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Reductive defluorination of fluoroalkanes

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This paper is dedicated to the memory of Professor Antonio González

Abstract—The reaction of an excess of lithium powder and a catalytic amount of DTBB with primary, secondary and tertiary fluoroalkanes in the presence of a substoichiometric amount of 1,2-bis(trimethylsilyl)benzene **1** afforded the corresponding alkanes resulting from a fluorine–hydrogen exchange. The method could be extended to non-geminal difluorides. The effect of the disilylated compound in the naphthalene-catalysed lithiation of fluorobenzene and benzyl fluoride was also studied. © 2003 Elsevier Science Ltd. All rights reserved.

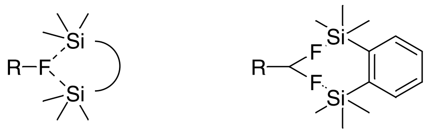
1. Introduction

The carbon–fluorine bond is the strongest one that a carbon atom can form.[1] Consequently, cleavage of this bond is not easy at all, especially in aliphatic derivatives. Defluorination procedures are important from an environmental point of view, due to the problematic degradation of fluoroalkanes in Nature.[2] Apart from methods involving loss of fluorine or hydrogen fluoride giving olefins,[3] most of the defluorination methodologies imply treatment with a metallic catalyst under very drastic reaction conditions.[4] In a few cases, defluorination could be achieved electrochemically,[5] using alkali metals under special conditions,[6] magnesium[7] or lithium aluminium hydride.[8]

On the other hand, in the last few years we have been developing an arene-catalysed lithiation reaction[9–13] which allows the preparation of different organolithium compounds under very mild reaction conditions. Thus, using this methodology, simple organolithium compounds can be prepared from non-halogenated materials[14] as well as functionalised organolithium compounds[15] by chlorine–lithium exchange[12] or by ring-opening of heterocycles.[16] In addition, this lithium activation has also been used for the generation of polylithium synthons[17] and for the activation of other metals,[18] especially nickel.[19] Recently, we have applied the arene-catalysed lithiation for the preparation of aryllithiums[20] or allylic and benzylic organolithium compounds[21] from the corresponding fluorides, working in the second case under Barbier-type reaction conditions.[22] However, when the same process was applied to aliphatic fluorides, the reaction failed, recovering the starting material unchanged. In this paper, we report a variant of the mentioned lithiation procedure which allows the defluorination of aliphatic fluorides under very mild reaction conditions.

2. Results and discussion

Continuing with our studies on the use of fluorocompounds as starting materials in lithiation processes, 1-fluorononane was allowed to react with an excess of lithium in the presence of a catalytic amount of naphthalene, but no reaction was observed after several hours at 20°C. However, we thought that our lithiation methodology could achieve the carbon–fluorine bond cleavage if we could find a good way to activate that bond. Recently, Maruoka et al.[23] reported that different disilylated compounds were able to form stable complexes with the fluoride anion of tetrabutylammonium fluoride via coordination of fluoride ion to both silicon atoms. This article prompted us to test some silicon containing compounds as additives in our lithiation reaction with the hope that they would activate the carbon–fluoride bond and facilitate its reductive cleavage by formation of a type **I** complex (Chart 1).



I **II**

Chart 1.

We started testing 1,2-bis(trimethylsilyl)benzene **1** (Table 1), since a similar compound gave the best results in Maruoka's work. Thus, a mixture of 1-fluorononane (1 mmol) and 1,2-bis(trimethylsilyl)benzene (0.15 mmol)

Keywords: lithium; lithiation; fluoroalkanes; alkyl fluorides; defluorination.

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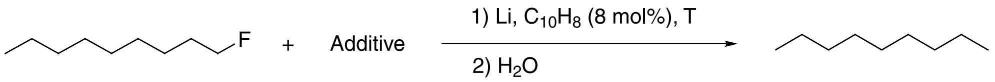
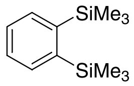
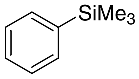
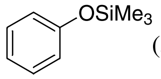
Table 1. Defluorination of 1-fluorononane in the presence of different additives **1**–**5**



Entry	Additive (no.)	Additive[a] (mmol)	T (°C)	t (h)	Yield of nonane (%)[b]	Yield of fluorononane (%)[b]
1	 (**1**)	0.15	0	3.5	64	–
2	$CH_2(SiMe_3)_2$ (**2**)	0.15	20	14	2	84
3	$(CH_2SiMe_3)_2$ (**3**)	0.15	20	18	22	58
4	 (**4**)	0.30	20	19	41	39
5	 (**5**)	0.30	20	19	21	30

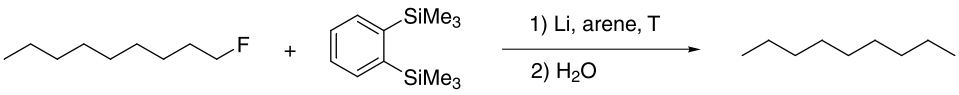
[a] Amounts of reagents used: fluorononane (1 mmol), additive (mmol indicated in the table), lithium (7 mmol), naphthalene (0.16 mmol), THF (7 mL).

