Copper-Catalyzed Regio- and Stereoselective Hydrothiolation of Allenamides, Enamides, and Ynamides

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Copper-catalyzed regio- and stereoselective hydrothiolation of allenamides, enamides and ynamides.

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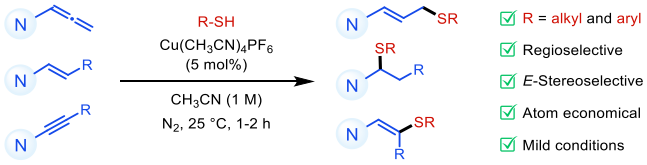
Supporting Information Placeholder

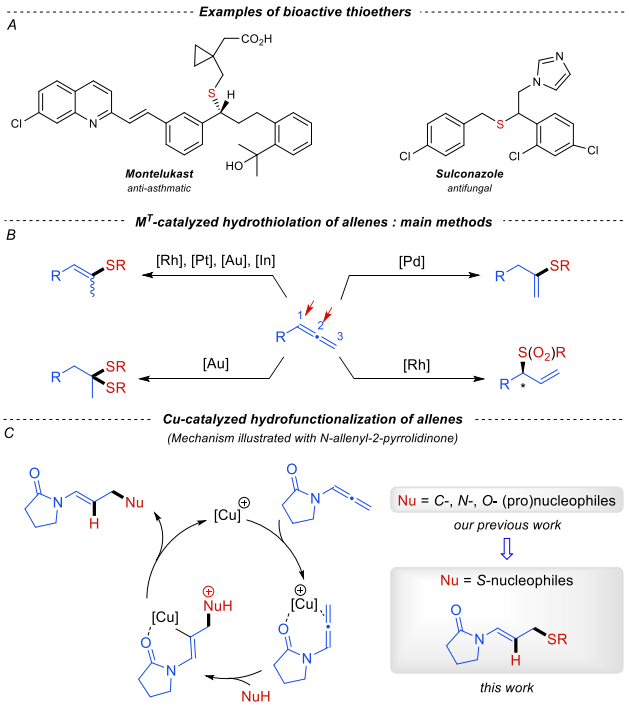


We report a simple protocol for the copper-catalyzed hydrothiolation of *N*-unsaturated precursors, i.e. allenamides, enamides and ynamides, under mild conditions. This method proceeds with a low loading of commercially available $Cu(CH_3CN)_4PF_6$ catalyst and enables the room temperature transformation of a wide range of aromatic and aliphatic thiols into allylic or vinylic thioethers, 1,3-dithioethers and thioaminals with good regio- and stereoselectivity.

INTRODUCTION

Thioethers or sulfides are widespread organosulfur motifs in both natural and synthethic molecules.[1-4] Indeed, many active pharmaceutical or agrochemical ingredients contain this functional group, such as for exemple Montelukast and Sulconazole (Scheme 1, A). Thioethers are also present in materials,[5] in ligands for catalysis[6] and in organic synthesis as key synthetic intermediates mainly toward sulfoxides and sulfones *via* oxidation.[7] Thus, the development of straightforward synthetic methods allowing the formation of C-S bonds remains an important challenge. Among these, hydrothiolation is an atom-economic tool consisting in directly adding a thiol to an unsaturated carbon-carbon bond. This approach has been well studied for alkenes, dienes and alkynes, involving either radical species, ionic intermediates or transition-metal catalysts.[8] In comparison, relatively few works related to the inter- or intramolecular hydrothiolation of allenes have been described. Those are mainly based on the use of palladium, gold and rhodium complexes as catalysts, and lead to the formation of vinylic or allylic thioethers by addition of the thiol on the C_1 (Rh[9]) or C_2 (Pd,[10] Au[11]) allenic carbon atoms (Scheme 1, B). Over the last years, our team has reported on a series of copper-catalyzed regio- and *E*-stereoselective additions of *C*-, *N*-, *O*- (pro)nucleophiles to the C_3 allenic carbon of terminal allenes and allenamides.[12] Concerning the mechanism (illustrated in Scheme 1C for the hydroamination of *N*-allenyl-2-pyrrolidinone), it was proposed that the allene moiety would coordinate to a cationic Cu species, with the carbonyl group of the substrate acting as a directing group. After addition of the nucleophile (NuH) onto the terminal double bond, hydrodemetallation with retention of configuration of the later would regenerate the catalyst and furnish the final product. The regio- and stereoselective outcomes of the Cu-catalyzed hydroamination of allenes were supported by DFT calculations and kinetic studies.[13]

Scheme 1. Hydrothiolation of allenes



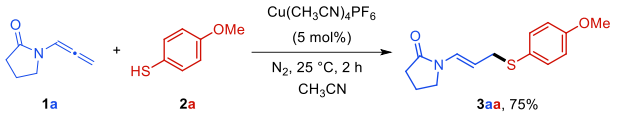
In this context, we disclose herein the first regioselective copper-catalyzed intermolecular hydrothiolation of allenamides, which takes place in the C_3 position,[14] and the extension of this

approach to enamides and ynamides. The synthesis of 1,3-dithioethers *via* a double intermolecular hydrothiolation of allenamides in the C_1 and C_3 position is also reported.

RESULTS AND DISCUSSION

Based on our previous works, we set out to study the model reaction between equimolar amounts of *N*-allenyl-2-pyrrolidinone **1a** and *p*-methoxythiophenol **2a** using 5 mol% of $Cu(CH_3CN)_4PF_6$ as the copper source (Table 1 and SI). Stirring the reaction for 2 h at room temperature in acetonitrile selectively furnished the (*E*) allylic product **3aa** as the sole regioisomer in 75% yield. In the absence of copper or with low catalyst loading or in the presence of air, the formation of a by-product (E/Z mixture) was observed, resulting from the addition of the thiol moiety on the central allenic carbon (entries 2 to 4). Different copper salts and solvents were investigated, and the combination $Cu(CH_3CN)_4PF_6$ in acetonitrile was found to be the most effective (entries 5 and 6). No positive ligand effect was observed when 2,2'-bipyridine was involved in the reaction (entry 7). The use of a base or the prior deprotonation of the thiophenol led to a suppression of the reactivity (entries 8 and 9). Finally, on a 10 mmol scale, thioether **3aa** was obtained in 68% yield (1.76g) (entry 10).

Table 1. Screening of reaction conditions for the copper-catalyzed hydrothiolation of allenamide 1a with 2a [a,b,c,d,e]

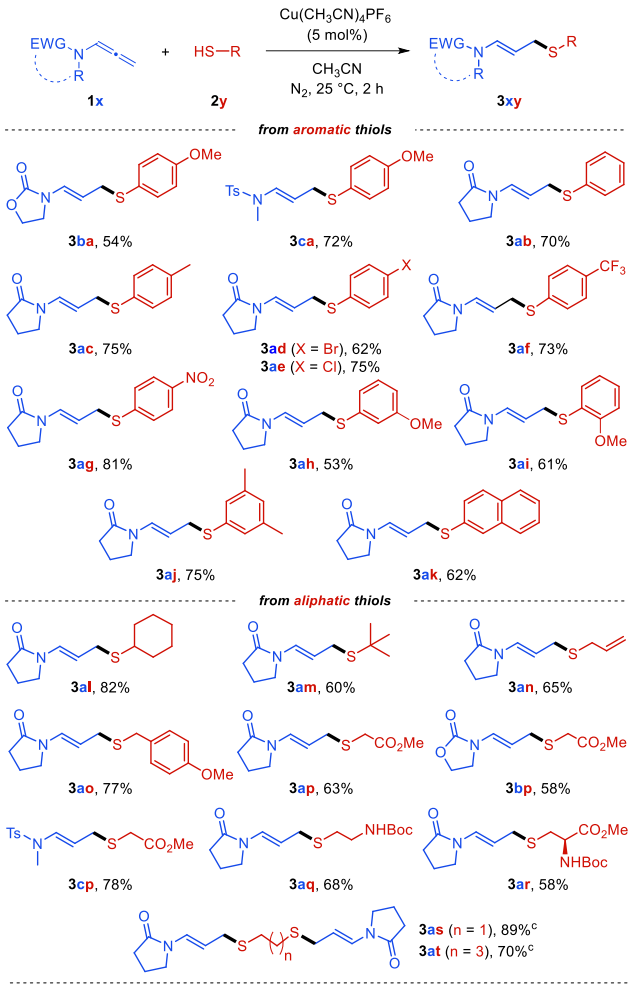


Entry	Deviation from above	Yield (%) [b]
1	None	75
2	Under open air	67 (12[c])
3	Without copper catalyst	3 (27[c])
4	With 1 mol% of $Cu(CH_3CN)_4PF_6$	45 (24[c])
5	With Cu_2O, CuO, CuI, $Cu(OTf)_2$ as copper source	50, 48, 67, 61
6	THF, DMF, CH_2Cl_2, 1,4-dioxane as solvent	58, 65, 67, 72
7	With 2,2'-bipyridine as ligand	33
8	With sodium *p*-methoxythiophenolate **2'a**	nr [d]
9	With K_2CO_3 as base	nr [d]
10	On a 10 mmol scale	68

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (1 equiv, 0.2 mmol), additives and copper source were placed in a Schlenk tube under nitrogen in 0.2 mL of dry solvent (1M) for 2 h at 25 °C. [b] Determined through ^1H NMR analysis using trichloroethylene (1 equiv, 0.2 mmol) as an internal standard. [c] Combined E/Z ^1H NMR yield of the regioisomer resulting from the addition of the thiol moiety on the central allenic carbon. [d] nr = no reaction.

