# Study on the Reactions of 3-Bromo-4-ethoxy-1,1,1-trifluoro-3-buten-2-one with Benzenethiols Promoted by $InCl_3$•$4H_2O$†

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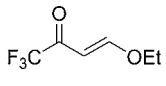
In the presence of $InCl_3$•$4H_2O$, the reaction of 3-bromo-4-ethoxy-1,1,1-trifluoro-3-buten-2-one **2** with a series of benzenethiols proceeds readily and gave both the addition-elimination product 3-bromo-1,1,1-trifluoro-4-thiophenyl-but-3-en-2-one and substitution product 1,1,1-trifluoro-3,4-bis-thiophenyl-but-3-en-2-one. The reactivity of benzenethiols is discussed in terms of their substituted group.

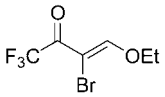
**Keywords** 3-bromo-4-ethoxy-1,1,1-trifluoro-3-buten-2-one, benzenethiols, coupling, addition-elimination, substitution, $Ad_NES_N$ mechanism

## Introduction

Trifluoromethyl substituted *α*,*β*-unsaturated ketones are of great importance, and are useful synthons to introduce trifluoromethyl group into molecules.[1,2] The methods for the synthesis of trifluoromethylated compounds have drawn considerable attention.[3,4] We have continued studying on the chemical transformation of (*E*)-4-ethoxy-1,1,1-trifluoro-3-buten-2-one **1**.[5] Recently, Gerus *et al.* reported a modified *α*,*β*-unsaturated ketone **2** with a $CF_3$ group, which was obtained from bromination of enone **1**.[6,7] The presence of bromine atom at the *α*-position, however, allows some new reactions of **2**, such as substitution of the bromine atom that is obviously different from enone **1**. However, to our best knowledge, very little is known about the reaction of *α*-bromo vinylic compound **2** with nucleophiles. The only reported examples are the reaction of **2** with nitrogen nucleophiles[6,8,9] and the reaction with sulfur nucleophiles has not been reported till now. Rosnati *et al.* have reported the reactions of phenol and benzenethiol with a number of vinyl bromides.[10] In their experiments, adducts and substituted products were obtained in the system $K_2CO_3$-acetone. However, the replacement of hydrogen atom by fluorine atom influenced profoundly the chemical property of **2**, when it reacted with thiols there were no adducts obtained. In this paper, we report the results of the reactions of **2** with a series of benzenethiols and discuss the possible reaction mechanism.



**1**



**2**

## Results and discussion

In the presence of $InCl_3$•$4H_2O$ (10 mol%), we found that the reaction of *α*-bromo Michael acceptor **2** (2 mmol) with thiophenol **3** (2 mmol) proceeds readily at room temperature to afford three products **3a** (9%), **3b** (16%) and **3c** (15%), respectively. Among them **3a** is the direct coupling product of thiophenol; **3b** is the product without the substitution of the vinylic bromine through addition of the thiophenol, followed by the elimination of an ethanol. On the basis of the formation of **3b**, **3c** might have been formed through nucleophilic substitution of the Michael substrates (Table 1, Entry 1).

How about the reaction under other conditions? During our careful investigations, we found that this type of reaction was extremely sensitive to reaction conditions. Firstly, we found if there was no catalyst in this system, the coupling reaction proceeded and the yield of **3a** was up to 64% (Table 1, Entry 2) and little products of **3b** and **3c** were isolated. Secondly, if we reduced the reaction temperature down to 0 ℃, the reaction time was prolonged obviously and the yield of **3a** was also increased, but no remarkable improving of

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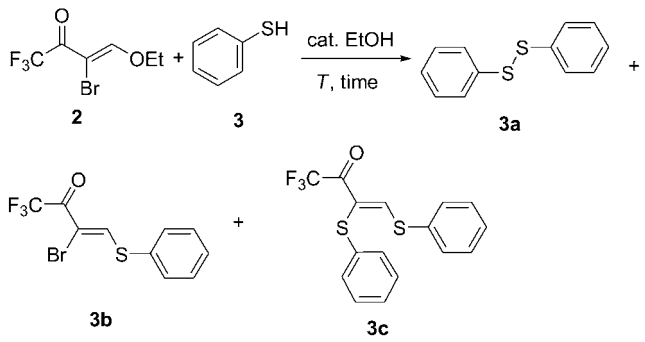
other products. Furthermore, it was unsuccessful that increasing the concentration of thiophenol in the solvent to increase the yield of **3b** and **3c**, and it only led to the raising yield of the coupling product (Table 1, Entry 4). Interestingly, when these two reagents were introduced into Rosnati's $K_2CO_3$-actone system, only the coupling product **3a** was isolated (Table 1, Entry 5). Clearly, in this reaction, the presence of catalyst $InCl_3$•$4H_2O$ is necessary and reducing or increasing the reaction temperature is unable to increase the yield of addition-elimination or substitution product.

**Table 1** Reaction results of **2** with thiophenol under different conditions




| Entry | Catalyst | Temp. | Time/h | Yield/% | | |
|---|---|---|---|---|---|---|
| | | | | **3a** | **3b** | **3c** |
| 1[a] | $InCl_3$•$4H_2O$ | r.t. | 12 | 9[c] | 16[c] | 15[c] |
| 2[a] | no | r.t. | 21 | 64[c] | 9[c] | 6[c] |
| 3[a] | $InCl_3$•$4H_2O$ | 0 ℃ | 48 | 69[c] | 14[c] | 8[c] |
| 4[b] | $InCl_3$•$4H_2O$ | r.t. | 24 | 80[d] | 4[d] | 6[d] |
| 5[b] | $K_2CO_3$-Acetone | r.t. | 2 | 96[d] | 0[d] | 0[d] |

[a] Molar ratio of **2** : **3**=1 : 1. [b] Molar ratio of **2** : **3**=1 : 4. [c] Isolated yield according to thiophenol. [d] Isolated yield according to 3-bromo-4-ethoxy-1,1,1-trifluoro-3-buten-2-one **2**.

