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Copper(I)-catalysed homo-coupling of aryldiazonium salts: synthesis of symmetrical biaryls

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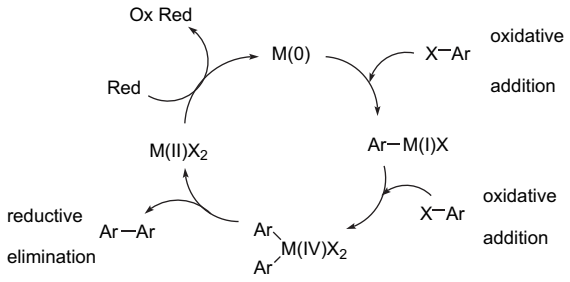
Abstract—Copper(I) triflate acts as an efficient stoichiometric reagent for the homo-coupling of aryldiazonium salts bearing electron-withdrawing group(s), to yield symmetrical biaryls in acetonitrile under mild reaction conditions. Aryldiazonium salts bearing electron-donating groups undergo the reaction by using catalytic amounts of a copper complex prepared in situ from copper(II) triflate and 2,2′-bipyridine with metallic copper as an ultimate reductant.

1. Introduction

Biaryls represent a very important class of organic compounds since numerous compounds of a natural origin, pharmaceuticals and optoelectronics contain this structural motif.[1,2] Thus aryl–aryl bond forming reactions have been the theme of numerous papers during the last century.[3,4] Several efficient reactions for synthesis of almost all types of biaryls have been developed. The first practical reported reaction was the Ullmann reaction, which involves heating aryl halide(s) with an excess of copper powder in (or without) suitable solvent, e.g. DMF, at elevated temperatures affording the corresponding (un)symmetrical biaryls.[5,6] Besides the Ullmann reaction and its numerous variants,[7–9] a great number of methods based on nickel- or palladium-catalysed homo- and cross-couplings of aryl halides and sulfonates to symmetrical and unsymmetrical biaryls have been developed.[10–21]

These reactions are catalysed by various nickel(0)-[10–17] or palladium(0)-complexes,[18–21] e.g. $M(PPh_3)_4$ (M=Ni, Pd), in the presence of stoichiometric reductants, e.g. active metals (Zn, Al, Mn),[12–16] tertiary amines,[18–21] isopropanol,[19–21] hydrazine,[22] tetrakis(dimethylamino)ethylene,[23] molecular hydrogen,[24] sodium hydride,[25] sodium formate,[26] hydroquinone,[27] etc. In all of these reactions, oxidative addition of catalytically active zero-valent nickel- or palladium-complexes to aryl electrophiles is taking place to form the respective arylnickel(II)-[28] or arylpalladium(II)-species.[29] These complexes further react in a second step of oxidative addition with another molecule of aryl electrophile to give the corresponding diarylnickel(IV),[10,28] or diarylpalladium(IV) complexes.[21,30] The latter diarylmetallic complexes are very unstable, and readily undergo the reductive elimination of the biaryl to produce nickel(II)- or palladium(II)-complexes.[10,28] The role of terminal reductants is to reduce nickel(II) or palladium(II) to the appropriate zero-valent complexes thus closing the catalytic cycle (Scheme 1).



Scheme 1.

The reaction mechanism of the Ullmann and related copper(0)- or copper(I)-mediated reactions is, at least partially, close to that presented in Scheme 1,[31] except that the reductive elimination proceeds from oligomeric diarylcopper-complexes,[32,33] and not from monomeric diarylcoppers. The difference between these reactions, and various reactions developed for the synthesis of unsymmetrical biaryls, e.g. Kharasch,[34] Negishi,[35] Stille,[36] or Suzuki–Miyaura reactions,[37] is the different method of in situ preparation of

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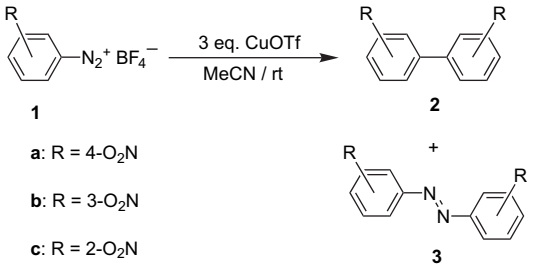
unstable diarylnickel- or diarylpalladium-complexes. The latter reactions proceed via unsymmetrical diarylmetallic complexes which, by reductive elimination, give unsymmetrical biaryls. Aryl halides and various types of aryl sulfonates[16,38] are extensively studied aryl electrophiles in both homo-coupling reactions catalysed by copper(I)-,[39–41] nickel-, or palladium-complexes, and in cross-coupling reactions with various arylmetallic reagents. On the other hand, aryldiazonium salts have been relatively neglected in the synthesis of biaryls. Aryldiazonium salts have found an application in the Gomberg–Bachmann–Hey reaction whose phase-transfer variant (ptGBH) provides an important, effective and inexpensive access to relatively simple unsymmetrical biaryls.[42] Furthermore, aryldiazonium salts have been also employed in the Pschorr reaction, which has been the premier method for the preparation of phenanthrene derivatives for a long time.[43] Additionally, aryldiazonium salts have been reported to participate in the Suzuki–Miyaura reaction with a great success.[44] More recently, Motherwell's group described that 2-tosyloxyphenyldiazonium- and 2-(*N*-tosyl-*N*-methylamino) phenyldiazonium-salts are suitable for synthesis of 2-hydroxy- and 2-alkylamino-biphenyls.[45] However, the synthesis of biaryls by homo-coupling of aryldiazonium salts has been barely explored.[46–48] This reaction, known as Gattermann synthesis of biaryls, was discovered as a side-reaction during studies on the Gattermann synthesis of aryl halides by reactions of aryldiazonium salts with copper(I) halides. A classical procedure for the homo-coupling of aryldiazonium salts to symmetrical biaryls employs an aqueous solution of copper(I) reagent prepared by reduction of an ammoniacal solution of copper(II) sulfate with hydroxylamine.[46,47] In particular, diphenic acid was obtained by this method in very high yield.[47] However, substrates lacking suitable co-ordinating groups in the *ortho*-position to the diazonium group give very low yields making this method rather useless. Cohen and co-workers[48] reported that copper(I) perchlorate (5 equiv) in the presence of copper(II) perchlorate (4 equiv) efficiently coupled 4-nitrophenyldiazonium tetrafluoroborate (**1a**; a single example) in acetone as solvent, at very high dilution, where a high yield of 4,4′-dinitrobiphenyl (**2a**) was obtained. According to these results, copper(I)-catalysed homo-coupling of aryldiazonium salts does proceed via arylcopper intermediates. Besides this excellent study, not much attention has been paid to the development of a practical method for coupling of aryldiazonium salts to biaryls.

