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Rhodium-Catalyzed Mono- and Divinylation of 1-Phenylpyrazoles and Related Compounds via Regioselective C−H Bond Cleavage

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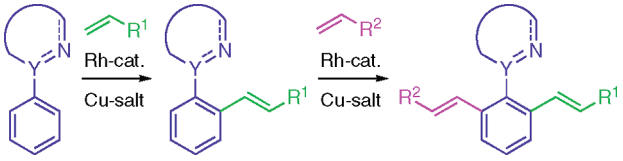

The selective 2-mono- and 2,6-divinylations of (*N*-containing heteroaryl)benzenes can be achieved effectively through rhodium-catalyzed oxidative coupling reactions with alkenes. The installation of two different vinyl groups is also possible by a simple one-pot manner. Thus, a series of 1,3-divinylbenzene derivatives, some of which exhibit solid-state fluorescence, is readily prepared.

Introduction

Transition metal-catalyzed C−C bond formation reactions via C−H bond cleavage have attracted much attention from the atom- and step-economic point of view, and various catalytic processes involving different modes to activate the ubiquitously available bond have been developed.[1] Among the most promising strategies is the chelation-assisted version with the aid of directing groups including carbonyl, imino, and pyridyl functions. Particularly, the vinylation at the ortho positions of arenes having such a functional group via oxidative coupling with readily available alkenes seems to be a useful method to selectively construct π-conjugated vinylarene frameworks, which can be widely seen in organic materials.[2] However, the straightforward vinylation with alkenes has not been extensively explored. As some rare examples, we demonstrated that 2-phenylphenols,[3] *N*-(arylsulfonyl)-2-phenylanilines,[4] and benzoic acids[4,5] undergo the direct oxidative vinylation under palladium or

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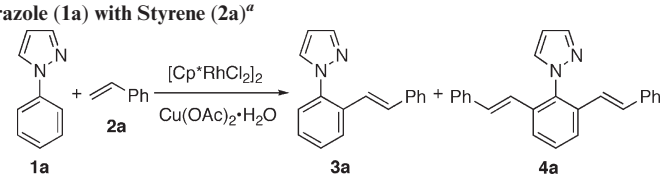
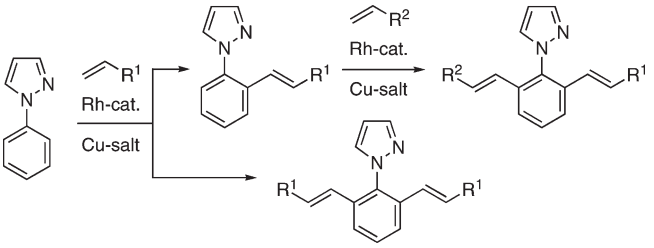
TABLE 1. Reaction of 1-Phenylpyrazole (1a) with Styrene (2a)[a]



						% yield[b]	
entry	**1** (mmol)	**2** (mmol)	$Cu(OAc)_2 \cdot H_2O$ (mmol)	temp (°C)	time (h)	**3a**	**4a**
1	0.5	0.5	1	60	10	72	27
2	1	0.5	1	60	3	81 (81)	7
3	0.5	1.2	2	60	10	3	67
4	0.5	1.2	2	100	2	0	90 (82)

[a]Reaction conditions: $[(Cp^*RhCl_2)_2]$ (0.005 mmol) and DMF (3 mL) under N_2. [b]GC yield. The value in parentheses indicates the yield after purification.

