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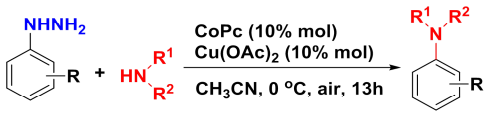
Li-Tao An,[b] Adedamola Shoberu,[a] Jian-Ping Zou*[a, c]

[a] *Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry and Chemical Engineering, Soochow University, 199 Renai Street, Suzhou, Jiangsu 215123, China.*

[b] *College of Chemistry and Chemical Engineering, Huaiyin Normal University, Huaian, 111 West Changjiang Road, Huai'an, Jiangsu, China, 223300.*

[c] *Key Laboratory of Synthetic Chemistry of Natural Substances, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China.*



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[a] *Key Laboratory of Organic Synthesis of Jiangsu Province,'College of Chemistry and Chemical Engineering, Soochow University, 199 Renai Street, Suzhou, Jiangsu 215123, China.*
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[c] *Key Laboratory of Synthetic Chemistry of Natural Substances, Shanghai Institute of Organic Chemistry, Chinese Academy of Science, Shanghai 200032, China.*

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ABSTRACT

The N-arylation of amines with arylhydrazines has been developed, achieving the selective cross-coupling of aryl radicals with amines to form N-aryl amines. The reaction uses air as an oxidant, CoPc and Cu(OAc)$_2$ as catalysts. The reaction proceeds under mild conditions in air through a relay process, arylhydrazines are oxidized to aryldiazenes by CoPc, further oxidized to aryl radicals by air (O_2), which are trapped by Cu(OAc)$_2$–amine complex, followed by reduction-elimination reaction to form N-aryl amines. Arylamines and arylhydrazines give the highest yields, but N-aryl-N-alkylamines and N-alkylamines can be used as well.

1. Introduction

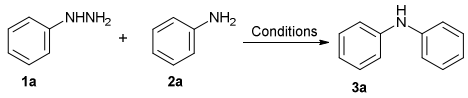
Diarylamines are ubiquitous core structures found in natural products, pharmaceuticals, agrochemicals, dyes and materials.[1] One of the most earliest approach towards preparing diarylamines[2] is the Ullmann reaction which was reported in early 1900's. Significant improvements on this approach has been described afterwards in literature.[3] Since Buchwald and Hartwig reported the Pd-catalyzed aromatic C-N bond-forming reaction, tremendous progress has been made in the area of transition-metal catalyzed N-arylation of arylamines.[4] Another important route to diarylamines is the reaction of anilines or aniline surrogates with stoichiometric arylmetal species or excess of hypervalent iodine reagents.[5] Other methods include the polyphosphoric acid-mediated reaction of nitroalkanes with arenes,[6] PhI(OAc)$_2$ / Bi(OTf)$_3$ / (Zn / CF_3COOH)-mediated reaction of arylsulfonyl amides with arylamines.[7] In recent years, research has focused mainly on metal-catalyzed amination reaction; examples include Ir-catalyzed C-H amination with anilines,[8a] Rh, Ru or Fe-catalyzed C-H amination with azides,[8b-g] Pd-catalyzed amination of aryl sulfides with anilines,[9] Pd-catalyzed reaction of nitroarenes and cyclohexanones.[10] The development of novel, efficient and cost-effective method for constructing such an important framework is still highly desirable. On the basis of our previous studies on arylhydrazines and C–N bond formation [11], arylhydrazines are known to be good radical precursors since they are easily oxidized by various oxidants to yield aryl radicals; these radicals can then react with alkenes, arenes, heteroarenes and C_{60} [12] to form C–C bonds. Inspired by this, we further investigated the possibility of catalytic C–N bond formation. Herein we report CoPc/Cu(OAc)$_2$-catalyzed N-arylation of amines with arylhydrazines using air as a sole oxidant for N-aryl amines synthesis.

2. Results and Discussion

At the outset of our investigation, the reaction between phenylhydrazine (**1a**) and aniline (**2a**) in the presence of Cu(OAc)$_2$ was selected for optimization. The initial result was quite promising; diphenylamine (**3a**) was obtained, although in only 10% yield (Table 1, entry 1). Meanwhile, no reactions were observed with CuPc and Mn(OAc)$_3$ (Table 1, entries 2-3). Hence, we turned to a two-component system such as CoPc/Cu(OAc)$_2$, FePc/Cu(OAc)$_2$ and Mn(OAc)$_3$/ Cu(OAc)$_2$. To our delight, the Mn(OAc)$_3$ / Cu(OAc)$_2$ system resulted in 45% yield of **3a** (Table 1, entries 4-6); in this case, a stochiometric amount of Mn(OAc)$_3$ was required. Notably, low yield of product was observed due to unconsumed aniline, thus the manner of addition of phenylhydrazine was changed. When phenylhydrazine was introduced successively at a rate of 0.2 mmol per hour, an improved yield of product was obtained (Table 1, entry 8). Encouraged by this result, the catalytic system in entry 8 was

replaced with CoPc/$Cu(OAc)_2$ system under the same conditions. To our surprise, the yield significantly increased from 20% to 60% thus indicating that the batch addition of phenylhydrazine is beneficial for this reaction (Table 1, entry 9). After screening the reaction temperature, time and ratio of **1a**/**2a** (Table 1, entries 9-14), the optimal reaction conditions were determined to be: phenylhydrazine (2.0 equiv), aniline (1.0 equiv), 10 mol% of CoPc and $Cu(OAc)_2$) in CH_3CN at 0 °C for 13 hours (Table 1, entry 12).

