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Imination of Sulfides and Sulfoxides with Sulfonylimino-λ³-Bromane under Mild, Metal-Free Conditions

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Abstract: Exposure of sulfides and sulfoxides to trifluoromethanesulfonylimino(aryl)-λ³-bromane in dichloromethane at 0 °C results in a facile transfer of the sulfonylimino group to sulfur atoms and affords *N*-triflylsulfilimines and -sulfoximines in high yields under transition-metal-free conditions. Imination of (*R*)-methyl *p*-tolyl sulfoxide proceeded with predominant retention of configuration at the stereogenic sulfur center. The Hammett plot afforded ρ values of −0.58 for *para*-substituted thioanisoles and −0.49 for their equivalent sulfoxides, which suggests a buildup of positive charge on the sulfur atoms of sulfides and sulfoxides in the transition state. Calculations suggest a bimolecular nucleophilic-substitution mechanism on the negatively charged nitrogen atom of the sulfonylimino-λ³-bromane, which involves the attack of a sulfide from the opposite side to bromine(III).

Keywords: bromine · hypervalent compounds · imination · sulfides · sulfoxides

Introduction

To introduce nitrogen functionalities directly into aliphatic molecules, hypervalent aryl(sulfonylimino)-λ³-iodanes and their derivatives are most frequently employed as the nitrogen sources in transition-metal-catalyzed nitrenoid reactions.[1] Recent developments in simple methodologies for the generation of imino-λ³-iodanes in situ have greatly enhanced research activity in this area.[2] Sulfonylimino-λ³-iodanes readily generate active metal–nitrenoid species under mild conditions[1] because of the hyper-leaving-group ability of aryl-λ³-iodanyl groups.[3] These species catalytically undergo both amination of unactivated aliphatic (sp^3) C–H bonds and transfer of the imino groups to olefins and heteroatom nucleophiles, which include nitrogen heterocycles, sulfides, and sulfoxides.[4–7] In the absence of metal catalysts, the nitrenoid-transfer reaction of imino-λ³-iodanes does not take place or requires harsh reaction conditions,[8] partly due to their insoluble nature in common organic media, evoked by the highly aggregated polymeric zigzag structure.[9]

Recently, we reported the synthesis of Group 17 analogue trifluoromethanesulfonylimino(aryl)-λ³-bromane (**1**).[10] The sulfonylimino-λ³-bromane **1** functions as an electrophilic imido-group donor and directly undergoes stereospecific aziridination of olefins with retention of stereochemistry and transylidation to iodobenzenes and pyridines.[11] Importantly, all of these reactions do not require the use of any transition-metal catalysts and proceed smoothly at room temperature. The iminobromane **1** is a dimeric species in the solid state and, therefore, is readily soluble in dichloromethane and acetonitrile.[10] In addition, the vastly enhanced nucleofugality of aryl-λ³-bromanyl groups[12] relative to aryl-λ³-iodanyl groups will result in the highly increased activity of **1** as an electrophilic nitrenoid species. Herein, we report a facile oxidative transfer of the sulfonylimino group of imino-λ³-bromane **1** to a wide range of sulfides and sulfoxides. The reaction affords excellent yields of *N*-triflylsulfilimines and -sulfoximines at 0 °C under metal-free conditions. Both sulfilimines and sulfoximines have found many applications as valuable synthons and reagents in organic synthesis and as chiral ligands, particularly for transition-metal catalysis.[13]

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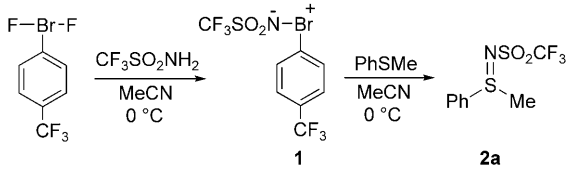
Results and Discussion

