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Hydrochalcogenation of Symmetrical and Unsymmetrical Buta-1,3-diynes with Diaryl Dichalcogenides: Facile Entry to (*Z*)-1-(Organylchalcogeno)but-1-en-3-yne Derivatives

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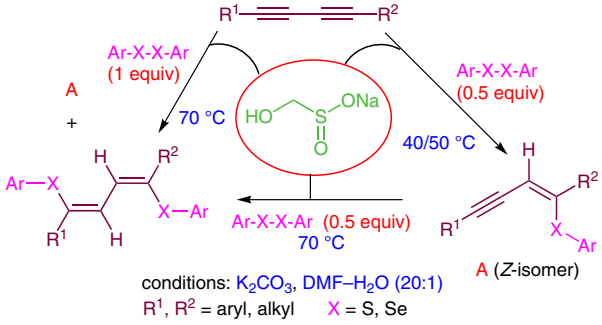

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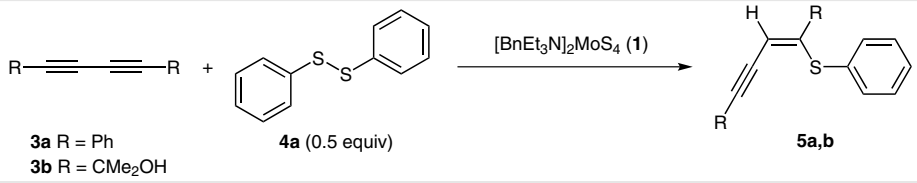
Abstract This work describes an efficient and stereoselective method for the hydrothiolation and -selenation of buta-1,3-diyne derivatives using diaryl disulfides or diselenides, respectively. In the presence of rongalite ($HOCH_2SO_2Na$) and potassium carbonate, buta-1,3-diynes undergo stereoselective addition of the thiolate or selenide anion generated in situ from diaryl disulfides or diselenides to afford the corresponding (*Z*)-1-sulfanyl- or (*Z*)-1-selanylalk-1-en-3-yne derivatives, respectively. The reaction of buta-1,3-diynes with diaryl disulfides or diselenides at higher temperature (70 °C) gave a mixture of monothiolation/selenation and bisthiolation/selenation products in moderate to good yields.

Key words hydrochalcogenation, buta-1,3-diynes, aryl dichalcogenides, rongalite, reductive cleavage

Hydrochalcogenation is the process of incorporating chalcogen and hydrogen atoms into an organic framework. In particular, the direct addition of chalcogenols to alkenes/alkynes has received greater attention recently due to the formation of products that are useful in the pharmaceutical industry and material science.[1] In this context, the thiol-yne reaction (also called alkyne hydrothiolation) is an organic reaction between a thiol and an alkyne that leads to the formation of an alkenyl sulfide.[1d,2]

Vinyl sulfides/selenides are used as important reagents and intermediates in organic synthesis. In the literature, various transformations are reported in which vinyl chalcogenides serve as reagents to access differently functionalized molecules.[3] For example, vinyl sulfides are generally converted into the corresponding aldehydes, ketones, or esters.[3b,e,4] Also cleavage of the C–S bond with metals furnishes the corresponding anionic species which can be easily trapped with electrophiles.[3j,k,m,4] Similarly, vinyl selenides form C–C bonds by cross-coupling reactions with magnesium or zinc reagents[3r–t] in the presence of a nickel catalyst. Despite their various applications, the synthesis of alkenyl chalcogenides has remained a challenge due to the problems of regio- and stereochemistry. Generally, the hydrothiolation of alkynes with thiols proceeds via a free radical or ionic pathway (acid- or base-catalyzed) or can be metal-catalyzed depending on the reaction conditions.[5]

Most commonly, vinyl chalcogenides can be synthesized from acetylenes by the addition of chalcogenide anions in a nucleophilic pathway. This addition takes place in a *trans* manner to form the (*Z*)-vinylic isomer with high stereoselectivity. The formation of nucleophilic species involves the reaction of chalcogenols with a strong base. There are many methods available in literature for the synthesis of vinyl sulfides. However, only a few methods are known for the synthesis of (*Z*)-1-(organylsulfanyl)enynes with high regio- and stereoselectivity.[2b,6] Such conjugated (*Z*)-1-(organylsulfanyl- or -selanyl)enynes are used as intermediates for the synthesis of an enediyne system as well as derivatives of thiophenes[6a,7] and selenophenes.[8] This prompted us to scan the literature methods for the synthesis of these compounds. Baroni et al. achieved the synthesis of (*Z*)-1-(organylsulfanyl)enynes by the reaction of symmetrical and unsymmetrical buta-1,3-diynes with in situ generated sodium organylthiolate anions under reflux conditions.[7] Perin and co-workers studied this reaction using a solid-catalyst system such as potassium fluoride/alumina with thiols in the presence of solvents like PEG-400 or glycerol.[9] Reducing agents such as sodium borohydride[3g,6b,8a,10] were used for the cleavage of dichalcogenides, which generates chalcogenide anions in situ, that were then used for hydrochalcogenation of symmetrical and unsymmetrical buta-1,3-diynes. Despite the advantages of the above methods, they



Scheme 1 Hydrothiolation of buta-1,3-diynes **3a**,**b** with diphenyl disulfide (**4a**) in the presence of **1**

have limitations such as the use of toxic, malodorous chalcogenols, harsh reaction conditions, and the formation of diastereomeric mixtures [(*E*) and (*Z*)] of (organylchalcogeno)enynes. Hence there is a need for newer methods to access these skeletons diastereospecifically. From our laboratory, we have reported that benzyltriethylammonium tetrathiomolybdate [$(BnEt_3N)_2MoS_4$, **1**] is a versatile reagent[11] in organic synthesis. The disulfide bond can be cleaved in situ using **1**, and the cleavage products can be trapped with various electrophiles.[11e,12] In light of this, we envisioned the use of **1** for the hydrochalcogenation of symmetrical and unsymmetrical buta-1,3-diynes.

We began our investigation by treating 1,4-diphenylbuta-1,3-diyne (**3a**, 1 equiv) with diphenyl disulfide (**4a**, 0.5 equiv) under various conditions in the presence of **1** (Scheme 1). Initially, the reaction between 1,4-diphenylbuta-1,3-diyne (**3a**) and diphenyl disulfide (**4a**, 0.5 equiv) was performed with benzyltriethylammonium tetrathiomolybdate (**1**, 2 equiv) in acetonitrile at room temperature. This resulted in the formation of only traces of the expected product, (*Z*)-sulfanylenyne **5a** after 12 hours (Table 1, entry 1).

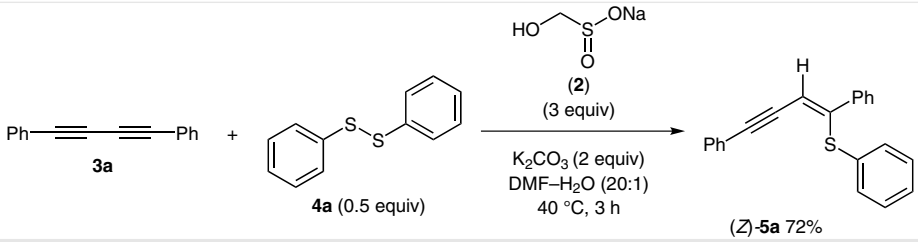
Heating the reaction mixture to 50 °C and the use of solvents such as toluene, tetrahydrofuran, ethanol, acetonitrile–ethanol (1:1) at this temperature did not furnish the product **5a** in reasonable yield (Table 1, entries 2–6). Then the reaction was performed with more reactive substrate such as 2,7-dimethylocta-3,5-diyne-2,7-diol[6b] (**3b**) in the presence of **1** in acetonitrile at 50 °C which gave the corresponding (*Z*)-sulfanylenyne **5b** in 33% yield. Considerable efforts to increase the yield of the reaction with various disulfides under different reaction conditions were unsuccessful.

Table 1 Screening for Hydrothiolation of Buta-1,3-diynes **3** with the Reagent **1** (Scheme 1)

Entry	Diyne	Solvent	Temp (°C)	Time (h)	Product	Yield[a] (%)
1	**3a**	MeCN	25	12	**5a**	trace
2	**3a**	MeCN	50	12	**5a**	trace
3	**3a**	toluene	50	12	**5a**	trace
4	**3a**	THF	50	12	**5a**	trace
5	**3a**	MeCN–EtOH (1:1)	50	12	**5a**	trace
6	**3a**	EtOH	50	24	**5a**	<5
7	**3b**	MeCN	50	12	**5a**	33[a]
8	**3b**	EtOH	50	12	**5b**	35[a]

[a] Yield of isolated product.