2. Results and discussion

We wish to report that copper(I) triflate acts as an efficient stoichiometric reagent for the homo-coupling of aryldiazonium salts **1a–i** to yield symmetrical biaryls **2a–i** (Scheme 2). Copper(I) triflate was conveniently prepared in situ by reduction of copper(II) triflate with copper bronze. The starting substrates must contain at least one electron-withdrawing group, e.g. nitro or carboxymethyl. Acetonitrile proved to be the most suitable reaction medium for this coupling reaction. Acetone, *N*,*N*-dimethylformamide, methanol, tetrahydrofuran, as well as mixtures of acetonitrile with methanol or water were tested as alternative reaction solvents, but reaction yields were significantly lower, presumably due to the fact that reduction of copper(II) triflate with copper bronze did not proceed adequately. Moreover, the reactions performed in THF and DMF gave predominant amounts of the parent arenes arising from aryldiazonium salt-reduction. When the preparation of CuOTf was carried out in acetonitrile, followed by dilution with methanol or water, significantly diminished yields were also obtained (Table 1). The optimal amount of copper(I) triflate proved to be 3 equiv per single aryl–aryl bond to be formed. The reactions start as soon as aryldiazonium salts are added to a clear solution of copper(I) triflate in acetonitrile. These reactions proceed smoothly at 0 °C to room temperature, with evolution of gaseous nitrogen, affording the respective biaryls **2a–i** in fair yields. Apart from homo-coupling, two possible side-reactions are proceeding simultaneously: the formation of azo-compounds **3d–f**, **i**, and the parent arenes from reduction.



Scheme 2.

Table 1. Copper(I) triflate-catalysed homo-coupling of aryldiazonium salts **1a–i** to yield symmetrical biaryls **2a–i** (Scheme 2)[a]

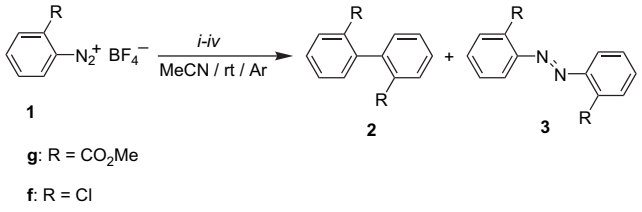
Entry	R	Product	Time[b] (h)	Yield of **2**[c] (%)	Yield of **3**[c] (%)
1	4-NO_2	**a**	20	66[d]	0
2	3-NO_2	**b**	18	82[e]	0
3	2-NO_2	**c**	18	70	0
4	4-Cl	**d**	24	58	20
5	3-Cl	**e**	22	47	33
6	2-Cl	**f**	20	5	44
7[f]	2-CO_2Me	**g**	24	96[g]	0
8	4-Cl-2-O_2N	**h**	20	80	0
9	4-Cl-2-Bz	**i**	22	65	24

[a] All reactions were performed at 0 °C (2 h) followed by room temperature in dried MeCN under an inert atmosphere (Ar) unless otherwise noted.
[b] Determined by a test with aqueous sodium β-naphthoxide. The disappearance of a red colour indicates the absence of the starting aryldiazonium salt.
[c] Yields of pure products isolated by chromatography.
[d] Nitrobenzene (28%) as reduction by-product was also isolated.
[e] Nitrobenzene (12%) was also isolated.
[f] In alternative reaction solvents the following yields (%) of **2g** were obtained: MeOH (6%); DMF (7%); THF (7%); acetone (33%); MeCN/MeOH (1:1; 85%); MeCN/H_2O (1:1; 71%). In all these reactions small amounts of methyl benzoate (2–7%) as reduction by-product were isolated, whilst in DMF (37%), and THF (44%) this became the major process.
[g] Methyl benzoate (4%) as reduction side-product was also isolated.

The reaction was generally shown to be strongly dependent on the electronic nature of the substituent(s) on the phenyl ring. Aryldiazonium salts bearing strong electron-withdrawing group(s), and those with co-ordinating, moderately strong electron-withdrawing groups *ortho* to the diazonium group, e.g. methoxycarbonyl, undergo the reaction smoothly giving the expected biaryls in moderate-to-high yields. Thus 2-methoxycarbonyl-substituted diazonium salt **1g** underwent the reaction to give an almost quantitative yield of biaryl **2g**. In contrast, aryldiazonium salts with moderately strong electron-withdrawing groups such as chloro, also afforded significant amounts of the corresponding azo-compounds. For instance, 2-chlorophenyldiazonium tetrafluoroborate (**1f**) gave a complex mixture with the predominant formation of 2,2′-dichloroazobenzene (**3f**) as the main product (44%). Although the chloro (halide) substituent is actually a σ-acceptor, it is also a π-donor. This might explain why results similar to those with electron-rich aryldiazonium salts were obtained.