Table 1. Optimization of the reaction conditions[a]

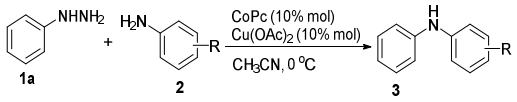


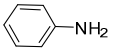
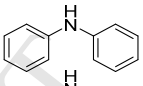
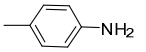
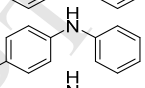
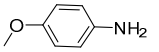
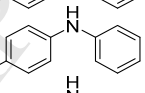
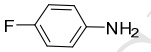
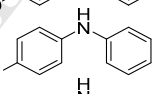
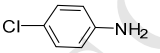
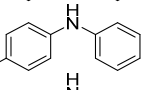
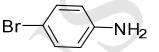
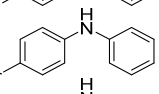
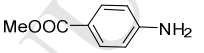
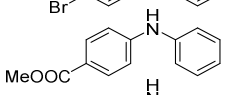
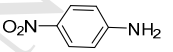
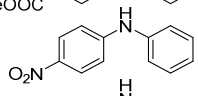
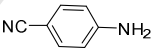
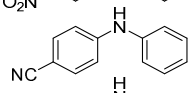
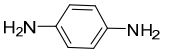
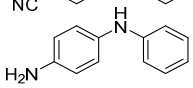
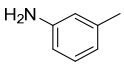
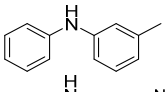
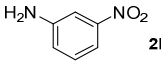
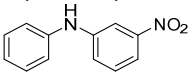
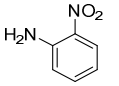
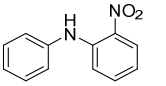
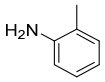
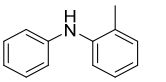
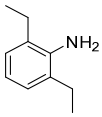
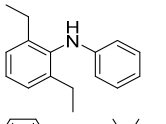
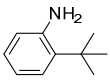
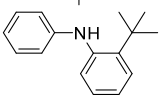
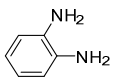
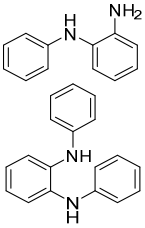
Entry	Cat.[b]	Temp. /°C	Time /h	**1a** (equiv)	Yield /%[c]
1	$Cu(OAc)_2$ (1 equiv)	0	3	1.5	10
2	CuPc (1 equiv)	0	3	1.5	N.D.
3	$Mn(OAc)_3$ (3 equiv)	0	3	1.5	trace
4	CoPc/$Cu(OAc)_2$	0	3	1.5	20
5	FePc/$Cu(OAc)_2$	0	3	1.5	18
6	$Mn(OAc)_3$(3 equiv)/$Cu(OAc)_2$	0	3	1.5	45
7	$Mn(OAc)_3$(3equiv) /$Cu(OAc)_2$	15	3	1.5	20
8	$Mn(OAc)_3$(3equiv) /$Cu(OAc)_2$	0	12	1.5	60[d]
9	CoPc/$Cu(OAc)_2$	0	12	1.5	60[d]
10	CoPc/$Cu(OAc)_2$	-5	12	1.5	22[d]
11	CoPc/$Cu(OAc)_2$	15	12	1.5	45[d]
12	CoPc/$Cu(OAc)_2$	0	13	2	80[d]
13	CoPc/$Cu(OAc)_2$	0	15	2	79[d]
14	CoPc/$Cu(OAc)_2$	0	13	2.5	80[d]

[a] Reaction conditions: **2a** (1.0 mmol), CH_3CN (4 mL) in air for all the reactions;
[b] Using 10% mol catalyst for all the reactions, except noted otherwise;
[c] Isolated yields;
[d] Phenylhydrazine was introduced successively at a rate of 0.2 mmol per hour.

The optimal conditions were applied to a variety of substituted anilines. Anilines with *para*-electron-donating groups such as CH_3 and OCH_3 produced the expected diarylamines in good yields (Table 2, entries 2-3); a slight reduction in yield was observed with *para*-NH_2 substrate since both NH_2 group could participate in the amination reaction (Table 2, entry 10). Anilines with *para*-electron-withdrawing groups such as F, Cl, Br, COOMe, NO_2 and CN all reacted smoothly although a slight drop in yield was observed (58-75%, Table 2, entries 4-9). With *ortho*-substituted anilines, results indicated that a small substituent such as CH_3, NH_2 had little effect on the yield. 2-Methylaniline gave the expected product **3n** in 75% yield similar to yields of products obtained from 3- and 4-methylanilines (Table 2, entries 2, 11 and 14). On the other hand, 2,6-diethylaniline and 2-*tert*-butylaniline gave moderate amounts of **3o** and **3p** respectively (Table 2, entries 15 and 16). In addition, lower yield of **3m** was obtained from 2-nitroaniline as compared with product yields obtained from 3- and 4-nitroanilines (Table 2, entries 8, 12 and 13). These results indicated that bulky groups at *ortho*-position of aniline could impede the reaction.

