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Study on the reactions of fluoroalkanesulfonyl azides with cycloalkenyl ether and aryl ynamines

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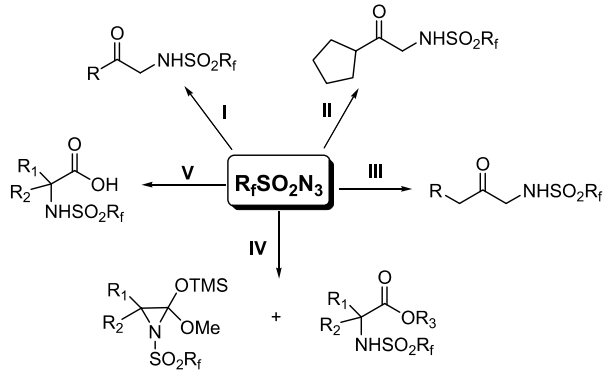
Abstract—The reactions of fluoroalkanesulfonyl azides **1** with some electron-rich compounds have been studied in detail. Cycloalkenyl vinyl ethers reacted with **1** readily at 0 °C to give the corresponding ring-contraction *N*-fluoroalkanesulfonyl amidine analogues **3**. In contrast, aryl ynamine generated in situ reacted with **1** affording fluorinated α-diazoamidines **9**, which were decomposed slowly at room temperature to form [1-diethylamino-2-(4-nitro-phenyl)-2-oxo-eth-(*Z*)-ylidene]-fluoroalkanesulfinyl imine **10** with elimination of nitrogen gas. Possible mechanisms for these reactions were proposed.

1. Introduction

Organic azides are versatile starting materials for the synthesis of a variety of nitrogen-containing compounds. The azido group can react with both nucleophilic and electrophilic reagents and can be used in 1,3-dipolar cycloaddition reactions. For example, Semenov[1] once studied the reaction of arylsulfonyl azides with 2-methoxy-1-phenyl-1-butene affording methyl *N*-aryl-sulfony-2-phenylbutyrimidates and *N*-(2-methoxy-1-phenyl-1-butenyl) arenesulfonamides, which were formed by decomposition of the unstable triazoline intermediates followed by the elimination of N_2 and the migration of hydrogen or ethyl group. Meanwhile they also reported the reactions of arylsulfonyl azides with cycloalkenyl ether and the expected ring-contraction products were obtained. It was noteworthy that all reactions were carried out under heating (~80 °C) conditions.

It has been well documented that the replacement of a hydrogen atom by a fluorine atom or a fluoroalkyl group in an organic molecule may profoundly influence its physical and biological properties.[2] Fluoroalkanesulfonyl azides **1** are more reactive than other nonfluorinated organic azides due to the strong electron-withdrawing property of the R_fSO_2 group. Since 1992 we have systematically studied their reactions with electron-rich olefins such as silyl enol ethers,[3] acyclic and cyclic vinyl ethers,[4] enamines etc.[5] Among them, the reactions of **1** and sily enol ethers afforded a novel approach to the formation of *N*-sulfonyl protected α-amino ketones, α-amino acids and β-amino-α-keto esters, respectively, (Scheme 1). Although various substrates containing enamine structure such as indole, carbazole and tetrakis(dimethylamino)ethylene (TDAE) were studied extensively, however, ynamine was still investigated rarely due to its relative difficult preparation and its easily hydrolysis. During our continued studying on the fluoro-alkanesulfonyl azides **1**, we found that they reacted



Reagents and conditions: (**I**) Silyl enol ethers, 0 °C; (**II**) Cyclic silyl enol ethers, 0 °C; (**III**) RCH=CHOTMS, 0 °C; (**IV**) Silyl ketene acetals, 0 °C; (**V**) Disilyl ketene acetals, 0 °C.

Scheme 1.

Keywords: Fluoroalkanesulfonyl azides; Cycloalkenyl ether; Ynamine; 1,3-Dipolar cycloaddition; Triazolines.
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smoothly at 0 °C or room temperature with cycloalkenyl ethers and in situ generated ynamine. Herein we report these results and discuss the reaction mechanisms.

2. Results and discussion

In our previous work on $R_fSO_2N_3$ **1**, we found that the reactions of acyclic and cyclic vinyl ethers gave two different products. In the case of acyclic vinyl ether it afforded the stable cycloproducts 1-fluoroalkanesulfonyl 1,2,3-triazolines.[4b] However, the reaction of **1** with dihydropyran did not give the corresponding *N*-fluoroalkanesulfonyl azilidines but *N*-fluoroalkanesulfonyl-tetrahydropyranon-2-imines.[4a] Similar to vinyl ether and dihydropyran, cycloalkenyl ether **2**, derived from cycloketone, containing an electron-rich double bond, reacted smoothly with **1** at 0 °C, this reaction finished within 10 min (monitored by TLC).

