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Regioselective addition reactions of 3-phenylsulfonyl-2-trifluoromethyl-1,3-butadiene with nucleophiles

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ABSTRACT

Reactions of 3-phenylsulfonyl-2-trifluoromethyl-1,3-butadiene (**1**) with heteroatom nucleophiles such as *pri*-amines, *pri*-alcohols, and thiols afforded the addition products **2**, **3**, and **5** regioselectively formed via addition of nucleophiles toward double bond attaching phenylsulfonyl group. Cyclization of **2a** in 2,2,2-trifluoroethanol at 60 °C for 2 h gave pyrrolidine **4a** in good yield. Similarly, compound **1** was also reacted with diethylmalonate in the presence of NaH to give addition product **7** in good yield.

1. Introduction

1,3-Butadienes have received much attention because they have been widely used in the Diels–Alder reaction to give the carbocyclic compounds [1]. The introduction of heterosubstituents has a significant influence on the reactivity, regioselectivity, and stereochemistry of the diene and also versatility in further reactions [2–6]. Sulfur-substituent within the diene unit, in particular, not only increases the reactivity of the diene but also adds control to the regioselectivity of the cycloaddition or addition reaction [7,8]. Numerous reactions related to the sulfur-substituted 1,3-butadienes have been well established in the previous literatures [9–12]. In the past several decades, much effort has been devoted to introduce the trifluoromethyl functionality into organic molecules because of the dramatic effects of functionality on their structure stability and reactivity of the resulting compounds [13–17]. Consequently, a variety of methods for the synthesis of trifluoromethylated dienes have been developed [18–22], but only scarce examples of their reactions are known [23,24]. Recently, we developed the method for the preparation of novel 2-trifluoromethyl-3-phenylthio-1,3-butadiene as a new building block which contains the trifluoromethyl and phenylthio functionality in the diene unit and examined the Diels–Alder reaction of this compound toward the dienophile [25]. Since the trifluoromethyl and sulfonyl group attached to 2- and 3-positions of the diene unit effects significant polarization of the double bond, this compound should be highly reactive toward nucleophilic addition because of its remarkably lowered LUMO energy level compared to 1,3-butadiene. Although nucleophilic addition reactions of doubly activated diene at the 2- and 3-positions have been well documented previously [26–28], there has been no report on the nucleophilic reaction of 3-phenylsulfonyl-2-trifluoromethyl-1,3-butadiene. Herein, we wish to report on the reactivity of 3-phenylsulfonyl-2-trifluoromethyl-1,3-butadiene toward the nucleophiles and its regioselectivity.

2. Results and discussion

When 3-phenylsulfonyl-2-trifluoromethyl-1,3-butadiene (**1**) was reacted with benzylamine in THF at the several reaction temperature (−78, −20, 25 °C) for 1 h, a messy reaction mixture was always obtained. However, treatment of **1** with benzylamine in methylene chloride at room temperature for 0.5 h resulted in the formation of addition product **2a** in 83% yield regioselectively. The use of co-solvent system (CH_2Cl_2:*t*-BuOH = 1:1) in this reaction dramatically increased the yield of **2a** up to 97% yield. There was no addition product at the double bond bearing a trifluoromethyl group. The other primary amines such as *n*-butylamine, *s*-butylamine, and *t*-butylamine also produced the addition products **2b–d** in 81–85% yields. The reaction of **1** with aniline in co-solvent

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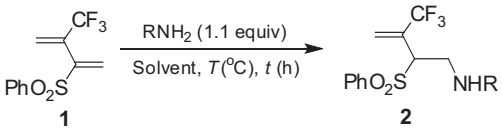
Table 1
Addition reaction of 2-trifluoromethyl-3-phenylsulfonyl-1,3-butadiene (**1**) with RNH_2.



Compound no.	R	Solvent	T (°C)	t (h)	Yield (%)[a]
2a	$CH_2C_6H_5$	THF	25	1	–[b]
2a	$CH_2C_6H_5$	THF	−78	1	–[b]
2a	$CH_2C_6H_5$	MC	25	0.5	83
2a	$CH_2C_6H_5$	MC:*t*-BuOH = 1:1	25	0.5	97
2b	*n*-C_4H_9	MC:*t*-BuOH = 1:1	25	0.5	85
2c	*s*-C_4H_9	MC:*t*-BuOH = 1:1	25	0.5	83
2d	*t*-C_4H_9	MC:*t*-BuOH = 1:1	25	0.5	81
2e	C_6H_5	MC:*t*-BuOH = 1:1	Reflux	24	51

[a] Isolated yield.
[b] A messy reaction mixture was obtained.

