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Graphical Abstract

Asymmetric Synthesis of Trifluoromethylated Aziridines from CF_3-substituted *N-tert*-Butanesulfinyl Ketimines

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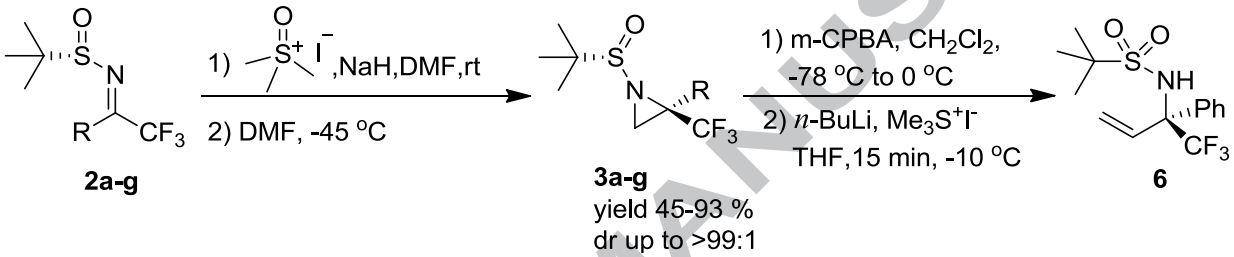

2a-g → **3a-g** yield 45-93 %, dr up to >99:1 → **6**

Asymmetric Synthesis of Trifluoromethylated Aziridines from CF_3-substituted *N-tert*-Butanesulfinyl Ketimines

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Abstract

A convenient and practical method for the asymmetric synthesis of trifluoromethylated aziridines was developed. The reactions of sulfur ylide with (*S*)-*N-tert*-butanesulfinyl ketimines gave trifluoromethylated aziridines **3** in moderate to excellent yields (45-93%) and good diastereoselectivities (86:14 to > 99:1 dr). The synthetic application of these aziridines were examined through the acidic deprotection of sulfinyl group and ring-opening reaction with dimethylsulfonium methylide to afford trifluoromethylated cyclopropylamine and α-trifluoromethylallylamine in 80 % and 67 % yield, respectively.

Keywords: Diasteroselective synthesis; CF_3-substituted; Aziridine; Sulfinamide

1. Introduction

Fluorine-containing compounds have attracted extensive attention due to the unique properties of fluorine (high electronegativity, low polarizability, relative small size) which induce modifications of physical properties for these compounds and make them suitable for use in life and material sciences.[1] Thereinto, as an essential fluorinated group, CF_3 group has attracted much attention and much effort has been paid in the development of new synthetic methods for

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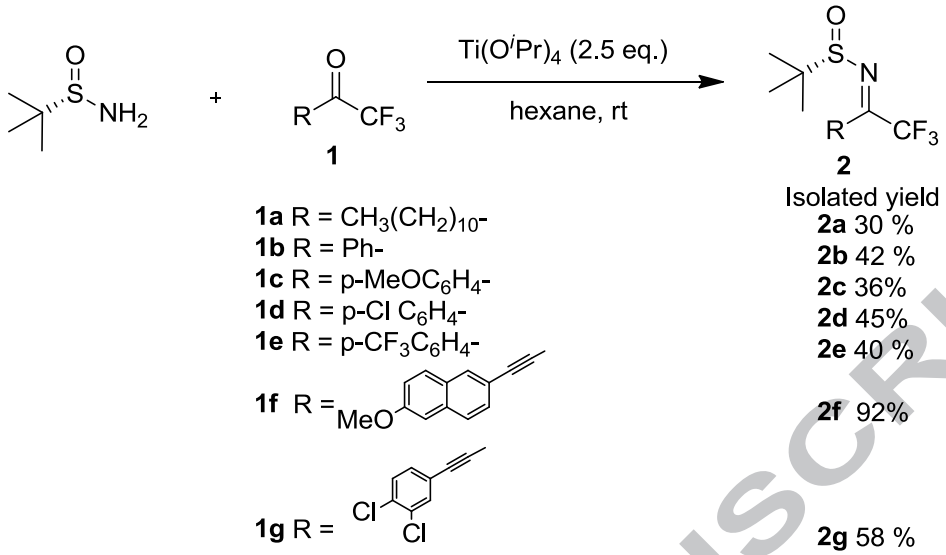
incorporation of the CF_3 group into diverse organic compounds.[2] However, although the introduction of CF_3 group usually results in an improvement of the biological properties of bioactive compounds,[3] the direct introduction of a CF_3 groups into heterocyclic compounds is often difficult.[4] Therefore, a building block approach can provide a useful alternative in some cases. One class of interesting heterocyclic derivatives is aziridines which are excellent building blocks for the preparation of a large variety of nitrogen-containing compounds due to the ease and predictable regioselectivity of their ring-opening reactions with nucleophiles.[5] In the last decade, numerous building block approaches for the preparation of trifluoromethylated aziridine derivatives have been reported.[6] However, few examples towards the asymmetric synthesis of trifluoromethylated aziridines can be found,[7] and at the same time CF_3 substituted chiral carbon center is an essential motif such as in the commercialized drugs Efavirenz (anti-HIV).[8] Here, we report an efficient method for the asymmetric synthesis of trifluoromethylated aziridines by using the inexpensive *N*-*tert*-butanesulfinyl group as a chiral auxiliary.[9]

