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Thermal conversion of primary alcohols to disulfides *via* xanthate intermediates: an extension to the Chugaev elimination
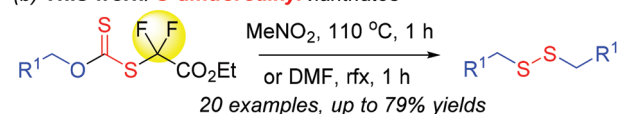
Wei He, Yong Ding, Jianzhuo Tu, Chuqiang Que, Zhanhui Yang* and Jiaxi Xu*

Heating primary *O*-alkyl *S*-(bromodifluoro(ethoxycarbonyl) methyl xanthates yields disulfides. This extends to the Chugaev elimination.

(a) *Chugaev elimination*: *S-methyl* xanthates

(b) *This work*: *S-difluoroalkyl* xanthates
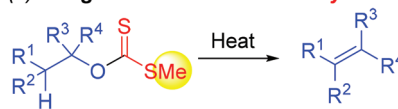
MeNO₂, 110 °C, 1 h
or DMF, rfx, 1 h
20 examples, up to 79% yields

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PAPER

Thermal conversion of primary alcohols to disulfides *via* xanthate intermediates: an extension to the Chugaev elimination†

Wei He, [iD] Yong Ding, Jianzhuo Tu, Chuqiang Que, Zhanhui Yang [iD] * and Jiaxi Xu [iD] *

Primary alcohols are converted into dialkyl disulfides *via* heating *in situ* generated *O*-alkyl *S*-difluoro(ethoxycarbonyl)methyl xanthates from ethyl bromodifluoroacetate and potassium xanthates, prepared from primary alcohols and carbon disulfide in the presence of KOH. The reaction mechanism is suggested as an alkyl C[1,3] shift followed by a radical mechanism. This extends to the Chugaev elimination which yields olefins. The current research provides easy access to dialkyl disulfides from commercially available primary alkanols.
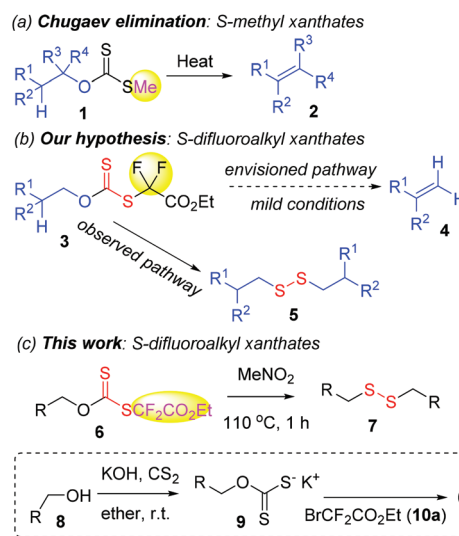
Introduction

In 1899, Chugaev unexpectedly discovered that the pyrolysis of xanthates derived from β-hydrogen-containing alcohols yielded olefins.[1] Subsequent studies showed that the reaction could convert sensitive alcohols with β-hydrogen atoms into the corresponding olefins without the rearrangement of the carbon skeletons under relatively mild conditions (Scheme 1a).[2] Therefore, the Chugaev elimination was intensively studied, and it found impressive utility,[2,3] for example, in natural product syntheses.[4] However, the Chugaev elimination mainly focuses on secondary xanthates (**1**, R^3 = H, $R^4 \neq$ H).[2] For more stable primary xanthates (**1**, $R^3 = R^4$ = H), much higher temperatures (>200 °C) are required, and the yields are unsatisfactory.

The xanthates used in the Chugaev reactions are always *S*-methyl ones. Out of our interest in xanthate chemistry,[5,6] we envisioned that when a suitable *S*-alkyl group was used instead of *S*-methyl, the elimination of primary xanthates might occur at lower temperatures and in higher yields (Scheme 1b). In light of the feasible elimination of CSF_2 molecules from structures with CF_2–S subunits,[7] we first tried the primary *S*-difluoro(ethoxycarbonyl)methyl xanthates **3**. However, the envisioned elimination products **4** were not observed. Unexpectedly, disulfides **5** were obtained. Subsequent studies

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†Electronic supplementary information (ESI) available: Copies of the ^{1}H NMR spectra of reaction mixtures and copies of the ^{1}H and ^{13}C NMR spectra of disulfides **7**. See DOI: 10.1039/c8ob00024g

(a) ***Chugaev elimination****: S-methyl xanthates*

(b) ***Our hypothesis****: S-difluoroalkyl xanthates*

(c) ***This work****: S-difluoroalkyl xanthates*

Scheme 1 The Chugaev olefin formation *versus* the current disulfide formation.

showed that *O*-arylmethyl/alkyl *S*-difluoro(ethoxycarbonyl)methyl xanthates **6** were especially susceptible to disulfide formation (**7**).

