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Reaction of α-(Trifluoromethyl)styrene with Anionic Initiators

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ABSTRACT: α-(Trifluoromethyl)styrene ($Q = 0.43$, $e = 0.90$) does not undergo radical homopolymerization. Anionic polymerization fails to produce appreciable amounts of polymer even in bulk at −78 °C in spite of its high e value. The resistance to anionic polymerization is primarily due to side reactions involving addition–elimination sequences (S_N2') when initiators are nucleophilic enough to add to the β-carbon of TFMST. Weaker anionic initiators such as pyridine and potassium *tert*-butoxide that effectively induce polymerization of methyl α-(trifluoromethyl)acrylate ($Q = 0.74$, $e = 2.5$) do not react with TFMST. Reactions of TFMST with several anionic initiators are described in detail.

Introduction

Methyl α-(trifluoromethyl)acrylate (MTFMA) is reluctant to undergo radical homopolymerization.[1,2] Alfrey-Price Q and e parameters for this fluoromonomer have been determined by Ito et al.[3] ($Q = 0.74$, $e = 2.5$) based on copolymerization analysis and the "mercury method"[4] and also by Iwatsuki et al.[2] ($Q = 0.8$, $e = 2.9$) using the Lüssi's method.[5] The high e value suggests that MTFMA should facilely undergo anionic polymerization. However, anionic initiators such as n-butyllithium (n-BuLi) or phenylmagnesium bromide (PhMgBr) typically employed for polymerization of methyl methacrylate (MMA) failed to produce high molecular weight polymers in good yield.[1] A similar anomalous behavior of ethyl α-(trifluoromethyl)acrylate in anionic polymerization has been noted by Narita et al.[6] Much weaker initiators such as pyridine[1,7] and organic and inorganic salts[7] successfully polymerize MTFMA to high molecular weight polymers. On the basis of GC/MS analysis of n-BuLi–MTFMA reaction products along with the literature survey, Ito and Schwalm suggested that n-BuLi reacts with the β-carbon of MTFMA followed by spontaneous elimination of LiF to form $CF_2{=}$, which then reacts with additional n-BuLi (addition–elimination sequence).[7]

Ueda and Ito extended the investigation of the effect of α-CF_3 group on the reactivity of vinyl monomers to α-(trifluoromethyl)styrene (TFMST).[8] TFMST fails to undergo radical homopolymerization even in bulk at low temperatures and does not self-propagate ($r_{TFMST} = 0$) in copolymerization with styrene (ST).[8] As is the case with MTFMA mentioned above, the Q and e parameters were determined by combining the copolymerization analysis with the mercury method[8] since Q and e values cannot be obtained only from the reactivity ratios when one of the ratios is 0. In spite of the favorable Q (0.43) and e (0.90) parameters and the fact that the mercury method has indicated that TFMST adds to a cyclohexyl radical 1.5 times and 7.5 times faster than MMA and ST, respectively, TFMST does not homopolymerize under radical conditions presumably due to the large steric hindrance and very low ceiling temperature.

Table I
Attempted Anionic Polymerization of TFMST at −78 °C

initiator (mol %)	THF/TFMST (mL/mL)	time (day)	initiation mode
KO-*t*-Bu/18-crown-6 (2.0)	2	5	*a*
KO-*t*-Bu/18-crown-6 (2.0)	0	4	*b*
PhMgBr (2.2)	2	3.6	*b*
PhMgBr (2.4)	0	5	*a*
EtMgBr (5.0)	0	6	*a*
n-BuLi (1.5)	1	3	*b*
n-BuLi (5.0)	0	7	*b*

[a] Mixed at room temperature and cooled to −78 °C. [b] Mixed at −78 °C.

Since TFMST ($e = 0.90$) is more electron-deficient than MMA ($e = 0.40$) and as electron-poor as methacrylonitrile ($e = 0.81$), we attempted anionic polymerization of TFMST with several initiators, which are discussed in this paper. Reactions of acrylic monomers with anionic initiators are quite complex due to the participation of the ester functionality. Therefore, TFMST should provide a good opportunity to study pathways of the reaction between α-CF_3-substituted vinyl monomers with anionic initiators without such complications as in the MTFMA case. Although there have been published several papers on the reaction of α-(fluoroalkyl)ethylenes with nucleophiles, systematic studies in relation to anionic polymerization have not been reported. In this paper are discussed primary pathways in the reaction of TFMST with various anionic initiators.

Results and Discussion

As summarized in Table I, anionic polymerizations of TFMST failed under several conditions despite its low electron density on the β-carbon ($e = 0.90$). Either bulk anionic polymerizations with a high initiator concentration at −78 °C or mixing TFMST with anionic initiators at room temperature followed by cooling to −78 °C did not

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Table II
1:1 Reaction of TFMST with Anionic Initiators in THF

entry	initiator	temp (°C)	time	unreacted TFMST (%)	unreacted initiator (%)	products (%) II	IV	V	VII	VIII
1	PhMgBr	0 → 25	3 days	17		27	11	41		
2	EtMgBr	0 → 25	2 days	40		21			32	
3	LiAlH$_4$	−78 → 25	12 h	20		80				
4	*n*-BuLi	−78	1 h	3		84	11			
5	PhLi	−78	1 h	10		62	30			
6	DPHLi	−78	1 h	5	14	63				
7	FlNa	0	2 h	2	19	39				7
8	FlK	0	1 h	10	34	57				25
9	FlLi	−78 → 0	30 min	7	<1	67				<1
10	KO-*t*-Bu 18-crown-6	25	4 days	>95						
11	naphthalene/Na	−78 → 25	24 h	100						