Phenyldiazonium tetrafluoroborate (**1j**), under the same reaction conditions, afforded a mixture of biphenyl (**2j**; 26%) and azobenzene (**3j**; 20%). Moreover, aryldiazonium salts **1j–p** without electron-withdrawing groups, or with electron-donating substituents on phenyl ring, could not be efficiently converted to the corresponding biaryls **2i–p** since poor yields (0–28%) were obtained. In these cases, formation of the respective azo-compounds **3j–p** became the major process (20–50%). The formation of azo-compounds in homo-couplings of electron-rich aryldiazonium salts with aqueous solution of the complex of copper(I) hydroxide and aqueous ammonia has been reported previously.[49]

Further improvement was achieved by using a catalytic variant of this stoichiometric copper(I) triflate-based method. The catalytic procedure was performed by stirring a mixture of aryldiazonium salt and catalytic amounts of copper(II) triflate (10–30 mol %) with an excess of copper bronze (3 equiv) in anhydrous acetonitrile (Scheme 3). Although this method in the model reaction of homo-coupling of 2-methoxycarbonylphenyldiazonium tetrafluoroborate (**1g**) to the respective 2,2′-dimethoxycarbonylbiphenyl (**2g**) gave lower yields (63–78% vs 97% in stoichiometric method), it allows the use of alternate copper(I) complexes (Table 2). A brief examination of the influence of 2,2′-bipyridine (bpy) (a widely explored ligand in the chemistry of copper complexes) showed that decreased electron-density at the copper(I)-centre is essential for increased selectivity with respect to biaryl versus azo-compound formation. Thus, in the homo-coupling reaction of 2-chlorophenyldiazonium



Scheme 3. (i) 10–30 mol % $Cu(OTf)_2$; 3 equiv Cu; (ii) 20 mol % $Cu(OTf)_2$; 20 mol % bpy; 3 equiv Cu; (iii) 3 equiv CuOTf; 2 equiv KOAc; (iv) 3 equiv CuOTf; 3 equiv bpy; 2 equiv KOAc.

Table 2. Catalyst effect on the homo-coupling reactions of 2-methoxycarbonylphenyl- (**1g**) and 2-chlorophenyl-diazonium tetrafluoroborates (**1f**) (Scheme 3)[a]

Entry	Reactant	$Cu(OTf)_2$ (mol %)	Ligand (mol %)	Additive (2 equiv)	Time[b] (h)	Yield of **2**[c] (%)	Yield of **3** (%)
1	**1g**	10	—	—	26	67[d]	—
2	**1g**	20	—	—	21	78[e]	—
3	**1g**	30	—	—	20	63[e]	—
4	**1g**	20	bpy (20)	—	20	59[f]	—
5	**1f**	20	—	—	22	18	27
6	**1f**	20	bpy (20)	—	22	27	20
7[g]	**1f**	300	—	KOAc	18	31	32
8	**1f**	20	bpy (20)	KOAc	26	0	Trace
9[h]	**1f**	300	bpy (300)	KOAc	20	36	40

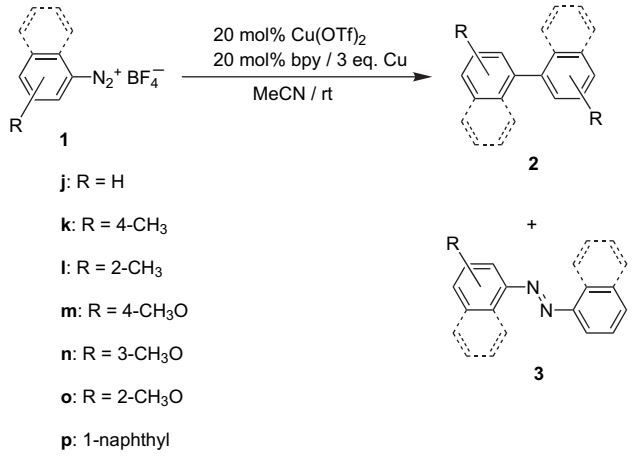
[a] All reactions were performed at 0 °C (2 h) and then at room temperature in anhydrous MeCN, in the presence of copper bronze (3 equiv) under an inert atmosphere (Ar) unless otherwise noted.
[b] Determined by a test with aqueous sodium β-naphthoxide. The disappearance of a red colour indicates the absence of the starting aryldiazonium salt.
[c] Yields of pure products isolated by chromatography.
[d] Reduction by-product, methyl benzoate (4%) was also isolated.
[e] Traces of reduction side-product, methyl benzoate were also detected (TLC).
[f] Reduction side-product methyl benzoate (15%) was also isolated.
[g] The reactions were conducted with previously prepared CuOTf.
[h] The reactions were performed with previously prepared Cu(bpy)OTf.

tetrafluoroborate (**1f**) the yield of expected 2,2′-dichlorobiphenyl (**2f**) was increased from 5% (Table 1, entry 6) to 27% (Table 2, entry 6) accompanied with significantly reduced amounts of the corresponding azo-compound **3f** (44% to 20%). Although the yield was still low, this method was further proved as reasonably effective in the homo-coupling reactions of aryldiazonium salts bearing electron-donating groups.

An alternative reaction pathway might include the copper(I)-catalysed homo-coupling of unstable aryldiazonium acetates generated in situ by reaction of the starting aryldiazonium salt and potassium acetate.[42] Unfortunately, 2-chlorophenyldiazonium tetrafluoroborate (**1f**) in reaction with an excess of CuOTf (3 equiv) in the presence of KOAc (2 equiv) gave almost equimolar amounts of expected 2,2′-dichlorobiphenyl (**2f**) and azo-compound **3f** in moderate yields (Table 2, entry 7). The use of a catalytic variant of this method, employing 20 mol % of $Cu(bpy)(OTf)_2$ in the presence of an excess of copper bronze (3 equiv) and potassium acetate (2 equiv) gave no reaction, presumably as a result of rapid decomposition of aryldiazonium acetate, prior to the desired homo-coupling reaction (entry 8). Additionally, no further improvement could be achieved by using the super-stoichiometric amounts of Cu(bpy)OTf (3 equiv) (entries 7 and 9).

This catalytic method based on copper(II) triflate and 2,2′-bipyridine (20 mol %) with copper bronze (3 equiv) as the ultimate reductant, in acetonitrile as solvent under ambient reaction conditions was further examined in the homo-coupling of electron-rich aryldiazonium salts **1j–p** (Scheme 4). Although the corresponding azo-compounds **3j–p** were still obtained in certain amounts, biaryls **2j**,**k**,**m–p** were isolated in moderate-to-good yields (Table 3). Unfortunately, the diazonium salt derived from the electron-rich aromatic compound 1-naphthyldiazonium tetrafluoroborate (**1p**)

failed to give the expected biaryl **2p** in practically useful yield.