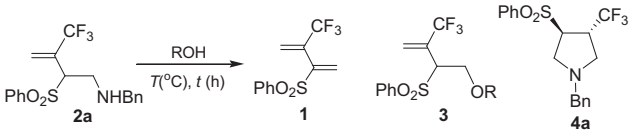
system at reflux for 24 h afforded the addition product **2e** in 51% yield. In contrast to the reaction with primary amines, secondary amines such as diethylamine, diisopropylamine, and pyrrolidine did not undergo the addition reaction with **1** even at the reflux temperature for 24 h. The results of these reactions were summarized in Table 1.

The addition products **2** still have an activated double bond which can be attacked by nitrogen nucleophile within **2**. Therefore, cyclization of **2a** was performed under the different reaction condition. Heating of **2a** in methanol at 60 °C for 2 h produced pyrrolidine derivative **4a** in 25% yield along with diene **1** (10%) and methanol addition product **3** (55%). Stereochemistry of **4a** (*trans*) was determined by ^{1}H NMR. When **2a** was heated for 10 h, **4a** was obtained in 16% yield, and diene **1** and **3** were obtained in 5% and 72% yields, respectively. The use of *t*-BuOH in this reaction provided the only diene **1** in 72% yield. However, **2a** was heated in 2,2,2-trifluoroethanol for 2 h to give **4a** in 71% yield along with diene **1** (6%) and **3** (15%). The longer reaction time (10 h) dramatically decreased the yield of **4a** (12%), but yield of **3** was increased up to 69%. The facility of the 5-*endo-trig* cyclization of **2a** is particularly surprising to us because of a disfavored process according to the Baldwin rule [29], although the similar 5-*endo-trig* cyclization of alkene with a CF_3 group was reported previously [30]. The result of cyclization reaction of **2a** was summarized in Table 2. These results indicate that **4a** undergoes the elimination reaction to give the diene **1** under the reaction condition, in which diene **1** was attacked by alcohol to afford the addition product **3**. The results were summarized in Scheme 1.

Since we proposed the reaction process for the formation of **3** in the cyclization of **2a** in Scheme 1, we examined the addition reaction of **1** with alcohols in the presence of amine. Treatment of **1** with excess of methanol in the presence of diisopropylamine (5 equiv.) in MC at room temperature for 16 h produced the addition product **3a** in 80% yield. Similar reaction with ethanol and 2,2,2-trifluoroethanol also provided the addition products **3b–c** in 71–74% yields. However, phenol, isopropyl alcohol and *t*-butyl alcohol were not reacted with **1** under the same reaction condition. The use of catalytic amount of NaH in this reaction resulted in the formation of a messy reaction mixture. The results of these reactions were summarized in Table 3.

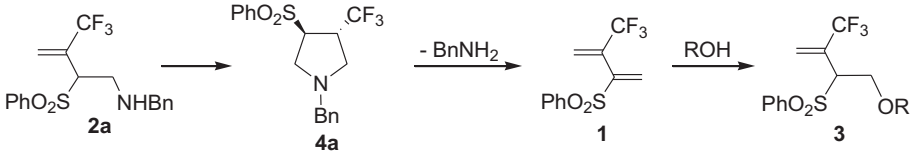
We have also examined the reaction of diene **1** with thiophenol and found that the reaction proceeded smoothly in THF at 0 °C for

Table 2
Cyclization reaction of **2a** in alcohols solvent.



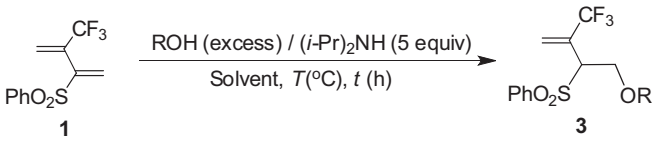
Entry	R	T (°C)	t (h)	Yield (%)[a]		
				1	**3**	**4a**
1	CH_3	25	10	45	36	0
2	CH_3	60	2	10	55	25
3	CH_3	60	10	5	72	16
4	*t*-C_4H_9	60	2	72	0	0
5	CF_3CH_2	60	2	6	15	71
6	CF_3CH_2	60	10	4	69	12

[a] Isolated yield.



Scheme 1.

Table 3
Addition reaction of 2-trifluoromethyl-3-phenylsulfonyl-1,3-butadiene (**1**) with alcohols.

