $^3J_{HH}$ = 4.1); 2.29–2.33 ($^3J_{HH}$ = 6, C*-C**H**$_2$-C*, AB system, 2 H); 2.5 (td, $^3J_{HF}$ = 11, $^3J_{HH}$ = 6, R$_F$C**H**$_2$, 2 H); 3.0–3.2 (m, $^3J_{HH}$ = 9, C**H**$_2$I, reverse, 2 H); 4.4 (m, 1HH$_A$, 1HH$_B$, J = 6.1, C***H**(CF$_3$), 1 H). ^{13}C NMR (CDCl$_3$): 130.7 (130.5), 127.9 (127.7), 125.2 (124.9), 122.4 (122.3) (q of d (two stereoisomers), C**F**$_3$ of TFP between two CH$_2$ groups in the normal adduct, $^1J_{CF}$ = 279.4, 1 C); 128.3 (128.15), 125.6 (125.4), 122.8 (122.7), 120.1 (119.9) (q of d, C**F**$_3$ of TFP adjacent to I, $^1J_{CF}$ = 275.9, 1 C); 122–105 (complex system assigned to n-C_6F_{13}-); 37.32, 37.05, 36.77, 36.49, 36.21 (qn (er and tr), C*H(CF$_3$) from the side of R$_F$, $^2J_{CF}$ = 27.6, 1 C); 35.83–35.40 (reverse, negligible, 1*C); 33.88, 32.89 ((er/tr), C**H**$_2$ between two C*, 1 C); 29.97 (29.92), 29.75 (29.70), 29.54 (29.48) (t of d (er/tr), R$_F$-C**H**$_2$, $^2J_{CF}$ = 20.9, 1 C); 19.94, 19.61, 17.24 (two q, C*H(CF$_3$)I, $^2J_{CF}$ = 32.2, 1 C); 5.62–4.59 (q of reverse adduct, negligible C**H**$_2$I, 1 C).

Run 8. Diadduct: $(CF_3)_2CF(C_3H_3F_3)_2$-I; 2-iodo-2H,3H,3H,4H,5H,5H-4,6-bis(trifluoromethyl)perfluoroheptane – normal adduct, 1-iodo-1H,1H,2H,3H,4H,4H-2,3,5-tris(trifluoromethyl)perfluorohexane – reverse adduct. ^{19}F NMR ($CDCl_3$): –69.6, –70.9, –71.5, –72.9 (assigned to C**F**$_3$ of both TFP (normal and reverse adducts), 6 F); –77.3, –78.5, –78.8 (t, (C**F**$_3$)$_2$, 6 F); –185.5, –187.2 (dt, C(**F**), 1 F). ^{1}H NMR ($CDCl_3$): 1.9–2.3 (m, *C-C**H**$_2$-C*, 2 H); 2.3–2.7 (m, R_F-C**H**$_2$, 2 H); 2.6–3.2 (m, *C**H**(CF$_3$)), 25% of one diastereoisomer overlapping with R_F-C**H**$_2$ protons and 75% in the range of 2.75–3.2; negligible reverse adduct (absence of signal at 3.5, 1 H)); 4.15–4.45 (m, *C**H**(CF$_3$)I, 1 H). ^{13}C NMR ($CDCl_3$): 130.8 (130.6), 128.0 (127.8), 125.2 (125.0), 122.4 (122.3) (q of d (coupling of two diastereoisomers), C**F**$_3$ of TFP between two CH_2 groups in normal adduct, $^1J_{CF}$ = 279.7, 1 C); 128.4 (128.16), 125.66 (125.42), 122.92 (122.68), 120.18 (119.94) (q of d, C**F**$_3$ adjacent to I in normal adduct, $^1J_{CF}$ = 276.7, 1 C); 125.04 (124.94), 122.27 (122.10), 119.39 (119.26), 116.55 (116.43), 124.79 (124.66), 121.95 (121.82), 119.11 (118.99), 116.27 (116.15) (two q of d, C**F**$_3$, $^1J_{CF}$ = 285.7, $^2J_{CF}$ = 28.17, 6 C); 92.63–89.02 (d of sept, C(F), $^1J_{CF}$ = 207.3, $^2J_{CF}$ = 32.2, 1 C); 38.10, 37.8, 37.6, 37.3, 37.0, 36.7 (sex, C*H(CF$_3$) of TFP between two CH_2 groups, $^2J_{CF}$ = 27.17, 1 C); 35.56, 33.29 (d, C**H**$_2$ of TFP-I, 1 C); 27.70, 27.51, 27.29, 27.10 (two d, C**H**$_2$, $^2J_{CF}$ = 19.1, 1 C); 19.53–18.55, 17.23–16.30 (d of q (tr/er), *C**H**(CF$_3$)I, $^2J_{CF}$ = 29.2, 1 C).