Table 2. Reactions of phenylhydrazine (**1a**) with substituted anilines (**2**)[a]



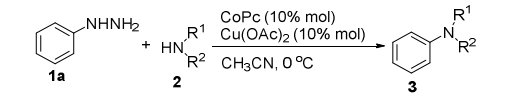
Entry	Aniline **2**		Product **3** and yield[b]
1		**2a**	 **3a**, 80%
2		**2b**	 **3b**, 79%
3		**2c**	 **3c**, 80%
4		**2d**	 **3d**, 70%
5		**2e**	 **3e**, 75%
6		**2f**	 **3f**, 75%
7		**2g**	 **3g**, 69%
8		**2h**	 **3h**, 58%
9		**2i**	 **3i**, 60%
10		**2j**	 **3j**, 72%
11		**2k**	 **3k**, 76%
12		**2l**	 **3l**, 56%
13		**2m**	 **3m**, 30%
14		**2n**	 **3n**, 75%
15		**2o**	 **3o**, 56%
16		**2p**	 **3p**, 58%
17		**2q**	 **3q**, 35% **3q'**, 40%

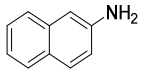
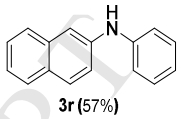
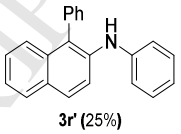
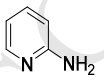
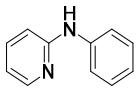
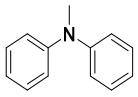
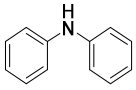
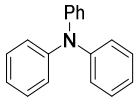
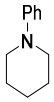
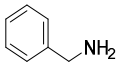
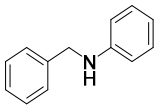
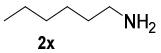
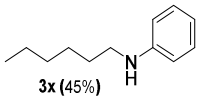
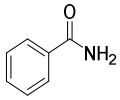
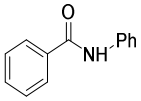
[a] Reaction conditions: phenylhydrazine (**1a**, 2.0 mmol in 2 mL CH_3CN) was introduced successively at a rate of 0.2 mmol per hour, arylamine (**2**, 1.0 mmol), 10 mol% of CoPc and $Cu(OAc)_2$ in CH_3CN (5 mL) at 0 °C for 13 h in air;
[b] Isolated yields.

With the above results in hand, we extended this procedure to different types of amino compounds. β-Aminonaphathalene (**2r**) produced majorly the expected product **3r** along with by-product **3r′** which was generated from the reaction of **3r** and phenyl radical (Table 3, entry 1). This indicated that the α-position of **2r** was more reactive. The electron-deficient 2-aminopyridine (**2s**) afforded the expected product **3s** in a moderate 58% yield (Table 3, entry 2). Reactions involving secondary amines such as N-methylaniline(**2t**), diphenylamine (**2u**) and piperidine (**2v**) were also tested; **2t** gave the expected product **3t** in 60% yield, however, no desired products were observed with **2u** and **2v** (Table 3, entries 3-5). Also, the reaction of phenylhydrazine (**1a**) with alkylamines such as benzylamine (**2w**) and *n*-hexylamine(**2x**) were performed, the expected products **3w** and **3x** were obtained in moderate yields (Table 3, entries 6-7). Finally, indole and benzamide were subjected to the reaction conditions; however no products were observed (Table 3, entries 8-9). These results indicated that this protocol is chemoselective. Subsequently, the effect of substitution on arylhydrazines was probed. As shown in Table 4, arylhydrazines (**1**) bearing electron-donating substituents such as CH_3 and OCH_3 afforded diarylamines (**3**) in very good yields (Table 4, entries 1-3). On the contrary, the presence of electron-withdrawing groups such as F, Cl, Br, $COOCH_3$ and NO_2 were unfavorable to the reaction; reduced yields ranging from 25-71% were observed (Table 4, entries 4-9). The effect of *ortho*-substituents on the reaction was also probed; arylhydrazines (**1**) with *ortho*-substituents such as CH_3 suppressed the reaction (Table 4, entry 10). Finally, the reaction of an alkylhydrazine, *tert*-butylhydrazine was carried out but no expected product was observed (Table 4, entry 11) thus indicating that alkylhydrazines are not suitable precursors for alkyl radical under this process.

