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A Highly Efficient Method for the Copper-Catalyzed Selective Synthesis of Diaryl Chalcogenides from Easily Available Chalcogen Sources

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An efficient protocol for copper-catalyzed C–S or C–Se bond formation between aryl iodides and easily available chalcogen sources leading to diaryl chalcogenides is reported. A variety of symmetrical diaryl sulfides and diaryl selenides were synthesized in good to excellent yields. Unsymmetrical diaryl sulfides were also obtained in moderate yields from two different aryl iodides by a one-pot tandem process. This strategy was further successfully utilized for the synthesis of 2-phenylbenzo[*b*]thiophene and of [1]benzothieno[3,2-*b*]-benzothiophene.

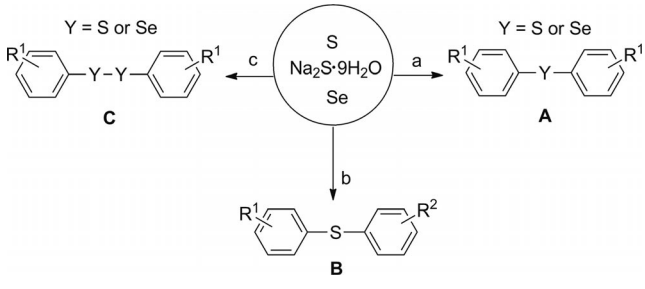
Introduction

Diaryl chalcogenides and their derivatives are important molecules frequently found in the biological and pharmaceutical fields.[1] Many compounds containing these systems are drugs with potential applications in the treatment of inflammation, cancer, human immunodeficiency virus (HIV), asthma, and Alzheimer's and Parkinson's diseases.[1g,2]

Traditional methods for the formation of carbon–chalcogen bonds, however, take place in toxic solvents such as HMPA and at high reaction temperatures.[3] To overcome these drawbacks, transition-metal-catalyzed cross-couplings of thiols with aryl halides have been explored.[1e,3a,4] Nickel,[5] palladium,[6] copper,[7,8] iron,[9] and cobalt catalysts[10] have recently emerged as appealing catalysts for this reaction, but these metal-catalyzed reactions require readily oxidizable, foul-smelling, expensive, and less available arene chalcogens.

The use of easily available chalcogen sources as coupling partners is of great interest as a means for the development of cost-efficient C–S and C–Se coupling procedures. Rabai's group employed Na_2S to synthesize diaryl sulfides from aryl iodides, although at relatively high temperatures (>150 °C).[11] Taniguchi further developed a well-designed system for the synthesis of mono- or dichalcogenides from aryl iodides in the presence of ligands and additives.[12] An elegant transformation for the preparation of benzothiazoles through intramolecular Cu-catalyzed thiolation and annulation with Na_2S as the sulfur source was reported by Ma's group.[13] The procedure was further extended to the formation of aryl thiols and aryl alkyl sulfide derivatives under ligand-free conditions.[14] Itoh and Mase developed palladium-catalyzed thiol cross-coupling reactions of aryl halides and thiol surrogates, such as 2-ethylhexyl 3-mercaptopropionate and 4-(2′-mercaptoethyl)pyridine hydrochloride.[6c,15] Hartwig further reported the use of a $Pd(OAc)_2$-CyPF-*t*Bu complex as a catalyst for the synthesis of unsymmetrical diaryl sulfides from TIPS-SH and two different aryl halides,[16] which is a striking improvement over the current methods. Nowadays, many more reagents are applied as chalcogen sources for the synthesis of diaryl chalcogenides; they include sulfur or selenium powder,[12] thiocyanates,[17] thioacetamide,[18] potassium ethyl xanthogenate,[19] potassium thioacetate,[20] thiourea,[21] selenoureas[22] and potassium selenocyanate.[23]

Only a few methods, however, have been used in the selective synthesis of symmetrical and unsymmetrical diaryl chalcogenides. As part of our ongoing efforts directed towards copper-catalyzed C–S or C–Se bond formation,[24] here we report a protocol for selective synthesis of diaryl chalcogenides from easily available chalcogen sources under ligand-free conditions (Scheme 1).



Scheme 1. Selective synthesis of diaryl chalcogenides and diaryl dichalcogenides.

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Results and Discussion

Initially, the ligand-free CuI-catalyzed *S*-arylation of iodobenzene with Na_2S was investigated. The highest yields (98%) were obtained in the polar solvent DMF (Table 1, Entry 4); moreover, with a reduction in the temperature to 100 °C, diphenyl disulfide (15% GC) was detected (Table 1, Entry 5). In view of the formation of Na_xS_y from Na_2S and S, we introduced S powder to the coupling reaction system to inhibit the formation of diphenyl sulfide.[25] Fortunately, this was the right choice, and diphenyl disulfide was obtained selectively in a yield of 96% (Table 1, Entry 9).

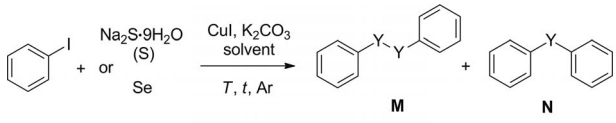
On the other hand, when we employed Se powder instead of Na_2S under the same conditions as for the synthesis of diphenyl sulfide (Table 1, Entry 4), only a 48% yield of diphenyl selenide was produced (Table 1, Entry 10), but with use of DMSO as a solvent, diphenyl selenide was obtained in 96% yield (Table 1, Entry 11). Finally, further control experiments were carried out: with the amount of Se powder increased from 1.2 to 3 equiv. and the temperature decreased to 90 °C, together with K_3PO_4 as base, diphenyl diselenide could be acquired selectively in 95% yield (Table 1, Entry 15).

