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β-(Trifluoromethyl)vinyl Sulfonium Salts: Preparation and Reactions with Active Methylene and Methenyl Compounds

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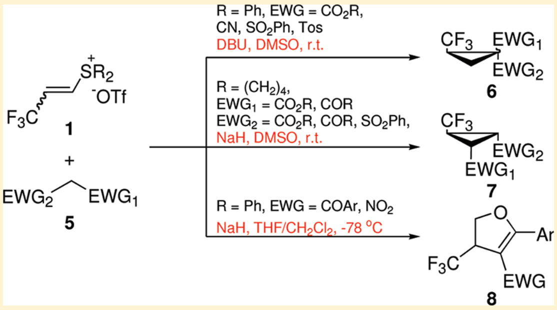
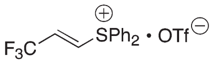
Supporting Information

ABSTRACT: Two trifluoromethyl-substituted building blocks β-(trifluoromethyl)vinyl sulfonium salts **1** and **2** were developed. Reactions of β-(trifluoromethyl)vinyl sulfonium salt **1** with active methylene compounds containing electron-withdrawing groups using DBU as the base in DMSO occurred to give trifluoromethyl-substituted cyclopropane derivatives **7** as the major products. In contrast, reactions of β-(trifluoromethyl)vinyl sulfonium salt **2** with active methylene compounds occurred with the migration of one of the electron-withdrawing groups to give the products **8** as the major products when NaH was used as the base in DMSO. Moreover, when NaH was used as base in THF/CH_2Cl_2 at −78 °C, reaction of β-(trifluoromethyl)vinyl sulfonium salt **1** gave trifluoromethyl-substituted 2,3-dihydrofuran derivatives **9** as the major products. A working mechanism was proposed to explain the different behaviors of the β-(trifluoromethyl)vinyl sulfonium salts **1** or **2** with active methylene compounds under these different conditions.



INTRODUCTION

Organofluorine compounds have attracted special attention in the field of drug discovery because of fluorine's unique physical and chemical properties.[1,2] Consequently, broad research efforts have been focused on the strategic introduction of fluorine substitution into drug-like molecules in medicinal and agricultural chemistry.[3] Among all the strategies, using fluorinated building-blocks that have both fluorine atom and substitutable functional groups are particularly attractive, since reactions of fluorinated building-blocks avoid the harsh reaction conditions and special equipments needed for handling fluorine or other fluorinated reagents.[1,4] On the other hand, because of the intrinsic electrophilic nature of the sulfonium ions, vinylsulfonium salts are well-known as good Michael acceptors that undergo addition reactions with various nucleophiles.[5] Typically, they are used and act as ethylene transfer reagents via initial Michael addition and subsequent elimination of thioether in the synthesis of cyclopropanes, oxiranes, aziridines, and other heterocycles.[6] Inspired by the diverse reactivity of vinylsulfonium salts and our long-term interest in development of trifluoromethylated building-blocks, we designed two β-trifluoromethyl-substituted vinylsulfoniums **1**[7] and **2**. We found that compounds **1** and **2** could be readily prepared from commercially available 3,3,3-trifluoropropene in five steps. Subsequent studies disclosed that reactions of various active methylene or methenyl compounds with β-(trifluoromethyl)-vinyl sulfonium salts **1** and **2** in the presence of different bases differed greatly. Three different products trifluoromethyl-substituted cyclopropane derivatives **7**,[8] trifluoromethyl-substituted cyclopropane derivatives **8** with one of the electron-withdrawing groups migrated, or trifluoromethyl-substituted 2,3-dihydrofuran derivatives **9** could be obtained. Herein, we disclose these findings and propose a working mechanism to explain the different behaviors of the β-trifluoromethyl-substituted vinylsulfonium salts **1** or **2** with active methylene compounds under different conditions.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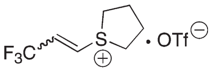
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RESULTS

1. Preparation of β-(Trifluoromethyl)vinyl Sulfonium Salts 1 and 2. β-(Trifluoromethyl)vinyl sulfonium salts **1** and **2** were readily prepared from commercially available 3,3,3-trifluoropropene in five steps, as illustrated in Scheme 1. Intermediate **3** was readily prepared in two steps in 40 g scale according to the reported literature procedure from 3,3,3-trifluoropropene.[9] Esterification of the resulting alcohol with 1.2 equiv of triflic anhydride and 1.2 equiv of pyridine in CH_2Cl_2 gave intermediate **4** in quantitative yield. Reaction of intermediate **4** with tetrahydrothiophene occurred smoothly in toluene at 100 °C to give a pale gray solid **5b** in 84% yield. Reaction of intermediate **4** with diphenyl sulfide was rather slow under the same conditions, mainly because of the low nucleophilicity of diphenyl sulfide. The diphenylsulfonium salt **5a** was obtained in 67% yield under

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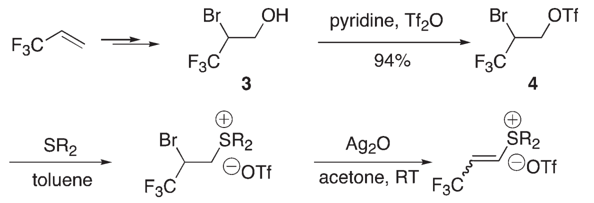
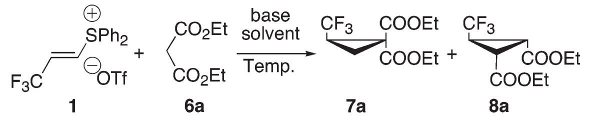
Scheme 1. Preparation of β-(Trifluoromethyl)vinyl Sulfonium Salts 1 and 2



R = Ph, 67%, **5a**
R = $(CH_2CH_2)_2$, 84%, **5b**

R = Ph, E/Z = 6:1, 93%, **1**
R = $(CH_2CH_2)_2$, E/Z = 6:1, 93%, **2**

Table 1. Optimization of the Conditions for the Reaction of β-(Trifluoromethyl)vinyl Diphenylsulfonium salt 1 with Ethyl Malonate 6a



				yield (%)[a]	
entry	base	solvent	temp, °C	7a	8a
1	DBU	CH_2Cl_2	0	80 (60)[b]	0
2	DBU	Et_2O/CH_2Cl_2	0	66	0
3	DBU	CH_3CN	0	92	0
4	DBU	DMF	RT	94	0
5	DBU	DMSO	RT	99	0
6	NaH	DMF	RT	89	7
7	NaH	HMPA	RT	90	7
8	NaH	DMSO	RT	85	15
9	NaH	DMSO	60	81	19
10	*n*BuLi	DMSO	RT	94	4
11	$LiN(TMS)_2$	DMSO	RT	96	0
12	$LiN(TMS)_2$	THF/HMPA	0	92	7
13	$KN(TMS)_2$	DMSO	RT	89	0

[a] Yields were determined by ^{19}F NMR analysis of the crude reaction mixture with α,α,α-trifluorotoluene as an internal standard. [b] Isolated yield.

solvent-free conditions at 100 °C for 48 h. Elimination of hydrobromide from intermediates **5a** and **5b** in the presence of stoichiometric amounts of Ag_2O in acetone at room temperature gave the desired building blocks **1** and **2**, respectively, in excellent yields. Compounds **1** and **2** prepared according to these procedures were *E*/*Z* mixtures (6:1), as determined by ^{19}F NMR and ^{1}H NMR spectroscopy.

Interestingly, the *Z*-isomer of **1** underwent isomerization to thermodynamically more stable *E*-isomer easily in the presence of 5 mol % Ag_2O or other weak nucleophiles such as triphenylphosphine, pyridine, or AgOAc (see Supporting Information), while no isomerization of *E*- or *Z*-isomer of **2** was observed under these conditions.

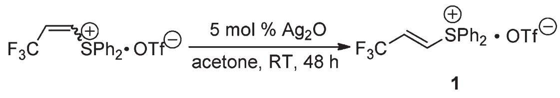


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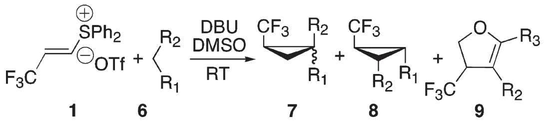
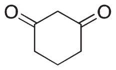
Table 2. Reactions of β-(Trifluoromethyl)vinyl Diphenylsulfonium Salt 1 with Active Methylene Molecules 6 in the Presence of DBU in DMSO[a]



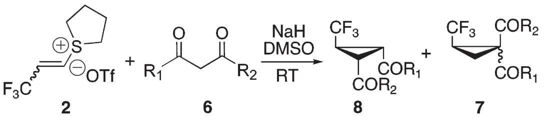
entry	6	R1	R2	7 : 8 : 9[b]	product	yield(%)[c]
1	**6a**	CO_2Et	CO_2Et	100:0:0	**7a**	87
2	**6b**	CO_2Me	CO_2Me	100:0:0	**7b**	79
3	**6c**	CO_2Bn	CO_2Bn	100:0:0	**7c**	93
4	**6d**	CN	CN	100:0:0	**7d**	86
5	**6e**	CN	CO_2Et	100:0:0	**7e**	81
6	**6f**	CN	SO_2Ph	100:0:0	**7f**	86
7	**6g**	CN	Ts	100:0:0	**7g**	95
8	**6h**	CO_2Me	SO_2Ph	100:0:0	**7h**	87[d]
9	**6i**	CO_2Et	SO_2Ph	100:0:0	**7i**	88[d]
10	**6j**	COPh	CO_2Et	22:6:72	**7j**	15[c]
11	**6k**	COMe	CO_2Et	50:6:44	**7k**	49[c,e]
12	**6l**	COPh	SO_2Ph	57:34:9	**7l**	57[c,e]
13	**6m**			28:0:72	**7m**	22[c]

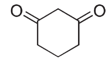
[a] Reaction conditions: **1** (0.3 mmol), **6** (0.36 mmol), and DBU (0.36 mmol) in DMSO (9 mL) for 10 min at room temperature. [b] Determined by ^{19}F NMR analysis of the crude reaction mixture with α,α,α-trifluorotoluene as an internal standard. [c] Isolated yield of 7. [d] Two diastereomers of 7 (3:1). [e] Unseperable mixture of three isomers.

2. Reaction of β-(Trifluoromethyl)vinyl Sulfonium Salt 1 with Active Methylene Compounds in the Presence of DBU in DMSO. With β-(trifluoromethyl)vinyl sulfonium salts **1** and **2** in hand, we began to study the reactions of β-(trifluoromethyl)-vinyl sulfonium salt **1** with active methylene molecules in the presence of different bases in different solvents. Reaction of β-(trifluoromethyl)vinyl diphenylsulfonium salt **1** with **6a** in the presence of 1.2 equiv of DBU as the base in CH_2Cl_2 occurred smoothly at 0 °C for less than 10 min to give the desired trifluoromethyl-substituted cyclopropane derivative **7a** in 60% yield and a minor side product trifluoromethyl propyne which was formed through elimination under basic conditions as determined by ^{19}F NMR spectroscopy (Table 1, entry 1).[10,11] The side product trifluoromethyl propyne was not observed when the reaction was conducted in polar solvents such as CH_3CN, DMF, or DMSO. As a result, reactions in these polar solvents gave higher yields (Table 1, entries 3−5). It was further found that the reaction was not sensitive to bases. Reactions in the presence of other bases such as NaH, n-BuLi, $LiN(TMS)_2$, or $KN(TMS)_2$ gave the desired products in good to excellent yields (Table 1, entries 6−13). Reactions using NaH as base in polar solvents such as DMF, HMPA, or DMSO, however, occurred to generate the desired product **7a** in 81−94% yield and a minor side product **8a** in less than 20% yield (Table 1, entries 8−10).

