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# A highly efficient and widely functional-group-tolerant catalyst system for copper(I)-catalyzed S-arylation of thiols with aryl halides

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ABSTRACT

A mild, general, and efficient copper-catalyzed system for C–S bond formation with high chemoselectivity and wide functional group tolerance is developed. With CuBr as catalyst and 1,2,3,4-tetrahydro-8-hydroxy-quinoline as ligand, the S-arylation of thiols with aryl halides performed well, the activated aryl iodides could take place even at room temperature, and the activated aryl bromides and chlorides give the corresponding products with good to excellent yields as well.

## 1. Introduction

The formation of C–S bond is a key step in synthetic organic chemistry due to the importance of related compounds in pharmaceuticals and functional materials.[1] As a method for the synthesis of sulfides, reduction of aryl sulfones and aryl sulfoxides requires strong reducing agents such as $LiAlH_4$.[2] In 1980, Migita and coworkers reported the first palladium-catalyzed C(aryl)–S bond formation from the corresponding aryl halides and thiols.[3] From then on, transition-metal-catalyzed C–S bond formation received particular interests. Because sulfur-containing compounds have strong coordinative properties and may poison the metal catalysts, literature reported for the transition-metal-catalyzed C–S cross-coupling reaction was limited since Migitas' study, which is in contrast with the C–N and C–O bond formation.[4] Although several transition metals such as palladium,[5] nickel,[6] copper,[7] cobalt,[8] iron,[9] and indium[10] have been reported for this purpose in the past decade, these catalytic systems still suffer from several common problems. For example, the high cost of palladium salts and phosphine ligands, metal toxicity, reagents needed in excess and few types of highly active ligands to choose restrict their applications, especially in large-scale process. Therefore, the development of traditional copper-catalyzed Ullmann-type C–S cross-coupling reactions is still attractive owing to the drawbacks of other metal-catalyzed systems.

In fact, the traditional copper-catalyzed C–S bond formation usually requires harsh conditions such as more than stoichiometric amounts of copper salts, polar solvent such as HMPA, and high temperature above 200 °C. It is noteworthy that only in the last few years attractive copper-catalyzed processes make a great contribution to this reaction. Copper-catalyzed Ullmann-type C–S coupling reaction could be accelerated by some special ligands such as phosphazene,[11] ethylene glycol,[12] neocuproine,[13] *N*-methylglycine,[14] oxime-phosphine oxide ligand,[15] tripod ligand,[16] benzotriazole,[17] 1,2-diaminocyclohexane,[18] β-ketoester,[19] L-proline,[20] and BINAM.[21] Indeed, significant progresses have been achieved through the use of the ligands. A popular opinion is that the use of ligands may increase the solubility of copper salts in the solvents. Very recently, copper-catalyzed reactions at high temperature without any ligand were reported.[22]

Yet, the development of this copper-catalyzed Ullmann-type reaction is required all the time as most catalytic systems still needed long reaction time (longer than 24 h), relatively high temperature ($\geq$110 °C), sometimes high catalyst loading. Another drawback is that the expensive aryl iodides were used to couple with thiols in most reported systems while cheap aryl bromides were mentioned in countable literatures.[14,17–21] In addition, high temperature is harmful for both asymmetrical synthesis and pharmaceutical. Therefore a mild, economic, and high-efficient catalytic system is still necessary for C–S coupling reaction aiming to decrease the temperature required for aryl iodides and also to increase the reactivity of aryl bromides.

Recently, we reported that *o*-aminophenol derivatives could accelerate the copper-catalyzed Ullmann-type N-arylation reaction.[23] Encouraged by the success in N-arylation reaction, we have investigated further copper-catalyzed S-arylation using *o*-aminophenol derivatives as ligands. In this paper, we report an extension of our catalytic system, which can catalyze Ullmann-type coupling of thiols with aryl halide for the formation of C–S bond.