Under the optimized conditions, thiol **2a** was successfully added to *N*-allenyl-2-oxazolidinone **1b** and *N*-allenyl, *N*-tosylmethylamine **1c**, affording **3ba** and **3ca** in medium to good yields (54 and 72%) (Scheme 2). The non-functionalized benzenethiol **2b** and a series of para-substituted derivatives with electron-donating or attracting groups were engaged with allenamide **1a**, leading to the allylic thioethers **3ab** to **3ag** in good yields (62-81%). It is interesting to note the good tolerance of our system to the position of the substituents. Indeed, the three regioisomers of methoxy-benzenethiols (*ortho* **2i**, *meta* **2h** and *para* **2a**) led to hydrothiolation products **3aa**, **3ah** and **3ai** in fairly similar yields (53-75%). Finally, the products **3aj** and **3ak** were formed in 62% and 75% yield from 3,5-dimethylbenzenethiol **2j** and 2-naphthalenethiol **2k**.

Scheme 2. [Cu]-catalyzed single hydrothiolation of allenamides [a,b]



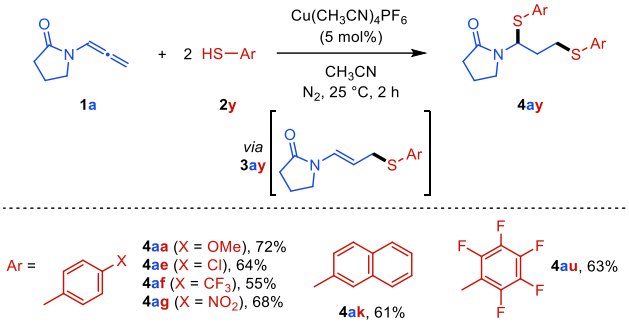
[a] Reaction conditions: **1x** (0.2 mmol), **2y** (1 equiv, 0.2 mmol), and $Cu(CH_3CN)_4PF_6$ (0.05 equiv, 0.01 mmol) were placed in a Schlenk tube under nitrogen in 0.2 mL of dry acetonitrile (1 M) for 2 h at 25 °C. [b] Isolated yields. [c] For **3as** and **3at**, a second equivalent of **1a** was added after 2 h and the medium was stirred for 2 h at 25 °C.

We then turned our attention to the reactivity of aliphatic thiols. The cyclohexyl- **2l**, tert-butyl- **2m** and allyl- **2n** thiol derivatives led to the corresponding thioethers **3al**-**3an** in good yields (60-82%). Benzylthiol **2o** could also be added to allene **1a**, affording compound **3ao** in 77% yield. Compounds **3ap**, **3bp** and **3cp** were then synthesized in good yield (58-78%) using the methyl ester **2p**. The protected amine **2q** also proved to be a suitable substrate for the hydrothiolation affording **3aq** in 68% yield, whereas in the absence of protection, no reaction was observed. Finally, the hydrothiolation of the allenamide **1a** with the α-amino acid derived from L-cysteine **2r** led to the formation of compound **3ar** in 58% yield. We then carried out the hydrothiolation of the allenamide **1a** with the aliphatic dithiols **2s** and

2t, using a different procedure, allowing us to obtain the double functionalized products **3as** and **3at** in high yields (70-89%).

During our optimization studies with **1a**, we observed that in the presence of an excess of thiol (>1 equiv), the formation of the 1,3-dithioether byproduct **4aa** occurred, resulting from a second hydrothiolation reaction (Scheme 3). The latter was never observed when less than one equivalent of thiol was used and, conversely, it was the only product obtained when more than 2 equivalents of thiol were used. We performed the addition of aromatic thiols and were able to obtain the compounds **4aa, 4ae, 4af, 4ag, 4ak** and **4au** in medium to good yields (55-72%) (Scheme 3). To the best of our knowledge, the one pot difunctionalization of allenes in two different positions has been sparsely reported.[15,16] It is noteworthy that the same products could be obtained *via* a single hydrothiolation of the isolated enamide intermediate **3ay** resulting itself from the single hydrothiolation of the starting allenamide **1a**. This hydrothiolation could not take place in the absence of copper.

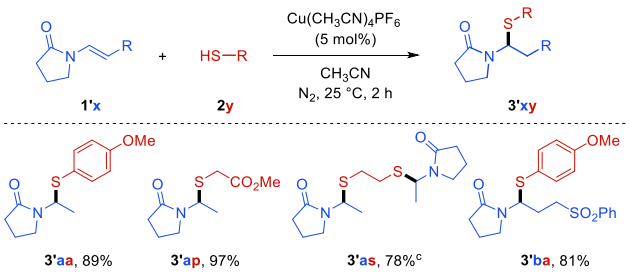
Scheme 3. [Cu]-catalyzed double 1,3-hydrothiolation of allenamides [a,b]



[a] Reaction conditions: **1a** (0.2 mmol), **2y** (2 equiv, 0.4 mmol), and $Cu(CH_3CN)_4PF_6$ (0.05 equiv, 0.01 mmol) were placed in a Schlenk tube under nitrogen in 0.2 mL of dry acetonitrile (1 M) for 2 h at 25 °C. [b] Isolated yields.

The formation of the double addition product led us to test the application of our catalytical system to different enamide substrates (Scheme 4). We first applied the reaction conditions to *N*-vinyl-2-pyrrolidinone **1'a**, a terminal enamide related to the model allenamide **1a**. The thioaminals **3'aa**, **3'ap** and **3'as** could be synthesized in very good yields (78-97%) using an aromatic (**2a**), an aliphatic (**2p**) and a 1,2-dithiol (**2s**) partner, respectively. This hydrothiolation reaction proceeded with full α-regioselectivity and did not take place in the absence of the copper catalyst.

Scheme 4. [Cu]-catalyzed α–selective hydrothiolation of enamides. [a,b,c]

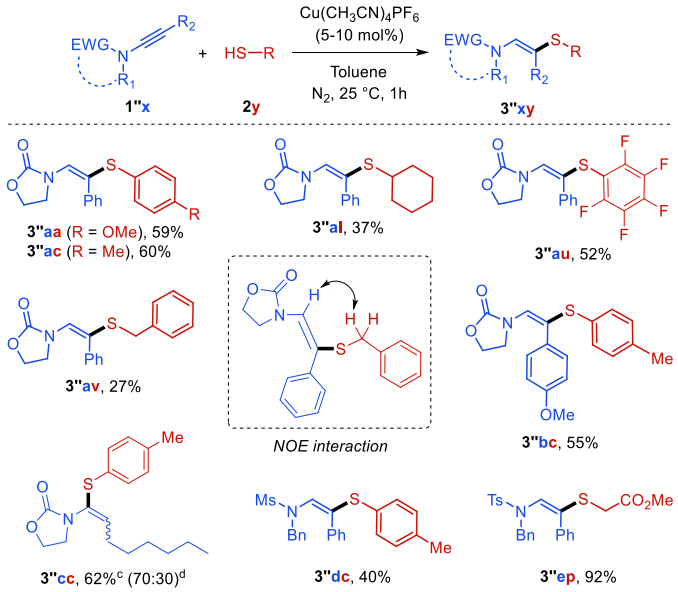


[a] Reaction conditions: **1'x** (0.2 mmol), **2y** (1 equiv, 0.2 mmol), and $Cu(CH_3CN)_4PF_6$ (0.05 equiv, 0.01 mmol) were placed in a Schlenk tube under nitrogen in 0.2 mL of dry acetonitrile (1M) for 2h at 25°C. [b] Isolated yields. [c] For **3'as**, a second equivalent of **1a** was added after 2h and the medium was stirred for another 2h at 25°C.

The substituted enamide **1'b**, prepared by hydrosulfonylation of allenamide **1a** in water in the presence of TFA and sodium benzene sulfinate according to the method previously reported by our team,[14a] could also be used in this reaction and provided the product **3'ba** in 81% yield. To the best of our knowledge, hydrothiolation of enamides has been previously reported with both α- and β- regioselectivities, but the observed α-regioselectivity was only described in the presence of a palladium catalyst or a ruthenium-based photocatalyst and visible light irradiation.[17,18]

We then turned our interest towards the reactivity of ynamides with thiols in the presence of a copper catalyst. For these substrates only a few examples of hydrothiolation have been reported, proceeding exclusively *via* radical pathways and hence leading to the β-thioethers.[19] To the best of our knowledge, aryl-substituted ynamides have not yet been described in this reaction. After a short parametric study (*see SI*), we found that toluene was the best solvent to perform the hydrothiolation of ynamide **1''a** (1-vinylpyrrolidin-2-one) with 4-methylbenzenethiol **2c** at room temperature. This rapid reaction led in one hour to the formation of β-thioether **3''ac** with exclusive *(E)* selectivity as confirmed by NOESY experiments (see below). This process did not take place in the absence of the copper catalyst. Several aromatic or aliphatic thiols were then used to perform the hydrothiolation of **1''a** or **1''b** thus affording the vinylic thioethers **3''aa, 3''ac**, **3''al**, **3''au**, **3''av** and **3''bc** in low to medium isolated yields (27-60%) (Scheme 5).

Scheme 5. [Cu]-catalyzed α- or β-hydrothiolation of ynamides. [a,b,c]



[a] Reaction conditions: **1''x** (2 equiv, 0.5 mmol), **2y** (1 equiv, 0.25 mmol), and $Cu(CH_3CN)_4PF_6$ (0.05 equiv, 0.01 mmol) were placed in a Schlenk tube under nitrogen in 0.25 mL of dry toluene (1 M) for 1 h at 25 °C. [b] Isolated yields. [c] For **3''cc**, 0.25 mmol (1 equiv) of **1''c** and 0.025 mmol (0.1 equiv) of $Cu(CH_3CN)_4PF_6$ were used. [d] E/Z ratio.

When alkyl substituted ynamide **1''c** was engaged with **2c**, we surprisingly observed the formation of the α-thioether **3''cc** with a loss of *(E)* selectivity. Electrodeficient thiophenols (*p*-NO_2 and *p*-CF_3) did not yield any product under these conditions. Finally, starting from sulfonamide derivatives **1''d** and **1''e** allowed to obtain the hydrothiolation products **3''dc** (40%) and **3''ep** (92%) in the presence of 4-methylbenzenethiol **2c** and methyl 2-mercaptoacetate **2p**, in medium to excellent yields. On compound **3''av**, the NOESY interaction between the two singlets corresponding to benzylic methylene group and vinylic proton undoubtedly confirm the *(E)* configuration. The relative stereochemistry of other compounds was attributed by analogy with **3''av**.