For further mechanistic insight, a series of control experiments have been done. First, the oxidation of phenylhydrazine (**1a**) with different oxidants including CoPc, Cu(II)–NH_2Ph complex (**8**) and air (O_2) were carried out, respectively. The results indicated that phenylhydrazine (**1a**) could be oxidized by CoPc or Cu(II)–NH_2Ph complex (**8**) to form phenyldiazine (**5a**)(Scheme 1, equations 1 and 2), however, the oxidation efficiency of **8** compared with CoPc is very low (Scheme 1, equations 3 and 4); the case with air (O_2) as oxidant gave a small amount of complicated mixtures after 12 h, while most of phenylhydrazine (**1a**) remained unchanged (Scheme 1, equation 5). On the basis of results obtained, it can conclude that CoPc played a main role in the oxidation of phenylhydrazine (**1a**) to phenyldiazine (**5a**). Second, to understand the oxidation process of phenyldiazine (**5a**), the reactions of **5a** with CoPc, Cu(II)–NH_2Ph complex (**8**) and air (O_2) were carried out, respectively. The results indicated that **5a** is difficult to be oxidized by CoPc and Cu(II)–NH_2Ph complex (**8**), while air (O_2) could oxidize **5a** easily to phenyl radical (**7a**), which was trapped by TEMPO to afford **10** (Scheme 1, equations 1 and 2). In addition, the result showed that phenyldiazine (**5a**) decomposed at 50 ^oC (Scheme 1, equation 1). Third, to have an insight into the action of Cu(II)–NH_2Ph complex (**8**), several control experiments have been done. The structure of CoPc and CuPc is shown in Scheme 2, cobalt ion coordinates with 4 nitrogen atoms of ligand phthalocyanine, it is difficult to coordinate with substrate aniline, so the reaction of phenylhydrazine (**1a**) with aniline (**2a**) gave no expected diphenylamine (**3a**) (Scheme 1, equation 6). CuPc is similar to CoPc, so using CuPc/CoPc as a catalytic system, no expected **3a** was found (Scheme 1, equation 7) because of copper ion in CuPc has no ability to coordinate with aniline. On the contrast, using $Cu(OAc)_2$/CoPc instead of CuPc/CoPc as a catalytic system, the reaction afforded diphenylamine (**3a**) in 80% yield (Scheme 1, equation 3) because of $Cu(OAc)_2$ is able to coordinate with aniline to form Cu(II)–NH_2Ph complex (**8**), it can further trap reactive phenyl radical (**7a**) to form complex **9** (Scheme 3).

Table 3 Reactions of phenylhydrazine (**1a**) with different types of amino compounds (**2**)[a]

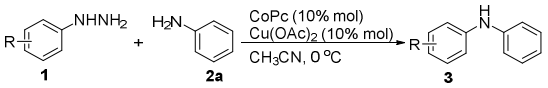


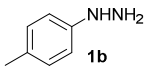
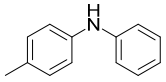
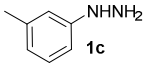
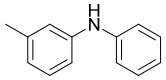
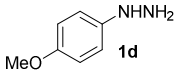
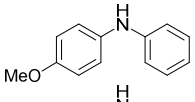
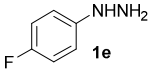
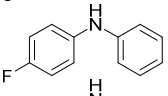
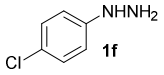
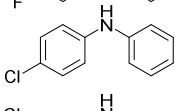
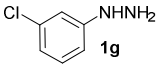
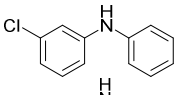
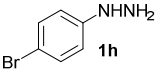
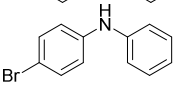
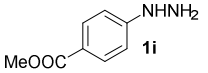
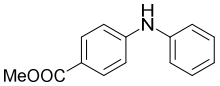
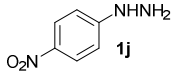
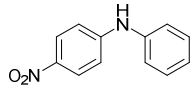
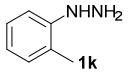
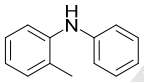
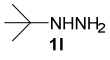
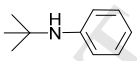
Entry	Amino compound **2**	Product **3** and yield[b]
1	 **2r**	 **3r** (57%)  **3r′** (25%)
2	 **2s**	 **3s** (58%)
3	 **2t**	 **3t** (60%)
4	 **2u**	 **3u** (trace)
5	 **2v**	 N.D. [c]
6	 **2w**	 **3w** (53%)
7	 **2x**	 **3x** (45%)
8	 **2y**	 N.D. [c]
9	 **2z**	 N.D. [c]

[a] Reaction conditions: phenylhydrazine (**1a**, 2.0 mmol in 2 mL CH_3CN) was introduced successively at a rate of 0.2 mmol per hour, amino compounds (**2**, 1.0 mmol), 10 mol% of CoPc and $Cu(OAc)_2$ in CH_3CN (5 mL) at 0 ^oC for 13 h in air;
[b] Isolated yields;
[C] Not detected.

Furthermore, $Cu(OAc)_2$-catalyzed reaction was also carried out, affording diphenylamine (**3a**) in only 6% yield (Scheme 1,

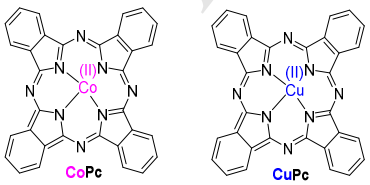
Table 4 Reactions of substituted hydrazines (**1**) with aniline (**2a**) [a]



Entry	Hydrazine **1**	Product **3** and yield [b]
1	 **1b**	 **3b**, 83%
2	 **1c**	 **3k**, 75%
3	 **1d**	 **3c**, 85%
4	 **1e**	 **3d**, 65%
5	 **1f**	 **3e**, 70%
6	 **1g**	 **3v**, 55%
7	 **1h**	 **3f**, 71%
8	 **1i**	 **3g**, 64%
9	 **1j**	 **3h**, 25%
10	 **1k**	 **3n**, 44%
11	 **1l**	 N.D.[c]