Under the optimized conditions (DBU as the base in DMSO (entry 5 in Table 1)), reactions of β-(trifluoromethyl)vinyl diphenylsulfonium salt **1** with a variety of active methylene molecules were studied. The results are summarized in Table 2. Reactions of active methylene molecules **6** containing electron-withdrawing groups such as ester, cyano, or sulfone occurred smoothly to give the desired products in good to excellent yields (Table 1, entries 1−9). Reactions of active methylene molecules

Table 3. Reaction of *β*-(Trifluoromethyl)vinyl Sulfonium Salt 2 with Active Methylene Compounds 6 in the Presence of NaH in DMSO[a]



entry	R$_1$	R$_2$	**6**	**8** : **7** [b]	product	yield(%)[c]
1	OEt	OEt	**6a**	89:11	**8a**	68
2	OMe	OMe	**6b**	100:0	**8b**	77
3	OBn	OBn	**6c**	100:0	**8c**	86
4	Ph	OEt	**6j**	92:8	**8j**	73[d]
5	Ph	Me	**6n**	100:0	**8n**	61
6	Me	Me	**6o**	100:0	**8o**	41
7	PhO$_2$S	COPh	**6l**	100:0	**8l**	79[e]
8	PhO$_2$S	COPh	**6l**	100:0	**8l**	66
9	PhO$_2$S	CO$_2$Me	**6h**	100:0	**8h**	94
10	PhO$_2$S	CO$_2$Et	**6i**	100:0	**8i**	91
11			**6m**	100:0	**8m**	58[f]

[a] Reaction conditions: **2** (0.3 mmol), **6** (0.36 mmol), and NaH (0.36 mmol) in DMSO (9 mL) for 10 min at room temperature. [b] Determined by ^{19}F NMR analysis of the crude reaction mixture with α,α,α-trifluorotoluene as an internal standard. [c] Isolated yield of **8**. [d] 12% of side product **9** was observed by ^{19}F NMR spectroscopy. [e] *β*-(Trifluoromethyl)vinyl sulfonium salt **1** was used. [f] 14% of side product **9** was observed by ^{19}F NMR spectroscopy.

containing two different electron-withdrawing groups theoretically could give two diastereomers. Two diastereomers (dr = 3:1) were isolated for the reactions of methyl phenylsulfonylacetate **6h** or ethyl phenylsulfonylacetate **6i** with *β*-(trifluoromethyl)vinyl diphenylsulfonium salt **1** (Table 2, entries 8 and 9). The major isomer was determined to have a cis relationship of the trifluoromethyl and carboxyl groups. However, reactions of active methylene molecules containing a cyano group and an ester group or a sulfonyl group gave only one product in high yields (Table 2, entries 5−7). The configuration of the product was determined to have a cis relationship of the trifluoromethyl and cyano group. The stereochemistry of these cyclopropanation products was established by comparing their ^{1}H NMR and ^{19}F NMR spectra with those reported in the literature.[8g]

Interestingly, when active methylene molecules containing a ketone group were reacted under these conditions, three isomers were isolated in different amounts. For example, reaction of ethyl acetoacetate with *β*-(trifluoromethyl)vinyl diphenylsulfonium salt **1** gave cyclopropane **7k**, its isomer **8k**, and a dihydrofuran derivative **9k** in 50%, 6%, and 44% yields, respectively, as determined by ^{19}F NMR spectroscopy.

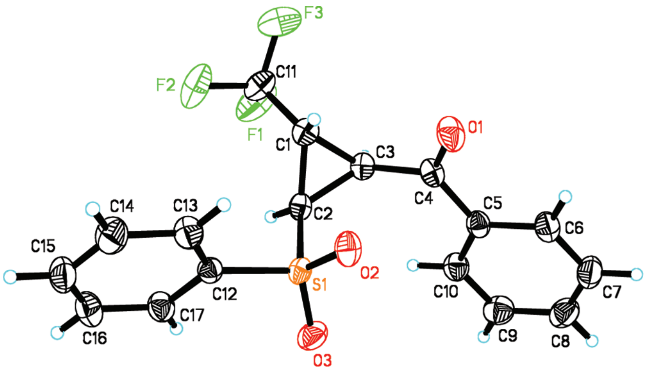
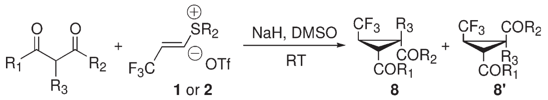
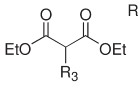
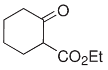
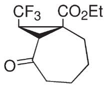


Figure 1. The ORTEP view of **8l** with thermal ellipsoids set at 30% probability level.

Table 4. Reaction of *β*-(Trifluoromethyl)vinyl Sulfonium Salts 1 or 2 with Active Methenyl Compounds in the Presence of NaH in DMSO[a]



entry	**1** or **2**	substrates		product	*dr*(**8**:**8'**)[b]	yield(%)[c]
1	**1**		R$_3$ = Bn	**8p**	89:11	90
2	**2**		Bn	**8p**	88:12	89
3	**1**		Ph	**8q**	86:14	68
4	**2**		Ph	**8q**	88:12	78
5	**1**		Me	**8r**	100:0	68
6	**1**			**8s** 		47

[a] Reaction conditions: **1** or **2** (0.3 mmol), active methenyl compound (0.36 mmol), and NaH (0.36 mmol) in DMSO (9 mL) for 10 min at room temperature. [b] Determined by ^{19}F NMR analysis of the crude reaction mixture with α,α,α-trifluorotoluene as an internal standard. [c] Isolated yield of **8**.

3. Reaction of *β*-(Trifluoromethyl)vinyl Sulfonium Salt 2 with Active Methylene Compounds in the Presence of NaH in DMSO. During the optimization of the conditions for the reaction of *β*-(trifluoromethyl)vinyl sulfonium salt **1** with diethylmalonate, it was found that a minor side product **8a** in which one of the electron-withdrawing groups migrated[12] was isolated when NaH was used as the base. Surprisingly, when *β*-(trifluoromethyl)vinyl sulfonium salt **2** was used under the same conditions (NaH as the base in DMSO), compound **8a** was isolated as the major product in 68% yield (Table 3, entry 1). The structure of compound **8a** was determined by measuring the coupling constant of cyclopropane proton ($^3J_{HH}$ = 6.0 Hz) in ^{1}H NMR spectroscopy. Reactions of other active methylene compounds with *β*-(trifluoromethyl)vinyl sulfonium salt **2** using NaH as the base occurred similarly to give **8** in good to excellent yields (Table 3). For example, reactions of diketones occurred smoothly to give compounds **8** in good yields (Table 3, entries 5−6, 11). Reactions of active methylene compounds with one sulfone group and one ketone group or ester group gave the corresponding compounds **8** exclusively in 66%, 94%, and 91% yields, respectively (Table 3, entries, 8−10).

The structures of compound **8** were further confirmed by X-ray crystallographic analysis. The X-ray structure of compound **8l** showed that the sulfone is cis to the ketone group and the trifluoromethyl group is trans to the sulfone or ketone group. The bond lengths of the carbon−carbon bonds in the trifluoromethyl-substituted cyclopropane are 1.489 and 1.497 Å, which are slightly shorter than those in cyclopropane (Figure 1).[8j]

4. Reaction of *β*-(Trifluoromethyl)vinyl Sulfonium Salts 1 and 2 with Active Methenyl Compounds in the Presence of NaH in DMSO. When active methenyl compounds were reacted with *β*-(trifluoromethyl)vinyl sulfonium salt **1** or **2** in the presence of NaH in DMSO, only the products with the migration

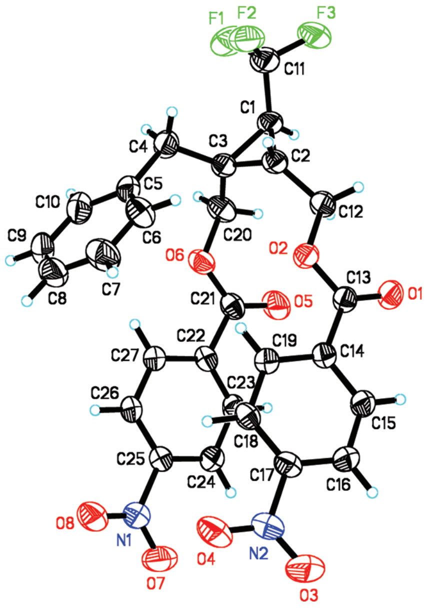
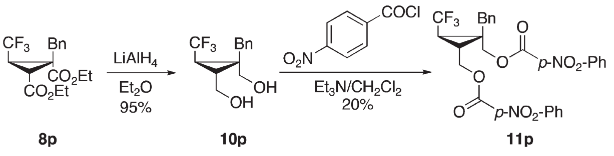


Figure 2. The ORTEP view of **11p** with thermal ellipsoids set at 30% probability level.

of one of the electron-withdrawing groups were observed (Table 4). It was found that reactions of β-(trifluoromethyl)vinyl sulfonium salt **1** or **2** with the same active methenyl compounds gave similar selectivities and yields (Table 4, entries 1−4). For example, reaction of β-(trifluoromethyl)vinyl sulfonium salt **1** with ethyl 2-benzylmalonate afforded the product in 90% in 89:11 diastereoselectivity (Table 4, entry 1), while the same reaction with β-(trifluoromethyl)vinyl sulfonium salt **2** gave the corresponding product in 89% yield in 88:12 diastereoselectivity (Table 4, entry 2). Interestingly, migration of carbonyl group was preferred for the active methenyl compounds containing both carbonyl group and ester group (Table 4, entry 6).

The relative configuration of compound **8p** was determined by X-ray crystallographic analysis of single crystals of its derivative **11p**. **11p** was obtained by first the reduction of **8p** with $LiAlH_4$, followed by esterification of the resulting diol with *p*-nitrobenzoyl chloride and recrystallization from chloroform/diethyl ether (eq 2). From the X-ray structure of **11p**, it was unambiguously determined that the trifluoromethyl group is cis to the benzyl group (Figure 2).

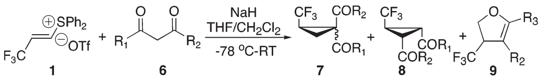


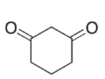
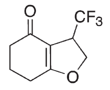
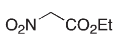
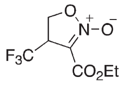
(2)

5. Reaction of β-(Trifluoromethyl)vinyl Sulfonium Salt 1 with Active Methylene Compounds in the Presence of NaH in THF/CH_2Cl_2 at −78 °C.

In some cases for the reaction of β-(trifluoromethyl)vinyl sulfonium salt **1** with active methylene compounds, trifluoromethyl-substitited 2,3-dihydrofuran derivatives[13] **9** were obtained as the major products (Table 2, entries 10 and 13). The reaction conditions were further investigated to determine if the formation of trifluoromethyl-substituted 2,3-dihydrofuran derivatives **9** is general toward other active methylene compounds. We studied the reaction of β-(trifluoromethyl)vinyl sulfonium salt **1** with ethyl 3-oxo-3-phenylpropanoate **6j** as a model reaction to optimize the conditions. It was found that reactions using NaH as the base in THF/CH_2Cl_2 (3:1, v/v) at −78 °C occurred to full conversion after 30 min to give compound **9j** as the major product and a small amount of compound **7j** (Table 5, entry 1). Other active methylene compounds with a ketone functional group also reacted to give compounds **9m**, **9u**−**9y** as the major products under these reaction conditions (Table 5, entries 2−8). Interestingly, reaction of ethyl 2-nitroacetate gave exclusively nitrone **9y** in quantitative yield (Table 5, entry 9).

