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Reactions of imines with 2,2-difluoro-2-fluorosulfonylacetyl fluoride

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ABSTRACT

Selected *N*-alkyl ketoimines having at least one methyl group at the imino carbon were reacted in a Stork enamine reaction with 2,2-difluoro-2-fluorosulfonylacetyl fluoride to yield enaminones carrying one fluorosulfonyldifluoromethylene function. In the case of *N*-tertbutyl methyl aldimine two of these groups were present in a triketone derivative. Taking a ethylene bis(imine) also a ring closure reaction was observed, proven by X-ray structure analysis.

1. Introduction

Enamino ketones are important synthetic precursors, e.g. in heterocyclic chemistry, and their synthesis is well-documented [1–4]. Fluorinated β-enamino ketones have attracted attention mainly due to their possible use in synthesis of pharmacologically important heterocycles [5,6]. These compounds were synthesized by regioselective condensation of fluoroalkyl-β-diketones using amines [7], the partial hydrolysis of 1,3-diimines to imidoyl chlorides and enolisable ketones [8] or by *C*-perfluoroalkylation of stable enamines [9,10]. Recently, a novel method for preparing fluorinated enamino ketones and diketones was introduced using perfluoroalkanoyl fluorides [11,12]. Commercially available 2,2-difluoro-2-fluorosulfonylacetyl fluoride has found many applications in organofluorine chemistry. This reagent was used as a source for difluorocarbene and, as an effective trifluoromethylating reagent [13,14]. 2,2-Difluoro-2-fluorosulfonylacetyl fluoride as acylating reagent in the case of amines and alcohols has been already described. [15–17] To the best of our knowledge the reactions of 2,2-difluoro-2-fluorosulfonylacetyl fluoride with imines have not been studied. The aim of this work is the synthesis of new aminovinyl ketones in the reaction of imines with 2,2-difluoro-2-fluorosulfonylacetyl fluoride.

2. Results and discussion

Selected imines **1a**–**i** reacted in a Stork enamine reaction [18,19] with equimolar amount of 2,2-difluoro-2-fluorosulfonylacetyl fluoride **2** to give the HF adducts of the corresponding fluorinated enaminones (aminovinyl ketones). Hydrogen fluoride was removed easily by extraction with sodium hydrogen carbonate solution to give the compounds **3a**–**g** in good to high yields (Scheme 1). The reactions proceeded at ambient temperature in 3–8 h. All the compounds obtained are non-moisture sensitive colorless oils or solids. It is notable that the aminovinyl ketones **3a**–**h** were obtained exclusively as the *Z*-isomers as a result of the formation an intramolecular hydrogen NH···O bond. The formation of the latter was proved by X-ray studies of compound **3f** (Fig. 1). The X-ray data show intramolecular hydrogen bonding N(1)H···O(1)C with 271.7 pm (**3f**) giving rise to almost planar six-membered ring systems. The respective distances in the enamino ketone system between the atoms N(1)–C(7) 132.2(3), C(7)–C(12) 140.4(3), C(12)–C(13) 139.7(3) pm are between a single and a double bond [20] indicating the expected delocalization with sp^2-hybridised carbon atoms. The O–C bond length O(1)–C(13) 124.2(3) pm of **3f** is slightly longer than a typical C=O double bond [20].

The reaction of **1h** with two equivalents of 2,2-difluoro-2-fluorosulfonylacetyl fluoride **2** under the same conditions mentioned above led to the corresponding product 4 h containing two alkanoyl fragments in good yield (Scheme 2).

When the diimine **1i** was reacted with two equivalents of **2**, the mixture of two colorless products **5i** and **6i** in a 1:1 ratio (100% conversion by ^{19}F NMR) was obtained (Scheme 3).