Then we explored the use of another reducing agent, sodium hydroxymethanesulfinate ($HOCH_2SO_2Na$, **2**, also called rongalite[13]) which has been studied in our laboratory for the cleavage of dichalcogenides and further utilized for ring-opening reactions of aziridines and epoxides.[14] Treatment of 1,4-diphenylbuta-1,3-diyne (**3a**, 1 equiv) and diphenyl disulfide (**4a**, 0.5 equiv) in *N*,*N*-dimethylformamide–water (20:1) with rongalite (**2**, 3 equiv) followed by the addition of potassium carbonate (2 equiv) at room temperature furnished [(*Z*)-4-phenyl-1-(phenylsulfanyl)but-1-en-3-ynyl]benzene (**5a**) in 35% yield after eight hours. In order to increase the yield of the reaction, we further raised the temperature of the reaction to 40 °C[15] which gave **5a** in 72% yield within three hours (Scheme 2).

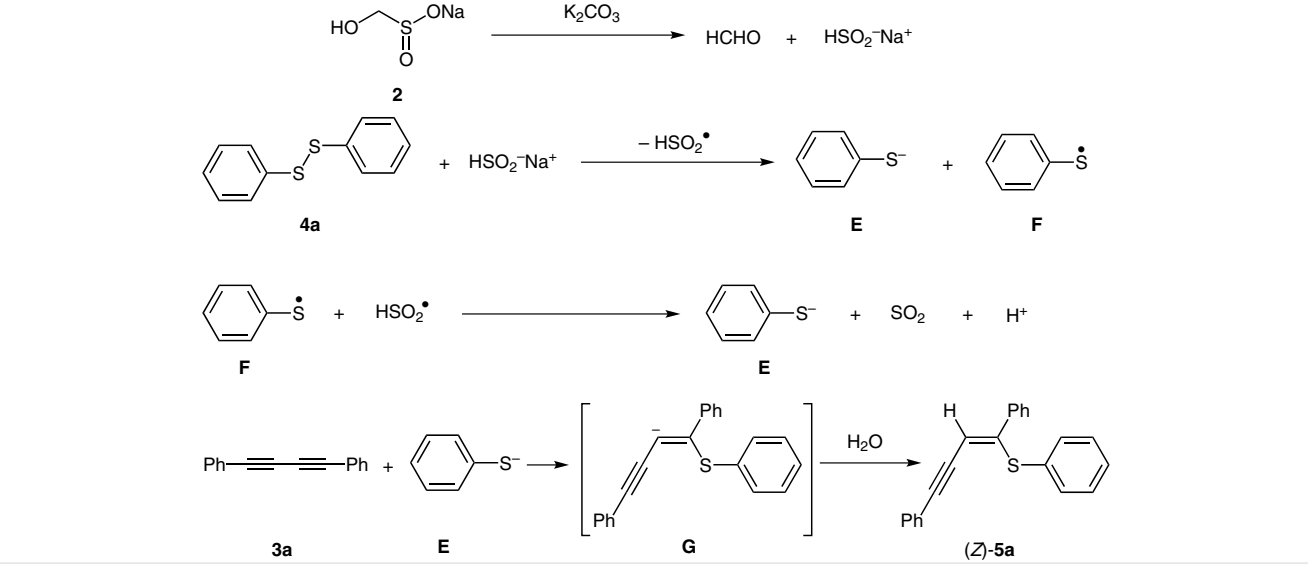


Scheme 2 Hydrothiolation of 1,4-diphenylbuta-1,3-diyne (**3a**) with diphenyl disulfide (**4a**) using rongalite (**2**)

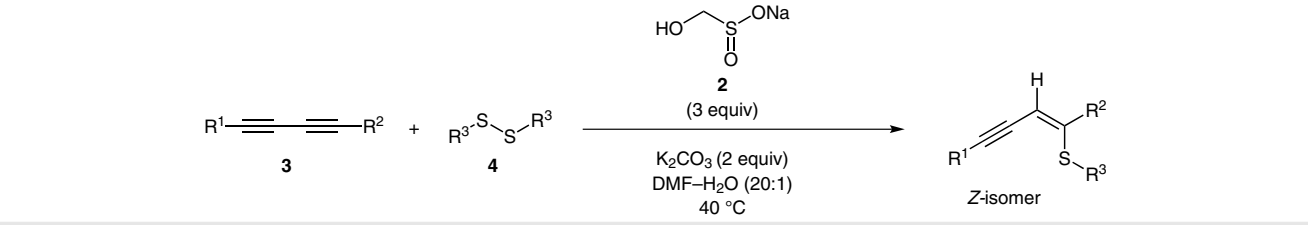
A mechanism has been proposed previously for the reduction of disulfide **4a** followed by the hydrothiolation of 1,4-diphenylbuta-1,3-diyne (**3a**) (Scheme 3).[6b,14,16] Initially, rongalite (**2**) undergoes decomposition to form formaldehyde and HSO_2^- in the presence of base followed by a single electron transfer to the disulfide to furnish the intermediates such as anionic species **E** and radical **F**.[14,16] The thiolate radical **F** further gets reduced to anionic species **E**, by another single electron transfer (SET) from the radical ($HSO_2^{\bullet}$).

This thiolate **E** undergoes *trans* addition to alkyne **3a** generating an intermediate **G** that on protonation gives the desired (*Z*)-sulfanylenyne derivative **5a**.[6b] This result encouraged us to study the scope of the reaction using various symmetrical and unsymmetrical buta-1,3-diynes **3b**–**g** with different disulfides **4a**–**g** under similar reaction conditions (Scheme 4).

The results of this investigation are summarized in Table 2. It can be observed from Table 2 that the symmetrical buta-1,3-diynes containing hydroxy groups such as 2,7-dimethylocta-3,5-diyne-2,7-diol (**3b**) and hexa-2,4-diyne-1,6-diol (**3c**) upon reaction with diphenyl disulfide (**4a**) in the presence of rongalite (**2**) for three hours give the corresponding (*Z*)-sulfanylenynes **5b** and **5c** in 82% and 83% yields, respectively (entries 1 and 2) whereas aliphatic 1,3-diyne such as hexadeca-7,9-diyne (**3d**) furnish only traces of the desired product **5d** even after 12 hours (entry 3).

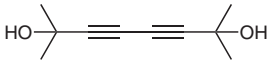
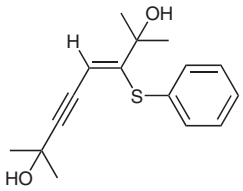
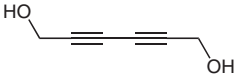
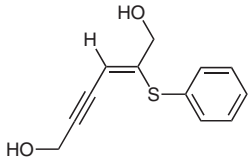
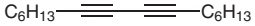
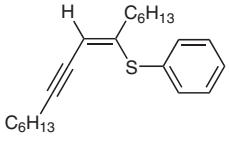
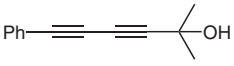
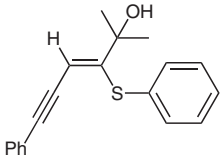
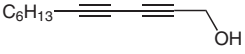
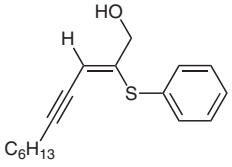
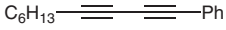
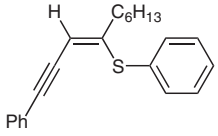
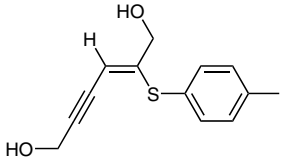
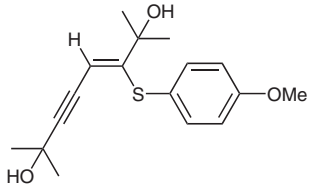
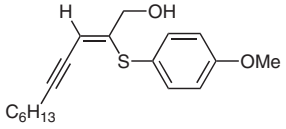


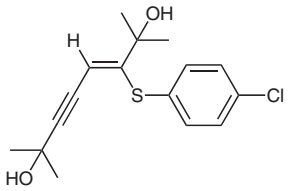
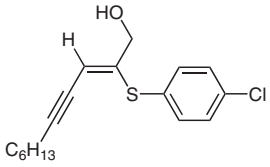
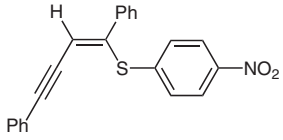
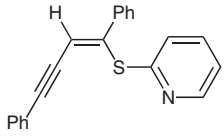
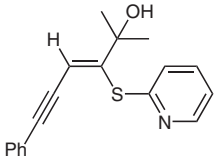
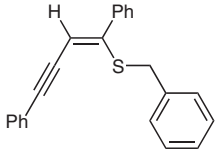
Scheme 3 Mechanism for the hydrothiolation reaction



