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Copper-catalyzed selective syntheses of Markovnikov-type hydrothiolation products and thioacetals by the reactions of thiols with alkenes bearing heteroatoms

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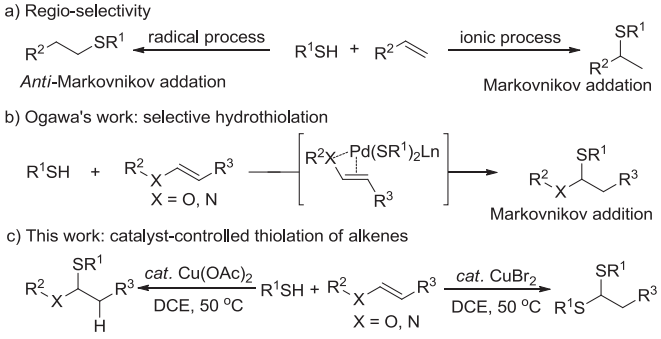
ABSTRACT

Catalyst-controlled divergent reactions of thiophenols with alkenes bearing heteroatoms have been developed. Markovnikov-type hydrothiolation products and thioacetals were synthesized selectively by switching copper catalysts.

1. Introduction

The construction of C–S bonds is one of significant goals in synthetic chemistry because of the numerous sulfur-containing natural products and pharmaceuticals as well as the increasing synthetic importance of sulfur-containing compounds.[1,2] Addition reactions of organosulfur compounds to alkenes present a general atom-economical method for C–S bond formation, and a great efforts have been made to tackle this challenge over the past decades.[3] *anti*-Markovnikov addition of thiols to alkenes has been well established since 1905 (thiol-ene reaction).[4] It usually undergoes a radical-type mechanism promoted by initiators, such as peroxides, AIBN or photochemistry (Scheme 1a, left).[5] In contrast, Markovnikov-type hydrothiolation of alkenes is far less developed (Scheme 1a, right), mainly because it lacks the driving force to achieve catalytic ionic process. The successful examples generally happened along with harsh reaction conditions.[6] Recently, some progress has been made by Ogawa group[7] and Duñach group.[8] In 2014, Ogawa and co-workers successfully realized catalytic Markovnikov-type hydrothiolation of alkenes with thiols assisted by the coordination of heteroatom and double bond to palladium (Scheme 1b).[7a]



Scheme 1. Addition reaction of organosulfur compounds to alkenes.

Controlling selectivity is one of great importance to chemistry, especially in transition-metal-catalyzed reactions.[9] Furthermore, exploring of selective methods to access divergent products from simple starting materials has attracted much more attentions from a synthetic point of view. Both the Markovnikov-type hydrothiolation products and thioacetals are present in natural products[10] and play important roles in organic synthesis.[11] Herein, we report an efficient and practical copper-catalyzed Markovnikov-type hydrothiolation of alkenes bearing heteroatoms, in which both Markovnikov-type hydrothiolation products and thioacetals can be selectively achieved by simply switching copper catalysts (Scheme 1c).

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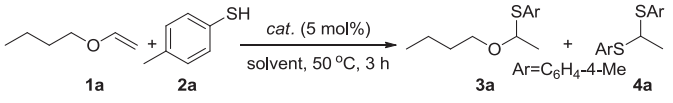
0040-4020/

2. Results and discussion

In 2013, we reported a Mn-catalyzed oxidative cyclization between thiophenols and alkynes for synthesis of benzothiophene derivatives using O_2 as oxidant.[12] To continue our efforts on C–S bond formation, we further investigated the reactions of thiophenols and alkenes. When the reactions of 1-(vinyloxy)butane **1a** and 4-methylbenzenethiol **2a** were carried out, the hydrothiolation product **3a** and the thioacetal **4a** were obtained (Table 1). Trace amount of **3a** and **4a** were observed in the presence of $Mn(OAc)_2$ (entry 1), while a full conversion of **1a** was achieved when the catalyst was switched to $FeCl_2$ (entry 2). **3a** and **4a** were obtained in 31% and 62% yields, respectively. Although **3a** was formed in only 34% yield using $Fe(OAc)_2$ as catalyst, the selectivity of the reaction is excellent (entry 3). To our delight, $Cu(OAc)_2$ turned out to be effective and selective catalyst for the formation of **3a** (entry 4). $Co(OAc)_2{\cdot}4H_2O$ showed lower efficiency compared with $Cu(OAc)_2$ (entry 5). Interestingly, **4a** turned out to be the major product when copper halides were applied as catalyst (entries 6–8) and an excellent yield of **4a** was achieved in 99% yield in the presence of $CuBr_2$ (entry 8). $CuSO_4$ also gave an excellent yield of **4a** (entry 9), while **4a** was obtained in only 43% when catalyzed by $Cu(OTf)_2$ (entry 10). It should be noted that strong Brφnsted acids were also effective for the formation of **4a** (entries 11 and 12). Trace amount of **3a** and **4a** were detected in other solvents, such as MeCN, PhMe and THF (entries 13–15), indicating that DCE is a suitable solvent for synthesis of **3a**. The reaction could also be carried out under nitrogen atmosphere (entries 16 and 17), however, a prolonged reaction time was needed to accomplish the desired reaction (entry 17). Importantly, **3a** was obtained in good yields under air (entries 18 and 19). These results suggested that oxygen could greatly accelerate the reaction rate.