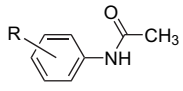
Scheme 4.

Table 3. Copper(II) triflate/2,2′-bipyridine-catalysed homo-coupling of aryldiazonium salts **1j–p** to yield symmetrical biaryls **2j**,**k**,**m–p** in the presence of copper bronze (Scheme 4)[a]

Entry	R	Product	Time[b] (h)	Yield of **2**[c] (%)	Yield of **3**[c] (%)
1	H	**j**	18	71	5
2	4-CH_3	**k**	16	60	10
3	2-CH_3	**l**	20	—[d]	—
4	4-CH_3O	**m**	24	47	21
5	3-CH_3O	**n**	22	79[e]	—
6	2-CH_3O	**o**	18	51	17
7	1-Naphthyl	**p**	24	7	21[f]

[a] All reactions were performed at room temperature in anhydrous MeCN under an inert atmosphere (Ar) unless otherwise noted.
[b] Determined by a test with aqueous sodium β-naphthoxide. The disappearance of a red colour indicates the absence of unreacted aryldiazonium salt.
[c] Yields of pure products isolated by preparative chromatography.
[d] *N*-(2-Tolyl)acetamide (**4l**) was isolated as the sole product (34%).[50]
[e] *N*-(3-Methoxyphenyl)acetamide (**4n**) was isolated as a by-product (17%).
[f] In the stoichiometric CuOTf-mediated method only azo-compound **3p** (31%) was isolated.

Also 2-tolyldiazonium tetrafluoroborate (**1l**) failed to give the biaryl **2l**, since *N*-(2-tolyl)acetamide (**4l**)[50] was isolated as the sole product. This kind of side-product was also detected in the homo-coupling reaction of 3-methoxyphenyldiazonium tetrafluoroborate (**1n**) where the corresponding acetamide derivative **4n** was isolated in a 27% yield.



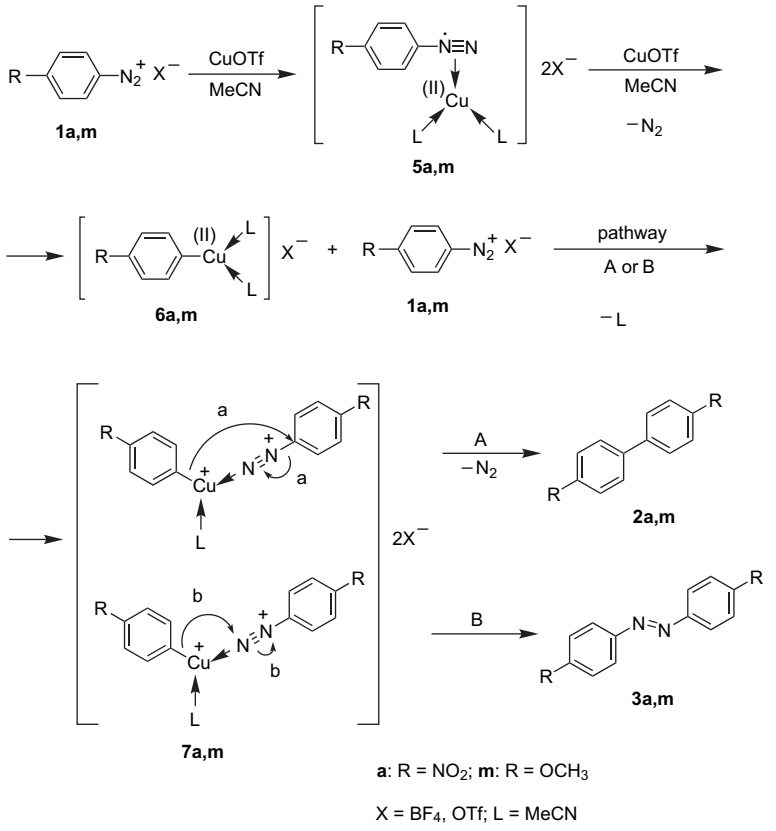
4l: R = 2-CH_3

4n: R = 3-CH_3O

The reaction presumably proceeds by one-electron reduction of the aryldiazonium salt, e.g. **1a**, with copper(I) to give complex **5** (Scheme 5). The formation of free aryl-radicals in copper(I)-induced decomposition of aryldiazonium salts is a well documented process.[48,51,52] From complex **5**, nitrogen can be eliminated to generate free aryl-radicals capable of intramolecular attack on the adjacent susceptible groups such as alkyl groups. As a result of this side-reaction pathway, the respective indazoles are obtained.[42,53] Also, nitrogen can be eliminated by nucleophilic substitution with acetonitrile (reaction solvent) to generate the *N*-aryl nitrilium ion, which upon addition of water gives the appropriate *N*-arylacetamides (Table 3, entries 3 and 5).[50] Alternatively, the complex **5** is reduced by another equivalent of copper(I) triflate forming the arylcopper(I) complex **6** (oxidative addition product). This reacts with another molecule of the starting aryldiazonium salt **1a** (**1m**) to give the complex **7a** (or **7m**; 2:1 stoichiometry). The formation of arylcopper(I) species in the reaction of 4-nitrophenyldiazonium tetrafluoroborate (**1a**) with an excess of copper(I) perchlorate is also well documented (although at very high dilution factor in acetone).[48] The complex **7a** (**7m**) undergoes two alternative reaction pathways. If the aromatic ring of complexed aryldiazonium salt bears an electron-withdrawing group(s), e.g. **1a**, the copper-assisted aromatic nucleophilic substitution of diazonium group (nitrogen as leaving group) with adjacent aryl-carbanion (S_N1-type), accompanied with elimination of molecular nitrogen, is the favoured reaction pathway. In this manner, the new aryl–aryl, C–C, bond is generated (pathway A). In contrast, electron-donating groups increase the electron-density at the nitrogen centre in complexed aryldiazonium salt-moiety, e.g. **1m**, to facilitate the copper-assisted addition of aryl-carbanion to the nitrogen centre (pathway B), which leads to the predominant formation of azo-compounds, e.g. **3m**. Possible aggregation (eventually dimerisation) of the complexes **6** and **7** cannot be excluded since analogous process is readily proceeding in numerous examples of known arylcopper complexes, e.g. $Ar_4Cu_6L_2$ ($L{=}CF_3CO_2^-$).[32,33] However, we believe that higher aggregation under our reaction conditions (homogeneous acetonitrile solution), in the absence of potentially bridged ligands (halogens, trifluoroacetate anion), cannot be a dominant process.

