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Mild Copper-Catalyzed Vinylation Reactions of Azoles and Phenols with Vinyl Bromides

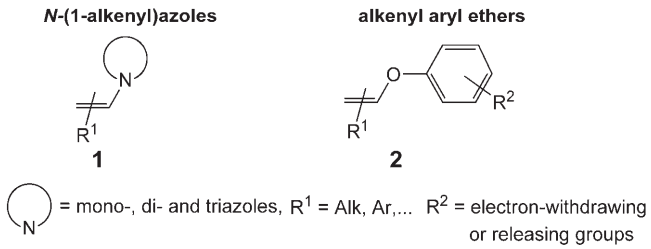
Marc Taillefer,*[a] Armelle Ouali,[a] Brice Renard,[a] and Jean-Francis Spindler[b]

Abstract: An efficient and straightforward copper-catalyzed method allowing vinylation of *N*- or *O*-nucleophiles with di- or trisubstituted vinyl bromides is reported. The procedure is applicable to a broad range of substrates since *N*-vinylation of mono-, di-, and triazoles as well as *O*-vinylation of phenol derivatives can be performed with catalytic amounts of copper iodide and inexpensive nitrogen ligands **3** or **8**. In the case of more hindered vinyl bromides, the use of the original bidentate chelator **8** was shown to be more efficient to promote the coupling reactions than our key tetradentate ligand **3**. The corresponding *N*-(1-alkenyl)-azoles and alkenyl aryl ethers are obtained in high yields and selectivities under very mild temperature conditions (35–110 °C for *N*-vinylation reactions and 50–80 °C for *O*-vinylation reactions). Moreover, to our knowledge, this method is the first example of a copper-catalyzed vinylation of various azoles. Finally, this protocol, practical on a laboratory scale and easily adaptable to an industrial scale, is very competitive compared to the existing methods that allow the synthesis of such compounds.

Keywords: copper · homogeneous catalysis · nitrogen heterocycles · phenols · vinylation

Introduction

N-(1-Alkenyl)azoles **1** and 1-alkenyl aryl ethers **2** (Scheme 1) are important classes of building blocks in organic synthesis as well as synthetic targets throughout the polymer and life science industries. Indeed, vinyl aryl ethers constitute useful intermediates in a wide range of reactions (for example, cycloaddition,[1] cyclopropanation,[2] or metathesis reactions[3]) and they find applications in the synthesis of natural product analogues,[4] biologically active molecules,[5] and polymers.[6] *N*-vinylazoles have also been widely used in the preparation of structural templates. In particular, 1-(1-alkenyl)benzotriazoles are of considerable interest because of their thermal and photochemical transformations.[7] Moreover, *N*-vinylazoles are highly reactive monomers that give rise to polymeric materials with various properties. For instance, poly(1-vinylimidazole)s and poly(1-vinyl-1,2,4-triazole)s are involved in the preparation of polymeric dyes, catalysts, and ion-exchange resins,[8] while poly(1-vinylindole)s display good photorefractive properties.[9] Otherwise, the vinyl group can act as an efficient protecting group of azole and phenol derivatives.[10] Interestingly, the *N*-vinylazole and the vinyl aryl ether moieties are found in numerous biologically active molecules. For example, vinylimidazole and 1-vinyl-1,2,4-triazole derivatives have been found to display antifungal activity[11,12] and 1-phenoxy-3-triazolyl-1-hexene derivatives constitute plant growth regulators.[13]



Scheme 1. Target molecules. Alk = alkyl, Ar = aryl.

The main routes to form *N*-(1-alkenyl)azoles **1** and alkenyl aryl ethers **2** (summarized in Scheme 2) are similar. They include alkylation of the azole or phenol with 1,2-dibromoethane[14a,b,h] or related compounds[2,14c–g] followed by dehydrohalogenation of the corresponding 2-haloethylazole or aryl 2-haloethyl ether in the presence of a base (Scheme

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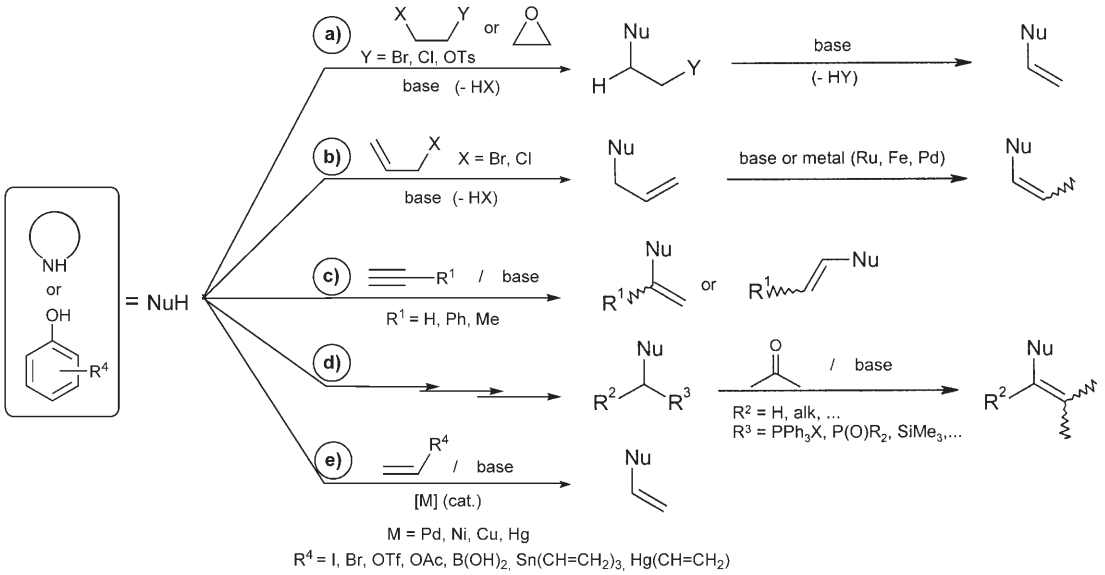


Scheme 2. Main routes to form *N*-vinylazoles and vinyl aryl ethers. Nu = nucleophile, Tf = trifluoromethansulfonyl, Ts = toluene-4-sulfonyl.

2a). Preparation of the desired 1-alkenyl derivatives can also be achieved by alkylation with allyl bromide and subsequent base-[15] or transition-metal-catalyzed isomerization[16] to yield the desired alkenyl derivatives (Scheme 2b). The major drawbacks of both procedures are the lack of generality and substrate scope. The synthesis of compounds **1** or **2** involving addition of the corresponding azole or phenol to an acetylenic compound in the presence of a strong base requires harsh conditions (high temperature (>125 °C) and pressure) and generally leads to the target products in poor yields (Scheme 2c).[17] Another way to prepare *N*-(1-alkenyl)-azoles involves creation of the carbon–carbon double bond by Wittig,[18e] Wittig–Horner,[19] Horner–Wadsworth–Emmons,[20] or Peterson[18] olefination reactions. These methods give access to a wide range of di-, tri-, or tetrasubstituted olefins but require time-consuming multistep syntheses and may thus suffer from low yields (Scheme 2d). Syntheses of alkenyl aryl ethers through olefination of carbonyl compounds have been achieved more efficiently.[21] More often than not, all of the above-mentioned procedures (Scheme 2a–d) lead to a mixture of *Z* and *E* stereoisomers. This last feature can be considered as a strong drawback and underlies the necessity to develop stereospecific methods.

The most appropriate methods for the synthesis of *N*-(1-alkenyl)azoles **1** and alkenyl aryl ethers **2** are thus based upon transition-metal-mediated coupling of azoles and phenols with different vinyl sources (Scheme 2e). *N*-vinylation of azoles with vinyl acetate in the presence of mercuric acetate has extensively been used to synthesize the corresponding *N*-vinylazoles.[22] The toxicity of mercury derivatives can, however, be considered disadvantageous for such methodologies. A general and efficient method for the synthesis of *N*-(1-alkenyl)monoazoles involves palladium-catalyzed vinylation by vinyl bromides to yield a wide range of target products under mild conditions (50–100 °C).[23] Palladium-based catalysts can also promote the cross-coupling of a wide range of phenols with vinyl triflates: alkenyl aryl ethers are thus obtained in good yields at 100 °C.[24] Nevertheless, the use of expensive palladium limits the attractiveness of these methods for industrial applications. As far as copper-mediated methods are concerned, those involving vinyl boronic acids (*N*- and *O*-vinylation)[25] or tetravinyltin (*O*-vinylation)[26] as vinylating agents display the major advantage of proceeding at room temperature but suffer from the requirements for stoichiometric amounts of the cupric acetate. A procedure involving vinylation of phenols by easily available vinyl bromides in the presence of the system CuI (25 mol %)/2,2,6,6-tetramethylheptane-3,5-dione (25 mol %) constitutes an attractive alternative to the above-mentioned methods.[27] It requires, however, high copper salt and ligand loadings and proceeds at a relatively high temperature (110 °C). More recently, a similar copper-mediated method involving *N*,*N*-dimethylglycine hydrochloride as the ligand (30 mol %) enabled the coupling of vinyl iodides and bromides with phenols under milder temperature conditions (60–90 °C).[28] It is worth noting that, although strategies involving the use of copper-based catalysts to promote *N*-amidation of vinyl halides have been reported,[29] no analogous method for achieving *N*-vinylation of azoles has been described, to the best of our knowledge.

The development of general, mild, cheap, stereospecific synthetic methodologies to create alkenyl C–N and C–O bonds and thus give access to *N*-(1-alkenyl)azoles **1** and alkenyl aryl ethers **2** is thus particularly challenging.

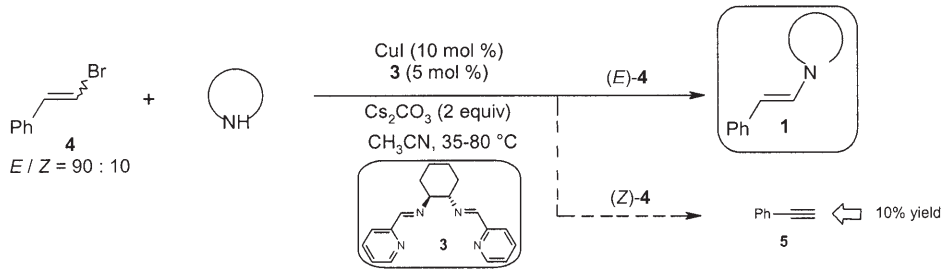
The quest for new catalysts to promote C–N, C–O, or C–C bond cross-coupling reactions has become a major topic in our group.[30,31] In that context, we developed catalysts involving copper salts and new nitrogen and/or oxygen ligands;[31c] these catalysts are able to promote arylation reactions of *N*-, *O*-, and *C*-nucleophiles that are useful for the synthesis of *N*-arylated heterocycles,[31c] *N*-arylated ami-

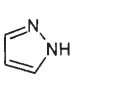
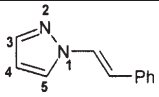
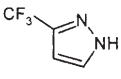
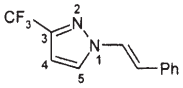
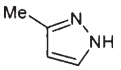
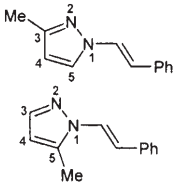
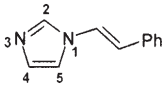
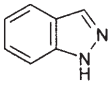
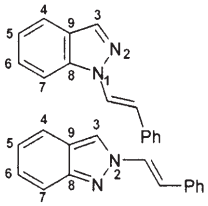
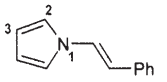
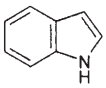
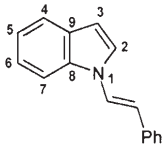
des,[31d] diaryl ethers,[31b] *C*-arylated malonic derivatives,[31b] or aryl nitriles.[31a] These copper-based methodologies are characterized by very mild reaction conditions with respect to the classical Ullmann condensations since most of these coupling reactions can be performed at temperatures of 25–80 °C. We now report further important synthetic utilizations of our catalytic systems, namely, the copper-catalyzed *N*-vinylation of azoles and the *O*-vinylation of phenol derivatives.

