

Note

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Air Oxidative Radical Oxysulfurization of Alkynes

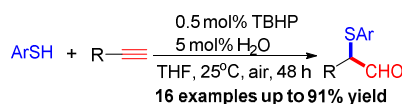
Leading to α -Thioaldehydes

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ABSTRACT: Air oxidative radical oxysulfurization of alkynes initiated by 0.5 mol % *tert*-butyl hydroperoxide with arylthiols is described. The reaction proceeded at room temperature in the presence of 5% mol water to afford selective α -thioaldehydes.

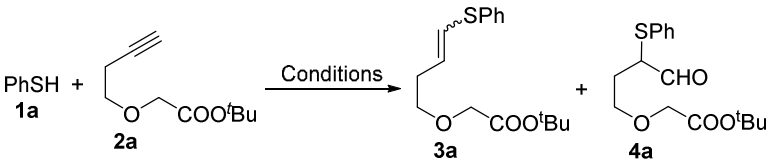
Recently, difunctionalization of alkenes and alkynes has become a powerful tool in synthetic organic chemistry.¹ The radical difunctionalization having advantages such as mild reaction conditions, high selectivity and convenient workup has made it more interesting.² Thiol–oxygen co-oxidation reactions (TOCO) provide attractive routes to functionalized valuable products with studies focusing mainly on olefins,³ only a few have been on alkynes.^{3a, 4} The first example of TOCO of alkynes appeared in the early 1960s when Griesbaum *et al.*^{4b} reported the reaction of thiophenol with phenylacetylene in an oxygen atmosphere to give the phenylglyoxal hemithioacetal. In 1993, the Isoe group found that the electroinitiated oxygenation of alkynes in the presence of thiophenol gave α -(phenylthio) carbonyl compounds.^{4c} Also, Renaud *et al.* reported that the reaction of terminal alkynes with thiophenol in the presence of AIBN afforded a

series of five-membered cyclic compounds.^{4e-g} In continuation of our efforts on difunctionalization reactions,⁵ herein, we report a new protocol, TBHP (*tert*-butyl hydroperoxide)-initiated water-catalyzed difunctionalization of terminal alkynes with thiophenol in air at room temperature to give α -thioaldehydes.

We began our studies by exploring the reaction of thiophenol (**1a**) with *tert*-butyl 2-(but-3-yn-1-yloxy) acetate (**2a**) in DMF at 25°C, however, alkenyl sulfide **3a** was obtained as the sole product (Table 1, entry 1). After screening of solvents, we were pleased to observe a mixture of products **3a** and **4a** in *tert*-butanol and ethereal solvents such as 1,4-dioxane, tetrahydrofuran (THF), and 1,2-dimethoxyethane (1,2-DME) (Table 1, entries 5-8). Interestingly, the addition of a catalytic amount of water into the reaction in THF slightly increased the yield of **4a** (Table 1, entry 9). More interesting was the fact that no formation of **4a** was observed in anhydrous THF (Table 1, entry 10). To improve the selectivity and yield of reaction, 0.5% mol of TBHP was added to the reaction and this led to a massive increase in the yield of **4a** to 75% (Table 1, entry 11). After screening the reaction time, temperature, amount of water and TBHP (Table 1, entries 11-20), the optimum reaction conditions were determined to be: thiophenol (**1a**, 2.0 equiv) and *tert*-butyl 2-(but-3-yn-1-yloxy) acetate (**2a**, 1 equiv) in THF at 25°C for 48 h in the presence of 0.5% mol TBHP and 5% mol H₂O to afford the selective α -thioaldehyde **4a** in good yield (Table 1, entry 12).

Under these conditions, reactions of a variety of terminal alkynes **2a-i** with thiophenol (**1a**) were carried out. The alkynes *tert*-butyl 2-(but-3-yn-1-yloxy) acetate (**2a**) and *n*-hexyne (**2b**) gave exclusively α -thioaldehydes (**4a** and **4b**) in excellent yields (Table 2, entries 1 and 2). However, the reaction of other chain terminal alkynes **2c-2g** gave majorly α -thioaldehydes **4c-4g** in moderate to good yields accompanied by alkenylsulfides **3c-3g** (Table 2, entries 3-7). In

Table 1. Optimization of the Reaction Conditions



Entry	Solvent	Ratio (1a:2a)	Temp (°C)	Time (h)	Yield(%) (3a)/(Z and E) ^a	Yield(%) (4a) ^a
1	DMF	2:1	25	24	37	0
2	Toluene	2:1	25	24	2.2	0
3	CH ₂ Cl ₂	2:1	25	24	29	0
4	CH ₃ CN	2:1	25	24	0	0
5	<i>t</i> BuOH	2:1	25	24	11	25
6	1,4-Dioxane	2:1	25	24	17	28
7	THF	2:1	25	24	15	29
8	1,2-DME	2:1	25	24	14	21
9 ^b	THF	2:1	25	24	20	38
10 ^c	THF	2:1	25	24	0	0
11 ^{b,d,e}	THF	2:1	25	24	25	75
12 ^{b,d,e}	THF	2:1	25	48	2	98
13 ^{b,d,e}	THF	2:1	25	72	9	90
14 ^{b,e}	THF	2:1	0	48	0	0
15 ^{b,e}	THF	2:1	13	48	27	0
16 ^{b,e}	THF	2:1	25	48	0	77
17 ^{b,e}	THF	2:1	40	48	70	25
18 ^{b,e}	THF	2:1	60	48	86	1.4
19 ^{d,e,f}	THF	2:1	25	48	12	70
20 ^{b,d,g}	THF	2:1	25	48	34	0

