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Transition-Metal-Free Olefinic C–H Azidoalkylthiolation *via* C(sp^3)–S Bond Cleavage of Vinylsulfonium Salts

Yuan He,[a, b] Zilong Huang,[a, b] Juan Ma,[a, b] Jie Lin,[a, b] Yong-Gui Zhou,[a,*] and Zhengkun Yu[a, c, d,*]

[a] Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian, Liaoning 116023, People's Republic of China
E-mail: zkyu@dicp.ac.cn; ygzhou@dicp.ac.cn
[b] University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China
[c] Innovation Academy for Green Manufacture, Chinese Academy of Sciences, Beijing 100190, People's Republic of China
[d] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, People's Republic of China
Fax: +86-411-8437-9227

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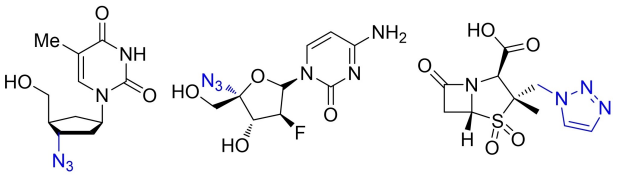
Abstract: A transition-metal-free olefinic C–H azidoalkylthiolation protocol was developed through C(sp^3)–S bond cleavage of vinylsulfonium salts with sodium azide in air under aqueous conditions. An interrupted Pummerer/nucleophilc azidoalkylation cascade was developed for such a process. The practicability of the synthetic protocol was demonstrated by scale-up preparation of the azidoalkylthiolated tetrasubstituted alkene products and their transformations to diverse triazole and tetrazole derivatives as well as azidoalkylthio-funtionalized *N*-heterocyclic compounds. The present synthetic methodology features broad substrate scopes and good functional group tolerance under mild conditions.

Keywords: azidoalkylation; vinyl sulfonium salts; C(sp^3)–H functionalization; sodium azide; C(sp^3)–S cleavage

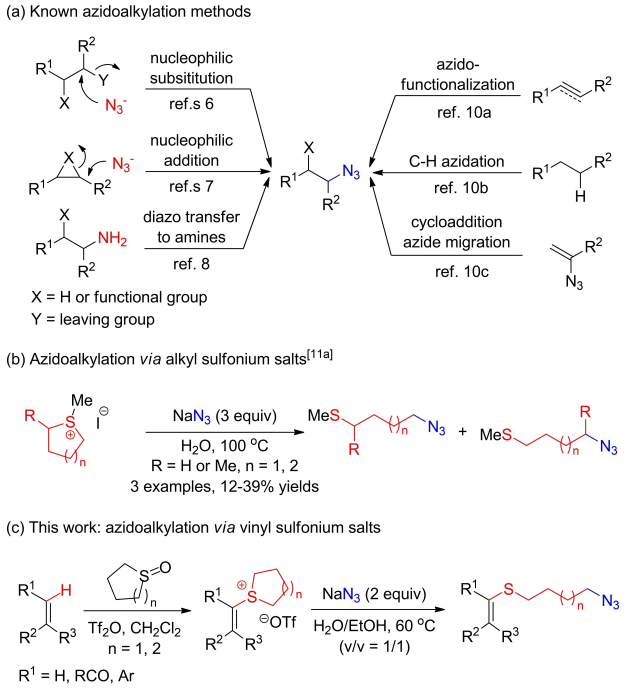
Introduction

Azido compounds are important intermediates in organic synthesis, and azido group (N_3) exists in some natural and synthetic functional materials. For example, alkylazido-substituted β-thymidines can act as anti-HIV drug[1] and HCV inhibitor,[2] and tazobactam with a thiazole structural motif which is generated from a N_3-containing compound (azide) has been used as a β-lactam antibiotic[3] (Scheme 1). Owing to the potential importance of N_3-bearing compounds and their derivatives various methods have been developed for the synthesis of diverse organic azides and their transformations.[4] Reactive azides usually serve as intermediates for a large number of transformations that afford amines, imines, amides, aziridines, triazoles, and other *N*-heterocycles.[5,6] These conversions are either based on [3+2] cycloadditions,[7] or Staudinger-type transformations.[8] Moreover, organic azides are convenient nitrene precursors, featuring no need of external oxidant and release of N_2 as the only by-product.[9a] In this context, development of sustainable methods for the establishment of C(sp^3)–N_3 bonds is extremely desired not only in organic synthesis but also in drug discovery.



Scheme 1. Representative biologically active alkyl azides and derivatives.

To access alkyl azides, three general methods have been developed: nucleophilic substitution, addition of an azido anion to electrophilic substrates and diazo transfer to primary amines with triflyl azide (Scheme 2a, left).[6–8] Azidoalkylation can also be achieved



Scheme 2. Azidoalkylation strategies.

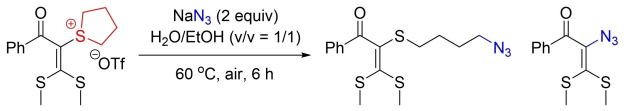
by means of azide compounds and specific radical sources.[9b–h] However, the classic nucleophilic substitution and addition reactions usually require substrate prefunctionalization and/or harsh (elaborate) reaction conditions, which leads to the target products in low yields with narrow substrate scopes, poor functional group tolerance, long reaction time, and/or complicated work-up manipulations. In addition, these known methods still remain a significant challenge in their practical applications. Thus, there has been an urgent need to develop applicable synthetic methodologies of complex alkyl azides. Radical-initiated azidation of C–C multiple bonds provides a powerful approach for the synthesis of functionalized alkyl azides.[10a] Regioselective introduction of an azido group through direct C(sp^3)–H transformation avoids prefunctionalization of the substrates and offers a straightforward access to the desired scaffold in high atom and step-economy.[10b] Cycloaddition, cyclization, and migration reactions of vinyl azides in which the azide functionality is kept in the final products are also potentially useful for the synthesis of alkyl azides which are difficult to be constructed by the conventional methods (Scheme 2a, right).[10c] It has been known that *S*-alkyl tetrahydro-1*H*-thiophen-1-ium salts and analogs can undergo nucleophilic ring-opening reactions with nucleophiles such as azide, thiolates, halogens, amines.[11] Unfortunately, in the case of azidoalkylation with sodium azide only three inefficient examples were reported (12–39% yields) through ring opening of the alkylsulfonium salts (Scheme 2b).[11a]

Arylsulfonium salts have been paid much attention as useful coupling partners[12] not only in light of their accessibility from simple arenes but also due to their versatility for many C–C[13] and C–X[14] bond formation reactions. As two types of common arylsulfonoum salts, aryl thianthrenium salts and dibenzothiophene sulfonium salts have been successfully applied for site-selective late-stage diversification of C–N cross-couplings.[14a,b] However, the analogs of aryl sulfonium salts, that is, vinylsulfonium salts, have been paid much less attention as applicable coupling partners.[15] Very recently, Wen and coworkers realized the synthesis of alkyl amines *via* the C(sp^3)–S bond cleavage of vinylsulfonium salts.[15g] During the continuous exploration of the multiple reactivities of functionalized olefins,[12b,16] we recently achieved palladium-catalyzed C–H fluoroalkylthiolation through C(sp^3)–S bond cleavage of vinylsulfonium salts with CsF.[17] We thus envisioned the possible azidoalkylthiolation of vinylsulfonium salts using a similar strategy. Herein, we report an interrupted Pummerer/transition-metal-free azidoalkylation cascade for olefinic C–H azidoalkylthiolation *via* vinylsulfonium salts (Scheme 2c).

Results and Discussion

Initially, the reaction of 1-(1,1-bis(methylthio)-3-oxo-3-phenylprop-1-en-2-yl)tetrahydro-1*H*-thiophen-1-ium trifluoro-methanesulfonate (**1 a**) and sodium azide (NaN_3) was conducted to screen the reaction conditions for the formation of 2-((4-azidobutyl)thio)-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (**2 a**). Vinylsulfonium salt **1 a** and its analogs were efficiently prepared from the readily available alkenes by the well-known interrupted Pummerer reaction (see the SI for details). The reaction conditions for the synthesis of **2 a** (93%) were optimized to: molar ratio of **1 a**: NaN_3 = 1:2, H_2O/EtOH (v/v = 1/1) as the solvent, 60 °C, and 6 h under an air atmosphere (Table 1, entry 1). The reaction reached 73% yield for the target product under aqueous conditions, and use of an organic solvent such as ethanol increased the yield to 81% (Table 1, entries 2 and 3). It is noteworthy that addition of an organic solvent improved the solubility of substrate **1 a** in the reaction medium, which thus increased the product yields to 92–94% (Table 1, entries 1, 4, and 5). Although the MeOH/H_2O solvent system behaved a little bit better than EtOH/H_2O did, the latter was chosen as the reaction medium due to the lower toxicity of ethanol. Change of trifluoromethanesulfonate anion with tetrafluoroborate or hexafluorophosphate diminished the yields to 69–73% (Table 1, entries 6 and 7). The counterions exhibited an obvious impact on the reactivity of the sulfonium salt presumably due to the electronegativity of the oxygen atom in OTf^- anion greater than those of the central atoms in BF_4^- and PF_6^- anions. In our case, OTf^- anion is more

Table 1. Screening of reaction conditions.[a]



1a **2a** **2a'**, N.D.