Obviously, two successive Stork reactions took place; the first to generate the intermediate $\mathbf{A^1}$, which is attacked by a second molecule of **2** to yield the linear product **5i** or to produce the cyclic compound **6i** via an intramolecular attack from the amine nitrogen in the tautomer $\mathbf{A^2}$ to the imine carbon under formation of a 2,2-dimethylimidazolidine where subsequently the N–H fragment

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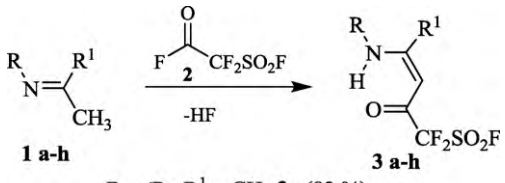
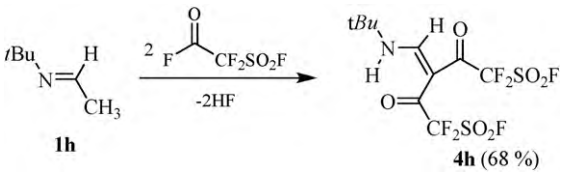


R = *i*Pr, R^1 = CH_3 **3a** (82 %)
R = *t*Bu, R^1 = Ph **3b** (55 %)
R = Bz, R^1 = CF_3 **3c** (78 %)
R = *c*Hex, R^1 = Ph **3d** (40 %)
R = *i*Pr, R^1 = Ph **3e** (67 %)
R = *t*Bu, R^1 = Ph-Cl **3f** (54 %)
R = *i*Pr, R^1 = H **3g** (76 %)
R = *t*Bu, R^1 = H **3h** (62 %)

Scheme 1.



Scheme 2.

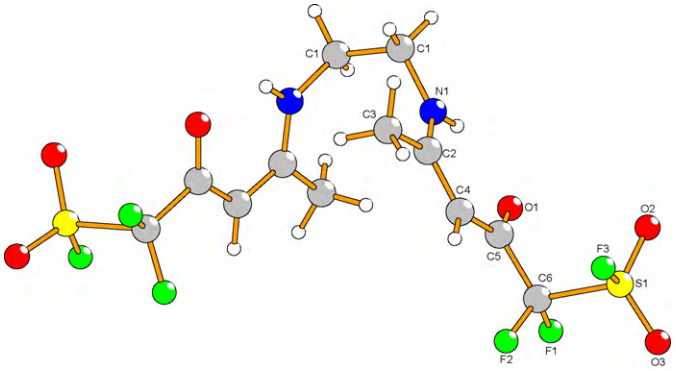


Fig. 2. Molecular structure of **5i**. Selected bond lengths (pm) and angles (°): N(1)–C(2)132.4(3), C(2)–C(4) 140.6(3), C(4)–C(5) 138.9(3), O(1)–C(5) 124.9(2), S(1)–F(3) 146.93(18), S(1)–O(2) 143.03(17), S(1)–O(3) 140.9(17);O(1)–C(5)–C(4) 128.63(19), C(5)–C(4)–C(2) 122.5218, N(1)–C(2)–C(4) 120.89(18), O(1)–C(5)–C(6) 115.2(17).

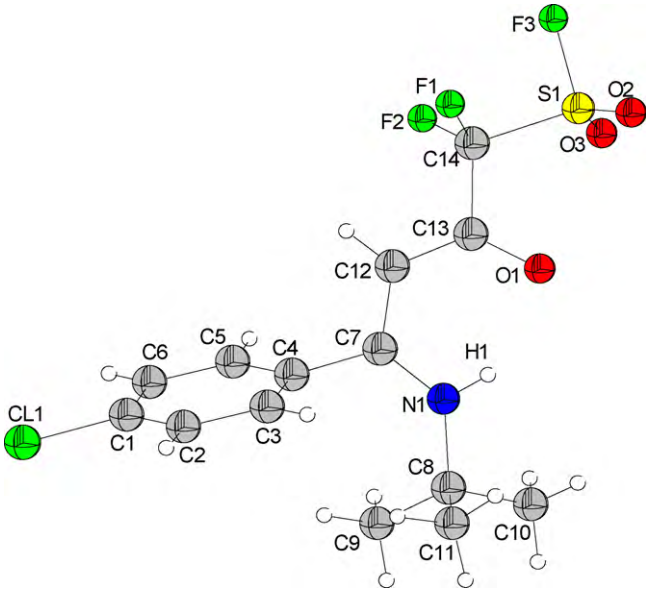


Fig. 1. Molecular structure of **3f**. Selected bond lengths (pm) and angles (°): N(1)–C(7)132.2(3), C(7)–C(12) 140.4(3), C(12)–C(13) 139.7(3), O(1)–C(13) 124.2(3), S(1)–F(3) 156.28(15), S(1)–O(2) 139.71(19), S(1)–O(3) 140.2(2);O(1)–C(13)–C(12) 129.2(2), C(13)–C(12)–C(7) 122.2(2), N(1)–C(7)–C(12) 120.9(2), O(1)–C(13)–C(14) 116.08(19).