Scheme 4 Hydrothiolation of symmetrical and unsymmetrical buta-1,3-diynes **3** with various disulfides **4**

Table 2 Regio- and Stereoselective Synthesis of (*Z*)-Sulfanylenynes (Scheme 4)

Entry	R^1—≡—≡—R^2		R^3SSR^3	Product		Time (h)	Yield[a] (%)
1	**3b**		**4a** $(PhS)_2$	**5b**		3	82
2	**3c**		**4a**	**5c**		3	83
3	**3d**		**4a**	**5d**		12	trace
4	**3e**		**4a**	**5e**		3	76
5	**3f**		**4a**	**5f**		3	73
6	**3g**		**4a**	**5g**		8	45
7	**3c**		**4b** $(4\text{-}MeC_6H_4S)_2$	**5h**		3	88
8	**3b**		**4c** $(4\text{-}MeOC_6H_4S)_2$	**5i**		3	85
9	**3f**		**4c**	**5j**		3	75

Entry	R^1—≡—≡—R^2	R^3SSR^3	Product	Time (h)	Yield[a] (%)
10	**3b**	**4d** $(4\text{-}ClC_6H_4S)_2$	**5k** 	4	76
11	**3f**	**4d**	**5l** 	4	65
12	**3a**	**4e** $(4\text{-}O_2NC_6H_4S)_2$	**5m** 	8	52
13	**3a**	**4f** $(2\text{-pyridylS})_2$	**5n** 	5	63
14	**3e**	**4f**	**5o** 	4	73
15	**3a**	**4g** $(BnS)_2$	**5p** 	12	–

[a] Yield of isolated product.

When the unsymmetrical buta-1,3-diynes **3e**–**g** were used, the reactions were completed in 3–8 hours and (*Z*)-sulfanylenynes **5e**–**g** were obtained in moderate to good yields with high chemoselectivity (Table 2, entries 4–6). The scope of the reaction was further demonstrated using other disulfides **4b**–**g** and it was found that aromatic disulfides bearing electron-releasing groups on the phenyl ring such as methyl or methoxy furnished the products in higher yields (entries 7–9) compared to disulfides bearing electron-withdrawing groups like chloro or nitro on the phenyl moiety (entries 10–12). The heteroaryl disulfide **4f** also reacted reasonably well with symmetrical and unsymmetrical buta-1,3-diynes under these conditions (entries 13 and 14).[17] However, alkyl disulfide such as dibenzyl disulfide (**4g**) failed to react with buta-1,3-diyne **3a** even after 12 hours (entry 15).

The reason for the reduced reactivity of the aliphatic symmetrical diacetylene hexadeca-7,9-diyne (**3d**) compared to other diacetylenes towards the benzenethiolate anion can be explained by close inspection of the mechanism of the reaction.[6b] Attack of the benzenethiolate anion on the diacetylene moiety develops a negative charge at the adjacent carbon (C2) and the possible transition states[6b] are shown in Figure 1. In case of **3a**, the incipient carbanion is stabilized by phenyl-substituted acetylenic group, which draws electrons efficiently (electronic factor) compared to transition state **A** of compound **3d** where the octynyl-substituted acetylene group is involved (Figure 1, **A**, **B**).

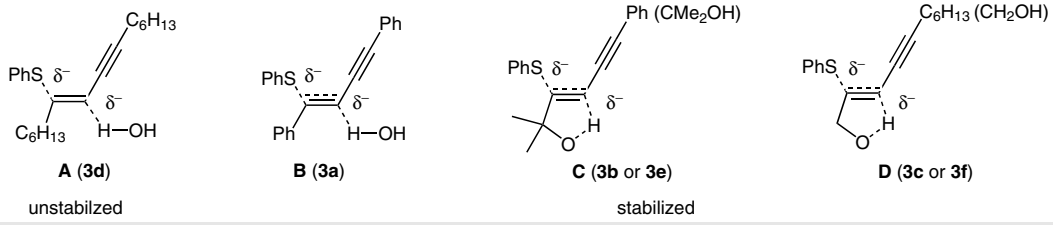


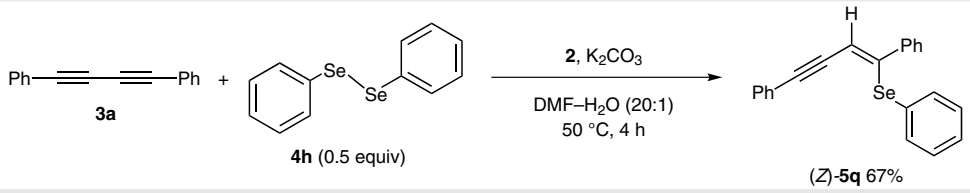
Figure 1 Possible transition states involved in the hydrothiolation reactions

This possibly explains the low reactivity of compound **3d**. The high reactivity of (hydroxymethyl)acetylene triple bonds over other diacetylenes bearing phenyl or alkyl substituents can be explained by the ease of formation of cyclic five-membered transition states[6b] **C** and **D** between the incipient carbanion at C2 and intramolecular hydrogen bonding (Figure 1, **C**, **D**). Additionally, steric as well as electronic factors play a vital role for these propargylic triple bonds (**3b**,**c**,**e**,**f**) in determining their reactivity (Table 2, entries 1, 2, 4, and 5).

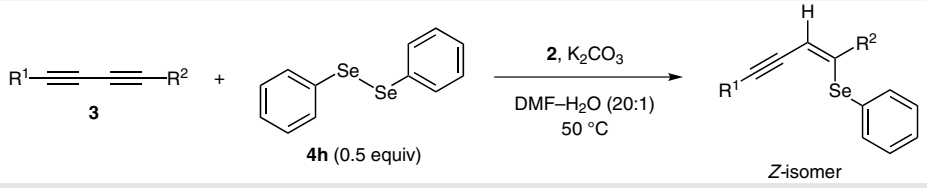
Like the aryl disulfides, aryl diselenides are also cleaved in the presence of rongalite (**2**).[14] Accordingly, diphenyl diselenide (**4h**) was treated with diacetylene **3a** in the presence of rongalite (**2**) and potassium carbonate at 50 °C.[18]

The reaction resulted in the formation of the corresponding (*Z*)-selenylenyne **5q** in 67% yield after four hours (Scheme 5).[15] The scope of the methodology was further extended to other buta-1,3-diynes (Scheme 6).

The results are presented in Table 3. Buta-1,3-diynes **3b** and **3c** bearing hydroxymethyl groups on both ends reacted with diselenide **4h** (4 h) in the presence of **2** to give the corresponding (*Z*)-selanylenynes **5r** and **5s**, respectively (entries 1 and 2). Aliphatic diacetylene such as hexadeca-7,9-diyne (**3d**) failed to react with diphenyl diselenide even after 12 hours (entry 3) whereas unsymmetrical buta-1,3-diynes **3e**–**g** gave the corresponding products **5u**–**w** in moderate to good yields (entries 4–6).