Synthesis of $R_F(C_3H_3F_3)_nCH_2CH(I)CH_2OCOCH_3$

In a 250-ml three-necked round-bottom flask equipped with a double condenser and a thermometer, a certain amount of monoadduct or diadduct produced in the previous reaction and a 1.2-fold excess of allyl acetate were introduced. Then, the mixture was heated up to 82 °C and stirred. When the temperature reached 80 °C, AIBN (C_0 = 0.015–0.050) was introduced stepwise during 10-h reaction time. No exothermicity was observed. After 10 h, the reaction was stopped; the crude product was cooled to room temperature, filtered and analyzed by GC. The reaction mixture was distilled to purify the iodoacetate. The retention times and boiling points are listed in Table III.

Run 3. n-$C_6F_{13}(C_3H_3F_3)CH_2CH(I)CH_2OCOCH_3$; 6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluoro-2-iodo-4-(trifluoromethyl)undecyl acetate. ^{19}F NMR ($CDCl_3$): –81.9 and from –111 to –127 (the same chemical shifts as those in Run 1); –71.39 and –72.59 (assigned to C**F**$_3$ of TFP in both diastereoisomers). ^{1}H NMR ($CDCl_3$): 2.05 (s, C**H**$_3$, 3 H); 2.4–2.6 (m, C***H**(CF$_3$), 1 H); 2.8–3.0 (m, C_6F_{13}C**H**$_2$, 2 H); 4.1–4.3 (m, C**H**$_2$OCOCH$_3$, 2 H); 4.4–4.5 (m, C***H**(I), 1 H).

Run 9. $(CF_3)_2CF(C_3H_3F_3)CH_2CH(I)CH_2OCOCH_3$; 6,7,7,7-tetrafluoroheptyl-2-iodo-4,6-bis(trifluoromethyl) acetate. ^{19}F NMR ($CDCl_3$): –71.2 and –72.3 (C**F**$_3$ of TFP (normal and reverse adducts), 3 F); –77.3 and –77.6 (m, (C**F**$_3$)$_2$C(F), $^3J_{FF}$ = 69.5, 6 F); –185.8, –187.1 (m, C(**F**), 1 F). ^{1}H NMR ($CDCl_3$): 2.02 (s, C**H**$_3$, 3 H); 2.1–2.2 (m, C**H**$_2$CH(I), 2 H); 2.25–2.60 (m, C(F)C**H**$_2$, 2 H); 2.8–3.1 (m, *C**H**(CF$_3$), 1 H); 4.1–4.25 (m, C**H**$_2$OCO, 2 H); 4.3–4.5 (m, C**H**(I), 1 H).

