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Deoxofluorination Reactions Using *N*,*N*-Disubstituted Aminodifluorosulfinium Tetrafluoroborate Salts

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ABSTRACT

The synthesis of *N*,*N*-disubstituted aminodifluorosulfinium tetrafluoroborate salts is reported, and their behavior as deoxofluorinating agent was evaluated. The deoxofluorination reactions were performed using a primary alcohol, a secondary alcohol and a ketone. Results show that subtle modification of the structure of the reagents can noticeably affect the reactivity and the selectivity in deoxofluorination reactions.

1. Introduction

The deoxofluorination reaction is one of the most effective approaches for the introduction of a fluorine atom into organic compounds. This transformation allows the direct conversion of an hydroxyl to a fluoride, a carbonyl group to a difluoromethylene, and a carboxylic acid to an acyl fluoride (or a trifluoromethyl in certain cases) (Fig. 1) [1,2].

Numerous reagents are able to perform deoxofluorination reactions on one, two or all of the above substrates including SF_4 [3], DAST (diethylaminosulfur trifluoride) [4], Deoxo-Fluor® (bis(2-methoxyethyl)aminosulfur trifluoride) [5], Yarovenko's reagent (*N*,*N*-diethyl-2-chloro-1,1,2-trifluoroethylamine) [6], Ishikawa's reagent (*N*,*N*-diethyl-1,1,2,3,3,3-hexafluoropropylamine) [7], TFEDMA (1,1,2,2-tetrafluoroethyl-*N*,*N*-dimethylamine) [8], DFI (2,2-difluoro-1,3-dimethylimidazolidine) [9], PBSF (perfluoro-1-butanesulfonyl fluoride) [10], Fluolead™ (4-*tert*-butyl-2,6-dimethylphenylsulfur trifluoride) [11], arylsulfur chlorotetrafluorides [12], and PhenoFluor™ (1,3-bis(2,6-diisopropylphenyl)-2,2-difluoro-2,3-dihydro-1*H*-imidazole) [13]. Among these, DAST and Deoxo-Fluor® are the most commonly used [2,14].

Recently, *N*,*N*-disubstituted aminodifluorosulfinium tetrafluoroborate salts, in particular *N*,*N*-diethylaminodifluorosulfinium tetrafluoroborate (XtalFluor-E®) and morpholinodifluorosulfinium tetrafluoroborate (XtalFluor-M®) have been reported as safer alternatives to DAST and Deoxo-Fluor® [15]. Indeed, these crystalline fluorinating agents are more easily handled and significantly more stable than DAST and its analogs. This is particularly true for DAST which is a thermally unstable and highly explosive liquid. While XtalFluor-E® and XtalFluor-M® are structurally related, those reagents have slightly different properties brought by the alkyl substituents on the amino group (diethyl *vs.* morpholino). For instance, in terms of stability, DSC analysis revealed that XtalFluor-E® had a decomposition temperature (T_{max}) at 205 °C with an exothermic heat ($-\Delta H$) of 1260 J/g while XtalFluor-M® had a T_{max} of 243 °C with a $-\Delta H$ = 773 J/g. In terms of reactivity, one or the other sometimes behaves better (yield and/or selectivity) [15]. With these results in mind, we became interested in evaluating the effect of other substituents on the amino moiety. Herein, we report the synthesis of three novel *N*,*N*-disubstituted aminodifluorosulfinium tetrafluoroborates (Fig. 2, compounds **1**–**3**) and their behavior in deoxofluorination reaction of various substrates.

2. Results and discussion

The synthesis of the new derivatives is shown in Scheme 1 [16]. First, pyrrolidine was converted to *N*-(trimethylsilyl)pyrrolidine in

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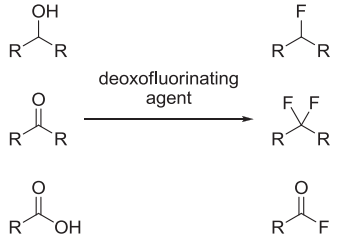


Fig. 1. Deoxofluorination reaction.

