FREE RADICAL REACTION OF DIISOPROPYL XANTHOGEN DISULFIDE WITH UNSATURATED SYSTEMS

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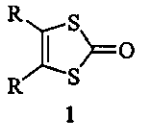
Abstract- 1,3-Dithiol-2-ones are prepared in one pot reaction from commercially available diisopropyl xanthogen disulfide (**2**) and alkynes under radical conditions. The 5-membered heterocycle is formed *via* a ring closure of vinyl radical (**7**) resulting from the thio radical addition of **5** to an alkyne. The reaction worked best for alkynes conjugated with a C=C double bond. The oxygen atoms of reagent (**2**) could be replaced by sulfur and this new reagent furnished 1,3-dithiol-2-thiones under radical conditions.

INTRODUCTION

Tetrathiafulvalenes are key constituents in the formation of charge transfer complexes with metal like properties[1a] and 1,3-dithiol-2-ones (**1**) are important building blocks in their preparations.[1b] These 5-membered heterocycles can be prepared in numerous ways which usually require many steps.[2] Our contribution in this area has been the subject of a recent communication, where we described a bimolecular one-pot reaction between diisopropyl xanthogen disulfide (**2**) and alkynes under radical conditions.[3] This methodology directly furnished compounds of type (**1**). With this approach, one avoided the need to prepare *S*-propargyl xanthogen of type (**3**) for every alkyne used. To further develop on this method, herein we wish to demonstrate i) that **2** is a useful synthetic reagent to transfer the 1,3-dithiol-2-one functionality, ii) the scope and limitations of this transfer reaction with alkynes and alkenes and iii) the flexibility of reagent (**2**) to be modified with different combination of heteroatoms to allow the transfer of other functionality such as 1,3-dithiol-2-thione.



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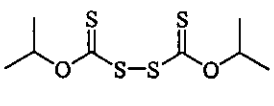

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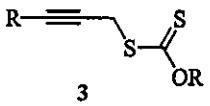

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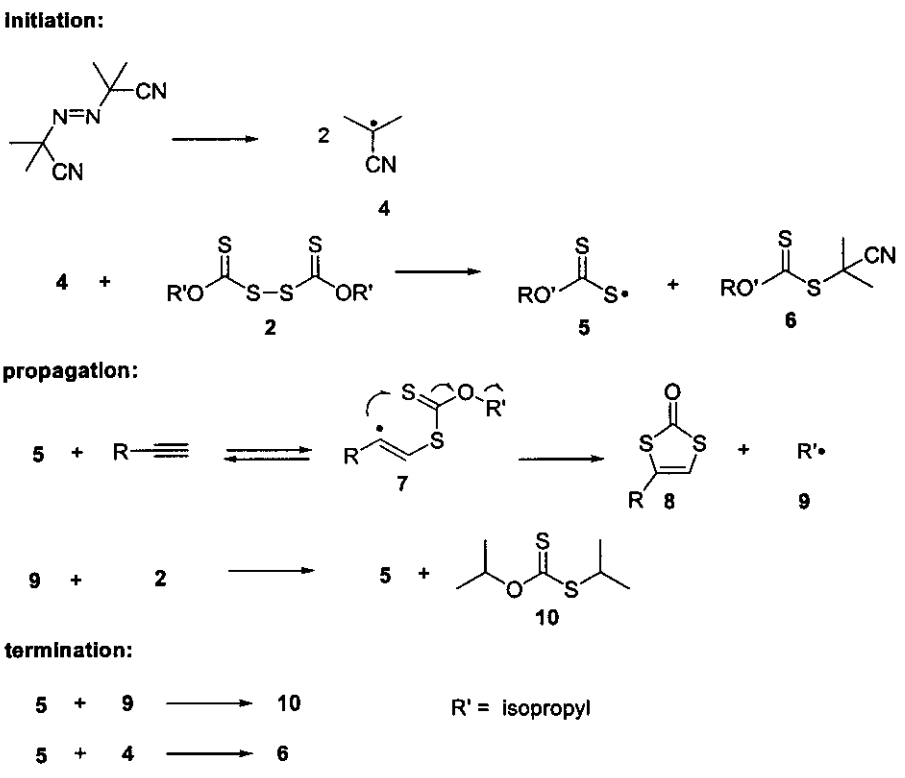
RESULTS AND DISCUSSION

We previously reported that terminal alkynes could be converted to **1** in a 0.1 M refluxing benzene solution with **2** and AIBN.[3] This radical reaction may be described by the three main steps of

a typical radical process (Scheme 1). The first step was the initiation event with the thermal decomposition of a catalytic amount of AIBN. The radical (**4**) thus generated would add to the carbon-sulfur double bond of **2** to give radical (**5**) and a neutral species (**6**). Addition of **5** on the less hindered side of the triple bond followed by a cyclization gives the desired heterocycle (**8**). For this sequence to be valid, the last step must be accompanied by the extrusion of an isopropyl radical (**9**). At this point, the propagation step would be mainly controlled by the addition of **9** on xanthogen (**2**). As for the termination step, many possibilities could occur such as the coupling of **5** with either **4** or **9**. This scenario was strongly supported by experimental evidence. Along with **8**, compounds (**6**) and (**10**) have been isolated and characterized from the reaction mixtures.

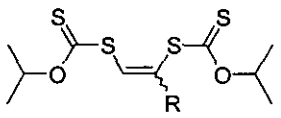
Scheme 1



The isopropyl group of xanthogen (**2**) also proved to be important for completion of the reaction. Fragmentation of xanthogens containing primary alkyl groups has been reported to be slow compared to secondary analogues.[4] This difference in rate was directly reflected in a low recovery of **8** when diethyl xanthogen disulfide was used. Under the same conditions, phenyacetylene and diethyl xanthogen disulfide furnished a 36% yield of 4-phenyl-1,3-dithiol-2-one.

At first, the reactions were run in a 1.0 M benzene solution with respect to the alkyne and appreciable amounts of side products were isolated. These products were identified as double-addition compounds of general structure (**11**), and probably arose from the addition of intermediate (**7**) to unreacted xanthogen (**2**). Mixtures of *E* and *Z* isomers were characterized in the case of phenylacetylene (**11a**), *m*-

methoxyphenylacetylene (**11b**) and *o*-bromophenylacetylene (**11c**). However, the amount of these compounds could be greatly reduced by decreasing the concentration of the reaction mixture. When the experiment was conducted at 0.1 M, only trace quantities of these side products were detected.