2. Results and discussion

Firstly, chiral CF_3-substituted (*S*)-*N*-*tert*- butylsulfinyl ketimines **2a**-**2g** were synthesized in 30-92 % yields according to the method established by Lu[10] *via* condensation of (*S*)-*tert*-butylsulfinyl amide and CF_3-substituted ketones **1a**-**1g** in the presence of 2.5 eq. of $Ti(O^iPr)_4$ (Scheme 1). As stated in the literature[10,11], most of these ketimines were displayed low hydrostability and need to be isolated quickly and prior to use. It is noteworthy that acetylenic ketimines **2f** and **2g** have higher hydrostability and can be isolated in yield of 92 % and 58 %, respectively.[12]

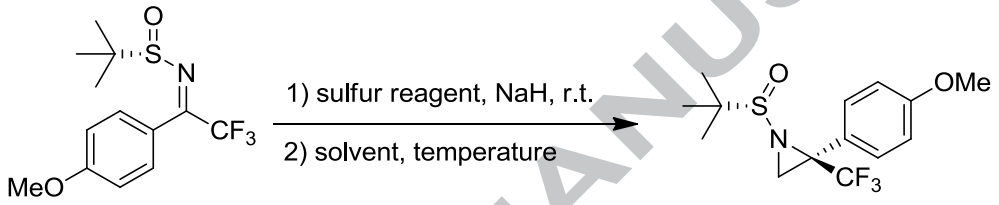


Scheme 1. Preparation of the CF_3-substituted (*S*)-*N*-*tert*-butanesulfinyl ketimines **2**.

With ketimines **2a**-**2g** in hand, the Corey-Chaykovsky aziridination[13] were then investigated (Table 2). Ketimine **2c** was chosen as the model substrate for optimization of the Corey-Chaykovsky aziridination condition. Initially, *in situ* generated dimethylsulfonium methylide was used as the sulfur ylide, and the reaction of **2c** with dimethylsulfonium methylide in DMSO at room temperature afforded a mixture of desired product **3c** in 55 % yield and 76:24 dr (Table 1, entry 1). However, we found that the reproducibility of this result was very poor. It was thought that the high reactivity of dimethylsulfonium methylide and the relatively unstable nature of the CF_3-substituted ketimine led to a multitude of undesired side reactions upon exposure to sodium hydride. Hence less reactive sulfur ylide derived from trimethyl sulfoxonium iodide (TMSOI) was then examined. To our delight, the highly strained aziridine **3c** was obtained in higher yield (93 %) and slight better diastereoselectivity (78:22) (Table 1, entry 2) when dimethyloxosulfonium methylide was used. In comparison to the reaction of **2c** with dimethylsulfonium methylide, the yield was significantly improved, and the reaction time was also shortened from 4 h to 1.5 h. Solvent effect was then investigated with TMSOI as the sulfur ylide precusor. Only trace products could be detected by ^{19}F NMR when low polar THF (Table 1, entry 3) or nonpolar toluene (Table 1, entry 4) was used as solvent. This result may due to the poor solubility of sulfur ylide in THF or toluene which retarded the progress of reaction. The effect of DMF (Table 1, entry 5) is comparable to that of DMSO, and **3c** was isolated in excellent total yield (95 %), however, the diastereoselectivity was still relatively