Table 1
Optimization of reaction Conditions[a]

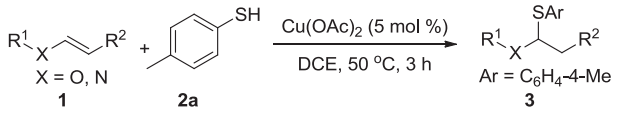


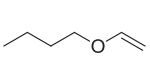
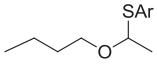
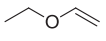
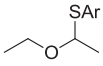
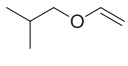
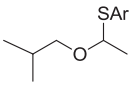
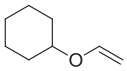
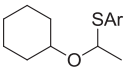
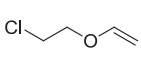
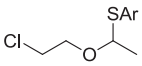
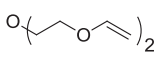
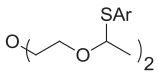
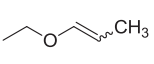
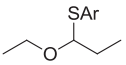
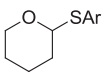
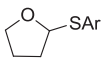
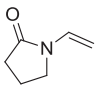
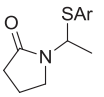
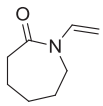
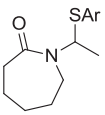
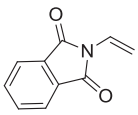
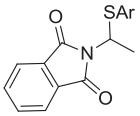
Entry	*cat.*	Solvent	**3a** (%)[b]	**4a** (%)[b]
1	$Mn(OAc)_2$	DCE	Trace	Trace
2	$FeCl_2$	DCE	31	62
3	$Fe(OAc)_2$	DCE	34	Trace
4	$Cu(OAc)_2$	DCE	91	Trace
5	$Co(OAc)_2{\cdot}4H_2O$	DCE	55	Trace
6	CuCl	DCE	40	60
7	$CuCl_2$	DCE	10	90
8	$CuBr_2$	DCE	Trace	99
9	$CuSO_4$	DCE	Trace	95
10	$Cu(OTf)_2$	DCE	Trace	43
11	TsOH	DCE	Trace	96
12	TfOH	DCE	Trace	94
13	$Cu(OAc)_2$	MeCN	6	Trace
14	$Cu(OAc)_2$	PhMe	Trace	Trace
15	$Cu(OAc)_2$	THF	Trace	Trace
16[c]	$Cu(OAc)_2$	DCE	34	Trace
17[d]	$Cu(OAc)_2$	DCE	90	Trace
18[e]	$Cu(OAc)_2$	DCE	80	Trace
19[f]	$Cu(OAc)_2$	DCE	91	Trace

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (2.0 mmol), cat. (0.025 mmol), DCE (5.0 mL), oxygen atmosphere, 50 °C, 3 h; unless otherwise noted.
[b] NMR yields were determined by ^1H NMR using an internal standard.
[c] Nitrogen atmosphere, 3 h.
[d] Nitrogen atmosphere, 8 h.
[e] Under air, 3 h.
[f] Under air, 5 h.

Subsequently, we investigated the generality of the methods for selective syntheses of **3** and **4** using $Cu(OAc)_2$ and $CuBr_2$ as catalyst, respectively (Tables 2–4). First, the scope and limitation of alkenes in the hydrothiolation reactions were investigated in the presence of $Cu(OAc)_2$ (Table 2). Both linear and cyclic vinyl ethers **1a**–**i** reacted with **2a** to give the corresponding hydrothiolation products **3a**–**i** selectively with good to excellent yields (entries 1–9). The reactions of the chloro-substituted and eudipleural polysubstitued substrates, **1e** and **1f**, proceeded efficiently (entries 5 and 6), which indicating a potential application in organic synthesis. In addition,

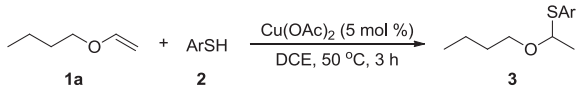
Table 2
Scope of the substrate **1**[a]



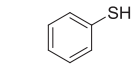
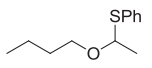
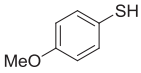
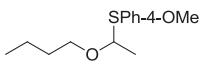
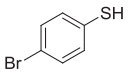
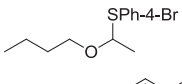
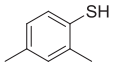
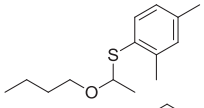
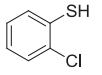
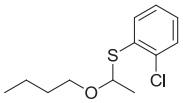
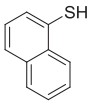
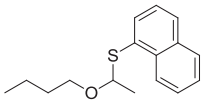
entry	1		3		yield (%)[b]
1		**1a**		**3a**	91(86)
2		**1b**		**3b**	89(76)
3[c]		**1c**		**3c**	80(68)
4		**1d**		**3d**	95(90)
5		**1e**		**3e**	70(57)
6[c]		**1f**		**3f**	70(64)
7[d]		**1g**		**3g**	87(80)
8		**1h**		**3h**	84(70)
9		**1i**		**3i**	88(77)
10		**1j**		**3j**	95(87)
11		**1k**		**3k**	92(84)
12		**1l**		**3l**	N.D.[e]

[a] Reaction conditions: **1** (0.5 mmol), **2a** (2.0 mmol), $Cu(OAc)_2$ (0.025 mmol), DCE (5.0 mL), oxygen atmosphere, 50 °C, 3 h.
[b] Reported yields were based on **1** and determined by ^1H NMR using an internal standard; the isolated yields were given in parentheses.
[c] The reaction time is 5 h.
[d] The reaction time is 7 h.
[e] Not Detected.