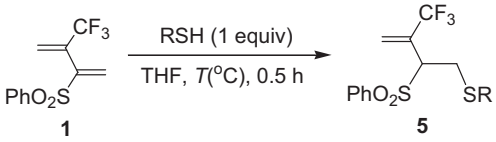


1 3

Compound no.	R	Solvent	T (°C)	t (h)	Yield (%)[a]
3a	CH_3	MC	25	16	80
3b	CH_3CH_2	MC	25	16	74
3c	CF_3CH_2	MC	25	8	71
3d	C_6H_5	MC	Reflux	30	–[b]
3e	i-C_3H_7	MC	25	30	–[b]
3f	t-C_4H_9	MC	25	30	–[b]

[a] Isolated yield.
[b] No reaction.

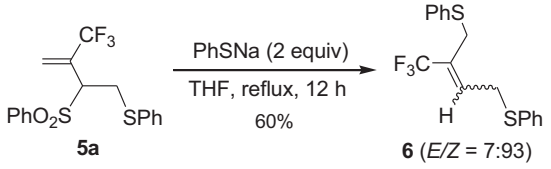
Table 4
Addition reaction of 2-trifluoromethyl-3-phenylsulfonyl-1,3-butadiene (**1**) with thiols.



1 5

Compound no.	R	T (°C)	Yield (%)[a]
5a	C_6H_5	25	–[b]
5a	C_6H_5	0	72
5b	n-C_3H_7	0	–[b]
5b	n-C_3H_7	−45	70

[a] Isolated yield.
[b] A messy reaction mixture was obtained.



5a 6 (*E*/*Z* = 7:93)

Scheme 2.

0.5 h, giving 72% yield. The use of excess thiophenol did not cause to increase the yield of **5a**. When the same reaction was performed at room temperature, a messy reaction mixture was obtained, but regioisomers were not detected. The reaction of diene **1** with alkanethiol was much faster than that with thiophenol and thus was controlled by lowing the reaction temperature. Therefore, diene **1** was reacted with 1-propanethiol in THF at −45 °C for 0.5 h to afford the addition product **5b** in 70% yield. The reaction at higher temperature resulted in the formation of a messy reaction mixture which does not include regioisomers. No addition products were obtained from the reaction of **1** with 2-propanethiol or 2-methyl-2-propanethiol. The result of these reaction was summarized in Table 4. The addition product **5a** was further reacted with sodium thiophenoxide (2.0 equiv.) in THF at reflux for 12 h to give the trifluoromethylated olefin **6** (*E*/*Z* = 7/93) in 60% yield (Scheme 2). Assignment of a *E*/*Z* isomer of **6** was based on the H–F coupling constant between H and CF_3. The ^{1}H NMR of *Z* isomer in which H and CF_3 group are arranged at the same side, showed that the H–F coupling constant is 1.6 Hz, whereas the H–F coupling constant of *E* isomer is not observed. Usually, in olefinic compounds bearing a CF_3 group, $^4J_{H-F}$ is ca. 2 Hz in the *cis* arrangement between H and CF_3 group and up to 1 Hz in the *trans* arrangement [31].

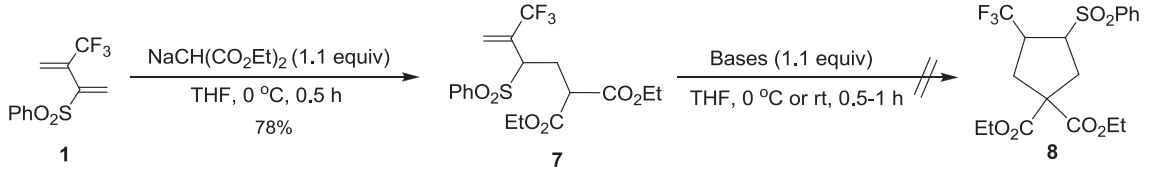
Finally, we have examined the reaction of diene **1** with carbon nucleophiles such as alkyllithium, aryllithium, alkynyllithium, sodium diethyl malonate and found that only sodium diethyl malonate underwent the addition reaction in THF at 0 °C for 0.5 h, giving 78% yield of addition product **7** (Scheme 3). Other carbon nucleophiles provided the messy reaction mixture even at low temperature. The reaction of **7** with bases such as NaH, NaOMe, *t*-BuOK for the cyclization of **7** did not provide a cyclization product **8** via 5-*endo*-*trig* cyclization which is considered as a disfavored process [29], but caused to regenerate the diene **1**.

3. Conclusion

In conclusion, we found that 2-trifluoromethyl-3-phenylsulfonyl-1,3-butadiene (**1**) underwent the addition reaction regiospecifically with heteroatom nucleophiles such as *pri*-amines, *pri*-alcohols, and thiols at the double bond attached with phenylsulfonyl group. Amine addition product **2a** underwent *5-endo-trig* cyclization to give pyrrolidine derivatives **4a**, but this compound underwent the elimination reaction to provide the diene **1** at the prolong reaction time. The diene **1** also reacted with diethylmalonate to afford the addition product **7**, but this compound did not undergo the *5-endo-trig* cyclization in the base condition.

