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Silver-Mediated [2 + 2 + 1] Cyclization Reaction of Diynes with Elemental Selenium/Sulfur To Synthesize 3,4-Substituted Cyclopenta[*c*]selenophenes/Cyclopenta[*c*]thiophenes

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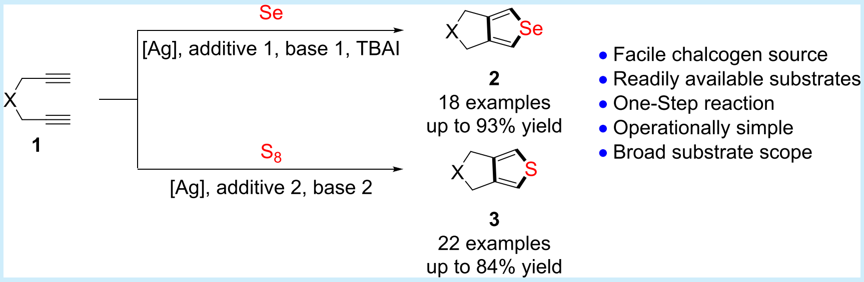

ABSTRACT: An efficient and atom-economical silver-mediated [2 + 2 + 1] cyclization protocol for the synthesis of 3,4-fused-ring-substituted and 2,5-unsubstituted selenophenes or thiophenes has been developed. Two C−Se/C−S bonds and one C−C bond were rapidly constructed in one step. Readily accessible substrates, commercially available elemental selenium/sulfur, and good functional group tolerance make this procedure attractive for the synthesis of π-conjugated material molecules.

3,4-Fused-ring-substituted thiophene and selenophene derivatives with unsubstituted 2,5-positions have received great attention owing to their wide applicability as precursors of conductive polymers (Figure 1).[1] Some of these polymers such as PEDOT and PEDOS have numerous advantages compared with other conducting polymers, and hold promise for diverse applications in several fields such as solar cells, organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and electrochromic devices.[2] However, the synthesis of such polythiophene and polyselenophene monomers is often difficult, and most of the known methods adopt multistep reactions, resulting in poor efficiency.[3] From the perspective view of organic synthesis, the [2 + 2 + 1] reaction of diynes with sulfur or selenium source to construct 3,4-fused-ring-substituted thiophenes or selenophenes is undoubtedly a straightforward and efficient method. Although there have been a few reports on this strategy, some limitations still exist. The classic Fagan−Nugent reaction can be used for the preparation of both thiophenes and selenophenes, but the functional-group compatibility is limited due to the highly reducing character of “Cp_2Zr”. At the same time, bis(silyl)-diynes were applied as substrates and further desiliconization is required (Scheme 1a).[4] Yamamoto and co-workers reported a luxurious Ruthenium catalyzed [2 + 2 + 1] cycloaddition of bis(silyl)diyne with a special sulfur donor, only one case of 3,4-fused-ring-substituted thiophene in moderate yield was obtained (Scheme 1b).[5] Recently, a one-step intramolecular radical cascade reaction of diynes with thioacetic acid in the presence of AIBN to synthesize thiophenes was realized by Zade’s group. However, it failed to be applied to the synthesis of selenophenes (Scheme 1c).[6] In this context, efficient and general protocols for accessing such compounds, especially selenophenes, which are more difficult to synthesize, are highly desirable. It is well-known, elemental sulfur or selenium widely exists in nature with low toxicity, stable properties under ambient conditions, and no unpleasant odor.[7] Thus, the development of an efficient and easy-to-operate [2 + 2 + 1] approach to efficiently construct 3,4-fused-ring-substituted thiophenes and selenophenes using diynes and elemental sulfur/selenium would be very attractive. Herein, we report a

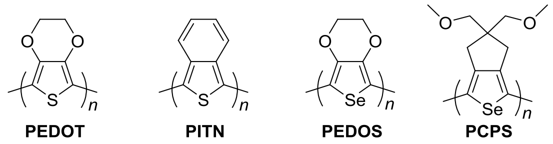

Figure 1. Representative 3,4-fused ring substituted polythiophenes and polyselenophenes.