Further experiments demonstrated that other thiophenols could also react with **2** under the same condition. The most significant results were summarized in Table 2. These showed that the substrate **2** reacted readily with thiophenols, however, the groups on the benzene influenced greatly the reactivities of these thiophenols. Thus the reactions of the two reagents afforded a different ratio of the three products.

Thiophenols **4**—**6** bearing electro-donor groups such as methyl or methoxyl, accounting for the stronger nucleophilic reactivity than thiophenol **3**, could react readily with $\alpha$-bromo vinyl compound **2**. In their products, the ratio of coupling products decreased, while the adding-elimination and substitution products became the major products. This phenomenon was obviously demonstrated that when **11** were applied in the reaction, there was almost no coupling product obtained. When halogen was introduced into thiophenol, the reactivity changed correspondingly. As a weak electron-donor fluorine atom influenced the nucleophilic reactivity hardly, the ratio of the products was the same as the thiophenol. On the other hand, when chlorine atom was introduced into the thiophenol molecular, the ratio of coupling products raised and reaction time was prolonged. Especially, the stronger electron-withdrawing nitryl weakened extremely the reactivity of the sulfur so that **12** appeared to have completely no reactivity in the reaction. It was worth to notice that phenol or sodium phenolate was unable to react with **2** under the same conditions. The reason must be the lower nucleophilic reactivity of the oxygen atom. All these results were summarized in the Figure 1, which showed clearly the whole current of the yields.

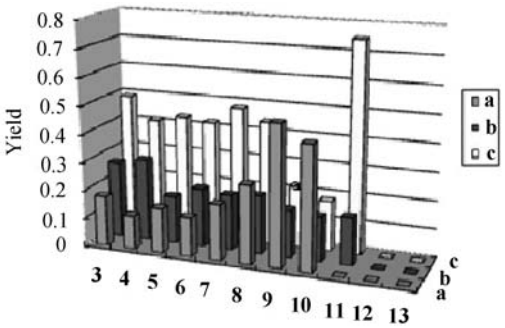



**Figure 1** Results of the reaction of **2** with substituted benzenethiols.

Naturely, we were interested in elucidating the mechanism of this $InCl_3$•$4H_2O$-mediated reaction of **2** with thiophenols. Despite some apparent difference, we thought that Rosnati's reaction of $\alpha$-bromo Michael acceptors with phenol or benzenethiol in the system $K_2CO_3$-acetone[10] could serve as a prototype for our $InCl_3$•$4H_2O$-promoted reaction. The results obtained in the reaction of **2** with thiophenols clearly indicated that there are two competition-reactions in this system. One is the simple coupling-reaction, which occurred between the thiophenols and gave the coupling products. The other occurred through a reaction sequence initiated by the conjugate additon of the reagent, followed by the elimination of ethanol on the newly generated $sp^3$ carbon atom and completed by nucleophilic substitution of the bromine ($Ad_NES_N$ mechanism).

The following facts support the proposed mechanism: (a) Coupling products **a** were isolated in all the reactions under different conditions. And we found the yield of **a** changed with the reaction time; the yield increased with the prolonged time. (b) The expected Michael-type adducts **A** have not been isolated, which could be accounted for the easy leaving of ethanol to produce the $\beta$-phenylsulfanyl vinylic bromides **b**. (c) Diphenylthio derivatives **c** were isolated from the reaction through formal substitution of the vinylic bromine. (d) Putting addition-elimination product **3b** with equivalent amount

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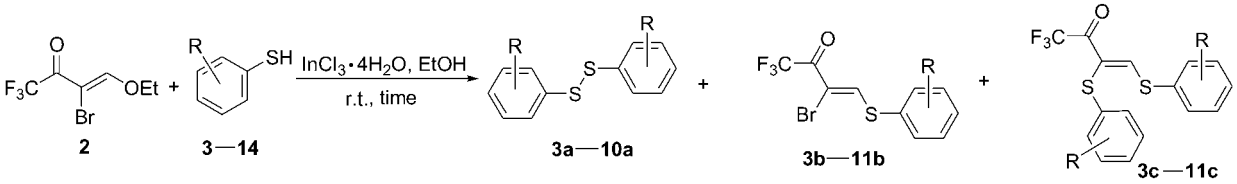
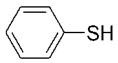
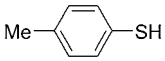
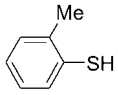
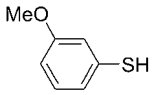
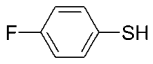
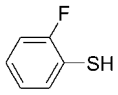
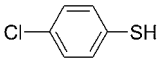
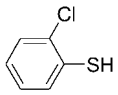
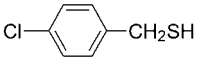
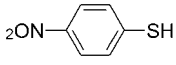
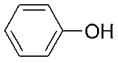
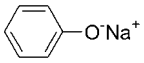
**Table 2** $InCl_3•4H_2O$-mediated reaction results of **2** with thiophenols[a]




| Entry | Thiophenols | Time | Products & yields/% | | |
|---|---|---|---|---|---|
| 1 |  **3** | 12 | **3a** (18) | **3b** (27) | **3c** (39) |
| 2 |  **4** | 12 | **4a** (12) | **4b** (29) | **4c** (41) |
| 3 |  **5** | 12 | **5a** (16) | **5b** (17) | **5c** (43) |
| 4 |  **6** | 12 | **6a** (14) | **6b** (21) | **6c** (42) |
| 5 |  **7** | 36 | **7a** (20) | **7b** (20) | **7c** (48) |
| 6 |  **8** | 24 | **8a** (28) | **8b** (21) | **8c** (44) |
| 7 |  **9** | 48 | **9a** (50) | **9b** (17) | **9c** (22) |
| 8 |  **10** | 48 | **10a** (44) | **10b** (16) | **10c** (18) |
| 9 |  **11** | 12 | trace | **11b** (17) | **11c** (75) |
| 10 |  **12** | 48 | — | — | — |
| 11 |  **13** | 48 | — | — | — |
| 12 |  **14** | 48 | — | — | — |