Sulfonylimino-λ^3-bromane **1** was prepared from aryl-(difluoro)-λ^3-bromane by facile ligand exchange with trifluoromethanesulfonamide ($TfNH_2$) on the bromane(III) in a high yield (Scheme 1).[10] Transimination between triflylimino-λ^3-bromane **1** and sulfides occurs even at 0°C under transition-metal-free conditions. Exposure of thioanisole to **1** (1.1 equiv) in acetonitrile at 0°C for 1 h under argon resulted in the formation of *N*-triflylsulfilimine **2a** in 64% yield, along with a small amount of *N*-triflylsulfoximine **3b** (2%) (Table 1, entry 1). ESI mass spectra of **1** in acetonitrile solution indicated coordination of a solvent molecule to the positively charged bromine(III) atom.[11a] The acetonitrile coordination enhances the thermal stability of **1** but probably reduces the nucleofugality of the aryl-λ^3-bromanyl group,[14] which, in turn, decreases the nitrenoid reactivity of the imino-λ^3-bromane **1**.



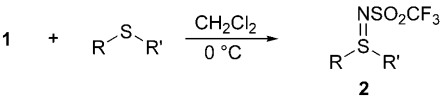
1 2a

Scheme 1. Synthesis of sulfonylimino-λ^3-bromane **1** from difluoro-λ^3-bromane and its transimination with thioanisole.

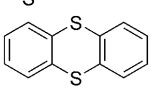
Changing the solvent to noncoordinating dichloromethane promoted the imination of thioanisole and afforded **2a** quantitatively within 10 min (Table 1, entry 2). No formation of sulfoximine **3b** was detected by ^{1}H NMR spectroscopy of the crude reaction mixture. Thioanisoles substituted with electron-donating (MeO or Me) or -withdrawing groups (Cl, Br, C(O)Me, CF_3, CN, or NO_2) were efficiently transformed into *N*-triflylsulfilimines **2b–j** under equimolar conditions. Benzyl, isopropyl, and diphenyl sulfides and cyclic sulfides such as tetrahydrothiophene, pentamethylene sulfide, and 1,4-oxathiane afforded the respective sulfilimines **2** in high yields. It is noted that use of imino-λ^3-iodane analogue *p*-$CF_3C_6H_4I{=}NSO_2CF_3$, instead of **1**, produced only trace amounts of sulfilimine **2a** under the reaction conditions and a large amount of thioanisole was recovered. These results clearly demonstrate a greater reactivity of imino-λ^3-bromane **1** toward thioanisole than that of the imino-λ^3-iodane (Table 1, entry 2 versus 3).

Oxidation of 1,3-dithiane afforded monosulfilimine **2t** selectively, whereas a 2:3 mixture of mono- and bis-sulfilimines **2u**/**2v** was produced from 1,4-dithiane (Table 1, entries 22 and 23). The triflylimino group (=NTf) in **2t** considerably decreases the nucleophilicity of the remaining sulfur atom toward the transimination because of its highly electron-withdrawing nature[15] but the extent of this induced effect is considerably reduced in monosulfilimine **2u**. The use of excess 1,4-dithiane (2 equiv) afforded **2u** predominantly, whereas excess λ^3-bromane **1** (2.5 equiv) gave **2v** exclusively (*cis*/*trans* = 69:31) in a high yield (Table 1, en-

Table 1. Synthesis of *N*-triflylsulfilimines **2**.[a]