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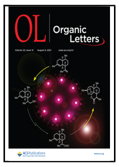

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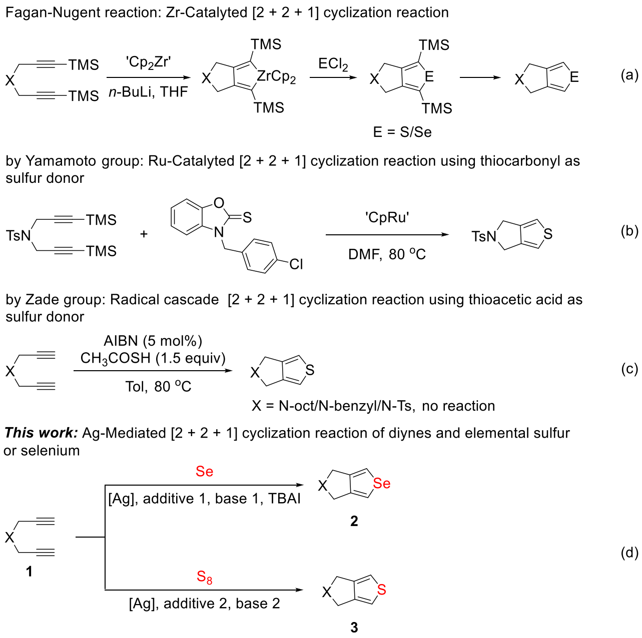
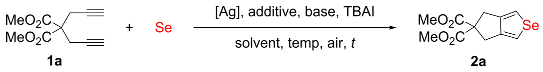
Scheme 1. [2 + 2 + 1] Approaches to Synthesize Cyclopenta[*c*]thiophene or Cyclopenta[*c*]selenophene



novel and atom-economical silver-mediated [2 + 2 + 1] cyclization reaction of readily available diynes with elemental selenium/sulfur to synthesize valuable 3,4-substituted cyclopenta[*c*]selenophenes/cyclopenta[*c*]thiophenes.

We initially conducted the investigation using dimethyl 2,2-di(prop-2-yn-1-yl)malonate **1a** with elemental selenium (3.0 equiv) in the presence of 2.0 equiv of AgOAc, 4.0 equiv of K_2CO_3, 10 mol % $Co(OAc)_2{\cdot}4H_2O$, and 1.5 equiv of TBAI at 60 °C in DCM. The results are depicted in Table 1. To our delight, cyclopenta[*c*]selenophene **2a** could be formed in 62% yield within 12 h (Table 1, entry 1). The structure of **2a** was confirmed by X-ray crystallography (CCDC 2089010). Interestingly, increasing the reaction temperature to 80 °C afforded **2a** in a higher yield of 82% (Table 1, entry 3). Next, we investigated the silver salts. Both Ag_2CO_3 and Ag_2O significantly reduced the reaction yield (Table 1, entries 4 and 5). Then, other bases, such as Na_2CO_3 and Cs_2CO_3 were tested. No better results were acheieved (Table 1, entries 6 and 7). Subsequently, different additives including $Co(OAc)_2$, $CoBr_2$, CoI_2, $Cu(OAc)_2$, $CuBr_2$, and $CuCl_2$ were screened, leading to product **2a** in 52–72% yields (Table 1, entries 8–13). The solvent effects on the reaction course were also examined. The reaction could also be performed in toluene or 1,4-dioxane, and **2a** was formed in lower yields of 46–51% (Table 1, entries 16 and 17). However, the yield of **2a** was dramatically decreased to 27% when DCE was employed (Table 1, entry 14). The reaction was hindered in a polar solvent like DMF (Table 1, entry 15). The amount of AgOAc was further investigated. When the amount of AgOAc was decreased to 1.0 equiv, **2a** was remarkable decreased to 44%