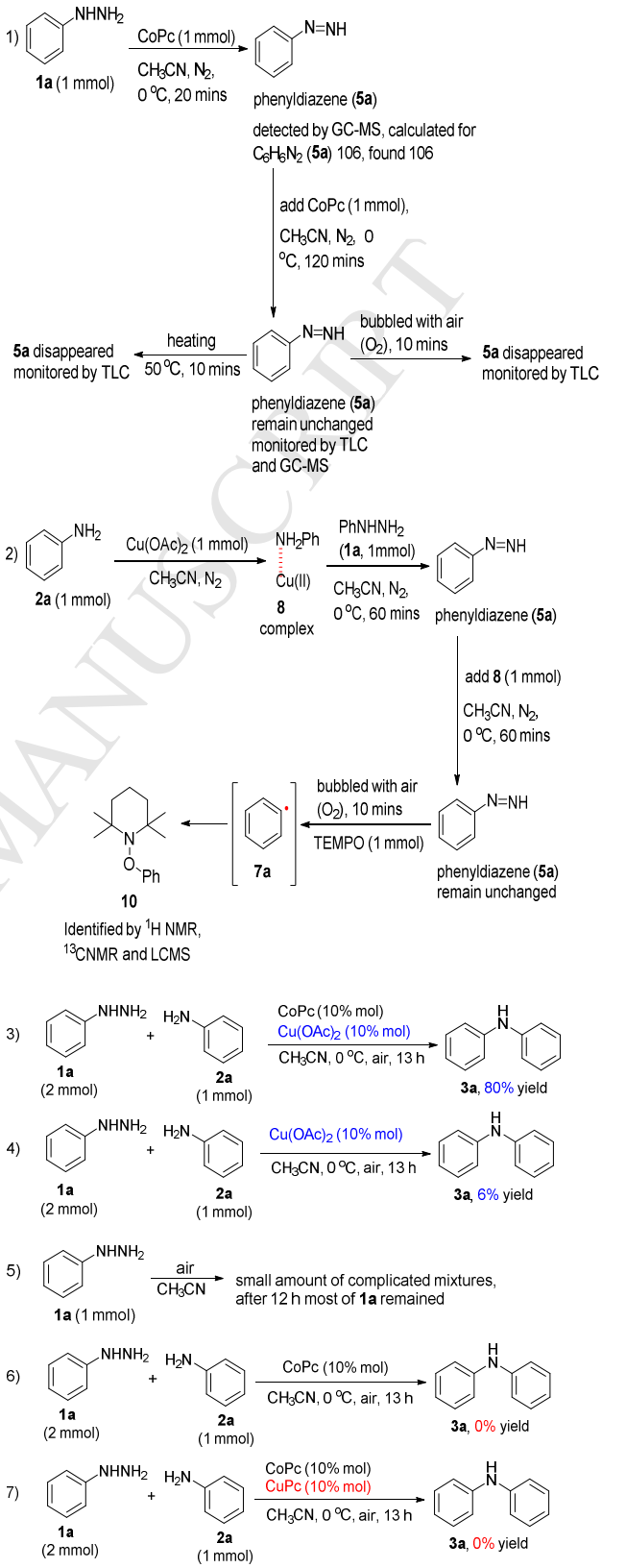
[a] Reaction conditions: substituted hydrazine (**1**, 2.0 mmol in 2 mL CH_3CN) was introduced successively at a rate of 0.2 mmol per hour, aniline (**2a**, 1.0 mmol), 10 mol% of CoPc and $Cu(OAc)_2$ in CH_3CN (5 mL) at 0 °C for 13 h in air;
[b] Isolated yields.
[c] Not detected.

equation 4) due to low efficiency of Cu(II)–NH_2Ph complex (**8**) oxidizing phenylhydrazine (**1a**) to phenyldiazine (**5a**), so the combination of CoPc/$Cu(OAc)_2$ is a better choice for N-arylation of amines with arylhydrazines leading to N-aryl amines.



Scheme 2. The structure of CoPc and CuPc

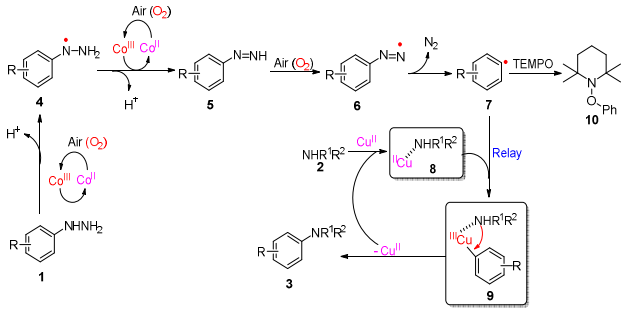
On the basis of results obtained, a plausible mechanism is proposed in Scheme 3. The arylhydrazines (**1**) can be oxidized by CoPc to form aryldiazenes (**5**) through successive oxidation processes *via* an intermediate arylhydrazyl radical (**4**).



Scheme 1. The oxidation of phenylhydrazine (**1a**) with CoPc, Cu(II)–NH_2Ph complex (**8**) and air (O_2)

Aryldiazenes (**5**) are easily oxidized to the aryldiazenyl radicals (**6**) by air (O_2), followed by release of N_2 to generate aryl radical (**7**). Aryl radical (**7**) can be trapped by complex **8** formed *in situ*

from $Cu(OAc)_2$ and amine (**2**) to produce complex **9**, followed by reductive elimination to afford product **3**.



Scheme 3. Proposed CoPc/$Cu(OAc)_2$ relay catalysis mechanism

3. Conclusion

In summary, we have developed a method for N-aryl amine synthesis through N-arylation of amines with arylhydrazines by employing air as a main oxidant, CoPc as a catalytic oxidant, and $Cu(OAc)_2$ as a catalyst. The best yields were achieved with arylamines and arylhydrazines, but N-aryl-N-alkylamines and N-alkylamines could be utilized as well. This protocol provides a general route to diarylamines, N-aryl-N-alkylamines and N,N-diary-N-alkyltriamines.