low (77:23). Fortunately, the dr value was increased from 77:23 to 83:17 as lowering the reaction temperature from room temperature to -45 °C (Table 1, entry 5 and 8). In addition, the variation of reaction temperature had no sensible difference on the yields and reaction time for the formation of trifluoromethylated aziridine (Table 1, entry 5, 6, 7 and 8). Considering that the concentration of sulfur ylide in the reaction system may have influence on the reaction diastereoselectivity, the charging sequence of the sulfur ylide and ketimine was then tested. Thankfully, the dropwise addition of sulfur ylide to **2c** in DMF at -45 °C led to a slight higher diastereoselectivity (89:11) (Table 1, entry 9).

Table 1. Optimization of the Corey-Chaykovsky aziridation of **2c** with sulfur ylide.



2c **3c**

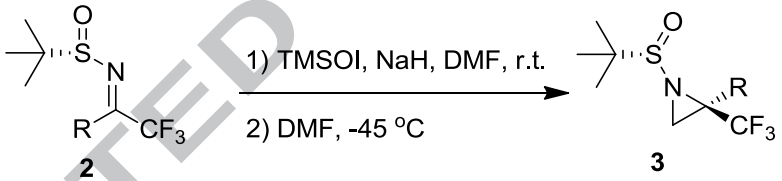
Entry	Reagent	Solvent	*t* (h)	T (°C)	dr[a](**3c**)	Yield[b](%)
1[c]	$Me_3S^+I^-$	DMSO	4	r.t.	76:24	55
2[c]	TMSOI	DMSO	1.5	r.t.	78:22	93
3[c]	TMSOI	THF	>48	r.t.	-[d]	trace
4[c]	TMSOI	Toluene	>48	r.t.	-[d]	trace
5[c]	TMSOI	DMF	1.5	r.t.	77:23	95
6[c]	TMSOI	DMF	1.5	0	79:21	92
7[c]	TMSOI	DMF	1.5	-30	82:18	93
8[c]	TMSOI	DMF	1.5	-45	83:17	93
9[e]	TMSOI	DMF	1.5	-45	89:11	93

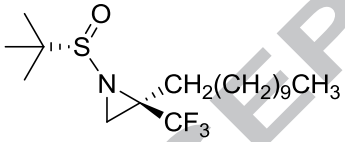
[a] Diastereomeric ratios were determined by ^{19}F NMR spectroscopy of the crude reaction mixture. [b] Total yield of two diastereoisomers after flash chromatography. [c] **2c** in DMF was slowly added to the sulfur ylide reaction mixture after 0.5 h. [d] Not determined. [e] The *in situ* generated sulfur ylide solution was slowly added to a solution of **2c** in DMF.

The scope with respect to chiral CF_3-substituted ketimines for the asymmetric aziridination under the optimized condition (the *in situ* generated sulfur ylide was added into a solution of ketimines in DMF at -45 °C) is presented in Table 2. Aromatic ketimines as well as aliphatic

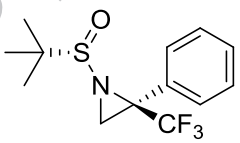
ketimines were underwent the aziridination smoothly to afford the corresponding aziridine products in moderate to excellent yield.[14,15] In general, the electron-withdrawing groups were beneficial to the construction of trifluoromethylated aziridines with good diastereoselectivities, but in lower yields (Table 2, **3d** and **3e**). The ketimine bearing an electron-donating group gave the highest yield (93 %) and lower diastereoselectivity (Table 2, **3c**). Usually, nucleophile was easy to react with electron-poor ketimines, but the reactivities of electron-poor ketoimines were further increased by trifluoromethyl group which resulted in a multitude of undesired side reactions. The acetylenic trifluoromethylated aziridines were also obtained in excellent diastereoselectivies (> 99:1 dr) and moderate yields (Table 2, **3f** and **3g**). The relatively lower yields of **3f** and **3g** may due to the higher electronegativity of Csp than that of Csp^2 making acetylenic ketimines **2f** and **2g** more reactive and leading to undesired side reactions. These results were contrast to the report of Stockman in which only three of nine ketimines exposed to dimthylsulfonium methylide furnished significant amounts of the desired aziridines.[16]