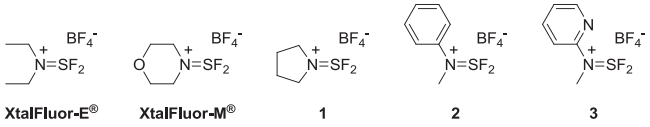
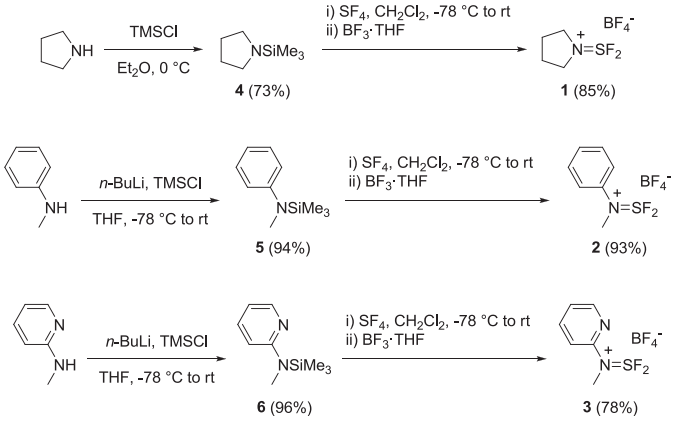


Fig. 2. *NN*-disubstituted aminodifluorosulfinium tetrafluoroborate salts under study.

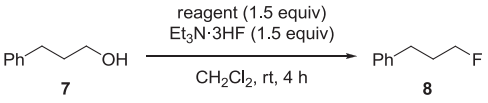


Scheme 1. Synthesis of *N,N*-disubstituted aminodifluorosulfinium tetrafluoroborate salts.

73% yield [17,18]. Reaction with SF_4 produced pyrrolidinosulfur trifluoride which was treated with BF_3·THF to generate **1** as the tetrafluoroborate salt in 85% yield [15]. Derivatives **2** and **3** were prepared in similar fashion by reacting *N*-methyl-*N*-(trimethylsilyl)aniline **5** [19] and *N*-trimethylsilyl-*N*-methyl-pyridin-2-amine **6** with SF_4 followed by treatment with BF_3·THF. In both cases, the aminodifluorosulfinium tetrafluoroborate salts **2** and **3** were obtained in good to excellent yields.

With the new reagents in hand, their reactivity in deoxofluorination reactions with a primary (Table 1), a secondary alcohol (Table 2), and a ketone (Table 3) was evaluated. In all cases, their reactivity and selectivity was compared to XtalFluor-E® and XtalFluor-M®.

Table 1
Deoxofluorination of a primary alcohol, 3-phenyl-1-propanol (**7**).



Entry	Reagent	Yield (%)[a]
1	XtalFluor-E®	88 (85)[b]
2	XtalFluor-M®	90
3	**1**	80
4	**2**	53
5	**3**	58

[a] Determined by ^{19}F and/or ^{1}H NMR analysis of the crude mixture using trifluoroethanol as an internal standard.
[b] Isolated yield, see Ref. [15]

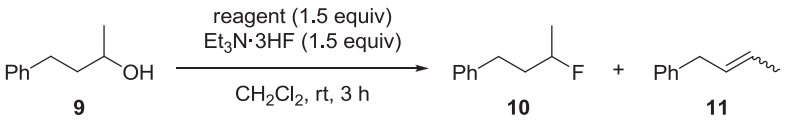
Hydrocinnamyl alcohol (**7**) was chosen as the model for a primary alcohol. As seen in Table 1, while XtalFluor-E® and XtalFluor-M® provided under standard conditions the desired alkyl fluoride **8** in excellent NMR yields (88 and 90% respectively), the other reagents, with the exception of **1** (entry 3) performed unsatisfactorily (53–58%). While in all cases, less than 6% of the starting alcohol (typically 1–2%) was left unreacted, NMR analysis of the reactions with reagents **2**–**3** showed significantly more side-products.