To explore the scope of substrates for the synthesis of symmetrical diaryl chalcogenides, various aryl iodides were investigated under the optimized conditions (Table 2). This protocol efficiently coupled various aryl iodides with Na_2S or Se powder to produce the corresponding products in excellent yields (**1a**–**2j**), demonstrating tolerance both towards electron-donating groups (e.g., Me, NH_2, and OMe) and towards electron-withdrawing groups (e.g., Cl, Br, NO_2, CF_3). It was also noted that the heterocyclic compounds 4-iodopyridine and 2-iodothiophene could also afford the corresponding products in good yields (**1j**, **2i**, **2j**). In addition, steric hindrance seemed to have little effect on these reactions, with groups at different positions resulting in similar high activities (**1b** vs. **1c**, **1d** vs. **1e**, and **2d** vs. **2e**). It is obvious that iodobenzene is more reactive than bromobenzene and chlorobenzene. Consequently, aryl iodides with bromo or chloro substituents exhibited an interesting chemoselectivity, proceeding exclusively at the iodo group (Table 2, **1d**, **1e**, **2d**, and **2e**). In the case of an aryl iodide bearing a free amino group the reaction proceeded without the need to protect the group and the C–S rather than the C–N coupling product (**1f**) was obtained in 96% yield.

Because the synthesis of unsymmetrical diaryl sulfides is a challenge, we further focused our interest on this issue. Recently our group reported a ligand-free bimetallic catalyst (Cu_2S/Fe) for the synthesis of unsymmetrical diaryl sulfides from aryl halides and diaryl disulfides.[24c] The catalyst systems were further used for efficient Se-arylation of diaryl diselenides with aryl halides, in which the role of iron was clarified as not only the reduction of CuS to form the true catalyst Cu_2S, but also the generation of Fe_xO_y in situ as a barrier to catalyst agglomeration to accelerate the reaction.[24d] Encouraged by the results in Table 1, we considered the possibility of generating unsymmetrical diaryl sulfides by addition of a different aryl halide into the first-step reaction mixture in a one-pot process.

With this in mind, some experiments were performed (Table 3). It was observed that the GC yield of the unsymmetrical diaryl sulfide **3a** rose from 72% to 95% on an increase in the amount of 1-iodo-4-methoxybenzene from 1 equiv. to 1.6 equiv. At the same time, the symmetrical di-

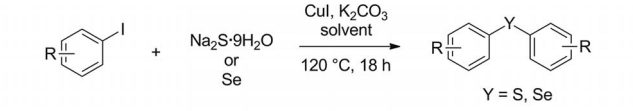
Table 1. Copper-catalyzed selective synthesis of diphenyl chalcogenides and/or diphenyl dichalcogenides.[a]

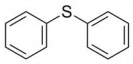
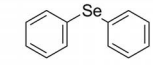
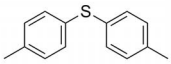
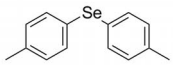
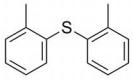
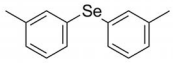
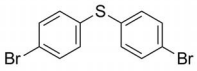
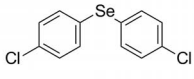
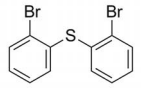
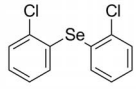
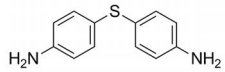
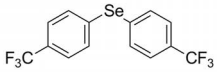
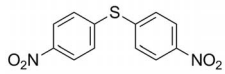
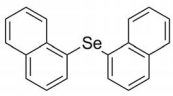
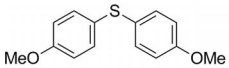
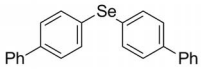
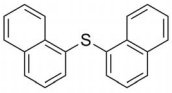
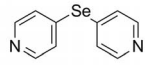
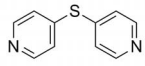
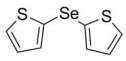


Entry	Chalcogen source [equiv.]	Solvent	*T* [°C]	M [%][b]	N [%][b]
1	Na_2S (0.6)	toluene	120	–	–
2	Na_2S (0.6)	EG	120	–	–
3	Na_2S (0.6)	DMSO	120	53	12
4	**Na_2S (0.6)**	**DMF**	**120**	**0**	**98 (94)**
5[c]	Na_2S (0.6)	DMF	100	15	61
6[c]	Na_2S (1.2)	DMF	100	43	57
7[c]	Na_2S (0.6) + S (0.6)	DMF	100	88	6
8[c,d]	Na_2S (0.8) + S (0.8)	DMF	100	97	2
9[c,d]	**Na_2S (1.0) + S (1.0)**	**DMF**	**100**	**96 (91)**	**0**
10	Se (0.6)	DMF	120	36	48
11	**Se (0.6)**	**DMSO**	**120**	**0**	**96 (94)**
12[e]	Se (1.2)	DMSO	120	66	26
13[e]	Se (1.2)	DMSO	100	77	10
14[e]	Se (3.0)	DMSO	90	89	5
15[f]	**Se (3.0)**	**DMSO**	**90**	**95 (90)**	**3**

[a] Reaction conditions: iodobenzene (1 mmol), $Na_2S{\cdot}9H_2O$ or Se (0.6 mmol), CuI (0.1 mmol), K_2CO_3 (1 mmol), and solvent (2 mL) stirred at 120 °C for 18 h under Ar. EG = ethylene glycol. [b] GC yields (isolated yields). [c] Without addition of K_2CO_3. [d] Reaction time: 15 h. [e] With 3 equiv. of K_2CO_3. [f] K_3PO_4 (3 equiv.) as the base.