Table 5. Reaction of β-(Trifluoromethyl)vinyl Sulfonium Salt 1 with Active Methylene Compounds 6 in the Presence of NaH in THF/CH_2Cl_2 at −78 °C[a]



entry	6	R_1	R_2	7:8:9[b]	9	yield(%)[c]
1	**6j**	Ph	OEt	5:8:87	**9j**	70
2	**6u**	4-O_2N-Ph	OEt	3:41:56	**9u**	50
3	**6v**	4-MeOPh	OEt	8:5:87	**9v**	84[b,d]
4	**6w**	4-BrPh	OEt	3:14:83	**9w**	82[b,d]
5	**6x**	2-thiophenyl	OEt	0:7:93	**9x**	80
6	**6n**	Me	Ph	2:89:9	**9n**	9[b,d]
7	**6o**	Me	Me	3:39:58	**9o**	57[b,d]
8	**6m**			 28:0:72	**9m**	64
9	**6y**				**9y**	99[e]

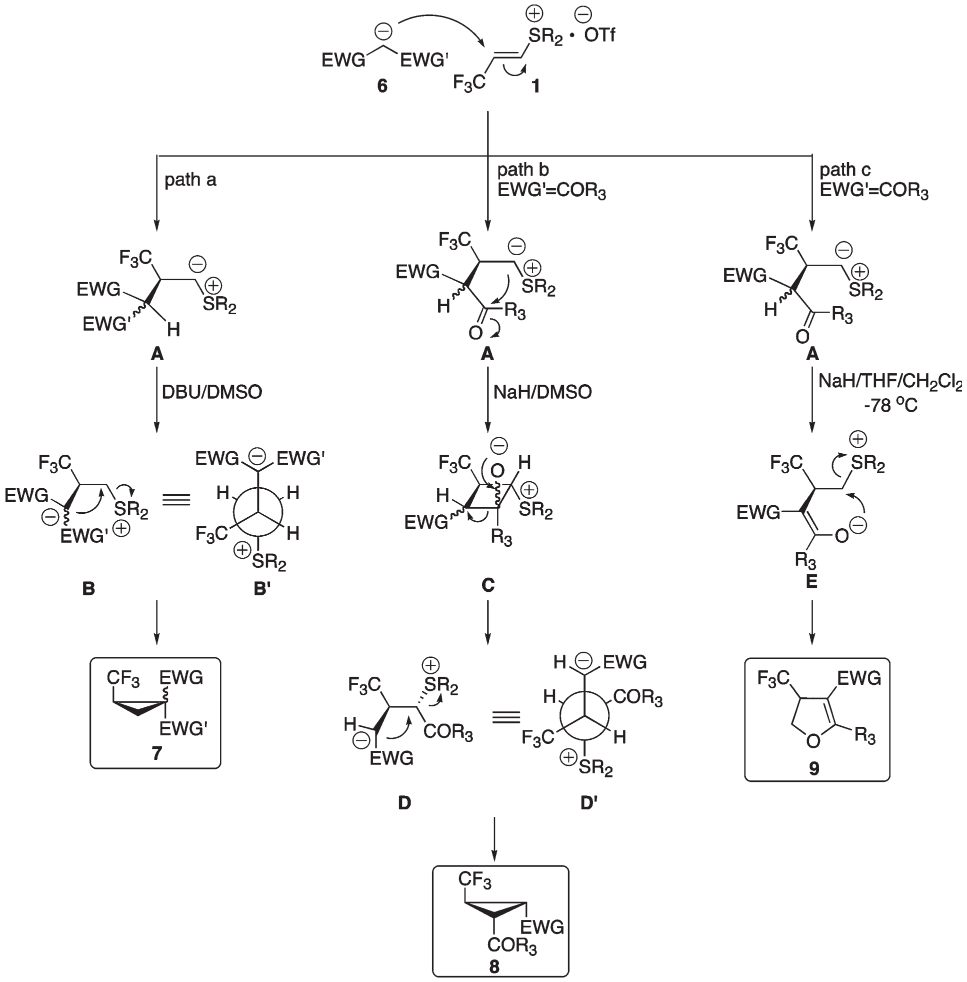
[a] Reaction conditions: **1** (0.3 mmol), active methenyl compound **6** (0.36 mmol), and NaH (0.36 mmol) in THF/CH_2Cl_2 (4.5 mL/1.5 mL) for 30 min at room temperature. [b] Determined by ^{19}F NMR analysis of the crude reaction mixture with α,α,α-trifluorotoluene as an internal standard. [c] Isolated yield of **9**. [d] Three isomers could not be separated. [e] DBU was used as base in DMSO.

■ DISCUSSION

We proposed a working mechanism to explain the different behaviors of the reaction between β-(trifluoromethyl)vinyl sulfonium salt **1** or **2** and active methylene molecules under different conditions. The β-(trifluoromethyl)vinyl sulfonium salt **1** or **2** was first nucleophilically attacked by deprotonated active methylene compounds to form intermediate **A**. When DBU was used as base in DMSO, the reaction proceeded through path a to form intermediate **B** via intramolecular deprotonation or reversible protonation/deprotonation through $DBU\cdot H^+$. **B′** as shown by its Newman projection is the most stable conformation of intermediate **B**, where the less sterically hindered EWG (EWG = electron-withdrawing group) is cis to the trifluoromethyl group. Intermediate **B′** then underwent an intramolecular nucleophilic substitution to form trifluoromethyl-substituted cyclopropane derivatives **7**.

When the reaction was conducted using NaH as the base in DMSO at room temperature, ylide **A** was formed where sodium is the counterion, as shown in path b. It is likely that this ylide is more nucleophilic than the ylide with $DBU\bullet H^+$ as the counterion. As a result, ylide **A** nucleophilically attacked the carbonyl

Scheme 2. Proposed Mechanism for the Reaction of β-(Trifluoromethyl)vinyl Sulfonium Salts 1 or 2 with Active Methenyl Compounds



group to form four-member ring intermediate **C** in which CF_3 was trans to Ph_2S^+ due to the steric hindrance. Subsequent retro-Aldol reaction generated the intermediate **D**, followed by intramolecular nucleophilic substitution to form trifluoromethyl-substituted cyclopropane derivatives **8**. Direct intramolecular substitution to form epoxide was unfavored because of the high ring strain in the resulting [2.1.0] bicyclic compound.

When the reaction was conducted using NaH as the base in THF/CH_2Cl_2 at −78 °C, a kinetically favored enol anion intermediate **E** was formed. Subsequent intramolecular nucleophilic substitution afforded trifluoromethyl-substituted dihydrofuran derivatives **9**, as shown in path c.

For reaction of β-(trifluoromethyl)vinyl sulfonium salts **1** or **2** with active methenyl compounds in the presence of NaH in DMSO, the reaction proceeded via path b to form intermediate **C**. Retro-Aldol reaction generated the intermediate **D**, where the less sterically hindered R group is cis to the trifluoromethyl group. Subsequent intramolecular nucleophilic substitution formed trifluoromethyl-substituted cyclopropane derivatives **8** (Scheme 2).

The reaction between β-(trifluoromethyl)vinyl sulfonium salt **1** or **2** and active methylene molecules differed greatly mainly due to the different properties of the ylides generated from these salts in the presence of base. The ylide generated from β-(trifluoromethyl)vinyl sulfonium salt **1** is more sterically hindered than the ylide from β-(trifluoromethyl)vinyl sulfonium salt **2**. In addition, the ylide from β-(trifluoromethyl)vinyl sulfonium salt **2** is more nucleophilic than ylide from β-(trifluoromethyl)vinyl sulfonium salt **1**. As a result, the nucleophilic addition of the ylide from β-(trifluoromethyl)vinyl sulfonium salt **2** to the carbonyl group was easier than the ylide from β-(trifluoromethyl)vinyl sulfonium salt **1**, as shown in mechanism path b.

■ CONCLUSION

In summary, we have developed two trifluoromethyl-substituted building block β-(trifluoromethyl)vinyl sulfonium salts **1** and **2**. Subsequent studies disclosed that reactions of various active methylene or methenyl compounds with β-(trifluoromethyl)vinyl sulfonium salt **1** or **2** differ greatly under different conditions. Reactions of β-(trifluoromethyl)vinyl sulfonium salt **1** with active methylene compounds containing electron-withdrawing groups such as ester, cyano, or sulfone using DBU as the base in DMSO afforded trifluoromethyl-substituted cyclopropane derivatives **7** as the major products. In contrast, reactions of β-(trifluoromethyl)vinyl sulfonium salt **2** with active methylene compounds occurred with the migration of one of the electron-withdrawing groups to give **8** as the major products when NaH was used as the base in polar solvent such as DMSO. Moreover, when NaH was used as base in THF/CH_2Cl_2 at −78 °C, reactions of β-(trifluoromethyl)vinyl sulfonium salt **1** gave trifluoromethyl-substituted 2,3-dihydrofuran derivatives **9** as the major products. A working mechanism was proposed to explain the different behaviors of the β-trifluoromethyl-substituted vinylsulfonium salts **1** or **2** with active methylene compounds under these different conditions.

EXPERIMENTAL SECTION

General Information. Unless otherwise noted, all reactions were performed in oven-dried glassware under an Ar atmosphere. Commercially obtained reagents were used without further purification. All solvents were purified by standard methods. ^1H, ^{13}C, ^{19}F NMR spectra were recorded on a 300 MHz (or 400 MHz), 100.5 MHz, or 282 MHz spectrometer. ^1H and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0, and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as internal standard. All reactions were monitored by TLC or ^{19}F NMR spectroscopy. Flash column chromatography was performed on silica gel (300−400 mesh) unless otherwise stated.

*Preparation of 2-Bromo-3,3,3-trifluoropropyl Trifluoromethanesulfonate **4**.*[14] Trifluoromethanesulfonic anhydride (18.5 g, 65.6 mmol) was added dropwise to a stirred solution of pyridine (5.45 g, 68.9 mmol) in anhydrous CH_2Cl_2 (90 mL) at −20 °C under argon, and the mixture was stirred for 10 min. 2-Bromo-3,3,3-trifluoropropanol (10.5 g, 54.4 mmol) was added dropwise. The cooling bath was removed, and the reaction was stirred overnight at room temperature. The resulting suspension was filtered and concentrated (*using a rotary evaporator, keeping the water bath temperature below 20 °C*), and petroleum ether (80 mL) was added. The mixture was filtered and concentrated again under reduced pressure to give the title product as a clear pale-brown oil (16.6 g, 94%). It was used directly in the next step without further purification. ^1H NMR (300 MHz, $CDCl_3$) δ 4.87−4.74 (m, 2 H), 4.50−4.41 (m, 1 H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −70.62 (d, J = 5.9 Hz, 3 F), −74.78 (s, 3 F); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 122.4 (q, J = 278 Hz), 118.5 (q, J = 319 Hz), 71.4, 41.1 (q, J = 34 Hz). IR (cm^{-1}): 2987, 1425, 1328, 1249, 1216, 1143, 1051, 990, 951, 814, 613.

