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Copper-Catalyzed Coupling of (*E*)-Bromostilbene with Phenols/Azole: ESI-MS Detection of Intermediates by Using an Ionically-Tagged Ligand

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Abstract: A system based on copper/1,10-phenanthroline efficiently promotes the coupling between phenols or pyrazole with (*E*)-bromostilbene. (*E*)-1-Aryloxy-1,2-diphenylethenes were obtained from the coupling with phenols in good to excellent yields (69–90%). The exception was the reaction involving a phenol containing an electron-withdrawing cyano group that required a longer reaction time and gave only 49% yield. Kinetic studies indicated the participation of the vinyl halide in the rate-determining step. Under the conditions employed, the activation of the vinyl halide *via* a radical pathway was discarded using a radical scavenger test. By using an ionically-tagged 1,10-phenanthroline derivative as the ligand, various copper-based ions were detected through ESI(+)-MS. These ions suggested that formation of the active species [phenCuOAr(HOAr)$_2$] precedes the vinyl halide activation.

Keywords: copper; cross-coupling; ESI-MS; ion-tagged ligand; vinylation

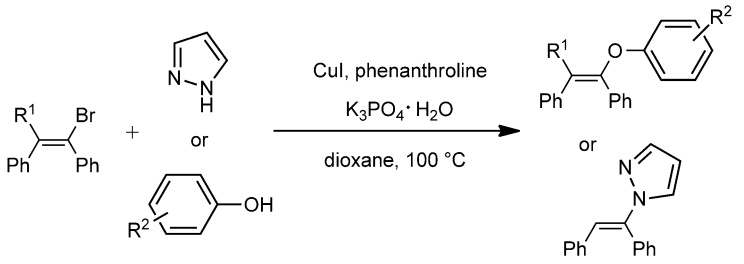
The copper-catalyzed coupling of phenols and azoles with aryl or vinyl halides providing aryl or vinyl ethers and amines represents a synthetic method that has clearly grown in importance in the last decade.[1] The judicious choice of appropriate ligands (e.g., diamines, amino acids, diketones, etc.) has allowed the use of milder conditions and lower amounts of copper. Therefore, the scope of the reaction has been extended and various synthetic intermediates[2] and targets[3] have been obtained.

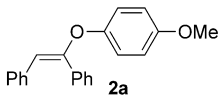
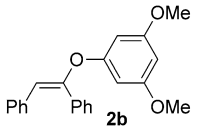
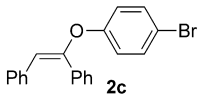
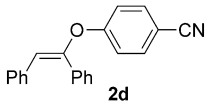
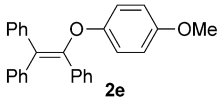
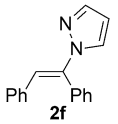
Most copper-catalyzed coupling reactions involve aryl halides as the electrophile partner, leading to C(aryl)–N or C(aryl)–O bond formation. However, vinylic amines and ethers are compounds widely used as intermediates in organic synthesis, and some excellent examples of copper-catalyzed vinylation of phenols and azoles have been reported. For instance, amino ethers,[4] *N*,*N*-dimethylglycine[2a] and pyridinyl-benzoimidazole[5] have been used as ligands in the coupling of vinyl bromides and iodides with phenols. In 2006, Taileffer and co-workers reported the coupling of phenols and azoles with β-bromostyrene.[6] The same group published a detailed study regarding the structure/activity of bi- and tetradentate nitrogen ligands in the arylation of phenols and azoles. These ligands were successfully used in N- and O-vinylation of 1-bromo-2-methylpropene.[7] A β-keto ester was also used as a ligand to efficiently couple styryl bromides with phenols, thiophenols and imidazoles.[8]

With respect to the reaction mechanism, it is currently believed that the reaction occurs *via* the formation of an intermediate, [L$_n$Cu(I)-Nu][9] (where L is the ligand and Nu is the nucleophile), prior to aryl halide activation. However, it remains unclear if this C–X activation occurs through an oxidative addition Cu(I)-Cu(III) process [as demonstrated in theoretical studies,[9e,10] reactions with well-defined Cu(III) compounds[11] and radical-presence tests[9d,12]] or *via* a radical SET/IAT Cu(I)-Cu(II) pathway (as shown in theoretical studies[13] and ESI-MS experiments in combination with radical scavenger tests[14]).