11

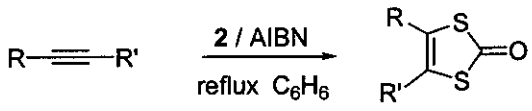
R =	**a**- phenyl	(4%, 3.3/1, E/Z)
	b- *m*-methoxyphenyl	(5%, 3.2/1, E/Z)
	c- *o*-bromophenyl	(16%, 4.9/1, E/Z)

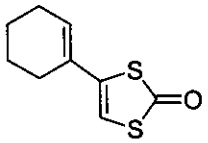
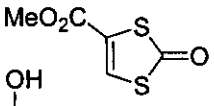
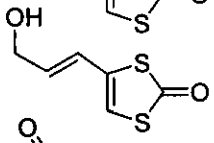
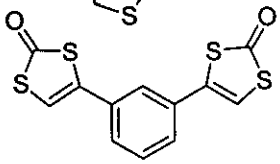
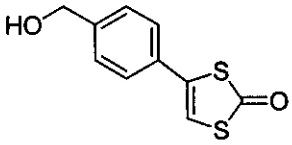
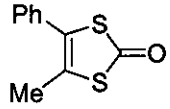
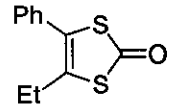
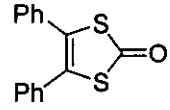
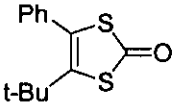
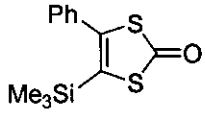
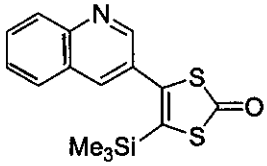
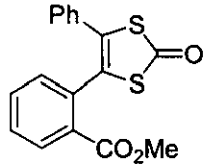
With the optimization of the reaction conditions and of reagent (**2**), we turned our attention at investigating the scope and limitations of this method. Several alkynes were submitted to a standard set of conditions (1.0 equivalent of alkyne, 1.1 equivalent of **2** and 0.45 equivalent of AIBN in a 0.1 M refluxing benzene solution) and the results are reported in Table 1. From the numerous alkynes studied, a trend in reactivity could be observed based on the α-substitution and one can classify the substrates into two categories. The first category of substrates contains monosubstituted (and some disubstituted) alkynes conjugated either with an aromatic ring or an olefin. Substitution pattern as well as functionality on the aromatic ring had little effect on the outcome of the reaction. This category furnished the best yields of **8**. The remaining alkynes fall into the second category. This includes aliphatic alkynes, bulky disubstituted alkynes and those conjugated with a carbonyl group. The conjugation with a carbonyl group resulted in a low yield of **8** and a low recovery of starting material. In a similar way, aliphatic alkynes gave unexpected low yields but, contrary to the carbonyl case, with a high recovery of starting material.

To rationalize the different behavior between the two categories of alkynes, the relative stability and the geometry of radical (**7**) may be invoked. The addition of a thio radical to an alkynes is a reversible process[5] and the resulting high energy vinyl radical can adopt one of two geometries depending of the α-R group. EPR studies on vinyl radicals suggested that the linear geometry is associated with α-aromatic groups while the bent geometry is associated with α-carbonyl groups.[6] The bent geometry would be also associated with α-alkyl groups.[7]

It has been postulated that the bent geometry which led to a cis-adduct resulted from an anti addition (kinetic) of the thio radical.[8] This vinyl radical may in turn equilibrate to the more stable *trans* isomer. Therefore, if the addition of **5** on an aliphatic alkyne produced first the *cis*-adduct, **7a** would have to isomerize to **7b** in order for a cyclization to occur. Although this equilibrium is usually fast,[9] it is probably slow relative to the elimination (reverse process) since most of the starting material was recovered. The same hypothesis may be applicable if the carbonyl group is conjugated with the triple bond. This time however, the reverse reaction does not have time to occur and the vinyl radical further reacts to generate a mixture of undefined products. In the case of **7c**, the linear geometry associated with the aromatic substituent gave an intermediate well suited to facilitate the subsequent cyclization.

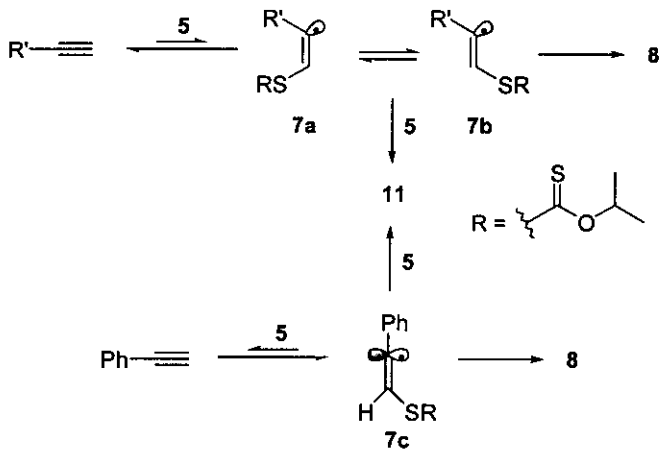
Table 1. Formation of 1,3-dithiol-2-ones from alkynes and 2.



Entry	Product	Yield (%)
1-	R= phenyl	80 (**13**)
2-	R= *o*-bromophenyl	59 (**14**)
3-	R= *m*-methoxyphenyl	78 (**15**)
4-	R= 3-quinolynyl	77 (**16**)
5-	R= *o*-carbomethoxyphenyl	81 (**17**)
6-	R= *p*-carbomethoxyphenyl	76 (**18**)
7-	R= octyl	27 (**19**)
8-	R= cyclohexyl	18 (**20**)
9-	R= *t*-butyl	12 (**21**)
10-	R= tributyltin	28 (**22**) (20)[a]
11-	R= benzyl	12 (**23**) (18)[b] (**24**) 0 (**23**) (32)[b,c] (**24**)
12-		76 (**25**)
13-		17 (**26**) (22)[b] (**27**)
14-		82 (**28**)
15-		50 (**29**)
16-		74 (**30**)
17-		75 (**31**)
18-		59[c] (**32**)
19-		40[c] (**33**)
20-		24[c] (**34**)
21-		12[c] (**35**)
22-		14[d] (**36**)
23-		51[d] (**37**) (41)[a]

[a] starting material left; [b] double addition product; [c] reaction run at 1.0 M; [d] reaction run at 0.5 M and 140° C with 1,1'-azobis(cyclohexanecarbonitrile).

