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Air Oxidative Radical Oxysulfurization of Alkynes Leading to α-Thioaldehydes

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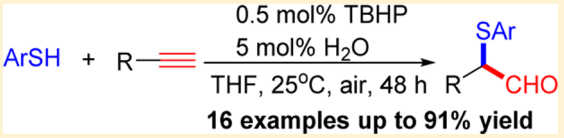
Supporting Information

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 H_2O 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 mainly α-thioaldehydes **4c−4g** in moderate to good yields accompanied by alkenylsufides **3c−3g** (Table 2, entries 3−7). In 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 alkenylsufides **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), and 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.

Afterward, 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

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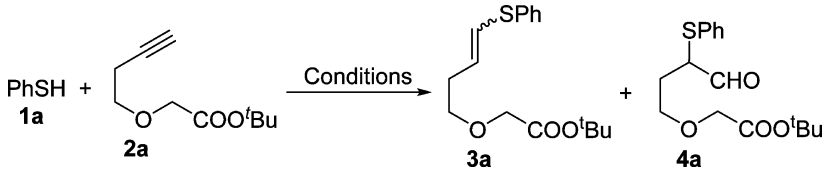
Table 1. Optimization of the Reaction Conditions



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_2Cl_2	2:1	25	24	29	0
4	CH_3CN	2:1	25	24	0	0
5	^{t}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

[a]Isolated yield. [b]Addition of 5% mol H_2O (1 μL). [c]Anhydrous THF. [d]Gas chromatography yield. [e]Addition of 0.5% mol TBHP (1 μL). [f]Addition of 4 μL H_2O. [g]Addition of 5% mol TBHP (10 μL).

well with **1a** to give exclusively alkenylsufides **3m**−**3n** (Table 2, entries 13 and 14). Reactions involving 5-hydroxypentyne (**2o**) and 4-hydroxybutyne (**2p**) also gave alkenylsufides **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^{t}Bu 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-methylbenzenethiol (**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 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.

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**.

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 H_2O to give radical **10** which then reacts with O_2 (air) to give peroxy radical **11**; this decomposes to form α-thioaldehyde **4a** and hydroperoxy radical

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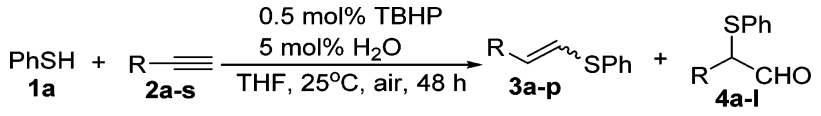
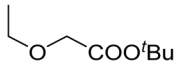
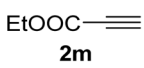
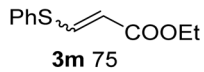
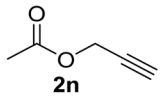
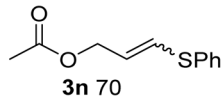
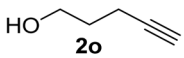
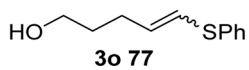
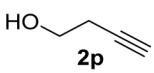
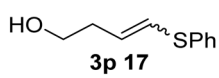
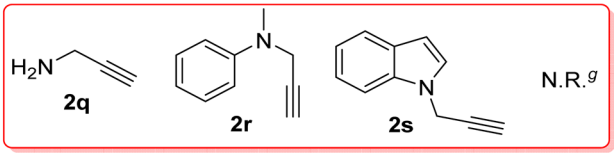
Table 2. Reactions of Thiophenol (1a) with Terminal Alkynes 2a–s[a]



Entry	2	R	Yield(%)[b] 3	4
1	**2a**		**3a** 0(2)[c]	**4a** 77(98)[c]
2	**2b**	*n*-butyl	**3b** 0(2)[c]	**4b** 78(98)[c]
3	**2c**	*n*-propyl	**3c**[d]	**4c** 64
4	**2d**	*n*-pentyl	**3d** 18	**4d** 71
5	**2e**	*n*-hexyl	**3e**[d]	**4e** 68
6	**2f**	*n*-heptyl	**3f** 28	**4f** 64
7	**2g**	*n*-octyl	**3g** 28	**4g** 60
8	**2h**	*t*-butyl	**3h** 46	**4h** 51
9	**2i**	cyclopropyl	**3i**[d]	**4i** 52
10	**2j**	Ph	complicated mixtures	
11	**2k**	$C_6H_5(CH_2)_2$	**3k** 0	**4k** 12[e]
12	**2l**	$C_6H_5(CH_2)_3$	**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]	

[a]Reaction 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 H_2O. [b]Isolated yield. [c]Analyzed by gas chromatography. [d]Mixture of alkenylsufide and diphenyldisulfide, they cannot be separated from each other. [e]Most of starting material **2k** did not react with **1a**. [f]Some of starting material **2l** did not react with **1a**. [g]N.R. represents no reaction.

12, which reacts with thiophenol (**1a**) to liberate thiophenyl radical **8**, for further propagation of the reaction cycle.