The reaction solvent, acetonitrile, obviously plays an important role in the reaction since it, acting as a ligand, stabilises the intermediate arylcopper species. Solvents which are not suitable ligands cannot facilitate the reaction efficiently (acetone), supress the reaction (toluene, MeOH), or cause totally different reaction pathways—the reduction of aryldiazonium salt to the parent arene (THF, DMF). The homo-coupling reactions conducted in THF or DMF showed that arylcopper intermediates, such as complexes **5**–**7**, are less stabilised and prone to homolytic decomposition with the generation of aryl-radicals. The latter reacts with the reaction solvent (hydrogen abstraction) such as THF or DMF[53] to give the corresponding reduction side-products, or attack the adjacent susceptible alkyl group, e.g. methyl, to form the respective indazole.[42]

In the Cu(bpy)OTf-catalysed method, copper bronze acts as the ultimate reductant for copper(II) complex formed during the course of the reaction, thus closing the catalytic cycle. We believe that this plausible mechanism is in good accordance with the experimental results, and provides reasonable



Scheme 5.

explanations for the main reaction pathways, as well as the described side-reactions.

3. Conclusion

Copper(I) triflate effectively catalyses the homo-coupling reaction of aryldiazonium tetrafluoroborates to the respective biaryls in acetonitrile as solvent under mild reaction conditions. The reaction is strongly dependent on the electronic nature of substituents in the aryldiazonium salts. The latter, bearing electron-withdrawing groups, were efficiently coupled to biaryls with copper(I) triflate as stoichiometric reagent (3 equiv per single aryl–aryl bond), whilst those without electron-withdrawing substituents effectively underwent the reaction employing catalytic amounts (20 mol %) of (2,2′-bipyridine)copper(II) triflate and copper bronze (3 equiv) as the ultimate reductant. To the best of our knowledge, these are the first applicable methods for synthesis of symmetrical biaryls from aryldiazonium salts. We believe that the methods will be a useful contribution to already existing methodology.

4. Experimental

4.1. General

IR spectra were recorded on a Perkin–Elmer Spectrum One spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on an AV Bruker (600 MHz) spectrometer, and shifts (δ) are given in parts per million downfield from TMS as an internal standard. TLC analyses were performed on Merck's (Darmstadt, Germany) DC-alufolien with Kieselgel 60 F_{254}. Preparative chromatography was carried out on silica gel, ϕ 0.063–0.2 mm (Merck, Germany). Melting points (mp) were determined using a Büchi B-540 instrument. The term room temperature (rt) means 20–25 °C. Copper(II) triflate was prepared by reaction of copper(II) oxide with trifluoromethanesulfonic acid (2 equiv) in water at rt (20 h). The thus obtained aqueous solution of copper(II) triflate was carefully brought to dryness by azeotropic removal of water with toluene, followed by high-vacuum drying (48 h), until dry (determined by IR spectrum). (2,2′-Bipyridine)-copper(II) triflate was prepared in situ by stirring equimolar amounts of copper(II) triflate and 2,2′-bipyridine in acetonitrile at rt for 1 h. Aryldiazonium salts **1a**–**p** were prepared by diazotisation of the respective anilines (1 equiv) with sodium nitrite (1 equiv) in cold (−3 to 0 °C/1 h) hydrochloric acid (3 equiv), followed by crystallisation (20 h/+4 °C) of the tetrafluoroborate salt by adding an aqueous solution of tetrafluoroboric acid (1.1 equiv).[54]

4.2. General procedure for homo-coupling of aryldiazonium salts bearing electron-withdrawing groups

To a solution of copper(II) triflate (1.09 g, 3 mmol, 1.5 equiv) in anhydrous acetonitrile (10 mL), copper bronze (0.19 g, 3 mmol, 1.5 equiv) was added, and the resulting suspension was refluxed under an argon atmosphere for 24 h. The clear solution of copper(I) triflate thus obtained was cooled to 0 °C and aryldiazonium salt (**1a**–**i**, 2 mmol) was

added at once. The reaction mixture was stirred at 0 °C–rt for 2 h, followed by additional stirring at rt as indicated in Table 1. The reaction mixtures were monitored for completion by testing an aliquot with an aqueous solution of sodium β-naphthoxide. The appearance of the red colour indicates the presence of unreacted starting diazonium salt. The reaction mixture was evaporated to dryness, diluted with water (20 mL) and extracted with dichloromethane (3×20 mL). The combined organic phases were dried (Na_2SO_4), filtered and evaporated to dryness. Crude products were purified by chromatography on silica gel (50 g).

4.2.1. 4,4′-Dinitrobiphenyl (2a). Pale yellow needles; yield 160 mg (66%); R_f (CH_2Cl_2/*n*-hexane, 2:1) 0.48; mp 191.5–196.1 °C; lit.[55] mp 237 °C (corr.); ν_{max} (KBr) 2921, 2319, 1600, 1511, 1476, 1375, 1343, 1108 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 8.32–8.31 (4H, m, arom.), 7.75–7.74 (4H, m, arom.); δ_C (600 MHz, $CDCl_3$) 148.0, 144.9, 128.2, 124.8, 124.3, 123.9.

4.2.2. 3,3′-Dinitrobiphenyl (2b). Pale yellow needles; yield 200 mg (82%); R_f (CH_2Cl_2/*n*-hexane, 2:1) 0.42; mp 177.2–179.8 °C; lit.[55] mp 200 °C (corr.); ν_{max} (KBr) 3079, 1526, 1464, 1348, 1266, 1104, 1083 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 8.52–8.51 (2H, m, arom.), 8.33–8.30 (2H, m, arom.), 8.00–7.97 (2H, m, arom.), 7.69–7.45 (2H, m, arom.); δ_C (600 MHz, $CDCl_3$) 140.3, 132.9, 130.2, 123.2, 122.0.