Scheme 2

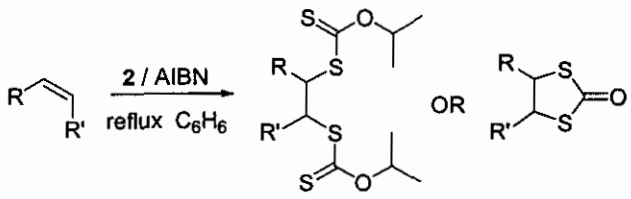


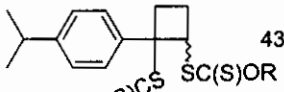
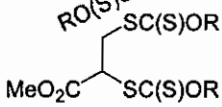
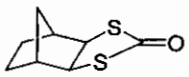
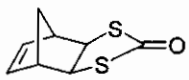
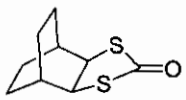
The type of substitution on the alkyne was another factor that influences the yield of the reaction. With phenylacetylene as a model compound, replacement of the terminal hydrogen by bulky groups was found to considerably decrease the yield of cycloaddition. The reaction proceeded well with hydrogen (80%) and methyl (75%), but larger groups such as ethyl decreased the yield drastically to only 6%. Interestingly, this yield could be improved by increasing the concentration of the reaction. Under the same conditions but in a 1.0 M benzene solution of alkyne, the isolated yield of adduct could be increased by a factor of 10 (59%). With very bulky groups such as *t*-butyl (24%) and trimethylsilyl (12%), the steric effect dominated the course of the reaction and low yields were again realized.

Beside alkynes, some cyclic alkenes were found to react with xanthogen (**2**) to afford double-addition products. However, most of the olefins examined such as phenylcyclopentene and 1,2-dichlorocyclobutene were unreactive in our reaction. Methyl acrylate and 1-(4-isopropylphenyl)cyclobutene are two examples that resulted in double-addition products. Unsaturated bicyclic systems were the only other class of compounds that furnished any cyclic products. Norbornylene was the best case with a 74% yield while bicyclo[2.2.2]octene provided only a 3% yield (Table 2).

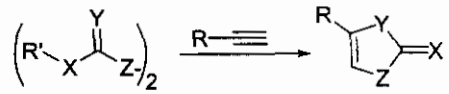
An interesting feature of a reagent such as **2** is the numerous modifications one can envision. For example, one can imagine that the heteroatoms of **2** may be changed by various combinations of oxygen, sulfur and selenium atoms. These modified reagents could lead to new heterocycles that would be difficult to prepare otherwise (eq. 1). We have tested one of these combinations where the oxygen of **2** has been replaced by sulfur atoms (**12**). This reagent was readily prepared in high yield (>80%) by the addition of the sodium salt of isopropyl thiol to carbon disulfide, followed by oxidation with iodine (eq. 2). Some representative alkynes were subjected to the standard set of conditions to yield 1,3-dithiol-2-thiones and these results are reported in Table 3. In all cases examined, considerably lower yields of 1,3-dithiol-2-thiones were obtained when compared to xanthogen (**2**) and these were accompanied by large quantities of unreacted starting material. The main reason for the lower yields, resides in the fact that **12** was thermally unstable under the reaction conditions and degradation of the reagent was observed with time.

Table 2. Radical addition of alkenes with 2.

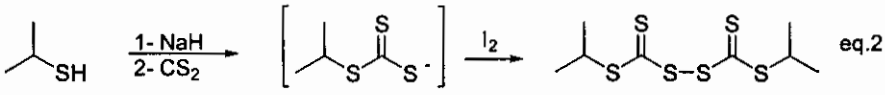


Entry	Product	Yield (%)
1-		43[a] **(38)**
2-		50[a] **(39)**
3-		74[a] **(40)**
4-		25 **(41)**
5-		3 (2)[a] **(42)**

[a] reaction run at 1.0 M R= isopropyl



eq. 1

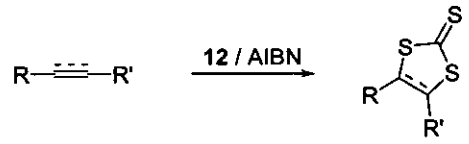


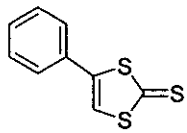
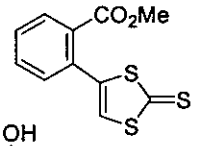
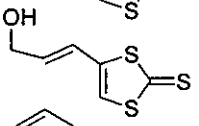
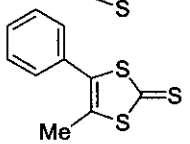
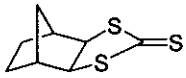
eq.2

12

In conclusion, we have shown that a combination of alkynes with either xanthogen (**2**) or (**12**) can lead to 1,3-dithiol-2-ones or 1,3-dithiol-2-thiones under radical conditions and this proceeded best when conjugated with a carbon-carbon double bond. Many functionality are tolerated and further manipulations can be envisioned to modify these building blocks. The yield of heterocycles was highly dependent on the substrates used. Some sterically hindered alkynes gave reasonable yields of 1,3-dithiol-2-ones by simply increasing the concentration. Side products such as those derived from a double-addition of thio radical (**5**) were reduced to a minimum by lowering the concentration of the reaction to 0.1 M. Finally, xanthogen (**2**) added to bicyclic alkenes and some strained cyclic alkenes to give either the expected heterocycles or double-addition products.

Table 3. Formation of 1,3-dithiol-2-thiones from alkynes/alkenes and 12.



Entry	Product	Yield (%)
1-		48 (**43**)
2-		54 (**44**) (25)[a]
3-		41 (**45**)
4-		22 (**46**) (70)[a]
5-		47 (**47**)

[a] Amount of starting material left.

EXPERIMENTAL SECTION

General procedure for the cycloaddition of xanthogen (2) with alkynes. A 0.1 M solution (unless otherwise mentionned) of alkyne, diisopropyl xanthogen disulfide (1.1 equivalent) and AIBN (0.45 equivalent) was refluxed in benzene for a minimum of 8 h. The mixture was cooled to rt and the solvent removed under reduced pressure. Purification by silica gel chromatography afforded the desired product. The MS spectra were recorded on a VG-ZAB instrument in a glycerol matrix (FAB^+).