*Preparation of (2-Bromo-3,3,3-trifluoropropyl) Diphenylsulfonium Trifluoromethanesulfonate **5a**.* 2-Bromo-3,3,3-trifluoropropyl trifluoromethanesulfonate **4** (9.5 g, 29.2 mmol) was added to diphenyl sulfide (20 mL). The stirred mixture was then heated to 100 °C for 48 h. The mixture was cooled to room temperature, and the solid was crystallized from CH_2Cl_2/Et_2O (ca. 5 mL/30 mL) to give compound **5** as white crystals (9.9 g, 67%): mp 90−91 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, J = 7.2 Hz, 4 H), 7.77−7.66 (m, 6 H), 5.08 (dd, J = 12.9, 3.3 Hz, 1 H), 4.89−4.77 (m, 2 H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −70.64 (d, J = 5.3 Hz, 3 F), −78.30 (s, 3 F); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 135.3, 135.2, 131.9, 131.8, 131.0, 131.0, 124.6, 124.0, 122.5 (q, J = 279 Hz), 120.7 (q, J = 320 Hz), 47.4, 39.4 (q, J = 36 Hz). Anal. Calcd. For $C_{16}H_{13}F_6O_3S_2Br$: C 37.59, H 2.56; Found: C 37.54, H 2.60. MS (ESI^+): m/z 360.9 [M^+], 362.9 [M + 2^+]; MS (ESI^-): m/z 148.9 [TfO^-]. IR (cm^{-1}): 3446, 3069, 3003, 2978, 1282, 1255, 1233, 1151, 1118, 1031, 757, 639.

*Preparation of (2-Bromo-3,3,3-trifluoropropyl) Tetramethylenesulfonium Trifluoromethanesulfonate **5b**.* To a solution of 2-bromo-3,3,3-trifluoropropyl trifluoromethanesulfonate **4** (14.1 g, 43.4 mmol) in toluene (35 mL) was added tetrahydrothiophene (4.43 g, 50.1 mmol). The mixture was heated to 100 °C for 5 h. After cooling to room temperature, Et_2O (20 mL) was added to facilitate the precipitation of the product. The mixture was then filtered and washed with Et_2O (30 mL) to give **5b** as a gray solid (15.2 g, 84%): mp 151−152 °C. ^1H NMR (400 MHz, acetone-d_6) δ 5.39 (m, 1 H), 4.30 (dd, J = 14.0, 4.4 Hz, 1 H), 4.14 (dd, J = 14.4, 10.4 Hz, 1 H), 3.98−3.88 (m, 4 H), 2.58−2.54 (m, 2 H), 2.46−2.42 (m, 2 H); ^{19}F NMR (282 MHz, acetone-d_6) δ −71.68 (d, J = 7.0 Hz, 3 F), −78.77 (s, 3 F); ^{13}C NMR (100.5 MHz, acetone-d_6) δ 123.3 (q, J = 278 Hz), 121.2 (q, J = 321 Hz), 46.4, 45.3, 44.1, 40.7 (q, J = 34 Hz), 28.9, 28.8. Anal. Calcd For $C_8H_{11}F_6O_3S_2Br$: C 23.25, H 2.68; Found: C 23.46, H 2.47. MS (ESI^+): m/z 263.0 [M^+ − OTf], 265.0 [M − OTf+2^+]; MS (ESI^-): m/z 149.0 [TfO^-]; HRMS (ESI^+) Calcd for $C_7H_{11}F_3BrS^+$ (M^+ − OTf): 262.9711, Found: 262.9715. IR (cm^{-1}): 2991, 2941, 1374, 1259, 1164, 1120, 1033, 641.

*Preparation of E-β-(Trifluoromethyl)vinyl Diphenylsulfonium Trifluoromethanesulfonate **1**.* To a stirred solution of (2-bromo-3,3,3-trifluoropropyl)diphenylsulfonium trifluoromethanesulfonate **5a** (4.8 g, 9.3 mmol) in acetone (15 mL) was added silver(I) oxide (1.3 g, 5.6 mmol) at room temperature. The reaction was stirred for 5−9 h as determined by ^{19}F NMR spectroscopy. Longer reaction time would lead to increased byproduct (δ = −62 ppm). The mixture was filtered and washed with acetone (10 mL). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was then diluted with acetone (10 mL), and a catalytic amount of Ag_2O (90 mg, 0.4 mmol) was added. The mixture of E/Z isomers (E:Z = 6:1, δ_E = −65 ppm, δ_Z = −60 ppm) was stirred at room temperature for 1−2 days until the disappearance of Z isomer as determined by ^{19}F NMR spectroscopy. The mixture was filtered, concentrated under vacuum. The residue was purified by flash column chromatography (CH_2Cl_2/acetone =2:1) to give **1** as a white solid (3.71 g, 93%): mp 71−72 °C [lit.[7] mp 68−70 °C]. ^1H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, J = 14.7 Hz, 1 H), 8.14−8.02 (m, 4 H), 7.80−7.67 (m, 6 H), 7.19 (m, 1 H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −64.7 (d, J = 6.2 Hz, 3 F), −78.4 (s, 3 F); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 137.2 (q, J = 37 Hz), 135.1, 131.7, 130.8, 126.6 (q, J = 6.6 Hz), 123.5, 120.5 (q, J = 320 Hz), 119.9 (q, J = 273 Hz).

*Preparation of E/Z-β-(Trifluoromethyl)vinyl Tetramethylenesulfonium Trifluoromethanesulfonate **2**.* To a stirred solution of (2-bromo-3,3,3-trifluoropropyl) tetramethylenesulfonium trifluoromethanesulfonate **5b** (4.1 g, 9.8 mmol) in acetone (15 mL) was added silver(I) oxide (1.4 g, 5.9 mmol) at room temperature (27 °C). The mixture was stirred overnight. The reaction was stirred for 5 h as determined by ^{19}F NMR spectroscopy. The mixture of E/Z isomers (E/Z = 6:1) was filtered and washed with acetone (15 mL). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (CH_2Cl_2/acetone = 2:1) to give **2** as a white solid (3.1 g, 93%, E/Z isomers): mp 61−63 °C for E/Z isomers. ^1H NMR (300 MHz, acetone-d_6) δ 7.54 (dd, J = 15.0, 1.5 Hz, 1 H), 7.25 (m, 1 H), 3.93 (m, 4 H), 2.43 (m, 4 H); ^{19}F NMR (282 MHz, acetone-d_6) δ −65.82 (dd, J = 6.2, 2.0 Hz, 3 F), −79.09 (s, 3 F); ^{13}C NMR (100.5 MHz, acetone-d_6) δ 132.6 (q, J = 36 Hz), 129.5 (q, J = 7.5 Hz), 121.1 (q, J = 288 Hz), 120.8 (q, J = 304 Hz), 47.5, 28.8. MS (ESI^+): m/z 183.0 [M^+ − OTf]; MS (ESI^-): m/z 148.9 [TfO^-]; HRMS (ESI^+) Calcd for $C_7H_{10}F_3S_1^+$ (M^+ − OTf): 183.0450, Found: 183.0443; HRMS (ESI^-) Calcd for $C_1F_3O_3S_1^-$ (OTf): 148.9526, Found: 148.9519. IR (cm^{-1}): 3058, 1652, 1322, 1263, 1158, 1035, 966, 640.

*Typical Procedure for Reaction of β-(Trifluoromethyl)vinyl Sulfonium Salt **1** with Active Methylene Compounds in the Presence of DBU in DMSO.* To a stirred solution of active methylene compound **6** (0.36 mmol) in DMSO (6 mL) was added DBU (0.36 mmol) under argon at room temperature. After 10 min, the reaction mixture was treated with a solution of **1** (130 mg, 0.3 mmol) in DMSO (3 mL) dropwise over 2−3 min. The reaction mixture was stirred for extra 5 min and then quenched with sat. NH_4Cl (aq, 15 mL). The mixture was then extracted with EtOAc (3 × 15 mL) and washed with water (2 × 20 mL) and brine (20 mL). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under vacuum. The residue was then purified by flash column chromatography.

7a *(Table 2, entry 1).*[15] Condition: **6a** (58 mg, 0.36 mmol), DBU (55 mg, 0.36 mmol), **1** (130 mg, 0.3 mmol), DMSO (6 + 3 mL). Eluent: petroleum ether/ethyl acetate = 40:1. **7a**: 67 mg, 87%, colorless oil. ^{1}H NMR (300 MHz, CDCl$_3$) δ 4.23 (m, 4 H), 2.55 (m, 1 H), 1.80 (dd, J = 7.2, 5.5 Hz, 1 H), 1.56 (dd, J = 9.7, 5.5 Hz, 1 H), 1.28 (m, 6 H); ^{19}F NMR (282 MHz, CDCl$_3$) δ −64.86 (d, J = 7.9 Hz, 3 F). MS (ESI$^+$): *m*/*z* 255.0 [M + H$^+$].

7b *(Table 2, entry 2).* Condition: **6b** (63 mg, 0.48 mmol), DBU (73 mg, 0.48 mmol), **1** (172 mg, 0.4 mmol), DMSO (6 + 3 mL). Eluent: petroleum ether/ethyl acetate = 30:1. **7b**: 72 mg, 79%, colorless oil. ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.80 (s, 3 H), 3.79 (s, 3 H), 2.58 (m, 1 H), 1.83 (dd, J = 6.6, 6.3 Hz, 1 H), 1.59 (dd, J = 9.6, 6.0 Hz, 1 H); ^{19}F NMR (282 MHz, CDCl$_3$) δ −64.61 (d, J = 7.3 Hz, 3 F); ^{13}C NMR (100.5 MHz, CDCl$_3$) δ 168.6, 165.6, 123.9 (q, J = 273 Hz), 53.4, 53.2, 32.8, 27.1 (q, J = 37 Hz), 15.5. MS (ESI$^+$): *m*/*z* 227 [M + H]$^+$; HRMS (ESI$^+$) Calcd for $C_8H_9F_3Na_1O_4$ (M + Na$^+$): 249.0345, Found: 249.0350. IR (cm^{-1}): 3011, 2961, 1743, 1270, 1151.

7c *(Table 2, entry 3).* Condition: **6c** (102 mg, 0.36 mmol), DBU (55 mg, 0.36 mmol), **1** (130 mg, 0.3 mmol), DMSO (6 + 3 mL). Eluent: petroleum ether/ethyl acetate = 40:1. **7c**: 107 mg, 93%, colorless oil. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.28 (m, 10 H), 5.14 (m, 4 H), 2.60 (m, 1 H), 1.85 (dd, = 7.0, 6.0 Hz, 1 H), 1.59 (dd, J = 9.0, 5.6 Hz, 1 H); ^{19}F NMR (282 MHz, CDCl$_3$) δ −64.68 (d, J = 7.9, 3 F); ^{13}C NMR (100.5 MHz, CDCl$_3$) δ 168.0, 164.9, 134.9, 134.8, 128.7, 128.6, 128.5, 128.5, 128.0, 124.1 (q, J = 273 Hz), 68.3, 68.1, 33.3, 27.5 (q, J = 38 Hz), 15.6. MS (EI$^+$): *m*/*z* 378 (M$^+$, 1.17), 91 (100), 107 (79.52), 181 (29.77); HRMS (EI$^+$) Calcd for $C_{20}H_{17}F_3O_4$ (M$^+$): 378.1079, Found: 378.1073. IR (cm^{-1}): 3036, 2958, 1738, 1269, 1148, 749, 697.

7d *(Table 2, entry 4).*[15] Condition: **6d** (24 mg, 0.36 mmol), DBU (55 mg, 0.36 mmol), **1** (180 mg, 0.42 mmol), DMSO (4 + 2 mL). Eluent: petroleum ether/ethyl acetate = 6:1. **7d**: 50 mg, 86%, colorless oil. ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.81−2.73 (m, 1 H), 2.21−2.18 (m, 2 H); ^{19}F NMR (282 MHz, CDCl$_3$) δ −64.87 (d, J = 6.2 Hz, 3 F). MS (EI$^+$): *m*/*z* 160 (M$^+$, 4.74), 64 (100), 69 (88.28), 82 (18.85).