## 2. Results and discussion

In a preliminary study, three ligands **A**, **B**, and **C** derived from *o*-aminophenol (see structures in Fig. 1) were tested to find the

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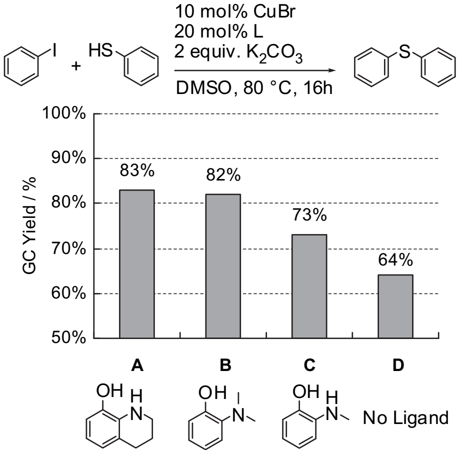
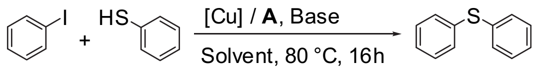


**Figure 1.** Ligand screening for S-arylation of thiophenol.

optimal ligand for S-arylation reaction under the condition used for N-arylation reaction.[23] $K_2CO_3$ was used instead of $Cs_2CO_3$ because the acidity of thiophenol was much stronger than substrates for N-arylation reaction. As shown in Figure 1, all ligands promoted the coupling reaction under the indicated conditions. Ligands **A** and **B** gave the higher GC yields compared with **C**. Without any ligand, the GC yield of diphenyl thioether is 64%, which is in agreement with the literature.[22c] We speculated that the synergistic electron-donating groups and flexible tetrahedral steric structures of ligands **A**, **B**, and **C** facilitated the oxidative addition and reductive elimination reaction.[23] Thus our study indicated that both ligands **A** and **B** were effective for the copper-catalyzed C–S coupling reaction. Considering the continuity of our research on the copper-catalyzed coupling reaction, the ligand **A** was chosen for the S-arylation reaction due to its low cost and commercial availability.

Some influencing factors, such as the copper salts, solvents, bases, molar ratio of ligand to copper salt, reaction time, etc., were briefly screened using this model reaction. As shown in Table 1, polar solvents $CH_3CN$, DMF, and DMSO can promote this reaction in a more efficient way compared with weakly polar solvent toluene, and DMSO was found to be the best choice. Although several copper salts could catalyze the reaction, CuBr was superior to others. Similarly, $K_2CO_3$ gave the best result among the bases examined. It was noted that the molar ratio of copper to ligand is important in the reaction. The yield of diphenyl thioether was dramatically decreased from 83% to 68% when the molar ratio of copper to ligand increased from 10:20 to 10:10 (Table 1, entries 7 and 12). Perhaps the structure of four-coordinate complex makes the copper ion more stable in reaction system relative to two-coordinate complex. The yield decreased to 51% while the catalyst loading decreased to 5 mol % (Table 1, entry 13). Detected by GC, byproduct diphenyl disulfide ranged from 5% to 15%. In order to avoid this side reaction, the iodobenzene was excess compared with thiophenol. After prolonging the reaction time to 24 h, the reaction gave a GC yield of 97% (Table 1, entry 14). Thus, the optimal reaction condition was obtained as shown in entry 14.

**Table 1**
Optimization of the reaction condition[a]



| Entry | [Cu]/L | Solvent | [Cu] | Base | Yield (%) |
|---|---|---|---|---|---|
| 1 | 10:20 | Toluene | CuCl | $K_2CO_3$ | 3 |
| 2 | 10:20 | $CH_3CN$ | CuCl | $K_2CO_3$ | 73 |
| 3 | 10:20 | DMF | CuCl | $K_2CO_3$ | 78 |
| 4 | 10:20 | DMSO | CuCl | $K_2CO_3$ | 80 |
| 5 | 10:20 | DMSO | CuI | $K_2CO_3$ | 47 |
| 6 | 10:20 | DMSO | $CuBr_2$ | $K_2CO_3$ | 38 |
| 7 | 10:20 | DMSO | CuBr | $K_2CO_3$ | 83 |
| 8 | 10:20 | DMSO | CuBr | $Cs_2CO_3$ | 62 |
| 9 | 10:20 | DMSO | CuBr | $K_3PO_4$ | 60 |
| 10 | 10:20 | DMSO | CuBr | KOH | 73 |
| 11 | 10:20 | DMSO | CuBr | $NEt_3$ | 27 |
| 12 | 10:10 | DMSO | CuBr | $K_2CO_3$ | 68 |
| 13 | 5:10 | DMSO | CuBr | $K_2CO_3$ | 51 |
| 14[b] | 10:20 | DMSO | CuBr | $K_2CO_3$ | 97 |