CONCLUSION

In conclusion, we have reported an efficient synthesis of allylic or vinylic thioethers, 1,3-dithioethers and thioaminals via an original copper-catalyzed hydrothiolation of allenamides, enamides and ynamides. For allenamides it represents the first Cu-catalyzed intermolecular hydrothiolation which takes place in the C_3 position. Performed under very mild temperature conditions and short reaction time, this general regio- and stereoselective hydrothiolation method proceeds in a total atom economical fashion.

EXPERIMENTAL PART

1. General considerations

All reactions were performed in oven-dried Schlenk flasks under nitrogen atmosphere. Unless otherwise mentioned, all reagents were purchased from commercial sources and were used without further purification and weighed in air without precautions. The solvents were distilled over Na/benzophenone or CaH_2. Allenamides **1a-c**[19,20], enamide **1'b**[16] and ynamides **1''a-e**[22] were synthetized according to previously described methods. Enamide **1'a** was commercially available. Thiol **2q** was synthesized following a reported procedure.[23]

^1H, $^1H\{^{19}F\}$, $^{13}C\{^1H\}$, $^{13}C\{^1H\}\{^{19}F\}$, $^{19}F\{^1H\}$ NMR and APT and NOESY spectra were recorded with a Bruker AC-400 MHz spectrometer in $CDCl_3$ or acetone-d_6, and the residual solvent protons (7.26 for ^1H) or carbons (77.16 for ^{13}C) were used as internal references. Structural assignments were made with additional information from gCOSY, gHSQC, and gHMBC experiments. Chemical shifts (δ) are reported in parts per million (ppm), and the coupling constants (*J*) are reported in Hertz (Hz). The following abbreviations are used: *s*, singlet; *d*, doublet; *dd*, doublet of doublets; *dt*, doublet of triplets; t, triplet; *hept*, heptuplet; and *m*, multiplet. A TOF-type mass analyzer was used for the HRMS measurements. Electrospray ionization (ESI) high-resolution mass spectra were recorded on a Waters SYNAPT G2-S (SN: UEB205) high-definition mass spectrometer in the positive ion mode from 100 to 1500 Da. Products were dissolved in either MeOH or a basic aqueous solution, depending on the case, and were introduced directly into the spectrometer. The capillary voltage was 3000 V, and the cone voltage was 30 V. The source and desolvation temperatures were 100 and 150 °C respectively. The data were reprocessed by the Masslynx 4.1 software.

2. General hydrothiolation procedures

2.1. General procedure A

In a flame-dried Schlenk tube of appropriate size was added the copper catalyst (5 mol%) under a stream of nitrogen. After a vacuum and backfill cycle, the solvent (1 M) was then added, followed by the allenamide/enamide (1.0 equiv, 0.2 mmol) and then the thiol (1.0 equiv, 0.2 mmol for mono hydrothiolation or 2.0 equiv, 0.4 mmol for double hydrothiolation), when liquids. If the thiol and allenamide/enamide are solids, they are introduced at the beginning, simultaneously with the catalyst. The addition of the thiol immediately changed the color of the reaction mixture. The mixture was stirred at 25 °C for 2 hours. After basic aqueous work-up using either NaOH 2 N or sat. Na_2CO_3 depending on the pKa of the thiol involved in the reaction, the organic phase was separated. The remaining aqueous phase was further extracted with CH_2Cl_2. The combined organic layers were dried over magnesium sulfate and concentrated under vacuum. Then, trichloroethylene (1.0 equiv, 0.2 mmol) was added as the internal standard to estimate the ^1H NMR yield. In most cases, the analytically pure hydrothiolation product could be obtained directly without further purification; however, purification by triethylamine-treated silica gel column chromatography was used if necessary.

2.2. General procedure B

In a flame-dried Schlenk tube of appropriate size was added the copper catalyst (5 mol%) under a stream of nitrogen. After a vacuum and backfill cycle, the solvent (1 M) was then added, followed by the allenamide/enamide (1.0 equiv, 0.2 mmol) and then the thiol (1.0 equiv, 0.2 mmol), when liquids. If the thiol and allenamide/enamide are solids, they are introduced at the beginning, simultaneously with the catalyst. The addition of the thiol immediately changed the color of the reaction mixture. The mixture was stirred at 25 °C for 2 hours. Then, allenamide/enamide (1.0 equiv, 0.2 mmol) is added to the reaction mixture and stirring continued for another 2 hours. After basic aqueous work-up using either NaOH 2 N or sat. Na_2CO_3 depending on the pKa of the thiol involved in the reaction, the organic phase was separated. The remaining aqueous phase was further extracted with CH_2Cl_2. The combined organic layers were dried over magnesium sulfate and concentrated under vacuum. Then, trichloroethylene (1.0 equiv, 0.2 mmol) was added as the internal standard to estimate the ^1H NMR yield. In most cases, the analytically pure hydrothiolation product could be obtained directly without further purification; however, purification by triethylamine-treated silica gel column chromatography was used if necessary.

2.3. General procedure C

In a flame-dried Schlenk tube of appropriate size was added the copper catalyst (5 mol%) under a stream of nitrogen. After a vacuum and backfill cycle with nitrogen, toluene (1 M) was then added, followed by the ynamide (2.0 equiv, 0.5 mmol) and then the thiol (1.0 equiv, 0.25 mmol), when liquids. If the ynamide is solid, it is introduced at the beginning, simultaneously with the catalyst. The addition of the thiol immediately changed the color of the reaction mixture. The mixture was stirred at 25 °C for 1 hour. Water was then added in the mixture and the product was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$, filtered and concentrated under vacuum. The crude mixture was purified by silica gel column chromatography (*n*-hexane/Et_2O) to obtain the corresponding hydrothiolation product.

3. Product Characterization data

(E)-1-(3-((4-methoxyphenyl)thio)prop-1-en-1-yl)pyrrolidin-2-one **3aa**

The reaction of *N*-allenyl-2-pyrrolidinone (**1a**, 0.2 mmol) with 4-methoxythiophenol (**2a**, 1.0 equiv, 0.2 mmol) according to the general procedure A afforded the corresponding hydrothiolation compound **3aa** as an off-white oil (39.5 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.30 (*m*, 2H), 6.87 – 6.81 (*d*, 1H + *m*, 2H), 4.95 (*dt*, *J* = 14.3, 7.6 Hz, 1H), 3.79 (*s*, 3H), 3.50 (*dd*, *J* = 7.6, 0.6 Hz, 2H), 3.48 – 3.44 (*m*, 2H), 2.45 (*m*, 2H), 2.10 – 2.04 (*m*, 2H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ 173.2, 159.3, 134.1, 126.0, 125.8, 114.7, 107.5, 55.5, 45.3, 37.2, 31.3, 17.5. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{18}NO_2S$ 264.1058, found 264.1053.

(E)-1-(3-(phenylthio)prop-1-en-1-yl)pyrrolidin-2-one **3ab**

The reaction of *N*-allenyl-2-pyrrolidinone (**1a**, 0.2 mmol) with thiophenol (**2b**, 1.0 equiv, 0.2 mmol) according to the general procedure A afforded the corresponding hydrothiolation compound **3ab** as an off-white oil (32.7 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 – 7.20 (*m*, 4H), 7.15 – 7.09 (*m*, 1H), 6.91 (*d*, *J* = 14.2 Hz, 1H), 4.92 (*dt*, *J* = 14.6, 7.5 Hz, 1H), 3.55 (*dd*, *J* = 7.5, 0.9 Hz, 2H), 3.44 – 3.35 (*m*, 2H), 2.39 (*m*, 2H), 2.07 – 1.97 (*m*, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 173.2, 135.9, 130.1, 129.1, 126.5, 126.4, 106.9, 45.3, 35.1, 31.3, 17.5. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{16}NOS$ 234.0940, found 234.0947.

(E)-1-(3-(*p*-tolylthio)prop-1-en-1-yl)pyrrolidin-2-one **3ac**

The reaction of *N*-allenyl-2-pyrrolidinone (**1a**, 0.2 mmol) with 4-methylthiophenol (**2c**, 1.0 equiv, 0.2 mmol) according to the general procedure A afforded the corresponding hydrothiolation compound **3ac** as an off-white oil (39.2 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 – 7.21 (*m*, 2H), 7.12 – 7.06 (*m*, 2H), 6.93 (*d*, *J* = 14.3 Hz, 1H), 4.97 (*dt*, *J* = 14.2, 7.5 Hz, 1H), 3.56 (*dd*, *J* = 7.5, 1.0 Hz, 2H), 3.49 – 3.42 (*m*, 2H), 2.45 (*m*, 2H), 2.31 (*s*, 3H), 2.12 – 2.03 (*m*, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 173.2, 136.7, 132.0, 130.9, 129.8, 126.2, 107.2, 45.2, 35.5, 31.2, 21.2, 17.5. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{18}NOS$ 248.1109, found 248.1108.

(E)-1-(3-((4-bromophenyl)thio)prop-1-en-1-yl)pyrrolidin-2-one **3ad**

The reaction of *N*-allenyl-2-pyrrolidinone (**1a**, 0.2 mmol) with 4-bromothiophenol (**2d**, 1.0 equiv, 0.2 mmol) according to the general procedure A afforded the corresponding hydrothiolation compound **3ad** as an off-white oil (38.7 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.37 (*m*, 2H), 7.20 – 7.16 (*m*, 2H), 6.98 (*d*, *J* = 14.3 Hz, 1H), 4.94 (*dt*, *J* = 14.5, 7.5 Hz, 1H), 3.59 (*dd*, *J* = 7.5, 1.1 Hz, 2H), 3.47 – 3.44 (*m*, 2H), 2.46 (*m*, 2H), 2.12 – 2.05 (*m*, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 173.3, 135.1, 132.1, 131.5, 126.6, 120.4, 106.4, 45.2, 35.1, 31.2, 17.5. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{15}BrNOS$ 312.0052, found 312.0058.