Run 4. n-$C_6F_{13}(C_3H_3F_3)_2CH_2CH(I)CH_2OCOCH_3$; 8,8,9,9,10,10,11,11,12,12,13,13,13-tridecafluoro-2-iodo-4,6-bis(trifluoromethyl) tridecanyl acetate. ^{19}F NMR ($CDCl_3$): –70 to –73 (complex system, 2 × C**F**$_3$ of TFP, 6 F); –81.6 (s, C**F**$_3$ of n-C_6F_{13}, 3 F); –111.8 to –127 (the same assignments as those in Run 1). ^{1}H NMR ($CDCl_3$): 2.05 (s, C**H**$_3$ from OCOC**H**$_3$, 3 H); 2.3 (*C-C**H**$_2$-*C, 2 H); 2.24 (C**H**$_2$CH(I), 2 H); 2.5 (*C**H**(CF$_3$) overlapping with 2.58, 1 H); 2.58 (m, R_F-C**H**$_2$, 2 H); 2.8 (m, *C**H**(CF$_3$), 1 H); 4.2 (m, C***H**(I), 1 H); 4.4 (m, ester C**H**$_2$OCOCH$_3$, 2 H).

Run 10. $(CF_3)_2CF(C_3H_3F_3)_2CH_2CH(I)CH_2OCOCH_3$; 8,9,9,9-tetrafluoro-2-iodo-4,6,8-tris(trifluoromethyl)nonyl acetate. ^{19}F NMR ($CDCl_3$): no signal at –67 (no reverse product); –70.5 to –72.77 (m, 2 × C**F**$_3$ of TFP, 6 F); –77.2 to –78.75 (m, (C**F**$_3$)$_2$, 6 F); –186.4, –187.14, –187.73 (t,

C(**F**), 1 F). ^{1}H NMR ($CDCl_3$): 1.6–1.9 (m, *C-C**H**$_2$-*C, 2 H); 2.02–2.25 (C**H**$_3$ in CH_3OCO, 3 H); 2.25–2.4 (C**H**$_2$-CHI, 2 H); 2.3–2.5 (R_F-C**H**$_2$, 2 H); 2.6–3.0 (*C**H**(CF_3), 1 H); 4.2 (m, 1 H of C**H**(I) + 1 H of *C**H**(CF_3)); 4.4 (m, ester C**H**$_2$OCOCH_3, 2 H).

Synthesis of $R_F(C_3H_3F_3)_nCH_2CH{=}CH_2$

Zn dust was activated with 1.2 g of a mixture of acetic acid/acetic anhydride (1:1), 40 ml of CH_3OH was added and they were introduced into 250-ml two-neck round-bottom flask with a reverse condenser and magnetic stirrer. The temperature was increased to 65 °C while stirring. The iodoacetate prepared in Run 3, Table III (60.05 g, 0.094 mol) in 30 ml MeOH was added dropwise under reflux to a Zn slurry within 3 h with vigorous stirring and then the reaction mixture was stirred for 2 h. A colorless product was obtained. The Zn complex was filtered off, the filtrate was diluted with CH_2Cl_2 (1:1 vol./vol.) and washed with 10% HCl aqueous solution (100 ml) and washed again with distilled water. The organic phase was added dropwise to anhydrous $MgSO_4$ under stirring to eliminate traces of water, filtered and twice distilled (Table III).

Run 5. n-$C_6F_{13}(C_3H_3F_3)CH_2CH{=}CH_2$; 6,6,7,7,8,8,8,9,9,10,10,11,11,11-tridecafluoro-4-(trifluoromethyl)undec-1-ene. ^{19}F NMR ($CDCl_3$): the same chemical shifts as those of n-$C_6F_{13}(C_3H_3F_3)CH_2CH(I)CH_2OCOCH_3$ except for the signal centred at –113 ppm which is simpler and gives only one peak at –72.0 (one diastereoisomer). ^{1}H NMR ($CDCl_3$): 2.2–2.6 (m, n-C_6F_{13}C**H** and C**H**$_2$-CH, 4 H); 2.6–2.8 (m, *C**H**(CF_3), 1 H); 5.1–5.4 (m, =C**H**$_2$, 2 H); 5.6–5.9 (m, =C**H**, 1 H). ^{13}C NMR ($CDCl_3$): 132.18 (132.08) (d (2 diastereoisomers), =**C**H, 1 C); 131.03, 128.26, 125.48, 122.71 (q, **C**F_3 of TFP, $^1J_{CF}$ = 279.0, 1 C); 120.4–104.9 (complex system, n-**C**$_6F_{13}$, 6 C); 118.8–118.7 (d, =**C**H$_2$, 1 C); 36.68–35.86 (q, *CH(CF_3), $^2J_{CF}$ = 27.2, 1 C); 32.68 (s, **C**H$_2$, 1 C); 28.18–27.75 (t, **C**H$_2$$R_F$, $^2J_{CF}$ = 21.13, 1 C).