[a] Reaction conditions: [Cu] (0.05 mmol), base (2 mmol), solvent (1 mL), iodobenzene (1 mmol), thiophenol (1.5 mmol), $N_2$. Yield (GC) was calibrated with diphenyl ether as an internal standard.

[b] Thiophenol (1 mmol), iodobenzene (1.5 mmol), 80 °C for 24 h.

By using the optimized reaction condition, we further investigated the scope of the Ullmann-type C–S coupling reaction of aryl iodides with thiols and the results are summarized in Table 2. As shown in Table 2, various substituted aryl iodides reacted with both aromatic and aliphatic thiols and gave the corresponding products with excellent yields. The aryl iodides with electron-donating groups, which deactivate the aryl iodides gave the desired diaryl thioethers in high yields (Table 2, entries 1–10). Electron-withdrawing groups such as nitro group dramatically increased the reactivity of aryl iodides and the coupling reaction took place even at room temperature (Table 2, entry 2). Whether the substitution of iodobenzene was at the *para*- or *ortho*-position, the C–S bond formation reaction gave excellent yields (Table 2, entries 3–9). Similarly in the case of thiols, both aliphatic and aromatic thiols with *para*- or *ortho*-substituted gave the corresponding products in excellent yields (Table 2, entries 11–17). All the results of *ortho*-substituted iodobenzene and thiophenol relative to the *para*-substitutions indicated that the effect of steric hindrance was unobvious. Moreover, the reaction showed a chemoselectivity to the thiols other than arylation on amino or hydroxyl groups. Monitoring the reaction of *p*-bromo iodobenzene with thiophenol at 80 °C by GC–MS, both *p*-bromo and *p*-iodo diphenyl thioethers were produced at a ratio of 1:1 approximately. It was noted that in the previous reported catalytic system the less reactive bromo group did not react when bromo and iodo groups coexist in the arene ring at 80 °C or above. By decreasing the temperature stepwise to 45 °C for 48 h, *p*-bromo diphenyl thioether became the sole product as we desired through the coupling reaction.

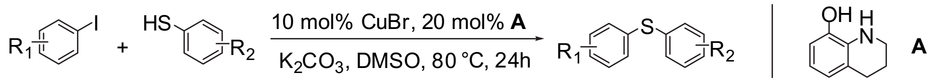
To the best of our knowledge, only few literatures reported that aryl bromides could react with thiols and gave satisfied yields by copper-catalyzed system.[17,19b,21] Encouraged by the result of *p*-bromo iodobenzene that *p*-iodo diphenyl thioether was formed under our optimized condition, aryl bromides were tried to react with thiophenol. At the initial stage, bromobenzene was tested but failed to form the corresponding product through the coupling reaction even the temperature was increased to 110 °C (Table 3, entry 1). To our delight, bromobenzene with electron-withdrawing groups such as nitro, cyano, keto, and aldehyde could react well under the condition used for aryl iodides, and the results are summarized in Table 3. It was noted that the presence of the electron-withdrawing groups dramatically increased the activity of aryl bromides and gave the good to excellent yields. Heterocyclic bromides such as 3-hydroxyl-2-bromo pyridine could also be applied to this coupling reaction and give a satisfactory yield of 62% (Table 3, entry 6). Even *p*-nitro chlorobenzene reacted well under our condition and an isolated yield of 95% was obtained (Table 3, entry 7).