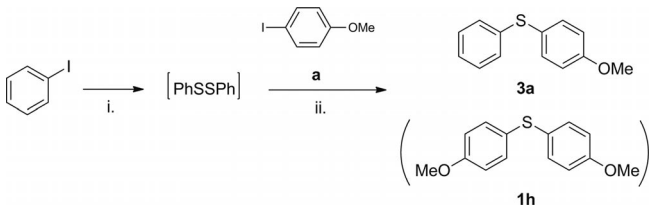
Table 2. Synthesis of symmetrical diaryl chalcogenides from aryl iodides and Na_2S or Se.[a]



Product	Yield [%][b]	Product	Yield [%][b]
	**1a**, 94		**2a**, 94
	**1b**, 91		**2b**, 88
	**1c**, 89		**2c**, 86
	**1d**, 94		**2d**, 91
	**1e**, 90		**2e**, 88
	**1f**, 96		**2f**, 89
	**1g**, 98		**2g**, 87
	**1h**, 81		**2h**, 87
	**1i**, 90		**2i**, 71
	**1j**, 86		**2j**, 73

[a] Reaction conditions: aryl iodide (1 mmol), $Na_2S·9H_2O$ (Se) (0.6 mmol), CuI (0.1 mmol), K_2CO_3 (1 mmol), and DMF (DMSO) (2 mL) stirred at 120 °C for 18 h under argon. [b] Isolated yields.

Table 3. Copper-catalyzed synthesis of the unsymmetrical diaryl sulfide **3a**.[a]



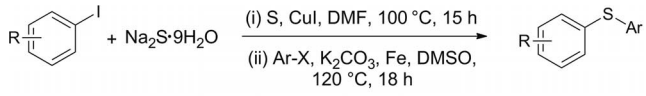
Entry	Equiv. of **a**	Yield [%] of **3a**[b]
1	1	72
2	1.2	86
3	1.5	90
4	1.6	95

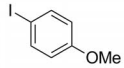
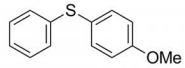
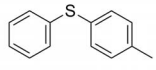
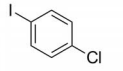
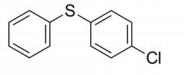
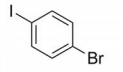
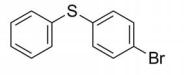
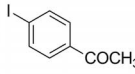
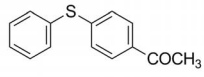
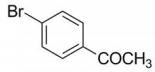
[a] Reaction conditions: i. iodobenzene (0.5 mmol), $Na_2S·9H_2O$ (1 equiv.), S (1 equiv.), CuI (0.1 equiv.), and DMF (1 mL) stirred at 100 °C for 15 h under argon. ii. 1-iodo-4-methoxybenzene, K_2CO_3 (1 mmol), Fe powder (0.3 mmol) and DMSO (2 mL) stirred at 120 °C for 18 h under argon. [b] GC yield determined was based on iodobenzene.

aryl sulfide formed from 1-iodo-4-methoxybenzene (Table 3, **1h**) was also observed, as would be expected because of the residue of excess sulfur source.

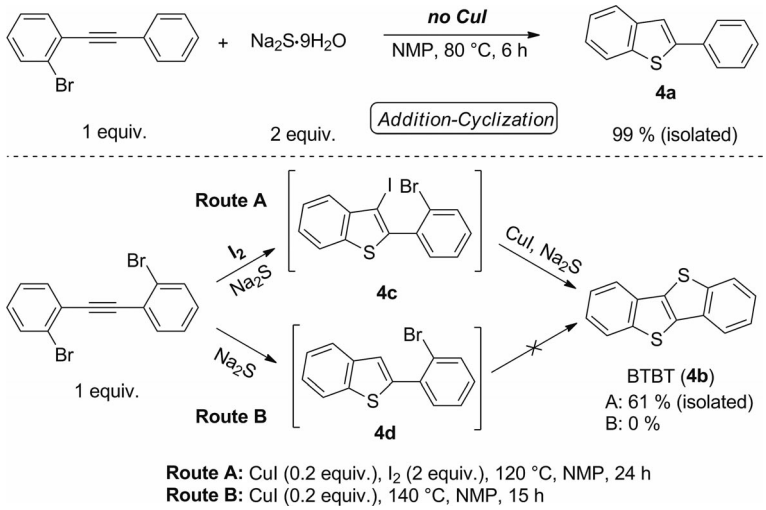
The scope of copper-catalyzed generation of disulfide in situ and its application in the one-pot synthesis of unsymmetrical diaryl sulfides were examined with several types of aryl halides. The outcome is summarized in Table 4. We observed that the electronic properties of different substituents on the aryl rings did not affect these coupling reaction to any great extent and that aryl halides bearing either elec-

Table 4. Synthesis of unsymmetrical diaryl sulfides from different aryl halides and Na_2S or S.[a]



Entry	Aryl iodide	Ar–X	Product	Yield [%][b]
1				**3a**, 75
2				**3b**, 80
3				**3c**, 79
4				**3d**, 78
5				**3e**, 60
6				**3e**, 64
7				**3f**, 78
8				**3f**, 80
9[c]				**3g**, 71
10[d]				**3h**, 79
11[d]				**3i**, 85
12[c]				**3j**, 78

[a] Reaction conditions: aryl iodide (0.5 mmol), $Na_2S·9H_2O$ (0.5 mmol), S powder (0.5 mmol), CuI (0.05 mmol), DMF (1 mL) stirred at 100 °C for 15 h under argon. Then Ar-X (0.8 mmol), K_2CO_3 (1 mmol), Fe powder (0.3 mmol), and DMSO (2 mL), stirred at 120 °C for another 18 h under argon. [b] Isolated yields. [c] The first-step coupling was performed at 80 °C. [d] The first-step coupling was performed at 110 °C.