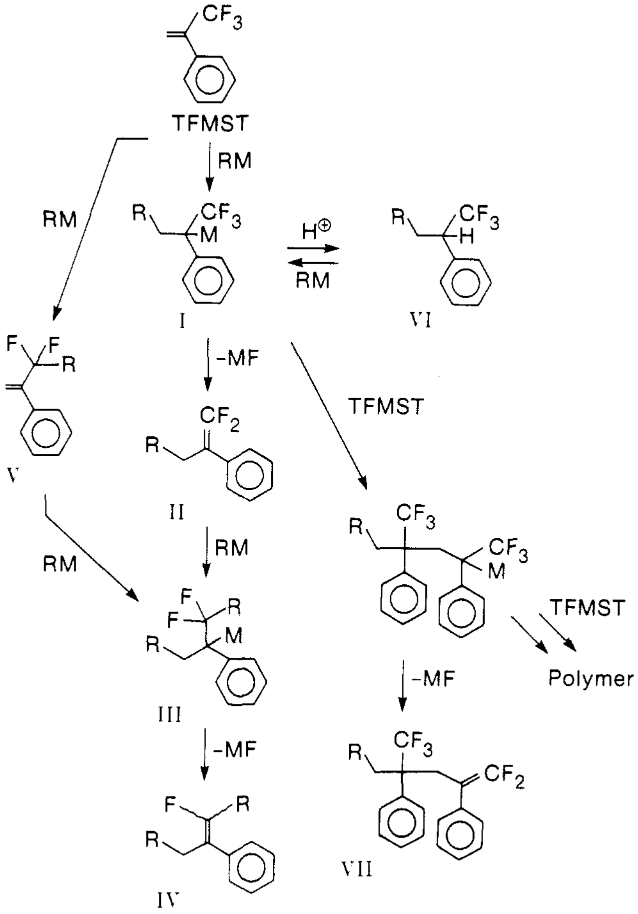
produce polymer. These conditions and procedures were employed because a very low ceiling temperature was anticipated.

As mentioned in Introduction, MTFMA suffers from similar problems in anionic polymerization with *n*-BuLi or PhMgBr.[1,7] However, owing to its very low electron density on the β-carbon ($e = 2.5$), MTFMA undergoes anionic polymerization when weak initiators such as pyridine or organic or inorganic salts are employed. The β-carbon of TFMST ($e = 0.90$, ^{13}C 120.2 ppm) is not expected to be much more electron negative than that of MMA ($e = 0.74$, ^{13}C 125.0 ppm) or methacrylonitrile ($e = 0.81$, ^{13}C 131.2 ppm) judging from the e values and ^{13}C chemical shifts. Thus, organometallic initiators would be still needed for successful initiation of anionic polymerization of TFMST. In consequence, side reactions involving addition–elimination sequences would become major pathways as pointed out in the case of MTFMA with *n*-BuLi or PhMgBr. In addition to the destructive side reactions, the propagation step in anionic polymerization of TFMST may suffer from a very low ceiling temperature.

We have investigated preferred pathways in the 1:1 reaction of TFMST with several anionic initiators (Scheme I) as summarized in Table II. We hoped that such studies would allow us to identify anionic initiators which favor propagation over side reactions. The reactions were first carried out at −78 °C, monitored by GC, and then brought to room temperature when the TFMST consumption was slow at lower temperatures. The reactions were in general much cleaner than that of MTFMA with *n*-BuLi which involves the participation of the ester functionality. The major common products were *gem*-difluoroolefins and trisubstituted fluoroethylenes. The proton-terminated addition product VI, which would be needed for successful propagation, was not detected in any 1:1 reactions we studied. The identification of the products was achieved by comparison of GC retention times, IR, ^{1}H, ^{13}C, and ^{19}F NMR spectra, elemental analysis, and GC/MS of the products with those of authentically synthesized samples. For example, *gem*-difluoroolefins exhibit characteristic IR absorption at ~1734 cm^{-1},[9] a triplet ^{13}C resonance at ~154 ppm (C=$\underline{\mathrm{C}}$F$_2$, $J_{\mathrm{CF}} = 289$ Hz) and a double doublet at ~92 ppm ($\underline{\mathrm{C}}$=CF$_2$, $J_{\mathrm{CF}} = 19$ and 15 Hz).

PhMgBr did not appreciably react with TFMST at −78 °C but slowly reacted at 25 °C, leaving 17% of unreacted TFMST after 3 days. In contrast to the other systems, the major product was a S$_{\mathrm{N}}$2 product V, which was confirmed by authentic synthesis (see Experimental Section). In Figures 1 and 2 are shown ^{1}H and ^{19}F NMR spectra, respectively, of the PhMgBr/TFMST reaction mixture and authentic samples. The ^{13}C spectrum of the reaction mixture also shows three major products and unreacted TFMST.

Scheme I
Possible Pathways in Reaction of TFMST with Nucleophiles



In Scheme I are demonstrated possible pathways in the reaction of TFMST with nucleophiles (RM). Although PhMgBr adds across the double bond of TFMST to form I, which spontaneously eliminates metal fluoride (MF) producing *gem*-difluoride II, the major pathway is the direct S$_{\mathrm{N}}$2 reaction onto the CF$_3$ group. This is quite surprising since it has been reported that the addition–elimination sequence is predominant in the reaction of α-(trifluoromethyl)olefins.[10-12] There is one report that describes the S$_{\mathrm{N}}$2 reaction between 3,3,3-trifluoropropene and ethoxide.[13] The *gem*-difluoride II could further react with a nucleophile to form III which is then immediately converted to monofluoroolefin IV through the MF elimination. As reported in the literature,[14,15] the monofluoro compound could further undergo the addition–elimination sequence in the excess of a nucleophile. However, in our 1:1 reactions the formation of such products was very