SCHEME 1. Mono- and Divinylation of 1-Phenylpyrazole with Alkenes

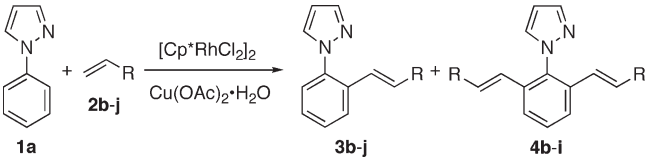


rhodium catalysis. Since them, some reports concerning monovinylation of limited substrates under palladium catalysis have been disclosed.[6] During our further studies of oxidative couplings using rhodium catalysts,[7] we have succeeded in conducting the ortho-vinylation of 1-phenylpyrazoles and related compounds with various alkenes in the presence of a rhodium catalyst and a copper oxidant (Scheme 1). Interestingly, not only monovinylated products but also divinylated ones can be obtained selectively, depending on the reaction conditions.[8] Furthermore, a stepwise, one-pot divinylation with two different alkenes can also be performed to afford the corresponding unsymmetrically substituted 1,3-divinylbenzene derivatives selectively.[9] These *m*-phenylene vinylene structures are common units in fine chemicals such as luminescent materials, liquid crystals, and nonlinear optical materials as well as herbicides.[10] The results obtained for the vinylation reactions are described herein.

Results and Discussion

In an initial attempt, 1-phenylpyrazole (**1a**) (0.5 mmol) was treated with styrene (**2a**) (0.5 mmol) in the presence of $[Cp^*RhCl_2]_2$ (0.005 mmol, 1 mol %) and $Cu(OAc)_2 \cdot H_2O$ (1 mmol) in DMF (3 mL) at 60 °C under N_2 for 10 h. As a result, mono- and divinylated products, **3a** and **4a**, were formed in 72% and 27% yields, respectively (entry 1 in Table 1, Cp* = pentamethylcyclopentadienyl).[11] Expectedly, the yield of **3a** was improved by using an excess amount of **1a** up to 81% (entry 2, conditions A). Meanwhile, the use of **1a** and **2a** in a ratio of 0.5:1.2 gave **4a** predominantly in 67% yield, along with a small amount of **3a** (entry 3). At 100 °C, **3a** completely disappeared, and **4a** was obtained exclusively in 90% yield (entry 4, conditions B).

TABLE 2. Reaction of 1-Phenylpyrazole (1a) with Alkynes 2[a]



					product, % yield[b]	
entry	**2**	R	conditions	time (h)	**3**	**4**
1	**2b**	4-MeC_6H_4	A	6	**3b**, 79 (69)	**4b**, 5
2	**2b**	4-MeC_6H_4	B	2		**4b**, 89 (86)
3	**2c**	4-(*t*-Bu)C_6H_4	A	7	**3c**, 80 (72)	
4	**2c**	4-(*t*-Bu)C_6H_4	B	6		**4c**, − (74)
5	**2d**	4-$MeOC_6H_4$	A	3	**3d**, 81 (74)	
6	**2d**	4-$MeOC_6H_4$	B	2		**4d**, − (64)
7	**2e**	4-ClC_6H_4	A	3	**3e**, − (74)	
8	**2e**	4-ClC_6H_4	B	2		**4e**, 68 (58)
9[c]	**2f**	2-naphthyl	A	7	**3f**, − (77)	
10[c]	**2f**	2-naphthyl	B	2		**4f**, 80 (77)
11	**2g**	CO_2(*n*-Bu)	A	2	**3g** , − (76)	
12	**2g**	CO_2(*n*-Bu)	B	2		**4g**, − (81)
13	**2h**	CO_2(*t*-Bu)	A[d]	2	**3h**, 62 (57)	
14	**2h**	CO_2(*t*-Bu)	B[d]	2		**4h**, − (78)
15	**2i**	CO_2Cy[e]	A[d]	1	**3i**, 85 (79)	
16	**2i**	CO_2Cy[e]	B[d]	2		**4i**, − (77)
17	**2j**	CN	A[d]	2	**3j**, − (76)[f]	

[a]Reaction conditions A: **1a** (1 mmol), **2** (0.5 mmol), $[(Cp^*RhCl_2)_2]$ (0.005 mmol), $Cu(OAc)_2 \cdot H_2O$ (1 mmol), DMF (3 mL) at 60 °C under N_2. Conditions B: **1a** (0.5 mmol), **2** (1.2 mmol), $[(Cp^*RhCl_2)_2]$ (0.005 mmol), $Cu(OAc)_2 \cdot H_2O$ (2 mmol), DMF (3 mL) at 100 °C under N_2. [b]GC yield. The value in parentheses indicates the yield after purification. [c]$[(Cp^*RhCl_2)_2]$ (0.01 mmol) was used. [d]After the vinylation reaction, the resulting mixture was treated with $PdCl_2(PhCN)_2$ (0.05 mmol) in mesitylene (3 mL) under N_2 at 150 °C for 15 h. [e]Cy = cyclohexyl. [f]*E*/*Z* = 3/1.