Scheme 2. One-pot syntheses of a BT derivative and of BTBT with $Na_2S·9H_2O$ as sulfur source.

tron-withdrawing or electron-donating groups worked well. As well as aryl iodides, aryl bromides bearing electron-withdrawing groups were also utilized for the synthesis of unsymmetrical diaryl sulfides, generating high yields (Table 4, Entries 6 and 8). An important parameter in the synthesis of disulfides is the temperature. With aryl iodides bearing electron-withdrawing groups the reaction temperature needs to be lowered to 80 °C to inhibit the symmetrical diaryl sulfides (**3g** and **3j**). In contrast, in cases of electron-donating groups on the aryl iodides higher reaction temperatures (110 °C) are required to achieve complete conversion (**3h** and **3i**). These results demonstrate that a wide range of diaryl sulfides can be accessed from the readily available sulfur source by this methodology.

The production of unsymmetrical selenides by the tandem procedure (based on Table 1, Entry 15) was also attempted. In these reactions, quantities of symmetrical selenide and diselenide (byproducts) formed from the second aryl halides were observed, due to the residue of excess selenium source (3 equiv.) in the first step. These caused great difficulties for separation and purification. We attempted to make some changes to the catalyst systems, including reaction time, temperature, and the amounts of the reactants, but unfortunately did not achieve good results.

The successful development of this facile synthetic procedure for diaryl sulfides was further utilized in the synthesis of 2-phenylbenzo[*b*]thiophene (BT derivative, Scheme 2) and [1]benzothieno[3,2-*b*]benzothiophene (BTBT). Both are important structural components in the development of organic optoelectronic materials, including organic photovoltaics[26,27] and field-effect transistors.[28]

As depicted in Scheme 2, 1-bromo-2-(phenylethynyl)-benzene in combination with Na_2S and in the presence of CuI as catalyst was capable of giving 2-phenylbenzo[*b*]thiophene (**4a**) in 100% GC yield. Control experiments, however, indicated that the reaction could also provide a 99% isolated yield of **4a** even without CuI. This observation suggested that the reaction proceeded through the addition of Na_2S with the adjacent acetylene moiety followed by an intramolecular coupling. Unfortunately, on application of the same procedure for the synthesis of BTBT with 1,2-bis(2-bromophenyl)ethyne as a substrate no reaction was observed even with use of higher temperatures and longer times. Addition of elemental iodine, however, afforded a 61% isolated yield of BTBT (**4b**). Monitoring the reaction by HPLC, we observed that the reaction in the absence of elemental iodine stopped after the generation of the intermediate **4d**. In the presence of iodine the proposed intermediate **4c** was formed, and this could react further with Na_2S by intramolecular C–S coupling to afford the product BTBT (**4b**).

Conclusions

In conclusion, a new Cu-catalyzed one-pot approach for selective synthesis of symmetrical diaryl chalcogenides and unsymmetrical diaryl sulfides with Na_2S or Se as chalcogen sources has been developed. This strategy was successfully extended to syntheses of benzo[*b*]thiophene and [1]benzothieno[3,2-*b*]benzothiophene.

Experimental Section

General Information: All reagents were obtained from commercial sources (>99%) and used without further purification unless otherwise noted. Analytical thin layer chromatography (TLC) was carried out with silica gel GF 254 precoated plates. Visualization was accomplished with a UV lamp. All products were characterized by NMR spectroscopy. ^1H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were recorded at 100 MHz in $CDCl_3$ as solvent. Chemical shifts are reported in ppm with use of TMS as internal standard. Gas chromatography analyses were performed with an FID detector. Gas chromatography/mass spectra (GC/MS) were recorded with an HP 6890 GC/5973 MSD instrument. High-resolution mass spectrometric data (HRMS) were obtained with MALDI micro MX or GCT instruments.

General Procedure for the Synthesis of Symmetrical Products: A flame-dried test tube containing a magnetic stirring bar was

charged with CuI (19 mg, 0.1 mmol), K_2CO_3 (138 mg, 1 mmol), Na_2S (Se) (0.6 mmol), the aryl iodide (1.0 mmol), and DMF (DMSO) (2 mL) under argon. The mixture was heated at the indicated temperature for 18 h and allowed to cool to room temperature. The resulting mixture was extracted with ethyl acetate (3× 25 mL). The combined organic layers were dried with Na_2SO_4 and then concentrated under vacuum. The residue was purified by column chromatography on silica gel with an eluent consisting of petroleum ether and ethyl acetate. All the physical data for known compounds were consistent with those reported in the literature.