4-Phenyl-1,3-dithiol-2-one (13). A solution of phenylacetylene (0.300 g, 2.9 mmol) was refluxed for 14 h. Purification by chromatography using 30% toluene in hexane gave 0.449 g (80%) of a solid identical to an authentic sample.[2f,10]

A second compound identified as the double addition product (**11**) was isolated (41 mg, 4%) in a 3.3/1 mixture of *E* and *Z* isomers. Characteristic displacements are: major isomer (oil); ^1H NMR (400 MHz, $CDCl_3$) δ 1.06 (6H, d, J= 6.2 Hz), 1.39 (6H, d, J= 6.2 Hz), 5.50 (1H, m), 5.77 (1H, m), 7.45 (2H, m) and 7.65 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 21.8, 42.8, 42.9, 128.2, 128.9, 129.0, 135.3, 216.9 and 221.9; HRMS calcd for $C_{16}H_{20}O_2S_4 + H^+$: 373.0424; Found: 373.0424. minor isomer (oil); ^1H NMR (400 MHz, $CDCl_3$) δ 1.11 (6H, d, J= 6.2 Hz), 1.41 (6H, d, J= 6.2 Hz), 5.50 (1H, m), 5.77 (1H,

m), 7.55 (1H, d, J= 6.9 Hz) and 7.86 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.8, 130.9 and 220.4. Products from the initiation and the propagation step were also isolated. **Diisopropyl dithiocarbonate,**[11] compound (**10**) was isolated as a pale yellow oil (0.245 g, 47%): ^1H NMR (400 MHz, $CDCl_3$) δ 1.34-1.38 (12H, m), 3.77 (1H, m), 5.77 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2, 22.2, 40.4, 77.1, 213.6; IR (neat) 2980, 2930, 2870, 1230, 1090, 1030 and 900 cm^{-1}; HRMS *m/z* calcd for $C_7H_{14}OS_2$+ H^+: 179.0564; Found: 179.0564; *Anal. Calcd* for $C_7H_{14}OS_2$: C, 47.15; H, 7.91; S, 35.96. Found: C, 46.38; H, 7.41; S, 35.34. ***O*-Isopropyl-*S*-isobutyronitrile dithiocarbonate**, compound (**6**) was isolated as a yellow oil (0.078 g; 15%): ^1H NMR (200 MHz, $CDCl_3$) δ 1.51 (6H, d, J= 6.3 Hz), 1.75 (6H, s), 5.82 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1, 27.1, 40.6, 79.5, 121.1 and 207.0; IR (neat) 2980, 2230, 1255, 1085, 1030 and 890 cm^{-1}; *Anal. Calcd* for $C_8H_{13}NOS_2$: C, 47.26; H, 6.44; N, 6.89; S, 31.54. Found: C, 47.13; H, 6.34; N, 7.12; S, 31.16.

4-(2-Bromophenyl)-1,3-dithiol-2-one (14). A solution of 2-bromophenylacetylene (0.132 g, 0.73 mmol) was refluxed for 14 h. Purification by chromatography using 10% toluene in hexane gave 0.118 g (59%) of an oil. ^1H NMR (400 MHz, $CDCl_3$) δ 6.71 (1H, s), 7.25 (1H, m), 7.35 (2H, m) and 7.65 (1H, d, J= 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 116.8, 122.9, 127.9, 130.7, 131.8, 132.9, 133.5, 133.7 and 192.7; *Anal. Calcd* for $C_9H_5OBrS_2$: C, 39.57; H, 1.84; S, 23.47. Found: C, 39.60; H, 1.82; S, 23.80.

A second compound identified as the double-addition product was isolated (54 mg, 16%) in a 4.9/1 mixture of *E* and *Z* isomers. Characteristic displacements are: major isomer (oil); ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 (6H, d, J= 6.2 Hz), 1.41 (6H, d, J= 6.2 Hz), 5.63 (1H, m), 5.75 (1H, m), 7.18 (1H, t, J= 6.8 Hz), 7.29 (1H, t, J= 6.8 Hz), 7.42 (1H, d, J= 7.7 Hz), 7.57 (1H, d, J= 7.9 Hz) and 7.76 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 21.2, 78.7, 79.0, 127.1, 130.2, 133.2, 136.6, 206.7 and 210.5; HRMS calcd for $C_{16}H_{19}O_2BrS_4$ + H^+: 450.9530; Found: 450.9529. minor isomer (oil); ^1H NMR (400 MHz, $CDCl_3$) δ 1.19 (6H, d, J= 6.2 Hz), 1.41 (6H, d, J= 6.2 Hz), 5.50 (1H, m), 5.75 (1H, m), 7.49 (1H, d, J= 7.7 Hz) and 7.79 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 122.8 and 139.2.

4-(3-Methoxyphenyl)-1,3-dithiol-2-one (15). A solution of 3-methoxyphenylacetylene (0.416 g, 3.14 mmol) was refluxed for 8 h. Purification by chromatography using 10% ethyl acetate in hexane gave 0.549 g (78%) of a solid; mp 53-54 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 3.82 (3H, s), 6.81 (1H, s), 6.88-6.93 (2H, m), 7.00 (1H, d, J= 7.7 Hz) and 7.30 (1H, t, J= 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 111.9, 112.2, 114.5, 118.8, 130.2, 133.9, 134.8, 160.0 and 192.4; *Anal. Calcd* for $C_{10}H_8O_2S_2$: C, 53.55; H, 3.60; S, 28.59. Found: C, 53.62; H, 3.76; S, 28.76.

A second compound identified as the double addition product was isolated (68 mg, 5%) in a 3.2/1 mixture of *E* and *Z* isomers. Characteristic displacements are: major isomer (oil); ^1H NMR (400 MHz, $CDCl_3$) δ 1.09 (6H, d, J= 6.2 Hz), 1.45 (6H, d, J= 6.2 Hz), 3.80 (3H, s), 5.52 (1H, m), 5.77 (1H, m), 6.82 (1H, m), 6.99 (1H, m), 7.05 (1H, d, J= 6.5 Hz), 7.23 (1H, m) and 7.65 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.2, 55.4, 78.4, 79.1 and 210.2; HRMS calcd for $C_{17}H_{22}O_3S_4$ + H^+ : 403.0530;

Found: *403.0530. minor isomer (oil);* ^1H NMR *(400 MHz,* $CDCl_3$) δ 1.16 (6H, d, J= 6.2 Hz), 1.47 (6H, d, J= 6.2 Hz), 3.83 (3H, s), 5.52 (1H, m), 5.77 (1H, m), 7.09 (1H, m), 7.17 (1H, d, J= 6.0 Hz) and 7.87 (1H, s).