We next turned our attention to a secondary alcohol, 4-phenylbutan-2-ol (**9**) since while with primary alcohol elimination is rarely observed, this side-reaction may become a competitive pathway with secondary alcohols. As such, we expected to detect the desired secondary fluoride **10** [15] with more or less of alkene **11** [20] (Table 2). Indeed, reaction of XtalFluor-E® and XtalFluor-M® gave **10** as the major product in moderate NMR yields (59–66%) along with *ca.* 17% of alkene **11**. A similar result was obtained with reagents **1** and **3** (entry 3 and 5). Notably, with reagent **2**, the presence of the alkene side-product was barely detectable (entry 4).

Finally, we investigated the deoxofluorination of a cyclic ketone, 1,4-dioxaspiro[4.5]decan-8-one (**12**), as six-membered ring systems are more prone to elimination [15]. In this case, we expected to observe fluoroalkene **14** [21,22], along with the desired difluoromethylene compound **13** [15,22] (Table 3). Reaction of both XtalFluor-E® and XtalFluor-M® provided **13** as the major product in moderate NMR yields (57–66%) along with *ca.* 10% of the fluoroalkene **14**. Reagents **1** (entry 3) and **3** (entry 5) behave similarly providing **13** in *ca.* 60% NMR yield along with *ca.* 10% of **14**. Interestingly, while reagent **2** provided compound **13** in a lower yield (45%), only trace amount of **14** were detected (entry 4).

In conclusion, we have reported the synthesis of novel *N,N*-disubstituted aminodifluorosulfinium tetrafluoroborate salts, and their behavior as deoxofluorinating agent was examined. The

Table 2
Deoxofluorination of a secondary alcohol, 4-phenylbutan-2-ol (**9**).



Entry	Reagent	Yield of **10** (%)[a]	Yield of **11** (%)[a]
1	XtalFluor-E®	66	16
2	XtalFluor-M®	59	18
3	**1**	64	14
4	**2**	52	3
5	**3**	72	16

[a] Determined by ^{19}F and/or ^{1}H NMR analysis of the crude mixture using trifluoroethanol as an internal standard.

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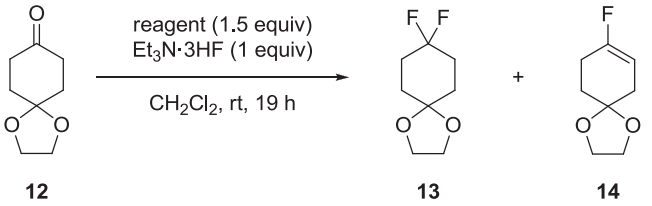
Table 3
Deoxofluorination of a ketone, 1,4-dioxaspiro[4.5]decan-8-one (**12**).



12 **13** **14**

Entry	Reagent	Yield of **13** (%)[a]	Yield of **14** (%)[a]
1	XtalFluor-E®	57	8
2	XtalFluor-M®	66 (76)[b]	11
3	**1**	60	12
4	**2**	45	<3
5	**3**	58	9

[a] Determined by ^{19}F and/or ^{1}H NMR analysis of the crude mixture using 2-fluoro-4-nitrotoluene as an internal standard.
[b] Isolated yield under slightly different conditions with no elimination observed, see Ref. [15].

results showed that subtle modification of the structure of the *N,N*-disubstituted aminodifluorosulfinium tetrafluoroborate salts can modify their reactivity and selectivity in deoxofluorination reactions of alcohol (primary and secondary) or ketones. However, while the new derivatives proved not to be superior to XtalFluor-E® and XtalFluor-M® in terms of deoxofluorinating capability, reagent **2**, *N*-methyl-*N*-phenylaminodifluorosulfinium tetrafluoroborate salt, showed promising results for reducing the elimination side-reaction with secondary alcohols and ketones.