^aIsolated yield. ^bAddition of 5% mol H₂O (1 μL). ^cAnhydrous THF. ^dGas chromatography yield. ^eAddition of 0.5% mol TBHP (1 μL). ^fAddition of 4 μL H₂O. ^gAddition of 5% mol TBHP (10 μL).

reactions involving the sterically hindered terminal alkynes such as *t*-butylacetylene (**2h**) and cyclopropyl acetylene (**2i**), low yields of α-thioaldehydes **4h-4i** were observed as the formation of alkenylsulfides **3h-3i** tends to predominate (Table 2, entries 8 and 9). The low yields of α-thioaldehydes underline the effect of bulky group attached to the C≡C triple bond. It is worth noting that the reaction of phenylacetylene (**2j**) with **1a** led to formation of complicated mixtures (Table 2, entry 10). This is probably due to the high reactivity of the conjugated alkenyl radical

generated from the reaction of thiyl radical with **2j**. Also, when alkyl group R = *n*-butyl (**2b**) was replaced with phenylethyl (**2k**) and phenylpropyl (**2l**), their reactions with **1a** produced **4k** and **4l** in low yields, 12% and 44% respectively (Table 2, entries 11 and 12), it was observed that most of starting substrate **2k** and **2l** remained unreacted at the end of reaction. From the results obtained, we reasoned that the yield of α -thioaldehydes depended mainly on the structure of the terminal alkynes.

Afterwards, the reactions of terminal alkynes having oxygen or nitrogen-containing substituent groups were investigated. Alkynes bearing an ester group at α - and β -positions all reacted well with **1a** to give exclusively alkenylsulfides **3m-3n** (Table 2, entries 13 and 14). Reactions involving 5-hydroxypentyne (**2o**) and 4-hydroxybutyne (**2p**) also gave alkenylsulfides **3o** and **3p** as the sole products in 77% and 17% yield respectively (Table 2, entries 15 and 16). Interestingly, the presence of the oxygen atom and COO^tBu groups in *tert*-butyl 2-(but-3-yn-1-yloxy) acetate (**2a**) led to formation of α -thioaldehyde, although the reason for this remained unknown. Furthermore, no reactions were observed with α -aminoalkynes (**2q-2s**) (Table 2). We reasoned that the amino group on the α -carbon could probably be impeding the radical reaction.

To know the effect of substitution on phenyl ring, a series of arylthiols containing electron-donating and electron-withdrawing groups were employed. In the reaction of 4-methyl benzenethiol (**1b**) with terminal alkyne **2a**, α -thioaldehyde (**4ba**) was obtained as the major product in 59% yield and alkenylsulfide (**3ba**) as minor product in 32% yield (Table 3, entry 1). On the contrary, the reaction of 2-methylbenzenethiol (**1c**) gave the alkenylsulfide (**3ca**) as major product in 70% yield and α -thioaldehyde (**4ca**) as minor product in 23% yield (Table 3, entry 2). In addition, the reaction of 2,6-dimethylbenzenethiol (**1d**) with **2a** gave alkenylsulfide (**3da**) as sole product in 84% yield (Table 3, entry 3). These results show that hindered arylthiyl radicals

Table 2. Reactions of Thiophenol (1a) with Terminal Alkynes 2a-s^a

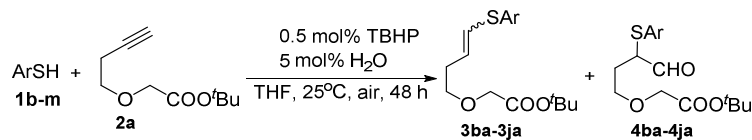
$\text{PhSH (1a)} + \text{R-C}\equiv\text{C- (2a-s)} \xrightarrow[\text{THF, 25}^\circ\text{C, air, 48 h}]{0.5 \text{ mol\% TBHP, 5 mol\% H}_2\text{O}} \text{R-C}\equiv\text{C-SPh (3a-p)} + \text{R-C(CHO)(SPh) (4a-l)}$				
Entry	2	R	Yield(%) ^b	
			3	4
1	2a		3a 0(2) ^c	4a 77(98) ^c
2	2b	<i>n</i> -butyl	3b 0(2) ^c	4b 78(98) ^c
3	2c	<i>n</i> -propyl	3c ^d	4c 64
4	2d	<i>n</i> -pentyl	3d 18	4d 71
5	2e	<i>n</i> -hexyl	3e ^d	4e 68
6	2f	<i>n</i> -heptyl	3f 28	4f 64
7	2g	<i>n</i> -octyl	3g 28	4g 60
8	2h	<i>t</i> -butyl	3h 46	4h 51
9	2i	cyclopropyl	3i ^d	4i 52
10	2j	Ph	complicated mixtures	
11	2k	C ₆ H ₅ (CH ₂) ₂	3k 0	4k 12 ^e
12	2l	C ₆ H ₅ (CH ₂) ₃	3l 0	4l 44 ^f
13	2m			3m 75
14	2n			3n 70
15	2o			3o 77
16	2p			3p 17
	2q	2r	2s	N.R. ^g

^aReaction conditions: thiophenol (1a, 2.0 equiv), *tert*-butyl 2-(but-3-yn-1-yloxy)acetate (2a, 1 equiv) in THF at 25°C for 48 h in the presence of 0.5% mol TBHP and 5% mol H₂O. ^bIsolated yield. ^cAnalyzed by gas chromatography. ^dMixture of alkenylsulfide and diphenyldisulfide, they can't be separated each other.