In this way, we report here the employment of an ESI(+)-MS technique in order to detect reaction intermediates in the copper-catalyzed vinylation of phenols. For this, we synthesized and used ionically-tagged 1,10-phenanthroline derivative ligand **L1** that

Table 1. C–O and C–N coupling of (*E*)-bromostilbene and 1,1,2-bromotriphenylethene.[a]



Entry	R^1/R^2	Product	Conversion [%]	Yield [%][b]
1	H/4-OMe	 **2a**	97	96 (83)
2	H/2,5-OMe	 **2b**	80	76 (69)
3	H/4-Br	 **2c**	100	97 (82)
4[c]	H/4-CN	 **2d**	56	51 (49)
5[d]	Ph/4-OMe	 **2e**	99	96 (90)
6[d]	H/pyrazole	 **2f**	85	85 (78)

[a] *Reaction conditions (for GC analysis):* vinyl bromide (0.5 mmol), phenol (0.75 mmol), $K_3PO_4{\cdot}H_2O$ (1 mmol), CuI (10 mol%), 1,10-phenanthroline (10 mol%), dioxane (2 mL).
[b] Yields refer to GC yields (with undecane as an internal standard). Values in brackets refer to yields of isolated products using a 2-mmol scale.
[c] CuI (20 mol%), 1,10-phenanthroline (20 mol%), 120 °C, 24 h.
[d] Reaction time: 24 h.

was used as a probe. Moreover, (*E*)-bromostilbene was used as substrate, allowing the synthesis of tri- and tetrasubstituted vinyl ethers and *N*-vinylpyrazole in good to excellent yields, using 1,10-phenanthroline as ligand. At the end, a viable mechanistic pathway of copper-catalyzed vinylations of phenols was proposed based on the results obtained from ESI(+)-MS, preliminary kinetic studies and a radical scavenger experiment.

We chose to study the C–O coupling of (*E*)-bromostilbene using CuI as the catalyst precursor and commercially available 1,10-phenanthroline as the ligand. Initially, we performed a screening of bases (Cs_2CO_3, K_2CO_3, CsF, KF and $K_3PO_4{\cdot}H_2O$), solvents (MeCN, DMF, PhMe and dioxane) and temperatures (50–100 °C). The optimized best results were obtained using a simple catalytic system composed of CuI (10 mol%), 1,10-phenanthroline (10 mol%) and $K_3PO_4{\cdot}H_2O$ (2 equiv) in dioxane at 100 °C for 6 h.

Table 1 describes the results obtained for the C–N and C–O coupling between phenols/azoles with (*E*)-bromostilbene (**1a**) and bromotriphenylethene (**1b**).

Good to excellent yields were obtained for the coupling of both an electron-rich phenol (Table 1, entry 1) and slightly electron-deficient phenols (Table 1, entries 2 and 3). However, when we used a phenol substituted with the electron-withdrawing CN group, the reaction gave only moderate substrate conversion and product yield even with longer reaction times, (Table 1, entry 4, 24 h) probably due to its poor nucleophilicity compared with the other phenols tested. It is worth mentioning that 4-bromophenol reacted not only as a nucleophile partner but also as an electrophile in the C_{aryl}–O coupling reaction. Under

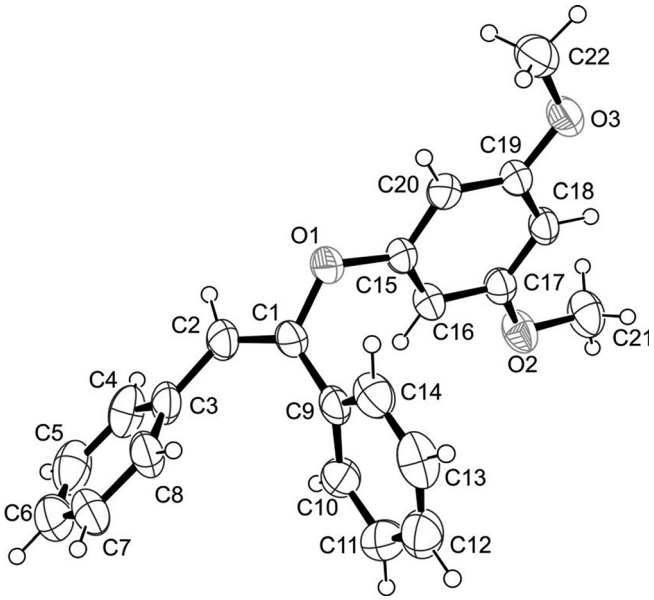


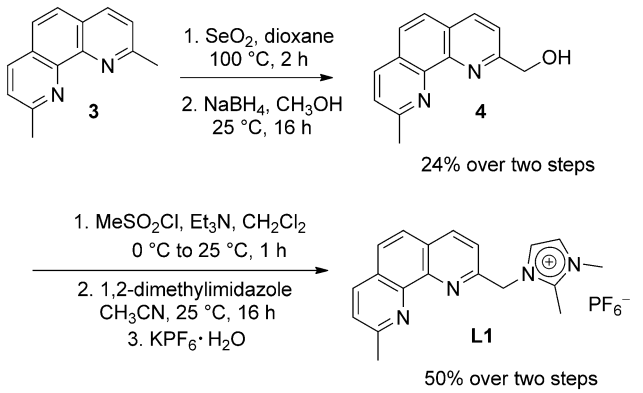
Figure 1. ORTEP diagram for the product **2b**.