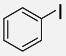
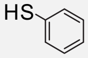
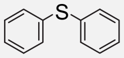
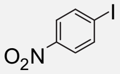
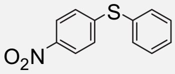
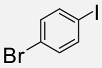
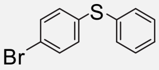
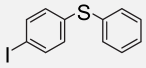
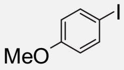
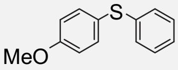
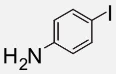
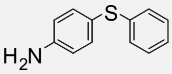
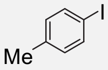
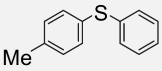
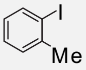
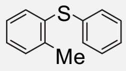
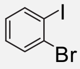
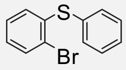
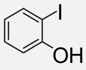
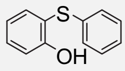
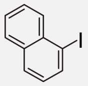
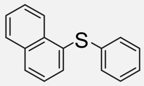
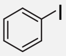
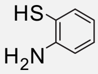
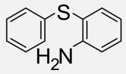
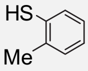
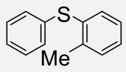
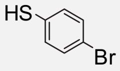
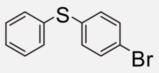
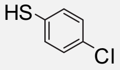
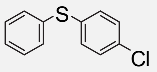
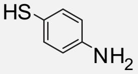
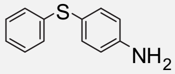
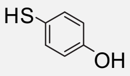
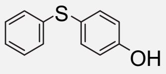
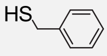
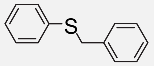
The results in Tables 2 and 3 showed that various functional groups such as –Br, –Cl, –CN, $-NO_2$, –Ac, –CHO, and especially free –OH and $-NH_2$, which were intolerant of Pd catalyzed systems, were tolerated by our catalytic system.

Aiming to obtain diaryl thioethers from less reactive aryl bromides with thiophenol under the reaction condition, we tried to change the base. The desired product was formed with good isolated yield when $K_2CO_3$ was replaced by the strong base *t*-BuOK

**Table 2**

The C–S coupling reaction of aryl iodides with thiols[a]



| Entry | Aryl iodide | Thiol | Product | Yield (%) |
|---|---|---|---|---|
| 1 |  |  |  | 92 |
| 2[b] |  | — |  | 98 (25 °C) |
| 3[c] |  | — |  2c  2c' | 86 (**2c** 45 °C, 48 h)<br>**2c**:**2c**′=52:48 (80 °C, 24 h)<br>**2c**:**2c**′=82:18 (60 °C, 24 h)<br>**2c**:**2c**′=97:3 (50 °C, 32 h) |
| 4 |  | — |  2d | 87 |
| 5 |  | — |  2e | 81 |
| 6 |  | — |  2f | 92 |
| 7 |  | — |  2g | 92 |
| 8 |  | — |  2h | 91 |
| 9 |  | — |  2i | 83 |
| 10 |  | — |  2j | 87 |
| 11 |  |  |  2k | 94 |
| 12 | — |  |  2g | 99 |
| 13 | — |  |  2c | 89 |
| 14 | — |  |  2l | 97 |
| 15 | — |  |  2e | 99 |
| 16 | — |  |  2m | 97 |
| 17 | — |  |  2n | 91 |

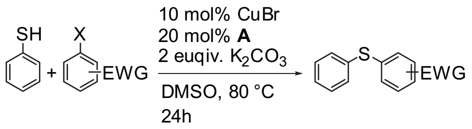
[a] Conditions: aryl iodide (1.5 mmol), thiols (1 mmol), CuBr (10 mol %), L (20 mol %), $K_2CO_3$ (2 mmol), DMSO (1 mL), 80 °C, 24 h. Isolated yield.

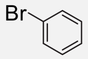
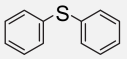
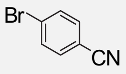
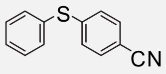
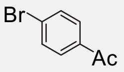
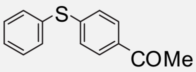
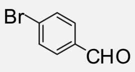
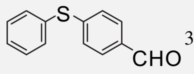
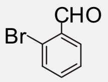
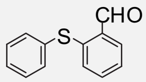
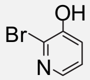
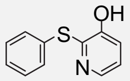
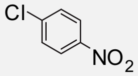
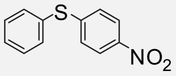
[b] React under 25 °C. The isolated yields were 96% (80 °C) and 97% (45 °C), respectively.