2

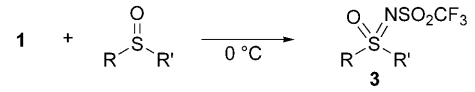
Entry	Sulfide	*t* [min]	**2**	Yield [%][b]	Entry	Sulfide	*t* [min]	**2**	Yield [%][b]
1[c]	PhSMe	60	**2a**	64	14	*i*PrSPh	10	**2l**	90
2	PhSMe	10	**2a**	100	15	$PhSCH_2Ph$	10	**2m**	81
3[d]	PhSMe	10	**2a**	2	16	PhSPh	10	**2n**	79
4	*p*-$MeOC_6H_4SMe$	10	**2b**	90	17	$PhSCH{=}CH_2$	10	**2o**	88
5	*p*-MeC_6H_4SMe	10	**2c**	81	18	$PhCH_2SCH_2Ph$	10	**2p**	89
6	*o*-ClC_6H_4SMe	10	**2d**	97	19		20	**2q**	92
7	*p*-ClC_6H_4SMe	10	**2e**	79	20		10	**2r**	93
8	*p*-BrC_6H_4SMe	10	**2f**	74	21		10	**2s**	93
9	*p*-$MeCOC_6H_4SMe$	10	**2g**	90	22		10	**2t**	83
10	*p*-$CF_3C_6H_4SMe$	10	**2h**	90	23		60	**2u**, **2v**	22, 31
11	*p*-NCC_6H_4SMe	10	**2i**	92	24[e]		120[f]	**2u**, **2v**	84, 5
12	*p*-$NO_2C_6H_4SMe$	10	**2j**	85	25[g]		10	**2v**	89
13	2,4,6-$Me_3C_6H_2SMe$	20	**2k**	89	26		60	**2w**	78

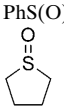
[a] Conditions: sulfide/bromane **1** (1.1 equiv), CH_2Cl_2, 0°C. [b] Isolated yield. [c] MeCN used as solvent. [d] *p*-$CF_3C_6H_4I{=}NTf$, which is poorly soluble in dichloromethane, was used. [e] 1,4-Dithiane (2 equiv) was used. [f] Conditions: −78 to 0°C over 2 h. [g] Bromane **1** (2.5 equiv) was used.

tries 24 and 25). Conjugation in thianthrene makes the selective monoimination to **2w** possible.

Imino-transfer reaction to sulfoxides with imino-λ^3-bromane **1** occurs smoothly under comparable conditions and the results given in Table 2 indicate the high yields obtained

Table 2. Transimination of imino-λ^3-bromane **1** with sulfoxides.[a]

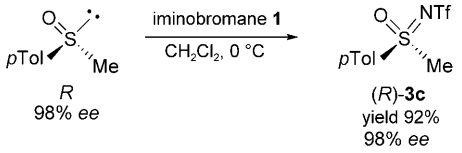


Entry	Sulfoxide	Solvent	t [min]	3	Yield [%][b]
1	MeS(O)Me	MeCN	10	**3a**	95
2	PhS(O)Me	CH_2Cl_2	10	**3b**	99
3	p-$MeC_6H_4S(O)Me$	CH_2Cl_2	10	**3c**	99
4	p-$BrC_6H_4S(O)Me$	CH_2Cl_2	10	**3d**	85
5	p-$NCC_6H_4S(O)Me$	CH_2Cl_2	30	**3e**	98
6	2,4,6-$Me_3C_6H_2S(O)Me$	CH_2Cl_2	360	**3f**	94
7	PhS(O)Ph	CH_2Cl_2	10	**3g**	87
8	$PhS(O)CH{=}CH_2$	CH_2Cl_2	30	**3h**	91
9		CH_2Cl_2	20	**3i**	93

[a] Conditions: Sulfoxide/bromane **1** (1.1 equiv), 0 °C. [b] Isolated yield.

for the formation of *N*-triflylsulfoximines **3**. The attempted Fe^{III}-catalyzed imination of sterically demanding mesityl methyl sulfoxide with *p*-nosylamide and iodosylbenzene led to the recovery of the sulfoxide,[7d] however, sulfoximine **3f** was obtained in high yield under our mild conditions (Table 2, entry 6). Similarly to the selective transimination of phenyl vinyl sulfide (Table 1, entry 17), the oxidative sulfoxide imination tolerates the double bond in phenyl vinyl sulfoxide (Table 2, entry 8).[16]

Scheme 2 depicts the stereochemical outcome of our metal-free transimination to sulfoxides. Comparison of the optical rotation of the product obtained from the reaction of

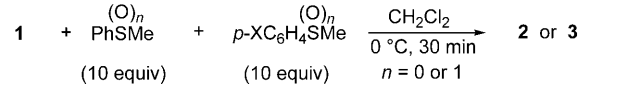


Scheme 2. Retention of configuration in the imination of chiral (*R*)-methyl *p*-tolyl sulfoxide.