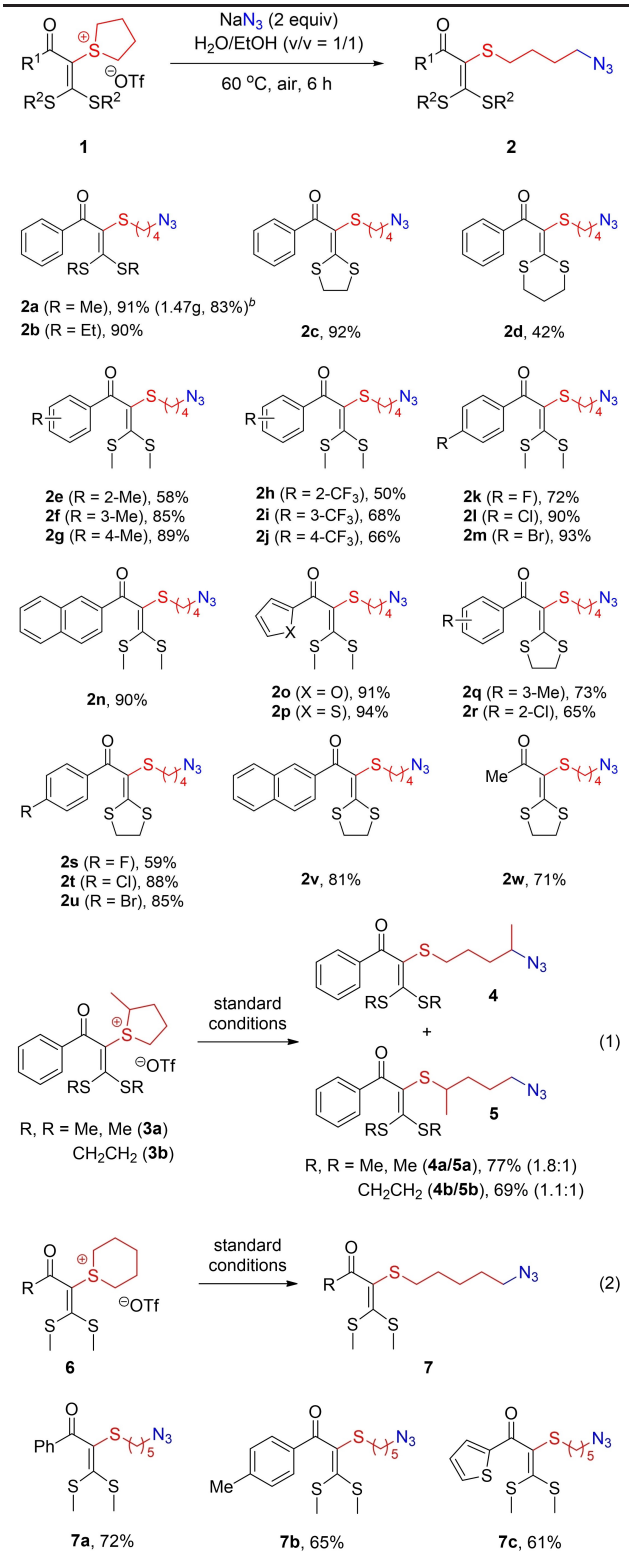
Entry	Variation	Yield of **2a**[b] [%]
1	none	93 (91)[c]
2	H_2O as the sole solvent	73
3	EtOH as the sole solvent	81
4	H_2O/MeCN (v/v = 1/1)	92
5	H_2O/MeOH (v/v = 1/1)	94
6	BF_4^- instead of OTf^-	73
7	PF_6^- instead of OTf^-	69
8	70 °C instead of 60 °C	86
9	50 °C instead of 60 °C	80
10	using covalent azide source instead of NaN_3[d]	trace
11	under 0.1 MPa O_2 atmosphere	90
12	under 0.1 MPa N_2 atmosphere	92

[a] Conditions: **1a** (0.3 mmol), NaN_3 (0.6 mmol), solvent (2 mL), air, 6 h.
[b] Determined by ^1H NMR analysis using 1,3,5-trimethoxylbenzene as the internal standard.
[c] Isolated yield given in parentheses.
[d] Using $TMSN_3$, *p*-TsN_3, or $Ph_2P(O)N_3$.

compatible with the alkenylsulfonium cation than other counterions. 60 °C seemed to be the appropriate reaction temperature (Table 1, entries 8 and 9). Covalent azide sources, i.e., trimethylsilyl azide, *p*-tosyl azide, and diphenylphosphoryl azide, failed to undergo the azidoalkylation reaction (Table 1, entry 10). For manipulation simplicity, the reaction was conducted under an air atmosphere (Table 1, entries 11 and 12). It should be noted that vinyl azide **2a′** was not detected in the reaction mixture under the stated conditions.

Next, the scope of vinylsulfonium salts **1** generated from di(alkylthio)-substituted alkenes, that is, ketene dithioacetals, was investigated under the optimal conditions (Table 2). This type of substrates showed moderate to excellent reactivity to form the target azidoalkylation products of type **2**. On a 5 mmol scale of **1a** product **2a** was still obtained in 83% yield. Di(ethylthio) and ethylene disulfide group-substituted vinylsulfonium salts (**1b–1c**) also efficiently reacted with NaN_3 to give products **2b–2c** (90–92%). However, cycloalkyldithio $S(CH_2)_3S$-substituted α-benzoyl vinylsulfonium salt **1d** only exhibited a moderate reactivity to generate **2d** (42%). The yield of **2d** is much lower than **2c**, which is a result of the unidentified side reactions. An obvious steric effect was observed from *ortho*-methyl group on the α-benzoyl moiety of vinylsulfonium **1e**, leading to **2e** in 58% yield, while 3- and 4-methyl-substituted ketene

Table 2. Scope of vinylsulfonium salts (**1**).[a]



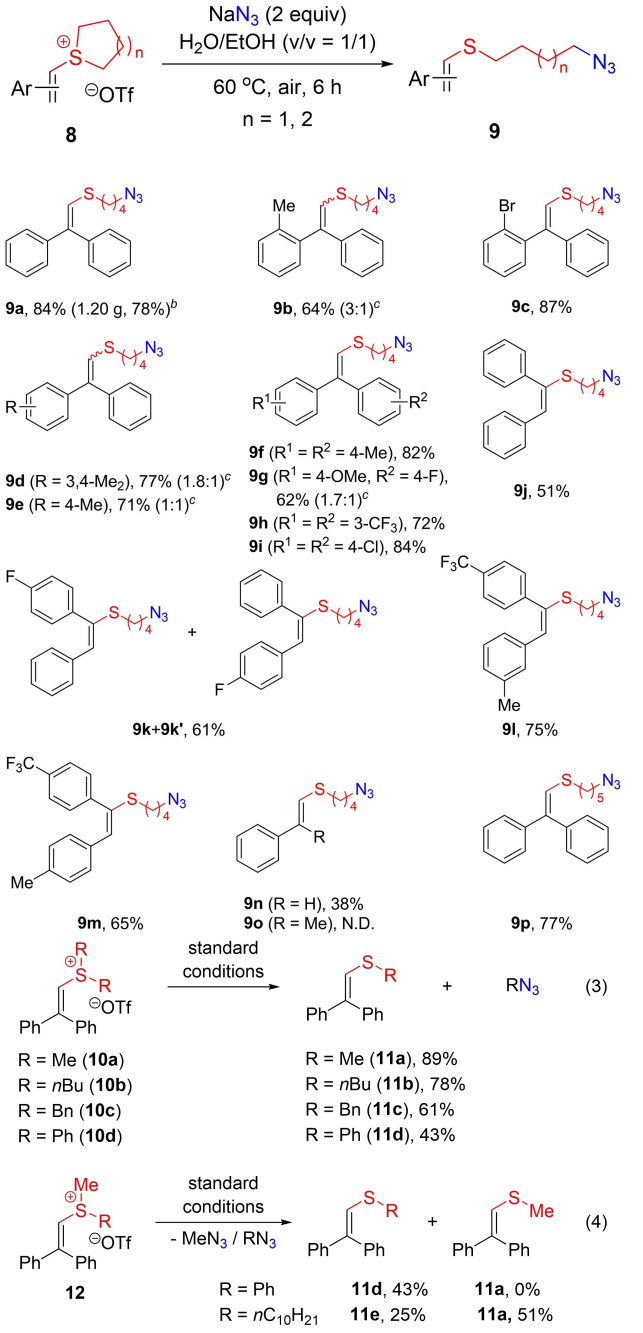
[a] Conditions: **1** (0.30 mmol), NaN_3 (0.60 mmol), H_2O/EtOH (v/v = 1/1, 2 mL), air, 60 °C, 6 h. Yields refer to the isolated products.
[b] **1** (5.0 mmol), NaN_3 (10.0 mmol), H_2O/EtOH (v/v = 1/1, 20 mL).

dithioacetals **1f** and **1g** efficiently reacted with NaN_3 to afford **2f** (85%) and **2g** (89%), respectively. Electron-withdrawing trifluoromethyl had an obvious negative impact on the reaction efficiency, resulting in **2h**–**2j** in 50–68% yields. 4-Halogen (F, Cl, and Br) functionalized vinylsulfonium salts **1k**–**1m** also reacted well with NaN_3 to give **2k**–**2m** (72–93%). The bulkiness of 2-naphthoyl did not affect generation of the target product (**2n**, 90%) either. It is noteworthy that α-heteroaroyl such as 2-furoyl or 2-thienoyl-substituted vinylsulfonium salts reacted well with NaN_3 to give **2o** and **2p** in 91–94% yields. In a similar fashion, cycloalkyldithio-substituted vinylsulfonium salts, that is, α-benzoyl ketene dithioacetals **1q**–**1u**, underwent the same type of reaction to form the corresponding products **2q**–**2u** (59–88%). The reactions of α-(2-naphthoyl) and α-acetyl-fuctionalized vinylsulfonium salts **1v** and **1w** with NaN_3 also smoothly proceeded to give **2v** and **2w** (71–81%).