General Procedure for the Synthesis of Unsymmetrical Diaryl Sulfides: A flame-dried test tube containing a magnetic stirring bar was charged with CuI (9.5 mg, 0.05 mmol), Na_2S (120 mg, 0.5 mmol), S (16 mg, 0.5 mmol), the first aryl iodide (0.5 mmol), and DMF (1 mL) under argon. The mixture was heated at the indicated temperature for 15 h. The reaction mixture was allowed to cool to room temperature, and the second aryl halide (0.8 mmol), Fe (16.8 mg, 0.3 mmol), K_2CO_3 (138 mg, 1 mmol), and DMSO (2 mL) were added. The mixture was further heated under argon at 120 °C for 18 h and allowed to cool to room temperature. The resulting mixture was extracted with ethyl acetate (3× 25 mL). The combined organic layers were dried with Na_2SO_4 and then concentrated under vacuum. The residue was purified by column chromatography on silica gel with an eluent consisting of petroleum ether and ethyl acetate. All the physical data for the known compounds were consistent with those reported in the literature.

General Procedure for the Synthesis of 2-Phenylbenzo[*b*]thiophene: A flame-dried test tube containing a magnetic stirring bar was charged with Na_2S (96 mg, 0.4 mmol), 1-bromo-2-(phenylethynyl)-benzene (51.4 mg, 0.2 mmol), and NMP (1 mL) under argon. The mixture was heated at 80 °C for 6 h, allowed to cool to room temperature, and extracted with ethyl acetate (3× 25 mL). The combined organic layers were dried with Na_2SO_4 and then concentrated under vacuum. The residue was purified by column chromatography on silica gel with petroleum ether, giving a white solid in 99% yield (0.0416 g). All the physical data were consistent with those reported in the literature.

General Procedure for the Synthesis of [1]Benzothieno[3,2-*b*]benzothiophene (BTBT): A flame-dried test tube containing a magnetic stirring bar was charged with CuI (7.6 mg, 0.04 mmol), Na_2S (192 mg, 0.8 mmol), I_2 (101.6 mg, 0.4 mmol), 1,2-bis(2-bromophenyl)ethyne (67.2 mg, 0.2 mmol), and NMP (1 mL) under argon. The mixture was heated at 120 °C for 24 h, allowed to cool to room temperature, and extracted with ethyl acetate (3× 25 mL). The combined organic layers were dried with Na_2SO_4 and then concentrated under vacuum. The residue was purified by column chromatography on silica gel with petroleum ether to give a white solid in 61% yield (0.0293 g). All the physical data were consistent with those reported in the literature.

1,2-Diphenyldisulfane: The crude product obtained by the General Procedure was purified on a silica gel column with petroleum ether to give a white solid in 91% yield (0.099 g). CAS: 882-33-7. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, J = 7.6 Hz, 4 H, Ar-H), 7.31–7.20 (m, 6 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.2, 129.2, 127.7, 127.3 ppm. GC-MS (EI): m/z = 218 $[M]^+$.

1,2-Diphenyldiselane: The crude product obtained by the General Procedure was purified on a silica gel column with petroleum ether to give a yellow solid in 90% yield (0.140 g). CAS: 1666-13-3. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62–7.60 (m, 4 H, Ar-H), 7.26–7.22 (m, 6 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 131.7, 131.1, 129.4, 127.9 ppm. GC-MS (EI): m/z = 314 $[M]^+$.

Diphenylsulfane (1a): The crude product obtained by the General Procedure was purified on a silica gel column with petroleum ether to give a colorless oil in 94% yield (0.087 g). CAS: 139-66-2. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.21 (m, 10 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.9, 131.2, 129.4, 127.2 ppm. GC-MS (EI): m/z = 186 $[M]^+$.

Di(*p*-tolyl)sulfane (1b): The crude product obtained by the General Procedure was purified on a silica gel column with petroleum ether to give a colorless oil in 91% yield (0.097 g). CAS: 620-94-0. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (d, J = 8.4 Hz, 4 H, Ar-H), 7.10 (d, J = 7.6 Hz, 4 H, Ar-H), 2.32 (s, 6 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.1, 132.8, 131.2, 130.1, 21.3 ppm. GC-MS (EI): m/z = 214 $[M]^+$.

Di(*o*-tolyl)sulfane (1c): The crude product obtained by the General Procedure was purified on a silica gel column with petroleum ether to give a white solid in 89% yield (0.095 g). CAS: 4537-05-7. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24–7.15 (m, 4 H, Ar-H), 7.12–7.04 (m, 4 H, Ar-H), 2.38 (s, 6 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.1, 134.4, 131.3, 130.6, 127.3, 126.9, 20.6 ppm. GC-MS (EI): m/z = 214 $[M]^+$.

Bis(4-bromophenyl)sulfane (1d): The crude product obtained by the General Procedure was purified on a silica gel column with petroleum ether to give a white solid in 94% yield (0.162 g). CAS: 3393-78-0. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, J = 8.8 Hz, 4 H, Ar-H), 7.19 (d, J = 8.4 Hz, 4 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.6, 132.8, 132.6, 121.7 ppm. GC-MS (EI): m/z (%) = 342 [M, Br^{79}, $Br^{79}]^+$, 344 (100) [M, Br^{79}, $Br^{81}]^+$, 346 [M, Br^{81}, $Br^{81}]^+$.

Bis(2-bromophenyl)sulfane (1e): The crude product obtained by the General Procedure was purified on a silica gel column with petroleum ether to give a white solid in 90% yield (0.155 g). CAS: 21848-84-0. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66–7.64 (m, 2 H, Ar-H), 7.26–7.22 (m, 2 H, Ar-H), 7.17–7.12 (m, 4 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.8, 133.7, 132.6, 129.0, 128.3, 126.0 ppm. GC-MS (EI,): m/z (%) = 342 [M, Br^{79}, $Br^{79}]^+$, 344 (100) m/z [M, Br^{79}, $Br^{81}]^+$, 346 [M, Br^{81}, $Br^{81}]^+$.