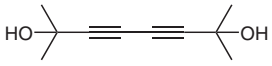
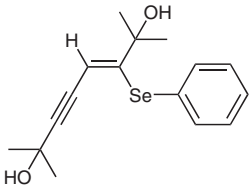
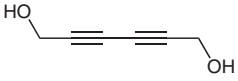
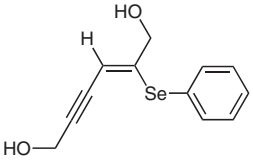
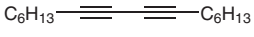
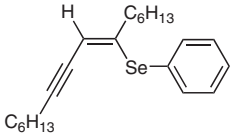
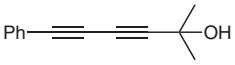
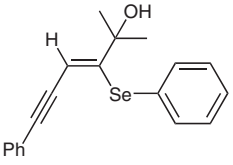
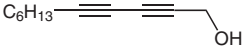
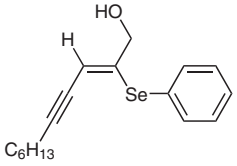
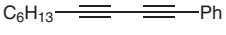
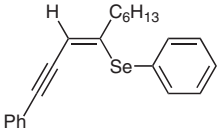


Scheme 5 Hydroselenation of **3a** with diphenyl diselenide (**4h**) mediated by rongalite (**2**)



Scheme 6 Hydroselenation of symmetrical and unsymmetrical buta-1,3-diynes with diphenyl diselenide (**4h**) mediated by rongalite (**2**)

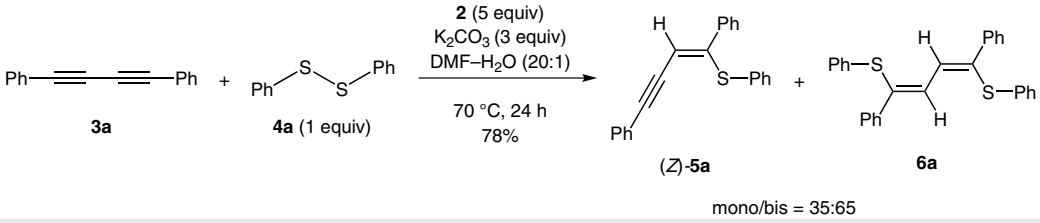
Table 3 Synthesis of (*Z*)-Selanylenynes from Various Buta-1,3-diynes (Scheme 6)

Entry	R^1—≡—≡—R^2		Product		Time (h)	Yield[a] (%)
1	**3b**		**5r**		4	72
2	**3c**		**5s**		4	75
3	**3d**		**5t**		12	–
4	**3e**		**5u**		5	68
5	**3f**		**5v**		7	62
6	**3g**		**5w**		8	42

[a] Yield of isolated product.

We then studied the reactivity of 1,4-diorganylbuta-1,3-diynes using one equivalent of diaryl dichalcogenide at 70 °C with excess rongalite (**2**) and potassium carbonate. Accordingly, the reaction was performed with 1,4-diphenylbuta-1,3-diyne (**3a**) and disulfide **4a** (1 equiv) in the presence of rongalite (**2**, 5 equiv) and potassium carbonate (3 equiv). Surprisingly, we found a mixture of mono- and bisthiolation products **5a** and **6a** (Scheme 7). This prompted us to search the literature for methods for the bischalcogenation of alkynes. Very few methods are reported such as the reaction of 1,4-diorganylbuta-1,3-diynes with thiols in the presence of strong bases[19] or alumina [20] under reflux conditions and metal-catalyzed (Pt or Ni)[21] dimerization–bisthiolation of alkynes.

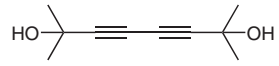
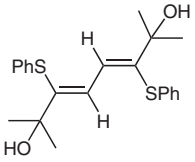
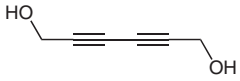
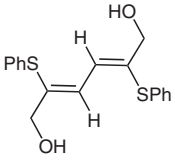
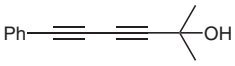
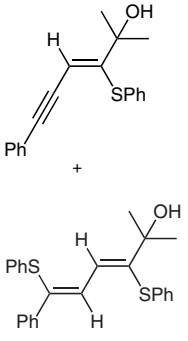
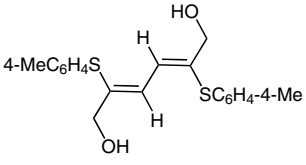
To study the scope of the reaction, the methodology was then extended to other buta-1,3-diynes using various disulfides and diselenides. The ratios of mono- and bischalcogenation products are presented in Table 4. It was found that butadiynes bearing hydroxymethyl groups on both ends reacted efficiently with diaryl disulfides to form only bisthiolation product (entries 1, 2, 4, and 5). For example, (3*Z*,5*Z*)-2,7-dimethyl-3,6-bis(phenylsulfanyl)octa-3,5-diene-2,7-diol (**6b**) was obtained as the sole product when buta-

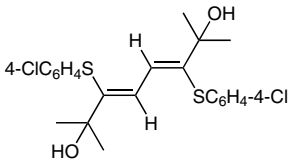
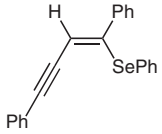
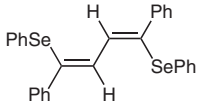
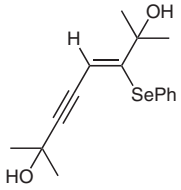
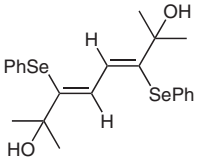
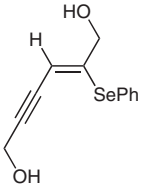
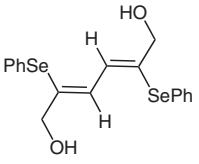


Scheme 7 Hydrothiolation of **3a** with diphenyl disulfide (**4a**) at 70 °C in the presence of rongalite (**2**)

1,3-diyne **3b** was reacted with disulfide **4a** for 12 hours under the reaction conditions described in Scheme 7 (entry 1). The unsymmetrical buta-1,3-diyne **3e** upon reaction with diphenyl disulfide (**4a**) gave a mixture of mono- and bisthiolation products (24 h, 78%) in the ratio 32:68 (entry 3). The reaction of diphenyl diselenide (**4h**) with diyne **3a** furnished the mono- and bisselenation products **5q** and **6g** in the ratio 48:52 after 24 hours (entry 6). Also the more reactive buta-1,3-diynes such as **3b** and **3c** on reaction with **4h** (24 h) resulted in a mixture of mono- and bisselenation products (entries 7 and 8).

Table 4 Synthesis of Mono- and Bischalcogenation Products from Buta-1,3-diynes **3** and Dichalcogenides **4** (Scheme 7)

Entry	R^1—≡—≡—R^2		R^3SSR^3	Product(s)		Ratio[a] mono/bis	Time (h)	Yield[b] (%)
1	**3b**		**4a** $(PhS)_2$	**6b**		0:100	12	82
2	**3c**		**4a**	**6c**		0:100	10	85
3	**3e**		**4a**	**5e** + **6d**		32:68	24	78
4	**3c**		**4b** $(4\text{-}MeC_6H_4S)_2$	**6e**		0:100	10	86

Entry	R^1—≡—≡—R^2	R^3SSR^3	Product(s)	Ratio[a] mono/bis	Time (h)	Yield[b] (%)
5	**3b**	**4d** $(4\text{-}ClC_6H_4S)_2$	**6f** 	0:100	16	76
			5q 			
6	**3a**	**4h** $(PhSe)_2$	+	48:52	24	52
			6g 			
			5r 			
7	**3b**	**4h**	+	40:60	24	62
			6h 			
			5s 			
8	**3c**	**4h**	+	34:66	24	66
			6i 			

[a] Ratio was determined from the yields of the isolated products.
[b] Total yield of isolated product(s).

The structure of **6g** from the bisselenation of **3a** was unambiguously determined by X-ray crystallographic analysis (Figure 2).

Then we decided to extend the methodology to the synthesis of mixed hydrochalcogenation products. In this regard, previously synthesized (*Z*)-(chalcogeno)enynes were treated with different dichalcogenides (Scheme 8) and the results are described in Table 5. Treatment of (*Z*)-sulfanylenyne **5c** (1 equiv) and 4-chlorophenyl disulfide (**4d**, 0.5 equiv) with rongalite (**2**, 3 equiv) and potassium carbonate (2 equiv) at 70 °C for 10 hours afforded the corresponding product **6j** in 80% yield whereas (*Z*)-sulfanylenyne **5h** under

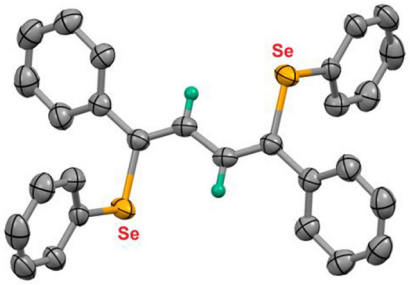
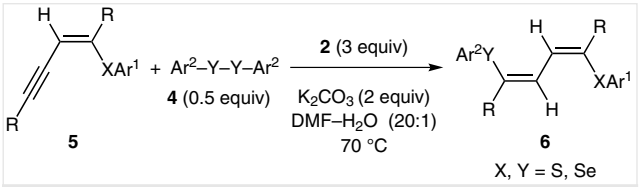