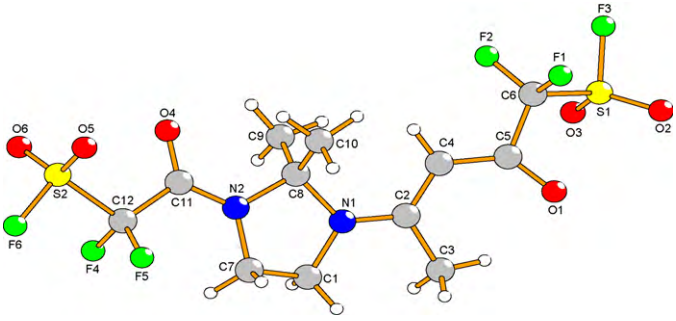
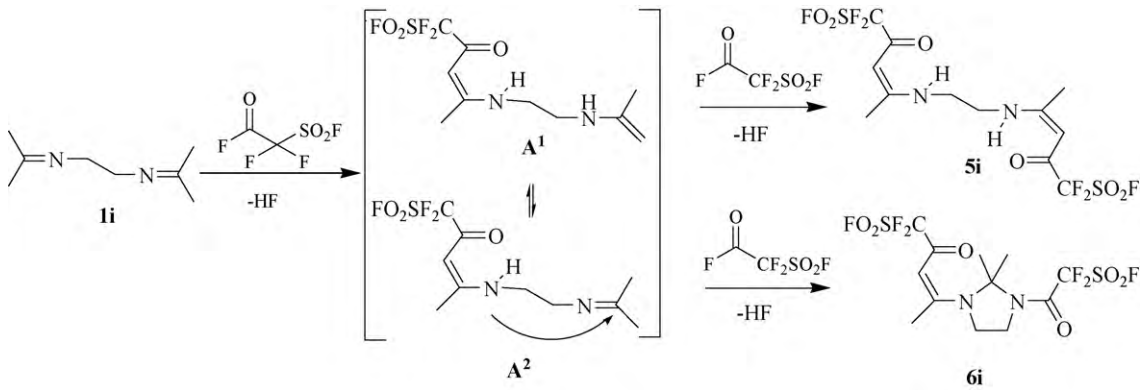


Fig. 3. Molecular structure of **6i**. Selected bond lengths (pm) and angels (°): N(1)–C(2) 133.2(3), N(1)–C(1) 147.4(3), N(1)–C(8) 149.8(3), N(2)–C(11) 133.3(3), C(7)–C(1) 150.7(4), C(2)–C(4) 139.4(3), C(4)–C(5) 140.2(4), O(1)–C(5) 123.6(3), S(1)–F(3) 155.4(2), S(1)–O(2) 140.1(2), S(1)–O(3) 140.5(2);O(1)–C(5)–C(4) 132.3(2), C(5)–C(4)–C(2) 124.9(2), N(1)–C(2)–C(4) 123.7(2), O(1)–C(5)–C(6) 111.8(2).

generated reacts with **2** giving rise to the amide **6i** via abstraction of HF.

Similar to compound **3f**, the X-ray analysis of **5i** (Fig. 2) shows a planar six-membered ring with distances among atoms (N(1)–C(2)132.4(3), C(2)–C(4) 140.6(3), C(4)–C(5) 138.9(3) pm), which indicates a delocalized double bond system. An intramolecular hydrogen bonding N(1)H···O(1)C with 271.9 pm was observed. The structure of compound **6i** was confirmed by X-ray analysis.



Scheme 3.

The ^{1}H, ^{19}F, ^{13}C NMR data of the products **3a–h**, **4h**, **5i**, **6i** (Fig. 3) are in accord with the proposed structures. The CF_2 group of the new compounds was observed in ^{13}C NMR as a triplet of doublets in the δ_C = 115.2–116 region, the C=O group appears as a triplet in the value about δ_C = 173.

3. Conclusion

We have studied the reaction of imines with 2,2-difluoro-2-fluorosulfonylacetyl fluoride as an acylating reagent. It has been shown that the corresponding aminovinyl ketones **3a–h** exist exclusively as **Z**-isomers as a result of the formation an intramolecular hydrogen NH···O bond. In the case of the aldimine **1h** an enamine dione is formed. Reacting the diimine **1i** with **2** surprisingly a ring closure product was observed.