Run 11. $(CF_3)_2CF(C_3H_3F_3)CH_2CH{=}CH_2$; 6,7,7,7-tetrafluoro-4,6-bis(trifluoromethyl)hept-1-ene. ^{19}F NMR ($CDCl_3$): –72.2 (C**F**$_3$ of TFP, 3 F); –78.8 and –78.4 (dt, (C**F**$_3$)$_2$, 6 F); –187.1 (m, C(**F**), 1 F). ^{1}H NMR ($CDCl_3$): 2.2–2.6 (m, C**H**$_2$CH=CH$_2$ + C(F)CH$_2$, 4 H); 2.6–3.0 (m, *C**H**(CF_3), 1 H); 5.05–5.4 (m, CH=C**H**$_2$, 2 H); 5.6–5.9 (m, CH$_2$=C**H**, 1 H). ^{13}C NMR ($CDCl_3$): 132.2 (=**C**H, 1 C); 131.1, 128.3, 125.5, 122.8 (q, **C**F_3 of TFP, $^1J_{CF}$ = 279.7, 1 C); 125.0, 122.1, 119.0, 116.5 (q of d, (**C**F_3)$_2$, $^1J_{CF}$ = 284.7, $^2J_{CF}$ = 27.2, 6 C); 119.4 (s, CH=**C**H$_2$, 1 C); 90 (d of sept, **C**(F), $^1J_{CF}$ = 206.3, $^2J_{CF}$ = 32.0, 1 C); 37.1 (q, *CH(CF_3), $^2J_{CF}$ = 27.2, 1 C); 33.27 (q, CH$_2$=CH**C**H$_2$, $^3J_{CF}$ = 2.0, 1 C); 25.5 (d, C(F)**C**H$_2$, $^2J_{CF}$ = 19.1, 1 C).

Run 6. n-$C_6F_{13}(C_3H_3F_3)_2CH_2CH{=}CH_2$; 8,8,9,9,10,10,11,11,12,12,13,13,13-tridecafluoro-4,6-bis(trifluoromethyl)tridec-1-ene. ^{19}F NMR ($CDCl_3$): –71.9 (d, C**F**$_3$ adjacent to allyl, 3 F); –72.6 (d, C**F**$_3$ of TFP to the C_6F_{13} side, 3 F); –82.0 (t, α C**F**$_3$ of n-C_6F_{13}, 3 F); the group of signals from –112 to –127 ppm belongs to C_5**F**$_{10}$ as in Run 1. ^{1}H NMR ($CDCl_3$): 1.6–1.8 and 50% from 1.8–2.2 (qn, *C-C**H**$_2$-C*, 2 H); 1.8–2.2 (m, C**H**$_2$CH=CH$_2$, 2 H); 2.2–2.6 (m, overlap of 2 H from C**H**$_2$ of R_FC**H**$_2$ and 1 H from *C**H**(CF_3)); 2.8 (m, *C**H**(CF_3), 1 H); 5.10–5.18 (m, =C**H**$_2$, 2 H); 5.58–5.84 (m, =C**H**, 1 H). ^{13}C NMR ($CDCl_3$): 133.03 (132.81) (d (diastereoisomers), =**C**H, 1 C); 131.73 (131.61), 128.96 (128.83), 126.18 (126.06), 123.41 (123.28) (q of d (diastereoisomers), **C**F_3 of TFP on the side of R_F, $^1J_{CF}$ = 279.2, 1 C); 131.10 (130.94), 128.32 (128.16), 125.55 (125.39), 122.78 (122.62) (q of t (diastereoisomers), **C**F_3 of TFP on the side of allyl, $^1J_{CF}$ = 279.01, $^2J_{CF}$ = 31.5, 1 C); 118.40 (118.28) (d, =**C**H$_2$, 1 C); 122–105.9 (complex system of **C**$_6F_{13}$, 6 C); 40.46 (40.39), 40.20 (40.14), 39.95 (39.88), 39.69 (39.63) (q of d (diastereoisomers), *CH(CF_3) from the side of R_F, $^2J_{CF}$ = 25.8, 1 C); 35.06, 34.80, 34.52, 34.25, 33.98 (q, *CH(CF_3) from the side of allyl, $^2J_{CF}$ = 27.25, 1 C); 32.60 (32.57), 32.22

