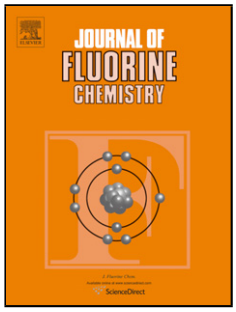

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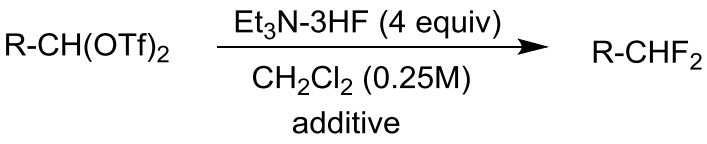

Synopsis

1,1-Difluoroalkanes are readily prepared from their respective 1,1-bistriflates by treatment with Et_3N-3HF.

Highlights

1,1-alkane bistriflates are readily prepared from aldehydes

1,1-difluoroalkanes are readily prepared from 1,1-bistriflates

Triethylamine trishydrofluoride is an excellent fluorinating reagent

Preparation of 1,1-Difluoroalkanes from Aldehydes via 1,1-*bis*-triflates. Advantageous Use of HF-Lewis Base Reagents

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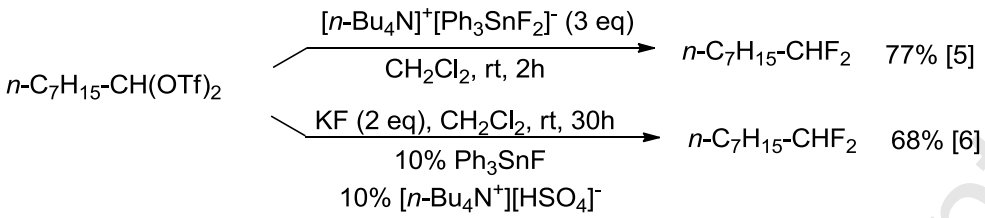
Abstract. Alkane-1,1-bistriflates, prepared in excellent yields by reaction of aldehydes with triflic anhydride, are converted to their respective 1,1-difluoroalkanes in good to excellent yield through reaction with fluorinating agent, triethylamine trishydrofluoride. Straight chain 1,1-bistriflates are more reactive than those substituted at the 2-position, but the latter are also converted successfully, without evidence of any rearrangement products.

1. Introduction

The most commonly used method for conversion of aldehydes to 1,1-difluoroalkanes involves use of one of many available, sulfur-based deoxofluorination reagents, such as SF_4, DAST (diethylaminosulfur trifluoride) [1], Deoxo-Fluor (*bis*(2-methoxyethyl)aminosulfur trifluoride) [2], Xtal-Fluor [3] and Fluolead[4]

Closer to the specific methodology to be described in this paper, is the work of Garcia Martinez [5] and that of Makosza [6], within whose papers the conversion of 1,1-bistriflates to 1,1-difluoroalkanes via nucleophilic substitution was reported (Scheme 1).

Scheme 1. Conversion of 1,1-bistriflates to 1,1-difluorides via nucleophilic substitution



There is always considerable interest in finding the lowest cost solution to a particular synthetic problem, and anhydrous HF is probably the least expensive available source of fluorine. This, combined with our own interest in the use of either anhydrous HF [7] or HF-Lewis base reagents [8] to carry out fluorine/halogen exchange processes and our current interest in the synthesis of *gem*-difluoroalkanes [9], led us to examine the use of various HF-Lewis base combinations for conversion of 1,1-bistriflates to 1,1-difluoroalkanes.