[a] Reactions were carried out in 3 mL ethanol with 2 mmol thiophenol, 2 mmol **2** and 0.15 mg $InCl_3•4H_2O$ under nitrogen atmosphere. [b] Isolated yields according to thiophenol.

benzenethiol, some substitution product **3c** could be isolated.

The following observations also point to the $Ad_NES_N$ mechanism. The reactivity of benzenethiol can be explained in terms of the nature of the substituent group on the benzene, which appears to be the main factor to affect the addition-elimination and the nucleophilic displacement of the bromine. Thus, all substrates with electron-donating groups which increase the nucleophilic activity could react readily with Michael-acceptor **2** and the yield of addition-elimination and substitution products was higher than the yield of coupling products (Table 1, Entries 2—4). By contrast, when benzene was substituted by strongly electron-drawing groups such as nitryl, which seriously weaken the reactivity of sulfur, there was no reaction occurred (Table 1, Entry 10). However, if halogen was introduced into benzene, due to the different electron-attracting power, the reaction results were different either (Table 1, Entries 5—9). Fluorine atom could be regarded as a weak electron-donor, so it enhanced the reactivity of sulfur. On the other hand, chlorine atom was a weak electron-drawer, which slightly decreased sulfur's reactivity, so the reaction time was prolonged, ultimately responsible for more benzenethiol undertaking the coupling reaction.

## Conclusion

In summary, we have the first reported the reaction of 3-bromo-4-ethoxy-1,1,1-trifluoro-3-buten-2-one with a series of benzenethiols in the presence of $InCl_3•4H_2O$. There are two-competition reactions in these system and three products are isolated, accounting for the proposed $Ad_NES_N$ mechanism.

## Experimental

### Materials and instruments

Melting points were measured on a Temp-Melt apparatus and were uncorrected. $^1H$, $^{13}C$ and $^{19}F$ NMR spectra were recorded on Bruker AM-300 instruments with $Me_4Si$ and $CFCl_3$ as the internal and external standards, respectively. FT-IR spectra were obtained with a Nicolet AV-360 spectrophotometer. Low-resolution mass spectra (LRMS) or high-resolution mass spectra (HRMS) were obtained on a Finnigan GC-MS 4021 or a Finnigan MAT-8430 instrument using the electron impact ionization technique (70 eV), respectively. Elemental analysis was performed by this institute. The material **2** was prepared according to the reference.[6,7]

### General procedure

**2** (2 mmol) was added into a 10 mL flask containing benzenethiosl (2 mmol) and 3 mL EtOH. Then $InCl_3•4H_2O$ (0.15 mg) was added into the mixture, which was stirred at r.t. TLC analysis was used to monitor the process. After the reaction finished, evaporating the solvent, the residue was purified by column chromatography on silica gel to give the products, respectively.

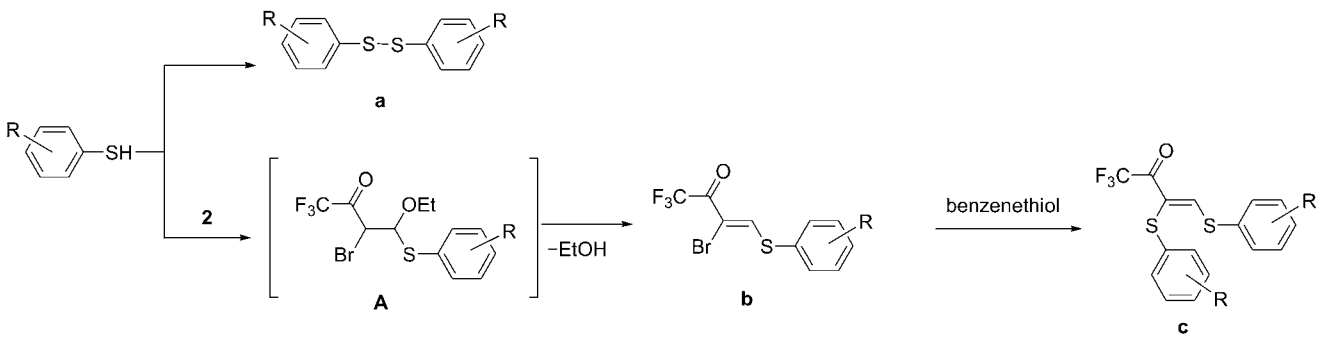
**Diphenyl disulfide (3a)** White solid, yield 18%. $^1H$ NMR ($CDCl_3$) $\delta$: 7.50 (dd, $J$=1.5, 8.4 Hz, 4H, Ph), 7.26—7.29 (m, 6H, Ph).

