Journal of Fluorine Chemistry 130 (2009) 474–483

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

On the isolation of neat allylic fluorides

Eunsung Lee, Dmitry V. Yandulov *

Department of Chemistry, Stanford University, Stanford, CA 94305-5080, United States

A R T I C L E I N F O

Article history:
Received 23 January 2009
Received in revised form 12 February 2009
Accepted 13 February 2009
Available online 3 March 2009

Keywords:
Cinnamyl fluoride
Geranyl fluoride
Cyclohexenyl fluoride
Allylic fluorides
Glass-mediated decomposition

A B S T R A C T

Neat cinnamyl fluoride, geranyl fluoride, 5-carbomethoxy-3-fluorocyclohexene and parent 3-fluorocyclohexene undergo spontaneous decomposition on contact with borosilicate glass or catalytic quantities of moderately strong acids that consists in polycondensation with elimination of HF initiated by electrophilic abstraction of F^-. Acid sensitivity of these allylic fluorides correlates with stability of respective allylic cations, exceeds that of parent benzyl fluoride, yet can be mitigated by the use of Teflon and PFA containers that permit their isolation and handling in the neat state.

1. Introduction

Organofluorine compounds continue to enjoy diverse applications in areas across the board from materials science to biomedical fields and provide a constant need for the development and improvement of methods of organofluorine synthesis [1]. Allylic fluorides constitute an important class of fluorinated intermediates due to the versatility with which allylic fluoride moiety can be constructed and elaborated on, including asymmetric transformations [2]. Against this background, we were struck to find the essential representatives of allylic fluorides family, viz. cinnamyl fluoride and geranyl fluoride, to suffer spontaneous decomposition in minutes after neat materials are isolated in common laboratory glass containers. We report here such decomposition to bear limiting stoichiometry of dehydrofluorination, present evidence of acid-catalyzed polycondensation and offer simple solutions to isolation and handling of small quantities of such materials, including parent and substituted cyclohexenyl fluorides.

2. Results and discussion

Notwithstanding several reported preparations of cinnamyl fluoride (**1**) [3,21] and geranyl fluoride (**2**) [3b,4] listing isolated yields, in our hands colorless, mobile liquids obtained initially upon distillation of these allylic fluorides within an hour inevitably converted to gelatinous forms of variable coloration, with complete transformation taking seconds after a sudden onset and resulting in etching of the borosilicate glass container. We were fortunate to find containers made of soda lime glass to impart sufficient stability to neat **1** and this allowed us to sample common laboratory materials for compatibility with **1**, attempt to identify the cause of the observed decomposition and seek means to prevent it. Fig. 1 summarizes the results of materials compatibility screen (Table 1). Without exception, neat **1** decomposed on contact with all borosilicate glass containers examined at RT under N_2, albeit over irreproducible times in any given material (average of six runs exceeded three standard deviations in only one case). Contrasting behavior of soda lime glass, which contains minimal amount of B_2O_3 and has not once been seen to cause decomposition of **1** at RT under N_2, suggested Lewis-acidic surface sites, such as three-coordinate boron [5], to be responsible for the unexpected reactivity. According to ^{1}H and ^{19}F NMR (Fig. 2), the gelatinous decomposition residues formed from neat **1** on contact with borosilicate glass at RT under N_2 contained significant amounts of organofluorine compounds devoid of **1** and dominated by dimers **3**, **3′** (Chart 1, *dr* = 80:20, >40% of organic F). The latter were isolated in 38% combined yield from similar mixtures formed in two analogous runs from neat **1** in a PFA container over several days at RT following a brief exposure to air. With connectivities assigned from extensive J_{FH} data, relative configurations of **3** and **3′** were assigned by correlating greater relative shielding of $C(3)H_2$ and $C(F)H_2$ protons observed in the ^{1}H NMR spectra of **3** and **3′**, respectively, to the proximity of C(5)Ph ring in the dominant staggered conformation around C4–C5 bond, identified with reasonable consistency by molecular mechanics and semiempirical methods (Chart 1).

---

* Corresponding author. Tel.: +1 650 725 9651; fax: +1 650 725 0259.
E-mail address: yandulov@stanford.edu (D.V. Yandulov).

0022-1139/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2009.02.012

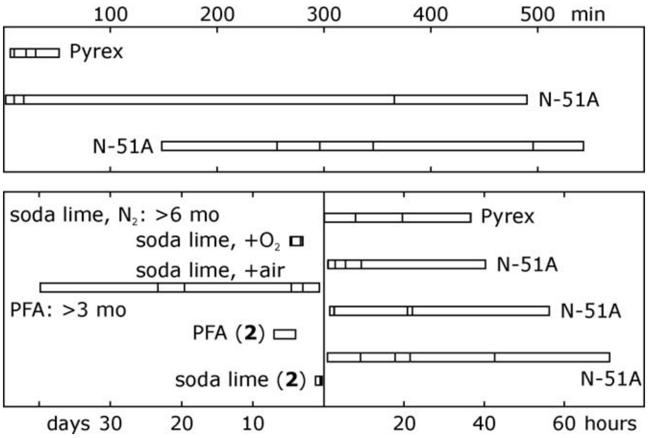


Fig. 1. Stability of neat **1** in eight different glass (Pyrex®, N-51A, soda lime: Table 1) and one PFA container at RT under N$_2$, unless otherwise indicated. Each horizontal bar spans the range of times to decomposition onset observed in six individual runs with the same material (3 for **2** in PFA) and marked with vertical bars.

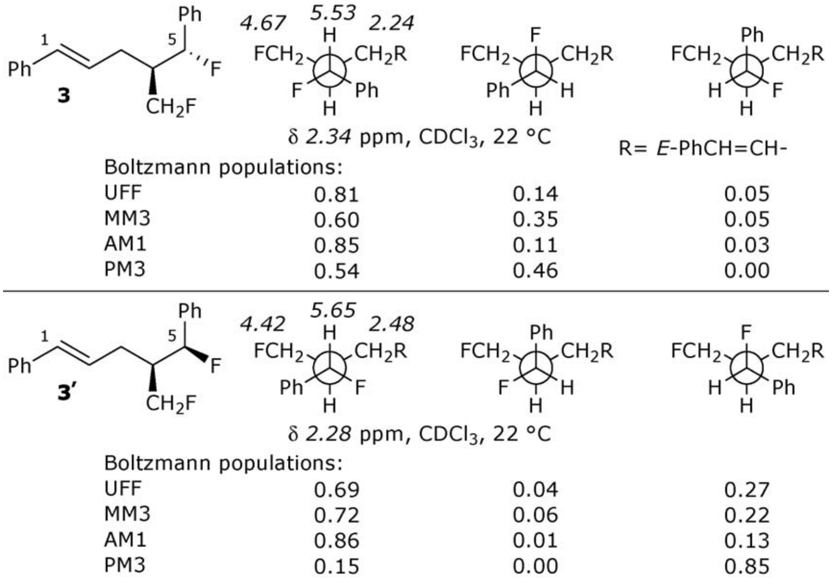
Table 1
Nominal composition of glasses (w/w, %) tested in Fig. 1.

	Soda lime[a]	Kimax® N-51A	Pyrex® 7740
SiO$_2$	68.7	72	81
B$_2$O$_3$	<0.02	12	13
Na$_2$O	13.3	6	4
Al$_2$O$_3$	2.7	7	2
K$_2$O	3.0	2	
CaO	10.1[b]	1	
BaO	2.0		

[a] Composition quoted for the specific material tested.

[b] CaO + MgO.

The reactivity of **1** was examined more closely in solution (Table 2). Thermally stable and resistant to bases, **1** reacted with catalytic quantities of various Brønsted and Lewis acids to yield product mixtures resembling those obtained from neat **1** by ^{1}H and ^{19}F NMR (Fig. 2) and featuring **3** in 40:60–100:0 *dr* [6] and up to 37% yield at full conversion. Activity of Brønsted acids, gauged qualitatively by the time to complete conversion, generally



Boltzmann populations:

UFF	0.81	0.14	0.05
MM3	0.60	0.35	0.05
AM1	0.85	0.11	0.03
PM3	0.54	0.46	0.00

Boltzmann populations:

UFF	0.69	0.04	0.27
MM3	0.72	0.06	0.22
AM1	0.86	0.01	0.13
PM3	0.15	0.00	0.85

Chart 1.

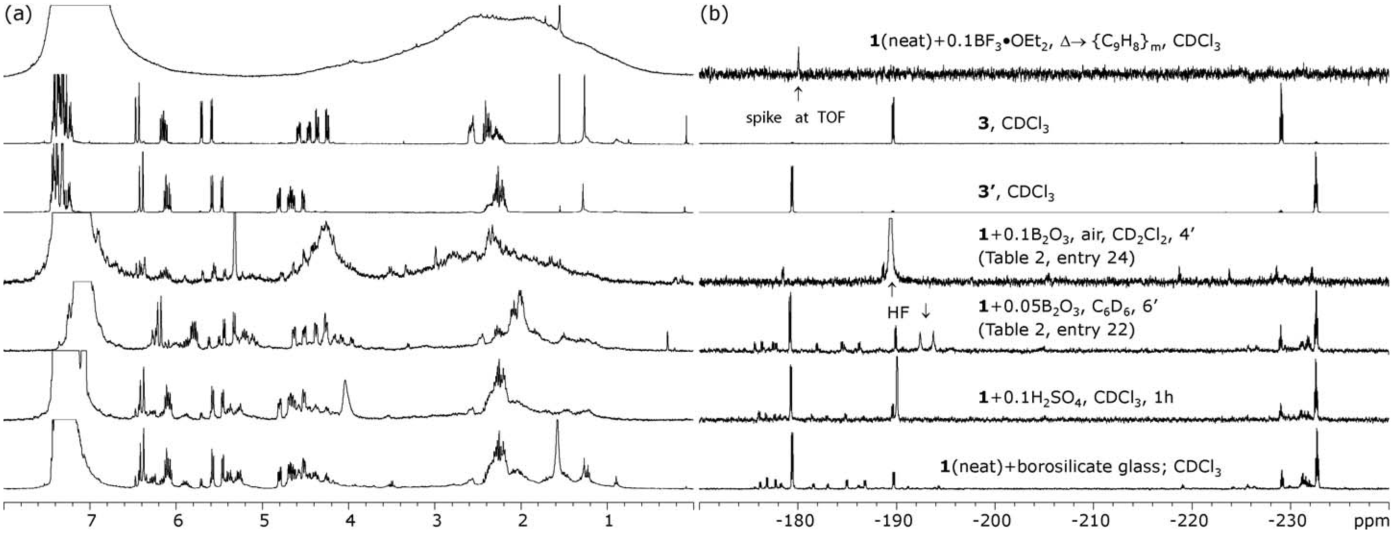


Fig. 2. (a) ^{1}H (400 MHz, 22 °C) and (b) ^{19}F (376 MHz, 22 °C) NMR spectra of the products of acid-catalyzed decomposition of **1**.

Table 2
NMR-tube reactivity of **1**[a].