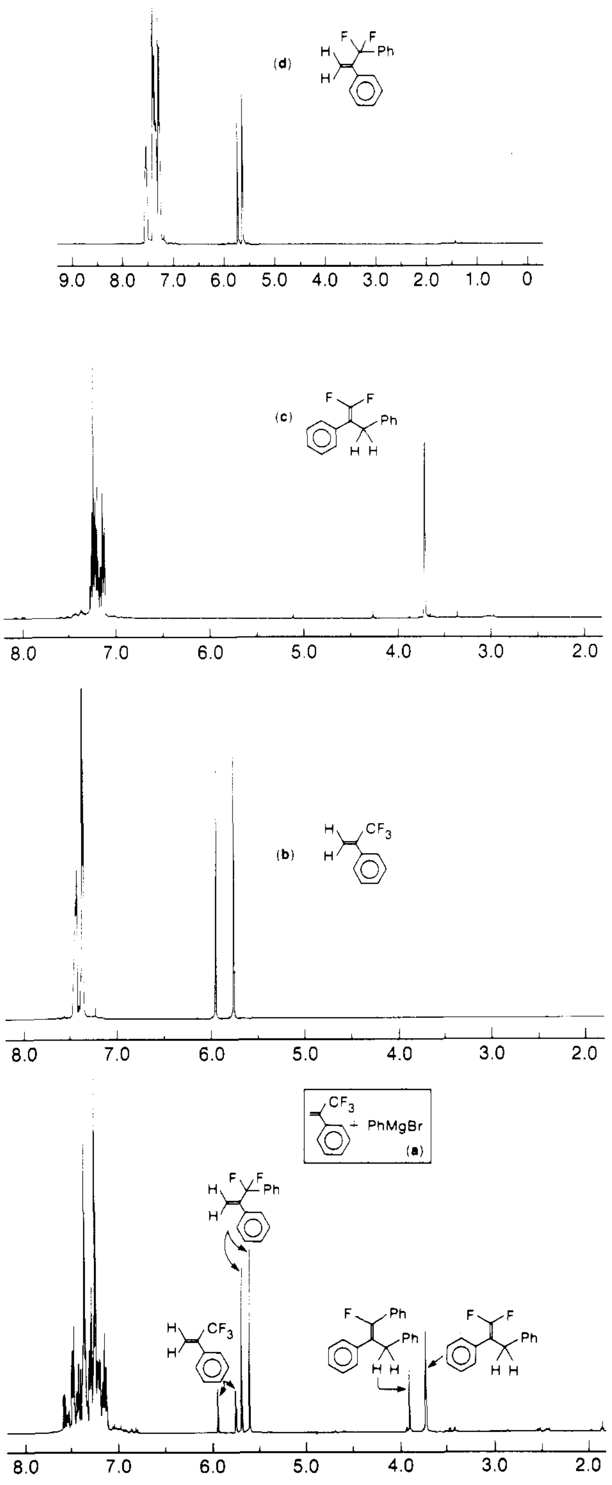


Figure 1. 400-MHz ^1H NMR spectra of (a) TFMST/PhMgBr reaction mixture, (b) TFMST, (c) authentic *gem*-difluoroolefin, and (d) authentic S_N2 product in $CDCl_3$.

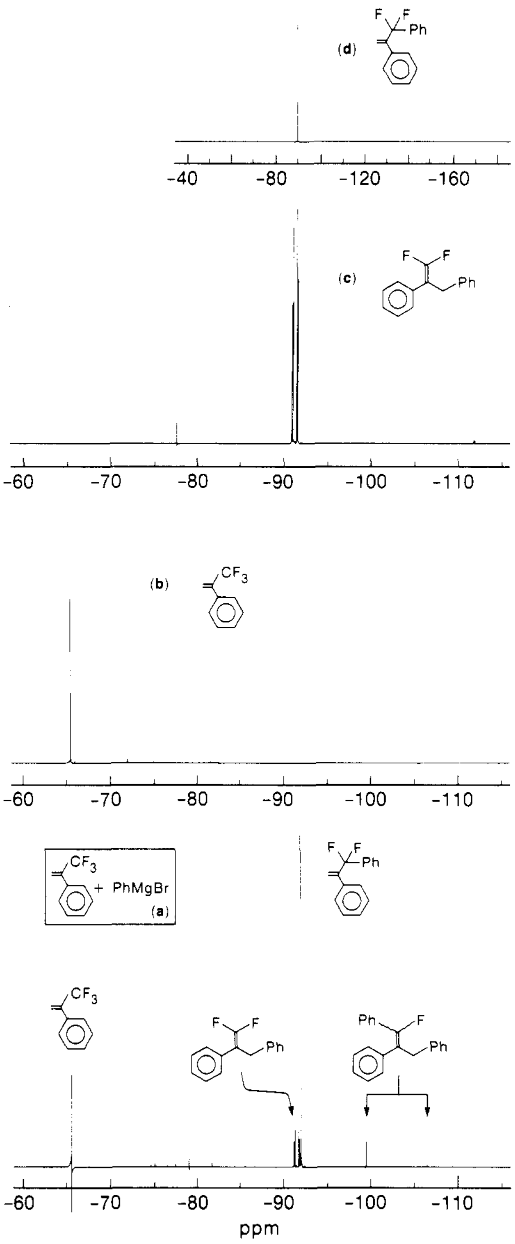


Figure 2. 376-MHz ^{19}F NMR spectra of (a) TFMST/PhMgBr reaction mixture, (b) TFMST, (c) authentic *gem*-difluoroolefin, and (d) authentic S_N2 product in $CDCl_3$.

minor. It would be unlikely that such a triple addition–elimination pathway could be found in anionic polymerization that employs a low concentration of initiators.

The monofluoroolefin IV could be also produced from the S_N2 product V through addition across the double bond followed by the MF elimination. In fact, this sequence appears to be a preferred pathway to the formation of IV in the PhMgBr reaction. The authentically prepared *gem*-difluoride II was treated with 1 equiv of PhMgBr. The reaction was very sluggish even at 25 °C and provided little *E*/*Z* selection whereas the treatment of TFMST with 1 equiv of PhMgBr almost exclusively produced one isomer (presumably *E*) as indicated in Figure 2. The monofluoroolefin was isolated from the reaction mixture as a crystalline material and the elemental analysis, IR, and ^1H, ^{13}C, and ^{19}F NMR agreed with the structure.

In order for the anionic polymerization to take place, addition of TFMST to I must compete with the MF elimination. However, our NMR analysis did not detect the protonated form VI which should have distinct CH resonances at 3.1–3.5 (^1H)[8] and at 47.3 ppm (^{13}C).[16] Even if TFMST added successfully to I before the MF elimination, the propagation might still suffer from termination through the elimination from the growing end as demonstrated in Scheme I. As shown in Table I, even bulk polymerization with PhMgBr did not produce polymer. Because the reaction of PhMgBr with TFMST is very sluggish at −78 °C, the initiator was mixed with neat TFMST at room temperature in one case to allow addition of the initiator to the β-carbon and then the mixture was cooled to −78 °C in an attempt to promote a propagation reaction. No polymer was obtained.

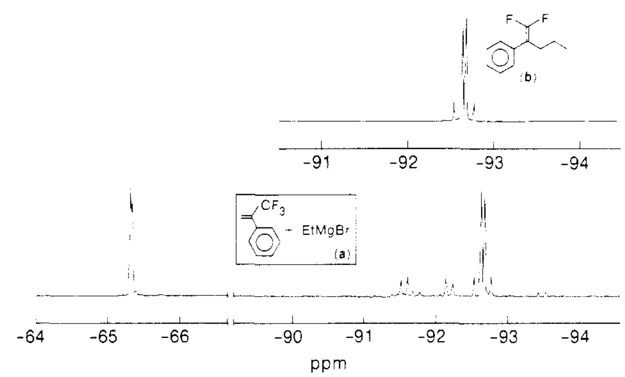


Figure 3. 470-MHz ^{19}F NMR spectra of (a) TFMST/EtMgBr reaction mixture and (b) authentic *gem*-difluoroolefin in $CDCl_3$.