Results and Discussion

***N*-Vinylation of mono- and diazoles by β-bromostyrenes**: Our initial exploration of reaction conditions focused on the coupling of pyrazole with β-bromostyrene, a commercial vinyl source available as a mixture of both *E* and *Z* isomers in a *E*-to-*Z* ratio of 90:10. The reaction was performed in the presence of CuI (10 mol %) and tetradentate ligand **3** (5 mol %) by using cesium carbonate as a base (Table 1, entry 1). We were pleased to find that, under these conditions, the coupling was successful, with (*E*)-β-bromostyrene being quantitatively and stereoselectively converted into (*E*)-β-styrylpyrazole (**1a**) after 30 h at 50 °C.[32] If reaction time is not an issue, it is even possible to perform the condensation at a lower temperature, with **1a** being obtained in 100 % yield after 55 h at 35 °C (Table 1, entry 1). Moreover, whatever the temperature, (*Z*)-β-bromostyrene was totally transformed into phenylacetylene by a competitive dehydrobromination reaction. Under basic conditions, *Z*-alkenyl bromides are indeed known to undergo an E2-type elimination more easily than the corresponding *E* isomers.[33] We thus decided to express the yields of (*E*)-β-styrylpyrazole (**1a**) with respect to (*E*)-β-bromostyrene.

Table 1. *N*-Vinylation of mono- and diazoles by β-bromostyrenes (*E*/*Z* = 90:10).[a]



Entry	Azole	*T* [°C]	*t* [h]	(*E*)-Styrylazole		(*E*)-**4** Conversion [%]	Yield of **1** [%][b]
1		50	30		**1a**	100	100 (94)
		35	55			100	100
2		50	30		**1b**	100	100 (98)
3		50	30		**1c** **1d**	100	70 (combined: 89) 30
4		50	30		**1e**	93	93 (90)
		60	24			100	100
5		60	24		**1f** **1g**	93	80 13
		80	24		**1f** **1g**	100	85 (80) 15 (9)
6		60	24		**1h**	76	75
		80	24			100	99 (89)
7		60	24		**1i**	74	74
		80	24			100	100 (83)

[a] Reaction conditions for yields of isolated products: β-bromostyrene (*E*/*Z* = 90:10, 2 mmol), azole (3 mmol), Cs_2CO_3 (4 mmol), CuI (0.20 mmol), ligand **3** (0.10 mmol), CH_3CN (1.2 mL); reaction conditions for yields measured by GC analysis: β-bromostyrene (*E*/*Z* = 90:10, 0.5 mmol), azole (0.75 mmol), Cs_2CO_3 (1 mmol), CuI (0.05 mmol), ligand **3** (0.025 mmol), CH_3CN (300 μL). [b] Yields refer to GC yields (with 1,3-dimethoxybenzene as an internal standard) and yields in brackets refer to yields of isolated products; yields are based on (*E*)-β-bromostyrene.

We afterwards investigated the coupling reactions of β-bromostyrene with various azoles under analogous conditions.[34] *N*-vinylations of substituted pyrazoles were first attempted and it was found that the presence of a substituent in position 3 did not affect the reactivity of the nitrogen heterocycle since 3-trifluoromethylpyrazole and 3-methylpyra-

zole were also quantitatively converted into the corresponding 1-(*E*)-β-styrylazoles within 30 h at 50 °C (Table 1, entries 2 and 3). In the case of these unsymmetrical pyrazoles, *N*-vinylation can theoretically lead to two regioisomers that result from the substitution of two tautomers at the NH position.[35] Structures can easily be assigned according to their $^{1}H/^{13}C$ NMR spectroscopic data, particularly if the coupling constant of hydrogen atoms on the *N*-substituted pyrazole ring (by a styryl group in our case) is considered: 1-β-styryl-3-substituted pyrazoles are expected to exhibit a $^{3}J_{H,H}$ value of 2.4–2.9 Hz, while the corresponding constant in 1-β-styryl-5-substituted pyrazoles is about 1.5–1.9 Hz.[36] Vinylation of 3-trifluoromethylpyrazole is however totally regioselective and exclusively gave rise to 1-(*E*)-β-styryl-3-trifluoromethylpyrazole (**1b**), which could be isolated in 98% yield. Such behavior was probably due to the inductive effect (−*I*) of the trifluoromethyl group, which deactivates the α-nitrogen atom and in this way favors substitution on the β atom. By contrast, 3-methylpyrazole led to the formation of two regioisomers, 1-(*E*)-β-styryl-3-methylpyrazole (**1c**) and 1-(*E*)-β-styryl-5-methylpyrazole (**1d**), in a 70:30 ratio with the major product being the former compound. The inductive effect of the methyl group (+*I*) is expected to favor vinylation on the α-nitrogen atom but this effect is probably counterbalanced by the induced steric hindrance, which is apparently predominant. The regioselectivity observed for condensation of 3-methylpyrazole and 3-trifluoromethylpyrazole with (*E*)-β-bromostyrene is similar to that already reported for *N*-arylation reactions of these nitrogen heterocycles.[31c]

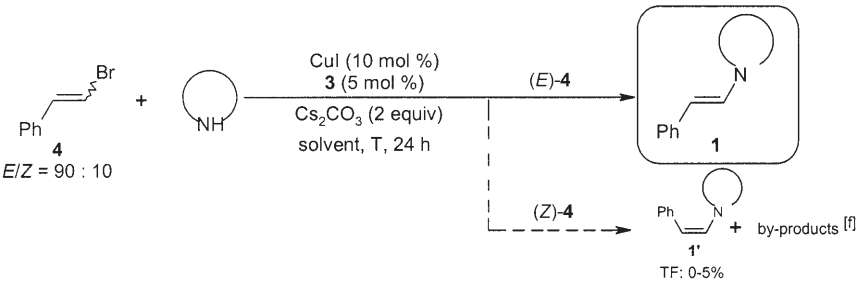
The scope of the process was also investigated in the case of other nitrogen heterocycles. Imidazole proved to be as reactive as pyrazole since 1-(*E*)-β-styrylimidazole (**1e**) could also be isolated in 90% yield (Table 1, entry 4) after 30 h at 50 °C. Our procedure is complementary to that involving addition of this nitrogen heterocycle across phenylacetylene in the presence of sodium, as described by Bourgeois and Lucrece (Scheme 2, c), a process that exclusively yields the *Z* stereoisomer.[17f] It is moreover both simpler and more efficient than the synthesis of alkylation/dehydrohalogenation (Scheme 2a) that was proposed by Cooper and Irwin, which leads to **1e** in 49% yield after alkylation of imidazole by styrene oxide, chlorination of the corresponding 1-(2-hydroxy-2-phenylethyl)imidazole by thionyl chloride, and subsequent dehydrochloration in the presence of KOH.[14f] *N*-vinylation of indazole by (*E*)-β-bromostyrene, almost quantitative after 24 h at 60 °C and quantitative at 80 °C (Table 1, entry 5), gave rise to a mixture of two regioisomers that were easily separated by column chromatography, 1-(*E*)-β-styrylindazole (**1f**) and, to a minor extent, 2-(*E*)-β-styrylindazole (**1g**). Indazoles **1f** and **1g**, which result from substitution on the N1 and N2 positions, respectively, are obtained in an approximately 6:1 ratio and can be distinguished by their NMR spectra. Both display a greater $J_{H6,H7}$ coupling constant than the $J_{H5,H6}$ one, but this difference is weaker in the case of the 1-substituted indazole ($J_{H6,H7}/J_{H5,H6}=1.1$ for **1f** and 1.3 for **1g**; see the Experimental Section).[37]

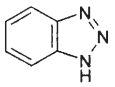
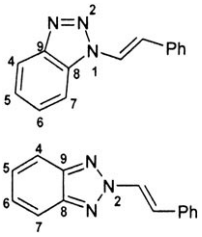
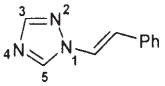
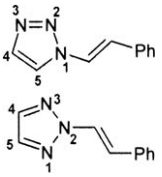
Furthermore, the same catalytic system was shown to efficiently promote *N*-vinylations of monoazoles such as pyrrole and indole (Table 1, entries 6 and 7). The couplings occurred at 60 °C, with 1-(*E*)-β-styrylpyrrole (**1h**) and 1-(*E*)-β-styrylindole (**1i**) being obtained in 75 and 74% yields, respectively, after 24 h at this temperature. An increase of the temperature of the reaction mixture allowed completion of the reaction within the same time and isolation of the target products in good yields. It is worth noting that the palladium-mediated preparation of **1h** and **1i** has already been reported: the *N*-vinylation of pyrrole by (*E*)-β-bromostyrene at 50 °C was not selective and gave rise to 1-(*E*)-β-styryl-pyrrole in poor yield, while quantitative *N*-vinylation of indole occurred at 85 °C.[23]

***N*-Vinylation of tri- and tetrazoles by β-bromostyrenes**: We then focused our attention on extending this methodology to the *N*-vinylation of tri- and tetrazoles (Table 2). We first investigated the *N*-vinylation of benzotriazole, 1,2,4-triazole, and 1,2,3-triazole by β-bromostyrene in the presence of the same catalytic system, CuI/**3** in a 2:1 ratio and cesium carbonate in acetonitrile at 80 °C. Unfortunately, the corresponding styryltriazoles were not formed under these conditions (Table 2, entries 1, 4, and 7). Yields were however significantly increased by replacing acetonitrile with *N*,*N*-dimethylformamide (DMF), in which the cesium salts of the triazoles were probably more soluble (Table 2, entries 2 and 5), and we were pleased to find that total conversion of (*E*)-β-bromostyrene occurred at 110 °C in this solvent (Table 2, entries 3 and 6). *N*-Substitution of 1,2,4-triazole (entry 6) regiospecifically took place at the N1(2) atom whose enhanced nucleophilicity in comparison with the N4 nitrogen atom could be due to an α effect. By contrast, *N*-vinylation of benzotriazole gave rise to two regioisomeric compounds, 1-(*E*)-β-styrylbenzotriazole (**1j**) and 2-(*E*)-β-styrylbenzotriazole (**1k**), which could be easily separated by column chromatography. The substitution preferentially occurred at the N1 position (ratio of **1j**/**1k** ≈ 10:1), which is in agreement with the highest electronic density being found on this atom in the benzotriazolate anion.[38] Once more, the structures of both regioisomers could be assigned according to their $^{1}H/^{13}C$ NMR spectra since the benzotriazole unit in the N2-substituted compound **1k** has a symmetry and thus displays equivalent signals for the protons and respective carbon atoms at positions 4 and 7 on the one hand and for the protons and respective carbon atoms at positions 5 and 6 on the other hand. The coupling reaction of 1,2,3-triazole and (*E*)-β-bromostyrene also led to a mixture of 1-(*E*)-β-styryl-1,2,3-triazole (**1m**) and 2-(*E*)-β-styryl-1,2,3-triazole (**1n**); both regioisomers were formed in comparable amounts (ratio of **1n**/**1m** ≈ 1.3:1). This result is in agreement with the fact that the electron densities on the N1 and N2 atoms of the triazole ring are similar.[38]