Table 1. Optimization Studies for the Synthesis of 2a[a]



entry	[Ag] (equiv)	base	additive	solvent	temp (°C)	*t* (h)	yield (%)
1	AgOAc (2)	K_2CO_3	$Co(OAc)_2{\cdot}4H_2O$	DCM	60	12	62
2	AgOAc (2)	K_2CO_3	$Co(OAc)_2{\cdot}4H_2O$	DCM	70	10	63
3	**AgOAc (2)**	**K_2CO_3**	**$Co(OAc)_2{\cdot}4H_2O$**	**DCM**	**80**	**10**	**82**
4	Ag_2CO_3 (2)	K_2CO_3	$Co(OAc)_2{\cdot}4H_2O$	DCM	80	10	48
5	Ag_2O (2)	K_2CO_3	$Co(OAc)_2{\cdot}4H_2O$	DCM	80	10	53
6	AgOAc (2)	Na_2CO_3	$Co(OAc)_2{\cdot}4H_2O$	DCM	80	10	28
7	AgOAc (2)	Cs_2CO_3	$Co(OAc)_2{\cdot}4H_2O$	DCM	80	10	39
8	AgOAc (2)	K_2CO_3	$Co(OAc)_2$	DCM	80	10	72
9	AgOAc (2)	K_2CO_3	$CoBr_2$	DCM	80	10	68
10	AgOAc (2)	K_2CO_3	CoI_2	DCM	80	10	68
11	AgOAc (2)	K_2CO_3	$Cu(OAc)_2$	DCM	80	10	52
12	AgOAc (2)	K_2CO_3	$CuBr_2$	DCM	80	10	55
13	AgOAc (2)	K_2CO_3	$CuCl_2$	DCM	80	10	55
14	AgOAc (2)	K_2CO_3	$Co(OAc)_2{\cdot}4H_2O$	DCE	80	10	27
15	AgOAc (2)	K_2CO_3	$Co(OAc)_2{\cdot}4H_2O$	DMF	80	10	trace
16	AgOAc (2)	K_2CO_3	$Co(OAc)_2{\cdot}4H_2O$	tol	80	10	46
17	AgOAc (2)	K_2CO_3	$Co(OAc)_2{\cdot}4H_2O$	1.4-dioxane	80	10	51
18	AgOAc (1)	K_2CO_3	$Co(OAc)_2{\cdot}4H_2O$	DCM	80	10	44
19	AgOAc (3)	K_2CO_3	$Co(OAc)_2{\cdot}4H_2O$	DCM	80	6	70
20[b]	AgOAc (2)	K_2CO_3	$Co(OAc)_2{\cdot}4H_2O$	DCM	80	10	64
21[c]	AgOAc (2)	K_2CO_3	$Co(OAc)_2{\cdot}4H_2O$	DCM	80	10	56
22[d]	AgOAc (2)	K_2CO_3	$Co(OAc)_2{\cdot}4H_2O$	DCM	80	10	61
23[e]	AgOAc (2)	K_2CO_3	$Co(OAc)_2{\cdot}4H_2O$	DCM	80	10	trace
24	–	K_2CO_3	$Co(OAc)_2{\cdot}4H_2O$	DCM	80	10	0
25	AgOAc (2)	–	$Co(OAc)_2{\cdot}4H_2O$	DCM	80	10	trace
26	AgOAc (2)	K_2CO_3	–	DCM	80	10	63

[a] Reaction conditions: **1a** (0.2 mmol), Se (0.6 mmol), [Ag] (0.4 mmol), base (0.8 mmol), additive (10 mol %), TBAI (0.3 mmol), solvent (2.0 mL), air, isolated yields. [b] K_2CO_3 (0.6 mmol). [c] Se (0.4 mmol). [d] Se (0.8 mmol). [e] Without TBAI.

yield (Table 1, entry 18). A slight erosion of the yield was gained when using 3.0 equiv of AgOAc (Table 1, entry 19). Decreasing the amount of K_2CO_3 to 3.0 equiv resulted in a lower product yield (Table 1, entry 20). Changing the amount of Se to 2.0 or 4.0 equiv did not produce better results (Table 1, entries 21 and 22). In addition, only a trace amount of **2a** was observed when the reaction was carried out without TBAI (Table 1, entry 23). TBAI may act as a phase transfer catalyst, increasing the dissolution of selenium and K_2CO_3 in the nonpolar solvent DCM. In the absence of silver salt or base, no product was obtained (Table 1, entries 24 and 25). Removal of the additive led to a 63% yield (Table 1, entry 26).