[c] There were two products including *p*-bromo and *p*-iodo diphenyl thioether monitored by GC–MS. Thiophenol was completely transformed.

(Table 4, entry 1b). Surprisingly, bromobenzene could also react at 60 °C and give a GC yield of 78% even without copper salts and ligand (Table 4, entry 1c). When we further investigated bromobenzene with electron-donating group, for example, *p*-methyl bromobenzene, two isomeric compounds *para*- and *meta*-tolyl phenyl thioether were detected at a ratio of 1:1 approximately (Table 4, entry 2). A similar result was obtained when *p*-methyl chlorobenzene reacted with thiophenol under 110 °C (Table 4, entry 3). All these results suggested that using *t*-BuOK as a base the reaction was carried out via a benzyne mechanism.[24]

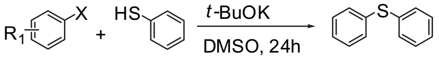
**Table 3**
The C–S coupling of activated aryl halides with thiophenol[a]



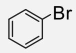
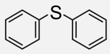
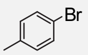
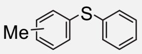
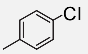
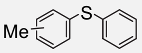
| Entry | Aryl halide | Product | Yield (%) |
|---|---|---|---|
| 1[b] |  |  2a | nd |
| 2 |  |  3a | 82 |
| 3 |  |  3b | 94 |
| 4 |  |  3c | 85 |
| 5 |  |  3d | 87 |
| 6 |  |  3e | 62 |
| 7 |  |  2b | 95 |

[a] Reaction conditions: aryl halide (1.5 mmol), thiophenol (1 mmol), CuBr (10 mol %), L (20 mol %), $K_2CO_3$ (2 mmol), DMSO (1 mL), 80 °C, 24 h. Isolated yield.
[b] Increasing the temperature to 110 °C. Not detected.

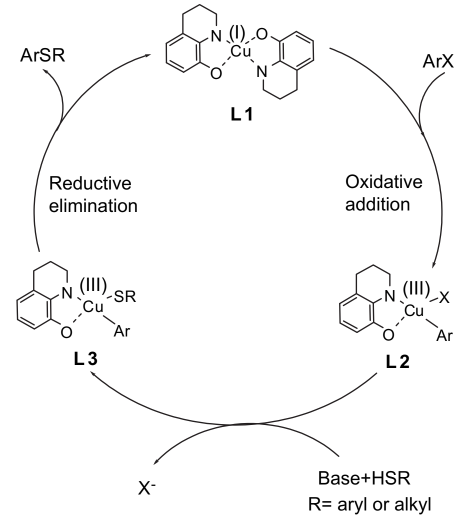
**Table 4**
The C–S coupling of aryl halides with thiophenol[a]



X=Br, Cl

| Entry | Aryl halide | Product | Yield (%) |
|---|---|---|---|
| 1 |  |  | 85[b]<br>78[c] |
| 2 |  |  *meta* : *para*= 1: 1 | 98[d] |
| 3 |  |  *meta* : *para*= 1: 1 | 92[e] |

[a] Reaction conditions: aryl bromide (1 mmol), thiophenol (1 mmol), *t*-BuOK (2 mmol), DMSO (1 mL), 24 h.
[b] 80 °C. Isolated yield.
[c] 60 °C for 16 h. GC yield using diphenyl ether as an internal standard.
[d] 80 °C. The conversion of *p*-methyl bromobenzene.
[e] 110 °C. The conversion of *p*-methyl chlorobenzene.