3. Experimental

All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions. ^{1}H, ^{13}C and ^{19}F spectra were recorded on a VARIAN Inova 400 or a BRUKER Advance 300 in $CDCl_3$ or CD_3CN at ambient temperature. Infrared spectra were recorded on a Thermo Scientific Nicolet 380 FT-IR spectrometer. High-resolution mass spectra were obtained on a LC/MS-TOF Agilent 6210 using electrospray ionization (ESI) [23]. XtalFluor-E® and Xtalfluor-M® were obtained from Aldrich. The *N,N*-disubstitutedaminodifluorosulfinium tetrafluoroborate salts **1–3** were synthesized by Manchester Organics Limited (UK).

3.1. Preparation of the N,N-disubstitutedaminodifluorosulfinium tetrafluoroborate salts

3.1.1. Preparation of pyrrolidinodifluorosulfinium tetrafluoroborate salt (*1*)

To an ice-cold solution of pyrrolidine (167 mL, 2.00 mol) in diethyl ether (500 mL) was added a solution of chlorotrimethylsilane (127 mL, 1.00 mol) in diethyl ether (100 mL) over 1 h. The solid was removed by filtration and washed with diethyl ether (100 mL). The filtrates were concentrated *in vacuo* then distilled at atmospheric pressure to give *N*-trimethylsilylpyrrolidine [17] (104 g, 73%) as a colorless liquid. b.p. 139–140 °C; ^{1}H NMR ($CDCl_3$) δ 2.91 (m, 4H), 1.74 (m, 4H), 0.09 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 48.33, 28.26, 3.50. To a 5 L flange necked flask fitted with magnetic stirrer, temp probe, bubbler and nitrogen inlet was added dichloromethane (150 mL) and then cooled to −78 °C. Sulfur tetrafluoride (70.6 g, 0.65 mol) was sub-surfaced while keeping the temperature below −65 °C. To the resulting solution was added dropwise a solution of *N*-trimethylsilylpyrrolidine (90 g, 0.62 mol) in dichloromethane (42 mL) while keeping the temperature below −60 °C. The resulting solution was allowed to slowly warm to room temperature and stirred overnight. To the resulting solution was added dichloromethane (558 mL) followed by boron trifluoride tetrahydrofuran complex (69 mL, 0.63 mol) dropwise over 1 h keeping the temperature below 25 °C. The suspension was stirred an additional 60 min, then filtered under a blanket of nitrogen. The solid material was rinsed with diethyl ether (3 × 150 mL), then dried under vacuum to provide pyrrolidinodifluorosulfinium tetrafluoroborate (121 g, 85%) as beige crystals: m.p. 105–113 °C; IR (ATR, ZnSe) ν = 1459, 1269, 1216, 1019, 822, 755 cm^{-1}; ^{1}H NMR (CD_3CN) δ 4.10–3.98 (m, 4H), 2.19–2.12 (m, 4H); ^{13}C NMR (CD_3CN) δ 53.1, 25.9; ^{19}F NMR (CD_3CN) δ 12.09 (q, 2F, J = 7.6 Hz), −151.26 (s, 4F); HRMS-ESI calcd for $C_4H_8NSF_2$ $[M]^{*+}$ 140.0346, found 140.0340.