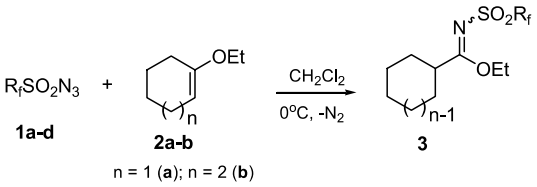
To a solution of cyclohexenyl ether **2a** in anhydrous CH_2Cl_2 was added slowly 1.33 equimolar amount of fluoroalkanesulfonyl azides **1a** at 0 °C, the nitrogen gas was released immediately. TLC analysis showed that the vinyl ether **2a** disappeared within 10 min and only one product was formed. According to the spectra data, the product was easily determined as an expected ring-contraction *N*-fluoroalkanesulfonyl amidine analogue **3aa**. The MS spectrum of **3aa** showed its quasi-molecular ion peak at *m/z* 548. A fragmental ion observed at *m/z* 69 indicated a cyclopentyl group should be involved in the molecular structure. Meanwhile a typical strong absorption at 1582 cm^{-1} in IR spectrum confirmed the existence of C=N functional group. By comparison of the ^1H NMR spectra of **2a** and **3aa**, it was observed that in **3aa** the two signals of ethoxy group (EtO) were shifted to lower field and a new multiple peak appeared at δ 3.49 ppm, which could be assigned to the CH linking cyclopentyl to other groups in the molecule. Combined with the elemental analysis result **3aa** was identified as 1-cyclopentyl-1-ethoxyl-*N*-fluoroalkanesulfonyl imine. Under the same reaction conditions other azides **1b–d** reacted with equimolar amount of **2a–b** gave the similar results. All these results were summarized in Table 1 (Scheme 2).

It was found in Table 1 that all the reactions finished within 10 min and the ring size of the cycloalkenyl ether had some influenced on the yields of **3**. In the case of the larger ring substrate cycloheptenyl ether **2b**, the relative lower yields were always obtained compared with that of cyclohexenyl ether **2a**, which might be due to the effect of the size of the ring in the ring-contraction process during the formation of **3**. According to previous studies and the above results, the possible mechanism for the formation of **3** was proposed (Scheme 3).

Table 1. Reaction results of fluoroalkanesulfonyl azides with cycloalkenyl ethers

Entry	Azides	Vinyl ether	Time (min)	Product	Yields[a]
1	**1a**	**2a**	10	**3aa**	71
2	**1b**	**2a**	10	**3ba**	70
3	**1c**	**2a**	10	**3ca**	61
4	**1d**	**2a**	10	**3da**	58
5	**1a**	**2b**	10	**3ab**	42
6	**1b**	**2b**	10	**3bb**	57
7	**1c**	**2b**	10	**3cb**	55
8	**1d**	**2b**	10	**3db**	53

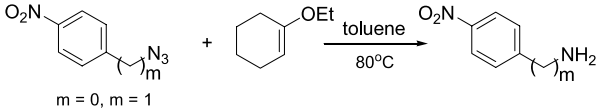
[a] Isolated yields.



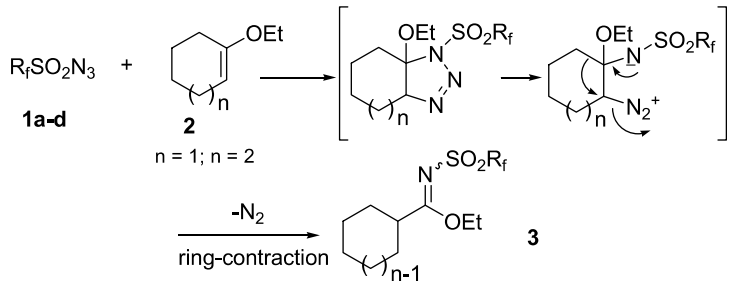
Scheme 2.

The reactions of fluoroalkanesulfonyl azides **1** with the six- and seven-membered cycloalkenyl ether **2a** (**2b**) afforded the ring-contraction products **3**, then how about the five-membered cyclopentenyl ether **2c**? Due to the larger tension of four-membered compound are very labile, the formation of ring-contraction product in the case of **2c** is impossible. Literature[6] reported that under heating the reaction of TsN_3 with **2c** in acetone could afford 1,2-disubstituted cyclopentene derivatives in high yield. However, under the similar reaction conditions (0 °C, 10 min), whatever solvents (CH_2Cl_2, Et_2O, CH_3CN, acetone) were used in the reaction of azide **1** and **2c**, the fluoroalkanesulfonyl amine $R_fSO_2NH_2$ was obtained as the major product (determined by the following ^{19}F NMR). In addition, another product, which had unsaturated bond (determined by $KMnO_4$ solution) and no fluorine atom (determined by ^{19}F NMR) was also isolated by the column chromatography, but due to its low boiling point it was removed completely when dried by oil pump.

During our investigation on the fluoroalkanesulfonyl azide **1**, we noticed that the similar reactions of electron-rich aryl azide **4** with **2** were studied rarely. Then our focus was turned to the reaction of aryl azides. It was found that no reaction occurred when 4-nitro-phenylazide **4a** reacted with cyclohexenyl ether **2a** at room temperature even it was prolonged to 12 h (monitored by TLC). Then heating the reaction up to 80 °C in toluene within 48 h, TLC analysis showed that the azide **4a** was not consumed completely and a new product was formed. After general work-up and recycling the unreacted **4a**, the new product, obtained in 86% yield, was identified as the corresponding 4-nitrophenylamine.[7] The same phenomena were also observed in the reaction of the 4-nitro-benzylazide with **2a**, the corresponding 4-nitro-benzylamine was also isolated.