[b] Yield determined by quantitative GLC, using commercially available 1-fluorononane, nonane and n-dodecane (internal standard) in the determination of response factors.

was treated with an excess of lithium (1:7 molar ratio) and a substoichiometric amount of naphthalene (1:0.16 molar ratio, 8 mol%) in THF at 0°C. After 3.5 h stirring at this temperature, the starting material was consumed and, after hydrolysis with water, nonane was formed in 64% yield (Table 1, entry 1). Some other silicon containing compounds were tested as additives and the results are collected in Table 1. Commercially available bis(trimethylsilyl)-methane **2** was not effective to promote the defluorination reaction. After 14 h at 20°C, only 2% of nonane was obtained together with 84% of unchanged starting material (Table 1, entry 2). When compound **3** was used as additive, only 3% of nonane was formed after 3 h at 0°C. Additional stirring for 18 h at 20°C led to 22% of nonane together with 58% of unreacted fluorononane. According to these results, it seems that the presence of an aromatic ring in the additive is crucial in order to get good results. It is also very important to have two silicon atoms in the additive in order to get dicoordination to the fluorine atom. When the defluorination was conducted in the presence of trimethylsilylbenzene **4** (0.30 equiv., in order to have the same concentration of silicon atoms), 41% yield of nonane and 39% of unchanged fluorononane were obtained after 19 h at 20°C (Table 1, entry 4). No improvement was observed with additive **5**, which possesses a more electrophilic silicon atom (Table 1, entry 5).

After having established that compound **1** was the best additive, we performed several experiments in order to optimise the reaction conditions (Table 2). First, we studied the effect of the amount of additive used, which was varied from 0.25 to 0.05 equiv. related to fluorononane. Increasing the amount of additive to 0.25 equiv. led to a reduction in the reaction time and a slight increase in yield (Table 2, entry 1), but the amount of by-products formed was higher than in the reaction with 0.15 equiv. of the additive. With 0.10 equiv. of **1**, a very small amount of the starting material did not react and a 48% yield of nonane was obtained after

Table 2. Optimisation of the reaction conditions in the defluorination of 1-fluorononane



1

Entry	**1**[a] (mmol)	Arene (%)	T (°C)	t (h)	Yield of nonane (%)[b]	Yield of fluorononane (%)[b]
1	0.25	$C_{10}H_8$ (**8**)	0	1	70	–
2	0.15	$C_{10}H_8$ (**8**)	0	3.5	64	–
3	0.10	$C_{10}H_8$ (**8**)	0	3.5	48	1
4	0.05	$C_{10}H_8$ (**8**)	0	7	39	21
5	0.15	$C_{10}H_8$ (**8**)	−30 to 0	3.5[c]	76	2
6	0.15	DTBB (**5**)	0	2.5	78	–
7	0.15	DTBB (**5**)	−30 to 0	3.5[c]	77	–
8	0.15	–	20	18	33	45

[a] Amounts of reagents used: fluorononane (1 mmol), additive **1** (mmol indicated in the table), lithium (7 mmol), arene (0.16 mmol of $C_{10}H_8$ or 0.10 mmol of DTBB), THF (7 mL).

[b] Yield determined by quantitative GLC, using commercially available 1-fluorononane, nonane and n-dodecane (internal standard) in the determination of response factors.

[c] The reaction was stirred for 1 h at −30°C and for 2.5 additional hours allowing the temperature to rise from −30 to 0°C.

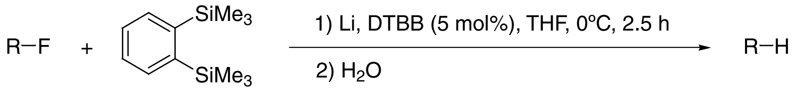
3.5 h at 0°C (Table 2, entry 3). The amount of unreacted fluorononane increased when 0.05 equiv. of **1** were used, even with an extended reaction time (Table 2, entry 4). Since full conversion, a good yield and few by-products were obtained when employing 0.15 equiv. of **1**, we decided to use that amount of additive in future experiments.

Next, the effect of temperature and the electron carrier were studied. When the mixture of lithium, naphthalene, 1-fluorononane and **1** (0.15 equiv.) in THF was stirred at −30°C for 1 h and additional 2.5 h allowing the temperature to rise to 0°C, the yield increased to 76% (Table 2, entry 5). However, 2% of unreacted fluorononane was recovered in this case. Using 4,4′-di-*tert*-butylbiphenyl (DTBB, 5 mol%) instead of naphthalene under the same reaction conditions, full conversion and 77% yield of the defluorination product was obtained (Table 2, entry 7). Finally, when the reaction was run at 0°C for 2.5 h using DTBB as an electron carrier, 78% yield of nonane was obtained and the starting material was not detected (Table 1, entry 6). The need of the use of the electron carrier was also established. No reaction was observed when a mixture of fluorononane, additive **1** and lithium were stirred for 3 h at 0°C. A small amount of defluorination product was formed when the latter reaction was stirred for 18 h at 20°C (Table 2, entry 8). According to the results collected in Table 2, we chose the reaction conditions in entry 6 as the optimal ones.

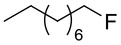
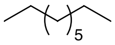
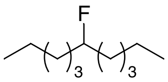
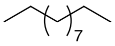
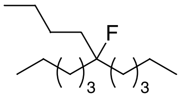
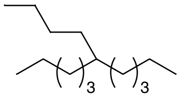
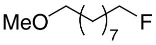
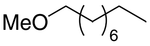
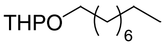
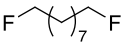
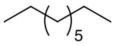
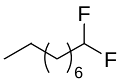
After having determined the optimal reaction conditions, we studied the scope of the defluorination reaction by testing different fluoroalkanes. Primary, secondary and tertiary alkyl fluorides were defluorinated in moderate to good yields when treated with an excess of lithium (1:7 molar ratio) and a catalytic amount of DTBB (1:0.10 molar ratio, 5 mol%) in the presence of additive **1** (Table 3, entries 1–3). In the case of 1-fluorononane, the reaction was complete after 2.5 h at 0°C. However, in reactions with secondary and tertiary alkyl fluorides, **6b** and **6c**, respectively, there was some unreacted starting material after 2.5 h and the defluorination did not proceed further when the reaction was stirred for a longer time. Increasing the amount of additive **1** to 0.25 equiv. led to full conversion of the starting fluoroalkane after 2.5 h at 0°C (Table 3, entries 2 and 3).