Table 2. Asymmetric synthesis of trifluoromethylated aziridines[a,b,c]

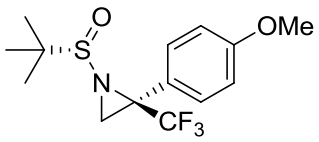




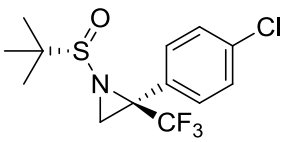
3a: 63 %
86:14 dr



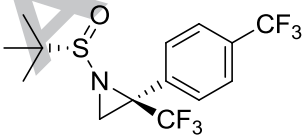
3b: 86 %
93:7 dr



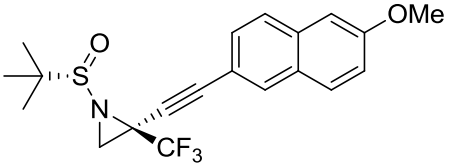
3c: 93 %
89:11 dr



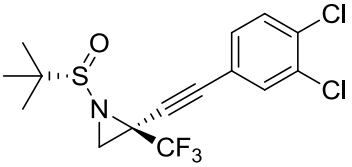
3d : 54 %
92:8 dr



3e: 61 %
92:8 dr



3f: 65 %
>99:1 dr



3g: 45 %
>99:1 dr

[a]Reaction conditions: ketimine **2** (0.5 mmol), TMSOI (1.5 mmol) and NaH (1.5 mmol) in DMF (5 mL), -45 °C, 1.5 h; the *in situ* generated sulfur ylide was added into a solution of ketimine in DMF over a 0.5 h period. [b]Diastereomeric ratios were determined by ^{19}F NMR spectroscopy of the crude reaction mixture. [c]Total isolated yield of two diastereoisomers after flash chromatography.

The absolute configuration of the chiral trifluoromethylated aziridine **3d** was determined by X-ray crystallographic analysis which indicated that the newly formed stereocenter was in *R* configuration (Fig. 1), and the stereocenter of other major products were tentatively assigned as *R* by analogy.[17] A possible mechanism was proposed based on the high diastereoselectivity observed and previous literatures.[18] The oxygen present in the dimethyloxosulfonium methylide can promote chelated transition state as shown in Fig. 2, in which both the sulfinyl oxygen and the dimethyloxosulfonium methylide oxygen chelate to the sodium ion. In this transition state, the CF_3 group prefers to occupy an equatorial position rather than an axial position due to the electrostatic repulsion between the CF_3 group and the lone pair of the sulfur atom, and the nucleophile attack the C=N bond from the least hindered face to form a chelated transition state.