2. Results and Discussion

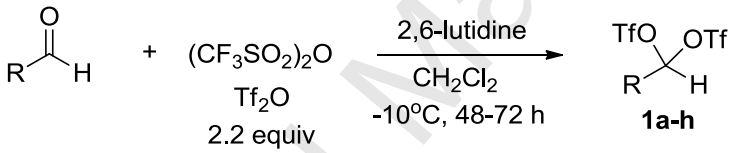
During an earlier study of the kinetic effects of fluorine substituents on nucleophilic substitution [10], we had the occasion to prepare 1-bromo-1-fluorononane from the 1,1-bistriflate via stepwise nucleophilic substitution using a method developed by Garcia-Martinez [11]. It was noticed that considerable 1,1-difluoroalkane was formed along with the desired bromo, fluoro compound, and although, as mentioned above, earlier work has shown that 1,1-difluorides can be prepared via from the bistriflate by nucleophilic substitution by fluoride, we thought that the process might be improved by

use of HF-Lewis base reagents as the source of fluoride in a presumed solvolytic process.

2.1. Preparation of 1,1-bistriflates

The requisite 1,1-bistriflates were readily prepared by the reaction of the respective aldehydes with triflic anhydride in the presence 2,6-lutidine, as shown in Scheme 2. Yields were as follows: **1a** (R = 3-heptyl), 95%; **1b** (R = *n*-octyl), 96%; **1c** (R = *n*-hexyl), 84%; **1d** (R = *n*-butyl), 80%; **1e** (R = benzyl), 54%; **1f** (R = isopropyl), 58%;

Scheme 2. Synthesis of 1,1-bistriflates



1g (R = cyclohexyl), 80%; **1h** (R = t-butyl), 84%. The ^{19}F NMR spectra of all of these bistriflates exhibited a characteristic singlet signal between -74.0 and -74.9 ppm in their ^{19}F NMR spectra along with a characteristic triplet (J_{HH} = 5-6 Hz) (**1b-e**) or doublet (J_{HH} = 2-5 Hz) (**1a, f-h**) at 6.3-6.5 ppm in their proton NMR spectra [12]. Proton and fluorine NMR spectra are provided in the Supplementary Data for all prepared bistriflates.

It was not possible to convert any *benzaldehyde* derivatives (i.e., R = Ph) to their respective bistriflates, nor were bistriflates able to be prepared from ketones, vinyl triflates being the only obtainable products [13].

2.2. Conversion of 1,1-bistriflates to 1,1-difluoroalkanes

In preliminary experiments using 2-ethylhexane-1,1-diyl bis(trifluoromethanesulfonate) (**1a**) in conjunction with THF-5HF, pyridine-HF, and Et_3N-3HF as sources of fluoride ion, it was found that, without an additive, only Et_3N-3HF had any significant effectiveness in this exchange reaction (Scheme 3, Table 1, entries 1-3). On the other hand, with addition of proton sponge (entries 4-7), the effectiveness of all three became enhanced, with that of Et_3N-3HF reaching the point of being satisfactory.

Scheme 3. Preliminary examination of HF/Lewis base effectiveness

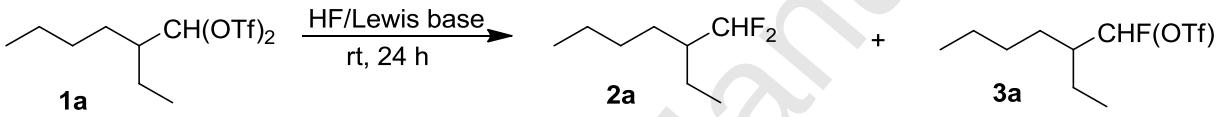


Table 1. Preliminary experiments using bistriflate, **1a**[a]

Entry	Reagent (Equiv)	Solvent	Additive	**2a** (%)[b]	**3a** (%)[b]
1	THF-5HF (30)	-	-	0	Trace
2	Pyr-HF (30)	-	-	Trace	0
3	Et_3N-3HF (20)	-	-	21.8	0
4	THF-5HF (30)	-	PS (4 eq)[c]	17.1	10.4
5	Pyr-HF (10)	CH_2Cl_2 (0.25M)	PS (4eq)[c]	17.5	Trace
6	Et_3N-3HF (5)	CH_2Cl_2 (0.25M)	PS (4eq)[c]	51.4	0
7	Et_3N-3HF (8)	CH_2Cl_2 (0.25M)	PS (1eq)[c]	85	0