(*R*)-methyl *p*-tolyl sulfoxide to that of authentic (*R*)-**3c**, prepared by triflylation of (*R*)-methyl *p*-tolyl sulfoximine,[7f] demonstrated predominant retention of configuration at the stereogenic sulfur center in the imination of the chiral sulfoxide with **1**.

To gain some insight into the mechanism, relative rates of the imino-group transfer for a series of *para*-substituted thioanisoles and their sulfoxides were measured by competitive reactions, in which a mixture of tenfold excess of each of two competing substrates was used (Table 3). Ratios of products **2** (or **3**) were analyzed by ^1H NMR spectroscopy of the crude reaction mixture. The electron-releasing *p*-Me

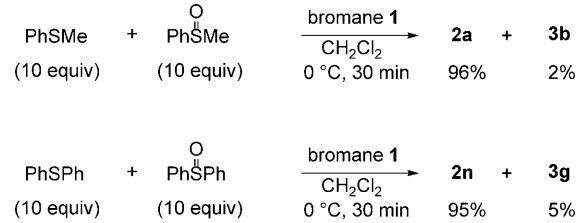
Table 3. Relative rates of thioanisoles and their sulfoxides.



Entry	Sulfide	k_{rel}
1	p-MeC_6H_4SMe	1.3
2	PhSMe	1.0
3	p-BrC_6H_4SMe	0.81
4	p-$CH_3C(O)C_6H_4SMe$	0.56
5	p-$CF_3C_6H_4SMe$	0.49
6	p-NCC_6H_4SMe	0.39
7	p-$NO_2C_6H_4SMe$	0.32
8	p-$MeC_6H_4S(O)Me$	1.1
9	PhS(O)Me	1.0
10	p-$BrC_6H_4S(O)Me$	0.82
11	p-$NCC_6H_4S(O)Me$	0.45

group increased the relative rates (k_{rel}) of the imino-transfer reaction slightly, both to the sulfide and the sulfoxide, whereas electron-withdrawing *p*-CN and *p*-NO_2 groups slowed down the reaction remarkably. The Hammett plot showed good correlations of the relative-rate factors with the σ_p constants of substituents[17] and afforded the reaction constants $\rho = -0.58$ ($r = 0.99$) and -0.49 ($r = 0.99$) for the imination of thioanisoles and sulfoxides, respectively. These negative ρ values suggest that imino-λ^3-bromane **1** functions as an electrophilic imino-transfer agent toward sulfur atoms. Comparable ρ values (-0.77 for thioanisoles and -0.76 for their sulfoxides) were reported in the oxenoid-transfer reactions with dimethyldioxirane in acetone at room temperature.[18] These ρ values evaluated in our imino-group transfer of **1** suggest a lesser buildup of positive charge on the sulfur atoms of sulfides and sulfoxides in the transition state relative to the oxenoid-transfer reactions and, therefore, earlier transition states.

The results from competitive iminations, which show that the more nucleophilic sulfides are much more reactive than sulfoxides, are in line with the above mechanistic considerations (Scheme 3). Similar preference for the formation of sulfilimines over sulfoximines was reported for transition-metal-catalyzed iminations with sulfonylimino-λ^3-iodanes.[7c,d]



Scheme 3. Competitive iminations between sulfides and sulfoxides.