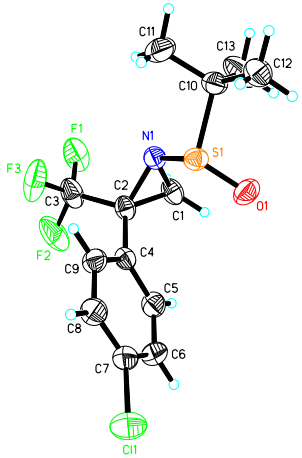


Figure 1. X-ray crystal structure of (S_s, *R*)-**3d**

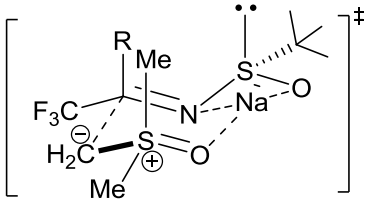
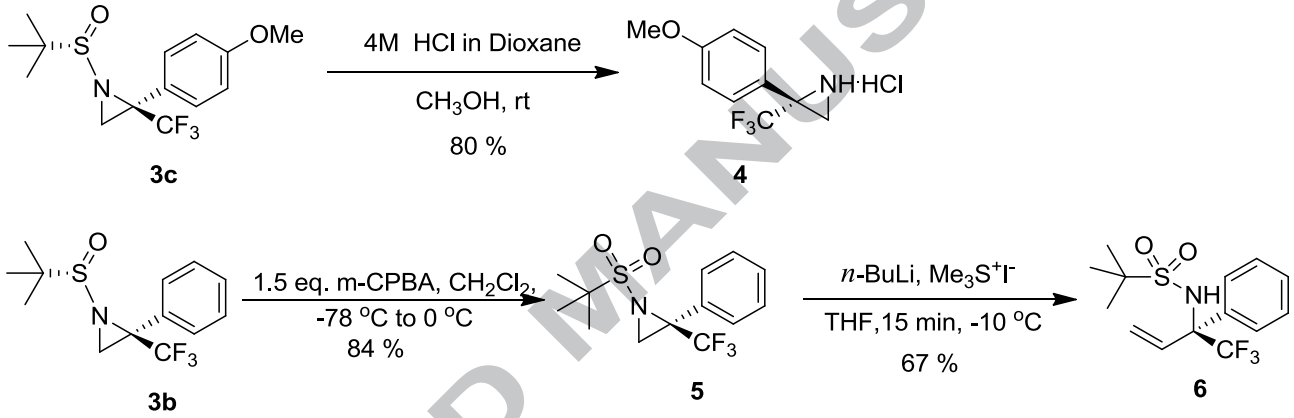


Figure 2. Transition state of the asymmetric aziridination.

To further demonstrate the synthetic utility of these aziridines, the removal of the sulfinyl group was firstly investigated. The deprotection of **3c** using HCl (4 M in dioxane) at room temperature gave the desired optically active trifluoromethylated aziridine hydrochloride **4** in 80 % yield. (Scheme 2). Aziridines are reactive substrates in ring-opening reactions with many nucleophiles due to their ring strain.[19] So the ring-opening reaction of **3b** with dimethylsulfonium methylide was then conducted, but no desired allylamine product was detected even in refluxing THF. This result

confirmed that the excess sulfur ylide will not complicate the aziridination reaction. In seeking a feasibility method to access trifluoromethylated allylic amines, we were attracted to a report from Hodgson and co-workers[20] that focused on the regiodefined conversion of *N*-sulfonylaziridines to allylic *N*-sulfonylamines using dimethylsulfonium methylide. According to Hodgson's method, the sulfinyl group in aziridine **3b** was oxidized into sulfonyl group with *m*-CPBA at -78 °C, then the ring-opening reaction of the resulted sulfonyl aziridine **5** [21] was conducted with *in situ* generated dimethylsulfonium methylide to afford chiral allylamine **6** in 67 % yield (Scheme 2).[22] This chiral α-trifluoromethylallylamine may act as important building block in organic chemistry.



Scheme 2

Conclusions

In summary, the chiral CF_3-substituted (*S*)-*N*-*tert*-butylsulfinyl ketimines displayed higher suitabilities than those of their non-fluorinated analogues as substrates for sulfur ylide mediated aziridination. The high stereo-directing nature of the chiral *tert*-butyl-sulfinyl group and the unique electronic property of trifluoromethyl group induced the good diastereoselectivity during the formation of aziridines. The removal of sulfinyl group from trifluoromethylated aziridine **3c** was readily achieved which provided convenient access to chiral CF_3-substituted aziridines. The synthetic utility of these aziridines was tentatively proved by the successful ring-opening reaction with dimethylsulfonium methylide.