Disulfides are of significant importance in biological and synthetic chemistry.[8] Thus, numerous synthetic methods have been developed. Generally, most reported methods rely on the oxidative coupling of thiols to construct the S–S bond,[9–11] and are limited due to the commercial shortage and/or tedious preparation of thiols or their equivalents. Therefore, it is still necessary to develop a facile synthetic method for disulfides from readily available materials.[12] Since xanthates **6** can be

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easily prepared from widely commercially available alkanols **8** (Scheme 1c), our current research provides a novel and convenient method to construct structurally diverse di(alkyl) disulfides.

Results and discussion

The reaction optimization commenced with the reaction of one equivalent of potassium xanthate **9a** with one equivalent of ethyl bromodifluoroacetate (**10a**). No reaction occurred between **9a** and **10a** in acetone at room temperature even though the reaction time was prolonged to 24 h (Table 1, entry 1). More violent conditions such as refluxing at 65 °C for 1 h led to the formation of disulfide **7a** in 10% yield (Table 1, entry 2). Further solvent optimization showed that polar aprotic solvents promoted the formation of disulfide **7a** (Table 1, entries 3–14), and nitromethane was the best choice (Table 1, entry 15). The ratios of **9a** and **10a** were also screened, and 1 : 1 was the most suitable one (see Table S1 in the ESI†). Shortening or prolonging the reaction time did not further improve the yields (Table 1, entries 16–18). The reaction in degassed nitromethane and under a nitrogen atmosphere still afforded comparable yields (Table 1, entry 19).
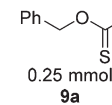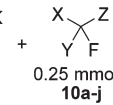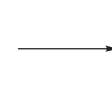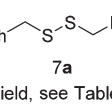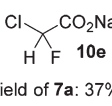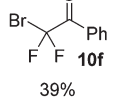
In the model reaction, xanthate **6a** (Scheme 1c, **6**, Ar = Ph) was generated, and the CF_2CO_2Et moiety of **6a** acted as a directing group. We wondered whether the yield of disulfide **7a** could be further improved when other directing groups

Table 1 Reaction condition optimization

Entry	Solvent	Temp. (°C)	Time (h)	Yield[a] (%)
1	Acetone	r.t.	24	n.r.
2	Acetone	65	1	10
3	MeCN	80	1	38
4	DMF	80	1	40
5	DMSO	80	1	18
6	THF	80	1	Trace
7	DCM	60	1	n.r.
8	EA	80	1	Trace
9[b]	EtOH	80	1	n.r.
10[b]	DMF	80	1	14
11	MeNO$_2$	80	1	45
12	MeNO$_2$	80/MW	0.5	45
13	HMPA	110	1	n.r
14	NMP	110	1	48
15	**MeNO$_2$**	**110**	**1**	**60/58[c]**
16	MeNO$_2$	110	0.33	46
17	MeNO$_2$	110	1.5	50
18	MeNO$_2$	110	2	58
19[d]	MeNO$_2$	110	1	54

[a] Yields based on ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as an internal standard. [b] Commercially received solvents without further drying. [c] Isolated yields. [d] In degassed nitromethane and under a nitrogen atmosphere. n.r. = no reaction occurred. MW = microwave irradiation.

Table 2 Screening of different fluoro reagents[a]

[a] Reactions were performed on a 0.25 mmol scale, and the yields were isolated ones. [b] n.r. is the abbreviation of no reaction.

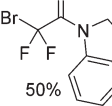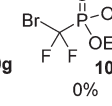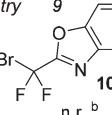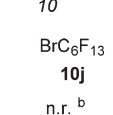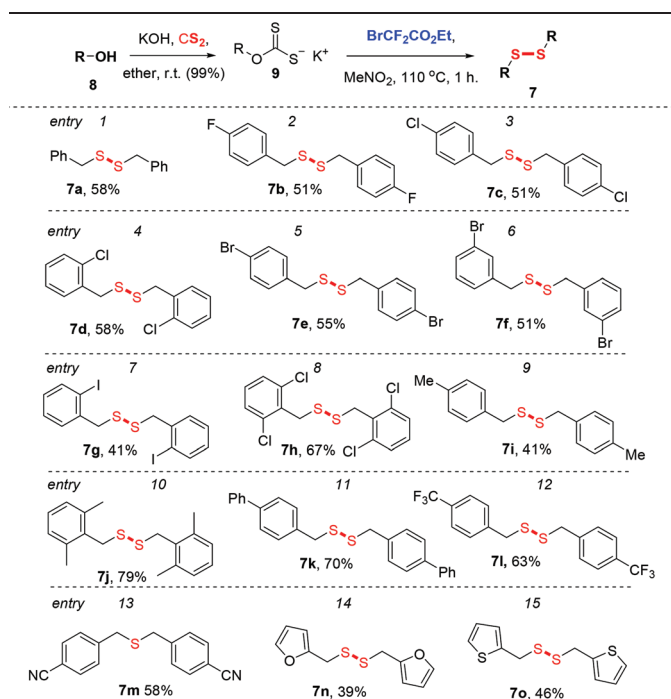were employed. Different fluoro or difluoro reagents **10b–j** were tested, and the results are presented in Table 2. The reactions of potassium xanthate **9a** with ethyl chlorodifluoroacetate (**10b**), bromodifluoroacetic acid (**10c**), ethyl bromofluoroacetate (**10d**), and sodium chlorodifluoroacetate (**10e**) delivered product **7a** in 58%, 0%, trace, and 37% yields, respectively (Table 2, entries 2–5). Bromodifluoroacetophenone (**10f**) and bromodifluoroacetamide (**10g**) succeeded in converting **9a** to disulfide **7a** in 39% and 50% yields, respectively (Table 2, entries 6 and 7), while diethyl bromodifluoromethanephosphonate (**10h**) afforded no product (Table 2, entry 8). 2-Bromodifluoromethylbenzo[*d*]oxazole (**10l**) and perfluorohexyl bromide (**10j**) failed to initiate the disulfide formation (Table 2, entries 9 and 10), possibly because their electrophilicities are too weak to undergo substitutions with **9a**.