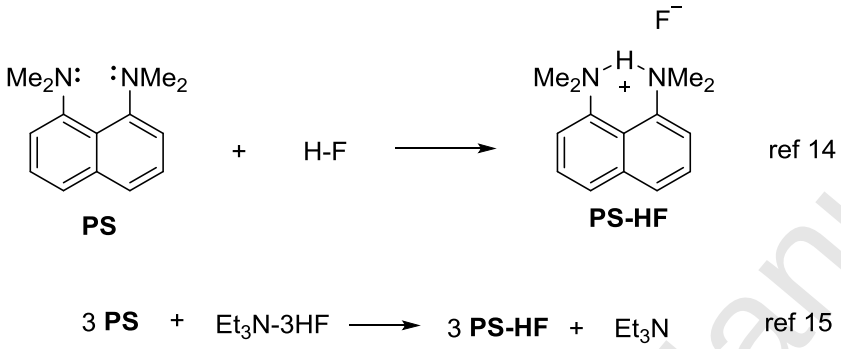
[a] all reactions run at rt for 24 h; [b] NMR yields; [c] PS = proton sponge (1,8-bis-(dimethylamino)-naphthalene

Because the reaction of bistriflate **1a** with any source of HF will generate two equivalents of very strong acid HOTf, two equivalents of base (i. e., Et_3N) will be consumed during the reaction; hence there is a logical necessity that an excess in equivalents of Et_3N-3HF be used in the reaction in order, at the minimum, to mitigate the impact of formation of HOTf on destruction of the structural integrity of Et_3N-3HF.

In fact proton sponge, 1,8-bis-(dimethylamino)-naphthalene, is known to form a

strong 1:1 complex with HF [14], and to effectively steal HF from Et_3N-3HF [15] (Scheme 4). This 1:1 complex is also known to be an effective source of nucleophilic fluoride ion for halogen-exchange reactions of heterocyclic systems [15,16]. Due to the

Scheme 4. Proton sponge – HF complex formation



steric interaction of its basic centers, proton sponge (**PS**) is an exceptionally strong amine base (pK_a = 12.1)[17,18]. It therefore would also act as a great scavenger for the protons of the triflic acid that is formed in the reaction.

2.2.1. Optimization experiments

It was considered that these results were sufficient to allow us to center our attention upon the use of Et_3N-3HF as the most efficient exchange reagent. Further experiments were carried out using Et_3N-3HF to optimize conditions and to test other amines as additives. Proton sponge was considered much too expensive to be used as additive in this reaction, unless it was determined to be absolutely necessary.

In the end, one equivalent of proton sponge proved adequate and two sufficient to obtain good yields (Entries 1-6, Table 2), but it was also found the DMAP (4-

(dimethylamino)pyridine) and TMEDA (1,2-(dimethylamino)ethane) were adequate, but not entirely equivalent replacements for proton sponge. The more reactive, straight-chain bistriflate, nonane-1,1-diyl bis(trifluoromethanesulfonate), (**1b**) was used for these optimization reactions (Scheme 5, Table 2)

Scheme 5. Optimization Experiments - testing various amines as additives

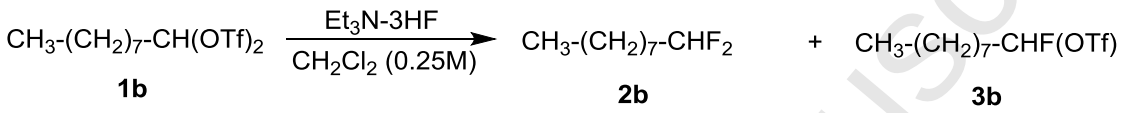


Table 2. Optimization experiments

Entry	Et_3N-3HF (equiv)	Additive (equiv)	Time (h)	Temp (^oC)	**2b** (%)[a]	**3b** (%)[a]
1	5	none	17	rt	66	
2	4	none	2.5	40	81	5
3	1	none	17	0	5	70
4	1	PS (1)	2.5	0	18	58
5	1	PS (1)	17	rt	69	
6	8	PS (1)	17	rt	85	
7	1	PS (2)	2.5	rt	62	
8	2	PS (2)	2.5	rt	80	
9	8	PS (2)	2.5	rt	92	
10	4	DMAP (0.2)	17	rt	81	
11	4	DMAP (2)	2.5	rt	77	
12	8	DMAP (2)	17	rt	87	
13	4	TMEDA (2)	2.5	rt	70	
14	4	TMEDA (0.2)	2,5	rt	44	47
15	4	TMEDA (0.2)	17	rt	86	