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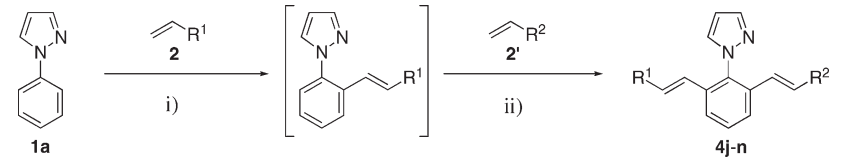
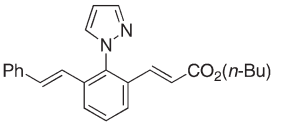
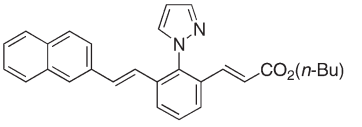
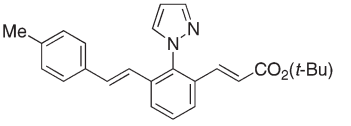
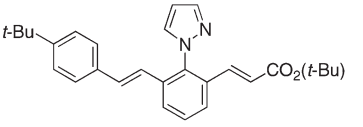
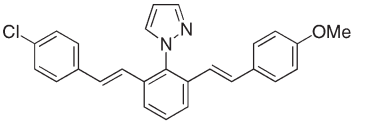
(11) It was confirmed by blank experiments that both the Rh-complex and the Cu-salt were needed in conducting the reaction effectively.

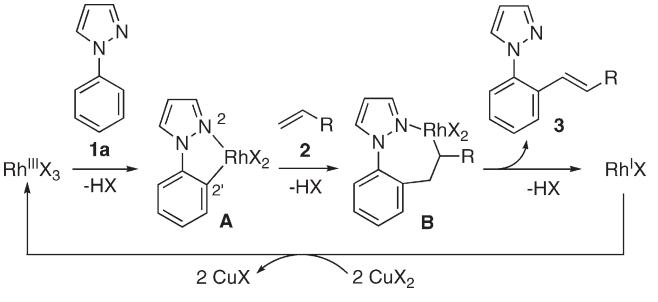
TABLE 3. Synthesis of Unsymmetrically Substituted Divinylbenzenes[a]



entry	2	R^1	2'	R^2	product, % yield[b]
					
1	**2a**	Ph	**2g**	CO_2(*n*-Bu)	**4j**, 70[c]
2	**2g**	CO_2(*n*-Bu)	**2a**	Ph	**4j**, 74[d,e]
					
3	**2f**	2-naphthyl	**2g**	CO_2(*n*-Bu)	**4k**, 63[f]
					
4[g]	**2b**	4-MeC_6H_4	**2h**	CO_2(*t*-Bu)	**4l**, 65[h]
					
5[g]	**2c**	4-(*t*-Bu)C_6H_4	**2h**	CO_2(*t*-Bu)	**4m**, 63
					
6	**2e**	4-ClC_6H_4	**2d**	4-$MeOC_6H_4$	**4n**, 55[i]

[a]Reaction conditions: (i) **1a** (0.6 mmol), **2** (0.5 mmol), [(Cp*$RhCl_2$)$_2$] (0.012 mmol), $Cu(OAc)_2 \cdot H_2O$ (2.4 mmol), DMF (3 mL) at 60 °C under N_2 for 2−7 h. (ii) **2'** (2 mmol) at 100 °C for 2 h. [b]Isolated yield. [c]**4a** (0.043 mmol) and **4g** (0.17 mmol) were also formed. [d]GC yield. [e]**4a** (0.17 mmol) and **4g** (0.055 mmol) were also formed. [f]**4g** (0.16 mmol) was also formed. The amount of **4f** was not determined. [g]After the vinylation reactions, the resulting mixture was treated with $PdCl_2(PhCN)_2$ (0.06 mmol) in mesitylene (3 mL) under N_2 at 150 °C for 15 h. [h]**4b** (0.012 mmol) was also formed. [i]**4d** (0.12 mmol) and **4e** (0.030 mmol) were also formed.