4-(3-Quinolinyl)-1,3-dithiol-2-one (16). A solution of 3-ethynylquinoline (0.252 g, 1.65 mmol) was refluxed for 18 h. Purification by chromatography using 30% ethyl acetate in hexane gave 0.323 g (77%) of a yellow solid. mp 157-159 °C; ^1H NMR *(400 MHz,* $CDCl_3$) δ 7.05 (1H, s), 7.58 (1H, t, J= 7.2 Hz), 7.73 (1H, t, J= 7.1 Hz), 7.81 (1H, d, J= 8.1 Hz), 8.04 (1H, d, J= 2.1 Hz), 8.09 (1H, d, J= 8.5 Hz) and 9.01 (1H, d, J= 2.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 113.8, 125.7, 127.3, 127.8, 128.0, 129.4, 130.4, 121.8, 133.3, 147.1, 147.8 and 191.4; *Anal. Calcd* for $C_{12}H_7NOS_2$: C, 58.75; H, 2.88; N, 5.71; S, 26.14. Found: C, 58.29; H, 2.91; N, 5.62; S, 26.35.

2-(2-Oxo-1,3-dithiol-4-yl)benzoic acid methyl ester (17). A solution of 2-ethynylbenzoic acid methyl ester (0.121 g, 0.75 mmol) was refluxed for 12 h. Purification by chromatography using 10% ethyl acetate in hexane gave 0.153 g (81%) of an oil. ^1H NMR (200 MHz, $CDCl_3$) δ 3.83 (3H, s), 6.52 (1H, s), 7.38 (1H, d, J= 7.5 Hz), 7.47 (1H, t, J= 7.5 Hz), 7.53 (1H, t, J= 7.5 Hz) and 7.77 (1H, d, J= 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.4, 114.1, 129.4, 130.5, 130.8, 131.1, 131.9, 132.9, 133.4, 166.9 and 192.9; *Anal. Calcd* for $C_{11}H_8O_3S_2$: C, 52.36; H, 3.20; S, 25.41. Found: C, 52.26; H, 3.21; S, 24.81.

4-(2-Oxo-1,3-dithiol-4-yl)benzoic acid methyl ester (18). A solution of 4-ethynylbenzoic acid methyl ester (0.250 g, 1.56 mmol) was refluxed for 12 h. The solution was brought to rt and 15 mL of hexane was added. Crystallization took place at 0 °C to yield 0.299 g (76%) of a white solid. mp 165-166 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 3.94 (3H, s), 7.00 (1H, s), 7.49 (2H, d, J= 8.7 Hz) and 8.78 (2H, d, J= 8.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.3, 113.9, 126.4, 130.4, 130.5, 133.8, 136.5, 166.2 and 191.6; HRMS calcd for $C_{11}H_8O_3S_2 + H^+$: 252.9993; Found: 252.9993.

4-Octyl-1,3-dithiol-2-one (19). A solution of 1-decyne (0.200 g, 1.45 mmol) was refluxed for 12 h. Purification by chromatography using 30% toluene in hexane gave 0.090 g (27%) of an oil. ^1H NMR (400 MHz, $CDCl_3$) δ 0.86 (3H, t, J= 6.6 Hz), 1.20-1.35 (10H, m), 1.57 (2H, q, J= 6.6 Hz), 2.54 (2H, t, J= 7.2 Hz) and 6.28 (1H, t, J= 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.6, 28.7, 29.0, 29.1, 29.3, 31.7, 32.8, 110.8, 136.7 and 193.9; *Anal. Calcd* for $C_{11}H_{18}OS_2$: C, 57.35; H, 7.88; S, 27.83. Found: C, 57.29; H, 7.90; S, 27.15.

4-Cyclohexyl-1,3-dithiol-2-one (20). A solution of ethynylcyclohexane (0.500 g, 4.6 mmol) was refluxed 18 h. Purification by chromatography using 30% toluene and 1% ethyl acetate in hexane gave 0.171 g (18%) of an oil. ^1H NMR (400 MHz, $CDCl_3$) δ 1.12 (1H, m), 1.30-1.40 (4H, m), 1.70 (1H, m), 1.83 (2H, m), 1.97 (2H, m), 2.52 (1H, m) and 6.29 (1H, d, J= 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.6, 26.0, 33.3, 42.1, 109.1, 142.6 and 193.7; HRMS calcd for $C_9H_{12}OS_2 + H^+$: 201.0408; Found: 201.0408.

4-*t*-Butyl-1,3-dithiol-2-one (21).[12] A solution of *t*-butylacetylene (0.400 g, 4.8 mmol) was refluxed 18 h. Purification by chromatography gave 0.103 g (12%) of an oil. ^1H NMR (400 MHz, $CDCl_3$) δ 1.30

(9H, s) and 6.30 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.5, 36.9, 108.7, 147.3 and 193.7; HRMS calcd for $C_7H_{10}OS_2$+ H^+: 175.0251; Found: 175.0251.

4-Tributyltin-1,3-dithiol-2-one (22). A solution of ethynyltributyltin (0.250 g, 0.76 mmol) was refluxed for 10 h. Purification by chromatography using 20% toluene in hexane gave 0.086 g (28%) of an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (9H, t, J= 7.3 Hz), 1.10 (6H, tt, J= 26.4, 7.9 Hz), 1.25-1.38 (6H, m), 1.45-1.60 (6H, m), 6.63 (1H, t, J= 17.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.9 (t, J= 177.0 Hz), 13.6, 27.1 (t, J= 29.5 Hz), 28.7 (t, J= 10.7 Hz), 122.2, 134.7, 199.5; MS (Electrospray) *m/z* 405 $C_{15}H_{28}OS_2{}^{116}Sn$ + H^+, 405; *Anal. Calcd* for $C_{15}H_{28}OS_2Sn$: C, 44.25; H, 6.93; S, 15.75. Found: C, 44.23; H, 7.03; S, 13.04.