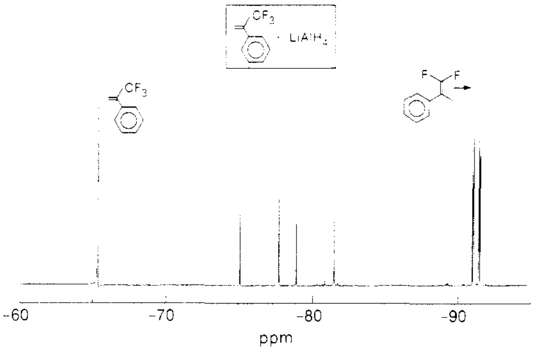


Figure 4. 376-MHz ^{19}F NMR spectrum of TFMST/LAH reaction mixture in $CDCl_3$.

Ethylmagnesium bromide (EtMgBr) did not appreciably react with TFMST at −78 °C and left 40% of unreacted TFMST after 2 days at 25 °C (Table II, entry 2). The major product was identified as the *gem*-difluoride II (21% by GC) which exhibits a characteristic quartet ^{19}F resonance [δ −92.6, −92.7 (J_{FF} = 45 Hz)] as shown in Figure 3 together with the spectrum of the authentically synthesized difluoroolefin. The difluoride did not undergo the second addition–elimination to form IV. However, there was another major product (32% by GC) which exhibits a well-separated CF_2 quartet [δ −91.6, −92.2 (J_{FF} = 44 Hz)] and a CF_3 singlet almost overlapping with the ^{19}F resonance of TFMST. These resonances are tentatively assigned to a dimer of the type VII (Scheme I) resulting from one-step propagation followed by the MF elimination. The ^{19}F quartet is similar to that of 1,1-difluoro-2-phenyl-2-benzylethylene (Figure 1) suggesting a similar magnetic environment. The ^{13}C NMR spectrum of the EtMgBr reaction mixture shows several resonances in the aliphatic region. Despite the possibility of the chain propagation in this case, anionic polymerization in bulk was not successful although EtMgBr and TFMST were mixed at room temperature to promote initiation and then cooled to −78 °C (Table I).

$LiAlH_4$ (LAH) was reacted with TFMST at −78 to 25 °C for 12 h (Table II, entry 3). The ratio of the *gem*-difluoride II to the unreacted TFMST was 4:1, as determined by GC. The ^{1}H and ^{13}C spectra of the main product II in the reaction agree with the literature.[17] The double addition–elimination product IV was not detected either by GC analysis or by NMR spectroscopies. However, as the ^{19}F NMR spectrum in Figure 4 indicates, a small additional CF_2 quartet is present suggesting occurrence of the one-step propagation as was the case with EtMgBr. In addition to a minor amount of VII, there are fairly strong ^{19}F resonances between the CF_3 and CF_2 regions corresponding to unidentified products, which were also observed in the PhMgBr reaction in a minute amount (cf. Figure 2).

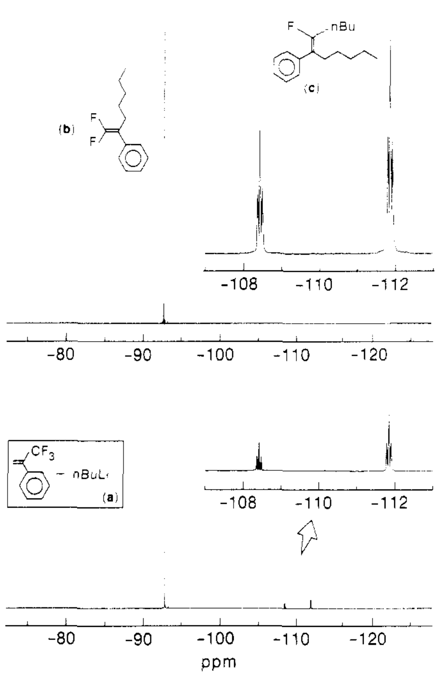


Figure 5. 376-MHz ^{19}F NMR spectra of (a) TFMST/*n*-BuLi reaction mixture, (b) authentic *gem*-difluoroolefin, and (c) isolated monofluoroolefin in $CDCl_3$.

Lithium reagents react rapidly with TFMST even at −78 °C (Table II, entries 4–6). The unreacted TFMST detected by GC after 1 h was 3 and 10% in the reactions with *n*-BuLi and phenyllithium (PhLi), respectively. (1,1-Diphenylhexyl)lithium (DPHLi) left 5% of TFMST after 1 h at −78 °C. In addition to 13% of diphenylethylene found unreacted in the reaction with *n*-BuLi, 1,1-diphenylhexane derived from the unreacted DPHLi amounted to 14%. In all the cases, the predominant products were the *gem*-difluoroolefin II (62–84%) and the monofluoroolefin IV (11–30%). The *gem*-difluoride was authentically prepared for comparison and converted to IV by reaction with *n*-BuLi, which assisted the assignment of ^{1}H, ^{13}C, and ^{19}F NMR spectra of the reaction mixtures. The ^{19}F NMR spectrum of the *n*-BuLi reaction mixture shown in Figure 5 is straightforward, consisting of a strong singlet due to the CF_2 group in II and two sets of much smaller triplets ascribed to the *E*/*Z* mixture of IV. The gem fluorine atoms in II are anisochronous and appear as an AB quartet as is the case with the product from the PhMgBr reaction (Figure 1, R = Ph in II). However, as the alkyl chain in R becomes longer (R = H → Et → *n*-Bu), the quartet becomes more and more degenerated (cf. Figures 2–5) and the fluorine atoms become accidentally isochronous when R = *n*-Bu. The fluorine atom in IV couples with the geminal methylene protons and gives rise to a triplet in the case where R = *n*-Bu whereas a singlet is characteristic to the monofluoroolefin with R = Ph (cf. Figure 2), which was confirmed by reacting the authentically prepared 1,1-difluoro-2-phenyl-2-benzylethylene with *n*-BuLi. The monofluoride thus formed still exhibits two sets of triplets, indicating that F couples with the geminal methylene protons rather than the vicinal methylene protons. *n*-BuLi does not provide *E*/*Z* selectivity in the reaction. Since *n*-BuLi adds to the β-carbon of TFMST rapidly even at −78 °C, anionic polymerization was attempted in bulk by mixing TFMST with a fairly high concentration (5 mol %) of *n*-BuLi at −78 °C, which failed to produce polymer.