SCHEME 2. Plausible Mechanism for the Vinylation of 1-Phenylpyrazole (1a) with Alkenes 2



Under monovinylation conditions A and divinylation conditions B, the reactions of methyl- (**2b**), *tert*-butyl- (**2c**), methoxy- (**2d**), and chloro- (**2e**) substituted styrenes with **1a** proceeded smoothly to give **3b**−**e** and **4b**−**e** selectively (entries 1−8 in Table 2). 2-Vinylnaphthalene (**2f**) and *n*-butyl acrylate (**2g**) also underwent the coupling reactions without any difficulties (entries 9−12). The reactions of **1a** with *tert*-butyl- (**2h**) and cyclohexyl- (**2i**) acrylates gave the corresponding vinylated products as mixtures of geometrical isomers. Fortunately, treatment of the *E*−*Z* mixtures with $PdCl_2(PhCN)_2$ (0.05 mmol) in mesitylene (3 mL) under N_2 at 150 °C for 15 h induced isomerization around their C=C double bonds to form thermodynamically stable *E*- and *E*,*E*-isomers (entries 13−16).[12] The reaction of acrylonitrile (**2j**) under conditions A also gave monovinylation product **3j** as an *E*−*Z* mixture (ca. 1:1). In contrast to the cases of **3h** and

(12) Yu, J.; Gaunt, M. J.; Spencer, J. B. *J. Org. Chem.* **2002**, *67*, 4627.

3i, however, the isomerization of **3j** could not be completed by treatment with the Pd-catalyst to result in an *E*-rich mixture (E/Z = 3/1, entry 17). The divinylation with **2j** was found to be sluggish and **3j** was obtained as a major product in 51% yield even under conditions B.

The reaction of **1a** with **2** seems to proceed via similar steps to those proposed for the oxidative coupling of **1a** with internal alkynes by using the $[Cp^*RhCl_2]_2/Cu(OAc)_2 \cdot H_2O$ system.[8b] Thus, as depicted in Scheme 2, coordination of the 2-*N* atom of **1a** to $Rh(III)X_3$ and the subsequent directed cyclorhodation at the 2′-position afford a rhodacycle **A**. Then, alkene insertion occurs to produce an intermediate **B**, which undergoes β-hydrogen elimination[13] to form **3** together with $HRh(III)X_2$. The latter releases HX to form the Rh(I)X species, which is reoxidized to $Rh(III)X_3$ by $Cu(OAc)_2$. The second vinylation may proceed by the same mechanism to produce **4**.

Next, the stepwise, one-pot synthesis of unsymmetrically substituted 1,3-divinylbenzene derivatives was examined. Thus, in the initial step, **1a** (0.6 mmol) was treated with **2a** (0.5 mmol) in the presence of $[Cp^*RhCl_2]_2$ (0.012 mmol) and $Cu(OAc)_2 \cdot H_2O$ (2.4 mmol) in DMF (3 mL) at 60 °C under N_2 for 2 h. Then, **2g** (2 mmol) was added as the second alkene, and the resulting mixture was kept at 100 °C for 2 h to give the corresponding divinylated product **4j** in 70% overall yield (entry 1 in Table 3). Reversing the addition order of alkenes **2a** and **2g** did not affect the final yield of **4j** (entry 2). A naphthyl-substituted derivative **4k** was also synthesized by the sequential coupling by using alkenes **2f** and **2g** (entry 3). Reactions using **2h** as the second alkene required the treatment with $PdCl_2(PhCN)_2$ to obtain *E*,*E*-**4*l*** and **4m** (entries 4 and 5), as in the symmetrical divinylation (entry 14 in Table 2). It should be noted that these *tert*-butoxycarbonyl-substituted products **4*l*** and **4m** were formed as luminescent solids (vide infra), while *n*-butoxycarbonyl derivatives **4j** and **4k** were obtained as oils. An unsymmetrically substituted 1,3-distyrylbenzene **4n** could also be constructed via successive divinylation with two styrenes **2e** and **2d** (entry 6).