4. Experimental

^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz Bruker AVANCEII^{++} NMR spectrometer with tetramethylsilane (TMS) as an internal standard and ^{19}F NMR spectra were also recorded on a 400 MHz Bruker AVANCEII^{++} NMR spectrometer with $CFCl_3$ as an internal standard and the upfield as negative. All chemical shifts (δ)



1 7 8

Scheme 3.

are expressed in parts per million and coupling constant (*J*) are given in Hertz. Mass spectra were obtained by using Agilent Technologies 6890N GC/5973 Network MSD (EI, 70 eV). Elemental analysis data were obtained by using EA1110 elemental analyzer. Melting points were determined in open capillary tubes and are uncorrected.

Commercially available reagents were purchased from Aldrich, Lancaster, Tokyo Kasei and Fluorochem. All solvents were dried by general purification method. Flash chromatography was performed on 40–60 μm silica gel (230–400 mesh).

4.1. General procedure for the preparation of 4-alkyl(or phenyl)amino-2-trifluoromethyl-3-phenylsulfonylbut-1-ene (**2**)

A 15 mL two-neck round bottom flask equipped with a magnetic stirrer bar, a septum and nitrogen tee connected to an argon source was charged with diene **1** (0.200 g, 0.76 mmol) and 4 mL of solvent (MC:*t*-BuOH = 1:1). The amine (0.84 mmol) was added into the reaction mixture which was then stirred at room temperature for 0.5 h (for alkylamine) or reflux for 24 h (for aniline). After the reaction mixture was stirred, it was extracted with methylene chloride twice, dried over anhydrous $MgSO_4$ and chromatographed on SiO_2 column. Elution with a mixture of *n*-hexane and ethyl acetate (4:1) provided the addition product **2**.

4.1.1. 4-Benzylamino-2-trifluoromethyl-3-phenylsulfonylbut-1-ene (**2a**)

2a was prepared in 97% yield (0.272 g) from the reaction of diene **1** with benzylamine according to the general procedure. **2a**: yellow oil; ^{1}H NMR ($CDCl_3$) δ 7.85–7.77 (m, 2H), 7.68–7.64 (m, 1H), 7.55–7.51 (m, 2H), 7.33–7.23 (m, 5H), 6.12 (s, 1H), 6.09 (s, 1H), 4.04 (t, *J* = 6.4 Hz, 1H), 3.79 (m, 2H), 3.51 (dd, *J* = 13.2, 6.4 Hz, 1H), 3.13 (dd, *J* = 13.2, 6.4 Hz, 1H), 1.86 (bs, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −69.53 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 137.6, 134.2, 131.5 (q, *J* = 32.2 Hz), 129.2, 129.1, 128.5, 128.0, 127.2, 125.5 (q, *J* = 6.0 Hz), 123.7, 62.2, 53.1, 49.4; MS, *m*/*z* (relative intensity) 369 (M^+, 1), 228 (3), 141 (3), 120 (57), 106 (6), 104 (5), 91 (100), 77 (16), 65 (8), 51 (7). Anal. Calcd for $C_{18}H_{18}F_3NO_2S$: C, 58.53; H, 4.91. Found: C, 58.31; H, 4.94.

4.1.2. 4-n-Butylamino-2-trifluoromethyl-3-phenylsulfonylbut-1-ene (**2b**)

2b was prepared in 85% yield (0.216 g) from the reaction of diene **1** with *n*-butylamine according to the general procedure. **2b**: yellow oil; ^{1}H NMR ($CDCl_3$) δ 7.83–7.82 (m, 2H), 7.69–7.65 (m, 1H), 7.57–7.53 (m, 2H), 6.16 (s, 1H), 6.11 (s, 1H), 4.04 (t, *J* = 6.4 Hz, 1H), 3.53 (dd, *J* = 13.2, 6.4 Hz, 1H), 3.12 (dd, *J* = 13.2, 6.4 Hz, 1H), 2.59 (t, *J* = 6.8 Hz, 2H), 1.55 (bs, 1H), 1.44 (m, 2H), 1.33 (m, 2H), 0.90 (t, *J* = 7.6 Hz, 3H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −69.60 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 134.5, 131.6 (q, *J* = 32.2 Hz), 129.6, 129.5, 125.7 (q, *J* = 6.0 Hz), 124.0, 62.0, 50.3, 48.9, 32.0, 20.3, 13.9; MS, *m*/*z* (relative intensity) 335 (M^+, 1), 292 (12), 150 (16), 141 (15), 122 (18), 86 (72), 82 (39), 77 (100), 51 (33). Anal. Calcd for $C_{15}H_{20}F_3NO_2S$: C, 53.72; H, 6.01. Found: C, 53.48; H, 5.98.