[a] NMR yields

2.2.2. Results using optimized method

Considering all information gleaned from the preliminary and optimization experiments, a variety of 1,1-bistriflates were examined under conditions that were chosen in order to provide optimal results for each individual substrate, with the results being given in Table 3 (Scheme 6). The *n*-alkyl 1,1-difluoroalkane products (R = primary) exhibited characteristic triplet of doublet signals at about -116 ppm in their ^{19}F NMR spectra (J_{HF} = 17.5 Hz and 57 Hz), and triplet of triplet signals at 5.8-5.9 ppm in their ^{1}H NMR spectra (J_{FH} = 57 Hz, and J_{HH} = 4.5 Hz), whereas the 2-substituted products (R = secondary) exhibited characteristic doublet of doublet signals at -123 to -124 ppm (J_{HF} = 57 Hz and 16 Hz) in their ^{19}F NMR spectra and triplet of doublet signals at about 5.7 ppm (J_{HF} = 57 Hz and J_{HH} = 1-2 Hz) in their ^{1}H NMR spectra.

The less sterically-hindered, *n*-alkyl 1,1-bistriflates (R = primary) were more reactive than the branched substrates (R = secondary). Arguably, the best results

Scheme 6. Conversion of 1,1-bistriflates to 1,1-difluorides

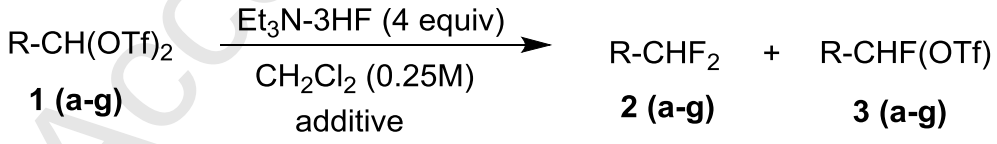


Table 3. Results under optimized conditons

Substr	R	Temp (^{o}C)	Time (hr)	Additive (equiv)	**2** (%)[b]	δ, ^{19}F NMR [Ref]	**3** (%)[b]	δ, ^{19}F NMR
1b	*n*-octyl	rt	17	TMEDA (0.4)	86	-116.2 [6]	0	-129.8, -75.5
1b	*n*-octyl	rt	2.5	PS (2)[a]	92		0	
1b	*n*-octyl	40	2.5	None	81		5	
1c	*n*- hexyl	40	2.5	TMEDA (0.4)	72	-116.2 [19]	0	
1c	*n*- hexyl	rt	2.5	PS (2)[a]	87		0	

1c	*n*- hexyl	40	2.5	None	78		0	
1d	*n*-butyl	40	2.5	TMEDA (0.4)	73	-116.1 [20]	0	
1d	*n*-butyl	rt	2.5	PS (2)[a]	78		0	
1d	*n*-butyl	40	2.5	None	66		0	
1e	$PhCH_2$	40	5	TMEDA (0.4)	76	-115.4 [6]	0	-117.94, -75.4
1e	$PhCH_2$	rt	17	PS (2)[a]	61		0	
1e	$PhCH_2$	40	5	None	67		0	
1a	3-heptyl	rt	40	TMEDA (0.4)	79	-123.3 [6]	0	-125.9, -75.4
1a	3-heptyl	40	5	TMEDA (0.4)	69		0	
1a	3-heptyl	rt	17	PS (2)[a]	60		13	
1a	3-heptyl	40	17	TMEDA (0.4)	73		17	
1f	isopropyl	40	7	TMEDA (0.4)	57	-124.2 [20]	2	
1f	isopropyl	rt	7	PS (2)[a]	66		0	
1f	isopropyl	40	7	TMEDA (0.4)	50		19	
1g	cyclohexyl	40	7	TMEDA (0.4)	79	-123.6 [20]	0	-125.6, -75.4
1g	cyclohexyl	rt	17	PS (2)[a]	79		3	
1g	cyclohexyl	40	17	None	54		4	
1h	*t*-butyl	rt	17	TMEDA (0.4)	0	-128.3 [1,20]	98	-129.8, -75.3
1h	*t*-butyl	60	17	TMEDA (0.4)	35		22	