Some divinylated products showed solid-state fluorescence in a range of 390−520 nm (see the Supporting Information). Notably, **4h** and **4*l*** exhibited relatively strong emissions compared to a typical emitter, anthracene, by factors of 3.0 and 2.3, respectively (λ_{emis} 394 and 405 nm, A and B versus D in Figure 1). It is apparent that the introduction of bulky *tert*-butyl groups at the appropriate positions of 1,3-divinylbenzene molecules significantly enhances the intensity of solid-state fluorescence.

We also examined the mono- and divinylations of other phenylazoles and a phenylpyridine with styrene (**2a**). 3-Methyl-1-phenylpyrazole (**1b**) underwent the reactions under conditions A and B to afford the corresponding mono- and divinylated products **5b** and **6b** in 84% and 88% yields, respectively (entries 1 and 2 in Table 4). In contrast, the divinylation of a sterically more hindered substrate, 3,5-dimethyl-1-phenylpyrazole (**1c**), was sluggish, and monovinylated product **5c** was produced predominantly under both conditions A and B (entry 3). As substrates in the present reactions, 2-phenylpyridine (**1d**) and 1-methyl-2-phenylimidazole (**1e**) could also be employed as well as phenylpyrazoles (entries 4−6). In the case with the latter substrate, only monovinylated product **5e** was obtained even under conditions B (entry 6). This may be due to similar steric reasons to those in the case with **1c**.

(13) The precedent dissociation of the 2-*N* atom in **B** may be involved, as in the reaction of **1a** with alkynes (see ref 8b).

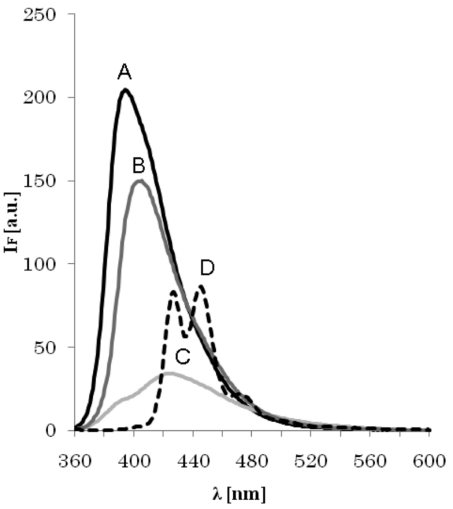


FIGURE 1. Fluorescence spectra of **4h** (A), **4*l*** (B), **4b** (C), and anthracene (D) in the solid state upon excitation at 350 nm.

In summary, we have demonstrated that the rhodium-catalyzed ortho-vinylation of phenylpyrazoles with alkenes proceeds efficiently via C−H bond cleavage. 2-Phenylpyridine and -imidazole also undergo the reaction. Some products possessing *tert*-butyl group(s) at the appropriate position(s) show relatively strong solid-state fluorescence.