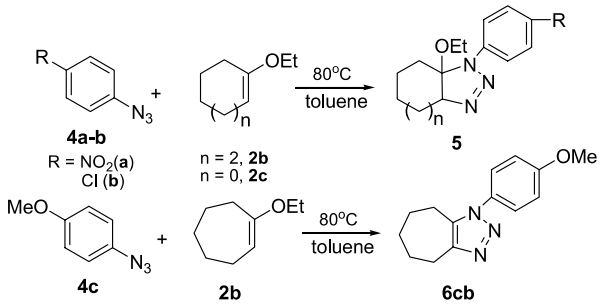


However, under the same reaction condition when mixing 4-nitro-phenylazide **4a** with cycloheptenyl ether **2b** the regiospecific [3+2] cycloadduct **5ab** was isolated successfully. This was further confirmed by the results of the reaction of **4a** and cyclopentenyl ether **2c**, the spectra data of cycloadduct **5ac** were consistence with the



Scheme 3.

literature.[8] Then other aryl azides **4b–c** were also applied to this reaction protocol (Scheme 4) and the results were listed in Table 2.



Scheme 4.

Table 2. Reaction results of aryl azides with cycloalkenyl ethers

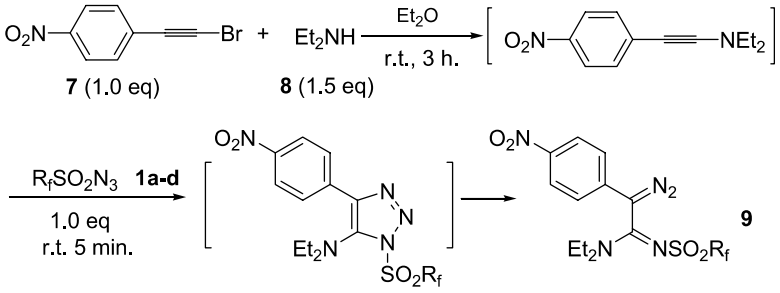
Entry	Azides (R=)	Vinyl ethers	Time (h)	Products	Yields[a]
1	R=NO_2 **4a**	**2b**	48	**5ab**	83
2	R=NO_2 **4a**	**2c**	48	**5ac**	77
3	R=Cl **4b**	**2b**	24	**5bb**	36
4	R=CH_3O **4c**	**2b**	48	**6cb**	40

[a] Based on the real azides participated in the reaction.

As seen in Table 2, the substituent R in aryl azides **4** had significant impact on the product and the isolated yields. During the same reaction time (48 h), the aryl azide with electron-rich substituent could react faster than that with electron-withdrawing one. Thus, a further elimination of one EtOH occurred and polysubstituted triazole **6cb** in stead of the corresponding **5cb** was obtained (Table 2, entry 1, 4). Meanwhile, the aryl azide with electron-withdrawing substitutent had higher isolated yields. When R=NO_2 the yield was 83%; however, when R=Cl the yield was decreased to 36% (Table 2, entry 1, 3).

In addition, the reactions of fluoroalkanesulfonyl azides **1** with ynamine were also studied. Considered the ynamine's easily hydrolysis, the 1,3-dipolar addition of fluoroalkanesulfonyl azide **1a** to *N*,*N*-diethylamino-*p*-nitrophenylacetylene generated in situ from 4-nitro-phenylacetylene bromide **7** and diethylamine **8** in anhydrous ether at room temperature was first investigated. No nitrogen gas was released and the reaction was finished in 5 min (monitored by TLC). The reaction mixture was directly purified by chromatography to afford the pure product *N*-[2-diazo-1-diethylamino-2-(4-nitro-phenyl)-eth-(*E*)-ylidene]-fluoroalkanesulfonyl imine **9a** in 75% yield (Scheme 5). A strong absorption at 2080 cm^{-1} in IR spectrum was observed, which was the typical absorption of $C{=}N^{+}{=}N^{-}$. Other azides **1**(**b–d**) reacted with arylacetylene bromide and diethyl amine gave similar α-diazoamidines in moderate yields. All these results were summarized in Table 3.

It was noteworthy that the α-diazoamidines **9** were unstable when kept at room temperature within 1–2 days and

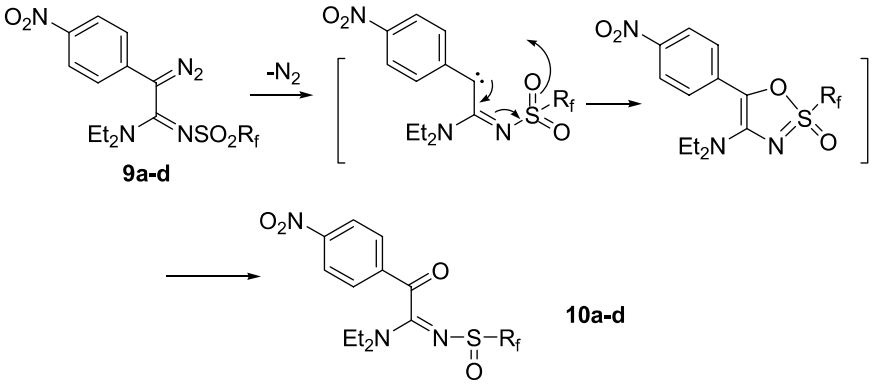


Scheme 5.

Table 3. Reaction results of fluoroalkanesulfonyl azides with arylynamine[a]

Entry	Azides	Arylacetylene bromide	Amine	Products	Yields (%)[b]
1	**1a**	**7**	**8**	**9a**	75
2	**1b**	**7**	**8**	**9b**	68
3	**1c**	**7**	**8**	**9c**	65
4	**1d**	**7**	**8**	**9d**	84

[a] Arylynamine was generated from **7** (1.0 equiv) and **8** (1.5 equiv).
[b] Isolated yields based on azides.