The process could be extended to some functionalised fluoroalkanes. Compounds **6d** and **6e** gave the corresponding defluorinated ethers under the optimal reaction conditions in moderate to good yields (Table 3, entries 4 and 5). The reductive defluorination of difluorides **6f** and **6g** was also investigated in order to check if mono- or direduction

Table 3. Reductive defluorination of fluoroalkanes **6** using additive **1**



6 **1** **7**

Entry	Fluoroalkane (no.)	**1**[a] (mmol)	Product (no.)[b]	Yield (%)[c]
1	 **(6a)**	0.15	 **(7a)**	32 (78)[d]
2	 **(6b)**	0.25	 **(7b)**	40[d]
3	 **(6c)**	0.25	 **(7c)**	79
4	 **(6d)**	0.15	 **(7d)**	46
5	 **(6e)**	0.15	 **(7e)**	86
6	 **(6f)**	0.30	 **(7a)**	28[d] (24)[d,e]
7	 **(6g)**	0.30	–[f]	–[f]
8	**6g**	2.00	–[f]	–[f]

[a] Amounts of reagents used: fluoroalkane **6** (1 mmol), additive **1** (mmol indicated in the table), lithium (7 mmol), DTBB (0.10 mmol), THF (7 mL). All reactions were set up as described in Section 4.

[b] All isolated compounds **7** were >95% pure (300 MHz ^{1}H NMR and/or GLC).

[c] Isolated yield after flash chromatography (silica gel, hexane) based on the starting fluoroalkane **6**.

[d] Yield determined by quantitative GLC, using commercially available alkane and *n*-dodecane (internal standard) in the determination of response factors.

[e] In brackets, yield of 1-fluorononane determined by quantitative GLC, using commercially available 1-fluorononane and *n*-dodecane (internal standard) in the determination of response factors.

[f] No reaction occurred.

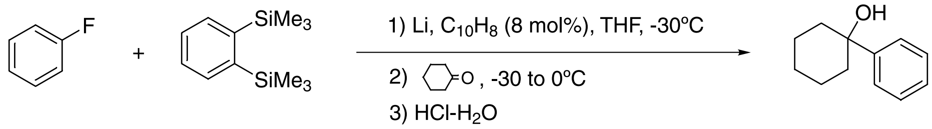
took place. When 1,9-difluorononane **6f** reacted for 2.5 h with an excess of lithium and a catalytic amount of DTBB in the presence of 0.30 equiv. of additive **1**, a mixture of nonane (28%) and 1-fluorononane (24%) was obtained (Table 3, entry 6). The defluorination did not proceed further with a prolonged reaction time. Concerning geminal difluoride **6g**, no reaction was observed under the same reaction conditions as for **6f**, the starting material being quantitatively recovered after work-up (Table 3, entry 7). As it was demonstrated at the beginning of this article, it is necessary to have coordination of fluorine to both silicon atoms of the additive in order for the complex to undergo reductive cleavage of the carbon–fluorine bond. We assume that the lack of reactivity in this case is due to the formation of chelate **II** (Chart 1), in which each fluorine atom is coordinated to only one silicon moiety. We even tried to accomplish the defluorination of **6g** by using 2 equiv. of additive **1**, but no reaction took place after stirring for 4.5 h at 0°C (Table 3, entry 8).

Fluoride **6a** was commercially available and it was used without further purification. The rest of the fluorides were prepared from the corresponding alcohols (for **6b–6f**) or aldehyde (for **6g**) by reaction with either DAST[24a] or bis(2-methoxyethyl)amino sulfur trifluoride[24b] following literature procedures. Secondary (**6b**) and tertiary (**6c**) fluorides showed to be relatively unstable. Hydrogen fluoride elimination took place to some extent when they were stored as pure liquids at room temperature. However, they could be stored for a longer time without apparent decomposition at 4°C in solution in hexane. The best results in defluorination reactions with **6b** and **6c** were obtained with freshly prepared fluorides.

Additive **1** could not be recovered after the defluorination reactions. As the reaction proceeds, it is gradually decomposing into several by-products that could contain trimethylsilyl groups (according to GC–MS), which could not be identified. However, the separation of the desired defluorination product from these by-products could easily be performed by flash chromatography (silica gel, hexane).

We also tried to trap the supposed intermediate organolithium reagent with a carbonyl compound as electrophile. Thus, a mixture of 1-fluorononane (1 mmol), additive **1** (1 mmol) and the electrophile (isobutyraldehyde or 3-pentanone, 1.2 mmol) was reacted with an excess of lithium (1:7 molar ratio) and DTBB (1:0.10 molar ratio, 5 mol%) in THF at 0°C, in a Barbier-type process.[22] After 1.5 h stirring at that temperature, the starting fluoride had disappeared completely and the major reaction product was nonane. The addition product to the electrophile was not detected (GC–MS, ^{1}H NMR). According to these results, it seems that the generated organolithium compound prefers to abstract a proton either from the carbon atom in α position to the carbonyl group of the electrophile or from the reaction medium[25] rather than add to the electrophile. In these tests, we used 1 equiv. of additive **1** in order to get a fast defluorination process, which would diminish the formation of pinacol-type coupling products resulting from the reaction of the electrophile with lithium.