4.1.3. 4-s-Butylamino-2-trifluoromethyl-3-phenylsulfonylbut-1-ene (**2c**)

2c was prepared in 83% yield (0.211 g) from the reaction of diene **1** with *s*-butylamine according to the general procedure. **2c**: yellow oil; ^{1}H NMR ($CDCl_3$) δ 7.85–7.83 (m, 2H), 7.68–7.65 (m, 1H), 7.57–7.53 (m, 2H), 6.17 (s, 1H), 6.11 (s, 1H), 4.00 (t, *J* = 6.4 Hz, 1H), 3.49 (dd, *J* = 13.2, 6.4 Hz, 1H), 3.15 (dd, *J* = 13.2, 6.4 Hz, 1H), 2.55 (m, 1H), 1.50 (bs, 1H), 1.41 (m, 1H), 1.29 (m, 1H), 0.98 (d, *J* = 6.4 Hz, 3H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −70.56 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 134.5, 131.8 (q, *J* = 32.2 Hz), 129.4, 129.3, 125.6 (q, *J* = 6.0 Hz), 124.0, 62.7, 53.9, 47.7, 29.7, 19.7, 10.3; MS, *m*/*z* (relative intensity) 335 (M^+, 1), 320 (5), 306 (55), 164 (15), 150 (52), 141 (15), 125 (10), 96 (12), 86 (46), 77 (100), 56 (15), 51 (38). Anal. Calcd for $C_{15}H_{20}F_3NO_2S$: C, 53.72; H, 6.01. Found: C, 53.52; H, 5.95.

4.1.4. 4-t-Butylamino-2-trifluoromethyl-3-phenylsulfonylbut-1-ene (**2d**)

2d was prepared in 81% yield (0.206 g) from the reaction of diene **1** with *t*-butylamine according to the general procedure. **2d**: yellow oil; ^{1}H NMR ($CDCl_3$) δ 7.85–7.83 (m, 2H), 7.68–7.64 (m, 1H), 7.56–7.53 (m, 2H), 6.19 (s, 1H), 6.10 (s, 1H), 3.93 (t, *J* = 6.4 Hz, 1H), 3.43 (dd, *J* = 12.4, 6.4 Hz, 1H), 3.06 (dd, *J* = 12.4, 6.4 Hz, 1H), 1.34 (bs, 1H), 1.06 (s, 9H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −70.56 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 134.5, 131.7 (q, *J* = 32.2 Hz), 129.5, 129.3, 125.6 (q, *J* = 6.0 Hz), 124.0, 64.2, 50.8, 44.0, 29.1; MS, *m*/*z* (relative intensity) 335 (M^+, 1), 262 (8), 252 (9), 172 (34), 153 (95), 121 (61), 91 (30), 77 (100), 51 (71). Anal. Calcd for $C_{15}H_{20}F_3NO_2S$: C, 53.72; H, 6.01. Found: C, 53.39; H, 6.07.

4.1.5. 4-Phenylamino-2-trifluoromethyl-3-phenylsulfonylbut-1-ene (**2e**)

2e was prepared in 51% yield (0.138 g) from the reaction of diene **1** with aniline according to the general procedure. **2e**: yellow oil; ^{1}H NMR ($CDCl_3$) δ 7.83–7.80 (m, 2H), 7.68–7.64 (m, 1H), 7.57–7.53 (m, 2H), 7.20–7.16 (m, 2H), 6.78–6.75 (m, 1H), 6.56–6.54 (m, 2H), 6.23 (s, 1H), 6.16 (s, 1H), 4.24–4.20 (m, 1H), 4.18–4.12 (m, 1H), 4.07 (t, *J* = 6.0 Hz, 1H), 3.74–3.67 (m, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −69.65 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 137.2, 134.0, 131.3 (q, *J* = 32.2 Hz), 129.5, 129.1, 128.7, 128.3, 125.5 (q, *J* = 6.0 Hz), 124.1, 120.4, 62.0, 52.9; MS, *m*/*z* (relative intensity) 355 (M^+, 8), 228 (3), 214 (9), 174 (8), 141 (8), 106 (100), 77 (89), 65 (24), 91 (7), 51 (30). Anal. Calcd for $C_{17}H_{16}F_3NO_2S$: C, 57.46; H, 4.54. Found: C, 57.19; H, 4.48.