In addition to the *gem*-difluoride (62%), the reaction of TFMST with PhLi (Table II, entry 5) produces a sig-

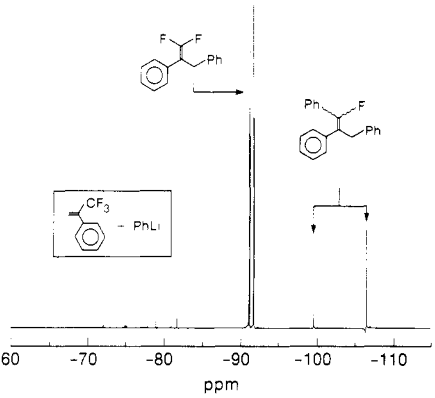


Figure 6. 470-MHz ^{19}F NMR spectrum of TFMST/PhLi reaction mixture in $CDCl_3$.

nificant amount of the monofluoroolefin IV (30%) but no S_N2 product V, which is in contrast to the PhMgBr reaction. The *E*/*Z* selection is poor in the PhLi reaction as the ^{19}F spectrum in Figure 6 indicates whereas the PhMgBr reaction almost exclusively produced one isomer (cf. Figure 2). In addition, while the authentic *gem*-fluoride II reacted rapidly with PhLi, the same reaction with PhMgBr was much more sluggish than the reaction of TFMST with PhMgBr in production of the monofluoroolefin IV as pointed out earlier. It is consequently concluded that the monofluoroolefin is produced predominantly through the S_N2 reaction followed by the addition–elimination in the case of the PhMgBr reaction whereas PhLi undergoes the double addition–elimination sequence to produce the same monofluoroolefin.

The *gem*-difluoride isolated from the reaction of TFMST with DPHLi (Table II, entry 6) exhibits a characteristic AB quartet ^{19}F resonances [δ −89.6, −91.2 (J_{FF} = 37.3 Hz)] with a large anisochronism (1.6 ppm), which resemble the smaller ^{19}F quartet observed in Figure 3 for the EtMgBr reaction. This spectral resemblance may be reflecting the similarity in the structure of II (where R = $CH_3(CH_2)_4CPh_2$) and VII, supporting our assumption of occurrence of the one-step propagation in the EtMgBr reaction. The ^{13}C NMR resonances of II isolated from the DPHLi reaction have been totally assigned with use of DEPT experiments.

Fluorenyl (Fl)sodium and -potassium were reacted with TFMST at 0 °C for 2 and 1 h, respectively (Table II, entries 7 and 8). In the former case unreacted initiator and TFMST amounted to 19 and 2%, respectively, and the latter reaction left 10% of TFMST and 34% of the unreacted initiator. FlLi reacted rapidly (30 min) with TFMST (−78 to 0 °C) almost quantitatively consuming TFMST (>99%) and FlLi (93%) (Table II, entry 9). In all the cases two major products were detected by GC as summarized in Table II. The low boiling fraction (mp 69–71 °C) was isolated from the FlLi reaction and the high boiling fraction (mp 120–122 °C) from the FlK reaction and subjected to NMR, IR, and elemental analyses. The low boiling compound shows a quartet characteristic to CF_2, and the ^1H and ^{13}C (Figure 7) spectra agree with those of structure II. The high boiling fraction exhibits only one set of CF_2 quartet with a larger anisochronism (2.6 ppm). The ^1H and ^{13}C spectra of the high boiling fraction lack the CH resonances due to the ring methine group. We have tentatively concluded that the high boiling product is a dimer of the type VIII. The fluorenyl initiator abstracts a proton from the tertiary benzylic CH of II to form a carbanion of II, which then undergoes the addition–elimination sequence with TFMST to form VIII (Scheme II). The ^1H NMR integration and chemical shift agree with the structure and elemental analysis also supports our conclusion. ^{13}C NMR spectra of II and VIII are compared in Figure 7.

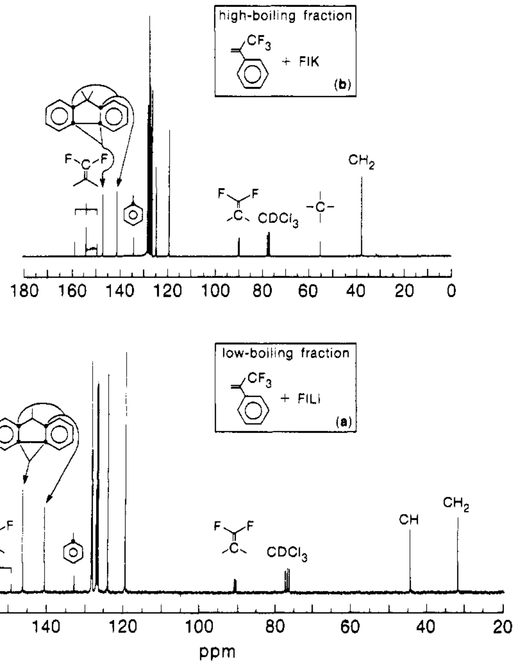
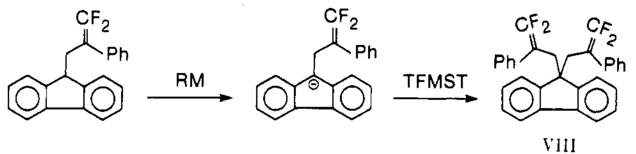


Figure 7. 62.9-MHz ^{13}C NMR spectra of (a) low-boiling and (b) high-boiling fractions of TFMST/FlLi(or K) reaction mixtures in $CDCl_3$.

Scheme II
Dimer Formation in Reaction of TFMST with Fluorenyl Initiators



Anionic polymerization of TFMST with DPHLi or fluorenyl initiators was not attempted because the absence of VI in the 1:1 model reactions suggested that polymerization would not occur.