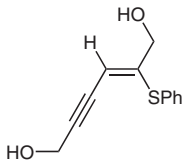
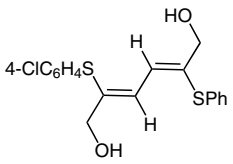
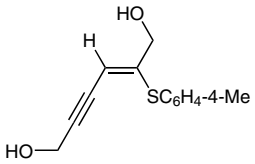
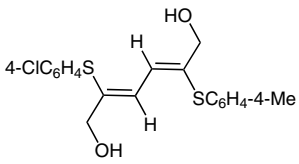
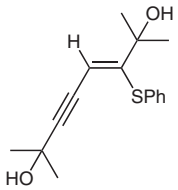
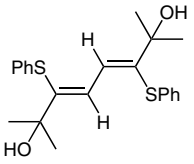
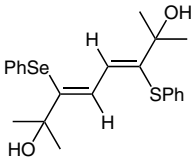
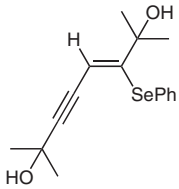
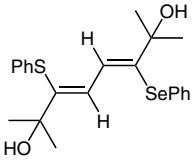
Figure 2 ORTEP of **6g** drawn with 50% ellipsoidal probability

similar conditions furnished mixed hydrothiolation product **6k** in 82% yield (entries 1 and 2). To study the reactivity of (*Z*)-sulfanylenyne **5b** with diphenyl disulfide (**4a**) as well as with diphenyl diselenide (**4h**), a set of reactions were performed separately and it was found that hydrothiolation of **5b** with **4a** proceeded smoothly in six hours to form the corresponding product **6b** (entry 3) whereas its hydroselenation with **4h** gave the desired product **6l** in only 52% yield after 24 hours (entry 4).



Scheme 8 Hydrochalcogenation of (*Z*)-(chalcogeno)enynes

Table 5 Synthesis of Mixed Chalcogenation Products by Hydrochalcogenation Reaction (Scheme 8)

Entry	(*Z*)-(Chalcogeno)enyne		Ar^2YYAr^2	Product		Time (h)	Yield[a] (%)
1	**5c**		**4d** $(4\text{-}ClC_6H_4S)_2$	**6j**		10	80
2	**5h**		**4d**	**6k**		10	82
3	**5b**		**4a** $(PhS)_2$	**6b**		6	85
4	**5b**		**4h** $(PhSe)_2$	**6l**		24	52
5	**5r**		**4a**	**6l**		24	50

[a] Yield of isolated product.

This indicated that the in situ generated benzenethiolate anion reacted more efficiently than the benzeneselenolate anion. This may be due to the rapid oxidative dimerization of selenols and also steric factors involved during hydroselenation. Then we studied the reactivity of structurally similar (*Z*)-selanylenyne **5r** with diphenyl disulfide (**4a**). When (*Z*)-selanylenyne **5r** was treated with **4a** in the presence of **2** under similar reaction conditions, it gave the mixed selanyl sulfide **6l** in 50% yield after 24 hours (entry 5). This demonstrates that the structurally similar (*Z*)-sulfanylenynes are more reactive than the corresponding (*Z*)-selanylenynes for this addition reaction.

In summary, we have developed an ecofriendly and metal-free method for the hydrochalcogenation of 1,4-diorganylbuta-1,3-diynes using rongalite as a reducing agent The significance of the method are high regio- and stereoselectivity, avoiding the use of toxic and malodorous chalcogenols, and an easy workup procedure. The scope of this method was also elaborated for the synthesis of bischalcogenation products under metal-free conditions at higher temperatures. Studies aimed at exploring the synthetic utility of these compounds are in progress.

All reactions were performed in oven dried apparatus and were stirred magnetically. IR spectra were recorded using a Jasco FT-IR instrument. ^{1}H and ^{13}C NMR spectra were recorded on 400 MHz (100 MHz, ^{13}C) NMR spectrometer and calibrated using TMS (for ^{1}H NMR) or residual undeuterated solvent (for ^{1}H and ^{13}C) as an internal reference. Mass spectra were recorded on a Q-TOF electrospray instrument. Melting point values reported are uncorrected. Commercial grade solvents were distilled prior to use. All buta-1,3-diyne derivatives were synthesized using reported protocols[22] and disulfides and diphenyl diselenide were purchased commercially. Spectral data of products obtained were consistent with the reported compounds.[6b,7,9,21]

(*Z*)-1-Sulfanyl or -selanylalk-1-en-3-ynes 5; General Procedure

To a well-stirred solution of 1,4-diorganylbuta-1,3-diyne (0.5 mmol, 1 equiv) in DMF–H_2O (20:1; 4 mL), the disulfide/diselenide (0.25 mmol, 0.5 equiv) was added followed by the addition of rongalite **2** (1.5 mmol, 3 equiv) and K_2CO_3 (1 mmol, 2 equiv). The mixture was stirred at 40 °C or 50 °C for the time indicated in Table 2 or 3. Completion of the reaction was monitored by TLC until consumption of the starting material. The mixture was allowed to attain r.t. and water was added followed by extraction with EtOAc (2 × 20 mL). The organic layer was separated, then washed with brine, extracted with EtOAc (2 × 5 mL), and dried (anhyd Na_2SO_4). The solvent was evaporated under vacuum and the crude product was purified by column chromatography (silica gel, 230–400 mesh, EtOAc–petroleum ether).

[(1*Z*)-4-Phenyl-1-(phenylsulfanyl)but-1-en-3-ynyl]benzene (5a)[6b]

White solid; yield: 112.5 mg (72%); mp 93–95 °C.

FTIR (neat): 3368 (br s), 1582 (s), 1478 (m), 1440 (m), 1018 (s), 754 (s), 738 (s), 688 cm^{-1} (s).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.02 (m, 15 H), 6.32 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.1, 138.3, 134.4, 131.5, 130.3, 128.6, 128.3, 128.2, 127.9, 126.3, 123.3, 112.2, 98.3, 87.6.

(3*Z*)-2,7-Dimethyl-3-(phenylsulfanyl)oct-3-en-5-yne-2,7-diol (5b)[6b]

White solid; yield: 113.3 mg (82%); mp 103–104 °C.

FTIR (KBr): 3283 (s), 2981 (m), 1580 (w), 1479 (w), 1363 (m), 1211 (m), 1164 (s), 1144 (m), 951 (m), 741 cm^{-1} (m).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.25 (m, 4 H), 7.15 (t, *J* = 7.2 Hz, 1 H), 6.44 (s, 1 H), 2.83 (br s, 1 H), 2.24 (br s, 1 H), 1.48 (s, 6 H), 1.23 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.0, 135.9, 128.7, 128.0, 125.6, 113.2, 103.8, 79.2, 74.6, 65.2, 30.5, 28.8.

(2*Z*)-2-(Phenylsulfanyl)hex-2-en-4-yne-1,6-diol (5c)[9]

White solid; yield: 91.4 mg (83%); mp 110–112 °C.

FTIR (KBr): 3402 (s), 2921 (w), 1637 (w), 1020 (s), 1004 (s), 752 cm^{-1} (m).

^{1}H NMR (400 MHz, CD_3COCD_3): δ = 7.45–7.43 (m, 2 H), 7.40–7.31 (m, 3 H), 6.16 (pent, *J* = 2.4, 1.6 Hz, 1 H), 4.44 (t, *J* = 5.6 Hz, 1 H), 4.35–4.34 (m, 2 H), 4.30–4.26 (m, 1 H), 4.01 (d, *J* = 5.6 Hz, 2 H).

^{13}C NMR (100 MHz, CD_3COCD_3): δ = 147.6, 132.5, 132.2, 129.3, 128.0, 108.0, 96.4, 80.7, 63.6, 50.5.

(3*Z*)-2-Methyl-6-phenyl-3-(phenylsulfanyl)hex-3-en-5-yn-2-ol (5e)[9]

White solid; yield: 111.7 mg (76%); mp 60–62 °C.

FTIR (KBr): 3441 (s), 2972 (m), 2199 (w), 1579 (w), 1440 (w), 1362 (m), 1210 (m), 1179 (s), 976 (m), 834 (m), 757 (s), 741 (m), 687 cm^{-1} (s).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 7.7 Hz, 2 H), 7.27–7.06 (m, 8 H), 6.63 (s, 1 H), 2.25 (br s, 1 H), 1.52 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.2, 135.4, 131.4, 128.8, 128.6, 128.3, 128.0, 125.9, 122.9, 114.2, 98.9, 86.6, 74.7, 29.1.

(2*Z*)-2-(Phenylsulfanyl)undec-2-en-4-yn-1-ol (5f)[6b]

Yellow oily liquid; yield: 100.2 mg (73%).