7e *(Table 2, entry 5).*[15] Condition: **6e** (54 mg, 0.48 mmol), DBU (73 mg, 0.48 mmol), **1** (172 mg, 0.4 mmol), DMSO (6 + 3 mL). Eluent: petroleum ether/ethyl acetate = 15:1. **7e**: 67 mg, 81%, colorless oil. ^{1}H NMR (300 MHz, CDCl$_3$) δ 4.33 (q, J = 7.2 Hz, 2 H), 2.66 (m, 1 H), 1.98 (m, 2 H), 1.38 (t, J = 7.2 Hz, 3 H); ^{19}F NMR (282 MHz, CDCl$_3$) δ −65.02 (d, J = 7.9 Hz, 3 F). *m*/*z* (ESI$^+$): 208 [M + H]$^+$.

7f *(Table 2, entry 6).*[15] Condition: **6f** (65 mg, 0.36 mmol), DBU (55 mg, 0.36 mmol), **1** (130 mg, 0.3 mmol), DMSO (6 + 3 mL). Eluent: petroleum ether/ethyl acetate = 15:1. **7f**: 72 mg, 86%, white solid: mp 104−105 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.99 (d, J = 7.2 Hz, 2 H), 7.82 (t, J = 7.5 Hz, 1 H), 7.69 (dd, J = 7.8, 7.8 Hz, 2 H), 2.88 (m, 1 H), 2.26 (dd, J = 9.6, 7.0 Hz, 1 H), 2.06 (dd, J = 7.2, 7.1 Hz, 1 H); ^{19}F NMR (282 MHz, CDCl$_3$) δ −65.32 (d, J = 7.0 Hz, 3 F). MS (EI$^+$): *m*/*z* 275 (M$^+$, 12.4), 77 (100), 141 (76.64), 51 (26.50).

7g *(Table 2, entry 7).* Condition: **6g** (70 mg, 0.36 mmol), DBU (55 mg, 0.36 mmol), **1** (130 mg, 0.3 mmol), DMSO (6 + 3 mL). Eluent: petroleum ether/ethyl acetate = 10:1. **7g**: 83 mg, 95%, white solid: mp 105−106 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.86 (d, J = 8.1 Hz, 2 H), 7.47 (d, J = 8.4 Hz, 2 H), 2.92−2.84 (m, 1 H), 2.50 (s, 3 H), 2.24 (m, 1 H), 2.03 (dd, J = 7.5, 6.9 Hz, 1 H); ^{19}F NMR (282 MHz, CDCl$_3$) δ −65.31 (d, J = 5.9 Hz, 3 F); ^{13}C NMR (100.5 MHz, CDCl$_3$) δ 147.3, 132.6, 130.6, 129.2, 122.3 (q, J = 274 Hz), 112.0, 35.49, 27.8 (q, J = 40 Hz), 21.8, 16.6 (q, J = 2.9 Hz). MS (ESI$^+$): *m*/*z* 290 [M + H]$^+$; HRMS (ESI$^+$) Calcd for $C_{12}H_{10}F_3NaNO_2S_1$ (M + Na$^+$): 312.0277, Found: 312.0269. IR (cm^{-1}): 3111, 3066, 3028, 2247, 1599, 1414, 1337, 1269, 1154, 627, 521.

7h/7h′ *(Table 2, entry 8).*[15] Condition: **6h** (77 mg, 0.36 mmol), DBU (55 mg, 0.36 mmol), **1** (130 mg, 0.3 mmol), DMSO (6 + 3 mL). Eluent: petroleum ether/ethyl acetate = 8:1. **7h**: 63 mg, 68%, oil. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.90 (d, J = 7.8 Hz, 2 H), 7.73 (t, J = 7.4 Hz, 1 H), 7.60 (dd, J = 7.7, 7.5 Hz, 2 H), 3.69 (s, 3 H), 2.70 (m, 1 H), 2.21 (dd, J = 10.1, 6.6 Hz, 1 H), 2.07 (dd, J = 7.7, 6.7 Hz, 1 H); ^{19}F NMR (282 MHz, CDCl$_3$) δ −63.29 (d, J = 7.2 Hz, 3 F); ^{13}C NMR (100.5 MHz, CDCl$_3$) δ 162.7, 137.8, 134.6, 129.2, 129.1, 123.3 (q, J = 273 Hz), 53.6, 49.2, 27.4 (q, J = 30 Hz), 13.6. MS (ESI$^+$): *m*/*z* 309.1 [M + H$^+$]. **7 h′**: 19 mg, 19%, oil. ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.04 (d, J = 7.6 Hz, 2 H), 7.68 (t, J = 7.5 Hz, 1 H), 7.57 (dd, J = 10.6, 3.0 Hz, 1 H), 3.66 (s, 3H), 2.60 (m, 2 H), 1.20 (dd, J = 9.6, 5.4 Hz, 1 H); ^{19}F NMR (282 MHz, CDCl$_3$) δ −56.71 (d, J = 7.2 Hz, 3 F); ^{13}C NMR (100.5 MHz, CDCl$_3$) δ 165.5, 139.8, 134.2, 129.5, 128.8, 123.2 (q, J = 274 Hz), 53.5, 49.7, 32.4 (q, J = 42 Hz), 17.9. MS (ESI$^+$): *m*/*z* 309 [M + H]$^+$; HRMS (ESI$^+$) Calcd for $C_{12}H_{11}F_3Na_1O_4S_1$ (M + H$^+$): 331.0222, Found: 331.0226. IR (cm^{-1}): 3111, 3064, 2959, 1743, 1335, 1275, 1144.

7i/7i′ *(Table 2, entry 9).* Condition: **6i** (83 mg, 0.36 mmol), DBU (55 mg, 0.36 mmol), **1** (130 mg, 0.3 mmol), DMSO (6 + 3 mL). Eluent: petroleum ether/ethyl acetate = 15:1. **7i**: 64 mg, 66%, white solid: mp 71−73 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.91 (d, J = 7.8 Hz, 2 H), 7.72 (t, J = 7.5 Hz, 1 H), 7.60 (dd, J = 7.8, 7.5 Hz, 2 H), 4.13 (m, 2H), 2.71 (m, 1 H), 2.21 (dd, J = 10, 6.6 Hz, 1 H), 2.07 (dd, J = 7.2, 7.1 Hz, 1 H), 1.14 (t, J = 7.1 Hz, 3 H); ^{19}F NMR (282 MHz, CDCl$_3$) δ −63.65 (d, J = 7.8 Hz, 3 F); ^{13}C NMR (100.5 MHz, CDCl$_3$) δ 162.0, 137.9, 134.5, 129.2, 129.1, 123.0 (q, J = 275 Hz), 63.1, 49.3, 27.4 (q, J = 39 Hz), 13.5, 13.5. MS (ESI$^+$): *m*/*z* 323 [M + H$^+$]; HRMS (ESI$^+$) Calcd for $C_{13}H_{13}F_3Na_1O_4S_1$ (M + Na$^+$): 345.03789, Found: 345.03841. IR (cm^{-1}): 3105, 3075, 3046, 2988, 1739, 1311, 1267, 1146. **7i′**: 22 mg, 22%, oil. ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.04 (d, J = 8.3 Hz, 2 H), 7.68 (t, J = 6.9 Hz, 1 H), 7.56 (dd, J = 8.1, 6.3 Hz, 2 H), 4.11 (q, J = 7.1 Hz, 2 H), 2.64 (m, 1 H), 2.55 (m, 1 H), 2.12 (dd, J = 9.8, 5.2 Hz, 1 H), 1.16 (t, J = 7.2 Hz, 3 H); ^{19}F NMR (282 MHz, CDCl$_3$) δ −56.51 (d, J = 7.3 Hz, 3 F); ^{13}C NMR (100.5 MHz, CDCl$_3$) δ 165.1, 140.0, 134.1, 129.5, 128.7, 123.3 (q, J = 274 Hz), 63.3, 49.6, 32.3 (q, J = 42 Hz), 18.1, 13.7. MS (ESI$^+$): *m*/*z* 323 [M + H$^+$], 340 [M + NH$_4^+$]; HRMS (ESI$^+$) Calcd for $C_{13}H_{13}F_3Na_1O_4S_1$ (M + Na$^+$): 345.03789, Found: 345.03811. IR (cm^{-1}): 3110, 3064, 2986, 2941, 1732, 1331, 1262, 1135.

7j *(Table 2, entry 10).* Condition: **6j** (38 mg, 0.2 mmol), DBU (22 mg, 0.22 mmol), **1** (103 mg, 0.24 mmol), DMSO (4 + 2 mL). Eluent: petroleum ether/ethyl acetate = 80:1. **7j**: 9 mg, 15%, oil. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.91 (d, J = 6.9 Hz, 2 H), 7.59 (d, J = 7.2 Hz, 1 H), 7.47 (d, J = 7.5 Hz, 2 H), 4.06 (m, 2 H), 2.94 (m, 1 H), 2.28 (dd, J = 6.9, 5.4 Hz, 1 H), 1.54 (dd, J = 8.1, 5.7 Hz, 1 H), 0.97 (t, J = 7.5 Hz, 3 H); ^{19}F NMR (282 MHz, CDCl$_3$) δ −61.44 (d, J = 8.2 Hz, 3 F); ^{13}C NMR (100.5 MHz, CDCl$_3$) δ 191.9, 166.8, 135.9, 133.5, 128.8, 128.3, 124.5 (q, J = 273 Hz), 62.3, 38.6, 26.0 (q, J = 39 Hz), 16.5, 13.44. MS (ESI$^+$): *m*/*z* 287 [M + H]$^+$, 309 [M + Na]$^+$; HRMS (ESI$^+$) Calcd for $C_{14}H_{13}F_3Na_1O_3$ (M + Na$^+$): 309.07090, Found: 309.07103. IR (cm^{-1}): 3051, 2985, 2940, 1745, 1690, 1600, 1450, 1413, 1316, 1274, 1209, 1151.

7m *(Table 2, entry 13).* Condition: **6m** (70 mg, 0.62 mmol), DBU (95 mg, 0.62 mmol), **1** (215 mg, 0.5 mmol), DMSO (6 + 3 mL). Eluent: petroleum ether/ethyl acetate = 2:1. **7m**: 20 mg, 19%, oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.82−2.58 (m, 4 H), 2.42 (m, 1 H), 2.33 (m, 1 H), 2.26−2.07 (m, 2 H), 2.0−1.97 (m, 1 H); ^{19}F NMR (282 MHz, CDCl$_3$) δ −59.76 (d, J = 7.9 Hz, 3 F); ^{13}C NMR (100.5 MHz, CDCl$_3$) δ 204.3, 200.8, 123.5 (q, J = 274 Hz), 43.0, 39.8, 39.3, 38.5 (q, J = 40 Hz), 17.5. MS (EI$^+$): *m*/*z* 206 (M$^+$, 46.99), 178 (100), 42 (67.19), 108 (66.97), 136 (50.75); HRMS (EI$^+$) Calcd for $C_9H_9F_3O_2$ (M$^+$): 206.0555, Found: 206.0560. IR (cm^{-1}): 3112, 2962, 1727, 1701, 1401, 1325, 1269, 1151, 1099.