(E)-1-(3-((4-chlorophenyl)thio)prop-1-en-1-yl)pyrrolidin-2-one **3ae**

The reaction of *N*-allenyl-2-pyrrolidinone (**1a**, 0.2 mmol) with 4-chlorothiophenol (**2e**, 1.0 equiv, 0.2 mmol) according to the general procedure A afforded the corresponding hydrothiolation compound **3ae** as an off-white oil (40.2 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (*s*, 4H), 6.96 (*d*, *J* = 14.3 Hz, 1H), 4.93 (*dt*, *J* = 14.6, 7.5 Hz, 1H), 3.58 (*dd*, *J* = 7.5, 1.0 Hz, 2H), 3.49 – 3.42 (*m*, 2H), 2.45 (*m*, 2H), 2.12 – 2.00 (*m*, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 173.2, 134.3, 132.4, 131.4, 129.1, 126.5, 106.4, 45.2, 35.2, 31.2, 17.4. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{15}ClNOS$ 268.0557, found 268.0555.

(E)-1-(3-((4-trifluoromethylphenyl)thio)prop-1-en-1-yl)pyrrolidin-2-one **3af**

The reaction of *N*-allenyl-2-pyrrolidinone (**1a**, 0.2 mmol) with 4-trifluoromethylthiophenol (**2f**, 1.0 equiv, 0.2 mmol) according to the general procedure A afforded the corresponding hydrothiolation compound **3af** as an off-white oil (44 mg, 73%). ^{1}H{^{19}F} NMR (400 MHz, $CDCl_3$): δ 7.53 – 7.47 (*m*, 2H), 7.39 – 7.32 (*m*, 2H), 7.07 (*d*, *J* = 14.3 Hz, 1H), 4.98 (*dt*, *J* = 14.5, 7.4 Hz, 1H), 3.68 (*dd*, *J* = 7.4, 1.1 Hz, 2H), 3.52 – 3.43 (*m*, 2H), 2.49 (*m*, 2H), 2.14 – 2.04 (*m*, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 173.3, 141.70 (*d*, *J* = 1.4 Hz), 128.1, 127.5 (*q*, *J* = 32 Hz), 126.7, 125.8 (*q*, *J* = 3.8 Hz), 124.2 (*q*, *J* = 272 Hz), 105.7, 45.2, 33.7, 31.2, 17.5. ^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$): δ -62.41. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for. $C_{14}H_{15}F_3NOS$ 302.0821, found 302.0825.

(E)-1-(3-((4-nitrophenyl)thio)prop-1-en-1-yl)pyrrolidin-2-one **3ag**

The reaction of *N*-allenyl-2-pyrrolidinone (**1a**, 0.2 mmol) with 4-nitrothiophenol (**2g**, 1.0 equiv, 0.2 mmol) according to the general procedure A afforded the corresponding hydrothiolation compound **3ag** as an off-white oil (45.1 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 – 8.06 (*m*, 2H), 7.36 – 7.29 (*m*, 2H), 7.12 (*d*, *J* = 14.3 Hz, 1H), 4.95 (*dt*, *J* = 14.5, 7.4 Hz, 1H), 3.73 (*dd*, *J* = 7.3, 1.1 Hz, 2H), 3.46 (*m*, 2H), 2.46 (*m*, 2H), 2.20 – 1.99 (*m*, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 173.3, 146.9, 145.2, 127.4, 126.8, 124.0, 104.7, 45.1, 33.1, 31.1, 17.4. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{15}N_2O_3S$ 279.0798, found 279.0805.

(E)-1-(3-((3-methoxyphenyl)thio)prop-1-en-1-yl)pyrrolidin-2-one **3ah**

The reaction of *N*-allenyl-2-pyrrolidinone (**1a**, 0.2 mmol) with 3-methoxythiophenol (**2h**, 1.0 equiv, 0.2 mmol) according to the general procedure A afforded the corresponding hydrothiolation compound **3ah** as an off-white oil (27.9 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (*t*, *J* = 8.0 Hz, 1H), 7.01 (*d*, *J* = 14.3 Hz, 1H), 6.91 (*ddd*, *J* = 7.7, 1.7, 0.9 Hz, 1H), 6.89 – 6.86 (*m*, 1H), 6.73 (*ddd*, *J* = 8.3, 2.5, 0.9 Hz, 1H), 4.99 (*dt*, *J* = 14.4, 7.5 Hz, 1H), 3.79 (*s*, 3H), 3.63 (*dd*, *J* = 7.5, 1.2 Hz, 2H), 3.51 – 3.45 (*m*, 2H), 2.46 (*m*, 2H), 2.09 (*m*, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 173.2, 159.9, 137.4, 129.9, 126.5, 121.9, 115.1, 112.2, 106.8, 55.4, 45.3, 34.8, 31.2, 17.5. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{18}NO_2S$ 264.1053, found 264.1055.

(E)-1-(3-((2-methoxyphenyl)thio)prop-1-en-1-yl)pyrrolidin-2-one **3ai**

The reaction of *N*-allenyl-2-pyrrolidinone (**1a**, 0.2 mmol) with 2-methoxythiophenol (**2i**, 1.0 equiv, 0.2 mmol) according to the general procedure A afforded the corresponding hydrothiolation compound **3ai** as an off-white oil (32.1 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (*dd*, *J* = 7.6, 1.7 Hz, 1H), 7.20 (*ddd*, *J* = 8.2, 7.5, 1.7 Hz, 1H), 6.95 (*d*, *J* = 14.3 Hz, 1H), 6.90 (*td*, *J* = 7.5, 1.2 Hz, 1H), 6.85 (*dd*, *J* = 8.2, 1.1 Hz, 1H), 4.97 (*dt*, *J* = 14.4, 7.6 Hz, 1H), 3.89 (s, 3H), 3.60 (*dd*, *J* = 7.6, 0.5 Hz, 2H), 3.45 – 3.41 (*m*, 2H), 2.46 – 2.39 (*m*, 2H), 2.09 – 2.02 (*m*, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 173.1, 157.9, 131.1, 128.0, 126.3, 123.7, 121.0, 110.7, 107.0, 55.9, 45.2, 33.4, 31.2, 17.5.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{18}NO_2S$ 264.1053, found 264.1052.

(E)-1-(3-((3,5-dimethylphenyl)thio)prop-1-en-1-yl)pyrrolidin-2-one **3aj**

The reaction of *N*-allenyl-2-pyrrolidinone (**1a**, 0.2 mmol) with 3,5-dimethylthiophenol (**2j**, 1.0 equiv, 0.2 mmol) according to the general procedure A afforded the corresponding hydrothiolation compound **3aj** as an off-white oil (39.2 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98 (*d*, *J* = 14.3 Hz, 1H), 6.94 (*m*, 2H), 6.81 (*m*, 1H), 4.98 (*dt*, *J* = 14.3, 7.6 Hz, 1H), 3.60 (*dd*, *J* = 7.5, 1.1 Hz, 2H), 3.49 – 3.42 (*m*, 2H), 2.45 (*m*, 2H), 2.27 (*s*, 6H), 2.13 – 2.00 (*m*, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 173.1, 138.5, 135.4, 128.3, 127.5, 126.3, 106.9, 45.2, 34.9, 31.2, 21.3, 17.5. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{20}NOS$ 262.1266, found 262.1257.

(E)-1-(3-(naphthalen-2-ylthio)prop-1-en-1-yl)pyrrolidin-2-one **3ak**

The reaction of *N*-allenyl-2-pyrrolidinone (**1a**, 0.2 mmol) with 2-naphthalenethiol (**2k**, 1.0 equiv, 0.2 mmol) according to the general procedure A afforded the corresponding hydrothiolation compound **3ak** as an off-white oil (35.1 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 – 7.71 (*m*, 4H), 7.50 – 7.38 (*m*, 3H), 7.04 (*d*, *J* = 14.3 Hz, 1H), 5.02 (*dt*, *J* = 14.6, 7.5 Hz, 1H), 3.73 (*dd*, *J* = 7.5, 1.1 Hz, 1H), 3.44 (*m*, 2H), 2.44 (*m*, 2H), 2.04 (*m*, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 173.3, 133.8, 133.4, 132.0, 128.5, 127.82, 127.80, 127.78, 127.2, 126.6, 126.5, 125.9, 106.9, 45.2, 34.8, 31.2, 17.4 (s). HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{18}NOS$ 284.1104, 284.1110.

(E)-1-(3-(cyclohexylthio)prop-1-en-1-yl)pyrrolidin-2-one **3al**

The reaction of *N*-allenyl-2-pyrrolidinone (**1a**, 0.2 mmol) with cyclohexylthiol (**2l**, 1.0 equiv, 0.2 mmol) according to the general procedure A afforded the corresponding hydrothiolation compound **3al** as an off-white oil (39.3mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.97 (*d*, *J* = 14.3 Hz, 1H), 4.97 (*dt*, *J* = 14.3, 7.6 Hz, 1H), 3.58 – 3.48 (*m*, 2H), 3.24 (expected *dd*, observed *d*, *J* = 7.6 Hz, 2H), 2.67 – 2.58 (*m*, 1H), 2.54 – 2.46 (*m*, 2H), 2.20 – 2.07 (*m*, 2H), 1.98 – 1.91 (*m*, 2H), 1.77 (*m*, 2H), 1.61 (*m*, 2H), 1.40 – 1.27 (*m*, 5H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 173.2, 125.2, 108.7, 45.3, 42.5, 33.5, 31.3, 30.5, 26.0, 25.9, 17.5. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{22}NOS$ 240.1422, found 240.1422.

(E)-1-(3-(tert-butylthio)prop-1-en-1-yl)pyrrolidin-2-one **3am**

The reaction of *N*-allenyl-2-pyrrolidinone (**1a**, 0.2 mmol) with 2-methyl-2-propanethiol (**2m**, 1.0 equiv, 0.2 mmol) according to the general procedure A afforded the corresponding hydrothiolation compound **3am** as an off-white oil (25.6 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05 (*d*, *J* = 14.4 Hz, 1H), 4.99 (*dt*, *J* = 14.8, 7.5 Hz, 1H), 3.52 (*m*, 2H), 3.29 (expected *dd*, observed *d*, *J* = 7.6 Hz, 2H), 2.49 (*m*, 2H), 2.17 – 2.07 (*m*, 2H), 1.35 (*s*, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 173.1, 125.5, 108.3, 45.3, 42.9, 31.3, 31.1, 29.2, 17.5. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{11}H_{20}NOS$ 214.1266, found 214.1264.