We then tried to extend our methodology to *N*-vinylation of tetrazole derivatives. Unfortunately, attempts to achieve the coupling reaction of 5-phenyltetrazole and β-bromostyrene at 110 °C was unsuccessful, with the vinylating agent

Table 2. *N*-Vinylation of tri- and tetrazoles by β-bromostyrenes (*E*/*Z* = 90:10).[a]



Entry	Azole	Solvent	*T* [°C]	(*E*)-Styrylazole **1**	(*E*)-**4** Conversion [%]	Yield of **1** [%][b]
1		CH_3CN	80	 **1j** **1k**	≈2[c]	<1 0
2		DMF	80		44[c]	40 2
3		DMF	110		100[c]	89 (87) 9 (7)
4		CH_3CN	80	 **1l**	≈2[c]	<1
5		DMF	80		54	54
6[d]		DMF	110		100	100 (94)
7		CH_3CN	80	 **1m** **1n**	≈2[c]	0 <1
8[d]		DMF	110		100	43 (38) 57 (50)
9		DMF	110	–	100[e]	0

[a] Reaction conditions for yields of isolated product: β-bromostyrene (*E*/*Z* = 90:10, 2 mmol), azole (3 mmol), Cs_2CO_3 (4 mmol), CuI (0.20 mmol), ligand **3** (0.10 mmol), CH_3CN (1.2 mL); reaction conditions for yields measured by GC analysis: β-bromostyrene (*E*/*Z* = 90:10) (0.5 mmol), azole (0.75 mmol), Cs_2CO_3 (1 mmol), CuI (0.05 mmol), ligand **3** (0.025 mmol), CH_3CN (300 μL). Byproducts detected whatever the solvent and the temperature: phenylacetylene **5** (≤5%) and diyne **6** (≤2%; structure given in Table 3). [b] Yields refer to GC yields (with 1,3-dimethoxybenzene as an internal standard) and yields in brackets refer to yields of isolated products; yields are based on (*E*)-β-bromostyrene. [c] Formation of **7** with ≤2% yield (structure given in Table 3). [d] (*Z*)-Styrylazoles **1′l**, **1′m**, and **1′n** formed from (*Z*)-**4** in 4–5% yield. [e] Total conversion of (*E*)- and (*Z*)-β-bromostyrene into styrene (30%) and enyne **7** (35%). [f] By-products detected whatever the solvent and the temperature: phenylacetylene **5** (5%) and diyne **6** (2%).

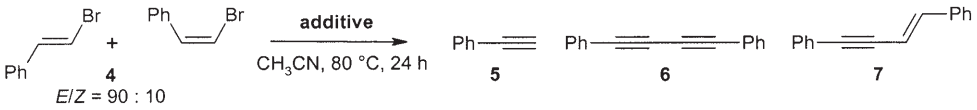
being quantitatively consumed to yield styrene and enyne **7** in 30 and 35% yields, respectively (Table 2, entry 9). The low reactivity of this nitrogen heterocycle may be attributed to its poor nucleophilicity. To our knowledge, the only method enabling metal-catalyzed *N*-vinylation of tetrazole derivatives involves mercuric acetate, whose disadvantages were mentioned in the Introduction.

By-products derived from (*Z*)-β-bromostyrene ((*Z*)-4) and proposed pathways to explain their formation: When *N*-vinylation of 1,2,4- and 1,2,3-triazoles was performed at 110°C, small amounts (4–5%)[39] of 1-(*Z*)-styryl-1,2,4-triazole (**1′l**), 1-(*Z*)-styryl-1,2,3-triazole (**1′m**), and 2-(*Z*)-styryl-1,2,3-triazole (**1′n**) were formed (Table 2, entries 6 and 8, footnote [d]). At this temperature, the side dehydrobromination of (*Z*)-β-bromostyrene ((*Z*)-**4**), which occurred exclusively in the case of mono- and diazoles (50–80°C; Table 1), was in competition with the *N*-vinylation of triazoles. It is noteworthy that, under these conditions, *N*-vinylation of the more hindered benzotriazole by (*Z*)-**4** was not observed (Table 2, entry 3).

Moreover, whatever the nature of the solvent (CH_3CN or DMF) and the temperature (80 or 110°C), (*Z*)-**4** also led to phenylacetylene (**5**; ≤5%) and to 1,4-diphenylbutadiyne (**6**; ≤2%; Table 2, footnote [a]). 1-(*E*)-4-diphenyl-but-1-en-3-yne (**7**), the major side product obtained from the *N*-vinylation of 5-phenyltetrazole (Table 2, entry 9), was also occasionally observed in small amounts (≤2%; Table 2, footnote [c]). To better understand the origin of these by-products, the mixture of both stereoisomers was heated for 24 h at 80°C in the presence of different additives (Table 3). The presence of only cesium carbonate led to quantitative dehydrobromination of the *Z* isomer, with the corresponding (*E*)-β-bromostyrene, in contrast, being totally recovered after 24 h at 80°C (Table 3, entry 2). Finally, it was highlighted that the combined action of both the catalytic system and cesium carbonate enabled two further copper-catalyzed side reactions (Table 3, entry 3): 1) the self-coupling of **5** to yield diyne **6** and 2) the cross-coupling of **5** with (*E*)-**4** to form enyne **7**. The ability of copper iodide to catalyze coupling reactions of acetylenic compounds and vinyl iodides to yield 1,3-enynes has also been recently reported.[40]

To sum up (Scheme 3), the more sterically encumbered (*Z*)-β-bromostyrene was less reactive than the correspond-

Table 3. Evolution of β-bromostyrenes ($E/Z = 90:10$) in the presence of different additives.[a]



Entry	Additives	Yield [%]				
		(*E*)-**4**	(*Z*)-**4**	**5**	**6**	**7**
1	no additive	90	10	0	0	0
2	Cs_2CO_3 (2 equiv)	90	0	10	0	0
3	CuI (10 mol%) + **3** (5 mol%) + Cs_2CO_3 (2 equiv)	85	0	<1	2	5

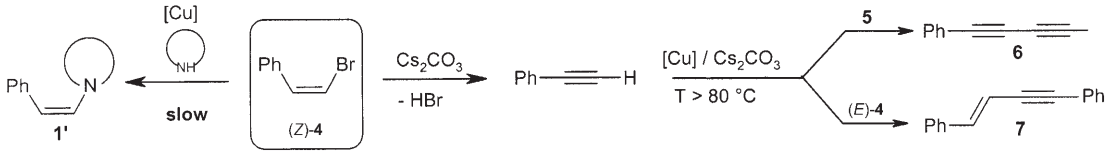
[a] The compositions of the final mixtures were determined by GC analysis with 1,3-dimethoxybenzene as an internal standard.

ing *E* isomer towards coupling with mono-, di-, and triazoles and was thus mainly or even quantitatively consumed by the above-mentioned side reactions, namely, dehydrobromination leading to **5** and, for reaction temperatures higher than 80 °C, further copper-catalyzed formation of diyne **6** and enyne **7**.

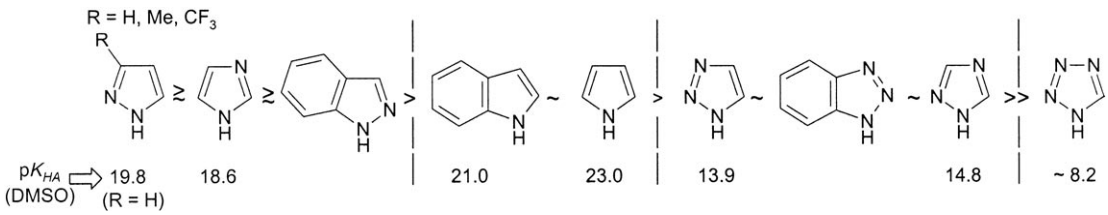
Comparative reactivities of nitrogen heterocycles: The order of reactivity in the azole series emerging from our studies is given in Scheme 4. Diazoles (pyrazoles, imidazole, indazole) were found to be the most reactive, since they underwent almost quantitative *N*-vinylation after 24–30 h at temperatures of 50–60 °C. We observed that less acidic monoazoles (pyrrole and indole) were a bit less reactive since a temperature of 80 °C was required to obtain (*E*)-β-styryl-monoazoles **1h** and **1i** in quantitative yields within the same time. Both pyrrole and indole exhibited similar reactivity, which could mean that the steric hindrance of the latter was counterbalanced by its greater ability to be deprotonated (pK_{HA} values are given in Scheme 4). Finally, despite their higher acidity and their consequently greater ease of ionization, triazoles required more forcing conditions than mono- and diazoles to undergo *N*-vinylation by (*E*)-β-bromostyrene (DMF, 110 °C). This result can be rationalized by invoking their poorer nucleophilicity.

The order we observed can reasonably be considered as a result of several parameters controlling the reactivity of the nitrogen heterocycle, among which are 1) the nucleophilicity, which is generally weaker when the azole displays more nitrogen atoms, 2) the ease of ionization, which can be estimated from the pK_{HA} values (Scheme 4), and 3) the ability to efficiently coordinate copper salts, which depends on both electronic and steric properties of the substrate.