Encouraged by the above results, we investigated the substrate range of the cyclization reaction. As shown in Figure 2, a variety of diynes **1** were tested, and the corresponding cyclopenta[*c*]selenophene products **2a**−**2r** were smoothly synthesized in 39−93% yields. Notably, various functional groups, including ester, nitrile, ketone, amide, sulfone, and silyl ether, were well tolerated under the reaction conditions.

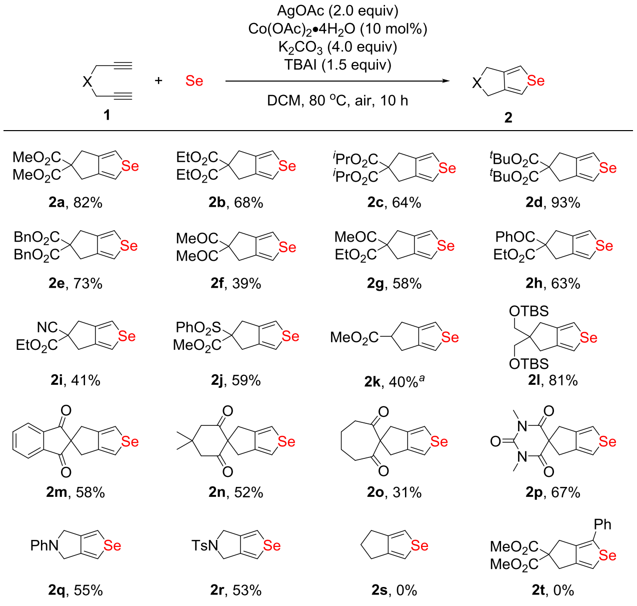
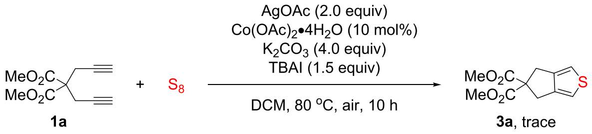


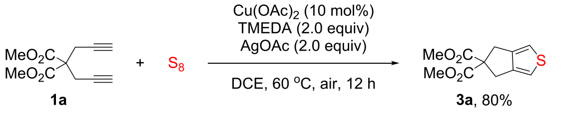
Figure 2. Substrate scope of diynes **1** to synthesize cyclopenta[*c*]selenophenes **2**. Reaction conditions: **1** (0.2 mmol), Se (0.6 mmol), AgOAc (0.4 mmol), K_2CO_3 (0.8 mmol), $Co(OAc)_2{\cdot}4H_2O$ (0.02 mmol), TBAI (0.3 mmol), DCM (2.0 mL), air, isolated yields. ^{a}60 °C.

However, when 1,6-heptadiyne was used, we did not observe the formation of corresponding product **2s**. In further investigations of the applicability, we found that diyne with a phenyl substituent at one triple bond failed to give the desired products **2t** under standard conditions, and the staring material was recovered. It indicates that terminal diacetylenes are indispensable to the formation of cyclopenta[*c*]selenophenes.

Subsequently, we tried to apply this method to the cyclization reaction of diyne **1a** with elemental sulfur to synthesize cyclopenta[*c*]thiophene. Unfortunately, only a trace amount of **3a** was detected (eq 1). In order to improve the yield of **3a**, different reaction parameters, such as temperature, silver salts, bases, additives, and solvents, were screened (see Supporting Information, Table S1). It was found that the best result for the preparation of **3a** was to use 1.0 equiv of S_8, 10 mol % $Cu(OAc)_2$, 2.0 equiv of AgOAc, and 2.0 equiv of TMEDA, at 60 °C in DCE for 12 h, providing the desired **3a** in 80% yield (eq 2).