(E)-1-(3-(allylthio)prop-1-en-1-yl)pyrrolidin-2-one **3an**

The reaction of *N*-allenyl-2-pyrrolidinone (**1a**, 0.2 mmol) with allyl mercaptan (**2n**, 1.0 equiv, 0.2 mmol) according to the general procedure A afforded the corresponding hydrothiolation compound **3an** as an off-white oil (25.6 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92 (*d*, *J* = 14.3 Hz, 1H), 5.81 – 5.69 (*m*, 1H), 5.14 – 5.03 (*m*, 2H), 4.88 (*dt*, *J* = 14.4, 7.6 Hz, 1H), 3.53 – 3.47 (*m*, 2H), 3.14 (*dd*, *J* = 7.6, 1.0 Hz, 2H), 3.09 – 3.06 (*m*, 2H), 2.46 (*m*, 2H), 2.14 – 2.04 (*m*, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 173.2, 155.8, 125.9, 107.6, 45.2, 32.0, 31.2, 31.1, 28.5, 17.5. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{10}H_{16}NOS$ 198.0947, found 198.0950.

(E)-1-(3-((4-methoxybenzyl)thio)prop-1-en-1-yl)pyrrolidin-2-one **3ao**

The reaction of *N*-allenyl-2-pyrrolidinone (**1a**, 0.2 mmol) with 4-methoxybenzylthiol (**2o**, 1.0 equiv, 0.2 mmol) according to the general procedure A afforded the corresponding hydrothiolation compound **3ao** as an off-white oil (42.7 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 – 7.19 (*m*, 2H), 6.92 (*d*, *J* = 14.3 Hz, 1H), 6.87 – 6.80 (*m*, 2H), 4.88 (*dt*, *J* = 14.4, 7.6 Hz, 1H), 3.79 (*s*, 3H), 3.62 (*s*, 2H), 3.53 – 3.43 (*m*, 2H), 3.10 (*d*, *J* = 7.4 Hz, 2H), 2.48 (*m*, 2H), 2.16 – 2.05 (*m*, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 173.2, 158.7, 130.3, 130.1, 125.8, 114.0, 107.9, 55.4, 45.3, 34.8, 31.7, 31.3, 17.5. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{20}NO_2S$ 278.1215, found 278.1214.

Methyl *(E)*-2-((3-(2-oxopyrrolidin-1-yl)allyl)thio)acetate **3ap**

The reaction of *N*-allenyl-2-pyrrolidinone (**1a**, 0.2 mmol) with methyl 2-mercaptoacetate (**2p**, 1.0 equiv, 0.2 mmol) according to the general procedure A afforded the corresponding hydrothiolation compound **3ap** as an off-white oil (28.9 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.99 (*d*, *J* = 14.3 Hz, 1H), 4.89 (*dt*, *J* = 14.3, 7.7 Hz, 1H), 3.72 (*s*, 3H), 3.55 – 3.47 (*m*, 2H), 3.31 (expected *dd*, observed *d*, *J* = 7.7 Hz, 2H), 3.17 (*s*, 2H), 2.48 (*m*, 2H), 2.16 – 2.06 (*m*, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 173.3, 171.1, 126.7, 106.5, 52.5, 45.2, 32.9, 32.0, 31.2, 17.5. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{10}H_{16}NO_3S$ 230.0851, found 230.0846.

Tert-butyl*(E)*-(2-((3-(2-oxopyrrolidin-1-yl)allyl)thio)ethyl)carbamate **3aq**

The reaction of *N*-allenyl-2-pyrrolidinone (**1a**, 0.2 mmol) with 2-(boc-amino)ethanethiol (**2q**, 1.0 equiv, 0.2 mmol) according to the general procedure A afforded the corresponding hydrothiolation compound **3aq** as an off-white oil (40.9 mg, 68%). 2-(boc-amino)ethanethiol was synthesized following a reported procedure.[22] ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.93 (*d*, *J* = 14.3 Hz, 1H), 4.90 (*dt*, J = 14.65, 7.68 Hz, 1H + *s*, 1H), 3.51 – 3.48 (*m*, 2H), 3.26 (*dd*, *J* = 12.3, 6.0 Hz, 2H), 3.18 (expected *dd*, observed *d*, *J* = 7.5 Hz, 2H), 2.57 (*s*, 2H), 2.45 (*m*, 2H), 2.12 – 2.04 (*m*, 2H), 1.41 (*s*, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 173.2, 155.8, 125.9, 107.6, 79.4, 60.4, 45.2, 39.7, 32.0, 31.2, 28.4, 17.5. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{25}N_2O_3S$ 301.1580, found 301.1590.

Methyl *(E)*-*N*-(tert-butoxycarbonyl)-*S*-(3-(2-oxopyrrolidin-1-yl)allyl)-L-cysteinate **3ar**

The reaction of *N*-allenyl-2-pyrrolidinone (**1a**, 0.2 mmol) with methyl (*tert*-butoxycarbonyl)-L-cysteinate (**2r**, 1.0 equiv, 0.2 mmol) according to the general procedure A afforded the corresponding hydrothiolation compound **3ar** as an off-white oil (41.6 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95 (*d*, *J* = 14.3 Hz, 1H), 5.30 (*d*, *J* = 8.1 Hz, 1H), 4.89 (dt, *J* = 14.8, 7.6 Hz, 1H), 4.51 (*dd*, *J* = 12.7, 5.2 Hz, 1H), 3.76 (*s*, 3H), 3.51 (*m*, 2H), 3.20 (*m*, 2H), 2.90 (*m*, 2H), 2.48 (*m*, 2H), 2.16 – 2.05 (*m*, 2H), 1.44 (*s*, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 173.3, 171.7, 155.2, 126.3, 107.1, 80.3, 52.8, 45.3, 33.4, 33.1, 31.2,

29.8, 28.4, 17.5. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{27}N_2O_5S$ 359.1641, found 359.1642.

1,1'-((1E,1'E)-(ethane-1,2-diylbis(sulfanediyl))bis(prop-1-ene-3,1-diyl))bis(pyrrolidin-2-one) **3as**

The reaction of *N*-allenyl-2-pyrrolidinone (**1a**, 0.4 mmol) with ethane-1,2-dithiol (**2s**, 1.0 equiv, 0.2 mmol) according to general procedure B afforded the corresponding hydrothiolation compound **3as** as an off-white oil (60.6 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95 (*d*, *J* = 14.3 Hz, 2H), 4.93 (*dt*, *J* = 14.5, 7.6 Hz, 2H), 3.57 – 3.47 (*m*, 4H), 3.22 (*d*, *J* = 7.5 Hz, 4H), 2.66 (*s*, 4H), 2.49 (*m*, 4H), 2.11 (*m*, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 173.4, 125.9, 107.8, 45.3, 32.5, 31.2, 30.8, 17.5. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{25}N_2O_2S_2$ 341.1352, found 341.1348.

1,1'-((1*E*,1'*E*)-(butane-1,4-diylbis(sulfanediyl))bis(prop-1-ene-3,1-diyl))bis(pyrrolidin-2-one) **3at**

The reaction of *N*-allenyl-2-pyrrolidinone (**1a**, 0.4 mmol) with butane-1,4-dithiol (**2t**, 1.0 equiv, 0.2 mmol) according to the general procedure B afforded the corresponding hydrothiolation compound **3at** as an off-white oil (51.6 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.93 (*d*, *J* = 14.3 Hz, 2H), 4.91 (*dt*, *J* = 14.5, 7.6 Hz, 2H), 3.54 – 3.46 (*m*, 4H), 3.17 (*dd*, *J* = 7.6, 1.0 Hz, 4H), 2.52 – 2.41 (*m*, 8H), 2.17 – 2.04 (*m*, 4H), 1.67 – 1.59 (*m*, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 173.2, 125.5, 108.1, 45.3, 32.2, 31.3, 30.5, 28.4, 17.5. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{29}N_2O_2S_2$ 369.1665, found 369.1662.

(E)-3-(3-((4-methoxyphenyl)thio)prop-1-en-1-yl)oxazolidin-2-one **3ba**

The reaction of *N*-allenyl-2-oxazolidinone (**1b**, 0.2 mmol) with 4-methoxythiophenol (**2a**, 1.0 equiv, 0.2 mmol) according to the general procedure A afforded the corresponding hydrothiolation compound **3ba** as an off-white oil (28.7 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.30 (*m*, 2H), 6.88 – 6.79 (*m*, 2H), 6.62 (*d*, *J* = 14.2 Hz, 1H), 4.84 (*dt*, *J* = 14.2, 7.6 Hz, 1H), 4.46 – 4.34 (*m*, 2H), 3.79 (*s*, 3H), 3.65 (*m*, 2H), 3.53 – 3.45 (*m*, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 159.4, 155.2, 134.2, 126.3, 125.1, 114.7, 106.3, 62.2, 55.4, 42.6, 36.8. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{16}NO_3S$ 266.0845, found 266.0850.

Methyl *(E)*-2-((3-(2-oxooxazolidin-3-yl)allyl)thio)acetate **3bp**

The reaction of *N*-allenyl-2-oxazolidinone (**1b**, 0.2 mmol) with methyl 2-mercaptoacetate **(2p**, 1.0 equiv, 0.2 mmol) according to the general procedure A afforded the corresponding hydrothiolation compound **3bp** as an off-white oil (26.8 mg, 58%). ^{1}H NMR (400 MHz, Acetone-d_6): δ 6.75 (*d*, *J* = 14.1 Hz, 1H), 4.88 (*dt*, *J* = 14.2, 7.7 Hz, 1H), 4.50 – 4.44 (*m*, 2H), 3.79 (*m*, 2H), 3.67 (*s*, 3H), 3.35 (*dd*, *J* = 7.7, 1.1 Hz, 2H), 3.24 (*s*, 2H). ^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6): δ 171.4, 155.8, 128.0, 105.8, 63.2, 52.3, 43.2, 32.6, 32.0. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_9H_{13}NNaO_4S$ 254.0463, found 254.0464.