Figure 1 shows the results for quantum chemical calculations[19] at the MP2 level[20,21] on the reaction of dimethyl sulfide with imino(phenyl)-λ^3-bromane **4**, a model of **1**. The

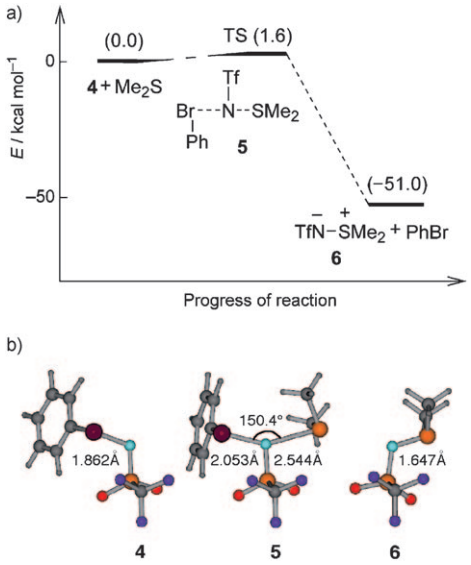
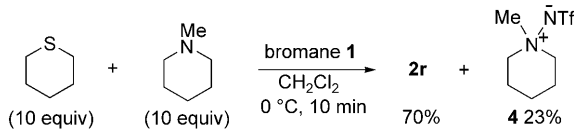


Figure 1. a) Energy profile for the reaction of imino-λ^3-bromane **4** with dimethyl sulfide. b) Calculated structures of **4**, transition state **5**, and sulfilimine **6** at the MP2 level of theory.

transition-state structure **5**, with a roughly linear Br-N-S bond angle (150.4°), was obtained and the activation energy for the transimination is predicted to be only 1.6 kcal mol^{-1}. The reaction involves nucleophilic attack of the sulfur lone-pair of electrons on the low-lying σ*(N−Br) orbital of **4** in an S_N2-type manner.[22] The length of the breaking N−Br bond (2.053 Å) in **5** is comparable to that of **4** (1.862 Å), whereas the length of the N−S bond that is formed (2.544 Å) is longer relative to that of sulfilimine **6** (1.647 Å).[23] These calculations suggest a very early transition state for the imination of dimethyl sulfide, which is directly reflected in a small negative ρ value of −0.58 for the reaction of thioanisoles (Table 3).

Direct transfer of the trifluoromethanesulfonylimino group of the imino-λ^3-bromane **1** to aliphatic trialkylamines also proceeds smoothly, even at 0 °C, under metal-free conditions and results in the selective formation of ammonium ylides in high yields.[11a] Scheme 4 shows the results for competitive transimination between a dialkyl sulfide and a tertiary alkylamine. Preferential formation of sulfilimine **2r**, derived from pentamethylene sulfide, over that of iminoammonium ylide **7** was observed in the reaction with bromane **1**.



Scheme 4. Competitive transimination between pentamethylene sulfide and *N*-methylpiperidine.

Conclusion

A facile oxidative transfer of the sulfonylimino group of imino-λ^3-bromane **1** to a variety of sulfides and sulfoxides was developed. The reaction affords excellent yields of *N*-triflylsulfilimines **2** and -sulfoximines **3** in dichloromethane at 0 °C under metal-free, equimolar conditions. Our results clearly indicate greater reactivity of the sulfonylimino-λ^3-bromane **1** than that of the equivalent imino-λ^3-iodane. Reaction of (*R*)-methyl *p*-tolyl sulfoxide demonstrated predominant retention of configuration at the stereogenic sulfur center after the imination with imino-λ^3-bromane **1**. Small negative ρ values (−0.58 and −0.49 for thioanisoles and their sulfoxides, respectively) evaluated in the imino-group transfer of **1** suggest a slight buildup of positive charge on the sulfur atoms of sulfides and sulfoxides in the transition state, hence, very early transition states, which were also predicted by quantum chemical calculations at the MP2 level. Calculations also indicated that the reaction involves nucleophilic attack of the sulfur atom on the low-lying σ*(N−Br) orbital of imino-λ^3-bromane **1** in an S_N2-type manner with a very low energy barrier.