Scheme 6.

decomposed gradually and converted into a new product **10** completely when it was exposed for a certain time. By comparison of the spectra data of **9** and **10**, it was found that in IR spectrum the strong absorption of diazo group (2080 cm^{-1}) was disappeared and a new strong absorption was observed at 1694 cm^{-1}, which might be attributed to the existence of conjugated carbonyl structure in **10**. The total numbers of hydrogen and fluorine atoms were retained as indicated in ^{1}H and ^{19}F NMR spectra, however, the chemical shifts and peak shapes of all protons in **10** had obvious changes, especially the chemical shift of fluorine signal attached to the sulfonyl (SO_2CF_2) changed from −116.7 to −125.6 ppm ($\Delta\delta$: ~9 ppm), which maybe resulted from the participation of sulfonyl group for the formation of product **10**. Other spectra data (MS, IR) and elemental analysis results substantiated the deduction and the possible mechanism was also proposed (Scheme 6).

3. Conclusions

In summary, the reactions of fluoroalkanesulfonyl azides **1** with cycloalkenyl ether and ynamine were studied in detail. A ring-contraction *N*-fluoroalkanesulfonyl amidine analogues **3** were obtained when **1** was reacted with cycloalkenyl vinyl ethers at 0 °C. On the other hand, in the case of aryl ynamine with **1** afforded fluorinated α-diazoamidines **9**, which were decomposed gradually at room temperature to form [1-diethylamino-2-(4-nitro-phenyl)-2-oxo-eth-(*Z*)-ylidene]-fluoroalkanesulfinyl imine **10**. Further chemical transformations of the fluorinated products are under way in our laboratory.

4. Experimental

Melting points were measured in Temp-Melt apparatus and were uncorrected. ^{1}H and ^{19}F NMR spectra were recorded in $CDCl_3$ (unless mentioned in text), Bruker AM-300 instruments with Me_4Si and $CFCl_3$ (with upfield negative) as the internal and external standards, respectively. IR spectra were obtained with a Nicolet AV-360 spectrophotometer. Lower resolution mass spectrum or high-resolution mass spectra (HRMS) were obtained on a Finnigan GC–MS 4021 or a Finnigan MAT-8430 instrument using the electron impact ionization technique (70 eV), respectively. Elemental analyses were performed by this Institute. All solvents were purified before use. Fluoroalkanesulfonyl azides **1**, cycloalkenyl ether **2** and arylacetylene bromide were prepared according to literature.[9–11]

4.1. General procedure for the reaction of fluoroalkanesulfonyl azides with cycloalkenyl ether

To a 10 mL round-bottom flask containing 1-ethoxycyclohexene **2a** (189 mg, 1.5 mmol) in 2 mL anhydrous CH_2Cl_2 was added slowly fluoroalkanesulfonyl azides **1a** (0.898 g, 2.0 mmol) at room temperature within 2 min. Then the mixture was continuously stirred at room temperature within 10 min until TLC analysis shown the reaction finished. The solvent was evaporated and the residue was purified on a silica column using petroleum ether–ether (50/1 v:v) as the eluant to give pure product **3aa** as a colorless oil (580 mg, 71%).

4.1.1. 1-Cyclopentyl-1-ethoxy-meth-(*Z*)-ylidene-(5′-iodo-3′-oxa-octafluoropentyl)-sulfonyl imine (3aa). Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.29 (2H, q, J=7.2 Hz), 3.53–3.43 (1H, m), 2.14–2.03 (2H, m), 1.86–1.59 (6H, m), 1.36 (3H, t, J=7.2 Hz). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −65.3 (2F, t, J=6.1 Hz, ICF_2), −81.4 (2F, t, J=12.8 Hz, CF_2O), −85.9 (2F, m, OCF_2), −117.8 (2F, s, CF_2S). IR (KBr) cm^{-1}: 2970, 2878, 1582, 1326, 1292, 1188, 1145, 914. MS: *m*/*z* (%) 548 (M^++1, 25), 478 ($M^+-C_5H_9$, 8), 227 ($IC_2F_4^+$, 5), 96 (M^++1−R_fSO_2–OEt, 100), 69 ($C_5H_9^+$, 65). Anal. Calcd for $C_{12}H_{14}F_8INO_4S$: C, 26.34; H, 2.58; N, 2.56%. Found: C, 26.47; H, 2.92; N, 2.59%.

4.1.2. 1-Cyclopentyl-1-ethoxy-meth-(*Z*)-ylidene-(5′-chloro-3′-oxa-octafluoropentyl)-sulfonyl imine (3ba). Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.29 (2H, q, J=7.2 Hz), 3.54–3.47 (1H, m), 2.14–2.05 (2H, m), 1.84–1.63 (6H, m), 1.35 (3H, t, J=7.2 Hz). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −74.2 (2F, s, $ClCF_2$), −81.5 (2F, t, J=12.8 Hz, CF_2O), −87.2 (2F, t, J=12.8 Hz, OCF_2), −117.9 (2F, s, CF_2S). IR (KBr) cm^{-1}: 2970, 2867, 1584, 1361, 1307, 1174, 1143, 970. MS: *m*/*z* (%) 457/455 (M^+, 2/6), 416/414 ($M^+-C_3H_5$, 23/60), 388/386 ($M^+-C_5H_9$, 38/100), 96 (M^++1−R_fSO_2–OEt, 87), 69 ($C_5H_9^+$, 59). Anal. Calcd for $C_{12}H_{14}ClF_8NO_4S$: C, 31.63; H, 3.10; N, 3.07%. Found: C, 31.71; H, 3.12; N, 3.38%.