Entry	Conditions[b]	Added reagent, *T* (°C)	Time	Conv. %	Inorg. F^-[c]	Org. F^-[d]	Other products identified[e]
1	B, C, 30, P	–[f]	44 h	<10	–	–	–
2	B, C, 30, P	–, +60	24 h	100	−157, −163	–	–
3	B, C, 50, T	–, +60	60 h	<10	–	–	–
4	S, 30, P	–, +145	18 h	<10	–	–	–
5	S, 45, P	4 CsF, +100	24 h	70	–	–	H/D exch. (70)[g]
6	S, 15, P	4 KOAc, +145	38 h	49	–	–	**4** (37)
7	D, 80, T	1.7 {HF}[h], +45	98 h	52	HF + HF_2^- (168), BF_4^- (179)	78:22 (29); (9)	–
8	D, 50, T	0.1 H_3PO_4[i]	51 h	100	−71, −73, −169, HF (28)	82:18 (12); (14)	
9	D, 60, T	0.1 TFA	26 h	96	HF (33)	83:17 (23); (10)	**5** (11)
10	D, 10, T	1.3 TFA	90 min	94	HF (83)	100:0 (12)	**5** (66)
11	D, 50, T	1.2 TFA	15 min	100	HF (81)	100:0 (12); (9)	**5** (37)
12	D, 60, T	0.1 HNO_3[j]	20 h	87	HF (42)	100:0 (15); (15)	**6** (3)
13	D, 60, P	0.1 HNO_3	15 min	100	−149, −150, −161 (47)	64:36 (7); (6)	**6** (tr.)
14	D, 50, T	1.3 HNO_3	6 h	95	HF (91)	–	**6** (75)
15	D, 50, P	1.1 HNO_3	70 min	99	−128, −149, −156, −161 (63)	100:0 (3); (12)	**6** (18)
16	D, 50, T	0.1 H_2SO_4[k]	25 min	98	HF (54)	82:18 (19); (14)	
17	D, 50, T	0.4 H_2SO_4	5 min	100	−171 (4), HF (58)	–; (9)	
18	D, 50, T	0.3 BHT, 0.1 H_2SO_4, air	1 h	100	−130 (10), HF (41)	100:0 (13); (19)	
19	D, 60, T	0.1 HOTf	3 min	100	HF (77)	–; (12)	
20	B, 100, T	0.05 B_2O_3	10 min	100	HF (13)	69:31 (37); (36)	
21	D, 50, T	0.1 B_2O_3	8 min	100	−148, −151 (7), HF (46)	62:38 (10); (10)	
22	D, 50, T	0.1 B_2O_3, air	8 min	100	−148, −151 (11), HF (43)	47:53 (9); (9)	
23	S, 90, T	0.1 B_2O_3, +60	24 h	<10	–	–	–
24	B, 50, P	$B_2O_3{\cdot}n Na_2O$[l]	91 h	<10	–	100:0 (2)	
25	D, 50, T	0.1 TMSOTf	10 min	100	HF (37), −157 (2)	78:22 (18); (15)	
26	D, 50, T	0.1 $BF_3{\cdot}OEt_2$	5 min	100	HF (51), BF_4^- (17)	59:41 (26); (20)	
27	B, 25, P	0.1 AgOTf	96 h	<10	–		
28	B, 50, T	1.0 **6** or **5**	21 h	<10	–	–	–

[a] All reactions at 22 °C under N_2 unless otherwise noted (**4**: cinnamyl acetate, **5**: cinnamyl trifluoroacetate, **6**: cinnamyl nitrate).

[b] Solvent (B = C_6D_6, C = $CDCl_3$, D = CD_2Cl_2, S = d_6-Me_2SO), mM **1**, NMR tube (P = Pyrex, T = Teflon insert).

[c] ^{19}F NMR chemical shifts of unidentified inorganic fluoride products observed between δ −71 and −195 ppm and assigned collectively to BF_3, SiF_4, PF_5 and F^- derivatives such as $BF_3{\cdot}H_2O$, BF_4^-, $SiF_4(H_2O)_n$, SiF_6^{2-}, HPO_3F^-, HF_2^-, $HF{\cdot}nH_2O$ and $F^-{\cdot}nH_2O$, with individual or combined ^{19}F NMR integrals in percent of that of initial **1** shown in parentheses (mol% yield of fluorine-containing products of **1**). HF was identified as a singlet at ^{19}F NMR δ −185 to −195 ppm and BF_4^- was identified by the presence of the minor ^{10}B isotopomer peak 0.05 ppm downfield from the ^{19}F NMR singlet at $\delta \sim -151$ ppm.

[d] **3** *dr* (mol% yield from initial **1** by ^{19}F NMR integration); (all other ^{19}F signals, mol% yield from initial **1** by ^{19}F NMR integration).

[e] mol% yield from initial **1** by ^1H NMR integration.

[f] None added/observed.

[g] *E*-PhCH = CH{H_nD_{2-n}}, $n = 1$ (50%), $n = 0$ (20%).

[h] 1.8[Bu_4N]HF_2 + 1.7$BF_3{\cdot}OEt_2$.

[i] 85 wt.% aq.

[j] 70 wt.% aq.

[k] 96 wt.% aq.

[l] 0.4 $NaBO_2{\cdot}4H_2O$ or 0.5 $Na_2B_4O_7{\cdot}10H_2O$.

correlated with their aqueous acidity and concentration. Inactivation of B_2O_3, exceedingly effective in non-coordinating media, by d_6-Me_2SO confirmed assignment of the acid function mediating decomposition of neat **1** to three-coordinate boron oxo sites on the surface of borosilicate glass [5,7]. Lack of inhibition by atmospheric oxygen and BHT [8] provided evidence against participation of radical intermediates in the acid-mediated solution decomposition of **1**. Dioxygen-triggered decomposition of neat **1** in soda lime glass (Fig. 1) and PFA may thus signify formation of acidic initiators by oxidative processes. All solution reactions of **1** with acids formed HF [9], in 13–91% yield with the total ^{19}F NMR mass balance of 54–102% [10] (Table 2). Accelerated decomposition of **1** by acids in solutions contained in glass tubes compared to Teflon inserts (entries 12–15) therefore stems from autocatalytic formation of H_2SiF_6 and $BF_3{\cdot}nOH_2$, both stronger acids than dilute HF [11], in reaction of HF with borosilicate glass [12]. Substitution of F^- with TFA and NO_3^-, effected in good yields with stoichiometric TFA and HNO_3, constitutes a side reactivity in the acid-catalyzed decomposition of **1**, as the yields of cinnamyl trifluoroacetate (**5**) and cinnamyl nitrate (**6**) did not correlate with rates of conversion of **1** and both were inert to **1** and B_2O_3 (Table 3).

Dimers **3**, observed almost invariably at complete conversion of **1** with catalytic acids in yields of up to 37% (Table 2), reacted further in the original reaction mixtures with formation and decay of other aliphatic fluoride intermediates in ^{19}F NMR (Fig. 3) and progressive loss of structured signals from ^1H NMR spectra. The aging occurred faster with use of stronger acids and heat and apparently precluded observation of **3** at complete conversion of **1** in the few rapid reactions with strong Brønsted acids (Table 2). Treatment of neat **1** with 0.1 equiv. $BF_3{\cdot}OEt_2$ at >100 °C followed by drying gave a yellow solid devoid of sharp ^1H NMR features and ^{19}F NMR signals (Fig. 2) that analyzed for elemental composition $\{C_9H_8\}_m$, was obtained in 89% yield and showed oligomeric peaks of four to ten C_9H_8 unit masses in ESI-MS (Fig. 4a). These results establish polycondensation with loss of HF as the limiting stoichiometry of acid-catalyzed decomposition of **1**.

Problems of instability of allylic fluorides have a sparse literature record [2e,g,13-15]. Evidently, only Hammond et al. observed **1** isolated in a round bottom flask to undergo "…gradual decomposition to a gelatinous solid… upon standing at room temperature" [3c]. Closest analogies to the observed behavior of **1** are found in the early studies of benzylic fluorides. The original report of synthesis and characterization of parent benzyl fluoride by Ingold and Ingold describes its autocatalytic dehydrofluorination to an opaque white glass of high molecular weight and composition $\{C_7H_6\}_n$ that can be initiated by concentrated H_2SO_4, HF, surface of only certain glass and "…may develop with almost explosive violence" [16a]. Subsequent studies by Miller and Swain revealed stabilizing influence of electron-withdrawing ring substituents in benzylic fluorides, utility of basic additives as chemical

Table 3
NMR-tube reactivity of other allylic derivatives[a].

Entry	Allyl-X	Conditions[b]	Added reagent, *T* (°C)	Time	Conv. %	Org. & inorg. F^- (% yield)[c]	Other products (% yield)
1	**6**	B, 20, P	0.1 B_2O_3	58 h	<10	–[d]	–
2	**5**	B, 30, P	0.1 B_2O_3	58 h	<10	–	–
3	**2**	C, 20, P	–	30 min	100	−147, −149, −161	**12**, α-terpinene, γ-terpinene, terpinolene
4		B, 20, P	–, +60	24 h	100	−161, −166	α-terpinene (42), γ-terpinene (12), terpinolene (tr.)
5		S, 20, P	–, +60	36 h	<10	–	–
6		C, 50, T	–, +60	195 h	90		**11** (60), **12** (12)
				445 h	100		**12** (60), α-terpinene (9), 4-fluoro-*p*-menth-1-ene (2)
7		B, 60, T	–, +60	24 h	100	−170 (3), HF (5)	**11** (10), **12** (59), α-terpinene (10), terpinolene (6)
8		B, 40, T	0.1 CsF, +60	24 h	<10	–	–
9	**7**	C, 70, P	–	20 min	100	−150 to −162 (23)	**14** (65)
10		S, 40, P	–	26 h	<10		
11		B, C, 20, T	–, +60	24 h	<10	–	–
12		B, 80, P	0.15 2,6-lutidine	30 min	<10	–	–
13	**13**	C, 90, P	–	25 h	<10	–	–
			–, +50	4 h	100	−152, −156, −161 (15)	**16** (21%), **15** (67)
14		B, 70, T	–, +60	59 h	<10	–	–

[a] All reactions at 22 °C under N_2 unless otherwise noted. Numbered structures are shown in Schemes 1 and 2.

[b] Solvent (B = C_6D_6, C = $CDCl_3$, D = CD_2Cl_2, S = d_6-Me_2SO), mM **1**, NMR tube (P = Pyrex, T = Teflon insert).

[c] ^{19}F NMR chemical shifts of unidentified organic and inorganic fluoride products, latter observed between δ −129 and −195 ppm and assigned collectively to BF_3, SiF_4 and F^- derivatives such as $BF_3{\cdot}H_2O$, BF_4^-, $SiF_4(H_2O)_n$, SiF_6^{2-}, HF_2^-, $HF{\cdot}nH_2O$ and $F^-{\cdot}nH_2O$, with individual or combined ^{19}F NMR integrals in percent of that of initial **1** shown in parentheses (mol% yield of fluorine-containing products of **1**). HF was identified as a singlet at ^{19}F NMR δ −185 to −195 ppm.