Experimental Section

General procedure for synthesis of *N*-triflyl-sulfilimines (2) and -sulfoximines (3)

Compound ***2a***: A solution of thioanisole (6.5 mg, 0.052 mmol) in dichloromethane (0.5 mL) was added dropwise to a stirred solution of **1** (21 mg, 0.058 mmol) in dichloromethane (0.6 mL) at 0 °C under argon and the mixture was stirred for 10 min. After addition of water (2 mL), the reaction mixture was extracted with dichloromethane (4×). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum to give an oil, which was purified by preparative TLC (hexane/dichloromethane 1:3) to give **2a** as a colorless oil (14.1 mg, 100%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89–7.81 (m, 2H), 7.73–7.60 (m, 3H), 3.03 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.6, 133.6, 130.5, 126.0, 120.2 (q, J(C,F) = 323 Hz), 39.7 ppm; IR (neat): $\tilde{\nu}$ = 3024, 2929, 1583, 1475, 1446, 1415, 1336, 1136, 1012, 739, 685, 611 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_8H_8F_3NNaO_2S_2$: 293.9846 [*M*+Na]$^+$; found: 293.9856; elemental analysis calcd (%) for $C_8H_8F_3NO_2S_2$: C 35.42, H 2.97, N 5.16; found: C 35.31, H 3.12, N 5.26.

Compound ***2k***: Colorless prisms (recrystallized from dichloromethane/hexane); m.p. 127–129 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.99 (s, 2H), 3.16 (s, 3H), 2.69 (s, 6H), 2.33 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.6, 140.5, 131.7, 126.8, 120.2 (q, J(C,F) = 323 Hz), 34.9, 21.2, 20.2 ppm; IR (KBr): $\tilde{\nu}$ = 3049, 2941, 1741, 1600, 1333, 1213, 1171, 1130, 1010, 972, 856, 768, 744, 627, 609 cm^{-1}; elemental analysis calcd (%) for $C_{11}H_{14}F_3NO_2S_2$: C 42.16, H 4.50, N 4.47; found: C 42.02, H 4.39, N 4.46.

Compound ***2o***: Colorless plates (recrystallized from dichloromethane/hexane); m.p. 56–58 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.76 (m, 2H), 7.71–7.59 (m, 3H), 6.55–6.45 (m, 2H), 6.29–6.18 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 133.7, 133.2, 132.1, 130.5, 127.4, 127.3, 120.2 ppm (q, J(C,F) = 323 Hz); IR (KBr): $\tilde{\nu}$ = 3105, 3070, 1473, 1446, 1335, 1203, 1174, 1132, 1011, 991, 957, 779, 756, 742, 687, 619, 607 cm^{-1}; elemental analysis calcd (%) for $C_9H_8F_3NO_2S_2$: C 38.16, H 2.85, N 4.94; found: C 38.09, H 2.98, N 5.08.

Compound ***2q***: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.42$–3.31 (m, 2H), 3.28–3.19 (m, 2H), 2.65–2.50 (m, 2H), 2.25–2.10 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 120.3$ (q, J(C,F) = 323 Hz), 52.4, 26.7 ppm; IR (neat): $\tilde{\nu} = 2954$, 2883, 1448, 1414, 1329, 1171, 997, 895, 768, 735, 609 cm^{-1}; elemental analysis calcd (%) for $C_5H_8F_3NO_2S_2$: C 25.53, H 3.43, N 5.95; found: C 25.52, H 3.44, N 6.25.

Compound ***2s***: Colorless plates (recrystallized from dichloromethane/hexane); m.p. 84–88 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.52$ (ddd, J = 13.2, 10.0, 2.0 Hz, 2H), 4.01 (dt, J = 13.2, 3.8 Hz, 2H), 3.22 (ddd, J = 14.0, 10.0, 3.8 Hz, 2H), 2.97 ppm (ddd, J = 14.0, 3.8, 2.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 120.2$ (q, J(C,F) = 323 Hz), 59.4, 42.1 ppm; IR (KBr): $\tilde{\nu} = 3012$, 2941, 2881, 1462, 1410, 1383, 1333, 1219, 1180, 1157, 1103, 1065, 1018, 991, 966, 833, 768, 741, 615 cm^{-1}; elemental analysis calcd (%) for $C_5H_8F_3NO_3S_2$: C 23.90, H 3.21, N 5.57; found: C 23.77, H 3.14, N 5.62.