4. Experimental Section

4.1. General

All reactions were performed in air. ^{1}H NMR (400 MHz) and ^{13}C NMR (125 or 100 MHz) spectra were determined on a Varian-Inova 300 MHz or 400 MHz spectrometer with $CDCl_3$ or DMSO-d_6 as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in ppm from internal TMS (δ), all coupling constants (J values) were reported in Hertz (Hz). Mass spectra were recorded on a microTOF-Q III (ESI). Column chromatography was performed with 300-400 mesh silica gel using flash column techniques. All of the reagents were used directly as obtained commercially unless otherwise noted.

4.2. General procedure for the preparation of N-aryl amines 3.

General procedure for N-arylation of amines(2) with arylhydrazines(1). Into a 25 mL round-bottom flask, amine **(2)** (1 mmol), $Cu(OAc)_2$ (0.02 g, 0.1 mmol) and acetonitrile (4 mL) were added, the mixture was stirred and cooled to 0 °C. Then, CoPc (0.057 g, 0.1 mmol) was added, the solution of arylhydrazine **(1)** (2 mmol) in acetonitrile (2 mL) was added successively at a rate of 0.2 mmol per hour while stirring for 13 hours in air. After completion of the reaction (monitored by TLC analysis (developing solvent: ethyl acetate/petroleum ether (1:8)), the mixture was filtered, concentrated, and the residue was further purified by column chromatography using ethyl acetate/petroleum ether (1:100) as eluent to afford N-aryl amine **3**.

4.3 Characterization

*Diphenylamine (**3a**).* [13]

White solid; m.p. 52–54 °C, yield 80% (135.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.29 (m, 4H), 7.07–7.09 (m, 4H), 6.93 (t, J = 7.3 Hz, 2H), 5.74 (br, s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1, 129.4, 121.0, 117.8. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{12}H_{12}N$ 170.1, found 170.1.

*4-Methyl-N-phenylaniline (**3b**).* [13]

White solid; m.p. 86–89 °C, yield 79% (144.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21–7.25 (m, 2H), 7.08 (d, J = 8.2 Hz, 2H), 6.99–7.01 (m, 4H), 6.87 (t, J = 7.3 Hz, 1H), 5.59 (br, s, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 140.3, 131.0, 129.9, 129.3, 120.3, 118.9, 116.9, 20.7. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{13}H_{14}N$ 184.1, found 184.1.

*4-Methoxy-N-phenylaniline (**3c**).* [13]

White solid; m.p. 99–101 °C, yield 80% (159.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (t, J = 7.7 Hz, 2H), 7.07 (d, J = 5.7 Hz, 2H), 6.83–6.91 (m, 5H), 5.49 (br, s, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 145.3, 135.8, 129.3, 122.2, 119.6, 115.6, 114.7, 55.6. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{13}H_{14}NO$ 200.1, found 200.1.

*4-Fluoro-N-phenylaniline (**3d**).* [13]

Brown solid; m.p. 35–36 °C, yield 70% (130.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22–7.25 (m, 2H), 6.95–7.06 (m, 6H), 6.90 (t, J =7.3 Hz, 1H), 5.59 (br, s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 156.9, 143.9, 138.9 (d, J = 2.4 Hz), 129.4, 120.6 (d, J = 8.2 Hz), 116.8, 116.0 (d, J = 22.5 Hz). MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{12}H_{11}FN$ 188.1, found 188.1.

*4-Chloro-N-phenylaniline (**3e**).* [13]

Brown solid; m.p. 66–68 °C, yield 74% (150.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27–7.29 (m, 2H), 7.18–7.22 (m, 2H), 7.04 (d, J = 7.7 Hz, 2H), 6.93–6.99 (m, 3H), 5.66 (br, s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.7, 141.9, 129.5, 129.3, 125.5, 121.5, 118.8, 118.1. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{12}H_{11}ClN$ 204.1, found 204.1.

*4-Bromo-N-phenylaniline (**3f**).* [1]

Brown solid; m.p. 85–86 °C, yield 75% (186.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, J = 8.7 Hz, 2H), 7.25–7.29 (m, 2H), 7.05 (d, J = 7.7 Hz, 2H), 6.92–6.98 (m, 3H), 5.66 (br, s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.5, 142.4, 132.2, 129.5, 121.7, 119.0, 118.3, 112.6. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{12}H_{11}BrN$ 248.0, found 248.0.

*Methyl 4-(phenylamino)benzoate (**3g**).* [14]

Colorless solid; m.p. 115–117 °C, yield 69% (156.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89–7.93 (m, 2H), 7.31–7.35 (m, 2H), 7.15–7.18 (m, 2H), 7.04–7.08 (m, 1H), 6.96–7.00 (m, 2H), 6.08 (br, s, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 148.1, 140.9, 131.5, 129.5, 123.1, 121.1, 120.4, 114.6, 51.7. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{14}H_{14}NO_2$ 228.1, found 228.1.

*4-Nitro-N-phenylaniline (**3h**).* [15]

Yellow solid; m.p. 132–134 °C, yield 58% (124.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, J = 9.1 Hz, 2H), 7.39 (t, J = 7.9 Hz, 2H), 7.15–7.22 (m, 3H), 6.94 (d, J = 9.1 Hz, 2H), 6.27 (br, s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.2, 139.8, 139.5, 129.8, 126.3, 124.7, 122.0, 113.7. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{12}H_{11}N_2O_2$ 215.1, found 215.1.