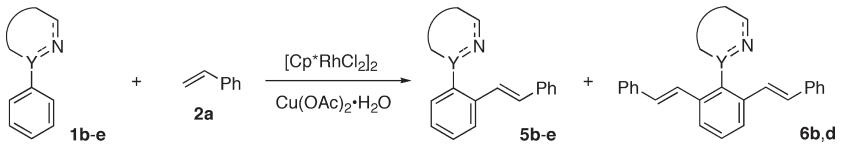
Experimental Section

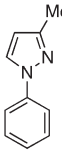
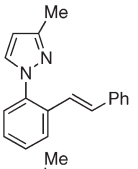
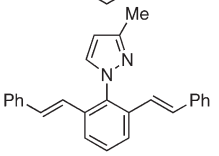
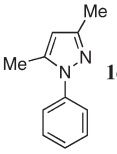
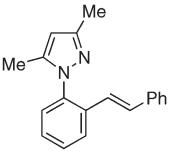
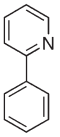
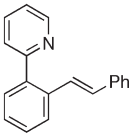
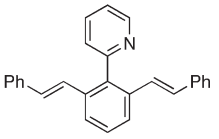
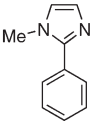
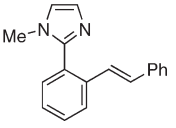
General Procedure for Monovinylation of Phenylpyrazoles 1 with Alkynes 2 under Conditions A. To a 20 mL two-necked flask were added pyrazole **1** (1 mmol), alkene **2** (0.5 mmol), $[(Cp^*RhCl_2)_2]$ (0.005 mmol, 1 mol %, 3 mg), $Cu(OAc)_2 \cdot H_2O$ (1 mmol, 200 mg), 1,2-diphenylethane (ca. 50 mg) as internal standard, and DMF (3 mL). The resulting mixture was stirred under N_2 at 60 °C. GC and GC-MS analyses of the mixtures confirmed formation of **3**. Then the reaction mixture was cooled to room temperature and extracted with Et_2O (100 mL) and ethylenediamine (2 mL). The organic layer was washed with water (100 mL, three times) and dried over Na_2SO_4. Product **3** was isolated by column chromatography on silica gel, using hexane−ethyl acetate as eluant.

1-[2-((*E*)-2-Phenylethenyl)phenyl]-1*H*-pyrazole (3a) (entry 2 in Table 1):[7f] oil; isolated yield 81%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.47 (dd, J = 1.8, 2.2 Hz, 1H), 6.94 (d, J = 16.2 Hz, 1H), 7.04 (d, J = 16.2 Hz, 1H), 7.20−7.27 (m, 1H), 7.28−7.34 (m, 2H), 7.35−7.46 (m, 5H), 7.65 (d, J = 2.2 Hz, 1H), 7.74−7.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 106.6, 123.9, 126.3, 126.6, 126.7, 127.9, 128.1, 128.4, 128.6, 131.2, 131.5, 133.0 137.0, 138.8, 140.7; HRMS m/z calcd for $C_{17}H_{14}N_2$ (M^+) 246.1157, found 246.1148.

General Procedure for Divinylation of Phenylpyrazoles 1 with Alkynes 2 under Conditions B. To a 20 mL two-necked flask were added pyrazole **1** (0.5 mmol), alkene **2** (1.2 mmol), $[(Cp^*RhCl_2)_2]$ (0.005 mmol, 1 mol %, 3 mg), $Cu(OAc)_2 \cdot H_2O$ (2 mmol, 399 mg), 1,2-diphenylethane (ca. 50 mg) as internal standard, and DMF (3 mL). The resulting mixture was stirred under N_2 at 100 °C. GC and GC-MS analyses of the mixtures confirmed formation of **4**. Then the reaction mixture was cooled to room temperature and extracted with Et_2O (100 mL) and ethylenediamine (4 mL). The organic layer was washed with water (100 mL, three times)

TABLE 4. Reaction of Phenylazoles or Phenylpyridine 1 with Styrene (2a)[a]



entry	1	conditions	time (h)	product, % yield[b]
1	 **1b**	A	6	 **5b**, 84[c]
2	**1b**	B	2	 **6b**, 88[d]
3	 **1c**	A	6	 **5c**, 90
4	 **1d**	A	10	 **5d**, 67[e]
5	**1d**	B	2	 **6d**, 82
6	 **1e**	B	6	 **5e**, 52

[a]Reaction conditions A: **1** (1 mmol), **2a** (0.5 mmol), [(Cp*RhCl$_2$)$_2$] (0.01 mmol), Cu(OAc)$_2\cdot$H$_2$O (1 mmol), DMF (3 mL) at 60 °C under N$_2$. Conditions B: **1** (0.5 mmol), **2a** (1.2 mmol), [(Cp*RhCl$_2$)$_2$] (0.01 mmol), Cu(OAc)$_2\cdot$H$_2$O (2 mmol), DMF (3 mL) at 100 °C under N$_2$. [b]Isolated yield. [c]**6b** was also formed in 12% yield. [d]**5b** was also formed in 7% yield. [e]**6d** was also formed in 10% yield.

and dried over Na_2SO_4. Product **4** was isolated by column chromatography on silica gel, using hexane−ethyl acetate as eluant.