Table 3
Scope of the substrate **2**[a]



1a **2** **3**

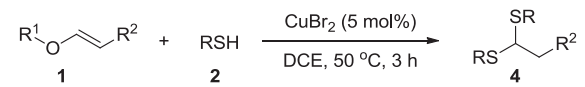
entry	2	3	yield (%)[b]
1	 **2b**	 **3m**	75(68)
2	 **2c**	 **3n**	90(84)
3	 **2d**	 **3o**	96(86)
4	 **2e**	 **3p**	80(72)
5	 **2f**	 **3q**	73(68)
6	 **2g**	 **3r**	90(84)

[a]Reaction conditions: **1a** (0.5 mmol), **2** (2.0 mmol), $Cu(OAc)_2$ (0.025 mmol), DCE (5.0 mL), oxygen atmosphere, 50 °C, 3 h.
[b]Reported yields were based on **1a** and determined by ^1H NMR using an internal standard; the isolated yields were given in parentheses.

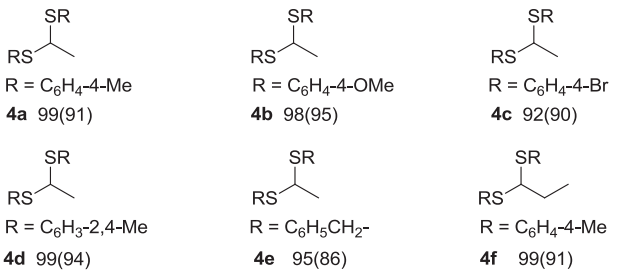
alkenes bearing nitrogen functional groups, **1j** and **1k**, also reacted smoothly with **2a**, affording the corresponding products in 95% and 92% yields, respectively (entries 10 and 11). However, the desired hydrothiolation product **3l** was not detected (entry 12), probably due to the lower electron density of **1l**.

Next, the scope of aryl thiols **2** in the hydrothiolation reactions was investigated in the presence of $Cu(OAc)_2$ (Table 3). A variety of thiophenols bearing both electron-donating and electron-withdrawing substituents on the aromatic ring reacted smoothly with **1a** to provide the desired products **3m**–**r** under the standard reaction conditions. It is worth noting that many synthetically relevant functional groups such as chloro and bromo were compatible with the conditions, revealing the possibility of further transformations by the well-established cross-coupling reactions.

Table 4
Scope of synthesis of thioacetals **4**[a,b]

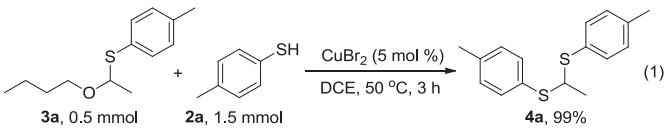


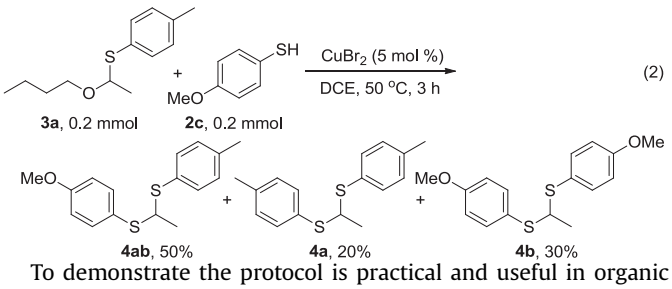
1 **2** **4**



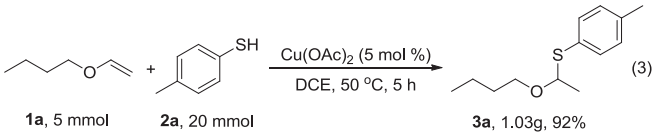
[a]Reaction conditions: **1a** (0.5 mmol), **2** (2 mmol), DCE (5.0 mL), oxygen atmosphere, 50 °C, 3 h.
[b]Reported yields were based on **1** and determined by ^1H NMR using an internal standard; the isolated yields were given in parentheses.

Furthermore, synthesis of thioacetals **4** was studied by the reactions of vinyl ethers **1** reacted with thiols **2** in the presence of $CuBr_2$ (Table 4). To our satisfaction, various thioacetals **4** were obtained in excellent yields under the standard reaction conditions. Importantly, the reaction of **1a** with phenylmethanethiol gave the corresponding thioacetals **4e** in 95% yield. When the hydrothiolation product **3a** was used to replace vinyl ether **1a**, the thioacetal **4a** was obtained in 99% yield in the presence of $CuBr_2$ (Eq. 1). The result indicated that the thioacetals **4** are generated by the reactions of the hydrothiolation products **3** with thiols **2**. Unfortunately, the attempts for selective synthesis of mixed thioacetals from **3** were not successful. For example, the reaction of **3a** and **2c** led to the desired mixed thioacetal **4ab** in 50% yield, accompanying with the formation of **4a** and **4b** (Eq. 2).