Under optimal conditions, different disulfides **7** were synthesized from the corresponding arylmethanols **8**. The results are summarized in Table 3. After treating with carbon disulfide (CS$_2$) and subsequent ethyl bromodifluoroacetate (BrCF$_2$CO$_2$Et) (**10a**), 4-fluorophenylmethanol (**8b**), 4-chlorophenylmethanol (**8c**), 2-chlorophenylmethanol (**8d**), 4-bromophenylmethanol (**8e**), 3-bromophenylmethanol (**8f**), and 2-iodophenylmethanol (**8g**) were readily converted into the corresponding disulfides **7b**, **7c**, **7d**, **7e**, **7f**, and **7g** in 51%, 51%, 58%, 55%, 51%, and 41% yields, respectively (Table 3, entries 2–7). The sterically more congested disulfide **7h** was also synthesized from 2,4-dichlorophenylmethanol (**8h**) in 67% yield (Table 3, entry 8). Notably, all the halogen atoms were well tolerated during the xanthation and disulfidation sequence. Disulfides with electron-rich aryls (**7i** and **7j**) as well as those with electron-deficient aryls (**7k** and **7l**) were prepared in 41–63% yields (Table 3, entries 9–13). Unexpectedly, the reaction of **9m** delivered sulfide **7m** in 58% yield (Table 3, entry 13). Heteroarylmethanols such as (furan-2-yl)methanol (**8n**)

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Table 3 Substrate extension[a,b]

a Potassium xanthates (0.25 mmol) and ethyl bromodifluoroacetate (0.25 mmol) were used. *b* Isolated yields.

and (thiophen-2-yl)methanol (**8o**) were also applicable in such a transformation to afford disulfides **7n** in 50% and **7o** in 63% yields (Table 3, entries 14 and 15).

Potassium xanthates derived from long-chain alkanols, for example, ethanol, phenylethanol, nopol, and citronellol, only afforded low yields of the corresponding disulfides **7** with impurities under optimal conditions (Scheme 2, top). However, by refluxing xanthates **9p** and **9q** in DMF, the corresponding disulfides **7p** and **7q** were formed in 42% and 47% yields, respectively (Scheme 2, bottom). Ethyl bromodifluoroacetate (**10a**) failed to completely convert xanthates **9r,s** into disulfides **7r,s** in DMF solvent. However, bromodifluoroacetamide
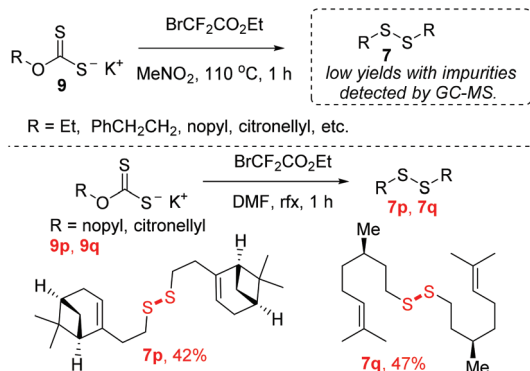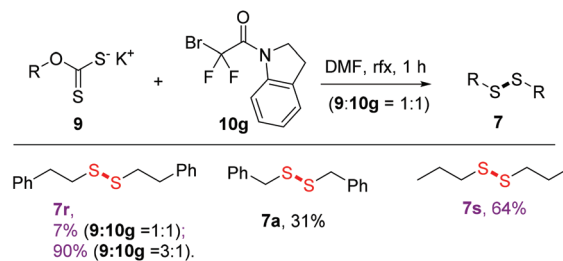

Scheme 2 Reactions of long-chain alkyl xanthates.

Scheme 3 Disulfide formation with bromodifluoroacetamide.

(**10g**) succeeded with disulfides **7r,s** generated in good yields in DMF (Scheme 3).

The generation of products **7** led us to consider a radical mechanism for the disulfide formation. Thus, radical probing experiments were conducted by adding a radical scavenger TEMPO into the reaction of **9a** and **10a** (Scheme 4). The addition of TEMPO resulted in significantly lower yields of **7a**. Thus, a radical mechanism is reasonable.