FTIR (neat): 3370 (m), 2955 (m), 2931 (s), 2858 (m), 2215 (w), 1583 (w), 1477 (w), 1100 (m), 1023 (m), 746 (m), 692 cm^{-1} (w).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 7.4 Hz, 2 H), 7.30–7.23 (m, 3 H), 6.01 (s, 1 H), 4.01 (d, *J* = 4.2 Hz, 2 H), 2.37–2.33 (m, 3 H), 1.56–1.26 (m, 8 H), 0.87 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.7, 132.2, 132.0, 128.9, 127.6, 110.8, 99.1, 76.9, 64.4, 31.2, 28.5, 28.4, 22.4, 19.7, 13.9.

[(3*Z*)-4-(Phenylsulfanyl)dec-3-en-1-ynyl]benzene (5g)[23]

Yellow liquid; yield: 72.1 mg (45%).

FTIR (neat): 3424 (s), 2954 (m), 2927 (s), 2855 (m), 1599 (m), 1440 (m), 1021 (m), 754 (m), 690 cm^{-1} (m).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.23 (m, 10 H), 5.84 (s, 1 H), 2.18 (t, *J* = 7.4 Hz, 2 H), 1.44–1.14 (m, 8 H), 0.83 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.7, 133.2, 132.6, 131.4, 128.9, 128.2, 127.9, 127.7, 123.5, 107.3, 95.9, 86.7, 36.1, 31.4, 28.5, 28.4, 22.4, 14.0.

(2*Z*)-2-[4-(Methylphenyl)sulfanyl]hex-2-en-4-yne-1,6-diol (5h)

Pale pink solid; yield: 103.1 mg (88%); mp 87–89 °C.

FTIR (neat): 3328 (s), 2924 (w), 2204 (w), 1339 (w), 1016 (s), 1004 (s), 973 (m), 814 cm^{-1} (m).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 8.0 Hz, 2 H), 7.11 (d, *J* = 7.9 Hz, 2 H), 5.98 (s, 1 H), 4.38 (s, 2 H), 3.98 (s, 2 H), 3.19 (br s, 2 H), 2.32 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.1, 138.4, 133.3, 129.8, 127.1, 106.8, 95.2, 81.8, 64.0, 51.3, 21.0.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{14}O_2SNa$: 257.0612; found: 257.0612.

(3*Z*)-3-[(4-Methoxyphenyl)sulfanyl]-2,7-dimethyloct-3-en-5-yne-2,7-diol (5i)

Yellow gummy mass; yield: 130.1 mg (85%).

FTIR (neat): 3426 (s), 2978 (s), 2932 (s), 1721 (m), 1594 (m), 1494 (s), 1463 (s), 1287 (m), 1246 (s), 1174 (m), 1032 (m), 947 (m), 825 cm^{-1} (m).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.32 (d, *J* = 8.6 Hz, 2 H), 6.84 (d, *J* = 8.6 Hz, 2 H), 6.32 (s, 1 H), 3.78 (s, 3 H), 2.31 (br s, 2 H), 1.48 (s, 6 H), 1.32 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.4, 154.9, 131.2, 126.5, 114.4, 111.7, 103.4, 79.2, 74.5, 65.3, 55.4, 30.8, 29.0.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{22}O_3SNa$: 329.1187; found: 329.1193.

(2*Z*)-2-[(4-Methoxyphenyl)sulfanyl]undec-2-en-4-yn-1-ol (5j)

Pale yellow liquid; yield: 114.2 mg (75%).

FTIR (neat): 3420 (s), 2957 (s), 2931 (s), 2858 (m), 2214 (w), 1720 (w), 1593 (w), 1494 (s), 1287 (m), 1248 (s), 1030 (s), 829 cm^{-1} (m).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 8.4 Hz, 2 H), 6.86 (d, *J* = 8.4 Hz, 2 H), 5.84 (s, 1 H), 3.98 (d, *J* = 5.5 Hz, 2 H), 3.80 (s, 3 H), 2.39 (t, *J* = 6.3 Hz, 2 H), 1.63–1.29 (m, 9 H), 0.88 (t, *J* = 6.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.0, 146.7, 135.7, 121.4, 114.6, 107.5, 99.1, 76.9, 64.3, 55.3, 31.3, 28.6, 28.5, 22.5, 19.8, 14.0.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{24}O_2SNa$: 327.1395; found: 327.1398.

(3*Z*)-3-[(4-Chlorophenyl)sulfanyl]-2,7-dimethyloct-3-en-5-yne-2,7-diol (5k)

Yellow gummy mass; yield: 118.1 mg (76%).

FTIR (neat): 3398 (s), 2981 (m), 2931 (w), 1719 (w), 1476 (s), 1363 (m), 1166 (m), 1091 (m), 1012 (w), 948 (m), 815 cm^{-1} (m).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.24 (br s, 4 H), 6.44 (s, 1 H), 2.37 (br s, 1 H), 1.94 (br s, 1 H), 1.47 (s, 6 H), 1.28 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.8, 134.4, 131.6, 129.4, 128.8, 114.0, 104.0, 79.0, 74.5, 65.4, 30.7, 28.9.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{19}ClO_2SNa$: 333.0692; found: 333.0694.

(2*Z*)-2-[(4-Chlorophenyl)sulfanyl]undec-2-en-4-yn-1-ol (5l)

Yellow liquid; yield: 100.4 mg (65%).

FTIR (neat): 3402 (m), 2955 (m), 2930 (s), 2858 (m), 1719 (w), 1475 (m), 1277 (w), 1093 (m), 1012 (m), 820 (w), 747 cm^{-1} (m).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.35 (d, *J* = 8.3 Hz, 2 H), 7.27 (d, *J* = 8.3 Hz, 2 H), 6.06 (s, 1 H), 4.05 (s, 2 H), 2.35 (t, *J* = 6.9 Hz, 2 H), 1.55–1.26 (m, 9 H), 0.88 (t, *J* = 6.3 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.0, 133.6, 133.2, 130.9, 129.1, 112.0, 99.6, 76.8, 64.5, 31.2, 28.5, 28.4, 22.5, 19.7, 14.0.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{21}ClOSNa$: 331.0899; found: 331.0901.

1-{[(1*Z*)-1,4-Diphenylbut-1-en-3-ynyl]sulfanyl}-4-nitrobenzene (5m)

Pale yellow solid; yield: 92.9 mg (52%); mp 169–171 °C.

FTIR (KBr): 3423 (s), 2926 (w), 2066 (w), 1641 (w), 1019 cm^{-1} (m).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.8 Hz, 2 H), 7.60–7.58 (m, 2 H), 7.43–7.29 (m, 10 H), 6.59 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.6, 145.0, 143.2, 137.5, 131.6, 129.3, 128.85, 128.78, 128.5, 128.4, 127.5, 123.8, 122.7, 116.0, 99.8, 87.0.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{15}NO_2SNa$: 380.0721; found: 380.0726.

2-{[(1*Z*)-1,4-Diphenylbut-1-en-3-ynyl]sulfanyl}pyridine (5n)

White solid; yield: 98.7 mg (63%); mp 77–79 °C.

FTIR (KBr): 3053 (w), 2188 (w), 1573 (m), 1558 (m), 1445 (m), 1424 (m), 1135 (w), 760 (s), 690 cm^{-1} (m).

^1H NMR (400 MHz, $CDCl_3$): δ = 8.36 (d, *J* = 3.9 Hz, 1 H), 7.65 (dd, *J* = 2.0, 7.7 Hz, 2 H), 7.43–7.25 (m, 9 H), 7.02 (d, *J* = 8.0 Hz, 1 H), 6.93–6.90 (m, 1 H), 6.54 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.5, 149.5, 144.1, 138.5, 136.3, 131.6, 128.8, 128.50, 128.47, 128.2, 127.4, 123.4, 123.0, 120.1, 115.1, 99.1, 87.5.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{16}NS$: 314.1003; found: 314.1007.

(3*Z*)-2-Methyl-6-phenyl-3-(pyridin-2-ylsulfanyl)hex-3-en-5-yn-2-ol (5o)

Yellow solid; yield: 107.8 mg (73%); mp 107–109 °C.

FTIR (KBr): 3394 (s), 2927 (s), 2196 (w), 1570 (w), 1421 (m), 1208 (m), 1130 (w), 768 (m), 750 (m), 683 cm^{-1} (w).

^1H NMR (400 MHz, $CDCl_3$): δ = 8.36 (d, *J* = 4.8 Hz, 1 H), 7.51 (dt, *J* = 1.4, 7.6 Hz, 1 H), 7.36 (d, *J* = 8.1 Hz, 1 H), 7.25 (br s, 5 H), 7.02–6.99 (m, 1 H), 6.65 (s, 1 H), 5.10 (br s, 1 H), 1.55 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.4, 150.8, 149.2, 136.7, 131.5, 128.5, 128.1, 122.8, 122.6, 120.2, 117.7, 98.4, 86.3, 73.4, 29.1.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{17}NOSNa$: 318.0929; found: 318.0916.