^eMost of starting material 2k did not react with 1a. ^fSome of starting material 2l did not react with 1a. ^gN.R. represents no reaction.

favor formation of the less hindered alkenylsulfides **3**. 4-Methoxybenzenethiol (**1e**) and 2-aminobenzenethiol (**1f**) did not give desired compounds due to self-coupling of the electron-rich arylthiyl radicals generated from **1e** and **1f** leading to diaryldisulfides (Table 3, entries 4 and 5). Arylthiols bearing F and Cl groups reacted with **2a** to form α -thioaldehydes (**4ga**, **4ha**, **4ia** and **4ja**) as major product in moderate to excellent yields (Table 3, entries 6-9). No reactions were observed with 4-nitrobenzenethiol **1k**, pyridylthiol **1l** and furylthiol **1m** (Table 3, entries 10-12). This is because the corresponding thiyl radicals could not be formed under the reaction condition.

Table 3. Reactions of Arylthiols **1 with Terminal Alkyne **2a**^a**

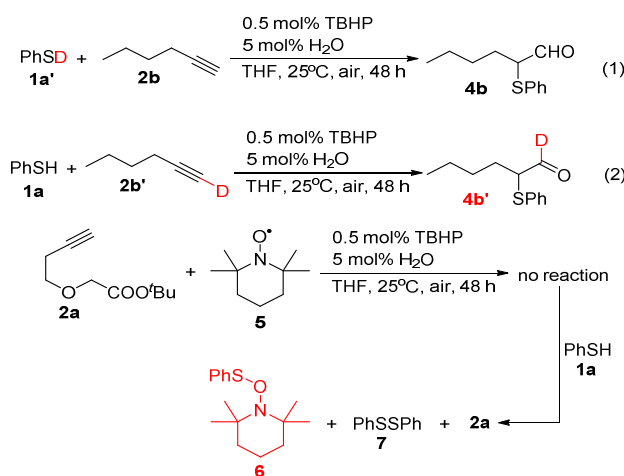


Entry	ArSH (1)	Products 3 , 4 and Yield(%) ^b	
1	4-CH ₃ C ₆ H ₄ SH (1b)	3ba 32	4ba 59
2	2-CH ₃ C ₆ H ₄ SH (1c)	3ca 70	4ca 23
3	2,6-(CH ₃) ₂ C ₆ H ₃ SH (1d)	3da 84	4da 0
4	4-CH ₃ OC ₆ H ₄ SH (1e)	N.R. ^c	
5	2-NH ₂ C ₆ H ₄ SH (1f)	N.R. ^c	
6	2-FC ₆ H ₄ SH (1g)	3ga 18	4ga 59
7	4-FC ₆ H ₄ SH (1h)	3ha <5	4ha 91
8	2-ClC ₆ H ₄ SH (1i)	3ia 15	4ia 61
9	3-ClC ₆ H ₄ SH (1j)	3ja 24	4ja 68
10	4-NO ₂ C ₆ H ₄ SH (1k)	N.R. ^c	
11		N.R. ^c	
12		N.R. ^c	

^aReaction conditions: arylthiol (**1**, 2.0 equiv), *tert*-butyl 2-(but-3-yn-1-yloxy)acetate (**2a**, 1 equiv) in THF at 25°C for 48 h in the presence of 0.5% mol TBHP and 5% mol H₂O. ^bIsolated yield. ^cN.R. indicates that the alkyne is not consumed and the desired α -thioaldehyde and/or alkenylsulfide were not isolated (0% yield).

As mentioned earlier, the reaction of *tert*-butyl 2-(but-3-yn-1-yloxy) acetate (**2a**) with thiophenol (**1a**) did not take place in anhydrous THF. Further experiment also showed that the same reaction did not take place when conducted in a nitrogen atmosphere, thus indicating that oxygen is necessary for reaction to occur. To understand how the reaction proceeds, a mechanistic study was done. An experiment using deuterium-labeled thiophenol (**1a'**) with *n*-hexyne (**2b**) was carried out and the unlabeled α -thioaldehyde (**4b**) was isolated as the product (Scheme 1, eq 1). However, the reaction of thiophenol (**1a**) with deuterium-labeled *n*-hexyne (**2b'**) gave the deuterated α -thioaldehyde (**4b'**) (Scheme 1, eq 2) thus indicating that the aldehydic proton originated from *n*-hexyne (**2b**). To know if the reaction proceeds via a radical pathway, the reaction of *tert*-butyl 2-(but-3-yn-1-yloxy) acetate (**2a**) with thiophenol (**1a**) was carried out in the presence of the radical inhibitor, TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) (**5**), and only 2,2,6,6-tetramethyl-1-((phenylthio)oxy)piperidine (**6**) and diphenyl disulfide (**7**) were isolated, with no detectable sign of α -thioaldehyde (**4a**). Further experiment showed that TEMPO did not react with **2a**.

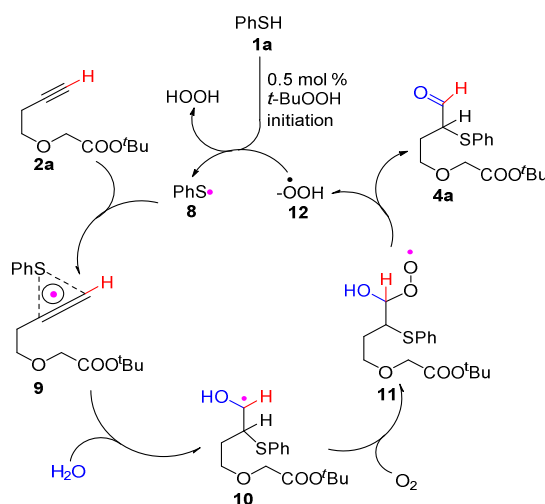
Scheme 1. Mechanistic Study



On the basis of above findings, a plausible mechanism is proposed in Scheme 2. The

thiophenyl radical **8** initiated by TBHP coordinates with terminal alkyne **2a** to form flexible radical **9**, followed by addition of H₂O to give radical **10** which then reacts with O₂ (air) to give peroxy radical **11**, this decomposes to form α -thioaldehyde **4a** and hydroperoxy radical **12**, which reacts with thiophenol (**1a**) to liberate thiophenyl radical **8**, for further propagation of the reaction cycle.