**(*Z*)-3-Bromo-1,1,1-trifluoro-4-phenylsulfanyl-but-3-en-2-one (3b)** Yellow solid (m.p. 36—38 ℃), yield 29%. $^1H$ NMR ($CDCl_3$) $\delta$: 8.55 (s, 1H, CH), 7.56—7.53 (m, 2H, Ph), 7.51—7.48 (m, 3H, Ph). $^{19}F$ NMR ($CDCl_3$) $\delta$: −68.93 (s, $CF_3$). $^{13}C$ NMR ($CDCl_3$) $\delta$: 171.3 (q, $^2J_{CF}$ =28 Hz, C=O), 157.6 (=CH), 131.4 ($C_6H_5$), 131.2 ($C_6H_5$), 130.0 ($C_6H_5$), 129.8 ($C_6H_5$), 115.8 (q, $^1J_{CF}$=232 Hz, $CF_3$), 112.4 (C=). IR $v$: 1703, 1532, 1125, 707 $cm^{-1}$. MS $m/z$ (%): 312 ($M^+$, 100), 310 ($M^+$, 100), 243 ($M^+$−$CF_3$, 79.71), 241 ($M^+$−$CF_3$, 75.09), 231 ($M^+$−Br, 6.57), 123 ($CF_3COC=CH^+$, 4.99), 69 ($CF_3$, 2.79). HRMS calcd for $C_{10}H_6BrF_3OS$ 310.116, found 309.930.

**(*Z*)-1,1,1-Trifluoro-3,4-bis-phenylsulfanyl-but-3-en-2-one (3c)** Yellow solid (m.p. 71—72 ℃), yield 37%. $^1H$ NMR ($CDCl_3$) $\delta$: 8.69 (s, 1H, CH), 7.56—7.46 (m, 5H, Ph), 7.33—7.19 (m, 5H, Ph). $^{19}F$ NMR ($CDCl_3$) $\delta$: −69.84 (s, $CF_3$). $^{13}C$ NMR ($CDCl_3$) $\delta$: 174.8 (q, $^2J_{CF}$ =27 Hz, C=O), 165.8 (=CH), 131.2 ($C_6H_5$), 129.9 ($C_6H_5$), 129.3 ($C_6H_5$), 128.8 ($C_6H_5$), 127.1 (C=), 118.0 (q, $^1J_{CF}$=232 Hz, $CF_3$). IR $v$: 1693, 1532, 1317, 1145, 1129, 883 $cm^{-1}$. MS $m/z$ (%): 246 ($M^+$−Ph-$H_2O$, 9.61), 177 ($M^+$−Ph-$H_2O$−$CF_3$, 92.27), 123 ($CF_3COC=CH^+$, 100), 109 ($PhS^+$, 1.58), 97 ($CF_3CO$, 8.54), 69 ($CF_3$, 76.08).

**Di-*p*-tolyl-disulfide (4a)** White solid, yield 12%. $^1H$ NMR ($CDCl_3$) $\delta$: 7.41 (d, $J$=8.4 Hz, 4H, Ph), 7.13 (d, $J$=8.1 Hz, 4H, Ph), 2.35 (s, 6H, Me).

**Scheme 3** Proposed $Ad_NES_N$ mechanism



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**(*Z*)-3-Bromo-1,1,1-trifluoro-4-*p*-tolylsulfanyl-but-3-en-2-one (4b)** Yellow solid (m.p. 55—57 ℃), yield 29%. $^1$H NMR ($CDCl_3$) $\delta$: 8.50 (s, 1H, CH), 7.41 (d, $J$= 8.1 Hz, 2H, Ph), 7.21 (d, $J$=5.4 Hz, 2H, Ph), 2.41 (s, 3H, Me). $^{19}$F NMR ($CDCl_3$) $\delta$: −68.63 (s, $CF_3$). IR $v$: 1694, 1532, 1376, 1148, 1127, 887 cm$^{-1}$. MS $m/z$ (%): 326 ($M^+$, 100), 324 ($M^+$, 98.72), 257 ($M^+-CF_3$, 79.77), 255 ($M^+-CF_3$, 77.82), 246 ($M^+-$Br, 17.42), 123 ($CF_3COC{=}CH^+$, 49.79), 69 ($CF_3$, 13.59). Anal. calcd for $C_{11}H_8BrF_3OS$: C 40.63, H 2.48; found C 40.21, H 2.67.

**(*Z*)-1,1,1-Trifluoro-3,4-bis-*p*-tolylsulfanyl-but-3-en-2-one (4c)** Yellow solid (m.p. 55—57 ℃), yield 41%. $^1$H NMR ($CDCl_3$) $\delta$: 8.57 (s, 1H, CH), 7.40 (d, $J$= 3.8 Hz, 2H, Ph), 7.28—7.24 (m, 4H, Ph), 7.11 (d, $J$= 7.5 Hz, 2H, Ph), 2.41 (s, 3H, Me), 2.33 (s, 3H, Me). $^{19}$F NMR ($CDCl_3$) $\delta$: −69.82 (s, $CF_3$). IR $v$: 1691, 1510, 1322, 1126, 896, 808 cm$^{-1}$. MS (ESI) $m/z$ (%): 369.2 ($M^+$+H). Anal. calcd for $C_{18}H_{15}F_3OS_2$: C 58.68, H 4.10; found C 58.92, H 4.16.

**Di-*o*-tolyl disulfide (5a)** White solid, yield 16%. $^1$H NMR ($CDCl_3$) $\delta$: 7.50—7.56 (m, 2H, Ph), 7.15—7.20 (m, 6H, Ph), 2.45 (s, 6H, Ph).