4.2. Preparation of N-benzyl-3-trifluoromethyl-4-phenylsulfonylpyrrolidine (**4a**)

A 15 mL two-neck round bottom flask equipped with a magnetic stirrer bar, a septum and nitrogen tee connected to an argon source was charged with olefin **2a** (0.185 g, 0.50 mmol) and 4 mL of 2,2,2-trifluoroethanol. The reaction mixture was heated at 60 °C for 2 h and then cooled down to room temperature. After evaporation of solvent, it was chromatographed on SiO_2 column. Elution with a mixture of *n*-hexane and ethyl acetate (3:1) provided the pyrrolidine **4a** in 71% yield (0.131 g). **4a**: yellow oil; ^{1}H NMR ($CDCl_3$) δ 7.91–7.89 (m, 2H), 7.71–7.67 (m, 1H), 7.60–7.56 (m, 2H), 7.32–7.20 (m, 6H), 3.79–3.75 (dt, *J* = 7.6, 4.8 Hz, 1H), 3.64 (d, *J* = 13.2 Hz, 1H), 3.56 (d, *J* = 13.2 Hz, 1H), 3.31–3.25 (m, 1H), 3.08 (dd, *J* = 10.4, 5.6 Hz, 1H), 2.94–2.84 (m, 2H), 2.70 (dd, *J* = 10.4, 5.6 Hz, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −70.74 (d, *J* = 11.3 Hz, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 137.8, 134.4, 131.5, 129.7, 129.1, 129.0, 128.7, 128.5, 127.6, 63.6, 58.9, 54.2, 53.60 (q, *J* = 7.0 Hz), 43.9 (q, *J* = 28.2 Hz), 31.2; MS, *m*/*z* (relative intensity) 369 (M^+, 1), 227 (81), 158 (100), 91 (90), 77 (22), 65 (10), 51 (8). Anal. Calcd for $C_{18}H_{18}F_3NO_2S$: C, 58.53; H, 4.91. Found: C, 58.21; H, 4.85.

4.3. General procedure for the preparation of 4-alkoxy-2-trifluoromethyl-3-phenylsulfonylbut-1-ene (**3**)

A 15 mL two-neck round bottom flask equipped with a magnetic stirrer bar, a septum and nitrogen tee connected to an argon source was charged with diene **1** (0.200 g, 0.76 mmol), diisopropylamine (0.384 g, 3.80 mmol), alcohol (3.80 mmol), and 3 mL of methylene chloride. The reaction mixture was then stirred

at room temperature for 8 h (2,2,2-trifluoroethanol) or 16 h (for methanol or ethanol). It was extracted with ether twice, dried over anhydrous $MgSO_4$ and chromatographed on SiO_2 column. Elution with a mixture of *n*-hexane and ethyl acetate (4:1) provided the addition product **3**.

4.3.1. 2-Trifluoromethyl-4-methoxy-3-phenylsulfonylbut-1-ene (**3a**)

3a was prepared in 80% yield (0.179 g) from the reaction of diene **1** with methanol according to the general procedure. **3a**: yellow oil; ^{1}H NMR ($CDCl_3$) δ 7.88–7.85 (m, 2H), 7.68–7.65 (m, 1H), 7.57–7.53 (m, 2H), 6.15 (m, 2H), 4.07–3.99 (m, 2H), 3.85 (dd, J = 10.0, 6.0 Hz, 1H), 3.28 (s, 3H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −69.09 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 134.4, 130.5 (q, J = 32.2 Hz), 129.4, 129.3, 125.9 (q, J = 5.0 Hz), 71.3, 62.6, 59.2; MS, *m*/*z* (relative intensity) 294 (M^+, 1), 172 (13), 153 (44), 141 (12), 121 (28), 91 (13), 83 (10), 77 (100), 65 (10), 51 (65). Anal. Calcd for $C_{12}H_{13}F_3O_3S$: C, 48.98; H, 4.45. Found: C, 48.81; H, 4.42.

4.3.2. 4-Ethoxy-2-trifluoromethyl-3-phenylsulfonylbut-1-ene (**3b**)

3b was prepared in 74% yield (0.173 g) from the reaction of diene **1** with ethanol according to the general procedure. **3b**: yellow oil; ^{1}H NMR ($CDCl_3$) δ 7.87–7.86 (m, 2H), 7.68–7.64 (m, 1H), 7.57–7.53 (m, 2H), 6.15 (s, 2H), 4.06 (q, J = 7.2 Hz, 2H), 3.88–3.83 (m, 1H), 3.43–3.40 (m, 2H), 1.05 (t, J = 7.2 Hz, 3H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −69.12 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 134.2, 130.6 (q, J = 32.2 Hz), 129.3, 129.1, 125.8 (q, J = 5.0 Hz), 71.0, 62.4, 60.1, 15.3; MS, *m*/*z* (relative intensity) 308 (M^+, 1), 262 (3), 172 (15), 153 (51), 141 (13), 121 (26), 91 (14), 83 (12), 77 (100), 65 (11), 51 (64). Anal. Calcd for $C_{13}H_{15}F_3O_3S$: C, 50.64; H, 4.90. Found: C, 50.31; H, 4.84.