Potassium *tert*-butoxide failed to induce any reactions at 25 °C even in the presence of 18-crown-6. TFMST did not react with sodium naphthalene at all, indicating that one-electron transfer to TFMST does not take place. It has been reported that α-(trifluoromethyl)vinyl acetate did not polymerize with sodium naphthalene.[18]

The addition–elimination sequence (S_N2' substitution) appears to be a universal phenomenon in the reaction of (trifluoromethyl)ethylenes[10,11] and similar fluoroethylenes[12] with hard nucleophiles. Alkyllithium reagents smoothly undergo the S_N2' displacement with such fluoroolefins. For example, Feiring has reported that 1-(trifluoromethyl)-ethenyl phenyl sulfide is readily converted by reaction with *n*-BuLi at −70 °C to *gem*-difluoroolefin, which further reacts with additional *n*-BuLi at somewhat higher temperature to give a 1:1 mixture of *E*/*Z* isomers of 5-fluoro-6-(phenylsulfenyl)undec-5-ene.[10] The addition–elimination sequence was also reported by Feiring in the reaction of (perfluoroalkyl)ethylenes with nucleophiles.[12] Ito[7] and Fuchikami[11] reported separately the reaction of methyl and sodium α-(trifluoromethyl)acrylates with nucleophiles, respectively, and found that *n*-BuLi undergoes the double addition–elimination sequences preferentially to form the monofluoroolefins. Grignard reagents converted the sodium acrylate only to the *gem*-difluoride,[11] suggesting that Grignard reagents react much more slowly with the *gem*-difluoride than alkyllithium reagents. The reaction of *gem*-difluoroolefins with nucleophiles has been also reported in the literature. Tanaka et al. reported that difluoroketene thioacetal underwent the S$_N$2′ substitution reaction with *n*-BuLi at room temperature to form monofluoroketene thioacetal in 90% yield and that the reactions with Grignard reagents were sluggish.[19] Koch et al.[20] studied nucleophilic reactions of sodium alkoxides in alcohol with various *gem*-difluoroalkenes of general structure PhCR=CF$_2$, determined rates and Arrhenius parameters, and found that the reaction proceeds via carbanion intermediates. The reports of Tanaka and Fuchikami support our proposed mechanism of the monofuoroolefin formation in the PhMgBr reaction with TFMST; that is, through the S$_N$2 product V rather than through the addition–elimination product II (Scheme I). However, the latter pathway cannot be totally discarded since our reaction of PhMgBr with the authentic II slowly produced monofluoroolefins and because Suda has noted a high reactivity of 3-(difluoromethylene)-4,4-dimethyloxolan-2-one toward benzylmagnesium bromide at −50 °C.[14]

Similar elimination reactions have been noted in the reaction of (trifluoromethyl)ethane bearing a benzylic hydrogen (similar to VI in Scheme I) with nucleophiles, especially alkoxides in alcohol. The base-catalyzed H–D exchange at carbon attached to the CF$_3$ group was studied by Cram and Wingrove,[21] who showed occurrence of competing elimination reaction to form geminal fluorides and suggested a carbanion intermediate for the reaction. It has been also pointed out that the elimination reaction in 2,2-bis(4-nitrophenyl)-1,1,1-trifluoroethane is via an (ElcB)$_R$ mechanism with methoxide/methanol changing to (ElcB)$_1$ or E2 with *tert*-butoxide/*tert*-butyl alcohol.

Conclusion

It is clear that anionic polymerization of TFMST suffers from the elimination reaction though, as pointed out by Kawabata and Tsuruta,[22] the pathways in the 1:1 reactions may differ from those in the polymerization reactions which employ a small amount of initiator. In the case of TFMST, the addition of a second monomer to I may compete with the elimination as suggested in the EtMgBr and LAH reactions. However, the chain may be terminated by the elimination reaction before a third monomer reacts with the chain end. In more reactive MTFMA,[1,7] the propagation seems to take place before the elimination occurs when weak initiators are employed, leading to formation of polymer. Even if an initiator which gives rise to minimum side reactions were found, the anionic polymerization of TFMST might not be successful due to a very low ceiling temperature. However, the proton-terminated addition product VI, which is needed for propagation to occur, was not detected in any reactions with various anionic initiators including DPHLi and fluorenyl initiators, suggesting that the addition–elimination sequence is the primary reason for the absence of anionic polymerization in the case of TFMST. The side reactions would have to be eliminated or minimized before the ceiling temperature effect could be discussed meaningfully.

Experimental Section

Measurements. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker AM-500 or AM-300, a Varian XL-400, or an IBM Instrument NR-250/AF or NR-200/AF spectrometer in deuteriochloroform (CDCl$_3$). ^{19}F chemical shifts measured in CDCl$_3$ are expressed in parts per million relative to CFCl$_3$ (external or internal standard). IR spectra were recorded on an IBM IR/32 spectrometer. Gas chromatographic analysis was made on a Hewlett-Packard 5890A chromatography equipped with a methylsilicone capillary column. High-resolution mass spectroscopic analysis (HRMS) was carried out by Shrader Laboratories, Detroit, MI. Combustion analysis was performed by Galbraith Laboratories, Knoxville, TN.

Materials. TFMST was prepared according to the procedure of Tarrant and Taylor,[23] as previously described.[8] Organolithium and organomagnesium reagents were purchased from Aldrich Chemical Co. and titrated with 2,5-dimethoxybenzyl alcohol[24] or *N*-phenyl-1-naphthylamine[25] immediately before use. 9-Fluorenyllithium,[26] -sodium,[27] and -potassium[28] as well as (1,1-diphenylhexyl)lithium[29] were prepared according to the literature. Potassium *tert*-butoxide, 18-crown-6 (recrystallized from hexanes), and LAH were purchased from Alfa. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone ketyl.

Attempted Anionic Polymerization. Anionic polymerization of TFMST with several initiators were carried out under high vacuum with use of a break-seal technique. Both housemade (*n*-BuLi, PhMgBr) and commercial initiators were used. After termination by adding methanol, reaction mixtures were poured into methanol or hexane without much precipitation.

Typical Procedure of Reaction between TFMST and Anionic Initiator. A flame-dried 25-mL round-bottomed flask was charged with TFMST (0.5 g, 3.1 mmol) in THF (5 mL). The solution was cooled to −78 °C and treated with 1.4 mL of 2.3 M solution of *n*-BuLi (3.2 mmol). The reaction was followed by GC analysis until less than 10% of the starting monomer remained (or until there was no change in the product distribution). The reaction was quenched with 10% HCl and washed with hexanes. The organic layer was separated and washed with water (2 × 25 mL) and brine (30 mL). The organic extract was dried over magnesium sulfate and concentrated to give 0.4 g of crude reaction mixture. Flash chromatography (silica gel, hexanes/ethyl acetate) allowed isolation of major products, which were then spectroscopically identified.