1-[2,6-Bis((*E*)-2-phenylethenyl)phenyl]-1*H*-pyrazole (4a) (entry 4 in Table 1):[7f] mp 170−171 °C; isolated yield 82%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.50 (d, J = 16.1 Hz, 2H), 6.52 (dd, J = 1.8, 2.2 Hz, 1H), 7.01 (d, J = 16.2 Hz, 2H), 7.19−7.24 (m, 2H), 7.25−7.33 (m, 8H), 7.46 (t, J = 7.7 Hz, 1H), 7.54 (d, J = 2.2 Hz, 1H), 7.69 (d, J = 7.7 Hz, 2H), 7.86 (d, J = 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 106.3, 123.2, 124.8, 126.7, 127.9, 128.6, 129.3, 131.6, 132.9, 136.2, 136.7, 137.0, 140.6; HRMS m/z calcd for $C_{25}H_{20}N_2$ (M^+) 348.1626, found 348.1623. Anal. Calcd for $C_{25}H_{20}N_2$: C, 86.17; H, 5.79; N, 8.04. Found: C, 85.91; H, 5.93; N, 7.89.

General Procedure for One-Pot Synthesis of Unsymmetrically Substituted 1,3-Divinylbenzenes 4j−n. To a 20 mL two-necked flask were added **1a** (0.6 mmol, 86 mg), alkyne **2** (0.5 mmol), [(Cp*RhCl$_2$)$_2$] (0.012 mmol, 2.4 mol %, 7 mg), Cu(OAc)$_2\cdot$H$_2$O (2.4 mmol, 479 mg), 1,2-diphenylethane (ca. 50 mg) as internal standard, and DMF (3 mL). The resulting mixture was stirred under N$_2$ at 60 °C for 2−7 h. Then alkene **2′** (2 mmol) was added and the reaction temperature was increased to 100 °C. After 2 h, the reaction mixture was cooled to room temperature and extracted with Et$_2$O (100 mL) and ethylene diamine (4 mL). The organic layer was washed with water (100 mL, three times) and dried over Na_2SO_4. Product **4** was isolated by column chromatography on silica gel, using hexane−ethyl acetate as eluant.

1-{2-[(*E*)-2-(*n*-Butoxycarbonyl)ethenyl]-6-[(*E*)-2-phenylethenyl]-phenyl}-1*H*-pyrazole (4j) (entry 1 in Table 3): oil; isolated yield 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, J = 7.4 Hz, 3H), 1.32−1.42 (m, 2H), 1.57−1.65 (m, 2H), 4.12 (t, J = 6.6 Hz, 2H), 6.29 (d, J = 16.1 Hz, 1H), 6.48 (d, J = 16.2 Hz, 1H), 6.53 (t, J = 2.2 Hz, 1H), 7.02 (d, J = 16.2 Hz, 1H), 7.11 (d, J = 16.1 Hz, 1H), 7.21−7.33 (m, 5H), 7.49 (dd, J = 7.7, 8.0 Hz, 1H), 7.53 (d, J = 2.2 Hz, 1H), 7.62 (d, J = 7.7 Hz, 1H), 7.80 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 2.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 19.1, 30.6, 64.4, 106.8, 121.3, 122.6, 125.9, 126.7, 127.2, 128.2,

128.6, 129.4, 132.2, 132.8, 133.4, 136.5, 136.7, 137.7, 139.2, 141.0, 166.3; HRMS *m*/*z* calcd for $C_{24}H_{24}N_2O_2$ (M^+) 372.1838, found 372.1840.

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Supporting Information Available: Characterization data of products. This material is available free of charge via the Internet at http://pubs.acs.org.