The reaction in Table 1, entry 19 indicates that oxygen did not play any role in the disulfide formation. Based on the results in Schemes 2 and 4, the mechanism is proposed and presented in Scheme 5. The potassium xanthates **9** directly undergo nucleophilic substitution with ethyl bromodifluoroacetate (**10a**), affording xanthates **6**. Under the reaction conditions, **6** undergo C[1,3]-rearrangement to form **11**. Such a rearrangement has been well demonstrated in the Chugaev elimination.[2a,13] The thermolysis of **11** eliminates CSF_2 and CO_2, and delivers two radicals, that is, ethyl radicals and acyl

Note: [1]*H NMR yield with 1,3,5-trimethoxybenzene as an internal standard.*
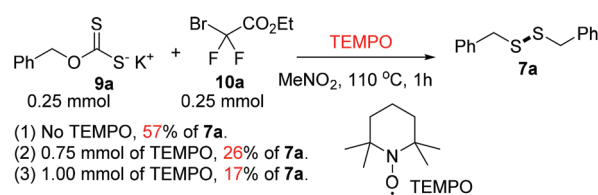
Scheme 4 Radical probing experiments.
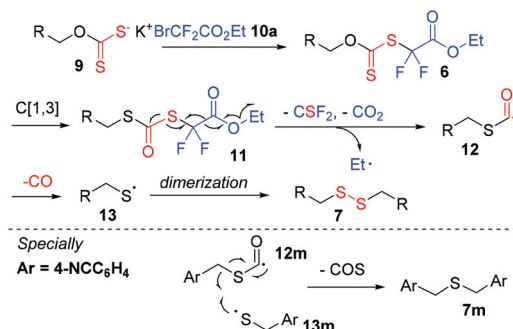
Scheme 5 Proposed mechanism for the formation of disulfides.

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radicals **12**. The elimination of CO from **12** affords alkanethio radicals **13**. Several research groups have demonstrated the elimination of the S=CF$_2$ molecule from structures with CF$_2$S subunits.[7] Although Zard and co-workers proposed an ionic mechanism for the formation of S=CF$_2$,[7d] we believe that our reaction follows a radical mechanism because TEMPO can inhibit the reaction. In our opinion, the driving force of the overall process is the release of the CSF$_2$ molecule. The alkanethio radicals **13** dimerize into the corresponding disulfides **7**.[10a,b,k] However, in a special case (Ar = 4-cyanophenyl), acyl radical **12m** directly reacts with an alkanethio radical **13m**, producing sulfide **7m** with the loss of O=C=S molecules.

The ethyl radical in the proposed mechanism was not trapped by the alkanethio radicals **13**. However, in the reactions of *O*-ethyl and *O*-phenylethyl xanthates **9t** and **9u** with ethyl bromodifluoroacetate (**10a**) in *N*,*N*-dimethylformamide (DMF), the corresponding ethyl propanethioates **14t** and **14u** were isolated in 64% and 87% yields, respectively. These products could be regarded as the experimental evidence for the existence of the ethyl radical, which in these cases were trapped by the corresponding alkoxythiocarbonyl radicals **15t** and **15u**. Interestingly, the difluoro xanthates **6t** and **6u** did not undergo C[1,3]-rearrangement
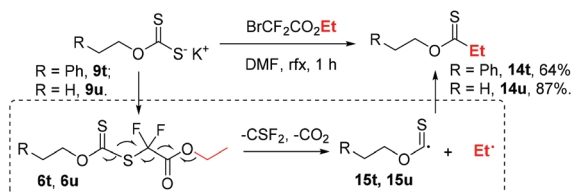
Scheme 6 Trapping the ethyl radical.
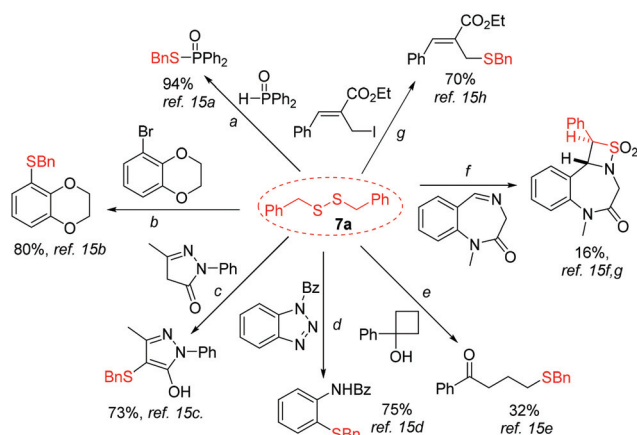
Scheme 7 Selected applications of disulfides from the literature. Conditions: (a) DMSO, 120 °C; (b) *s*-BuLi, THF, −78 °C; (c) DMSO, cat. I$_2$, 80 °C; (d) [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF$_6$), DIPEA, Bz$_2$O, DMSO, r.t., blue LEDs (455 nm); (e) Mn(OAc)$_3$, bpy, IBX, MeCN; (f) (i). NCS, MeCN-H$_2$O, 0–15 °C; (ii) THF, r.t., 24 h. (g) (*t*-BuO)$_2$, MeCN, 80 °C.