3.1.2. Preparation of N-methyl-N-phenylaminodifluorosulfinium tetrafluoroborate salt (*2*)

To a stirring solution of *N*-methylaniline (80 g, 0.75 mol) in diethyl ether (600 mL) cooled at −78 °C was added *n*-butyllithium (2.4 M in hexane; 342 mL, 0.82 mol) keeping the temperature below −60 °C. The resulting slurry was stirred for 1 h then chlorotrimethylsilane (114 mL, 0.90 mol) was added while keeping the temperature below −70 °C. The reaction was allowed to warm to room temperature overnight then filtered to remove the precipitated white solid. The filtrates were concentrated *in vacuo* then distilled under high vacuum to yield the *N*-trimethylsilyl-*N*-methylaniline [19] (126 g, 94%) as a colorless/straw colored liquid. b.p. 48 °C/0.6 mmHg; ^{1}H NMR ($CDCl_3$) δ 7.27 (t, 2H, J = 9 Hz), 6.94 (d, 2H, J = 8 Hz), 6.85 (t, 1H, J = 7 Hz,), 2.95 (s, 3H), 0.33 (s, 9H). To a 5 L flange necked flask fitted with magnetic stirrer, temp probe, bubbler and nitrogen inlet was added dichloromethane (150 mL) and then cooled to −78 °C. Sulfur tetrafluoride (57.1 g, 0.53 mol) was sub-surfaced while keeping the temperature below −65 °C. To the resulting solution was added dropwise a solution of *N*-trimethylsilyl-*N*-methylaniline (91.2 g, 0.51 mol) in dichloromethane (42 mL) while keeping the temperature below −70 °C. The resulting solution was allowed to slowly warm to room temperature and stirred overnight. To the resulting solution was added dichloromethane (558 mL) followed by boron trifluoride tetrahydrofuran complex (56 mL, 0.51 mol) dropwise over 70 min keeping the temperature below 25 °C. The suspension was stirred an additional 60 min, then filtered under a blanket of nitrogen. The solid material was rinsed with diethyl ether (3 × 150 mL), then dried under vacuum to provide *N*-methyl-*N*-phenylaminodifluorosulfinium tetrafluoroborate salt (124 g, 93%) as dark-gray crystals: m.p. 144–150 °C; IR (ATR, ZnSe) ν = 1287, 1004, 964, 836, 764, 692 cm^{-1}; ^{1}H NMR (CD_3CN) δ 7.71–7.47 (m, 5H), 3.79 (t, J = 7.6 Hz, 1H); ^{13}C NMR (CD_3CN) δ 132.8, 131.5, 128.0, 122.7, 43.8; ^{19}F NMR (CD_3CN) δ 14.33 (s, 2F), −150.41 (s, 4F); HRMS-ESI calcd for $C_7H_8NSF_2$ $[M]^{*+}$ 176.0346, found 176.0342.

3.1.3. Preparation of N-methyl-N-(2-pyridyl)aminodifluorosulfinium tetrafluoroborate salt (*3*)

To a stirring solution of 2-methylaminopyridine (19.5 g, 0.18 mol) in diethyl ether (120 mL) cooled at −78 °C was added *n*-butyllithium (2.4 M in hexane; 85 mL, 0.20 mol) keeping the temperature below −70 °C. The resulting slurry was stirred for 1 h then chlorotrimethylsilane (28.2 mL, 0.22 mol) was added while keeping the temperature below −70 °C. The reaction was allowed to warm to room temperature overnight then filtered to remove the precipitated white solid. The filtrates were concentrated *in vacuo* then distilled under high vacuum to yield the *N*-trimethylsilyl-*N*-methyl-2-aminopyridine (31.9 g, 96%) as a colorless liquid. b.p. 50 °C/0.5 mmHg; ^{1}H NMR ($CDCl_3$) δ 8.12 (m, 1H), 7.49 (m, 1H), 6.62 (m, 1H), 6.51 (t, J = 8 Hz, 1H), 2.86 (s, 3H), 0.33 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 160.74, 145.94, 136.05, 111.38, 105.03, 30.91, 0.00. To a 5 L flange necked flask fitted with magnetic stirrer, temp probe, bubbler and nitrogen inlet was added dichloromethane