[d] None added/observed.

stabilizers and positive effects of strictly anhydrous conditions and scratch-free, fire-polished glassware in handling such compounds [16b,c]. The sudden nature of glass-mediated decomposition of BnF on storage was highlighted more recently in a safety alert of an explosive incident [16d] and decomposition residue of neat BnF was likened to hyperbranched polymers well known to result from Friedel–Crafts condensation of heavier benzylic halides or alcohol [17].

Related to the behavior of BnF, the overall acid-catalyzed decomposition of **1** is proposed to follow a series of basic steps shown in Scheme 1. The observed products of allylic substitution (**5**, **6**) and regioselectivity of dimerization to **3** signify electrophilic activation of **1** at the allylic, as opposed to olefinic [18], position and formation of anion-stabilized cinnamyl cation $\mathbf{8}^+$ as a reactive intermediate. Acid-mediated fluoride abstraction proposed for **1** finds ample precedent in solvolysis of 1°-, 2°-, 3°-alkyl fluorides, Ph_3CF, BnF, BzF, a fluorinated allylic fluoride [19,16c], and engenders fluorides with the highest Friedel–Crafts alkylation reactivity of aliphatic halides in general [18]. Thus, **3** results from regioselective addition of $\mathbf{8}^+$ to **1** and trapping of the resulting benzylic $\mathbf{9}^+$ with F^-. The allylic and benzylic carbocations so formed can further lead to oligomeric products via a combination of cationic addition polymerization (**CA**), and Friedel-Crafts polycondensation pathways with aromatic (**AC**) or olefinic substitution (**OC**). Because **CA** faces greater steric hindrance to C–C bond formation [20] than do both polycondensation pathways and since benzylic carbocations alkylate olefins with good regioselectivity to aromatic substitution, e.g., in styrene [21,18], we consider **OC** to be the favored pathway by which acid-catalyzed dehydrofluorination of **1** takes place. This pathway is well suited for rapid formation of higher oligomers, since acid lability of the condensation dimer **10** is enhanced relative to that of its precursor **1** by electron-donating β-substitution [21a].

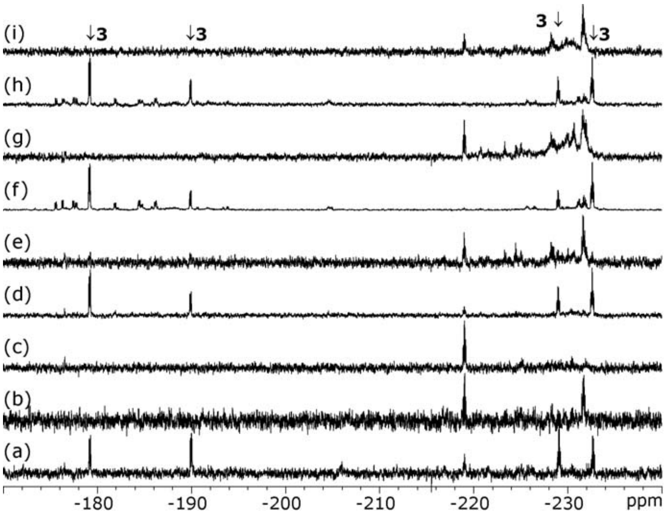


Fig. 3. ^{19}F NMR spectra (376 MHz, 22 °C) showing aging of the initial products of decomposition of **1** (30–50 mM, C_6D_6, Pyrex® NMR tubes) formed in the following reactions: **1** + 0.1 $BF_3{\cdot}OEt_2$, RT, 8 min (a), RT, 5 h 20 min (b), +100 °C, 24 h (c); **1** + 0.1 TMSOTf, RT, 15 min (d), RT, 7 h 30 min (e); **1** + 0.1 B_2O_3, RT, 8 min (f), RT, 9 h (g); **1** + 0.1 TFA, RT, 7 h 30 min (h), RT, 3d 19 h (i). Signals of **3** and **3′** are marked with arrows.

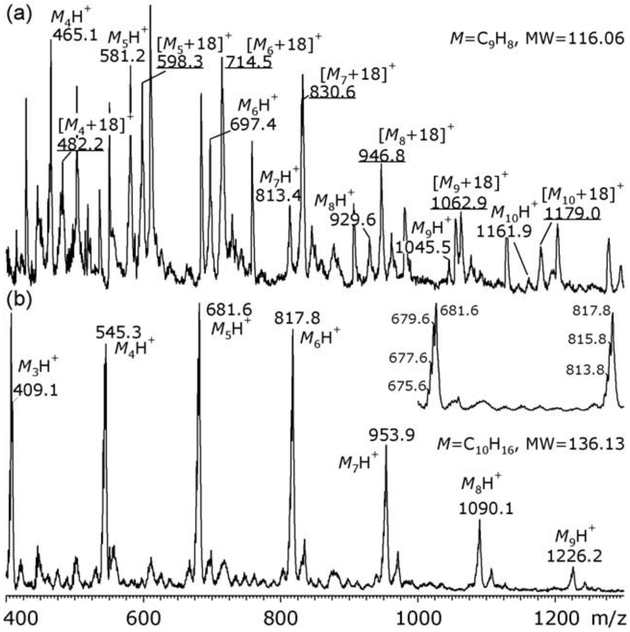
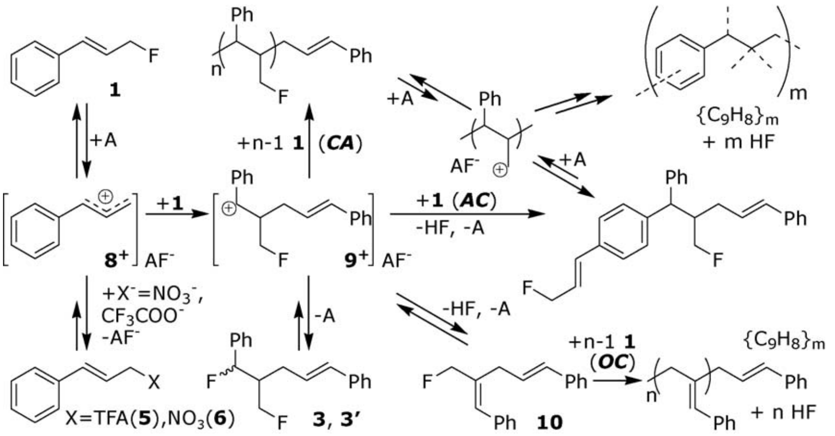


Fig. 4. ESI-MS spectra of the products of complete dehydrofluorination of (a) **1** ($\{C_9H_8\}_m$, THF:MeOH 1:1, satd. NH_4Cl) and (b) **2** ($\{C_{10}H_{16}\}_m$, THF:MeOH 1:2).



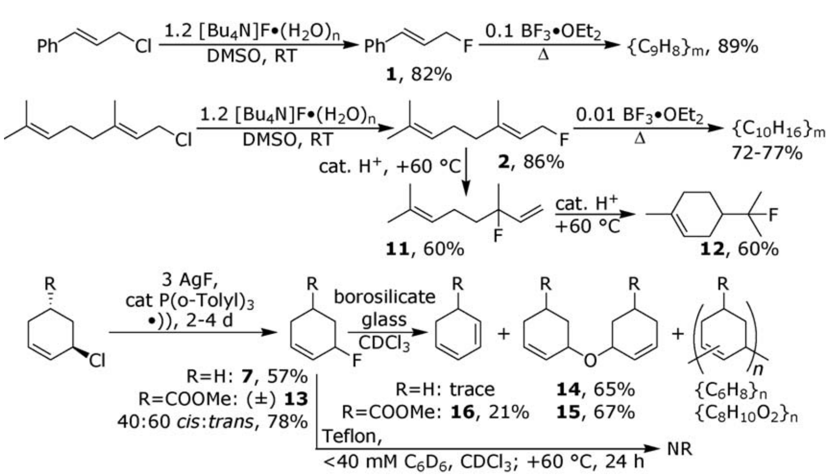
Scheme 1. Mechanism of acid-catalyzed decomposition of **1**.

Acid lability of **1** is greater than that of BnF, which can be nitrated [16a] (cf. Table 2). This enables **3** to persist past full conversion of **1** in most cases before reacting more slowly at the benzylic fluoride during the aging phase, via the intermediacy of $\mathbf{9}^+$ [6]. Most resistant to acids, unactivated aliphatic fluorides (^{19}F NMR $\delta < -220$ ppm) disappear last from **1**/acid reaction mixtures on extended aging (Fig. 3), via, e.g., Friedel–Crafts electrophilic activation (Scheme 1). Although the structure of the final, dehydrofluorinated oligomeric material $\{C_9H_8\}_m$ is not known, pathways available for its formation, and subsequent cross-linking, can in principle render each monomer unit connected at one or more of all but the aromatic ipso positions, as schematically shown in Scheme 1.

2.1. Other allylic fluorides

Geranyl fluoride (**2**) exhibits greater sensitivity than does **1** and suffers decomposition (Fig. 1) not only in soda lime glass (6–29 h), but also in PFA containers over 4–7 days at RT, possibly due to the presence or accumulation of trace contaminants. It is nevertheless possible to isolate **2** reproducibly in 86% yield (Scheme 2) by distillation in a Teflon/PFA assembly and store it for months at -35 °C under N_2. Triggering instantaneous decomposition of **2** in pentane solution or neat with 0.01 equiv. $BF_3{\cdot}OEt_2$ followed by heating of the initial decomposition products at $>$100 °C and vacuum-drying produced yellow to purple solids devoid of sharp ^{1}H NMR features and ^{19}F NMR signals that analyzed for elemental composition $\{C_{10}H_{16}\}_m$, were obtained in 71–77% yield and showed oligomeric peaks of three to nine $C_{10}H_{16}$ unit masses in ESI-MS (Fig. 4b). As for **1**, these results establish polycondensation with loss of HF as the limiting stoichiometry of acid-catalyzed decomposition of **2**, which we presume to stem from analogous acid-mediated fluoride abstraction and involve several intramolecular elimination and cyclization routes [22] in addition to pathways outlined for **1** in Scheme 1. Without added reagents in 50 mM $CDCl_3$ solution in a Teflon insert at +60 °C, **2** undergoes isomerization to linaloyl fluoride (**11**) followed by cyclization to α-terpinyl fluoride (**12**) in good yields (Scheme 2). The isomerization of **2** is analogous to that of respective alcohols [22b] and is catalyzed by adventitious acid, as evidenced by inhibition by CsF (Table 3).