***O*-Vinylation of phenol derivatives by β-bromostyrenes**: The scope of the above-described methodology was then extended to vinylation of phenol derivatives by (*E*)-β-bromostyrene. The same catalytic system involving copper iodide (10 mol%) and ligand **3** (5 mol%) was found to efficiently promote the coupling reaction of electron-neutral and electron-rich phenols (Table 4, entries 1–3). *O*-vinylation of less reactive substrates substituted with more electron-withdrawing chloro and fluoro groups also proved to be successful (Table 4, entries 4 and 5). In all cases, β-styryl aryl ethers were formed in high yields and selectivities and the coupling reactions proceeded under very mild temperature conditions in comparison with the existing methods (Scheme 1). Moreover, lower ligand loadings than in other copper-mediated *O*-vinylation reactions can be employed.[27,28] Our methodology encountered, however, some limitation in the case of phenols bearing the strongly electron-withdrawing nitro group (Table 4, entry 6); *O*-vinylation of 4-nitrophenol did not occur, even under more forcing conditions (DMF, 110 °C; Table 4, footnote [c]). The poor reactivity of such acidic phenols in Ullmann-type couplings is well-known.[41] Finally, whatever the nature of the phenol derivative, no traces of (*Z*)-styryl aryl ethers resulting from *O*-vinylation by (*Z*)-β-bromostyrene ((*Z*)-**4**) were detected. As for azoles, (*Z*)-**4** proved to be less reactive than its corresponding *E*

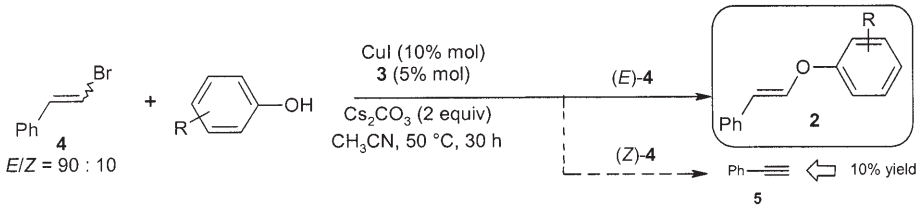


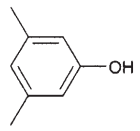
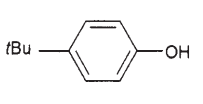
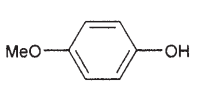
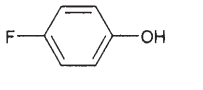
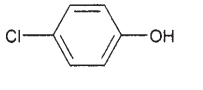
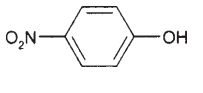
Scheme 3. Formation of by-products derived from (*Z*)-β-bromostyrene ((*Z*)-**4**).



Scheme 4. Order of reactivity in the azole series for *N*-vinylation by (*E*)-β-bromostyrene. DMSO = dimethyl sulfoxide.

Table 4. *O*-Vinylation of substituted phenols by β-bromostyrenes (*E*/*Z* = 90:10).[a]



Entry	Phenol	(*E*)-β-Styryl aryl ether **2**[a]	(*E*)-**4** Conversion [%]	Yield of **2** [%][b]
1		**2a**	92	92 (75)
2		**2b**	100	100 (90)
3		**2c**	95	95 (82)
4		**2d**	100	100 (82)
5		**2e**	89	89 (74)
6[c]		**2f**	0	–

[a] Reaction conditions for yields of isolated products: β-bromostyrene (*E*/*Z* = 90:10, 5 mmol), phenol (7.5 mmol), Cs_2CO_3 (10 mmol), CuI (0.5 mmol), ligand **3** (0.25 mmol), CH_3CN (3 mL); reaction conditions for yields measured by GC analysis: β-bromostyrene (*E*/*Z* = 90:10, 0.5 mmol), phenol (0.75 mmol), Cs_2CO_3 (1 mmol), CuI (0.05 mmol), ligand **3** (0.025 mmol), CH_3CN (300 μL). [b] Yields refer to GC yields (with 1,3-dimethoxybenzene as an internal standard) and yields in brackets refer to yields of isolated products after purification by column chromatography on alumina; yields are based on (*E*)-β-bromostyrene. [c] DMF, 110 °C.

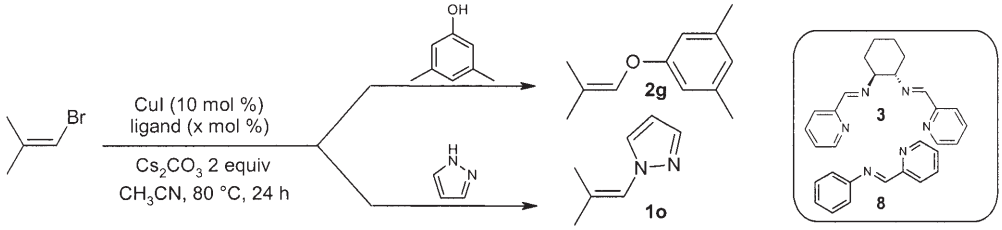
were here formed in poor yields after 24 h at 80 °C (21 % and 5 %, respectively; Table 5, entries 1 and 4). It was noticed that an increase of the ligand loading (from 5 % up to 20 %) significantly improved the efficiency of both coupling reactions (Table 5, entries 2 and 5). Finally, we were pleased to find that quantitative *O*-vinylation of 3,5-dimethylphenol could be achieved by replacing tetradentate ligand **3** with the original bidentate ligand **8** and that ether **2g** could thus be isolated in 89 % yield (Table 5, entry 3). The action of ligand **8** also improved the yield for *N*-vinylation of pyrazole since *N*-vinylpyrazole **1o** was obtained in 55 % after 24 h at 80 °C (Table 5, entry 6) and the outcome of this reaction could be improved by increasing the reaction time. The weaker steric hindrance of ligand **8**, in comparison with that of ligand **3**, may allow the promotion of the coupling of more encumbered substrates, such as 1-bromo-2-methylpropene. These last results highlight the necessity of having a diverse range of ligand frameworks to tune the behavior of our catalytic systems with a view to extending their scope. We have already underlined this fact in the case of arylation reactions of *N*-, *C*-, and *O*-nucleophiles.[30,31]

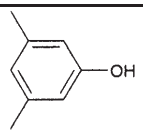
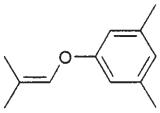
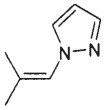
isomer and was quantitatively converted into phenylacetylene (**5**).

***N*-/*O*-Vinylation by 1-bromo-2-methylpropene**: The scope of the process with respect to the vinyl bromide structure was next investigated. 1-bromo-2-methylpropene was chosen as the vinylating agent: this trisubstituted substrate is more sterically encumbered than (*E*)-β-bromostyrene and cannot undergo dehydrobromination as (*Z*)-β-bromostyrene did. The coupling of 3,5-dimethylphenol and pyrazole with 1-bromo-2-methylpropene was first carried out in the presence of the catalytic system involving copper iodide (10 mol %) and ligand **3** (5 mol %), with cesium carbonate as a base, in acetonitrile. Whereas these conditions enabled quantitative vinylation of both nucleophiles by (*E*)-β-bromostyrene under very mild conditions (Table 1, entry 1 and Table 4, entry 1), the expected 3,5-dimethylphenyl 2-methyl-1-propenyl ether (**2g**) and 1-(2-methyl-1-propenyl)pyrazole (**1o**)

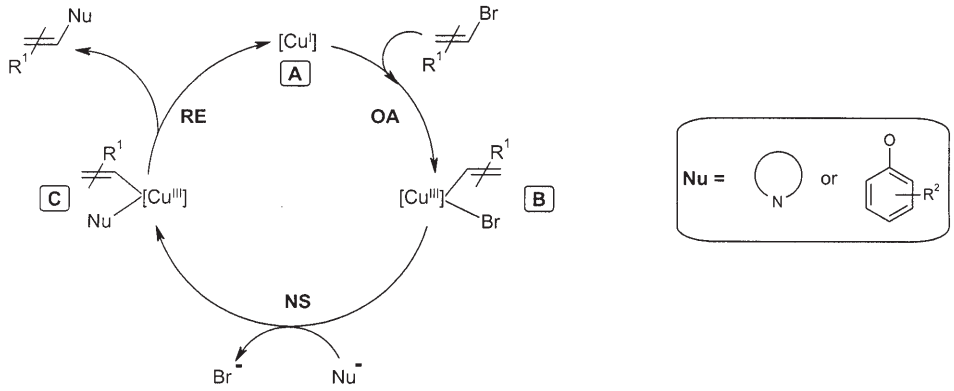
Proposed mechanism for N- and O-vinylation of azoles and phenols by vinyl bromides: The proposed mechanism for the *N*- and *O*-vinylation reactions with vinyl bromides is similar to that we described for arylation reactions with our copper-based systems (Scheme 5).[31a,d] To our knowledge, no mechanism has been proposed in the literature for copper-catalyzed vinylations of nucleophiles. The first step should involve oxidative addition of the vinyl bromide to the catalytically active copper species **A**, which is thought to be a copper(I) complex involving ligands. The resulting copper(III) intermediate **B** should undergo a nucleophilic substitution of the copper-bound bromide by a nucleophile to give **C**. The third step should consist of the reductive elimination of *N*-(1-alkenyl)azoles **1** or alkenyl aryl ethers **2** and the subsequent regeneration of the active copper(I) species. It is

Table 5. Vinylation of pyrazole and 3,5-dimethyphenol by 1-bromo-2-methylpropene.[a]



Entry	Nucleophile	Ligand (mol%)	Product		Yield [%][b]
1		**3** (5)		**2g**	21
2		**3** (20)			50
3		**8** (20)			100 (89)
4		**3** (5)		**1o**	5
5		**3** (20)			35
6		**8** (20)			55 (47)

[a] Reaction conditions for yields of isolated products: nucleophile (2 mmol), 1-bromo-2-methylpropene (3 mmol), Cs_2CO_3 (4 mmol), CuI (0.2 mmol), ligand **8** (0.4 mmol), CH_3CN (1.2 mL); reaction conditions for yields measured by GC analysis: nucleophile (0.5 mmol), 2-methyl-1-bromopropene (0.75 mmol), Cs_2CO_3 (1 mmol), CuI (0.05 mmol), ligand **3** or **8** (see Table), CH_3CN (300 μL). [b] Yields refer to GC yields (with 1,3-dimethoxybenzene as an internal standard) and yields in brackets refer to yields of isolated products after purification by column chromatography on silica gel or alumina; yields are based on nucleophile.



Scheme 5. Possible mechanism for copper-catalyzed *N*- and *O*-vinylation of azoles and phenols by vinyl bromides. OA = oxidative addition, NS = nucleophilic substitution, RE = reductive elimination.

worth noting that the nucleophilic substitution step could also precede the oxidative addition step.

The poorer reactivity of the more hindered (*Z*)-β-bromostyrene and 1-bromo-2-methylpropene towards *N*- and *O*-nucleophiles in comparison with that of (*E*)-β-bromostyrene may be explained by their lower ease for performing oxidative addition on the copper(I) complex. Indeed, Jutand has shown that oxidative addition of (*Z*)-β-bromostyrene on palladium-based catalysts was significantly slower (35 times slower) than that of the corresponding *E* isomer, probably because of its greater steric hindrance.[42] The improved efficiency of bidentate ligand **8** over that of tetradentate ligand **3** for achieving *N*- and *O*-vinylations with the trisubstituted 1-bromo-2-methylpropene could be rationalized by invoking the smaller steric bulk it generates on the active copper(I) species **A**. The latter species would consequently more easily accept sterically hindered substrates during the oxidative addition.

Conclusion

We have developed a straightforward and efficient method allowing quantitative *N*-vinylation of nitrogen heterocycles by (*E*)-β-bromostyrene under the catalysis of an inexpensive copper-based system involving CuI (10 mol%) and tetradentate ligand **3** (5 mol%). This method is general since it is applicable to a wide range of mono-, di-, and triazoles and, to the best of our knowledge, this is the first copper catalytic system allowing *N*-vinylation of these substrates. (*E*)-styryl aryl ethers could also be obtained in high yields and selectivities by *O*-vinylation of various substituted phenols with (*E*)-β-bromostyrene under similar conditions. Finally, it was noticed that (*Z*)-β-bromostyrene was less reactive than the corresponding *E* isomer and mainly gave rise to byproducts. This copper-based methodology could successfully be extended to *N*- and *O*-vinylation with more encumbered vinylating agents such as the trisubstituted 1-bromo-2-methylpropene. In this case, the less hindered bidentate ligand **8** was shown to be more efficient for promoting the coupling.