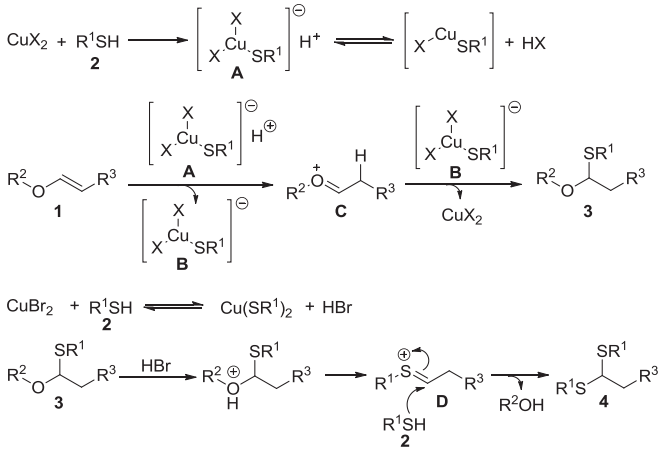
To demonstrate the protocol is practical and useful in organic synthesis, Gram-scale synthesis was investigated (Eq. 3). A 5 mmol-scale of **1a** reacted with **2a** in the presence of $Cu(OAc)_2$ providing **3a** in 1.03 g (92% isolated yield).



A plausible mechanism for the formation of **3** and **4** is described in Scheme 2.[13] A copper thiolate intermediate **A** is generated in situ, and oxygen might accelerate this transportation process. Protonation of alkene **1** leads to an oxonium ion intermediate **C**.[14] Followed by thiolation of **C** with **B** gives Markovnikov-type hydrothiolation product **3**. When $CuBr_2$ is applied as catalyst, a thionium ion intermediate **D** will be subsequently generated due to the HBr generation from the reaction with thiol.[15] The reaction of **D** with thiol **2** generates thioacetal **4** by releasing an alcohol. However, in the case of $Cu(OAc)_2$ as catalyst, the reaction with thiol generates more weaker acetic acid, which cannot accelerate the hydrothiolation.

3. Conclusions

In conclusion, we have developed selective and efficient methods for synthesis of Markovnikov-type hydrothiolation products and thioacetals from the same starting materials, thiophenols



Scheme 2. Proposed mechanism.

and alkenes, by simply switching copper catalysts. The developed protocols are general and practical. Efforts to understand the reaction mechanism and apply this catalytic system to other substrates are under way.

4. Experimental section

4.1. General information

^{1}H NMR spectra were recorded on 400 or 600 MHz spectrometer and the chemical shifts were reported in parts per million (δ) relative to internal standard TMS (0 ppm) for $CDCl_3$. The peak patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). ^{13}C NMR spectra were obtained at 100 or 150 MHz and referenced to the internal solvent signals (central peak is 77.0 ppm in $CDCl_3$). $CDCl_3$ were used as the NMR solvent. HRMS measurements were recorded on a FTMS analyzer using an ESI source in the positive mode. Flash column chromatography was performed over silica gel 200–300. All reagents were weighed and handled in air at room temperature. All reagents were purchased from a commercial source and used without further purification. 1,2-Dichloroethane (DCE) was freshly distilled with calcium hydride before use.

4.2. General procedure for synthesis of hydrothiolation product 3

A dried Schlenk tube was evacuated and then filled with oxygen through an oxygen balloon, then $Cu(OAc)_2$ (4.5 mg, 0.025 mmol) was added under oxygen atmosphere. The Schlenk tube was sealed with a rubber plug, evacuated, and filled with oxygen through an oxygen balloon. Alkene **1** (0.5 mmol), thiophenol **2** (2.0 mmol) and DCE (5.0 mL) were added sequentially. The reaction mixture was vigorously stirred at 50 °C for 3 h. After cooling down to room temperature, the resulting reaction solution was filtered through a pad of silica with ethyl acetate as eluent. The solvent was evaporated in vacuo to give the crude product **3**. NMR yield was determined by ^{1}H NMR using dibromomethane as an internal standard. Solvent was evaporated and the residue was purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether) to afford the product **3**.

4.2.1. (1-Butoxyethyl)(p-tolyl)sulfane ***(3a)****.*[7a] Isolated by flash column chromatography (ethyl acetate/petroleum ether=1:20, R_f=0.4) in 86% yield (96.3 mg). Colorless oil; IR (KBr): ν_{max} 2993, 2362, 1770, 1759, 1216, 1105, 1056, 912, 808, 744 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J*=8.0 Hz, 2H), 7.11 (d, *J*=8.0 Hz, 2H), 4.82 (q, *J*=6.4 Hz, 1H), 3.94–3.85 (m, 1H), 3.47–3.38 (m, 1H), 2.34 (s, 3H), 1.63–1.53 (m, 2H), 1.48 (d, *J*=6.4 Hz, 3H), 1.44–1.34 (m, 2H), 0.93 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 134.2, 129.4, 129.1, 84.7, 67.8, 31.5, 22.5, 21.1, 19.4, 13.9.