Scheme 2. Proposed Mechanism for the Reaction of Terminal Alkyne **2a with Thiophenol (**1a**)**



In conclusion, a new protocol for the oxysulfurization of alkynes *via* the reaction of arylthiols with alkynes has been developed. The reaction was initiated by 0.5 mol % TBHP at room temperature in the presence of 5 mol % water, with air (O₂) as sole oxidant to afford the selective α -thioaldehydes in moderate to good yields. This method is straightforward, requires no other oxidant or additive, and involves simple manipulations. The α -thioaldehydes obtained can be directly applied in syntheses of organic, medicinal and other functional compounds.

EXPERIMENTAL SECTION

General Methods. ¹H NMR (400 MHz) and ¹³C NMR (101 MHz) spectra were determined with CDCl₃ or DMSO-*d*₆ as solvent and tetramethylsilane (TMS) as internal standard. Chemical

shifts were reported in parts per million (ppm) from internal TMS (δ); all coupling constants (J values) were reported in hertz (Hz). High-resolution mass spectra were recorded on a TOF machine (ESI). Column chromatography was performed with 300–400 mesh silica gel using flash column techniques. All of the reagents were used directly as obtained commercially unless otherwise noted.

Preparation of 2-(Arylthio) aldehydes 4. *Typical procedure for the preparation of tert-butyl 2-(4-oxo-3-(phenylthio)butoxy) acetate (4a).* To a solution of THF (10 mL), *tert*-butyl 2-(but-3-yn-1-yloxy)acetate (**2a**, 0.184 g, 1 mmol) and thiophenol (0.22 g, 2 mmol) was added TBHP (1 μ L) and H₂O (1 μ L), the mixture was stirred at 25°C for 48 h. After the completion of the reaction, the solvent was evaporated under vacuum to yield the crude product, which was purified by column chromatography (silica gel, petroleum ether/EtOAc = 40:1) to give *tert*-butyl 2-(4-oxo-3-(phenylthio)butoxy)acetate (**4a**).

Tert-butyl 2-(4-oxo-3-(phenylthio)butoxy)acetate (4a). Yellow oil, 72% yield (223 mg); ¹H NMR (400 MHz, CDCl₃): δ 9.52 (d, J = 2.8 Hz, 1H), 7.42–7.40 (m, 2H), 7.34–7.23 (m, 3H), 3.93 (d, J = 3.3 Hz, 2H), 3.90–3.82 (m, 1H), 3.78–3.62 (m, 2H), 2.24–2.12 (m, 1H), 1.94–1.86 (m, 1H), 1.47 (s, 9H); ¹³C NMR (101 MHz, CDCl₃): δ 189.9, 164.9, 129.0, 126.6, 124.6, 123.9, 77.2, 64.2, 63.5, 49.2, 23.7, 23.5; HRMS (ESI) m/z : (M+Na)⁺ Calcd for C₁₆H₂₂O₄SNa 333.1137, found 333.1134.

*2-(Phenylthio)hexanal (4b).*⁶ Yellow oil, 78% yield (162 mg); ¹H NMR (400 MHz, CDCl₃): δ 9.34 (d, J = 4.3 Hz, 1H), 7.38–7.34 (m, 2H), 7.30–7.24 (m, 3H), 3.52–3.46 (m, 1H), 1.84–1.74 (m, 1H), 1.71–1.59 (m, 1H), 1.56–1.28 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H); ¹³C NMR (101 MHz, DMSO-*d*₆): δ 190.8, 128.2, 127.3, 124.6, 123.6, 52.3, 24.5, 23.0, 17.8, 9.4, 9.2; MS (ESI) m/z : (M+H)⁺ Calcd for C₁₂H₁₇OS 209.1, found 209.1.

2-(Phenylthio)pentanal (**4c**).⁷ Yellow oil, 64% yield (124 mg); ¹H NMR (400 MHz, CDCl₃): δ 9.37 (d, *J* = 4.3 Hz, 1H), 7.42–7.35 (m, 2H), 7.33–7.26 (m, 3H), 3.58–3.50 (m, 1H), 1.80–1.74 (m, 1H), 1.71–1.42 (m, 3H), 0.97 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 195.3, 132.8, 131.9, 129.2, 128.1, 56.6, 29.9, 20.2, 13.8; MS (ESI) *m/z*: (M+H)⁺ Calcd for C₁₁H₁₅OS 195.1, found 195.1.

2-(Phenylthio)heptanal (**4d**).⁸ Yellow oil, 71% yield (157 mg); ¹H NMR (400 MHz, CDCl₃): δ 9.36 (d, *J* = 2.1 Hz, 1H), 7.40–7.36 (s, 2H), 7.30–7.22 (m, 3H), 3.52–3.50 (m, 1H), 1.91–1.73 (m, 1H), 1.73–1.61 (m, 1H), 1.61–1.52 (m, 1H), 1.49–1.39 (m, 1H), 1.20–1.15 (m, 4H), 0.89 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 195.3, 132.7, 131.9, 129.1, 128.1, 56.8, 31.4, 27.8, 26.6, 22.4, 14.0. MS (ESI) *m/z*: (M+H)⁺ Calcd for C₁₃H₁₉OS 223.1, found 223.1.