the studied conditions, the reaction was chemoselective and only the product obtained from C_{vinyl}–Br bond activation was observed (Table 1, entry 3). The tetrasubstituted vinyl ether **2e** was obtained in 90% yield (Table 1, entry 5). The same method was then extended to the N-nucleophile pyrazole and the *N*-vinylpyrazole **2f** was obtained in 78% yield.

The vinyl ethers (**2a**–**2d**) have only been obtained in the literature as the *Z* isomer by a gold-catalyzed hydrophenoxylation of diphenylacetylene.[15] We were able to obtain an X-ray crystal structure of compound **2b** that unambiguously established the *E* configuration (Figure 1). As we have observed for Pd-catalyzed coupling reactions,[16] the configuration of the double bond remained unchanged during the vinyl bromide activation reaction and the product showed the same stereochemistry as the substrate.

After the synthesis of vinylic compounds, we tried to determine the reaction mechanism through ESI(+)-MS analyses and radical scavenger tests (Scheme 4). Recently, two studies concerning the use of ESI(+)-MS to determine the intermediates of the copper-catalyzed arylation of amines were published.[14,17] Our group has published some studies concerning the utilization of ionophilic ligands in organometallic biphasic catalysis.[18] This type of ionically-tagged ligand is also very useful for detecting intermediates in ESI(+)-MS experiments because neutral species are transformed into ionic species by the ionophilic ligand. For this reason, we synthesized the ligand **L1** as demonstrated in Scheme 1.

In the first step, neocuproine **3** was oxidized to the corresponding monoaldehyde using SeO_2. After filtration, $NaBH_4$ and methanol were added to the solution and alcohol **4** was obtained in 24% yield over two



Scheme 1. Synthesis of the ligand **L1**.

steps. In order to introduce a good leaving group, alcohol **4** was treated with $MeSO_2Cl$ and Et_3N. The mesylated intermediate was then reacted with 1,2-dimethylimidazole. After that, the counter-ion was exchanged by the addition of KPF_6, giving the desired ionophilic ligand **L1** in 12% overall yield. Before a final purification, ESI-MS analysis (Figure 2) indi-

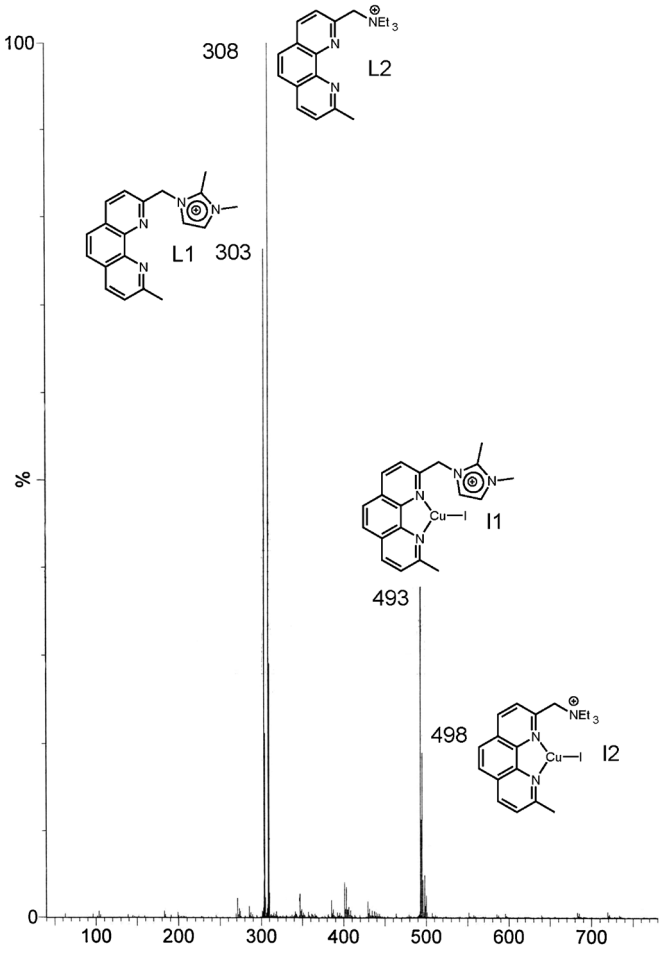
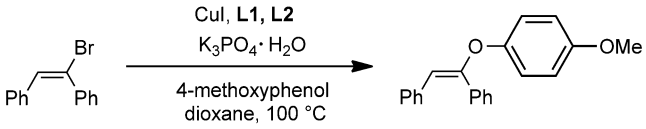


Figure 2. ESI(+)-mass spectrum of the reaction between CuI, **L1** and **L2**.