4. Experimental

The ^{1}H (200.13 MHz), ^{13}C (50.32 MHz) and ^{19}F (188.31 MHz) NMR spectra were recorded on a Bruker DPX-200 spectrometer using $CDCl_3$ as solvent and TMS or CCl_3F as internal standards. MS (EI) and HRMS spectra were obtained on a Varian MAT CH7A instrument at 70 eV. The X-ray structural study was carried out 173(2) K on a Siemens P4 diffractometer using graphite monochromated Mo Kα radiation (λ = 71.073 pm) and the low temperature device LT2. All reactions were carried out under the inert atmosphere (nitrogen) and monitored by ^{19}F NMR spectroscopy. The ketimines have been prepared according to literature procedures. *N*-(1-Methylethyliden)-2-propanamin **1a** [21], 2-methyl-*N*-(1-phenylethyliden)-2-propanamin **1b** [22], *N*-(1-phenylethyliden)propan-2-amin **1e** [22], *N*-ethyliden-2-propanamin **1g** [23], *N*-ethyliden-2-methyl-2-propanamin **1h** [23], ethylen-bis(2-imino-propan) **1i** [24].

4.1. Reactions of 1a–i with 2,2-difluoro-2-fluorosulfonylacetyl fluoride

General procedure: 2,2-Difluoro-2-fluorosulfonylacetyl fluoride **2** was condensed to a solution of ketimine in anhydrous diethylether at −196 °C. After stirring for several hours at room temperature the reaction mixture was washed twice with a saturated $NaHCO_3$ solution. The organic layer was separated, dried over Na_2SO_4, all volatiles removed in vacuum and the residue was purified by SiO_2 gel column chromatography or crystallization to give the corresponding products **3a–h**, **4h**, **5i**, **6i**.

4.1.1. (Z)-1,1-Difluoro-4-(isopropylamino)-2-oxopent-3-ene-1-sulfonyl fluoride 3a (82%)

Colorless oil; ^{1}H NMR ($CDCl_3$): δ 1.28 (d, *J* = 6.1 Hz, 6H), 2.15 (s, 3H), 3.86 (sep, *J* = 6.1 Hz, 1H), 5.37 (s, 1H), 11.21 (bs, 1H, NH); ^{13}C NMR ($CDCl_3$): δ 19.8 (s, CH_3), 24.1 (s, CH_3), 48 (s, CH), 93.7 (s, CH), 115.8 (td, *J* = 302.5 Hz, *J* = 24.9 Hz, CF_2), 171.9 (s, C), 172.4 (t, *J* = 22.3 Hz, C=O); ^{19}F NMR ($CDCl_3$): δ 38.4 (s, 1F, SF), −104.4 (s, 2F, CF_2); MS (EI) *m*/*z* (%): 259 $[M]^+$(15), 178 $[M\text{-}SO_2F]^+$ (10), 126 $[M\text{-}CF_2SO_2F]^+$ (100); HRMS for $[M]^+$ ($C_8H_{12}F_3NO_3S$): calculated 259.0490, found 259.0489.

4.1.2. (Z)-4-(tert-Butylamino)-1,1-difluoro-2-oxo-4-phenylbut-3-ene-1-sulfonyl fluoride 3b (55%)

Colorless crystals; mp. 88 °C; ^{1}H NMR ($CDCl_3$): δ 1.26 (s, 9H), 5.37 (s, 1H), 7.32–7.36 (m, 2H), 7.45–7.47 (m, 3H), 11.7 (s, 1H, NH); ^{13}C NMR ($CDCl_3$): δ 31.8 (s, CH_3), 56.7 (s, C), 93.5 (s, CH), 116.1 (td, *J* = 302.3 Hz, *J* = 25.5 Hz, CF_2), 127.8 (s, CH), 128.8 (s, CH), 130.5 (s, CH), 135.4 (s, CH), 172.1 (s, C), 172.6 (t, *J* = 22.9 Hz, C=O); ^{19}F NMR ($CDCl_3$): δ = 43.9 (s, 1F), −99.3 (s, 2F); MS (EI) *m*/*z* (%): 335 $[M]^+$ (15), 202 $[M\text{-}CF_2\text{–}SO_2F]^+$ (60), 146 [M-*t*-Bu, –$CF_2SO_2F]^+$ (100), 57 [*t*-Bu]$^+$ (47); HRMS for $[M]^+$ ($C_{14}H_{16}F_3NO_3S$): calculated 335.0803, found 335.0801.