4-Benzyl-1,3-dithiol-2-one (23). A solution of 3-phenyl-1-propyne (0.250 g, 2.15 mmol) was refluxed for 15 h. Purification by chromatography using 20% toluene in hexane gave 0.054 g (12%) of an oil, identical to an authentic sample.[13] ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.8, 112.5, 127.4, 128.8, 128.9, 135.4, 136.3, 193.4; *Anal. Calcd* for $C_{10}H_8OS_2$: C, 57.66; H, 3.87. Found: C, 57.51; H, 4.36.

A second compound identified as the double-addition **(24)** product was isolated (0.146 g; 18%) in a 2.7/1 mixture of *E* and *Z* isomers. Characteristic displacements are: major isomer (oil); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (6H, d, J= 6.2 Hz), 1.41 (6H, d, J= 6.2 Hz), 3.79 (2H, s), 5.70 (1H, m), 5.79 (1H, m) and 7.43 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 21.2, 40.9, 78.3, 78.9, 206.6 and 211.0; *Anal. Calcd* for $C_{17}H_{22}O_2S_4$: C, 52.82; H, 5.74. Found: C, 52.87; H, 5.76. minor isomer (oil); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (6H, d, J= 6.2 Hz) and 3.78 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.9, 78.4, 78.5, 207.9 and 208.1.

4-(Cyclohex-1-enyl)-1,3-dithiol-2-one (25). A solution of 1-ethynylcyclohexene (0.350 g, 3.3 mmol) was refluxed 10 h. Purification by chromatography using 30% toluene in hexane gave 0.497 g (76%) of an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.55 (2H, m), 1.72 (2H, m), 2.16 (2H, m), 2.27 (2H, m), 5.86 (1H, m) and 6.40 (1H, d, J= 0.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 22.1, 25.4, 25.7, 109.4, 130.4, 130.6, 137.1 and 192.5; HRMS calcd for $C_9H_{10}OS_2$+ H^+: 199.0251; Found: 199.0252

2-Oxo-1,3-dithiol-4-carboxylic acid methyl ester (26). A 1.0 M solution of methyl propiolate (0.213 g, 2.53 mmol) was refluxed for 16 h. Purification by chromatography using 10% ethyl acetate in hexane gave 0.074g (17%) of a pink solid. mp 73-75 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.89 (3H, s), 7.80 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 53.1, 125.8, 129.1, 159.4, 190.6; IR (KBr) 3090, 3050, 2970, 1710, 1630, 1440, 1300, 1060 and 730 cm^{-1}; HRMS calcd for $C_5H_4O_3S_2$+ H^+: 175.9602; Found: 175.9601; *Anal. Calcd* for $C_5H_4O_3S_2$: C, 34.08; H, 2.29; S, 36.39. Found: C, 33.92; H, 2.27; S, 37.31. A second compound identified as the double addition product **(27)** was isolated (0.139 g, 22%) in a 8/1 mixture of *E* and *Z* isomers. Characteristic displacements are: major isomer (oil); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.33 (6H, d, J= 6.3 Hz), 1.39 (6H, d, J= 6.3 Hz), 3.79 (3H, s), 5.67 (1H, m), 5.80 (1H, m) and 8.58 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1, 21.4, 52.8, 78.6, 79.8, 116.7, 151.2, 163.1, 207.7 and 210.5;

HRMS calcd for $C_{12}H_{18}O_4S_4 + H^+$: 355.0166; Found: 355.0168. minor isomer (oil); ^1H NMR (200 MHz, $CDCl_3$) δ 1.33 (6H, d, J= 6.3 Hz), 1.37 (6H, d, J= 6.3 Hz), 3.82 (3H, s) and 7.61 (1H, s).

4-(3-Hydroxyprop-1-enyl)-1,3-dithiol-2-one (28). A solution of pent-2-en-4-yn-1-ol (0.150 g, 1.83 mmol) was refluxed for 12 h. Purification by chromatography using 40% ethyl acetate in hexane gave 0.262g (82%) of a white solid. mp 83-85 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.48 (1H, t, J= 5.6 Hz), 4.28 (2H, t, J= 4.0 Hz), 5.87 (1H, dt, J= 15.7 and 5.0 Hz), 6.43 (1H, dt, J= 15.7 and 0.6 Hz) and 6.55 (1H, d, J= 0.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 62.2, 114.9, 123.2, 133.3, 133.4 and 192.1; *Anal. Calcd* for $C_6H_6O_2S_2$: C, 41.36; H, 3.47; S, 36.80. Found: C, 41.45; H, 3.61; S, 37.46.

1,3-Bis(2-oxo-1,3-dithiol-4-yl)benzene (29). A solution of 1,3-diethynylbenzene (0.257 g, 2.0 mmol), xanthogen (**5**) (1.21 g, 4.48 mmol) and AIBN (0.277 g, 2.04 mmol) was refluxed for 17 h. Purification by crystallization using toluene gave 0.314 g (50%) of a pale orange solid. mp 188-190 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 6.90 (2H, s) and 7.43 (4H, m); ^{13}C NMR (100 MHz, dioxane-d8 at 60 °C) δ 114.6, 124.8, 127.5, 130.6, 133.9, 134.9 and 191.1; *Anal. Calcd* for $C_{12}H_6O_2S_4$: C,46.46; H, 1.95; S, 41.31. *Found: C, 46.76; H, 1.97; S, 42.01.*

4-(4-Hydroxymethylphenyl)-1,3-dithiol-2-one (30). A solution of 4-ethynylphenyl alcohol (0.366 g, 2.77 mmol) was refluxed for 15 h. Purification by chromatography using 40% ethyl acetate in toluene gave 0.457 g (74%) of a pale yellow solid. mp 107-109 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.76 (1H, t, J= 5.5 Hz), 4.71 (2H, d, J= 5.3 Hz), 6.82 (1H, s) and 7.40 (4H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 64.5, 111.6, 126.4, 127.5, 131.8, 134.7, 142.0, 192.6; IR (KBr) 3310 (br), 3050, 1630, 1005 and 780 cm^{-1}; *Anal. Calcd* for $C_{10}H_8O_2S_2$: C, 53.55; H, 3.59; S, 28.59. Found: C, 53.48; H, 3.77; S, 28.43.

4-Methyl-5-phenyl-1,3-dithiol-2-one (31).[14] A solution of 1-phenyl-1-propyne (0.250 g, 2.15 mmol) was refluxed for 17 h. Purification by chromatography using 50% toluene in hexane gave 0.338 g (75%) of an oil. ^1H NMR (400 MHz, $CDCl_3$) δ 2.23 (3H, s), 7.35-7.45 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.1, 124.7, 127.8, 129.3, 131.3 and 191.4; HRMS calcd for $C_{10}H_8O_2S_2 + H^+$: 209.0095; Found: 209.0094.