(E)-*N*-(3-((4-methoxyphenyl)thio)prop-1-en-1-yl)-*N*,4-dimethylbenzenesulfonamide **3ca**

The reaction of *N*,4-dimethyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (**1c**, 0.2 mmol) with 4-methoxythiophenol (**2a**, 1.0 equiv, 0.2 mmol) according to the general procedure A afforded the corresponding hydrothiolation compound **3ca** as an orange oil (52.3 mg, 72%). ^{1}H NMR (400 MHz, Acetone-d_6): δ 7.55 – 7.50 (*m*, 2H), 7.39 – 7.34 (*m*, 2H), 7.34 – 7.29 (*m*, 2H), 6.92 – 6.86 (*m*, 2H), 6.79 (*d*, *J* = 13.9 Hz, 1H), 4.83 (*dt*, *J* = 14.1, 7.4 Hz, 1H), 3.80 (*s*, 3H), 3.54 (*dd*, *J* = 7.4, 1.1 Hz, 2H), 2.81 (*s*, 3H), 2.41 (*s*, 3H). ^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6): δ 160.0, 144.7, 135.6, 134.3, 131.0, 130.6, 127.7, 126.5, 115.3, 107.3, 55.6, 36.4, 32.6, 21.4. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{22}NO_3S_2$ 364.1036, found 364.1035.

Methyl *(E)*-2-((3-((*N*,4-dimethylphenyl)sulfonamido)allyl)thio)acetate **3cp**

The reaction of *N*,4-dimethyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (**1c**, 0.2 mmol) with methyl 2-mercaptoacetate (**2p**, 1.0 equiv, 0.2 mmol) according to the general procedure A afforded the corresponding hydrothiolation compound **3cp** as a yellow oil (51.4 mg, 78%). ^{1}H NMR (400 MHz, Acetone-d_6): 7.74 – 7.67 (*m*, 2H), 7.53 – 7.30 (*m*, 2H), 6.89 (*d*, *J* = 13.9 Hz, 1H), 4.76 (*dt*, *J* = 14.0, 7.7 Hz, 1H), 3.69 (*s*, 3H), 3.29 (*dd*, *J* = 7.7, 0.9 Hz, 2H), 3.10 (*s*, 2H), 2.89 (*s*, 3H), 2.42 (*s*, 3H). ^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6): δ 171.3, 145.0, 135.4, 131.8, 130.7, 127.9, 106.6, 52.4, 32.7, 32.6, 31.5, 21.4. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{20}NO_4S_2$ 330.0828, found 330.0825 ; $[M+NH_4]^+$ Calcd for $C_{14}H_{23}N_2O_4S_2$ 347.1094, found 347.1092 ; $[M+Na]^+$ Calcd for $C_{14}H_{19}NNaO_4S_2$ 352.0648, found 352.0647.

1-(1,3-bis((4-methoxyphenyl)thio)propyl)pyrrolidin-2-one **4aa**

The reaction of *N*-allenyl-2-pyrrolidinone (**1a**, 0.2 mmol) with 4-methoxythiophenol (**2a**, 2 equiv, 0.4 mmol) according to the general procedure A afforded the corresponding hydrothiolation compound **4aa** as a pale yellow oil (58.1 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.33 (*m*, 2H), 7.33 – 7.29 (*m*, 2H), 6.86 – 6.82 (*m*, 2H), 6.81 – 6.77 (*m*, 2H), 5.64 (*dd*, *J* = 9.1, 6.0 Hz, 1H), 3.79 (*s*, 3H), 3.76 (*s*, 3H), 3.55 (*ddd*, *J* = 9.7, 8.5, 5.8 Hz, 1H), 3.12 (*ddd*, *J* = 9.7, 8.2, 5.7 Hz, 1H), 2.86 (*ddd*, *J* = 13.4, 9.6, 5.9 Hz, 1H), 2.73 (*ddd*, *J* = 13.4, 9.6, 5.6 Hz, 1H), 2.26 (*ddd*, *J* = 16.8, 9.3, 6.8 Hz, 1H), 2.12 – 1.98 (*m*, 2H), 1.97 – 1.85 (*m*, 2H), 1.85 – 1.76 (*m*, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 175.1, 160.0, 159.4, 135.6, 134.1, 125.6, 122.7, 114.8, 114.6, 59.5, 55.4, 55.3, 41.6, 33.0, 32.6, 31.2, 18.0. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{26}NO_3S_2$ 404.1349, found 404.1351.

1-(1,3-bis((4-chlorophenyl)thio)propyl)pyrrolidin-2-one **4ae**

The reaction of *N*-allenyl-2-pyrrolidinone (**1a**, 0.2 mmol) with 4-chlorothiophenol (**2e**, 2 equiv, 0.4 mmol) according to the general procedure A afforded the corresponding hydrothiolation compound **4ae** as a pale yellow oil (52.6 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.21 (*m*, 8H), 5.82 (*dd*, *J* = 8.6, 6.3 Hz, 1H), 3.51 (*ddd*, *J* = 9.6, 8.4, 5.8 Hz, 1H), 3.19 (*ddd*, *J* = 9.7, 8.3, 5.6 Hz, 1H), 2.97 (*ddd*, *J* = 13.4, 9.1, 5.9 Hz, 1H), 2.86 (*ddd*, *J* = 13.4, 9.1, 6.0 Hz, 1H), 2.31 (*ddd*, *J* = 17.0, 9.4, 6.6 Hz, 1H), 2.14 (*ddd*, *J* = 17.0, 9.6, 6.6 Hz, 1H), 2.11 – 1.99 (*m*, 2H), 1.98 – 1.90 (*m*, 1H), 1.87 – 1.78 (*m*, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 175.3, 133.5, 131.6, 129.35, 129.31, 58.5, 41.8, 32.6, 31.3, 31.2, 18.0. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{20}Cl_2NOS_2$ 412.0358, found 412.0362.

1-(1,3-bis((4-trifluoromethyl)phenyl)thio)propyl)pyrrolidin-2-one **4af**

The reaction of *N*-allenyl-2-pyrrolidinone (**1a**, 0.2 mmol) with 4-trifluoromethylthiophenol (**2f**, 2 equiv, 0.4 mmol) according to the general procedure A afforded the corresponding hydrothiolation compound **4af** as a pale yellow oil (52.7 mg, 55%). ^{1}H {^{19}F} NMR (400 MHz, $CDCl_3$): δ 7.58 – 7.49 (*m*, 4H), 7.45 (*m*,

2H), 7.38 (*m*, 2H), 5.99 (*dd*, *J* = 8.4, 6.6 Hz, 1H), 3.50 (*ddd*, *J* = 9.6, 8.5, 5.9 Hz, 1H), 3.25 (*ddd*, *J* = 9.7, 8.3, 5.5 Hz, 1H), 3.09 (*ddd*, *J* = 13.5, 8.9, 6.0 Hz, 1H), 2.98 (*ddd*, *J* = 13.5, 8.8, 6.2 Hz, 1H), 2.36 (*ddd*, *J* = 17.0, 9.4, 6.6 Hz, 1H), 2.24 – 2.14 (*m*, 2H), 2.13 – 2.04 (*m*, 1H), 1.97 (*m*, 1H), 1.90 – 1.78 (*m*, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 175.4 (*s*), 141.0 (*d*, *J* = 1.4 Hz), 138.1 (*d*, *J* = 1.4 Hz), 130.4 (*s*), 128.3 (*s*), 126.0 (*qd*, *J* = 3.8, 1.2 Hz), 57.4 (*s*), 42.0 (*s*), 32.5 (*s*), 31.2 (*s*), 29.8 (*s*), 18.0 (*s*). ^{19}F $\{^{1}H\}$ NMR (377 MHz, $CDCl_3$): δ -62.5, -62.6. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{20}F_6NOS_2$ 480.0885, found 480.0881.

1-(1,3-bis((4-nitrophenyl)thio)propyl)pyrrolidin-2-one **4ag**

The reaction of *N*-allenyl-2-pyrrolidinone (**1a**, 0.2 mmol) with 4-nitrothiophenol (**2g**, 2 equiv, 0.4 mmol) according to the general procedure A afforded the corresponding hydrothiolation compound **4ag** as a pale yellow oil (59.0 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 – 8.05 (*m*, 4H), 7.51 – 7.43 (*m*, 2H), 7.39 – 7.31 (*m*, 2H), 6.07 (*dd*, *J* = 8.2, 6.8 Hz, 1H), 3.50 (*ddd*, *J* = 9.6, 8.5, 5.9 Hz, 1H), 3.30 (*ddd*, *J* = 9.7, 8.4, 5.6 Hz, 1H), 3.16 (*ddd*, *J* = 13.6, 8.5, 6.1 Hz, 1H), 3.06 (*ddd*, *J* = 13.4, 8.5, 6.4 Hz, 1H), 2.40 (*ddd*, *J* = 17.1, 9.4, 6.6 Hz, 1H), 2.31 – 2.21 (*m*, 2H), 2.15 (*ddd*, *J* = 14.3, 8.2, 2.1 Hz, 1H), 2.08 – 1.95 (*m*, 1H), 1.95 – 1.83 (*m*, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 175.5, 146.3, 146.0, 145.6, 142.8, 129.3, 127.0, 124.25, 124.22, 56.9, 42.0, 32.1, 31.1, 29.0, 17.9. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{20}N_3O_5S_2$ 434.0839, found 434.0825 ; $[M+Na]^+$ Calcd for $C_{19}H_{19}N_3NaO_5S_2$ 456.0658, found 456.0653.