Typical Procedure for Reaction of β-(Trifluoromethyl)vinyl Sulfonium Salt ***2*** *with Active Methylene Compounds in the Presence of NaH in DMSO.* To a stirred solution of active methylene compound **6** (0.36 mmol) in DMSO (6 mL) was added NaH (60% in oil, 14.4 mg, 0.36 mmol) under argon at room temperature. After 10 min, a solution of **2** (100 mg, 0.3 mmol) in DMSO (3 mL) was added dropwise over 2−3 min.

The reaction mixture was stirred for extra 5 min and then quenched with sat. NH_4Cl (aq, 15 mL). The mixture was then extracted with EtOAc (3 × 15 mL) and washed with water (2 × 20 mL) and brine (20 mL). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under vacuum. The residue was then purified by flash column chromatography.

***8a** (Table 3, entry 1).* Condition: **6a** (71 mg, 0.44 mmol), NaH (19.7 mg, 0.49 mmol), **2** (171 mg, 0.52 mmol), DMSO (6 + 3 mL). Eluent: petroleum ether/ethyl acetate = 120:1. **8a**: 77 mg, 68%, oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.19 (q, J = 7.2 Hz, 4 H), 2.79 (m, 1 H), 2.42 (d, J = 6.0 Hz, 2 H), 1.28 (t, J = 7.2 Hz, 6 H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −67.08 (d, J = 6.2 Hz, 3 F); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 166.7, 123.9 (q, J = 272 Hz), 61.81, 25.4 (q, J = 39 Hz), 24.1 (q, J = 2.2 Hz), 14.0. MS (ESI$^+$): m/z 255.1 [M + H]$^+$; HRMS (ESI$^+$) Calcd for $C_{10}H_{13}F_3Na_1O_4$ (M + Na$^+$): 277.0658, Found: 277.0668. IR (cm^{-1}): 3059, 2987, 2938, 1744, 1400, 1378, 1351, 1319, 1259, 1146, 1041.

***8b** (Table 3, entry 2).* Condition: **6b** (49 mg, 0.36 mmol), NaH (14.4 mg, 0.36 mmol), **2** (99 mg, 0.3 mmol), DMSO (4 + 2 mL). Eluent: petroleum ether/ethyl acetate = 20:1. **8b**: 49 mg, 77%, oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.74 (m, 6 H), 2.80 (m, 1 H), 2.44 (d, J = 6.0 Hz, 2 H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −67.10 (d, J = 6.2 Hz, 3 F); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 167.3, 123.8 (q, J = 271 Hz), 52.7, 25.6 (q, J = 39 Hz), 23.8 (q, J = 2.2 Hz). MS (ESI$^+$): m/z 227 [M + H]$^+$; HRMS (ESI$^+$) Calcd for $C_8H_9F_3Na_1O_4$ (M + Na$^+$): 249.0345, Found: 249.0343. IR (cm^{-1}): 3059, 2960, 1747, 1438, 1368, 1323, 1259, 1214, 1145.

***8c** (Table 3, entry 3).* Condition: **6c** (144 mg, 0.51 mmol), NaH (20.3 mg, 0.51 mmol), **2** (141 mg, 0.42 mmol), DMSO (6 + 3 mL). Eluent: petroleum ether/ethyl acetate = 70:1. **8c**: 138 mg, 86%, oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34−7.29 (m, 10 H), 5.06 (s, 4 H), 2.85 (m 1 H), 2.48 (d, J = 6.0 Hz, 2 H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −66.97 (d, J = 6.2 Hz, 3 F); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 166.5, 135.1, 128.7, 128.6, 128.6, 123.9 (q, J = 271 Hz), 67.6, 25.6 (q, J = 39 Hz), 24.2 (q, J = 2.2 Hz). MS (EI$^+$): m/z 378 (M$^+$, 0.14), 107 (100), 91 (79.37), 181 (19.39), 92 (15.96). HRMS (EI$^+$) Calcd for $C_{20}H_{17}F_3O_4$ (M$^+$): 378.1079, Found: 378.1076. IR (cm^{-1}): 3066, 3036, 2959, 1747, 1456, 1392, 1352, 1316, 1262, 1147, 739, 698.

***8j** (Table 3, entry 4).* Condition: **6j** (54 mg, 0.28 mmol), NaH (9.6 mg, 0.24 mmol), **2** (66 mg, 0.2 mmol), DMSO (4 + 2 mL). Eluent: petroleum ether/ethyl acetate = 100:1. **8j**: 42 mg, 73%, white solid: mp 71−73 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, J = 7.7 Hz, 2 H), 7.62 (t, J = 7.5 Hz, 1 H), 7.50 (dd, J = 7.8, 7.2 Hz, 2 H), 4.04 (q, J = 7.0 Hz, 2 H), 3.14 (dd, J = 10.0, 6.1 Hz, 1 H), 3.02 (m, 1 H), 2.65 (dd, J = 10.0, 5.7 Hz, 1 H), 1.08 (t, J = 7.1 Hz, 3 H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −67.19 (d, J = 5.9 Hz, 3 F); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 190.8, 166.8, 136.1, 133.9, 128.8, 128.5, 124.3 (q, J = 272 Hz), 61.7, 28.2, 25.4, 25.2 (q, J = 38 Hz), 13.9. MS (ESI$^+$): m/z 287 [M + H]$^+$; HRMS (ESI$^+$) Calcd for $C_{14}H_{13}F_3Na_1O_3$ (M + Na$^+$): 309.0709, Found: 309.0713. IR (cm^{-1}): 3068, 3038, 2981, 2933, 1727. 1686, 1356, 1266, 1131.

***8n** (Table 3, entry 5).* Condition: **6n** (39 mg, 0.24 mmol), NaH (9.6 mg, 0.24 mmol), **2** (66 mg, 0.2 mmol), DMSO (3 + 1.5 mL). Eluent: petroleum ether/ethyl acetate = 12:1. **8n**: 35 mg, 61%, white solid: mp 107−109 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, J = 8.1 Hz, 2 H), 7.62 (t, J = 7.8 Hz, 1 H), 7.50 (dd, J = 7.2, 7.2 Hz, 2 H), 3.22 (dd, J = 9.6, 6.0 Hz, 1 H), 3.03 (m, 1 H), 2.79 (dd, J = 9.9, 6.0 Hz, 1 H), 2.27 (s, 3 H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −66.58 (d, J = 6.2 Hz, 3 F); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 199.8, 191.3, 136.1, 134.0, 128.9, 128.5, 124.4 (q, J = 271 Hz), 32.2, 30.7, 29.8, 25.8 (q, J = 38 Hz); MS (ESI$^+$): m/z 257 [M + H]$^+$; HRMS (ESI$^+$) Calcd for $C_{13}H_{11}F_3Na_1O_2$ (M + Na$^+$): 279.0603, Found: 279.0606. IR (cm^{-1}): 3062, 3037, 2922, 1710, 1682, 1324, 1265, 1139.

***8o** (Table 3, entry 6).* Condition: **6o** (37 mg, 0.37 mmol), NaH (9.6 mg, 0.24 mmol), **2** (66 mg, 0.2 mmol), DMSO (3 + 1.5 mL). Eluent: petroleum ether/ethyl acetate = 5:1. **8o**: 16 mg, 41%, white solid: mp 87−89 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.80 (m, 1 H), 2.61 (d, J = 6.0 Hz, 2 H), 2.30 (s, 6 H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −66.81 (d, J = 6.2 Hz, 3 F); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 200.1, 124.1 (q, J = 271 Hz), 32.2, 30.5, 25.8 (q, J = 38 Hz); MS (ESI$^+$): m/z 195 [M + H]$^+$; HRMS (ESI$^+$) Calcd for $C_8H_9F_3Na_1O_2$ (M + Na$^+$): 217.0447, Found: 217.0449. IR (cm^{-1}): 3063, 3020, 2926, 1712, 1369, 1323, 1256, 1142.

***8l** (Table 3, entry 7).* Condition: **6l** (52 mg, 0.2 mmol), NaH (8.8 mg, 0.22 mmol), **2** (80 mg, 0.24 mmol), DMSO (3 + 1.5 mL). Recrystallization from petroleum ether/ethyl acetate. **8l**: 47 mg, 66%, needle crystals: mp 165−166 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, J = 7.2 Hz, 2 H), 7.73 (d, J = 7.5 Hz, 2 H), 7.59 (m, 2 H), 7.40 (m, 4 H), 3.42−3.37 (m, 2 H), 2.26 (dd, J = 9.0, 7.8 Hz, 1 H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −67.15 (d, J = 4.0 Hz, 3 F); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 187.5, 138.9, 136.0, 134.3, 134.1, 129.4, 128.9, 128.8, 127.9, 123.6 (q, J = 273 Hz), 43.3, 30.0, 24.3 (q, J = 40 Hz). Anal. Calcd. for $C_{17}H_{13}F_3O_3S$: C: 57.62 H: 3.70; Found C: 57.59 H: 3.85. MS (ESI$^+$): m/z 355 [M + H]$^+$; HRMS (ESI$^+$) Calcd for $C_{17}H_{13}F_3NaO_3S_1$ (M + Na$^+$): 377.0430, Found: 377.0437. IR (cm^{-1}): 3043, 3029, 1686, 1449, 1343, 1317, 1279, 1153, 1141, 736.

***8h** (Table 3, entry 9).* Condition: **8h** (76 mg, 0.36 mmol), NaH (14.4 mg, 0.36 mmol), **2** (99 mg, 0.3 mmol), DMSO (4 + 2 mL). Eluent: petroleum ether/ethyl acetate = 7:1. **8h**: 87 mg, 94%, white solid: mp 84−85 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.2 Hz, 2 H), 7.71 (dd, J = 7.6, 7.2 Hz, 1 H), 7.61 (dd, J = 8.0, 7.6 Hz, 2 H), 3.80 (s, 3 H), 3.14−3.11 (m, 2 H), 2.63 (dd, J = 9.6, 7.2 Hz, 1 H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −66.73 (d, J = 4.2 Hz, 3 F); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 164.7, 139.2, 134.5, 129.5, 127.95, 123.2 (q, J = 273 Hz), 53.2, 41.3 (q, J = 1.5 Hz), 25.8 (q, J = 3.0 Hz), 25.0 (q, J = 40 Hz). MS (EI$^+$): m/z 308 (M$^+$, 0.81), 77 (100), 141 (30.05), 277 (21.64), 185 (21.25); HRMS (EI$^+$) Calcd for $C_{12}H_{11}F_3O_4S$ (M$^+$): 308.0330, Found: 308.0332. IR (cm^{-1}): 3054, 3036, 2960, 1755, 1736, 1449, 1348, 1330, 1280, 1258, 1159, 1133, 733.

***8i** (Table 3, entry 10).* Condition: **6i** (89 mg, 0.39 mmol), NaH (14.4 mg, 0.36 mmol), **2** (99 mg, 0.3 mmol), DMSO (4 + 2 mL). Eluent: petroleum ether/ethyl acetate = 6:1. **8i**: 89 mg, 91%, solid: mp 92−93 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, J = 7.5 Hz, 2 H), 7.71 (dd, J = 7.5, 7.2 Hz, 1 H), 7.59 (dd, J = 7.8, 7.2 Hz, 2 H), 4.29−4.23 (m, 2 H), 3.13 (m, 2 H), 2.63 (dd, J = 9.6, 7.2 Hz, 1 H), 1.32 (t, J = 7.2 Hz, 3 H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −66.99 (d, J = 5.1 Hz, 3 F); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 164.2, 139.3, 134.4, 129.5, 128.0, 123.3 (q, J = 272 Hz), 62.6, 41.4 (q, J = 2.2 Hz), 26.0 (q, J = 2.2 Hz), 25.0 (q, J = 40 Hz), 13.9. MS (EI$^+$): m/z 322 (M$^+$), 77 (100), 277 (33.68), 141 (26.32), 125 (24.22); HRMS (EI$^+$) Calcd for $C_{13}H_{13}F_3O_4S$ (M$^+$): 322.0487, Found: 322.0488. IR (cm^{-1}): 3044, 2988, 1743, 1448, 1372, 1331, 1280, 1211, 1155, 737, 688.