**Scheme 1.** Possible mechanism for copper-catalyzed C–S bond formation.

On the basis of the results, we proposed the following mechanism for this CuBr catalyzed Ullmann-type C–S cross-coupling reaction (see Scheme 1).[14,17,21,25] Firstly, four-coordinate $[\mathrm{Cu}^{\mathrm{I}}]$ complex **L1** was formed by the ligand **A** coordinated to the cuprous bromide according to the molar ratio of ligand to copper in the experiment. The $[\mathrm{Cu}^{\mathrm{III}}]$ intermediate **L2** was then generated by oxidation addition of aryl halide by replacing one ligand **A** to $[\mathrm{Cu}^{\mathrm{I}}]$ complex. In the presence of base, thiols reacted with the $[\mathrm{Cu}^{\mathrm{III}}]$ intermediate **L2** and gave the intermediate **L3**, which gave the desired product and regenerated the active $[\mathrm{Cu}^{\mathrm{I}}]$ complex **L1** through a reductive elimination. By this mechanism, the ligand **A** may play a dual role of both increasing the solubility of copper salts and promoting the oxidative addition and reductive elimination of substitution to $[\mathrm{Cu}^{\mathrm{I}}]$ complex. Searching for more evidence about the mechanism is undergoing in our laboratory.

## 3. Conclusion

In conclusion, we have developed a very simple, economical, and highly efficient catalytic system for copper-catalyzed C–S bond formation of both aromatic and aliphatic thiols with aryl halides. Both activated aryl bromides and aryl chlorides reacted well with thiols under the same condition and gave excellent yields. Aryl iodides with electron-withdrawing groups could give the corresponding product almost quantitatively even at room temperature. It was still very attractive that inactive bromobenzene and even chlorobenzene were able to react with thiols without any copper catalyst although the coupling reaction using strong base underwent a benzyne mechanism. Because of the simplicity and commercial availability of the ligand 1,2,3,4-tetrahydro-8-hydroxy-quinoline and more attractive reaction conditions than others, we believe that this type of reaction is of great importance not only in academic research but also in large-scale synthesis of aromatic thioethers.

## 4. Experimental

### 4.1. General information

All reagents were obtained from commercial source and used without further purification. The reactions were carried out under $N_2$ atmosphere. Gas chromatography analyses were performed with an FID detector. All products were isolated by column chromatography on silica gel (200–300 mesh) using petroleum ether (60–90 °C) and ethyl acetate as eluate. Compounds described in the literature were characterized by comparison of their $^1H$ NMR, $^{13}C$ NMR spectra, and MS to the reported data. $^1H$ NMR and $^{13}C$ NMR spectra were measured in $CDCl_3$ and chemical shifts were reported in parts per million relative to TMS. High resolution mass spectrometric (HRMS) data were performed on Q-Tof MS.

### 4.2. Experimental procedure for all compounds

*4.2.1. Method for ligands derived from o-aminophenol.* The three ligands derived from *o*-aminophenol have been reported before.[23]

All the physical data of the three ligands were in agreement with those reported.

*4.2.2. General procedure for diaryl thioethers.* A flame-dried Schlenk test tube with a magnetic stirring bar was charged with CuBr (14 mg, 0.1 mmol), ligand (30 mg, 0.2 mmol), $K_2CO_3$ (276 mg, 2.0 mmol), thiol (1.0 mmol), aryl halide (1.5 mmol), and DMSO (1 mL) under $N_2$. The mixture reacted at 80 °C for 24 h, then cooled to ambient temperature, and the resulting mixture was extracted with ethyl acetate (3×30 mL). The combined organic layers were dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether) to provide the desired product. All the physical data of the known compounds were in agreement with those reported in the literatures.

*4.2.2.1. 2-(Phenylthio)pyridin-3-ol (**3e**).* General procedure was followed. Thiolphenol (103 μL, 1.0 mmol) and 2-bromopyridin-3-ol (261 mg, 1.5 mmol) were used to obtain the product 2-(phenylthio)pyridin-3-ol (138 mg, 62% yield) as white solid. Column chromatography (petroleum ether/ethyl acetate=4:1). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.20 (dd, $J$=4.4, 1.2 Hz, 1H), 7.32–7.20 (m, 7H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 153.5, 142.8, 141.4, 133.2, 130.1, 129.5, 127.6, 125.5, 123.1 ($CDCl_3$, 77.2); MS (ESI, $m/z$) 204 $[M+H]^+$, 226 $[M+Na]^+$; HRMS (ESI) calcd for $C_{11}H_9NOS$ $(M-H)^+$ 202.0327, found 202.0319. Mp: 119.4–120.6 °C.

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## Supplementary data

Experimental procedures and characterization of the products. This material is available free of charge via ScienceDirect. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.09.085.

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