(150 mL) and then cooled to −78 °C. Sulfur tetrafluoride (23.7 g, 0.22 mol) was sub-surfaced while keeping the temperature below −70 °C. To the resulting solution was added dropwise a solution of *N*-trimethylsilyl-*N*-methyl-2-aminopyridine (38.0 g, 0.21 mol) in dichloromethane (42 mL) while keeping the temperature below −70 °C. The resulting solution was allowed to slowly warm to room temperature and stirred overnight. To the resulting solution was added dichloromethane (500 mL) followed by boron trifluoride tetrahydrofuran complex (23.3 mL, 0.21 mol) dropwise over 35 min keeping the temperature below 21 °C. The suspension was stirred an additional 60 min, then filtered under a blanket of nitrogen. The solid material was rinsed with diethyl ether (3 × 150 mL), then dried under vacuum to provide *N*-methyl-*N*-(2-pyridyl)aminodifluorosulfinium tetrafluoroborate (43.6 g, 78%) as white crystals. m.p. 80–86 °C; IR (ATR, ZnSe) ν = 1617, 1302, 1231, 1030, 986, 766, 674 cm^{-1}; ^1H NMR (CD_3CN) δ 8.39 (m, 1H), 8.20 (ddd, *J* = 8.3, 7.6, 1.7 Hz, 1H), 7.59 (ddd, *J* = 7.6, 5.1, 0.9 Hz, 1H), 7.50 (dt, *J* = 8.4, 0.9 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (CD_3CN) δ 148.7, 147.0, 143.8, 124.9, 112.1, 33.8; ^{19}F NMR (CD_3CN) −9.11 (s, 2F), −151.23 (s, 4F); HRMS-ESI calcd for $C_6H_7N_2SF_2$ $[M]^{*+}$ 177.0298, found 177.0288.

3.2. Deoxofluorination reactions

3.2.1. Deoxofluorination of 3-phenyl-1-propanol (Table 1)

To a solution of triethylamine trihydrofluoride (1.5 equiv.) in dichloromethane (6.0 mL/1 mmol of alcohol) at room temperature was added the *N*,*N*-disubstituted aminodifluorosulfinium tetrafluoroborate salt (1.5 equiv.) followed by 3-phenylpropan-1-ol (0.5–2.7 mmol scale, 1 equiv.). After 3 h of stirring under nitrogen, the reaction mixture was quenched at room temperature with a 5% aqueous sodium bicarbonate solution, stirred for 15 min, and the resulting mixture was extracted twice using dichloromethane. The organic phases were combined, dried over sodium sulfate and solvents were evaporated under low-vacuum at 40 °C. NMR yield was calculated by integration of ^{19}F NMR and/or ^1H NMR signals of the resulting crude material + internal standard (trifluoroethanol).

3.2.2. Deoxofluorination of 4-phenylbutan-2-ol (Table 2)

To a solution of triethylamine trihydrofluoride (2 equiv.) in dichloromethane (3.0 mL/1 mmol of alcohol) at room temperature was added the *N*,*N*-disubstituted aminodifluorosulfinium tetrafluoroborate (1.5 equiv.) followed by 4-phenylbutan-2-ol (0.5–1.0 mmol scale, 1 equiv.). After 3 h of stirring under nitrogen, the reaction mixture was quenched at room temperature with a 5% aqueous sodium bicarbonate solution, stirred for 15 min, and the resulting mixture was extracted twice using dichloromethane. The organic phases were combined, dried over sodium sulfate and solvents were evaporated under low-vacuum at 40 °C. NMR yield was calculated by integration of ^{19}F and/or ^1H NMR signals of the resulting crude material + internal standard (trifluoroethanol).

3.2.3. Deoxofluorination of 1,4-dioxaspiro[4.5]decan-8-one (Table 3)

To a solution of triethylamine trihydrofluoride (1 equiv.) in dichloromethane (2 mL) at room temperature was added the *N*,*N*-disubstituted aminodifluorosulfinium tetrafluoroborate (1.5 equiv.) followed by 1,4-dioxaspiro[4.5]decan-8-one (1.0 mmol, 1 equiv.). After 3 h of stirring under nitrogen, the reaction mixture was quenched at room temperature with a 5% aqueous sodium bicarbonate solution, stirred for 15 min, and the resulting mixture was extracted twice using dichloromethane. The organic phases were combined, dried over sodium sulfate and solvents were evaporated under low-vacuum at 40 °C. NMR yield was calculated by integration of ^{19}F NMR and/or ^1H NMR signals of the resulting crude material + internal standard (2-fluoro-4-nitrotoluene).