(1)



(2)

With the optimized reaction conditions in hand, the substrate scope of diynes **1** for the synthesis of cyclopenta[*c*]thiophenes **3** was examined (Figure 3). Various functionalized diynes could successfully react with elemental sulfur under standard conditions, offering the desired thiophene products in moderate to good yields (**3a**−**3v**). The functionalities such as ester, nitrile, ketone, amide, sulfone, and silyl ether, were all well compatible. Similarly, neither 1,6-heptadiyne nor diyne with a phenyl substituent at one triple bond could deliver the corresponding thiophene products by this method (**3w**, **3x**).

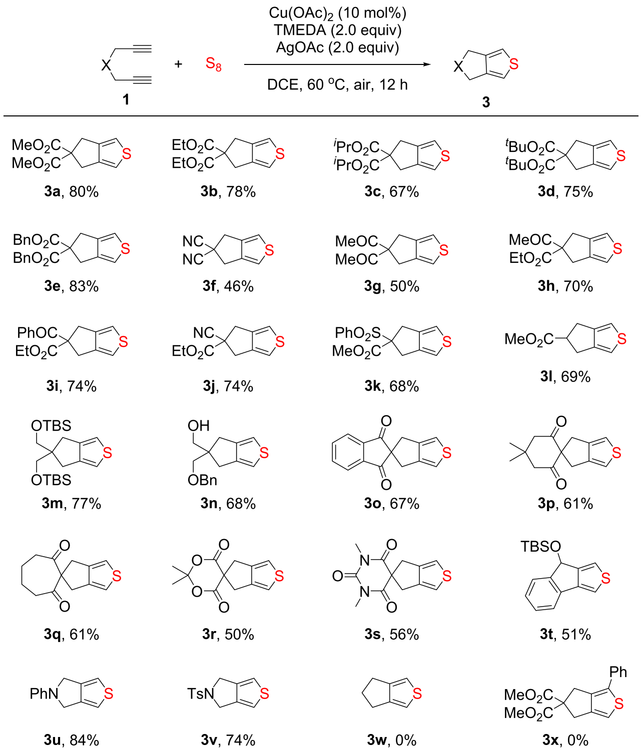
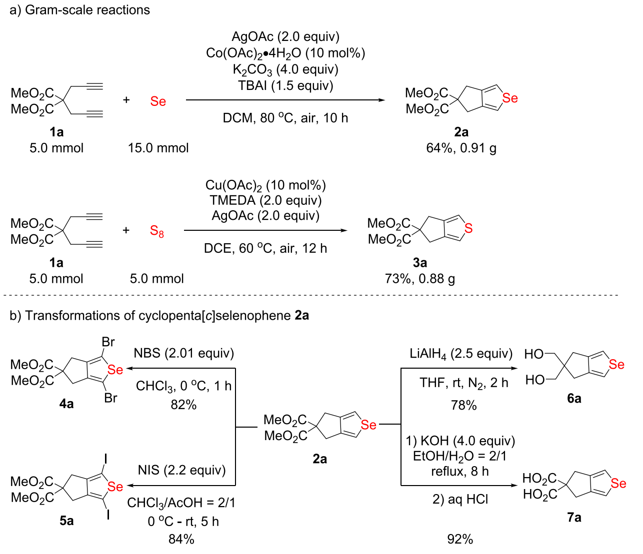


Figure 3. Substrate scope of diynes **1** to synthesis cyclopenta[*c*]thiophenes **3**. Reaction conditions: **1** (0.2 mmol), S_8 (0.2 mmol), AgOAc (0.4 mmol), TMEDA (0.4 mmol), $Cu(OAc)_2$ (0.02 mmol), DCE (2.0 mL), air, isolated yields.

We next investigated the potential synthetic utility of these synthetic strategies. First, gram-scale reactions were performed, and we obtained the corresponding products **2a** and **3a** in 64% and 73% yields, respectively (Scheme 2a). Then, further derivatization of cyclopenta[*c*]selenophene **2a** was carried out. For example, **2a** could react with NBS or NIS to give its 2,5-dibromo or diiodo product **4a** or **5a** in 82% and 84% yields, respectively.[2b] Besides, the ester groups of **2a** could be reduced to hydroxyl groups by lithium aluminum hydride, providing **6a**