Table 2. Results of the ESI(+)-MS experiments.[a]



Exp.	Sequence of addition/time	Copper-based ion	CG results
1	1. CuI + (**L1** + **L2**)/1 h	1. **I1**, **I2**	No coupling products
	2. phenol + base/1 h	2. none	
	3. (*E*)-bromostilbene/1 h	3. none	
2	1. CuI + (**L1** + **L2**)/1 h	1. **I1**, **I2**	34% yield
	2. (*E*)-bromostilbene/1 h	2. **I1**	
	3. phenol + base/1 h	3. **I1**–**I10**	
3	all reagents/1 h	**I1**–**I10**	38% yield

[a] *Reaction conditions:* see Table 1.

cated the presence of the by-product **L2** that was formed from the reaction of the mesylated intermediate with Et_3N as the nucleophile. We decided to use the mixture of **L1** and **L2** for the ESI-MS experiments since both could be a potential probe in the search for intermediates.

A mixture of **L1** and **L2** was used as a probe to detect intermediates in the coupling between (*E*)-bromostilbene and 4-methoxyphenol catalyzed by CuI. Three different experiments were performed, varying the sequence of the addition of reagents as shown in Table 2.

In the first experiment (Exp. 1), CuI, **L1** and **L2** were allowed to react for 1 h in dioxane at 100 °C and the mixture was analyzed by ESI(+)-MS. Thereby, the ions **I1** and **I2** and the free ligands **L1** and **L2** were detected (Figure 2). The fact that there was free ligand even in the presence of a chelating diamine could indicate that a portion of the copper was not in solution, but in a copper reservoir as previously suggested.[19] Next, we added 4-methoxyphenol and $K_3PO_4{\cdot}H_2O$; however, after 1 h of reaction, no copper-based ions were observed. The same result (no ions detected) was obtained after the addition of (*E*)-bromostilbene. Finally, the reaction was analyzed by GC and the coupling product **2a** was also not observed.

Next, we decided to change the order of addition (Exp. 2), starting with CuI + (**L1** + **L2**) (Exp. 2-1) followed by bromostilbene (Exp. 2-2) and phenol + base (Exp. 2-3). Initially, the same ions **I1** and **I2** were observed. After the addition of (*E*)-bromostilbene, no changes were observed on the mass spectrum, indicating that the halides did not react directly with intermediates **I1** and **I2** and, consequently, the formation of a phenoxide species precedes halide activation. Finally, after the addition of the phenol and the base, a complete change in the ESI(+)-MS was observed and various ions could be identified (the ions are shown in Figure 3). In Exp. 3, where all reagents were added simultaneously, the same ions as observed in Exp. 2–3 were detected. The proposed ions are shown in Figure 3. Concerning the structure of the intermediates, at first, it is important to note that the theoretical and experimental isotopic distributions of the proposed copper ions are in agreement (see the Supporting Information). It is also noteworthy that some copper-based intermediates formed from the attack of the phenol to the benzylic position of the ligands **L1** and **L2** were observed (**I5**, **I7** and **I9**) in conjunction with the respective leaving group dimethylimidazole ($m/z = 96$) and triethylamine ($m/z = 101$). Several $[Cu(phen)_2]^+$ species were detected (**I6**, **I7** and **I9**). These species are similar to those described by Taillefer and co-workers as very active catalysts in the arylation of phenols, even at very low concentrations of copper (10 ppm).[19] Another important intermediate detected was **I10**. In this species, the ionophilic probe was not cleaved and it contains a Cu–OAr bond. The formation of species Cu–Nu has been described in the arylation of phenols[20] and other nucleophiles.[9] These species have been reported as capable to react with aryl halides under mild conditions.[9,20] Moreover, some species of copper-containing phenol molecules as the ligand were observed (**I8** and **I10**), indicating that the phenol can act as a nucleophile and as a ligand.