2-(Phenylthio)octanal (**4e**). Yellow oil, 68% yield (160 mg). ¹H NMR (400 MHz, CDCl₃): δ 9.36 (d, *J* = 4.3 Hz, 1H), 7.38 (dd, *J* = 7.5, 2.0 Hz, 2H), 7.33–7.27 (m, 3H), 3.52 (td, *J* = 7.4, 4.3 Hz, 1H), 1.87–1.75 (m, 1H), 1.73–1.59 (m, 1H), 1.52–1.38 (m, 2H), 1.36–1.28 (m, 6H), 0.88 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 195.3, 132.7, 131.9, 129.1, 128.1, 56.8, 31.5, 28.9, 27.8, 26.9, 22.5, 14.0; HRMS (ESI) *m/z*: (M+H)⁺ Calcd for C₁₄H₂₁OS 237.1313, found 237.1323.

2-(Phenylthio)nonanal (**4f**). Yellow oil, 64% yield (160 mg). ¹H NMR (400 MHz, CDCl₃): δ 9.36 (d, *J* = 4.1 Hz, 1H), 7.40–7.36 (m, 2H), 7.32–7.28 (m, 3H), 3.54–3.48 (m, 1H), 1.82–1.76 (m, 1H), 1.72–1.60 (m, 1H), 1.60–1.38 (m, 2H), 1.32–1.28 (m, 8H), 0.87 (t, *J* = 6.6 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 195.3, 132.7, 131.9, 129.1, 128.1, 56.8, 31.7, 29.2, 29.0, 27.8, 26.9, 22.6, 14.1; HRMS (ESI) *m/z*: (M+H)⁺ Calcd for C₁₅H₂₃OS 251.1470, found 251.1515.

2-(Phenylthio)decanal (**4g**). Yellow oil, 60% yeild (158 mg). ¹H NMR (400 MHz, CDCl₃): δ 9.34 (d, *J* = 4.3 Hz, 1H), 7.41–7.32 (m, 2H), 7.28–1.24 (m, 3H), 3.49 (td, *J* = 7.3, 4.4 Hz, 1H), 1.84–1.74 (m, 1H), 1.68–1.60 (m, 1H), 1.56–1.36 (m, 2H), 1.26–1.20 (m, 10H), 0.86 (t, *J* = 6.7

Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 195.3, 132.7, 131.9 (d, $J = 7.1$ Hz, 2H), 7.27 (dd, $J = 15.4$, 7.5 Hz, 3H), 3.24 (d, $J = 6.4$ Hz, 1H), 1.17 (s, 9H); ^{13}C NM, 129.1, 128.1, 56.8, 31.8, 29.3, 29.2, 29.1, 27.8, 26.9, 22.6, 14.1; HRMS (ESI) m/z : (M+H) $^+$ Calcd for $\text{C}_{16}\text{H}_{25}\text{OS}$ 265.1626, found 265.1622.

3,3-Dimethyl-2-(phenylthio)butanal(4h). Yellow oil, 51% yield (106 mg); ^1H NMR (400 MHz, CDCl_3): δ 9.47 (d, $J = 6.4$ Hz, 1H), 7.37 R (101 MHz, CDCl_3): δ 195.9, 132.8, 129.9, 128.4, 69.3, 34.3, 28.5; HRMS (ESI) m/z : (M+K) $^+$ Calcd for $\text{C}_{12}\text{H}_{16}\text{OSK}$ 247.0559, found 247.0542.

2-Cyclopropyl-2-(phenylthio)acetaldehyde(4i). Yellow oil, 52% yield (100 mg). ^1H NMR (400 MHz, CDCl_3): δ 9.42 (d, $J = 4.5$ Hz, 1H), 7.40–7.34 (m, 2H), 7.30–7.24 (m, 3H), 2.91–2.83 (m, 1H), 1.05–0.95 (m, 1H), 0.78–0.66 (m, 2H), 0.53–0.38 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 194.5, 133.1, 129.1, 129.0, 128.1, 127.5, 127.1, 62.1, 9.4, 5.7, 4.3; HRMS (ESI) m/z : (M+H) $^+$ Calcd for $\text{C}_{11}\text{H}_{13}\text{OS}$ 193.0687, found 193.0681.

4-Phenyl-2-(phenylthio)butanal (4k). Yellow oil, 12% yield (30 mg); ^1H NMR (400 MHz, CDCl_3): δ 9.52 (d, $J = 3.4$ Hz, 1H), 7.46 (ddd, $J = 6.5$, 3.8, 1.5 Hz, 2H), 7.41–7.35 (m, 5H), 7.32–7.25 (m, 3H), 3.56 (td, $J = 13.7$, 6.9 Hz, 1H), 3.00–2.82 (m, 2H), 2.30–2.15 (m, 1H), 2.12–1.96 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3): δ 194.4, 139.9, 132.8, 130.8, 128.7, 128.16, 128.10, 127.9, 125.9, 55.5, 32.2, 28.7; HRMS (CI-TOF) m/z : M^+ Calcd for $\text{C}_{16}\text{H}_{16}\text{OS}$ 256.0922, found 256.0914.

5-Phenyl-2-(phenylthio)pentanal (4l). Yellow oil, 44% yield (120 mg); ^1H NMR (400 MHz, CDCl_3): δ 9.37 (d, $J = 4.0$ Hz, 1H), 7.37–7.32 (m, 2H), 7.32–7.26 (m, 5H), 7.22–7.16 (m, 3H), 3.51 (td, $J = 6.9$, 4.0 Hz, 1H), 2.70–2.64 (m, 2H), 1.96–1.58 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3): δ 195.3, 141.6, 136.7, 133.3, 131.8, 130.1, 129.4, 129.3, 128.69, 128.66, 128.5, 127.8,

127.4, 126.3, 57.1, 35.7, 28.8, 27.5; HRMS (ESI) m/z : (M+Na)⁺ Calcd for C₁₇H₁₈OSNa 293.0976, found 293.0967.