(32.20) (CH_2 adjacent to vinyl, 1 C); 30.51, 30.09, 29.88 (t, R_FCH_2, $^2J_{CF}$ = 21.5, 1 C); 27.52 (s, CH_2 from *C-CH_2-*C, 1 C).

Run 12. $(CF_3)_2CF(C_3H_3F_3)_2CH_2CH{=}CH_2$; 8,9,9,9-tetrafluoro-4,6,8-tris(trifluoromethyl)non-1-ene. ^{19}F NMR ($CDCl_3$): –71.7, –72.2, –72.5 (t, 2 × CF_3 in TFP, 6 F); –77.7 to –78.9 (dt, $(CF_3)_2$, 6 F); –186.9, –187.4 (m, C(F), 1 F). ^{1}H NMR ($CDCl_3$): 1.55–2.2 (m, CH_2 from *C-CH_2-C*, 2 H); 2.0–2.2 (m, allyl CH_2, 2 H); 2.3–2.5 (m, 2 H of R_F-CH_2 + 25% of diastereoisomer *CH(CF_3) from the side of R_F); 2.9 (m, 1 H of *CH(CF_3) from the side of the allyl); 5.20 (m, =CH_2, 2 H); 5.7 (m, CH=CH_2, 1 H). ^{13}C NMR ($CDCl_3$): 133.21 (132.89) (d, CH_2=CH-, 1 C); 131.76 (131.61), 128.98 (128.83), 126.20 (126.05), 123.43 (123.28) (q, CF_3 of TFP on the side of R_F, $^1J_{CF}$ = 279.7, 1 C); 131.18 (131.00), 128.40 (128.22), 125.62 (125.45), 122.84 (122.67) (q, CF_3 of TFP adjacent to allyl, $^1J_{CF}$ = 279.7, 1 C); 125.10 (125.06), 124.82 (124.79), 122.26 (122.23), 121.98 (121.95), 116.59 (116.55), 116.30 (116.26) (two qq, $(CF_3)_2$, $^1J_{CF}$ = 285.7, $^2J_{CF}$ = 28.17, 2 C); 188.29 (118.24) (d, CH=CH_2, 1 C); 92.74–88.77 (d of sept, C(F), $^1J_{CF}$ = 206.25, $^2J_{CF}$ = 32.2, 1 C); 40.37–39.38 (qn, *CH(CF_3), $^2J_{CF}$ = 25.15, 1 C); 35.85–34.68 (qn of d, *CH(CF_3) adjacent to allyl, $^2J_{CF}$ = 27.16, 1 C); 32.78–32.75 (d, CH_2 adjacent to vinyl, 1 C); 32.10, 32.08, 31.91 (t, CH_2 between 2*C, 1 C); 28.94, 27.70 (two d, CH_2-R_F, $^2J_{CF}$ = 19.12, 1 C).

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