[a] 8 equiv of Et_3N-3HF used; [b] NMR yields

were generally obtained, when using 2 equivalents of proton sponge as additive, along with 8 equivalents of Et_3N-3HF. Under these conditions 78-92% yields were obtained for *n*-alkyl substrates (**1b-1d**), with 60-79% yields being obtained for the 2-substituted substrates (**1a, f** & **g**). Alternatively, using only 4 equivalents of Et_3N-3HF combined with 0.4 equivalents of TMEDA gave equally good results (72-86% yields for *n*-alkyl substrates (**1b-1d**) and 73-79% yields being obtained for 2-substituted substrates (**1a, f** & **g**)). Competitive results were also obtained for the straight chain, *n*-alkyl 1,1-bistriflate substrates when *no* additive was added (Yields of 66-81%), but all 2-substituted substrates required an additive in order to obtain decent conversions.

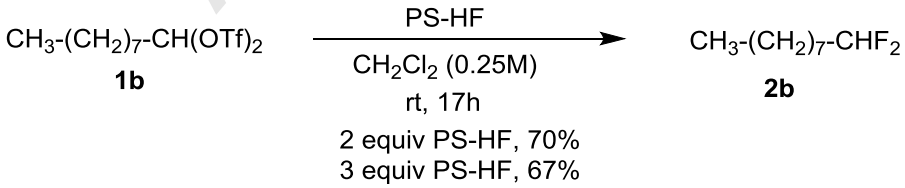
Conditions for at least partial conversion of the neopentyl substrate, **1h**, were able to be found, but heating at 60 ^{o} for 17 hours was required in order to obtain 35% conversion. When the reaction was carried out at room temperature, only the monofluoro product was formed (98%). No rearrangement products were able to be

detected from either this system or any of the other 2-substituted alkyl systems (**1a**, **f**, or **g**). This lack of rearrangement products was surprising, considering the expectation that these reactions, particularly that of the neopentyl substrate, might proceed via a solvolytic process involving carbocations. Apparently all of the observed reactions are proceeding via an S_N2 mechanism.

2.3. Use of pure proton-sponge – HF complex

It had earlier been noted that the 1:1 complex of proton sponge with HF was itself a good nucleophilic source of fluoride anion [15,16]. Indeed Darabantu found that combinations of Et_3N-3HF with **PS** also acted as excellent sources of nucleophilic fluoride anion for use in nucleophilic aromatic substitution reactions of heterocyclic halides [15]. However, to our knowledge no one has reported the use of either **PS-HF** or combinations of Et_3N-3HF as sources of fluoride ion in S_N2 reactions, which is the probable mechanism for the reactions with our bistriflates. It was therefore decided to examine the use of pure **PS-HF** in our bistriflate reaction, with the result (Scheme 7) that use of **PS-HF** alone proved to give results similar, but slightly inferior to those of the Et_3N-3HF/PS mixtures in reactions with *n*-nonyl bistriflate (**1b**).