*4-(Phenylamino)benzonitrile (**3i**).* [16]

Yellow solid; m.p. 97–98 °C, yield 60% (116.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, J = 8.6 Hz, 2H), 7.36 (t, J = 7.8 Hz, 2H), 7.17 (d, J = 7.8 Hz, 2H), 7.12 (t, J = 7.4 Hz, 1H), 6.97 (d, J = 8.6 Hz, 2H), 6.09 (br, s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.0, 140.0, 133.8, 129.7, 124.0, 121.3, 119.9, 114.9, 101.5. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{13}H_{11}N_2$ 195.1, found 195.1.

*N-Phenyl-1,4-benzenediamine (**3j**).* [17]

Brown solid; m.p. 69–71 °C, yield 72% (132.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (dd, J = 8.2, 7.6 Hz, 2H), 6.97 (d, J = 8.4 Hz, 2H), 6.85 (d, J = 7.8 Hz, 2H), 6.79 (t, J = 7.3 Hz, 1H), 6.67 (d, J = 8.4 Hz, 2H), 5.39 (br, s, 1H), 3.18 (br, s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.9, 142.1, 133.9, 129.3, 12.3, 119.0, 116.2, 115.1. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{12}H_{13}N_2$ 185.1, found 185.1.

*3-Methyl-N-phenylaniline (**3k**).* [14]

Yellow solid; m.p. 30–31 °C, yield 76%(139.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (t, J = 7.8 Hz, 2H), 7.13 (t, J = 8.1 Hz, 1H), 7.03 (d, J = 8.1 Hz, 2H), 6.86–6.92 (m, 3H), 6.73 (d, J = 7.5 Hz, 1H), 5.59 (br, s, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 143.2, 139.3, 129.4, 129.3, 122.0, 120.9, 118.6, 117.9, 115.0, 21.6. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{13}H_{14}N$ 184.1, found 184.1.

*3-Nitro-N-phenylaniline (**3l**).* [15]

Yellow solid; m.p. 86–88 °C, yield 56% (120.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (t, J = 2.1 Hz, 1H), 7.69 (dd, J = 8.0, 1.2 Hz, 1H), 7.27–7.38 (m, 4H), 7.14 (d, J = 7.6 Hz, 2H), 7.08 (t, J = 7.4 Hz, 1H), 5.94 (br, s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.3, 145.1, 140.9, 130.0, 129.7, 123.2, 121.8, 119.9, 114.7, 110.3. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{12}H_{11}N_2O_2$ 215.1, found 215.1.

*2-Nitro-N-phenylaniline (**3m**).* [18]

Yellow solid; m.p. 74–75 °C, yield 30% (64.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.49 (br, s, 1H), 8.20 (dd, J = 8.6, 1.3 Hz, 1H), 7.42 (t, J = 7.8 Hz, 1H), 7.39–7.33 (m, 1H), 7.21–7.29 (m, 4H), 6.75–6.79 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.1, 138.7, 135.7, 133.2, 129.7, 126.7, 125.6, 124.4, 117.5, 116.0. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{12}H_{11}N_2O_2$ 215.1, found 215.1.

*2-Methyl-N-phenylaniline (**3n**).* [19]

Brown solid; m.p. 39–40 °C, yield 75% (137.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (t, J = 7.8 Hz, 3H), 7.18 (d, J = 7.2 Hz, 1H), 7.12 (t, J = 7.6 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 6.91–6.86 (m, 1H), 5.28 (br, s, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 141.2, 131.0, 129.4, 128.4, 126.8, 122.1, 120.5, 118.9, 117.5, 18.0. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{13}H_{14}N$ 184.1, found 184.1.

*2,6-Diethyl-N-phenylaniline (**3o**).* [20]

Amber oil, yield 56% (126.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11–7.23 (m, 5H), 6.72 (t, J = 7.3 Hz, 1H), 6.48 (d, J = 7.7 Hz, 2H), 5.14 (br, s, 1H), 2.58 (q, J = 7.5 Hz, 4H), 1.14 (t, J = 7.6 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.3, 142.3, 136.9, 129.2, 126.7, 126.5, 117.9, 113.2, 24.7, 14.7. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{16}H_{20}N$ 226.2, found 226.2.

*2-(tert-Butyl)-N-phenylaniline (**3p**).* [21]

Yellow oil, yield 58% (130.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (dd, J = 7.9, 1.4 Hz, 1H), 7.27 (dd, J = 7.9, 1.3 Hz, 1H), 7.14–7.23 (m, 3H), 7.04–7.08 (m, 1H), 6.79–6.82 (m, 3H), 5.39 (br, s, 1H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.0, 143.4, 141.2, 129.3, 127.1, 126.9, 126.0, 123.9, 119.2, 116.0, 34.9, 30.6. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{16}H_{20}N$ 226.2, found 226.2.

*N-Phenylbenzene-1,2-diamine (**3q**).* [22]

Brown solid; m.p. 78–80 °C, yield 35% (64.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18–7.23 (m, 2H), 7.11 (d, J = 7.7 Hz, 1H), 7.01 (t, J = 7.3 Hz, 1H), 6.72–6.83 (m, 5H), 5.12 (br, s, 1H), 3.64 (br, s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4, 141.9, 129.3, 128.6, 125.7, 124.9, 119.3, 119.2, 116.2, 115.2. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{12}H_{13}N_2$ 185.1, found 185.1.