[(1*Z*)-4-Phenyl-1-(phenylselanyl)but-1-en-3-ynyl]benzene (5q)[3g]

Pale yellow solid; yield: 120.3 mg (67%); mp 68–69 °C.

FTIR (KBr): 3344 (s), 1577 (s), 1482 (m), 1460 (m), 1055 (m), 1021 (s), 622 cm^{-1} (s).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.05 (m, 15 H), 6.40 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.1, 139.3, 133.0, 131.4, 129.9, 128.7, 128.3, 128.2, 128.0, 126.9, 123.2, 112.6, 97.6, 88.3.

(3*Z*)-2,7-Dimethyl-3-(phenylselanyl)oct-3-en-5-yne-2,7-diol (5r)[3g]

Pale yellow solid; yield: 116.4 mg (72%); mp 104–106 °C.

FTIR (neat): 3367 (s), 2980 (m), 1577 (w), 1438 (w), 1362 (m), 1209 (m), 1164 (s), 947 (m), 735 cm^{-1} (m).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 7.3 Hz, 2 H), 7.27–7.18 (m, 3 H), 6.51 (s, 1 H), 2.39 (br s, 1 H), 1.79 (br s, 1 H), 1.50 (s, 6 H), 1.27 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.3, 131.9, 130.4, 129.0, 126.3, 114.4, 102.4, 80.1, 74.8, 65.3, 30.7, 29.1.

(2*Z*)-2-(Phenylselanyl)hex-2-en-4-yne-1,6-diol (5s)

White solid; yield: 100.2 mg (75%); mp 113–115 °C.

FTIR (KBr): 3338 (s), 3263 (s), 2917 (w), 2211 (w), 1587 (w), 1410 (m), 1334 (m), 1085 (m), 1012 (s), 999 (s), 745 cm^{-1} (s).

^1H NMR (400 MHz, CD_3COCD_3): δ = 7.62–6.30 (m, 6 H), 4.37–4.33 (m, 3 H), 4.24 (t, *J* = 6.1 Hz, 1 H), 4.02 (d, *J* = 6.0 Hz, 2 H).

^{13}C NMR (100 MHz, CD_3COCD_3): δ = 146.8, 135.3, 129.5, 128.5, 108.0, 96.0, 81.4, 65.1, 50.5.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_{12}O_2SeNa$: 290.9901; found: 290.9903.

(3*Z*)-2-Methyl-6-phenyl-3-(phenylselanyl)hex-3-en-5-yn-2-ol (5u)

Pale yellow oily liquid; yield: 116.0 mg (68%).

FTIR (neat): 3394 (s), 2976 (s), 2199 (w), 1577 (w), 1476 (w), 1362 (m), 1211 (m), 1174 (s), 828 (m), 756 (s), 735 (s), 689 cm^{-1} (s).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.11 (m, 10 H), 6.71 (s, 1 H), 2.39 (br s, 1 H), 1.51 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.4, 131.4, 131.2, 131.0, 129.0, 128.2, 128.0, 126.5, 122.9, 115.4, 97.2, 87.5, 75.0, 29.3.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{18}OSeNa$: 365.0421; found: 365.0422.

(2*Z*)-2-(Phenylselanyl)undec-2-en-4-yn-1-ol (5v)

Yellow liquid; yield: 99.6 mg (62%).

FTIR (neat): 3370 (s), 2954 (m), 2930 (s), 2858 (m), 2215 (w), 1088 (w), 1009 (w), 740 cm^{-1} (m).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 7.5 Hz, 2 H), 7.33–7.26 (m, 3 H), 6.15 (s, 1 H), 4.05 (d, *J* = 4.4 Hz, 2 H), 2.37 (t, *J* = 6.9 Hz, 2 H), 1.68–1.26 (m, 9 H), 0.89 (t, *J* = 6.9 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.3, 135.2, 129.2, 128.3, 126.9, 111.0, 98.7, 77.7, 65.8, 31.3, 28.6, 28.5, 22.5, 19.7, 14.0.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{22}OSeNa$: 345.0734; found: 345.0730.

[(3*Z*)-4-(Phenylselanyl)dec-3-en-1-ynyl]benzene (5w)

Yellow liquid; yield: 77.1 mg (42%).

FTIR (neat): 3424 (m), 2955 (m), 2928 (s), 2855 (m), 1579 (m), 1439 (m), 1022 (w), 755 (s), 740 (m), 690 cm^{-1} (m).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.63–7.28 (m, 10 H), 6.00 (s, 1 H), 2.19 (t, *J* = 7.4 Hz, 2 H), 1.42–1.12 (m, 8 H), 0.83 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.9, 135.8, 131.3, 129.0, 128.19, 128.17, 128.0, 127.9, 123.5, 107.9, 95.4, 87.3, 37.4, 31.4, 28.9, 28.3, 22.4, 14.0.

^{77}Se NMR (100 MHz, $CDCl_3$): δ = 428.3.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{24}SeNa$: 391.0941; found: 391.0939.

Compounds 6a–i; General Procedure

To a well stirred solution of 1,4-diorganylbuta-1,3-diyne (0.5 mmol, 1 equiv) in DMF–H_2O (20:1; 4 mL), dichalcogenide (0.5 mmol, 1 equiv) was added followed by the addition of rongalite (2.5 mmol, 5 equiv) and K_2CO_3 (1.5 mmol, 3 equiv). The mixture was stirred at 70 °C for the time indicated in Table 4. Then the mixture was allowed to attain r.t. and water was added followed by extraction with EtOAc (2 × 20 mL). The organic layer was separated, then washed with brine, extracted with EtOAc (2 × 5 mL), and dried (anhyd Na_2SO_4). The solvent was evaporated under vacuum and the crude product was purified by column chromatography (silica gel, 230–400 mesh, EtOAc–petroleum ether).

[(1*Z*,3*Z*)-4-Phenyl-1,4-bis(phenylsulfanyl)buta-1,3-dienyl]benzene (6a)[2b]

Yellow solid; yield: 107.1 mg (51%); mp 194–196 °C.

FTIR (KBr): 3051 (m), 1579 (m), 1478 (m), 1439 (w), 1075 (w), 1024 (w), 892 (m), 764 (s), 736 (s), 700 (s), 688 cm^{-1} (s).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.75 (s, 2 H), 7.63 (d, *J* = 7.5 Hz, 4 H), 7.26–7.04 (m, 16 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.6, 138.1, 135.6, 133.4, 128.8, 128.7, 128.3 (overlapped 2 signals), 127.9, 125.8.

(3*Z*,5*Z*)-2,7-Dimethyl-3,6-bis(phenylsulfanyl)octa-3,5-diene-2,7-diol (6b)

White solid; yield: 158.3 mg (82%); mp 152–153 °C.

FTIR (KBr): 3300 (s), 2970 (m), 1581 (m), 1478 (m), 1440 (m), 1358 (m), 1171 (m), 1133 (m), 838 (s), 739 (s), 688 cm^{-1} (m).

^1H NMR (400 MHz, CD_3COCD_3): δ = 7.42 (s, 2 H), 7.32 (t, *J* = 7.7 Hz, 4 H), 7.21–7.15 (m, 6 H), 3.93 (br s, 2 H), 1.27 (s, 12 H).

^{13}C NMR (100 MHz, CD_3COCD_3): δ = 146.8, 138.8, 132.3, 129.7, 128.3, 126.3, 74.9, 29.7.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{26}O_2S_2Na$: 409.1272; found: 409.1273.

(2*Z*,4*Z*)-2,5-Bis(phenylsulfanyl)hexa-2,4-diene-1,6-diol (6c)

White solid; yield: 140.4 mg (85%); mp 133–135 °C.

FTIR (KBr): 3253 (s), 3158 (m), 2899 (w), 1582 (m), 1478 (m), 1440 (m), 1070 (s), 978 (m), 893 (m), 736 (s), 688 cm^{-1} (m).

^1H NMR (400 MHz, CD_3COCD_3): δ = 7.61 (s, 2 H), 7.34–7.23 (m, 10 H), 4.47 (t, *J* = 5.9 Hz, 2 H), 4.15 (d, *J* = 5.9 Hz, 4 H).

^{13}C NMR (100 MHz, CD_3COCD_3): δ = 138.6, 135.3, 130.3, 130.0, 129.9, 127.4, 65.4.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{18}O_2S_2Na$: 353.0646; found: 353.0645.