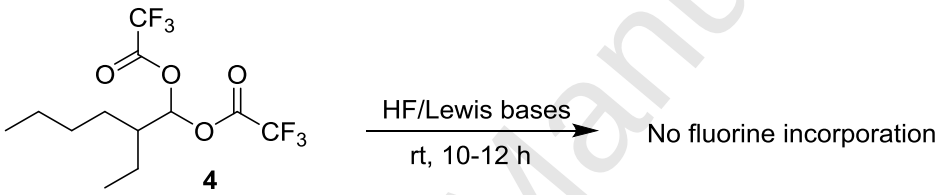
Scheme 7. Use of proton sponge – HF in conversion of bistriflates



2.4. Possible alternative use of 1,1-bis(trifluoroacetates)

A recent report of a ketone acylal, cyclohexane-1,1-diyl bis(trifluoroacetate) being successfully converted to 1,1-difluorocyclohexane using pyridine-HF with catalysis by trifluoroacetic acid [21], led us to also examine and compare the reactivity of an analogous aldehyde acylal, 2-ethylhexane-1,1-diyl bis(trifluoroacetate), (**4**) under various conditions of exchange (Scheme 8).

Scheme 8. 1,1-bistrifluoroacetates unreactive with HF-Lewis base reagents



Bistrifluoroacetate **4** proved to be completely unreactive with any of the HF-Lewis base reagents, with no fluorine incorporation being obtained after stirring overnight at room temperature. Neither addition of catalytic CF_3CO_2H to pyridine-HF, nor addition of proton sponge to Et_3N-3HF led to observable exchange.

3. Conclusions

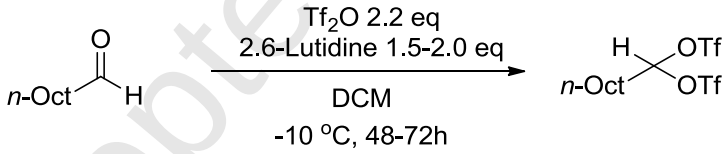
Triethylamine trishydrofluoride proved to be an excellent reagent for the purpose of converting alkane 1,1-bistriflates to the respective 1,1-difluoroalkanes in a process that occurs without observable rearrangement. Thus, this two-step procedure for conversion of aldehydes to 1,1-difluoroalkanes should be considered a good alternative to the use of deoxofluorinating reagents for this purpose.

4. Experimental

4.1. General information

All NMR spectra were run using $CDCl_3$ as solvent, unless otherwise specified. ^{1}H NMR spectra were recorded at 300 MHz, with chemical shifts being reported in ppm downfield relative to TMS. ^{19}F NMR spectra were recorded at 282 MHz, with chemical shifts being reported in ppm downfield relative to $CFCl_3$. ^{13}C NMR spectra were recorded at 75 MHz with proton decoupling, and chemical shifts are reported in ppm downfield relative to TMS. as the reference. All reagents were purchased at commercial quality and were used without further purification.

4.2. Typical procedure for preparation of 1,1-bistriflates. Nonane-1,1-diyl bis(trifluoromethanesulfonate ***(1b)***



A solution of trifluoromethanesulfonic anhydride (4.2 g, 15 mmol) in dichloromethane (5 mL) was slowly added to a stirred solution of nonanal (1.0 g, 7 mmol) and 2.6-lutidine (1.1 g, 10 mmol) in dichloromethane (30 mL) at 0 ^{o}C. After stirring for 5 h, the reaction mixture was sealed and left in a freezer for 48-72 h at -10 ^{o}C, after which time the reaction was complete, as determined by ^{19}F-NMR. The solvent was then removed by rotary evaporation at room temperature and the residue extracted with pentane (2×40 mL). The pentane extract was washed with aqueous 1.0 M hydrochloric acid (50 mL),

saturated sodium bicarbonate solution (50 mL), and brine (50 mL), after which the organic phase was dried with magnesium sulfate and the solvent removed by rotary evaporation at room temperature to obtain a product that required no additional purification before being used in the next step: nonane-1,1-diyl bis(trifluoromethanesulfonate (2.8 g, 6.6 mmol, 94%); ^{1}H NMR, δ 0.87 (t, *J* = 6.8 Hz, 3H), 1.28-1.50 (m, 12H), 2.08-2.15 (m, 2H), 6.48 (t, *J* = 5.1 Hz, 1H); ^{19}F NMR, δ -74.9 (s, 6F).

Proton and fluorine NMR spectra of all bistriflates are included in the Supplementary Data for this paper.