4.1.3. 1-Cyclopentyl-1-ethoxy-meth-(*Z*)-ylidene-(1′,1′,2′,2′,4′,4′,5′,5′-octafluoro-3′-oxa-pentyl)-sulfonyl imine

(3ca). Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.87 (1H, tt, J=3.0, 52.8 Hz), 4.29 (2H, q, J=7.2 Hz), 3.52–3.48 (1H, m), 2.14–2.05 (2H, m), 1.86–1.61 (6H, m), 1.35 (3H, t, J=7.2 Hz). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −81.2 (2F, t, J=13.1 Hz, CF_2O), −89.0 (2F, m, OCF_2), −118.0 (2F, s, CF_2S), −137.9 (2F, d, J=52.7 Hz, HCF_2). IR (KBr) cm^{-1}: 2968, 2879, 1583, 1359, 1326, 1144, 1010, 907. MS: *m/z* (%) 421 (M^+, 1), 380 ($M^+-C_3H_5$, 8), 352 ($M^+-C_5H_9$, 18), 96 ($M^+ +1-R_fSO_2$–EtO, 100), 69 ($C_5H_9^+$, 54). Anal. Calcd for $C_{12}H_{15}F_8NO_4S$: C, 34.21; H, 3.59; N, 3.32%. Found: C, 34.32; H, 3.59; N, 3.27%.

4.1.4. 1-Cyclopentyl-1-ethoxy-meth-(*Z*)-ylidene-perfluorobutylsulfonyl imine (3da). Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.30 (2H, q, J=7.2 Hz), 3.53–3.48 (1H, m), 2.12–2.06 (2H, m), 1.85–1.64 (6H, m), 1.36 (3H, t, J=7.2 Hz). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −81.2 (3F, t, J=8.5 Hz, CF_3), −114.4 (2F, t, J=13.8 Hz, CF_2), −121.3 (2F, t, J=4.8 Hz, CF_2S), −126.5 (2F, t, J=14.1 Hz, CF_2). IR (KBr) cm^{-1}: 2967, 2878, 1583, 1360, 1237, 1140, 1012. MS: *m/z* (%) 382 ($M^+-C_3H_5$, 12), 354 ($M^+-C_5H_9$, 25), 96 ($M^+ +1-R_fSO_2$–EtO, 100), 69 ($C_5H_9^+$, 93). Anal. Calcd for $C_{12}H_{14}F_9NO_3S$: C, 34.05; H, 3.33; N, 3.31%. Found: C, 34.14; H, 3.36; N, 3.31%.

4.1.5. 1-Cyclohexyl-1-ethoxy-meth-(*Z*)-ylidene-(5′-iodo-3′-oxa-octafluoropentyl)-sulfonyl imine (3ab). Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.29 (2H, q, J=7.2 Hz), 3.16–3.09 (1H, m), 2.01–1.42 (8H, m), 1.36 (3H, t, J=7.2 Hz), 1.32–1.20 (2H, m). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −65.1 (2F, t, J=5.8 Hz, ICF_2), −81.3 (2F, t, J=13.3 Hz, CF_2O), −85.7 (2F, m, OCF_2), −117.5 (2F, s, CF_2S). IR (KBr) cm^{-1}: 2938, 2861, 1584, 1332, 1292, 1186, 1146, 915. MS: *m/z* (%) 561 (M^+, 1), 478 ($M^+-C_6H_{11}$, 3), 227 ($IC_2F_4^+$, 8), 110 ($M^+ +1-R_fSO_2$–OEt, 100), 83 ($C_6H_{11}^+$, 65). Anal. Calcd for $C_{13}H_{16}F_8INO_4S$: C, 27.82; H, 2.87; N, 2.50%. Found: C, 27.89; H, 2.93; N, 2.46%.

4.1.6. 1-Cyclohexyl-1-ethoxy-meth-(*Z*)-ylidene-(5′-chloro-3′-oxa-octafluoropentyl)-sulfonyl imine (3bb). Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.28 (2H, q, J=7.2 Hz), 3.16–3.07 (1H, m), 2.01–1.40 (8H, m), 1.36 (3H, t, J=7.2 Hz), 1.32–1.19 (2H, m). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −74.1 (2F, s, $ClCF_2$), −81.3 (2F, t, J=13.7 Hz, CF_2O), −87.1 (2F, t, J=12.6 Hz, OCF_2), −117.6 (2F, s, CF_2S). IR (KBr) cm^{-1}: 2939, 2862, 1585, 1360, 1305, 1187, 1142, 977. MS: *m/z* (%) 471/469 (M^+, 0.6/1.6), 388/386 ($M^+-C_6H_{11}$, 2/5), 110 ($M^+ +1-R_fSO_2$–OEt, 100), 83 ($C_6H_{11}^+$, 71). Anal. Calcd for $C_{13}H_{16}ClF_8NO_4S$: C, 33.24; H, 3.43; N, 2.98%. Found: C, 33.23; H, 3.43; N, 2.90%.