Acknowledgements

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12 Data for **2f**: Pale yellow solid, m.p. 82~83 ^{o}C; IR (KBr, cm^{-1}) : 3348, 2190, 162, 1575, 119, 1149, 1039; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.38 (s, 9 H), 2.95 (s, 3 H), 7.14 (s, 1 H), 7.20 (d, *J* = 9.0 Hz, 1 H), 7.61 (d, *J* =8.5 Hz, 1 H), 7.75 (dd, *J* = 14.5, 8.8 Hz, 2 H), 8.16 (s,1 H); ^{13}C NMR (101 MHz, $CDCl_3$) : δ 22.8, 55.4, 60.3, 79.9, 106.0, 109.2, 114.4, 117.8 (q, *J* (F,C) =280.8 Hz), 120.0, 127.2, 128.1, 128.9, 130.1, 134.5, 136.0, 145.6 (q, *J*(F,C) =40.4 Hz), 159.7; ^{19}F NMR (375 MHz, $CDCl_3$): δ -71.33; Anal. Calcd for $C_{19}H_{18}F_3NO_2S$: C 59.83, H 4.76, N 3.67, Found C 59.97, H 4.68, N 3.65. **2g**: Yellow solid, m.p. 71~72 ^{o}C; IR cm^{-1} : 2973, 2199, 1583, 1466, 1207, 1158, 1114 ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.37 (s, 9 H), 7.50 (s, 2 H), 7.75 (s, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 22.9, 60.9, 80.5, 104.3,117.6 (q, *J*(F,C) = 279.7 Hz), 119.7, 130.8, 131.9, 133.2, 134.3, 136.3, 144.4 (q, *J*(F,C) = 40.4 Hz); ^{19}F NMR (375 MHz, $CDCl_3$): δ -71.40; HR-ESI-MS m/z calcd for $C_{14}H_{13}Cl_2F_3NOS$ [M + H^{+}] : 370.0047, found 370.0043.

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14 General procedure for the preparation of aziridines. NaH (1.5 mmol) was added to a stirred suspension of trimethyl sulfoxonium iodide (TMSOI) (1.5 mmol) in anhydrous DMF (3 mL) at room temperature. After stirring at room temperature for 0.5 h, the sulfur ylide mixture was added dropwise to a solution of **2** (0.5 mmol) in anhydrous DMF (2 mL) at -45 °C, and the reaction was stirred at -45 °C over 1.5 h. After quenching with brine, the cloudy mixture was

filtered through Celite, and washed with ethyl acetate, afforded a biphasic solution which was separated, the aqueous layer was extracted with ethyl acetate (10 mL×3) and washed with brine (5 mL×3). The combined organic layers were dried (Na_2SO_4), and solvent was evaporated in vacuo. The residue was purified by column chromatography with petroleum ether/ethyl acetate as eluent to give trifluoromethylated aziridine **3.**