4.1.3. (Z)-4-(Benzylamino)-1,1,5,5,5-pentafluoro-2-oxopent-3-ene-1-sulfonyl fluoride 3c (78%)

Colorless crystals; mp. 31 °C; ^{1}H NMR ($CDCl_3$): δ 4.73 (d, *J* = 5.8 Hz, 2H), 6.10 (s, 1H), 7.32–7.35 (m, 2 H), 7.39–7.43 (m, 3H), 11.0 (bs, 1H, NH); ^{13}C NMR ($CDCl_3$): δ 50.0 (s), 87.3 (s), 115.2 (dt, *J* = 303.2 Hz, *J* = 27.9 Hz, CF_2), 119.3 (q, *J* = 278.9 Hz), 128.1 (s), 129.4 (s), 129.8 (s), 134.8 (s), 154.8 (q, *J* = 33.9 Hz), 178.1 (t, *J* = 22.6 Hz, C=O); ^{19}F NMR ($CDCl_3$): δ = 39.7 (s, 1F), −68.3 (s, 3F), −106.0(s, 2F); MS (EI) *m*/*z* (%): 361 $[M]^+$ (10), 278 $[M\text{-}SO_2F]^+$ (50); HRMS for $[M]^+$ ($C_{12}H_9F_6NO_3S$): calculated 361.0207, found 361.0219.

4.1.4. (Z)-4-(Cyclohexylamino)-1,1-difluoro-2-oxo-4-phenylbut-3-ene-1-sulfonyl fluoride 3d (40%)

Yellow crystals, mp. 55 °C; ^{1}H NMR ($CDCl_3$): δ 1.20–1.24 (m, 3 H), 1.41–1.45 (m, 4H), 1.53–1.58 (m, 4H), 3.40–3.48 (m, 1H), 5.48 (s, 1H), 7.23–7.25 (m, 2H), 7.51–7.56 (m, 3H), 11.40 (bs, 1H, NH); ^{13}C NMR ($CDCl_3$): δ 23.9 (s), 24.8 (s), 33.6 (s), 53.9 (s), 91.1 (s), 115.5 (td, *J* = 302.4 Hz, *J* = 25.5 Hz, CF_2), 126.9 (s), 128.8 (s), 130.6 (s), 133.4 (s), 170.1 (s), 172.4 (t, *J* = 21.2 Hz, C=O); ^{19}F NMR ($CDCl_3$): δ 38.8 (s, 1F), −104.2 (s, 2F); MS (EI) *m*/*z* (%): 361 $[M]^+$ (27), 278 $[M\text{-}SO_2F]^+$ (94), 228 $[M\text{-}CF_2SO_2F]^+$ (100); HRMS for $[M]^+$ ($C_{16}H_{18}F_3NO_3S$): calculated 361.0960, found 361.0959.

4.1.5. (Z)-1,1-Difluoro-4-(isopropylamino)-2-oxo-4-phenylbut-3-ene-1-sulfonyl fluoride 3e (67%)

Colorless oil, ^{1}H NMR ($CDCl_3$): δ 1.27 (d, *J* = 6.3 Hz, 6H), 3.76–3.82 (m, 1H), 5.47 (s, 1H), 7.34–7.40 (m, 2H), 7.50–7.54 (m, 3H), 11.26 (bs, 1H, NH); ^{13}C NMR ($CDCl_3$): δ 24.1 (s), 48.0 (s), 91.5 (s), 116.3 (td, *J* = 302.3 Hz, *J* = 25.6 Hz, CF_2), 127.4 (s), 129.5 (s), 131.1 (s), 133.9 (s), 170.8 (s), 173.2 (t, *J* = 21.2 Hz, C=O); ^{19}F NMR ($CDCl_3$): δ 43.9 (s, 1F), −99.1 (s, 2F); MS (EI) *m*/*z* (%): 321 $[M]^+$ (22), 238 $[M\text{-}SO_2F]^+$ (42), 188 $[M\text{-}CF_2SO_2F]^+$ (100); HRMS for $[M]^+$ ($C_{13}H_{14}F_3NO_3S$): calculated 321.0647, found 321.0642.