In order to further probe into the C-S bond reactivity of vinylsulfonium salts, the substituent and size effects from the cycloalkylsulfonium ring were explored [Eq.s (1–2)]. The vinylsulfonium salts derived from 2-methyltetrahydro-1*H*-thiophene, that is, vinylsulfonium salts **3a** and **3b**, with NaN_3 gave a mixture of two inseparable azidoalkylation products **4a**/**5a** (77%, 1.8:1) and **4b**/**5b** (69%, 1.1:1) *via* different aliphatic C–S bond cleavages of the cycloalkylsulfonium ring [Eq. (1)], which reveals that the sterically hindered C(sp^3)–S bond is easier to be cleaved. However, the corresponding vinylsulfonium salt of thietane ($(CH_2)_3S$) was decomposed quickly under the standard conditions. To our delight, the vinylsulfonium salts (**6**) of tetrahydro-2*H*-thiopyrans could efficiently react with NaN_3 to afford the target C_5-azidoalkylthio functionality-bearing products **7a**–**7c** (61–72%) [Eq. (2)]. Unfortunately, the vinylsulfonium salts derived from the large-ring aliphatic cyclic sulfoxides $C_nH_{2n}S{=}O$ ($n \geq 6$) could not be successfully prepared by the known methods, we thus failed to further expand the azidoalkylthio chain. Vinyl thianthrenium and dibenzothiophenium salts were also tested under the standard conditions, which exhibited a negative steric/electronic effect to result in none of the target azidoalkylthiolation products.

The scope of other types of vinylsulfonium salts, that is, styryl sulfonium salts (**8**), was also investigated (Table 3). 1,1-Diphenyl-substituted vinylsulfonium salt **8a** reacted with NaN_3 under the optimal conditions to give the target product **9a** in 84% yield. A gram-scale preparation also efficiently produced compound **9a** (78%). When two different aryls were installed at the same terminus of the vinyl moiety, a mixture of two isomeric azidoalkylation products were usually isolated. Thus, compounds **9b** (64%, *E*/*Z* = 3:1), **9d** (77%, *E*/*Z* = 1.8:1), **9e** (71%, *E*/*Z* = 1:1), and **9g** (62%, *E*/*Z* = 1.7:1) were obtained. It should be noted that in the cases of using unsymmetrical alkenylsulfonium salts the *E*/*Z* ratios of the isolated azidoalkylation products remain unchanged as compared to those of the starting sulfonium salts. It is notable that a steric

Table 3. Scope of styrylsulfonium salts (**8**).[a]



[a] Conditions: **8** (0.30 mmol), NaN_3 (0.60 mmol), H_2O/EtOH (v/v = 1/1, 2 mL), air, 60 °C, 6 h. Yields refer to the isolated products.

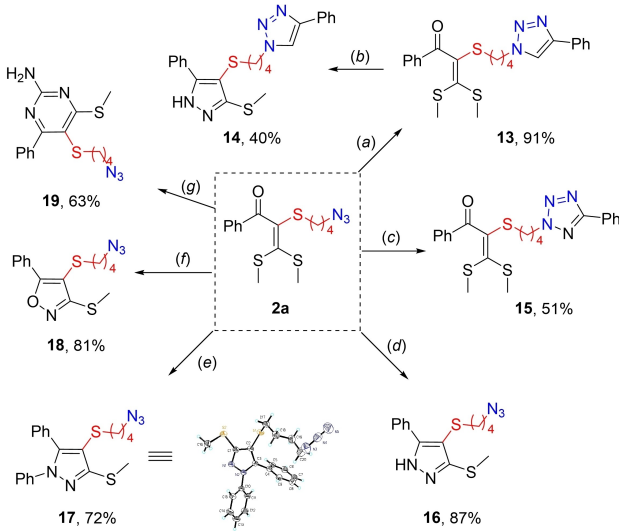
[b] 8 (5.0 mmol), NaN_3 (10.0 mmol), H_2O/EtOH (v/v = 1/1, 20 mL).

[c] The *E*/*Z* isomer ratio was determined from the isolated products by ^{1}H NMR analysis.

effect was observed from the *ortho*-methyl group, leading to **9b** in 64% yield, while the negative steric effect could be compensated by the electronic effect of the *ortho*-bromo group to result in **9c** (87%) as a single (*E*)-isomer. In the cases of placing two same aryls at the same terminus of the vinyl moiety, single isomeric products **9f** and **9h**–**9i** (72–84%) were efficiently generated. 1,2-Diaryl-functionalized vinylsulfonium salts, that is, the sulfonium salts of 1,2-stilbenes, also reacted well with NaN_3 under the stated conditions, giving **9j**–**9m** (51–75%). Compared to the formation of **9j** (51%) a positive substituent effect facilitated the production of **9k**/**9k′** (61%) and **9l** (75%). Compound **8k** is a mixture of regioisomers which resulted in **9k**/**9k′** as a mixture with the same regioisomer ratio. It is noteworthy that the monoaryl-functionalized sulfonium salt, that is, styrylsulfonium salt **8n**, was readily decomposed under the stated conditions that the corresponding target product **9n** was only formed in 38% yield. The low yield of **9n** is presumably attributed to the competitive nucleophilic attack of N_3^- anion at the *β*-position of the alkenylsulfonium salt.[15h–j] An additional aryl at the vinyl moiety gives extra stabilization to the 1,1- and 1,2-diarylvinylsulfonium salts **8a**–**8m** due to the conjugation effect, which renders them to react with NaN_3 more efficiently to afford the target products in decent yields. Unexpectedly, the sulfonium salt of 2-methylstyrene (**8o**) seldomly underwent the same type of azidoalkylation reaction to form the corresponding product **9o**. Interestingly, the 1,1-diphenyl vinylsulfonium salt (**8p**) of six-membered cyclic tetrahydro-2*H*-thiopyran underwent the ring-opening azidoalkylation to afford the corresponding product **9p** (77%) bearing a C_5-azidoalkylthio chain.

The reactivities of open-chain vinylsulfonium salts was then comparatively investigated [Eq.s (3–4)]. Treatment of vinylsulfonium salt **10a** (R=Me) derived from 1,1-stilbene and dimethylsulfoxide (DMSO) with NaN_3 under the standard conditions gave both methylthiolated alkene **11a** (89%) and methyl azide. Sulfonium salts **10b**–**10d** behaved in a fashion similar to form **11b**–**11d** (43–78%) [Eq. (3)]. The vinylsulfonium salt of methyl phenyl thioether (**12a**) predominantly underwent the azidation through C-S cleavage of the S-C(methyl) bond to form **11d** (43%) with formation of MeN_3. No PhSMe was detected from the reaction mixture by GC-MS analysis, suggesting that no S-C(phenyl) bond cleavage occurred in the reaction of **12a** with NaN_3. In the case of using the vinylsulfonium salt of methyl decyl thioether (**12b**), two kinds of C(sp^3)–S bond cleavages proceeded to give **11e** (25%) and **11a** (51%) [Eq. (4)]. Notably, MeN_3 and decyl azide were detected by GC-MS analysis in the reaction mixtures, respectively (See the SI for details). In all the cases, no vinyl azides were detected as the side products. This type of reactions can be considered as an alternative method to access vinyl thioethers.

To investigate the applicability of the present synthetic protocol, the resultant azidoalkylthiolated alkene **2a** was transformed under diverse reaction conditions (Scheme 3). Two transformable moieties, that is, azido and α-oxo ketene dithioacetal, exist in compounds of type **2**. Organic azides have been found broad synthetic utilities in copper-catalyzed azide-alkyne cycloaddition[7] and Staudinger bioconjugation.[8] A [3+2] cycloaddition reaction of **2a** with phenylacetylene was conducted to selectively afford vinylthioalkyl-functionalized triazole **13** in 91% yield (Scheme 3a). Further condensation of **13** with hydrazine gave thioalkyl-linked bis(*N*-heterocycle) **14** (40%) (Scheme 3b). Usually, such a bis(heterocycle) is difficult to be constructed by a conventional method.[18] Vinylthioalkyl-functionalized tetrazole **15** (51%) was accessed from the reaction of **2a** and benzoyl cyanide (Scheme 3c). Notably, the azido functionality could withstand various reaction conditions in the present work. In refluxing ethanol **2a** reacted with hydrazine hydrate and phenylhydrazine to give azidoalkylthio-functionalized multisubstituted pyrazoles **16** (87%) and **17** (72%) (Scheme 3d and 3e), respectively. In a similar fashion, isoxazole **18** (81%) was prepared by the condensation of **2a** with hydroxylamine (Scheme 3f). Interestingly, azidoalkylthio-functionalized



Scheme 3. Product derivatization. Reagents and conditions:[a] Phenylacetylene (2 equiv.), CuBr (10 mol%), 1,4-dioxane (2 mL), air, 80 °C, 12 h.[b] Hydrazine hydrate (10 equiv.), EtOH (2 mL), air, 80 °C, 12 h.[c] Benzoyl cyanide (2 equiv.), MeCN (2 mL), air, 130 °C, 36 h.[d] Hydrazine hydrate (10 equiv.), EtOH (2 mL), air, 80 °C, 12 h.[e] Phenylhydrazine (2 equiv.), EtOH (2 mL), air, 80 °C, 24 h.[f] Hydroxylamine hydrochloride (10 equiv.), K_2CO_3 (10 equiv.), EtOH (2 mL), air, 80 °C, 12 h.[g] Guanidine nitrate (2 equiv.), K_2CO_3 (2 equiv.), MeCN (2 mL), air, 100 °C, 36 h.

pyrimidine **19** was also produced by the reaction with guanidine nitrate in 63% yield (Scheme 3g). It should be noted that the molecular structure of compound **17** was further confirmed by the X-ray single-crystal crystallographic determinations, verifying formation of the present *N*-heterocycle and establishment of the azidoalkylthio functionality in the C-H azidoalkylthiolation products (see the SI for details).

Control experiments were conducted to probe into the reaction mechanism. The reaction of **1 a** with NaN_3 was carried out in the presence of 3.0 equiv. of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or 2,6-di-*tert*-butyl-4-methylphenyl (BHT) under the standard conditions (see the SI for details). These radical-trapping reagents could not inhibit the ring-opening azidoalkylthiolation reaction, leading to **2 a** in 78–85% yields, which excludes a radical pathway. We reasonably speculate that this reaction is a nucleophilic substitution process of azide anion (N_3^-) *via* aliphatic C-S bond cleavage of the cycloalkylsulfonium ring.