Starting from alcohols, different methods to synthesize disulfides have been reported,[12] including sequential thiol formation with Lawesson's reagent and the oxidative coupling of thiols.[14] The application of Lawesson's reagent generates a large amount of solid waste (4-methoxyphenyl)(thioxo)phosphine oxide in the vessels. However, in our mechanistically totally different method, the sulfur donor, carbon disulfide, and the radical initiator, ethyl bromodifluoroacetate, are cheaper chemicals. They are also traceless in the vessels, that is, the byproducts are either volatile gases or well soluble in water, making the purification more convenient.

The synthesized disulfides **7** are very useful reagents in organic synthesis. For example, various reports have demonstrated that disulfide **7a** can act as a sulfenyl or sulfonyl donor to undergo different kinds of reactions, affording structurally diverse and synthetically important products (Schemes and 7).[15]

Conclusion

By simply treating primary alkanols with carbon disulfide in the presence of potassium hydroxide at room temperature and then reacting the resulting potassium xanthates with ethyl bromodifluoroacetate at high temperatures, a series of disulfides are obtained in moderate yields. The proposed mechanism involves a radical process preceded by C[1,3]-rearrangement and the subsequent elimination of CO, CO$_2$, and S=CF$_2$ molecules. The current study provides easy access to synthetically important disulfides from readily available or naturally occurring primary alkanols. In the current disulfide formation, the primary *O*-alkyl *S*-difluoro(ethoxycarbonyl)methyl xanthates are key intermediates, while in the Chugaev elimination, secondary *O*-alkyl *S*-methyl xanthates are preferred substrates. The present study is extensive yet orthogonal to the Chugaev elimination, and provides a new observation in xanthate chemistry.

Experimental

General information

All the solvents were dried and freshly distilled under vacuum prior to use. Melting points were obtained on a Yanaco MP-500 melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer in CDCl$_3$ with TMS as an internal standard and the chemical shifts (δ) are reported in parts per million (ppm). The IR spectra (KBr pellets, ν [cm^{-1}]) were recorded on a Nicolet 370 FTIR spectrometer. HRMS measurements were carried out on an Agilent LC/MS TOF mass spectrometer. TLC analyses were performed on silica gel plates, and the plates were visualized with UV light. PE is the abbreviation for petroleum ether (60–90 °C), and EA for ethyl acetate. The spectra of the known products are identical with those reported.

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General procedure for the synthesis of potassium xanthates (9a–t)

Q5 Pure potassium xanthates **9** were prepared following a reported procedure.[16] To a 100 mL flask were sequentially added alcohol **8** (10 mmol), potassium hydroxide (560 mg, 10 mmol) and ether (25 mL). Carbon disulfide (0.75 mL, 12 mmol) was dissolved in ether (25 mL), and the solution was slowly added into the 100 mL flask. The resulting solution was stirred at room temperature for 12 h. Vacuum filtration, washing with ether (10 mL), and drying afforded the crude potassium xanthate. The crude potassium xanthate was recrystallized from acetone and petroleum ether, and pure potassium xanthates **9** were obtained in excellent yields. The synthesized potassium xanthates are known compounds, and their NMR spectra are identical with those reported.

General procedure for the synthesis of disulfides 7a–t

To a 15 mL heavy-wall reaction tube were sequentially added potassium xanthate **9** (0.25 mmol), ethyl bromodifluoroacetate (**10a**) (55.3 mg, 0.25 mmol), and dry $MeNO_2$ (1.0 mL). The tube was sealed without inert protection and immersed in a pre-heated oil-bath at 110 °C, and heated for 1 h. Upon cooling to room temperature, the reaction mixture was diluted with ethyl acetate (5 mL) and washed with brine (5 mL × 3). The organic phase was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was subjected to chromatography on silica gel with PE and EA as eluents to afford pure disulfides **7**.

General procedure for screening different fluoro or difluoro reagents

To a 15 mL heavy-wall reaction tube were sequentially added potassium *S*-benzyl xanthate (**9a**) (55 mg, 0.25 mmol), fluoro or difluoro reagents **10a–j** (0.25 mmol), and dry $MeNO_2$ (1.0 mL). A similar experimental procedure to the above afforded disulfide **7a** in different isolated yields (see Table 2).

1,2-Dibenzyldisulfane (7a).[10a] Yellowish green oil. Yield: 18 mg, 58%. R_f = 0.5 (PE : EA = 50 : 1, v/v). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.35–7.20 (m, 10H), 3.59 (s, 4H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 137.5, 129.5, 128.6, 127.5, 43.4.