Selected data: **3a**, dr 84:16; IR(KBr, cm^{-1}): 2926, 2858, 1459, 1163, 1082; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, J = 6.6 Hz , 3 H), 1.21-1.35 (m, 27 H), 1.93 (t, J = 8.2 Hz, 2 H), 2.22 (s, 1 H), 2.58 (s, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 14.1, 22.3, 22.7, 26.2, 26.3, 26.7, 29.2, 29.31, 29.5, 29.6 (d, $J_{(F,C)}$ = 2.0 Hz), 29.7, 30.8 (q, $J_{(F,C)}$ = 123.2 Hz), 31.9, 43.0 (q, $J_{(F,C)}$ = 34.3 Hz), 58.1, 124.0 (q, $J_{(F,C)}$ = 277.7 Hz); ^{19}F NMR (375 MHz, $CDCl_3$): δ -73.33; HR-ESI-MS m/z calcd for $C_{18}H_{35}F_3NOS$ [M+H^+]: 370.2391, found 370.2377. **3b**, Pale yellow solid, m.p. 39~40 ^{o}C; dr 93:7; IR (KBr, cm^{-1}): 2969, 1638, 1344, 1164, 1086; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (s, 9 H), 2.56 (s, 1 H), 3.15 (s, 1 H), 7.35-7.66 (m, 5 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 22.5, 25.5, 45.7 (q, $J_{(F,C)}$ = 36.4 Hz), 57.7, 123.4 (q, $J_{(F,C)}$ = 277.8 Hz), 127.9, 128.6, 130.1, 130.7; ^{19}F NMR (375 MHz, $CDCl_3$): δ -73.44; HR-ESI-MS m/z calcd for $C_{13}H_{16}F_3NNaOS$ [M + Na^+]: 314.0803, found 314.0791. **3c**, Colorless oil, dr 86:14; IR (KBr, cm^{-1}): 2965, 1607, 1460, 1174, 1088; ^{1}H NMR(400 MHz, $CDCl_3$): δ 1.24 (s, 9 H),2 .54 (s, 1 H), 3.12 (s, 1 H), 3.82 (s, 3 H), 6.93 (d, J = 8.2 Hz, 2 H), 7.43 (d, J = 8.0 Hz, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 22.4, 25.7, 45.2 (q, $J_{(F,C)}$ = 36.4 Hz), 55.2, 57.6, 114.0, 119.7, 123.5 (q, $J_{(F,C)}$ = 277.8 Hz), 132.0, 160.7; ^{19}F NMR (375 MHz, $CDCl_3$): δ -73.59; HR-ESI-MS m/z calcd for $C_{14}H_{19}F_3NO_2S$ [M + H^+]: 322.1088, found 322.1081. **3d**,white solid, m.p.63~64 ^{o}C; dr 92:8; IR (KBr, cm^{-1}): 2961, 1585, 1338, 1174, 1089; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (s, 9 H), 2.56 (s, 1 H), 3.12 (s, 1 H), 7.42 (dd, J = 19.4 Hz, 7.7 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 22.4, 25.5, 45.1 (q, $J_{(F,C)}$ = 36.4 Hz), 57.8, 123.4(q, $J_{(F,C)}$ =277.8 Hz), 126.4, 129.0, 132.0, 136.5; ^{19}F NMR (375 MHz, $CDCl_3$): δ -73.48; HR-ESI-MS m/z calcd for $C_{13}H_{15}ClF_3NNaOS$ [M + Na^+]: 348.0413, found 348.0421. **3e**, white solid, m.p.87~88 ^{o}C; dr 92:8; IR (KBr, cm^{-1}): 2957, 1580, 1331, 1174, 1080 ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.26 (s, 9 H), 2.60 (s, 1 H), 3.16 (s, 1 H), 7.67 (dd, J = 18.4 Hz, 7.9 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 22.4, 25.4, 45.2 (q, $J_{(F,C)}$ = 37.4 Hz), 57.9, 123.1 (q, $J_{(F,C)}$ =

278.8 Hz), 123.6 (q, $J_{(F,C)}$ = 273.7 Hz), 125.5 (q, $J_{(F,C)}$ = 4.0 Hz), 131.2, 131.9, 132.2 (q, $J_{(F,C)}$ = 33.3 Hz); ^{19}F NMR(375 MHz, $CDCl_3$): δ -63.01, -73.31; HR-ESI-MS m/z calcd for $C_{14}H_{16}F_6NOS$ [M + H^+]: 360.0857, found 360.0861. **3f**, pale yellow solid, m.p. 82~83 ^oC; IR (KBr, cm^{-1}): 3064, 2959, 2233, 1619, 1174, 1086; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (s, 9 H), 2.56 (s, 1 H), 3.10 (s, 1 H), 3.94 (s, 3 H), 7.12 (d, *J* = 1.8 Hz, 1 H), 7.18 (dd, *J* = 8.9 Hz, *J* = 2.3 Hz, 1 H), 7.52 (d, *J* = 8.4 Hz, 1.2 Hz, 1 H), 7.70 (dd, *J* = 12.7 Hz, *J* = 8.8 Hz, 2 H), 8.00 (s, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 24.0, 38.2 (q, $J_{(F,C)}$ = 41.4 Hz), 38.3, 55.3, 61.6, 75.7, 90.0, 105.8, 115.7, 119.5, 121.5 (q, $J_{(F,C)}$ = 277.7 Hz), 126.9, 128.2, 128.8, 129.5, 132.5, 134.8, 158.7; ^{19}F NMR (375 MHz, $CDCl_3$): δ -74.28; HR-ESI-MS m/z calcd for $C_{20}H_{21}F_3NO_2S$ [M + H^+]: 418.1065, found 418.1045. **3g**, yellow solid, m.p. 68~69; IR cm^{-1} 3060, 2959, 2231, 1598, 1174, 1086 ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.29 (s, 9 H), 2.53 (s, 1 H), 3.04 (s, 1 H), 7.34 (d, *J* =8.3 Hz, 1 H), 7.40 (d, *J* =8.3 Hz, 1 H), 7.60 (s, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 22.4, 29.0, 35.6 (q, $J_{(F,C)}$ =40.9 Hz), 58.0, 79.5, 87.1, 120.8, 121.9 (q, $J_{(F,C)}$ =276.7 Hz), 130.4, 131.3, 132.7, 133.7, 134.1; ^{19}F NMR (375 MHz, $CDCl_3$): δ -74.21; HR-ESI-MS m/z calcd for $C_{15}H_{14}Cl_2F_3NNaOS$ [M+Na^+]: 406.0023, found 406.0027.