3-Fluorocyclohexene (**7**) [15] and its novel derivative **13** were prepared from respective chlorides by halide exchange with AgF and isolated in good yields with help of Teflon/PFA equipment (Scheme 2). In agreement with previous reports, **7** is remarkably intolerant of borosilicate glass, however can be maintained without significant decomposition in 20 mM C_6D_6 or $CDCl_3$ solutions in a Teflon insert at +60 °C over 24 h, or 40 mM d_6-Me_2SO solution in a borosilicate NMR tube at RT for 26 h (Table 3). Consistent with electrophilic mode of activation of allylic fluorides to decomposition, the less electron-rich **13** exhibit increased stability to glass. Elimination and hydrolysis account for up to 88% of products formed on decomposition of **7** and **13** on contact with borosilicate glass (Table 3), which include oligomeric cyclohexadienes $\{C_6H_8\}_{5-11}$ and $\{C_8H_{10}O_2\}_{3-14}$ observed by ESI-MS.



Scheme 2. Synthesis and decomposition of allylic fluorides.

3. Conclusions

Some of the simplest known allylic fluorides, including cinnamyl fluoride which lacks aliphatic β-hydrogens, are susceptible to acid-catalyzed elimination of HF that is initiated by electrophilic abstraction of the fluoride with moderately strong Brønsted or Lewis acids and results from polycondensation. Acid sensitivity of cinnamyl fluoride exceeds that of parent benzyl fluoride and is elevated in the other allylic fluorides examined by structural features that stabilize corresponding allylic cations. Lewis acidic sites on the surface of borosilicate glass, such as three-coordinate boron oxo, are particularly effective in promoting such reactivity in neat liquids that therefore are best contained in soda lime glass, Teflon or PFA vessels, refrigerated under N_2, stabilized by mild bases and/or stored in solutions. Allylic cations that result from the loss of F^- undergo addition, elimination, cyclization and hydrolysis by water from etching of silica glass by the evolving HF, which also makes decomposition of neat materials autocatalytic. Although oligomeric materials ultimately dominate organic products of acid-mediated decomposition of allylic fluorides studied here, isolation of addition dimers of cinnamyl fluoride in modest yield suggests that selectivity of electrophilic activation of allylic fluorides may be optimized for olefin carbofluorination [23], as it has been in related transformations [3f,13]. Conversely, mitigation of adventitious acids by resorting to ordinary Teflon/PFA containers permits isolation and handling of such electron-rich allylic fluorides as geranyl fluoride and secondary 5-carbomethoxy-3-fluorocyclohexene and 3-fluorocyclohexene in the neat state.

4. Experimental

4.1. General experimental procedures

All air- and moisture-sensitive manipulations were performed using oven- and flame-dried glassware, standard Schlenk and glovebox techniques under an atmosphere of nitrogen, with solvents dried and deoxygenated by appropriate methods. All starting materials and reagents were obtained from commercial suppliers and used as received unless otherwise stated. *CAUTION: pure neat allylic fluorides described here undergo spontaneous and potentially exothermic polymerization with release of HF on contact with borosilicate glass or traces of acids; stability is imparted under air atmosphere.* ^{1}H, ^{13}C{^{1}H} and ^{19}F NMR spectra were recorded on Varian 400 and 500 MHz spectrometers and referenced to the residual protio solvent peaks (^{1}H: $CDCl_3$, δ 7.27; C_6D_6, δ 7.16; CD_2Cl_2, δ 5.32; $(CD_3)_2SO$, δ 2.49; CD_3CN, δ 1.93 relative to Me_4Si), solvent ^{13}C signals ($CDCl_3$, δ 77.23; C_6D_6, δ 128.39; CD_2Cl_2, δ 54.00; $(CD_3)_2SO$, δ 39.51; relative to Me_4Si), dissolved or external neat PhF (^{19}F, −113.15 ppm relative to $CFCl_3$) or dissolved C_6F_6 (^{19}F, −164.9 ppm relative to $CFCl_3$). Signals are listed in ppm, coupling constants in Hz, and multiplets identified as s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, sx = sextet, sp = septet, m = multiplet, br = broad. Where identified, heteronuclear couplings were confirmed by selective homo- and heteronuclear decoupling, which was also used in ^{1}H and ^{19}F NMR signal assignments of **3**, **3′** and **13**. Complete assignments of ^{1}H and ^{13}C signals of **13** were additionally based on ^{1}H–^{1}H COSY, ^{13}C DEPT and ^{1}H–^{13}C HSQC methods. In situ conversion was quantified by integration of fully relaxed ^{1}H and ^{19}F NMR spectra vs. internal standards; relative integral values are accurate to ±10% in the 2σ sense.

4.2. Tetrabutylammonium fluoride, hydrate $[Bu_4N]F{\cdot}(H_2O)_n$

Material available commercially as a 1 M THF solution or neat semi-solid was dried at RT to solid consistency and recrystallized from dry THF at −35 °C. The resultant white, crystalline solid was collected by filtration, washed with cold THF and dried at RT under <10 mTorr vacuum to constant weight. Material purity and water content were determined by integration of ^{1}H (δ ~5.8 (H_2O) and 3.47 ($N(CH_2C_3H_7)_4^+$)) and ^{19}F (δ ~−110 ($F(H_2O)_n^-$) and −152 (HF_2^-)) NMR spectra recorded in C_6D_6, assuming the material to be a mixture of the only species observed by NMR, $[Bu_4N]F{\cdot}(H_2O)_n$ and $[Bu_4N]HF_2$ [24]. Solid of a typical composition $[Bu_4N]F{\cdot}(H_2O)_2$ (91%, w/w) forms a homogeneous solution in C_6D_6 at 50 mM and although NMR signals of $F^-(H_2O)_n$ and $N(CH_2CH_2CH_2CH_3)_4^+$ may appear as several closely lying peaks due to ion-pairing, depending on the water content, same ^{1}H and ^{19}F NMR integration values are obtained from spectra recorded in d_8-THF that are free from ion-pairing effects.

4.3. Tetrabutylammonium bifluoride $[Bu_4N]HF_2$

$[Bu_4N]F{\cdot}(H_2O)_{2.3}$ (91.3 wt.%, 503 mg, 1.52 mmol) was dried to constant weight at 60 °C under <10 mTorr vacuum (38 h) in a glass container. The resulting colorless oil crystallized on cooling to −35 °C and remained solid at RT. Yield 264 mg (0.94 mmol, 103%). Spectral data are in accord with those of a commercial material.

4.4. [(1E)-3-fluoroprop-1-en-1-yl]benzene (cinnamyl fluoride, **1**)

Cinnamyl chloride (610 mg, 4.00 mmol) was added to Me_2SO (10 mL) solution of $Bu_4NF{\cdot}(H_2O)_{1.7}$ (1.53 g, 93.0 wt.%, 4.87 mmol) in a 20 mL scintillation vial in the glovebox. After stirring for 24 h at RT, the solution was poured to 30 mL of CH_2Cl_2 in a 120 mL separatory funnel, washed with 7× 10 mL of water, dried over $MgSO_4$ and filtered through Celite. The filtrate in a 100 mL RBF was concentrated to ~2 mL (regular borosilicate glassware can be used up to this point) and the solution was transferred to a soda lime glass bottle. The product **1** was distilled at ~30 °C under <10 mTorr vacuum in a soda lime assembly (Fig. 5) and collected as a colorless oil at 0 °C, *d* 1.03 g/mL. Yield 453 mg (3.33 mmol, 83%; repeat synthesis: 81%); this quantity of neat material can be stored over extended periods in a soda lime container under N_2 at −35 °C. Spectral data are in accord with literature values [3b,c,21].

4.5. [(1E)-5-fluoro-4-(fluoromethyl)-5-phenylpent-1-en-1-yl]benzene (**3** and **3′**)

Cinnamyl fluoride (**1**, 70 mg, 514 μmol) in a 7 mL PFA vial under N_2 was exposed to air for 10 s and stored at RT for 3 days. The resultant pale purple gel was chromatographed on silica gel (85% hexanes–CH_2Cl_2) to afford **3** (96:4 *dr*, R_f 0.30, 22 mg, 81 μmol, 32%) and **3′** (97:3 *dr*, R_f 0.33, 4.7 mg, 17 μmol, 7%) as colorless oils.

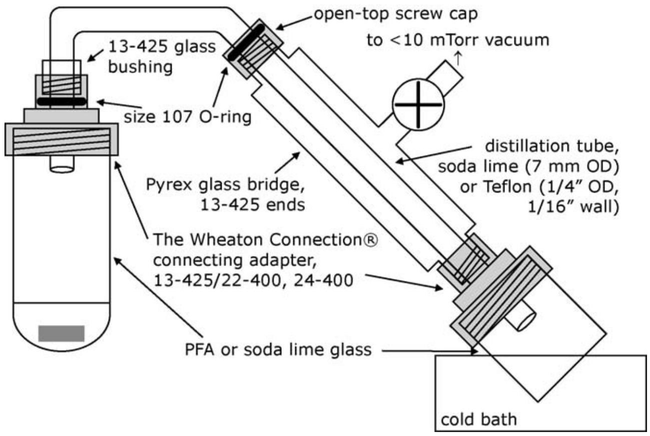


Fig. 5. Soda lime and Teflon/PFA vacuum-distillation assembly.

3, ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C): δ 7.46–7.21 (m, 10H, C_6H_5), 6.40 (dt, $^{3}J_{\text{H1-H2}}$ = 15.6, $^{4}J_{\text{H1-H3,3}'}$ = 1.4, 1H, C(1)H), 6.10 (ddd, $^{3}J_{\text{H1-H2}}$ = 15.6, $^{3}J_{\text{H2-H3,3}'}$ = 7.7, 6.7, 1H, C(2)H), 5.53 (dd, $^{2}J_{\text{F-H5}}$ = 46.3, $^{3}J_{\text{H5-H4}}$ = 7.4, 1H, C(5)H), 4.75 (dddd, $^{2}J_{\text{HF}}$ = 47.4, $^{2}J_{\text{HH}}$ = 9.4, $^{3}J_{\text{H-H4}}$ = 4.5, $J_{\text{F5-H}}$ = 1, 1H, C(4)C*H*H'F), 4.58 (dddd, $^{2}J_{\text{HF}}$ = 46.7, $^{2}J_{\text{HH}}$ = 9.3, $^{3}J_{\text{H-H4}}$ = 3.6, $J_{\text{F5-H}}$ = 1.1, 1H, C(4)CH*H'*F), 2.34 (m, $^{3}J_{\text{H4-H3}'}$ = 8.3, $^{3}J_{\text{H4-H3}}$ = 5.2, 1H, C(4)H), 2.28 (m, $^{2}J_{\text{H3-H3}'}$ = 13.7, 1H, C(3)H'), 2.20 (m, 1H, C(3)H). ^{13}C NMR (126 MHz, $CDCl_3$, 22 °C): δ 138.1 (d, J = 20.0), 137.3, 133.2, 129.0 (d, J = 2.1), 128.8 (d, J = 8.4), 127.5, 126.6, 126.55, 126.53, 126.3, 93.6 (dd, J = 173.9, 5.1), 81.8 (dd, J = 168.6, 5.3), 45.9 (dd, J = 21.5, 18.4), 30.1 (dd, J = 5.2, 4.2). ^{19}F NMR (376 MHz, $CDCl_3$, 22 °C): δ −179.4 (dd, $^{2}J_{\text{F-H5}}$ = 46.4, $^{3}J_{\text{F-H4}}$ = 14.6, 1F, C(5)F), −232.6 (td, $^{2}J_{\text{HF}}$ = 47.0, $^{3}J_{\text{F-H4}}$ = 26.1, 1F, C(4)CH_2F). Anal. Calcd. for $C_{18}H_{18}F_2$: C, 79.39; H, 6.66. Found: C, 79.11; H, 6.74.