4,4′-Thiodianiline (1f): The crude product obtained by the General Procedure was purified on a silica gel column with ethyl acetate/petroleum ether (1:2) to give a brown solid in 96% yield (0.104 g). CAS: 139-65-1. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15 (d, J = 8.0 Hz, 4 H, Ar-H), 6.60 (d, J = 8.0 Hz, 4 H, Ar-H), 3.67 (s, 4 H, NH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.8, 132.9, 125.2, 115.9 ppm. GC-MS (EI): m/z = 216 $[M]^+$.

Bis(4-nitrophenyl)sulfane (1g): The crude product obtained by the General Procedure was purified on a silica gel column with ethyl acetate/petroleum ether (1:10) to give a yellow solid in 98% yield (0.135 g). CAS: 1223-31-0. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (d, J = 8.8 Hz, 4 H, Ar-H), 7.50 (d, J = 9.2 Hz, 4 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.3, 142.8, 131.3, 124.8 ppm. GC-MS (EI): m/z = 276 $[M]^+$.

Bis(4-methoxyphenyl)sulfane (1h): The crude product obtained by the General Procedure was purified on a silica gel column with ethyl acetate/petroleum ether (1:50) to give a colorless oil in 81% yield (0.100 g). CAS: 3393-77-9. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (d, J = 8.8 Hz, 4 H, Ar-H), 6.83 (d, J = 8.8 Hz, 4 H, Ar-H), 3.78 (s, 6 H, OCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.1, 132.9, 127.6, 114.9, 55.5 ppm. GC-MS (EI): m/z = 246 $[M]^+$.

Bi(naphthalen-1-yl)sulfane (1i): The crude product obtained by the General Procedure was purified on a silica gel column with petroleum ether to give a white solid in 90% yield (0.129 g). CAS: 607-

53-4. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43–8.40 (m, 2 H, Ar-H), 7.89–7.87 (m, 2 H, Ar-H), 7.78–7.76 (m, 2 H, Ar-H), 7.55–7.51 (m, 4 H, Ar-H), 7.32–7.30 (m, 4 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.3, 132.8, 132.6, 130.1, 128.8, 128.2, 126.9, 126.6, 126.0, 125.3 ppm. GC-MS (EI): m/z = 286 $[M]^+$.

Bi(pyridin-4-yl)sulfane (1j): The crude product obtained by the General Procedure was purified on a silica gel column with ethyl acetate/petroleum ether (2:1) to give a slightly yellow solid in 86% yield (0.081 g). CAS: 37968-97-1. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.55 (d, J = 4.8 Hz, 4 H, Ar-H), 7.25 (d, J = 4.8 Hz, 4 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.1, 143.7, 124.6 ppm. GC-MS (EI): m/z = 188 $[M]^+$.

Diphenylselane (2a): The crude product obtained by the General Procedure was purified on a silica gel column with petroleum ether to give a colorless oil in 94% yield (0.110 g). CAS: 1132-39-4. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.45 (m, 4 H, Ar-H), 7.26–7.24 (m, 6 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.1, 131.3, 129.5, 127.5 ppm. GC-MS (EI): m/z = 154 $[M - 80]^+$, 234 $[M]^+$.

Di(*p*-tolyl)selane (2b): The crude product obtained by the General Procedure was purified on a silica gel column with petroleum ether to give a slightly yellow solid in 88% yield (0.115 g). CAS: 22077-55-0. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (d, J = 8.0 Hz, 4 H, Ar-H), 7.06 (d, J = 8.0 Hz, 4 H, Ar-H), 2.31 (s, 6 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.3, 133.2, 130.2, 127.9, 21.3 ppm. GC-MS (EI): m/z = 182 $[M - 80]^+$, 262 $[M]^+$.

Di(*m*-tolyl)selane (2c): The crude product obtained by the General Procedure was purified on a silica gel column with petroleum ether to give a slightly yellow oil in 86% yield (0.112 g). CAS: 22077-57-2. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (s, 2 H, Ar-H), 7.25 (d, J = 7.2 Hz, 2 H, Ar-H), 7.16–7.12 (m, 2 H, Ar-H), 7.05 (d, J = 7.6 Hz, 2 H) 2.29 (s, 6 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.2, 133.7, 131.1, 130.2, 129.2, 128.3, 21.4 ppm. GC-MS (EI): m/z = 182 $[M - 80]^+$, 262 $[M]^+$.

Bis(4-chlorophenyl)selane (2d): The crude product obtained by the General Procedure was purified on a silica gel column with petroleum ether to give a slightly yellow solid in 91% yield (0.137 g). CAS: 58235-79-3. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (d, J = 8.8 Hz, 4 H, Ar-H), 7.24 (d, J = 8.4 Hz, 4 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.5, 134.0, 129.8, 129.2 ppm. GC-MS (EI): m/z = 222 $[M - 80]^+$, 302 $[M]^+$.

Bis(2-chlorophenyl)selane (2e): The crude product obtained by the General Procedure was purified on a silica gel column with petroleum ether to give a white solid in 88% yield (0.133 g). CAS: 116929-15-8. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.44 (m, 2 H, Ar-H), 7.27–7.23 (m, 4 H, Ar-H), 7.16–7.13 (m, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.6, 134.4, 130.5, 130.0, 129.3, 127.8 ppm. GC-MS (EI): m/z = 222 $[M - 80]^+$, 302 $[M]^+$.