Whatever the nature of the nucleophile (either azole or phenol) and the vinylating agent, coupling reactions proceed under mild temperature conditions (35–110 °C for *N*-vinylation reactions; 50–80 °C for *O*-vinylation reactions) and by

using particularly low copper and ligand loadings. Thus, this practical protocol, which is very competitive compared to all of the existing methods for the synthesis of *N*-(1-alkenyl)-azoles and 1-alkenyl aryl ethers, can easily be adapted for industrial applications.

Work to extend the scope of our vinylation method to other vinyl bromides and chlorides as well as to other nucleophiles is in progress in our laboratory. Other applications of our copper catalytic systems and a general mechanistic study concerning copper-catalyzed arylations and vinylations of nucleophiles will also be reported soon.

Experimental Section

General: Column chromatography was performed with SDS 60 A C.C silica gel (35–70 μm). Thin-layer chromatography was carried out by using Merck silica gel 60 F_{254} plates. Products were characterized by their NMR, GC/MS, and IR spectra. NMR spectra were recorded at 20 °C on DRX-250 and DRX-400 spectrometers working at 250.13 and 400.13 MHz, respectively, for ^{1}H spectra, at 62.90 and 100.61 MHz, respectively, for ^{13}C spectra, and at 236.36 and 376.50 for ^{19}F spectra. Coupling constants are reported in Hz and chemical shifts (δ) in ppm relative to tetramethylsilane for ^{1}H and $\{^1H\}^{13}C$ spectra ($\delta = 77.00$ ppm for the $CDCl_3$ signal in the ^{13}C spectra) and in ppm relative to $CFCl_3$ for $\{^1H\}^{19}F$ spectra. The first-order peak patterns are indicated as s (singlet), d (doublet), t (triplet), and q (quadruplet). Complex non-first-order signals are indicated as m (multiplet) and broad signals as br. ^{13}C NMR signals were assigned by using HMQC and HMBC sequences. Gas chromatography–mass spectrometry (GC/MS) spectra were recorded on an Agilent Technologies 6890 N instrument with an Agilent 5973 N mass detector (EI) and an HP5-MS 30 m × 0.25 mm capillary apolar column (stationary phase: 5% diphenyldimethylpolysiloxane film, 0.25 μm). GC/MS method: initial temperature = 45 °C, initial time = 2 min, gradient = 10 °C min^{-1}, final temperature = 250 °C, final time = 10 min. IR spectra were recorded on a Nicolet 210 FT-IR instrument (a neat thin film for liquid products and a KBr pellet or carbon tetrachloride solution for solid products). FAB+ and high-resolution mass spectra were recorded on a JEOL JMS-DX300 spectrometer (3 keV, xenon) in a *meta*-nitrobenzylalcohol matrix. Melting points were determined by using a Büchi B-540 apparatus and are uncorrected.

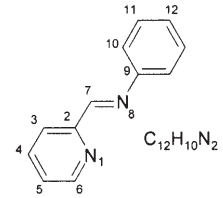
Materials: All reactions were carried out in 35-mL Schlenk tubes or in Carousel "reaction stations RR98030" Radley tubes, under a pure and dry nitrogen atmosphere. Acetonitrile was distilled from P_4O_{10} and DMF was distilled under vacuum from $MgSO_4$; both were stored protected from light over 4-Å activated molecular sieves under a nitrogen atmosphere. Cesium carbonate (Aldrich) was ground to a fine powder and stored under vacuum in the presence of P_4O_{10}. All other solid materials were stored in the presence of P_4O_{10} in a bench-top desiccator under vacuum at room temperature and weighed in air. Copper(I) iodide was purified according to literature procedures[43] and stored protected from light. The synthesis of ligand **1** was reported in our previous papers[30] and the procedure to obtain ligand **7** is reported below. Vinyl halides, azoles, and phenols were purchased from commercial sources (Aldrich, Acros, Avocado, Fluka, or Lancaster). Solids were recrystallized in an appropriate solvent.[44] Liquids were distilled under vacuum and stored under an atmosphere of nitrogen.

General procedure for the *N*-vinylation of azoles and *O*-vinylation of phenols by β-bromostyrenes (2-mmol scale): After standard cycles of evacuation and back-filling with dry and pure nitrogen, an oven-dried Radley tube equipped with a magnetic stirring bar was charged with CuI (38.0 mg, 0.2 mmol), ligand **3** (29.2 mg, 0.1 mmol), the nucleophile if a solid (the azole or the phenol, 3 mmol), and Cs_2CO_3 (1.303 g, 4 mmol). The tube was evacuated and back-filled with nitrogen. β-Bromostyrene (256 μL, 3 mmol) and the nucleophile if a liquid were added by syringe under a stream of nitrogen at room temperature, followed by anhydrous and degassed solvent (acetonitrile or DMF, 1.2 mL). The tube was sealed under a positive pressure of nitrogen and the mixture was stirred and heated to the required temperature for the required time period. After cooling to room temperature, the mixture was diluted with dichloromethane (≈25 mL) and filtered through a plug of celite, with the filter cake being further washed with dichloromethane (≈5 mL). The filtrate was washed twice with water (≈10 mL × 2). The collected aqueous phases were extracted twice with dichloromethane (≈10 mL × 2). The organic layers were collected, dried over $MgSO_4$, filtered, and concentrated in vacuo to yield a brown oil. The crude product obtained was purified by silica gel or alumina chromatography with an appropriate eluent (mentioned below for each target product).

General procedure for the *N*-vinylation of pyrazole and *O*-vinylation of 3,5-dimethylphenol by 1-bromo-2-methylpropene (2-mmol scale): After standard cycles of evacuation and back-filling with dry and pure nitrogen, an oven-dried Radley tube equipped with a magnetic stirring bar was charged with CuI (38.0 mg, 0.2 mmol), ligand **8** (72.8 mg, 0.4 mmol), the nucleophile (136.2 mg of pyrazole or 244.4 mg of 3,5-dimethylphenol, 2 mmol), and Cs_2CO_3 (1.303 g, 4 mmol). The tube was evacuated and back-filled with nitrogen. 1-bromo-2-methylpropene (307 μL, 3 mmol) was added by syringe under a stream of nitrogen at room temperature, followed by anhydrous and degassed acetonitrile (1.2 mL). The tube was sealed under a positive pressure of nitrogen and the mixture was stirred and heated to 80 °C for 24 h. The workup was the same as that for vinylation by β-bromostyrenes.

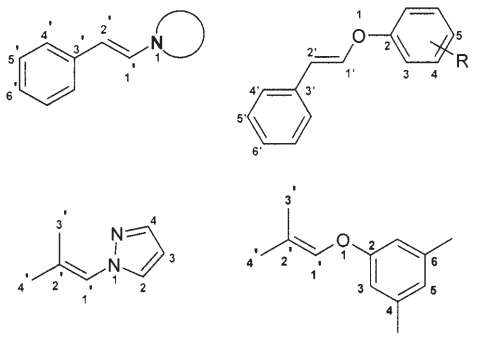
General procedure for reactivity comparisons or screening of reaction conditions (0.5-mmol scale): The above procedures were applied on a 0.5-mmol scale. After heating for the required time period at the required temperature, the reaction mixture was allowed to cool to room temperature and was diluted with dichloromethane (5 mL). 1,3-Dimethoxybenzene (65 μL, as an internal standard) was added. A small sample of the reaction mixture was taken and filtered through a plug of celite, with the filter cake being further washed with dichloromethane. The filtrate was washed three times with water and analyzed by gas chromatography. The GC yields were determined by obtaining correction factors by using authentic samples of the expected products.

8



$C_{12}H_{10}N_2$

2-Pyridylidenaminobenzene (8): Anhydrous magnesium sulphate (18.0 g, 0.15 mol) and rac-*trans*-1,2-diaminocyclohexane (9.31 g, 0.10 mol) were successively added to a solution of 2-pyridylaldehyde (10.7 g, 0.10 mol) in absolute ethanol (60 mL). The mixture was stirred for 16 h at room temperature and filtered through a frit. The solid was discarded and the filtrate was concentrated in vacuo. Trituration in pentane led to the precipitation of the desired product (16 g, 88%): ^{1}H NMR ($CDCl_3$): $\delta = 8.75$ (ddd, 1H, $^3J_{H5,H6} = 4.9$, $^4J_{H4,H6} = 1.8$, $^5J_{H3,H6} = 1.0$ Hz, H6), 8.64 (brs, 1H, H7), 8.24 (ddd, 1H, $^3J_{H3,H4} = 7.9$, $^4J_{H3,H5} = 1.3$, $^5J_{H3,H6} = 1.0$ Hz, H3), 7.86 (dddd, 1H, $^3J_{H3,H4} = 7.9$, $^3J_{H4,H5} = 7.5$, $^4J_{H4,H6} = 1.8$, $^5J_{H4,H7} = 0.6$ Hz, H4), 7.41 (ddd, 2H, $^3J_{H4,H5} = 7.5$, $^3J_{H5,H6} = 4.9$, $^4J_{H3,H5} = 1.3$ Hz, H5), 7.45 (m, 2H, H11), 7.31 ppm (m, 3H, H10, H12); ^{13}C NMR: $\delta = 160.43$ (C7), 154.34 (C2), 150.77 (C9), 149.51 (C6), 136.45 (C4), 129.04 (C11), 126.54 (C12), 124.94 (C5), 121.68 (C3), 120.92 ppm (C10); GC/MS (EI): rt = 19.39 min, *m*/*z*: 182; IR (CCl_4): $\tilde{\nu} = 3050$, 2893, 1622 (m, C=N), 1588, 1563, 1483, 1463, 1449, 1431, 1345, 1199, 1165, 1144, 1090, 989, 978, 912, 873, 778, 762, 739, 689, 666, 618, 550, 534, 405 cm^{-1}.



***N*-Alkenylazoles and alkenyl aryl ethers**: Chemical shifts have been assigned by using the following numbering systems. The numbering systems of the different azole moieties are given in Table 1 and Table 2.

***N*-Alkenylazoles**:

1-(*E*)-Styrylpyrazole (1a): *N*-Vinylation of pyrazole (204 mg, 3 mmol) was achieved by following the general procedure (acetonitrile, 50 °C, 30 h). The crude oily residue was purified by flash chromatography on silica gel (eluent: hexanes/CH_2Cl_2 100:0→50:50) to provide the desired product (290 mg, 94 % yield) as a white solid: M.p. 53–54 °C (hexanes/CH_2Cl_2; Lit.:[31d] 53 °C (hexanes/CH_2Cl_2)); ^{1}H NMR (CD_2Cl_2): δ = 7.75 (d, $^3J_{H4,H5}$ = 2.3 Hz, H5), 7.68 (d, $^3J_{H3,H4}$ = 1.3 Hz, H3), 7.59 (d, $^3J_{H1',H2'}$ = 14.5 Hz, H1′), 7.50 (m, H4′), 7.40 (m, H5′), 7.34 (m, H6′), 7.10 (d, $^3J_{H1',H2'}$ = 14.5 Hz, H2′), 6.45 ppm (m, H4); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 141.13 (C3), 135.09 (C3′), 128.89 (C5′), 128.14 (C1′), 127.60 (C6′), 126.48 (C5), 126.26 (C4′), 116.88 (C2′), 107.34 ppm (C4); GC/MS (EI): rt = 18.81 min, *m*/*z*: 169; R_f = 0.30 (dichloromethane); IR (KBr): $\tilde{\nu}$ = 3138, 3121, 3078, 3024, 2964, 1656, 1596, 1517, 1441, 1394, 1378, 1337, 1261, 1227, 1091, 1046, 967, 939, 911, 860, 851, 778, 760, 748, 690, 608, 585, 502, 480 cm^{-1}.