**(*Z*)-3-Bromo-1,1,1-trifluoro-4-*o*-tolylsulfanyl-but-3-en-2-one (5b)** Yellow solid (m.p. 75—76 ℃), yield 17%. $^1$H NMR ($CDCl_3$) $\delta$: 8.42 (s, 1H, CH), 7.52—7.49 (m, 1H, Ph), 7.38—7.33 (m, 3H, Ph), 2.48 (s, 3H, Me). $^{19}$F NMR ($CDCl_3$) $\delta$: −68.90 (s, $CF_3$). $^{13}$C NMR ($CDCl_3$) $\delta$: 171.7 (q, $^2J_{CF}$=27 Hz, C=O), 158.0 (=CH), 133.0 ($C_6H_4$), 131.4 ($C_6H_4$), 130.4 ($C_6H_4$), 127.6 ($C_6H_4$), 115.6 (q, $^1J_{CF}$=232 Hz, $CF_3$), 112.6 (C=), 20.8 ($CH_3$). IR $v$: 1705, 1533, 1316, 885 cm$^{-1}$. MS $m/z$ (%): 326 ($M^+$, 100), 344 ($M^+$, 97.72), 257 ($M^+-CF_3$, 79.58), 255 ($M^+-CF_3$, 77.20), 245 ($M^+-$Br, 18.61), 123 ($CF_3COCCH$, 14.01), 69 ($CF_3$, 11.74). HRMS calcd for $C_{11}H_8BrF_3OS$ 323.142, found 323.944.

**(*Z*)-1,1,1-Trifluoro-3,4-bis-*o*-tolylsulfanyl-but-3-en-2-one (5c)** Yellow solid (m.p. 75—76 ℃), yield 43%. $^1$H NMR ($CDCl_3$) $\delta$: 8.49 (s, 1H, CH), 7.48 (d, $J$= 7.5 Hz, 1H, Ph), 7.36—7.26 (m, 3H, Ph), 7.19—7.11 (m, 4H, Ph), 2.50 (s, 3H, Me), 2.42 (s, 3H, Me). $^{19}$F NMR ($CDCl_3$) $\delta$: −69.46 (s, $CF_3$). IR $v$: 3057, 1690, 1511, 1195, 1119, 756 cm$^{-1}$. MS $m/z$ (%): 368 ($M^+$, 100), 299 ($M^+-CF_3$, 4.06), 245 ($M^+-$SPhMe, 16.90), 188 ($M^+-$2PhMe, 4.23), 124 ($CF_3COCCH_2$, 23.21), 69 ($CF_3$, 9.54). Anal. calcd for $C_{18}H_{15}F_3OS_2$: C 58.68, H 4.10; found C 58.76, H 4.18.

**Bis-(3-methoxy-phenyl)-disulfide (6a)** White solid, yield 14%. $^1$H NMR ($CDCl_3$) $\delta$: 7.23—7.27 (m, 2H, Ph), 7.05—7.09 (m, 4H, Ph), 6.76—6.80 (m, 2H, Ph), 3.78 (s, 6H, Me).

**(*Z*)-3-Bromo-1,1,1-trifluoro-4-(3-methoxy-phenylsulfanyl)-but-3-en-2-one (6b)** Yellow liquid, yield 21%. $^1$H NMR ($CDCl_3$) $\delta$: 8.57 (s, 1H, CH), 7.40—7.36 (m, 1H, Ph), 7.12—7.11 (m, 1H, Ph), 7.05—7.03 (m, 2H, Ph), 3.85 (s, 3H, Me). $^{19}$F NMR ($CDCl_3$) $\delta$: −68.91 (s, $CF_3$). $^{13}$C NMR ($CDCl_3$) $\delta$: 174.7 (q, $^2J_{CF}$= 28 Hz, C=O), 165.9 (=CH), 134.2 ($C_6H_4$), 130.8 ($C_6H_4$), 123.2 ($C_6H_4$), 120.7($C_6H_4$), 117.8 (q, $^1J_{CF}$=232 Hz, $CF_3$), 116.2 ($C_6H_4$), 114.0 ($C_6H_4$), 112.7 (C=), 55.4 ($CH_3$). IR $v$: 1779, 1698, 1593, 1126, 705 cm$^{-1}$. MS $m/z$ (%): 342 ($M^+$, 23.19), 340 ($M^+$, 21.63), 273 ($M^+-CF_3$, 10.22), 271 ($M^+-CF_3$, 9.67), 261 ($M^+-$Br, 12.66), 164 ($M^+-$Br$-CF_3CO$, 100), 139 ($M^+-$SphOMe, 11.57), 69 ($CF_3$, 13.59). HRMS calcd for $C_{11}H_8BrF_3O_2S$ 339.141; found 339.947.

**(Z)-1,1,1-Trifluoro-3,4-bis-(3-methoxy-phenylsulfanyl)-but-3-en-2-one (6c)** Yellow oil, yield 42%. $^1$H NMR ($CDCl_3$) $\delta$: 8.70 (s, 1H, CH), 7.7 (t, $J$=8.1 Hz, 1H, Ph), 7.22 (t, $J$=7.8 Hz, 1H, Ph), 7.10—7.07 (m, 1H, Ph), 7.03—6.96 (m, 2H, Ph), 6.90—6.85 (m, 2H, Ph), 6.9—6.76 (m, 1H, Ph), 3.85 (s, 3H, Me), 3.80 (s, 3H, Me). $^{19}$F NMR ($CDCl_3$) $\delta$: −69.86 (s, $CF_3$). $^{13}$C NMR ($CDCl_3$) $\delta$: 176.8 (q, $^2J_{C\text{-}F}$=28 Hz, C=O), 157.5 (=CH), 132.2 ($C_6H_4$), 130.9 ($C_6H_4$), 123.2 ($C_6H_4$), 116.9 ($C_6H_4$), 116.8 ($C_6H_4$), 115.6 ($C_6H_4$), 114.6 (q, $^1J_{C\text{-}F}$=232 Hz, $CF_3$), 112.4 (C=), 55.5 ($CH_3$). IR $v$: 1696, 1591, 1480, 1123, 713 cm$^{-1}$. MS $m/z$ (%): 400 ($M^+$, 11.11), 261 ($M^+-$SPhOMe, 17.46), 191 ($M^+-$SphOMe$-CF_3$, 15.67), 140 (HSPhOMe, 30.84), 124 ($CF_3COCCH_2$, 8.62), 69 ($CF_3$, 11.69). HRMS calcd for $C_{18}H_{15}F_3O_3S_2$ 400.429, found 400.043.