Conclusions

In conclusion, an olefinic C-H azidoalkylthiolation strategy was developed by means of an interrupted Pummerer/nucleophilc azidoalkylation cascade. Multi-substituted azidoalkylthiolated alkenes can be accessed through ring-opening azidoalkylation of vinylsulfonium salts under air conditions. The synthetic protocol has been shown potentials for the synthesis of diverse azidoalkylthiolated *N*-heterocycles.

Experimental Section

General Considerations

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a 400 MHz spectrometer and all chemical shift values refer to $CDCl_3$ ($\delta(^1H)$, 7.26 ppm and $\delta(^{13}C)$, 77.16 ppm). X-Ray crystallographic analysis was achieved by the Analysis Center, Dalian Institute of Chemical Physics, Chinese Academy of Sciences. The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre on quoting the deposition numbers CCDC 2080911 for **17**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www. ccdc.cam.ac.uk). The HRMS analysis was obtained by ESI on a GC-TOF mass spectrometer. Column chromatographic purifications were performed on silica gel. All the chemical reagents were purchased from commercial sources and used as received unless otherwise indicated. NaN_3 is of great acute toxicity, which requires attention during experimental operation.

Typical Procedure for the Synthesis of Compounds (2) and (9) – Synthesis of 2 a

A mixture of 1-(1,1-bis(methylthio)-3-oxo-3-phenylprop-1-en-2-yl)tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfo-nate (**1 a**) (138 mg, 0.3 mmol), NaN_3 (39 mg, 0.6 mmol), and 2 mL H_2O/EtOH (1/1, v/v) was stirred at 60 °C for 6 h under an air atmosphere. After **1 a** was completely consumed by TLC monitoring on silica gel, all the volatiles were evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60–90 °C)/ethyl acetate = 30:1, v/v), affording **2 a** (97 mg, 91%) as a yellow liquid.

2-((4-Azidobutyl)thio)-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (2 a): 90 mg, 85%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.00–7.84 (m, 2 H), 7.56 (m, 1 H), 7.51–7.43 (m, 2 H), 3.25–3.10 (m, 2 H), 2.60 (m, 2 H), 2.42 (s, 3 H), 2.06 (s, 3 H), 1.60 (m, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 191.1, 138.9, 135.9, 133.8, 132.8, 129.4, 128.8, 50.9, 33.0, 27.7, 26.7, 18.4, and 16.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{20}N_3OS_3$ 354.0768; Found 354.0763.

2-((4-Azidobutyl)thio)-3,3-bis(ethylthio)-1-phenylprop-2-en-1-one (2 b): 103 mg, 90%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.03–7.91 (m, 2 H), 7.59 (s, 1 H), 7.47 (t, J = 7.6 Hz, 2 H), 3.20 (s, 2 H), 2.93 (q, J = 7.3 Hz, 2 H), 2.68–2.53 (m, 4 H), 1.62 (m, 4 H), 1.34 (t, J = 7.3 Hz, 3 H), 1.01 (t, J = 7.4 Hz, 3 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 191.6, 141.4, 136.0, 133.8, 130.1, 129.6, 128.9, 51.0, 32.9, 29.2, 27.8, 27.7, 26.7, 15.3, and 14.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{24}N_3OS_3$ 382.1081; Found 382.1079.

2-((4-Azidobutyl)thio)-2-(1,3-dithiolan-2-ylidene)-1-phenylethanone (2 c): 97 mg, 92%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.78–7.69 (m, 2 H), 7.44 (m, 1 H), 7.41–7.31 (m, 2 H), 3.53 (m, 2 H), 3.36 (m, 2 H), 3.06 (t, J = 6.4 Hz, 2 H), 2.45 (t, J = 6.6 Hz, 2 H), 1.44 (m, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 192.0, 176.8, 138.7, 131.1, 128.9, 127.6, 114.0, 50.8, 40.7, 35.6, 35.5, 27.6, and 26.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{18}N_3OS_3$ 352.0612; Found 352.0614.

2-((4-Azidobutyl)thio)-2-(1,3-dithian-2-ylidene)-1-phenylethanone (2 d): 46 mg, 42%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.9 Hz, 2 H), 7.51–7.30 (m, 3 H), 3.54 (t, J = 6.5 Hz, 2 H), 3.43–3.31 (m, 2 H), 3.11 (t, J = 6.9 Hz, 2 H), 2.45 (t, J = 7.0 Hz, 2 H), 1.38 (m, 4 H), 1.26–1.17 (m, 2 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 192.1, 176.5, 138.8, 131.1, 129.0, 127.6, 114.3, 51.2, 40.7, 35.9, 35.6, 28.6, 28.3, and 25.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{20}N_3OS_3$ 366.0768; Found 366.0770.

2-((4-Azidobutyl)thio)-3,3-bis(methylthio)-1-(*o*–tolyl)prop-2-en-1-one (2 e): 64 mg, 58%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 7.7 Hz, 1 H), 7.42 (m, 1 H), 7.27 (m, 2 H), 3.24 (t, J = 6.2 Hz, 2 H), 2.79–2.65 (m, 5 H), 2.43 (s, 3 H), 1.95 (s, 3 H), 1.72–1.62 (m, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 193.1, 141.0, 140.7, 136.0, 133.1, 132.4, 132.3, 131.1, 125.6, 50.9, 32.9, 22.8, 26.7, 21.8, 17.9, and 16.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{22}N_3OS_3$ 368.0925; Found 368.0924.

2-((4-Azidobutyl)thio)-3,3-bis(methylthio)-1-(*m*–tolyl)prop-2-en-1-one (2 f): 94 mg, 85%; yellow liquid. ^1H NMR

(400 MHz, CDCl3) δ 7.78 (s, 1 H), 7.71 (d, J=7.4 Hz, 1 H), 7.38 (m, 2 H), 3.20 (t, J=6.2 Hz, 2 H), 2.61 (t, J=6.7 Hz, 2 H), 2.42 (m, 6 H), 2.08 (s, 3 H), 1.62 (m, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, CDCl3) δ 191.2, 139.1, 138.7, 135.7, 134.6, 132.3, 129.6, 128.6, 126.8, 50.8, 32.8, 27.7, 26.6, 21.4, 18.3, and 16.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{22}N_3OS_3$ 368.0925; Found 368.0926.

2-((4-Azidobutyl)thio)-3,3-bis(methylthio)-1-(*p*-tolyl)prop-2-en-1-one (2 g): 98 mg, 89%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J=8.2 Hz, 2 H), 7.29 (d, J=8.3 Hz, 2 H), 3.20 (t, J=6.2 Hz, 2 H), 2.61 (t, J=6.7 Hz, 2 H), 2.43 (m, 6 H), 2.10 (s, 3 H), 1.62 (m, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 190.8, 144.8, 139.4, 133.3, 131.9, 129.6, 50.9, 32.8, 27.7, 26.7, 21.9, 18.4, and 16.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{22}N_3OS_3$ 368.0925; Found 368.0928.

2-((4-Azidobutyl)thio)-3,3-bis(methylthio)-1-(2-(trifluoromethyl)phenyl)prop-2-en-1-one (2 h): 63 mg, 50%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.87–7.79 (m, 1 H), 7.70–7.65 (m, 1 H), 7.61 (m, 2 H), 3.24 (t, J=6.3 Hz, 2 H), 2.76–2.67 (m, 2 H), 2.48 (s, 3 H), 2.07 (s, 3 H), 1.74–1.61 (m, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 189.7, 144.8, 137.6, 136.7, 131.7, 131.5, 130.5, 129.4 (J=32.5 Hz), 127.9 (J=5.9 Hz), 123.6 (J=272.2 Hz), 51.0, 33.6, 27.9, 26.7, 18.9, and 16.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{19}F_3N_3OS_3$ 422.0642; Found 422.0644.

2-((4-Azidobutyl)thio)-3,3-bis(methylthio)-1-(3-(trifluoromethyl)phenyl)prop-2-en-1-one (2 i): 86 mg, 68%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1 H), 8.08 (d, J=7.8 Hz, 1H), 7.83 (d, J=7.8 Hz, 1 H), 7.62 (t, J=7.8 Hz, 1 H), 3.22 (m, 2 H), 2.62 (m, 2 H), 2.44 (d, J=3.4 Hz, 3 H), 2.07 (d, J=3.3 Hz, 3 H), 1.72–1.53 (m, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 189.6, 136.9, 136.6, 135.8, 132.6, 131.5 (J=32.6 Hz), 130.0 (J=3.5 Hz), 129.5, 126.0 (J=3.8 Hz), 122.7 (J=270.0 Hz), 50.9, 33.4, 27.8, 26.8, 18.4, and 16.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{19}F_3N_3OS_3$ 422.0642; Found 422.0641.

2-((4-Azidobutyl)thio)-3,3-bis(methylthio)-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (2 j): 83 mg, 66%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J=8.3 Hz, 1 H), 7.74 (d, J=8.3 Hz, 2 H), 3.23 (s, 2 H), 2.62 (t, J=6.5 Hz, 2H), 2.45 (s, 3 H), 2.08 (s, 3 H), 1.63 (td, J=6.8, 3.5 Hz, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 189.9, 138.8, 137.2, 135.6, 134.8 (J=32.5 Hz), 129.7, 125.9 (J=3.6 Hz), 123.7 (J=271.3 Hz), 50.9, 33.4, 27.8, 26.8, 18.5, and 16.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{19}F_3N_3OS_3$ 422.0642; Found 422.0636.