*N^1, N^2-Diphenylbenzene-1,2-diamine (**3q'**).* [23]

Brown solid; m.p. 107–108 °C, yield 40% (104.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21–7.29 (m, 6H), 6.91–7.04 (m, 8H), 5.57 (br, s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 134.9, 129.3, 123.0, 120.6, 120.3, 117.3. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{18}H_{17}N_2$ 261.1, found 261.1.

*N-Phenylnaphthalen-2-amine (**3r**).* [14]

White solid; m.p. 107–108 °C, yield 57% (125.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.6 Hz, 2H), 7.64 (d, J = 8.2 Hz, 1H), 7.43 (d, J = 1.8 Hz, 1H), 7.38–7.42 (m, 1H), 7.28–7.32 (m, 3H), 7.22 (dd, J = 8.8, 2.3 Hz, 1H), 7.15–7.17 (m, 2H), 6.98 (t, J = 7.3 Hz, 1H), 5.82 (br, s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.7, 140.6, 134.6, 129.5, 129.4, 129.3, 127.7, 126.6, 126.5, 123.7, 121.8, 120.1, 118.5, 112.1. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{16}H_{14}N$ 220.1, found 220.1.

*N,1-Diphenylnaphthalen-2-amine (**3r'**).* [24]

Brown oil, yield 25% (73.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74–7.78 (m, 2H), 7.58 (d, J = 8.9 Hz, 1H), 7.51 (t, J = 7.4 Hz, 2H), 7.41–7.45 (m, 1H), 7.33–7.38 (m, 3H), 7.27–7.30 (m, 2H), 7.19–7.24 (m, 2H), 7.00 (d, J = 7.7 Hz, 2H), 6.92 (t, J = 7.3 Hz, 1H), 5.53 (br, s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6, 138.1, 136.7, 133.9, 131.0, 129.39, 129.38, 129.3, 128.4, 128.0, 127.9, 126.4, 125.3, 125.0, 123.4, 121.5, 118.9, 118.7. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{22}H_{18}N$ 296.1, found 296.1.

*N-Phenylpyridin-2-amine (**3s**).* [25]

Colorless solid; m.p. 106–108 °C, yield 58% (98.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19–8.20 (m, 1H), 7.45–7.49 (m, 1H), 7.33 (s, 2H), 7.32 (s, 2H), 7.08 (br, s, 1H), 7.02–7.06 (m, 1H), 6.88 (d, J = 8.4 Hz, 1H), 6.70–6.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.2, 148.3, 140.5, 137.8, 129.3, 122.8, 120.5, 114.9, 108.2. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{11}H_{11}N_2$ 171.1, found 171.1.

*N-Methyl-N-phenylaniline (**3t**).* [26]

Brown oil, yield 60% (110.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.29 (m, 4H), 7.01–7.03 (m, 4H), 6.93–6.97 (m, 2H), 3.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.0, 129.2, 121.3, 120.5, 40.3. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{13}H_{14}N$ 184.1, found 184.1.

*3-Chloro-N-phenylaniline (**3v**).* [18]

Brown oil, yield 55% (112.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26–7.30 (m, 2H), 7.13 (t, J = 8.0 Hz, 1H), 7.05–7.07 (m, 2H), 6.96–7.01 (m, 2H), 6.83–6.87 (m, 2H), 5.67 (br, s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 142.0, 135.0, 130.4, 129.5, 122.1, 120.5, 119.0, 116.7, 115.2. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{12}H_{11}ClN$ 204.1, found 204.1.

*N-Benzylaniline (**3w**).* [27]

Brown oil, yield 53% (97.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23–7.36 (m, 5H), 7.16 (t, J = 7.8 Hz, 2H), 6.70 (t, J = 7.3 Hz, 1H), 6.61 (d, J = 8.1 Hz, 2H), 4.29 (s, 2H), 3.98 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2, 139.5, 129.3, 128.7, 127.6, 127.3, 117.6, 112.9, 48.4; MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{13}H_{14}N$ 184.1, found 184.1.

*N-Hexylaniline (**3x**).* [27]

Brown oil, yield 45% (79.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (t, J = 7.9 Hz, 2H), 6.68 (t, J = 7.3 Hz, 1H), 6.60 (d, J = 7.7 Hz, 2H), 3.58 (br, s, 1H), 3.10 (t, J = 7.1 Hz, 2H), 1.57–1.65 (m, 2H), 1.30–1.43 (m, 6H), 0.90 (t, J = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.5, 129.2, 117.0, 112.7, 44.0, 31.7, 29.6, 26.9, 22.6, 14.1. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{12}H_{20}N$ 178.2, found 178.2.

2,2,6,6-Tetramethyl-1-phenoxypiperidine (***10***).[28]

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.12 (m, 4H), 6.89–6.80 (m, 1H), 1.67–1.54 (m, 5H), 1.45–1.39 (m, 1H), 1.24 (s, 6H), 1.02 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.1, 128.2, 119.4, 113.4, 59.8, 39.3, 32.1, 20.0, 16.6. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{15}H_{23}NOH$ 234.1, found 234.1.

Supplementary data

The copies of the ^{1}H NMR and ^{13}C NMR spectra for the products are available.

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