1-(*E*)-Styryl-3-trifluoromethylpyrazole (1b): *N*-Vinylation of 3-trifluoromethylpyrazole (408 mg, 3 mmol) was achieved by following the general procedure (acetonitrile, 50 °C, 30 h). The crude oily residue was purified by flash chromatography on silica gel (eluent: hexanes/CH_2Cl_2 100:0→50:50) to provide the desired product (430 mg, 98 % yield) as a colorless oil: ^{1}H NMR (CD_2Cl_2): δ = 7.80 (dq, $^3J_{H4,H5}$ = 2.5, $^5J_{H5,F}$ = 0.9 Hz, H5), 7.57 (d, $^3J_{H1',H2'}$ = 14.5 Hz, H1′), 7.52 (m, H4′), 7.43 (m, H5′), 7.35 (m, H6′), 7.23 (d, $^3J_{H1',H2'}$ = 14.5 Hz, H2′), 6.45 ppm (dd, $^3J_{H4,H5}$ = 2.5, $^4J_{H4,F}$ = 0.5 Hz, H4); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 144.26 (q, $^2J_{C3,F}$ = 38.0 Hz, C3), 134.52 (C3′), 129.99 (C5), 129.31 (C5′), 128.68 (C6′), 126.86 (C4′), 126.00 (C1′), 121.67 (q, $^1J_{C6,F}$ = 269.0 Hz, C6), 120.14 (C2′), 105.90 ppm (q, $^3J_{C4,F}$ = 1,5 Hz, C4); ^{19}F NMR (CD_2Cl_2): δ = −62.43 ppm (s); GC/MS (EI): rt = 18.46 min, *m*/*z*: 238; HRMS: calcd for $C_{12}H_9N_2F_3$ [M^+]: 238.0718; found: 238.0718; R_f = 0.65 (dichloromethane); IR (KBr): $\tilde{\nu}$ = 3151, 3083, 3064, 3032, 1660, 1483, 1389, 1265, 1226, 1170, 1132, 1056, 1004, 965, 939, 785, 764 748, 691, 668, 508 cm^{-1}.

1-(*E*)-Styryl-3-methylpyrazole (1c) and 1-(*E*)-styryl-5-methylpyrazole (1d): *N*-Vinylation of 3-methylpyrazole (242 μL, 3 mmol) was achieved by following the general procedure (acetonitrile, 50 °C, 30 h). The crude oily residue was purified by flash chromatography on silica gel (eluent: hexanes/CH_2Cl_2 100:0→50:50) to provide a mixture of the regioisomers **1c** and **1d** (300 mg, 89 % yield, **1c**/**1d** = 70:30) as a colorless oil: **1c**: ^{1}H NMR (CD_2Cl_2): δ = 7.60 (d, $^3J_{H4,H5}$ = 2.4 Hz, H5), 7.49 (d, $^3J_{H1',H2'}$ = 14.4 Hz, H1′), 7.47 (m, H4′), 7.40 (m, H5′), 7.29 (m, H6′), 7.03 (d, $^3J_{H1',H2'}$ = 14.4 Hz, H2′), 6.23 (d, $^3J_{H4,H5}$ = 2.4 Hz, H4), 2.21 ppm (s, CH_3); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 151.51 (C3), 135.88 (C3′), 129.42 (C5), 129.16 (C5′), 127.58 (C6′), 126.78 (C1′), 126.34 (C4′), 115.56 (C2′), 107.49 (C4), 13.89 ppm (C6); GC/MS (EI): rt = 19.50 min, *m*/*z*: 184; R_f = 0.38 (dichloromethane); IR (KBr): $\tilde{\nu}$ = 3134, 3107, 3081, 3060, 3028, 2984, 2927, 1657, 1601, 1577, 1553, 1534, 1450, 1415, 1397, 1365, 1334, 1299, 1226, 1203, 1191, 1094, 1073, 1056, 989, 938, 924, 862, 827, 783, 747, 692, 673, 651, 591, 581, 510, 491 cm^{-1}; **1d**: ^{1}H NMR (CD_2Cl_2): δ = 7.55 (br, $^3J_{H3,H4}$ = 0.9 Hz, H3), 7.49 (m, H4′), 7.47 (dd, $^3J_{H1',H2'}$ = 14.4, $^5J_{H1',H4}$ = 0.9 Hz, H1′), 7.40 (m, H5′), 7.29 (m, H6′), 7.27 (d, $^3J_{H1',H2'}$ = 14.4 Hz, H2′), 6.17 (sextet, $^3J_{H3,H4}$ = 0.9, $^4J_{H4,H6}$ = 0.9, $^5J_{H1',H4}$ = 0.9 Hz, H4), 2.31 ppm (br s, CH_3); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 140.75 (C3), 139.16 (C5), 136.08 (C3′), 129.16 (C5′), 127.72 (C6′), 126.53 (C4′), 123.40 (C1′), 117.65 (C2′), 107.04 (C4), 11.24 ppm (C6); GC/MS (EI): rt = 19.87 min, *m*/*z*: 184; R_f = 0.38 (dichloromethane); IR (KBr): same as for **1c**.

1-(*E*)-Styrylimidazole (1e): *N*-Vinylation of imidazole (204 mg, 3 mmol) was achieved by following the general procedure (acetonitrile, 50 °C, 30 h). The crude oily residue was purified by flash chromatography on silica gel (eluent: hexanes/CH_2Cl_2 100:0→50:50) to provide the desired product (280 mg, 90 % yield) as a white solid: M.p. 86–87 °C (dichloromethane/hexane; Lit.:[45] 87–88 °C (diethyl ether)); ^{1}H NMR (CD_2Cl_2): δ = 7.78 (t, $^4J_{H2,H4}$ = $^4J_{H2,H5}$ = 1.2 Hz, H2), 7.47 (m, H4′), 7.43 (d, $^3J_{H1',H2'}$ = 14.6 Hz, H1′), 7.41 (m, H5′), 7.35 (dd, $^3J_{H4,H5}$ = 3.9, $^4J_{H2,H4}$ = 1.2 Hz, H4), 7.33 (m, H6′), 7.14 (m, H5), 6.81 ppm (d, $^3J_{H1',H2'}$ = 14.6 Hz, H2′); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 136.87 (C2), 135.05 (C3′), 130.61 (C5), 129.28 (C5′), 128.30 (C6′), 126.50 (C4′), 123.24 (C1′), 118.75 (C2′), 116.64 ppm (C4); GC/MS (EI): rt = 20.03 min, *m*/*z*: 169; R_f = 0.25 (dichloromethane); IR (KBr): $\tilde{\nu}$ = 3148, 3109, 3095, 3069, 3032, 3000, 1656, 1511, 1496, 1485, 1454, 1291, 1252, 1217, 1199, 1162, 1105, 1078, 1019, 937, 903, 838, 826, 761, 728, 695, 655, 618, 582, 509 cm^{-1}.

1-(*E*)-Styrylindazole (1f) and 2-(*E*)-styrylindazole (1g): *N*-Vinylation of indazole (354 mg, 3 mmol) was achieved by following the general procedure (acetonitrile, 80 °C, 24 h). The crude oily residue was purified by flash chromatography on silica gel (eluent: hexanes/CH_2Cl_2 100:0→50:50) to provide **1f** (317 mg, 80 % yield) and **1g** (35 mg, 9 % yield) as white solids: **1f**: M.p. 124–126 °C; ^{1}H NMR (CD_2Cl_2): δ = 8.20 (dd, $^4J_{H3,H4}$ = 1.0, $^5J_{H1',H3}$ = 0.9 Hz, H3), 7.88 (dd, $^3J_{H1',H2'}$ = 14.2, $^5J_{H1',H3}$ = 0.9 Hz, H1′), 7.83 (ddd, $^3J_{H6,H7}$ = 8.0, $^4J_{H5,H7}$ = 1.0, $^5J_{H4,H7}$ = 1.0 Hz, H7), 7.73 (dddd, $^3J_{H4,H5}$ = 8.0, $^4J_{H3,H4}$ = 1.0, $^4J_{H4,H6}$ = 1.0, $^5J_{H4,H7}$ = 1.0 Hz, H4), 7.57 (m, H4′), 7.54 (ddd, $^3J_{H4,H5}$ = 8.0, $^3J_{H5,H6}$ = 7.0, $^4J_{H5,H7}$ = 1.0 Hz, H5), 7.42 (m, H5′), 7.30 (d, $^3J_{H1',H2'}$ = 14.2 Hz, H2′), 7.29 (m, H6′), 7.29 ppm (ddd, $^3J_{H6,H7}$ = 8.0, $^3J_{H5,H6}$ = 7.0, $^4J_{H4,H6}$ = 1.0 Hz, H6); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 139.12 (C8), 136.36 (C3), 136.32 (C3′), 129.18 (C5′), 127.69 (C5), 127.48 (C6′), 126.33 (C4′), 125.34 (C9), 123.75 (C1′), 122.29 (C6), 121.75 (C7), 115.53 (C2′), 109.75 ppm (C4); GC/MS (EI): rt = 24.19 min, *m*/*z*: 220; HRMS: calcd for $C_{15}H_{13}N_2$ [M^++H]: 221.1079; found: 221.1079; R_f = 0.65 (dichloromethane); IR (KBr): $\tilde{\nu}$ = 3109, 3052, 3024, 1653, 1613, 1597, 1576, 1490, 1468, 1449, 1423, 1361, 1326, 1290, 1268, 1216, 1177, 1156, 1147, 1116, 1024, 1003, 985, 964, 940, 908, 860, 844, 763, 755, 743, 690, 630, 578, 507, 434 cm^{-1}; **1g**: M.p. 122–124 °C; ^{1}H NMR (CD_2Cl_2): δ = 8.21 (d, $^4J_{H3,H4}$ = 0.9 Hz, H3), 7.81 (d, $^3J_{H1',H2'}$ = 14.4 Hz, H1′), 7.71 (ddd, $^3J_{H6,H7}$ = 8.5, $^4J_{H5,H7}$ = 0.9, $^5J_{H4,H7}$ = 0.9 Hz, H7), 7.70 (dddd, $^3J_{H4,H5}$ = 7.7, $^4J_{H3,H4}$ = 0.9, $^4J_{H4,H6}$ = 0.9, $^5J_{H4,H7}$ = 0.9 Hz, H4), 7.59 (m, H4′), 7.54 (d, $^3J_{H1',H2'}$ = 14.4 Hz, H2′), 7.44 (m, H5′), 7.37 (m, H6′), 7.34 (ddd, $^3J_{H4,H5}$ = 7.7, $^3J_{H5,H6}$ = 6.5, $^4J_{H5,H7}$ = 0.9 Hz, H5), 7.12 ppm (ddd, $^3J_{H6,H7}$ = 8.5, $^3J_{H5,H6}$ = 6.5, $^4J_{H4,H6}$ = 0.9 Hz, H6); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 148.84 (C8), 133.79 (C3′), 128.15 (C5′), 127.46 (C6′), 126.24 (C1′), 126.00 (C5), 125.84 (C4′), 121.57 (C3), 121.55 (C6), 121.19 (C9), 120.19 (C2′), 119.54 (C7), 116.66 ppm (C4); GC/MS (EI): rt = 25.23 min, *m*/*z*: 220; HRMS: calcd for $C_{15}H_{13}N_2$ [M^++H]: 221.1079; found: 221.1081; R_f = 0.25 (dichloromethane); IR (KBr): $\tilde{\nu}$ = 3123, 3061, 2964, 1655, 1626, 1516, 1396, 1378, 1332, 1262, 1160, 1140, 1097, 1022, 942, 800, 754, 695, 641, 614, 511, 442 cm^{-1}.