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References

[1] (a) T. Hiyama, Organofluorine Compounds: Chemistry and Applications, Springer-Verlag, Berlin, Germany, 2001;
(b) K. Uneyama, Organofluorine Chemistry, Blackwell Publishing Ltd., Oxford, United Kingdom, 2006.
[2] K.L. Kirk, Org. Process Res. Dev. 12 (2008) 305–321.
[3] W.R. Hasek, W.C. Smith, V.A. Engelhardt, J. Am. Chem. Soc. 82 (1960) 543–551.
[4] W.J. Middleton, J. Org. Chem. 40 (1975) 574–578.
[5] (a) G.S. Lal, G.P. Pez, R.J. Pesaresi, F.M. Prozonic, H. Cheng, J. Org. Chem. 71 (1999) 7048–7054;
(b) G.S. Lal, G.P. Pez, R.J. Pesaresi, F.M. Prozonic, J. Chem. Soc. Chem. Commun. (1999) 215–216.
[6] N.N. Yarovenko, M.A. Raksha, Zh. Obshch. Khim. 29 (1959) 2159–2163.
[7] A. Takaoka, H. Iwakiri, N. Ishikawa, Bull. Chem. Soc. Jpn. 52 (1979) 3377–3380.
[8] V.A. Petrov, S. Swearingen, W. Hong, W.C. Petersen, J. Fluorine Chem. 109 (2001) 25–31.
[9] H. Hayashi, H. Sonoda, K. Fukumura, T. Nagata, J. Chem. Soc. Chem. Commun. (2002) 1618–1619.
[10] (a) B. Bennua-Skalmowski, H. Vorbrüggen, Tetrahedron Lett. 36 (1995) 2611–2614;
(b) P. M. Savu, D. Snustad, U.S. Patent 6 248 889, 2001.
[11] T. Umemoto, R.P. Singh, Y. Xu, N. Saito, J. Am. Chem. Soc. 132 (2010) 18199–18205.
[12] T. Umemoto, R.P. Singh, J. Fluorine Chem. 140 (2012) 17–27.
[13] F. Sladojevich, S.I. Arlow, P. Tang, T. Ritter, J. Am. Chem. Soc. 135 (2013) 2470–2473.
[14] R.P. Singh, J.M. Shreeve, Synthesis (2002) 2561–2578.
[15] (a) F. Beaulieu, L.-P. Beauregard, G. Courchesne, M. Couturier, F. Laflamme, A. L'Heureux, Org. Lett. 11 (2009) 5050–5053;
(b) A. L'Heureux, F. Beaulieu, C. Bennet, D.R. Bill, S. Clayton, F. Laflamme, M. Mirmehrabi, S. Tadayon, D. Tovell, M. Couturier, J. Org. Chem. 75 (2010) 3401–3411.
[16] The new *N*,*N*-disubstitutedaminodifluorosulfinium tetrafluoroborate salts were synthesized by Manchester Organics Limited, UK
[17] W.K.D. Brill, J. Nielsen, M.H. Caruthers, J. Am. Chem. Soc. 113 (1991) 3972–3980.
[18] 1-(Trimethylsilyl)pyrrolidine is also commercially available
[19] C.J. Smith, M.W.S. Tsang, A.B. Holmes, R.L. Danheiser, J.W. Tester, Org. Biomol. Chem. 3 (2005) 3767–3781.
[20] A. Scrivanti, V. Beghetto, M. Bertoldini, U. Matteoli, Eur. J. Org. Chem. (2012) 264–268.
[21] M.A. Tius, J.K. Kawakami, Synth. Commun. 22 (1992) 1461–1471.
[22] (a) A. Flohr, R. Jakob-Roetne, R.D. Norcross, C. Riemer, U.S. Patent 149036, 2003.;
(b) J.P. Powers, M. Degraffenreid, X. He, L. Julian, D. Sun, X. Yan, Y. Rew, D.L. McMinn, U.S. Patent 293392, 2006.
[23] The most abundant peak for all the compounds was the protonated amine generated after the loss of the SF_2 fragment.