4.1.7. 1-Cyclohexyl-1-ethoxy-meth-(*Z*)-ylidene-(1′,1′,2′,2′,4′,4′,5′,5′-octafluoro-3′-oxa-pentyl)-sulfonyl imine (3cb). Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.87 (1H, tt, J=3.0, 52.5 Hz), 4.29 (2H, q, J=7.2 Hz), 3.17–3.07 (1H, m), 2.01–1.40 (8H, m), 1.36 (3H, t, J=7.2 Hz), 1.32–1.20 (2H, m). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −80.9 (2F, t, J=12.8 Hz, CF_2O), −88.8 (2F, m, OCF_2), −117.7 (2F, s, CF_2S), −137.66 (2F, d, J=52.5 Hz, HCF_2). IR (KBr) cm^{-1}: 2939, 2862, 1585, 1358, 1329, 1187, 1009. MS: *m/z* (%) 435 (M^+, 1), 352 ($M^+-C_6H_{11}$, 4), 110 ($M^+ +1-R_fSO_2$–EtO, 100), 83 ($C_6H_{11}^+$, 70). Anal. Calcd for $C_{13}H_{17}F_8NO_4S$: C, 35.87; H, 3.94; N, 3.22%. Found: C, 36.06; H, 3.93; N, 3.23%.

4.1.8. 1-Cyclohexyl-1-ethoxy-meth-(*Z*)-ylidene-perfluorobutylsulfonyl imine (3db). Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.29 (2H, q, J=7.2 Hz), 3.17–3.07 (1H, m), 2.02–1.42 (8H, m), 1.36 (3H, t, J=7.2 Hz), 1.33–1.20 (2H, m). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −81.0 (3F, t, J=10.0 Hz, CF_3), –114.1 (2F, t, J=15.1 Hz, CF_2), –121.1 (2F, m, CF_2S), –126.2 (2F, m, CF_2). IR (KBr) cm^{-1}: 2939, 2862, 1584, 1359, 1238, 1140, 1012. MS: *m/z* (%) 437 (M^+, 2), 354 ($M^+-C_6H_{11}$, 4), 110 ($M^+ +1-R_fSO_2$–EtO, 100), 83 ($C_6H_{11}^+$, 78). Anal. Calcd for $C_{13}H_{16}F_9NO_3S$: C, 35.70; H, 3.69; N, 3.20%. Found: C, 35.74; H, 3.79; N, 3.55%.

4.2. General procedure for the reaction of aryl azides with cycloalkenyl ether

To a 10 mL round-bottom flask containing 1-ethoxy-cycloheptene **2b** (227 mg, 1.62 mmol) in 2 mL anhydrous toluene was added 4-nitro phenyl azides **4a** (0.246 g, 1.5 mmol) at room temperature under N_2. Then the mixture was continuously stirred and heated to 80 °C. After 48 h TLC analysis showed the azide **4a** was not consumed completely. The solvent was evaporated and the residue was chromatographed on a silica column using petroleum ether–ether (20/3 v:v) as eluant to give pure product **5ab** as a yellowish solid (253 mg, 83%). Meanwhile, 80 mg of 4-nitro-phenyl azides **4a** was recycled.

4.2.1. 8a-Ethoxy-1-(4-nitro-phenyl)-1,3a,4,5,6,7,8,8a-octahydro-cycloheptatriazole (5ab). Yellowish solid. Mp 128–130 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.25 (2H, dd, J=9.0, 1.5 Hz, AA′BB′), 7.65 (2H, dd, J=9.6, 1.5 Hz, AA′BB′), 4.62 (1H, t, J=5.4 Hz), 3.19–3.14 (1H, m), 2.93–2.88 (1H, m), 2.44–1.21 (10H, m), 1.16 (3H, t, J=7.2 Hz). IR (KBr) cm^{-1}: 2940, 2859, 1593, 1516, 1493, 1338, 1045, 860. MS: *m/z* (%) 275 (M^+−Et, 5), 259 (M^+−EtO, 5), 193 ($M^+-C_2H_4-C_6H_{11}$, 47), 137 (M^+−EtO–$C_6H_4NO_2$, 12), 83 ($C_6H_{11}^+$, 93), 55 ($C_4H_7^+$, 100). Anal. Calcd for $C_{15}H_{20}N_4O_3$: C, 59.21; H, 6.58; N, 18.42%. Found: C, 59.18; H, 6.78; N, 18.15%.

4.2.2. 1-(4-Chloro-phenyl)-8a-ethoxy-1,3a,4,5,6,7,8,8a-octahydro-cycloheptatriazole (5bb). Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.46–7.27 (4H, m), 4.50 (1H, t, J=5.1 Hz), 3.17–3.11 (1H, m), 2.99–2.93 (1H, m), 2.52–1.23 (10H, m), 1.17 (3H, t, J=6.9 Hz). IR (KBr) cm^{-1}: 2930, 2856, 1597, 1491, 1455, 1346, 1065, 1039, 829. MS: *m/z* (%) 295/293 (M^+, 1/3), 238/236 ($M^+-C_4H_9$, 3/9), 182 ($M^+-C_6H_4Cl$, 25), 113/111 ($ClC_6H_4^+$, 51), 55 ($C_4H_7^+$, 100). HRMS (MALDI/DHB) for $[M+OH]^+$: $C_{15}H_{21}ClN_3O_2$ Calcd 310.1326. Found: 310.1317.