*4.2.1. Heptane-1,1-diyl bis(trifluoromethanesulfonate (**1c)***

^{1}H NMR, δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.28-1.51 (m, 8H), 2.08-2.16 (m, 2H), 6.48 (t, *J* = 5.2 Hz, 1H); ^{19}F NMR, δ -74.9 (s, 6F).

*4.2.2. Pentane-1,1-diyl bis(trifluoromethanesulfonate (**1d)***

^{1}H NMR, δ 0.96 (t, *J* = 7.1 Hz, 3H), 1.41-1.48 (m, 4H); 2.09-2.16 (m, 2H), 6.48 (t, *J* = 5.4 Hz, 1H); ^{19}F NMR, δ -74.9 (s, 6F).

*4.2.3. 2-Phenylethane-1,1-diyl bis(trifluoromethanesulfonate (**1e)***

^{1}H NMR, δ 3.40 (d, *J* = 5.1 Hz, 2H), 6.54 (t, *J* = 5.5 Hz, 1H), 7.23-7.40 (m, 5H); ^{19}F NMR, δ -74.8 (s, 6F) [22] .

*4.2.4. 2-Ethylhexane-1,1-diyl bis(trifluoromethanesulfonate (**1a**)*

^{1}H NMR, δ 0.90-1.05 (m, 6H), 1.34-1.61 (m, 8 H), 1.86-1.91 (m, 1H), 6.52 (d, *J* = 5.4 Hz, 1H); ^{19}F NMR, δ -74.8 (s, 6F).

*4.2.5. Cyclohexylmethane-1,1-diyl bis(trifluoromethanesulfonate (**1f**)*

^{1}H NMR, δ 1.18-1.36 (m, 5H), 1.73-2.05 (m, 6H), 6.31 (d, *J* = 2.4 Hz, 1H); ^{19}F NMR, δ -74.7 (s, 6F).

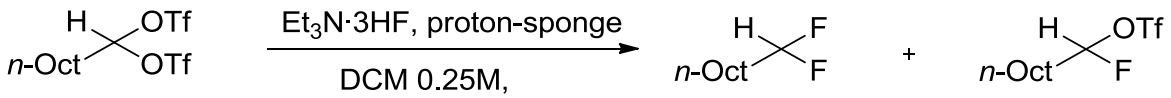
*4.2.6. 2-methylpropane-1,1-diyl bis(trifluoromethanesulfonate (**1g**)*

^{1}H NMR, δ 1.14 (d, *J* = 7.2, 6H), 2.31-2.36 (m, 1H), 6.56 (d, *J* = 3.3, 1H); ^{19}F NMR, δ -74.7 (s, 6F) [12].

*4.2.7. 2,2-Dimethylpropane-1,1-diyl bis(trifluoromethanesulfonate (**1h**)*

^{1}H NMR, δ 1.13 (s, 9H), 6.63 (s, 1H); ^{19}F NMR, δ -74.0 (s, 6F) [22].

*4.3. Typical preparation of 1,1-difluoroalkanes: 1,1-difluorononane **(2b)***



Triethylamine-tris-hydrofluoride, Et_3N-3HF, (7.2 g, 45 mmol) was added to a stirred suspension of proton-sponge (1.50 g, 7 mmol) in dichloromethane (15 mL) at 0 ^{o}C. After stirring this mixture for 10 min. at 0 ℃, a solution of nonane-1,1-diyl bis(trifluoromethanesulfonate (**1b**) (2.4 g, 5.7 mmol) in dichloromethane (5 mL) was slowly added and the mixture stirred for an additional 5.5 h. At that time, 30 mL of pentane was added to the reaction mixture, which was then filtered to remove all solids. To the filtrate was added 30 mL of half-saturated sodium bicarbonate and the mixture was stirred for 20 min at room temperature. The organic layer was then separated, washed with half-saturated sodium hydrogen carbonate, 1.0 M hydrochloric acid (30 mL) and brine (50 mL). The organic phase was dried with magnesium sulfate, and the solvent was removed by a rotary evaporation at room temperature to obtain crude product (1.35 g). The 1,1-difluorononane was purified by column chromatography (silica gel, pentane), with the pentane being removed carefully to provide 0.72 g (77%) of colorless liquid product, **2b** [6,23]: ^{1}H NMR, δ 0.88 (t, J = 6.5 Hz, 3H), 1.28-1.47 (m, 12H), 1.73-1.82 (m, 2H), 5.79 (tt, J = 4.4 and 57 Hz, 1H); ^{19}F NMR, δ -116.2 (td, J = 17.5 and 57 Hz, 2F); ^{13}C NMR, δ 11.2, 13.9, 20.5-20.6 (m, 2C), 22.9, 26.9 (t, J = 4.6 Hz), 29.0, 43.5 (t, J = 18 Hz), 119.2 (t, J = 237 Hz).