4.2.2. (1-Ethoxyethyl)(p-tolyl)sulfane ***(3b)****.* Isolated by flash column chromatography (ethyl acetate/petroleum ether=1:20, R_f=0.5) in 76% yield (74.5 mg). Colorless oil; IR (KBr): ν_{max} 3412, 2976, 1770, 1757, 1637, 1616, 1492, 1442, 1398, 1371, 1245, 1149, 1105, 808 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J*=8.0 Hz, 2H), 7.11 (d, *J*=8.0 Hz, 2H), 4.82 (q, *J*=6.4 Hz, 1H), 4.03–3.89 (m, 1H), 3.54–3.41 (m, 1H), 2.33 (s, 3H), 1.48 (d, *J*=6.4 Hz, 3H), 1.22 (t, *J*=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 134.3, 129.5, 129.0, 84.6, 63.4, 22.7, 21.1, 14.9; HRMS calcd for $C_{11}H_{16}NaOS$ (M+Na)$^+$: 219.0814; found: 219.0805.

4.2.3. (1-Isobutoxyethyl)(p-tolyl)sulfane ***(3c)****.* Isolated by flash column chromatography (ethyl acetate/petroleum ether=1:20, R_f=0.7) in 68% yield (76.2 mg). Colorless oil; IR (KBr): ν_{max} 2956, 2927, 1768, 1757, 1490, 1375, 1245, 1103, 1089, 1055, 912, 808, 742 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J*=8.0 Hz, 2H), 7.10 (d, *J*=8.0 Hz, 2H), 4.82 (q, *J*=6.4 Hz, 1H), 3.65 (dd, *J*=9.2, 6.8 Hz, 1H), 3.20 (dd, *J*=9.2, 6.8 Hz, 1H), 2.32 (s, 3H), 1.94–1.77 (m, 1H), 1.47 (d, *J*=6.4 Hz, 3H), 0.95–0.89 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 134.1, 129.4, 129.1, 84.9, 74.8, 28.3, 22.5, 21.1, 19.5; HRMS calcd for $C_{13}H_{20}NaOS$ (M+Na)$^+$: 247.1127; found: 247.1112.

4.2.4. (1-(Cyclohexyloxy)ethyl)(p-tolyl)sulfane ***(3d)****.* Isolated by flash column chromatography (ethyl acetate/petroleum ether=1:20, R_f=0.5) in 90% yield (112.5 mg). Colorless oil; IR (KBr): ν_{max} 2929, 2854, 1772, 1490, 1448, 1367, 1245, 1099, 1087, 1055, 972, 808 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J*=8.0 Hz, 2H), 7.10 (d, *J*=8.0 Hz, 2H), 4.95 (q, *J*=6.4 Hz, 1H), 3.84–3.71 (m, 1H), 2.33 (s, 3H), 1.95–1.82 (m, 2H), 1.79–1.67 (m, 2H), 1.58–1.50 (m, 1H), 1.45 (d, *J*=6.4 Hz, 3H), 1.41–1.15 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 134.5, 129.4, 128.9, 81.6, 74.7, 33.1, 31.1, 25.7, 24.3, 24.0, 23.2, 21.1; HRMS calcd for $C_{15}H_{22}NaOS$ (M+Na)$^+$: 273.1284; found: 273.1273.

4.2.5. (1-(2-Chloroethoxy)ethyl)(p-tolyl)sulfane ***(3e)****.* Isolated by flash column chromatography (ethyl acetate/petroleum ether=1:20, R_f=0.6) in 57% yield (66.0 mg). Colorless oil; IR (KBr): ν_{max} 2980, 1768, 1757, 1490, 1445, 1373, 1242, 1107, 1051, 912, 810, 744 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J*=8.0 Hz, 2H), 7.12 (d, *J*=8.0 Hz, 2H), 4.90 (q, *J*=6.4 Hz, 1H), 4.17–4.08 (m, 1H), 3.76–3.68 (m, 1H), 3.67–3.62 (m, 2H), 2.34 (s, 3H), 1.50 (d, *J*=6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 134.2, 129.5, 128.4, 84.9, 67.7, 42.7, 22.2, 21.1; HRMS calcd for $C_{11}H_{15}ClNaOS$ (M+Na)$^+$: 253.0424; found: 253.0414.

4.2.6. (((Oxybis(ethane-2,1-diyl))bis(oxy))bis(ethane-1,1-diyl))bis(p-tolylsulfane) ***(3f)****.* Isolated by flash column chromatography (ethyl acetate/petroleum ether=1:10, R_f=0.3) in 66% yield (133.9 mg). Colorless oil; IR (KBr): ν_{max} 2976, 2926, 2866, 1768, 1757, 1492, 1371, 1245, 1103, 1087, 912, 810, 742 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J*=8.0 Hz, 4H), 7.10 (d, *J*=8.0 Hz, 4H), 4.94–4.84 (m, 2H), 4.11–3.98 (m, 2H), 3.73–3.59 (m, 6H), 2.32 (s, 6H), 1.48 (d, *J*=6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 134.1, 129.4, 128.8, 84.9, 70.2, 70.1, 66.9, 22.4, 21.0; HRMS calcd for $C_{22}H_{30}NaO_3S_2$ (M+Na)$^+$: 429.1529; found: 429.1518.

4.2.7. (1-Ethoxypropyl)(p-tolyl)sulfane ***(3g)****.* Isolated by flash column chromatography (ethyl acetate/petroleum ether=1:20,

R_f=0.6) in 80% yield (84.0 mg). Colorless oil; IR (KBr): ν_{max} 2980, 2935, 1768, 1759, 1490, 1375, 1246, 1058, 912, 744 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J=8.0 Hz, 2H), 7.10 (d, J=8.0 Hz, 2H), 4.53 (t, J=6.4 Hz, 1H), 4.05–3.92 (m, 1H), 3.53–3.40 (m, 1H), 2.32 (s, 3H), 1.84–1.64 (m, 2H), 1.22 (t, J=7.2 Hz, 3H), 0.99 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 134.1, 129.4, 129.3, 90.9, 63.5, 29.1, 21.1, 14.8, 10.8; HRMS calcd for $C_{12}H_{18}NaOS$ $(M+Na)^+$: 233.0971; found: 233.0959.