4.2.3. 2,2′-Dinitrobiphenyl (2c). Pale yellow needles; yield 170 mg (70%); R_f (CH_2Cl_2/*n*-hexane, 2:1) 0.65; mp 121.2–124.5 °C; lit.[39] mp 127.5–128 °C; ν_{max} (KBr) 3093, 1588, 1578, 1530, 1460, 1357, 1258, 1147, 1058 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 8.24–8.21 (2H, m, arom.), 7.72–7.67 (2H, m, arom.), 7.63–7.57 (2H, m, arom.), 7.32–7.29 (2H, m, arom.); δ_C (600 MHz, $CDCl_3$) 134.1, 133.3, 130.8, 129.0, 124.7.

4.2.4. 4,4′-Dichlorobiphenyl (2d). Colourless needles; yield 130 mg (58%); R_f (CH_2Cl_2/*n*-hexane, 1:4) 0.63; mp 139.5–143.6 °C; lit.[56] mp 142–144 °C; ν_{max} (KBr) 2925, 2345, 1904, 1643, 1588, 1473, 1388, 1298, 1088, 1019, 1003 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 7.51–7.48 (4H, m, arom.), 7.44–7.41 (4H, m, arom.); δ_C (600 MHz, $CDCl_3$) 138.3, 133.6, 128.9, 128.1.

4.2.5. 4,4′-Dichloroazobenzene (3d). Orange needles; yield 50 mg (20%); R_f (CH_2Cl_2/*n*-hexane, 1:4) 0.41; mp 178.7–181.6 °C; ν_{max} (KBr) 2920, 2343, 1907, 1632, 1577, 1478, 1402, 1282, 1221, 1150, 1082, 1008 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 7.90–7.87 (4H, m, arom.), 7.52–7.50 (4H, m, arom.); δ_C (600 MHz, $CDCl_3$) 148.0, 144.9, 128.2, 124.8, 124.3, 123.9.

4.2.6. 3,3′-Dichlorobiphenyl (2e). Viscous colourless oil; yield 105 mg (47%); R_f (*n*-hexane) 0.59; ν_{max} (KBr) 3064, 2930, 1593, 1560, 1463, 1396, 1260, 1161, 1102; δ_H (600 MHz, $CDCl_3$) 7.60–7.48 (2H, m, arom.), 7.46–7.30 (6H, m, arom.); δ_C (600 MHz, $CDCl_3$) 141.5, 134.7, 130.0, 127.8, 127.1, 125.1.

4.2.7. 3,3′-Dichloroazobenzene (3e). Viscous pale yellow oil; yield 83 mg (33%); R_f (CH_2Cl_2/2-PrOH, 9.5:0.5) 0.49; ν_{max} (KBr) 3070, 2964, 1585, 1568, 1463, 1416, 1302, 1262, 1199, 1087, 1066, 1021 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 7.89 (2H, s, arom.), 7.84–7.81 (2H, m, arom.), 7.53–7.45 (4H, m, arom.); δ_C (600 MHz, $CDCl_3$) 153.0, 135.1, 131.1, 130.1, 122.5, 121.8.

4.2.8. 2,2′-Dichlorobiphenyl (2f). Pale yellow needles; yield 11 mg (5%) in stoichiometric CuOTf-method (Table 1, entry 6), and 60 mg (27%) in catalytic method (Table 2, entry 6); R_f (CH_2Cl_2/*n*-hexane, 1:4) 0.64; ν_{max} (KBr) 3056, 2924, 2321, 1963, 1927, 1592, 1521, 1462, 1424, 1319, 1296, 1241, 1128, 1084, 1057, 1036, 1005 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 7.51–7.46 (2H, m, arom.), 7.45–7.36 (2H, m, arom.), 7.35–7.31 (2H, m, arom.), 7.30–7.24 (2H, m, arom.); δ_C (600 MHz, $CDCl_3$) 138.2, 133.4, 131.1, 129.3, 129.1, 126.4.

4.2.9. *trans*-2,2′-Dichloroazobenzene (3f). Orange needles; yield 111 mg (44%) in stoichiometric CuOTf-method (Table 1, entry 6), and 50 mg (20%) in catalytic method (Table 2, entry 6); R_f (CH_2Cl_2/*n*-hexane, 1:4) 0.48; mp 119.7–121.3 °C; ν_{max} (KBr) 3060, 2925, 1973, 1906, 1630, 1581, 1465, 1442, 1431, 1299, 1252, 1218, 1158, 1060, 1031 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 7.79–7.76 (2H, m, arom.), 7.58–7.55 (2H, m, arom.), 7.44–7.32 (4H, m, arom.); δ_C (600 MHz, $CDCl_3$) 148.6, 135.7, 132.1, 130.6, 127.3, 118.0.

4.2.10. 2,2′-Dimethoxycarbonylbiphenyl (2g). Pale yellow needles; yield 260 mg (96%); R_f (CH_2Cl_2/EtOAc, 9.5:0.5) 0.61; mp 69.7–71.4 °C; lit.[12] mp 70–72 °C; ν_{max} (KBr) 2951, 1728, 1598, 1434, 1258, 1127 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 8.02–7.99 (2H, m, arom.), 7.55–7.49 (2H, m, arom.), 7.44–7.39 (2H, m, arom.), 7.21–7.18 (2H, m, arom.), 3.60 (6H, s, 2×COOCH_3); δ_C (600 MHz, $CDCl_3$) 167.1, 143.0, 131.2, 130.0, 129.6, 129.1, 126.9, 51.6.

4.2.11. 4,4′-Dichloro-2,2′-dinitrobiphenyl (2h). Colourless needles; yield 250 mg (80%); R_f (CH_2Cl_2/*n*-hexane, 1:1) 0.58; mp 51.3–53.3 °C; ν_{max} (KBr) 3077, 1590, 1566, 1534, 1466, 1352, 1274, 1251, 1159, 1099, 1051 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 7.89–7.88 (m, 4H, arom.), 7.52–7.51 (m, 2H, arom.); δ_C (600 MHz, $CDCl_3$) 133.4, 133.2, 132.7, 125.6, 125.4.