3′, ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C): δ 7.44–7.20 (m, 10H, C_6H_5), 6.45 (dt, $^{3}J_{\text{H1-H2}}$ = 15.9, $^{4}J_{\text{H1-H3,3}'}$ = 1.5, 1H, C(1)H), 6.14 (ddd, $^{3}J_{\text{H1-H2}}$ = 15.7, $^{3}J_{\text{H2-H3,3}'}$ = 8.4, 6.4, 1H, C(2)H), 5.65 (dd, $^{2}J_{\text{F-H5}}$ = 46.8, ^{3}J$_{\text{H5-H4}}$ = 5.9, 1H, C(5)H), 4.52 (dddd, $^{2}J_{\text{HF}}$ = 47.0, $^{2}J_{\text{HH}}$ = 9.4, $^{3}J_{\text{H-H4}}$ = 5.9, $J_{\text{F5-H}}$ = 1.7, 1H, C(4)C*H*H'F), 4.31 (ddd, $^{2}J_{\text{HF}}$ = 47.1, $^{2}J_{\text{HH}}$ = 9.4, $^{3}J_{\text{H-H4}}$ = 4.0, 1H, C(4)CH*H'*F), 2.57 (m, $^{2}J_{\text{H3-H3}'}$ = 14.3, $^{3}J_{\text{H4-H3}}$ = 4.2, $^{3}J_{\text{F-H3}}$ = 2.3, 1H, C(3)H), 2.39 (m, $^{3}J_{\text{H4-H3}'}$ = 9.3, 1H, C(3)H'), 2.28 (m, 1H, C(4)H). ^{13}C NMR (126 MHz, $CDCl_3$, 22 °C): δ 138.5 (d, J = 20.4), 137.4, 132.9, 128.8, 128.7 (d, J = 1.3), 127.5, 127.1, 126.3, 125.9 (d, J = 7.6), 93.5 (dd, J = 174.5, 4.0), 82.5 (dd, J = 168.8, 6.1), 46.4 (dd, J = 22.9, 18.1), 29.0 (dd, J = 5.5, 4.3), one signal obscured. ^{19}F NMR (376 MHz, $CDCl_3$, 22 °C): δ −189.7 (dd, $^{2}J_{\text{F-H5}}$ = 46.8, $^{3}J_{\text{F-H4}}$ = 20.4 Hz, 1F, C(5)F), −229.1 (td, $^{2}J_{\text{HF}}$ = 46.9, $^{3}J_{\text{F-H4}}$ = 23.9, 1F, C(4)CH_2F). Anal. Calcd. for $C_{18}H_{18}F_2$: C, 79.39; H, 6.66. Found: C, 79.66; H, 6.41.

4.6. Preparative scale dehydrofluorination of 1

Neat liquid **1** (35.9 mg, 264 μmol) was treated with $BF_3{\cdot}Et_2O$ (3.1 μL, 24.5 μmol, 0.1 equiv.) in a closed 7 mL PFA vial, immediately producing visible smoke and turning into a deep purple solid. After standing for 5 min, the vial was vented to N_2, then heated closed under N_2 at +100 °C for 13 h and dried at +100 to 130 °C for 14 h, producing a yellow solid. Yield 27.3 mg (235 μmol, 89%). ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C): δ 8.5–5.5 (br), 4.5–0.0 (br). Anal. Calcd. for C_9H_8: C, 93.06; H, 6.94. Found: C, 92.89; H, 6.68. ESI-MS (THF:MeOH 1:1, satd. NH_4Cl): 465.1 (M_4H^+), 581.2 (M_5H^+), 697.4 (M_6H^+), 813.4 (M_7H^+), 929.6 (M_8H^+), 1045.5 (M_9H^+), 1161.9 ($M_{10}H^+$); 482.2 $[M_4+18]^+$, 598.3 $[M_5+18]^+$, 714.5 $[M_6+18]^+$, 830.6 $[M_7+18]^+$, 946.8 $[M_8+18]^+$, 1062.9 $[M_9+18]^+$, 1179.0 $[M_{10}+18]^+$; $M = C_9H_8$ (Fig. 4a).

In another preparation, neat **1** contained in a PFA vial was decomposed by contact with Pyrex glass over several minutes at RT and the initial products subjected to aging under 1 atm N_2 at +90 °C for 3d. ESI-MS spectrum of the resulting pale brown solid showed series of signals consistent with elemental composition of partly dehydrofluorinated oligomers of **1**, $\{C_9H_8\}_m(HF)_nNa^+$, m = 5–16, n = 1–5.

4.7. (2E)-3-phenylprop-2-en-1-yl trifluoroacetate (cinnamyl trifluoroacetate, 5*)*

A CH_2Cl_2 solution (5 mL) of cinnamyl alcohol (280 mg, 2.09 mmol) was treated at RT with trifluoroacetic anhydride (657 mg, 3.13 mmol) and the mixture was stirred for 30 min. Distillation at +70 °C under <10 mTorr vacuum afforded cinnamyl trifluoroacetate as a colorless liquid, which was collected at 0 °C. Yield 385 mg (1.67 mmol, 80%). ^{1}H NMR (500 MHz, $CDCl_3$, 22 °C): δ 7.45–7.43 (m, 2H, H_o), 7.39–7.31 (m, 3H, H_m, H_p), 6.78 (d, 1H, $^{3}J_{\text{H2-H3}}$ = 16.0, C(3)H), 6.31 (dt, 1H, $^{3}J_{\text{H2-H3}}$ = 15.8, $^{3}J_{\text{H2-H1}}$ = 6.9, C(2)H), 5.00 (dd, 2H, $^{3}J_{\text{H2-H1}}$ = 6.9, $^{4}J_{\text{H3-H1}}$ = 0.8, C(1)H_2); data are in accord with literature values [25]. ^{13}C NMR (126 MHz, $CDCl_3$, 22 °C): δ 157.6 (q, J = 42.5, C(O)O), 137.33, 137.32, 135.6, 129.0, 127.1, 120.3, 114.7 (q, J = 285.8, CF_3), 68.8. ^{19}F NMR (376 MHz, $CDCl_3$, 22 °C): δ −74.8.

4.8. (2E)-3-phenylprop-2-en-1-yl nitrate (cinnamyl nitrate, 6*)*

Cinnamyl chloride (150 mg, 0.98 mmol) and $AgNO_3$ (334 mg, 1.97 mmol) were stirred in 10 mL of CH_3CN for 24 h. The solution was filtered through Celite and filtrate distilled at +50 °C under <10 mTorr vacuum to yield cinnamyl nitrate as a colorless liquid, which was collected at +5 °C. The product crystallized at −35 °C and remained solid at room temperature, mp 29–30 °C. Yield 80 mg (0.45 mmol, 46%). Spectral data are in accord with literature values [26].

4.9. (2E)-1-fluoro-3,7-dimethylocta-2,6-diene (geranyl fluoride, 2*)*

Geranyl chloride [27] (298 mg, 1.73 mmol) was added to Me_2SO (5 mL) solution of $Bu_4NF{\cdot}(H_2O)_{1.7}$ (660 mg, 93.0 wt.%, 2.10 mmol) in a scintillation vial in the glovebox. After stirring for 24 h at RT, the solution was poured to 15 mL of CH_2Cl_2 in a 120 mL separatory funnel, washed with 7× 7 mL of water, dried over $MgSO_4$, and filtered through Celite. The filtrate was collected in a 100 mL RBF, concentrated and transferred to a 26 mL PFA tube. The solution was concentrated further to 2 mL, the product **2** was vacuum-distilled (<10 mTorr) in a Teflon/PFA assembly (Fig. 5) and collected as a colorless oil at 0 °C, *d* 0.86 g/mL. Yield 235 mg (1.50 mmol, 87%; repeat synthesis: 85%); this quantity of neat material can be stored over extended periods in a PFA container under N_2 at −35 °C. ^{1}H NMR (400 MHz, d_6-Me_2SO, 22 °C): δ 5.43 (d × t × sx, $^{3}J_{\text{FH}}$ = 9.3, $^{3}J_{\text{H1-H2}}$ = 7.2, $^{4}J_{\text{H2-C(3)CH}}$ = $^{4}J_{\text{H2-C(4)H,H'}}$ = 1.3, 1H, C(2)H), 5.06 (t × sp, $^{3}J_{\text{H6-H5,5}'}$ = 6.8, $^{4}J_{\text{H6-C(7)CH}}$ = $^{4}J_{\text{H6-C(8)H}}$ = 1.4, 1H, C(6)H), 4.87 (dd, $^{2}J_{\text{HF}}$ = 47.8, $^{3}J_{\text{H1-H2}}$ = 7.3, 2H, C(1)H_2), 2.09–2.00 (m, 4H, C(4)H_2, C(5)H_2), 1.67 (dd, J_{FH} = 4.8, $^{4}J_{\text{H2-C(3)CH}}$ = 1.5, 3H, C(3)CH_3), 1.63 (d, $^{4}J_{\text{H6-CH}}$ = 1.2, 3H, CH_3), 1.56 (d, $^{4}J_{\text{H6-CH}}$ = 1.0, 3H, CH_3). ^{13}C NMR (101 MHz, d_6-Me_2SO, 22 °C): δ 143.4 (d, $^{3}J_{\text{CF}}$ = 11.2, C3), 131.1, 123.6, 119.0 (d, $^{2}J_{\text{CF}}$ = 17.2, C2), 78.9 (d, $^{1}J_{\text{CF}}$ = 154.4, C1), 38.9 (d, J_{CF} = 2.6), 25.7 (d, J_{CF} = 3.4), 25.5, 17.5, 16.1 (d, $^{4}J_{\text{CF}}$ = 3.4, C(3)CH_3); data are in accord with literature values [3b,4]. ^{19}F NMR (376 MHz, d_6-Me_2SO, 22 °C): δ −205.5 (t × d × sx, $^{2}J_{\text{HF}}$ = 47.8, $^{3}J_{\text{F-H2}}$ = 9.6, $J_{\text{F-C(3)CH}}$ = $J_{\text{F-H4,4}'}$ = 4.8).