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 (O_2) 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

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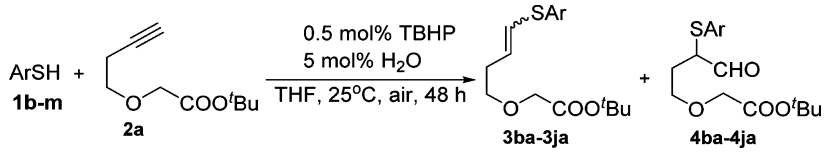
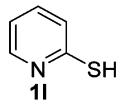
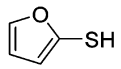
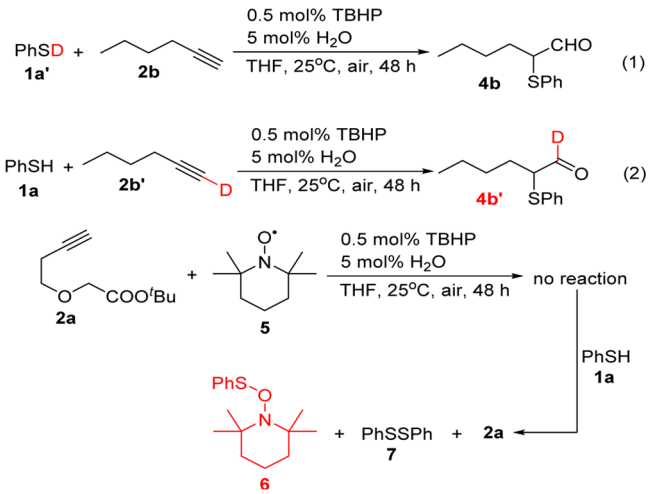
Table 3. Reactions of Arylthiols 1 with Terminal Alkyne 2a[a]



Entry	ArSH (**1**)	Products **3**, **4** and Yield(%)[b]	
1	4-$CH_3C_6H_4SH$ (**1b**)	**3ba** 32	**4ba** 59
2	2-$CH_3C_6H_4SH$ (**1c**)	**3ca** 70	**4ca** 23
3	2,6-$(CH_3)_2C_6H_3SH$ (**1d**)	**3da** 84	**4da** 0
4	4-$CH_3OC_6H_4SH$ (**1e**)		N.R.[c]
5	2-$NH_2C_6H_4SH$ (**1f**)		N.R.[c]
6	2-FC_6H_4SH (**1g**)	**3ga** 18	**4ga** 59
7	4-FC_6H_4SH (**1h**)	**3ha** <5	**4ha** 91
8	2-ClC_6H_4SH (**1i**)	**3ia** 15	**4ia** 61
9	3-ClC_6H_4SH (**1j**)	**3ja** 24	**4ja** 68
10	4-$NO_2C_6H_4SH$ (**1k**)		N.R.[c]
11	 **1l**		N.R.[c]
12	 **1m**		N.R.[c]

[a]Reaction 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 H_2O. [b]Isolated yield. [c]N.R. indicates that the alkyne is not consumed and the desired α-thioaldehyde and/or alkenylsulfide were not isolated (0% yield).

Scheme 1. Mechanistic Study



applied in syntheses of organic, medicinal and other functional compounds.

EXPERIMENTAL SECTION

General Methods. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra were determined with $CDCl_3$ 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 μL) and H_2O (1 μL), and 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**).

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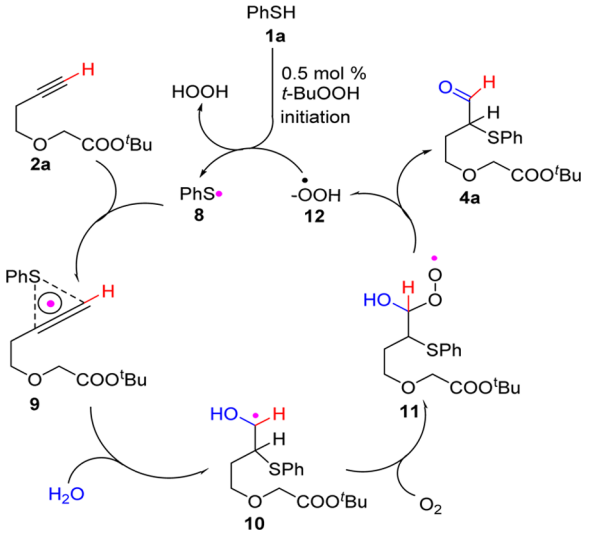
Scheme 2. Proposed Mechanism for the Reaction of Terminal Alkyne 2a with Thiophenol (1a)



*tert-Butyl 2-(4-oxo-3-(phenylthio)butoxy) Acetate (**4a**).* Yellow oil, 72% yield (223 mg); ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (101 MHz, $CDCl_3$): 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 $C_{16}H_{22}O_4SNa$ 333.1137, found 333.1134.

*2-(Phenylthio)hexanal (**4b**).*[6] Yellow oil, 78% yield (162 mg); ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C 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 $C_{12}H_{17}OS$ 209.1, found 209.1.