**Bis-(4-fluoro-phenyl)-disulfide (7a)** White solid, yield 20%. $^1$H NMR ($CDCl_3$) $\delta$: 7.62 (d, $J$=8.7 Hz, 4H), 7.21 (d, $J$=8.7 Hz, 4H). $^{19}$F NMR ($CDCl_3$) $\delta$: −110.18 (s).

**(*Z*)-3-Bromo-1,1,1-trifluoro-4-(4-fluoro-phenylsulfanyl)-but-3-en-2-one (7b)** Yellow solid (m.p. 30—32 ℃), yield 20%. $^1$H NMR ($CDCl_3$) $\delta$: 8.44 (s, 1H, CH), 7.57—7.52 (m, 2H, Ph), 7.20—7.15 (m, 2H, Ph). $^{19}$F NMR ($CDCl_3$) $\delta$: −69.02 (s, $CF_3$), −110.08 (1F, s). $^{13}$C NMR ($CDCl_3$) $\delta$: 181.6 (q, $^2J_{CF}$=29 Hz, C=O), 163.6 (=CH), 137.7 ($C_6H_4$), 136.2 ($C_6H_4$), 131.3 ($C_6H_4$), 129.8 ($C_6H_4$), 119.1 (q, $^1J_{CF}$=232 Hz, $CF_3$), 115.9 (C=). IR $v$: 1693, 1592, 1492, 1318, 1152 cm$^{-1}$. MS $m/z$ (%): 330 ($M^+$, 43.80), 328 ($M^+$, 50.37), 261 ($M^+-CF_3$, 56.65), 259 ($M^+-CF_3$, 57.51), 152 ($M^+-CF_3COCBr$, 80.37), 127 ($FPhS^+$, 91.14), 83 ($CF_3CH$, 100), 69 ($CF_3$, 60.33). HRMS calcd for $C_{10}H_5BrF_4OS$ 328.106, found 328.925.

**(*Z*)-1,1,1-Trifluoro-3,4-bis-(4-fluoro-phenylsulfanyl)-but-3-en-2-one (7c)** Yellow solid (m.p. 71—73 ℃), yield 48%. $^1$H NMR ($CDCl_3$) $\delta$: 8.47 (s, 1H, CH), 7.52 (dd, $J$=6.9, 1.8 Hz, 2H, Ph), 7.39 (dd, $J$=9.0, 5.1 Hz, 2H, Ph), 7.17 (t, $J$=8.4 Hz, 2H, Ph), 7.02 (t, $J$=8.7 Hz, 2H, Ph). $^{19}$F NMR ($CDCl_3$) $\delta$: −69.91 (s, $CF_3$), −110.18 (1F, s), −113.88 (1F, s). IR $v$: 1694, 1591, 1490, 1233, 830 cm$^{-1}$. MS $m/z$ (%): 376 ($M^+$, 68.69), 307 ($M^+-CF_3$, 2.15), 201 ($M^+-CF_3CO-$FPh+H, 1.80), 152 (CH=CHSPhF, 100), 69 ($CF_3$, 29.92). Anal. calcd for $C_{16}H_9F_5OS_2$: C 51.06, H 2.41; found C 51.20, H 2.43.

  

**Bis-(2-fluoro-phenyl)-disulfide (8a)** White solid, yield 28%. $^1$H NMR ($CDCl_3$) $\delta$: 7.60 (t, $J$=7.8 Hz, 2H, Ph), 7.25—7.29 (m, 2H, Ph), 7.07—7.13 (m, 4H, Ph). $^{19}$F NMR ($CDCl_3$) $\delta$: −110.23 (s).

**(*Z*)-3-Bromo-1,1,1-trifluoro-4-(2-fluoro-phenylsulfanyl)-but-3-en-2-one (8b)** Yellow solid (m.p. 39—40 ℃), yield 21%. $^1$H NMR ($CDCl_3$) $\delta$: 8.45 (s, 1H, CH), 7.57—7.47 (m, 2H, Ph), 7.27—7.23 (m, 2H, Ph). $^{19}$F NMR ($CDCl_3$) $\delta$: −69.02 (s, $CF_3$). IR $v$: 1699, 1534, 1492, 1149, 1129, 878 cm$^{-1}$. MS $m/z$ (%): 330 ($M^+$, 64.23), 328 ($M^+$, 60.83), 261 ($M^+-CF_3$, 66.73), 259 ($M^+-CF_3$, 61.68), 152 ($M^+-CF_3COCBr$, 100), 127 ($FPhS^+$, 46.64), 69 ($CF_3$, 42.66). Anal. calcd for $C_{10}H_5BrF_4OS$: C 36.49, H 1.53; found C 37.01, H 1.67.