4.1.6. (Z)-4-(tert-Butylamino)-4-(4-chlorophenyl)-1,1-difluoro-2-oxobut-3-ene-1-sulfonyl fluoride 3f (54%)

Colorless crystals; mp. 76 °C; ^{1}H NMR ($CDCl_3$): δ 1.26 (s, 9H), 5.32 (s, 1H), 7.20–7.32 (m, 2H), 7. 36–7.43 (m, 2H), 11.63 (bs, 1H, NH); ^{13}C NMR ($CDCl_3$): δ 31.8 (s), 56.7 (s), 93.4 (s), 116.1 (td, *J* = 302.3 Hz, *J* = 25.7 Hz, CF_2), 129.2 (s), 133.8 (s), 136.8 (s), 170.8 (s), 172.8 (t, $^{2}J_{CF}$ = 21.4 Hz, C=O); ^{19}F NMR ($CDCl_3$): δ 38.9 (s, 1F), −104.5 (s, 2F); MS (EI) *m*/*z* (%) = 369 $[M]^+$ (15), 286 $[M\text{-}SO_2F]^+$ (30), 236 $[M\text{-}CF_2SO_2F]^+$ (90), 180 [M-*t*-Bu]$^+$ (100), 57 [*t*-Bu]$^+$ (80); HRMS for $[M]^+$ ($C_{14}H_{15}ClF_3NO_3S$): calculated 369.0413, found 369.0426.

4.1.7. (Z)-1,1-Difluoro-4-(isopropylamino)-2-oxobut-3-ene-1-sulfonyl fluoride 3g (76%)

Colorless oil; ^{1}H NMR ($CDCl_3$): δ 1.35 (d, *J* = 6.8 Hz, 6H), 3.65 (sep, *J* = 6.8 Hz, 1H), 5.49 (d, *J* = 6.8 Hz, 1H), 7.29 (dd, *J* = 13.8 Hz, *J* = 6.8 Hz, 1H), 10.47 (s, 1H, NH); ^{13}C NMR ($CDCl_3$): δ 23.7 (s), 52.2 (s), 88.2 (s), 115.6 (td, *J* = 302.2 Hz, *J* = 25.6 Hz, CF_2), 157.1 (s), 175.2 (t, $^{2}J_{CF}$ = 21.9 Hz, C=O); ^{19}F NMR ($CDCl_3$): δ 38.9 (s, 1F), −104.8 (s, 2F); MS (EI) *m*/*z* (%): 245 $[M]^+$ (35), 112 $[M\text{-}CF_2SO_2F]^+$ (100); HRMS for $[M]^+$ ($C_7H_{10}F_3NO_3S$): calculated 245.0334, found 245.0336.

4.1.8. (Z)-4-(tert-Butylamino)-1,1-difluoro-2-oxobut-3-ene-1-sulfonyl fluoride 3h (62%)

Colorless crystals; mp. 65 °C; ^{1}H NMR ($CDCl_3$): δ 1.24 (s, 9H), 5.51 (dt, *J* = 6.9 Hz, *J* = 1.3 Hz, 1H), 7.38 (dd, *J* = 14.3 Hz, *J* = 6.9 Hz, 1H, CH), 10.81 (bs, 1H, NH); ^{13}C NMR ($CDCl_3$): δ 29.6 (s), 54.4 (s), 87.8 (s), 115.6 (td, *J* = 302.1 Hz, *J* = 25.8 Hz, CF_2), 154.5 (s), 174.5 (t, *J* = 21.6 Hz, C=O); ^{19}F NMR ($CDCl_3$): δ 43.1 (s, 1F), −100.5 (s, 2F); MS (EI) *m*/*z* (%) = 259 $[M]^+$ (40), 126 $[M\text{-}CF_2\text{–}SO_2F]^+$ (55), 70 [M-*t*-

Bu, $-CF_2SO_2F]^+$ (100), 57 [*t*-Bu]$^+$(90); HRMS for $[M]^+$ ($C_8H_{12}F_3NO_3S$): calculated 259.0490, found 259.0488.