4.2.3. 1-(4-Methoxy-phenyl)-1,4,5,6,7,8-hexahydro-cycloheptatriazole (6cb). Yellowish solid. Mp 104–106 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.32 (2H, dd, J=9.0, 2.1 Hz, AA′BB′), 7.02 (2H, dd, J=9.0, 2.4 Hz, AA′BB′), 3.87 (3H, s), 2.96 (2H, t, J=6.0 Hz), 2.69 (2H, t, J=5.7 Hz), 1.87–1.67 (6H, m). IR (KBr) cm^{-1}: 2927, 2844, 1515, 1457, 1252, 1233, 1176, 1032, 841. MS: *m/z* (%) 243 (M^+, 11), 214 ($M^+-C_2H_5$, 89), 200 ($M^+-C_3H_7$,

100). Anal. Calcd for $C_{14}H_{17}N_3O$: C, 69.14; H, 7.00; N, 17.28%. Found: C, 69.18; H, 7.02; N, 17.08%.

4.3. General procedure for the reaction of fluoroalkanesulfonyl azides with in situ generated ynamine

At room temperature, to a 10 mL round-bottom flask containing 1-bromo-2-(4-nitro-phenyl)ethyne **7** (100 mg, 0.44 mmol) in 3 mL anhydrous diethyl ether was added slowly diethyl amine **8** (0.07 mL, 0.66 mmol). Then the mixture was continuously stirred at room temperature. TLC analysis showed the reaction finished within 3 h. Then fluoroalkanesulfonyl azides **1d** (143 mg, 0.44 mmol) was added dropwise to the reaction system. The original yellowish color turned to carmine immediately. TLC analysis showed that azide **1** was disappeared within 5 min. The solvent was evaporated and the residue was chromatographed on a silica column using petroleum ether–ether (1/1 v:v) as the eluant to give pure diazo product **9d** as a yellowish solid (203 mg, 85%).

4.3.1. [2-Diazo-1-diethylamino-2-(4-nitro-phenyl)-eth-(*Z*)-ylidene]-(5′-iodo-3′-oxa-octafluoropentyl)-sulfonyl imine (9a). Yellowish solid. Mp 78–80 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.28 (2H, d, J=7.2 Hz), 7.10 (2H, d, J=7.2 Hz), 3.62–3.49 (4H, m), 1.31–1.21 (6H, m). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −65.2 (CF_2, t, J=6.1 Hz), −81.5 (CF_2, t, J=11.7 Hz), −85.8 (CF_2, t, J=12.8 Hz), −116.7 (CF_2, s). IR (KBr) cm^{-1}: 2978, 2080, 1593, 1549, 1440, 1340, 1172, 1145. MS: *m/z* (%) 640 (MH^+-N_2, 1), 296 ($M^+-N_2-R_f$, 32), 163 ($O_2NC_6H_4CH{=}N_2^+$, 100). HRMS (+ESI) for $[M+Na]^+$: $C_{16}H_{14}F_8IN_5O_5SNa$ Calcd 689.9530. Found: 689.9524.

4.3.2. [2-Diazo-1-diethylamino-2-(4-nitro-phenyl)-eth-(*Z*)-ylidene]-(5′-chloro-3′-oxa-octafluoropentyl)-sulfonyl imine (9b). Yellowish solid. Mp 58–60 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.27 (2H, d, J=7.2 Hz), 7.09 (2H, d, J=7.2 Hz), 3.63–3.40 (4H, m), 1.37–1.20 (6H, m). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −74.1 (CF_2, s), −81.5 (CF_2, t, J=12.8 Hz), −87.2 (CF_2, t, J=12.0 Hz), −116.8 (CF_2, s). IR (KBr) cm^{-1}: 2988, 2945, 2082, 1562, 1533, 1449, 1349, 1308, 1176, 1137. MS: *m/z* (%) 550/548 (MH^+-N_2, 2/5), 296 ($M^+-N_2-R_f$, 93), 163 ($O_2NC_6H_4CH{=}N_2^+$, 100). Anal. Calcd for $C_{16}H_{14}ClF_8N_5O_5S$: C, 33.37; H, 2.45; N, 12.16%. Found: C, 33.66; H, 2.56; N, 11.81%.

4.3.3. [2-Diazo-1-diethylamino-2-(4-nitro-phenyl)-eth-(*Z*)-ylidene]-(1′,1′,2′,2′,4′,4′,5′,5′-octafluoro-3′-oxa-pentyl)-sulfonyl imine (9c). Yellowish solid. Mp 54–56 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.24 (2H, d, J=8.7 Hz), 7.08 (2H, d, J=8.7 Hz), 5.85 (1H, tt, J=3.0, 52.5 Hz), 3.64–3.47 (4H, m), 1.42–1.18 (6H, m). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −81.0 (CF_2, t, J=12.7 Hz), −88.9 (CF_2, m), −116.8 (CF_2, s), −137.7 (CF_2, d, J=52.5 Hz). IR (KBr) cm^{-1}: 2989, 2945, 2081, 1594, 1557, 1442, 1342, 1136. MS: *m/z* (%) 514 (MH^+-N_2, 5), 296 ($M^+-N_2-R_f$, 100), 163 ($O_2NC_6H_4CH{=}N_2^+$, 61). HRMS (+ESI) for $[M+Na]^+$: $C_{16}H_{15}F_8N_5O_5SNa$ Calcd 564.0564. Found: 564.0561.