In order to observe the participation of radical intermediates in the catalytic cycle, we performed the coupling of (*E*)-bromostilbene with 4-methoxyphenol in the absence and presence of 2,6-di-*tert*-butyl-4-methylphenol (BHT), a well-known radical scavenger. No significant differences were observed in the absence (conversion: 37%), with 10 mol% (conversion: 41%) or 100 mol% (conversion: 41%) of the radical inhibitor (Scheme 2). The presence of a radical mechanism was proposed for the coupling reaction of iodotoluene with diphenylamine using TEMPO as a radical

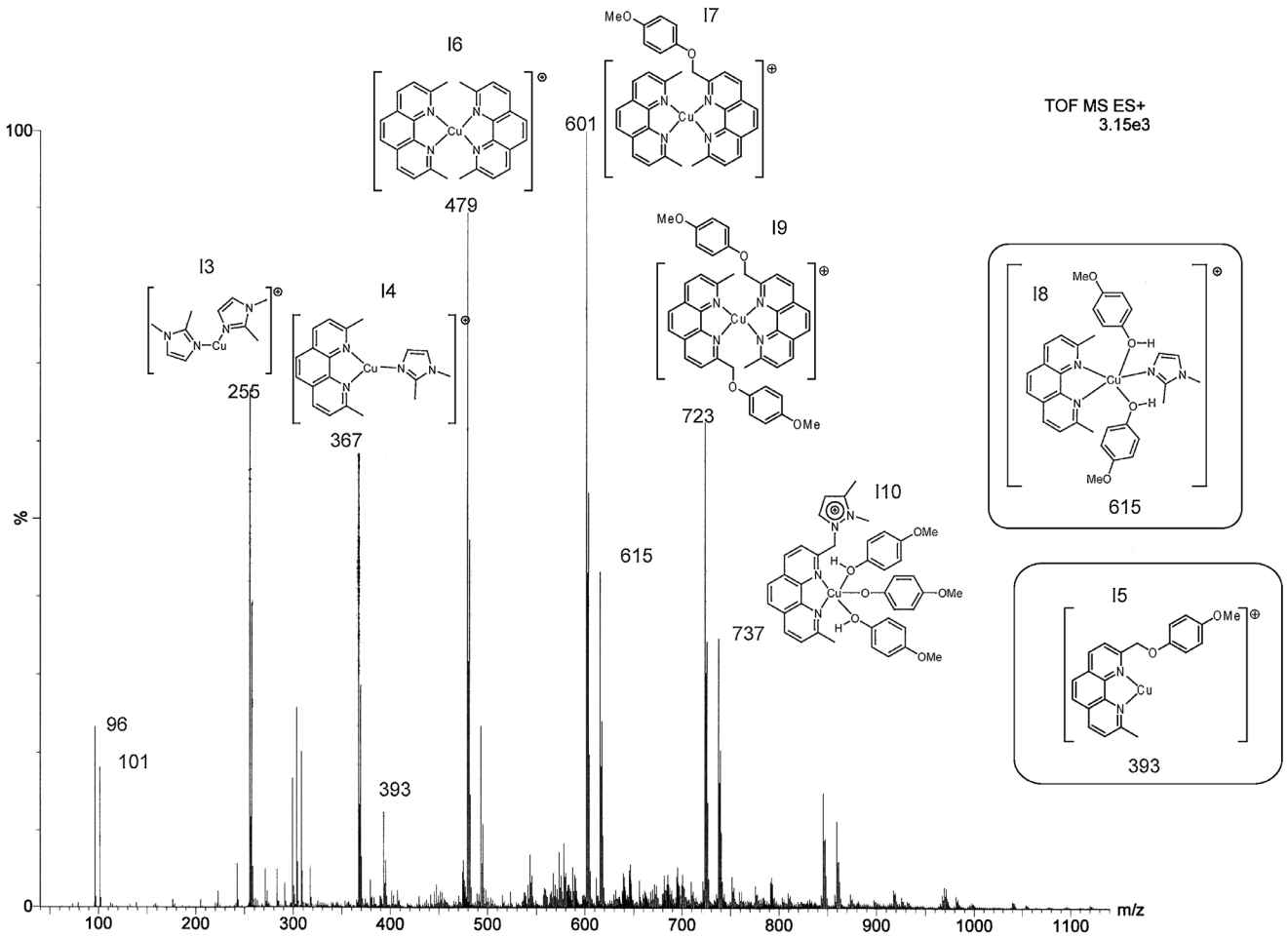
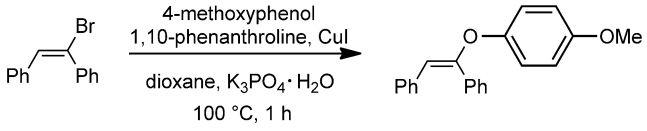


Figure 3. ESI(+)-mass spectrum of the reaction between (*E*)-bromostilbene and 4-methoxyphenol, using the ligands **L1** and **L2**, and $K_3PO_4 \cdot H_2O$ as base.