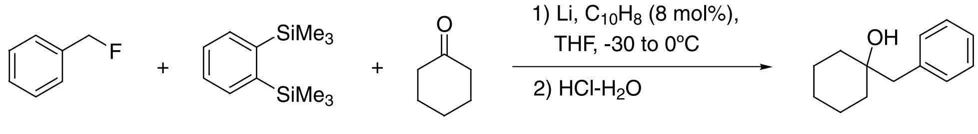
In previous papers, we have been able to prepare organolithium compounds from fluoroarenes[20] and from allylic and benzylic fluorides[21] using our arene-catalysed lithiation procedure. After having demonstrated that additive **1** was able to facilitate the reductive cleavage of the carbon-fluorine bond in fluoroalkanes, we decided to investigate if it could also improve the results we had obtained in the lithiation of aromatic, allylic and benzylic fluorides. Thus, a mixture of fluorobenzene **8** (1 mmol) and additive **1** (0.15 mmol) was treated with an excess of lithium (1:7 molar ratio) and a catalytic amount of naphthalene (1:0.16 molar ratio, 8 mol%) in THF at −30°C. After 30 min, cyclohexanone was added and the reaction was stirred for 3 h allowing the temperature to rise to 0°C. After hydrolysis with water and usual work-up, the expected addition product **9** was isolated in 72% yield (Eq. (1)). A parallel experiment was set up without additive **1**, and the yield was 71%.



8 **1** (0.15 equiv.) **9** (72%)
(71% in the absence of **1**

(1)

On the other hand, naphthalene-catalysed lithiation of a mixture of benzyl fluoride **10** (1 mmol) and additive **1** (0.15 mmol) in the presence of cyclohexanone (1.2 mmol) (Barbier-type reaction conditions) gave the expected product **11** in 43% yield (Eq. (2)). A parallel reaction under the same conditions but in the absence of additive **1** gave compound **11** in 45% yield. According to these results, it seems that the use of the disilylated compound **1** does not cause any effect on the lithiation of both aromatic and benzylic fluorides, probably due to the high rate with which our lithiation procedure is able to cleave the carbon–fluoride bond in those cases.



10 **1** (0.15 equiv.) **11** (43%)
(45% in the absence of **1**

(2)

Concerning the starting fluorides, fluorobenzene **8** was commercially available and benzyl fluoride **10** was prepared as previously described by us.[21]

3. Conclusions

From the results described in this paper, we conclude that disilylated compound **1** is a very efficient additive to promote the reductive cleavage of the carbon–fluorine bond of fluoroalkanes in combination with an excess of lithium and a catalytic amount of an arene. It has been demonstrated that primary, secondary and tertiary monofluorides and non-geminal difluorides can easily be converted into the corresponding defluorinated products in moderate to good yield under mild reaction conditions. Our procedure has shown to be a good alternative for the defluorination methods that have already been reported.

4. Experimental

4.1. General

For general information, see Ref. 26. t_r values are given in min under the conditions described in Ref. 26, unless otherwise stated. Flash chromatography was performed using silica gel 60 of 0.040–0.063 mm. Additives **1** and **2**, fluorides **6a** and **8**, naphthalene, DTBB, cyclohexanone and the starting materials needed for the preparation of fluorides **6b**–**6g** were commercially available (Acros, Aldrich) and were used without further purification. Additives **3**[27] and **5**[28] were prepared according to literature procedures. Additive **4**,[20] benzyl fluoride **10**[21] and lithium powder[26] were prepared as previously reported by us. Commercially available anhydrous THF (99.9%, water content≤0.006%, Acros) was used as solvent in all the lithiation reactions. CH_2Cl_2 was dried by refluxing it with phosphorous pentoxide under Ar and distilled before use.

4.2. Preparation of the required alcohols (precursors of fluorides 6b–6e)

4.2.1. 6-Undecanol. 6-Undecanone (2.0 mL, 9.5 mmol) was dropwise added to a stirred suspension of lithium aluminium hydride (454 mg, 13.0 mmol) in anhydrous THF (10 mL), under Ar, at 0°C. The mixture was stirred for 2 h allowing the temperature to rise to 20°C. Then, the reaction was quenched following a literature procedure.[29] After filtration of the solids, solvent was evaporated (15 Torr) and pure (^{1}H NMR) 6-undecanol was obtained in 90% yield. Physical, spectroscopic and analytical data follow: colourless oil; R_f 0.34 (hexane/ethyl acetate: 4/1); t_r 7.0 [T_{column}=60°C (3 min) and 60–270°C (15°C min^{-1})]; ν (film) 3353 (OH), 1128 cm^{-1} (CO); δ_H 0.91 (6H, t, J=6.7 Hz, 2×Me), 1.19–1.51 (16H, m, 8×CH$_2$), 1.60 (1H, s, OH), 3.53–3.68 (1H, m, CHO); δ_C 14.01 (2C, 2×Me), 22.6 (2C), 25.3 (2C), 31.9 (2C), 35.3 (2C) (8×CH$_2$), 72.0 (CO); m/z 172 (M$^+$, <1%), 101 (43), 83 (100), 57 (15), 56 (11), 55 (86); HRMS: M$^+$, found 172.1789. $C_{11}H_{24}O$ requires 172.1827.