4.3.3. 4-(2,2,2-Trifluoroethoxy)-2-trifluoromethyl-3-phenylsulfonylbut-1-ene (**3c**)

3c was prepared in 71% yield (0.195 g) from the reaction of diene **1** with 2,2,2-trifluoroethanol according to the general procedure. **3c**: yellow oil; ^{1}H NMR ($CDCl_3$) δ 7.88–7.85 (m, 2H), 7.70–7.67 (m, 1H), 7.59–7.55 (m, 2H), 6.18 (s, 2H), 4.25 (dd, J = 10.0, 6.0 Hz, 1H), 4.13–4.03 (m, 2H), 3.82 (q, J = 8.4 Hz, 2H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −69.26 (s, 3F), −74.05 (t, J = 9.4 Hz, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 134.6, 129.9 (q, J = 32.2 Hz), 129.4, 129.3, 126.5 (q, J = 5.2 Hz), 71.0, 69.0 (q, J = 34.2 Hz), 62.7, 59.2; MS, *m*/*z* (relative intensity) 362 (M^+, 2), 279 (7), 263 (14), 189 (13), 143 (10), 129 (13), 121(18), 113 (100), 101 (10), 97 (9), 83 (20), 77 (74), 51 (35). Anal. Calcd for $C_{13}H_{12}F_6O_3S$: C, 43.10; H, 3.34. Found: C, 42.91; H, 3.36.

4.4. General procedure for the preparation of 4-alkylthio(or arylthio)-2-trifluoromethyl-3-phenylsulfonylbut-1-ene (**5**)

A 15 mL two-neck round bottom flask equipped with a magnetic stirrer bar, a septum and nitrogen tee connected to an argon source was charged with diene **1** (0.200 g, 0.76 mmol) and 3 mL of THF. The reaction mixture was then cooled to 0 °C (thiophenol) or −45 °C (propanethiol) and then thiol (0.76 mmol) was added into the mixture. After stirring for 0.5 h, the reaction mixture was extracted with ether twice, washed with 10% NaOH, dried over anhydrous $MgSO_4$ and chromatographed on SiO_2 column. Elution with a mixture of *n*-hexane and ethyl acetate (4:1) provided the addition product **5**.

4.4.1. 2-Trifluoromethyl-3-phenylsulfonyl-4-phenylthiobut-1-ene (**5a**)

5a was prepared in 72% yield (0.204 g) from the reaction of diene **1** with thiophenol according to the general procedure. **5a**: yellow oil; ^{1}H NMR ($CDCl_3$) δ 7.80–7.78 (m, 2H), 7.70–7.66 (m, 1H), 7.56–7.52 (m, 2H), 7.26–7.21 (m, 5H), 6.19 (s, 1H), 6.07 (s, 1H), 3.88 (dd, J = 11.6, 3.2 Hz, 1H), 3.82 (dd, J = 13.6, 3.2 Hz, 1H), 3.23 (dd, J = 13.6, 11.6 Hz, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −68.46 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 134.7, 133.8, 131.7 (q, J = 32.2 Hz), 130.5, 129.5, 129.4, 127.5, 126.4 (q, J = 5.0 Hz), 62.3, 34.4; MS, *m*/*z* (relative intensity) 372 (M^+, 1), 231 (100), 198 (10), 177 (9), 135 (8), 109 (80), 77 (52), 65 (16), 51 (21). Anal. Calcd for $C_{17}H_{15}F_3O_2S_2$: C, 54.83; H, 4.06. Found: C, 54.55; H, 4.02.

4.4.2. 2-Trifluoromethyl-3-phenylsulfonyl-4-propylthiobut-1-ene (**5b**)

5b was prepared in 70% yield (0.2180 g) from the reaction of diene **1** with propanethiol according to the general procedure. **5b**: yellow oil; ^{1}H NMR ($CDCl_3$) δ 7.89–7.81 (m, 2H), 7.69–7.67 (m, 1H), 7.59–7.55 (m, 2H), 6.20 (s, 1H), 6.08 (s, 1H), 3.94 (dd, J = 11.2, 3.2 Hz, 1H), 3.38 (dd, J = 13.6, 3.2 Hz, 1H), 2.97 (dd, J = 13.6, 11.6 Hz, 1H), 2.46 (t, J = 7.2 Hz, 2H), 1.59–1.51 (m, 2H), 0.94 (t, J = 7.2 Hz, 3H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −68.76 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 134.4, 131.8 (q, J = 32.2 Hz), 129.4, 129.1, 125.9 (q, J = 5.0 Hz), 123.4, 62.6, 34.7, 31.5, 22.5, 13.0; MS, *m*/*z* (relative intensity) 338 (M^+, 1), 197 (100), 155 (45), 153 (34), 141 (12), 115 (13), 77 (95), 51 (43). Anal. Calcd for $C_{14}H_{17}F_3O_2S_2$: C, 49.69; H, 5.06. Found: C, 49.31; H, 4.99.