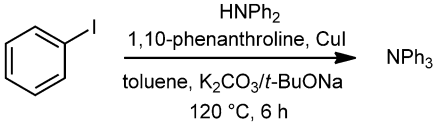
scavenger.[14] When we used BHT for the same reaction and under similar conditions as described in the literature, we also observed a significant decrease in the yield (Scheme 3). Therefore, at least for the reaction conditions used in our work for the coupling of (*E*)-bromostilbene with phenol, the radical pathway is not operational. Further evidence for the non-involvement of radicals is the maintenance of the *E* stereochemistry in the coupling product, because in a radical pathway an isomeric *E*/*Z* mixture would be expected.

Additionally, we performed some preliminary kinetic studies in order to determine the involvement of the phenol and the halide in the rate-determining step. We carried out a series of reactions by varying the concentration of 4-methoxyphenol or bromostilbene. These reactions were stopped with low conversions and the initial rates were determined; therefore, we were able to determine the reaction order as a function of phenol and vinyl halide. As expected, a first-order reaction was obtained for the halide, indicating its participation in the rate-determining step (see the Supporting Information). On the other hand,



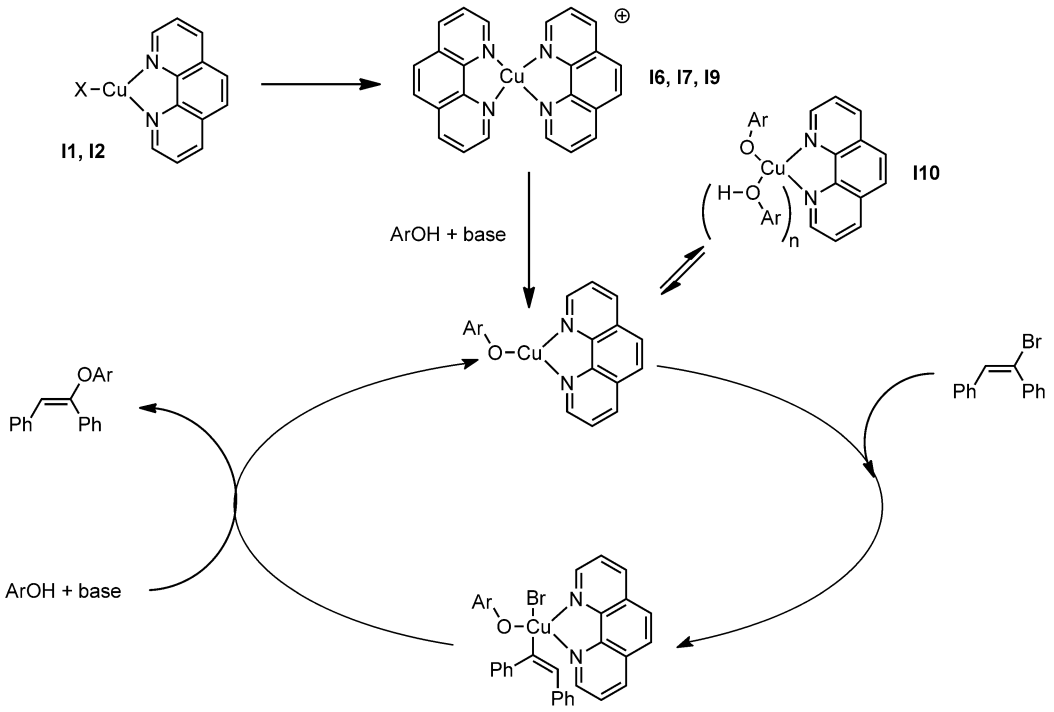
	conv.:	yield:
absence of inhibitor	37%	36%
BHT 10 mol%:	41%	37%
BHT 100 mol%:	41%	38%

Scheme 2. Radical scavenger test using BHT in C–O vinylation.



	conv.:	yield:
absence of inhibitor	38%	33%
BHT 100 mol%:	2%	2%

Scheme 3. Radical scavenger test using BHT in C–N arylation.



Scheme 4. Catalytic cycle proposed for the copper-catalyzed vinylation of phenols.

we found that the reaction rate was also dependent on the phenol concentration in a variable order dependence on the phenol concentration. These results are in agreement with the ESI-MS experiments which indicate that the phenol can act as a nucleophile and as a ligand.

Based on the results obtained from ESI(+)-MS, preliminary kinetic studies and the radical scavenger experiment we propose viable mechanistic pathways for the copper/1,10-phenanthroline-catalyzed vinylation of phenols. At first the coordination of the ligand to CuI takes place, providing a species (phen)CuI, which was detected as **I1** and **I2** in the ESI(+)-MS. Thereafter, an intermediate $[(phen)_2Cu]^+$ is formed. The formation of this intermediate was supported by the detection of **I6**, **I7** and **I9**. Next, the formed intermediate Cu–OAr was detected as **I10** which is reported to be capable to react with the organic halides.[20] In terms of vinyl halide activation, since the radical pathway is not operational, we can argue in favour of an oxidative addition to form a Cu(III) intermediate. Although these species are not common, arylcopper(III) complexes have been identified recently,[11a,21] and arylcopper(III) intermediates containing nitrogen ligands are calculated to be kinetically accessible under the reaction conditions.[9d] Then, the [(phen)-CuOAr] intermediate would be reformed by a putative reductive elimination followed by attack of the phenoxide to the copper species.