4.2.2. 6-Butyl-6-Undecanol. n-BuLi (6.5 mL 1.6 M solution in hexane, 10.4 mmol) was dropwise added to a stirred solution of 6-undecanone (2.0 mL, 9.5 mmol) in anhydrous THF (10 mL), under Ar, at 0°C. The mixture was stirred for 2 h allowing the temperature to rise to 20°C. Then, water (10 mL) was added and the mixture was extracted with ethyl acetate (3×10 mL). The combined organic phases were washed with water (10 mL) and brine (10 mL) and then dried over magnesium sulfate. After evaporation of the solvents (15 Torr), the resulting residue was purified by column chromatography (silica gel, hexane/ethyl acetate), giving 84% of the titled compound. Physical, spectroscopic and analytical data follow: colourless oil; R_f 0.29 (hexane/ethyl acetate: 9/1); t_r 9.7 [T_{column}=60°C (3 min) and 60–270°C (15 °C min^{-1})]; ν (film) 3456 (OH), 1145 cm^{-1} (CO); δ_H 0.71–0.99 (9H, m, 3×Me), 1.08–1.62 (23H, m, 11×CH$_2$ and OH); δ_C 14.0 (3C, 3×Me), 22.6 (2C), 23.1 (2C), 23.3, 25.65, 32.45 (2C), 38.9, 39.15 (2C) (11×CH$_2$), 74.3 (CO); m/z 210 (M$^+$−H$_2$O, 1%), 158 (10), 157 (100), 97 (17), 83 (43), 71 (13), 69 (53), 58 (22), 57 (39), 56 (17), 55 (99); HRMS: M$^+$−H$_2$O, found 210.2322. $C_{15}H_{30}$ requires 210.2347.

4.2.3. 9-Methoxy-1-nonanol.[30] n-BuLi (6.4 mL 1.7 M solution in hexane, 11.1 mmol) was dropwise added to a stirred solution of 1,9-nonanediol (1.815 g, 11.1 mmol) in THF (20 mL), under Ar, at 0°C. A white solid appeared, which could not be dissolved even after addition of 10 more mL of THF. Methyl iodide (0.7 mL, 12.2 mmol) was added and the reaction was stirred at 20°C for 60 h. Then, water (10 mL) was added and the mixture was extracted with ethyl acetate (3×15 mL). The combined organic phases were washed with water (10 mL) and brine (10 mL) and then dried over magnesium sulfate. Evaporation of the solvents gave a mixture of starting diol, 9-methoxy-1-nonanol and 1,9-dimethoxynonane. Column chromatography of the crude mixture gave the titled compound in 16% yield. Physical and spectroscopic data follow: colourless oil; R_f 0.36 (hexane/ethyl acetate: 1/1); t_r 9.9; ν (film) 3400 (OH), 1117, 1057 cm^{-1} (CO); δ_H 1.04–1.44, 1.47–1.69 [10H and 4H, respectively, 2m, (CH_2)$_7$CO], 1.77 (1H, s, OH), 3.33 (3H, s, Me), 3.37 (2H, t, J=6.6 Hz, CH_2OMe), 3.63 (2H, t, J=6.6 Hz, CH_2OH); δ_C 25.7, 26.1, 29.3, 29.4, 29.5, 29.6, 32.75 [(CH$_2$)$_7$CO], 58.45 (Me), 62.9 (CH$_2$OH), 72.9 (CH$_2$OMe); m/z 125 (M$^+$−H$_2$O−MeOH, <1%), 99 (11), 96 (50), 95 (53), 85 (19), 83 (26), 82 (14), 81 (11), 71 (47), 70 (13), 69 (42), 67 (100), 58 (14), 57 (28), 56 (25), 55 (95), 54 (60), 53 (11).

4.2.4. 9-(Tetrahydro-2-pyranyloxy)-1-nonanol.[31] The title compound was prepared according to a literature procedure.[31] Physical and spectroscopic data follow: greenish oil; R_f 0.47 (hexane/ethyl acetate: 1/1); t_r 13.8; ν (film) 3410 (OH), 1128, 1071, 1030 cm^{-1} (CO); δ_H 1.00–1.37, 1.40–1.89 [10H each, 2m, (CH_2)$_7$CO and (CH_2)$_3$CH], 2.10 (1H, s, OH), 3.25–3.38, 3.40–3.50, 3.62–3.74, 3.76–3.94 (1H each, 4m, 2×CH_2OCH), 3.56 (2H, t, J=6.7 Hz, CH_2OH), 4.48–4.60 (1H, m, CH); δ_C 19.5, 25.35, 25.6, 26.05, 29.2, 29.25, 29.4, 29.6, 30.65, 32.65 [(CH$_2$)$_7$CO and (CH$_2$)$_3$CH], 62.15, 62.7, 67.55 (3×CH$_2$O), 98.7 (CH); m/z 244 (M$^+$, <1%), 101 (20), 85 (100), 84 (11), 83 (17), 69 (29), 67 (12), 57 (14), 56 (20), 55 (34).

4.3. Synthesis of fluorides 6b–6e using DAST as fluorinating agent: general procedure[24a]

To a solution of DAST (0.41 mL, 3.1 mmol) in dry CH_2Cl_2

(3 mL), under Ar, at −78°C, the solution of the corresponding alcohol (3.1 mmol) was dropwise added (ca. 10 min). The reaction was stirred for ca. 5 h allowing the temperature to rise to 20°C. After hydrolysis with water (5 mL) at 0°C, the organic phase was separated, diluted with CH_2Cl_2 (10 mL), washed with water (3×5 mL) and dried over magnesium sulfate. Solvent was evaporated (15 Torr) and the resulting residue was purified by column chromatography (silica gel, hexane), affording the expected fluoride in the following yields: **6b** (50%), **6c** (42%), **6d** (44%) and **6e** (40%). Physical, spectroscopic and analytical data follow.