Compound ***2t***: Colorless needles (recrystallized from dichloromethane/hexane); m.p. 134–135 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.29$ (br d, J = 12.8 Hz, 1H), 4.10 (d, J = 12.8 Hz, 1H), 3.61–3.53 (m, 1H), 3.20 (dt, J = 13.1, 2.6 Hz, 1H), 2.82–2.73 (m, 1H), 2.71–2.59 (m, 2H), 2.46–2.33 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 120.2$ (q, J(C,F) = 323 Hz), 49.3, 49.2, 28.0, 27.7 ppm; IR (KBr): $\tilde{\nu} = 2997$, 2929, 1433, 1336, 1217, 1178, 1138, 1086, 999, 924, 891, 820, 771, 748, 727, 652, 613 cm^{-1}; elemental analysis calcd (%) for $C_5H_8F_3NO_2S_3$: C 22.47, H 3.02, N 5.24; found: C 22.58, H 3.04, N 5.24.

Compound ***2u***: Colorless oil; ^{1}H NMR (400 MHz, [D$_6$]acetone): $\delta = 3.72$–3.59 (m, 4H), 3.46–3.36 (m, 2H), 2.91–2.78 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 120.2$ (q, J(C,F) = 322 Hz), 43.8, 19.1 ppm; IR (neat): $\tilde{\nu} = 2981$, 2929, 1408, 1335, 1186, 1130, 1018, 945, 895, 771, 742, 609 cm^{-1}; elemental analysis calcd (%) for $C_5H_8F_3NO_2S_3$: C 22.47, H 3.02, N 5.24; found: C 22.23, H 3.06, N 5.01.

Compound cis-***2v***: Colorless prisms (recrystallized from acetone/hexane); m.p. 192 °C (decomposition); ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta = 4.04$–3.91 (m, 4H), 3.84–3.71 ppm (m, 4H); ^{13}C NMR (75 MHz, [D$_6$]acetone): $\delta = 121.2$ (q, J(C,F) = 322 Hz), 40.3 ppm; IR (KBr): $\tilde{\nu} =$ 3010, 2931, 1417, 1336, 1225, 1182, 1157, 1136, 1039, 989, 908, 775, 746, 613 cm^{-1}; HRMS (ESI): m/z: calcd for $C_6H_8F_6N_2NaO_4S_4$: 436.9169 $[M+Na]^+$; found: 436.9167.

Compound trans-***2v***: White powder (recrystallized from acetone); m.p. 254–255 °C (decomposition); ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta = 4.07$ (d, J = 11.5 Hz, 4H), 3.52 ppm (d, J = 11.5 Hz, 4H); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 119.8$ (q, J(C,F) = 323 Hz), 32.0 ppm; IR (KBr): $\tilde{\nu} =$ 2991, 2947, 1412, 1333, 1223, 1180, 1119, 1003, 899, 777, 750, 627 cm^{-1}; elemental analysis calcd (%) for $C_6H_8F_6N_2O_4S_4$: C 17.39, H 1.95, N 6.76; found: C 17.63, H 2.22, N 7.02.