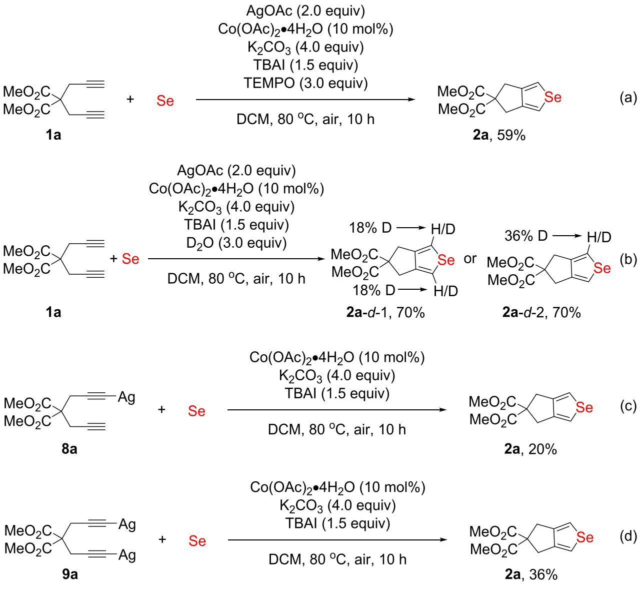
Scheme 2. Gram-Scale Reactions and Synthetic Transformations



in 78% yield.[8] Moreover, the ester groups could also be hydrolyzed to formic acid groups, furnishing **7a** in good yield of 92% (Scheme 2b).[9]

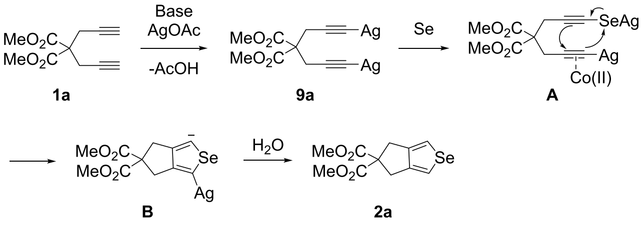
In order to clarify the reaction mechanism, several mechanistic experiments were performed (Scheme 3). First, we carried out the reaction of **1a** with elemental selenium under the optimized reaction conditions in the presence of radical scavenger TEMPO (3.0 equiv), and a 59% yield of **2a** was obtained as well (Scheme 3a). This indicated that a radical reaction pathway may not be involved in the reaction process. Next, when 4.0 equiv of D_2O were added to the reaction system, deuterium incorporation (18% or 36%) was observed at the 2,5-positions or 2-position of selenophene **2a**. This result showed that the cyclization reaction may be terminated by the hydrolysis at the 2-position of **2a** (Scheme 3b). When diynyl monosilver **8a** was used, the selenophene **2a** was obtained in 20% yield in the absence of AgOAc (Scheme 3c). However, the yield of **2a** increased to 36% when diynyl disilver **9a** was used (Scheme 3d). These results suggested that **9a** may be the intermediate of this reaction.

Scheme 3. Control Experiments



Based on the above experimental results and the previous reports,[10,11] a plausible reaction mechanism has been proposed in Scheme 4. Initially, in the presence of a base, **1a** reacts with AgOAc to obtain **9a**. Next, the selenium atom inserts into a carbon−silver bond of **9a** to generate intermediate **A**. Subsequently, intramolecular cyclization followed by protonation leads to the final product **2a**.

Scheme 4. Plausible Reaction Mechanism for the Formation of 2a



In summary, we have developed an efficient and atom-economical [2 + 2 + 1] cyclization protocol for the synthesis of diverse 3,4-substituted cyclopenta[*c*]selenophenes or cyclopenta[*c*]thiophenes starting from easily accessible diynes and elemental selenium/sulfur. Two C−Se/C−S bonds and one C−C bond were rapidly constructed in one step. It is noteworthy that the newly developed process is robust and operationally simple because neither an anhydrous solvent nor an inert atmosphere is necessary. This strategy provides an appealing choice for the synthesis of π-conjugated material molecules.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c02018.

Experimental details and spectroscopic characterization of all new compounds (PDF)

Accession Codes

CCDC 2089010 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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