***8m** (Table 3, entry 11).* Condition: **8m** (55 mg, 0.49 mmol), NaH (19.2 mg, 0.48 mmol), **2** (133 mg, 0.4 mmol), DMSO (6 + 3 mL). Eluent: petroleum ether/ethyl acetate = 3:1. **8m**: 48 mg, 58%, solid: mp 105−106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.97 (m, 1 H), 2.69−2.62 (m, 4 H), 2.54 (d, J = 6.4 Hz, 2 H), 2.01−1.95 (m, 1 H), 1.73−1.66 (m, 1 H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −67.09 (d, J = 5.1 Hz, 3 F); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 203.0, 123.4 (q, J = 273 Hz), 41.3, 31.2 (q, J = 1.7 Hz), 28.6 (q, J = 39 Hz), 22.1. MS (EI$^+$): m/z 206 (M$^+$, 9.12), 178 (100), 136 (72.84), 108 (27.17), 55 (19.64); HRMS (EI$^+$) Calcd for $C_9H_9F_3O_2$ (M$^+$): 206.0555, Found: 206.0559. IR (cm^{-1}): 3070, 2972, 1690, 1456, 1334, 1298, 1267, 1222, 1147, 1130.

***8p** (Table 4, entries 1 and 2).* Condition: **6p** (125 mg, 0.5 mmol), NaH (22.5 mg, 0.56 mmol), **1** (270 mg, 0.62 mmol), DMSO (6 + 3 mL). Eluent: petroleum ether/ethyl acetate = 80:1. **8p**: 140 mg, 80%, oil, mixed with trace amount of **6p** (**8p**: **6p** = 13:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (m, 5 H), 4.18 (q, J = 7.2 Hz, 2 H), 4.03 (m, 2 H), 3.43 (d, J = 15.3 Hz, 1 H), 3.12 (d, J = 15.3 Hz, 1 H), 2.94 (m, 1 H), 2.41 (d, J = 6.6 Hz, 1 H), 1.29 (t, J = 7.2 Hz, 3 H), 1.08 (t, J = 7.2 Hz, 3 H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −60.72 (d, J = 7.6 Hz, 3 F).

Preparation of ***10p***. To a suspension of $LiAlH_4$ (330 mg, 8.6 mmol) in Et_2O (5 mL) was added a solution of **7p** (381 mg, 1.1 mmol) in Et_2O (5 mL) dropwise at room temperature under argon. The mixture was stirred at room temperature for 2 h and was then heated to reflux for 1 h. After cooling to room temperature, the mixture was quenched with EtOH, diluted with H_2O and extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layer was dried over Na_2SO_4, filtered, concentrated under vacuum. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 1:1) to give **10p** as a pale yellow oil (275 mg, 95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35−7.26 (m, 5 H), 4.10 (dd, *J* = 12.0, 5.1 Hz, 1 H), 3.95 (d, *J* = 12.0 Hz, 1 H), 3,39 (dd, *J* = 11.7, 10.8 Hz, 1 H), 3.23 (d, *J* = 12.3 Hz, 1 H), 3.10 (d, *J* = 14.7 Hz, 1 H), 2.89 (d, *J* = 14.7 Hz, 1 H), 2.70 (br, 2 H), 1.86 (m, 1 H), 1.45 (m, 1 H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −59.34 (d, *J* = 7.9 Hz, 3 F); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 138.4, 129.3, 128.8, 126.9, 126.0 (q, *J* = 272 Hz), 64.9, 61.7, 36.7, 32.5, 29.3 (q, *J* = 37 Hz), 28.5. MS (ESI$^+$): *m/z* 283 [M + Na]$^+$; HRMS (ESI$^+$) Calcd for $C_{13}H_{15}F_3Na_1O_2$ (M + Na$^+$): 283.0916, Found: 283.0913. IR (cm^{-1}): 3347, 3030, 2832, 2891, 1456, 1278, 1132, 1099, 1030, 729, 702.

Preparation of ***11p***. To a solution of **10p** (50 mg, 0.19 mmol) in CH_2Cl_2 (1.5 mL) were added NEt_3 (158 mg, 1.56 mmol) and 4-nitrobenzoyl chloride (286 mg, 1.54 mmol) at room temperature. The mixture was then heated to reflux for 2 days. After cooling to room temperature, the solvent was then removed under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 5:1) to give compound **11p** as a solid (21 mg, 20%). ^{1}H NMR: (300 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.4 Hz, 2 H), 8.23 (d, *J* = 9.0 Hz, 2 H), 8.11 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.4 Hz, 2 H), 7.26−7.20 (m, 5 H), 4.83 (dd, *J* = 12.3, 6.6 Hz, 1 H), 4.40 (d, *J* = 11.7 Hz, 1 H), 4.26 (d, *J* = 12.3 Hz, 1 H), 4.18 (d, *J* = 11.7 Hz, 1 H), 3.25 (d, *J* = 14.7 Hz, 1 H), 2.78 (d, *J* = 14.4 Hz, 1 H), 2.33 (m, 1 H), 2.02 (m, 1 H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −59.59 (d, *J* = 7.9 Hz, 3F); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 164.3, 164.1, 150.8, 150.8, 137.6, 134.8, 134.7, 130.8, 129.2, 128.8, 127.0, 125.4 (q, *J* = 272 Hz), 123.7, 123.5, 66.2, 63.7, 35.6, 30.5, 30.2 (q, *J* = 36 Hz), 26.1 (q, *J* = 2.4 Hz). MS (ESI$^+$): *m/z* 581 [M + Na]$^+$; HRMS (ESI$^+$) Calcd for $C_{27}H_{21}F_3N_2Na_1O_8$ (M + Na$^+$): 581.1142, Found: 581.1163. IR (cm^{-1}): 3112, 2922, 1725, 1525, 1349, 1274, 1103, 718.

8p*′ (Table 4, entries 1 and 2).* Seventeen milligrams, 10%, oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (t, *J* = 6.8 Hz, 2 H), 7.19 (d, *J* = 7.2 Hz, 1 H), 7.09 (d, *J* = 7.2 Hz, 2 H), 4.20−4.06 (m, 4 H), 3.62 (d, *J* = 15.6 Hz, 1 H), 3.08 (d, *J* = 6.4 Hz, 1 H), 3.03 (d, *J* = 15.6 Hz, 1 H), 2.50 (m, 1 H), 1.23 (t, *J* = 7.2 Hz, 3 H), 1.14 (t, *J* = 7.2 Hz, 3 H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −62.63 (d, *J* = 5.9 Hz, 3 F); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 168.7, 167.5, 136.9, 128.4, 128.4, 126.8, 124.0 (q, *J* = 272 Hz), 62.1, 61.8, 38.1, 34.6, 32.3 (q, *J* = 39 Hz), 27.2, 14.0, 13.7. MS (ESI$^+$): *m/z* 345 [M + H]$^+$; HRMS (ESI$^+$) Calcd for $C_{17}H_{19}F_3NaO_4$ (M + Na$^+$): 367.1128, Found: 167.1132. IR (cm^{-1}): 3034, 2984, 2937, 1732, 1456, 1374, 1281, 1239, 1191, 1153, 1125, 1044.

Typical Procedure To Remove Small Amount of Compound ***6*** *via Decarboxylation.* To a solution of **8** or **9** (mixed with 1,3-dicarbonyl compound **6** or **7**, isolated from cyclopropantion reaction) in DMSO (1 mL) were added NaCl (10−20 equiv) and H_2O (20−30 equiv) at room temperature in a sealed tube. The mixture was then heated to 150 °C for 2−3 days. After cooling to room temperature, the mixture was diluted with H_2O and extracted with ethyl acetate (3 × 10 mL). The combined organic layer was wash with H_2O (2 × 15 mL) and brine (15 mL), dried over Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography.

8q *(Table 4, entries 3 and 4).* Condition: (1) **6q** (158 mg, 0.67 mmol), NaH (19.7 mg, 0.5 mmol), **2** (176 mg, 0.41 mmol), DMSO (6 + 3 mL). Eluent: petroleum ether/ethyl acetate = 80:1. (2) NaCl (435 mg, 7.4 mmol), H_2O (206 mg, 11.4 mmol), DMSO (1 mL). Eluent: petroleum ether/ethyl acetate = 80:1. **8q**: 56% for two steps, oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46−7.34 (m, 5 H), 4.24 (q, *J* = 7.2 Hz, 2 H), 4.09 (m, 2 H), 3.10 (m, 1 H), 2.82 (d, *J* = 6.3 Hz, 1 H), 1.33 (t, *J* = 7.2 Hz, 3 H), 1.15 (t, *J* = 7.2 Hz, 3 H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −61.67 (d, *J* = 7.1 Hz, 3 F); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 168.1, 167.64, 132.3, 129.5, 128.7, 123.9 (q, *J* = 273 Hz), 62.1, 61.9, 42.5, 30.6 (q, *J* = 37 Hz), 29.0, 14.1, 13.8. MS (EI$^+$): *m/z* 330 (M$^+$, 10.94), 183 (100), 229 (87.86), 284 (87.03), 115 (75.12); HRMS (EI$^+$) Calcd for $C_{16}H_{17}F_3O_4$ (M$^+$): 330.1079, Found: 330.1078. IR (cm^{-1}): 3062, 2985, 2940, 1745, 1467, 1449, 1372, 1345, 1265, 1182, 1136, 703.

8q*′ (Table 4, entries 3 and 4).* Twelve milligrams, 12%, oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (m, 5 H), 4.25−4.03 (m, 2 H), 3.98 (q, *J* = 7.2 Hz, 2 H), 3.18 (d, *J* = 6.0 Hz, 1 H), 2.96 (m, 1 H), 1.18 (t, *J* = 7.2 Hz, 3 H), 1.06 (d, *J* = 7.2 Hz, 3 H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −63.28 (d, *J* = 5.9 Hz, 3 F); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 167.2, 166.9, 133.5, 129.1, 128.7, 128.6, 124.2 (q, *J* = 273 Hz), 62.4, 61.5, 42.2, 30.9 (q, *J* = 38 Hz), 28.3, 13.9, 13.7. MS (EI$^+$): *m/z* 330 (M$^+$, 54.96), 115 (100), 183 (91.2), 228 (79.49), 133 (61.52); HRMS (EI$^+$) Calcd for $C_{16}H_{17}F_3O_4$ (M$^+$): 330.1079, Found: 330.1081. IR (cm^{-1}): 3062, 2985, 2940, 1736, 1467, 1449, 1371, 1345, 1282, 1257, 1165, 1134, 1036, 737, 698.