*4.10. Preparative scale dehydrofluorination of (*2*)*

Neat liquid **2** (28.9 mg, 185 μmol) in a 7 mL PFA vial was treated with $BF_3{\cdot}Et_2O$ (0.23 μL, 1.8 μmol, 0.01 equiv.), immediately producing visible smoke and turning into a deep purple solid. The solid was evacuated at RT for 3 h, heated closed under N_2 atmosphere at +90 °C for 25 h and dried at +100 to 125 °C for 3 days, becoming light purple. Yield 19.4 mg (142 μmol, 77%). ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C): δ 6.96 (br), 5.33 (br), 5.23 (br), 5.10 (br), 4.69 (br), 3.17–0.5 (br). Anal. Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.03; H, 11.68. ESI-MS (THF:MeOH 1:2): 409.1 (M_3H^+), 545.3 (M_4H^+), 681.6 (M_5H^+), 817.8 (M_6H^+), 953.9 (M_7H^+), 1090.1 (M_8H^+), 1226.2 (M_9H^+); $M = C_{10}H_{16}$ (Fig. 4b). In a separate reaction, **2** (28.7 mg, 184 μmol) dissolved in 0.5 mL of pentane in a Teflon insert was treated with $BF_3{\cdot}Et_2O$ (0.23 μL, 1.9 μmol, 0.01 equiv.), immediately producing orange coloration and precipitation of an orange solid. After 30 h at RT ^{19}F NMR showed near complete conversion of organofluorine intermediates. The reaction mixture was rinsed out to a 7 mL PFA vial with help of CH_2Cl_2, evaporated to dryness and the residue dried under <10 mTorr vacuum at +100 to 120 °C for 24 h, remaining yellow. Yield 17.9 mg (131 μmol, 71%). ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C): δ 6.96 (br), 5.33 (br), 5.23 (br), 5.10 (br), 4.69 (br), 3.17–0.5 (br). Anal. Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 87.88; H, 11.60.

4.11. Thermolysis of 2 in C_6D_6 in a Teflon NMR tube insert

A $CDCl_3$ solution of **2** (0.4 mL, 50 mM, Teflon insert capped with a Teflon cap inside a J. Young tube) containing an internal ^{19}F NMR standard was heated to +60 °C. After 8d 3 h, ^{1}H and ^{19}F spectra showed formation of 3-fluoro-3,7-dimethylocta-1,6-diene (linaloyl fluoride, **11**) in 60% yield by ^{19}F NMR integration. **11**, ^{1}H NMR (400 MHz, $CDCl_3$, Teflon insert, 22 °C): δ 5.89 (td, $^3J_{H2\text{-}H1cis} = {}^3J_{HF} = 17.8$, $^3J_{H2\text{-}H1trans} = 11.0$, 1H, C(2)H), 5.27 (dt, $^3J_{H2\text{-}H1cis} = 17.4$, $^2J_{HH} = {}^4J_{HF} = 1.3$, 1H, C(1)$H_{cis}$), 5.13 (dt, $^3J_{H2\text{-}H1trans} = 10.9$, $_2J_{HH} = {}^4J_{HF} = 1.0$, 1H, C(1)$H_{trans}$), 5.10 (t, $^3J_{H6\text{-}H5,5'} = 7.0$, 1H, C(6)H), 2.14-1.98 (m, 2H), 1.77-1.65 (m, 2H), 1.69 (s, 3H, CH_3), 1.61(s, 3H, CH_3), 1.42 (d, $^3J_{FH} = 21.8$, 3H, C(3)CH_3). ^{13}C NMR (101 MHz, C_6D_6, Teflon insert, 22 °C): δ 141.6 (d, $J = 22.5$, C2), 132.0, 124.8, 113.4 (d, $J = 11.2$, C1), 95.9 (d, $J = 171.7$, C3), 41.0 (d, $J = 23.2$, C4), 26.1, 25.9 (d, $J = 25.1$, C(3)CH_3), 23.1 (d, $J = 4.9$, C5), 17.9; data are in accord with literature values [4]. ^{19}F NMR (376 MHz, $CDCl_3$, Teflon insert, 22 °C): δ −148.5 (m, $^3J_{H4\text{-}F} = 23.3$, $^3J_{C(3)CH\text{-}F} = 21.1$, $^3J_{H2\text{-}F} = 18.3$, $^3J_{H4'\text{-}F} = 16.6$). After 18d 13 h of thermolysis, ^{1}H and ^{19}F NMR spectra showed formation of 4-(1-fluoro-1-methylethyl)-1-methylcyclohexene (α-terpinyl fluoride, **12**), in 60% yield by ^{19}F NMR integration. **12**, ^{1}H NMR (400 MHz, $CDCl_3$, Teflon insert, 22 °C): δ 5.39 (br s, 1H, C(2)H), 2.12–1.61 (m, 7H), 1.67 (s, 3H), 1.33 (d, $^3J_{FH} = 22.0$, 3H, C(F)CH_3), 1.32 (d, $^3J_{FH} = 22.0$, 3H, C(F)CH_3). ^{19}F NMR (376 MHz, $CDCl_3$, Teflon insert, 22 °C): δ −140.4 (sp × d, $^3J_{F\text{-}C(F)CH3} = 22.0$, $^3J_{F\text{-}H4} = 11.5$); data are in accord with literature values [14]. ^{13}C NMR (101 MHz, C_6D_6, Teflon insert, 22 °C): δ 134.1, 121.1, 97.1 (d, $J = 167.6$, C(4)CF), 44.2 (d, $J = 22.1$, C4), 31.2 (C6), 27.3 (d, $J = 7.1$), 25.3 (d, $J = 25.1$, C(4)CCH_3), 24.5 (d, $J = 5.2$), 24.2 (d, $J = 25.4$, C(4)CCH_3), 23.9.

4.12. 3-Fluorocyclohexene (7)

A 26 mL PFA tube was loaded with AgF (653 mg, 5.15 mmol), P(o-Tolyl)$_3$ (52 mg, 0.17 mmol), Et_2O (10 mL) and 3-chlorocyclohexene (200 mg, 1.72 mmol) in the glovebox and the mixture was sonicated at 20 °C in the dark for 4 days, after which time complete conversion was established by NMR. The solids were centrifuged and the colorless solution was decanted off to a clean PFA tube. After removing most of the ether at 350 Torr/RT, the residue was distilled at 10 Torr/RT in a Teflon/PFA assembly described in Fig. 5. The distillate collected in a PFA vial at −40 °C was additionally dried under <10 mTorr vacuum at −78 °C for 2–3 h and quickly transferred to a −35 °C glovebox freezer under N_2. Yield 106 mg (93.5 wt.% pure (1.6 wt.% 1,4-cyclohexadiene, 1.3 wt.% Et_2O, and 3.6 wt.% 4-chlorocyclohexene as impurities), 0.99 mmol, 58%; repeat synthesis: 56%); neat material can be stored over a few weeks in a PFA container under N_2 at −35 °C. ^{1}H NMR (500 MHz, C_6D_6, Teflon insert, 22 °C): δ 5.79–5.74 (m, 1H), 5.66 (dq, $^3J_{H1\text{-}H2} = 10.2$, $J_{HH} = 3.4$, 1H), 4.75 (dq, $^2J_{HF} = 49.5$, $J_{HH} = 4.5$, 1H, C(3)H), 1.83–1.64 (m, 2H), 1.58–1.42 (m, 3H), 1.22–1.16 (m, 1H). ^{19}F NMR (376 MHz, C_6D_6, Teflon insert, 22 °C): δ −165.9 (m); data are in accord with literature values [15b]. ^{13}C NMR (126 MHz, C_6D_6, Teflon insert, 22 °C): δ 133.6 (d, $J = 9.3$, C1), 126.6 (d, $J = 18.5$, C2), 85.6 (d, $J = 164.2$, C3), 29.8 (d, $J = 20.0$, C4), 25.4 (d, $J = 9.3$, C5), 18.7 (d, $J = 3.5$, C6). GC retention time, $T = 2.5'$; HP-5MS column (30 m, ID 0.25 mm, film thickness 25 μm); 50°(5′) → 20°/′ → 250°(5′); sample stabilized with 0.2 equiv. Et_3N in pentane in a glass vial. EI-MS: m/z (int) 100 (M^+, 55), 99 (14), 85 (66), 80 (35), 79 (34), 77 (16), 72 (100), 67 (11), 59 (30), 54(32), 53 (11), 51 (16).

4.13. Preparative scale dehydrofluorination of 7

A C_6D_6 (0.5 mL) solution of **7** (30 mg, 0.30 mmol) was poured from a Teflon NMR tube insert to a borosilicate glass vial, turning from colorless to deep blue-purple within a minute. After 10 min, the reaction was quenched with CsF (45.5 mg, 0.30 mg) to absorb HF and distilled under <10 mTorr vacuum at +55 °C, to yield dicyclohex-2-en-1-yl ether (**14**) as a colorless liquid, collected at +5 °C. Yield 10 mg (52:48 dr, 56 μmol, 37%). Diastereomeric ratio was determined by ^{13}C and ^{1}H NMR integration. Spectral data are in accord with literature values [28]. Another sample of **7** in C_6D_6 solution was decomposed on contact with borosilicate glass and decomposition products aged as formed for a month at RT. ESI-MS of the reaction mixture in C_6D_6 showed series of signals consistent with elemental composition of cyclohexadiene oligomers, $\{C_6H_8\}_n(H,OH)^+$, $n = 5$–11.

4.14. cis/trans-Methyl 5-fluorocyclohex-3-ene-1-carboxylate (13)