1,2-Bis(4-fluorobenzyl)disulfane (7b).[11d] Orange oil. Yield: 18 mg, 51%. R_f = 0.5 (PE : EA = 50 : 1, v/v). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.24–7.14 (m, 4H), 7.06–6.92 (m, 4H), 3.59 (s, 4H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 162.4 (d, *J* = 246.4 Hz), 133.2 (d, *J* = 3.3 Hz), 131.0 (d, *J* = 8.1 Hz), 115.54 (d, *J* = 21.5 Hz), 42.54.

1,2-Bis(4-chlorobenzyl)disulfane (7c).[10a] Yellowish green oil. Yield: 20 mg, 51%. R_f = 0.6 (PE : EA = 50 : 1, v/v). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.30 (d, *J* = 8.4 Hz, 4H), 7.16 (d, *J* = 8.4 Hz, 4H), 3.58 (s, 4H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 135.9, 133.5, 130.8, 128.8, 42.6.

1,2-Bis(2-chlorobenzyl)disulfane (7d).[11e] Colorless crystals, m.p. 93–94 °C. Yield: 23 mg, 58%. R_f = 0.5 (PE : EA = 50 : 1, v/v). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.32–7.27 (m, 2H), 7.22–7.12 (m, 6H), 3.72 (s, 4H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 135.1, 134.3, 131.7, 129.9, 129.1, 126.8, 41.2.

1,2-Bis(4-bromobenzyl)disulfane (7e).[11b] Colorless crystals, m.p. 73–75 °C. Yield: 28 mg, 55%. R_f = 0.5 (PE : EA = 50 : 1, v/v). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.45 (d, *J* = 8.3 Hz, 4H), 7.09 (d, *J* = 8.3 Hz, 4H), 3.56 (s, 4H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 136.5, 131.8, 131.2, 121.6, 42.7.

1,2-Bis(3-bromobenzyl)disulfane (7f).[11e] Orange oil. Yield: 26 mg, 51%. R_f = 0.5 (PE : EA = 50 : 1, v/v). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.45–7.35 (m, 4H), 7.24–7.13 (m, 4H), 3.55 (s, 4H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 139.7, 132.5, 130.7, 130.2, 128.1, 122.6, 42.7. IR (film, KBr) ν cm^{-1} 2920, 1774, 1763, 1752, 1736, 1719, 1697, 1676, 1670, 1664, 1618, 1592, 1568, 1523, 1508, 1499, 1473, 1426, 1384, 1198, 1180, 1070, 997, 885, 846, 784, 721, 698, 679, 669. ESI-HRMS [M + H]$^+$ calcd for $C_{14}H_{13}Br_2S_2^+$ *m/z* 402.8820, found 402.8815.

1,2-Bis(2-iodobenzyl)disulfane (7g).[12a] Colorless crystals, m.p. 94–96 °C. Yield: 25 mg, 41%. R_f = 0.5 (PE : EA = 50 : 1, v/v). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.84 (d, *J* = 7.8, 2H), 7.34–7.26 (m, 4H), 7.00–6.93 (m, 2H), 3.81 (s, 4H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 139.9, 131.1, 129.3, 128.4, 100.8, 48.6. IR (film, KBr) ν cm^{-1} 2921, 2850, 1770, 1584, 1562, 1462, 1435, 1412, 1374, 1290, 1225, 1160, 1126, 1045, 1012, 943, 856, 758, 723, 646. ESI-HRMS [M + H]$^+$ calcd for $C_{14}H_{13}I_2S_2^+$ *m/z* 498.8543, found 498.8530.

1,2-Bis(2,6-dichlorobenzyl)disulfane (7h). Colorless crystals, m.p. 105–107 °C. Yield: 32 mg, 67%. R_f = 0.5 (PE : EA = 50 : 1, v/v). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.31 (d, *J* = 8.0 Hz, 4H), 7.14 (dd, *J* = 8.0, 8.0 Hz, 2H), 4.28 (s, 4H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 136.0, 133.8, 129.1, 128.5, 39.6. IR (film, KBr) ν cm^{-1} 2926, 2851, 1735, 1580, 1561, 1436, 1215, 1200, 1180, 1122, 1088, 875, 777, 761, 737, 677. ESI-HRMS [M + H]$^+$ calcd for $C_{14}H_{11}Cl_4S_2^+$ *m/z* 382.9051, found 382.9046.

1,2-Bis(4-methylbenzyl)disulfane (7i).[10a] Yellowish green oil. Yield: 14 mg, 41%. R_f = 0.5 (PE : EA = 50 : 1, v/v). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.14 (s, 8H), 3.61 (s, 4H), 2.34 (s, 6H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 137.3, 134.4, 129.4, 129.3, 43.2, 21.3.

1,2-Bis(2,6-dimethylbenzyl)disulfane (7j). Orange oil. Yield: 30 mg, 79%. R_f = 0.5 (PE : EA = 50 : 1, v/v). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.19–6.54 (m, 6H), 3.59 (s, 4H), 2.32 (s, 12H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 138.1, 137.2, 129.2, 127.4, 43.4, 21.4. IR (film, KBr) ν cm^{-1} 3015, 2917, 2860, 1774, 1735, 1701, 1685, 1676, 1648, 1637, 1571, 1560, 1508, 1465, 1376, 1300, 1217, 1165, 1123, 1050, 954, 848, 734, 708, 686, 617. ESI-HRMS [M + H]$^+$ calcd for $C_{18}H_{23}S_2^+$ *m/z* 303.1236, found 303.1238.