*2-(Phenylthio)pentanal (**4c**).*[7] Yellow oil, 64% yield (124 mg); ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (101 MHz, $CDCl_3$): 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 $C_{11}H_{15}OS$ 195.1, found 195.1.

*2-(Phenylthio)heptanal (**4d**).*[8] Yellow oil, 71% yield (157 mg); ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (75 MHz, $CDCl_3$): 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 $C_{13}H_{19}OS$ 223.1, found 223.1.

*2-(Phenylthio)octanal (**4e**).* Yellow oil, 68% yield (160 mg); ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (75 MHz, $CDCl_3$): 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 $C_{14}H_{21}OS$ 237.1313, found 237.1323.

*2-(Phenylthio)nonanal (**4f**).* Yellow oil, 64% yield (160 mg); ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (75 MHz, $CDCl_3$): 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 $C_{15}H_{23}OS$ 251.1470, found 251.1515.

*2-(Phenylthio)decanal (**4g**).* Yellow oil, 60% yield (158 mg); ^{1}H NMR (400 MHz, $CDCl_3$): 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 $C_{16}H_{25}OS$ 265.1626, found 265.1622.

*3,3-Dimethyl-2-(phenylthio)butanal (**4h**).* Yellow oil, 51% yield (106 mg); ^{1}H 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 $C_{12}H_{16}OSK$ 247.0559, found 247.0542.

*2-Cyclopropyl-2-(phenylthio)acetaldehyde (**4i**).* Yellow oil, 52% yield (100 mg); ^{1}H 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 $C_{11}H_{13}OS$ 193.0687, found 193.0681.

*4-Phenyl-2-(phenylthio)butanal (**4k**).* Yellow oil, 12% yield (30 mg); ^{1}H NMR (400 MHz, CDCl3): 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 $C_{16}H_{16}OS$ 256.0922, found 256.0914.

*5-Phenyl-2-(phenylthio)pentanal (**4l**).* Yellow oil, 44% yield (120 mg); ^{1}H 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 $C_{17}H_{18}OSNa$ 293.0976, found 293.0967.

*Ethyl (Z/E)-3-(Phenylthio)acrylate (**3m**).*[9] Yield 77% (150 mg); ^{1}H NMR (400 MHz, $CDCl_3$): 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 $C_{11}H_{13}O_2S$ 209.1, found 209.1.

*(Z/E)-3-(Phenylthio)allyl Acetate (**3n**).*[10] Yield 70% (146 mg); ^{1}H NMR (400 MHz, $CDCl_3$): 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 $C_{11}H_{12}O_2S$ 208.0558, found 208.0558.

*(Z/E) 5-(Phenylthio)pent-4-en-1-ol (**3o**).* Yield 77% (149 mg); ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (101 MHz, $CDCl_3$): *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 $C_{11}H_{14}OS$ 194.0765, found 194.0763.

*(Z/E) 4-(Phenylthio)but-3-en-1-ol (**3p**).*[11] Yellow oil, 17% yield (30 mg); ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{1}H 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,

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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); ^{1}H 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); ^{1}H 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); ^{1}H 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: $(M + H)^+$ Calcd for $C_{17}H_{24}O_4S$ 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); ^{1}H 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 $C_{18}H_{26}O_3S$ 322.1603, found 322.1619.

*tert-Butyl 2-(4-oxo-3-((2-Fluorophenyl)thio)butoxy)acetate (**4ga**).* Yellow oil, 59% yield (193 mg). ^{1}H 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: $(M + H)^+$ Calcd for $C_{16}H_{22}O_4FS$ 329.1223, found 329.1217.

*tert-Butyl 2-(4-Oxo-3-((4-fluorophenyl)thio)butoxy)acetate (**4ha**).* Yellow oil, 91% yield (298 mg); ^{1}H 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 $C_{16}H_{21}O_4FS$ 328.1145, found 328.1154.

*tert-Butyl 2-(4-Oxo-3-((2-chlorophenyl)thio)butoxy)acetate (**4ia**).* Yellow oil, 61% yield (210 mg); ^{1}H 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 $C_{16}H_{22}O_4ClS$ 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 $C_{16}H_{21}O_3SCl$ 328.0900, found 328.0905.

*tert-Butyl 2-(4-Oxo-3-((3-chlorophenyl)thio)butoxy)acetate (**4ja**).* Yellow oil, 68% yield (234 mg); ^{1}H 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: $(M - C_4H_8)^+$ Calcd for $C_{12}H_{13}O_4SCl$ 288.0223, found 288.0219.

*Hex-1-yne-1-d (**2b′**).* ^{1}H NMR (400 MHz, $CDCl_3$): 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′**).* ^{1}H NMR (400 MHz, $CDCl_3$): 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 $C_{12}H_{15}OSD$ 209.0985, found 209.0992.

*2,2,6,6-Tetramethyl-1-((phenylthio)oxy)piperidine (**6**).*[12] ^{1}H NMR (400 MHz, $CDCl_3$): 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 $C_{15}H_{24}NOS$ 266.2, found 266.2.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H, ^{13}C NMR spectra for compounds **3** and **4**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00641.

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Notes

The authors declare no competing financial interest.

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