4.3.4. [2-Diazo-1-diethylamino-2-(4-nitro-phenyl)-eth-(*Z*)-ylidene]-perfluorobutyl-sulfonyl imine (9d). Yellowish solid. Mp 90–92 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.28 (2H, d, J=9.0 Hz), 7.10 (2H, d, J=9.0 Hz), 3.69–3.57 (4H, m), 1.42–1.20 (6H, m). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −81.0 (CF_3, t, J=9.3 Hz), −113.2 (CF_2, t, J=13.5 Hz), −121.2 (CF_2, t, J=6.3 Hz), −126.2 (CF_2, m). IR (KBr) cm^{-1}: 2988, 2081, 1557, 1441, 1343, 1235, 1138. MS: *m/z* (%) 516 (MH^+-N_2, 5), 296 ($M^+-N_2-R_f$, 76), 163 ($O_2NC_6H_4CH{=}N_2^+$, 90), 150 (100). Anal. Calcd for $C_{16}H_{14}F_9N_5O_4S$: C, 35.37; H, 2.60; N, 12.89%. Found: C, 35.43; H, 2.66; N, 12.99%.

4.4. General procedure for the decomposition reactions of α-diazoamidines 9

At room temperature α-diazoamidines **9** decomposed slowly within 4–7 days accompanying release N_2. Finally the diazo compound **9** converted completely into one new kind of fluoroalkanesulfinyl imine **10**.

4.4.1. [1-Diethylamino-2-(4-nitro-phenyl)-2-oxo-eth-(*Z*)-ylidene]-(5′-iodo-3′-oxa-octafluoropentyl)-sulfinyl imine (10a). Yellowish oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.40 (2H, d, J=8.7 Hz), 8.07 (2H, d, J=9.0 Hz), 3.69 (2H, br), 3.19 (2H, q, J=6.9 Hz), 1.36 (3H, t, J=7.2 Hz), 1.15 (3H, t, J=6.9 Hz). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −65.4 (CF_2, t, J=5.6 Hz), −81.9 (CF_2, t, J=11.7 Hz), −86.0 (CF_2, m), −125.6 (CF_2, m). IR (KBr) cm^{-1}: 2978, 2919, 1694, 1558, 1523, 1346, 1292, 1187, 1134. MS: *m/z* (%) 640 (MH^+, 1), 296 (M^+-R_f, 100), 150 ($O_2NC_6H_4CO^+$, 56). HRMS (+ESI) for $[M+Na]^+$: $C_{16}H_{14}F_8IN_3O_5SNa$ Calcd 661.9469. Found: 661.9466.

4.4.2. [1-Diethylamino-2-(4-nitro-phenyl)-2-oxo-eth-(*Z*)-ylidene]-(5′-chloro-3′-oxa-octafluoropentyl)-sulfinyl imine (10b). Yellowish oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.40 (2H, d, J=9.0 Hz), 8.08 (2H, d, J=9.0 Hz), 3.67 (2H, br), 3.20 (2H, q, J=7.2 Hz), 1.38 (3H, t, J=7.2 Hz), 1.21 (3H, t, J=7.2 Hz). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −74.2 (CF_2, s), −81.9 (CF_2, m), −87.2 (CF_2, m), −125.6 (CF_2, m). IR (KBr) cm^{-1}: 2989, 1697, 1560, 1533, 1349, 1307, 1225, 1133, 977. MS (+ESI): *m/z* (%) 548($[M+H]^+$, 100). HRMS (+ESI) for $[M+Na]^+$: $C_{16}H_{14}ClF_8N_3O_5SNa$ Calcd 570.0113. Found: 570.0110.

4.4.3. [1-Diethylamino-2-(4-nitro-phenyl)-2-oxo-eth-(*Z*)-ylidene]-(1′,1′,2′,2′,4′,4′,5′,5′-octafluoro-3′-oxa-pentyl)-sulfinyl imine (10c). Yellowish oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.39 (2H, d, J=9.0 Hz), 8.06 (2H, d, J=8.4 Hz), 5.88 (1H, tt, J=3.0, 52.5 Hz), 3.68 (2H, br), 3.18 (2H, q, J=6.9 Hz), 1.34 (3H, t, J=7.2 Hz), 1.13 (3H, t, J=7.2 Hz). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −81.2 (CF_2, s), −88.8 (CF_2, m), −125.9 (CF_2, m), −137.8 (CF_2, d, J=53.6 Hz). IR (KBr) cm^{-1}: 2989, 2945, 1695, 1563, 1533, 1441, 1349, 1284, 1139. MS: *m/z* (%) 296 (M^+-R_f, 100), 150 ($O_2NC_6H_4CO^+$, 96). HRMS (+ESI) for $[M+Na]^+$: $C_{16}H_{15}F_8N_3O_5SNa$ Calcd 536.0503. Found: 536.0500.

4.4.4. [1-Diethylamino-2-(4-nitro-phenyl)-2-oxo-eth-(*Z*)-ylidene]-perfluorobutyl-sulfinyl imine (10d). Yellowish solid. Mp 74–76 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.41 (2H, d, J=7.2 Hz), 8.07 (2H, d, J=8.7 Hz), 3.68 (2H, br), 3.20 (2H, q, J=6.9 Hz), 1.36 (3H, t, J=7.2 Hz), 1.15 (3H, t, J=7.2 Hz). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −81.2 (CF_3, m), −122.2 (CF_2, s), −122.4 (CF_2, s), −126.6 (CF_2, m).

IR (KBr) cm^{-1}: 2987, 2944, 1696, 1560, 1441, 1349, 1228, 1211, 1139. MS: *m/z* (%) 516 (MH^+, 3), 296 ($M^+ - R_f$, 100), 150 ($O_2NC_6H_4CO^+$, 79). Anal. Calcd for $C_{16}H_{14}F_9N_3O_4S$: C, 37.29; H, 2.74; N, 8.15%. Found: C, 37.65; H, 3.11; N, 8.15%.

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