1-(1,3-bis(naphthalen-2-ylthio)propyl)pyrrolidin-2-one **4ak**

The reaction of *N*-allenyl-2-pyrrolidinone (**1a**, 0.2 mmol) with 2-naphtalenethiol (**2k**, 2 equiv, 0.4 mmol) according to the general procedure A afforded the corresponding hydrothiolation compound **4ak** as a pale yellow oil (54.1 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 – 7.69 (*m*, 8H), 7.52 – 7.40 (*m*, 6H), 6.01 (*dd*, *J* = 8.8, 6.2 Hz, 1H), 3.55 (*ddd*, *J* = 9.7, 8.4, 5.9 Hz, 1H), 3.21 (*ddd*, *J* = 9.4, 8.2, 5.6 Hz, 1H), 3.16 (*ddd*, *J* = 13.4, 9.3, 5.8 Hz, 1H), 3.02 (*ddd*, *J* = 13.4, 9.4, 5.8 Hz, 1H), 2.32 – 2.18 (*m*, 2H), 2.17 – 2.07 (*m*, 1H), 2.03 (*ddd*, *J* = 16.9, 8.1, 3.9 Hz, 1H), 1.94 – 1.82 (*m*, 1H), 1.80 – 1.68 (*m*, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 175.3, 133.8, 133.6, 133.0, 132.5, 132.1, 130.9, 130.0, 129.2, 128.74, 128.67, 128.1, 127.85, 127.84, 127.83, 127.6, 127.3, 126.75, 126.66, 126.4, 126.0, 58.3, 41.9, 32.8, 31.2, 30.9, 17.9. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{26}NOS_2$ 444.1450, found 444.1440 ; $[M+Na]^+$ Calcd for $C_{27}H_{25}NNaOS_2$ 466.1270, found 466.1261.

1-(1,3-bis((perfluorophenyl)thio)propyl)pyrrolidin-2-one **4au**

The reaction of *N*-allenyl-2-pyrrolidinone (**1a**, 0.2 mmol) with 2,3,4,5,6-pentafluorothiophenol (**2u**, 2 equiv, 0.4 mmol) according to the general procedure A afforded the corresponding hydrothiolation compound **4au** as a pale yellow oil (65.9 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.65 (*dd*, *J* = 8.5, 6.8 Hz, 1H), 3.73 (*dt*, *J* = 9.4, 7.2 Hz, 1H), 3.24 (*dt*, *J* = 9.5, 6.9 Hz, 1H), 2.99 – 2.84 (*m*, 2H), 2.36 – 2.26 (*m*, 1H), 2.22 – 2.08 (*m*, 2H), 2.08 – 1.93 (*m*, 3H). $^{13}C\{^{1}H,^{19}F\}$ NMR (101 MHz, $CDCl_3$): 175.4, 148.4, 147.8, 142.7, 141.9, 137.9, 137.7, 60.0, 41.5, 33.2, 31.7, 30.9, 17.8. ^{19}F $\{^{1}H\}$ NMR (377 MHz, $CDCl_3$) δ -132.18 (*dd*, *J* = 52.4, 18.9 Hz), -149.41 (*t*, *J* = 20.8 Hz), -151.55 (*t*, *J* = 20.7 Hz), -160.33 (*t*, *J* = 22.2 Hz). HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{12}F_{10}NOS_2$ 524.0195, found 524.0192.

1-(1-((4-methoxyphenyl)thio)ethyl)pyrrolidin-2-one **3'aa**

The reaction of *N*-vinyl-2-pyrrolidinone (**1'a**, 0.2 mmol) with 4-methoxythiophenol (**2a**, 1.0 equiv, 0.2 mmol) according to the general procedure A afforded the corresponding hydrothiolation compound **3'aa** as a pale yellow oil (44.7 mg, 89%). ^{1}H NMR (400 MHz, Acetone-d_6): δ 7.41 – 7.36 (*m*, 2H), 6.91 – 6.85 (*m*, 2H), 5.67 (*q*, *J* = 7.0 Hz, 1H), 3.80 (*d*, *J* = 2.0 Hz, 3H), 3.66 – 3.57 (*m*, 1H), 3.42 – 3.34 (*m*, 1H), 2.21 – 2.12 (*m*, 1H), 2.05 – 1.98 (*m*, 1H), 1.98 – 1.92 (*m*, 1H), 1.92 – 1.81 (*m*, 1H), 1.45 (*d*, *J* = 7.0 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, Acetone-d_6): 174.0, 160.8, 136.4, 124.4, 115.1, 56.3, 55.6, 41.5, 31.4, 19.1, 18.4. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{18}NO_2S$ 252.1053, found 252.1054.

Methyl 2-((1-(2-oxopyrrolidin-1-yl)ethyl)thio)acetate **3'ap**

The reaction of *N*-vinyl-2-pyrrolidinone (**1'a**, 0.2 mmol) with methyl 2-mercaptoacetate (**2p**, 1.0 equiv, 0.2 mmol) according to the general procedure A afforded the corresponding hydrothiolation compound **3'ap** as a pale yellow oil (43.5 mg, 97%).^{1}H NMR (400 MHz, Acetone-d_6): δ 5.60 (*q*, *J* = 7.1 Hz, 1H), 3.67 (*s*, 3H), 3.56 (*ddd*, *J* = 9.3, 7.5, 6.6 Hz, 1H), 3.36 (*ddd*, *J* = 9.2, 7.4, 6.3 Hz, 1H), 3.33 (*d*, *J* = 9.1 Hz, 2H), 2.34 – 2.26 (*m*, 2H), 2.07 – 1.98 (*m*, 2H), 1.40 (*d*, *J* = 7.0 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, Acetone-d_6): δ 175.1, 171.0, 53.6, 52.5, 41.3, 33.4, 31.5, 19.0, 18.3. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_9H_{16}NO_3S$ 218.0845, found 218.0844.

1,1'-((ethane-1,2-diylbis(sulfanediyl))bis(ethane-1,1-diyl))bis(pyrrolidin-2-one) **3'as**

The reaction of *N*-vinyl-2-pyrrolidinone (**1'a**, 0.4 mmol) with ethane-1,2-dithiol (**2s**, 1.0 equiv, 0.2 mmol) according to the general procedure B afforded the corresponding hydrothiolation compound **3'as** as a pale white oil (49.4 mg, 78%).^{1}H NMR (400 MHz, $CDCl_3$): δ 5.46 (*dq*, *J* = 8.8, 7.0 Hz, 2H), 3.56 – 3.47 (*m*, 2H), 3.22 (*ddd*, *J* = 9.7, 7.8, 6.6 Hz, 2H), 2.68 – 2.48 (*m*, 4H), 2.47 – 2.26 (*m*, 4H), 2.04 – 1.91 (*m*, 4H), 1.31 (*d*, *J* = 7.0 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 174.84, 174.81, 51.1, 51.0, 40.9, 40.92, 31.41, 31.40, 30.6, 30.4, 19.11, 19.06, 17.8 (2C). HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{25}N_2O_2S_2$ 317.1352, found 317.1360.

1-(1-((4-methoxyphenyl)thio)-3-(phenylsulfonyl)propyl)pyrrolidin-2-one **3'ba**

The reaction of *(E)*-1-(3-(phenylsulfonyl)prop-1-en-1-yl)pyrrolidin-2-one (**1'b**, 0.2 mmol) with 4-methoxythiophenol (**2a**, 2 equiv, 0.4 mmol) according to the general procedure A afforded the corresponding hydrothiolation compound **3'ba** as a pale yellow oil (65.7 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 – 7.88 (*m*, 2H), 7.75 – 7.67 (*m*, 1H), 7.65 – 7.58 (*m*, 2H), 7.34 – 7.27 (*m*, 2H), 6.85 – 6.76 (*m*, 2H), 5.49 (*dd*, *J* = 8.6, 6.8 Hz, 1H), 3.78 (*s*, 3H), 3.65 – 3.56 (*m*, 1H), 3.24 (*m*, 2H), 3.10 – 2.99 (*m*, 1H), 2.33 – 2.19 (*m*, 3H), 2.15 – 2.04 (*m*, 1H), 1.99 – 1.82 (*m*, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): 175.4, 160.2, 138.7, 135.6, 134.1, 132.7, 129.5, 129.2, 128.4, 128.1, 121.8, 114.68, 114.67, 58.9, 55.3, 53.4, 41.6, 31.0, 25.7, 17.8. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{24}NO_4S_2$ 406.1147, found 406.1149.

(E)-3-(2-((4-methoxyphenyl)thio)-2-phenylvinyl)oxazolidin-2-one **3''aa**

The reaction of 3-(phenylethynyl)oxazolidin-2-one (**1''a**, 0.5 mmol) with 4-methoxylthiophenol (**2a**, 0.25 mmol) according to the general procedure C afforded the corresponding hydrothiolation compound **3''aa** as a white solid (48.4 mg, 59%). ^{1}H

NMR (400 MHz, Acetone-d_6): δ 7.50 – 7.42 (*m*, 4H), 7.38 – 7.33 (*m*, 2H), 7.28 (*m*, 1H), 7.02 – 6.94 (*m*, 2H), 6.81 (*s*, 1H), 4.21 (*dd*, *J* = 8.6, 7.2 Hz, 2H), 3.84 (*s*, 3H), 3.79 (*dd*, *J* = 8.6, 7.2 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, Acetone-d_6): δ 160.2, 154.5, 135.2, 134.0, 131.2, 129.3, 128.5, 128.3, 127.8, 122.0, 114.9, 62.4, 54.8, 44.8. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{17}NO_3S$ 328.1002, found 328.1004.