*Ethyl (Z/E)-3-(phenylthio)acrylate (3m).*⁹ 77% yield (150 mg); ¹H NMR (400 MHz, CDCl₃): δ *Z*-isomer 7.78 (d, J = 14.9 Hz, 1H), 7.53–7.45 (m, 2H), 7.42–7.36 (m, 3H), 5.91 (d, J = 10.2 Hz, 1H), 4.26 (q, 2H), 1.33 (t, J = 7.2 Hz, 3H); *E*-isomer 7.78 (d, J = 14.9 Hz, 1H), 7.53–7.45 (m, 2H, ArH), 7.42–7.36 (m, 3H), 5.65 (d, J = 14.9 Hz, 1H), 4.16 (q, 2H), 1.26 (t, J = 7.0 Hz, 3H); MS (ESI) m/z : (M+H)⁺ Calcd for C₁₁H₁₃O₂S 209.1, found 209.1.

*(Z/E)-3-(phenylthio)allyl acetate(3n).*¹⁰ 70% yield (146 mg); ¹H NMR (400 MHz, CDCl₃): δ *Z* isomer 7.47–7.30 (m, 5H), 6.52 (dt, J = 15.1, 1.2 Hz, 1H), 6.00–5.73 (m, 1H), 4.83 (dd, J = 6.5, 1.2 Hz, 2H), 2.15 (s, 3H); *E* isomer 7.47–7.30 (m, 5H), 6.58 (dt, J = 15.1, 1.2 Hz, 1H), 6.00–5.73 (m, 1H), 4.65 (dd, J = 6.6, 1.2 Hz, 2H), 2.12 (s, 3H); HRMS (CI-TOF) m/z : M⁺ Calcd for C₁₁H₁₂O₂S 208.0558, found 208.0558.

(Z/E) 5-(Phenylthio)pent-4-en-1-ol (3o). 77% yield (149 mg); ¹H NMR (400 MHz, CDCl₃): δ *Z* isomer 7.42–7.31 (m, 4H), 7.28–7.21 (m, 1H), 6.29 (dt, J = 9.2, 1.2 Hz, 1H), 5.88 (dt, J = 9.2, 7.4 Hz, 1H), 3.73 (td, J = 6.4, 4.1 Hz, 2H), 2.40 (qd, J = 7.4, 1.2 Hz, 2H), 1.86 (s, 1H), 1.81–1.70 (m, 2H); *E* isomer 7.42–7.31 (m, 4H), 7.28–7.21 (m, 1H), 6.24 (dt, J = 14.9, 1.3 Hz, 1H (*E*)), 6.12–5.98 (m, 1H (*Z*)), 3.73 (td, J = 6.4, 4.1 Hz, 2H), 2.35–2.27 (m, 2H), 1.86 (s, 1H), 1.81–1.70 (m, 2H); ¹³C NMR (101 MHz, CDCl₃): *Z+E* δ 136.0, 132.3, 129.03, 128.98, 128.91, 128.6, 126.3, 126.2, 123.7, 121.7, 62.2, 62.1, 31.9, 31.8, 29.4, 25.4; HRMS (CI-TOF) m/z : M⁺ Calcd for C₁₁H₁₄OS 194.0765, found 194.0763.

*(Z/E) 4-(Phenylthio)but-3-en-1-ol (3p).*¹¹ Yellow oil, 17% yield (30 mg); ¹H NMR (400 MHz, CDCl₃): δ *Z* isomer 7.43–7.30 (m, 4H), 7.27–7.23 (m, 1H), 6.41 (d, J = 9.3 Hz, 1H), 6.03–5.84 (m, 1H), 3.75 (t, J = 6.3 Hz, 2H), 2.59 (td, J = 7.4, 1.0 Hz, 2H), 1.96 (s, 1H); *E* isomer 7.43–7.30

(m, 4H), 7.27–7.23 (m, 1H), 6.33 (d, $J = 15.0$ Hz, 1H), 6.03–5.84 (m, 1H), 3.79 (t, $J = 6.4$ Hz, 2H), 2.53–2.42 (m, 2H), 1.96 (s, 1H); HRMS (CI-TOF) m/z : M^+ Calcd for $C_{10}H_{12}OS$ 180.0609, found 180.0599.

(*Z/E*) *Tert-butyl 2-((4-(p-tolylthio) but-3-en-1-yl)oxy)acetate (3ba)*. Yellow oil, 70% yield (215 mg); 1H NMR (300 MHz, $CDCl_3$): δ 7.25 (d, $J = 8.0$ Hz, 2H), 7.11 (d, $J = 7.6$ Hz, 2H), 6.24 (t, $J = 11.4$ Hz, 1H), 6.02–5.71 (m, 1H), 4.08–3.88 (m, 2H), 3.72–3.46 (m, 2H), 2.56 (dd, $J = 13.4, 6.7$ Hz, 1H), 2.46 (dd, $J = 13.4, 6.6$ Hz, 1H), 2.32 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $Z+E$ δ 168.7, 168.6, 135.5, 135.4, 131.3, 131.0, 129.4, 128.7, 128.6, 128.5, 126.7, 125.0, 123.6, 80.6, 80.5, 69.6, 69.3, 67.8, 67.7, 32.3, 28.5, 27.1, 20.0; HRMS (CI-TOF) m/z : $(M+H)^+$ Calcd for $C_{17}H_{25}O_3S$ 309.1524, found 309.1526.

Tert-butyl 2-(4-oxo-3-(p-tolylthio)butoxy)acetate (4ba). Yellow oil, 23% yield (75 mg); 1H NMR (400 MHz, $CDCl_3$): δ 9.51 (d, $J = 2.0$ Hz, 1H), 7.29 (d, $J = 7.8$ Hz, 2H), 7.10 (d, $J = 7.8$ Hz, 2H), 3.98–3.88 (m, 2H), 3.78 (td, $J = 7.3, 2.2$ Hz, 1H), 3.74–3.62 (m, 2H), 2.32 (s, 3H), 2.18–2.10 (m, 1H), 1.92–1.82 (m, 1H), 1.48 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.4, 168.5, 137.9, 133.3, 128.9, 128.8, 127.5, 126.0, 107.7, 80.7, 67.8, 67.1, 53.0, 27.1, 20.1; HRMS (CI-TOF) m/z : M^+ Calcd for $C_{17}H_{24}O_4S$ 324.1395, found 324.1395.