4.1.9. 3-((tert-Butylamino)methylene)-1,1,5,5-tetrafluoro-2,4-dioxopentane-1,5-disulfonyl difluoride **4h** *(45%)*

Colorless crystals; mp. 120 °C; ^{1}H NMR (CD_3CN): δ 1.50 (s, 9H), 8.23 (d, J = 15.3 Hz, 1H), 11.11 (bs, 1H, NH); ^{13}C NMR (CD_3CN): δ 28.4 (s), 58.8 (s), 101.1 (s), 118.7 (td, J = 312.1 Hz, J = 33.4 Hz, CF_2), 157.1 (s), 177.1 (t, J = 22.2 Hz, C=O); ^{19}F NMR ($CDCl_3$): δ 40.2 (s, 1F), 39.7 (s, 1F), −96.8 (s, 2F), −97.6 (s, 2F); MS: (EI) m/z (%): 419 $[M]^+$ (15), 336 $[M\text{-}SO_2F]^+$ (5), 286 $[M\text{-}CF_2SO_2F]^+$ (75), 57 [*t*-Bu]$^+$ (100); HRMS for $[M]^+$ ($C_{10}H_{11}F_6NO_6S_2$): calculated 418.9932, found 418.9928.

4.1.10. (3Z,3′Z)-4,4′-(Ethane-1,2-diylbis(azanediyl))bis(1,1-difluoro-2-oxopent-3-ene-1-sulfonyl fluoride) **5i** *(46%)*

Colorless crystals; mp. 135 °C; ^{1}H NMR (CD_3CN): δ 2.12 (s, 6H), 3.65–3.81 (m, 4H), 5.53 (s, 2H), 11.16 (bs, 2H, NH); ^{13}C NMR (CD_3CN): δ 19.7(s), 44.4 (s), 91.4 (s), 117.5 (td, J = 302 Hz, J = 25.7 Hz, CF_2), 172.5 (t, $^2J_{CF}$ = 25.6 Hz, C=O), 173.9 (s); ^{19}F NMR (CD_3CN): δ 42.7 (s, 1F), −99.1 (s, 2F, CF_2); MS (EI) m/z (%) 460 $[M]^+$ (15), 377 $[M\text{-}SO_2F]^+$ (20), 327 $[M\text{-}CF_2SO_2F]^+$ (60), 299 $[M\text{-}CO\text{–}CF_2SO_2F]^+$ (40); HRMS for $[M]^+$ ($C_{12}H_{14}F_6N_2O_3S_2$): calculated 460.0197, found 460.0195.

4.1.11. (3Z,3′Z)-4,4′-(Ethane-1,2-diylbis(azanediyl))bis(1,1-difluoro-2-oxopent-3-ene-1-sulfonyl fluoride) **6i** *(42%)*

Colorless crystals; mp. 143 °C; ^{1}H NMR (CD_3CN): δ 1.94 (s, 6H), 2.67 (s, 3H), 3.86–4.05 (m, 4H), 5.45 (s, 1H); ^{13}C NMR (CD_3CN): δ 20.9 (s), 21.3(s), 26.4 (s), 42.4 (s), 43.9 (s), 83.5 (s), 94.4 (s), 117.5 (td, J = 302 Hz, J = 25.7 Hz, CF_2), 123.7 (td, J = 305 Hz, J = 27.2 Hz, CF_2) 150.9 (t, $^2J_{CF}$ = 23.5 Hz, C=O), 171.6 (s), 173.4 (t, $^2J_{CF}$ = 25.6 Hz, C=O); ^{19}F NMR (CD_3CN): δ 37.2 (s, 1F), 38.2 (s, 1F), −103.5 (s, 2F), −104.4 (s, 2F); MS (EI) m/z (%) = 460 $[M]^+$ (20), 405 $[M\text{-}NH\text{–}C(CH_3)\text{=}CH]^+$ (100), 327 $[M\text{-}CF_2SO_2F]^+$ (55), 299 $[M\text{-}CO\text{–}CF_2SO_2F]^+$ (40). HRMS for $[M]^+$ ($C_{12}H_{14}F_6N_2O_3S_2$): calculated 460.0197, found 460.0195.

4.2. X-ray crystal structure determination of **3f**, **5i** *and* **6i**

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 775065 (**3f**), CCDC 775066 (**5i**) and CCDC 775067 (**6i**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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