4.2.8. 2-(p-Tolylthio)tetrahydro-2H-pyran ***(3h)***.[16] Isolated by flash column chromatography (ethyl acetate/petroleum ether=1:20, R_f=0.5) in 70% yield (72.8 mg). Colorless oil; IR (KBr): ν_{max} 2937, 2862, 1770, 1757, 1492, 1438, 1242, 1186, 1103, 1076, 1035, 1004, 914, 808, 721 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J=8.0 Hz, 2H), 7.10 (d, J=8.0 Hz, 2H), 5.20–5.06 (m, 1H), 4.23–4.10 (m, 1H), 3.63–3.50 (m, 1H), 2.32 (s, 3H), 2.07–1.94 (m, 1H), 1.91–1.75 (m, 2H), 1.68–1.54 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 131.6, 131.4, 129.5, 85.6, 64.6, 31.5, 25.5, 21.7, 21.0.

4.2.9. 2-(p-Tolylthio)tetrahydrofuran ***(3i)***.[17] Isolated by flash column chromatography (ethyl acetate/petroleum ether=1:20, R_f=0.5) in 77% yield (74.7 mg). Colorless oil; IR (KBr): ν_{max} 2976, 2949, 2868, 1768, 1757, 1492, 1375, 1242, 1049, 912, 808, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J=8.0 Hz, 2H), 7.10 (d, J=8.0 Hz, 2H), 5.61–5.53 (m, 1H), 4.06–3.97 (m, 1H), 3.97–3.89 (m, 1H), 2.38–2.29 (m, 1H), 2.31(S, 3H), 2.06–1.80 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 131.7, 129.5, 87.4, 67.1, 32.5, 24.7, 21.0.

4.2.10. 1-(1-(p-Tolylthio)ethyl)pyrrolidin-2-one ***(3j)***.[7a] Isolated by flash column chromatography (ethyl acetate/petroleum ether=1:1, R_f=0.2) in 87% yield (102.2 mg). Colorless oil; IR (KBr): ν_{max} 2976, 1768, 1691, 1597, 1490, 1458, 1411, 1375, 1282, 1199, 1058, 808, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J=8.0 Hz, 2H), 7.08 (d, J=8.0 Hz, 2H), 5.83 (q, J=6.8 Hz, 1H), 3.64–3.54 (m, 1H), 3.37–3.26 (m, 1H), 2.30 (s, 3H), 2.29–2.21 (m, 1H), 2.15–2.04 (m, 1H), 1.99–1.74 (m, 2H), 1.47 (d, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 137.7, 132.8, 129.5, 129.1, 54.8, 41.2, 31.1, 21.1, 18.8, 17.6.

4.2.11. 1-(1-(p-Tolylthio)ethyl)azepan-2-one ***(3k)***. Isolated by flash column chromatography (ethyl acetate/petroleum ether=1:5, R_f=0.3) in 84% yield (110.5 mg). White solid; IR (KBr): ν_{max} 2964, 2927, 2856, 1643, 1492, 1438, 1411, 1259, 1182, 1145, 1091, 1062, 975, 806, 729 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J=8.0 Hz, 2H), 7.07 (d, J=8.0 Hz, 2H), 6.45 (q, J=6.8 Hz, 1H), 3.52–3.43 (m, 1H), 3.34–3.24 (m, 1H), 2.42–2.32 (m, 2H), 2.29 (s, 3H), 1.69–1.46 (m, 6H), 1.41 (d, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 136.7, 130.9, 130.1, 129.5, 56.3, 42.6, 37.3, 29.8, 29.0, 23.2, 21.0, 19.1; HRMS calcd for $C_{15}H_{21}NNaOS$ $(M+Na)^+$: 286.1236; found: 286.1227.

4.2.12. (1-Butoxyethyl)(phenyl)sulfane ***(3m)***.[7a] Isolated by flash column chromatography (ethyl acetate/petroleum ether=1:10, R_f=0.6) in 68% yield (71.4 mg). Colorless oil; IR (KBr): ν_{max} 2958, 2929, 2870, 1768, 1757, 1475, 1371, 1246, 1109, 912, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51–7.44 (m, 2H), 7.33–7.23 (m, 3H), 4.89 (q, J=6.4 Hz, 1H), 3.94–3.82 (m, 1H), 3.50–3.37 (m, 1H), 1.63–1.52 (m, 2H), 1.50 (d, J=6.4 Hz, 3H), 1.45–1.33 (m, 2H), 0.92 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.7, 133.1, 128.6, 127.4, 84.6, 67.7, 31.5, 22.5, 19.4, 13.9.