4.3.1. 6-Fluoroundecane (6b). Colourless oil; t_r 5.4 [T_{column}=60°C (3 min) and 60–270°C (15°C min^{-1})]; ν (film) 1015 cm^{-1} (CF); δ_H 0.92 (6H, t, J=6.4 Hz, 2×Me), 1.23–1.77 (16H, m, 8×CH_2), 4.35–4.49, 4.51–4.69 (1H, m, CHF); δ_C 13.95 (2C, 2×Me), 22.55 (2C), 31.7 (2C) [2×Me(CH_2)$_2$], 24.8 (2C, d, J=4.4 Hz, 2×CH_2CH_2CF), 35.1 (2C, d, J=20.8 Hz, 2×CH_2CF), 94.6 (d, J=165.8 Hz, CF); m/z 154 (M^+−HF, 2%), 126 (11), 111 (23), 98 (22), 97 (43), 84 (36), 83 (45), 82 (12), 71 (18), 70 (82), 69 (71), 61 (13), 59 (10), 57 (57), 56 (98), 55 (100); HRMS: M^+−HF, found 154.1752. $C_{11}H_{22}$ requires 154.1721.

4.3.2. 6-Butyl-6-fluoroundecane (6c). Colourless oil; t_r 8.8 [T_{column}=60°C (3 min) and 60–270°C (15°C min^{-1})]; ν (film) 1056 cm^{-1} (CF); δ_H 0.79–1.04 (9H, m, 3×Me), 1.22–1.44 [16H, m, 2×Me(CH_2)$_3$$CH_2CF$ and Me(CH_2)$_2$-CH_2CF], 1.50–1.71 (6H, m, 3×CH_2CF); δ_C 14.0 (3C, 3×Me), 22.6 (3C, 3×MeCH_2), 23.0 (d, J=5.5 Hz, $MeCH_2$-CH_2CH_2CF), 25.55 (2C, d, J=5.5 Hz, 2×$MeCH_2CH_2CH_2$-CH_2CF), 32.3 (2C, 2×$MeCH_2CH_2CH_2CH_2CF$), 36.75 (d, J=23.1 Hz, $MeCH_2CH_2CH_2CF$), 37.0 (2C, d, J=23.0 Hz, 2×$MeCH_2CH_2CH_2CH_2CF$), 99.3 (d, J=169.1 Hz, CF); m/z 210 (M^+−HF, 2%), 158 (13), 111 (11), 97 (70), 83 (100), 71 (12), 69 (52), 57 (33), 56 (14), 55 (54); M^+−HF, found 210.2355. $C_{15}H_{30}$ requires 210.2347.

4.3.3. 9-Fluorononyl methyl ether (6d). Colourless oil; R_f 0.45 (hexane/ethyl acetate: 4/1); t_r 7.7; ν (film) 1127, 1043 cm^{-1} (CO and CF); δ_H 1.22–1.49, 1.50–1.85 [10H and 4H, respectively, 2m, (CH_2)$_7$CO], 3.31 (3H, s, Me), 3.35 (2H, t, J=6.6 Hz, CH_2O), 4.41 (2H, dt, J=47.3, 6.2 Hz, CH_2F); δ_C 26.05, 29.1, 29.35, 29.4, 29.6 [(CH_2)$_5$CO], 25.05 (d, J=5.5 Hz, CH_2CH_2CF), 30.35 (d, J=19.8 Hz, CH_2CF), 58.45 (Me), 72.9 (CH_2O), 84.1 (d, J=163.6 Hz, CF); m/z 144 (M^+−MeOH, 18%), 116 (53), 102 (13), 97 (11), 96 (14), 95 (19), 88 (46), 83 (42), 82 (45), 81 (37), 74 (21), 71 (11), 70 (50), 69 (67), 68 (58), 67 (28), 59 (12), 57 (18), 56 (57), 55 (100), 54 (31), 53 (12); HRMS: M^+−MeOH, found 144.1333. $C_9H_{17}F$ requires 144.1314.

4.3.4. 2-(9-Fluorononyloxy)tetrahydropyran (6e). Greenish oil; R_f 0.49 (hexane/ethyl acetate: 4/1); t_r 12.3; ν (film) 1129, 1073, 1031 cm^{-1} (CO and CF); δ_H 1.04–1.95 [20H, m, (CH_2)$_7$CF and (CH_2)$_3$CH], 3.32–3.45, 3.46–3.58, 3.68–3.81, 3.83–3.95 (1H each, 4m, 2×CH_2O), 4.42 (2H, dt, J=47.3, 6.2 Hz, CH_2F), 4.55–4.66 (1H, m, CH); δ_C 19.65, 25.45, 26.15, 29.15, 29.35, 29.4, 29.7, 30.75 [(CH_2)$_5$CO and (CH_2)$_3$CH], 25.1 (d, J=5.5 Hz, CH_2CH_2CF), 30.35 (d, J=19.8 Hz, CH_2CF), 62.3, 67.6 (2×CH_2O), 84.2 (d, J=163.6 Hz, CF), 98.7 (CH); m/z 246 (M^+, <1%), 101 (10), 85 (100), 84 (10), 69 (29), 57 (20), 56 (29), 55 (23); HRMS: M^+, found 246.1976. $C_{14}H_{27}FO_2$ requires 246.1995.