Under N_2, a 26 mL PFA tube was charged with AgF (436 mg, 3.47 mmol), P(o-Tolyl)$_3$ (35 mg, 0.12 mmol), C_6H_6 (6 mL) and *trans*-methyl 5-chlorocyclohex-3-ene-1-carboxylate [29] (202 mg, 1.16 mmol). The mixture was sonicated at +20 °C in the dark for 44 h, at which time complete conversion of the chloride was established by NMR of an aliquot. The solids were centrifuged off and the clear supernatant solution was decanted to a clean PFA tube in the glovebox. The product **13** was vacuum-distilled (<10 mTorr) in a Teflon/PFA assembly described in Fig. 5 and collected as a colorless oil at +5 °C, d 1.05 g/mL (approximately by weight of a 10 μL volume). Yield 158 mg (95%, w/w pure (1.7%, w/w methyl benzoate and 3.2% (w/w) 1-carbomethoxy-2,4-cyclohexadiene identified as impurities), 0.95 mmol, 82%; repeat synthesis: 74%); neat material can be stored over extended periods in a PFA container under N_2 at −35 °C. The ratio *cis*:*trans* = 40:60 was determined by ^{1}H NMR integration. In a C_6D_6 solution (>0.1 M **13**) contained in a borosilicate glass NMR tube, elimination of HF occurs on the timescale of hours at RT producing 1-carbomethoxy-2,4-cyclohexadiene and lowering *cis*:*trans* ratio. ^{1}H NMR (400 MHz, C_6D_6, 22 °C): δ 5.67-5.60 (m, 1H, *cis*-C(4)H (5.63) [30], *trans*-C(4)H (5.62) [30]), 5.57 (dddd, $^3J_{H3\text{-}H4} = 10.1$, $^3J_{HF} = 3.5$, $J_{HH} = 5.2$, 2.8, 0.6H, *trans*-C(3)H), 5.41 (ddddd, $^3J_{H3\text{-}H4} = 10.2$, $J_{HH} = 4.5$, 2.8, 1.6, $^3J_{HF} = 2.2$, *cis*-C(3)H), 4.77 (dm, $^2J_{HF} = 49.0$, 0.4H, *cis*-C(5)H), 4.63 (dm, $^2J_{HF} = 48.2$, 0.6H, *trans*-C(5)H), 3.30 (s, 1.2H, *cis*-$COOCH_3$), 3.28 (s, 1.8H, *trans*-$COOCH_3$), 2.73 (dddd, $^3J_{H1\text{-}H6a} = 12.7$, $^3J_{H1\text{-}H2a} = 11.1$, $^3J_{H1\text{-}H2e} = 5.2$, $^3J_{H1\text{-}H6e} = 3.1$, 0.6H, *trans*-C(1)H), 2.28 (ddtt, $^3J_{HF} = 15.8$, $^2J_{HH} = 14.5$, $^3J_{H6e\text{-}H1} = {}^3J_{H6e\text{-}H5} = 3.0$, $^4J_{HH} = 1.3$, 1.3, 0.6H, *trans*-C(6)H_e), 2.23-2.15 (m, 0.8H, *cis*-C(6)H (2.19) [30], *cis*-C(1)H (2.18) [30]), 2.13–1.82 (m, 2.4H, *cis*-C(2)H+*trans*-C(2)H (2.1) [30], *trans*-C(2)H (1.98) [30], *cis*-C(6)H (1.91), *cis*-C(2)H (1.86) [30]), 1.53 (dddd, $^3J_{HF} = 36.4$, $^2J_{HH} = 14.5$, $^3J_{H1\text{-}H6a} = 12.8$, $^3J_{H6a\text{-}H5} = 3.9$, 0.6H, *trans*-C(6)$H_a$). ^{13}C NMR (101 MHz, C_6D_6, 22 °C)): δ 175.0 (*trans*-C(O)OMe), 173.9 (d, $^4J_{CF} = 1.5$, *cis*-C(O)OMe), 132.9 (d, $^3J_{CF} = 10.1$, *trans*-C3), 130.0 (d, $^3J_{CF} = 9.3$, *cis*-C3), 127.6 (d, $^2J_{CF} = 21.3$, *cis*-C4), 124.9 (d, $^2J_{CF} = 16.5$, *trans*-C4), 87.4 (d, $^1J_{CF} = 164.9$, *cis*-C5), 83.7 (d, $^1J_{CF} = 164.9$, *trans*-C5), 51.7 (*cis*-C(O)OCH_3), 51.6 (*trans*-C(O)OCH_3), 37.6 (d, $^3J_{CF} = 8.2$, *cis*-C1), 35.1, (*trans*-C1), 32.2 (d, $^2J_{CF} = 20.2$, *cis*-C6), 32.1 (d, $^2J_{CF} = 21.7$, *trans*-C6), 28.1 (d, $^4J_{CF} = 3.7$, *trans*-C2), 27.7 (d, $^4J_{CF} = 2.6$, *cis*-C2). ^{19}F NMR (376 MHz, C_6D_6, 22 °C)): δ −162.1 (m, 0.6F, *trans*-C(5)F), −172.4 (dm, $^2J_{HF} = 48.3$, 0.4F, *cis*-C(5)F). Anal. Calcd. for $(C_8H_{11}FO_2)_{0.951}\cdot(C_8H_8O_2)_{0.017}\cdot(C_8H_{10}O_2)_{0.032} = C_8H_{10.917}O_2F_{0.951}$: C, 61.14; H, 7.00. Found: C, 61.54; H, 6.71. Relative configurations of isomers of **13** were assigned on the basis of J_{HH} and J_{HF} coupling constants, measured by selective decoupling of signals assigned with help of J_{CF} constants, ^{1}H–^{1}H COSY, ^{13}C DEPT and ^{1}H–^{13}C HSQC spectra. Specifically, *trans*-configuration of the major isomer was established from assignment of C(1)H as axial and C(5)H as equatorial (Chart 2). These assignments were consistent with available NOE data, limited in scope and magnitude by signal overlap.

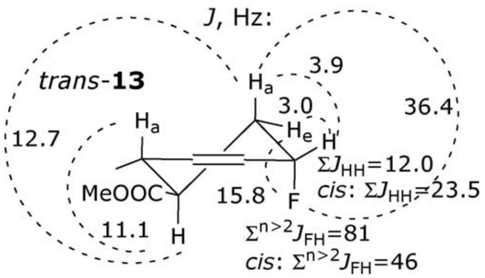


Chart 2.

4.15. Preparative scale dehydrofluorination of 13

A sample of **13** (30 mg, 0.19 mmol) in a C_6D_6 solution (0.6 mL) in a J. Young tube turned from colorless to light green-blue within a day. The reaction mixture was transferred to a PFA vial and distilled under <10 mTorr vacuum at +130 °C to yield dimethyl 5,5′-oxybiscyclohex-3-ene-1-carboxylate (**15**) as a colorless liquid collected at +18 °C. Yield 7.5 mg (25 μmol, 27%). Isolated material is a mixture of at least 6 diastereomers of **15** according to GC, ^{13}C NMR and elemental analysis. ^1H NMR (500 MHz, $CDCl_3$, 22 °C): δ 5.94–5.66 (m, 4H,), 4.33–3.94 (m, 2H), 3.70 (s, 6H), 2.90–2.58 (m, 2H), 2.42–2.11 (m, 6H), 1.81–1.63 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 22 °C): δ 176.38, 176.34, 176.32, 175.25, 175.23, 175.21, 129.9, 129.80, 129.78, 129.77, 129.7, 129.49, 129.48, 128.1, 127.85, 127.77, 127.76, 127.7, 127.1, 127.0, 126.9, 126.7, 72.62, 72.56, 72.4, 72.2, 68.8, 68.53, 68.51, 68.47, 52.05, 51.97, 51.96, 38.8, 38.65, 38.57, 35.04, 34.95, 34.90, 34.88, 32.61, 32.55, 32.19, 32.16, 31.5, 31.1, 31.0, 27.99, 27.98, 27.75, 27.74, 27.71. GC retention times, T (FID % of total): 15.89′ (15.6%), 15.91′ (23.2%), 16.14′ (21.6%), 16.18′ (24.0%), 16.38′ (6.2%), 16.41′ (7.3%); HP-5MS column (30 m, ID 0.25 mm, film thickness 25 μm); 50°(5′) → 20°/′ → 250°(10′). Anal. Calcd. for $C_{16}H_{22}O_5$: C, 65.29; H, 7.53. Found: C, 65.55; H, 7.39. The yellow oil of the distillation residue showed series of signals in ESI-MS (THF:MeOH 1:1) consistent with elemental composition of oligomers of **16**, $\{C_8H_{10}O_2\}_nNa^+$, $n = 3–14$.

4.16. Screen of compatibility of neat 1 and 2 with various materials (Fig. 1, Table 1)

Materials of eight common laboratory glass containers were drawn into ~10 μL capillaries, flame-sealed at one end, fitted with a sleeve of a Teflon cannula (16 AWG, standard wall) over the open end, washed with DI water and dried at +160 °C for overnight together with plugs made of the same material. The capillaries were loaded with ~3–5 μL of neat **1** or **2**, pipetted with a length of a Teflon cannula (24 AWG, thin wall), plugged to prevent evaporation and positioned in front of a Logitech QuickCam® Pro 9000 web camera, all inside a glovebox. For runs under air or O_2 (grade 2.6) atmosphere, capillaries loaded in the glovebox under N_2 were placed under appropriate atmosphere inside a secondary glass container, plugged promptly in the air and returned for video monitoring into the secondary glass container maintained under air. Decomposition typically manifested itself by formation of gas bubbles and change of liquid consistency to a gelatinous solid of various coloration that evolved over ~2 min. The time of decomposition onset was recorded at the first sign of gas evolution to within a minute. Stability of **1** in soda lime and PFA containers was monitored periodically by visual inspection of appearance and ^1H and ^{19}F NMR spectra taken on the neat liquid contained in plugged capillaries made of soda lime in triplicate; no decomposition was observed over 6 (soda lime) and 3 (PFA) months at RT under N_2 atmosphere. Analogous tests of **2** in PFA produced semi-solid white products at times recorded to within 24 h.

4.17. NMR-tube reactivity studies of 1 (Table 2) and other allylic derivatives (Table 3)

All experiments listed in Tables 2 and 3 were done with internal standards using flame-dried J. Young tubes with and without Teflon inserts under N_2, unless otherwise stated. Nominal quantities of liquid fluorides were measured approximately, by volume in a soda lime glass capillary (**1** only) or a length of a Teflon cannula (24 AWG, thin wall) calibrated manually. In reactions with accurately measured, dissolved internal standards, actual amount of allylic fluoride present initially in solution was determined by ^1H and/or ^{19}F NMR integration and was used to calculate its actual concentration and stoichiometric quantities of reagents that were added subsequently to the NMR tube solution. In general, the nominal and actual, integration-based quantities agreed to within 10% of each other. The listed reaction times mark the end of the acquisition of the last spectrum used in quantification.

Acknowledgments

We thank Stanford University for funding and L. Chen for initial observations.

References

[1] (a) M. Pagliaro, R.J. Ciriminna, Mater. Chem. 15 (2005) 4981–4991;
(b) P. Maienfisch, R.G. Hall, Chimia 58 (2004) 93–99;
(c) R.E. Banks, B.E. Smart, J.C. Tatlow (Eds.), Organofluorine Chemistry: Principles and Commercial Applications, Plenum Press, New York, 1994;
(d) T. Hiyama, Organofluorine Compounds: Chemistry and Applications, Springer, New York, 2000.

[2] (a) M.C. Pacheco, S. Purser, V. Gouverneur, Chem. Rev. 108 (2008) 1943–1981;
(b) L. Hunter, D. O'Hagan, A.M.Z. Slawin, J. Am. Chem. Soc. 128 (2006) 16422–16423;
(c) M. Tredwell, V. Gouverneur, Org. Biomol. Chem. 4 (2006) 26–32;
(d) R. Roig, J.M. Percy, Sci. Synth. 34 (2005) 331–343;
(e) M. Prakesch, D. Grée, R. Grée, Tetrahedron 59 (2003) 8833–8841;
(f) M. Prakesch, D. Grée, R. Grée, Acc. Chem. Res. 35 (2002) 175–181;
(g) M. Prakesch, D. Grée, R. Grée, J. Org. Chem. 66 (2001) 3146–3151;
(h) V. Madiot, D. Grée, R. Grée, Tetrahedron Lett. 40 (1999) 6403–6406;
(i) S. Legoupy, C. Crévisy, J.-C. Guillemin, R. Grée, J. Fluorine Chem. 93 (1999) 171–173;
(j) R.L. Grée, J.-P. Lellouche, in: V.A. Soloshonok (Ed.), Enantiocontrolled Synthesis of Fluoro-Organic Compounds, John Wiley & Sons Ltd., Chichester, 1999, pp. 63–106;
(k) F. Benayoud, L. Chen, G.A. Moniz, A.J. Zapata, G.B. Hammond, Tetrahedron 54 (1998) 15541–15554;
(l) A. Boukerb, D. Grée, M. Laabassi, R. Grée, J. Fluorine Chem. 88 (1998) 23–27;
(m) F.A. Davis, P.V.N. Kasu, G. Sundarababu, H. Qi, J. Org. Chem. 62 (1997) 7546–7547;
(n) D.M. Gree, C.J.M. Kermarrec, J.T. Martelli, R. Gree, J.-P. Lellouche, L.J. Toupet, J. Org. Chem. 61 (1996) 1918–1919;
(o) M. El-Khoury, Q. Wang, M. Schlosser, Tetrahedron Lett. 31 (1996) 9047–9048;
(p) J.M. Dolence, C.D. Poulter, Tetrahedron 52 (1996) 119–130;
(q) M. Ceruti, S. Amisano, P. Milla, F. Viola, F. Rocco, M. Jung, L. Cattel, J. Chem. Soc. Perkin Trans. 1 (1995) 889–893.