(*Z/E*) *Tert-butyl 2-((4-(o-tolylthio)but-3-en-1-yl)oxy)acetate (3ca)*. Yellow oil, 32% yield (99 mg); 1H NMR (400 MHz, $CDCl_3$): δ 7.32–7.30 (m, 1H), 7.18–7.10 (m, 3H), 6.24–6.14 (m, 1H), 5.99–5.82 (m, 1H), 4.0–3.96 (m, 2H), 3.68–3.56 (m, 2H), 2.65–2.55 (m, 1H), 2.54–2.45 (m, 1H), 2.38 (s, 1.5H, (*Z* isomer)), 2.35 (s, 1.5 H, (*E* isomer)), 1.48 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ $Z+E$ 169.1, 137.09, 137.06, 134.7, 134.3, 130.9, 129.7, 128.83, 128.77, 128.6, 126.06, 126.05, 126.03, 125.9, 124.4, 122.9, 81.13, 81.09, 70.2, 69.9, 68.3, 68.2, 32.9, 29.0, 27.6, 20.0, 19.7. HRMS (CI-TOF) m/z : M^+ Calcd for $C_{17}H_{24}O_3S$ 308.1446, found 308.1431.

Tert-butyl 2-(4-oxo-3-(o-tolylthio)butoxy)acetate(4ca). Yellow oil, 59% yield (191 mg); ^1H NMR (400 MHz, CDCl_3): δ 9.43 (d, $J = 3.4$ Hz, 1H), 7.43–7.36 (m, 1H), 7.24–7.09 (m, 3H), 3.99–3.87 (m, 2H), 3.88–3.80 (m, 1H), 3.70 (td, $J = 5.2, 1.3$ Hz, 2H), 2.45 (s, 3H), 2.33–2.14 (m, 1H), 2.07–1.83 (m, 1H), 1.47 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3): δ 194.5, 169.4, 140.4, 133.4, 131.2, 130.7, 128.3, 126.7, 81.8, 68.8, 68.2, 53.5, 28.8, 28.1, 20.9; HRMS (CI-TOF) m/z : ($\text{M}+\text{H}$) $^+$ Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_4\text{S}$ 324.1395, found 324.1377.

Tert-butyl (E/Z)-2-((4-((2,6-dimethylphenyl)thio)but-3-en-1-yl)oxy)acetate(3da). Yellow oil, 84% yield (270 mg); ^1H NMR (400 MHz, CDCl_3): δ *Z* isomer 7.13–6.97 (m, 3H), 5.71 (dt, $J = 9.3, 1.3$ Hz, 1H), 5.64–5.55 (m, 1H), 3.93 (s, 2H), 3.57 (t, $J = 6.8$ Hz, 2H), 2.52 (qd, $J = 6.8, 1.3$ Hz, 2H), 2.40 (s, 6H), 1.42 (s, 9H); *E* isomer 7.13–6.97 (m, 3H), 5.87 (dt, $J = 14.9, 1.3$ Hz, 1H), 5.16–5.06 (m, 1H), 3.84 (s, 2H), 3.40 (t, $J = 7.0$ Hz, 2H), 2.39 (s, 6H), 2.27 (qd, $J = 7.0, 1.3$ Hz, 2H), 1.40 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3): δ *Z+E* 169.23, 169.17, 142.7, 142.1, 132.4, 130.2, 128.3, 128.0, 127.73, 127.69, 127.6, 127.3, 124.4, 124.3, 122.8, 81.1, 81.0, 70.5, 69.9, 68.3, 32.7, 28.8, 27.7, 27.6, 21.6, 21.2; HRMS (CI-TOF) m/z : M^+ Calcd for $\text{C}_{18}\text{H}_{26}\text{O}_3\text{S}$ 322.1603, found 322.1619.

Tert-butyl 2-(4-oxo-3-((2-fluorophenyl)thio)butoxy)acetate(4ga). Yellow oil, 59% yield (193 mg). ^1H NMR (400 MHz, CDCl_3): δ 9.45 (s, 1H), 7.37 (t, $J = 7.0$ Hz, 1H), 7.30–7.22 (m, 1H), 7.02 (t, $J = 7.7$ Hz, 2H), 3.88 (t, $J = 10.4$ Hz, 2H), 3.78 (t, $J = 6.7$ Hz, 1H), 3.71–3.59 (m, 2H), 2.12 (dd, $J = 13.7, 6.1$ Hz, 1H), 1.84 (dd, $J = 14.0, 5.6$ Hz, 1H), 1.41 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3): δ 194.2, 169.5, 162.9 (d, $J = 247.3$ Hz), 136.7, 131.2 (d, $J = 8.1$ Hz), 124.7 (d, $J = 7.7$ Hz), 116.2 (d, $J = 23.2$ Hz), 81.7, 68.5 (d, $J = 74.1$ Hz), 53.5, 28.4, 28.1; HRMS (CI-TOF) m/z : ($\text{M}+\text{H}$) $^+$ Calcd for $\text{C}_{16}\text{H}_{22}\text{O}_4\text{FS}$ 329.1223, found 329.1217.