4.4. Preparation of fluorides 6f and 6g using bis(2-methoxyethyl)amino sulfur trifluoride as fluorinating agent[24b]

4.4.1. 1,9-Difluorononane (6f).[32] A solution of bis(2-methoxyethyl)amino sulfur trifluoride (1.7 mL, 9.2 mmol) in CH_2Cl_2 (2 mL) was dropwise added to a solution of 1,9-nonanediol (1.512 g, 9.3 mmol) in dry CH_2Cl_2 (6 mL), under Ar, at −78°C (on cooling the latter solution to −78°C, it became solid). The reaction mixture was stirred for ca. 5 h allowing the temperature to rise to 20°C. Then, a saturated aqueous solution of $NaHCO_3$ was slowly added until the gas evolution ceased. Layers were separated and the aqueous phase was extracted with CH_2Cl_2 (3×15 mL). The combined organic phases were dried over magnesium sulfate. After evaporation of the solvent (15 Torr), the resulting residue was purified by column chromatography (silica gel, hexane), giving difluoride **6f** in 10% yield. Physical and spectroscopic data follow: colourless oil; t_r 4.4 [T_{column}=60°C (3 min) and 60–270°C (15°C min^{-1})]; ν (film) 1048 cm^{-1} (CF); δ_H 1.17–1.51 [10H, m, (CH_2)$_5$$CH_2CF$], 1.59–1.81 (4H, m, 2×$CH_2CF$), 4.42 (4H, dt, J=47.5, 6.2 Hz, 2×CH_2F); δ_C 25.1 (2C, d, J=5.5 Hz, 2×CH_2CH_2-CF), 29.1 (2C, 2×$CH_2CH_2CH_2CF$), 29.35 [CH_2(CH_2)$_3$CF], 30.35 (2C, d, J=18.7 Hz, 2×CH_2CF), 84.1 (2C, d, J=164.7 Hz, 2×CF); m/z 144 (M^+−HF, <1%), 88 (14), 83 (28), 74 (17), 70 (22), 69 (58), 67 (12), 61 (31), 59 (13), 57 (20), 56 (38), 55 (100).

4.4.2. 1,1-Difluorononane (6g). To a solution of nonanal (5.4 mL, 30.0 mmol) in dry CH_2Cl_2 (10 mL), under Ar, at 20°C was successively added a solution of bis(2-methoxyethyl)amino sulfur trifluoride (9.4 mL, 51.0 mmol) in dry CH_2Cl_2 (6 mL) and absolute ethanol (0.35 mL, 6.0 mmol). The reaction mixture was stirred for 4.5 h at 20°C and then it was quenched and worked-up as described above for 1,9-difluorononane. Purification of the crude residue by column chromatography (silica gel, hexane) afforded difluoride **6g** in 38% yield. Physical, spectroscopic and analytical data follow: colourless oil; t_r 2.6 [T_{column}=60°C (3 min) and 60–270°C (15°C min^{-1})]; ν (film) 1048 cm^{-1} (CF); δ_H 0.89 (3H, t, J=6.6 Hz, Me), 1.05–1.57 [12H, m, Me(CH_2)$_6$], 1.69–1.92 (2H, m, CH_2CF), 5.78 (1H, tt, J=57.0, 4.5 Hz, CHF); δ_C 14.05 (Me), 22.65, 29.35, 31.6, 31.8 [Me(CH_2)$_4$], 22.15 (t, J=5.5 Hz, CH_2CH_2CF), 28.95–29.2 (m, CH_2CH_2-CH_2CF), 34.15 (t, J=20.3 Hz, CH_2CF), 117.5 (t, J=238.2 Hz, CF_2); m/z 164 (M^+, 2%), 98 (15), 95 (23), 87 (12), 85 (26), 83 (12), 82 (28), 81 (20), 73 (32), 71 (65), 70 (38), 69 (28), 68 (13), 67 (13), 61 (16), 59 (22), 57 (100), 56 (51), 55 (79), 53 (13), 51 (20). HRMS: M^+, found 164.1375. $C_9H_{18}F_2$ requires 164.1377.

4.5. DTBB catalysed defluorination of fluorides 6 in the presence of additive 1. Isolation of compounds 7: general procedure

To a green suspension of lithium powder (50 mg, 7.2 mmol) and DTBB (27 mg, 0.10 mmol), under Ar, at 0°C, was dropwise added a solution of the corresponding fluoride **6**

(1.0 mmol) and additive **1** [0.15 mmol (for **6a**, **6d** and **6e**), 0.25 mmol (for **6b** and **6c**) or 0.30 mmol (for **6f** and **6g**)] in THF (2 mL). After 2.5 h stirring at 0°C, the reaction was hydrolysed with water (5 mL) at the same temperature and acidified with 2 M HCl (5 mL). The mixture was extracted with ethyl acetate (3×15 mL) and the combined organic phases were washed with saturated aqueous $NaHCO_3$ (5 mL), water (5 mL) and brine (5 mL), being then dried over magnesium sulfate. After evaporation of the solvents (15 Torr), the resulting residue was purified by flash chromatography [silica gel, hexane (for **7a**–**7c**) or hexane/ethyl acetate (for **7d**, **7e**)], affording the expected products in the yields indicated in Table 3. Compounds **7a** and **7b** were characterized by comparison with authentic samples (commercially available). For compounds **7c**–**7e**, physical, spectroscopic and analytical (for **7c**) data follow.