4.2.13. (1-Butoxyethyl)(4-methoxyphenyl)sulfane ***(3n)***.[7a] Isolated by flash column chromatography (ethyl acetate/petroleum ether=1:20, R_f=0.2) in 84% yield (100.8 mg). Colorless oil; IR (KBr): ν_{max} 2958, 2931, 2870, 1591, 1492, 1244, 1103, 1089, 1033, 827, 744 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43–7.37 (m, 2H), 6.89–6.82 (m, 2H), 4.73 (q, J=6.4 Hz, 1H), 3.96–3.87 (m, 1H), 3.80 (s, 3H), 3.46–3.34 (m, 1H), 1.62–1.53 (m, 2H), 1.43 (d, J=6.4 Hz, 3H), 1.43–1.33 (m, 2H), 0.93 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 136.5, 122.8, 114.2, 84.9, 68.0, 55.3, 31.5, 22.5, 19.4, 13.9.

4.2.14. (4-Bromophenyl)(1-butoxyethyl)sulfane ***(3o)***. Isolated by flash column chromatography (ethyl acetate/petroleum ether=1:20, R_f=0.7) in 86% yield (123.8 mg). Colorless oil; IR (KBr): ν_{max} 2956, 2931, 2870, 1768, 1471, 1384, 1371, 1246, 1109, 1085, 1010, 912, 815, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46–7.39 (m, 2H), 7.36–7.30 (m, 2H), 4.87 (q, J=6.4 Hz, 1H), 3.91–3.80 (m, 1H), 3.48–3.37 (m, 1H), 1.65–1.53 (m, 2H), 1.48 (d, J=6.4 Hz, 3H), 1.44–1.32 (m, 2H), 0.92 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.1, 132.2, 131.7, 121.7, 84.5, 67.7, 31.4, 22.4, 19.4, 13.9; HRMS calcd for $C_{12}H_{17}BrNaOS$ $(M+Na)^+$: 311.0076; found: 311.0080.

4.2.15. (1-Butoxyethyl)(2,4-dimethylphenyl)sulfane ***(3p)***. Isolated by flash column chromatography (ethyl acetate/petroleum ether=1:20, R_f=0.7) in 72% yield (85.7 mg). Colorless oil; IR (KBr): ν_{max} 2955, 1768, 1757, 1475, 1373, 1242, 1097, 1055, 912, 812, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J=8.0 Hz, 1H), 7.03 (s, 1H), 7.95 (d, J=8.0 Hz, 1H), 4.84 (q, J=6.4 Hz, 1H), 3.90–3.80 (m, 1H), 3.46–3.35 (m, 1H), 2.41 (s, 3H), 2.29 (s, 3H), 1.61–1.51 (m, 2H), 1.47 (d, J=6.4 Hz, 3H), 1.41–1.33 (m, 2H), 0.91 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 137.6, 134.7, 131.0, 129.0, 127.0, 84.9, 67.8, 31.5, 22.5, 21.1, 21.0, 19.4, 13.9; HRMS calcd for $C_{14}H_{22}NaOS$ $(M+Na)^+$: 261.1284; found: 261.1301.

4.2.16. (1-Butoxyethyl)(2-chlorophenyl)sulfane ***(3q)***. Isolated by flash column chromatography (ethyl acetate/petroleum ether=1:20, R_f=0.6) in 68% yield (83.0 mg). Colorless oil; IR (KBr): ν_{max} 2958, 2929, 1452, 1373, 1247, 1105, 1035, 750, 661 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.66–7.59 (m, 1H), 7.44–7.36 (m, 1H), 7.23–7.15 (m, 2H), 5.07 (q, J=6.4 Hz, 1H), 3.86–3.77 (m, 1H), 3.50–3.42 (m, 1H), 1.58 (d, J=6.4 Hz, 3H), 1.57–1.51 (m, 2H), 1.41–1.30 (m, 2H), 0.90 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 134.0, 133.3, 129.7, 128.1, 126.9, 84.3, 67.2, 31.5, 22.1, 19.3, 13.8; HRMS calcd for $C_{12}H_{17}ClNaOS$ $(M+Na)^+$: 267.0581; found: 267.0573.

4.2.17. (1-Butoxyethyl)(naphthalen-1-yl)sulfane ***(3r)***. Isolated by flash column chromatography (ethyl acetate/petroleum ether=1:20, R_f=0.5) in 85% yield (109.2 mg). Colorless oil; IR (KBr): ν_{max} 2956, 2931, 1768, 1759, 1373, 1242, 1097, 1055, 912, 796, 771, 744 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J=8.4 Hz, 1H), 7.87–7.74 (m, 3H), 7.59–7.47 (m, 2H), 7.45–7.38 (m, 1H), 4.98 (q, J=6.4 Hz, 1H), 3.95–3.86 (m, 1H), 3.49–3.39 (m, 1H), 1.60–1.51 (m, 2H), 1.48 (d, J=6.4 Hz, 3H), 1.41–1.31 (m, 2H), 0.90 (t, J=7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.0, 134.0, 133.4, 131.0, 128.6, 128.4, 126.4, 126.1, 126.0, 125.5, 85.6, 68.1, 31.5, 22.7, 19.4, 13.8; HRMS calcd for $C_{16}H_{21}OS$ $(M+H)^+$: 261.1308; found: 261.1302.