In summary, we have described herein the efficient coupling between (*E*)-bromostilbene and nucleophiles. Through ESI(+)-MS, we described the formation of the species [LCuI], $[L_2Cu]^+$ [LCu(I)–OAr] that is preceding halide activation. Furthermore, with kinetic studies and radical inhibition studies, we could determine the participation of the halide in the rate-determining step and the non-involvement of radicals in the reaction pathway, respectively. Further studies concerning the application of this reaction and mechanistic studies are in progress in our group.

Experimental Section

Typical Procedure for the Coupling of (*E*)-Bromostilbene or Bromotriphenylethene with Phenols or Azoles

An oven-dried resealable Schlenk flask was charged with (*E*)-bromostilbene or bromotriphenylethene (2.0 mmol), phenol or azole (3.0 mmol), 1,10-phenanthroline (36 mg, 0.2 mmol), CuI (38 mg, 0.2 mmol) and $K_3PO_4 \cdot H_2O$ (4 mmol, 920 mg), evacuated and back-filled with argon. Then, dioxane (8 mL) was added, and the reaction mixture was stirred at 100 °C for the desired time (6 h for phenols and 24 h for azoles). Next, the reaction mixture was cooled, filtered and analyzed by GC and GC-MS. The product was further purified by column chromatography (silica gel in hexane/ethyl acetate) and analyzed by ^{1}H NMR and ^{13}C NMR. Crystalline samples were obtained through crystallization in hot ethanol.

Synthesis of the Ionophilic Ligand L1

In a typical synthesis, 2,9-dimethyl-1,10-phenanthroline **3** (2.00 g, 9.60 mmol) was stirred with selenium dioxide (1.60 g, 14.40 mmol) in 60 mL of dioxane. The reaction mixture was heated at 100 °C for 2 h. After that, the mixture was filtered and the dioxane was evaporated. Next, sodium borohydride (2.0 g, 0.05 mol) and 100 mL of methanol were added and the mixture was stirred at room temperature for 16 h. The volume was reduced to 25 mL, water was added and the crude product was extracted with chloroform. At the end the product was purified by column chromatography (alumina) resulting in (2-methyl-1,10-phenanthrolin-9-yl)methanol **4**; yield: 24%. The characterization data of product **4** were in agreement with those in the literature.[22]

Product **4** was then stirred with methanesulphonyl chloride (0.34 g, 3.00 mmol) and triethylamine (0.35 g, 3.45 mmol) in 20 mL of dichloromethane for 1 h at 25 °C. Then, the mixture was filtered through a neutral alumina plug and the solution was concentrated to a volume of 5 mL. Next, a solution of 1,2-dimethyl-1*H*-imidazole (0.38 g, 3.91 mmol) in 20 mL of acetonitrile were added and the mixture was stirred for 16 h at 25 °C. The solvent was then evaporated and the resulting solid was washed with ethyl ether (3×10 mL). Finally, a solution of potassium hexafluorophosphate (0.85 g, 4.60 mmol) in 20 mL of water was added, giving a pale yellow solid. The solid was filtered and dried under vacuum, furnishing **L1**; global yield: 515 mg (12%).

Characterization of New Products

(*E*)-1-(4-Methoxyphenoxy)-1,2-diphenylethene (2a): White solid, yield: 83%, mp 79–80 °C. IR (KBr): ν = 3053, 2960, 2839, 1644, 1505, 1226, 1205 cm^{-1}; MS (EI, 70 eV): *m*/*z* (rel. intensity) = 302 (26, M^+), 197 (32), 178 (80), 152 (19), 124 (100), 109 (17); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.77 (s, 3H), 6.07 (s, 1H), 6.84 (d, *J* = 9.1 Hz, 2H), 7.17–6.99 (m, 7H), 7.33–7.23 (m, 3H), 7.50–7.43 (m, 2H); ^{13}C NMR: δ = 55.5, 111.4, 114.6, 120.6, 126.0, 128.0, 128.2, 128.7, 128.8, 129.5, 134.7, 135.8, 149.6, 155.0, 155.5; elem. anal. calcd. for $C_{21}H_{18}O_2$: C 83.42, H 6.00; found: C 83.47, H 6.09.