1,2-Bis([1,1′-biphenyl]-4-ylmethyl)disulfane (7k). Colorless crystals, m.p. 184–185 °C. Yield: 35 mg, 70%. R_f = 0.4 (PE : EA = 50 : 1, v/v). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.62–7.53 (m, 8H), 7.47–7.41 (m, 4H), 7.38–7.30 (m, 6H), 3.71 (s, 4H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 140.8, 140.5, 136.5, 130.0, 128.9, 127.5, 127.4, 127.2, 43.2. IR (film, KBr) ν cm^{-1} 3054, 2986, 2931, 1606, 1562, 1487, 1450, 1405, 1265, 1129, 959, 895,

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842, 767, 735, 704. ESI-HRMS $[M + H]^+$ calcd for $C_{26}H_{23}S_2^+$ m/z 399.1236, found 399.1231.

1,2-Bis(4-trifluoromethylbenzyl)disulfane (7l). Colorless crystals, m.p. 144–146 °C. Yield: 30 mg, 63%. R_f = 0.5 (PE : EA = 50 : 1, v/v). ^{1}H NMR (400 MHz, chloroform-d) δ 7.59 (d, J = 8.0, 4H), 7.33 (d, J = 8.0, 4H), 3.65 (s, 4H). ^{13}C NMR (101 MHz, chloroform-d) δ 141.5 (q, J = 1.2 Hz), 129.8, 128.3, 125.6 (q, J = 3.8 Hz), 124.2 (q, J = 271.7 Hz), 42.7. IR (film, KBr) ν cm^{-1} 3066, 2924, 2228, 1736, 1720, 1686, 1648, 1638, 1606, 1554, 1501, 1459, 1414, 1384, 1292, 1231, 1196, 1179, 1104, 1061, 958, 845, 826, 783, 669, 653, 553. ESI-HRMS $[M + H]^+$ calcd for $C_{16}H_{13}F_6S_2^+$ m/z 383.0357, found 383.0347.

4,4′-(Thiobis(methylene))dibenzonitrile (7m).[17] Yellowish green oil. Yield: 19 mg, 58%. R_f = 0.5 (PE : EA = 10 : 1, v/v). ^{1}H NMR (400 MHz, chloroform-d) δ 7.62 (d, J = 8.2 Hz, 4H), 7.32 (d, J = 8.2 Hz, 4H), 3.63 (s, 4H). ^{13}C NMR (101 MHz, chloroform-d) δ 142.7, 132.4, 130.0, 118.6, 111.5, 42.6.

1,2-Bis(furan-2-ylmethyl)disulfane (7n).[10g] Yellowish green oil. Yield: 11 mg, 39%. R_f = 0.3 (PE : EA = 50 : 1, v/v). ^{1}H NMR (400 MHz, chloroform-d) δ 7.41–7.38 (m, 2H), 6.35–6.32 (m, 2H), 6.23 (d, J = 3.2 Hz, 2H), 3.69 (s, 4H). ^{13}C NMR (101 MHz, chloroform-d) δ 150.3, 142.6, 110.9, 109.1, 35.8.

1,2-Bis(thiophen-2-ylmethyl)disulfane (7o).[18] Yellowish green oil. Yield: 15 mg, 46%. R_f = 0.3 (PE : EA = 50 : 1, v/v). ^{1}H NMR (400 MHz, chloroform-d) δ 7.20–7.15 (m, 2H), 6.90–6.85 (m, 4H), 3.80 (s, 4H). ^{13}C NMR (101 MHz, chloroform-d) δ 139.9, 127.4, 127.1, 125.8, 37.8. IR (film, KBr) ν cm^{-1} 3105, 2923, 2851, 1722, 1642, 1434, 1402, 1236, 1181, 1115, 1075, 1037, 882, 845, 746, 700. ESI-HRMS $[M + H]^+$ calcd for $C_{10}H_{11}S_4^+$ m/z 258.9738, found 258.9743.

1,2-Bis(2-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl)disulfane (7p). Yellowish green oil. Yield: 19 mg, 42%. R_f = 0.8 (PE : EA = 100 : 1, v/v). ^{1}H NMR (400 MHz, chloroform-d) δ 5.29–5.25 (m, 2H), 2.73–2.66 (m, 4H), 2.40–2.14 (m, 10H), 2.11–2.05 (m, 2H), 2.04–1.97 (m, 2H), 1.27 (s, 6H), 1.16 (d, J = 8.4 Hz, 2H), 0.83 (s, 6H). ^{13}C NMR (101 MHz, chloroform-d) δ 146.3, 117.8, 45.8, 40.9, 38.2, 37.2, 36.9, 31.8, 31.4, 26.4, 21.4. IR (film, KBr) ν cm^{-1} 3026, 2984, 2915, 2831, 1654, 1585, 1467, 1432, 1381, 1364, 1346, 1330, 1301, 1265, 1205, 1181, 1166, 1134, 1114, 1098, 1081, 1044, 956, 929, 886, 842, 791, 740, 706, 642, 622. ESI-HRMS $[M + H]^+$ calcd for $C_{22}H_{35}S_2^+$ m/z 363.2175, found 363.2182.