Tert-butyl 2-(4-oxo-3-((4-fluorophenyl)thio)butoxy)acetate(4ha). Yellow oil, 91% yield (298

mg); ^1H NMR (400 MHz, CDCl_3): δ 9.50 (d, $J = 2.8$ Hz, 1H), 7.47–7.37 (m, 2H), 7.03–6.96 (m, 2H), 3.93 (d, $J = 2.2$ Hz, 2H), 3.81–3.76 (m, 1H), 3.75–3.62 (m, 2H), 2.20–2.10 (m, 1H), 1.92–1.82 (m, 1H), 1.47 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3): δ 194.1, 169.5, 163.2 (d, $J = 249.5$ Hz), 138.8 (d, $J = 8.7$ Hz), 136.5 (d, $J = 8.4$ Hz, 1H), 131.3 (d, $J = 8.3$ Hz), 116.4 (d, $J = 22.0$ Hz), 81.8, 68.8, 68.1, 54.3, 28.2, 28.1; HRMS (CI-TOF) m/z : M^+ Calcd for $\text{C}_{16}\text{H}_{21}\text{O}_4\text{FS}$ 328.1145, found 328.1154.

Tert-butyl 2-(4-oxo-3-((2-chlorophenyl)thio)butoxy)acetate(4ia). Yellow oil, 61% yield (210 mg); ^1H NMR (400 MHz, CDCl_3): δ 9.51 (dd, $J = 2.8, 1.3$ Hz, 1H), 7.44 (td, $J = 7.7, 1.7$ Hz, 1H), 7.36–7.29 (m, 1H), 7.13–7.05 (m, 2H), 3.93 (d, $J = 4.6$ Hz, 2H), 3.85 (td, $J = 7.2, 2.8$ Hz, 1H), 3.77–3.65 (m, 2H), 2.24–2.14 (m, 1H), 1.97–1.81 (m, 1H), 1.47 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3): δ 194.2, 169.4, 136.6, 131.2, 131.1, 124.7, 116.3, 116.0, 81.7, 68.8, 68.1, 53.4, 28.4, 28.1; HRMS (CI-TOF) m/z : M^+ Calcd for $\text{C}_{16}\text{H}_{22}\text{O}_4\text{ClS}$ 345.0927, found 345.0939.

Tert-butyl (Z/E)-2-((4-((3-chlorophenyl)thio)but-3-en-1-yl)oxy)acetate(3ja). Yellow oil, 24% yield (79 mg); δ 7.32 (dd, $J = 6.4, 4.6$ Hz, 1H), 7.27–7.16 (m, 3H), 6.30 (dd, $J = 11.9, 10.5$ Hz, 1H), 6.15–6.00 (m, 1H), 4.02 (s, 2H), 3.66 (t, $J = 6.5$ Hz, 2H), 2.62 (ddd, $J = 13.6, 6.8, 1.2$ Hz, 1H), 2.58–2.52 (m, 1H), 1.52 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3): δ Z+E 169.1, 169.0, 138.1, 137.8, 134.3, 134.2, 134.1, 130.6, 129.5, 129.4, 127.6, 127.3, 126.1, 125.8, 125.7, 125.6, 122.9, 121.6, 81.16, 81.10, 69.8, 69.7, 68.3, 68.2, 32.9, 29.1, 27.6; HRMS (CI-TOF) m/z : M^+ Calcd for $\text{C}_{16}\text{H}_{21}\text{O}_3\text{SCl}$ 328.0900, found 328.0905.

Tert-butyl 2-(4-oxo-3-((3-chlorophenyl)thio)butoxy)acetate(4ja). Yellow oil, 68% yield (234 mg); ^1H NMR (400 MHz, CDCl_3): δ 9.46 (d, $J = 3.4$ Hz, 1H), 7.55–7.34 (m, 2H), 7.28–7.14 (m, 2H), 3.93 (d, $J = 3.8$ Hz, 2H), 3.71 (t, $J = 5.7$ Hz, 2H), 2.30–2.20 (m, 1H), 2.11–1.93 (m, 1H), 1.47 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3): δ 193.4, 168.4, 135.5, 132.6, 129.1, 128.1, 126.4, 80.8,

67.8, 67.1, 52.0, 27.6, 27.1; HRMS (CI-TOF) m/z : (M-C₄H₈)⁺ Calcd for C₁₂H₁₃O₄SCl 288.0223, found 288.0219.

Hex-1-yne-1-d (2b'). ¹H NMR (400 MHz, CDCl₃): δ 2.19 (t, J = 6.9 Hz, 2H), 1.93 (s, 0.13H), 1.59–1.36 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H).

2-(Phenylthio)hexanal-1-d (4b'). ¹H NMR (400 MHz, CDCl₃): δ 9.36 (d, J = 4.3 Hz, 0.13H), 7.42–7.34 (m, 2H), 7.33–7.27 (m, 3H), 3.51 (t, J = 7.2 Hz, 1H), 1.84–1.76 (m, 1H), 1.68–1.62 (m, 1H), 1.45–1.28 (m, 4H), 0.92 (t, J = 7.1 Hz, 3H). HRMS (CI-TOF) m/z : M⁺ Calcd for C₁₂H₁₅OSD 209.0985, found 209.0992.

2,2,6,6-Tetramethyl-1-((phenylthio)oxy)piperidine (6).¹² ¹H NMR (400 MHz, CDCl₃): δ 7.75–7.63 (m, 2H), 7.50–7.34 (m, 3H), 1.84 (s, 1H), 1.67 (s, 4H), 1.57 (s, 4H), 1.51 (s, 3H), 1.48 (s, 3H), 1.38 (s, 1H), 0.91 (s, 2H); MS (ESI-TOF) m/z : (M+H)⁺ Calcd for C₁₅H₂₄NOS 266.2, found 266.2.

ASSOCIATED CONTENT

Supporting Information

¹H, ¹³C NMR spectra for compounds **3** and **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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