(*E*)-1-(3,5-Dimethoxyphenoxy)-1,2-diphenylethene (2b): White solid, yield: 69%, mp 95–96 °C. IR (KBr): ν = 3020, 2967, 2837, 1595, 1475, 1355, 1205, 1137, 1064 cm^{-1}; MS (EI, 70 eV): *m*/*z* (rel. intensity) = 332 (45, M^+), 227 (18), 178 (100), 154 (63), 125 (24), 105 (31); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.72 (s, 6H), 6.13 (t, *J* = 2.2 Hz, 1H), 6.27 (d, *J* = 2.2 Hz, 2H), 6.33 (s, 1H), 7.17–7.07 (m, 5H), 7.27–7.23 (m, 3H), 7.46–7.40 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.3, 94.9, 97.0, 115.2, 126.5, 128.1, 128.3, 128.8, 129.3, 134.3, 135.4, 152.5, 158.5, 161.3; elem. anal. calcd. for $C_{22}H_{20}O_3$: C 79.50, H 6.06; found: C 79.58, H 5.96. Crystals suitable for X-ray diffraction analyses were obtained by recrystallization from ethanol. CCDC 850009 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

(*E*)-1-(4-Bromophenoxy)-1,2-diphenylethene (2c): White solid, yield: 82%, mp 88–90 °C. IR (KBr): ν = 3058, 3023, 1644, 1581, 1480, 1230, 1054 cm^{-1}; MS (EI, 70 eV): *m*/*z* (rel. intensity) = 352 (10), 350 (10, M^+), 178 (100), 152 (17); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.32 (s, 1H), 6.98 (d, *J* = 8.9 Hz, 2H), 7.22–7.07 (m, 5H), 7.32–7.24 (m, 3H), 7.38 (d, *J* = 8.9 Hz, 2H), 7.49–7.42 (m, 2H); ^{13}C NMR: δ = 115.0, 115.2, 120.3, 126.6, 128.2, 128.4, 128.8, 129.0, 129.4, 132.5, 133.9, 135.1, 152.7, 155.7; elem. anal. calcd. for $C_{20}H_{15}BrO$: C 68.39, H 4.30; found: C 68.18, H 4.32.

4-[(*E*)-1,2-Diphenylvinyloxy]benzonitrile (2d): White solid, yield: 49%, mp: 98–99 °C. IR (KBr): ν = 3096, 3057, 2224, 1649, 1601, 1502, 1446, 1242, 1169 cm^{-1}; MS (EI, 70 eV): *m*/*z* (rel. intensity) = 297 (32), 179 (87), 178 (100), 165 (6), 152 (21), 106 (6), 105 (76), 77 (13); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.48 (s, 1H), 7.09 (d, *J* = 9.0 Hz, 2H), 7.30–7.13 (m, 8H), 7.41–7.34 (m, 2H), 7.52 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 105.5, 117.9, 118.0, 118.8, 127.2, 128.3, 128.5, 128.8, 129.2, 129.2, 133.2, 134.0, 134.4, 150.6, 160.5; elem. anal. calcd. for $C_{21}H_{15}NO$: C 84.82, H 5.08, N 4.71; found: C 84.47, H 5.12, N, 4.69.

1-[(*E*)-1,2-diphenylvinyl]-1*H*-pyrazole (2e): Colourless oil, yield: 78%. IR (neat): ν = 3057, 3024, 1641, 1598, 1514, 1498, 1444, 1392, 1321, 1193 cm^{-1}; MS (EI, 70 eV): *m*/*z* (rel. intensity) = 245 (61, M^+), 178 (100), 152 (12); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.25 (dd, *J* = 2.4, 1.84 Hz, 1H), 6.99–6.92 (m, 2H), 7.11–7.01 (m, 3H), 7.24–7.18 (m, 2H), 7.41–7.24 (m, 5H), 7.63 (d, *J* = 1.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 106.4, 118.7, 126.7, 127.9, 128.9, 129.1, 129.2, 130.3, 134.2, 135.0, 138.0, 140.7; elem. anal. calcd. for $C_{17}H_{14}N_2$: C 82.90, H 5.73, N 11.37; found: C 82.90, H 5.93, N 11.27.

L1: Pale yellow solid, yield: 12%, mp: 295 °C (decomp.). ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.80 (s, 3H), 2.90 (s, 3H), 3.90 (s, 3H), 5.90 (s, 2H), 7.60–7.80 (m, 4H), 7.91–7.98 (m, 2H), 8.38 (d, *J* = 8.2 Hz, 1H), 8.54 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 10.2, 25.1, 34.8, 52.5, 121.0, 121.6, 122.4, 123.8, 125.1, 126.7, 126.8, 127.7, 136.5, 137.6, 144.2, 144.4, 146.4, 153.4, 158.6; HR-MS: *m*/*z* = 303.1616, calcd. for $C_{19}H_{19}N_4$: 303.1604.

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