8r *(Table 4, entry 5).* Condition: **6r** (52 mg, 0.3 mmol), NaH (14.4 mg, 0.36 mmol), **1** (172 mg, 0.4 mmol), DMSO (6 + 3 mL). Eluent: petroleum ether/ethyl acetate = 30:1. **8r**: 26 mg, 32%, oil (excess **6r** was removed under reduced pressure by oil pump). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.20−4.12 (m, 4 H) 2.08 (m, 1 H), 2.40 (d, *J* = 6.3 Hz, 1 H), 1.55 (s, 3 H), 1.30−1.24 (m, 6 H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −61.15 (d, *J* = 8.2 Hz, 3 F); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 169.4, 167.7, 124.5 (q, *J* = 273 Hz), 61.9, 61.6, 32.3, 31.1, 29.9 (q, *J* = 37 Hz), 15.1, 14.1, 14.0. MS (ESI$^+$): *m/z* 269 [M + H]$^+$; HRMS (ESI$^+$) Calcd for $C_{11}H_{15}F_3Na_1O_4$ (M + Na$^+$): 291.0815, Found: 291.0816. IR (cm^{-1}): 2987, 2943, 1744, 1452, 1373, 1346, 1269, 1153, 1185, 1125, 1099, 1024.

8s *(Table 4, entry 6).* Condition: **6s** (73 mg, 0.43 mmol), NaH (9.6 mg, 0.24 mmol), **1** (86 mg, 0.2 mmol), DMSO (4 + 2 mL). Eluent: petroleum ether/ethyl acetate = 15:1. **8s**: 25 mg, 47%, oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.16−4.11 (m, 2 H), 3.02 (m, 1 H), 2.56 (m, 1 H), 2.29 (d, *J* = 6.4 Hz, 1 H), 2.28−1.82 (m, 7 H), 1.25 (t, *J* = 7.2 Hz, 3 H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −60.78 (d, *J* = 8.2 Hz, 3 F); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 202.5, 167.3, 124.7 (q, *J* = 273 Hz), 61.6, 41.4 (q, *J* = 1.6 Hz), 41.3, 32.0 (q, *J* = 5 Hz), 30.5, 27.9 (q, *J* = 38 Hz), 26.3, 24.1, 14.1. MS (ESI$^+$): *m/z* 265 [M + H]$^+$; HRMS (ESI$^+$) Calcd for $C_{12}H_{15}F_3Na_1O_3$ (M + Na$^+$): 287.08655, Found: 287.08671. IR (cm^{-1}): 3041, 2943, 2869, 1740, 1450, 1372, 1344, 1295, 1261, 1190, 1135, 1102.

Typical Procedure for Reaction of β-(Trifluoromethyl)vinyl Sulfonium Salts ***1*** *and* ***2*** *with Active Methenyl Compounds in the Presence of NaH in DMSO.* To a stirred solution of active methylene compound **6** (0.36 mmol) in THF (4.5 mL) was added NaH (60% in oil, 14.4 mg, 0.36 mmol) under argon at room temperature. After 10 min, a solution of **1** (129 mg, 0.3 mmol) in CH_2Cl_2 (3 mL) was added dropwise over 2−3 min. The reaction mixture was stirred for extra 5 min and then quenched with sat. NH_4Cl (aq, 15 mL), extracted with CH_2Cl_2 (3 × 15 mL), and washed with water (2 × 20 mL) and brine (20 mL). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under vacuum. The residue was then purified by flash column chromatography.

9j *(Table 5, entry 1).* Condition: **6j** (40 mg, 0.21 mmol), NaH (9.6 mg, 0.24 mmol), **1** (112 mg, 0.26 mmol), THF/CH_2Cl_2 (4 + 0.8 mL). Eluent: petroleum ether/ethyl acetate = 100:1. **9j**: 42 mg, 70%, oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.4 Hz, 2 H), 7.47−7.38 (m, 3 H), 4.74 (dd, *J* = 10.5, 3.0 Hz, 1 H), 4.58 (dd, *J* = 10.2, 9.9 Hz, 1 H), 4.18−4.07 (m, 3 H), 1.21 (t, *J* = 7.2 Hz, 3 H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −73.40 (d, *J* = 7.9 Hz, 3 F); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 170.1, 163.7, 131.4, 129.9, 128.8, 127.7, 126.3 (q, *J* = 281 Hz), 98.8, 69.9 (q, *J* = 3.7 Hz), 60.2, 48.1 (q, *J* = 29 Hz), 14.1. MS (EI$^+$): *m/z* 286 (M$^+$, 46.14), 105 (100), 77 (86.03), 217 (83.00), 115 (64.56), 241 (64.56), 145 (61.70), 171 (59.75); HRMS (EI$^+$) Calcd for $C_{14}H_{13}F_3O_3$ (M$^+$): 286.0817, Found: 286.0820. IR (cm^{-1}): 2984, 2909, 1709, 1624, 1598, 1494, 1362, 1335, 1227, 1149, 1124, 1088, 939, 763, 696.

***8u** (Table 5, entry 2).* Condition: (1) **6u** (86 mg, 0.36 mmol), NaH (14.4 mg, 0.36 mmol), **1** (130 mg, 0.3 mmol), THF/CH_2Cl_2 (4.5 + 1.5 mL). Eluent: petroleum ether/ethyl acetate = 12:1. **8u** and **6u**: 53 mg; (2) NaCl (44 mg, 0.75 mmol), H_2O (44 mg, 2.44 mmol), DMSO (1.2 mL); Eluent: petroleum ether/ethyl acetate = 10:1; **8u**: 27 mg, 27% for two steps, solid: mp 129−130 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 (d, J = 8.4 Hz, 2 H), 8.20 (d, J = 8.7 Hz, 2 H), 4.06 (q, J = 7.2 Hz, 2 H), 3.15 (dd, J = 9.9, 6.0 Hz, 1 H), 3.05 (m, 1 H), 2.73 (dd, J = 9.9, 6.0 Hz, 1 H), 1.13 (t, J = 7.2 Hz, 3 H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −67.22 (d, J = 5.9 Hz, 3 F); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 189.7, 166.6, 150.8, 140.4, 129.46, 124.1, 124.0 (q, J = 271 Hz), 62.0, 28.2, 25.7, 25.4 (q, J = 39 Hz), 13.9. MS (EI$^+$): m/z 331 (M$^+$, 5.60), 150 (100), 286 (24.41), 104 (15.59), 76 (11.12); HRMS (EI$^+$) Calcd for $C_{14}H_{12}F_3O_5N$ (M$^+$): 331.0668, Found: 331.0664. IR (cm^{-1}): 3110, 3079, 3037, 1724, 1692, 1524, 1355, 1321, 1265, 1226, 1146.

***9u** (Table 5, entry 2).* Condition: **6u** (86 mg, 0.36 mmol), NaH (14.4 mg, 0.36 mmol), **1** (130 mg, 0.3 mmol), THF/CH_2Cl_2 (4.5 + 1.5 mL). Eluent: petroleum ether/ethyl acetate = 12:1. **9u**: 50 mg, 50%, solid: mp 62−63 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 9.2 Hz, 2 H), 8.00 (d, J = 8.8 Hz, 2 H), 4.80 (dd, J = 10.8, 3.6 Hz, 1 H), 4.66 (dd, J = 10.4, 10.0 Hz, 1 H), 4.22−4.13 (m, 3 H), 1.23 (t, J = 7.2 Hz, 3 H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −72.42 (d, J = 8.2 Hz, 3 F); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 167.1, 163.1, 149.2, 134.7, 131.1, 125.9 (q, J = 281 Hz), 122.8, 101.5, 70.4 (q, J = 2.9 Hz), 60.7, 48.2 (q, J = 30 Hz), 14.0. MS (EI$^+$): m/z 331 (M$^+$, 40.87), 115 (100), 262 (96.50), 190 (78.95), 76 (73.24); HRMS (EI$^+$) Calcd for $C_{14}H_{12}NF_3O_5$ (M$^+$): 331.0668, Found: 331.0670. IR (cm^{-1}): 3117, 2983, 2915, 1709, 1631, 1593, 1526, 1350, 1228, 1127, 1090, 1029, 1015, 859, 834.

***9x** (Table 5, entry 5).* Condition: **6x** (122 mg, 0.6 mmol), NaH (24.8 mg, 0.6 mmol), **1** (192 mg, 0.45 mmol), THF/CH_2Cl_2 (6 + 3 mL). Eluent: petroleum ether/ethyl acetate = 30:1. **9x**: 104 mg, 80%, solid: mp 50−51 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (d, J = 3.9 Hz, 1 H), 7.58 (d, J = 5.1 Hz, 1 H), 7.12 (dd, J = 5.2, 4.8 Hz, 1 H), 4.72 (dd, J = 12.9, 2.4 Hz, 1 H), 4.54 (dd, J = 10.2, 9.9 Hz, 1 H), 4.32−4.20 (m, 2 H), 4.06 (m, 1 H), 1.31 (t, J = 7.2 Hz, 3 H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −72.51 (d, J = 7.3 Hz, 3 F); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 163.9, 163.0, 134.2, 131.9, 130.1, 127.4, 126.2 (q, J = 281 Hz), 96.7, 69.7 (q, J = 9 Hz), 60.3, 48.2 (q, J = 30 Hz), 14.2. MS (EI$^+$): m/z 292 (M$^+$, 41.86), 111 (100), 223 (89.45), 292 (41.86), 247 (38.74); HRMS (EI$^+$) Calcd for $C_{12}H_{11}F_3O_3S$ (M$^+$): 292.0381, Found: 292.0386. IR (cm^{-1}): 3079, 2982, 1689, 1603, 1424, 1358, 1263, 1221, 1143, 1080, 1053, 738.

***9m** (Table 5, entry 8).* Condition: **6m** (70 mg, 0.62 mmol), DBU (95 mg, 0.62 mmol), **1** (215 mg, 0.5 mmol), DMSO (6 + 3 mL). Eluent: petroleum ether/ethyl acetate = 3:1. **9m**: 66 mg, 64%, oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.73 (dd, J = 10.8, 4.0 Hz, 1 H), 4.58 (dd, J = 10.8, 10.0 Hz, 1 H), 3.92 (m, 1 H), 2.59−2.43 (m, 3 H), 2.37−2.29 (m, 1 H), 2.11−2.04 (m, 2 H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −72.50 (d, J = 7.9 Hz, 3 F); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 193.3, 181.4, 125.8 (q, J = 277 Hz), 109.1, 72.6 (q, J = 3.1 Hz), 43.9 (q, J = 32 Hz), 36.7, 24.1, 21.1. MS (EI$^+$): m/z 206 (M$^+$, 33.75), 178 (100), 206 (33.75); HRMS (EI$^+$) Calcd for $C_9H_9F_3O_2$ (M$^+$): 206.0555, Found: 206.0556. IR (cm^{-1}): 2955, 1664, 1629, 1425, 1407, 1270, 1236, 1220, 1185, 1124, 997, 979.

***9y** (Table 5, entry 9).* Condition: **6y** (67 mg, 0.5 mmol), DBU (51 mg, 0.33 mmol), **1** (86 mg, 0.2 mmol), DMSO (3 + 1.5 mL). Eluent: petroleum ether/ethyl acetate = 8:1. **9y**: 43 mg, 99%, solid: mp 55−56 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.76 (d, J = 9.0 Hz, 1 H), 4.67 (dd, J = 9.0, 9.0 Hz, 1 H), 4.39−4.27 (m, 3 H), 1.35 (t, J = 7.2 Hz, 3 H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −71.56 (d, J = 7.1 Hz, 3 F); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 157.7, 124.6 (q, J = 281 Hz), 103.6, 64.2 (q, J = 2.9 Hz), 62.3, 47.8 (q, J = 32 Hz), 14.0. MS (ESI$^+$): m/z 228 [M + H]$^+$; HRMS (ESI$^+$) Calcd for $C_7H_8F_3N_1Na_1O_4$ (M + Na$^+$): 250.0298, Found: 249.0298. IR (cm^{-1}): 2994, 1729, 1620, 1407, 1390, 1372, 1283, 1244, 1171, 1026, 905, 769, 754.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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