(E)-3-(2-phenyl-2-(*p*-tolylthio)vinyl)oxazolidin-2-one **3''ac**

The reaction of 3-(phenylethynyl)oxazolidin-2-one (**1''a**, 0.5 mmol) with 4-methylthiophenol (**2c**, 0.25 mmol) according to the general procedure C afforded the corresponding hydrothiolation compound **3''ac** as a white solid (46.8 mg, 60%). ^1H NMR (400 MHz, Acetone-d_6): δ 7.46 (*m*, 2H), 7.40 (*m*, 2H), 7.36 (*m*, 1H), 7.28 (*m*, 1H), 7.22 (*m*, *J* = 8.5 Hz, 2H), 6.87 (*s*, 1H) 4.21 (*dd*, *J* = 8.8, 7.0 Hz, 2H), 3.80 (*dd*, *J* = 8.9, 7.1 Hz, 2H), 2.35 (*s*, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, Acetone-d_6): δ 154.5, 138.0, 135.2, 131.3, 130.5, 130.0, 129.9, 128.7, 128.5, 128.3, 127.9, 62.0, 44.8, 20.2. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{17}NO_2S$ 312.1053, found 312.1050.

(E)-3-(2-(cyclohexylthio)-2-phenylvinyl)oxazolidin-2-one **3''al**

The reaction of 3-(phenylethynyl)oxazolidin-2-one (**1''a**, 0.5 mmol) with cyclohexylthiol (**2l**, 0.25 mmol) according to the general procedure C afforded the corresponding hydrothiolation compound **3''al** as colorless liquid (28.1 mg, 37%). ^1H NMR (400 MHz, Acetone-d_6): δ 7.27 (*d*, *J* = 7.6 Hz, 2H), 7.19 (*t*, *J* = 7.6 Hz, 2H), 7.11 (*t*, *J* = 7.3 Hz, 1H), 6.66 (*s*, 1H), 4.42 – 4.31 (*m*, 2H), 3.89 – 3.78 (*m*, 2H), 2.90 – 2.79 (*m*, 1H), 1.61 (*m*, 2H), 1.52 – 1.39 (*m*, 1H), 1.33 – 1.07 (*m*, 7H). $^{13}C\{^1H\}$ NMR (101 MHz, Acetone-d_6): δ 154.6, 135.3, 132.6, 129.9, 128.5, 128.2, 127.8, 62.3, 45.0, 44.1, 33.0, 25.6, 25.5. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{22}NO_2S$ 304.1366, found 304.1368.

(E)-3-(2-((perfluorophenyl)thio)-2-phenylvinyl)oxazolidin-2-one **3''au**

The reaction of 3-(phenylethynyl)oxazolidin-2-one (**1''a**, 0.5 mmol) with 2,3,4,5,6-pentafluorothiophenol (**2u**, 0.25 mmol) according to the general procedure C afforded the corresponding hydrothiolation compound **3''au** as a yellow oil (50.3 mg, 52%). ^1H NMR (400 MHz, Acetone-d_6): δ 7.49 – 7.47 (m, 2H), 7.43 – 7.31 (m, 3H), 7.17 (s, 1H), 4.48 – 4.44 (m, 2H), 3.99 – 3.95 (m, 2H). $^{13}C\{^1H,^{19}F\}$ NMR (101 MHz, Acetone-d_6): δ 154.7, 142.6, 135.7, 134.2, 129.5, 128.9, 128.7, 128.5, 127.4, 125.2, 106.1, 62.5, 44.4. $^{19}F\{^1H\}$ NMR (377 MHz, $CDCl_3$) δ -133.51, -152.82, -163.21. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{11}F_5NO_2S$ 388.0425, found 388.0424.

(E)-3-(2-(benzylthio)-2-phenylvinyl)oxazolidin-2-one **3''av**

The reaction of 3-(phenylethynyl)oxazolidin-2-one (**1''a**, 0.5 mmol) with benzylmercaptan (**2u**, 0.25 mmol) according to the general procedure C afforded the corresponding hydrothiolation compound **3''av** as a brown oil (21.1 mg, 27%). The NOESY interaction between the two singlets corresponding to benzylic methylene group and vinylic proton undoubtedly confirm the *(E)* configuration. ^1H NMR (400 MHz, Acetone-d_6): δ 7.47 – 7.43 (*m*, 2H), 7.41 – 7.32 (*m*, 6H), 7.32 – 7.25 (*m*, 2H), 6.73 (*s*, 1H), 4.40 (*dd*, *J* = 8.7, 7.2 Hz, 2H), 4.03 (*s*, 2H), 3.81 (*dd*, *J* = 8.7, 7.2 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, Acetone-d_6): δ 154.8, 138.0, 135.1, 131.6, 129.0, 128.6, 128.4, 128.1, 127.9, 127.1, 62.3, 44.8, 36.9. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{17}NO_2S$ 312.1053, found 312.1047.

(E)-3-(2-(4-methoxyphenyl)-2-(*p*-tolylthio)vinyl)oxazolidin-2-one **3''bc**

The reaction of 3-((4-methoxyphenyl)ethynyl)oxazolidin-2-one (**1''b**, 0.5 mmol) with 4-methylthiophenol (**2c**, 0.25 mmol) according to the general procedure C afforded the corresponding hydrothiolation compound **3''bc** as a white solid (47 mg, 55%). ^1H NMR (400 MHz, Acetone-d_6): δ 7.27 – 7.21 (*m*, 4H), 7.05 – 7.03 (*m*, 2H), 6.78 – 6.77 (*m*, 2H), 6.74 (*s*, 1H), 4.08 (*dd*, *J* = 16.0, 8.2 Hz, 2H), 3.73 – 3.55 (*m*, 5H), 2.17 (*s*, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, Acetone-d_6): δ 159.6, 137.7, 131.1, 130.9, 130.7, 130.0, 129.3, 129.1, 127.7, 127.1, 113.9, 62.4, 54.9, 44.9, 20.2. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{20}NO_3S$ 342.1158, found 342.1159.

3-(3-oxo-1-(*p*-tolylthio)oct-1-en-1-yl)oxazolidin-2-one **3''cc**

The reaction of 3-(oct-1-yn-1-yl)oxazolidin-2-one (**1''c**, 0.25 mmol) with 4-methylthiophenol (**1c**, 0.25 mmol) according to a modified procedure C (5 mol% of copper catalyst and a 1:1 ratio of the ynamide and thiophenol derivative) afforded a mixture of E/Z isomers of the corresponding hydrothiolation compound **3''cc** as a colorless liquid (51.6 mg, 62%, E/Z ratio : 70:30).

Diastereomer (E)-**3''cc**: ^1H NMR (400 MHz, Acetone-d_6): δ 7.13 (*d*, *J* = 7.5 Hz, 2H), 7.01 (*d*, *J* = 7.9 Hz, 2H), 5.85 (*t*, *J* = 7.1 Hz, 1H), 4.07 (*t*, *J* = 7.8 Hz, 2H), 3.57 (*t*, *J* = 7.8 Hz, 2H), 2.17 (*s*, 3H), 2.03 (*q*, *J* = 7.3 Hz, 2H), 1.12-1.20 (*m*, 6H), 0.72-0.78 (*m*, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 155.1, 137.0, 136.3, 129.8, 129.6, 127.3, 62.2, 45.0, 31.6, 22.4, 20.1, 13.4.

Diastereomer (Z)-**3''cc**: ^1H NMR (400 MHz, Acetone-d_6) δ 7.11 (*d*, *J* = 7.1 Hz, 2H), 7.02 (*d*, *J* = 7.7 Hz, 2H), 6.03 (*t*, *J* = 7.6 Hz, 1H), 3.98 (*t*, *J* = 7.9 Hz, 2H), 3.57 (*t*, *J* = 7.9 Hz, 2H), 2.30 (*q*, *J* = 6.9 Hz, 2H), 2.17 (*s*, 3H), 1.13-1.19 (*m*, 6H), 0.72-0.77 (*m*, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 153.9, 136.7, 135.2, 129.9, 129.8, 129.1, 127.8, 61.4, 45.3, 31.3, 22.2, 20.0, 13.3.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{23}NO_3S$ 304.1366, found 304.1368.

(E)-*N*-benzyl-*N*-(2-phenyl-2-(*p*-tolylthio)vinyl)methanesulfonamide **3''dc**

The reaction of *N*-benzyl-*N*-(phenylethynyl)methanesulfonamide (**1''d**, 0.5 mmol) with 4-methylthiophenol (**2c**, 0.25 mmol) according to the general procedure C afforded the corresponding hydrothiolation compound **3''dc** as a white solid (41 mg, 40%). ^1H NMR (400 MHz, Acetone-d_6): δ 7.38 (*m*, 2H), 7.25 (*m*, 2H), 7.18 – 7.00 (*m*, 10H), 6.35 (*s*, 1H), 4.46 (*s*, 2H), 2.81 (*s*, 3H), 2.20 (*s*, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, Acetone-d_6): δ 138.7, 135.3, 135.1, 135.0, 134.6, 132.8, 130.3, 130.0, 129.6, 128.6, 128.2, 128.0, 53.0, 40.3, 20.0. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{24}NO_2S_2$ 410.1243, found 410.1231.

Methyl *(E)*-2-((2-((*N*-benzyl-4-methylphenyl)sulfonamido)-1-phenylvinyl)thio)acetate **3''ep**

The reaction of *N*-benzyl-4-methyl-*N*-(phenylethynyl)benzenesulfonamide (**1''e**, 0.5 mmol) with methyl 2-mercaptoacetate (**2p**, 0.25 mmol) according to the general procedure C afforded the corresponding hydrothiolation compound **3''ep** as a colorless oil (107.5 mg, 92%). ^1H NMR (400 MHz, Acetone-d_6): δ 7.70 – 7.67 (m,2H), 7.26 – 7.23 (m, 4H), 7.07 – 6.97 (m, 8H), 6.58 (s, 1H), 4.43 (s *broad*, 2H), 3.52 (s, 3H), 3.38 (s *broad*, 2H), 2.28 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, Acetone-d_6): δ 169.2, 144.4, 136.8, 135.2, 135.1, 134.6, 133.3, 129.7, 129.6,

128.8, 128.4, 128.1, 128.03, 127.99, 127.9, 52.6, 51.9, 36.8, 20.7. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{26}NO_4S_2$ 468.1298, found 468.1288.

ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Experimental procedures, product characterization data (NMR and HRMS), and copies of ^1H and ^{13}C NMR spectra of all the new synthesized compounds (PDF).

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