2-((4-Azidobutyl)thio)-1-(4-fluorophenyl)-3,3-bis(methylthio)prop-2-en-1-one (2 k): 80 mg, 72%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.07–7.90 (m, 2 H), 7.16 (t, J=8.5 Hz, 2 H), 3.22 (t, J=6.0 Hz, 2 H), 2.61 (t, J=6.6 Hz, 2 H), 2.44 (s, 3 H), 2.10 (s, 3 H), 1.63 (m, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 189.6, 166.1 (J=254.5 Hz), 138.2, 133.5, 132.2 (J=2.9 Hz), 132.1 (J=9.4 Hz), 116.0 (J=21.9 Hz), 50.9, 33.1, 27.7, 26.7, 18.4, and 16.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{19}FN_3OS_3$ 372.0674; Found 372.0670.

2-((4-Azidobutyl)thio)-1-(4-chlorophenyl)-3,3-bis(methylthio)prop-2-en-1-one (2 l): 105 mg, 90%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.94–7.79 (m, 2 H), 7.55–7.39 (m, 2 H), 3.21 (t, J=6.2 Hz, 2 H), 2.60 (m, 2 H), 2.43 (s, 3 H), 2.09 (s, 3 H), 1.62 (m, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 190.0, 140.3, 138.0, 134.3, 134.0, 130.8, 129.3, 50.9, 33.2, 27.8, 26.7, 18.5, and 16.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{19}ClN_3OS_3$ 388.0379; Found 388.0380.

2-((4-Azidobutyl)thio)-1-(4-bromophenyl)-3,3-bis(methylthio)prop-2-en-1-one (2 m): 121 mg, 93%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J=8.6 Hz, 2 H), 7.61 (d, J=8.6 Hz, 2 H), 3.21 (s, 2 H), 2.59 (d, J=6.2 Hz, 2 H), 2.43 (s, 3 H), 2.08 (s, 3 H), 1.67–1.56 (m, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 190.1, 137.8, 134.7, 134.1, 132.2, 130.9, 129.0, 50.9, 33.2, 27.8, 26.7, 18.5, and 16.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{19}BrN_3OS_3$ 431.9874; Found 431.9868.

2-((4-Azidobutyl)thio)-3,3-bis(methylthio)-1-(naphthalen-2-yl)prop-2-en-1-one (2 n): 109 mg, 90%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ δ 9.07 (d, J=8.5 Hz, 1 H), 8.10–7.97 (m, 2 H), 7.90 (d, J=8.1 Hz, 1 H), 7.67 (m, 1 H), 7.57 (m, 1 H), 7.49 (m, 1 H), 3.19 (t, J=6.5 Hz, 2 H), 2.74 (t, J=7.0 Hz, 2 H), 2.44 (s, 2 H), 1.90 (s, 2 H), 1.64 (m, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 193.0, 141.3, 134.3, 134.1, 133.5, 133.4, 131.3, 131.2, 128.7, 128.7, 126.7, 126.2, 124.3, 50.9, 32.9, 27.8, 26.6, 18.2, and 16.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{22}N_3OS_3$ 404.0925; Found 404.0923.

2-((4-Azidobutyl)thio)-1-(furan-2-yl)-3,3-bis(methylthio)prop-2-en-1-one (2 o): 94 mg, 91%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1 H), 7.09 (d, J=3.4 Hz, 1 H), 6.51 (d, J=1.8 Hz, 1 H), 3.16 (s, 2 H), 2.60 (s, 2 H), 2.35 (s, 3 H), 2.08 (s, 3 H), 1.56 (s, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 178.8, 151.6, 147.5, 136.5, 136.1, 139.6, 112.4, 50.6, 32.8, 27.5, 26.5, 18.4, and 16.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{18}N_3O_2S_3$ 344.0561; Found 344.0566.

2-((4-Azidobutyl)thio)-3,3-bis(methylthio)-1-(thiophen-2-yl)prop-2-en-1-one (2 p): 101 mg, 94%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (m, 2 H), 7.12 (m, 1 H), 3.19 (t, J=6.3 Hz, 2 H), 2.65 (t, J=6.8 Hz, 2 H), 2.40 (s, 3 H), 2.13 (s, 3 H), 1.60 (m, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 183.7, 143.0, 138.2, 135.0, 134.1, 134.0, 128.3, 50.7, 33.0, 27.6, 26.6, 18.5, and 16.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{18}N_3OS_4$ 360.0333; Found 360.0330.

2-((4-Azidobutyl)thio)-2-(1,3-dithiolan-2-ylidene)-1-(*m*-tolyl)ethenone (2 q): 80 mg, 73%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J=7.7 Hz, 2 H), 7.34–7.22 (m, 2 H), 3.55 (t, J=6.4 Hz, 2 H), 3.39 (t, J=6.4 Hz, 2 H), 3.10 (t, J=6.3 Hz, 2 H), 2.49 (t, J=6.4 Hz, 2 H), 2.39 (s, 3 H), 1.54–1.38 (m, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 192.3, 176.1, 138.7, 137.3, 131.9, 129.4, 127.5, 126.1, 114.1, 50.9, 40.7, 35.6, 35.6, 27.6, 26.1, and 21.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{20}N_3OS_3$ 366.0768; Found 366.0766.

2-((4-Azidobutyl)thio)-1-(2-chlorophenyl)-2-(1,3-dithiolan-2-ylidene)ethenone (2 r): 75 mg, 65%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.49–7.23 (m, 4 H), 3.64 (m, 2 H), 3.40 (m, 2 H), 3.15 (m, 2 H), 2.52 (m, 2 H), 1.50 (m, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 191.0, 180.6, 140.0, 131.0, 130.3, 129.4, 128.4, 126.3, 114.3, 50.9, 41.3, 35.4, 35.4, 27.8, and 26.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{17}ClN_3OS_3$ 386.0222; Found 386.0220.

2-((4-Azidobutyl)thio)-2-(1,3-dithiolan-2-ylidene)-1-(4-fluorophenyl)ethenone (2s): 66 mg, 59%; yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–7.72 (m, 2 H), 7.16–6.93 (m, 2 H), 3.53 (m, 2 H), 3.37 (m, 2 H), 3.09 (t, J = 6.5 Hz, 2 H), 2.44 (t, J = 6.7 Hz, 2 H), 1.52–1.38 (m, 4 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.5, 177.1, 164.4, (J = 250.6 Hz), 134.7 (J = 3.3 Hz), 131.6 (J = 8.8 Hz), 114.6 (J = 21.6 Hz), 113.6, 50.9, 40.7, 35.6, 35.6, 27.6, and, 26.1. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{15}H_{17}FN_3OS_3$ 370.0518; Found 370.0517.

2-((4-Azidobutyl)thio)-1-(4-chlorophenyl)-2-(1,3-dithiolan-2-ylidene)ethenone (2t): 102 mg, 88%; yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76–7.63 (m, 2 H), 7.42–7.29 (m, 2 H), 3.54 (dd, J = 7.5, 5.5 Hz, 2 H), 3.37 (dd, J = 7.5, 5.5 Hz, 2 H), 3.10 (t, J = 6.5 Hz, 2 H), 2.44 (t, J = 6.7 Hz, 2 H), 1.58–1.34 (m, 4 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.6, 177.9, 137.2, 137.0, 130.5, 127.9, 113.5, 50.8, 40.8, 35.7, 35.6, 27.6, and 26.1. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{15}H_{17}ClN_3OS_3$ 386.0222; Found 386.0221.

2-((4-Azidobutyl)thio)-1-(4-bromophenyl)-2-(1,3-dithiolan-2-ylidene)ethenone (2u): 110 mg, 85%; yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69–7.55 (m, 2 H), 7.55–7.42 (m, 2 H), 3.53 (m, 2 H), 3.35 (m, 2 H), 3.09 (t, J = 6.5 Hz, 2 H), 2.43 (t, J = 6.7 Hz, 2 H), 1.44 (m, 4 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.6, 178.1, 137.5, 130.8, 130.6, 125.7, 113.4, 50.8, 40.8, 35.6, 35.5, 27.6, and 26.1. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{15}H_{17}BrN_3OS_3$ 429.9717; Found 429.9711.

2-((4-Azidobutyl)thio)-2-(1,3-dithiolan-2-ylidene)-1-(naphthalen-2-yl)ethenone (2v): 98 mg, 81%; yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1 H), 7.96–7.79 (m, 4 H), 7.53 (m, 2 H), 3.56 (t, J = 6.4 Hz, 2 H), 3.40 (t, J = 6.4 Hz, 2 H), 3.01 (s, 2 H), 2.46 (d, J = 6.1 Hz, 2 H), 1.44 (m, 4 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.9, 176.5, 136.1, 134.6, 132.3, 129.9, 129.2, 127.8, 127.7, 127.3, 126.5, 125.7, 114.3, 50.9, 40.8, 35.7, 35.7, 27.7, and 26.2. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{19}H_{20}N_3OS_3$ 402.0768; Found 402.0761.

1-((4-Azidobutyl)thio)-1-(1,3-dithiolan-2-ylidene)propan-2-one (2w): 67 mg, 77%; yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.51 (m, 2 H), 3.33–3.20 (m, 4 H), 2.70 (t, J = 7.0 Hz, 2 H), 2.43 (s, 3 H), 1.76–1.61 (m, 4 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.4, 177.0, 114.6, 51.0, 41.3, 35.5, 35.2, 28.1, 27.5, and 26.1. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{10}H_{15}N_3OS_3$ 290.0455; Found 290.0456.

2-((4-Azidopentyl)thio)-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (4a) and 2-((5-Azidopentan-2-yl)thio)-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (5a): 85 mg, 77%; yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03–7.85 (m, 2 H), 7.68–7.54 (m, 1 H), 7.54–7.43 (m, 2 H), 3.69 (s, 0.45 H), 3.35 (m, 0.62 H), 3.16 (t, J = 6.3 Hz, 0.57 H), 2.61 (t, J = 7.1 Hz, 1.38 H), 2.44 (t, J = 3.3 Hz, 3 H), 2.08 (t, J = 7.2 Hz, 3 H), 1.62 (qdd, J = 9.2, 7.3, 3.6 Hz, 2.49 H), 1.55–1.44 (m, 1.37 H), 1.25 (d, J = 6.8 Hz, 0.87 H), 1.18 (d, J = 6.5 Hz, 1.82 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.2, 191.1, 139.0, 137.6, 136.4, 135.8, 135.7, 133.7, 133.6, 132.5, 129.5, 129.4, 128.8, 128.7, 67.1, 57.4, 51.1, 43.2, 34.9, 34.1, 33.1, 26.1, 26.0, 21.6, 19.3, 18.5, 18.3, 16.3, 16.2. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{16}H_{22}N_3OS_3$ 368.0925; Found 368.0924.