4.2.12. 4,4′-Dichloro-2,2′-dibenzoylbiphenyl (2i). Colourless needles; yield 280 mg (65%); R_f (CH_2Cl_2/*n*-hexane, 4:1) 0.65; mp 152.0–155.8 °C; ν_{max} (KBr) 3081, 3060, 3010, 2925, 1658, 1593, 1582, 1464, 1450, 1389, 1318, 1289, 1263, 1250, 1182, 1160, 1137, 1099, 1054, 1026 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 7.81 (d, 4H, *J* 7.4 Hz, arom.), 7.64–7.62 (m, 2H, arom.), 7.50–7.48 (m, 4H, arom.), 7.42–7.39 (m, 4H, arom.), 7.37–7.36 (m, 2H, arom.); δ_C (600 MHz, $CDCl_3$) 193.5, 139.9, 135.8, 133.9, 132.9, 131.2, 131.0, 130.0, 129.5, 128.8, 128.7.

4.2.13. *trans*-4,4′-Dichloro-2,2′-dibenzoylazobenzene (3i). Yellow needles; yield 110 mg (24%); R_f (CH_2Cl_2/*n*-hexane, 4:1) 0.39; mp 152.0–155.8 °C; ν_{max} (KBr) 3057, 2924, 1664, 1594, 1463, 1449, 1378, 1317, 1284, 1235, 1179, 1156, 1115, 1102, 1025, 1000 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 7.68 (d, 4H, *J* 7.9 Hz, arom.), 7.47–7.25 (m, 12H, arom.); δ_C (600 MHz, $CDCl_3$) 195.7, 139.5, 137.3, 136.4, 133.2, 133.2, 132.6, 130.2, 130.1, 129.0, 128.1.

4.3. General procedure for homo-coupling of aryldiazonium salts without electron-withdrawing groups

To a solution of copper(II) triflate (145 mg, 0.4 mmol, 20 mol %) in anhydrous acetonitrile (10 mL), 2,2′-bipyridine (bpy, 62 mg, 0.4 mmol, 20 mol %) was added, and the resulting mixture was stirred at rt for 1 h under an argon atmosphere. Then, copper bronze (0.38 g, 6 mmol, 3 equiv), and aryldiazonium salt (**1j–p**, 2 mmol) were added, and the resulting suspension was stirred at rt under an argon atmosphere for the time indicated in Table 3. The reaction mixture was evaporated to dryness, diluted with water (20 mL) and then extracted with dichloromethane (3×20 mL). The combined organic phases were dried (Na_2SO_4), filtered, and evaporated to dryness. Crude products were purified by preparative chromatography on silica gel (50 g).

4.3.1. Biphenyl (2j). Colourless needles; yield 110 mg (71%); R_f (CH_2Cl_2/*n*-hexane, 1:2) 0.65; mp 67.2–70.0 °C; lit.[26] mp 69–70 °C (corr.); ν_{max} (KBr) 3033, 1569, 1480, 1429, 1344, 1170, 1042, 1007 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 7.59–7.56 (4H, m, arom.), 7.44–7.39 (4H, m, arom.), 7.34–7.16 (2H, m, arom.); δ_C (600 MHz, $CDCl_3$) 141.1, 128.6, 127.1, 127.0.

4.3.2. *trans*-Azobenzene (3j). Orange needles; yield 10 mg (5%); R_f (CH_2Cl_2/*n*-hexane, 2:1) 0.44; mp 70.1–73.2 °C; ν_{max} (KBr) 3062, 2319, 1957, 1898, 1769, 1583, 1483, 1453, 1300, 1222, 1151, 1071, 1020 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 7.94–7.92 (4H, m, arom.), 7.53–7.51 (4H, m, arom.), 7.48–7.46 (2H, m, arom.); δ_C (600 MHz, $CDCl_3$) 152.6, 130.9, 129.0, 122.7.

4.3.3. 4,4′-Dimethylbiphenyl (2k). Colourless needles; yield 110 mg (60%); R_f (CH_2Cl_2/*n*-hexane, 1:2) 0.67; mp 121.5–122.0 °C; lit.[57] mp 120.7–121.5 °C; ν_{max} (KBr) 2914, 1903, 1562, 1501, 1445, 1311, 1178, 1113, 1036 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 7.49–7.46 (4H, m, arom.), 7.24–7.21 (4H, m, arom.), 2.38 (6H, s, 2×C*H*$_3$); δ_C (600 MHz, $CDCl_3$) 138.2, 136.6, 129.3, 126.7, 21.0.

4.3.4. *trans*-4,4′-Dimethylazobenzene (3k). Orange needles; yield 22 mg (10%); R_f (CH_2Cl_2/*n*-hexane, 1:2) 0.48; mp 137.1–140.8 °C; ν_{max} (KBr) 3021, 2921, 1598, 1501, 1411, 1294, 1208, 1152, 1108, 1035, 1010 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 7.83–7.80 (4H, m, arom.), 7.31–7.28 (4H, m, arom.), 2.41 (6H, s, 2×C*H*$_3$); δ_C (600 MHz, $CDCl_3$) 150.7, 141.1, 129.6, 122.6, 21.5.

4.3.5. *N*-(2-Tolyl)acetamide (4l). Colourless needles; yield 101 mg (34%); R_f (CH_2Cl_2/2-PrOH, 9.5:0.5) 0.45; mp 105–108 °C; ν_{max} (KBr) 3294, 1655 (C=O, amide), 1588, 1529, 1486, 1459, 1369, 1287, 1270 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 7.59 (1H, d, *J* 8.1 Hz, arom.), 7.45 (1H, s, N*H*), 7.13 (2H, s, arom.), 7.07–7.03 (1H, m, arom.), 2.19 (3H, s, COC*H*$_3$), 2.12 (3H, s, C*H*$_3$); δ_C (600 MHz, $CDCl_3$) 168.6, 135.5, 130.3, 130.0, 126.3, 125.3, 123.9, 23.8, 17.6.