**(*Z*)-1,1,1-Trifluoro-3,4-bis-(2-fluoro-phenylsulfanyl)-but-3-en-2-one (8c)** Yellow solid (m.p. 55—56 ℃), yield 44 %. $^1$H NMR ($CDCl_3$) $\delta$: 8.51 (s, 1H, CH), 7.53—7.49 (m, 2H, Ph), 7.31—7.20 (m, 4H, Ph), 7.13—7.09 (m, 2H, Ph). $^{19}$F NMR ($CDCl_3$) $\delta$: −70.06 (s, $CF_3$), −108.59 (s, 1F), −109.82 (s, 1F). IR $v$: 1698, 1516, 1474, 1200, 1120 cm$^{-1}$. MS $m/z$ (%): 376 ($M^+$, 100), 307 ($M^+-CF_3$, 6.82), 200 ($M^+-CF_3CO-FPh$, 0.31), 155 ($CF_3COCH=CHS^+$, 0.72), 120 (COCSHCHSH, 1.93), 69 ($CF_3$, 19.29). Anal. calcd for $C_{16}H_9F_5OS_2$: C 51.06, H 2.41; found C 51.39, H 2.63.

**Bis-(4-chloro-phenyl)-disulfide (9a)** White solid, yield 50%. $^1$H NMR ($CDCl_3$) $\delta$: 7.42 (d, $J$=8.7 Hz, 4H, Ph), 7.29 (d, $J$=6.9 Hz, 4H).

**(*Z*)-3-Bromo-4-(4-chloro-phenylsulfanyl)-1,1,1-trifluoro-but-3-en-2-one (9b)** Yellow solid, m.p. 35—37 ℃, yield 17%. $^1$H NMR ($CDCl_3$) $\delta$: 8.44 (s, 1H, CH), 7.57—7.50 (m, 2H, Ph), 7.16—7.15 (m, 2H, Ph). $^{19}$F NMR ($CDCl_3$) $\delta$: −69.02 (s, $CF_3$). $^{13}$C NMR ($CDCl_3$) $\delta$: 177.2 (q, $^2J_{CF}$=27 Hz, C=O), 165.9 (=CH), 131.3 ($C_6H_4$), 130.6 ($C_6H_4$), 129.9 ($C_6H_4$), 129.5 ($C_6H_4$), 122.3 (C=), 117.1 (q, $^1J_{CF}$=232 Hz, $CF_3$). MS $m/z$ (%): 346 or 344 ($M^+$+H, 15.14 or 12.31), 277 or 275 ($M^+-CF_3$, 19.45 or 25.71), 143 ($o$-$ClPhS^-$, 9.62), 123 ($CF_3COCCH$, 5.25), 69 ($CF_3$, 46.84). HRMS calcd for $C_{10}H_5BrClF_3OS$ 343.8885, found 343.8887.

**(*Z*)-3,4-Bis-(4-chloro-phenylsulfanyl)-1,1,1-trifluoro-but-3-en-2-one (9c)** Yellow solid (m.p. 62—64 ℃), yield 22%. $^1$H NMR ($CDCl_3$) $\delta$: 8.54 (s, 1H, CH), 7.43—7.47 (m, 4H, Ph), 7.25—7.29 (m, 4H, Ph). $^{19}$F NMR ($CDCl_3$) $\delta$: −69.95 (s, $CF_3$). IR $v$: 1697, 1475, 1487, 1092 cm$^{-1}$. MS $m/z$ (%): 409 ($M^+$, 38.86), 374 ($M^+$−Cl, 13.66), 340 ($M^+-CF_3$, 1.99), 265 ($M^+-o$-ClPhS, 1.09), 167 ($M^+-o$-ClPhS−$CF_3CO$−H, 100), 143 ($o$-ClPhS, 26.66), 69 ($CF_3$, 28.21). Anal. calcd for $C_{16}H_9C_{l2}F_3OS_2$: C 46.96, H 2.22; found C 47.36, H 2.22.

**Bis-(2-chloro-phenyl)-disulfide (10a)** White solid, yield 44%. $^1$H NMR ($CDCl_3$) $\delta$: 7.56 (dd, $J$=1.8, 7.8 Hz, 2H, Ph), 7.37 (dd, $J$=1.5, 7.8 Hz, 2H, Ph), 7.21—7.19 (m, 4H, Ph).

**(*Z*)-3-Bromo-4-(2-chloro-phenylsulfanyl)-1,1,1-trifluoro-but-3-en-2-one (10b)** Yellow solid, m.p. 45—46 ℃, yield 16%. $^1$H NMR ($CDCl_3$) $\delta$: 8.44 (s, 1H, CH), 7.61—7.54 (m, 2H, Ph), 7.46—7.37 (m, 2H, Ph). $^{19}$F NMR ($CDCl_3$) $\delta$: −69.12 (s, $CF_3$). $^{13}$C NMR ($CDCl_3$) $\delta$: 171.2 (q, $^2J_{CF}$=27 Hz, C=O), 155.7 (=CH), 134.5 ($C_6H_4$), 133.7 ($C_6H_4$), 130.6 ($C_6H_4$), 130.2 ($C_6H_4$), 129.5 ($C_6H_4$), 115.1 (q, $^1J_{CF}$=232 Hz, $CF_3$), 113.2 (C=). IR $v$: 1706, 1534, 1123, 701 cm$^{-1}$. MS $m/z$ (%): 346 ($M^+$, 71.31), 344 ($M^+$, 54.64), 277 ($M^+-CF_3$, 100), 275 ($M^+-CF_3$, 75.81), 265 ($M^+$−Br, 5.27), 143 ($o$-ClPhS, 25.60), 123 ($CF_3COCCH$, 3.51), 69 ($CF_3$, 34.04). HRMS calcd for $C_{10}H_5BrClF_3OS$ 343.8885, found 343.8853.