4.5.1. 6-Butylundecane (7c). Colourless oil; t_r 8.2 [T_{column}=60°C (3 min) and 60–270°C (15°C min^{-1})]; ν (film) 2957, 2926, 2858, 1466, 1378 cm^{-1} (CH); δ_H 0.89 (9H, t, J=6.9 Hz, 3×Me), 1.09–1.49 (23H, m, 11×CH_2 and CH); δ_C 14.15 (3C, 3×Me), 22.75 (2C), 23.2, 26.4 (2C), 29.0, 32.45 (2C), 33.4, 33.7 (2C) (11×CH_2), 37.4 (CH); m/z 212 (M^+, <1%), 154 (13), 140 (29), 99 (15), 85 (59), 71 (57), 57 (100), 56 (14), 55 (25); M^+, found 212.2486. $C_{15}H_{32}$ requires 212.2504.

4.5.2. Methyl nonyl ether (7d).[33] Colourless oil; R_f 0.59 (hexane/ethyl acetate: 4/1); t_r 6.5; ν (film) 1120, 1031 cm^{-1} (CO); δ_H 0.87 (3H, t, J=6.7 Hz, $MeCH_2$), 1.15–1.46, 1.49–1.68 [10H and 4H, respectively, 2m, $(CH_2)_7Me$], 3.32 (3H, s, MeO), 3.36 (2H, t, J=6.6 Hz, CH_2O); δ_C 14.05 ($MeCH_2$), 22.65, 26.15, 29.25, 29.5, 29.55, 29.65, 31.85, [$(CH_2)_7Me$], 58.45 (MeO), 72.95 (CH_2O); m/z 158 (M^+, <1%), 126 (37), 98 (43), 97 (37), 84 (29), 83 (45), 82 (20), 71 (15), 70 (76), 69 (60), 68 (28), 57 (30), 56 (100), 55 (70).

4.5.3. 2-Nonyloxytetrahydropyran (7e).[34] Greenish oil; R_f 0.60 (hexane/ethyl acetate: 4/1); t_r 11.5; ν (film) 1128, 1076, 1032 cm^{-1} (CO); δ_H 0.86 (3H, t, J=6.5 Hz, Me), 1.01–1.95 [20H, m, $Me(CH_2)_7$ and $(CH_2)_3CH$], 3.32–3.46, 3.47–3.59, 3.69–3.81, 3.83–3.96 (1H each, 4m, 2×CH_2O), 4.55–4.67 (1H, m, CH); δ_C 14.05 (Me), 19.65, 22.6, 25.5, 26.2, 29.25, 29.45, 29.5, 29.7, 30.75, 31.85 [$Me(CH_2)_7$ and $(CH_2)_3CH$], 62.25, 67.65 (2×CH_2O), 98.7 (CH); m/z 228 (M^+, <1%), 85 (100), 84 (11), 71 (11), 57 (19), 56 (27), 55 (18).

4.6. Naphthalene-catalysed lithiation of fluorobenzene 8 in the presence of additive 1

To a green suspension of lithium powder (70 mg, 10.0 mmol) and naphthalene (20 mg, 0.16 mmol) in THF (5 mL), under Ar, at −30°C, was dropwise added (ca. 20 min) a solution of fluorobenzene **8** (1.0 mmol) and additive **1** (38 μL, 0.15 mmol) in THF (2 mL). After 15 min stirring at the same temperature [the starting material was consumed (GLC)], cyclohexanone (0.13 mL, 1.2 mmol) was added and the mixture was stirred for ca. 3 h allowing the temperature to rise to 0°C. The resulting mixture was then hydrolysed with water (10 mL), acidified with 2 M HCl and extracted with ethyl acetate (3×20 mL). The organic layers were successively washed with a saturated solution of $NaHCO_3$ (5 mL), water (5 mL) and brine (5 mL), being then dried over sodium sulfate. After evaporation of the solvents (15 Torr), the resulting residue was purified by column chromatography (silica gel, hexane/ethyl acetate) giving compound **9** in 72% yield. Another reaction that was set up in parallel in the absence of additive **1** gave 71% yield of the expected product. Compound **9**, previously prepared in our laboratory,[35] was characterised by comparison of its physical and spectroscopic data with an authentic sample.

4.7. Naphthalene-catalysed lithiation of benzyl fluoride 10 in the presence of additive 1 and cyclohexanone

To a green suspension of lithium powder (70 mg, 10.0 mmol) and naphthalene (20 mg, 0.16 mmol) in THF (5 mL), under Ar, at −30°C, was dropwise added (ca. 20 min) a solution of fluoride **10** (1.0 mmol), additive **1** (38 μL, 0.15 mmol) and cyclohexanone (0.13 mL, 1.2 mmol) in THF (2 mL). The mixture was stirred for ca. 3 h allowing the temperature to rise to 0°C. The reaction was then hydrolysed with water (10 mL), acidified with 2 M HCl and extracted with ethyl acetate (3×20 mL). The combined organic layers were successively washed with a saturated solution of $NaHCO_3$ (5 mL), water (5 mL) and brine (5 mL), being then dried over sodium sulfate. After evaporation of the solvents (15 Torr), the resulting residue was purified by column chromatography (silica gel, hexane/ethyl acetate), affording compound **11** in 43% yield. Another reaction that was set up in parallel in the absence of additive **1** gave 45% yield of the expected product. Compound **11**, previously prepared in our laboratory,[36] was characterised by comparison of its physical and spectroscopic data with an authentic sample.

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