4.3.6. 4,4′-Dimethoxybiphenyl (2m). Colourless needles; yield 101 mg (47%); R_f (CH_2Cl_2) 0.74; mp 177.2–180.3 °C; lit.[58] mp 182–183 °C; ν_{max} (KBr) 3056, 2923, 1567, 1488, 1463, 1423, 1261, 1241, 1128, 1084, 1057, 1034 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 7.49–7.46 (4H, m, arom.), 6.97–6.94 (4H, m, arom.), 3.84 (6H, s, 2×OC*H*$_3$); δ_C (600 MHz, $CDCl_3$) 158.5, 133.3, 127.6, 114.0, 55.2.

4.3.7. *trans*-4,4′-Dimethoxyazobenzene (3m). Yellow needles; yield 51 mg (21%); R_f (CH_2Cl_2) 0.59; mp 155.4–158.7 °C; ν_{max} (KBr) 3016, 2839, 2033, 1599, 1579, 1497, 1457, 1439, 1318, 1244, 1178, 1144, 1103, 1023 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 7.91–7.87 (4H, m, arom.), 7.02–6.98 (4H, m, arom.), 3.88 (6H, s, 2×OC*H*$_3$); δ_C (600 MHz, $CDCl_3$) 161.4, 146.9, 124.2, 114.0, 55.4.

4.3.8. 3,3′-Dimethoxybiphenyl (2n). Colourless liquid; yield 170 mg (79%); R_f (CH_2Cl_2/*n*-hexane, 2:1) 0.51; ν_{max} (KBr) 3054, 3029, 3000, 2957, 2939, 2835, 1599, 1575, 1477, 1412, 1317, 1299, 1291, 1235, 1204, 1170, 1092, 1056, 1047, 1031 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 7.34–7.29 (m, 2H, arom.), 7.17–7.11 (m, 4H, arom.), 6.89–6.85 (m, 2H, arom.), 3.81 (s, 6H, 2×OC*H*$_3$); δ_C (600 MHz, $CDCl_3$) 159.7, 142.4, 129.6, 119.5, 112.8, 112.6, 55.0.

4.3.9. *N*-(3-Methoxyphenyl)acetamide (4n). Colourless needles; yield 56 mg (17%); R_f (CH_2Cl_2/2-PrOH, 9.5:0.5) 0.42; ν_{max} (KBr) 3308, 3207, 3147, 3090, 3002, 2961, 2938, 2836, 1668, 1599, 1549, 1494, 1455, 1428, 1371, 1286, 1264, 1198, 1157, 1084, 1045 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 8.10 (s, 1H, N*H*), 7.29–7.28 (m, 1H, arom.), 7.21–7.08 (m, 1H, arom.), 7.03–7.00 (m, 1H, arom.), 6.67–6.64 (m, 1H, arom.), 3.75 (s, 3H, OC*H*$_3$), 2.15 (s, 3H, NHCOC*H*$_3$); δ_C (600 MHz, $CDCl_3$) 168.8, 159.8, 139.1, 129.4, 112.0, 109.7, 105.6, 55.0, 24.3.

4.3.10. 2,2′-Dimethoxybiphenyl (2o). Pale yellow needles; yield 110 mg (51%); R_f (CH_2Cl_2) 0.70; mp 139.8–142.5 °C; ν_{max} (KBr) 2962, 2930, 1914, 1601, 1590, 1500, 1482, 1456, 1429, 1299, 1284, 1237, 1164, 1112, 1022, 1001 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 7.33–7.30 (2H, m, arom.), 7.24–7.23 (2H, m, arom.), 7.00–6.98 (2H, m, arom.), 6.97–6.96 (2H, m, arom.), 3.75 (6H, s, 2×OC*H*$_3$); δ_C (600 MHz, $CDCl_3$) 156.9, 131.3, 128.5, 127.5, 120.2, 111.0, 55.6.

4.3.11. *trans*-2,2′-Dimethoxyazobenzene (3o). Red needles; yield 42 mg (17%); R_f (CH_2Cl_2) 0.41; mp 143.1–147.6 °C; ν_{max} (KBr) 2966, 2839, 2040, 1924, 1593, 1584, 1488, 1467, 1436, 1307, 1279, 1243, 1158, 1119, 1023 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 7.64–7.62 (2H, m, arom.), 7.42–7.39 (2H, m, arom.), 7.07–7.05 (2H, m, arom.), 7.01–6.98 (2H, m, arom.), 4.00 (6H, s, 2×OC*H*$_3$); δ_C (600 MHz, $CDCl_3$) 156.7, 142.8, 132.0, 120.6, 117.4, 112.4, 56.2.

4.3.12. 1,1′-Binaphthyl (2p). Colourless needles; yield 18 mg (7%); mp 156.1–158.9 °C; lit.[59] mp 158–160 °C; ν_{max} (KBr) 3039, 2963, 1927, 1821, 1568, 1502, 1384, 1327, 1259, 1210, 1130, 1012 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 8.00–7.97 (4H, m, arom.), 7.65–7.60 (2H, m, arom.), 7.55–7.48 (2H, m, arom.), 7.45–7.40 (4H, m, arom.), 7.35–7.28 (2H, m, arom.); δ_C (600 MHz, $CDCl_3$) 138.3, 133.4, 132.7, 128.0, 127.8, 127.7, 126.4, 125.9, 125.7, 125.3.

4.3.13. *trans*-1,1′-Azobinaphthyl (3p). Pale orange needles; yield 60 mg (21%); R_f (CH_2Cl_2/*n*-hexane, 1:2) 0.52;

mp 171.8–175.2 °C; ν_{max} (KBr) 3047, 2922, 1588, 1507, 1388, 1341, 1261, 1211, 1153, 1088, 1016 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 9.07–9.03 (2H, m, arom.), 8.02–7.93 (6H, m, arom.), 7.70–7.57 (6H, m, arom.); δ_C (600 MHz, $CDCl_3$) 148.1, 134.3, 131.4, 131.3, 127.8, 126.8, 126.4, 125.5, 123.5, 112.2.

The catalyst effect of various amounts (10–30 mol %) of copper(I) triflate and (2,2′-bipyridine)copper(II) triflate on the model reactions of **1f** and **1g** was performed analogously to the procedures described above. The results from this study are presented in Table 2.

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