1,1-Difluoro-2,4,4-triphenyl-1-nonene: ^{1}H NMR (250 MHz) δ 7.25–7.24 (m, 15 H), 3.30 (b s, 2 H), 1.90–1.87 (m, 2 H), 1.08–0.72 (m, 9 H); ^{13}C NMR (62.9 MHz) δ 154.5 (t, J_{CF} = 289 Hz), 135.2, 128.7, 128.2, 128.1, 127.7, 126.9, 125.9, 90.5 (dd, J_{CF} = 19.0, 15.0 Hz), 50.8, 37.6, 35.8, 32.3, 24.0, 22.6, 14.2; $^{1\,9}$F NMR (188.3 MHz) δ −89.6 (d, J_{FF} = 37.4 Hz), −91.2 (d, J_{FF} = 37.2 Hz); IR (film) 3080, 3052, 3017, 2958, 2930, 2870, 1736, 1597, 1500, 1448, 1244, 1125, 769, 733, 705 cm^{-1}; HRMS calcd for $C_{18}H_{24}$ ($m^{\bullet +} - C_9H_7F_2$) *m/e* 237.1622, *m/e* 237.1635.

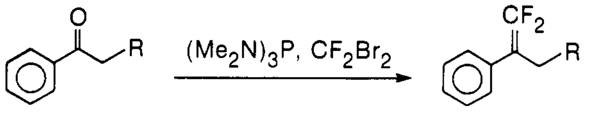
9*H*-9-(3,3-Difluoro-2-phenyl-2-propylidene)fluorene: mp 69–71 °C; ^{1}H NMR (250 MHz) δ 7.89–7.13 (m, 13 H), 3.98 (t, J = 7.1 Hz), 3.13–2.92 (m, 2 H); ^{13}C NMR (62.9 MHz) δ 154.2 (t, J_{CF} = 287 Hz), 146.4, 140.8, 133.2 (t, J_{CF} = 3.3 Hz), 128.7, 128.5 (t, J_{CF} = 3.1 Hz), 127.6, 127.3, 127.0, 124.5, 119.8, 91.1 (dd, J_{CF} = 20.0, 13.0 Hz), 44.7, 32.2; ^{19}F NMR (188.3 MHz) δ −89.0 (d, J_{FF} = 39.0 Hz), −89.9 (d, J_{FF} = 39.1 Hz); IR (KBr) 3070, 3019, 2962, 1741, 1727, 1500, 1452, 1297, 1238, 1122, 983, 781, 742, 706 cm^{-1}. Anal. Calcd for $C_{22}H_{16}F_2$: C, 83.00; H, 5.07; F, 11.94. Found: C, 81.65; H, 5.16; F, 12.08.

9,9-Bis(3,3-difluoro-2-phenyl-2-propylidene)fluorene: mp 120–122 °C; ^{1}H NMR (250 MHz) δ 7.52–6.58 (m, 18 H), 3.13–3.11 (m, 4 H); ^{13}C NMR (62.9 MHz) δ 153.9 (t, J_{CF} = 289 Hz), 146.8, 140.9, 133.9, 128.1, 128.08, 127.5, 127.1, 126.5, 126.2, 124.5, 119.0, 89.8 (dd, J_{CF} = 20.0, 16.5 Hz), 55.2, 37.8; ^{19}F NMR (188.3 MHz) δ −89.2 (d, J_{FF} = 38.4 Hz), −91.8 (d, J_{FF} = 38.4 Hz); IR (KBr) 3070, 3028, 1734, 1500, 1455, 1239, 1125, 920, 767, 745, 705 cm^{-1}. Anal. Calcd for $C_{31}H_{22}F_4$: C, 79.13; H, 4.71; F, 16.15. Found: C, 78.94; H, 4.63; F, 16.24.

1-Fluoro-1,2,3-triphenylpropene (*E*/*Z* mixture): mp 117–119 °C; ^{1}H NMR (400 MHz) δ 7.56–7.12 (m, 15 H), 3.91 (s); ^{13}C NMR (100.6 MHz) δ 156.0, 153.6, 139.14, 139.11, 136.9, 132.9, 132.7, 129.2, 128.85, 128.80, 128.4, 128.3, 128.2, 128.16, 128.1, 127.1, 126.1, 117.8, 117.7, 37.41, 37.39; ^{19}F NMR (376.2 MHz) δ −99.1, −106.1; IR (KBr) 3070, 3031, 1666, 1597, 1503, 1450, 1258, 1097, 1062, 953, 794, 778, 747, 714 cm^{-1}. Anal. Calcd for $C_{21}H_{17}F$: C, 87.47; H, 5.94; F, 6.59. Found: C, 87.28; H, 6.09; F, 6.81.

5-Fluoro-6-phenyl-5-undecene (*E*/*Z* mixture): ^{1}H NMR (400 MHz) δ 7.32–7.13 (m, 5 H), 2.41–2.29 (m, 2 H), 2.10–2.07 (m, 1 H), 1.56–1.26 (m, 1 H), 0.97–0.80 (m, 6 H); ^{19}F NMR (376.2 MHz) δ −111.8 (t, J_{HF} = 22.9 Hz), −108.3 (t, J_{HF} = 22.9 Hz); IR (film)

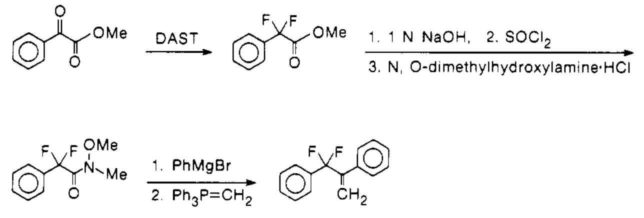
Scheme III
Authentic Synthesis of *gem*-Difluoroolefins (II)



II

R = Et, Bu, Ph

Scheme IV
Authentic Synthesis of S_N2 Product V



V

3064, 3025, 2966, 2933, 2867, 1683, 1498, 1465, 1219, 1175, 903, 769, 706 cm^{-1}; HRMS calcd for $C_{17}H_{25}F$ m/e 248.1928, m/e 248.1936 ($m^{\bullet+}$).

Authentic Synthesis of *gem*-Difluoroolefins (II). The *gem*-difluoroolefins were separately synthesized from aryl ketones by using the procedure of Burton[30] (Scheme III). Spectroscopic data of the authentic difluoroolefins thus prepared are shown below.