2-((4-Azidopentyl)thio)-2-(1,3-dithiolan-2-ylidene)-1-phenylethanone (4b) and 2-((5-Azidopentan-2-yl)thio)-2-(1,3-dithiolan-2-ylidene)-1-phenylethanone (5b): 76 mg, 69%; yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.88 (m, 0.5 H), 7.75 (d, J = 8.0 Hz, 1.5 H), 7.59–7.34 (m, 3 H), 5.29 (s, 0.25 H), 3.55 (m, 1.5 H), 3.48 (m, 0.5 H), 3.38 (m, 2 H), 3.22 (m, 0.5 H), 3.02 (m, 0.7 H), 2.69 (m, 0.4 H), 2.46 (m, 0.9 H), 1.65 (m, 0.8 H), 1.54–1.21 (m, 3.6 H), 1.12 (d, J = 6.5 Hz, 1.2 H), 1.07 (d, J = 6.8 Hz, 1.0 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 192.4, 192.1, 177.1, 176.7, 138.8, 138.9, 132.1, 131.2, 131.2, 129.3, 129.1, 128.6, 127.9, 127.7, 127.6, 114.2, 114.0, 108.4, 57.6, 51.1, 45.4, 40.8, 40.7, 35.9, 35.6, 35.6, 35.5, 34.9, 26.0, 25.7, 21.1, 19.5. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{16}H_{20}N_3OS_3$ 366.0768; Found 366.0761.

2-((5-Azidopentyl)thio)-3,3-bis(methylthio)-1-phenylprop-2-en-1-one (7a): 70 mg, 72%; yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (m, 2 H), 7.61–7.56 (m, 1 H), 7.50–7.46 (m, 2 H), 3.19 (t, J = 6.8 Hz, 2 H), 2.59 (t, J = 7.3 Hz, 2 H), 2.43 (s, 3 H), 2.07 (s, 3 H), 1.52 (m, 4 H), 1.45–1.32 (m, 2 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.2, 139.5, 133.9, 133.8, 132.1, 129.5, 128.9, 51.3, 33.3, 29.1, 28.4, 25.7, 18.4, and 16.3. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{16}H_{22}N_3OS_3$ 368.0925; Found 368.0926.

2-((5-Azidopentyl)thio)-3,3-bis(methylthio)-1-(*p*-tolyl)prop-2-en-1-one (7b): 75 mg, 65%; yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.2 Hz, 2 H), 7.25–7.18 (m, 2 H), 2.51 (t, J = 7.3 Hz, 2 H), 2.38–2.32 (m, 7 H), 2.02 (s, 3 H), 1.98 (s, 3 H), 1.45 (dt, J = 15.7, 7.9 Hz, 4 H), 1.32 (d, J = 6.7 Hz, 2 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.9, 144.8, 140.3, 133.5, 130.7, 129.6, 129.6, 34.0, 33.2, 29.1, 28.6, 27.8, 21.9, 18.4, 16.3, and 15.5. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{17}H_{24}N_3OS_3$ 382.1081; Found 382.1087.

2-((5-Azidopentyl)thio)-3,3-bis(methylthio)-1-(thiophen-2-yl)prop-2-en-1-one (7c): 68 mg, 61%; yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (m, 2 H), 7.14 (m, 1 H), 3.21 (t, J = 6.8 Hz, 2 H), 2.66 (t, J = 7.3 Hz, 2 H), 2.44 (s, 3 H), 2.16 (s, 3 H), 1.63–1.35 (m, 6 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 184.0, 143.4, 139.1, 135.1, 134.3, 133.5, 128.4, 51.3, 33.4, 29.1, 28.4, 25.8, 18.7, and 16.4. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{14}H_{20}N_3OS_4$ 374.0489; Found 374.0487.

(4-Azidobutyl)(2,2-diphenylvinyl)sulfane (9a): 78 mg, 84%; yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.20 (m, 10 H), 6.63 (s, 1 H), 3.35 (t, J = 6.5 Hz, 2 H), 2.85 (t, J = 7.0 Hz, 2 H), 1.95–1.68 (m, 4 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.9, 139.6, 139.1, 129.8, 128.4, 128.3, 127.6, 127.1, 127.0, 125.6, 51.0, 34.3, 27.8, and 27.4. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{18}H_{20}N_3S$ 310.1378; Found 310.1365.

(*E*)-(4-Azidobutyl)(2-phenyl-2-(*o*-tolyl)vinyl)sulfane (9b) and (*Z*)-(4-Azidobutyl)(2-phenyl-2-(*o*-tolyl)vinyl)sulfane (9b'): 62 mg, 64%; yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–6.98 (m, 9 H), 6.65 (s, 0.7 H), 6.10 (s, 0.2 H), 3.18 (dd, J = 8.2, 4.6 Hz, 2 H), 2.82–2.58 (m, 2 H), 2.04 (s, 2.2 H), 1.94 (s, 0.7 H), 1.78–1.50 (m, 4 H).^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.8. 139.9, 139.4, 138.9, 138.8, 138.0, 136.6, 136.5, 130.4, 130.4, 130.3, 129.9, 128.8, 128.5, 128.1, 127.9, 127.5, 127.1, 126.8, 126.6, 126.2, 125.8, 125.7, 125.4, 51.0, 34.8, 33.7, 27.8, 27.8, 27.7, 27.4, 20.4, and 19.5. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{19}H_{22}N_3S$ 324.1534; Found 324.1535.

(*E*)-(4-Azidobutyl)(2-(2-bromophenyl)-2-phenylvinyl)sulfane (9c): 101 mg, 87%; yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.45 (m, 2 H), 7.39–7.25 (m, 7 H), 6.60 (s, 1 H), 3.35 (t, J= 6.5 Hz, 2 H), 2.84 (t, J=6.9 Hz, 2 H), 1.79 (m, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.9, 139.6, 139.1, 129.8, 128.4, 128.4, 127.6, 127.1, 127.0, 125.6, 51.1, 34.4, 27.8, and 27.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{19}BrN_3S$ 388.0483; Found 388.0484.

(*E*)-(4-Azidobutyl)(2-(3,4-dimethylphenyl)-2-phenylvinyl)sulfane (9 d) and (*Z*)-(4-Azidobutyl)(2-(3,4-dimethylphenyl)-2-phenylvinyl)sulfane (9 d'): 78 mg, 77%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.32–6.80 (m, 8 H), 6.39 (d, J=3.4 Hz, 1 H), 3.17 (t, J=6.4 Hz, 2 H), 2.66 (t, J=6.9 Hz, 2 H), 2.15 (m, 6 H), 1.75–1.50 (m, 4 H).$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.1. 138.8, 138.6, 138.3, 138.2, 136.0, 135.5, 135.4, 135.0, 134.5, 129.7, 128.7, 128.6, 127.3, 127.2, 126.5, 126.2, 126.1, 125.9, 124.0, 123.6, 123.4, 50.0, 33.3, 33.3, 26.8, 26.8, 26.4, 18.9, 18.7, and 18.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{24}N_3S$ 338.1691; Found 338.1695.

(*E*)-(4-Azidobutyl)(2-phenyl-2-(*p*-tolyl)vinyl)sulfane (9 e) and (*Z*)-(4-Azidobutyl)(2-phenyl-2-(*p*-tolyl)vinyl)sulfane (9 e'): 69 mg, 71%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.31–7.09 (m, 7 H), 6.99 (d, J=3.3 Hz, 2 H), 6.41 (d, J= 3.0 Hz, 1 H), 3.17 (t, J=6.3 Hz, 2 H), 2.66 (td, J=6.9, 3.1 Hz, 2 H), 2.27 (s, 1.5 H), 2.22 (s, 1.5 H), 1.72–1.53 (m, 4 H).$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.0. 139.7, 139.1, 139.1, 139.1, 137.3, 136.7, 136.6, 129.7, 129.6, 129.1, 129.0, 128.3, 128.3, 127.5, 127.1, 127.0, 126.9, 125.2, 124.6, 51.0, 34.3, 34.3, 27.8, 27.4, 21.4, and 21.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{22}N_3S$ 324.1534; Found 324.1540.

(4-Azidobutyl)(2,2-di-*p*-tolylvinyl)sulfane (9 f): 83 mg, 82%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.09 (s, 4 H), 6.99 (q, J=8.3 Hz, 4 H), 6.36 (s, 1 H), 3.17 (t, J=6.4 Hz, 2 H), 2.66 (t, J=6.9 Hz, 2 H), 2.27 (s, 3 H), 2.22 (s, 3 H), 1.75–1.51 (m, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 138.3, 138.1, 136.2, 135.7, 135.7, 128.6, 128.0, 128.0, 126.0, 123.1, 50.9, 33.3, 26.8, 26.4, 20.4, and 20.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{24}N_3S$ 338.1691; Found 338.1687.

(*Z*)-(4-Azidobutyl)(2-(4-fluorophenyl)-2-(4-methoxyphenyl)vinyl)sulfane (9 g) and (*E*)-(4-Azidobutyl)(2-(4-fluorophenyl)-2-(4-methoxyphenyl)vinyl)sulfane (9 g'): 67 mg, 62%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.15 (m, 2.1 H), 7.09–6.90 (m, 3.2 H), 6.90–6.76 (m, 1.7 H), 6.75–6.63 (m, 1.2 H), 6.32 (s, 0.6 H), 6.30 (s, 0.4 H), 3.70 (s, 1.3 H), 3.67 (s, 1.7 H), 3.18 (t, J=6.4 Hz, 2 H), 2.76–2.53 (m, 2 H), 1.69–1.53 (m, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.9 (J=245.2 Hz), 158.9, 158.8, 138.4 (J=3.1 Hz), 137.8, 137.7, 135.6 (J=3.3 Hz), 134.5, 131.6, 131.5 (J=7.9 Hz), 130.9, 128.7 (J=7.9 Hz), 128.1, 124.6, 123.7, 115.2 (J=21.3 Hz), 115.0 (J=21.2 Hz), 113.7, 55.1, 50.9, 34.3, 27.7, and 27.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{20}FN_3OS$ 357.1311; Found 357.1310.