Bis[4-(trifluoromethyl)phenyl]selane (2f): The crude product obtained by the General Procedure was purified on a silica gel column with petroleum ether to give a white solid with low melting point in 89% yield (0.164 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.53 (m, 8 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.3, 133.3, 130.2 (q, J = 32 Hz), 126.5 (d, J = 4 Hz), 124.1 (q, J = 270 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –63.2 (s, 6 F) ppm. GC-MS (EI): m/z = 290 $[M - 80]^+$, 370 $[M]^+$. HRMS (Tof EI) m/z calcd. for $C_{16}H_6F_6Se$ (M^+) 369.9695; found 369.9687.

Di(naphthalen-1-yl)selane (2g): The crude product obtained by the General Procedure was purified on a silica gel column with petroleum ether to give a slightly yellow solid in 87% yield (0.145 g). CAS: 227010-30-2. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32–8.30 (m, 2 H), 7.78–7.69 (m, 4 H, Ar-H), 7.47–7.43 (m, 6 H, Ar-H), 7.18 (t, J = 8.0 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.2, 133.7, 132.3, 130.0, 128.8, 128.5, 127.2, 127.0, 126.5, 126.2 ppm. GC-MS (EI): m/z = 334 $[M]^+$.

Di(biphenyl-4-yl)selane (2h): The crude product obtained by the General Procedure was purified on a silica gel column with petroleum ether to give a slightly yellow solid in 87% yield (0.167 g). CAS: 73151-89-0. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.55 (m, 8 H, Ar-H), 7.52–7.49 (m, 4 H, Ar-H), 7.44–7.41 (m, 4 H, Ar-H), 7.36–7.32 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.54, 140.51, 133.5, 130.3, 129.0, 128.2, 127.7, 127.1 ppm. GC-MS (EI): m/z = 386 $[M]^+$. HRMS (MALDI Tof): calcd. for $C_{24}H_{18}Se$ $[M]^+$ 386.0574; found 386.0564.

Di(pyridin-4-yl)selane (2i): The crude product obtained by the General Procedure was purified on a silica gel column with ethyl acetate/petroleum ether (2:1) to give a slightly yellow oil in 71% yield (0.084 g). CAS: 87385-48-6. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51 (d, J = 5.6 Hz, 4 H, Ar-H), 7.36 (d, J = 6.0 Hz, 4 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.4, 140.4, 127.3 ppm. GC-MS (EI): m/z = 236 $[M]^+$.

Di(thiophen-2-yl)selane (2j): The crude product obtained by the General Procedure was purified on a silica gel column with petroleum ether to give a colorless oil in 73% yield (0.090 g). CAS: 95108-98-8. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (dd, J_1 = 5.2, J_2 = 1.2 Hz, 2 H, Ar-H), 7.26 (dd, J_1 = 3.6, J_2 = 1.2 Hz, 2 H, Ar-H), 6.93 (dd, J_1 = 5.2, J_2 = 3.6 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.9, 131.1, 128.1, 126.4 ppm. GC-MS (EI): m/z = 166 $[M - 80]^+$, 246 $[M]^+$.

(4-Methoxyphenyl)(phenyl)sulfane (3a): The crude product obtained by the General Procedure was purified on a silica gel column with ethyl acetate/petroleum ether (1:50) to give a slightly yellow oil in 75% yield (0.081 g). CAS: 5633-57-8. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, J = 8.8 Hz, 2 H, Ar-H), 7.25–7.21 (m, 2 H, Ar-H), 7.18–7.11 (m, 3 H, Ar-H), 6.89 (d, J = 8.8 Hz, 2 H, Ar-H), 3.81 (s, 3 H, OCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.0, 138.8, 135.6, 129.1, 128.3, 125.9, 124.4, 115.1, 55.5 ppm. GC-MS (EI): m/z = 216 $[M]^+$.

Phenyl(*p*-tolyl)sulfane (3b): The crude product obtained by the General Procedure was purified on a silica gel column with petroleum ether to give a slightly yellow oil in 80% yield (0.080 g). CAS: 3699-01-2. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (d, J = 8.0 Hz, 2 H, Ar-H), 7.27–7.22 (m, 4 H, Ar-H), 7.18–7.15 (m, 1 H, Ar-H), 7.12 (d, J = 8.0 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.7, 137.3, 132.4, 131.4, 130.2, 129.9, 129.2, 126.5, 21.3 ppm. GC-MS (EI): m/z = 200 $[M]^+$.

(4-Chlorophenyl)(phenyl)sulfane (3c): The crude product obtained by the General Procedure was purified on a silica gel column with petroleum ether to give a colorless oil in 79% yield (0.087 g). CAS: 13343-26-5. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.22 (m, 9 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.2 134.8, 133.1, 132.2, 131.5, 129.49, 129.46, 127.6 ppm. GC-MS (EI): m/z = 220 $[M]^+$, 222 $[M + 2]^+$.

(4-Bromophenyl)(phenyl)sulfane (3d): The crude product obtained by the General Procedure was purified on a silica gel column with petroleum ether to give a colorless oil in 78% yield (0.103 g). CAS: 65662-88-6. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, J = 8.4 Hz, 2 H, Ar-H), 7.36–7.24 (m, 5 H, Ar-H), 7.16 (d, J = 8.4 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.7, 135.1, 132.4, 132.3, 131.8, 129.5, 127.7, 121.1 ppm. GC-MS (EI): m/z = 264 $[M]^+$, 266 $[M + 2]^+$.