1,2-Bis((R)-3,7-dimethyloct-6-en-1-yl)disulfane (7q). Yellowish green oil. Yield: 20 mg, 47%. R_f = 0.8 (PE : EA = 100 : 1, v/v). ^{1}H NMR (400 MHz, chloroform-d) δ 5.09 (t, J = 7.2 Hz, 2H), 2.77–2.62 (m, 4H), 2.06–1.90 (m, 4H), 1.74–1.70 (m, 2H), 1.68 (s, 6H), 1.61 (s, 6H), 1.58–1.44 (m, 4H), 1.40–1.29 (m, 2H), 1.23–1.12 (m, 2H), 0.90 (d, J = 6.4 Hz, 6H). ^{13}C NMR (101 MHz, chloroform-d) δ 131.4, 124.8, 37.1, 37.0, 36.6, 31.8, 25.9, 25.6, 19.4, 17.8. IR (film, KBr) ν cm^{-1} 2961, 2915, 2852, 2727, 1673, 1451, 1377, 1350, 1266, 1218, 1181, 1108, 1082, 984, 827, 741, 706. ESI-HRMS $[M + H]^+$ calcd for $C_{20}H_{39}S_2^+$ m/z 343.2488, found 343.2482.

1,2-Diphenethyldisulfane (7r).[10f] Yellowish green oil. Yield: 31 mg, 90%. R_f = 0.6 (PE : EA = 50 : 1, v/v). ^{1}H NMR (400 MHz, chloroform-d) δ 7.37–7.30 (m, 4H), 7.29–7.21 (m, 6H),

3.07–3.01 (m, 4H), 3.00–2.94 (m, 4H). ^{13}C NMR (101 MHz, chloroform-d) δ 140.1, 128.7, 128.6, 126.5, 40.3, 35.8.

1,2-Dipropyldisulfane (7s).[10c] Yellowish green oil. Yield: 12 mg, 64%. R_f = 0.8 (PE : EA = 100 : 1, v/v). ^{1}H NMR (400 MHz, chloroform-d) δ 2.67 (t, J = 7.2, 4H), 1.71 (qt, J = 7.4, 7.2 Hz, 4H), 0.99 (t, J = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, chloroform-d) δ 41.3, 22.6, 13.3.

General procedure for the radical probing experiments

To a 15 mL heavy-wall reaction tube were sequentially added potassium S-benzyl xanthate (9a) (55 mg, 0.25 mmol), TEMPO (0.75 mmol, 117 mg; or 1.00 mmol, 156 mg), ethyl bromodifluoroacetate (10a) (55.3 mg, 0.25 mmol), and dry MeNO$_2$ (1.0 mL). The tube was sealed and immersed in a pre-heated oil-bath at 110 °C, and heated for 1 h. Upon cooling to room temperature, mesitylene (0.125 mmol, 21 mg) was added. A similar workup procedure afforded a residue, which was subjected to ^{1}H NMR spectroscopy to determine the yields of 7a.

General procedure for the preparation of propanethioates 14

To a 15 mL heavy-wall reaction tube were sequentially added potassium xanthate 9t or 9u (0.25 mmol), ethyl bromodifluoroacetate (10a) (55.3 mg, 0.25 mmol), and dry DMF (1.0 mL). The tube was sealed without inert protection and immersed in a preheated oil-bath, and refluxed for 1 h. A similar workup afforded propanethioates 14.

O-(2-Phenylethyl)propanethioate (14t). Yellowish oil. Yield: 31 mg, 64%. R_f = 0.5 (PE : EA = 50 : 1, v/v). ^{1}H NMR (400 MHz, chloroform-d) δ = 7.35–7.28 (m, 2H), 7.27–7.21 (m, 3H), 4.79 (t, J = 7.1 Hz, 2H), 3.11 (t, J = 7.1 Hz, 2H), 3.08 (q, J = 7.4 Hz, 2H), 1.30 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, chloroform-d) δ = 215.0, 137.4, 129.1, 128.7, 126.9, 73.8, 34.8, 30.2, 13.6.

O-Ethyl propanethioate (14u).[19] Yellowish oil. Yield: 26 mg, 87%. R_f = 0.8 (PE : EA = 100 : 1, v/v) ^{1}H NMR (400 MHz, chloroform-d) δ = 4.65 (q, J = 7.1 Hz, 2H), 3.12 (q, J = 7.4 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H), 1.34 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, chloroform-d) δ = 215.2, 69.8, 30.2, 13.9, 13.6.

Conflicts of interest

There are no conflicts to declare.

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