(4-Azidobutyl)(2,2-bis(3-(trifluoromethyl)phenyl)vinyl)sulfane (9 h): 96 mg, 72%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.55–7.36 (m, 6 H), 7.30 (t, J= 7.8 Hz, 1 H), 7.20 (d, J=7.8 Hz, 1 H), 6.63 (s, 1 H), 3.23 (t, J=6.4 Hz, 2 H), 2.76 (t, J=7.0 Hz, 2 H), 1.76–1.59 (m, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.1, 139.6, 136.0, 133.2, 131.1 (J=32.2 Hz), 131.1 (J=31.9 Hz), 130.4, 129.4, 129.2, 129.1, 126.6 (J=3.8 Hz), 124.7 (J=3.6 Hz), 124.2 (J= 270.8 Hz), 123.9 (J=3.6 Hz), 123.5 (J=3.7 Hz), 51.0, 34.5, 27.8, and 27.6. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{18}F_6N_3S$ 446.1126; Found 446.1137.

(4-Azidobutyl)(2,2-bis(4-chlorophenyl)vinyl)sulfane (9 i): 95 mg, 84%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.40–7.04 (m, 8 H), 6.50 (s, 1 H), 3.23 (t, J=6.4 Hz, 2 H), 2.73 (dd, J=8.3, 5.5 Hz, 2 H), 1.75–1.56 (m, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.1, 139.6, 136.8, 131.7, 130.4, 129.3, 128.6, 127.5, 127.3, 127.1, 51.0, 34.5, 27.8, and 27.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}Cl_2N_3S$ 378.0598; Found 378.0604.

(*E*)-(4-Azidobutyl)(1,2-diphenylvinyl)sulfane (9 j): 47 mg, 51%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (m, 5 H), 7.12 (m, 3 H), 6.98 (m, 2 H), 6.84 (s, 1 H), 3.27 (t, J= 6.0 Hz, 2 H), 2.55 (t, J=6.7 Hz, 2 H), 1.80–1.65 (m, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 137.9, 137.7, 136.7, 129.7, 129.0, 128.8, 128.2, 128.1, 127.8, 126.7, 51.0, 31.2, 27.9, and 26.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{20}N_3S$ 310.1378; Found 310.1370.

(*E*)-(4-Azidobutyl)(2-(4-fluorophenyl)-1-phenylvinyl)sulfane (9 k) and (*E*)-(azidomethyl)(2-(4-fluorophenyl)-1-phenylvinyl)sulfane (9 k'): 60 mg, 61%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.23 (s, 4 H), 7.12–6.60 (m, 6 H), 3.14 (m, 2 H), 2.42 (m, 2 H), 1.68–1.49 (m, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.5 (J=246.4 Hz), 161.5 (J= 245.5 Hz), 137.6, 137.5, 136.6 (J=3.7 Hz), 133.8, 132.8 (J= 3.5 Hz), 131.6, 131.5, 130.6, 130.5, 129.7, 129.0, 128.9, 128.3, 128.2, 128.1, 126.8, 126.7, 115.8 (J=21.5 Hz), 115.0 (J= 21.4 Hz), 51.0, 31.3, 31.2, 27.9, 27.8, 26.5, and 26.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{19}FN_3S$ 328.1284; Found 328.1285.

(*E*)-(4-Azidobutyl)(2-(*m*-tolyl)-1-(4-(trifluoromethyl)phenyl)vinyl)sulfane (9 l): 88 mg, 75%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J=16.3 Hz, 1 H), 7.51 (s, 4 H), 7.37 (s, 1 H), 7.25 (d, J=7.9 Hz, 1 H), 6.95 (dd, J=17.0, 12.1 Hz, 2 H), 3.13 (t, J=6.4 Hz, 2 H), 2.73 (t, J=6.8 Hz, 2 H), 2.27 (s, 3H), 1.57 (m, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.1, 138.2, 137.4, 132.4, 131.8, 129.6, 129.4 (J= 33.8 Hz), 129.3, 128.7, 126.9, 126.8, 125.7 (J=3.9 Hz), 124.3 (J=270.2 Hz), 51.0, 34.8, 27.9, 26.4, and 21.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}F_3N_3S$ 392.1408; Found 392.1406.

(*E*)-(4-azidobutyl)(2-(*p*-tolyl)-1-(4-(trifluoromethyl)phenyl)vinyl)sulfane (9 m): 76 mg, 65%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J=8.0 Hz, 2 H), 7.39 (d, J=8.0 Hz, 2 H), 6.84 (d, J=7.8 Hz, 2 H), 6.73 (d, J=7.9 Hz, 2 H), 3.15 (d, J=5.4 Hz, 2 H), 2.40 (t, J=6.1 Hz, 2 H), 2.16 (s, 3 H), 1.57 (d, J=2.8 Hz, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.2, 137.2, 134.7, 133.3, 130.3, 130.0 (J=32.3 Hz), 130.0, 129.1, 129.0, 125.7 (J=3.6 Hz), 124.2 (J=271.8 Hz), 51.0, 31.4, 27.8, 26.4, and 21.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}F_3N_3S$ 392.1408; Found 392.1411.

(*E*)-(4-Azidobutyl)(styryl)sulfane (9 n): 27 mg, 38%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (m, 5 H), 6.76 (d, J=15.6 Hz, 1 H), 6.55 (d, J=15.6 Hz, 1 H), 3.35 (t, J=6.3 Hz, 2 H), 2.87 (t, J=6.7 Hz, 2 H), 1.81 (m, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 137.0, 128.7, 127.4, 127.0, 125.5, 124.7,

50.9, 32.1, 27.9, and 26.6. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{16}N_3S$ 234.1065; Found 234.1069.

(5-Azidopentyl)(2,2-diphenylvinyl)sulfane (9 o): 75 mg, 77%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.31–7.10 (m, 10 H), 6.47 (s, 1 H), 3.16 (t, $J=6.7$ Hz, 2 H), 2.67 (t, $J=7.3$ Hz, 2 H), 1.65–1.49 (m, 4 H), 1.40 (d, $J=6.8$ Hz, 2 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.0, 139.6, 138.8, 129.8, 128.4, 128.3, 127.6, 127.1, 126.9, 126.0, 51.3, 34.7, 29.9, 28.5, and 25.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{22}N_3S$ 324.1534; Found 324.1542.

Typical procedure for the Synthesis of Compounds (11) – Synthesis of 11 a

A mixture of (2,2-diphenylvinyl)dimethylsulfonium trifluoromethanesulfonate (**10 a**) (117 mg, 0.3 mmol), NaN_3 (39 mg, 0.6 mmol), and 2 mL H_2O/EtOH (1/1, v/v) was stirred at 60 °C for 6 h under an air atmosphere. After **10 a** was completely consumed by TLC monitoring on silica gel, all the volatiles were evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60–90 °C)/ethyl acetate = 30:1, v/v), affording **11 a** (60 mg, 89%) as a yellow liquid.

(2,2-Diphenylvinyl)(methyl)sulfane (11 a): 60 mg, 89%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.34–7.11 (m, 10 H), 6.47 (s, 1 H), 2.28 (s, 3 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.9, 139.6, 138.6, 129.8, 128.4, 128.4, 127.7, 127.6, 127.1, 127.0, and 18.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{15}S$ 227.0894; Found 227.0896.

***n*-Butyl(2,2-diphenylvinyl)sulfane (11 b)**: 63 mg, 78%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.39–7.04 (m, 10 H), 6.50 (s, 1 H), 2.68 (t, $J=7.4$ Hz, 2 H), 1.70–1.50 (m, 2 H), 1.35 (dd, $J=14.9$, 7.4 Hz, 2 H), 0.84 (t, $J=7.4$ Hz, 3 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.1, 139.8, 138.5, 129.9, 128.4, 128.3, 127.5, 127.1, 126.9, 126.5, 34.7, 32.6, 21.9, and 13.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{21}S$ 269.1364; Found 269.1355.

Benzyl(2,2-diphenylvinyl)sulfane (11 c): 55 mg, 61%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.29–7.12 (m, 14 H), 7.05 (d, $J=1.3$ Hz, 1 H), 6.49 (s, 1 H), 3.86 (s, 2 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.9, 139.6, 139.3, 137.8, 129.8, 129.1, 128.8, 128.4, 128.3, 127.7, 127.4, 127.2, 127.0, 124.8, and 39.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{19}S$ 303.1207; Found 303.1220.

(2,2-Diphenylvinyl)(phenyl)sulfane (11 d): 37 mg, 43%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.61–6.97 (m, 15 H), 6.76 (s, 1 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.6, 141.2, 139.3, 136.6, 129.9, 129.6, 129.2, 128.5, 128.4, 127.9, 127.4, 127.3, 126.9, and 124.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{17}S$ 289.1051; Found 289.1057.

Synthesis of 3,3-bis(methylthio)-1-phenyl-2-((4-(4-phenyl-1H-1,2,3-triazol −1-yl)butyl)thio)prop-2-en-1-one (13)

A mixture of 2-((4-azidobutyl)thio)-3,3-bis(methylthio) −1-phenylprop-2-en-1-one (**2 a**) (106 mg, 0.3 mmol), phenylacetylene (61 mg, 0.6 mmol), and CuBr (4.3 mg, 0.03 mmol) in 2 mL 1,4-dioxane was stirred at 80 °C for 12 h. After **2 a** was completely consumed by TLC monitoring on silica gel, all the volatiles were evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60–90 °C)/ethyl acetate = 30:1, v/v), affording **13** (124 mg, 91%) as a yellow solid.