1-(*E*)-Styrylpyrrole (1h): *N*-Vinylation of pyrrole (208 μL, 3 mmol) was achieved by following the general procedure (acetonitrile, 80 °C, 24 h). The crude oily residue was purified by flash chromatography on silica gel (eluent: hexanes/CH_2Cl_2 100:0→50:50) to provide the desired product (260 mg, 89 % yield) as a white solid: M.p. 98–101 °C (dichloromethane; Lit.:[46] 98–100 °C (diethyl ether/water)); ^{1}H NMR (CD_2Cl_2): δ = 7.44 (m, H4′), 7.39 (d, $^3J_{H1',H2'}$ = 14.6 Hz, H1′), 7.38 (m, H5′), 7.27 (m, H6′), 7.05 (AA′ system, H2), 6.66 (d, $^3J_{H1',H2'}$ = 14.6 Hz, H2′), 6.30 ppm (XX′ system, H3); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 136.18 (C3′), 129.15 (C5′), 127.34 (C6′), 127.28 (C1′), 126.03 (C4′), 119.42 (C2), 114.33 (C2′), 110.70 ppm (C3); GC/MS (EI): rt = 18.28 min, *m*/*z*: 169; $R_{f=}$ 0.35 (hexanes); IR (KBr): $\tilde{\nu}$ = 3126, 3098, 3063, 3027, 2965, 1659, 1596, 1520, 1481, 1449, 1374, 1339, 1321, 1306, 1288, 1230, 1200, 1153, 1097, 1072, 1049, 1026, 969, 940, 828, 802, 750, 728, 690, 614, 582, 506, 477 cm^{-1}.

1-(*E*)-Styrylindole (1i): *N*-Vinylation of indole (351 mg, 3 mmol) was achieved by following the general procedure (acetonitrile, 80 °C, 24 h). The

crude oily residue was purified by flash chromatography on silica gel (eluent: hexanes/ethyl acetate 100:0→80:20) to provide the desired product (220 mg, 83% yield) as a white solid: M.p. 115–117°C;[23] ^{1}H NMR (CD_2Cl_2): δ=8.78 (d, $^3J_{H1',H2'}$=14.5 Hz, H1′), 7.67 (ddd, $^3J_{H4,H5}$=7.9, $^4J_{H4,H6}$=1.3, $^5J_{H4,H7}$=0.9 Hz, H4), 7.63 (dddd, $^3J_{H6,H7}$=8.3, $^4J_{H5,H7}$=1.0, $^5J_{H3,H7}$=0.7, $^5J_{H4,H7}$=0.9 Hz, H7), 7.61 (d, $^3J_{H2,H3}$=3.4 Hz, H2), 7.53 (m, H4′), 7.41 (m, H5′), 7.33 (ddd, $^3J_{H6,H7}$=8.3, $^3J_{H5,H6}$=7.1, $^4J_{H4,H6}$=1.3 Hz, H6), 7.28 (m, H6′), 7.21 (ddd, $^3J_{H4,H5}$=7.9, $^3J_{H5,H6}$=7.1, $^4J_{H5,H7}$=1.0 Hz, H5), 6.77 (d, $^3J_{H1',H2'}$=14.5 Hz, H2′), 6.73 ppm (ddd, $^3J_{H2,H3}$=3.4, $^5J_{H3,H7}$=0.7, $^5J_{H3,H1'}$=0.7 Hz, H3); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ=136.55 (C3′), 136.13 (C8), 129.63 (C9), 129.18 (C5′), 127.26 (C6′), 126.03 (C4′), 124.16 (C7), 123.94 (C1′), 123.12 (C6), 121.51 (C5), 121.28 (C4), 114.31 (C2′), 110.00 (C2), 105.62 ppm (C3); GC/MS (EI): rt=24.34 min, m/z: 219; R_f=0.80 (ethyl acetate/hexanes 1:4); IR (KBr): $\tilde{\nu}$=3114, 3043, 3024, 1650, 1596, 1518, 1461, 1365, 1326, 1269, 1230, 1200, 1120, 1089, 1012, 935, 745, 717, 695 cm^{-1}.

1-(*E*)-Styrylbenzotriazole (1j) and 2-(*E*)-styrylbenzotriazole (1k): *N*-Vinylation of benzotriazole (357 mg, 3 mmol) was achieved by following the general procedure (DMF, 110°C, 24 h). The crude oily residue was purified by flash chromatography on silica gel (eluent: hexanes/dichloromethane) to provide **1j** (354 mg, 87% yield) and **1k** (36 mg, 7% yield) as white solids: **1j:** M.p. 116–119°C (dichloromethane/hexanes; Lit.:[47] 115–116°C (benzene/chloroform)); ^{1}H NMR (CD_2Cl_2): δ=8.14 (ddd, $^3J_{H4,H5}$=8.4, $^4J_{H4,H6}$=1.0, $^4J_{H4,H7}$=0.9 Hz, H4), 8.03 (d, $^3J_{H1',H2'}$=14.6, H1′), 7.86 (ddd, $^3J_{H6,H7}$=8.4, $^4J_{H5,H7}$=0.9, $^4J_{H4,H7}$=0.9, H7), 7.65 (ddd, $^4J_{H4,H6}$=1.0, $^3J_{H5,H6}$=7.0, $^3J_{H6,H7}$=8.4 Hz, H6), 7.63 (m, H4′), 7.54 (d, $^3J_{H1',H2'}$=14.6, H2′), 7.50 (m, H5), 7.48 (m, H5′), 7.39 ppm (m, H6′); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ=146.32 (C9), 131.57 (C3′), 134.50 (C8), 128.96 (C5′), 128.26 (C6 or C6′), 128.39 (C6 or C6′), 126.56 (C4′), 124.57 (C5), 121.89 (C1′), 120.72 (C2′), 120.17 (C4), 110.17 ppm (C7); GC/MS (EI): rt=25.00 min, m/z: 221; R_f=0.38 (dichloromethane/hexane 3:1); IR (KBr): $\tilde{\nu}$=3069, 3060, 3035, 1655, 1609, 1598, 1486, 1455, 1400, 1326, 1307, 1286, 1267, 1242, 1208, 1164, 1142, 1117, 1076, 1058, 999, 944, 917, 779, 766, 747, 695 cm^{-1}; **1k**: M.p. 104–107°C (dichloromethane/hexanes); ^{1}H NMR (CD_2Cl_2): δ=8.10 (d, $^3J_{H1',H2'}$=14.6 Hz, H1′), 7.92 (AA′ system, $^3J_{H4,H5}$=$^3J_{H6,H7}$=8.8, $^4J_{H4,H6}$=$^3J_{H5,H7}$=1.0, $^5J_{H4,H7}$=1.0 Hz, H4, H7), 7.88 (d, $^3J_{H1',H2'}$=14.6 Hz, H2′), 7.65 (m, H4′), 7.48 (m, H5′), 7.47 (XX′ system, $^3J_{H4,H5}$=$^3J_{H6,H7}$=8.8, $^3J_{H5,H6}$=6.7, $^4J_{H4,H6}$=$^3J_{H5,H7}$=1.0 Hz, H5, H6), 7.41 ppm (m, H6′); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ=143.58 (C8, C9), 132.53 (C3′), 127.71 (C5′), 127.67 (C6′), 125.94 (C5, C6), 125.90 (C1′), 125.82 (C4′), 123.06 (C2′), 116.68 ppm (C4, C7); GC/MS (EI): rt=23.94 min, m/z: 221; $R_{f=}$0.20 (dichloromethane/hexanes 3:1); IR (KBr): $\tilde{\nu}$=3083, 3032, 2964, 1562, 1498, 1447, 1341, 1330, 1291, 1261, 1205, 1187, 1144, 1098, 1021, 958, 917, 887, 844, 801, 756, 741, 693, 624 cm^{-1}.

1-(*E*)-Styryl-1,2,4-triazole (1l): *N*-Vinylation of 1,2,4-triazole (207 mg, 3 mmol) was achieved by following the general procedure (DMF, 110°C, 24 h). The crude oily residue was purified by flash chromatography on silica gel (eluent: hexanes/ethyl acetate) to provide **1l** (322 mg, 94% yield) as an oil: ^{1}H NMR (CD_2Cl_2): δ=8.37 (s, H5), 8.06 (s, H3), 7.60 (d, $^3J_{H1',H2'}$=14.3 Hz, H1′), 7.51 (m, H4′), 7.42 (m, H5′), 7.35 (m, H6′), 7.30 ppm (d, $^3J_{H1',H2'}$=14.3 Hz, H2′); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ=152.66 (C3), 142.93 (C5), 134.51 (C3′), 129.32 (C5′), 128.37 (C6′), 126.94 (C4′), 122.62 (C1′), 121.10 ppm (C2′); GC/MS (EI): rt=19.13 min, m/z: 171; HRMS: calcd for $C_{10}H_{10}N_3$ [M^++H]: 172.0875; found: 172.0880; R_f=0.65 (ethyl acetate/hexanes 2:1); IR (KBr): $\tilde{\nu}$=3119, 3086, 3029, 2865, 1705, 1661, 1601, 1505, 1451, 1420, 1362, 1346, 1300, 1275, 1241, 1196, 1136, 1015, 1001, 943, 863, 780, 749, 693, 672, 647, 586, 509 cm^{-1}.