4-Ethyl-5-phenyl-1,3-dithiol-2-one (32). A 1.0 M solution of 1-phenyl-1-butyne (0.400 g, 3.07 mmol) was refluxed for 12 h. Purification by chromatography using 50% toluene in hexane gave 0.401 g (59%) of an oil. ^1H NMR (300 MHz, $CDCl_3$) δ 2.00 (3H, t, J= 7.5 Hz), 2.60 (2H, q, J= 7.5 Hz) and 7.35-7.45 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.3, 23.1, 127.1, 128.8, 128.9, 129.3, 131.4, 132.5 and 191.6; HRMS calcd for $C_{11}H_{10}OS_2 + H^+$: 223.0252; Found: 223.0251.

3,4-Diphenyl-1,3-dithiol-2-one (33). A 1.0 M solution of diphenylacetylene (0.260 g, 1.46 mmol) was refluxed for 12 h. Purification by chromatography using 35% toluene in hexane gave 0.156 g (40%) of a white solid, identical to an authentic sample.[2f] mp 109-110 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 7.25 (10H,m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 128.6, 128.7, 129.5, 131.6 and 190.6; HRMS calcd for

$C_{15}H_{10}OS_2 + H^+$: 271.0251; Found: 271.0252.

4-*t*-Butyl-5-phenyl-1,3-dithiol-2-one (34). A 1.0 M solution of 2,3-dimethyl-4-phenyl-3-propyne (0.400 g, 2.5 mmol) was refluxed 12 h. Purification by chromatography using 50% toluene in hexane gave 0.151 g (24%) of a white solid. mp 129 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31 (9H, s), 7.20-7.29 (3H, m) and 7.36-7.40 (2H, m); ^{13}C NMR NMR (75 MHz, $CDCl_3$) δ 32.4, 38.3, 126.5, 128.4, 128.9, 130.3, 132.9, 140.3 and 191.0; *Anal. Calcd* for $C_{13}H_{14}OS_2$: C, 62.48; H, 5.73; S, 26.13. Found: C, 62.36; H, 5.64; S, 25.61.

4-Trimethylsilyl-5-phenyl-1,3-dithiol-2-one (35). A 1.0 M solution of trimethylsilylacetylene (0.600 g, 3.44 mmol) was refluxed for 14 h. Purification by chromatography using 40% toluene in hexane gave 0.112 g (12%) of a white solid. mp 86-87 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.06 (9H, s) and 7.25-7.41 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.42, 128.5, 129.4, 129.6, 131.5, 134.2, 140.3 and 195.6; *Anal. Calcd* for $C_{12}H_{14}OS_2Si$: C, 54.09; H, 5.30; S, 24.06. Found: C, 53.52; H, 5.30; S, 24.76.

4-Trimethylsilyl-5-(3-quinolinyl)-1,3-dithiol-2-one (36). A 0.5 M solution of 3-quinolynyltrimethylsilylacetylene (0.180 g, 0.80 mmol) was refluxed in xylene with azobis(cyclohexanecarbonitrile) for 8 h. Purification by chromatography using 17% ethyl acetate in hexane gave 0.034 g (13%) of a white solid; mp 146-148 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.10 (9H, s), 7.65 (1H, t, J= 7.3 Hz), 7.75-7.95 (2H, m), 8.10-8.25 (2H, m) and 8.90 (1H, d, J= 2.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.50, 77.1, 126.8, 127.3, 127.7, 127.9, 129.5, 130.7, 134.2, 136.1, 136.5, 147.9, 150.0 and 194.6; HRMS calcd for $C_{15}H_{15}NOS_2Si + H^+$: 318.0443; Found: 318.0442.

4-(2-Methoxycarbonylphenyl)-5-phenyl-1,3-dithiol-2-one (37). A 0.5 M solution of methyl 2-phenylethynylbenzoate (0.230 g, 0.98 mmol) was refluxed in xylene with azobis(cyclohexanecarbonitrile) for 15 h. Purification by chromatography using 20% ethyl acetate in hexane gave 0.163 g (51%) of an oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.80 (3H, s), 7.10-7.50 (8H, m) and 7.86 (1H, dd J= 6.8 and 1.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.3, 127.1, 127.3, 128.3, 128.4, 128.9, 129.1, 130.6, 131.2, 131.3, 131.9, 132.1, 166.3 and 190.6; HRMS calcd for $C_{17}H_{12}O_3S_2 + H^+$: 329.0306; Found: 329.0305.

1,2-Bis(isopropoxythiocarbonylthio)-1-(4-isopropylphenyl)cyclobutane (38). A 1.0 M solution of 1-(4-isopropylphenyl)cyclobutene (0.250 g, 1.45 mmol) was refluxed for 16 h. Purification by chromatography using 30% toluene in hexane gave 0.275 g (43%) of an oil as a mixture of *cis* and *trans* isomers (1.7/1); Characteristic displacements are: major isomer (oil); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (6H, d, J= 6.9 Hz), 1.31 (6H, d, J= 6.9 Hz), 4.94 (1H, dd, J= 7.7 and 1.6 Hz), 5.53 (1H, m), 5.70 (1H, m), 7.14 (2H, d, J= 8.2 Hz) and 7.36 (2H, d, J= 8.3 Hz). minor isomer (oil); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.05 (1H, m), 3.27 (1H, m), 4.66 (1H, t, J= 6.9 Hz), 5.53 (1H, m) and 5.70 (1H, m) HRMS calcd for $C_{22}H_{30}O_2S_4 + H^+$: 443.1207; Found: 443.1207.