(3*Z*,5*Z*)-2-Methyl-6-phenyl-3,6-bis(phenylsulfanyl)hexa-3,5-dien-2-ol (6d)

Gummy mass; yield: 107.2 mg (53%).

FTIR (neat): 3413 (br), 1653 (br), 1219 (w), 1018 (m), 772 cm^{-1} (s).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 10.4 Hz, 1 H), 7.41–7.04 (m, 16 H), 2.22 (br s, 1 H), 1.47 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.8, 139.6, 139.4, 137.1, 135.7, 133.0, 132.3, 129.1, 128.9, 128.8, 128.5, 128.3, 128.0, 127.2, 126.0, 125.7, 75.1, 29.4.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{25}H_{24}OS_2Na$: 427.1166; found: 427.1170.

(2*Z*,4*Z*)-2,5-Bis[(4-methylphenyl)sulfanyl]hexa-2,4-diene-1,6-diol (6e)

White solid; yield: 154.2 mg (86%); mp 147–149 °C.

FTIR (KBr): 3247 (br), 2920 (m), 1492 (m), 1074 (s), 1029 (s), 879 (m), 808 cm^{-1} (s).

^{1}H NMR (400 MHz, CD_3COCD_3): δ = 7.53 (s, 2 H), 7.24 (d, *J* = 8.0 Hz, 4 H), 7.16 (d, *J* = 8.0 Hz, 4 H), 4.35 (t, *J* = 6.0 Hz, 2 H), 4.11 (d, *J* = 5.9 Hz, 4 H), 2.31 (s, 6 H).

^{13}C NMR (100 MHz, CD_3COCD_3): δ = 139.0, 137.7, 131.4, 131.1, 130.7, 128.8, 65.3, 21.0.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{22}O_2S_2Na$: 381.0959; found: 381.0959.

(3*Z*,5*Z*)-3,6-Bis[(4-chlorophenyl)sulfanyl]-2,7-dimethylocta-3,5-diene-2,7-diol (6f)

White solid; yield: 173.1 mg (76%); mp 134–136 °C.

FTIR (KBr): 3314 (br), 2971 (m), 2929 (w), 1475 (m), 1358 (w), 1172 (m), 1093 (m), 1012 (w), 836 (m), 817 cm^{-1} (m).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22 (d, *J* = 8.4 Hz, 4 H), 7.17 (s, 2 H), 7.10 (d, *J* = 8.4 Hz, 4 H), 2.04 (br s, 2 H), 1.32 (s, 12 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.6, 135.6, 131.7, 131.2, 129.1, 128.9, 74.5, 29.0.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{24}Cl_2O_2S_2Na$: 477.0492; found: 477.0491.

[(1*Z*,3*Z*)-4-Phenyl-1,4-bis(phenylselanyl)buta-1,3-dienyl]benzene (6g)

Pale yellow solid; yield: 69.8 mg (27%); mp 182–184 °C.

FTIR (KBr): 3446 (br), 2922 (w), 2852 (w), 1646 (w), 1436 (m), 1250 (w), 1021 (w), 873 (m), 762 (s), 738 (s), 688 cm^{-1} (s).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (s, 2 H), 7.56 (d, *J* = 7.7 Hz, 4 H), 7.30–7.11 (m, 16 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.1, 138.3, 135.6, 131.2, 131.1, 129.0, 128.4, 128.21, 128.16, 126.4.

Anal. Calcd for $C_{28}H_{22}Se_2$: C, 65.12; H, 4.29. Found: C, 65.29; H, 4.41.

(3*Z*,5*Z*)-2,7-Dimethyl-3,6-bis(phenylselanyl)octa-3,5-diene-2,7-diol (6h)

Pale yellow solid; yield: 89.3 mg (37%); mp 147–149 °C.

FTIR (KBr): 3298 (s), 2970 (s), 1676 (m), 1576 (m), 1476 (m), 1358 (m), 1133 (m), 888 (m), 824 (m), 733 (s), 688 cm^{-1} (m).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.19 (m, 10 H), 7.02 (s, 2 H), 3.03 (br s, 2 H), 1.29 (s, 12 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.6, 136.6, 131.8, 130.5, 129.1, 126.4, 74.6, 29.1.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{26}O_2Se_2Na$: 505.0161; found: 505.0163.

(2*Z*,4*Z*)-2,5-Bis(phenylselanyl)hexa-2,4-diene-1,6-diol (6i)

Pale yellow solid; yield: 92.4 mg (44%); mp 118–119 °C.

FTIR (KBr): 3266 (m), 2896 (w), 2847 (w), 1576 (m), 1474 (w), 1232 (w), 1060 (s), 1021 (m), 886 (m), 730 (s), 687 cm^{-1} (m).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.45 (m, 4 H), 7.31 (s, 2 H), 7.28–7.26 (m, 6 H), 4.19 (s, 4 H), 1.88 (br s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.2, 132.7, 131.6, 129.4, 128.8, 127.5, 67.1.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{18}O_2Se_2Na$: 448.9535; found: 448.9531.

Hydrochalcogenation of (*Z*)-(Chalcogeno)enynes; General Procedure

To a stirred solution of (*Z*)-(chalcogeno)enyne (0.5 mmol, 1 equiv), dichalcogenide (0.25 mmol, 0.5 equiv) in DMF–H_2O (20:1; 4 mL), rongalite (1.5 mmol, 3 equiv), and K_2CO_3 (1 mmol, 2 equiv) were added and the mixture was stirred at 70 °C for the time indicated in Table 5. Then the mixture was allowed to attain r.t. and water was added followed by extraction with EtOAc (2 × 20 mL). The organic layer was separated, then washed with brine, extracted with EtOAc (2 × 5 mL), and dried (anhyd Na_2SO_4). The solvent was evaporated under vacuum and the crude product was purified by column chromatography (silica gel, 230–400 mesh, EtOAc–petroleum ether).

(2*Z*,4*Z*)-2-[(4-Chlorophenyl)sulfanyl]-5-(phenylsulfanyl)hexa-2,4-diene-1,6-diol (6j)

White solid; yield: 146.0 mg (80%); mp 138–140 °C.

FTIR (KBr): 3449 (br), 1648 (m), 1090 (w), 1068 (m), 1010 cm^{-1} (w).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.49–7.24 (m, 11 H), 5.44–5.39 (m, 2 H), 3.99–3.96 (m, 4 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 138.6, 137.2, 134.2, 133.7, 131.7, 130.9, 129.8, 129.69, 129.66, 129.6, 128.5, 127.2, 64.2, 64.1.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{17}ClO_2S_2Na$: 387.0256; found: 387.0256.

(2*Z*,4*Z*)-2-[(4-Chlorophenyl)sulfanyl]-5-[4-(methylphenyl)sulfanyl]hexa-2,4-diene-1,6-diol (6k)

White solid; yield: 155.4 mg (82%); mp 162–164 °C.

FTIR (KBr): 3455 (br), 1640 (w), 1086 (m), 1030 (m), 882 cm^{-1} (w).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.16 (m, 10 H), 5.43 (t, *J* = 5.8 Hz, 1 H), 5.34 (t, *J* = 5.8 Hz, 1 H), 3.98 (d, *J* = 5.5 Hz, 2 H), 3.92 (d, *J* = 5.3 Hz, 2 H), 2.28 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.5, 137.1, 136.6, 133.8, 131.6, 130.7, 130.5, 130.4, 130.0, 129.8, 129.7, 127.1, 64.3, 63.9, 21.0.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{19}ClO_2S_2Na$: 401.0413; found: 401.0415.

(3*Z*,5*Z*)-2,7-Dimethyl-3-(phenylselanyl)-6-(phenylsulfanyl)octa-3,5-diene-2,7-diol (6l)

White solid; yield: 112.7 mg (52%); mp 155–157 °C.

FTIR (KBr): 3307 (br), 2970 (s), 1578 (w), 1476 (m), 1358 (m), 1168 (m), 1133 (m), 888 (m), 833 (m), 735 (s), 688 cm^{-1} (m).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 7.8 Hz, 2 H), 7.27–7.02 (m, 10 H), 2.13 (br s, 1 H), 2.04 (br s, 1 H), 1.31 (s, 6 H), 1.27 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.4, 145.7, 137.1, 132.6, 132.5, 130.7, 129.8, 129.1, 128.9, 127.7, 126.5, 125.7, 74.6, 74.4, 29.1, 28.9.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{26}O_2SSeNa$: 457.0717; found: 457.0737.

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Supporting Information

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