1-(*E*)-Styryl-1,2,3-triazole (1m) and 2-(*E*)-styryl-1,2,3-triazole (1n): *N*-Vinylation of 1,2,3-triazole (138 μL, 3 mmol) was achieved by following the general procedure (DMF, 110°C, 24 h). The crude oily residue was purified by flash chromatography on silica gel (eluent: ethyl acetate/dichloromethane) to provide **1m** (130 mg, 38% yield) as a white solid and **1n** (180 mg, 50% yield) as a greenish solid: **1m**: M.p. 95–97°C (ethyl acetate/dichloromethane); ^{1}H NMR (CD_2Cl_2): δ=7.96 (d, $^3J_{H4,H5}$=1.1 Hz, H5), 7.86 (d, $^3J_{H1',H2'}$=14.9 Hz, H1′), 7.79 (dd, $^3J_{H4,H5}$=1.1 Hz, $^5J_{H1',H4}$=0.5 Hz, H4), 7.55 (m, H4′), 7.49 (m, H5′), 7.38 (m, H6′), 7.27 ppm (d, $^3J_{H1',H2'}$=14.9 Hz, H2′); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ=134.29 (C4), 134.15 (C3′), 129.37 (C5′), 129.09 (C6′), 127.08 (C4′), 123.45 (C1′), 121.94 (C2′), 121.60 ppm (C5); GC/MS (EI): rt=20.29 min, m/z: 171; HRMS: calcd for $C_{10}H_9N_3$ [M^+]: 171.0802; found: 171.0796; R_f=0.50 (ethyl acetate/dichloromethane 1:1); IR (KBr): $\tilde{\nu}$=3140, 3123, 3108, 3030, 2963, 1658, 1578, 1489, 1477, 1454, 1435, 1311, 1285, 1262, 1227, 1207, 1178, 1156, 1107, 1076, 1025, 1015, 940, 802, 752, 697, 670, 636, 584, 507, 469 cm^{-1}; **1n**: M.p. 45–48°C (ethyl acetate/dichloromethane); ^{1}H NMR (CD_2Cl_2): δ=7.86 (d, $^3J_{H1',H2'}$=14.4 Hz, H1′), 7.80 (s, H4, H5), 7.55 (m, H4′), 7.47 (d, $^3J_{H1',H2'}$=14.4 Hz, H2′), 7.43 (m, H5′), 7.35 ppm (m, H6′); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ=134.67 (C4, C5), 133.50 (C3′), 128.11 (C5′), 127.45 (C6′), 125.85 (C4′), 125.66 (C1′), 119.30 ppm (C2′); GC/MS (EI): rt=17.48 min, m/z: 171; HRMS: calcd for $C_{10}H_{10}N_3$ [M^++H]: 172.0875; found: 172.0867; R_f=0.70 (ethyl acetate/dichloromethane 1:1); IR (KBr): $\tilde{\nu}$=3117, 3084, 3058, 3030, 2964, 1654, 1601, 1541, 1576, 1494, 1448, 1410, 1374, 1332, 1258, 1151, 1071, 1029, 962, 945, 865, 823, 790, 748, 694, 672, 588, 512, 479 cm^{-1}.

1-(2-Methyl-1-propenyl)pyrazole (1o): *N*-Vinylation of pyrazole by 2-methyl-1-bromopropene was achieved by following the general procedure. The crude oily residue was purified by flash chromatography on silica gel (eluent: dichloromethane) to provide **1o** (115 mg, 47% yield) as a colorless oil:[48] ^{1}H NMR (CD_2Cl_2): δ=7.60 (d, $^3J_{H4,H5}$=1.8 Hz, H5), 7.46 (d, $^3J_{H3,H4}$=2.4 Hz, H3), 6,70 (dq, $^4J_{H1',H3'}$ or $^4J_{H1',H4'}$=1.6, $^4J_{H1',H4'}$ or $^4J_{H1',H3'}$=1.4 Hz, H1′), 6.32 (dd, $^3J_{H3,H4}$=2.4, $^3J_{H4,H5}$=1.8 Hz, H4), 1.88 (d, $^4J_{H1',H3'}$ or $^4J_{H1',H4'}$=1.6 Hz, H3′ or H4′), 1.85 ppm (d, $^4J_{H1',H4'}$ or $^4J_{H1',H3'}$=1.4 Hz, H4′ or H3′); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ=143.25 (C3), 132.57 (C5), 123.05 (C1′), 121.94 (C2′), 105.05 (C4), 20.12 (C3′ or C4′), 19.25 ppm (C4′ or C3′); GC/MS (EI): rt=9.81 min, m/z: 122; R_f=0.35 (dichloromethane).

Alkenyl aryl ethers:

3,5-Dimethylphenyl (*E*)-styryl ether (2a): *O*-Vinylation of 3,5-dimethylphenol (363 mg, 3 mmol) was achieved by following the general procedure (acetonitrile, 50°C, 30 h). The crude oily residue was purified by flash chromatography on alumina (eluent: hexanes) to provide **2a** (336 mg, 75% yield) as a colorless oil: ^{1}H NMR (CD_2Cl_2): δ=7.25 (m, 5H, H4′, H5′, H6′), 7.21 (d, 1H, $^3J_{H1',H2'}$=12.4 Hz, H1′), 6.79 (m, 1H, H5), 6.72 (m, 2H, H3), 6.37 (d, 1H, $^3J_{H1',H2'}$=12.4 Hz, H2′), 2.35 ppm (s, 6H, CH_3); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ=157.17 (C2), 143.67 (C1′), 139.59 (C4), 135.28 (C3′), 128.66 (C5′), 126.53 (C5), 125.60 (C4′), 124.96 (C6′), 114.61 (C3), 113.18 (C2′), 21.33 ppm (C6); GC/MS (EI): rt=22.00 min, m/z: 224; R_f=0.76 (hexanes).

4-*tert*-Butylphenyl (*E*)-styryl ether (2b): *O*-Vinylation of 4-*tert*-butylphenol (450 mg, 3 mmol) was achieved by following the general procedure (acetonitrile, 50°C, 30 h). The crude oily residue was purified by flash chromatography on alumina (eluent: hexanes) to provide **2b** (482 mg, 90% yield) as a colorless oil: ^{1}H NMR (CD_2Cl_2): δ=7.42 (m, 2H, H4), 7.27 (m, 5H, H4′, H5′, H6′), 7.24 (d, 1H, $^3J_{H1',H2'}$=12.4 Hz, H1′), 7.06 (m, 2H, H3), 6.39 (d, 1H, $^3J_{H1',H2'}$=12.4 Hz, H2′), 1.36 ppm (s, 9H, CH_3); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ=154.89 (C2), 146.15 (C1′), 143.91 (C5), 137.27 (C3′), 128.66 (C5′), 126.51 (C4), 126.35 (C6′), 125.58 (C4′), 116.49 (C3), 113.01 (C2′), 34.28 (C6), 31.46 ppm (C7); GC/MS (EI): rt=23.52 min, m/z: 252; R_f=0.76 (hexanes).

4-Methoxyphenyl (*E*)-styryl ether (2c): *O*-Vinylation of 4-methoxyphenol (372 mg, 3 mmol) was achieved by following the general procedure (acetonitrile, 50°C, 30 h). The crude oily residue was purified by flash chromatography on alumina (eluent: hexanes/dichloromethane) to provide **1c** (370 mg, 82% yield) as a colorless oil; ^{1}H NMR (CD_2Cl_2): δ=7.26 (m, 5H, H4′, H5′, H6′), 7.18 (d, 1H, $^3J_{H1',H2'}$=12.5 Hz, H1′), 7.06 (m, 2H, H4), 6.93 (m, 2H, H3), 6.31 (d, 1H, $^3J_{H1',H2'}$=12.5 Hz, H2′), 3.83 ppm (s, 3H, CH_3); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ=155.65 (C5), 150.90 (C2), 144.72 (C1′), 135.26 (C3′), 128.60 (C5′), 126.38 (C6′), 125.47 (C4′), 118.32 (C3), 114.67 (C4), 112.29 (C2′), 55.56 ppm (C6); GC/MS (EI): rt=23.45 min, m/z: 226; $R_{f=}$0.42 (hexanes).

4-Fluorophenyl (*E*)-styryl ether (2d): *O*-Vinylation of 4-fluorophenol (336 mg, 3 mmol) was achieved by following the general procedure (acetonitrile, 50°C, 30 h). The crude oily residue was purified by flash chromatography on alumina (eluent: hexanes) to provide **1d** (351 mg, 82% yield) as a white solid: ^{1}H NMR (CD_2Cl_2): δ=7.29 (m, 5H, H4′, H5′, H6′), 7.16 (d, 1H, $^3J_{H1',H2'}$=12.4 Hz, H1′), 7.07 (m, 4H, H3, H4), 6.36 ppm (d, 1H, $^3J_{H1',H2'}$=12.4 Hz, H2′); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ=158.76 (d,

$^1J_{C5',F}$ = 242.0 Hz, C5), 153.13 (C2), 143.83 (C1′), 134.93 (C3′), 128.69 (C5′), 126.72 (C6′), 125.63 (C4′), 118.40 (d, $^3J_{C3',F}$ = 8.0 Hz, C3), 116.21 (d, $^2J_{C4',F}$ = 23.0 Hz, C4), 113.50 ppm (C2′); GC/MS (EI): rt = 19.80 min, *m*/*z*: 214; $R_{f=}$0.71 (hexanes).

4-Chlorophenyl (*E*)-styryl ether (2e): *O*-Vinylation of 4-chlorophenol (386 mg, 3 mmol) was achieved by following the general procedure (acetonitrile, 50 °C, 30 h). The crude oily residue was purified by flash chromatography on alumina (eluent: hexanes) to provide **1e** (340 mg, 74 % yield) as a white solid: ^{1}H NMR (CD_2Cl_2): δ = 7.22–7.36 (m, 5H, H4′,H5′, H6′), 7.16 (d, 1H, $^3J_{H1',H2'}$ = 12.4 Hz, H1′), 7.07 (m, 4H, H3, H4), 6.36 ppm (d, 1H, $^3J_{H1',H2'}$ = 12.4 Hz, H2′); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 155.64 (C2), 142.88 (C1′), 134.72 (C3′), 129.63 (C5′), 128.69 (C4), 128.21 (C5), 126.83 (C6′), 125.68 (C4′), 118.15 (C3), 114.31 ppm (C2′); GC/MS (EI): rt = 21.95 min, *m*/*z*: 230; R_f = 0.74 (hexanes).

3,5-Dimethylphenyl 2-methylpropenyl ether (2g): *O*-Vinylation of 3,5-dimethylphenol by 2-methyl-1-bromopropene was achieved by following the general procedure. The crude oily residue was purified by flash chromatography on alumina (eluent: hexanes) to provide **2g** (313 mg, 89 % yield) as a colorless oil: ^{1}H NMR ($CDCl_3$): δ = 6.72 (m, H3), 6.67 (m, H5), 6.24 (dq, $^4J_{H1',H3'}$ or $^4J_{H1',H4'}$ = 1.6, $^4J_{H1',H4'}$ or $^4J_{H1',H3'}$ = 1.4 Hz, H1′), 2.36 (m, H6), 1.78 (d, $^4J_{H1',H3'}$ or $^4J_{H1',H4'}$ = 1.6 Hz, H3′ or H4′), 1.76 ppm (d, $^4J_{H1',H4'}$ or $^4J_{H1',H3'}$ = 1.4 Hz, H4′ or H3′); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 158.31 (C2), 139.73 (C1′), 135.80 (C4), 124.08 (C5), 117.59 (C2′), 113.96 (C3), 21.79 (C6), 19.95 (C3′ or C4′), 15.59 ppm (C4′ or C3′); GC/MS (EI): rt = 14.98 min, *m*/*z*: 176; R_f = 0.72 (hexanes).

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