**(*Z*)-3,4-Bis-(2-chloro-phenylsulfanyl)-1,1,1-trifluoro-but-3-en-2-one (10c)** Yellow solid, m.p. 53—55 ℃, yield 18%. $^1$H NMR ($CDCl_3$) $\delta$: 8.60 (s, 1H, CH), 7.60—7.53 (m, 2H, Ph), 7.44—7.36 (m, 3H, Ph), 7.20—7.16 (m, 3H, Ph). $^{19}$F NMR ($CDCl_3$) $\delta$: −70.07 (s, $CF_3$). IR $v$: 1697, 1513, 1452, 1121, 749 cm$^{-1}$. MS $m/z$ (%): 409 ($M^+$, 11.00), 339 ($M^+-CF_3$, 4.01), 265 ($M^+-o$-ClPhS, 8.23), 168 ($M^+-o$-ClPhS−$CF_3CO$, 100), 143 ($o$-ClPhS, 36.68), 123 ($CF_3COCCH$, 2.39), 69 ($CF_3$, 16.90). Anal. calcd for $C_{16}H_9Cl_2F_3OS_2$: C 46.96, H 2.22; found C 47.07, H 2.33.

**Bis-(4-chloro-benzyl)-disulfide (11a)** White solid (trace); $^1$H NMR ($CDCl_3$) $\delta$: 7.30 (d, $J$=8.1 Hz, 4H, Ph), 7.16 (d, $J$=8.7 Hz, 4H, Ph), 3.60 (s, 4H, $CH_2$).

**(*Z*)-3-Bromo-4-(4-chloro-benzylsulfanyl)-1,1,1-trifluoro-but-3-en-2-one (11b)** Yellow solid, m.p. 24—26 ℃, yield 17%. $^1$H NMR ($CDCl_3$) $\delta$: 8.34 (s, 1H, CH), 7.54 (d, $^3J_{HH}$=8 Hz, 2H, Ph), 7.27 (d, $^3J_{HH}$=8 Hz, 2H, Ph), 4.18 (s, 2H, $CH_2$). $^{19}$F NMR ($CDCl_3$) $\delta$: −69.01 (s, $CF_3$). $^{13}$C NMR ($CDCl_3$) $\delta$: 174.6 (q, $^2J_{CF}$=27 Hz, C=O), 165.9 (=CH), 131.3 ($C_6H_4$), 130.5 ($C_6H_4$), 129.9 ($C_6H_4$), 128.9 ($C_6H_4$), 122.3 (C=), 116.2 (q, $^1J_{CF}$=232 Hz, $CF_3$), 21.2 ($CH_2$). IR $v$: 1697, 1533, 1491, 1317, 1016 cm$^{-1}$. MS $m/z$ (%): 360 ($M^+$, 6.99), 358 ($M^+$, 6.30), 281 ($M^+$−Br, 1.63), 123 ($CF_3COC=CH^+$, 100), 69 ($CF_3$, 5.37). Anal. calcd for $C_{11}H_7BrClF_3OS$: C 36.74, H 1.96; found C 37.46, H 2.19.

**(*Z*)-3,4-Bis-(4-chloro-benzylsulfanyl)-1,1,1-trifluoro-but-3-en-2-one (11c)** Yellow solid, m.p. 46—48 ℃, yield 75%. $^1$H NMR ($CDCl_3$) $\delta$: 8.16 (s, 1H, CH), 7.36 (d, $^3J_{HH}$=9 Hz, 3H, Ph), 7.21—7.08 (m, 5H, Ph), 4.00 (s, 2H, $CH_2$), 3.90 (s, 2H, $CH_2$). $^{19}$F NMR ($CDCl_3$) $\delta$: −69.47 (s, $CF_3$). IR $v$: 1685, 1513, 1491, 1201, 1128 cm$^{-1}$. MS $m/z$ (%): 311 ($M^+-CH_2PhCl$, 9.45), 243 ($M^+-CH_2PhCl-CF_3$, 0.62), 125 ($CF_3COC=CH$, 100), 69 ($CF_3$, 3.79). Anal. calcd for $C_{18}H_{13}Cl_2F_3OS_2$: C 49.44, H 3.00; found C 49.59, H 3.30.

## References


1 Nenajdenko, V. G.; Sanin, A. V.; Balenkova, E. S. *Molecules* **1997**, *2*, 186.

2 Plenkiewicz, H.; Dmowskiand, W.; Lipínski, M. *J. Fluorine*


  

CHINESE JOURNAL OF CHEMISTRY

*Chem.* **2001**, *111*, 227.
3 Singh, R. P.; Shreeve, J. M. *Tetrahedron* **2000**, *56*, 7613.
4 Uneyama, K. *J. Fluorine Chem.* **1999**, *97*, 11.
5 Zhu, S. Z.; Wang, Y. L.; Peng, W. M.; Song, L. P.; Jin, G. F. *Curr. Org. Chem.* **2002**, *6*, 1057.
6 Gerus, I. I.; Kacharova, L. M.; Vdovenko, S. I. *Synthesis* **2001**, 431.
7 Kacharova, L. M.; Kacharov, A. D.; Gerus, I. I. *J. Fluorine Chem.* **2001**, *111*, 29.
8 Kacharova, L. M.; Gerus, I. I.; Kacharov, A. D. *J. Fluorine Chem.* **2002**, *117*, 193.
9 Schlosser, M.; Volle, J. N.; Leroux, F.; Schenk, K. *Eur. J. Org. Chem.* **2002**, *17*, 2913.
10 Rosnati, V.; Saba, A.; Salimbeni, A.; Vettori, U. *Gazzetta Chimica Iraliata* **1981**, *111*, 249.

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