Products **2a** and **2b** were satisfactorily isolated in this manner, whereas other products were not isolated, and their yields were obtained solely by ^{19}F NMR. All of the 1,1-difluoro alkane products have been previously prepared, and references to papers containing their earlier-obtained spectral data are provided.

4.3.1. 1,1-difluoroheptane ***(2c)***[19]

^{19}F NMR, δ -116.2 (td, *J* = 17.5 and 57 Hz, 2F).

4.3.2. 1,1-difluoropentane ***(2d)***[20]

^{19}F NMR, δ -116.1 (td, *J* = 17.5 and 57 Hz).

4.3.3. 1,1-difluoro-2-phenylethane ***(2e)***[6]

^{1}H NMR, δ 3.41 (dt, *J* = 4.5 and 18 Hz, 2H), 5.92 (tt, *J* = 4.5 and 57 Hz), 1H), ^{19}F NMR, δ -115.3 (td, *J* = 17.5 and 57 Hz, 2F); ^{13}C NMR, δ 40.9 (t, *J* = 45 Zh), 116.6 (t, *J* = 241 Hz), 127.4, 128.6, 129.8.

4.3.4. 1,1-difluoro-2-ethylhexane ***(2a)***[6,20]

^{1}H NMR, δ 0.91-0.95 (m, 6H), 1.32-1.55 (m, 9H), 5.71 (dt, *J* = 1.4 and 57 Hz, 1H); ^{19}F NMR, δ -123.45 (dd, *J* = 16 and 57 Hz); ^{13}C NMR, δ 14.1, 22.2 (t, *J* = 5.7 Hz), 22.7, 29.1 (m), 29.4, 31.8, 34.1 (t, *J* = 21 Hz), 117.5 (t, *J* = 238 Hz).

4.3.5. (difluoromethyl)cyclohexane ***(2f)***[6,20]

^{1}F NMR, δ –123.6 (dd, *J* = 16 and 57 Hz, 2F).

4.3.6. 1,1-difluoro-2-methylpropane ***(2g)[20]***

^{19}F NMR, δ -124.1 (dd, *J* = 16 and 57 Hz, 2F).

*4.3.7. 1,1-difluoro-2,2-dimethylpropane **(2h)***[1,20]

^{19}F NMR, δ -128.3 (d, *J* = 57 Hz, 2F).

*4.3.8. 1-fluorononanyl trifluoromethanesulfonate (**3b**)*

Under conditions where the partially fluorinated product, 1-fluorononanyl trifluoromethanesulfonate (**3b**) was formed as the major product (Table 2, Entry 3), it was isolated by first washing the reaction mixture sequentially by satd. $NaHCO_3$, 1*N*-HCl, and satd. $NaHCO_3$, which after careful evaporation of the dichloromethane solvent was further purified by silica gel chromatography (pentane): ^{1}H NMR, δ 0.89 (t, *J* = 7.2 Hz, 3H), 1.54 (m, 12H), 1.92-2.02 (m, 2H), 6.13 (td, *J* = 5.2 and 55 Hz, 1H); ^{19}F NMR, δ -75.4 (d, *J* = 7.3 Hz, 3F), -119.2 (m, 1F).

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Appendix A. Supplementary data

Supplementary data associated with this paper, including copies of proton and fluorine NMR spectra of all new compounds, can be found in the online version.

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