[3] (a) J. Ichikawa, K. Sugimoto, T. Sonoda, H. Kobayashi, Chem. Lett. (1987) 1985–1988;
(b) O.S. Park, H.J. Son, W.Y. Lee, Arch. Pharm. Res. 10 (1987) 239–244;
(c) D.J. de Mendonca, C.A. Digits, E.W. Navin, T.C. Sanders, G.B. Hammond, J. Chem. Ed. 72 (1995) 736–739;
(d) N. Yoneda, T. Fukuhara, Chem. Lett. (2001) 222–223;
(e) N. Yoneda, T. Fukuhara, K. Shimokawa, K. Adachi, S. Oishi, US Patent 6,784,327 (2004).
(f) K. Hirano, H. Yorimitsu, K. Oshima, Org. Lett. 6 (2004) 4873–4875;
(g) B.P. Bandgar, S.V. Bettigeri, Monatsh. Chem. 135 (2004) 1251–1255;
(h) B.P. Bandgar, V.T. Kamble, A.V. Biradar, Monatsh. Chem. 136 (2005) 1579–1582.

[4] D.V. Banthorpe, M.J. Ireland, J. Prakt. Chem. 338 (1996) 279–282.

[5] (a) L.D. Pye, V.D. Fréchette, N.J. Kreidl (Eds.), Borate Glasses: Structure, Properties, and Application Materials Science Research, vol. 12, Plenum Press, New York, 1979;
(b) S. Prasad, T.M. Clark, T.H. Sefzik, H.-T. Kwak, Z. Gan, P.J. Grandinetti, J. Non-Cryst. Solids 352 (2006) 2834–2840.

[6] The diastereomers of **3** formed in the reaction of **1** with 0.1 B_2O_3 in C_6D_6 in 10 min were observed by NMR to undergo acid-catalyzed equilibration during the following hour.

[7] Apparent lack of reactivity of the latter with solutions of **1** in non-basic solvents is partly due to dilution of neat **1** (7.6 M) by a factor of ~100, which alone decreases

the rate of a surface reaction by the same or greater factor; full decomposition was indeed accomplished by heating 30 mM solutions of **1** in C_6D_6 or $CDCl_3$ for 24 h in borosilicate NMR tubes, while analogous runs in Teflon inserts resulted in no reaction (Table 2).

[8] (a) D.B. Priddy, Styrene Plastics Kirk-Othmer Encyclopedia of Chemical Technology (online), Wiley–Interscience, New York, vol. 23, 2006, pp. 358–416;
(b) K.S. Khuong, W.H. Jones, W.A. Pryor, K.N. Houk, J. Am. Chem. Soc. 127 (2005) 1265–1277;
(c) The retardation seen with 0.3 equiv. of BHT was similar to the base effect of 0.3 equiv. of MeOH. Complete inhibition of decomposition of **1** at 0, 0 and 25% conversion in reactions with 0.1 equiv. H_2SO_4, 0.1 B_2O_3 and 0.1 $BF_3{\cdot}OEt_2$ was effected by 0.15, 0.25 and 0.15 equiv. TEMPO, respectively, as a result of its acid-mediated disporportionation that consumes stoichiometric equivalent of the acid: J.M. Bobbitt, C.L. Flores, Heterocycles 27 (1988) 509–533. Z. Ma, J.M. Bobbitt, J. Org. Chem. 56 (1991) 6110–6114. S. Kishioka, T. Ohsaka, K. Tokuda, Electrochim. Acta 48 (2003) 1589–1594. X. Wang, R. Liu, Y. Jin, X. Liang, Chem. Eur. J. 14 (2008) 2679–2685.

[9] Identified by ^{19}F NMR spectra of reactions in Teflon inserts as a singlet at δ −185 to −195 ppm that decoalesced into a J_{FH} = 441 Hz doublet in spectra of entry 19 reaction following dilution with ether and cooling below RT. D.K. Hindermann, C.D. Cornwell, J. Chem. Phys. 48 (1968) 2017–2025. C. MacLean, E.L. Mackor, J. Chem. Phys. 34 (1961) 2207–2208. G.J. Schrobilgen, J. Chem. Soc., Chem. Commun. (1988) 863–865.

[10] With the median mass balance of 83%, we suspect the deficiencies to stem from partial escape of HF to the gas phase and leaking out of Teflon insert over periods of days, as well as formation of multiple organofluorine intermediates with low intensity signals (Fig. 2b). Reactions in Pyrex tubes showed lower ^{19}F NMR mass balance, of 34–79% with a median of 60%, due to precipitation/adsorption of inorganic fluoro anions as metal salts on the glass surface.

[11] (a) E.T. Urbansky, Chem. Rev. 102 (2002) 2837–2854;
(b) D. Fărcaşıu, A. Ghenciu, J. Catal. 134 (1992) 126–133;
(c) K.W. Kolasinski, J. Electrochem. Soc. 152 (2005) J99–J104.

[12] (a) A.J. Muscat, A.G. Thorsness, G. Montaño-Miranda, J. Vac. Sci. Technol. A 19 (2001) 1854–1861;
(b) D.M. Knotter, J. Am. Chem. Soc. 122 (2000) 4345–4351;
(c) G.A.C.M. Spierings, J. Mater. Sci. 28 (1993) 6261–6273;
(d) R.A. Smith, Fluorine Compounds, Inorganic, Hydrogen Kirk-Othmer Encyclopedia of Chemical Technology (online), vol. 13, Wiley–Interscience, New York, 2005, pp. 1–26.

[13] K. Hirano, K. Fujita, H. Yorimitsu, H. Shinokubo, K. Oshima, Tetrahedron Lett. 45 (2004) 2555–2557.

[14] M. Wüst, D.B. Little, M. Schalk, R. Croteau, Arch. Biochem. Biophys. 387 (2001) 125–136.

[15] (a) G.A. Olah, M. Nojima, I. Kerekes, J. Am. Chem. Soc. 96 (1974) 925–927;
(b) M. Hudlicky, J. Fluorine Chem. 32 (1986) 441–452.

[16] (a) C.K. Ingold, E.H. Ingold, J. Chem. Soc. (1928) 2249–2262;
(b) J. Bernstein, J.S. Roth, W.T. Miller Jr., J. Am. Chem. Soc. 70 (1948) 2310–2314;
(c) C.G. Swain, R.E.T. Spalding, J. Am. Chem. Soc. 82 (1960) 6104–6107;
(d) S.S. Szucs, Chem. Eng. News 68 (34) (1990) 4.

[17] Y.H. Kim, O. Webster, J. Macromol, Sci. Polym. Rev. C42 (2002) 55–89.

[18] (a) G.A. Olah, Friedel–Crafts Chemistry, Wiley, New York, 1973, pp. 40, 81, 432;
(b) G.A. Olah (Ed.), Friedel–Crafts and Related Reactions, vol. 2, Interscience, New York, 1964, pp. 313, 428, 767.

[19] (a) W.T. Miller Jr., J. Bernstein, J. Am. Chem. Soc. 70 (1948) 3600–3604;
(b) N.B. Chapman, J.L. Levy, J. Chem. Soc. (1952) 1677–1682;
(c) C.W.L. Bevan, R.F. Hudson, J. Chem. Soc. (1953) 2187–2189;
(d) C.G. Swain, R.B. Mosley, J. Am. Chem. Soc. 77 (1955) 3727–3731;
(e) C.G. Swain, T.E.C. Knee, A. MacLachlan, J. Am. Chem. Soc. 82 (1960) 6101–6104;
(f) T.J. Dougherty, J. Am. Chem. Soc. 86 (1964) 2236–2240;
(g) M.M. Toteva, J.P. Richard, J. Am. Chem. Soc. 124 (2002) 9798–9805.

[20] (a) A. Mizote, T. Tanaka, T. Higashimura, S. Okamura, J. Polym. Sci., Part A: Polym. Chem. 3 (1965) 2567–2578;
(b) V.C. Armstrong, Z. Katovic, A.M. Eastham, Can. J. Chem. 49 (1971) 2119–2124.

[21] (a) H. Mayr, W. Striepe, J. Org. Chem. 48 (1983) 1159–1165;
(b) G.A. Olah, S.J. Kuhn, D.G. Barnes, J. Org. Chem. 29 (1964) 2685–2687.

[22] (a) J.A. Miller, H.C.S. Wood, Angew. Chem., Int. Ed. 3 (1964) 310–311;
(b) O. Cori, L. Chayet, L.M. Perez, C.A. Bunton, D. Hachey, J. Org. Chem. 51 (1986) 1310–1316.

[23] P. Wolfrum, in: B. Baasner, H. Hagemann, J.C. Tatlow (Eds.), Organo-Fluorine Compounds, Methods of Organic Chemistry (Houben-Weyl), vol. E10, E10b1, Thieme Verlag, Stuttgart, 1999, p. 308.

[24] $2F^- + H_2O = HF_2^- + OH^-$ acid–base equilibrium is strongly shifted to the left in Me_2SO: H. Sun, S.G. DiMagno, J. Am. Chem. Soc. 127 (2005) 2050–2051.

[25] J.J. Gajewski, K.R. Gee, J. Jurayj, J. Org. Chem. 55 (1990) 1813–1822.

[26] (a) M. Ochiai, E. Fujita, M. Arimoto, H. Yamaguchi, Chem. Pharm. Bull. 32 (1984) 5027–5030;
(b) P. Frøyen, Phosphorous, Sulfur Silicon Relat. Elem. 129 (1997) 89–97.

[27] S. Nowotny, C.E. Tucker, C. Jubert, P. Knochel, J. Org. Chem. 60 (1995) 2762–2772.

[28] A. Uzarewicz, R. Dresler, Pol. J. Chem. 71 (1997) 181–195.

[29] J.-E. Bäckvall, K.L. Granberg, A. Heumann, Isr. J. Chem. 31 (1991) 17–24.

[30] Chemical shifts of overlapping resonances determined from ^{1}H–^{13}C HSQC spectrum.