1,1-Difluoro-2,3-diphenyl-1-propene: ^{1}H NMR (400 MHz) δ 7.29–7.14 (m, 10 H), 3.72 (t, J = 2.2 Hz); ^{13}C NMR (100.6 MHz) δ 154.3 (t, J_{CF} = 290 Hz), 138.4, 133.5, 128.5, 128.3, 128.2 (t, J_{CF} = 4.3 Hz), 127.2, 126.4, 91.7 (dd, J_{CF} = 21.1, 14.5 Hz), 33.9; ^{19}F NMR (376.2 MHz) δ -90.9 (d, J_{FF} = 39.7 Hz), -91.4 (d, J_{FF} = 39.7 Hz); IR (film) 3086, 3062, 3033, 2928, 1734, 1603, 1495, 1453, 1247, 1019, 1000, 920, 744, 703 cm^{-1}; HRMS calcd for $C_{15}H_{12}F_2$ m/e 230.0876, m/e 230.0891 ($m^{\bullet+}$).

1,1-Difluoro-2-phenyl-1-pentene: ^{1}H NMR (400 MHz) δ 7.36–7.24 (m, 5 H), 2.39–2.34 (m, 2 H), 1.43–1.34 (m, 2 H), 0.89 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (100.6 MHz) δ 153.7 (t, J_{CF} = 292 Hz), 133.9, 128.4, 128.2 (t, J_{CF} = 2.1 Hz), 127.1, 92.1 (dd, J_{CF} = 20.1, 13.9 Hz), 29.6, 20.9, 13.4; ^{19}F NMR (470.6 MHz) δ -92.6 (d, J_{FF} = 45.1 Hz), -92.7 (d, J_{FF} = 45.2 Hz); IR (film) 3055, 3016, 2969, 2938, 2875, 1734, 1498, 1450, 1308, 1247, 951, 762, 700 cm^{-1}; HRMS calcd for $C_{11}H_{12}F_2$ m/e 182.0875, m/e 182.0890 ($m^{\bullet+}$).

1,1-Difluoro-2-phenyl-1-heptene: ^{1}H NMR (400 MHz) δ 7.35–7.20 (m, 5 H), 2.40–2.35 (m, 2 H), 1.37–1.24 (m, 6 H), 0.85 (t, J = 6.9 Hz, 3 H); ^{13}C NMR (100.6 MHz) δ 153.6 (t, J_{CF} = 290 Hz), 134.0, 128.4, 128.3, (t, J_{CF} = 2.2 Hz), 127.1, 92.8 (dd, J_{CF} = 19.0, 15.4 Hz), 31.2, 27.7, 27.4, 22.3, 13.9; ^{19}F NMR (376.2 MHz) δ -92.7 (s); IR (film) 3055, 3023, 2956, 2930, 2861, 1734, 1502, 1453, 1309, 1242, 1141, 928, 773, 703 cm^{-1}; HRMS calcd for $C_{13}H_{16}F_2$ m/e 210.1196, m/e 210.1209 ($m^{\bullet+}$).

Authentic Preparation of 3,3-Difluoro-2,3-diphenyl-1-propene (V). The authentic synthesis was accomplished according to Scheme IV. Treatment of methyl benzoylformate with (diethylamino)sulfur trifluoride (DAST)[31] gave the methyl α,α-difluorophenylacetate in 76% yield. Hydrolysis of the ester followed by the procedure of Weinreb[32] gave the *N*,*O*-dimethylhydroxylamide in overall yield of 62%. Subsequent addition of PhMgBr followed by the Wittig reaction gave the desired product in 21% yield: ^{1}H NMR (250 MHz) δ 7.67–7.20 (m, 10 H), 5.81 (d, J = 17.7 Hz, 1 H), 5.40 (d, J = 11.1 Hz, 1 H); ^{13}C NMR (62.9 MHz) δ 145.5 (t, J_{CF} = 26.4 Hz), 134.2 (t, J_{CF} = 24.2 Hz), 129.7, 128.3, 128.2, 128.1, 125.9, (t, J_{CF} = 5.8 Hz), 122.4 (q, J_{CF} = 246 Hz), 119.3 (t, J_{CF} = 4.1 Hz); IR (film) 3058, 3031, 1498, 1456, 1264, 1247, 1152, 1044, 1003, 950, 783, 708 cm^{-1}; HRMS calcd for $C_{15}H_{12}F_2$ m/e 230.0928, m/e 230.0918 ($m^{\bullet+}$).

Authentic Preparation of Monofluoroolefins (IV). The authentic *gem*-difluoroolefins prepared as above were treated with an excess of *n*-BuLi, PhLi, or PhMgBr in THF.

1-Fluoro-1,2,3-triphenylpropene (*E*/*Z* mixture): ^{19}F NMR (282.4 MHz) δ -99.4 (s, *E*), -106.3 (t, J_{HF} = 3.1–3.4 Hz, *Z*).

3-Fluoro-1,2-diphenyl-2-heptene (*E*/*Z* mixture): ^{19}F NMR (282.4 MHz) δ -106.3 (t, J_{HF} = 23.4–23.7 Hz, *E*), -110.1 (tt, J_{HF} = 23.0, 2.5 Hz, *Z*).

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Registry No. TFMST, 384-64-5; II (R = Ph), 116635-32-6; II (R = Et), 83567-85-5; II (R = Bu), 116635-33-7; V, 116635-34-8; BuLi, 109-72-8; KOBu-*t*, 865-47-4; PhMgBr, 100-58-3; EtMgBr, 925-90-6; $LiAlH_4$, 16853-85-3; PhLi, 591-51-5; DPHLi, 3462-81-5; FlNa, 3531-83-7; FlK, 7307-10-0; FlLi, 881-04-9; Na, 3481-12-7; 18-crown-6, 17455-13-9; 1,1-difluoro-2,4,4-triphenyl-1-nonene, 116635-27-9; 9*H*-9-3,3-difluoro-2-phenyl-2-propylidenefluorene, 116635-28-0; 9,9-bis(3,3-difluoro-2-phenyl-2-propylidene)fluorene, 116635-29-1; 1-fluoro-1,2,3-triphenylpropene, 116635-30-4; 5-fluoro-6-phenyl-5-undecene, 116635-31-5; 3-fluoro-1,2-diphenyl-2-heptene, 116635-35-9.

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