1-[4-(Phenylthio)phenyl]ethanone (3e): The crude product obtained by the General Procedure was purified on a silica gel column with ethyl acetate/petroleum ether (1:50) to give a slightly yellow solid in 60% yield (0.068 g) or 64% yield (0.073 g) when 1-(4-bromophenyl)ethanone was employed. CAS: 10169-55-8. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, J = 8.4 Hz, 2 H, Ar-H), 7.50–7.47 (m, 2 H, Ar-H), 7.41–7.38 (m, 3 H, Ar-H), 7.20 (d, J = 8.4 Hz, 2 H, Ar-H), 2.54 (s, 3 H, $COCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.2, 145.0, 134.5, 134.0, 132.1, 129.8, 129.0, 128.9, 127.5, 26.6 ppm. GC-MS (EI): m/z = 228 $[M]^+$.

(4-Nitrophenyl)(phenyl)sulfane (3f): The crude product obtained by the General Procedure was purified on a silica gel column with ethyl acetate/petroleum ether (1:50) to give a yellow oil in 78% yield (0.090 g) or 80% yield (0.092 g) when 1-bromo-4-nitrobenzene was employed. CAS: 952-97-6. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, J = 8.8 Hz, 2 H, Ar-H), 7.55–7.52 (m, 2 H, Ar-H), 7.46–7.44 (m, 3 H, Ar-H), 7.16 (d, J = 9.2 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.6, 145.4, 134.8, 130.4, 130.1, 129.8, 126.7, 124.1 ppm. GC-MS (EI): m/z = 231 $[M]^+$.

(4-Chlorophenyl)(4-nitrophenyl)sulfane (3g): The crude product obtained by the General Procedure was purified on a silica gel column with ethyl acetate/petroleum ether (1:50) to give a yellow solid in 71% yield (0.094 g). CAS: 21969-11-9. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, J = 8.8 Hz, 2 H, Ar-H), 7.48–7.40 (m, 4 H, Ar-H), 7.18 (d, J = 9.2 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.7, 145.7, 136.1, 135.9, 130.4, 129.2, 127.0, 124.2 ppm. GC-MS (EI): m/z = 265 $[M]^+$, 267 $[M + 2]^+$.

(4-Methoxyphenyl)(4-nitrophenyl)sulfane (3h): The crude product obtained by the General Procedure was purified on a silica gel column with ethyl acetate/petroleum ether (1:50) to give a yellow solid in 79% yield (0.103 g). CAS: 22865-50-5. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, J = 8.8 Hz, 2 H, Ar-H), 7.48 (d, J = 8.8 Hz, 2 H, Ar-H), 7.08 (d, J = 8.8 Hz, 2 H, Ar-H), 6.99 (d, J = 8.8 Hz, 2 H, Ar-H), 3.86 (s, 3 H, OCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.2, 150.2, 145.0, 137.2, 125.6, 124.0, 120.1, 115.8, 55.6 ppm. GC-MS (EI): m/z = 261 $[M]^+$.

(4-Nitrophenyl)(*p*-tolyl)sulfane (3i): The crude product obtained by the General Procedure was purified on a silica gel column with ethyl acetate/petroleum ether (1:50) to give a yellow solid in 85% yield (0.104 g). CAS: 22865-48-1. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, J = 7.6 Hz, 2 H, Ar-H), 7.42 (d, J = 6.8 Hz, 2 H, Ar-H), 7.25 (d, J = 7.6 Hz, 2 H, Ar-H), 7.11 (d, J = 7.6 Hz, 2 H, Ar-H), 2.40 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.4, 145.2, 140.3, 135.2, 130.9, 126.5, 126.2, 124.0, 21.4 ppm. GC-MS (EI): m/z = 245 $[M]^+$.

(4-Chlorophenyl)(4-methoxyphenyl)sulfane (3j): The crude product obtained by the General Procedure was purified on a silica gel column with ethyl acetate/petroleum ether (1:50) to give a white solid in 78% yield (0.098 g). CAS: 20912-69-0. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, J = 8.8 Hz, 2 H, Ar-H), 7.17 (d, J = 8.8 Hz, 2 H, Ar-H), 7.06 (d, J = 8.4 Hz, 2 H, Ar-H), 6.89 (d, J = 8.8 Hz, 2 H, Ar-H), 3.80 (s, 3 H, OCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.2, 137.5, 135.7, 131.7, 129.4, 129.1, 123.8, 115.2, 55.5 ppm. GC-MS (EI): m/z = 250 $[M]^+$, 252 $[M + 2]^+$.

2-Phenylbenzo[*b*]thiophene (4a): The crude product obtained by the General Procedure was purified on a silica gel column with petroleum ether to give a white solid in 99% yield (0.0416 g). CAS: 1207-95-0; m.p. 174.8–175.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82–7.70 (m, 4 H, Ar-H), 7.53 (s, 1 H, Ar-H), 7.43–7.28 (m, 5 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.4, 140.9, 139.7, 134.5, 129.1, 128.4, 126.7, 124.7, 124.5, 123.7, 122.4, 119.6 ppm. GC-MS (EI): m/z = 210 $[M]^+$.

[1]Benzothieno[3,2-*b*]benzothiophene (4b): The crude product obtained by the General Procedure was purified on a silica gel column with petroleum ether to give a white solid in 61% yield (0.0293 g). CAS: 248-70-4; m.p. 219–219.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92–7.87 (m, 4 H, Ar-H), 7.47–7.38 (m, 4 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.6, 133.7, 133.4, 125.2, 125.1, 124.2, 121.8 ppm. GC-MS (EI): m/z = 240 $[M]^+$.

Supporting Information (see footnote on the first page of this article): Experimental procedures, characterization data and copies of the original ^{1}H NMR and ^{13}C NMR spectra of all compounds.

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