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21 Aziridine **3b** (120 mg, 0.39 mmol) was dissolved in CH_2Cl_2 (5 mL) and cooled to -78 ^oC, *m*-CPBA (120 mg, 0.59 mmol) was then added in one portion. The reaction mixture was allowed to warm up to 0 ^oC and stirred for 1 h at 0 ^oC. Subsequently the reaction mixture was poured into a saturated aqueous solution of $NaHCO_3$ (5 mL) and extracted with dichloromethane (5 mL×3). The combined organic phases were washed with 2 N NaOH (5 mL×3) and dried (Na_2SO_4), filtered and evaporated in vacuo. The residue was then purified by column chromatography with

petroleum ether/ethyl acetate as eluant to give aziridine **5** (102 mg, 84 %). White solid, m.p.120~121 ^{o}C; IR (KBr, cm^{-1}): 2989, 1638, 1345, 1311, 1166, 1122; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.50 (s, 9 H), 2.98 (s, 1 H), 3.28 (s, 1 H), 7.46 (m, 3 H),7.70 (d, *J* = 7.3 Hz, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 24.0, 36.1, 49.6 (q, $J_{(F,C)}$ = 47.5 Hz), 61.7, 122.8 (q, $J_{(F,C)}$ = 278.8 Hz), 126.8, 128.2, 130.4, 131.5; ^{19}F NMR (375 MHz, $CDCl_3$): δ -73.39; HR-ESI-MS m/z calcd for $C_{13}H_{16}F_3NNaO_2S$ [M+ Na^+]: 330.0752 , found 330.0745.

22 *n*-BuLi (1.5 M in THF, 0.60 mL, 0.9 mmol) was added dropwise to a stirred suspension of trimethylsulfonium iodide (184 mg, 0.9 mmol) in THF (5 mL) at -10 °C and keep stirring for 15 min. Aziridine **5** (70 mg, 0.22 mmol) in THF (2 mL) was added dropwise at -20 °C, and the reaction mixture was stirred for further 3 h. After quenching with brine solution, the layers were separated. The aqueous layer was extracted with ethyl acetate; the combined organic layers were dried (Na_2SO_4), and solvent was evaporated in vacuo. The residue was purified by column chromatography with petroleum ether/ethyl acetate as eluent to give allylic sulfonamide **6** (48 mg, 67 %). Yellow oil, IR (KBr, cm^{-1}): 2927, 1636, 1456, 1318, 1170, 1129; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.46 (s, 9 H), 4.63 (s, 1 H), 5.43 (d, *J* = 17.6 Hz, 1 H), 5.65 (d, *J* = 11.2 Hz, 1 H), 6.43 (dd, *J* = 17.7 Hz, *J* = 11.2 Hz, 1 H), 7.34-7.50 (m, 3 H), 7.67 (d, *J* = 7.4 Hz, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 24.5, 58.4, 61.2, 70.0 (q, $J_{(F,C)}$ = 27.3 Hz), 121.9, 124.8 (q, $J_{(F,C)}$ = 287.9 Hz), 128.3, 129.0, 132.1, 135.4; ^{19}F NMR (375 MHz, $CDCl_3$): δ -73.33; HR-ESI-MS m/z calcd for $C_{14}H_{18}F_3NNaO_2S$ [M + Na^+]: 344.0908, found 344.0912.