4.3. General procedure for synthesis of thioacetal 4

A dried Schlenk tube was evacuated and then filled with oxygen through an oxygen balloon, then $CuBr_2$ (5.6 mg, 0.025 mmol) was added under oxygen atmosphere. The Schlenk tube was sealed with a rubber plug, evacuated, and filled with oxygen through an oxygen balloon. Alkene **1** (0.5 mmol), thiophenol **2** (2.0 mmol) and DCE (5.0 mL) were added sequentially. The reaction mixture was vigorously stirred at 50 °C for 3 h. After cooling down to room temperature, the resulting reaction solution was filtered through a pad of silica with ethyl acetate as eluent. The solvent was evaporated in vacuo to give the crude product **4**. NMR yield was determined by ^1H NMR using dibromomethane as an internal standard. Solvent was evaporated and the residue was purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether) to afford the product **4**.

*4.3.1. Ethane-1,1-diylbis(p-tolylsulfane) (**4a**).* Isolated by flash column chromatography (ethyl acetate/petroleum ether=1:20, R_f=0.7) in 91% yield (124.6 mg). Colorless oil; IR (KBr): ν_{max} 2976, 1770, 1757, 1490, 1240, 1049, 912, 808, 744 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J=8.0 Hz, 4H), 7.12 (d, J=8.0 Hz, 4H), 4.42 (q, J=6.8 Hz, 1H), 2.34 (s, 6H), 1.55 (d, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 133.5, 130.3, 129.6, 52.8, 22.6, 21.2; HRMS calcd for $C_{16}H_{18}NaS_2$ $(M+Na)^+$: 297.0742; found: 297.0743.

*4.3.2. Ethane-1,1-diylbis((4-methoxyphenyl)sulfane) (**4b**).* Isolated by flash column chromatography (ethyl acetate/petroleum ether=1:20, R_f=0.3) in 95% yield (145.4 mg). Colorless oil; IR (KBr): ν_{max} 2960, 1770, 1589, 1490, 1284, 1244, 1170, 1029, 912, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J=8.8 Hz, 4H), 6.85 (d, J=8.8 Hz, 4H), 4.24 (q, J=6.8 Hz, 1H), 3.80 (s, 6H), 1.50 (d, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 136.1, 124.2, 114.3, 55.3, 54.3, 22.5; HRMS calcd for $C_{16}H_{18}NaO_2S_2$ $(M+Na)^+$: 329.0640; found: 329.0645.

*4.3.3. Ethane-1,1-diylbis((4-bromophenyl)sulfane) (**4c**).* Isolated by flash column chromatography (ethyl acetate/petroleum ether=1:20, R_f=0.7) in 90% yield (180.5 mg). Colorless oil; IR (KBr): ν_{max} 2968, 2920, 1770, 1757, 1558, 1472, 1384, 1246, 1008, 912, 814, 743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J=8.4 Hz, 4H), 7.30 (d, J=8.4 Hz, 4H), 4.47 (q, J=6.8 Hz, 1H), 1.58 (d, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.5, 132.7, 132.0, 122.3, 52.3, 22.5; HRMS calcd for $C_{14}H_{12}Br_2NaS_2$ $(M+Na)^+$: 424.8639; found: 424.8652.

*4.3.4. Ethane-1,1-diylbis((2,4-dimethylphenyl)sulfane) (**4d**).* Isolated by flash column chromatography (ethyl acetate/petroleum ether=1:20, R_f=0.8) in 94% yield (141.9 mg). Colorless oil; IR (KBr): ν_{max} 2972, 2920, 1770, 1757, 1474, 1246, 1047, 912, 813, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J=8.0 Hz, 2H), 7.01 (s, 2H), 6.95 (d, J=8.0 Hz, 2H), 4.33 (q, J=6.8 Hz, 1H), 2.34 (s, 6H), 2.28 (s, 6H), 1.57 (d, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 137.9, 133.9, 131.2, 130.2, 127.1, 52.2, 22.7, 21.0, 20.7; HRMS calcd for $C_{18}H_{22}NaS_2$ $(M+Na)^+$: 325.1055; found: 325.1060.

*4.3.5. Ethane-1,1-diylbis(benzylsulfane) (**4e**).*[18] Isolated by flash column chromatography (ethyl acetate/petroleum ether=1:20, R_f=0.2) in 86% yield (117.3 mg). Colorless oil; IR (KBr): ν_{max} 2964, 1757, 1494, 1452, 1371, 1240, 1049, 912, 741, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32–7.18 (m, 10H), 3.85 (d, J=13.2 Hz, 2H), 3.73 (d, J=13.2 Hz, 2H), 3.63 (q, J=6.8 Hz, 1H), 1.52 (d, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 128.9, 128.5, 126.9, 44.5, 34.9, 22.5.

*4.3.6. Propane-1,1-diylbis(p-tolylsulfane) (**4f**).* Isolated by flash column chromatography (ethyl acetate/petroleum ether=1:20, R_f=0.8) in 91% yield (131.0 mg). Colorless oil; IR (KBr): ν_{max} 3477, 3414, 2966, 1770, 1759, 1616, 1490, 1450, 1240, 1049, 912, 808, 742, 623, 495 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41–7.33 (m, 4H), 7.16–7.06 (m, 4H), 4.23 (t, J=6.6 Hz, 1H), 2.34 (s, 6H), 1.88–1.78 (m, 2H), 1.11 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 133.3, 130.6, 129.6, 60.8, 28.8, 21.1, 11.7; HRMS calcd for $C_{17}H_{20}NaS_2$ $(M+Na)^+$: 311.0899; found: 311.0904.

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Supplementary data

Supplementary data(Copies of ^1H and ^{13}C NMR spectra of all new compounds) associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2016.05.050.

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