Compound ***2w***: Colorless needles (recrystallized from dichloromethane/hexane); m.p. 131–132 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.04$ (dd, J = 7.7, 1.3 Hz, 2H), 7.77 (dd, J = 7.7, 1.3 Hz, 2H), 7.66 (dt, J = 1.3, 7.7 Hz, 2H), 7.60 ppm (dt, J = 1.3, 7.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 131.9, 131.3, 130.0, 129.4, 126.2, 120.3 ppm (q, J(C,F) = 323 Hz); IR (KBr): $\tilde{\nu} = 3078$, 2999, 1572, 1450, 1338, 1217, 1165, 1132, 1043, 972, 752, 702, 611 cm^{-1}; elemental analysis calcd (%) for $C_{13}H_8F_3NO_2S_3$: C 42.97, H 2.22, N 3.85; found: C 42.92, H 2.44, N 3.84.

Compound ***3c***: Colorless plates (recrystallized from diethyl ether/hexane); m.p. 89–91 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.92$ (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 3.49 (s, 3H), 2.51 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 147.0$, 134.1, 130.8, 127.4, 119.2 (q, J-(C,F) = 321 Hz), 47.0, 21.8 ppm; IR (KBr): $\tilde{\nu} = 3020$, 2925, 1581, 1475, 1454, 1410, 1358, 1342, 1321, 1259, 1201, 1138, 1097, 1061, 991, 976, 796, 741, 688, 627 cm^{-1}; HRMS (ESI): m/z: calcd for $C_9H_{10}F_3NNaO_3S_2$: 323.9952 $[M+Na]^+$; found: 323.9952; elemental analysis calcd (%) for $C_9H_{10}F_3NO_3S_2$: C 35.88, H 3.35, N 4.65; found: C 35.71, H 3.53, N 4.65.

Compound ***3f***: Colorless needles (recrystallized from dichloromethane/hexane); m.p. 93–94 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.06$ (s, 2H), 3.56 (s, 3H), 2.72 (s, 6H), 2.35 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 145.2$, 139.7, 133.4, 131.3, 119.2 (q, J(C,F) = 321.4 Hz), 47.0, 22.8, 21.1 ppm; IR (KBr): $\tilde{\nu} = 3022$, 2978, 2941, 1603, 1560, 1456, 1385, 1344, 1263, 1186, 1138, 1066, 958, 860, 791, 766, 741, 706, 623 cm^{-1}; elemental analysis calcd (%) for $C_{11}H_{14}F_3NO_3S_2$: C 40.11, H 4.28, N 4.25; found: C 39.99, H 4.21, N 4.20.

Compound ***3h***: Colorless needles (recrystallized from dichloromethane/hexane); m.p. 50–51 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.01$ (d, J = 7.8 Hz, 2H), 7.78 (t, J = 7.2 Hz, 1H), 7.67 (dd, J = 7.8, 7.2 Hz, 2H), 6.85 (dd, J = 16.2, 9.4 Hz, 1H), 6.64 (d, J = 16.2 Hz, 1H), 6.36 ppm (d, J = 9.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 136.3$, 136.2, 135.3, 131.1, 130.2, 127.9, 119.2 ppm (q, J(C,F) = 321 Hz); IR (KBr): $\tilde{\nu} = 3111$, 3087, 3024, 2966, 1444, 1385, 1344, 1265, 1194, 1130, 1095, 1061, 997, 958, 798, 771, 742, 690, 640 cm^{-1}; elemental analysis calcd (%) for $C_9H_8F_3NO_3S_2$: C 36.12, H 2.69, N 4.68; found: C 35.86, H 2.76, N 4.89.

Compound ***3i***: White needles (recrystallized from ethyl acetate/hexane); m.p. 58–59 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.86$–3.74 (m, 2H), 3.50–3.37 (m, 2H), 2.49–2.32 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 119.2 (q, J(C,F) = 321 Hz), 54.9, 23.3 ppm; IR (KBr): $\tilde{\nu} = 3018$, 2976, 2945, 1450, 1400, 1350, 1286, 1203, 1134, 1101, 1045, 903, 787, 750, 727, 656, 634 cm^{-1}; elemental analysis calcd (%) for $C_5H_8F_3NO_3S_2$: C 23.90, H 3.21, N 5.57; found: C 24.14, H 3.19, N 5.73.

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