4.5. Preparation of 1,4-bis(phenylthio)-2-trifluoromethylbut-2-ene (**6**)

A 15 mL two-neck round bottom flask equipped with a magnetic stirrer bar, a septum and nitrogen tee connected to an argon source was charged with NaH (1.0 mmol) and 3 mL of THF. Then, thiophenol (0.110 g, 1.0 mmol) was added into the mixture and then stirred at room temperature for 0.5 h. The compound **5a** (0.186 g, 0.5 mmol) added into the mixture and then it was heated at reflux temperature for 12 h. After cooling the reaction mixture, it was extracted with ether twice, washed with 10% NaOH, dried over anhydrous $MgSO_4$ and chromatographed on SiO_2 column. Elution with *n*-hexane provided the product **6** (*E*/*Z* = 93:7) in 60% yield (0.102 g). **6**: yellow oil; ^{1}H NMR ($CDCl_3$) δ 7.40–7.26 (m, 10H), 6.28 (tq, J = 7.6, 1.6 Hz, 1H, *E*-isomer), 5.71 (t, J = 7.6 Hz, 1H, *Z*-isomer), 3.62 (d, J = 7.6 Hz, 2H, *Z*-isomer), 3.56 (s, 2H, *Z*-isomer), 3.33 (s, 2H, *E*-isomer), 3.20 (dq, J = 7.6, 1.6 Hz, 2H, *E*-isomer); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −60.53 (s, 3F, *Z*-isomer), −67.88 (s, 3F, *E*-isomer); MS, *m*/*z* (relative intensity) 340 (M^+, 1), 230 (52), 197 (32), 177 (20), 153 (15), 109 (100), 77 (10), 65 (41), 51 (10). Anal. Calcd for $C_{17}H_{15}F_3S_2$: C, 59.98; H, 4.44. Found: C, 59.57; H, 4.39.

4.6. Preparation of diethyl 2-[3-trifluoromethyl-2-phenylsulfonylbut-3-enyl]malonate (**7**)

A 15 mL two-neck round bottom flask equipped with a magnetic stirrer bar, a septum and nitrogen tee connected to an argon source was charged with NaH (1.1 mmol) and 3 mL of THF. Then, diethyl malonate (0.176 g, 1.1 mmol) was added into the mixture and then stirred at room temperature for 0.5 h. Diene **1** (0.288 g, 1.1 mmol) was added into the mixture at 0 °C and then the mixture was stirred at 0 °C for 0.5 h. The reaction mixture was extracted with ether twice, dried over anhydrous $MgSO_4$ and chromatographed on SiO_2 column. Elution with a mixture of *n*-hexane and ethyl acetate (4:1) provided the addition product **7** in 78% yield (0.362 g). **7**: yellow oil; ^{1}H NMR ($CDCl_3$) δ 7.88–7.86 (m, 2H), 7.70–7.67 (m, 1H), 7.59–7.55 (m, 2H), 6.22 (s, 1H), 6.17 (s, 1H), 4.21 (m, 4H), 4.04 (dd, J = 10.4, 3.2 Hz, 1H), 3.44 (dd, J = 10.4, 4.8 Hz, 1H), 2.83–2.75 (m, 1H), 2.39–2.32 (m, 1H), 1.27–1.20 (m, 6H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −69.33 (s, 3F); ^{13}C NMR

(100 MHz, $CDCl_3$) δ 168.4, 168.0, 137.2, 134.6, 131.6 (q, J = 32.2 Hz), 129.5, 129.4, 126.5 (q, J = 5.0 Hz), 123.7, 62.2, 62.0, 60.3, 48.7, 29.5, 14.1; MS, m/z (relative intensity) 422 (M^+, 1), 377 (10), 331 (10), 281 (100), 253 (13), 235 (11), 225 (12), 207 (81), 179 (30), 163 (27), 141 (28), 115 (70), 77 (90), 51 (32). Anal. Calcd for $C_{18}H_{21}F_3O_6S$: C, 51.18; H, 5.01. Found: C, 51.05; H, 5.04.

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