3,3-Bis(methylthio)-1-phenyl-2-((4-(4-phenyl-1*H*-1,2,3-triazol-1-yl)butyl)thio)prop-2-en-1-one (13): 124 mg, 91%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97–7.89 (m, 2 H), 7.81 (m, 3 H), 7.56 (d, $J=7.4$ Hz, 1 H), 7.44 (dt, $J=15.1$, 7.8 Hz, 4 H), 7.33 (d, $J=7.4$ Hz, 1 H), 4.33 (t, $J=7.1$ Hz, 2 H), 2.64 (t, $J=7.1$ Hz, 2 H), 2.41 (s, 3 H), 2.08–1.93 (m, 5 H), 1.66–1.54 (m, 2 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 191.1, 147.7, 138.0, 135.7, 133.8, 130.7, 129.4, 128.8, 128.1, 125.7, 119.6, 49.7, 32.8, 29.0, 26.5, 18.3, and 16.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{26}N_3OS_3$ 456.1238; Found 456.1231.

Synthesis of 1-(4-((3-(methylthio)-5-phenyl-1H-pyrazol-4-yl)thio)butyl) −4-phenyl-1H-1,2,3-triazole (14)

A mixture of 3,3-bis(methylthio)-1-phenyl-2-((4-(4-phenyl-1*H*-1,2,3-triazol-1-yl)butyl)thio)prop-2-en-1-one (**13**) (137 mg, 0.3 mmol), and hydrazine hydrate (150 mg, 3 mmol) in 2 mL EtOH was stirred at 80 °C for 12 h. After **13** was completely consumed by TLC monitoring on silica gel, all the volatiles were evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60–90 °C)/ethyl acetate = 30:1, v/v), affording **14** (51 mg, 40%) as a yellow liquid.

1-(4-((3-(Methylthio)-5-phenyl-1*H*-pyrazol-4-yl)thio)butyl)-4-phenyl-1*H*-1,2,3-triazole (14): 57 mg, 40%; yellow solid, m.p.: 96–97 °C. ^1H NMR (400 MHz, d_6-DMSO) δ 13.43 (s, 1 H), 8.43 (s, 1 H), 7.84 (d, $J=7.6$ Hz, 4 H), 7.55–7.38 (m, 5 H), 7.33 (d, $J=7.2$ Hz, 1 H), 4.24 (t, $J=6.6$ Hz, 2 H), 2.61 (t, $J=6.7$ Hz, 2 H), 2.49 (s, 3 H), 1.91–1.71 (m, 2 H), 1.44–1.29 (m, 2 H). $^{13}C\{^1H\}$ NMR (100 MHz, d_6-DMSO) δ 152.5, 146.7, 146.1, 131.3, 129.3, 129.1, 128.2, 127.9, 125.6, 121.6, 104.4, 49.5, 35.2, 28.9, 26.1, and 14.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{24}N_5S_2$ 422.1473; Found 422.1464.

Synthesis of 3,3-bis(methylthio)-1-phenyl-2-((4-(5-phenyl-2H-tetrazol-2-yl) butyl)thio)prop-2-en-1-one (15)

A mixture of 2-((4-azidobutyl)thio)-3,3-bis(methylthio)-1- phenylprop-2-en-1-one (**2 a**) (106 mg, 0.3 mmol) and benzoyl cyanide (79 mg, 0.6 mmol), in 2 mL MeCN was stirred at 130 °C for 36 h. After **2 a** was completely consumed by TLC monitoring on silica gel, all the volatiles were evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60–90 °C)/ethyl acetate = 30:1, v/v), affording **15** (70 mg, 51%) as a yellow liquid.

3,3-Bis(methylthio)-1-phenyl-2-((4-(5-phenyl-2*H*-tetrazol-2-yl)butyl)thio)prop-2-en-1-one (15): 70 mg, 51%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.51–8.35 (m, 2 H), 7.89 (m, 2 H), 7.78–7.65 (m, 1 H), 7.61–7.51 (m, 3 H), 7.46 (m, 2

H), 4.68 (t, J = 7.3 Hz, 2 H), 2.65 (t, J = 7.1 Hz, 2 H), 2.41 (s, 3 H), 2.11–1.94 (m, 5 H), 1.70–1.55 (m, 3 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 191.1, 181.6, 149.5, 138.1, 135.8, 135.3, 135.1, 134.1, 133.8, 131.2, 129.5, 129.0, 128.9, 49.4, 32.8, 28.8, 26.4, 18.5, and 16.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{25}N_4O_2S_3$ 485.1140; Found 485.1133.

Synthesis of 4-((4-azidobutyl)thio)-3-(methylthio)-5-phenyl-1H-pyrazole (16)

A mixture of 2-((4-azidobutyl)thio)-3,3-bis(methylthio)-1- phenylprop-2-en-1-one (**2 a**) (106 mg, 0.3 mmol), and hydrazine hydrate (150 mg, 3 mmol) in 2 mL EtOH was stirred at 80 °C for 12 h. After **2 a** was completely consumed by TLC monitoring on silica gel, all the volatiles were evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60–90 °C)/ethyl acetate = 30:1, v/v), affording **16** (83 mg, 87%) as a yellow liquid.

4-((4-Azidobutyl)thio)-3-(methylthio)-5-phenyl-1*H*-pyrazole (16): 83 mg, 87%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.94–7.65 (m, 2 H), 7.61–7.27 (m, 3 H), 3.03 (t, J = 6.9 Hz, 2 H), 2.56 (t, J = 6.8 Hz, 2 H), 2.42 (s, 3 H), 1.52 (m, 2 H), 1.40 (m, 2 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.8, 148.0, 129.3, 129.0, 128.7, 127.6, 106.7, 50.8, 35.4, 27.5, 26.1, and 15.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{18}N_5S_2$ 320.1004; Found 320.1006.

Synthesis of 4-((4-azidobutyl)thio)-3-(methylthio)-1,5-diphenyl-1H-pyrazole (17)

A mixture of 2-((4-azidobutyl)thio)-3,3-bis(methylthio)-1- phenylprop-2-en-1-one (**2 a**) (106 mg, 0.3 mmol) and phenylhydrazine (65 mg, 0.6 mmol) in 2 mL EtOH was stirred at 80 °C for 24 h. After **2 a** was completely consumed by TLC monitoring on silica gel, all the volatiles were evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60–90 °C)/ethyl acetate = 30:1, v/v), affording **17** (85 mg, 72%) as a yellow solid.

4-((4-Azidobutyl)thio)-3-(methylthio)-1,5-diphenyl-1*H*-pyrazole (17): 85 mg, 72%; yellow solid, m.p.: 105–106 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (m, 3 H), 7.29 (m, 7 H), 3.03 (t, J = 6.6 Hz, 2 H), 2.67 (s, 3 H), 2.61 (t, J = 6.5 Hz, 2 H), 1.55–1.34 (m, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.1, 146.9, 139.7, 130.1, 129.2, 128.8, 128.7, 128.2, 127.1, 124.5, 109.3, 50.8, 35.1, 27.2, 26.1, and 14.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{22}N_5S_2$ 396.1317; Found 396.1314.

Synthesis of 4-((4-azidobutyl)thio)-3-(methylthio)-5-phenylisoxazole (18)

A mixture of 2-((4-azidobutyl)thio)-3,3-bis(methylthio)-1- phenylprop-2-en-1-one (**2 a**) (106 mg, 0.3 mmol), hydroxylamine hydrochloride (209 mg, 3 mmol), and K_2CO_3 (415 mg, 3 mmol) in 2 mL EtOH was stirred at 80 °C for 12 h. After **2 a** was completely consumed by TLC monitoring on silica gel, all the volatiles were evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60–90 °C)/ethyl acetate = 30:1, v/v), affording **18** (78 mg, 81%) as a yellow liquid.

4-((4-Azidobutyl)thio)-3-(methylthio)-5-phenylisoxazole (18): 78 mg, 81%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.27–8.03 (m, 2 H), 7.63–7.42 (m, 3 H), 3.13 (t, J = 6.7 Hz, 2 H), 2.72 (t, J = 6.9 Hz, 2 H), 2.63 (s, 3 H), 1.67–1.51 (m, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.8, 165.9, 130.8, 128.9, 127.3, 127.3, 104.4, 50.9, 34.9, 27.7, 26.5, and 13.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{17}N_4OS_2$ 321.0844; Found 321.0842.

Synthesis of 5-((4-azidobutyl)thio)-4-(methylthio)-6-phenylpyrimidin-2-amine (19)

A mixture of 2-((4-azidobutyl)thio)-3,3-bis(methylthio)-1- phenylprop-2-en-1-one (**2 a**) (106 mg, 0.3 mmol), guanidine nitrate (73 mg, 0.6 mmol), and K_2CO_3 (83 mg, 0.6 mmol) in 2 mL MeCN was stirred at 100 °C for 36 h. After **2 a** was completely consumed by TLC monitoring on silica gel, all the volatiles were evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60–90 °C)/ethyl acetate = 30:1, v/v), affording **19** (66 mg, 63%) as a yellow liquid.

5-((4-Azidobutyl)thio)-4-(methylthio)-6-phenylpyrimidin-2-amine (19): 66 mg, 63%; yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.66–7.55 (m, 2 H), 7.49–7.38 (m, 3 H), 5.25 (s, 2 H), 3.02 (t, J = 6.6 Hz, 2 H), 2.55–2.35 (m, 5 H), 1.44–1.22 (m, 4 H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 178.1, 169.1, 160.9, 138.5, 129.4, 129.2, 127.9, 112.4, 50.9, 35.2, 27.6, 26.1, and 14.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{19}N_6S_2$ 347.1113; Found 347.1119.

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