2,3-Bis(isopropoxythiocarbonylthio)propanoic acid methyl ester (39). A 1.0 M solution of methyl

acrylate (0.205 g, 2.38 mmol) was refluxed for 16 h. Purification by chromatography using 10% ethyl acetate in hexane gave 0.427 g (50%) of an oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.41 (12 H, d, J= 6.2 Hz), 3.55-3.75 (2H, m), 3.78 (3H, s), 4.68 (1H, t, J= 7.7 Hz) and 5.70-5.90 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 21.3, 36.4, 50.2, 53.0, 78.6, 79.1, 169.8, 209.3 and 212.3; *Anal. Calcd* for $C_{12}H_{20}O_4S_4$: C, 40.43; H, 5.65; S, 35.97. Found: C, 40.01; H, 5.72; S, 36.38.

exo-3,5-Dithiatricyclo[5.2.1.0^{2,6}]decan-4-one (40). A 1.0 M solution of norbornylene (0.250 g, 2.66 mmol) was refluxed for 15 h. Purification by chromatography using toluene gave 0.457 g (74%) of a white solid identical to an authentic sample.[15] mp 87 °C.

exo-3,5-Dithiatricyclo[5.2.1.0^{2,6}]dec-8-en-4-one (41). A solution of norbornadiene (0.400 g, 4.3 mmol) was refluxed 12 h. Purification by chromatography using 30% hexane was followed by crystallization in hexane to give 0.189 g (25%) of a white solid. mp 104-105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.76 (1H, dt, J= 8.0 and 1.9 Hz), 2.14 (1H, d, J= 9.9 Hz), 3.03 (2H, m), 3.86 (2H, d, J= 2.1 Hz) and 6.17 (2H, t, J= 1.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.3, 49.5, 51.5, 136.2 and 198.9; *Anal. Calcd* for $C_8H_8OS_2$: C, 52.49; H, 4.39; S, 36.99. Found: C, 52.49; H, 4.39; S, 37.00.

exo-3,5-Dithiatricyclo[6.2.1.0^{2,6}]undecan-4-one (42). A solution of bicyclo[2.2.2]octene (0.400 g, 3.7 mmol) was refluxed for 12 h. Purification by chromatography using 30% hexane in toluene gave 0.021 g (3%) of a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47 (2H, m), 1.59 (2H, m), 1.70-1.80 (4H, m), 2.15 (2H, m) and 4.35 (2H, d, J= 0.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.5, 25.3, 29.6, 52.3 and 197.8; HRMS calcd for $C_9H_{12}OS_2 + H^+$: 201.0408; Found: 201.0408.

4-Phenyl-1,3-dithiol-2-thione (43). A solution of phenylacetylene (0.400 g, 3.92 mmol) was refluxed for 14 h. Purification by chromatography using 10% ethyl acetate in hexane gave 0.394 g (48%) of a red solid.[16] mp 116-118 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.12 (1H, s) and 7.43 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.8, 126.4, 129.3, 129.7, 131.0, 146.2 and 212.2; *Anal. Calcd* for $C_9H_6S_3$: C, 51.40; H, 2.88; S, 45.73. Found: C, 51.86; H, 2.95; S, 45.59.

4-(2-Methoxycarbonylphenyl)-1,3-dithiol-2-thione (44). A solution of methyl 2-ethynylbenzoate (0.444 g, 2.77 mmol) was refluxed 15 h. Purification by chromatography using 20% ethyl acetate in hexane gave 0.405 g (54%) of a yellow solid. mp 129-131 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.88 (3H, s), 6.86 (1H, s), 7.40-7.60 (3H, m) and 7.97 (1H, dt, J= 7.0 and 1.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.6, 124.8, 129.9, 130.8, 131.3, 132.2, 144.8 and 212.9; *Anal. Calcd* for $C_{11}H_8O_2S_3$: C, 49.23; H, 3.00; S, 35.84. Found: C, 49.22; H, 2.99; S, 35.84.

4-(3-Hydroxyprop-1-enyl)-1,3-dithiol-2-thione (45). A solution of 2-penten-4-yn-1-ol (0.340 g, 4.14 mmol) was refluxed for 16 h. Purification by chromatography using 50% ethyl acetate in hexane gave 0.323 g (41%) of a yellow solid. mp 100-102 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.83 (1H, br s), 4.31 (2H, d, J= 3.7 Hz), 5.95 (1H, dt, J= 15.8 and 4.8 Hz), 6.50 (1H, dd, J= 15.8 and 1.3 Hz) and 6.84 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 63.3, 120.9, 124.5, 134.6, 144.1 and 211.8; *Anal. Calcd* for $C_6H_6OS_3$: C,

37.87; H, 3.18; S, 50.55. Found: C, 38.06; H, 3.15; S, 51.60.

4-Methyl-5-phenyl-1,3-dithiol-2-thione (46). A solution of 1-phenyl-1-propyne (0.600 g, 5.16 mmol) was refluxed for 12 h. Purification by chromatography using 50% hexane in toluene gave 0.258 g (22%) of a yellow solid.[17] mp 70-71 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.26 (3H, s) and 7.30-7.50 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.4, 128.9, 129.2, 129.9, 135.8, 139.1 and 211.0; HRMS calcd for $C_{10}H_8S_3 + H^+$: 224.9866; Found: 224.9867.

exo-3,5-Dithiatricyclo[5.2.1.0^{2,6}]decane-4-thione (47). A 1.0 M solution of norbornylene (0.342 g, 3.63 mmol) was refluxed for 15 h. Purification by chromatography using 10% ethyl acetate in hexane gave 0.342 g (47%) of yellow solid.[18] mp 111-113 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.32 (2H, d, J= 7.9 Hz), 1.52 (1H, d, J= 11.0 Hz), 1.70 (2H, d, J= 8.8 Hz), 2.27 (1H, d, J= 11.0 Hz), 2.48 (2H, s) and 4.41 (2H, d, J= 2.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.6, 33.1, 44.8, 67.5 and 218.4 *Anal. Calcd* for $C_8H_{10}S_3$: C, 47.49; H, 4.98; S, 47.53. Found: C, 47.46; H, 5.06; S, 47.52.

Bis(diisopropylthiothiocarbonyl) disulfide (12). 2-Propanethiol (12.2 mL, 131.3 mmol) was added dropwise to a mixture of sodium hydride (4.14 g of 80%, 137.9 mmol) in 150 mL of THF at 0 °C. The mixture was warmed to rt after 30 min and stirred overnight. Carbon disulfide (11.0 g, 144.4 mmol) was added dropwise to the white suspension at 0° C, to give an orange solution. After 2 h, iodine (16.66 g, 65.7mmol) in 200 mL of Et_2O was added portionwise at 0 °C. The mixture was filtered through celite to afford after purification by column chromatography on silical gel using hexane, 16.0 g (81%) of an brown-red oil.[19] ^{1}H NMR (200 MHz, acetone-d_6) δ 1.42 (12H, d, J= 6.9 Hz) and 4.05 (2H, m, J= 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 43.5 and 220.3; IR (neat) 2960, 2920, 2860, 1440, 1360, 1065, 1040 and 830 cm^{-1}.

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